Title

Targeted Rapid Synthesis of Redox-Active Dodecaborane Clusters

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Publication Date

2015

UNIVERSITY OF CALIFORNIA

Los Angeles

Targeted Rapid Synthesis of Redox-Active Dodecaborane Clusters

A thesis submitted in partial satisfaction

of the requirements for the degree Master of Science

in Chemistry

by

Alex Ian Wixtrom

2016

ABSTRACT OF THE THESIS

Targeted Rapid Synthesis of Redox-Active Dodecaborane Clusters

by

Alex Ian Wixtrom

Master of Science in Chemistry
University of California, Los Angeles, 2016
Professor Alexander Michael Spokoyny, Chair

We have developed a fast, efficient route to obtain targeted perfunctionalized ether-linked alkyl and benzyl derivatives of the *closo*-$[B_{12}(OH)_{12}]^{2-}$ icosahedral dodecaborate cluster via microwave-assisted synthesis. These icosahedral boron clusters exhibit unique properties including three-dimensional delocalization of the cage-bonding electrons, tunable photophysical properties, and a high degree of stability in air in both solid and solution states. Several $B_{12}(OR)_{12}$ clusters have been prepared with reaction times ranging from hours to several minutes using microwave-assisted synthesis. This represents a significant improvement upon previously reported protocols due to a dramatic reduction in required reaction times and the elimination of the need for inert atmosphere conditions. The robust nature of the new microwave-based method has been further demonstrated through the targeted synthesis of several new derivatives, which feature desired properties such as redox potentials up to 0.6 V more positive than previously known $B_{12}(OR)_{12}$ cluster compounds or substituents that allow further facile functionalization *via* thiol "click" S_NAr. We further demonstrate the ability to synthesize hybrid, vertex-differentiated cluster species $B_{12}(OR)_{11}(OR')$

via a single-step one-pot reaction that was formerly accessible only via multi-step reaction sequence.

The thesis of Alex Ian Wixtrom is approved.

Richard B. Kaner
Joseph Ambrose Loo
Dante A. Simonetti
Alexander Michael Spokoyny, Committee Chair

University of California, Los Angeles
2016

To my parents, for their encouragement and support,
and for always inspiring me to work hard in pursuit of my goals.

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Acknowledgements

I would like to thank the members of my thesis committee, my colleagues in the Spokoyny lab, and Dr. Alexander Spokoyny for providing an intellectually stimulating research environment. I would like to thank Dr. Liban Saleh for commenting on the manuscript.

Chapter 1: Introduction to Icosahedral Boron Cluster Chemistry

In 1912, the first borane compounds were discovered by Alfred Stock.[1–3] For decades these boron hydride compounds were considered exotic, with little practical value outside of academic curiosity, and their inherent pyrophoric properties made synthesis and characterization difficult. Borane chemistry was revitalized in the 1940's when certain borane compounds (pentaborane B_5H_9 and decaborane $B_{10}H_{14}$) were thought to be superior alternatives to hydrocarbons for rocket fuels.[2,3] This notion was based on the fact that the energy contained in the B-H bond was greater than the C-H bond in traditional hydrocarbon fuels. Research efforts to produce high-energy fuels ultimately failed due to the discovery that borates formed from borane combustion clog jet engines, thus eliminating any potential efficiency gains from the higher energy,[3,4] yet the interest in development of these fuels had successfully sparked the "renaissance era" of boron chemistry. A key discovery that elucidated a more accurate understanding of borane chemistry was Lipscomb's concept of three-center two-electron bonding.[5] In his 1954 study, Lipscomb predicted the existence of an icosahedral boron hydride $B_{12}H_{12}$, which Longuet-Higgins and Roberts posited would only be stable as a dianion in a theoretical molecular orbital-based approach in 1955.[5,6] In 1959 the possible formation of the predicted $[B_{12}H_{12}]^{2-}$ was observed by Shapiro and Williams[7], and a year later in 1960 the triethylammonium salt of $[B_{12}H_{12}]^{2-}$ was isolated in a relatively low yield by Hawthorne and co-workers.[8]

The "renaissance era" in the field of boron cluster chemistry was led by the pioneering work of Hawthorne, Knoth, and Muetterties over the next few decades.[2,9–22] Their investigations resulted in significantly improved synthetic methods to produce $[B_{12}H_{12}]^{2-}$ on a much larger scale in high yields (>90%)[2] and the discovery that boron clusters can undergo facile functionalization chemistry in a similar fashion to some classical organic molecules such as benzene, unlocking entirely new avenues of functionalized boron cluster development.[3,23,24] As mentioned above, many boron hydride clusters were considered exotic and highly unstable species for many decades, undergoing rapid degradation if exposed to heat, acids, or bases. Even the widespread attempts to produce viable rocket fuels from these boranes was impeded by the unavoidable combustion products negatively impacting the jet engine performance.[3,4] However, now that $[B_{12}H_{12}]^{2-}$ salts had been synthesized in greater yields, full characterization provided evidence of the surprising stability of the icosahedral cluster. $[B_{12}H_{12}]^{2-}$ salts were heated to 95 °C in strongly acidic (3 N HCl) and basic (3 N NaOH) media with little to no observed degradation, and heating the cluster to 810 °C under vacuum also resulted in no observable decomposition.[16]

The remarkable thermal stability exhibited by $[B_{12}H_{12}]^{2-}$ along with exceptional stability in acids and bases and the potential for functionalization of the cluster were very exciting discoveries, inspiring many groups to investigate possible novel boron cluster derivatives. The first persubstitution of the cluster where all 12 vertices of the icosahedron were functionalized was demonstrated by Knoth and co-workers. Knoth and his group were able to persubstitute $[B_{12}H_{12}]^{2-}$ with several halogens, successfully isolating $[B_{12}F_{12}]^{2-}$, $[B_{12}Cl_{12}]^{2-}$, $[B_{12}Br_{12}]^{2-}$ and $[B_{12}I_{12}]^{2-}$ derivatives.[20,25] More recent studies have expanded upon these early persubstitution examples to produce additional derivatives of $[B_{12}H_{12}]^{2-}$ with improved synthetic methods and non-halogen functional groups, including $[B_{12}Me_{12}]^{2-}$ and $[B_{12}(OH)_{12}]^{2-}$.[26–30] The latter of these species, *closo*-$[B_{12}(OH)_{12}]^{2-}$, is a particularly interesting derivative due to the possibility of further functionalization of the cluster *via* formation of ether, ester, carbonate, and carbamate linkages.[29,31–33]

The exceptional stability of the parent dodecaborate cluster $[B_{12}H_{12}]^{2-}$ is one attractive feature of these boron cluster species, but another unique property is the three-dimensional delocalization of two cage-bonding electrons across all of the boron atoms contained within. While Longuet-Higgins and Roberts concluded that the parent $[B_{12}H_{12}]^{2-}$ could only exist as a dianion[6], the successful formation of various derivatives led others to investigate the possibility of oxidizing the cluster to produce radical 1- or neutral clusters. Controlled oxidation of the $[B_{12}H_{12}]^{2-}$ anion lead to irreversible degradation of the cluster due to the formation of a B–B linked dimer,[21] though several of the synthesized perfunctionalized derivatives were observed to undergo reversible redox behavior.[34] Rupich and co-workers reported the single electron oxidation of $[B_{12}X_{12}]^{2-}$ to form a stable radical $[B_{12}X_{12}]^{1-}$,[35] and a recent study by Weber and co-workers confirmed the identity of the oxidized radical $[B_{12}Cl_{12}]^{1-}$ species.[36]

The possible redox state of perfunctionalized clusters were further investigated by Hawthorne and co-workers *via* the characterization of $B_{12}(OCH_2Ph)_{12}$ in three distinct redox states. These three redox states (*closo*-$[B_{12}(OCH_2Ph)_{12}]^{2-}$, *hypocloso*-$[B_{12}(OCH_2Ph)_{12}]^{1-}$, and *hypercloso*-$[B_{12}(OCH_2Ph)_{12}]^{0}$) are accessible via two sequential and quasi-reversible one-electron oxidation reactions of the parent dianionic species.[37] Hawthorne's group later demonstrated the synthesis of several other benzyl and alkyl functionalized $B_{12}(OR)_{12}$ clusters and characterized the redox behavior of these new derivatives, which exhibited similarly reversible behavior.[31] The parent $[B_{12}(OH)_{12}]^{2-}$ cluster these derivatives originated from was also shown to be capable of undergoing a one-electron oxidation by Schleid and co-workers, forming a stable radical $[B_{12}(OH)_{12}]^{1-}$ species.[38] Perhaps the most intriguing feature of these cluster derivatives is that the redox potential of ether-linked $B_{12}(OR)_{12}$ species can be rationally tuned as a function of the O-bound substituent, similar to metal-based redox-active inorganic complexes.[31,34,39] This is a very interesting feature warranting further studies to probe the extent of this tunable nature, yet all reported synthetic routes to produce perfunctionalized $B_{12}(OR)_{12}$ clusters to date require either extremely long reaction times (weeks) or highly specialized high-pressure equipment. All of these synthetic routes also require strict inert atmospheric conditions, further adding to the difficulty of producing new derivatives.[29,31,37] A new method to produce perfunctionalized $B_{12}(OR)_{12}$ clusters under less stringent inert atmosphere conditions in significantly shorter time would allow for much more rapid exploration of novel derivatives, allowing for targeted synthesis of cluster with specific properties for a plethora of applications.

Chapter 2: Rapid Synthesis of Redox-Active Dodecaborane $B_{12}(OR)_{12}$ Clusters Under Ambient Conditions

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We have developed a fast and efficient route to obtain perfunctionalized ether-linked alkyl and benzyl derivatives of the *closo*-$[B_{12}(OH)_{12}]^{2-}$ icosahedral dodecaborate cluster via microwave-assisted synthesis. These icosahedral boron clusters exhibit three-dimensional delocalization of the cage-bonding electrons, tunable photophysical properties, and a high degree of stability in air in both solid and solution states. A series of *closo*-$[B_{12}(OR)_{12}]^{2-}$, *hypocloso*-$[B_{12}(OR)_{12}]^{1-}$ and *hypercloso*-$[B_{12}(OR)_{12}]^{0}$ clusters have been prepared with reaction times ranging from hours to several minutes. This method is superior to previously reported protocols since it dramatically decreases the reaction times required and eliminates the need for inert atmosphere conditions. The generality of the new microwave-based method has been further demonstrated through the synthesis of several new derivatives, which feature redox potentials up to 0.6 V more positive than previously known $B_{12}(OR)_{12}$ cluster compounds. We further show how this method can be applied to a one-pot synthesis of hybrid, vertex-differentiated species $B_{12}(OR)_{11}(OR')$ that was formerly accessible only via multi-step reaction sequence.

Introduction

The existence of an icosahedral dodecaborate [$B_{12}H_{12}$] cluster was first predicted by Lipscomb and co-workers in 1954.[5] In a subsequent theoretical molecular orbital-based approach published in 1955[6], Longuet-Higgins and Roberts predicted that such a cluster would only be stable as dianionic $[B_{12}H_{12}]^{2-}$. A 1959 study by Shapiro and Williams[7] suggested the possible formation of a $[B_{12}H_{12}]^{2-}$ icosahedron, and in 1960 this cluster was first successfully isolated and characterized as a triethylammonium salt by Pitochelli and Hawthorne, albeit in a relatively low yield.[8] Subsequent pioneering studies by Hawthorne, Knoth, Muetterties, and others initiated a new era in the field of boron cluster chemistry.[2,9–22] Specifically, these groups have shown that $[B_{12}H_{12}]^{2-}$ can be prepared on a large scale in a high yield (>90%)[2] and undergo facile functionalization chemistry that parallels some properties of classical organic molecules (*e.g.* benzene).[3,23,24] This was an exciting discovery, since previously many boron hydride clusters were perceived as highly unstable species prone to fast degradation by heat, acids, and bases. Conversely, $[B_{12}H_{12}]^{2-}$ salts were shown to be stable in acids and bases, and were thermally stable as high as 810 °C with no observable decomposition.[16] Knoth and co-workers were the first to demonstrate the persubstitution of $[B_{12}H_{12}]^{2-}$, producing halogenated $[B_{12}F_{12}]^{2-}$, $[B_{12}Cl_{12}]^{2-}$, $[B_{12}Br_{12}]^{2-}$ and $[B_{12}I_{12}]^{2-}$ derivatives.[20,25] In the past two decades, persubstitution of $[B_{12}H_{12}]^{2-}$ was improved with new synthetic methods and extended towards other functional groups including $[B_{12}Me_{12}]^{2-}$ and $[B_{12}(OH)_{12}]^{2-}$.[26–30] Among the perfunctionalized derivatives synthesized, *closo*-$[B_{12}(OH)_{12}]^{2-}$ is particularly appealing, as it is capable of undergoing further functionalization by forming ether, ester, carbonate, and carbamate linkages.[29,31–33]

While controlled oxidation of the parent $[B_{12}H_{12}]^{2-}$ anion leads to an irreversible cluster degradation forming a B–B linked dimer,[21] several perfunctionalized variants have been previously observed to undergo reversible redox behavior.[34] For example, Rupich reported that $[B_{12}X_{12}]^{2-}$ could undergo a single electron oxidation to form a stable radical $[B_{12}X_{12}]^{1-}$,[35] which was recently isolated and structurally confirmed as the oxidized radical $[B_{12}Cl_{12}]^{1-}$ species by Weber and co-workers.[36] Hawthorne and co-workers reported that the perfunctionalized $B_{12}(OCH_2Ph)_{12}$ cluster can exist in three distinct redox states accessible via two sequential and quasi-reversible one-electron oxidation reactions of the parent dianionic *closo* species.[37] The same group later showed that other benzyl and alkyl functionalized $B_{12}(OR)_{12}$ clusters can be synthesized, and all of these species exhibit similarly reversible redox behavior.[31] Schleid and co-workers subsequently showed that the parent $[B_{12}(OH)_{12}]^{2-}$ cluster can undergo a one-electron oxidation to form a stable radical $[B_{12}(OH)_{12}]^{1-}$ species.[38] Interestingly, the redox potential of the ether-linked $B_{12}(OR)_{12}$ species can be rationally tuned as a function of the O-bound substituent, reminiscent of many metal-based redox-active inorganic complexes.[31,34,39] Unfortunately, all of the reported synthetic routes towards $B_{12}(OR)_{12}$ clusters currently require either extremely long reaction times (weeks) or highly specialized high-pressure equipment. Furthermore, in all cases strict inert atmospheric conditions are also required for their synthesis.[29,31,37]

Herein we report a rapid, scalable, and robust synthetic route to a wide range of perfunctionalized $B_{12}(OR)_{12}$ cluster derivatives utilizing a bench-top microwave reactor. This technology has emerged over the past several decades and has been successfully employed in a large number of synthetic schemes[40] which necessitate the reaction heating above the boiling point of the solvent. Our work shows that the microwave-based method enables synthesis of perfunctionalized ether-linked boron clusters within minutes and does not require the use of inert atmosphere and rigorously dried solvents. We further show the synthetic utility of our method in the preparation of previously unknown $B_{12}(OR)_{12}$ derivatives featuring highly oxidizing redox potentials as well as vertex-differentiated molecular architectures. Synthesized cluster species were all isolated and characterized using solution-based NMR and IR spectroscopic tools and mass spectrometry. Electron delocalization of the radical state in these species was further evaluated by electron paramagnetic resonance (EPR) spectroscopy and elucidated by X-ray photoelectron spectroscopy (XPS).

Results and Discussion

The tetrabutylammonium (TBA) salt of *closo*-$[B_{12}(OH)_{12}]^{-2}$ (TBA_2**[1]**) was chosen for use with our microwave synthesis due to its enhanced solubility in organic solvents compared to alkali metal salts of **1** (Figure 1).[31] The synthesis of TBA_2**[1]** was adapted from previously reported protocols by Hawthorne and co-workers (see SI for details).[31,41,42]

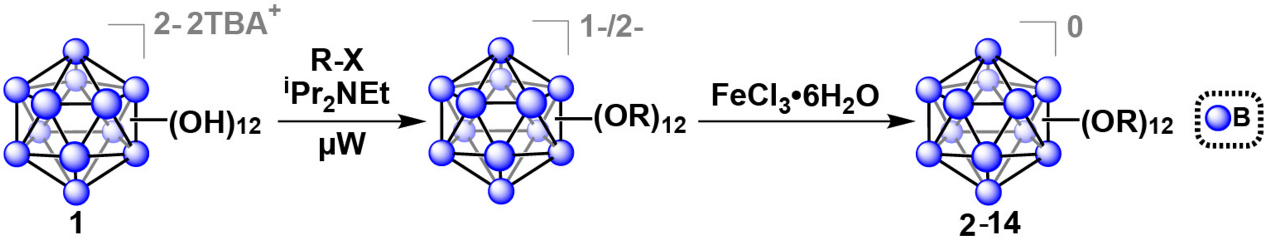


Figure 1. Synthetic route to produce functionalized ether-linked derivatives of the *hypercloso* boron clusters (**2-14**) via microwave-assisted synthesis. Precursor synthesis of **[1]**$^{2-}$ was adapted from previously described methods (see SI for details).[31,41,42]

Oxygen-free, anhydrous conditions (oven-dried glassware, dried and distilled solvents, nitrogen atmosphere) were initially employed for microwave-assisted syntheses of alkyl- and benzyl-functionalized *closo*-$[B_{12}(OH)_{12}]^{2-}$ **[1]** ether-linked derivatives, due to previously described high-pressure and reflux-based methods necessitating stringent air and moisture free conditions. To our surprise, we discovered that microwave reactions utilizing previously reported conditions (benzyl bromide and TBA_2[**1**] in the presence of *N*,*N*-diisopropylethylamine (DIEA, Hünig's base) in acetonitrile) are driven at a much higher rate, resulting in quantitative formation of a mixture of charged 1-/2- TBA salts of **2** within 15 minutes at 140 °C, as indicated by *in situ* ^{11}B NMR spectroscopy. Specifically, no parent ^{11}B NMR resonance at δ –18 corresponding to the $[B_{12}(OH)_{12}]^{2-}$ starting material is observed, and a singlet at δ –16 can be seen instead. Concomitant presence of $\mathbf{[2]^{1-}}$ radical species in the product mixture can be deduced from the diagnostic pink color of the solution and its measured signature EPR signal (G-factor = 2.008121). Oxidation of the reaction mixture using $FeCl_3{\cdot}6H_2O$ in 90/10 ethanol/acetonitrile followed by column chromatography on silica gel produces the pure neutral cluster $\mathbf{[2]^{0}}$ in 63% yield (Figure 2). Oxidation can be conveniently monitored by ^{11}B NMR, where the fully oxidized cluster $\mathbf{[2]^{0}}$ exhibits a downfield resonance shift at δ 41.8. Overall, this represents a significant reduction in reaction duration from the originally reported 6 days and 4 hours required for reflux and high-pressure reactor methods, respectively, while retaining similar yield.[31]

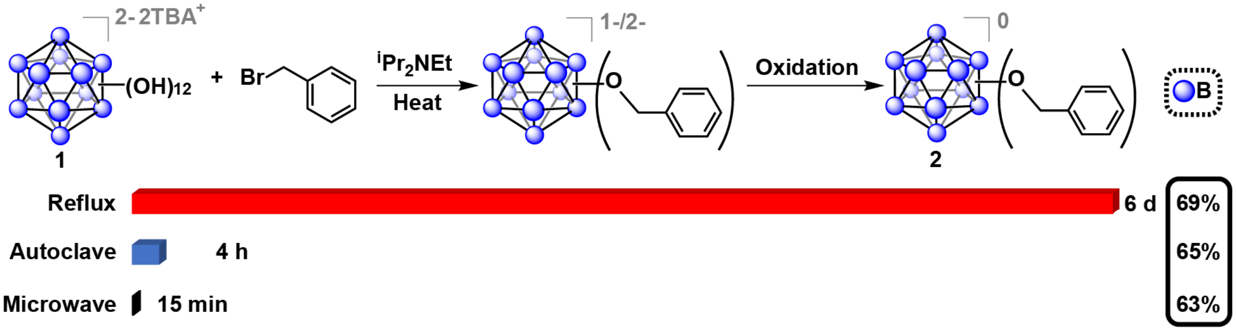
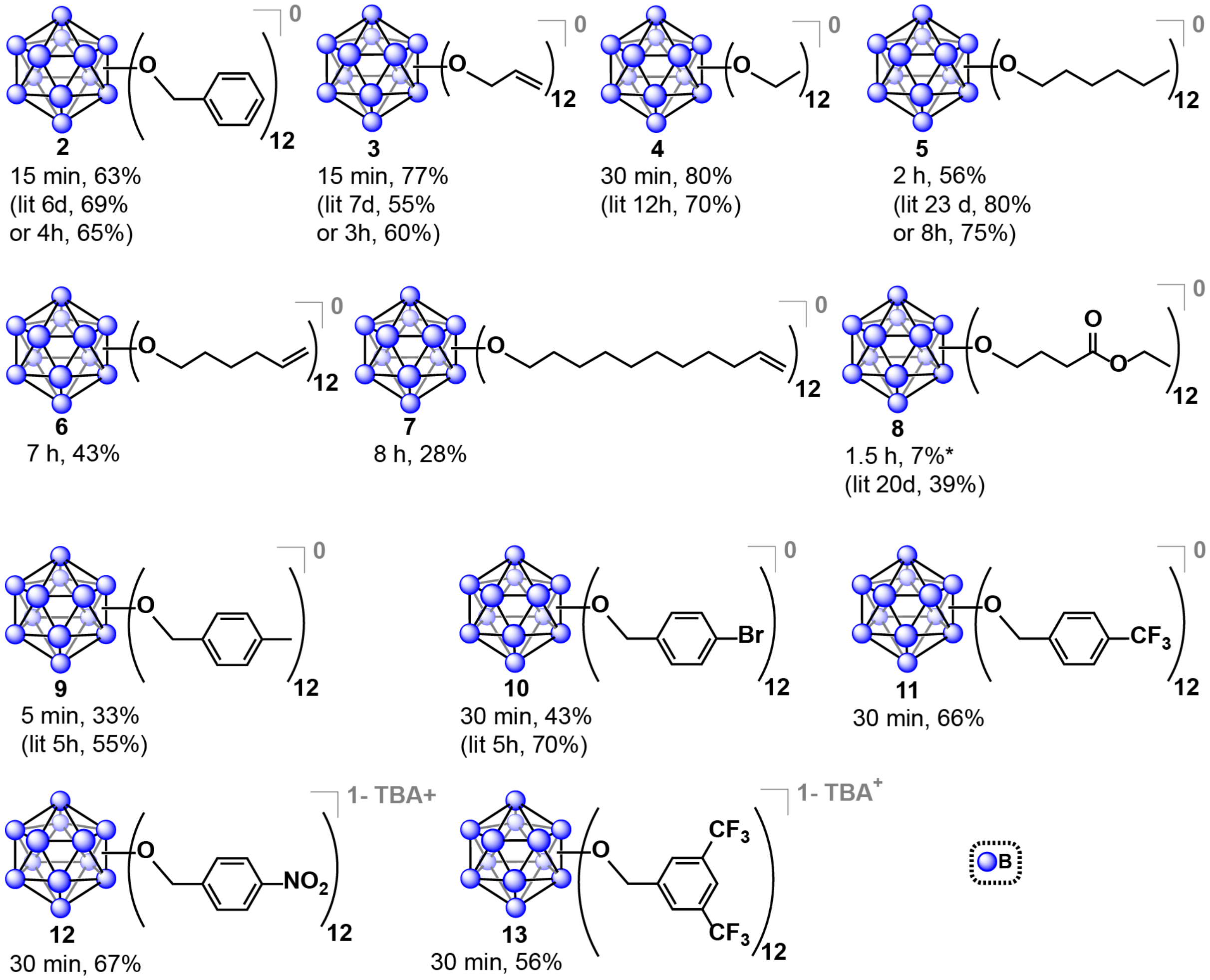


Figure 2. Synthesis of **2** from TBA_2**[1]** using microwave-based method along with two previously reported methods indicating dramatic reduction in reaction time without compromising the isolated yield of $\mathbf{[2]^{0}}$.[31]

Encouraged by these results, we then optimized the microwave reaction times with allyl bromide and bromoethane reagents independently, and in both cases observed that complete substitution can be accomplished within 15 - 30 minutes at 140 °C. These compounds were isolated in their fully oxidized neutral form in a similar fashion to **[2]^{0}**, (compounds **[3]^{0}** and **[4]^{0},** respectively; Figure 3). Notably, previously reported high-pressure reactor synthesis of these species required 3 and 12 hours, respectively, for alkylation to occur at all twelve vertices, suggesting that the microwave-based method can be generally applied to several classes of ether-linked $B_{12}(OR)_{12}$ clusters and is potentially superior to the previously developed methods.[31]

The relatively short perfunctionalization reaction times made possible by this new microwave technique prompted us to investigate whether it would be possible to utilize ambient synthetic conditions. Specifically, we hypothesized that the fast rate of product formation would outcompete the rate of degradation stemming from the presence of adventitious air and moisture during the synthesis. We therefore tested the synthesis of **2** using as-received non-dried acetonitrile (see SI) with the reagents added to a reaction vessel open to air. The open-air synthesis of **2** proceeded with full conversion in 15 minutes as indicated by ^{11}B NMR spectroscopy on the crude mixture. Following the normal work-up procedure (see SI), **[2]^{0}** was isolated in a 63% yield, suggesting that rigorous exclusion of air and moisture is not necessary for this transformation. This open-air synthesis method was successfully used for all subsequent ether-based cluster syntheses reported in this work. We decided to further explore the scope of this transformation by using longer-chain alkyl substituents. Hexyl chain substitution required increased reaction times compared to the shorter ethyl substituent, yet persubstitution was still achieved within two hours, as opposed to 8 hours when using a high-pressure reactor[31] (isolated as **[5]^{0}**, Figure 3). This increased reaction time likely stems from the increase in the length and size of the alkyl reagent affecting the kinetics of the reaction.[43,44] To further probe the limits of the microwave-based method we tested hexene- and undecene-based electrophiles, and even with the requisite increase in reaction time to 7 and 8 hours respectively, persubstitution proceeded to full conversion. Neutral **[6]^{0}** and **[7]^{0}** were isolated in 43% and 28% yields, respectively, after oxidation and normal purification procedures (Figure 3). These derivatives have not been synthesized prior to this report, and their preparation illustrates how one can dramatically increase the size of these ether-based dodecaborate clusters via a direct linkage of large substituents featuring terminal olefins onto $[B_{12}(OH)_{12}]^{2-}$.



2
15 min, 63%
(lit 6d, 69%
or 4h, 65%)

3
15 min, 77%
(lit 7d, 55%
or 3h, 60%)

4
30 min, 80%
(lit 12h, 70%)

5
2 h, 56%
(lit 23 d, 80%
or 8h, 75%)

6
7 h, 43%

7
8 h, 28%

8
1.5 h, 7%*
(lit 20d, 39%)

9
5 min, 33%
(lit 5h, 55%)

10
30 min, 43%
(lit 5h, 70%)

11
30 min, 66%

12
30 min, 67%

13
30 min, 56%

Figure 3. Synthesized $B_{12}(OR)_{12}$ clusters via microwave-based method. Yields are reported for the species isolated in a designated oxidation state as an average of two independent trials. For previously synthesized species, reported yield is given for comparison.[31] **Additional 8% of 1-/2- non-oxidized species collected.*

Based on the success of the long-chain olefin-containing moieties, we investigated the compatibility of this system with less stable reagents by using ethyl 4-bromobutyrate with TBA_2[**1**]. Perfunctionalization with ethyl butyrate has been challenging using prior synthetic methods, requiring multiple-step sequential additions of the alkyl halide and Hünig's base for 20 days while being handled under inert atmosphere conditions.[45] However, utilizing microwave-assisted synthesis, the same product (Figure 3, **[8]^{0}**) was obtained via a single 1.5 hour reaction, followed by oxidation with $FeCl_3 \cdot 6H_2O$ overnight and purification with column chromatography on Sephadex^{TM} and silica gel.

Benzyl-substituted ether-based clusters can feature a high degree of electrochemical tunability as a function of the substituents attached to the aromatic ring.[39] Our method allows for the efficient synthesis of clusters containing both electron-rich (**9**) and electron-withdrawing (**10**) benzyl derivatives in yields matching previous methods but with significantly reduced reaction times (Figure 3). We were further intrigued by the possibility of extending the accessible electrochemical window for this class of compounds by utilizing benzyl halide precursors containing highly electron-withdrawing substituents. The perfunctionalized cluster featuring a trifluoromethyl (CF_3) group attached to the *para* position of the benzyl moiety was prepared using our method in 30 minutes, and following oxidation the isolated neutral compound **[11]^{0}** was obtained in 66% yield (Figure 3). The oxidation potential of [**11**]$^{1-}$/[**11**]$^{0-}$ ($E_{1/2}$ = 0.56 V vs Fc/Fc^{+}) measured by cyclic voltammetry (CV) is particularly notable since it is higher than any reported $B_{12}(OR)_{12}$ cluster to date (previously 0.09 V vs Fc/Fc^{+}).[39] Plotting the Hammett constants of various benzyl substituents[44] versus the redox potentials of $[B_{12}(OR)_{12}]$ clusters perfunctionalized with these groups[39] (Figure 4) indicates the oxidation potential of these clusters can be rationally extended beyond the previously reported electrochemical window.

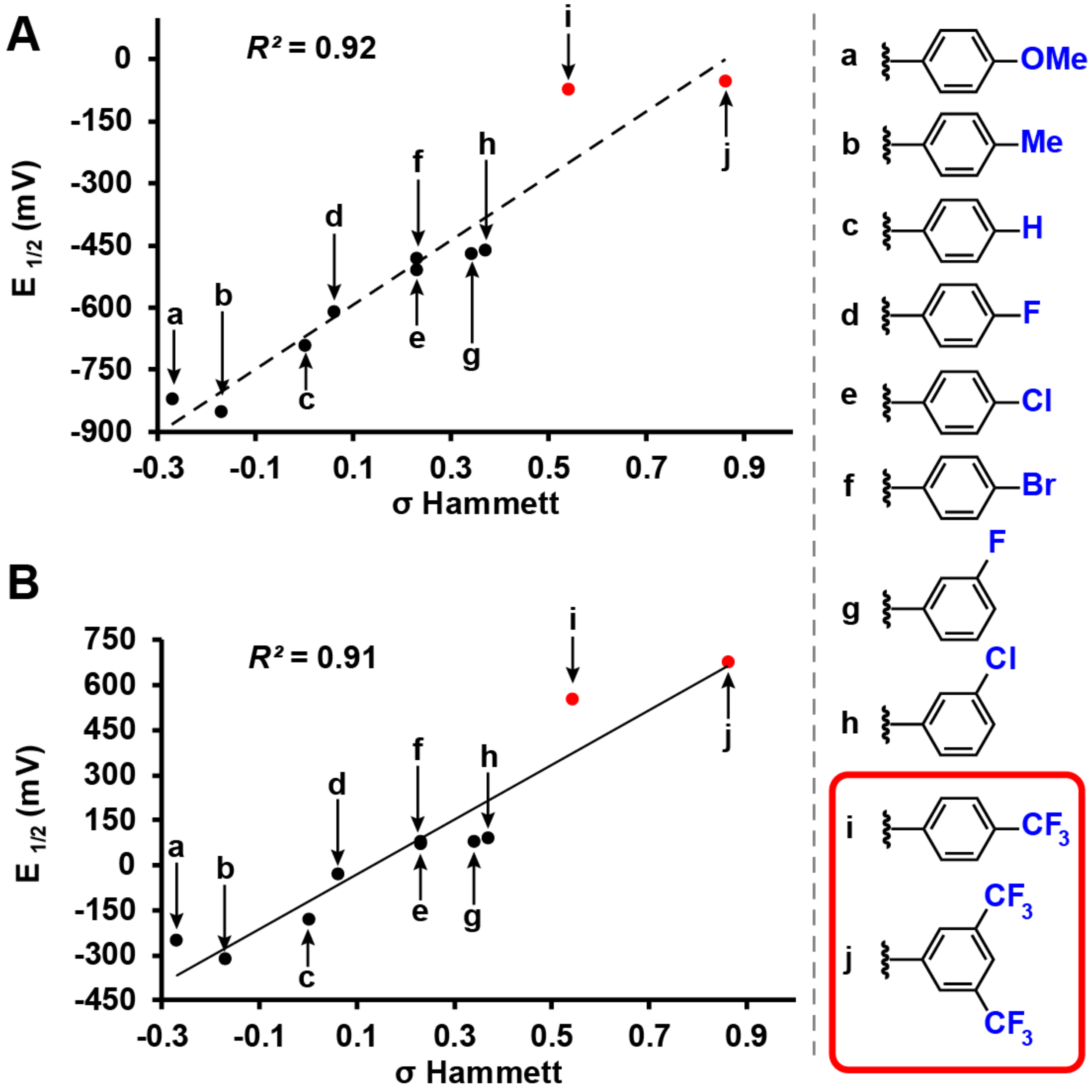


Figure 4. (a) Redox potential of $[B_{12}(OR)_{12}]^{2-/1-}$ and (b) $[B_{12}(OR)_{12}]^{1-/0}$ substituted with various benzyl substituents plotted vs Hammett constants.[3,44] Previously characterized[39] (black) and new (red) $[B_{12}(OR)_{12}]^0$ clusters are shown.

For example, according to the trend suggested by this Hammett plot, a *para*-nitrobenzyl-substituted cluster should exhibit a higher 1-/0 oxidation potential than **11** (Figure 3 and Figure 4).[44] The perfunctionalized cluster **12** featuring *para*-nitro (NO_2) substituent attached to the benzyl was successfully synthesized using our method in 30 minutes, however, oxidation of the reaction mixture containing [**12**]$^{2-/1-}$ with $FeCl_3{\cdot}6H_2O$ did not produce any *hypercloso*-neutral species **[12]^{0}**. Instead, the radical cluster species **[12]$^{1-}$** was isolated as the only product in 67% yield (Figure 3). This is not surprising, given the predicted oxidation potential for the [**12**]$^{1-}$/**[12]^{0}** redox couple is more positive than the oxidizing strength of $FeCl_3{\cdot}6H_2O$.[46] Attempts to use stronger chemical oxidants (e.g. ceric ammonium nitrate) resulted in cluster degradation. Furthermore, insufficient solubility of **[12]$^{1-}$** as a TBA salt precluded us from obtaining CV measurements for this derivative. Nevertheless, convinced we could expand the electrochemical window for $B_{12}(OR)_{12}$ species featuring benzyl-based substituents, we turned our attention to a potentially more soluble compound containing a 3,5-*bis*(trifluoromethyl)benzyl group instead.

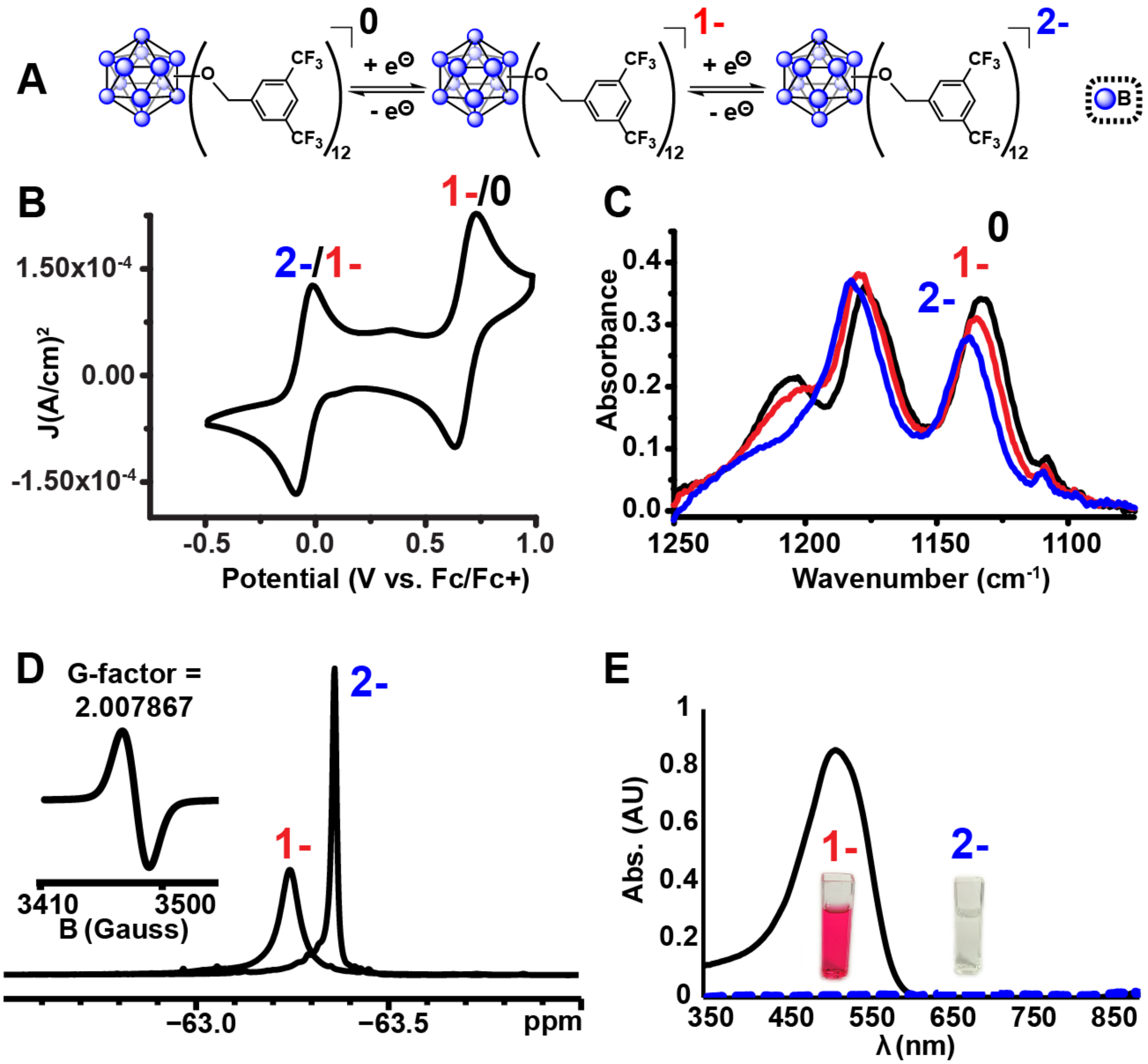


Figure 5. (a) Reversible redox activity of **13**; (b) Cyclic voltammogram (CV) demonstrating two independent, one-electron oxidation/reduction waves between 2-/1-, and 1-/0 states (1 mM **13** with 0.1 M $TBAPF_6$ in CH_2Cl_2; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudoreference electrode behind a CoralPor tip; referenced to an internal ferrocene standard); (c) Infrared spectroelectrochemical (IRSEC)[47,48] analysis of 0/1-/2- states of **13**; (d) ^{19}F NMR spectra of **[13]**$^{1-}$ and **[13]**$^{2-}$ with EPR of **[13]**$^{1-}$ (inset); (e) UV-Vis spectra of **[13]**$^{1-}$ and **[13]**$^{2-}$.

Using the microwave method described above, cluster **13** was synthesized in 30 minutes. Interestingly, unlike all of the synthesized clusters reported thus far, the post-microwave reaction mixture was colorless, which is a characteristic feature of the pure dianionic state **[13]**$^{2-}$ for these clusters. The lack of color persisted even after column chromatography purification on silica gel in air. The identity of the pure isolated TBA salt of **[13]**$^{2-}$ (73% yield) was validated by full spectroscopic characterization and mass spectrometry (see SI). Oxidation of **[13]**$^{2-}$ with $FeCl_3·6H_2O$ did not produce the neutral cluster, rather the pure **[13]**$^{1-}$ radical species was isolated in 78% yield, resulting in 56% net yield for **[13]**$^{1-}$ species starting from TBA_2[**1**]. Use of stronger chemical oxidants such as ceric ammonium nitrate (CAN) degraded the boron cage, producing a diagnostic ^{11}B NMR resonance at δ 20 characteristic of borates.[49] Nevertheless, we were able to observe neutral cluster **[13]**^{0} electrochemically via infrared spectroelectrochemistry (IR-SEC) and cyclic voltammetry (CV) in CH_2Cl_2 (Figure 5, B, C). CVs of **[13]**$^{1-}$ as the TBA salt in CH_2Cl_2 showed two quasi-reversible redox features at -0.05 V and 0.68 V vs Fc/Fc^{+}, corresponding to the 2-/1- and 1-/0 transitions, respectively. IR-SEC experiments where the applied potential was increased to more positive potentials incrementally on the TBA salt of **[13]**$^{2-}$ showed subtle changes in the IR stretching modes for all three oxidation states of [**13**] around 1130-1140 cm^{-1} and 1200-1220 cm^{-1}. The shift in these IR bands assigned to the B–O bond[50] to higher wavenumbers from **[13]**$^{2-}$/**[13]**$^{1-}$/**[13]**^{0} is consistent with those observed in the same region for the analogous *para*-CF_3 compound **[11]**^{0} which can be isolated in its neutral form via direct synthesis (see SI). The high oxidation potential for the **[13]**$^{1-}$/**[13]**^{0} redox couple observed from cyclic voltammetry ($E_{1/2}$ = 0.70 V vs Fc/Fc^{+}) is notable since it is the highest observed 1-/0 oxidation potential for the $B_{12}(OR)_{12}$ class of clusters reported to date[39] and is ~130 mV higher that the *para*-CF_3 benzyl cluster **11**. ^{19}F NMR spectroscopy provides another diagnostic handle on the oxidation state of this compound (Figure 5, D). ^{11}B NMR spectra for these clusters typically show a singlet around δ -14 to -16 for the 2- state, though the 1- state is silent due to the presence of the paramagnetic radical (confirmed by EPR, Figure 5D (inset)). However, with ^{19}F NMR spectroscopy, a shift from a singlet resonance in **[13]**$^{2-}$ at δ -63.36 to a broad singlet at δ -63.24 for

[13]$^{1-}$ was observed. This broadening is consistent with the paramagnetic nature of **[13]**$^{1-}$**,** where F atoms are located far enough from the unpaired electron-carrying B_{12}-based cluster core to be resolved by ^{19}F NMR spectroscopy.

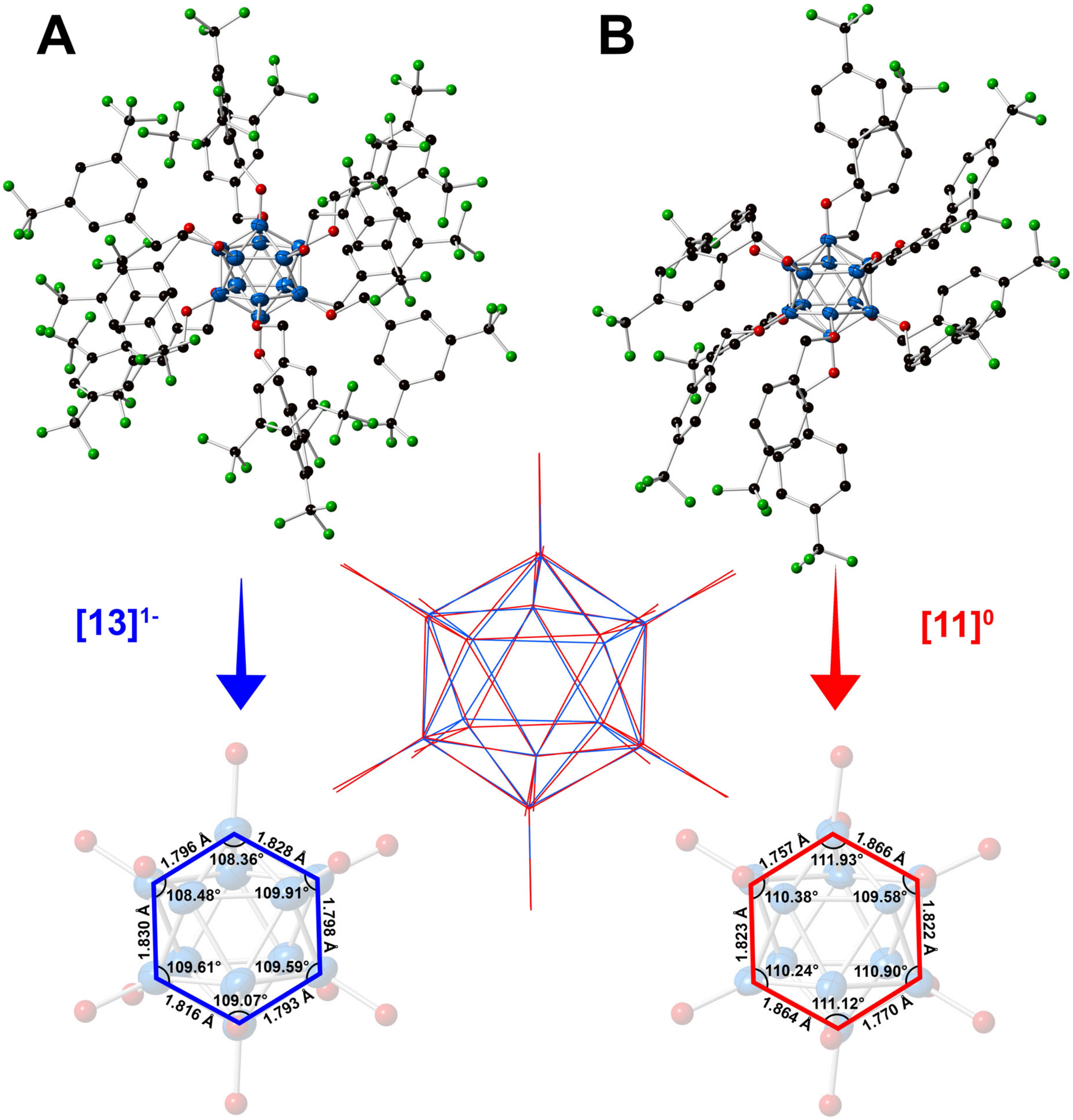


Figure 6. (A-B) Solid state X-ray structures for **[13]**$^{1-}$ and **[11]**^{0} shown with 50% thermal ellipsoid probabilities for the boron atoms (hydrogen atoms omitted for clarity). B atoms are blue, O – red, C – black, and F – green. Selected bond lengths and angles of the boron cores (substituents omitted for clarity) for **[11]**^{0} and **[13]**$^{1-}$ are shown on the bottom. Overlay of the two cores (**[13]**$^{1-}$ in blue, **[11]**^{0} in red) is depicted in the middle.

The structural parameters of the boron clusters featuring persubstituted vertices can exhibit significant distortions in the solid state as a function of the substituent and the redox state as determined by X-ray crystallographic studies. Specifically, **[2]**$^{2-}$ exhibits nearly identical B–B bond distances (1.781(4) – 1.824(4) Å) and angles (B–B–B 107.798°<a<109.229°) as expected for a perfect icosahedron, yet as the cluster is oxidized to the electron-deficient **[2]**$^{1-}$ the structure expands and distorts slightly, with further distortion observed in the neutral state.[37] Additionally, the B–O bond lengths decrease as the cluster is oxidized from **[2]**$^{2-}$**,** which contains the longest average B–O distances, to the neutral **[2]**^{0} state with the shortest B–O distances.[37] This observed trend of B–B bond lengthening, B–O bond contraction, and B–B–B angle distortion within the core as a function of cluster oxidation state is supported qualitatively by the crystal structures for neutral **[11]**^{0} and radical **[13]**$^{1-}$ (Figure 6), which show comparable changes to those observed between **[2]**$^{1-}$ and **[2]**^{0}. Selected bond lengths and angles for **[11]**^{0} and **[13]**$^{1-}$ are shown in Figure 6.

X-ray photoelectron spectroscopy (XPS) has been widely used to study oxidation states in inorganic compounds.[51–54] We therefore decided to utilize this technique to further elucidate the oxidation state and effect of functionalization for these boron clusters. Boron XPS spectra for several representative clusters synthesized in our study (Figure 7) indicate a clear trend observed in the shift of B–B bond peak energies depending on the redox state of the functionalized cluster. The observed geometric distortion of these boron cluster icosahedra with oxidation from 2- to 1- and further to neutral species results in an increased B–B binding energy (Figure 7A). The nature of the substituents also produces a clear trend in these measurements, as compound **13** also exhibits an increase in B–B binding energy as the cluster increases in oxidation state from **[13]**$^{2-}$ to **[13]**$^{1-}$ (Figure 7B), yet both are higher in energy than that of neutral cluster **[11]**^{0}. However, despite the change in oxidation potential and binding energy observed from the XPS data from substituent effects, the nature of the electron radical delocalization throughout the boron-based core remains consistent. A single, broad symmetric EPR signal centered between 3450 and 3500 Gauss was observed for all cluster species isolated in the radical form with *g* values ranging between 2.0079 and 2.0081 depending on the substituent (see SI). Due to the 3D delocalization of the single electron across the 12 boron nuclei comprising the cluster, there exist a large number of possible hyperfine couplings.[36] Overlap of these hyperfine couplings ultimately gives rise to the single broad line observed in the EPR spectra.

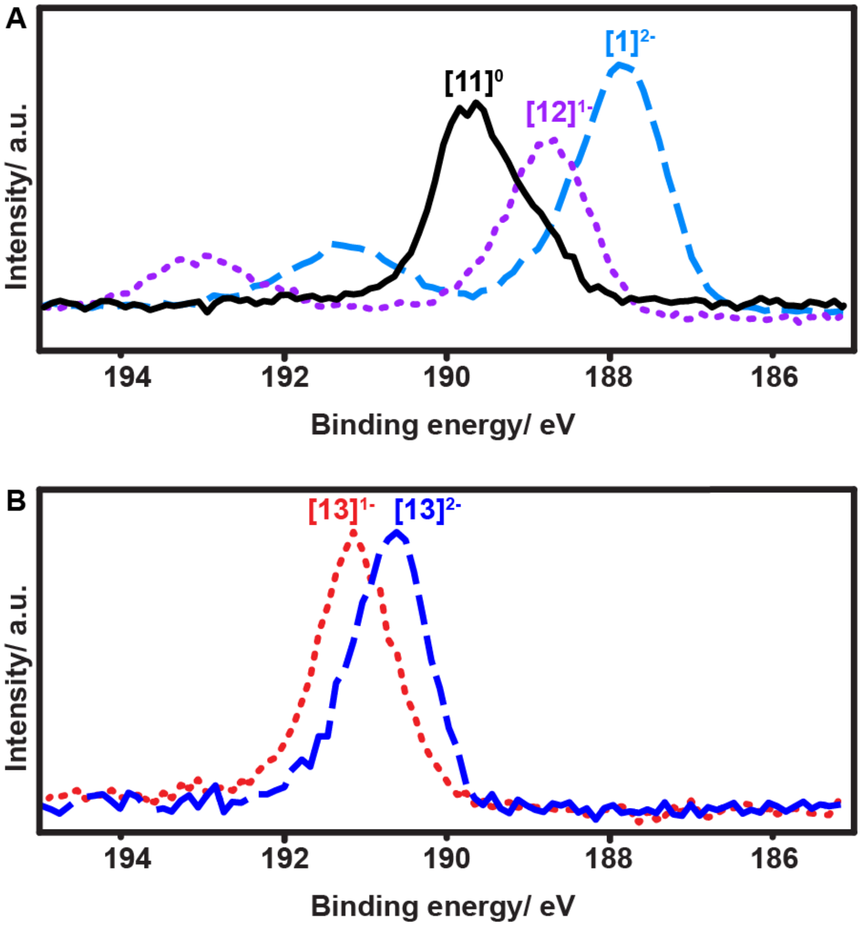


Figure 7. (a) Boron XPS spectra for TBA$_2$**[1]**$^{2-}$, TBA**[12]**$^{1-}$, and **[11]**^{0} showing an increase in B–B bond energy with increasing oxidation state; (b) Boron XPS spectra for TBA$_2$**[13]**$^{2-}$ and TBA**[13]**$^{1-}$ indicating the higher B-B bond energies of the **[13]**$^{2-}$ and **[13]**$^{1-}$ anions compared to the other substituted clusters.

In addition to previously mentioned benefits such as shortened reaction durations and the lack of stringent requirements for inert reaction conditions, microwave-assisted synthesis allows for one-pot, single-step reactions that would otherwise require more elaborate protocols.

Monosubstitution of a benzyl ligand followed by persubstitution of the remaining eleven vertices has previously required a lengthy process involving multi-step syntheses,[55] whereas we demonstrate a one-pot approach enabled by our microwave-based method. For example, mixed-substituent $B_{12}(OEt)_{11}(OBn)$ cluster (**14**, Figure 8) can be formed in a single step simply by adding a stoichiometric amount of the desired reagents into a single reaction vessel.

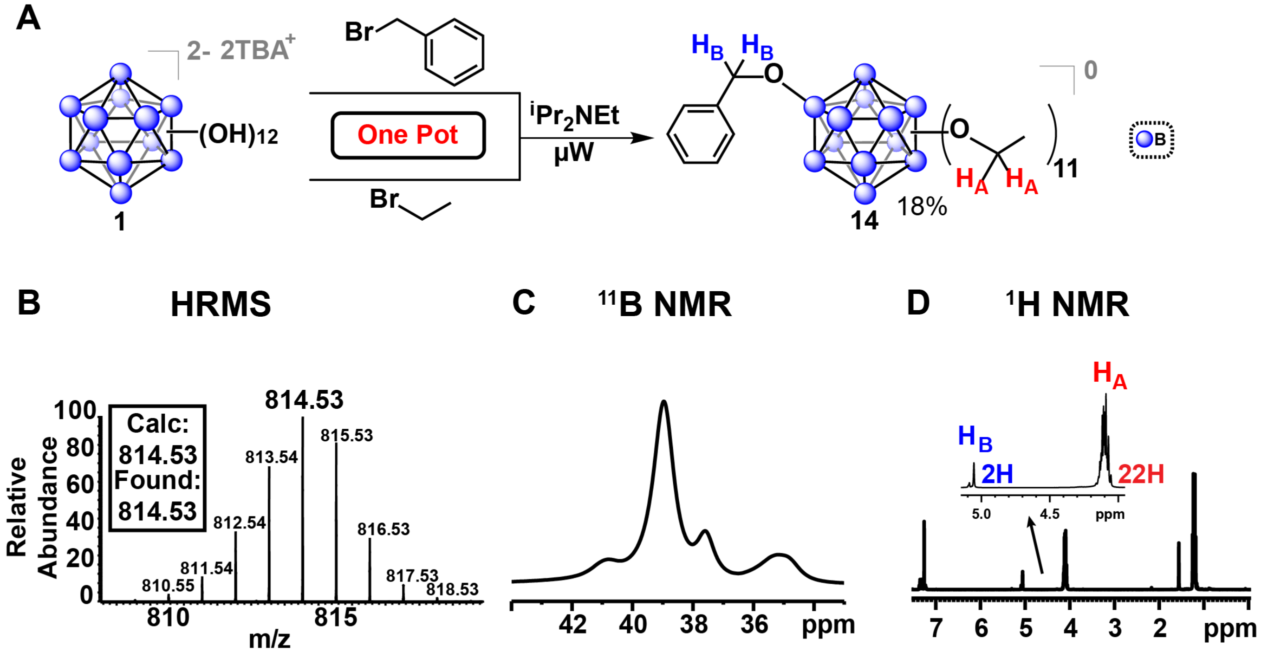


Figure 8. One-pot synthesis of vertex-differentiated *hypercloso* cluster [**14**]^0 from a 60:1:1 molar mixture of benzyl bromide:bromoethane:TBA$_2$[**1**]. Isolated yield of **[14]^0** was 18% (compound **[4]^0** was also formed as an additional product of the reaction). ^{11}B NMR spectra indicates loss of the icosahedral symmetry due to vertex differentiation, ^{1}H NMR integrations show 24H (CH_2) and 36H (CH_3) for the 11 ethyl groups and 2H (CH_2) and 5H (Ph) for the single benzyl moiety.

This reaction was completed in 30 minutes, producing three distinct species as a mixture which were oxidized with $FeCl_3 \cdot 6H_2O$ as previously described and subsequently isolated via column chromatography on silica: the perfunctionalized ethyl cluster **[4]^0**, a small amount (<5%) of di-substituted $[B_{12}(OEt)_{10}(OBn)_2]^0$ clusters, and the desired **[14]^0** in 18% yield. This method represents a significantly faster route to produce this class of [$B_{12}(OR)_{11}(OR^{'})$] mixed-substituent clusters.

Conclusions

A rapid microwave-assisted synthetic route to perfunctionalized ether-linked $B_{12}(OR)_{12}$ clusters is disclosed and the robust nature of the technique demonstrated by the synthesis and characterization of multiple derivatives of **1**. For previously synthesized compounds, reaction duration was significantly reduced and prior requirements for oxygen-free and anhydrous reaction conditions were eliminated. Our method also allows for a unique one-pot synthesis of mixed-substituent clusters with good selectivity under the same open-air conditions. The cluster species described here maintain the attractive properties of earlier derivatives, behaving as redox-active cores which show delocalization of electrons throughout the entire 3D boron cage, while the new functional groups provide a significant expansion to the available tuneable redox potential window for this class of clusters.

Acknowledgements

We gratefully acknowledge Department of Chemistry and Biochemistry at UCLA for start-up funds. Portions of this material are based upon work supported by the National Science Foundation (CHE-1048804). E.A.Q. acknowledges USPHS of the National Institute of Heath for the predoctoral training fellowship under the National Research Service Award (T32GM008496). C.W.M. and C.P.K. acknowledge support for this work from the AFOSR through a Basic Research Initiative (BRI) grant (FA9550-12-1-0414). We would like to thank Kent Kirlikovali for assisting with EPR sample preparation. We thank Dr Liban Saleh for commenting on the manuscript.

Experimental and Supporting Information

General considerations.

Initial microwave synthesis reactions were carried out under an inert atmosphere of nitrogen using standard glovebox techniques. All post-microwave work-up and characterization was performed under ambient conditions. All reactions designated as “open-air” were carried out and worked up under ambient conditions. The “ambient conditions” for this manuscript refer to room temperature (20 - 25 °C) and uncontrolled laboratory air.

Materials.

Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. MilliQ water described in this manuscript refers to purified potable water with a resistivity at 25 °C of ≤18.2 MΩ·cm. $[NEt_3H]_2[B_{12}H_{12}]$ was purchased from Boron Specialties (USA). Ethanol (200 proof) was purchased from Decon Labs and used as received. $FeCl_3 \cdot 6H_2O$ (≥97%), $CsOH \cdot 1H_2O$ (≥99.5%), H_2O_2 (30% in H_2O), $[N^nBu_4]OH$ (40% in H_2O), bromoethane (≥99%), 6-bromo-1-hexane (98%) allyl bromide (99%), 4-nitrobenzyl bromide (99%), acetonitrile (≥99.9%), CH_2Cl_2 (≥99.5%), ethyl acetate (≥99.5%), hexanes (≥98.5%), methanol (≥99.8%), *N*,*N*-diisopropylethylamine (≥99%), and tetrabutylammonium hexafluorophosphate (≥99.0%, electrochemical grade and 98%, recrystallized from ethanol and dried under vacuum at 90 °C) were purchased from Sigma-Aldrich. Benzyl bromide (99%) and ethyl 4-bromobutyrate (98%) were purchased from Alfa Aesar, and 4-methylbenzyl bromide (98%) was purchased from Acros. 6-bromo-1-hexene (98%), undec-10-enyl bromide (95%), 4-trifluoromethylbenzyl bromide

(99%), and 3,5-bis($(CF_3)_2$-benzyl bromide (97%) were purchased from Oakwood. All reagents were used as received unless otherwise indicated.

Instruments.

