

Supporting Information

Arene extrusion as an approach to reductive elimination at boron: Implication of carbene-ligated haloborylene as a transient reactive intermediate

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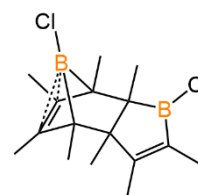
Synthetic details and characterization data

General considerations: all manipulations were performed in a Vacuum Atmospheres model MO-40M glovebox under an inert atmosphere of purified N₂ or using standard Schlenk techniques. All solvents were obtained anhydrous and oxygen-free by bubble degassing (argon) and purified by passing through columns of alumina and Q5.¹ Once collected, solvents were stored over activated 4 Å molecular sieves (20 wt%) inside the glovebox.² All glassware was oven-dried for at least 6 h prior to use, at temperatures greater than 150 °C. Deuterated solvents were purchased from Cambridge Isotope Labs and were degassed three times by the freeze-pump-thaw method and stored over activated 4 Å molecular sieves for 48 h in the glovebox prior to use. 4 Å molecular sieves (Millipore-Sigma) were dried by heating at 200 °C under dynamic vacuum for at least 48 h prior to use.

Cp₂Zr(C₄Me₄),³ (PhB(C₄Me₄))₂,⁴ EtCAAC,^{5, 6} CyCAAC,^{5, 6} and IMes,⁷ were prepared according to literature procedures. 2-Butyne was purchased from Millipore-Sigma and degassed by the freeze-pump-thaw method and stored over activated 4 Å molecular sieves for 48 h in the glovebox prior to use. Bis(triphenylphosphine)iminium chloride ([PPN]Cl) and tetramethylammonium fluoride ([TMA]F) were purchased from Millipore-Sigma and dried by heating at 120 °C under a dynamic vacuum for at least 6 h prior to use. Unless otherwise noted, all other chemicals were purchased commercially and used as received.

NMR spectra were obtained on Bruker Avance 400, Avance 401, Neo 402, Neo 500, and Neo 501 spectrometers. ¹H and ¹³C NMR spectra were referenced to residual CD₂Cl₂ (¹H = 5.32 ppm, ¹³C = 54.0 ppm) or C₆D₆ (¹H = 7.16 ppm, ¹³C = 128.06 ppm). HRMS were obtained on high-resolution JEOL AccuTOF 4G LC-plus equipped with an ionSense DART (Direct Analysis in Real Time) source. Elemental analyses were obtained on Thermo Scientific™ FlashSmart™ Elemental Analyzers. Samples were removed from the glovebox in sealed vials and briefly handled in air prior to data collection.

Synthesis of 1^{Cl}: to a pentane (250 mL) suspension of Cp₂Zr(C₄Me₄) (10.0 g, 30.3 mmol, 1 equiv), BCl₃ (1M in hexanes, 32 mL, 32 mmol, 1.06 equiv) was added dropwise at 25 °C. The color of the suspension immediately changed from red to brown. The suspension was stirred overnight at 25 °C and then filtered. The filtrate was concentrated to approx. 15 mL to obtain a dark brown solution. The solution was cooled at -35 °C and the product precipitated as brown crystalline solids (4.3 g, 92%).



¹H NMR (500 MHz, C₆D₆): 0.94 (s, 3H, CH₃), 1.00 (s, 3H, CH₃), 1.18 (s, 3H, CH₃), 1.28 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.50 (s, 3H, CH₃), 1.54 (s, 3H, CH₃). **¹¹B NMR** (161 MHz, C₆D₆): 3.38 (s, B-C(CH₃)-C(CH₃)=C), 66.23 (br. s, B-C(CH₃)=C(CH₃)-C). **¹³C{¹H} NMR** (126 MHz, C₆D₆): 11.23 (s, CH₃), 11.44 (s, CH₃), 11.75 (s, CH₃), 11.98 (s, CH₃), 14.99 (s, CH₃), 15.13 (s, CH₃), 18.08 (s, CH₃), 52.34 (br. s, B-C-CH₃), 53.10 (br. s,

B-C-CH₃), 66.48 (s, B-C(CH₃)=C(CH₃)-C), 129.49 (s, B-C(CH₃)-C(CH₃)=C), 132.20 (s, B-C(CH₃)-C(CH₃)=C), 183.62 (s, B-C(CH₃)=C(CH₃)-C). **HRMS** (m/z): [M+H]⁺ calcd. for C₁₆H₂₅B₂Cl₂, 309.15194; found 309.15171. **Elemental analysis**: calcd. for C₁₆H₂₄B₂Cl₂, C, 62.22; H, 7.83; found: C, 61.73; H, 7.89.

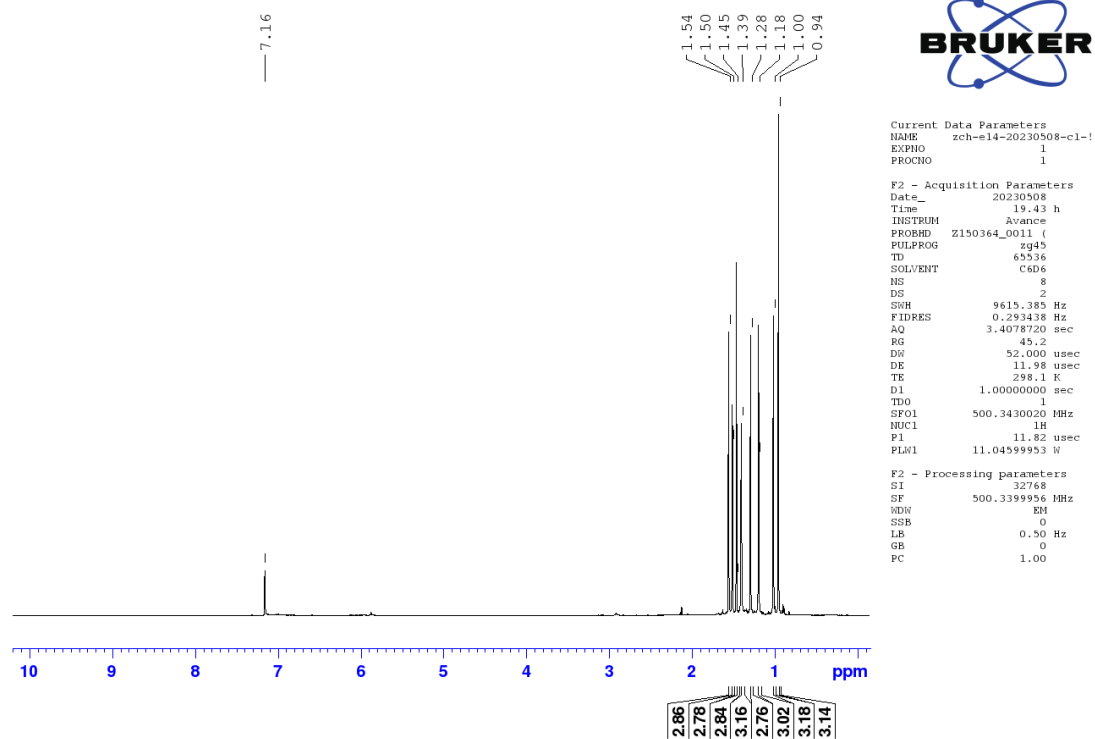


Figure S1. ¹H NMR spectrum of 1^{Cl} in C₆D₆

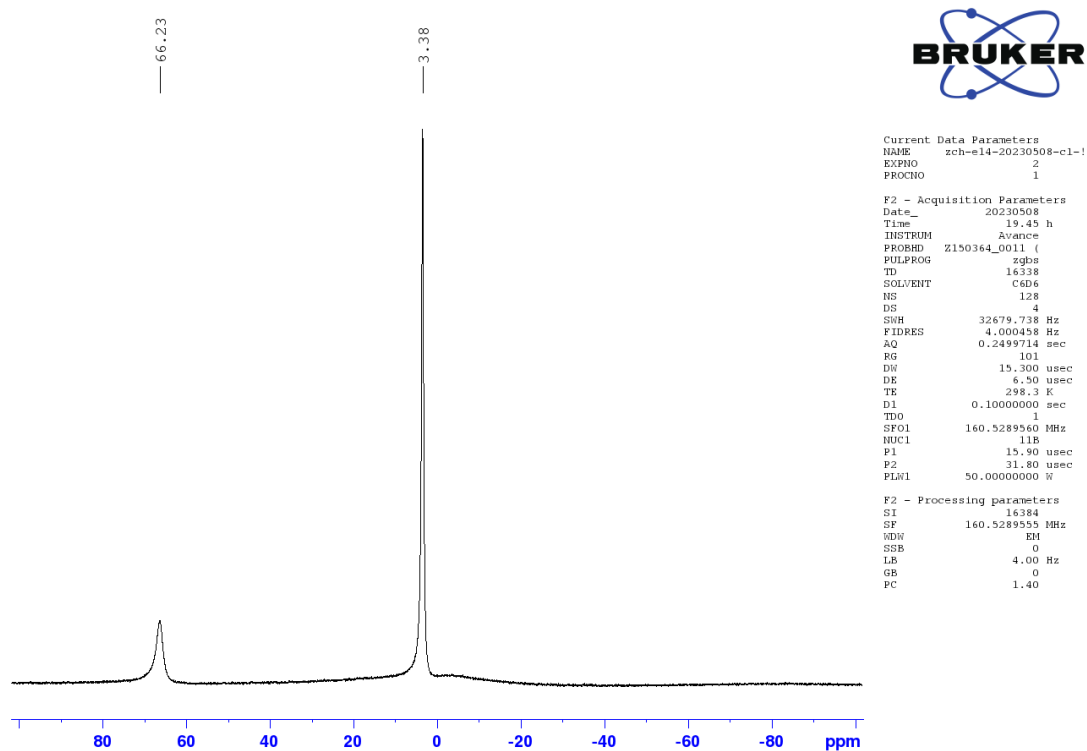


Figure S2. ¹¹B NMR spectrum of 1^{Cl} in C₆D₆

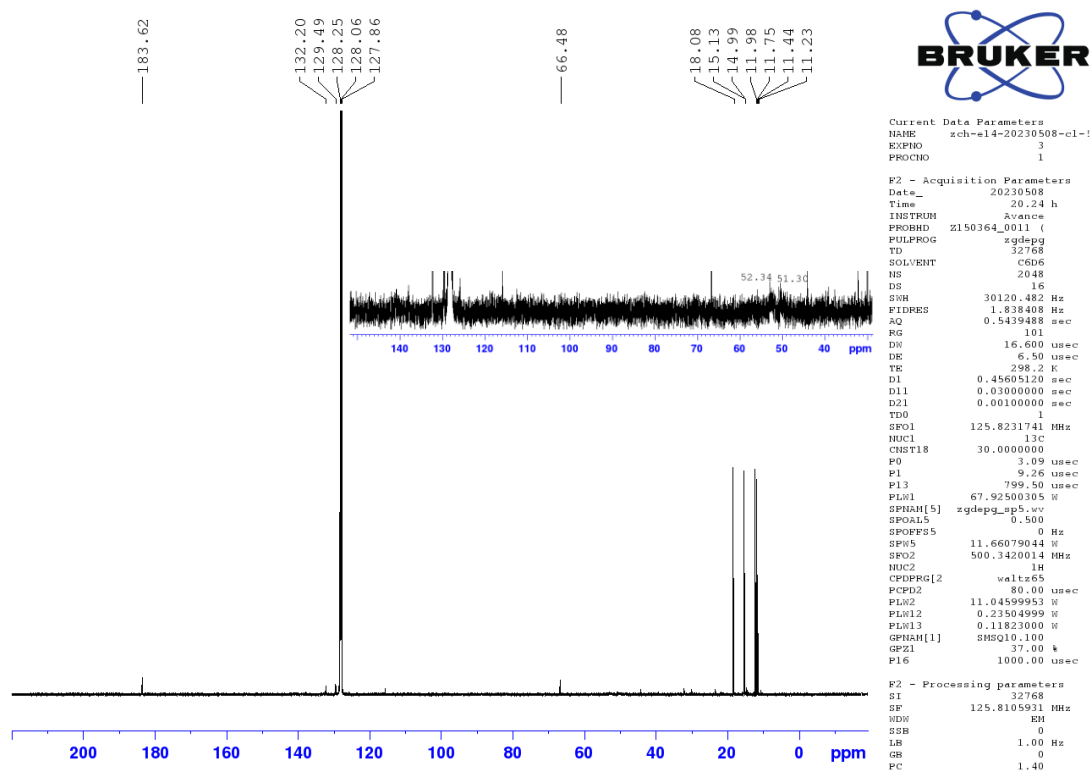
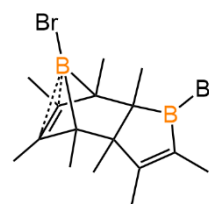


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1^{Cl} in C_6D_6

Synthesis of 1^{Br} : to a pentane (100 mL) suspension of $\text{Cp}_2\text{Zr}(\text{C}_4\text{Me}_4)$ (1.71 g, 5.2 mmol, 1.0 equiv), BBr_3 (1.37 g, 5.46 mmol, 1.05 equiv) was added dropwise at 25 °C. The color of the suspension immediately changed from red to light brown. The suspension was stirred overnight at 25 °C and then filtered. All volatiles in the red-brown filtrate were removed under reduced pressure to obtain a brown solid (872 mg, 84%). The purity of the crude product was acceptable based on the NMR spectra.



^1H NMR (500 MHz, C_6D_6): 0.93 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.59 (s, 3H, CH_3); ^{11}B NMR (161 MHz, C_6D_6): -3.90 (s, $\text{B}-\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{C}$), 67.62 (br. s, $\text{B}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{C}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): 11.96 (s, CH_3), 12.12 (s, CH_3), 12.37 (s, CH_3), 12.57 (s, CH_3), 12.84 (s, CH_3), 15.32 (s, CH_3), 15.45 (s, CH_3), 18.20 (s, CH_3), 51.25 (br. s, $\text{B}-\text{C}-\text{CH}_3$), 54.36 (br. s, $\text{B}-\text{C}-\text{CH}_3$), 68.02 (s, $\text{B}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{C}$), 130.85 (s, $\text{B}-\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{C}$), 142.47 (br. s, $\text{B}-\text{C}-\text{CH}_3$), 183.99 (s, $\text{B}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{C}$). HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{16}\text{H}_{25}\text{B}_2\text{Br}_2$, 397.05091; found 397.05166. **Elemental analysis:** calcd. for $\text{C}_{16}\text{H}_{24}\text{B}_2\text{Br}_2$, C, 48.31; H, 6.08; found: C, 48.11; H, 5.95.

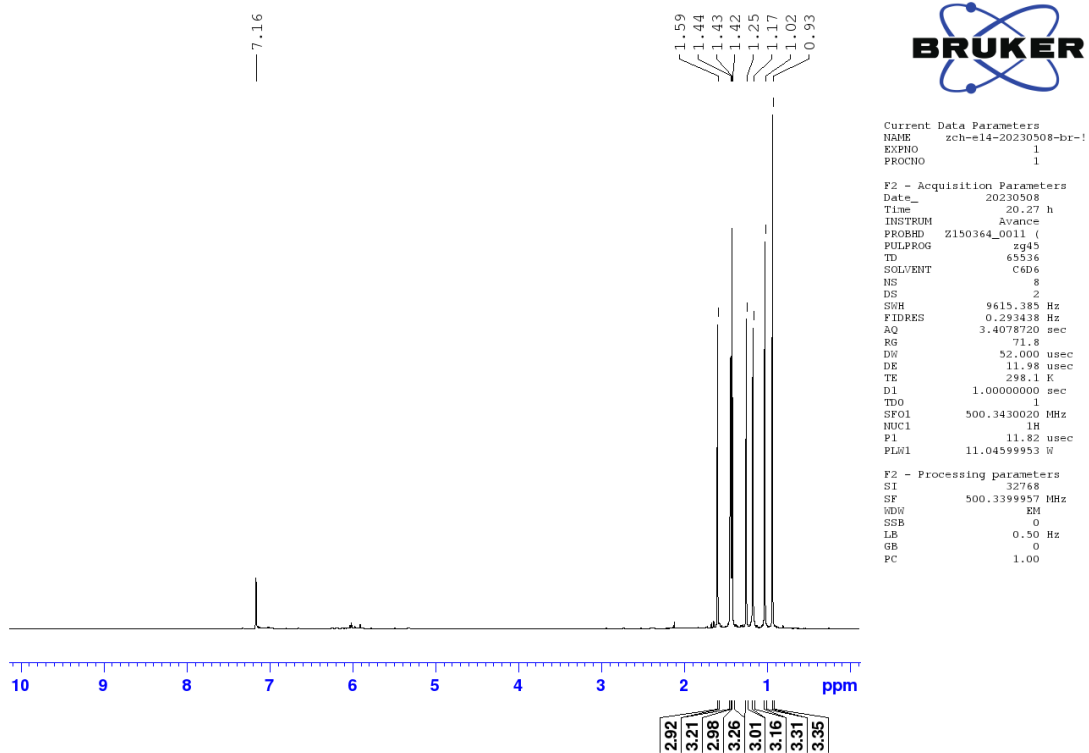


Figure S4. ^1H NMR spectrum of 1^{Br} in C_6D_6

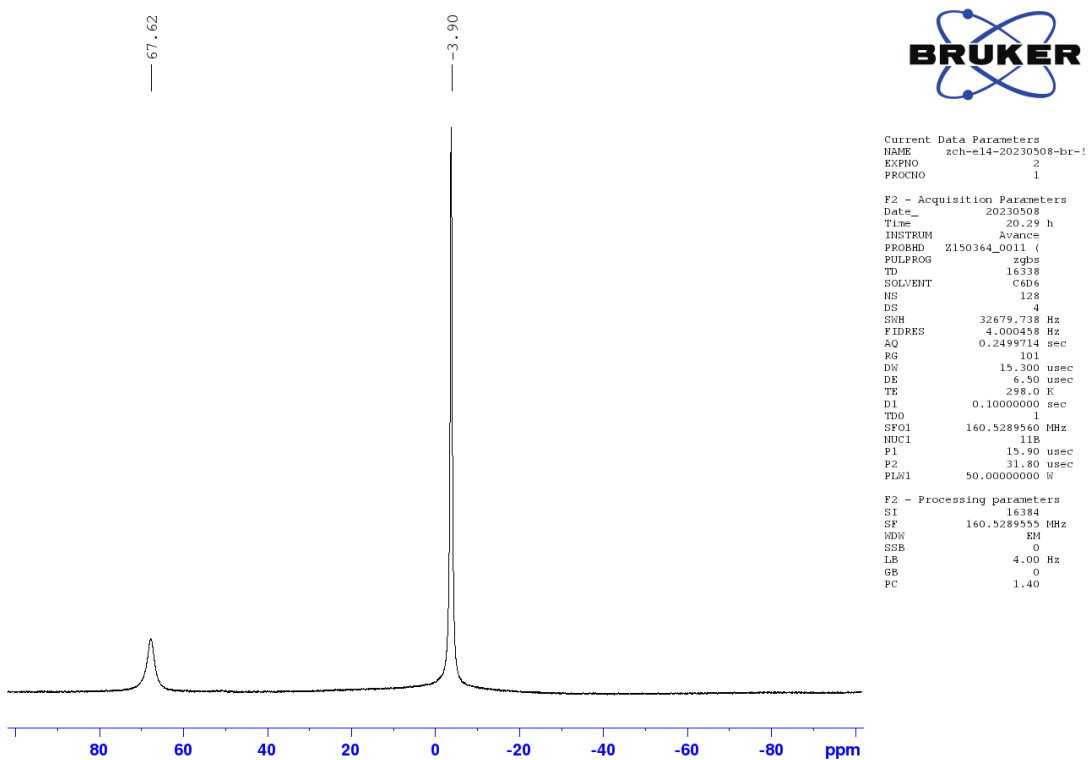


Figure S5. ^{11}B NMR spectrum of 1^{Br} in C_6D_6

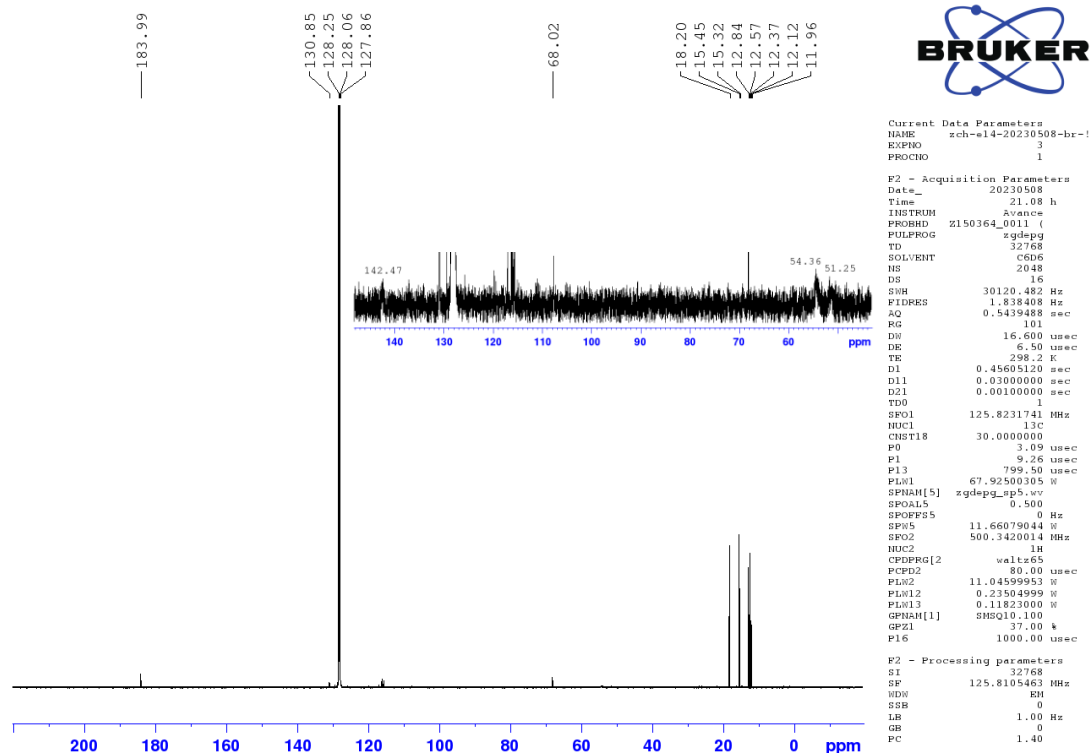
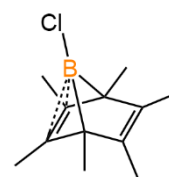


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1^{Br} in C_6D_6

Synthesis of 2^{Cl} : inside the glovebox, compound 1^{Cl} (730 mg, 2.36 mmol, 1.0 equiv) and 2-butyne (510 mg, 9.44 mmol, 4.0 equiv) were dissolved in toluene (7 mL) in a Schlenk flask. The flask was taken out of the glovebox and heated at 55 °C overnight to obtain an orange solution. The flask was then connected to a dynamic vacuum for approx. 10 mins to remove the remaining 2-butyne. The solution was heated at 70 °C for another 6 hours. All volatiles in the solution were removed under vacuum to obtain an orange oil (980 mg, 99%). The purity of the crude product was acceptable based on the NMR spectra.

^1H NMR (500 MHz, C_6D_6): 1.41 (s, 6H, CH_3), 1.52 (s, 12H, CH_3); ^{11}B NMR (161 MHz, C_6D_6): -7.50 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): 11.11 (s, C-CH_3), 11.64 (s, C-CH_3), 60.11 (br. s, B-C-CH_3), 126.95 (s, C=C). HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{12}\text{H}_{19}\text{BCl}$, 209.12683; found 209.12579. Elemental analysis: calcd. for $\text{C}_{12}\text{H}_{18}\text{BCl}$, C, 69.12; H, 8.70; found: C, 69.42; H, 8.75.



