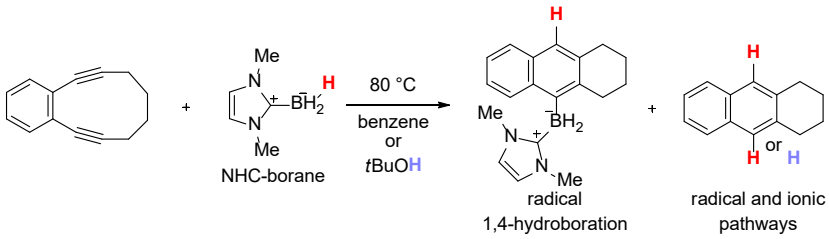
N-Heterocyclic Carbene Boranes are Hydrogen Donors in Masamune–Bergman Reactions of Benzo[3,4]cyclodec-3-ene-1,5-diynes

Takashi Watanabe,[†] Steven J. Geib,[‡] Dennis P. Curran,*[,‡] and Tsuyoshi Taniguchi*[,†]

[†]School of Pharmaceutical Sciences, Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

[‡]Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA



Abstract: Thermal reactions of benzo[3,4]cyclodec-3-ene-1,5-diyne with N-heterocyclic carbene boranes (NHC-boranes) provided mixtures of 9-borylated 1,2,3,4-tetrahydroanthracenes along with 1,2,3,4-tetrahydroanthracene. These products indicate that NHC-boranes serves as hydrogen donors to a *p*-benzyne intermediate formed by the Masamune-Bergman reaction. Experimental results support a radical mechanism in non-polar solvents, but suggest that ionic mechanisms compete in the production of 1,2,3,4-tetrahydroanthracene when the reaction is performed in a polar solvent.

INTRODUCTION

Reactive intermediates have a long track record of use in organic synthesis.[1] Benzynes (and more generally arynes) are widely used to synthesize functionalized aromatic compounds.[2] While *o*-benzyne intermediates are most common, *p*-benzyne and related diradicals are also important because they are intermediates in various cycloaromatization reactions.[2b,3] In the 1970s, cycloaromatization of enediynes was

independently reported by Masamune[4] and Bergman,[5a] and Bergman proposed *p*-benzyne, which is a 1,4-biradical, as a key intermediate.[5] Naturally occurring enediyne compounds show antibiotic and cytotoxic activity,[6] and *p*-benzyne intermediates formed from such enediynes cause DNA cleavage.[7] Today there are extensive experimental and theoretical studies on the Masamune-Bergman reaction.[8] In synthetic applications, 1,4-cyclohexadiene has often been used as a hydrogen donor to *p*-benzyne intermediates to isolate cycloaromatization products.

Some types of boranes can serve as hydrogen atom donors in radical reactions,[9] and therefore might serve as replacements of 1,4-cyclohexadiene in reactions on *p*-benzynes. However, investigation of this simple hypothesis is not straightforward because many boranes would hydroborate enediynes before they had a chance to form *p*-benzyne intermediates. Therefore, there has been no example of the reaction between *p*-benzyne and borane compounds.

As a class, N-heterocyclic carbene boranes (NHC-boranes) are stable to air and water,[10] and they do not hydroborate unstrained alkenes or alkynes (unless a catalyst is added).[11] NHC complexes of borane (NHC–BH_3) do not release free borane (BH_3) even under thermal conditions (stable at least at 120 °C). Many *B*-substituted NHC-boranes (NHC–BH_2R) are also stable and isolable by silica gel chromatography (especially when R = alkenyl or aryl). Capitalizing on this lack of reactivity towards alkynes, we have recently shown that NHC-boranes react selectively with *o*-benzyne intermediates formed by thermal hexadehydro-Diels–Alder reactions of various polyynes (Figure 1a).[12]

Similarly, we have recently shown that typical Masamune-Bergman reaction substrates such as benzo[3,4]cyclodec-3-ene-1,5-diyne **1** undergo neither direct 1,2-hydroboration reactions with NHC-boranes nor Masamune-Bergman reactions. Instead, under conditions conducive to radical chain reactions (di-*tert*-butylhyponitrite, $PhCF_3$, 100 ˚C), **1** predominantly undergoes a net hydroboration reaction that is interrupted by a radical cyclization (Figure 1b, left).[13] We wondered whether the radical chain reaction with **1** could be suppressed, thereby allowing the Masamune-Bergman to occur in its place (Figure 1b, right). Accomplishing this may not be as easy as it sounds because the *p*-benzyne intermediates are themselves potential chain initiators.

Herein we report that NHC-boranes serve as hydrogen donors in the

Masamune-Bergman reaction of **1** and related substrates, forming both anthracenes and borylated anthracenes. Mechanistic studies suggest that both radical and ionic pathways can lead to cycloaromatization products, depending on reaction conditions.

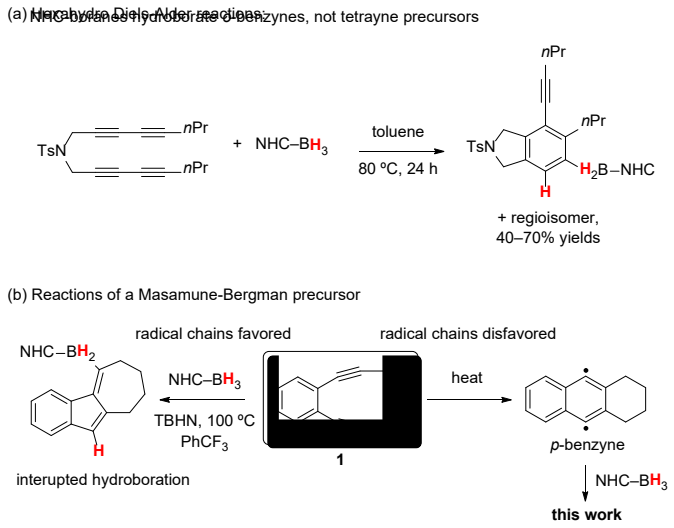


Figure 1. Reactions of NHC-boranes with *o*- and *p*-benzyne precursors

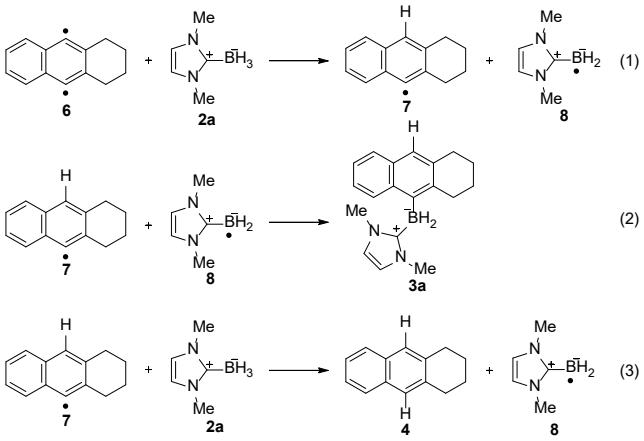
RESULTS AND DISCUSSION

We chose 10-membered cyclic diyne **1** as the *p*-benzyne precursor because it is stable yet has moderately strained alkynes. The Masamune-Bergman reaction takes place at a temperature of about 80 ˚C in the presence of appropriate radical trapping reagents.[8b] We initially studied the reaction of diyne **1** with readily available 1,3-dimethylimidazol-2-ylidene borane (diMe-Imd-BH_3, **2a**). This reaction proceeded slowly in benzene (0.2 M) at 80 ˚C in the presence of 2 equiv of diMe-Imd-BH_3 (**2a**), and the starting material **1** was almost completely consumed in 168 hours (1 week). Solvent evaporation and purification by silica gel chromatography gave three products, 9-NHC-boryl-1,2,3,4-tetrahydroanthracene **3a**, 1,2,3,4-tetrahydroanthracene (**4**) and 5-NHC-boryl-6,7,8,9-tetrahydrobenzo[*a*]azulene **5a** in 18%, 42% and 4% yields, respectively (Table 1, entry 1).

Formation of compounds **3a** and **4** indicates that the Masamune-Bergman reaction predominated. Benzo[*a*]azulene **5a** is the previously observed radical chain product,[13a] now formed in only small amounts. Further experiments were guided by the notion that the mechanism of the Masamune-Bergman reaction with diMe-Imd-BH_3 (**2a**) would be

similar to that of previous examples with 1,4-cyclohexadiene.[8] As shown in Scheme 1 (eq 1), the 1,4-biradical (*p*-benzyne) **6** generated by cycloaromatization of diyne **1** abstracts a hydrogen atom from NHC-borane **2a** to form aryl radical **7** and NHC-boryl radical **8**.[14] If this radical pair recombines,[8a] then the 1,4-hydroboration product **3a** is formed (eq 2). On the other hand, if aryl radical **7** reacts with another NHC-borane **2a**, then 1,2,3,4-tetrahydroanthracene (**4**) is produced along with NHC-boryl radical **8** (eq 3). The isolation of small amounts of 5-borylated 6,7,8,9-tetrahydrobenzo[*a*]azulene **5a** supports formation of NHC-boryl radical **8** because this radical can mediate the chain to make **5a**.[13a]

Scheme 1. Proposed mechanism of the Masamune-Bergman reaction with NHC-borane **2a**.

