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Vinyl Carbocations Generated under Basic Conditions and Their Intramolecular C–H Insertion Reactions

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Abstract

Here we report the surprising discovery that high-energy vinyl carbocations can be generated under strongly basic conditions, and that they engage in intramolecular sp^3 C–H insertion reactions through the catalysis of weakly coordinating anion salts. This approach relies on the unconventional combination of lithium hexamethyldisilazide base and the commercially available catalyst, triphenylmethyl tetrakis(pentafluorophenyl)-borate. These reagents form a catalytically active lithium species that enables the application of vinyl cation C–H insertion reactions to heteroatom-containing substrates.

From the lessons learned about structure and bonding arising from the great classical vs nonclassical ion debate of the mid-20th century, to the syntheses of pharmaceuticals and materials, carbocations have played a prominent role in the development of modern organic chemistry.^{1–3} Such electron-deficient species are typically generated under Brønsted acidic or Lewis acidic conditions, as exemplified by independent studies by Norris, Kehrman, and Baeyer on the formation of the resonance-stabilized triphenylmethyl (trityl) cation.^{4–6} In the 1960s, elegant studies by Olah demonstrated that superacidic media, such as “magic acid”, could be utilized to generate a variety of nonstabilized alkyl carbocations.⁷ Later, Reed et al. showed that, when paired with appropriately robust and weakly coordinating anions (WCAs), savagely Lewis acidic silylium ions could be utilized to access, and in some cases isolate in crystalline form, a variety of otherwise reactive carbocations.^{8,9} Even more reactive carbocations, such as aryl or vinyl cations, are often generated in a similar fashion and have found limited synthetic utility, save for the Balz–Schiemann and Sandmeyer reactions.^{10,11} While Brønsted acidic, highly oxidizing “magic acid”, and potent electrophiles like silylium ions are useful in generating such reactive carbocations for the conversion of hydrocarbons, they hinder application of these strategies in the syntheses of

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Supporting Information

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Procedures and characterization data (PDF)

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heteroatom-rich complex molecules, such as those utilized for materials and pharmaceuticals.^{12–14}

Recently, aryl and vinyl carbocations have been found to undergo fast and high-yielding insertion reactions into unactivated sp^3 C–H bonds (Figure 1a,b).^{15,16} In these systems the substrate scope was limited due to the electro-philicity of the silylium ion. In an effort to expand these C–H functionalization chemistries to additional synthetic applications, we posited that tempering the Lewis acidity of our active catalytic species would greatly expand the scope of vinyl carbocation C–H insertion reactions (Figure 1c). Here we report the discovery that high-energy vinyl carbocations can be generated under strongly basic conditions, and that they engage in intramolecular sp^3 C–H insertion reactions through the catalysis of weakly coordinating anions. Importantly, this system features commercially available tetraaryl borate salts instead of exotic carborane salts and is demonstrated to be applicable to heteroatom-containing substrates.

Inspired by work from Michl and others, we hypothesized that Li cations, paired with WCAs, could serve as Lewis acids capable of converting vinyl triflates into reactive vinyl cations.^{17–19} To evaluate this hypothesis, we considered cyclooctenyl triflates (e.g., **1**, Figure 2a) that undergo facile ionization by silylium cations to form vinyl carbocations.¹⁶ These cations subsequently engage in transannular C–H insertion reactions to generate bicyclooctane products in excellent yield. We postulated that nucleophilic attack of a lithium base on $[Ph_3C]^+[WCA]^-$ would yield the active $[Li]^+[WCA]^-$ catalyst (Figure 2a). $[Li]^+[WCA]^-$ -mediated triflate abstraction would then afford a persistent vinyl cation, **2**, which would undergo transannular C–H insertion to form bicyclic secondary cation **3** (Figure 2a). Importantly, we envisioned that deprotonation of this cation by a lithium base would generate alkene products **4** and concomitantly regenerate the active $[Li]^+[WCA]^-$ catalyst.