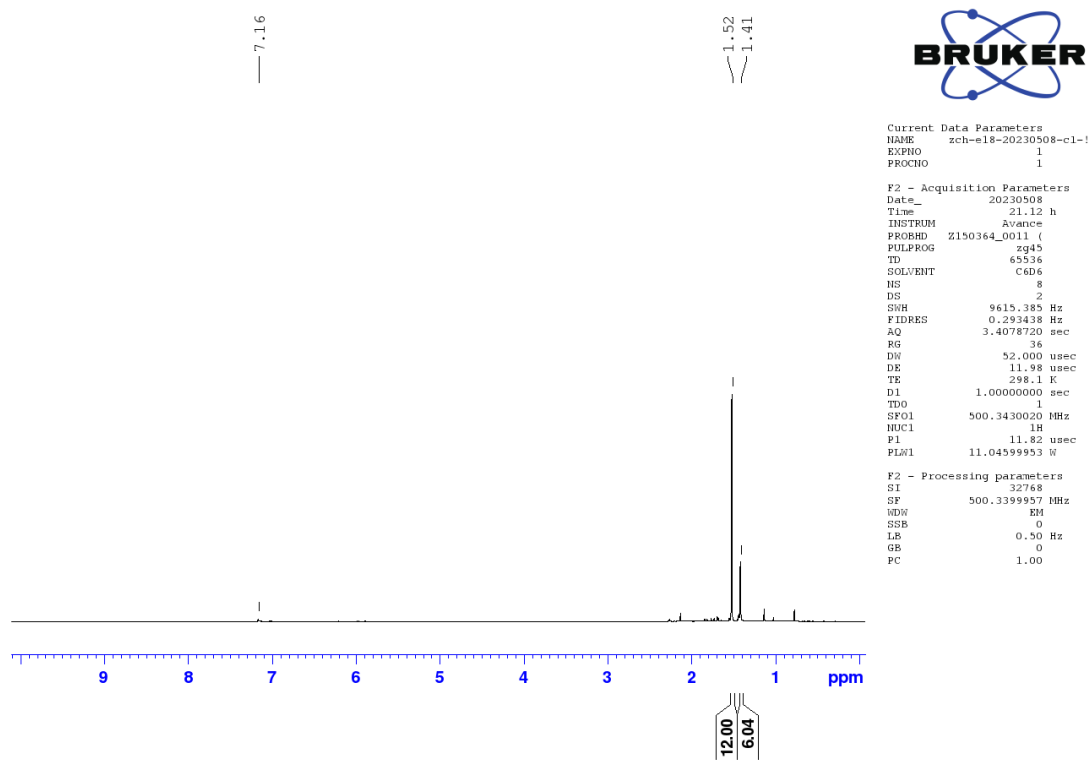


Figure S7. ^1H NMR spectrum of 2^{Cl} in C_6D_6

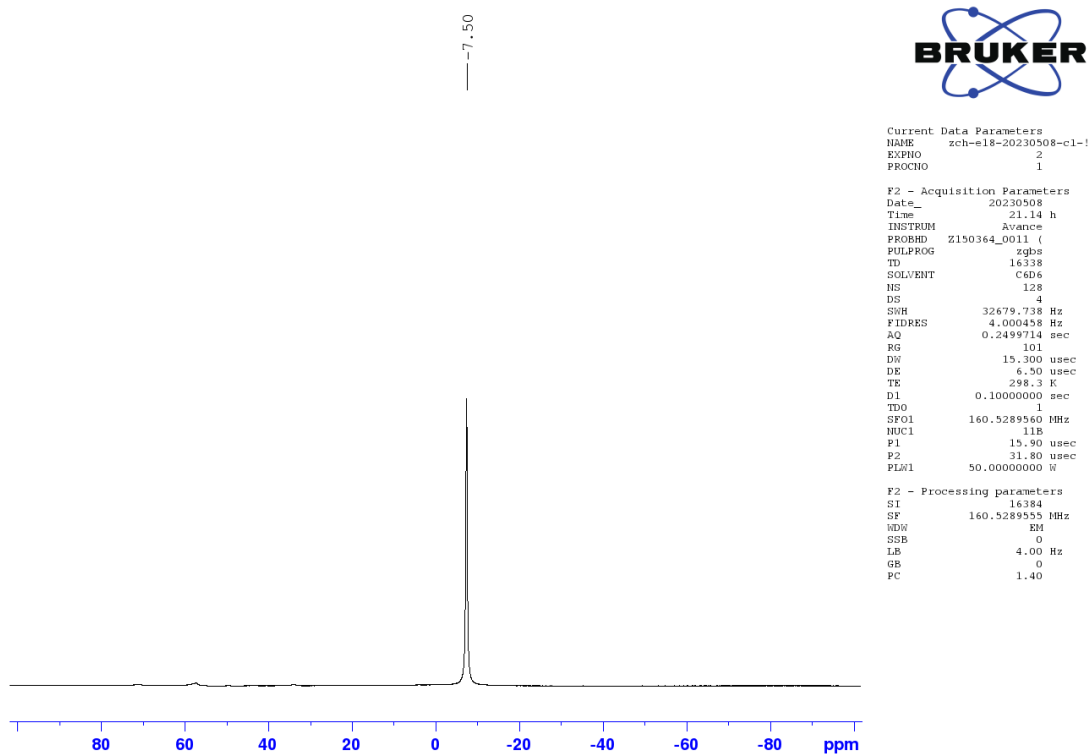


Figure S8. ^{11}B NMR spectrum of 2^{Cl} in C_6D_6

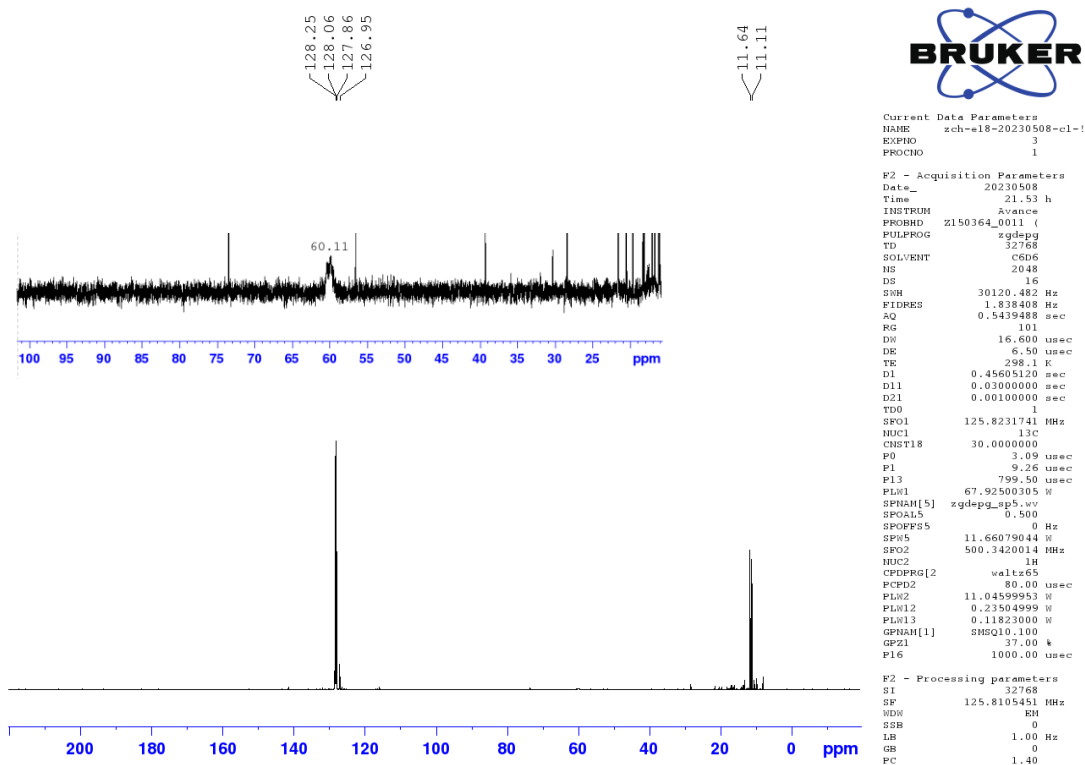
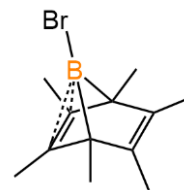
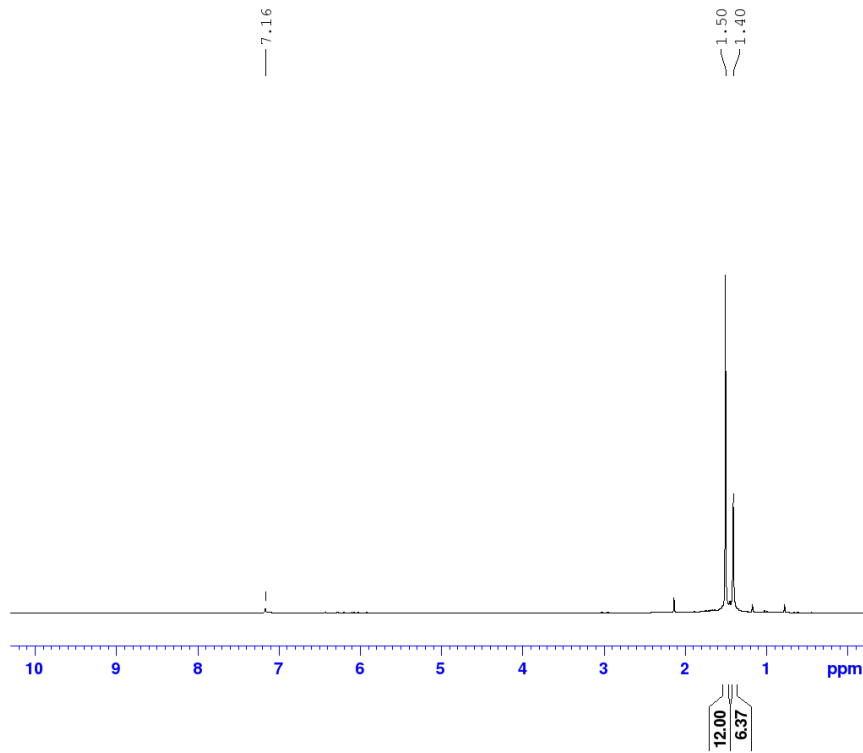


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2^{Cl} in C_6D_6

Synthesis of 2^{Br} : inside the glovebox, compound 1^{Br} (730 mg, 1.83 mmol, 1.0 equiv) and 2-butyne (395 mg, 7.32 mmol, 4.0 equiv) were dissolved in toluene (11 mL) in a Schlenk flask. The flask was taken out of the glovebox and heated at 60 °C for one day to obtain an orange solution. All volatiles in the solution were removed under vacuum to obtain an orange oil (907 mg, 98%). The purity of the crude product was acceptable based on the NMR spectra.



^1H NMR (500 MHz, C_6D_6): 1.40 (s, 6H, CH_3), 1.50 (s, 12H, CH_3); ^{11}B NMR (161 MHz, C_6D_6): -11.30 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): 11.84 (s, C-CH_3), 11.99 (s, C-CH_3), 60.77 (br. s, B-C-CH_3), 126.44 (s, C=C). **HRMS** (m/z): not detected. **Elemental analysis:** calcd. for $\text{C}_{12}\text{H}_{18}\text{BBr}$, C, 56.97; H, 7.17; found: C, 56.33; H, 7.13.

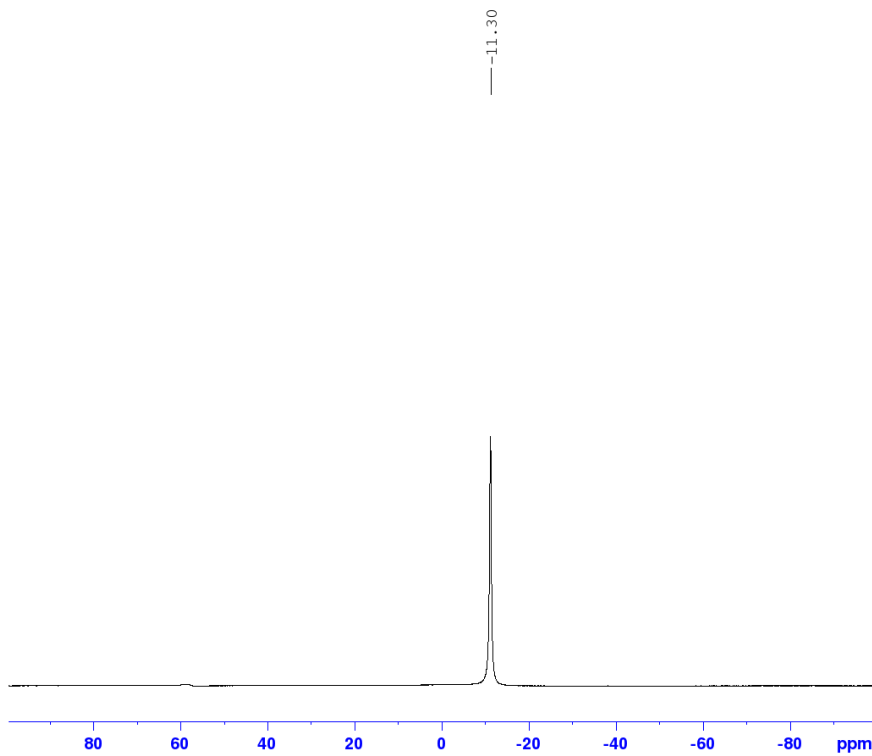


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Figure S10. ^1H NMR spectrum of 2^{Br} in C_6D_6



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Figure S11. ^{11}B NMR spectrum of 2^{Br} in C_6D_6

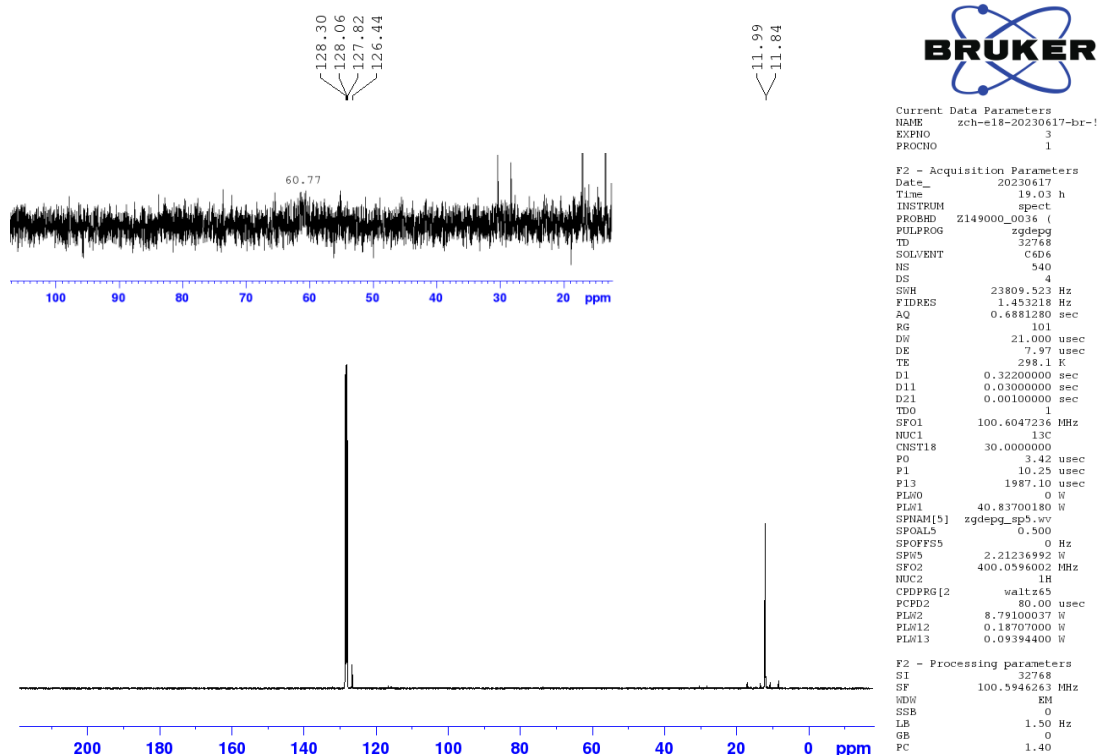
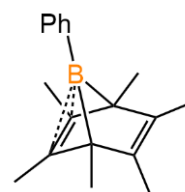
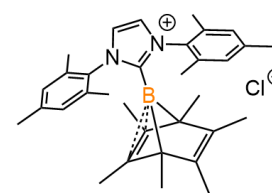


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2^{Br} in C_6D_6

Synthesis of 2^{Ph} : inside the glovebox, compound 1^{Ph} (600 mg, 1.53 mmol, 1.0 equiv) and 2-butyne (331 mg, 6.12 mmol, 4.0 equiv) were dissolved in toluene (20 mL) in a Schlenk flask. The flask was taken out of the glovebox and heated at 60 °C for one day to obtain a light brown solution. All volatiles in the solution were removed under vacuum to obtain an off-white solid. The solid was washed with hexanes (5 mL) and dried under vacuum to obtain the final product. A second crop of the product, a crystalline solid, was obtained by cooling the remaining hexanes solution at -35 °C (combined yield: 635 mg, 83%). The NMR spectra were in accordance with those in literature.⁴



Synthesis of 6: in a vial, a toluene (5 mL) solution of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (*i*Mes) (182 mg, 0.60 mmol, 1.0 equiv) was slowly added to a toluene (1 mL) solution of 2^{Cl} (125 mg, 0.60 mmol, 1.0 equiv). The solution was left to stand still overnight, and colorless crystalline solids gradually precipitated. The mother liquid was removed, and the remaining solids were dissolved in DCM (0.5 mL). Hexanes (0.5 mL) was slowly added to the DCM solution. The solution was then cooled at -35°C overnight to obtain colorless crystalline solids (67%, 206 mg).



^1H NMR (500 MHz, DCM): 0.95 (s, 6H, B-C- CH_3), 1.35 (s, 12H, B-C(CH_3)-C(CH_3)), 2.05 (s, 12H, $\text{C}^{\text{Mes}}\text{H}_3$), 2.39 (s, 6H, $\text{C}^{\text{Mes}}\text{H}_3$), 7.10 (s, 4H, $\text{C}^{\text{Mes}}\text{H}$), 7.80 (s, 2H, N- CH); ^{11}B NMR (161 MHz, DCM): -16.44 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DCM): 11.78 (s, $\text{C}^{\text{norbomadiene}}\text{CH}_3$), 12.98 (s, $\text{C}^{\text{norbomadiene}}\text{CH}_3$), 18.43 (s, *o*- $\text{C}^{\text{Mes}}\text{CH}_3$), 21.22 (s, *p*- $\text{C}^{\text{Mes}}\text{CH}_3$), 59.86 (br. s, B-

$\underline{C}(\text{CH}_3)$, 124.38 (s, *p*- $\underline{C}^{\text{Mes}}\text{CH}_3$), 126.35 (br. s, $\text{B}-\underline{C}(\text{CH}_3)-\underline{C}(\text{CH}_3)$), 127.54 (s, $\text{N}-\underline{\text{C}}\text{H}$), 130.29 (s, $\underline{C}^{\text{Mes}}\text{H}$), 135.17 (s, *m*- $\underline{C}^{\text{Mes}}\text{CH}_3$), 141.80 (s, *o*- $\underline{C}^{\text{Mes}}\text{CH}_3$). **HRMS** (*m/z*): $[\text{M}]^+$ calcd. for $\text{C}_{33}\text{H}_{42}\text{BN}_2$, 477.34410; found 477.34156. **Elemental analysis**: calc. for $\text{C}_{33}\text{H}_{42}\text{BN}_2\text{Cl}$ + 1.1 DCM, C, 67.54; H, 7.35; N, 4.62; found: C, 67.66; H, 7.40; N, 4.70.

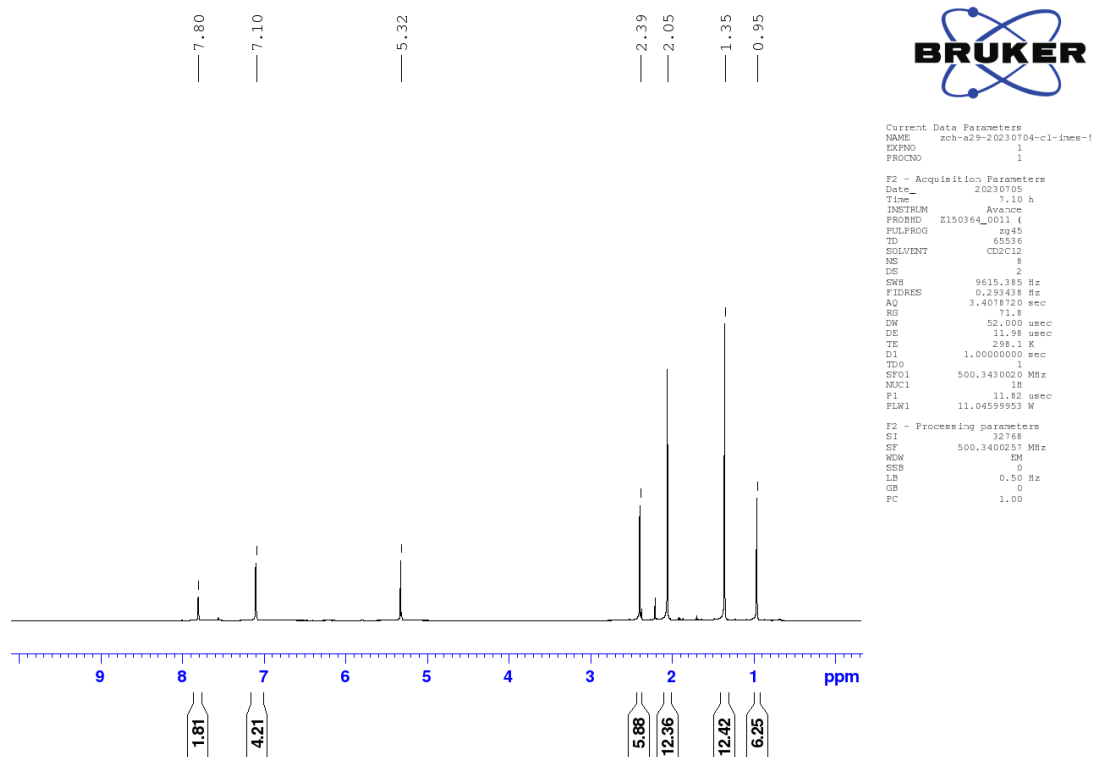


Figure S13. ^1H NMR spectrum of **6** in d_2 -DCM.

