Nickel-Catalyzed Cross-Coupling Reactions: Stereospecific Arylations, Formation of 2-PyridylZinc Reagents & Directed Hydroarylation of Alkynes

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Nickel-Catalyzed Cross-Coupling Reactions: Stereospecific Arylations, Formation of 2-PyridylZinc Reagents & Directed Hydroarylation of Alkynes

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Luke Edward Hanna

Dissertation Committee:
Professor Elizabeth R. Jarvo, Chair
Professor Vy M. Dong
Professor Christopher D. Vanderwal

2016

DEDICATION

To

my parents, family and friends

in recognition of their inspiring character, love and support

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Tollefson E. J.; Hanna L. E.; Jarvo, E. R.; "Stereospecific Nickel-Catalyzed Cross-Coupling Reactions of Benzylic Ethers and Esters" *Acc. Chem. Res.* **2015**, *48*, 2344.**

Hanna, L. E.; Jarvo E. R. "Selective Cross-Electrophile Coupling By Dual Catalysis" *Angew. Chem. Int. Ed.* **2015**, *54*, 15618.**

Konev, M. O.; Hanna, L. E.; Jarvo E. R. "Nickel-Catalyzed Reductive Cross-Electrophile Coupling Reaction of Primary and Secondary Benzylic Esters With Aryl Halides" *Angew. Chem. Int. Ed.* **2016**, *55*, 6730.

Hanna, L. E.; Konev, M. O.; Jarvo E. R. "Facile Nickel Catalyzed Hydroarylation of Alkynes Enabled by Carbamate Directing Groups" *Manuscript in preparation*

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241st American Chemical Society National Conference; March 2011; Anaheim, CA; “Mechanistic studies of an unusual rearrangement of iminoxyl radicals derived from benzylketoximes”

239th American Chemical Society National Conference; March 2010; San Francisco, “Synthesis and Studies of *N*-Aryl Isophthalates as Drugs for Maintenance of Pluripotent Stem Cells”

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ABSTRACT OF THE DISSERTATION

Nickel-Catalyzed Cross-Coupling Reactions:
Stereospecific Arylations, Formation of 2-PyridylZinc Reagents
& Directed Hydroarylation of Alkynes

by

Luke E. Hanna

Doctor of Philosophy in Chemistry

University of California, Irvine, 2016

Professor Elizabeth R. Jarvo, Chair

Cross-coupling technology has become an indispensable tool for the rapid and efficient synthesis of complex molecules. Over the past few decades a foundational understanding of organometallic chemistry has been laid using palladium and other precious metals. Recent research on first row base metal catalysts such as nickel, cobalt and iron has uncovered new and complementary modes of reactivity compared to their more well-studied precious metal counterparts. While nickel sits one row above palladium on the periodic table, ongoing research has illustrated that nickel possesses a unique reactivity profile. Thus, while nickel is commonly thought of as a cheaper alternative to palladium, research in the field of nickel catalysis has demonstrated far more potential than this. The unique propensity of nickel to undergo single electron chemistry as well as its ability to break strong carbon oxygen bonds make research into nickel reactivity an immensely beneficial endeavor to the fields of inorganic, organometallic and synthetic organic chemistry.

Chapter 1 describes the development of a stereospecific Suzuki coupling of benzylic carbamates and pivalates with aryl- and heteroarylboronic esters. The reaction proceeds with selective inversion or retention at the electrophilic carbon, depending on the identity of the ligand used. Tricyclohexylphosphine ligand provides products with retention of configuration at the electrophilic carbon, while an N-heterocyclic carbene ligand SIMes provides products with inversion.

Chapter 2 discusses the development of a regio- and stereoselective nickel-catalyzed hydroarylation of alkynes using propargylic carbamates as directing groups. The reaction proceeds under mild reaction conditions using arylboronic acids in the absence of base. A range of heterocycles and functional groups are tolerated under the reaction conditions. Additionally, the method is applied to the synthesis of tamoxifen.

Chapter 3 details a nickel-catalyzed cross-electrophile coupling reaction of benzylic esters and aryl halides. Both inter- and intramolecular variants proceed under mild reaction conditions. A range of heterocycles and functional groups are tolerated under the reaction conditions. Additionally, the first example of a stereospecific cross-electrophile coupling of a secondary benzylic ester is described.

Chapter 4 presents secondary benzylzinc reagents generated from 2-pyridylcarbinols using a nickel catalyst and diethylzinc. Substrates are activated in situ using a chlorophosphate reagent. Quenching the organozinc reagents allows for facile deoxygenation of 2-pyridylcarbinols in a one-pot reaction with straightforward incorporation of a deuterium label from deuteromethanol. An intramolecular conjugate addition of a secondary benzylzinc reagent with an α,β-unsaturated ester is also demonstrated.

Chapter 1

Nickel-Catalyzed Stereospecific Suzuki Cross-Coupling: A Novel Approach to Optically Enriched Triarylmethanes

1.1 Introduction

Triarylmethanes are a diverse class of compounds, from their early uses as precursors to dyes, their utility has since expanded to include a range of chemical and biological applications (Figure 1.1).[1] For example, triarylmethanes have been used as compounds for live cell imaging, selective sensors for metal ions, anticancer and antitubercular agents, potassium ion channel blockers, and even have applications to material science.[1,2] Hence, the synthesis of triarylmethanes is a rich and growing area of research. Given the wide ranging applications of triarylmethanes, many methods have emerged to access racemic mixtures;[3] however, methods that address their asymmetric synthesis have notably been limited.[4] In this Chapter, an account of the development of a stereospecific nickel-catalyzed Suzuki cross-coupling that can access a library of enantioenriched triarylmethanes is described.

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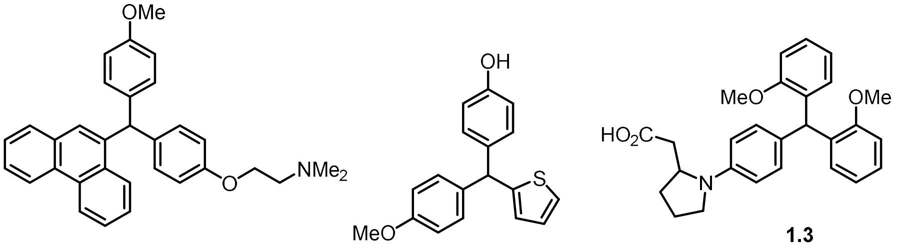
Figure 1.1. Examples of biologically active triarylmethanes



1.1
IC$_{50}$ = 3.88 μM
breast cancer MCF-7 cells
(Tamoxifen analogue)

1.2
anti-tuberculosis

1.3
GPR40 modulator
(diabetes treatment)

The mechanisms of alkyl cross-coupling reactions are hardwired with implications for the stereochemical outcome at the reactive centers.[5] Simple changes to the reaction conditions do not typically perturb the inherent bias for racemization, retention, or inversion at the reactive centers. For example, palladium-catalyzed reactions of alkyl electrophiles are typically stereospecific and proceed with inversion at the stereogenic center,[6,7] while nickel-catalyzed reactions of alkyl halides proceed with racemization at the electrophilic carbon[8] and judicious use of a chiral catalyst permits stereoconvergent reactions.[9] Overcoming the intrinsic preference, such that a reaction that typically proceeds with inversion at the stereogenic center can proceed with retention is quite unusual, and requires a significant change to the mechanism of the transformation. For stereospecific reactions, special cases using α-chiral *transmetallating agents* have been reported where modification of reaction conditions or substrate structure can effect a switch in the sense of

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[5] Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417.

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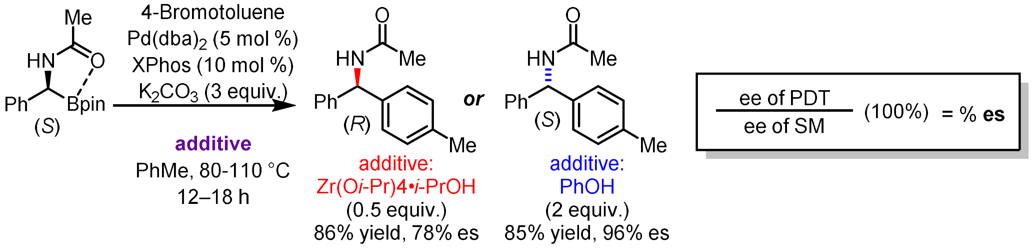
[9] (a) Saito, B.; Fu, G.C. *J. Am. Chem. Soc.* **2008**, *130*, 6694. (b) Wilsily, A.; Tramutola, F.; Owston, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2012** *134*, 5794, and cited therein. (c) Glorius, F. *Angew. Chem. Int. Ed.* **2008**, *47*, 8347.

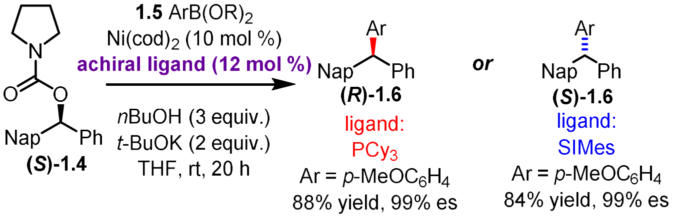
absolute configuration.[10] Transmetallation typically occurs with retention at the stereogenic center;[11,12] select examples that proceed with inversion have been reported.[13] In seminal contributions, Hiyama demonstrated that palladium-catalyzed couplings of alkylsilanes could proceed with retention or inversion, depending on the reaction conditions.[14,15] Recently, the Suginome group has developed stereodivergent reactions of α-(acetylamino)benzylboronic esters that are controlled by choice of additive to afford, selectively, either retention or inversion (Scheme 1.1a).

Scheme 1.1. Control of product stereochemistry in stereospecific reactions

a) Stereodivergent cross-coupling of chiral transmetallating agents.



b) This work: stereodivergent cross-coupling of chiral alkyl electrophiles.



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[10] For a discussion, see: Molander, G. A.; Wisniewski, S. R. *J. Am. Chem. Soc.* **2012**, *134*, 16856.

[11] For labeling studies, see: (a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. (b) Ridgway, B. H.; Woerpel, K. A. *J. Org. Chem.* **1998**, *63*, 458. (c) Matos, K.; Soderquist, J. A. *J. Org. Chem.* **1998**, *63*, 461. (d) Taylor, B. L. H.; Jarvo, E. R. *J. Org. Chem.* **2011**, *76*, 7573.

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[13] (a) LaBadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 669. (b) Kells, K. W.; Chong, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 15666. (c) Sandrock, D. L.; Jean-Gérard, L.; Chen, C.-Y.; Dreher, S. D.; Molander, G. A. *J. Am. Chem. Soc.* **2010**, *132*, 17108. (d) Ohmura, T.; Awano, T.; Suginome, M. *J. Am. Chem. Soc.* **2010**, *132*, 13191. (e) Lee, J. C. H.; McDonald, R.; Hall, D. G. *Nat. Chem.* **2011**, *3*, 894.

[14] (a) Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793. (b) Hiyama, T. *J. Organomet. Chem.* **2002**, *653*, 58.

[15] For enantiodivergent reactions of alkyllithium reagents: Stymiest, J. L.; Bagutski, V.; French, R. M.; Aggarwal, V. M. *Nature*, **2008**, *456*, 778.

In this Chapter, we demonstrate catalyst control of the stereochemical course with respect to the *electrophilic* partner in a cross-coupling reaction. Stereospecific nickel-catalyzed cross-coupling reactions of benzylic alcohol derivatives typically proceed with inversion at the electrophilic carbon.[16,17] Nickel-catalyzed cross-coupling of benzylic esters where the achiral ligand structure dictates if the reaction proceeds with retention or inversion (Scheme 1.1b). Use of SIMes, an N-heterocyclic carbene (NHC) ligand, affords inversion, while PCy_3 gives retention. To the best of our knowledge, these results constitute the first cross-coupling reactions of alkyl electrophiles that proceed via two distinct stereospecific mechanistic pathways to provide either retention or inversion at the electrophilic carbon.

In previous work, we established the synthesis of enantioenriched triarylmethanes by stereospecific nickel-catalyzed cross-coupling of ethers with aryl Grignard reagents.[16b] As part of our ongoing interest in developing nickel-catalyzed stereospecific reactions of alkyl electrophiles, we chose to examine cross-coupling reactions of arylboronic esters for triarylmethane synthesis. The functional group tolerance and availability of a wide range of boronic esters makes them attractive coupling partners.

1.2 Development of a Stereospecific Cross-Coupling Reaction of Arylboronic Esters

We began by examining a range of benzylic alcohol derivatives (Table 1.1). Our initial reaction conditions resulted in a modest conversion of carbonate **(*S*)-1.4** and low enantiospecificity (es) (entry 1).[18] To our surprise, in contrast to the Kumada coupling, the product, **(*R*)-1.6**, results

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[16] (a) Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. *J. Am. Chem. Soc.* **2011**, *133*, 389. (b) Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790. (c) Greene, M. A.; Yonova, I. M.; Williams, F. J.; Jarvo, E. R. *Org. Lett.* **2012**, *14*, 4293. (d) For a review, see: Taylor, B. L. H.; Jarvo, E. R. *Synlett*, **2011**, *19*, 2761.

[17] For recent studies of the stereochemical course of nickel-catalyzed reactions of epoxides and aziridines, see: (a) Beaver, M. G.; Jamison, T. F. *Org. Lett.* **2011**, *13*, 4140. (b) Sylvester, K. T.; Wu, K.; Doyle, A. G. *J. Am. Chem. Soc.* **2012**, *134*, 9541. (c) Lin, B. L.; Clough, C. R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 2890.

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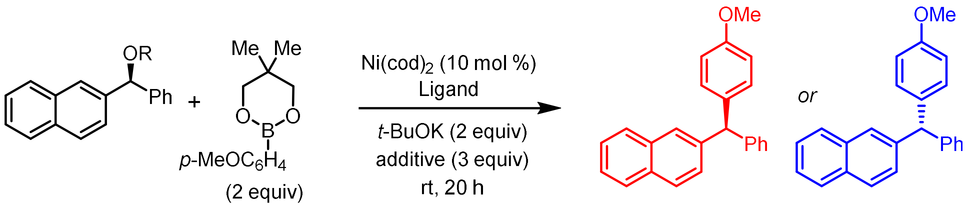
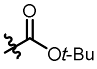
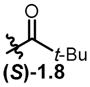
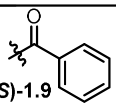
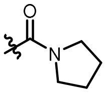
from *retention* at the electrophilic carbon. An improvement to 43% es was observed when the solvent was changed from toluene to THF (entry 2). Alcohol additives further improved the yield and stereochemical fidelity of the reaction, with *n*-BuOH providing the highest es, 87% (entry 4). More sterically encumbered alcohols provided more modest improvements, while water and the electron-deficient alcohol trifluoroethanol proved detrimental to the reaction (entries 3, 5, and 7). The enantiospecificity of the reaction showed a marked dependence on the identity of the leaving group. While the use of pivalate **(*S*)-1.8** in the cross-coupling reaction resulted in lower enantiomeric excess of the product (entry 8), the benzoate and carbamate derivatives **(*S*)-1.9** and **(*S*)-1.4** showed a significant increase in product ee, providing 91 and 95% es, respectively (entries 8, 10, and 12). An additional small improvement in yield and es resulted from using a 1:1 mixture of THF/toluene as the solvent (c.f. entries 12 and 15).

Table 1.1. Optimization of Stereospecific Suzuki Cross-coupling



(*R*)-1.6 **(*S*)-1.6**

Entry	R	ligand^a	solvent	additive	% yield^b	es^c	retention/ inversion
1	 **(*S*)-1.7**	PCy_3	PhMe	none	46	7	retention
2		PCy_3	THF	none	53	43	retention
3		PCy_3	THF	H_2O	74	10	retention
4		PCy_3	THF	*n*-BuOH	76	87	retention
5		PCy_3	THF	*i*-PrOH	46	78	retention
6		PCy_3	THF	*t*-BuOH	55	43	retention
7		PCy_3	THF	F_3CCH_2OH	< 5	na	retention
8	 **(*S*)-1.8**	PCy_3	THF	*n*-BuOH	53	76	retention
9		SIMes	THF	*n*-BuOH	60	77	inversion
10	 **(*S*)-1.9**	PCy_3	THF	*n*-BuOH	57	91	retention
11		SIMes	THF	*n*-BuOH	83	>99	inversion
12	 **(*S*)-1.4**	PCy_3	THF	*n*-BuOH	62	95	retention
13		PCy_3	THF/PhMe	none	67	35	retention
14		SIMes	THF/PhMe	none	82	92	inversion
15		**PCy_3**	**THF/PhMe**	***n*-BuOH**	**88**	**99**	**retention**
16		**SIMes**	**THF/PhMe**	***n*-BuOH**	**84**	**99**	**inversion**

[a] PCy_3 (20 mol %), SIMes (11 mol %). [b] Isolated yield after column chromatography. [c] Enantiospecificity (es)=$ee_{product}/ee_{starting\ material}$ x100%.

We examined other ligands[19] under the reaction conditions and found that the NHC ligand SIMes[20] afforded comparable yields and enantiospecificity of **1.6**, however, the major product was the (*S*)-enantiomer, resulting from *inversion* at the electrophilic carbon.[21] Catalyst-control of the stereochemical outcome of the reaction was consistent across the range of esters and carbamates that we examined: PCy_3 and SIMes reliably afforded opposite enantiomers of product (entries 8–11, 15 and 16).[22] Under the optimal reaction conditions, addition of *n*-BuOH was found to improve stereochemical fidelity when using either ligand (c.f. entries 13–16).

1.3 Investigation of Scope in Aryl Boronic Ester

Having optimized reaction conditions for the stereospecific synthesis of either enantiomer of product, we turned our attention to the scope of the reaction with respect to the boronic ester (Table 1.2). Electron-donating and withdrawing substituents on the arylboronic ester are well tolerated under the reaction conditions (entries 1–6). Reaction conditions are mild and allow for broad functional group tolerance. Boronic esters containing ketone, free alcohol and carbamate functional groups all undergo cross-coupling in good yield and es (entries 9–13). Heterocyclic boronic esters including pyrimidine, furan, and indole undergo smooth cross-coupling (entries 14–19). The reaction conditions developed for the formation of either enantiomer of **1.6** are general across the range of boronic esters that we examined: of 20 examples, 18 provide high es. Therefore, by choosing the appropriate ligand, PCy_3 or SIMes, either enantiomer of a given product can be obtained from the same enantiomer of starting material.

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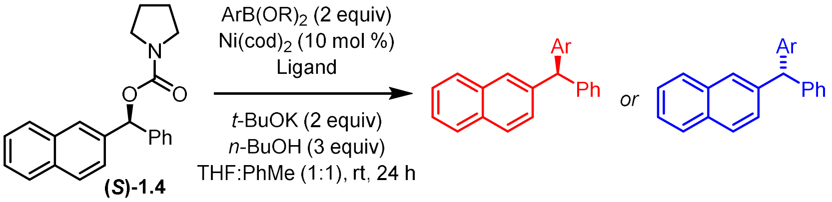
[19] For results with other ligands, see the Experimental Details (table 1.4)

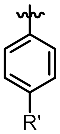
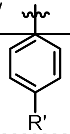
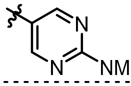
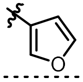
[20] SIMes = 1,3-Bis(2,6-diisopropylphenyl)-4,5-di-hydroimidazoliumtetrafluoroborate

[21] Comparison of NHC to PR_3: (a)Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 841. (b)Dorta, R., Stevens, E. D., Scott, N. M., Costabile, C., Cavallo, L., Hoff, C. D., Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127,2485.* (c)Kelly, R. A., III; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202.

[22] Changing PCy_3 loading from 20 mol % to 11 mol % does not affect the stereochemical outcome; see the Experimental Details.

Table 1.2. Investigation of Scope with respect to Aryl Boronic Ester[a]



Entry	Ar	ligand[b]	yield (%)[c]	SM ee (%)[d]	product ee (%)[d]	es (%)	retention/ inversion
1	 R' = OMe	PCy_3	88	93	92	98	retention
2	OMe	SIMes	84	93	93	>99	inversion
3	NMe_2	PCy_3	86	93	92	99	retention
4	NMe_2	SIMes	71	93	92	98	inversion
5	F	PCy_3	82	93	90	97	retention
6	F	SIMes	80	97	88	91	inversion
7	CF_3	PCy_3	88	97	57	59	retention
8	CF_3	SIMes	70	93	91	98	inversion
9	COMe	PCy_3	76	93	89	96	retention
10	COMe	SIMes	99	98	97	99	inversion
11	 R' = CH_2OH	PCy_3	67	93	82	88	retention
12	CH_2NHBoc	PCy_3	84	93	91	98	retention
13	CH_2NHBoc	SIMes	84	98	95	97	inversion
14		PCy_3	86	93	89	96	retention
15[d]		SIMes	75	98	92	94	inversion
16		PCy_3	79	93	94	>99	retention
17		SIMes	65	98	82	84	inversion
18		PCy_3	90	93	93	99	retention
19		SIMes	71	93	92	98	inversion

[a]All data are average of two experiments unless otherwise indicated. [b]PCy3 (20 mol %), SIMes (11 mol %).
[c]Isolated yield after column chromatography. [d]Determined by chiral SFC chromatography. [e]Data obtained from a single experiment.

1.4 Stereochemical Course of the Cross-Coupling Reaction

To demonstrate the stereochemical course of the reaction with either catalyst, we utilized X-ray crystallographic analysis. We first showed that the reaction proceeds with inversion when SIMes is used as the ligand by comparison of the optical rotation of the triarylmethane **(*R*)-1.12** with the literature value (Scheme 1.2a).[23,24] This product corresponds to net inversion at the benzylic carbon during the Suzuki–Miyaura cross-coupling reaction. Previous work in our group demonstrated that cross-coupling of aryl Grignard reagents and benzylic ethers also results in inversion at the benzylic carbon and assigned the absolute configuration of **(*R*)-1.12** based on X-ray crystallographic analysis. The stereochemical course of the Suzuki–Miyaura cross-coupling

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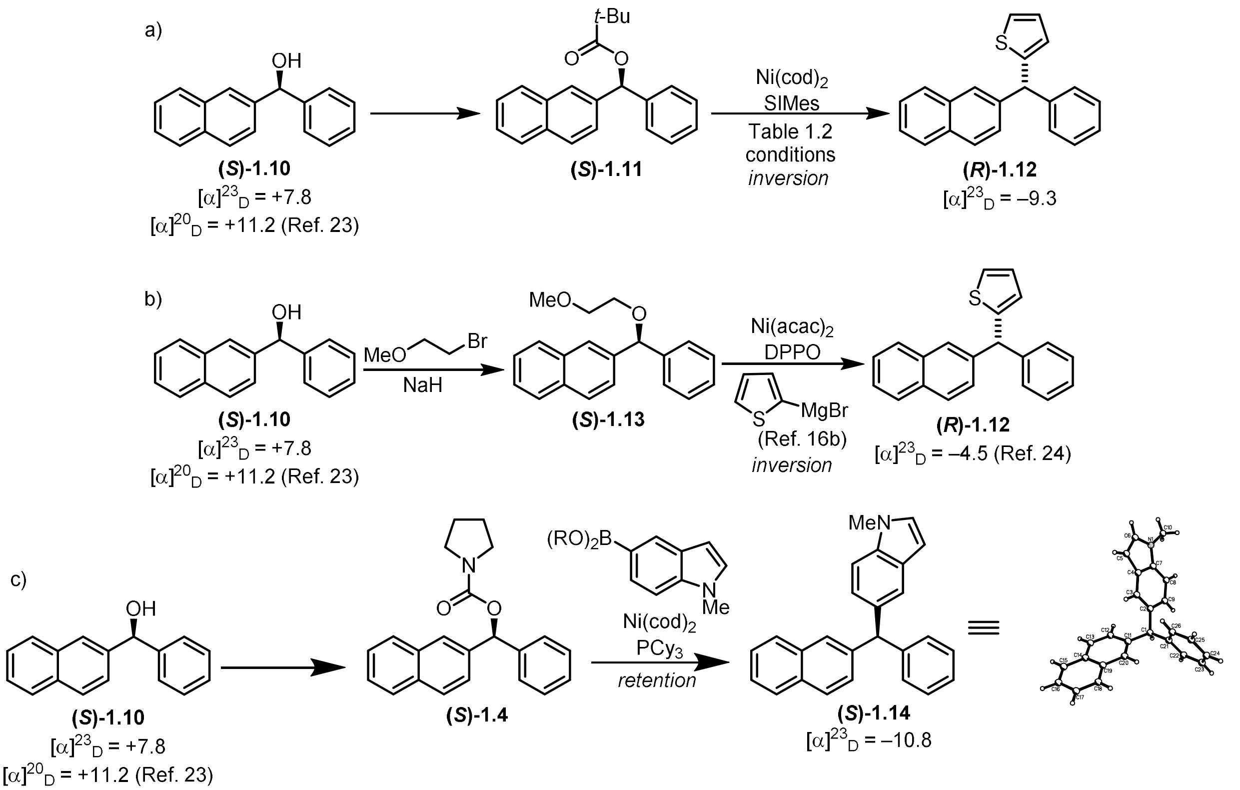
[23] For optical rotation data for **1.10**, see: (a) Yamamoto, Y.; Kurihara, K.; Miyaura, N. *Angew. Chem. Int. Ed.* **2009**, *48*, 4414. (b) Shannon, J.; Bernier, D.; Rawson, D.; Woodward, S. *Chem. Commun.* **2007**, 3945. (c) Tjosaas, F.; Anthonsen, T.; Jacobsen, E. E. *ARKIVOC* **2008**, (6), 8190.

[24] For characterization data for **1.12** including optical rotation and X-ray crystallographic data, see: Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 7790.

reaction when PCy_3 is used as the ligand provides the opposite enantiomer. Based on the absolute configuration of ***(S)*-1.14**, the reaction proceeds with retention at the benzylic carbon (Scheme 1.2c).

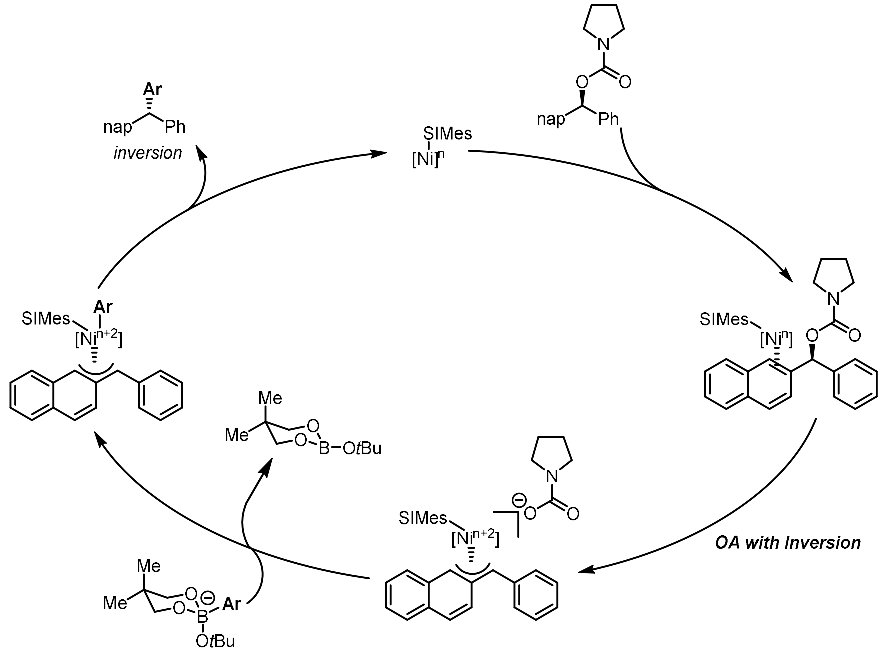
Scheme 1.2. Demonstration of stereochemical course of cross-coupling reaction



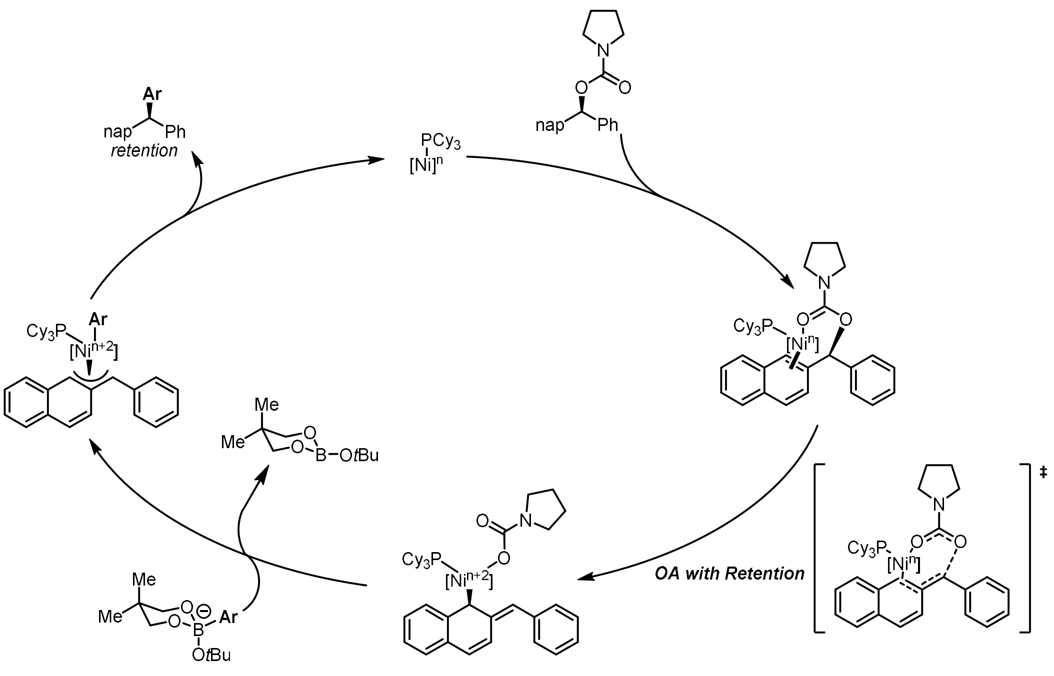
A mechanistic model for obtaining either product of retention or inversion is shown in Scheme 1.3b. We propose that when PCy_3 ligand is employed, the carbamate leaving group coordinates to the nickel catalyst. This coordination event directs the oxidative addition of the catalyst to the substrate, resulting in oxidative addition with retention. Transmetallation followed by reductive elimination with retention leads to formation of product with overall retention. In contrast, when SIMes is used as the ligand, coordination of the carbamate to the catalyst prior to oxidative addition does not occur. Without precoordination of the nickel catalyst to the leaving group, oxidative addition proceeds with inversion, ultimately affording triarylmethane products with overall inversion.

Scheme 1.3. Current mechanistic model for stereodivergent pathways using PCy_3 or SIMes

a) Catalytic cycle for Ni-SiMes catalyst; oxidative addition with *inversion* of configuration



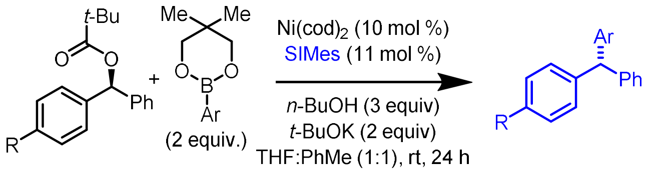
b) Catalytic cycle for Ni-PCy_3 catalyst; oxidative addition with *retention* of configuration

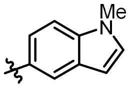
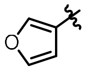
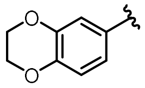


1.5 Scope of the Oxidative Addition Partner

We set as our goal the cross-coupling of oxidative addition partners that do not include a naphthalene moiety. Electrophiles that only have simple benzene rings are typically less reactive in cross-coupling reactions,[16c] and were not competent for triarylmethane synthesis via Kumada coupling.[16b] Indeed, neither the corresponding carbamates nor the use of PCy$_3$ as ligand provide acceptable yields of product. However, benzhydryl pivalates undergo smooth cross-coupling under our optimized reaction conditions when SIMes is used as the ligand (Table 1.3). Efficient cross-coupling was achieved for pivalates with a range of arylboronic esters, including an indoleboronic ester (entries 1–3). Heterocyclic functionality was also tolerated on the electrophile: furan- and benzodioxane- substituted pivalates couple in good yield and excellent es (entries 4 and 5).

Table 1.3. Scope of Substrates Bearing Non-extended Arenes [a]



Entry	R'	Ar	yield (%)[b]	SM ee (%)[c]	product ee (%)[c]	es (%)
1	Ph	*p*-MeOC$_6$H$_4$	85	96	84	88
2	Ph	*p*-(Me$_2$N)C$_6$H$_4$	75	82	79	96
3	Ph		66	96	96	>99
4			80	93	87	94
5			60	93	93	99

[a] All data are average of two experiments. [b] Isolated yield after column chromatography. [c] Determined by chiral SFC chromatography.

1.6 Conclusions

In summary, we have developed a nickel-catalyzed Suzuki-Miyaura cross-coupling reaction for the synthesis of enantioenriched triarylmethanes. Reactions proceed with high stereochemical fidelity. Achiral ligand identity controls if the reaction proceeds with inversion or retention at the electrophilic carbon; therefore either enantiomer of product can be formed from a single enantiomer of starting material. This method expands the range of triarylmethanes that may be prepared in enantioenriched form, as simple benzhydryl pivalates and a variety of functionalized arylboronic esters, including heterocyclic compounds, can be used in the reaction.

1.7 Experimental Details

General Procedures

All reactions were carried out under an atmosphere of N_2, or Ar when noted. All glassware was oven- or flame-dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and toluene (PhMe) were degassed with Ar and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 ºC for 12 h) to remove H_2O. All other solvents utilized were purchased "anhydrous" commercially, or purified as described. ^1H NMR spectra were recorded on Bruker DRX-400 (400 MHz ^1H, 100 MHz ^{13}C, 376.5 MHz ^{19}F), GN-500 (500 MHz ^1H, 125.7 MHz ^{13}C), or CRYO-500 (500 MHz ^1H, 125.7 MHz ^{13}C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), triplet (t), doublet of triplets (dt), doublet of doublet of triplets (ddt), triplet of triplets (tt), quartet (q), multiplet (m)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 ºC. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum 1000 FT-IR Systems and are reported in terms of frequency of absorption (cm^{-1}). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F_{254} precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with $KMnO_4$, ceric ammonium molybdate (CAM), or *p*-anisaldehyde (PAA) solutions. Flash chromatography was performed using Silica Gel 60 (170-400 mesh) from Fisher Scientific. Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. Optical rotations were measured on a Rudolph Research

Analytical Autopol IV Automatic Polarimeter. SFC determinations of enantiopurity were performed on a Berger Analytical instrument using a Daicel™ Chiralpak® column (OD-H, OJ-H, or AD-H; 100 bar, 50 °C, 215 nm). High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. Boronic esters were prepared from the corresponding boronic acids and 2,2-dimethylpropane-1,3-diol.[25] Boronic acids were generously donated from Frontier, stored at 4 ºC, and used as received. 1,8-bis(1,5-cyclooctadiene)nickel was purchased from Strem, stored in a glovebox freezer (–20 °C) under an atmosphere of N_2, and used as received. Tricyclohexylphosphine (PCy_3), (1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydroimidazoliumtetrafluoroborate (SIMes), and tris(di-benzylideneacetone)dipalladium ($Pd_2(dba)_3$) were purchased from Strem, stored in a glovebox, and used as received. All other reagents were purchased commercially and used as received.

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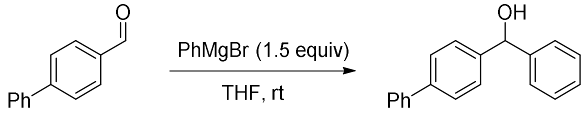
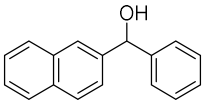
[25] Tivola, B. P.; Deagostino, A.; Prandi, C.; Venturello, P. *Org. Lett.* **2002**, *4*, 1275.

Synthesis and Characterization of Substrates

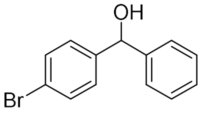
A. Representative procedure for synthesis of diarylmethyl alcohols.



***Rac*-1.15** In a flame-dried round-bottom flask, to a solution of biphenyl-4-carboxaldehyde (1.04 g, 5.68 mmol, 1.00 equiv) in THF (10 mL) was added phenylmagnesium bromide (0.71 M in THF, 12 mL, 8.5 mmol, 1.5 equiv). After stirring at room temperature for 4 h, saturated ammonium chloride (10 mL) was added and the reaction was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine (3 x 5 mL), dried over $MgSO_4$, and concentrated in vacuo to afford ***rac*-1.15** as a white solid (1.2 g, 4.7 mmol, 55%). Analytical data are consistent with the values listed for **(*S*)-1.15** (vide infra).

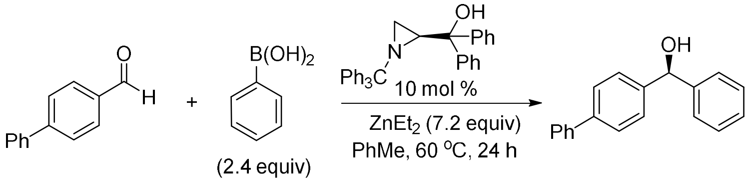


***Rac*-1.10** Using the representative procedure A outlined above, the following amounts of reagents were used: 2-naphthaldehyde (6.24 g, 40.0 mmol, 1.00 equiv), phenylmagnesium bromide (58 mL, 0.83 M in THF, 48 mmol, 1.2 equiv), and THF (25 mL). The reaction mixture was purified by silica gel flash column chromatography (5–20% EtOAc/hexanes) to afford the product as a white solid (6.74 g, 28.7 mmol, 72%). Analytical data are consistent with the values listed for **(*S*)-1.10** (vide infra).



***Rac*-1.16** Using the representative procedure A outlined above, the following amounts of reagents were used: 4-bromobenzaldehyde (1.85 g, 10.0 mmol, 1.00 equiv), phenylmagnesium bromide (7.0 mL, 1.7 M in THF, 12 mmol, 1.2 equiv), and THF (10 mL). The crude reaction mixture was purified by flash chromatography (5–20% EtOAc/hexanes) to afford the product as a white solid (1.92 g, 7.29 mmol, 73%). Analytical data is consistent with the values listed below for **(*S)*-1.16**.

B. *Representative procedure for enantioselective synthesis of diarylmethyl alcohols by asymmetric arylation.*



Enantioenriched alcohols were prepared according to a modified procedure of Braga and co-workers.[26]

(*S*)-1.15 To a solution of phenylboronic acid (0.732 g, 6.00 mmol, 2.40 equiv) in toluene (10 mL) was added diethylzinc (18 mL, 18 mmol, 1.0 M in toluene, 7.2 equiv), and the solution was allowed to stir at 60 °C for 12 h. Upon cooling to room temperature, (*S*)-(1-tritylaziridin-2-yl)diphenylmethanol (0.084 g, 0.06 mmol, 0.01 equiv) was added as a solution in toluene (5 mL) and the reaction mixture was allowed to stir for 10 minutes before the addition of a solution of biphenyl-4-carboxaldehyde (0.456 g, 2.50 mmol, 1.00 equiv) in toluene (5 mL). After stirring 12 h at room temperature, 1 N hydrochloric acid (10 mL) was added and the product was extracted

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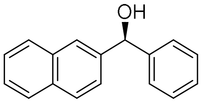
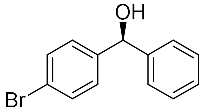
[26] Braga, A. R.; Paixao, M. W.; Westeman, B.; Schneider, P. H.; Wessjohan, L.A. *J. Org. Chem.* **2008**, *73*, 2879.

with EtOAc (3 x 10 mL). The combined organics were washed with brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. The product was purified by flash column chromatography (0–1% EtOAc/benzene) and then recrystallized from hexanes and EtOAc to upgrade the ee (0.488 g, 1.85 mmol, 75% yield, 96% ee). **TLC R$_f$** = 0.2 (benzene); **m.p.** = 90–92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (m, 4H), 7.40 (m, 6H), 7.32 (m, 4H), 5.81 (s, 1H), 2.32 (d, *J* = 2.8, 1H); **^{13}C NMR** δ (100 MHz, $CDCl_3$) δ 143.8, 142.9, 140.9, 140.6, 128.9, 128.7, 127.8, 127.4, 127.38, 127.2, 127.1, 126.7, 76.1; **IR** (neat) 3361, 3029, 1408, 1006, 763 cm^{-1}; **HRMS (**TOF MS ES+) *m / z* calcd for $C_{19}H_{16}O$ $(M + Na)^+$ 283.1099, found 283.1110; **[α]^{23}$_D$** +4.72 (*c* 1.10, $CHCl_3$); **SFC** analysis (AD-H, 15% IPA, 3 mL/min) indicated 96% ee: t_R (major) = 18.9 minutes, t_R (minor) = 20.5 minutes.

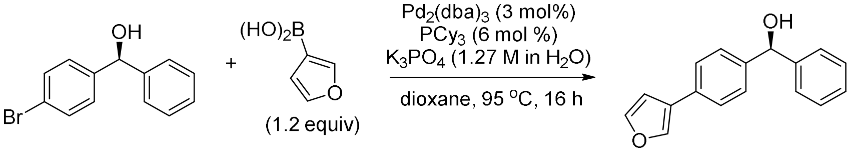


(*S*)-1.10 Using the representative procedure B outlined above, the following amounts of reagents were used: phenylboronic acid (0.732 g, 6.00 mmol, 2.4 equiv), diethylzinc (18 mL, 18 mmol, 1.0 M in toluene), (*S*)-diphenyl(1-tritylaziridin-2-yl)methanol (116 mg, 0.250 mmol, 0.100 equiv), and 2-naphthaldhyde (0.390 g, 2.50 mmol, 1.00 equiv). The product was purified by flash chromatography (10–20% EtOAc/hexanes) to afford the product as a white solid (0.608 g, 2.59 mmol, 93%, 89% ee). The product was then recrystallized from hexanes to upgrade the ee (99% ee). Analytical data is consistent with literature values.**Error! Bookmark not defined.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.82 (dt, *J* = 9.2, 2.6 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.49–7.40 (m, 5H), 7.35 (t, *J* = 7.0 Hz, 2H), 7.29 (dt, *J* = 7.4, 1.5 Hz, 1H), 6.02 (d, *J* = 3.5 Hz, 1H), 2.29 (d, *J* = 3.5 Hz, 1H); **[α]^{23}$_D$** +7.8 (*c* 0.92, $CHCl_3$), literature [α]^{20}$_D$ +11.2 (*c* 0.83, $CHCl_3$); **SFC** analysis (OD-H, 20% 2-propanol, 3 mL/min) indicated >99% ee: t_R (major) = 6.4 min, t_R (minor) = 7.3 min.



(*S*)-1.16 Using the representative procedure B outlined above, the following amounts of reagents were used: phenylboronic acid (0.732 g, 6.00 mmol, 2.4 equiv), diethylzinc (18 mL, 18 mmol, 1.0 M in toluene), (*S*)-(1-tritylaziridin-2-yl)diphenylmethanol (116 mg, 0.250 mmol, 0.100 equiv), and 4-bromobenzaldehyde (0.463 g, 2.50 mmol, 1.00 equiv). The product was purified by flash chromatography (10–20% EtOAc/hexane) to afford the product as a white solid (0.608 g, 2.31 mmol, 93%, 92% ee). The product was then recrystallized from hexanes to yield higher enantiopurity (96% ee). Analytical data is consistent with literature values.[27] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.36–7.30 (m, 4H), 7.29–7.25 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.76 (d, *J* = 3.3 Hz, 1H), 2.34 (d, *J* = 3.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.5, 142.8, 131.7, 128.8, 128.3, 128.0, 126.6, 121.5, 75.8; **$[\alpha]^{23}_D$** +17.5 (*c* 1.65, $CHCl_3$); **SFC** analysis (AD-H, 10% IPA, 2.5 mL/min) indicated 96% ee: t_R (major) = 10.4 minutes, t_R (minor) = 9.8 minutes.

C. *Representative procedure for the Suzuki cross-coupling of aryl bromide* ***(S)-1.17*** *with aryl boronic acids.*



(*S*)-1.17 The product was prepared according to a modified procedure by Fu and co-workers.[28] Tris(dibenzylideneacetone)dipalladium (55 mg, 0.060 mmol, 0.030 equiv) and tricyclohexylphosphine (39 mg, 0.14 mmol, 0.070 equiv) were weighed out into a flame dried two neck, round bottom flask inside a glovebox. The flask was fitted with septa, removed from the

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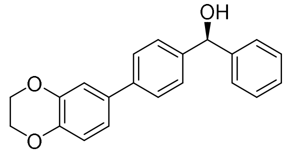
[27] Wu, X.; Liu, X.; Zhao, G. *Tetrahedron: Asymmetry* **2005**, *16*, 2299.

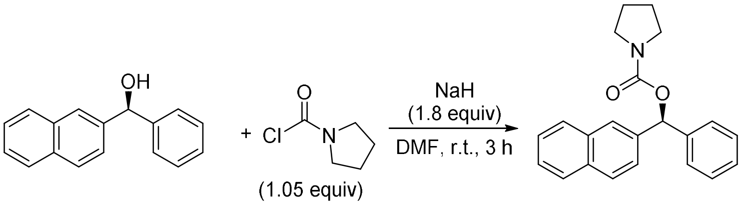
[28] Kudo, N.; Perseghini, M.; Fu, G. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 1282.

glovebox, and 3-furanboronic acid (0.262 g, 2.20 mmol, 1.10 equiv), ***(S)*-1.16** (0.526 g, 2.00 mmol, 1.00 equiv), aqueous potassium phosphate (2.7 mL, 3.4 mmol, 1.3 M in H_2O, 1.7 equiv) and dioxane (6 mL) were added. The reaction flask was fitted with a reflux condenser and heated to 95 ºC for 16 h. After cooling, the solvent was removed under reduced pressure. The resultant residue was purified by flash column chromatography (10–20% EtOAc/hexane) to afford ***(S)*-1.17** as a yellow solid (0.437 g, 1.75 mmol, 87%, 97% ee). **TLC R_f** = 0.2 (4:1 hexane/EtOAc); **m.p.** = 97–99 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.45 (s, 2H), 7.43 (s, 1H), 7.37 (t, *J* = 8.2 Hz, 3H), 7.33 (t, *J* = 7.3 Hz, 3H), 7.27 (d, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 5.82 (s, 1H), 2.32 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.9, 143.8, 142.7, 138.6, 131.8, 128.7, 127.8, 127.1, 126.7, 126.2, 126.1, 108.9, 76.1; **IR** (neat) 3279, 1160, 1012, 780, 699 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{17}H_{14}O_2$ $(M + Na)^+$ 273.0891, found 273.0883; **$[\alpha]^{29}_D$** –37.3 (*c* 1.00, $CHCl_3$); **SFC** analysis (OD-H, 13% IPA, 2.5 mL/min) indicated 97% ee: t_R (major) = 12.9 minutes, t_R (minor) = 14.7 minutes.



***(S)*-1.18** Using representative procedure C outlined above, the following amounts of reagents were used: tris(dibenzylideneacetone)dipalladium (28 mg, 0.030 mmol, 0.030 equiv), tricyclohexylphosphine (20 mg, 0.07 mmol, 0.070 equiv), 1,4-benzodioxane-6-boronic acid (0.198 g, 1.10 mmol, 1.10 equiv), ***(S)*-1.16** (0.263 g, 1.00 mmol, 1.00 equiv), aqueous potassium phosphate (1.4 mL, 1.7 mmol, 1.3 M in H_2O, 1.7 equiv) and dioxane (3 mL). The product was purified by flash column chromatography (10–30% EtOAc/hexane) to afford ***(S)*-1.18** as a brown solid (0.296 g, 0.929 mmol, 93%, 96% ee). **TLC R_f** = 0.2 (4:1 hexane/EtOAc); **TLC R_f** = 0.3 (30% EtOAc/hexanes); **m.p.** = 108–110 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.7 Hz, 2H), 7.40 (q, J = 7.8 Hz, 4H), 7.34 (t, J = 7.2 Hz, 2H), 7.27 (d, J = 7.3 Hz, 1H), 7.08 (d, J = 1.9 Hz, 1H), 7.04 (dd, J = 8.5, 2.1 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 5.85 (s, 1H), 4.36 (s, 4H), 2.35 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.9, 143.8, 143.3, 142.5, 140.0, 134.5, 128.7, 127.7, 127.1, 127.0, 126.6, 120.2, 117.7, 115.9, 76.2, 64.6, 64.5; **IR** (neat) 3550, 1494, 1304, 1284, 1070 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{21}H_{18}O_3$ $(M + Na)^+$ 341.1154, found 341.1147; **$[\alpha]^{29}_D$** +3.1 (*c* 1.04, $CHCl_3$); **SFC** analysis (AD-H, 14% IPA, 2.5 mL/min) indicated 96%: t_R (major) = 6.9 minutes, t_R (minor) = 8.8 minutes.

Preparation of protected carbinols.



(*S*)-1.4 The product was prepared according to a modified procedure by Zhang and co-workers.[29] To a suspension of NaH (0.153 g, 6.37 mmol, 1.80 equiv) in DMF (3 mL) was added a solution of **(*S*)-1.10** (0.823 g, 3.54 mmol, 1.00 equiv) in DMF (2 mL) at 0 °C. The mixture was stirred for 1 h before addition of neat 1-pyrollidinecarbonyl chloride (0.41 mL, 3.7 mmol, 1.1 equiv) at room temperature. After stirring for 3 h, the reaction was quenched with saturated aqueous ammonium chloride (6 mL), and the product was extracted with methylene chloride (3 x 10 mL). The combined organics were washed with brine (5 mL), dried over Na_2SO_4, and concentrated in vacuo. The product was purified by flash column chromatography (20% EtOAc/hexane) to afford **(*S*)-1.4** as a white solid (0.963 g, 2.91 mmol, 83%, 94% ee): **TLC R_f** = 0.2 (20% EtOAc/hexanes); **m.p.** = 151–153 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.82–7.77 (m, 3H), 7.47–7.44 (m, 3H),

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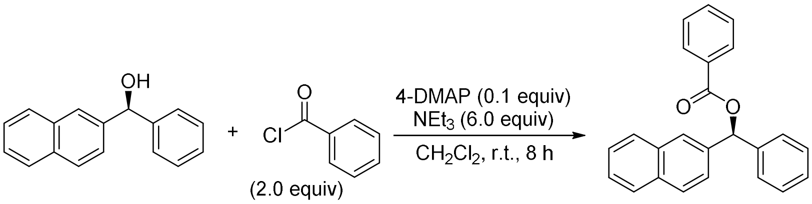
[29] DeKorver, K. A.; Johnson, W. L.; Zhang, Y.; Hsung, R. P.; Dai, H.; Deng, J.; Lohse, A. G.; Zhang, Y. S. *J. Org. Chem.* **2011**, *76*, 5092.

7.41 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 3.40 (t, *J* = 6.7 Hz, 2H), 1.90 (dt, *J* = 13.3, 6.7 Hz, 2H), 1.84 (dt, *J* = 13.3, 6.7 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.2, 141.4 138.7, 133.2, 133.0, 128.5, 128.4 128.3, 127.8, 127.7, 127.2, 126.3, 126.2, 126.1, 125.2, 77.4, 46.4, 46.0, 25.9, 25.0; **IR** (neat) 1690, 1412, 1102, 828, 765 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{21}NO_2$ $(M + Na)^+$ 354.1470, found 354.1463; **$[\alpha]^{29}_D$** +45.9 (*c* 1.15, $CHCl_3$); **SFC** analysis (OD-H, 18% IPA, 2.5 mL/min) indicated 93% ee: t_R (major) = 7.1 minutes, t_R (minor) = 6.6 minutes.



(*S*)-1.9 The product was prepared according to a modified procedure by Hassner and co-workers.[30] To a 25 mL round bottom flask was added alcohol **(*S*)-1.10** (0.175 g, 0.750 mmol, 1.00 equiv), and 4-(dimethylamino)pyridine (9.0 mg, 0.075 mmol, 0.10 equiv). The flask was evacuated and backfilled with nitrogen before addition of methylene chloride (6 mL), triethylamine (0.48 mL, 4.5 mmol, 6.0 equiv), and benzoyl chloride (0.18 mL, 1.5 mmol, 2.0 equiv). After stirring for 8 h, the reaction was quenched with 1 M HCl (6 mL), and the product was extracted with methylene chloride (3 x 10 mL). The combined organics were washed with brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. The product was purified by flash column chromatography (5–10% EtOAc/hexane) to afford **(*S*)-1.9** as a white solid (0.177 g, 0.523 mmol, 70%, 89% ee): **TLC R$_f$** = 0.4 (10% EtOAc/hexanes); **m.p.** = 91–93 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.9 Hz, 2H), 8.00 (s, 1H), 7.91–7.90 (m, 3H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.61–7.53 (m, 6H), 7.45 (t, *J* = 7.1

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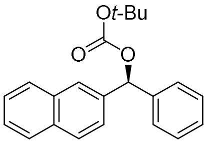
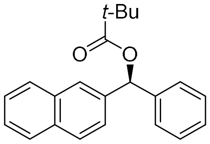
[30] Basel, Y.; Hassner, A. *J. Org. Chem.* **2000**, *65*, 6368.

Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.7, 140.3, 137.7, 133.3, 133.2, 133.1, 130.3, 130.0, 128.7, 128.6, 128.3, 128.2, 127.8, 127.4, 126.44, 126.40, 126.3, 125.1, 77.7; **IR** (neat) 1712, 1259, 1108, 732, 700 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{24}H_{18}O_2$ $(M + Na)^+$ 361.1205, found 361.1201; **$[\alpha]^{29}{}_D$** +10.0 (*c* 0.99, $CHCl_3$); **SFC analysis** (OD-H, 10.0% IPA, 2.5 mL/min) indicated 89% ee: t_R (major) = 6.5 minutes, t_R (minor) = 6.3 minutes.

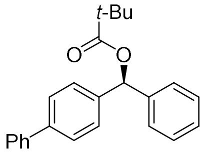


(*S*)-1.7 The product was prepared according to a modified procedure by Hassner and co-workers.[30] To a 25 mL round bottom flask was added alcohol **(*S*)-1.10** (0.234 g, 1.00 mmol, 1.00 equiv), and 4-(dimethylamino)pyridine (12 mg, 0.010 mmol, 0.10 equiv). The flask was evacuated and backfilled with nitrogen before addition of methylene chloride (8 mL), triethylamine (0.10 mL, 1.2 mmol, 1.2 equiv), and di-*tert*-butyl dicarbonate (0.228 g, 1.05 mmol, 1.05 equiv). After stirring for 8 h, the reaction was quenched with 1 M HCl (6 mL), and the product was extracted with methylene chloride (3 x 10 mL). The combined organics were washed with brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. The product was purified by flash column chromatography (5–10% EtOAc/hexane) to afford **(*S*)-1.7** as a white solid (0.284 g, 0.849 mmol, 85%, 88% ee): **TLC R_f** = 0.4 (9:1 hexane/EtOAc); **m.p.** = 90–92 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.83 (d, *J* = 7.0 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.48–7.45 (m, 2H), 7.43 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 1H), 1.47 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.1, 140.1, 137.6, 133.2, 133.1, 128.7, 128.5, 128.3, 128.1, 127.8, 127.2, 126.4, 126.3, 126.0, 125.0, 82.7, 80.0, 27.9; **IR** (neat) 1742, 1270, 1251, 1150, 1081 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{22}O_3$ $(M + Na)^+$ 357.1467, found 357.1467; **$[\alpha]^{29}{}_D$** –19.3 (*c* 0.90, $CHCl_3$); **SFC analysis** (AD-H, 5% IPA, 3.0 mL/min) indicated 88% ee: t_R (major) = 5.6

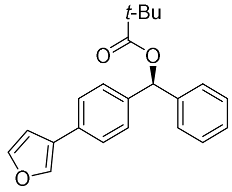
minutes, t_R (minor) = 6.1 minutes.



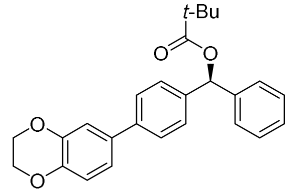
***(S)*-1.8** The product was prepared according to a modified procedure by Hassner and co-workers.[30] To a 25 mL round bottom flask was added alcohol ***(S)*-1.10** (0.281 g, 1.20 mmol, 1.20 equiv), and 4-(dimethylamino)pyridine (15 mg, 0.012 mmol, 0.10 equiv). The flask was evacuated and backfilled with nitrogen before addition of methylene chloride (8 mL), triethylamine (0.19 mL, 2.6 mmol, 2.2 equiv), and trimethylacetyl chloride (0.160 mL, 1.26 mmol, 1.05 equiv). After stirring for 8 h, the reaction was quenched with 1M HCl (6 mL), and the product was extracted with methylene chloride (3 x 10 mL). The combined organics were washed with brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. The product was purified by flash column chromatography (5–10% EtOAc/hexane) to afford ***(S)*-1.8** as a white solid (0.334 g, 1.05 mmol, 88%, 82% ee): **TLC R_f** = 0.5 (10% EtOAc/hexanes); **m.p.** = 80–83 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.48–7.45 (m, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 1.27 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.4, 140.6, 138.0, 133.2, 133.0, 128.6, 128.5, 128.3, 127.9, 127.8, 127.1, 126.4, 126.3, 126.1, 125.0, 76.8, 39.1, 27.3; **IR** (neat) 1721, 1276, 1148, 1123, 823 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{22}H_{22}O_2$ $(M + Na)^+$ 341.1518, found 341.1526; **$[\alpha]^{29}_D$** –37.4 (*c* 1.18, $CHCl_3$); **SFC analysis** (AD-H, 5.0% IPA, 3.0 mL/min) indicated 82% ee: t_R (major) = 6.8 minutes, t_R (minor) = 7.1 minutes.



(*S*)-1.19 The product was prepared according to a modified procedure by Zhang and co-workers.[29] NaH (500 mg, 20.8 mmol, 4.00 equiv) was suspended in 40 mL of dry DMF and cooled to 0 °C. To this solution, alcohol **(*S*)-1.15** (1.28 g, 4.92 mmol, 1.00 equiv) in dry DMF (10 mL) was added dropwise. The mixture was allowed to stir at 0 °C for 30 minutes after which pivaloyl chloride (4.3 mL, 35 mmol, 7.0 equiv) was added dropwise. The reaction was stirred at 0 °C for 1.5 hours then warmed to room temperature and stirred for 22 hours. The reaction was quenched by consecutive addition of water (5 x 2 mL) and stirring for 3 minutes. The reaction was diluted with more water (10 mL) and the organics were extracted with EtOAc (3 x 30 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by flash chromatography (0–1% Et_2O/petroleum ether) yielding **(*S*)-1.19** as a white solid (1.56 g, 4.53 mmol, 92%). **TLC R_f** = 0.4 (10% Et_2O:petroleum ether); **m.p.** = 109–110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 6.1, 1.9 Hz, 4H), 7.35 (m, 10H), 6.87 (s, 1H), 1.27 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.4, 140.8, 140.6, 139.8, 128.9, 128.7, 127.9, 127.8, 127.5, 127.40, 127.38, 127.2, 127.0, 76.5, 39.1, 27.3; **IR** (neat) 3029, 2974, 1722, 1275, 1138 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{24}H_{24}O_2$ $(M + Na)^+$ 367.1674, found 367.1681; **$[\alpha]^{23}_D$** –23.6 (*c* 1.09, $CHCl_3$); **SFC** analysis (AD-H, 10% IPA, 3 mL/min) indicated 96% ee: t_R (minor) = 4.0 minutes, t_R (major) = 6.4 minutes.



(*S*)-1.20 The product was prepared according to a modified procedure by Zhang and co-workers.[29] To a suspension of NaH (72 mg, 3.0 mmol, 2.0 equiv) in DMF (3 mL) was added a solution of **(*S*)-1.17** (0.374 g, 1.50 mmol, 1.00 equiv) in DMF (2 mL) at 0 ºC. The mixture was stirred for 1 h before addition of neat trimethylacetyl chloride (0.200 mL, 1.60 mmol, 1.05 equiv) at room temperature. After stirring for 3 h, the reaction was quenched with saturated aqueous ammonium chloride (6 mL), and the product was extracted with methylene chloride (3 x 10 mL). The combined organics were washed with brine (5 mL), dried over Na_2SO_4, and concentrated in vacuo. The product was purified by flash column chromatography (30% Et_2O/hexane) to afford **(*S*)-1.20** as a pale yellow solid (0.427 g, 1.28 mmol, 85%, 93% ee): **TLC R_f** = 0.2 (4:1 hexane/Et_2O); **m.p.** = 105–108 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.45 (s, 2H), 7.43 (s, 1H), 7.35 (s, 4H), 7.33 (s, 2H), 7.29–7.26 (m, 1H), 1.26 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.4, 143.8, 140.6, 139.5, 138.7, 132.1, 128.6, 127.9, 127.6, 127.0, 126.2, 126.1, 108.9, 76.5, 39.0, 27.3; **IR** (neat) 1724, 1159, 1138, 757, 699 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{22}O_3$ $(M + Na)^+$ 357.1467, found 357.1475; **$[\alpha]^{29}_D$** –26.0 (c 1.25, $CHCl_3$); **SFC** analysis (OJ-H, 8% IPA, 2.0 mL/min) indicated 93% ee: t_R (major) = 3.6 minutes, t_R (minor) = 4.2 minutes.

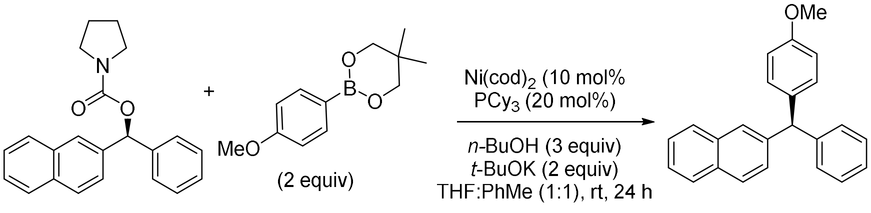


(*S*)-1.21 The product was prepared according to a modified procedure by Zhang and co-workers.[29] To a suspension of NaH (35 mg, 1.4 mmol, 1.8 equiv) in DMF (3 mL) was added a solution of

(*S*)-1.18 (0.254 g, 0.800 mmol, 1.00 equiv) in DMF (2 mL) at 0 ºC. The mixture was stirred for 1 h before addition of neat trimethylacetyl chloride (0.103 mL, 0.840 mmol, 1.05 equiv) at room temperature. After stirring for 3 h, the reaction was quenched with saturated aqueous ammonium chloride (6 mL), and the product was extracted with methylene chloride (3 x 10 mL). The combined organics were washed with brine (5 mL), dried over Na_2SO_4, and concentrated in vacuo. The product was purified by flash column chromatography (30% Et_2O/hexanes) to afford **(*S*)-1.21** as a tan solid (0.232 g, 0.576 mmol, 73%, 94% ee): **TLC R_f** = 0.1 (20% Et_2O/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.37–7.32 (m, 6H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.08 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.84 (s, 1H), 4.27 (s, 4H), 1.27 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.4, 143.8, 143.4, 140.7, 140.2, 139.3, 134.4, 128.7, 127.9, 127.4, 127.0, 126.9, 120.2, 117.7, 115.9, 76.5, 64.6, 64.5, 39.0, 27.3; **IR** (neat) 1723, 1494, 1309, 1147, 1068 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{26}H_{26}O_4$ $(M + Na)^+$ 425.1729, found 425.1715; **$[\alpha]^{29}_D$** –20.3 (c 0.96, $CHCl_3$); **SFC** analysis (OD-H, 30% MeOH, 2.5 mL/min) indicated 94% ee: t_R (major) = 6.9 minutes, t_R (minor) = 8.8 minutes.

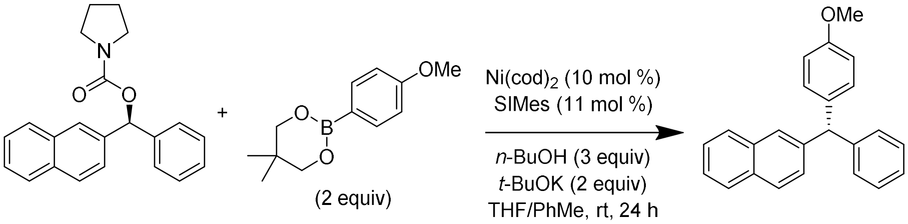
Procedures for Cross-Coupling Reactions

A. Procedure for the synthesis of products with retention (Table 2).



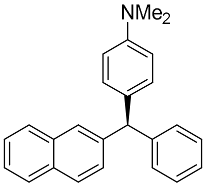
(*R*)-1.6 To a flame dried vial in a glovebox was added 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.20 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-methoxyphenyl)-1,3,2-dioxaborinane (88 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The reaction was stirred for 24 hours before removing the vial from the glovebox, opening to atmosphere, and running through a silica gel plug (1:1 Et_2O:hexane). The combined organics were concentrated in vacuo, internal standard (PhTMS, 0.20 mmol) was added and ^{1}H NMR yield was collected. The product was purified by flash chromatography (1–3% Et_2O/pentane) to afford **(*R*)-1.6** as a colorless oil. First run: (56.0 mg, 0.173 mmol, 86%, 93% ee). Second run: (56.4 mg, 0.174 mmol, 87%, 93% ee). Analytical data is consistent with literature values:[13b] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81–7.76 (m, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.72–7.67 (m, 1H), 7.46 (s, 1H), 7.42 (dt, *J* = 9.5, 3.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 3H), 7.24–7.19 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.65 (s, 1H), 3.78 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.2, 144.1, 142.0, 136.0, 133.5, 132.2, 130.6, 129.6, 128.4, 128.2, 128.0, 127.9, 127.8, 127.6, 126.4, 126.1, 125.7, 113.8, 56.2, 55.3; **$[\alpha]^{23}_D$** –0.77 (*c* 2.70, $CHCl_3$); **SFC** analysis (AD-H, 15% IPA, 2.5 mL/min) indicated 93% ee: t_R (major) = 13.9 minutes, t_R (minor) = 13.2 minutes.

B. Procedure for the synthesis of products with inversion of configuration.



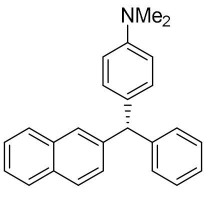
(*S*)-1.6 To a flame dried vial in a glovebox was added 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 μL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-methoxyphenyl)-1,3,2-dioxaborinane (88 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The reaction was stirred for 24 hours before removing the vial from the glovebox, opening to atmosphere, and running through a silica gel plug (1:1 Et_2O:hexane). The combined organics were concentrated in vacuo, internal standard (PhTMS, 0.20 mmol) was added and ^1H NMR yield was collected. The product was purified by flash chromatography (1–3% Et_2O/pentane) to afford **(*S*)-1.6** as a colorless oil. First run: (53.2 mg, 0.164 mmol, 82%, 93% ee). Second run: (56.0 mg, 0.173 mmol, 86%, 93% ee). Analytical data is consistent with the values listed above for **(*R*)-1.6** **$[\alpha]^{23}_D$** +2.1 (*c* 2.70, $CHCl_3$); **SFC** analysis (AD-H, 15% IPA, 2.5 mL/min) indicated 90% ee: t_R (major) = 13.2 minutes, t_R (minor) = 13.9 minutes.

Characterization Data for Products

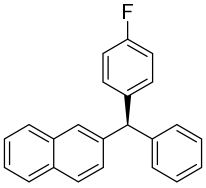


(*R*)-1.22 Using representative procedure A outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.20 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-

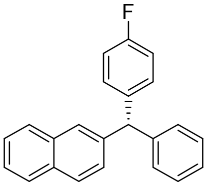
butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-dimethylaminophenyl)-1,3,2-dioxaborinane (83 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash chromatography (1–3% Et_2O/pentane) to afford the product as a colorless oil. First run: (49.8 mg, 0.148 mmol, 80%, 90% ee). Second run: (52.6 mg, 0.167 mmol, 84%, 90% ee). Analytical data is consistent with literature values:[13b] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80–7.75 (m, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.71–7.67 (m, 1H), 7.48 (s, 1H), 7.40 (dt, *J* = 9.4, 3.3 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.61 (s, 1H), 2.90 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.2, 144.6, 142.5, 133.6, 132.2, 131.8, 130.3, 129.6, 128.4 (2C), 128.0, 127.8, 127.7, 127.6, 126.3, 126.0, 125.6, 112.6, 56.2, 40.8; **IR** (neat) 3054, 3023, 2879, 1612, 1350 cm^{-1}; **$[\alpha]^{23}_D$** –9.43 (*c* 2.28, $CHCl_3$); **SFC** analysis (AD-H, 20% MeOH, 3 mL/min) indicated 92% ee: t_R (major) = 4.2 min, t_R (minor) = 4.8 min.



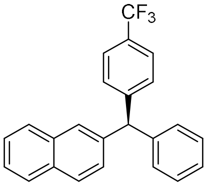
(*S*)-1.22 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-dimethylaminophenyl)-1,3,2-dioxaborinane (83 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash chromatography (1–3% Et_2O/pentane) to afford the product as a colorless oil. First run: (42.1 mg, 0.125 mmol 62%, 92% ee). Second run: (53.6 mg, 79%, 0.159 mmol, 92% ee). Analytical data is consistent with the values listed above for **(*R*)-1.22** **$[\alpha]^{23}_{D}$** +8.0 (*c* 1.00, $CHCl_3$); **SFC** analysis (AD-H, 20% MeOH, 3 mL/min) indicated 92% ee: t_R (major) = 3.9 min, t_R (minor) = 4.6 min.



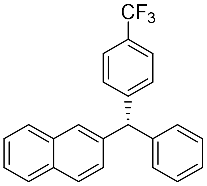
(*R*)-1.23 Using representative procedure A outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.2 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 μL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-fluorophenyl)-1,3,2-dioxaborinane (83 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash chromatography (1–3% Et_2O/pentane) to afford the product as a colorless oil. First run: (49.8 mg, 0.159 mmol, 80%, 90% ee). Second run: (52.6 mg, 0.168 mmol, 84%, 90% ee). Analytical data is consistent with literature values:[13b] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81–7.77 (m, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.71–7.67 (m, 1H), 7.45–7.39 (m, 3H), 7.31–7.21 (m, 4H), 7.15–7.07 (m, 4H), 6.97 (t, *J* = 8.8 Hz, 2H), 5.70 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.6 (d, *J* = 245 Hz), 143.6, 141.4, 139.5 (d, *J* = 3 Hz), 133.5, 132.3, 131.1 (d, *J* = 8 Hz), 129.6, 128.6, 128.1, 128.05, 127.99, 127.8, 127.7, 126.7, 126.2, 125.9, 115.3 (d, *J* = 21 Hz), 56.3; **$[\alpha]^{23}_{D}$** +4.5 (*c* 4.47, $CHCl_3$); **SFC** analysis (OJ-H, 12% IPA, 2.5 mL/min) indicated 90% ee: t_R (major) = 9.4 minutes, t_R (minor) = 8.7 minutes.



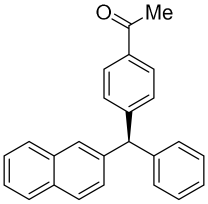
(*S*)-1.23 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-fluorophenyl)-1,3,2-dioxaborinane (83 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash chromatography (1–3% Et_2O/pentane) to afford the product as a colorless oil. First run: (49.8 mg, 0.159 mmol, 80%, 88% ee). Second run: (50.0 mg, 0.168 mmol, 84%, 88% ee). Analytical data is consistent with literature values:[13b] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81–7.77 (m, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.71–7.67 (m, 1H), 7.45–7.39 (m, 3H), 7.31–7.21 (m, 4H), 7.15–7.07 (m, 4H), 6.97 (t, *J* = 8.8 Hz, 2H), 5.70 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.6 (d, *J* = 245 Hz), 143.6, 141.4, 139.5 (d, *J* = 3 Hz), 133.5, 132.3, 131.1 (d, *J* = 8 Hz), 129.6, 128.6, 128.1, 128.05, 127.99, 127.8, 127.7, 126.7, 126.2, 125.9, 115.3 (d, *J* = 21 Hz), 56.3; **$[\alpha]^{23}_D$** –3.6 (*c* 4.10, $CHCl_3$); **SFC** analysis (OJ-H, 12% IPA, 2.5 mL/min) indicated 88% ee: t_R (major) = 9.7 minutes, t_R (minor) = 10.6 minutes.



(*R*)-1.24 Using representative procedure A outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.2 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.00 equiv), 5,5-dimethyl-2-(4-trifluoromethylphenyl)-1,3,2-dioxaborinane (103 mg, 0.400 mmol, 2.00 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (1% Et_2O/pentane) to afford the product as a colorless oil. First run: (64.4 mg, 0.178 mmol, 89%, 57% ee). Second run: (62.1 mg, 0.172 mmol, 86%, 57% ee). **TLC R_f** = 0.4 (pentane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85–7.79 (m, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.74–7.68 (m, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.49–7.41 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.29–7.22 (m, 4H), 7.14 (d, *J* = 7.6 Hz, 2H), 5.75 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.0, 142.9, 140.6, 133.5, 132.4, 130.0, 129.6, 128.9 (q, *J* = 32.4 Hz), 128.7, 128.3, 128.02, 128.00, 127.9, 127.7, 126.9, 126.4, 126.1, 125.5 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.9 Hz), 56.9; **IR** (neat) 3057, 1600, 1323, 1119 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{15}H_{16}O$ $(M)^+$ 362.1282, found 362.1273; **$[\alpha]^{23}_D$** +4.84 (*c* 0.915, $CHCl_3$); **SFC** analysis (AD-H, 5% IPA, 2.5 mL/min) indicated 57% ee: t_R (major) = 7.7 minutes, t_R (minor) = 7.0 minutes.

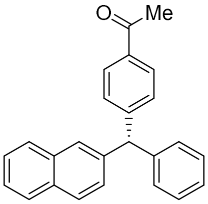


(*S*)-1.24 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.00 equiv), 5,5-dimethyl-2-(4-trifluoromethylphenyl)-1,3,2-dioxaborinane (103 mg, 0.400 mmol, 2.00 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (1% Et_2O/pentane) to afford the product as a colorless oil. First run: (52.8 mg, 0.146 mmol, 73%, 91% ee). Second run: (48.6 mg, 0.134 mmol, 67%, 90% ee). **TLC R_f** = 0.4 (pentane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85–7.79 (m, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.74–7.68 (m, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.49–7.41 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.29–7.22 (m, 4H), 7.14 (d, *J* = 7.6 Hz, 2H), 5.75 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.0, 142.9, 140.6, 133.5, 132.4, 130.0, 129.6, 128.9 (q, *J* = 32.4 Hz), 128.7, 128.3, 128.02, 128.00, 127.9, 127.7, 126.9, 126.4, 126.1, 125.5 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.9 Hz), 56.9; **IR** (neat) 3057, 1600, 1323, 1119 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{15}H_{16}O$ $(M)^+$ 362.1282, found 362.1273; **$[\alpha]^{23}_D$** –16.5 (*c* 1.00, $CHCl_3$); **SFC** analysis (AD-H, 5% IPA, 2.5 mL/min) indicated 89% ee: t_R (major) = 6.6 minutes, t_R (minor) = 7.3 minutes.

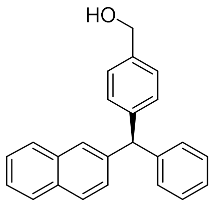


(*R*)-1.25 Using representative procedure A outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.20 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 μL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-acetylphenyl)-1,3,2-dioxaborinane (93 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (10% EtOAc/hexanes) to afford the product as an amorphous white solid. First run: (50.8 mg, 0.151 mmol, 76%, 89% ee). Second run: (51.0 mg, 0.152 mmol, 76%, 89% ee). **TLC R_f** = 0.4 (20% EtOAc/hexanes); **^{1}H**

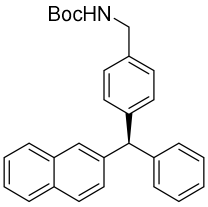
NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.73–7.69 (m, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.63–7.57 (m, 1H), 7.40–7.30 (m, 3H), 7.21 (q, *J* = 7.7 Hz, 2H), 7.19–7.10 (m, 4H), 7.05 (d, *J* = 7.5 Hz, 2H), 5.65 (s, 1H), 2.47 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.9, 149.4, 142.9, 140.7, 135.6, 133.5, 132.3, 129.9, 129.6, 128.7, 128.6, 128.3, 127.97, 127.95, 127.9, 127.7, 126.9, 126.3, 126.0, 57.0, 26.7; **IR** (neat) 3055, 2923, 1679, 1600, 1506 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{25}H_{20}O$ $(M)^+$ 336.1514, found 3316.1514; **$[\alpha]^{23}_D$** –17.2 (*c* 2.3, $CHCl_3$); **SFC** analysis (OD-H, 20% IPA, 3.0 mL/min) indicated 89% ee: t_R (major) = 6.3 minutes, t_R (minor) = 5.9 minutes.



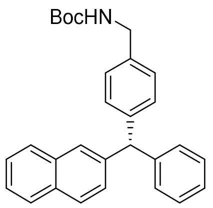
(*S*)-1.25 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.67 mg, 0.0220 mmol, 0.11 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-acetylphenyl)-1,3,2-dioxaborinane (93 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (10% EtOAc/hexanes) to afford the product as an amorphous white solid. First run: (66.5 mg, 0.198 mmol, 99%, 97% ee). Second run: (66.0 mg, 0.196 mmol, 98%, 97% ee). **TLC R_f** = 0.4 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.73–7.69 (m, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.63–7.57 (m, 1H), 7.40–7.30 (m, 3H), 7.21 (q, *J* = 7.7 Hz, 2H), 7.19–7.10 (m, 4H), 7.05 (d, *J* = 7.5 Hz, 2H), 5.65 (s, 1H), 2.47 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.9, 149.4, 142.9, 140.7, 135.6, 133.5, 132.3, 129.9, 129.6, 128.7, 128.6, 128.3, 127.97, 127.95, 127.9, 127.7, 126.9, 126.3, 126.0, 57.0, 26.7; **IR** (neat) 3055, 2923, 1679, 1600, 1506 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{25}H_{20}O$ $(M)^+$ 336.1514, found 3316.1514; **[α]^{29}D** +5.05 (*c* 1.01, $CHCl_3$); **SFC** analysis (OD-H, 20% IPA, 3.0 mL/min) indicated 97% ee: t_R (major) = 5.9 minutes, t_R (minor) = 6.5 minutes.



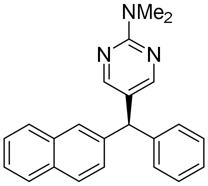
(*R*)-1.26 Using representative procedure A outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.20 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-hydroxymethylphenyl)-1,3,2-dioxaborinane (88 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (10% EtOAc/hexane) to afford the product as an oil. First run: (51.0 mg, 0.157 mmol, 79%, 82% ee). Second run: (50.0 mg, 0.154 mmol, 77%, 81% ee). **TLC R$_f$** = 0.2 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82–7.76 (m, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.71–7.66 (m, 1H), 7.46 (s, 1H), 7.41 (dt, *J* = 9.5, 4.4 Hz, 2H), 7.34–7.24 (m, 5H), 7.24–7.19 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 4H), 5.69 (s, 1H), 4.64 (d, *J* = 4 Hz, 2H), 1.77 (t, *J* = 4.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.7, 143.3, 141.5, 139.1, 133.5, 132.3, 129.9, 129.6, 128.5, 128.1, 128.02, 127.96, 127.9, 127.7, 127.3, 126.6, 126.1, 125.8, 65.2, 56.8; **IR** (neat) 3330 (br), 2953, 1600, 1506 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{24}H_{18}O$ $(M - 2H)^+$ 322.1358, found 322.1364; **[α]^{23}D** –18.3 (*c* 1.66, $CHCl_3$); **SFC** analysis (AD-H, 30% MeOH, 2.5 mL/min) indicated 89% ee: t_R (major) = 4.3 minutes, t_R (minor) = 6.1 minutes.



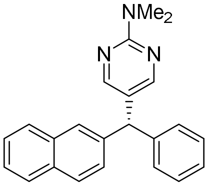
(*R*)-1.27 Using representative procedure A outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.2 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-{[(tert-butoxycarbonyl)amino]methyl}phenyl)-1,3,2-dioxaborinane (128 mg, 0.400 mmol, 2.00 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (15–25% Et_2O/hexanes) to afford the product as a white solid. First run: (71.0 mg, 0.168 mmol, 84%, 92% ee). Second run: (70.5 mg, 0.166 mmol, 83%, 89% ee). **TLC R_f** = 0.3 (20% EtOAc/hexanes); **m.p.** = 57 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81–7.76 (m, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.71–7.66 (m, 1H), 7.45 (s, 1H), 7.41 (dt, *J* = 9.5, 1.0 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 3H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 1H), 4.83 (br s, 1H), 4.29 (d, *J* = 5.1 Hz, 2H), 1.45 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.0, 143.7, 142.9, 141.5, 137.1, 133.5, 132.2, 129.9, 129.6, 128.5, 128.1, 128.01, 127.95, 127.8, 127.64, 127.59, 126.5, 126.1, 125.8, 79.5, 56.7, 44.4, 28.5; **IR** (neat) 3346, 2876, 1698, 1600, 1365 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{29}H_{29}O_2N$ $(M + Na)^+$ 446.2096, found 446.2078; **$[\alpha]^{23}_D$** –14.3 (*c* 4.4, $CHCl_3$); **SFC** analysis (AS-H, 20% MeOH, 2.5 mL/min) indicated 92% ee: t_R (major) = 4.3 minutes, t_R (minor) = 4.7 minutes.



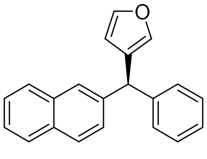
(*S*)-1.27 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-{[(tert-butoxycarbonyl)amino]methyl}phenyl)-1,3,2-dioxaborinane (128 mg, 0.400 mmol, 2.00 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (15–25% Et_2O/hexanes) to afford the product as a white solid. First run: (84.0 mg, 0.198 mmol, 99%, 96% ee). Second run: (75.4 mg, 0.178 mmol, 89%, 94% ee). **TLC R_f** = 0.3 (20% EtOAc/hexanes); **m.p.** = 57 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81–7.76 (m, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.71–7.66 (m, 1H), 7.45 (s, 1H), 7.41 (dt, *J* = 9.5, 1.0 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 3H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 1H), 4.83 (br s, 1H), 4.29 (d, *J* = 5.1 Hz, 2H), 1.45 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.0, 143.7, 142.9, 141.5, 137.1, 133.5, 132.2, 129.9, 129.6, 128.5, 128.1, 128.01, 127.95, 127.8, 127.64, 127.59, 126.5, 126.1, 125.8, 79.5, 56.7, 44.4, 28.5; **IR** (neat) 3346, 2876, 1698, 1600, 1365 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{29}H_{29}O_2N$ $(M + Na)^+$ 446.2096, found 446.2078; **$[\alpha]^{29}_D$** +22.1 (*c* 1.01, $CHCl_3$); **SFC** analysis (AS-H, 20% MeOH, 2.5 mL/min) indicated 96% ee: t_R (major) = 4.5 minutes, t_R (minor) = 4.3 minutes.



(*S*)-1.28 Using representative procedure A outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.20 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-((dimethylamino)-5-pyrimidinylphenyl)-1,3,2-dioxaborinane (94 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (5% EtOAc/benzene) to afford the product as a white solid. First run: (58.2 mg, 0.171 mmol, 86%, 89% ee). Second run: (58.6 mg, 0.173 mmol, 86%, 89% ee). **TLC** **R_f** = 0.5 (5% EtOAc/benzene); **m.p.** = 45–47 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.73–7.67 (m, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.64–7.59 (m, 1H), 7.40 (s, 1H), 7.33 (dt, *J* = 9.5, 3.5 Hz, 2H), 7.23–7.16 (m, 3H), 7.15–7.10 (m, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 2.39 (s, 1H), 3.08 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.3, 158.5, 142.9, 140.7, 133.5, 132.3, 129.8, 128.7, 128.3, 127.9, 127.67, 127.65, 127.6, 126.8, 126.3, 125.9, 123.6, 51.7, 37.2; **IR** (neat) 3054, 3023, 2861, 1599, 1531 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{23}H_{21}N_3$ $(M + H)^+$ 340.1814, found 340.1819; **$[\alpha]^{23}_D$** +15.7 (*c* 2.51, $CHCl_3$); **SFC** analysis (AD-H, 30% MeOH, 2.5 mL/min) indicated 89% ee: t_R (major) = 4.6 minutes, t_R (minor) = 6.4 minutes.

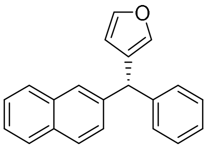


(*S*)-1.28 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 μL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-((dimethylamino)-5-pyrimidinylphenyl)-1,3,2-dioxaborinane (94 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (5% EtOAc/benzene) to afford the product as a white solid (50.8 mg, 0.150 mmol, 75%, 92% ee). **TLC R_f** = 0.5 (5% EtOAc/benzene); **m.p.** = 45–47 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.73–7.67 (m, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.64–7.59 (m, 1H), 7.40 (s, 1H), 7.33 (dt, *J* = 9.5, 3.5 Hz, 2H), 7.23–7.16 (m, 3H), 7.15–7.10 (m, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 2.39 (s, 1H), 3.08 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.3, 158.5, 142.9, 140.7, 133.5, 132.3, 129.8, 128.7, 128.3, 127.9, 127.67, 127.65, 127.6, 126.8, 126.3, 125.9, 123.6, 51.7, 37.2; **IR** (neat) 3054, 3023, 2861, 1599, 1531 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{23}H_{21}N_3$ $(M + H)^+$ 340.1814, found 340.1819; **$[\alpha]^{29}_D$** –13.2 (*c* 0.675, $CHCl_3$); **SFC** analysis (AD-H, 30% MeOH, 2.5 mL/min) indicated 92% ee: t_R (major) = 6.1 minutes, t_R (minor) = 4.5 minutes.

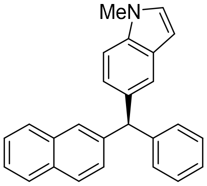


(*S*)-1.29 Using representative procedure A outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.20 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 μL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(3-furanyl)-1,3,2-dioxaborinane (72 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene

(1 mL). The product was purified by flash column chromatography (0.5–1% Et_2O/pentane) to afford the product as a white solid. First run: (45.8 mg, 0.161 mmol, 80%, 94% ee). Second run: (44.0 mg, 0.155 mmol, 78%, 94% ee). **TLC R_f** = 0.5 (1% Et_2O/pentane); **m.p.** = 65–67 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83–7.69 (m, 3H), 7.60 (s, 1H), 7.47–7.37 (m, 3H), 7.34 (dd, *J* = 8.6, 1 Hz, 1H), 7.31–7.16 (m, 5H), 6.97 (s, 1H), 6.26 (s, 1H), 5.42 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.4, 143.3, 141.3, 141.1, 133.5, 132.4, 129.0, 128.6, 128.3, 128.1, 128.0, 127.7, 127.6, 127.1, 126.7, 126.2, 125.8, 111.6, 48.3; **IR** (neat) 3145, 3024, 1599, 1492 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{21}H_{16}O$ $(M)^+$ 284.1201, found 284.1203; **$[\alpha]^{23}_D$** +22.3 (*c* 1.67, $CHCl_3$); **SFC** analysis (AD-H, 5% IPA, 2.5 mL/min) indicated 94% ee: t_R (major) = 12.2 minutes, t_R (minor) = 11.3 minutes.

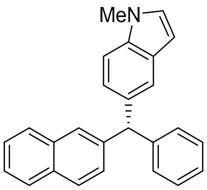


(*R*)-1.29 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 μL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(3-furanyl)-1,3,2-dioxaborinane (72 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (0.5–1% Et_2O/pentane) to afford the product as a white solid. First run: (35.5 mg, 0.125 mmol, 62.5 %, 82% ee). Second run: (38.7 mg, 0.136 mmol, 68%, 84% ee). **TLC R_f** = 0.5 (1% Et_2O/pentane); **m.p.** = 65–67 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83–7.69 (m, 3H), 7.60 (s, 1H), 7.47–7.37 (m, 3H), 7.34 (dd, *J* = 8.6, 1 Hz, 1H), 7.31–7.16 (m, 5H), 6.97 (s, 1H), 6.26 (s, 1H), 5.42 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.4, 143.3, 141.3, 141.1, 133.5, 132.4, 129.0, 128.6, 128.3, 128.1, 128.0, 127.7, 127.6, 127.1, 126.7, 126.2, 125.8, 111.6, 48.3; **IR** (neat) 3145, 3024, 1599, 1492 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{21}H_{16}O$ $(M)^+$ 284.1201, found 284.1203; **[α]^{29}$_D$** –22.0 (*c* 1.00, $CHCl_3$); **SFC** analysis (AD-H, 5% IPA, 2.5 mL/min) indicated 84% ee: t_R (major) = 12.2 minutes, t_R (minor) = 13.4 minutes.

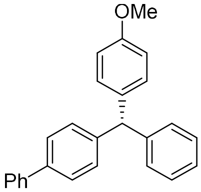


(*S*)-1.14 Using representative procedure A outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), tricyclohexylphosphine (11 mg, 0.040 mmol, 0.20 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1*H*-indole (97 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.4** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (5–20% Et_2O/hexane, 0.5% TEA) to afford the product as a white solid. First run: (63.4 mg, 0.182 mmol, 91%, 92% ee). Second run: (61.4 mg, 0.178 mmol, 89%, 93% ee). **TLC R$_f$** = 0.3 (20% Et_2O/hexane); **m.p.** = 49–52 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80–7.75 (m, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.70–7.64 (m, 1H), 7.50 (s, 1H), 7.40 (dt, *J* = 9.3, 4.9 Hz, 2H), 7.37–7.31 (m, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.25–7.16 (m, 4H), 7.07 (dd, *J* = 8.7, 1.0 Hz, 1H), 6.98 (d, *J* = 2.9 Hz, 1H), 6.36 (d, *J* = 2.9 Hz, 1H), 5.83 (s, 1H), 3.72 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.7, 142.6, 135.6, 134.9, 133.5, 132.2, 129.8, 129.2, 128.55, 128.52, 128.4, 128.0, 127.9, 127.8, 127.6, 126.3, 126.0, 125.6, 123.9, 121.7, 109.2, 101.1, 57.1, 33.0; **IR** (neat) 3022, 2884, 1599, 1489 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{26}H_{21}N$ $(M + Na)^+$ 370.1572, found 370.1576; **[α]^{23}$_D$** –10.8 (*c* 1.00, $CHCl_3$); **SFC** analysis (AD-H, 20% MeOH, 2.5 mL/min) indicated 93% ee: t_R (major)

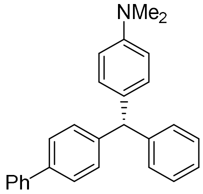
= 8.1 minutes, t_R (minor) = 9.0 minutes. Single crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of hexane into a solution of **(*S*)-1.14** in benzene at 4 °C.



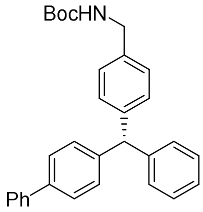
***(R)*-1.14** Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.3 mg, 0.021 mmol, 0.11 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1*H*-indole (97 mg, 0.40 mmol, 2.0 equiv), **(*S*)-2.1** (66 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (5–20% Et_2O/hexanes, 0.5% TEA) to afford the product as a white solid. First run: (41.5 mg, 0.119 mmol, 57%, 92% ee). Second run: (57.0 mg, 0.164 mmol, 82%, 92% ee). Analytical data is consistent with the values listed above for **(*S*)-1.4** **$[\alpha]^{23}_{D}$** +6.0 (*c* 0.9, $CHCl_3$); **SFC** analysis (AD-H, 20% MeOH, 2.5 mL/min) indicated 93% ee: t_R (major) = 8.9 minutes, t_R (minor) = 8.1 minutes.



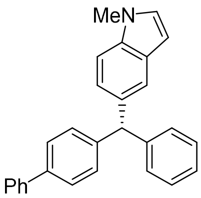
(*R*)-1.30 Using representative procedure B above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.3 mg, 0.0210 mmol, 0.11 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5,5-dimethyl-2-(4-methoxyphenyl)-1,3,2-dioxaborinane (88 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.19** (69 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (1–3% Et_2O/hexanes) to afford the product as a colorless oil. First run: (54.8 mg, 0.156 mmol, 78%, 81% ee). Second run: (55.8 mg, 0.159 mmol, 80%, 81% ee). **TLC R_f** = 0.4 (10% Et_2O/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2, 2H), 7.51 (d, *J* = 7.1, 2H), 7.42 (t, *J* = 7.1, 2H), 7.29 (m, 3H), 7.19 (m, 5H), 7.06 (d, *J* = 7.8, 2H), 6.83 (d, *J* = 8.2, 2H) 5.53 (s, 1H), 3.78 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.2, 144.3, 143.5, 141.0, 139.2, 136.2, 130.5, 129.9, 129.5, 128.9, 128.5, 128.3, 127.15, 127.14, 126.4, 113.9, 55.9, 55.4; **IR** (neat) 3020, 2996, 1508, 1244, 1030 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{26}H_{22}O$ $(M + Na)^+$ 350.1671, found 367.1679; **[α]$^{23}_{D}$** +1.2 (*c* 1.01, $CHCl_3$), **SFC** analysis (AD-H, 10% MeOH, 2.5 mL/min) indicated 84% ee: t_R (minor) = 21.5 minutes, t_R (major) = 19.8 minutes.



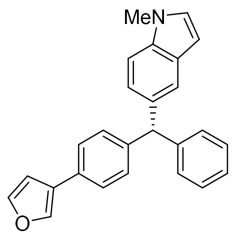
(*R*)-1.31 Using representative procedure B above, the following amounts and reagents: 1,8-bis(1,5-cyclooctadiene)nickel (8.3 mg, 0.030 mmol, 0.10 equiv), 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (12 mg, 0.030 mmol, 0.10 equiv), potassium *tert*-butoxide (64 mg, 0.60 mmol, 2.0 equiv), 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-*N,N*-dimethylaniline (134 mg, 0.600 mmol, 2.00 equiv), **(*S*)-1.19** (103 mg, 0.300 mmol, 1.00 equiv) and 1-butanol (54 µL, 0.90 mmol, 3.00 equiv). Purified by flash column chromatography (0–10% Et_2O/hexanes) to afford **(*R*)-1.32,** as a light yellow oil (55 mg, 0.15 mmol, 75%). **TLC R_f** = 0.3 (10% Et_2O/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2, 2H), 7.49 (d, *J* = 8.2, 2H), 7.41 (t, *J* = 7.7, 2H), 7.29 (m, 3H), 7.27 (s, 1H) 7.21 (m, 5H), 7.02 (dd, *J* = 8.6, 2H) 6.67 (d, *J* = 8.9, 2H), 6.4 (d, *J* = 2.8, 1H), 5.5 (s, 1H), 2.9 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.2, 144.7, 143.9, 141.1, 139.0, 131.9, 130.2, 129.9, 129.5, 128.8, 128.4, 127.20, 127.15, 127.1, 126.3, 112.7, 55.7, 40.8; **IR** (neat) 3024, 2841, 2360, 1613, 1485, 1347, 763 cm^{-1}; **HRMS** (TOF MS EI+) *m / z* calcd for $C_{27}H_{25}O$ (M + Na)$^+$ 364.2065, found 364.2061; **[α]^{23}D** –2.9 (*c* 1.07, $CHCl_3$); **SFC** analysis (AD-H, 16% MeOH, 3.0 mL/min) indicated 79% ee: t_R (minor) = 26.3 minutes, t_R (major) = 11.6 minutes.



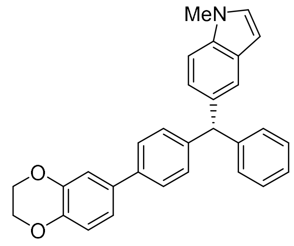
(*S*)-1.32 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.67 mg, 0.022 mmol, 0.11 equiv), potassium *tert*-butoxide (45 mg, 0.4 mmol, 2.0 equiv), *tert*-butyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzylcarbamate (127.3 mg, 0.200 mmol, 2.00 equiv), **(*S*)-1.19** (68.9 mg, 0.200 mmol, 1.00 equiv) and 1-butanol (54 µL, 0.60 mmol, 3.0 equiv). Purified by flash column chromatography (0–15 % EtOAc/Hexane) to afford to afford the desired triarylmethane as a clear colorless oil (48.5 mg, 54%); **TLC R$_f$** = 0.1 (9:1 Hexanes:EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 1.5, *J* = 8.4, 2H), 7.51 (d, *J* = 8.3, 2H), 7.39 (t, *J* = 7.5, 2H), 7.29 (m, 3H), 7.25 (m, 3H), 7.15 (m, 6H), 5.56 (s, 1H), 4.82 (s, 1H), 4.30 (d, *J* = 5.3, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.0, 143.9, 143.13, 143.05, 140.9, 139.3, 137.1, 129.9, 129.8, 129.5, 128.9, 128.5, 127.6, 127.3, 127.16, 127.14, 126.5, 56.3, 44.3, 28.5; **IR** (neat) 3294, 3028, 1695, 1486, 1316, 1016, 757 cm^{-1}; **HRMS** (TOF MS EI+) *m / z* calcd for $C_{31}H_{31}NO_2$ [M+Na]$^+$ 472.2253, found 472.2261. **[α]^{29}D** –8.2 **SFC** analysis (AS-H, 20% MeOH, 2.5 mL/min) indicated 92% ee: t_R (major) = 6.86 minutes, t_R (minor) = 7.47 minutes.



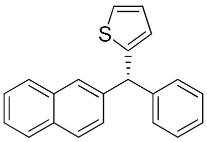
(*R*)-1.33 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1*H*-indole (97 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.19** (69 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified by flash column chromatography (5–20% Et_2O/hexane, 0.5% TEA) to afford the product as a white solid. First run: (61.0 mg, 0.163mmol, 82%, 96% ee). Second run: (37.8 mg, 0.101 mmol, 51%, 96% ee). **TLC R_f** = 0.3 (10% EtOAc/hexanes); **m.p.** = 54–55 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4, 2H), 7.49 (d, *J* = 8.2, 2H), 7.37 (t, *J* = 7.4, 2H), 7.27 (m, 3H), 7.26 (s, 1H) 7.22 (m, 9H), 7.07 (dd, *J* = 1.3, 8.6, 1H) 6.87 (d, *J* = 3.0, 1H), 6.37 (d, *J* = 2.8, 1H), 5.70 (s, 1H), 3.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 144.2, 141.1, 138.9, 135.6, 135.1, 130.1, 129.7, 129.2, 128.8, 128.6, 128.4, 127.17, 127.15, 127.0, 126.2, 123.8, 121.6, 109.2, 101.1, 56.7, 32.9; **IR** (neat) 3025, 2360, 1486, 1449, 1246, 1006, 760 cm^{-1}; **HRMS** submitted; **$[\alpha]^{23}_D$** –5.2; **SFC** analysis (AD-H, 25% MeOH, 2.5 mL/min) indicated 96% ee: t_R (major) = 11.3 minutes, t_R (minor) = 16.1 minutes.



(*R*)-1.34 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 μL, 0.60 mmol, 3.0 equiv), 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1*H*-indole (97 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.20** (67 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified twice by flash column chromatography (6% Et_2O/hexane and then 60% benzene/pentane) to afford the desired triarylmethane as a white solid. First run: (58.5 mg, 0.161 mmol, 80%, 87% ee). Second run: (58.5 mg, 0.161 mmol, 80%, 87% ee). **TLC R$_f$** = 0.6 (40% pentane/benzene); **m.p.** = 149–151 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.34 (s, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.23 (s,1H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.15–7.09 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 4H), 6.95 (d, *J* = 8.6 Hz, 1H), 6.90 (d, *J* = 2.8 Hz, 1H), 6.57 (s, 1H), 6.29 (d, *J* = 2.8 Hz, 1H), 5.58 (s, 1H), 3.63 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.9, 143.9, 141.7, 138.5, 135.6, 135.0, 130.3, 130.1, 129.7, 129.2, 128.5, 128.3, 126.4, 126.2, 125.8, 123.7, 121.5, 109.2, 109.0, 101.1, 56.7, 33.0; **IR** (neat) 3145, 3024, 1599, 1492 cm^{-1}; **$[\alpha]^{23}_D$** –3.1 (*c* 2.24, $CHCl_3$); **HRMS** submitted; **SFC** analysis (OJ-H, 30% MeOH, 3.0 mL/min) indicated 87% ee: t_R (major) = 23.6 minutes, t_R (minor) = 26.2 minutes.



(*R*)-1.35 Using representative procedure B outlined above, the following amounts of reagents were used: 1,8-bis(1,5-cyclooctadiene)nickel (5.5 mg, 0.020 mmol, 0.10 equiv), 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (8.27 mg, 0.0210 mmol, 0.105 equiv), potassium *tert*-butoxide (45 mg, 0.40 mmol, 2.0 equiv), 1-butanol (54 µL, 0.60 mmol, 3.0 equiv), 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1*H*-indole (97 mg, 0.40 mmol, 2.0 equiv), **(*S*)-1.21** (67 mg, 0.20 mmol, 1.0 equiv), tetrahydrofuran (1 mL) and toluene (1 mL). The product was purified twice by flash column chromatography (6% EtOAc/hexanes and then 70% benzene/pentane) to afford the desired triarylmethane as a white solid. First run: (51.4 mg, 0.119 mmol, 60%, 93% ee). Second run: (52.0 mg, 0.121 mmol, 60%, 93% ee). **TLC R$_f$** = 0.3 (40% pentane/benzene); **m.p.** = 81–84 ºC; **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.43 (s, *J* = 8.0 2H), 7.33 (s, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 (s,1H), 7.22–7.14 (m, 5H), 7.10 (s, 1H), 7.06 (dt, *J* = 8.2, 2.0 Hz, 2H), 7.01 (d, *J* = 2.7 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.39 (d, *J* = 2.5 Hz, 1H), 5.69 (s, 1H), 4.27 (s, 4H), 3.76 (s, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 144.9, 143.8, 143.7, 143.1, 138.4, 135.6, 135.1, 134.8, 130.0, 129.7, 129.2, 128.6, 128.4, 126.6, 126.2, 123.8, 121.6, 120.2, 117.6, 115.8, 109.2, 101.1, 64.58, 64.56, 56.7, 33.0; **IR** (neat) 2916, 1586, 1513, 1449 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{30}H_{25}O_2N$ $(M + Na)^+$ 454.1783, found 454.1772; **[α]^{23}$_D$** –8.2 (*c* 2.36, CHCl$_3$); **SFC** analysis (OD-H, 25% IPA, 2.5 mL/min) indicated 93% ee: t$_R$ (major) = 23.6 minutes, t$_R$ (minor) = 26.2 minutes.

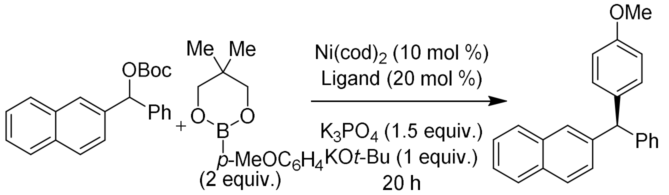


(*R*)-1.12 Prepared according to general procedure B using the following amounts and reagents: Ni(cod)$_2$ (2.8 mg, 0.010 mmol, 0.10 equiv), 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (3.9 mg, 0.010 mmol, 0.10 equiv), potassium *tert*-butoxide (22 mg, 0.20 mmol, 2.0 equiv), 5,5-dimethyl-2-(thiophen-2-yl)-1,3,2-dioxaborinane (39.2 mg, 0.200 mmol, 2.00 equiv), **(*S*)-1.4** (33.1 mg, 0.100 mmol, 1.00 equiv) and 1-butanol (27 µL, 0.30 mmol, 3.0 equiv). Purified by flash column chromatography (0–5% Et$_2$O/hexanes) to afford the desired triarylmethane as a yellow solid (11.4 mg, 0.0379 mmol, 38%). Analytical data is consistent with literature values.[13b] **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.84–7.72 (m, 3H), 7.61 (s, 1H), 7.37–7.41 (m, 2H), 7.37 (dd, *J* = 1.6, 8.5), 7.34–7.20 (m, 6H), 6.95 (t, *J* = 4.3), 6.73 (d, *J* = 3.3), 5.84 (s, 1H); **^{13}C NMR** δ (125 MHz, CDCl$_3$) δ 147.8, 143.7, 141.4, 133.5, 132.4, 129.1, 128.6, 128.2, 128.1, 127.7, 127.5, 127.4, 126.9, 126.8, 126.7, 126.2, 125.9, 124.8, 52.3 **$[\alpha]^{25}_{D}$** –9.3 (*c* 0.57, CHCl$_3$).

Tables of results using alternative ligands and bases.

Other ligands and bases were tested under reaction conditions similar to Table 1.1. Representative examples are shown below.

Table 1.4. Examination of additional ligands in the cross-coupling reaction



Entry	ligand	yield[a]
1	DPEphos (Bis[(2-diphenylphosphino)phenyl] ether)	< 5%
2	Cy-DPEphos (Bis[(2-dicyclohexylphosphino)phenyl] ether)	< 5%
3	DPPO (1,8-bis(diphenylphosphino)octane)	13%
4	PPh_3 (triphenylphosphine)	22%
5	$P(t\text{-}Bu)_3$ tri-*tert*-butylphosphine	< 5%
6	XPhos (2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl)	< 5%
7	SPhos (2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl)	< 5%
8	SIPr-HBF_4 (1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium tetrafluoroborate	31%
9	tricyclohexylphosphine	86%
10	PCy_3 tricylohexylphosphine (11 mol %)	83%
11	SIMes-HBF_4 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate	84%
12	None	< 5%

[a] Determined by ^1H NMR analysis using an internal standard ($PhSiMe_3$).

1H spectrum

(S)- 1.15

```
Current Data Parameters
USER              lhanna
NAME      LEH-1-77-c1-f40-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121101
Time               10.41
INSTRUM           drx400
PROBHD   5 mm GNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
AQ           5.1118579 sec
RG                 143.7
DW              78.000 usec
DE                4.50 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1               12.00 usec
PL1              -0.60 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF         400.1300345 MHz
WDW                   no
SSB                    0
LB                0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             3601.17 Hz
F2P              0.000 ppm
F2                0.00 Hz
PPMCM          0.39474 ppm/cm
HZCM         157.94608 Hz/cm
```

13C spectrum with 1H decoupling

```
Current Data Parameters
USER              lhanna
NAME          LEH-1-77-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
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Time               11.10
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PROBHD   5 mm GNP H/F/P
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH          24154.590 Hz
FIDRES        0.368570 Hz
AQ           1.3566452 sec
RG               14596.5
DW              20.700 usec
DE               20.39 usec
TE               298.0 K
D1          0.10000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1               11.00 usec
PL1               0.00 dB
SFO1       100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2           mlev16
NUC2                  1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             16.20 dB
SFO2       400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF         100.6127632 MHz
WDW                   no
SSB                    0
LB                0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.50 cm
F1P            150.000 ppm
F1            15091.91 Hz
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F2             6036.77 Hz
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HZCM         397.15564 Hz/cm
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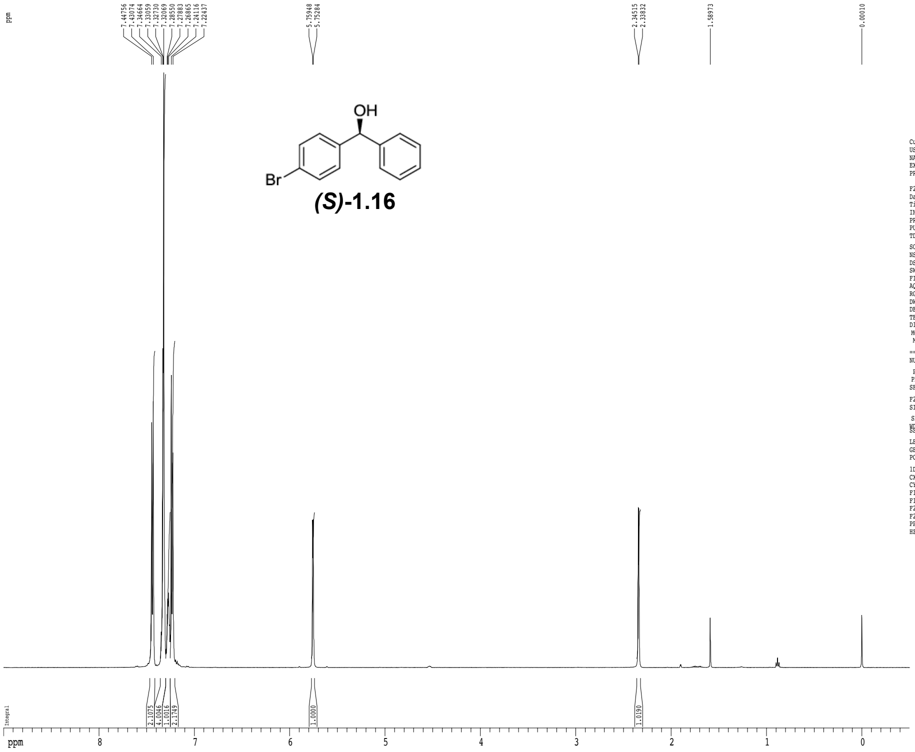
1H spectrum



(S)-1.16

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EXPNO                  1
PROCNO                 1

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PULPROG             zg30
TD                 81728
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DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
 MCREST       0.00000000 sec
 MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
 P1                 7.50 usec
 PL1                1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
 SF          500.2200406 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
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HZCM           208.42502 Hz/cm
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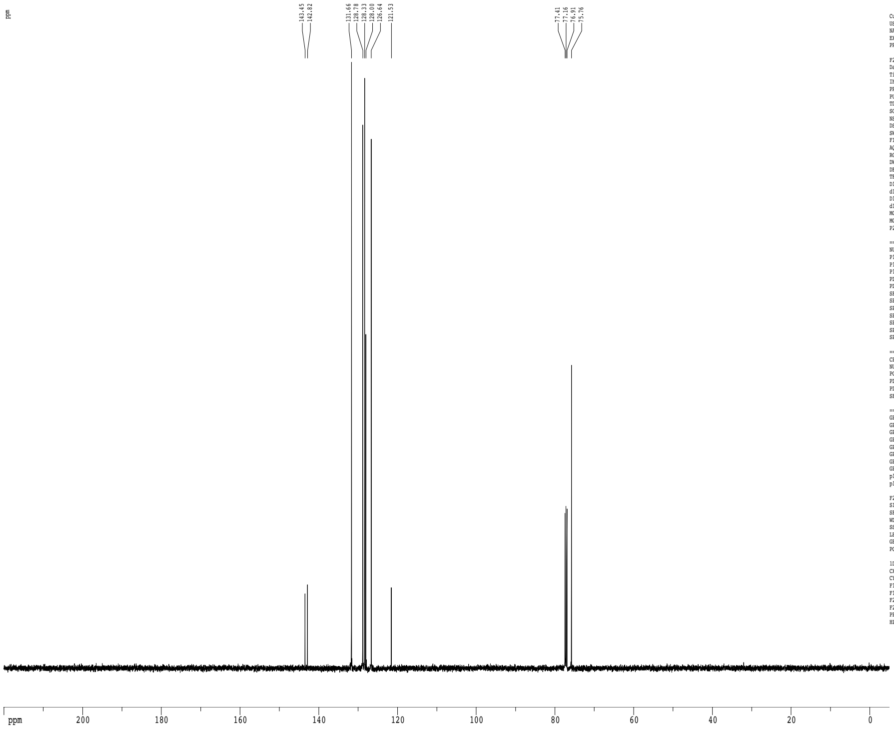
Z-restored spin-echo 13C spectrum with 1H decoupling



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EXPNO                  1
PROCNO                 1

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PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT           CDCl3T
NS                   126
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                2580.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804131 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              220.000 ppm
F1              27671.69 Hz
F2P               -5.000 ppm
F2               -628.90 Hz
PPMCM            9.86842 ppm/cm
HZCM          1241.25415 Hz/cm
```
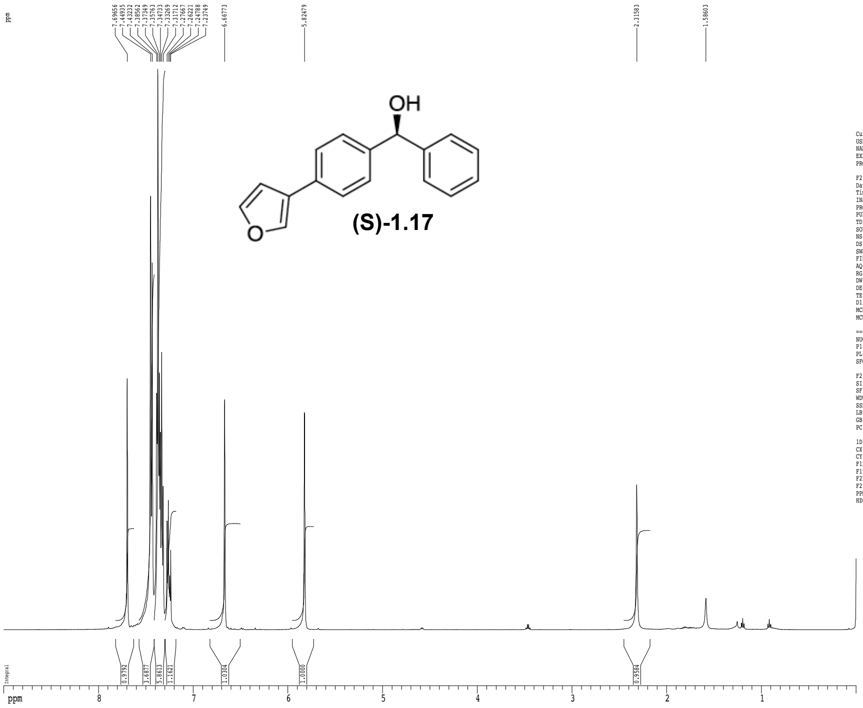
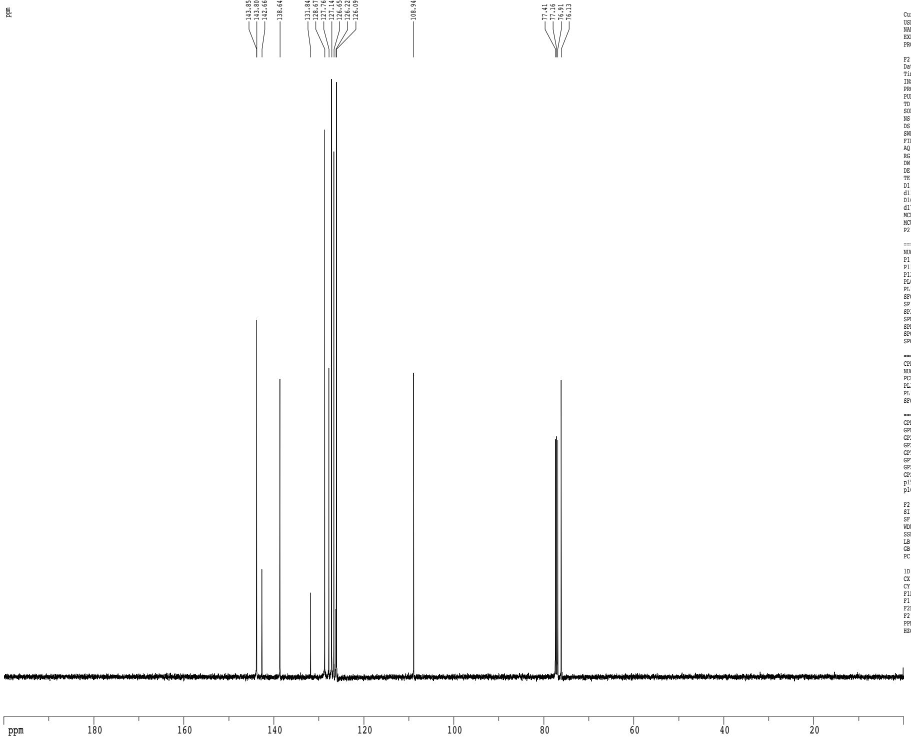

1H spectrum



(S)-1.17

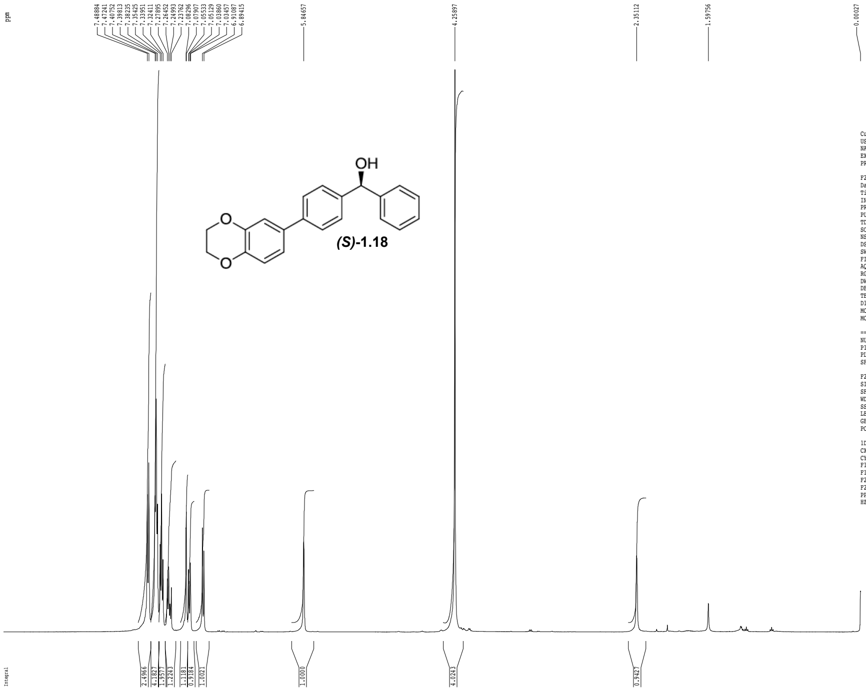
```
Current Data Parameters
USER              greene
NAME           mrh-4-133
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121117
Time               10.00
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0999398 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200421 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              greene
NAME           mrh-4-133
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121117
Time               10.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   295
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0814105 sec
RG                9195.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804127 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            8.77193 ppm/cm
HZCM          1103.33691 Hz/cm
```

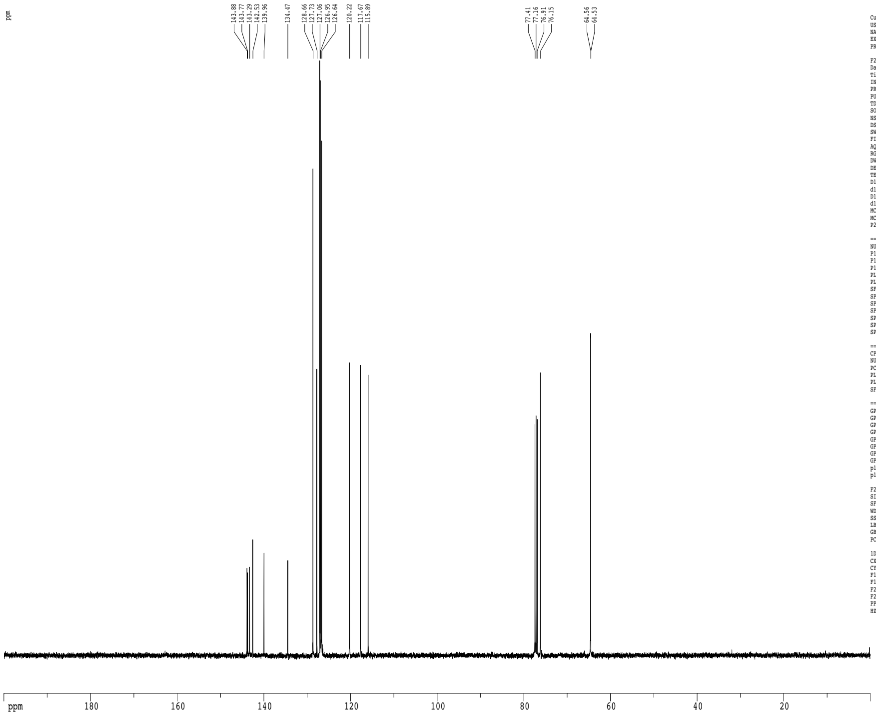
1H spectrum



(S)-1.18

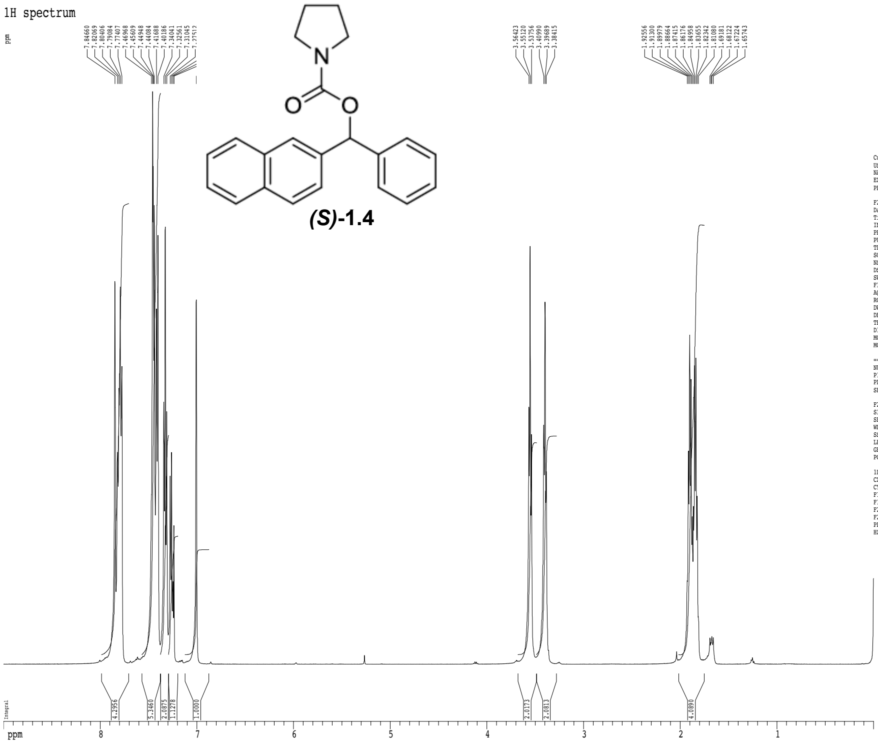
```
Current Data Parameters
USER            greene
NAME         mrh-4-138
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20121117
Time              9.35
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               81728
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0999398 sec
RG                 6.3
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                7.50 usec
PL1               1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI               65536
SF         500.2200418 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                4.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             4501.98 Hz
F2P              0.000 ppm
F2                0.00 Hz
PPMCM          0.39474 ppm/cm
HZCM         197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER            greene
NAME         mrh-4-138
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20121117
Time              9.40
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT          CDCl3
NS                 299
DS                  16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0814105 sec
RG              5792.6
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               31.00 usec

======== CHANNEL f1 ========
NUC1               13C
P1               15.50 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP1               3.20 dB
SP2               3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1            0.00 Hz
SPOFF2            0.00 Hz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.60 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI               65536
SF         125.7804131 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            200.000 ppm
F1            25156.08 Hz
F2P              0.000 ppm
F2                0.00 Hz
PPMCM          8.77193 ppm/cm
HZCM        1103.33691 Hz/cm
```

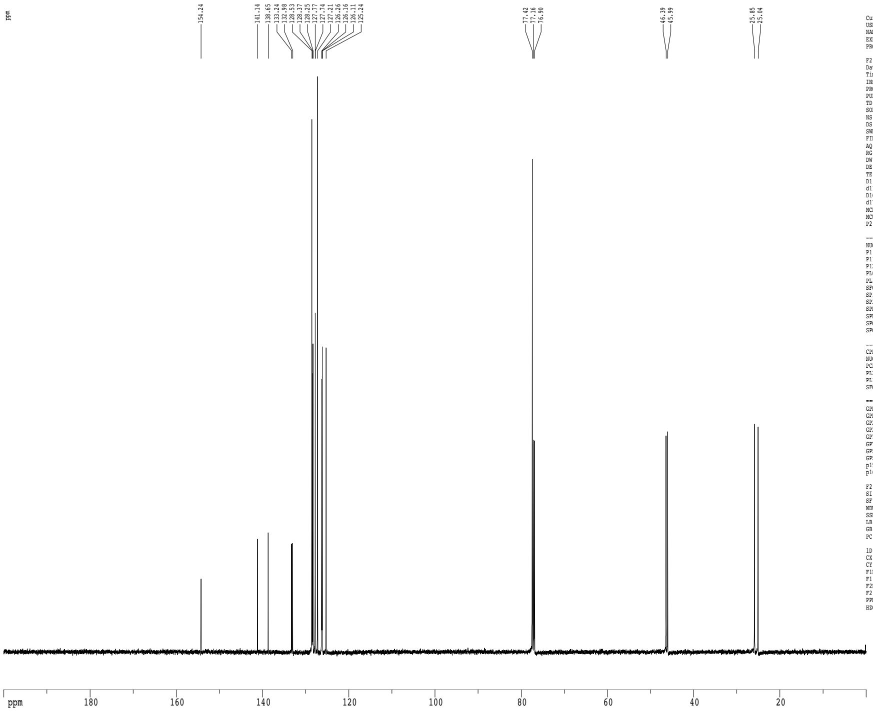
1H spectrum



***(S)*-1.4**

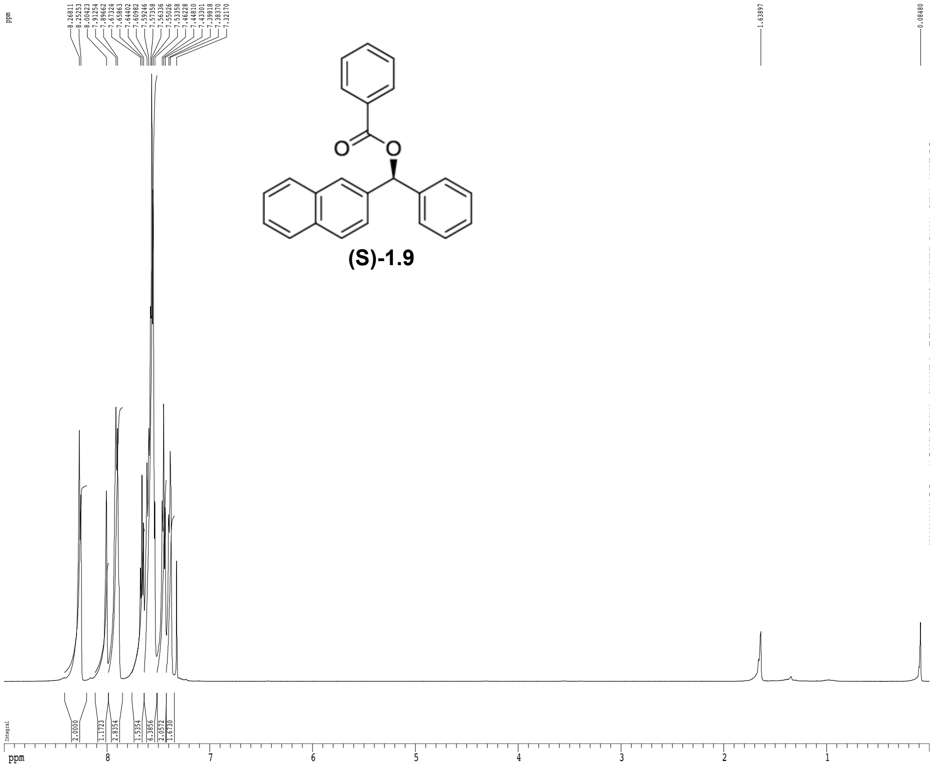
```
Current Data Parameters
USER              greene
NAME           mrh-3-259
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121117
Time                9.00
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0999398 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200429 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              greene
NAME           mrh-3-259
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121117
Time                9.06
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   360
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0814105 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804150 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            8.77193 ppm/cm
HZCM          1103.33704 Hz/cm
```

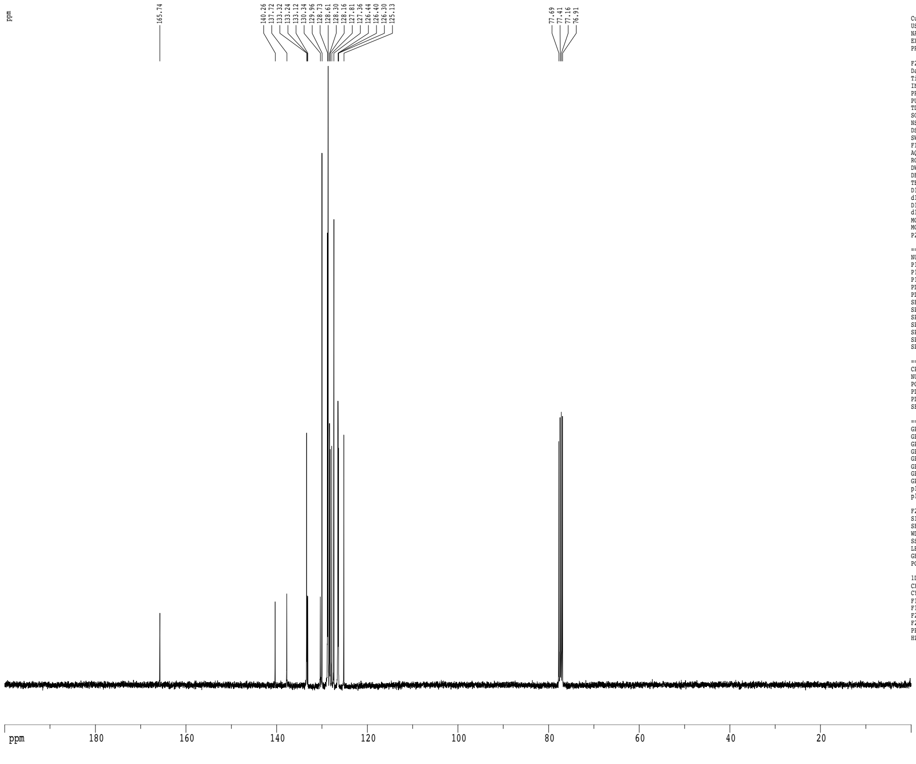
1H spectrum



(S)-1.9

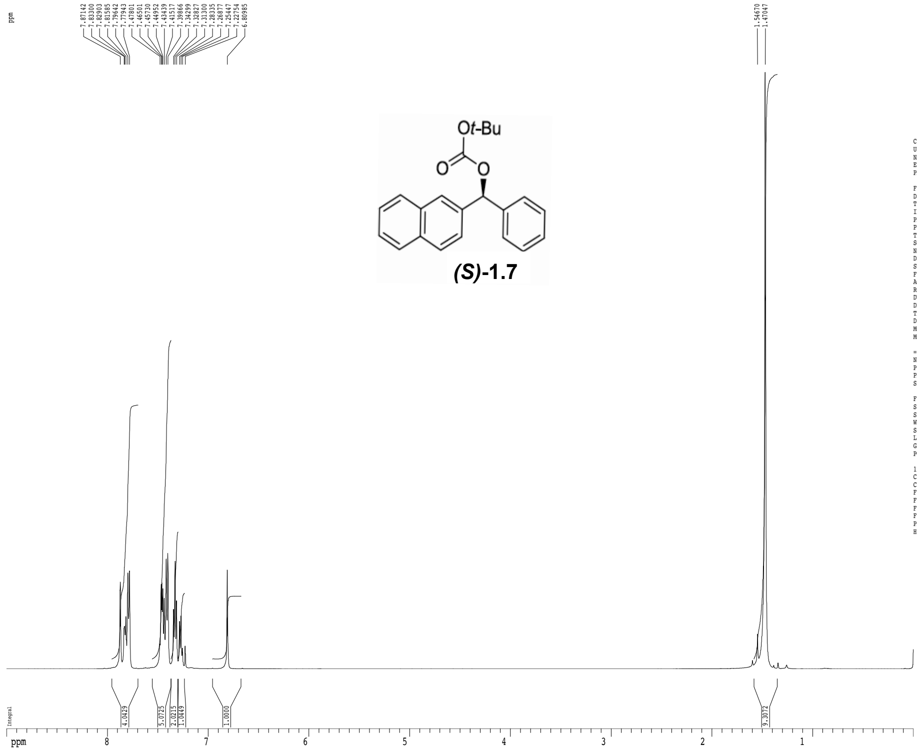
```
Current Data Parameters
USER              greene
NAME          mrh-3-146
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121118
Time                9.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                    16
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              greene
NAME          mrh-3-146
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121118
Time                9.10
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   546
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0814105 sec
RG               11585.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804122 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            8.77193 ppm/cm
HZCM          1103.33691 Hz/cm
```

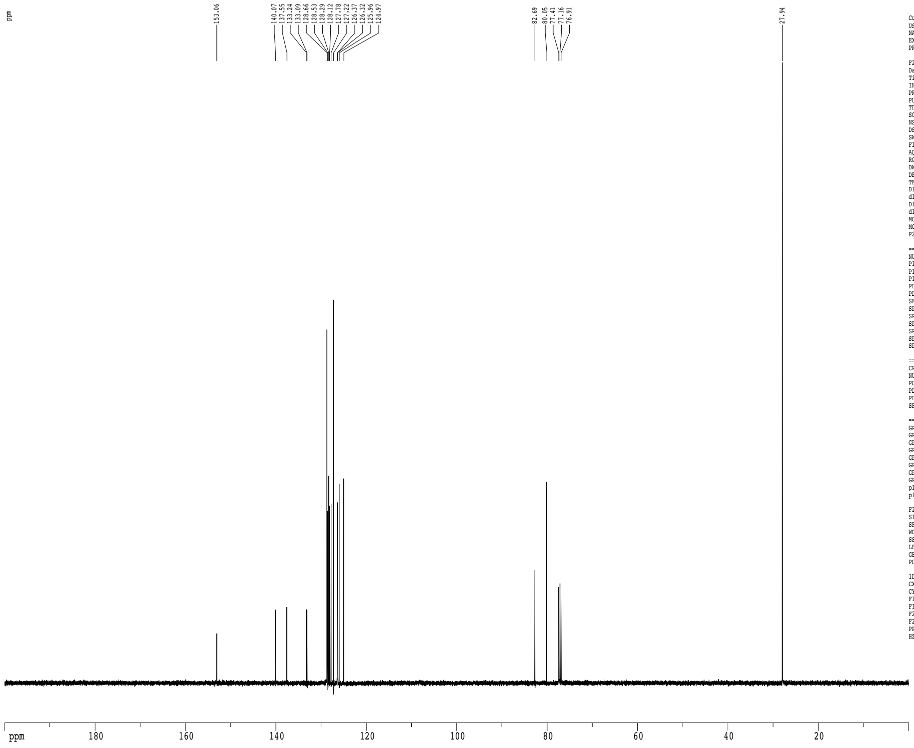
1H spectrum



(S)-1.7

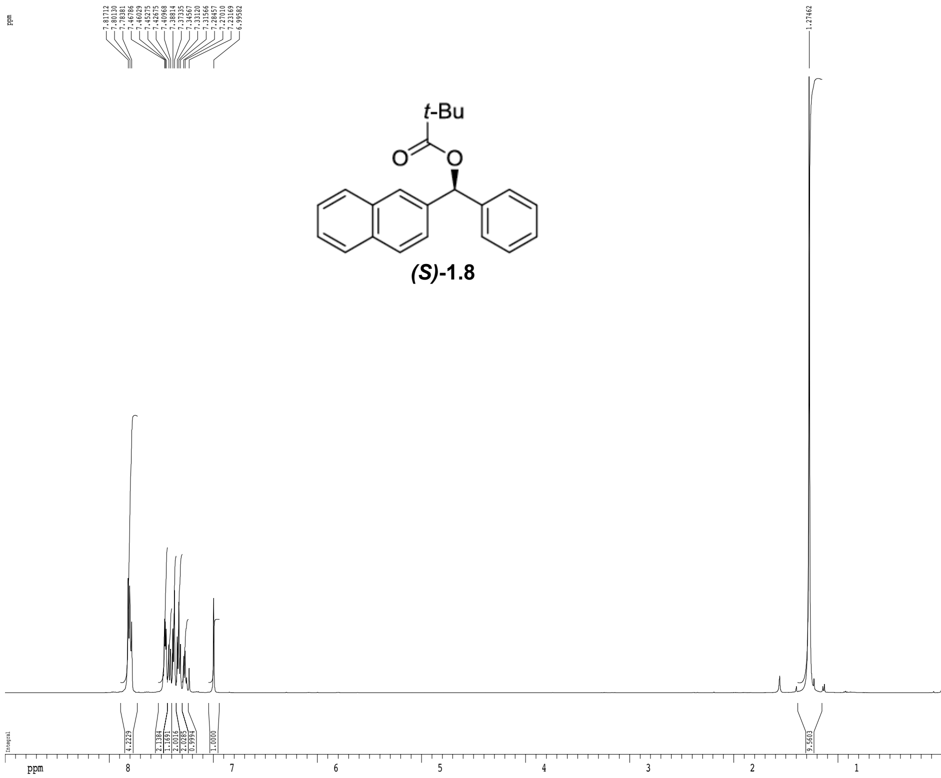
```
Current Data Parameters
USER              greene
NAME          mrh-3-123a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121117
Time                8.35
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0999398 sec
RG                  10.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200469 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              greene
NAME          mrh-3-123a
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121117
Time                8.57
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   296
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0814105 sec
RG                  4096
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804140 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            8.77193 ppm/cm
HZCM          1103.33691 Hz/cm
```

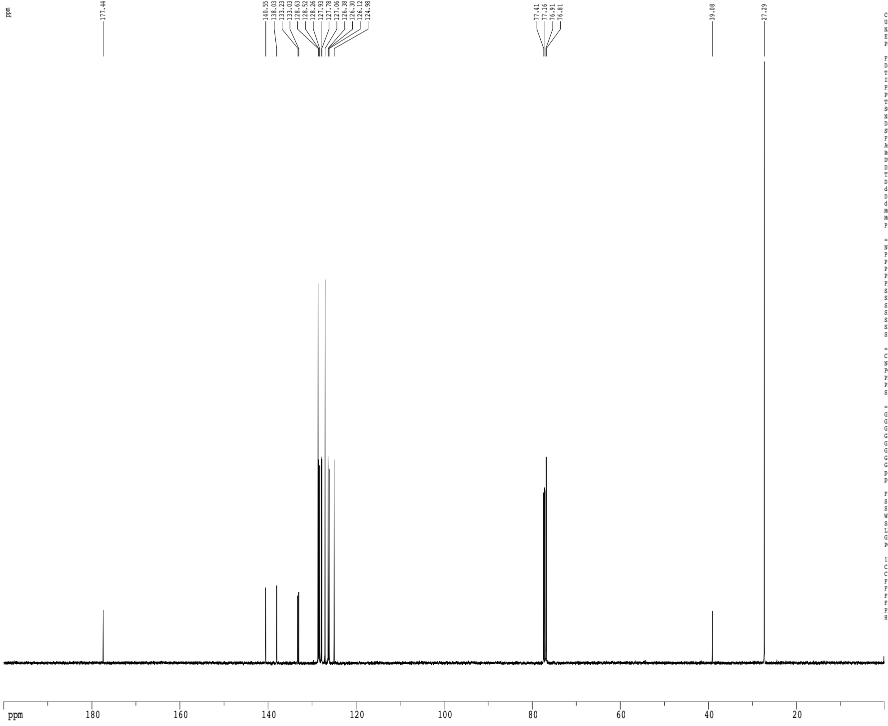
1H spectrum



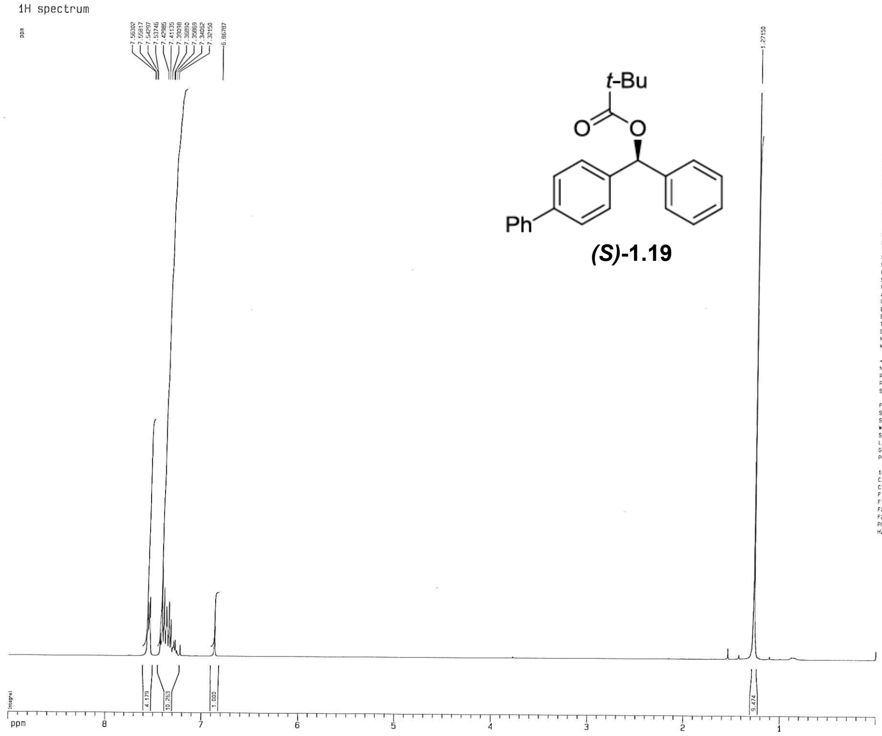
***(S)*-1.8**

```
Current Data Parameters
USER                greene
NAME             mrh-3-190
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121117
Time                  9.24
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0999398 sec
RG                     5.7
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200451 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                  0.000 ppm
F2                    0.00 Hz
PPMCM              0.39474 ppm/cm
HZCM             197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER                greene
NAME             mrh-3-190
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121117
Time                  9.31
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     266
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0814105 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                   31.00 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   15.50 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   3.20 dB
SP2                   3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1                0.00 Hz
SPOFF2                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.60 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804127 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                200.000 ppm
F1                25156.08 Hz
F2P                  0.000 ppm
F2                    0.00 Hz
PPMCM              8.77193 ppm/cm
HZCM            1103.33691 Hz/cm
```