To validate key elementary steps in the putative cycle, we conducted density functional theory (DFT) calculations (Figure 2b). Beginning with triflate **1** and the $[Li]^+[WCA]^-$ complex, using $HCB_{11}Cl_{11}^-$ as our WCA model, we found that Li^+ dissociation from the anion followed by ligation to the triflate moiety occurs with only a modest enthalpic cost, as modeled with implicit dichloromethane (DCM) solvation (**5**, Figure 2b). Li^+ ligation to the triflate while it is still coordinated to the WCA does not offer any significant energetic advantage, and subsequent triflate abstraction to provide cyclic vinyl cation **2** likely occurs with the free Li^+ ion. The exact role the anion plays during triflate abstraction is still being investigated, though preliminary calculations suggest that facile separation of the catalyst ion-pair is vital for generation of the vinyl cation. Once the vinyl cation is generated, the potential energy surface appears insensitive to the effects of the WCA, resulting in similar barriers and energetics using either the independent, free ions or calculating the cation(s) and WCA as tight ion-pairs. In the C–H insertion transition state **TS₁**, complexation of the electron-deficient carbon with the C5 C–H is followed by a favorable transannular C–H insertion to give secondary nonclassical cation **6**, which can undergo a 1,2-hydride shift to the more stable tertiary cation. Alternatively, if vinyl cation **2** is coordinated to the WCA, **TS₁** may directly lead to either the secondary cation or the tertiary cation. Finally, either cation species can proceed via E1 elimination to form the three possible isomeric alkene products.

Beginning with cyclooctenyl triflate **1**, a screen of several Li bases, trityl salt catalysts, and general reaction conditions was undertaken. We were gratified to find that using a catalytic amount (5 mol%) of $[\text{Ph}_3\text{C}]^+[\text{HCB}_{11}\text{Cl}_{11}]^-$ and 1.5 equiv of LiHMDS base in *o*-difluorobenzene (*o*-DFB) solvent produced a mixture of bicyclooctene products **4** in 4 h, in a combined yield of 84% (Table SI-1). Remarkably, deleterious nucleophilic quenching or elimination products were not observed, despite the utilization of the highly basic hexamethyldisilazide anion in the presence of a high-energy, reactive vinyl cation intermediate. Pleasingly, commercially available $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ was superior in this reaction, providing the bicyclooctene products **4** in 98% GC yield in 30 min at room temperature, obviating the need for the rarer $[\text{HCB}_{11}\text{Cl}_{11}]^-$ anion. Chlorinated solvents, which are traditionally unstable under silylium catalysis,²⁰ were also competent media for these reactions, albeit providing the products in lower yield (Table SI-1). Moreover, unlike silylium-mediated reductive coupling conditions,^{15,16} here we generate olefinic products that can be further functionalized.^{21,22}

While our initial studies of Li^+ ion-generated vinyl cations demonstrated exquisite reactivity and conversion, we sought to validate our hypothesis that the use of Li^+ ions would improve the substrate compatibility of vinyl cation reactions. To explore functional group tolerance, a variety of 3-arylcyclooctenyl triflates were prepared (Figure 3). We were pleased to find that the benzylmorpholine derivative underwent conversion to bicyclic styrene **7**, in 42% NMR yield after 1 h. Similarly, heteroatom-containing thioethers and ethers were also competent under the reaction conditions (**8–10**, 38%, 38%, and 60% NMR yield of the depicted olefin isomer, respectively). An electron-deficient arene was tolerated, producing styrenyl trifluoromethyl derivative **11** in 50% NMR yield. We also found that 3-phenylcyclooctenyl triflate provided bicyclic styrene **12** in 46% NMR yield. The overall efficiency of the transannular C–H insertion reactions was high, with combined ca. yields of the styrenyl-, tri-, and tetra-substituted olefin isomer products ranging from 48% to 97% (Figure 3).^{23a} Isolation of each individual olefin isomer proved difficult; however, the major styrenyl product can be purified with ease. Thus, isolated yields given refer to this major product, and approximate overall yields of the olefin isomers are also given.^{23a}