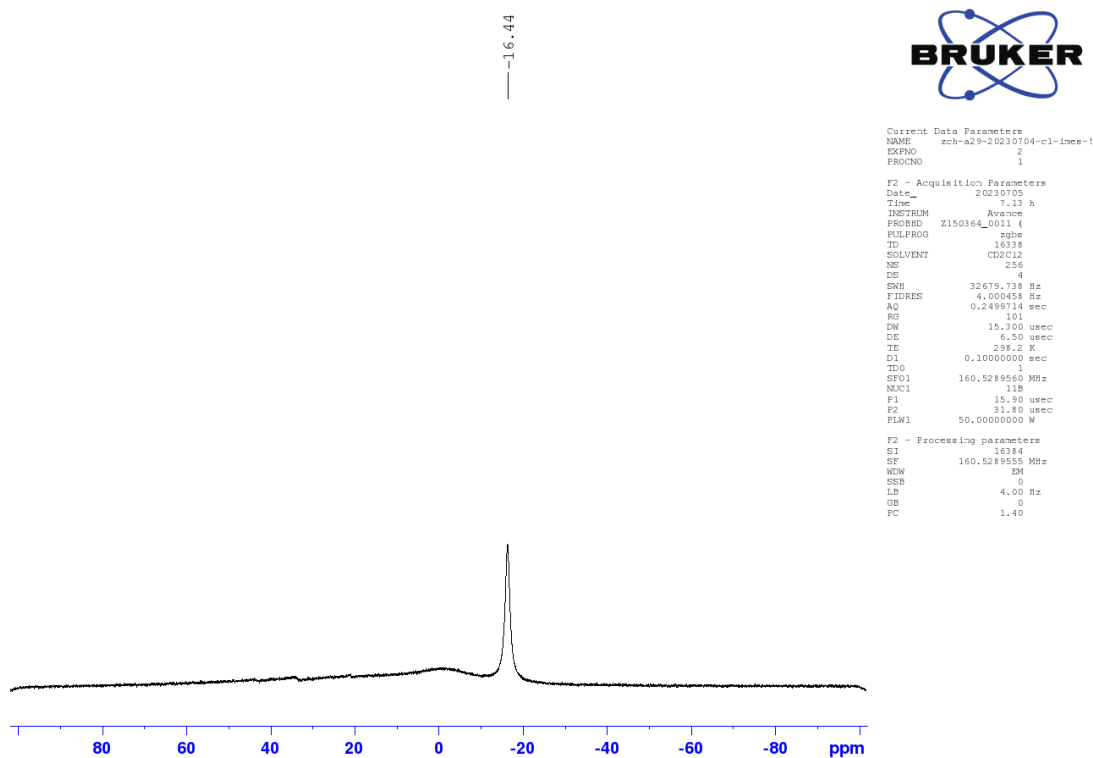


Figure S14. ^{11}B NMR spectrum of **6** in d_2 -DCM.

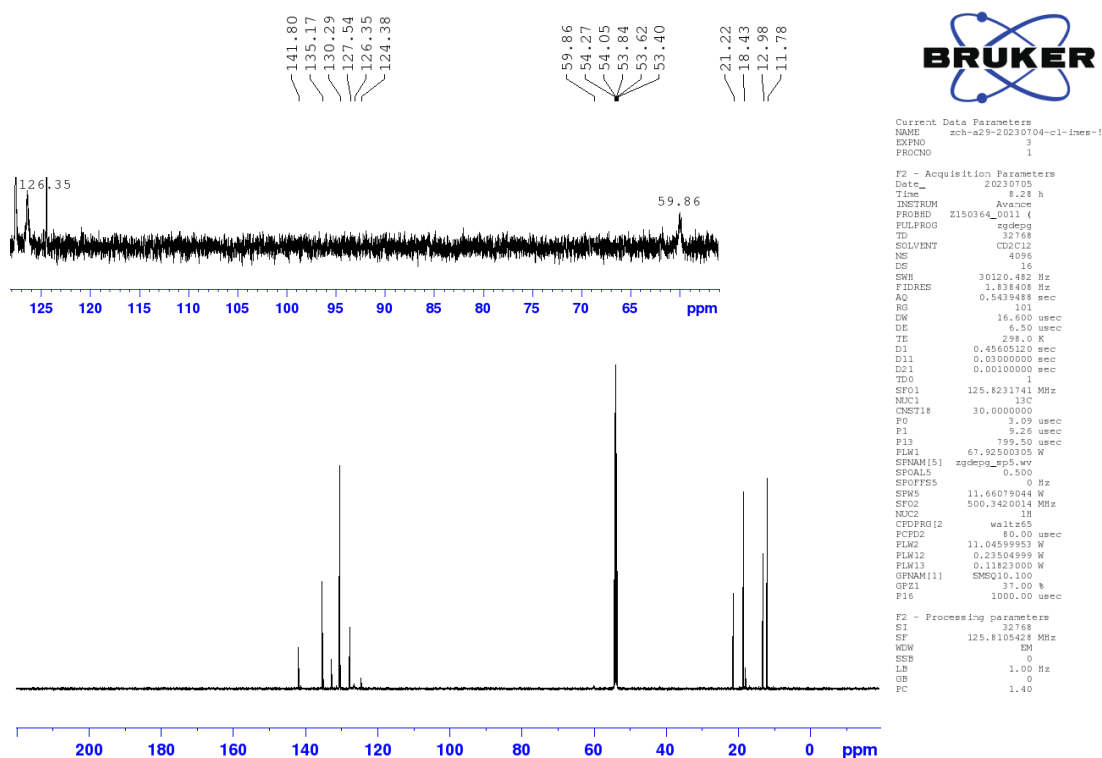
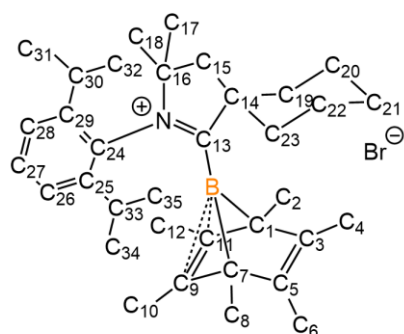
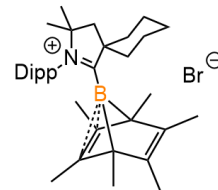


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** in d_2 -DCM.

Synthesis of 7: in a vial, a toluene (10 mL) solution of cyclic(alkyl)(amino) carbene CyCAAC (604 mg, 1.85 mmol, 1.0 equiv) was slowly added to a toluene (1 mL) solution of **2**^{Br} (468 mg, 1.85 mmol, 1.0 equiv). The solution was left to stand still overnight, and yellowish crystalline solids precipitated. The solids were separated from mother liquid by filtration. The solids were washed with toluene (2 mL) and dried under vacuum to afford the final product (56%, 601 mg).



^1H NMR (500 MHz, DCM): 1.00 (s, 6H, C_2H_3 and C_8H_3), 1.23 (d, $J = 6.6$, 6H, C_{32}H_3 and C_{35}H_3 , or C_{31}H_3 and C_{34}H_3), 1.32 (m, 1H, C_{21}H), 1.35 (d, $J = 6.6$, 6H, C_{32}H_3 and C_{35}H_3 , or C_{31}H_3 and C_{34}H_3), 1.35 (br. s, 6H, C_4H_3 and C_6H_3 , or C_{10}H_3 and C_{12}H_3), 1.51 (m, 2H, C_{20}H and C_{22}H), 1.58 (s, 6H, C_{17}H_2 and C_{18}H_2), 1.59 (m, 4H, C_{19}H_2 and C_{23}H_2), 1.86 (m, 1H, C_{21}H), 1.91 (m, 2H, C_{20}H and C_{22}H), 2.07 (br. s, 6H, C_4H_3 and C_6H_3 , or C_{10}H_3 and C_{12}H_3), 2.34 (s, 2H, C_{15}H_2), 2.54 (sept, $J = 6.6$, 2H, C_{30}H and C_{33}H), 7.35 (d, $J = 7.8$, 2H, C_{26}H and C_{28}H), 7.53 (t, $J = 7.8$, 1H, C_{27}); **^{11}B NMR** (161 MHz, DCM): -13.27 (s); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126

MHz, DCM): 12.60 (br. s, C₁₀ and C₁₂, or C₄ and C₆), 12.96 (s, C₂ and C₈), 14.11 (br. s, C₁₀ and C₁₂, or C₄ and C₆), 22.16 (s, C₂₀ and C₂₂), 24.90 (s, C₂₁), 24.14 (s, C₃₁ and C₃₄, or C₃₂ and C₃₅), 27.92 (s, C₃₁ and C₃₄, or C₃₂ and C₃₅), 29.44 (s, C₃₀ and C₃₃), 35.60 (s, C₁₉ and C₂₃), 35.65 (s, C₁₇ and C₁₈), 45.21 (s, C₁₅), 61.53 (br. s, C₁ and C₇), 61.68 (s, C₁₄), 84.26 (s, C₁₆), 125.52 (br. s, C₃ and C₅, or C₉ and C₁₁), 126.42 (s, C₂₇), 131.60 (s, C₂₆ and C₂₈), 131.61 (br. s, C₃ and C₅, or C₉ and C₁₁), 133.84 (s, C₂₅ and C₂₉), 145.91 (s, C₂₄), 209.70 (only observed by HMBC, C₁₃). (Some assignments of the peaks were accomplished by the assistance of 2D spectra) **HRMS** (m/z): [M]⁺ calcd. for C₃₅H₅₃BN, 498.42710; found 498.42844. **Elemental analysis**: calcd. for C₃₅H₅₃BNBr, C, 72.67; H, 9.23; N, 2.42; found, C, 72.83; H, 9.14; N, 2.28.

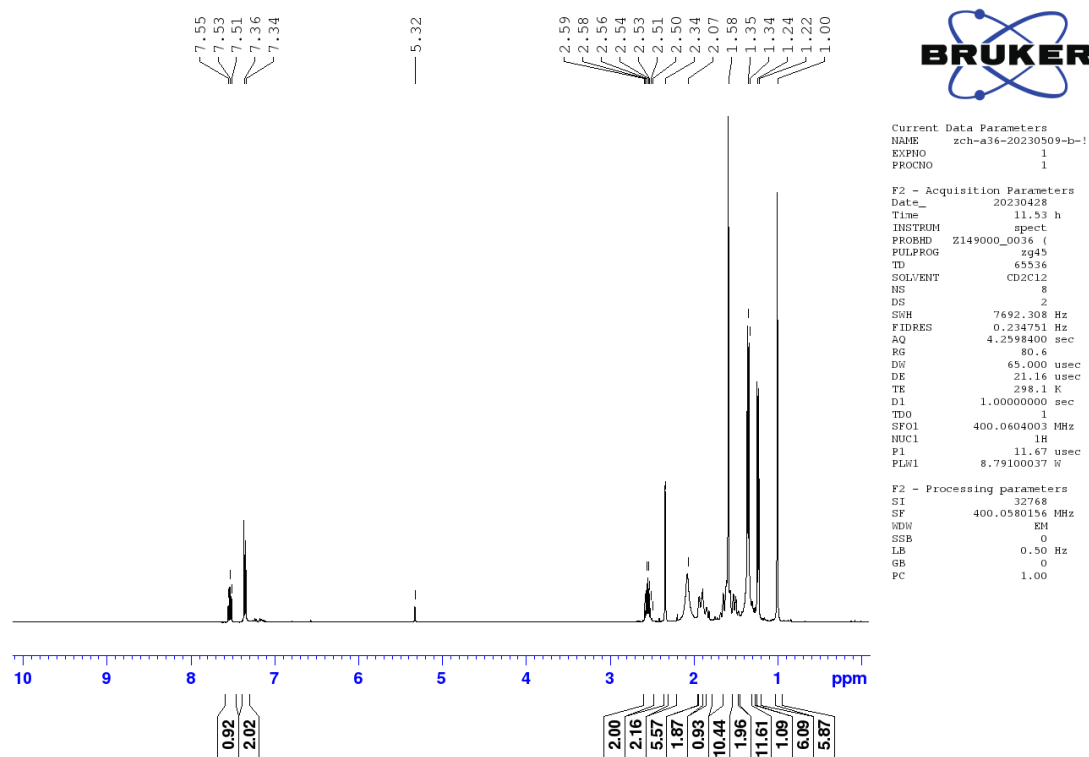
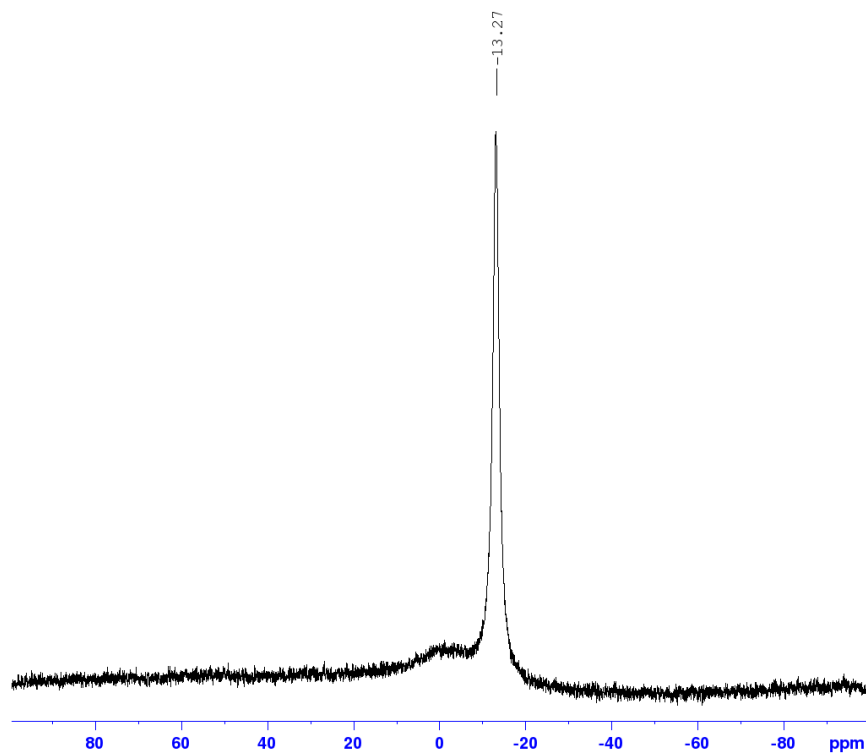


Figure S16. ¹H NMR spectrum of **7** in d₂-DCM.



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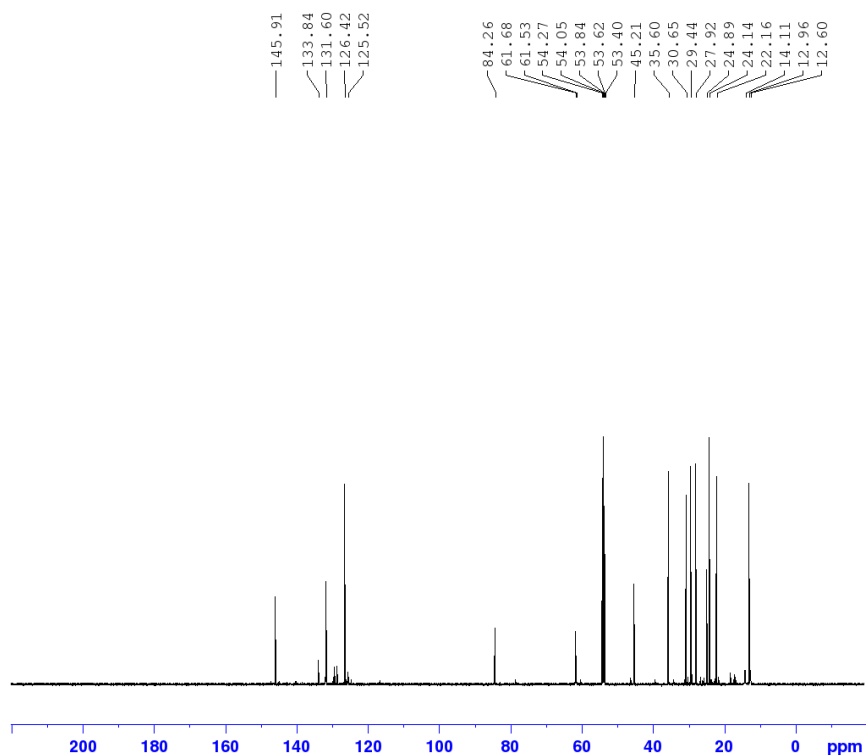
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P2         26.00 usec
PLN1      39.99399948 N

F2 - Processing parameters
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Figure S17. ^{11}B NMR spectrum of **7** in d_2 -DCM.



```

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PROCNO    1

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FIDRES    1.838408 Hz
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RG         101
DW         16.600 usec
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TE         298.1 K
D1         0.45605120 sec
D11        0.03000000 sec
D21        0.00100000 sec
TD0        1
SFO1      125.8231741 MHz
NUC1       13C
CHST18    30.0000000
P0         3.09 usec
P1         9.26 usec
P13        799.50 usec
PLN1      67.92500305 N
SPNAM[5]  zgpgpg_ap5.vv
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SFO2       500.3420014 MHz
NUC2        1H
CPDPRG[2] waltz65
PCPD2      80.00 usec
PLW2       11.04599953 N
PLW12      0.23504999 N
PLW13      0.11823000 N
GPNAM[1]   SMSQ10.100
GPZ1       37.00 k
P16        1000.00 usec

F2 - Processing parameters
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GB          0
PC          1.40

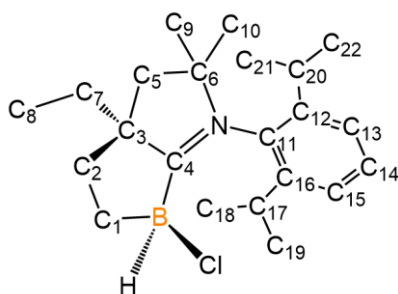
```

Figure S18. $^{13}\text{C}^8$ NMR spectrum of **7** in d_2 -DCM.

The reaction of 2^{Cl} with Et^{CAAC} : to a toluene (100 mL) solution of 2^{Cl} (505 mg, 2.42 mmol, 1.0 equiv), a toluene (20 mL) solution of Et^{CAAC} (1.22 g, 2.42 mmol, 1.0 equiv) was slowly added at 25 °C while stirring. The solution immediately turned orange and then gradually

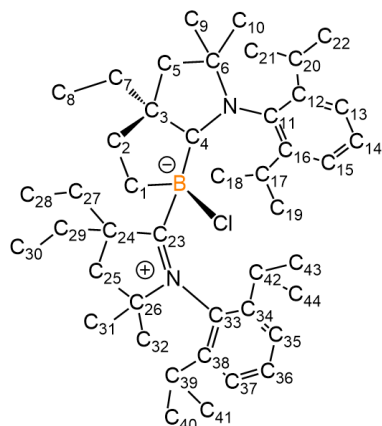
turned yellow. The solution was stirred overnight and then concentrated to approx. 20 mL. The concentrated solution was cooled at $-35\text{ }^{\circ}\text{C}$ for approx. 20 minutes and compound **3** was precipitated as white crystalline solids (59 mg, 6.8%). After compound **3** was isolated from the mother liquid by filtration, the solution was concentrated to approx. 10 mL and stored at $-35\text{ }^{\circ}\text{C}$ for 2 days. Compound **3**, **4**, and hexamethylbenzene precipitated as a mixture. The mother liquid was removed and the remaining solids were washed with hexanes (10 mL \times 2) and dried to afford compound **3** and **4** as a ratio of 1:1.4 (172 mg in total).

NMR yield determination: to a toluene (1 mL) solution of **2**^{Cl} (10.4 mg, 0.05 mmol, 1.0 equiv), a toluene (1 mL) solution of ^{Et}CAAC (15.7 mg, 0.05 mmol, 1.0 equiv) was slowly added at $25\text{ }^{\circ}\text{C}$ while stirring. The solution was stirred overnight. Acenaphthene (7.7 mg, 0.05 mmol, 1.0 equiv) was then added to the solution as an internal reference. All volatiles in the solution were removed under vacuum and the remaining solids were dissolved in deuterated DCM. The ¹H NMR spectrum suggested that the yield of **3**, **4** and C₆Me₆ were 37%, 24%, and 64%, respectively.



¹H NMR (500 MHz, C₆D₆): 0.76 (s, 3H, C₉H₃ and C₁₀H₃), 0.92 (t, $J = 7.3$, 3H, C₈H₃), 1.04 (s, 3H, C₉H₃ and C₁₀H₃), 1.07 (d, $J = 6.7$, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.13 (d, $J = 6.7$, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.22 (m, 1H, C₂H), 1.30 (d, $J = 6.7$, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.40 (d, $J = 13.2$, 1H, C₅H), 1.53 (d, $J = 6.7$, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.56 to 1.71 (m, 2H, C₁H₂), 1.76 (d, $J = 13.2$, 1H, C₅H), 1.83 (dq, $J = 14.3$, $J = 7.3$, 1H, C₇H), 2.38 (ddd, $J = 12.7$, $J = 8.8$, $J = 3.2$, 1H, C₂H), 2.46 (sept, $J = 6.7$, 1H, C₁₇H₃ or C₂₀H₃), 2.71 (dq, $J = 14.3$, $J = 7.3$, 1H, C₇H), 2.90 (sept, $J = 6.7$, 1H, C₁₇H₃ or C₂₀H₃), 3.08 (br. s, 1H, BH), 6.98 (dd, $J = 7.6$, $J = 1.3$, 1H, C₁₅H or C₁₃H), 7.03 (dd, $J = 7.9$, $J = 1.3$, 1H, C₁₅H or C₁₃H), 7.11 (t, $J = 7.7$, 1H, C₁₄H); **¹H{¹¹B} NMR** (400 MHz, C₆D₆): 0.76 (s, 3H, C₉H₃ and C₁₀H₃), 0.92 (t, $J = 7.3$, 3H, C₈H₃), 1.04 (s, 3H, C₉H₃ and C₁₀H₃), 1.07 (d, $J = 6.7$, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.13 (d, $J = 6.7$, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.22 (m, 1H, C₂H), 1.30 (d, $J = 6.7$, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.40 (d, $J = 13.2$, 1H, C₅H), 1.53 (d, $J = 6.7$, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.56 to 1.71 (m, 2H, C₁H₂), 1.76 (d, $J = 13.2$, 1H, C₅H), 1.83 (dq, $J = 14.3$, $J = 7.3$, 1H, C₇H), 2.38 (ddd, $J = 12.7$, $J = 8.8$, $J = 3.2$, 1H, C₂H), 2.46 (sept, $J = 6.7$, 1H, C₁₇H₃ or C₂₀H₃), 2.71 (dq, $J = 14.3$, $J = 7.3$, 1H, C₇H), 2.90 (sept, $J = 6.7$, 1H, C₁₇H₃ or C₂₀H₃), 3.08 (dd, $J = 8.6$, $J = 3.9$, 1H, BH), 6.98 (dd, $J = 7.6$, $J = 1.3$, 1H, C₁₅H or C₁₃H), 6.03 (dd, $J = 7.9$, $J = 1.3$, 1H, C₁₅H or C₁₃H), 7.11 (t, $J = 7.7$, 1H, C₁₄H). **¹¹B NMR** (161 MHz, C₆D₆): -10.87 (d, $J = 86.0$); **¹¹B{¹H} NMR** (161 MHz, C₆D₆): -10.87 (s); **¹³C{¹H} NMR** (126 MHz,

C₆D₆): 9.70 (s, C₈), 20.23 (br. s, C₁), 23.99 (s, C₁₈ or C₁₉ or C₂₁ or C₂₂), 24.36 (s, C₁₈ or C₁₉ or C₂₁ or C₂₂), 25.86 (s, C₁₈ or C₁₉ or C₂₁ or C₂₂), 26.99 (s, C₁₈ or C₁₉ or C₂₁ or C₂₂), 28.32 (s, C₉ or C₁₀), 28.83 (s, C₉ or C₁₀), 29.11 (s, C₁₇ or C₂₀), 29.16 (s, C₇), 29.81 (s, C₁₇ or C₂₀), 35.82 (s, C₂), 47.05 (s, C₅), 64.76 (s, C₃), 84.83 (s, C₆), 125.02 (s, C₁₃ or C₁₅), 125.36 (s, C₁₃ or C₁₅), 130.00 (s, C₁₄), 132.39 (s, C₁₁), 145.47 (s, C₁₂ or C₁₆), 145.58 (s, C₁₂ or C₁₆). (Some assignments of the peaks were accomplished by the assistance of 2D spectra)
HRMS (m/z): [M]⁺ calcd. for C₂₂H₃₅BCIN, 359.25511; found 359.25608. **Elemental analysis**: calcd. for C₂₂H₃₅BCIN, C, 73.44; H, 9.81; N, 3.89; found: C, 73.71; H, 9.64; N, 3.75.