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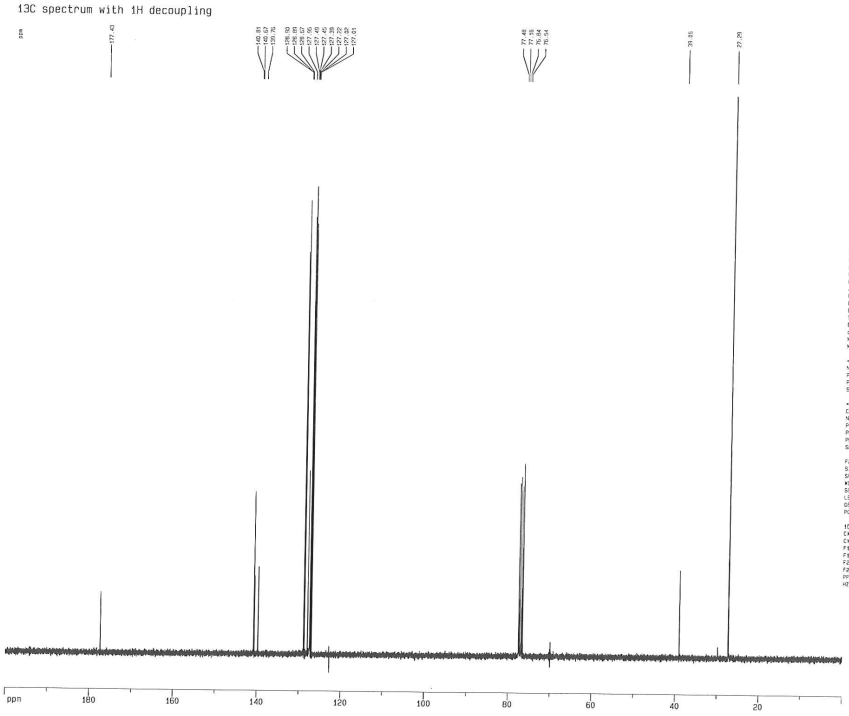
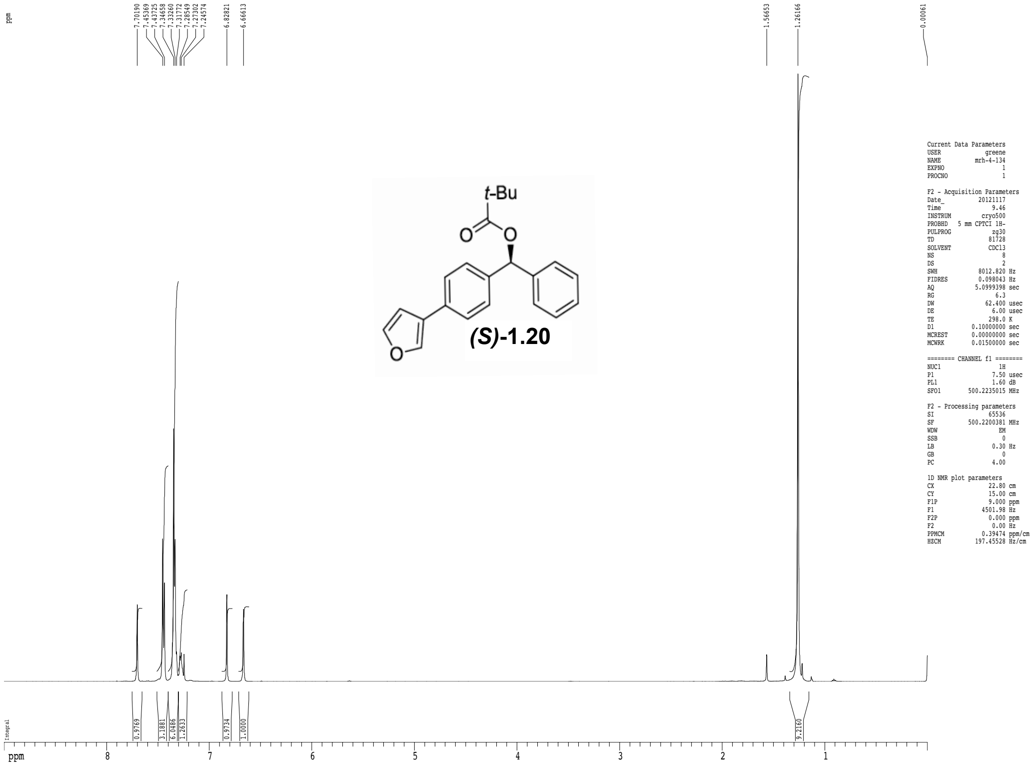
```
Current Data Parameters
USER                  lhanna
NAME      LEH-1-121-c2-H1
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121005
Time                  13.58
INSTRUM              drx400
PROBHD    5 mm QNP H/F/P
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ            5.1118579 sec
RG                     90.5
DW               78.000 usec
DE                 4.50 usec
TE                  298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1               12.00 usec
PL1                -0.60 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                    65536
SF           400.1300353 MHz
WDW                      no
SSB                       0
LB                  0.00 Hz
GB                        0
PC                     2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P               9.000 ppm
F1               3601.17 Hz
F2P               0.000 ppm
F2                  0.00 Hz
PPMCM         0.39474 ppm/cm
HZCM        157.94509 Hz/cm
```



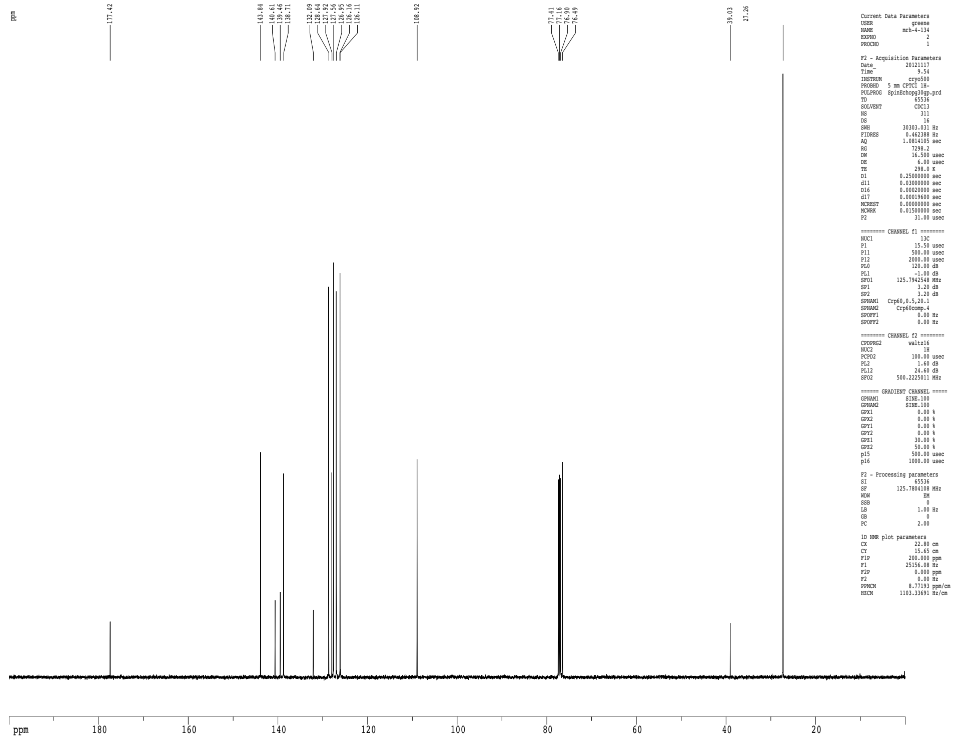
```
Current Data Parameters
USER                  lhanna
NAME     LEH-1-121-c2-C13
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121005
Time                  13.54
INSTRUM              drx400
PROBHD    5 mm QNP H/F/P
PULPROG              zgdc30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ            1.3566452 sec
RG                    13004
DW               20.700 usec
DE                20.39 usec
TE                  298.0 K
D1           0.10000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1               11.00 usec
PL1                 0.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2              mlev16
NUC2                     1H
PCPD2            80.00 usec
PL2                 0.00 dB
PL12               16.20 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                    65536
SF           100.6127624 MHz
WDW                      no
SSB                       0
LB                  0.00 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P             200.000 ppm
F1              20122.55 Hz
F2P               0.000 ppm
F2                  0.00 Hz
PPMCM         8.77193 ppm/cm
HZCM        882.55812 Hz/cm
```

1H spectrum



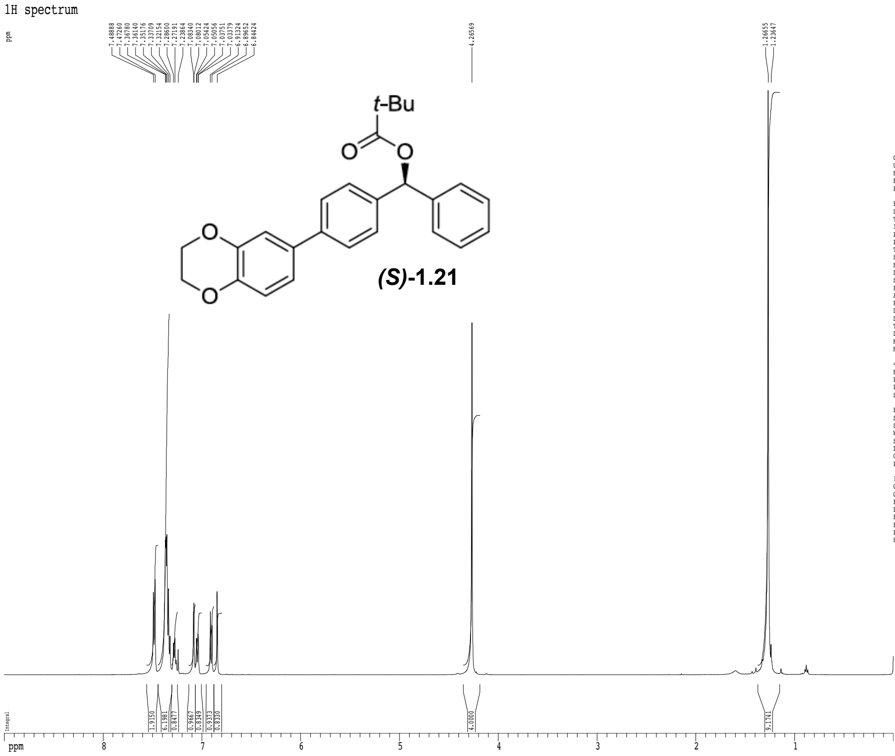
```
Current Data Parameters
USER              greene
NAME           mrh-4-134
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121117
Time                9.46
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0999398 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200381 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              greene
NAME           mrh-4-134
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121117
Time                9.54
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   311
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0814105 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804108 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            8.77193 ppm/cm
HZCM          1103.33691 Hz/cm
```

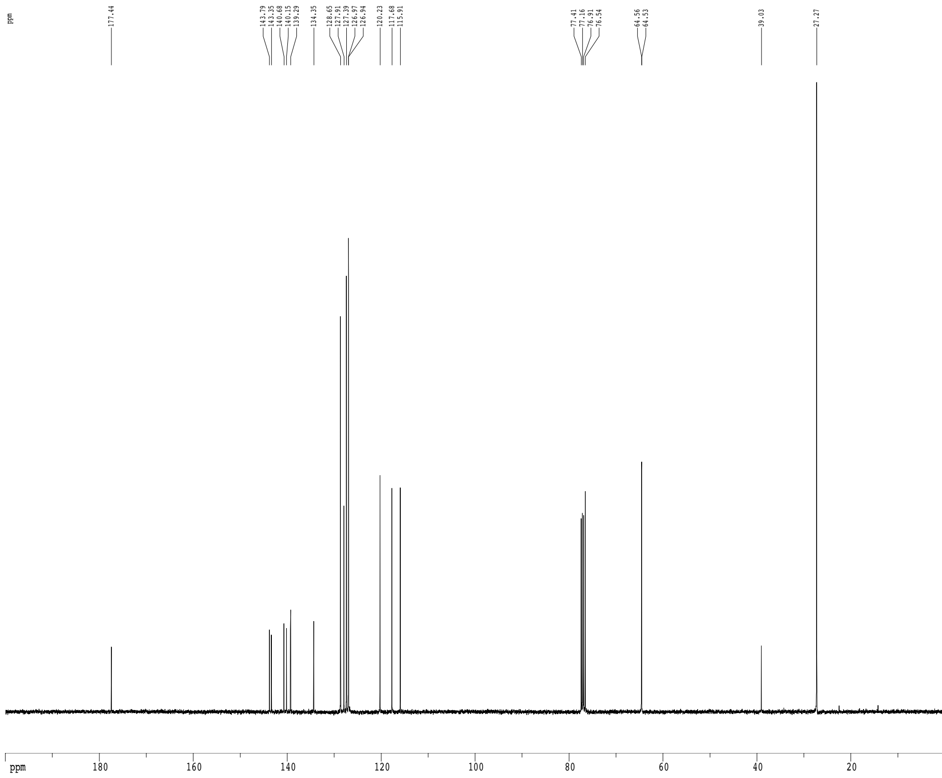
1H spectrum



(S)-1.21

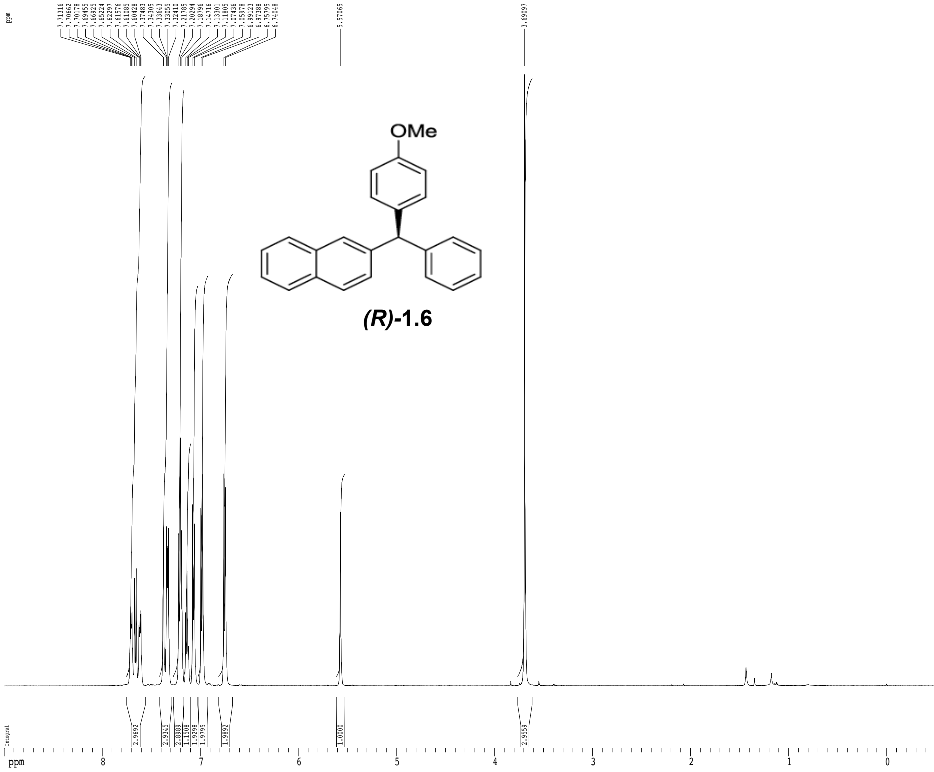
```
Current Data Parameters
USER                 greene
NAME             mrh-4-139
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20121117
Time                   9.14
INSTRUM             cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG                zg30
TD                    81728
SOLVENT               CDCl3
NS                        8
DS                        2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0999398 sec
RG                      5.7
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                     7.50 usec
PL1                    1.60 dB
SFO1            500.2235015 MHz

F2 - Processing parameters
SI                    65536
SF              500.2200413 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00

1D NMR plot parameters
CX                    22.80 cm
CY                    15.00 cm
F1P                   9.000 ppm
F1                  4501.98 Hz
F2P                   0.000 ppm
F2                     0.00 Hz
PPMCM               0.39474 ppm/cm
HZCM              197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER                 greene
NAME             mrh-4-139
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20121117
Time                   9.20
INSTRUM             cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                    65536
SOLVENT               CDCl3
NS                      253
DS                       16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0814105 sec
RG                     4096
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                    31.00 usec

======== CHANNEL f1 ========
NUC1                    13C
P1                    15.50 usec
P11                  500.00 usec
P12                 2000.00 usec
PL0                  120.00 dB
PL1                   -1.00 dB
SFO1            125.7942548 MHz
SP1                    3.20 dB
SP2                    3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1                 0.00 Hz
SPOFF2                 0.00 Hz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    1.60 dB
PL12                  24.60 dB
SFO2            500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1             SINE.100
GPNAM2             SINE.100
GPX1                   0.00 %
GPX2                   0.00 %
GPY1                   0.00 %
GPY2                   0.00 %
GPZ1                  30.00 %
GPZ2                  50.00 %
p15                  500.00 usec
p16                 1000.00 usec

F2 - Processing parameters
SI                    65536
SF              125.7804127 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     2.00

1D NMR plot parameters
CX                    22.80 cm
CY                    15.65 cm
F1P                 200.000 ppm
F1                 25156.08 Hz
F2P                   0.000 ppm
F2                     0.00 Hz
PPMCM               8.77193 ppm/cm
HZCM             1103.33691 Hz/cm
```

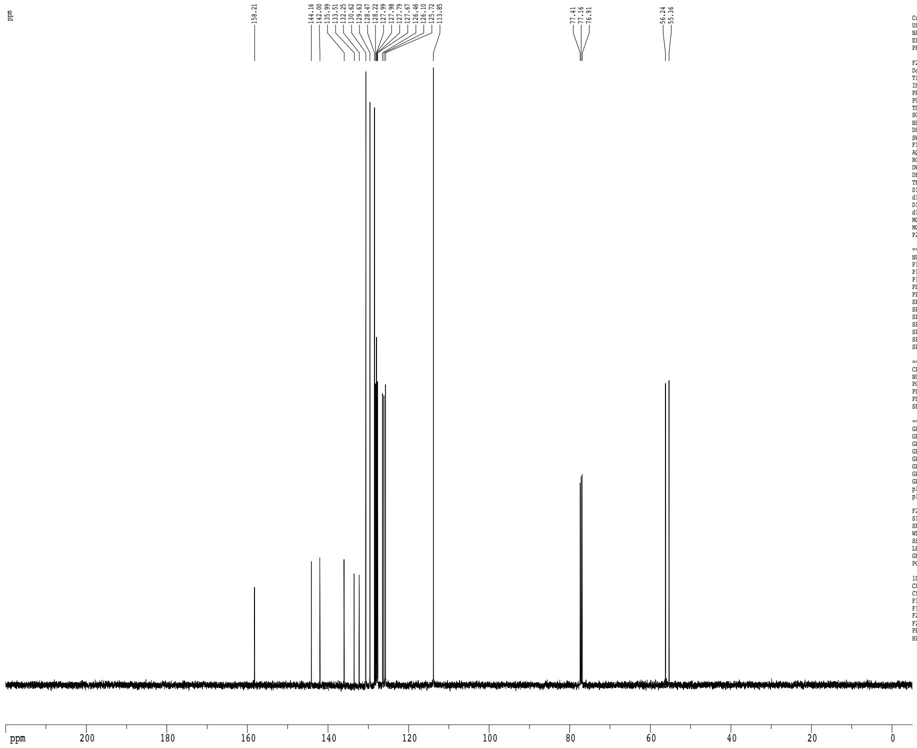
1H spectrum



(R)-1.6

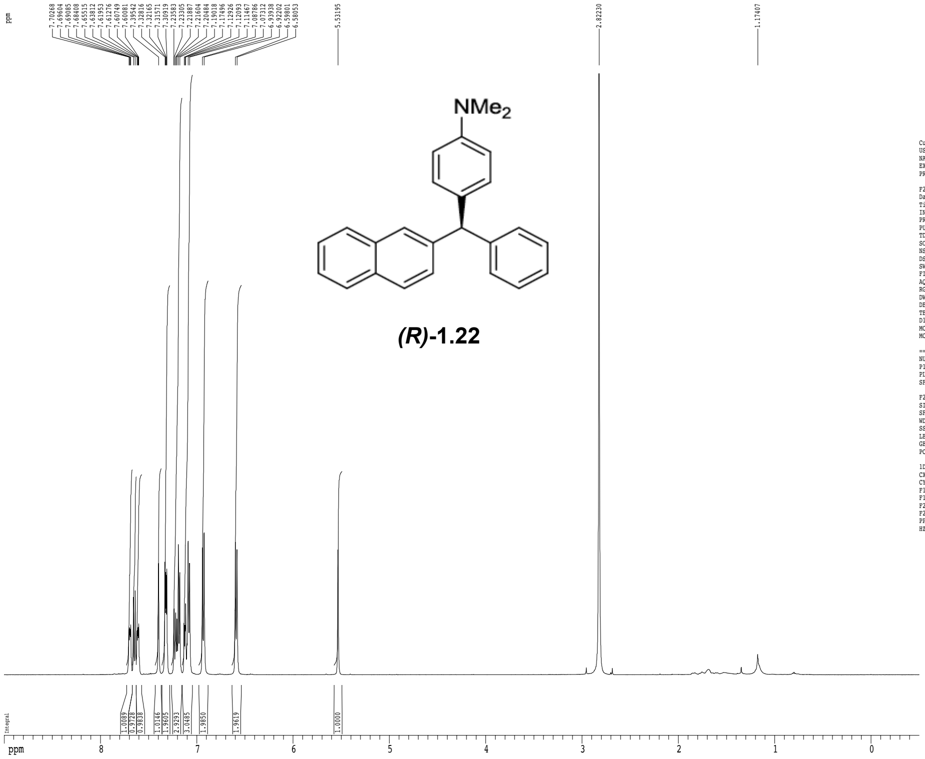
```
Current Data Parameters
USER               mharri
NAME      MRH-III-264-1HNMR
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120928
Time                10.49
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      1
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998774 sec
RG                      5
DW                 62.400 usec
DE                   6.00 usec
TE                  298.1 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200931 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42505 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER               mharri
NAME      MRH-III-264-13CNMR
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120928
Time                10.52
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT            CDCl3T
NS                    110
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                11585.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  31.00 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  15.50 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  3.20 dB
SP2                  3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.60 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804140 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               220.000 ppm
F1               27671.69 Hz
F2P                -5.000 ppm
F2                -628.90 Hz
PPMCM             9.86842 ppm/cm
HZCM           1241.25415 Hz/cm
```

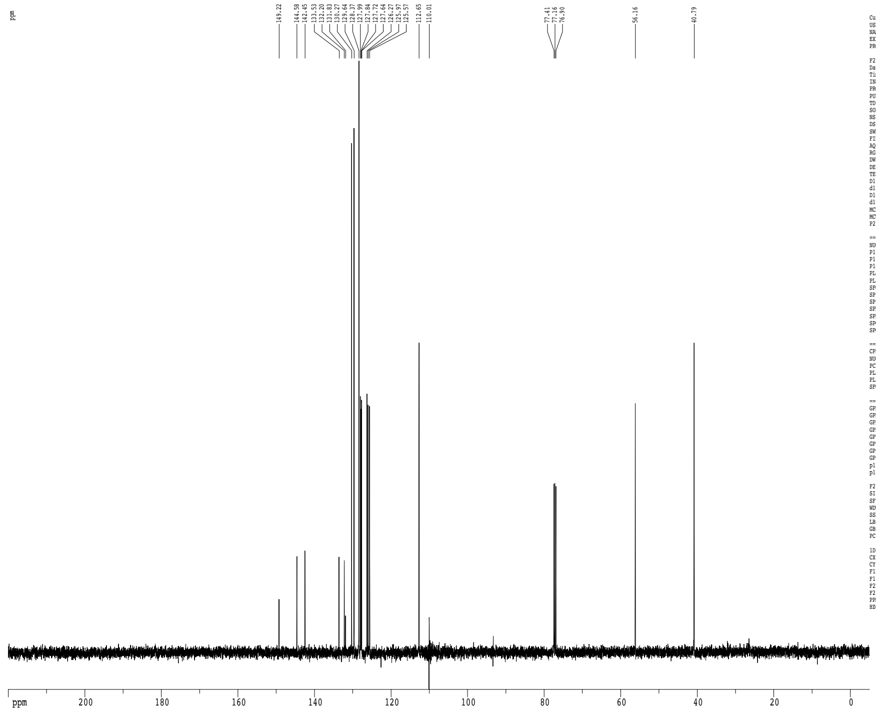
1H spectrum



(R)-1.22

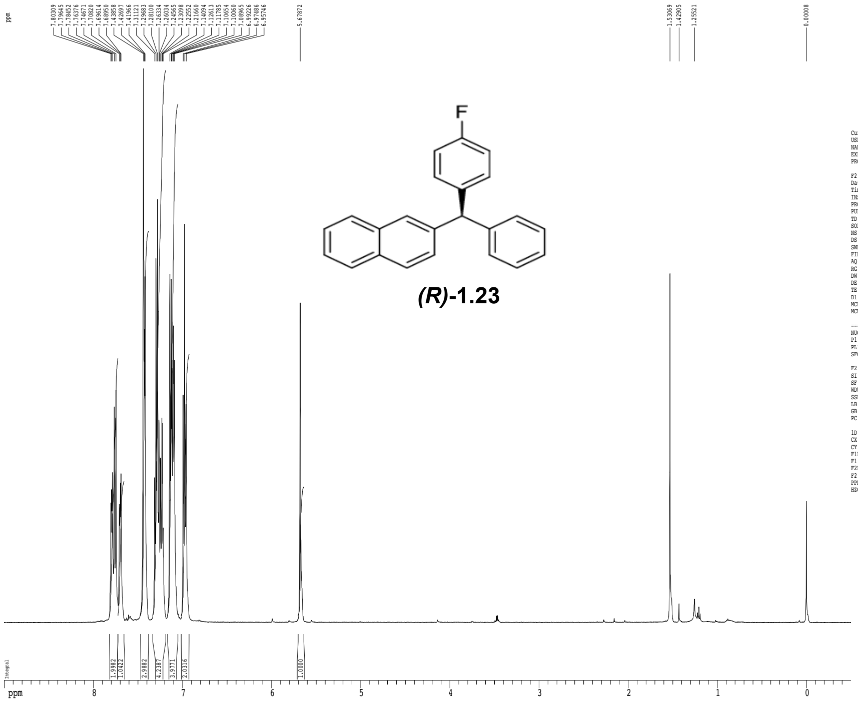
```
Current Data Parameters
USER              mharri
NAME     MRH-III-269-1HNMR
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120928
Time               10.55
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     1
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2201002 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42505 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mharri
NAME     MRH-III-269-13CNMR
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120928
Time               10.57
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT           CDCl3T
NS                   175
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                     5
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804168 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              220.000 ppm
F1              27671.69 Hz
F2P               -5.000 ppm
F2               -628.90 Hz
PPMCM            9.86842 ppm/cm
HZCM          1241.25415 Hz/cm
```

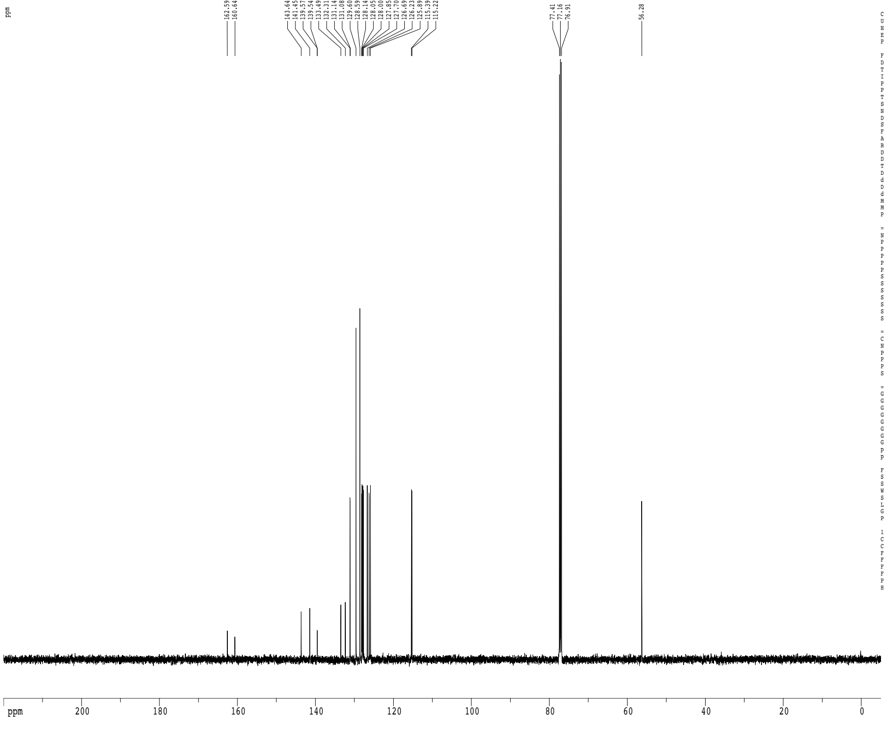
1H spectrum



***(R)*-1.23**

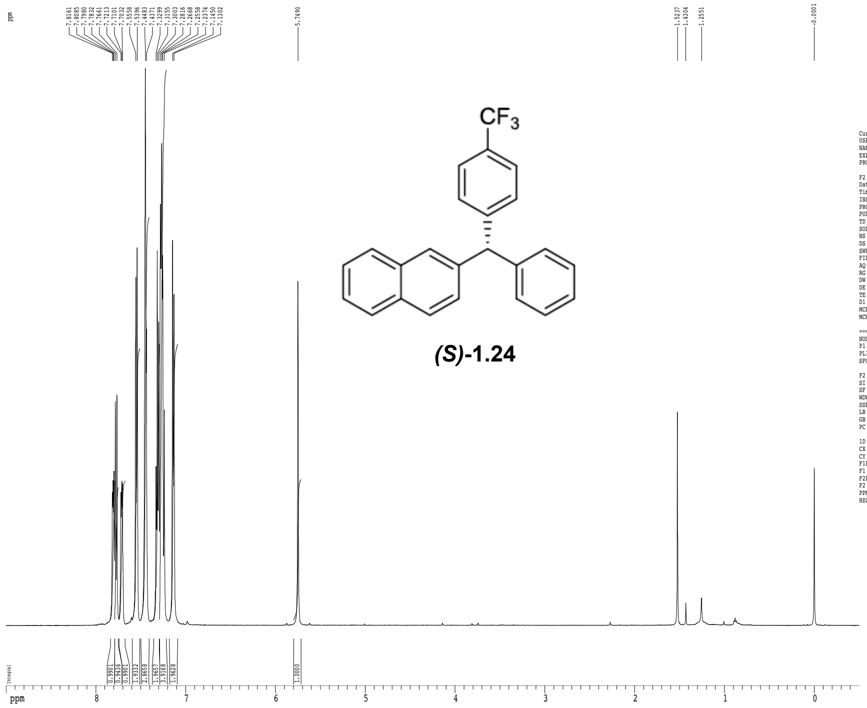
```
Current Data Parameters
USER               mharri
NAME     MRH-III-275-1HNMR
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120925
Time                19.34
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT            CDCl3T
NS                      1
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998774 sec
RG                      5
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200480 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42503 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER               mharri
NAME     MRH-II-101-A-C13CNMR
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20111130
Time                15.11
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    968
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                11585.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  31.00 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  15.50 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  3.20 dB
SP2                  3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.60 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               220.000 ppm
F1               27671.69 Hz
F2P                -5.000 ppm
F2                -628.90 Hz
PPMCM             9.86842 ppm/cm
HZCM           1241.25415 Hz/cm
```

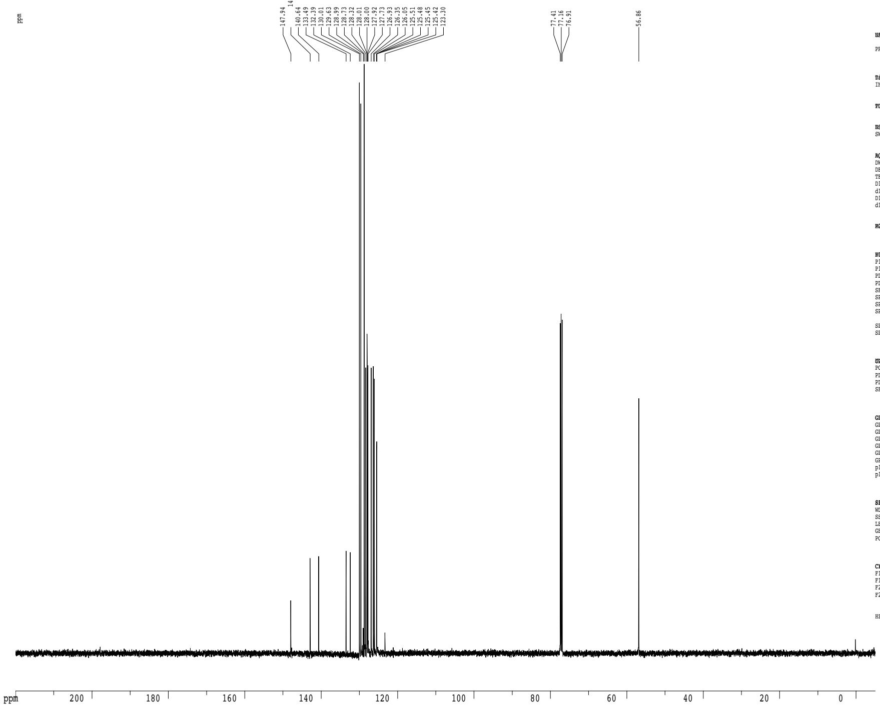
1H spectrum



(S)-1.24

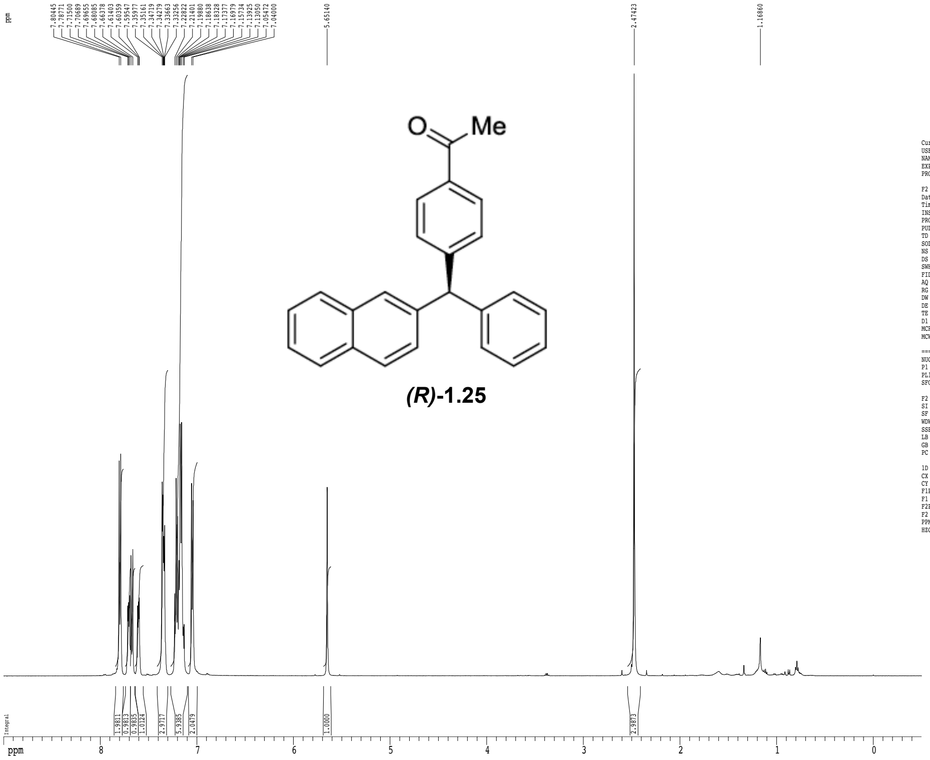
```
Current Data Parameters
USER              mharri
NAME     MRH-IV-29-1HNMR
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121019
Time               14.43
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     3
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200421 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME    MRH-IV-29-13CNMR  mharri
   EXPNO             2
PROCNO                1


     F2 - Acquisition Parameters
Date_                          20121019
INSTRUM             14.46
             cryo500
                         PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg5536.prd
              CDCl3T
  SOLVENT          317
NS                    16
SWH           30303.031 Hz
                         0.462388 Hz
  FIDRES    1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                           6.00 usec
TE                298.0 K
D1          0.25000000 sec
d11                          0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
            0.00000000 sec
    MCREST                   0.01500000 sec
MCWRK       31.00 usec


    ======== CHANNEL f1 ========
NUC1                             13C
P11                          15.50 usec
P12              2500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1        125.7942548 MHz
SP1                          3.20 dB
SP2                3.20 dB
SPNAM1   Crp60,0.5,20.1
                      SPNAM2      Crp60comp.4
SPOFF1             0.00 Hz
SPOFF2                     0.00 Hz


       ======== CHANNEL f2 ========
CPDPRG2          1H                 waltz16
PCPD2             100.00 usec
PL2                          1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz


      ====== GRADIENT CHANNEL =====
GPNAM2         SINE.100             SINE.100
GPX1           0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2               50.00 %
p15
p16                          500.00 usec
               1000.00 usec

  F2 - Processing parameters
SF          125.7804099 MHz 65536
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00


  1D NMR plot parameters22.80cm
CX                          15.65 cm
F1P            220.000 ppm
F1             27671.69 Hz
F2P              -5.000 ppm
F2              -628.90 Hz
                  9.86842 ppm/cm
   PPMCM    1241.25415 Hz/cm
HZCM
```

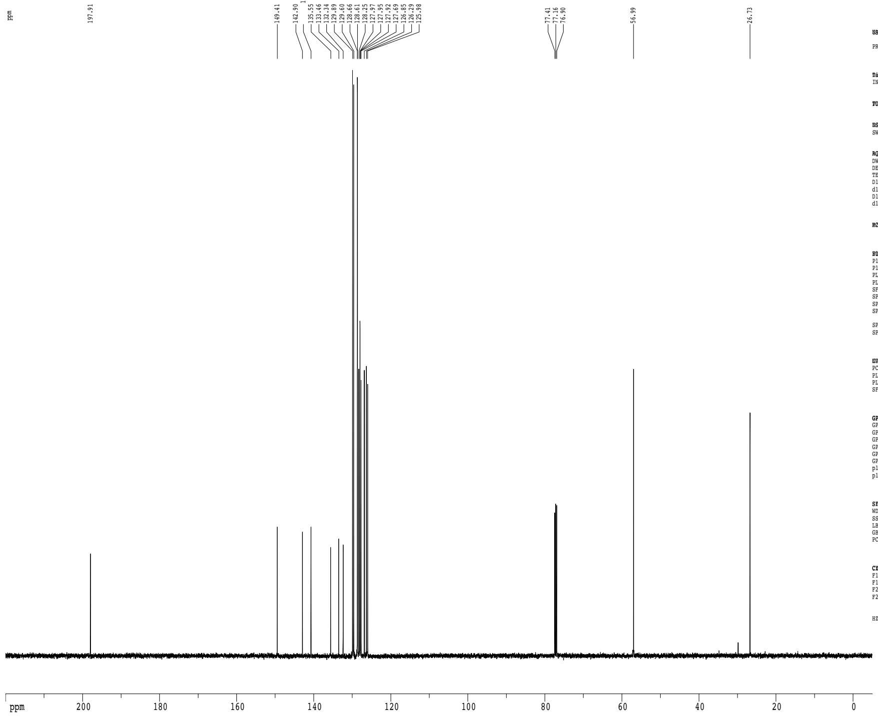
1H spectrum



(R)-1.25

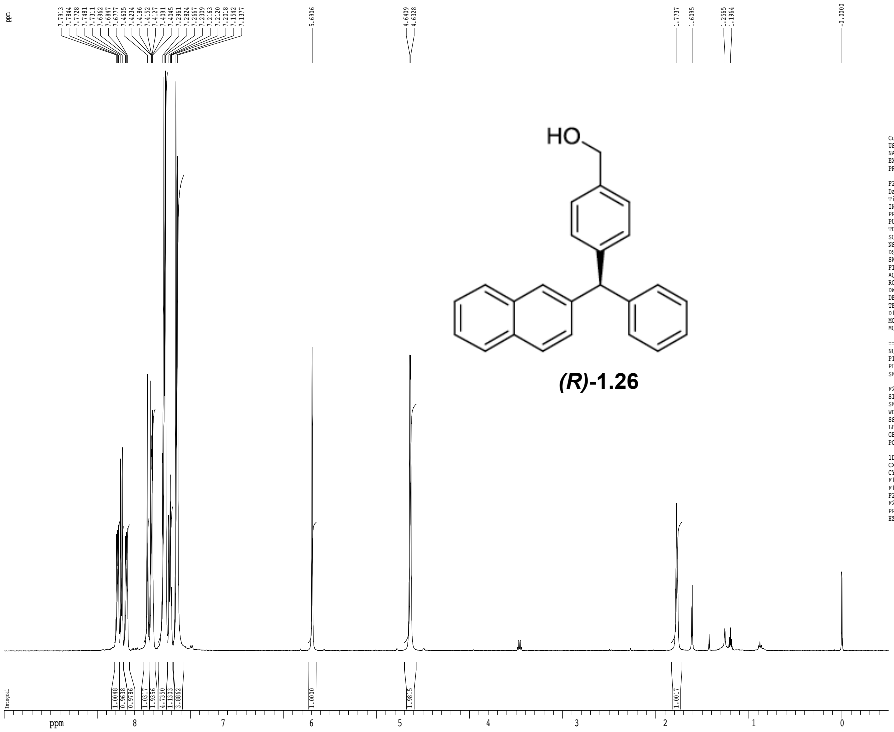
```
Current Data Parameters
USER              mharri
NAME     MRH-III-283-1HNMR
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120928
Time               11.10
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     1
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200951 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42505 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
    Current Data Parameters
USER     MRH-III-283-13CNMRmharri
    EXPNO            3
PROCNO                1

     F2 - Acquisition Parameters
Date_                            20120928
INSTRUM             11.13
             cryo500
                        PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
              CDCl3T
  SOLVENT          106
NS                    16
SWH           30303.031 Hz
                       0.462388 Hz
  FIDRES     1.0813940 sec
AQ                7298.2
DW                16.500 usec
DE                          6.00 usec
TE                298.0 K
D1          0.25000000 sec
d11                         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec

     MCREST                 0.00000000 sec
MCWRK       0.01500000 sec

    ======== CHANNEL f1 ========
NUC1                             13C
P11                         15.50 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                         3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
                    SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2                     0.00 Hz

       ======== CHANNEL f2 ========
CPDPRG2         1H                  waltz16
PCPD2
PL2                        100.00 usec
PL12              24.00 dB
SFO2        500.2225011 MHz

      ====== GRADIENT CHANNEL =====
GPNAM1         SINE.100             SINE.100
GPX1           0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1             30.00 %
GPZ2              50.00 %
p15
p16                         500.00 usec
               1000.00 usec

  F2 - Processing parameters
SI          125.7804177 MHz 65536
WDW                 EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

  1D NMR plot parameters22.00cm
CY                          15.65 cm
F1P            220.000 ppm
F1             27671.69 Hz
F2P              -5.000 ppm
F2              -628.90 Hz
                 9.86842 ppm/cm
    PPMCM    1241.25415 Hz/cm
HZCM
```

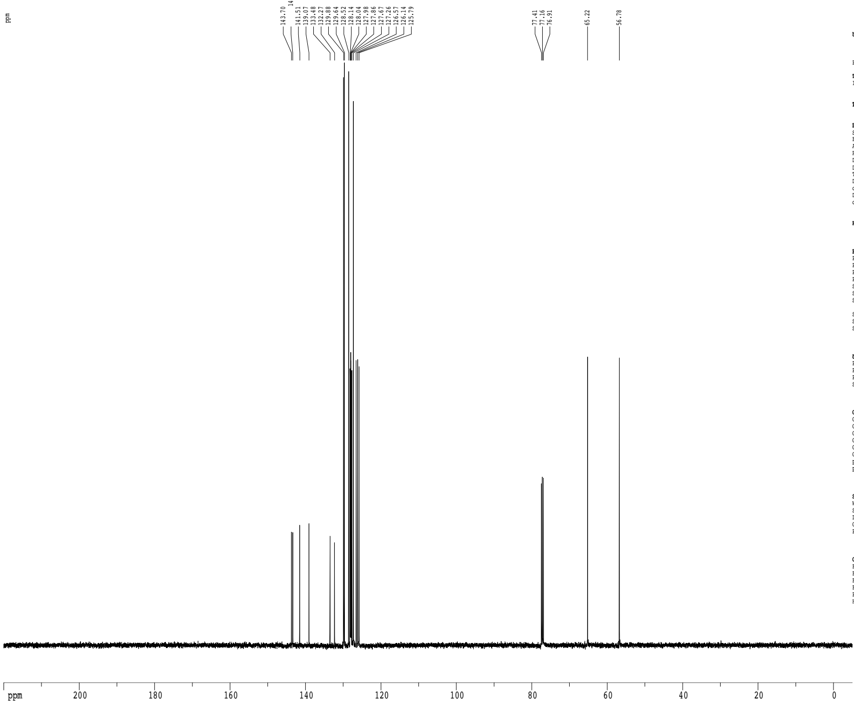
1H spectrum



***(R)*-1.26**

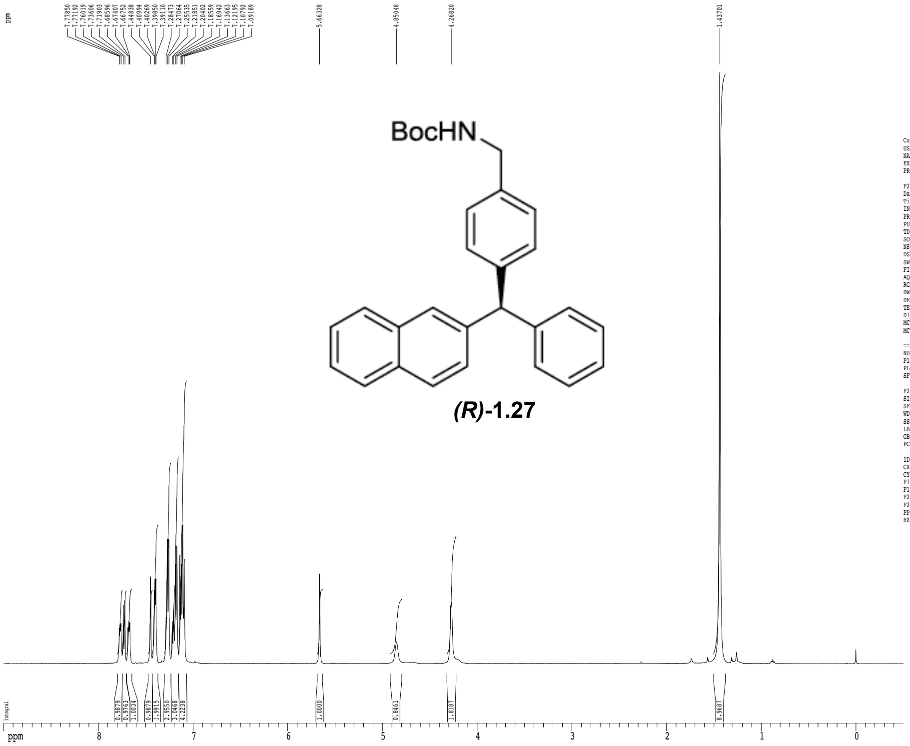
```
Current Data Parameters
USER            mharri
NAME     MRH-IV-26-1HNMR
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20121019
Time             14.34
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               81728
SOLVENT          CDCl3
NS                   1
DS                   2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998774 sec
RG                 3.2
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                7.50 usec
PL1               1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI               65536
SF         500.2200546 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                4.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             4501.98 Hz
F2P             -0.500 ppm
F2             -250.11 Hz
PPMCM          0.41667 ppm/cm
HZCM         208.42503 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
    Current Data Parameters
USER     MRH-IV-26-13CNMR  mharri
    EXPNO             2
                       1

PROCNO
     F2 - Acq20121019n Parameters
Date_                       14.36
INSTRUM             cryo500

                          PROBHD   5 mm CPTCI 1H-
TDLPROG  SpinEchop65536.prd
                CDCl3T
  SOLVENT          101
NS                     16
SWH           30303.031 Hz
FIDRES                     0.462388 Hz
AQ           1.0813940 sec
RG                 4096
DW               16.500 usec
DE                          6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11                         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec

     MCREST                 0.00000000 sec
MCWRK       0.01500000 sec


    ======== CHANNEL f1 ========
NUC1                           13C
P11                         15.50 usec
P12              2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                         3.20 dB
SP2
                                               3.20 dB
SPNAM1   Crp60,0.5,20.1
SPOFF1      0.00 Hz    SPNAM2      Crp60comp.4
SPOFF2             0.00 Hz


       ======== CHANNEL f2 ========
CPDPRG2         1H                 waltz16
PCPD2
PL2                         100.00 usec
PL12              24166.00dB
SFO2        500.2225011 MHz


      ====== GRADIENT CHANNEL =====
GPNAM1          SINE.100           SINE.100
GPX1            0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec


  F2 - Processing parameters
SI          125.7804168 MHz 65536
WDW                 EM
SSB                          0
LB                   1.00 Hz
GB
PC                     0
                2.00

  1D NMR plot parameters
CX                 15.65 22.80 cm
F1P            220.000 ppm
F1             27671.69 Hz
F2P             -5.000 ppm
F2             -628.90 Hz
PPMCM          9.86842 ppm/cm
HZCM      1241.25415 Hz/cm
```

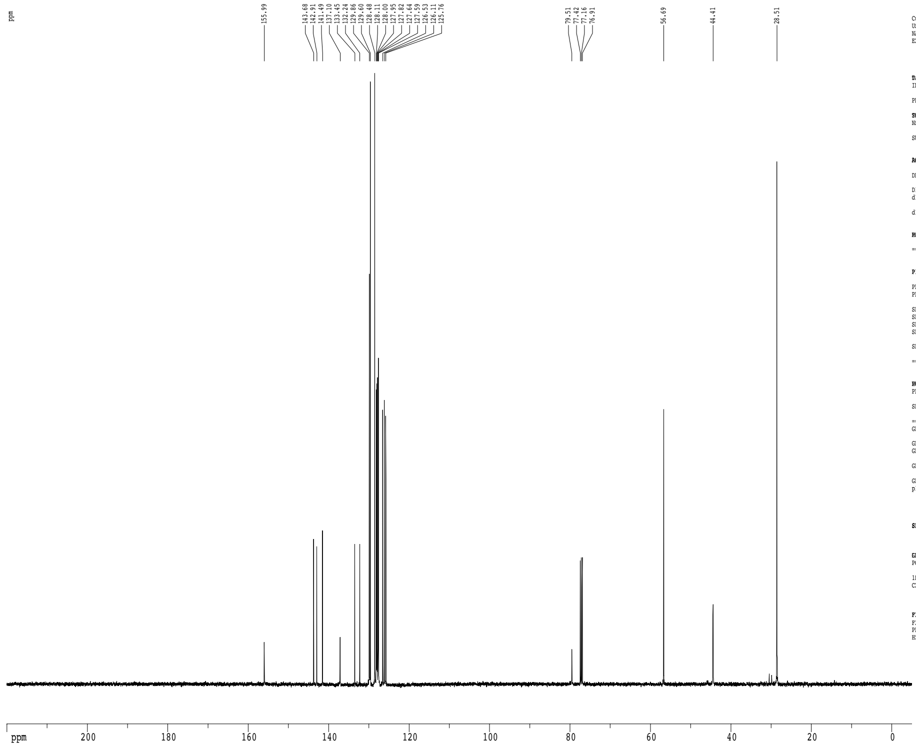
1H spectrum



(R)-1.27

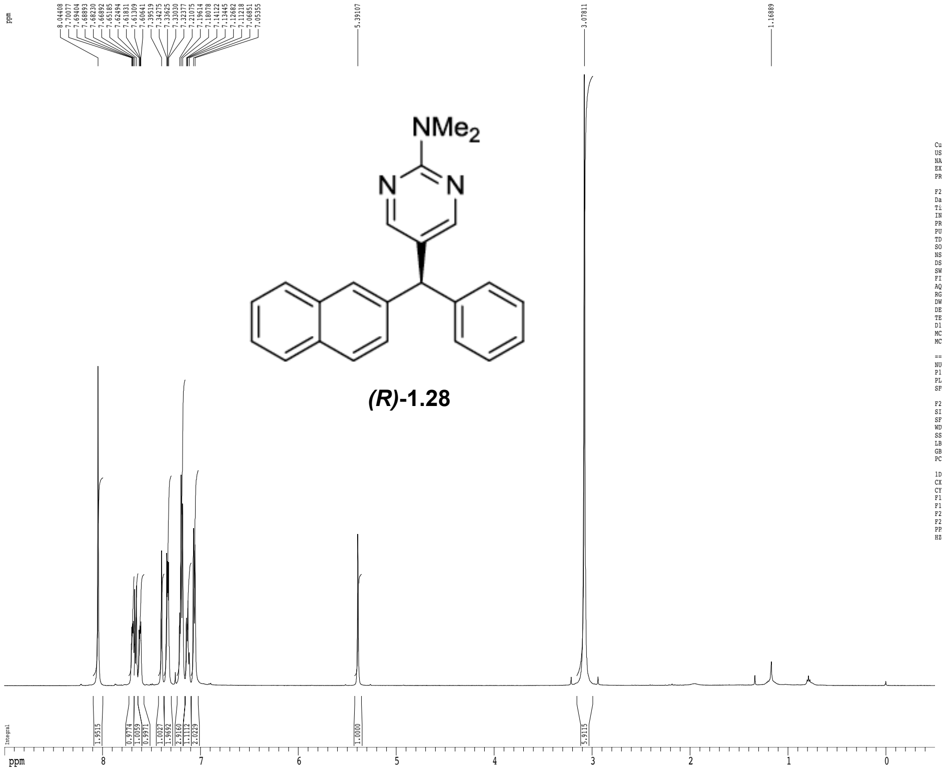
```
Current Data Parameters
USER            mharri
NAME     MRH-III-294-1HNMR
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20121015
Time              15.33
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    1
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200672 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42503 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER            mharri
NAME     MRH-III-294-13CNMR
EXPNO                1
     PROCNO            1

     F2 - Acquisition Parameters
Date_            15.35         20121015
INSTRUM

                cryo500
PROBHD   5 mm CPTCI 1H-
  PULPROG  SpinEchopg30gp.prd
SOLVENT         CDCl3T       65536
NS                 101
  DS                  16
SWH           30303.031 Hz
                           0.462388 Hz
  FIDRES     1.0813940 sec
AQ                5792.6
  DW              16.500 usec
DE
  TE                     6.00 usec
D1           0.25000000Ksec
d11          0.03000000 sec
   D16                      0.00020000 sec
d17          0.00019600 sec
             0.00000000 sec
     MCREST                 0.01500000 sec
MCWRK              31.00 usec

======== CHANNEL f1 ========
                       13C
  NUC1             15.50 usec
P11
   P12                      500.00 usec
PL0             2000.00 dBec
PL1                -1.00 dB
   SFO1     125.7942548 MHz
SP1                         3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
      SPOFF1       0.00 Hz
SPOFF2                     0.00 Hz

======== CHANNEL f2 ========
                waltz16
    CPDPRG2             1H
NUC2               100.00 usec
PL2
   PL12                     1.60 dB
SFO2        500.2225601dBHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
      GPNAM2           SINE.100
GPX1           0.00 %
GPX2               0.00 %
    GPY1                  0.00 %
GPY2
    GPZ1                  0.00 %
GPZ2             350000%%
p15
   p16                      500.00 usec
               1000.00 usec

  F2 - Processing parameters
SF          125.7804238 MHz 65536
  WDW                       EM
                         0
  SSB              1.00 Hz
GB                       0
PC                 2.00

1D NMR plot parameters
CX                 22.80 cm
  CY                       15.65 cm

  F1P                      220.000 ppm
F2P            27570000ppm
F2               -628.90 Hz
PPMCM            9.86842 ppm/cm
HZCM          1241.25427 Hz/cm
```

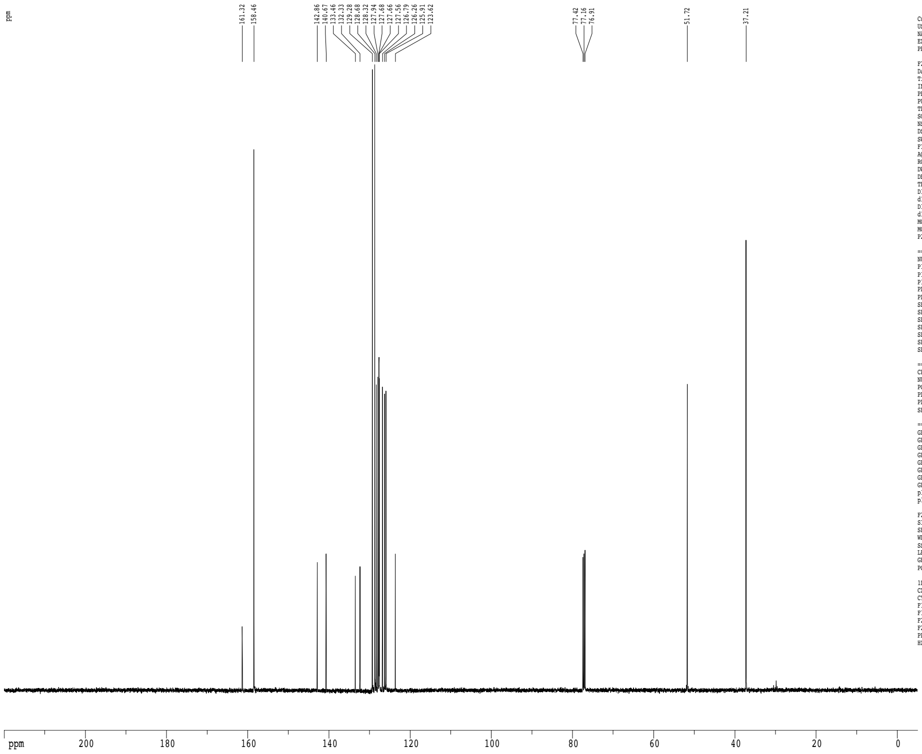
1H spectrum



(R)-1.28

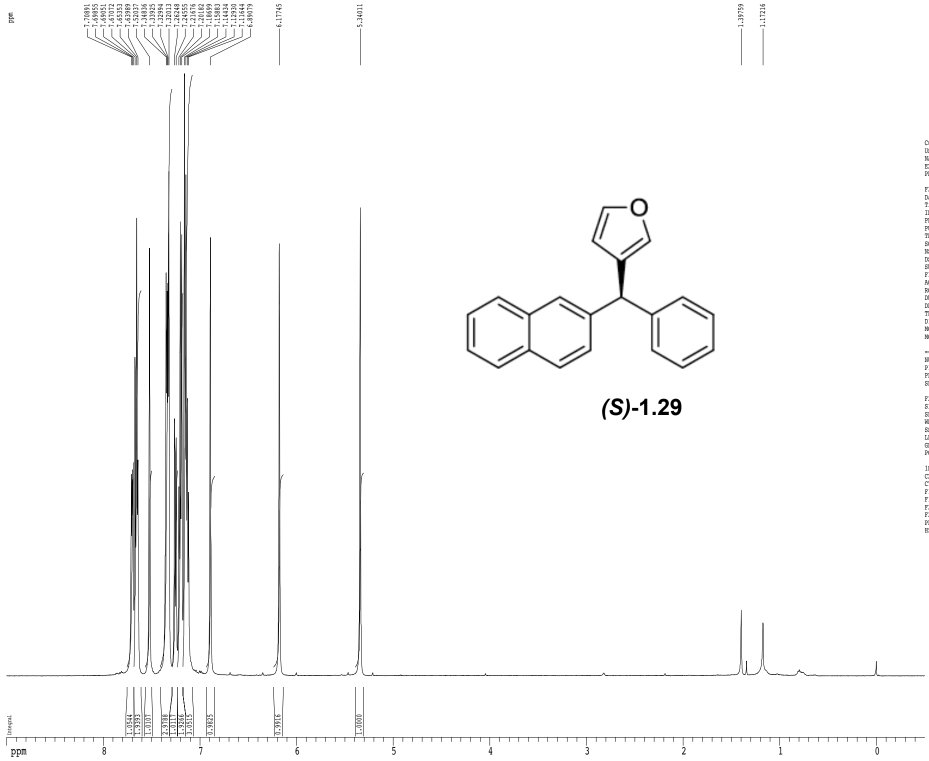
```
Current Data Parameters
USER              mharri
NAME     MRH-III-285-1HNMR
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120928
Time               11.16
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     1
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200930 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42505 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mharri
NAME    MRH-III-285-13CNMR
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120928
Time               11.19
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT           CDCl3T
NS                   109
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804177 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              220.000 ppm
F1              27671.69 Hz
F2P               -5.000 ppm
F2               -628.90 Hz
PPMCM            9.86842 ppm/cm
HZCM          1241.25415 Hz/cm
```

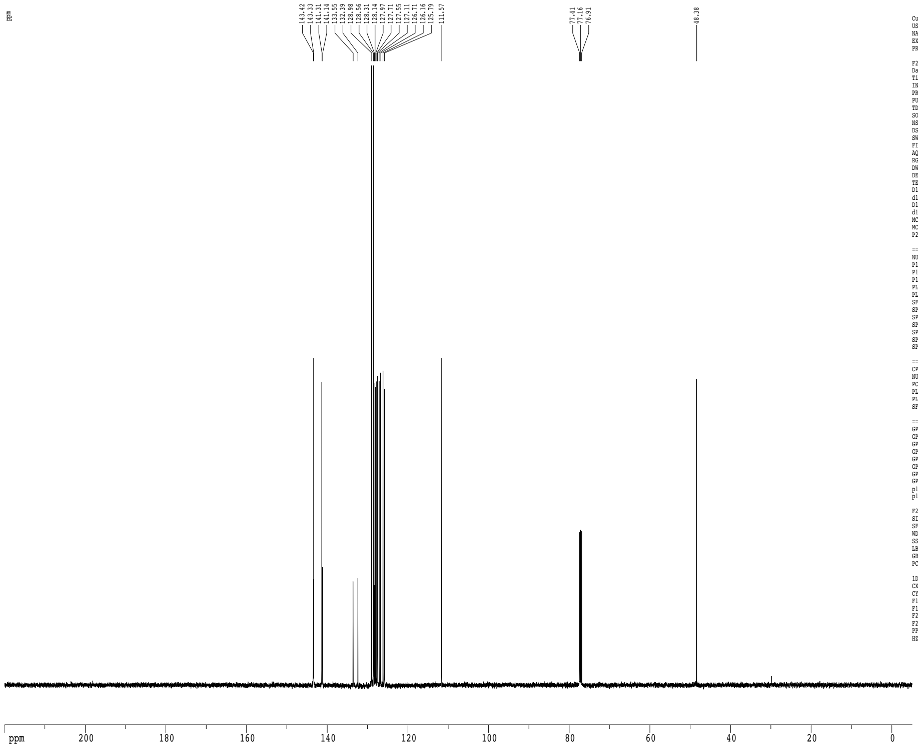
1H spectrum



(S)-1.29

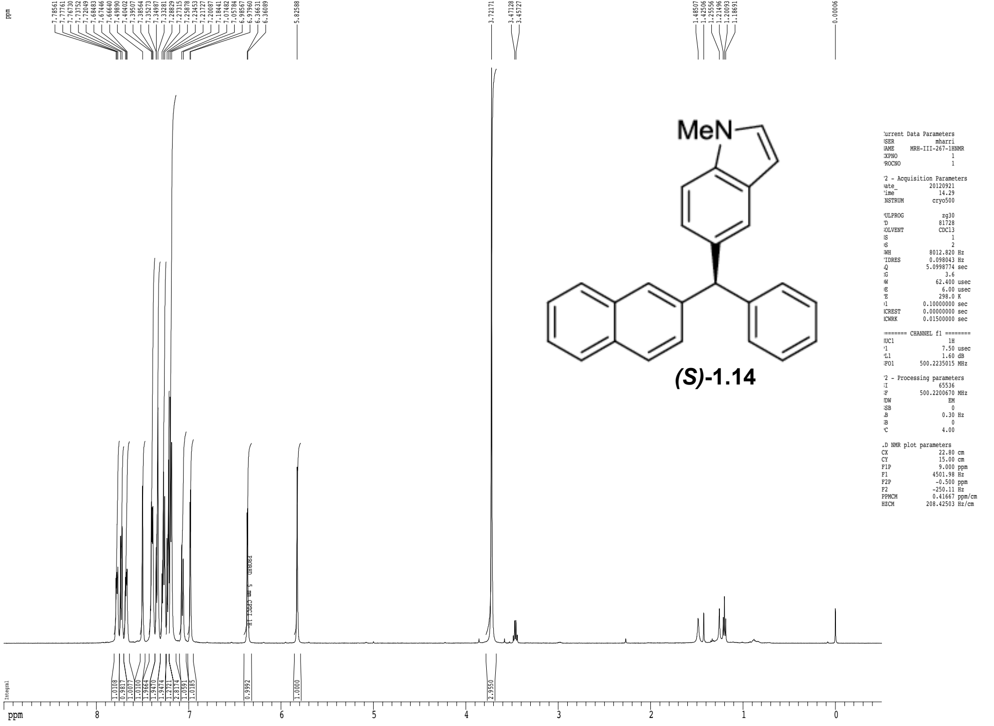
```
Current Data Parameters
USER              mharri
NAME     MRH-III-277-1HNMR
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120928
Time               11.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     1
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.1 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2201019 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42505 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

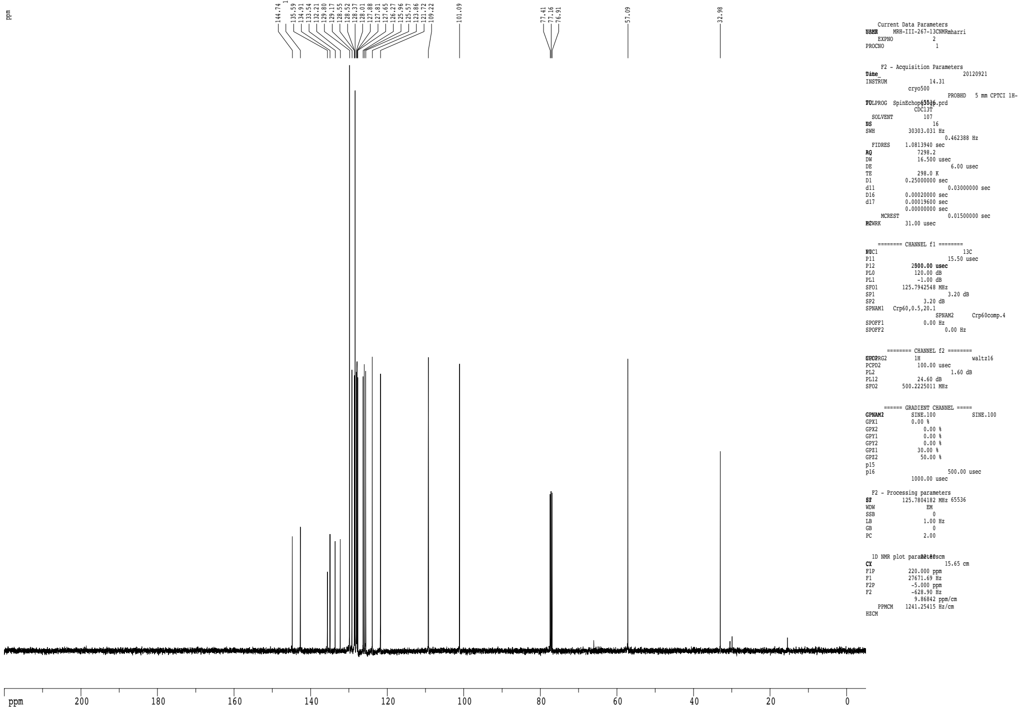


```
Current Data Parameters
USER              mharri
NAME     MRH-III-277-13CNMR
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120928
Time               11.07
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT           CDCl3T
NS                   102
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.1 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804159 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              220.000 ppm
F1              27671.69 Hz
F2P               -5.000 ppm
F2               -628.90 Hz
PPMCM            9.86842 ppm/cm
HZCM          1241.25415 Hz/cm
```

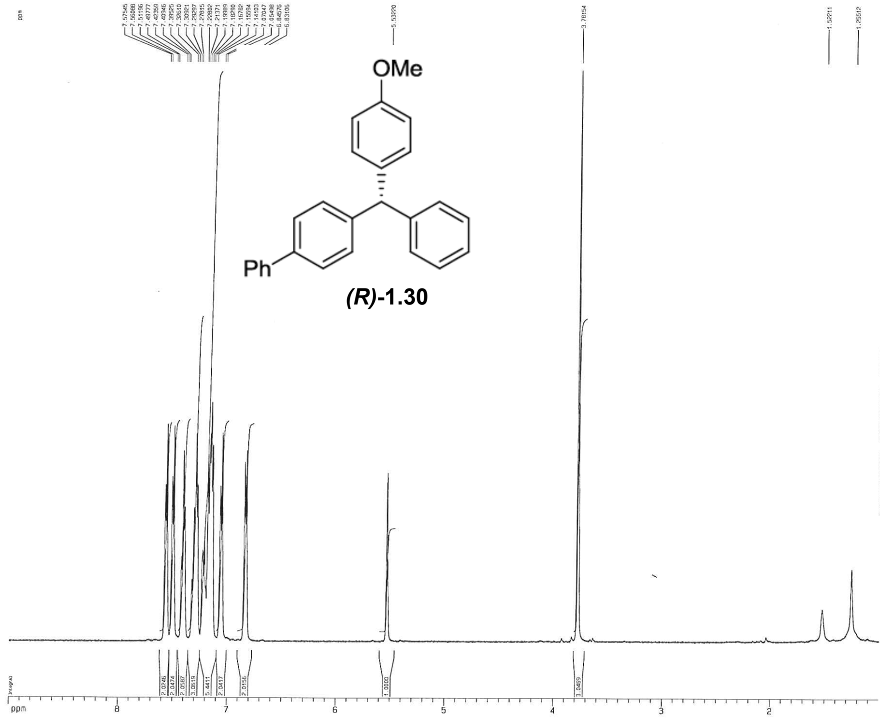
1H spectrum



Z-restored spin-echo 13C spectrum with 1H decoupling



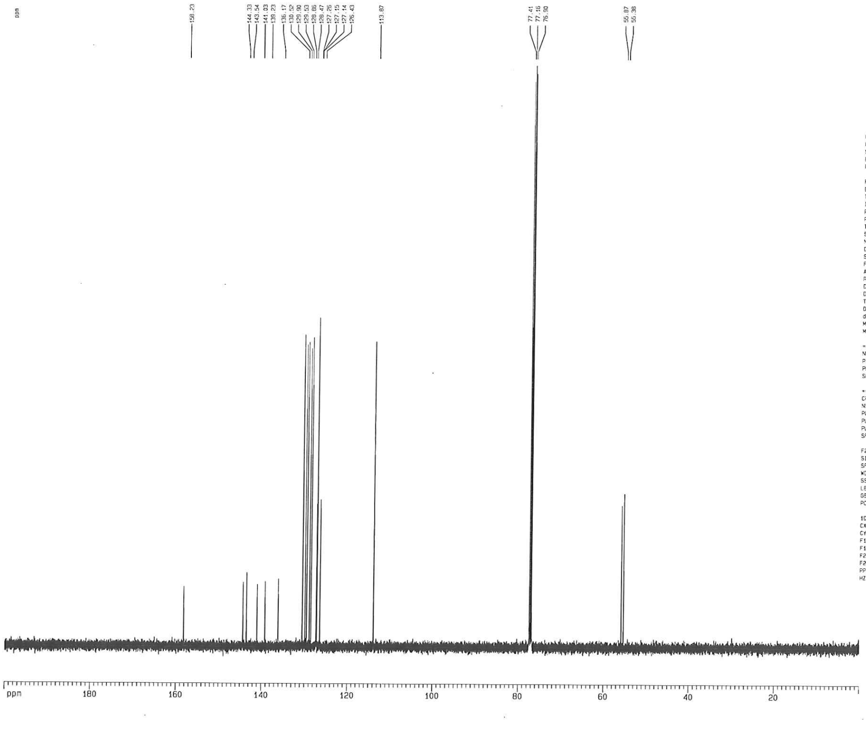
1H spectrum



(R)-1.30

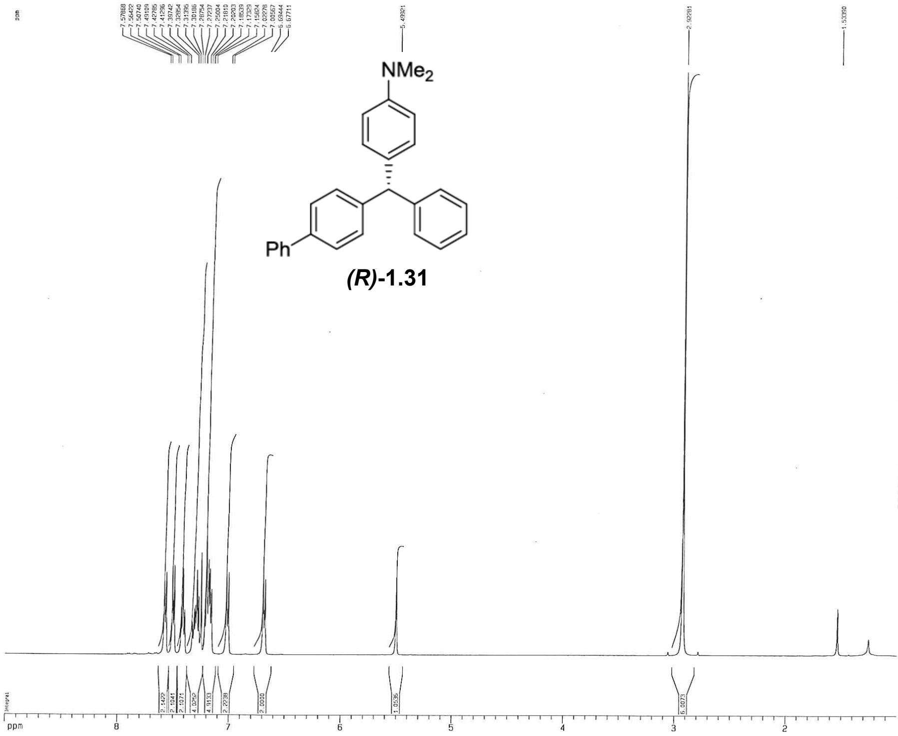
```
Current Data Parameters
USER            lhanna
NAME       LEH-1-118-c2
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20121023
Time             18.44
INSTRUM          gn500
PROBHD   5 mm broadband
PULPROG           zg30
TD               81728
SOLVENT          CDC13
NS                   8
DS                   2
SWH           6012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0938774 sec
RG               143.7
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.20 usec
PL1              -5.00 dB
SFO1       499.4034958 MHz

F2 - Processing parameters
SI               65536
SF         499.4000425 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             4494.60 Hz
F2P              1.000 ppm
F2              499.40 Hz
PPMCM          0.35088 ppm/cm
HZCM         175.22809 Hz/cm
```

13C spectrum with 1H decoupling



```
Current Data Parameters
USER            lhanna
NAME      LEH-1-118-C13
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20121023
Time             19.47
INSTRUM          gn500
PROBHD   5 mm broadband
PULPROG         zgdc30
TD               65535
SOLVENT          CDC13
NS                1024
DS                   4
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG              7298.2
DW              16.500 usec
DE                4.50 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1                7.70 usec
PL1               0.00 dB
SFO1       125.5880432 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -3.00 dB
PL12             13.20 dB
SFO2       499.4024970 MHz

F2 - Processing parameters
SI               65536
SF         125.5742201 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            200.000 ppm
F1            25114.84 Hz
F2P              0.000 ppm
F2                0.00 Hz
PPMCM          8.77193 ppm/cm
HZCM        1101.52832 Hz/cm
```

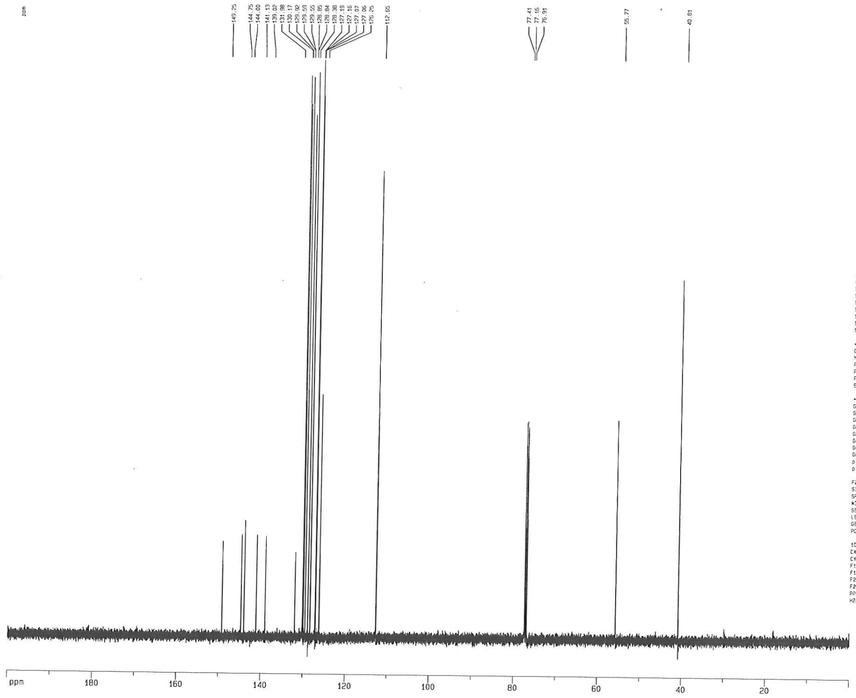
1H spectrum



***(R)*-1.31**

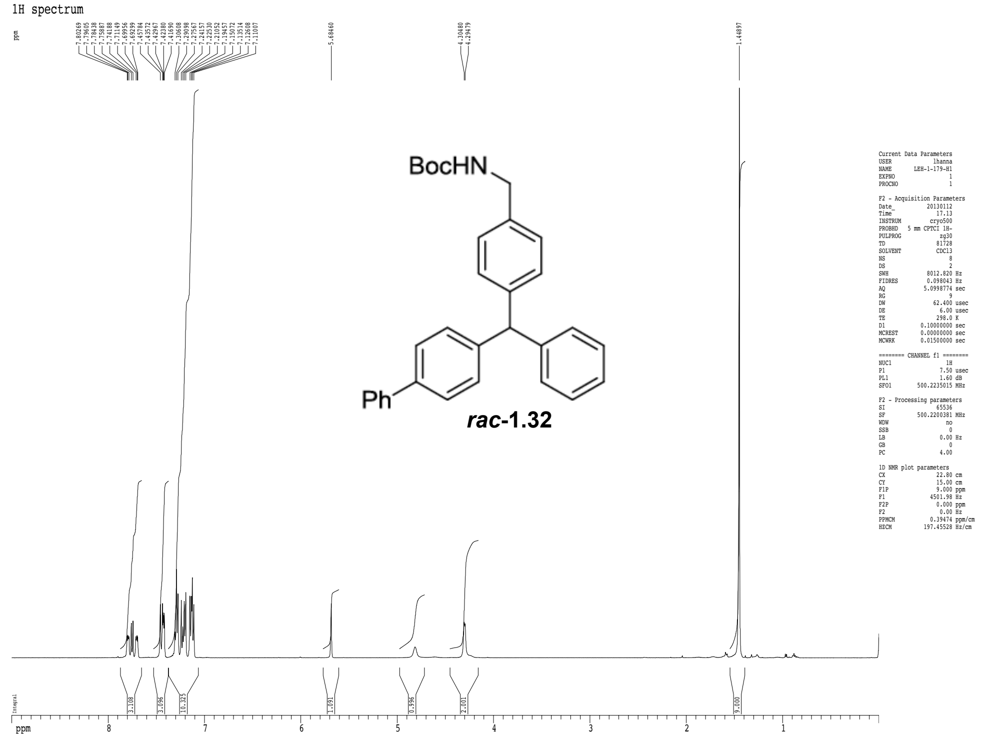
```
Current Data Parameters
USER            lhanna
NAME     LEH-1-148-c3-f25-2
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20121118
Time             14.31
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               81728
SOLVENT          CDCl3
NS                  40
DS                   2
SWH          8012.820 Hz
FIDRES       0.098043 Hz
AQ          5.0998774 sec
RG                 5.7
DW             62.400 usec
DE               6.00 usec
TE              298.0 K
D1         0.10000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               7.50 usec
PL1              1.60 dB
SFO1      500.2235015 MHz

F2 - Processing parameters
SI               65536
SF        500.2200354 MHz
WDW                 no
SSB                  0
LB               0.00 Hz
GB                   0
PC                4.00

1D NMR plot parameters
CX              22.60 cm
CY              15.00 cm
F1P             9.000 ppm
F1            4501.98 Hz
F2P             1.000 ppm
F2             500.22 Hz
PPMCM         0.35088 ppm/cm
HZCM        175.51581 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



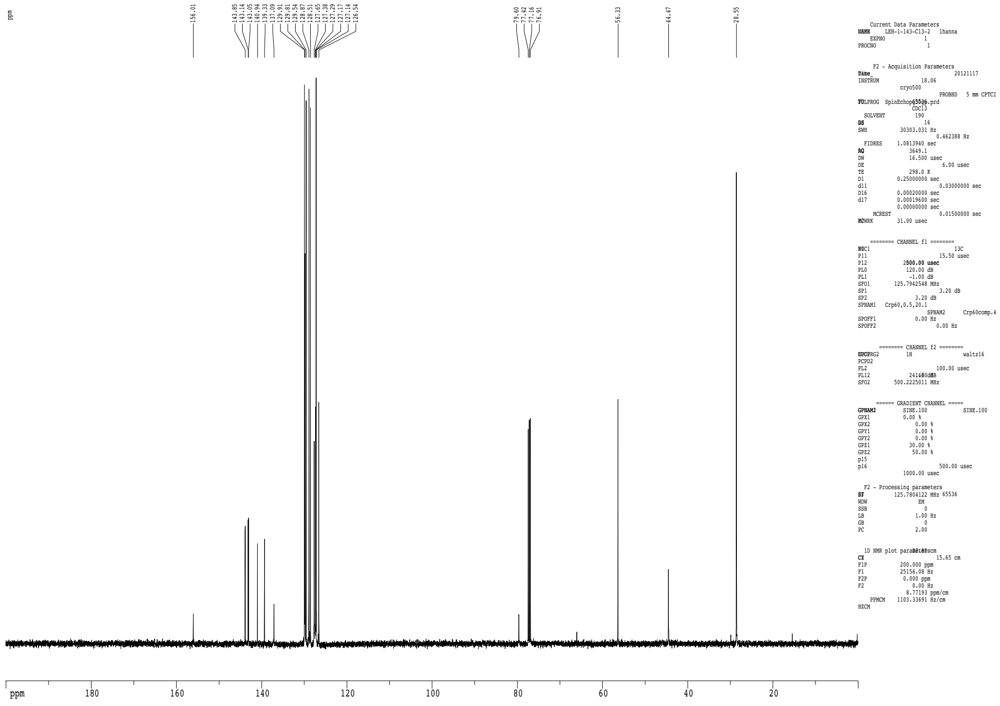
```
Current Data Parameters
USER            lhanna
NAME        LEH-1-148-C13
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20121117
Time             23.20
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT          CDCl3
NS                 325
DS                  16
SWH         30303.031 Hz
FIDRES       0.462388 Hz
AQ          1.0813940 sec
RG              9195.2
DW             16.500 usec
DE               6.00 usec
TE              298.0 K
D1         0.25000000 sec
d11        0.03000000 sec
D16        0.00020000 sec
d17        0.00019500 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec
P2              31.00 usec

======== CHANNEL f1 ========
NUC1               13C
P1              15.50 usec
P11            500.00 usec
P12           2000.00 usec
PL0            120.00 dB
PL1             -1.00 dB
SFO1      125.7942549 MHz
SP1              3.20 dB
SP2              3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2     Crp60comp.4
SPOFF1           0.00 Hz
SPOFF2           0.00 Hz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2          100.00 usec
PL2              1.60 dB
PL12            24.60 dB
SFO2      500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPX1             0.00 %
GPX2             0.00 %
GPY1             0.00 %
GPY2             0.00 %
GPZ1            30.00 %
GPZ2            50.00 %
p15            500.00 usec
p16           1000.00 usec

F2 - Processing parameters
SI               65536
SF        125.7804094 MHz
WDW                 no
SSB                  0
LB               0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX              22.60 cm
CY              15.65 cm
F1P           200.000 ppm
F1           25156.08 Hz
F2P             0.000 ppm
F2               0.00 Hz
PPMCM         8.77193 ppm/cm
HZCM       1103.33691 Hz/cm
```

1H spectrum

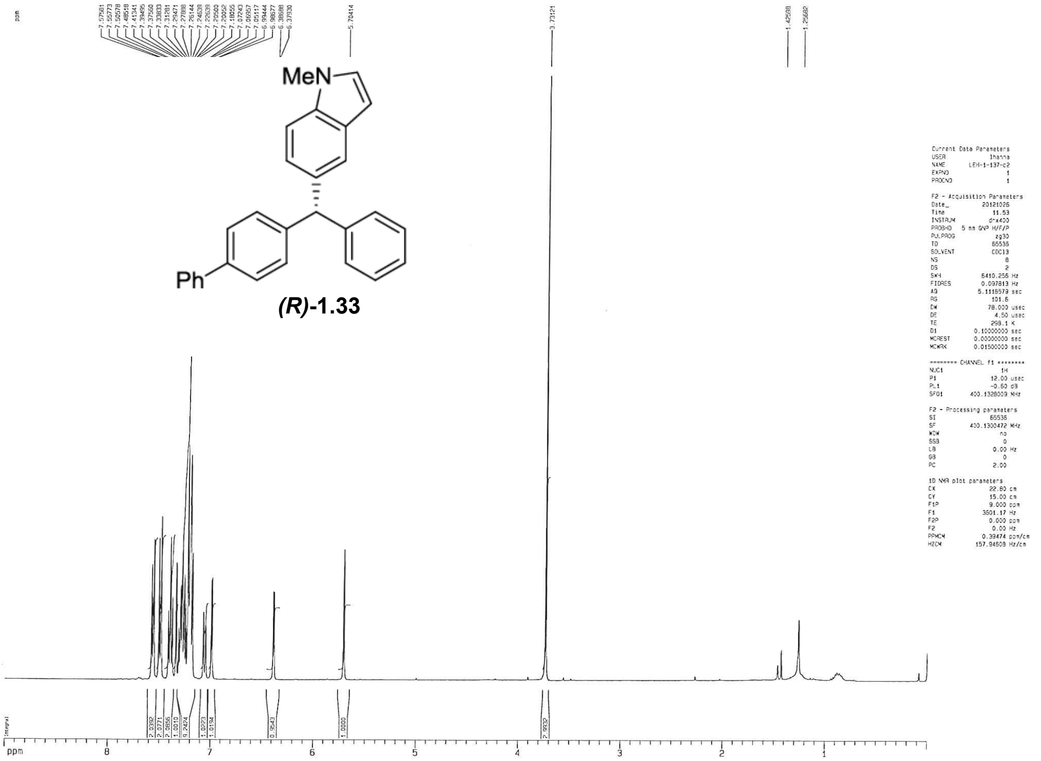


***rac*-1.32**

Z-restored spin-echo 13C spectrum with 1H decoupling

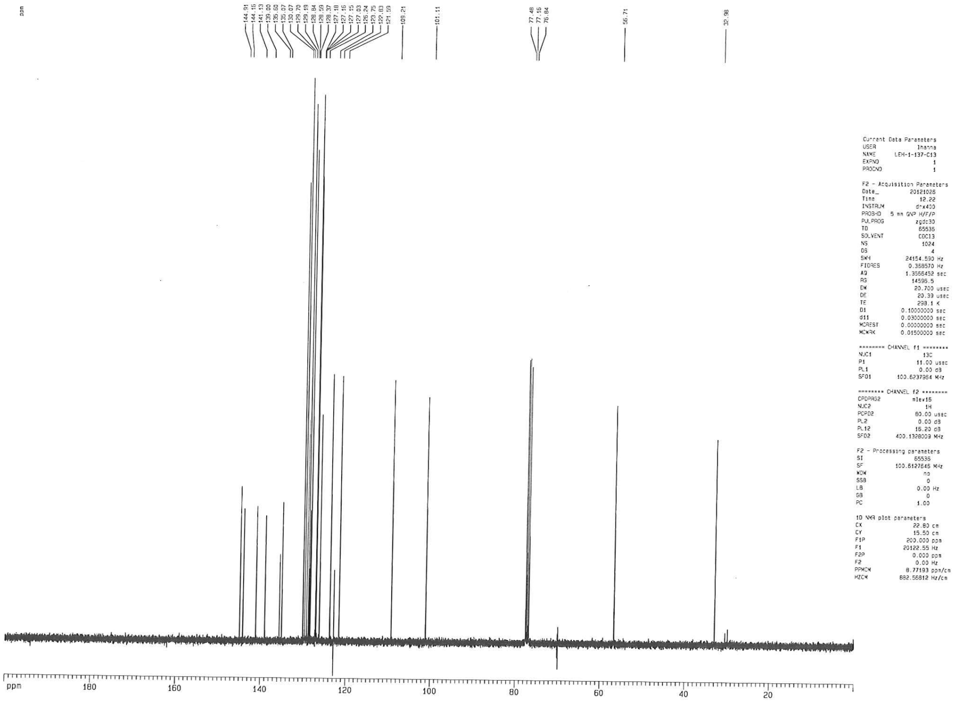


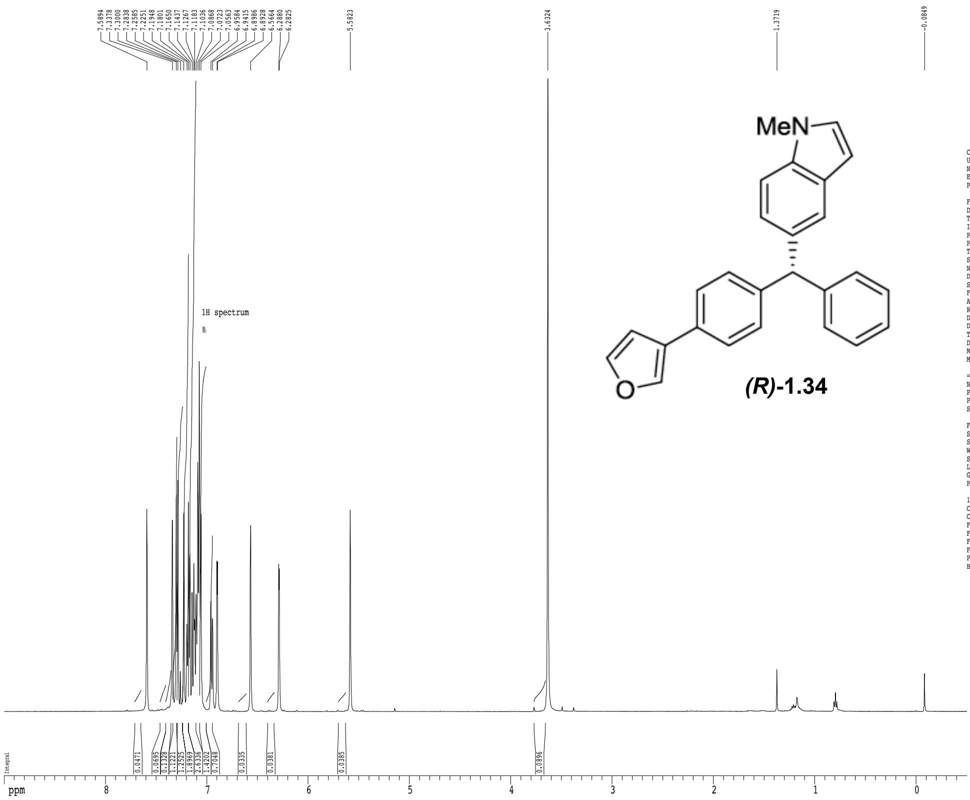
1H spectrum



***(R)*-1.33**

13C spectrum with 1H decoupling

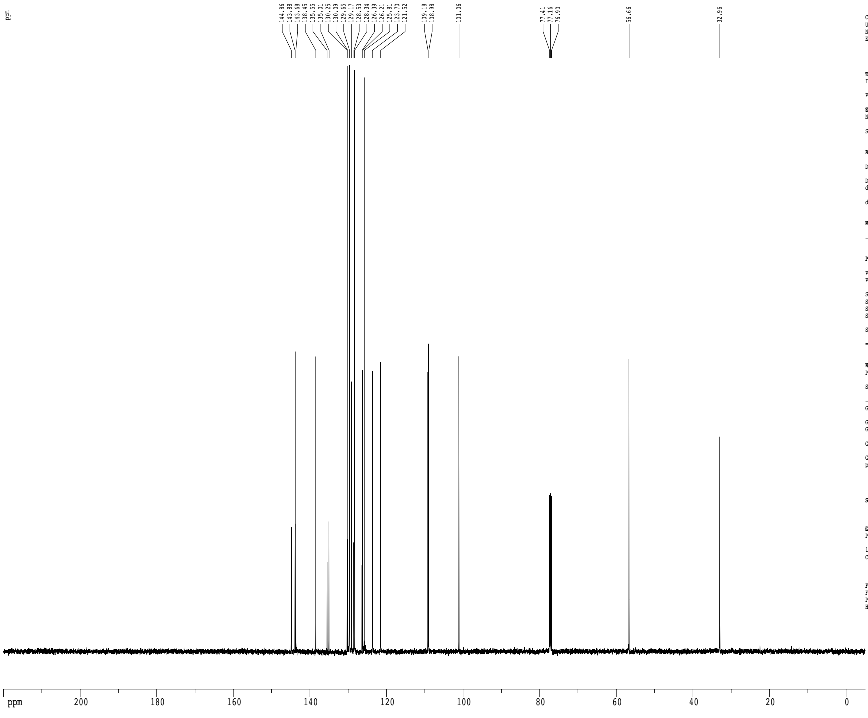




***(R)*-1.34**

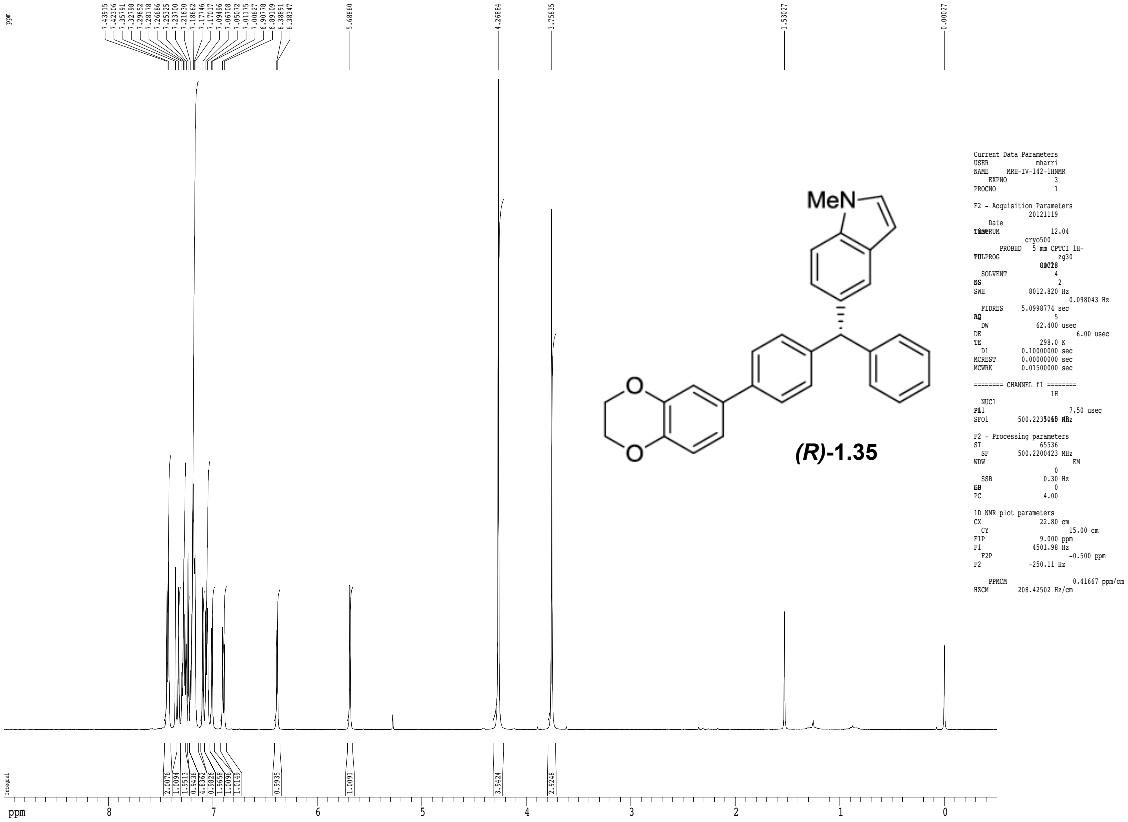
```
Current Data Parameters
USER              mharri
NAME      MRH-IV-135-1HNMR
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121118
Time               18.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     2
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                     4
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2201117 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42506 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

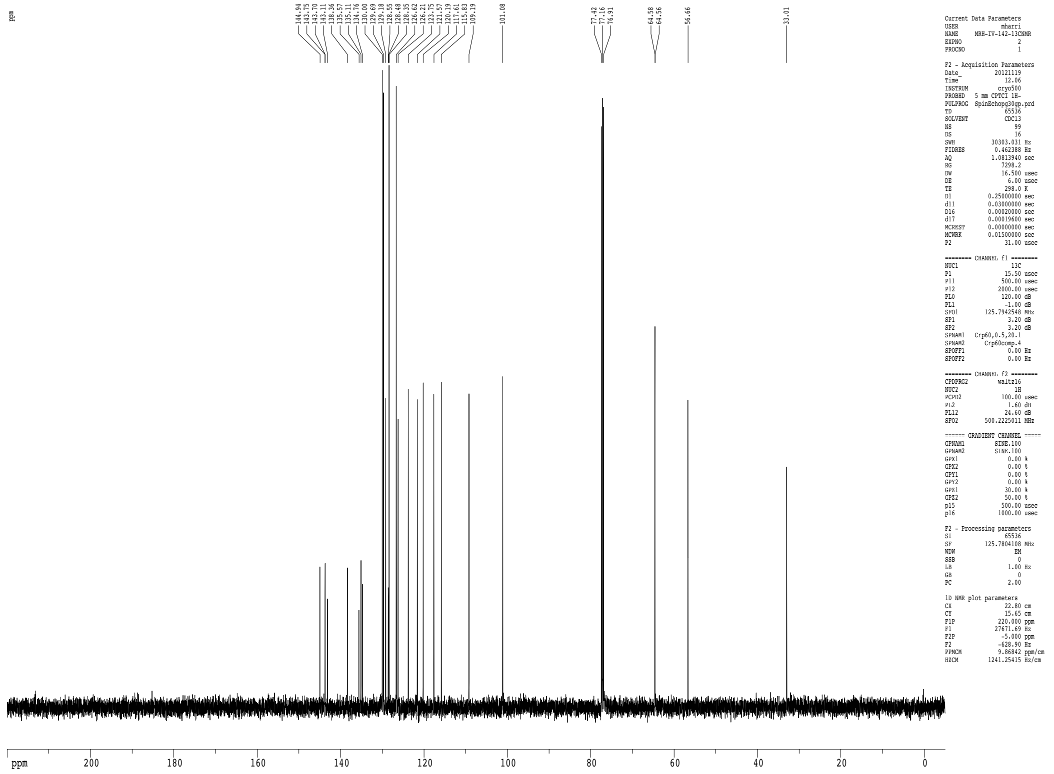


```
Current Data Parameters
USER              mharri
NAME      MRH-IV-135-13CNMR
EXPNO                  2
     PROCNO             1


     F2 - Acquisition Parameters
Date_              18.46          20121118
INSTRUM
                cryo500
PROBHD   5 mm CPTCI 1H-
  PULPROG  SpinEchopg30gp.prd
SOLVENT         CDCl3T        65536
NS                 101
  DS                  16
SWH          30303.031 Hz
                         0.462388 Hz
  FIDRES     1.0813940 sec
AQ                7298.2
  DW             16.500 usec
DE
  TE                       6.00 usec
D1           0.25298000Ksec
d11          0.03000000 sec
   D16                       0.00020000 sec
d17          0.00019600 sec
             0.00000000 sec
     MCREST                  0.01500000 sec
MCWRK              31.00 usec

======== CHANNEL f1 ========
                      13C
  NUC1             15.50 usec
P11
   P12                       500.00 usec
PL0             2120.00 dBec
PL1                -1.00 dB
   SFO1     125.7942548 MHz
SP1                          3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
      SPOFF1       0.00 Hz
SPOFF2                      0.00 Hz

======== CHANNEL f2 ========
                waltz16
    CPDPRG2            1H
PCPD2             100.00 usec
PL2
   PL12                     1.60 dB
SFO2        500.2225601dBHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
      GPNAM2            SINE.100
GPX1            0.00 %
GPX2                0.00 %
    GPY1                    0.00 %
GPY2
    GPZ1                   0.00 %
GPZ2              350000%%
p15
   p16                       500.00 usec
                1000.00 usec

  F2 - Processing parameters
SF          125.7804201 MHz 65536
  WDW                       EM
                       0
  SSB              1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
  CY                        15.65 cm

  F1P                       220.000 ppm
F2P           27670069ppHz
F2               -628.90 Hz
PPMCM            9.86842 ppm/cm
HZCM          1241.25415 Hz/cm
```

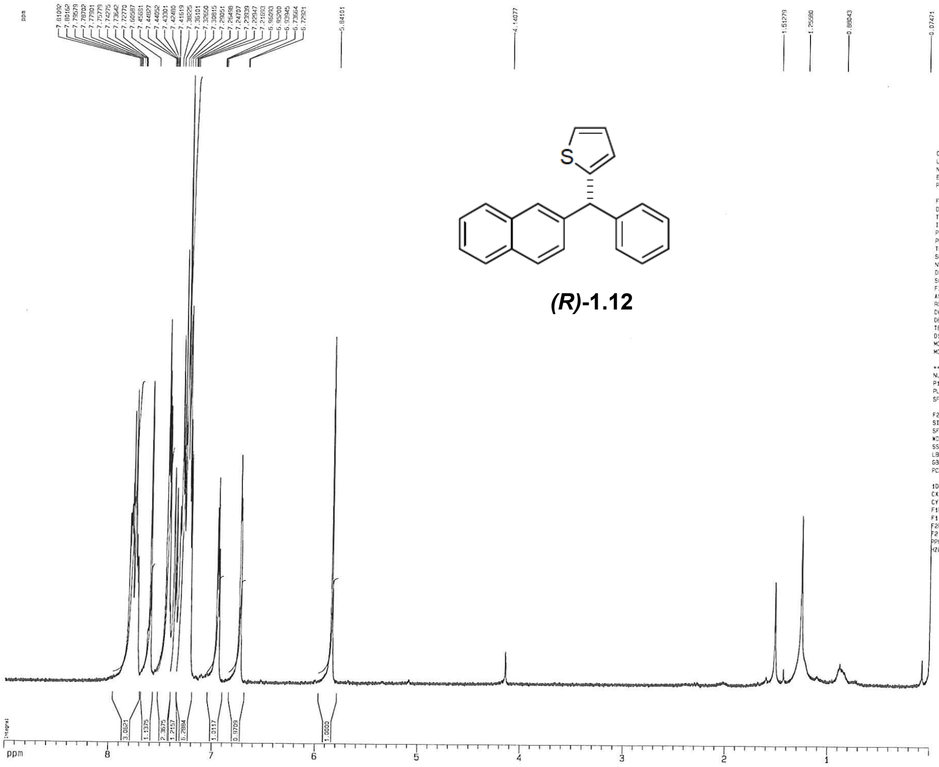
1H spectrum


(R)-1.35

Z-restored spin-echo 13C spectrum with 1H decoupling



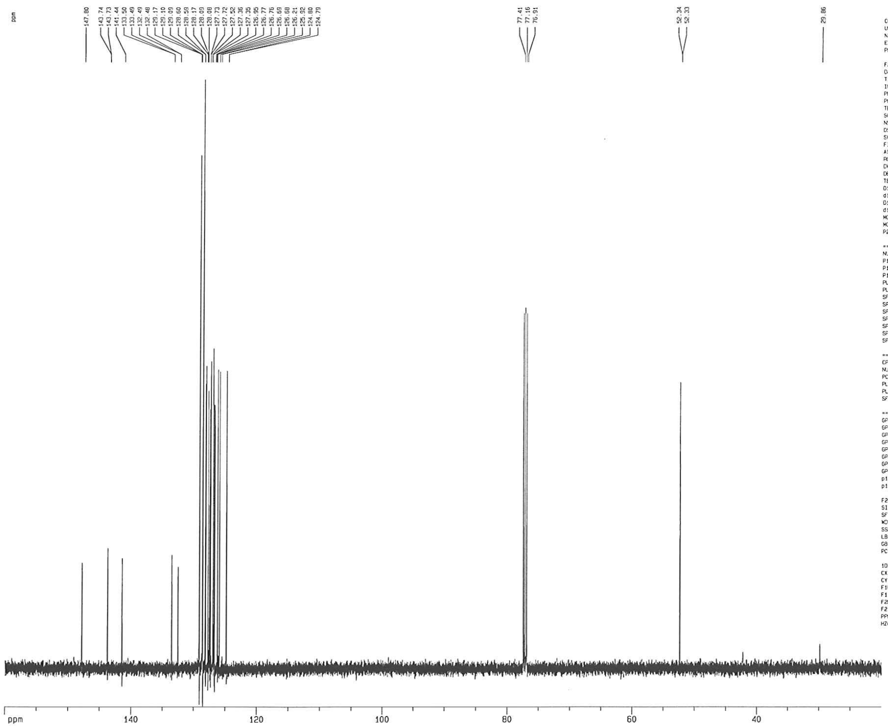
1H spectrum



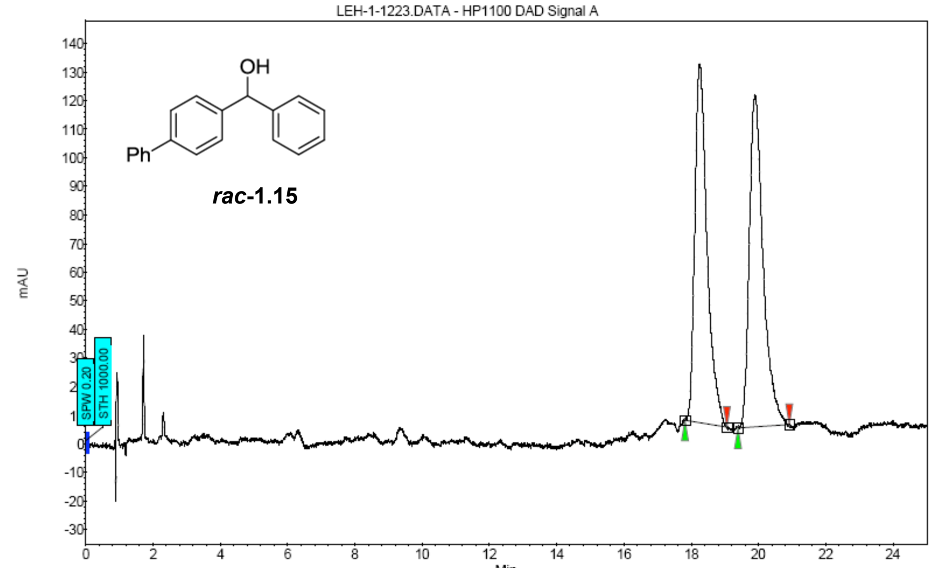
(R)-1.12

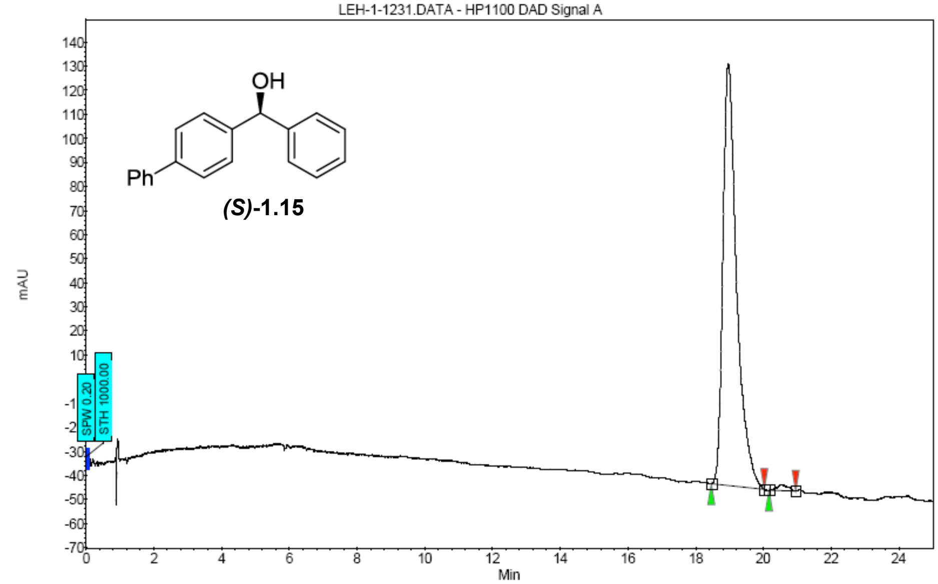
```
Current Data Parameters
USER              lhanna
NAME       LEH-1-150-c2-plg
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121123
Time               20.31
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH          6410.256 Hz
FIDRES       0.097813 Hz
AQ          5.1118579 sec
RG                   256
DW            78.000 usec
DE              4.50 usec
TE               298.1 K
D1        0.10000000 sec
MCREST    0.00000000 sec
MCWRK     0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1             12.00 usec
PL1              -0.60 dB
SFO1       400.1326009 MHz

F2 - Processing parameters
SI                 65536
SF         400.1300295 MHz
WDW                   no
SSB                    0
LB               0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX               22.60 cm
CY               15.00 cm
F1P              9.000 ppm
F1             3601.17 Hz
F2P              0.000 ppm
F2                0.00 Hz
PPMCM      0.39474 ppm/cm
HZCM     157.94508 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

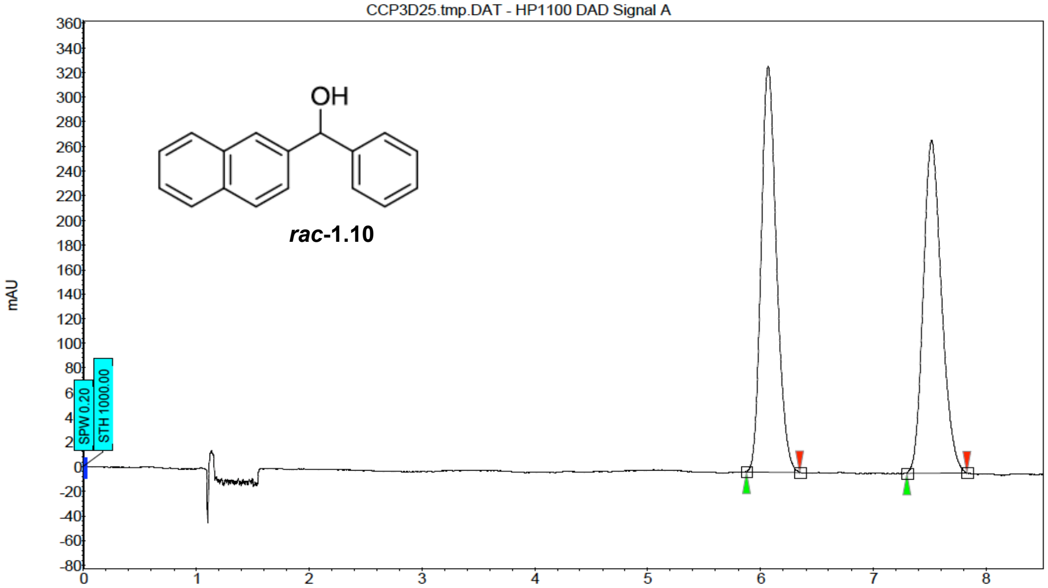


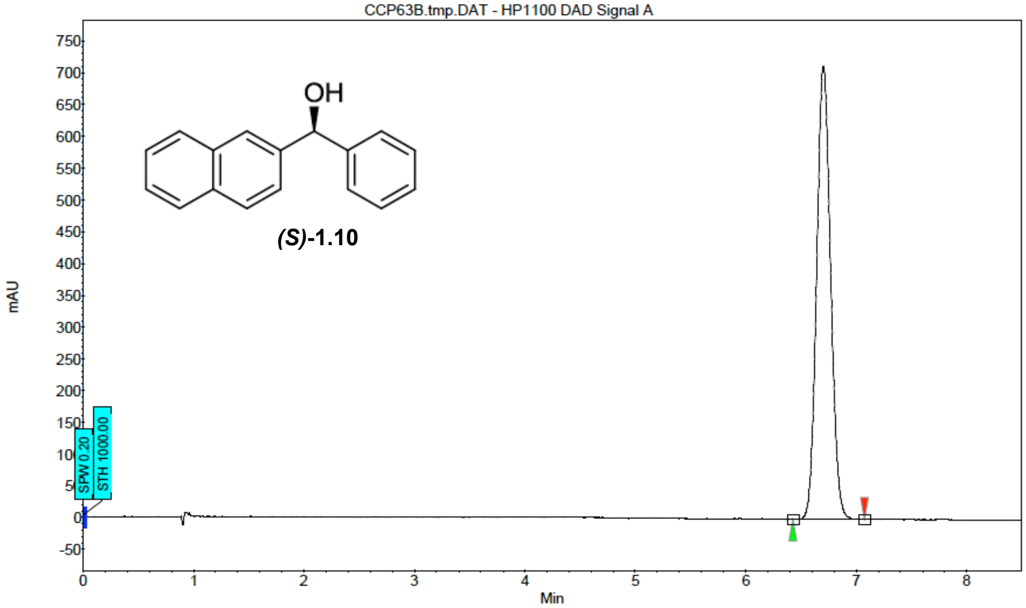
```
Current Data Parameters
USER              lhanna
NAME          LEH-1-150-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121128
Time               14.18
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   184
DS                    16
SWH         30303.031 Hz
FIDRES       0.462388 Hz
AQ          1.0813940 sec
RG                5160.6
DW            16.500 usec
DE              6.00 usec
TE               298.0 K
D1        0.25000000 sec
d11       0.03000000 sec
D16       0.00020000 sec
d17       0.00019600 sec
MCREST    0.00000000 sec
MCWRK     0.01500000 sec
P2             31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1             15.50 usec
P11           500.00 usec
P12          2000.00 usec
PL0            120.00 dB
PL1             -1.00 dB
SFO1       125.7942548 MHz
SP1              3.20 dB
SP2              3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1           0.00 Hz
SPOFF2           0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2         100.00 usec
PL2              1.60 dB
PL12            24.60 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15           500.00 usec
p16          1000.00 usec

F2 - Processing parameters
SI                 65536
SF         125.7804103 MHz
WDW                   no
SSB                    0
LB               0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX               22.60 cm
CY               15.65 cm
F1P            160.000 ppm
F1            20124.87 Hz
F2P             20.000 ppm
F2             2515.61 Hz
PPMCM      6.14035 ppm/cm
HZCM     772.33588 Hz/cm
```



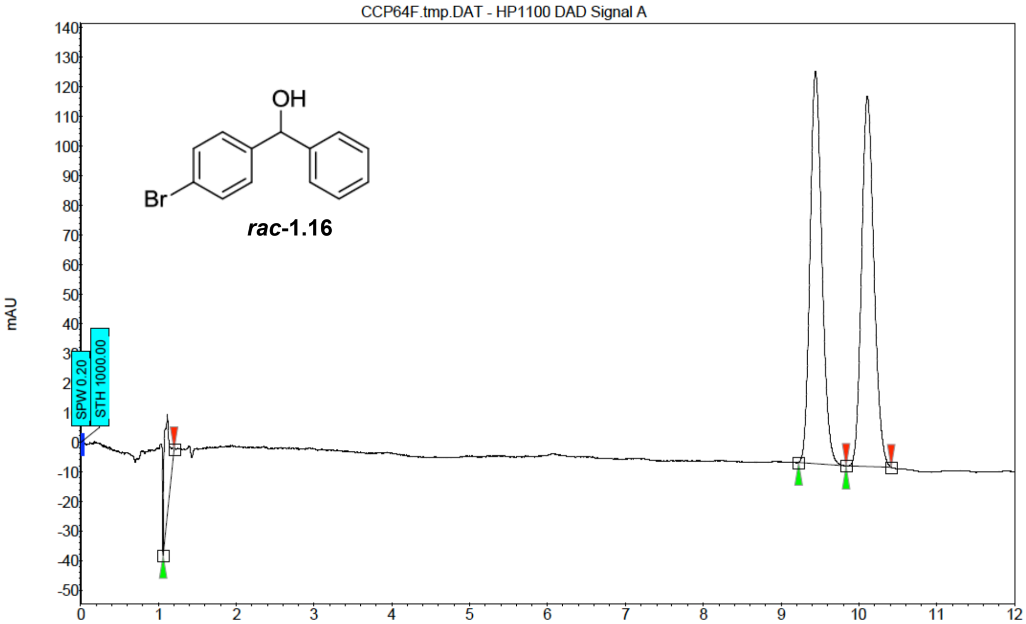


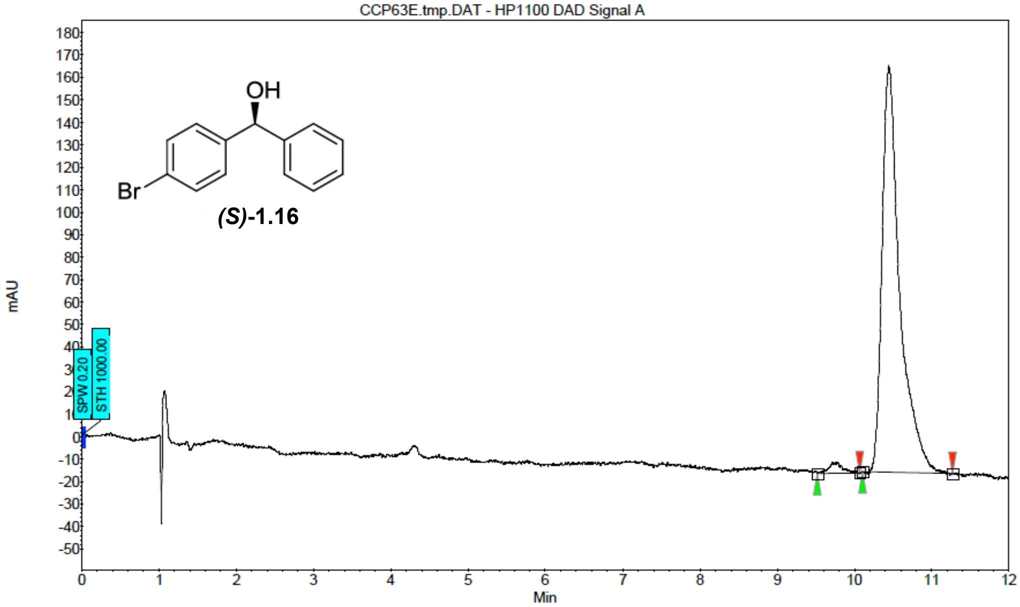
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	18.46	18.97	20.02	0.00	98.91	175.3	82.1	98.914
2	UNKNOWN	20.17	20.55	20.95	0.00	1.09	2.4	0.9	1.086
Total						100.00	177.7	83.0	100.000



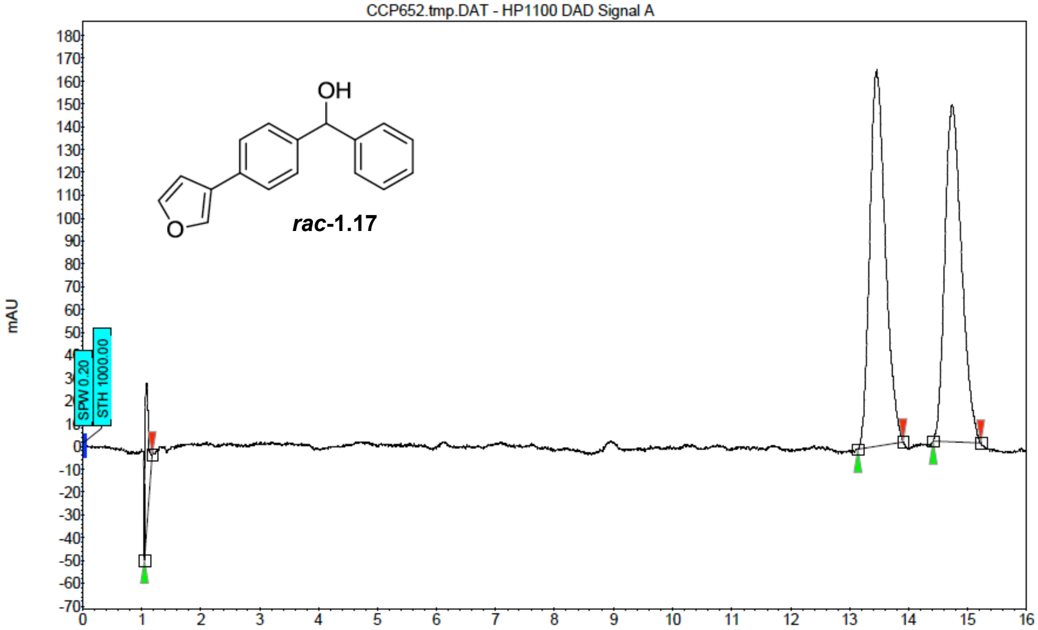


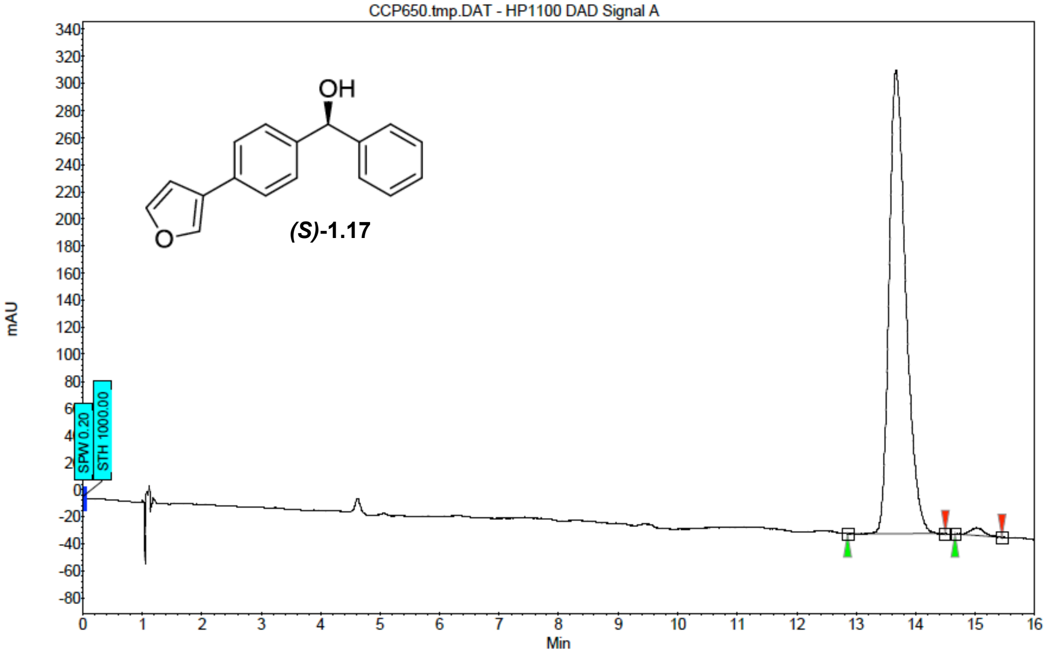
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.43	6.70	7.08	0.00	100.00	712.9	104.3	100.000
Total						100.00	712.9	104.3	100.000



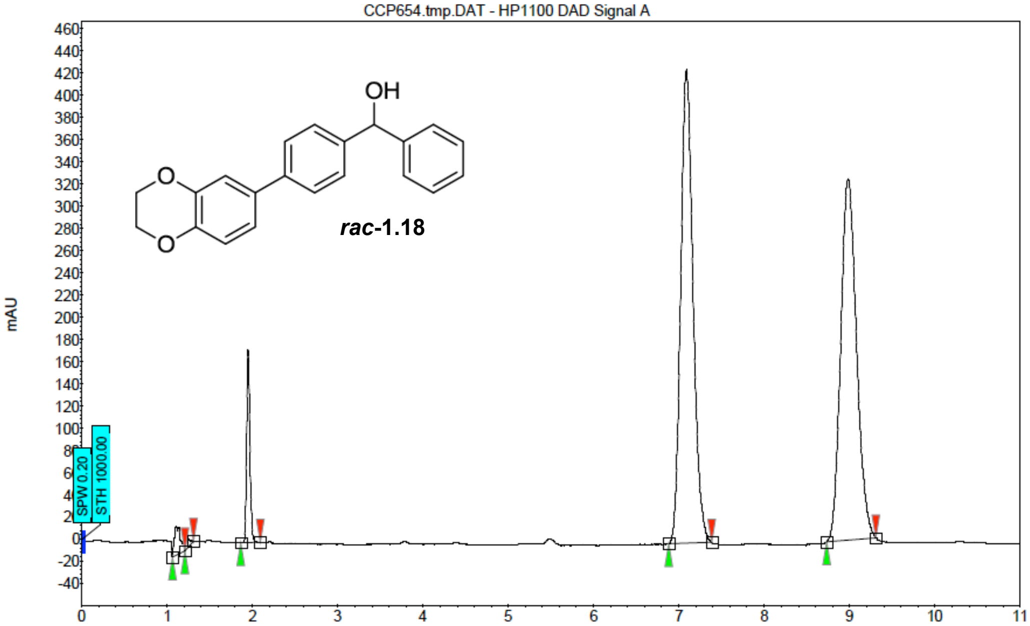


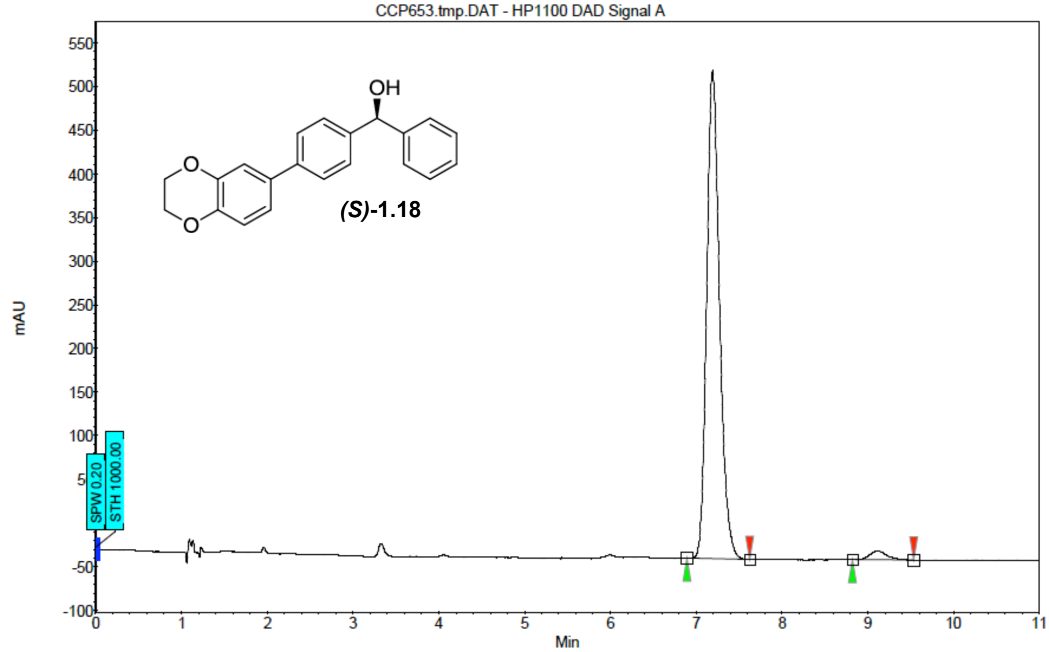
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	9.52	9.76	10.07	0.00	2.16	4.9	1.1	2.164
1	UNKNOWN	10.10	10.44	11.27	0.00	97.84	181.0	47.8	97.836
Total						100.00	185.8	48.9	100.000



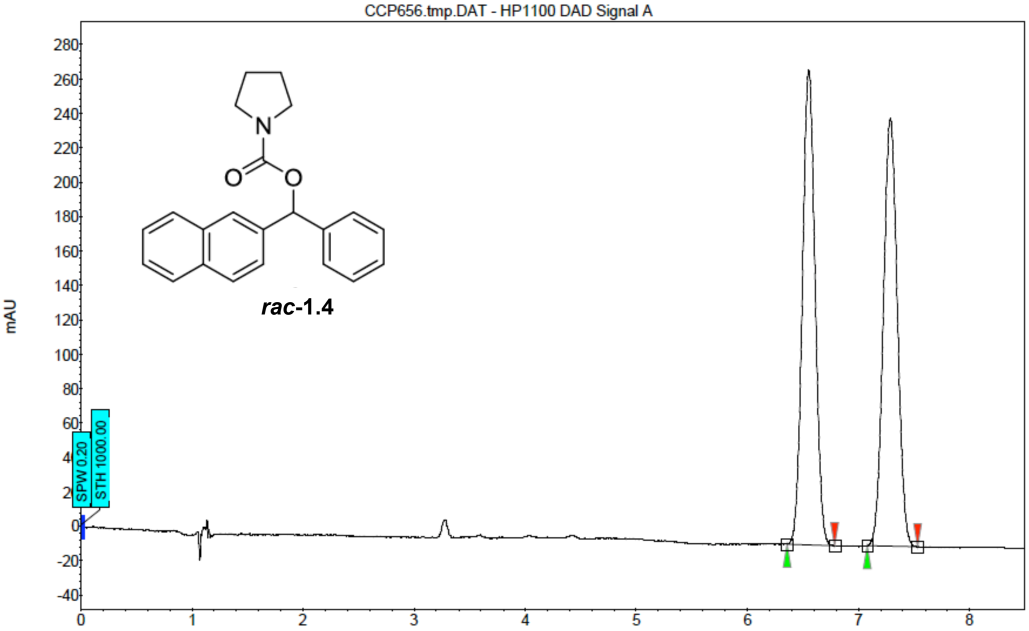


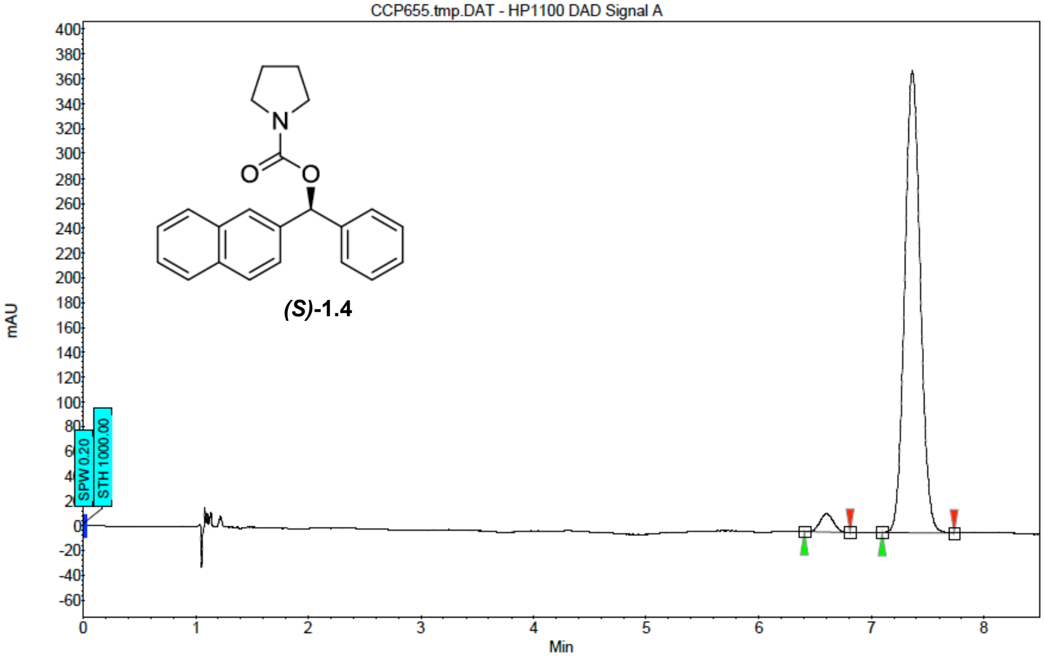
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	12.86	13.67	14.50	0.00	98.57	341.7	111.0	98.571
2	UNKNOWN	14.66	15.02	15.45	0.00	1.43	5.9	1.6	1.429
Total						100.00	347.6	112.6	100.000



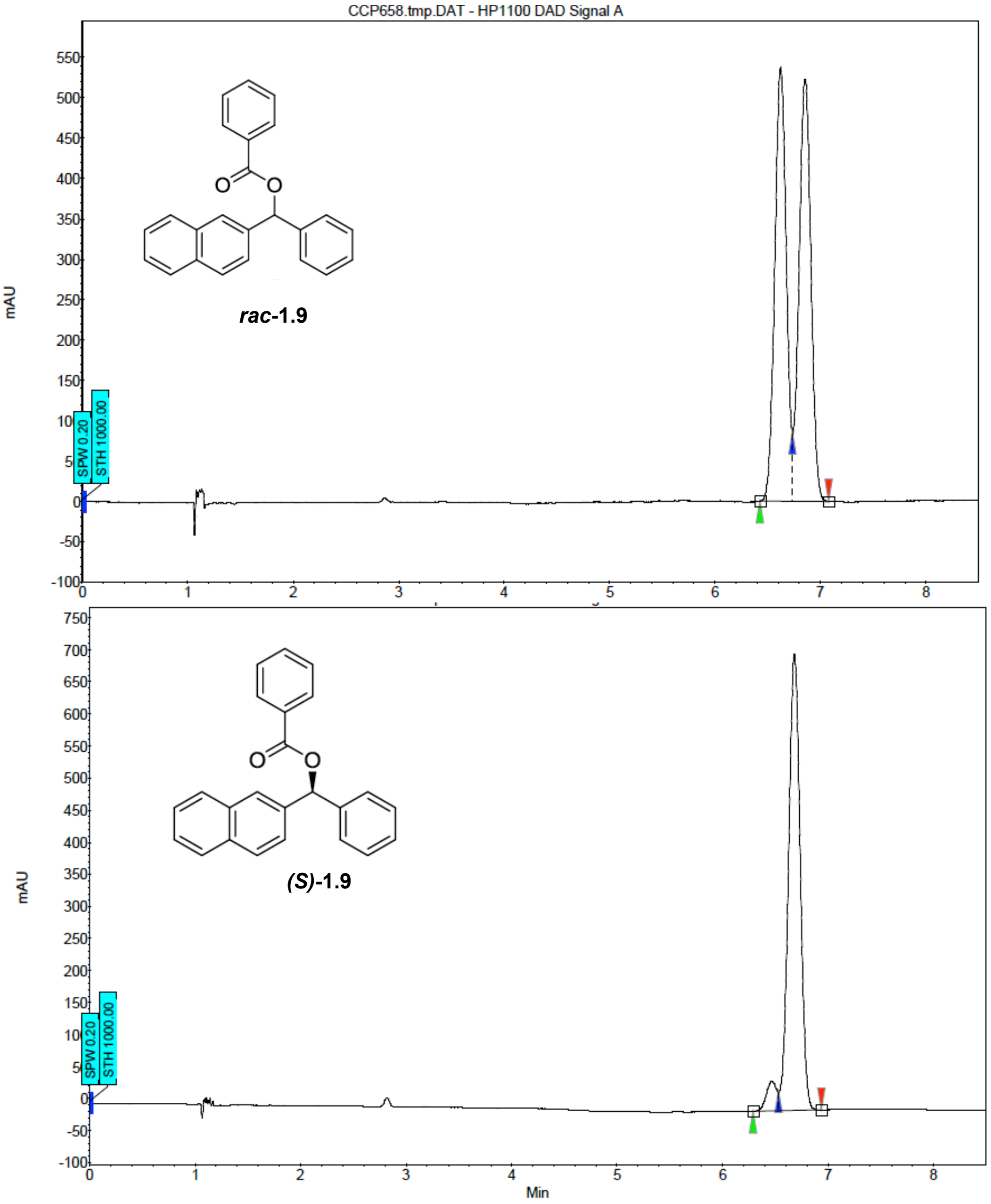


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.89	7.19	7.62	0.00	97.79	558.2	96.4	97.790
2	UNKNOWN	8.82	9.11	9.53	0.00	2.21	9.8	2.2	2.210
Total						100.00	568.0	98.6	100.000

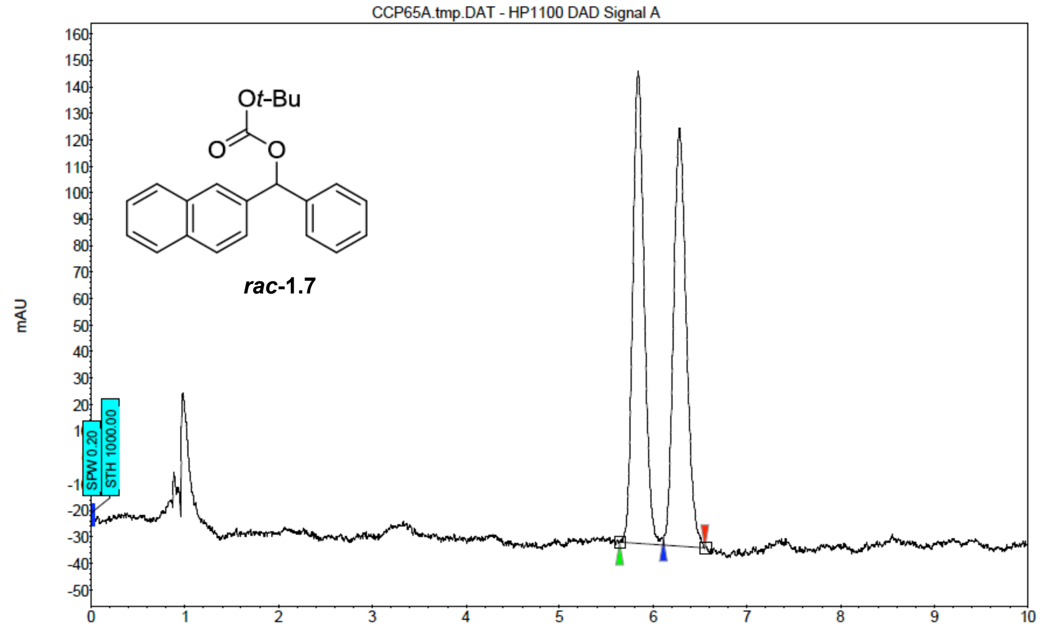


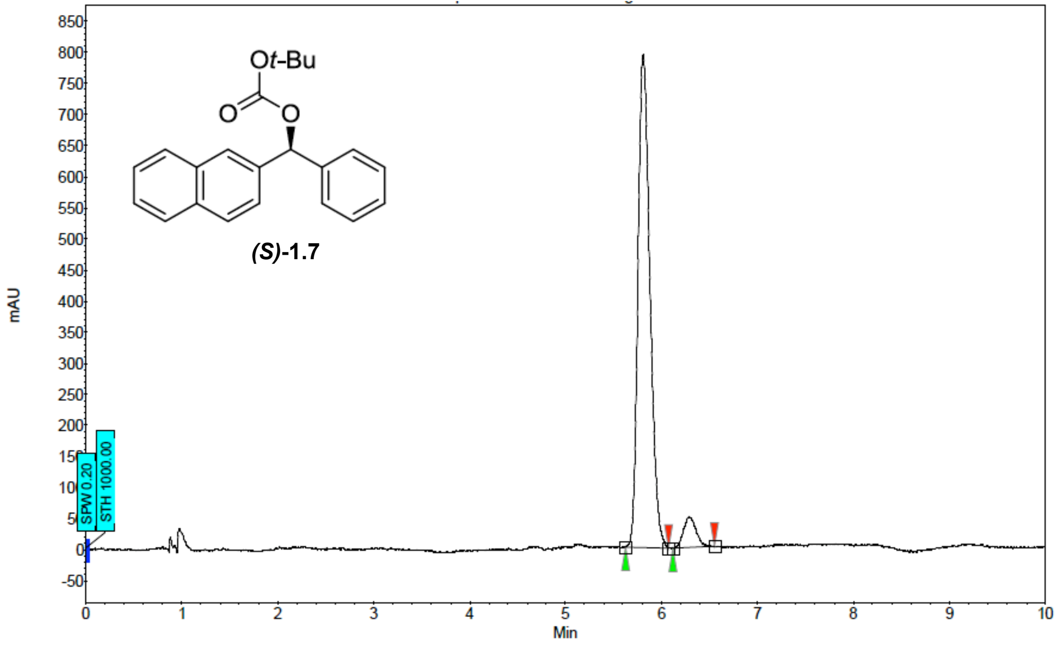


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.41	6.60	6.81	0.00	3.40	14.9	2.1	3.400
2	UNKNOWN	7.10	7.37	7.74	0.00	96.60	372.0	59.5	96.600
Total						100.00	386.9	61.6	100.000

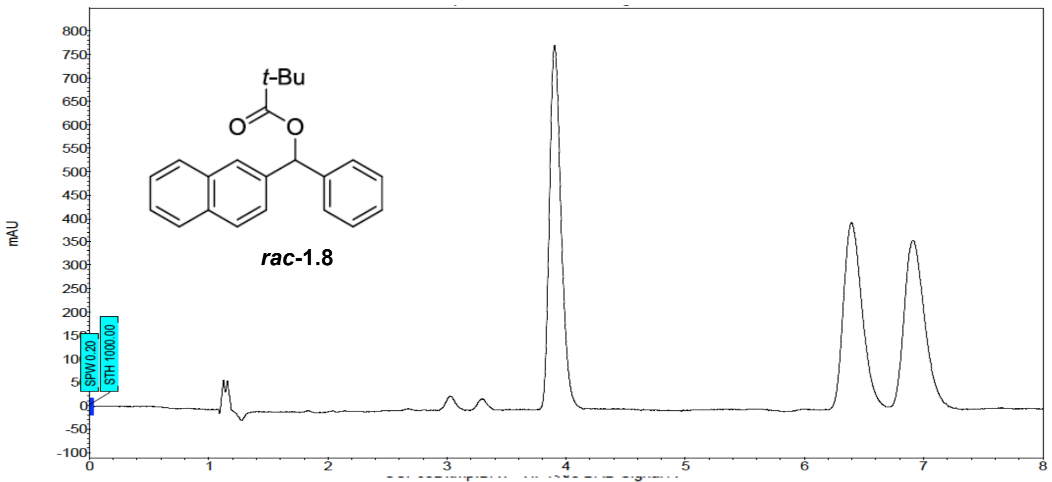


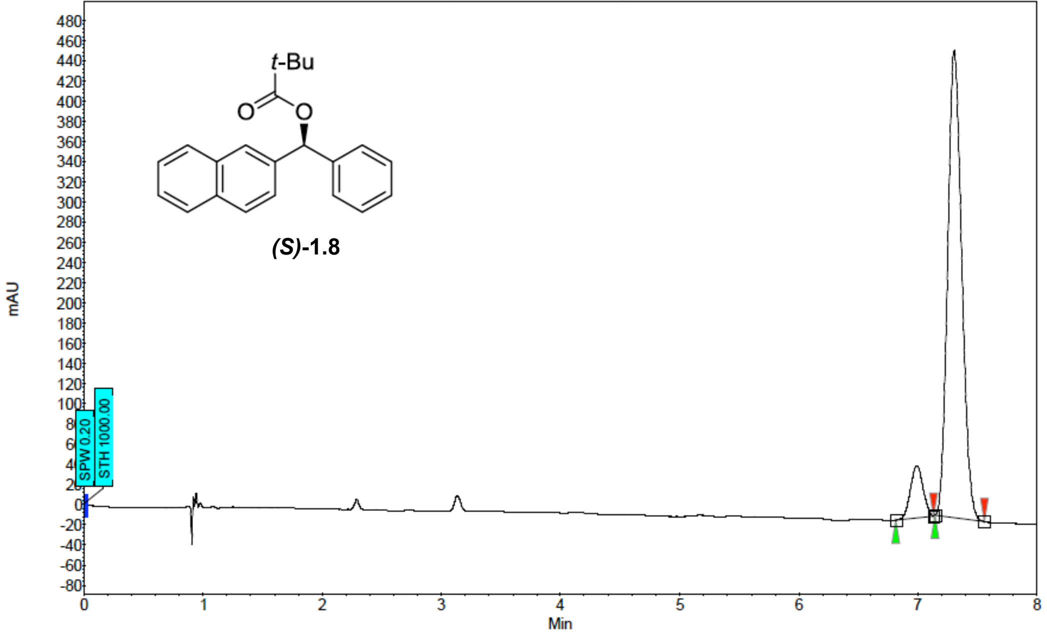
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.29	6.47	6.53	0.00	5.45	46.2	5.2	5.451
2	UNKNOWN	6.53	6.68	6.94	0.00	94.55	711.7	90.9	94.549
Total						100.00	757.9	96.2	100.000