Bruker AV400 and AV500 spectrometers were used to obtain ^{11}B, $^{13}C\{^1H\}$, ^1H, and ^{19}F NMR spectra and Bruker Topspin software was used to process the NMR data. $^{13}C\{^1H\}$ and ^1H NMR spectra were referenced to residual solvent resonances in deuterated solvents (due to high humidity H_2O resonances are often present). ^{11}B and ^{19}F NMR spectra were referenced to $BF_3 \cdot Et_2O$ and $CFCl_3$ standards, respectively. A Bruker EMX EPR spectrometer was used to acquire EPR spectra, with all spectra collected in CH_2Cl_2 at ambient temperature. Mass spectrometry data was acquired using a Thermo Scientific^{TM} Q-Exactive^{TM} Plus instrument with a quadrupole mass filter and Orbitrap mass analyzer. IR spectroscopy was acquired on solid samples using a PerkinElmer Spectrum Two FT-IR spectrometer equipped with a diamond universal ATR probe. X-ray photoelectron spectroscopy (XPS) data was acquired using an AXIS Ultra DLD instrument (Kratos Analytical Inc., Chestnut Ridge, NY, USA) with a monochromatic Al Kα X-ray source (10 mA for survey and high-resolution scans). A 300 x 700 nm oval spot size and ultrahigh vacuum (10^{-9} Torr) were used, with 160 eV pass energy for survey spectra and 20 eV for high-resolution spectra of B 1s using a 200 ms dwell time and 20 scans. All XPS peaks were externally referenced to the C 1s signal at 284.6 eV. The experimental setup and design of the infrared-spectroelectrochemistry (IR-SEC) cell has been published previously.[47,48]

X-ray data collection and processing parameters.

For [**11**] and [**13**]$^{1-}$, a single crystal was mounted on a nylon loop using perfluoropolyether oil and cooled rapidly to 100 K with a stream of cold dinitrogen. Diffraction data were measured using a Bruker APEX-II CCD diffractometer using Mo-K_{α} radiation. The cell refinement and data reduction were carried out using Bruker SAINT and the structure was solved with SHELXS-97. All subsequent crystallographic calculations were performed using SHELXL-2013.

Cyclic voltammetry and IRSEC.

Cyclic voltammetry was performed on [**11**] and [**14**] using a CH Instruments CHI630D potentiostat with a glassy carbon disc working electrode, platinum wire counter electrode, and Ag/Ag$^+$ wire pseudoreference. All experiments were conducted in 0.1M [N^{n}Bu$_4$]PF$_6$/CH$_2$Cl$_2$ with 0.5 mM analyte concentrations (11.2 mg in 10 mL for [**11**] and 3.7 mg in 10 mL for [**14**]). The CH$_2$Cl$_2$ was dried in house with a custom drying system running through two alumina columns prior to use. The solution was degassed by bubbling Ar, and the cyclic voltammetry was performed under Ar gas. For [**11**], a scan rate of 0.1 mV/s was used with Fc/Fc$^+$ as an external standard. For [**14**], a scan rate of 0.5 mV/s was used with Fc/Fc$^+$ as an internal standard.

IRSEC and cyclic voltammetry for [**13**] were performed using a Pine Instrument Company model AFCBP1 bipotentiostat and BAS Epsilon potentiostat, respectively. For IR-SEC, as the potential was scanned, thin-layer bulk electrolysis was monitored by Fourier-Transform Reflectance IR off the electrode surface. All experiments were conducted in 0.1 M [N^{n}Bu$_4$]PF$_6$/CH$_2$Cl$_2$ solutions with analyte concentrations of ~5 mM (13.9 mg in 1 mL) prepared under a nitrogen atmosphere. The IR-SEC cell used a glassy carbon working electrode, Pt wire counter electrode, and Ag wire pseudoreference electrode. The anionic $[N^nBu_4]_2[\mathbf{13}]^{2-}$ was used for IRSEC, starting at resting potential and increasing to more oxidizing potentials stepwise.

Microwave Synthesis.

Microwave reactions were performed using a CEM Discover SP microwave synthesis reactor. Except where noted otherwise, all reactions were performed in glass 10 mL microwave reactor vials purchased from CEM with silicone/PTFE caps. Flea micro PTFE-coated stir bars were used in the vials with magnetic stirring set to high and 15 seconds of premixing prior to the temperature ramping. All microwave reactions were carried out at 140 °C with the pressure release limit set to 250 psi (no reactions exceeded this limit to trigger venting) and the maximum wattage set to 250W (the power applied was dynamically controlled by the microwave instrument and did not exceed this limit for any reactions). Column chromatography was performed using 2.0 - 2.25 cm inner diameter glass fritted chromatography columns with 20-30 cm of slurry-packed silica gel to ensure full separation of reagents and products. Unfiltered pressurized air was used to assist column chromatography.

Dicesium Dodecahydroxy-*closo*-dodecaborate Cs_2[1].

$CsOH{\cdot}H_2O$ (14.00 g, 83.4 mmol) was dissolved in methanol (130 mL) in a 300 mL glass round bottom flask. $[NEt_3H]_2[B_{12}H_{12}]$ (13.3758 g, 38.9 mmol) was added along with a PTFE-coated stir bar, and the reaction was left to stir vigorously for 18 h at ambient temperature. The cloudy suspension was then filtered through a 60 mL fritted glass funnel and washed with methanol (3 x 20 mL). The resulting white solid was dried on the frit for 1.5 h then left under high vacuum for 12 h and complete conversion to Cs_2[*closo*-$B_{12}H_{12}$] was confirmed by the absence of amine resonances in the ^{1}H NMR spectrum. Alternatively, commercially-obtained $Cs_2[B_{12}H_{12}]$ (98%, Strem) can be utilized for hydroxylation.

Note: The perhydroxylation procedure described herein should always be undertaken with caution and careful planning in order to ensure the $Cs_2[B_{12}H_{12}]$ reagent is pure and contains no organic contaminants. Blast shielding to contain any possible explosions should be utilized. Under no circumstances should the hydrogen peroxide used in the reaction come into contact with any organic material or solvents due to the possibility of an explosion. Synthesis of $Cs_2[B_{12}(OH)_{12}]$ and the ion exchange to produce $[N^nBu_4]_2[B_{12}(OH)_{12}]$ have been described elsewhere,[41,42] but will be reported here for convenience. $Cs_2[B_{12}H_{12}]$ (15.0 g, 36.8 mmol) was added to a glass three-necked round bottom flask with a water-cooled condensing coil in the top slot. The rear neck outlet contained a stopcock for venting pressure, and the front outlet was sealed with a glass stopper and secured with a plastic Keck clip. The apparatus was suspended in a silicone oil bath on a hot plate and secured, with a blast shield in front as a precaution against any potential explosion. The oil bath was heated to 95 °C, and a 50 mm oval PTFE stir bar was added to the flask, and the reaction was initiated with the addition of H_2O_2 (50 mL, 30% in H_2O). The flask was stoppered and the mixture allowed to stir at that temperature for 2 h. After 2 h, additional H_2O_2 (12 mL) was added, with the flask being vented, the glass stopper removed, and upon completion of addition, re-stoppering the flask. This addition of H_2O_2 was repeated every 2 h until a total volume of 60 mL was added to the reaction mixture. Upon completion of the addition, the oil bath temperature was increased to 105 °C, and additional H_2O_2 aliquots (10-15 mL) were added every 2 - 3 days, cooling the solution in the flask by raising it out of the oil bath and leaving it to cool for 20 – 30 minutes prior to each addition. After 14 days, the progress of the reaction was assessed *via* ^{11}B NMR, with reaction completion indicated by the appearance of a broad resonance at -18.0 ppm corresponding to $Cs_2[B_{12}(OH)_{12}]$ and the disappearance of the resonance at -16 ppm corresponding to unreacted

$Cs_2[B_{12}H_{12}]$. Once the reaction is complete (as assessed by ^{11}B NMR), the mixture was cooled to 2 – 8 °C and cold MilliQ water was used to transfer the solution and solid product to a 150 mL glass fritted filter funnel. The crude product was washed with additional MilliQ water prior to drying on the filter frit under water-aspirator vacuum for 6 – 12 hours. Yield: 18.8 g (85 %).

From this point, N^nBu_4 will be referred to as TBA. For the cation exchange, Dowex 50X8 (100-200 mesh, hydrogen form, Sigma-Aldrich) was washed with MilliQ water in a 500 mL glass beaker until neutral (decanting and discarding the wash fractions), and [TBA]OH (40% in H_2O) was added in 10 mL increments until basic with magnetic stirring using a 50 mm PTFE coated standard stir bar. After 30 minutes, the pH was assessed again, and if no longer basic, additional [TBA]OH was added to restore basicity and left to stir overnight covered with a watch glass. The resin was slurry-packed into a 5 x 30 cm column wrapped with heating tape (controller set to hold temperature at 50 °C), and washed with MilliQ water until neutral. $Cs_2[B_{12}(OH)_{12}]$ (5.996 g, 10.0 mmol) was dissolved in boiling water (600 mL), cooled to 50 °C and slowly added to column. The product was washed with an additional 750 mL of 50 °C water, and the product was concentrated *in vacuo* and lyophilized to produce pure $TBA_2[\mathbf{1}]$. Yield: 6.90 g (85 %). $TBA_2[\mathbf{1}]$ is a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 4.66 (s, 12H, $O\underline{H}$), 3.08 (m, 8H, $N\text{-}\underline{CH_2}$), 1.54 (m, 8H, $N\text{-}CH_2\underline{CH_2}$), 1.25 (m, 8H, $N\text{-}(CH_2)_2\underline{CH_2}$), 0.84 (m, 12H, $N\text{-}(CH_2)_3\underline{CH_3}$). $^{11}B\{^1H\}$ NMR (128 MHz, D_2O): δ -17.9. *Note: $TBA_2[\mathbf{1}]$ is air-stable, but hygroscopic. Store under inert atmosphere or in a sealed desiccator to prevent excess absorption of water over extended periods of time under storage.*

General ether alkylation/benzylation of TBA2[1] to B12(OR)12 microwave procedure.

Reactions were performed using TBA_2[**1**] which was weighed and placed into a 10 mL glass microwave vial and transferred out of a nitrogen-filled glovebox, being opened to the air prior to synthesis. The acetonitrile solvent, base, and alkyl reagents were all used under ambient temperature and pressure conditions with no additional purification or drying. *Note: the initial inert-atmosphere trials mentioned in the main text for* ***2****,* ***3****, and* ***4*** *were prepared inside a nitrogen-filled glovebox using rigorously anhydrous solvent. Once the PTFE/silicone cap was placed on the microwave vial it was transferred out of the glovebox and the reactions were performed identically to the open-air reactions.* TBA_2[**1**] (50.0 mg, 0.061 mmol) was transferred to a 10 mL glass microwave vial containing a flea micro stir bar and dissolved in acetonitrile (1 mL). *N*,*N*-diisopropylethylamine (Hünig's base, 0.2 mL, 1.15 mmol) and alkyl halide (7.6 mmol) were added, and a PTFE/silicone cap was placed on the microwave vial. The mixture was heated to 140 °C with stirring in the microwave for 5 min to 8 hrs (depending upon the alkyl halide), with the progress of the reaction monitored *via* ^{11}B NMR spectroscopy. Multiple resonances between -14 and -16 ppm are first observed, indicating partial substitution of the 12 vertices. The reaction has reached completion when these resonances coalesce to a broad singlet resonance between -14 and -16 ppm corresponding to the fully substituted $[B_{12}(OR)_{12}]^{2-}$ species. The color of the reaction mixture is typically a faint yellow initially, with the completed reaction mixture changing to a pink/purple, faint pink, or deep red/orange color indicative of the 1- species. Upon completion of the reaction, excess acetonitrile and base were removed *via* rotary evaporation. With the exception of **3**, **4**, **6,** and **14** the remaining reaction mixture containing product and unreacted alkyl halide were separated *via* column chromatography with silica gel. The unreacted alkyl halide (clear and colorless or slightly yellow/orange, UV active) was eluted first, followed by the elution of the remaining pink/purple product mixture consisting of 1-/2- species (note that the 2- species is colorless). The excess solvent was removed *via* a rotary evaporator, and the remaining 1-/2- product mixture was dissolved in a 90/5/5 ethanol/acetonitrile/MilliQ H_2O or 90/10 ethanol/acetonitrile mixture and transferred to a 50 mL round bottom flask. $FeCl_3 \cdot 6H_2O$ (0.3 g, 1.11 mmol) was added to the dissolved mixture, and subsequently stirred vigorously for 12-24 h at ambient temperature. The solvent was removed from the resulting dark orange/brown mixture *via* rotary evaporation, and the neutral [*hypercloso*-$B_{12}(OR)_{12}]^0$ or radical TBA[*hypocloso*-$B_{12}(OR)_{12}]^{1-}$ product was separated from the $FeCl_3 \cdot 6H_2O$ *via* column chromatography with silica gel. A dark orange, yellow-orange, or red-orange band consisting of neutral [*hypercloso*-$B_{12}(OR)_{12}]^0$ was eluted with CH_2Cl_2, with a pink/purple band containing charged 1-/2- species eluting next if any product was not fully oxidized. The red or orange fraction containing the desired neutral closomer was dried with rotary evaporation followed by high vacuum, and the above procedure for oxidation could be repeated on the remaining 1-/2- mixture to obtain additional neutral product if any non-fully oxidized product remains. *Note: if the final oxidized product appears to have any impurities (via ^{1}H NMR spectroscopy), eluting the product through an additional silica plug or short column with 1:1 CH_2Cl_2/hexanes should remove any contaminants.*

Dodeca(benzyloxy)-*hypercloso*-dodecaborane [2]

TBA$_2$[**1**] (50.0 mg, 0.061 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 1 mL acetonitrile. *N,N*-diisopropylethylamine (0.2 mL, 1.15 mmol) and benzyl bromide (1.74 mL, 14.7 mmol) were added along with a flea micro stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 15 min. The volatiles were removed *via* rotary evaporation, and the excess reagent was eluted through a slurry-packed silica gel column with 65/35 hexanes/ethyl acetate, and the pink/purple product mixture was eluted with CH_2Cl_2.

The CH_2Cl_2 was removed *via* rotary evaporation, the remaining charged 1-/2- product mixture was dissolved in 5 mL 90/5/5 ethanol/acetonitrile/H_2O, $FeCl_3 \cdot 6H_2O$ (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and an orange band containing the neutral product was separated from the $FeCl_3 \cdot 6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed *via* rotary evaporation and the final neutral product **2** was dried under high vacuum to obtain an isolated yield of 54.3 mg (63%). Compound **2** is a dark orange solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.08 - 7.19 (m, 60H, C_6H_5), 5.25 (s, 24H, O-$\underline{CH_2}$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 140.8, 128.4, 127.3, 73.4. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 41.8. HRMS (Orbitrap): *m/z* calculated for $C_{84}H_{84}B_{12}O_{12}$ (M^-), 1414.72 Da; found, 1414.72 Da.

Dodeca(allyloxy)-*hypercloso*-dodecaborane [3]

Note: this reaction should be performed with minimal exposure to light. TBA_2[**1**] (100.0 mg, 0.122 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 2 mL acetonitrile. *N,N*-diisopropylethylamine (0.4 mL, 2.30 mmol) and allyl bromide (1.28 mL, 14.68 mmol) were added along with a flea micro stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 15 min. The volatiles and excess reagent were removed *via* rotary evaporation and the purple 1-/2- product mixture was dissolved in 5 mL 90/10 ethanol/acetonitrile, $FeCl_3 \cdot 6H_2O$ (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 12-24 h (wrapped in foil to avoid excessive light exposure). Following oxidation, the solvent mixture was removed *via* rotary evaporation, and a yellow band containing the neutral product was separated from the $FeCl_3 \cdot 6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed *via* rotary evaporation and the final neutral product **3** was dried under high vacuum to obtain an isolated yield of 76.8 mg (77%). Compound **3** is a dark yellow-orange viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.91 – 5.99 (m, 12H, CH), 5.21 (dq, 12H, CH), 5.05 (dq, 12H, CH), 4.62 (m, 24H, O-$\underline{CH_2}$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.9, 114.2, 71.6. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 41.1. HRMS (Orbitrap): *m/z* calculated for $C_{36}H_{60}B_{12}O_{12}$ (M^-), 814.53 Da; found, 814.53 Da. *Note: Compound* ***3*** *should be stored at -20 °C or used immediately.*

Dodeca(ethoxy)-*hypercloso*-dodecaborane [4]

TBA$_2$[**1**] (50.0 mg, 0.061 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 1 mL acetonitrile. *N,N*-diisopropylethylamine (0.2 mL, 1.15 mmol) and bromoethane (1.65 mL, 22.1 mmol) were added along with a flea micro stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 30 min. The volatiles and excess reagent were removed *via* rotary evaporation, the remaining charged 1-/2- product mixture was dissolved in 4 mL 90/5/5 ethanol/acetonitrile/H_2O, $FeCl_3{\cdot}6H_2O$ (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and an orange band containing the neutral product was separated from the $FeCl_3{\cdot}6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed *via* rotary evaporation and the final neutral product **4** was dried under high vacuum to obtain an isolated yield of 32.7 mg (80%). Compound **4** is a dark orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.09 (q, 24H, O-$\underline{CH_2}$), 1.24 (t, 36H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 66.8, 17.8. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 37.7. HRMS (Orbitrap): *m/z* calculated for $C_{24}H_{60}B_{12}O_{12}$ (M^-), 670.53 Da; found, 670.53 Da.

Dodeca(hexoxy)-*hypercloso*-dodecaborane [5]

TBA$_2$[**1**] (99.0 mg, 0.121 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 2 mL acetonitrile. *N,N*-diisopropylethylamine (0.4 mL, 2.30 mmol) and 6-bromo-1-hexane (2.85 mL, 20.3 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 2 h. The volatiles were removed *via* rotary evaporation at 65 °C, the remaining charged 1-/2- product mixture was dissolved in 5 mL 90/5/5 ethanol/acetonitrile/H$_2$O, FeCl$_3$·6H$_2$O (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and an orange band containing the neutral product was separated from the FeCl$_3$·6H$_2$O through a slurry-packed silica gel column with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ was removed *via* rotary evaporation and the final neutral product **5** was dried under high vacuum to obtain an isolated yield of 91.4 mg (56%). Compound **5** is a dark yellow-orange oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.02 (t, 24H, O-$\underline{CH_2}$), 1.54 (m, 24H, $CH_2\underline{CH_2}(CH_2)_3CH_3$), 1.31, (m, 72H, $CH_2CH_2\underline{(CH_2)_3}CH_3$), 0.89 (m, 36H, CH$_3$). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 70.2, 32.2, 31.8, 25.9, 22.8, 14.1. ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ 42.0. HRMS (Orbitrap): *m/z* calculated for $C_{72}H_{156}B_{12}O_{12}$ (M$^-$), 1343.28 Da; found, 1343.28 Da.

Dodeca(6-hexeneoxy)-*hypercloso*-dodecaborane [6]

Note: this reaction should be performed with minimal exposure to light. TBA$_2$[**1**] 50.0 mg (0.061 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 1 mL acetonitrile. *N,N*-diisopropylethylamine (0.2

mL, 1.15 mmol) and 6-bromo-1-hexene (0.59 mL, 4.41 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 7 h. The volatiles and excess reagent were removed *via* rotary evaporation, and the remaining charged 1-/2- product mixture was dissolved in 5 mL 90/10 ethanol/acetonitrile, $FeCl_3 \cdot 6H_2O$ (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and an orange band containing the neutral product was separated from the $FeCl_3 \cdot 6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed *via* rotary evaporation and the final neutral product **6** was dried under high vacuum to obtain an isolated yield of 35.0 mg (43%). Compound **6** is a dark yellow-orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79 (m, 12H, CH), 4.95 (m, 24H, $\underline{CH_2}CH$), 4.02 (t, 24H, O-$\underline{CH_2}$), 2.05 (q, 24H, $(CH_2)_3\underline{CH_2}CH_2CH$), 1.56 (m, 24H, $CH_2\underline{CH_2}(CH_2)_3CH$), 1.43 (m, 24H, $(CH_2)_2\underline{CH_2}(CH_2)_2CH$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 139.1, 114.2, 70.1, 33.6, 31.7, 25.5. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 41.6. HRMS (Orbitrap): *m/z* calculated for $C_{72}H_{132}B_{12}O_{12}$ (M^-), 1319.09 Da; found, 1319.10 Da.

Dodeca(11-undeceneoxy)-*hypercloso*-dodecaborane [7]

Note: this reaction should be performed with minimal exposure to light. TBA_2[**1**] (50.0 mg, 0.061 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 1 mL acetonitrile. *N,N*-diisopropylethylamine (0.2 mL, 1.15 mmol) and undec-10-enyl bromide (1.54 mL, 7.33 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was reacted at 140 °C with stirring in the microwave for 8 h. The volatiles were removed *via* rotary evaporation, the excess reagent was eluted through a slurry-packed silica gel column with hexanes, and the product mixture yellow-orange and red-orange fractions were eluted with CH_2Cl_2 followed by a pink fraction with ethyl acetate. The CH_2Cl_2/ethyl acetate was removed *via* rotary evaporation, the remaining charged 1-/2- product mixture was dissolved in 9 mL 49/49/2 ethanol/CH_2Cl_2/acetonitrile, $FeCl_3 \cdot 6H_2O$ (0.5 g, 1.85 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and a dark brown/black band containing the neutral product was separated from the $FeCl_3 \cdot 6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed *via* rotary evaporation and the final neutral product **7** was dried under high vacuum to obtain an isolated yield of 37.1 mg (28%). Compound **7** is a dark, brown/black oil. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.81 (m, 12H, CH), 4.98 (m, 12H, *trans*-$C\underline{H}_2CH$), 4.91 (m, 12H, *cis*-$C\underline{H}_2CH$), 4.01 (t, 24H, O-$\underline{CH_2}$), 2.03 (m, 24H, O-$CH_2\underline{CH_2}$), 1.54 (m, 24H, O-$(CH_2)_2\underline{CH_2}$), 1.32 (m, 144H, O-$(CH_2)_3\underline{(CH_2)_6}CH_2CH$. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 139.3, 113.8, 70.4, 33.9, 32.3, 29.9, 29.7, 29.6, 29.3, 29.1, 26.2. $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ 41.5. *m/z* calculated for $C_{132}H_{252}B_{12}O_{12}$ (M^-), 2161.03 Da; due to solubility issues, the molecule was incompatible with our M.S. instrument.

Dodeca(ethylbutyratoxy)-*hypercloso*-dodecaborane [8]

TBA_2[**1**] (100.0 mg, 0.122 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 2 mL acetonitrile. *N*,*N*-diisopropylethylamine (0.4 mL, 2.30 mmol) and ethyl 4-bromobutyrate (1.08 mL, 7.55 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 1.5 h. The volatiles were removed *via* rotary evaporation, and the reaction mixture was eluted through Sephadex LH-20 size exclusion column with methanol, with the pink fraction containing the desired 1-/2- product collected. The methanol was removed *via* rotary evaporation, and the charged 1-/2- product mixture was oxidized by eluting through a slurry-packed silica gel column with 90/10 CH_2Cl_2/ethanol, collecting the orange fraction. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and the product was purified by eluting through a short (15 cm) silica gel column slurry-packed with 1:1 hexanes/ethyl ether, with ~50 mL 1:1 hexanes/ethyl ether followed by ~50 mL ethyl ether eluting an orange band. The volatiles were removed *via* rotary evaporation, and the final neutral product **8** was dried under high vacuum to obtain an isolated yield of 14.0 mg (7%). *Note: ~8% additional 1-/2- product was collected from the first silica column, and by repeating the oxidation step with the charged 1-/2- mixture additional* **8** can be isolated. Compound **8** is an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.11 (q, 24H, O-$\underline{CH_2}$), 4.03 (t, 24H, COO$\underline{CH_2}$), 2.34 (t, 24H, $\underline{CH_2}$COO), 1.87 (m, 24H, O-$CH_2\underline{CH_2}$), 1.24 (t, 36H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ, 173.3, 69.7, 60.3, 30.9, 27.4, 14.2. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 41.9. HRMS (Orbitrap): *m/z* calculated for $C_{72}H_{132}B_{12}O_{36}$ (M^-), 1702.97 Da; found, 1702.97 Da.

Dodeca(4-methylbenzyloxy)-*hypercloso*-dodecaborane [9]

TBA$_2$[**1**] (48.0 mg, 0.059 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 1 mL acetonitrile. *N,N*-diisopropylethylamine (0.2 mL, 1.15 mmol) and 4-methylbenzyl bromide (1.362 g, 7.36 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 5 min. The volatiles were removed *via* rotary evaporation, and the excess reagent was eluted through a slurry-packed silica gel column with 90/10 hexanes/ethyl acetate, and the pink/purple product mixture was eluted with acetonitrile. The volatiles were removed *via* rotary evaporation, the remaining charged 1-/2- product mixture was dissolved in 5 mL 90/10 ethanol/acetonitrile, $FeCl_3{\cdot}6H_2O$ (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and a dark orange band containing the neutral product was separated from the $FeCl_3·6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed via rotary evaporation and the final neutral product **9** was dried under high vacuum to obtain an isolated yield of 30.9 mg (33%). Compound **9** is a brown/orange viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.98 (m, 48H, C_6H_4), 5.17 (s, 24H, CH_2), 2.31 (s, 36H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 137.9, 136.4, 128. 7, 127.3, 72.8, 21.2. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 41.6. HRMS (Orbitrap): *m/z* calculated for $C_{96}H_{108}B_{12}O_{12}$ (M^-), 1582.90 Da; found, 1582.91 Da.

Dodeca(4-bromobenzyloxy)-*hypercloso*-dodecaborane [10]

TBA$_2$[**1**] (50.0 mg, 0.061 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 1 mL acetonitrile. *N,N*-diisopropylethylamine (0.2 mL, 1.15 mmol) and 4-bromobenzyl bromide (1.358 g, 7.36 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 30 min. The volatiles were removed *via* rotary evaporation, and the excess reagent was eluted through a slurry-packed silica gel column with hexanes, and the red-pink product mixture was eluted with CH_2Cl_2 followed by ethyl acetate. The volatiles were removed *via* rotary evaporation, the remaining charged 1-/2- product mixture was dissolved in 5 mL 90/10 ethanol/acetonitrile, $FeCl_3·6H_2O$ (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and a dark orange band containing the neutral product was separated from the $FeCl_3·6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed via rotary evaporation and the final neutral product **10** was dried under high vacuum to obtain an isolated yield of 62.5 mg (43%). Compound **10** is a dark-orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, 24H, *m*-$C_6\underline{H}_4$), 6.86 (d, 24H, *o*-$C_6\underline{H}_4$), 5.07 (s, 24H, O-$\underline{CH_2}$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ, 138.5, 131.6, 128.5, 121.6, 72.6. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 41.4. HRMS (Orbitrap): *m/z* calculated for $C_{84}H_{72}B_{12}Br_{12}O_{12}$ (M^-), 2361.63 Da; found, 2361.63 Da.

Dodeca(4-trifluoromethylbenzyloxy)-*hypercloso*-dodecaborane [11]

TBA$_2$[**1**] (50.0 mg, 0.061 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 1 mL acetonitrile. *N,N*-diisopropylethylamine (0.2 mL, 1.15 mmol) and 4-trifluoromethylbenzyl bromide (1.765 g, 7.5 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was reacted at 140 °C with stirring in the microwave for 30 min. The volatiles were removed *via* rotary evaporation, and the excess reagent was eluted through a slurry-packed silica gel column with hexanes, and the pink/purple product mixture was eluted with acetonitrile. The acetonitrile was removed *via* rotary evaporation, the remaining charged 1-/2- product mixture was dissolved in 5 mL of 90/10 ethanol/acetonitrile, $FeCl_3 \cdot 6H_2O$ (0.4 g, 1.48 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and an orange band containing the neutral product was separated from the $FeCl_3 \cdot 6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed *via* rotary evaporation and the final neutral product **11** was dried under high vacuum to obtain an isolated yield of 89.6 mg (66%). Compound **11** is a red-orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 - 7.48 (m, 24H, *m*-$C_6\underline{H}_4$), 7.06 - 7.15 (m, 24H, *o*-$C_6\underline{H}_4$), 5.27 (s, 24H, O-$\underline{CH_2}$). ^{13}C{^{1}H}

NMR (125 MHz, $CDCl_3$): δ 143.0, 130.6, 126.6, 125.7, 125.0, 122.8, 72.9. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 41.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.76 (s, 36F). HRMS (Orbitrap): *m/z* calculated for $C_{96}H_{72}B_{12}F_{36}O_{12}$ (M^-), 2231.57 Da; found, 2231.56 Da. Crystallized from $CDCl_3$ and pentane at room temperature for 1 week to obtain a single crystal for X-ray diffraction analysis.

Dodeca(4-nitrobenzyloxy)-*hypocloso*-dodecaborane [12]$^{1-}$

TBA$_2$[**1**] (50.0 mg, 0.061 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 1 mL acetonitrile. *N,N*-diisopropylethylamine (0.2 mL, 1.15 mmol) and 4-nitrobenzyl bromide (1.585 g, 7.34 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 30 min. The volatiles were removed *via* rotary evaporation, and the excess reagent was eluted through a slurry-packed silica gel column with 50/50 hexanes/CH_2Cl_2, and the orange product mixture was eluted with acetonitrile. The volatiles were removed *via* rotary evaporation, the remaining charged 1-/2- product mixture was dissolved in 5 mL 90/10 ethanol/acetonitrile, $FeCl_3\cdot 6H_2O$ (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and the product mixture was washed with 150 – 200 mL ethanol in a glass fritted 30 mL filter funnel to remove the remaining $FeCl_3\cdot 6H_2O$. The remaining orange radical 1- product TBA[**12**]$^{1-}$ was removed from the funnel and dried under high vacuum to obtain an isolated yield of 89.0 mg (66%). Compound TBA[**12**]$^{1-}$ is an orange solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.49 - 7.41 (m, 48H, C_6H_4). *Note: The CH_2 signal is masked and all other peaks are quite broad due to the paramagnetic radical state of the molecule.* $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 191.26, 147.47, 140.59, 130.55, 124.24. *Note: The CH_2 signal is masked and all other peaks are quite* *broad due to the paramagnetic radical state of the molecule.* No resonances are visible by ^{11}B NMR due to paramagnetic broadening (a trace resonance at 20.4 ppm is indicative of borates, which result from decomposition). HRMS (Orbitrap): *m/z* calculated for $C_{84}H_{72}B_{12}N_{12}O_{36}$ (M^-), 1954.54 Da; found, 1954.54 Da.

Dodeca(3,5-bis(trifluoromethyl)$_2$benzyloxy)-*hypocloso*-dodecaborane [13]$^{1-}$

TBA$_2$[**1**] (99.0 mg, 0.121 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 2 mL acetonitrile. *N,N*-diisopropylethylamine (0.4 mL, 2.30 mmol) and 3,5-bis(trifluoromethyl)benzyl bromide (2.68 mL, 14.6 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 30 min. The volatiles were removed *via* rotary evaporation, and the excess reagent was eluted through a slurry-packed silica gel column with 65/35 hexanes/ethyl acetate, and the colorless/very light pink product mixture was eluted with CH_2Cl_2. After removal of the CH_2Cl_2 *via* rotary evaporation, compound TBA$_2$[**13**]$^{2-}$, a clear, colorless solid, was dried under high vacuum to obtain an isolated yield of 313.6 mg (73%). After spectroscopic characterization, the dianionic TBA$_2$[**13**]$^{2-}$ was dissolved in 5 mL 90/10 ethanol/acetonitrile, 0.3 g (1.11 mmol) $FeCl_3 \cdot 6H_2O$ was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and a red-purple band containing [**13**]$^{1-}$ was separated from the $FeCl_3 \cdot 6H_2O$ through a slurry-packed silica gel column with CH_2Cl_2. The CH_2Cl_2 was removed *via* rotary evaporation and the final isolated radical [**13**]$^{1-}$ was dried under high vacuum to obtain an isolated yield of 226.4 mg (56%). Compound [**13**]$^{1-}$ is a red-purple solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 8.74 (m, 36H, C_6H_3), 3.13 (m, 8H, N-$\underline{CH_2}$), 1.65 (m, 8H, N-$CH_2\underline{CH_2}$), 1.47 (m, 8H, N-$(CH_2)_2\underline{CH_2}$), 1.05 (m, 12H, N-$(CH_2)_3\underline{CH_3}$). *Note: The CH_2 signal for the cluster is masked and all other peaks* *are quite broad due to the paramagnetic radical state of the molecule.* $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 189.0, 132.7, 132.5, 129.4, 124.6, 122.5, 121.0, 68.0, 59.2, 59.2, 59.1, 30.9, 25.6, 23.8, 19.7, 19.7, 13.4. No resonances are visible by ^{11}B NMR, due to paramagnetic broadening. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.22 (s, 72F). HRMS (Orbitrap): *m/z* calculated for $C_{108}H_{60}B_{12}F_{72}O_{12}$ (M^-), 3047.42 Da; found, 1523.71 (z=2) Da. Crystallized from $CDCl_3$ and pentane at room temperature for 1 week to obtain a single crystal for X-ray diffraction analysis.

Benzyloxy undeca(ethoxy)-hypercloso-dodecaborane [14]

TBA_2[**1**] (100.0 mg, 0.122 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 2 mL acetonitrile. *N,N*-diisopropylethylamine (0.4 mL, 2.30 mmol), benzyl bromide (0.0204 g, 0.119 mmol) and bromoethane (0.8055g, 7.39 mmol) were added along with a stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 30 min. The volatiles and excess bromoethane were removed *via* rotary evaporation, the remaining charged 1-/2- product mixture was dissolved in 5 mL 90/10 ethanol/acetonitrile, $FeCl_3·6H_2O$ (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 12-24 h. Following oxidation, the solvent mixture was removed *via* rotary evaporation, and the product mixture was separated from the $FeCl_3·6H_2O$ with CH_2Cl_2. The CH_2Cl_2 was removed *via* rotary evaporation, and the product mixture was loaded onto a long (30 – 35 cm) silica gel column slurry-packed with 80/20 CH_2Cl_2/hexanes, and the products were separated by eluting fractions with 80/20 CH_2Cl_2/hexanes. The first orange band eluted contained randomly di-substituted $benzyl_2ethyl_{10}$ species, followed by an orange band with the neutral closomer **14**, with extra **4** in a third yellow-orange band eluting last. *Note: The fractions overlap, and due to the similar colors of the different products, thin layer chromatography (TLC) with 80/20 CH_2Cl_2/hexanes was performed on the fractions near the band* *edges to determine which fractions contained a mixture of products.* The fractions containing only a single species according to TLC that eluted after the di-substituted product and prior to the pure **4** bands were combined. The volatiles were removed *via* rotary evaporation, and the final neutral product **14** was dried under high vacuum to obtain an isolated yield of 15.7 mg (18%). Compound **14** is a yellow-orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 5H, C_6H_5), 5.07 (m, 2H, $\underline{CH_2}C_6H_5$), 4.10 (m, 22H, $\underline{CH_2}CH_3$), 1.22 (m, 33H, $CH_2\underline{CH_3}$).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 141.2, 128.0, 126.6, 71.6, 66.8, 17.7. ^{11}B NMR (128 MHz, $CDCl_3$): δ 39.0, 35.2. HRMS (Orbitrap): *m/z* calculated for $C_{29}H_{62}B_{12}O_{12}$ (M^-), 732.54 Da; found, 732.54 Da.

Chapter 3: Additional $B_{12}(OR)_{12}$ Derivatives and Future Work

The $B_{12}(OR)_{12}$ clusters synthesized in this work have myriad future applications due to their unique properties including expanded redox potential windows for these classes of clusters and post-functionalization growth of the cluster. Targeted development of novel clusters with desired functional groups has already yielded promising initial results in two of these research directions in studies led by collaborators, with efforts on other projects ongoing. The principle focus of all immediate future work is to investigate the unique multivalent interactions possible with the perfunctionalized clusters, and the many potential applications these characteristics enable. Each of these avenues will require future studies to elucidate the full potential of the novel clusters synthesized in this study, yet early results have also been promising. The further study of these applications requiring unique, multivalent clusters with diverse functional groups is significantly accelerated due to the microwave-assisted synthetic methods developed in this work allowing for targeted synthesis of new clusters specifically designed for their intended usage scenarios. The first example of this directed synthesis of novel $B_{12}(OR)_{12}$ clusters for immediate application is demonstrated by the formation of two "scaffold" clusters for organomimetic atomically precise nanoparticles.

Two additional $B_{12}(OR)_{12}$ species were synthesized utilizing the general microwave-based methods to be used for multivalent organomimetic nanoparticle synthesis. After achieving successful perfunctionalization with highly electron-withdrawing substituents (as described in the previous chapter) for multiple compounds, the inclusion of perfluorinated groups was investigated. These groups would allow facile post-functionalization *via* established *para*-fluorine S_NAr "click" chemistry.[56] Utilizing identical conditions to the benzyl species [**2**], perfunctionalization of the cluster with 2,3,4,5,6-pentafluorobenzyl groups was accomplished by simply replacing the aryl halide (benzyl bromide) with commercially available 2,3,4,5,6-pentafluorobenzyl bromide. This new species (Figure 9, **15**) was intended for use to serve as a well-defined rigid core molecular scaffold from which to construct atomically precise organomimetic nanoparticles *via* the aforementioned facile post-functionalization. Initial trials by Elaine A. Qian and co-workers (unpublished work) with small thiol-containing molecules yielded promising results, yet larger groups were slow to fully react with all 12 sites on the cluster, or failed to react entirely. The most likely cause of this decreased reactivity was steric hindrance due to the bulky perfluorinated benzyl rings preventing close approach of the larger thiol-containing molecules. To remedy this issue, yet another novel cluster (Figure 9, **16**) was synthesized featuring a phenyl "spacer" to alleviate the steric hindrance and enhance the speed of the S_NAr reaction.

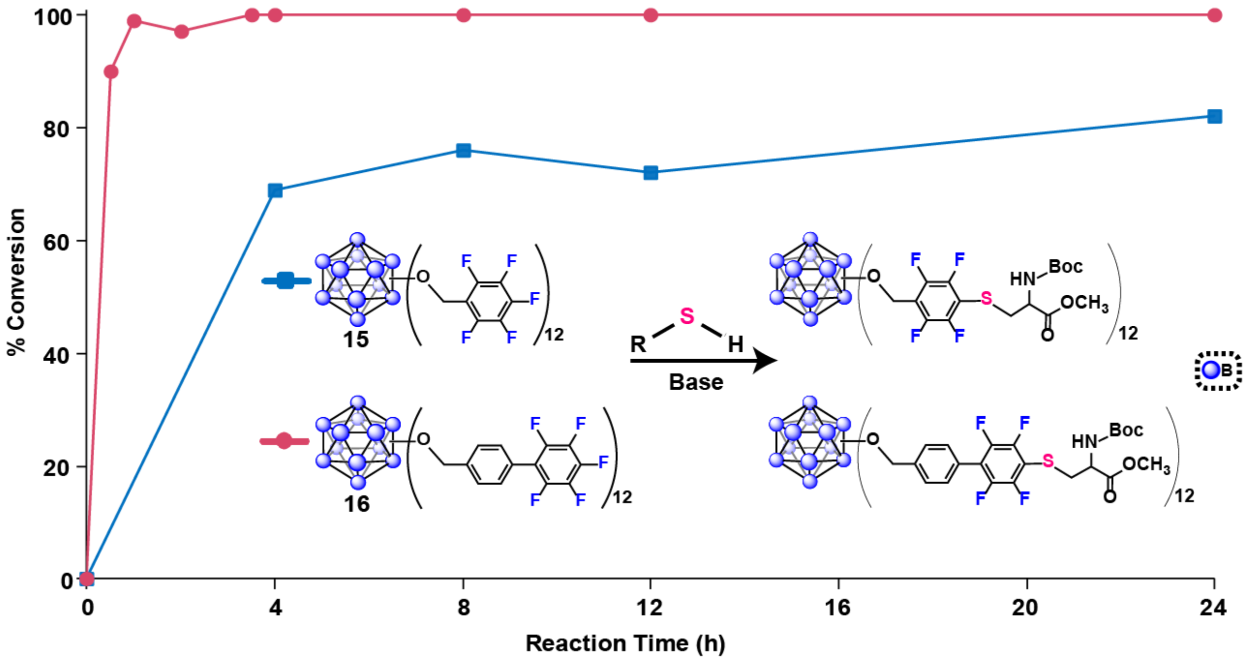


Figure 9. Compounds **15** and **16;** Reaction duration and conversion for *para*-fluorine S_NAr reactions of Boc-cysteine with compounds **15** and **16**.

To prepare compound **16**, the brominated precursor reagent Br-$CH_2C_6H_4C_6F_5$ was obtained *via* reduction of 4-(pentafluorophenyl)benzaldehyde with $NaBH_4$ in EtOH/THF (1:2) to form the benzyl alcohol and subsequent treatment with PBr_3 to obtain the desired benzyl bromide (Figure 10).

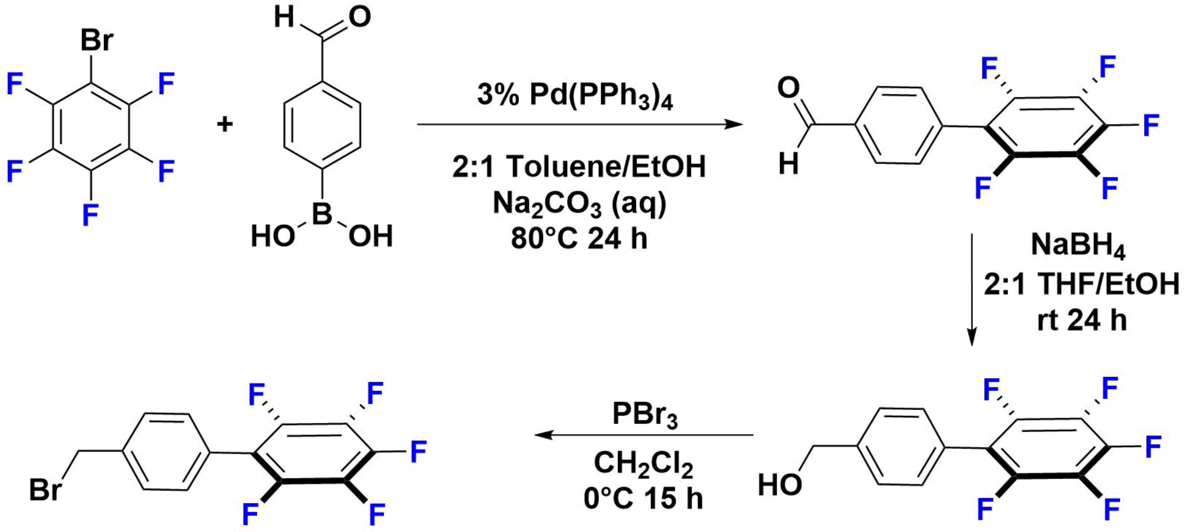


Figure 10. Synthesis of the Br-$CH_2C_6H_4C_6F_5$ reagent precursor for preparation of compound **16**.

Compound **16** was synthesized using the general microwave procedure with the developed Br-$CH_2C_6H_4C_6F_5$ reagent, once again only requiring an increase in reaction duration (to 1 h) and slight alteration of the column chromatography gradients for purification. Reactions of **16** with thiols were significantly more efficient than the first generation **15**, as demonstrated by the time required to fully substitute all 12 vertices with a bulky thiol-containing functional group (Figure 9). Compound **16** also allowed for more rapid attachment of larger and longer substituents, including sugars and polyethylene glycol (PEG). The synthesis of new perfunctionalized clusters with diverse substituents to enable specific applications (e.g. *para*-fluorine/thiol S_NAr click chemistry) is indicative of the robust nature of the microwave technique as a tool for targeted cluster design. Further studies investigating additional clusters with branched or further extended phenyl chains with terminal perfluorinated rings will probe the limits of this technique, and post-functionalization with thiol-containing groups will allow formation of myriad organomimetic nanoparticles with diverse multivalent applications based on the nature of the thiol groups decorating the rigid core.

Another application for these clusters with promising initial results is photo-initiated polymerization of styrenes. During the attempted synthesis of a $B_{12}(OR)_{12}$ derivative containing a polymerizable vinyl group on the substituent, *in situ* polymerization occurred in the microwave vial forming an insoluble solid, which was later determined to be a heavily crosslinked species. This led us to question if other clusters could be utilized to deliberately polymerize common monomers *via* photoexcitation, since the perfunctionalized clusters absorb in the visible region once oxidized to their neutral state. Initial trials by Marco S. Messina and co-workers (unpublished work) employing the benzyl (**2**) and pentafluorobenzyl (**15**) clusters to polymerize a variety of styrene derivatives were successful, resulting in polymer formation with high yields and low polydispersity (Figure 11). Another route being explored is the use of alkene-containing clusters such as compounds **3**, **6**, and **7** to construct heavily crosslinked polymers by incorporating styrene or other monomers. Further investigation of photopolymerization utilizing more oxidizing clusters, a broader substrate scope, and elucidation of the mechanism are ongoing.

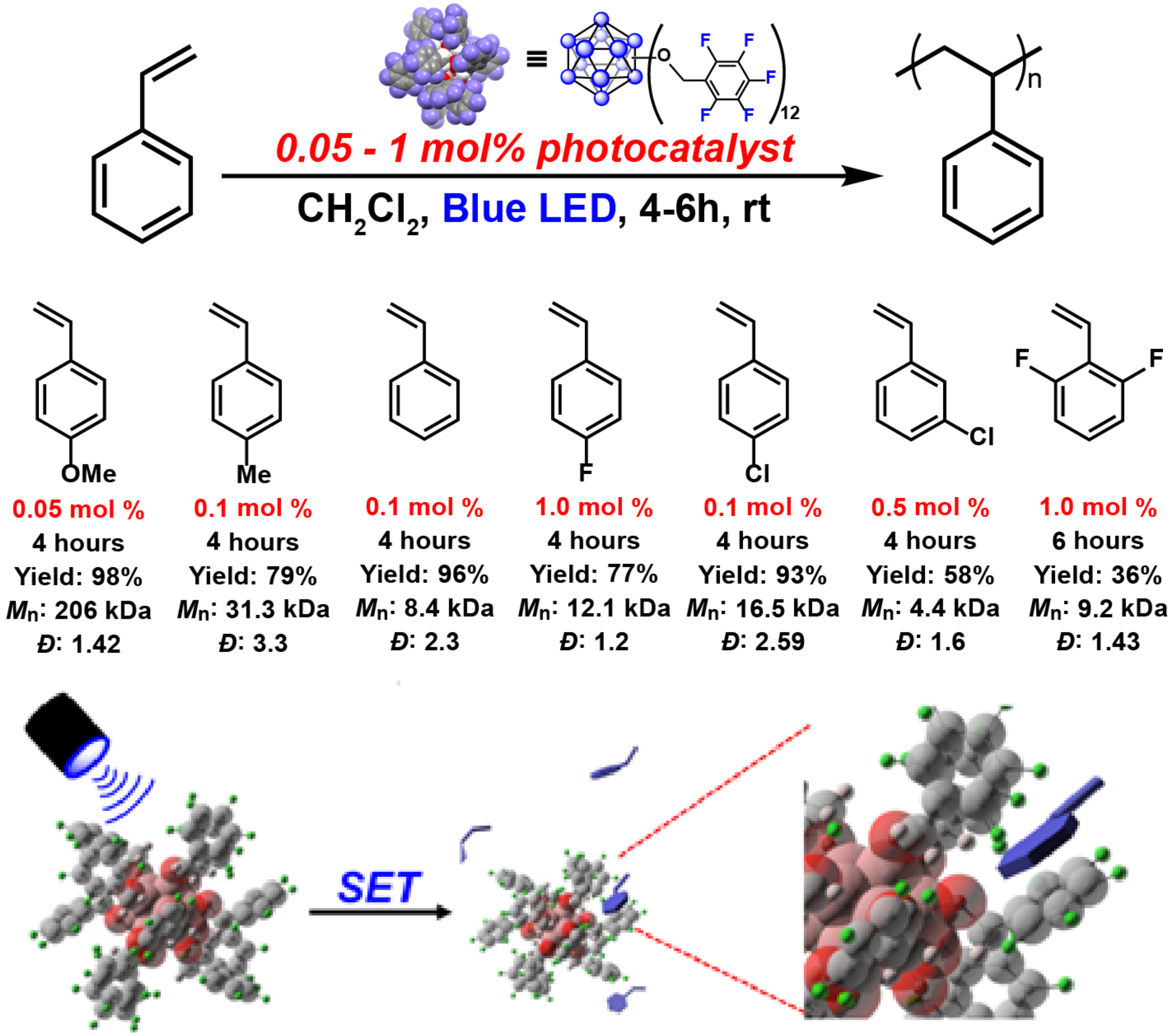


Figure 11. Photopolymerization of styrene derivatives utilizing compound **15**. Initial substrate scope with yields, average molecular weight, and polydispersity index.

These initial studies by collaborators have demonstrated the successful facile modifications to the cluster made possible by the developed microwave-assisted synthetic route yielding viable materials for the desired applications, and further studies for both applications are in progress. Immediate future work in new directions are based on exploiting the multivalent capabilities of the functionalized clusters for additional applications in several areas. One such application would be the formation of a tetrafluoroido-containing cluster to probe the multivalent halogen bonding interactions possible with such a cluster (Figure 12). This cluster would be synthesized using the general microwave synthetic procedure and utilizing a similar route to form the brominated reagent as shown in Figure 10. Recent studies have elucidated many possible applications incorporating XB halogen bonding, including the construction of molecular capsules[57], supramolecular rotors[58], and other molecular recognition scenarios[59]. The unique multivalent interactions a cluster-based approach allow could lead to interesting self-assembly of three-dimensional complexes of the perfunctionalized tetrafluoriodo cluster and various XB acceptors.

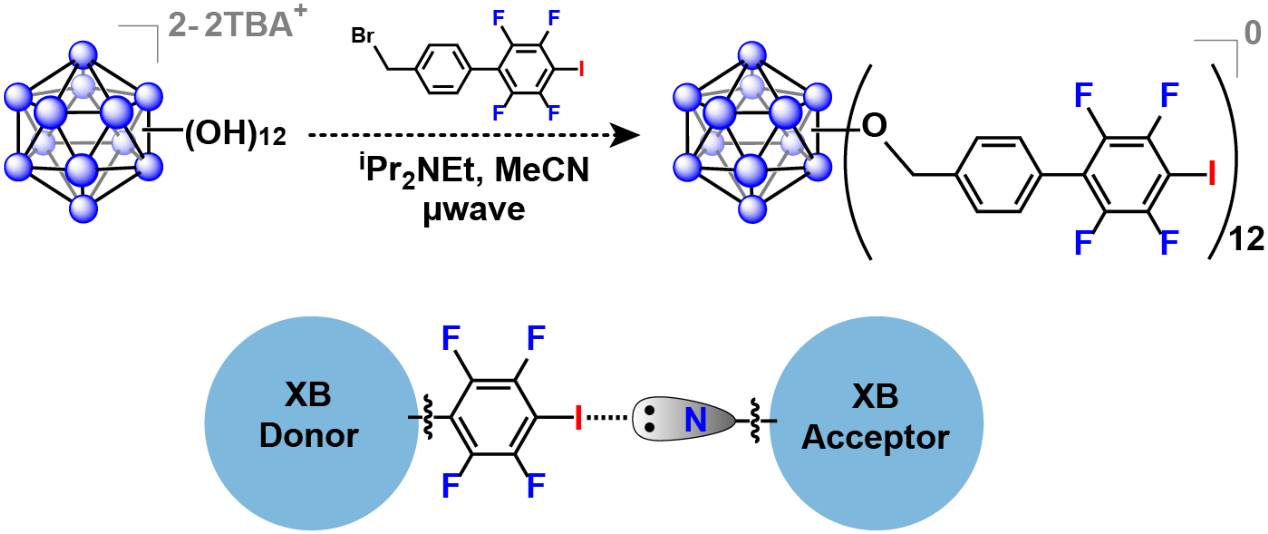


Figure 12. Synthesis of proposed tetrafluoroiodo perfunctionalized cluster (top); scheme of XB donor-acceptor halogen bonding (bottom).

Formation of new classes of charge transfer complexes with various tetrathiafulvalene (TTF) compounds could be another use for the clusters synthesized in this work, as any phenyl ring-containing species such as **2**, **9-13**, and **15** could potentially form charge transfer complexes with TTF compounds, provided the redox potential of the neutral cluster is high enough to oxidize the TTF to TTF$^+$. Initial NMR tube scale trials of this reaction with **15** have been promising, with early NMR spectroscopic data indicating the formation of a $[TTF]^+[\mathbf{15}]^-$ ion pair. Full characterization of this reaction product and reactions with other TTF compounds is ongoing.

Energy storage is yet another application these novel boron clusters could be used for, in two possible battery architectures. Flow batteries have been considered for large-scale energy storage, due to their design accommodating the creation of very large batteries without the hazards or complexities associated with traditional batteries.[60] The design of a flow battery is fairly simple (Figure 13), yet given the right anodic and cathodic materials the potential energy density can be quite high, and recent studies have shown remarkable progress in advancing the performance of such devices.[60–64] The molecules utilized in the anodic and cathodic chambers must be reversibly redox-active, stable compounds. The boron clusters synthesized in this work have exhibited redox potentials significantly higher than any previously reported $B_{12}(OR)_{12}$ clusters, so by utilizing a pair of clusters with widely separated oxidation potentials a flow battery could be constructed. The performance of such a device could potentially be improved as more clusters are developed with even higher redox potentials.

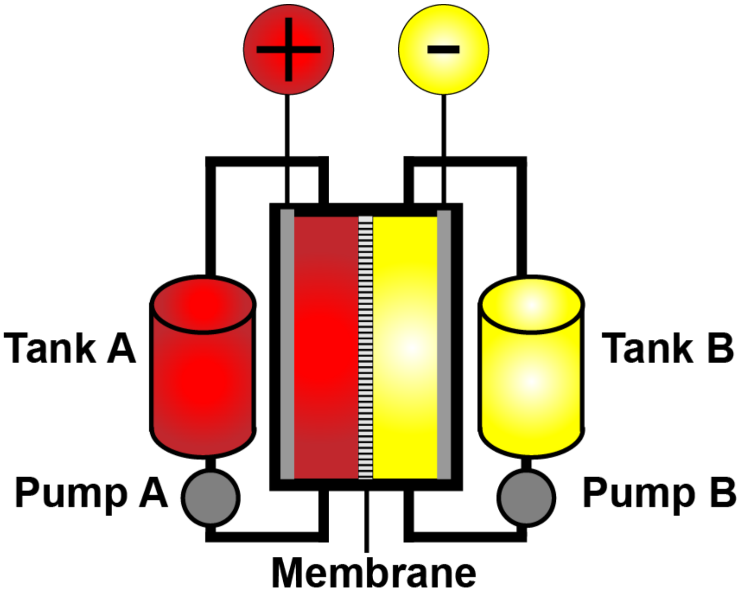


Figure 13. Flow battery general schematic, with anodic and cathodic chambers, pumps to circulate redox-active materials in solution past a membrane.

Flow batteries have the benefits of being easily scalable and simple to produce, but are not practical for use in smaller devices such as phones, tablets, and other personal electronics. Recent studies have demonstrated the successful formation of fully organic batteries utilizing nitroxyl radical polymers.[65] This class of battery could be extremely useful for many device applications where traditional rigid, heavy Li-ion or similar batteries are not suitable. Lightweight and flexible metal-free batteries could be invaluable for incorporation into many devices, though instability of the nitroxyl radical polymers utilized in current prototypes limits their immediate application. An alternative metal-free radical battery based on polymers containing redox-active stable radical icosahedral boron clusters (Figure 14) would potentially alleviate the stability issues due to the more robust nature of the boron clusters, while also allowing higher voltage performance due to the tunable wide redox potential window of the substituted $B_{12}(OR)_{12}$ clusters. A proposed first prototype based on this architecture would contain two different synthesized clusters with polymerizable functional groups. This would allow for photoinduced polymerization on the surface of indium tin oxide (ITO)-coated polyethylene terephthalate (PET) with a thin layer of electrolyte sandwiched in between the different cluster polymer layers (Figure 14). Two potential candidates among those synthesized so far would be the perfunctionalized allyl cluster (**3**) as one half of the cell, with a vinyl-containing derivative of the vertex-differentiated cluster **14** as the opposing half. This 4-vinylbenzyl cluster derivative (**17**, Figure 14) was successfully synthesized by employing the methods developed for **14** and exchanging the benzyl bromide for 4-vinylbenzyl bromide. Once again, this demonstrates the kind of facile modifications to form novel cluster derivatives with desired properties (in this case a single polymerizable terminal alkene) enabled by our microwave-assisted method. Both **3** and **17** are readily soluble in organic solvents, so *via* spin-coating or drop-casting a layer of each could be deposited onto PET substrates and photopolymerized with UV light similarly to the preparation methods used in the aforementioned nitroxyl-based fully-organic metal-free battery.[65]

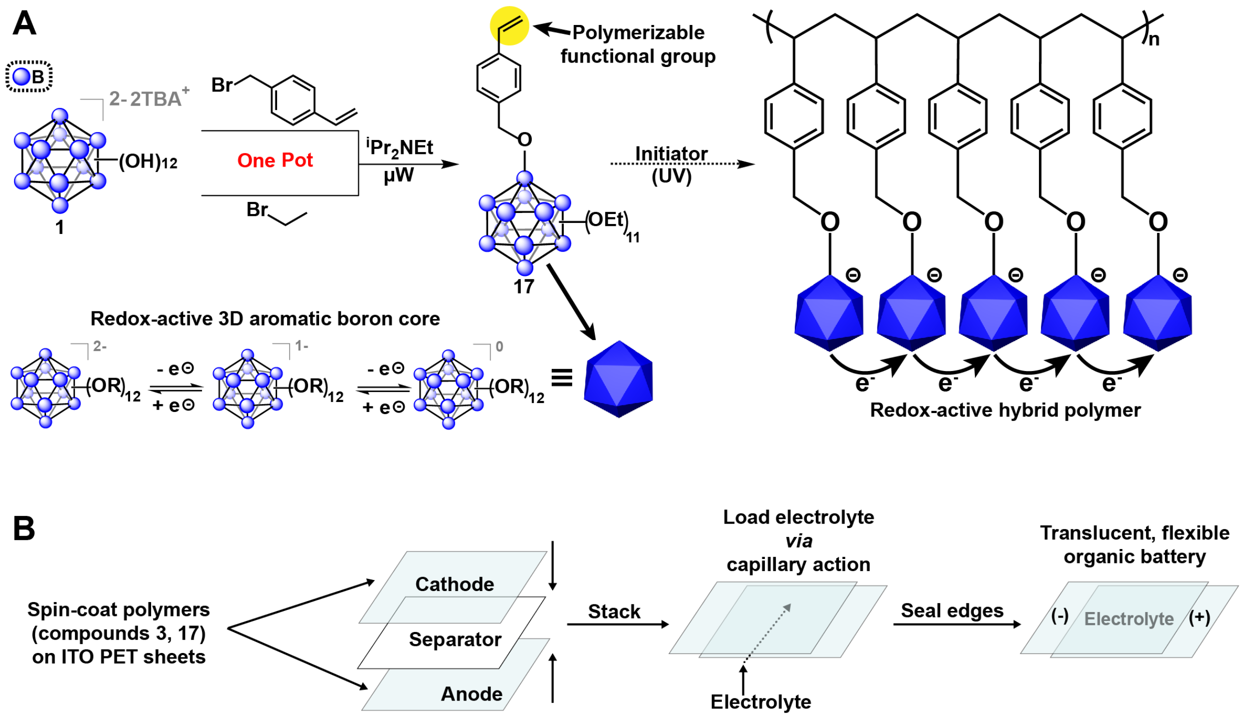


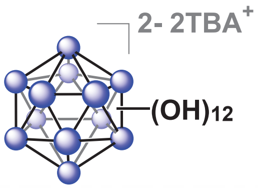
Figure 14. Scheme for synthesis of compound **17** (A) and proposed polymerization; schematic of a radical translucent, flexible organic battery from polymerized compounds **3** and **17**.