¹H NMR (500 MHz, C₆D₆): 0.09 (m, 1H, C₁H), 0.21 (m, 1H, C₁H), 0.50 (t, *J* = 7.4, 3H, C₂₈H₃ or C₃₀H₃), 0.67 (s, 3H, C₉H₃ or C₁₀H₃), 0.74 (t, *J* = 7.5, 3H, C₂₈H₃ or C₃₀H₃), 0.75 (s, 3H, C₉H₃ or C₁₀H₃), 0.97 (m, 3H, C₈H₃), 0.98 (d, *J* = 6.6, 3H, C₄₀H₃ or C₄₁H₃ or C₄₃H₃ or C₄₄H₃), 1.05 (d, *J* = 6.6, 3H, C₄₀H₃ or C₄₁H₃ or C₄₃H₃ or C₄₄H₃), 1.17 (s, 3H, C₃₁H₃ or C₃₂H₃), 1.22 (s, 3H, C₃₁H₃ or C₃₂H₃), 1.24 (d, *J* = 6.6, 3H, C₄₀H₃ or C₄₁H₃ or C₄₃H₃ or C₄₄H₃), 1.25 (d, *J* = 6.7, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.39 (d, *J* = 6.8, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.40 (m, 1H, C₅H), 1.48 (m, 1H, C₅H), 1.51 (m, 2H, C₂₇H₂ or C₂₉H₂), 1.53 (d, *J* = 6.8, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.63 (d, *J* = 6.8, 3H, C₁₈H₃ or C₁₉H₃ or C₂₁H₃ or C₂₂H₃), 1.63 (d, *J* = 6.5, 3H, C₄₀H₃ or C₄₁H₃ or C₄₃H₃ or C₄₄H₃), 1.64 (m, 1H, C₇H), 1.70 (m, 1H, C₂H), 1.76 (m, 1H, C₇H), 1.78 (m, 1H, C₂₇H or C₂₉H), 1.90 (m, 1H, C₂₇H or C₂₉H), 1.99 (s, 2H, C₂₅H₂), 2.45 (sept., *J* = 6.6, 1H, C₃₉H₃ or C₄₂H₃), 2.73 (m, 1H, C₂H), 3.51 (sept., *J* = 6.5, 1H, C₃₉H₃ or C₄₂H₃), 3.56 (sept., *J* = 6.7, 1H, C₁₇H₃ or C₂₀H₃), 3.62 (s, 1H, C₄H), 5.02 (sept., *J* = 6.8, 1H, C₁₇H₃ or C₂₀H₃), 6.88 (dd, *J* = 7.1, *J* = 2.1, 1H, C₃₅H₃ or C₃₇H₃), 7.04 (m, 1H, C₃₅H₃ or C₃₆H₃ or C₃₇H₃), 7.06 (m, 1H, C₃₅H₃ or C₃₆H₃ or C₃₇H₃), 7.15 (m, 1H, C₁₃H₃ or C₁₄H₃ or C₁₅H₃), 7.19 (m, 1H, C₁₃H₃ or C₁₄H₃ or C₁₅H₃), 7.30 (m, 1H, C₁₃H₃ or C₁₄H₃ or C₁₅H₃); **¹¹B NMR** (161 MHz, C₆D₆): 2.95 (s); **¹³C{¹H} NMR** (126 MHz, C₆D₆): 10.84 (s, C₂₈ or C₃₀), 10.94 (s, C₂₈ or C₃₀), 11.17 (s, C₈), 22.43 (br. s, C₁), 23.69 (s, C₁₈ or C₁₉ or C₂₁ or C₂₂), 24.56 (s, C₁₈ or C₁₉ or C₂₁ or C₂₂), 25.13 (s, C₄₀ or C₄₁ or C₄₃ or C₄₄), 25.68 (s, C₄₀ or C₄₁ or C₄₃ or C₄₄), 26.36 (s, C₉ or C₁₀), 26.88 (s, C₄₀ or C₄₁ or C₄₃ or C₄₄), 27.25 (s, C₄₀ or C₄₁ or C₄₃ or C₄₄), 27.29 (s, C₁₇ or C₂₀), 27.57 (s, C₁₈ or C₁₉ or C₂₁ or C₂₂), 27.87 (s, C₁₈ or C₁₉ or C₂₁ or C₂₂), 28.20 (s, C₉ or C₁₀), 28.60 (s, C₃₉ or C₄₂), 28.81 (s, C₃₉ or C₄₂), 29.65 (s, C₁₇ or C₂₀), 30.41 (s, C₃₁ or C₃₂), 30.50 (s, C₃₁ or C₃₂), 32.73 (s, C₂₇ or C₂₉), 32.78 (s, C₂), 33.33 (s, C₇), 34.86 (s, C₂₇ or C₂₉), 42.43 (s, C₅), 56.14 (s, C₂₄), 56.34 (s, C₂₇ or C₂₉), 56.37 (s, C₃), 61.59 (s, C₂₆), 65.12 (s, C₆), 77.40 (br. s, C₄), 124.87 (s, C₃₅ or C₃₇),

124.93 (s, C₁₃ or C₁₄ or C₁₅), 125.18 (s, C₁₃ or C₁₄ or C₁₅), 125.31 (s, C₃₅ or C₃₆ or C₃₇), 126.61 (s, C₁₃ or C₁₄ or C₁₅), 129.85 (s, C₃₅ or C₃₆ or C₃₇), 136.52 (s, C₃₄ or C₃₈), 145 (s, C₃₄ or C₃₈), 146.42 (s, C₃₃), 149.28 (s, C₁₂ or C₁₆), 149.60 (s, C₁₁), 152.30 (s, C₁₂ or C₁₆).
 (Some assignments of the peaks were accomplished by the assistance of 2D spectra)
HRMS (m/z): [M+H]⁺ calcd. for C₄₄H₇₁BCIN₂, 673.53988; found 673.54293.

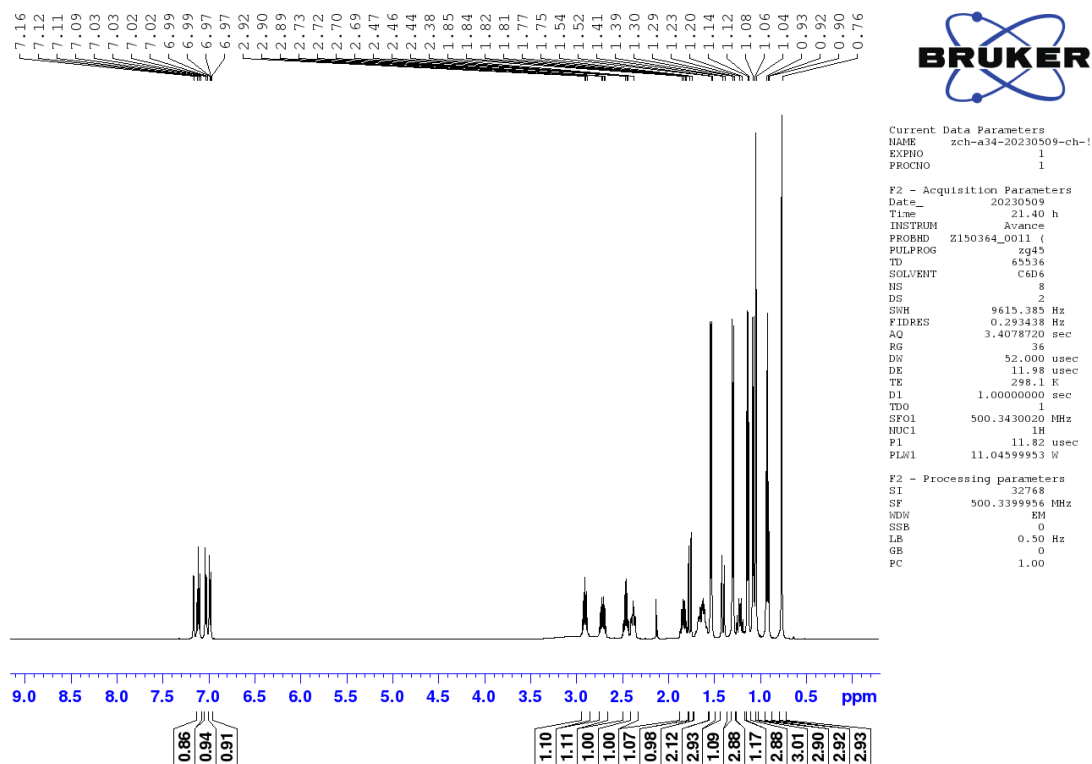


Figure S19. ¹H NMR spectrum of **3** in C₆D₆.

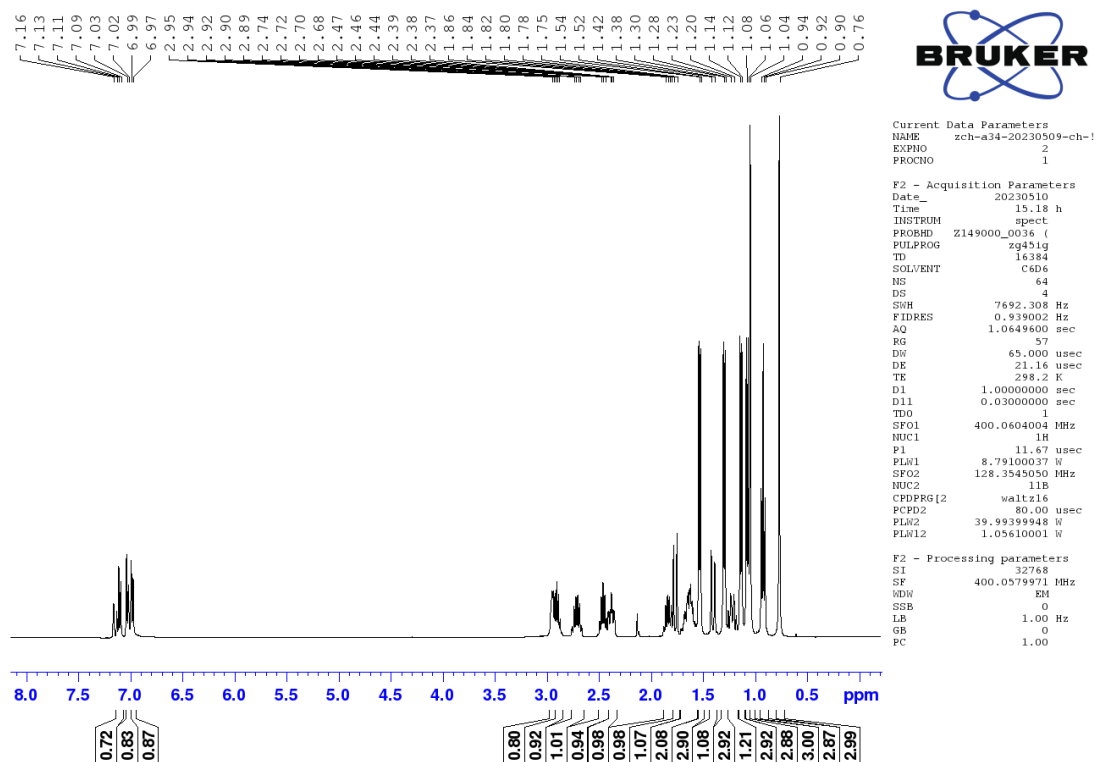


Figure S20. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **3** in C_6D_6 .

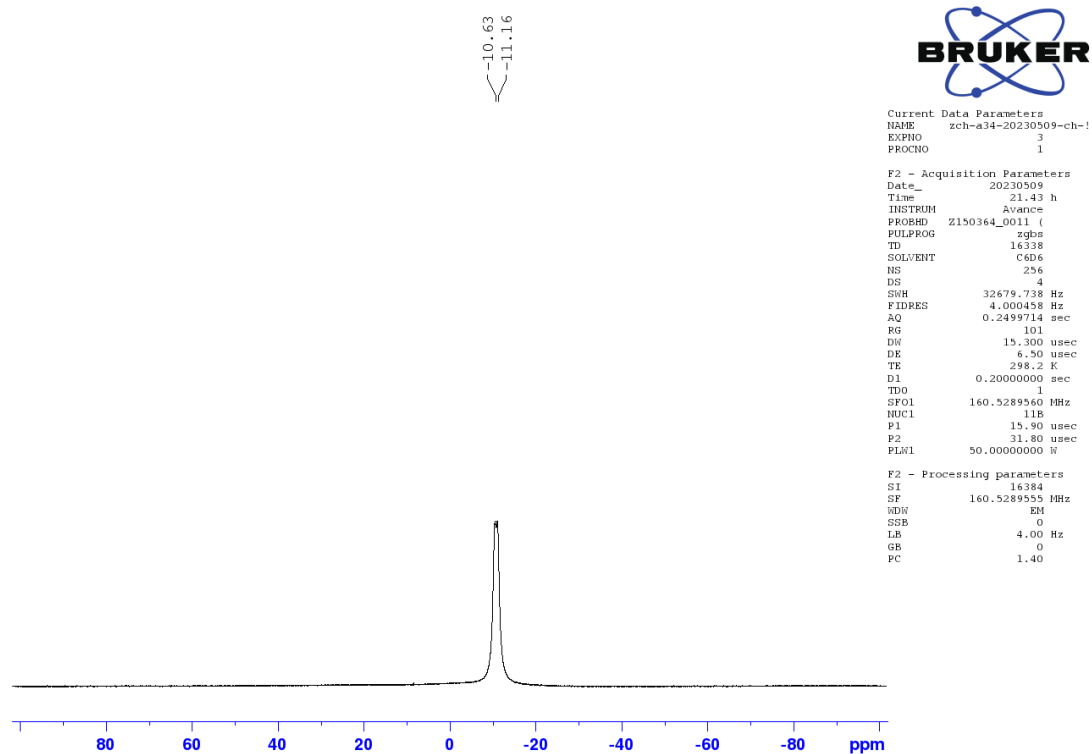
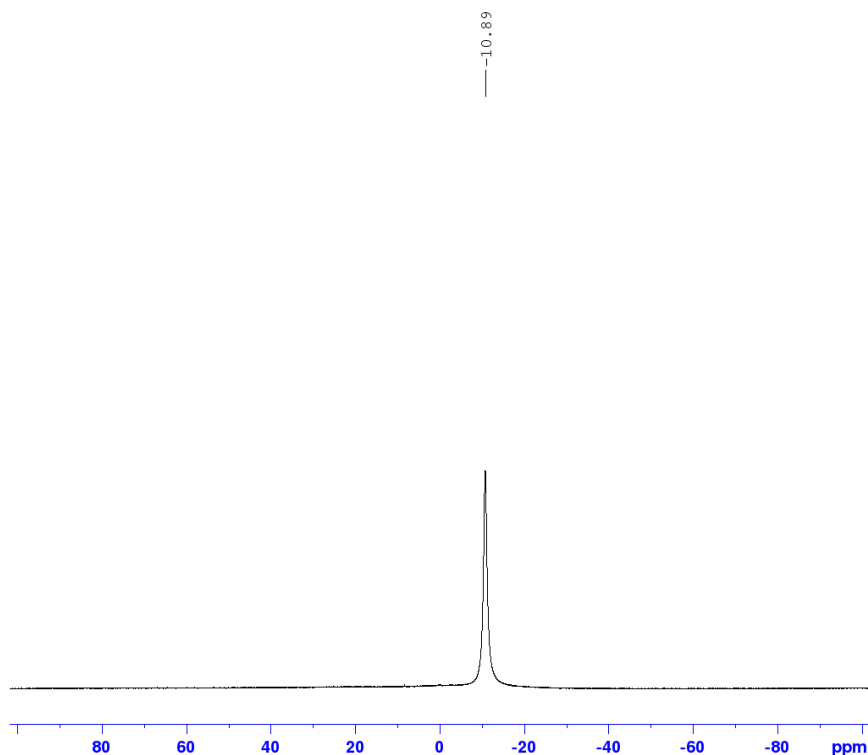


Figure S21. ^{11}B NMR spectrum of **3** in C_6D_6 .

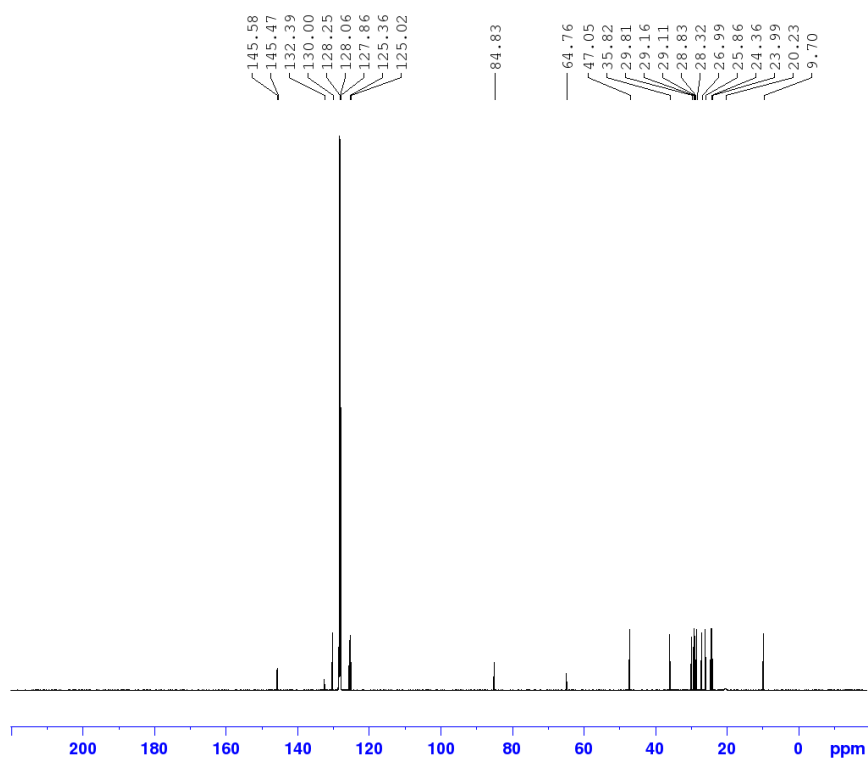


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 PULPROG zgpg3g
 TD 16338
 SOLVENT C6D6
 NS 256
 DS 4
 SNR 32679.738 Hz
 FIDRES 4.000458 Hz
 AQ 0.2499714 sec
 RG 101
 DW 15.300 usec
 DE 6.50 usec
 TE 298.1 K
 D1 0.20000000 sec
 D2 0 sec
 TDO 1
 SF01 160.5289560 MHz
 HUC1 11B
 P1 15.90 usec
 P2 31.80 usec
 PLW1 50.00000000 W
 SF02 500.3425000 MHz
 HUC2 1H
 CPDPRG[2] waltz64
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 PLW2 11.04599953 W
 PLW12 0.23504999 W

F2 - Processing parameters
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 SF 160.5289555 MHz
 WDW EM
 SSB 0
 LB 4.00 Hz
 GB 0
 PC 1.40

Figure S22. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3** in C_6D_6 .



Current Data Parameters
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 PROCNO 1

F2 - Acquisition Parameters
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 Time 22.25 h
 INSTRUM Avance
 PROBRD Z150364_0011 ((
 PULPROG zgpg3g
 TD 32768
 SOLVENT C6D6
 NS 2948
 DS 16
 SWH 30120.482 Hz
 FIDRES 1.838408 Hz
 AQ 0.5439488 sec
 RG 101
 DW 16.600 usec
 DE 6.50 usec
 TE 298.1 K
 D1 0.45605120 sec
 D11 0.03000000 sec
 D21 0.00100000 sec
 TDO 1
 SF01 125.8231741 MHz
 HUC1 13C
 CHST18 30.0000000
 P0 3.09 usec
 P1 9.26 usec
 P13 799.50 usec
 PLW1 67.92500305 W
 SPNAM[5] zgpg3g_sp5.vv
 SPOAL5 0.500
 SPOFF5 0 Hz
 SPW5 11.66079044 W
 SF02 500.3420014 MHz
 HUC2 1H
 CPDPRG[2] waltz65
 PCPD2 80.00 usec
 PLW2 11.04599953 W
 PLW12 0.23504999 W
 PLW13 0.11823000 W
 GPHAM[1] SHSQ10.100
 GPZ1 37.00 k
 F16 1000.00 usec

F2 - Processing parameters
 SI 32768
 SF 125.8105465 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in C_6D_6 .

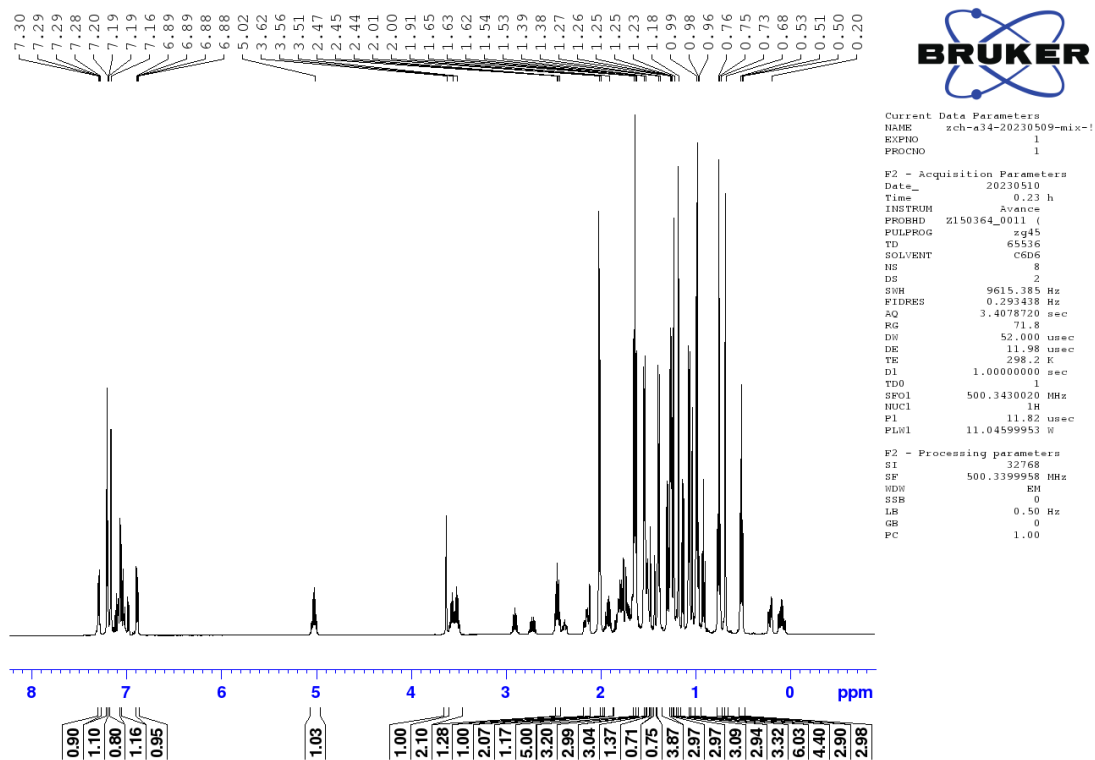


Figure S24. ^1H NMR spectrum of mixed **3** and **4** in C_6D_6 . Only the signals belonging to **4** were labeled and integrated.