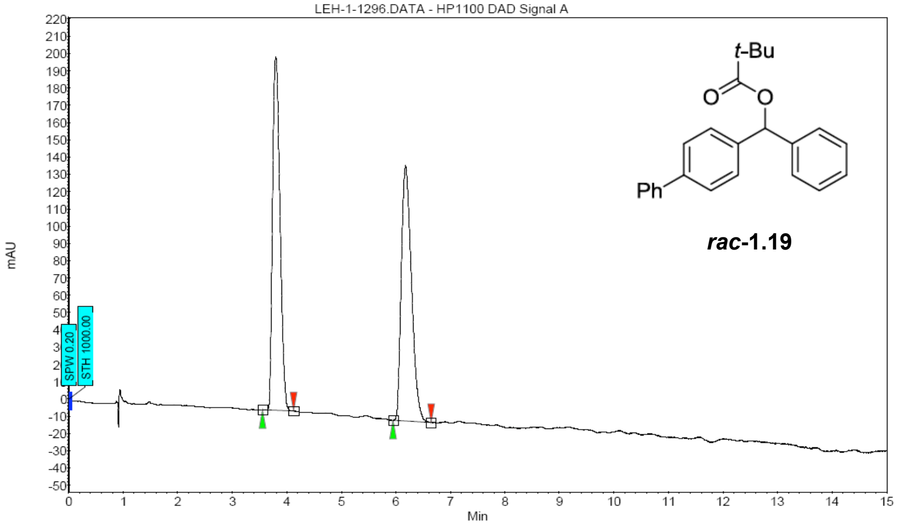


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.63	5.81	6.08	0.00	93.79	791.8	113.4	93.788
2	UNKNOWN	6.12	6.29	6.55	0.00	6.21	50.0	7.5	6.212
Total						100.00	841.8	120.9	100.000

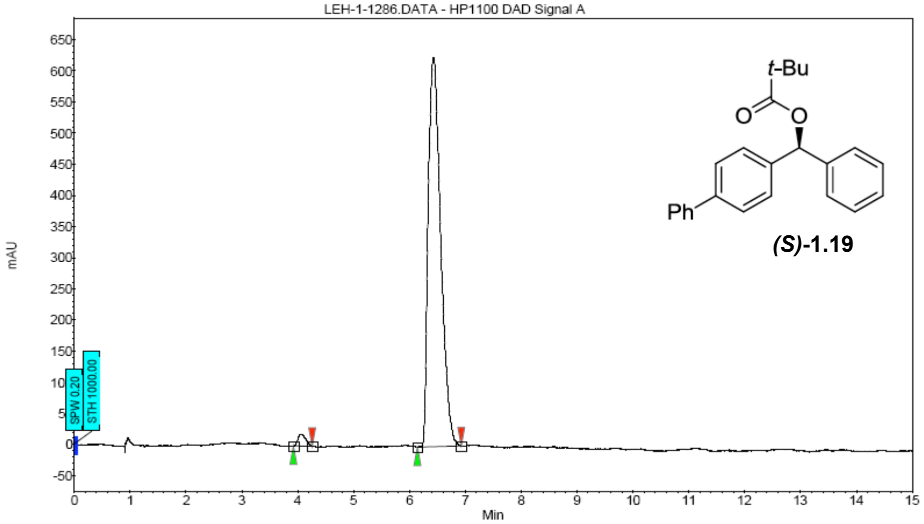




Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.82	6.99	7.13	0.00	9.06	51.7	6.3	9.058
2	UNKNOWN	7.14	7.30	7.56	0.00	90.94	463.0	63.5	90.942
Total						100.00	514.7	69.9	100.000

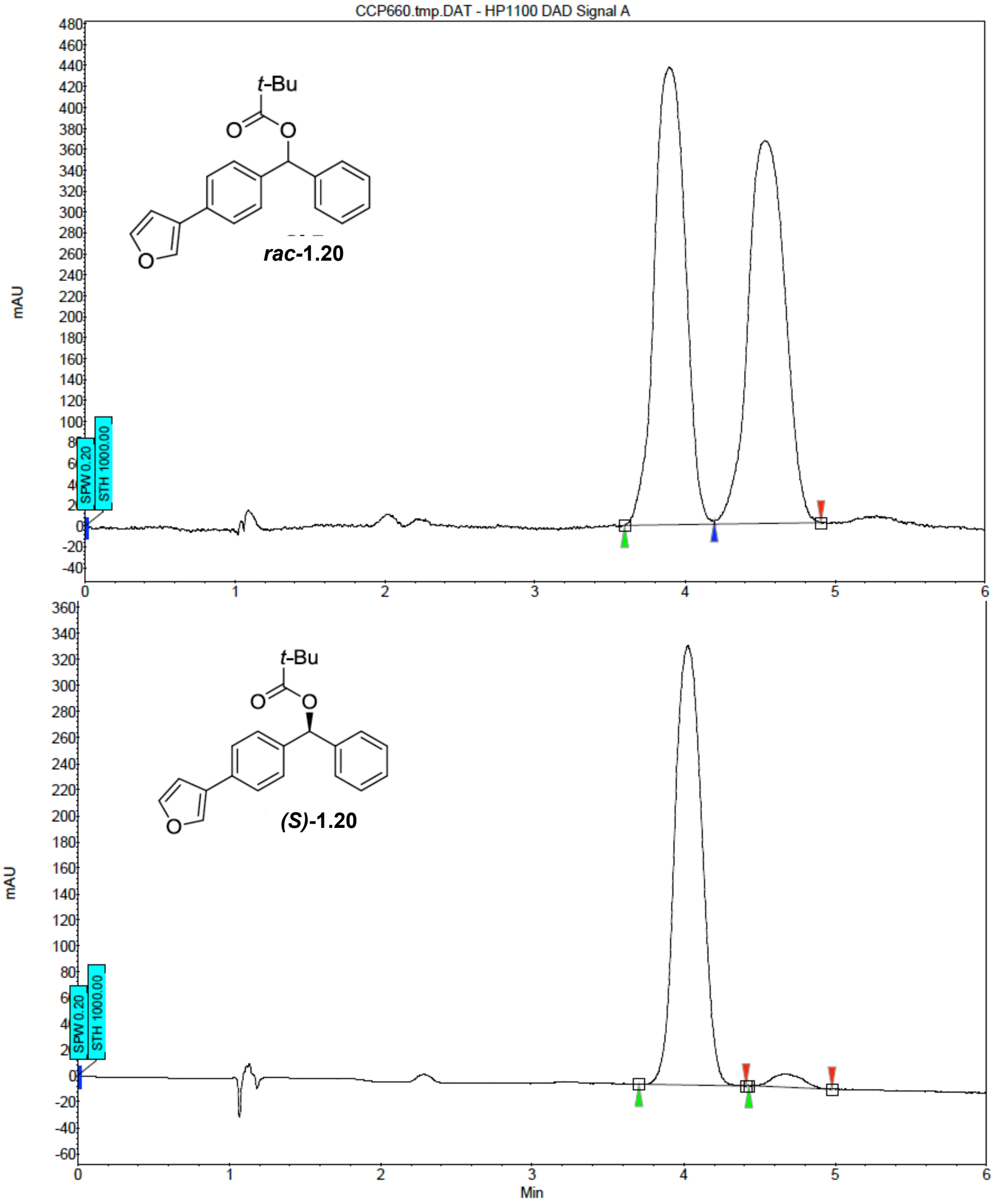


***rac*-1.19**

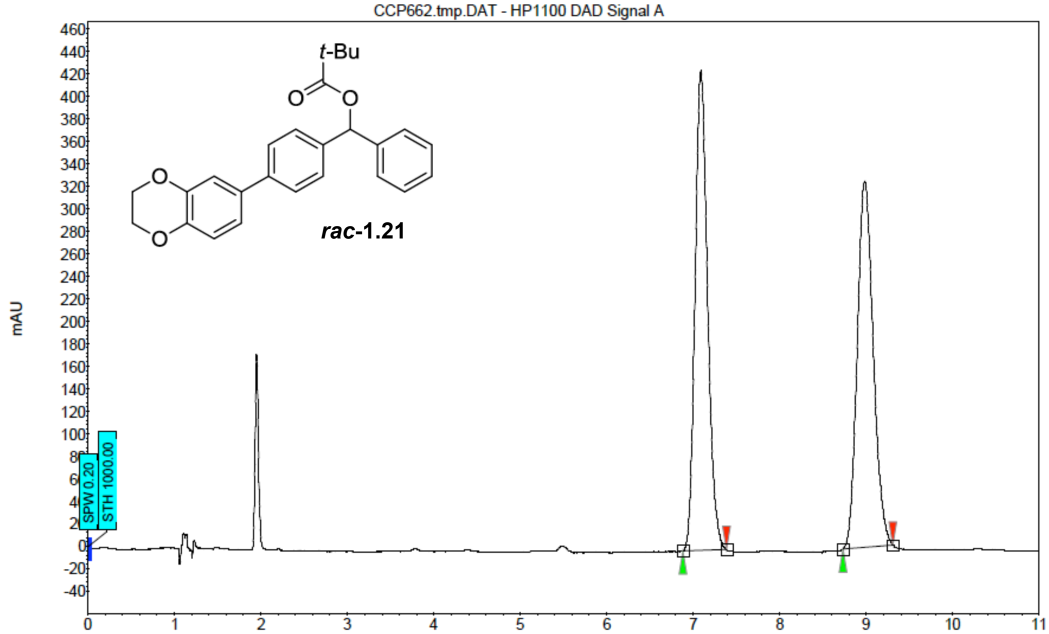


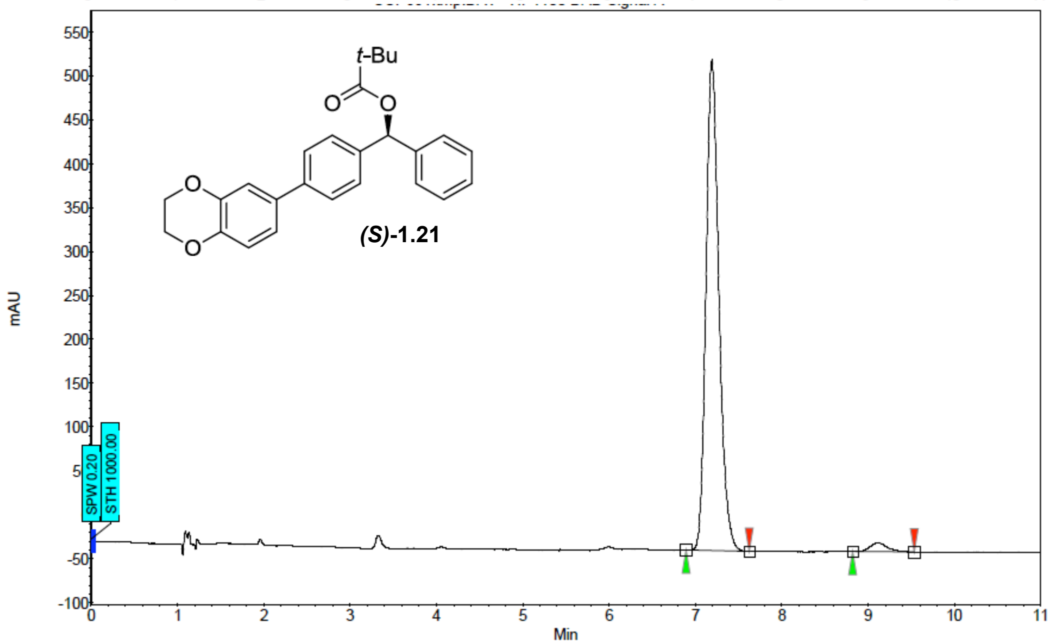
***(S)*-1.19**

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	3.93	4.06	4.26	0.00	1.88	19.0	3.1	1.877
1	UNKNOWN	6.14	6.43	6.93	0.00	98.12	625.4	161.3	98.123
Total						100.00	644.3	164.4	100.000

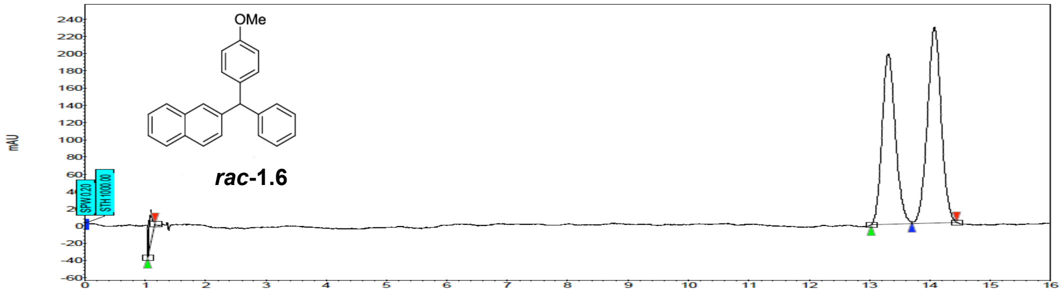


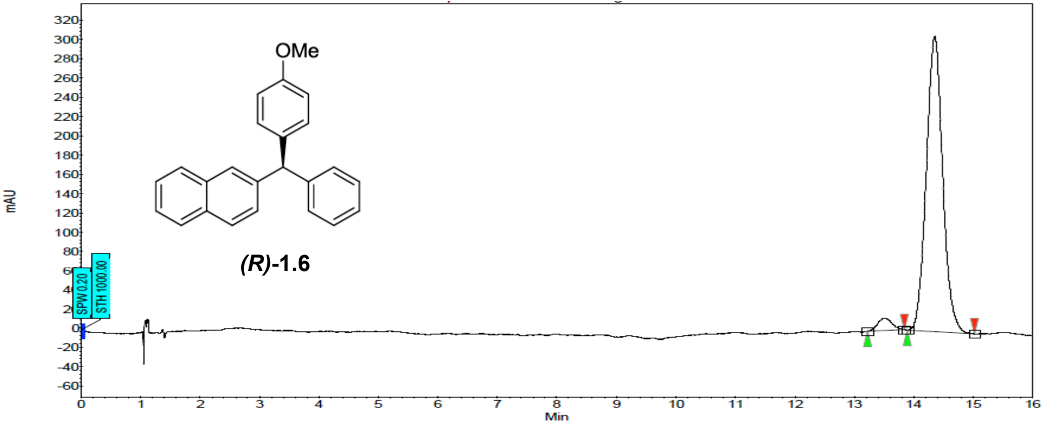
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.70	4.03	4.41	0.00	96.61	337.3	69.5	96.611
2	UNKNOWN	4.43	4.66	4.98	0.00	3.39	10.1	2.4	3.389
Total						100.00	347.4	71.9	100.000



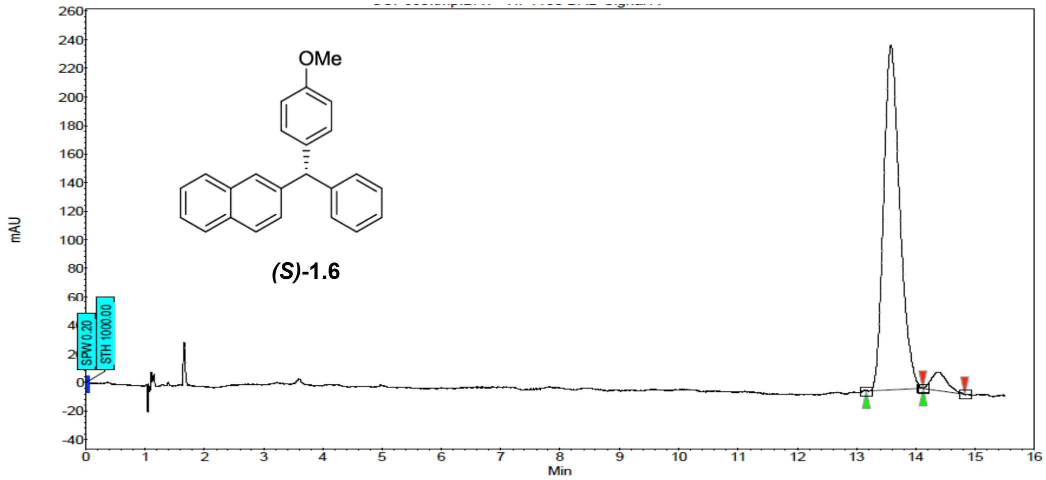


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.89	7.19	7.62	0.00	97.79	558.2	96.4	97.790
2	UNKNOWN	8.82	9.11	9.53	0.00	2.21	9.8	2.2	2.210
Total						100.00	568.0	98.6	100.000

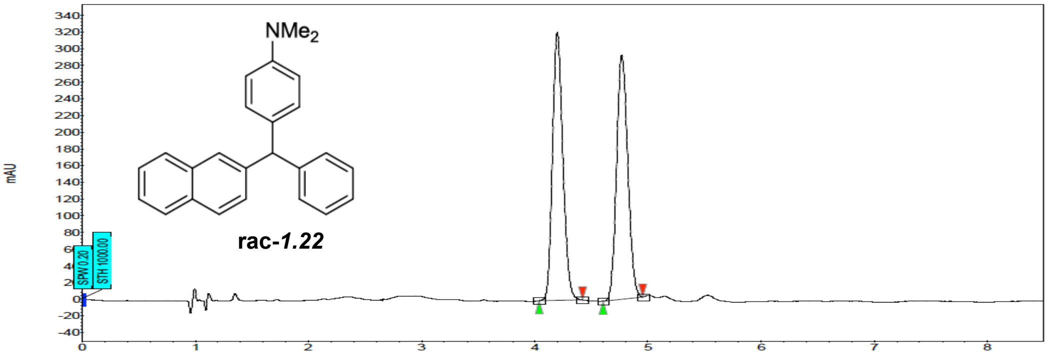


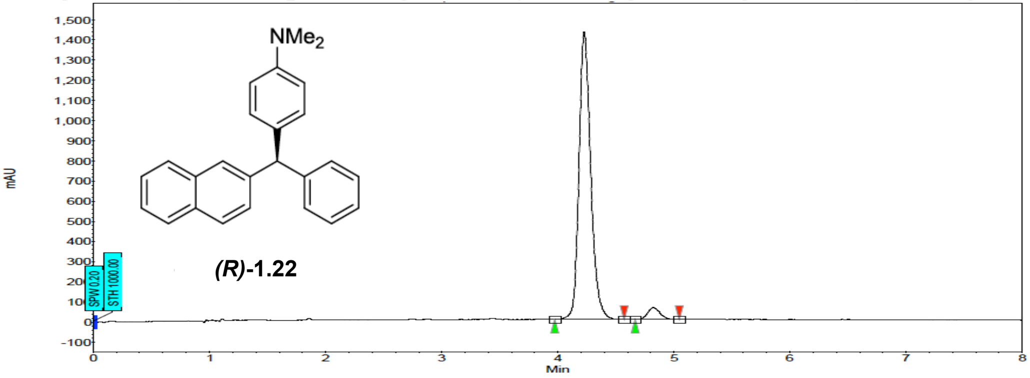


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	13.22	13.52	13.84	0.00	3.51	13.0	3.6	3.505
2	UNKNOWN	13.89	14.35	15.02	0.00	96.49	306.8	98.0	96.495
Total						100.00	319.8	101.6	100.000

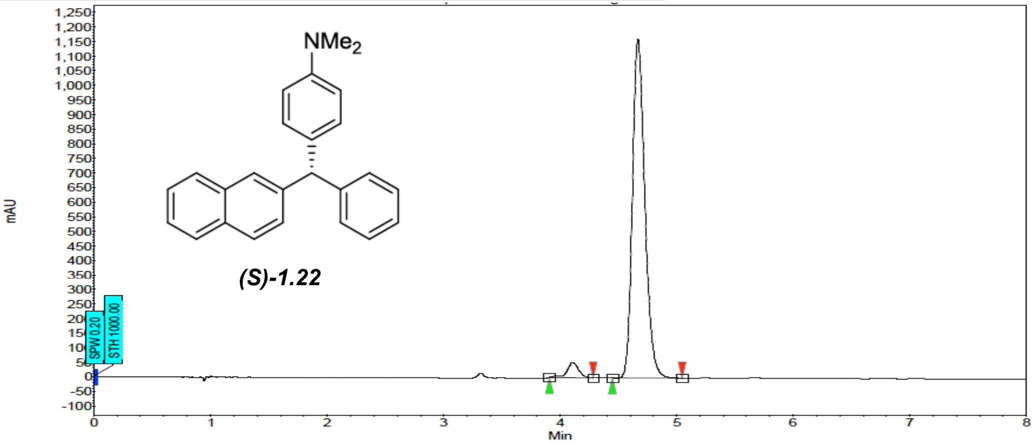


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	13.16	13.58	14.11	0.00	95.00	241.1	76.1	94.998
2	UNKNOWN	14.12	14.40	14.83	0.00	5.00	12.9	4.0	5.002
Total						100.00	254.0	80.1	100.000

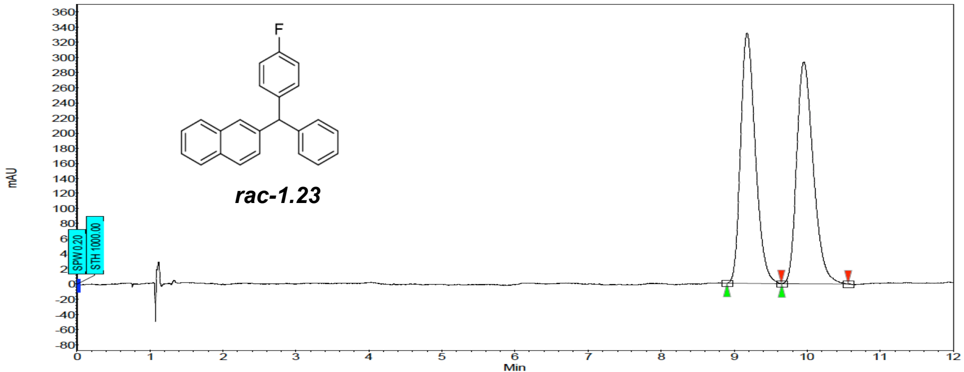


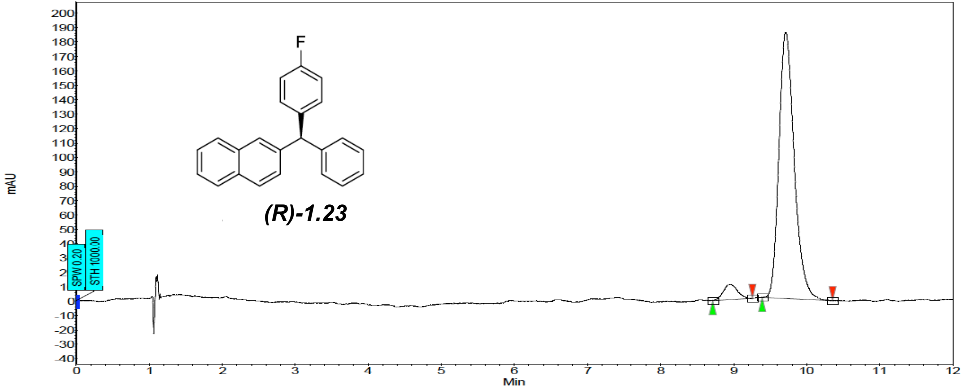


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.98	4.23	4.57	0.00	95.82	1425.1	166.4	95.819
2	UNKNOWN	4.67	4.83	5.05	0.00	4.18	59.1	7.3	4.181
Total						100.00	1484.1	173.7	100.000

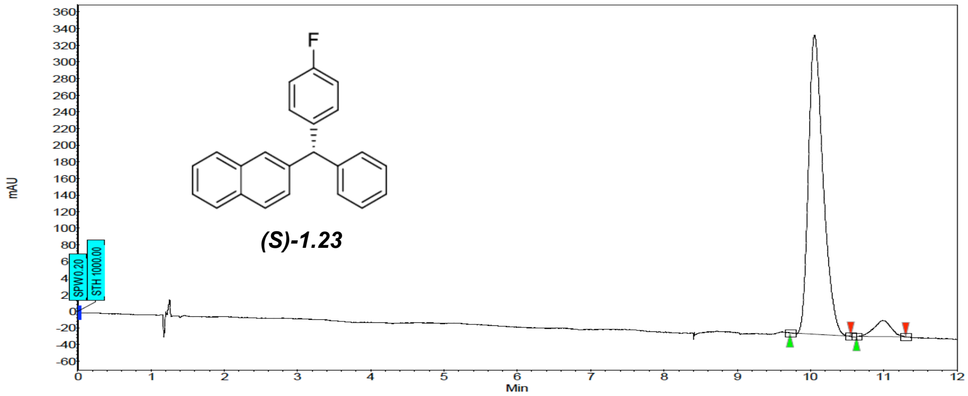


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	3.91	4.11	4.29	0.00	4.01	52.1	6.0	4.006
1	UNKNOWN	4.45	4.67	5.05	0.00	95.99	1160.9	143.0	95.994
Total						100.00	1213.0	148.9	100.000

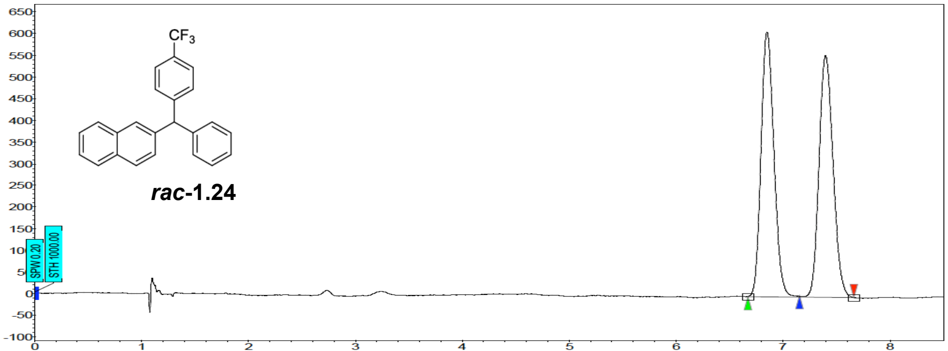


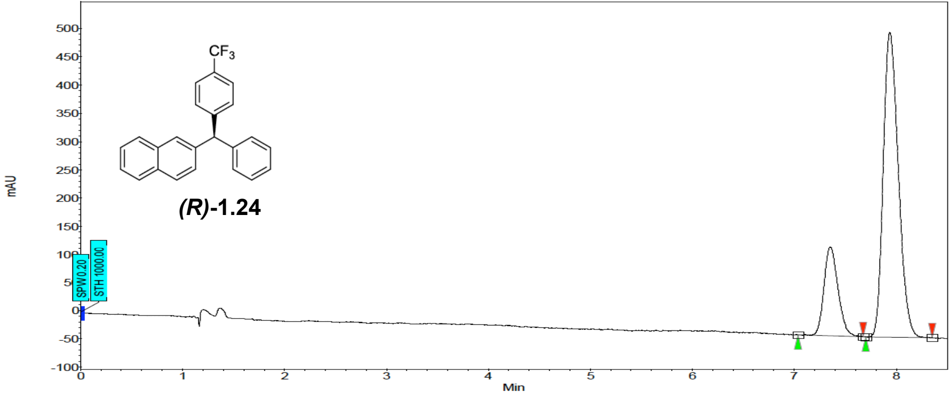


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	8.71	8.96	9.26	0.00	4.97	10.6	2.4	4.971
2	UNKNOWN	9.39	9.71	10.35	0.00	95.03	185.0	45.1	95.029
Total						100.00	195.6	47.5	100.000

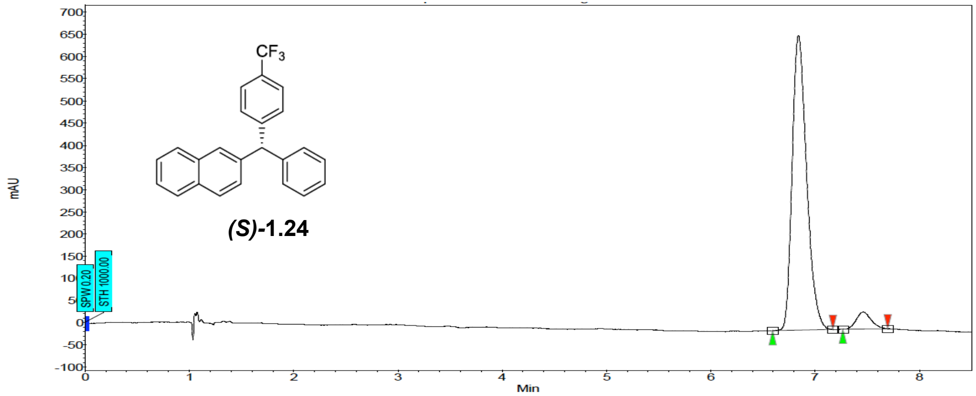


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.72	10.06	10.55	0.00	94.00	359.5	82.9	94.005
2	UNKNOWN	10.63	10.98	11.30	0.00	6.00	19.5	5.3	5.995
Total						100.00	379.0	88.2	100.000

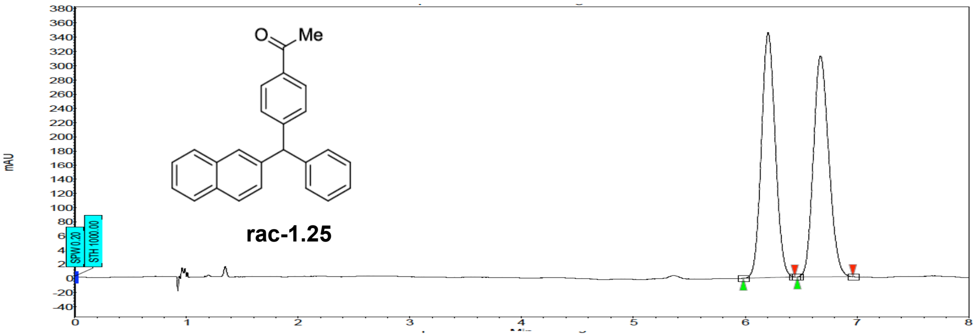




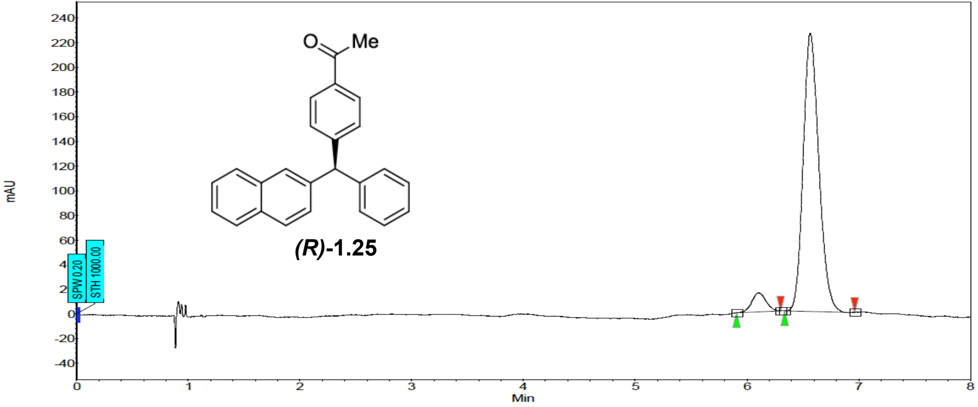
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.04	7.35	7.67	0.00	21.30	157.7	25.0	21.299
2	UNKNOWN	7.70	7.94	8.35	0.00	78.70	540.3	92.5	78.701
Total						100.00	698.0	117.6	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.59	6.84	7.17	0.00	94.37	663.8	106.4	94.372
2	UNKNOWN	7.27	7.46	7.70	0.00	5.63	38.2	6.3	5.628
Total						100.00	702.1	112.7	100.000

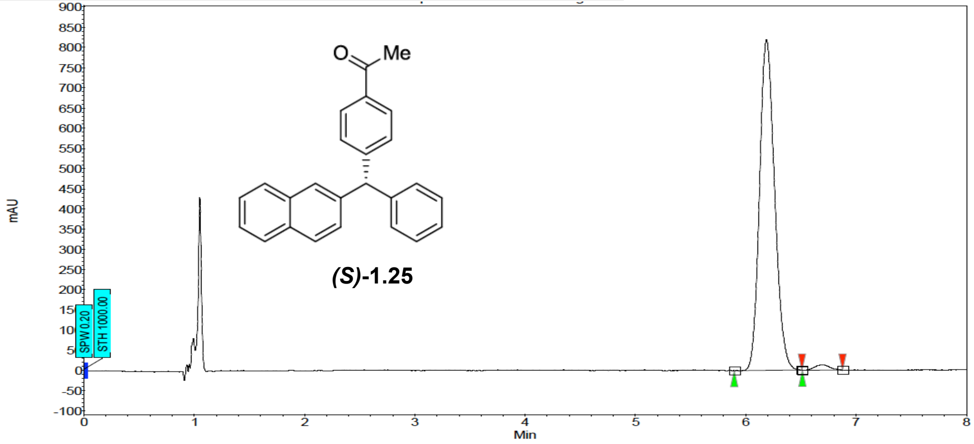


rac-1.25



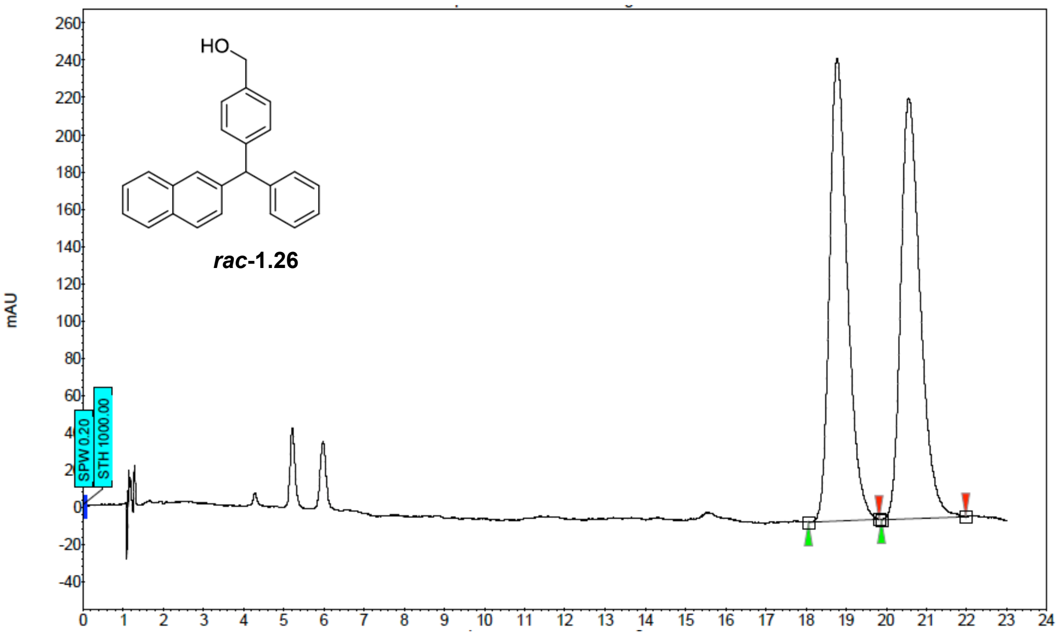
***(R)*-1.25**

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	5.91	6.11	6.30	0.00	5.73	15.4	2.3	5.725
1	UNKNOWN	6.34	6.57	6.96	0.00	94.27	225.7	37.1	94.275
Total						100.00	241.1	39.4	100.000

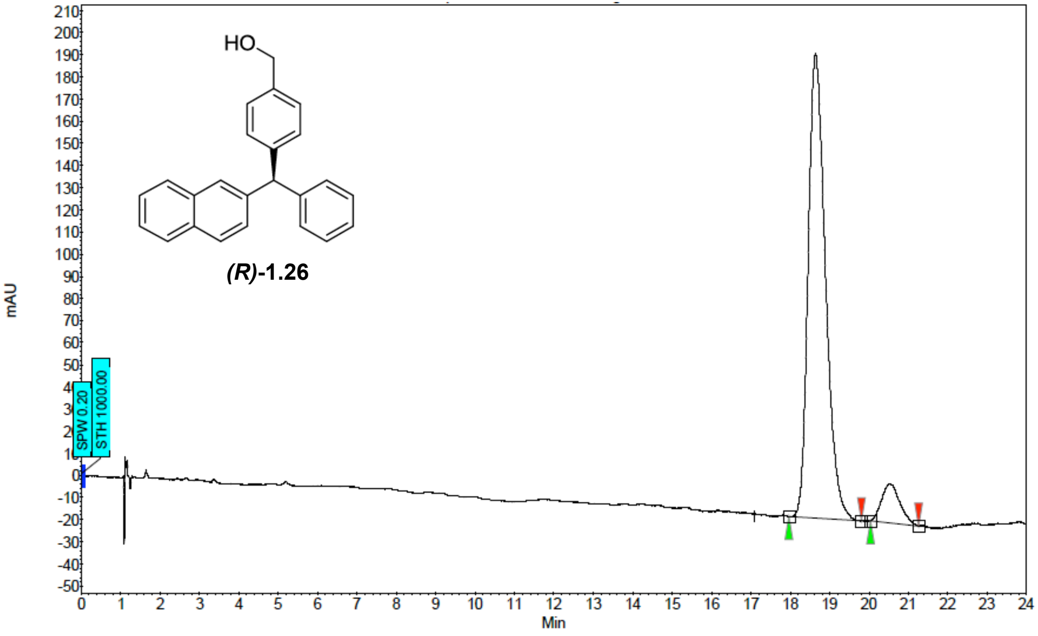


***(S)*-1.25**

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.90	6.19	6.51	0.00	98.37	818.9	129.1	98.371
2	UNKNOWN	6.51	6.69	6.88	0.00	1.63	13.7	2.1	1.629
Total						100.00	832.6	131.2	100.000

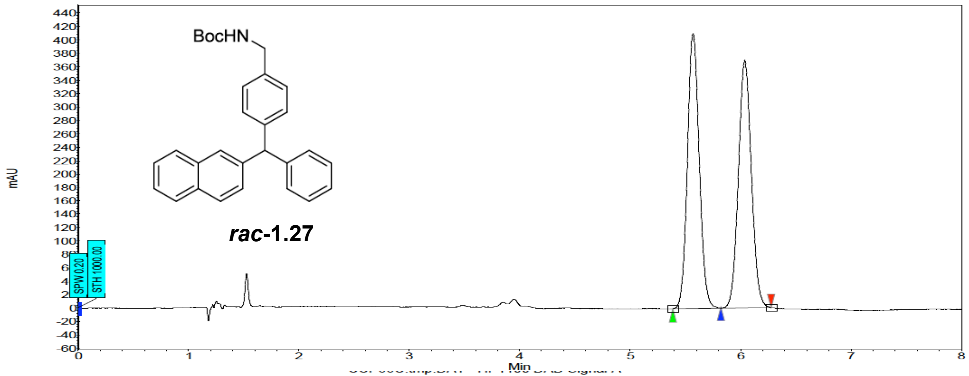


***rac*-1.26**

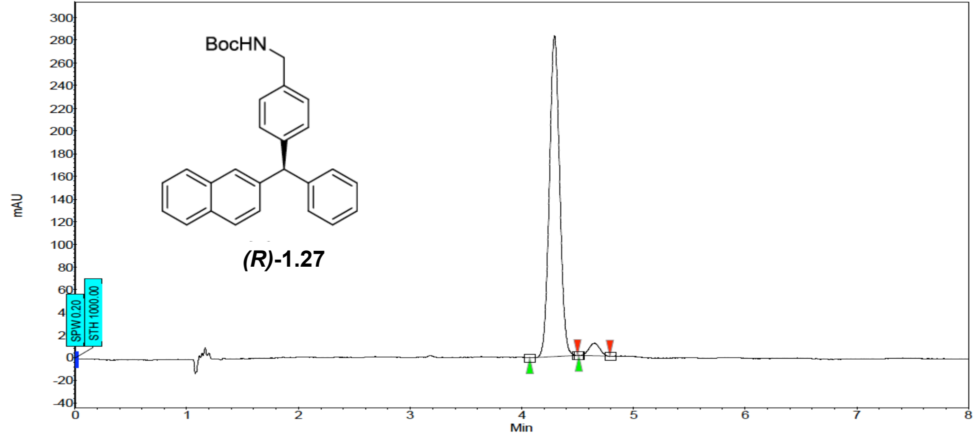


***(R)*-1.26**

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	17.97	18.64	19.81	0.00	91.88	209.7	106.3	91.876
2	UNKNOWN	20.04	20.53	21.26	0.00	8.12	17.7	9.4	8.124
Total						100.00	227.3	115.7	100.000

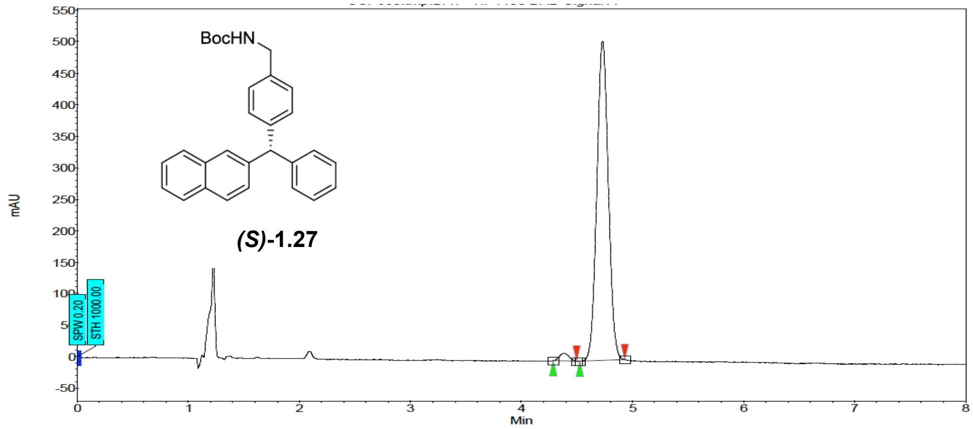


***rac*-1.27**



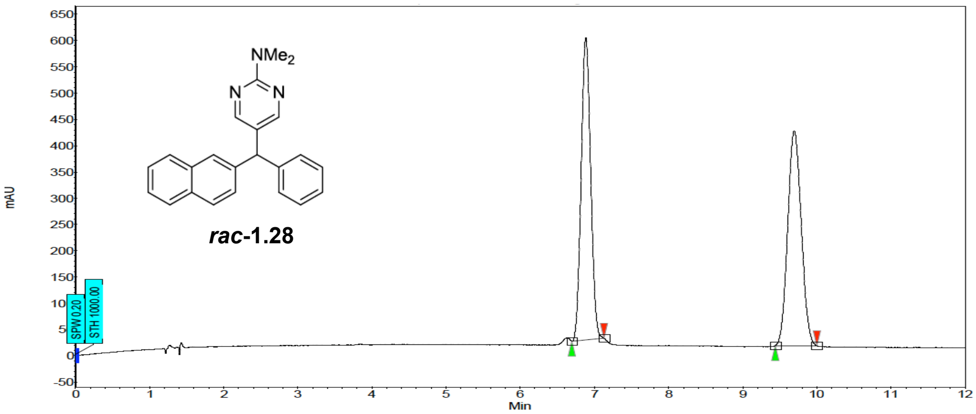
***(R)*-1.27**

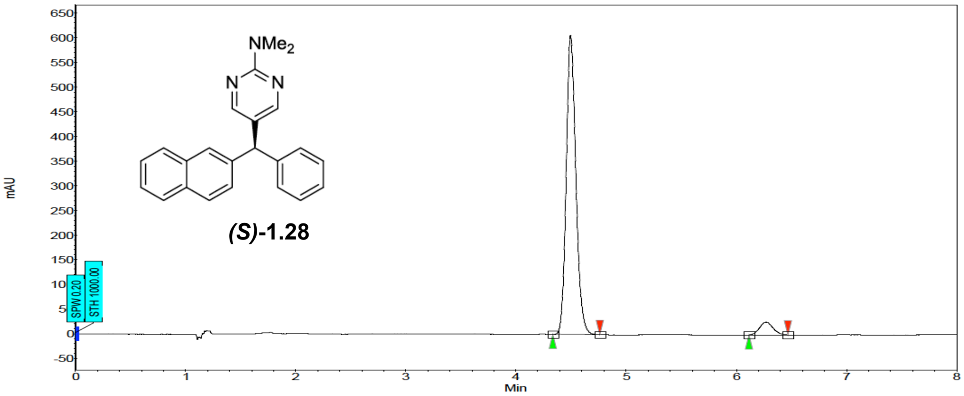
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.07	4.29	4.50	0.00	96.08	283.0	30.0	96.085
2	UNKNOWN	4.51	4.66	4.79	0.00	3.92	11.0	1.2	3.915
Total						100.00	294.0	31.2	100.000



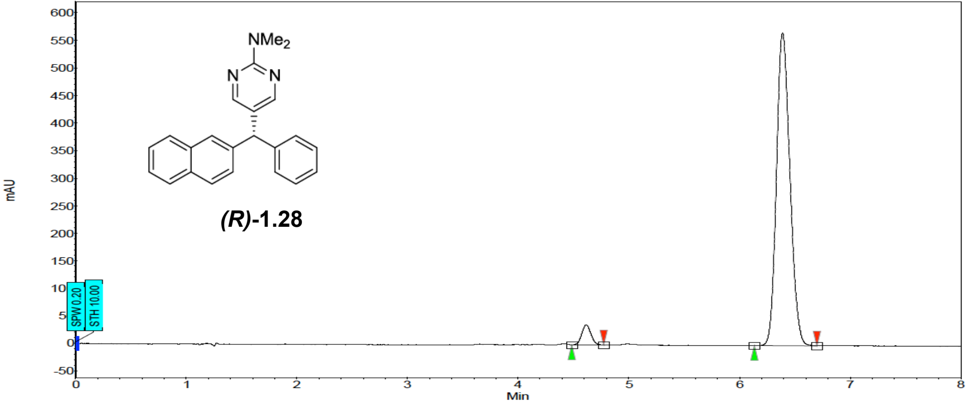
***(S)*-1.27**

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.29	4.39	4.50	0.00	1.92	11.9	1.2	1.924
2	UNKNOWN	4.53	4.73	4.93	0.00	98.08	506.5	60.4	98.076
Total						100.00	518.5	61.6	100.000

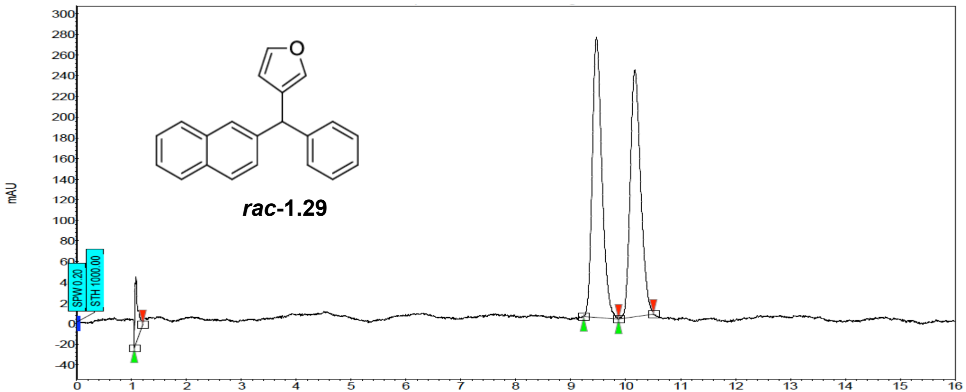




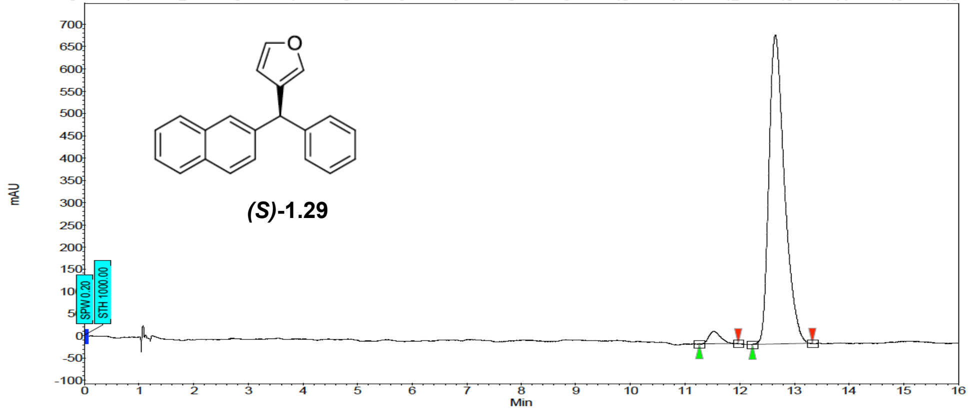
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.33	4.50	4.76	0.00	94.50	606.4	62.5	94.501
2	UNKNOWN	6.12	6.27	6.47	0.00	5.50	25.7	3.6	5.499
Total						100.00	632.1	66.2	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.48	4.62	4.77	0.00	4.20	36.6	3.5	4.201
2	UNKNOWN	6.13	6.39	6.70	0.00	95.80	567.9	79.6	95.799
Total						100.00	604.4	83.1	100.000

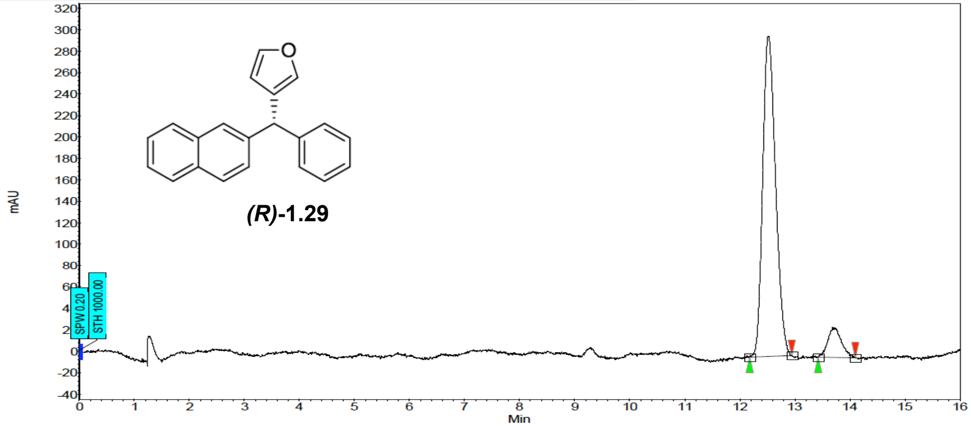


***rac*-1.29**



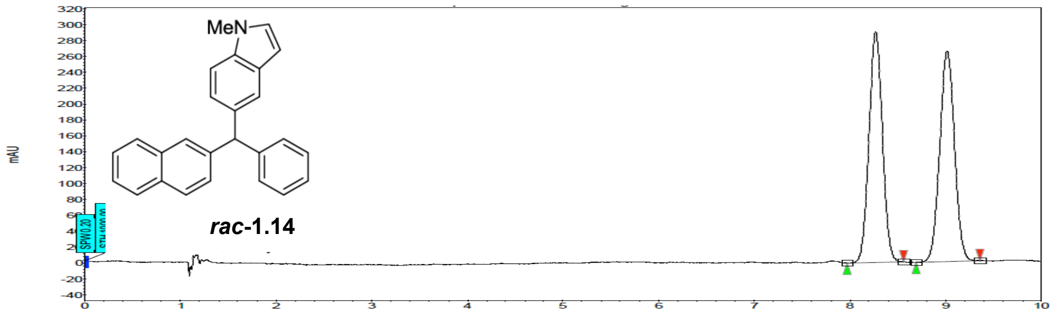
***(S)*-1.29**

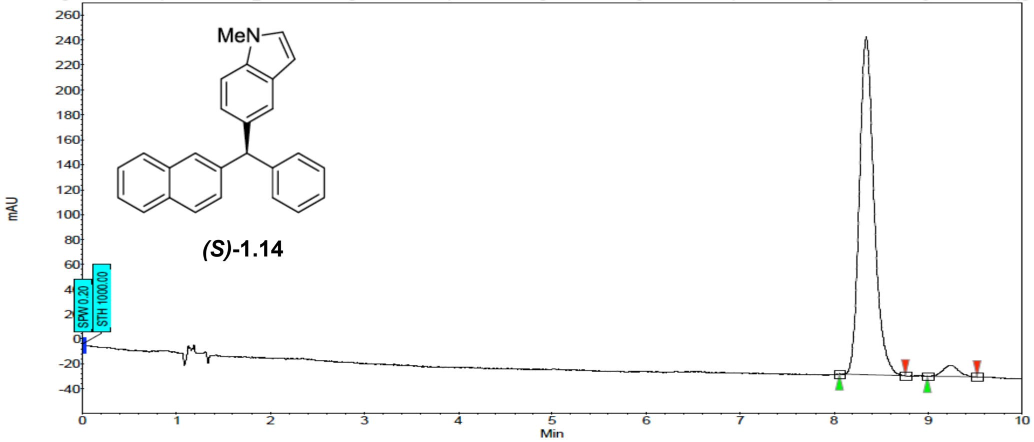
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	11.26	11.53	11.97	0.00	2.94	28.1	6.9	2.937
1	UNKNOWN	12.23	12.65	13.32	0.00	97.06	694.1	227.6	97.063
Total						100.00	722.3	234.5	100.000



***(R)*-1.29**

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	12.18	12.52	12.95	0.00	90.99	298.5	80.3	90.991
2	UNKNOWN	13.42	13.69	14.10	0.00	9.01	27.8	7.9	9.009
Total						100.00	326.3	88.2	100.000





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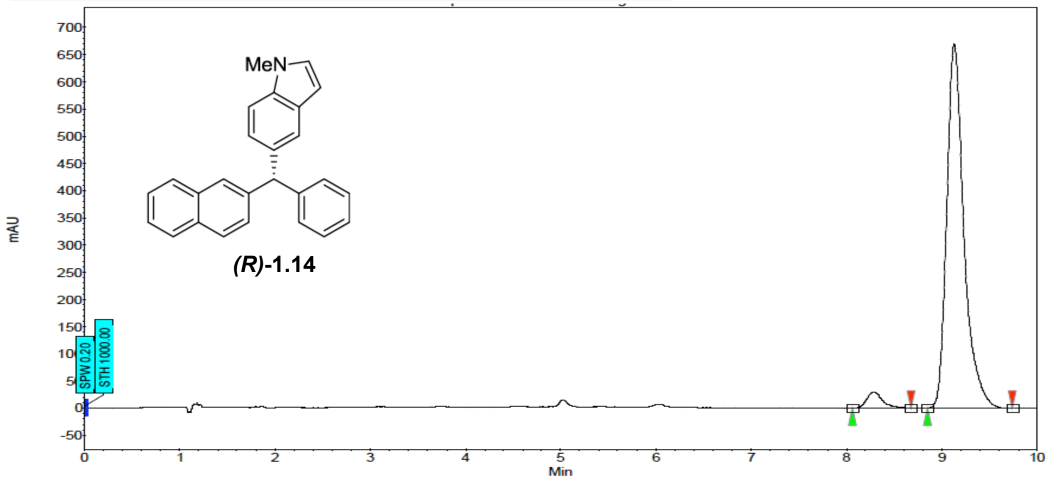
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	8.05	8.34	8.76	0.00	96.61	270.9	49.0	96.606
2	UNKNOWN	8.99	9.24	9.52	0.00	3.39	8.9	1.7	3.394
Total						100.00	279.8	50.7	100.000



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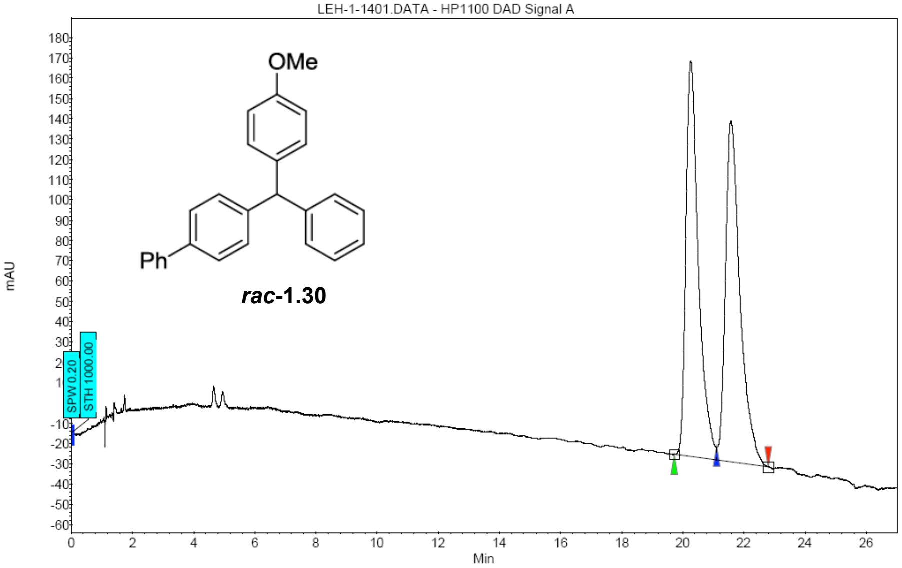
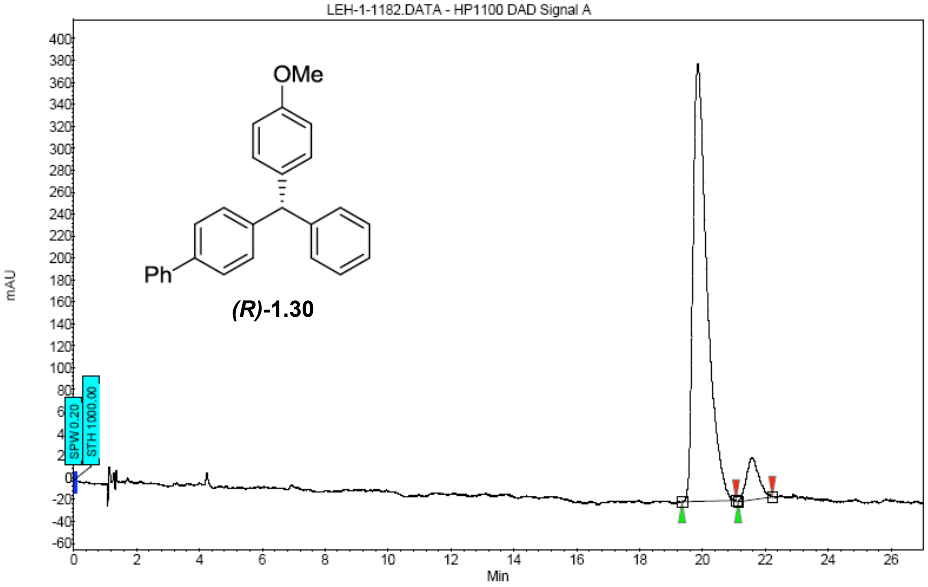
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	8.06	8.28	8.67	0.00	3.91	29.8	5.7	3.910
2	UNKNOWN	8.85	9.13	9.73	0.00	96.09	668.3	139.6	96.090
Total						100.00	698.2	145.3	100.000

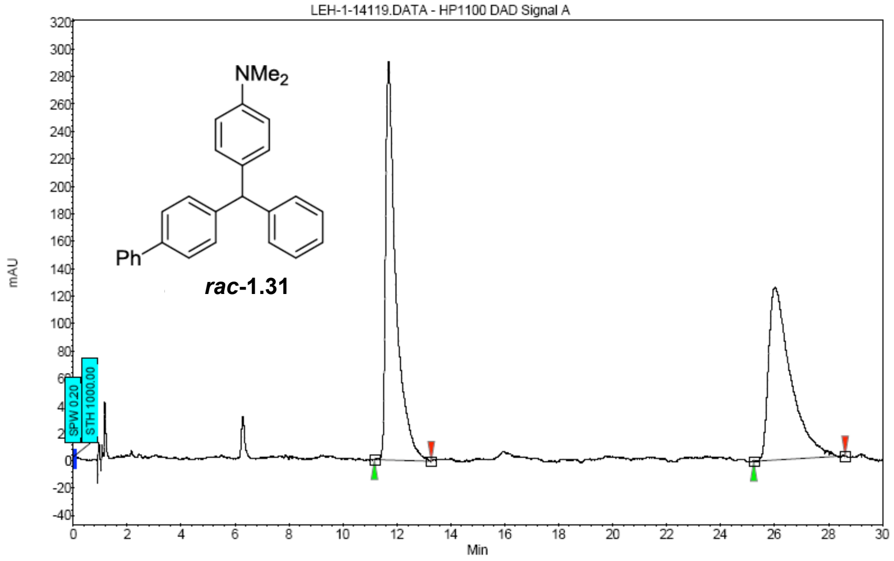


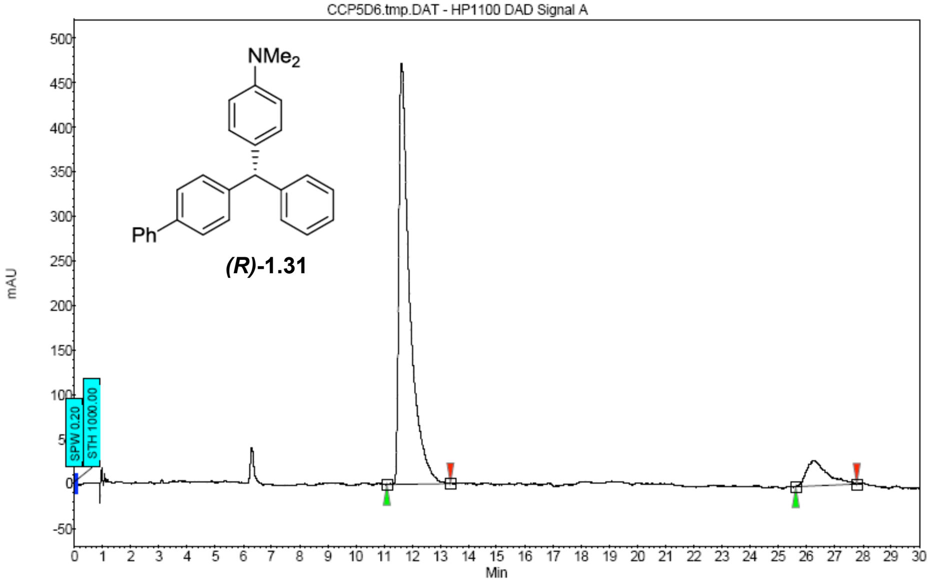
***rac*-1.30**



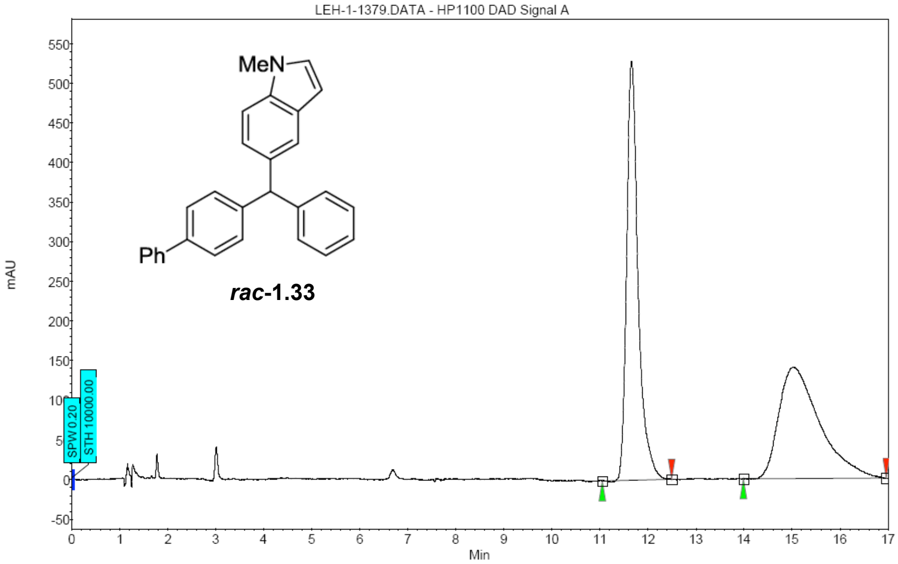
***(R)*-1.30**

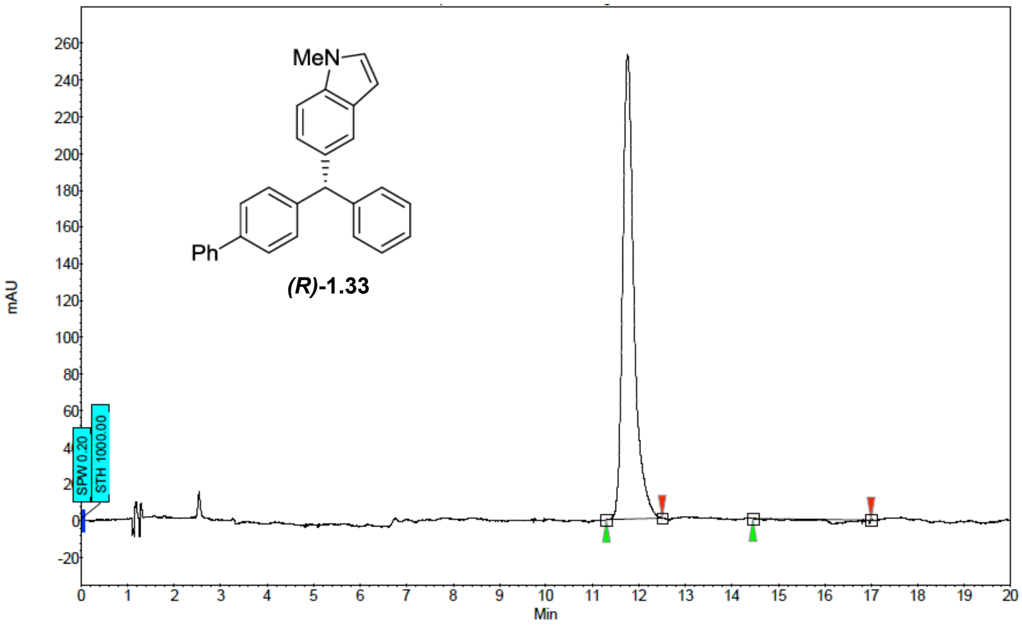
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	19.35	19.85	21.07	0.00	92.25	398.9	207.1	92.249
2	UNKNOWN	21.13	21.57	22.22	0.00	7.75	38.6	17.4	7.751
Total						100.00	437.5	224.5	100.000



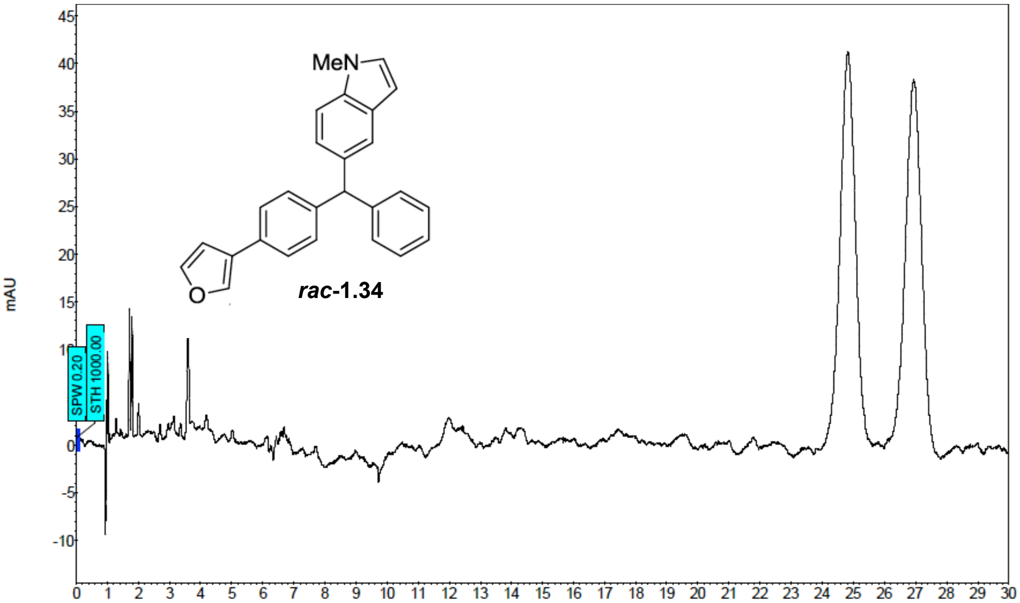


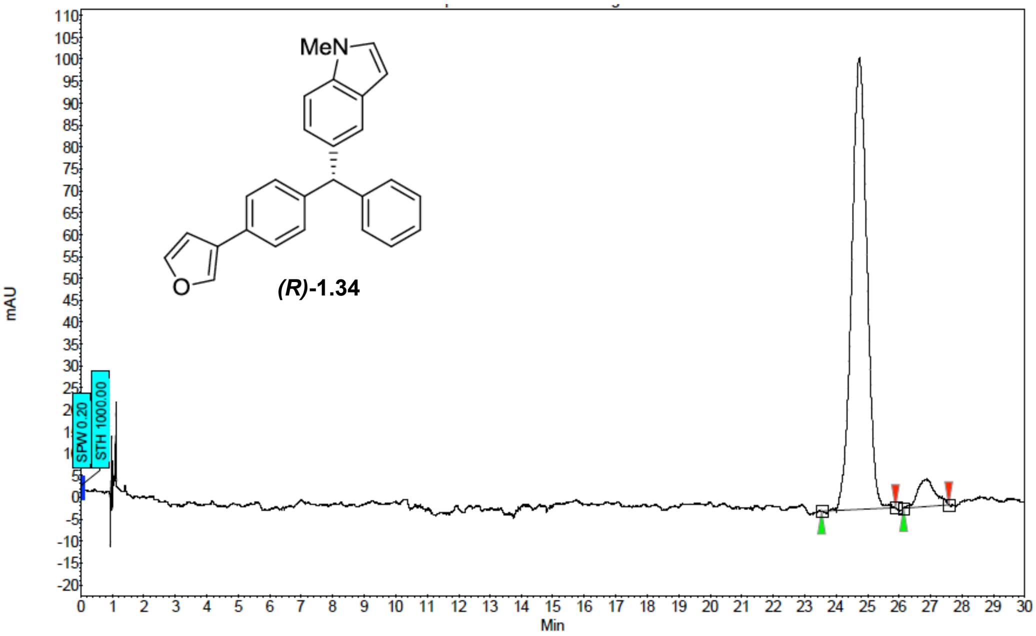
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	11.09	11.62	13.35	0.00	89.58	472.3	210.6	89.580
2	UNKNOWN	25.61	26.26	27.77	0.00	10.42	28.2	24.5	10.420
Total						100.00	500.5	235.1	100.000



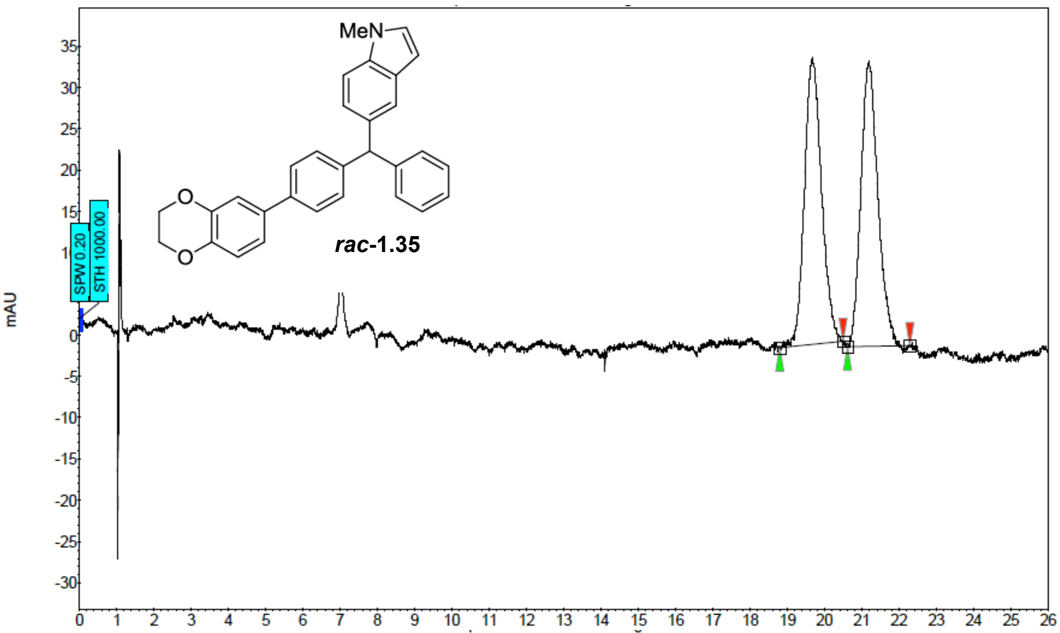


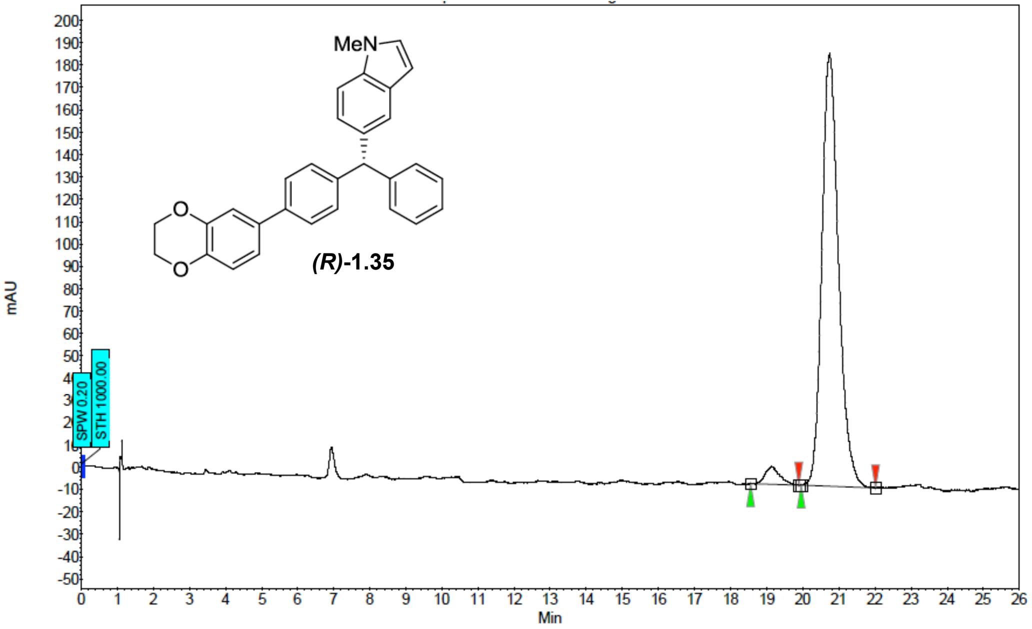
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	11.31	11.76	12.51	0.00	97.87	252.3	70.7	97.873
2	UNKNOWN	14.45	16.15	17.00	0.00	2.13	2.3	1.5	2.127
Total						100.00	254.6	72.2	100.000





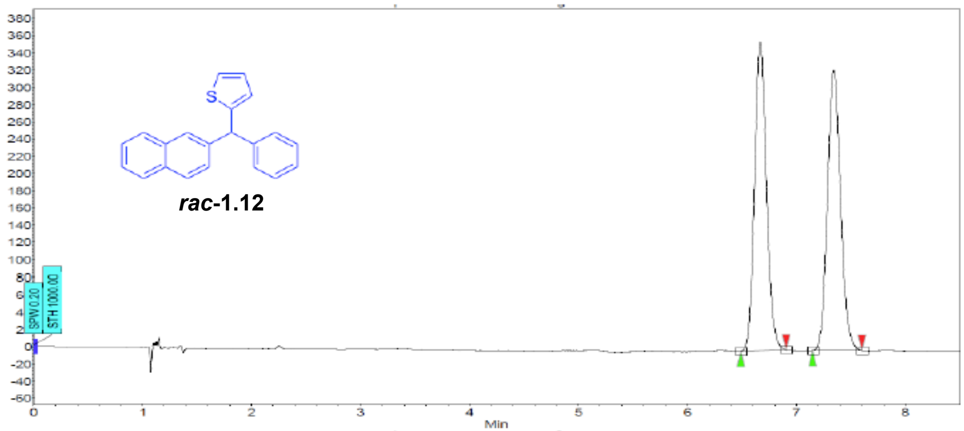
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	23.55	24.74	25.88	0.00	93.55	103.0	57.7	93.545
2	UNKNOWN	26.15	26.89	27.58	0.00	6.45	6.2	4.0	6.455
Total						100.00	109.2	61.7	100.000





Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	18.56	19.13	19.88	0.00	3.46	7.8	3.7	3.464
2	UNKNOWN	19.96	20.74	22.01	0.00	96.54	193.6	103.4	96.536
Total						100.00	201.4	107.1	100.000

SFC traces (complete SFC data can be found in section X):



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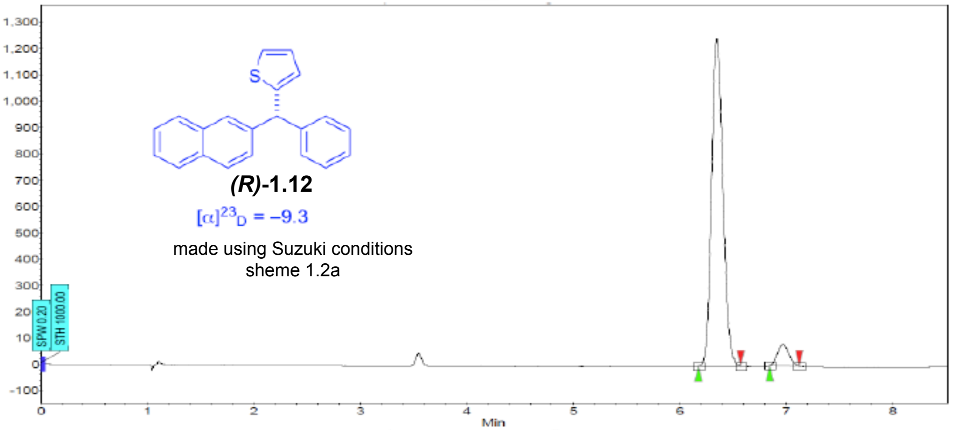
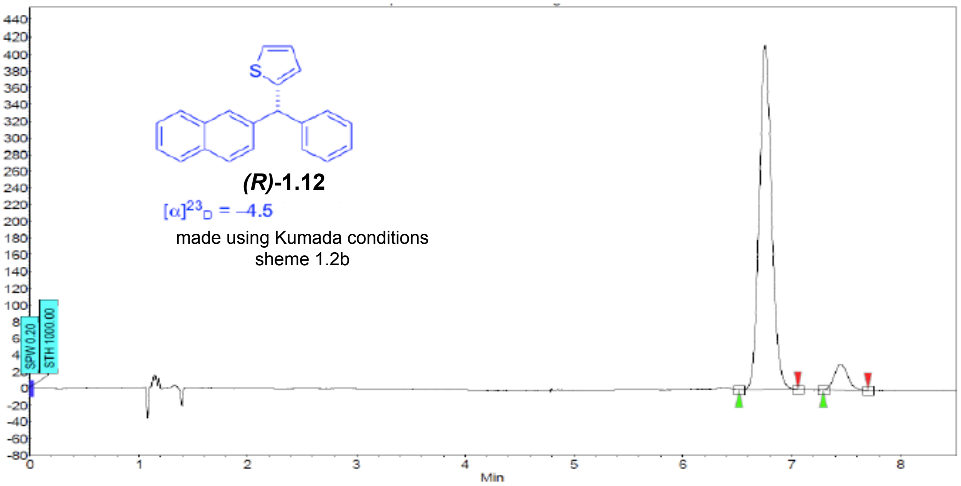


***(R)*-1.12**

$[\alpha]^{23}_{D} = -9.3$

made using Suzuki conditions
sheme 1.2a



***(R)*-1.12**

$[\alpha]^{23}_{D} = -4.5$

made using Kumada conditions
sheme 1.2b

Chapter 2

Propargylic Carbamates Facilitate Regio- and Stereoselective Nickel-Catalyzed Hydroarylation of Alkynes

2.1 Introduction

Functionalized alkenes are present in pharmaceuticals[1] and natural products, and are commonly used as building blocks in synthesis[2] and polymer chemistry[3] (Figure 2.1).[4] Hydroarylation reactions of alkynes offer an alternative manifold for the facile synthesis of substituted alkenes. The major challenges associated with hydroarylation of alkynes has primarily been control of regioisomeric ratios and control of *E/Z* stereochemistry of the resulting olefin without relying on steric or electronic biases in the substrate.[5] For example, early work from Hayashi demonstrated that Rh(I) catalysts cleanly furnished hydroarylated products using symmetrical alkynes and arylboronic acids, however, using unsymmetrical starting materials that lacked strong electronic or steric bias resulted in mixtures of regioisomers (Scheme 2.1a).[6] The Lautens group judiciously addressed this problem with the use of pyridine or alcohol directing

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[1] (a) Liu, X.; Shimizu, M.; Hiyama, T. *Angew. Chem. Int. Ed.* **2004**, *43*, 879. (b) Levenson, A. S.; Jordan, V. C. *Eur. J. Cancer,* **1999**, *35*, 1628. (c) Prasit, P.; Wang, Z.; Brideau, C.; Chan, C. C.; Charleson, S.; Cromlish, W.; Ethier, D.; Evans, J. F.; Ford-Hutchinson, A. W.; Gauthier, J. Y.; Gordon, R.; Guay, J.; Gresser, M.; Kargman, S.; Kennedy, B.; Leblanc, Y.; Leger, S.; Mancini, J.; O´ 'Neill, G. P.; Ouellet, M.; Percival, M. D.; Perrier, H.; Riendeau, D.; Rodger, I.; Tagari, P.; Therien,´ M.; Vickers, P.; Wong, E.; Xu, L. J.; Young, R. N.; Zamboni, R.; Boyce, S.; Rupniak, N.; Forrest, M.; Visco, D.; Patrick, D. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1773. (d) Fallis, A. G.; Forgione, P. *Tetrahedron*, **2001**, *28*, 5899.

[2] For examples of alkene utility in synthesis: (a) Hoffmann, N. *Chem. Rev.* **2008**, *108*, 1052. (b) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835. (c) Nicolaou, K.C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. *Angew. Chem. Int. Ed.* **2002**, *41*, 1668.

[3] Hall, H. K. *Angew. Chem., Int. Ed.* **1983**, *22*, 440.

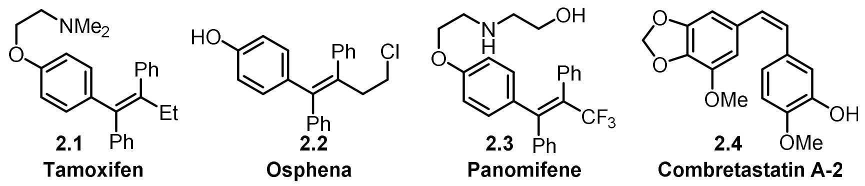
[4] (a) Example of natural products: Williams, R.B.; Norris, A.; Slebodnick, C.; Merola, J.; Miller, J. S.; Andriantsiferana, R.; Rasamison, V. E.; Kingston, D. G. I. *J. Nat. Prod.* **2005**, *68*, 1371. (b) Lin, C. M.; Ho, H. H.; Pettit, G. R.; Hamel, E. *Biochemistry* **1989**, *28*, 6984.

[5] for examples using electronic biased substrates (a) Lin, P.-S.; Jeganmohan, M.; Cheng, C.-H. *Chem. - Eur. J.* **2008**, 14, 11296. (b) Bai, Y.; Yin, J.; Kong, W.; Mao, M.; Zhu G. *Chem. Commun.*, **2013**,*49*, 7650. (c) Cui, W.; Yin, J.; Zheng, R.; Cheng, C.; Bai, Y.; Zhu, G. J. Org. Chem. 2014, 79, 3487. Also see reference 6 for examples of steric and electronic bias

[6] (a)Hayashi, T.; Inoue, K.; Taniguchi, N.; Ogasawara, M. *J. Am. Chem. Soc.* **2001**, *123*, 9918. (b)Zhang, W.; Liu, M.; Wu, H.; Ding, J.; Cheng, J. *Tetrahedron Lett.* **2008**, 49, 5214. (c) Genin, E.; Michelet, V.; Genêt, J.-P. *Tetrahedron Lett.* **2004**, 45, 4157.

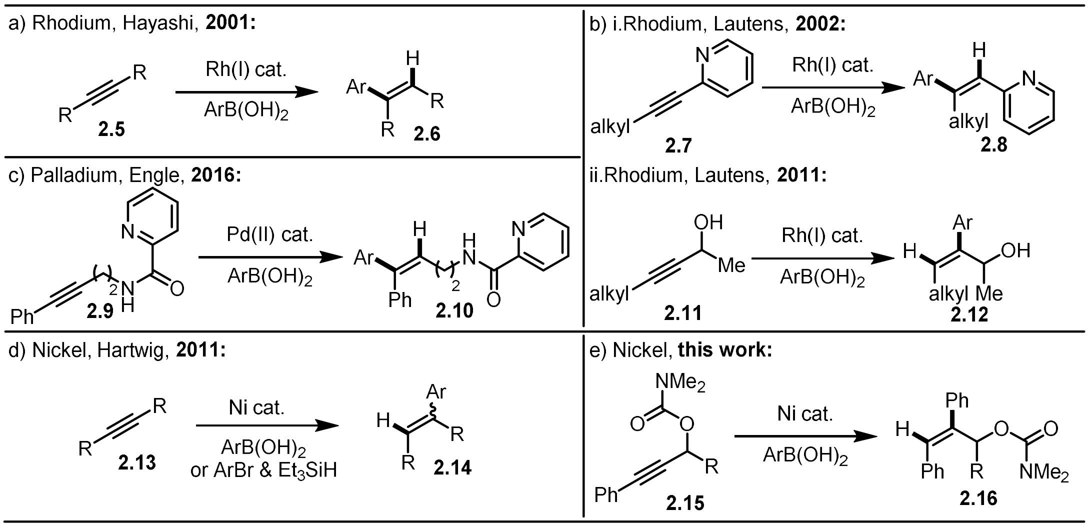
groups that could deliver hydroarylated products with excellent regio- and stereocontrol (Scheme 2.1b).[7] Efforts to employ group 10 metals such as palladium and nickel in hydroarylation reactions have been explored with low regio- and sterocontrol (Scheme 2.1d).[8] However, Engle and co-workers have recently reported the use of pendant directing groups that address these obstacles with great success in palladium-catalyzed reactions (Scheme 2.1c).[9] To date, hydroarylation reactions that use nickel catalysts suffer from both regio- and stereocontrol of the resulting olefin. (Scheme 2d).

Figure 2.1. Examples of pharmaceutical agents and natural products bearing alkenes



2.1 **Tamoxifen** **2.2** **Osphena** **2.3** **Panomifene** **2.4** **Combretastatin A-2**

Scheme 2.1. Summary of transition metal catalyzed hydroarylations using boronic acids



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[7] (a) Panteleev, J.; Huang, R. Y.; Lui, E. K. J.; Lautens, M. *Org. Lett.* **2011**, *13*, 5314. (b) Lautens, M; Yoshida, M. *Org. Lett.* **2002**, *4*, 123.

[8] (a)Shirakawa, E.; Takahashi, G.; Tsuchimoto, T.; Kawakami, Y. *Chem. Commun.* **2001**, 2688 (b) Hartwig, J. F. *Science* **2011**, 333, 1423. (c) Oh, C. H.; Jung, H. H.; Kim, K. S.; Kim, N. *Angew. Chem., Int. Ed.* **2003**, 42, 805. (d) Xu, X.; Chen, J.; Gao, W.; Wu, H.; Ding, J.; Su,W. *Tetrahedron* **2010**, 66, 2433

[9] Liu, Z.; Derosa, J.; Engle, K. M. *J. Am. Chem. Soc.*, **2016**, *138*, 13076.

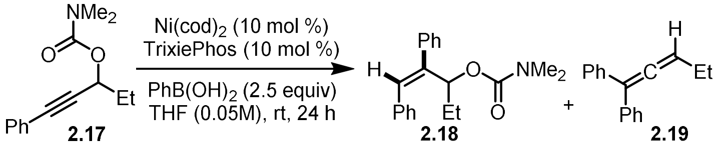
Moving forward, efforts in our group have focused on the use of base metals and propargylic directing groups to address this challenge. Previous work in our group has demonstrated that carbamates can serve as directing groups for nickel catalysts in Suzuki coupling reactions. Thus, we hypothesized that propargylic carbamates could also serve as directing groups for hydroarylation reactions as well. Herein, we report a regio- and stereoselective hydroarylation of alkynes under mild conditions (Scheme 2.1e).

2.2 Development of Nickel-Catalyzed Directed Hydroarylation

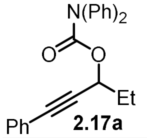
We began our investigation by investigating a range of propargylic directing groups including pivalates, carbonates and carbamates. Using pivalates and carbonates as directing groups led to undesired formation of allene **2.19** while still forming small amounts of desired product. A mixture of byproducts and only 10% hydroarylated product was observed when free secondary propargyl alcohols were used. Interestingly, nearly identical results were observed without the alcohol or directing groups present (Table 2.1, entries 4 and 5). Employing bulky carbamates such as diisopropyl carbamate led to a severe decrease in product formation. However, moving to sterically smaller alkyl groups such as pyrrolidine carbamate led to an increase in product formation, with a dimethyl carbamate giving the highest yields. A range of ligands were investigated during the optimization. The reaction performs well with monodentate phosphine ligands. During further studies of ligand effects, it was uncovered that catalysts with sterically bulky Buchwald type ligands such as TrixiePhos were uniquely capable of suppressing the formation of allene, while still furnishing the desired product in good yields.

Interestingly, the reaction performs much better in the absence of bases such as *t*-BuOK and K_3PO_4, commonly used bases for transmetallation of Suzuki reagents. Furthermore, the addition of just one equivalent of LiCl to the reaction mixture led to a complete shutdown of reactivity and recovery of only starting material (Table 2.1, entry 12). Additionally, during an investigation of solvents, it was found that the use of strongly coordinating solvents such as DMF also shut down reactivity (Table 2.1, entry 11).

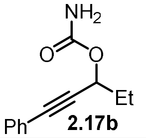
Table 2.1. Optimization of hydroarylation reaction conditions



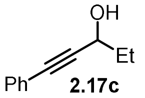
entry	variation from standard conditions	recovered **2.17** (%)^a	**2.18** (%)^a	**2.19** (%)^a
1	none	<2	70	<2
2	**2.17a** instead of **2.17**	57	16	14
3	**2.17b** instead of **2.17**	81	8	<2
4	**2.17c** instead of **2.17**	73	20	<2
5	**2.20** instead of **2.17**	57	19	<2
6	no nickel	100	0	0
7	no ligand	8	55	15
8	SPhos instead of TrixiePhos	16	63	2
9	BrettPhos instead of TrixiePhos	11	50	9
10	CPhos instead of TrixiePhos	12	50	12
11	DMF instead of THF	86	13	7
12	1 equivalent of LiCl	100	0	0
13	1 equivalent of K_3PO_4	10	40	6
14	PhBpin instead of $PhB(OH)_2$	78	8	4
15	$(PhBO)_3$ instead of $PhB(OH)_2$	65	19	6



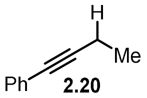
2.17a



2.17b



2.17c



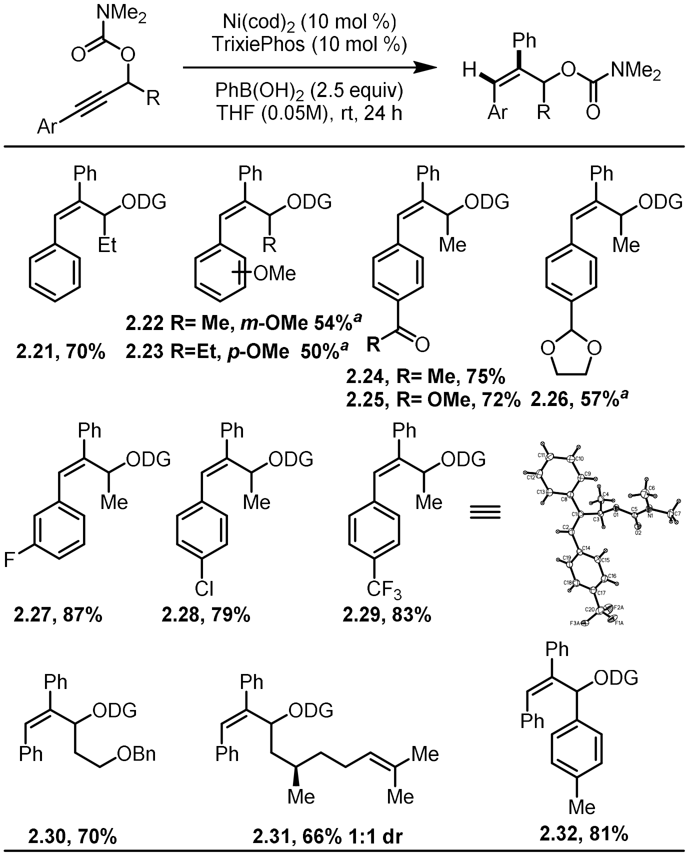
2.20

^{a}Yied determined by ^1H NMR spectroscopy using PhTMS as internal standard.

2.3 Scope of Substrates for Hydroarylation

Having identified suitable reaction conditions for model substrate **2.17**, we turned our attention to interrogating a broad scope of internal alkynes (Table 2.2). Substrates bearing electron-deficient arenes provided the highest yields of hydroarylated product at room temperature while electron-rich arenes required heating (Table 2.2, entry **2.22** and **2.23**). Ketone and ester substituents were well tolerated, however, free aldehydes were not. Gratifyingly, this oxidation state can still be incorporated as an acetal, although heating is required. The presence of aryl fluorides and chlorides did not produce the corresponding Suzuki-coupled products, allowing for further orthogonal functionalization (Table 2.2, entry **2.27** and **2.28**). An X-ray crystallographic structure of trifluoromethyl-substituted **2.29** was obtained, supporting the completely regioselective *cis*-hydroarylation. Benzyl-protected alcohols on the alkyl moiety of the starting materials were carried through the reaction untouched. Citronellal-derived substrate **2.31** shows that alkenes do not shut down reactivity and can be manipulated in downstream reactions. Surprisingly, sp^2-hybridized side chains yielding both allylic and benzylic-activated carbamates did not undergo Tsuji-Trost type cross-coupling and provided products in high yields (entry **2.32**).

Table 2.2. Investigation of scope in alkynes for hydroarylation



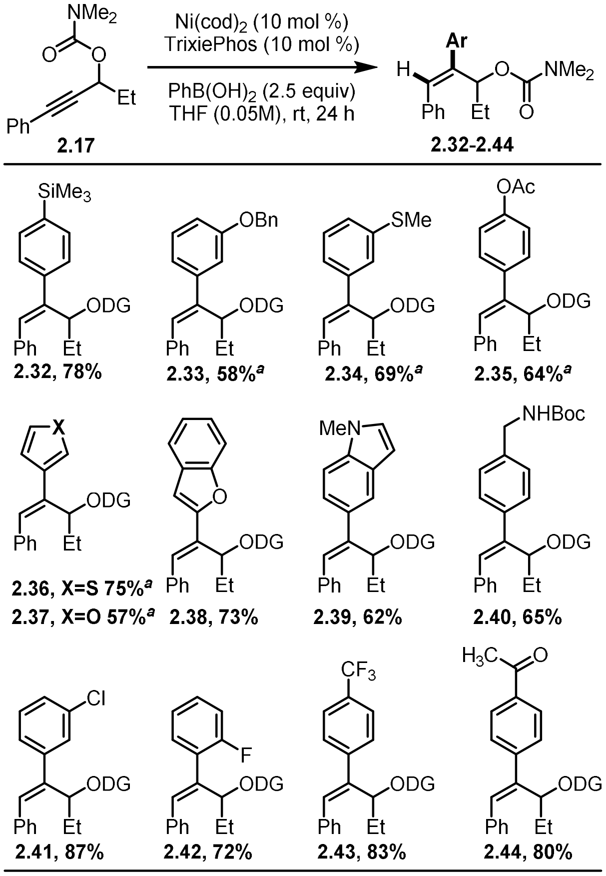
2.21, 70%
2.22 R= Me, *m*-OMe 54%[a]
2.23 R=Et, *p*-OMe 50%[a]
2.24, R= Me, 75%
2.25, R= OMe, 72%
2.26, 57%[a]
2.27, 87%
2.28, 79%
2.29, 83%
2.30, 70%
2.31, 66% 1:1 dr
2.32, 81%

yield is that of isolated compound after column chromatography.

2.4 Scope of ArylBoronic Acid for Hydroarylation

Next, we turned our attention to investigating the scope of arylboronic acids (Table 2.3). Again, a similar trend in sensitivity to electronics was observed and electron-deficient arylboronic acids provided the highest yields at room temperature while electron-rich arylboronic acids required heating. A variety of functional groups were well-tolerated, allowing for the incorporation of phenyl TMS, acetoxy, ether, thioether, and trifluoromethyl moieties (Table 2.3, entries **2.32**-**2.34** & **2.43**). Ketones and Boc-protected amines were also well tolerated and provided hydroarylated product in good yields. Chloro- and fluorophenyl products, such as **2.41** and **2.42** did not participate in either hydrodehalogenation or cross-coupling. Furthermore, boronic acids containing heterocycles such as furan and thiophene underwent hydroarylation smoothly at elevated temperatures while benzofuran and indoleboronic acids could be coupled at room temperature. (Table 2.3, entries **2.38** and **2.39**).

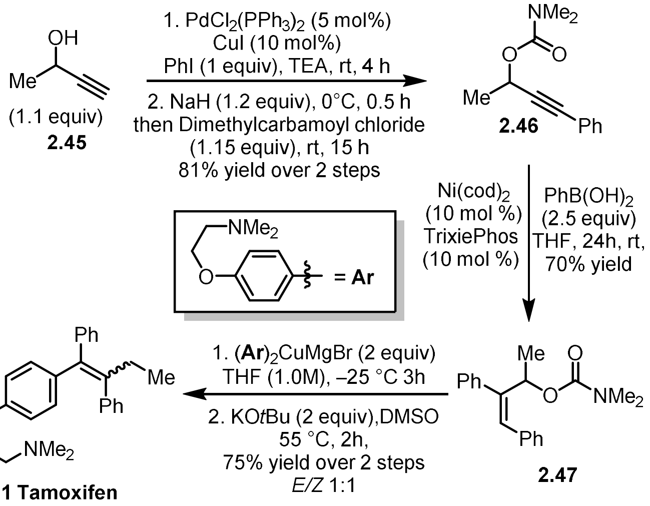
Table 2.3. Investigation of scope in aryl boronic acid



2.5 Synthesis of Tamoxifen

Functionalized allylic alcohols are common synthetic building blocks en route to more complex molecular scaffolds. Allylic carbamates can be used in Tsuji-Trost chemistry as well as copper-mediated substitutions allowing for a range of back-to-back transition-metal-catalyzed reactions following hydroarylation. Scheme 2.2 demonstrates one of the many synthetic uses of these products. **2.47** can be converted to tamoxifen in two steps via a cuprate-mediated allylic substitution of the allylic carbamate followed by isomerization of the double bond to form the conjugated target **2.13**. As previously stated, these alkenes are known to be biologically active, and have been described to have anti-cancer activity. Hence, the herein described method can serve as a useful platform to generate a library of tamoxifen-like structures for SAR studies.

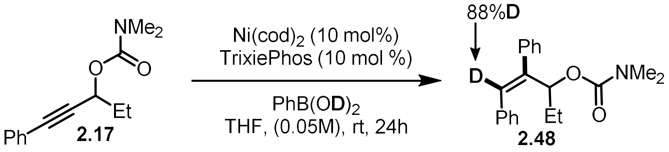
Scheme 2.2. Synthesis of Tamoxifen



2.6 Mechanistic Studies and Deuterium Labeling

Lastly, we were interested gaining insight into the mechanism of the reaction by determining the origin of the hydrogen atom in our hydroarylation reaction. Initial attempts to replace phenylboronic acid with phenyl boroxine and deuterium oxide resulted in low yields of product (17-30%) with 99% deuterium incorporation. However, using $PhB(OD)_2$ led to a 68% yield of product **2.48** with 88% deuterium incorporation (Equation 2.3). These results led us to definitively conclude that the acidic protons in the boronic acid were the source of hydrogen in the hydroarylation. These results are consistent with a mechanism that involves a directed hydrometalation to afford a vinylnickelintermediate, which can then undergo transmetallation and reductive elimination to furnish the desired product. This is also consistent with the previously proposed hydoarylation reactions that do not require base.[8c]

***Equation 2.3.* Deuterium Labeled Boronic Acid Reveals Origin of Hydrogen in Reaction**



2.7 Conclusion

In conclusion, we have developed a regio- and stereoselective nickel-catalyzed hydroarylation of alkynes using a propargyl carbamate as a directing group. The reaction is tolerant of a range of functional groups and heterocycles. Furthermore, the synthesis of tamoxifen can be completed in two, operationally simple, steps in good overall yield.

2.8 Experimental Details

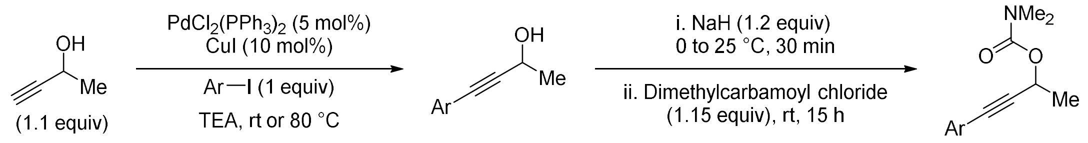
General Procedures

All hydroarylations were carried out under an atmosphere of N_2, or Ar when noted. All glassware was oven- or flame-dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and dimethylacetamide (DMA) were degassed with Ar and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 ºC for 12 h) to remove H_2O. All other solvents utilized were purchased "anhydrous" commercially, or purified as described. ^1H NMR spectra were recorded on Bruker DRX-400 (400 MHz ^1H, 100 MHz ^{13}C, 376.5 MHz ^{19}F) or CRYO-500 (500 MHz ^1H, 125.7 MHz ^{13}C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), triplet (t), doublet of triplets (dt), doublet of doublet of triplets (ddt), triplet of triplets (tt), quartet (q), quintet (quin), apparent doublet (ad), apparent triplet (at), multiplet (m)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 ºC. Infrared (IR) spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm^{-1}). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F_{254} precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with $KMnO_4$, ceric ammonium molybdate (CAM), or *p*-anisaldehyde (PAA) solutions. Flash chromatography was performed using Silica Gel 60 (170-400 mesh) from Fisher Scientific. Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Automatic Polarimeter. High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. Bis(cyclooctadiene)nickel Ni(cod)$_2$ complex was purchased from Strem, stored in a glovebox under an atmosphere of N$_2$, and used as received. All other reagents were purchased commercially and used as received.

GENERAL METHODS FOR STARTING MATERIAL SYNTHESIS

The general methods for starting material synthesis will be used throughout the rest of the SI. In each instance a general method is used, it is specified by letter (A, B, etc.) and the exact amounts of reagents used for each reaction are listed for the specific compounds synthesized.

METHOD A: SONOGASHIRA COUPLING, CARBAMATE INSTALLATION



SONOGASHIRA COUPLING:

The products were prepared according to a modified procedure reported by Lautens.[10] To 100 mL round bottom flask equipped with a stir bar was added PdCl$_2$(PPh$_3$)$_2$ (5 mol%), CuI (10 mol%), 1-butyne-3-ol (1.1 equiv), aryl iodide (1.0 equiv), and triethyl amine (25 mL). The reaction was stirred at room temperature for 4 hours. The reaction mixture was then filtered through silica to remove palladium and copper, and the silica was washed with diethyl ether. The solvents were removed under reduced pressure to provide the crude product as a dark yellow-brown oil. The crude mixtures were carried forward to carbamate installation without further purification.

CARBAMATE INSTALLATION:

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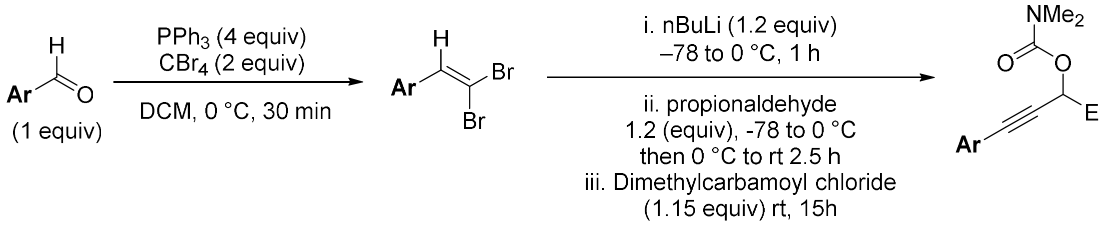
[10] Panteleev, J.; Huang, R. Y.; Lui, E. K. J.; Lautens, M. *Org. Lett.* **2011**, *13*, 5314

To a 100 mL round bottom flask was added NaH (1.1 equiv) and THF (30 mL). The suspension was cooled to 0 °C in an ice bath and a solution of the alcohol (1 M in THF) was added dropwise over 15 minutes. The ice bath was then removed and the mixture was allowed to warm to room temperature before dimethylcarbamoyl chloride (1.15 equiv) was added. The reaction was stirred overnight at room temperature for 15 hours after which the mixture was quenched with saturated aqueous ammonium chloride, extracted with ethyl ether, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography.

METHOD B: COREY-FUCHS, 1, 2 ADDITION, CARBAMATE INSTALLATION



COREY-FUCHS:

The product was prepared according to a modified procedure reported by Hoppe.[11] To a 250 mL round bottom flask was added PPh_3 (40 mmol, 4 equiv) and dichloromethane (35 mL) and was cooled to 0 °C, after which CBr_4 (20 mmol, 2 equiv) was added as a solution in dichloromethane (15 mL). The aryl aldehyde (10 mmol, 1 equiv) was then added as a solution in dichloromethane (10 mL) dropwise over the course of 10 minutes. The reaction was stirred for 30 min at 0 °C before the solvent was removed and the crude yellow oil was purified by column chromatography.

1, 2 ADDITION, CARBAMATE INSTALLATION:

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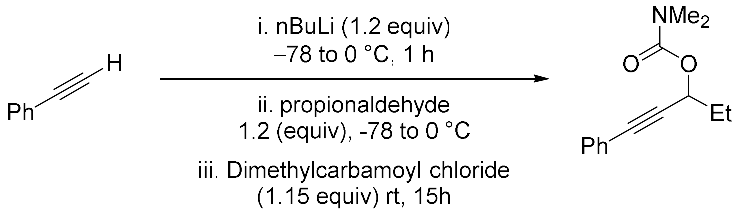
[11] Oestreich, M; Fröhlich, R.; Hoppe, D. *J. Org. Chem*. **1999**, *64*, 8616

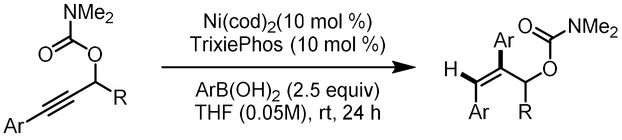
To a 250 mL round bottom flask was added *gem*-dibromo styrene and THF (50 mL). The solution was cooled to –78 °C in a dry ice and acetone bath after which *n*-BuLi (1.2 equiv) was added dropwise over the course for 20 min. The bath was then removed and the reaction was allowed to warm to room temperature and stirred for 30 minutes before it was cooled back down to –78 °C, and a solution of propionaldehyde (1M in THF) was added dropwise over the course of 10 minutes. The reaction was allowed to warm to room temperature and stirred for 4 hours before being quenched with dimethylcarbamoyl chloride (1.15 equiv). The resulting mixture was stirred overnight at room temperature for 15 hours before being quenched with saturated aqueous ammonium chloride and extracted with ethyl ether, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography.

METHOD C: 1, 2 ADDITION, CARBAMATE INSTALLATION



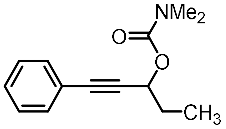
To a 250 mL round bottom flask was added phenyl acetylene (1 equiv) and THF (50 mL). The solution was cooled to –78 °C in a dry ice and acetone bath after which *n*-BuLi (1.2 equiv) was added dropwise over the course for 20 min. The bath was then removed and the reaction was allowed to warm to room temperature and stirred for 30 minutes before it was cooled back down to –78 °C, and a solution of propionaldehyde (1M in THF) was added dropwise over the course of 10 minutes. The reaction was allowed to warm to room temperature and stirred for 4 hours before being quenched with dimethylcarbamoyl chloride (1.15 equiv). The resulting mixture was stirred overnight at room temperature for 15 hours before being quenched with saturated aqueous ammonium chloride and extracted with ethyl ether, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography.

METHOD D: NICKEL CATALYZED HYDROARYLATION



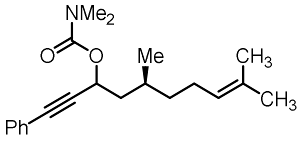
In a glove box, a flame dried 7 mL dram vial was charged with $Ni(cod)_2$ (5.5 mg, 0.02 mmol, 0.10 equiv), TrixiePhos (8.0 mg, 0.02 mg, 0.10 equiv), arylboronic acid (0.5 mmol, 2.5 equiv), and the alkyne (0.2 mmol, 1.0 equiv) and dissolved in THF (4 mL). The reaction was then stirred for 24 hours at 24℃ or 85℃ depending on the substrate and arylboronic acid used. The crude reaction mixture was then filtered through a pad of silica and eluted with Et_2O to remove the catalyst and then concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to isolate pure product.

CHARACTERIZATION FOR STARTING MATERIALS

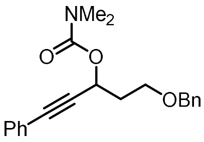


2.49. The product was prepared according to general method C using propionaldehyde (1.9 mL, 26.8 mmol), phenylacetylene (2.9 mL, 26.4 mmol) *n*-BuLi (11.4 mL, 28.5 mmol) and dimethylcarbamoyl chloride (2.5 mL, 27.5 mmol). The product was purified by flash column chromatography (20% Et_2O/pentane) to afford the title compound as a colorless oil (4.4 g, 19 mmol, 72% yield). **TLC R_f** = 0.4 (12% EtOA/hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49–7.41

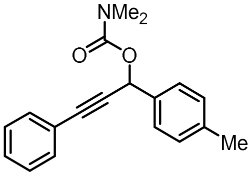
(m, 2H), 7.33–7.28 (m, 3H), 5.5 (t, *J* = 6.48 Hz, 1 H), 2.94 (s, 6H), 1.89 (quintet *J* = 7.5 Hz, 2H) 1.08 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 156.0, 132.2, 128.7, 128.5, 122.9, 87.6, 85.2, 66.9, 28.9, 9.8; **IR** (neat) 2970, 2935, 1702, 1489, 1128, 1392 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{14}H_{17}NO_2Na$ $(M + Na)^+$ 254.1157, found 254.1151



2.50. The product was prepared according to general method C using citronellal (2.0 mL, 11.0 mmol), phenylacentylene (1.1 mL, 10 mmol,) *n*-BuLi (4.4 mL, 11 mmol) and dimethylcarbamoyl chloride (1.0 ml, 11 mmol). The product was purified by flash column chromatography (20% Et$_2$O/pentane) to afford the title compound as a colorless oil (3.3 g, 10 mmol, 92% yield). **TLC R$_f$** = 0.4 (20% Et$_2$O/pentane); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.46–7.40 (m, 2H), 7.31–7.27 (m, 3H), 5.65–5.58 (m, 1H), 5.14–5.07 (m, 1H), 2.94 (s, 6H) 2.08–1.84, (m, 3H), 1.83–1.65 (m, 5H), 1.60 (s, 3H), 1.47–1.37 (m, 1H), 1.29–1.18 (m, 1H), 1.00–0.96 (m, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 156.1, 156.0, 132.21, 132.19, 131.66, 131.65, 128.68, 128.66, 128.49, 128.48, 124.91, 124.90, 123.0, 88.3, 88.0, 85.3, 85.0, 64.9, 64.4, 42.8, 42.5, 37.4, 37.2, 29.7, 29.4, 26.0, 25.66, 25.62, 19.97, 19.89, 18.0; **IR** (neat) 2955, 2924, 1705, 1489, 1392, 1178 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{21}H_{29}NO_2Na$ $(M + Na)^+$ 350.2096, found 350.2083

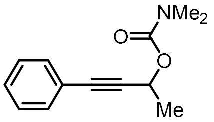


2.51. The product was prepared according to general method C using phenyl acetylene (0.45 mL, 4.1 mmol), *n*-BuLi (1.9 mL, 4.6 mmol), 3-(benzyloxy)propanal (660 mg, 4.0 mmol), and dimethyl carbamoyl chloride (1.1 mL, 11 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a colorless oil (1.1 g, 3.4 mmol, 85% yield). **TLC R$_f$** = 0.3 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43–7.38 (m, 2H), 7.36–7.23 (m, 8H), 5.73 (t, *J* = 6.7 Hz, 1H), 4.53 (s, 2H), 3.74–3.62 (m 2H), 2.93 (s, 3H), 2.89 (s, 3H), 2.28–2.12 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.8, 138.6, 132.2, 128.8, 128.7, 128.5, 128.0, 127.8, 122.8, 87.5, 85.4, 73.3, 66.4, 63.4, 35.9;**IR** (neat) 2931, 2863, 1699, 1490, 1395, 1184 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{21}H_{23}NO_3Na$ $(M + Na)^+$ 360.1576, found 360.1564

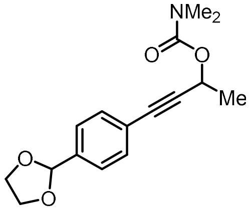


2.52. The product was prepared according to general method C using phenyl acetylene (1.1 mL 10 mmol) *n*-BuLi (4.8 mL, 12 mmol), *p*-Tolualdehyde (1.2 mL, 2.0 mmol), and dimethyl carbamoyl chloride (0.41mL, 4.4 mmol). The product was purified by flash column chromatography (20% Et_2O/pentanes) to afford the title compound as a colorless oil (1.14 g, 3.38mmol, 85% yield). **TLC R$_f$** = 0.3 (20% Et_2O/pentane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52–7.46, (m, 4H), 7.34–7.27 (m, 3H), 7.22–7.18 (m, 2H), 6.63 (s, 1H), 2.94 (s, 6H), 2.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.8, 138.9, 135.5, 132.2, 129.6, 128.9, 128.5, 127.9, 122.8, 87.0, 86.8, 67.2, 21.6; **IR** (neat)

2929, 1697, 1490, 1394, 1175 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{19}NO_2Na$ (M + Na)$^+$ 316.1313, found 316.1313

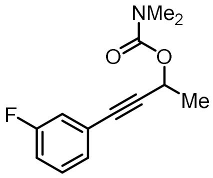


2.53. The product was prepared according to general method A using $PdCl_2(PPh_3)_2$ (90 mg), CuI (45 mg) 1-butyne-3-ol (0.54 mL, 7.0 mmol), aryl iodide (0.78 mL, 7.0 mmol), trielthyl amine (30 mL), dimethylcarbamoyl chloride (0.71 mL, 7.7 mmol), NaH (200 mg, 8.4 mmol), THF (25 mL) The product was purified by flash column chromatography (20% Et_2O/pentanes) to afford the title compound as a colorless oil (1.3 g, 6.0 mmol, 86% yield). **TLC** $\mathbf{R_f}$ = 0.4 (12% EtOA/hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46–7.42 (m ,2H), 7.32–7.25 (m, 3H), 5.65 (q, *J* = 6.6 Hz, 1H), 2.93 (s, 6H), 1.59 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.8, 132.1, 128.7, 128.5, 122.8, 88.6, 84.4, 61.9, 20.2; **IR** (neat) 2986, 2935, 1699, 1489, 1392, 1177 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{13}H_{15}NO_2Na$ (M + Na)$^+$ 240.1001, found 240.0989

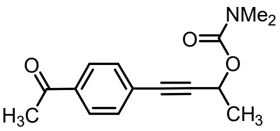


2.54 The product was prepared according to general method A using $PdCl_2(PPh_3)_2$ (350 mg, 0.5 mmol), CuI (190 mg, 1.0 mmol) 1-butyne-3-ol (0.83 mL, 11 mmol), aryl bromide (2.3g, 10 mmol), trielthyl amine (30 mL), dimethylcarbamoyl chloride (1.0 mL, 11 mmol), NaH (290 mg, 12 mmol), THF (25 mL) The product was purified by flash column chromatography (12% EtOAc/hexanes) to afford the title compound as a pale yellow oil (2.3 g, 8.0 mmol, 80% yield). **TLC** $\mathbf{R_f}$ = 0.2 (12%

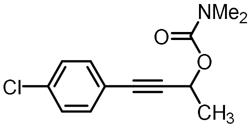
EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47–7.39 (m, 4H), 5.79 (s,1H), 5.64 (q, *J* = 6.7 Hz, 1H), 4.14–3.99 (m , 4H), 2.94 (s, 6H), 1.58 (d, 3, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.9, 138.4, 132.2, 126.7, 123.7, 103.6, 89.2, 84.1, 65.6, 62.0, 22.3; **IR** (neat) 2985, 2886, 1699, 1391, 1176, 1079 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{16}H_{19}NO_4Na$ (M + Na)$^+$ 312.1212, found 312.1197



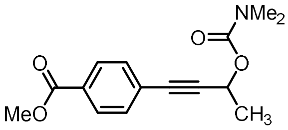
2.55 The product was prepared according to general method A using $PdCl_2(PPh_3)_2$ (250 mg, 0.35 mmol), CuI (130 mg, 0.70 mmol) 1-butyne-3-ol (0.58 mL, 7.7 mmol), aryl iodide (0.82 mL, 7.0 mmol), trielthyl amine (30 mL), dimethylcarbamoyl chloride (0.71 mL, 7.7 mmol), NaH (200 mg, 8.2 mmol), THF (25 mL) The product was purified by flash column chromatography (12% EtOAc/hexanes) to afford the title compound as a pale yellow oil (1.9 g, 8.2 mmol, 82% yield). **TLC R_f** = 0.4 (12% EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29–7.20 (m, 2H), 7.16–7.12 (m ,1H), 7.05–6.98 (m, 1H), 5.63 (q, *J* = 6.8 Hz, 1H), 2.94 (s, 6H), 1.58 (d, *J* = 6.8 Hz , 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246.0 Hz) 155.8, 130.1 (d, *J* = 8.8 Hz) 128.1 (d, *J* = 3.2 Hz) 124.7 (d, *J* = 9.7 Hz), 119.0 (d, *J* = 22.7 Hz), 116.1 (d, *J* = 21.4 Hz), 89.7, 83.2, 61.9, 22.2; **IR** (neat) 2936, 1701, 1579, 1486, 1392, 1170 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{13}H_{14}FNO_2Na$ (M + Na)$^+$ 258.0906, found 258.0905



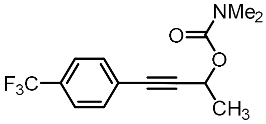
2.56. The product was prepared according to general method A using $PdCl_2(PPh_3)_2$ (180 mg, 0.25 mmol), CuI (95 mg, 0.50 mmol) 1-butyne-3-ol (0.43 mL, 5.5 mmol), aryl iodide (1.2 g, 5.0 mmol), trielthyl amine (30 mL), dimethylcarbamoyl chloride (0.51 mL, 5.5 mmol), NaH (140 mg, 6 mmol), THF (25 mL) The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (0.86 g, 3.3 mmol, 66% yield). **TLC R$_f$** = 0.4 (12% EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 5.65 (q, *J* = 6.7 Hz, 1H), 2.95 (s, 6H), 2.60 (s, 3H), 1.60 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.7, 155.8, 136.7, 132.3, 128.4, 127.8, 92.0, 83.6, 61.8, 27.0, 22.1; **IR** (neat) 2987, 2936, 1701, 1682, 1392, 1260, 1176 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{15}H_{17}NO_3Na$ $(M + Na)^+$ 282.1106, found 282.1102



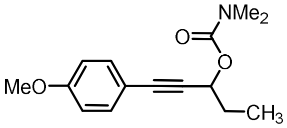
2.57. The product was prepared according to general method A using $PdCl_2(PPh_3)_2$ (180 mg, 0.25 mmol), CuI (95 mg, 0.50 mmol) 1-butyne-3-ol (0.43 mL, 5.5 mmol), aryl iodide (1.2 g, 5.0 mmol), trielthyl amine (30 mL), dimethylcarbamoyl chloride (0.51 mL, 5.5 mmol), NaH (140 mg, 6 mmol), THF (25 mL) The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (0.89 g, 3.6 mmol, 71% yield). **TLC R$_f$** = 0.4 (12% EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.62 (q, *J* = 6.7 Hz, 1H), 2.94 (s, 6H), 1.58 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.8, 134.8, 133.4, 128.9, 121.4, 89.8, 83.3, 61.9, 22.2; **IR** (neat) 2987, 2934, 1701, 1488, 1391, 1177 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{13}H_{14}ClNO_2Na$ (M + Na)$^+$ 274.0611, found 274.0617



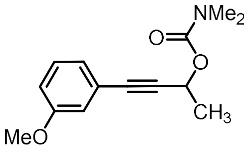
2.58. The product was prepared according to general method A using $PdCl_2(PPh_3)_2$ (180 mg, 0.25 mmol), CuI (95 mg, 0.50 mmol) 1-butyne-3-ol (0.43 mL, 5.5 mmol), aryl iodide (1.3 g, 5.0 mmol), trielthyl amine (30 mL), dimethylcarbamoyl chloride (0.51 mL, 5.5 mmol), NaH (140 mg, 6 mmol), THF (25 mL) The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (1.0 g, 3.8 mmol, 75% yield). **TLC R$_f$** = 0.3 (15% EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* 8.6 = Hz, 2H), 5.64 (q, *J* = 6.7 Hz, 1H), 3.92 (s, 3H), 2.95 (s, 6H) 1.59 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 155.8, 132.1, 130.0, 129.7, 127.6, 91.7, 83.7, 61.9, 52.6, 22.1; **IR** (neat) 2988, 2936, 1701, 1393, 1272, 1174, 1085 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{15}H_{17}NO_4Na$ (M + Na)$^+$298.1055, found 298.1047



2.59. The product was prepared according to general method A using $PdCl_2(PPh_3)_2$ (180 mg, 0.25 mmol), CuI (95 mg, 0.50 mmol) 1-butyne-3-ol (0.43 mL, 5.5 mmol), aryl iodide (0.73 mL, 5.0 mmol), trielthyl amine (30 mL), dimethylcarbamoyl chloride (0.51 mL, 5.5 mmol), NaH (140 mg, 6 mmol), THF (25 mL) The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (1.0 g, 3.7 mmol, 73% yield). **TLC R$_f$** = 0.4 (15% EtOAc/Hexanes);**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58–7.52 (m, 4H), 5.64 (q, *J* 7.0 = Hz, 1H), 2.95 (s, 6H), 1.59 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.8, 132.4, 130.5 (q, *J* = 32.8 Hz), 126.7 (q, *J* = 1.8 Hz), 124.1 (q, *J* = 271.9 Hz) 125.5 (q, *J* = 3.7 Hz), 91.2, 83.1, 61.8, 22.0; **IR** (neat) 2938, 1703, 1394, 1319, 1165, 1064 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{14}H_{14}F_3NO_2Na$ $(M + Na)^+$ 308.0874, found 308.0863

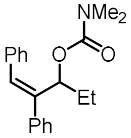


2.60. The product was prepared according to general method B using *p*-methoxy benzaldehyde (1.2 mL 10 mmol) CBr_4 (6.6 g, 20 mmol), PPh_3 (10.5 g 40.0 mmol), *n*-BuLi (8.4 mL, 21 mmol) propionaldehyde (0.72 mL, 10 mmol) and dimethyl carbamoyl chloride (1.0 mL, 11 mmol). The product was purified by flash column chromatography (12 % EtOAc/Hex) to afford the title compound as a pale yellow oil (1.2 g, 4.5 mmol, 45% yield). **TLC R$_f$** = 0.3 (12% EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.7, Hz, 2H), 5.50 (t, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 2.94 (s, 6H), 1.87 (quintet *J* = 7.2 Hz, 2H), 1.07 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.0, 156.1, 133.7, 115.1, 114.1, 86.3, 85.1, 67.0, 55.6, 29.0, 9.8; **IR** (neat) 2962, 2930, 1698, 1509, 1248, 1176 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{15}H_{19}NO_3Na$ $(M + Na)^+$ 284.1263, found 284.1265

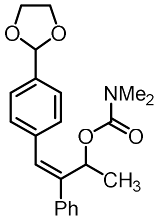


2.61. The product was prepared according to general method A using $PdCl_2(PPh_3)_2$ (180 mg, 0.25 mmol), CuI (95 mg, 0.50 mmol) 1-butyne-3-ol (0.43 mL, 5.5 mmol), aryl iodide (0.73 mL, 5.0 mmol), trielthyl amine (30 mL), dimethylcarbamoyl chloride (0.51 mL, 5.5 mmol), NaH (140 mg, 6 mmol), THF (25 mL) The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (1.0 g, 3.7 mmol, 73% yield). **TLC R$_f$** = 0.3 (12% EtOAc/Hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.20 (t, *J* = 7.7 Hz, 1H), 7.06–7.02 (m, 1H), 6.99–6.95 (m ,1H), 6.89–6.84 (m ,1H), 5.64 (q, *J* = 6.9 Hz, 1H), 3.79 (s, 3H), 2.94 (s, 6H), 1.58 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 159.5, 155.9, 129.6, 124.7, 123.8, 116.9, 115.5, 88.5, 84.4, 62.0, 55.6, 22.3; **IR** (neat) 2936, 1700, 1574, 1392, 1173 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{13}H_{17}NO_3Na$ $(M + Na)^+$ 270.1106, found 270.1097

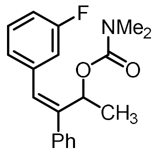
CHARACTERIZATION OF PRODUCTS



2.21 The product was prepared according to general method D using alkyne **2.49** (46.3 mg, 0.2 mmol), phenyl boronic acid (60 mg, 0.5 mmol), Ni(cod)$_2$ (5.5 mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (43.3 mg, 70% yield). **TLC R$_f$** = 0.4 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.51–7.46 (m, 2H), 7.43–7.23 (m, 8H), 6.71 (s, 1H), 5.84 (t, *J* = 6.85 Hz, 1H), 2.88 (s, 3H), 2.7 (s, 3H), 1.85 (m, 1H), 1.65 (m ,3H), 0.82 (t, *J* = 7.83 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) 156.3, 141.9, 141.4, 137.3, 132.6, 129.2, 128.9, 128.6, 128.2, 127.5, 127.3, 75.6, 27.5, 10.5; **IR** (neat) 2968, 2934, 1699, 1598, 1443 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{20}H_{23}NO_2Na$ $(M + Na)^+$ 332.1627, found 332.1611

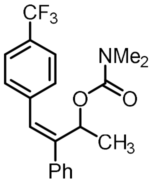


2.26. The product was prepared according to general method D using alkyne **2.54** (57.9 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5 mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (41.9 mg, 57% yield). **TLC R$_f$** = 0.3 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.51–7.45 (m, 4H), 7.41–7.28 (m, 5H), 6.64 (s, 1H), 6.02 (q, *J* = 6.9 Hz, 1H), 5.83 (s, 1H), 4.16–4.01 (m, 4H), 2.86 (s, 3H), 2.70 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) 156.1, 143.4, 141.0, 138.1, 137.0, 131.0, 129.2, 128.9, 128.2, 127.6, 126.8, 103.9, 70.6, 65.7, 65.6, 30.1, 20.8; **IR** (neat) 2926, 1698, 1442, 1390, 1183, 1080 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{25}NO_4Na$ (M + Na)$^+$ 390.1681, found 390.1668

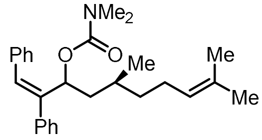


2.27 The product was prepared according to general method D using alkyne **2.55** (47.1 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (54.5 mg, 87% yield). **TLC R$_f$** = 0.3 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.48–7.44 (m, 2H), 7.39–7.29 (m, 4H), 7.17–7.13 (m, 1H), 7.10–7.05

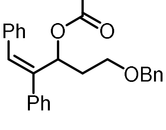
(m, 1H), 6.93 (dt, *J* = 8.4 , *J* = 2.4 Hz, 1H), 6.58 (s, 1H), 5.99 (q, *J* = 6.8 Hz, 1H), 2.87 (s, 3H), 2.71 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.9 (d, *J* = 245.5 Hz) 156.0, 144.2, 140.8, 139.4 (d, *J* = 7.9 Hz), 130.1 (d, *J* = 8.3 Hz), 130.0 (d, *J* = 1.8 Hz), 128.9, 128.3, 127.7, 124.9, (d, *J* = 3.2 Hz), 116.1 (d, *J* = 21.7 Hz), 114.3 (d, *J* = 21.3 Hz), 70.4, 20.8; **IR** (neat) 2985, 2933, 1698, 1489, 1391, 1180 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{20}FNO_2Na$ (M + Na)$^+$ 336.1376, found 336.1362



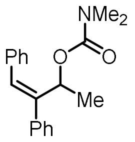
2.29. The product was prepared according to general method D using alkyne **2.59** (57.1 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), $Ni(cod)_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (60.3mg, 83% yield). **TLC R$_f$** = 0.4 (10% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65–7.61 (m, 2H), 7.51–7.46 (m, 4H), 7.40–7.31 (m, 3H), 6.63 (s, 1H), 5.95 (q, *J* = 6.7 Hz, 1H), 2.87 (s, 3H), 2.68 (s, 3H), 1.40 (d, *J=6.7* Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.0, 144.9, 140.9 (q, *J* = 1.4 Hz), 140.6, 129.7, 129.4, 129.3 (q, *J* = 132.4 Hz), 128.8, 128.4, 127.9, 125.6 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 271.9), 70.4, 20.8; **IR** (neat) 2980, 2934, 1700, 1615, 1393, 1323, 1121 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{20}H_{20}F_3NO_2Na$ (M + Na)$^+$ 386.1344, found 386.1335



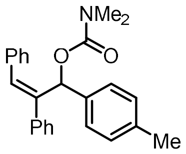
2.31. The product was prepared according to general method D using alkyne **2.50** (65.5 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (53.5 mg, 66% yield). **TLC R$_f$** = 0.6 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.50–7.44 (m, 2H), 7.44–7.40 (m, 2H), 7.38–7.32 (m, 4H), 7.31–7.27 (m, 1H), 7.27–7.22 (m, 1H), major diastereomer 6.69 (s, 0.52H), minor diastereomer 6.64 (s, 0.46H), 6.06–5.99 (m, 1H), 4.99–4.91 (m, 1H), major diastereomer 2.92– 2.80 (m, 3H) minor diastereomer 2.77-2.58 (m, 3H), 1.97–1.72 (m, 2H), 1.69–1.59 (m, 4H), 1.54–1.49 (m, 3H), 1.49–133 (m, 2H), 1.22–0.90 (m, 2H), minor diastereomer 0.73 (d, *J* = 6.6 Hz, 1.3H) major diastereomer 0.68 (d, *J* = 6.7 Hz, 1.59H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 156.3, 156.2, 143.1, 142.4, 141.28, 141.24, 137.4, 137.3, 132.3, 131.33, 131.28, 131.26, 129.10, 129.09, 128.90, 128.89, 128.6, 128.5, 128.19, 128.16, 127.48, 127.45, 127.3, 127.2, 125.03, 125.01, 73.2, 72.7, 41.9, 41.3, 37.5, 37.0, 29.6, 29.4, 26.01, 26.00, 25.7, 25.4, 19.9, 19.4, 17.9; **IR** (neat) 3022, 2959, 1700, 1493, 1392, 1186 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{27}H_{35}NO_2Na$ (M + Na)$^+$ 428.2566, found 428.2574



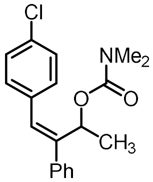
2.30. The product was prepared according to general method D using alkyne **2.51** (67.5 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (58.2 mg, 70% yield). **TLC** $\mathbf{R_f}$ = 0.6 (20% EtOAc/hexanes); ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.48–7.40 (m, 4H), 7.36–7.19 (m, 11H), 6.67 (s, 1H), 6.16 (dd, *J* =8.9 Hz, *J* = 5.3 Hz 1H), 4.35 (s, 2H), 3.50–3.40 (m, 2H), 2.84 (s, 3H), 2.64 (s, 3H), 2.22–2.12 (m, 1H), 2.06, 1.97 (m, 1H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 156.1, 141.9, 141.2, 138.7, 137.1, 132.3, 129.3, 128.9, 128.6, 128.5, 128.2, 127.9, 127.7, 127.5, 127.3, 73.1, 71.6, 67.0, 35.0; **IR** (neat) 3056, 2927, 1699, 1494, 1391, 1179 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{27}H_{29}NO_3Na$ $(M + Na)^+$ 438.2045, found 438.2048



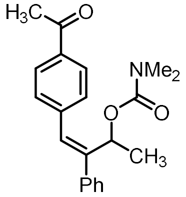
2.47 The product was prepared according to general method D using alkyne **2.53** (43.5 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (41.9 mg, 71% yield). **TLC** $\mathbf{R_f}$ = 0.4 (15% EtOAc/hexanes); ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.51–7.47 (m, 2H), 7.40–7.24 (m, 7H), 6.65 (s, 1H), 6.05 (q, *J* = 6.6 Hz, 1H), 2.87 (s, 3H), 2.72 (s, 3H), 1.40 (d, *J* = 6.7 Hz, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 156.1, 142.9, 141.2, 137.1, 131.5, 129.2, 129.0, 128.7, 128.2, 127.5, 127.4, 70.5, 20.8; **IR** (neat) 3022, 2932, 1698, 1491,m 1392, 1185 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{21}NO_2Na$ $(M + Na)^+$ 318.1470, found 318.1469



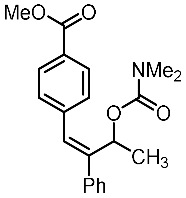
2.32 The product was prepared according to general method D using alkyne **2.52** (58.7 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (60.2 mg, 81% yield). **TLC R$_f$** = 0.4 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.52 (d, J = 8.1 Hz, 2H), 7.45–7.38 (m, 4H), 7.34–7.28 (m, 6H), 7.22 (s, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.05, (s, 1H), 2.92 (s, 3H), 2.68 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 156.1, 140.5, 140.4, 137.4, 137.03, 136.94, 132.4, 129.4, 129.2, 128.78, 128.76, 128.1, 127.6, 127.5, 126.7, 74.6, 21.5; **IR** (neat) 3023, 2923, 1703, 1492, 1389, 1173 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{25}H_{25}NO_2Na$ (M + Na)$^+$ 394.1783, found 394.1784



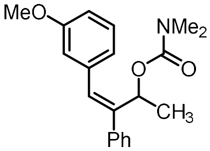
2.28 The product was prepared according to general method D using alkyne **2.57** (50.3 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (52.1 mg, 79% yield). **TLC R$_f$** = 0.5 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.48–7.44 (m, 2H), 7.38–7.28 (m, 7H), 6.57 (s, 1H), 5.99 (q, *J* = 6.7 Hz, 1H) 2.87 (s, 3H), 2.72 (s, 3H), 1.38 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 156.0, 143.7, 140.8, 135.6, 133.3, 130.5, 130.1, 128.85, 128.82, 128.3, 127.7, 70.3, 20.7; **IR** (neat) 2977, 2930, 1698, 1490, 1391, 1183 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{20}ClNO_2Na$ (M + Na)$^+$ 352.1080, found 352.1077



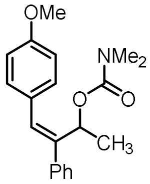
2.24. The product was prepared according to general method D using alkyne **2.56** (51.9 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (50.6mg, 75% yield). **TLC R$_f$** = 0.3 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00–7.95 (m, 2H), 7.51–7.45 (m, 4H), 7.40–7.31 (m, 3H), 6.66 (s, 1H), 6.01 (q, *J* = 6.7 Hz, 1H), 2.87 (s, 3H), 2.72 (s, 3H), 2.61 (s, 3H), 1.40 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.0, 144.8, 142.1, 140.6, 135.9, 130.3, 129.4, 128.83, 128.76, 128.3, 127.8, 70.3, 27.0, 20.7; **IR** (neat) 2979, 2931, 1699, 1682, 1267, 1182 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{21}H_{23}NO_3Na$ (M + Na)$^+$ 360.1576, found 360.1572



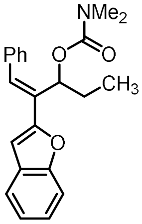
2.25 The product was prepared according to general method D using alkyne **2.58** (55.1 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (50.9mg, 72% yield. **TLC R$_f$** = 0.3 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.06–8.03 (m, 2H), 7.50–7.46 (m, 2H), 7.46–7.42 (m, 2H), 7.39–7.31 (M, 3H), 6.65 (s, 1H), 5.99 (q, *J* = 6.7 Hz, 1H), 3.92 (s, 3H), 2.86 (s, 3H), 2.69 (s, 3H), 1.43 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 167.2, 156.0, 144.7, 142.0, 140.7, 130.3, 129.9, 129.2, 128.9, 128.8, 128.3, 127.8, 70.4, 52.4, 20.7; **IR** (neat) 2929, 1718, 1698, 1391, 1275, 1178 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{21}H_{23}NO_4Na$ (M + Na)$^+$ 376.1525, found 376.1522



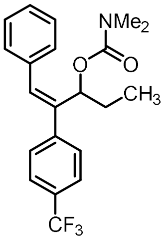
2.22 The product was prepared according to general method D using alkyne **2.61** (49.5 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (35.1 mg, 54% yield). **TLC R$_f$** = 0.3 (12% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.50–7.46 (m, 2H), 7.39–7.26 (m, 4H), 6.98–6.94 (m, 1H), 6.93–6.90 (m, 1H), 6.85–6.80 (m, 1H), 6.63 (s, 1H), 6.06 (q, *J* = 6.4 Hz 1H), 3.83 (s, 3H), 2.87 (s, 3H) 2.74 (s, 3H), 1.40 (d, *J* = 6.6 Hz 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 159.8, 143.1, 141.1, 138.5, 131.5, 129.7, 128.9, 128.2, 127.6, 121.6, 114.4, 113.4, 70.6, 55.5, 20.8; **IR** (neat) 2928, 1697, 1488, 1391, 1268, 1182 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{20}H_{23}NO_3Na$ (M + Na)$^+$ 348.1576, found 348.1577



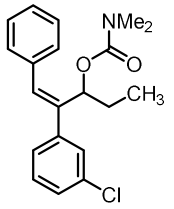
2.23 The product was prepared according to general method D using alkyne **2.61** (49.5 mg, 0.2 mmol), phenyl boronic acid (61 mg, 0.5 mmol), Ni(cod)$_2$ (5.5 mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (32.5 mg, 50% yield). **TLC R$_f$** = 0.3 (12% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.50–7.46 (m, 2H), 7.39–7.26 (m, 5H), 6.94–6.88 (m, 2H), 6.65 (S, 1H), 5.89 (t, *J* = 7.34 Hz, 1H), 3.82 (s, 3H), 2.89 (s, 3H), 2.78 (s, 3H), 1.84 (m, 1H), 1.64 (m, 1H), 0.82 (t, *J* = 7.58 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 158.9, 141.5, 140.5, 132.5, 130.5, 129.7, 128.9, 128.2, 127.3, 114.1, 75.5, 55.6, 27.4, 10.5; **IR** (neat) 2929, 1698, 1573, 1442, 1298, 1033 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{21}H_{25}NO_3Na$ $(M + Na)^+$ 362.1732, found 362.1730



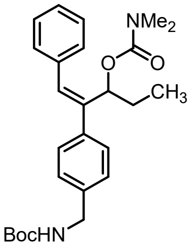
2.38 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 2-benzofuranylboronic acid (81 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (51.0 mg, 73% yield). **TLC R$_f$** = 0.3 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.57–7.50 (m, 4H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.31–7.23 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.96 (s, 1H), 6.03 (dd, *J* = 8.6, *J* = 6.4 Hz, 1H), 2.93 (s, 3H), 2.88 (s, 3H), 2.18–2.08 (m, 1H), 1.96–1.86 (m, 1H), 0.90 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.3, 154.4, 154.3, 136.6, 130.8, 130.5, 129.5, 129.4, 128.8, 127.8, 124.8, 123.1, 121.2, 111.2, 105.3, 74.0, 28.1, 10.8; **IR** (neat) 3057, 2967, 1699, 1451, 1390, 1181 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{23}NO_3Na$ $(M + Na)^+$ 372.1576, found 372.1582



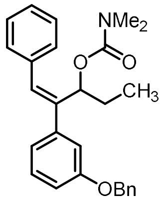
2.43 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 4-(Trifluoromethyl) phenyl boronic acid (95.0 mg, 0.5 mmol), $Ni(cod)_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (62.6 mg, 83% yield). **TLC R$_f$** = 0.4 (15% EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63–7.58 (m, 4H), 7.43–7.36, (m , 4H), 7.31–7.26 (m, 1H), 6.73 (s, 1H), 5.85 (t, *J* = 7.3 Hz, 1H), 2.89 (s, 3H), 2.73 (s, 3H), 1.88–1.80 (m, 1H), 1.68–1.59 (m,1H), 0.83 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.2, 145.1 (q, *J* = 1.4 Hz), 140.9, 136.7, 133.7, 129.6 (q, *J* = 32.4 Hz)129.23, 129.16, 128.7, 127.7, 125.2 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 127.4 Hz) 75.4, 27.6, 10.5; **IR** (neat) 2969, 2934, 1699,1322, 1164, 1122 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{21}H_{22}F_3NO_2Na$ $(M + Na)^+$ 400.1500, found 400.1489



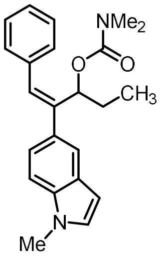
2.41 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 3-chlorophenylboronic acid (78 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (59.8 mg, 87% yield). **TLC R$_f$** = 0.4 (15% EtOAc/Hex); **^{1}H NMR** (500 MHz,CDCl$_3$) δ 7.51–7.49 (m, 1H), 7.42–7.34 (m, 5H), 7.31–7.26 (m, 3H), 6.71 (s, 1H), 5.83 (dd, *J* = 8.1, *J* = 6.7, Hz, 1H), 2.89 (s, 3H), 2.76 (s, 3H), 1.88–1.78 (m, 1H), 1.67–1.58 (m, 1H), 0.82 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz,CDCl$_3$) δ 156.2, 143.1, 140.7, 136.8, 134.0, 133.3, 129.5, 129.2, 129.1, 128.7, 127.59, 127.58, 127.1, 75.3, 27.5, 10.5; **IR** (neat) 2968, 2933, 1699, 1472, 1390, 1182 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{20}H_{22}ClNO_2Na$ (M + Na)$^+$, 366.1237 found 366.1227



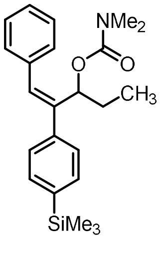
2.40 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 4-(tert-butoxycarbonylaminomethyl)phenylboronic acid (126 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (57.0 mg, 65% yield). **TLC R$_f$** = 0.3 (25% EtOAc/Hex); **^{1}H NMR** (500 MHz,$CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.42–7.33 (m, 4H), 7.29–7.23 (m, 3H), 6.69 (s, 1H), 5.83 (t, *J* = 7.2 Hz, 1H), 4.88 (s, 1H), 4.34 (d, *J* = 5.5 Hz, 2H), 2.88 (s, 3H), 2.74 (s, 3H), 1.88–1.78 (m, 1H), 1.66–1.58 (m, 1H), 1.48 (s, 9H), 0.80 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz,$CDCl_3$) δ 156.3, 141.5, 140.4, 137.2, 132.6, 129.18, 129.11, 128.6, 127.3, 75.6, 44.7, 28.8, 27.5, 10.5; **IR** (neat) 3339, 2970, 2932, 1699, 1507, 1175 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{26}H_{34}N_2O_4Na$ $(M + Na)^+$, 461.2416 found 461.2411



2.33 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 3-benzyloxyphenylboronic acid (114 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (48.2 mg, 58% yield). **TLC R$_f$** = 0.3 (25% EtOAc/Hex); **^{1}H NMR** (500 MHz,$CDCl_3$) δ 7.47–7.43 (m, 2H), 7.41–7.31 (m, 6H), 7.28–7.23 (m, 2H), 7.15–7.13 (m, 1H), 7.12–7.09 (m, 1H), 6.93 (ddd, *J* = 8.3, *J* = 2.6 *J* = 0.7 Hz, 1H), 6.72 (s, 1H), 5.82 (dd, *J* = 7.8, *J* = 6.8 Hz, 1H), 5.09 (s, 2H), 2.89 (s, 3H), 2.73 (s, 3H), 1.89–1.79 (m, 1H), 1.70–1.60 (m, 1H), 0.81 (t, *J* = 7.5, 3H); **^{13}C NMR** (125 MHz,$CDCl_3$) δ 158.7, 156.3, 142.8, 141.7, 137.4, 137.2, 132.7, 129.20, 129.18, 128.9, 128.6, 128.3, 127.8, 127.4, 121.7, 115.7, 113.8, 75.6, 70.3, 27.5, 10.6; **IR** (neat) 2967, 2930, 1698, 1574, 1391, 1182 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{27}H_{29}NO_3Na$ $(M + Na)^+$, 438.2045 found 438.2029

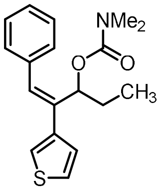


2.39 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 1-Methyl-5-indolylboronic acid (87 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (44.9 mg, 62% yield). **TLC R$_f$** = 0.2 (15% EtOAc/Hex); **^{1}H NMR** (500 MHz,CDCl$_3$) δ 7.75–7.74 (m, 1H), 7.44–7.34 (m, 5H), 7.31–7.28 (m, 1H), 7.26–7.22 (m, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 6.74 (s, 1H), 6.49 (dd, *J* = 3.2 *J* = 0.7 Hz, 1H), 5.88 (t, *J* = 7.3 Hz, 1H), 3.80 (s, 3H), 2.89 (s, 3H), 2.74 (s, 3H), 1.91–1.81 (m, 1H), 1.73–1.64 (m, 1H), 0.81 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz,CDCl$_3$) δ 156.5, 142.7, 137.9, 136.4, 132.7, 132.0, 129.5, 129.2, 128.5, 127.0, 123.0, 121.2, 108.8, 101.4, 76.2, 33.2, 27.6, 10.6; **IR** (neat) 2964, 2931, 2695, 1488, 1391, 1186 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{23}H_{26}N_2O_2Na$ $(M + Na)^+$, 385.1892 found 385.1900

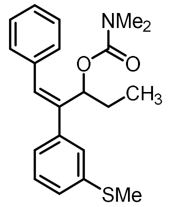


2.32 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 4-trimethylsilylphenylboronic acid (97 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure

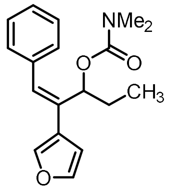
Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (59.5 mg, 78% yield). **TLC** $\mathbf{R_f}$ = 0.5 (15% EtOAc/Hex); **^{1}H NMR** (500 MHz,$CDCl_3$) δ 7.52–7.46 (m, 4H), 7.41–7.34 (m, 4H), 7.28–7.23 (m, 1H), 6.73 (s, 1H), 5.86 (dd, *J* = 7.7 *J* = 6.7 Hz, 1H), 2.89 (s, 3H), 2.75 (s, 3H), 1.89–1.80 (m,1H), 1.70–1.60 (m, 1H), 0.81 (t, *J* = 7.5 Hz, 3H), 0.29 (s, 9H); **^{13}C NMR** (125 MHz,$CDCl_3$) δ 156.4, 141.76, 141.74, 139.5, 137.4, 133.3, 132.8, 129.2, 128.6, 128.2, 127.3, 75.6, 27.5, 10.5, –0.7; **IR** (neat) 2955, 1703, 1460, 1392, 1248, 1183 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{23}H_{31}NO_2SiNa$ $(M + Na)^+$, 404.2022 found 404.2018



2.36 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 3-thienylboronic acid (64 mg, 0.5 mmol), $Ni(cod)_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (47.3mg, 75% yield). **TLC** $\mathbf{R_f}$ = 0.4 (15% EtOAc/Hex); **^{1}H NMR** (500 MHz,$CDCl_3$) δ 7.45–7.34 (m, 4H), 7.33–7.28 (m, 2H), 7.28–7.24 (m, 2H), 6.95 (s, 1H), 5.89 (dd, *J* = 8.1, *J* = 6.9 Hz, 1H), 2.88 (s, 3H), 2.85 (s, 3H), 1.98–1.87 (m, 1H), 1.77–1.68 (m, 1H), 0.83 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz,$CDCl_3$) δ 156.3, 140.8, 137.2, 136.3, 131.1, 129.2, 128.7, 128.0, 127.4, 125.0, 122.5, 75.3, 27.7, 10.6; **IR** (neat) 2969, 1702, 1491, 1390, 1183 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{18}H_{21}NO_2SNa$ $(M + Na)^+$, 338.1191 found 338.1184

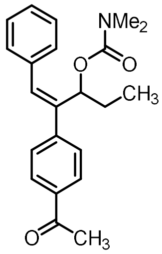


2.34 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 3-methylthiophenylboronic acid (84 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (49.1mg, 69% yield). **TLC R$_f$** = 0.4 (15% EtOAc/Hex); **^{1}H NMR** (500 MHz,CDCl$_3$) δ 7.42–7.35 (m, 5H), 7.30–7.24 (m, 3H), 7.20 (dt, *J* = 7.1, *J*= 1.8 Hz, 1H) 6.70 (s, 1H), 5.83 (dd, *J* = 8.0, *J* = 6.7 Hz, 1H), 2.89 (s, 3H), 2.75 (s, 3H), 2.51 (s, 3H), 1.88–1.79 (m, 1H), 1.69–1.60 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz,CDCl$_3$) δ 156.3, 142.0, 141.5, 138.2, 137.1, 132.9, 129.2, 128.7, 128.6, 127.4, 127.2, 125.8, 125.6, 75.5, 27.5, 16.2, 10.5; **IR** (neat) 2966, 1698, 1584, 1443, 1390, 1182 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{21}H_{25}NO_2SNa$ (M + Na)$^+$, 378.1504 found 378.1510

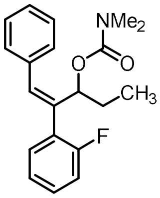


2.37 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 3-furanboronic acid (56 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (34.1 mg, 57% yield). **TLC R$_f$** = 0.3 (15% EtOAc/Hex); **^{1}H NMR** (500 MHz,CDCl$_3$) δ 7.67 (s, 1H), 7.43–7.40 (m, 2H), 7.39–7.34 (m, 2H), 7.27–7.23 (m, 2H), 6.88

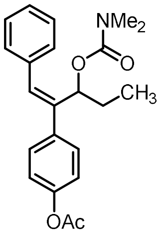
(s, 1H), 6.65–6.63 (m, 1H), 5.87 (dd, *J* =8.3, *J* = 6.6 Hz, 1H), 2.90 (s, 6H), 2.0–1.89 (m, 1H), 1.78–1.69 (m, 1H), 0.84 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (125 MHz,$CDCl_3$) δ 156.3, 142.8, 140.5, 137.1, 132.6, 129.2, 129.1, 128.7, 127.3, 124.2, 109.8, 75.2, 27.7, 10.6; **IR** (neat) 2971, 1698, 1491, 1394, 1264, 1188 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{18}H_{21}NO_3Na$ (M + Na)$^+$, 322.1419 found 322.1426



2.44 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 4-acetylphenylboronic acid (82 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et_2O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (56.2 mg, 80% yield). **TLC R$_f$** = 0.2 (12% EtOAc/Hex); **^{1}H NMR** (500 MHz,$CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H) 7.60 (d, *J* = 8.3 Hz, 2H), 7.43–7.35 (m, 4H), 7.31–7.27 (m, 1H), 6.77 (s, 1H), 5.87 (dd, *J* = 7.7 , *J* =6.8 Hz, 1H), 2.88 (s, 3H), 274 (s, 3H), 2.63 (s, 3H), 1.93–1.80 (m, 1H) 1.71–1.59 (m, 1H) 0.82 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** 198.2, 156.2, 146.4, 141.2, 136.8, 136.2, 133.7, 129.2, 129.1, 128.7, 128.4, 127.7, 75.4, 27.7, 27.0, 10.5; **IR** (neat) 2963, 2925, 1698, 1681, 1602, 1265, 1180 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{25}NO_3Na$ (M + Na)$^+$, 374.1732 found 374.1729

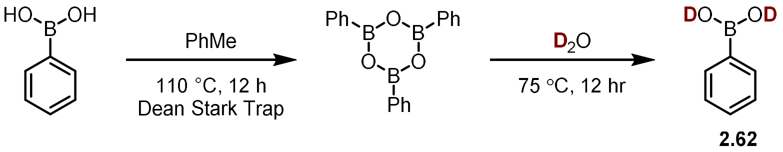


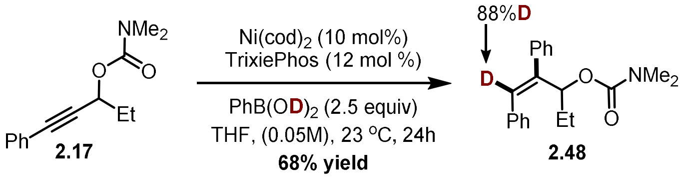
2.44 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 2-fluorophenylboronic acid (70 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (47.1 mg, 72% yield). **TLC R$_f$** = 0.4 (12% EtOAc/Hex); **^{1}H NMR** (500 MHz,CDCl$_3$) δ 7.41–7.43 (m, 2H), 7.40–7.35 (m, 2H), 7.33–7.26 (m, 3H), 7.14–7.06 (m, 2H), 6.60 (s, 1H), 5.87 (dd, *J* = 8.4 , *J* = 6.0 Hz, 1H), 2.89 (s, 3H), 2.68 (s, 3H), 1.81–1.58 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz,CDCl$_3$) δ 160.6 (d, *J* = 245.5 Hz), 156.4, 134.1, (*J* = 1.4 Hz), 132.3 (*J* = 3.7 Hz), 131.9, 129.3, 129.21, 129.18, 128.7, 127.5, 123.6 (d, *J* = 3.7), 115.7 (d, *J* = 23.1 Hz), 75.3, 27.3, 10.5; **IR** (neat) 2931, 1698, 1487, 1391, 1182 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{20}H_{22}FNO_2$ (M)$^+$, 327.1635 found 327.1630

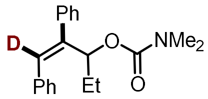


2.35 The product was prepared according to general method D using alkyne **2.17** (46.3 mg, 0.2 mmol), 4-acetoxyphenylboronic acid (90 mg, 0.5 mmol), Ni(cod)$_2$ (5.5mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (47.0 mg, 64% yield). **TLC R$_f$** = 0.3 (12% EtOAc/Hex); **^{1}H NMR** (500 MHz,CDCl$_3$) δ 7.51–7.47 (m, 2H), 7.41–7.33 (m ,4H), 7.28–7.23 (m, 1H), 7.10–7.05 (m, 2H), 6.70 (s, 1H), 5.83 (dd, *J* = 8.0 , *J* = 6.6 Hz, 1H), 2.87 (s, 3H), 2.72 (s, 3H), 2.32 (s, 3H), 1.91–1.79 (m, 1H), 1.71–1.60 (m ,1H), 0.82 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz,CDCl$_3$) δ 169.8, 156.3, 150.2, 141.1, 139.0, 137.2, 132.8, 129.9, 129.2, 128.6, 127.4, 121.3, 75.6, 27.5, 21.5, 10.6; **IR** (neat) 2926, 1760, 1698, 1503, 1186, 1166 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{25}NO_4Na$ (M + Na)$^+$, 390.1681 found 390.1684

DEUTERIUM LABELING EXPERIMENTS

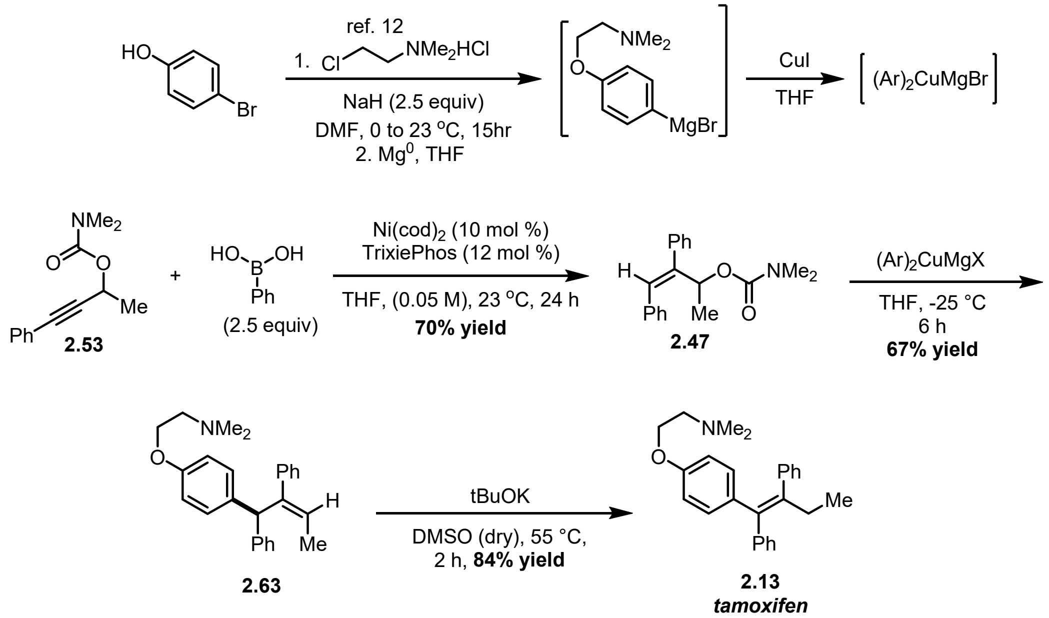






2.48 The product was prepared according to general method D using alkyne **2.17** (43.5 mg, 0.2 mmol), phenyl boronic acid-D$_2$ **2.62** (62 mg, 0.5 mmol), Ni(cod)$_2$ (5.5 mg, 0.02 mmol), TrixiePhos (8.0 mg, 0.02 mmol). The reaction mixture was eluted through a silica plug (with pure Et$_2$O) and concentrated under reduced pressure. Purified by flash column chromatography to afford the title compound as a pale yellow oil (42.2 mg, 68% yield). **TLC R$_f$** = 0.4 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.51–7.46 (m, 2H), 7.43–7.23 (m, 8H), 6.71 (s, (12% H incorporation, 1H), 5.84 (t, *J* = 6.85 Hz, 1H), 2.88 (s, 3H), 2.7 (s, 3H), 1.85 (m, 1H), 1.65 (m, 3H), 0.82 (t, *J* = 7.83 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) 156.3, 141.9, 141.4, 137.3, 132.6, 129.2, 128.9, 128.6, 128.2, 127.5, 127.3, 75.6, 27.5, 10.5; **IR** (neat) 2966, 2932, 1698, 1493, 1390, 1179 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{20}H_{22}DNO_2Na$ (M + Na)$^+$ 333.1689, found 333.1677.