The boron cluster-containing polymers for the cathode and anode could both be rationally tuned for optimal performance, as the substituents attached to the boron core have been demonstrated to significantly modify the redox potential[39], and the backbone polymer could also be modified for enhanced performance.

Chapter 4: Conclusion

In conclusion, a new microwave-based method for synthesizing $B_{12}(OR)_{12}$ derivatives under ambient conditions was demonstrated. This method was successfully employed to synthesize several known derivatives with significantly reduced reaction times compared to previously reported protocols, while completely eliminating the need for handling in inert atmosphere. Additionally, the robust nature of the microwave-assisted synthesis method allowed the formation of novel $B_{12}(OR)_{12}$ species with diverse substituents for targeted applications. Hybrid vertex-differentiated $B_{12}(OR)_{11}(OR')$ clusters were also synthesized *via* a one-pot, single-step reaction, previously inaccessible except through lengthy multi-step protocols. There are many exciting applications for these newly developed $B_{12}(OR)_{12}$ clusters, with very promising initial results meriting further investigation. The targeted synthesis of clusters with specific functional groups for desired applications using the developed microwave method allows for significantly more rapid investigation of new research directions. The primary focus of the immediate future work utilizing this system will be exploring the possible multivalent interactions enabled by the three-dimensional nature of the perfunctionalized cluster.

Supplementary Spectra



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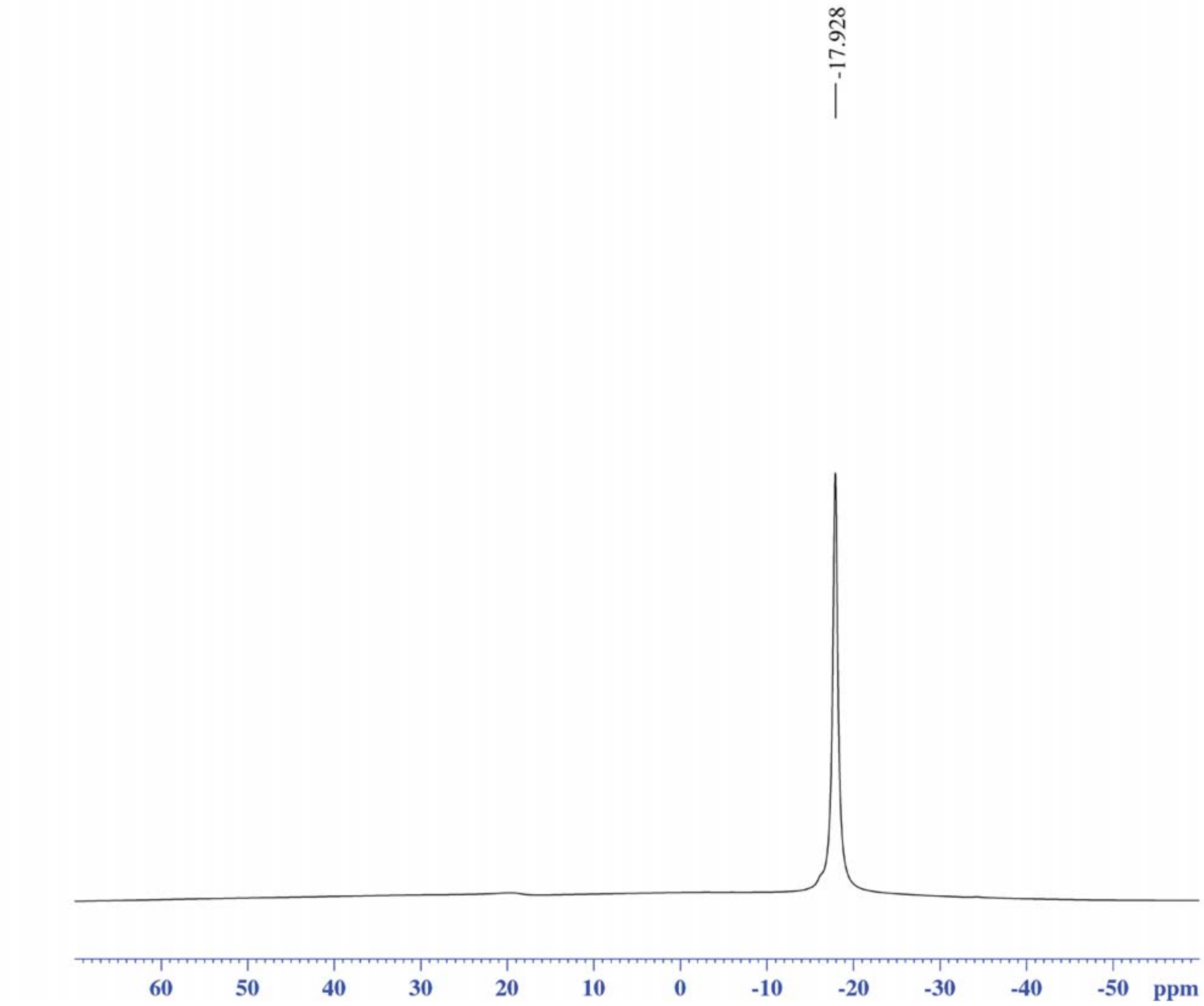

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PLW12      0.36111000 W

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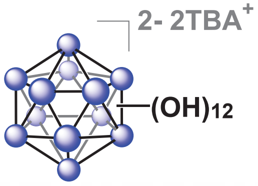

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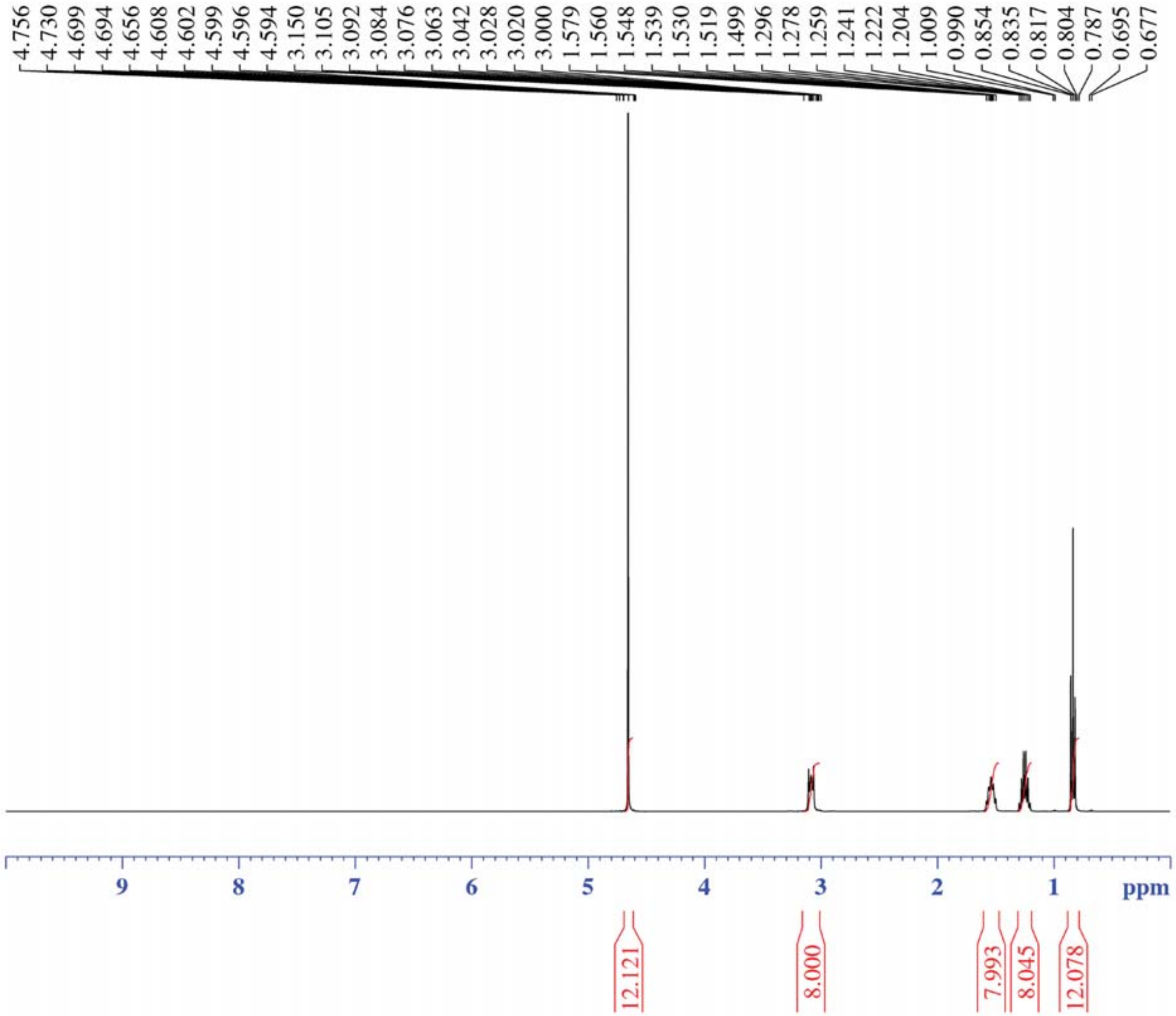

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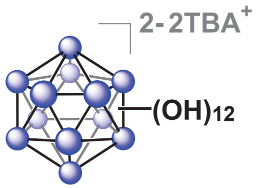
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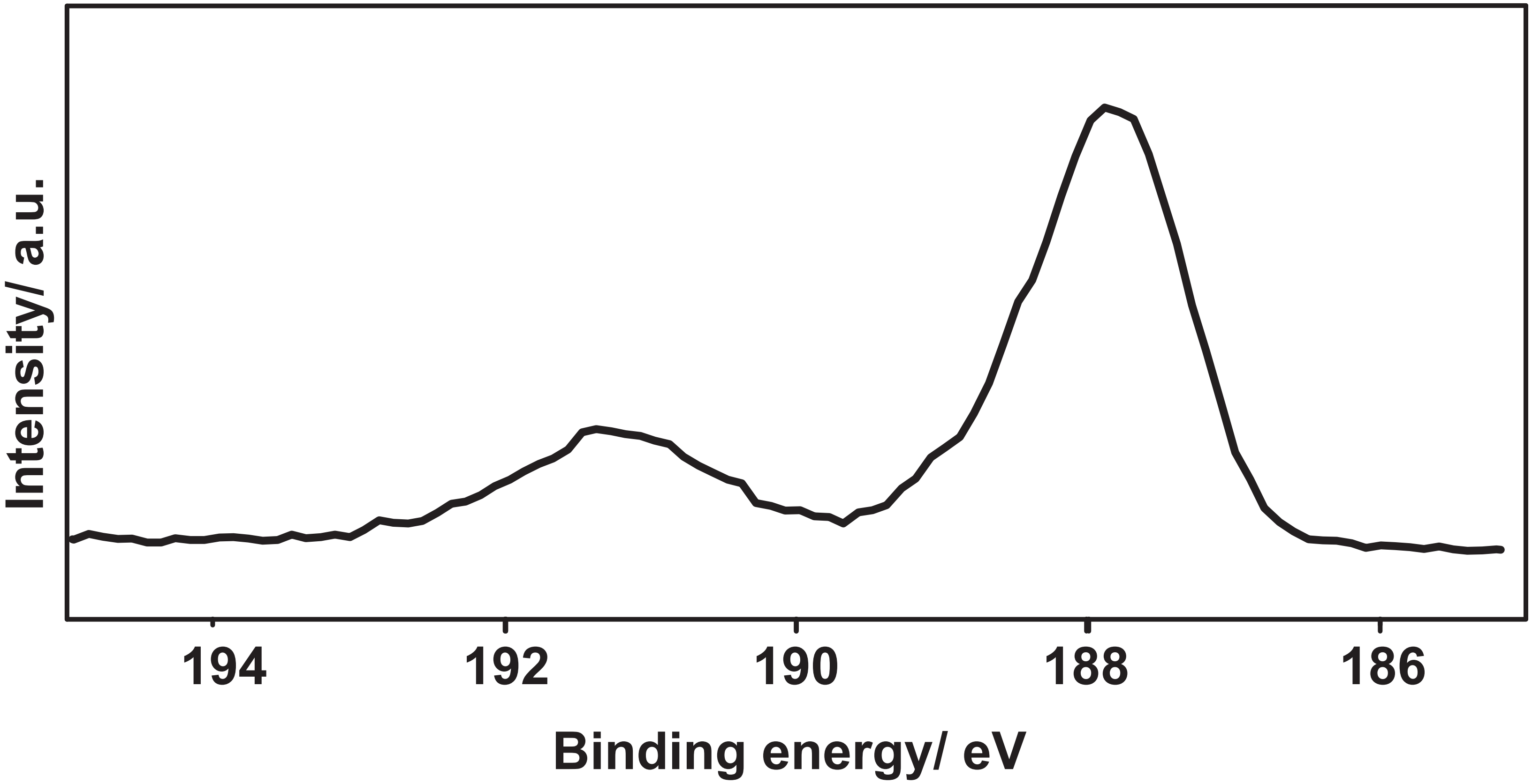
(OH)$_{12}$

B 1s XPS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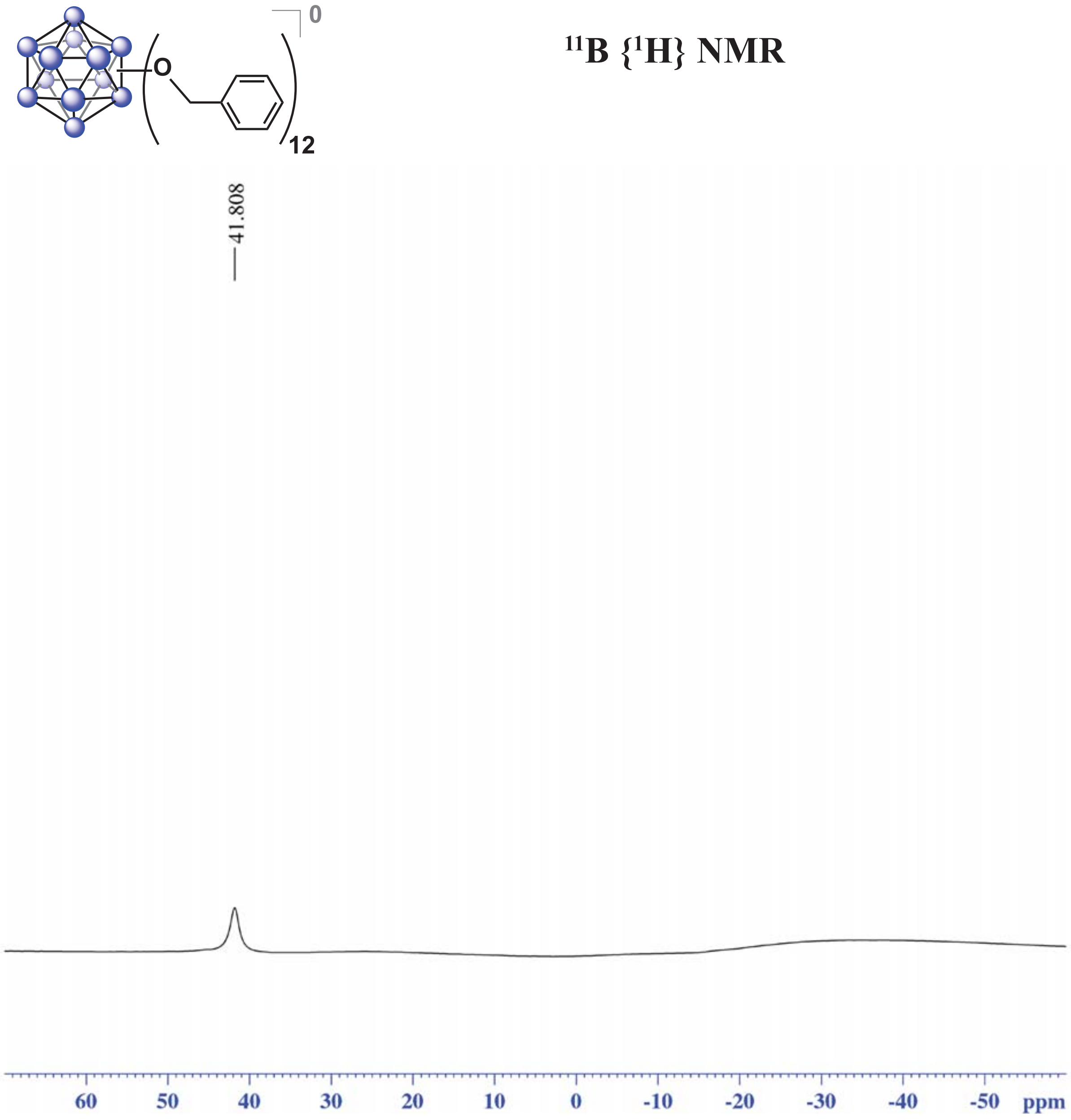
Binding energy/ eV



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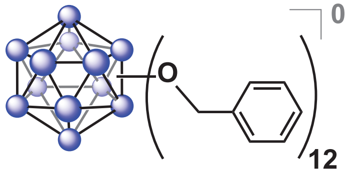

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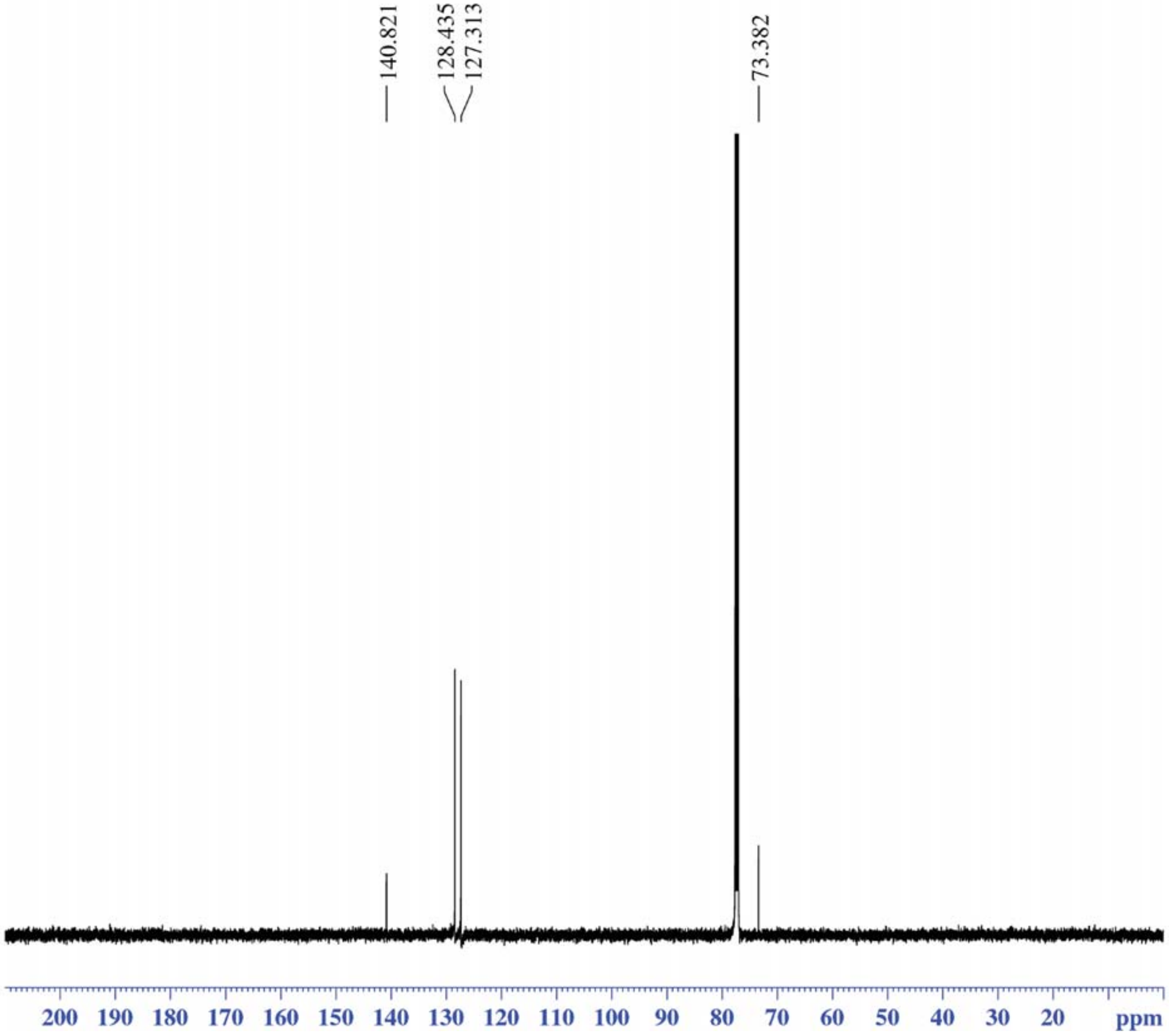

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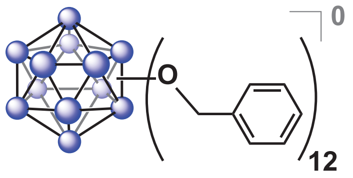

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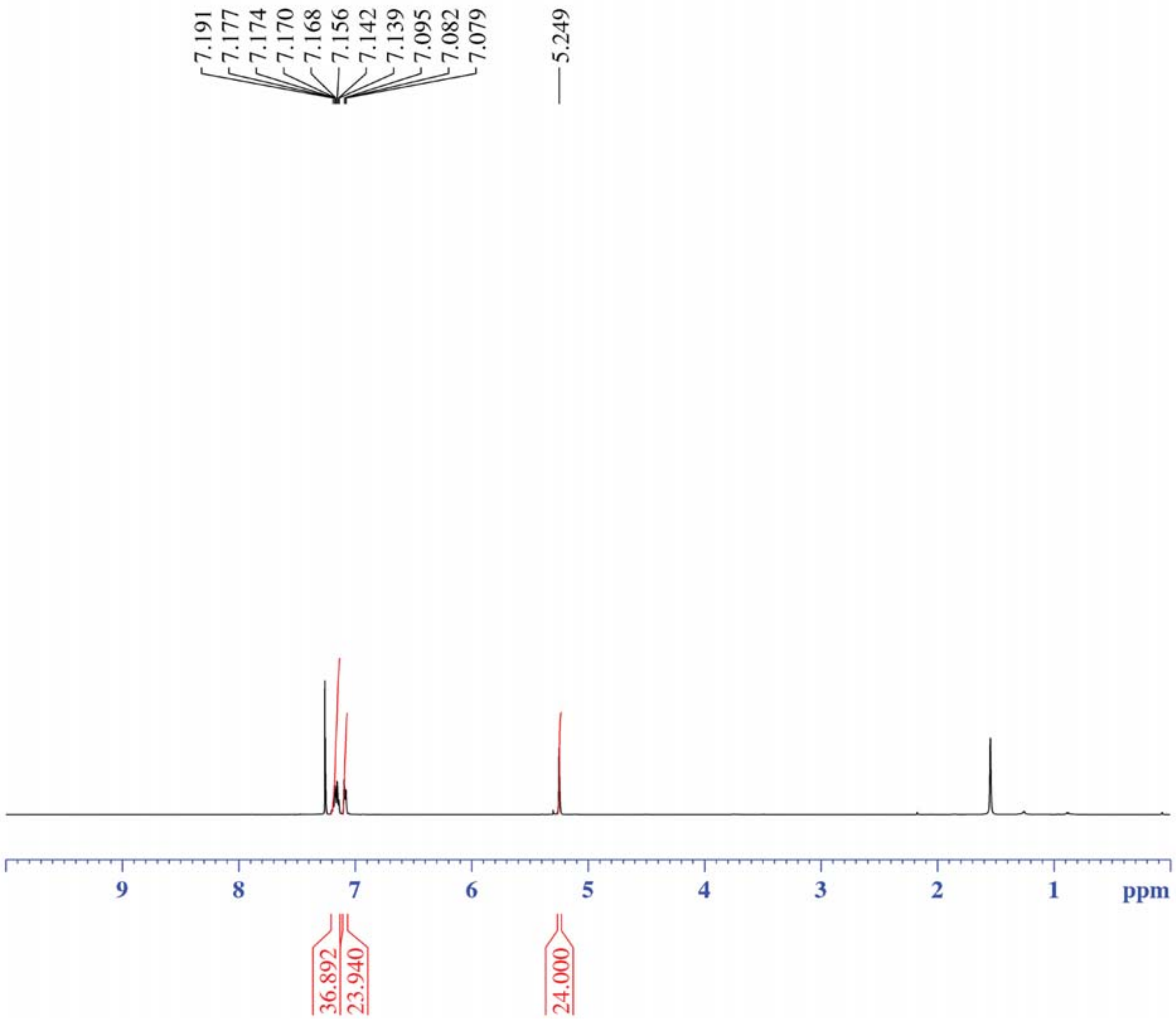

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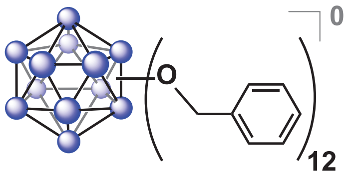

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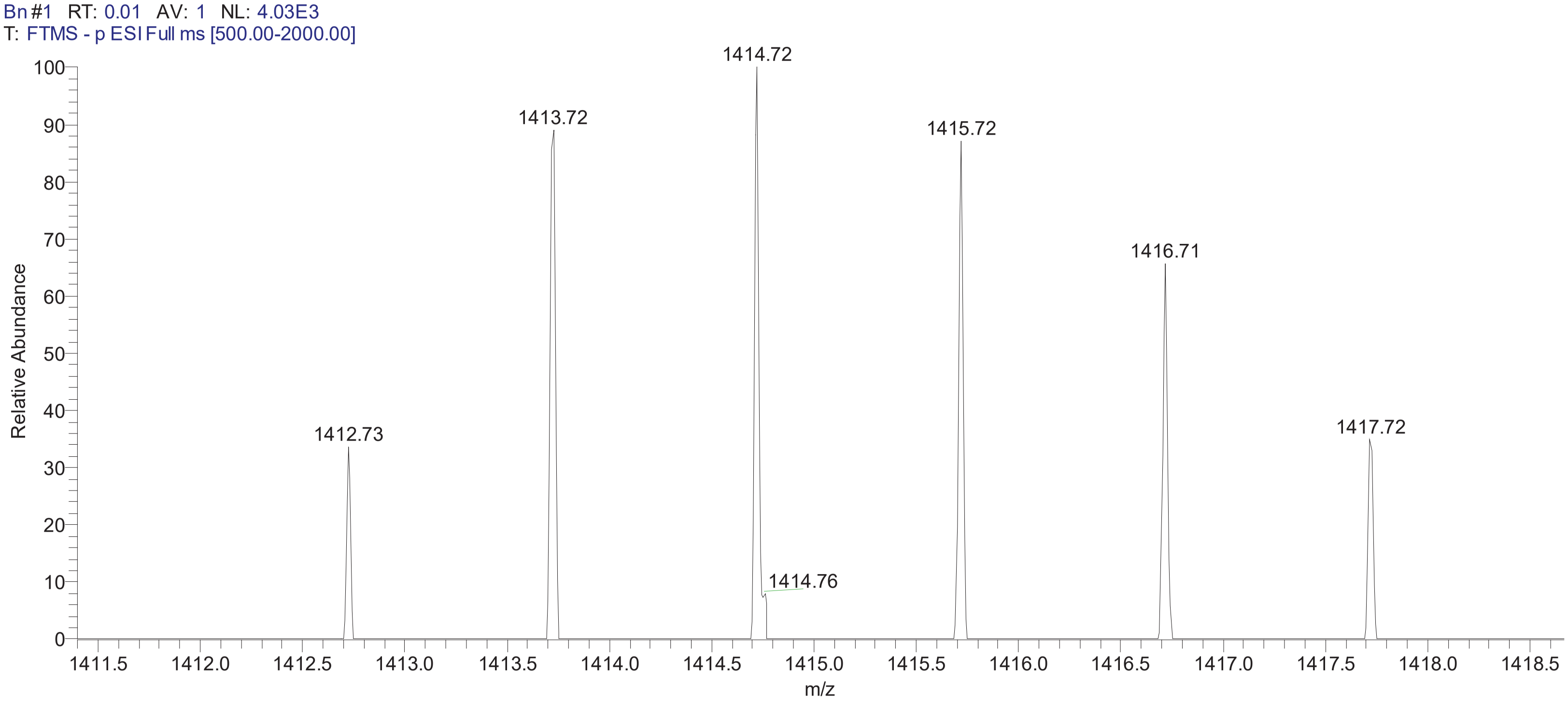

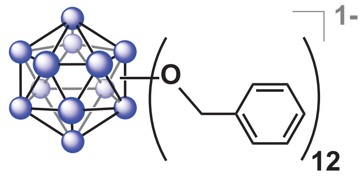

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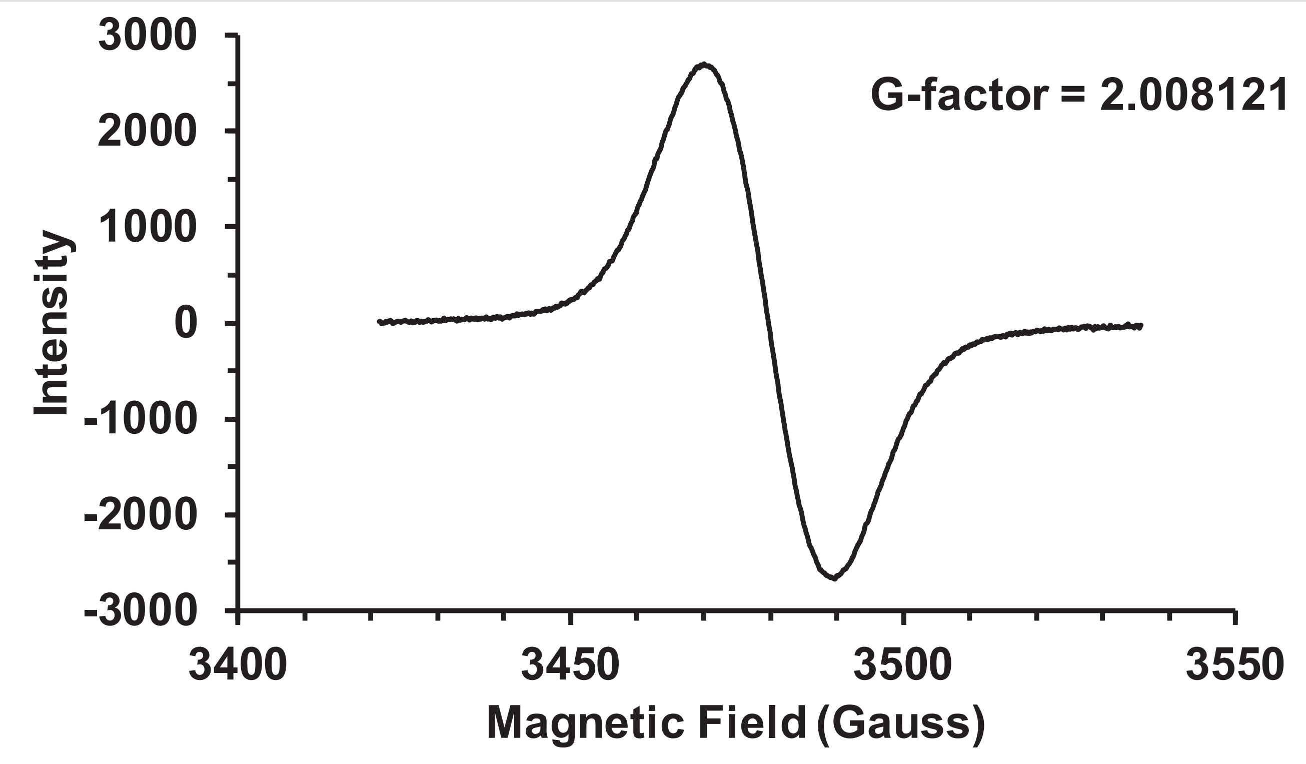

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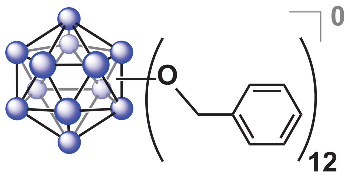

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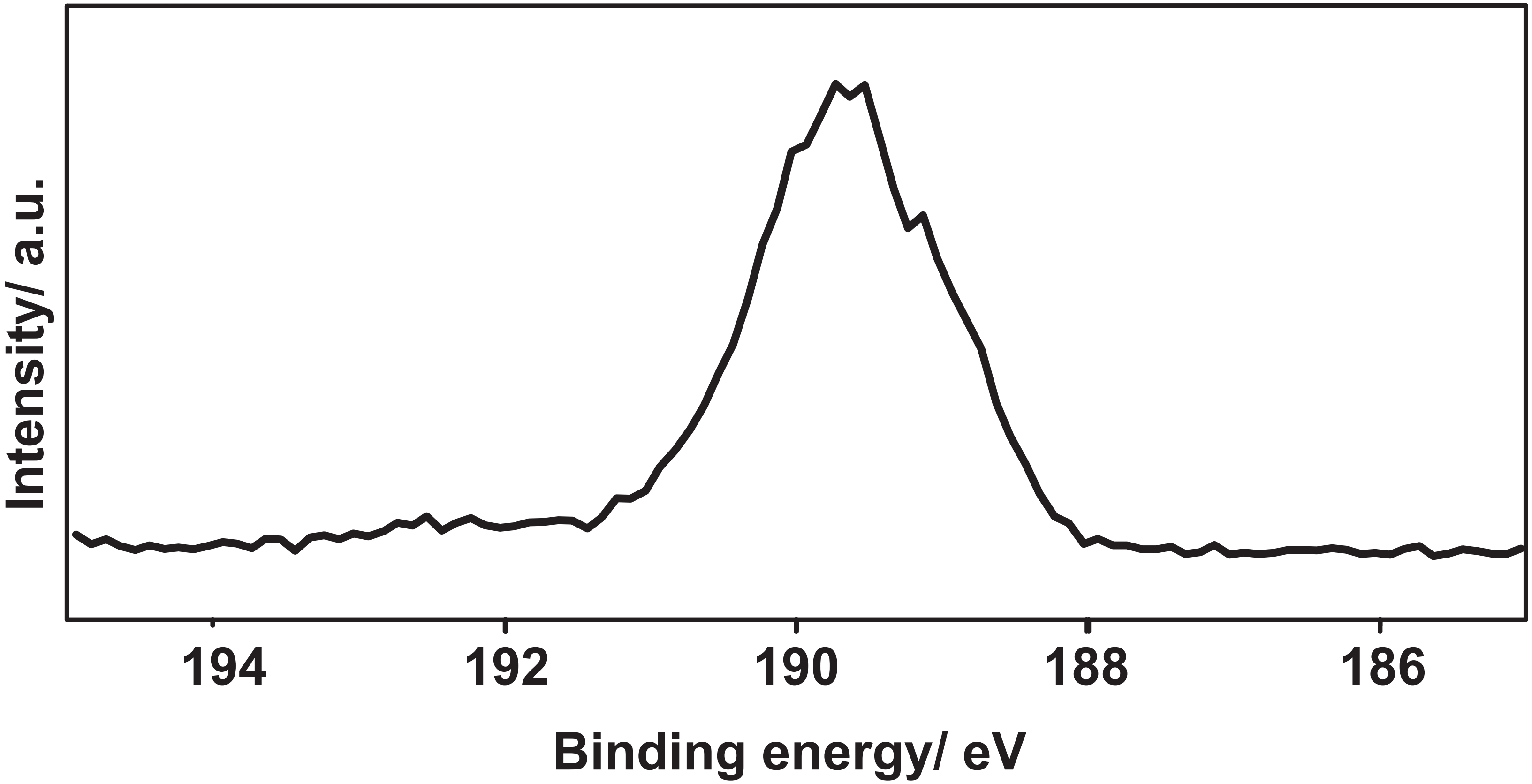
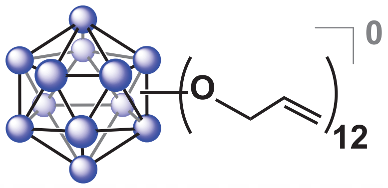
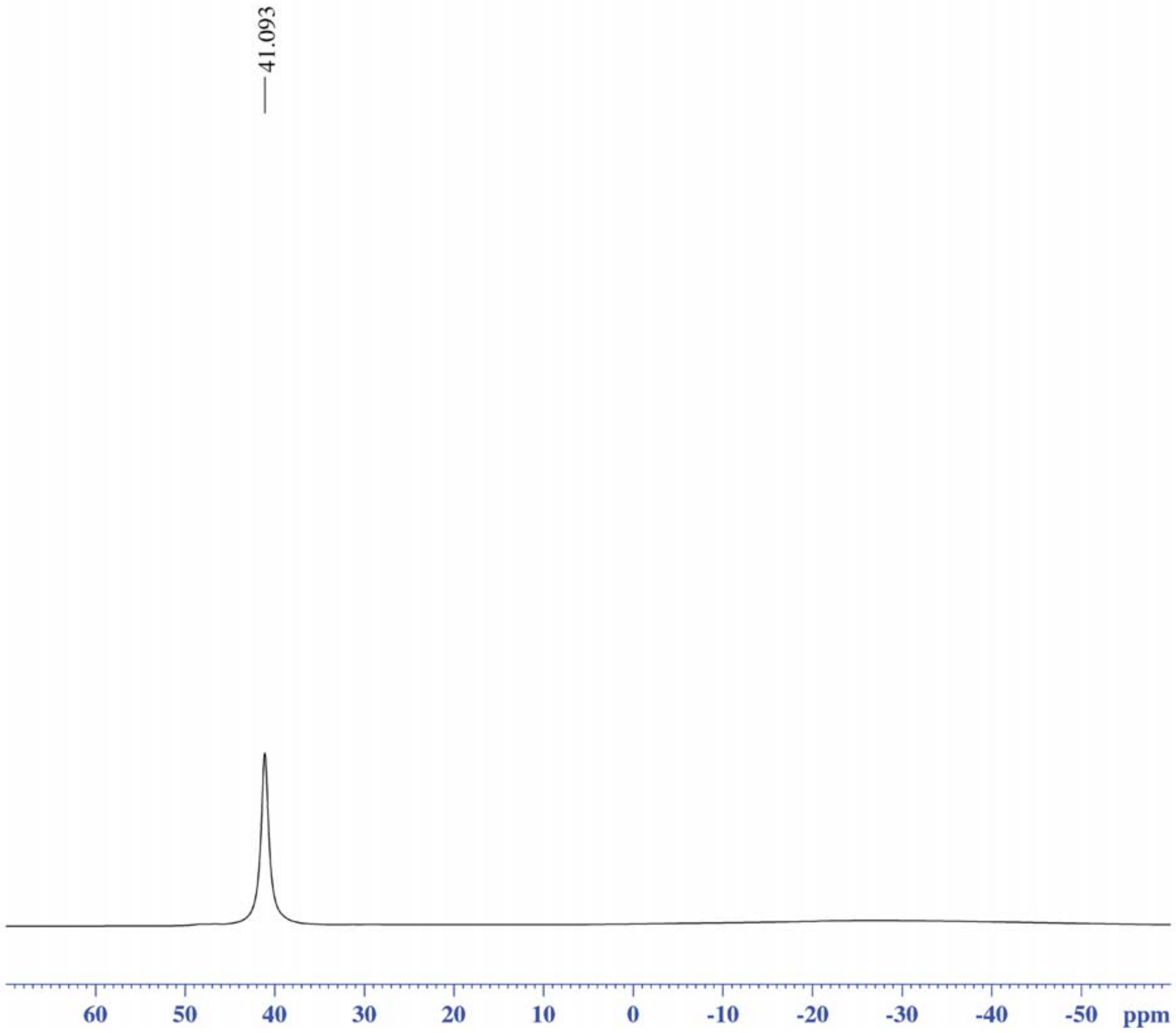




$^{11}B\ \{^{1}H\}$ NMR



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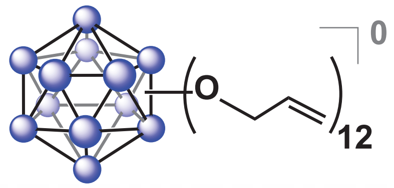

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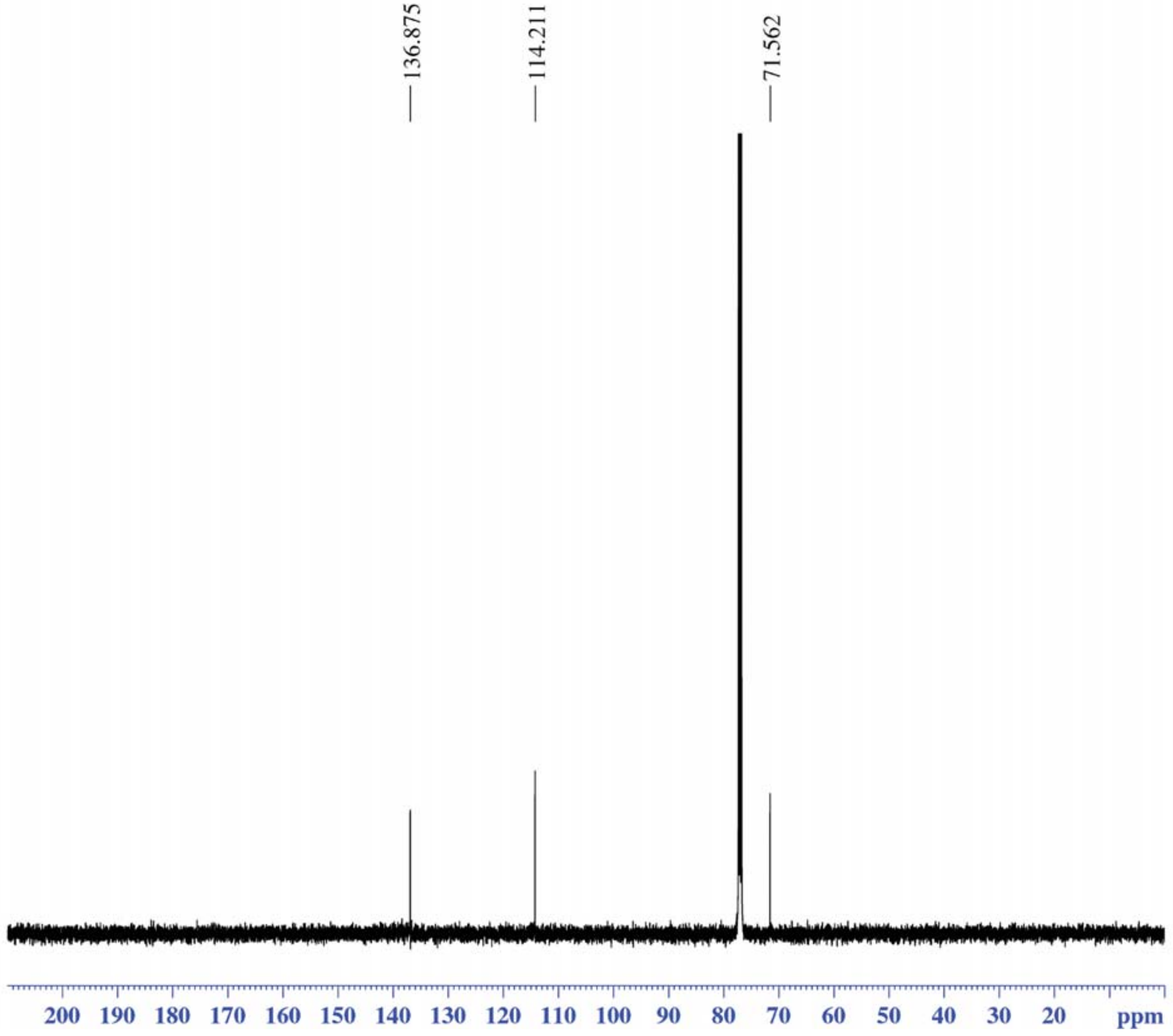

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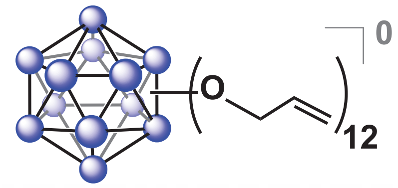

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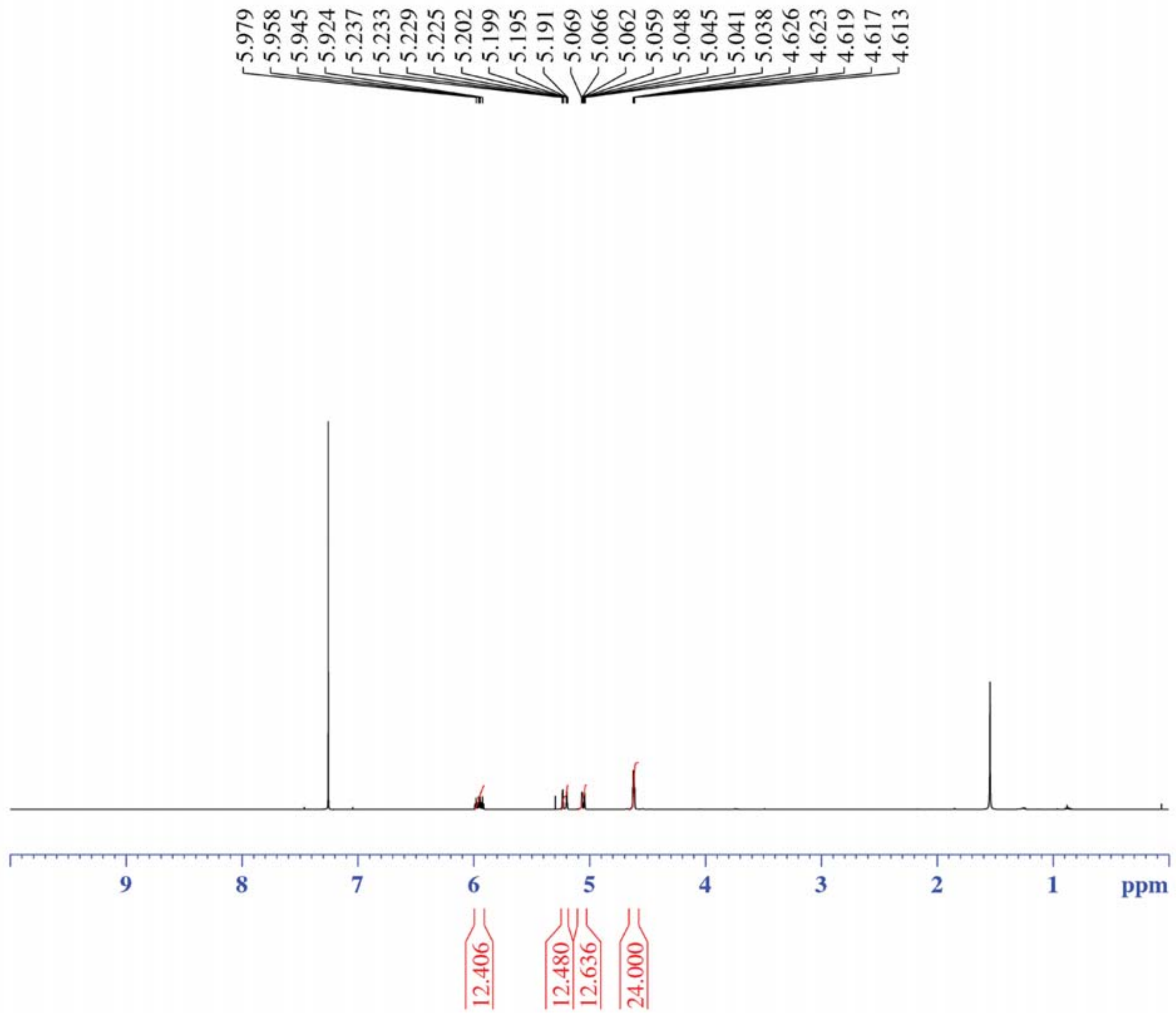

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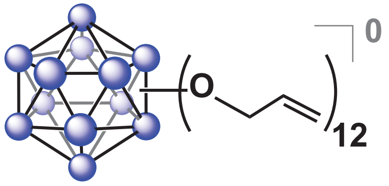
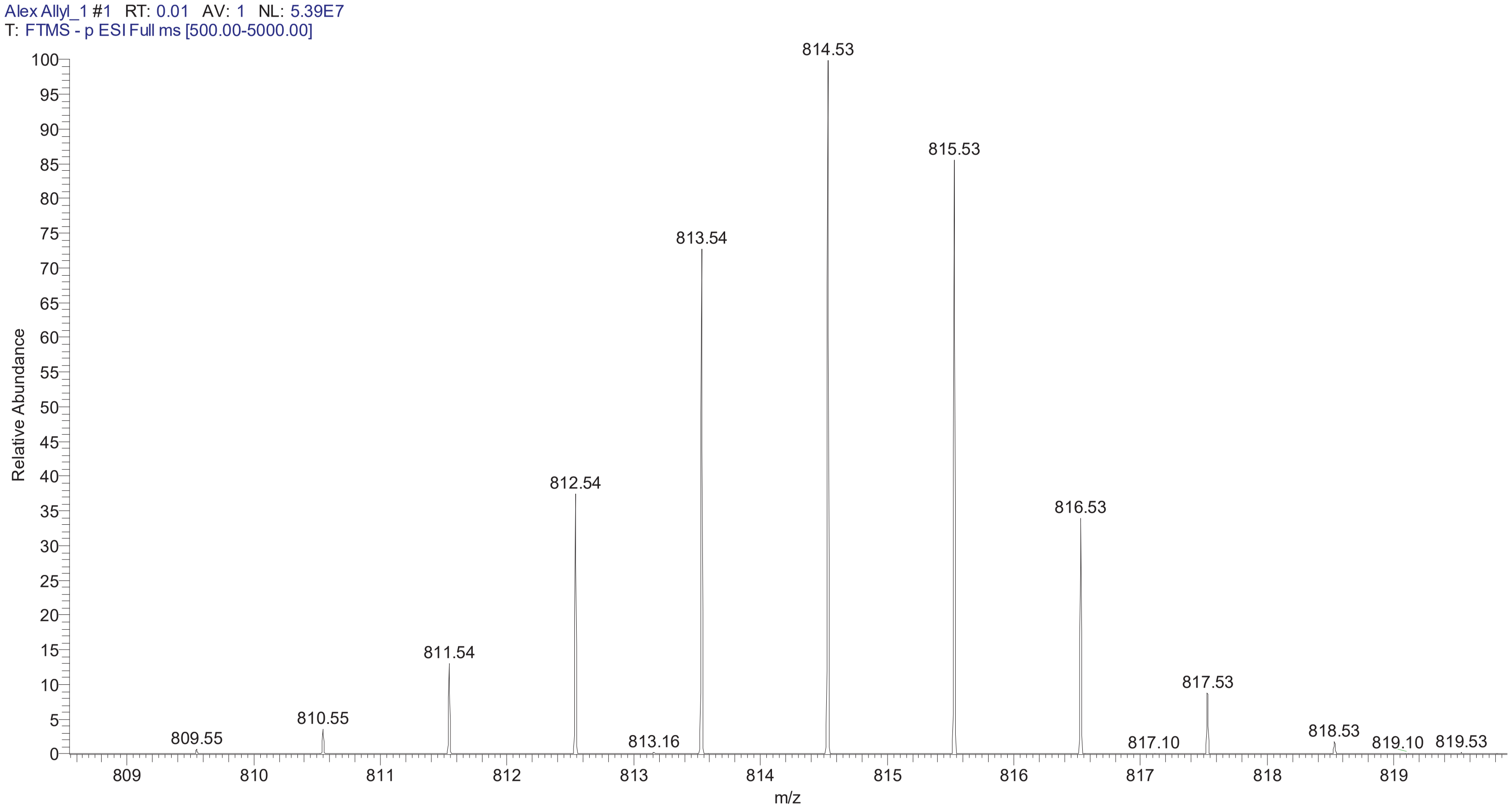
SFO1      500.1330008 MHz
NUC1                1H
P1               10.00 usec
PLW1       13.50000000 W

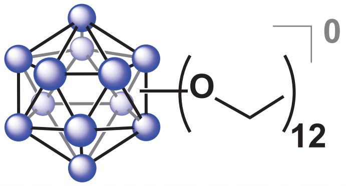
F2 - Processing parameters
SI               65536
SF        500.1300146 MHz
WDW                 EM
SSB     0
LB                0.30 Hz
GB      0
PC                1.00
```

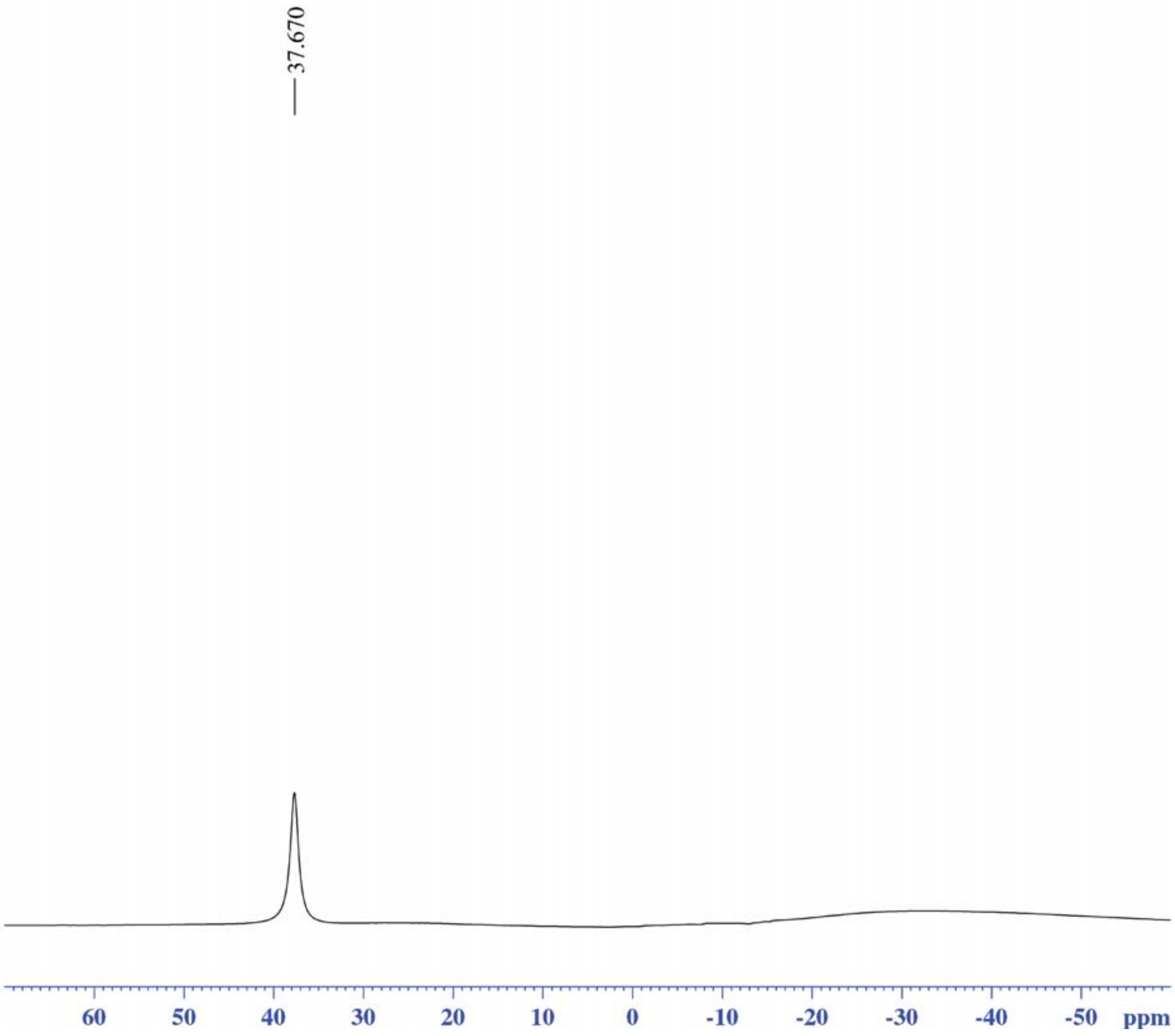


Q Exactive
High-Res Mass Spec



$^{11}B\ \{^1H\}$ NMR





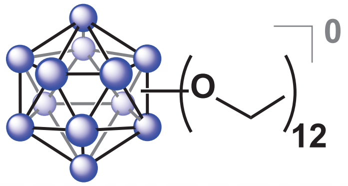
```
Current Data Parameters
NAME        B12(O-Et)12
EXPNO              100
PROCNO               1

F2 - Acquisition Parameters
Date_         20150412
Time             19.11
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG        zgdc.js
TD                5096
SOLVENT          CDCl3
NS                1024
DS                   0
SWH         51020.406 Hz
FIDRES      10.011854 Hz
AQ          0.0499408 sec
RG             189.85
DW              9.800 usec
DE               6.50 usec
TE              299.1 K
D1         0.00000400 sec
D11        0.03000000 sec
TD0                  1

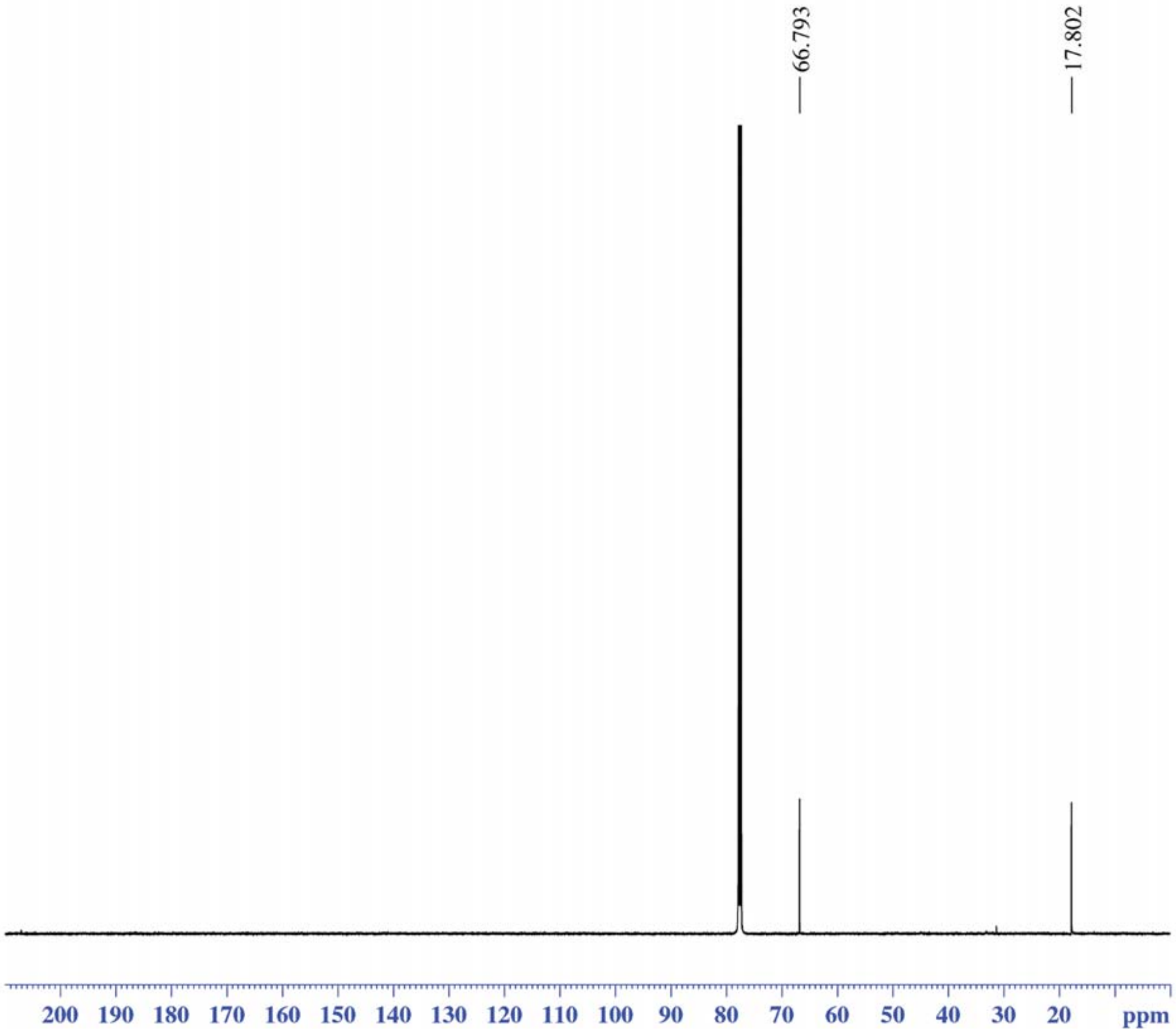
======== CHANNEL f1 ========
SFO1      128.3776052 MHz
NUC1              11B
P1              10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 ========
SFO2      400.1324008 MHz
NUC2               1H
CPDPRG[2          waltz16
PCPD2           90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W