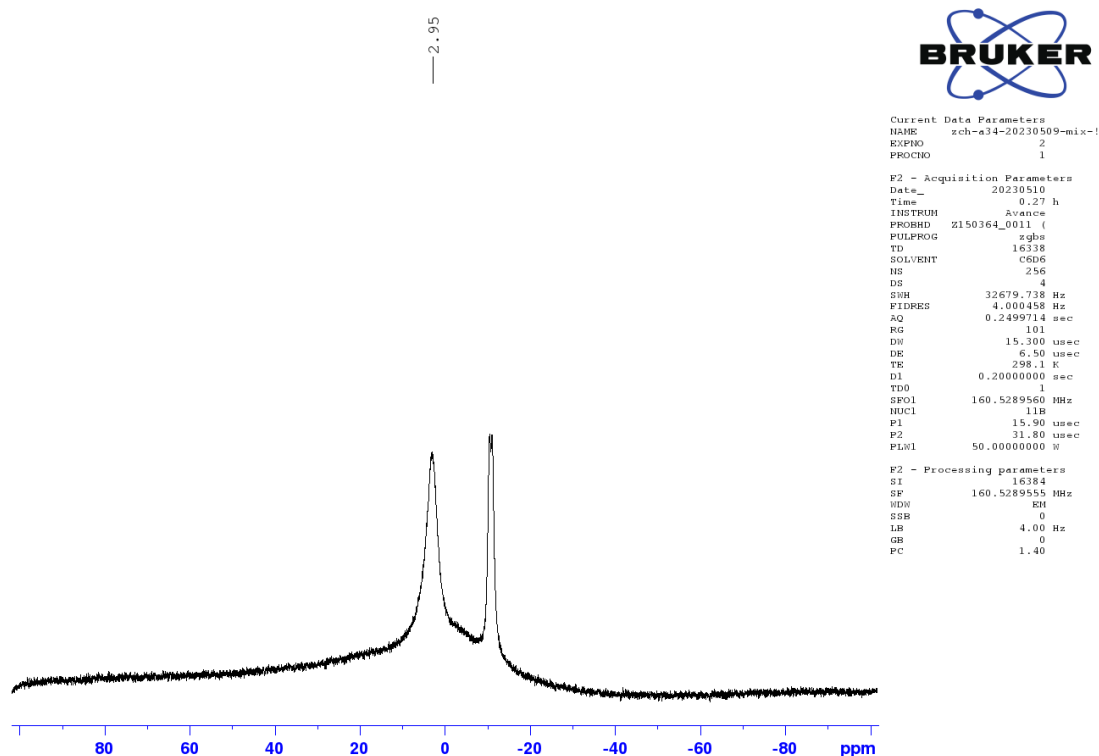


Figure S25. ^{11}B NMR spectrum of mixed **3** and **4** in C_6D_6 . Only the signals belonging to **4** were labeled.

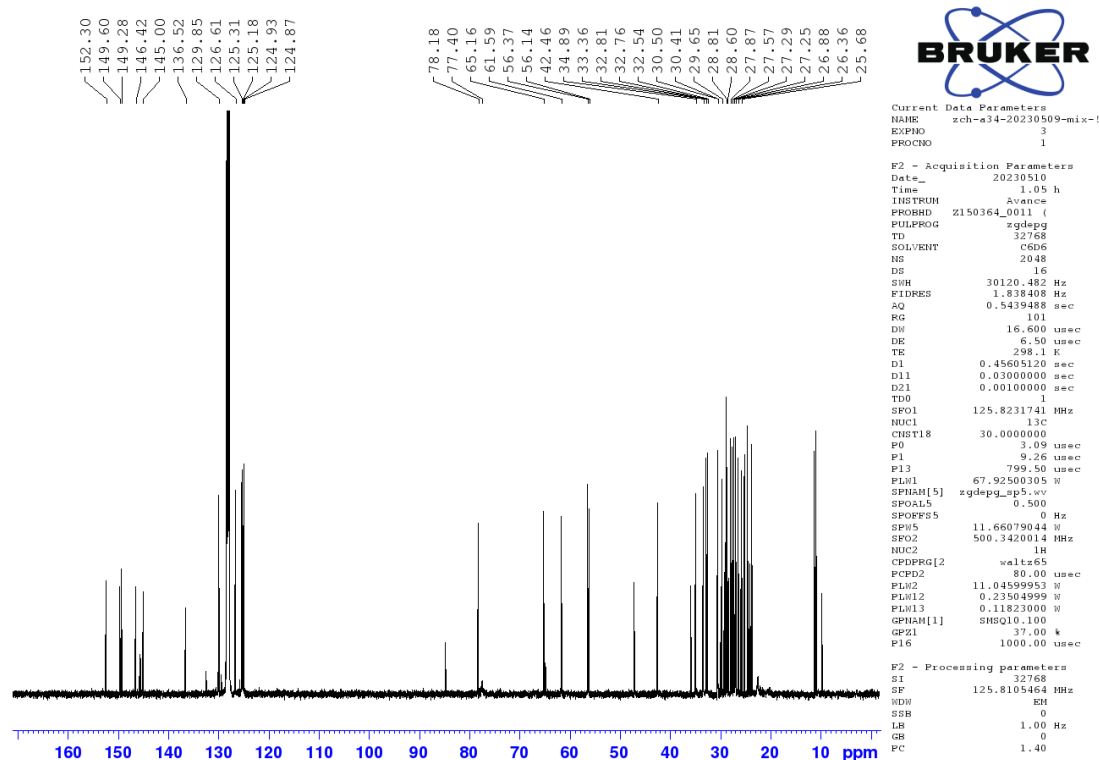


Figure S26. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of mixed **3** and **4** in C_6D_6 . Only the signals belonging to **4** were labeled.

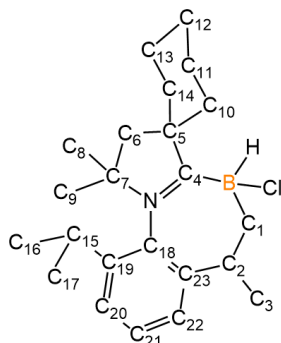
The reaction of 2^{Cl} with $^{\text{Cy}}\text{CAAC}$: to a toluene (60 mL) solution of 2^{Cl} (371 mg, 1.78 mmol, 1.0 equiv), a toluene (20 mL) solution of $^{\text{Cy}}\text{CAAC}$ (580 mg, 1.78 mmol, 1.0 equiv) was slowly added at 25 °C while stirring. The solution immediately turned orange and solids precipitated. The solution was stirred overnight to afford a dark orange suspension. All volatiles in the suspension were removed under reduced pressure, and the remaining solids were washed with hexanes (40 mL \times 2). The washed solids were dissolved in DCM (2 mL), and hexanes (1 mL) was slowly added. The solution was stored at -35 °C for 2 days and white solids precipitated from the solution. The mother liquid was removed by filtration and the solids were dried under vacuum to afford compound 5^{Cl} (270 mg, 41%) as a white powder.

NMR yield determination: to a toluene (1 mL) solution of 2^{Cl} (10.4 mg, 0.05 mmol, 1.0 equiv), a toluene (1 mL) solution of $^{\text{Cy}}\text{CAAC}$ (16.3 mg, 0.05 mmol, 1.0 equiv) was slowly added at 25 °C while stirring. The solution was stirred overnight. Acenaphthene (7.7 mg, 0.05 mmol, 1.0 equiv) was then added to the solution as an internal reference. All volatiles in the solution were removed under vacuum and the remaining solids were dissolved in deuterated DCM. The ^1H NMR spectrum suggested that the yield of 5^{Cl} and C_6Me_6 was 62% and 74%, respectively.

The reaction of **7 with $[\text{PPN}]\text{Cl}$:** compound **7** (28.3 mg, 0.05 mmol, 1.0 equiv) and $[\text{PPN}]\text{Cl}$ (143 mg, 0.25 mmol, 5.0 equiv) were suspended in toluene and the mixture was stirred overnight at room temperature. All volatiles in the solution were removed under vacuum to

afford a mixture of **5^{Cl}**, [PPN]Br, and C₆Me₆. The ¹H NMR spectrum (in C₆D₆) suggested that the ratio of **5^{Cl}** and C₆Me₆ was 1.0:1.1.

The product was characterized as two diastereomers.



Major Isomer (67%):

¹H NMR (500 MHz, C₆D₆): 0.70 (s, 3H, C₈H₃ or C₉H₃), 0.93 (s, 3H, C₈H₃ or C₉H₃), 1.02 (d, *J* = 6.6, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.07 (tt, *J* = 12.7, *J* = 3.6, 2H, C₁₂H₃), 1.13 (d, *J* = 6.9, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.15 (1H, C₁₀H or C₁₄H), 1.32 (d, *J* = 6.6, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.34 (1H, C₁₀H or C₁₄H), 1.56 (1H, C₆H), 1.56 (2H, C₁₁H or C₁₃H), 1.59 (m, 2H, C₁H₂), 1.59 (2H, C₁₁H or C₁₃H), 1.70 (d, *J* = 13.7, 1H, C₆H), 2.56 (m, 1H, C₂H or C₁₅H), 2.65 (sept, *J* = 6.9, 1H, C₂H or C₁₅H), 3.00 (br. s, 1H, BH), 3.37 (dt, *J* = 13.5, *J* = 4.0, 1H, C₁₀H or C₁₄H), 3.43 (dt, *J* = 13.4, *J* = 4.0, 1H, C₁₀H or C₁₄H), 7.04 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.07 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.15 (m, 1H, C₂₀H or C₂₁H or C₂₂H); **¹H{¹¹B} NMR** (400 MHz, C₆D₆): 0.70 (s, 3H, C₈H₃ or C₉H₃), 0.93 (s, 3H, C₈H₃ or C₉H₃), 1.02 (d, *J* = 6.6, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.07 (tt, *J* = 12.7, *J* = 3.6, 2H, C₁₂H₃), 1.13 (d, *J* = 6.9, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.15 (1H, C₁₀H or C₁₄H), 1.32 (d, *J* = 6.6, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.34 (1H, C₁₀H or C₁₄H), 1.56 (1H, C₆H), 1.56 (2H, C₁₁H or C₁₃H), 1.59 (m, 2H, C₁H₂), 1.59 (2H, C₁₁H or C₁₃H), 1.70 (d, *J* = 13.7, 1H, C₆H), 2.56 (m, 1H, C₂H or C₁₅H), 2.65 (sept, *J* = 6.9, 1H, C₂H or C₁₅H), 3.01 (m, 1H, BH), 3.37 (dt, *J* = 13.5, *J* = 4.0, 1H, C₁₀H or C₁₄H), 3.43 (dt, *J* = 13.4, *J* = 4.0, 1H, C₁₀H or C₁₄H), 7.04 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.07 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.15 (m, 1H, C₂₀H or C₂₁H or C₂₂H); **¹¹B NMR** (161 MHz, C₆D₆): -7.95 (br. d, *J* = 67.6); **¹¹B{¹H} NMR** (161 MHz, C₆D₆): -7.99 (s); **¹³C{¹H} NMR** (126 MHz, C₆D₆): 20.86 (s, C₃ or C₁₆ or C₁₇), 21.74 (s, C₃ or C₁₆ or C₁₇), 22.15 (s, C₁₁ or C₁₃), 22.34 (s, C₁₂), 25.11 (s, C₁₁ or C₁₃), 25.88 (s, C₃ or C₁₆ or C₁₇), 28.41 (s, C₈ or C₈), 29.99 (s, C₈ or C₉), 30.10 (s, C₂ or C₁₅), 32.01 (s, C₁₀ or C₁₄), 34.47 (s, C₂ or C₁₅), 34.74 (s, C₁₀ or C₁₄), 40.48 (br. s, C₁), 46.85 (s, C₆), 58.60 (s, C₅), 77.57 (s, C₇), 122.30 (s, C₂₀ or C₂₁ or C₂₂), 124.17 (s, C₂₀ or C₂₁ or C₂₂), 129.78 (s, C₂₀ or C₂₁ or C₂₂), 133.28 (s, C₁₈ or C₁₉ or C₂₃), 143.34 (s, C₁₈ or C₁₉ or C₂₃), 144.37 (s, C₁₈ or C₁₉ or C₂₃).

Minor Isomer (33%):

¹H NMR (500 MHz, C₆D₆): 0.58 (s, 3H, C₈H₃ or C₉H₃), 1.01 (2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.09 (2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.12 (3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.25 (1H, C₁H), 1.30 (3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.39 (s, 3H, C₈H₃ or C₉H₃), 1.46 (1H, C₁₀H or C₁₄H), 1.46 (1H, C₆H), 1.47 (3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.51 (2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.61 (1H, C₆H), 1.73 (1H, C₁₀H or C₁₄H), 1.85 (1H, C₁H), 1.92 (1H, C₁₀H or C₁₄H), 1.99 (1H, C₁₀H or C₁₄H), 2.75 (1H, C₂H or C₁₅H), 3.46 (1H, C₂H or C₁₅H), 6.99 (m, 1H, C₂₀H or C₂₁H or C₂₂H),

7.06 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.14 (m, 1H, C₂₀H or C₂₁H or C₂₂H); ¹H{¹¹B} NMR (400 MHz, C₆D₆): 0.58 (s, 3H, C₈H₃ or C₉H₃), 1.01 (2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.09 (2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.12 (3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.25 (1H, C₁H), 1.30 (3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.39 (s, 3H, C₈H₃ or C₉H₃), 1.46 (1H, C₁₀H or C₁₄H), 1.46 (1H, C₆H), 1.47 (3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.51 (2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.61 (1H, C₆H), 1.73 (1H, C₁₀H or C₁₄H), 1.85 (1H, C₁H), 1.92 (1H, C₁₀H or C₁₄H), 1.99 (1H, C₁₀H or C₁₄H), 2.75 (1H, C₂H or C₁₅H), 3.46 (1H, C₂H or C₁₅H), 3.54 (m, 1H, BH), 6.99 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.06 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.14 (m, 1H, C₂₀H or C₂₁H or C₂₂H); ¹B NMR (161 MHz, C₆D₆): -4.73 (br. d, J = 137.4); ¹¹B{¹H} NMR (161 MHz, C₆D₆): -4.78 (s); ¹³C{¹H} NMR (126 MHz, C₆D₆): 19.72 (s, C₃ or C₁₆ or C₁₇), 23.44 (s, C₁₁ or C₁₂ or C₁₃), 24.62 (s, C₁₁ or C₁₂ or C₁₃), 26.14 (s, C₃ or C₁₆ or C₁₇), 26.24 (s, C₁₁ or C₁₂ or C₁₃), 26.94 (s, C₈ or C₉), 27.80 (s, C₁₁ or C₁₃), 27.96 (s, C₈ or C₉), 28.38 (s, C₂ or C₁₅), 30.77 (s, C₂ or C₁₅), 32.44 (s, C₁₀ or C₁₄), 33.41 (s, C₁₀ or C₁₄), 37.98 (s, C₁), 44.14 (s, C₅), 49.16 (s, C₆), 71.31 (s, C₇), 123.15 (s, C₂₀ or C₂₁ or C₂₂), 126.30 (s, C₂₀ or C₂₁ or C₂₂), 126.91 (s, C₂₀ or C₂₁ or C₂₂), 135.03 (s, C₁₈ or C₁₉ or C₂₃), 142.46 (s, C₁₈ or C₁₉ or C₂₃), 146.46 (s, C₁₈ or C₁₉ or C₂₃). (Some assignments of the peaks were accomplished by the assistance of 2D spectra) HRMS (m/z): [M+H]⁺ calcd. for C₂₃H₃₆BCIN, 372.26849; found 372.26728. **Elemental analysis:** calcd. for C₂₃H₃₅BCIN, C, 74.30; H, 9.49; N, 3.77; found, C, 74.58; H, 9.29; N, 3.67.

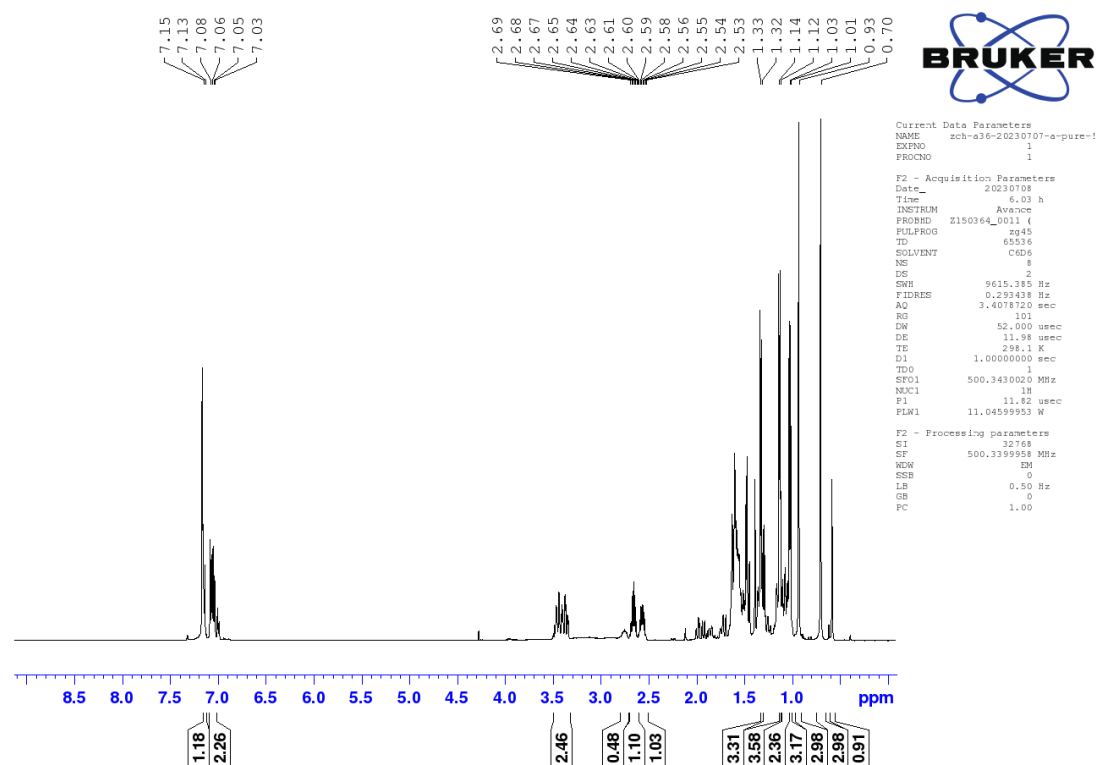


Figure S27. ¹H NMR spectrum of **5**^{Cl} in C₆D₆. Only the signals belonging to the major isomer were labeled and integrated.

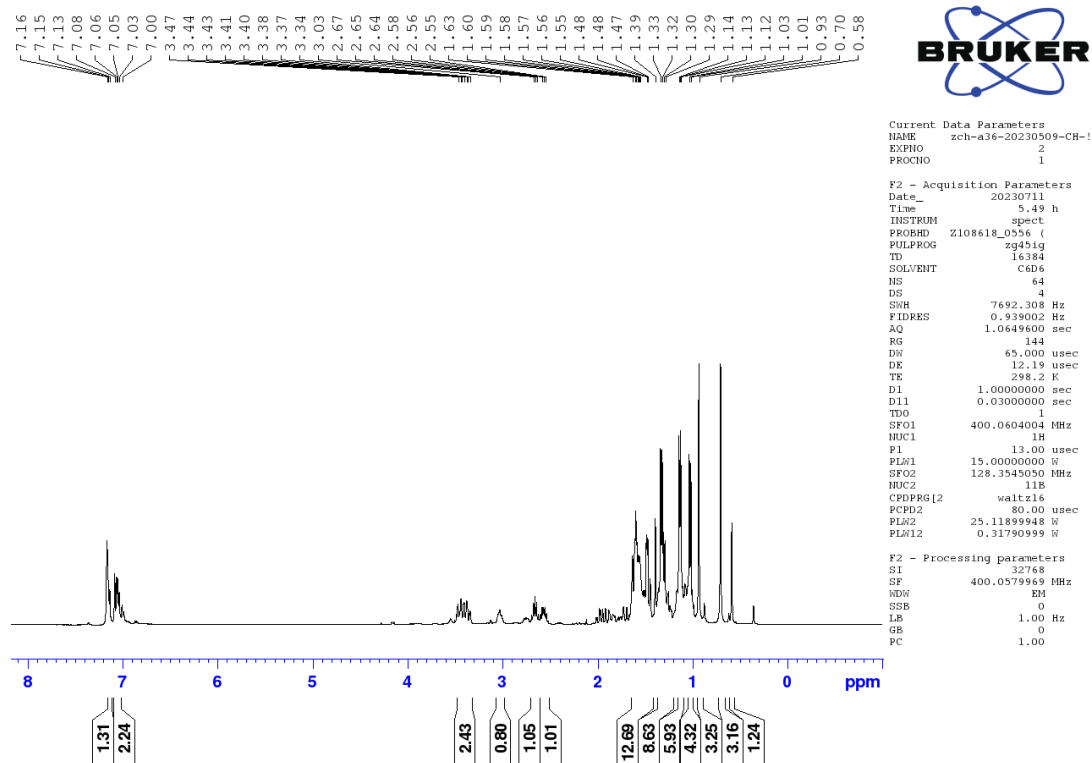


Figure S28. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of 5^{Cl} in C_6D_6 . Only the signals belonging to the major isomer were labeled and integrated.

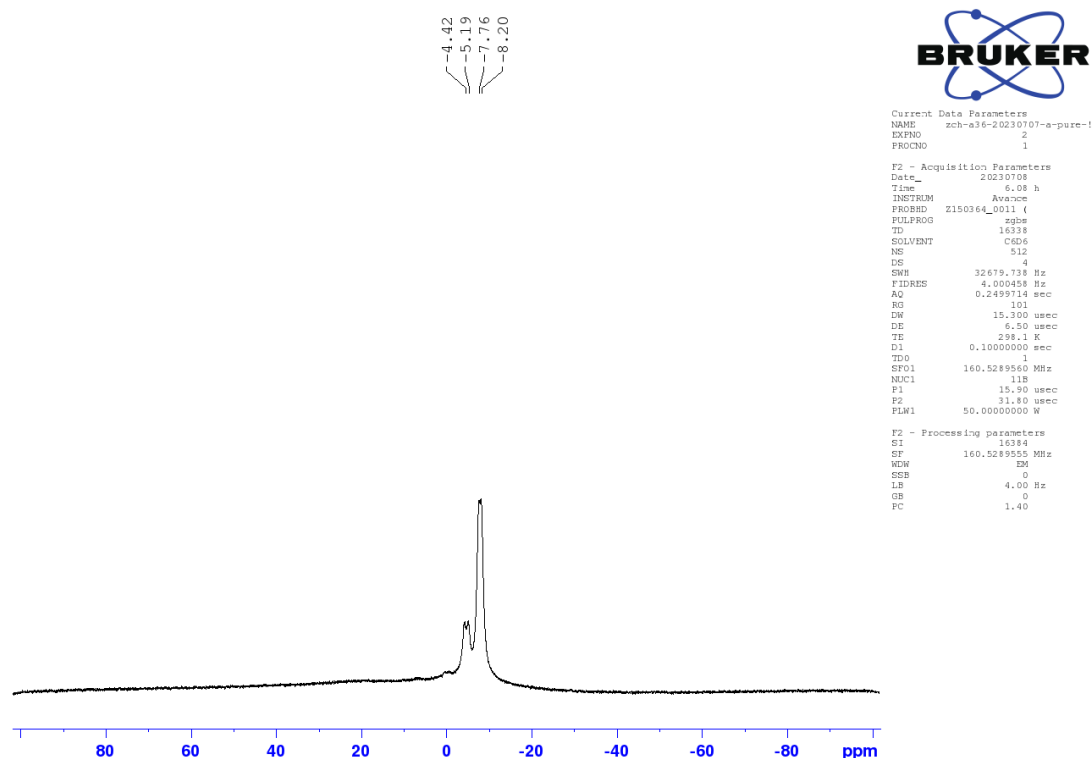


Figure S29. ^{11}B NMR spectrum of 5^{Cl} in C_6D_6 .