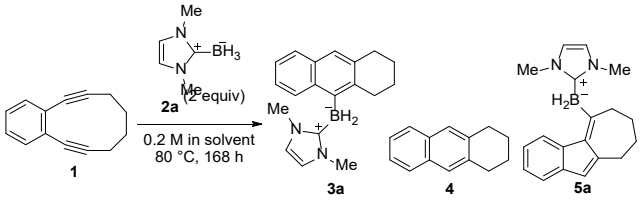


To assess whether the coupling reaction between aryl radical **7** and NHC-boryl radical **8** (Scheme 1, eq 2) occurred in a solvent cage,[8a,15] we conducted reactions of diyne **1** with NHC-borane **2a** in various solvents. Reactions in acetonitrile and dimethyl sulfoxide provided borylated product **3a** in 15% and 16% yields, respectively, and 1,2,3,4-tetrahydroanthracene (**4**) in 48% and 39% yields, respectively (Table 1, entries 2 and 3). When the reaction was performed in *tert*-butyl alcohol (*t*BuOH), borylated product **3a** was obtained in slightly improved yield (25%) along with 1,2,3,4-tetrahydroanthracene (**4**, 44%) (entry 4). 5-Borylated 6,7,8,9-tetrahydrobenzo[*a*]azulene **5a** was formed in only trace amounts in these reactions in polar solvents.

Because viscous liquids induce large cage effect in some radical reactions,[17] we tested representative ionic liquids and obtained **3a** in slightly improved yields (25−28%,

entries 5–8) compared to benzene, acetonitrile and DMSO. As usual, **4** was formed in about 40% yield. These small improvements suggest that cage effects are not especially important. Indeed, about the same yields of both **3a** and **4** can be obtained simply by conducting the reaction in non-viscous *tert*-butyl alcohol.[16]

Table 1. Reactions of diyne **1** with diMe-Imd-BH_3 (**2a**) in various solvents



entry	solvent	yield (%)[b]		
		3a	**4**	**5a**
1	PhH	18	42	4
2	MeCN	15	48	trace
3	DMSO	16	39	trace
4	*t*BuOH	25	44	trace
5[d]	[bmin]BF_4	25	43	n.d.
6[d]	[emin]OAc	25	43	n.d.
7[d]	[$P_{1,3}$]TFSA	28	40	n.d.
8[d]	[$PP_{1,3}$]TFSA	28	37	n.d.

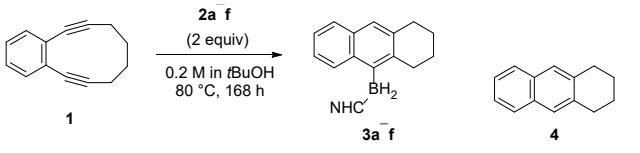
[a]Conditions: **1** (0.2 mmol), **2a** (0.4 mmol), in solvent (1 mL) at 80 ˚C for 168 h. [b]Yield of isolated products. [c]0.1 M. [d]Reaction time is 240 h. [bmin]BF_4: 1-butyl-3-methylimidazolium tetrafluoroborate. [emin]OAc: 1-ethyl-3-methylimidazolium acetate. [$P_{1,3}$]TFSA: 1-methyl-1-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide. [$PP_{1,3}$]TFSA: 1-methyl-1-propylpyperidinium bis(trifluoromethanesulfonyl)imide.

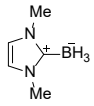
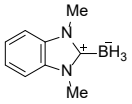
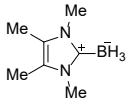
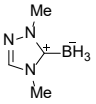
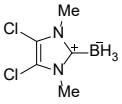
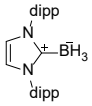
We next surveyed reactions of other NHC-boranes in *t*BuOH to understand the effect of NHC ligands. Reaction conditions were the same as Table 1, entry 4, and results are shown in Table 2. The reaction of 1,3-dimethylbenzimidazol-2-ylidene borane (**2b**) gave borylated product **3b** and 1,2,3,4-tetrahydroanthracene (**4**) in 22% and 41% yields, respectively (Table 2, entry 2). However, when 1,3,4,5-tetramethylimidazol-2-ylidene borane (**2c**) was used, borylated product **3c** was hardly detected in ^{11}B NMR analysis of the crude product, and only 1,2,3,4-tetrahydroanthracene (**4**) was isolated in 37% yield (entry 3). ^1H NMR of the crude product showed several unidentified products, indicating that side reactions could compete with the Masamune-Bergman reaction

probably because of high nucleophilicity of **2c** having electron-donating 4,5-dimethyl groups.[18]

Reactions with 1,4-dimethyl-1,2,4-triazolium-5-ylidene borane (**2d**) and 4,5-dichloro-1,3-dimethylimidazol-2-ylidene borane (**2e**) were similar to each other. Borylated products **3d** and **3e** were obtained in about 20% yield, but 1,2,3,4-tetrahydroanthracene (**4**) was obtained in lower yields compared to the prior examples (19% and 18% yields, entries 4 and 5). Small amounts of 5-borylated 6,7,8,9-tetrahydrobenzo[*a*]azulenes (analogous to **5a**) and unidentified side products were detected by NMR analysis of the crude product in these cases. The reaction with bulky dipp-imidazolylidene borane **2f** (dipp being 2,6-diisopropylphenyl) was sluggish, and low conversion of diyne **1** was observed probably due to a steric factor (entry 6).

Table 2. Preparative reactions of **1** with various NHC-boranes **2a−f** in *t*BuOH.



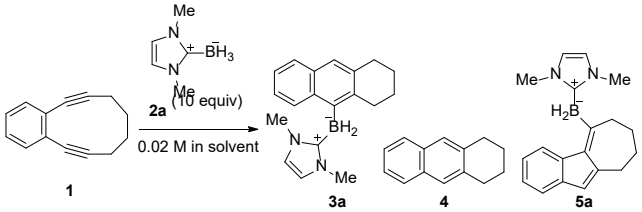
entry 1		**2a**	25%	44%
entry 2		**2b**	22%	41%
entry 3		**2c**	trace	37%
entry 4		**2d**	note[b]	18%
entry 5		**2e**	22%	18%
entry 6		**2f**	n.d	12%

[a]Conditions: **1** (0.2 mmol), **2b-f** (0.4 mmol), in *t*BuOH (1 mL) at 80 ˚C for 168 h. [b]**3d** was isolated as a mixture including inseparable impurities. **3d**:**4** = ca. 1:1 (^{1}H NMR analysis of the crude product).

The total yield of Masamune-Bergman products was less than 70% in all examples in Table 2, indicating that side reactions competed. We hypothesized that yields of 5-borylated 6,7,8,9-tetrahydrobenzo[*a*]azulenes such as **5a** and other side products could be minimized by reducing the concentration of precursor **1** (a potential chain initiator) while maintaining a relatively high concentration of **2a** (to trap the *p*-benzyne species).

Therefore, we conducted a thermal reaction of **1** in benzene at 0.02 M with 10 equiv of NHC-borane **2a**. The reaction was complete after 168 h at 80 ˚C and afforded borylated product **3a** and 1,2,3,4-tetrahydroanthracene (**4**) in 32% and 55% yields, respectively (Table 3, entry 1). The mass balance of Masamune-Bergman products was improved (87% at 0.02 M compared to 69% at 0.2 M). As expected, 5-borylated 6,7,8,9-tetrahydrobenzo[*a*]azulene **5a** and other side products were not detected. A similar reaction in benzotrifluoride ($PhCF_3$) provided **3a** in slightly improved yield (38%), again with a good total yield (91%, entry 2).[19] The use of half as much NHC-borane **2a** (5 equiv) required a longer reaction time (240 h) and gave a somewhat lower total yield (77%, entry 3). Elevating the temperature to 100 ˚C and then 120 ˚C (entries 4 and 5) shortened the reaction times (24 h and 6 h), but gave significant amounts of chain product **5a** (19% and 28%) at the expense of **3a** and **4**. Clearly higher temperatures favor chain reactions. Reactions in *t*BuOH and an ionic liquid did not work well under the dilute conditions with excess **2a** (entries 6 and 7).

Table 3. The reaction of **1** with **2a** under dilute conditions



entry	solvent	temp (˚C)	time (h)	yield (%)[b]		
				3a	**4**	**5a**
1	benzene	80	168	32	55	0
2	$PhCF_3$	80	168	38	53	0
3[c]	$PhCF_3$	80	240	31	46	0
4	$PhCF_3$	100	24	27	48	19
5[d]	$PhCF_3$	120	6	20	41	28

6	*t*BuOH	80	240	8	38	0
7	$[P_{1,3}]$TFSA	80	240	18	38	0

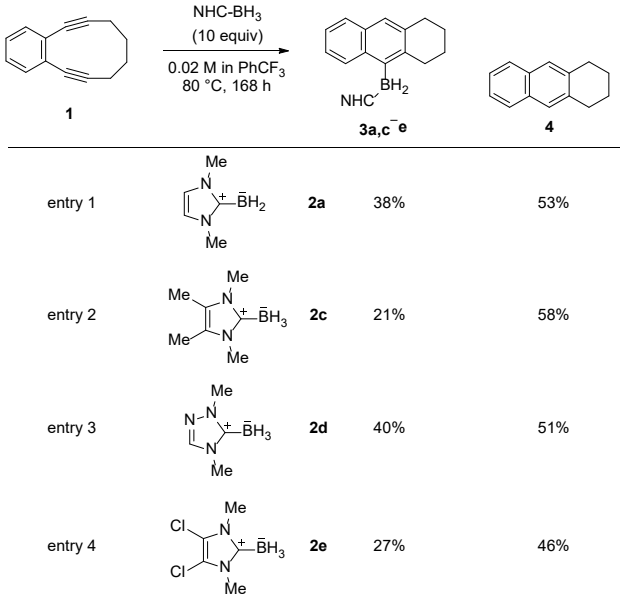
[a]Conditions: **1** (0.15 mmol), **2a** (1.5 mmol), in solvent (7.5 mL) at 80−120 ˚C. [b]Yield of isolated products. [c]5 equiv (0.75 mmol) of **2a** was used. [d]The reaction was performed in a sealed tube.