In addition to 3-aryl-derived substrates, 2-substituted vinyl triflate **13** yielded silyl enol ether products **14** in 92% overall yield. These examples highlight the functional group tolerance of these newly discovered conditions, standing in stark contrast to the previously reported Lewis acid-mediated insertion reactions of vinyl cations.^{16,11,12} In fact, when heteroatom-containing substrates **7** and **9** were subjected to the previously optimized silylium conditions, no reactivity was observed.^{23b}

Having demonstrated that cyclic vinyl triflates undergo transannular C–H insertion reactions under Li-WCA catalysis, we sought to further expand the scope of our method to annulation reactions. Benzosuberone-derived triflates with tethered alkyl chains stood out as potential candidates for several reasons: (1) the 7-membered ring triflate would have a low barrier for vinyl cation formation,²⁴ (2) the possibility of insertion into 1° C–H bonds could be probed, and (3) the large number of benzosuberone derivatives that have been identified as potential therapeutics.²⁵ Gratifyingly, upon exposure to 10 mol% of $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and 1.1 equiv of LiHMDS, propylbenzoxepinyl triflate afforded tricycle **15** in 84% yield (3.3:1

isomer ratio) after 2 h (Figure 4). Further, 2-substituted pinacol boronic ester, anisole, and protected aniline benzosuberone derivatives were successfully converted to their corresponding tricyclic styrene products **16–18** in 44–66% yield. Similarly, 2-halogenated benzosuberonyl triflates provided styrene products **19–20** in 72% and 82% NMR yield. Functionalization at other positions of the fused aryl system afforded tricyclic styrene products **21–24** in good to excellent yields (61–93%). These examples not only highlight the vastly improved heteroatom compatibility of these conditions but also demonstrate the C–H insertion reactivity of benzylic vinyl cations into 1° C–H bonds. Finally, insertion into a benzylic 2° C–H bond was also possible, offering styrene **25** in 76% yield.

With our scope studies in hand, we began our investigation into the mechanistic underpinnings of this transformation. Initially, because hexamethyldisilazane has been previously used as a silyl transfer reagent,²⁶ we sought to discount the formation of silylium intermediates. In this regard, we found that NaHMDS and KHMDS were not competent under standard reaction conditions, supporting our hypothesis that Li⁺ rather than Me₃Si⁺ from HMDS is the active species (Table SI-1). Instead, we attribute this discrepancy in reactivity to the enhanced Lewis acidity of Li⁺ ions compared to Na⁺ and K⁺ ions, as demonstrated via Gutmann–Beckett experiments (Figure 5a).^{27,28} From these observations, we propose that the lithium ion is the active Lewis acid in our catalytic regime. To corroborate this mechanistic proposal, we treated triflate **26** with stoichiometric [Li]⁺ [B(C₆F₅)₄]⁻, resulting in the formation of LiOTf and full consumption of the triflate starting material (Figure 5b). Notably, we also observed reduced tricycle **27** in 15% yield as well as other intractable mixtures of products.^{23c}

Additionally, we wanted to verify the *in situ* formation of a [Li]⁺[WCA]⁻ salt under our reaction conditions. Here we exposed [Ph₃C]⁺ [B(C₆F₅)₄]⁻ to 1 equiv of LiHMDS and observed rapid formation of [Li]⁺ [B(C₆F₅)₄]⁻ by ⁷Li, ¹¹B, and ¹⁹F NMR (Figure 5c). To confirm the intermediacy of a vinyl cation species in our system, we synthesized 2-phenylvinyl triflate **28**, as 2-substituted cyclic vinyl cations have been previously reported to undergo ring-contractive rearrangement to exocyclic vinyl cations (Figure 5d).^{29,30} Under the reaction conditions, we observed formation of ring-contracted product **29** and transannular insertion product **30**. The cycloheptene derivative **29** is a result of C–H insertion into cyclohexane from the ring-contracted exocyclic vinyl cation **31**. Finally, to further validate our C–H insertion step, we looked to disprove the possibility of 1,5-hydride migration,^{31,32} given the selectivity in generating five-membered rings throughout our scope studies. Exposing tert-butyl derivative **32** to our reaction conditions yielded cyclohexene product isomers **33** in 85% NMR yield and a 1:1 ratio (Figure 5e). These observations disfavor a 1,5-hydride migration pathway. Instead, these studies suggest a concerted (but possibly highly asynchronous) C–H insertion mechanism, where formation of a five-membered ring is based solely on kinetic preference.