SYNTHESIS OF TAMOXIFEN

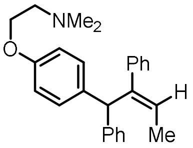


2.53

2.47

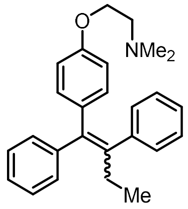
2.63

2.13
tamoxifen



2.63. The Grignard reagent was prepared by adding to Taillefer's method 25 mL round bottom flask: aryl bromide (0.80 g, 3.3 mmol), magnesium turnings (160 mg, 6.6 mmol, 2 equiv), THF (3 mL), and 1,2-dibromoethane (70 µL). The mixture was stirred at room temperature for 3 hours, resulting in a solution of ~ 0.55 M of Grignard reagent. To a 7 dram vial was added CuI (76 mg, 0.40 mmol) and Grignard reagent (1.5 mL, 0.80 mmol) at 0 °C, and the mixture was stirred for 30 minutes. The mixture was then cooled to -25 °C and a solution of allylic carbamate (30 mg, 0.10

mmol, 0.1 M in THF) was added dropwise over 40 minutes. The mixture was stirred for 6 hours at –25 °C then quenched with saturated aqueous ammonium chloride, extracted with EtOAc, dried over Mg_2SO_4 and concentrated under reduced pressure. The product was purified by reverse-phase HPLC with H_2O/CH_3CN (ZORBAX SB-C18 column, gradient elution of 40–70% CH3CN w/ 0.1% TFA) to afford the compound as a colorless oil (24.1 mg, 65% yield). **TLC** $\mathbf{R_f}$ = 0.3 (15% EtOAc/hexanes w/ 5% NEt_3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5H), 7.27–7.16 (m, 7H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.24 (q, *J* = 7.0 Hz, 1H), 5.08 (s, 1H), 4.30 (t, *J* = 3.8 Hz, 2H), 3.53 (t, *J* = 3.9 Hz, 2H), 2.99 (s, 6H), 1.58 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.7, 144.2, 142.9, 141.8, 136.8, 131.2, 129.8, 129.1, 128.5, 128.3, 126.8, 126.6, 126.5, 114.3, 62.6, 58.9, 57.2, 44.3, 15.3; **IR** (neat) 3027, 1609, 1509, 1238, 1175^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{26}H_{29}NOH$ $(M + H)^+$ 372.2327, found 372.2328



2.13 The product was prepared according to a modified procedure reported by Taillefer.[12] **2.63** (9.1 mg, 0.024 mmol) was dissolved in dry DMSO (0.8 mL) and KO*t*Bu (14 mg, 0.12 mmol, 5 equiv) was added. The mixture was then heated at 50 °C for 5 h. The crude reaction mixture was then filtered through a pad of silica and eluted with Et_2O then concentrated under reduced pressure. The product was purified by flash column chromatography to afford the title compound as a colorless oil (7.6 mg, 84% yield, 1:1 *E:Z*). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38–7.33 (m, 2H),

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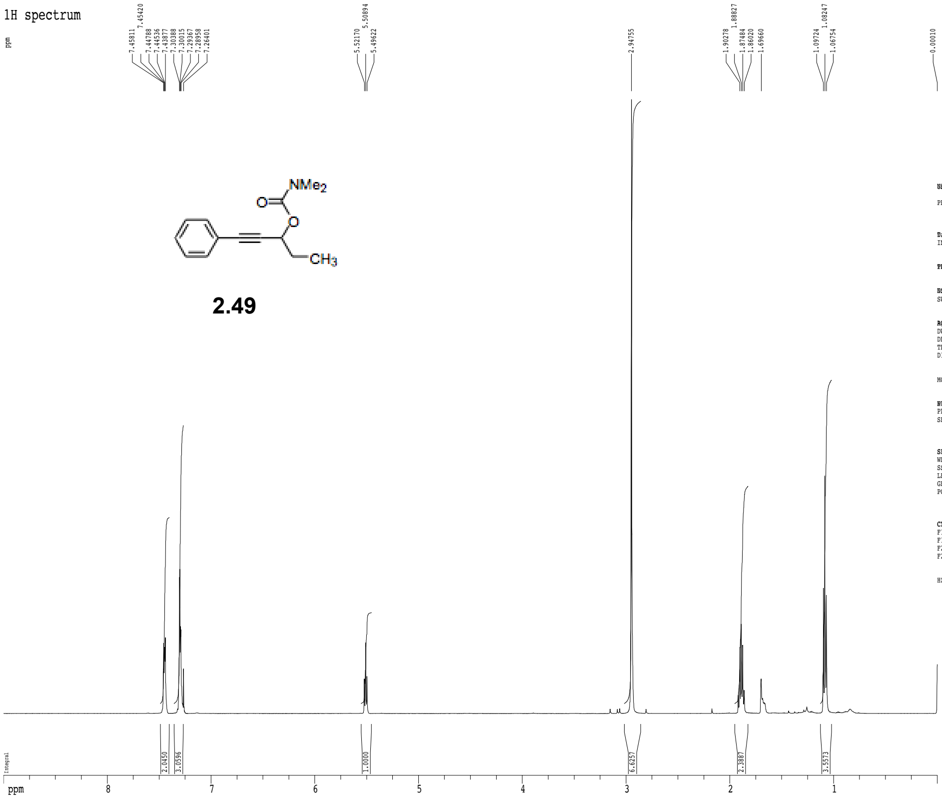
[12] Danoun, G.; Tlili, A.; Monnier, F.; Taillefer, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 12815

7.30–7.23 (m, 4H), 7.21–7.08 (m, 12H), 7.02–6.97 (m, 2H), 6.93–6.87 (m, 4H), 6.80–6.75 (m, 2H), 6.59–6.55 (m, 2H), 4.10 (t, *J* = 6.1 Hz, 1H), 3.94 (t, *J* = 6.0 Hz, 1H), 2.76 (t, *J* = 5.8 Hz, 1H), 2.65 (t, *J* = 5.8 Hz, 1H), 2.52 (q, *J* = 7.4 Hz, 1H), 2.47 (q, *J* = 7.4 Hz, 1H), 2.36 (s, 6H), 2.29 (s, 6H), 0.94 (q, *J* = 8.6 Hz, 6H).

1H spectrum



2.49

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PROCNO                1


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PULPROG                      zg30
                16022
  SOLVENT             8CDCl3
NS                    2
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                          0.500114 Hz
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RG                 12.7
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             0.00000000 sec
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MCWRK

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WDW                 no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 4.00


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F1              4501.98 Hz
F2P              0.000 ppm
F2                 0.00 Hz

    PPMCM                   0.39474 ppm/cm
HZCM        197.45528 Hz/cm
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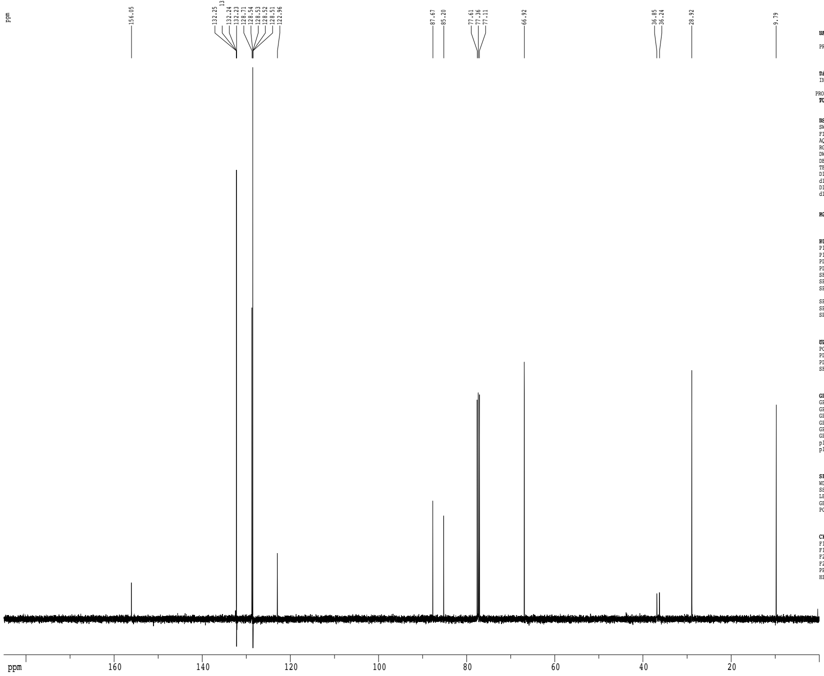
Z-restored spin-echo 13C spectrum with 1H decoupling



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PROCNO                1


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                  CDCl3
  SOLVENT          251
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FIDRES                     0.462388 Hz
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RG               7298.2
DW               16.500 usec
DE                           6.00 usec
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d17          0.00019600 sec

     MCREST                0.00000000 sec
MCWRK          0.01500000 sec


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P12             2000.00 usec
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PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                        2.70 dB
SP2
                                       2.70 dB
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SPOFF1      0.00 Hz    SPNAM2      Crp60comp.4
SPOFF2             0.00 Hz


       ======== CHANNEL f2 ========
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PCPD2            100.00 usec
PL2                          1.60 dB
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SFO2        500.2225011 MHz


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GPY2               0.00 %
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GPZ2              50.00 %
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p16            1000.00 usec


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SSB                   0
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GB
PC                    0
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  1D NMR plot parameters
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F1            23269.37 Hz
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PPMCM
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         1020.58649 Hz/cm
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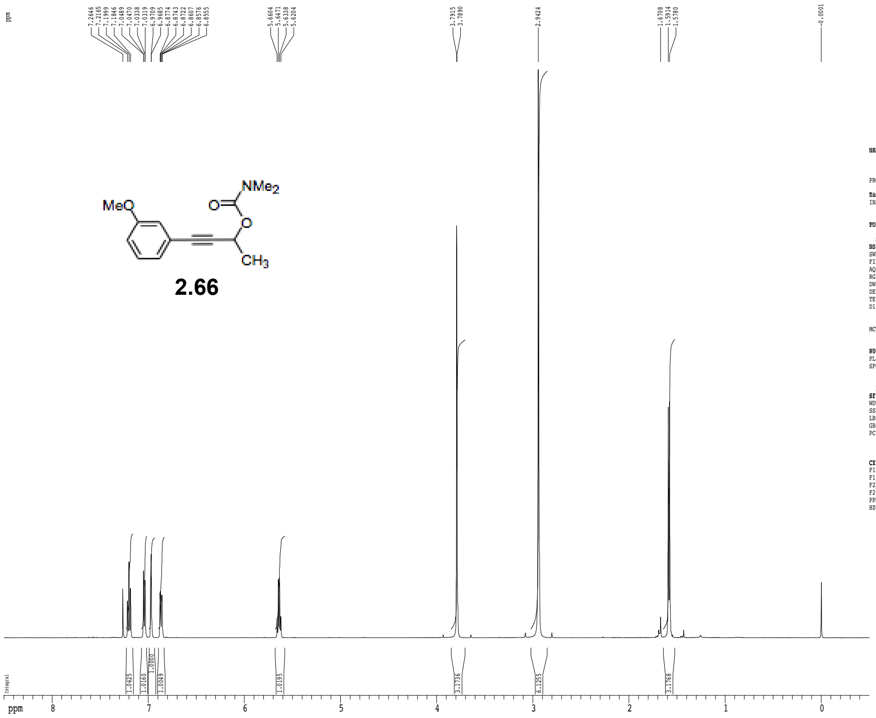
1H spectrum



2.66

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                       1

PROCNO
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                  32048
  SOLVENT             8CDCl3
NS                    2
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FIDRES                      0.250026 Hz
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RG                 5.7
DW               62.400 usec
DE                            6.00 usec
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            0.00000000 sec
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MCWRK

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  F2 - Processing parameters
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WDW                no
SSB                          0
LB                   0.00 Hz
GB
PC                 0
               4.00

  1D NMR plot parameters
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HZCM        197.45528 Hz/cm
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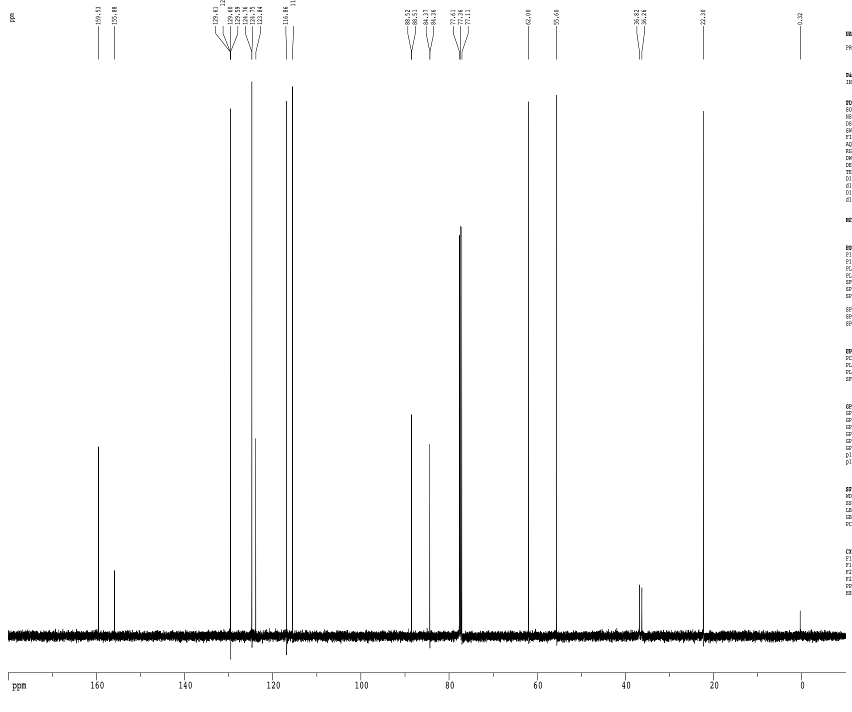
Z-restored spin-echo 13C spectrum with 1H decoupling



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PROCNO                1


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NS
DS
SWH                387
FIDRES        0.462388 Hz
AQ     30303.031 Hz
RG                    1.0813940 sec
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TE                298.0 K
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MCWRK       33.10 usec


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NUC1            16.55 usec      13C
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1  125.7942548 MHz
SP1         2.70 dB
SP2
                                                  2.70 dB
SPNAM1   Crp60,0.5,20.1
SPOFF1      0.00 Hz    SPNAM2      Crp60comp.4
SPOFF2             0.00 Hz


       ======== CHANNEL f2 ========
CPDPRG2          1H                waltz16
PCPD2        100.00 usec
PL2              1.60 dB
PL12            24.50 dB
SFO2  500.2225011 MHz


      ====== GRADIENT CHANNEL =====
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GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec


  F2 - Processing parameters
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WDW                no
SSB                 0
LB                   0.00 Hz
GB
PC                  0
              2.00

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CX                15.65 22.80 cm
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F1            22640.47 Hz
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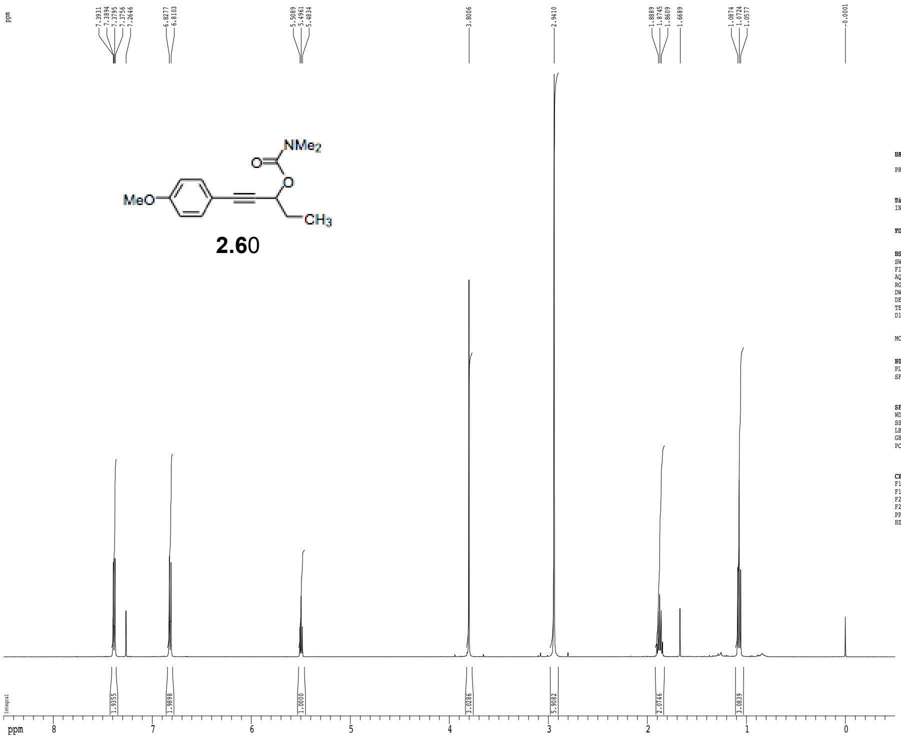
1H spectrum



2.60

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PROCNO                   1

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INSTRUM             cryo500

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                  32048
  SOLVENT               8CDCl3
NS                       2
SWH              8012.820 Hz
FIDRES                         0.250026 Hz
AQ            1.9998451 sec
RG                     5.7
DW                  62.400 usec
DE                               6.00 usec
TE                  298.0 K
D1            0.10000000 sec

     MCREST                    0.00000000 sec
MCWRK         0.01500000 sec

    ======== CHANNEL f1 ========
NUC1                                 1H
PL1                            7.50 usec
SFO1          500.2235069 MHz

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WDW                  no
SSB                    0
LB                      0.00 Hz
GB
PC                     0
                4.00

  1D NMR plot parameters
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F1P                 8.500 ppm
F1              4251.87 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM             0.39474 ppm/cm
HZCM          197.45528 Hz/cm
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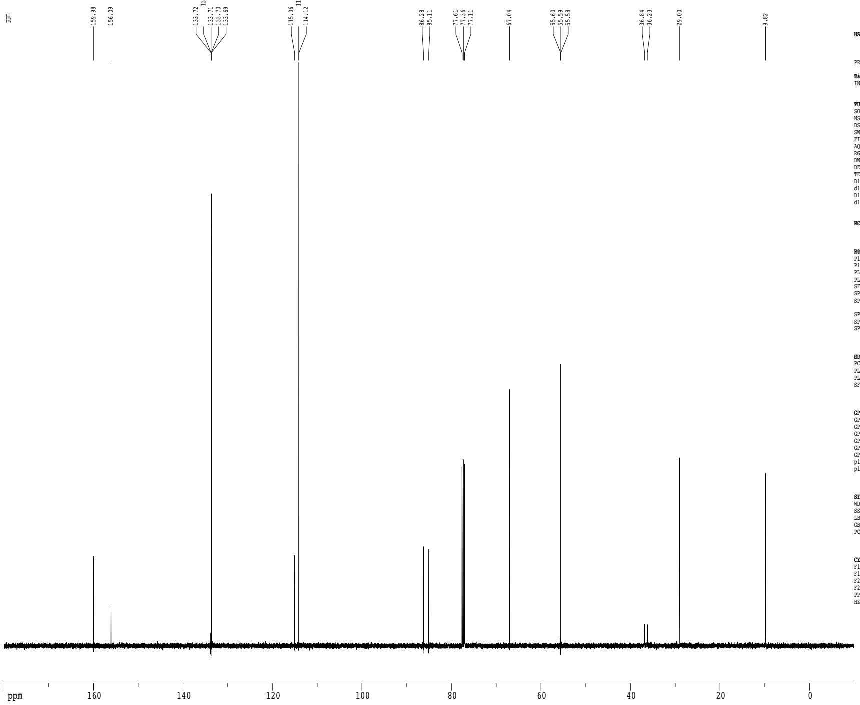
Z-restored spin-echo 13C spectrum with 1H decoupling



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                      1

PROCNO
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DS                      16
SWH           30303.031 Hz
FIDRES                     0.462388 Hz
AQ
RG                  1.0813940 sec
DW            4597.6
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TE                298.0 K
D1       0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
              0.00000000 sec
     MCREST                 0.01500000 sec
MCWRK         33.10 usec


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NUC1               16.55 usec      13C
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P12               2000.00 usec
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PL1                 -1.00 dB
SFO1        125.7942548 MHz
SP1                          2.70 dB
SP2
                                              2.70 dB
SPNAM1   Crp60,0.5,20.1
SPOFF1      0.00 Hz    SPNAM2      Crp60comp.4
SPOFF2              0.00 Hz

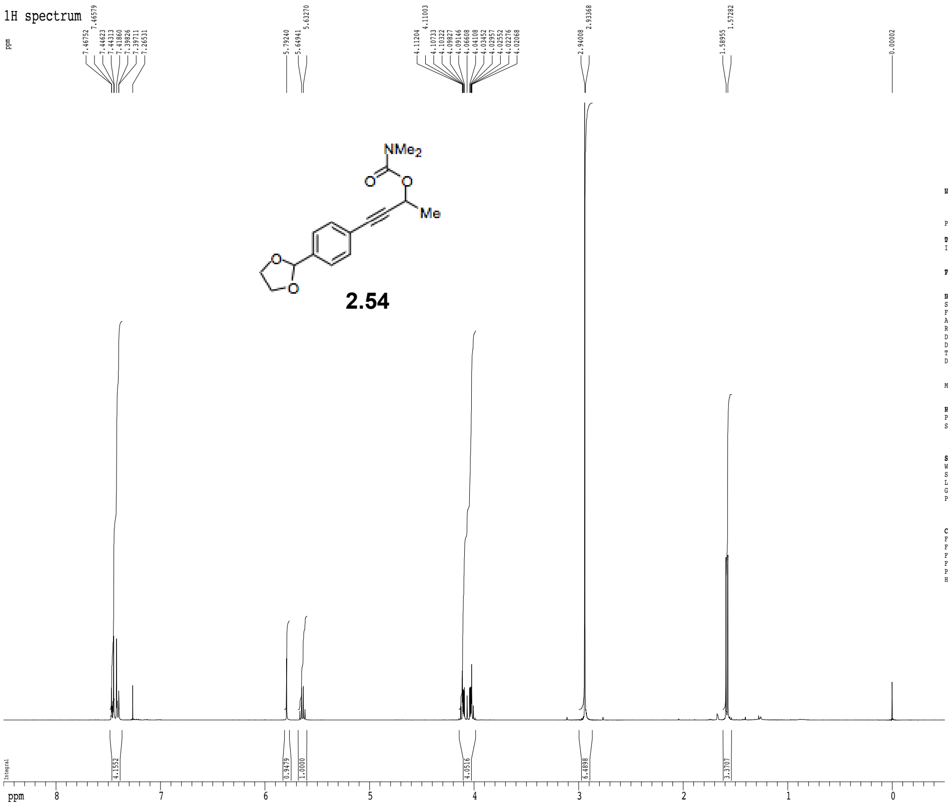

       ======== CHANNEL f2 ========
CPDPRG2          1H                 waltz16
PCPD2        100.00 usec
PL2               1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz


      ====== GRADIENT CHANNEL =====
GPNAM1          SINE.100            SINE.100
GPX1            0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1              30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec


  F2 - Processing parameters
SI          125.7803847 MHz 65536
WDW                  no
SSB                    0
LB                      0.00 Hz
GB
PC                     0
               2.00

  1D NMR plot parameters
CX                   15.65 22.80 cm
F1P             180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM             8.33333 ppm/cm
HZCM       1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
NAME     LEH-6-245-c1-f55  lhanna
EXPNO             1
PROCNO            1

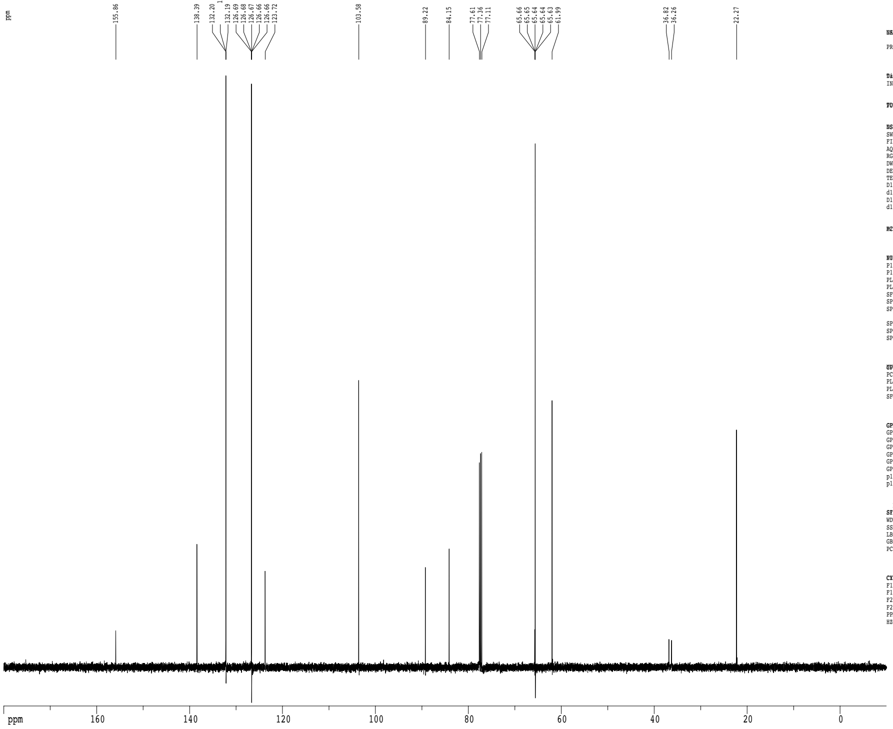
F2 - Acquisition Parameters
Date_            2014
Time               17.37
INSTRUM          drx400
PROBHD    5 mm QNP H/F/P
PULPROG            zg30
TD                25640
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.250010 Hz
AQ            1.9999700 sec
RG                  181
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1                0.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300192 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                15.00 cm
CY                22.80 cm
F1P               8.500 ppm
F1              3401.10 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.39474 ppm/cm
HZCM          157.94606 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
NAME     LEH-6-245-C13   lhanna
EXPNO             1
PROCNO            1

F2 - Acquisition Parameters
Date_            2014
Time               12.19
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG  SpinEchopg.prd
TD                65536
SOLVENT           CDCl3
NS                  148
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                  2050
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P11               16.55 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2   Crp60comp.4
SPOFF1             0.00 Hz
SPOFF2             0.00 Hz

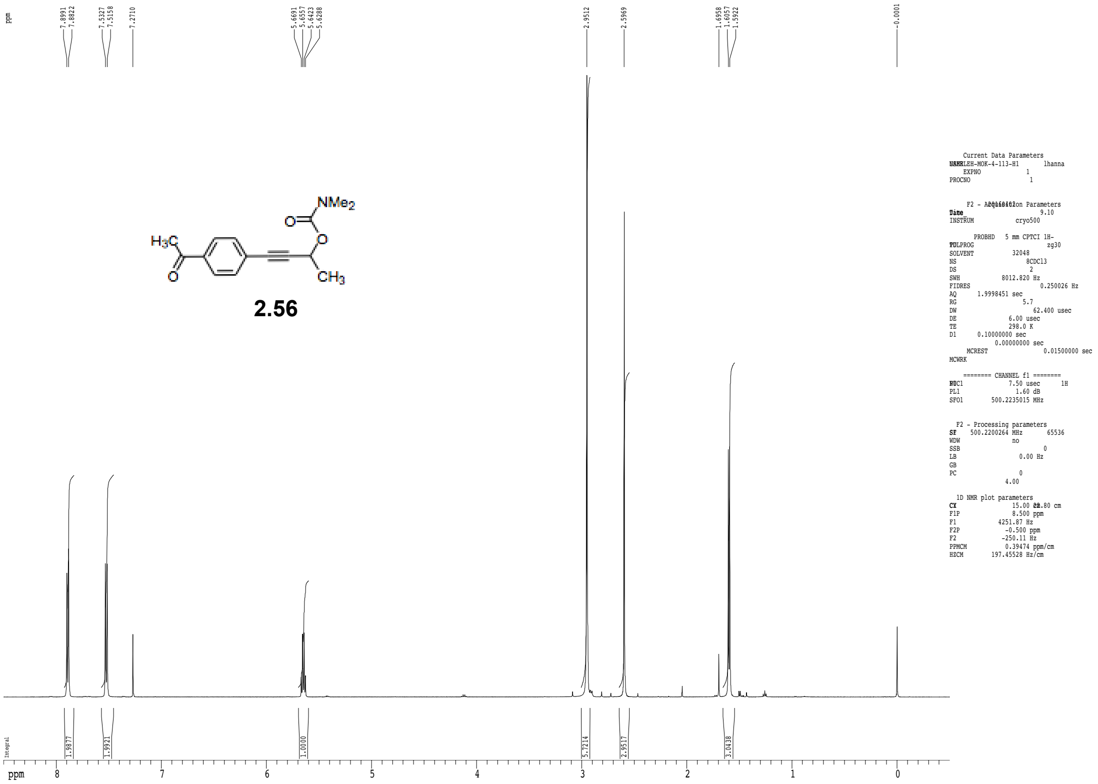
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1             0.00 %
GPX2             0.00 %
GPY1             0.00 %
GPY2             0.00 %
GPZ1            30.00 %
GPZ2            50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803857 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

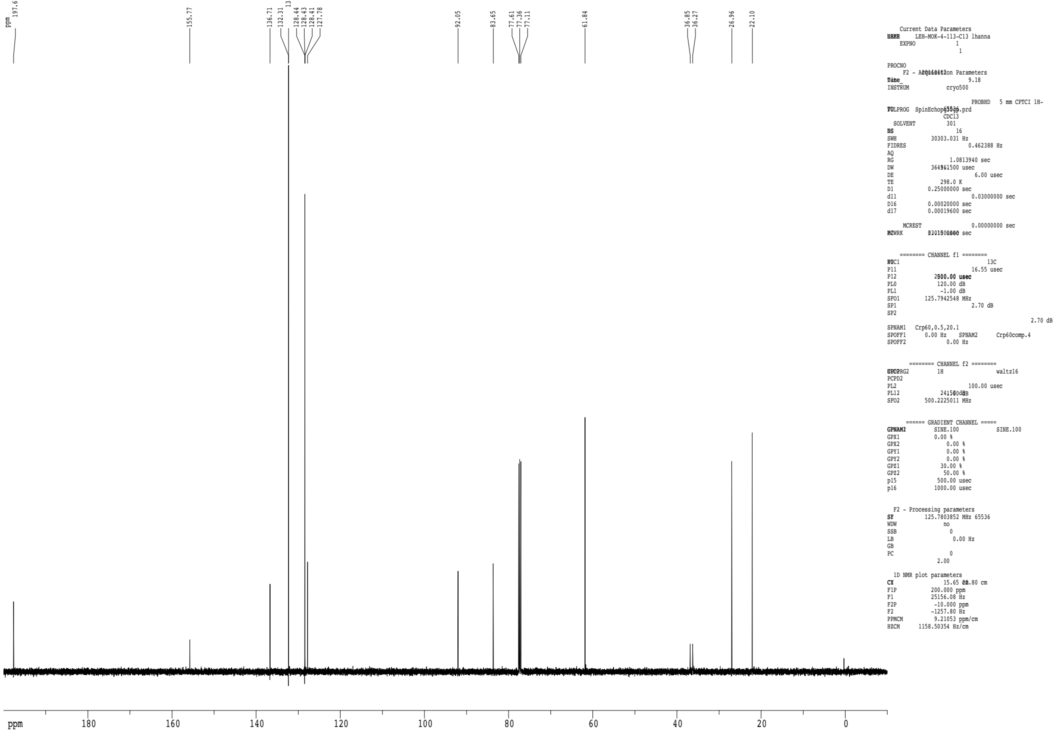
1D NMR plot parameters
CX                15.65 cm
CY                22.80 cm
F1P             180.000 ppm
F1             22640.47 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM           8.33333 ppm/cm
HZCM         1048.16992 Hz/cm
```

1H spectrum

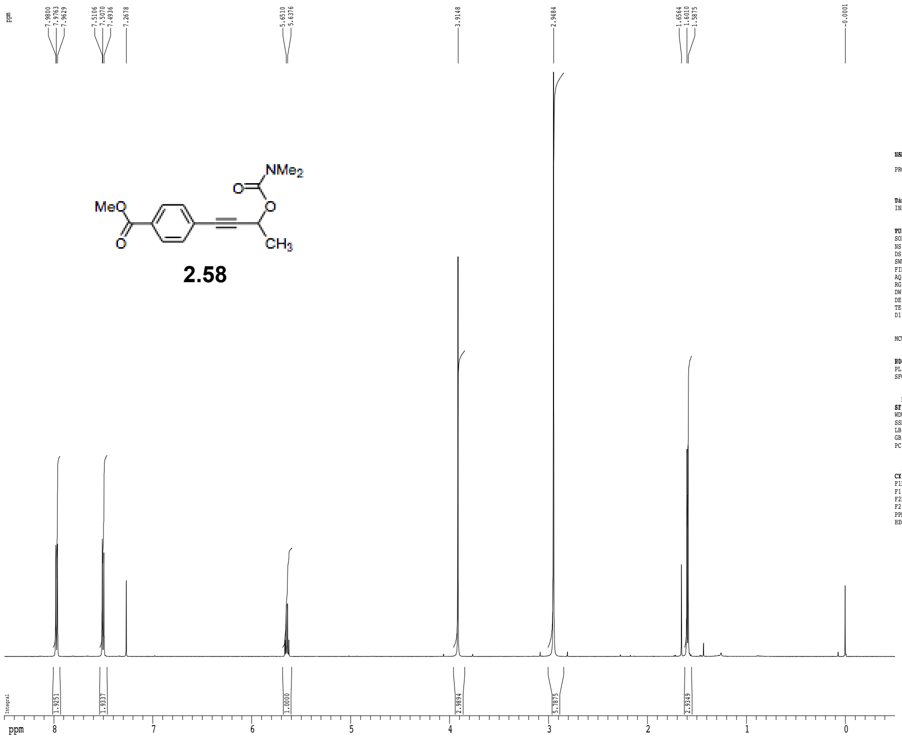


2.56

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



2.58

```
    Current Data Parameters
NAME     LEH-6-192-R-H1         USER lhanna
    EXPNO              1
PROCNO                 1


     F2 - Acquisition Parameters
Date_      20160404                Time 15.27
INSTRUM              cryo500

       PROBHD   5 mm CPTCI 1H-
PULPROG                          zg30
SOLVENT           32048
NS                         8CDCl3
DS                          2
SWH              8012.820 Hz
FIDRES                        0.250026 Hz
AQ             1.9998451 sec
RG                   5.7
DW                      62.400 usec
DE                   6.00 usec
TE                   298.0 K
D1       0.10000000 sec

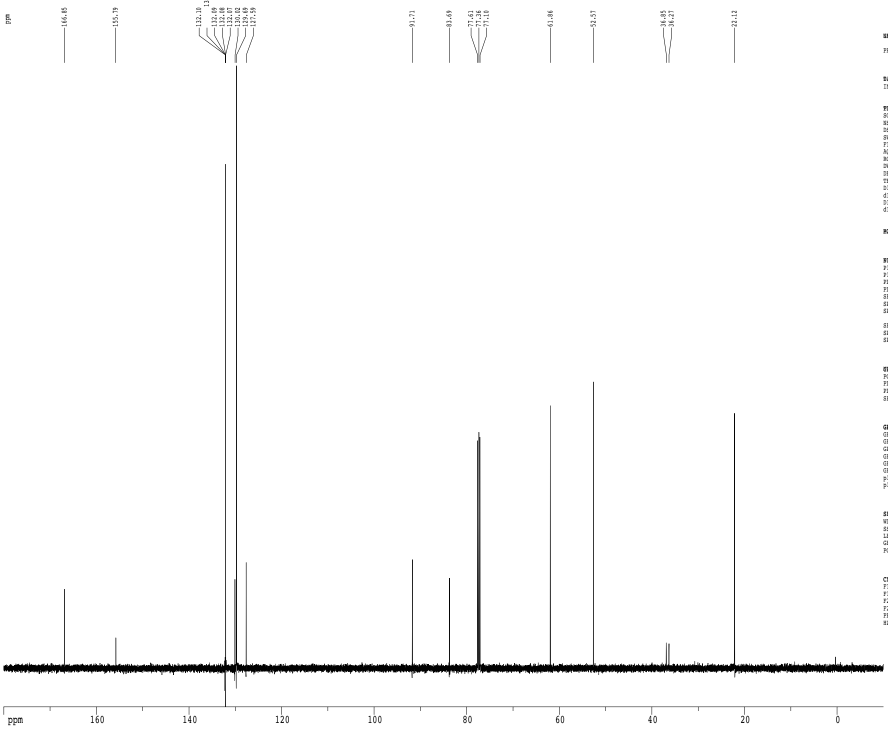
     MCREST                    0.00000000 sec
MCWRK          0.01500000 sec

    ======== CHANNEL f1 ========
NUC1 P1              7.50 usec       1H
PL1                    1.60 dB
SFO1          500.2235015 MHz


  F2 - Processing parameters
SI SF          500.2200274 MHz 65536
WDW                   no
SSB                     0
LB                       0.00 Hz
GB
PC                      0
                    4.00

  1D NMR plot parameters
CX                    15.00 22.80 cm
F1P                    8.500 ppm
F1                 4251.87 Hz
F2P                   -0.500 ppm
F2                   -250.11 Hz
PPMCM                 0.39474 ppm/cm
HZCM          197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     LEH-6-192-R-C13        USER lhanna
    EXPNO             1
PROCNO                 1


     F2 - Acquisition Parameters
Date_      20160404               Time 15.31
INSTRUM              cryo500

                           PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd   65536
SOLVENT             CDCl3
NS                   306
DS                      16
SWH            30303.031 Hz
FIDRES                       0.462388 Hz
AQ
RG                    1.0813940 sec
DW             7298.2
DE                  6.00 usec       16.500 usec
TE                  298.0 K
D1       0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec

     MCREST                    0.00000000 sec
MCWRK HZ      0.01500000 sec  


    ======== CHANNEL f1 ========
NUC1 P1             16.55 usec      13C
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1        125.7942548 MHz
SP1                          2.70 dB
SP2
                                             2.70 dB
SPNAM1   Crp60,0.5,20.1
SPOFF1      0.00 Hz    SPNAM2      Crp60comp.4
SPOFF2             0.00 Hz

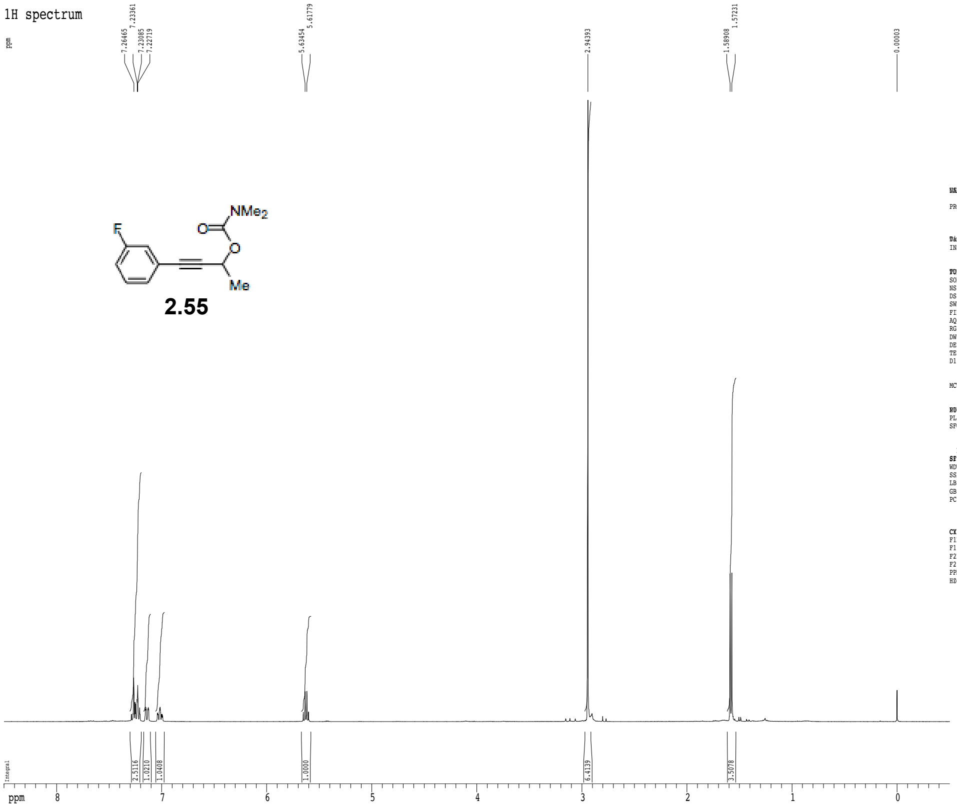

      ======== CHANNEL f2 ========
CPDPRG2 NUC2          1H                  waltz16
PCPD2        100.00 usec
PL2               1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz


     ====== GRADIENT CHANNEL =====
GPNAM1 GPNAM2         SINE.100              SINE.100
GPX1           0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1              30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec


  F2 - Processing parameters
SI SF          125.7803843 MHz 65536
WDW                 no
SSB                   0
LB                     0.00 Hz
GB
PC                    0
                 2.00

  1D NMR plot parameters
CX                  15.65 22.80 cm
F1P               180.000 ppm
F1                22640.47 Hz
F2P                -10.000 ppm
F2                -1257.80 Hz
PPMCM              8.33333 ppm/cm
HZCM        1048.16992 Hz/cm
```

1H spectrum



2.55

```
    Current Data Parameters
NAME     LEH-6-244-crude        lhanna
    EXPNO               1
PROCNO                  1

     F2 - Acquisition Parameters
Date_        20160506          14.56
INSTRUM               drx400

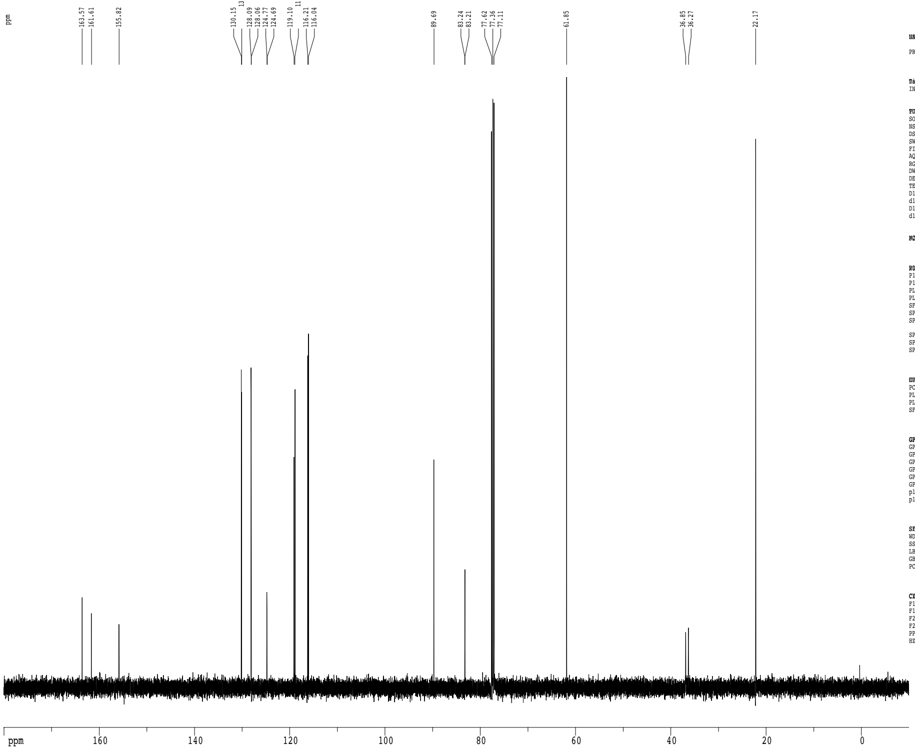
       PROBHD   5 mm QNP H/F/P
PULPROG                        zg30
SOLVENT             25640
NS                        CDCl3
DS
SWH                   8
FIDRES            0.250210 Hz
AQ      6410.256 Hz
RG                    1.9999700 sec
DW              228.1
DE                 4.50 usec      78.000 usec
TE                 298.0 K
D1      0.10000000 sec
      0.00000000 sec
     MCREST  0.01500000 sec
MCWRK

    ======== CHANNEL f1 ========
NUC1              12.00 usec       1H
PL1                   0.00 dB
SFO1 400.1328009 MHz


  F2 - Processing parameters
SI    400.1300195 MHz       65536
WDW                   no
SSB                     0
LB                        0.00 Hz
GB
PC                      0
                  2.00

  1D NMR plot parameters
CX                    15.00 22.80 cm
F1P                   8.500 ppm
F1              3401.10 Hz
F2P                  -0.500 ppm
F2                 -200.07 Hz
PPMCM               0.39474 ppm/cm
HZCM         157.94606 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     LEH-6-244-C13          lhanna
    EXPNO              1
PROCNO                  1


     F2 - Acquisition Parameters
Date_        20160510           12.25
INSTRUM               cryo500

                           PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd   65536
SOLVENT             CDCl3
NS
DS
SWH                 228
FIDRES         0.462388 Hz
AQ     30303.030 Hz sec
RG                      2048
DW                           16.500 usec
DE                 6.00 usec
TE                 298.0 K
D1      0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
      0.00000000 sec
     MCREST  0.01500000 sec
MCWRK        33.10 usec


    ======== CHANNEL f1 ========
NUC1              16.55 usec      13C
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1  125.7942548 MHz
SP1         2.70 dB
SP2
                                               2.70 dB
SPNAM1   Crp60,0.5,20.1
SPOFF1      0.00 Hz    SPNAM2      Crp60comp.4
SPOFF2              0.00 Hz

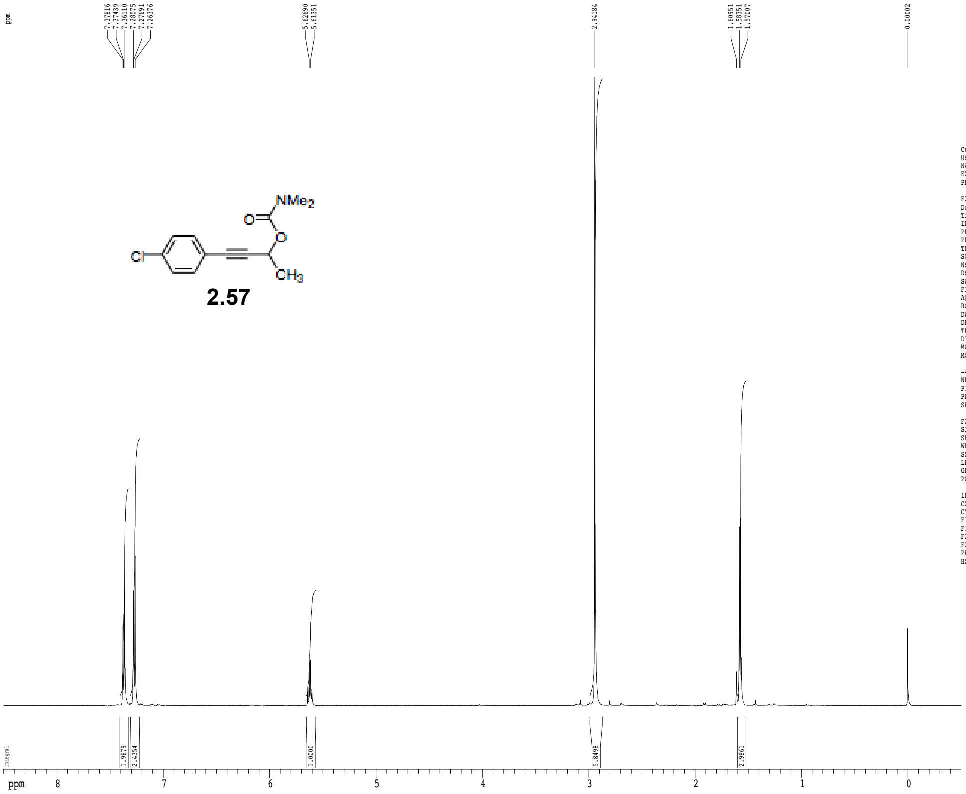

       ======== CHANNEL f2 ========
CPDPRG2          1H                  waltz16
PCPD2        100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2  500.2225011 MHz


      ====== GRADIENT CHANNEL =====
GPNAM1         SINE.100             SINE.100
GPX1           0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1             30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec


  F2 - Processing parameters
SI    125.7803833 MHz       65536
WDW                  no
SSB                    0
LB                       0.00 Hz
GB
PC                     0
                 2.00

  1D NMR plot parameters
CX                   15.65 22.80 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P               -10.000 ppm
F2               -1257.80 Hz
PPMCM             8.33333 ppm/cm
HZCM      1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER            lhanna
NAME     LEH-MOK-4-141-H1
EXPNO                1
PROCNO               1

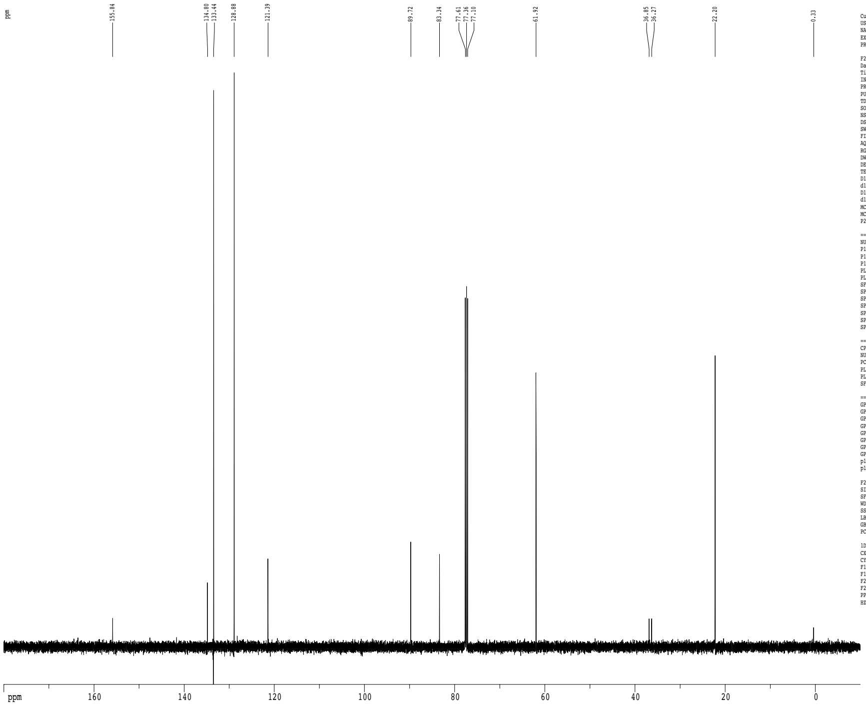
F2 - Acquisition Parameters
Date_         20160402
Time              9.59
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               32048
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.250026 Hz
AQ           1.9998451 sec
RG                   8
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                7.50 usec
PL1               1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI               65536
SF         500.2200296 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                4.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              8.500 ppm
F1             4251.87 Hz
F2P             -0.500 ppm
F2             -250.11 Hz
PPMCM          0.39474 ppm/cm
HZCM         197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER            lhanna
NAME     LEH-MOK-4-141-C13
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20160402
Time             10.06
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT          CDCl3
NS                 359
DS                  16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG              7298.2
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1               13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1            0.00 Hz
SPOFF2            0.00 Hz

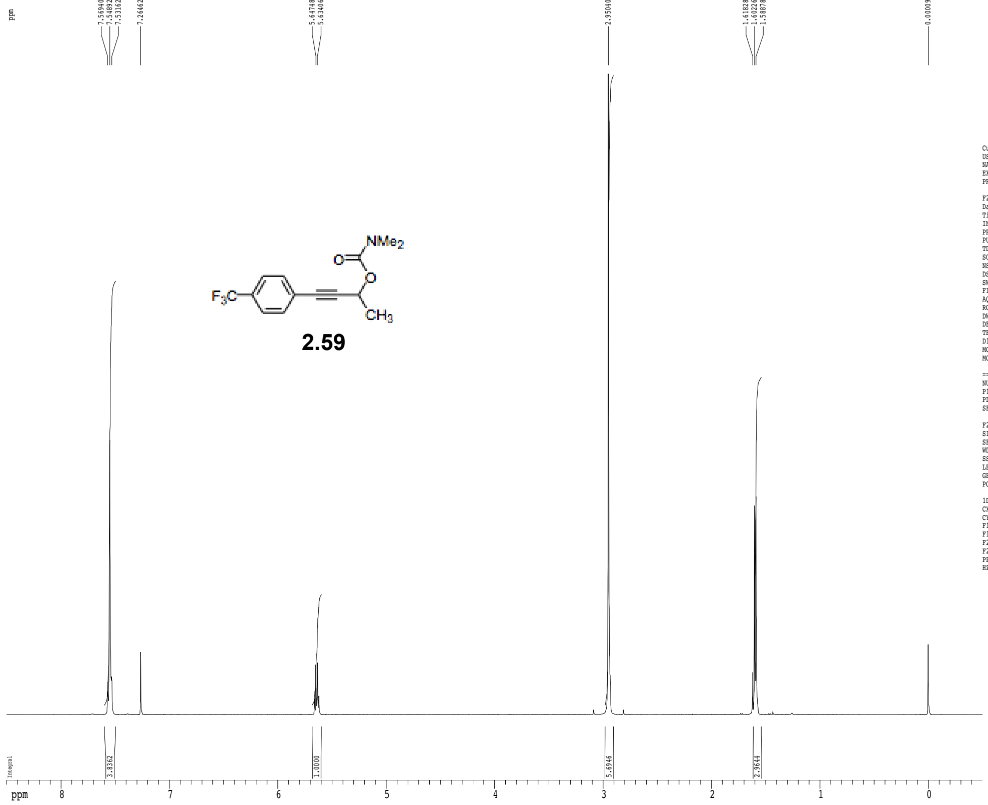
======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI               65536
SF         125.7803838 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            180.000 ppm
F1            22640.47 Hz
F2P            -10.000 ppm
F2            -1257.80 Hz
PPMCM          8.33333 ppm/cm
HZCM        1048.16992 Hz/cm
```

1H spectrum



2.59

```
Current Data Parameters
USER              lhanna
NAME     LEH-MOK-4-112-H1
EXPNO                  1
PROCNO                 1

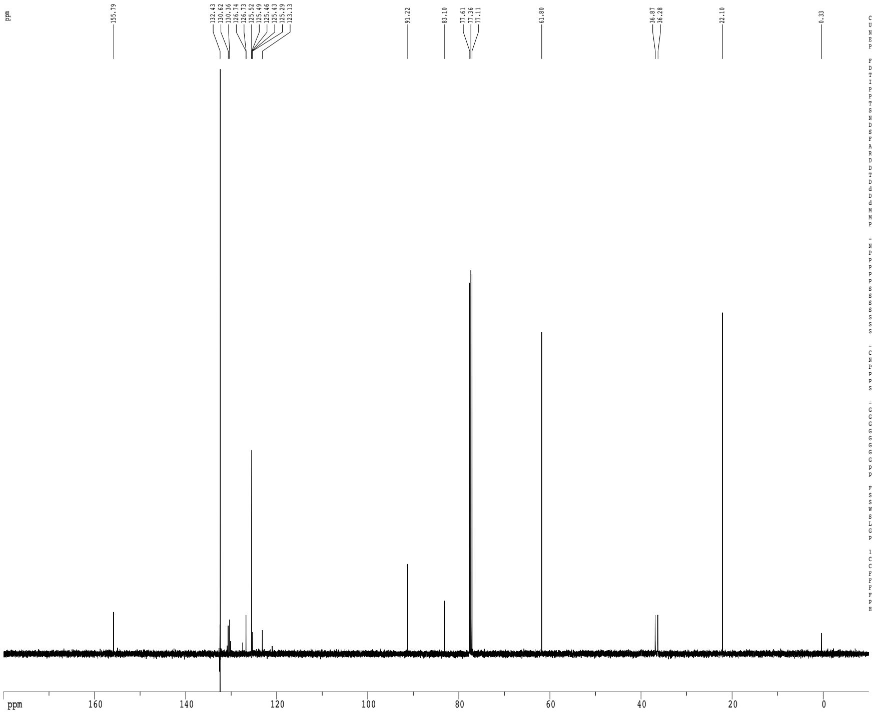
F2 - Acquisition Parameters
Date_           20160402
Time                9.30
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200294 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               4251.87 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              lhanna
NAME     LEH-MOK-4-112-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160402
Time                9.34
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

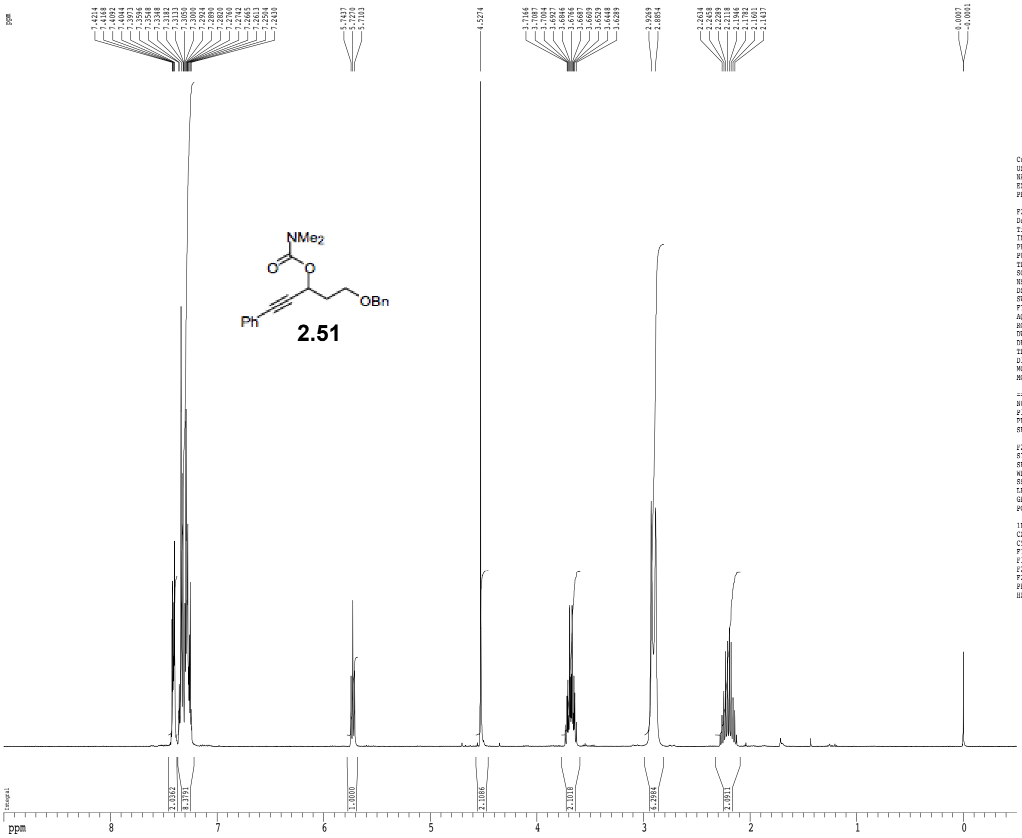
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803829 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER              mkonev
NAME      MOK-IV-151hchar
EXPNO                  1
PROCNO                 1

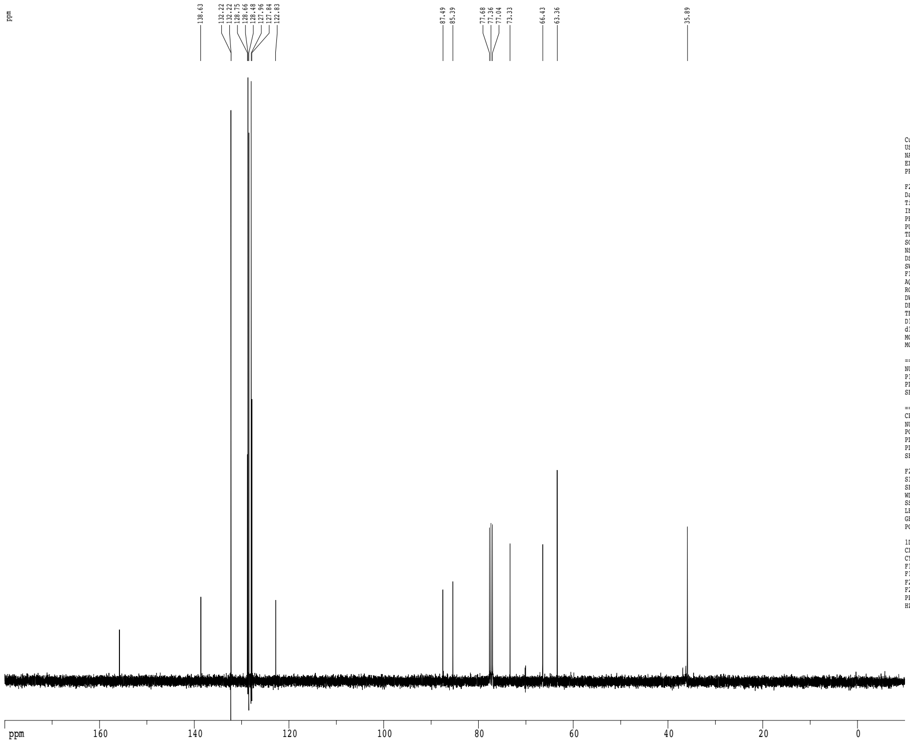
F2 - Acquisition Parameters
Date_           20160408
Time                9.18
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 51280
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.125005 Hz
AQ             3.9998901 sec
RG                   114
DW                78.000 usec
DE                  4.50 usec
TE                 298.1 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300252 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME      MOK-IV-151cchar
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160408
Time                9.20
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   392
DS                     4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ             1.3566452 sec
RG                9195.2
DW                20.700 usec
DE                 20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

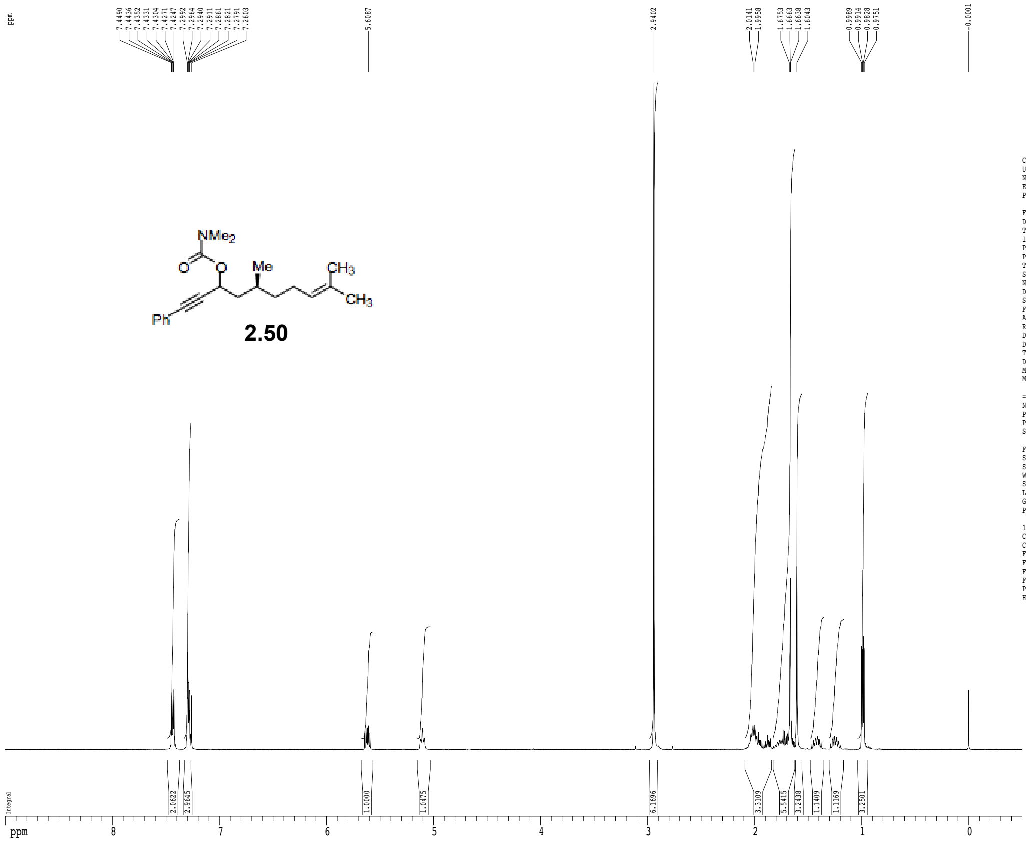
======== CHANNEL f1 ========
NUC1                 13C
P1                  7.75 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2           mlev16
NUC2                  1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               17.70 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127423 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              180.000 ppm
F1              18110.29 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM            8.33333 ppm/cm
HZCM           838.43951 Hz/cm
```

1H spectrum



2.50

```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-149hchar
EXPNO                  1
PROCNO                 1

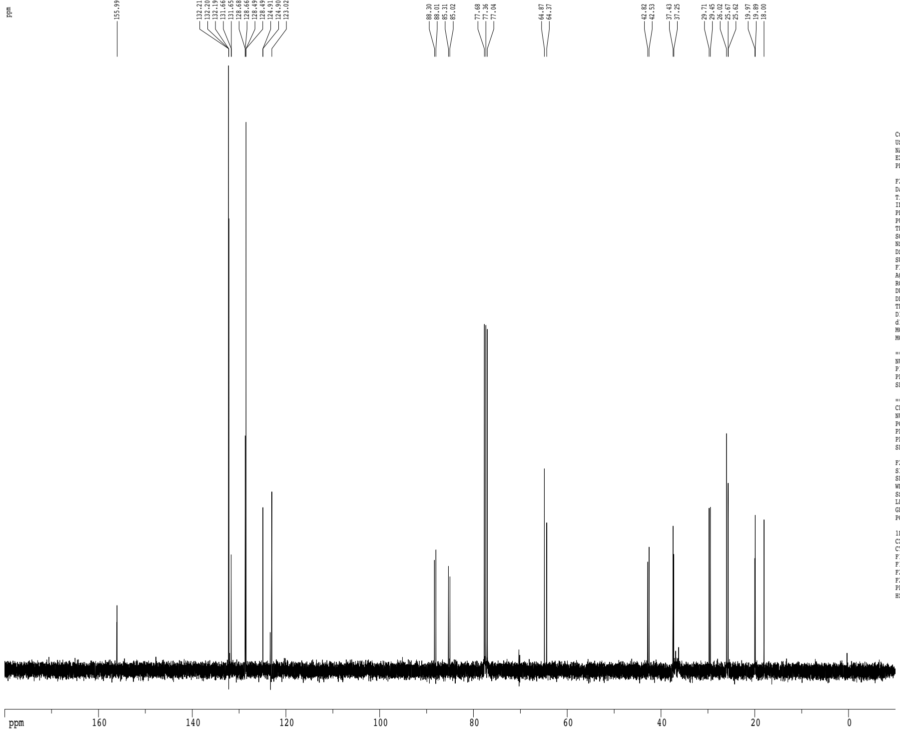
F2 - Acquisition Parameters
Date_          20160408
Time               9.02
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                51280
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.125005 Hz
AQ            3.9998901 sec
RG                 90.5
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1                0.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300213 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-149cchar
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20160408
Time               9.05
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  504
DS                    4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ            1.3566452 sec
RG               9195.2
DW               20.700 usec
DE                20.39 usec
TE                298.0 K
D1           0.10000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

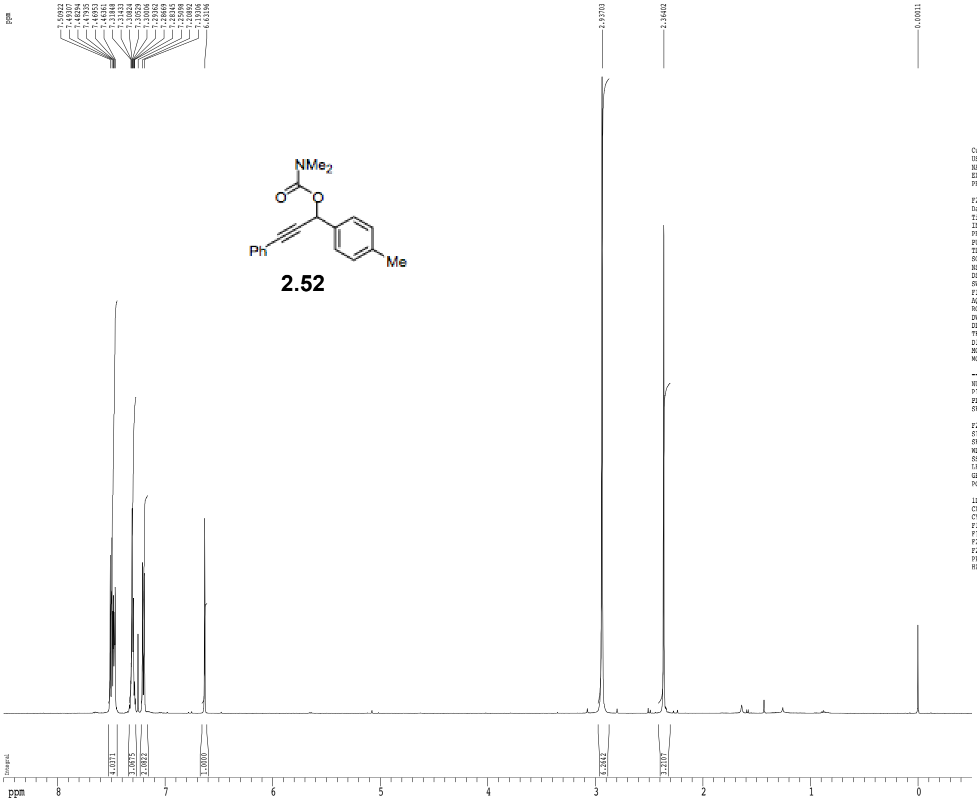
======== CHANNEL f1 ========
NUC1                13C
P1                 7.75 usec
PL1               -3.00 dB
SFO1        100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          mlev16
NUC2                 1H
PCPD2             90.00 usec
PL2                0.00 dB
PL12              17.70 dB
SFO2        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          100.6127401 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.50 cm
F1P             180.000 ppm
F1             18110.29 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz
PPMCM           8.33333 ppm/cm
HZCM          838.43951 Hz/cm
```

1H spectrum



2.52

```
Current Data Parameters
USER             mkonev
NAME      MOK-IV-123hchar
EXPNO                 1
PROCNO                1

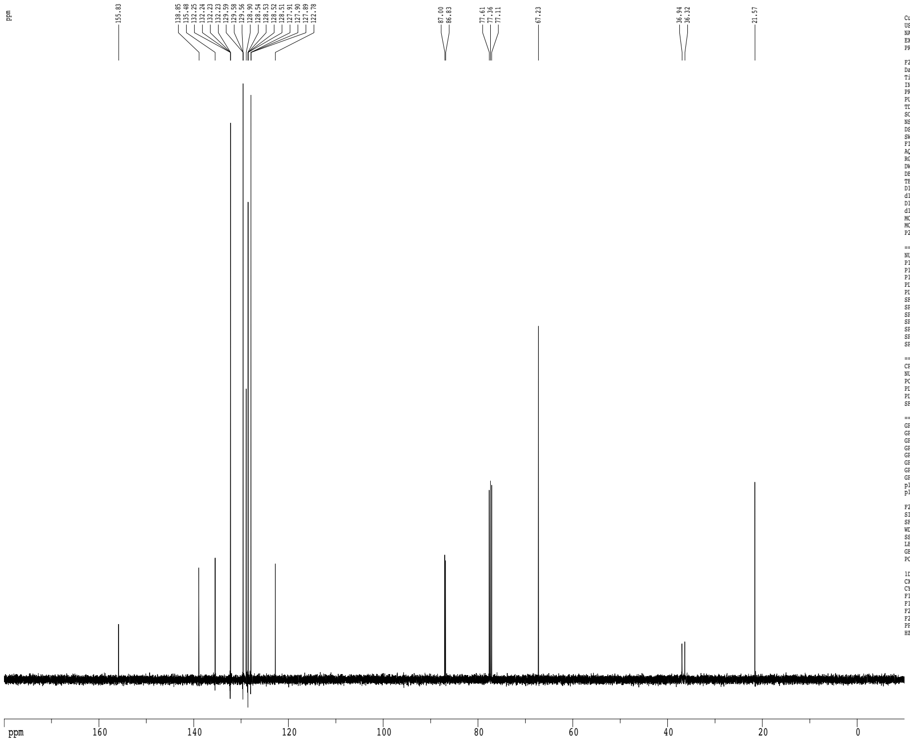
F2 - Acquisition Parameters
Date_          20160517
Time              10.49
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9998451 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200357 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               8.500 ppm
F1              4251.87 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.39474 ppm/cm
HZCM          197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER             mkonev
NAME      MOK-IV-123cchar
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160517
Time              10.51
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  152
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               5792.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1             0.00 Hz
SPOFF2             0.00 Hz

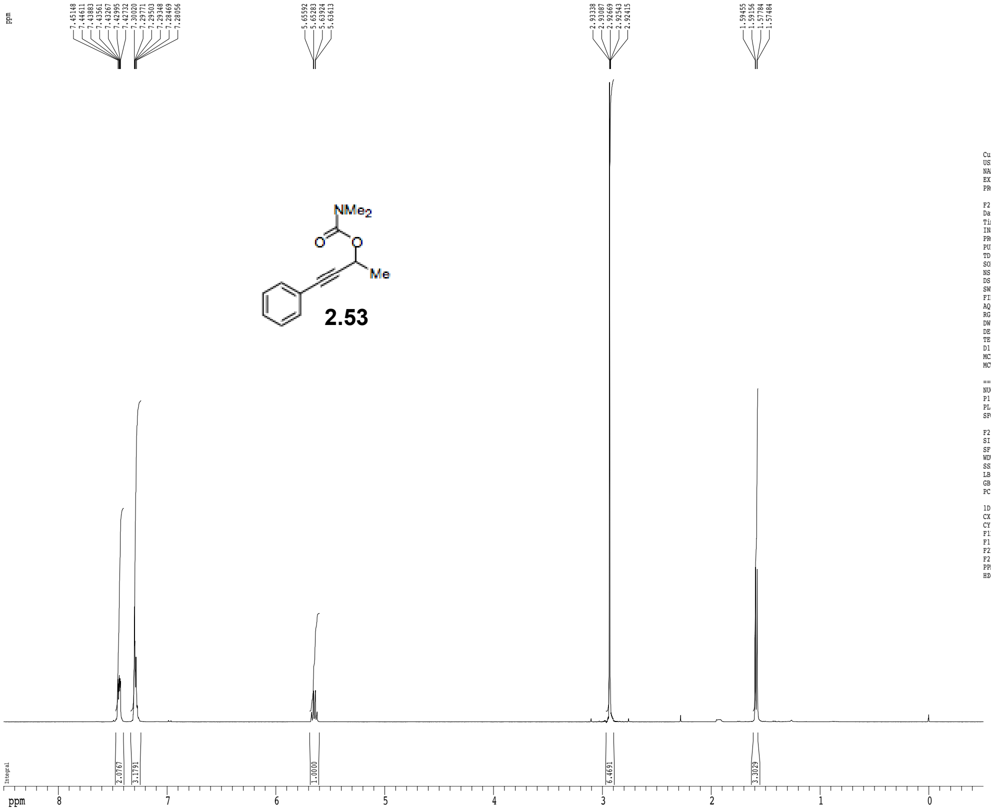
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803866 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             180.000 ppm
F1             22640.47 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM           8.33333 ppm/cm
HZCM         1048.16992 Hz/cm
```

1H spectrum



2.53

```
Current Data Parameters
USER              lhanna
NAME        LEH-6-213-c1-f
EXPNO                  1
PROCNO                 1

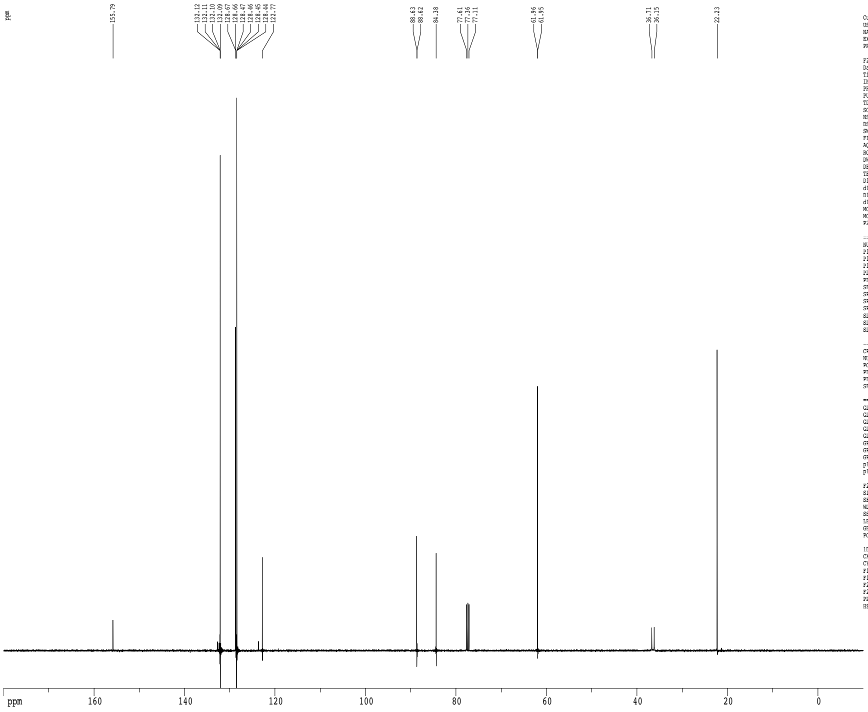
F2 - Acquisition Parameters
Date_           20160415
Time               12.34
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 25640
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.250010 Hz
AQ             1.9999700 sec
RG                  71.8
DW                78.000 usec
DE                  4.50 usec
TE                 297.9 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300166 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               3401.10 Hz
F2P               -0.500 ppm
F2               -200.07 Hz
PPMCM            0.39474 ppm/cm
HZCM           157.94606 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              lhanna
NAME         LEH-6-213-c13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160419
Time                9.34
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   141
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

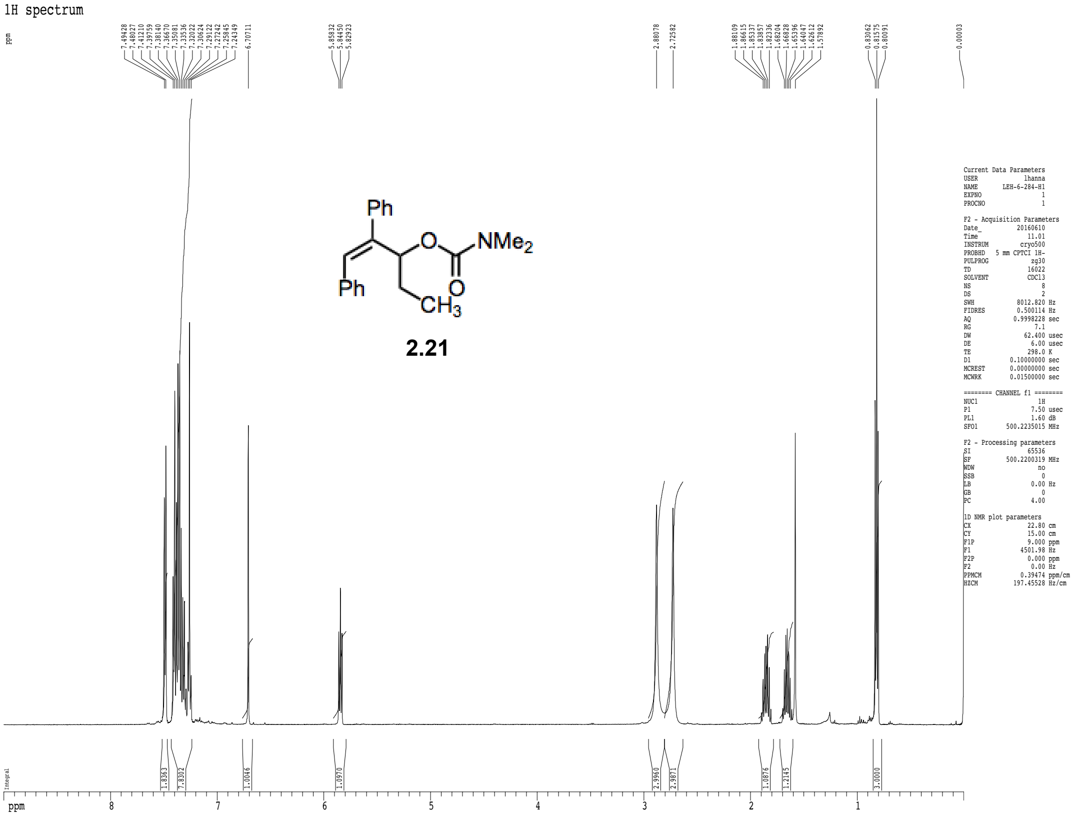
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

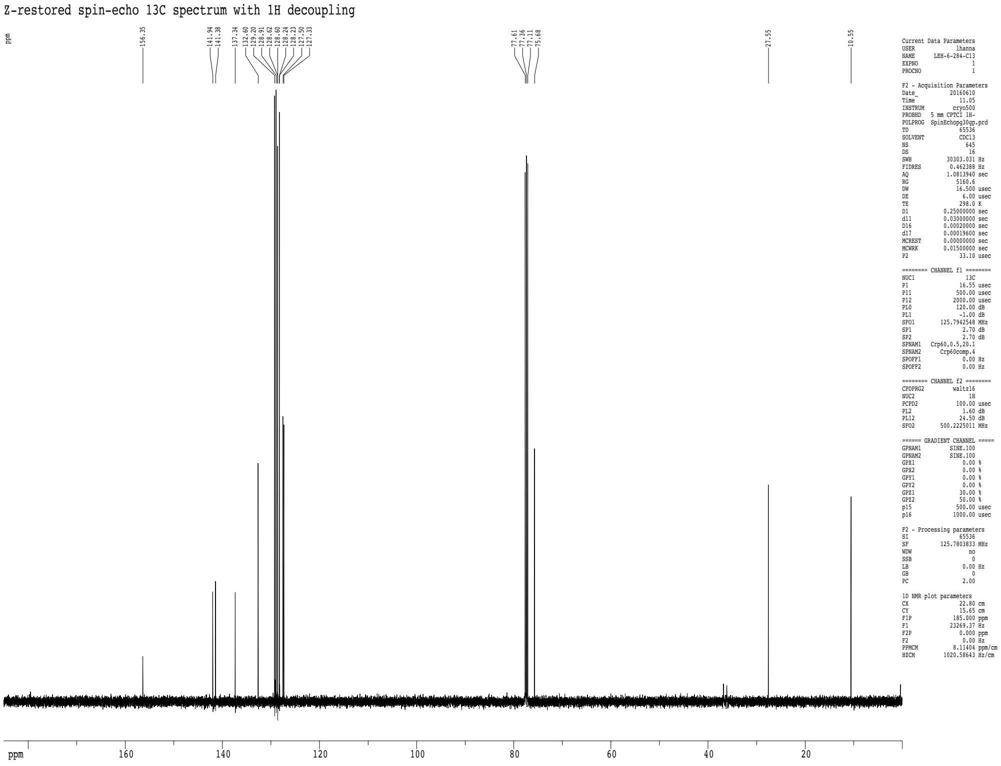
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

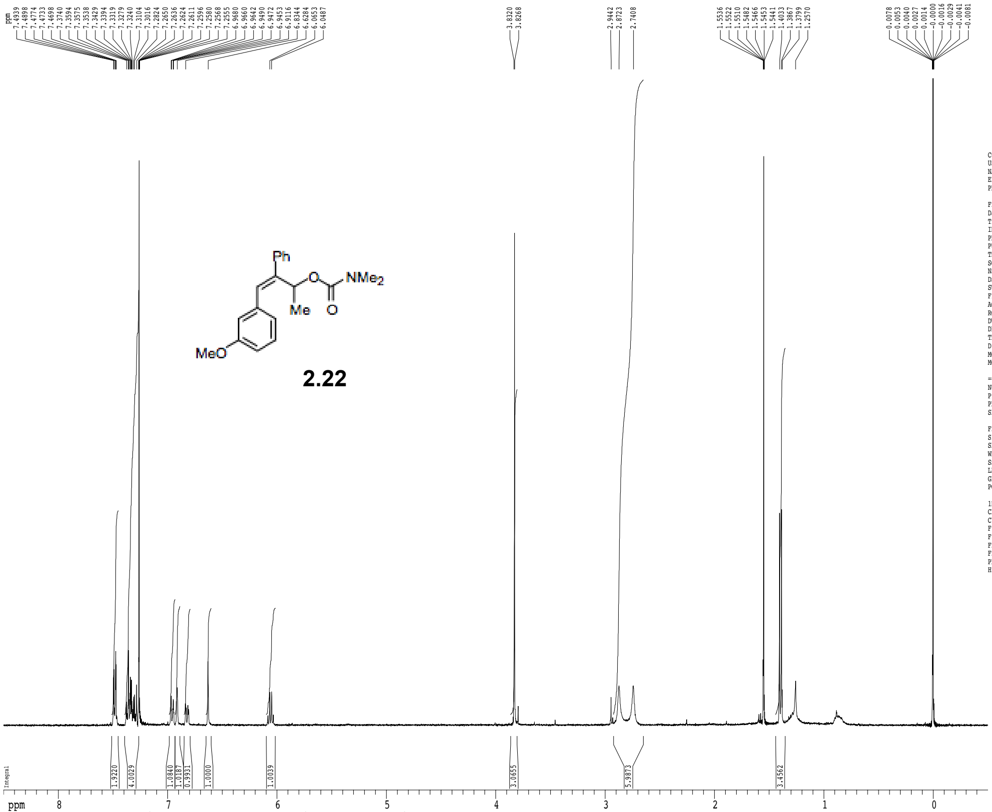
F2 - Processing parameters
SI                 65536
SF           125.7803949 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.17004 Hz/cm
```


1H spectrum


Z-restored spin-echo 13C spectrum with 1H decoupling

1H spectrum



```
Current Data Parameters
USER                lhanna
NAME     LEH-6-222-c1-f-16
EXPNO                    1
PROCNO                   1

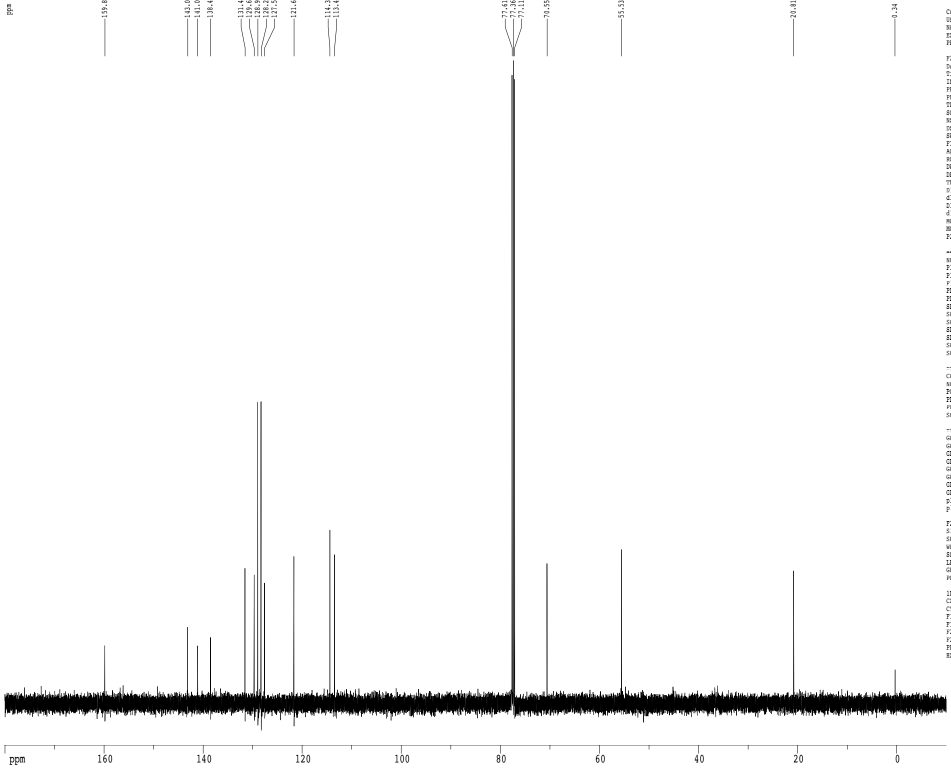
F2 - Acquisition Parameters
Date_             20160429
Time                 13.27
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG               zg30
TD                   25640
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               6410.256 Hz
FIDRES            0.250010 Hz
AQ               1.9999700 sec
RG                  1149.4
DW                  78.000 usec
DE                    4.50 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                   0.00 dB
SFO1           400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300213 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  8.500 ppm
F1                 3401.11 Hz
F2P                 -0.500 ppm
F2                 -200.07 Hz
PPMCM              0.39474 ppm/cm
HZCM             157.94608 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER                mkonev
NAME         LEH-6-222cchar
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160430
Time                 17.50
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     296
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813940 sec
RG                  2580.3
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

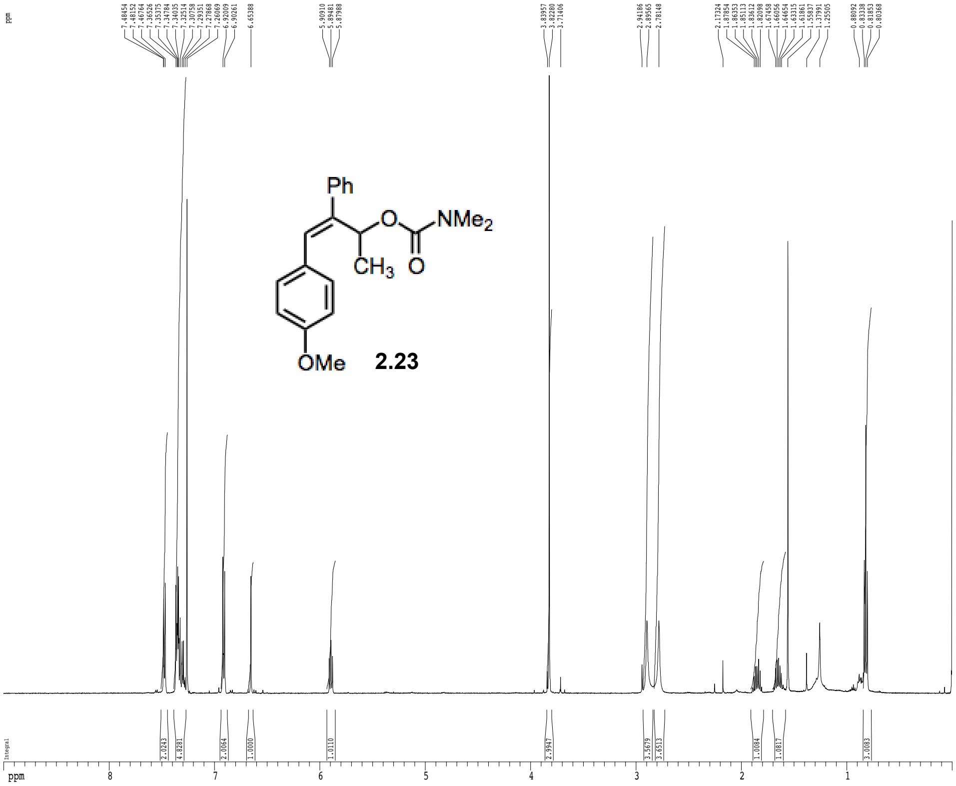
======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   2.70 dB
SP2                   2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1                0.00 Hz
SPOFF2                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.50 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7803829 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                180.000 ppm
F1                22640.47 Hz
F2P                -10.000 ppm
F2                -1257.80 Hz
PPMCM              8.33333 ppm/cm
HZCM            1048.16992 Hz/cm
```



1H spectrum

2.23

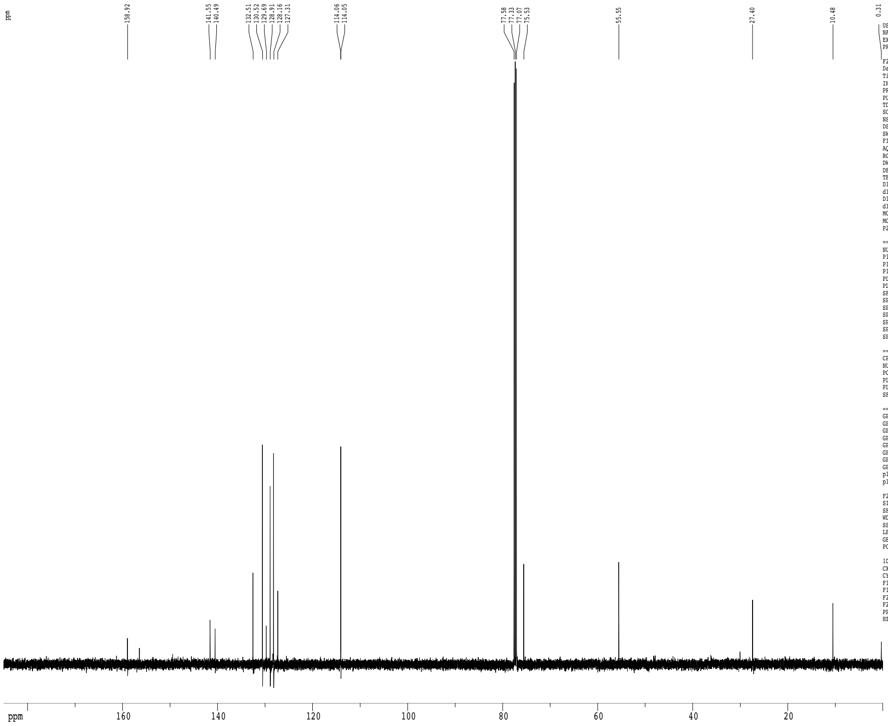
```
Current Data Parameters
USER              lhanna
NAME     LEH-6-210-re-H1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160608
Time               12.53
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200309 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```



Z-restored spin-echo 13C spectrum with 1H decoupling

```
USER              lhanna
NAME    LEH-6-210-re-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160608
Time               13.05
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

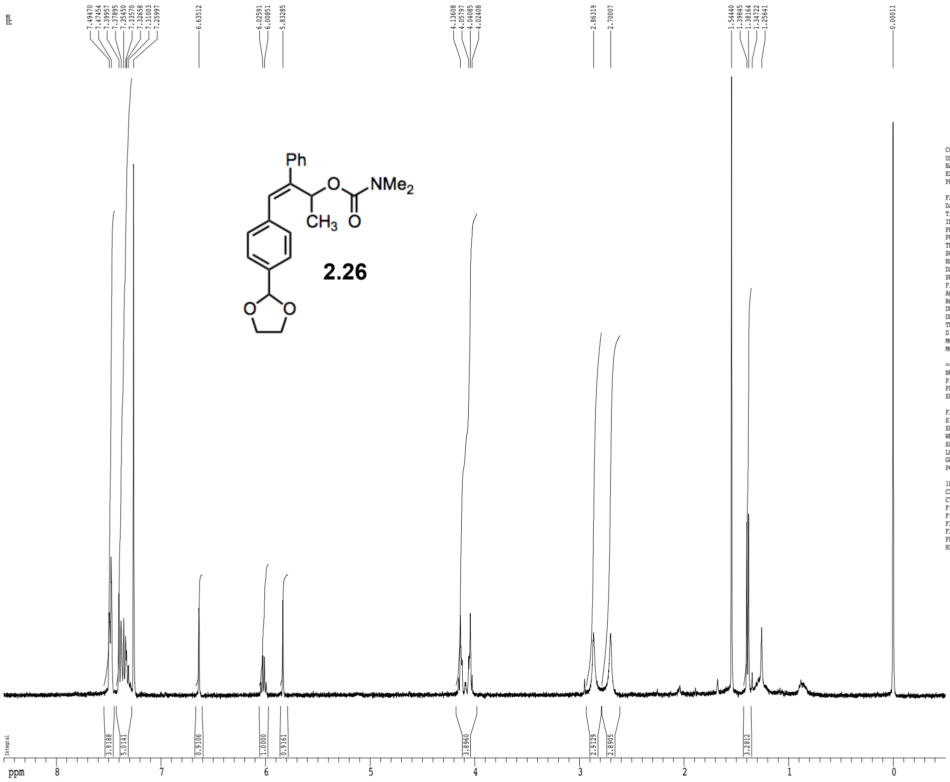
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803866 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              185.000 ppm
F1              23269.37 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            8.11404 ppm/cm
HZCM          1020.58649 Hz/cm
```

1H spectrum



2.26

```
Current Data Parameters
USER              lhanna
NAME     LEH-6-255-c1-fb50
EXPNO                  1
PROCNO                 1

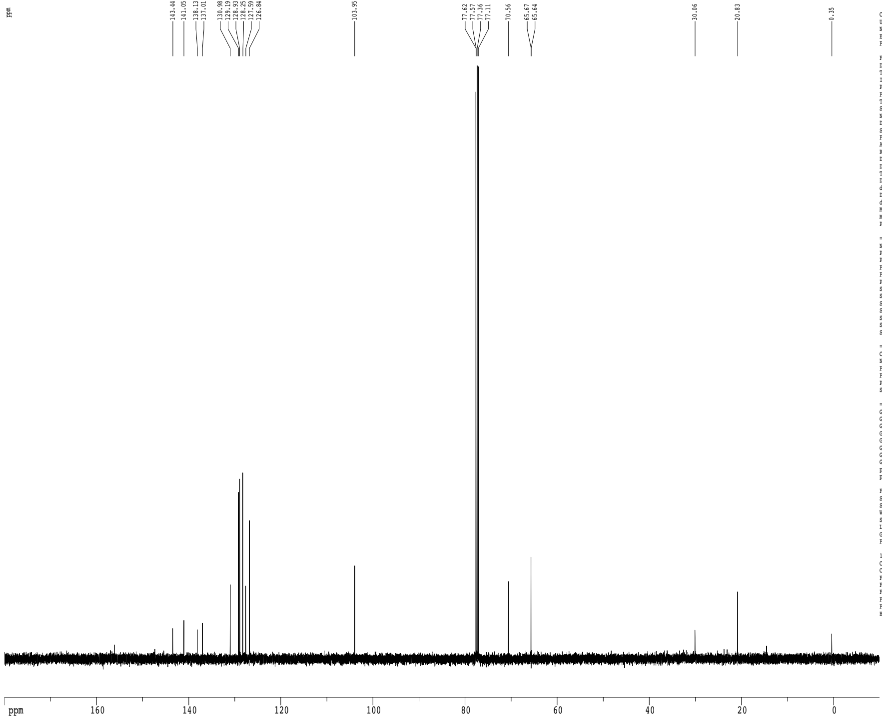
F2 - Acquisition Parameters
Date_           20160520
Time               13.44
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 25640
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.250010 Hz
AQ             1.9999700 sec
RG                1149.4
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300214 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               3401.11 Hz
F2P               -0.500 ppm
F2               -200.07 Hz
PPMCM            0.39474 ppm/cm
HZCM           157.94608 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              lhanna
NAME         LEH-6-255-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160520
Time               16.44
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                2896.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

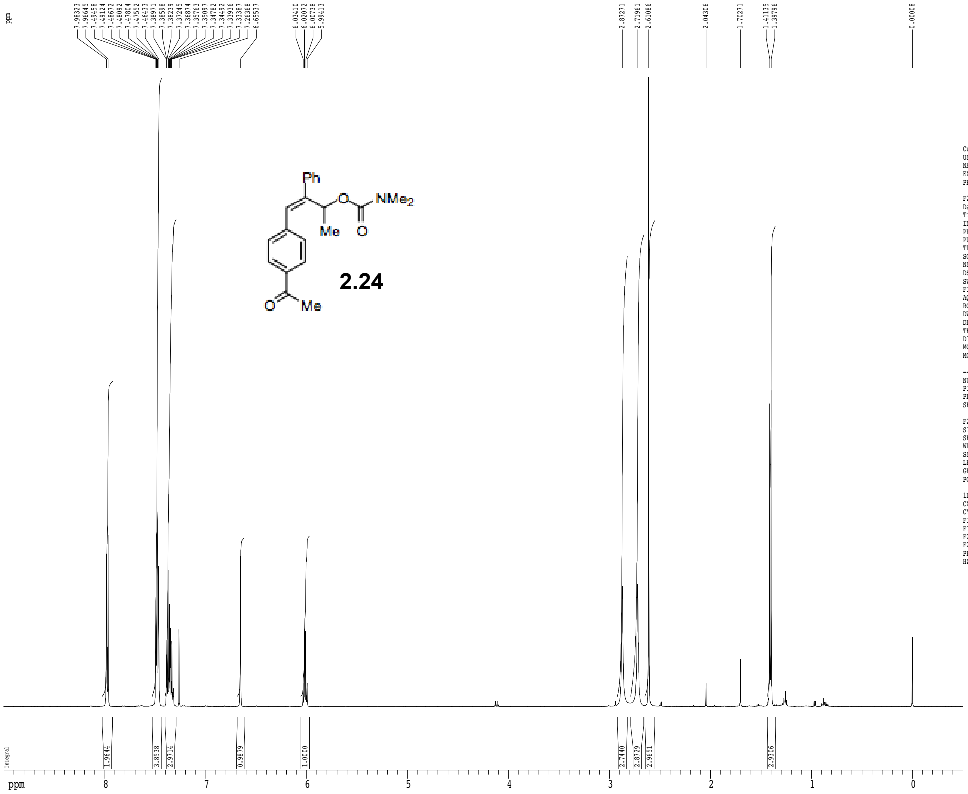
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803824 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-158hchar2
EXPNO                  1
PROCNO                 1

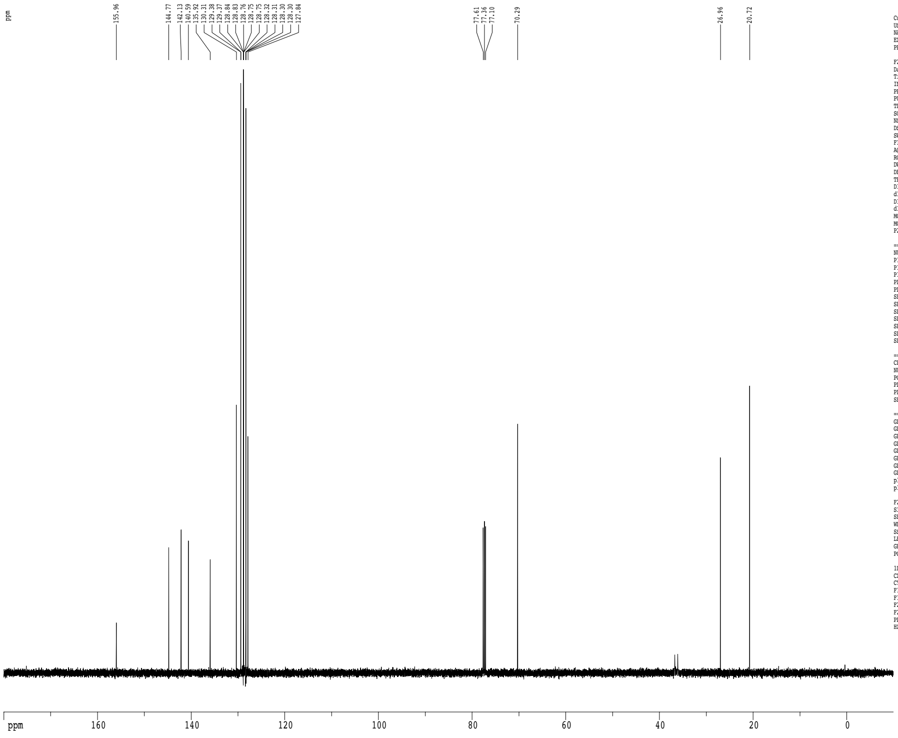
F2 - Acquisition Parameters
Date_           20160413
Time               16.12
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                     9
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200297 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-158cchar2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160413
Time               16.16
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG               10321.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

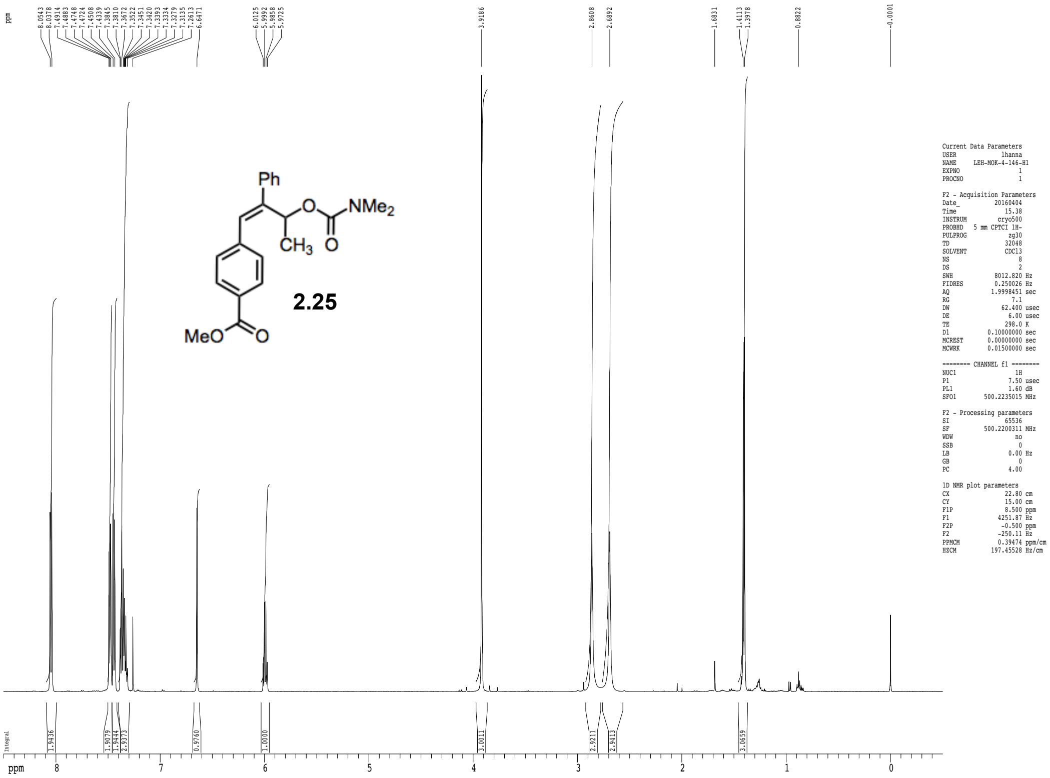
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

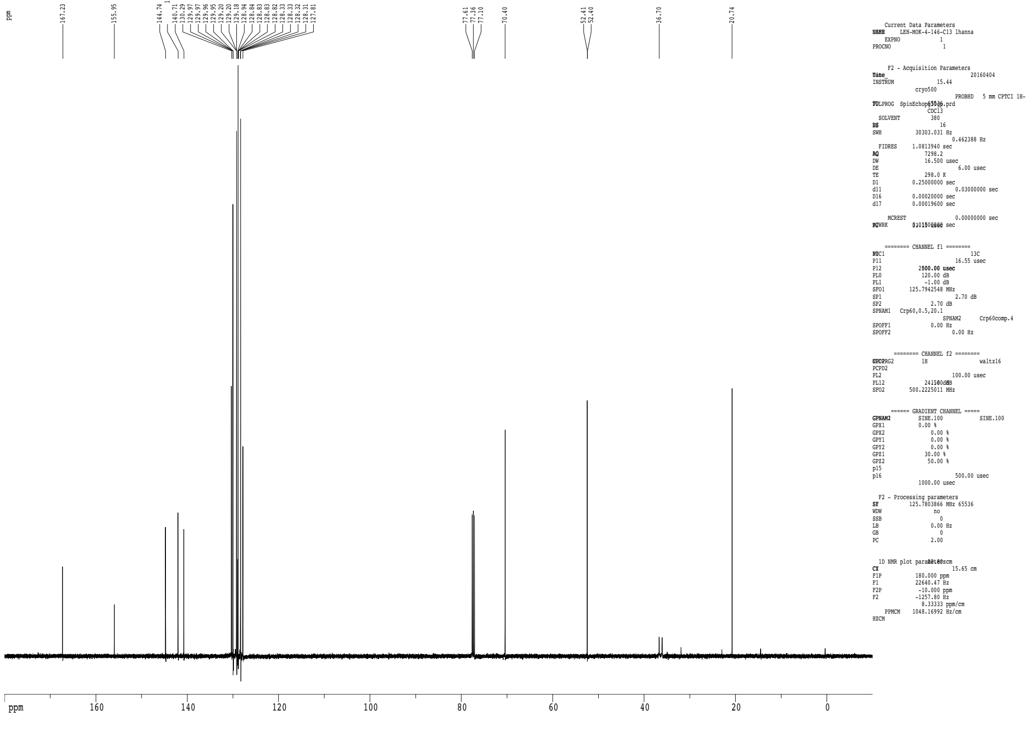
F2 - Processing parameters
SI                 65536
SF           125.7803870 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

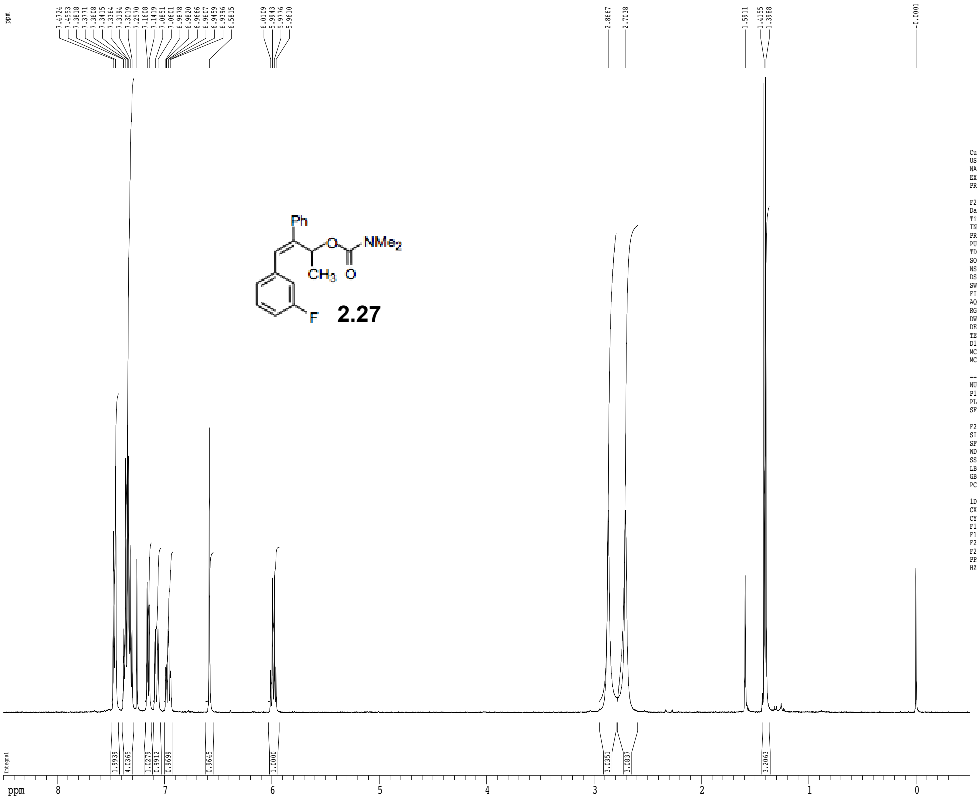
1H spectrum



Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



2.27

```
Current Data Parameters
USER               lhanna
NAME         LEH-6-257-c1
EXPNO                   1
PROCNO                  1

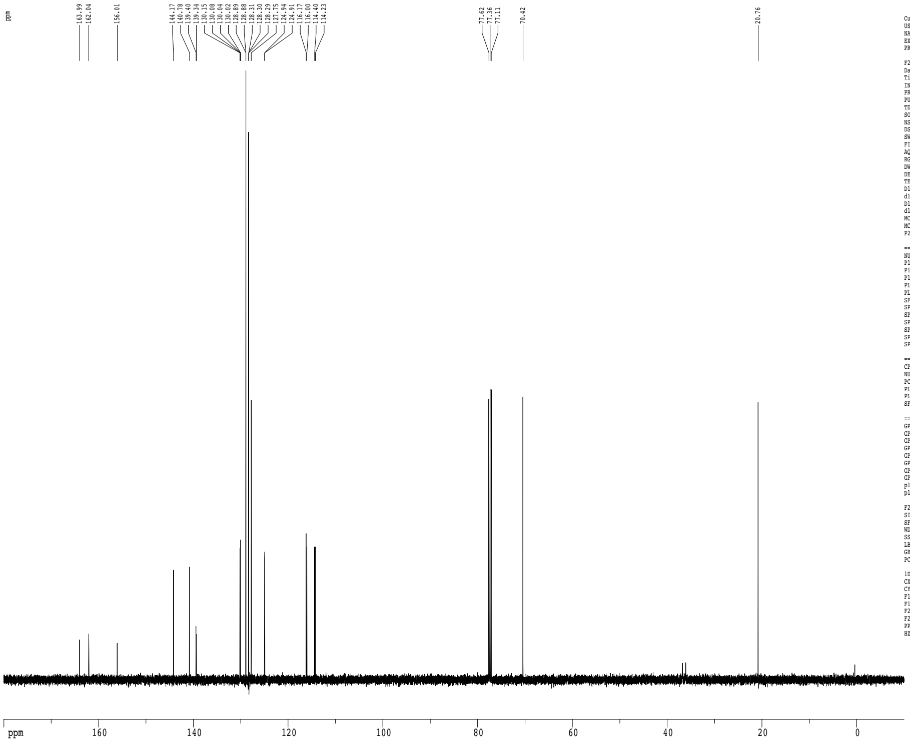
F2 - Acquisition Parameters
Date_            20160520
Time                13.40
INSTRUM            drx400
PROBHD   5 mm QNP H/F/P
PULPROG              zg30
TD                  25640
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             6410.256 Hz
FIDRES          0.250010 Hz
AQ             1.9999700 sec
RG                  287.4
DW                 78.000 usec
DE                   4.50 usec
TE                  298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                  0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                  65536
SF           400.1300225 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 8.500 ppm
F1                3401.11 Hz
F2P                -0.500 ppm
F2                -200.07 Hz
PPMCM             0.39474 ppm/cm
HZCM            157.94608 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER               lhanna
NAME        LEH-6-247-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160520
Time                17.08
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    280
DS                     16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                   6502
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1         125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

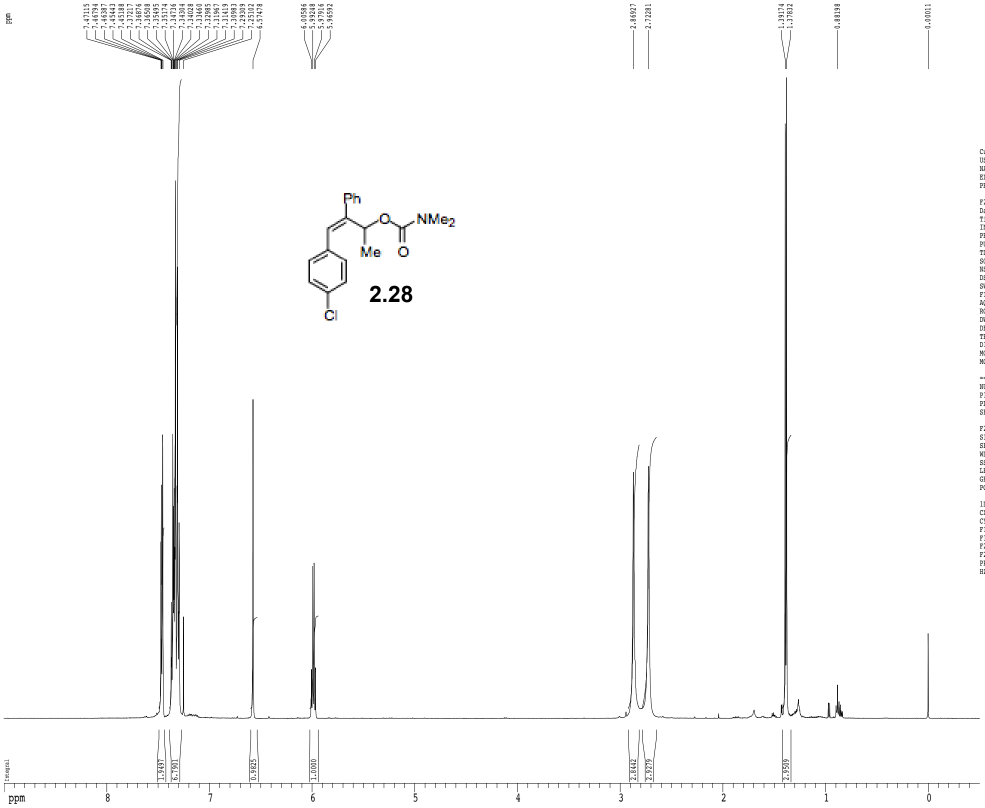
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF           125.7803838 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               180.000 ppm
F1               22640.47 Hz
F2P               -10.000 ppm
F2               -1257.80 Hz
PPMCM             8.33333 ppm/cm
HZCM           1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-157hchar
EXPNO                  1
PROCNO                 1

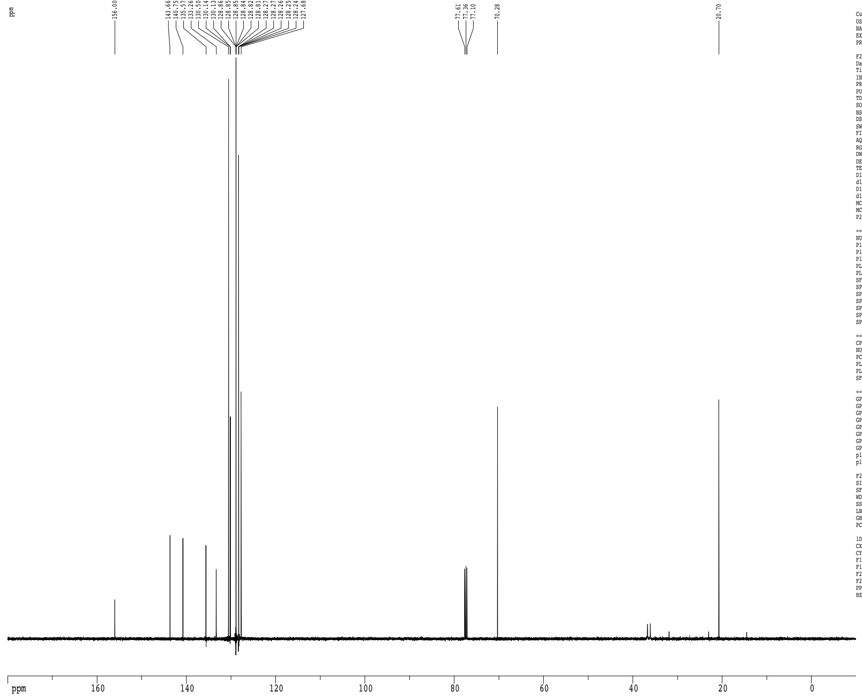
F2 - Acquisition Parameters
Date_           20160412
Time               14.51
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200358 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME    MOK-IV-157cchar2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160412
Time               14.56
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  3251
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

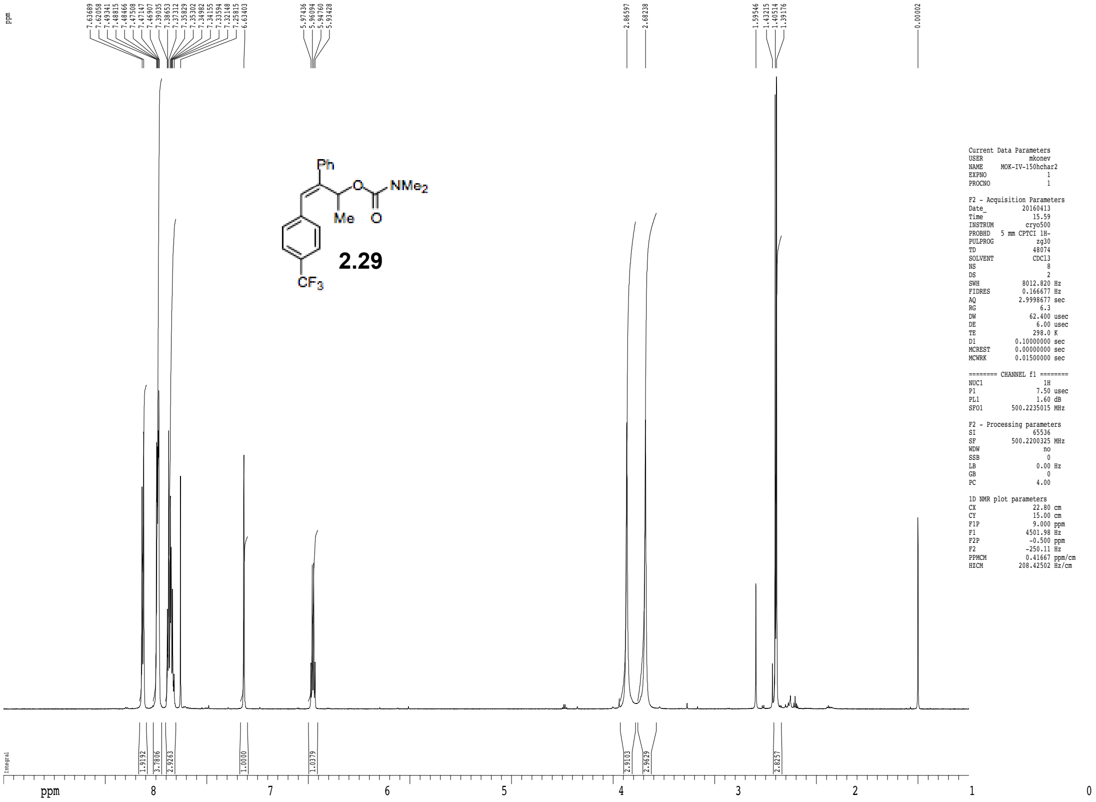
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803889 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



2.29

```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-150hchar2
EXPNO                  1
PROCNO                 1

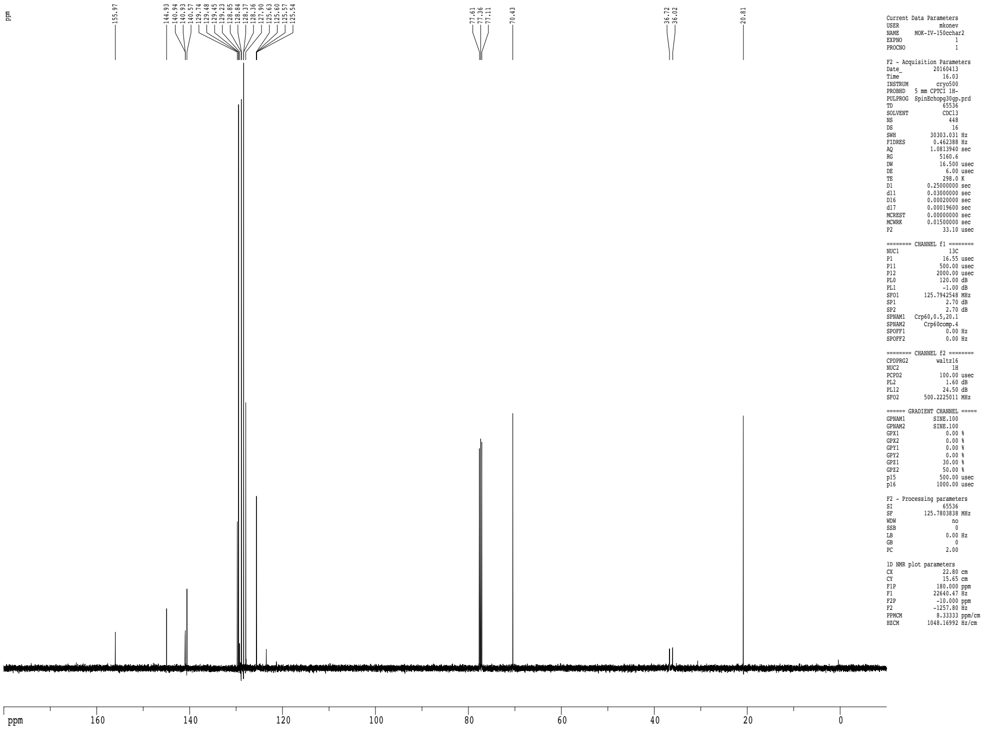
F2 - Acquisition Parameters
Date_           20160413
Time               15.59
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200325 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-150cchar2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160413
Time               16.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   448
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                5160.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

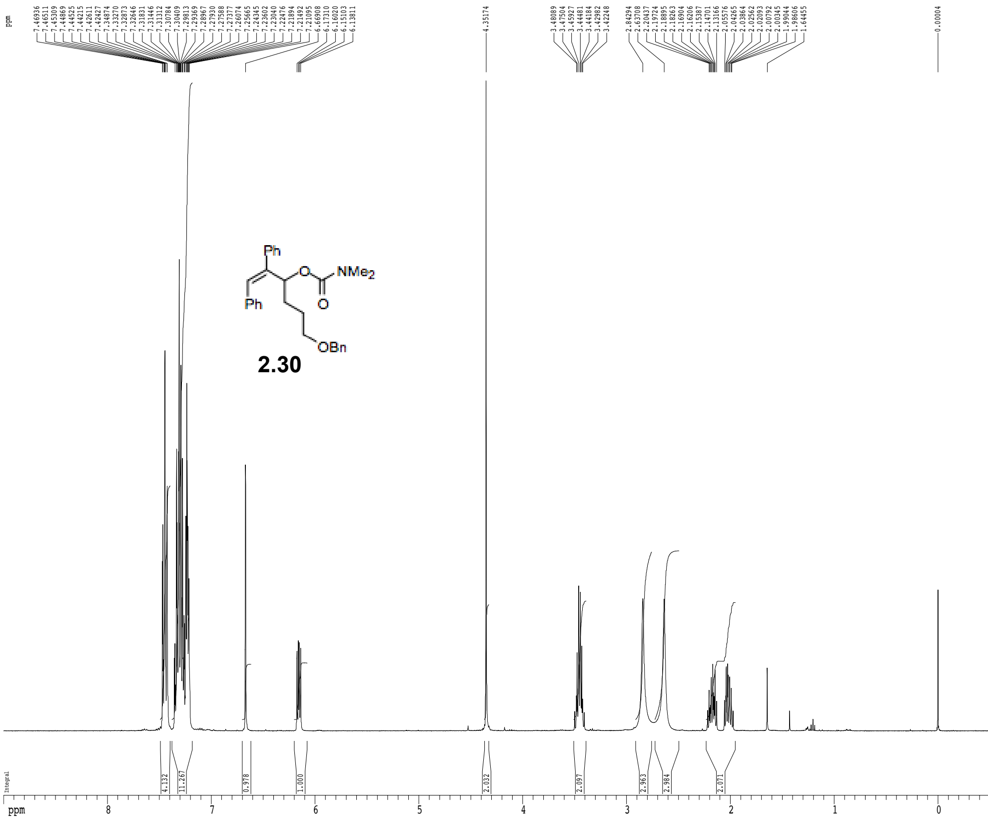
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803838 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



2.30