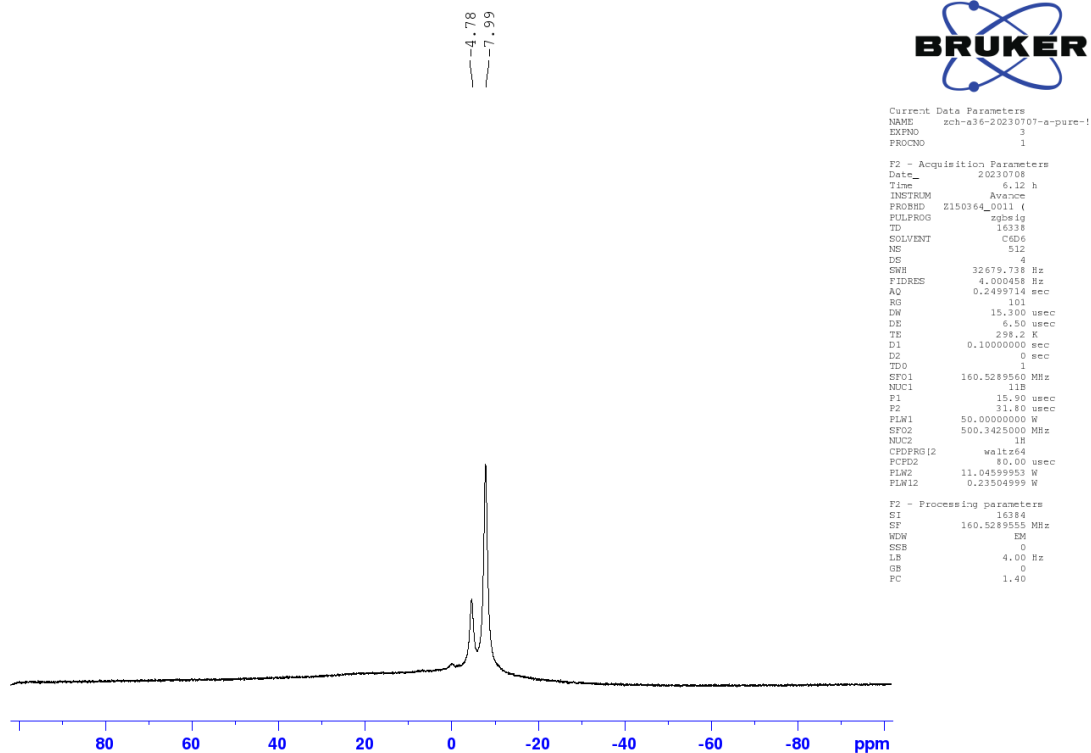


Figure S30. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 5^{Cl} in C_6D_6 .

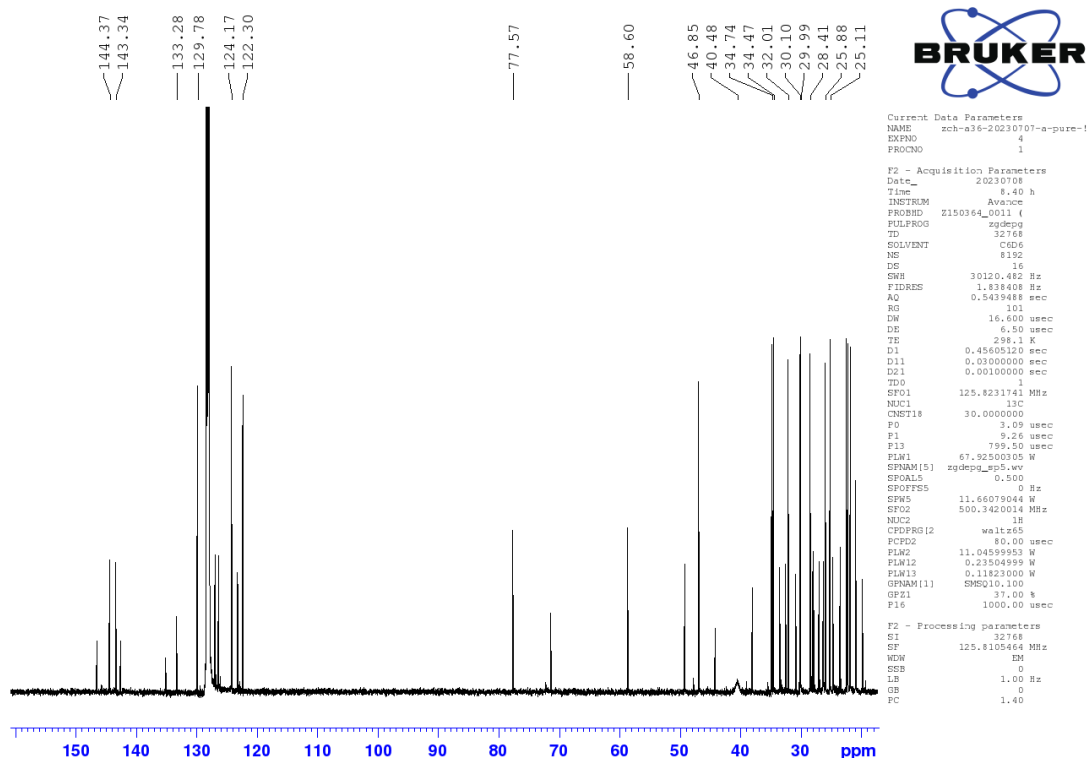
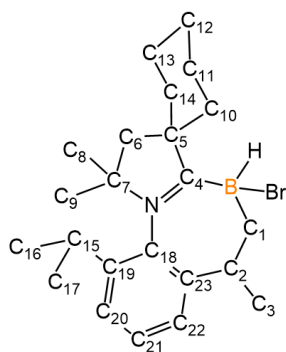


Figure S31. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5^{Cl} in C_6D_6 . Only the signals belonging to the major isomer were labeled.

Heating 7 in toluene: in a Schlenk tube, toluene (20 mL) was added to **7** (587 mg, 1.01 mmol) to form a yellow suspension. The suspension was stirred and heated at 110 °C for

18 hours. The yellow suspension gradually converted to a homogeneous solution. All volatiles in the solution were removed under reduced pressure, and the remaining solids were washed with hexanes (30 mL×2). The washed solids were dissolved in DCM (1 mL), and hexanes (1 mL) was slowly added. The solution was stored at –35 °C for 2 days and white solids precipitated from the solution. The mother liquid was removed by filtration and the solids were dried to afford compound **5^{Br}** (142 mg, 34%) as a white powder. The two portions of 30 mL hexanes solution were combined and evaporated under vacuum. The remaining solids were sublimed at 100 °C, 250 mTorr for 4 hours. The remaining solids were dissolved in DCM (0.5 mL), added with hexanes (1.5 mL), and the mixture was stored at –35 °C for 2 days. The mother liquid was removed, and the remaining crystalline solids were dried under vacuum. The recrystallization process was repeated twice to afford compound **8** (overall yield: 15 mg, 3%).

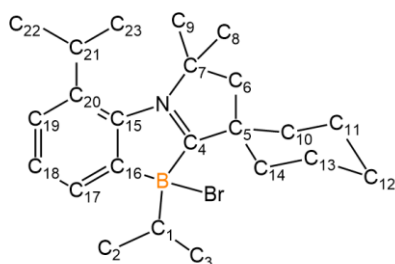
NMR yield determination: in a Schlenk tube, toluene (1 mL) was added to **7** (28.9 mg, 0.05 mmol, 1.0 equiv) to form a yellow suspension. The suspension was stirred and heated at 110 °C for 18 hours. The yellow suspension gradually converted to a homogeneous solution. Acenaphthene (7.7 mg, 0.05 mmol, 1.0 equiv) was then added to the solution as an internal reference. All volatiles in the solution were removed under vacuum and the remaining solids were dissolved in deuterated DCM. The ¹H NMR spectrum suggested that the yield of **8**, **5^{Br}** and C₆Me₆ were 57%, 35% and 92%, respectively.



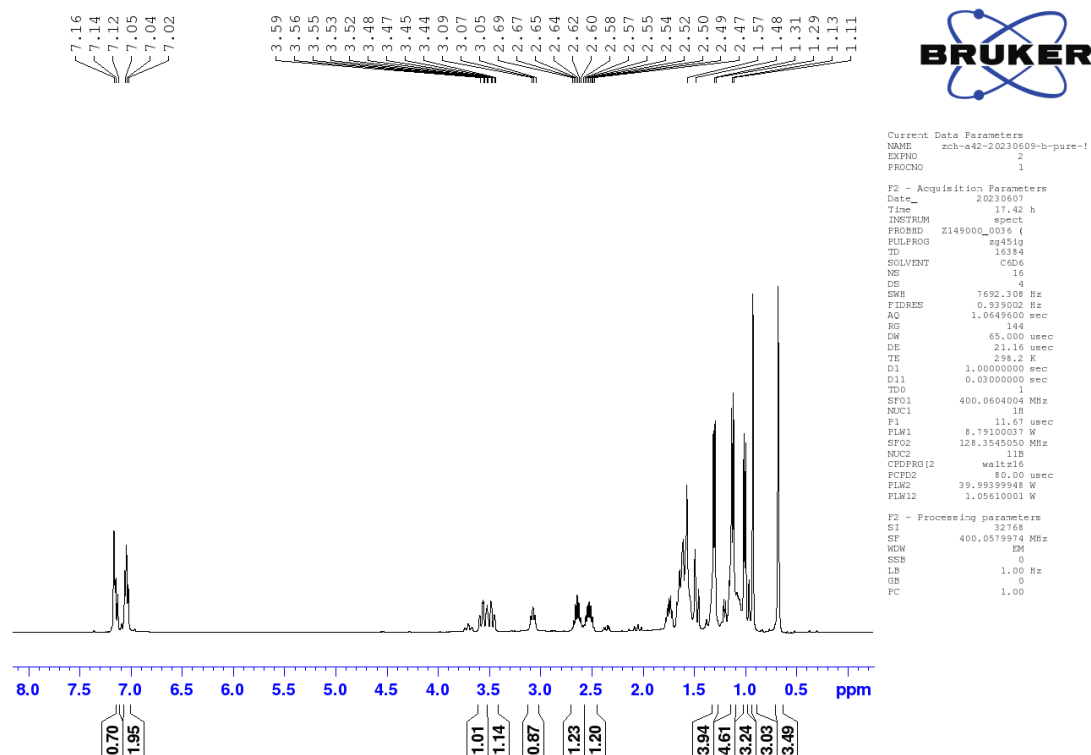
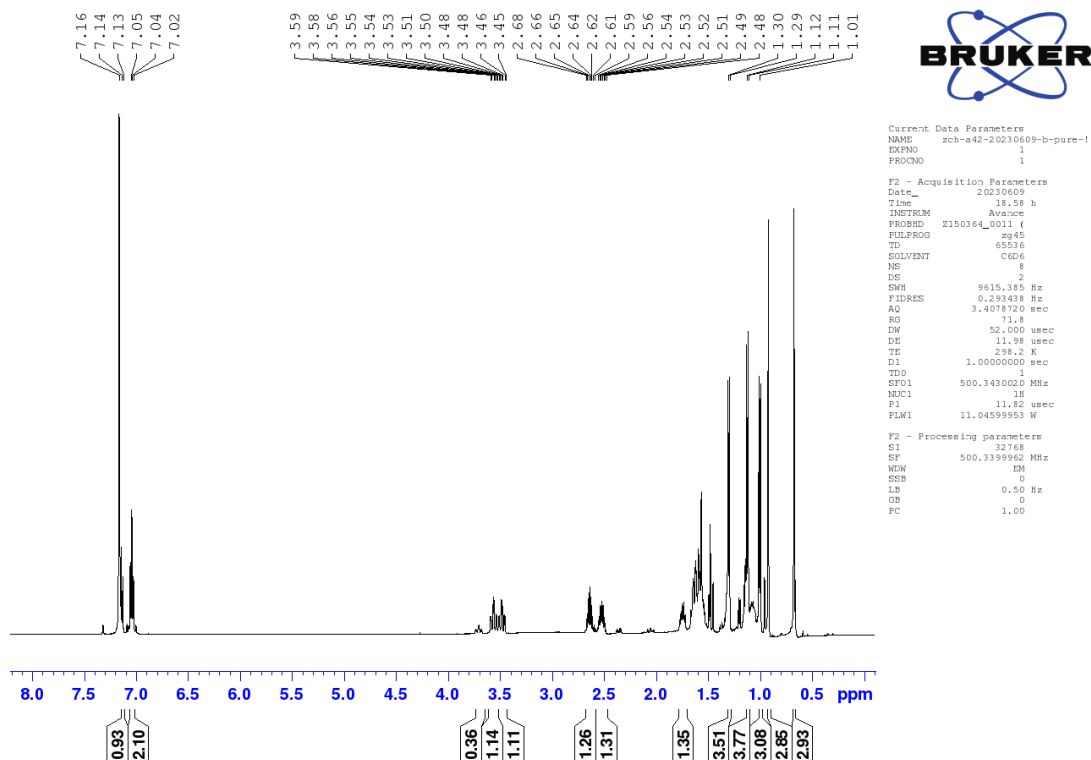
Major Isomer (85%):

¹H NMR (500 MHz, C₆D₆): 0.67 (s, 3H, C₈H₃ or C₉H₃), 0.92 (s, 3H, C₈H₃ or C₉H₃), 1.00 (d, *J* = 6.7, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.07 (m, 2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.12 (d, *J* = 6.8, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.12 (m, 1H, C₁₀H or C₁₄H), 1.30 (m, 1H, C₁₀H or C₁₄H), 1.30 (d, *J* = 6.7, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.46 (1H, C₆H), 1.56 (m, 2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.57 (d, *J* = 13.6, 1H, C₆H), 1.61 (m, 2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.63 (m, 1H, C₁H), 1.73 (m, 1H, C₁H), 2.52 (sept, *J* = 6.7, 1H, C₂H or C₁₅H), 2.64 (sept, *J* = 6.7, 1H, C₂H or C₁₅H), 3.01 (br. s, 1H, BH), 3.48 (td, *J* = 13.2, *J* = 3.5, 1H, C₁₀H or C₁₄H), 3.56 (td, *J* = 13.4, *J* = 4.0 1H, C₁₀H or C₁₄H), 7.04 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.04 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.13 (m, 1H, C₂₀H or C₂₁H or C₂₂H); **¹H{¹¹B} NMR** (400 MHz, C₆D₆): 0.67 (s, 3H, C₈H₃ or C₉H₃), 0.92 (s, 3H, C₈H₃ or C₉H₃), 1.00 (d, *J* = 6.7, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.07 (m, 2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.12 (d, *J* = 6.8, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.12 (m, 1H, C₁₀H or C₁₄H), 1.30 (m, 1H, C₁₀H or C₁₄H), 1.30 (d, *J* = 6.7, 3H, C₃H₃ or C₁₆H₃ or C₁₇H₃), 1.46 (1H, C₆H), 1.56 (m, 2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.57 (d, *J* = 13.6, 1H,

C₆H), 1.61 (m, 2H, C₁₁H₂ or C₁₂H₂ or C₁₃H₂), 1.63 (m, 1H, C₁H), 1.73 (m, 1H, C₁H), 2.52 (sept, *J* = 6.7, 1H, C₂H or C₁₅H), 2.64 (sept, *J* = 6.7, 1H, C₂H or C₁₅H), 3.07 (t, *J* = 8.4 1H, BH), 3.48 (td, *J* = 13.2, *J* = 3.5, 1H, C₁₀H or C₁₄H), 3.56 (td, *J* = 13.4, *J* = 4.0 1H, C₁₀H or C₁₄H), 7.04 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.04 (m, 1H, C₂₀H or C₂₁H or C₂₂H), 7.13 (m, 1H, C₂₀H or C₂₁H or C₂₂H); **¹¹B NMR** (161 MHz, C₆D₆): -10.73 (br. s, FWHM = 353.9 Hz); **¹¹B{¹H} NMR** (161 MHz, C₆D₆): -10.59 (br. s, FWHM = 205.9 Hz); **¹³C{¹H} NMR** (126 MHz, C₆D₆): 20.66 (s, C₃ or C₁₆ or C₁₇), 21.74 (s, C₃ or C₁₆ or C₁₇), 22.19 (s, C₁₁ or C₁₂ or C₁₃), 22.35 (s, C₁₁ or C₁₂ or C₁₃), 25.00 (s, C₁₁ or C₁₂ or C₁₃), 25.79 (s, C₃ or C₁₆ or C₁₇), 28.42 (s, C₈ or C₉), 29.95 (s, C₈ or C₉), 30.11 (s, C₂ or C₁₅), 32.07 (s, C₁₀ or C₁₄), 34.93 (s, C₂ or C₁₅), 35.02 (s, C₁₀ or C₁₄), 40.37 (br. s, C₁), 47.01 (s, C₆), 58.80 (s, C₅), 77.57 (s, C₇), 122.34 (s, C₂₀ or C₂₁ or C₂₂), 124.28 (s, C₂₀ or C₂₁ or C₂₂), 129.88 (s, C₂₀ or C₂₁ or C₂₂), 133.29 (s, C₁₈ or C₁₉ or C₂₃), 143.27 (s, C₁₈ or C₁₉ or C₂₃), 143.96 (s, C₁₈ or C₁₉ or C₂₃). (Some assignments of the peaks were accomplished by the assistance of 2D spectra)
 Minor Isomer (15%): most of the peaks are hard to identify.
¹¹B NMR (161 MHz, C₆D₆): -5.38 (br. s); **¹¹B{¹H} NMR** (161 MHz, C₆D₆): -5.47 (br. s).
HRMS (m/z): [M]⁺ calcd. for C₂₃H₃₅BBrN, 415.20459; found 415.20369.



¹H NMR (500 MHz, C₆D₆): 0.77 (d, *J* = 6.9, 3H, C₂H₃ or C₃H₃), 0.98 (1H, C₁₁H or C₁₂H or C₁₃H), 1.00 (1H, C₁₁H or C₁₂H or C₁₃H), 1.06 (d, *J* = 6.9, 3H, C₂₂H₃ or C₂₃H₃), 1.09 (d, *J* = 6.9, 3H, C₂H₃ or C₃H₃), 1.16 (1H, C₁₁H or C₁₂H or C₁₃H), 1.17 (s, 3H, C₈H₃ or C₉H₃), 1.28 (s, 3H, C₈H₃ or C₉H₃), 1.40 (m, 1H, C₁₀H or C₁₄H), 1.45 (1H, C₁₁H or C₁₂H or C₁₃H), 1.49 (1H, C₁₁H or C₁₂H or C₁₃H), 1.51 (1H, C₁₁H or C₁₂H or C₁₃H), 1.74 (d, *J* = 6.8, 3H, C₂H₃ or C₃H₃), 1.78 (m, 1H, C₁₀H or C₁₄H), 1.78 (1H, C₆H), 1.82 (1H, C₆H), 2.26 (td, *J* = 13.4, *J* = 3.2, 1H, C₁₀H or C₁₄H), 2.86 (td, *J* = 13.9, *J* = 3.6, 1H, C₁₀H or C₁₄H), 3.27 (sept, *J* = 6.8, 1H, C₂₁H), 7.02 (dd, *J* = 7.8, *J* = 1.3, 1H, C₁₉H), 7.18 (m, 1H, C₁₈H), 7.86 (d, *J* = 6.6, 1H, C₁₇H); **¹¹B NMR** (161 MHz, C₆D₆): -4.71 (s); **¹³C{¹H} NMR** (126 MHz, C₆D₆): 20.31 (s, C₂ or C₃), 21.41 (s, C₂ or C₃), 22.15 (s, C₁₁ or C₁₂ or C₁₃), 22.44 (s, C₁₁ or C₁₂ or C₁₃), 23.70 (s, C₂₂ or C₂₃), 24.81 (s, C₂₂ or C₂₃), 25.37 (s, C₁₁ or C₁₂ or C₁₃), 27.67 (s, C₈ or C₉), 29.32 (s, C₈ or C₉), 29.45 (s, C₂₁), 33.81 (s, C₁₀ or C₁₄), 38.15 (s, C₁₀ or C₁₄), 52.66 (s, C₅), 53.85 (s, C₆), 70.87 (s, C₇), 125.89 (s, C₁₉), 128.35 (s, C₁₈), 130.70 (s, C₁₇), 134.69 (s, C₁₅ or C₂₀), 141.26 (s, C₁₅ or C₂₀). (Some assignments of the peaks were accomplished by the assistance of 2D spectra) **HRMS** (m/z): [M+H]⁺ calcd. for C₂₃H₃₆BBrN, 416.21240; found 416.21000.



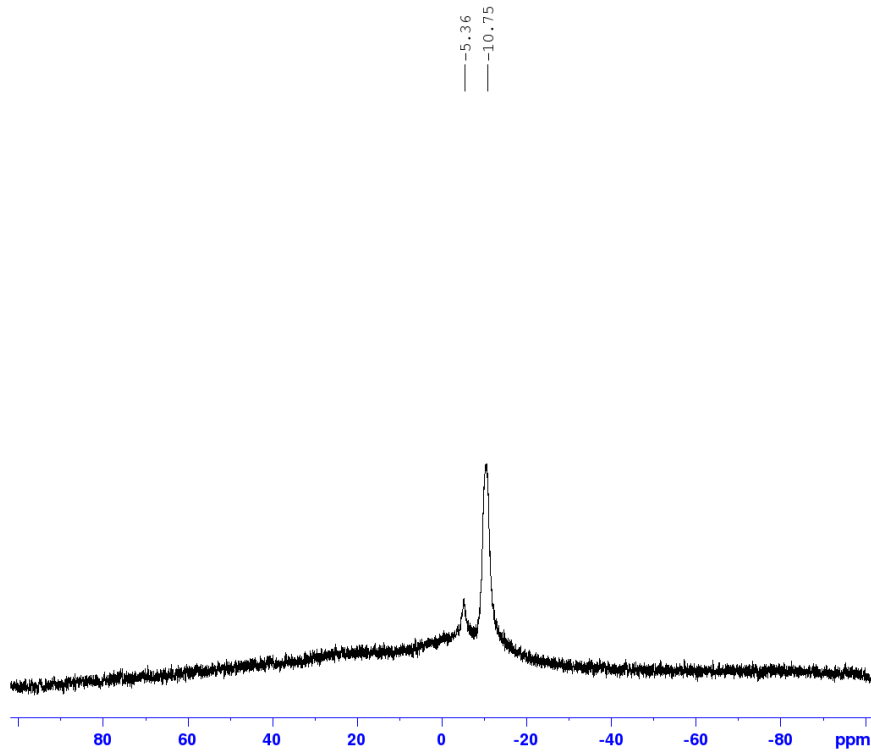


Figure S34. ^{11}B NMR spectrum of 5^{Br} in C_6D_6 .