We next tested representative NHC-boranes under the dilute conditions of Table 3, entry 2 (0.02 M, $PhCF_3$, 80˚C), and results are shown in Table 4. The reaction of 1,3,4,5-tetramethylimidazol-2-ylidene borane (**2c**) afforded the corresponding borylated product **3c** in 21% yield (entry 2) along with 58% of **5**. Compare this to the reaction in *t*BuOH, where only a trace of **3c** was formed (Table 2, entry 2). Reaction with 1,4-dimethyl-1,2,4-triazolium-5-ylidene borane (**2d**) gave borylated product **3d** and 1,2,3,4-tetrahydroanthracene (**4**) in 40% and 51% yields, respectively (entry 3). Finally, the reaction of 4,5-dichloro-1,3-dimethylimidazol-2-ylidene borane (**2e**) provided the borylated product **3e** and 1,2,3,4-tetrahydroanthracene (**4**) in 27% and 46% yields, respectively (entry 4).

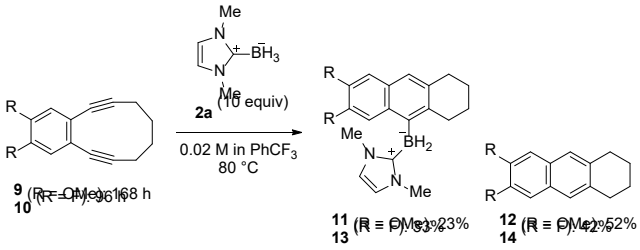
Overall, combined yields of Masamune-Bergman products were improved in these reactions, and radical chain products were not observed. Most of the unreacted NHC-boranes could be recovered by silica gel chromatography after the reaction, if desired.

Reactions of **2a** with two substituted diynes **9** and **10** were tested under the conditions of Table 4 and the results are shown in Scheme 2. Product yields were roughly comparable to those with **1**. The dimethoxy analog **9** gave borylated and non-borylated products **11** and **12** in 23 and 52% yields, respectively. Difluoro analog **10** gave **11** and **14** in 33% and 40% yields.

Table 4. Reactions of **1** with several NHC-boranes under dilute conditions [a]Conditions: **1** (0.15 mmol), **2a,c−e** (1.5 mmol), in $PhCF_3$ (7.5 mL) at 80 ˚C for 168 h.

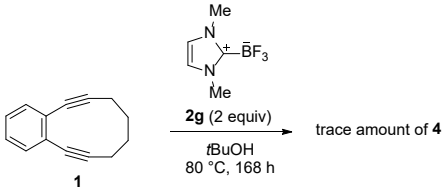


Scheme 2. Reactions of substituted diynes **9** and **10** with **2a**.



We tried to reveal the hydrogen source in the reaction between diyne **1** and NHC-boranes. When diMe-Imd-BF_3 (**2g**) was used instead of diMe-Imd-BH_3 (**2a**), the reaction in *t*BuOH was hardly induced, though a trace amount of **4** was detected. This indicates that B–H bonds in the NHC-borane are required to promote the Masamune-Bergman reaction (Scheme 3).[20]

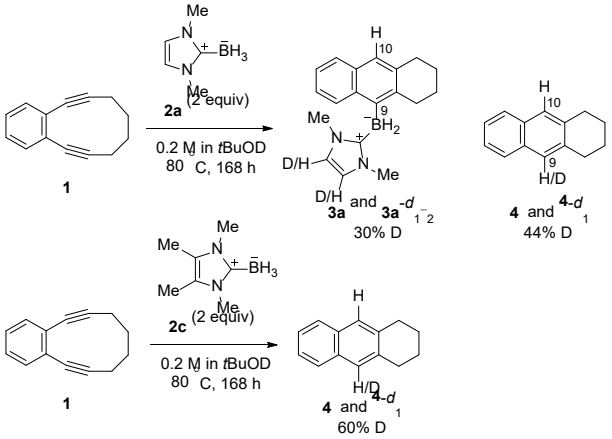
Scheme 3. The reaction of **1** with diMe-Imd-BF_3 (**2g**) in *t*BuOH.



We next performed the reaction of diyne **1** with NHC-borane **2a** in *t*BuOD (Scheme 4).

^{1}H NMR analysis of product **4** indicated that a deuterium atom was partially introduced to the C9 and/or C10 positions (22% D based on two hydrogens on C9 and C10). When NHC-borane **2c** was used instead of **2a**, the ratio of the introduced deuterium atom was increased (30% D based on two hydrogens on C9 and C10). Mass spectrometry analysis indicated production of compound **4** and 9-deuterio-1,2,3,4-tetrahydroanthracene (**4**-d_1) in both cases. Therefore, the ratio of a deuterium atom incorporated on C9 is simply estimated as 44% for **2a** and 60% for **2c**, respectively (Scheme 4). These results suggested that an ionic pathway participates in the reaction because O–H bonds of typical alcohols could not be hydrogen sources to radicals due to their large BDEs. For product **3a**, no deuterium atom was detected on the naphthalene ring, but hydrogen atoms on sp^2-carbons of the NHC were partially replaced with deuterium atoms (30% D) (Scheme 4). Since hydrogen-deuterium exchange on sp^2-carbons of NHCs occurs under basic conditions,[21] this result indicates generation of a strong base in *situ*. The reaction of **1** with **2a** in DMSO-d_6 produced **4**-d_1 (50% D), and this also supports generation of a highly basic anion (not shown in Scheme 4, see the experimental section).

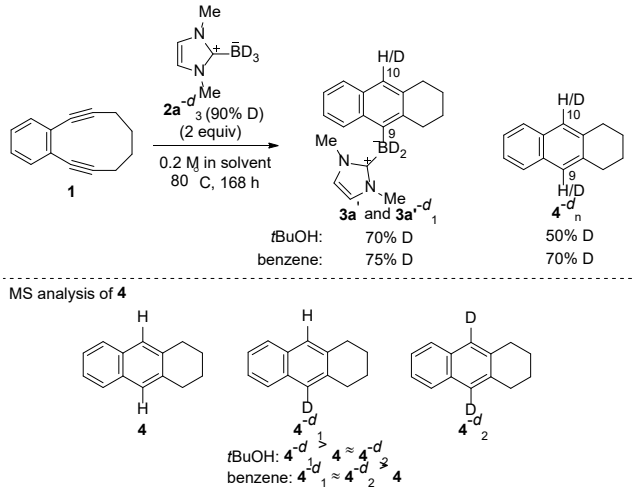
Scheme 4. The reaction of **1** with NHC-boranes in *t*BuOD.



Subsequently, we tested the reaction of diyne **1** with diMe-Imd-BD$_3$ (**2a**-d_3, ca. 90% D) in *t*BuOH or benzene (Scheme 5). These reactions provided borylated product **3a'**-d_1 having a deuterium atom on a C10 position (70% D in *t*BuOH, 75% D in benzene) and compound **4** having deuterium atoms on C9 and/or C10 positions (50% D in *t*BuOH, 70% in benzene). The deuterium enrichment on the C10 position of **3a'** was less than that of the deuterated NHC-borane, but it could be rationalized by the kinetic isotope effect because hydrogen abstraction is a rate-determining step in cycloaromatization of diyne **1**.[8d] Mass spectrometry analysis of product **4**-d_n in this reaction indicated that the

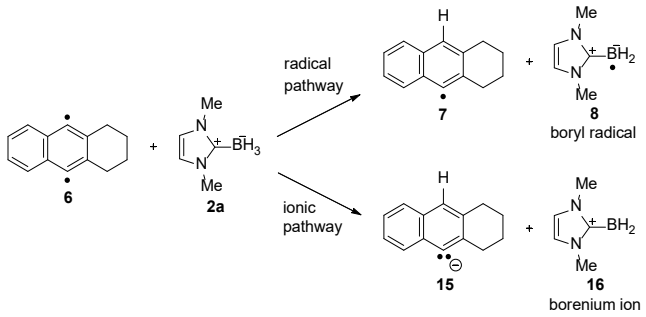
isomer distribution consisted of **4** (d_0), **4**-d_1 and **4**-d_2. Production of **4** and a portion of **4**-d_1 would occur due to 90% D purity of the deuterated NHC-borane as in the case of product **3a'**. **4**-d_1 was a major isomer in *t*BuOH, whereas both **4**-d_1 and **4**-d_2 were equally major isomers in benzene. These results also indicate that there is the ionic pathway in *t*BuOH.

Scheme 5. The reaction of **1** with diMe-Imd-BD_3.