F2 - Processing parameters
SI               32768
SF        128.3776050 MHz
WDW                 EM
SSB      0
LB              50.00 Hz
GB       0
PC               1.40
```



^{13}C NMR



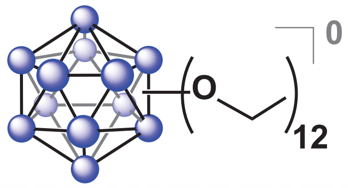
```
Current Data Parameters
NAME        B12(O-Et)12
EXPNO              10
PROCNO              1

F2 - Acquisition Parameters
Date_        20150420
Time            21.23
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT          CDCl3
NS                 64
DS                  2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ         1.0485760 sec
RG             204.54
DW             16.000 usec
DE              18.00 usec
TE              298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

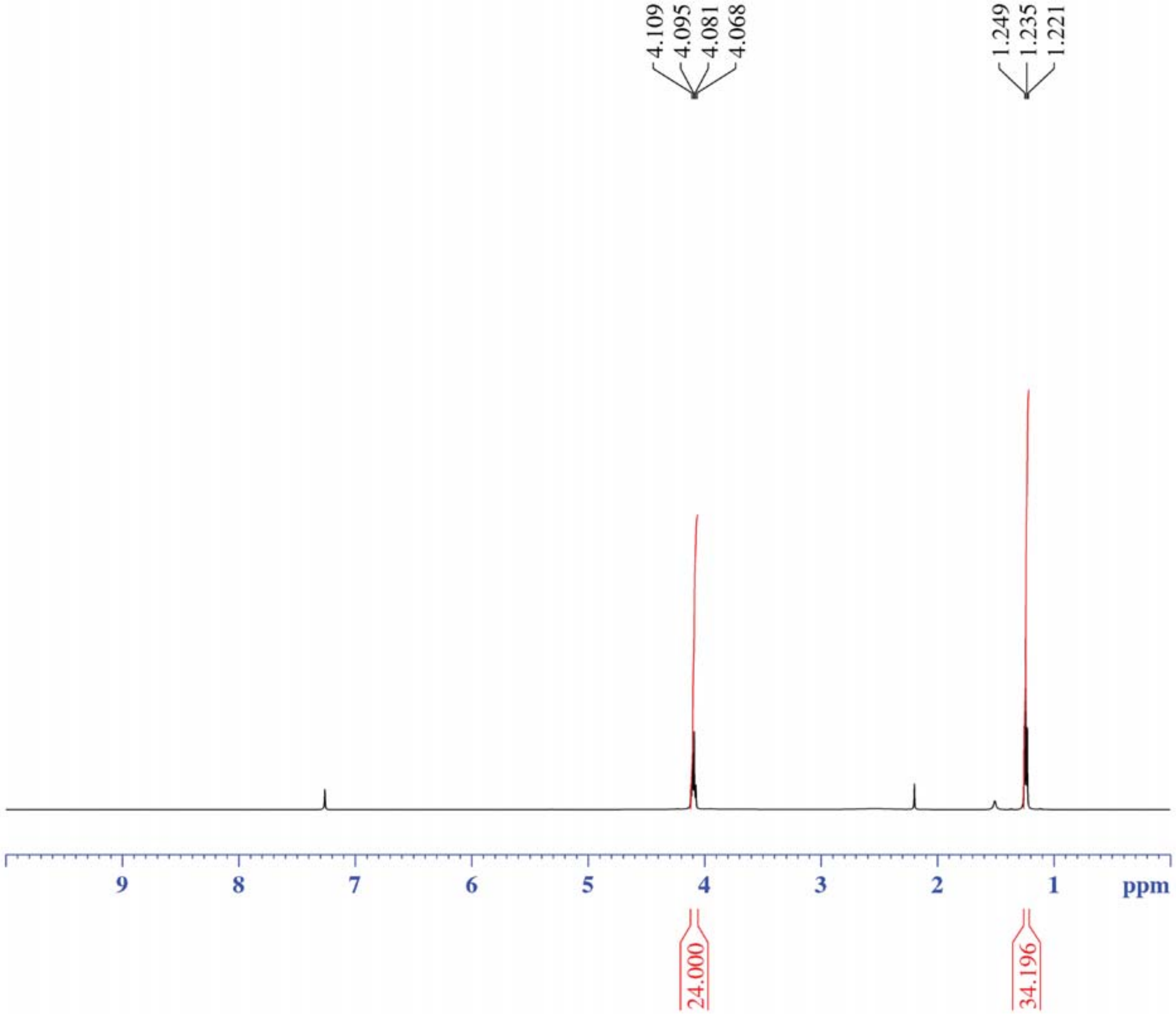
======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec
PLW1      23.00000000 W

======== CHANNEL f2 ========
SFO2      500.1330008 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           80.00 usec
PLW2      13.50000000 W
PLW12      0.21094000 W
PLW13      0.13500001 W

F2 - Processing parameters
SI             131072
SF        125.7577890 MHz
WDW                EM
SSB     0
LB              1.00 Hz
GB      0
PC              1.40
```



^{1}H NMR

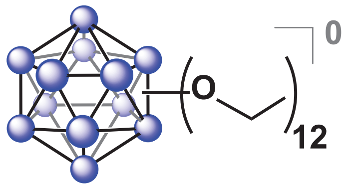


```
Current Data Parameters
NAME       B12(O-Et)12
EXPNO              11
PROCNO              1

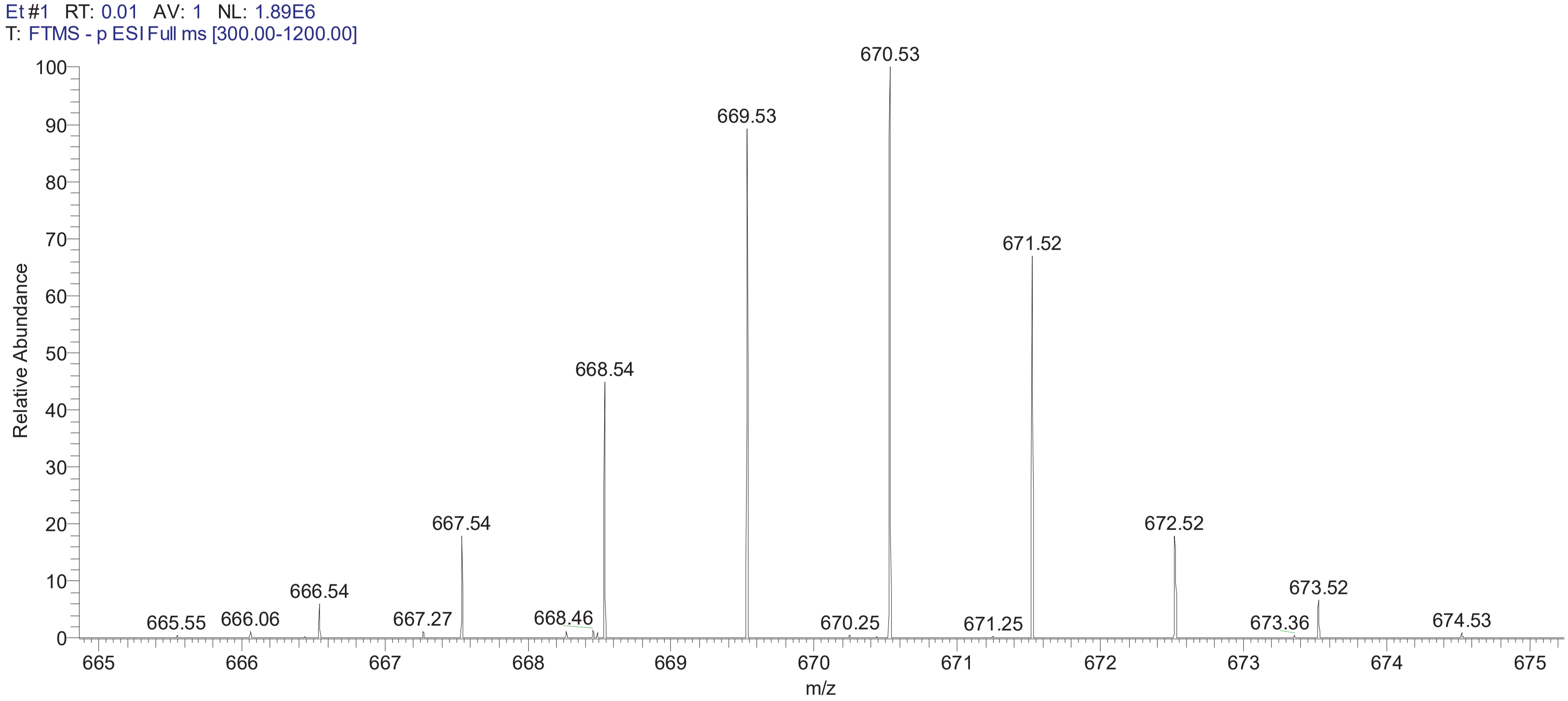
F2 - Acquisition Parameters
Date_        20150420
Time            21.30
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 64
DS                  0
SWH      10000.000 Hz
FIDRES    0.152588 Hz
AQ       3.2767999 sec
RG              52.41
DW         50.000 usec
DE          10.00 usec
TE            298.0 K
D1     2.00000000 sec
TD0                 1

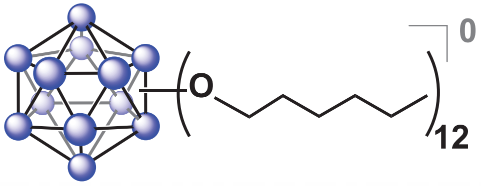
======== CHANNEL f1 ========
SFO1    500.1330008 MHz
NUC1               1H
P1          10.00 usec
PLW1    13.50000000 W

F2 - Processing parameters
SI              65536
SF      500.1300115 MHz
WDW                EM
SSB    0
LB            0.30 Hz
GB     0
PC               1.00
```

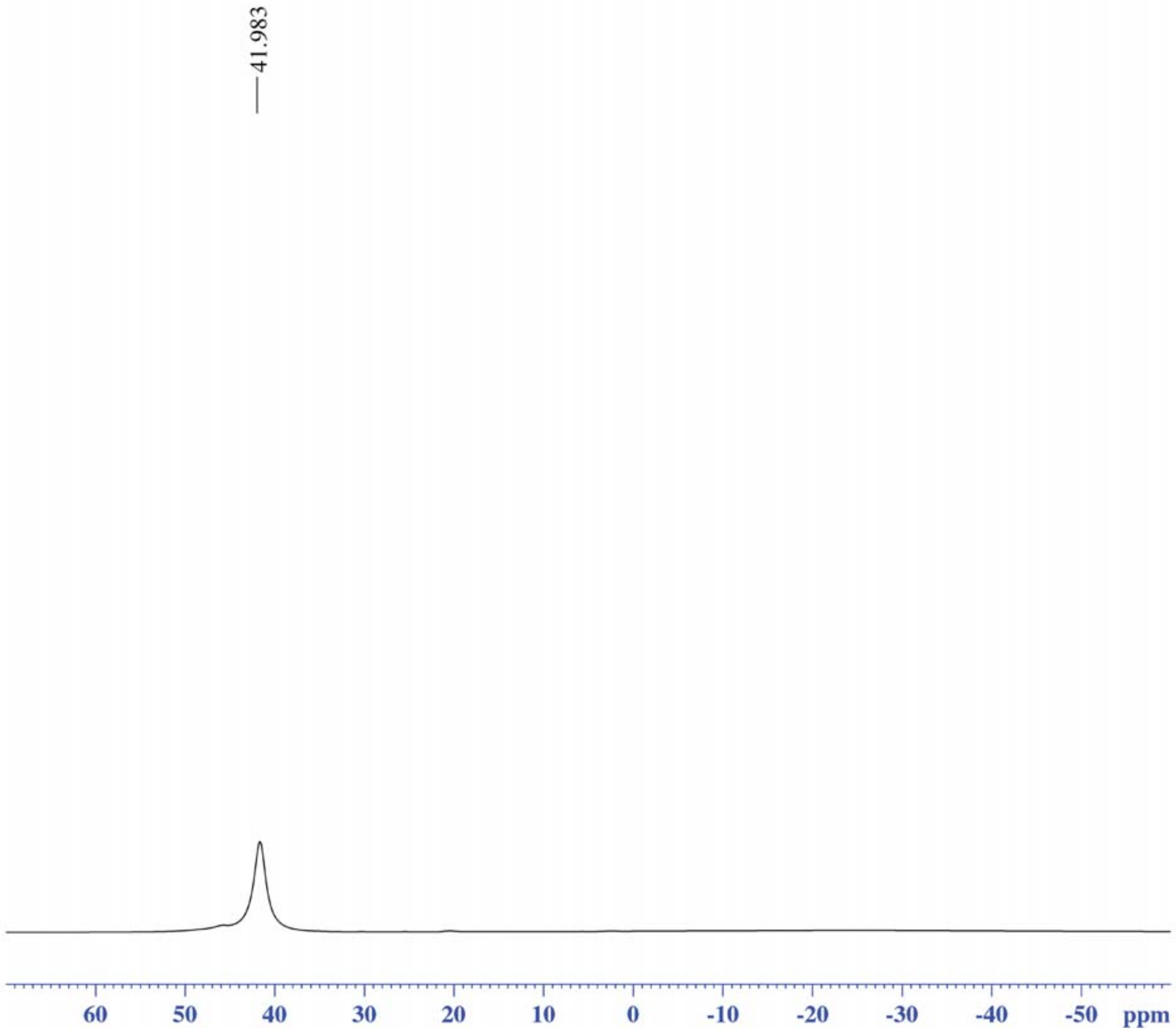


Q Exactive
High-Res Mass Spec





^{11}B {^{1}H} NMR



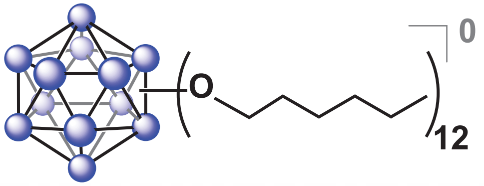
```
Current Data Parameters
NAME     B12(O-Hexyl)12
EXPNO              20
PROCNO              1

F2 - Acquisition Parameters
Date_         20150610
Time             15.09
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG        zgdc.js
TD                5096
SOLVENT          CDCl3
NS                1024
DS                   0
SWH        51020.406 Hz
FIDRES     10.011854 Hz
AQ        0.0499408 sec
RG              189.85
DW           9.800 usec
DE            6.50 usec
TE             299.2 K
D1      0.00000400 sec
D11     0.03000000 sec
TD0                  1

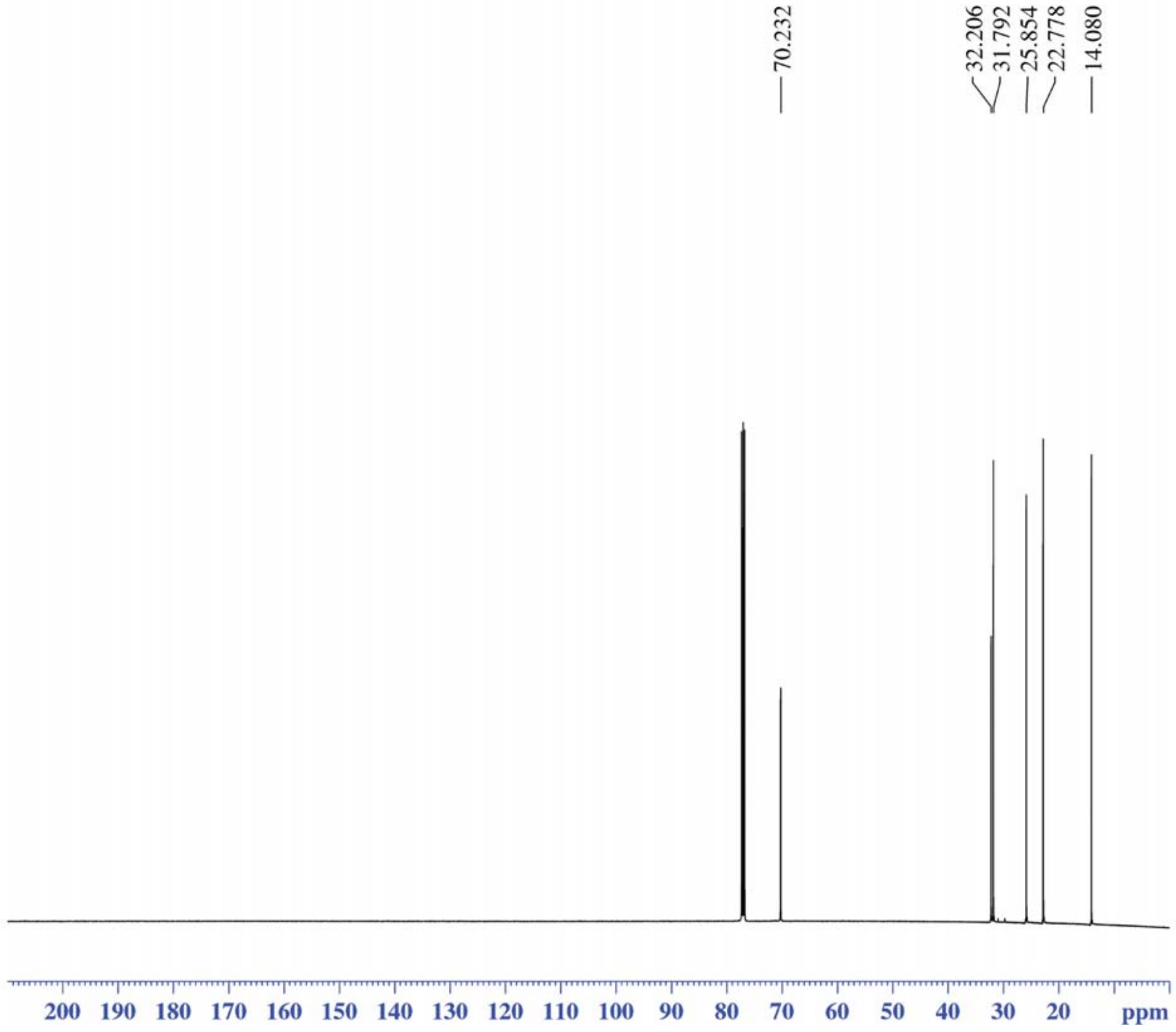
======== CHANNEL f1 ========
SFO1     128.3776052 MHz
NUC1               11B
P1            10.00 usec
PLW1       52.00000000 W

======== CHANNEL f2 ========
SFO2     400.1324008 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2         90.00 usec
PLW2       13.00000000 W
PLW12       0.36111000 W

F2 - Processing parameters
SI               32768
SF       128.3776050 MHz
WDW                 EM
SSB    0
LB            50.00 Hz
GB     0
PC                1.40
```



^{13}C NMR



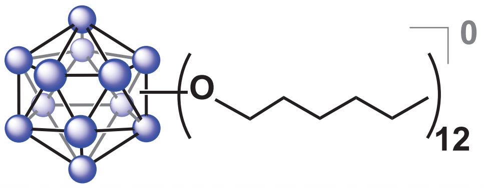
```
Current Data Parameters
NAME     B12(O-Hexyl)12
EXPNO              200
PROCNO               1

F2 - Acquisition Parameters
Date_          20150829
Time              20.52
INSTRUM           av500
PROBHD   5 mm DCH 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH          31250.000 Hz
FIDRES        0.476837 Hz
AQ           1.0485760 sec
RG               204.54
DW               16.000 usec
DE                18.00 usec
TE                298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1

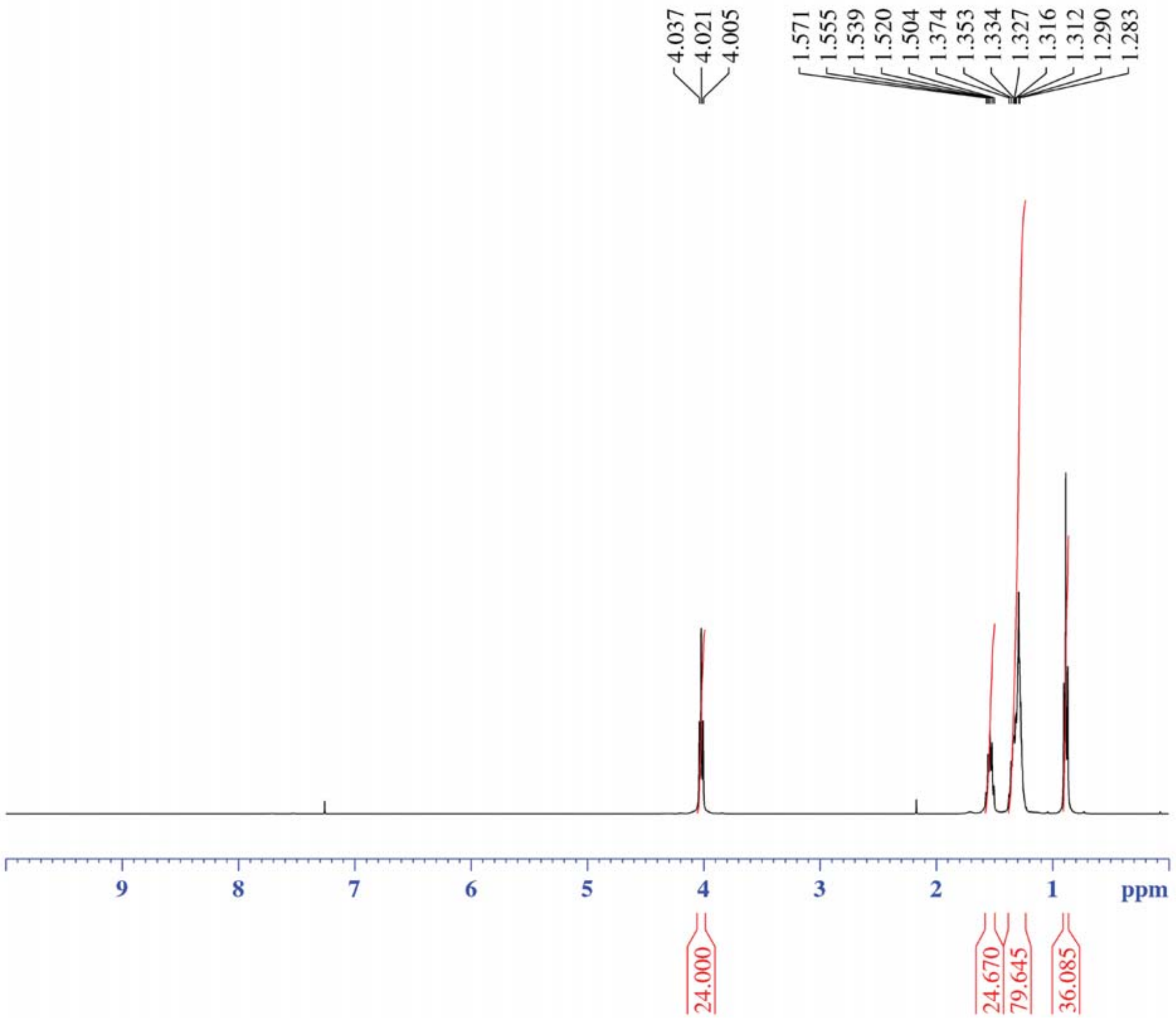
======== CHANNEL f1 ========
SFO1        125.7722511 MHz
NUC1                13C
P1                 9.63 usec
PLW1        23.00000000 W

======== CHANNEL f2 ========
SFO2        500.1330008 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        13.50000000 W
PLW12        0.21094000 W
PLW13        0.13500001 W

F2 - Processing parameters
SI               131072
SF          125.7577890 MHz
WDW                  EM
SSB     0
LB                 1.00 Hz
GB      0
PC                 1.40
```



^{1}H NMR

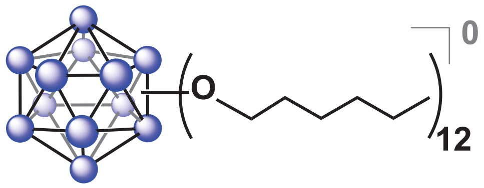


```
Current Data Parameters
NAME     B12(O-Hexyl)12
EXPNO              21
PROCNO              1

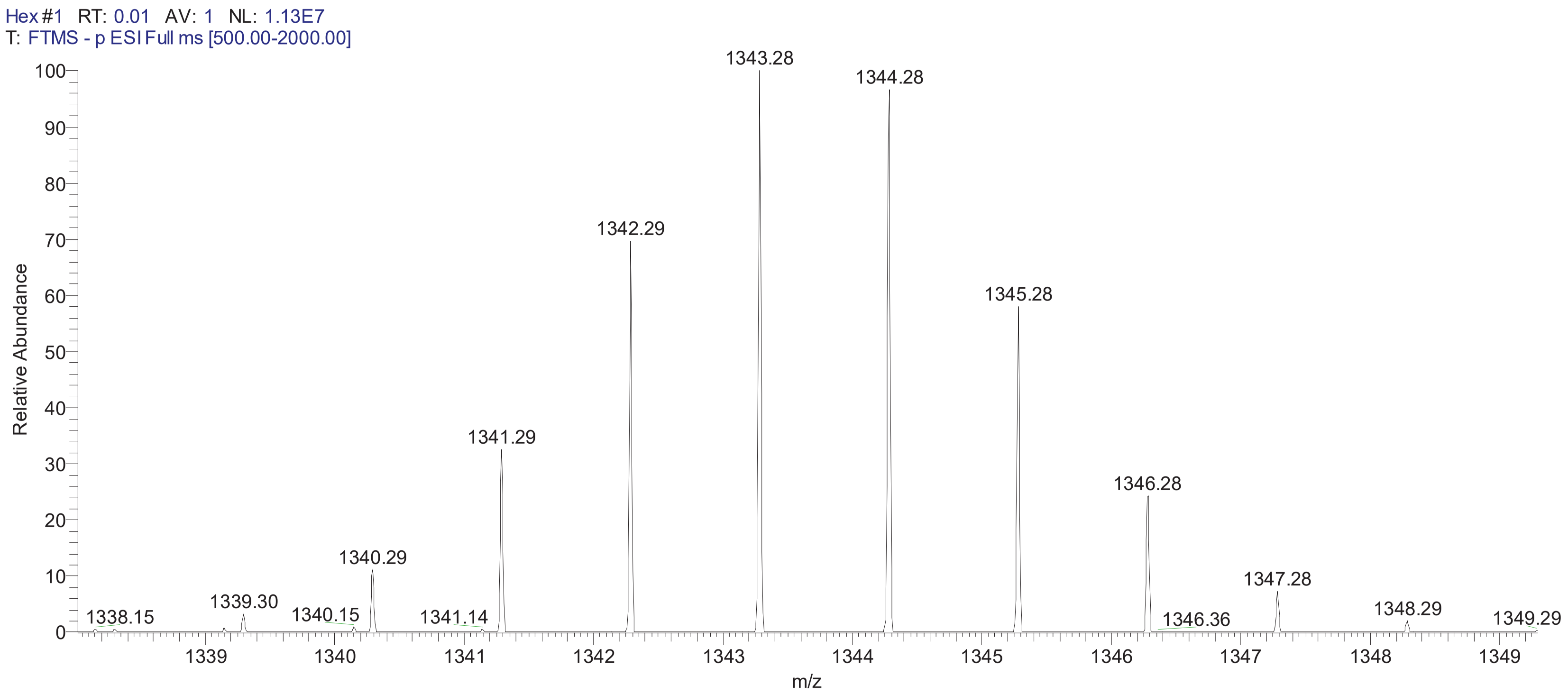
F2 - Acquisition Parameters
Date_        20150610
Time            15.11
INSTRUM         av400
PROBHD  5 mm PABBO BB/
PULPROG          zg30
TD              52882
SOLVENT         CDCl3
NS                  8
DS                  0
SWH         8012.820 Hz
FIDRES      0.151523 Hz
AQ         3.2998369 sec
RG              28.22
DW             62.400 usec
DE               6.50 usec
TE              299.0 K
D1        2.00000000 sec
TD0                 1

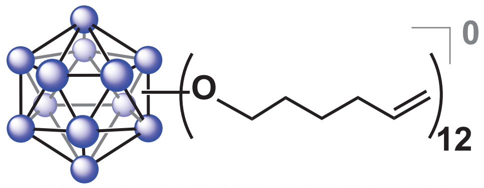
======== CHANNEL f1 ========
SFO1     400.1324008 MHz
NUC1              1H
P1             15.00 usec
PLW1     13.00000000 W

F2 - Processing parameters
SI              65536
SF       400.1300184 MHz
WDW                EM
SSB    0
LB              0.30 Hz
GB     0
PC              1.00
```

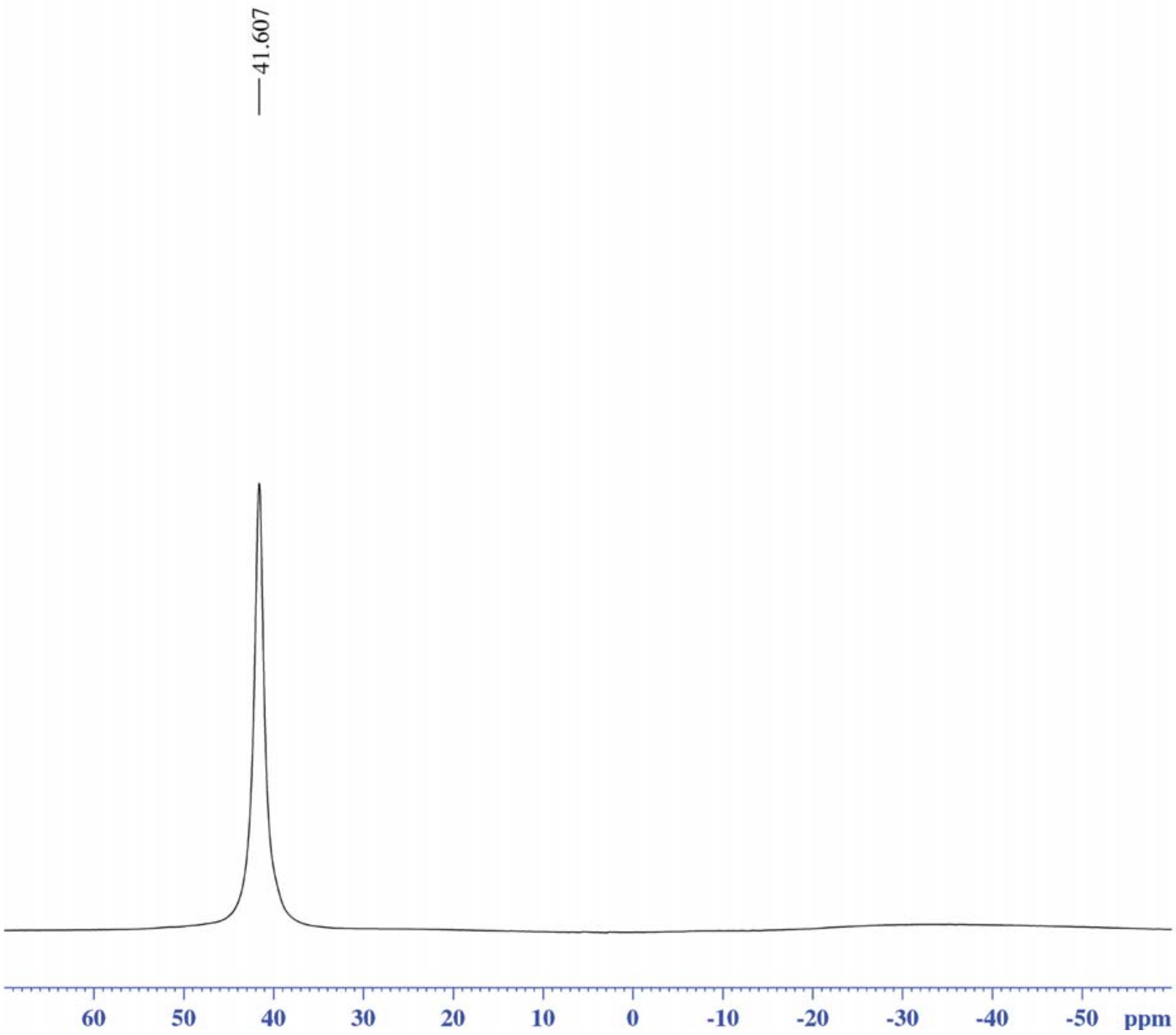


Q Exactive
High-Res Mass Spec





^{11}B {^{1}H} NMR



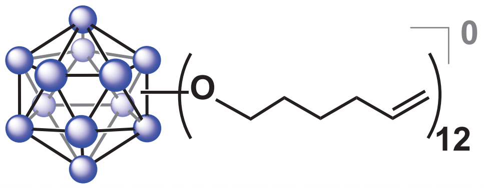
```
Current Data Parameters
NAME         Oct05-2015
EXPNO                51
PROCNO                1

F2 - Acquisition Parameters
Date_          20151005
Time              15.01
INSTRUM           av400
PROBHD   5 mm PABBO BB/
PULPROG         zgdc.js
TD                 5096
SOLVENT           CDCl3
NS                 1024
DS                    0
SWH         51020.406 Hz
FIDRES      10.011854 Hz
AQ          0.0499408 sec
RG              189.85
DW               9.800 usec
DE                6.50 usec
TE               299.1 K
D1          0.05000000 sec
D11         0.03000000 sec
TD0                   1

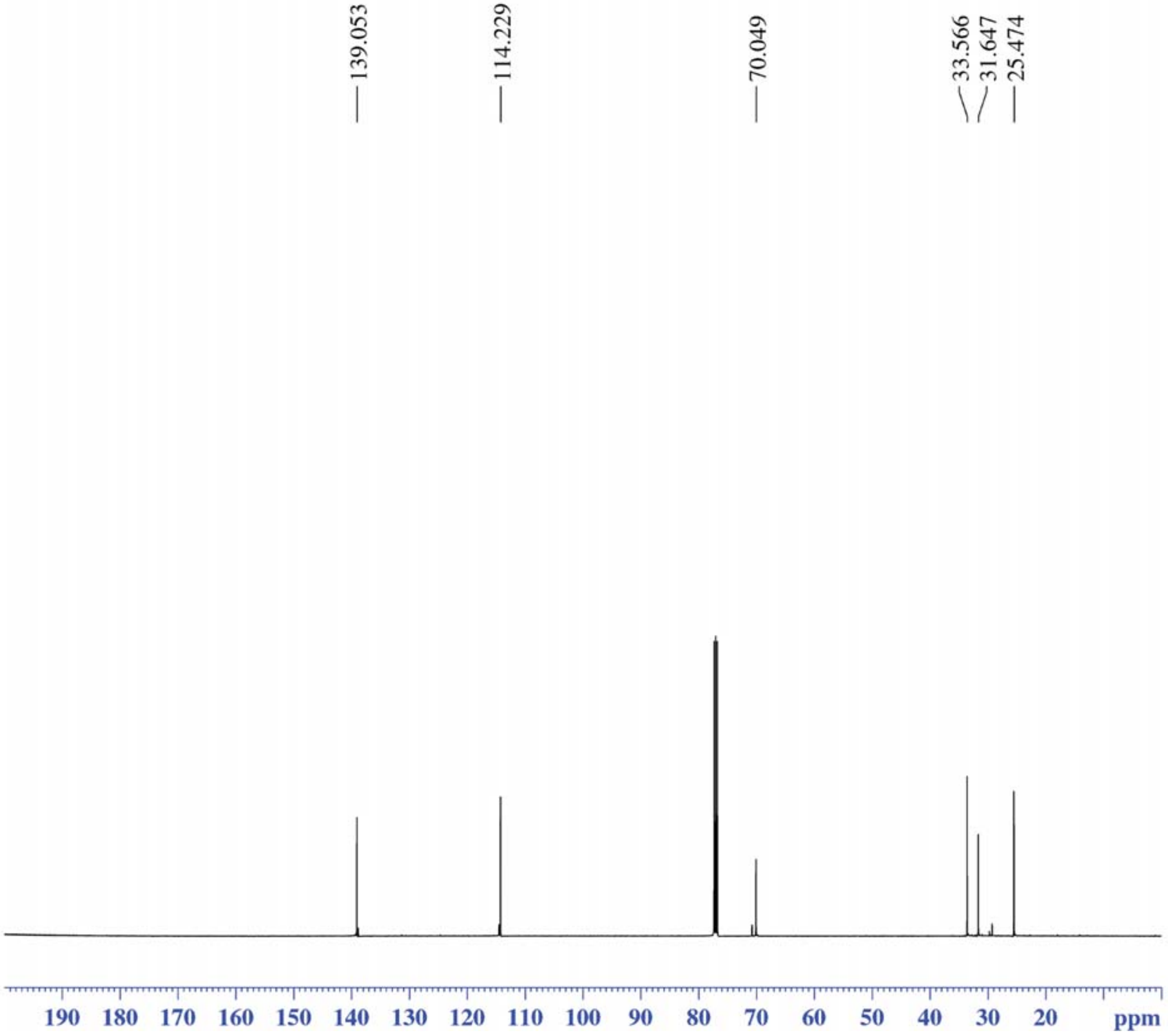
======== CHANNEL f1 ========
SFO1      128.3776052 MHz
NUC1              11B
P1              10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 ========
SFO2      400.1324008 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W

F2 - Processing parameters
SI                32768
SF        128.3776161 MHz
WDW                  EM
SSB     0
LB                10.00 Hz
GB      0
PC                 1.40
```



^{13}C NMR



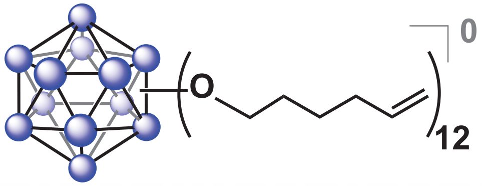
```
Current Data Parameters
NAME     B12(O-Hexene)12
EXPNO              20
PROCNO              1

F2 - Acquisition Parameters
Date_      20151021
Time          17.44
INSTRUM       av500
PROBHD  5 mm DCH 13C-1
PULPROG      zgpg30
TD          65536
SOLVENT       CDCl3
NS            256
DS              2
SWH       31250.000 Hz
FIDRES     0.476837 Hz
AQ        1.0485760 sec
RG           204.54
DW           16.000 usec
DE            18.00 usec
TE            298.0 K
D1      2.00000000 sec
D11     0.03000000 sec
TD0               1

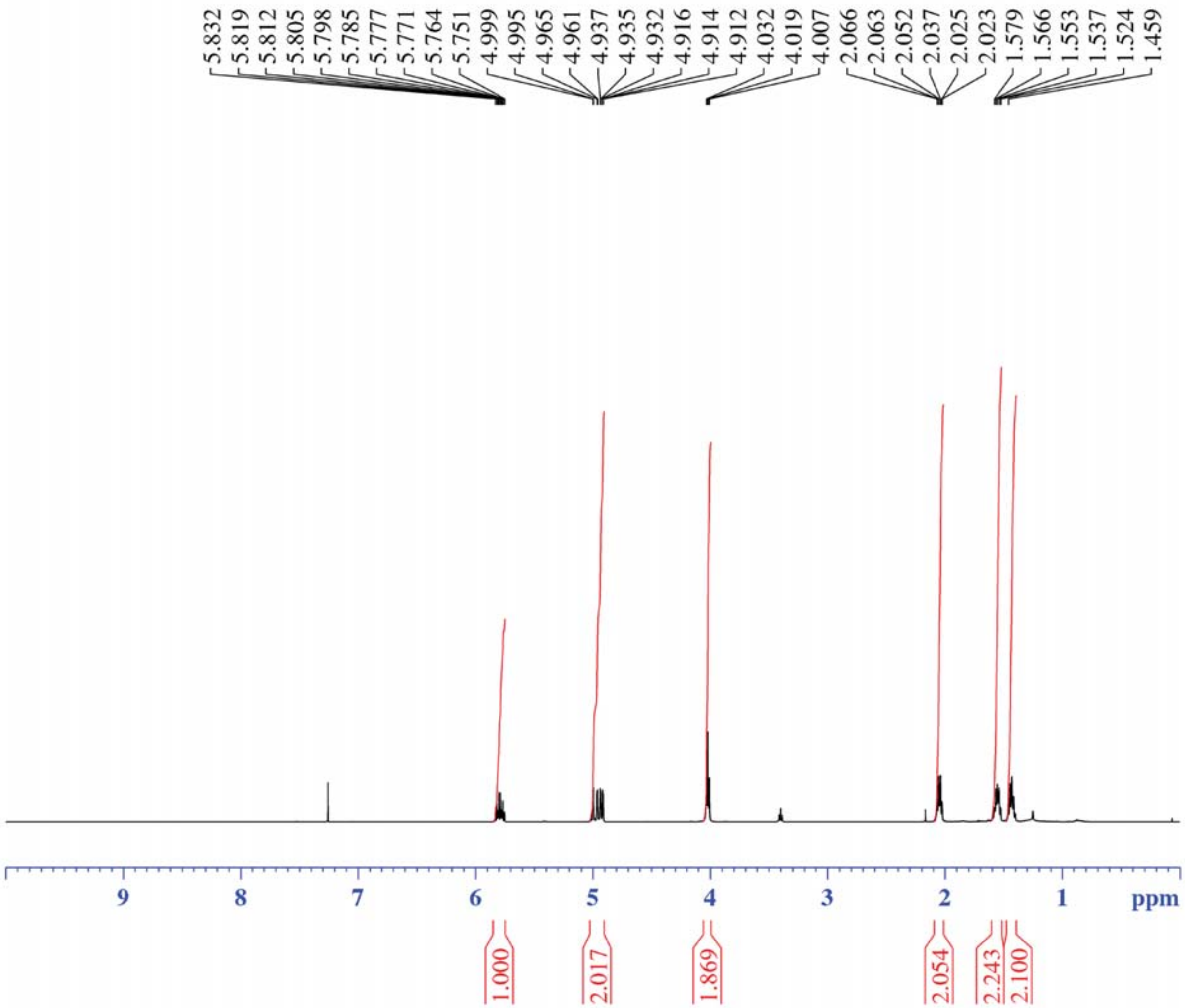
======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1             13C
P1              9.63 usec
PLW1     23.00000000 W

======== CHANNEL f2 ========
SFO2     500.1330008 MHz
NUC2              1H
CPDPRG[2      waltz16
PCPD2          80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.13500001 W

F2 - Processing parameters
SI          131072
SF     125.7577890 MHz
WDW             EM
SSB    0
LB            1.00 Hz
GB     0
PC            1.40
```



^{1}H NMR

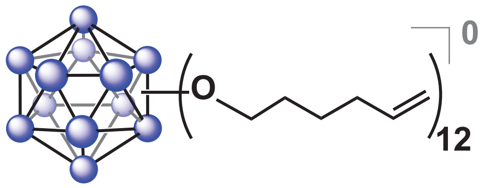


```
Current Data Parameters
NAME     B12(O-Hexene)12
EXPNO               21
PROCNO               1

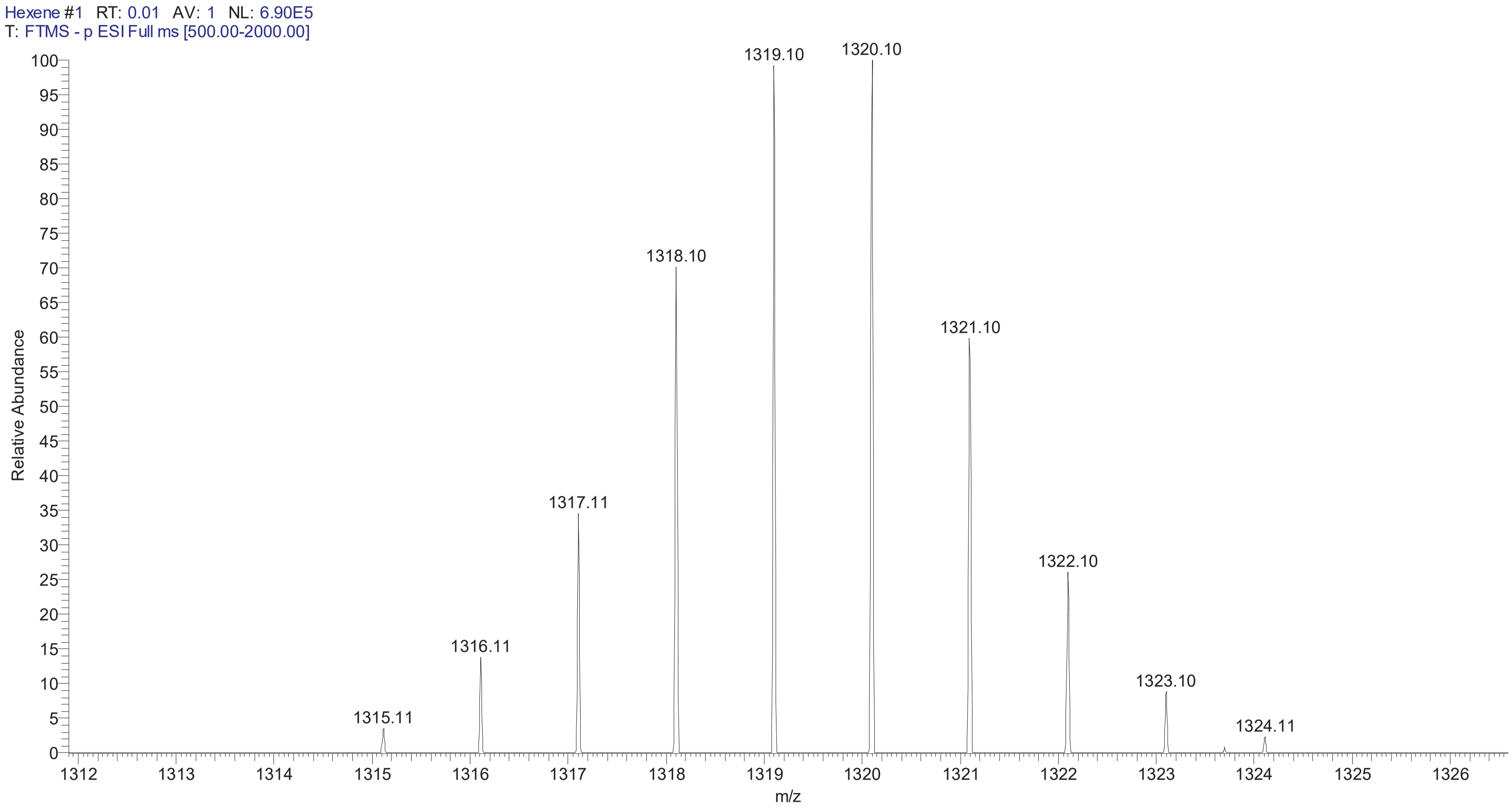
F2 - Acquisition Parameters
Date_         20151021
Time             17.48
INSTRUM          av500
PROBHD  5 mm DCH 13C-1
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ        3.2767999 sec
RG               33.91
DW          50.000 usec
DE          10.00 usec
TE             298.0 K
D1      2.00000000 sec
TD0                  1

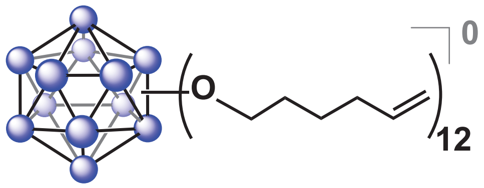
======== CHANNEL f1 ========
SFO1     500.1330008 MHz
NUC1                1H
P1           10.00 usec
PLW1      13.50000000 W

F2 - Processing parameters
SI               65536
SF       500.1300146 MHz
WDW                 EM
SSB     0
LB             0.30 Hz
GB      0
PC                1.00
```

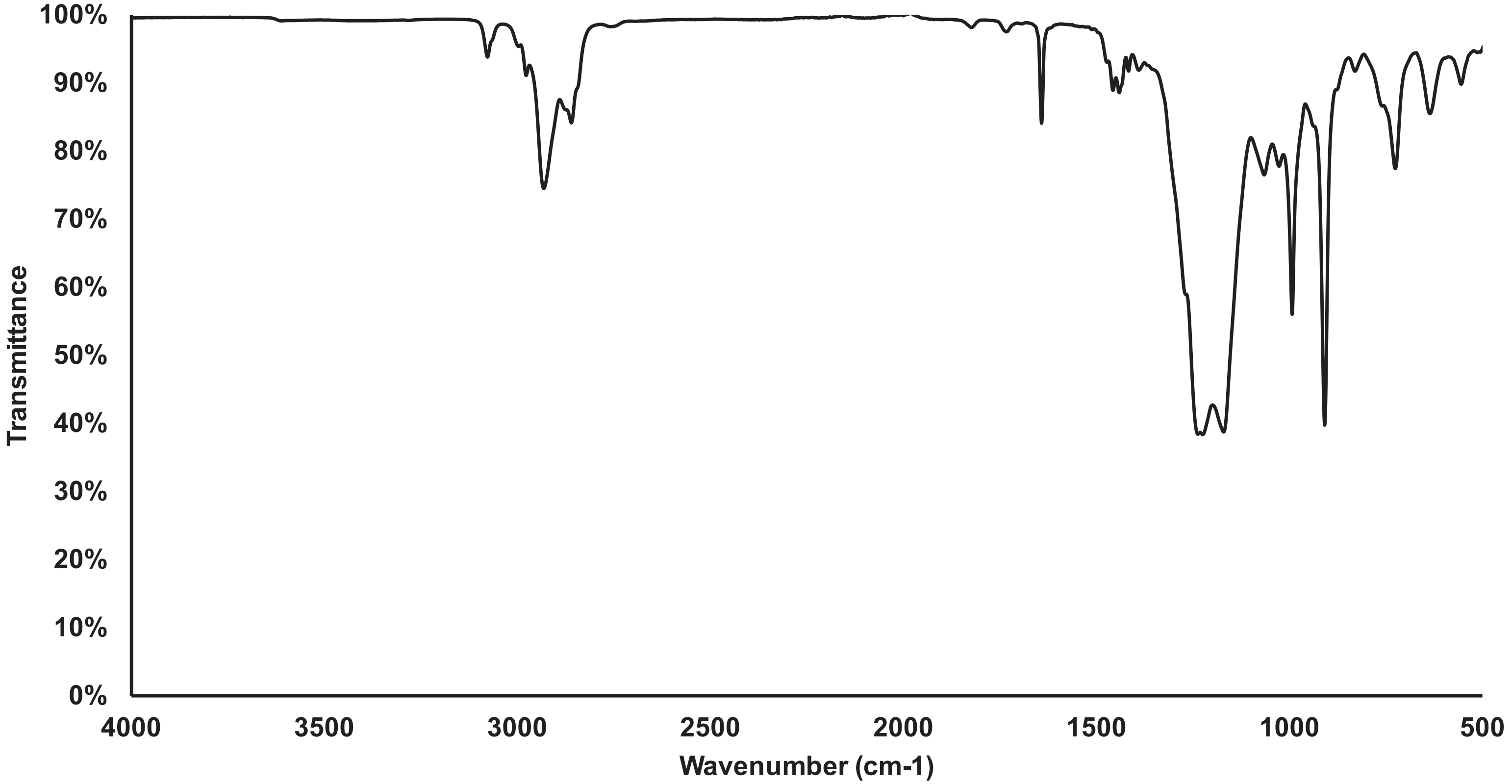


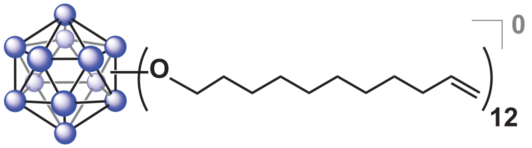
Q Exactive
High-Res Mass Spec



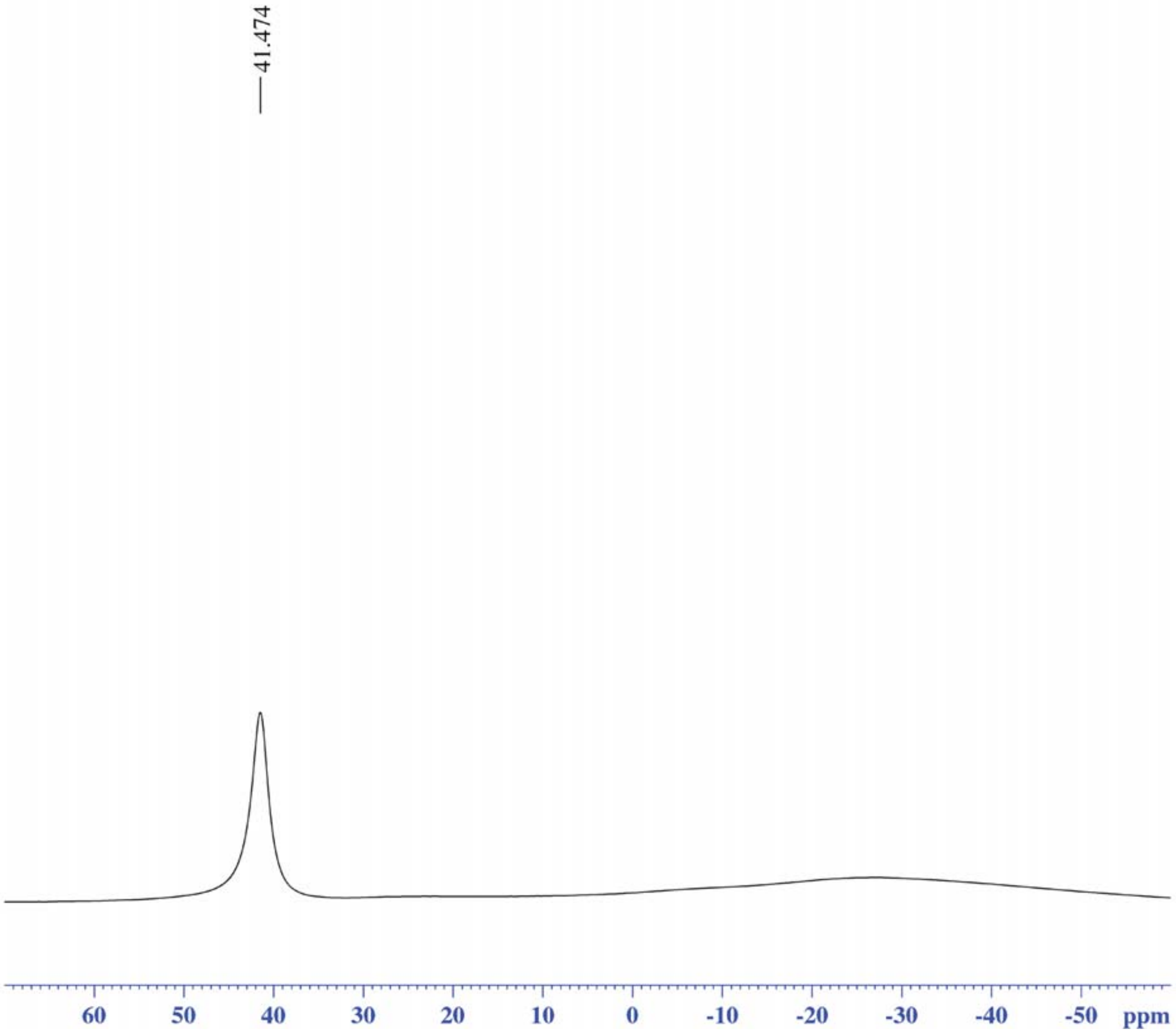

O
12
0

IR


Transmittance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)



^{11}B {^{1}H} NMR



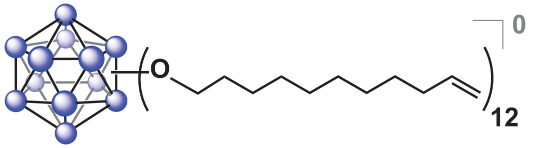
```
Current Data Parameters
NAME     B12(O-1-undecene)12
EXPNO              20
PROCNO              1

F2 - Acquisition Parameters
Date_         20150626
Time             12.16
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG        zgdc.js
TD                5096
SOLVENT         CD2Cl2
NS                1024
DS                   0
SWH         51020.406 Hz
FIDRES      10.011854 Hz
AQ          0.0499408 sec
RG              189.85
DW               9.800 usec
DE                6.50 usec
TE               299.1 K
D1          0.00000400 sec
D11         0.03000000 sec
TD0                  1