Over 100 years after Norris, Kehrman, and Baeyer's pioneering studies on the formation of carbocations under Brønsted and Lewis acidic conditions, we show that it is possible to generate such species in highly basic media. Importantly, this catalytic regime represents a new strategy in synthetic chemistry where lithium bases can be utilized to fuel [Li]⁺[WCA]⁻-catalyzed, intramolecular C–H insertion reactions of carbocations. This study highlights the

power of main-group-catalyzed C–H functionalization reactions in a field dominated by transition-metal-based systems. The commercial availability of the catalyst, the simple reaction protocols described above, and the resulting vast improvement in functional group compatibility render this strategy an attractive approach to build molecules for academic as well as industrial pursuits.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

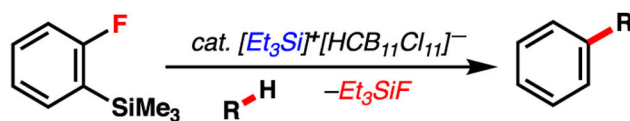
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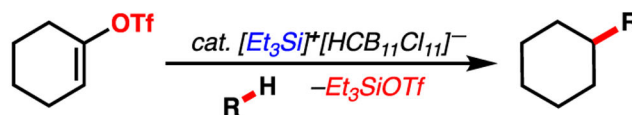
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a Silylium-catalyzed C–H insertion reactions of phenyl cationsShao and Bagdasarian, *Science*, 2017

R = alkyl

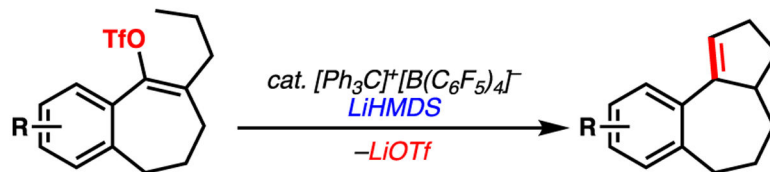
b Silylium-catalyzed C–H insertion reactions of vinyl cationsPopov, *Science*, 2018

R = alkyl

- Hyperelectrophilic Et_3Si^+
- Rare and exotic carborane anions
- Poor substrate compatibility

c Li^+ -catalyzed C–H insertion reactions of vinyl cations

This research



Milder Lewis acid



Commercial catalyst



Heteroatom compatibility

Figure 1.

Insertion reactions of di-coordinated carbocations. (a) C–H insertion reactions of aryl cations (b) Previous C–H insertion reactions of vinyl cations (c) C–H insertion reactions of vinyl cations under basic conditions.