Perrin and co-workers reported nucleophilic addition of halide anions to a *p*-benzyne intermediate to form an aryl anion in polar solvents.[22] Since NHC-boranes work as a good hydride source,[23] a hydride transfer from NHC-BH_3 **2a** to *p*-benzyne **6** could occur to produce the corresponding aryl anion **15** followed by protonation to give product **4** (Scheme 6). Results of Schemes 4 and 5 indicated that such an ionic pathway could compete with the radical pathway in the reaction between *p*-benzyne **6** and NHC-borane **2a**. An improvement in yield of **3a** by the cage effect might be offset by the ionic pathway in ionic liquids because ionic liquids also could be a proton source to a strongly basic anion (Table 1). However, hydride addition to diyne **1** followed by cyclization cannot be fully excluded in our case because a small amount of the corresponding diene was detected in the reaction in *t*BuOH.[16,24]

Scheme 6. Possible pathways in the reaction between *p*-benzyne and **2a**



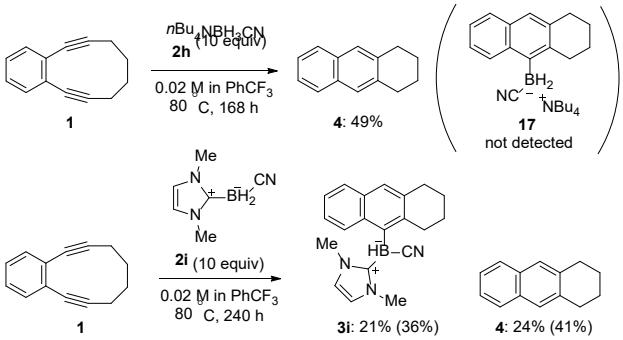
Do these ionic pathways contribute to production of borylated compound **3a** in an apolar solvent? The combination between aryl anion **15** and NHC-borenium ion **16** would give borylated product **3a** if the ionic pathway proceeded in an apolar solvent.

To address this question, we tested the reaction of **1** with tetra-*n*-butylammonium cyanoborohydride (*n*Bu_4NBH_3CN, **2h**) in the diluted solution in $PhCF_3$ (Scheme 7). Interestingly, starting **1** was almost completely consumed in 168 hours, and 1,2,3,4-tetrahydroanthracene (**4**) was obtained in 49% yield, indicating that *n*Bu_4NBH_3CN (**2h**) could work as a hydrogen donor to the *p*-benzyne intermediate. However, neither compound **17** nor other borylated products were detected by ^{11}B NMR analysis of the crude product. The nucleophilicity of *n*Bu_4NBH_3CN (**2h**) is similar to that of NHC-boranes,[23] so the absence of **17** suggests that an ionic process is not important in apolar solvents.[25] On the other hand, since it is known that *n*Bu_4NBH_3CN (**2h**) works as a hydrogen donor to radicals,[9c] the radical pathway in apolar solvents is sensible. If hydrogen transfer from *n*Bu_4NBH_3CN (**2h**) to aryl radical **7** is more favorable than recombination of a radical pair, then **17** would not be produced.

When diMe-Imd-BH_2CN **2i**[26] was used instead of *n*Bu_4NBH_3CN (**2h**), the reaction was much slower than that of diMe-Imd-BH_3 **2a**, and the conversion of **1** was 59% in 240 hours. However, borylated product **3i** and 1,2,3,4-tetrahydroanthracene (**4**) were obtained in roughly equal yields (Scheme 7). In this case, the ionic pathway would hardly contribute to the reaction due to the low nucleophilicity of NHC-borane **2i** having a cyano group on a boron atom. Therefore, these results also indicate that the radical mechanism predominates in the production of borylated compounds in apolar solvents. Borylated compound **17** might not be produced because of the difference in the properties of boryl radicals (NHC-boryl radicals and cyanoborane radical anion) formed by the radical pathway. Results shown in Table 4 indicated a weak impact of the electron density of NHC-boranes, and this is consistent with the exclusive radical pathway in apolar solvents because the impact of NHC-boranes is not large in the

radical hydrogen transfer reaction.[14] Thus, the ionic pathway is unlikely to contribute to production of borylated compounds in benzene and $PhCF_3$.

Scheme 7. The reaction of **1** with nBu$_4$NBH$_3$CN (**2h**) or **2i**. Yield in parentheses is based on recovered **1**.



X-ray crystal structures of three representative borylated compounds **3a**, **3d** and **3i** were shown in Figure 2 as the ORTEP representations.[27] Crystals of these compounds were grown from benzene/*n*-pentane, benzene/*n*-hexane and ethyl acetate/*n*-hexane solutions, respectively. Those structures are consistent with the assignments that the compounds were Masamune-Bergman products.

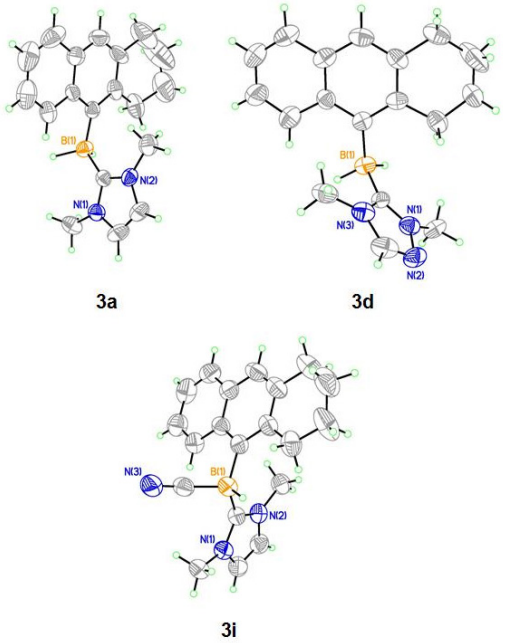


Figure 2. ORTEP representations of X-ray crystal structures of **3a**, **3d**, and **3i** with

ellipsoids drawn at the 50% probability level.

CONCLUSIONS

We investigated the reactions of the typical *p*-benzyne intermediate formed from 10-membered cyclic diyne **1** with NHC-boranes. NHC-borane **2a** can induce the Masamune-Bergman reaction of **1** to provide 9-NHC-boryl-1,2,3,4-tetrahydroanthracene **3a**, indicating formal 1,4-hydroboration of *p*-benzyne, along with typical 1,2,3,4-tetrahydroanthracene (**4**). However, a radical chain reaction of **1** mediated by the NHC-boryl radical often competed with the Masamune-Bergman reaction to provide 5-NHC-boryl-6,7,8,9-tetrahydrobenzo[*a*]azulene **5a**. The results largely depended on reaction conditions such as solvents, concentration and temperature. We revealed that the use of excessive amounts of NHC-boranes in a highly diluted solution in benzene or $PhCF_3$ exclusively caused the Masamune-Bergman reaction.

We found that both radical and ionic pathways could participate in the first hydrogen donation to the *p*-benzyne intermediate. Generation of the corresponding aryl anion was suggested by reactions in *t*BuOD and DMSO-d_6 to give compound **4** partially including a deuterium atom.

Our study provided new insights into the reactions between *p*-benzyne and borane complexes. 1,4-Hydroboration of *p*-benzyne could be a new approach for synthesis of organoboron compounds, though the product yield is moderate at present. Such an approach will be applicable to other reactive intermediates formed from related cycloaromatization reactions. We anticipate that a combination of a highly reactive species with the organoboron chemistry will serve for the development of new synthetic methodologies and organoboron materials in the future.

EXPERIMENTAL SECTION

General remarks. All reactions were performed in oven-dried glassware under a nitrogen atmosphere unless otherwise noted. A pressure vessel [ACE GLASS Inc. (15 mL)] was used as required. All reagents purchased commercially were used without further purification unless otherwise noted. Dehydrated benzene, acetonitrile and dimethyl sulfoxide were purchased from Kanto Chemical Co., Inc. Benzotrifluoride was purchased from Tokyo Chemical Industry Co., Ltd. and dried with activated molecular sieves 4A (activation method: heating with a heat gun in vacuo) before use. Thin-layer

chromatography (TLC) analysis was performed by illumination with a UV lamp (254 nm) or staining with PMA and heating to monitor the reaction. Melting points are uncorrected. IR spectra were recorded on a FT-IR spectrometer. NMR spectra were recorded on 400 MHz (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{11}B: 128 MHz, ^{19}F: 376 MHz) and 600 MHz (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{11}B: 192 MHz, ^{19}F: 564 MHz, ^{2}H NMR 92 MHz) spectrometers. Chemical shifts (δ) are quoted relative to tetramethylsilane (^{1}H NMR, δ 0 ppm), the signals of the residual solvent (^{13}C NMR, $CDCl_3$: δ 77.00 ppm, ^{2}H NMR, $CDCl_3$: δ 7.26 ppm), boron trifluoride diethyl ether complex (^{11}B NMR, external standard: δ 0 ppm, error: <±1 ppm) and hexafluorobenzene (^{19}F NMR, external standard: δ −164.9 ppm, error: not calibrated). The resonances for carbons bonded to boron in the ^{13}C NMR spectra were not typically observed. NMR spectra were recorded at 295−298 K. Silica gel column chromatography was carried out on silica gel 60N (spherical, neutral, 40−50 μm). Mass spectra were recorded on a TOF-MS spectrometer in direct analysis in real time (DART) mode.