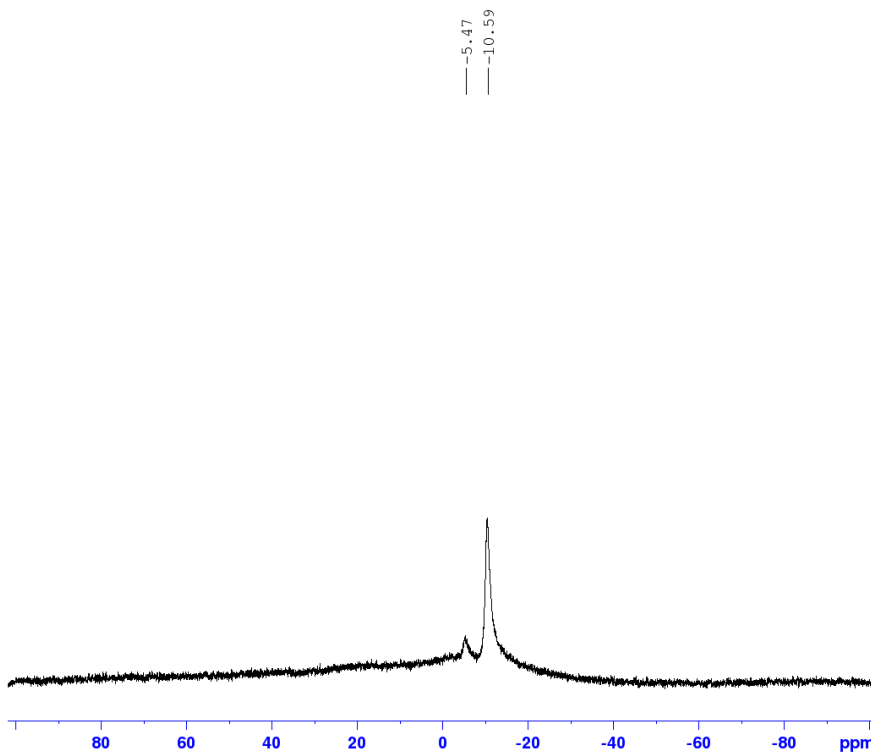


Figure S35. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 5^{Br} in C_6D_6 .

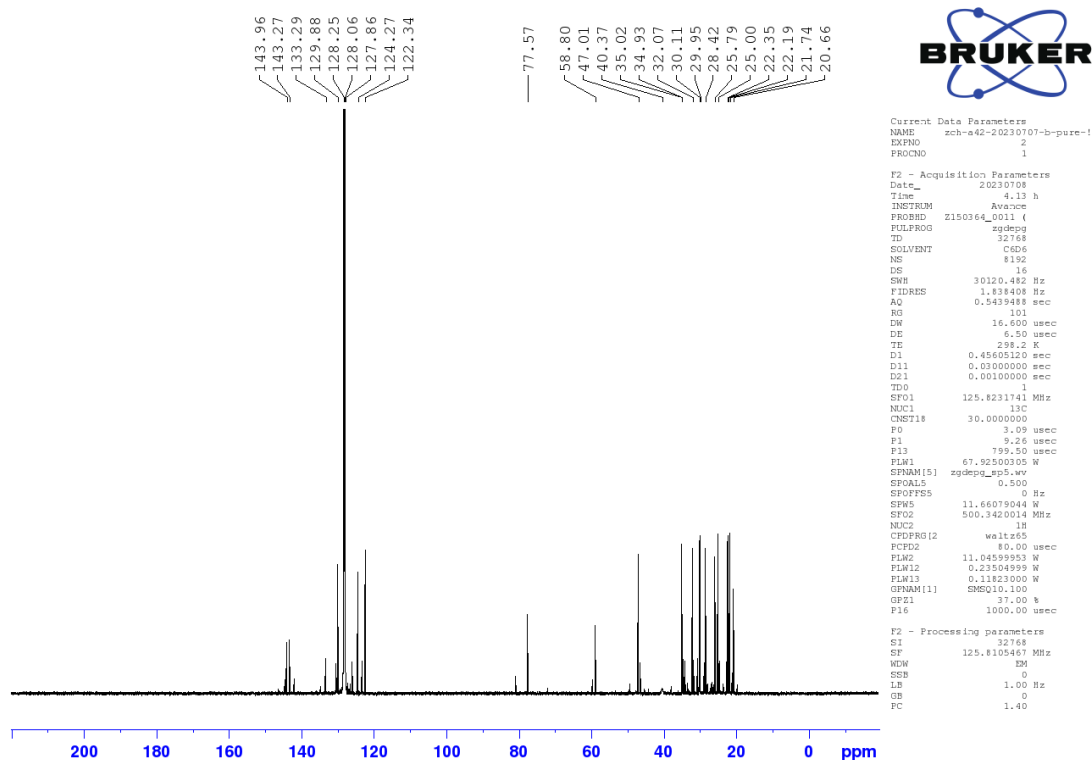


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5^{Br} in C_6D_6 . Only the signals belonging to the major isomer were labeled.

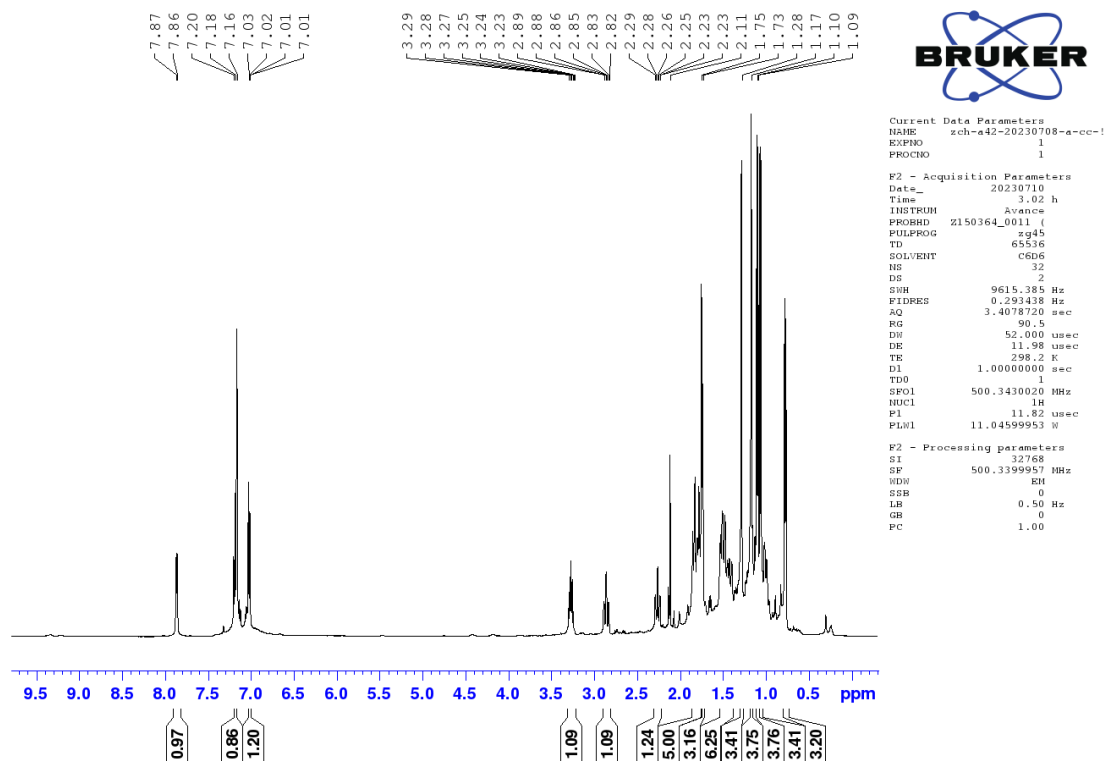
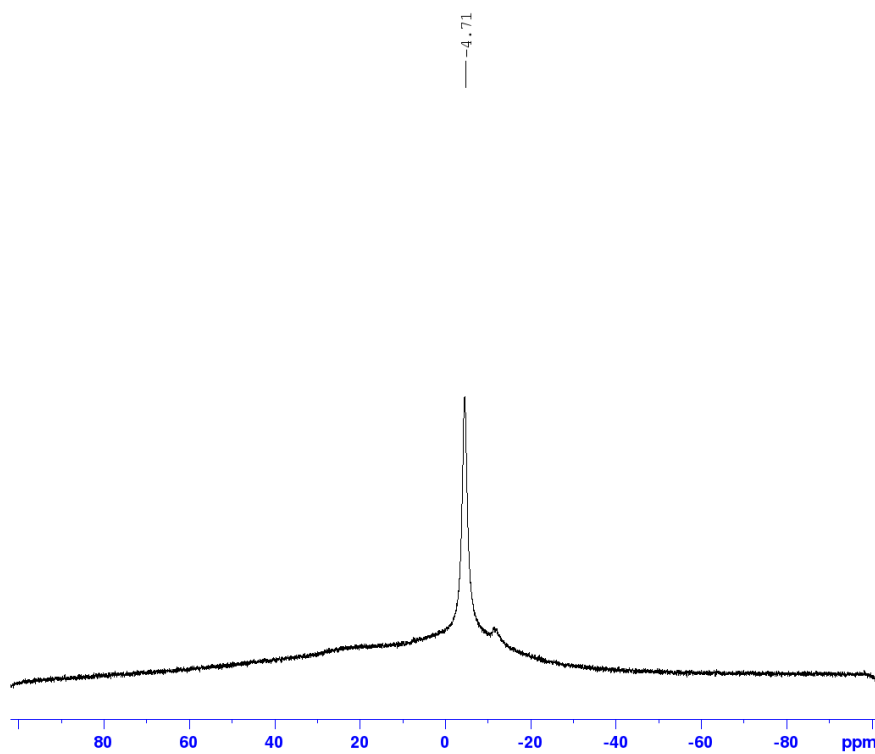


Figure S37. ^1H NMR spectrum of 8 in C_6D_6 .



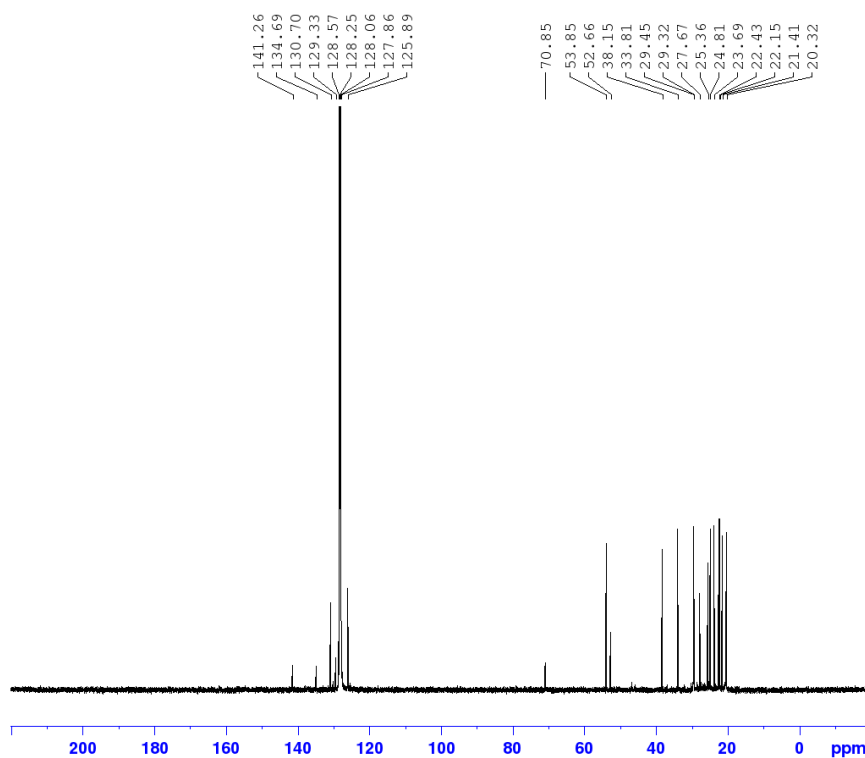
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Current Data Parameters
NAME      zch-a42-20230708-a-cc-1
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    20230710
Time     3.07 h
INSTRUM  Avance
PROBHD   Z150364_0011 (
PULPROG  zgpg
TD        16538
SOLVENT  C6D6
NS        512
DS        4
SWH       32679.738 Hz
FIDRES    4.000458 Hz
AQ        0.2499714 sec
RG        101
DN        15.300 usec
DE        6.50 usec
TE        298.1 K
D1        0.10000000 sec
TD0       1
SF01      160.5289560 MHz
NUC1      11B
P1        15.90 usec
P2        31.80 usec
PLW1     50.00000000 W

F2 - Processing parameters
SI        16384
SF        160.528955 MHz
WDW       EM
SSB       0
LB        4.00 Hz
GB        0
PC        1.40
  
```

Figure S38. ^{11}B NMR spectrum of **8** in C_6D_6 .



```

Current Data Parameters
NAME      zch-a42-20230708-a-cc-1
EXPNO    3
PROCNO   1

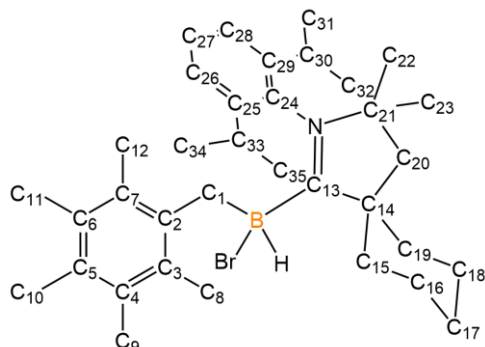
F2 - Acquisition Parameters
Date_    20230710
Time     5.34 h
INSTRUM  Avance
PROBHD   Z150364_0011 (
PULPROG  zgpgpg
TD        32768
SOLVENT  C6D6
NS        8192
DS        16
SWH       30120.482 Hz
FIDRES    1.838408 Hz
AQ        0.5439488 sec
RG        101
DN        16.600 usec
DE        6.50 usec
TE        298.2 K
D1        0.45605120 sec
D11       0.03000000 sec
D21       0.00100000 sec
TD0       1
SF01      125.8231741 MHz
NUC1      13C
CNST18   30.0000000
P0        3.09 usec
P1        8.25 usec
P13       799.50 usec
PLW1     67.92500305 W
SFRM[5]  zgpgpg5.vv
SFOAL5    0.500
SPOFF55  0 Hz
SPW5     11.66079044 W
SPW2     500.3420014 MHz
NUC2      1H
OPDPRG[2] waltz65
PCPDZ    80.00 usec
PLW2     11.04599953 W
PLW12    0.23504999 W
PLW13    0.11823000 W
GPMHM[1] SMSQ10.100
GPZ1     37.00 k
P16      1000.00 usec

F2 - Processing parameters
SI        32768
SF        125.8105465 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
```

Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** in C_6D_6 .

Heating 7 in DCM (or o-difluorobenzene): in a Schlenk tube, **7** (172 mg, 0.29 mmol) was dissolved in DCM (10 mL). The solution was stirred and heated at 50 °C overnight. All volatiles in the solution were removed under reduced pressure, and the remaining solids

were recrystallized in DCM/hexanes at $-35\text{ }^{\circ}\text{C}$, affording compound **11** as a white solid (87.1 mg, 52%). This reaction was also conducted using *o*-difluorobenzene as solvent instead of DCM. The reaction was heated at $85\text{ }^{\circ}\text{C}$ for 2 days, and the isolated yield improved from 52% to 73%.



$^1\text{H NMR}$ (500 MHz, C_6D_6): 0.80 (br. s, 3H, C_{22}H_3 or C_{23}H_3), 1.01 (br. s, 3H, C_{22}H_3 or C_{23}H_3), 1.08 (6H, C_{31}H_3 and C_{32}H_3 , or C_{34}H_3 and C_{35}H_3), 1.33 (6H, C_{31}H_3 and C_{32}H_3 , or C_{34}H_3 and C_{35}H_3), 1.59 (m, 1H, C_{20}H), 1.77 (m, 1H, C_{20}H), 2.16 (s, 3H, C_{10}H_3), 2.19 (6H, C_8H_3 and C_{12}H_3 , or C_9H_3 and C_{11}H_3), 2.16 (s, 3H, C_{10}H_3), 2.19 (1H, C_1H), 2.56 (1H, C_1H), 2.57 (s, 6H, C_8H_3 and C_{12}H_3 , or C_9H_3 and C_{11}H_3), 2.69 (m, 1H, C_{30}H or C_{34}H), 3.19 (m, 1H, C_{30}H or C_{34}H), 7.00 (m, 1H, C_{26}H or C_{27}H or C_{28}H), 7.02 (m, 1H, C_{26}H or C_{27}H or C_{28}H), 7.08 (m, 1H, C_{26}H or C_{27}H or C_{28}H), C_{15}H_2 - C_{19}H_2 : 1.22 (br. m), 1.47 (br. m), 1.60 (br. m), 1.76 (br. m), 2.33 (br. m), 2.42 (br. m), 2.53 (br. m), 3.03 (br. m), 3.12 (br. m); **$^1\text{H}\{^{11}\text{B}\}$ NMR** (400 MHz, C_6D_6): 0.80 (br. s, 3H, C_{22}H_3 or C_{23}H_3), 1.01 (br. s, 3H, C_{22}H_3 or C_{23}H_3), 1.08 (6H, C_{31}H_3 and C_{32}H_3 , or C_{34}H_3 and C_{35}H_3), 1.33 (6H, C_{31}H_3 and C_{32}H_3 , or C_{34}H_3 and C_{35}H_3), 1.59 (m, 1H, C_{20}H), 1.77 (m, 1H, C_{20}H), 2.16 (s, 3H, C_{10}H_3), 2.19 (6H, C_8H_3 and C_{12}H_3 , or C_9H_3 and C_{11}H_3), 2.16 (s, 3H, C_{10}H_3), 2.19 (1H, C_1H), 2.56 (1H, C_1H), 2.57 (s, 6H, C_8H_3 and C_{12}H_3 , or C_9H_3 and C_{11}H_3), 2.69 (m, 1H, C_{30}H or C_{34}H), 3.05 (m, 1H, BH), 3.19 (m, 1H, C_{30}H or C_{34}H), 7.00 (m, 1H, C_{26}H or C_{27}H or C_{28}H), 7.02 (m, 1H, C_{26}H or C_{27}H or C_{28}H), 7.08 (m, 1H, C_{26}H or C_{27}H or C_{28}H), C_{15}H_2 - C_{19}H_2 : 1.22 (br. m), 1.47 (br. m), 1.60 (br. m), 1.76 (br. m), 2.33 (br. m), 2.42 (br. m), 2.53 (br. m), 3.03 (br. m), 3.12 (br. m); **$^{11}\text{B NMR}$** (161 MHz, C_6D_6): -8.03 (s); **$^{11}\text{B}\{^1\text{H}\}$ NMR** (161 MHz, C_6D_6): -8.06 (s); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, C_6D_6): 17.10 (s, C_{10}), 17.40 (s, C_8 and C_{12} , or C_9 and C_{11}), 18.89 (s, C_8 and C_{12} , or C_9 and C_{11}), 17.10 (s, C_{10}), 23.42 (br. s, C_{31} or C_{32} or C_{34} or C_{35}), 24.77 (br. s, C_{31} or C_{32} or C_{34} or C_{35}), 26.05 (br. s, C_{31} or C_{32} or C_{34} or C_{35}), 26.99 (br. s, C_{22} or C_{23}), 28.26 (br. s, C_{31} or C_{32} or C_{34} or C_{35}), 28.87 (br. s, C_{30} or C_{33}), 29.36 (br. s, C_{30} or C_{33}), 30.55 (br. s, C_{22} or C_{23}), 45.96 (s, C_{20}), 59.89 (s, C_{14}), 77.38 (s, C_{21}), 124.34 (br. s, C_{26} or C_{27} or C_{28}), 126.15 (br. s, C_{26} or C_{27} or C_{28}), 129.26 (s, C_5), 129.66 (s, C_{26} or C_{27} or C_{28}), 131.39 (s, C_3 and C_7 , or C_4 and C_6), 131.83 (s, C_3 and C_7 , or C_4 and C_6), 133.89 (s, C_{24} or C_{25} or C_{29}), 139.95 (s, C_1), 144.64 (s, C_{24} or C_{25} or C_{29}), 147.47 (s, C_{24} or C_{25} or C_{29}), C_{15} - C_{19} : 22.49 (br. s), 23.62 (br. s), 25.65 (s), 35.49 (br. s), 39.63 (br. s). (Some assignments of the peaks were accomplished by the assistance of 2D spectra) **HRMS** (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{35}\text{H}_{54}\text{BBrN}$, 578.35326; found 578.35728. **Elemental analysis**: calcd. for $\text{C}_{35}\text{H}_{53}\text{BBrN}$, C, 72.66; H, 9.23; N, 2.42; found: C, 72.79; H, 9.08; N, 2.17.

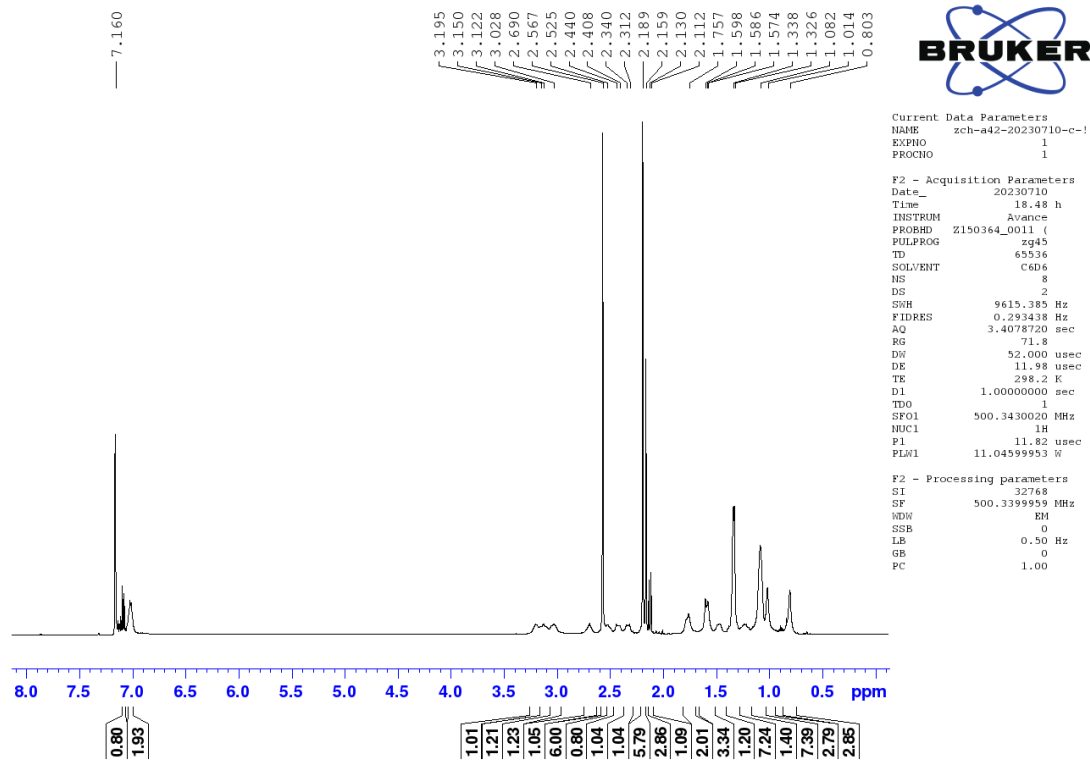


Figure S40. ^1H NMR spectrum of **9** in C_6D_6 .

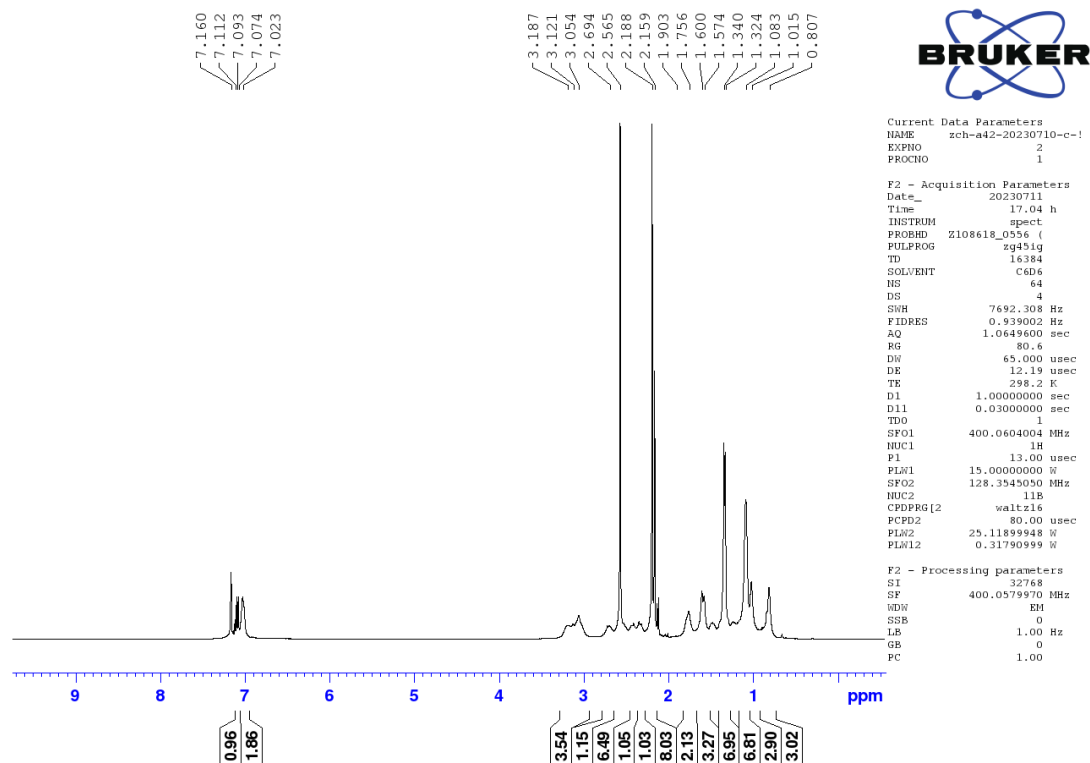


Figure S41. $^1\text{H}^9$ NMR spectrum of **9** in C_6D_6 .

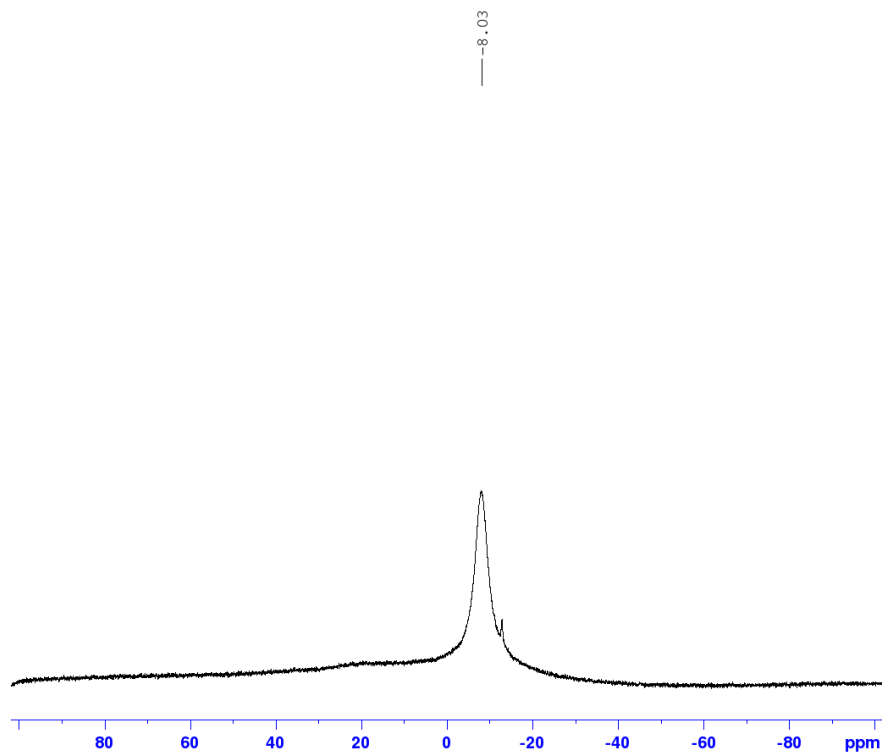


Figure S42. ^{11}B NMR spectrum of **9** in C_6D_6 .