```
Current Data Parameters
USER              mkonev
NAME      MOK-IV-156hchar
EXPNO                  1
PROCNO                 1

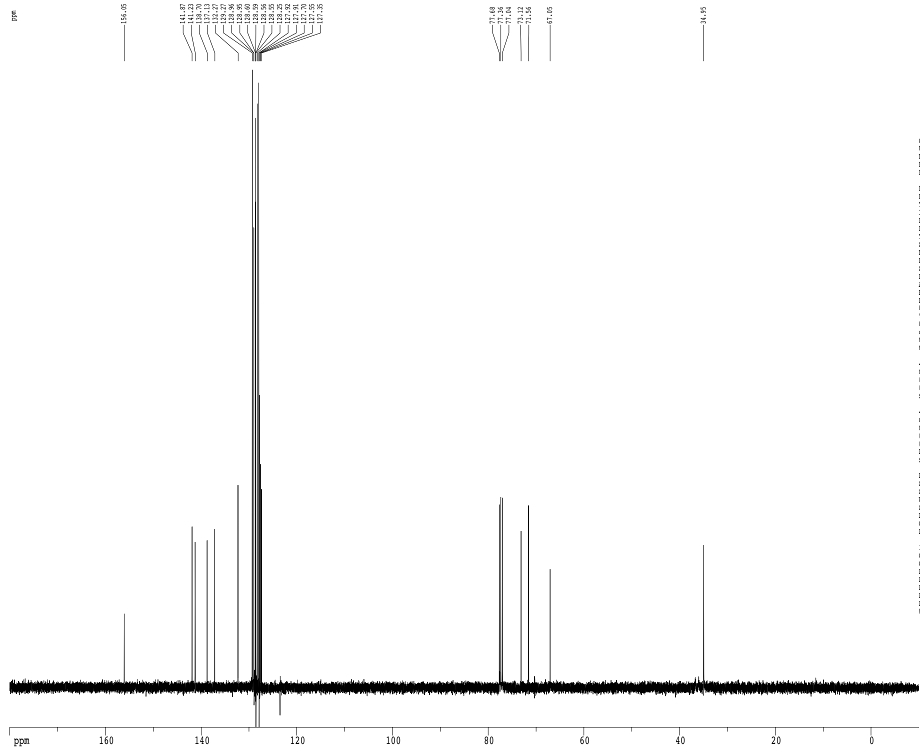
F2 - Acquisition Parameters
Date_           20160410
Time               17.27
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                 101.6
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300309 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME      MOK-IV-156cchar
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160410
Time               17.30
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   384
DS                     4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ             1.3566452 sec
RG               14596.5
DW                20.700 usec
DE                 20.39 usec
TE                 298.1 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

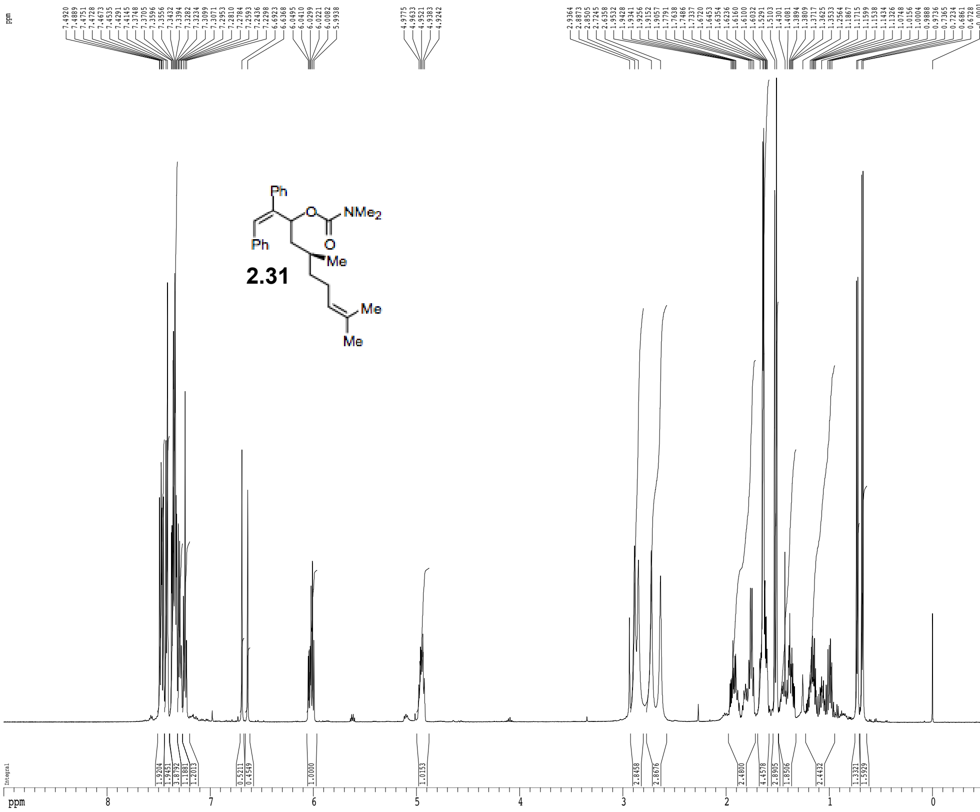
======== CHANNEL f1 ========
NUC1                 13C
P1                  7.75 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2           mlev16
NUC2                  1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               17.70 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127431 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              180.000 ppm
F1              18110.29 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM            8.33333 ppm/cm
HZCM           838.43951 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-153hchar
EXPNO                  1
PROCNO                 1

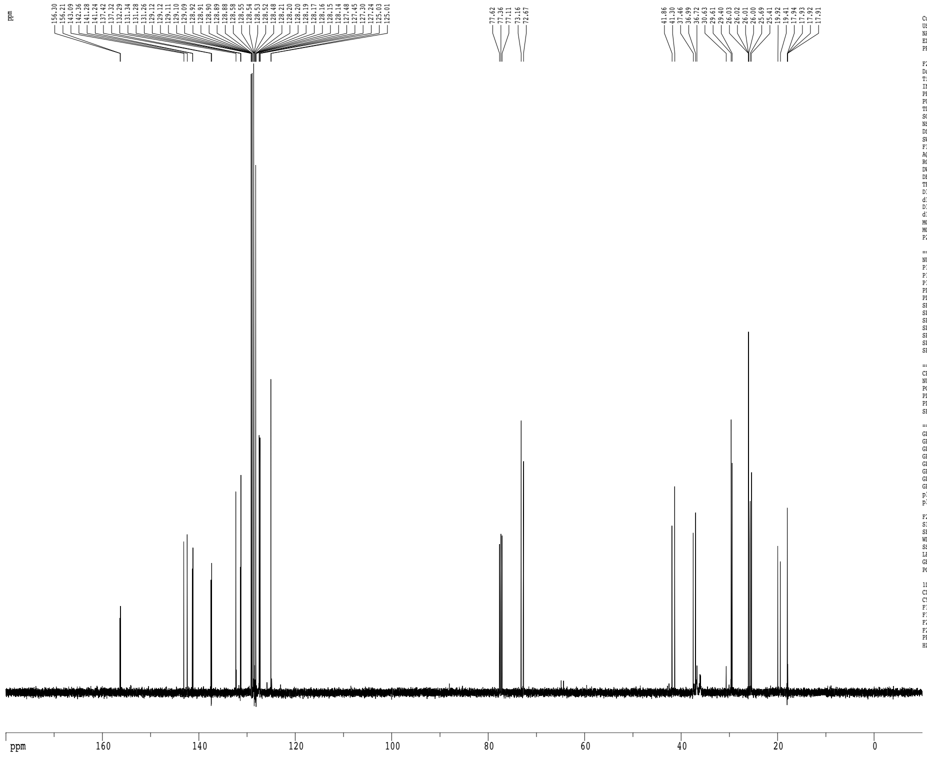
F2 - Acquisition Parameters
Date_           20160408
Time               16.39
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200395 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-153cchar
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160408
Time               16.43
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                2580.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

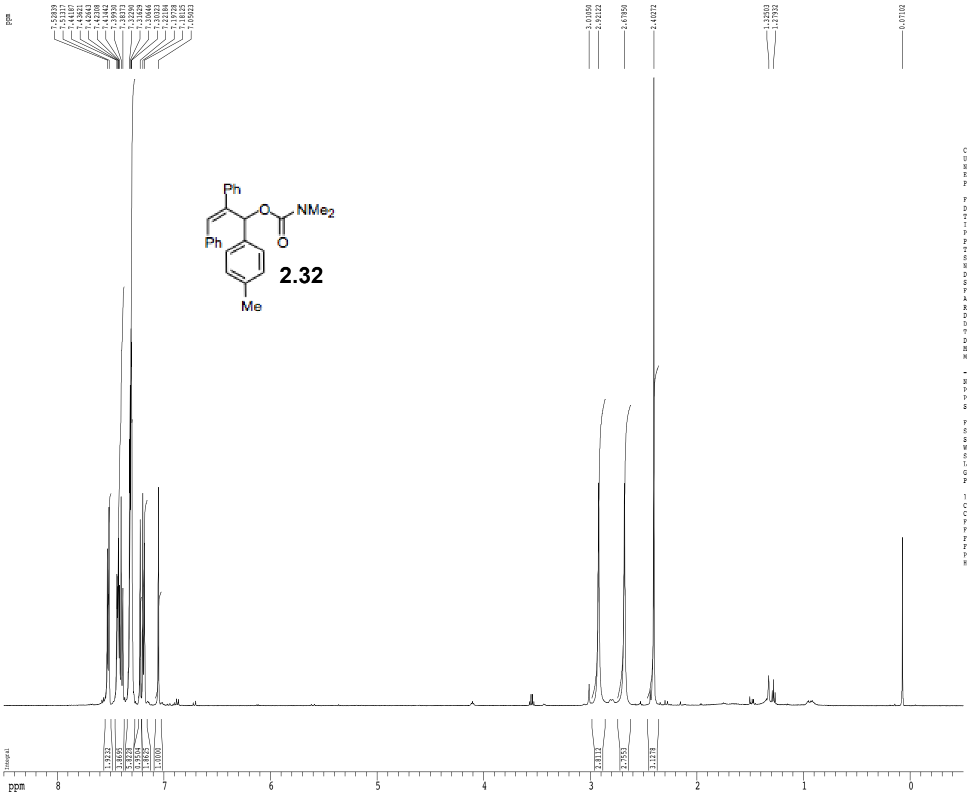
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803884 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



2.32

```
Current Data Parameters
USER              mkonev
NAME      MOK-IV-173hchar
EXPNO                  1
PROCNO                 1

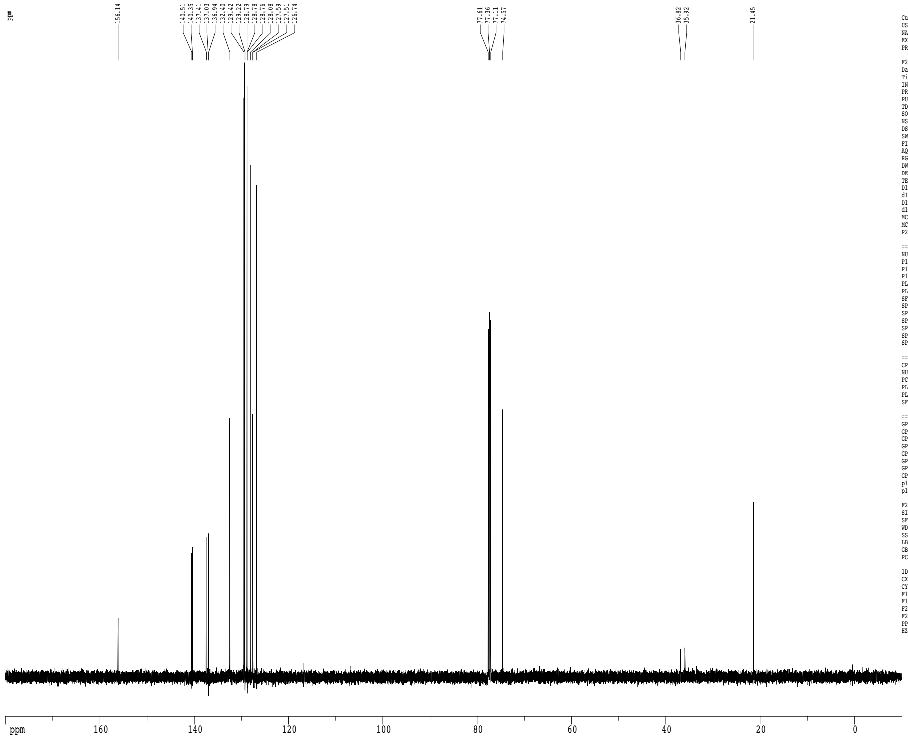
F2 - Acquisition Parameters
Date_           20160517
Time               10.35
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               4251.87 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-173cchar2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160517
Time               10.42
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   304
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  8192
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

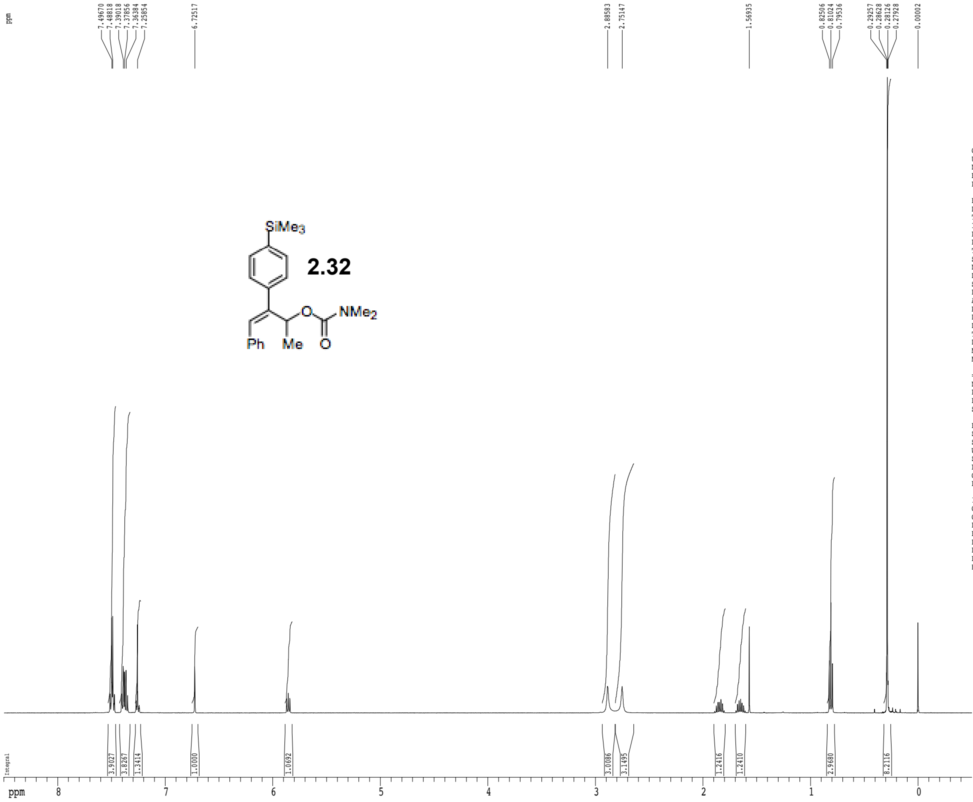
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803843 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



2.32

```
Current Data Parameters
USER               mkonev
NAME        LEH-6-234hchar
EXPNO                   1
PROCNO                  1

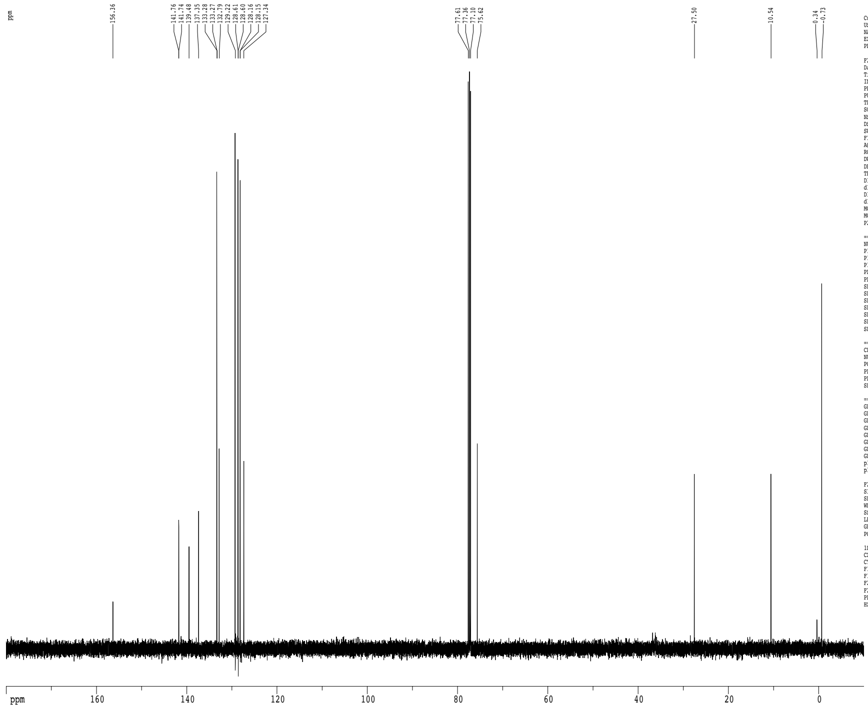
F2 - Acquisition Parameters
Date_            20160504
Time                16.32
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  32048
SOLVENT            CDCl3T
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.250026 Hz
AQ              1.9998451 sec
RG                    7.1
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200322 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 8.500 ppm
F1                4251.87 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.39474 ppm/cm
HZCM            197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER               mkonev
NAME        LEH-6-234cchar
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160504
Time                16.35
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    336
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

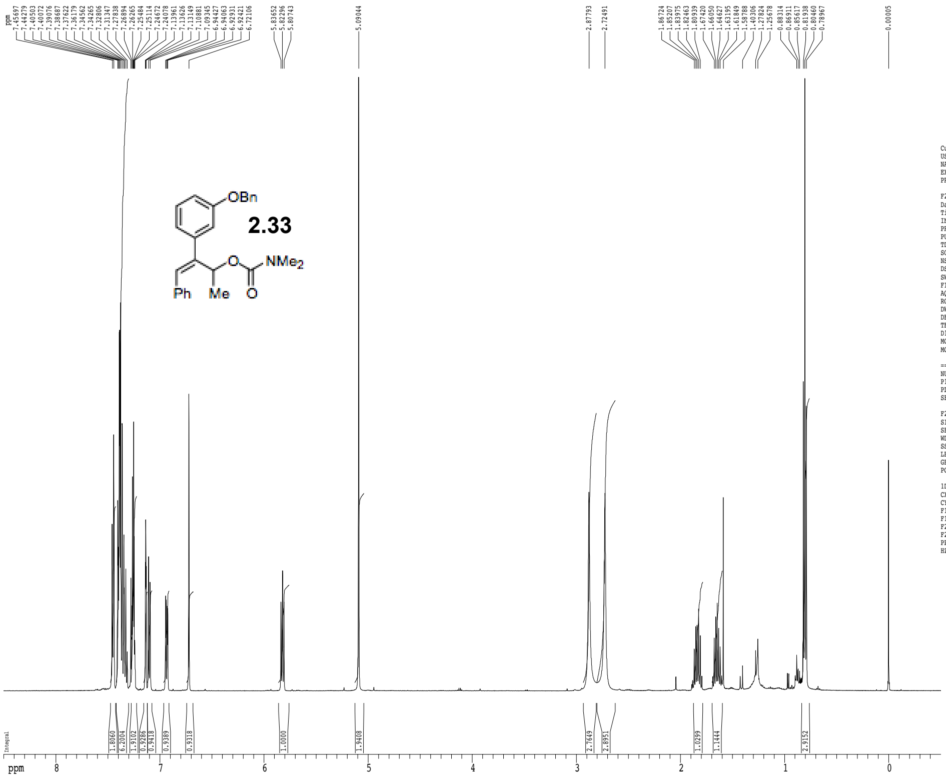
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7803829 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               180.000 ppm
F1               22640.47 Hz
F2P               -10.000 ppm
F2               -1257.80 Hz
PPMCM             8.33333 ppm/cm
HZCM           1048.16992 Hz/cm
```

1H spectrum



2.33

```
Current Data Parameters
USER              mkonev
NAME     LEH-6-232hchar
EXPNO                 1
PROCNO                1

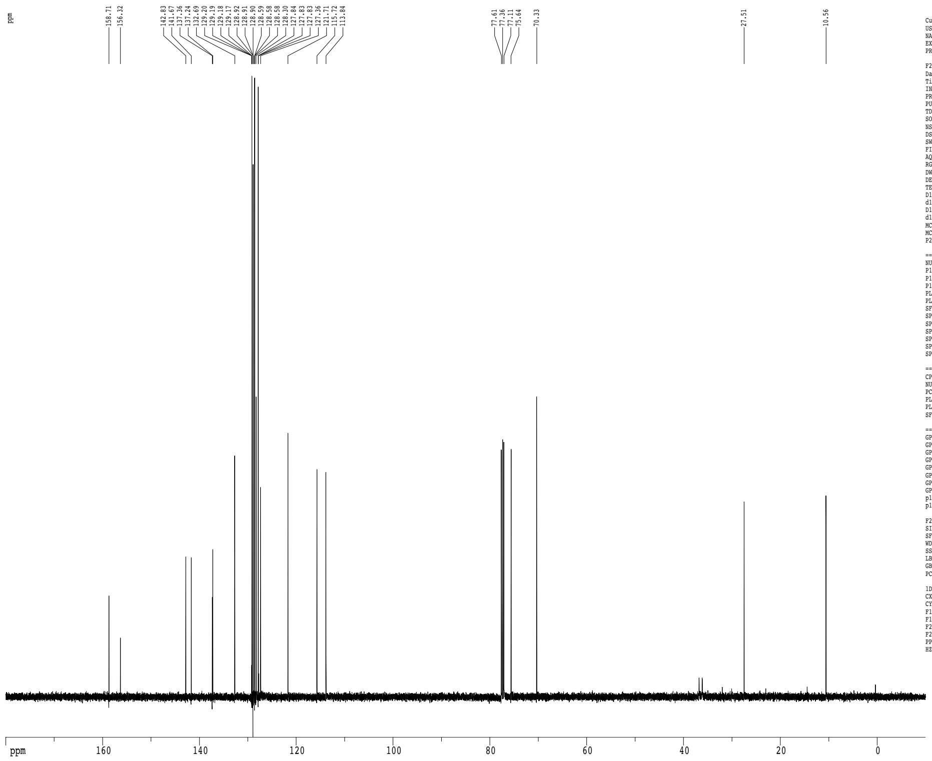
F2 - Acquisition Parameters
Date_          20160429
Time              16.43
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9998451 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200359 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               8.500 ppm
F1              4251.87 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.39474 ppm/cm
HZCM          197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME     LEH-6-232cchar
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160429
Time              16.48
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  376
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1             0.00 Hz
SPOFF2             0.00 Hz

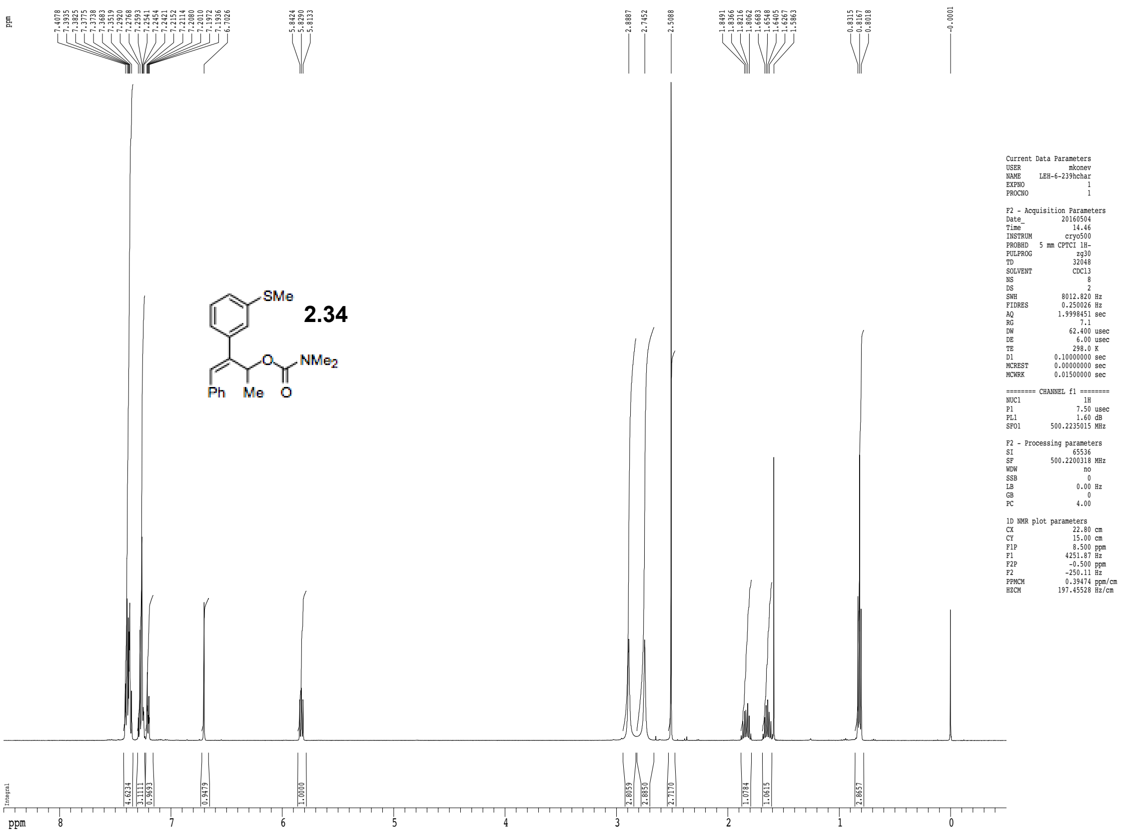
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803852 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             180.000 ppm
F1             22640.47 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM           8.33333 ppm/cm
HZCM         1048.16992 Hz/cm
```

1H spectrum



2.34

```
Current Data Parameters
USER              mkonev
NAME     LEH-6-239hchar
EXPNO                  1
PROCNO                 1

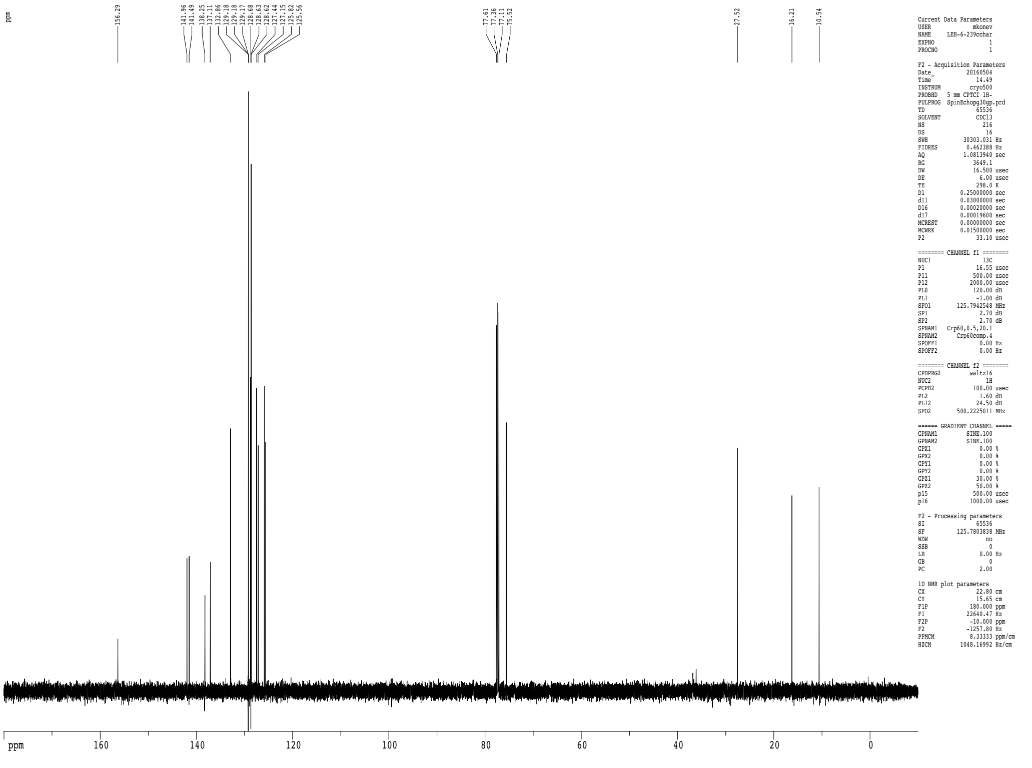
F2 - Acquisition Parameters
Date_           20160504
Time               14.46
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200318 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               4251.87 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME     LEH-6-239cchar
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160504
Time               14.49
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   216
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                3649.1
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

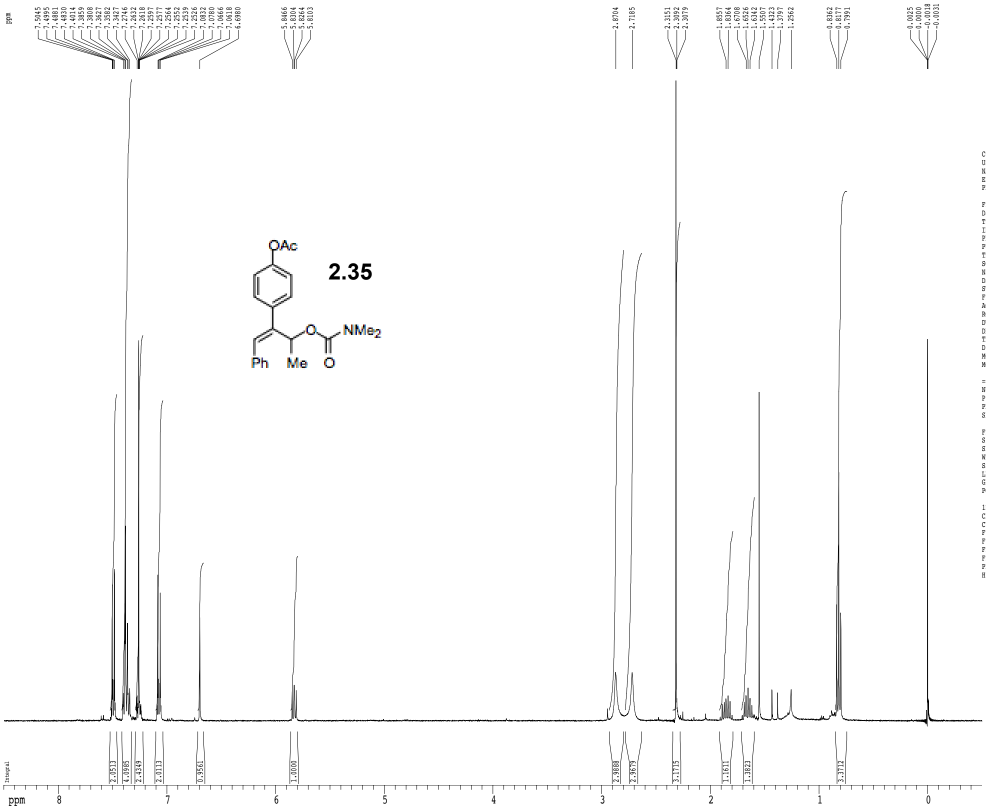
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803838 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER              lhanna
NAME     LEH-6-224-c2-f10
EXPNO                  1
PROCNO                 1

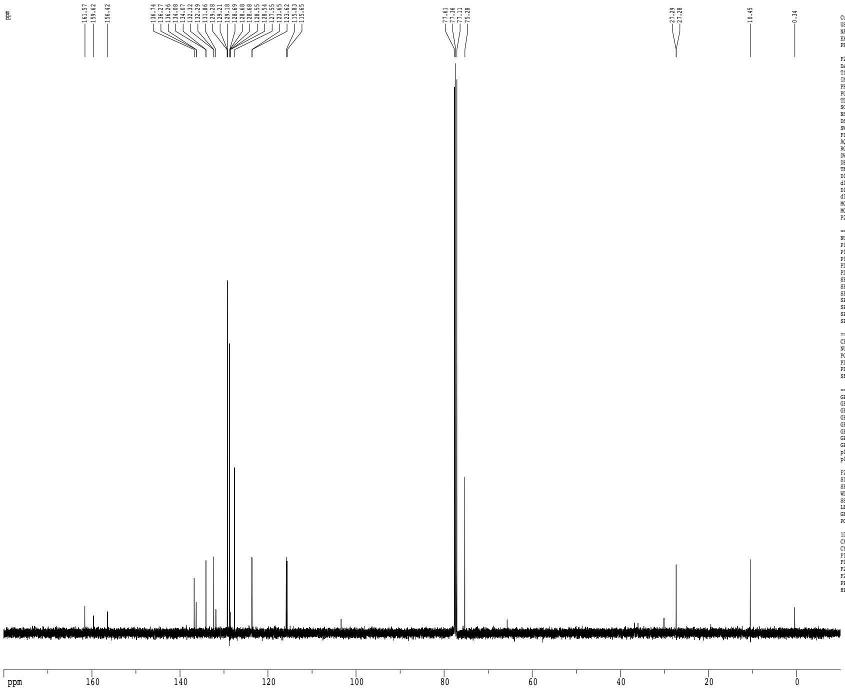
F2 - Acquisition Parameters
Date_           20160430
Time               18.10
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 25640
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.250010 Hz
AQ             1.9999700 sec
RG                 724.1
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300215 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               3401.11 Hz
F2P               -0.500 ppm
F2               -200.07 Hz
PPMCM            0.39474 ppm/cm
HZCM           157.94608 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              lhanna
NAME        LEH-6-225-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160510
Time               12.01
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   763
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  4096
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

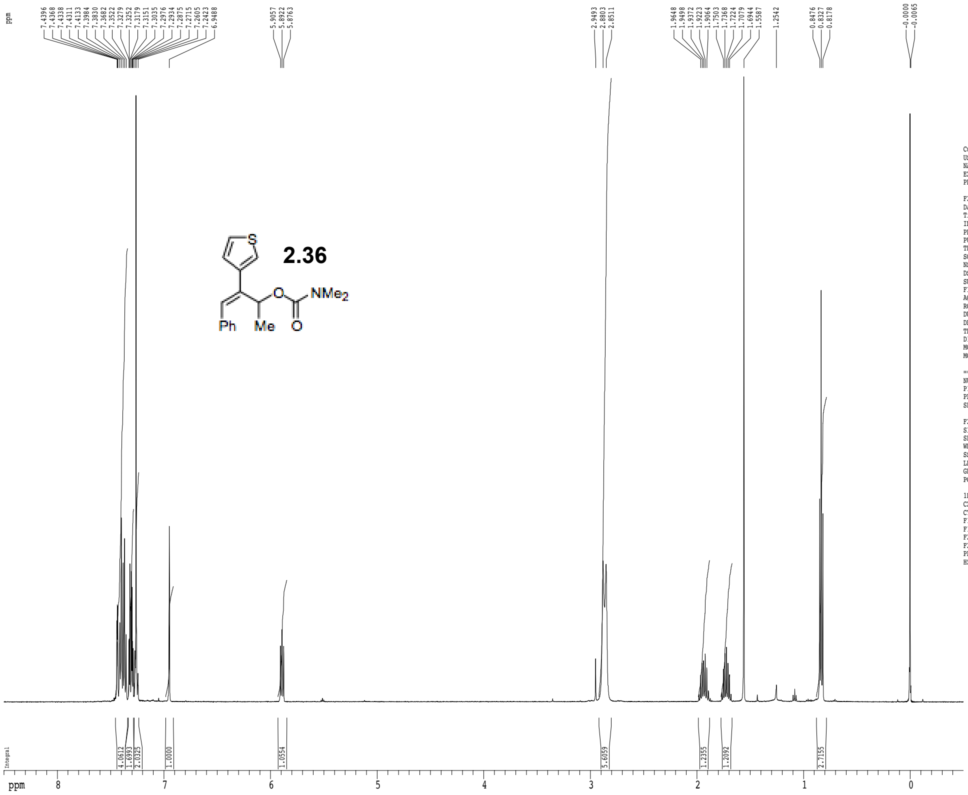
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803829 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER              mkonev
NAME     LEH-6-238hchar2
EXPNO                  1
PROCNO                 1

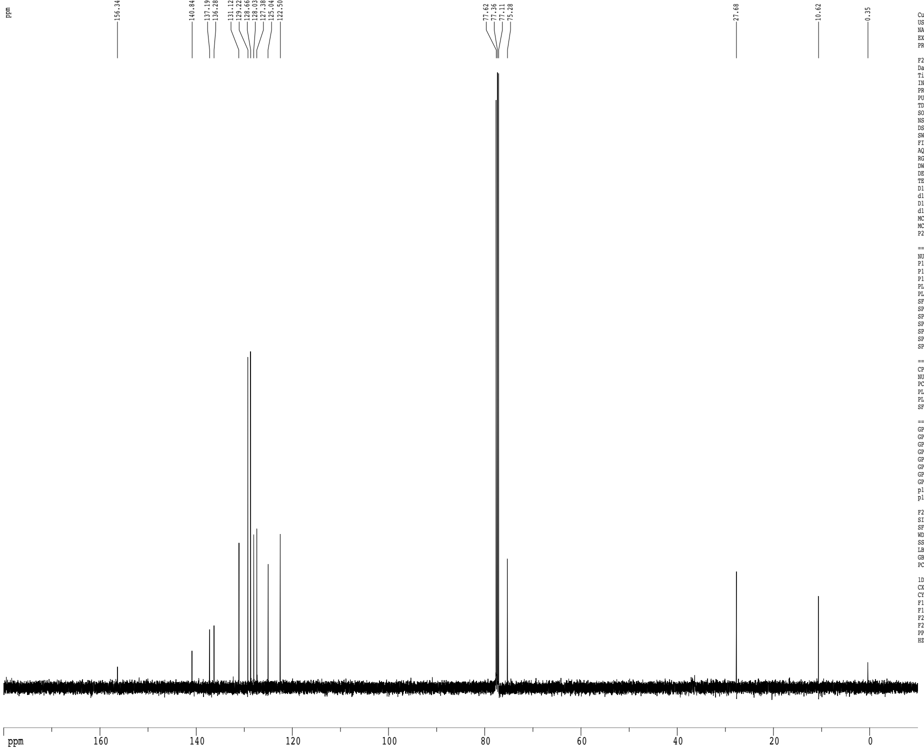
F2 - Acquisition Parameters
Date_           20160505
Time               16.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                     9
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200310 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               4251.87 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME     LEH-6-238cchar2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160505
Time               16.47
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   928
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG               10321.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

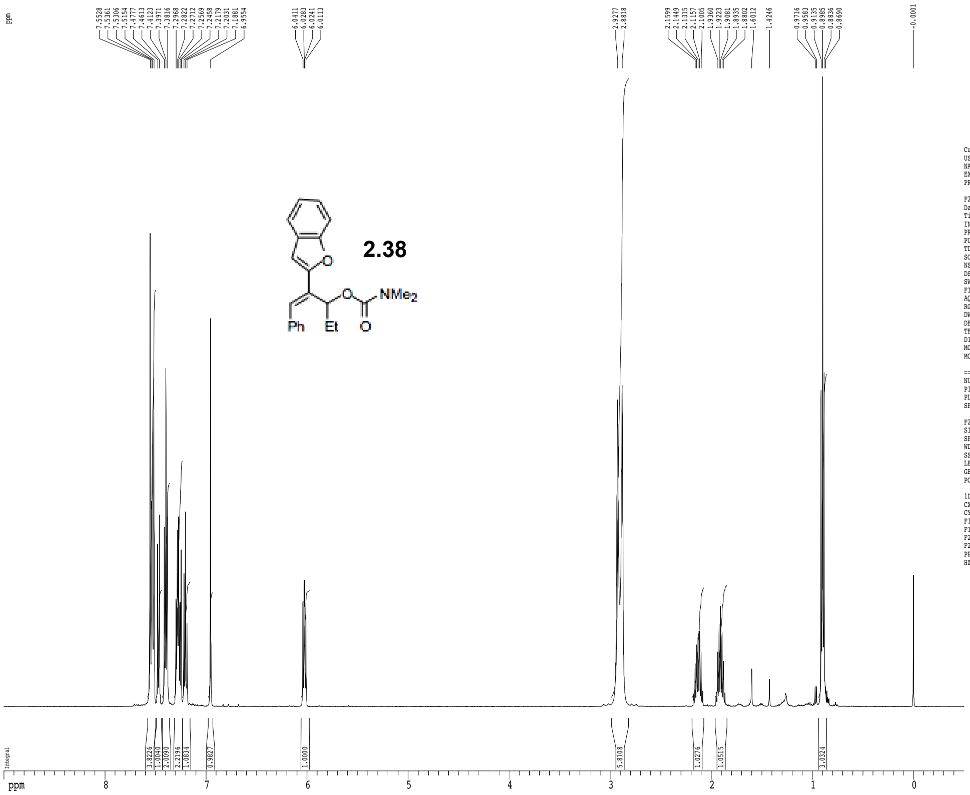
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803824 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER            mkonev
NAME     MOK-IV-160hchar
EXPNO                1
PROCNO               1

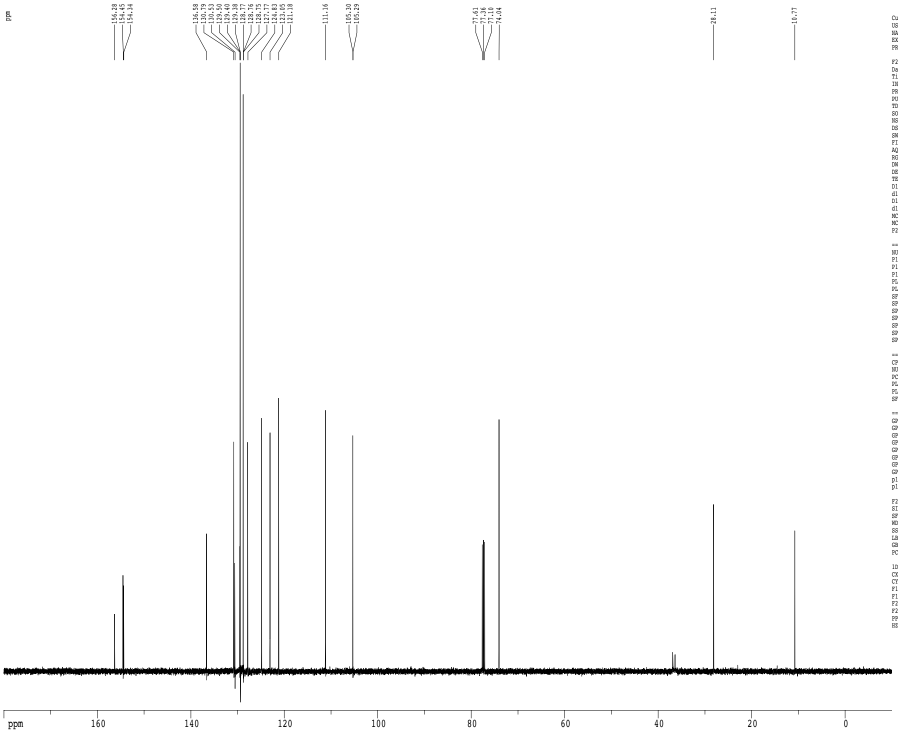
F2 - Acquisition Parameters
Date_         20160415
Time             13.10
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               48074
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.166677 Hz
AQ           2.9998677 sec
RG                   9
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                7.50 usec
PL1               1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI               65536
SF         500.2200386 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                4.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             4501.98 Hz
F2P             -0.500 ppm
F2             -250.11 Hz
PPMCM          0.41667 ppm/cm
HZCM         208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER            mkonev
NAME     MOK-IV-160cchar
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20160415
Time             13.15
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT          CDCl3
NS                 160
DS                  16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG              5792.6
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1               13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1            0.00 Hz
SPOFF2            0.00 Hz

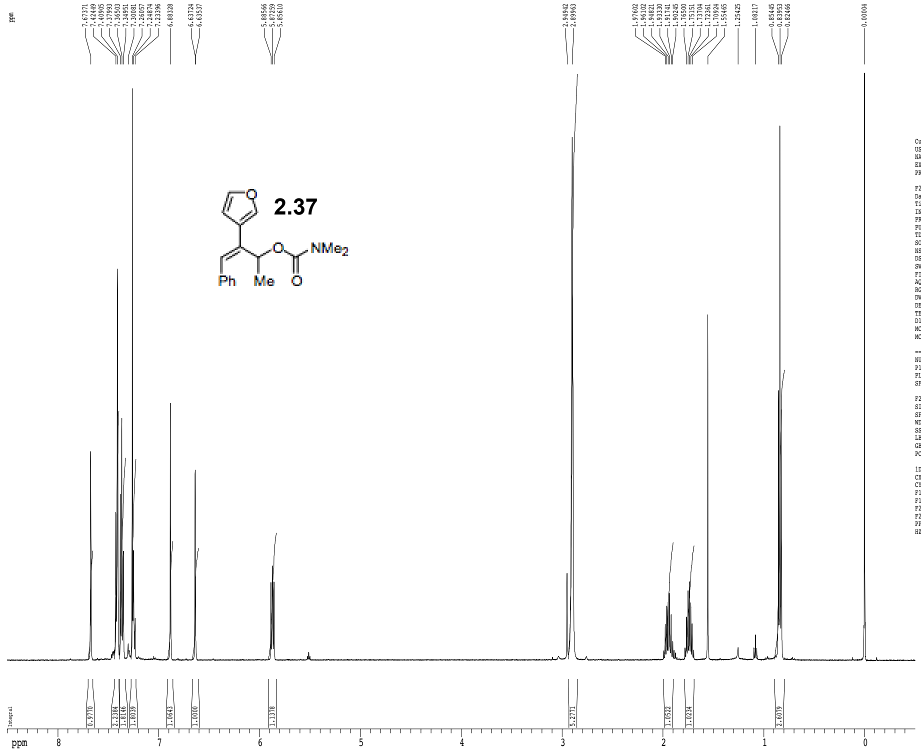
======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI               65536
SF         125.7803870 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            180.000 ppm
F1            22640.47 Hz
F2P            -10.000 ppm
F2            -1257.80 Hz
PPMCM          8.33333 ppm/cm
HZCM        1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER             mkonev
NAME      MOK-IV-168hchar
EXPNO                 1
PROCNO                1

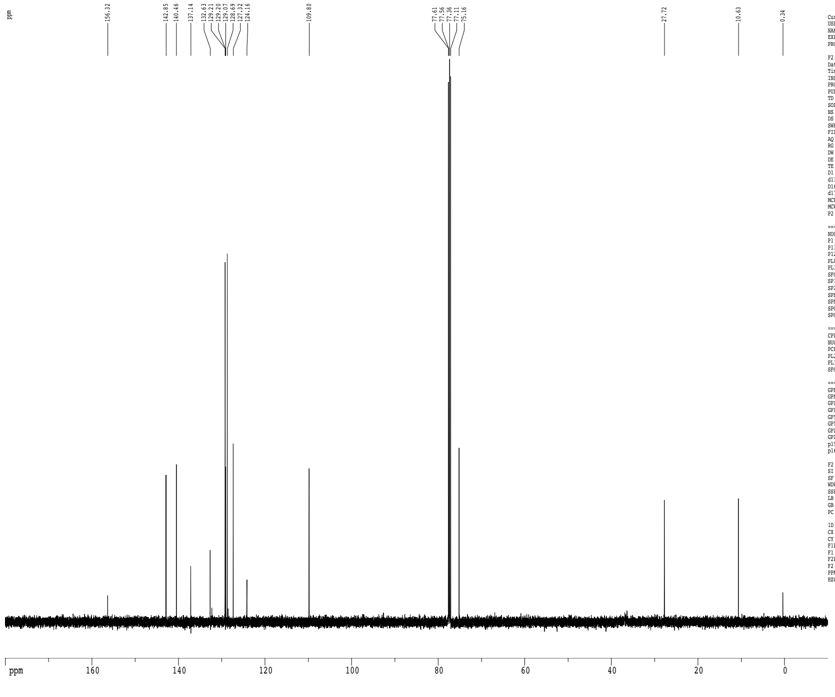
F2 - Acquisition Parameters
Date_          20160428
Time              22.16
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9998451 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200309 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               8.500 ppm
F1              4251.87 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.39474 ppm/cm
HZCM          197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER             mkonev
NAME      MOK-IV-168cchar
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160428
Time              22.19
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               5792.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

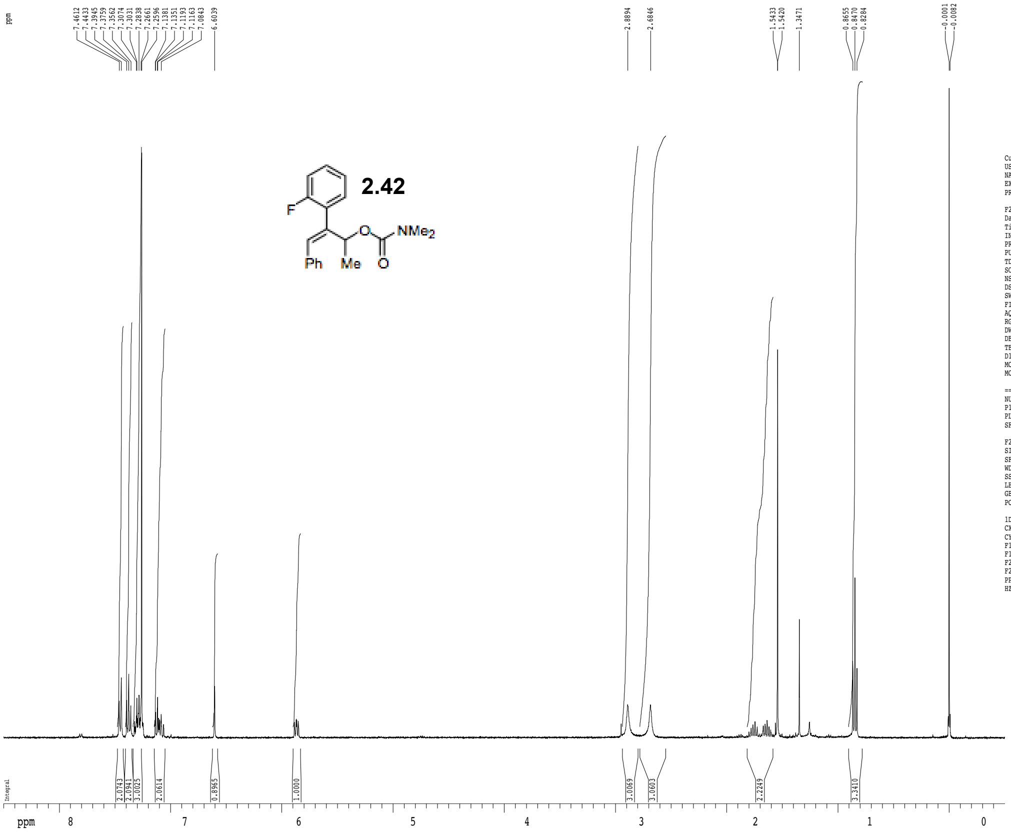
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1             0.00 Hz
SPOFF2             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803824 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             180.000 ppm
F1             22640.47 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM           8.33333 ppm/cm
HZCM         1048.16992 Hz/cm
```



1H spectrum

2.42

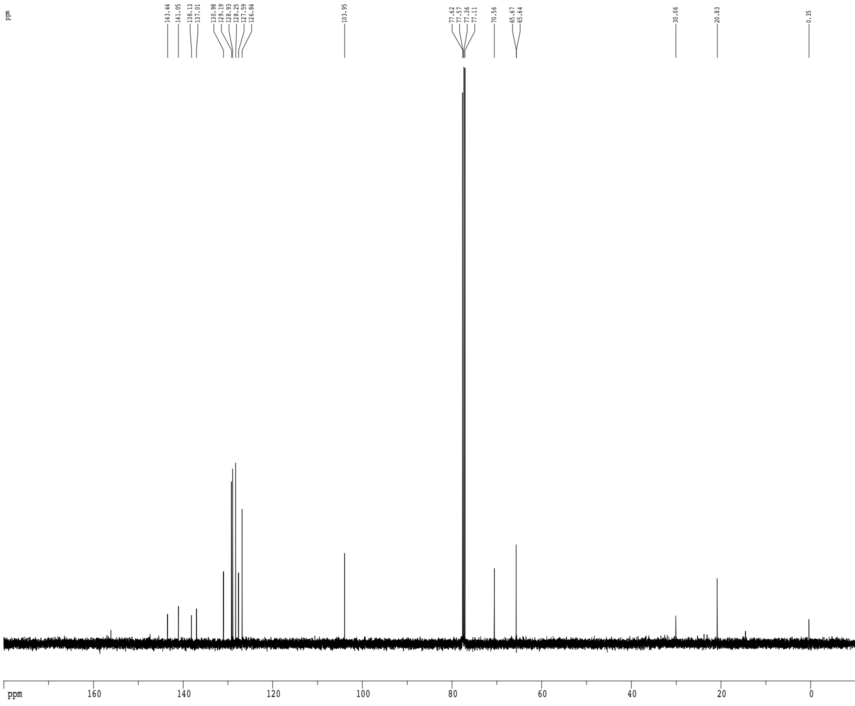
```
Current Data Parameters
USER             lhanna
NAME     LEH-6-235-c1-f49
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160506
Time              10.57
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                25640
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.250010 Hz
AQ            1.9999700 sec
RG               1149.4
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1                0.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300216 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               8.500 ppm
F1              3401.11 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.39474 ppm/cm
HZCM          157.94608 Hz/cm
```



Z-restored spin-echo 13C spectrum with 1H decoupling

```
Current Data Parameters
USER             lhanna
NAME        LEH-6-255-C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160520
Time              16.44
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               2896.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1             0.00 Hz
SPOFF2             0.00 Hz

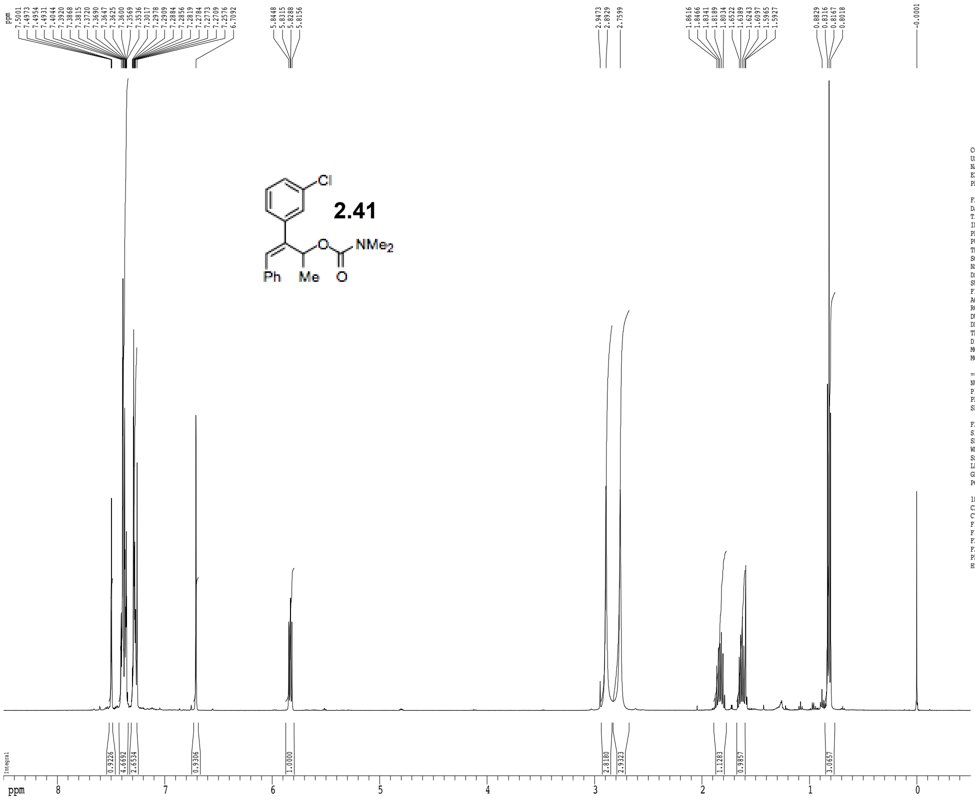
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803824 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             180.000 ppm
F1             22640.47 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM           8.33333 ppm/cm
HZCM         1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER              mkonev
NAME       LEH-6-229hchar
EXPNO                  1
PROCNO                 1

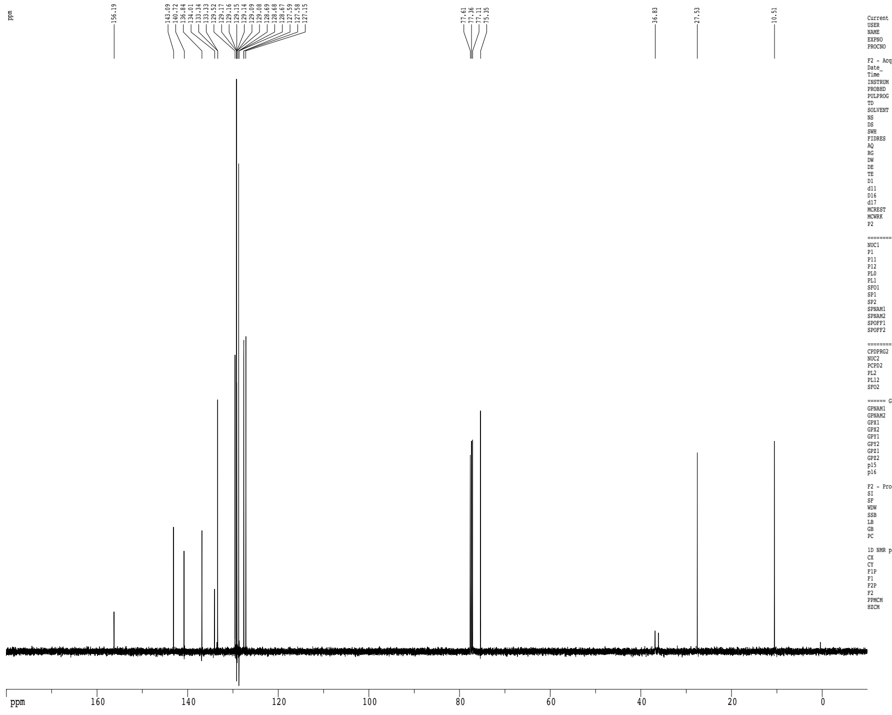
F2 - Acquisition Parameters
Date_           20160429
Time               16.14
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200326 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               4251.87 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME       LEH-6-229cchar
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160429
Time               16.18
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG   SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   368
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

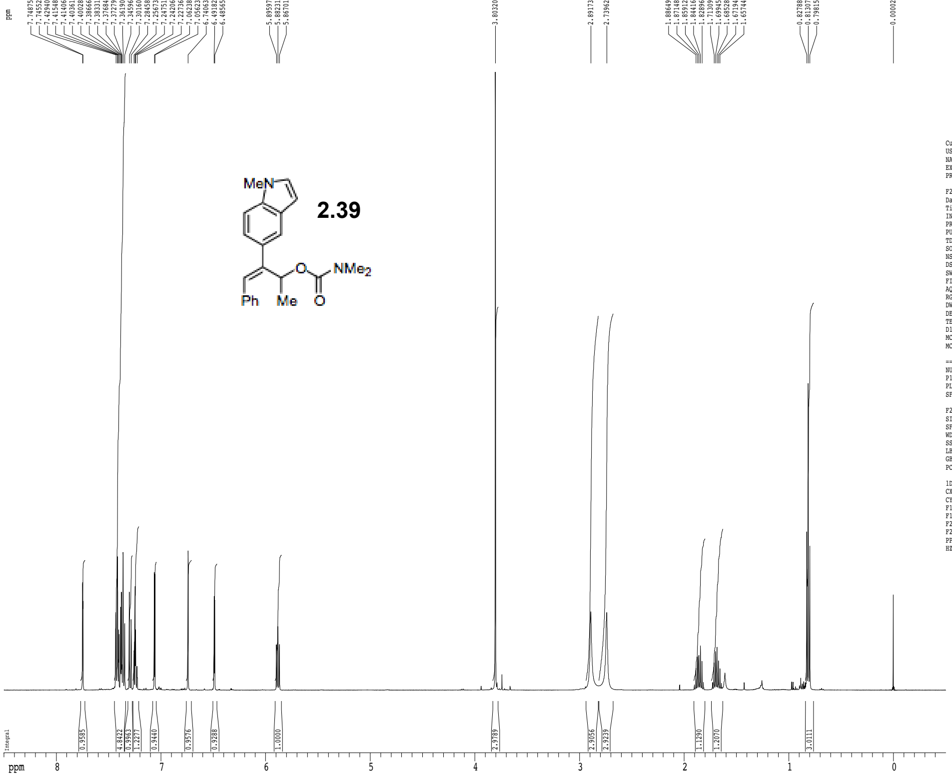
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803838 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



2.39

```
Current Data Parameters
USER             mkonev
NAME     LEH-6-233hchar
EXPNO                 1
PROCNO                1

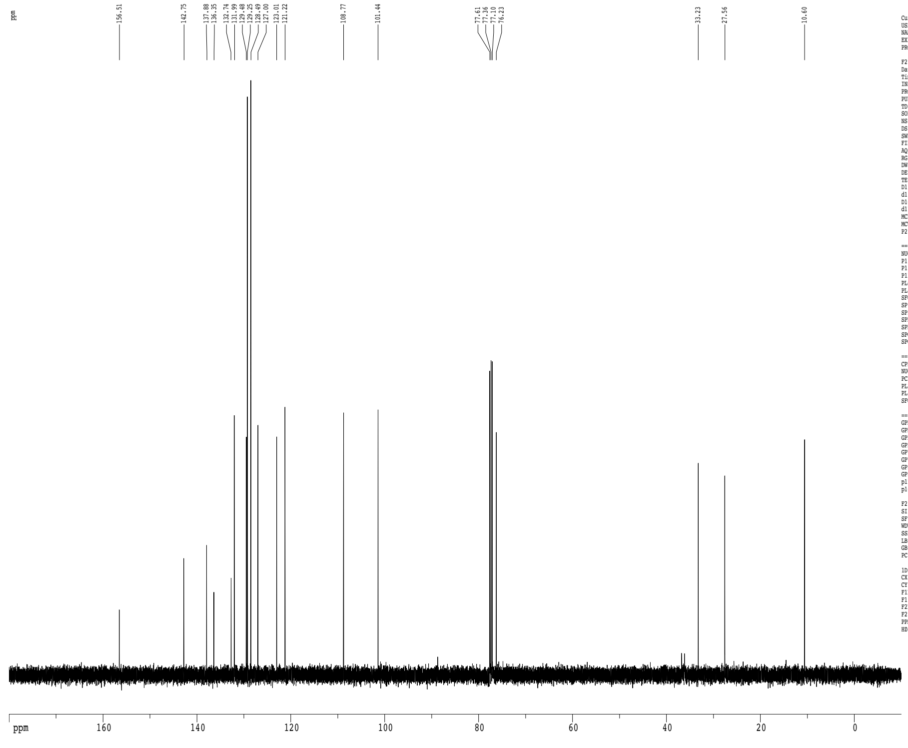
F2 - Acquisition Parameters
Date_          20160507
Time              15.17
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9998451 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200375 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               8.500 ppm
F1              4251.87 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.39474 ppm/cm
HZCM          197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER             mkonev
NAME     LEH-6-233cchar
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160507
Time              15.19
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   72
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1             0.00 Hz
SPOFF2             0.00 Hz

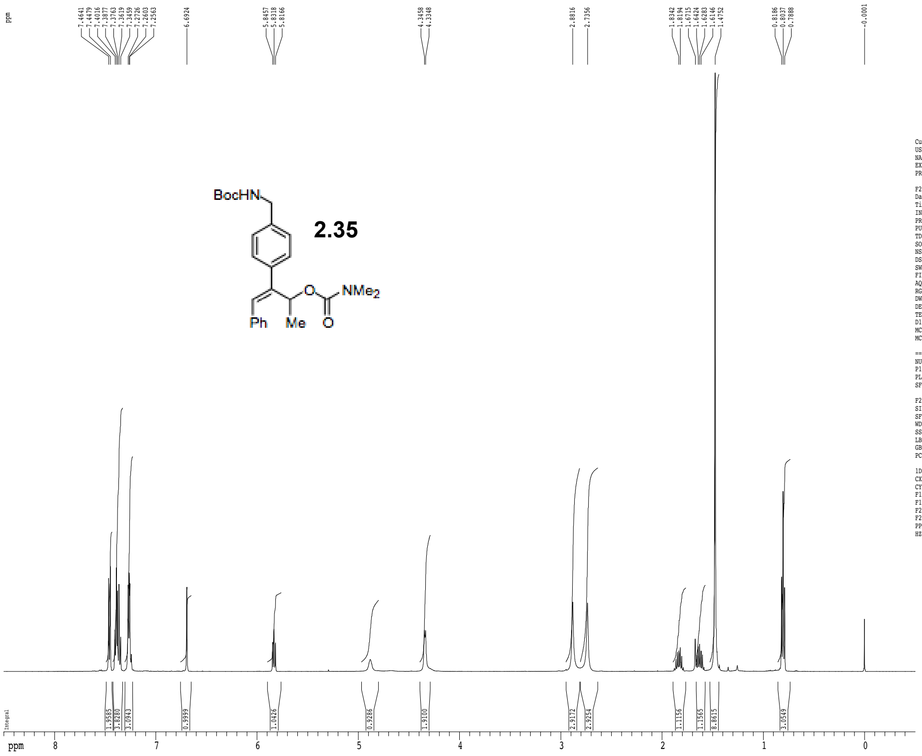
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803861 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             180.000 ppm
F1             22640.47 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM           8.33333 ppm/cm
HZCM         1048.16992 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER              mkonev
NAME      LEH-6-230hchar2
EXPNO                  1
PROCNO                 1

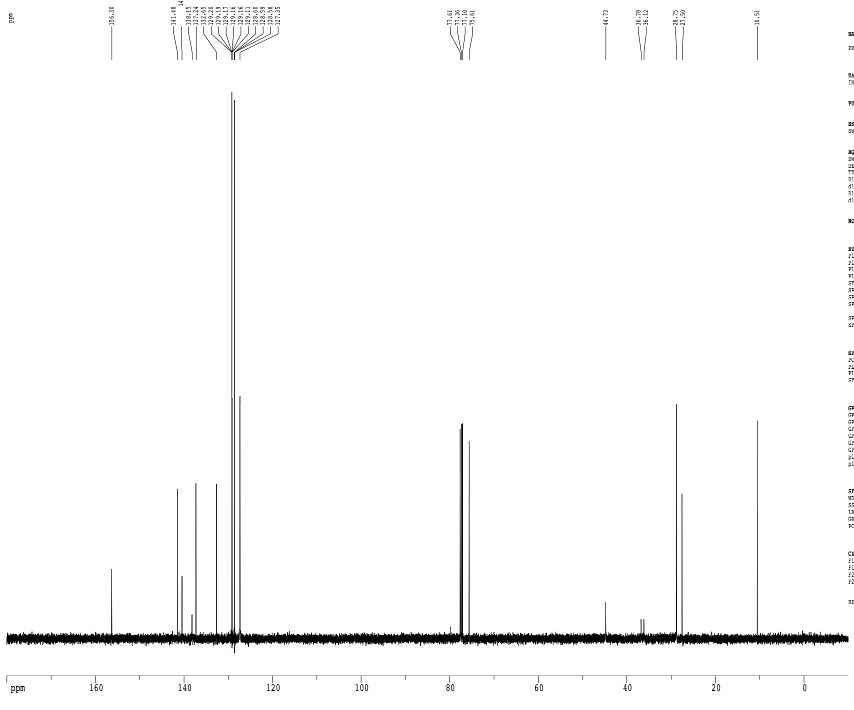
F2 - Acquisition Parameters
Date_           20160502
Time               16.59
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200310 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               4251.87 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     LEH-6-230cchar2   mkonev
    EXPNO             1
PROCNO                 1


     F2 - Acquisition Parameters
Date_                            20160502
INSTRUM             17.04
              cryo500
                           PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
                  CDCl3
  SOLVENT          208
NS                   16
SWH           30303.031 Hz
                          0.462388 Hz
  FIDRES     1.0813940 sec
RG                4597.6
DW                16.500 usec
DE                         6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11                        0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec

     MCREST                0.00000000 sec
MCWRK         0.01500000 sec


    ======== CHANNEL f1 ========
NUC1                            13C
P11                        16.55 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                        2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
                 SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2                     0.00 Hz

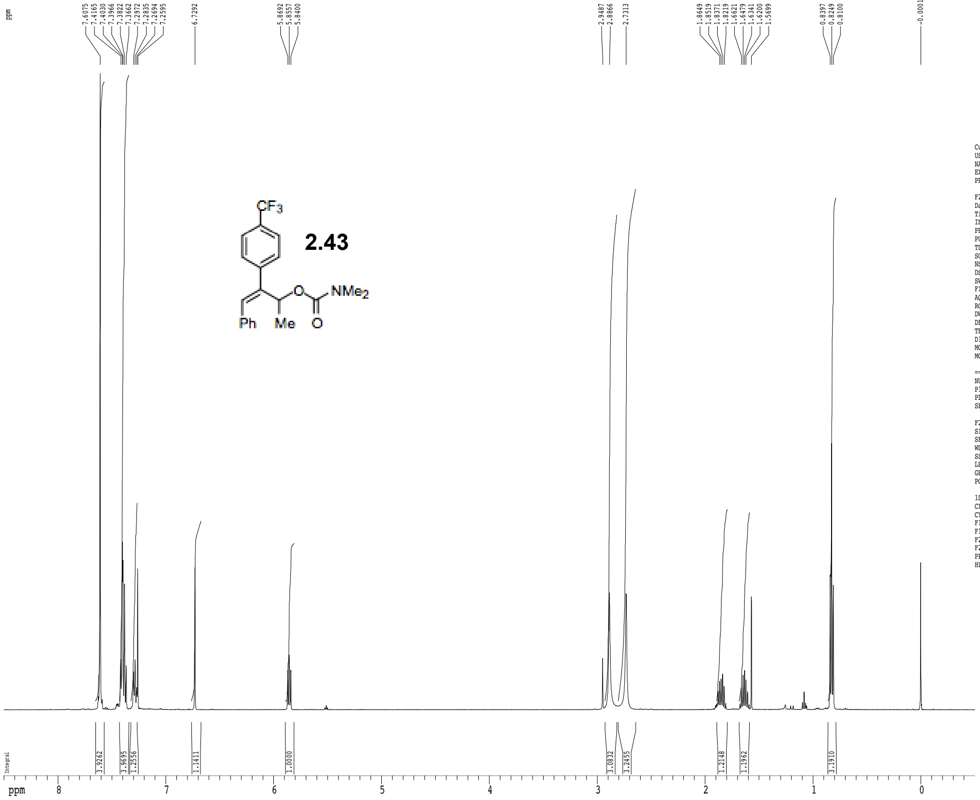

       ======== CHANNEL f2 ========
CPDPRG2         1H                waltz16
PCPD2
PL2                        100.00 usec
PL12               24.50 dB
SFO2        500.2225011 MHz


      ====== GRADIENT CHANNEL =====
GPNAM1         SINE.100           SINE.100
GPX1           0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1              30.00 %
GPZ2               50.00 %
p15
p16                        500.00 usec
               1000.00 usec

  F2 - Processing parameters
SI          125.7803857 MHz 65536
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00


  1D NMR plot parameters22.00 cm
CX                         15.65 cm
F1P           180.000 ppm
F1            22640.47 Hz
F2P            -10.000 ppm
F2            -1257.80 Hz
                8.33333 ppm/cm
    PPMCM    1048.16992 Hz/cm
HZCM
```

1H spectrum



```
Current Data Parameters
USER              mkonev
NAME        LEH-6-227hchar
EXPNO                  1
PROCNO                 1

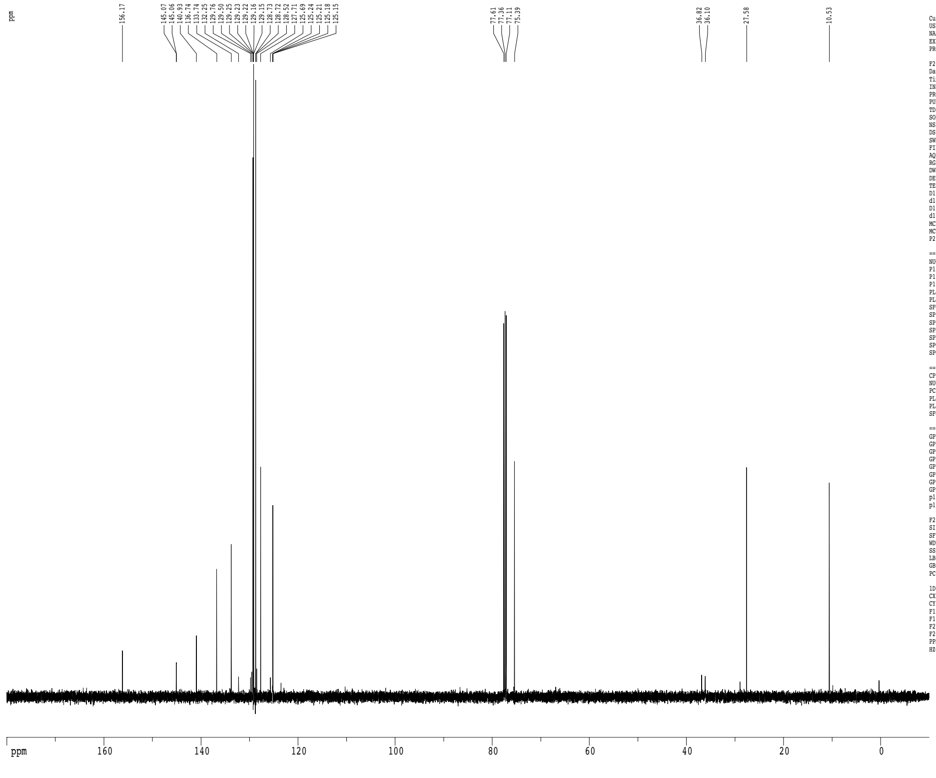
F2 - Acquisition Parameters
Date_           20160429
Time                0.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200318 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               4251.87 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME      LEH-6-227cchar
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160429
Time                0.20
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   568
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

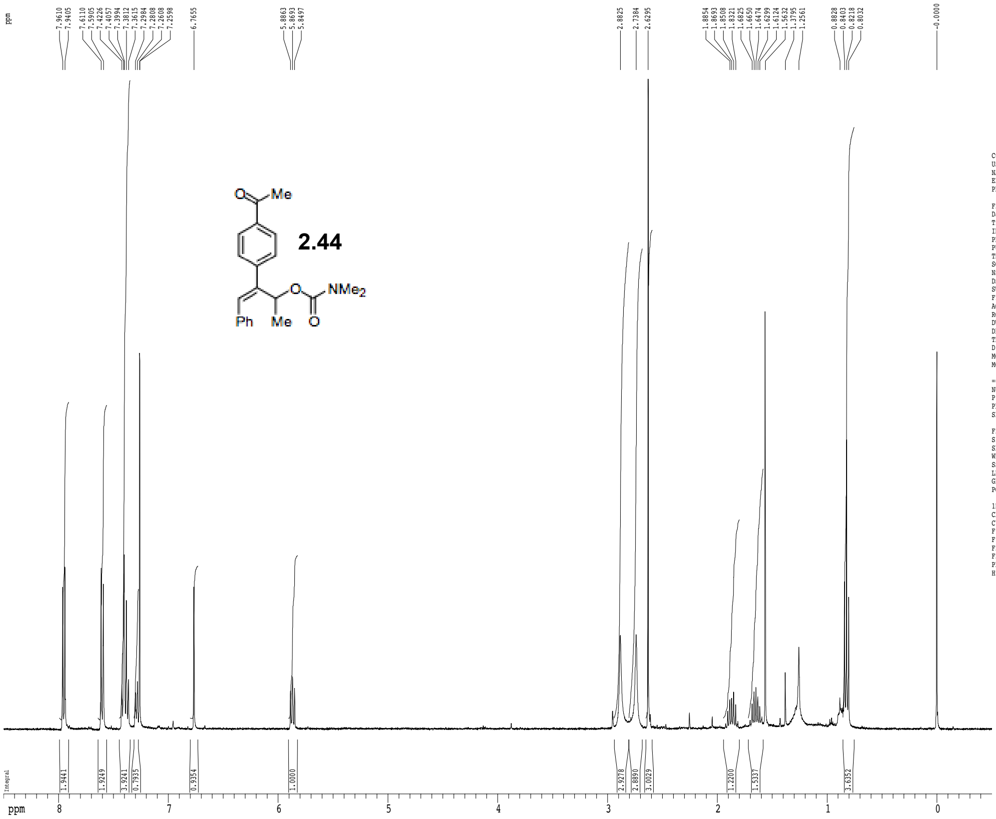
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803829 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.16992 Hz/cm
```

1H spectrum



2.44

```
Current Data Parameters
USER              lhanna
NAME     LEH-6-228-c1-f-11
EXPNO                  1
PROCNO                 1

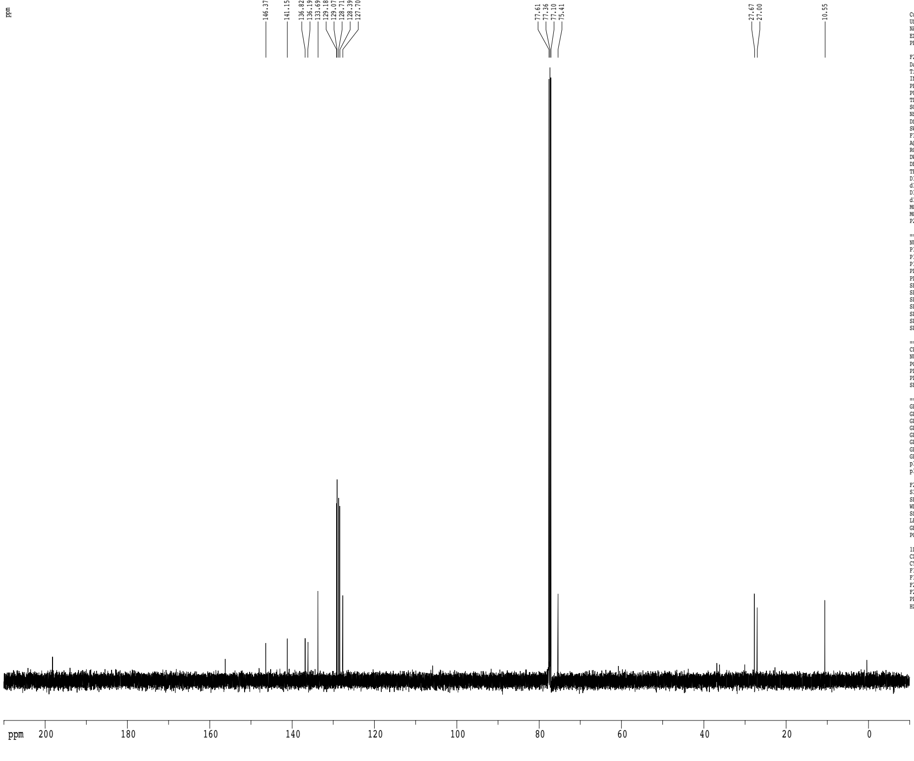
F2 - Acquisition Parameters
Date_           20160429
Time                9.50
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 25640
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.250010 Hz
AQ             1.9999700 sec
RG                 724.1
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300211 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               3401.11 Hz
F2P               -0.500 ppm
F2               -200.07 Hz
PPMCM            0.39474 ppm/cm
HZCM           157.94608 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              lhanna
NAME     LEH-6-228-c1-f11-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160429
Time               14.02
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   801
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  8192
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

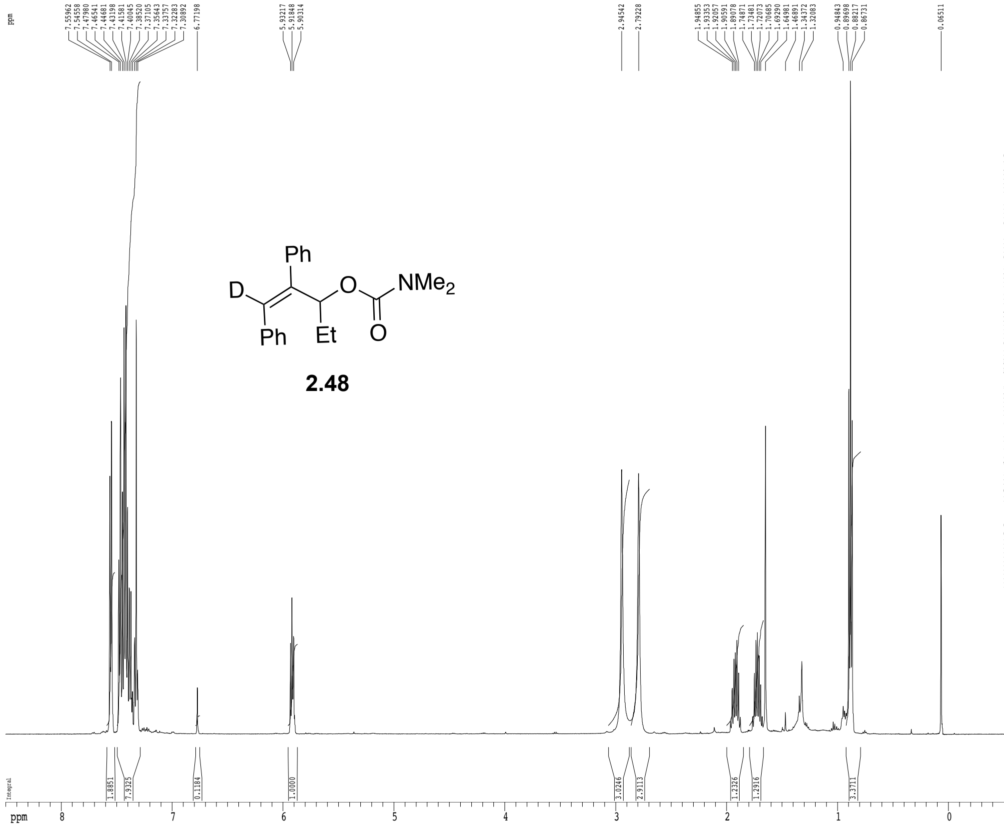
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803829 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              210.000 ppm
F1              26413.88 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            9.64912 ppm/cm
HZCM          1213.67041 Hz/cm
```

1H spectrum



2.48

```
Current Data Parameters
USER              lhanna
NAME         LEH-7-009-H1
EXPNO                  1
PROCNO                 1

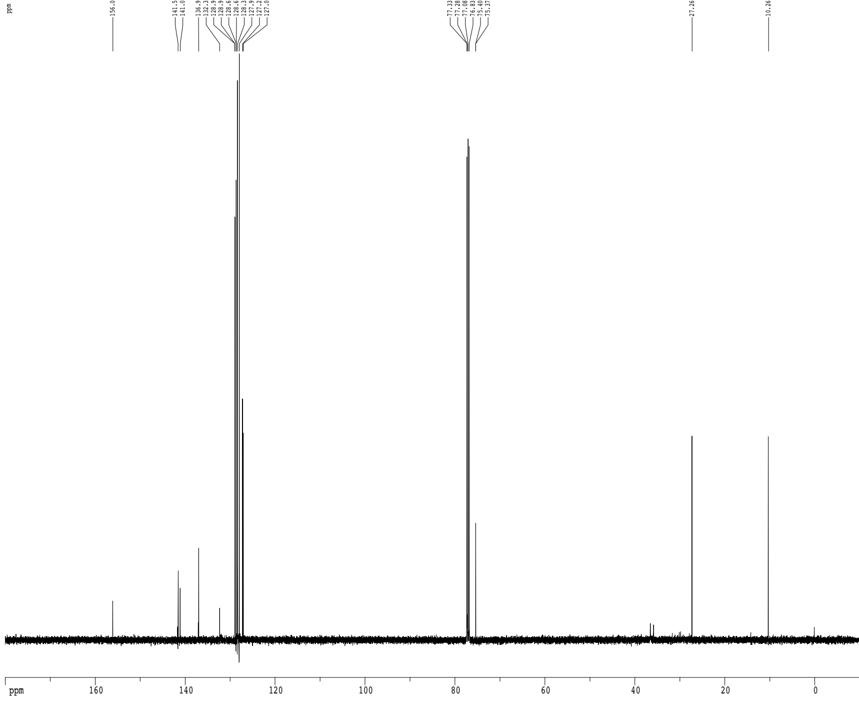
F2 - Acquisition Parameters
Date_           20160623
Time               10.59
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 16022
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.500114 Hz
AQ             0.9998228 sec
RG                  12.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               4251.87 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              lhanna
NAME        LEH-7-009-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160623
Time               10.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

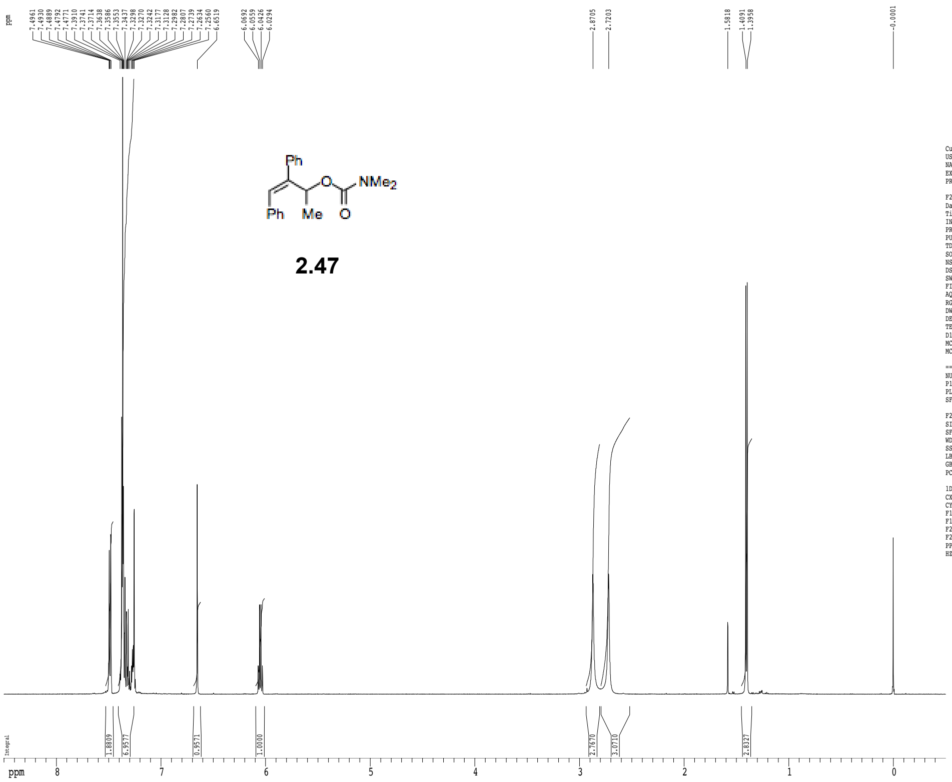
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804190 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.17017 Hz/cm
```

1H spectrum



2.47

```
Current Data Parameters
USER               mkonev
NAME     MOK-IV-172hchar
EXPNO                   1
PROCNO                  1

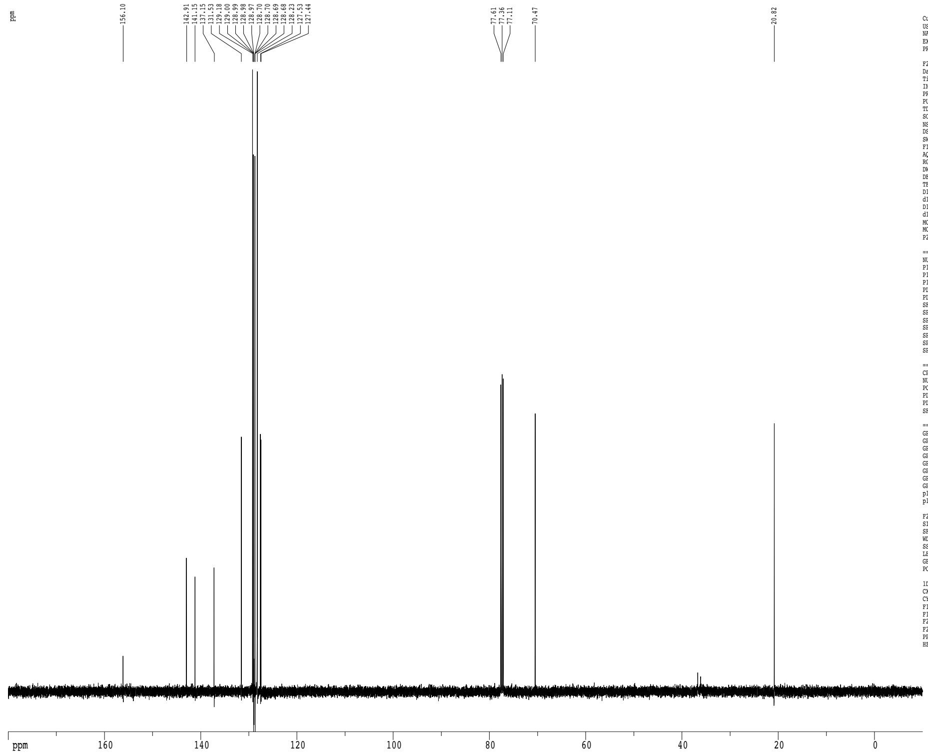
F2 - Acquisition Parameters
Date_            20160517
Time                15.59
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  32048
SOLVENT           CDCl3T
NS                      8
DS                      2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                    6.3
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200335 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 8.500 ppm
F1                4251.87 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.39474 ppm/cm
HZCM            197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER               mkonev
NAME     MOK-IV-172cchar
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160517
Time                16.02
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    273
DS                     16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                   4096
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

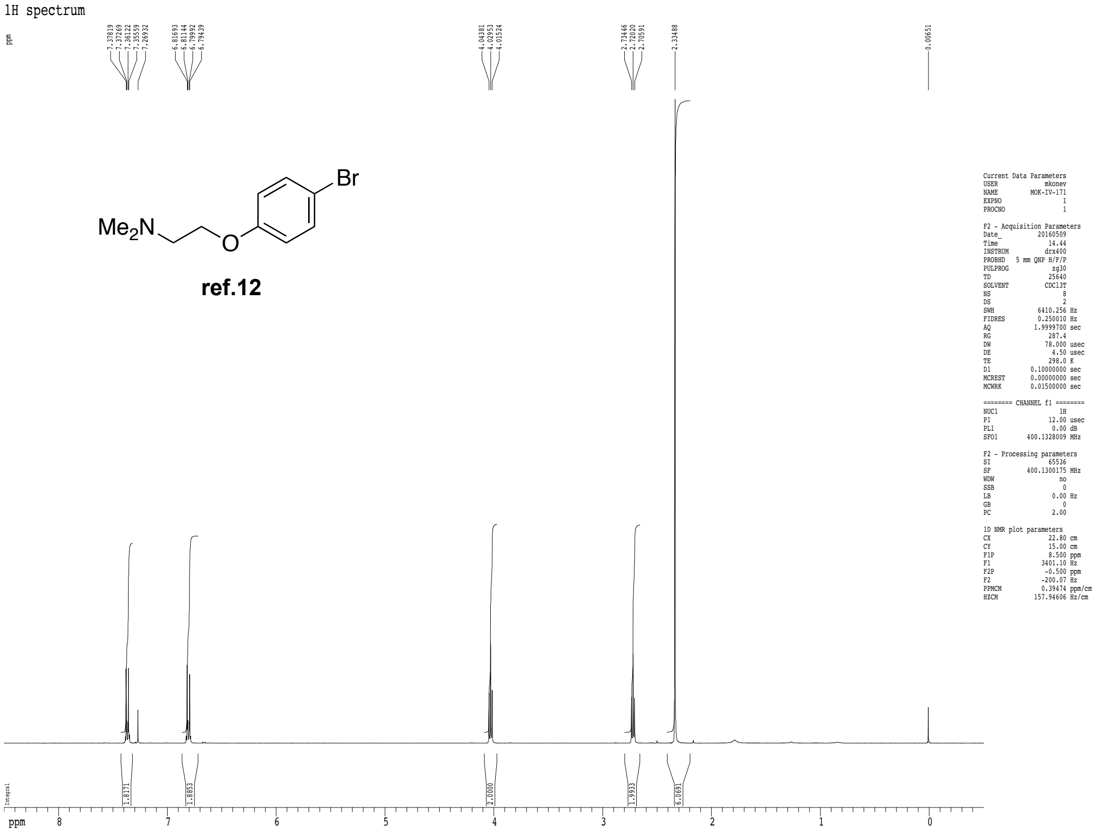
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7803838 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               180.000 ppm
F1               22640.47 Hz
F2P               -10.000 ppm
F2               -1257.80 Hz
PPMCM             8.33333 ppm/cm
HZCM           1048.16992 Hz/cm
```



ref.12

```
Current Data Parameters
USER              mkonev
NAME          MOK-IV-171
EXPNO                  1
PROCNO                 1

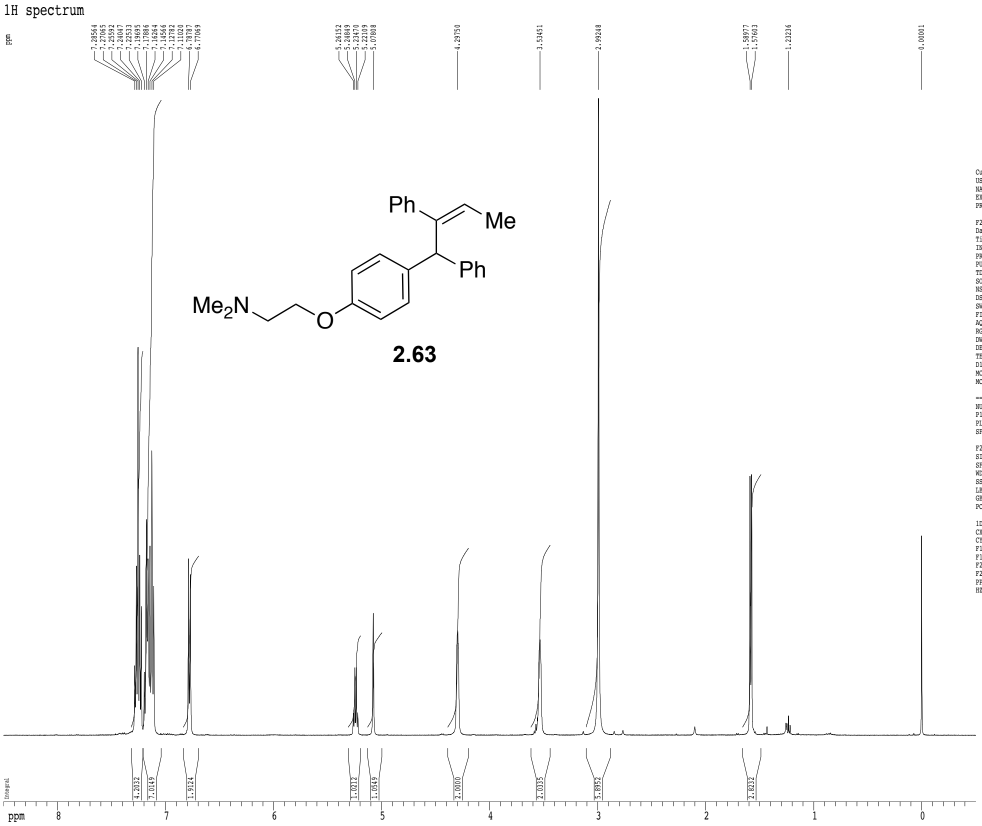
F2 - Acquisition Parameters
Date_           20160509
Time               14.44
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 25640
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.250010 Hz
AQ             1.9999700 sec
RG                 287.4
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               3401.10 Hz
F2P               -0.500 ppm
F2               -200.07 Hz
PPMCM            0.39474 ppm/cm
HZCM           157.94606 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER               mkonev
NAME        MOK-IV-sn2ch2
EXPNO                   1
PROCNO                  1

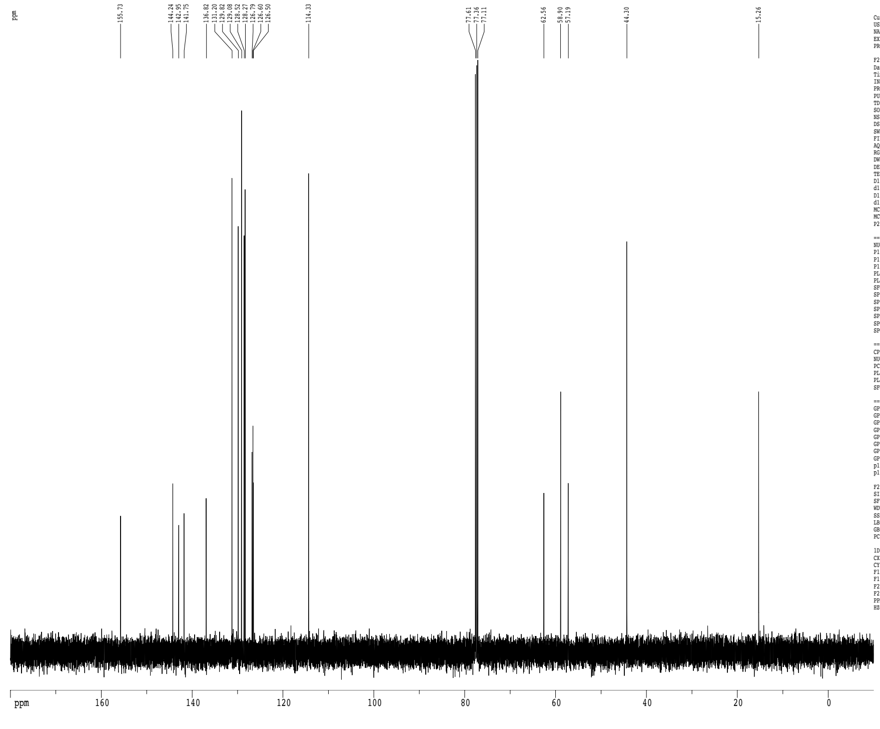
F2 - Acquisition Parameters
Date_            20160912
Time                13.45
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998774 sec
RG                      9
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200331 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 8.500 ppm
F1                4251.87 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.39474 ppm/cm
HZCM            197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER               mkonev
NAME          MOK-IV-sn2c
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160912
Time                13.43
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT            CDCl3T
NS                     79
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                 4597.6
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

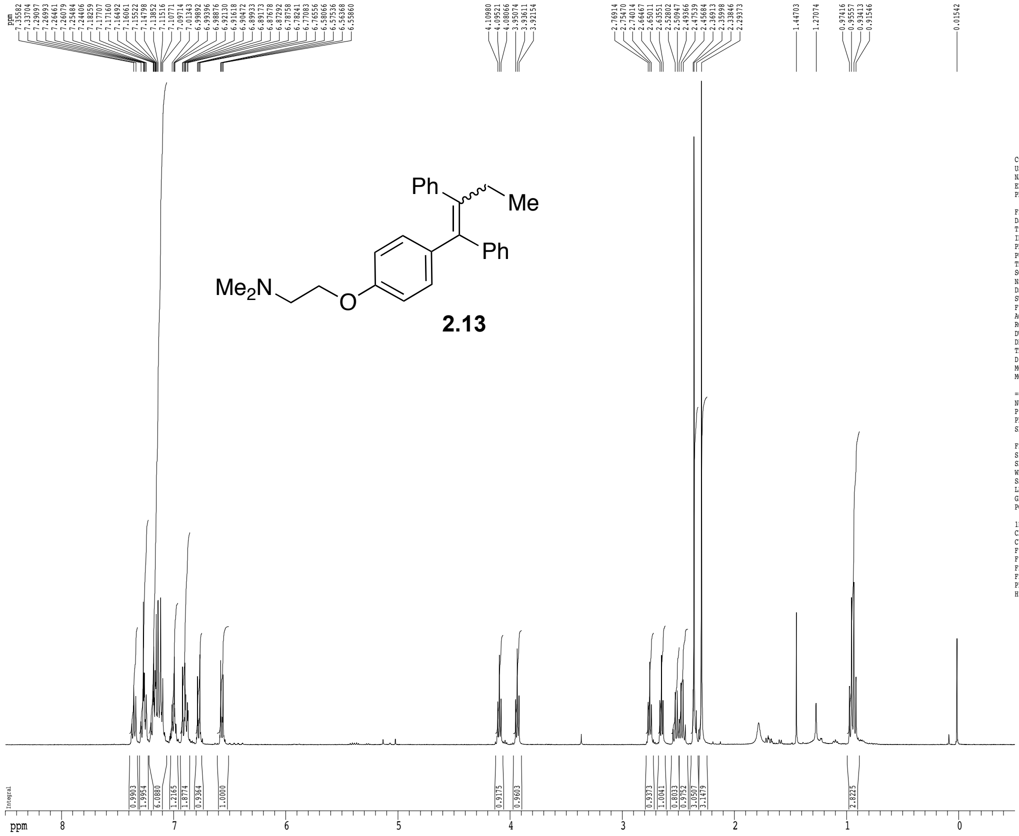
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7803833 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               180.000 ppm
F1               22640.47 Hz
F2P               -10.000 ppm
F2               -1257.80 Hz
PPMCM             8.33333 ppm/cm
HZCM           1048.16992 Hz/cm
```