Starting materials. All *N*-heterocyclic carbene−boranes were prepared according to the established procedure.[14,28–32] All starting 10-membered cyclic diynes were prepared by alkylation of the corresponding 1,2-diethynylbenzenes with *n*-butyllithium and 1,4-diiodobutane according to an established method.[8b,13a]

General procedure for the reaction between benzo[3,4]cyclodec-3-ene-1,5-diyne (1) and NHC-boranes at 0.2 M (General procedure A). The reaction of 1 with 1,3-dimethylimidazol-2-ylidene borane (2a) (Table 1). A stirred solution of **1** (36.1 mg, 0.20 mmol) and **2a** (44.0, mg, 0.40 mmol) in solvent (1 mL) was heated for 168 h at 80 ˚C. After cooling to room temperature, the volatile solvent was removed under reduced pressure [When the solvent having a high boiling point was used (DMSO or ionic liquids), the reaction mixture was diluted with water, extracted with *n*-hexane/EtOAc (1:1), dried with brine and $MgSO_4$, and concentrated under reduced pressure]. NMR analysis of the crude product was conducted as required. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1). The second elution gave (1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1,2,3,4-tetrahydroanthracen-9-yl)dihydroborate (**3a**) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (1H, d, J = 7.2 Hz), 7.64 (1H, dd, J = 7.2, 2.4 Hz), 7.35 (1H, s), 7.27–7.21 (2H, m), 6.70 (2H, s), 3.45 (6H, s), 2.95 (2H, t, J = 6.0 Hz), 2.80 (2H, t, J = 6.0 Hz), 2.72 (2H, br-q, $J_{H–B}$ = 83 Hz), 1.81–1.74 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 137.1, 135.4, 132.2, 129.1, 127.4,

124.4, 123.3, 123.0, 120.2, 35.9, 31.3, 31.0, 24.5, 23.3; ^{11}B NMR (128 MHz, $CDCl_3$): δ –28.8 (t, J_{B-H} = 83 Hz); IR (nujol, cm^{-1}): ν_{max} 2285, 1475, 1232,; mp: 149–150.5 ºC (gradually decomposed from 120 ºC); MS (DART+): *m*/*z* 289 (100%); HRMS (DART+): calcd for $C_{19}H_{22}{}^{11}BN_2$ $[M-H]^+$ 289.1876, found 289.1879. The first elution gave 1,2,3,4-tetrahydroanthracene (**4**) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.69 (2H, m), 7.53 (1H, s), 7.36–7.33 (2H, m) 3.00–2.92 (4H, m), 1.90–1.82 (4H, m); MS (DART+): *m*/*z* 183 (100%). Analytical data of **4** were consistent with the previously reported characterization.[8b] A small amount (typically <5%) of unreacted **1** or side products (typically <5%) contaminated **4**. In such the case, the yield of **4** was calculated in ^{1}H NMR spectra. The third elution gave (1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(6,7,8,9-tetrahydrobenzo[*a*]azulen-5-yl)dihydrob orate (**5a**) as a yellow solid: Analytical data of **5a** were consistent with the previously reported characterization.[13a] Representative results: Benzene (0.2 M): **3a** (10.5 mg, 18%), **4** (15.2 mg, 42%) contaminated by **1** (4%), **5a** (2.6 mg, 4%); *t*BuOH: **3a** (14.4 mg, 25 %), **4** (16.1 mg, 44%), **5a** (<1 mg, trace). Small amounts of (5*Z*,11*Z*)-7,8,9,10-tetrahydrobenzo[10]annulene (**18**) and benzo[3,4]cyclodec-3-ene-1,6-diyne (**19**) were often detected in ^{1}H NMR spectra of **4** obtained by reactions in polar solvents (each ca. 2%). These were tentatively identified by ^{1}H and ^{2}H NMR and mass spectrometry analysis. **18**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.07 (4H, m), 6.64 (2H, d, *J* = 9.6 Hz), 6.13 (2H, dt, *J* = 9.6, 4.4 Hz), 2.42–2.37 (4H, m), 1.74–1.65 (4H, m). (**19**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.07 (4H, m), 3.29 (2H, s), 2.60–2.58 (2H, m), 2.54 (2H, app. t, *J* = 5.6 Hz), 1.74–1.65 (4H, m). MS (DART+) of **4** obtained by the reaction in *t*BuOH: *m*/*z* 181 (18%), 183 (97%), 185 (100%).

The reaction of 1 with 1,3-dimethylbenzo[*d*]imidazol-2-ylidene borane (2b) (Table 2, entry 2). According to the general procedure A, a solution of **1** (36.1 mg, 0.20 mmol) and **2b** (63.2 mg, 0.40 mmol) in *t*BuOH (1 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 3:1). The second elution gave (1,3-dimethylbenzo[*d*]imidazol-3-ium-2-yl)(1,2,3,4-tetrahydroanthracen-9-yl)dihydrobo rate (**3b**) (14.8 mg, 22%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (1H, d, *J* = 9.0 Hz), 7.66 (1H, d, *J* = 7.8 Hz), 7.39–7.37 (5H, m), 7.28–7.22 (2H, m), 3.70 (6H, s), 2.96 (2H, t, *J* = 6.0 Hz), 2.95 (2H, br-q, J_{H-B} = 87 Hz), 2.84 (2H, t, *J* = 6.0 Hz), 1.78–1.74 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.8, 137.0, 135.6, 133.3, 132.3, 129.1, 127.5, 124.7, 123.9, 123.4, 123.3, 110.5, 31.9, 31.3, 24.5, 23.3; ^{11}B NMR (192 MHz,

$CDCl_3$): δ –28.3 (t, $J_{B–H}$ = 87 Hz); IR (nujol, cm^{-1}): ν_{max} 2289, 1456, 1377; mp: 110–112 ºC; HRMS (DART+): calcd for $C_{23}H_{24}{}^{11}BN_2$ $[M–H]^+$ 339.2033, found 339.2037. The first elution gave 1,2,3,4-tetrahydroanthracene (**4**) (14.9 mg, 41%). The third elution gave a mixture including a small amount of (1,3-dimethylbenzo[*d*]imidazol-3-ium-2-yl)(6,7,8,9-tetrahydrobenzo[*a*]azulen-5-yl)dihydroborate.[13a]

The reaction of 1 with 1,3,4,5-tetramethylimidazol-2-ylidene borane (2c) (Table 2, entry 3). According to the general procedure A, a solution of **1** (36.1 mg, 0.20 mmol) and **2c** (55.2, mg, 0.40 mmol) in *t*BuOH (1 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1) to give **4** (14.0 mg, 38%). **18** and **19** (each ca. 2%) were detected in the ^{1}H NMR spectrum of **4**. Trace amounts of (1,2,3,4-tetrahydroanthracen-9-yl)(1,3,4,5-tetramethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3c**) and (6,7,8,9-tetrahydrobenzo[*a*]azulen-5-yl)(1,3,4,5-tetramethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate[13a] were detected by NMR analysis of the crude product.

The reaction of 1 with 1,4-dimethyl-1,2,4-triazol-5-ylidene borane (2d) (Table 2, entry 4). According to the general procedure A, a solution of **1** (36.1 mg, 0.20 mmol) and **2d** (44.4, mg, 0.40 mmol) in *t*BuOH (1 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1). The second elution gave impure (1,4-dimethyl-4*H*-1,2,4-triazol-1-ium-5-yl)(1,2,3,4-tetrahydroanthracen-9-yl)dihydroborate (**3d**) (11.4 mg as a mixture). Since a pure compound was obtained in the reaction shown in Table 4, characterization data was described therein. The first elution gave **4** (6.5 mg, 18%). **15** and **16** (each ca. 2%) were detected in the ^{1}H NMR spectrum of **4**. The ratio of **3d**:**4** was approximately estimated as 1:1 by ^{1}H NMR analysis of the crude product. The third elution gave a mixture including a small amount of 1,4-dimethyl-4*H*-1,2,4-triazol-1-ium-5-yl)(6,7,8,9-tetrahydrobenzo[*a*]azulen-5-yl)dihydroborate.[13a]

The reaction of 1 with 4,5-dichloro-1,3-dimethylimidazol-2-ylidene borane (2e) (Table 2, entry 5). According to the general procedure A, a solution of **1** (36.1 mg, 0.20 mmol) and **2e** (71.5, mg, 0.40 mmol) in *t*BuOH (1 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 5:1). The second elution gave

(4,5-dichloro-1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1,2,3,4-tetrahydroanthracen-9-yl)dihydroborate (**3e**) (15.5 mg, 22%) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 (1H, d, J = 7.2 Hz), 7.65 (1H, dd, J = 7.2, 2.4 Hz), 7.37 (1H, s), 7.28–7.24 (2H, m), 3.48 (6H, s), 2.95 (2H, t, J = 6.0 Hz), 2.81 (2H, t, J = 6.0 Hz), 2.75 (2H, br-q, J_{H-B} = 83 Hz), 1.83–1.75 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.8, 136.9, 135.6, 132.3, 128.8, 127.5, 124.9, 123.5, 123.4, 116.1, 33.3, 31.2, 24.4, 23.2; ^{11}B NMR (192 MHz, $CDCl_3$): δ –27.9 (t, J_{B-H} = 83 Hz); IR (nujol, cm^{-1}): ν_{max} 2322, 1600, 1456, ; HRMS (DART+): calcd for $C_{19}H_{20}{}^{11}B^{35}Cl_2N_2$ $[M-H]^+$ 357.1097, found 357.1094. The first elution gave 1,2,3,4-tetrahydroanthracene (**4**) (6.7 mg, 18%). The third elution gave a mixture including a small amount of (4,5-dichloro-1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(6,7,8,9-tetrahydrobenzo[*a*]azulen-5-yl)dihydroborate.[13a]

The reaction of 1 with 1,3-bis(2,6-diiopropylphenyl)imidazol-2-ylidene borane (2g) (Table 2, entry 6). According to the general procedure A, a solution of **1** (36.1 mg, 0.20 mmol) and **2g** (160.2, mg, 0.40 mmol) in *t*BuOH (1 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1). The first elution gave a mixture of **4** (4.5 mg, 12%) and unreacted **1** (14.4 mg, 40%). Yields were calculated in the ^{1}H NMR spectrum of the isolated mixture. No borylated products were detected by ^{11}B NMR analysis of the crude product. The second elution gave unreacted **2g** (109.9 mg, 69%)

General procedure for the reaction between benzo[3,4]cyclodec-3-ene-1,5-diynes and borane reagents at 0.02 M (General procedure B). The reaction of 1 with 2a (Table 3, entry 2). A stirred solution of **1** (27.0 mg, 0.15 mmol) and **2a** (165.0 mg, 1.50 mmol) in $PhCF_3$ (7.5 mL) was heated for 168 h at 80 ˚C. After cooling to room temperature, the solvent was removed under reduced pressure. The resultant crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1) to give **3a** (16.8 mg, 38%) and **4** (14.4 mg, 53%). The third elution gave unreacted **2a** (124.0 mg, 75% recovery).