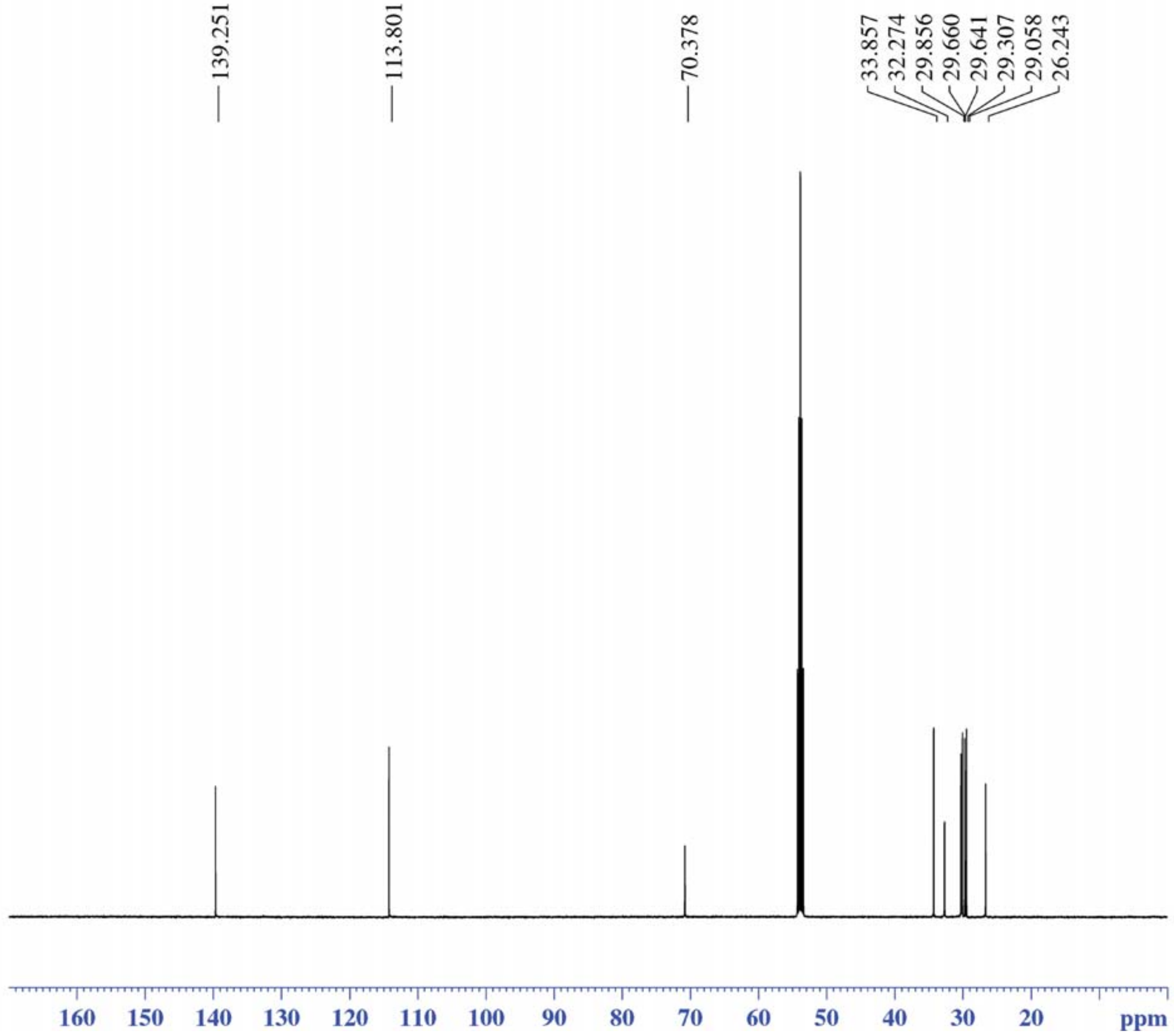
======== CHANNEL f1 ========
SFO1      128.3776052 MHz
NUC1              11B
P1              10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 ========
SFO2      400.1324008 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2           90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W

F2 - Processing parameters
SI              32768
SF        128.3776050 MHz
WDW                EM
SSB     0
LB              50.00 Hz
GB      0
PC               1.40
```



^{13}C NMR



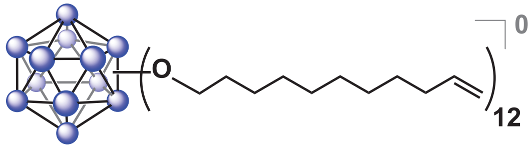
```
Current Data Parameters
NAME         Jun26-2015
EXPNO              10
PROCNO              1

F2 - Acquisition Parameters
Date_       20150626
Time           14.05
INSTRUM        av500
PROBHD  5 mm DCH 13C-1
PULPROG       zgpg30
TD             65536
SOLVENT       CD2Cl2
NS                64
DS                 2
SWH       31250.000 Hz
FIDRES     0.476837 Hz
AQ        1.0485760 sec
RG            204.54
DW            16.000 usec
DE             18.00 usec
TE             298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1

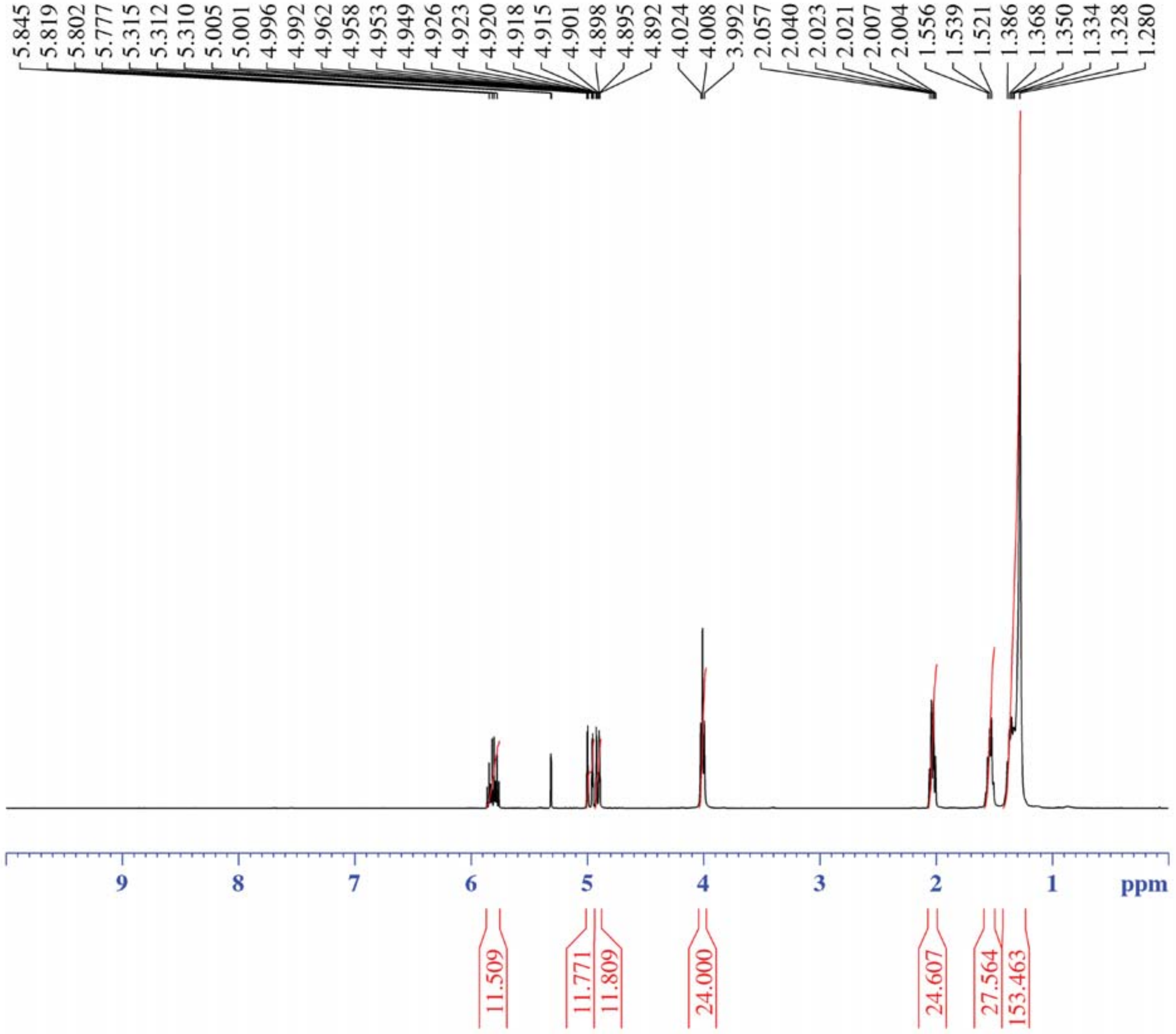
======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec
PLW1      23.00000000 W

======== CHANNEL f2 ========
SFO2      500.1330008 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2           80.00 usec
PLW2      13.50000000 W
PLW12      0.21094000 W
PLW13      0.13500001 W

F2 - Processing parameters
SI            131072
SF       125.7577890 MHz
WDW               EM
SSB     0
LB             1.00 Hz
GB      0
PC              1.40
```



^{1}H NMR

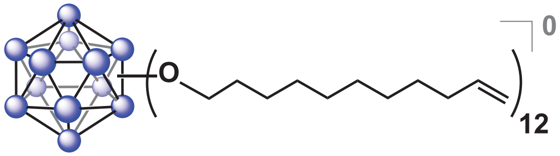


```
Current Data Parameters
NAME     B12(O-1-undecene)12
EXPNO              21
PROCNO              1

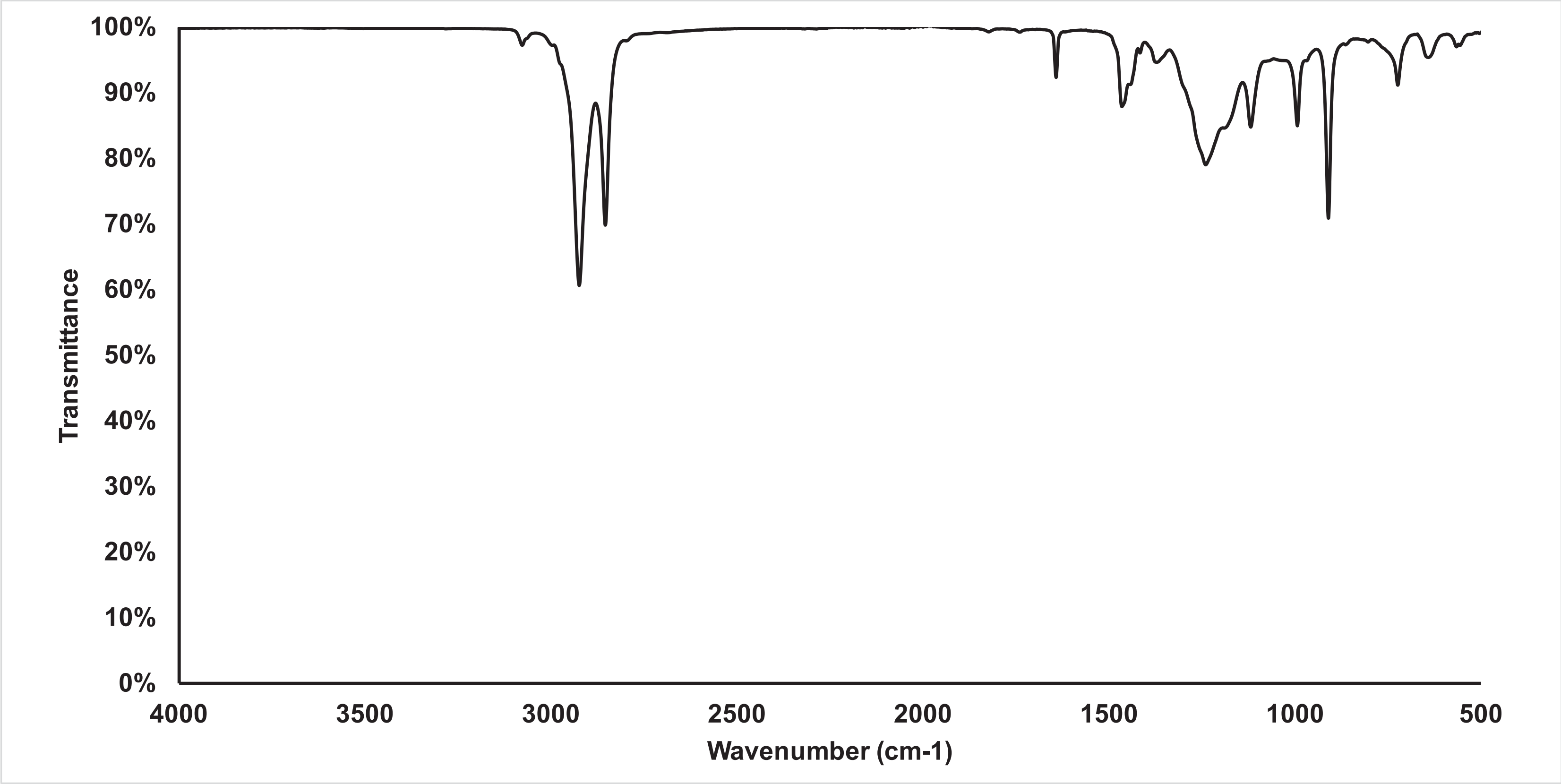
F2 - Acquisition Parameters
Date_        20150626
Time            12.18
INSTRUM         av400
PROBHD  5 mm PABBO BB/
PULPROG          zg30
TD              52882
SOLVENT        CD2Cl2
NS                  8
DS                  0
SWH        8012.820 Hz
FIDRES     0.151523 Hz
AQ        3.2998369 sec
RG              83.63
DW         62.400 usec
DE           6.50 usec
TE            299.0 K
D1       2.00000000 sec
TD0                 1

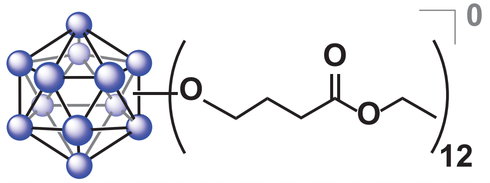
======== CHANNEL f1 ========
SFO1     400.1324008 MHz
NUC1               1H
P1          15.00 usec
PLW1    13.00000000 W

F2 - Processing parameters
SI              65536
SF       400.1300184 MHz
WDW                EM
SSB    0
LB            0.30 Hz
GB     0
PC               1.00
```

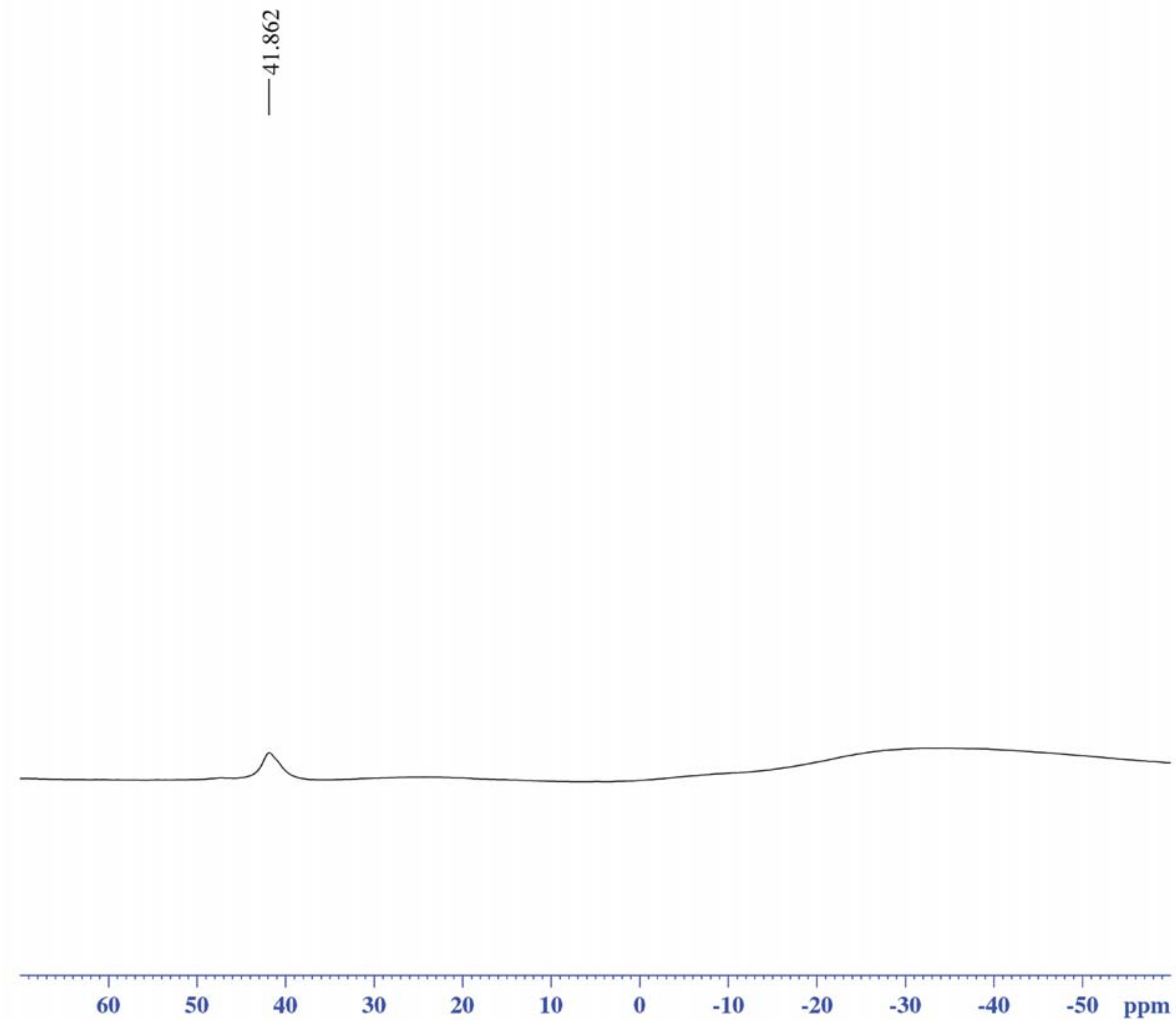

O
0
12

IR


Transmittance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)



^{11}B {^{1}H} NMR



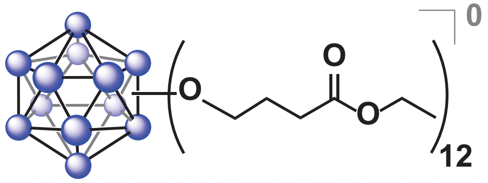
```
Current Data Parameters
NAME     B12(O-EtButyr)12
EXPNO              110
PROCNO               1

F2 - Acquisition Parameters
Date_          20150412
Time              19.19
INSTRUM           av400
PROBHD   5 mm PABBO BB/
PULPROG         zgdc.js
TD                 5096
SOLVENT           CDCl3
NS                 1024
DS                    0
SWH        51020.406 Hz
FIDRES     10.011854 Hz
AQ         0.0499408 sec
RG               189.85
DW            9.800 usec
DE             6.50 usec
TE              299.1 K
D1       0.00000400 sec
D11      0.03000000 sec
TD0                   1

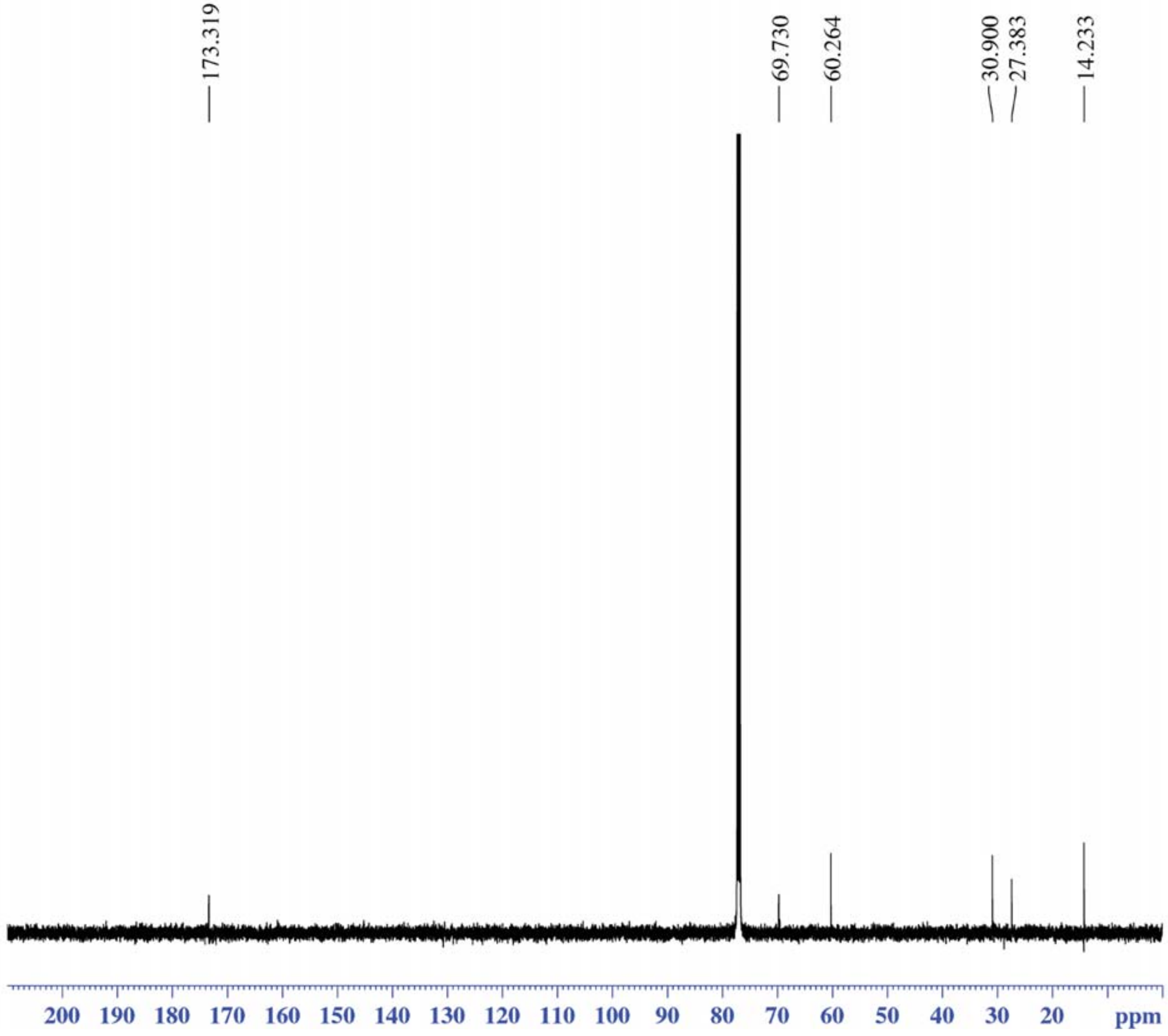
======== CHANNEL f1 ========
SFO1      128.3776052 MHz
NUC1                 11B
P1            10.00 usec
PLW1       52.00000000 W

======== CHANNEL f2 ========
SFO2      400.1324008 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2         90.00 usec
PLW2       13.00000000 W
PLW12       0.36111000 W

F2 - Processing parameters
SI                32768
SF        128.3776050 MHz
WDW                  EM
SSB      0
LB             50.00 Hz
GB       0
PC                 1.40
```



^{13}C NMR



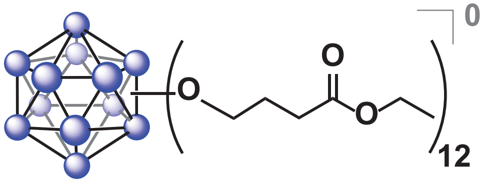
```
Current Data Parameters
NAME     B12(O-EtButyr)12
EXPNO              60
PROCNO              1

F2 - Acquisition Parameters
Date_        20150406
Time            23.42
INSTRUM         av500
PROBHD  5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 64
DS                  2
SWH      31250.000 Hz
FIDRES    0.476837 Hz
AQ       1.0485760 sec
RG             204.54
DW         16.000 usec
DE          18.00 usec
TE            298.0 K
D1     2.00000000 sec
D11    0.03000000 sec
TD0                 1

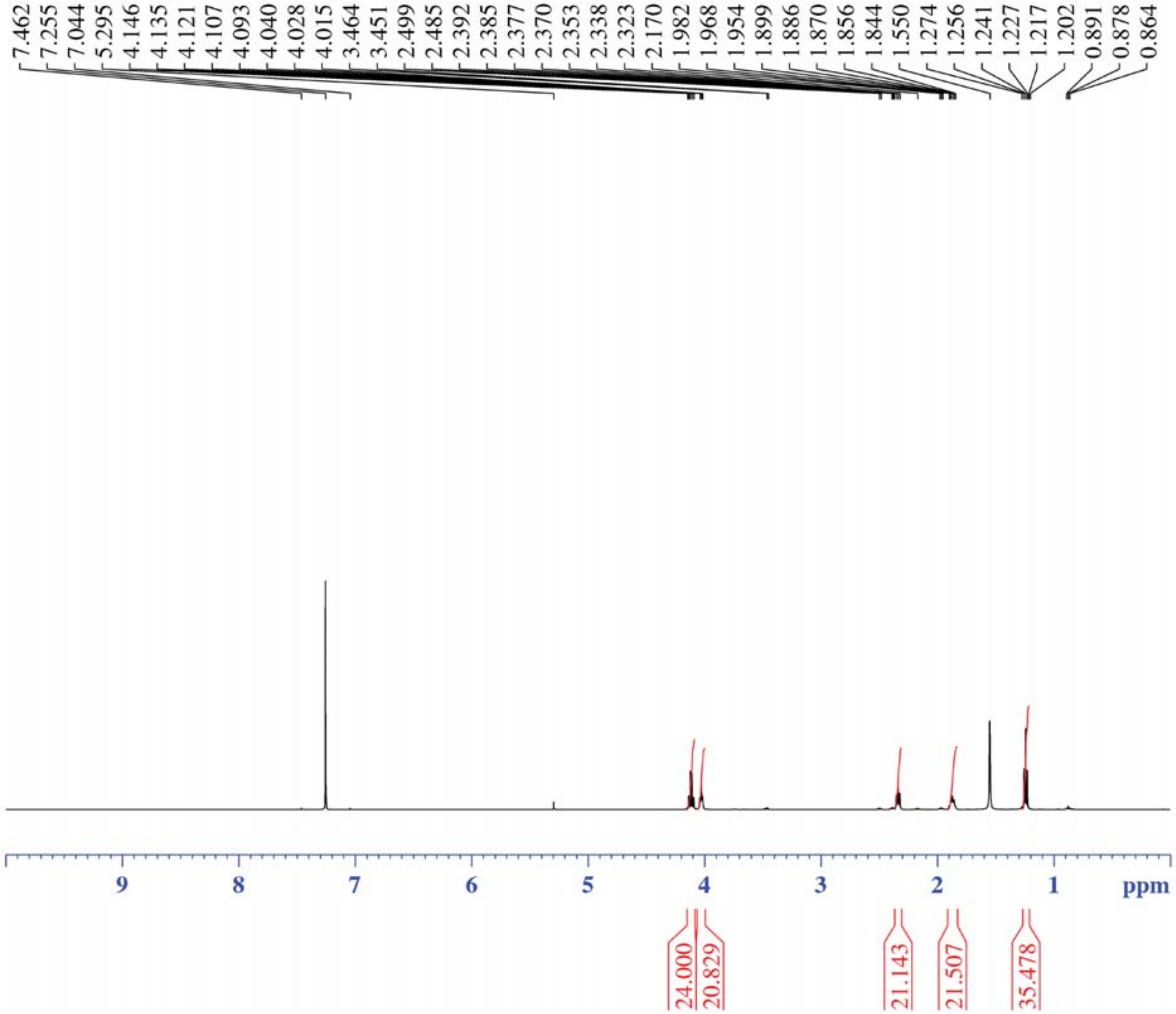
======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1              13C
P1            9.63 usec
PLW1    23.00000000 W

======== CHANNEL f2 ========
SFO2     500.1330008 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2         80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.13500001 W

F2 - Processing parameters
SI             131072
SF     125.7577890 MHz
WDW                EM
SSB    0
LB            1.00 Hz
GB     0
PC              1.40
```



^{1}H NMR

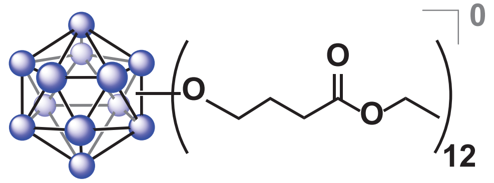


```
Current Data Parameters
NAME     B12(O-EtButyr)12
EXPNO              61
PROCNO              1

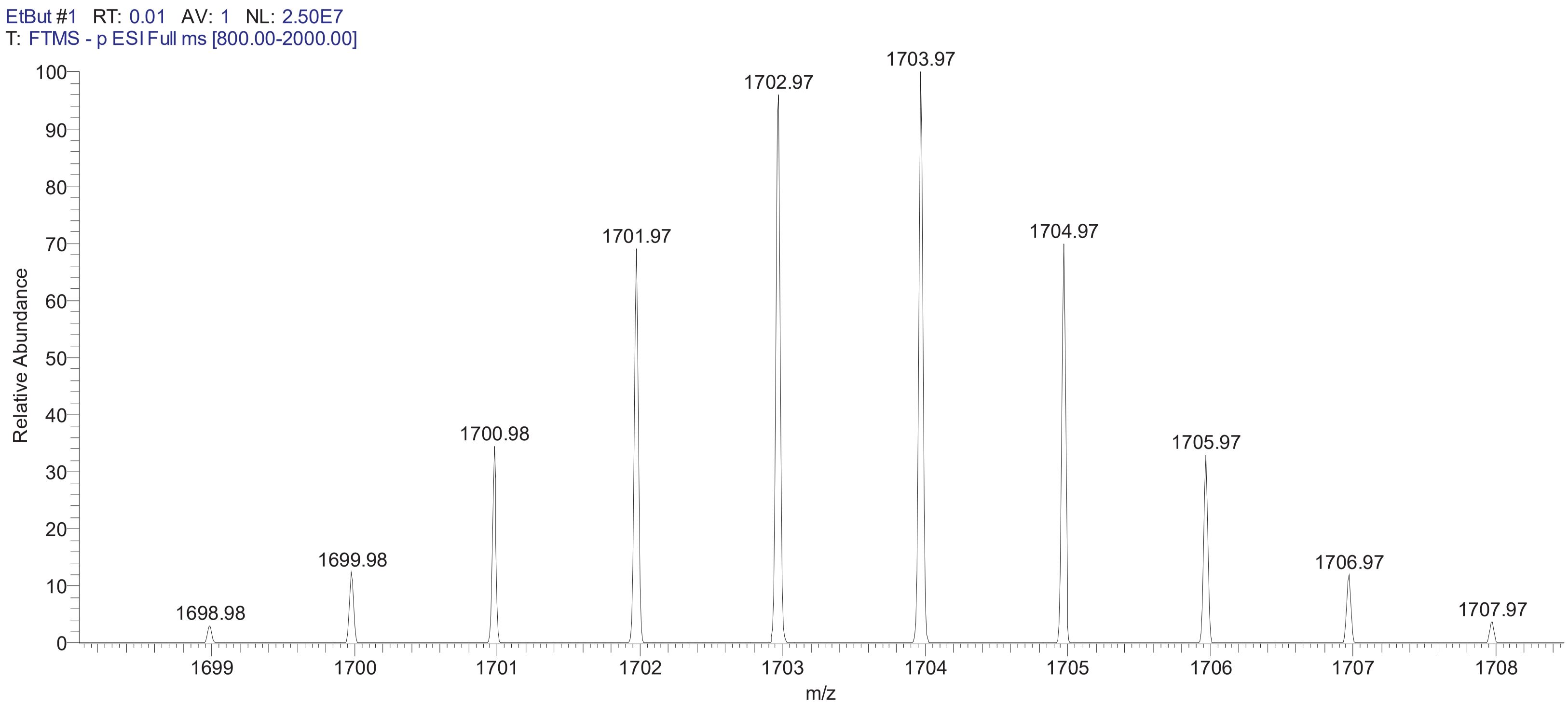
F2 - Acquisition Parameters
Date_        20150406
Time            23.44
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                  8
DS                  0
SWH       10000.000 Hz
FIDRES     0.152588 Hz
AQ        3.2767999 sec
RG              59.34
DW         50.000 usec
DE          10.00 usec
TE             298.0 K
D1     2.00000000 sec
TD0                 1

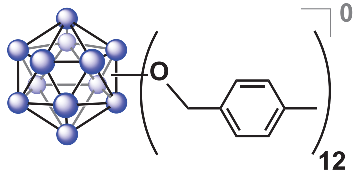
======== CHANNEL f1 ========
SFO1     500.1330008 MHz
NUC1                1H
P1          10.00 usec
PLW1    13.50000000 W

F2 - Processing parameters
SI              65536
SF      500.1300146 MHz
WDW                EM
SSB   0
LB            0.30 Hz
GB    0
PC               1.00
```

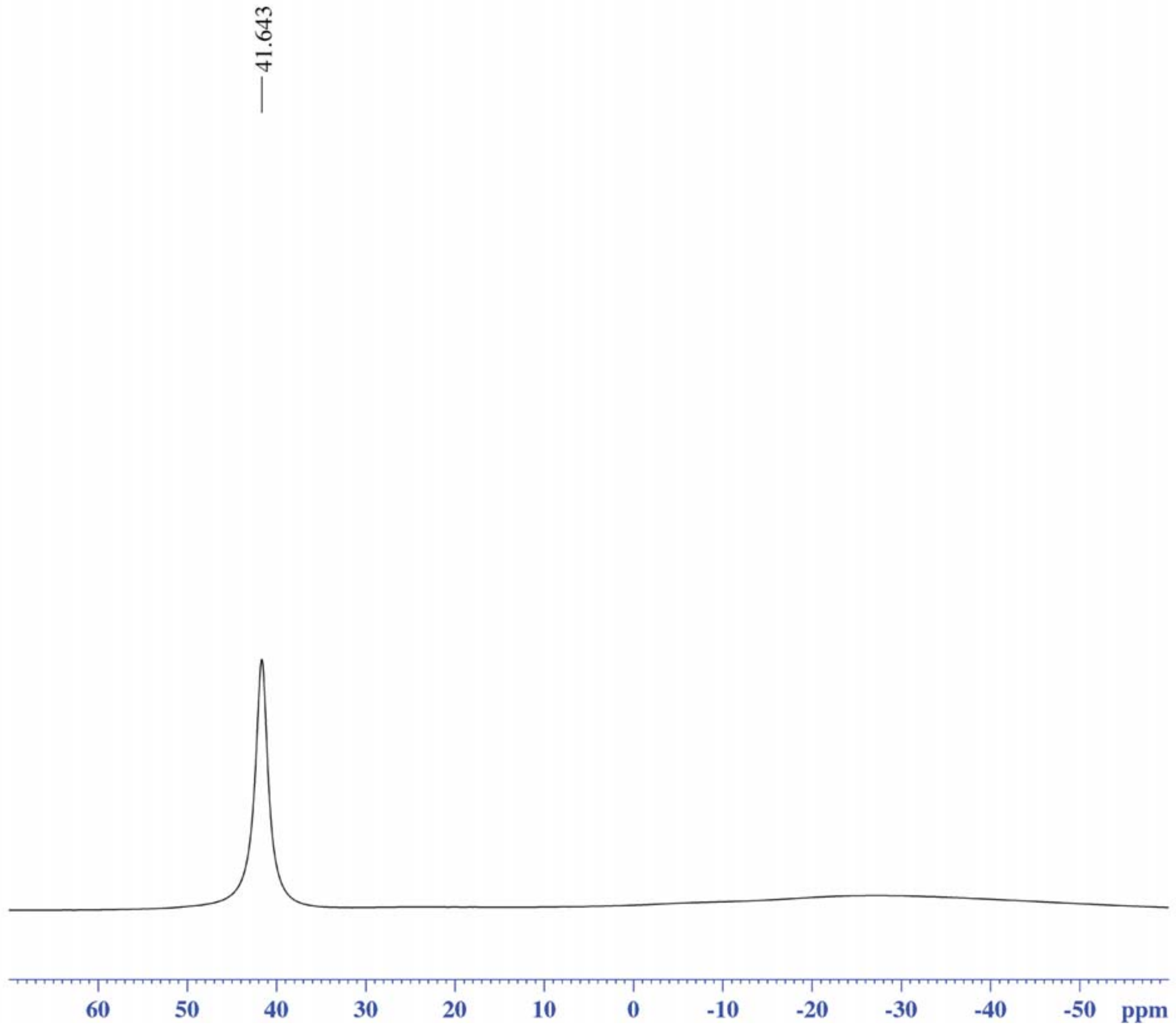


Q Exactive
High-Res Mass Spec





$^{11}B\ \{^1H\}$ NMR



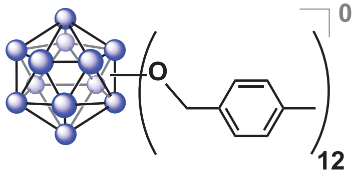
```
Current Data Parameters
NAME          Aug29-2015
EXPNO                160
PROCNO                 1

F2 - Acquisition Parameters
Date_         20150829
Time             21.02
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG        zgdc.js
TD                5096
SOLVENT          CDCl3
NS                1024
DS                   0
SWH       51020.406 Hz
FIDRES    10.011854 Hz
AQ       0.0499408 sec
RG              189.85
DW           9.800 usec
DE            6.50 usec
TE             299.3 K
D1      0.00000400 sec
D11     0.03000000 sec
TD0                  1

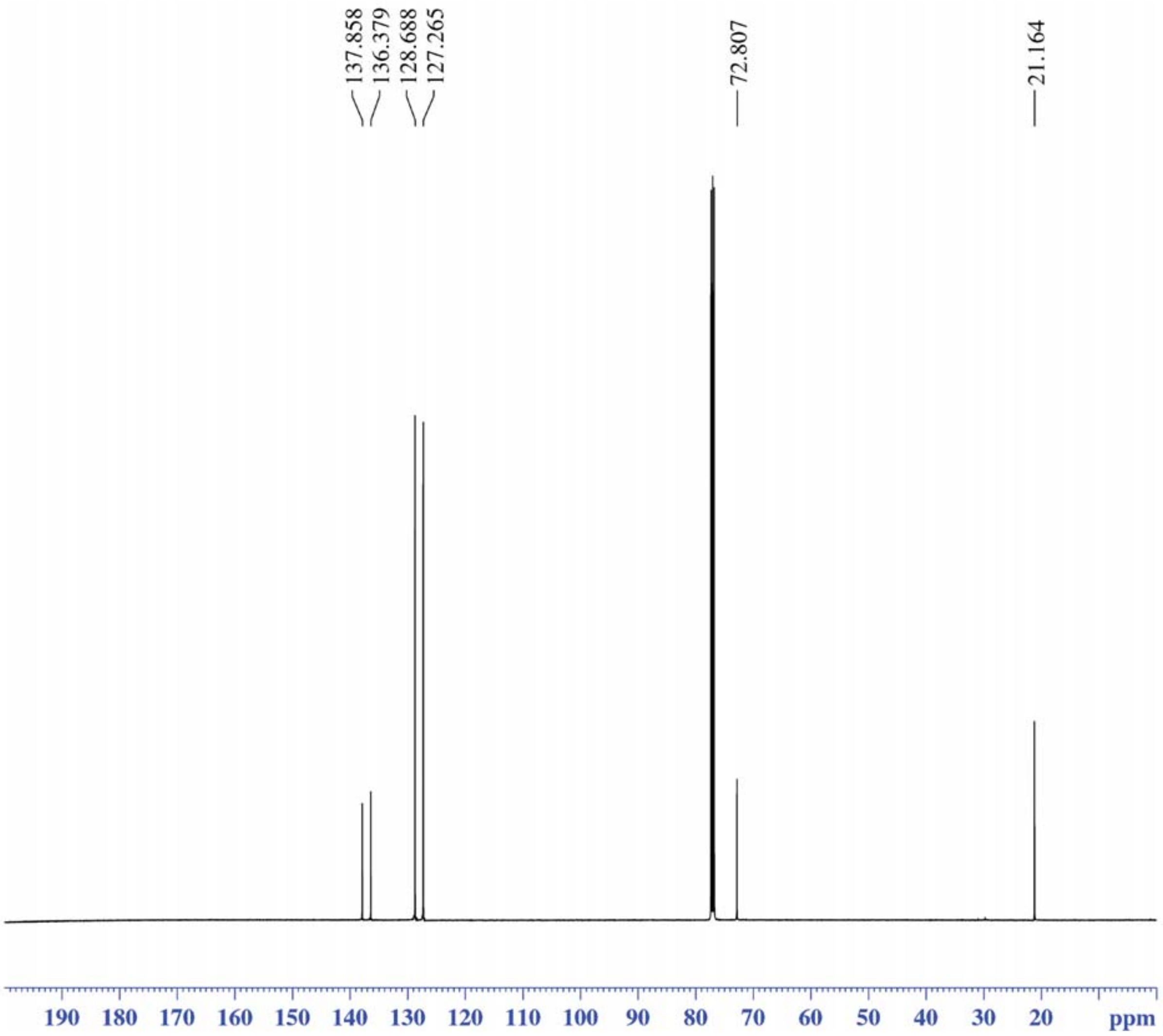
======== CHANNEL f1 ========
SFO1     128.3776052 MHz
NUC1             11B
P1             10.00 usec
PLW1     52.00000000 W

======== CHANNEL f2 ========
SFO2     400.1324008 MHz
NUC2              1H
CPDPRG[2      waltz16
PCPD2          90.00 usec
PLW2     13.00000000 W
PLW12     0.36111000 W

F2 - Processing parameters
SI               32768
SF     128.3776050 MHz
WDW                 EM
SSB      0
LB            50.00 Hz
GB       0
PC                1.40
```



^{13}C NMR



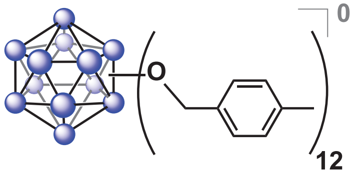
```
Current Data Parameters
NAME     B12(O-4-MeBn)12
EXPNO              60
PROCNO              1

F2 - Acquisition Parameters
Date_       20150829
Time           22.04
INSTRUM          av500
PROBHD  5 mm DCH 13C-1
PULPROG         zgpg30
TD             65536
SOLVENT          CDCl3
NS               256
DS                 2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ         1.0485760 sec
RG            204.54
DW            16.000 usec
DE             18.00 usec
TE             298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1

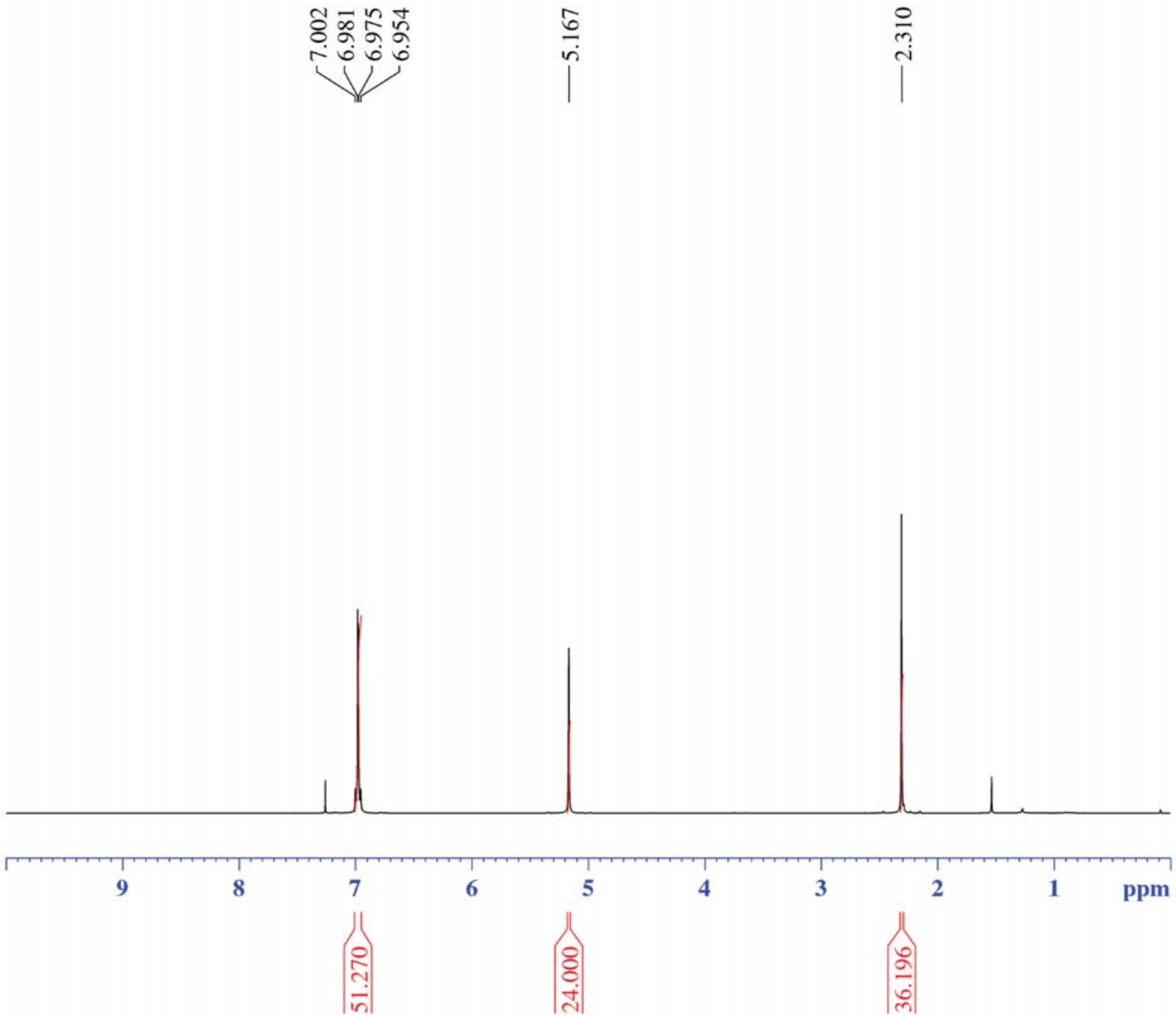
======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec
PLW1      23.00000000 W

======== CHANNEL f2 ========
SFO2      500.1330008 MHz
NUC2               1H
CPDPRG[2          waltz16
PCPD2            80.00 usec
PLW2       13.50000000 W
PLW12       0.21094000 W
PLW13       0.13500001 W

F2 - Processing parameters
SI            131072
SF      125.7577890 MHz
WDW               EM
SSB     0
LB              1.00 Hz
GB      0
PC              1.40
```



^{1}H NMR

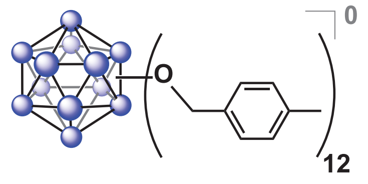


```
Current Data Parameters
NAME     B12(O-4-MeBn)12
EXPNO              161
PROCNO               1

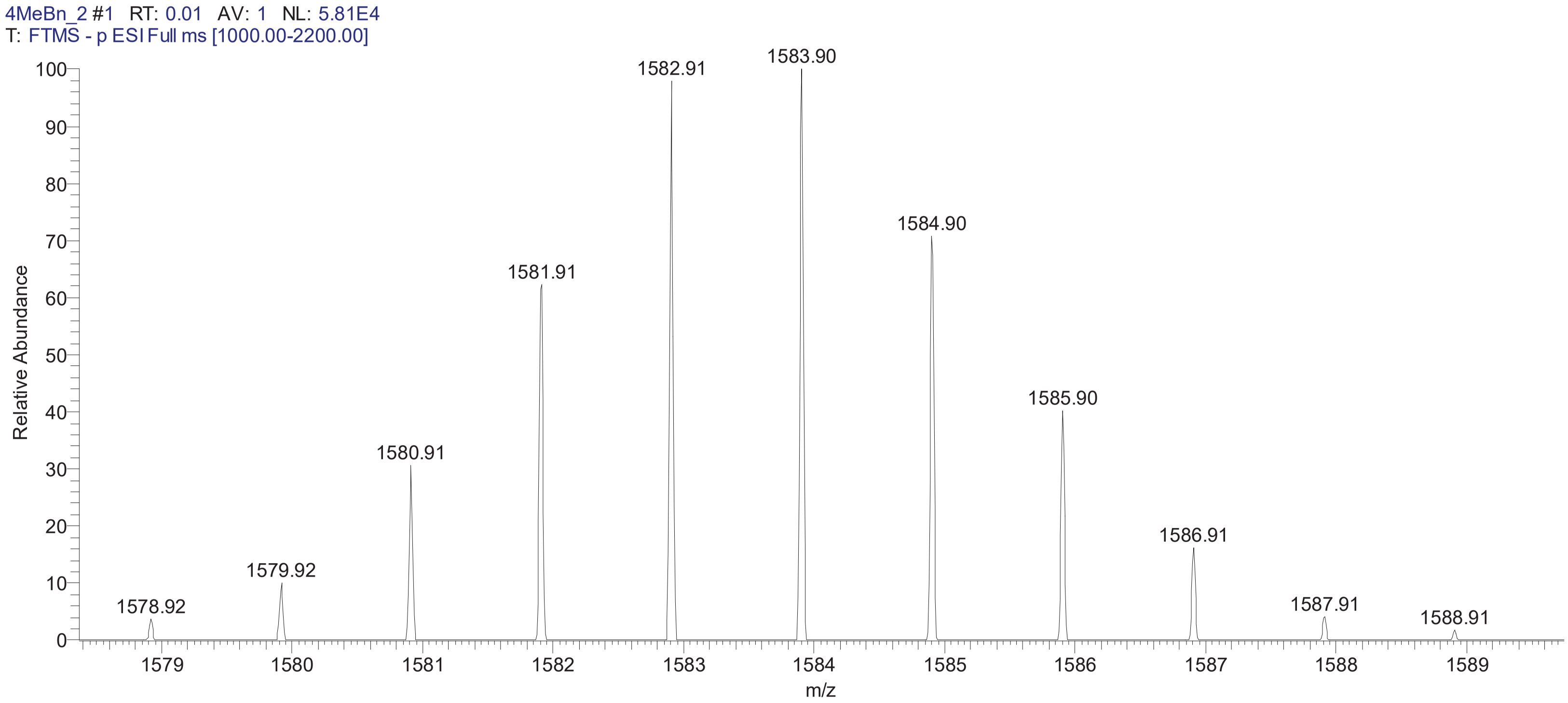
F2 - Acquisition Parameters
Date_        20150829
Time            21.05
INSTRUM         av400
PROBHD  5 mm PABBO BB/
PULPROG          zg30
TD              52882
SOLVENT         CDCl3
NS                 32
DS                  0
SWH        8012.820 Hz
FIDRES     0.151523 Hz
AQ        3.2998369 sec
RG             155.85
DW         62.400 usec
DE           6.50 usec
TE            299.0 K
D1      2.00000000 sec
TD0                 1

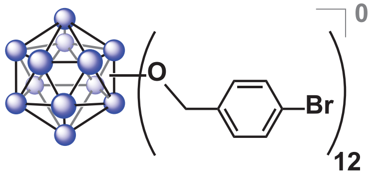
======== CHANNEL f1 ========
SFO1     400.1324008 MHz
NUC1              1H
P1           15.00 usec
PLW1     13.00000000 W

F2 - Processing parameters
SI              65536
SF       400.1300184 MHz
WDW                EM
SSB    0
LB              0.30 Hz
GB     0
PC               1.00
```

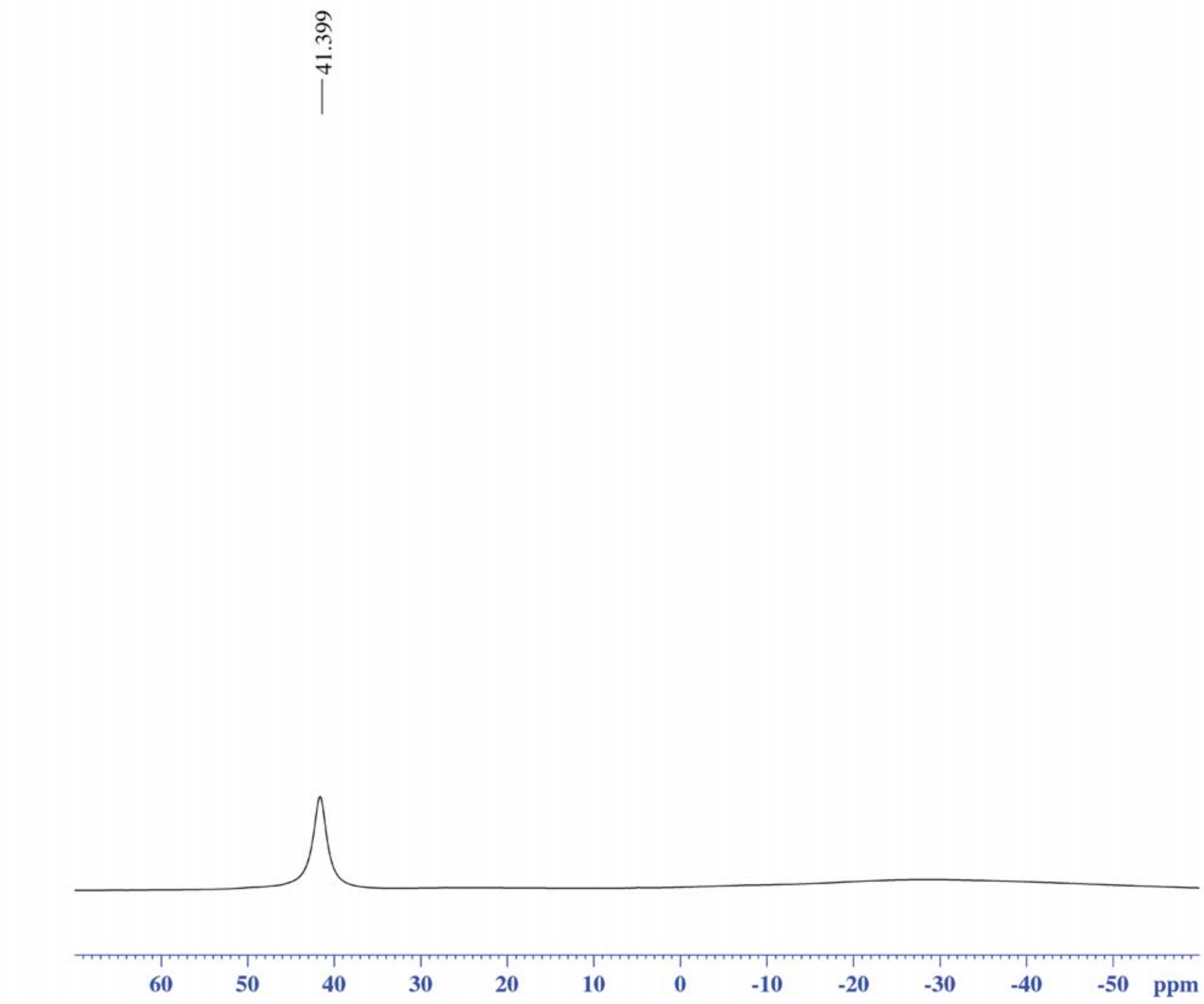


Q Exactive
High-Res Mass Spec





$^{11}B\ \{^1H\}$ NMR



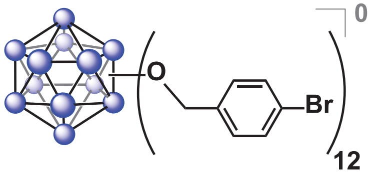
```
Current Data Parameters
NAME     B12(O-4-BrBn)12
EXPNO              10
PROCNO              1

F2 - Acquisition Parameters
Date_         20150624
Time             10.50
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG        zgdc.js
TD                5096
SOLVENT          CDCl3
NS                1024
DS                   0
SWH       51020.406 Hz
FIDRES    10.011854 Hz
AQ        0.0499408 sec
RG              189.85
DW           9.800 usec
DE            6.50 usec
TE              299.1 K
D1       0.00000400 sec
D11      0.03000000 sec
TD0                  1

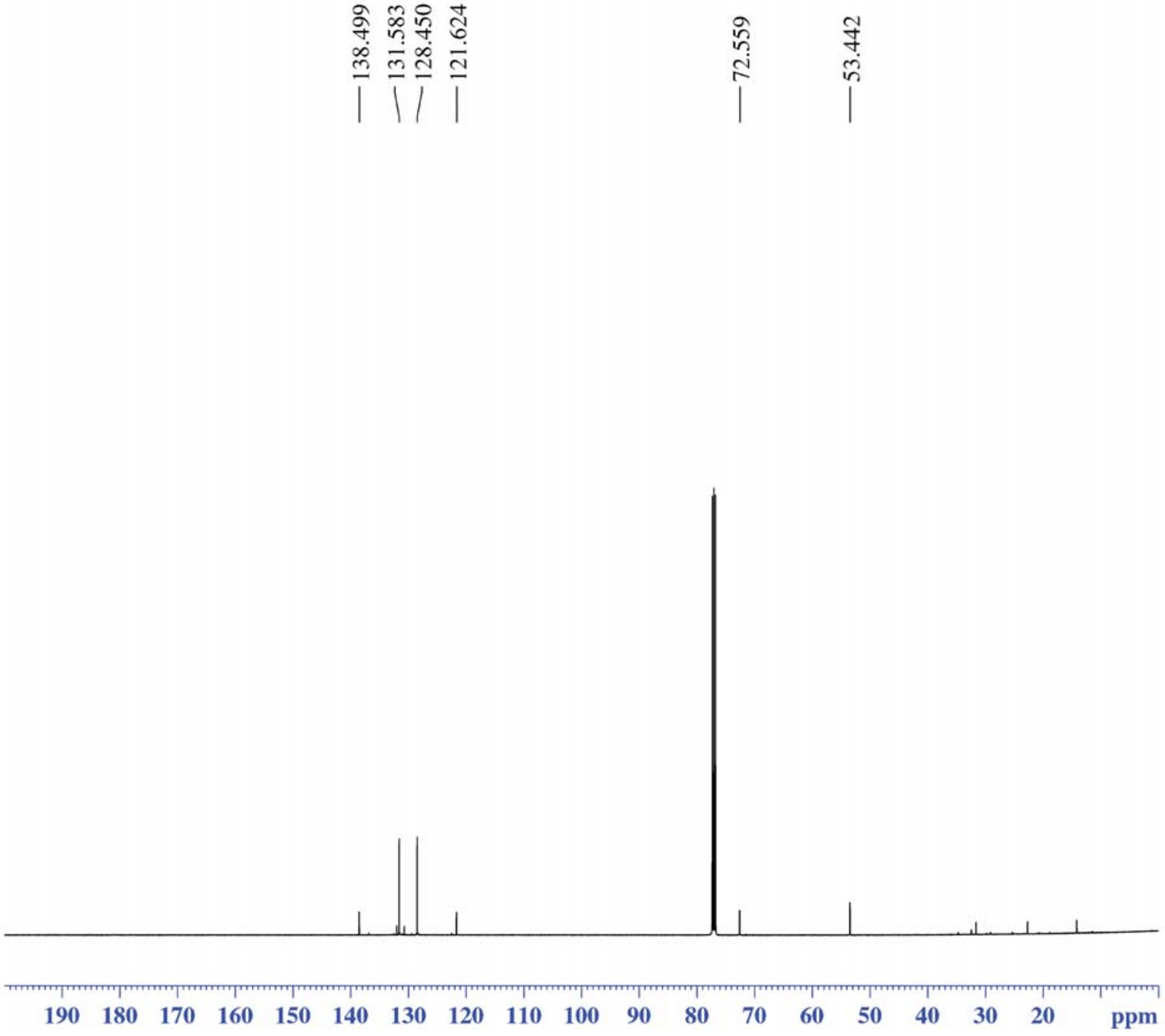
======== CHANNEL f1 ========
SFO1     128.3776052 MHz
NUC1                 11B
P1            10.00 usec
PLW1       52.00000000 W

======== CHANNEL f2 ========
SFO2     400.1324008 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2         90.00 usec
PLW2       13.00000000 W
PLW12       0.36111000 W

F2 - Processing parameters
SI                 32768
SF       128.3776050 MHz
WDW                   EM
SSB      0
LB              50.00 Hz
GB       0
PC                  1.40
```



^{13}C NMR



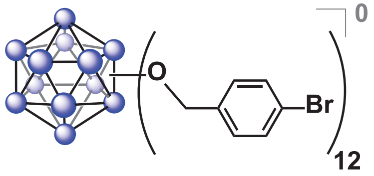
```
Current Data Parameters
NAME     B12(O-4-BrBn)12
EXPNO             10
PROCNO             1

F2 - Acquisition Parameters
Date_        20151021
Time            17.14
INSTRUM          av500
PROBHD   5 mm DCH 13C-1
PULPROG         zgpg30
TD              65536
SOLVENT          CDCl3
NS                256
DS                  2
SWH         31250.000 Hz
FIDRES       0.476837 Hz
AQ          1.0485760 sec
RG             204.54
DW             16.000 usec
DE              18.00 usec
TE              298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