1H spectrum



2.13

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Current Data Parameters
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NAME      MOK-IV-197conc
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
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Time               13.32
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 32050
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6410.256 Hz
FIDRES          0.200008 Hz
AQ             2.4999499 sec
RG                 228.1
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.500 ppm
F1               3401.10 Hz
F2P               -0.500 ppm
F2               -200.07 Hz
PPMCM            0.39474 ppm/cm
HZCM           157.94606 Hz/cm
```

Chapter 3

Intramolecular Nickel-Catalyzed Reductive Cross-Electrophile Coupling Reactions of Benzylic Esters with Aryl Halides

3.1 Introduction

Nickel-catalyzed reductive cross-electrophile coupling reactions have recently undergone rapid advances in synthetic utility and mechanistic understanding.[1] Their mild reaction conditions can provide advantages to traditional cross-coupling reactions. For example, reductive coupling reactions offer an attractive strategy toward intramolecular cyclization reactions because they do not require installation of both electrophilic and organometallic functional groups into the starting material.[2] We envisioned a cross-electrophile reductive coupling reaction would provide straightforward synthesis of 1-arylindanes and tetralins, common motifs in natural products and pharmaceutical agents (Scheme 3.1).[3,4] While intermolecular reductive coupling reactions have undergone rapid development in recent years,[1,5] few intramolecular variants have been reported. The Peng group disclosed a stoichiometric nickel-catalyzed reductive coupling reaction to access nitrogen- and oxygen-containing heterocycles (Scheme 3.2a).[6] In 2014, Gong and coworkers

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[1] (a) Knappke, E. I. C.; Grupe, G.; Gartner, D.; Corpet, M.; Gosmini, C.; Wangelin, A. J. V. *Chem. Eur. J.* **2014**, *20*, 6828. (b) Weix, D. *Acc. Chem. Res*. **2015**, *48*, 1767. (c) Moragas, T.; Correa, A.; Martin, R. *Chem. Eur. J.* **2014**, *20*, 8242. (d) Gu, J.; Wang, X.; Xue, W.; Gong, H. *Org. Chem. Front.* **2015**, *2*, 1141.

[2] Traditional cross-coupling reactions have had a transformative impact on synthesis. For reviews, see: (a) Bulger, P. G.; Sarlah, D.; Nicolaou, K. C. *Angew. Chem. Int. Ed.* **2005**, *44*, 4442. (b) Chemler, S. R.; Trauner, D.; Danishefsky, S. J. *Angew. Chem. Int. Ed*. **2001**, *40*, 4544.

[3] For lead references in alternative methods for synthesis of indanes and tetralins, see: (a) Parham, W. E.; Bradsher, C. K.; Reames, D. C. *J. Org. Chem.* **1981**, *46*, 4804. (b) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc*. **1989**, *111*, 314. (c) Bailey, W. F.; Longstaff, S. C. *J. Org. Chem.* **1998**, *63*, 432. (d) Segura, J. L.; Martin, N. *Chem. Rev.* **1999**, *99*, 3199. (f) Begouin, J-M.; Capitta, F.; Wu, X.; Niggemann, M. *Org. Lett*, **2013**, *15*, 1370. (g) Wang, Y.-M.; Bruno, N. C.; Placeres, A. L.; Zhu, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **2015**, *137*, 10524.

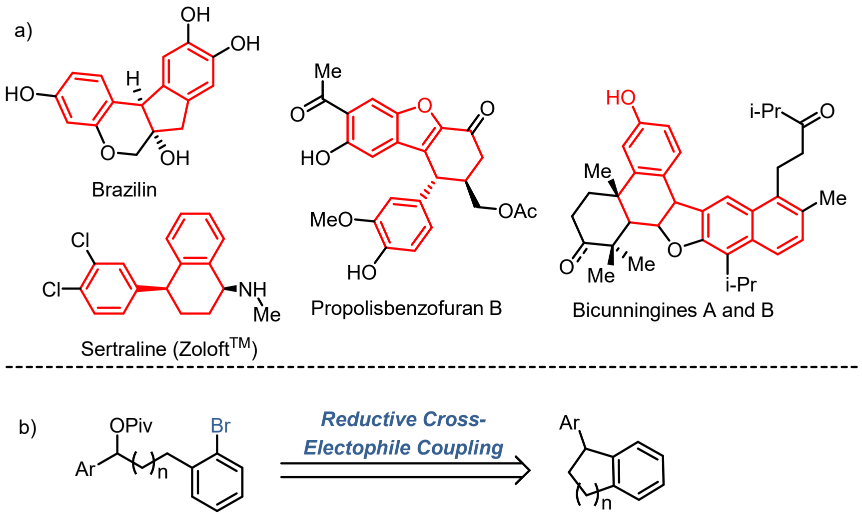
[4] For representative nickel-catalyzed reactions that generate indanes, see: (a) Deng, R.; Sun, L.; Li, Z. *Org. Lett.*, **2007**, *9*, 5207. (b) Watson, M. P.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2008**, *130*, 12594. (c) Arp, F. O.; Fu, G. C. *J. Am. Chem. Soc*. **2005**, *127*, 10482.

[5] For lead references, see: (a) Kadunce, N. T.; Reisman S. E. *J. Am. Chem. Soc.* **2015**, *137*, 10480. (b) Ackerman, L. K. G.; Lovell, M. M.; Weix, D. J. *Nature* **2015**, *524*, 454.

[6] Yan, C. S.; Peng, Y.; Xu, X. B.; Wang, Y. W. *Chem. Eur. J.* **2012**, *18*, 6039.

reported a catalytic intramolecular cyclization of dihaloalkanes to access 5- and 6-membered rings (Scheme 3.2b).[7] Recently, much interest has focused on the use of C–O electrophiles in reductive coupling reactions.[8,9] Our laboratory has reported a reductive ring-contraction of 4-chlorotetrahydropyrans to generate cyclopropanes (Scheme 3.2c).[10] To further expand the scope of intramolecular cross-electrophile coupling reactions, we targeted cyclization reactions of benzylic esters with aryl halides to afford valuable indanes and tetralins (Scheme 3.2d). These reactions would also complement recent efforts to develop intermolecular reductive coupling reactions to include alcohol derivatives.[11] In this chapter we report the intramolecular reductive cross-electrophile coupling reactions of benzylic pivalates with aryl halides and provide evidence for a stereospecific cyclization reaction.

Scheme 3.1. Intramolecular Reductive Cross-Electrophile Coupling Reaction for The Synthesis of Indanes and Tetralins.



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[7] Xue, W.; Xu, H.; Liang, Z.; Qian, Q.; Gong, H. *Org. Lett.* **2014**, *16*, 4984.

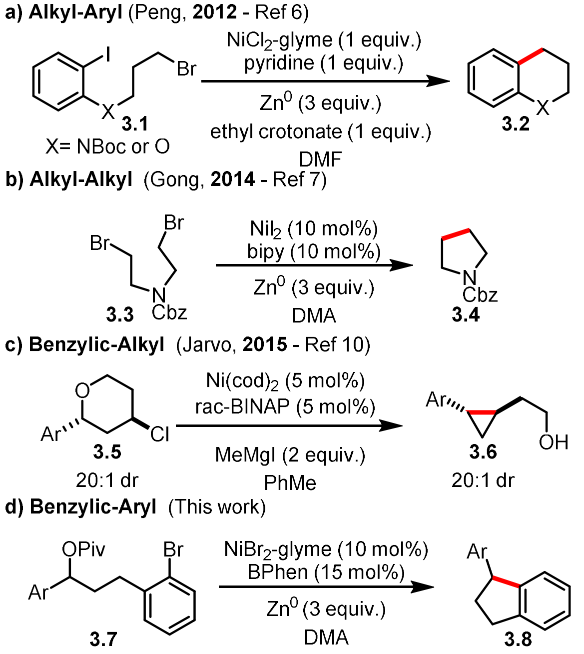
[8] (a) Weix, D. *Acc. Chem. Res*. **2015**, *48*, 1767. (b) Moragas, T.; Correa, A.; Martin, R. *Chem. Eur. J.* **2014**, *20*, 8242. (c) Gu, J.; Wang, X.; Xue, W.; Gong, H. *Org. Chem. Front.* **2015**, *2*, 1141.

[9] For intermolecular reductive coupling reactions of benzylic alcohol derivatives, see: (a) Correa, A.; Leon, T.; Martin, R. *J. Am. Chem. Soc.* **2014**, *136*, 1062. (b) Ackerman, L. K. G.; Anka-Lufford, L. L.; Naodovic, M.; Weix, D. J. *Chem. Sci.* **2015**, *6*, 1115.

[10] Tollefson, E. J.; Erickson, L. W.; Jarvo, E. R. *J. Am. Chem. Soc.* **2015**, *137*, 9760.

[11] For intermolecular reductive coupling of allylic esters with halides, see: Anka-Lufford, L. L.; Prinsell, M. R.; Weix, D. J. *J. Org. Chem.* **2012**, *77*, 9989. (b) Cui, X.; Wang, S.; Zhang, Y.; Deng, W.; Qian, Q.; Gong, H. *Org. Biomol. Chem.* **2013**, *11*, 3094.

Scheme 3.2. Nickel-Catalyzed Intramolecular Reductive Cross-Electrophile Coupling Reactions



3.2 Development of Nickel-Catalyzed Reductive Cross-Electrophile Coupling

We designed secondary benzylic pivalate **3.9** as a model substrate, based on our previous work in cross-coupling reactions of benzylic electrophiles.[12] These substrates are easily prepared by lithiation of an arene and addition into the corresponding bromophenyl aldehyde. Additionally, benzylic pivalate esters are less reactive than their halide counterparts. Reaction of **3.9** in the presence of catalytic quantities of $NiBr_2$-glyme, bathophenanthroline (BPhen), and Zn^0 provided desired product **3.10** in excellent yield with negligible yields of hydrodehalogenation (Table 3.1, entry 1). Less sterically encumbered esters, such as acetate, provided lower conversion under the reaction conditions (entry 2). Alternative reducing agents such as Mn^0 also led to lower yields (entry 3). Utilizing phosphine and other aromatic nitrogen-containing ligands, such as bipy or pybox, resulted in a dramatic decrease in product formation (entries 4–7). In the absence of a ligand

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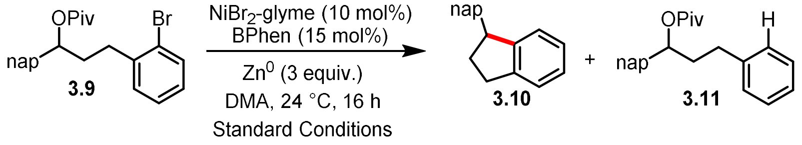
[12] Tollefson, E. J.; Hanna, L. E.; Jarvo, E. R. *Acc. Chem. Res.* **2015**, *48*, 2344. For a related transformation, see: Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 3307.

or a nickel catalyst, the desired cyclization does not occur (entries 8 and 9). Additives known to promote reactivity in other reductive cross-electrophile coupling reactions were also examined.[13] The addition of either pyridine or NaI favored hydrodehalogenation (entries 10 and 11).

Table 3.1. Optimization of reductive coupling reaction conditions



Entry	Variation From Standard Conditions	Recovered **3.9** (%)[a]	**3.10** (%)[a]	**3.11** (%)[a]
1	none	<2	90	<2
2	Ac instead of Piv	59	9	13
3	Mn instead of Zn	80	<2	<2
4	dppf instead of BPhen	26	25	49
5	bipy instead of BPhen	20	42	25
6	terpyridine instead of BPhen	86	<2	3
7	pybox instead of BPhen	98	<2	<2
8	no ligand	100	<2	<2
9	no $NiBr_2$-glyme	93	<2	<2
10	pyridine (40 mol%)	25	4	61
11	NaI (25 mol%)	<2	25	68
12	$NiCl_2$-glyme instead of $NiBr_2$-glyme	12	79	4
13	DMF instead of DMA	<2	44	35

[a]Determined by ^1H NMR spectroscopy using PhTMS as internal standard.

3.3 Scope of Intramolecular Reductive Coupling

Having established conditions for the cyclization of model substrate **3.9**, we set out to investigate the scope of the transformation (Table 3.2). Cyclization of a series of naphthylic esters provides tetralins **3.12** and **3.14**, which correspond to the core of bicunningines A and B,[14] and tetracyclic indanes **3.10, 3.13,** and **3.15.** Benzofuran and benzothiophene moieties were well-tolerated, providing good yields for both indanes and tetralins (**3.16–18, 3.20–21**). Additionally, substrates containing N-heterocycles were found to undergo the desired cyclization. Pyridine-

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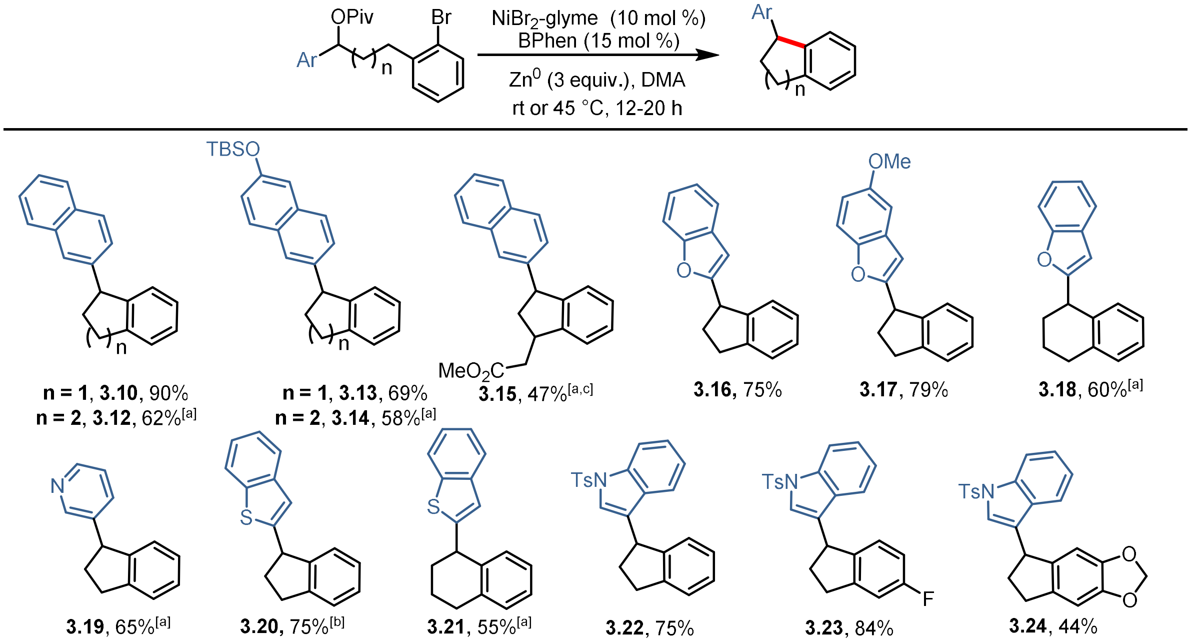
[13] (a) Everson, D. A.; Shrestha, R.; Weix, D. J. *J. Am. Chem. Soc.* **2010**, *132*, 920. (b) Cherney, A. H.; Reisman, S. E. *J. Am. Chem. Soc.* **2014**, *136*, 14365.

[14] Hou, X.-F.; Yao, S.; Mandi, A.; Kurtan, T.; Tang, C.-P.; Ke, C.-Q.; Li, X.-Q.; Ye, Y. *Org. Lett.* **2012**, *14*, 460.

substituted indane **3.19** can be synthesized in 65% yield and *N*-tosylindoles **3.22–24** were obtained in good yields. Substrates containing methoxy-, fluoro-, silyl- and ester substituents were also well-tolerated under the reaction conditions. Notably, these cyclization reactions proceed smoothly without the aid of a Thorpe-Ingold effect.[15]

Table 3.2. Scope of intramolecular cross-electrophile coupling



[a]Reaction run with 15 mol% NiBr$_2$-glyme and 45 °C. [b]Reaction run at 45 °C. [c]Both sm and product are 1:1 dr.

3.4 Scope of Enantiospecific Intramolecular Reductive Coupling

Finally, we sought to determine whether the intramolecular cyclization could proceed in an enantiospecific fashion. While several examples of stereoconvergent reductive coupling reactions have been reported,[16] to the best of our knowledge, there is only one example of an enantiospecific reductive coupling reaction.[8] Subjecting **(*R*)-3.9** to the optimized conditions afforded **(*S*)-3.10** in 90% yield in 88% enantiomeric excess with 92% enantiospecificity (Table

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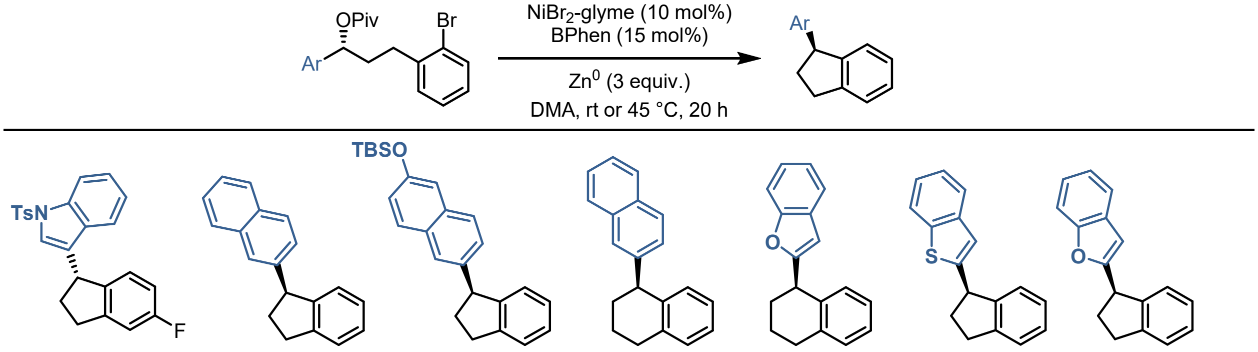
[15] Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc. Trans.* **1915**, *107*, 1080.

[16] Cui, X.; Wang, S.; Zhang, Y.; Deng, W.; Qian, Q.; Gong, H. *Org. Biomol. Chem.* **2013**, *11*, 3094. Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 7442. Cherney, A. H.; Reisman, S. E. *J. Am. Chem. Soc*. **2014**, *136*, 14365. Kadunce, N. T.; Reisman S. E. *J. Am. Chem. Soc.* **2015**, *137*, 10480. Ackerman, L. K. G.; Anka-Lufford, L. L.; Naodovic, M.; Weix, D. J. *Chem. Sci.* **2015**, *6*, 1115.

3.3). Based on comparison of **(*S*)-3.10** to literature values, [17,18] the reductive cross-electrophile coupling reaction proceeds with inversion at the benzylic center. Indane **3.13** was also formed with high enantiospecificy, as was tetralin **3.12**. Notably, all three of these substrates contain the naphthylic ether moiety which we hypothesize is prone to rapid and stereospecific oxidative addition reactions. [12] Substrates wherein the ester is activated by a heterocycle such as benzofuran, benzothiophene, or indole provided lower enantiospecificity.[19] This change in stereoselectivity likely correlates to a change in the reaction mechanism. Investigation of the mechanistic details is ongoing.

Table 3.3. Nickel-catalyzed stereospecific reductive cyclization



(*S*)-**3.23**	(*S*)-**3.10**	(*S*)-**3.13**	(*S*)-**3.12**	(*S*)-**3.18**	(*S*)-**3.20**	(*S*)-**3.16**
75% yield	90% yield	69% yield	62% yield	60% yield	75% yield	69% yield
0% es^{a,b}	92% es^{a}	96% es^{a}	83% es^{a}	50% es^{c}	0% es^{a}	28% es^{a}

a) NiBr$_2$-glyme (10 mol%), rt. b) Starting material 23% ee c) NiBr$_2$-glyme (15 mol%), 45 °C

3.5 Conclusion

In summary, the intramolecular reductive cyclization for the synthesis of indanes and tetralins has been developed. The reactions are tolerant of a variety of heterocycles and functional groups. We have also demonstrated stereospecific cross-electrophile coupling reactions of benzylic esters for synthesis of enantioenriched 1-arylindanes and tetralins.

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[17] (a) Yu, N-U.; Xu, M-H. *J. Org. Chem.* **2013**, *78*, 2736. (b) Yue, G.; Lei, K.; Hirao, H.; Zhou, J. *Angew. Chem. Int. Ed.* **2015**, *54*, 6531.

[18] For complete details, see the experimental details.

[19] When enantioenriched starting materials were employed, products **3.16**, **3.18**, **3.20**, and **3.23** were formed with <50% es. For details, see the experimental details.

3.6 Experimental Details

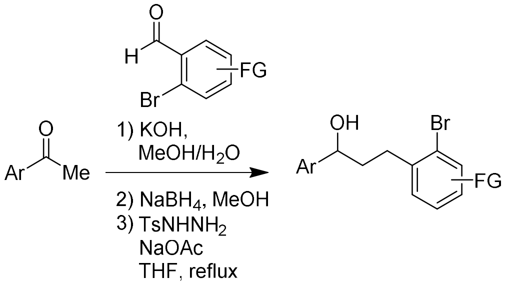
General Procedures

All reactions were carried out under an atmosphere of N_2, or Ar when noted. All glassware was oven- or flame-dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and dimethylacetamide (DMA) were degassed with Ar and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 ºC for 12 h) to remove H_2O. All other solvents utilized were purchased "anhydrous" commercially, or purified as described. ^{1}H NMR spectra were recorded on Bruker DRX-400 (400 MHz ^{1}H, 100 MHz ^{13}C, 376.5 MHz ^{19}F) or CRYO-500 (500 MHz ^{1}H, 125.7 MHz ^{13}C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), triplet (t), doublet of triplets (dt), doublet of doublet of triplets (ddt), triplet of triplets (tt), quartet (q), quintet (quin), apparent doublet (ad), apparent triplet (at), multiplet (m)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 ºC. Infrared (IR) spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm $^{-1}$). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F_{254} precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with $KMnO_4$, ceric ammonium molybdate (CAM), or *p*-anisaldehyde (PAA) solutions. Flash chromatography was performed using Silica Gel 60 (170-400 mesh) from Fisher Scientific. Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Automatic Polarimeter. SFC determinations of enantiopurity were performed on a Berger Analytical instrument using a Daicel™ Chiralpak® column (OD-H, OJ-H, or AD-H; 100 bar, 50 °C, 215 nm). High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. Nickel(II) bromide ethylene glycol dimethyl ether complex was purchased from Aldrich, stored in a glovebox under an atmosphere of N_2, and used as received. Zinc powder (100 Mesh) was purchased from Alfa Aesar and used as received. All other reagents were purchased commercially and used as received.

General methods for starting material synthesis

The general methods for starting material synthesis will be used throughout the rest of the SI. In each instance a general method is used, it is specified by letter (A, B, etc.) and the exact amounts of reagents used for each reaction are listed for the specific compounds synthesized.

METHOD A: ALDOL CONDENSATION, SODIUM BOROHYDRIDE REDUCTION, AND DIIMIDE REDUCTION



The products were prepared according to a modified procedure reported by Franzen.[20] To a 250 mL round bottom flask equipped with a stir bar was added ketone (1.0 equiv), aldehyde (1.0 equiv), KOH (2.0 equiv), and MeOH (30 mL). The reaction was stirred overnight at room temperature. The resulting solid was filtered, washed with water, dried by vacuum filtration, and taken on to

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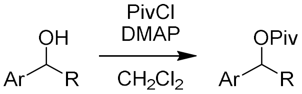
[20] Wang, Y.; Franzen, R. *Synlett.*, **2012**, *23*, 925.

the next step without further purification. The unpurified chalcone was taken up in MeOH (50 mL) and $NaBH_4$ (1.2 equiv) was added in two portions over 10 minutes. Upon complete reaction of starting material, as judged by TLC, the mixture was quenched with careful addition of saturated NH_4Cl (15 mL). EtOAc (50 mL) was added, the layers were separated, and the aqueous layer was extracted with EtOAc (3 x 30 mL). The organic extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure and the unpurified allylic alcohol was taken on to the next step without further purification. The unpurified residue was dissolved in THF (100 mL) and tosylhydrazide (4.0 equiv) and NaOAc•3H_2O (4.0 equiv) were added. The reaction vessel was equipped with a reflux condenser and the mixture was heated at reflux for 24 hours. The mixture was cooled to room temperature and quenched with H_2O (30 mL), and the aqueous layer was extracted with EtOAc (3 x 40 mL). The organic extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The product was then purified by flash column chromatography.

METHOD B: PIVALATION OF BENZYLIC ALCOHOLS



The product was prepared according to a modified procedure reported by Martin.[21] To a solution of benzylic alcohol (1.0 equiv) in CH_2Cl_2 (20 mL) was added pivaloyl chloride (1.1 equiv) and dimethylaminopyridine (1.1 equiv). The reaction was allowed to stir overnight at room temperature. The reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The organic extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography.

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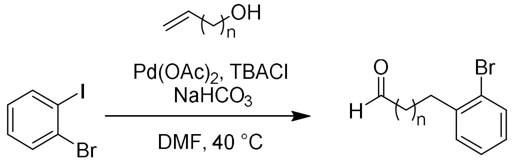
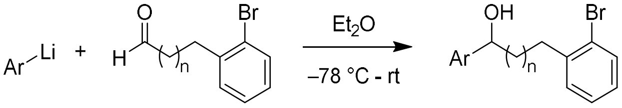
[21] Zarate, C.; Martin, R. *J. Am. Chem. Soc.*, **2014**, *136*, 2236

METHOD C: HECK REACTION FOR THE PREPARATION OF 2-BROMOPHENYLALDEHYDES



The product was prepared according to a modified procedure reported by Tietze.[22] A flame-dried 100 mL round bottom flask equipped with a stir bar and septum was charged with TBACl (1.0 equiv), $NaHCO_3$ (2.5 equiv), $Pd(OAc)_2$ (0.05 equiv), and dry DMF (30 mL). The mixture was stirred for 5 minutes followed by simultaneous addition of 1,2-iodobromobenzene (1.0 equiv), and alkenol (1.5 equiv). The reaction mixture was heated to 40 °C and stirred for 30 hours. The reaction was slowly quenched with saturated NH_4Cl (25 mL) and extracted with EtOAc (3 x 30 mL). The organic extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography.

METHOD D: ARENE LITHIATION/LITHIUM-HALOGEN EXCHANGE, THEN ADDITION INTO ALDEHYDE



The product was prepared according to a modified procedure reported by O'Doherty.[23] A flame-dried 25 mL round bottom flask equipped with a stir bar and septum was charged with Et_2O (6 mL) and arene (1.3 equiv) and cooled to –78 °C. *n*-BuLi (2.5 M in hexanes, 1.4 equiv) was added dropwise over 10 minutes. The mixture was stirred cold for 30 minutes and then allowed to warm to room temperature and stir for an additional 20 minutes. A separate flask of requisite aldehyde

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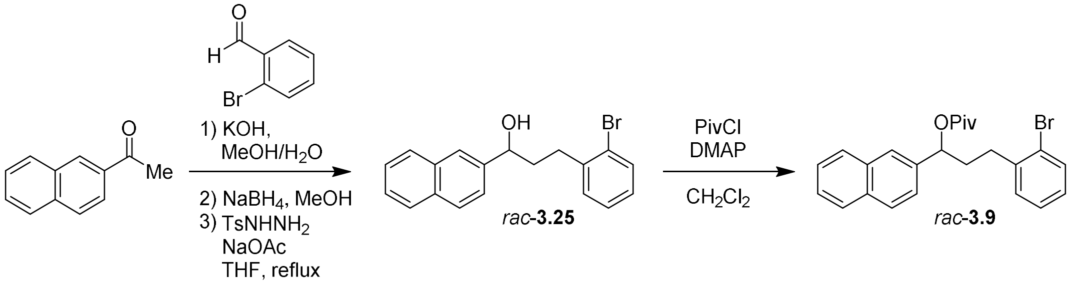
[22] Tietze, L. F.; Hungerland, T.; Dufert, A.; Objartel, I.; Stalke, D. *Chem. Eur. J.*, **2012**, *18*, 3286

[23] Guo, H.; O'Doherty, G.A. *Org. Lett.* **2006**, *8*, 1609

(1.0 equiv) dissolved in Et_2O (10 mL) was cooled to –78 °C. The solution of aryl lithium was added dropwise over 30 minutes to the aldehyde. The reaction was warmed to room temperature overnight. The mixture was quenched with saturated NH_4Cl (15 mL). Layers separated and the aqueous layer was extracted with EtOAc (3 x 25 mL). The organic extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography.

SYNTHESIS AND CHARACTERIZATION OF STARTING MATERIALS FOR TABLE 3.2

Scheme 3.3: Synthesis of starting material for formation of *rac*-3.10 (Table 3.2)

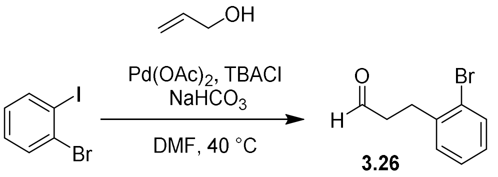


rac-**3.25**The product was prepared according to general method A using 2-acetonaphthone (3.4 g, 20 mmol), 2-bromobenzaldehyde (2.3 mL, 20 mmol), and KOH (2.2 g, 40 mmol). Then $NaBH_4$ (1.0 g, 25 mmol), tosylhydrazide (15 g, 80 mmol) and NaOAc•$3H_2O$ (11 g, 80 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (6.2 g, 18 mmol, 91% over 3 steps). **TLC R$_f$** = 0.6 (10% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.78 (m, 4H), 7.54–7.43 (m, 4H), 7.24–7.18 (m, 2H), 7.04 (ddd, *J* = 8.1, 6.2, 3.3 Hz, 1H), 4.89 (t, *J* = 6.4 Hz, 1H), 2.97–2.76 (m, 2H), 2.22–2.09 (m, 2H), 2.05 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.9, 141.3, 133.5, 133.3, 133.1, 130.7, 128.6, 128.2, 127.92, 127.90, 127.7, 126.4, 126.1, 124.9, 124.7, 124.3, 74.3, 39.0, 32.8; **IR** (neat) 3365, 3054, 2929, 1601, 1470, 1021 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{17}BrONa$ (M + Na)$^+$ 363.0360, found 363.0368.

rac-**3.9.** The product was prepared according to general method B using *rac*-**3.25** (1.7 g, 5.0 mmol), pivaloyl chloride (0.68 mL, 5.5 mmol, 1.1 equiv) and dimethylaminopyridine (0.67 g, 5.5 mmol, 1.1 equiv). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (1.7 g, 4.1 mmol, 82%). **TLC R$_f$** = 0.7 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.74 (m, 4H), δ 7.52–7.39 (m, 4H), δ 7.22–7.11 (m, 2H), 7.00 (t, *J* = 7.0 Hz, 1H), 5.95 (t, *J* = 6.5 Hz, 1H), 2.94–2.68 (m, 2H), 2.36–2.11 (m, 2H), 1.26 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 140.9, 138.2, 133.5, 133.3, 133.2, 130.6, 128.7, 128.3, 128.1, 128.0, 127.8, 126.5, 126.3, 125.8, 124.6, 124.3, 75.5, 39.2, 36.9, 32.8, 27.5; **IR** (neat) 3055, 2969, 1725, 1471, 1279, 1147, 1025 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{24}H_{25}BrO_2Na$ (M + Na)$^+$ 447.0936, found 447.0926.

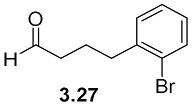
Synthesis of building blocks 3.26 and 3.27.

Aldehydes **3.26** and **3.27** were employed as building blocks in the synthesis of the starting materials for compounds **3.12 and 3.13, 3.18-21** (Table 3.2).



3.26 The product was prepared according to general method C using TBACl (5.6 g, 20.0 mmol), $NaHCO_3$ (4.2 g, 50 mmol), $Pd(OAc)_2$ (0.11 g, 0.5 mmol), iodobromobenzene (2.6 mL, 20 mmol, 1.0 equiv), and allyl alcohol (2.1 mL, 30 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (2.4 g, 10 mmol, 52%). Analytical data is consistent with literature values.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ

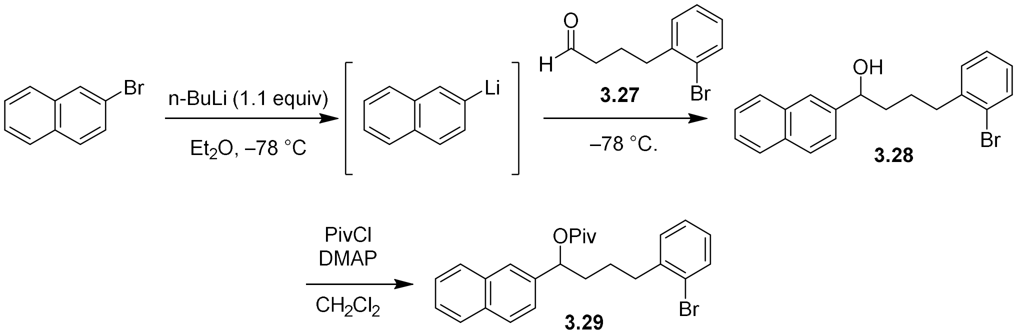
9.84 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.28–7.20 (m, 2H), 7.08 (q, *J* = 4.1 Hz, 1H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H).



3.27

3.27 The product was prepared according to general method C using TBABr (6.5 g, 20.0 mmol), $NaHCO_3$ (4.2 g, 50 mmol), $Pd(OAc)_2$ (0.11 g, 0.5 mmol), iodobromobenzene (2.6 mL, 20 mmol, 1.0 equiv), and 3-buten-1-ol (2.6 mL, 30 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (2.4 g, 10 mmol, 52%). Analytical data is consistent with literature values.[24] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.25–7.18 (m, 2H), 7.07 (dd, *J* = 7.9, 2.2 Hz, 1H), 2.79 (dt *J* = 7.5 Hz, 2H), 2.50 (td, *J* = 7.4, 1.5 Hz, 2H), 1.97 (d, *J* = 7.5 Hz, 2H).

Scheme 3.4: Synthesis of starting material for formation of 3.12 (Table 3.2)



3.28 The product was prepared according to general method D using 2-bromonaphthalene (1.25 g, 6.00 mmol), *n*-BuLi (2.6 mL, 2.5 M in hexane, 6.6 mmol), and **3.27** (1.36 g, 6.00 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (1.89 g, 5.31 mmol, 85%).

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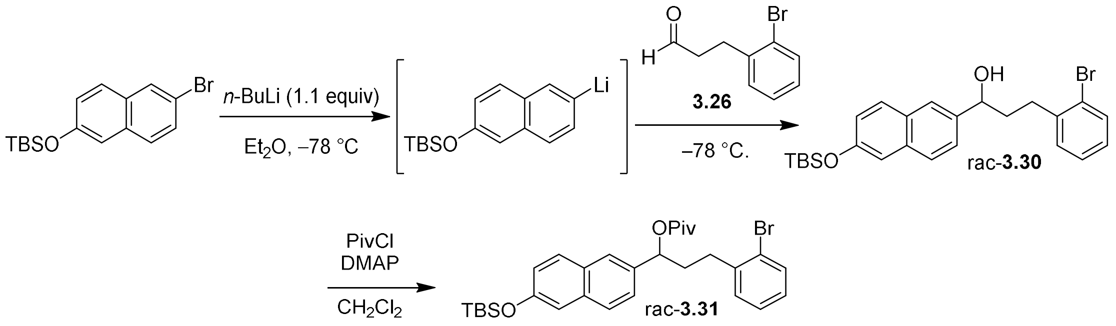
[24] Gibson, S. E.; Jones, J. O.; McCague R.; Tozer, M. J.; Whitcombe, N. J. *Synlett*, **1999**, 954

3.29 The product was prepared according to general method B using *rac*-**3.28** (0.18 g, 0.50 mmol), pivaloyl chloride (0.080 mL, 0.60 mmol) and dimethylaminopyridine (0.80 g, 0.60 mmol). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (0.18 g, 0.40 mmol, 80%). **TLC R_f** = 0.4 (12% Et_2O/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85–7.78 (m, 3H), 7.76 (s, 1H), 7.52–7.41 (m, 4H), 7.19 (td, *J* = 7.2, 1.2 Hz, 1H), 7.14 (dd, *J* = 7.6, 1.27 Hz, 1H), 7.03 (td, *J* = 7.6, 1.9 Hz, 1H), 5.91 (dd, *J* = 8.0, 5.6 Hz, 1H), 2.76 (t, *J* = 7.9 Hz, 2H), 2.07 (dddd, *J* = 13.4, 10.2, 8.0, 5.1 Hz, 1H), 1.93 (ddt, *J* = 13.8, 11.2, 5.6 Hz, 1H), 1.78–1.58 (m, 2H), 1.22 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.8, 141.4, 138.5, 133.3, 133.2, 133.0, 130.5, 128.5, 128.2, 127.8, 127.8, 127.6, 126.3, 126.1, 125.6, 124.6, 124.3, 75.6, 39.0, 36.3, 36.0, 27.4, 26.0; **IR** (neat) 2971, 2866, 1726, 1500, 1279, 1148 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{25}H_{27}BrO_2$ $(M)^+$ 438.1194, found 438.1187.

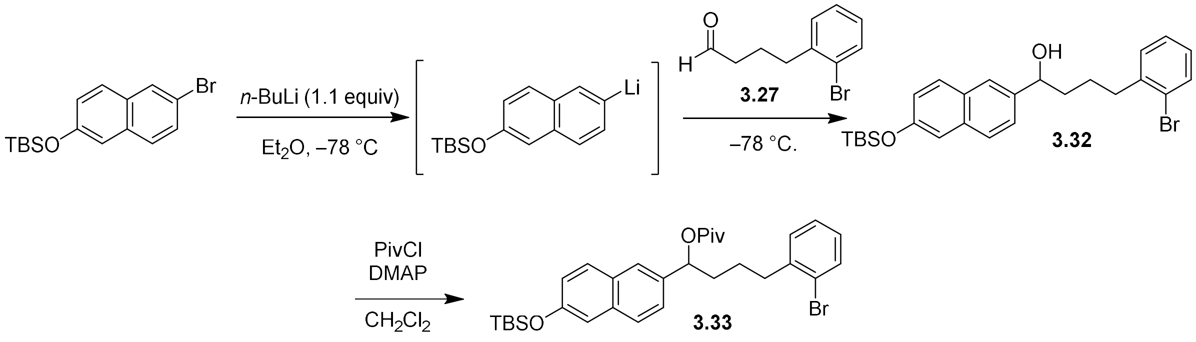
Scheme 3.5: Synthesis of starting material for formation of 3.13 (Table 3.2)



rac-**3.30** The product was prepared according to general method D using 2-bromo-6-(*tert*-butyldimethylsiloxy) naphthalene (2.02 g, 6.00 mmol), *n*-BuLi (2.6 mL, 2.5 M in hexane, 6.6 mmol), and **3.26** (1.4 g, 6.0 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (1.9 g, 4.0 mmol, 67%).

rac-**3.31** The product was prepared according to general method B using *rac*-**3.30** (0.47 g, 1.0 mmol), pivaloyl chloride (0.13 mL, 1.1 mmol) and dimethylaminopyridine (0.13 g, 1.1 mmol). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (0.45 g, 0.81 mmol, 81%). **TLC R$_f$** = 0.5 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.73–7.66 (m, 3H), 7.50 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.22–7.13 (m, 3H), 7.07 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.02 (ddd, *J* = 8.0, 6.9, 2.3 Hz, 1H), 5.91 (dd, *J* = 8.3, 5.3 Hz, 1H), 2.86 (ddd, *J* = 14.0, 11.2, 5.0 Hz, 2H), 2.73 (ddd, *J* = 13.5, 10.7, 5.7 Hz, 2H), 2.35–2.10 (m, 2H), 1.25 (s, 9H), 1.01 (s, 9H), 0.24 (s, 6H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 177.8, 153.9, 140.9, 136.1, 134.5, 133.0, 130.5, 129.6, 129.1, 127.9, 127.7, 127.3, 125.5, 124.54, 124.50, 122.5, 114.9, 75.5, 39.1, 36.7, 32.7, 27.4, 25.9, 18.4, -4.2; **IR** (neat) 2956, 2930, 1728, 1605, 1505, 1261, 1152 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for C$_{30}$H$_{39}$BrO$_3$Si (M + Na)$^+$ 554.1852, found 554.1850.

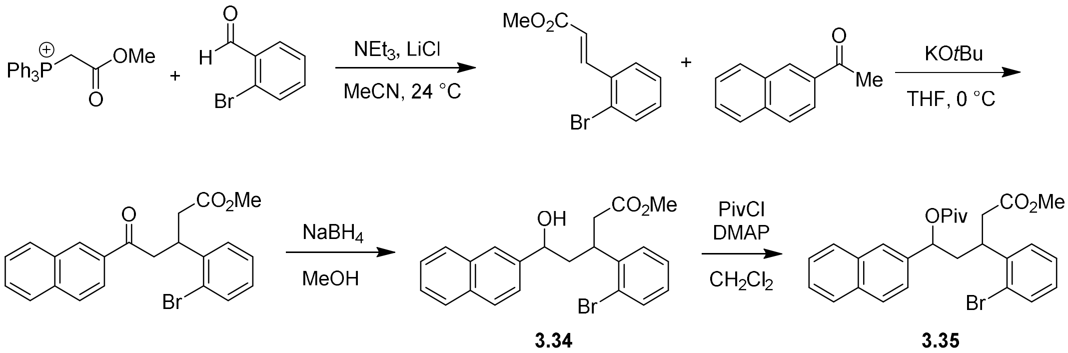
Scheme 3.6: Synthesis of starting material for formation of 3.14 (Table 3.2)



3.32. The product was prepared according to general method D using 2-bromo-6-(*tert*-butyldimethylsiloxy) naphthalene (1.01 g, 3.00 mmol), *n*-BuLi (1.3 mL, 2.5 M in hexane, 3.3 mmol), and **3.27** (0.68 g, 3.0 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (1.4 g, 2.9 mmol, 98%).

3.33 The product was prepared according to general method B using **3.32** (0.75 g, 1.5 mmol), pivaloyl chloride (0.22 mL, 1.8 mmol) and dimethylaminopyridine (0.22 g, 1.8 mmol). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (0.33 g, 0.77 mmol, 96%). **TLC R$_f$** = 0.5 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.70–7.64 (m, 3H), 7.49 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.38 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.19–7.11 (m, 3H), 7.06 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.00 (ddd, *J* = 8.0, 7.0, 2.1 Hz, 1H), 5.88 (dd, *J* = 7.8, 5.6 Hz, 1H), 2.75 (t, *J* = 7.9 Hz, 2H), 2.11–1.85 (m, 2H), 1.80–1.56 (m, 2H), 1.21 (s, 9H), 1.01 (s, 9H), 0.23 (s, 6H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 177.9, 153.9, 141.5, 136.5, 134.5, 133.1, 130.6, 129.7, 129.2, 127.8, 127.7, 127.3, 125.5, 124.7, 122.6, 115.1, 75.8, 39.1, 36.4, 36.1, 27.5, 26.1, 26.0, 18.5, -4.04; **IR** (neat) 2954, 2929, 1726, 1605, 1479, 1260, 1150 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{31}H_{41}BrO_3SiNa$ (M + Na)$^+$ 591.1906, found 591.1910.

Scheme 3.7: Synthesis of starting material for formation of 3.15 (Table 3.2)



3.34 The product was prepared according to a modified procedure reported by Liu.[25] A 100 mL round bottom flask charged with LiCl (0.50 g, 10 mmol, 1.0 equiv) and a Teflon stir bar was flame-dried under vacuum. Once cooled to room temperature, the flask was removed from vacuum and charged with MeCN (50 mL), 2-bromobenzaldehyde (1.2 mL, 10 mmol, 1.0 equiv), trimethyl phosphonoacetate (2.00 mL, 12.5 mmol, 1.25 equiv), and triethylamine (1.4 mL, 10 mmol, 1.0 equiv), then sealed and stirred at 24 °C for 12 hr. The reaction mixture was passed through a cake

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[25] Pan, X.; Liu, Z. *Tetrahedron*, **2014**, *70*, 4602

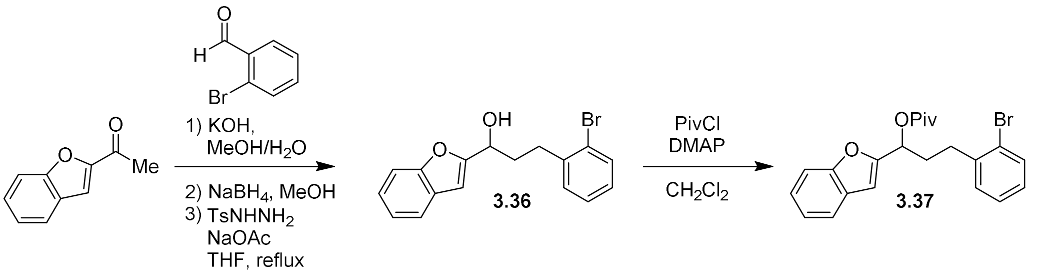
of silica and the solvent was removed under reduced pressure affording a clear, colorless oil that was taken directly to the next step in the synthetic sequence.

A 100 mL round bottom flask containing methyl (*E*)-3-(2-bromophenyl)-acrylate was charged with 2-acetonaphthone (1.7 g, 10 mmol, 1.0 equiv), dissolved in THF (40 mL) and cooled to -5 °C in a brine-ice bath. Following this, potassium *tert*-butoxide (1.2 g, 10 mmol, 1.0 equiv) was added and the reaction was stirred at -5 °C to 0 °C for 3 hrs. The reaction was then quenched with saturated NH_4Cl (20 mL) and extracted with Et_2O (45 mL). The ether layer was then washed with brine and dried over Na_2SO_4, filtered and concentrated under vacuum. The unpurified product was purified by flash column chromatography (gradient: hexanes to 15% Et_2O/hexanes). The fractions containing product were concentrated in a 100 mL round bottom flask, dissolved in MeOH (45 mL), cooled to 0 °C and $NaBH_4$ (0.45 g, 12 mmol 1.2 equiv) was added. The reaction was allowed to warm to room temperature over the course of 30 min and stirred for an additional 2 hr. The unpurified mixture was then concentrated under reduced pressure and the unpurified oil was passed through a cake of silica with ethyl ether to afford the title compound as a pale yellow oil (1.4 g, 3.3 mmol, 33% over 3 steps).

3.35 The product was prepared according to general method B using **3.34** (1.3 g, 3.3 mmol), pivaloyl chloride (0.45 mL, 3.7 mmol) and dimethylaminopyridine (0.46 g, 3.8 mmol). The product was purified by flash column chromatography (10% Et_2O/hexanes) to afford the title compound as a colorless oil (1.6 g, 3.2 mmol, 99%, 1:1 dr). **TLC R$_f$** = 0.35 (12% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84–7.76 (m, 3H), 7.63 (s, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.49–7.43 (m, 2H), 7.40 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.35–7.28 (m, 2H), 7.11–7.06 (m, 1H), 5.79 (t, *J* = 7.3 Hz, 1H), 3.68 (quint, *J* = 7.2 Hz, 1H), 3.56 (s, 3H), 2.68 (dd, *J* = 15.4, 7.2 Hz, 1H), 2.61 (dd, *J*

= 15.5, 7.2 Hz, 1H), 2.49 (dt, *J* = 15.4, 8.2 Hz, 1H), 2.26–2.17 (m, 1H), 1.20 (s, 9H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 177.8, 172.0, 141.9, 137.5, 133.4, 133.27, 133.24, 128.6, 128.4, 128.2, 128.0, 127.8, 126.3, 126.2, 126.1, 124.8, 124.1, 74.0, 51.8, 40.8, 39.7, 38.9, 37.2, 27.2; **IR** (neat) 3056, 2972, 1728 (b), 1600, 1471, 1278, 1148, 1021 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{27}H_{29}BrO_4Na$ (M + Na)$^+$ 519.1147, found 519.1132.

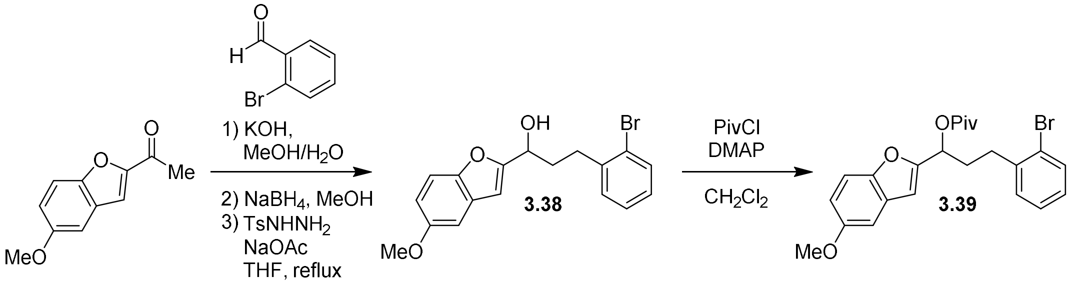
Scheme 3.8: Synthesis of starting material for formation of 3.16 (Table 3.2)



3.36 The product was prepared according to general method A using 2-benzofuran methyl ketone (2.9 g, 18 mmol), 2-bromobenzaldehyde (2.1 mL, 18 mmol), and KOH (2.0 g, 36 mmol). Then NaBH$_4$ (0.76 g, 20 mmol), tosylhydrazide (7.5 g, 40 mmol) and NaOAc•3H$_2$O (5.4 g, 40 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (2.1 g, 6.3 mmol, 35% over 3 steps).

3.37 The product was prepared according to general method B using **3.36** (0.66 g, 2.0 mmol), pivaloyl chloride (0.27 mL, 2.2 mmol) and dimethylaminopyridine (0.27 g, 2.2 mmol). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (0.59 g, 1.4 mmol, 70%). **TLC R$_f$** = 0.5 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.51 (d, *J* = 8.3 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.27–7.12 (m, 4H), 7.02–6.94 (m, 1H), 6.67 (s, 1H), 6.04 (t, *J* = 6.8 Hz, 1H), 2.90–2.72 (m, 2H), 2.41–2.27 (m, 2H), 1.25 (s, 9H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 177.8, 155.6, 155.2, 140.6, 133.2, 130.7, 129.8, 128.3, 127.9, 124.74, 124.68, 123.2, 121.5, 111.6, 104.9, 68.8, 39.3, 33.3, 32.4, 27.5; **IR** (neat) 2970, 1729, 1453, 1278, 1142 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{23}BrO_3Na$ (M + Na)$^+$ 437.0728, found 437.0725.

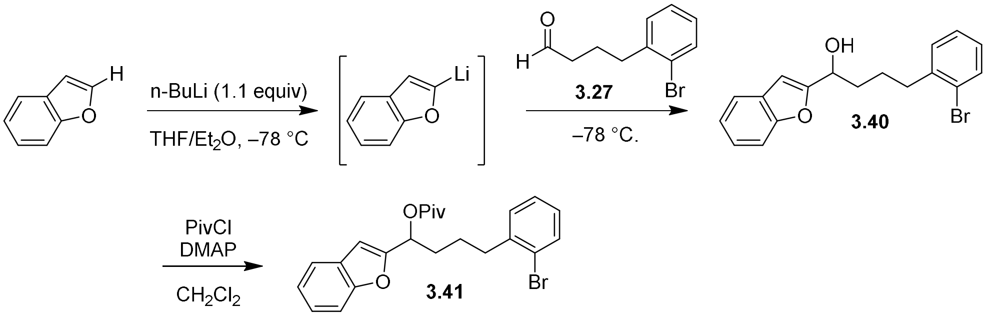
Scheme 3.9: Synthesis of starting material for formation of 3.17 (Table 3.2)



3.38 The product was prepared according to general method A using 2-acyl-5-methoxybenzofuran (2.0 g, 10 mmol), 2-bromobenzaldehyde (1.2 mL, 10 mmol), and KOH (1.2 g, 21 mmol). Then $NaBH_4$ (0.95 g, 25 mmol), tosylhydrazide (5.4 g, 29 mmol) and NaOAc•$3H_2O$ (3.9 g, 29 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (2.0 g, 5.5 mmol, 55% over 3 steps).

3.39 The product was prepared according to general method B using **3.38** (0.50 g, 1.6 mmol), pivaloyl chloride (0.19 mL, 1.6 mmol) and dimethylaminopyridine (0.19 g, 1.6 mmol). The product was purified by flash column chromatography (12% EtOAc/hexanes) to afford the title compound as a colorless oil (0.52 g, 1.2 mmol, 75%). **TLC R$_f$** = 0.4 (12% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.20–7.16 (m, 2H), 7.01 (ddd, *J* = 7.9, 6.0, 3.2 Hz, 1H), 6.99 (d, *J* = 2.6 Hz, 1H), 6.87 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.62 (t, *J* = 0.6 Hz, 1H), 6.00 (t, *J* = 6.6 Hz, 1H), 3.78 (s, 3H), 2.90–2.72 (m, 2H), 2.41–2.26 (m, 2H), 1.25 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 156.34, 156.32, 150.1, 140.6, 133.2, 130.7, 128.8, 128.2, 127.9, 124.6, 113.5, 112.0, 105.0, 103.9, 68.8, 56.1, 39.2, 33.2, 32.3, 27.4; **IR** (neat) 2968, 1729, 1617, 1476, 1204, 1192 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{25}BrO_4Na$ $(M + Na)^+$ 467.0834, found 467.0832.

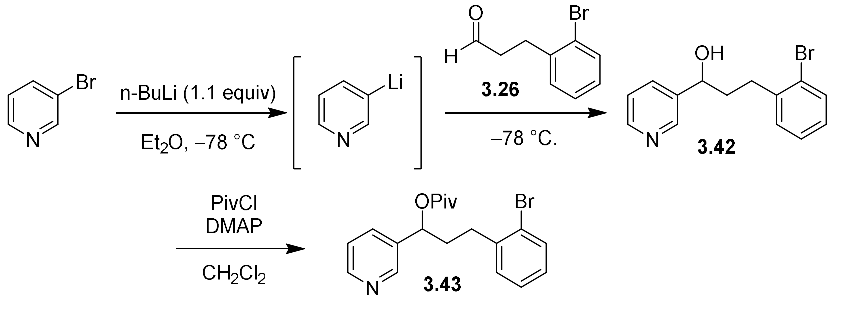
Scheme 3.10: Synthesis of starting material for formation of 3.18 (Table 3.2)



3.40 The product was prepared according to general method D using benzofuran (0.66 mL, 6.0 mmol), *n*-BuLi (2.6 mL, 2.5 M in hexane, 6.6 mmol), and **3.27** (1.0 g, 4.5 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (1.4 g, 3.8 mmol, 84%).

3.41 The product was prepared according to general method B using **3.40** (0.28 g, 0.80 mmol), pivaloyl chloride (0.11 mL, 0.90 mmol) and dimethylaminopyridine (0.11 g, 0.90 mmol). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (0.33 g, 0.77 mmol, 96%). **TLC R$_f$** = 0.5 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.21–7.11 (m, 3H), 7.00 (td, *J* = 7.8, 1.8 Hz, 1H), 6.63 (s, 1H), 6.01 (t, *J* = 6.8 Hz, 1H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.18–2.03 (m, 2H), 1.80–1.60 (m, 2H), 1.21 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 155.9, 155.1, 141.4, 133.1, 130.6, 128.2, 128.0, 127.7, 124.7, 124.6, 123.1, 121.4, 111.6, 104.6, 69.0, 39.2, 36.0, 32.7, 27.4, 25.7; **IR** (neat) 3057, 2969, 2869, 1728, 1471, 1454, 1278, 1254, 1143 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{23}H_{25}BrO_3Na$ (M + Na)$^+$ 451.0885, found 451.0891.

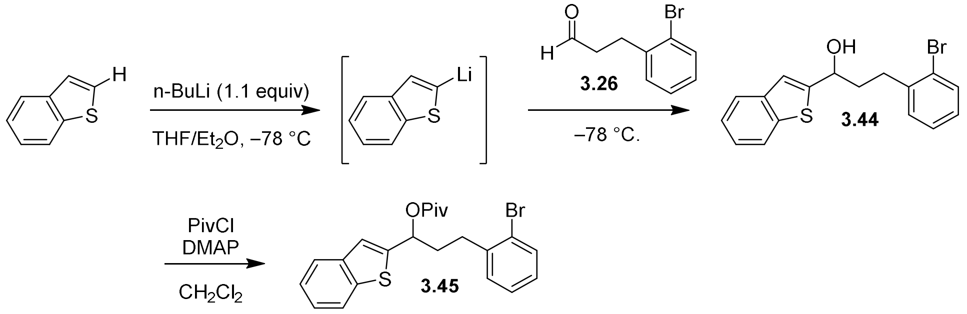
Scheme 3.11: Synthesis of starting material for formation of 3.19 (Table 3.2)



3.42 The product was prepared according to general method D using 3-bromopyridine (0.39 g, 4.0 mmol), *n*-BuLi (1.7 mL, 2.5 M in hexane, 4.4 mmol), and **3.26** (0.85 g, 4.0 mmol) and –78 °C. The product was purified by flash column chromatography (1% NEt_3 in EtOAc) to afford the title compound as a yellow oil (0.72 g, 2.5 mmol, 62%).

3.43 The product was prepared according to general method B using **3.42** (0.58 g, 1.5 mmol), pivaloyl chloride (0.22 mL, 1.8 mmol) and dimethylaminopyridine (0.22 g, 1.8 mmol). The product was purified by flash column chromatography (50% EtOAc/hexanes) to afford the title compound as a colorless oil (0.40 g, 1.1 mmol, 70%). **TLC** $\mathbf{R_f}$ = 0.2 (12% EtOAc/hexanes); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.4 Hz, 1H), 8.54 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.65 (dt, *J* = 8.2, 1.8 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.27 (dd, *J* = 7.3, 4.8 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.16 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.05 (td, *J* = 7.8, 1.5 Hz, 1H), 5.80 (dd, *J* = 8.2, 5.1 Hz, 1H), 2.89–2.68 (m, 2H), 2.30–2.05 (m, 2H), 1.25 (s, 9H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 177.7, 149.5, 148.3, 140.4, 136.4, 134.1, 133.2, 130.5, 128.2, 127.9, 124.5, 123.6, 73.2, 39.1, 36.6, 32.5, 27.4; **IR** (neat) 3055, 2970, 1728, 1471, 1279, 1146 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{22}BrNO_2Na$ (M + Na)$^+$ 398.0732, found 398.0746.

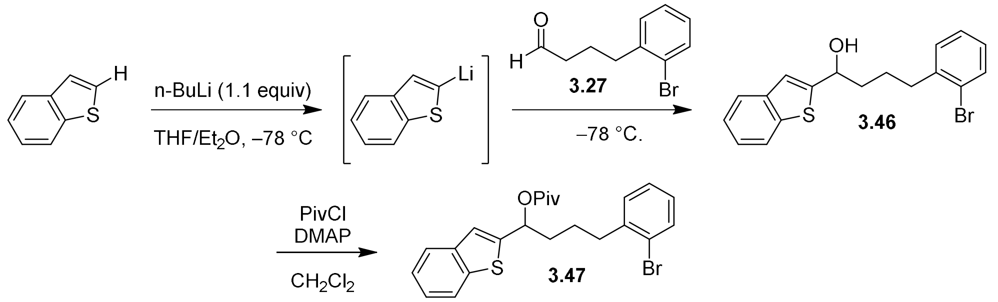
Scheme 3.12: Synthesis of starting material for formation of 3.20 (Table 3.2)



3.44 The product was prepared according to general method D using benzothiophene (0.54 g, 4.0 mmol), *n*-BuLi (1.7 mL, 2.5 M in hexane, 4.4 mmol), and **3.26** (0.85 g, 4.0 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (1.1 g, 3.2 mmol, 79%).

3.45 The product was prepared according to general method B using **3.44** (0.21 g, 0.60 mmol), pivaloyl chloride (0.08 mL, 0.7 mmol) and dimethylaminopyridine (0.080 g, 0.70 mmol). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (0.21 g, 0.48 mmol, 79%). **TLC R$_f$** = 0.5 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.40–7.30 (m, 3H), 7.28–7.20 (m, 2H), 7.01 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.21 (dd, *J* = 7.6, 5.7 Hz, 1H), 2.99–2.79 (m, 2H), 2.46–2.27 (m, 2H), 1.32 (s, 9H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 177.7, 144.4, 140.5, 139.7, 139.5, 133.2, 130.6, 129.8, 128.2, 127.9, 124.7, 124.6, 124.0, 122.7, 122.3, 71.4, 39.2, 36.6, 32.6, 27.4; **IR** (neat) 3058, 2970, 1728, 1477, 1457, 1277, 1140, 1028 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{23}BrO_2SNa$ (M + Na)$^+$ 453.0500, found 453.0512.

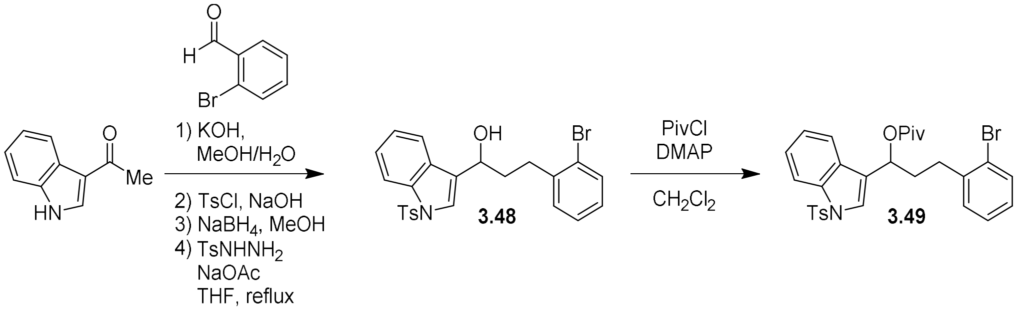
Scheme 3.13: Synthesis of starting material for formation of 2.21 (Table 3.2)



3.46 The product was prepared according to general method D using benzothiophene (0.34 g, 2.5 mmol), *n*-BuLi (1.1 mL, 2.5 M in hexane, 2.2 mmol), and **3.27** (0.45 g, 2.0 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (0.72 g, 2.0 mmol, 99%).

3.47 The product was prepared according to general method B using **3.46** (0.72 g, 2.0 mmol), pivaloyl chloride (0.27 mL, 2.3 mmol) and dimethylaminopyridine (0.27 g, 2.3 mmol). The product was purified by flash column chromatography (12% Et_2O/hexanes) to afford the title compound as a colorless oil (0.46 g, 1.0 mmol, 50%). **TLC** R_f = 0.6 (12% Et_2O/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81–7.77 (m, 1H), 7.73–7.69 (m, 1H), 7.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.35–7.27 (m, 2H), 7.23–7.15 (m, 3H), 7.04 (ddd, *J* = 7.9, 7.0, 2.1 Hz, 1H), 6.12 (dd, *J* = 7.6, 6.0 Hz, 1H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.17–1.96 (m, 2H), 1.82–1.61 (m, 2H), 1.22 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.6, 144.5, 141.1, 139.4, 139.3, 132.9, 130.4, 127.7, 127.5, 124.5, 124.40, 124.35, 123.7, 122.4, 121.8, 71.4, 38.9, 35.9, 35.8, 27.2, 25.7; **IR** (neat) 3054, 2972, 1725, 1438, 1264, 1146 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{23}H_{25}BrO_2SNa$ $(M + Na)^+$ 467.0656, found 467.0652.

Scheme 3.14: Synthesis of starting material for formation of 3.22 (Table 3.2)



3.48 The product was prepared according to general method A using 3-acetylindole (1.6 g, 10 mmol), 2-bromobenzaldehyde (1.9 g, 10 mmol), and KOH (1.2 g, 22 mmol). The indolyl chalcone was then tosylated according to a modified procedure reported by Carreira. A using tosyl chloride (2.2 g, 12 mmol), TBABr (0.34 g, 0.12 mmol), and NaOH (30% w/v) and benzene.[26] The chalcone was then reduced by $NaBH_4$ (0.38 g, 10 mmol), and tosylhydrazide (7.5 g, 40 mmol) and $NaOAc•3H_2O$ (5.5 g, 40 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (3.6 g, 7.4 mmol, 74% over 4 steps).

3.49 The product was prepared according to general method B using **3.48** (0.78 g, 1.6 mmol), pivaloyl chloride (0.25 mL, 2.0 mmol) and dimethylaminopyridine (0.25 g, 2.0 mmol). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title product as a colorless oil (0.86 g, 1.5 mmol, 94%). **TLC R_f** = 0.6 (15% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 6.5 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.17–7.06 (m, 4H), 6.96 (td, *J* = 7.7, 1.7 Hz, 1H), 6.14 (t, *J* = 6.6 Hz, 1H), 2.84–2.64 (m, 2H), 2.39–2.19 (m, 2H), 2.17 (s, 3H), 1.21 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 145.3, 140.6, 135.7, 135.3, 133.1, 130.6,

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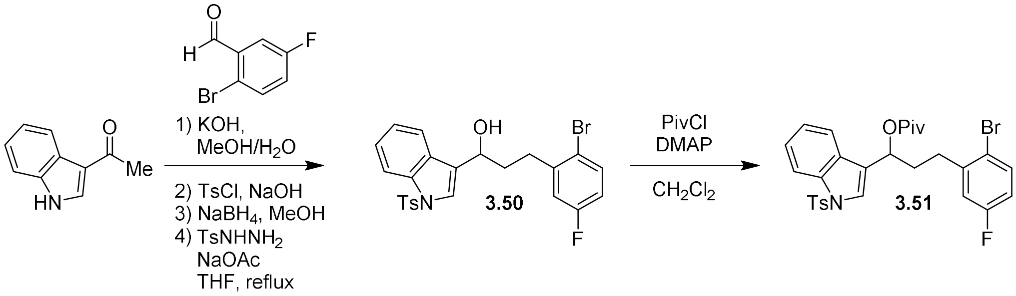
[26] Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.*, **2006**, *128*, 11693.

130.2, 129.1, 128.2, 127.9, 127.0, 125.3, 124.6, 124.3, 123.7, 122.3, 120.6, 114.2, 68.9, 39.2, 35.1, 32.7, 27.5, 21.7; **IR** (neat) 3053, 2972, 1725, 1596, 1446, 1370, 1174, 1152, 1122 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{29}H_{30}BrNO_4SNa$ (M + Na)$^+$ 590.0977, found 590.0964.

Scheme 3.15: Synthesis of starting material for formation of 3.23 (Table 3.2)

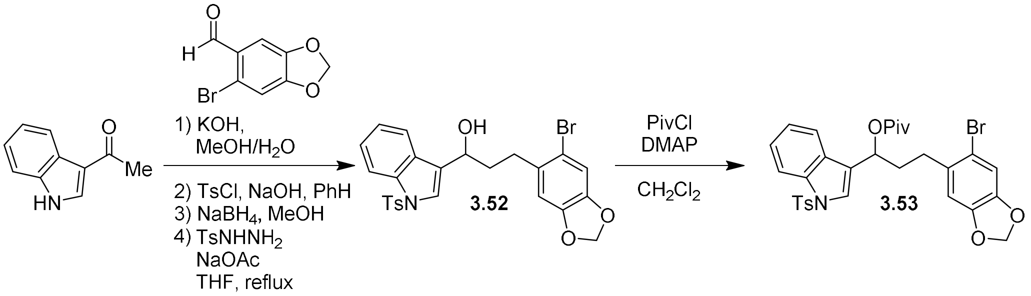


3.50 The product was prepared according to general method A using 3-acetylindole (1.6 g, 10 mmol), 2-bromo-5-fluorobenzaldehyde (2.0 g, 10 mmol), and KOH (1.4 g, 23 mmol). The indolyl chalcone was then tosylated according to a modified procedure reported by Carreira using tosyl chloride (2.2 g, 12 mmol), TBABr (0.34 g, 0.12 mmol), and NaOH (30% w/v) and benzene. The chalcone was then reduced by $NaBH_4$ (0.40 g, 10 mmol), and tosylhydrazide (7.5 g, 40 mmol) and NaOAc•$3H_2O$ (5.5 g, 40 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (3.6 g, 7.4 mmol, 64% over 4 steps).

3.51 The product was prepared according to general method B using **3.50** (0.75 g, 1.5 mmol), pivaloyl chloride (0.25 mL, 2.0 mmol) and dimethylaminopyridine (0.24 g, 2.0 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title product as a yellow oil (0.66 g, 1.1 mmol, 73%). **TLC R$_f$** = 0.6 (15% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.42 (dd, *J* = 8.7, 6.3 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.85 (dd, *J* = 9.3, 3.0 Hz, 1H), 6.77 (td, *J* = 8.3, 3.0 Hz, 1H), 6.11 (t, *J* = 6.6

Hz, 1H), 2.80–2.61 (m, 2H), 2.36–2.17 (m, 5H), 1.21 (s, 9H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 177.8, 162.1 (d, *J* = 247 Hz), 145.3, 142.7 (d, *J* = 7 Hz), 135.7, 135.3, 134.2 (d, *J* = 8 Hz), 130.1, 129.0, 127.0, 125.2, 124.2, 123.6, 122.0, 120.5, 118.6 (d, *J* = 3 Hz), 117.3 (d, *J* = 22 Hz), 115.3 (d, *J* = 22 Hz), 114.1, 68.8, 39.2, 34.7, 32.7, 27.4, 21.8; **IR** (neat) 3068, 2972, 1726, 1598, 1370, 1174, 1121 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{29}H_{29}BrFNO_4SNa$ (M + Na)$^+$ 608.0883, found 608.0860.

Scheme 3.16: Synthesis of starting material for formation of 3.24 (Table 3.2)



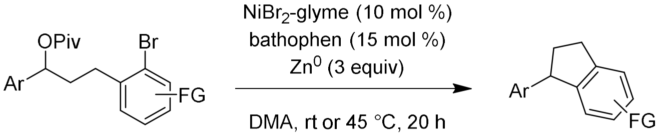
3.52 The product was prepared according to general method A using 3-acetylindole (1.6 g, 10 mmol), 2-bromo-5-fluorobenzaldehyde (2.3 g, 10 mmol), and KOH (1.4 g, 23 mmol). The indolyl chalcone was then tosylated according to a modified procedure reported by Carreira using tosyl chloride (2.2 g, 12 mmol), TBABr (0.34 g, 0.12 mmol), and NaOH (30% w/v) and benzene. The chalcone was then reduced by NaBH$_4$ (0.40 g, 10 mmol), and tosylhydrazide (7.5 g, 40 mmol) and NaOAc•3H$_2$O (5.5 g, 40 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a yellow oil (3.6 g, 7.4 mmol, 11% over 4 steps).

3.53 The product was prepared according to general method B using **3.52** (0.60 g, 1.1 mmol), pivaloyl chloride (0.16 mL, 1.3 mmol) and dimethylaminopyridine (0.16 g, 1.3 mmol). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title product as a yellow oil (0.25 g, 0.41 mmol, 36%). **TLC R$_f$** = 0.5 (15% EtOAc/hexanes); **^{1}H NMR**

(400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.58 (s, 1H), 7.30 (td, *J* = 8.4, 1.3 Hz, 1H), 7.22 (td, *J* = 8.1, 1.2 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.93 (s, 1H), 6.59 (s, 1H), 6.08 (t, *J* = 6.6 Hz, 1H), 5.89 (s, 2H), 2.73–2.54 (m, 2H), 2.32–2.11 (m, 5H), 1.20 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 147.7, 147.1, 145.3, 135.7, 135.3, 133.5, 130.1, 129.0, 127.0, 125.2, 124.2, 123.6, 122.2, 120.6, 114.4, 114.1, 113.0, 110.1, 101.9, 68.8, 39.2, 35.2, 32.6, 27.4, 21.8; **IR** (neat) 2971, 1724, 1476, 1369, 1174, 1121 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{30}H_{30}BrNO_6SNa$ $(M + Na)^+$ 634.0875, found 634.0860.

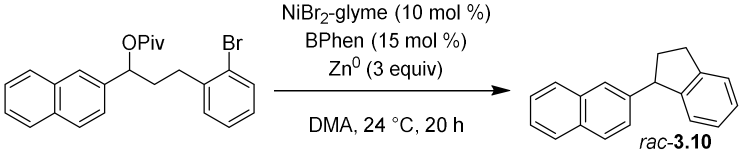
GENERAL PROCEDURES FOR REDUCTIVE CROSS-ELECTROPHILE COUPLING REACTIONS

METHOD E: INTRAMOLECULAR REDUCTIVE COUPLING REACTIONS



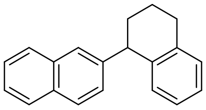
In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with $NiBr_2$•glyme (10 or 15 mol %), bathophenanthroline (15 mol %), Zn^0 (3 equiv), DMA (0.60 mL), and substrate (1.00 equiv). The reaction was stirred for 20 h before removing the vial from the glovebox. The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography.

CHARACTERIZATION OF PRODUCTS IN TABLE 3.2



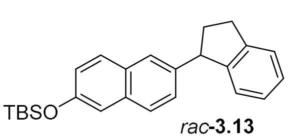
rac-**3.10**

rac-**3.10**. The product was prepared according to general method E using $NiBr_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and *rac*-**3.9** (85.1 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (44.0 mg, 0.180 mmol, 90%). **TLC R$_f$** = 0.3 (100% hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.71 (m, 3H), 7.63 (s, 1H), 7.44–7.36 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.26 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 4.48 (t, *J* = 8.3 Hz, 1H), 3.12–2.92 (m, 2H), 2.65–2.55 (m, 1H), 2.19–2.07 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 144.7, 143.1, 133.9, 132.7, 128.6, 127.98, 127.96, 126.99, 126.95, 126.82, 126.78, 126.3, 125.7, 125.4, 124.8, 52.1, 36.8, 32.3; **IR** (neat) 3050, 3018, 2937, 1599, 1506, 1477, 1457 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{19}H_{16}$ $(M)^+$ 224.1252, found 224.1257.



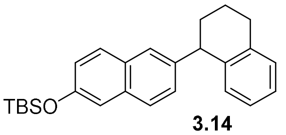
rac-**3.12**

rac-**3.12**. The product was prepared according to general method E using $NiBr_2$•glyme (3.1 mg, 0.010 mmol, 10 mol %), bathophenanthroline (5.0 mg, 0.015 mmol, 15 mol %), Zn^0 (18.8 mg, 0.300 mmol, 3 equiv), DMA (0.40 mL), and **3.29** (44.0 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (10% EtOAc/hexanes) to afford the title compound as a colorless oil (16 mg, 0.062 mmol, 62%). **TLC R$_f$** = 0.3 (hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.84–7.73 (m, 3H), 7.53 (s, 1H), 7.49–7.41 (m, 2H), 7.29–7.23 (m, 1H), 7.21–7.11 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.28 (t, *J* = 7.0 Hz, 1H), 3.02–2.84 (m, 2H), 2.27–2.18 (m, 1H), 2.03–1.90 (m, 2H), 1.86–1.75 (m, 1H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 145.1, 139.4, 137.8, 133.6, 132.3, 130.5, 129.2, 128.1, 127.79, 127.77, 127.5, 127.4, 126.2, 126.1, 125.9, 125.5, 46.0, 33.3, 30.0, 21.4; **IR** (neat) 3053, 2925, 2854, 1599, 1448 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{20}H_{18}$ (M)$^+$ 258.1408, found 258.1415.



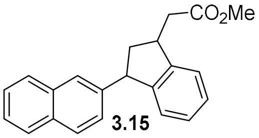
rac-**3.13**

rac-**3.13**. The product was prepared according to general method E using NiBr$_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.31** (111 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et$_2$O) and concentrated under reduced pressure. The product was purified by flash column chromatography (10% EtOAc/hexanes) to afford the title compound as a colorless oil (51.7 mg, 0.138 mmol, 69%). **TLC R$_f$** = 0.3 (hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.64 (dd, *J* = 8.6, 6.8 Hz, 2H), 7.57 (s, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.23–7.10 (m, 4H), 7.05 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 4.47 (t, *J* = 8.4 Hz, 1H), 3.13–2.93 (m, 2H), 2.66–2.57 (m, 1H), 2.13 (dq, *J* = 12.7, 8.8 Hz, 1H), 1.02 (s, 9H), 0.23 (s, 6H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 153.3, 147.1, 144.6, 140.8, 133.6, 129.5, 129.2, 127.2, 127.1 126.8, 126.6, 126.4, 125.2, 124.6, 122.4, 115.0, 51.8, 36.7, 32.1, 25.9, 18.5, –4.1; **IR** (neat) 2954, 2928, 1602, 1478, 1258 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{25}H_{30}OSi$ $(M)^+$ 374.2066, found 374.2054.



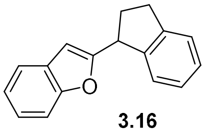
3.14

3.14. The product was prepared according to general method E using $NiBr_2$•glyme (3.1 mg, 0.010 mmol, 5.0 mol %), bathophenanthroline (5.0 mg, 0.015 mmol, 7.5 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.33** (113.9 mg, 0.200 mmol, 1.00 equiv). After 8 hours, the reaction vial was taken out of the oil bath. In the glovebox, an additional amount of $NiBr_2$•glyme (3.1 mg, 0.010 mmol, 5 mol %) and bathophenanthroline (5.0 mg, 0.015 mmol, 7.5 mol %) was added to the reaction mixture. The reaction vial was put back into the oil bath for the remainder of the reaction time. The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% pentane) to afford the title compound as a colorless oil (29.8 mg, 0.120 mmol, 58%). **TLC R$_f$** = 0.2 (pentane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.6, 6.9 Hz, 2H), 7.45 (s, 1H), 7.18 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.16–7.10 (m, 3H), 7.04 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.04–6.99 (m, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 1H), 3.02–2.82 (m, 2H), 2.26–2.15 (m, 1H), 2.00–1.88 (m, 2H), 1.84–1.73 (m, 1H), 1.01 (s, 9H), 0.23 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 142.8, 139.5, 137.7, 133.3, 130.4, 129.3, 129.04, 129.02, 127.6, 127.2, 126.8, 126.0, 125.7, 122.1, 114.8, 45.7, 33.2, 29.9, 25.8, 21.2, 18.3, -4.3; **IR** (neat) 3053, 2928, 1633, 1602, 1478, 1259 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{26}H_{32}OSi$ $(M)^+$ 388.2222, found 388.2227.



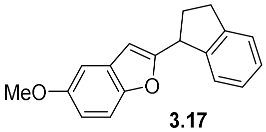
3.15

3.15. The product was prepared according to general method E using NiBr$_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.35** (99.5 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et$_2$O) and concentrated under reduced pressure. The product was purified by flash column chromatography (10% EtOAc/hexanes) to afford the titlecompound as a colorless oil (29.7 mg, 0.094 mmol, 47%, 1:1 dr). **TLC R$_f$** = 0.6 (10% EtOAc in hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.82–7.73 (m, 3H), 7.60–7.57 (m, 1H), 7.47–7.40 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.27–7.22 (m, 2H), 7.18 (tdd, *J* = 7.5, 1.5, 0.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 4.62 (t, *J* = 7.7 Hz, 1H), 3.87–3.78 (m, 1H), 3.72 (s, 3H), 2.76 (dd, *J* = 15.5, 6.1 Hz, 1H), 2.57 (dd, *J* = 15.4, 8.9 Hz, 1H), 2.51–2.36 (m, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 173.3, 146.4, 146.3, 142.6, 133.7, 132.6, 128.5, 127.86, 127.85, 127.6, 127.4, 126.7, 126.5, 126.2, 125.7, 124.1, 123.1, 51.9, 49.9, 42.5, 40.6, 40.2; **IR** (neat) 3051, 2949, 1734, 1599, 1435, 1250, 1164 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{20}O_2Na$ (M + Na)$^+$ 339.1361, found 339.1367.



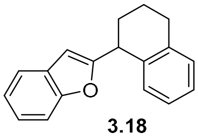
3.16

3.16. The product was prepared according to general method E using NiBr$_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.37** (83.1 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (neat Et$_2$O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (35.1 mg, 0.150 mmol, 75%). **TLC R$_f$** = 0.7 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.54–7.50 (m, 1H), 7.48–7.44 (m, 1H), 7.36–7.29 (m, 2H), 7.27–7.19 (m, 4H), 6.43 (s, 1H), 4.61 (t, *J* = 7.7 Hz, 1H), 3.19–2.98 (m, 2H), 2.66–2.37 (m, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 161.1, 155.2, 144.2, 143.5, 129.0, 127.5, 126.7, 125.1, 124.9, 123.6, 122.7, 120.7, 111.2, 102.4, 45.1, 32.4, 31.8; **IR** (neat) 3066, 3022, 2942, 1597, 1583, 1453, 1252 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{17}H_{14}ONH_4$ (M + NH$_4$)$^+$ 252.1388, found 252.1386.



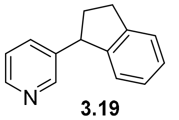
3.17

3.17. The product was prepared according to general method E using NiBr$_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.39** (89.0 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et$_2$O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (41.2 mg, 0.156 mmol, 79%). **TLC R$_f$** = 0.3 (6% Et$_2$O/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.31–7.26 (m, 2H), 7.25–7.14 (m, 3H), 6.95 (d, *J* = 2.6 Hz, 1H), 6.81 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.34–6.32 (m, 1H), 4.53 (t, *J* = 7.7 Hz, 1H), 3.82 (s, 3H), 3.14–2.93 (m, 2H), 2.61–2.51 (m, 1H) 2.41–2.30 (m, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 162.0, 156.0, 150.2, 144.2, 143.5, 129.5, 127.5, 126.7, 125.0, 124.9, 112.0, 111.5, 103.5, 102.6, 56.2, 45.1, 32.3, 31.8; **IR** (neat) 3068, 2929, 1615, 1599, 1474, 1202, 1030 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{18}H_{16}O_2NH_4$ (M + NH$_4$)$^+$ 282.1494, found 282.1494.



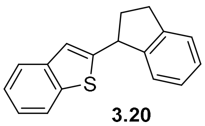
3.18

3.18. The product was prepared according to general method E using NiBr$_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.41** (85.9 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et$_2$O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (29.8 mg, 0.120 mmol, 60%). **TLC R$_f$** = 0.8 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.44 (t, *J* = 8.3 Hz, 2H), 7.23 (td, *J* = 7.7, 1.4 Hz, 1H), 7.20–7.09 (m, 5H), 6.19 (s, 1H), 4.33 (t, *J* = 5.7 Hz, 1H), 2.91–2.78 (m, 2H), 2.35–2.08 (m, 2H), 1.95–1.75 (m, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 162.6, 155.5, 137.6, 136.0, 130.1, 129.6, 128.9, 126.9, 125.9, 123.5, 122.7, 120.6, 111.2, 104.3, 39.9, 29.6, 28.7, 20.5; **IR** (neat) 3064, 2926, 2858, 1453, 1253 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for C$_{18}$H$_{16}$OH (M + H)$^+$ 249.1279, found 249.1276.



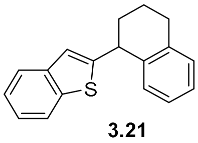
3.19

3.19. The product was prepared according to general method E using NiBr$_2$•glyme (9.2 mg, 0.030 mmol, 15 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.43** (75.3 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et$_2$O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (25.4 mg, 0.130 mmol, 65%). **TLC R$_f$** = 0.1 (12% EtOAc: hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.52 (d, *J* = 1.8 Hz, 1H), 8.50 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.45 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.25–7.20 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 4.37 (t, *J* = 8.2 Hz, 1H), 3.13–2.95 (m, 2H), 2.63 (dtd, *J* = 12.8, 7.9, 7.9, 3.9 Hz, 1H), 2.08 (dq, *J* = 12.7, 8.7 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.0, 148.0, 145.7, 144.3, 140.8, 135.3, 127.0, 126.6, 124.7, 124.6, 123.6, 49.0, 36.5, 31.9; **IR** (neat) 3020, 2925, 1574, 1478, 1423 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{14}H_{13}NH$ (M + H)$^+$ 196.1126, found 196.1119.



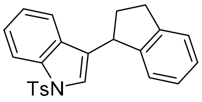
3.20

3.20. The product was prepared according to general method E using $NiBr_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.45** (86.3 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% pentane) to afford the title compound as a colorless oil (37.6 mg, 0.150 mmol, 75%). **TLC R$_f$** = 0.5 (pentane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.32–7.14 (m, 6H), 7.06 (s, 1H), 4.68 (t, *J* = 7.8 Hz, 1H), 3.14–2.90 (m, 2H), 2.66 (dtd, *J* = 12.6, 7.9, 4.6 Hz, 1H), 2.25 (dq, *J* = 12.7, 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.2, 145.6, 143.9, 140.2, 139.7, 127.4, 126.8, 125.2, 124.8, 124.4, 123.9, 123.2, 122.5, 120.9, 47.4, 36.6, 31.9; **IR** (neat) 3060, 2922, 1567, 1475, 1456, 1133 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{17}H_{14}OH$ (M + H)$^+$ 251.0894, found 251.0894.



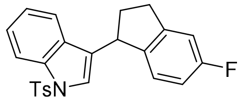
3.21

3.21. The product was prepared according to general method E using $NiBr_2$•glyme (9.2 mg, 0.030 mmol, 15 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.47** (89.0 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (29.1 mg, 0.110 mmol, 55%). **TLC R_f** = 0.5 (hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.32–7.27 (m, 1H), 7.25–7.08 (m, 5H), 6.87 (s, 1H), 4.46 (t, *J* = 5.9 Hz, 1H), 2.96–2.79 (m, 2H), 2.29–2.07 (m, 2H), 2.00–1.75 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.0, 139.8, 139.6, 137.9, 137.1, 130.2, 129.3, 126.6, 125.8, 124.1, 123.6, 123.0, 122.3, 122.1, 41.2, 32.8, 29.4, 20.4; **IR** (neat) 3060, 2915, 1456, 1435, 1308, 1129 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{18}H_{16}S$ $(M)^+$ 264.0973, found 264.0966.



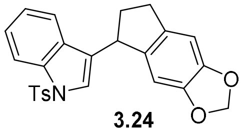
3.22

3.22. The product was prepared according to general method E using $NiBr_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.49** (114 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (59.4 mg, 0.153 mmol, 75%). **TLC R_f** = 0.4 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.34–7.26 (m, 3H), 7.25–7.09 (m, 6H), 7.01 (d, *J* = 7.6 Hz, 1H), 4.53 (t, *J* = 8.1 Hz, 1H), 3.08–2.92 (m, 2H), 2.55 (dtd, *J* = 12.4, 7.8, 4.6 Hz, 1H), 2.32 (s, 3H), 2.12 (dq, *J* = 12.6, 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.99, 144.98, 144.2, 136.0, 135.5, 130.6, 130.0, 127.2, 127.0, 126.7, 126.4, 124.90, 124.86, 124.8, 123.3, 123.2, 120.4, 114.1, 42.3, 34.2, 31.9, 21.8; **IR** (neat) 3065, 2926, 2850, 1596, 1446, 1368, 1171 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{24}H_{21}NO_2SNa$ $(M + Na)^+$ 410.1191, found 410.1193.



3.23

3.23. The product was prepared according to general method E using NiBr$_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.51** (117.3 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et$_2$O) and concentrated under reduced pressure. The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (68.1 mg, 0.168 mmol, 84%). **TLC R$_f$** = 0.4 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.98 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.32–7.27 (m, 2H), 7.23–7.20 (m, 3H), 7.16 (td, *J* = 7.7, 0.9 Hz, 1H), 7.01–6.97 (m, 1H), 6.92 (dd, *J* = 8.3, 5.4 Hz, 1H), 6.81 (td, *J* = 9.0, 2.3 Hz, 1H), 4.49 (t, *J* = 8.1 Hz, 1H), 3.05–2.91 (m, 2H), 2.57 (dtd, *J* = 12.6, 8.0, 4.7 Hz, 1H), 2.35 (s, 3H), 2.17 (dq, *J* = 12.7, 8.3 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 162.3 (d, *J* = 243 Hz), 146.2 (d, *J* = 8 Hz), 144.8, 140.2 (d, *J* = 2 Hz), 135.8, 135.3, 130.2, 129.9, 126.8, 125.5 (d, *J* = 9 Hz), 126.0, 124.7, 123.1, 123.0, 120.1 113.9, 113.4 (d, *J* = 22 Hz), 111.7 (d, *J* = 22 Hz), 41.4, 34.4, 31.7, 21.6; **IR** (neat) 2923, 1595, 1482, 1368, 1172, 1121 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{24}H_{20}FNO_2SNa$ (M + Na)$^+$ 428.1096, found 428.1081.

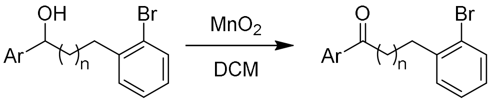


3.24

3.24. The product was prepared according to general method E using NiBr$_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and **3.53** (122.5 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et$_2$O) and concentrated under reduced pressure. The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a colorless oil (38.0 mg, 0.088 mmol, 44%). **TLC R$_f$** = 0.5 (15% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.35–7.26 (m, 2H), 7.24–7.12 (m, 4H), 6.76 (s, 1H), 6.43 (s, 1H), 5.92 (d, *J* = 8.3 Hz, 2H), 4.43 (t, *J* = 7.7 Hz, 1H), 2.97–2.81 (m, 2H), 2.60–2.48 (m, 1H), 2.33 (s, 3H), 2.13 (dq, *J* = 12.7, 7.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 146.9, 145.0, 137.7, 137.0, 136.1, 135.5, 130.5, 130.0, 127.0, 126.6, 124.9, 123.3, 123.2, 120.4, 114.1, 105.33, 105.31, 101.2, 42.2, 34.6, 31.7, 21.8; **IR** (neat) 2926, 1596, 1474, 1367, 1172, 1120, 1021 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{25}H_{21}NO_4SNa$ $(M + Na)^+$ 454.1089, found 454.1085.

VIII. SYNTHESIS AND CHARACTERIZATION OF ENANTIOENRICHED ESTERS FOR TABLE 4 AND STEREOSPECIFIC INTRAMOLECULAR REDUCTIVE CROSS-ELECTROPHILE COUPLING REACTION

METHOD G: MANGANESE DIOXIDE OXIDATION OF BENZYLIC ALCOHOLS



The product was prepared according to a modified procedure reported by Wipf.[27] To a solution of *rac*-benzylic alcohol (1.0 equiv) in CH_2Cl_2 (30 mL) was added in a single portion MnO_2 (8 equiv). The reaction was allowed to stir overnight at room temperature. The resulting slurry was filtered through celite, and the celite was washed with CH_2Cl_2. Solvent was removed under reduced pressure to afford the pure title compound.

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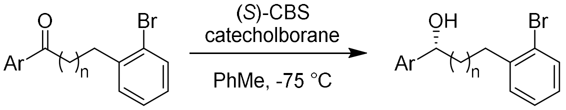
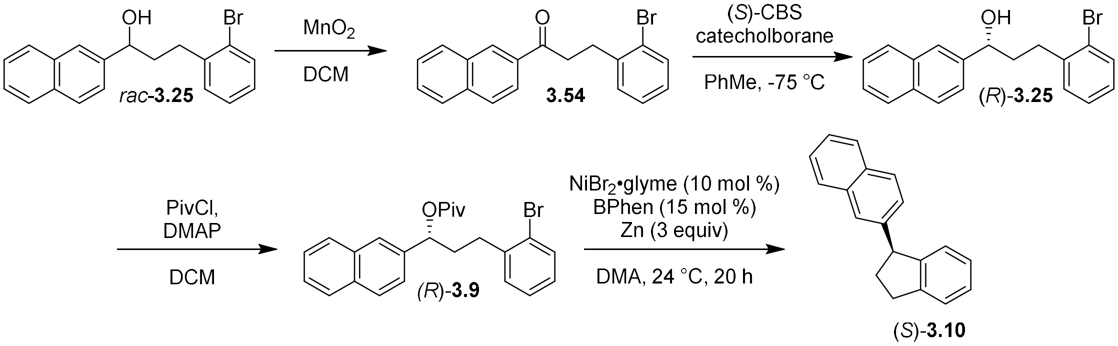
[27] Wipf, P.; Xu, W. *J. Org. Chem.* **1996**, *61*, 6556

METHOD H: CBS REDUCTION OF BENZYLIC KETONES



The product was prepared according to a modified procedure reported by Okamura.[28] In a glovebox, (*S*)-Me-CBS (0.100 equiv) was added to a 50 mL flame-dried round bottom flask equipped with a stir bar. The flask was capped with a septum and removed from the box. Benzylic ketone (1.0 equiv) was added to the flask as a solution in PhMe (20 mL). The reaction was then cooled to –78 °C and catecholborane (2.0 equiv) was added dropwise. After stirring for 24 h at –78 °C, the reaction was warmed to ambient temperature and quenched with water. Saturated $NaHCO_3$ (15 mL) was added to the reaction flask and the mixture was extracted with EtOAc (3 x 30 mL). The combined organics were washed with brine, dried over MgSO4, and concentrated under reduced pressure. The product was purified by flash column chromatography to afford the title compound.

Scheme 3.17: Synthesis of starting material and formation of (*S*)- 3.10 (Table 3.3)



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[28] Okamoto, K.; Hayashi, T. *Org. Lett.* **2007**, *9*, 5067

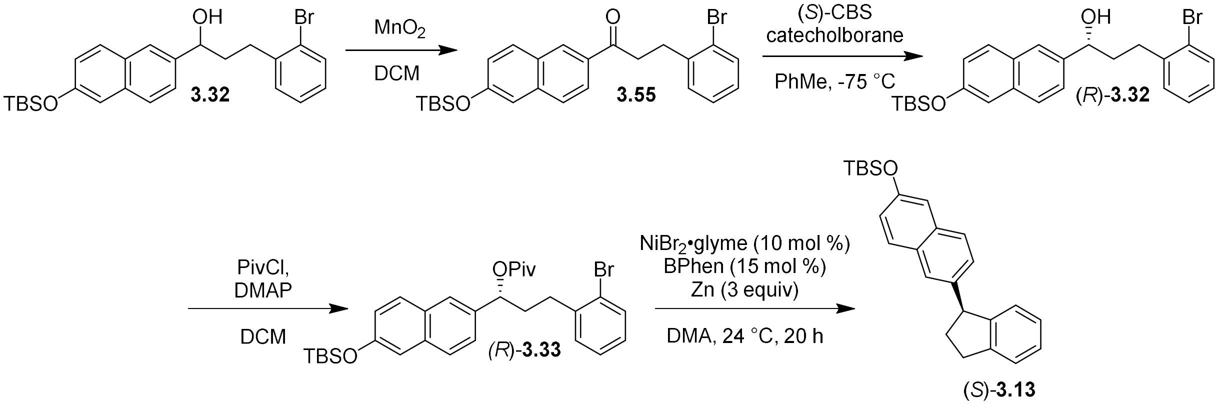
3.54. The product was prepared according to general procedure G using *rac*-**3.25** (1.32 g, 3.86 mmol, 1.0 equiv), MnO_2 (2.08 g, 24.0 mmol, 6.22 equiv). The product was purified by flash column chromatography to afford the pure title compound as a yellow oil (0.962 g, 2.84 mmol, 74%). **TLC R_f** = 0.6 (10% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.04 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 8.6 Hz, 2H), 7.61–7.50 (m, 3H), 7.34 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.27–7.21 (m, 1H), 7.08 (td, *J* = 7.8, 1.8 Hz, 1H), 3.44 (t, *J* = 8.3 Hz, 2H), 3.24 (t, *J* = 8.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 140.9, 135.8, 134.3, 133.2, 132.8, 131.1, 130.0, 129.8, 128.7 (2C), 128.3, 128.0, 127.9, 127.0, 124.6, 124.1, 39.0, 31.2; **IR** (neat) 3057, 2928, 1677, 1626, 1469, 1182, 1122 cm^{-1}; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{15}BrONa$ $(M + Na)^+$ 361.0204, found 361.0218.

(*R*)**-3.25**. The product was prepared according to a general procedure H using (*S*)-Me-CBS (98 mg, 0.28 mmol, 0.100 equiv), **3.54** (0.96 g, 2.8 mmol, 1.0 equiv), and catecholborane (0.59 mL, 5.5 mmol, 2.0 equiv). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (0.91 g, 2.6 mmol, 94%, 96% ee). Analytical data is consistent with the values listed for **3.25** (vide supra).

(*R*)**- 3.9.** The product was prepared according to general method B using (*R*)-**3.25** (0.60 g, 1.7 mmol, 1.0 equiv), pivaloyl chloride (0.24 mL, 1.9 mmol, 1.1 equiv) and dimethylaminopyridine (0.24 g, 1.9 mmol, 1.1 equiv). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (0.49 g, 1.1 mmol, 66%). Analytical data is consistent with the values listed for *rac*-**9** (vide supra). $[\alpha]^{28}_D$ +39 (c 1.7, $CHCl_3$); **SFC** analysis (OD-H, 6% IPA, 2.5 mL/min) indicated 96% ee: t_R (major) = 13.6 minutes, t_R (minor) = 14.9 minutes.

(*S*)- **3.10**. The product was prepared according to general method E using $NiBr_2$•glyme (6.2 mg, 0.020 mmol, 10 mol %), bathophenanthroline (10.0 mg, 0.030 mmol, 15 mol %), Zn^0 (39.6 mg, 0.600 mmol, 3 equiv), DMA (0.60 mL), and (*R*)- **3.9** (85.1 mg, 0.200 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (44.0 mg, 0.180 mmol, 90%, 88% ee). Analytical data is consistent with the values listed for *rac*-**3.10** (vide supra); $[\alpha]^{28}_D$ +10 (c 0.9, $CHCl_3$); **SFC** analysis (OD-H, 6.0% IPA, 2.5 mL/min) indicated 88% ee: t_R (major) = 11.3 minutes, t_R (minor) = 10.5 minutes.

Scheme 3.18: Synthesis of starting material and formation of (*S*)- 3.13 (Table 3.3)



3.55. The product was prepared according to general procedure G using *rac*-**3.32** (0.94 g, 2.0 mmol, 1.0 equiv), MnO_2 (1.8 g, 20.0 mmol, 10 equiv). The product was purified by flash column chromatography to afford the pure title compound as a yellow oil (0.56 g, 1.2 mmol, 60%). **TLC** R_f = 0.4 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.98 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.51 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.30

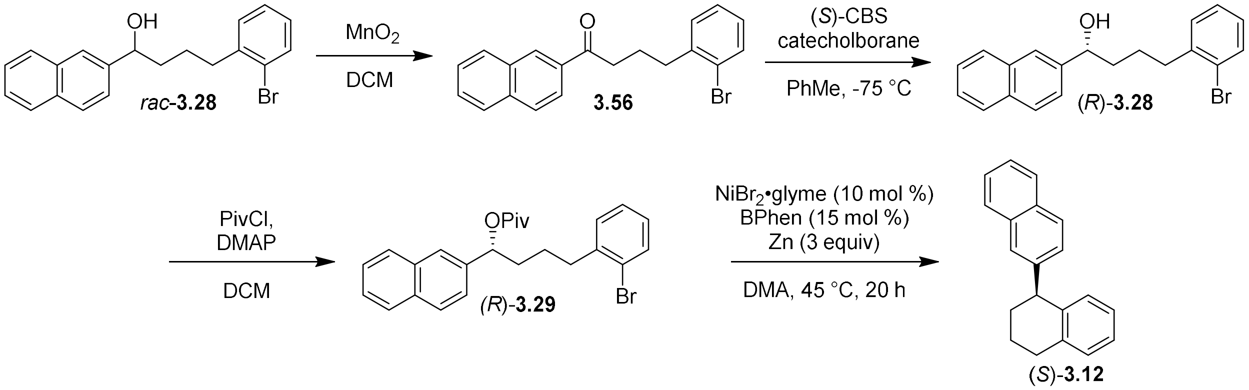
(dd, *J* = 7.7, 1.6 Hz, 1H), 7.22–7.17 (m, 2H), 7.10 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.02 (td, *J* = 7.6, 1.6 Hz, 1H), 3.37 (t, *J* = 7.9 Hz, 2H), 3.20 (t, *J* = 7.8 Hz, 2H), 1.00 (s, 9H), 0.25 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.5, 156.0, 140.8, 137.3, 133.0, 132.4, 131.4, 130.9, 129.8, 128.2, 128.1, 127.8, 127.2, 124.5, 124.4, 123.1, 115.0, 38.6, 31.1, 25.8, 18.4, -4.1; **IR** (neat) 3056, 2954, 1680, 1598, 1467, 1256 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{25}H_{29}BrO_2Si$ $(M)^+$ 468.1120, found 468.1132.

(*R*)**-3.32**. The product was prepared according to a general procedure H using (*S*)-Me-CBS (66 mg, 0.24 mmol, 0.200 equiv), **3.55** (0.56 g, 1.2 mmol, 1.0 equiv), and catecholborane (0.26 mL, 2.4 mmol, 2.0 equiv). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (0.42 g, 0.90 mmol, 75%). Analytical data is consistent with the values listed for **3.32** (vide supra).

(*R*)**-3.33** The product was prepared according to general method B using (*R*)-**3.32** (0.40 g, 0.85 mmol, 1.0 equiv), pivaloyl chloride (0.12 mL, 0.98 mmol, 1.1 equiv) and dimethylaminopyridine (0.14 g, 1.0 mmol, 1.1 equiv). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (0.23 g, 0.41 mmol, 52%). Analytical data is consistent with the values listed for *rac*-**3.33** (vide supra). $[\alpha]^{27.5}_{D}$ +67 (c 3.7, $CHCl_3$); **SFC** analysis (OD-H, 8% IPA, 2.5 mL/min) indicated 96% ee: t_R (major) = 8.1 minutes, t_R (minor) = 8.9 minutes.

(*S*)- **3.13**. The product was prepared according to general method E using $NiBr_2$•glyme (3.1 mg, 0.010 mmol, 10 mol %), bathophenanthroline (5.0 mg, 0.015 mmol, 15 mol %), Zn^0 (18.6 mg, 0.300 mmol, 3 equiv), DMA (0.40 mL), and (*R*)-**3.33** (55.5 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (26 mg, 0.069 mmol, 69%, 92% ee). Analytical data is consistent with the values listed for *rac*-**3.13** (vide supra); $[\alpha]^{26.6}_{D}$ +91 (c 0.55, $CHCl_3$); **SFC** analysis (AD-H, 7.0% IPA, 2.5 mL/min) indicated 92% ee: t_R (major) = 7.1 minutes, t_R (minor) = 8.6 minutes.

Scheme 3.19: Synthesis of starting material and formation of (*S*)- 3.12 (Table 3.3)



3.56. The product was prepared according to general procedure G using *rac*-**3.28** (1.79 g, 5.03 mmol, 1.0 equiv), MnO_2 (4.4 g, 51 mmol, 10 equiv). The product was purified by flash column chromatography to afford the pure title compound as a yellow oil (1.22 g, 3.69 mmol, 73%). **TLC** $\mathbf{R_f}$ = 0.5 (12% Et_2O/hexanes); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.03 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.97–7.93 (m, 1H), 7.91–7.85 (m, 1H), 7.58 (dddd, *J* = 18.5, 7.7, 6.6, 1.3 Hz, 3H), 7.29–7.22 (m, 3H), 7.07 (ddd, *J* = 8.0, 7.0, 2.1 Hz, 1H), 3.17 (t, *J* = 7.3 Hz, 2H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.20–2.11 (m, 2H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 200.0, 141.2, 135.7, 134.4, 133.0, 132.7, 130.7, 129.86, 129.74, 128.62, 128.58, 128.0, 127.9, 127.7, 126.9, 124.8, 124.1, 38.0, 35.6, 24.7; **IR**

(neat) 2939, 2893, 1679, 1620, 1438, 1165 cm^{-1}; **HRMS** (TOF MS CI+) *m / z* calcd for $C_{20}H_{17}BrOH$ (M + H)$^+$ 353.0541, found 353.0442.

(*R*)**-3.28**. The product was prepared according to a general procedure H using (*S*)-Me-CBS (67 mg, 0.29 mmol, 0.100 equiv), **3.56** (1.0 g, 2.9 mmol, 1.0 equiv), and catecholborane (0.62 mL, 5.8 mmol, 2.0 equiv). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (0.83 g, 2.3 mmol, 80%). Analytical data is consistent with the values listed for **3.28** (vide supra).

(*R*)**-3.29.** The product was prepared according to general method B using (*R*)-**3.28** (0.728 g, 2.05 mmol, 1.0 equiv), pivaloyl chloride (0.30 mL, 2.4 mmol, 1.2 equiv) and dimethylaminopyridine (0.33 g, 2.7 mmol, 1.3 equiv). The product was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (0.23 g, 0.41 mmol, 52%). Analytical data is consistent with the values listed for *rac*-**3.29** (vide supra). $[\alpha]^{27.6}_{D}$ +84 (c 2.1, $CHCl_3$); **SFC** analysis (OD-H, 6% IPA, 2.5 mL/min) indicated 94% ee: t_R (major) = 18.2 minutes, t_R (minor) = 21.6 minutes.

(*S*)**- 3.12**. The product was prepared according to general method E using $NiBr_2$•glyme (3.1 mg, 0.010 mmol, 10 mol %), bathophenanthroline (5.0 mg, 0.015 mmol, 15 mol %), Zn^0 (18.6 mg, 0.300 mmol, 3 equiv), DMA (0.40 mL), and (*R*)**-3.29** (44.0 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (16 mg, 0.062 mmol, 62%, 78% ee). Analytical data is consistent with the values listed for *rac*-**3.12** (vide supra); $[\alpha]^{27.6}_{D}$ +43 (c 0.66, $CHCl_3$); **SFC** analysis (OD-H, 6.0% IPA, 2.5 mL/min) indicated 78% ee: t_R (major) = 12.5 minutes, t_R (minor) = 16.8 minutes.

STEREOCHEMICAL PROOF

Enantioenriched alcohol (*R*)-**3.25** was prepared by enantioselective CBS reduction (vida supra). Absolute configuration of (*R*)-**3.25** and (*R*)- **3.9** were assigned based on the accepted model for selectivity in CBS reductions.[29]

The absolute configuration of the enantioenriched indane **3.10** was assigned by derivatization of known enantioenriched indanone (*S*)-**3.58** to indane (*S*)-**3.10.** Enantioenriched (*S*)-**3.58** was prepared by an asymmetric reductive Heck reaction as reported by Zhou. The stereochemistry was verified by comparison of the optical rotation to the literature value. Reduction to indane (*S*)- **3.10** and subsequent comparison of the optical rotation and SFC data matched that of (*S*)-**3.10** synthesized by the reductive cross-electrophile coupling reaction. This product corresponds to net inversion at the benzylic center in the reductive cross-electrophile coupling reaction.

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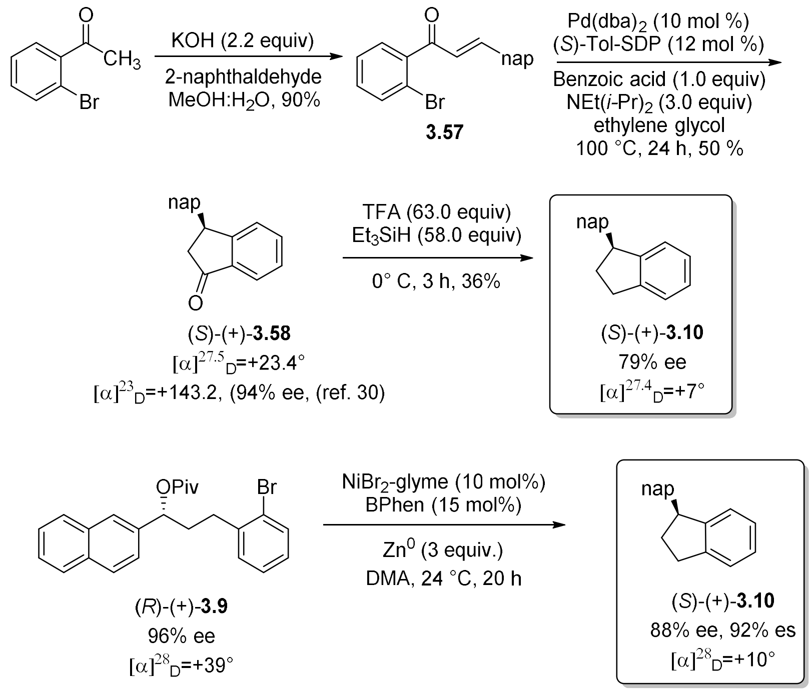
[29] Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1986

Scheme 3.20: Stereochemical course of the reductive cross-electrophile coupling reaction (Table 3.3).



3.57. The product was prepared according to a modified procedure reported by Zhou.[30] To a 100 mL round bottom flask equipped with a stir bar was added 2'-bromoacetophenone (0.67 mL, 5.0 mmol, 1.0 equiv), naphthaldehyde (0.78 g, 5.0 mmol, 1.0 equiv), KOH (0.62 g, 11 mmol, 2.2 equiv), and MeOH/H_2O (15:15 mL). The reaction was stirred overnight at room temperature. The resulting solid was filtered, washed with MeOH/H_2O, and dried by vacuum filtration to afford the title compound as a solid (1.3 g, 4.5 mmol, 90 % yield).

(*S*)-**3.58.** The product was prepared according to a modified procedure reported by Zhou.[15] In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with Pd(dba)$_2$ (14 mg,

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[30] Yue, G.; Lei, K.; Hirao, H.; Zhou, J. *Angew. Chem. Int. Ed.* **2015**, *54*, 6531

0.025 mmol, 10 mol %), (*S*)- Tol-SDP (18 mg, 0.03 mmol, 12 mol %), benzoic acid (30 mg, 0.25 mmol, 1.0 equiv) and degassed ethylene glycol (1.25 mL). After stirring for 10 min, N-diisopropylethylamine (130 μL, 1.5 mmol, 3.0 equiv) and **3.57** (85 mg, 0.25 mmol, 1.0 equiv) were added and the mixture was taken out of the glove box. The reaction was stirred for 24 h in a pre-warmed oil bath at 100 °C then allowed to cool to room temperature. The reaction mixture was eluted through a silica plug (with Et_2O) and concentrated under reduced pressure. The product was purified by flash column chromatography (0%-10% Et_2O/hexanes) to afford the title compound as a colorless oil (27 mg, 0.13 mmol, 50% yield). Analytical data is consistent with literature values.[31] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 1H), 7.84–7.77 (m, 3H), 7.67 (s, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.50–7.43 (m, 3H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.15 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.77 (dd, *J* = 8.2, 3.7 Hz, 1H), 3.31 (dd, *J* = 19.3, 8.1 Hz, 1H), 2.79 (dd, *J* = 19.3, 3.9 Hz, 1H).

(*S*)**- 3.10**. A 20 ml scintillation vial was charged with **3.58** (27 mg, 0.13 mmol, 1.0 equiv), dissolved in TFA (0.5 ml) and cooled to 0 °C in an ice bath. Et_3SiH (1.0 ml) was added dropwise over the course of 20 min and the reaction was allowed to stir for 3 h at 0 °C. The reaction was then allowed to warm to room temperature, was concentrated under reduced pressure, and the residue was taken up and purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (9.2 mg, 0.038 mmol, 36% yield, 79% ee). Analytical data is consistent with the values listed for (*S*)-**10** (vide supra). $[\alpha]^{27.4}_{D}$ +7 (c 0.46, $CHCl_3$); **SFC** analysis (OD-H, 6.0% IPA, 2.5 mL/min) indicated 79% ee: t_R (major) = 11.4 minutes, t_R (minor) = 10.6 minutes.

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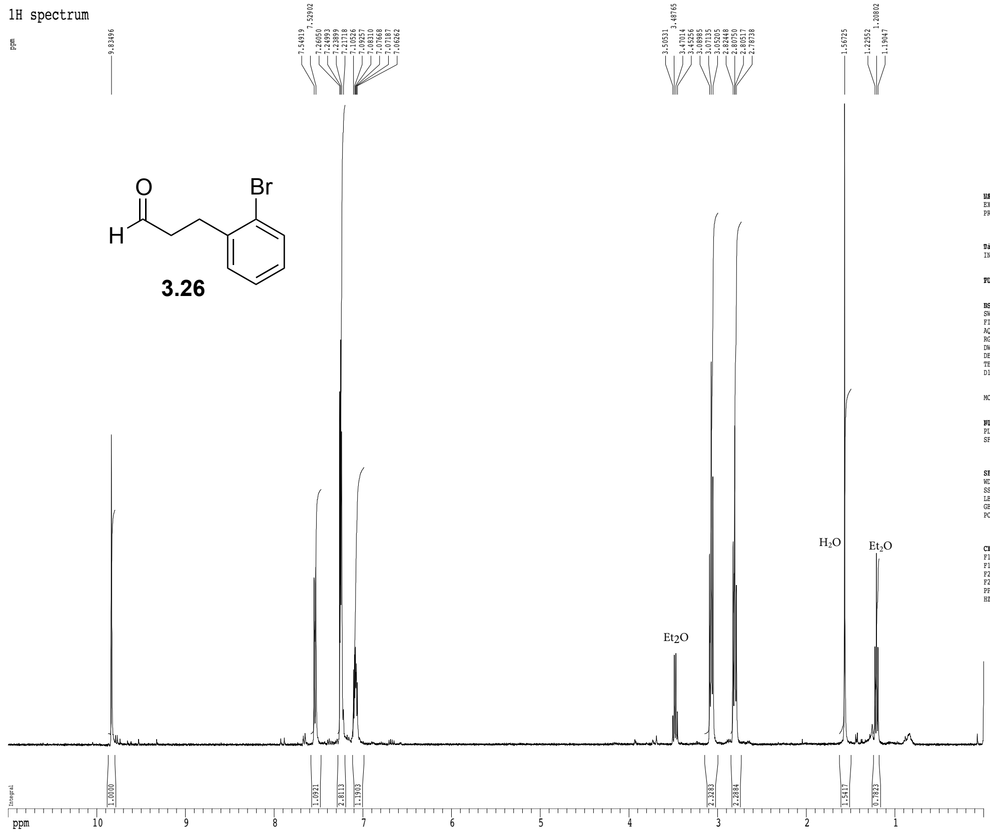
[31] Yu, N-U.; Xu, M-H. *J. Org. Chem.*, **2013**, *78*, 2736.



3.26

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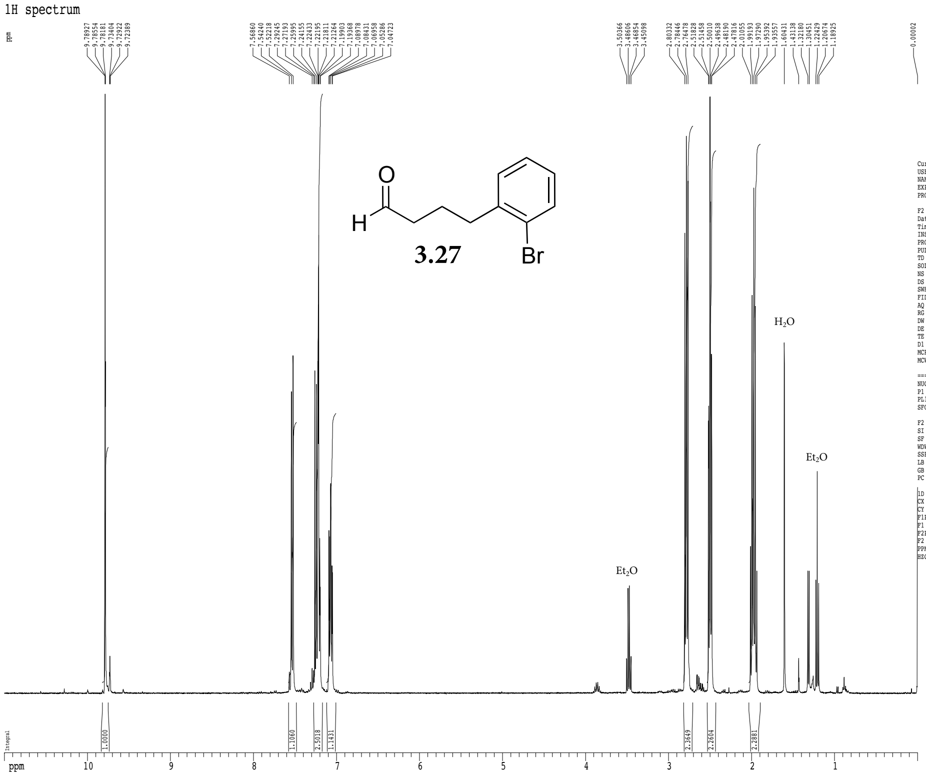

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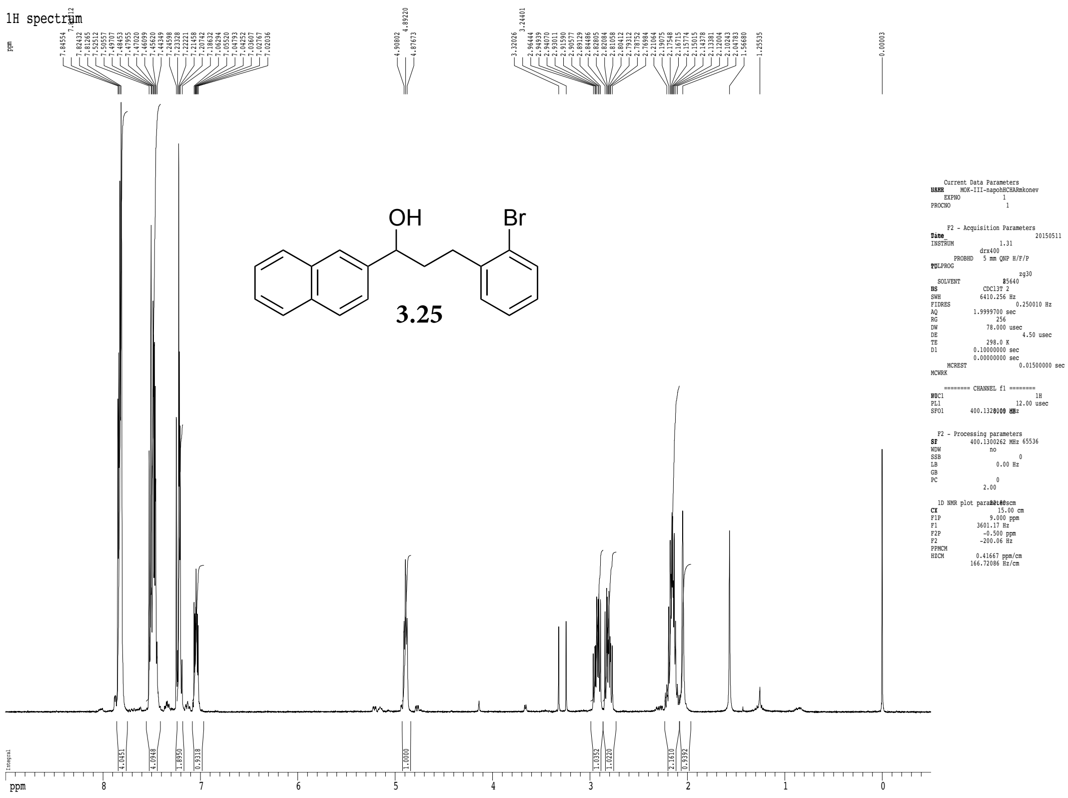
1H spectrum



3.25

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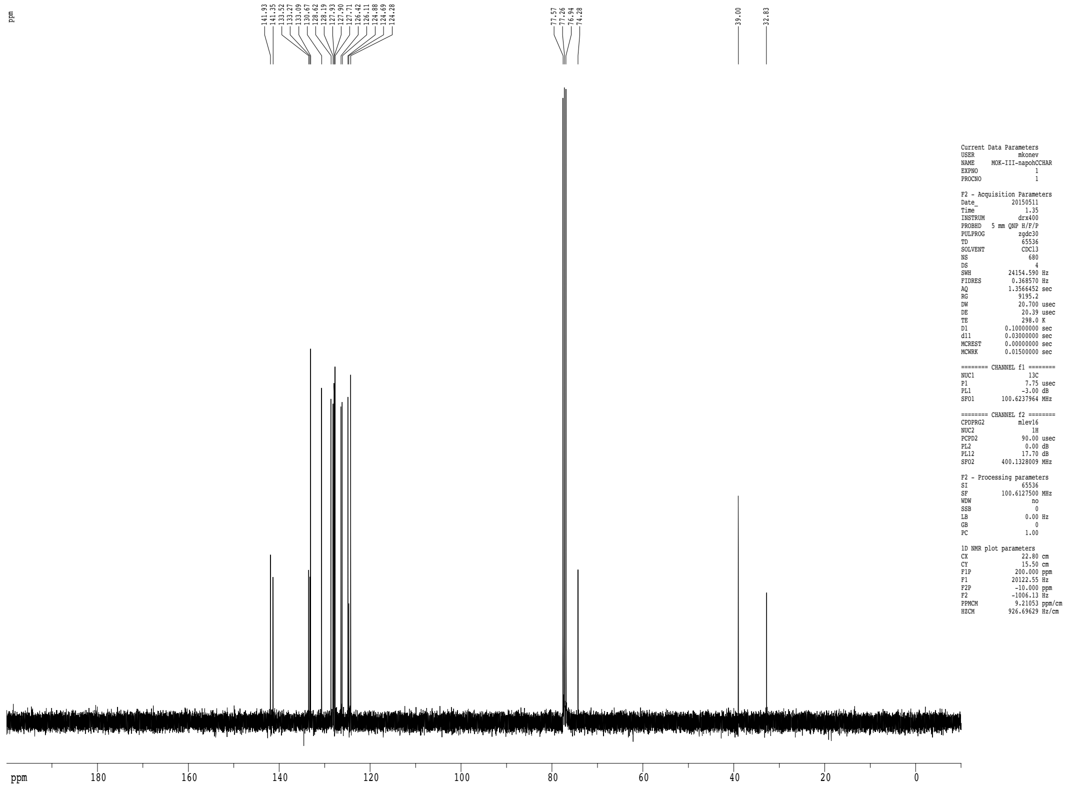
13C spectrum with 1H decoupling



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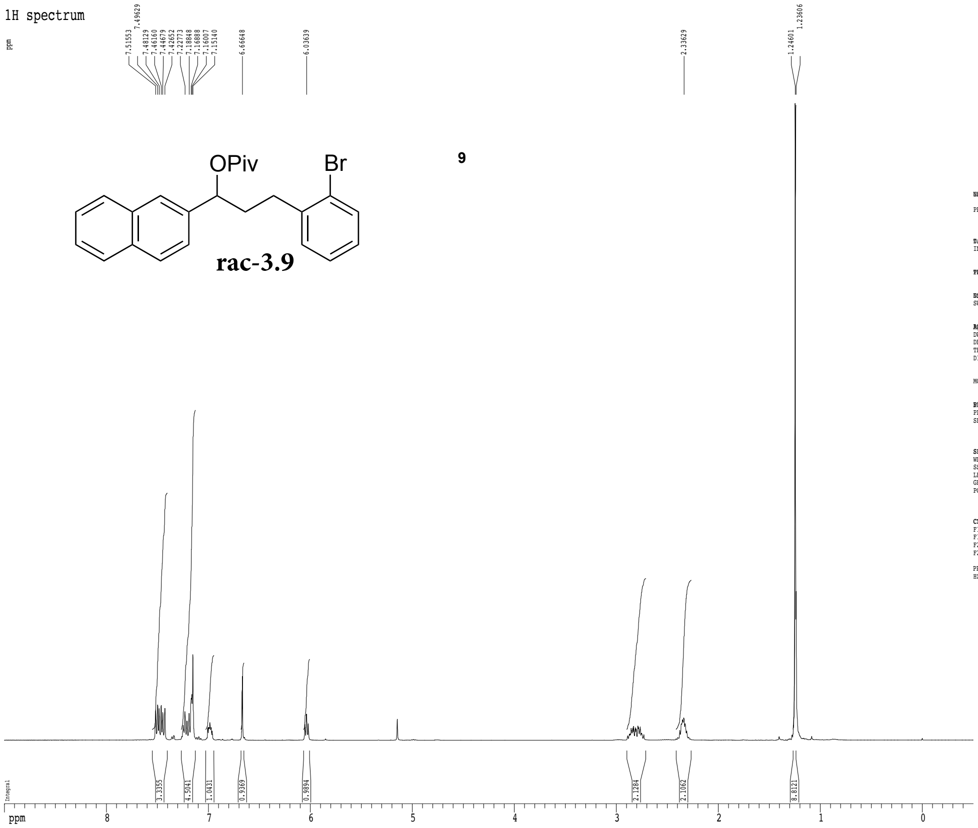

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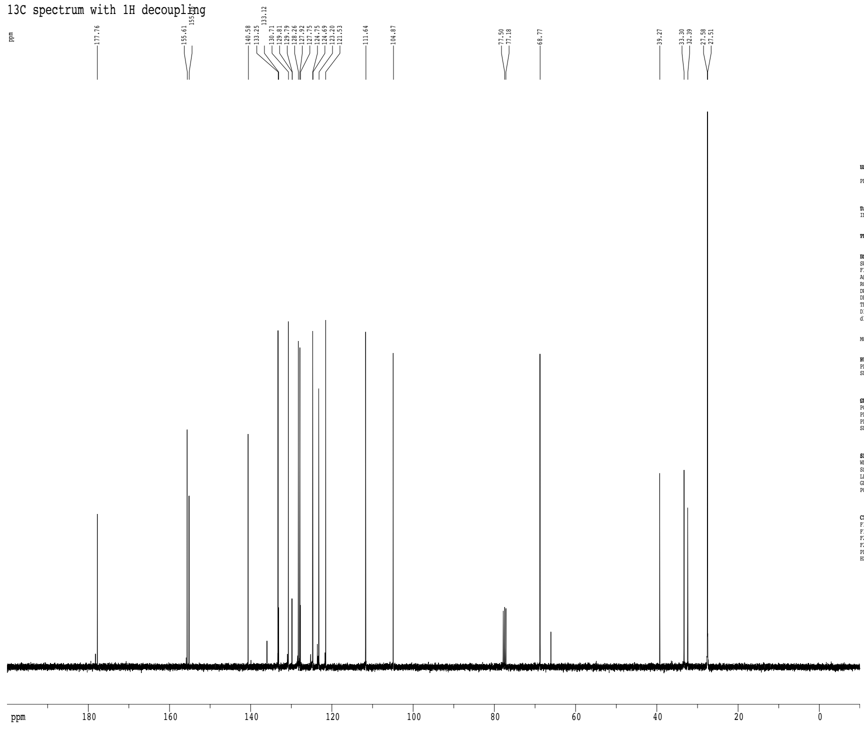

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MCWRK

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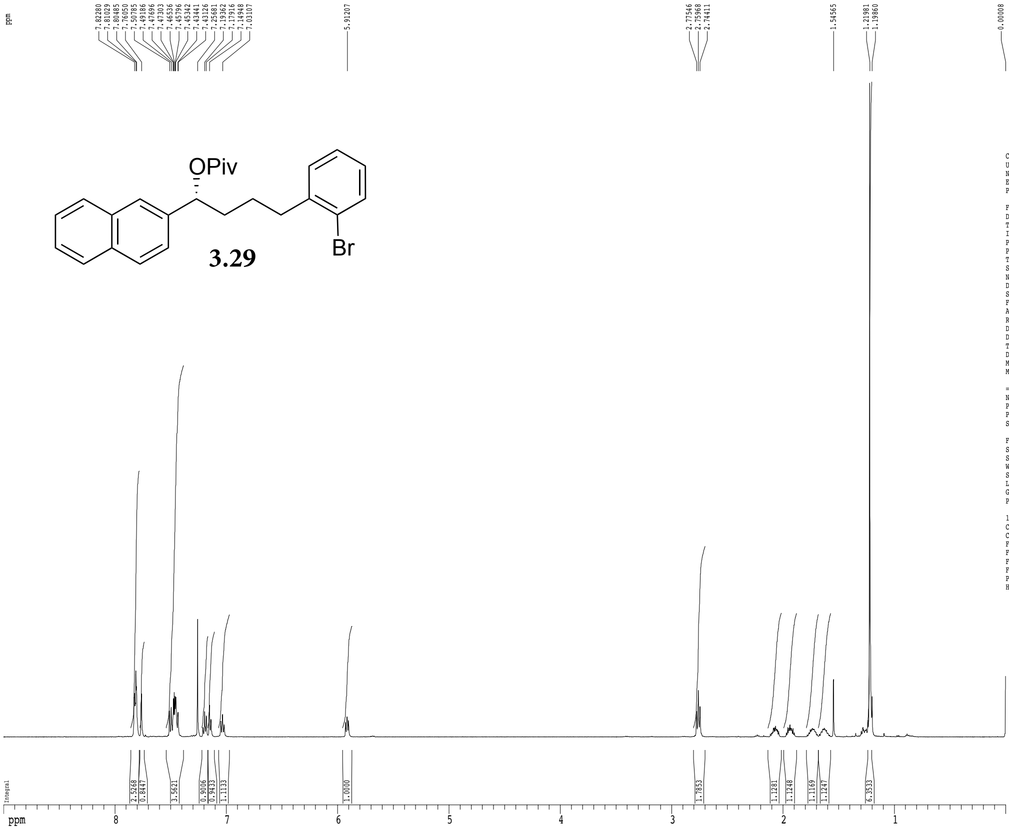
SFO1         100.6237964 MHz


       ======== CHANNEL f2 ========
CPDPRG2           1H                mlev16
PCPD2
PL2                         90.00 usec
PL12              17.00 dB
SFO2         400.1328009 MHz


  F2 - Processing parameters
SI           100.6127500 MHz 65536
WDW                 no
SSB                           0
LB                   0.00 Hz
GB
PC                   0
                1.00

  1D NMR plot parameters
CX                          15.50 cm
F1P            200.000 ppm
F1             20122.55 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz
PPMCM
HZCM                       9.21053 ppm/cm
            926.69629 Hz/cm
```

1H spectrum



3.29

```
Current Data Parameters
USER               lhanna
NAME          LEH-6-080-b
EXPNO                   1
PROCNO                  1

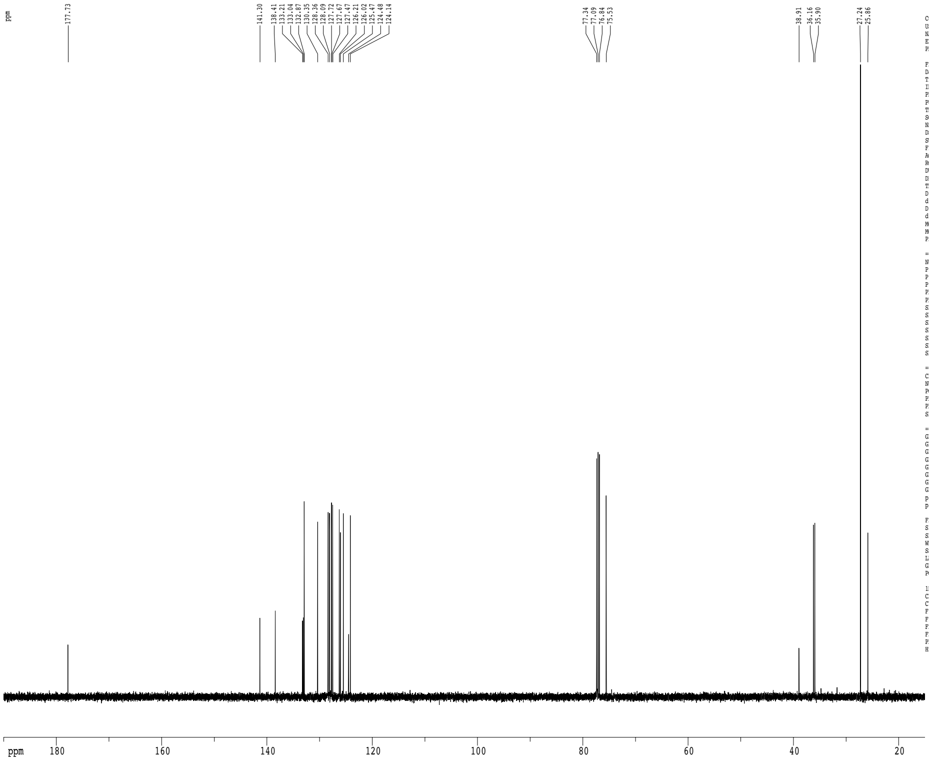
F2 - Acquisition Parameters
Date_            20151110
Time                18.23
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  32048
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.250026 Hz
AQ              1.9998451 sec
RG                    6.3
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200337 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                 0.000 ppm
F2                   0.00 Hz
PPMCM             0.39474 ppm/cm
HZCM            197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER               lhanna
NAME        LEH-6-080-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151110
Time                18.47
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    401
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                   4096
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

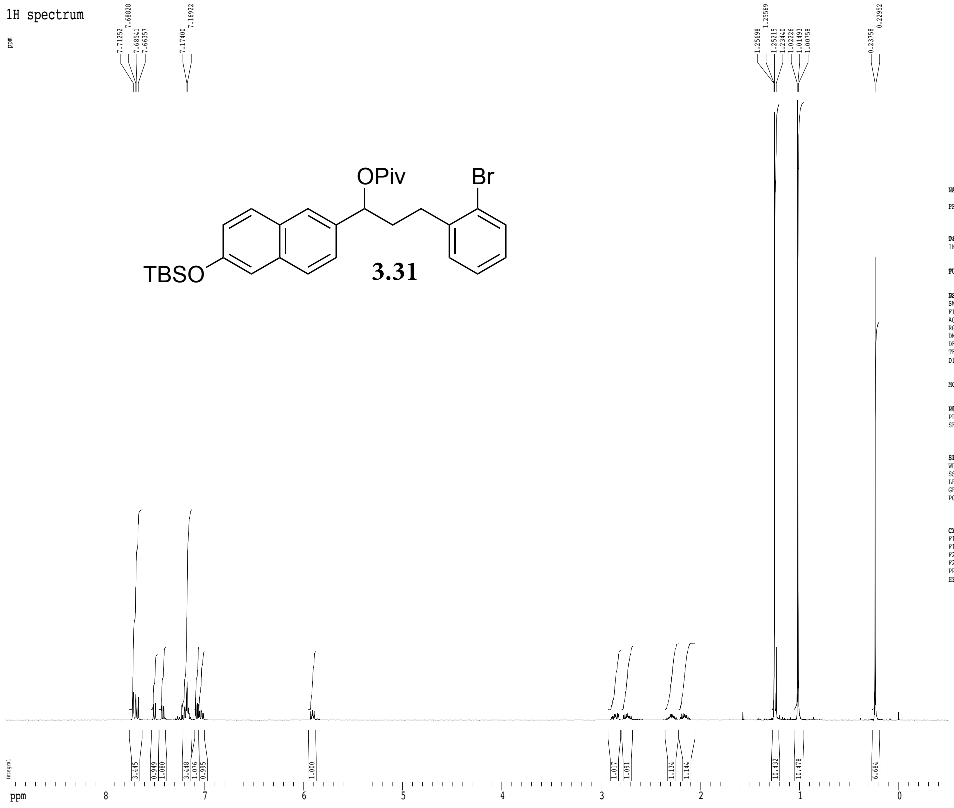
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804190 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               190.000 ppm
F1               23898.28 Hz
F2P                15.000 ppm
F2                1886.71 Hz
PPMCM             7.67544 ppm/cm
HZCM            965.41992 Hz/cm
```

1H spectrum



3.31

```
    Current Data Parameters
NAME     MOK-IV-otbspivee  mkonev
  EXPNO              1
PROCNO               1


     F2 - Acquisition Parameters
Date_          20151124      15.58
INSTRUM            drx400

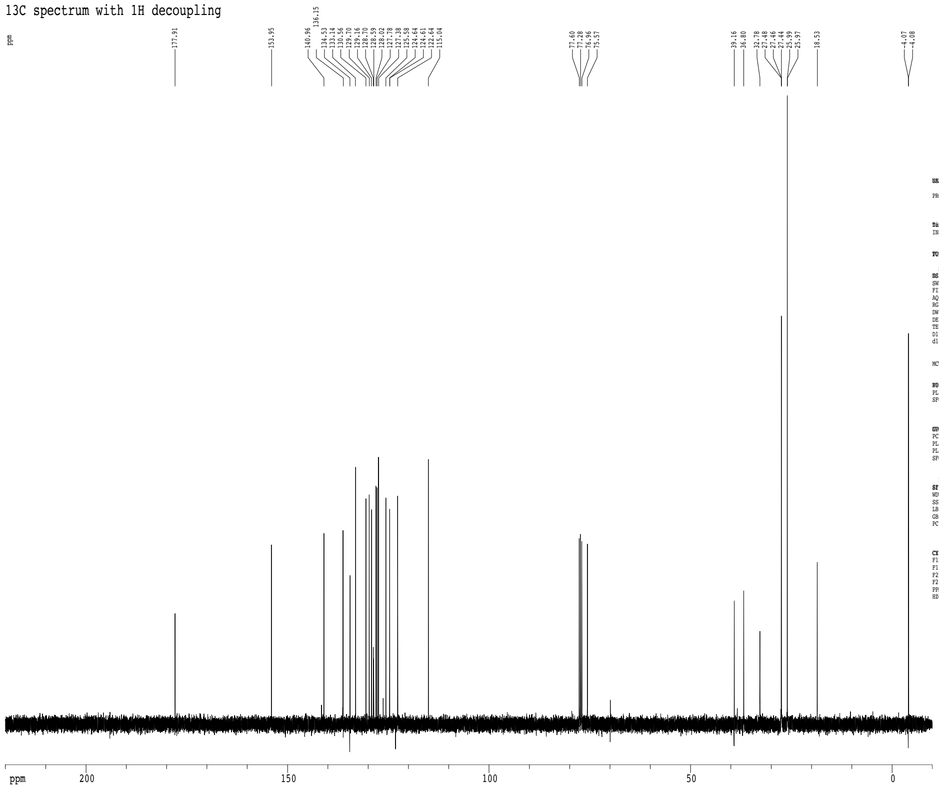
      PROBHD   5 mm QNP H/F/P
PULPROG
                               zg30
  SOLVENT            25640
DS              CDCl3T 2
SWH           6410.256 Hz
FIDRES                    0.250010 Hz
AQ          1.9999700 sec
RG                  64
DW              78.000 usec
DE                             4.50 usec
TE              298.0 K
D1          0.10000000 sec
            0.00000000 sec
     MCREST                 0.01500000 sec
MCWRK

    ======== CHANNEL f1 ========
NUC1                              1H
PL1                         12.00 usec
SFO1        400.1328009 MHz


  F2 - Processing parameters
SI          400.1300332 MHz 65536
WDW                 no
SSB                          0
LB                    0.00 Hz
GB
PC                    0
                 2.00

  1D NMR plot parameters   22.00 cm
CX                          15.00 cm
F1P                   9.000 ppm
F1             3601.17 Hz
F2P                 -0.500 ppm
F2                 -200.06 Hz
PPMCM
HZCM                         0.41667 ppm/cm
            166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     MOK-IV-otbspiveecarbmkonev
  EXPNO              1
PROCNO               1


     F2 - Acquisition Parameters
Date_          20151124      16.00
INSTRUM            drx400

      PROBHD   5 mm QNP H/F/P
PULPROG        zgdc30
                    65536
                          CDCl3
  SOLVENT         224
DS                  4
SWH           24154.590 Hz
FIDRES                 0.368570 Hz
AQ          1.3566452 sec
RG              9195.2
DW              20.700 usec
DE                        20.39 usec
TE              297.9 K
D1          0.10000000 sec
d11                         0.03000000 sec

    MCREST                  0.00000000 sec
MCWRK       0.01500000 sec

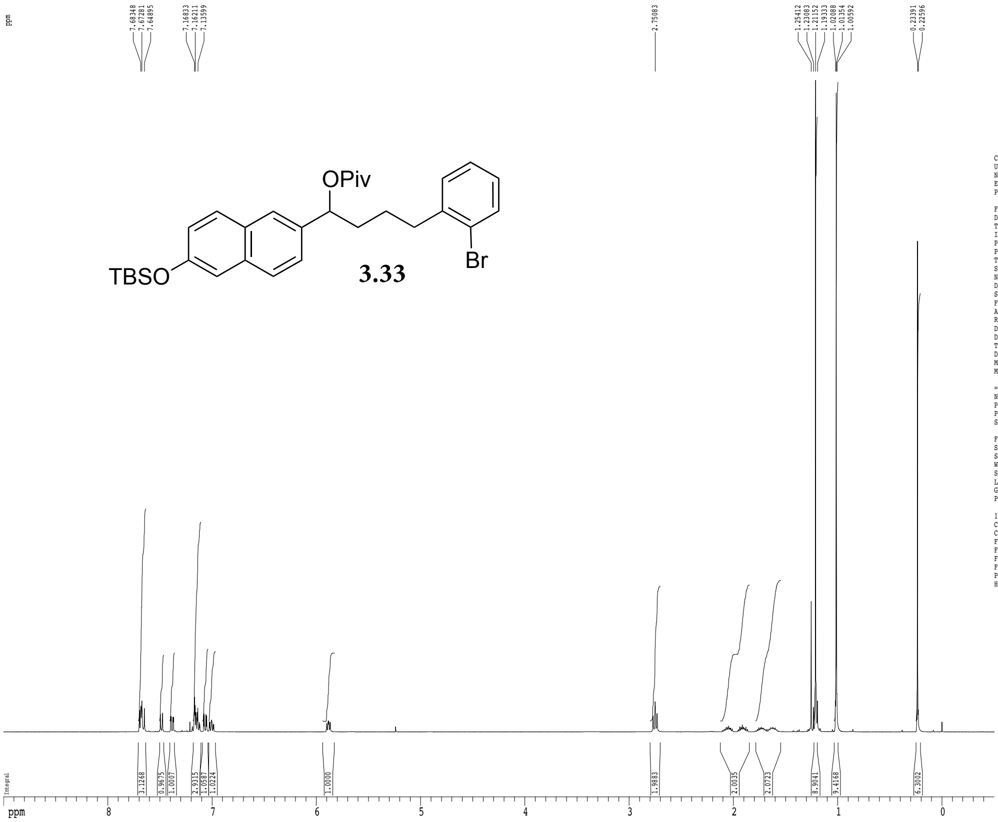
    ======== CHANNEL f1 ========
NUC1                            13C
PL1                        7.75 usec
SFO1        100.6237964 MHz
                     3.00 dB

      ======== CHANNEL f2 ========
CPDPRG2           1H                mlev16
PCPD2
PL2                         90.00 usec
PL12             17.00 dB
SFO2        400.1328009 MHz


  F2 - Processing parameters
SI          100.6127500 MHz 65536
WDW                 no
SSB                   0
LB                      0.00 Hz
GB
PC                    0
                1.00

  1D NMR plot parameters  22.00 cm
CX                          15.50 cm
F1P             220.000 ppm
F1              22134.80 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM
HZCM                         10.08772 ppm/cm
          1014.95319 Hz/cm
```

1H spectrum



3.33

```
Current Data Parameters
USER              mkonev
NAME     MOK-III-270hchar
EXPNO                  1
PROCNO                 1

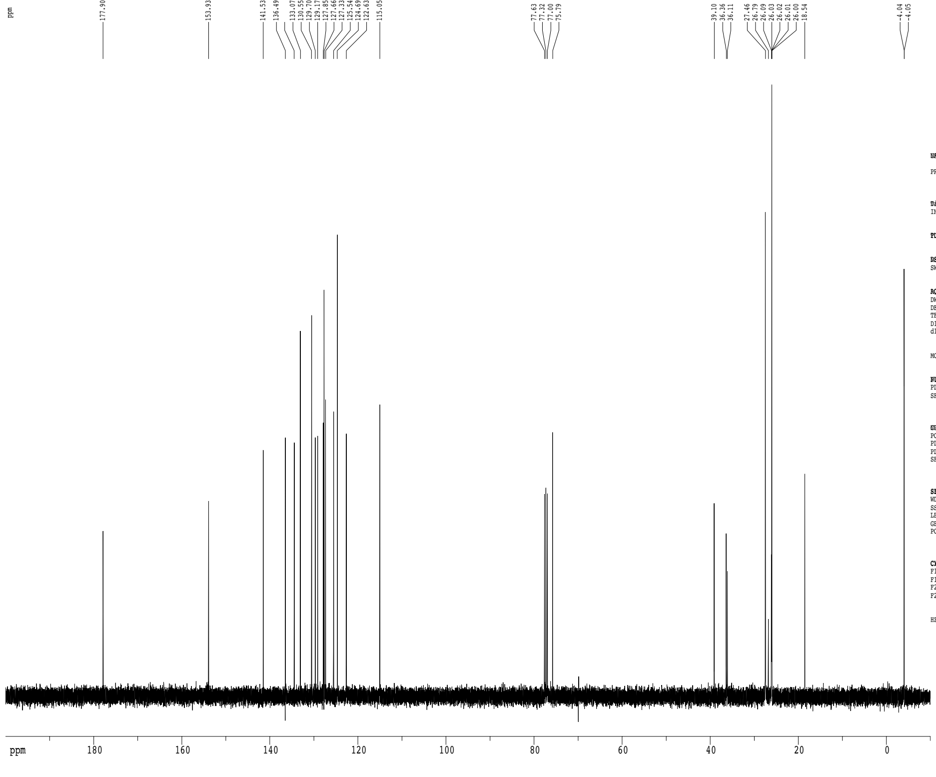
F2 - Acquisition Parameters
Date_           20150816
Time               15.57
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 51280
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.125005 Hz
AQ             3.9998901 sec
RG                    32
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300405 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
   Current Data Parameters
NAME     MOK-III-270cchar  mkonev
   EXPNO             1
PROCNO                1


    F2 - Acquisition Parameters
Date_                            20150816
INSTRUM              15.59
                drx400
      PROBHD   5 mm QNP H/F/P
PULPROG              65536
                         CDCl3
  SOLVENT           96
DS                   4
SWH           24154.590 Hz
                       0.368570 Hz
  FIDRES     1.3566452 sec
AQ              9195.2
DW              20.700 usec
DE                          20.39 usec
TE                298.0 K
D1           0.10000000 sec
d11                        0.03000000 sec
             0.00000000 sec
    MCREST                 0.01500000 sec
MCWRK

   ======== CHANNEL f1 ========
NUC1                              13C
PL1                         7.75 usec
SFO1       100.6237964 MHz

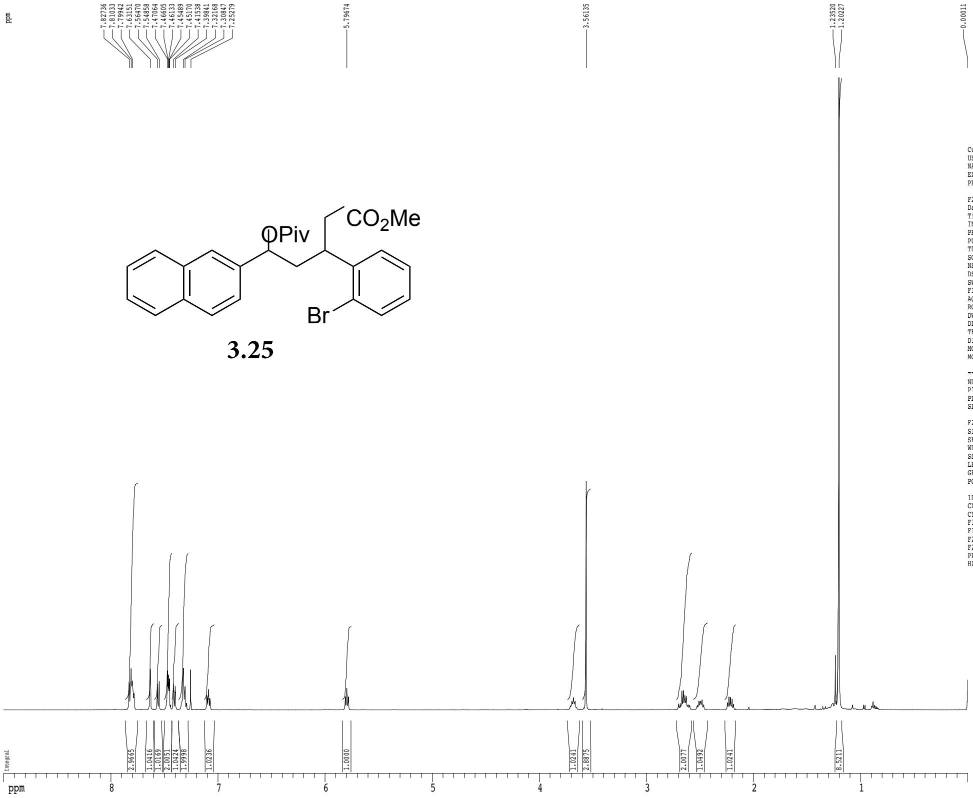

      ======== CHANNEL f2 ========
CPDPRG2         1H                mlev16
PCPD2
PL2                          90.00 usec
PL12            17.00 dB
SFO2       400.1328009 MHz


  F2 - Processing parameters
SI         100.6127500 MHz 65536
WDW                no
SSB                 0
LB               0.00 Hz
GB                  0
PC               1.00


  1D NMR plot parameters 22.00 cm
CX                         15.50 cm
F1P           200.000 ppm
F1            20122.55 Hz
F2P            -10.000 ppm
F2            -1006.13 Hz

    PPMCM                  9.21053 ppm/cm
HZCM       926.69629 Hz/cm
```

1H spectrum



3.25

```
Current Data Parameters
USER              lhanna
NAME         LEH-6-017-H1
EXPNO                  1
PROCNO                 1

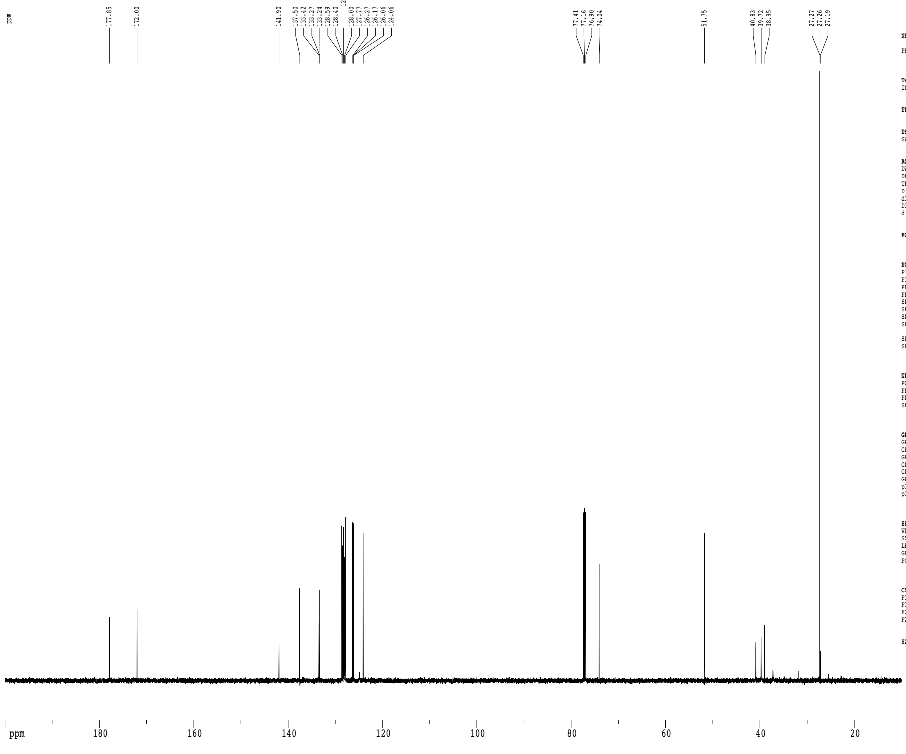
F2 - Acquisition Parameters
Date_           20150731
Time               14.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9998451 sec
RG                    16
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200341 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.39474 ppm/cm
HZCM           197.45528 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
    Current Data Parameters
USER     LEH-6-017-c2-f11  lhanna
    EXPNO              1
PROCNO                 1


     F2 - Acquisition Parameters
Date_                           20150731
INSTRUM            14.29
              cryo500
                         PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
                  CDCl3
  SOLVENT          513
DS                     16
SWH           30303.031 Hz
                         0.462388 Hz
  FIDRES     1.0813940 sec
AQ                 8192
DW               16.500 usec
DE                         6.00 usec
TE               298.0 K
D1           0.25000000 sec
d11                         0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
             0.00000000 sec
     MCREST                 0.01500000 sec
MCWRK        33.10 usec


    ======== CHANNEL f1 ========
NUC1                           13C
P11                         16.55 usec
P12              2500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                         2.70 dB
SP2                  2.70 dB
SPNAM1   Crp60,0.5,20.1
                       SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2                      0.00 Hz

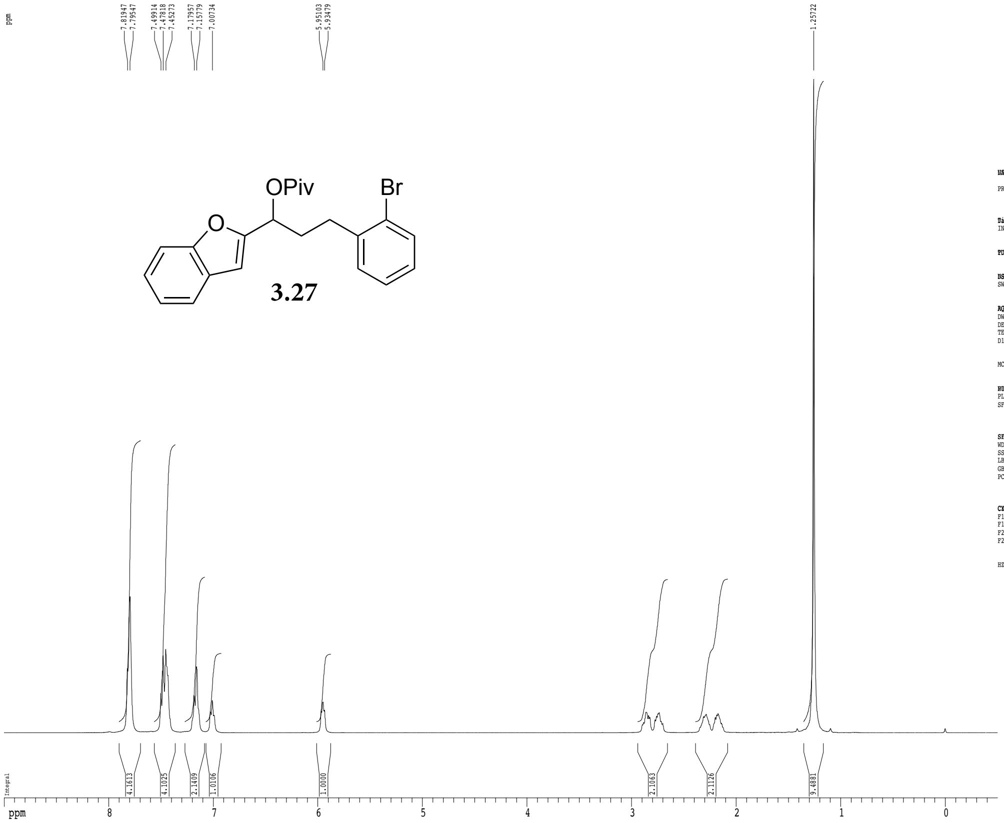

       ======== CHANNEL f2 ========
CPDPRG2          1H                 waltz16
PCPD2             100.00 usec
PL2                        1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz


      ====== GRADIENT CHANNEL =====
GPNAM1           SINE.100            SINE.100
GPX1             0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1               30.00 %
GPZ2                50.00 %
p15
p16                         500.00 usec
                 1000.00 usec

  F2 - Processing parameters
SI          125.7804103 MHz 65536
WDW                  no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 2.00


  1D NMR plot parameters cm
CX                          15.65 cm
F1P             200.000 ppm
F1              25156.08 Hz
F2P              10.000 ppm
F2               1257.80 Hz
                  8.33333 ppm/cm
    PPMCM     1048.17017 Hz/cm
HZCM
```

1H spectrum



```
    Current Data Parameters
NAME     MOK-III-bf5pivHCHARmkonev
    EXPNO             1
PROCNO                1

     F2 - Acquisition Parameters
Date_                          20150509
INSTRUM               21.22
              drx400
       PROBHD   5 mm QNP H/F/P
PULPROG                    zg30
                32050
  SOLVENT             8CDC13
NS                     2
SWH            6410.256 Hz
                           0.200008 Hz
  FIDRES     2.4999499 sec
RG                    32
DW                78.000 usec
DE                           4.50 usec
TE                298.0 K
D1             0.10000000 sec
               0.00000000 sec
     MCREST                  0.01500000 sec
MCWRK

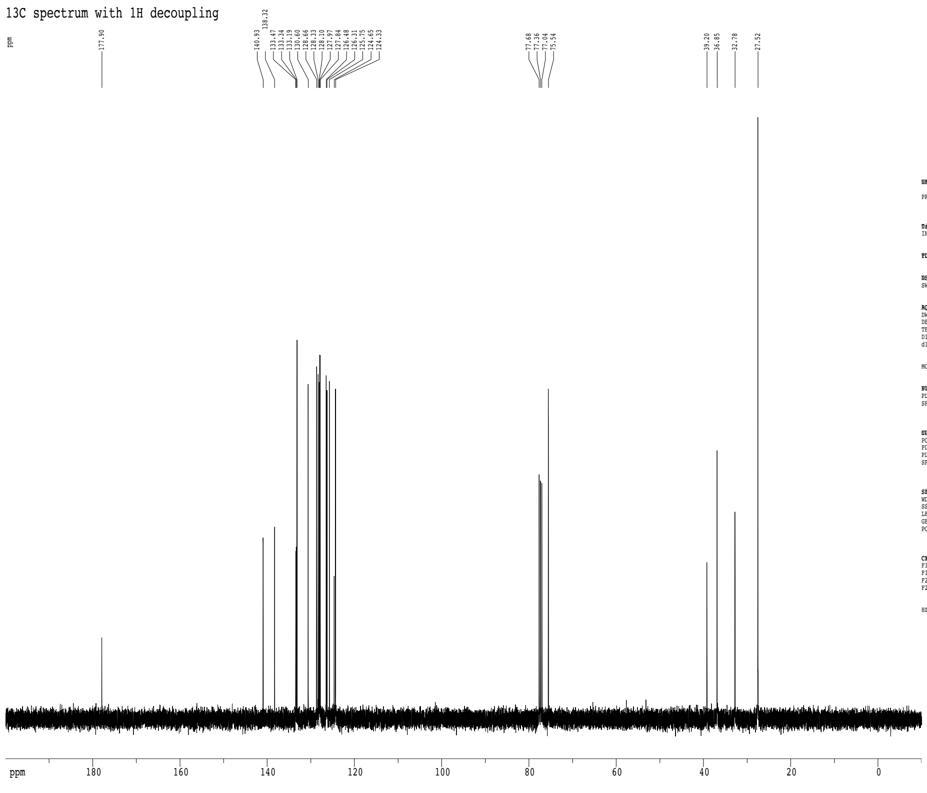
    ======== CHANNEL f1 ========
NUC1                             1H
PL1                        12.00 usec
SFO1        400.1328009 MHz

  F2 - Processing parameters
SI          400.1300480 MHz 65536
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

  1D NMR plot parameters
CX                         15.00 cm
F1P               9.000 ppm
F1             3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz

    PPMCM                    0.41667 ppm/cm
HZCM        166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     MOK-III-bf5pivCCHARmkonev
    EXPNO             1
PROCNO                1

     F2 - Acquisition Parameters
Date_                        20150509
INSTRUM              21.25
             drx400
       PROBHD   5 mm QNP H/F/P
PULPROG              65536
                          CDC13
  SOLVENT          152
NS                   4
SWH           24154.590 Hz
                        0.368570 Hz
  FIDRES     1.3566452 sec
RG                9195.2
DW                20.700 usec
DE                        20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11                       0.03000000 sec
              0.00000000 sec
    MCREST                0.01500000 sec
MCWRK

    ======== CHANNEL f1 ========
NUC1                           13C
PL1                       7.75 usec
SFO1        100.6237964 MHz

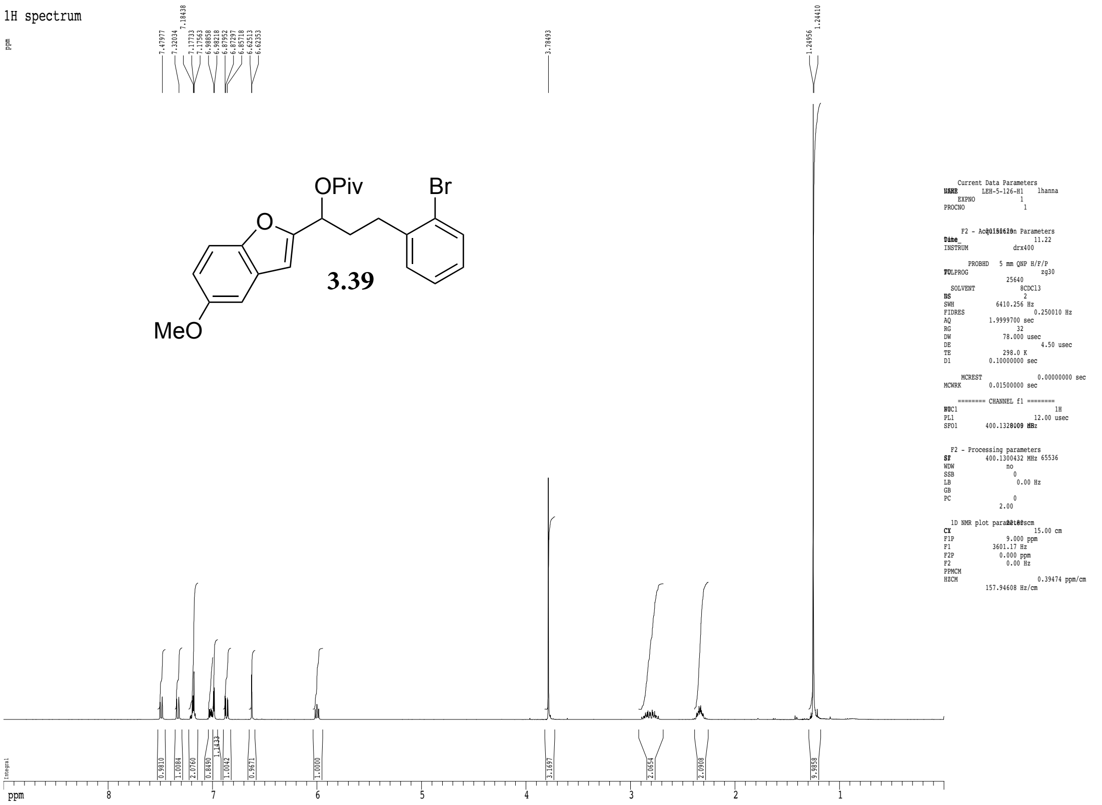
        ======== CHANNEL f2 ========
CPDPRG2          1H                 mlev16
PCPD2
PL2                        90.00 usec
PL12             17.00 dB
SFO2        400.1328009 MHz

  F2 - Processing parameters
SI          100.6127500 MHz 65536
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

  1D NMR plot parameters
CX                    15.50 cm
F1P           200.000 ppm
F1            20122.55 Hz
F2P            -10.000 ppm
F2            -1006.13 Hz

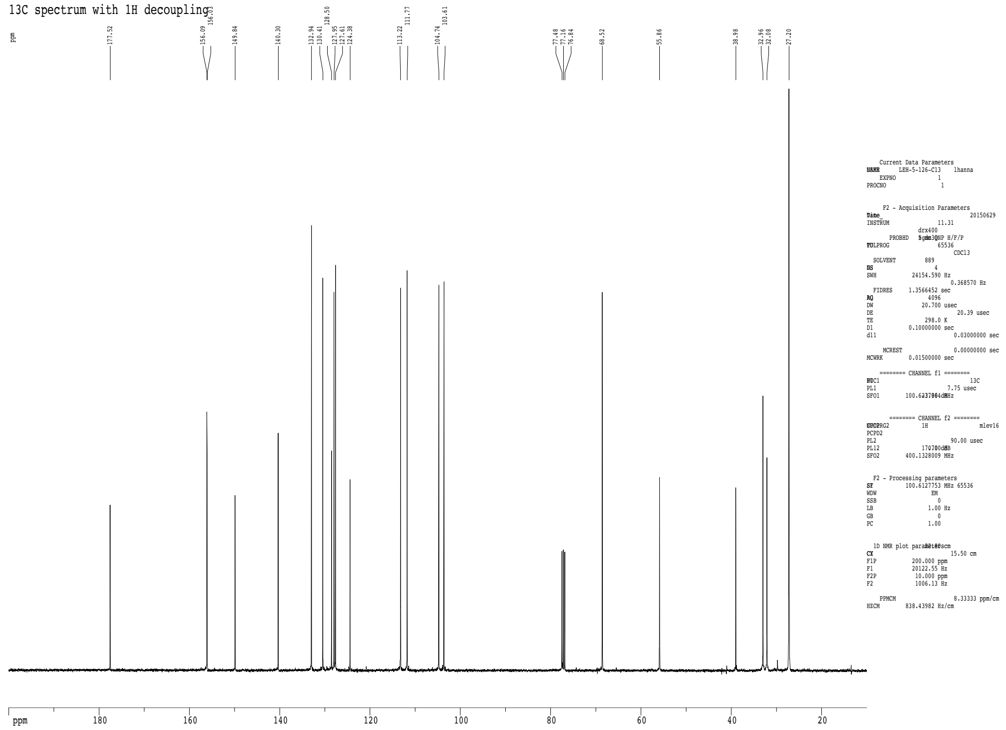
    PPMCM                9.21053 ppm/cm
HZCM        926.69629 Hz/cm
```

1H spectrum

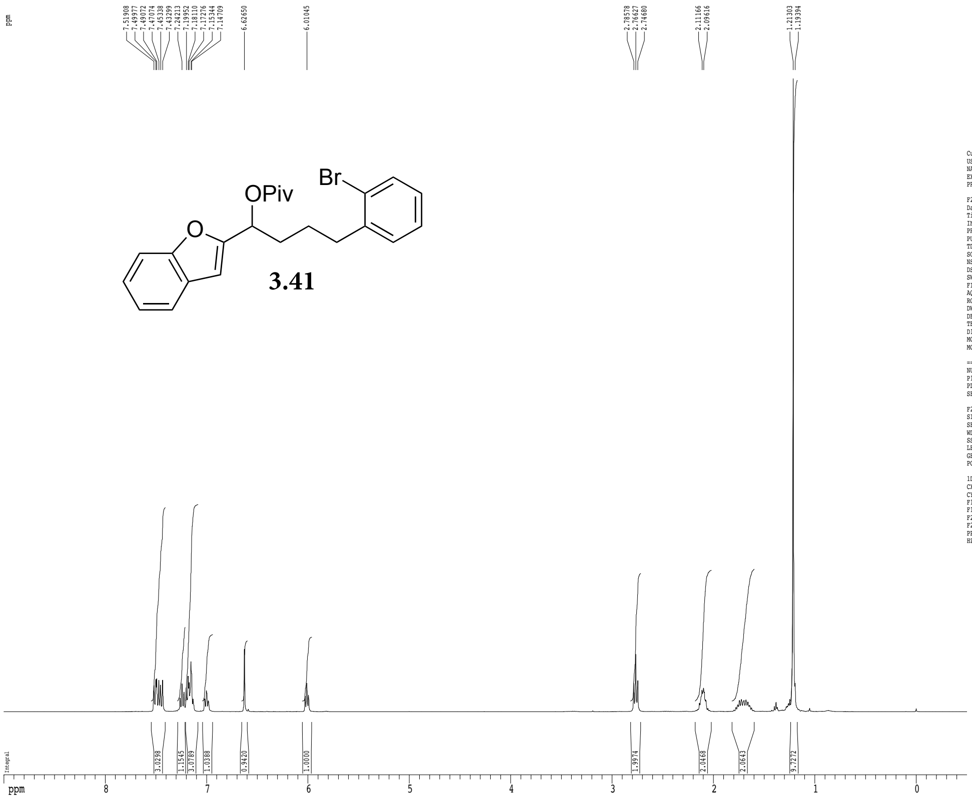


3.39

13C spectrum with 1H decoupling



1H spectrum



3.41

```
Current Data Parameters
USER              mkonev
NAME     MOK-III-bf6pivHCHAR
EXPNO                  1
PROCNO                 1

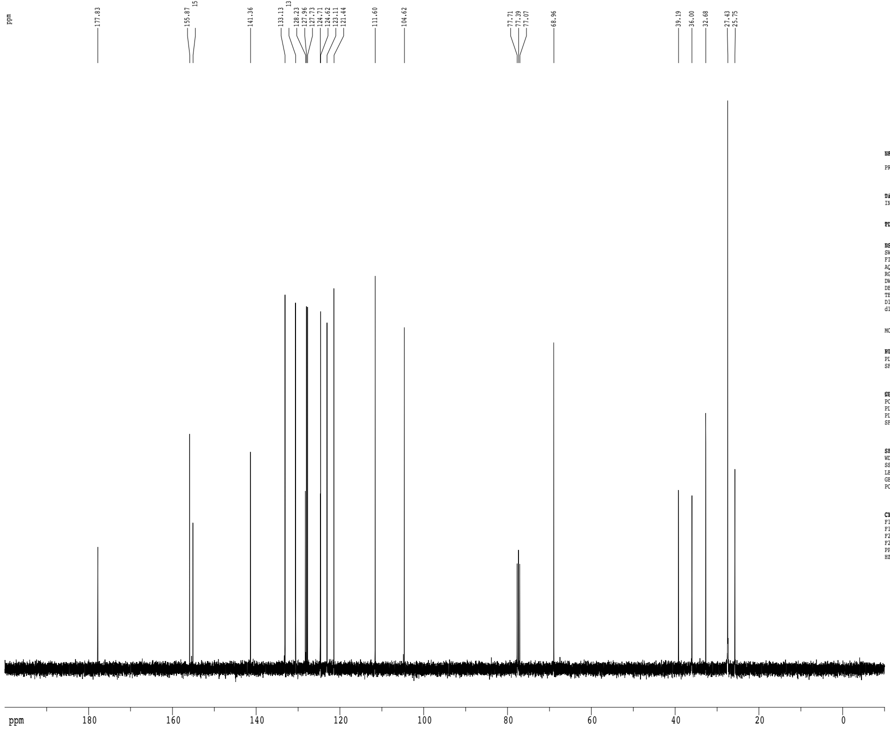
F2 - Acquisition Parameters
Date_          20150510
Time               4.20
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                32050
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.200008 Hz
AQ            2.4999499 sec
RG                   32
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1                0.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300505 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
USER     MOK-III-bf6pivCCHARmkonev
    EXPNO            1
PROCNO                1


     F2 - Acquisition Parameters
Date_                           20150510
INSTRUM             4.21
               drx400
      PROBHD   5 mm QNP H/F/P
PULPROG              65536
                          CDCl3
  SOLVENT           80
DS                    4
SWH           24154.590 Hz
FIDRES                      0.368570 Hz
AQ           1.3566452 sec
RG               7298.2
DW               20.700 usec
DE                          20.39 usec
TE                298.1 K
D1           0.10000000 sec
d11                          0.03000000 sec
             0.00000000 sec
    MCREST                   0.01500000 sec
MCWRK

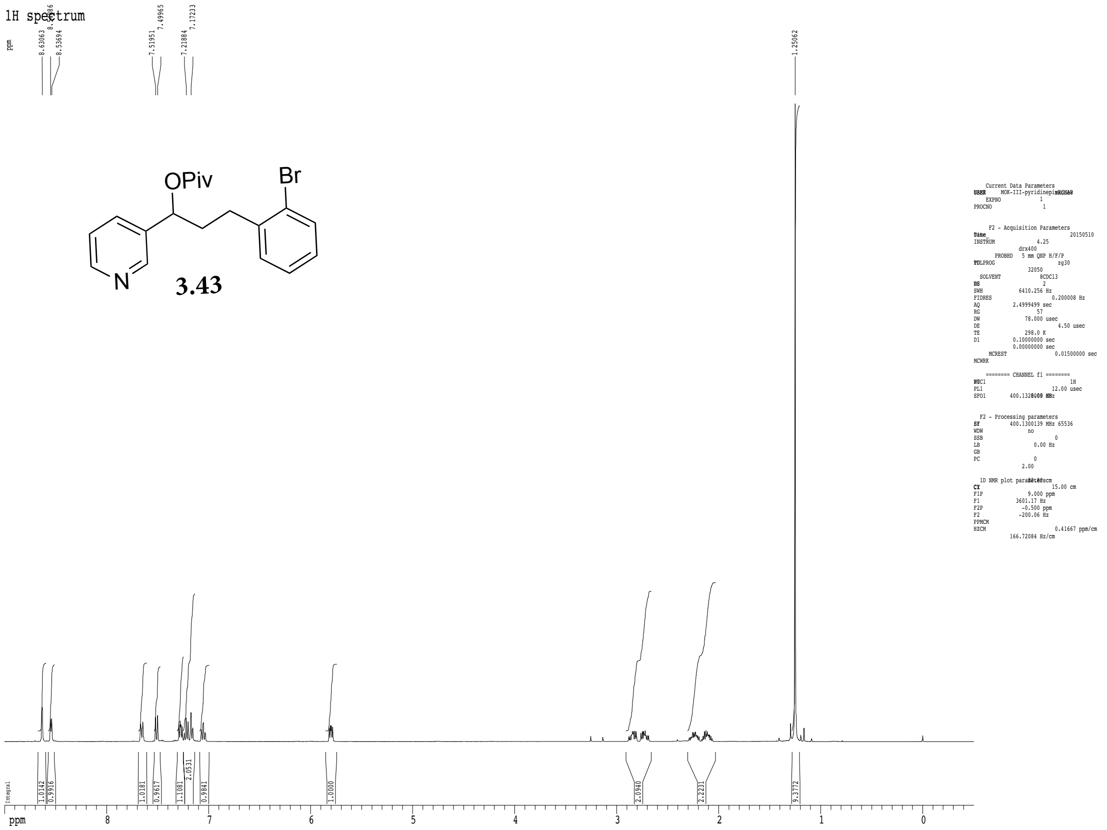
    ======== CHANNEL f1 ========
NUC1                           13C
PL1                         7.75 usec
SFO1       100.6237964dB MHz


       ======== CHANNEL f2 ========
CPDPRG2          1H                mlev16
PCPD2
PL2                         90.00 usec
PL12             170700dB
SFO2       400.1328009 MHz


  F2 - Processing parameters
SF         100.6127500 MHz 65536
WDW                 no
SSB                         0
LB                  0.00 Hz
GB
PC                     0
                  1.00

  1D NMR plot parameters cm
CX                        15.50 cm
F1P          200.000 ppm
F1           20122.55 Hz
F2P           -10.000 ppm
F2           -1006.13 Hz
PPMCM
HZCM                         9.21053 ppm/cm
             926.69629 Hz/cm
```

1H spectrum



```
    Current Data Parameters
USER      MOK-III-pyridinepimCHAR
    EXPNO            1
PROCNO               1

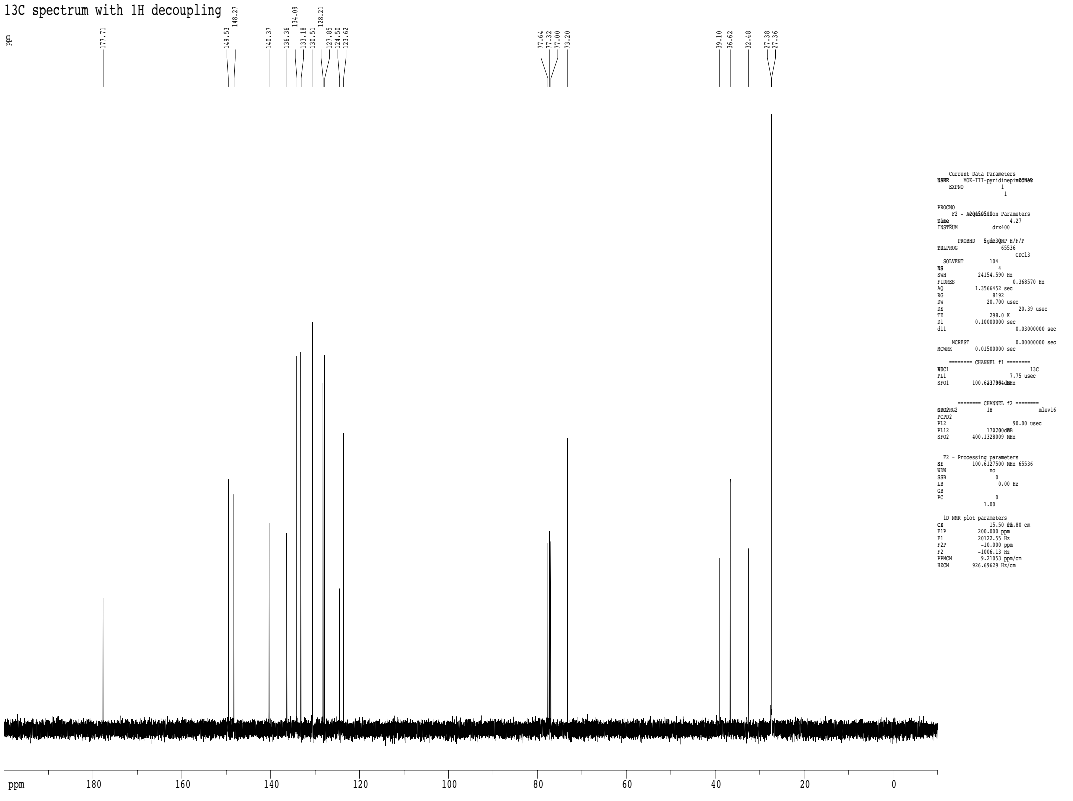
     F2 - Acquisition Parameters
Date_                           20150510
INSTRUM            4.25
              drx400
       PROBHD   5 mm QNP H/F/P
PULPROG                     zg30
                 32050
  SOLVENT             8CDCl3
NS                    2
SWH            6410.256 Hz
FIDRES                     0.200008 Hz
AQ           2.4999499 sec
RG                   57
DW              78.000 usec
DE                           4.50 usec
TE              298.0 K
D1           0.10000000 sec
             0.00000000 sec
     MCREST                 0.01500000 sec
MCWRK

    ======== CHANNEL f1 ========
NUC1                            1H
PL1                        12.00 usec
SFO1         400.1328009 MHz

  F2 - Processing parameters
SI           400.1300139 MHz 65536
WDW               no
SSB                         0
LB                  0.00 Hz
GB
PC                    0
              2.00

  1D NMR plot parameters cm
CX                         15.00 cm
F1P               9.000 ppm
F1             3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM
HZCM                        0.41667 ppm/cm
             166.72084 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
USER      MOK-III-pyridinepimCHAR
    EXPNO            1
                      1

PROCNO
     F2 - Acquisition Parameters 20150510
Date_                     4.27
INSTRUM            drx400

       PROBHD   5 mm QNP H/F/P zgdc30
PULPROG                65536
                            CDCl3
  SOLVENT         104
NS                    4
SWH           24154.590 Hz
FIDRES                    0.368570 Hz
AQ           1.3566452 sec
RG                 8192
DW              20.700 usec
DE                          20.39 usec
TE                298.0 K
D1           0.10000000 sec
d11                         0.03000000 sec

     MCREST                 0.00000000 sec
MCWRK        0.01500000 sec

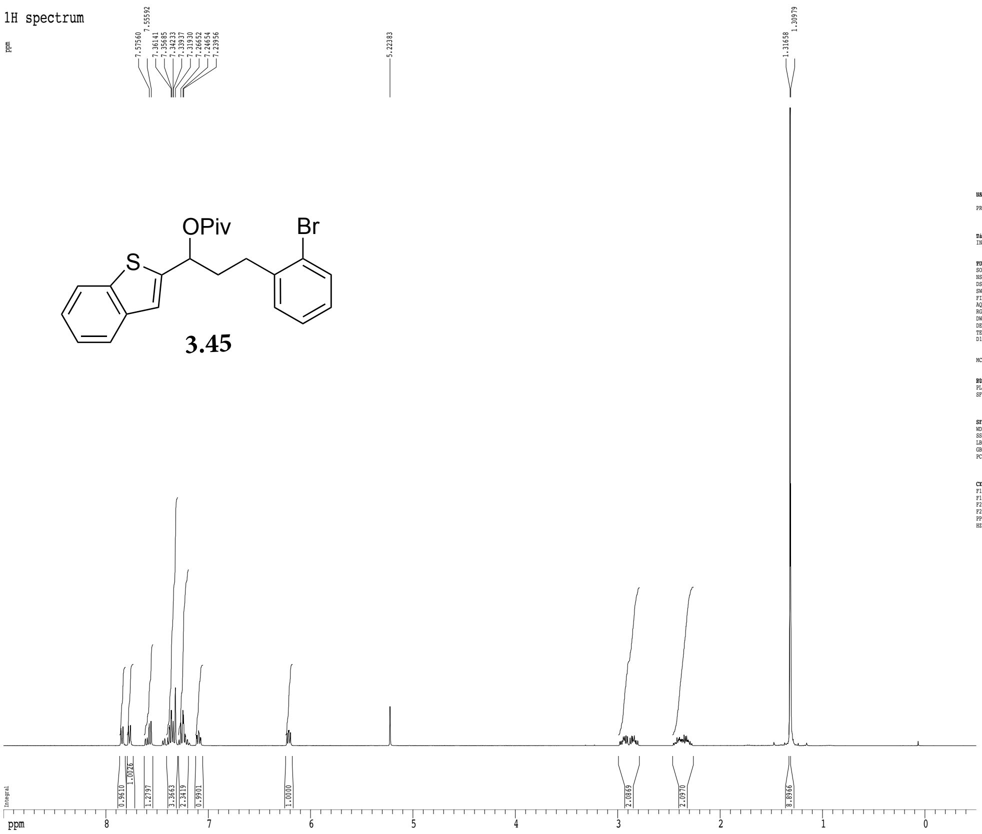
    ======== CHANNEL f1 ========
NUC1                              13C
PL1                        7.75 usec
SFO1         100.6237964 MHz

      ======== CHANNEL f2 ========
CPDPRG2          1H               mlev16
PCPD2
PL2                          90.00 usec
PL12              17.00 dB
SFO2         400.1328009 MHz

  F2 - Processing parameters
SI           100.6127500 MHz 65536
WDW               no
SSB                 0
LB                   0.00 Hz
GB
PC                  0
               1.00

  1D NMR plot parameters
CX                15.50 22.80 cm
F1P           200.000 ppm
F1            20122.55 Hz
F2P            -10.000 ppm
F2            -1006.13 Hz
PPMCM           9.21053 ppm/cm
HZCM         926.69629 Hz/cm
```