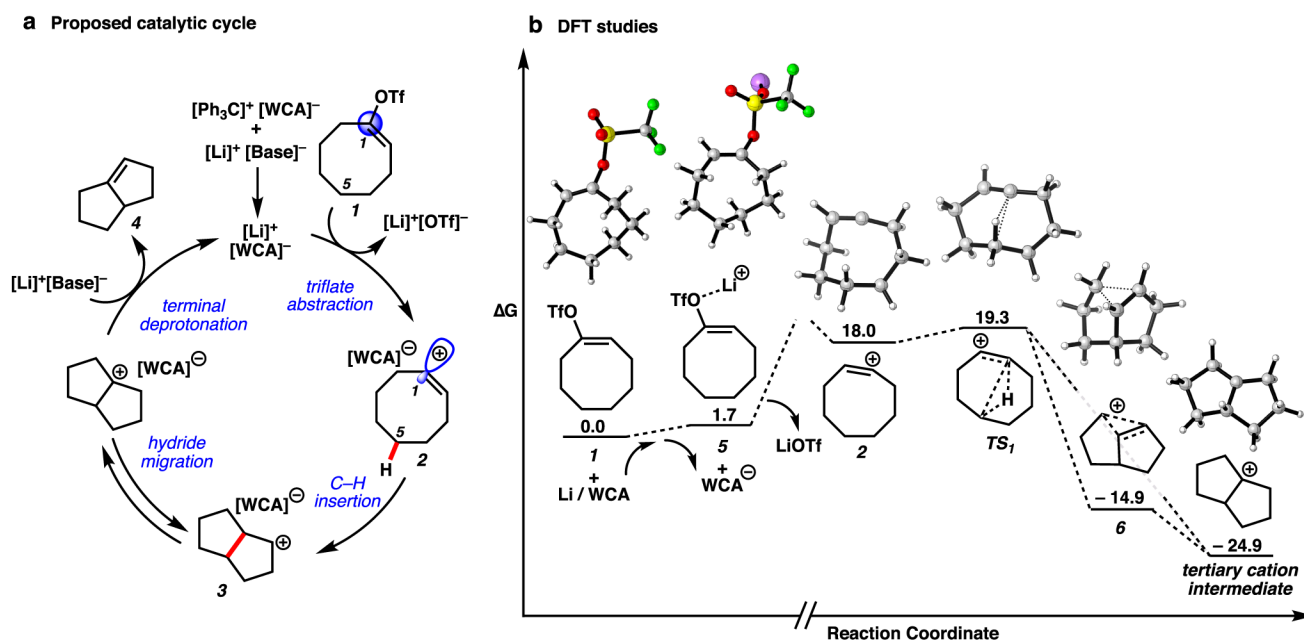


Figure 2. Proposed mechanism for lithium-mediated intramolecular C–H insertion reactions of vinyl cations. (a) Envisioned catalytic cycle of transannular insertion reactions of cyclooctenyl triflate 1. (b) Density functional theory (DFT) calculations supporting key mechanistic steps proposed in (a) starting from triflate 1 and $[\text{Li}]^+[\text{WCA}]^-$ complex using $[\text{HCB}_{11}\text{Cl}_{11}]^-$ as the model anion. G units are reported in kcal/mol. Calculations were performed using $\omega\text{B97XD}/6\text{-}311+\text{G}(\text{d},\text{p})\text{-SMD}(\text{DCM})$.

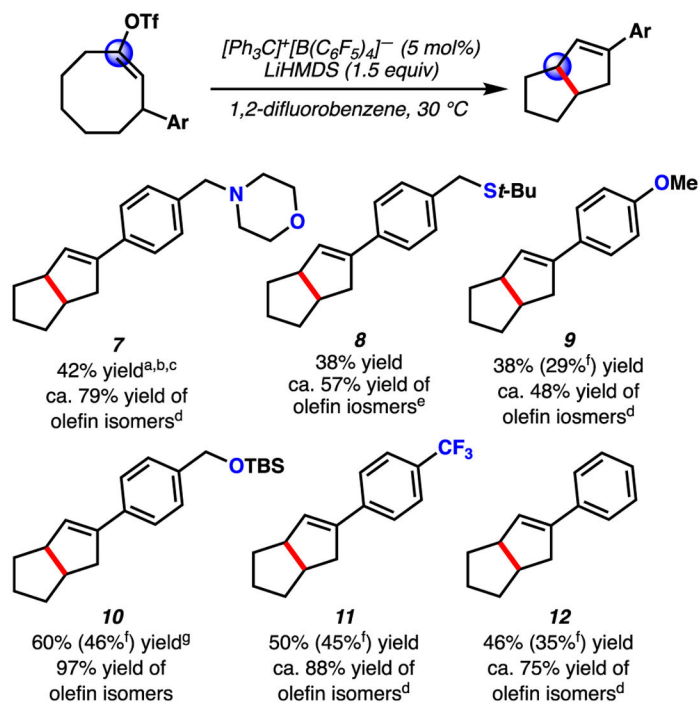
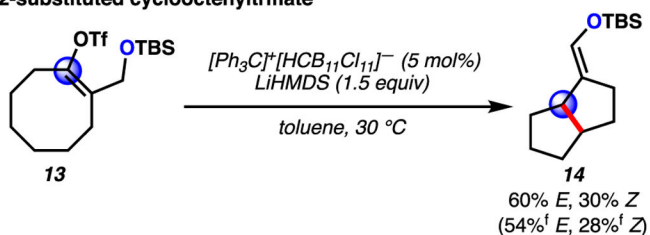
a 3-aryl cyclooctenyltriflates**b 2-substituted cyclooctenyltriflate**