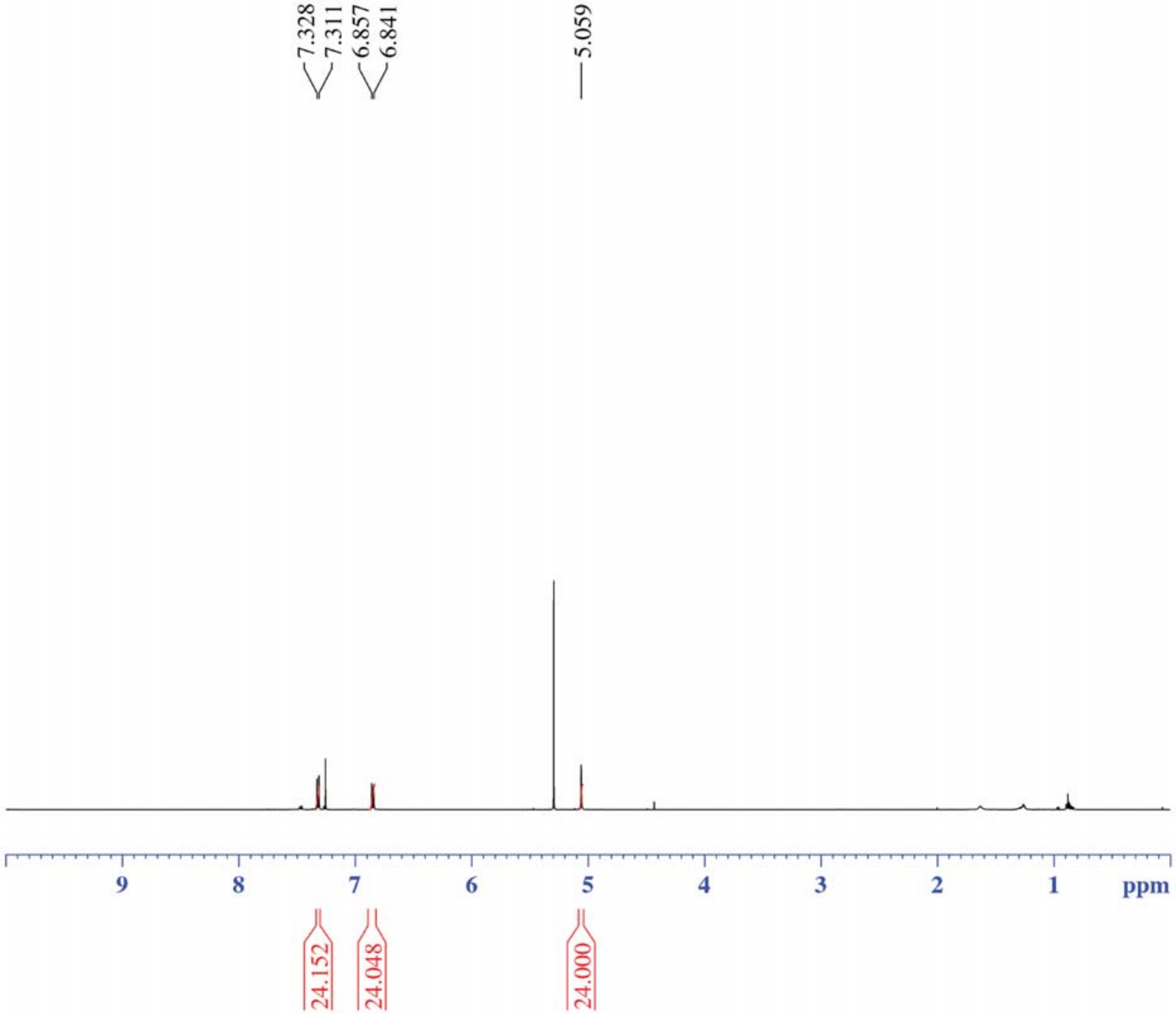
======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec
PLW1      23.00000000 W

======== CHANNEL f2 ========
SFO2      500.1330008 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2      13.50000000 W
PLW12      0.21094000 W
PLW13      0.13500001 W

F2 - Processing parameters
SI             131072
SF      125.7577890 MHz
WDW                EM
SSB      0
LB               1.00 Hz
GB       0
PC               1.40
```



^{1}H NMR

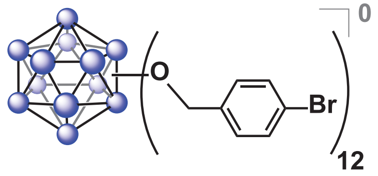


```
Current Data Parameters
NAME     B12(O-4-BrBn)12
EXPNO              11
PROCNO              1

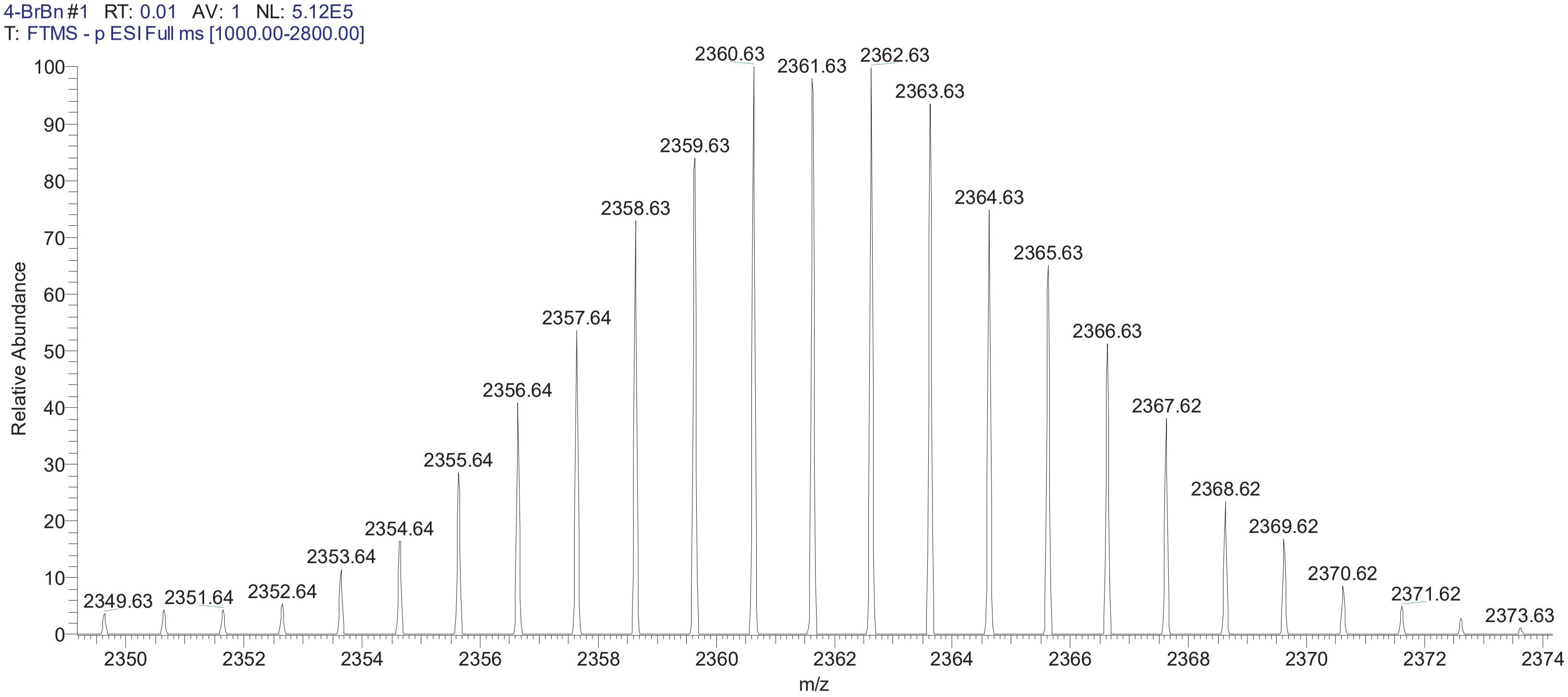
F2 - Acquisition Parameters
Date_        20151021
Time            17.27
INSTRUM         av500
PROBHD  5 mm DCH 13C-1
PULPROG          zg30
TD            65536
SOLVENT          CDCl3
NS               32
DS                0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ         3.2767999 sec
RG             42.29
DW            50.000 usec
DE             10.00 usec
TE             298.0 K
D1        2.00000000 sec
TD0                1

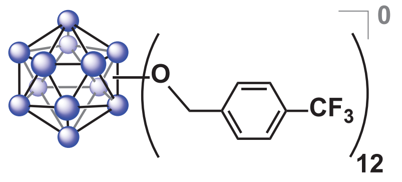
======== CHANNEL f1 ========
SFO1      500.1330008 MHz
NUC1               1H
P1              10.00 usec
PLW1      13.50000000 W

F2 - Processing parameters
SI            65536
SF       500.1300146 MHz
WDW                EM
SSB   0
LB            0.30 Hz
GB    0
PC            1.00
```

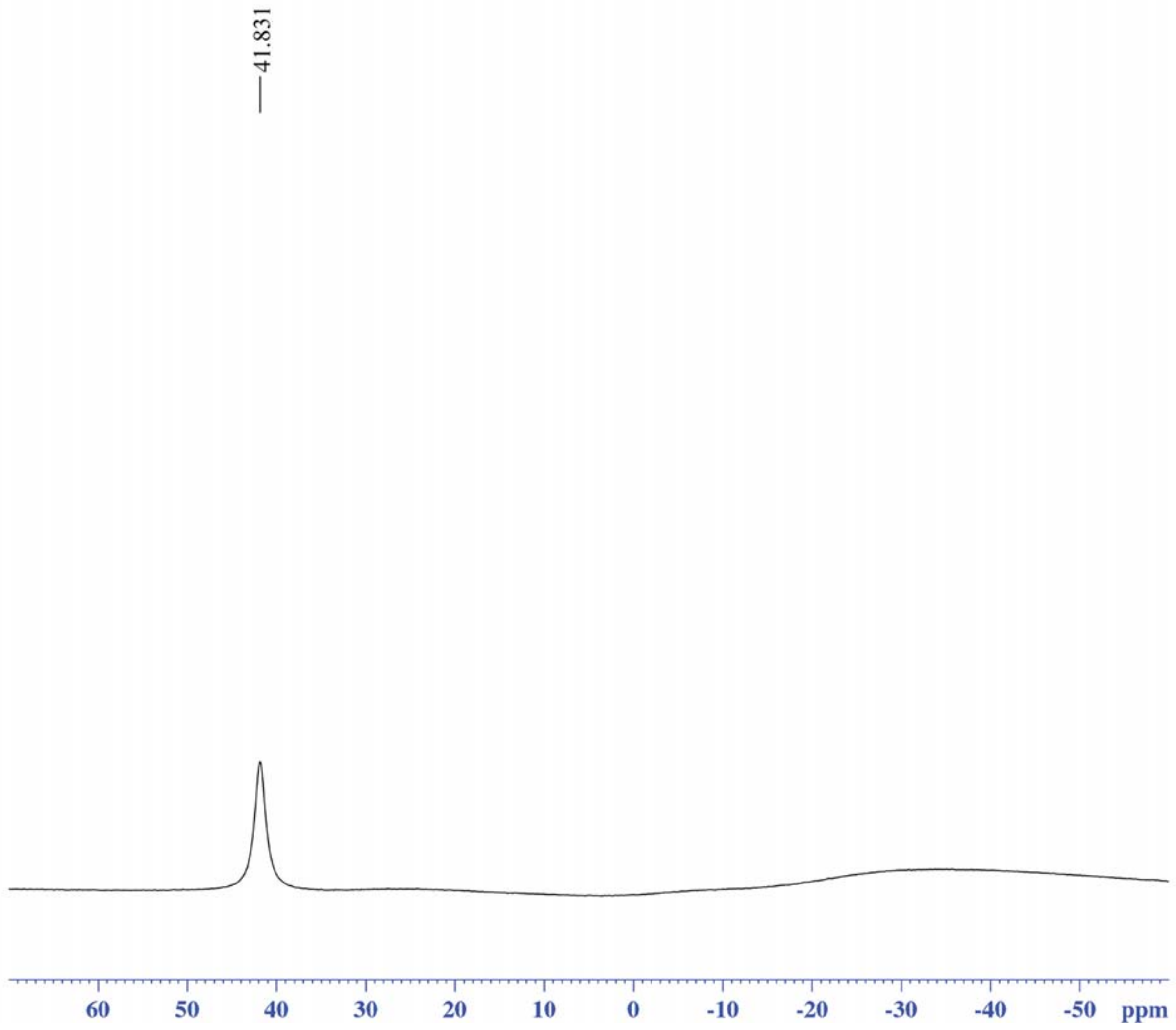


Q Exactive
High-Res Mass Spec





^{11}B {^{1}H} NMR



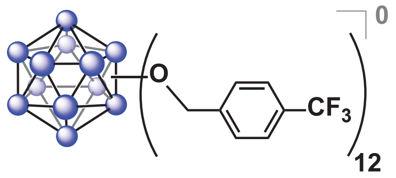
```
Current Data Parameters
NAME     B12(O-4-TFMBn)12
EXPNO              40
PROCNO              1

F2 - Acquisition Parameters
Date_         20150927
Time             14.58
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG        zgdc.js
TD                5096
SOLVENT          CDCl3
NS                1024
DS                   0
SWH        51020.406 Hz
FIDRES     10.011854 Hz
AQ         0.0499408 sec
RG              189.85
DW              9.800 usec
DE               6.50 usec
TE               299.3 K
D1       0.05000000 sec
D11      0.03000000 sec
TD0                  1

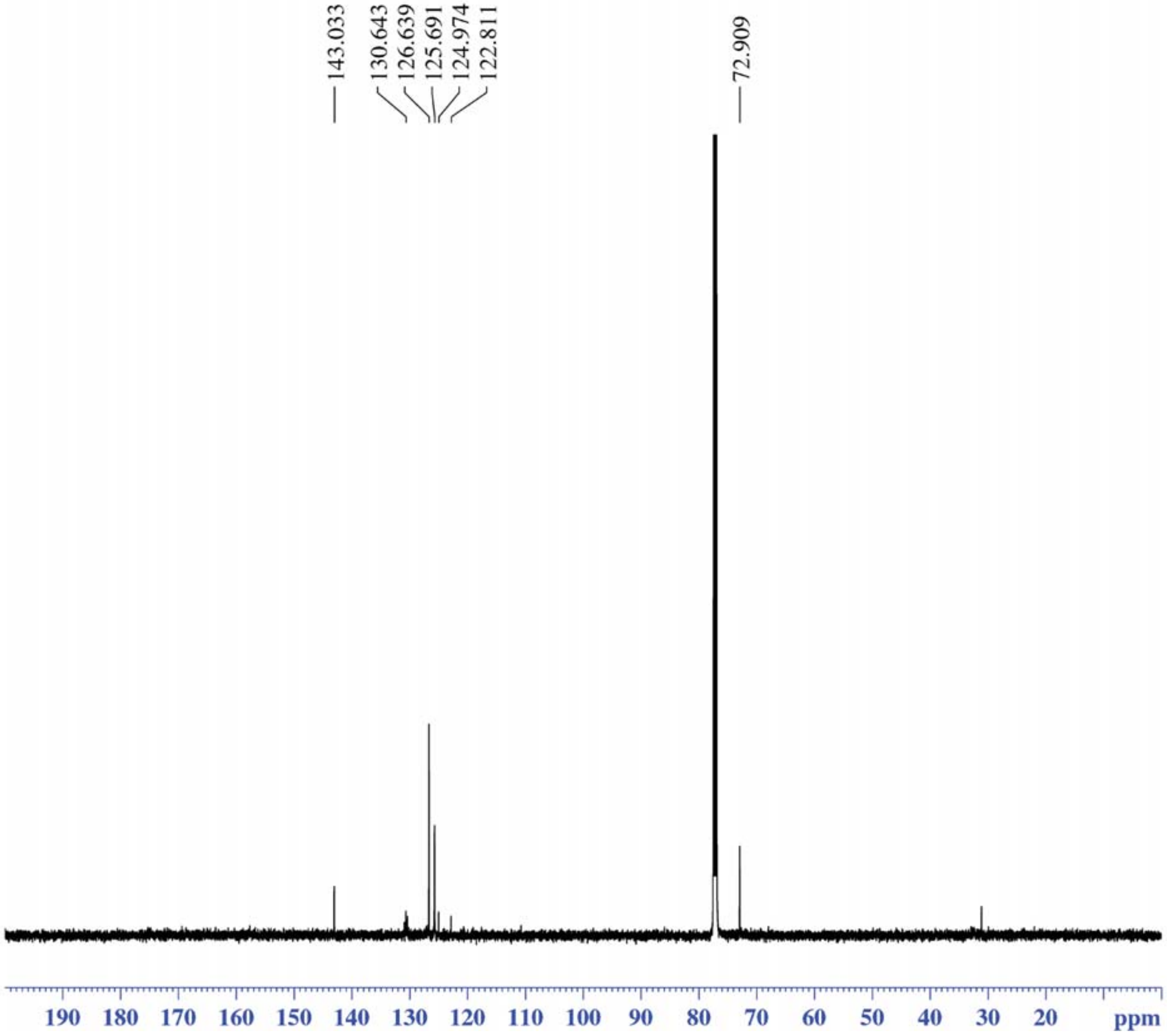
======== CHANNEL f1 ========
SFO1     128.3776052 MHz
NUC1               11B
P1             10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 ========
SFO2     400.1324008 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2          90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W

F2 - Processing parameters
SI               32768
SF       128.3776161 MHz
WDW                 EM
SSB     0
LB             10.00 Hz
GB      0
PC                1.40
```



^{13}C NMR



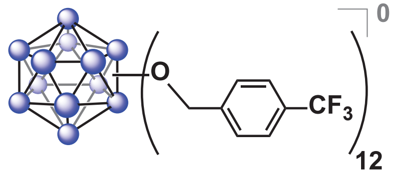
```
Current Data Parameters
NAME     B12(O-4-TFMBn)12
EXPNO              20
PROCNO              1

F2 - Acquisition Parameters
Date_        20150928
Time           13.45
INSTRUM          av500
PROBHD   5 mm DCH 13C-1
PULPROG         zgpg30
TD             65536
SOLVENT          CDCl3
NS                64
DS                 2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ        1.0485760 sec
RG            204.54
DW            16.000 usec
DE             18.00 usec
TE             298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                1

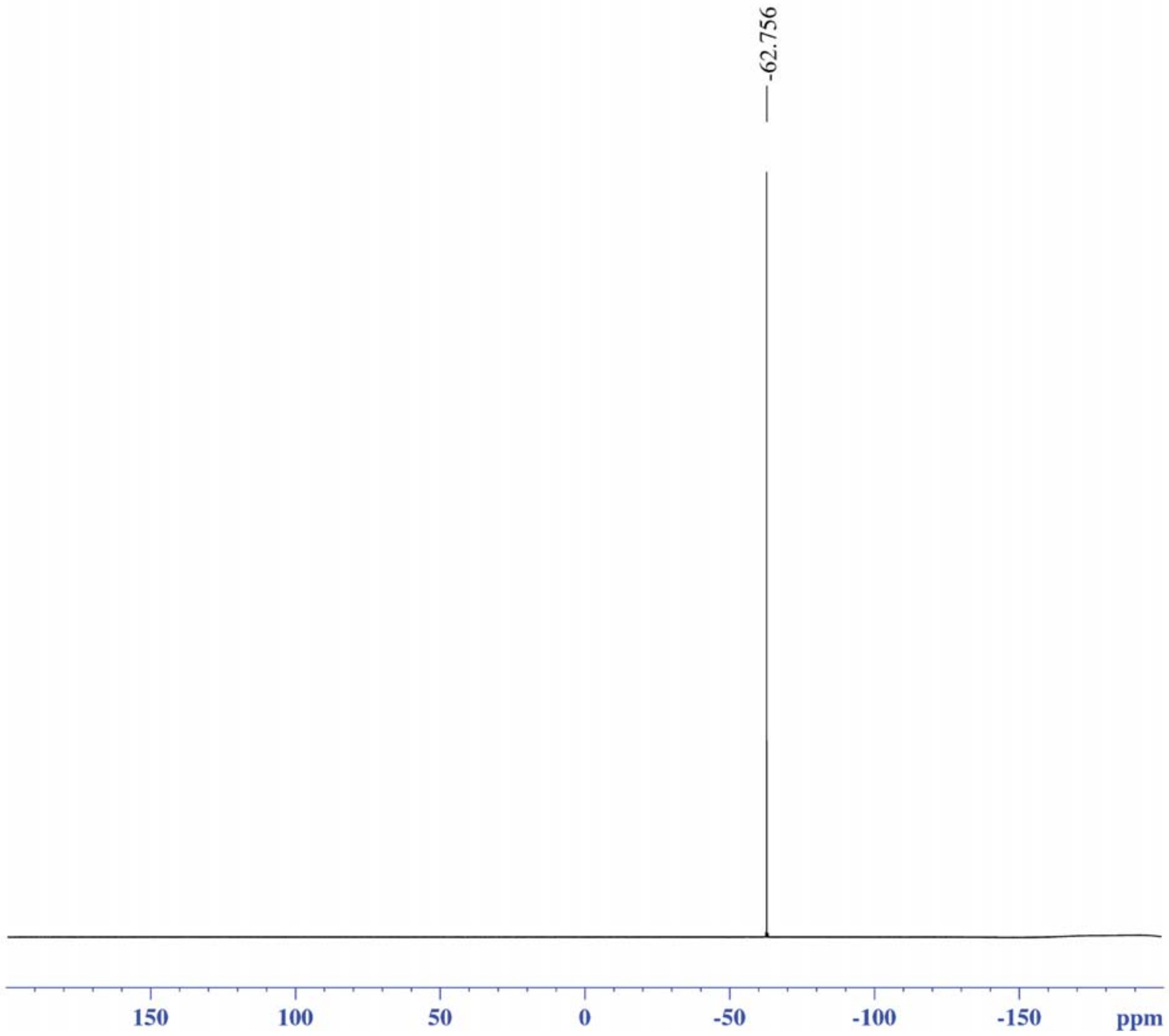
======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1             13C
P1              9.63 usec
PLW1     23.00000000 W

======== CHANNEL f2 ========
SFO2      500.1330008 MHz
NUC2              1H
CPDPRG[2         waltz16
PCPD2          80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.13500001 W

F2 - Processing parameters
SI            131072
SF       125.7577722 MHz
WDW              EM
SSB     0
LB              1.00 Hz
GB      0
PC              1.40
```



^{19}F NMR

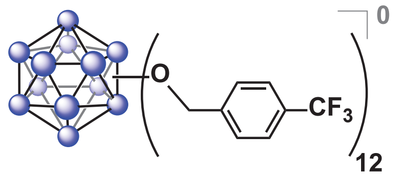


Current Data Parameters
NAME B12(O-4-TFMBn)12
EXPNO 42
PROCNO 1

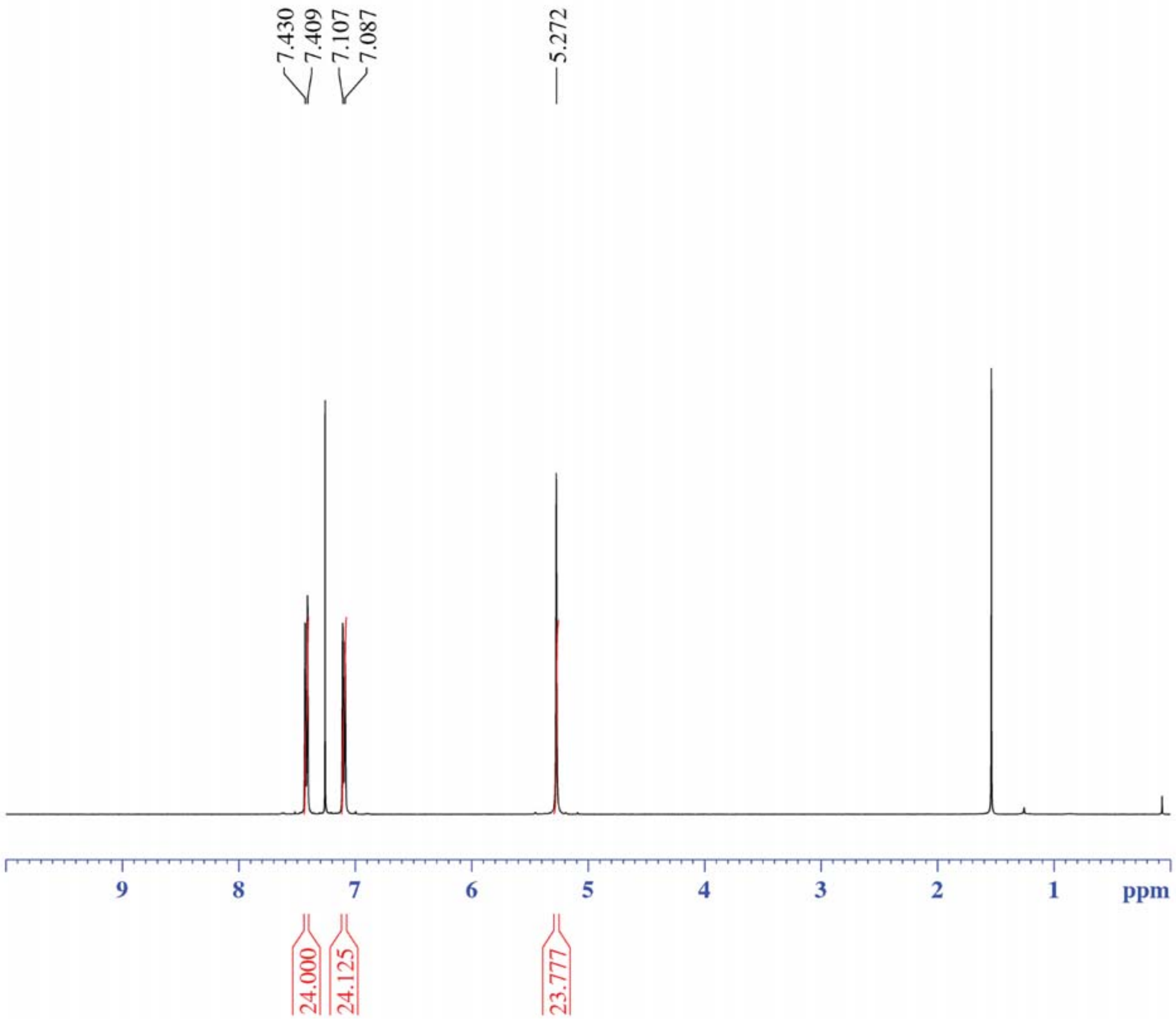
F2 - Acquisition Parameters
Date_ 20150927
Time 15.05
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqn30
TD 262144
SOLVENT CDCl3
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 376.4983660 MHz
NUC1 19F
P1 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



^{1}H NMR

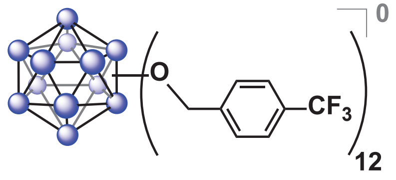


```
Current Data Parameters
NAME     B12(O-4-TFMBn)12
EXPNO             41
PROCNO             1

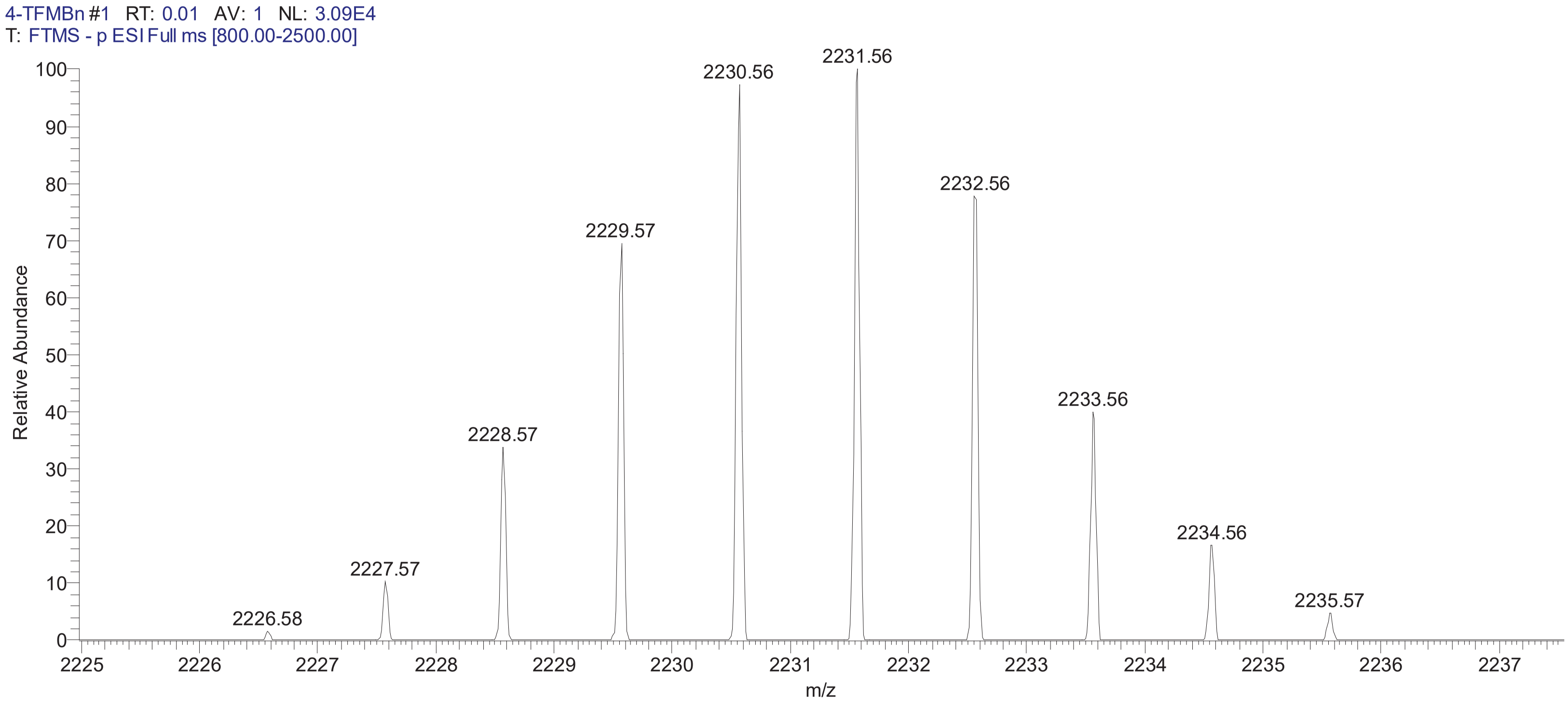
F2 - Acquisition Parameters
Date_        20150927
Time            15.01
INSTRUM         av400
PROBHD  5 mm PABBO BB/
PULPROG          zg30
TD              52882
SOLVENT         CDCl3
NS                 32
DS                  0
SWH        8012.820 Hz
FIDRES     0.151523 Hz
AQ       3.2998369 sec
RG             189.85
DW         62.400 usec
DE           6.50 usec
TE            299.0 K
D1      2.00000000 sec
TD0                 1

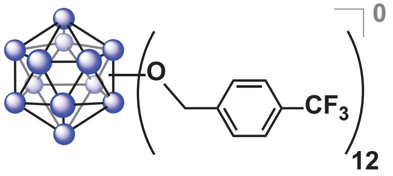
======== CHANNEL f1 ========
SFO1     400.1324008 MHz
NUC1               1H
P1            15.00 usec
PLW1      13.00000000 W

F2 - Processing parameters
SI              65536
SF       400.1300184 MHz
WDW                EM
SSB   0
LB            0.30 Hz
GB    0
PC             1.00
```

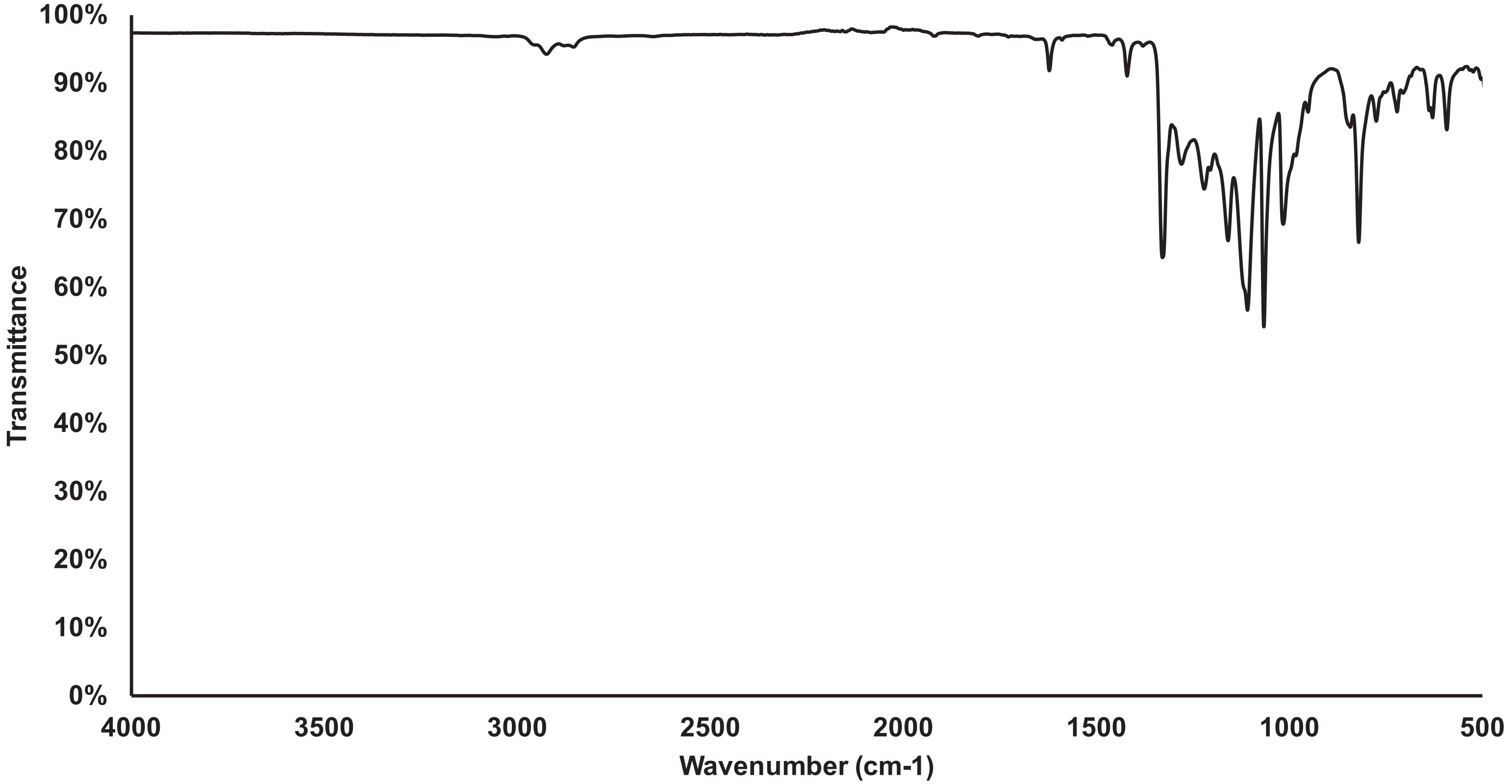


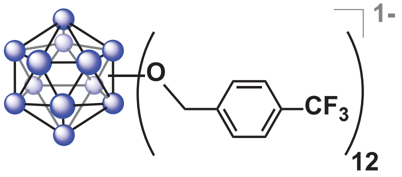
Q Exactive
High-Res Mass Spec



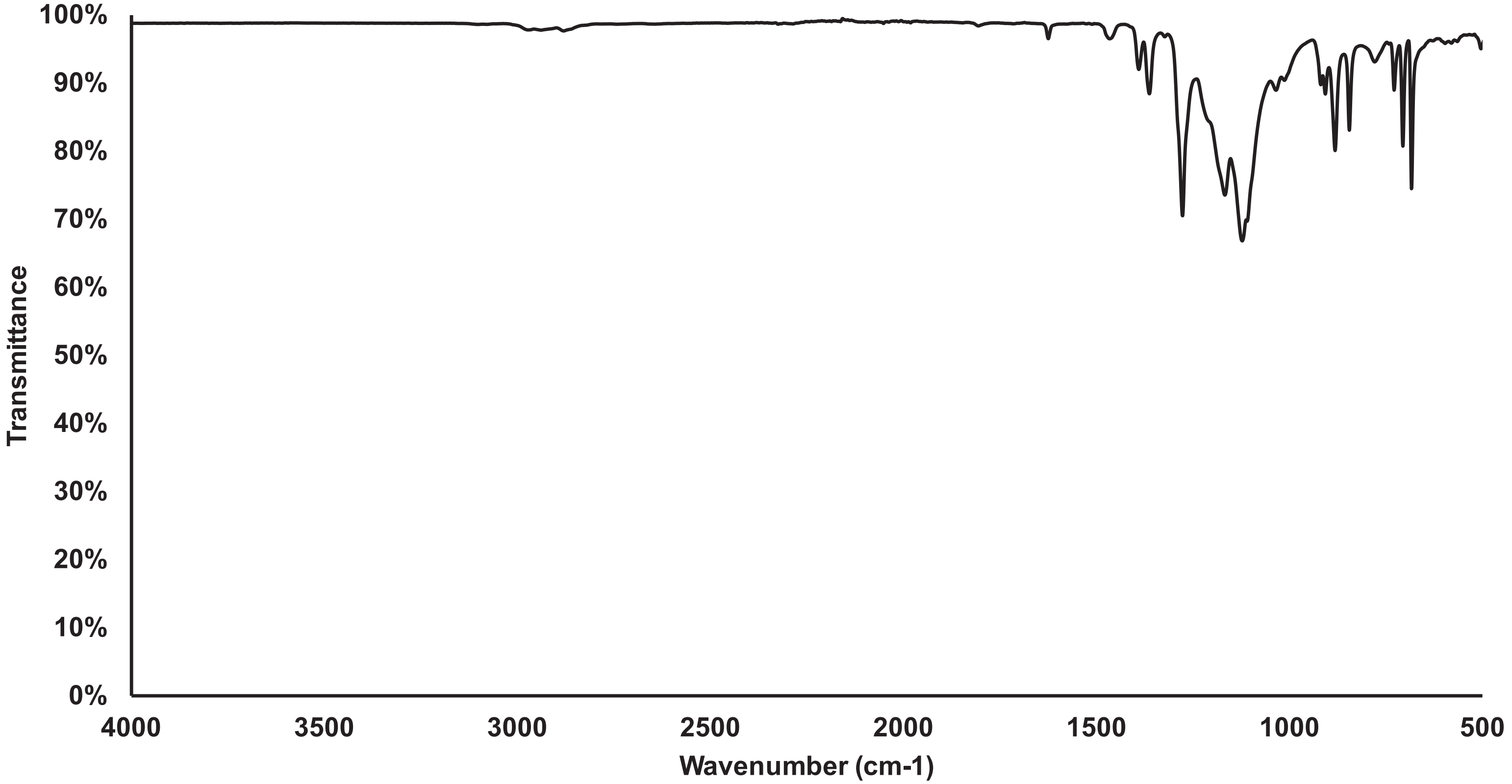

O
CF3
12
0

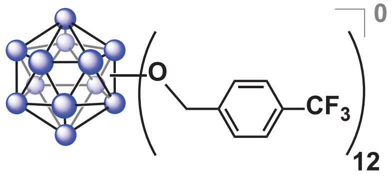
IR


Transmittance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

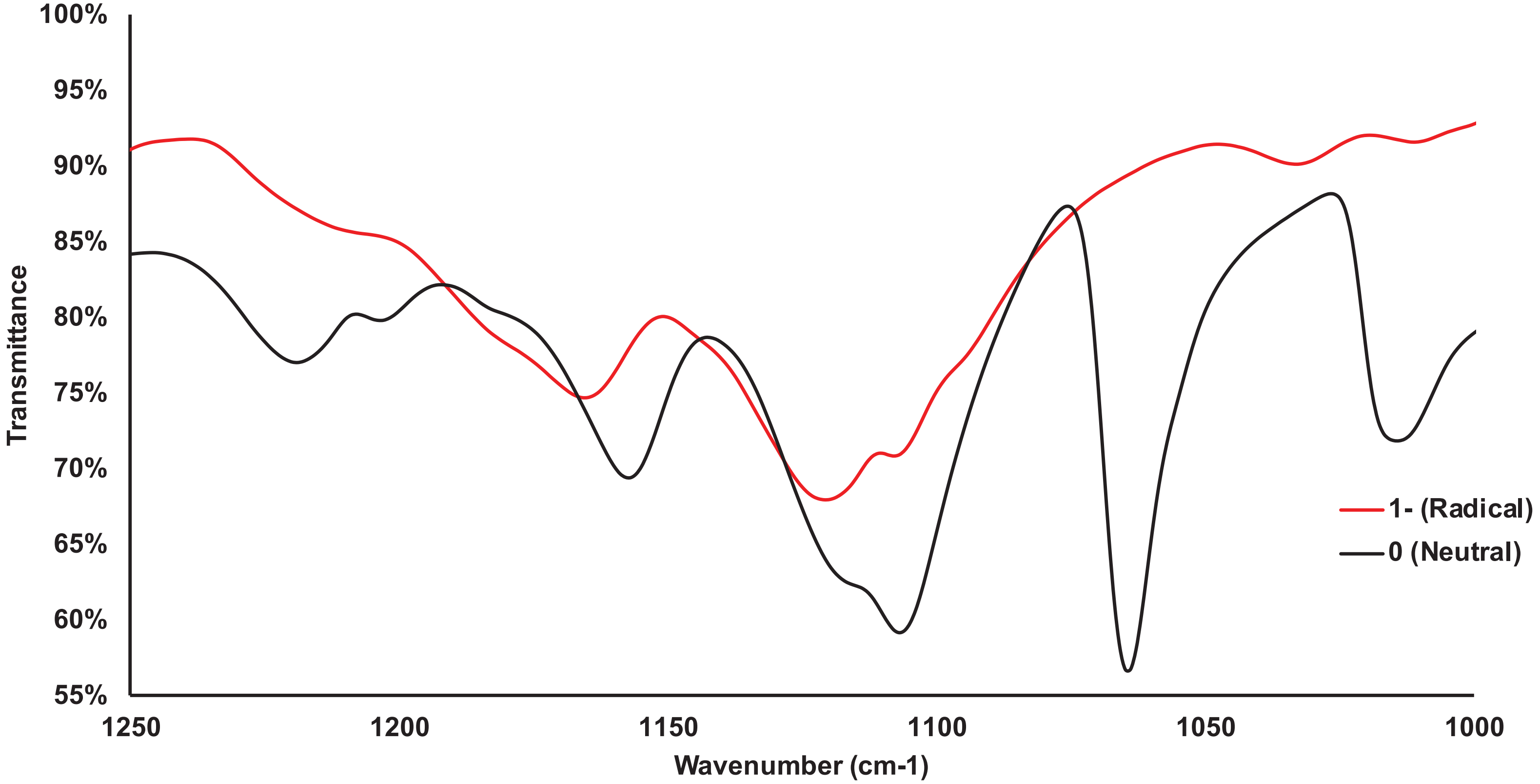

1-
O
CF3
12

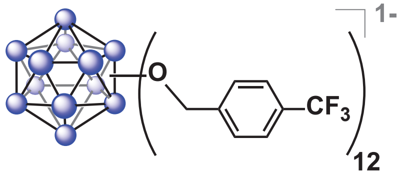
IR


Transmittance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

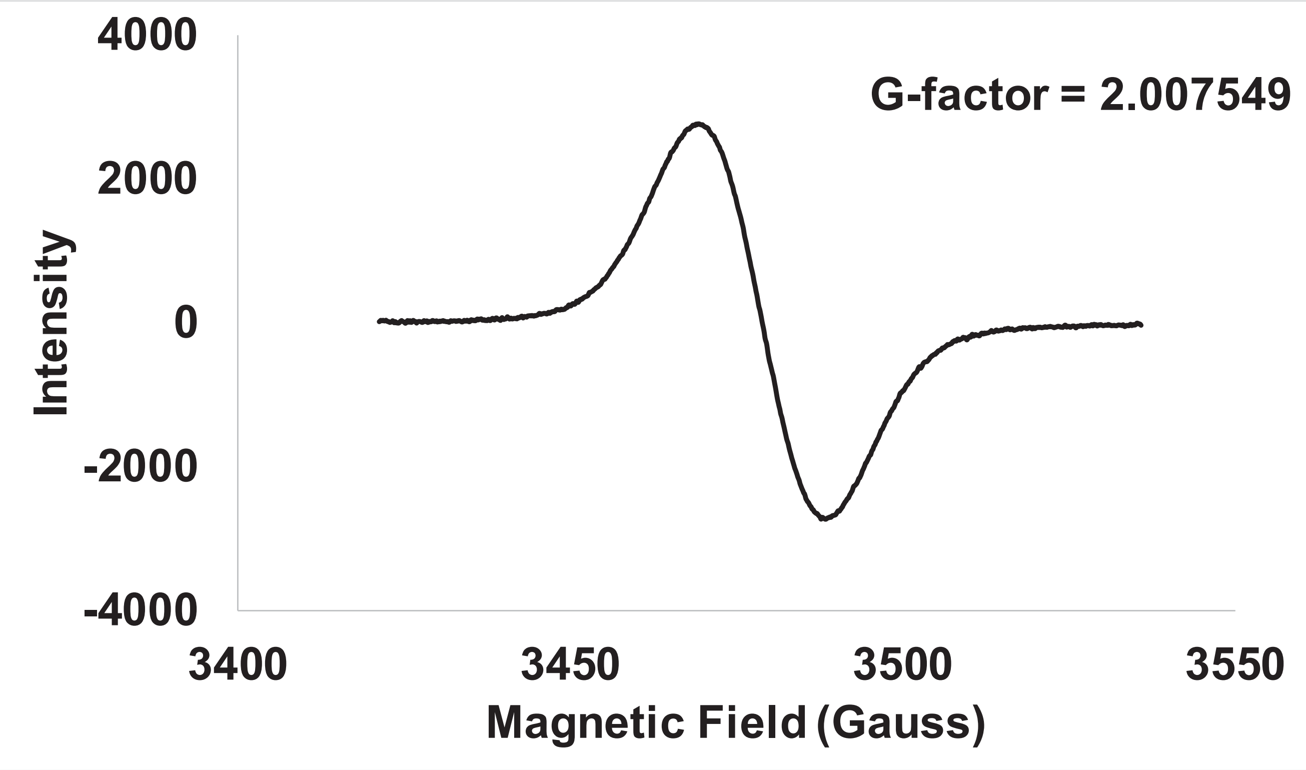

O
CF3
12
0

IR

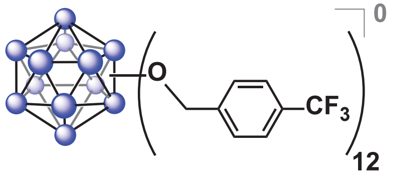

Transmittance
100%
95%
90%
85%
80%
75%
70%
65%
60%
55%
1250
1200
1150
1100
1050
1000
Wavenumber (cm-1)
1- (Radical)
0 (Neutral)



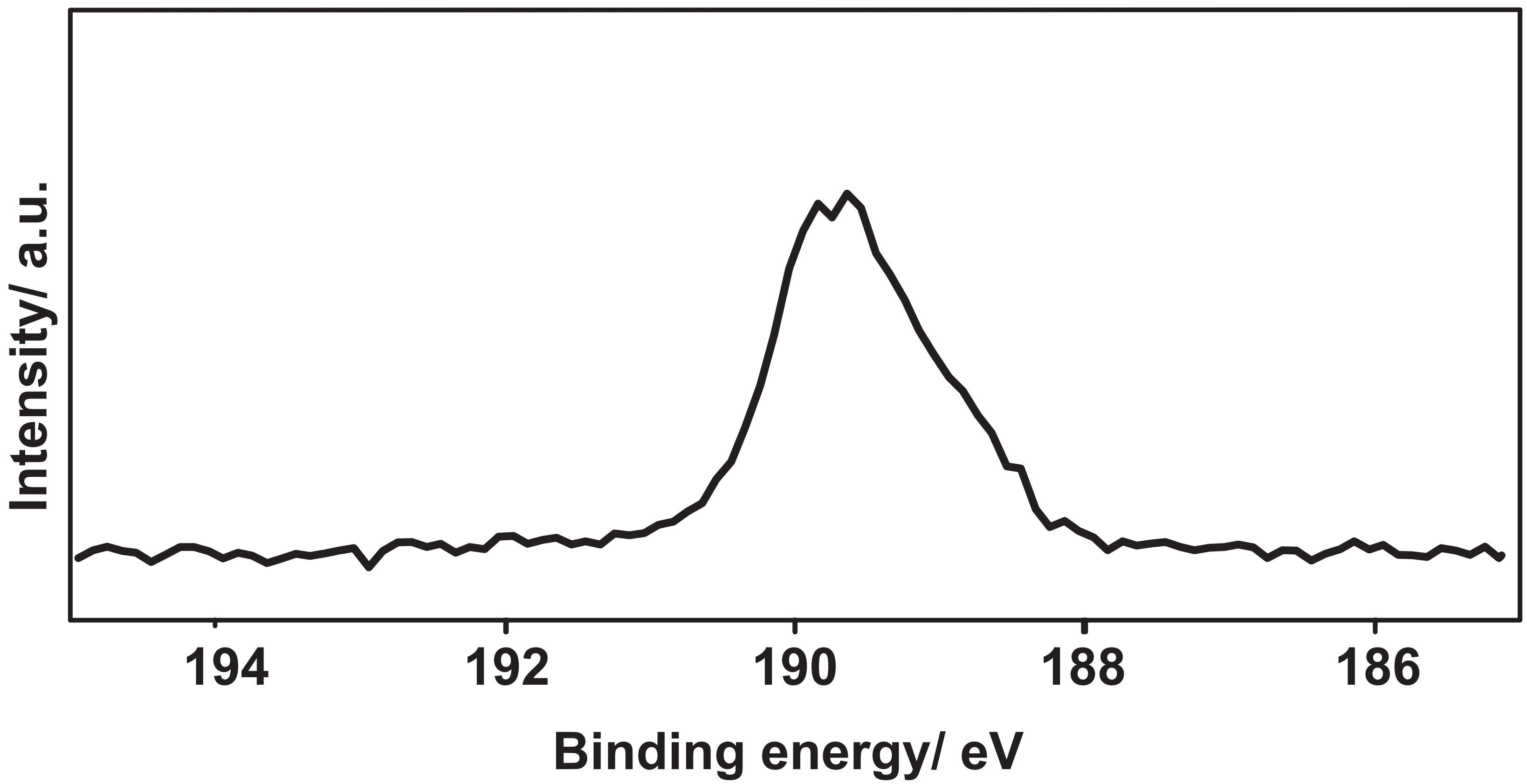
EPR

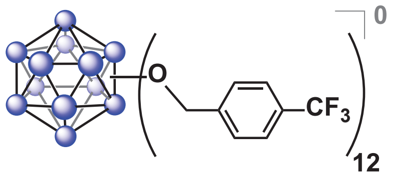


DOS	Format
ANZ	1024
MIN	-2733.186523
MAX	2772.813477
JSS	0
GST	3421.274884
GSI	114.543004
JUN	G
JON	Bruker BioSpin GmbH
JDA	9/25/2015
JTM	13:33
JRE	c:\programfiles\bruker-emx\syscal\st0103.cal
JEX	field-sweep
JSD	1
HCF	3478.546386
HSW	114.543004
EMF	0
RCT	20.48
RTC	20.48
RRG	8.93E+03
RMA	4
MF	9.773981
MP	6.38E-01
MPD	25

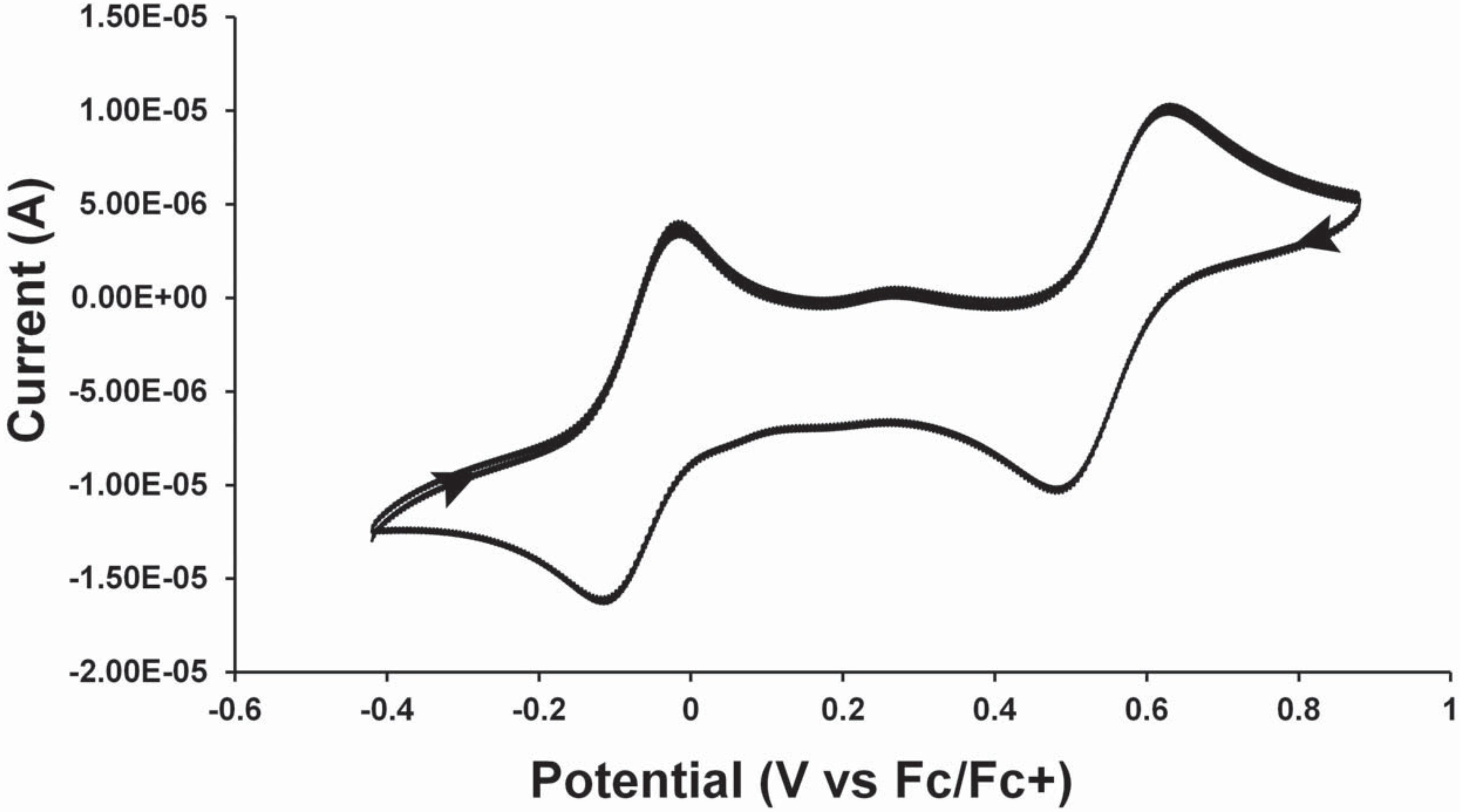


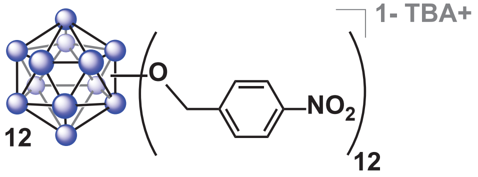
B 1s XPS





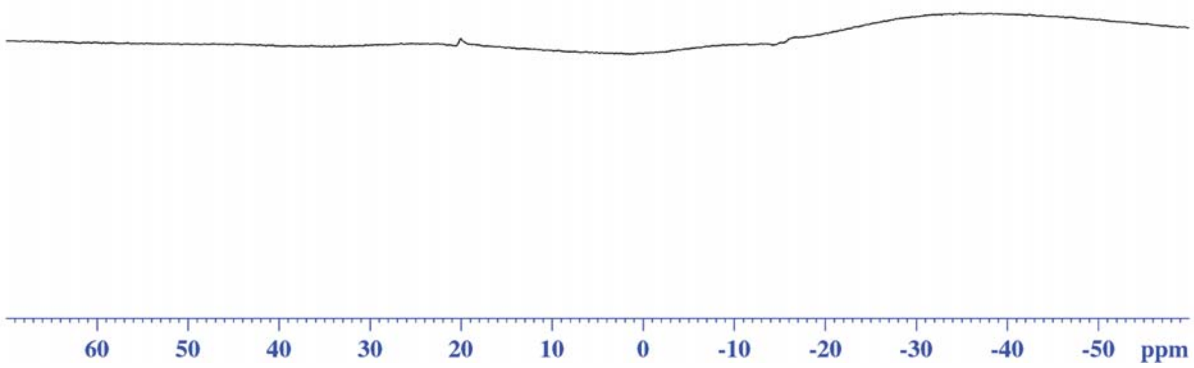
Cyclic voltammetry





12

^{11}B {^{1}H} NMR



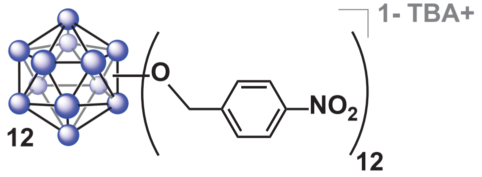
```
Current Data Parameters
NAME     B12(O-4-NO2Bn)12
EXPNO              60
PROCNO              1

F2 - Acquisition Parameters
Date_         20151101
Time            19.40
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG        zgdc.js
TD               5096
SOLVENT        Acetone
NS               1024
DS                  0
SWH        51020.406 Hz
FIDRES     10.011854 Hz
AQ         0.0499408 sec
RG             189.85
DW            9.800 usec
DE             6.50 usec
TE             299.0 K
D1       0.05000000 sec
D11      0.03000000 sec
TD0                 1