1H spectrum



```
    Current Data Parameters
NAMEUSERMOK-III-benzothiopivHCHARonev
    EXPNO             1
PROCNO                1

     F2 - Acquisition Parameters
Date_   20150510           4.31
INSTRUM            drx400

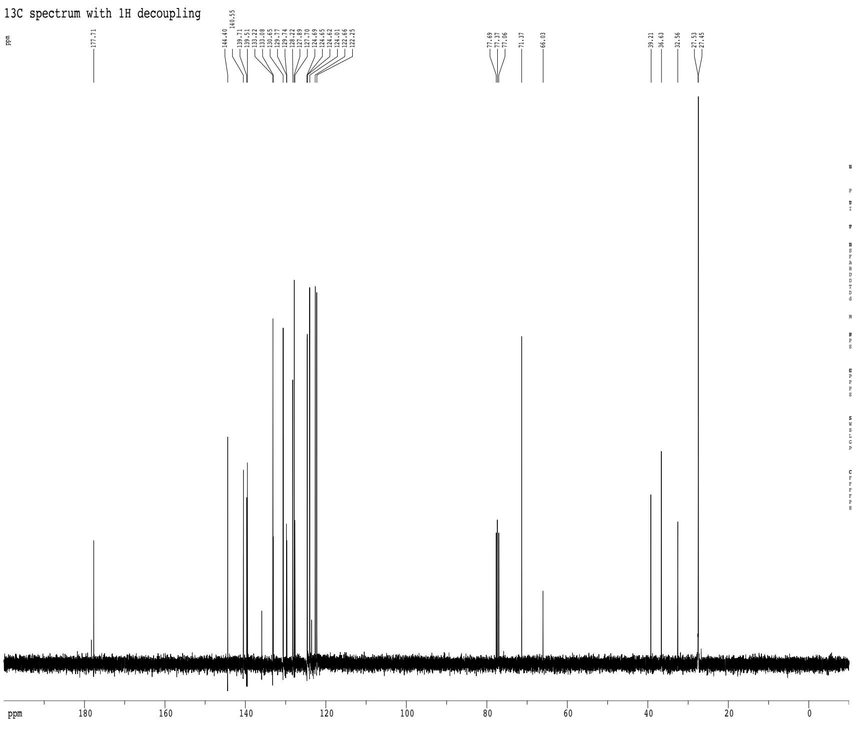
       PROBHD   5 mm QNP H/F/P
PULPROG                      zg30
SOLVENT           32050
NS                    8CDCl3
DS                     2
SWH           6410.256 Hz
FIDRES                       0.200008 Hz
AQ          2.4999499 sec
RG                32
DW                  78.000 usec
DE                4.50 usec
TE                298.0 K
D1      0.10000000 sec
            0.00000000 sec
     MCREST                   0.01500000 sec
MCWRK

    ======== CHANNEL f1 ========
NUC1           12.00 usec       1H
PL1                0.00 dB
SFO1       400.1328009 MHz

  F2 - Processing parameters
SI         400.1300175 MHz 65536
WDW                no
SSB                         0
LB                   0.00 Hz
GB
PC                    0
               2.00

  1D NMR plot parameters
CX                 15.00 22.80 cm
F1P                 9.000 ppm
F1             3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM        166.72084 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
NAMEUSER     MOK-III-benzothiopivHCHAR
    EXPNO            1
                      1

PROCNO
     F2 - Acquisition Parameters
Date_   20150510           4.32
INSTRUM            drx400

       PROBHD   5 mm QNP H/F/P
PULPROG   zgdc30    65536
                         CDCl3
  SOLVENT           64
NS DS                4
SWH           24154.590 Hz
FIDRES                    0.368570 Hz
AQ
RG                 1.3566452 sec
DW            9195.2700 usec
DE                          20.39 usec
TE                298.0 K
D1           0.10000000 sec
d11                        0.03000000 sec
             0.00000000 sec
     MCREST                0.01500000 sec
MCWRK

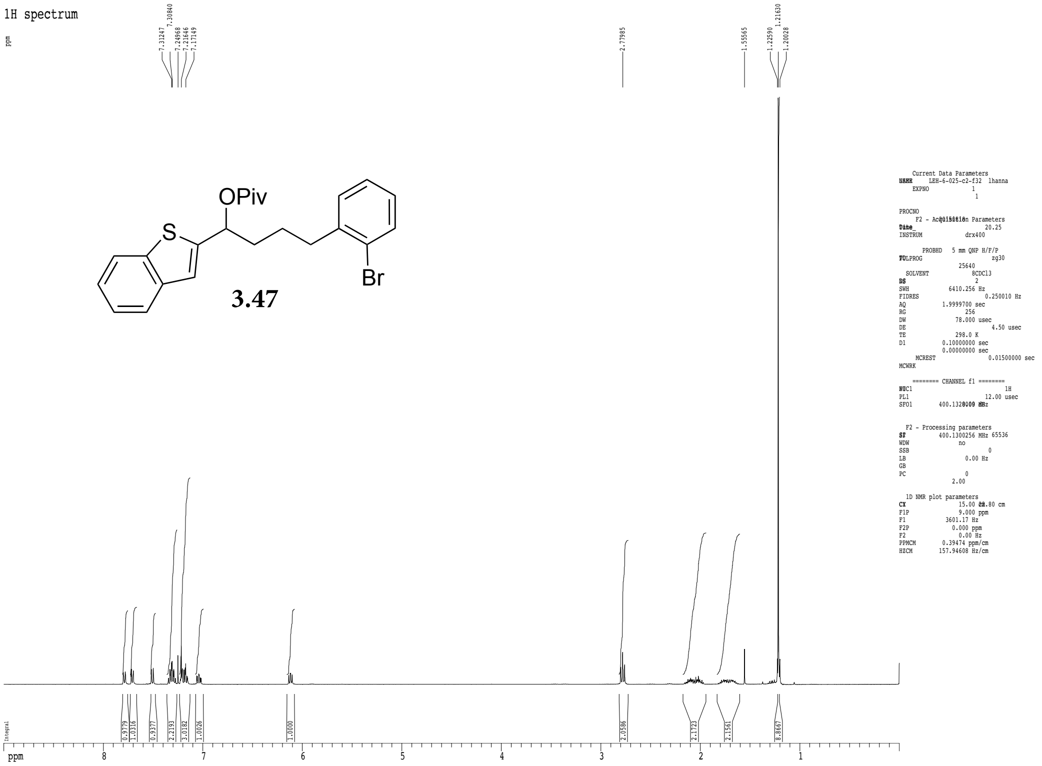
    ======== CHANNEL f1 ========
NUC1                            13C
PL1                      7.75 usec
SFO1       100.6237964 dB MHz

      ======== CHANNEL f2 ========
CPDPRG2          1H              mlev16
PCPD2
PL2                       90.00 usec
PL12             17.00 dB
SFO2       400.1328009 MHz

  F2 - Processing parameters
SI         100.6127500 MHz 65536
WDW                no
SSB                         0
LB                   0.00 Hz
GB
PC                    0
              1.00

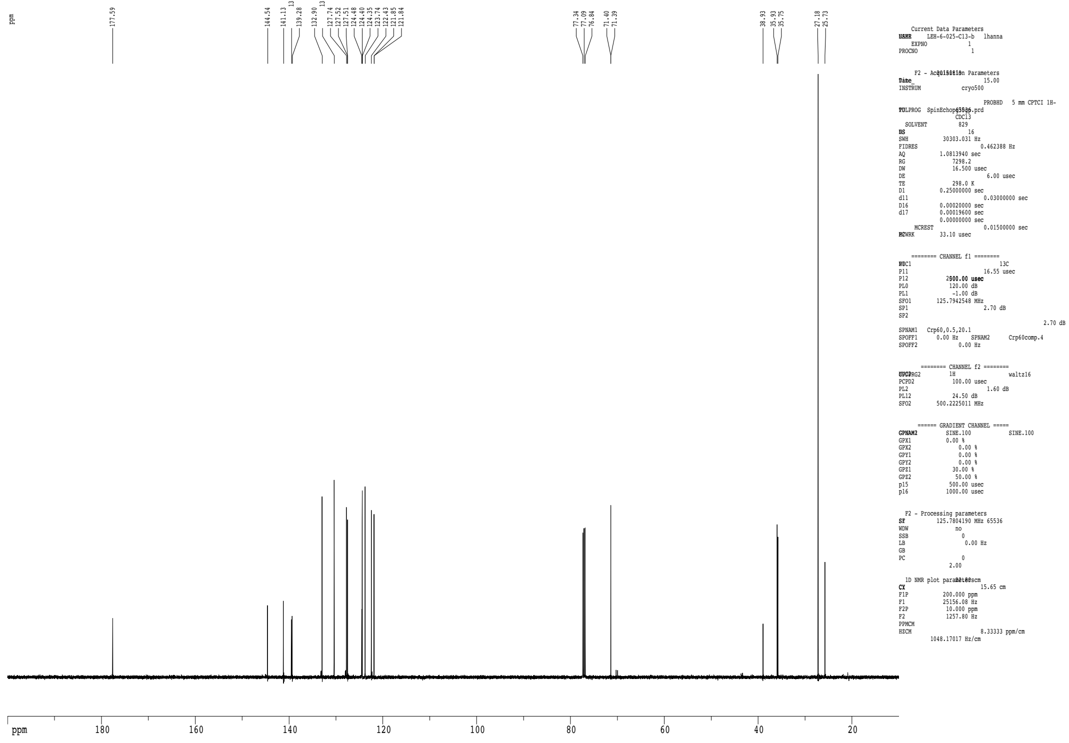
  1D NMR plot parameters
CX                15.50 22.80 cm
F1P           200.000 ppm
F1            20122.55 Hz
F2P            -10.000 ppm
F2            -1006.13 Hz
PPMCM          9.21053 ppm/cm
HZCM        926.69629 Hz/cm
```

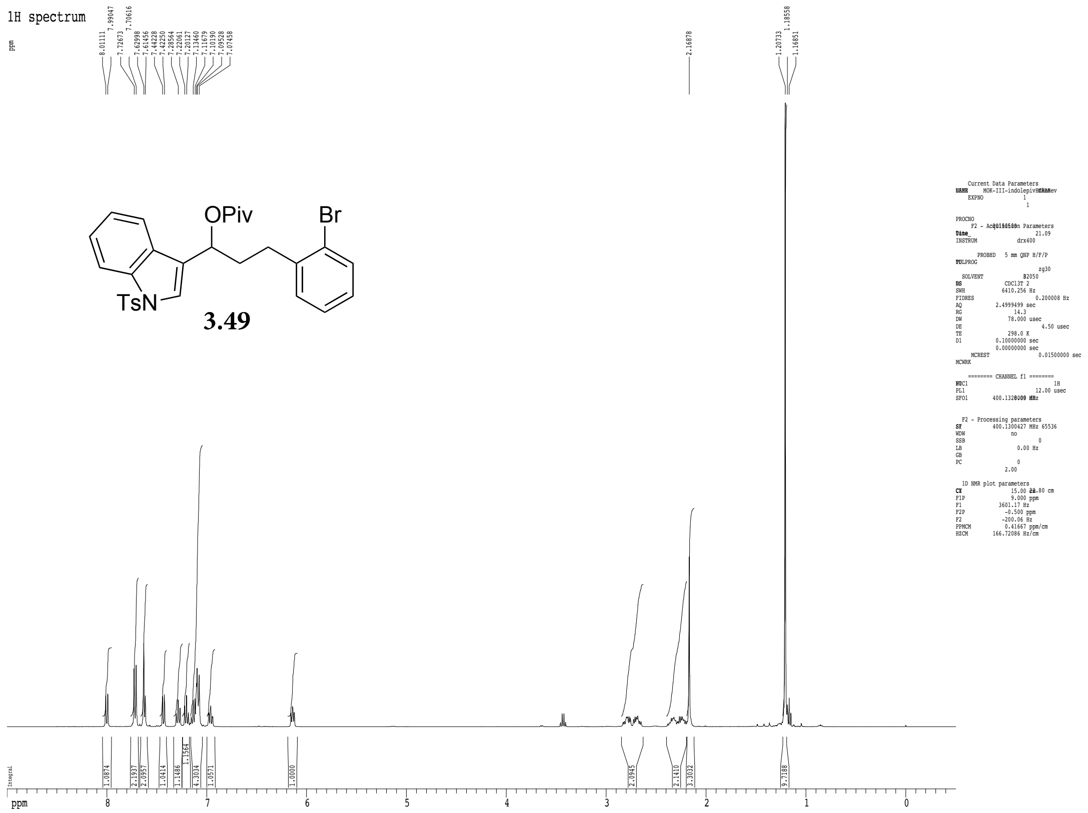
1H spectrum



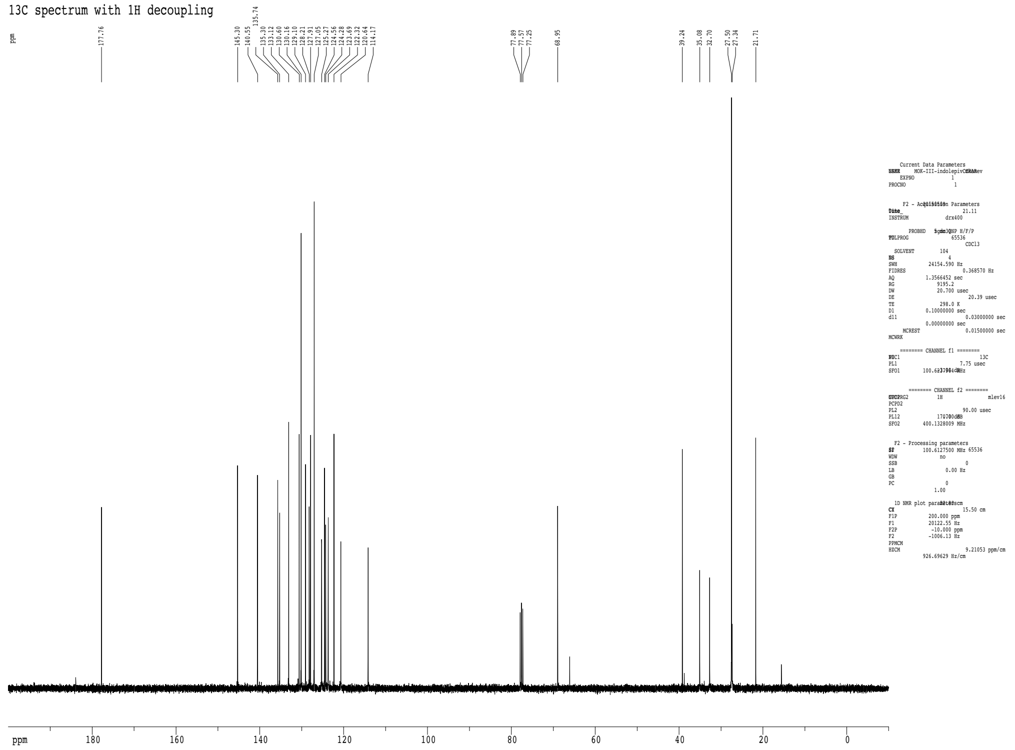
3.47

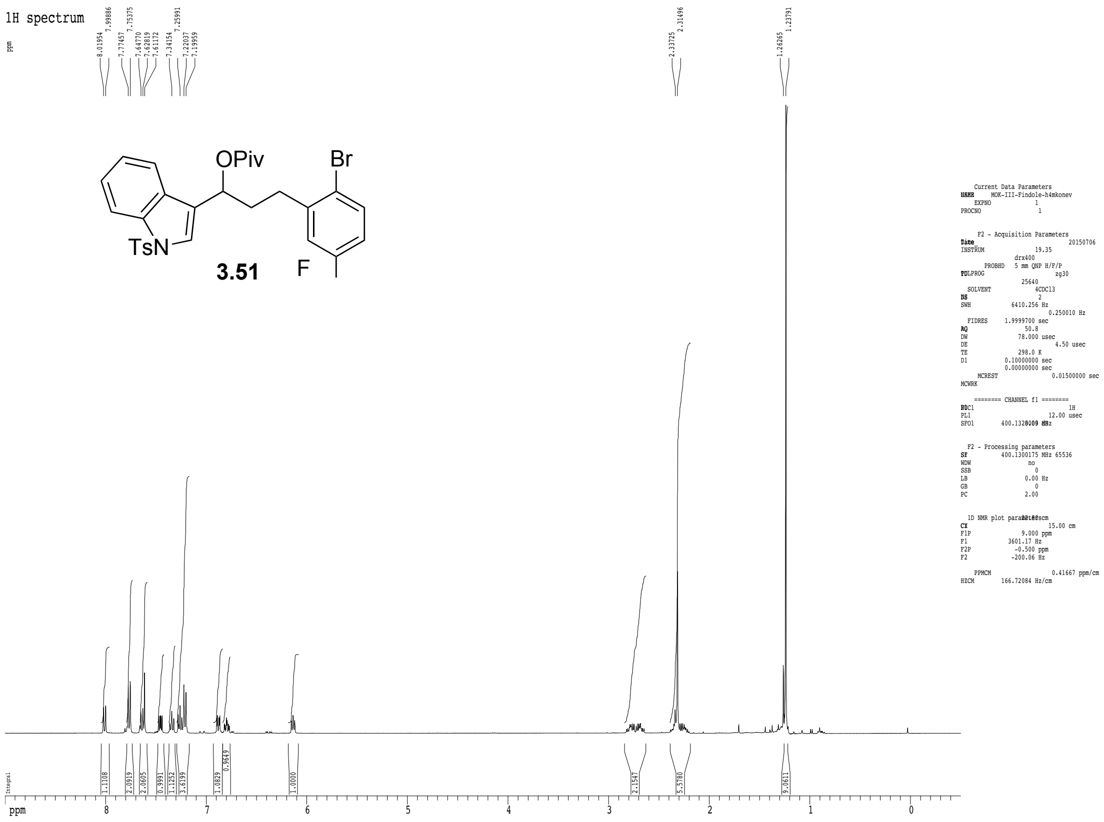
Z-restored spin-echo 13C spectrum with 1H decoupling




1H spectrum
ppm
8.01111
7.99047
7.72673
7.70616
7.62998
7.61456
7.44228
7.42250
7.28564
7.22061
7.20127
7.13460
7.11679
7.10190
7.09528
7.07458
2.16878
1.20733
1.18558
1.16851
OPiv
Br
TsN
Integral
1.0874
2.1937
2.0957
1.0414
1.1486
1.1564
4.3034
1.0571
1.0000
2.0945
2.1410
3.3032
9.7188
ppm
8
7
6
5
4
3
2
1
0

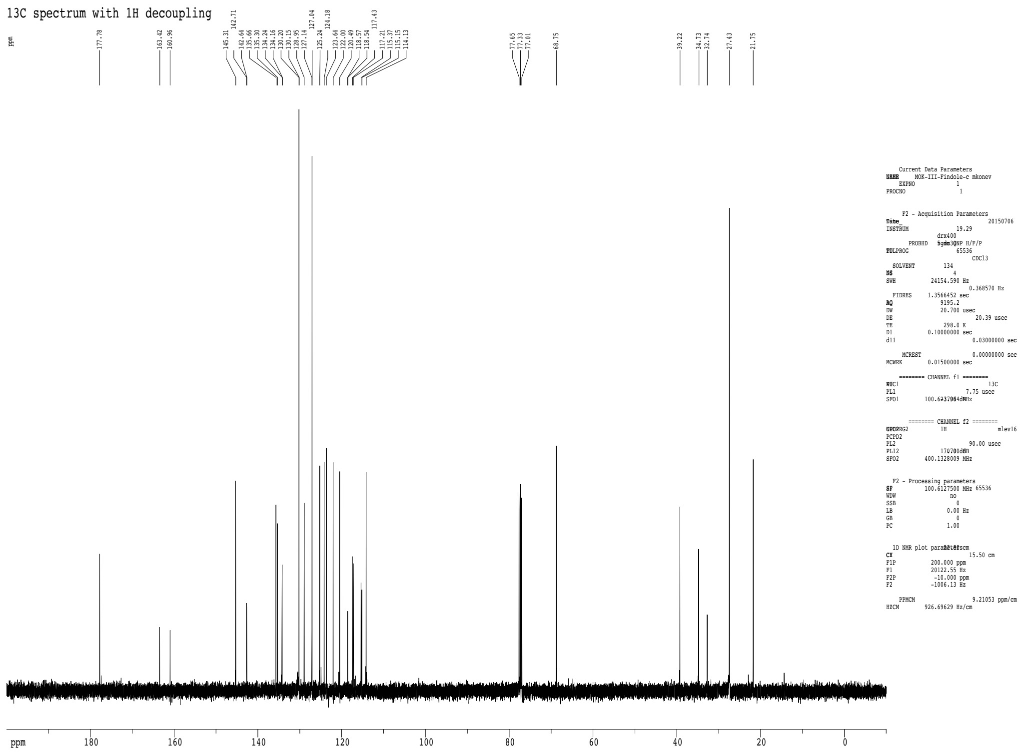
3.49


13C spectrum with 1H decoupling
ppm
177.76
145.30
140.55
135.74
135.30
133.12
130.60
130.16
129.10
128.21
127.91
127.05
125.27
124.56
124.28
123.69
122.32
120.64
114.17
77.89
77.57
77.25
68.95
39.24
35.08
32.70
27.50
27.34
21.71
ppm
180
160
140
120
100
80
60
40
20
0



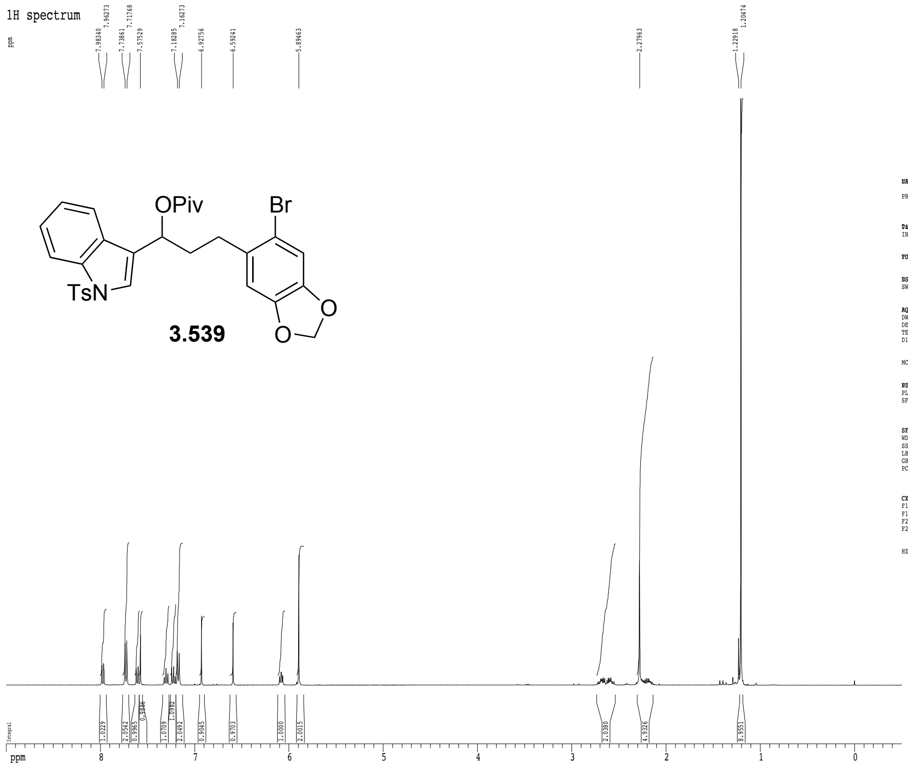
3.51

1H spectrum
ppm
8.01954
7.99886
7.77457
7.75375
7.64770
7.62819
7.61172
7.34154
7.25991
7.22037
7.19959
2.33725
2.31496
1.26265
1.23791
OPiv
Br
TsN
F
Integral
1.1108
2.0919
2.0605
0.9991
1.1252
3.6199
1.0829
0.9649
1.0000
2.1547
5.5780
9.0611
ppm
8
7
6
5
4
3
2
1
0
Current Data Parameters
NAME MOK-III-Findole-h4mkonev
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150706
Time 19.35
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 25640
SOLVENT CDCl3
NS 4
DS 2
SWH 6410.256 Hz
FIDRES 0.250010 Hz
AQ 1.9999700 sec
RG 50.8
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm



13C spectrum with 1H decoupling
ppm
177.78
163.42
160.96
145.31
142.71
142.64
135.66
135.30
134.24
134.16
130.20
130.15
128.95
127.14
127.04
125.24
124.18
123.64
122.00
120.49
118.57
118.54
117.43
117.21
115.37
115.15
114.13
77.65
77.33
77.01
68.75
39.22
34.73
32.74
27.43
21.75
ppm
180
160
140
120
100
80
60
40
20
0
Current Data Parameters
NAME MOK-III-Findole-c mkonev
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150706
Time 19.29
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 134
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 9195.2
DW 20.700 usec
DE 20.39 usec
TE 298.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 7.75 usec
PL1
SFO1 100.6237964 MHz
======== CHANNEL f2 ========
CPDPRG2 mlev16
NUC2 1H
PCPD2 90.00 usec
PL2
PL12
SFO2 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 100.6127500 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69629 Hz/cm

1H spectrum



3.539

```
    Current Data Parameters
NAME     MOK-III-02MePiv-H mkonev
   EXPNO              1
PROCNO                 1


     F2 - Acquisition Parameters
Date_                              20150709
INSTRUM              21.46
             drx400
       PROBHD   5 mm QNP H/F/P
PULPROG                       zg30
               51280
  SOLVENT              8CDCl3
NS                      2
SWH            6410.256 Hz
                            0.125005 Hz
  FIDRES     3.9998901 sec
AQ                    32
DW               78.000 usec
DE                               4.50 usec
TE               298.0 K
D1           0.10000000 sec
             0.00000000 sec
     MCREST                  0.01500000 sec
MCWRK

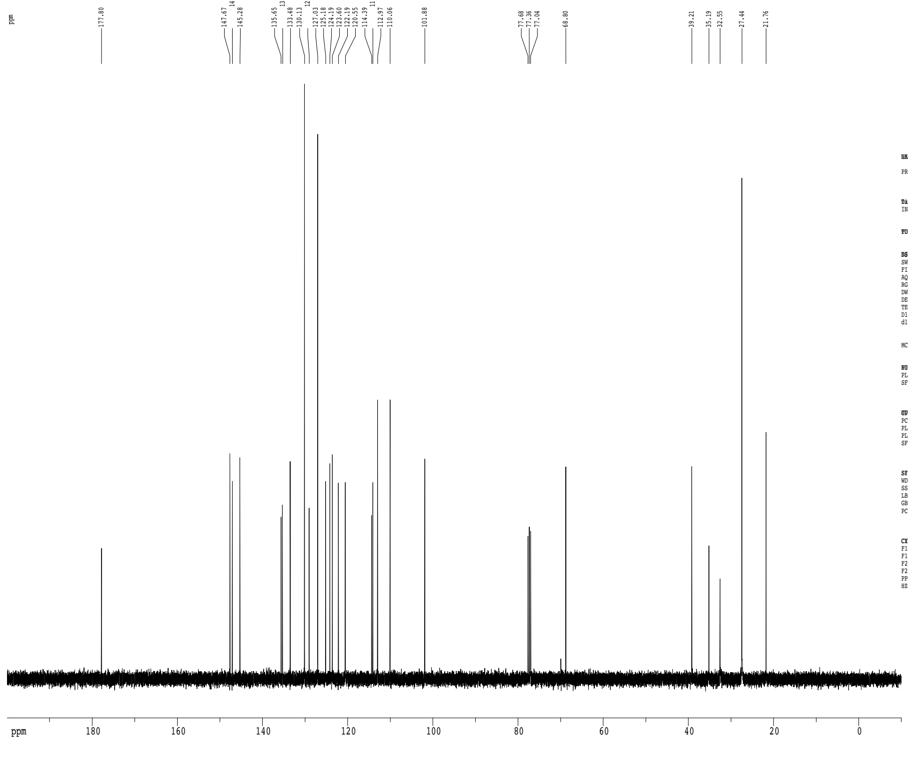
    ======== CHANNEL f1 ========
NUC1                               1H
PL1                         12.00 usec
SFO1         400.1328009 MHz


  F2 - Processing parameters
SF           400.1300280 MHz 65536
WDW                    no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00


  1D NMR plot parameters 22.00 cm
CX                           15.00 cm
F1P                 9.000 ppm
F1               3601.17 Hz
F2P                -0.500 ppm
F2                -200.06 Hz

    PPMCM                    0.41667 ppm/cm
HZCM         166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     MOK-III-02MePiv-C mkonev
   EXPNO              1
PROCNO                 1


     F2 - Acquisition Parameters 20150709
Date_                        21.47
INSTRUM              drx400

       PROBHD   5 mm QNP H/F/P zgdc30
PULPROG                65536
                            CDCl3
  SOLVENT            96
NS                      4
SWH            24154.590 Hz
FIDRES                       0.368570 Hz
AQ           1.3566452 sec
RG                9195.2
DW                20.700 usec
DE                             20.39 usec
TE                 298.0 K
D1           0.10000000 sec
d11                            0.03000000 sec
             0.00000000 sec
     MCREST                  0.01500000 sec
MCWRK

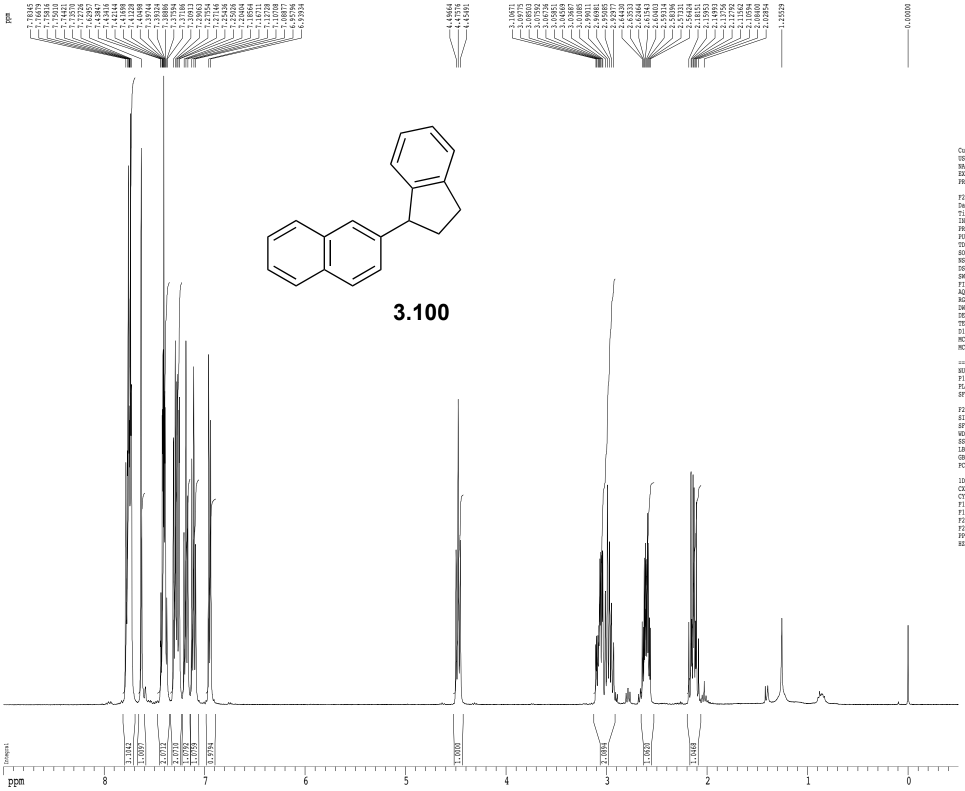
    ======== CHANNEL f1 ========
NUC1                              13C
PL1                         7.75 usec
SFO1         100.6237964 MHz -3.00 dB


       ======== CHANNEL f2 ========
CPDPRG2           1H                  mlev16
PCPD2
PL2                         90.00 usec
PL12              17.00 -0.70 dB
SFO2         400.1328009 MHz


  F2 - Processing parameters
SF           100.6127500 MHz 65536
WDW                   no
SSB                      0
LB                    0.00 Hz
GB
PC                       0
                  1.00

  1D NMR plot parameters 22.00 cm
CX                          15.50 cm
F1P             200.000 ppm
F1              20122.55 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM
HZCM                          9.21053 ppm/cm
             926.69629 Hz/cm
```

1H spectrum



3.100

```
Current Data Parameters
USER              mkonev
NAME     MOK-III-napxchCHAR
EXPNO                  1
PROCNO                 1

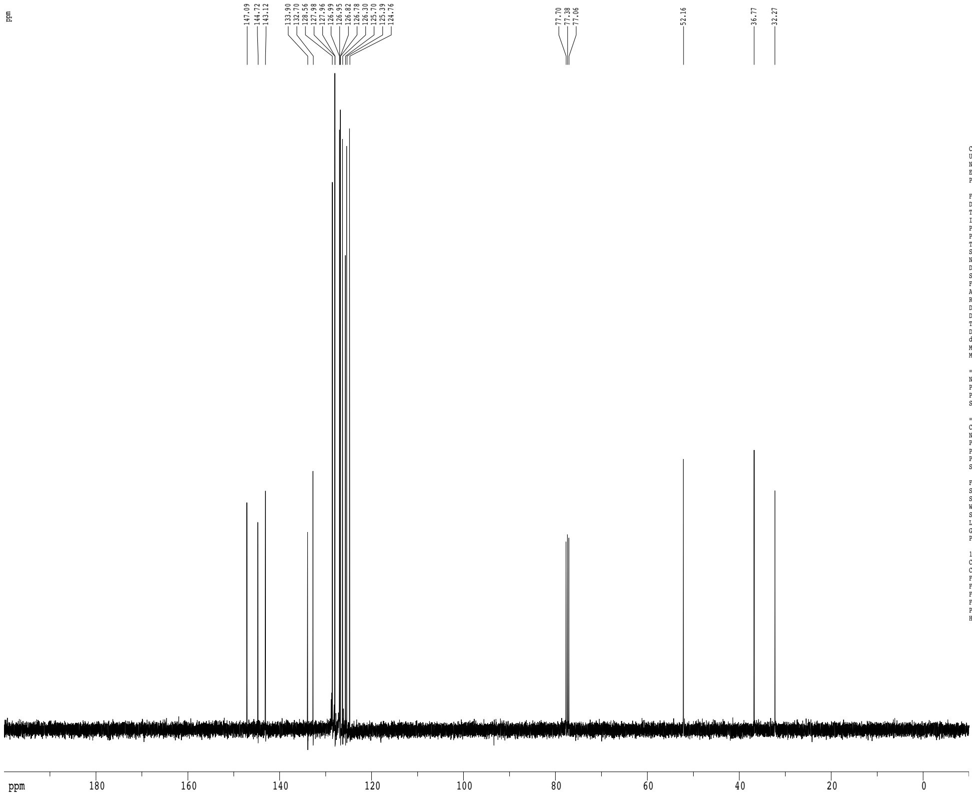
F2 - Acquisition Parameters
Date_           20150509
Time               11.10
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 32050
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.200008 Hz
AQ             2.4999499 sec
RG                    57
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300733 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72087 Hz/cm
```

13C spectrum with 1H decoupling



```
Current Data Parameters
USER              mkonev
NAME     MOK-III-napxcCCHAR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150509
Time               11.12
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   136
DS                     4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ             1.3566452 sec
RG                 13004
DW                20.700 usec
DE                 20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

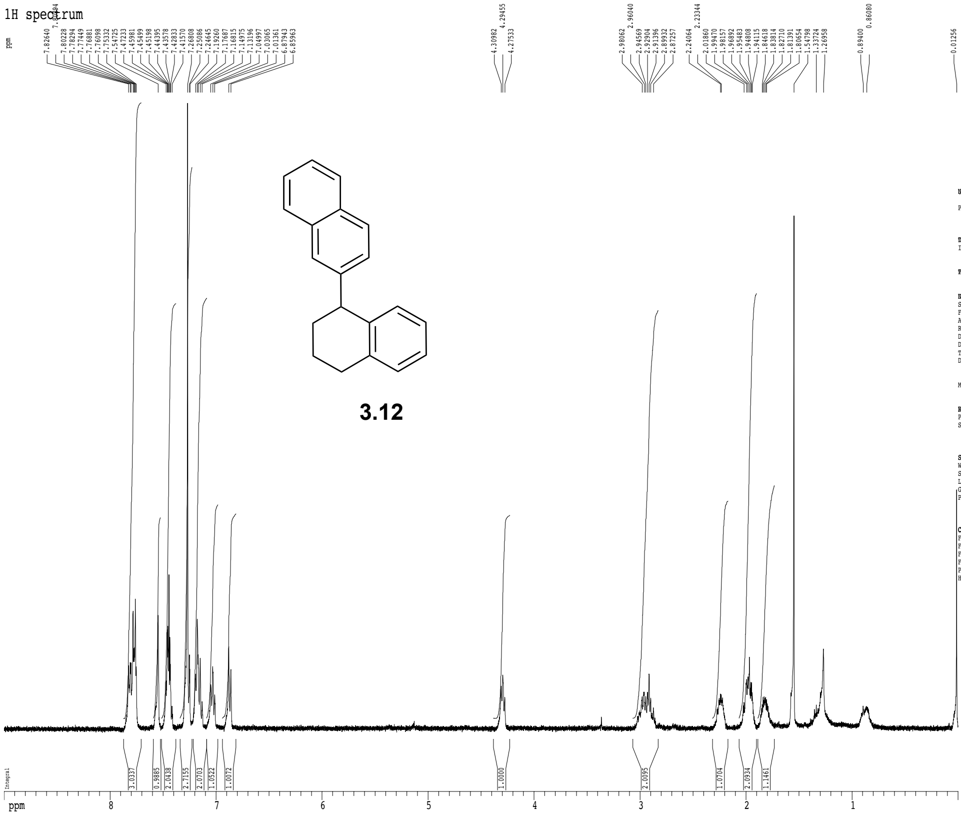
======== CHANNEL f1 ========
NUC1                 13C
P1                  7.75 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2           mlev16
NUC2                  1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               17.70 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127500 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              200.000 ppm
F1              20122.55 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM            9.21053 ppm/cm
HZCM           926.69629 Hz/cm
```

1H spectrum



3.12

```
   Current Data Parameters
NAME      LEH-6-085-c1-f12b lhanna
   EXPNO              1
PROCNO                1

     F2 - Acquisition Parameters
Date_                    16.55
INSTRUM             drx400
      PROBHD   5 mm QNP H/F/P
PULPROG                   zg30
                 65536
  SOLVENT            CDCl3
NS                    2
SWH           6410.256 Hz
FIDRES                 0.097813 Hz
AQ           5.1118579 sec
RG                724.1
DW               78.000 usec
DE                        4.50 usec
TE               298.0 K
D1           0.10000000 sec

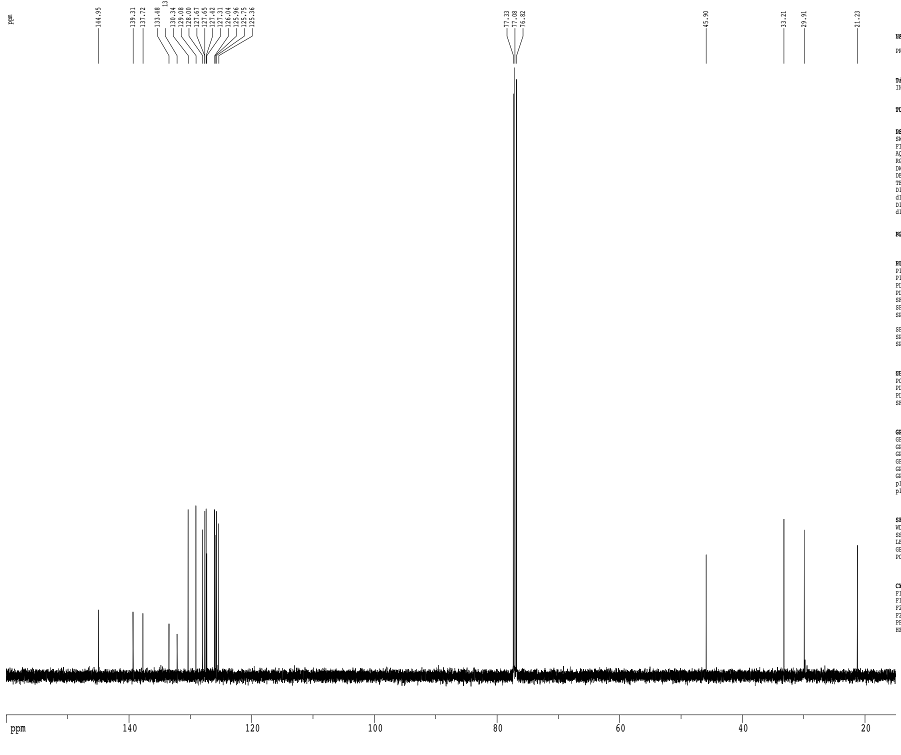
     MCREST                 0.00000000 sec
MCWRK        0.01500000 sec

    ======== CHANNEL f1 ========
NUC1                          1H
PL1                    12.00 usec
SFO1       400.1328009 MHz

  F2 - Processing parameters
SI         400.1300175 MHz 65536
WDW               no
SSB                 0
LB                   0.00 Hz
GB
PC                  0
               2.00

  1D NMR plot parameters
CX                     15.00 cm
F1P               9.000 ppm
F1             3601.17 Hz
F2P              0.000 ppm
F2                0.00 Hz
PPMCM
HZCM                     0.39474 ppm/cm
           157.94606 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     LEH-6-085-f12-C13 lhanna
   EXPNO              1
PROCNO                 1

     F2 - Acquisition Parameters
Date_                    19.12
INSTRUM            cryo500
                          PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
                65536
                  CDCl3
  SOLVENT          979
DS                   16
SWH          30303.031 Hz
FIDRES                 0.462388 Hz
AQ          1.0813940 sec
RG              7298.2
DW              16.500 usec
DE                      6.00 usec
TE              298.0 K
D1          0.25000000 sec
d11                     0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec

     MCREST                 0.00000000 sec
MCWRK       0.01500000 sec

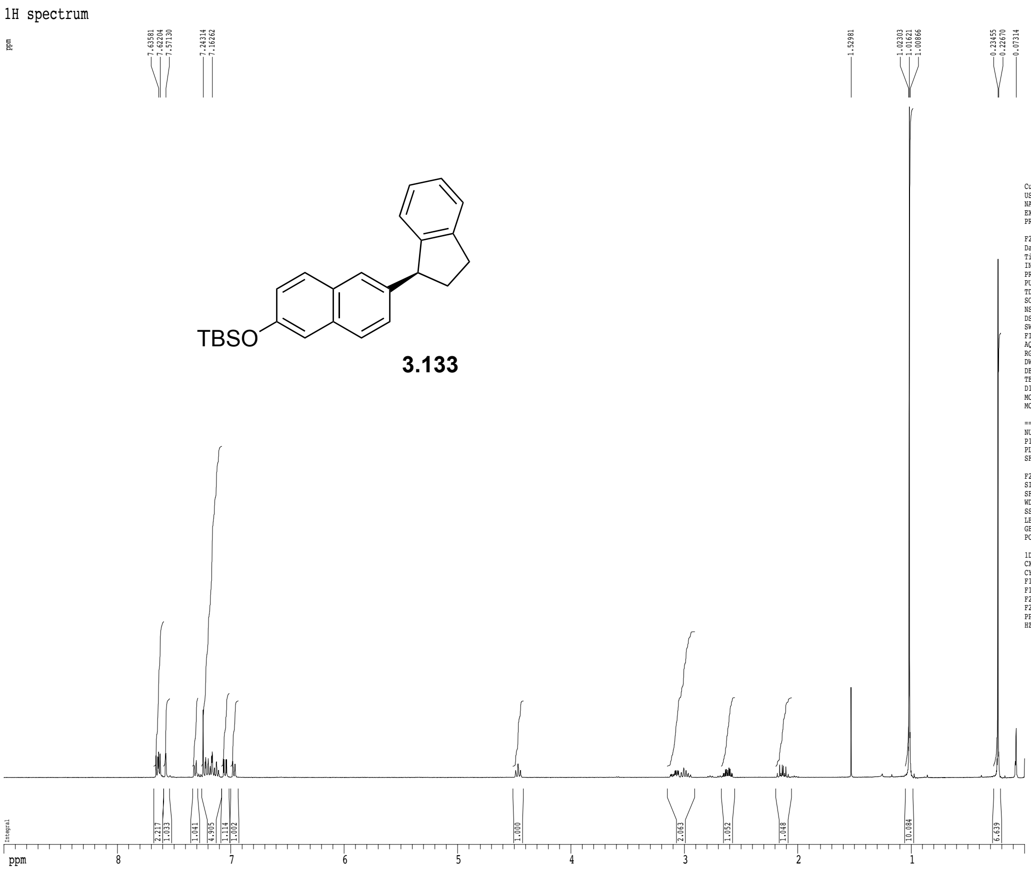
    ======== CHANNEL f1 ========
NUC1                          13C
P11                     16.55 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP1                     2.70 dB
SP2
                                     2.70 dB
SPNAM1   Crp60,0.5,20.1
SPOFF1      0.00 Hz    SPNAM2      Crp60comp.4
SPOFF2            0.00 Hz

      ======== CHANNEL f2 ========
CPDPRG2        1H                waltz16
PCPD2           100.00 usec
PL2                        1.60 dB
PL12            24.50 dB
SFO2       500.2225011 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1          SINE.100            SINE.100
GPX1           0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1              30.00 %
GPZ2               50.00 %
p15              500.00 usec
p16             1000.00 usec

  F2 - Processing parameters
SI         125.7804190 MHz 65536
WDW               no
SSB                 0
LB                   0.00 Hz
GB
PC                  0
               2.00

  1D NMR plot parameters
CX                     15.65 cm
F1P           160.000 ppm
F1            20124.87 Hz
F2P            15.000 ppm
F2             1886.71 Hz
PPMCM
HZCM                     6.35965 ppm/cm
           799.91937 Hz/cm
```


1H spectrum

3.133

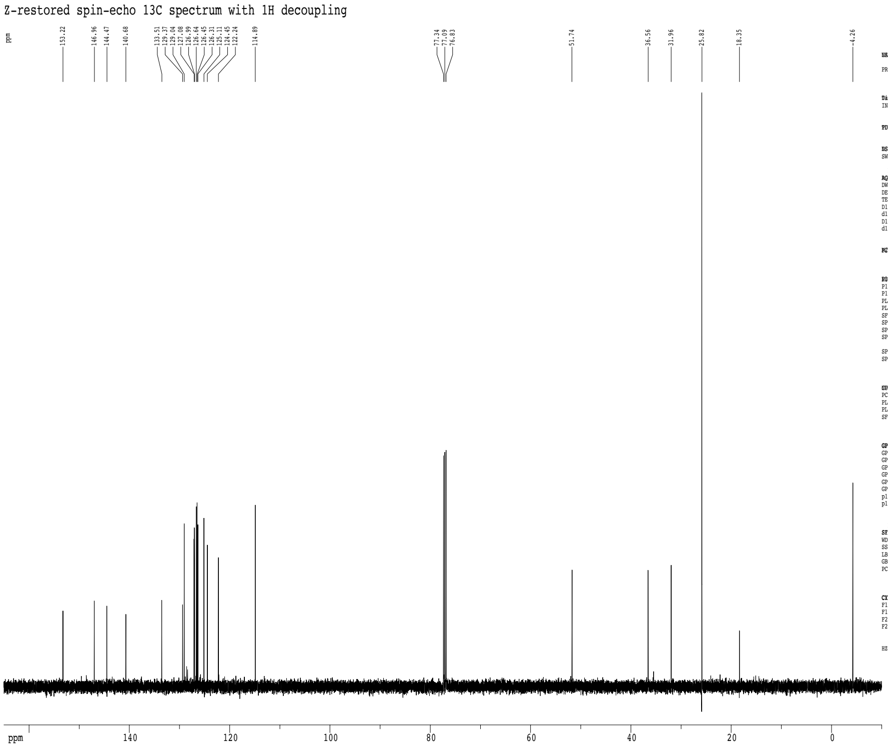
```
Current Data Parameters
USER              lhanna
NAME        LEH-6-089-f24
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151124
Time               12.09
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                   256
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                 0.00 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300283 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.39474 ppm/cm
HZCM           157.94608 Hz/cm
```


Z-restored spin-echo 13C spectrum with 1H decoupling

```
   Current Data Parameters
NAME      LEH-089-C13-b    lhanna
   EXPNO            1
PROCNO               1

    F2 - Acquisition Parameters
Date_                           20151124
INSTRUM              12.39
             cryo500
                           PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg65536.prd
                 CDCl3
  SOLVENT         137
NS                   16
SWH          30303.031 Hz
                           0.462388 Hz
  FIDRES     1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                          6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11                         0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec

    MCREST                  0.00000000 sec
MCWRK        0.01500000 sec

    ======== CHANNEL f1 ========
NUC1                            13C
P11                         16.55 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1         125.7942548 MHz
SP1                         2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
                     SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2                      0.00 Hz

      ======== CHANNEL f2 ========
CPDPRG2         1H                 waltz16
PCPD2             100.00 usec
PL2                         1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

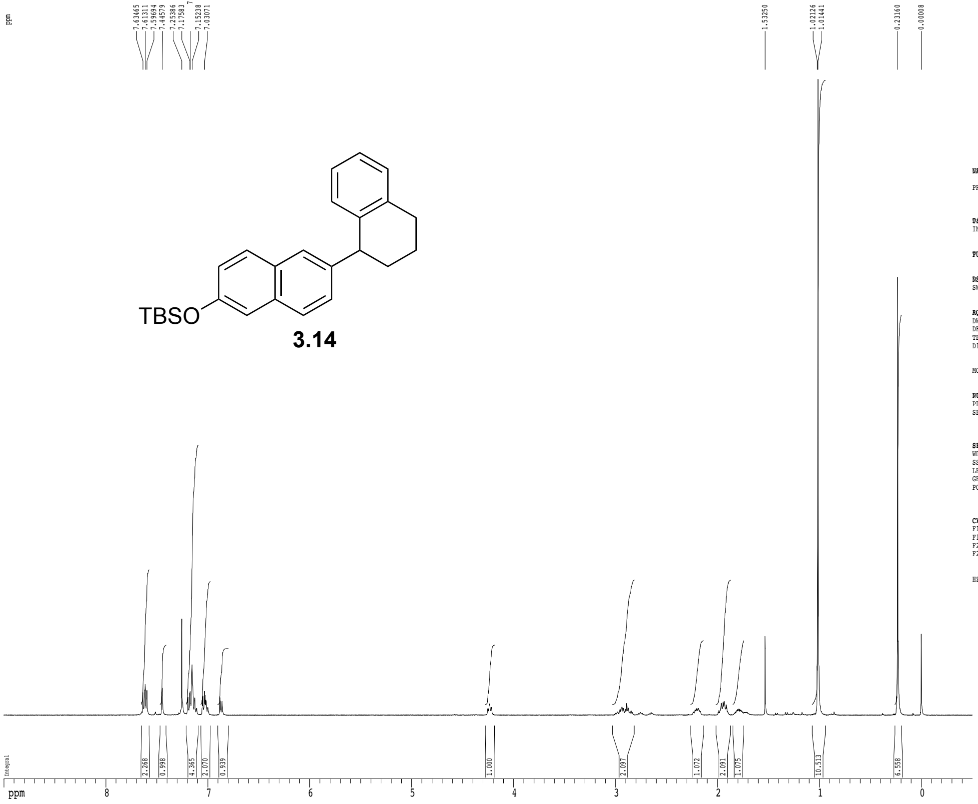
     ====== GRADIENT CHANNEL =====
GPNAM1         SINE.100            SINE.100
GPX1           0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1             30.00 %
GPZ2              50.00 %
p15
p16                         500.00 usec
               1000.00 usec

  F2 - Processing parameters
SI          125.7804190 MHz 65536
WDW                 no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

  1D NMR plot parameters22.80cm
CX                        15.65 cm
F1P           165.000 ppm
F1            20753.77 Hz
F2P            -10.000 ppm
F2            -1257.81 Hz

    PPMCM                   7.67544 ppm/cm
HZCM         965.41992 Hz/cm
```

1H spectrum



```
    Current Data Parameters
USER       MOK-III-272h    mkonev
    EXPNO              1
PROCNO                  1

     F2 - Acquisition Parameters
Date_                               20150817
INSTRUM                 14.06
                drx400
      PROBHD   5 mm QNP H/F/P
PULPROG                        zg30
                  25640
  SOLVENT               8CDCl3
DS                        2
SWH             6410.256 Hz
                             0.250010 Hz
  FIDRES     1.9999700 sec
RG                      512
DW                  78.000 usec
DE                             4.50 usec
TE                  298.0 K
D1             0.10000000 sec

     MCREST                    0.00000000 sec
MCWRK          0.01500000 sec

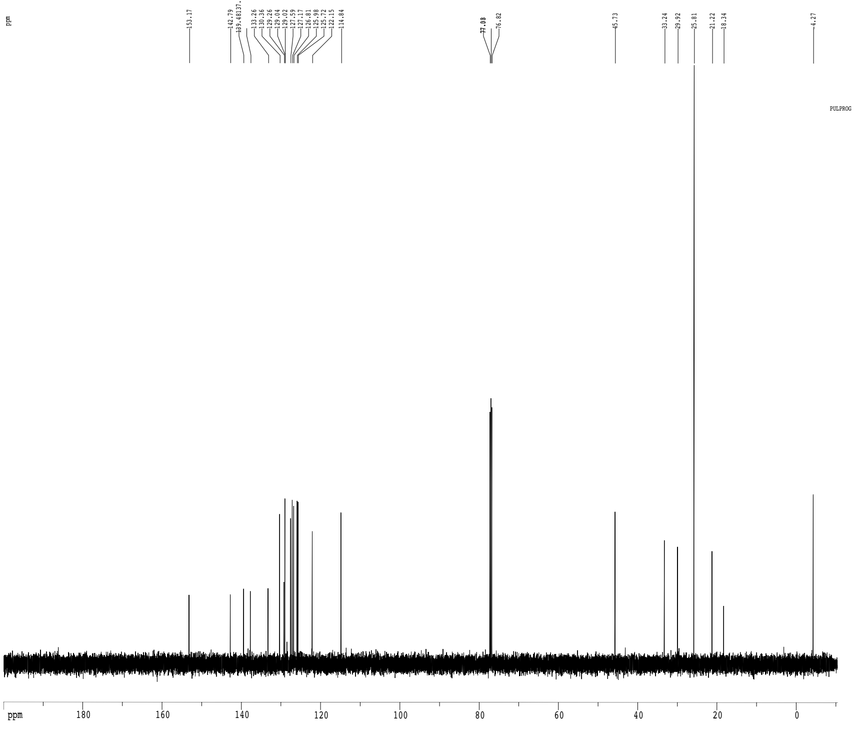
    ======== CHANNEL f1 ========
NUC1                               1H
PL1                          12.00 usec
SFO1          400.1328009 MHz

  F2 - Processing parameters
SI             400.1300240 MHz 65536
WDW                     no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     2.00

  1D NMR plot parameters cm
CX                           15.00 cm
F1P                    9.000 ppm
F1                3601.17 Hz
F2P                   -0.500 ppm
F2                  -200.06 Hz

    PPMCM                      0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
NAME  Current Data Parameters  MOK-III-272h  USER  mkonev
EXPNO                  11
PROCNO

Date_F2 - Acquisition Parameters20150818
INSTRUM
              cryo50015.21
PULPROG  SpinEchopg30gp.prdPROBHD   5 mm CPTCI 1H-
                       CDCl3
                          7216
DSSOLVENT
SWH            30303.031 Hz0.462388 Hz

              1.0813940 sec
RGFIDRES              8192
DW                  16.500 usec6.00 usec
DE
TE                  298.0 K
D1             0.25000000 sec0.03000000 sec
d11
D16            0.00020000 sec
d17            0.00019600 sec
               0.00000000 sec0.01500000 sec

MCWRKMCREST         33.10 usec

NUC1======== CHANNEL f1 ========13C
P11
P12               2500.00 usec16.55 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1          125.7942548 MHz2.70 dB
SP1
SP2                    2.70 dB
SPNAM1   Crp60,0.5,20.1SPNAM2      Crp60comp.4

SPOFF1                 0.00 Hz0.00 Hz
SPOFF2

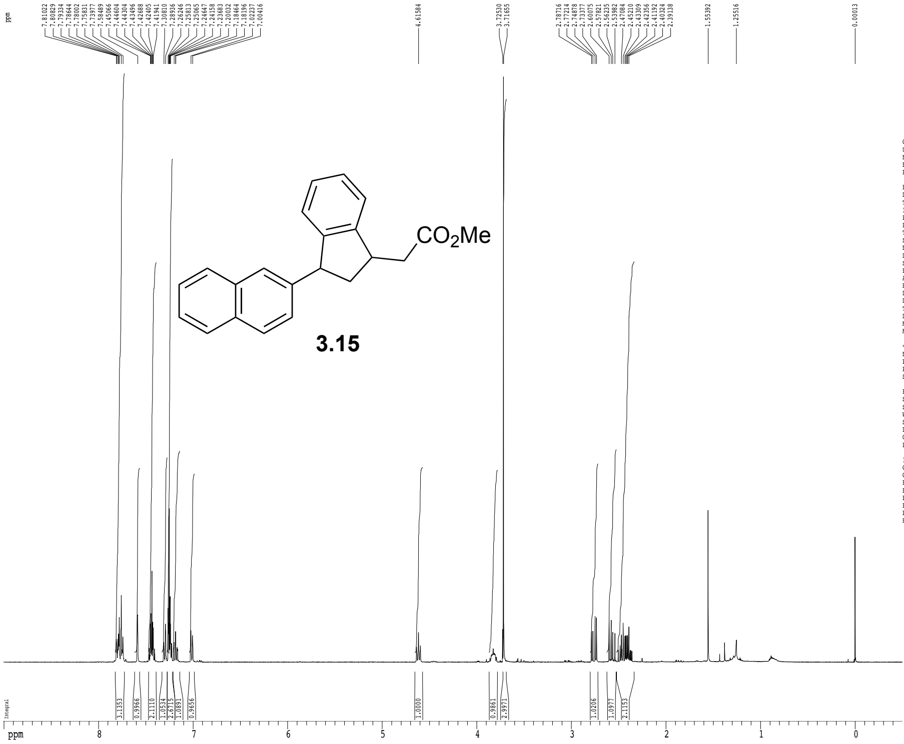
CPDPRG2======== CHANNEL f2 ========waltz16
PCPD2               100.00 usec1.60 dB
PL2
PL12                 24.50 dB
SFO2          500.2225011 MHz

GPNAM2====== GRADIENT CHANNEL =====SINE.100
GPX1             0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1               30.00 %
GPZ2                50.00 %
p15
p16
                 1000.00 usec500.00 usec

SIF2 - Processing parameters 125.7804190 MHz 65536
WDW                     no0
SSB
LB                     0.00 Hz
GB                        0
PC                     2.00

                    22.80 cm15.65 cm
CX1D NMR plot parameters
F1P              200.000 ppm
F1              25156.08 Hz
F2P              -20.000 ppm
F2              -2515.61 Hz
                  9.64912 ppm/cm
               1213.67078 Hz/cm
HZCMPPMCM
```

1H spectrum



```
Current Data Parameters
USER              mkonev
NAME     MOK-III-subprod-H
EXPNO                  1
PROCNO                 1

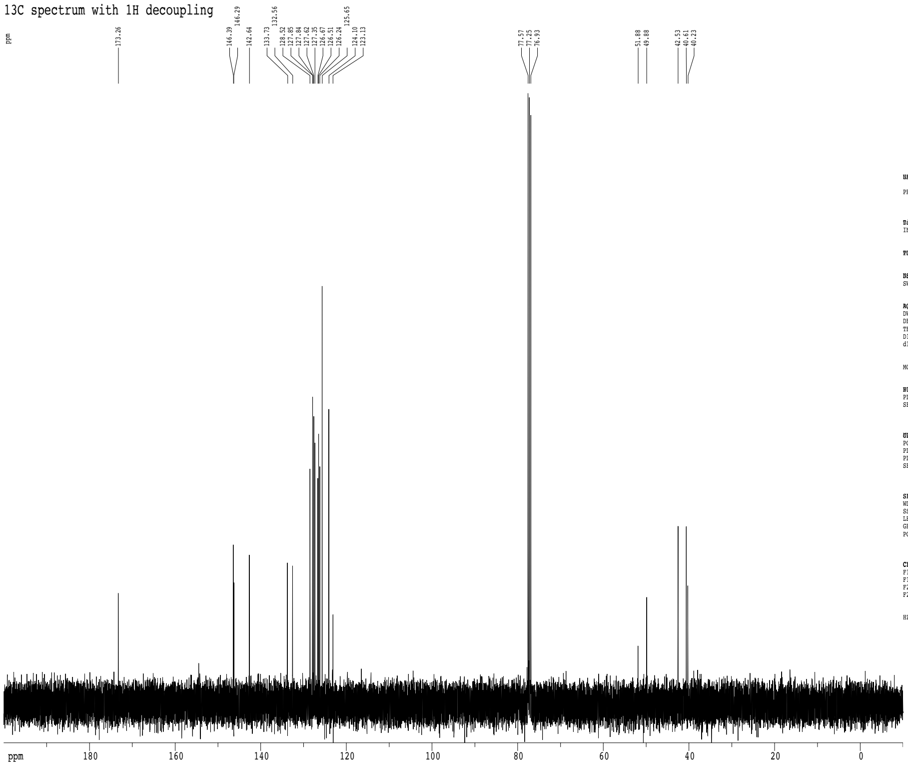
F2 - Acquisition Parameters
Date_          20150709
Time              14.08
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                287.4
DW               78.000 usec
DE                 4.50 usec
TE                298.1 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1                0.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300254 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     MOK-III-subprod-C mkonev
    EXPNO              1
PROCNO                  1


     F2 - Acquisition Parameters
Date_                           20150709
INSTRUM                14.10
               drx400
       PROBHD   5gdm30NP H/F/P
PULPROG                65536
                           CDCl3
  SOLVENT         239
NS                    4
SWH           24154.590 Hz
                           0.368570 Hz
  FIDRES     1.3566452 sec
RG                  9195.2
DW                  20.700 usec
DE                             20.39 usec
TE                   298.0 K
D1            0.10000000 sec
d11                           0.03000000 sec
              0.00000000 sec
     MCREST                   0.01500000 sec
MCWRK

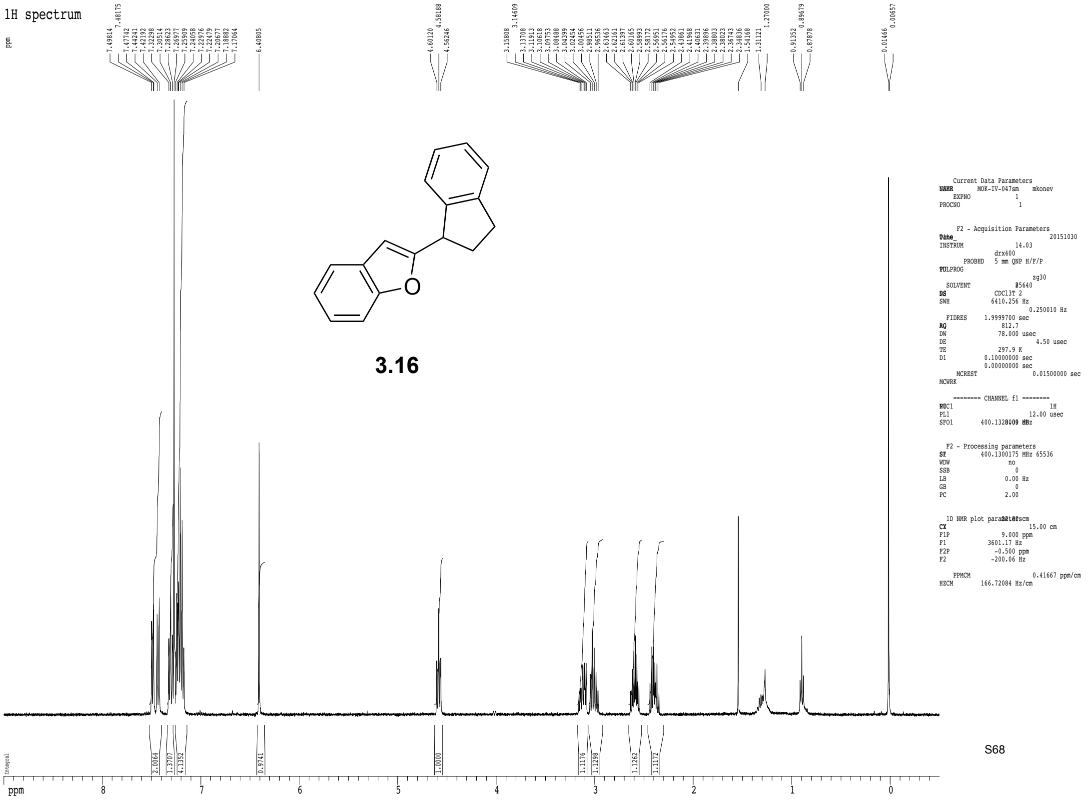
    ======== CHANNEL f1 ========
NUC1                               13C
PL1                          7.75 usec
SFO1         100.6237064dBHz


       ======== CHANNEL f2 ========
CPDPRG2            1H                  mlev16
PCPD2
PL2                          90.00 usec
PL12               170700dB
SFO2         400.1328009 MHz


  F2 - Processing parameters
SF          100.6127500 MHz 65536
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00


  1D NMR plot parameters cm
CX                         15.50 cm
F1P           200.000 ppm
F1            20122.55 Hz
F2P            -10.000 ppm
F2            -1006.13 Hz

    PPMCM                     9.21053 ppm/cm
HZCM         926.69629 Hz/cm
```


1H spectrum

3.16

```
    Current Data Parameters
NAME       MOK-IV-047sm    mkonev
    EXPNO              1
PROCNO                  1


     F2 - Acquisition Parameters
Date_                              20151030
INSTRUM                14.03
                drx400
       PROBHD   5 mm QNP H/F/P
PULPROG
                               zg30
  SOLVENT              85640
NS              CDCl3T 2
SWH           6410.256 Hz
                             0.250010 Hz
  FIDRES     1.9999700 sec
AQ                 812.7
DW                78.000 usec
DE                              4.50 usec
TE                297.9 K
D1            0.10000000 sec
              0.00000000 sec
     MCREST                    0.01500000 sec
MCWRK

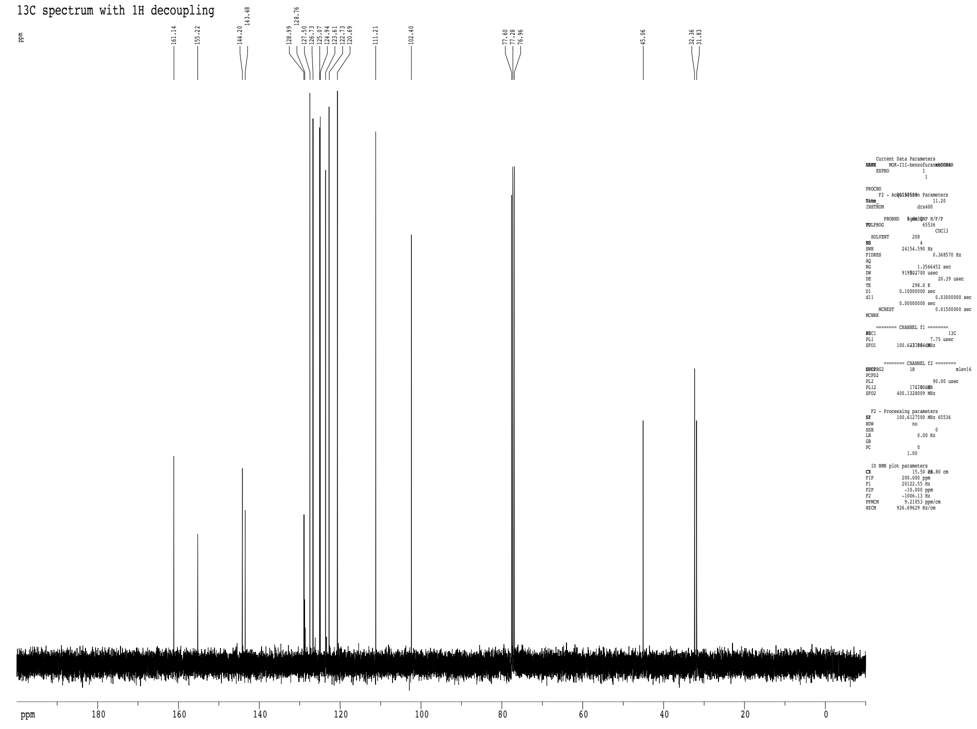
    ======== CHANNEL f1 ========
NUC1                               1H
PL1                            12.00 usec
SFO1        400.1328009 MHz


  F2 - Processing parameters
SI          400.1300175 MHz 65536
WDW                 no
SSB                   0
LB                  0.00 Hz
GB                    0
PC                  2.00


  1D NMR plot parameters cm
CX                             15.00 cm
F1P                9.000 ppm
F1             3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz

    PPMCM                      0.41667 ppm/cm
HZCM        166.72084 Hz/cm
```

S68


13C spectrum with 1H decoupling

```
    Current Data Parameters
NAME     MOK-III-benzofuranmkOCHaR
    EXPNO            1
                      1

PROCNO
     F2 - Acquisition Parameters
Date_                      11.20
INSTRUM             drx400

       PROBHD   5 mm QNP H/F/P
PULPROG                65536
                            CDCl3
  SOLVENT         208
NS                   4
SWH           24154.590 Hz
FIDRES                     0.368570 Hz
AQ
RG                   1.3566452 sec
DW            919.2700 usec
DE                           20.39 usec
TE                298.0 K
D1           0.10000000 sec
d11                         0.03000000 sec
             0.00000000 sec
     MCREST                 0.01500000 sec
MCWRK

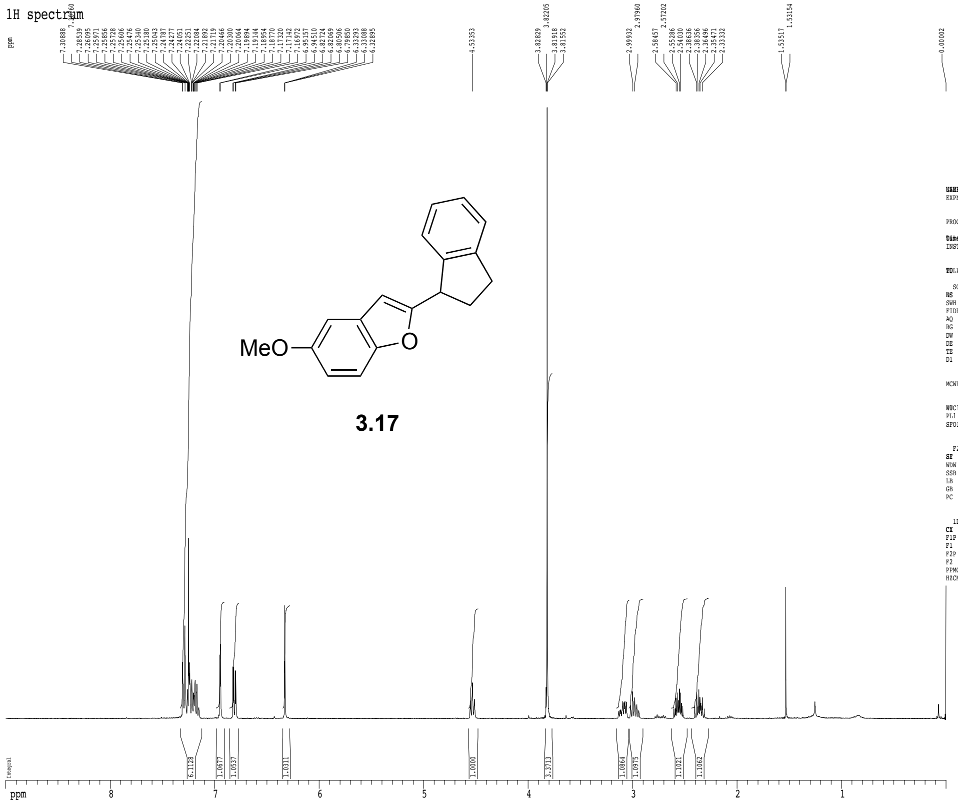
    ======== CHANNEL f1 ========
NUC1                              13C
PL1                         7.75 usec
SFO1        100.6237064 MHz


      ======== CHANNEL f2 ========
CPDPRG2           1H                mlev16
PCPD2
PL2                          90.00 usec
PL12              17.00 dB
SFO2        400.1328009 MHz


  F2 - Processing parameters
SI          100.6127500 MHz 65536
WDW                no
SSB                        0
LB                  0.00 Hz
GB
PC                  0
                 1.00

  1D NMR plot parameters
CX                15.50 20.80 cm
F1P             200.000 ppm
F1              20122.55 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM            9.21053 ppm/cm
HZCM        926.69629 Hz/cm
```

1H spectrum



3.17

```
    Current Data Parameters
NAME LEH-5-232-c3          lhanna
EXPNO                1
                      1

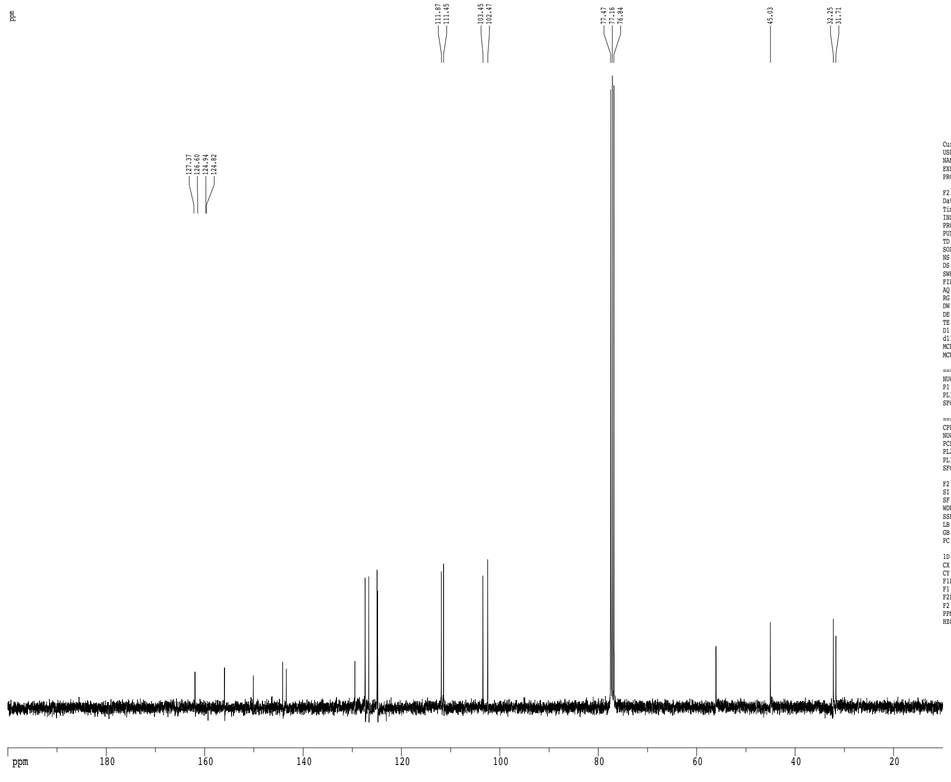
PROCNO
    F2 - Acquisition Parameters
Date_                           20150706
INSTRUM              9.54
           drx400
     PROBHD   5 mm QNP H/F/P
PULPROG                     zg30
              25640
  SOLVENT             8CDCl3
NS                     2
SWH            6410.256 Hz
FIDRES                     0.250010 Hz
AQ           1.9999700 sec
RG                456.1
DW               78.000 usec
DE                          4.50 usec
TE               298.0 K
D1           0.10000000 sec
                           0.00000000 sec
     MCREST  0.01500000 sec
MCWRK

    ======== CHANNEL f1 ========
NUC1                              1H
PL1                        12.00 usec
SFO1         400.1328009 MHz


  F2 - Processing parameters
SF           400.1300255 MHz 65536
WDW               no
SSB                        0
LB                  0.00 Hz
GB
PC                  0
              2.00

  1D NMR plot parameters 22.80 cm
CX                         15.00 cm
F1P               9.000 ppm
F1           3601.17 Hz
F2P             0.000 ppm
F2               0.00 Hz
PPMCM
HZCM                        0.39474 ppm/cm
         157.94608 Hz/cm
```

13C spectrum with 1H decoupling



```
Current Data Parameters
USER              lhanna
NAME      LEH-5-232-c3-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150706
Time                10.04
INSTRUM            drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    889
DS                      4
SWH             24154.590 Hz
FIDRES           0.368570 Hz
AQ              1.3566452 sec
RG                  13004
DW                 20.700 usec
DE                  20.39 usec
TE                  298.0 K
D1             0.10000000 sec
d11            0.03000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

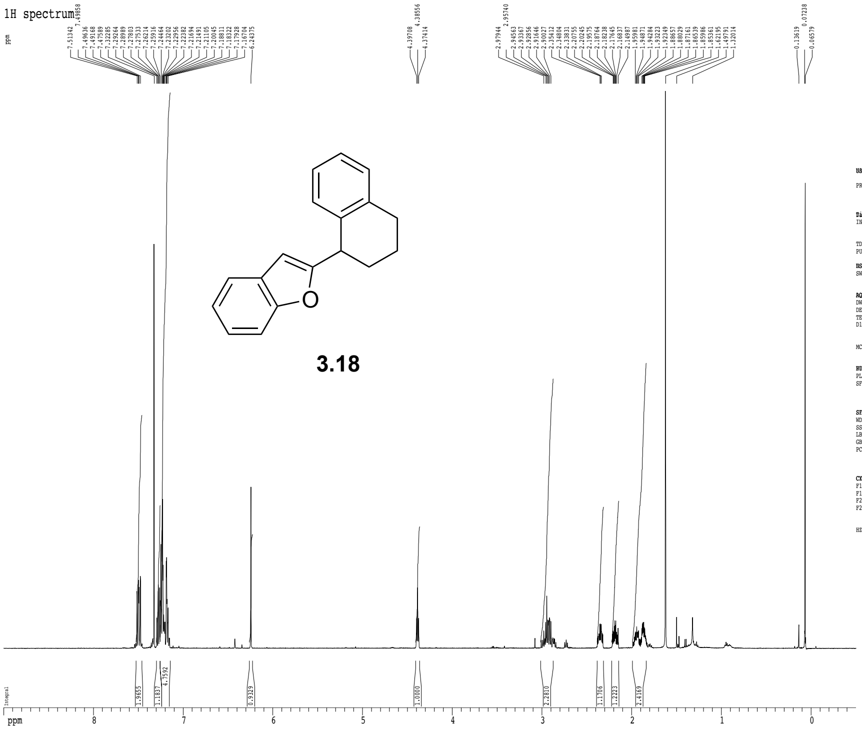
======== CHANNEL f1 ========
NUC1                  13C
P1                   7.75 usec
PL1                 -3.00 dB
SFO1          100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2            mlev16
NUC2                   1H
PCPD2               90.00 usec
PL2                  0.00 dB
PL12                17.70 dB
SFO2          400.1328009 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127587 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.50 cm
F1P               200.000 ppm
F1               20122.55 Hz
F2P                10.000 ppm
F2                1006.13 Hz
PPMCM             8.33333 ppm/cm
HZCM            838.43970 Hz/cm
```

1H spectrum



3.18

```
    Current Data Parameters
USER      MOK-III-BF6-H    mkonev
   EXPNO              1
PROCNO                 1


     F2 - Acquisition Parameters
Date_                8.50         20150707
INSTRUM


                         cryo500
TD     PROBHD   5 mm CPTCI 1Hg30
PULPROG            48074
  SOLVENT              8CDCl3
DS                     2
SWH            8012.820 Hz
                            0.166677 Hz
  FIDRES     2.9998677 sec
AQ                    7.1
DW                 62.400 usec
DE                            6.00 usec
TE                 298.0 K
D1            0.10000000 sec

     MCREST                   0.00000000 sec
MCWRK         0.01500000 sec

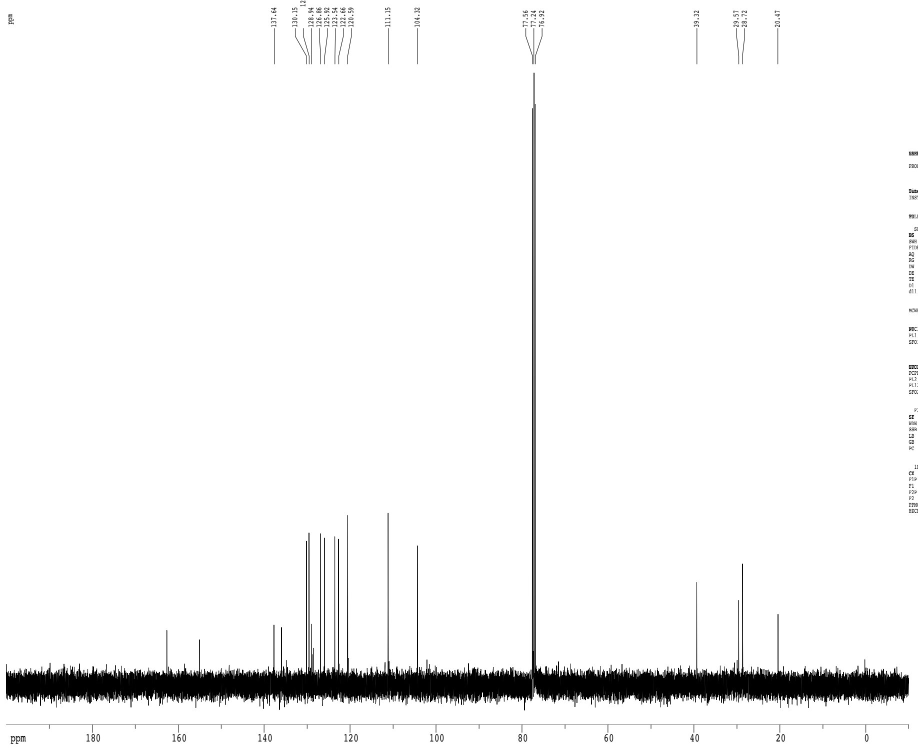
    ======== CHANNEL f1 ========
NUC1                                1H
PL1                         7.50 usec
SFO1        500.2235069 dBz


  F2 - Processing parameters
SF          500.2200000 MHz 65536
WDW                   no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   4.00


  1D NMR plot parameters22.00cm
CX                          15.00 cm
F1P                9.000 ppm
F1             4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz

    PPMCM                     0.41667 ppm/cm
HZCM        208.42500 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     MOK-III-benzofuran6koCCMAR
   EXPNO              1
PROCNO                 1


     F2 - Acquisition Parameters
Date_          20150510       11.30
INSTRUM              drx400

       PROBHD   5 mm QNP H/F/P
PULPROG                65536
                                CDCl3
  SOLVENT         426
DS                     4
SWH           24154.590 Hz
FIDRES                       0.368570 Hz
AQ            1.3566452 sec
RG               14596.5
DW                20.700 usec
DE                            20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11                           0.03000000 sec
              0.00000000 sec
    MCREST                    0.01500000 sec
MCWRK

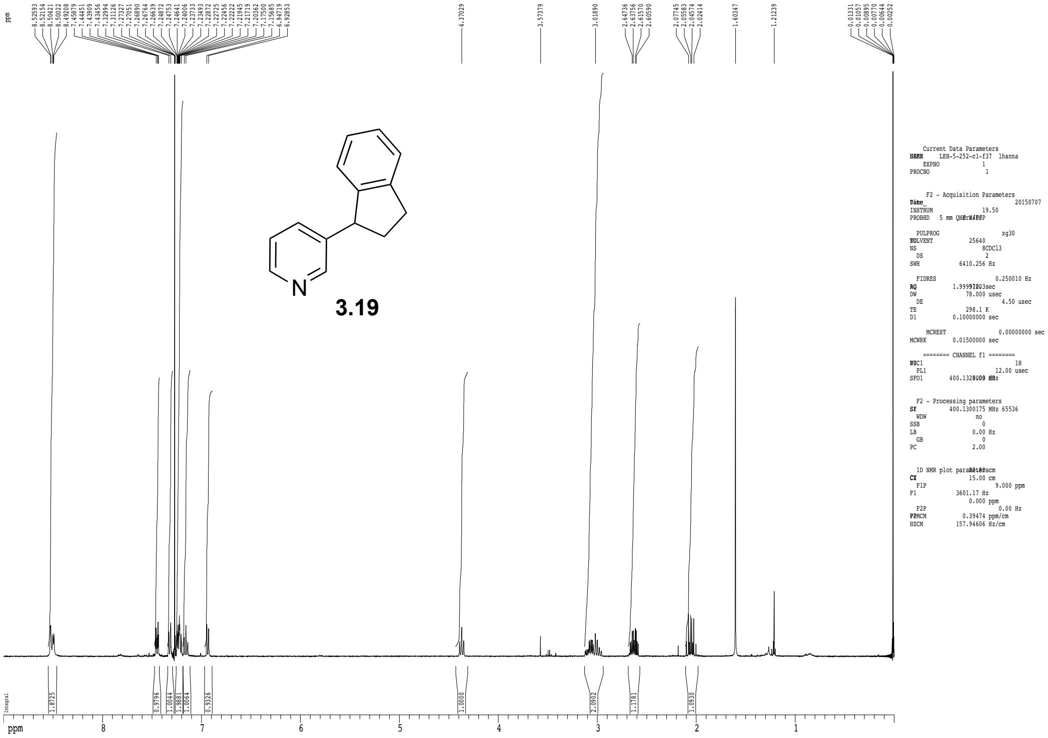
    ======== CHANNEL f1 ========
NUC1                                13C
PL1                         7.75 usec
SFO1        100.6237964 dBMHz


       ======== CHANNEL f2 ========
CPDPRG2          1H                 mlev16
PCPD2
PL2                          90.00 usec
PL12             17.00 dB
SFO2        400.1328009 MHz


  F2 - Processing parameters
SF          100.6127500 MHz 65536
WDW                   no
SSB                     0
LB                     0.00 Hz
GB
PC                      0
                 1.00

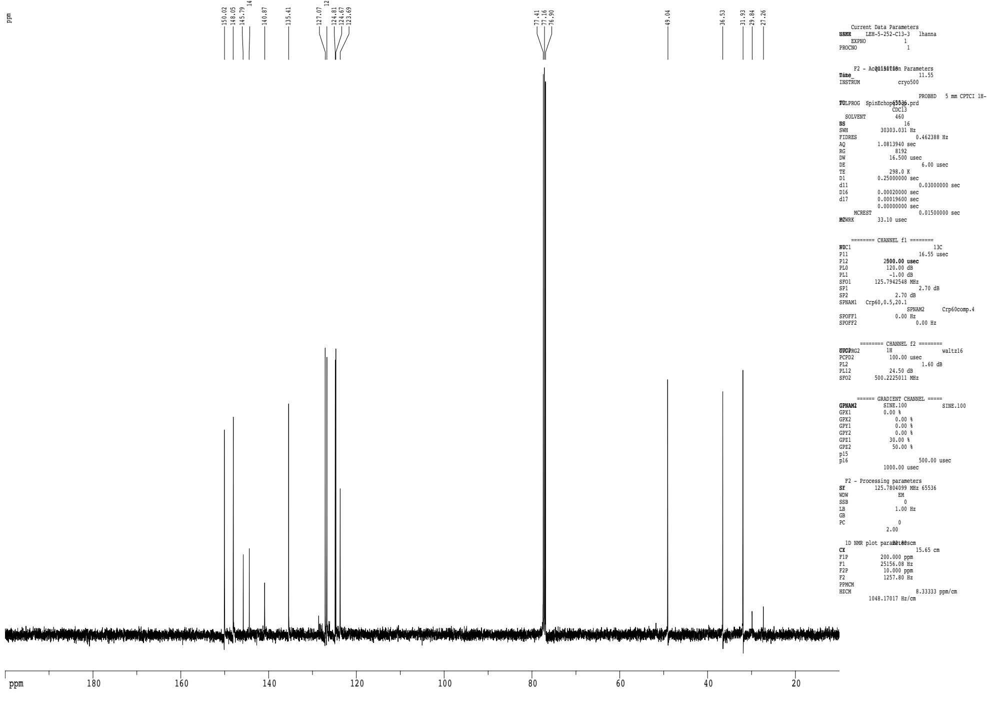
  1D NMR plot parameters22.00cm
CX                          15.50 cm
F1P            200.000 ppm
F1             20122.55 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz
PPMCM
HZCM                         9.21053 ppm/cm
            926.69629 Hz/cm
```

1H spectrum

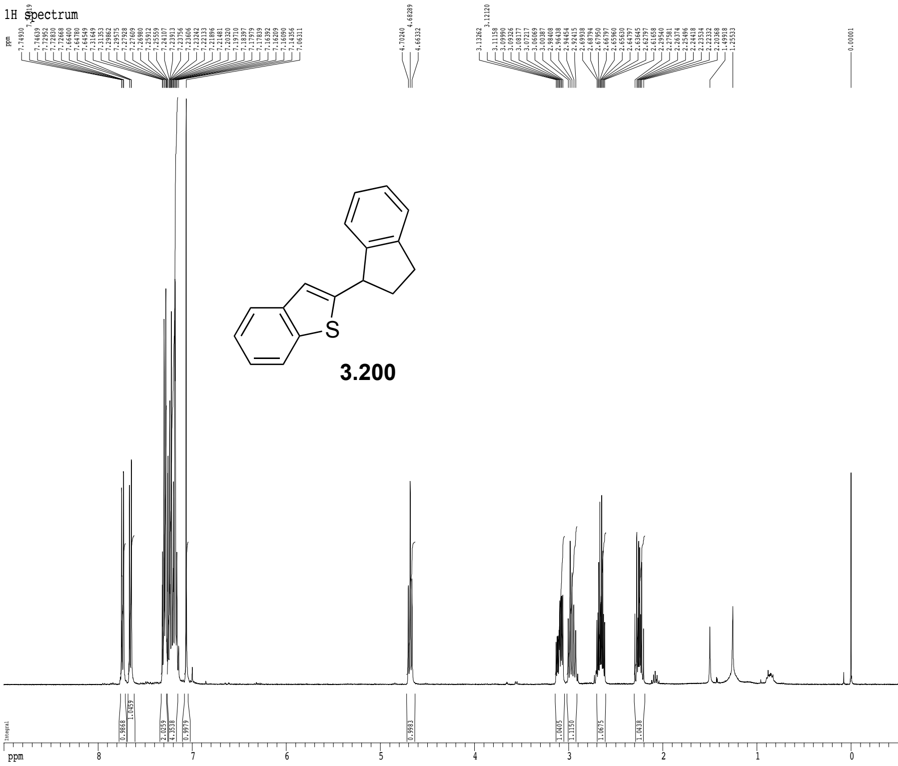


3.19

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



```
    Current Data Parameters
NAME       MOK-III-234-h    mkonev
    EXPNO              1
PROCNO                  1


     F2 - Acquisition Parameters
Date_                               20150627
INSTRUM                14.50
                drx400
       PROBHD   5 mm QNP H/F/P
PULPROG
                            zg30
  SOLVENT              81280
NS              CDCl3T 2
SWH             6410.256 Hz
                           0.125005 Hz
  FIDRES      3.9998901 sec
RG                    181
DW                 78.000 usec
DE                            4.50 usec
TE                 298.0 K
D1            0.10000000 sec

     MCREST                   0.00000000 sec
MCWRK         0.01500000 sec

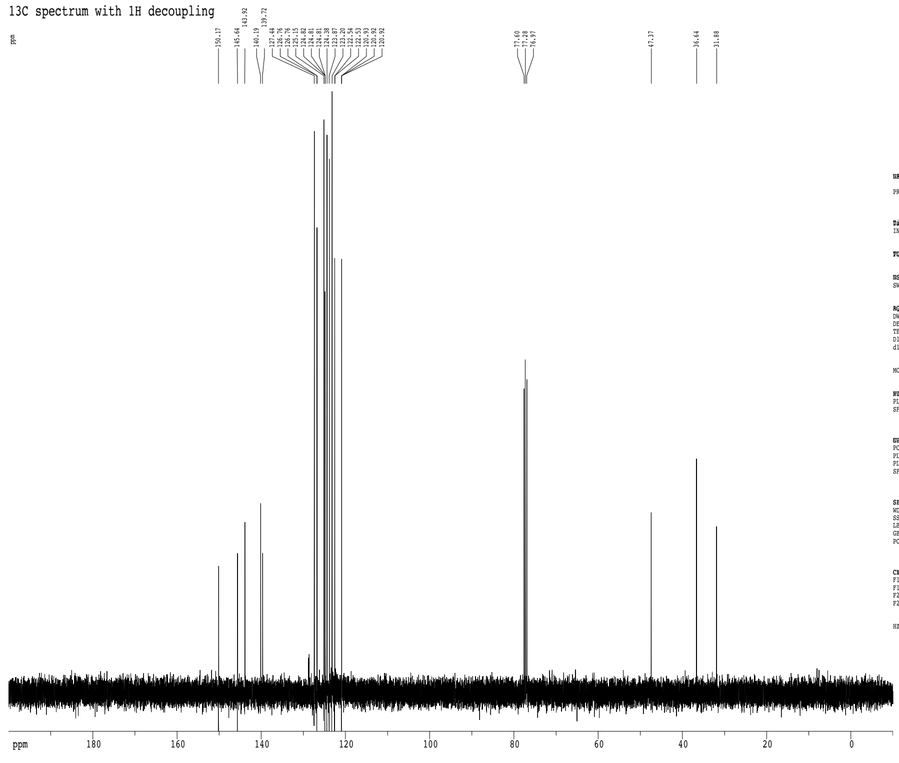
    ======== CHANNEL f1 ========
NUC1                               1H
PL1                            12.00 usec
SFO1          400.1328009 MHz


  F2 - Processing parameters
SI            400.1300380 MHz 65536
WDW                     no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     2.00


  1D NMR plot parameters  22.00 cm
CX                             15.00 cm
F1P                    9.000 ppm
F1                3601.17 Hz
F2P                  -0.500 ppm
F2                 -200.06 Hz

    PPMCM                     0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME       MOK-III-234-c    mkonev
    EXPNO              1
PROCNO                  1


     F2 - Acquisition Parameters
Date_                              20150627
INSTRUM                14.54
                drx400
       PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30 65536
                            CDCl3
  SOLVENT         176
NS                    4
SWH           24154.590 Hz
                          0.368570 Hz
  FIDRES     1.3566452 sec
RG                 9195.2
DW                 20.700 usec
DE                            20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11                           0.03000000 sec

     MCREST                   0.00000000 sec
MCWRK         0.01500000 sec

    ======== CHANNEL f1 ========
NUC1                               13C
PL1                         7.75 usec
SFO1          100.6237964 MHz

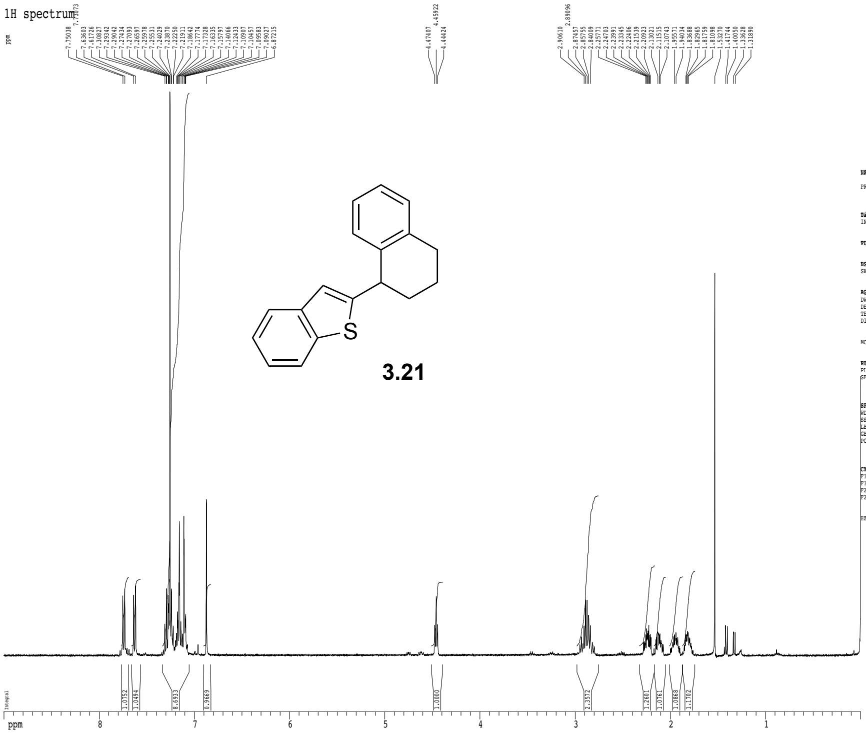

       ======== CHANNEL f2 ========
CPDPRG2           1H                  mlev16
PCPD2
PL2                          90.00 usec
PL12                 17.00 dB
SFO2          400.1328009 MHz


  F2 - Processing parameters
SI            100.6127500 MHz 65536
WDW                     no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00


  1D NMR plot parameters  22.00 cm
CX                             15.50 cm
F1P             200.000 ppm
F1              20122.55 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz

    PPMCM                     9.21053 ppm/cm
HZCM          926.69629 Hz/cm
```

1H spectrum



3.21

```
    Current Data Parameters
NAME     LEH-6-029-c1-Freezlhanna
   EXPNO              1
PROCNO                 1


     F2 - Acquisition Parameters
Date_                            20150825
INSTRUM               11.54
              drx400
       PROBHD   5 mm QNP H/F/P
PULPROG                     zg30
                25640
  SOLVENT             8CDCl3
NS                     2
SWH            6410.256 Hz
                          0.250010 Hz
  FIDRES     1.9999700 sec
AQ                912.3
DW                78.000 usec
DE                          4.50 usec
TE                298.0 K
D1            0.10000000 sec
              0.00000000 sec
     MCREST                0.01500000 sec
MCWRK

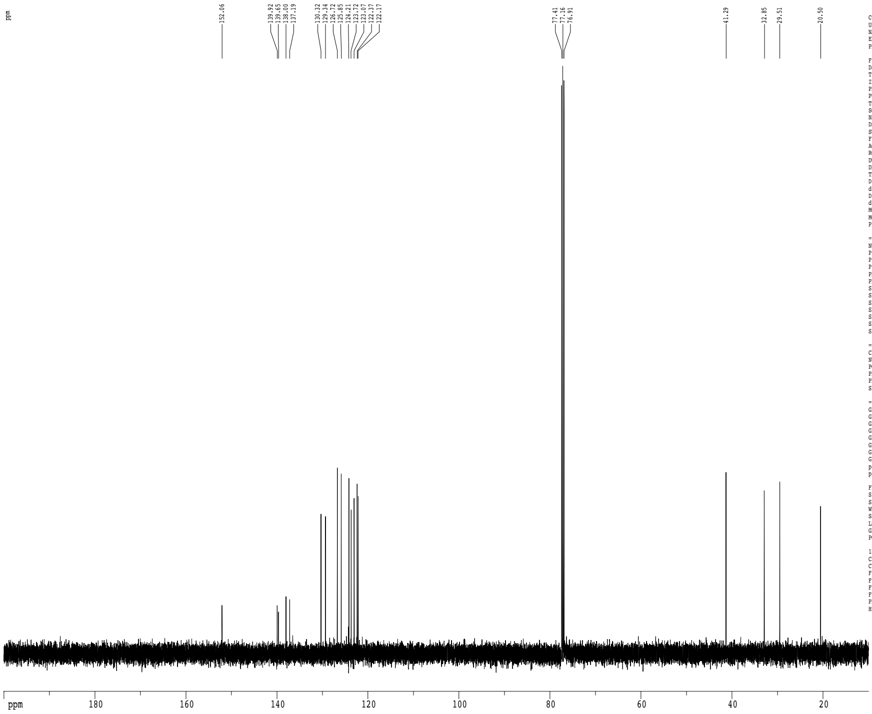
    ======== CHANNEL f1 ========
NUC1                             1H
PL1                         12.00 usec
SFO1        400.1328009 MHz


  F2 - Processing parameters
SI          400.1300231 MHz 65536
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00


  1D NMR plot parameters
CX                          15.00 cm
F1P               9.000 ppm
F1            3601.17 Hz
F2P             0.000 ppm
F2                0.00 Hz

    PPMCM                  0.39474 ppm/cm
HZCM        157.94608 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
Current Data Parameters
USER              lhanna
NAME      LEH-6-029-C13-b
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150825
Time               16.08
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   285
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

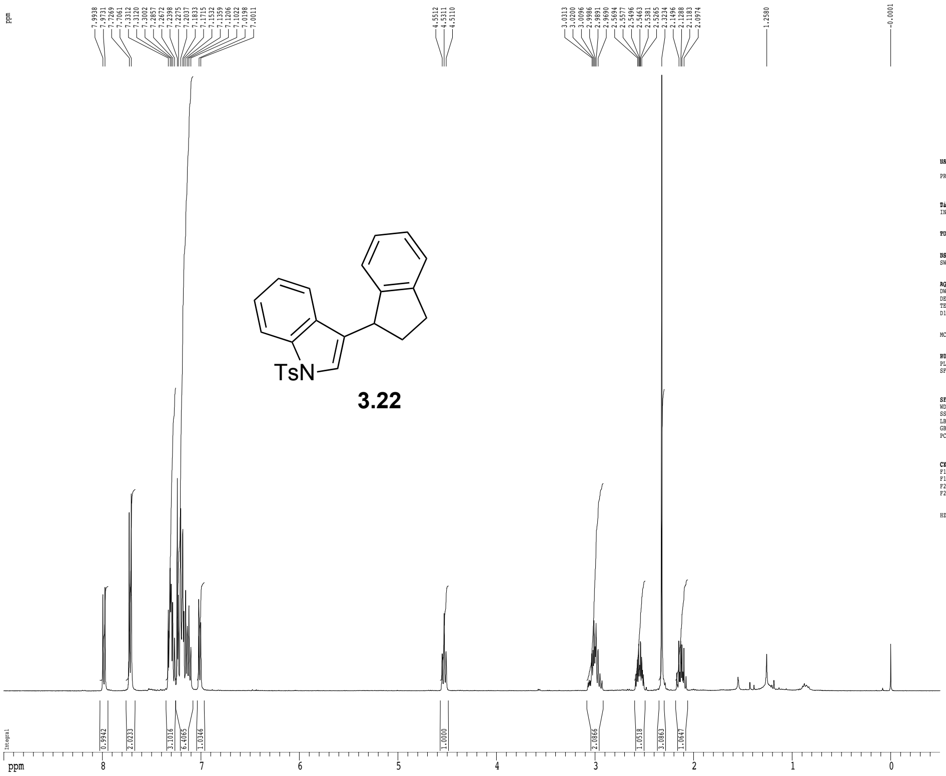
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804080 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P               10.000 ppm
F2               1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.17017 Hz/cm
```

1H spectrum



3.22

```
    Current Data Parameters
NAME     MOK-III-indolexcHCMARnev
  EXPNO              1
PROCNO               1


     F2 - Acquisition Parameters
Date_                             20150509
INSTRUM               10.58
                drx400
       PROBHD   5 mm QNP H/F/P
PULPROG                        zg30
                 32050
  SOLVENT             8CDCl3
NS                    2
SWH             6410.256 Hz
                            0.200008 Hz
  FIDRES      2.4999499 sec
RG                 101.6
DW                78.000 usec
DE                               4.50 usec
TE                298.0 K
D1           0.10000000 sec

     MCREST                  0.00000000 sec
MCWRK        0.01500000 sec

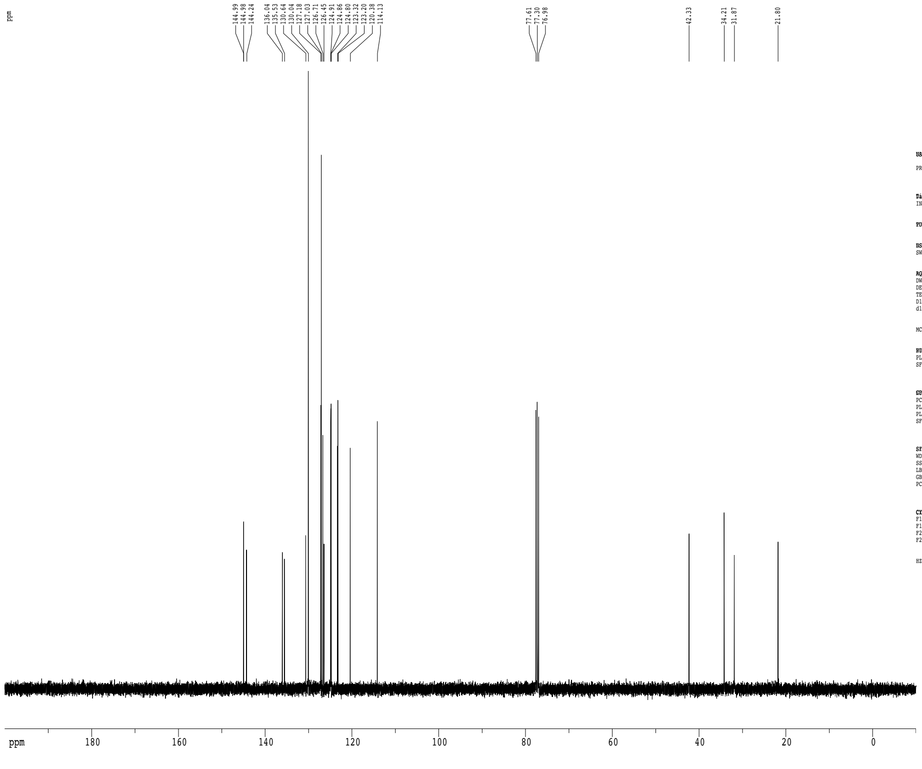
    ======== CHANNEL f1 ========
NUC1                             1H
PL1                         12.00 usec
SFO1        400.1328009 MHz


  F2 - Processing parameters
SF          400.1300335 MHz 65536
WDW                 no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00


  1D NMR plot parameters cm
CX                          15.00 cm
F1P                9.000 ppm
F1             3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz

    PPMCM                    0.41667 ppm/cm
HZCM        166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
    Current Data Parameters
USER     MOK-III-indolexcCCHARnev
  EXPNO              1
PROCNO               1


     F2 - Acquisition Parameters
Date_                             20150509
INSTRUM               11.02
                drx400
       PROBHD   5 mm QNP H/F/P
PULPROG               65536
                          CDCl3
  SOLVENT          344
DS                    4
SWH            24154.590 Hz
                         0.368570 Hz
  FIDRES      1.3566452 sec
RG                 8192
DW                20.700 usec
DE                           20.39 usec
TE                298.0 K
D1           0.10000000 sec
d11                          0.03000000 sec

     MCREST                  0.00000000 sec
MCWRK        0.01500000 sec

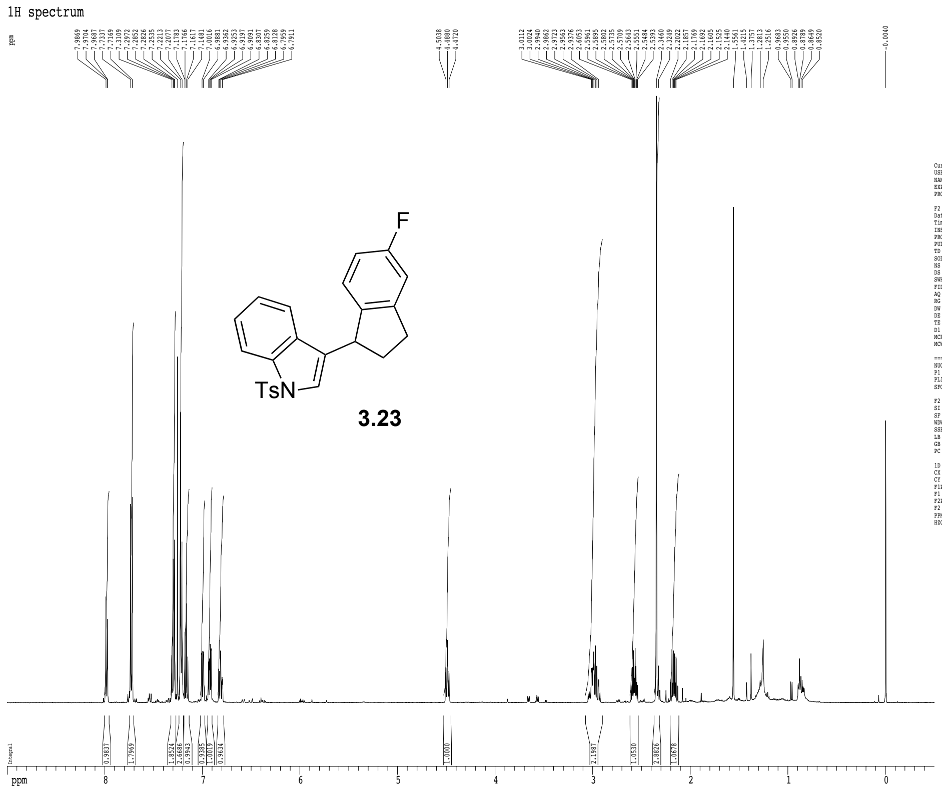
    ======== CHANNEL f1 ========
NUC1                             13C
PL1                         7.75 usec
SFO1        100.6237964 MHz


       ======== CHANNEL f2 ========
CPDPRG2          1H                 mlev16
PCPD2
PL2                         90.00 usec
PL12            17.00 dB
SFO2        400.1328009 MHz


  F2 - Processing parameters
SF          100.6127500 MHz 65536
WDW                 no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00


  1D NMR plot parameters cm
CX                          15.50 cm
F1P              200.000 ppm
F1             20122.55 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz

    PPMCM                    9.21053 ppm/cm
HZCM        926.69629 Hz/cm
```



3.23

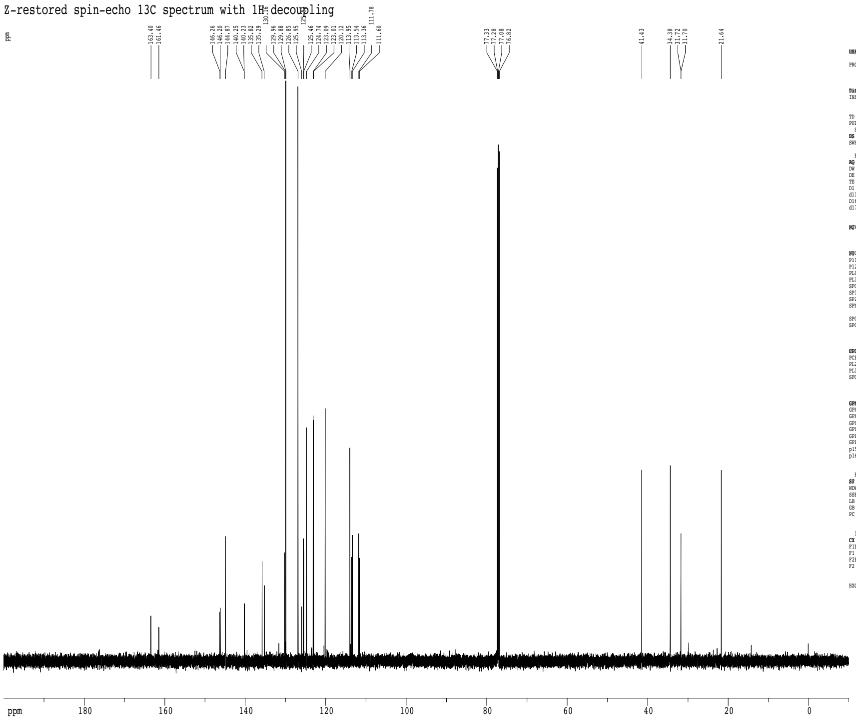
```
Current Data Parameters
USER              mkonev
NAME     MOK-III-Findoleprod-H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150708
Time                8.59
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 40062
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.200010 Hz
AQ             2.4999187 sec
RG                     8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200347 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```



```
    Current Data Parameters
NAME     MOK-III-Findoleprodkonev
   EXPNO              1
PROCNO                 1


     F2 - Acquisition Parameters
Date_              9.03         20150708
INSTRUM


                                          cryo500
TD                 65536    PROBHD   5 mm CPTCI 1H-
PULPROG   SpinEchopgCDCl3.prd
  SOLVENT          672
NS                     16
SWH            30303.031 Hz
                            0.462388 Hz
  FIDRES     1.0813940 sec
AQ                 5160.6
DW                16.500 usec
DE                           6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11                         0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec

     MCREST                 0.00000000 sec
MCWRK         0.01500000 sec


    ======== CHANNEL f1 ========
NUC1                            13C
P11                         16.55 usec
P12              2500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1         125.7942548 MHz
SP1                         2.70 dB
SP2                  2.70 dB
SPNAM1   Crp60,0.5,20.1
                       SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2                     0.00 Hz

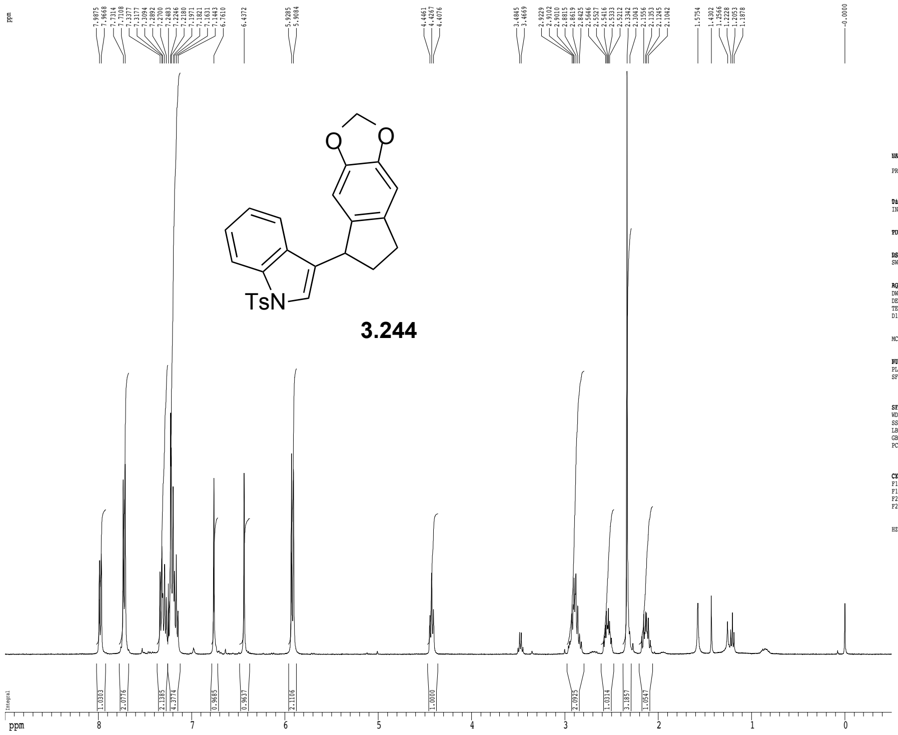

      ======== CHANNEL f2 ========
CPDPRG2           1H                 waltz16
PCPD2              100.00 usec
PL2                          1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz


     ====== GRADIENT CHANNEL =====
GPNAM1          SINE.100           SINE.100
GPX1            0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1              30.00 %
GPZ2               50.00 %
p15
p16                          500.00 usec
                1000.00 usec

  F2 - Processing parameters
SI           125.7804190 MHz 65536
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00


  1D NMR plot parameters22.80cm
CX                          15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
                  9.21053 ppm/cm
    PPMCM    1158.50378 Hz/cm
HZCM
```

1H spectrum



3.244

```
    Current Data Parameters
NAME     MOK-III-256-h1    mkonev
   EXPNO              1
PROCNO                 1


     F2 - Acquisition Parameters
Date_                            20150715
INSTRUM               10.04
                drx400
       PROBHD   5 mm QNP H/F/P
PULPROG
                                zg30
  SOLVENT             88460
DS              CDCl3T 2
SWH            6410.256 Hz
                              0.166673 Hz
  FIDRES     2.9999299 sec
RG                    181
DW                78.000 usec
DE                              4.50 usec
TE                298.0 K
D1            0.10000000 sec
              0.00000000 sec
     MCREST                     0.01500000 sec
MCWRK

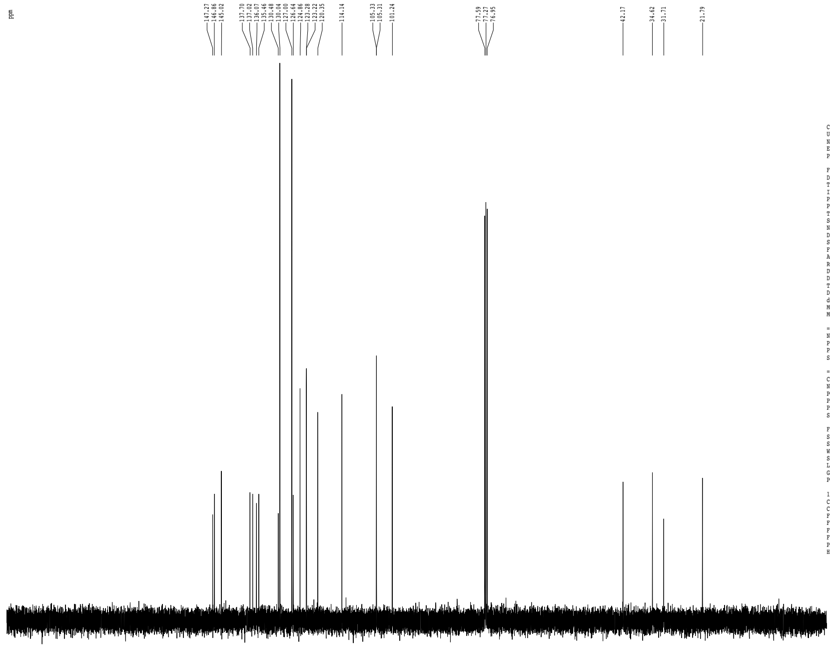
    ======== CHANNEL f1 ========
NUC1                             1H
PL1                           12.00 usec
SFO1         400.1328009 MHz


  F2 - Processing parameters
SF           400.1300266 MHz 65536
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00


  1D NMR plot parameters 22.80 cm
CX                            15.00 cm
F1P                  9.000 ppm
F1              3601.17 Hz
F2P                -0.500 ppm
F2                -200.06 Hz

    PPMCM                       0.41667 ppm/cm
HZCM        166.72086 Hz/cm
```

13C spectrum with 1H decoupling



```
Current Data Parameters
USER               mkonev
NAME       MOK-III-256-c1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150715
Time                10.06
INSTRUM            drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    344
DS                      4
SWH             24154.590 Hz
FIDRES           0.368570 Hz
AQ              1.3566452 sec
RG                14596.5
DW                 20.700 usec
DE                  20.39 usec
TE                  298.0 K
D1             0.10000000 sec
d11            0.03000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

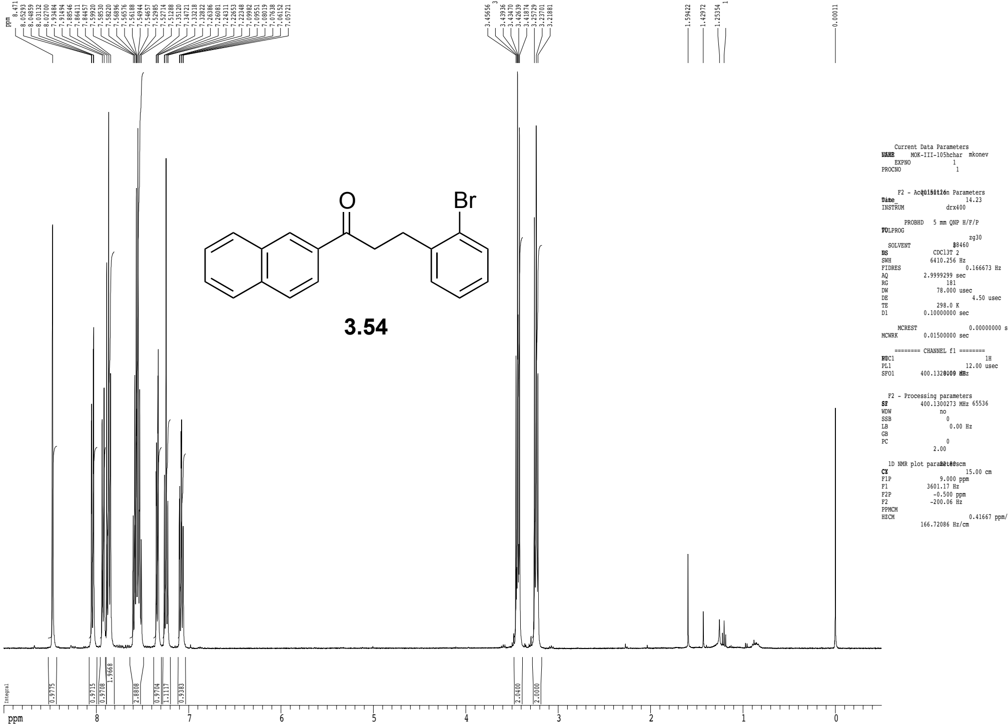
======== CHANNEL f1 ========
NUC1                  13C
P1                   7.75 usec
PL1                 -3.00 dB
SFO1          100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2            mlev16
NUC2                   1H
PCPD2               90.00 usec
PL2                  0.00 dB
PL12                17.70 dB
SFO2          400.1328009 MHz

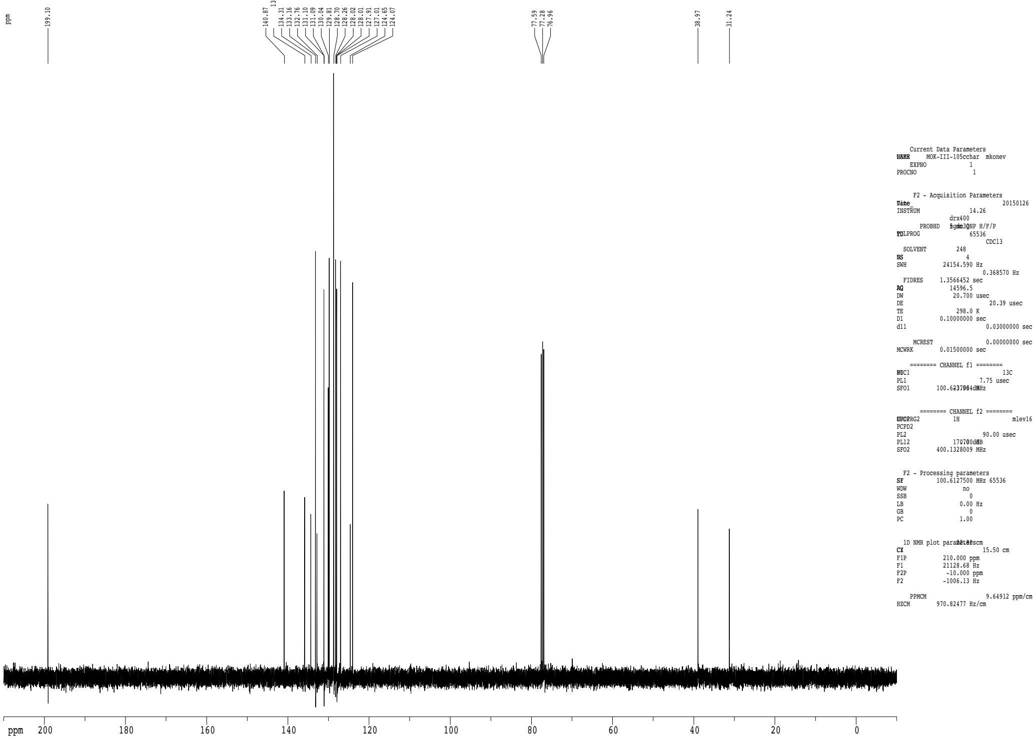
F2 - Processing parameters
SI                  65536
SF            100.6127500 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.50 cm
F1P               200.000 ppm
F1               20122.55 Hz
F2P               -10.000 ppm
F2               -1006.13 Hz
PPMCM             9.21053 ppm/cm
HZCM            926.69629 Hz/cm
```

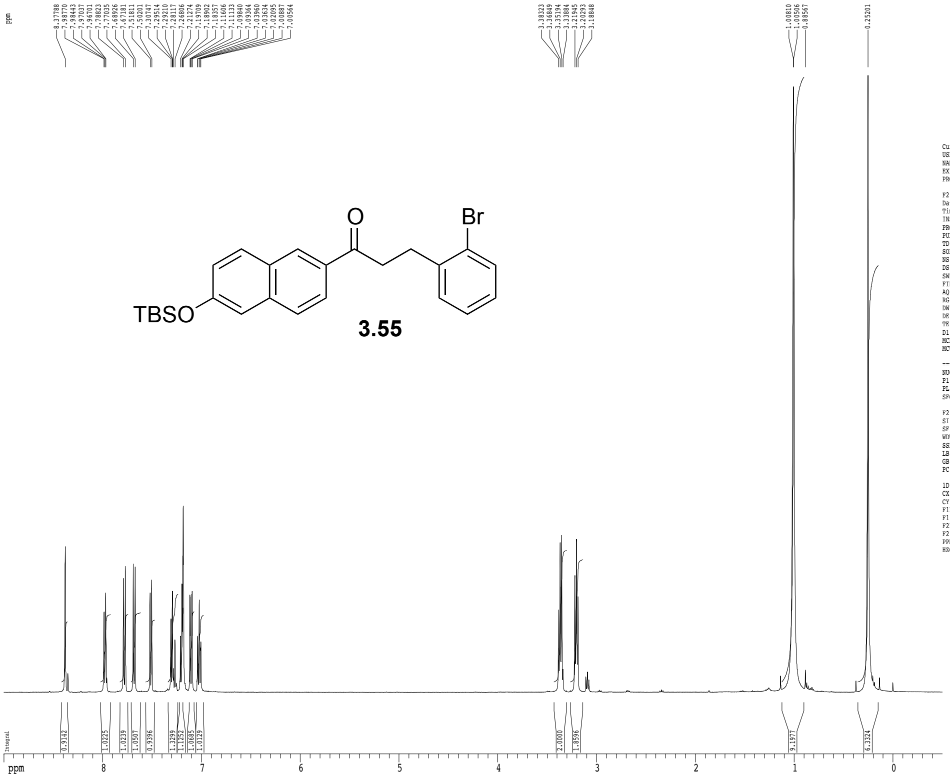
1H spectrum



13C spectrum with 1H decoupling



1H spectrum



```
Current Data Parameters
USER              mkonev
NAME     MOK-IV-062hchar
EXPNO                  1
PROCNO                 1

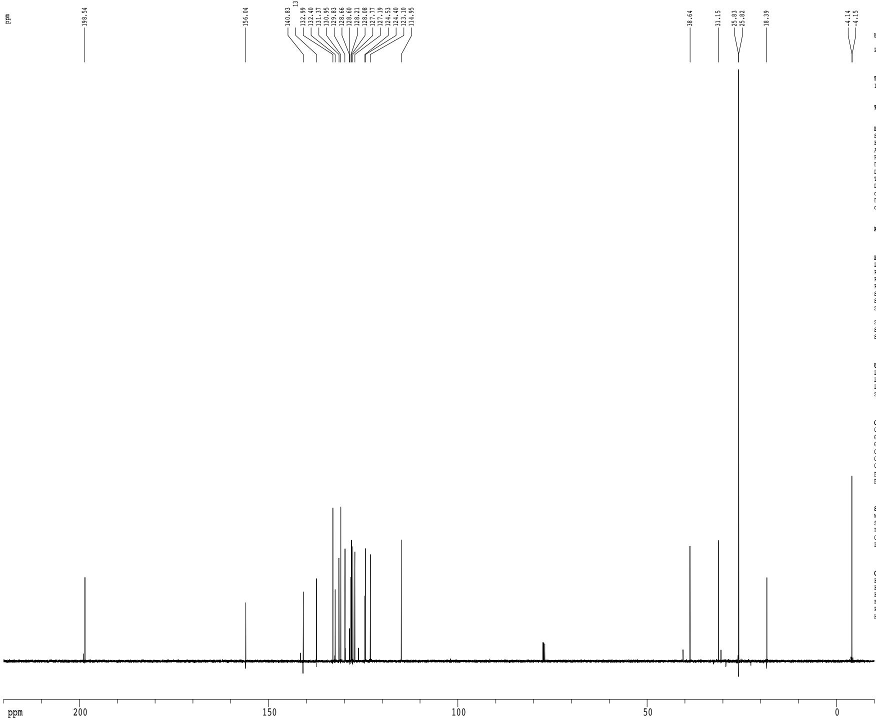
F2 - Acquisition Parameters
Date_           20151117
Time                1.48
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                   2.8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200627 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42503 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```
    Current Data Parameters
NAME     MOK-IV-062cchar3  mkonev
    EXPNO             1
PROCNO                 1


     F2 - Acquisition Parameters
Date_                          20151117
INSTRUM            1.54
           cryo500
                        PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
                CDCl3
  SOLVENT           16
NS                     16
SWH           30303.031 Hz
FIDRES                 0.462388 Hz
AQ            1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                          6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11                         0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec

     MCREST                 0.00000000 sec
MCWRK         0.01500000 sec

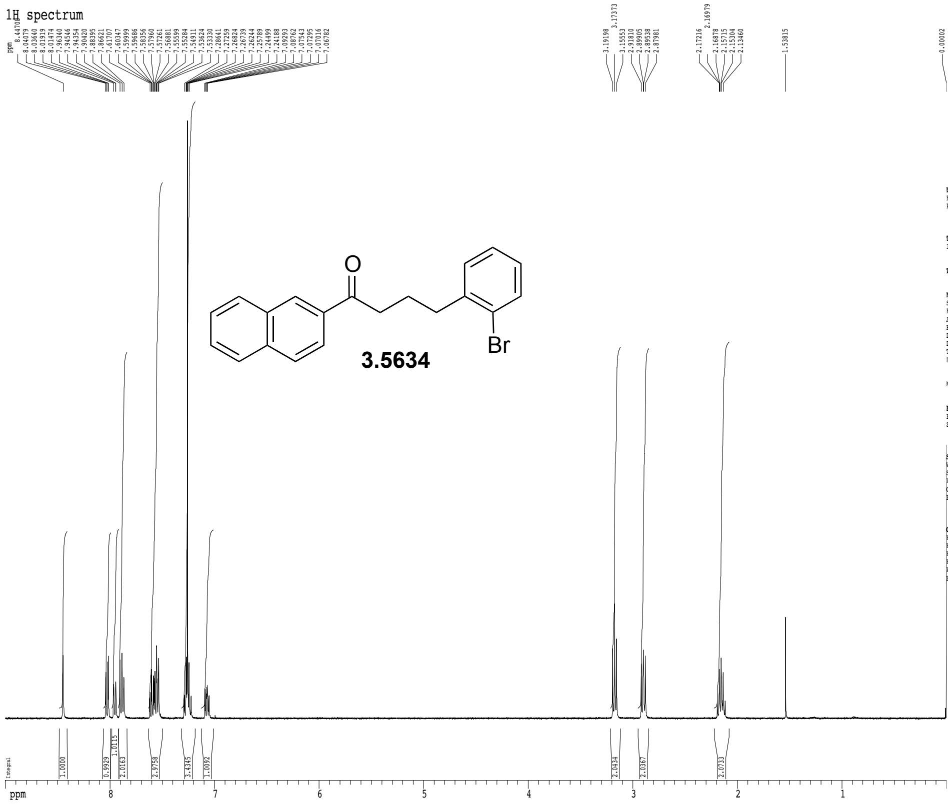

    ======== CHANNEL f1 ========
NUC1                         13C
P11                         16.55 usec
P12              2500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                         2.70 dB
SP2
                                              2.70 dB
SPNAM1   Crp60,0.5,20.1
SPOFF1      0.00 Hz    SPNAM2      Crp60comp.4
SPOFF2              0.00 Hz


        ======== CHANNEL f2 ========
CPDPRG2         1H                 waltz16
PCPD2
PL2                         100.00 usec
PL12               24.50 dB
SFO2         500.2225011 MHz


      ====== GRADIENT CHANNEL =====
GPNAM2         SINE.100             SINE.100
GPX1           0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1             30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec


  F2 - Processing parameters
SF           125.7804190 MHz 65536
WDW                no
SSB                  0
LB                     0.00 Hz
GB
PC                   0
               2.00

  1D NMR plot parameters 22.80 cm
CX                          15.65 cm
F1P            220.000 ppm
F1             27671.69 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM
HZCM                        10.08772 ppm/cm
          1268.83765 Hz/cm
```


1H spectrum

3.5634

```
Current Data Parameters
NAME         LEH-6-081-b    lhanna
EXPNO                 1
PROCNO                 1


   F2 - Acquisition Parameters
Date_                        14.34
INSTRUM             drx400

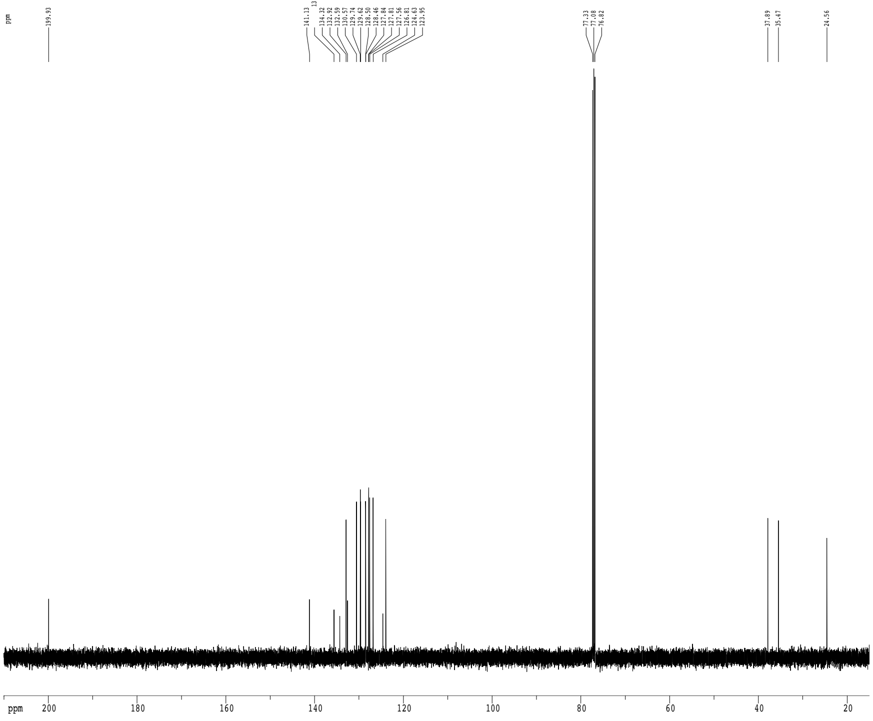
     PROBHD   5 mm QNP H/F/P
PULPROG                      zg30
                  64100
  SOLVENT             8CDCl3
NS                     2
SWH            6410.256 Hz
FIDRES                       0.100004 Hz
AQ            4.9998498 sec
RG                812.7
DW               78.000 usec
DE                          4.50 usec
TE               298.0 K
D1            0.10000000 sec

     MCREST                 0.00000000 sec
MCWRK         0.01500000 sec

    ======== CHANNEL f1 ========
NUC1                              1H
PL1                          12.00 usec
SFO1        400.1328009 MHz


  F2 - Processing parameters
SF          400.1300224 MHz 65536
WDW               no
SSB                 0
LB                   0.00 Hz
GB
PC                  0
              2.00

  1D NMR plot parameters cm
CX                           15.00 cm
F1P               9.000 ppm
F1            3601.17 Hz
F2P             0.000 ppm
F2                0.00 Hz
PPMCM
HZCM                          0.39474 ppm/cm
              157.94608 Hz/cm
```


Z-restored spin-echo 13C spectrum with 1H decoupling

```
Current Data Parameters
NAME      LEH-6-081-C13    lhanna
   EXPNO             1
PROCNO               1


    F2 - Acquisition Parameters
Date_                          20151117
INSTRUM            18.06
           cryo500
                         PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
               CDCl3
  SOLVENT          892
NS                    16
SWH          30303.031 Hz
                         0.462388 Hz
  FIDRES     1.0813940 sec
AQ                7298.2
DW                16.500 usec
DE                        6.00 usec
TE               298.0 K
D1           0.25000000 sec
d11                      0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec

    MCREST               0.00000000 sec
MCWRK        0.01500000 sec

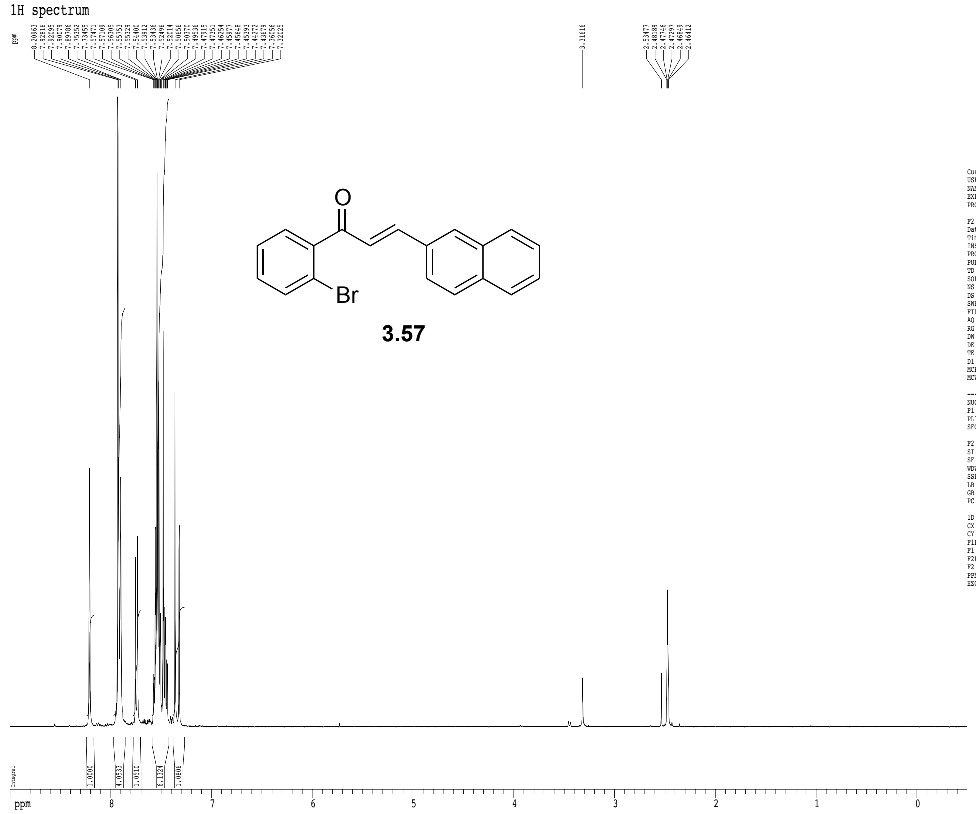

    ======== CHANNEL f1 ========
NUC1                          13C
P11                      16.55 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                      2.70 dB
SP2                2.70 dB
SPNAM1   Crp60,0.5,20.1
                    SPNAM2      Crp60comp.4
SPOFF1             0.00 Hz
SPOFF2                   0.00 Hz


      ======== CHANNEL f2 ========
CPDPRG2          1H                waltz16
PCPD2
PL2                      100.00 usec
PL12               24.00 dB
SFO2        500.2225011 MHz


      ====== GRADIENT CHANNEL =====
GPNAM1           SINE.100            SINE.100
GPX1            0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1              30.00 %
GPZ2               50.00 %
p15
p16                        500.00 usec
               1000.00 usec

  F2 - Processing parameters
SF          125.7804190 MHz 65536
WDW                no
SSB                  0
LB                 0.00 Hz
GB                   0
PC                 2.00


  1D NMR plot parameters cm
CX                          15.65 cm
F1P           210.000 ppm
F1            26413.89 Hz
F2P            15.000 ppm
F2             1886.71 Hz
                8.55263 ppm/cm
    PPMCM    1075.75366 Hz/cm
HZCM
```



3.57

```
Current Data Parameters
USER             mkonev
NAME     MOK-IV-chalcone
EXPNO                 1
PROCNO                1

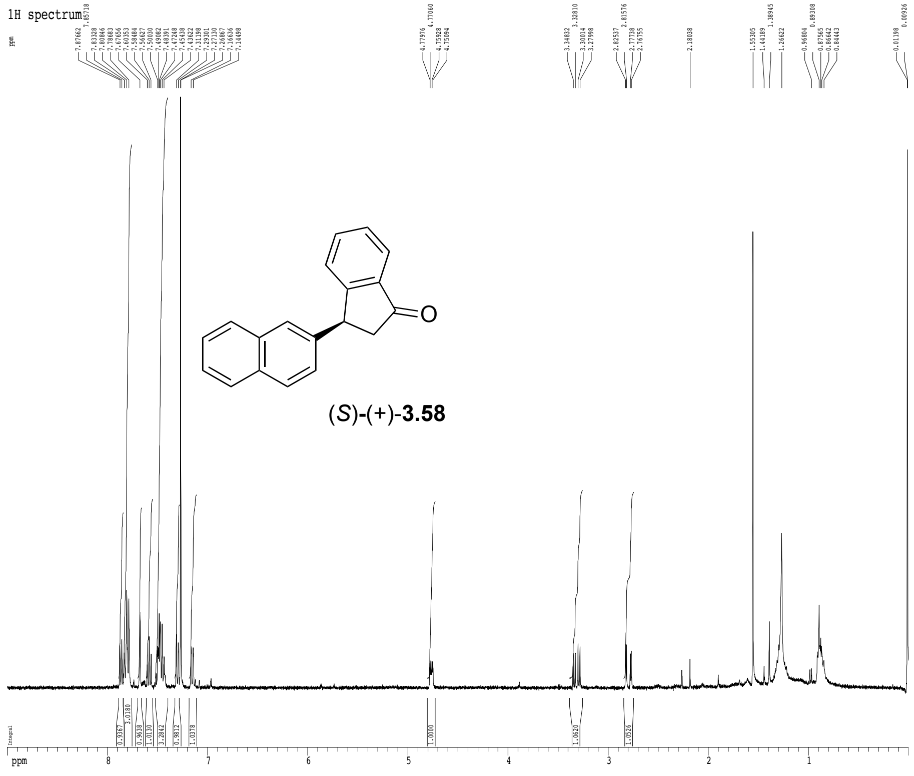
F2 - Acquisition Parameters
Date_          20151112
Time              17.24
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                203.2
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1                0.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

S96



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F2P               0.000 ppm
F2                 0.00 Hz

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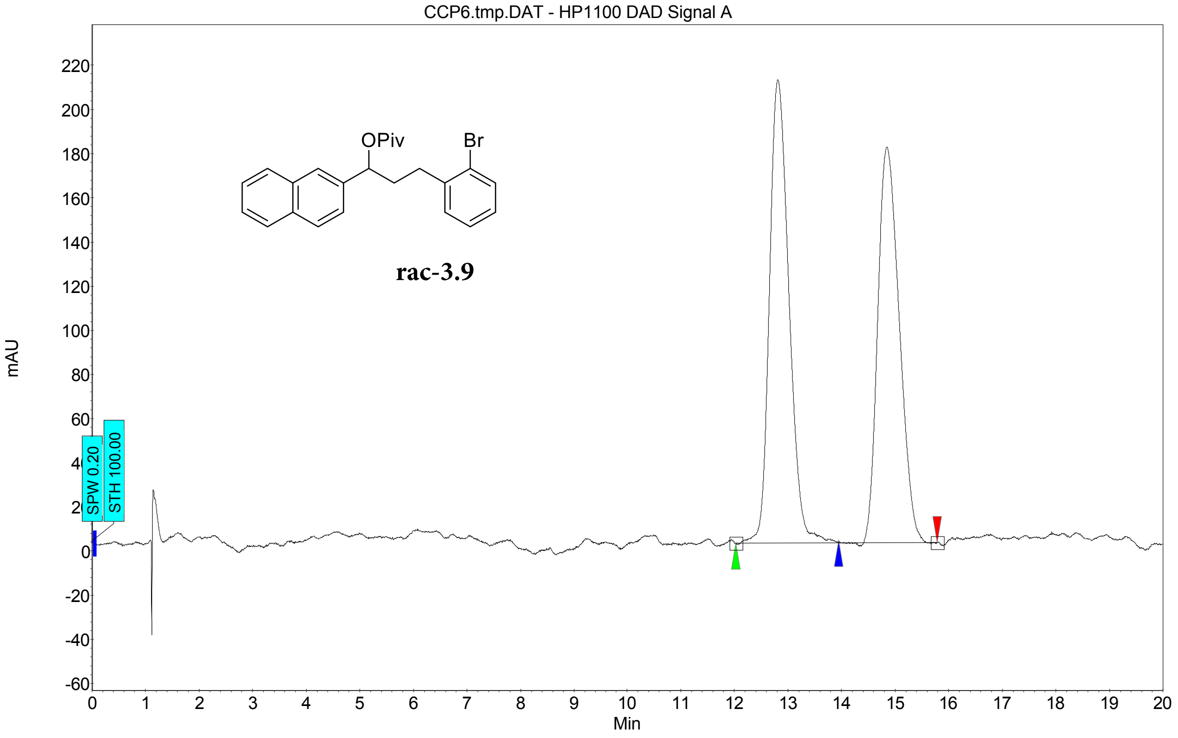