The reaction of 1 with 2c (Table 4, entry 2). According to the general procedure B, a solution of **1** (27.0 mg, 0.15 mmol) and **2c** (207.0, mg, 1.50 mmol) in $PhCF_3$ (7.5 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 3:1). The second elution gave (1,2,3,4-tetrahydroanthracen-9-yl)(1,3,4,5-tetramethyl-1*H*-imidazol-3-ium-2-yl)dihydro

borate (**3c**) (10.1 mg, 21%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (1H, d, J = 14.4 Hz), 7.63 (1H, dd, J = 7.8, 1.8 Hz), 7.35 (1H, s), 7.26–7.21 (2H, m), 3.78 (6H, s), 2.95 (2H, t, J = 6.0 Hz), 2.82 (2H, t, J = 6.0 Hz), 2.72 (2H, br-q, J_{H-B} = 87 Hz), 2.07 (6H, s), 1.80–1.75 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.7, 137.1, 135.4, 132.2, 129.2, 127.4, 124.3, 123.2, 123.1, 122.9, 32.1, 31.3, 31.0, 24.5, 23.3, 8.8; ^{11}B NMR (192 MHz, $CDCl_3$): δ –28.4 (t, J_{B-H} = 87 Hz); IR (neat, cm^{-1}): ν_{max} 2333, 2291, 1436; mp: 78.5–80 ºC; HRMS (DART+): calcd for $C_{21}H_{26}{}^{11}BN_2$ $[M-H]^+$ 317.2189, found 317.2191. The first elution gave **4** (15.8 mg, 58%). The third elution gave unreacted **2c** (61.7 mg, 30% recovery).

The reaction of 1 with 2d (Table 4, entry 3). According to the general procedure B, a solution of **1** (27.0 mg, 0.15 mmol) and **2d** (166.4 mg, 1.50 mmol) in $PhCF_3$ (7.5 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 3:1 to 2:1). The second elution gave give **3d** (17.5 mg, 40%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (1H, d, J = 8.0 Hz), 7.72 (1H, s), 7.64 (1H, dd, J = 6.8, 2.4 Hz), 7.38 (1H, s), 7.29–7.22 (2H, m), 6.70 (2H, s), 3.64 (3H, s), 3.40 (3H, s), 2.95 (2H, t, J = 6.0 Hz), 2.82 (2H, t, J = 6.0 Hz), 2.74 (2H, br-q, J_{H-B} = 87 Hz), 1.82–1.74 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 140.1, 137.1, 135.6, 132.2, 128.8, 127.5, 125.0, 123.5, 123.4, 38.0, 33.6, 31.3, 31.2, 24.4, 23.2; ^{11}B NMR (128 MHz, $CDCl_3$): δ –29.2 (t, J_{B-H} = 87 Hz); IR (nujol, cm^{-1}): ν_{max} 2322, 1462,; mp: 128–129 ºC; HRMS (DART+): calcd for $C_{18}H_{21}{}^{11}BN_3$ $[M-H]^+$ 290.1829, found 290.1836. The first elution gave **4** (14.0 mg, 51%). The third elution gave unreacted **2d** (111.8 mg, 67% recovery).

The reaction of 1 with 2e (Table 4, entry 4). According to the general procedure B, a solution of **1** (27.0 mg, 0.15 mmol) and **2e** (268.3, mg, 1.50 mmol) in $PhCF_3$ (7.5 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 20:1 to 10:1) to give **3e** (14.8 mg, 27%) and **4** (12.7 mg, 46%). The third elution gave unreacted **2e** (99.3 mg, 37% recovery).

The reaction of 4,5-dimethoxybenzo[3,4]cyclodec-3-ene-1,5-diyne (9) with 2a (Scheme 2). According to the general procedure B, a solution of **9** (36.1 mg, 0.15 mmol) and **2a** (165.0, mg, 1.50 mmol) in $PhCF_3$ (7.5 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1). The third elution gave (6,7-dimethoxy-1,2,3,4-tetrahydroanthracen-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl

)dihydroborate (**11**) (12.1 mg, 23%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (1H, s), 7.22 (1H, s), 6.96 (1H, s), 6.73 (2H, s), 3.96 (3H, s), 3.90 (3H, s), 3.47 (6H, s), 2.90 (2H, t, J = 6.0 Hz), 2.66 (2H, t, J = 6.0 Hz), 2.64 (2H, br-q, $J_{H–B}$ = 83 Hz), 1.76–1.73 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.6, 147.2, 137.8, 133.6, 132.6, 127.7, 123.1, 120.2, 108.6, 105.7, 55.5, 55.4, 35.9, 31.1, 30.7, 24.7, 23.4; ^{11}B NMR (192 MHz, $CDCl_3$): δ –28.8 (t, $J_{B–H}$ = 83 Hz); IR (nujol, cm^{-1}): ν_{max} 2316, 2276, 1465, 1244, 1149; mp: 183–185 ºC (gradually decomposed from 170 ºC); HRMS (DART+): calcd for $C_{21}H_{26}{}^{11}BN_2O_2$ $[M–H]^+$ 349.2087, found 349.2096. The first elution gave 6,7-dimethoxy-1,2,3,4-tetrahydroanthracene (**12**) (18.9 mg, 52%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (1H, s), 6.99 (1H, s), 3.96 (6H, s), 2.92–2.90 (4H, m), 1.86–1.83 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.9, 134.2, 127.7, 125.3, 105.4, 55.7, 29.6, 23.5; IR (nujol, cm^{-1}): ν_{max} 1512, 1259, 1151; mp: 177–179 ºC; HRMS (DART+): calcd for $C_{16}H_{19}O_2$ $[M+H]^+$ 243.1385, found 243.1388. The second elution gave unreacted **2a** (121.1 mg, 73% recovery).

The reaction of 4,5-difluorobenzo[3,4]cyclodec-3-ene-1,5-diyne (10) with 2a (Scheme 2). According to the general procedure B, a solution of **10** (32.4 mg, 0.15 mmol) and **2a** (165.0, mg, 1.50 mmol) in $PhCF_3$ (7.5 mL) was heated for 96 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1 to 1:1). The second elution gave (6,7-difluoro-1,2,3,4-tetrahydroanthracen-9-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**13**) (15.9 mg, 33%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (1H, dd, J = 15.0, 9.0 Hz), 7.31 (1H, d, J = 12.0, 9.0 Hz), 7.25 (1H, s), 6.74 (2H, s), 3.45 (6H, s), 2.90 (2H, t, J = 6.0 Hz), 2.70 (2H, t, J = 6.0 Hz), 2.63 (2H, br-q, $J_{H–B}$ = 83 Hz), 1.77–1.73 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.6 (dd, J = 246, 17.3 Hz), 148.3 (dd, $J_{C–F}$ = 242, 15.2 Hz), 133.9 (d, $J_{C–F}$ = 7.2 Hz), 128.8 (d, $J_{C–F}$ = 5.8 Hz), 123.7 (d, $J_{C–F}$ = 2.9 Hz), 115.0 (d, $J_{C–F}$ = 17.3 Hz), 112.0 (d, $J_{C–F}$ = 14.4 Hz), 35.9, 31.1, 30.8, 24.3, 23.1; ^{11}B NMR (192 MHz, $CDCl_3$): δ –28.7 (t, $J_{B–H}$ = 83 Hz); ^{19}F NMR (564 MHz, $CDCl_3$): δ –144.9, –145.8; IR (nujol, cm^{-1}): ν_{max} 2320, 2287, 1506, 1464,; mp: 110–112 ºC; HRMS (DART+): calcd for $C_{19}H_{20}{}^{11}BF_2N_2$ $[M–H]^+$ 325.1688, found 325.1684. The first elution gave 6,7-fluoro-1,2,3,4-tetrahydroanthracene (**14**) (13.9 mg, 42%) contaminated by a small amount of **10** (7%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (2H, s), 7.39 (2H, dd, J = 9.6 Hz), 2.94–2.92 (4H, m), 1.86–1.84 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.5 (dd, $J_{C–F}$ = 248, 17.0 Hz), 136.7, 128.6 (t, $J_{C–F}$ = 4.2 Hz), 126.0, 112.4 (dd, $J_{C–F}$ = 12.9, 4.4 Hz), 29.6, 23.2; ^{19}F NMR (564 MHz, $CDCl_3$): δ –141.3; IR (nujol, cm^{-1}): ν_{max} 1462, 1377; mp: 122.5–124 ºC; HRMS

(DART+): calcd for $C_{14}H_{13}F_2$ $[M+H]^+$ 219.0985, found 219.0987. The third elution gave unreacted **2a** (127.3 mg, 77% recovery).