Figure 3. Cyclooctenyl triflate scope. (a) C–H insertion reactions of 3-arylcyclooctenyl triflates. (b) C–H insertion reaction of 2-substituted vinyl triflate **13**. Yields were determined by NMR using an internal standard. Conditions: ^a3 equiv of LiHMDS. ^bCyclohexane as solvent. ^c70 °C. ^dYield determined by GC-FID.^{23a}^eYield determined by LCMS.^{23a} ^fIsolated yield. ^gMethylene chloride as solvent.

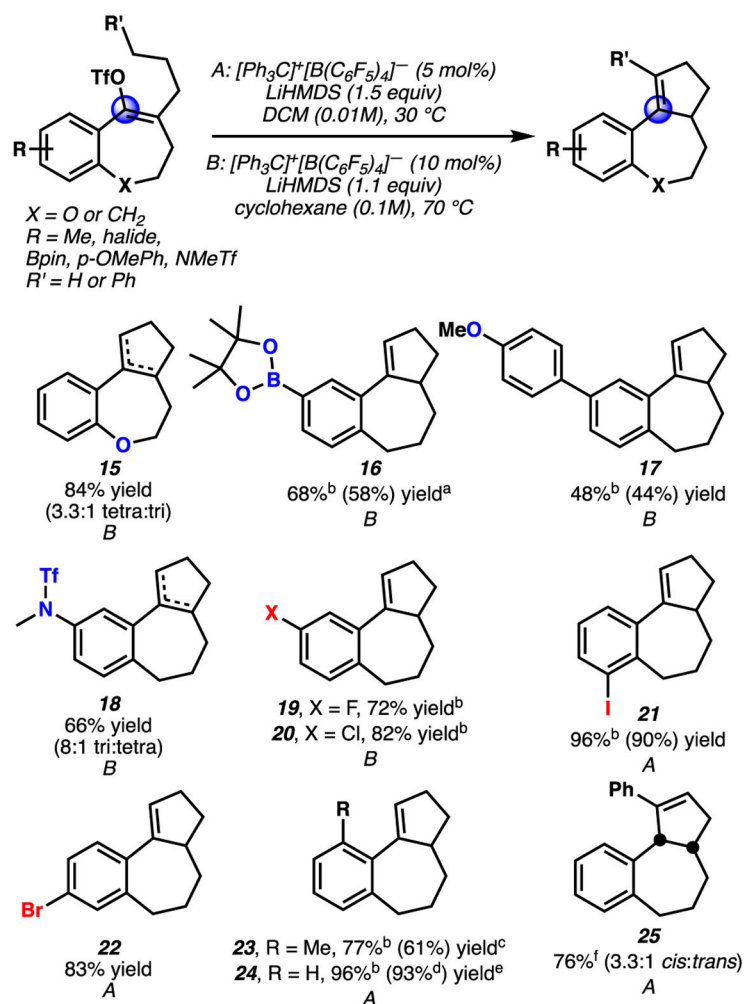


Figure 4. Benzosuberonyl triflate substrate scope. Isolated yields. Conditions: ^a30 °C. ^bYield determined by NMR using an internal standard. ^c0.0167 M. ^d1 mmol scale. ^e5 mol% $[Ph_3C]$ + $[HCB_{11}Cl_{11}]^-$. ^f-40 °C.