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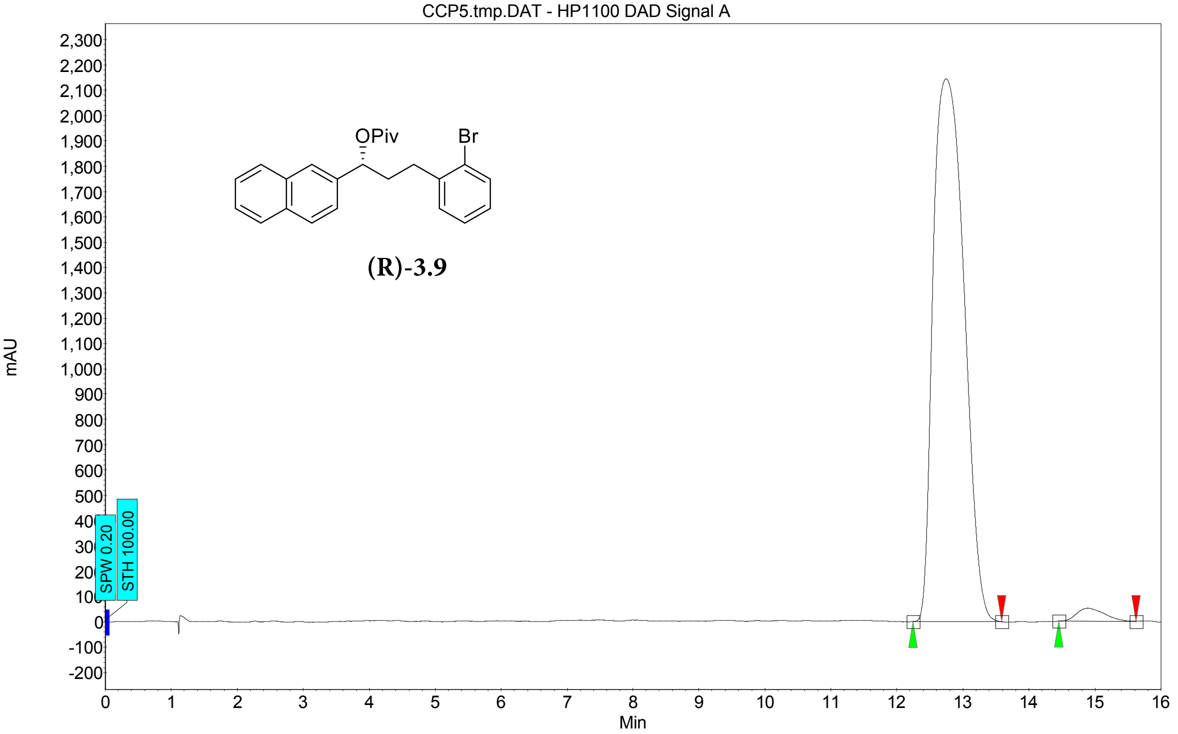

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1	UNKNOWN	12.25	12.74	13.59	0.00	97.90	2143.7	1166.3	97.901
2	UNKNOWN	14.45	14.90	15.62	0.00	2.10	51.7	25.0	2.099
Total						100.00	2195.5	1191.3	100.000

Method Name:MOK-II-266rac
Run Name:LEH-6-080-D3

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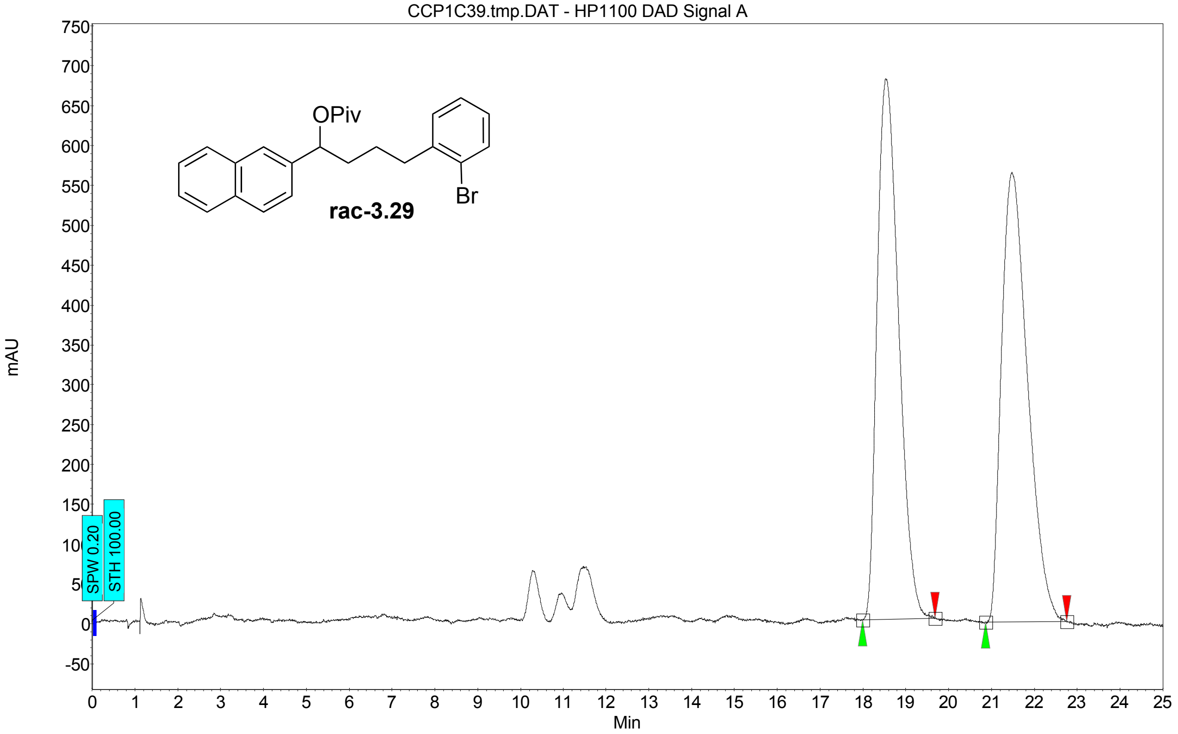

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2	UNKNOWN	20.86	21.48	22.75	0.00	50.15	564.1	397.9	50.154
Total						100.00	1242.2	793.3	100.000

Method Name:MOK-II-266rac
Run Name:LEH-5-084-A3

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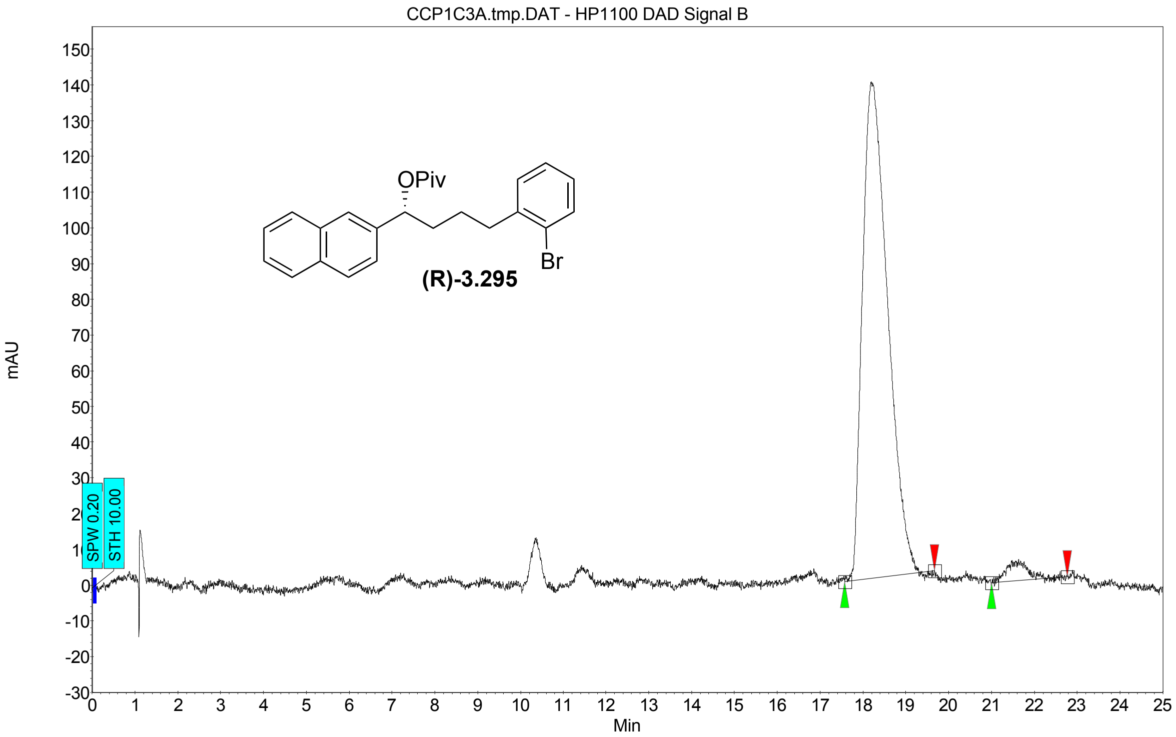

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2	UNKNOWN	21.01	21.63	22.76	0.00	3.16	5.9	3.1	3.158
Total						100.00	144.7	97.3	100.000

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Run Name:MOK-IV-racopiv5tbs3

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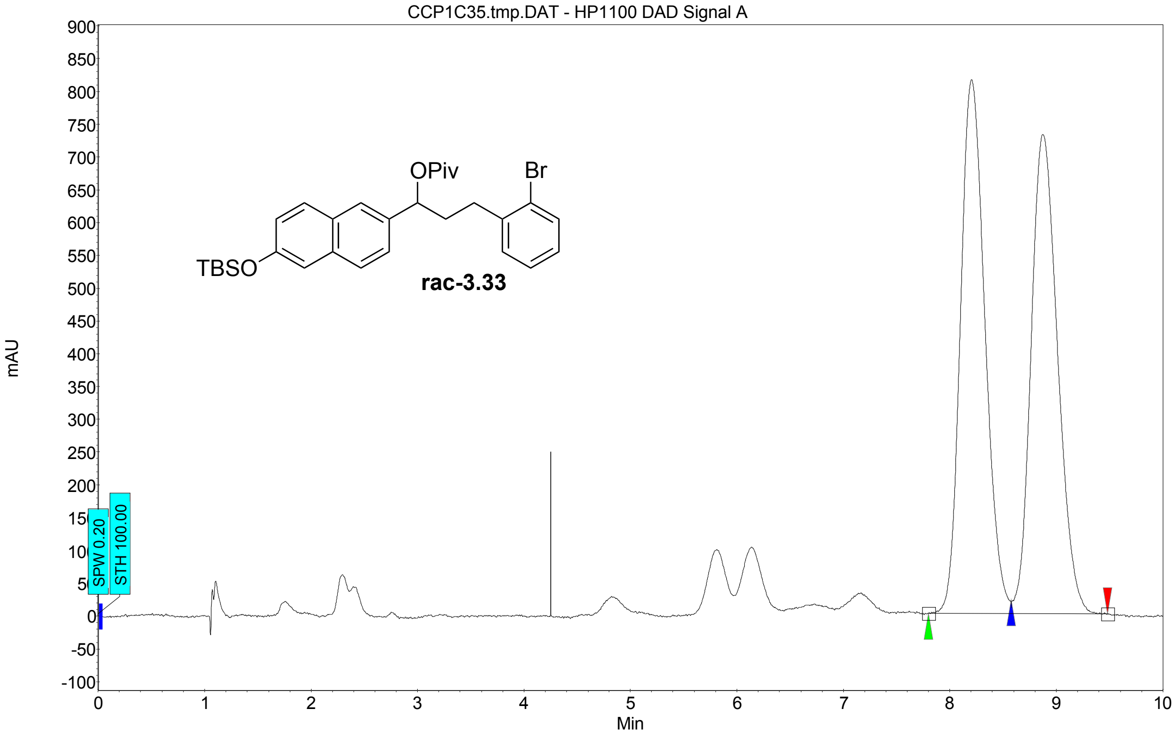
Time:7:00:17 PM



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2	UNKNOWN	8.58	8.87	9.48	0.00	49.35	730.6	211.1	49.349
Total						100.00	1544.2	427.7	100.000

Method Name:MOK-IV-5otbspiv
Run Name:MOK-IV-eeopiv5tbs2

Date:11/24/2015
Time:7:01:31 PM

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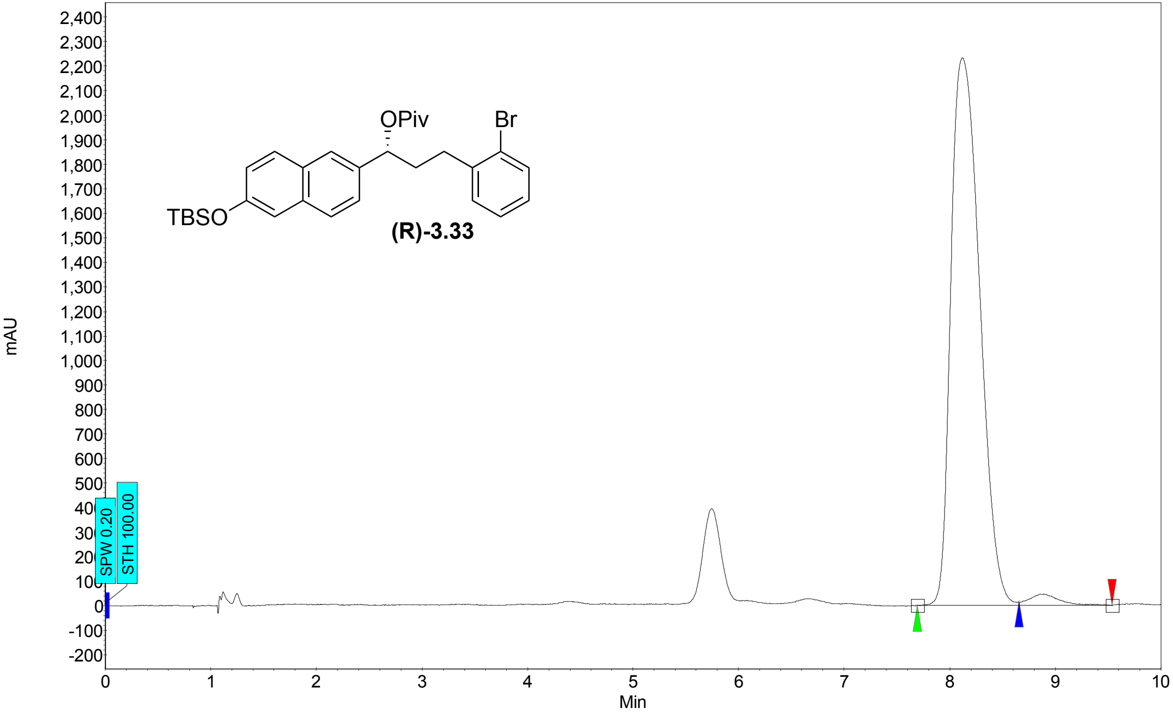

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1	UNKNOWN	7.69	8.12	8.65	0.00	97.92	2231.6	705.5	97.918
2	UNKNOWN	8.65	8.86	9.54	0.00	2.08	45.6	15.0	2.082
Total						100.00	2277.2	720.5	100.000

Method Name:MOK-II-266rac
Run Name:MOK-2-266rac3

Date:9/7/2015
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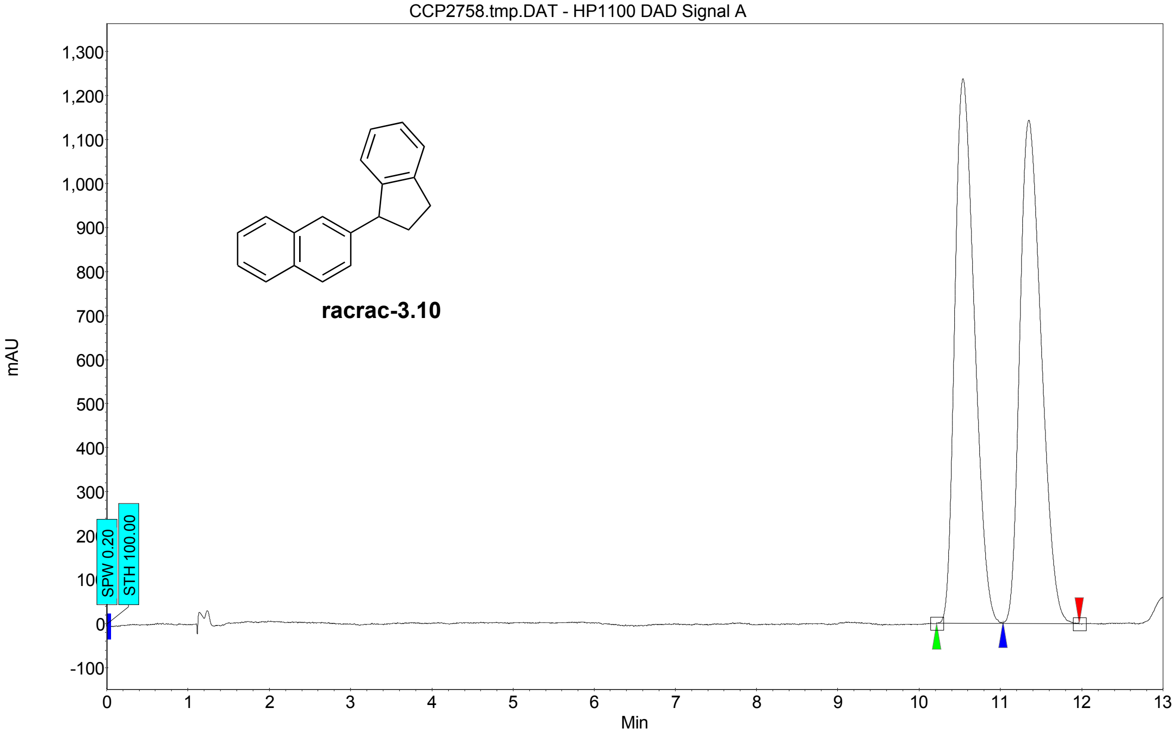

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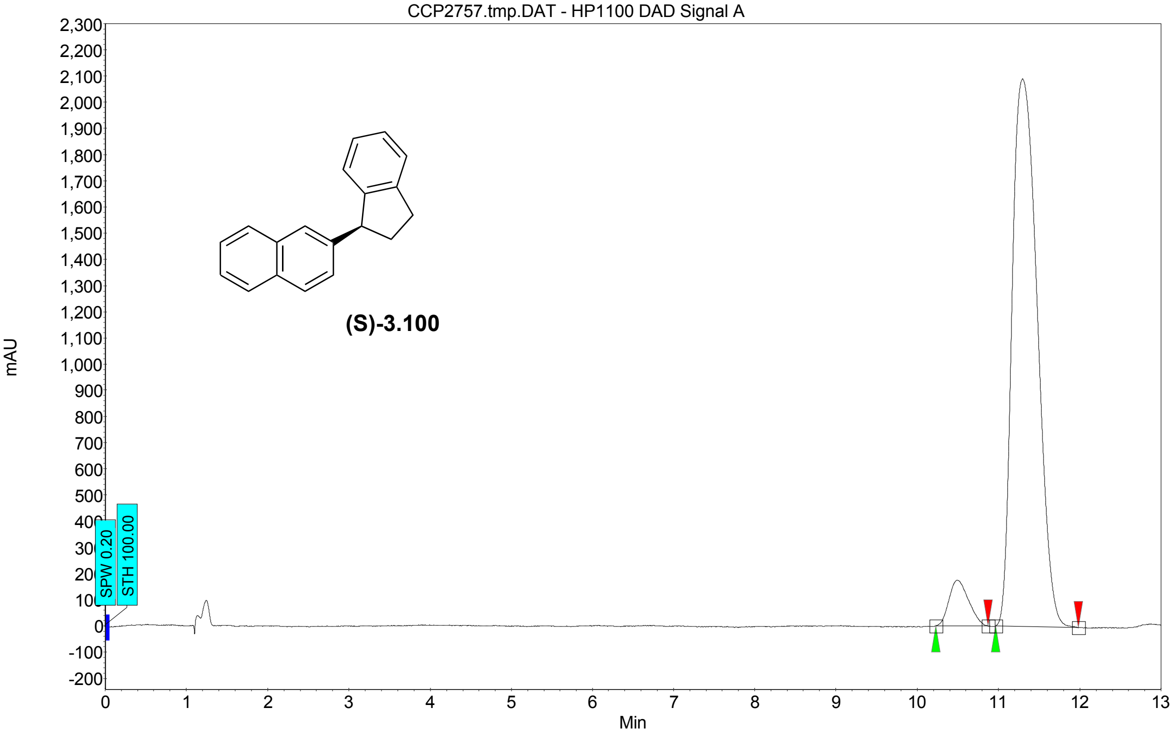
1	UNKNOWN	10.21	10.54	11.04	0.00	49.76	1237.1	347.4	49.764
2	UNKNOWN	11.04	11.35	11.97	0.00	50.24	1143.6	350.7	50.236
Total						100.00	2380.8	698.2	100.000

Method Name:MOK-II-266rac
Run Name:LEH-5-151-pub3

Date:9/7/2015
Time:3:03:27 PM



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
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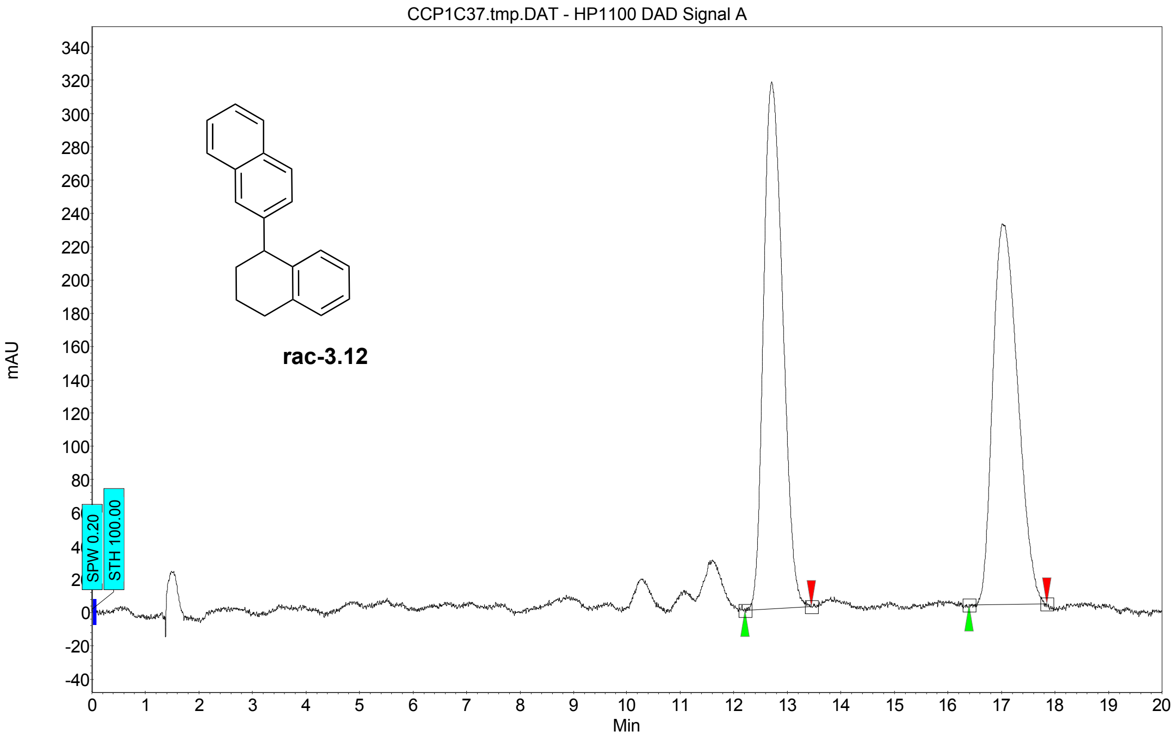
2	UNKNOWN	10.23	10.50	10.87	0.00	6.12	174.1	48.8	6.121
1	UNKNOWN	10.96	11.30	11.98	0.00	93.88	2091.5	747.8	93.879
Total						100.00	2265.6	796.6	100.000

Method Name:MOK-266-NAP-6-Pdt
Run Name:LEH-6-083-F1

Date:11/24/2015
Time:7:04:23 PM



rac-3.12

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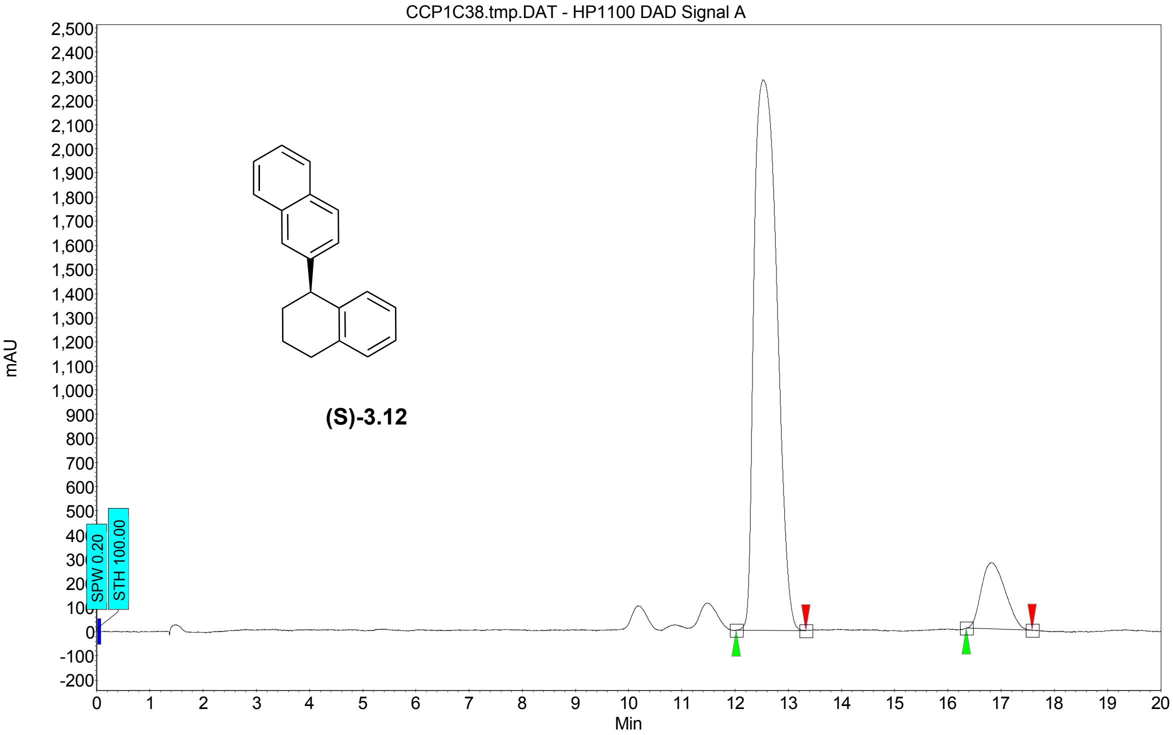
1	UNKNOWN	12.21	12.71	13.45	0.00	51.53	316.7	131.5	51.529
2	UNKNOWN	16.40	17.02	17.84	0.00	48.47	228.9	123.7	48.471
Total						100.00	545.7	255.3	100.000

Method Name:MOK-266-NAP-6-Pdt
Run Name:LEH-6-085-A1

Date:11/24/2015
Time:7:06:01 PM



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1	UNKNOWN	12.02	12.53	13.33	0.00	88.75	2280.2	1130.7	88.750
2	UNKNOWN	16.35	16.81	17.57	0.00	11.25	273.6	143.3	11.250
Total						100.00	2553.9	1274.1	100.000

Method Name:MOK-IV-ractbsprodMETH
Run Name:MOK-IV-otbsracprod1

Date:11/24/2015
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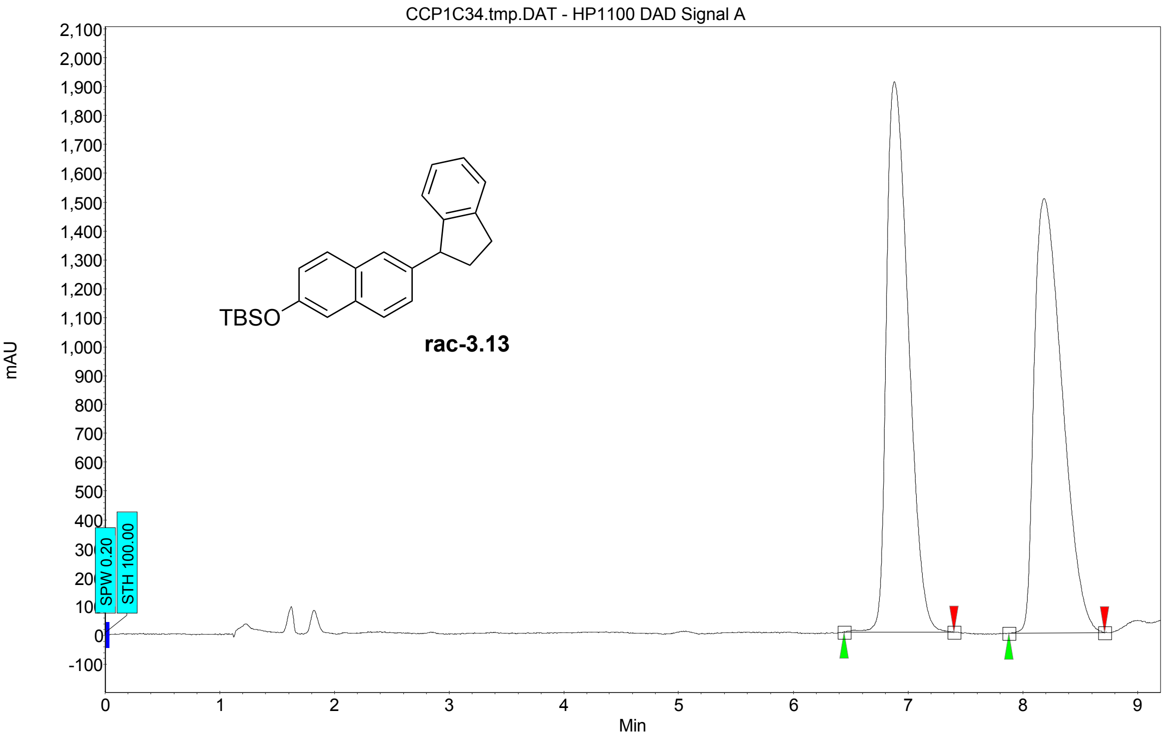

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1	UNKNOWN	6.44	6.88	7.40	0.00	49.85	1904.4	421.7	49.849
2	UNKNOWN	7.88	8.19	8.71	0.00	50.15	1503.7	424.3	50.151
Total						100.00	3408.1	846.0	100.000

Method Name:MOK-IV-ractbsprodMETH
Run Name:MOK-IV-otbseeprod2

Date:11/24/2015
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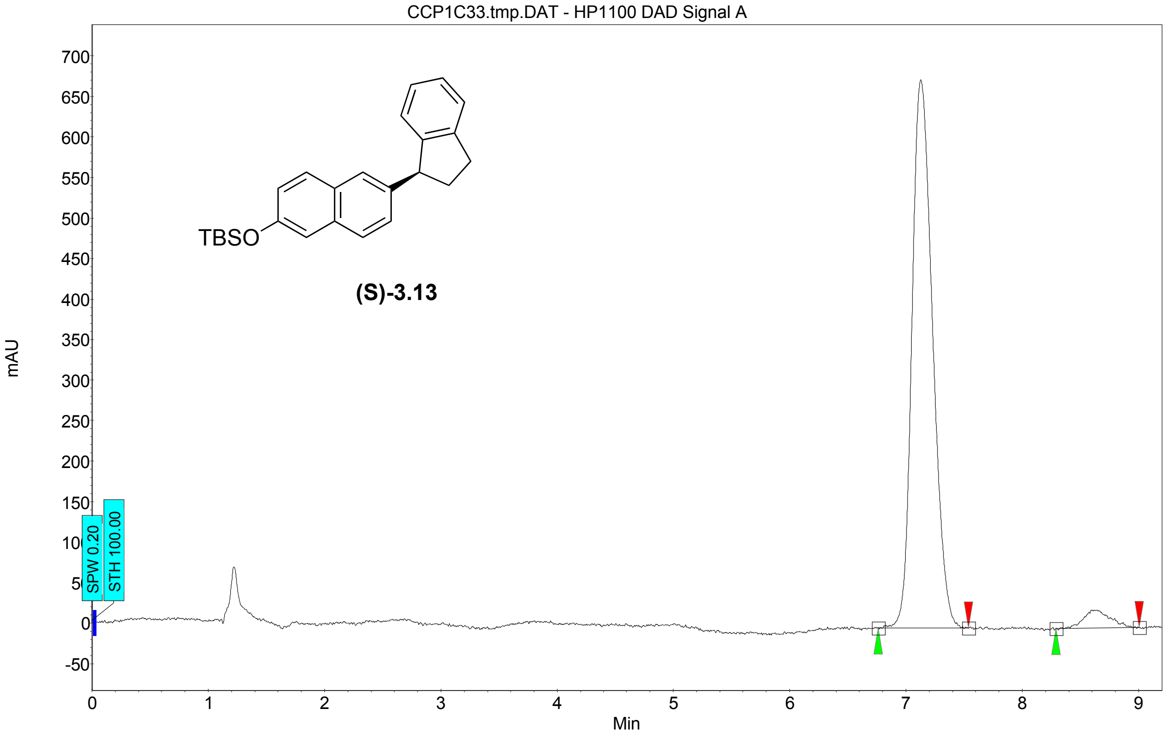

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
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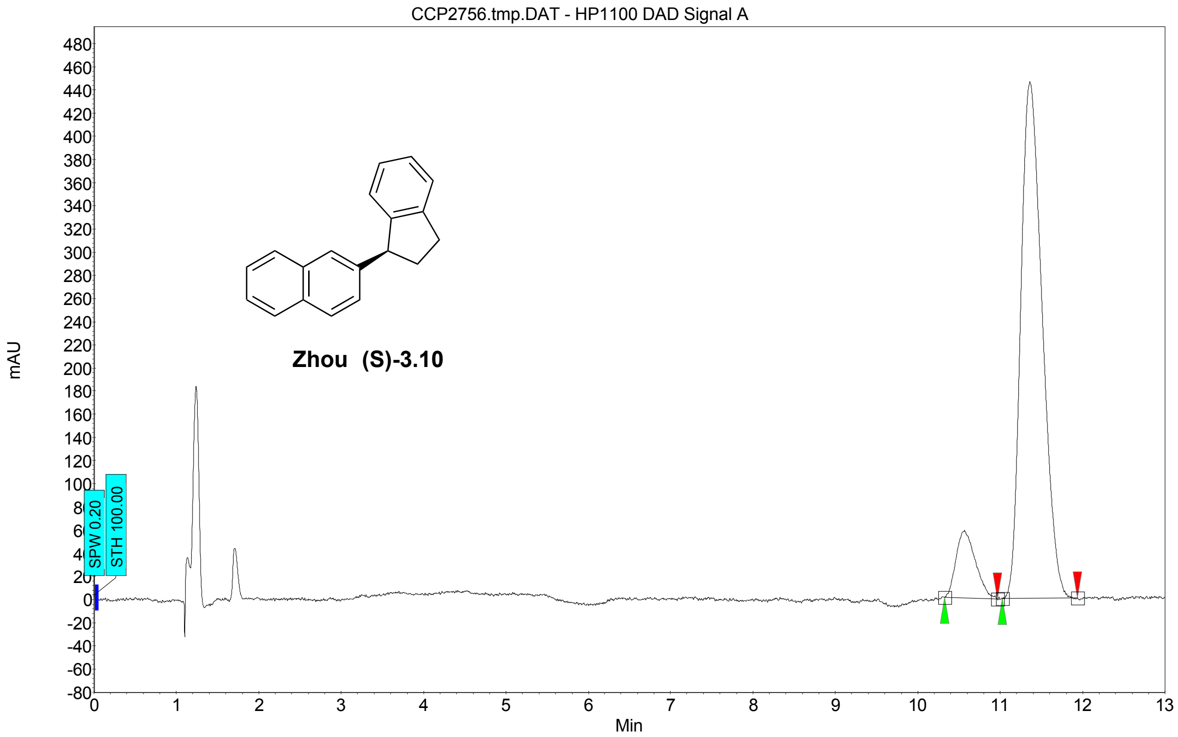
1	UNKNOWN	6.76	7.13	7.53	0.00	95.85	676.0	138.3	95.849
2	UNKNOWN	8.29	8.61	9.00	0.00	4.15	22.6	6.0	4.151
Total						100.00	698.6	144.3	100.000

Method Name:MOK-II-266rac
Run Name:LEH-5-036-realeezhou3

Date:9/7/2015
Time:2:49:52 PM



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	10.33	10.57	10.96	0.00	10.54	58.2	15.8	10.536
2	UNKNOWN	11.03	11.36	11.93	0.00	89.46	446.0	134.4	89.464
Total						100.00	504.2	150.3	100.000

Chapter 4

Nickel-Catalyzed Generation of 2-PyridylZinc Reagents: Applications to Deoxygenation and Intramolecular Conjugate Additions

4.1 Introduction

Functionalized organozinc reagents are critical for the construction of natural products and other complex organic molecules.[1,2] Their tendency to undergo selective reactions with transition metals enables the construction of new carbon–carbon bonds under mild reaction conditions. Methods to prepare functionalized organozincs are diverse and are an important topic of continuing research.[3] However, the preparation of benzylzinc reagents present particular challenges. While benzylzinc reagents can be prepared by insertion of elemental zinc with primary benzylic halides (Scheme 4.1a), secondary benzylic halides frequently provide low yields due to formation of stable radicals that undergo competitive Wurtz-type coupling. Exchange of alkylboron reagents with a zinc (II) species provides an alternative method for the preparation of secondary benzylzinc reagents, but relies on synthesis of the requisite alkylboron reagent (Scheme 4.1b).[4] Fragmentation of bulky homobenzylic zinc alkoxides is a creative approach that circumvents formation of benzylic radicals (Scheme 4.1c).[5]

---

[1] (a) G.S. Silverman, in: P.E. Rakita (Ed.), Handbook of Grignard reagents, Marcel Dekker, New York, 1996. (b) Knochel, P.; Leuser, H.; Gong, L.-Z.; Perrone, S.; Kneisel, F. F. Handbook of Functionalized Organometallics: Applications in Synthesis; Knochel, P., Ed.; Wiley: Weinheim, 2005; p 251.

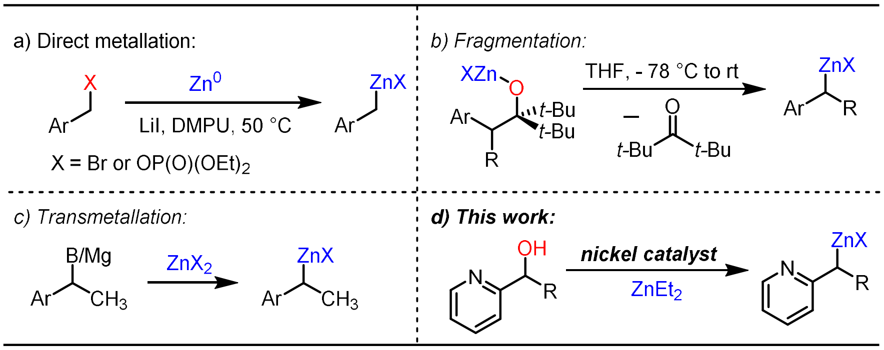
[2] (a) Knochel, P.; Leuser, H.; Gong, L.-Z.; Perrone, S.; Kneisel, F. F. Polyfunctional Zinc Organometallics for Organic Synthesis. In *Handbook of Functionalized Organometallics: Applications in Synthesis*; Knochel, P., Ed.; Wiley: Weinheim, 2005; p 251. For specific examples in total synthesis, see: (b) Fürstner, A.; Weintritt, H. *J. Am. Chem. Soc.* **1998**, *120*, 2817. (c) Masaki, H.; Maeyama, J.; Kamada, K.; Esumi, T.; Iwabuchi, Y.; Hatakeyama, S. *J. Am. Chem. Soc.* **2000**, *122*, 5216. (d) Aoyagi, S.; Hirashima, S.; Saito, K.; Kibayashi, C. *J. Org. Chem.* **2002**, *67*, 5517.

[3] (a) Klatt, T.; Markiewicz, J. T.; Sämann, C.; Knochel, P. *J. Org. Chem.* **2014**, *79*, 4253. (b) Stathakis, C. I.; Manolikakes, S. M.; Knochel, P. *Org. Lett.* **2013**, *15*, 1302. (c) Colombe, J. R.; Bernhardt, S.; Stathakis, C.; Buchwald, S. L.; Knochel, P. **2013**, *15*, 5754. (d) Quinio, P.; François, C.; Cuesta, A. E.; Steib, A. K.; Achrainer, F.; Zipse, H.; Karaghiosoff, K.; Knochel, P. *Org. Lett.* **2015**, *17*, 1010.

[4] (a) Langer, F.; Knochel, P. *Tetrahedron Lett.* **1995**, *36*, 4591. (b) Hupe, E.; Calaza, M. I.; Knochel, P. *J. Organomet. Chem.* **2003**, *680*, 136.

[5] Piazza, C.; Millot, N.; Knochel, P. *J. Organomet. Chem.* **2001**, *624*, 88.

Scheme 4.1 Summary of methods for preparation of benzylic zinc reagents



Transition-metal catalysis offers alternative strategies for formation of organometallic reagents.[6,7,8] Formation of benzylnickel complexes can be accomplished by oxidative addition of nickel catalysts with benzylic electrophiles.[9] We reasoned that, with catalytic quantities of a nickel catalyst and in the presence of a super-stoichiometric organozinc reagent such as diethylzinc, transmetallation would generate the desired organozinc reagent. The Shi group has reported a related synthesis of primary benzylic Grignard reagents from benzylic alcohols.[10] In this chapter, we report nickel-catalyzed formation of secondary benzylzinc reagents from readily accessible 2-pyridylcarbinols (Scheme 4.1d). Activation of the alcohol is achieved using diethylchlorophosphate;[11] quenching with methanol provides the products of deoxygenation in a one-pot reaction. We propose that the pyridyl substituent serves as a directing group and stabilizes

---

[6] (a) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508. (b) Rosen, B. M.; Huang, C.; Percec, V. *Org. Lett.* **2008**, *10*, 2597. (c) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am Chem. Soc.* **2002**, *124*, 390.

[7] Gao, F.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 10961.

[8] Dao, H. T.; Baran, P. S. *Angew. Chem. Int. Ed.* **2014**, *53*, 14382.

[9] (a) Wisniewska, H. M.; Swift, E. C.; Jarvo, E. R. *J. Am. Chem. Soc.* **2013**, *135*, 9083. (b) Do, H-Q.; Chandrashekar, E. R. R.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 16288

[10] Yu, D-G.; Wang, X.; Zhu, R-Y.; Luo, S.; Zhang, X-B.; Wang, B-Q.; Wang, L.; Shi, Z-J. *J. Am. Chem. Soc.* **2012**, *134*, 14638.

[11] Phosphate esters generated in situ are effective electrophiles in nickel-catalyzed transformations, see: (a) Ackerman, L. K. G.; Anka-Lufford, L. L.; Naodovic, M.; Weix, D. J. *Chem. Sci.* **2015**, *6*, 1115.

the benzylzinc reagent.[12,13] This method provides reduction of hydroxymethylpyridines with incorporation of deuterium in the benzylic position, which can be useful probing metabolic pathways.

4.2 Development of Nickel-Catalyzed Formation of 2-Pyridyl Benzylzinc Reagents

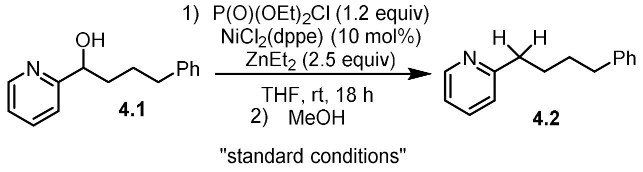
We examined 2-pyridyl carbinol **4.1** as our model substrate. Reactions were performed employing diethylchlorophosphate to activate the alcohol, a series of nickel catalysts, and diethylzinc as transmetallating agent. We found that at room temperature, Ni(dppe)Cl_2 furnishes the desired deoxygenated product **4.2** in high yield (Table 4.1, entry1). The data in Table 4.1 illustrate how changes in the reaction parameters affect the transformation. When the nickel catalyst or diethylchlorophosphate are omitted, the reaction does not afford desired product (entries 2–4). These results are consistent with a mechanism of benzylic alcohol activation prior to reaction with a nickel catalyst. The use of a non-polar solvent or $ZnMe_2$ instead of $ZnEt_2$ does not significantly affect the efficiency of the reaction (entries 5 and 6). A decreased yield of **4.2** was observed when catalysts ligated by other bidentate or monodentate phosphine ligands were used in the reaction (entries 7-10). Under optimized conditions, the reaction scales well, providing desired product in high yield when run on gram scale (entry 11).

---

[12] General pyridyl directing groups: (a) Reviews on removable pyridine directing groups (a) Itami, K.; Mitsudo, K.; Nokami, T.; Kamei, T.; Koike, T.; Yoshida, J-I. *J. Organomet. Chem.* **2002**, *653*, 105. (b) Itami, K.; Yoshida, J-I *Synlett.* **2006**, *2*, 157. Direcred reactions by Chatani/Murai (a) Chatani, N.; Inoue, S.; Yokata, K.; Tatamidani, H.; Fukumoto, Y. *Pure. Appl. Chem.* **2010**, *82*, 1443. (b) Chatani, N.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **1999**, *121*, 8645. (c) Tatamidani, H.; Yokata, K.; Kakiuchi, F.; Chatani, N. *J. Org. Chem.* **2004**, *69*, 5615. More recent publications: (a) Wang, J.; Chen, W.; Zuo, S.; Liu, L.; Zhang, X.; Wang, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 12334. (b) Lei, Z-Q.; Pan, F.; Li, H.; Li, Y.; Zhang, X-S.; Chen, K.; Wang, X.; Li, Y-X.; Sun, J.; Shi, Z-J. *J. Am. Chem. Soc.* **2015**, *137*, 5012. Pyridine is a privileged directing group in C–H bond activation, see: (a) Suggs, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 489. (b) Lim, Y–G.; Kang, J–B.; Kim, Y. H. *J. Chem. Soc., Perkin Trans.* **1996**, *1*, 2201. (c) Jun, C–H.; Hwang, D–C.; Na, S–J. *Chem. Commun.* **1998**, 1405. (d) Chatani, N.; Ishii, Y.; Ie, Y.; Kakiuchi F.; Murai, S. *J. Org. Chem.* **1998**, *63*, 5129. (e) Chatani, N.; Asaumi, T.; Ikeda, T.; Yorimitsu, S.; Ishii, Y.; Kakuichi, F.; Murai, S. *J. Am. Chem. Soc.* **2000**, *122*, 12882.

[13] Bioactive references: (a) Shi, N.; Lu, C.; Ho, C. C.; Shen, Y. *Rec. Nat. Prod.* **2013**, *7*, 1. (b) Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856. (c) Kubota, T.; Ishiguro Y.; Yamamoto, S.; Fromont, J.; Kobayashi, J. *Heterocycles* **2010**, *80*, 1407. (d) Fischer, D. F.; Sarpong, R. *J. Am. Chem. Soc.* **2010**, *132*, 5926. Actos (Takeda). Ligand references: (a) Chelucci, G.; Thummel, R. P. *Chem. Rev.* **2002**, *102*, 3129.

Table 4.1. Effect of Reaction Parameters on the Efficiency of Deoxygenation of **4.1**

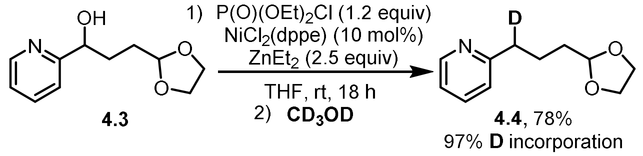


entry	change from standard conditions	yield (%)[a]
1	none	77
2	dppe instead of $NiCl_2$(dppe)	< 5
3	no $NiCl_2$(dppe)	< 5
4	no $P(O)(OEt)_2Cl$	< 5
5	PhMe instead of THF	72
6	$ZnMe_2$ instead of $ZnEt_2$	74
7	$NiCl_2$•DME / DPEphos instead of $NiCl_2$(dppe)	42
8	$NiCl_2$•DME / dppf instead of $NiCl_2$(dppe)	55
9	$NiCl_2$•DME / PCy_3 instead of $NiCl_2$(dppe)	21
10	$NiCl_2$•DME / PPh_3 instead of $NiCl_2$(dppe)	50
11	Run on 1.0 g scale of **1**	72[b]

4.3 Exploration of Scope of Deoxygenation of 2-pyridyl Alcohols

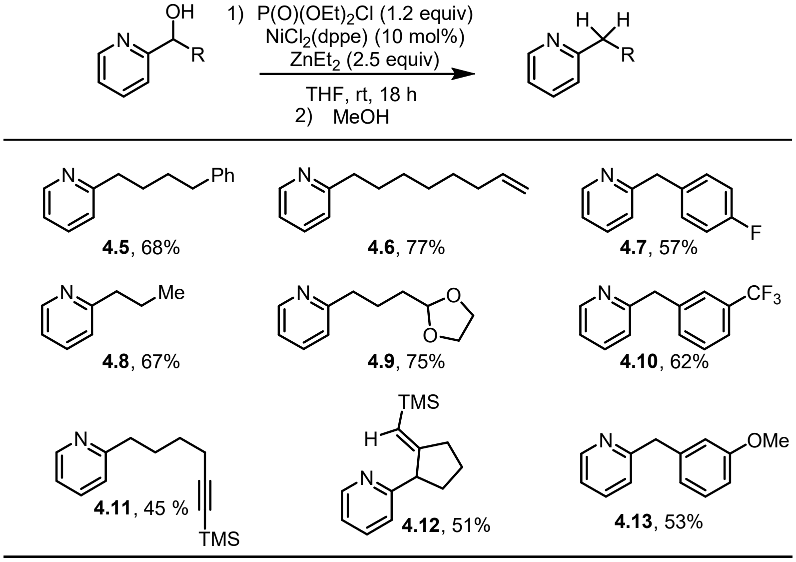
Having developed robust conditions for the deoxygenation of **4.1**, we turned our attention to investigating the source of "H" found in the product. We proposed that **4.2** is formed from the methanol quench of the benzylzinc reagent generated in situ. To test our hypothesis, we performed an isotopic labeling study with methanol-d4. Upon quenching the deoxygenation reaction of **4.3** with CD_3OD, we observed high yield and high deuterium incorporation of the corresponding product **4.4** (eq 4.1). The result of the isotopic labeling experiment provides strong support for our proposed hypothesis that the reaction proceeds by formation of a benzylzinc reagent.

Equation 4.1. Deuterium incorporation via quenching with deuteromethanol



Next, we examined the formation of alkylzinc reagents from a range of benzylic alcohols (Table 4.2). Secondary benzylic alcohols bearing alkyl chains are well tolerated under the reaction conditions (entries **4.5**, and **4.8**). Substrates containing acetal and alkene functionalities provide deoxygenated products in good yield (**4.6** and **4.11**). The high yield of **4.6** demonstrates excellent orthogonality to hydroboration transmetallation procedures often used to prepare secondary benzylic zinc reagents.[14] Of particular note, is the formation of byproduct **4.12**, isolated from reactions desired to produce only **4.11**. We hypothesize this by product is the result of a metallo-ene reaction resulting from the proposed benzylic reagent which has been previously described.[15]

Table 4.2 Scope of Deoxygenation



A mechanism consistent with the formation of the proposed benzylic zinc reagents is outlined in Figure 1. The active catalyst is formed by reduction of Ni(dppe)Cl_2 with $ZnEt_2$ to give the reduced Ni(0)(dppe) species. The Ni(0) catalyst then undergoes oxidative addition into the phosphorylated alcohol to form a benzylic Ni(II) intermediate. Transmetallation results in formation of the benzylic zinc reagent and an ethylnickel complex. β-Hydride elimination followed by loss of ethylene yields a nickel hydride intermediate. This intermediate undergoes a

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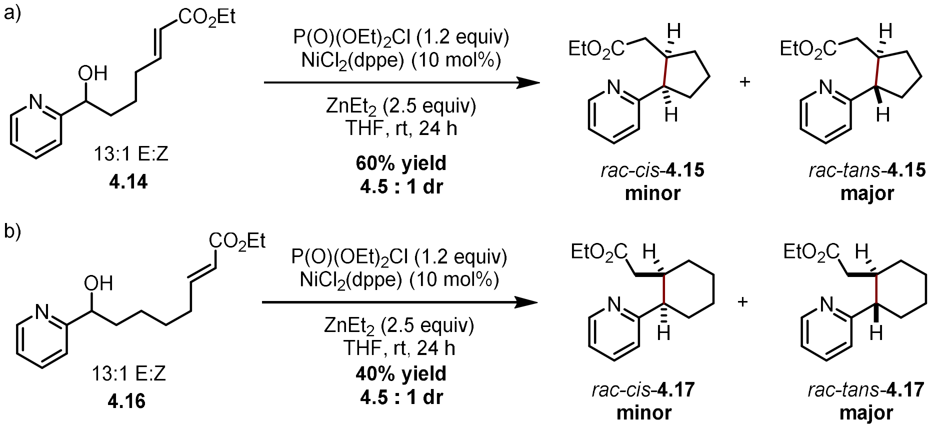
[14] Hupe, E.; Calaza, M. I.; Knochel, P. *J. Organomet. Chem.* **2003**, *680*, 136.

[15] Meyer, C.; Marek, I.; Courtemanche, G.; Normant, J.-F. *J. Org. Chem.* **1995**, *60*, 863.

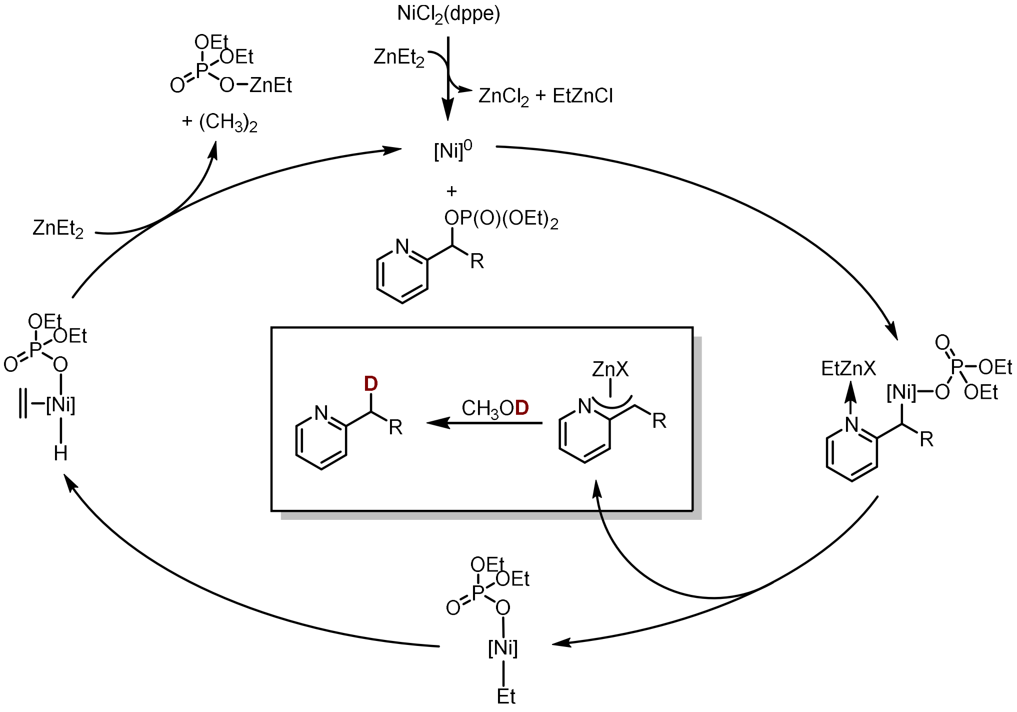
final transmetallation of an ethyl group from zinc followed by reductive elimination to form ethane and regenerate the Ni(0) catalyst.

Scheme 4.2. Intramolecular 1,4-addition



To further demonstrate the utility of this methodology, we coupled the formation of a benzylic zinc reagent to an intramolecular conjugate addition (Scheme 4.2). We anticipated that upon forming the corresponding benzylzinc reagent from **4.14** or **4.16**, cyclization should occur to afford cyclopentane **4.15** or cyclohexane **4.17** (Scheme 4.2 a and b respectively). 2-Pyridyl carbinol **4.14** and **4.16** bearing a pendant α,β-unsaturated ester underwent smooth cyclization to produce the desired product in modest yield and 4.5:1 diastereomeric ratio. Upon investigation of smaller ring sized such as 3-membered rings yielded no cyclization product, this was also the case when we attempted to produce 7-membered rings using this methodology.

Figure 4.1. Proposed Mechanism for formation of 2-pyridyl zinc reagent



4.4 Conclusion

In summary, we have developed a concise route to secondary organozinc reagents directly from benzylic alcohols. We have successfully applied this methodology to the formal hydrogenolysis of a range of 2-pyridyl carbinols. The reaction proceeds in high yield and with straightforward incorporation of deuterium from deuteromethanol. The reaction has been applied to an intramolecular 1,4-addition. Further exploration of the reactivity of these compounds and elucidation of mechanistic details are underway.

4.5 Experimental Details

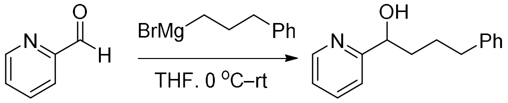
GENERAL PROCEDURES

All reactions were carried out under an atmosphere of N_2, or Ar when noted. All glassware was oven- or flame-dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and toluene (PhMe) were degassed with Ar and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 ºC for 12 h) to remove H_2O. All other solvents utilized were purchased "anhydrous" commercially, or purified as described. ^1H NMR spectra were recorded on Bruker DRX-400 (400 MHz ^1H, 100 MHz ^{13}C, 376.5 MHz ^{19}F), GN-500 (500 MHz ^1H, 125.7 MHz ^{13}C), or CRYO-500 (500 MHz ^1H, 125.7 MHz ^{13}C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), triplet (t), doublet of triplets (dt), doublet of doublet of triplets (ddt), triplet of triplets (tt), quartet (q), quintet (quin), apparent doublet (ad), apparent triplet (at), multiplet (m)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 ºC. Infrared (IR) spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm^{-1}). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F_{254} precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with $KMnO_4$, ceric ammonium molybdate (CAM), or *p*-anisaldehyde (PAA) solutions. Flash chromatography was performed using Silica Gel 60 (170-400 mesh) from Fisher Scientific. Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. [1,2-Bis(diphenylphosphino)ethane]dichloronickel(II) was purchased from Strem, stored in a glovebox under an atmosphere of N_2, and used as received. Diethylzinc ($ZnEt_2$) and diethyl chlorophosphate were purchased from Sigma and used as received. 1-isoquinolinecarboxaldehyde was prepared from selenium (IV) oxide oxidation of 1-methylisoquinoline by a procedure reported by Long.[i] All other reagents were purchased commercially and used as received.

SYNTHESIS AND CHARACTERIZATION OF ALL SUBSTRATES

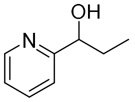
Synthesis of Benzylic Alcohols

General Procedure A. *Grignard addition to aldehydes.*

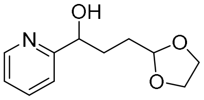


4.18. In a flame-dried round-bottom flask, to a solution of 2-pyridinecarboxaldehyde (1.43 mL, 15.0 mmol, 1.00 equiv) in THF (30 mL) was added at 0 °C (3-phenylpropyl)magnesium bromide (1.6 M in THF, 10 mL, 16 mmol, 1.1 equiv). After stirring at room temperature for 1 h, saturated ammonium chloride (25 mL) was added at 0 °C and the reaction was extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with brine (1 x 40 mL), dried over Na_2SO_4, and concentrated in vacuo. The product was purified by column flash chromatography (25–40% EtOAc/hexanes) to afford the title compound as a yellow solid (1.70 g, 7.50 mmol, 50%). **TLC R_f** = 0.16 (20% EtOAc/hexanes, UV active); **m.p.** = 58–60 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, J = 4.8 Hz, 1H), 7.66 (td, J = 7.8, 1.8 Hz, 1H), 7.29–7.23 (m, 2H), 7.22–7.13 (m, 5H), 4.75 (s, 1H), 4.19 (s, 1H), 2.71–2.59 (m, 2H), 1.91–1.82 (m, 1H), 1.80–1.67 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.9, 148.2, 142.4, 136.7, 128.5, 128.3, 125.8, 122.3, 120.4, 72.5, 38.2, 35.8, 26.9; **IR**

(neat) 3192, 2925, 2861, 1594, 1492, 1452 cm^{-1}; **HRMS** (TOF MS ES+) m / z calcd for $C_{15}H_{17}NONa$ (M + Na)$^{+}$ 227.1310, found 227.1315.



4.19 Prepared according to a procedure reported by Braga[16], the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.38 mL, 4.00 mmol, 1.00 equiv), ethylmagnesium bromide (2.4 M in Et_2O, 2.0 mL, 4.8 mmol, 1.2 equiv), and THF (15 mL). Analytical data is consistent with literature values.[17] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dt, *J* = 4.9, 1.3 Hz, 1H), 7.68 (td, *J* = 7.6, 1.8 Hz, 1H), 7.25 (dd, *J* = 7.8 Hz, 0.5 Hz, 1H), 7.20 (ddd, *J* = 7.6, 4.9, 0.5 Hz, 1H), 4.73–4.66 (m, 1H), 4.17 (d, *J* = 5.5 Hz, 1H), 1.95–1.84 (m,



4.20 Using representative procedure A outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv), hept-6-en-1-ylmagnesium bromide (1.2 M in THF, 9.2 mL, 11 mmol, 1.1 equiv), and THF (10 mL). The product was purified by column flash chromatography (25–40% EtOAc/hexanes) to afford the title compound as a yellow oil (1.31 g, 6.38 mmol, 64%). Analytical data is consistent with literature values.[18] **TLC R$_f$** = 0.1 (50% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55–8.50 (m, 1H), 7.67 (td, *J* = 7.8, 1.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.21–7.15 (m, 1H), 4.93–4.88 (m, 1H), 4.83–4.75 (m, 1H), 4.33 (d, *J* = 5.4 Hz, 1H), 3.99–3.80 (m, 4H), 2.07–1.95 (m, 1H), 1.87–1.74 (m,

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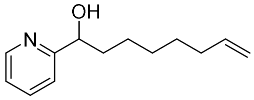
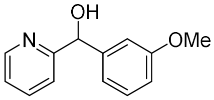
[16] Braga, A. L.; Paixao, M. W.; Ludtke, D. S.; Silveira, C. C.; Rodrigues, O. E. D. *Org. Lett.* **2003**, *5*, 2365.
[17] Moody, C. J.; Morfitt, C. N. *Synthesis* **1998**, *7*, 1039.
[18] Gebert, A.; Barth, M.; Linden, A.; Widmer, U.; Heimgartner, H. *Helv. Chim. Acta* **2012**, *95*, 737.

3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 161.9, 148.3, 136.7, 122.3, 120.4, 104.4, 72.38, 64.9, 32.5, 29.5.

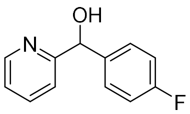


4.21 Using representative procedure A outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv), hept-6-en-1-ylmagnesium bromide (1.2 M in THF, 9.2 mL, 11 mmol, 1.1 equiv), and THF (10 mL). The product was purified by column flash chromatography (25–40% EtOAc/hexanes) to afford the title compound as a red oil (1.31 g, 6.38 mmol, 64%). **TLC R$_f$** = 0.4 (40% EtOAc/hexanes, UV active); ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.7 Hz 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 5.5 Hz, 1H), 5.79 (ddt, *J* = 17.2, 10.2, 6.9 Hz, 1H), 4.98 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.2 Hz, 1H), 4.73 (dd, *J* = 7.7, 4.4 Hz, 1H), 4.25 (br s, 1H), 2.03 (dd, *J* = 10.2, 6.9 Hz, 2H), 1.87–1.77 (m, 1H) 1.74–1.65 (m, 1H), 1.50–1.24 (m, 6H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 162.4, 148.3, 139.2, 136.7, 122.3, 120.4, 114.3, 72.9, 38.7, 33.8, 29.2, 28.9, 25.2; **IR** (neat) 3260, 2926, 1594 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{13}H_{19}ONNa$ $(M + Na)^+$ 228.1364, found 228.1364.

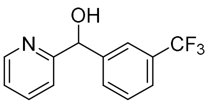


4.22 Using representative procedure A outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv) (3-methoxyphenyl)magnesium bromide (0.92 M in THF, 13 ml, 12 mmol, 1.2 equiv), and THF (20 mL). The product was purified by column flash chromatography (20–40% EtOAc/hexanes) to afford the title compound as a yellow oil (0.62 g, 3.1 mmol, 62%). Analytical data is consistent with literature values.[6] **TLC R$_f$**

= 0.2 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.4 Hz, 1H), 7.62 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29–7.14 (m, 3H), 6.96 (d, *J* = 6.7 Hz, 1H), 6.93 (s, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 5.27 (d, *J* = 3.6 Hz, 1H), 5.29 (d, *J* = 4.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.6, 159.8, 147.8, 144.8, 136.9, 129.6, 122.5, 121.4, 119.5, 113.5, 112.5, 74.9, 55.3.



4.23 Using representative procedure A outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.36 mL, 3.8 mmol, 1.1 equiv) (4-fluorophenyl)magnesium bromide) (0.27 M in THF, 15 ml, 4.0 mmol, 1.2 equiv), and THF (20 mL). The product was purified by column flash chromatography (20–40% EtOAc/hexanes) to afford the title compound as a yellow oil. (0.60 g, 3.0 mmol, 78%). Analytical data is consistent with literature values.[19] **TLC R_f** = 0.2 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.7 Hz, 1H), 7.62 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.36–7.30 (m, 2H), 7.23–7.17 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.05–6.97 (m, 2H), 5.73 (s, 1H), 5.31 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.4, 161.5, 160.6, 147.9, 139.1 (d, J_{CF} = 2.77 Hz), 137.0, 128.9 (d, J_{CF} = 8.3 Hz), 122.6 (d, J_{CF} = 161.8 Hz), 115.6 (d, J_{CF} = 21.5 Hz), 74.31.



4.24 Using representative procedure A outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv) (3-(trifluoromethyl)phenyl)magnesium bromide (0.50 M in THF, 20 ml, 10 mmol, 1.2 equiv), and

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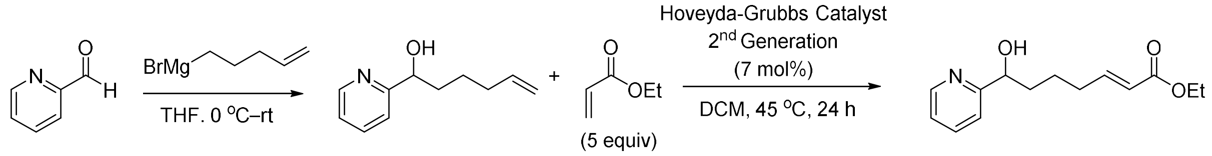
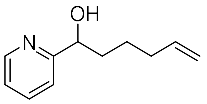
[19] Kamitani, M.; Ito, M.; Itazaki, M.; Nakazawa, H. *Chem.Commun.* **2014**, *50*, 7941.

THF (20 mL). The product was purified by column flash chromatography (20–40% EtOAc/hexanes) to afford the title compound as a yellow oil (0.60 g, 3.0 mmol, 78%). Analytical data is consistent with literature values.[20] **TLC R$_f$** = 0.2 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.0 Hz, 1H), 7.69–7.62 (m, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.25–7.20 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 5.80 (s, 1H), 5.44 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.9, 148.0, 144.2, 137.1, 130.8 (q *J* = 32.4 Hz), 130.4, 129.0, 124.8, 124.7 (q, *J* = 4.16 Hz), 123.8 (q, *J* = 3.70 Hz), 122.8, 121.2, 74.4.

Synthesis of Substrate for Scheme 4.2





4.25 Using representative procedure A outlined above, the following amounts of reagents were used: 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol, 1.0 equiv), pent-4-en-1-ylmagnesium bromide (1.1 M in THF, 10 mL, 11 mmol, 1.1 equiv), and THF (15 mL). The product was purified by column flash chromatography (20–40% EtOAc/hexanes) to afford the title compound as a yellow oil (0.784 g, 4.40 mmol, 44%). **TLC R$_f$** = 0.4 (40% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.5 Hz, 1H), 7.68 (td, *J* = 7.6, 1.5 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.19 (dd, *J* = 6.9, 5.1 Hz, 1H), 5.79 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 4.99 (dd, *J* = 17.1, 1.6 Hz, 1H), 4.94 (d, *J* = 10.3 Hz, 1H), 4.80–4.78 (m, 1H), 4.25 (s, 1H), 2.16–2.02 (m, 2H), 1.89–1.78

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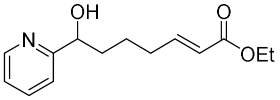
[20] Agai, B.; Proszenyak, A.; Tarkanyi, G.; Vida, L.; Faigl, F. *Eur. J. Org. Chem.* **2004**, 3623.

(m, 1H), 1.74–1.62 (m, 1H), 1.58–1.47 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.3, 148.3, 138.8, 136.8, 122.4, 120.4, 114.7, 72.7, 38.1, 33.8, 24.6; **IR** (neat) 3260, 2936, 1594 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{11}H_{15}ONNa$ $(M + Na)^+$ 200.1051, found 200.1056.



4.14 The title compound was prepared according to a modified procedure reported by Grubbs.[21] In a glovebox, a flame-dried bomb flask was charged with a stir bar, **SI-10** (0.71 g, 4.0 mmol, 1.0 equiv), and Hoveyda-Grubbs Catalyst 2nd Generation (178 mg, 0.280 mmol, 0.0700 equiv). The flask was removed from the glovebox, and anhydrous CH_2Cl_2 (50 mL) and ethyl acrylate (2.2 mL, 20 mmol, 5.0 equiv) were added. The flask was sealed and heated to reflux over 24 h. The flask was then cooled to ambient temperature, and the solvent was removed in vacuo. The residue was purified by flash column chromatography to afford the title compound as a pale yellow oil (125 mg, 0.501 mmol, 13%, 13:1 E:Z). **TLC R_f** = 0.1 (40% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.4 Hz, 1H), 7.68 (td, *J* = 7.6, 1.5 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.20 (dd, *J* = 6.9, 5. Hz, 1H), 6.93 (dt, *J* = 15.5, 7.1 Hz, 1H), 5.80 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.75 (dd, *J* = 7.2, 4.3 Hz, 1H), 4.33 (br s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.28–2.18 (m, 2H), 1.90–1.81 (m, 1H), 1.75–1.66 (m, 1H), 1.64–1.55 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 162.0, 148.9, 148.3, 136.8, 122.4, 121.7, 120.4, 72.5, 60.2, 38.0, 32.1, 23.7, 14.3; **IR** (neat) 2938, 1730 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{14}H_{19}NO_3Na$ $(M + Na)^+$ 272.1263, found 272.1271.

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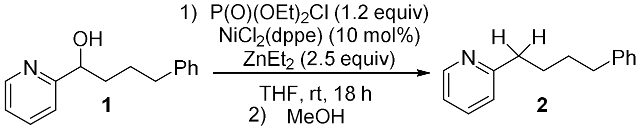
[21] Chatterjee, A. K; Choi, T–L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360.

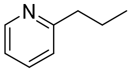
NICKEL CATALYZED FORMATION OF ALKYL ZINC REAGENTS AND DEOXYGENATION OF BENZYLIC CARBINOLS

Synthesis of Products for table 4.2

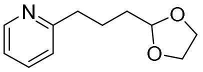
General Procedure A. *Deoxygenation of benzylic carbinols*



In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with $NiCl_2$(dppe) (11 mg, 0.020 mmol, 0.10 equiv), alcohol **1** (45 mg, 0.20 mmol, 1.0 equiv) and diethyl chlorophosphate (35 µl, 0.24 mmol, 1.2 equiv) and suspended in THF (1.6 mL). The reaction vial was capped with a screw-cap, fitted with a septum and removed from the glove box. The reaction was placed under N_2, and stirred at which point diethyl zinc (1 M in PhMe, 0.5 mL, 0.5 mmol, 2.5 equiv) was added at room temperature resulting in an immediate color change from slightly orange to transparent yellow. The reaction was then sealed with parafilm and allowed to stir for 18 hours at 24 °C after which the reaction typically is dark brown or black. The reaction was quenched with MeOH and filtered through a plug of silica gel (100% EtOAc). The solvent was removed under reduced vacuum and the crude purified by flash column chromatography (12% EtOAc, 1% triethyl amine in hexanes) to afford the title compound as a pale yellow oil (29 mg, 0.13 mmol, 69%). **TLC R_f** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.56 (td, *J* = 2.0, 7.7 Hz, 1H), 7.29–7.23 (m, 2H), 7.19–7.14 (m, 3H), 7.13–7.06 (m, 2H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.83–1.74 (m, 2H) 1.74–1.64 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.2, 149.3, 142.6, 136.3, 128.5, 128.3, 125.7, 122.7, 120.9, 38.3, 35.8, 31.3, 29.6; **IR** (neat) 3025, 2926, 2855, 2359, 2341, 1598 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for $C_{16}H_{18}ONH_4$ $(M + NH_4)^+$ 211.1361, found 211.1351.



4.8 Using representative procedure B outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 0.10 equiv), alcohol **SI-1** (28 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 □l, 0.24 mmol, 1.2 equiv), THF (1.6 mL) and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (16 mg, 0.13 mmol, 67%). Analytical data is consistent with literature values.[ii] **TLC R_f** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 6.5 Hz, 1H), 2.77 (t, *J* = 7.8 Hz, 2H), 1.76 (sex, *J* = 7.7 Hz, 2H), 0.97 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4, 149.3, 136.3, 122.9, 121.0, 40.5, 23.2, 14.0.



4.9 Using representative procedure B outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 0.10 equiv), alcohol **3** (42 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μl, 0.24 mmol, 1.2 equiv), THF (1.6 mL) and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (12% EtOAc/hexanes) to afford the title compound as a pale yellow oil (31 mg, 0.15 mmol, 74 %). Analytical data are consistent with literature values.[22] **TLC R_f** = 0.1 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.9 Hz, 1H), 7.57 (td, *J* = 7.6, 1.6 Hz, 1H),

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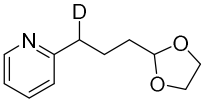
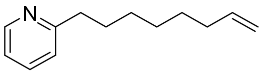
[22] Kitbunnadaj, R.; Zuiderveld, O.P.; Christophe, B.; Hulscher, S.; Menge, W.M.P.B.; Gelens, E.; Snip, E.; Bakker, R.A.; Celanire, S.; Gillard, M.; Talaga, P.; Timmerman, H.; Leurs, R. *J. Med. Chem.* **2004**, *47*, 2414.

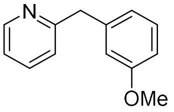
7.14 (d, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.6, 5.3 Hz, 1H), 4.89 (t, *J* = 6 Hz, 1H), 4.00–3.79 (m, 4H), 2.84 (t, *J* = 7.7 Hz, 2H), 1.92–1.82 (m, 2H), 1.76–1.68 (m, 2H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 161.8, 149.3, 136.3, 122.8, 121.1, 104.5, 64.9, 38.1, 33.4, 24.2.



4.4 Using representative procedure B outlined above, the following amounts of reagents were used: NiCl$_2$(dppe) (11 mg, 0.020 mmol, 0.10 equiv), alcohol **3** (42 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 µl, 0.24 mmol, 1.2 equiv), THF (1.6 mL) and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The reaction was quenched with CD$_3$OD from a sealed ampoule (1 mL) and the product was purified by flash column chromatography (12 % EtOAc, 1% triethyl amine, in hexane) to afford the title compound as a pale yellow oil (30 mg, 0.15 mmol, 78%). **TLC R$_f$** = 0.1 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.52 (d, *J* = 4.6 Hz, 1H), 7.58 (td, *J* = 7.7, 1.9 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.11–7.08 (m, 1H), 4.89 (t, *J* = 4.7 Hz, 1H), 4.01–3.79 (m, 4H), 2.87–2.79 (m, 1H), 1.91–183 (m, 2H), 1.76–1.68 (m, 2H); **^{2}H NMR** (500 MHz, CHCl$_3$) 3.10 (s, 1D) **^{13}C NMR** (125 MHz, CDCl$_3$) δ 161.8, 149.3, 136.3, 122.8, 121.1, 104.5, 64.9, 38.1, 33.4, 24.2; **IR** (neat) 2922, 2874, 1591, 1567, 1473, 1410 cm^{-1}; **HRMS** (TOF MS CI+) *m* / *z* calcd for C$_{16}$H$_{18}$ONH$_4$ (M + NH$_4$)$^+$ 195.1244, found 195.1251.



4.6 Using representative procedure B outlined above, the following amounts of reagents were used: NiCl$_2$(dppe) (11 mg, 0.020 mmol, 0.10 equiv), alcohol **SI-3** (41 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 µl, 0.24 mmol, 1.2 equiv), THF (1.6 mL) and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (15% EtOAc/hexanes) to afford the title compound as a pale yellow oil (29 mg, 0.15 mmol, 77%). **TLC R$_f$** = 0.2 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.52 (d, *J* = 4.5 Hz, 1H), 7.58 (td, *J* = 7.6, 1.5 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 7.3, 5.5 Hz, 1H), 5.80 (ddt, *J* = 17.1, 10.4, 3.3 Hz, 1H), 4.98 (dd, *J* = 17.1, 1.1 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.03 (dd, *J* = 13.5, 6.5 Hz, 2H), 1.72 (quint, *J* = 7.6 Hz, 2H), 1.44–1.30 (m, 6H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 162.2, 149.3, 139.3, 136.3, 122.8, 121.0, 114.3, 38.6, 33.9, 30.0, 29.6, 29.1, 28.9; **IR** (neat) 3075, 2925, 1589 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{13}H_{19}NNa$ (M + Na)$^+$ 212.1415, found 212.1406.



4.13 Using representative procedure B outlined above, the following amounts of reagents were used: NiCl$_2$(dppe) (11 mg, 0.020 mmol, 0.10 equiv), alcohol **SI-7** (43 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 μl, 0.24 mmol, 1.2 equiv), THF (1.6 mL) and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (20 % EtOAc, 10% DCM, in hexanes) to afford the title compound as a pale yellow oil (21.5 mg, 0.120 mmol, 54%). Analytical data are consistent with literature values.[23] **TLC R$_f$** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.54 (d, *J* = 4.3 Hz, 1H), 7.57 (td, *J* = 7.6, 1.7, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.12 (s, 1H), 7.10 (t, *J* = 3.2 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.81 (s, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.13 (s, 2H), 3.77 (s, 3H),

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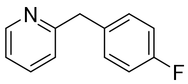
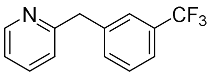
[23] Chen, X.; Zhou, L.; Li, Y.; Xie, T.; Zhou, S. *J. Org. Chem.* **2014**, *79*, 230.

^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 159.8, 149.4, 141.1, 136.6, 129.6, 123.2, 121.5, 121.3, 114.9, 111.9, 55.2, 44.8.



4.7 Using representative procedure B outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 0.10 equiv), alcohol **SI-8** (43 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 µl, 0.24 mmol, 1.2 equiv), THF (1.6 mL) and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The crude product was pre-absorbed to a minimal amount of silica and purified by flash column chromatography (12 % EtOAc, 1% triethyl amine, in hexane) to afford the title compound as a pale yellow oil (20.3 mg, 0.120 mmol, 60%). Analytical data are consistent with literature values.[24] **TLC R_f** = 0.3 (20% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (ddd, J = 4.9, 1.9, 1.0 Hz, 1H), 7.58 (td, J = 7.6, 1.9 Hz, 1H), 7.24–7.19 (m, 2H), 7.14–7.07 (m, 2H), 7.01–6.95 (m, 2H), 4.12 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.5 (d, J_{CF} = 244.14 Hz), 160.6, 149.4, 136.6, 135.1 (d, J_{CF} = 3.24 Hz), 130.5 (d, J_{CF} = 7.87 Hz), 123.0, 121.3, 115.3 (d, J_{CF} = 21.2 Hz), 43.8.



4.10 Using representative procedure B outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 0.10 equiv), alcohol **SI-9** (51 mg, 0.20 mmol, 1.0 equiv),

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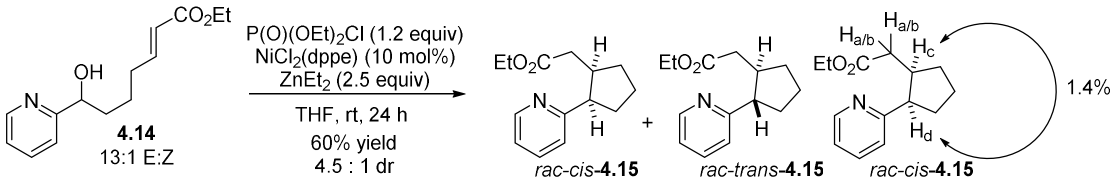
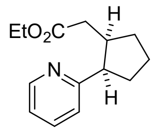
[24] De Houwer, J.; Tehrani, K. A.; Maes, B. U. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 2745.

diethyl chlorophosphate (35 µl, 0.24 mmol, 1.2 equiv), THF (1.6 ML) and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (30–50% EtOAc/hexanes) to afford the title compound as a pale yellow oil (29.4 mg, 0.124 mmol, 62%). Analytical data are consistent with literature values[10] **TLC R_f** = 0.2 (10% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.9 Hz, 1H), 7.61 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.53 (s, 1H), 7.50–7.38 (m, 3H), 7.17–7.09 (m, 2H), 4.21 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.8, 149.6, 140.4, 136.8, 132.5, 128.9, 125.8, 125.7, 123.4, 123.3, 123.2, 121.6, 44.3.

<u>Intramolecular 1,4-addition (Scheme 4.2)</u>



4.15 Using representative procedure B outlined above, the following amounts of reagents were used: $NiCl_2$(dppe) (11 mg, 0.020 mmol, 0.10 equiv), alcohol **16** (50 mg, 0.20 mmol, 1.0 equiv), diethyl chlorophosphate (35 µl, 0.24 mmol, 1.2 equiv), THF (1.6 mL) and diethyl zinc (1.0 M in PhMe, 0.50 mL, 0.50 mmol, 2.5 equiv). The product was purified by flash column chromatography (20% EtOAc/hexanes) to afford the title compound as a mixture 2.5:1 mixture of diastereomers (37 mg, 0.16 mmol, 80%). H_c was integrated to determine the ratio of diastereomers. Flash column chromatography (5–10% EtOAc/hexanes) was performed a second time to isolate analytically pure cis diastereomer (19 mg, 0.081 mmol, 40%) and a 1:1 mixture of diastereomers (16 mg, 0.07 mmol, 34%). The cis diastereomer was assigned based on the nOe correlation shown.



TLC R_f = 0.1 (10% EtOAc/hexanes, UV active); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.7 Hz, 1H), 7.56 (td, *J* = 7.7, 2.0 Hz, 1H), 7.12–7.07 (m, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.43 (q, *J* = 8.0 Hz, 1H), 2.79–2.71 (m, 1H), 2.14–2.04 (m, 2H), 2.02–1.90 (m, 4H), 1.75–1.67 (m, 1H), 1.63–1.54 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.6, 163.2, 149.2, 136.0, 123.5, 121.2, 60.2, 49.8, 40.8, 36.2, 31.9, 30.2, 24.2, 14.3; **IR** (neat) 2935, 1716 cm^{-1}; **HRMS** (TOF MS ES+) *m* / *z* calcd for $C_{14}H_{19}NO_2Na$ $(M + Na)^+$ 256.1313, found 256.1316.

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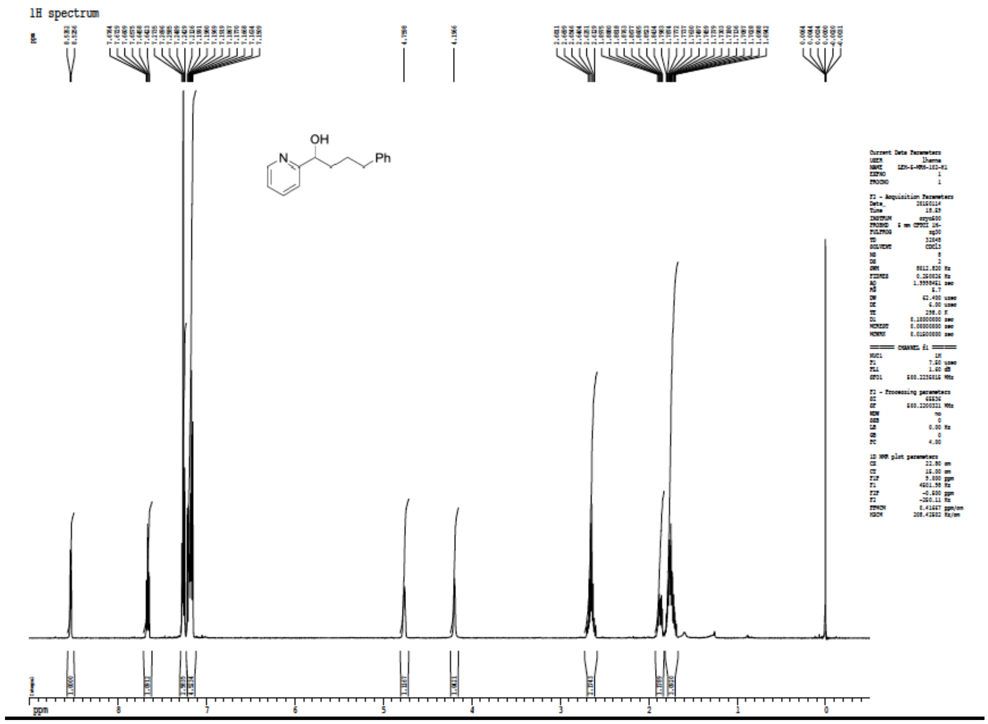
[i] Cao, B.; Wang, Y.; Ding, K.; Neamati, N.; Long, Y-Q. *Org. Biomol. Chem.* **2012**, *10*, 1239.

[ii] Groenhagen, U.; Maczka, M.; Dickschat, J. S.; Schulz, S. *Beilstein J. Org. Chem.* **2014**, *10*, 1421.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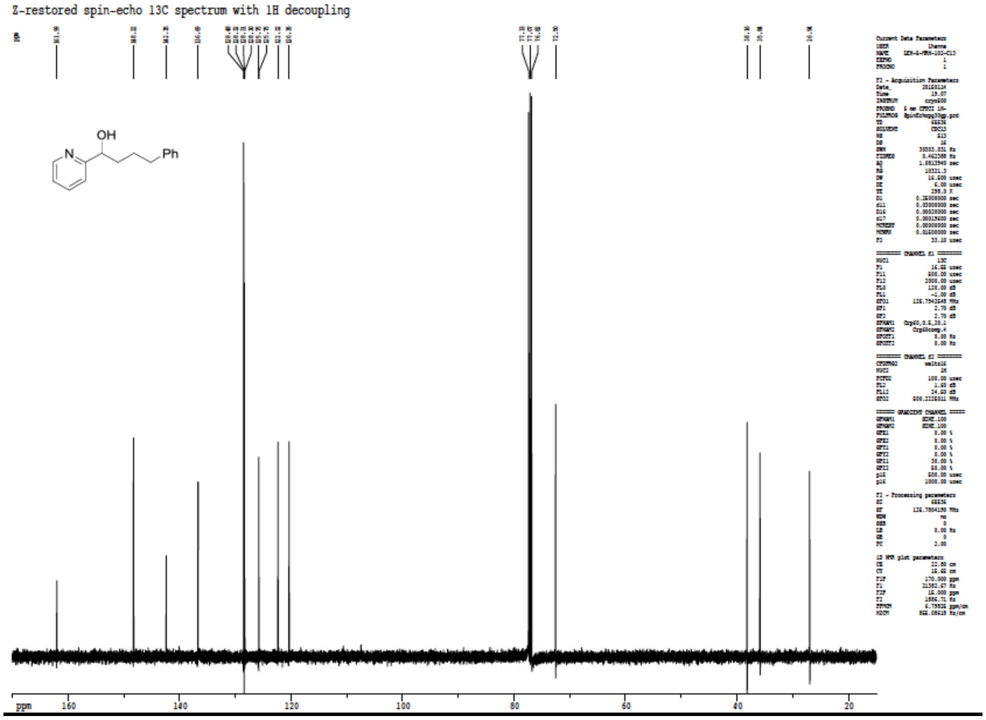
Z-restored spin-echo 13C spectrum with 1H decoupling
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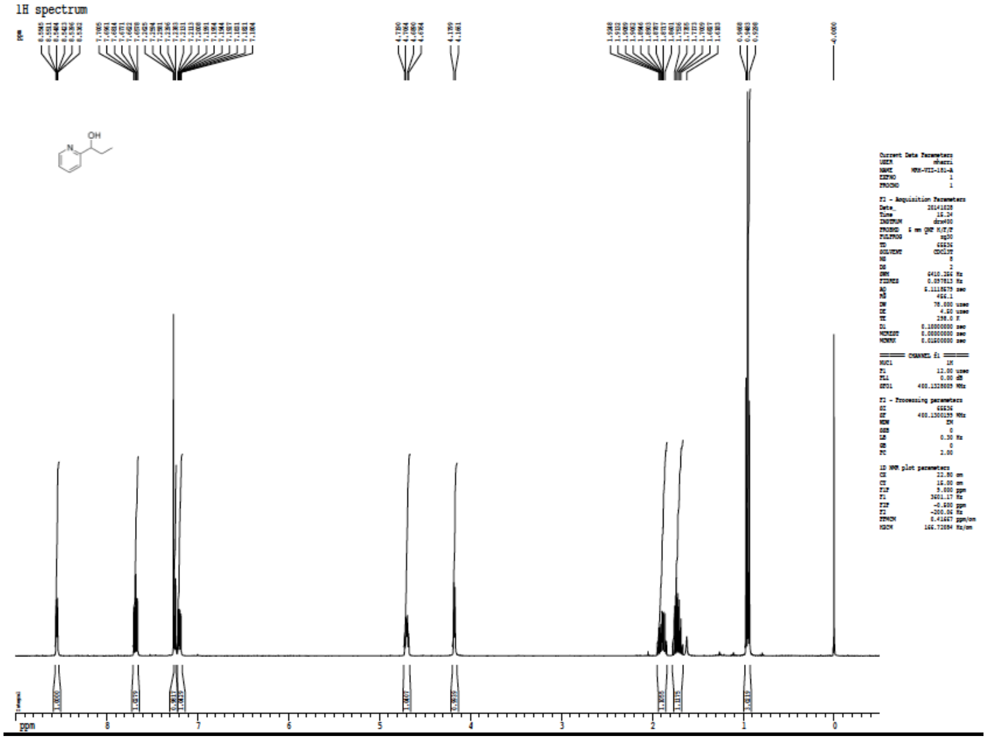
20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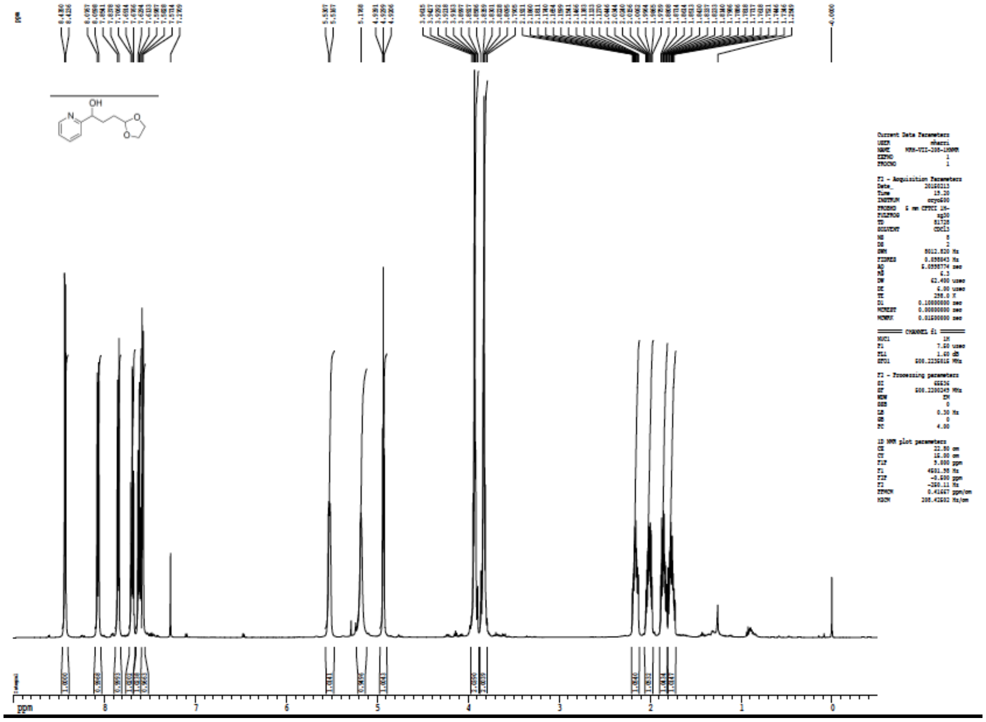
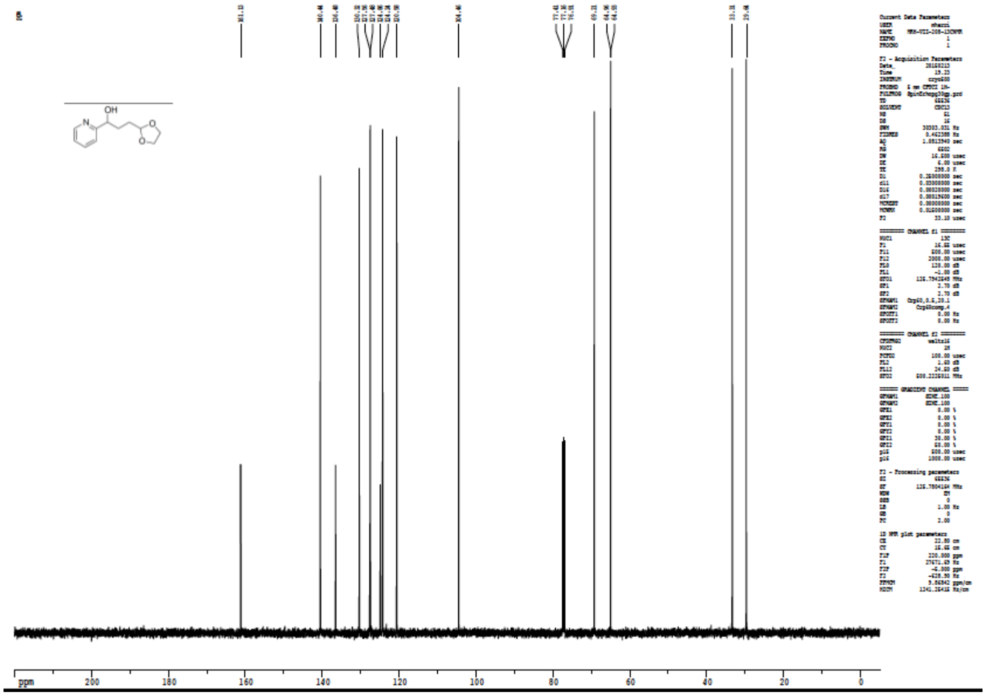
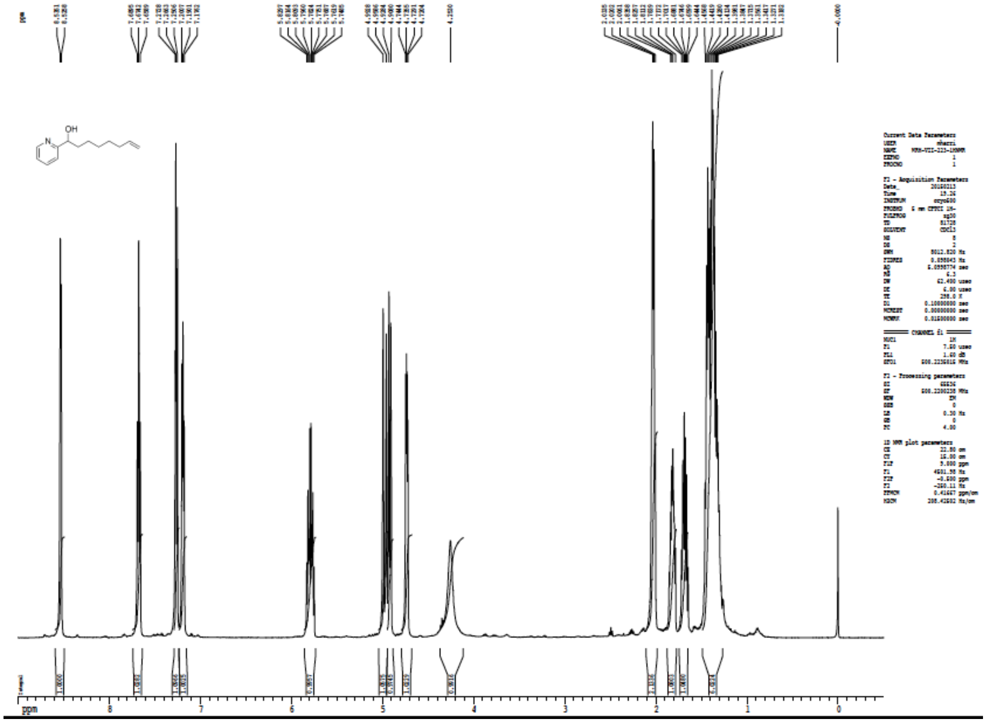
1H spectrum



Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



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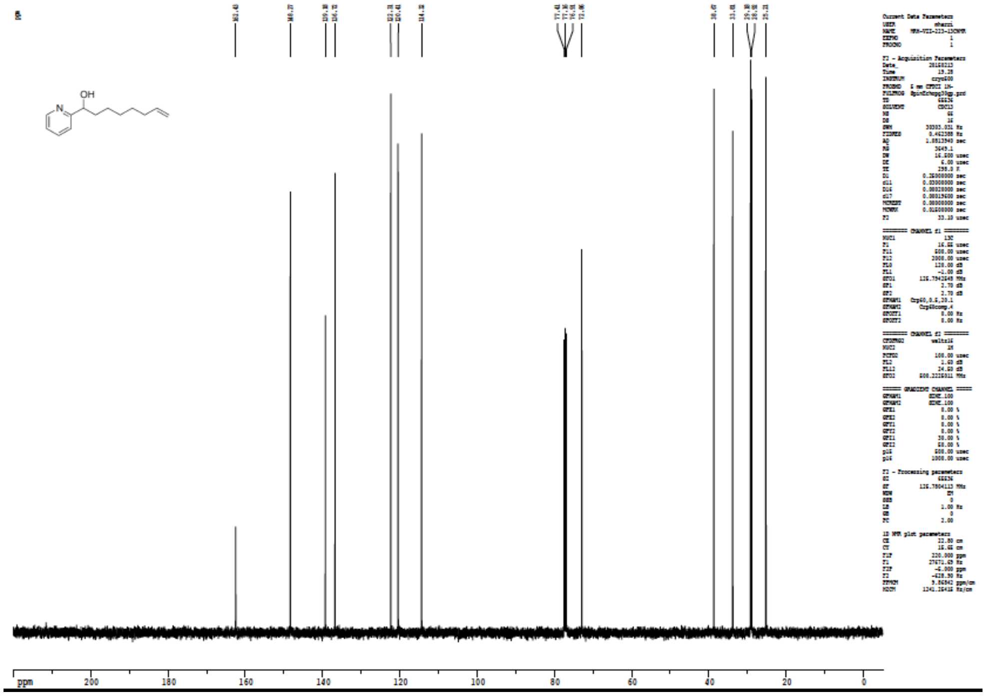
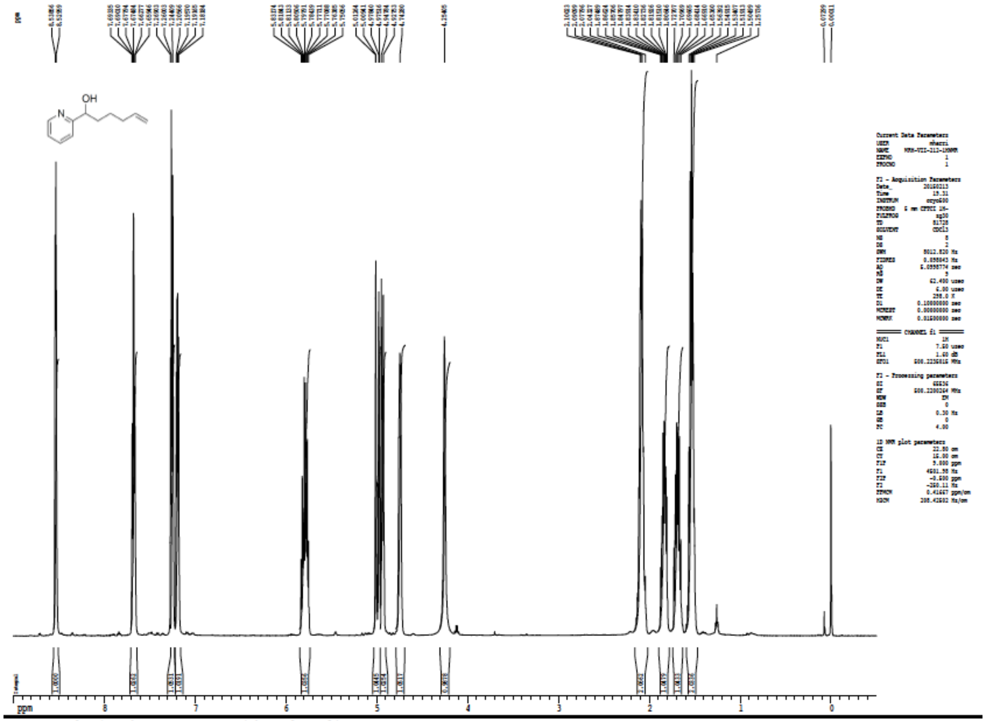


1H spectrum



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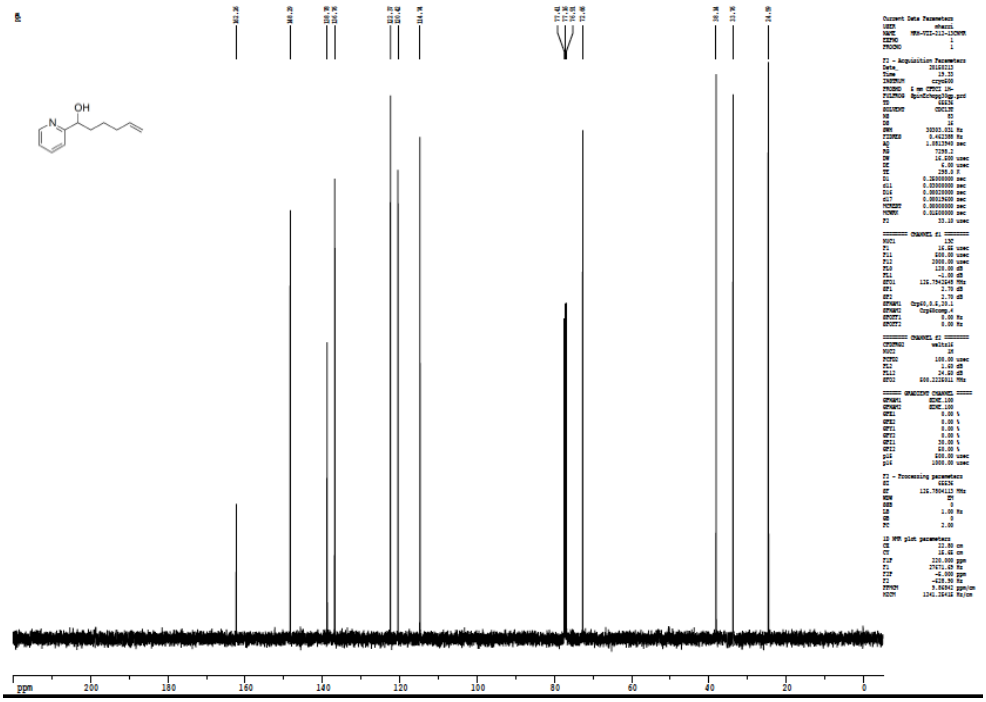
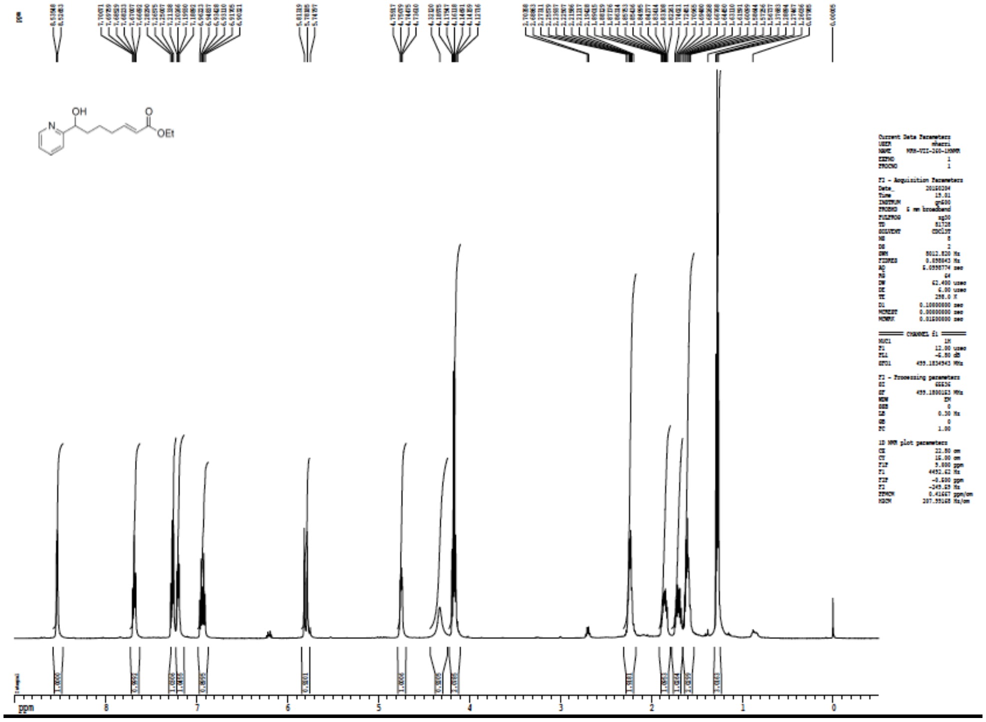
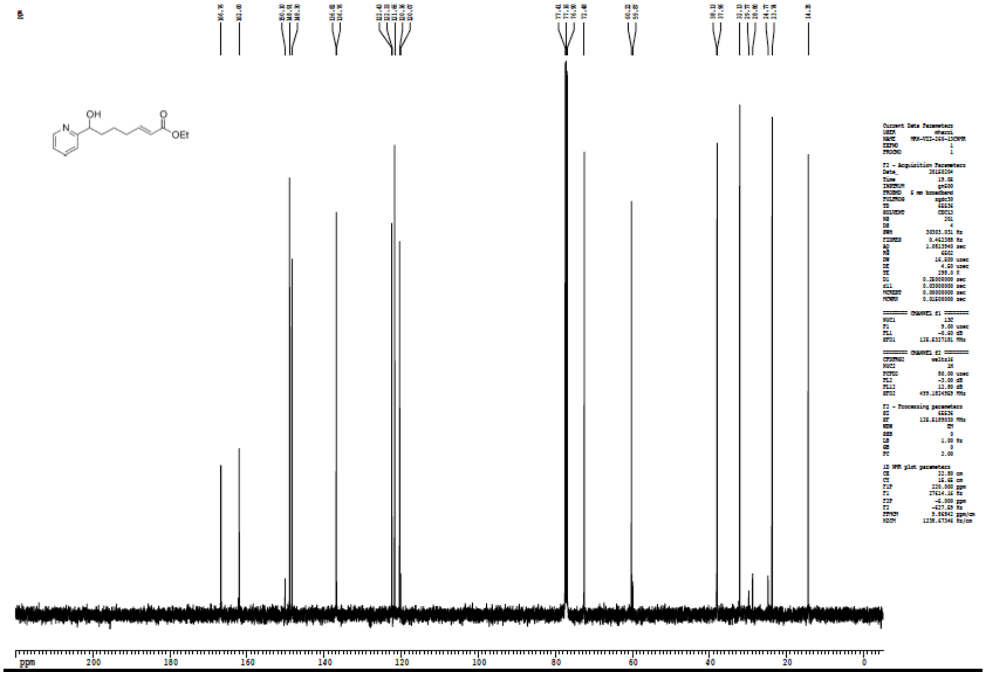


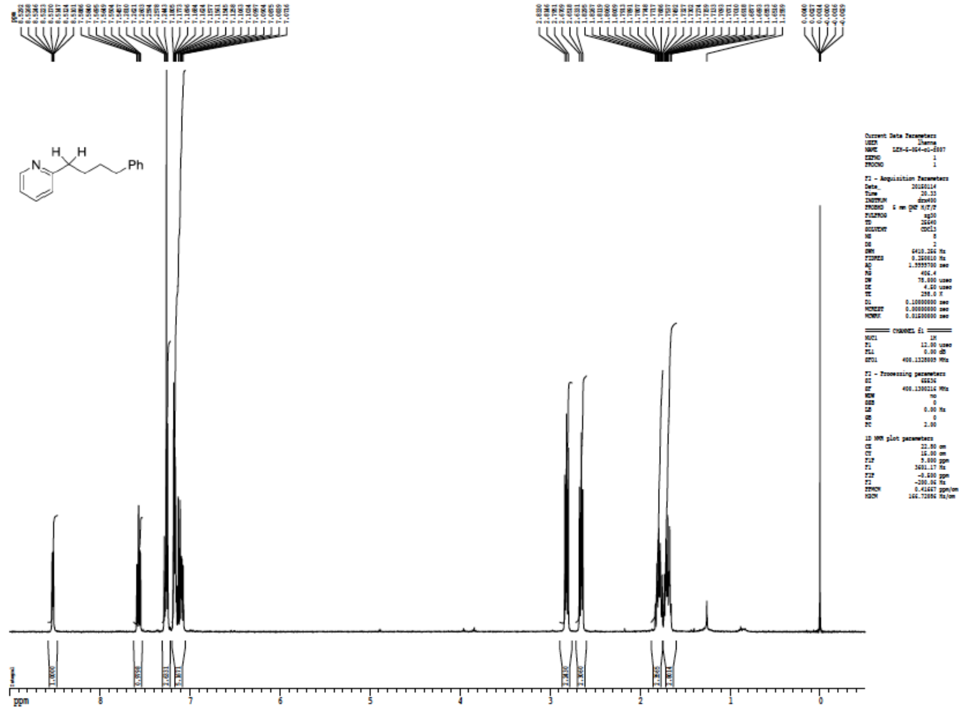
1H spectrum



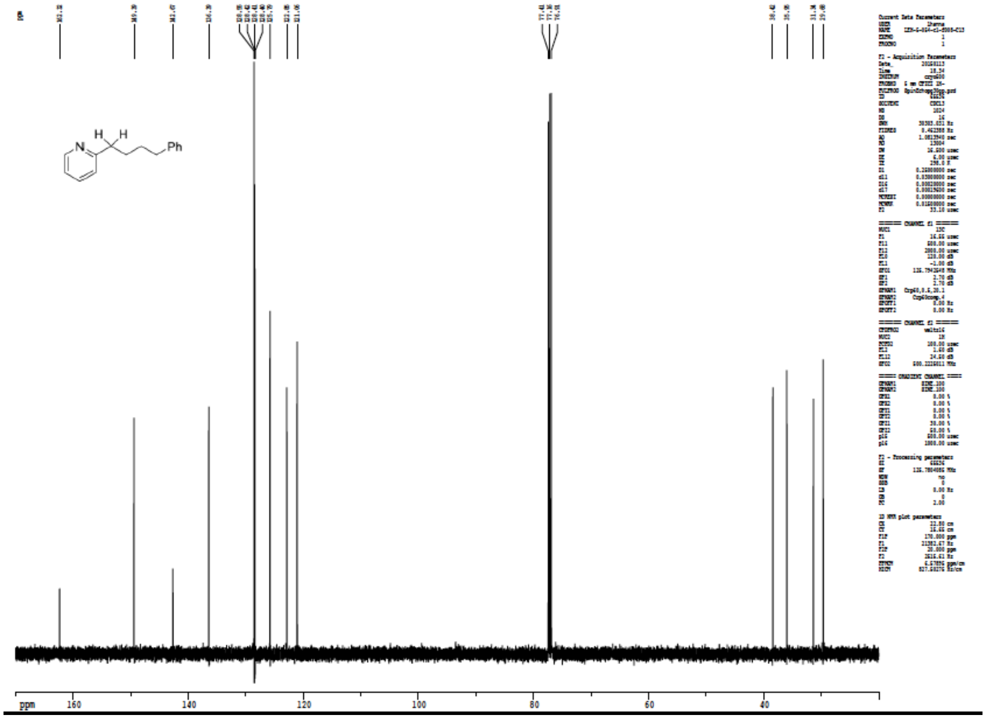
13C spectrum with 1H decoupling



1H spectrum



Z-restored spin-echo 13C spectrum with 1H decoupling



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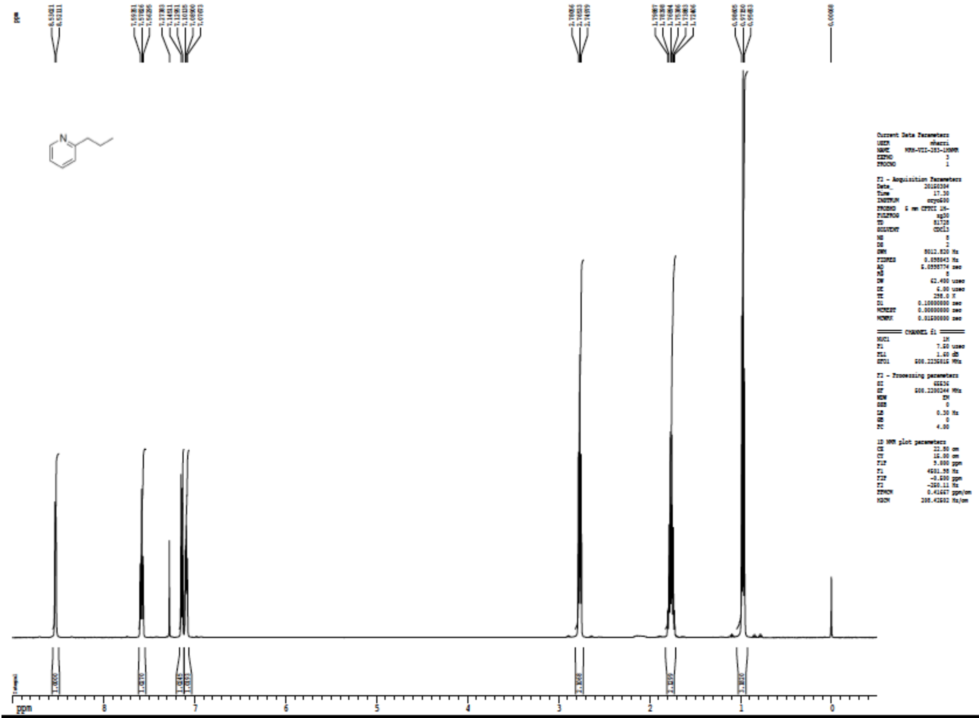
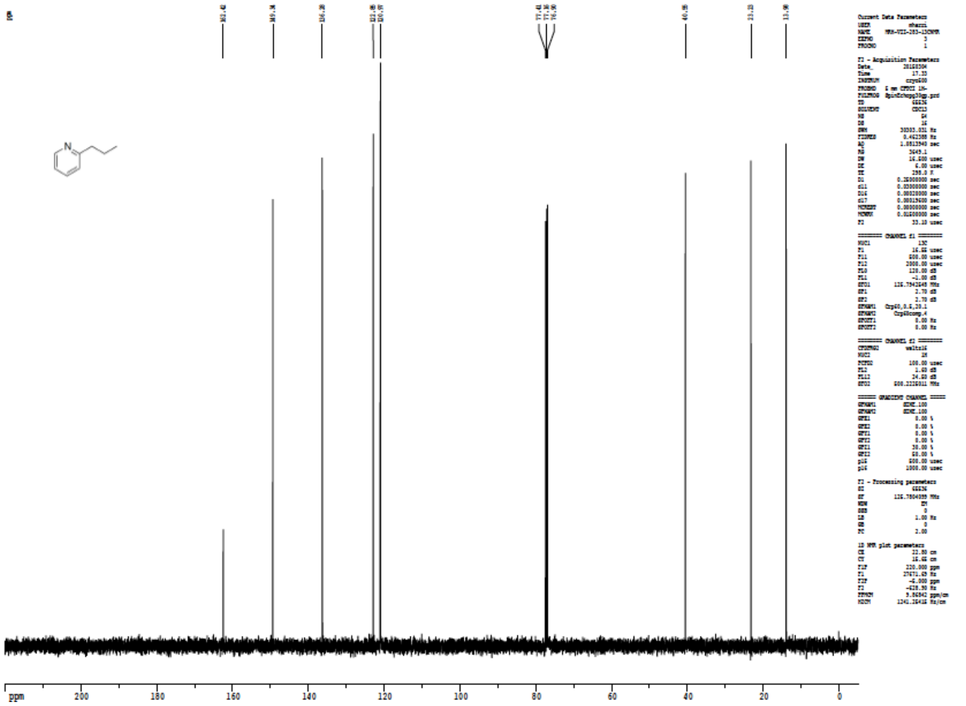
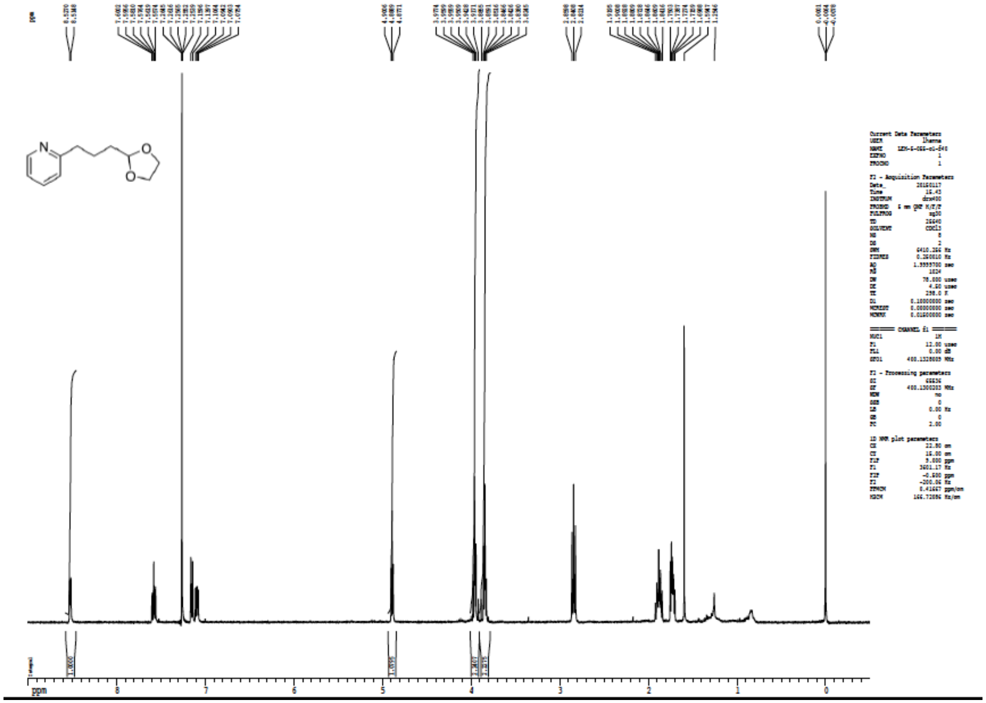


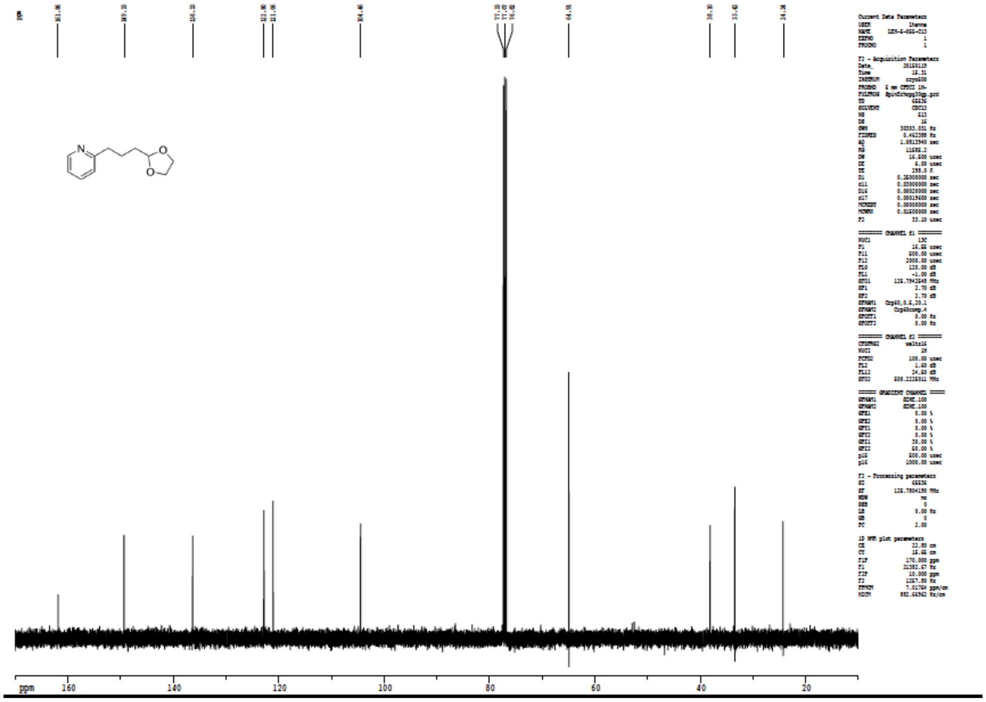
Z-restored spin-echo 13C spectrum with 1H decoupling



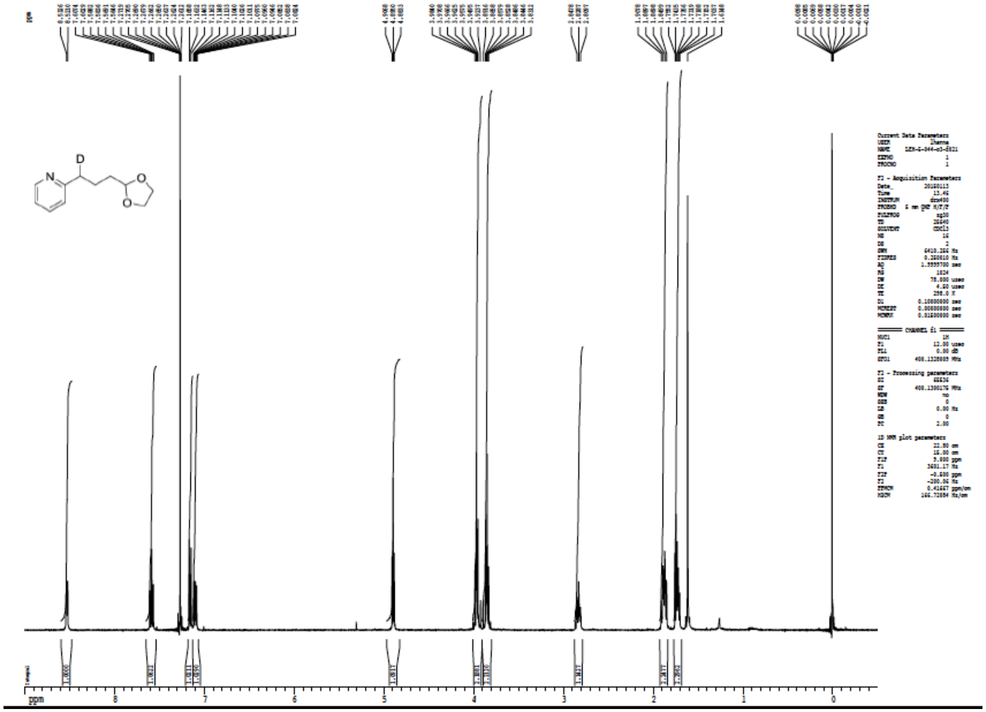
1H spectrum



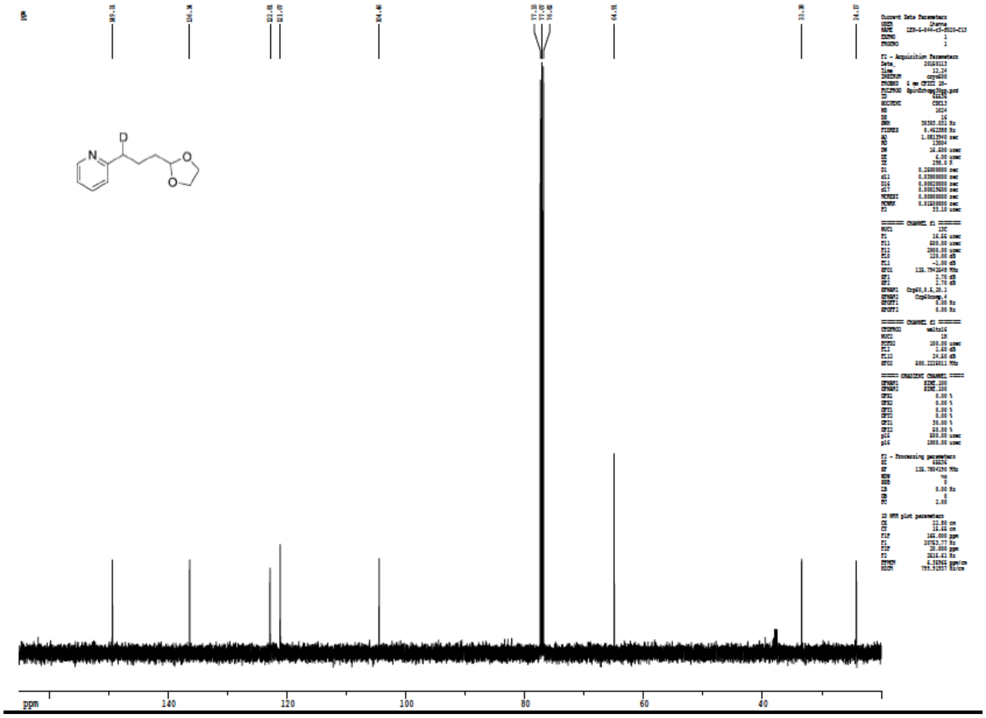
Z-restored spin-echo 13C spectrum with 1H decoupling



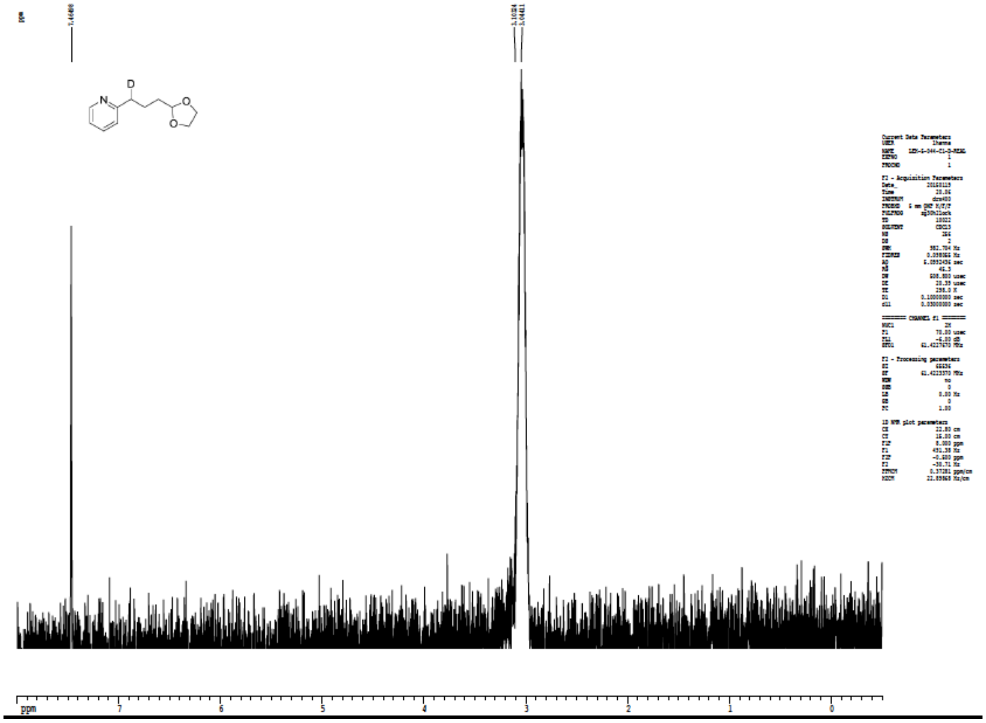
1H spectrum



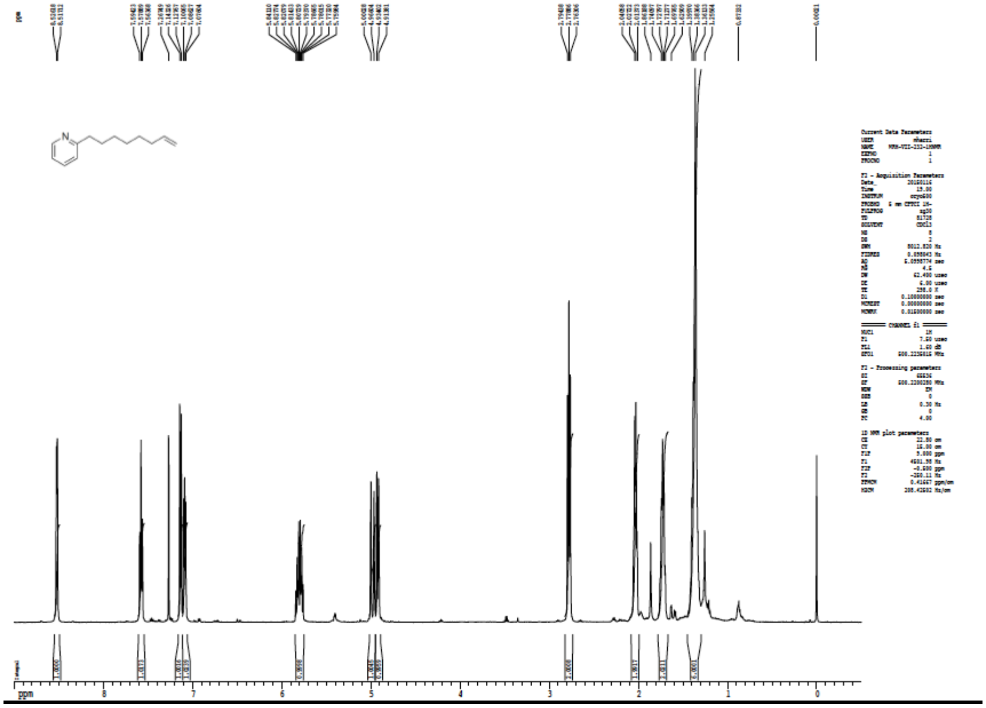
Z-restored spin-echo 13C spectrum with 1H decoupling



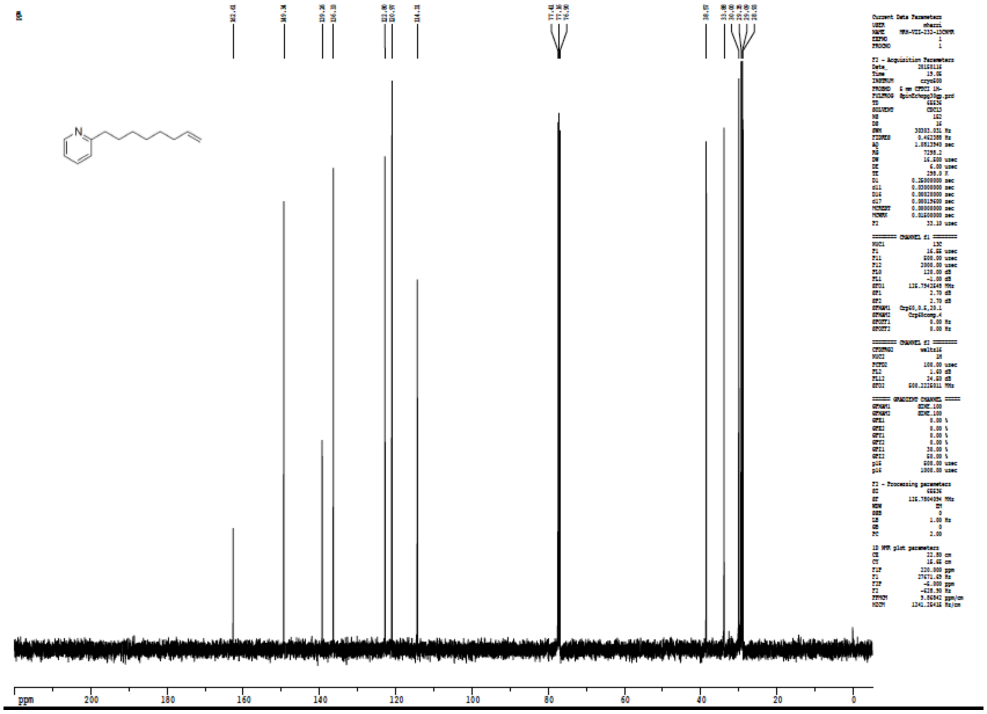
2H spectrum (measure via lock channel without changing any cables)

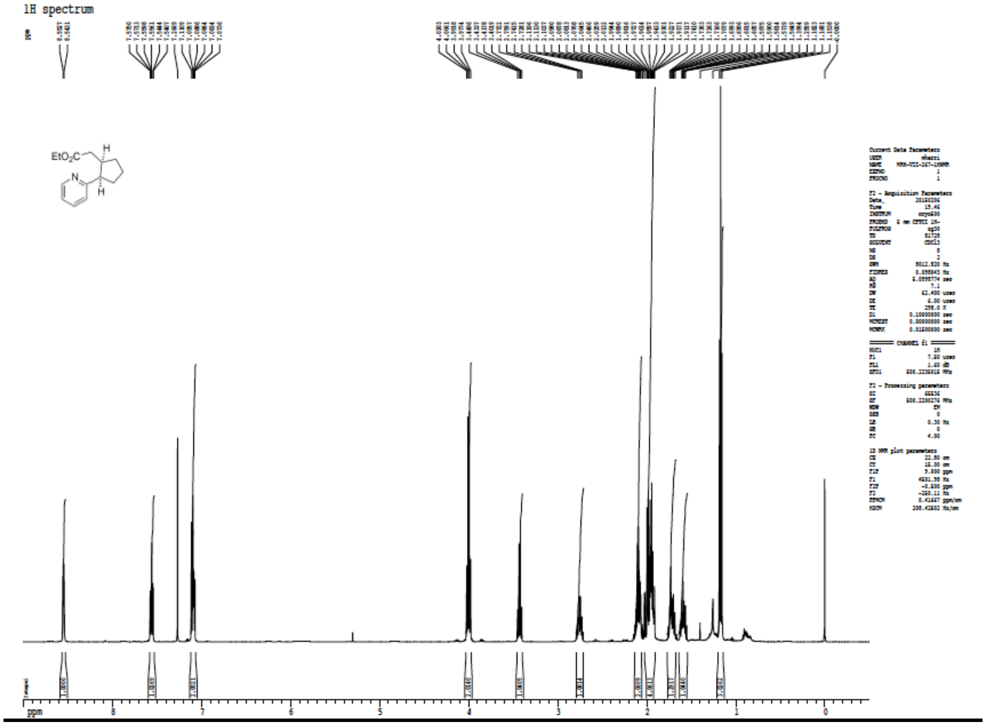


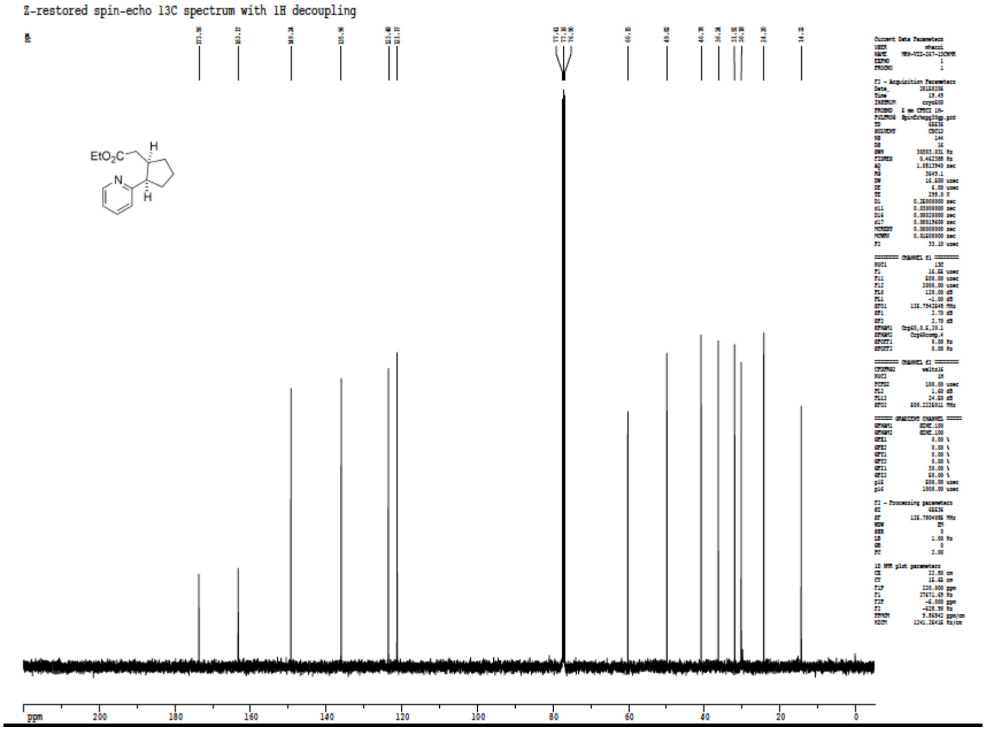
1H spectrum

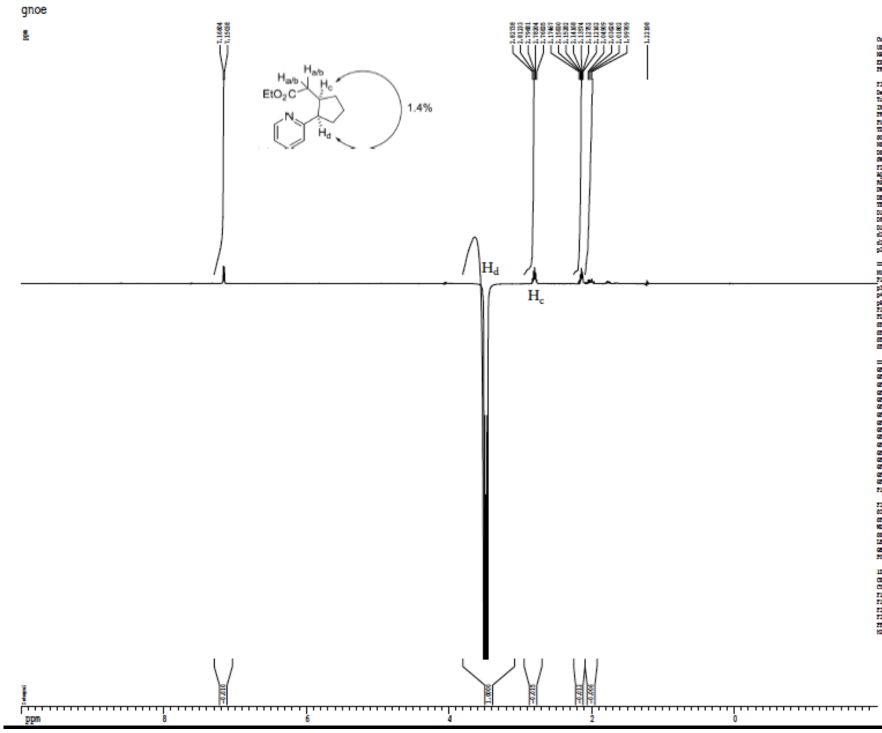


Z-restored spin-echo 13C spectrum with 1H decoupling




1H spectrum
EtO2C
H
N
H
ppm
8
7
6
5
4
3
2
1
0


Z-restored spin-echo 13C spectrum with 1H decoupling
EtO2C
H
N
H
ppm
200
180
160
140
120
100
80
60
40
20
0



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Current Data Parameters
USER              mherzi
NAME      MRH-VII-267-NOE
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160206
Time                19.58
INSTRUM           cryo600
PROBHD   5 mm CPTCI 1H-
PULPROG        gnoeloo.wu
TD                  65536
SOLVENT             CDCl3T
NS                    160
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   80.6
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.60000000 sec
D16            0.00020000 sec
d21            0.33376600 sec
d22            0.16359659 sec
p2                  16.00 usec

====== CHANNEL f1 ======
NUC1                   1H
P1                   7.60 usec
p3                  22.60 usec
p4                  30.00 usec
p6                  20.00 usec
P12              40000.00 usec
PL1                  1.60 dB
SFO1          600.2217416 MHz
SP1                 61.60 dB
SPNAM1          gauss1.512
SPOFF1               0.00 Hz

==== GRADIENT CHANNEL ===
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            600.2200000 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  60.00 cm
F1P                10.000 ppm
F1                6002.20 Hz
F2P                -2.000 ppm
F2               -1000.44 Hz
PPMCM             0.52632 ppm/cm
HZCM            263.27368 Hz/cm
```