The reaction of 1 with 1,3-dimethylimidazol-2-ylidene trifluoroboron (2g) (Scheme 3). According to the general procedure A, a solution of **1** (18.0 mg, 0.10 mmol) and **2g** (32.8, mg, 0.20 mmol) in *t*BuOH (1 mL) was heated for 168 h at 80 ˚C. After removal of the solvent, NMR analysis of the crude material showed that the reaction hardly proceeded, though the signal of a trace amount of **4** was detected.

The reaction of 1 with 2a in *t*BuOD (Scheme 4). According to the general procedure A, a solution of **1** (27.0 mg, 0.15 mmol) and **2a** (33.0 mg, 0.30 mmol) in *t*BuOD (0.75 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1). The second elution gave a mixture of **3a** and **3a**-$d_{1–2}$ having deuterium atom(s) on the NHC: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (1.4H, s, C4-H and/or C5-H of NHC); ^{2}H NMR (92 MHz, $CHCl_3$): δ 6.77 (br-s), 3.36 (br-s, <5% D, N-Me of NHC); MS (DART+): *m*/*z* 289 (100%), 290 (74%), 291 (33%). The first elution gave a mixture of **4** and 9-deuterio-1,2,3,4-tetrahydroanthracene (**4**-d_1) including a small amount of 3,3,8,8-tetradeuteriobenzo[3,4]cyclodec-3-ene-1,6-diyne (**19**-d_4). **4** and **4**-d_1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (1.55H, s, C9-H and C10-H); ^{2}H NMR (92 MHz, $CHCl_3$): δ 7.59 (br-s). **19**-d_4: ^{1}H NMR (400 MHz, $CDCl_3$): No signals at δ 3.29 and 2.60–2.58 ppm; ^{2}H NMR (92 MHz, $CHCl_3$): δ 3.29 (br-s), 2.60 (br-s). MS (DART+) of the mixture: *m*/*z* 183 (100%), 184 (58%), 185 (13%).

The reaction of 1 with 2c in *t*BuOD (Scheme 4). According to the general procedure A, a solution of **1** (27.0 mg, 0.15 mmol) and **2c** (41.4 mg, 0.30 mmol) in *t*BuOD (0.75 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1) to give a mixture of **4** and **4**-d_1 including a small amount of **19**-d_4. **4** and **4**-d_1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (1.4H, s, C9-H and C10-H); ^{2}H NMR (92 MHz, $CHCl_3$): δ 7.58 (br-s), 2.97 (br-s, <5% D, C1-H and C4-H). **19**-d_4: ^{1}H NMR (400 MHz, $CDCl_3$): No signals at δ 3.29 and 2.60–2.58 ppm; ^{2}H NMR (92 MHz, $CHCl_3$): δ 3.28 (br-s), 2.60 (br-s). MS (DART+) of the mixture: *m*/*z* 183 (62%), 184 (53%), 185 (15%).

The reaction of 1 with 2a in DMSO-d_6. According to the general procedure A, a solution of **1** (27.0 mg, 0.15 mmol) and **2a** (33.0 mg, 0.30 mmol) in DMSO-d_6 (0.75

mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1) to give a mixture of **4** and 9-deuterio-1,2,3,4-tetrahydroanthracene (**4**-d_1) including a small amount of 3,3,8,8-tetradeuteriobenzo[3,4]cyclodec-3-ene-1,6-diyne (**19**-d_4). **4** and **4**-d_1 (small amounts of deuterium atoms were incorporated on C1 and C4 probably because of a strong basicity of an anion generated from DMSO-d_6): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (1.50H, s, C9-H and C10-H), 3.00–2.92 (3.66H, m, C1-H and C4-H); ^{2}H NMR (92 MHz, $CHCl_3$): δ 7.59 (br-s), 2.97 (br-s, C1-H and C4-H). **19**-d_4: ^{1}H NMR (400 MHz, $CDCl_3$): No signals at δ 3.29 and 2.60–2.58 ppm; ^{2}H NMR (92 MHz, $CHCl_3$): δ 3.29 (br-s), 2.60 (br-s). MS (DART+) of the mixture: *m*/*z* 183 (61%), 184 (78%), 185 (40%). **3a** and **3a**-$d_{1–2}$ having deuterium atom(s) on the NHC was also detected, but the ratio of incorporated deuterium atoms showed a broad range (20–100% D) in a few trials.

The reaction of 1 with 2a-*d*$_3$ (90% D) in *t*BuOH (Scheme 5). According to the general procedure A, a solution of **1** (27.0 mg, 0.15 mmol) and **2a**-d_3 (90% D) (34.0 mg, 0.30 mmol) in *t*BuOH (0.75 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1). The second elution gave a mixture of **3a'** and **3a'**-d_1 contaminated by unreacted **2a**-d_3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (0.3H, s); ^{2}H NMR (92 MHz, $CHCl_3$): δ 7.41 (br-s), 2.75 (br-d, $J_{D–B}$ = 13.5 Hz); MS (DART+): *m*/*z* 290 (76%), 291 (100%). The first elution gave a mixture of **4**, **4**-d_1 and 9,10-dideuterio-1,2,3,4-tetrahydroanthracene (**4**-d_2) including a small amount of (5*E*,11*E*)-6,11-dideuterio-7,8,9,10-tetrahydrobenzo[10]annulene (**20**-d_2). **4**, **4**-d_1 and **4**-d_2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (1H, s, C9-H and C10-H); ^{2}H NMR (92 MHz, $CHCl_3$): δ 7.59 (br-s). **20**-d_2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.21 (4H, m) 6.45 (2H, s), 2.42–2.38 (4H, m), 1.82–1.77 (4H, m); ^{2}H NMR (92 MHz, $CHCl_3$): δ 5.71 (br-s). MS (DART+) of the mixture: *m*/*z* 183 (43%), 184 (100%), 185 (33%).

The reaction of 1 with 2a-*d*$_3$ (90% D) in benzene (Scheme 5). According to the general procedure A, a solution of **1** (27.0 mg, 0.15 mmol) and **2a-*d*$_3$** (90% D) (33.9 mg, 0.30 mmol) in benzene (0.75 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1). The second elution gave a mixture of (1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1,2,3,4-tetrahydroanthracen-9-yl)dideuteriobora te (**3a'**) and (1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(10-deuterio-1,2,3,4-tetrahydroanthracen-9-yl)di

deuterioborate (**3a'**-d_1): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (0.25H, s); ^{2}H NMR (92 MHz, $CHCl_3$): δ 7.40 (br-s), 2.73 (br-d, $J_{D–B}$ = 12.9 Hz); MS (DART+): *m*/*z* 290 (61%), 291 (100%). The first elution gave a mixture of **4**, **4**-d_1 and **4**-d_2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (0.6H, s, C9-H and C10-H); ^{2}H NMR (92 MHz, $CHCl_3$): δ 7.59 (br-s); MS (DART+): *m*/*z* 183 (42%), 184 (100%), 185 (96%).

The reaction of 1 with tetra-*n*-butylammonium cyanoborohydride (2h) (Scheme 7). According to the general procedure B, a solution of **1** (27.0 mg, 0.15 mmol) and **2h** (423.5 mg, 1.50 mmol) in $PhCF_3$ (7.5 mL) was heated for 168 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 2:1) to give **4** (13.5 mg, 49%). ^{11}B NMR analysis of the crude product showed no production of borylated compounds.

The reaction of 1 with 1,3-dimethylimidazol-2-ylidene cyanoborane (2i) (Scheme 7). According to the general procedure B, a solution of **1** (27.0 mg, 0.15 mmol) and **2i** (202.5 mg, 1.50 mmol) in $PhCF_3$ (7.5 mL) was heated for 240 h at 80 ˚C. The crude product was purified by flash chromatography on silica gel (*n*-hexane/EtOAc, 1:3). The second elution gave The second elution gave cyano(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1,2,3,4-tetrahydroanthracen-9-yl)hydrobo rate (**3i**) (10.1 mg, 21%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23 (1H, d, *J* = 9.0 Hz), 7.66 (1H, dd, *J* = 6.0, 2.4 Hz), 7.43 (1H, s), 7.30–7.26 (2H, m), 6.78 (2H, s), 3.62 (1H, br-q, $J_{H–B}$ = 87 Hz), 3.56 (6H, s), 3.10–3.05 (1H, m), 2.94 (2H, t, *J* = 6.0 Hz), 2.64–2.59 (1H, m), 1.84–1.72 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.6, 136.1, 135.9, 132.4, 127.73, 127.71, 126.4, 124.0, 123.8, 121.6, 36.7, 30.94, 30.88, 24.1, 22.9; ^{11}B NMR (192 MHz, $CDCl_3$): δ –28.8 (d, $J_{B–H}$ = 87 Hz); IR (neat, cm^{-1}): ν_{max} 2360, 2183, 1577; mp: 141−143 ºC; HRMS (DART+): calcd for $C_{20}H_{23}{}^{11}BN_3$ $[M+H]^+$ 316.1985, found 316.1992. The first elution gave a mixture of **4** (6.6 mg, 24%) and unreacted **1** (11.2 mg, 41%). Yields were calculated in the ^{1}H NMR spectrum of the isolated mixture.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: curran@pitt.edu (D.P.C), tsuyoshi@p.kanazawa-u.ac.jp (T.T)

ORCID

Dennis P. Curran: 0000-0001-9644-7728

Tsuyoshi Taniguchi: 0000-0002-4945-480X

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Crystal structures (CIF)

Copies of NMR spectra and ORTEP diagrams for crystal structures (PDF)

ACKNOWLEDGEMENTS

We are thankful to Dr. Tetsuo Fujie (Kanazawa University) for assistance in NMR analysis. This work was supported by MEXT/JSPS KAKENHI Grant-in-Aid for Scientific Research (C) (Grant No. 16K08159). D.P.C thanks the US National Science Foundation for support.