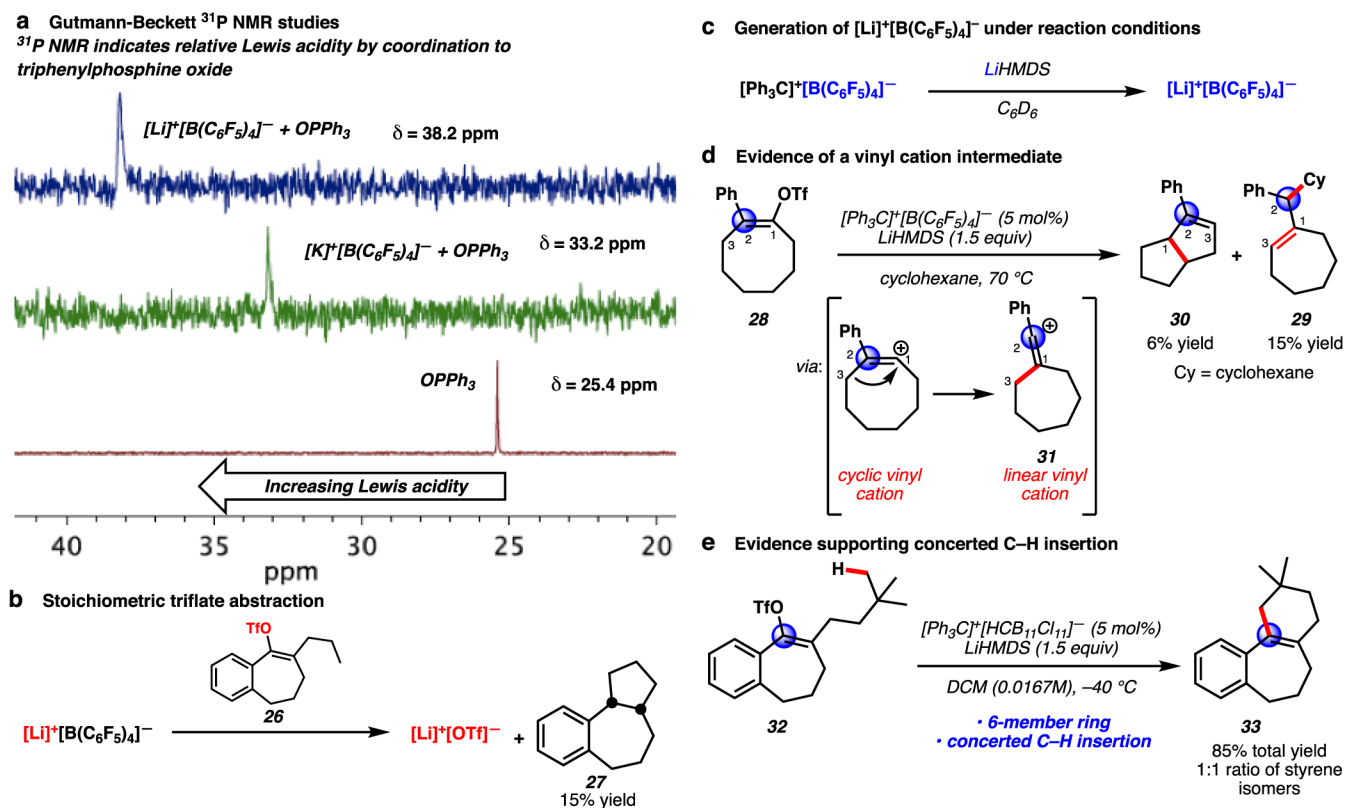


Figure 5. Mechanistic studies of base-mediated C–H insertion reactions. Yields were determined by NMR using an internal standard. (a) Gutmann–Beckett Lewis acidity assessment of alkali metal cations. (b) Stoichiometric triflate abstraction by $[\text{Li}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. (c) *In situ* formation of active catalyst. (d) Observation of ring-contracted products. (e) Formation of six-membered-ring products.