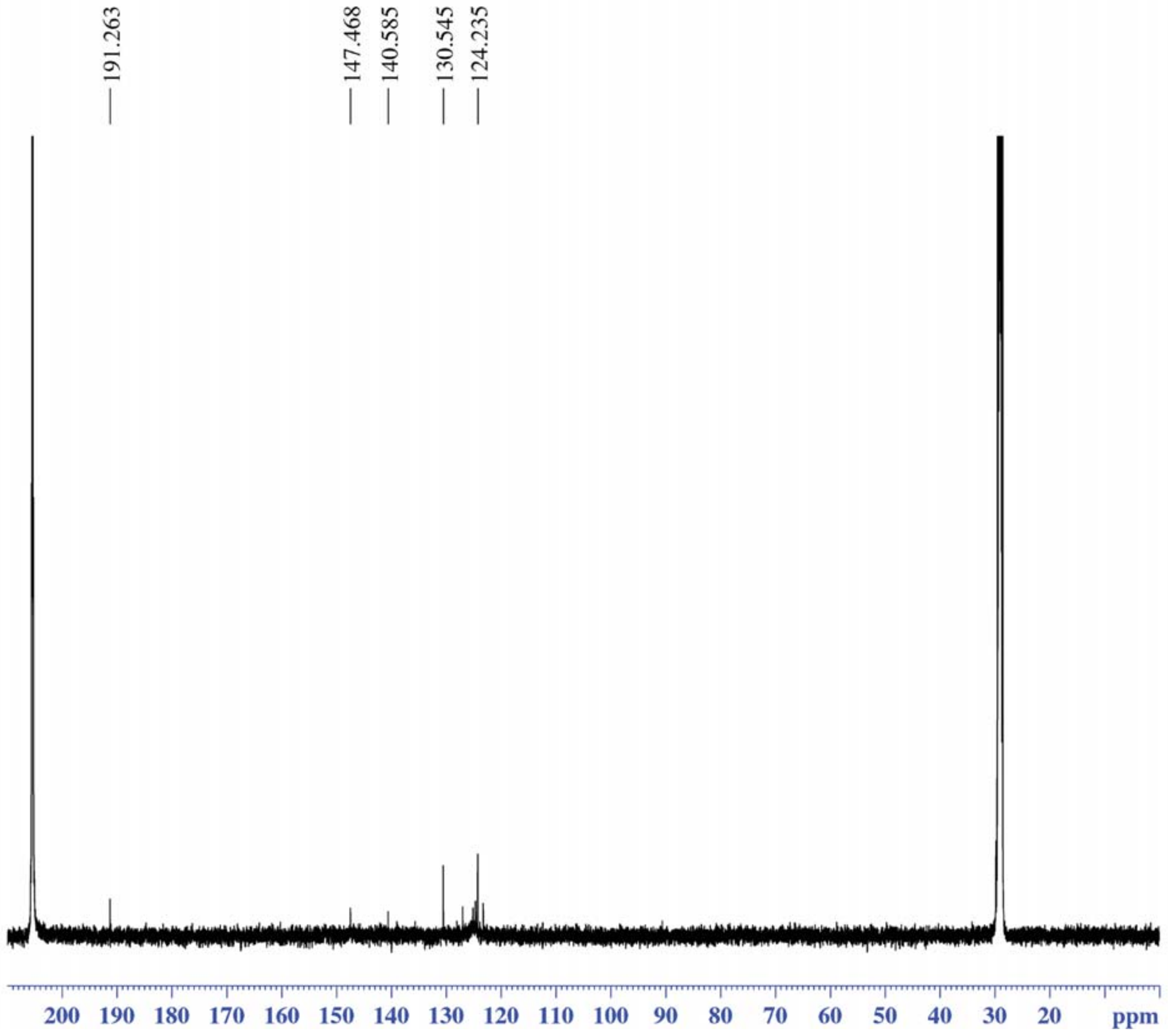
======== CHANNEL f1 ========
SFO1     128.3776052 MHz
NUC1              11B
P1            10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 ========
SFO2     400.1324008 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2         90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W

F2 - Processing parameters
SI              32768
SF       128.3776161 MHz
WDW                EM
SSB     0
LB             10.00 Hz
GB      0
PC               1.40
```



^{13}C NMR



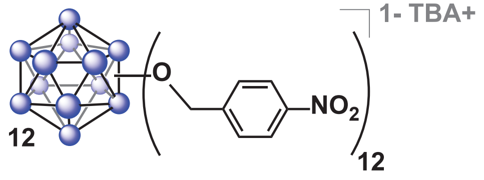
```
Current Data Parameters
NAME     B12(O-4-NO2Bn)12
EXPNO              10
PROCNO              1

F2 - Acquisition Parameters
Date_        20151103
Time            11.12
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT        Acetone
NS                128
DS                  2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ         1.0485760 sec
RG             204.54
DW            16.000 usec
DE             18.00 usec
TE             298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                 1

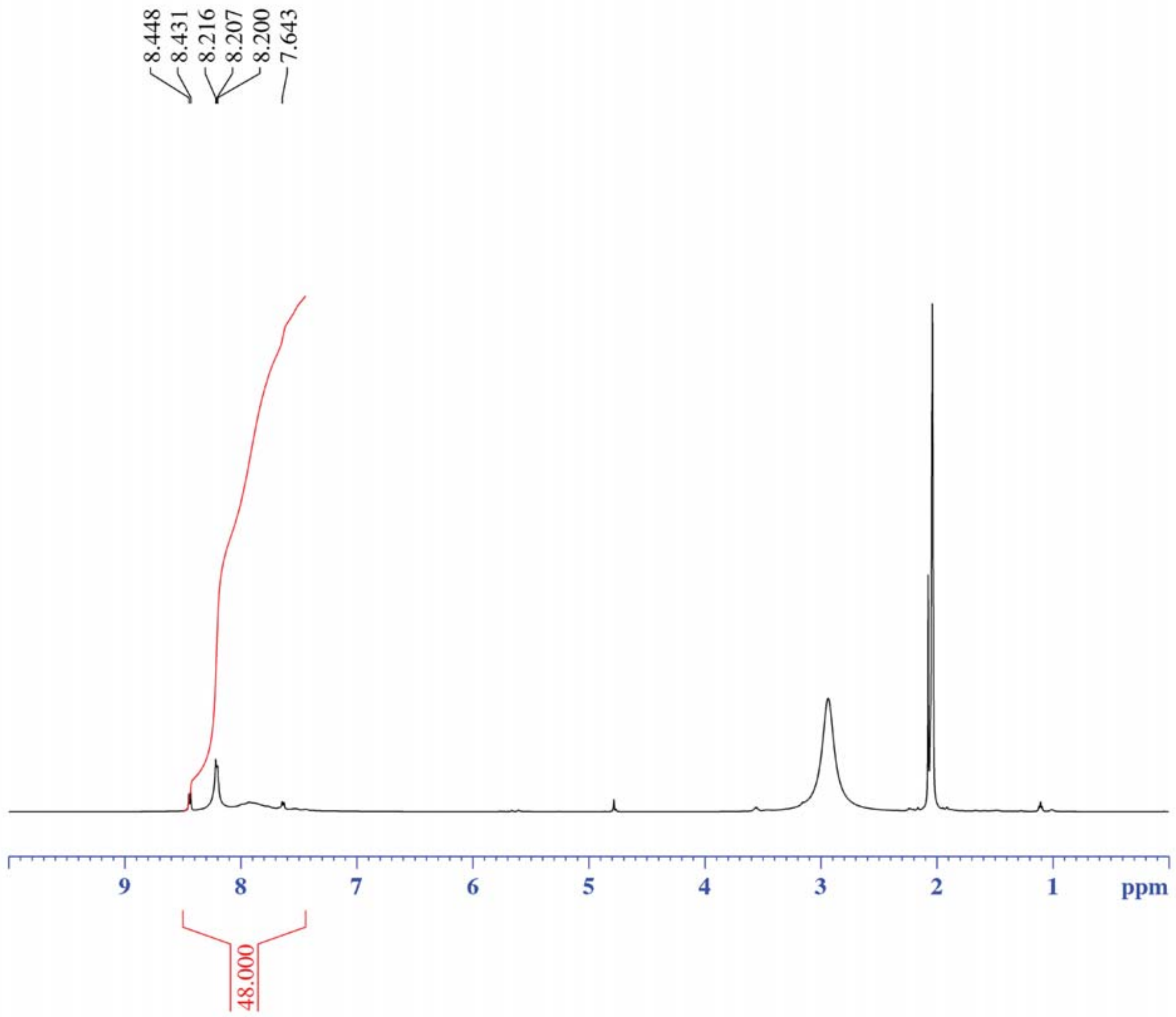
======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec
PLW1      23.00000000 W

======== CHANNEL f2 ========
SFO2      500.1330008 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2           80.00 usec
PLW2      13.50000000 W
PLW12      0.21094000 W
PLW13      0.13500001 W

F2 - Processing parameters
SI             131072
SF        125.7577890 MHz
WDW                EM
SSB     0
LB              1.00 Hz
GB      0
PC              1.40
```



^{1}H NMR

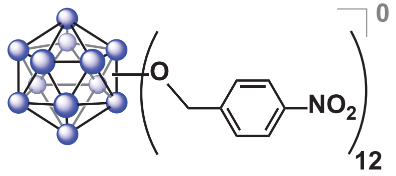


```
Current Data Parameters
NAME     B12(O-4-NO2Bn)12
EXPNO              11
PROCNO              1

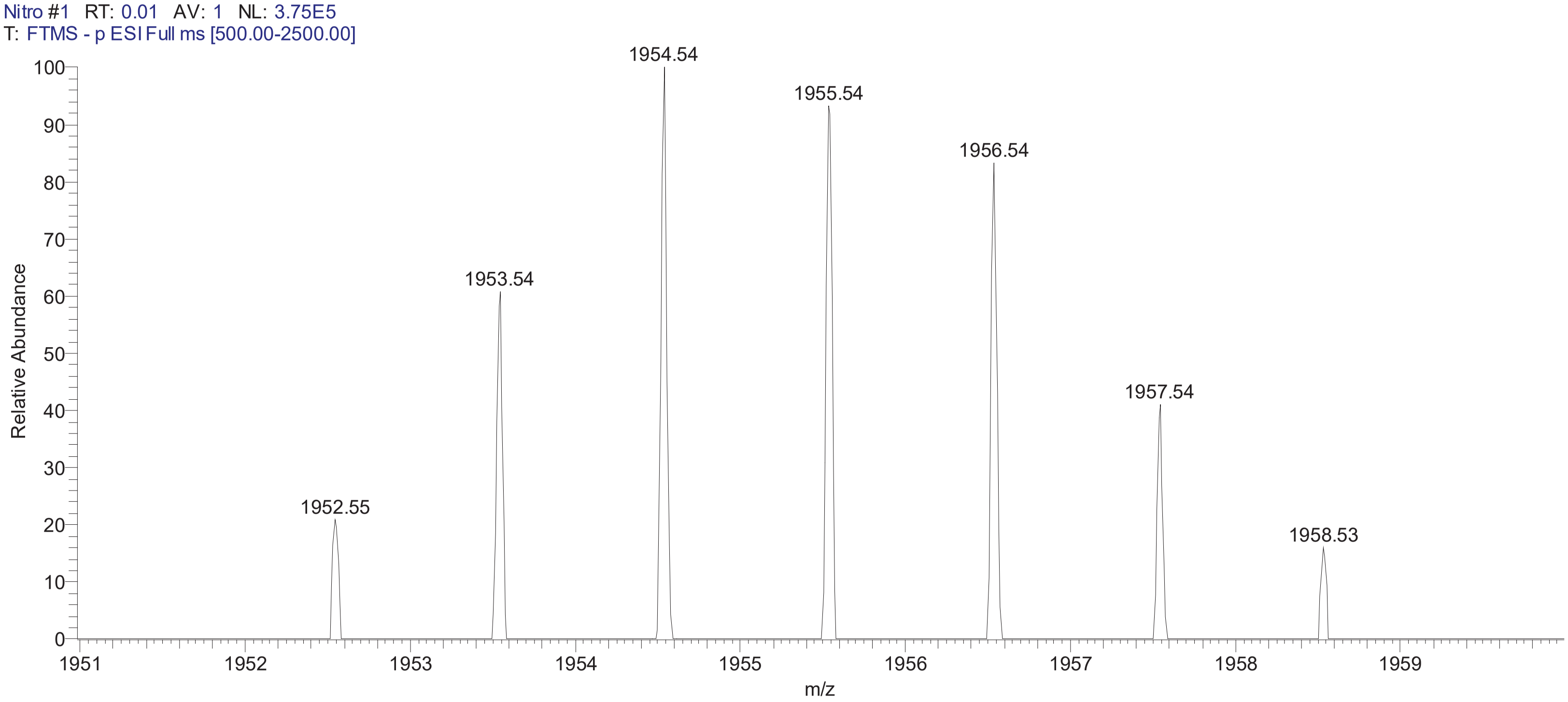
F2 - Acquisition Parameters
Date_         20151103
Time             11.16
INSTRUM          av500
PROBHD  5 mm DCH 13C-1
PULPROG           zg30
TD               65536
SOLVENT        Acetone
NS                  32
DS                   0
SWH         10000.000 Hz
FIDRES       0.152588 Hz
AQ          3.2767999 sec
RG               52.41
DW              50.000 usec
DE              10.00 usec
TE              298.0 K
D1        2.00000000 sec
TD0                  1

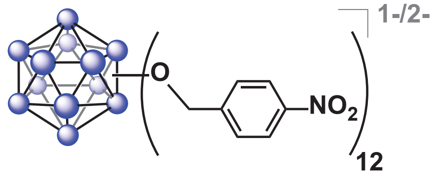
======== CHANNEL f1 ========
SFO1      500.1330008 MHz
NUC1                1H
P1             10.00 usec
PLW1      13.50000000 W

F2 - Processing parameters
SI               65536
SF       500.1300146 MHz
WDW                 EM
SSB    0
LB                0.30 Hz
GB     0
PC                1.00
```

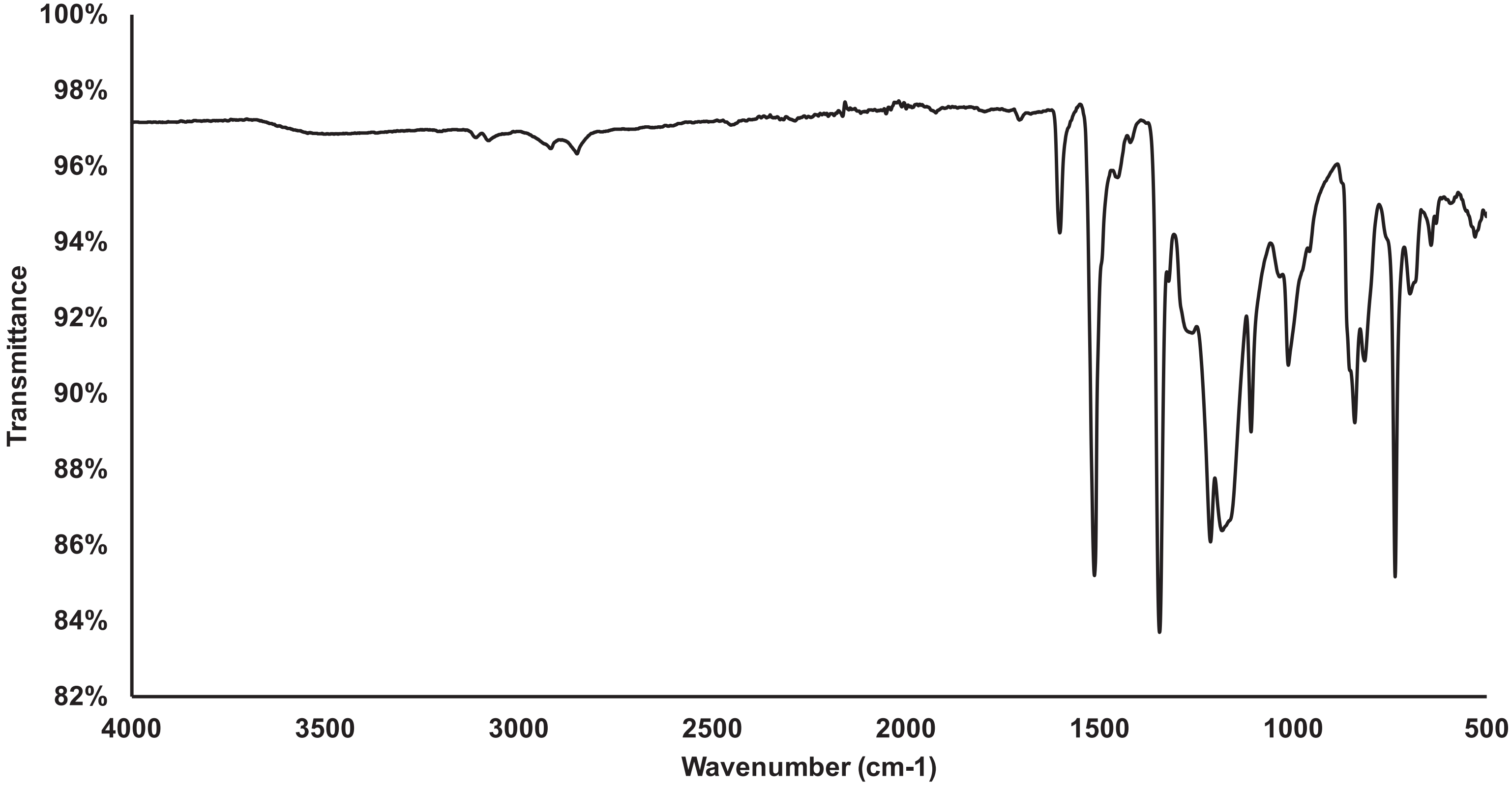


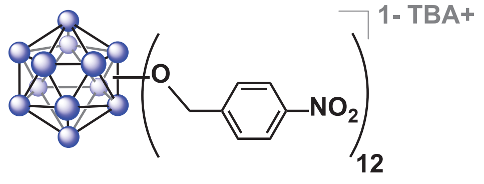
Q Exactive
High-Res Mass Spec



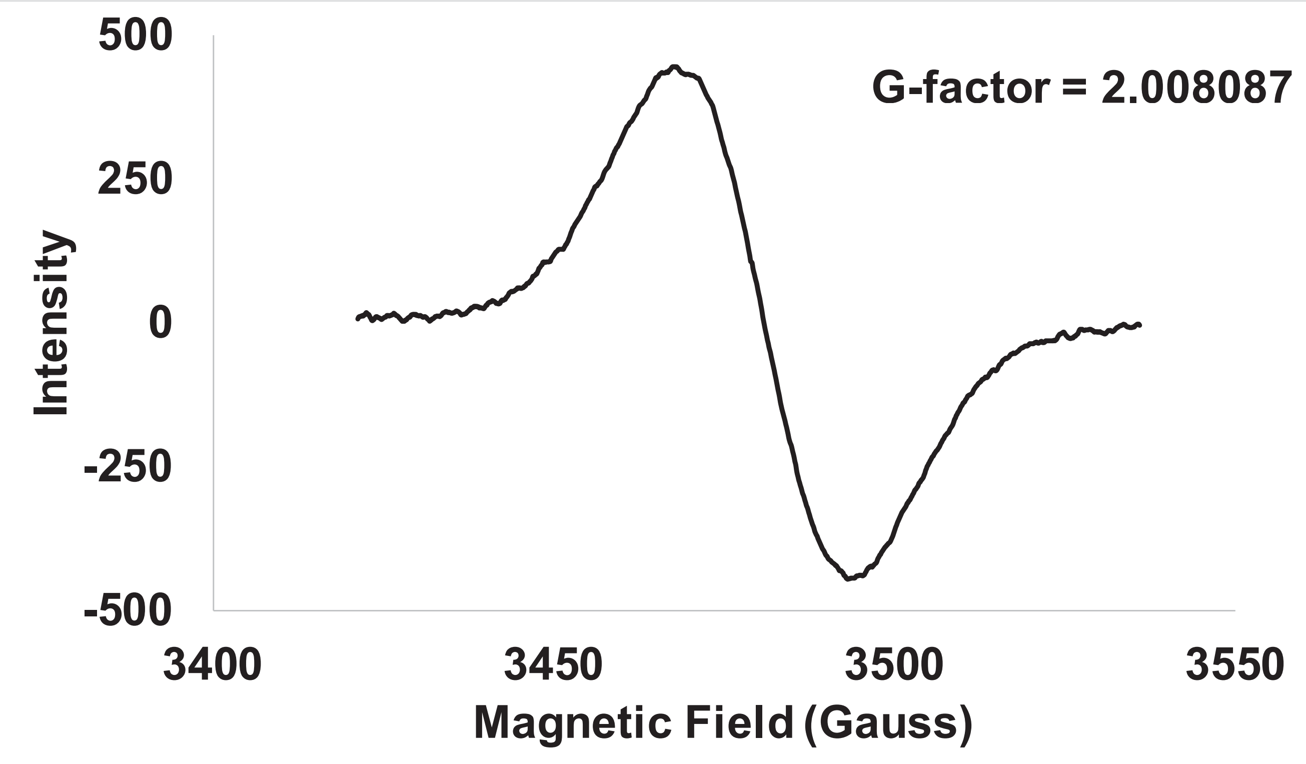

O
NO2
12
1-/2-

IR

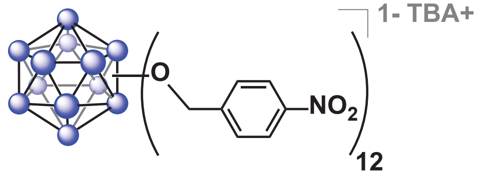

Transmittance
100%
98%
96%
94%
92%
90%
88%
86%
84%
82%
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)



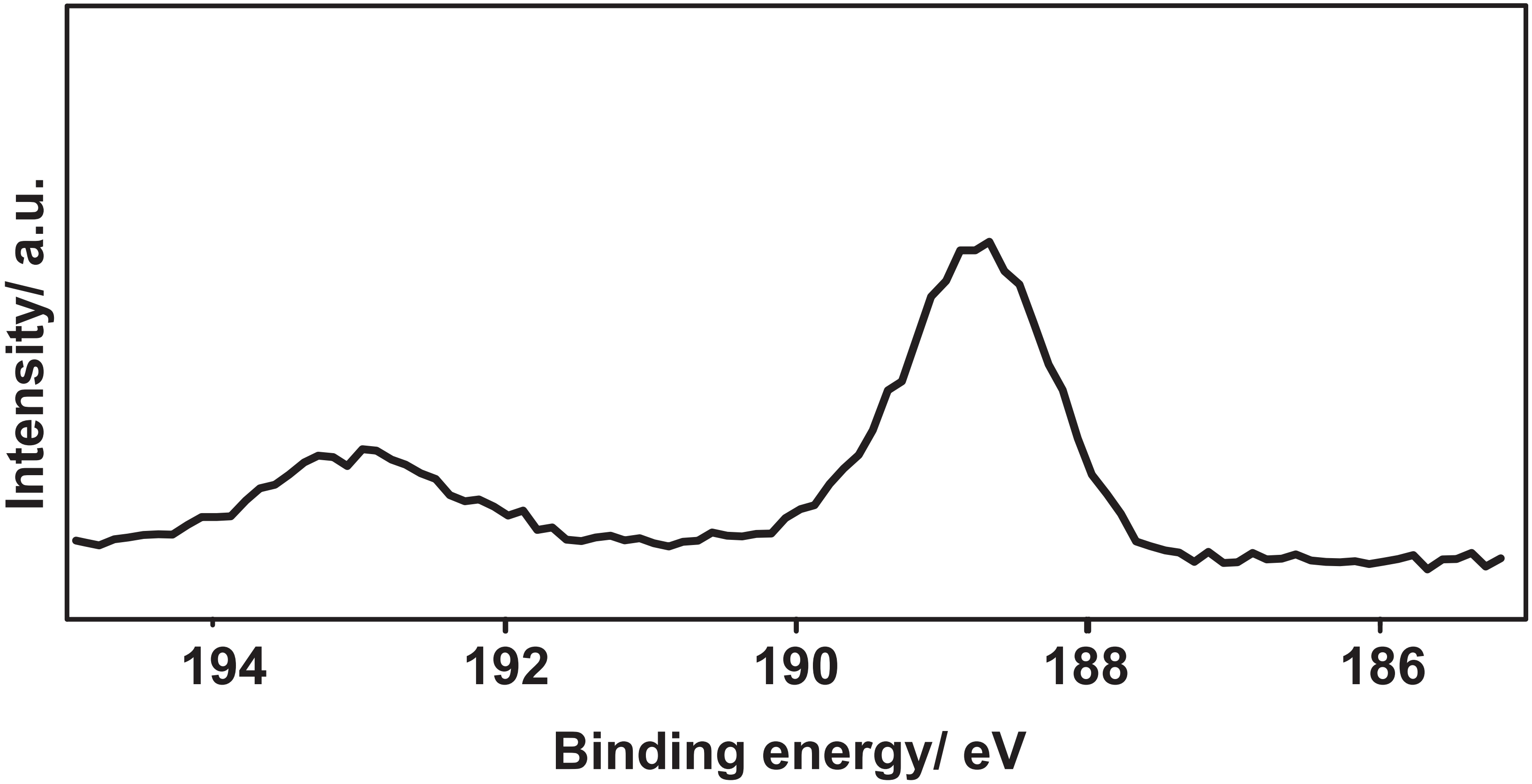
EPR

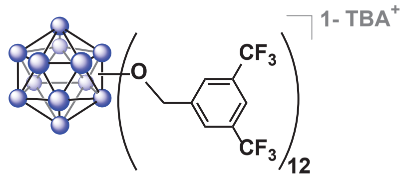


DOS	Format
ANZ	1024
MIN	-445.813477
MAX	444.186523
JSS	0
GST	3421.28
GSI	114.54
JUN	G
JON	Bruker BioSpin GmbH
JDA	9/29/2015
JTM	16:26
JRE	c:\programfiles\bruker-emx\syscal\st0103.cal
JEX	field-sweep
JSD	1
HCF	3478.55
HSW	114.54
EMF	0
RCT	20.48
RTC	163.84
RRG	8.93E+03
RMA	4
MF	9.776609
MP	6.38E-01
MPD	25


O
NO2
12
1- TBA+

B 1s XPS


Intensity/ a.u.
194
192
190
188
186
Binding energy/ eV



^{11}B {^{1}H} NMR

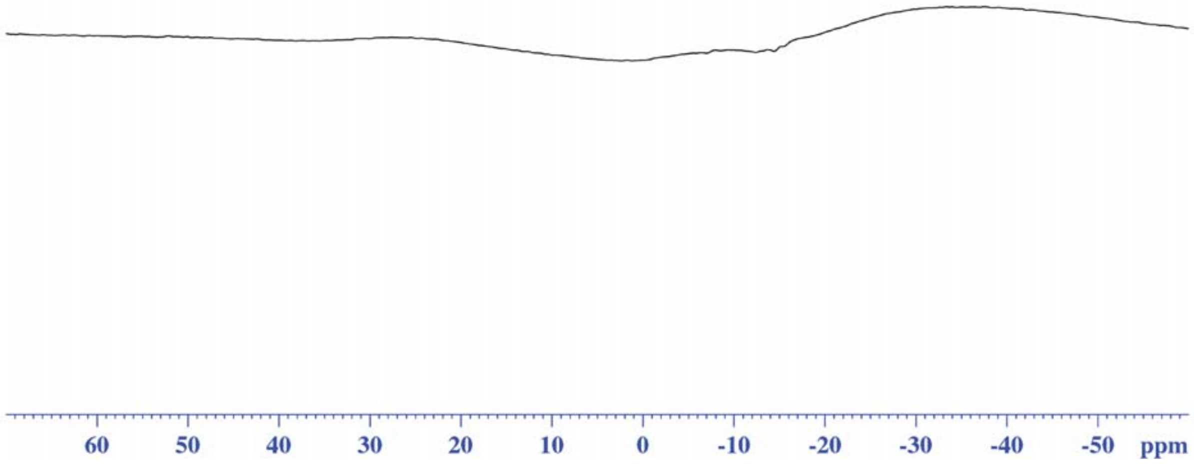
```
Current Data Parameters
NAME      B12(O-3,5-bisTFMBn)12
EXPNO              210
PROCNO               1

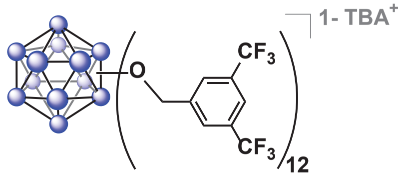
F2 - Acquisition Parameters
Date_          20150824
Time              20.51
INSTRUM           av400
PROBHD   5 mm PABBO BB/
PULPROG         zgdc.js
TD                 5096
SOLVENT           CDCl3
NS                 1024
DS                    0
SWH        51020.406 Hz
FIDRES     10.011854 Hz
AQ        0.0499408 sec
RG               189.85
DW            9.800 usec
DE             6.50 usec
TE              299.2 K
D1       0.00000400 sec
D11      0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1      128.3776052 MHz
NUC1                  11B
P1             10.00 usec
PLW1        52.00000000 W

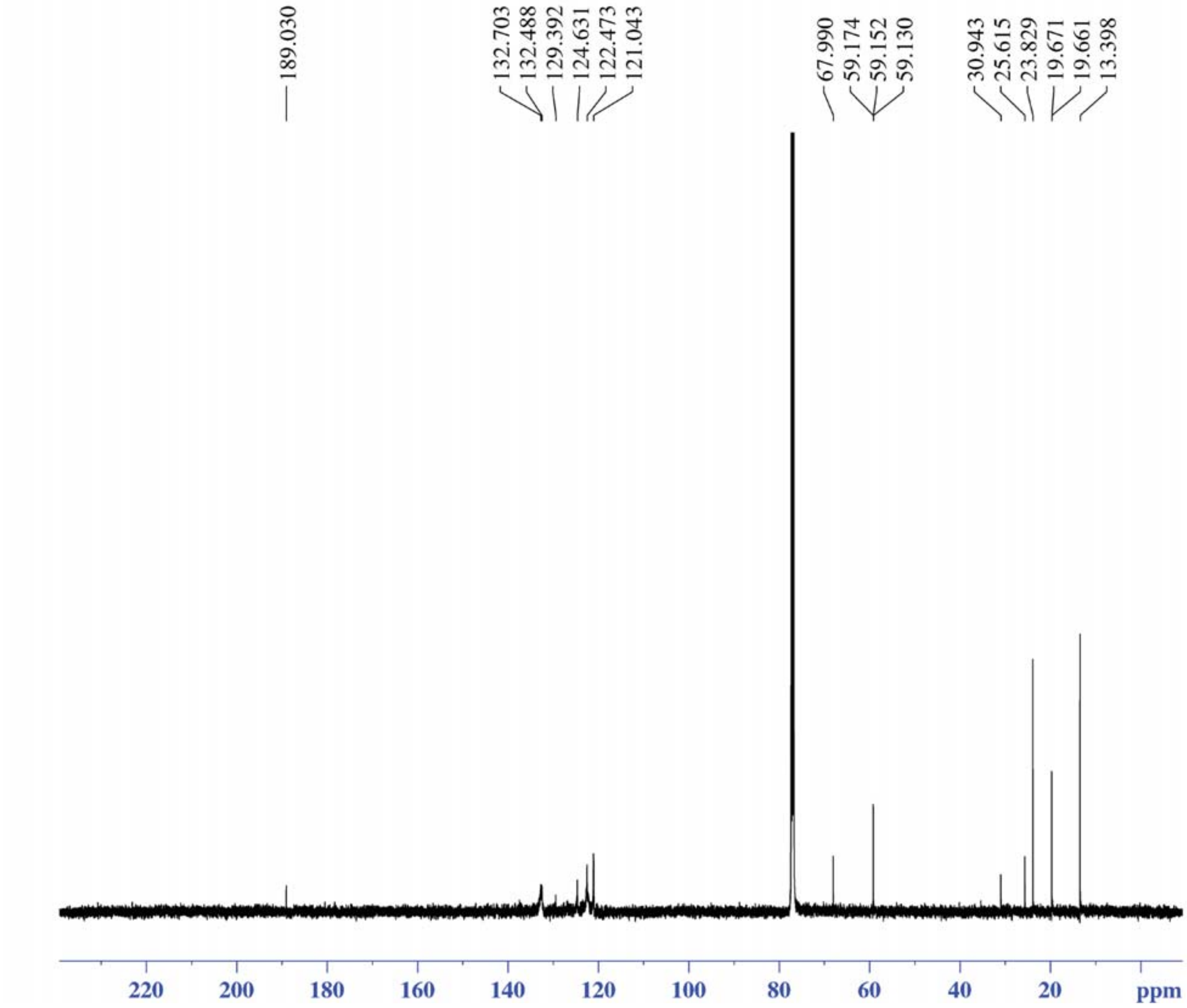
======== CHANNEL f2 ========
SFO2      400.1324008 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2          90.00 usec
PLW2        13.00000000 W
PLW12        0.36111000 W

F2 - Processing parameters
SI                32768
SF       128.3776050 MHz
WDW                  EM
SSB     0
LB             50.00 Hz
GB      0
PC                 1.40
```





^{13}C NMR



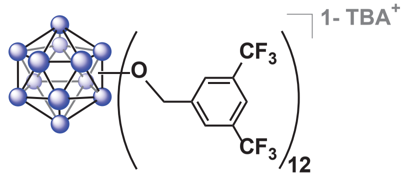
```
Current Data Parameters
NAME     B12(O-3,5-bisTFMBn)12
EXPNO               300
PROCNO                1

F2 - Acquisition Parameters
Date_        20150829
Time            21.11
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                256
DS                  2
SWH       31250.000 Hz
FIDRES     0.476837 Hz
AQ        1.0485760 sec
RG             204.54
DW          16.000 usec
DE           18.00 usec
TE             298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                 1

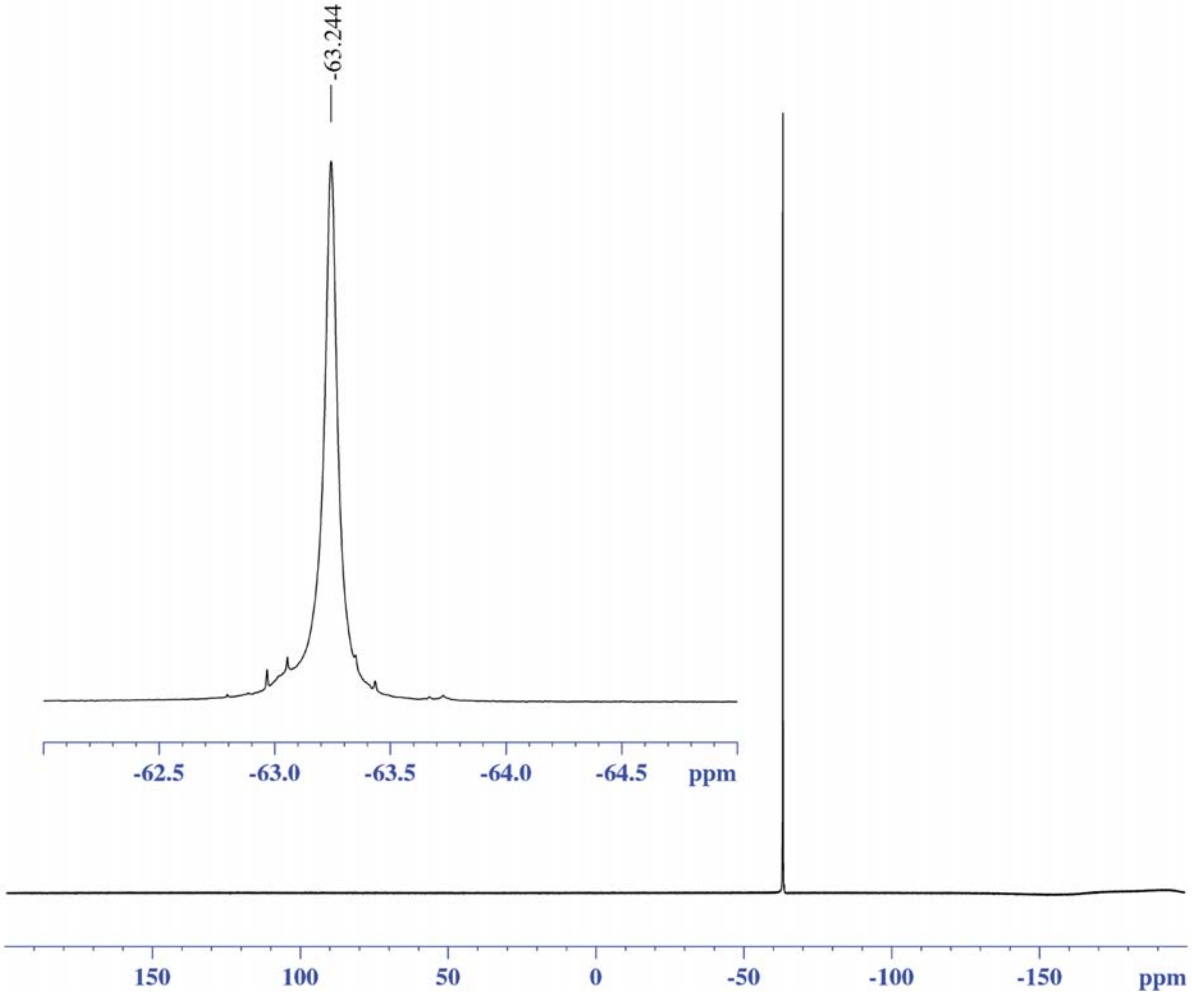
======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1             13C
P1             9.63 usec
PLW1     23.00000000 W

======== CHANNEL f2 ========
SFO2     500.1330008 MHz
NUC2              1H
CPDPRG[2       waltz16
PCPD2        80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.13500001 W

F2 - Processing parameters
SI             131072
SF       125.7577890 MHz
WDW                EM
SSB      0
LB              1.00 Hz
GB       0
PC              1.40
```



^{19}F NMR

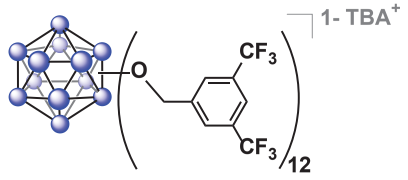


```
Current Data Parameters
NAME     B12(O-3,5-bisTFMBn)12
EXPNO             212
PROCNO              1

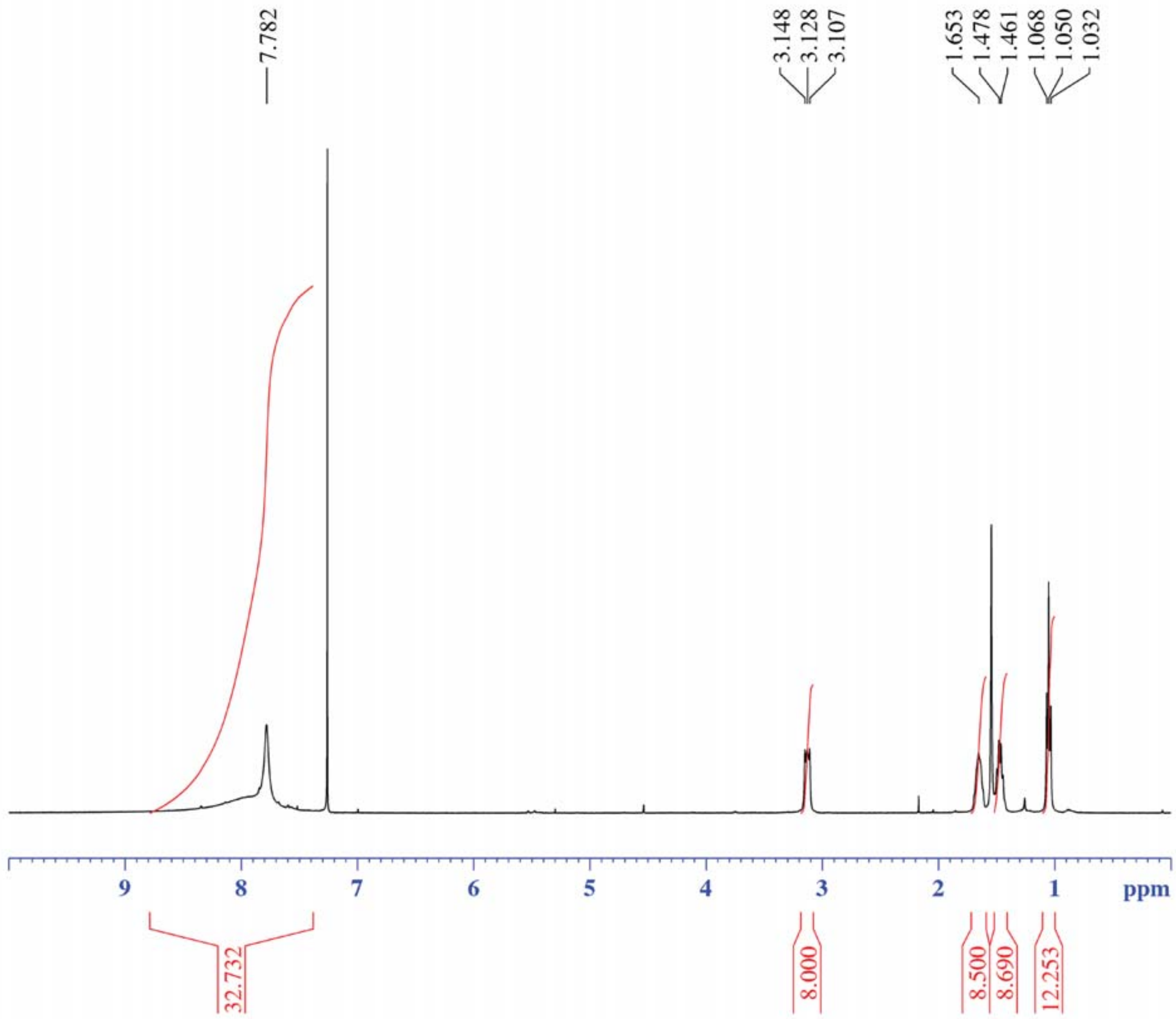
F2 - Acquisition Parameters
Date_         20150824
Time             21.00
INSTRUM          av400
PROBHD  5 mm PABBO BB/
PULPROG       zgflqn30
TD              262144
SOLVENT          CDCl3
NS                  64
DS                   0
SWH        150000.000 Hz
FIDRES       0.572205 Hz
AQ          0.8738133 sec
RG              189.85
DW               3.333 usec
DE                6.50 usec
TE               299.0 K
D1         2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1      376.4983660 MHz
NUC1              19F
P1               14.50 usec
PLW1       17.00000000 W

F2 - Processing parameters
SI              262144
SF        376.4983660 MHz
WDW                 EM
SSB     0
LB                1.00 Hz
GB      0
PC                1.00
```



^{1}H NMR

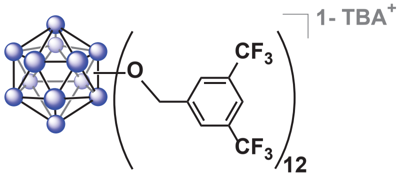


```
Current Data Parameters
NAME     B12(O-3,5-bisTFMBn)12
EXPNO              211
PROCNO               1

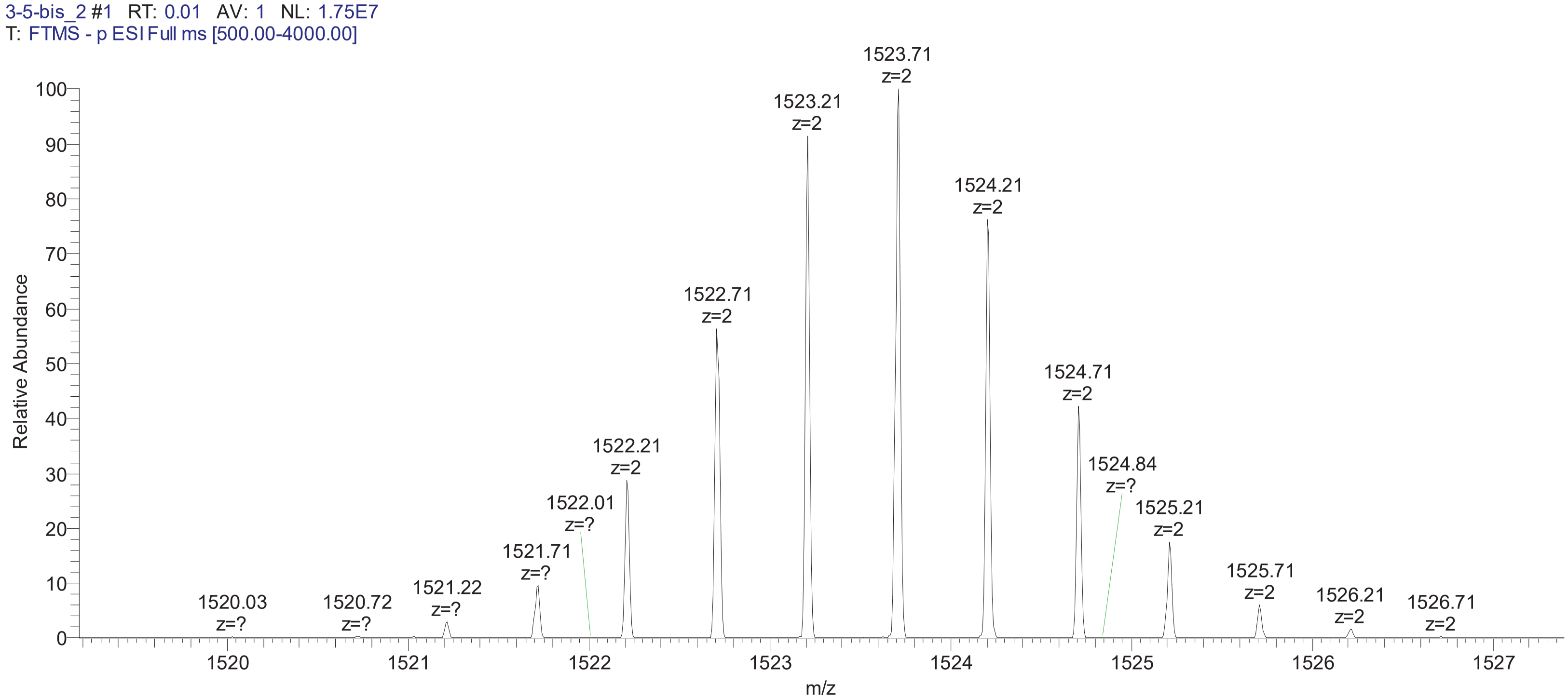
F2 - Acquisition Parameters
Date_          20150824
Time              20.54
INSTRUM           av400
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                52882
SOLVENT           CDCl3
NS                   32
DS                    0
SWH         8012.820 Hz
FIDRES      0.151523 Hz
AQ        3.2998369 sec
RG               189.85
DW          62.400 usec
DE            6.50 usec
TE              299.0 K
D1       2.00000000 sec
TD0                   1

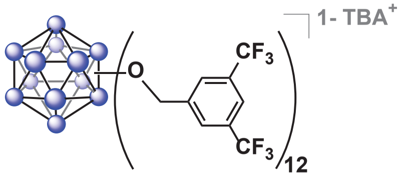
======== CHANNEL f1 ========
SFO1     400.1324008 MHz
NUC1                 1H
P1           15.00 usec
PLW1      13.00000000 W

F2 - Processing parameters
SI                65536
SF       400.1300184 MHz
WDW                  EM
SSB     0
LB              0.30 Hz
GB      0
PC                 1.00
```

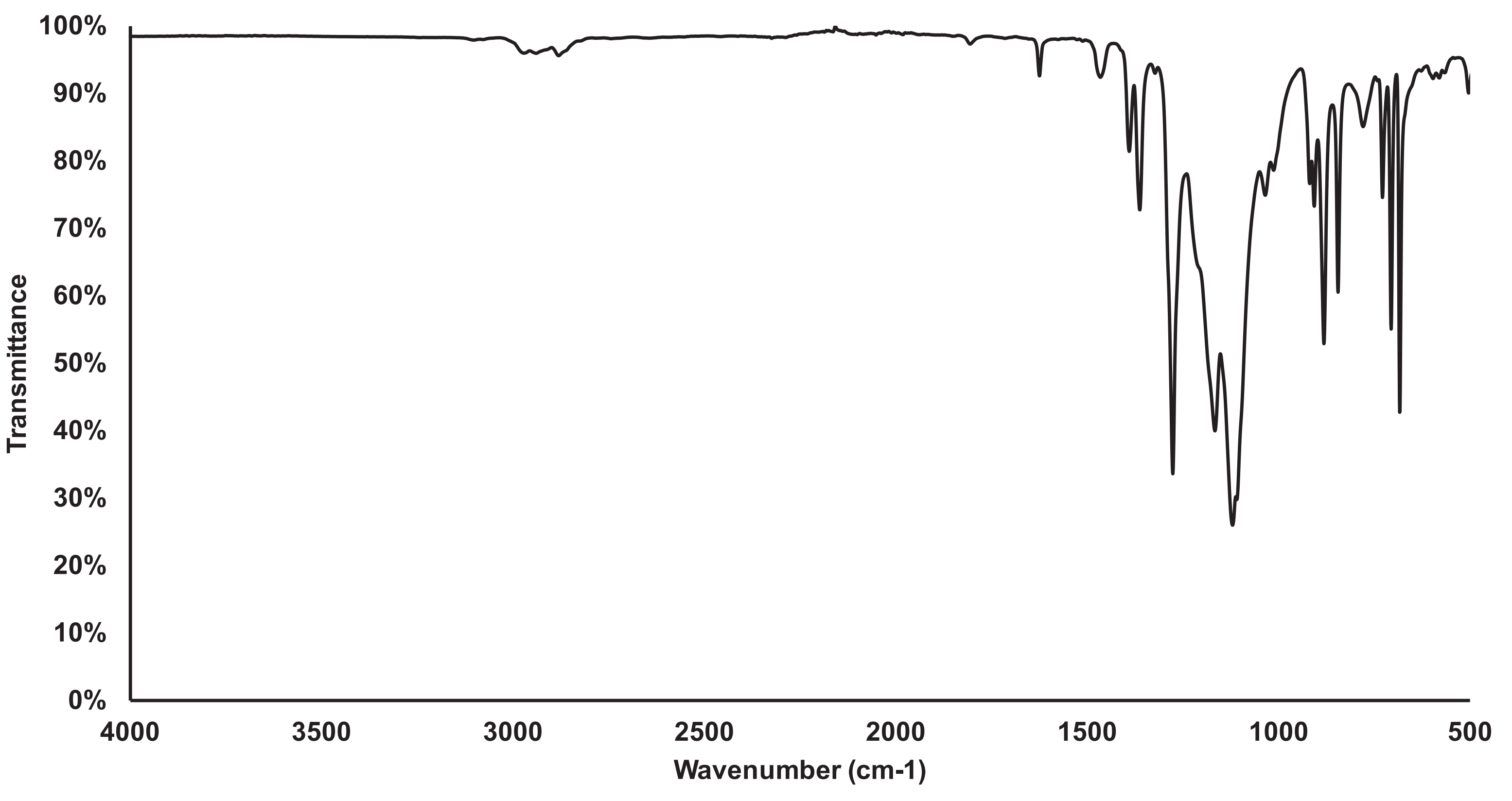


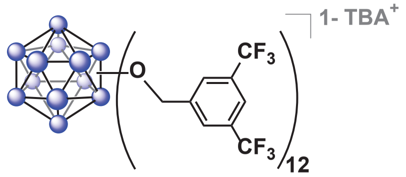
Q Exactive
High-Res Mass Spec



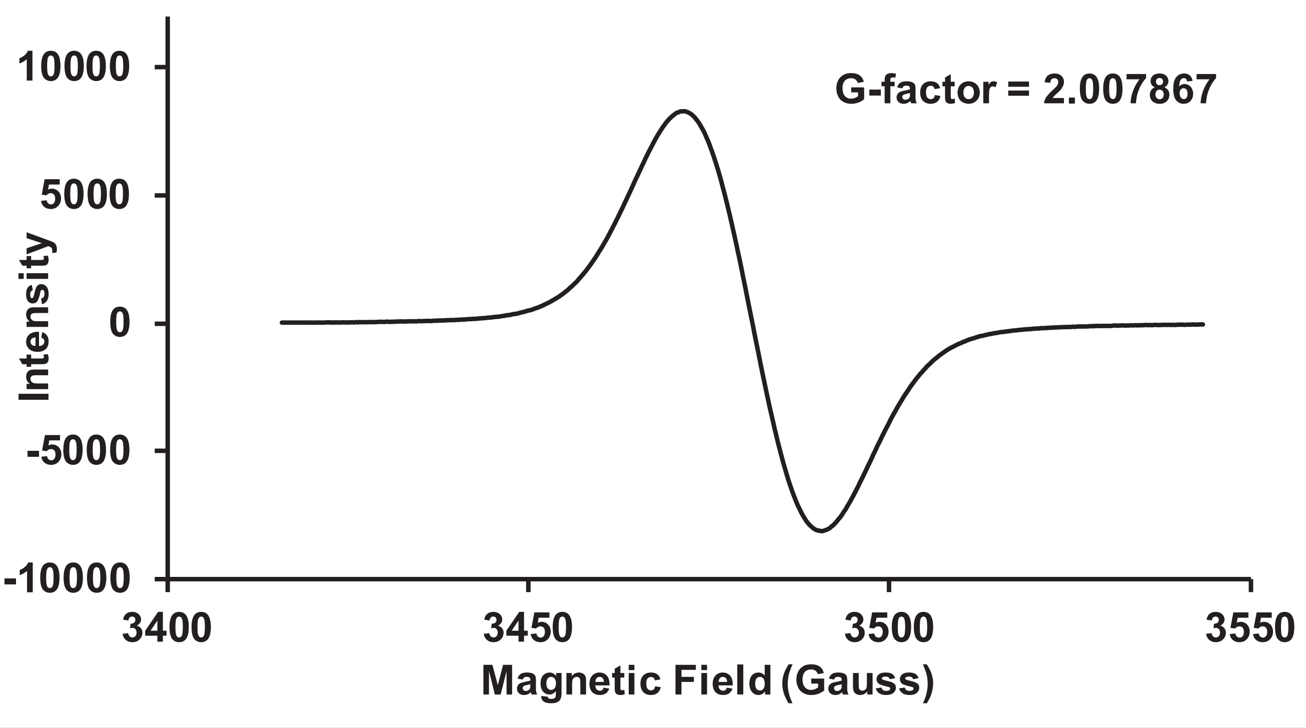

O
CF3
CF3
12
1- TBA+

IR


Transmittance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)



EPR



DOS	Format
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MAX	8283.838867
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GST	3415.875
GSI	127.47
JUN	G
JON	Bruker BioSpin GmbH
JDA	6/4/2015
JTM	16:02
JRE	c:\programfiles\bruker-emx\syscal\st0103.cal
JEX	field-sweep
JSD	1
HCF	3479.61
HSW	127.47
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RRG	2.83E+03
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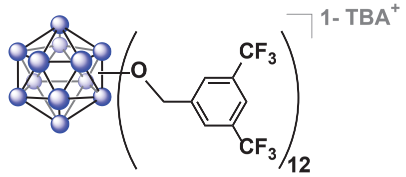
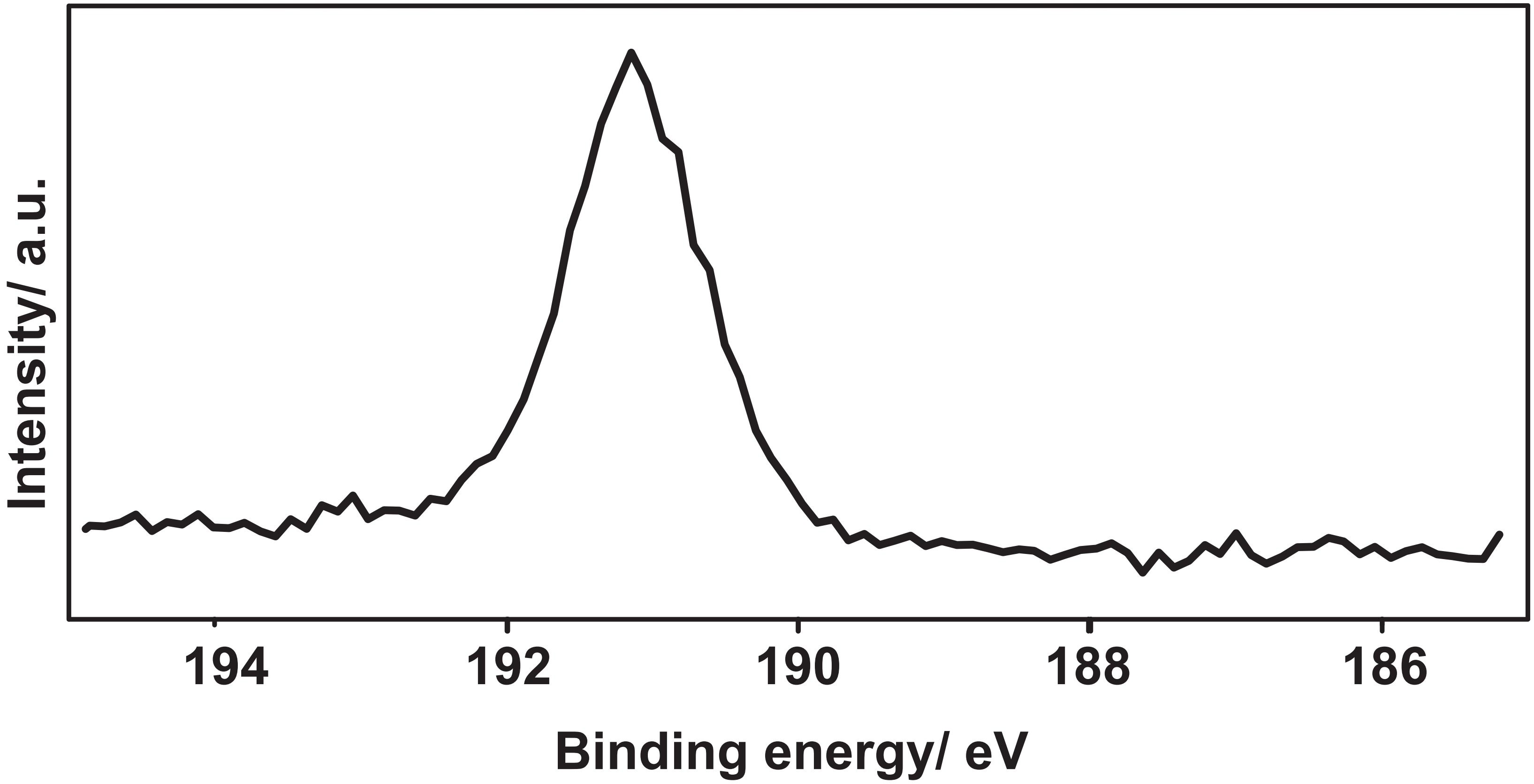
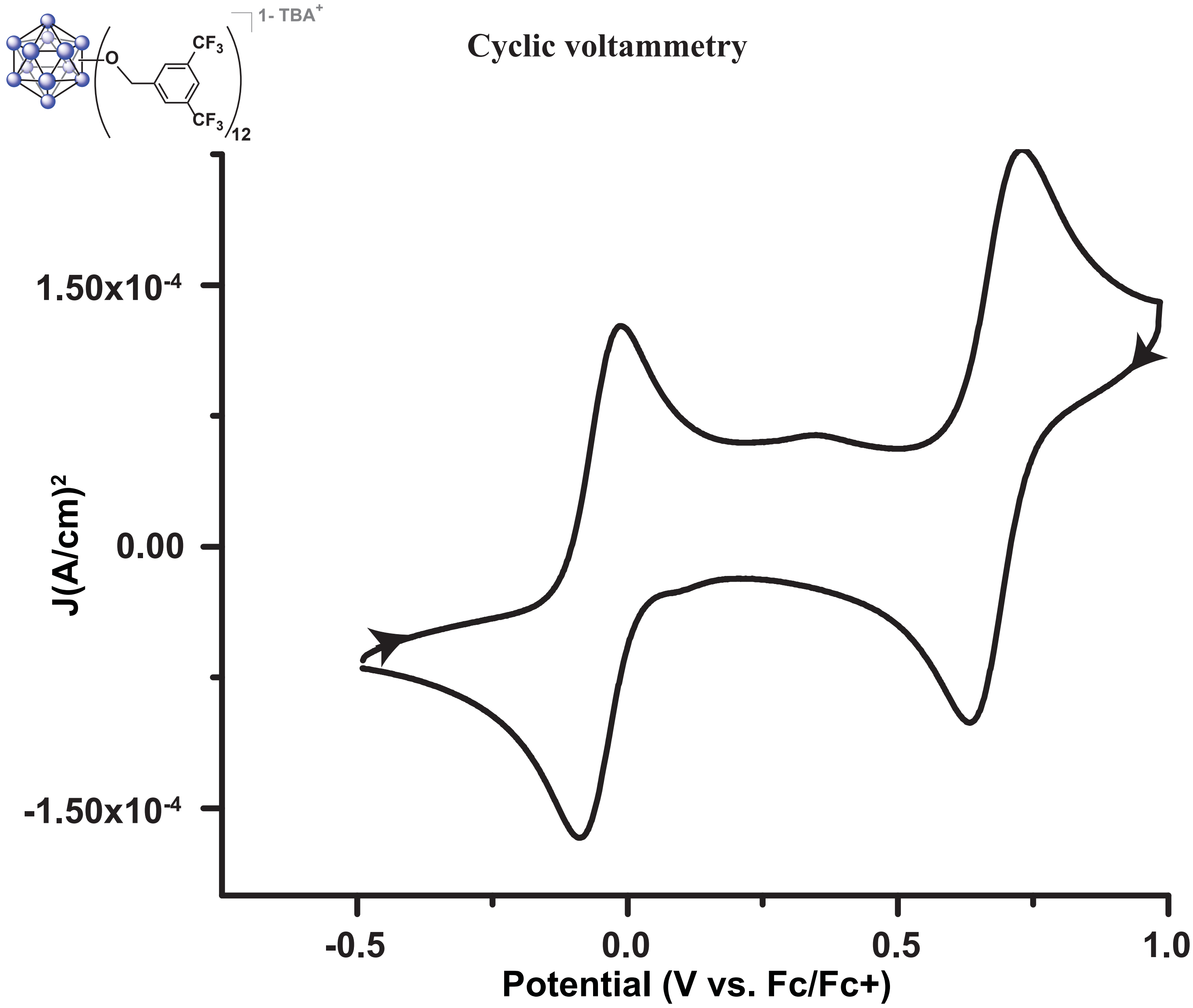
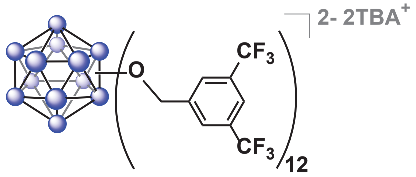

O
CF3
CF3
12
1- TBA+

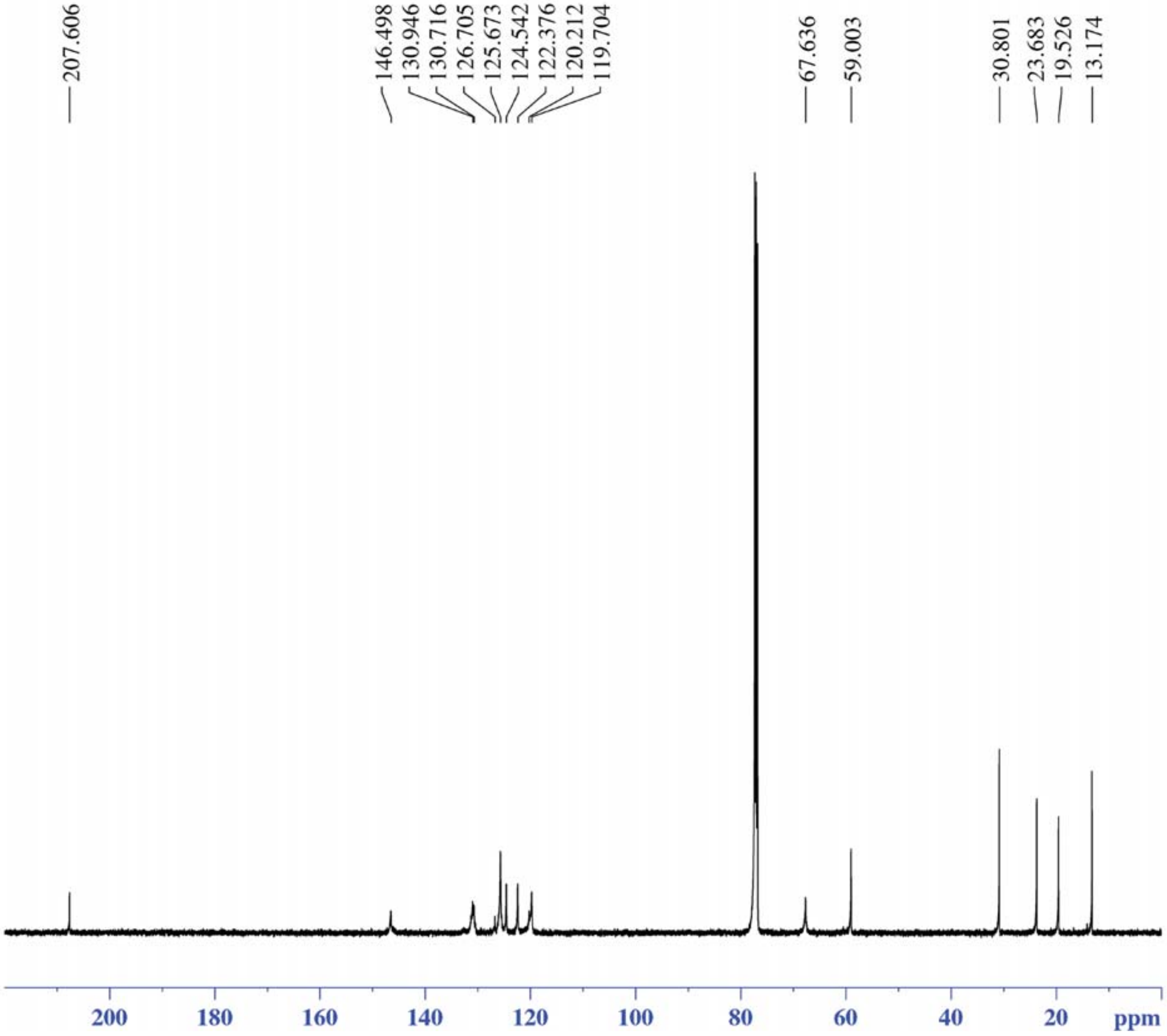
B 1s XPS


Intensity/ a.u.
194
192
190
188
186
Binding energy/ eV


Cyclic voltammetry
O
CF3
CF3
12
1- TBA+
J(A/cm)2
1.50x10-4
0.00
-1.50x10-4
-0.5
0.0
0.5
1.0
Potential (V vs. Fc/Fc+)



^{13}C NMR