References

1. (a) *Reactive Intermediate Chemistry*; Moss, R. A.; Platz, M. S.; Jones, Jr., M., Eds; John Wiley & Sons, Inc: Hoboken, New Jersey, **2004**. (b) Singh, M. S. *Reactive Intermediates in Organic Chemistry: Structure, Mechanism, and Reactions*; Wiley-VCH: Weinheim, Germany, **2014**.
2. Selected reviews on aryne chemistry: (a) Pellissier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701-730. (b) Wenk, H. H.; Winkler, M.; Sander, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 502-528. (c) Yoshida, H.; Ohshita, J.; Kunai, A. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 199-219. (d) Tadross, P. M.; Stoltz, B. M. *Chem. Rev.* **2012**, *112*, 3550-3577. (e) Bhunia, A.; Yetra, S. R.; Biju, A. T. *Chem. Soc. Rev.* **2012**, *41*, 3140-3152. (f) Gampe, C. M.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3766-3778. (g) Dubrovskiy, A. V.; Markina, N. A.; Larock, R. C. *Org. Biomol. Chem.* **2013**, *11*, 191-218. (h) Goetz, A. E.; Shah, T. K.; Garg, N. K. *Chem. Commun.* **2015**, *51*, 34-45.
3. Mohamed, R. K.; Peterson, P. W.; Alabugin, I. V. *Chem. Rev.* **2013**, *113*, 7089-7129.

4. Darby N.; Kim, C. U.; Salaün, J. A.; Shelton, K. W.; Takada, S.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1971**, 1516-1517.
5. (a) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660-661. (b) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25-31. (c) Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082-4090.
6. Reviews: (a) Nicolaou, K. C.; Dai, W. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387−1416. (b) Nicolaou, K. C.; Smith, A. L. *Acc. Chem. Res.* **1992**, *25*, 497−503. (c) Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang, D. *Tetrahedron* **1996**, *52*, 6453−6518. A recent example: (d) Williams, D. E.; Bottriell, H.; Davies, J.; Tietjen, I.; Brockman, M. A.; Andersen, R. J. *Org. Lett.* **2015**, *17*, 5304-5307.
7. Kar, M.; Basak, A. *Chem. Rev.* **2007**, *107*, 2861-2890.
8. Representative examples: (a) Nicolaou, K. C.; Zuccarello, G.; Riemer, C.; Estevez, V. A.; Dai, W.-M. *J. Am. Chem. Soc.* **1992**, *114*, 7360−7371. (b) Semmelhack, M. F.; Neu, T.; Foubelo, F. *J. Org. Chem.* **1994**, *59*, 5038–5047. (c) Grissom, J. W.; Calkins, T. L.; McMillen, H. A.; Jiang, Y. *J. Org. Chem.* **1994**, *59*, 5833–5835. (d) Kaneko, T.; Takahashi, M.; Hirama, M. *Tetrahedron Lett.* **1999**, *40*, 2015–2018. (e) Basak, A.; Mandal, S.; Bag, S. S. *Chem. Rev.* **2003**, *103*, 4077–4094. (f) Pandithavidana, D. R.; Poloukhtine, A.; Popik, V. V. *J. Am. Chem. Soc.* **2009**, *131*, 351–356. (g) Doubleday, C.; Boguslav, M.; Howell, C.; Korotkin, S. D.; Shaked, D. *J. Am. Chem. Soc.* **2016**, *138*, 7476–7479. (h) Schuler, B.; Fatayer, S.; Mohn, F.; Moll, N.; Pavliček, N.; Meyer, G.; Peña, D.; Gross, L. *Nat. Chem.* **2016**, *8*, 220–224.
9. (a) Roberts, B. P. *Chem. Soc. Rev.* **1999**, *28*, 25-35. (b) Hioe, J.; Karton, A.; Martin, J. M. L.; Zipse, H. *Chem. Eur. J.* **2010**, *16*, 6861–6865. (c) Kawamoto, T.; Ryu, I. *Org. Biomol. Chem.* **2014**, *12*, 9733–9742.
10. Curran, D. P.; Solovyev, A.; Makhlouf Brahmi, M.; Fensterbank, L.; Malacria, M.; Lacôte, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 10294–10317.
11. (a) Pan, X.; Boussonnière, A.; Curran, D. P. *J. Am. Chem. Soc.* **2013**, *135*, 14433–14437. (b) Boussonnière, A.; Pan, X.; Geib, S. J.; Curran, D. P. *Organometallics* **2013**, *32*, 7445–7450.
12. Watanabe, T.; Curran, D. P.; Taniguchi, T. *Org. Lett.* **2015**, *17*, 3450–3453.
13. (a) Watanabe, T.; Hirose, D.; Curran, D. P.; Taniguchi, T. *Chem. Eur. J.* **2017**, *23*, 5404–5409. (b) Other examples of borylative radical cyclizations: Ren, S.-C.; Zhang, F.-L.; Qi, J.; Huang, Y.-S.; Xu, A.-Q.; Yan, H.-Y.; Wang, Y.-F. *J. Am. Chem. Soc.* **2017**, *139*, 6050–6053.
14. Solovyev, A.; Ueng, S.-H.; Monot, J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Curran. D. P. *Org. Lett.* **2010**, *12*, 2998–3001.

15. For the radical cage effect: Barry, J. T.; Berg, D. J.; Tyler, D. R. *J. Am. Chem. Soc.* **2016**, *138*, 9389–9392 and references therein.
16. Small amounts of inseparable impurities were often detected in ^{1}H NMR spectra of **4** obtained by reactions in polar solvents, and (5*Z*,11*Z*)-7,8,9,10-tetrahydrobenzo[10]annulene and benzo[3,4]cyclodec-3-ene-1,6-diyne were tentatively identified.
17. (a) Nishiyama, Y.; Terazima, M.; Kimura, Y. *Chem. Phys. Lett.* **2010**, *491*, 164–168. (b) Osawa, K.; Terazima, M.; Kimura, Y. *Chem. Phys. Lett.* **2013**, *564*, 21–25.
18. Taniguchi, T.; Curran, D. P. *Org. Lett.* **2012**, *14*, 4540–4543.
19. Hasegawa, E.; Ogawa, Y.; Kakinuma, K.; Tsuchida, H.; Tosaka, E.; Takizawa, S.; Muraoka, H.; Saikawa, T. *Tetrahedron* **2008**, *64*, 7724–7728.
20. Semmelhack and co-workers reported that the reaction of diyne **1** in the absence of 1,4-cyclohexadiene gave **4** in 11% yield.[8b]
21. Curran, D. P.; Boussonnière, A.; Geib, S. J.; Lacôte, E. *Angew. Chem., Int. Ed.* **2012**, *51*, 1602-1605.
22. (a) Perrin, C. L.; Rodgers, B. L.; O'Connor, J. M. *J. Am. Chem. Soc.* **2007**, *129*, 4795–4799. (b) Perrin, C. L.; Reyes-Rodríguez, G. J. *J. Am. Chem. Soc.* **2014**, *136* 15263–15269.
23. Horn, M.; Mayr, H.; Lacôte, E.; Merling, E.; Deaner, J.; Wells, S.; McFadden, T.; Curran, D. P., *Org. Lett.* **2012**, *14*, 82–85.
24. Schottelius, M. J.; Chen, P. *J. Am. Chem. Soc.* **1996**, *118*, 4896-4903.
25. Although β-elimination of tetra-*n*-butylammonium by aryl anion **24** cannot be ruled out, the reaction of **24** with generated Lewis acidic cyanoborane would be likely.
26. Kawamoto, T.; Geib, S. J.; Curran, D. P. *J. Am. Chem. Soc.* **2015**, *137*, 8617–8622.
27. CCDC 1567028, CCDC 1567029 and CCDC 1567030 contain the supplementary crystallographic data for these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
28. Walton, J. C.; Makhlouf Brahmi, M.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Chu, Q.; Ueng, S.-H.; Solovyev, A.; Curran, D. P. *J. Am. Chem. Soc.* **2010**, *132*, 2350–2358.
29. Ueng, S.-H.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. *Org. Lett.* **2010**, *12*, 3002–3005.
30. Kuhn, N.; Henkel, G.; Kratz, T.; Kreutzberg, J.; Boese, R.; Maulitz, A. H. *Chem. Ber.* **1993**, *126*, 2041−2045.

31. Solovyev, A.; Ueng, S.-H.; Monot, J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Curran, D. P. *Org. Lett.* **2010**, *12*, 2998−3001.
32. Gardner, S.; Kawamoto, T.; Curran, D. P. *J. Org. Chem.* **2015**, *80*, 9794−9797.