```
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EXPNO             700
PROCNO              1

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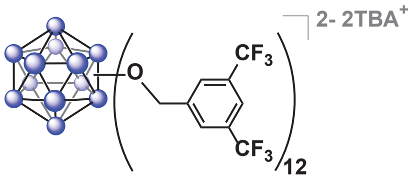
Date_         20150829
Time             22.21
INSTRUM          av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                256
DS                  2
SWH         31250.000 Hz
FIDRES       0.476837 Hz
AQ          1.0485760 sec
RG             204.54
DW             16.000 usec
DE              18.00 usec
TE              298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                 1

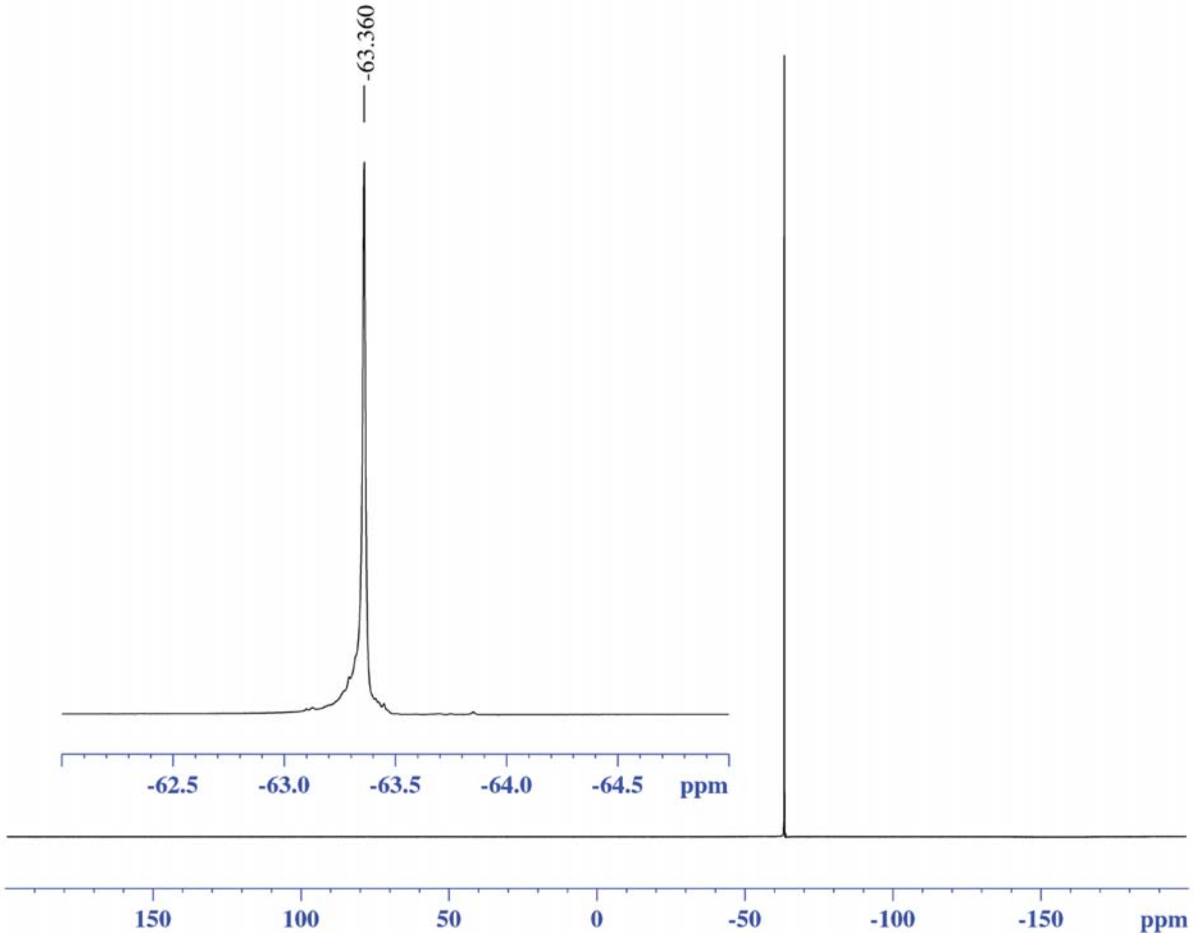
======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec
PLW1      23.00000000 W

======== CHANNEL f2 ========
SFO2      500.1330008 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2           80.00 usec
PLW2      13.50000000 W
PLW12      0.21094000 W
PLW13      0.13500001 W

F2 - Processing parameters
SI             131072
SF        125.7577890 MHz
WDW                EM
SSB      0
LB               1.00 Hz
GB       0
PC               1.40
```



^{19}F NMR

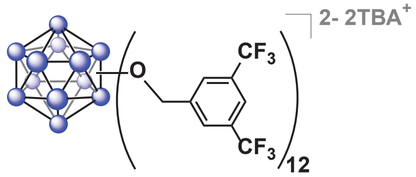


```
Current Data Parameters
NAME     B12(O-3,5-bisTFMBn)12
EXPNO              121
PROCNO               1

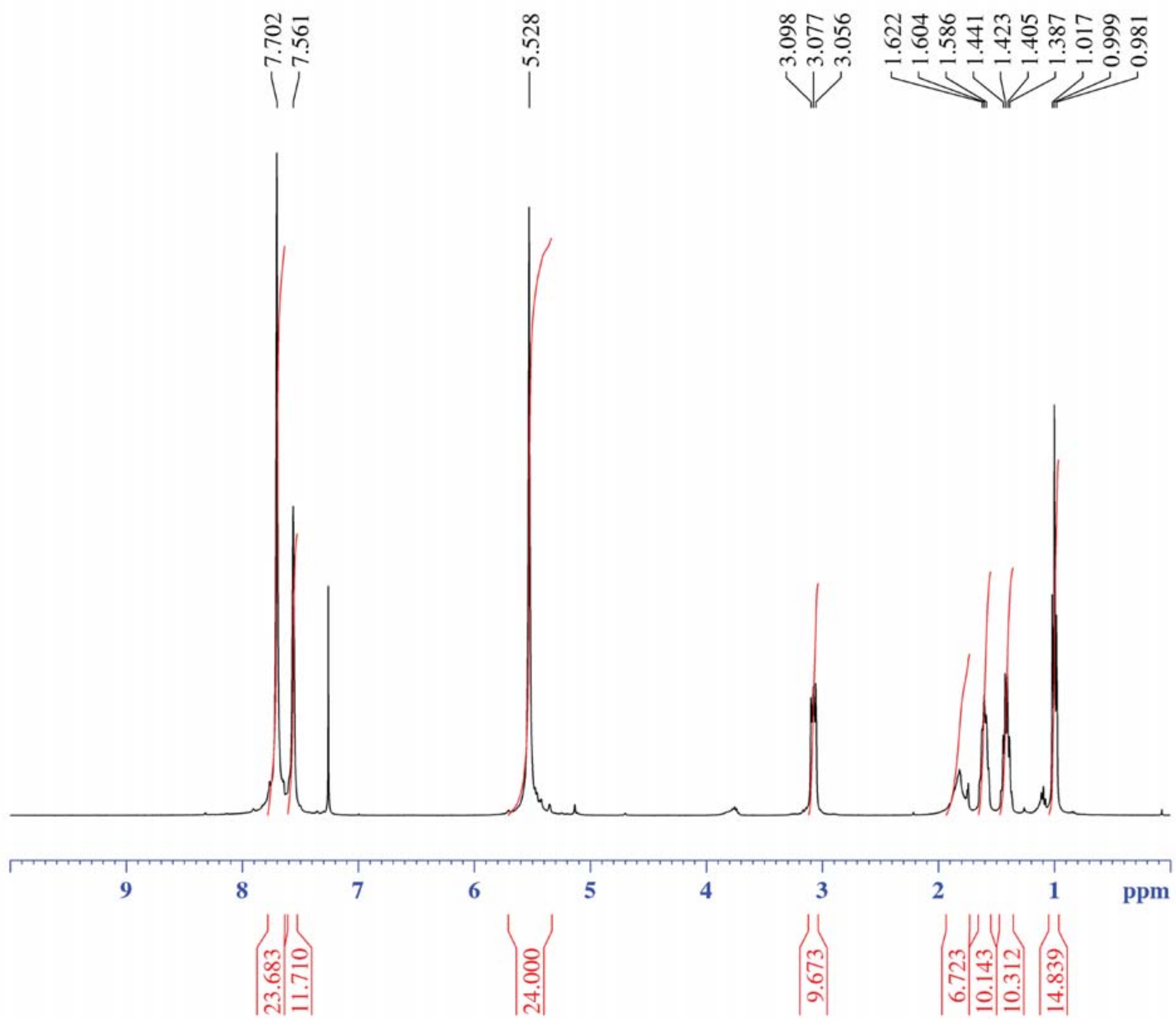
F2 - Acquisition Parameters
Date_          20150824
Time              17.26
INSTRUM           av400
PROBHD   5 mm PABBO BB/
PULPROG        zgflqn30
TD               262144
SOLVENT           CDCl3
NS                   32
DS                    0
SWH        150000.000 Hz
FIDRES       0.572205 Hz
AQ          0.8738133 sec
RG               189.85
DW              3.333 usec
DE               6.50 usec
TE               299.0 K
D1         2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1      376.4983660 MHz
NUC1                19F
P1              14.50 usec
PLW1      17.00000000 W

F2 - Processing parameters
SI               262144
SF        376.4983660 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.00
```



^{1}H NMR

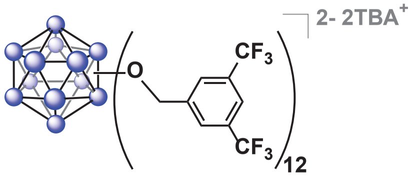


```
Current Data Parameters
NAME     B12(O-3,5-bisTFMBn)12
EXPNO              122
PROCNO               1

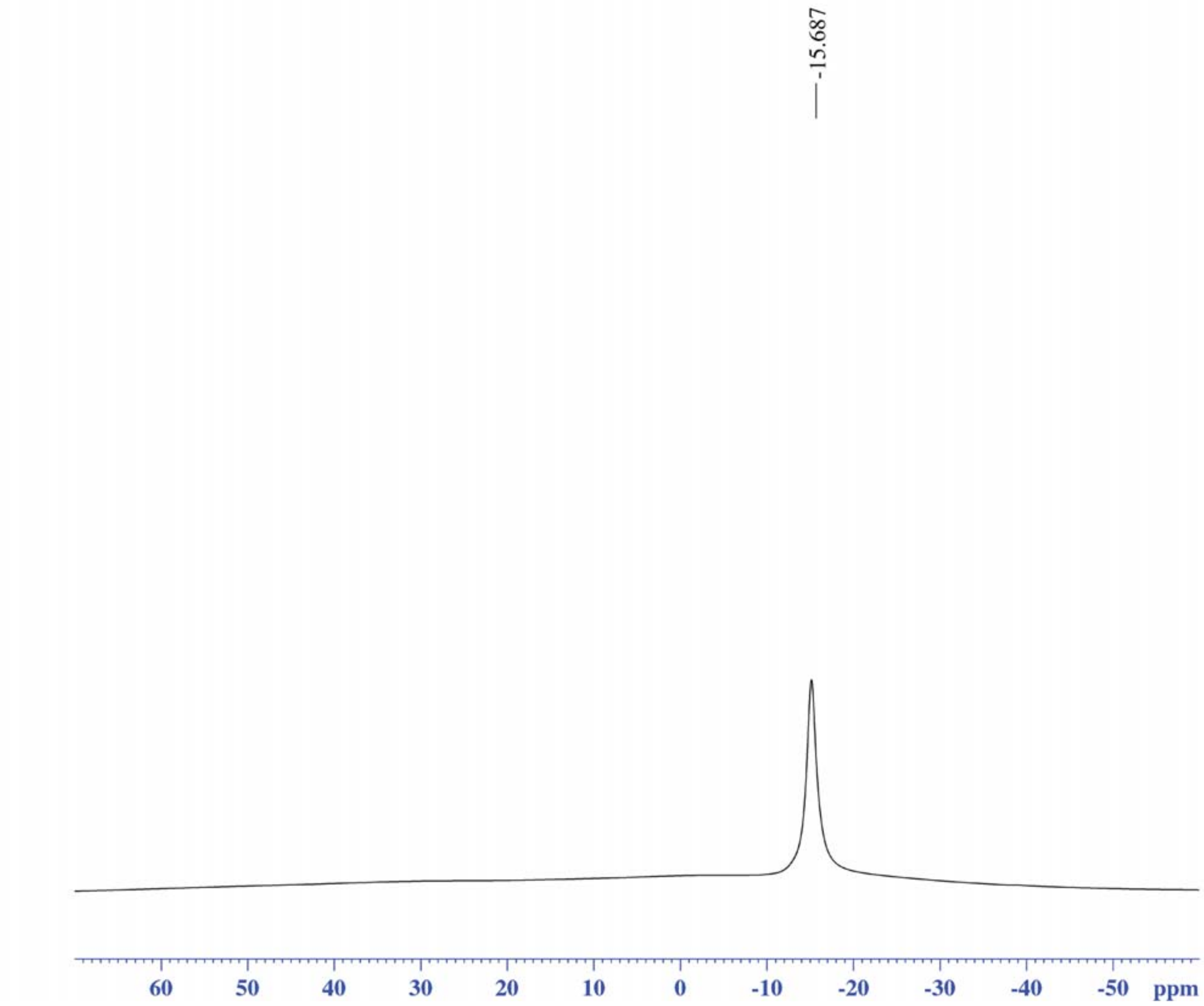
F2 - Acquisition Parameters
Date_         20150824
Time             17.32
INSTRUM          av400
PROBHD  5 mm PABBO BB/
PULPROG           zg30
TD               52882
SOLVENT          CDCl3
NS                  64
DS                   0
SWH         8012.820 Hz
FIDRES      0.151523 Hz
AQ        3.2998369 sec
RG              155.85
DW          62.400 usec
DE            6.50 usec
TE             299.0 K
D1     2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1     400.1324008 MHz
NUC1              1H
P1           15.00 usec
PLW1     13.00000000 W

F2 - Processing parameters
SI             65536
SF     400.1300184 MHz
WDW               EM
SSB    0
LB           0.30 Hz
GB     0
PC              1.00
```



^{11}B {^{1}H} NMR



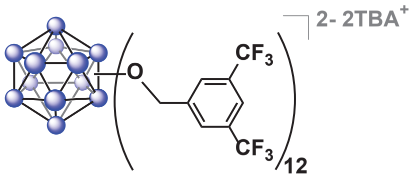
```
Current Data Parameters
NAME     B12(O-3,5-bisTFMBn)12
EXPNO              120
PROCNO               1

F2 - Acquisition Parameters
Date_          20150824
Time             17.23
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG        zgdc.js
TD                5096
SOLVENT          CDCl3
NS                1024
DS                   0
SWH        51020.406 Hz
FIDRES     10.011854 Hz
AQ        0.0499408 sec
RG              189.85
DW           9.800 usec
DE            6.50 usec
TE             299.2 K
D1       0.00000400 sec
D11      0.03000000 sec
TD0                  1

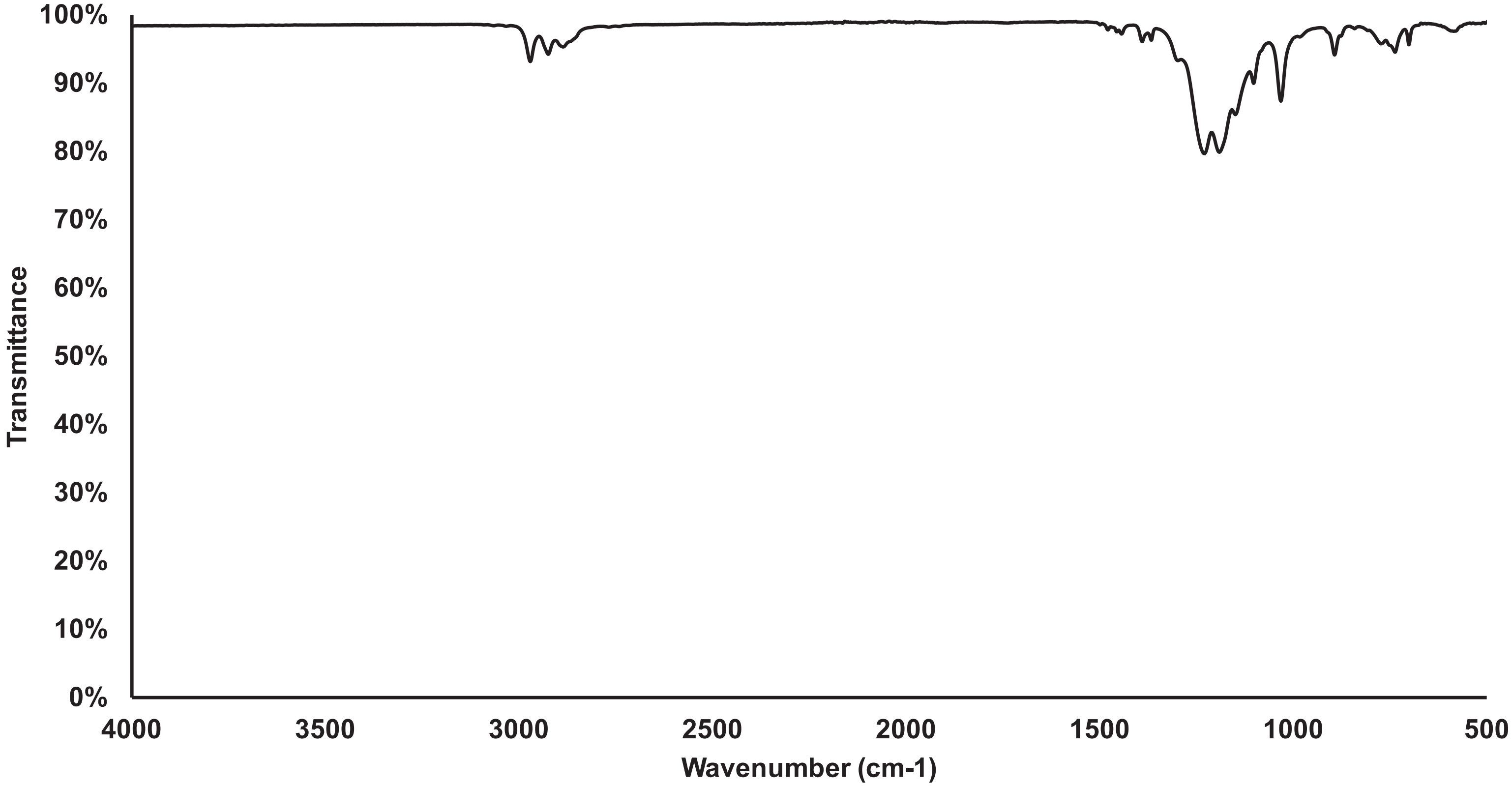
======== CHANNEL f1 ========
SFO1     128.3776052 MHz
NUC1               11B
P1            10.00 usec
PLW1       52.00000000 W

======== CHANNEL f2 ========
SFO2     400.1324008 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2         90.00 usec
PLW2       13.00000000 W
PLW12       0.36111000 W

F2 - Processing parameters
SI               32768
SF       128.3776050 MHz
WDW                 EM
SSB      0
LB            50.00 Hz
GB       0
PC                1.40
```


O
CF3
CF3
12
2- 2TBA+

IR


Transmittance
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20%
10%
0%
4000
3500
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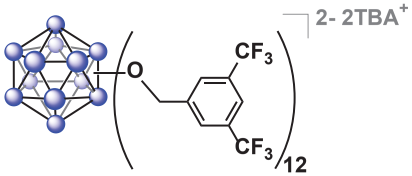
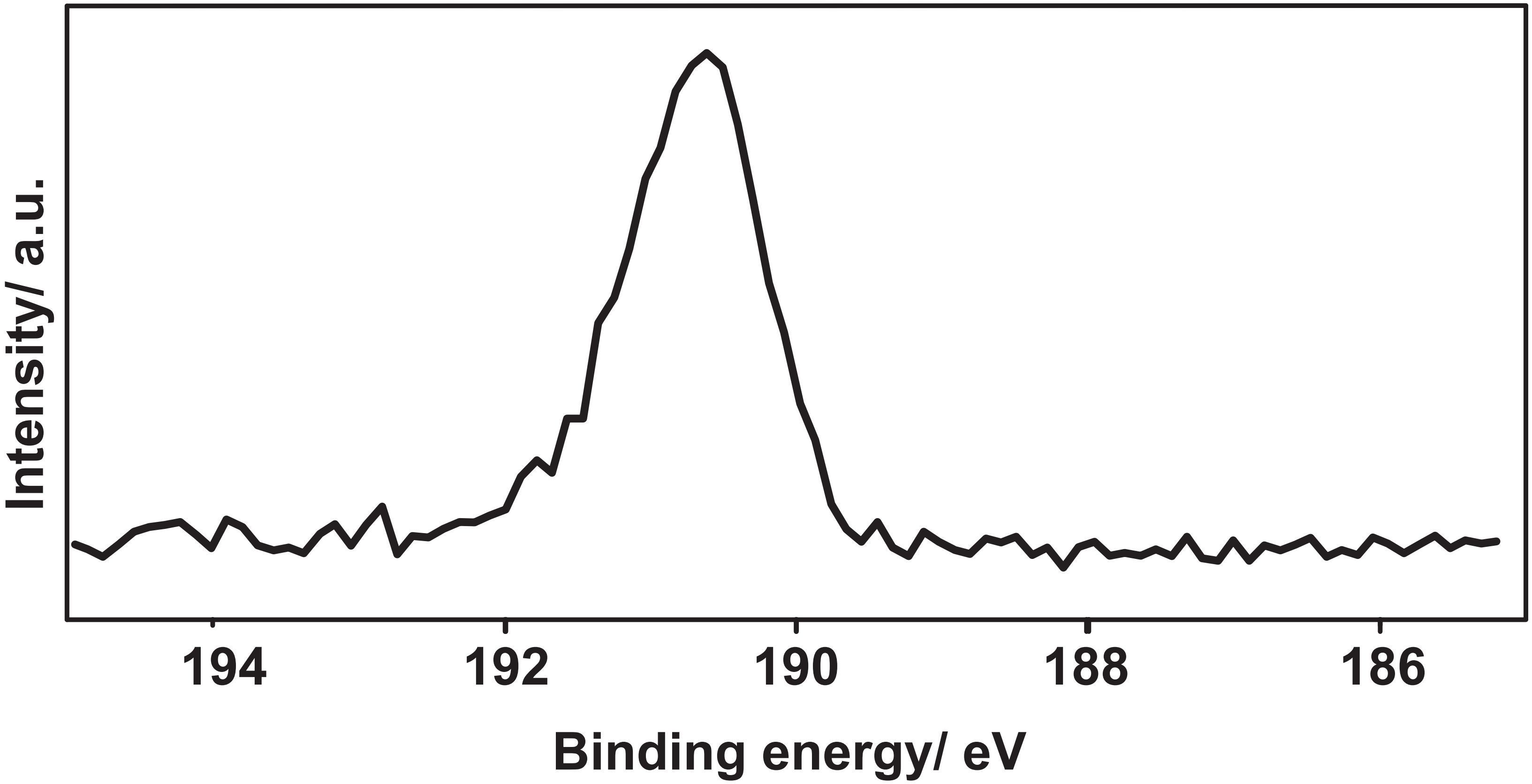
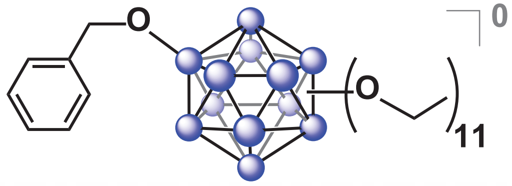
1500
1000
500
Wavenumber (cm-1)

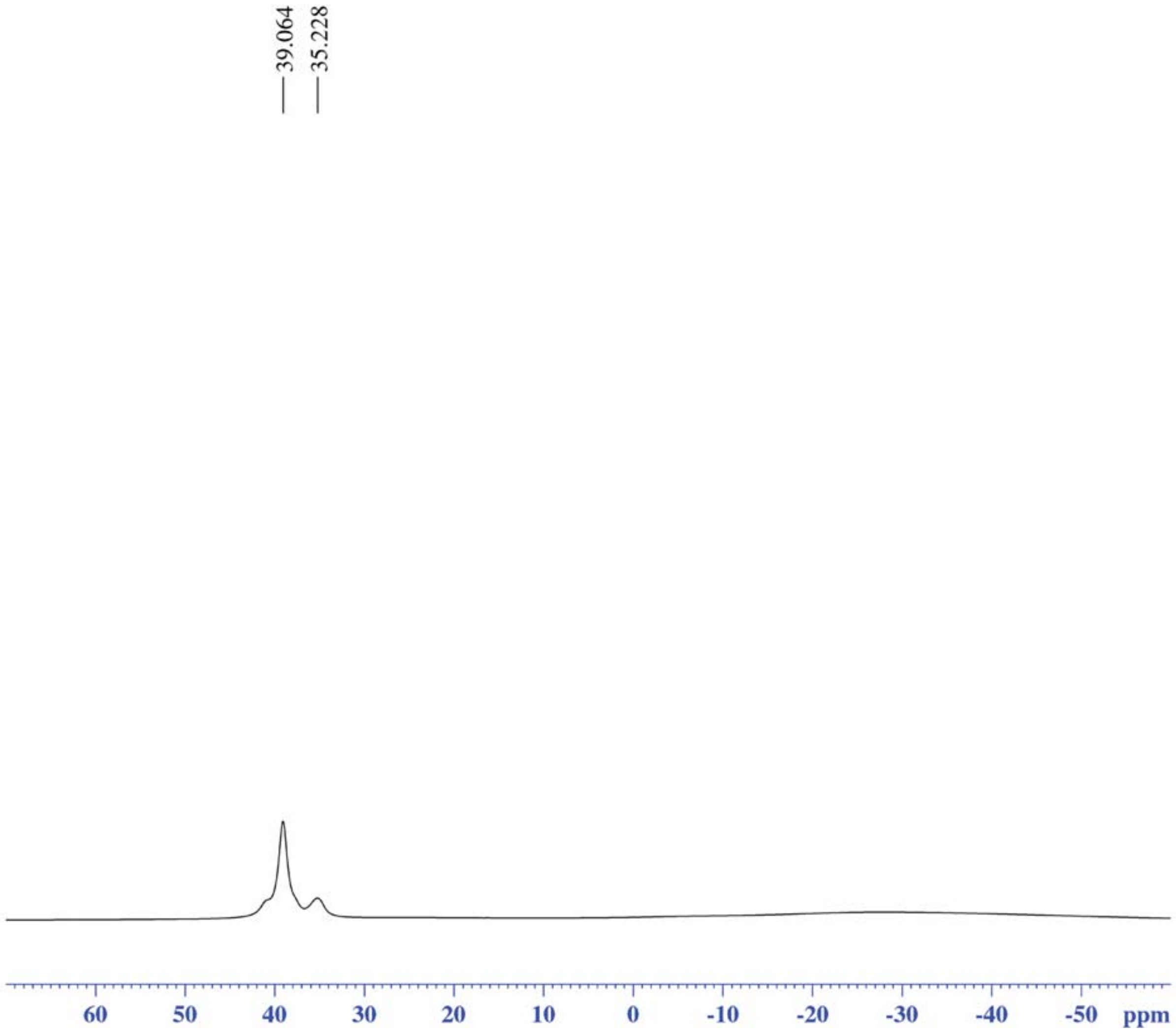

O
CF3
CF3
12
2- 2TBA+

B 1s XPS


Intensity/ a.u.
194
192
190
188
186
Binding energy/ eV



^{11}B {^{1}H} NMR



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Current Data Parameters
NAME     B12(O-Bn)(O-Et)11
EXPNO              30
PROCNO              1

F2 - Acquisition Parameters
Date_          20150517
Time              15.01
INSTRUM           av400
PROBHD   5 mm PABBO BB/
PULPROG         zgdc.js
TD                 5096
SOLVENT           CDCl3
NS                 1024
DS                    0
SWH        51020.406 Hz
FIDRES     10.011854 Hz
AQ        0.0499408 sec
RG               189.85
DW           9.800 usec
DE            6.50 usec
TE              299.1 K
D1       0.00000400 sec
D11      0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1     128.3776052 MHz
NUC1                11B
P1           10.00 usec
PLW1      52.00000000 W

======== CHANNEL f2 ========
SFO2     400.1324008 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2        90.00 usec
PLW2      13.00000000 W
PLW12      0.36111000 W

F2 - Processing parameters
SI                32768
SF       128.3776050 MHz
WDW                  EM
SSB        0
LB             50.00 Hz
GB         0
PC                 1.40
```
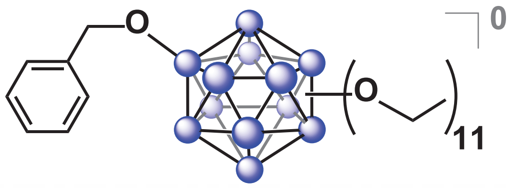
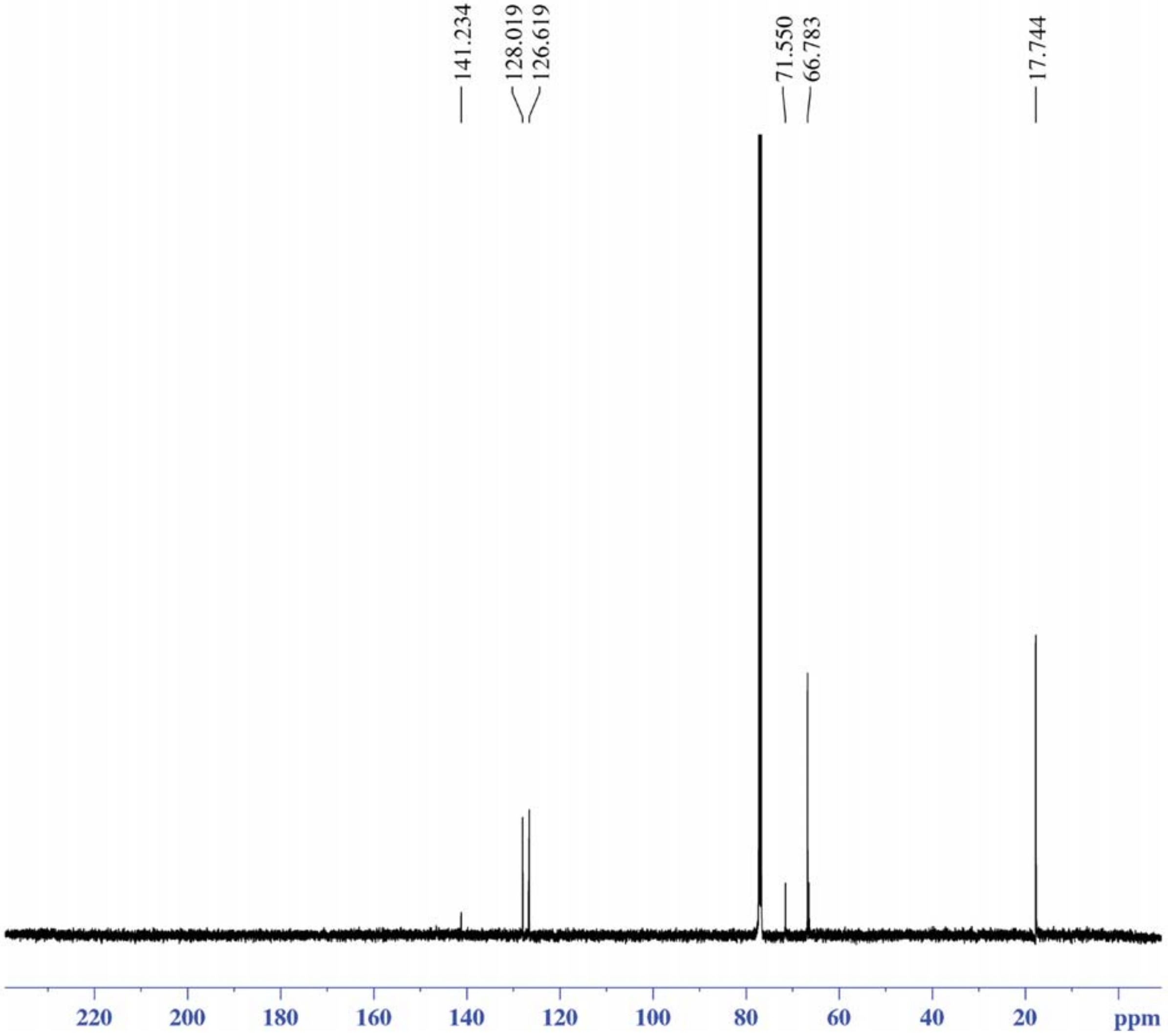



^{13}C NMR



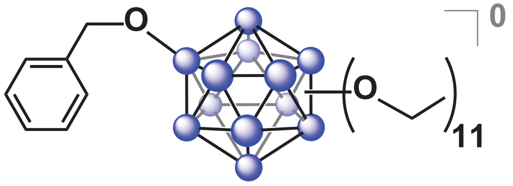
Current Data Parameters
NAME B12(O-Bn)(O-Et)11
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150517
Time 16.29
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 13.13
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

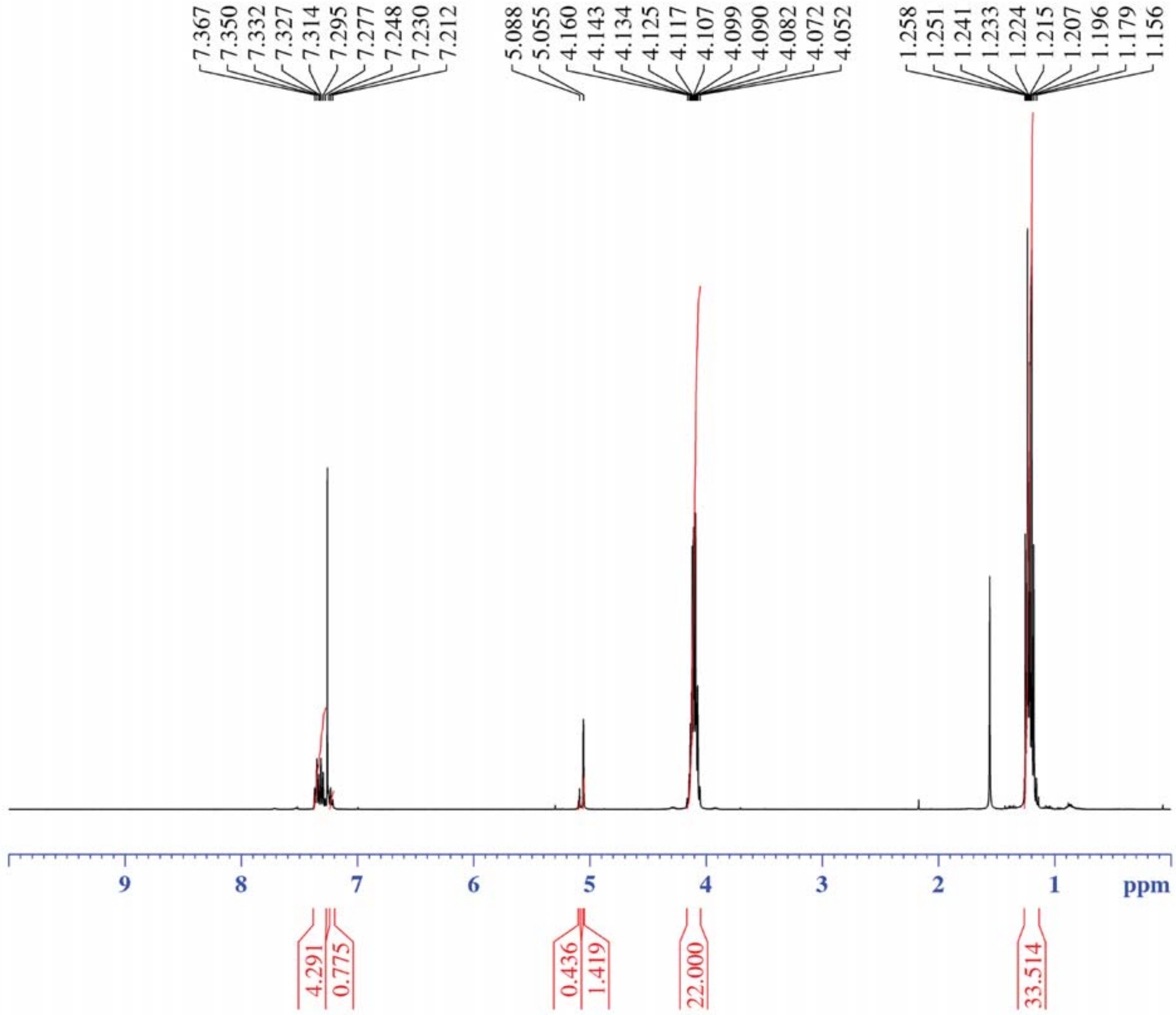
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W

======== CHANNEL f2 ========
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W

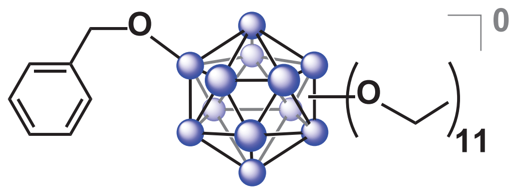
F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



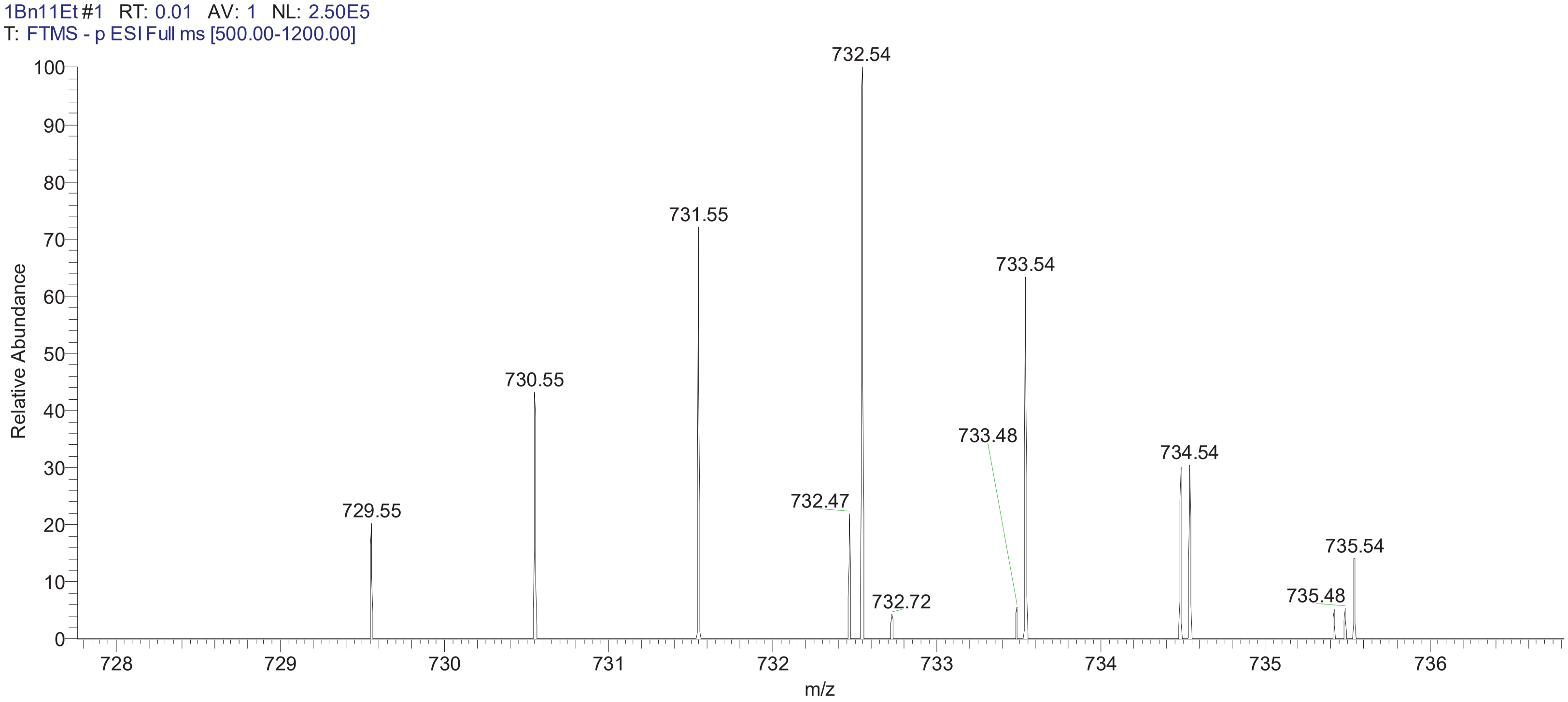
^{1}H NMR

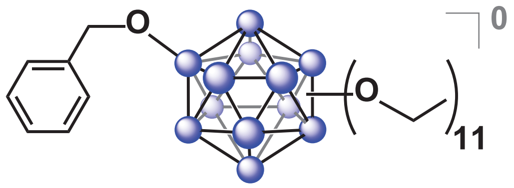


```
Current Data Parameters
NAME     B12(O-Bn)(O-Et)11
EXPNO              31
PROCNO              1

F2 - Acquisition Parameters
Date_       20150517
Time          15.05
INSTRUM        av400
PROBHD  5 mm PABBO BB/
PULPROG         zg30
TD            52882
SOLVENT         CDCl3
NS               32
DS                0
SWH       8012.820 Hz
FIDRES    0.151523 Hz
AQ       3.2998369 sec
RG           155.85
DW          62.400 usec
DE            6.50 usec
TE            299.0 K
D1     2.00000000 sec
TD0               1

======== CHANNEL f1 ========
SFO1     400.1324008 MHz
NUC1              1H
P1            15.00 usec
PLW1     13.00000000 W

F2 - Processing parameters
SI            65536
SF      400.1300184 MHz
WDW               EM
SSB     0
LB              0.30 Hz
GB      0
PC              1.00
```

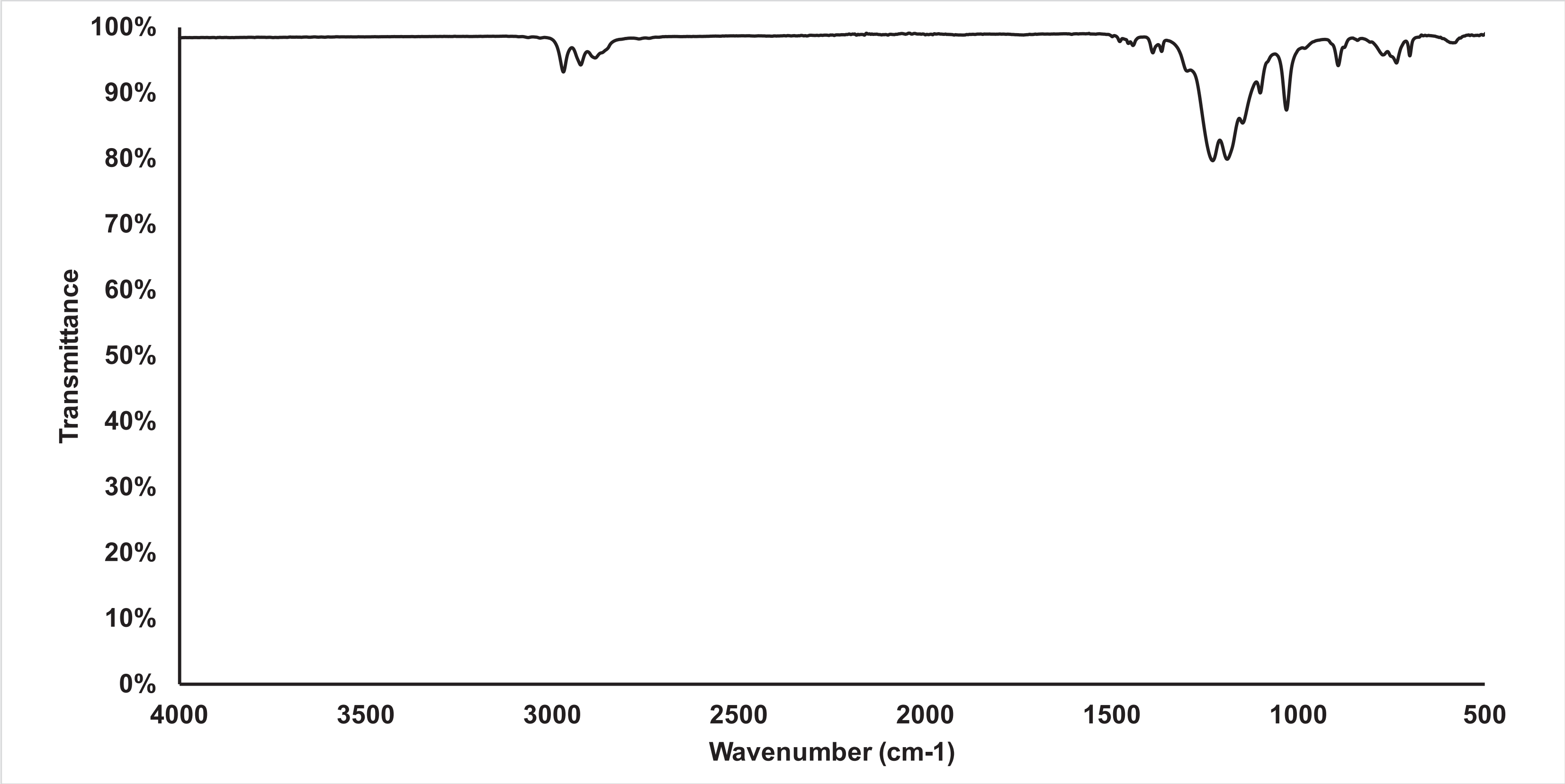


Q Exactive
High-Res Mass Spec




O
O
11
0

IR


Transmittance
100%
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70%
60%
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20%
10%
0%
4000
3500
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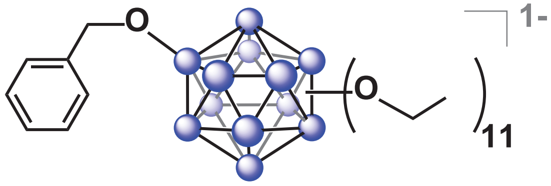
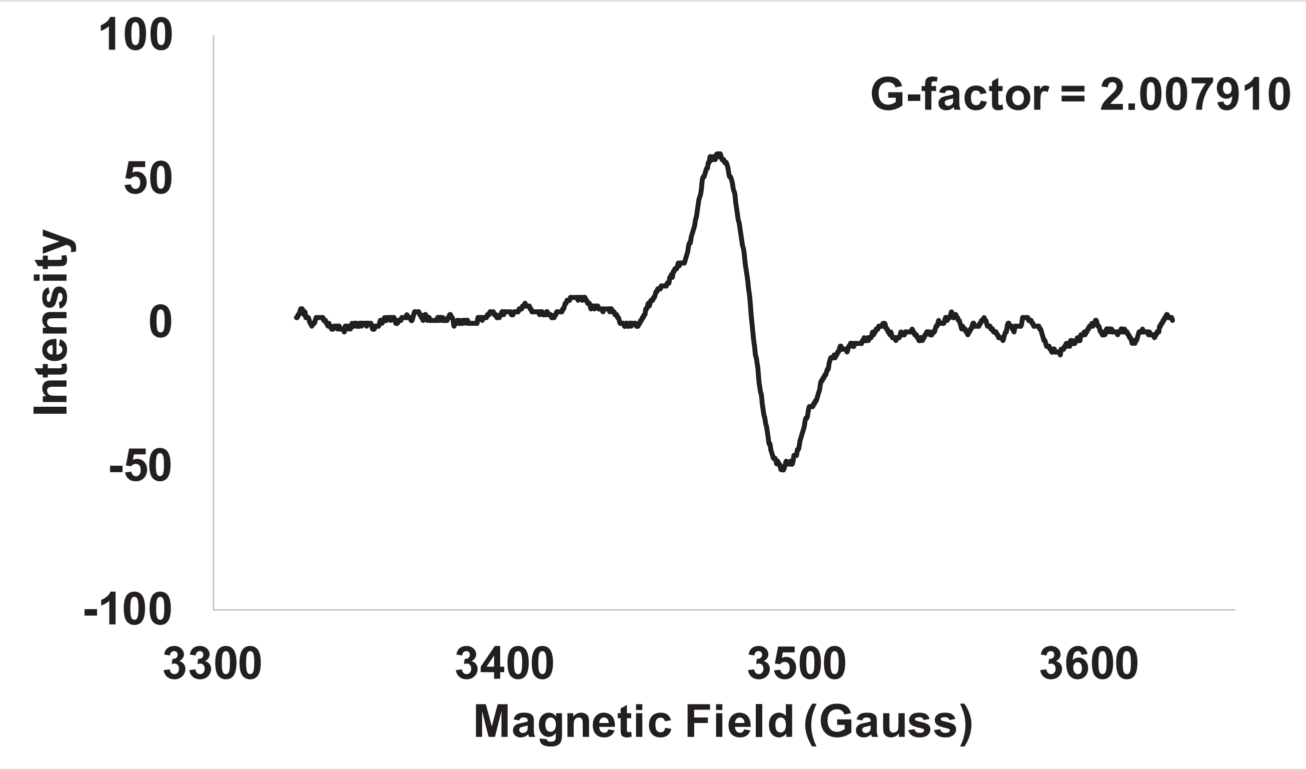
1500
1000
500
Wavenumber (cm-1)



EPR



DOS	Format
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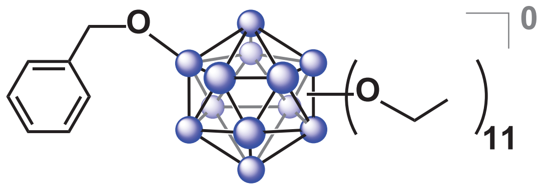
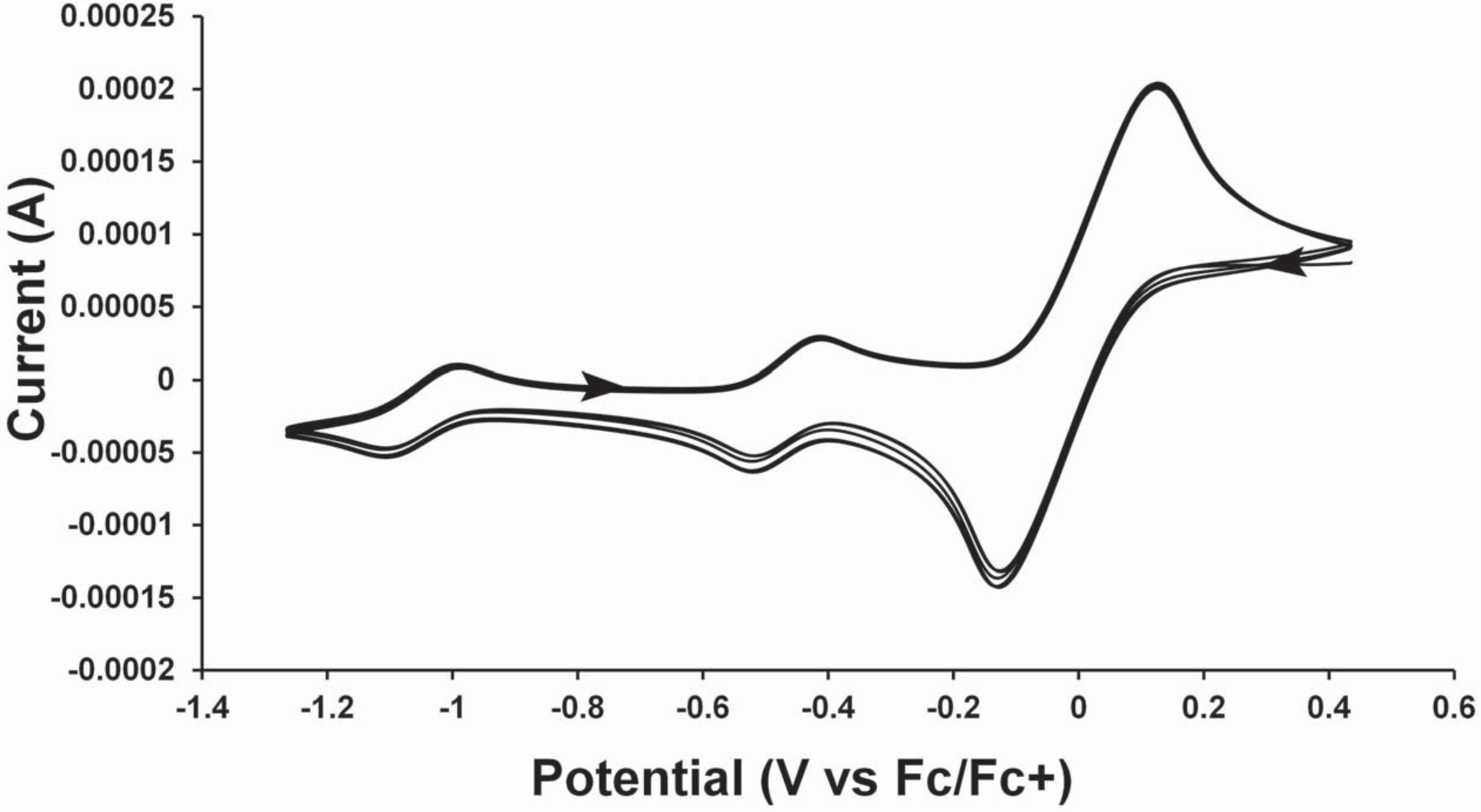
GST	3328.55
GSI	300
JUN	G
JON	Bruker BioSpin GmbH
JDA	11/2/2015
JTM	20:39
JRE	c:\programfiles\bruker-emx\syscal\st0103.cal
JEX	field-sweep
JSD	1
HCF	3478.55
HSW	300
EMF	0
RCT	20.48
RTC	327.68
RRG	8.93E+03
RMA	4
MF	9.77575
MP	2.54E+00
MPD	19



Cyclic voltammetry



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