```

Current Data Parameters
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EXPNO    3
PROCNO   1

F2 - Acquisition Parameters
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Time     18.53 h
INSTRUM  Avance
PROBHD   Z150364_0011 (
PULPROG  zgbs
TD       16338
SOLVENT  C6D6
NS       512
DS       4
SWH      32679.738 Hz
FIDRES   4.000458 Hz
AQ       0.2499714 sec
RG       101
DW       15.300 usec
DE       6.50 usec
TE       298.2 K
D1       0.1000000 sec
TD0      1
SF01     160.5289560 MHz
NUC1     11B
P1       15.90 usec
P2       31.80 usec
PLW1     50.0000000 W

F2 - Processing parameters
SI       16384
SF       160.5289555 MHz
WDW      EM
SSB      0
LB       4.00 Hz
GB       0
PC       1.40
  
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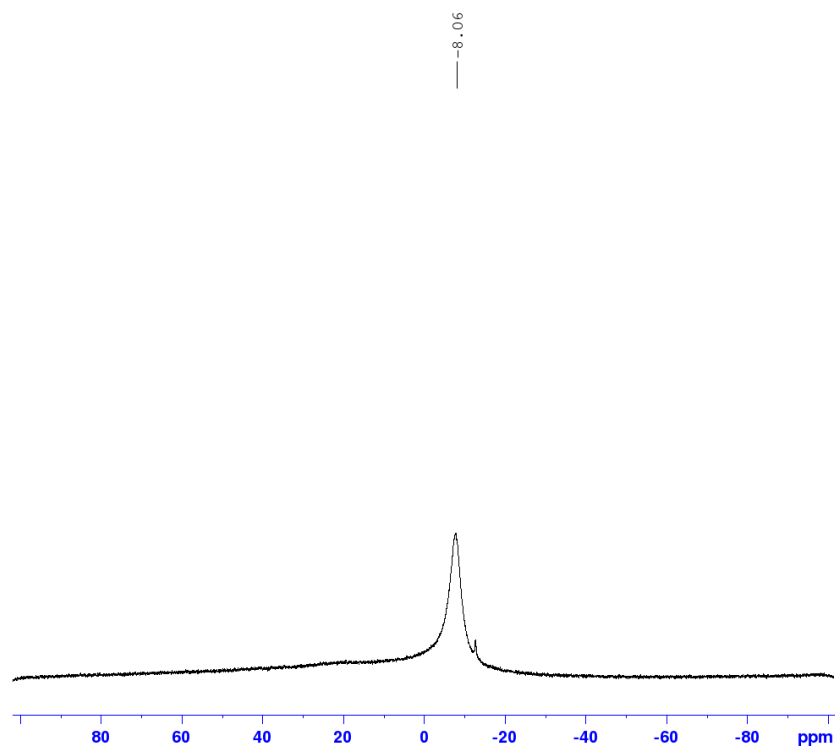


Figure S43. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **9** in C_6D_6 .



```

Current Data Parameters
NAME      zch-a42-20230710-c-1
EXPNO    4
PROCNO   1

F2 - Acquisition Parameters
Date_    20230710
Time     18.57 h
INSTRUM  Avance
PROBHD   Z150364_0011 (
PULPROG  zgbsig
TD       16338
SOLVENT  C6D6
NS       512
DS       4
SWH      32679.738 Hz
FIDRES   4.000458 Hz
AQ       0.2499714 sec
RG       101
DW       15.300 usec
DE       6.50 usec
TE       298.0 K
D1       0.1000000 sec
D2       0 sec
TD0      1
SF01     160.5289560 MHz
NUC1     11B
P1       15.90 usec
P2       31.80 usec
PLW1     50.0000000 W
SF02     500.3425000 MHz
NUC2     1H
CPDPRG2  waltz64
PCPD2    80.00 usec
PLW2     11.04599953 W
PLW12    0.23504999 W

F2 - Processing parameters
SI       16384
SF       160.5289555 MHz
WDW      EM
SSB      0
LB       4.00 Hz
GB       0
PC       1.40
  
```

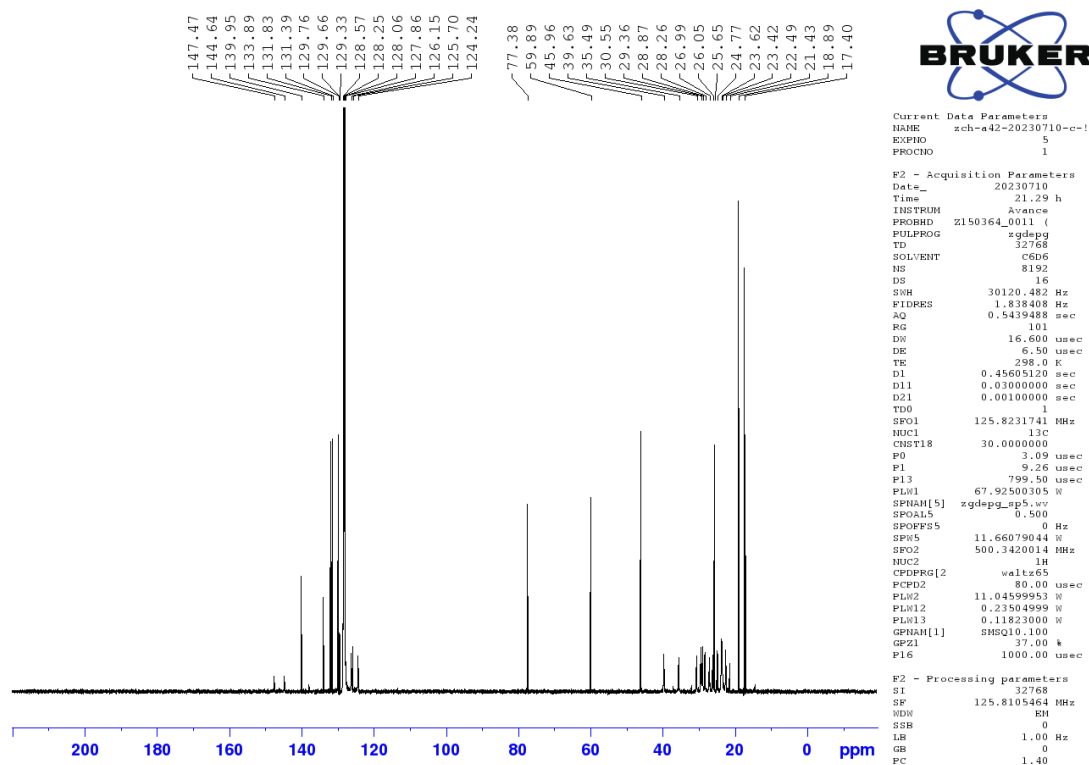
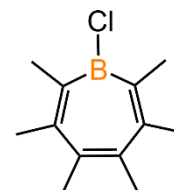


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** in C_6D_6 .

Synthesis of 10^{Cl} (mixed with 2^{Cl}): in a vial, compound 1^{Cl} (15.4 mg, 0.05 mmol, 1.0 equiv) and 2-butyne (27 mg, 0.50 mmol, 10.0 equiv) was dissolved in toluene (2 mL). The solution was stirred at 25 °C for 2 days. All volatiles in the solution were removed under vacuum to obtain a mixture of 10^{Cl} and 2^{Cl} as an orange oil (1: 0.8, respectively).



^1H NMR (500 MHz, C_6D_6): 1.77 (s, 6H, CH_3), 1.82 (s, 6H, CH_3), 2.26 (s, 6H, CH_3); ^{11}B NMR (161 MHz, C_6D_6): 54.73 (br. s); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): 19.56 (s, CH_3), 20.38 (s, CH_3), 21.51 (s, CH_3), 135.90 (s, $\text{C}-\text{CH}_3$), 152.39 (s, $\text{C}-\text{CH}_3$).

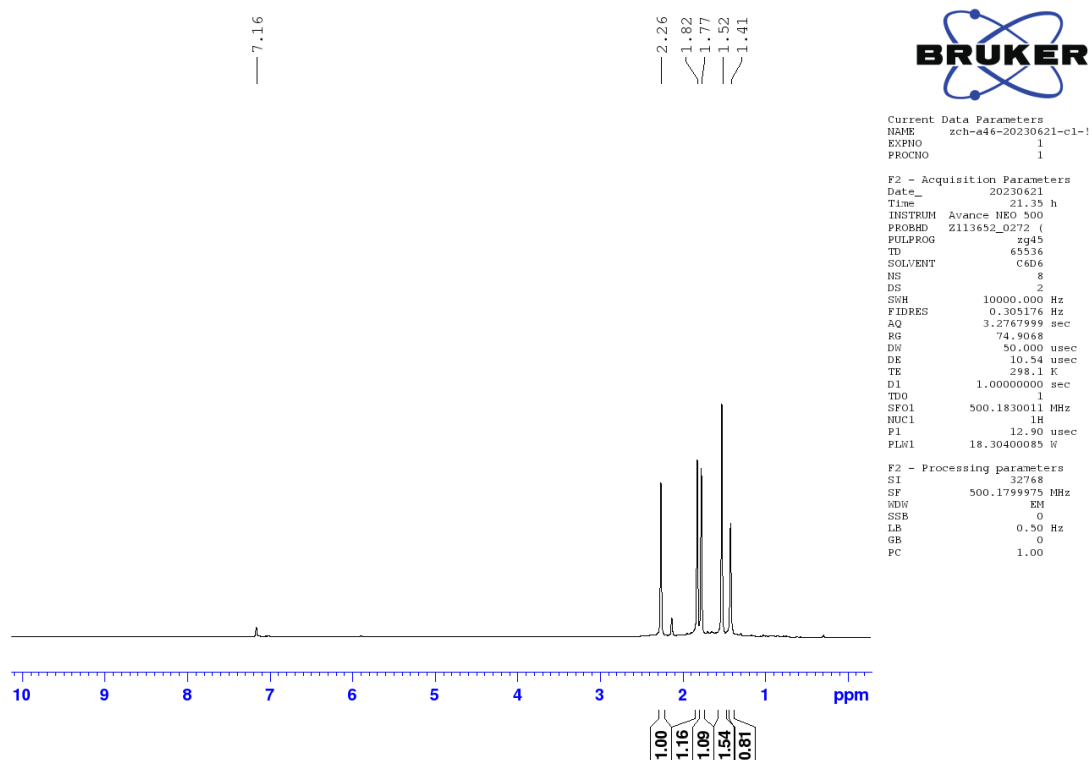


Figure S45. ^1H NMR spectrum of 10^{Cl} mixed with 2^{Cl} in C_6D_6 .

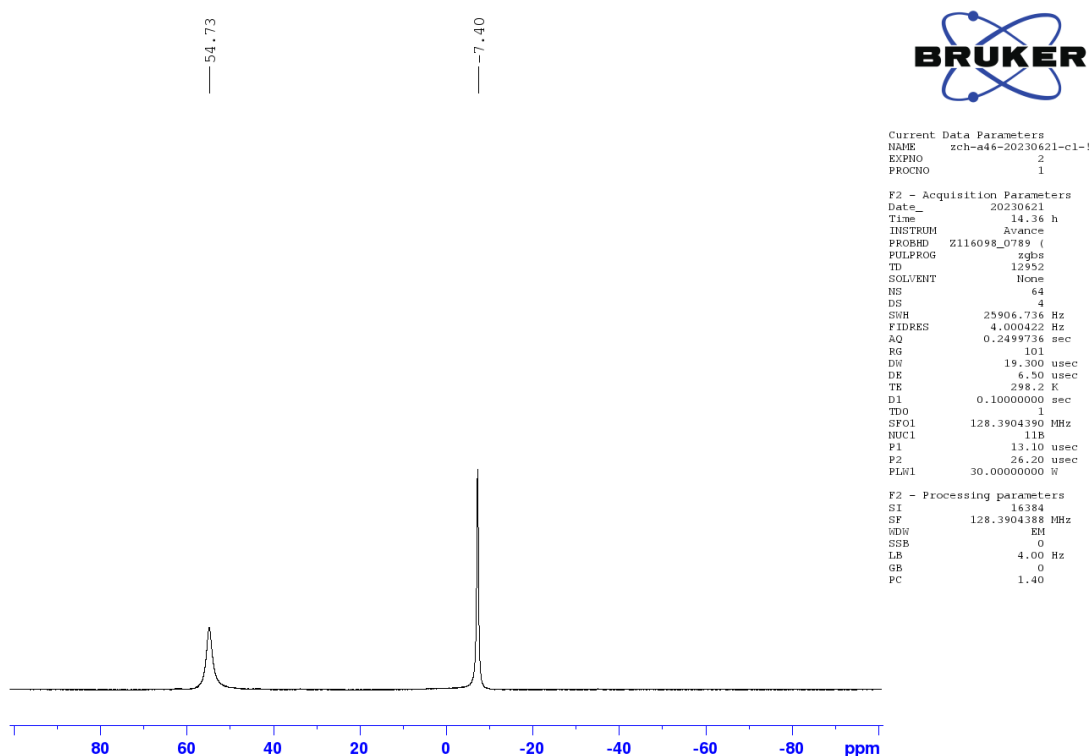


Figure S46. ^{11}B NMR spectrum of 10^{Cl} mixed with 2^{Cl} in C_6D_6 .

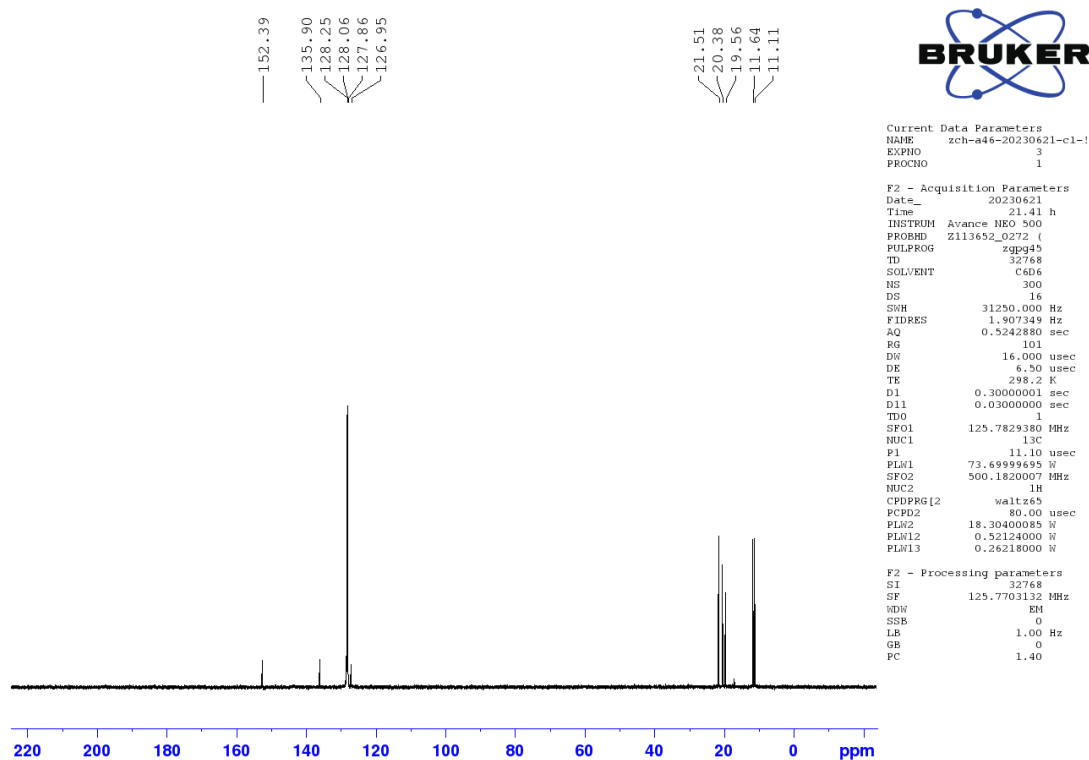
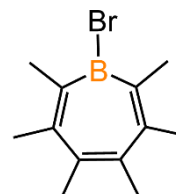


Figure S47. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 10^{Cl} mixed with 2^{Cl} in C_6D_6 .

Synthesis of 10^{Br} (mixed with 2^{Br}): in a vial, compound 1^{Br} (19.9 mg, 0.05 mmol, 1.0 equiv) and 2-butyne (27 mg, 0.50 mmol, 10.0 equiv) was dissolved in toluene (2 mL). The solution was stirred at 25 °C for 2 days. All volatiles in the solution were removed by vacuum to obtain a mixture of 10^{Br} and 2^{Br} as an orange oil (1 : 1, respectively).



^1H NMR (500 MHz, C_6D_6): 1.74 (s, 6H, CH_3), 1.79 (s, 6H, CH_3), 2.33 (s, 6H, CH_3); ^{11}B NMR (161 MHz, C_6D_6): 57.94 (br. s); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): 20.34 (s, $\underline{\text{C}}\text{H}_3$), 20.96 (s, $\underline{\text{C}}\text{H}_3$), 21.56 (s, $\underline{\text{C}}\text{H}_3$), 136.14 (s, $\underline{\text{C}}-\text{CH}_3$), 151.48 (s, $\underline{\text{C}}-\text{CH}_3$).

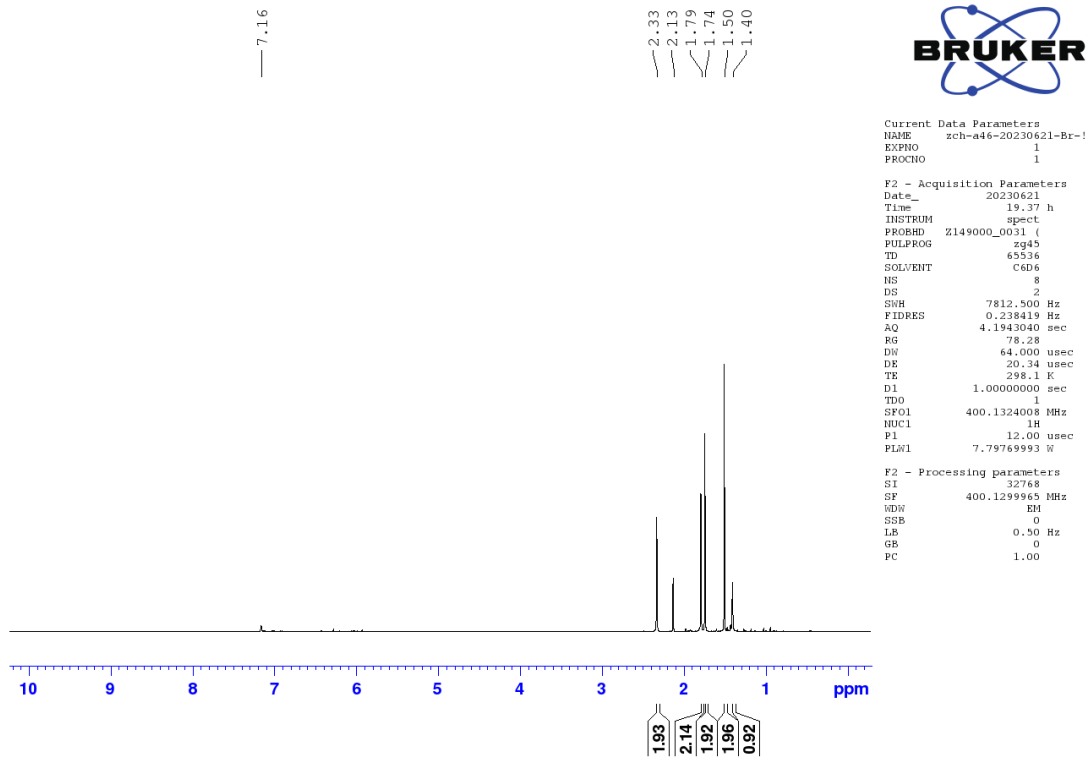


Figure S48. ^1H NMR spectrum of 10^{Br} mixed with 2^{Br} in C_6D_6 .

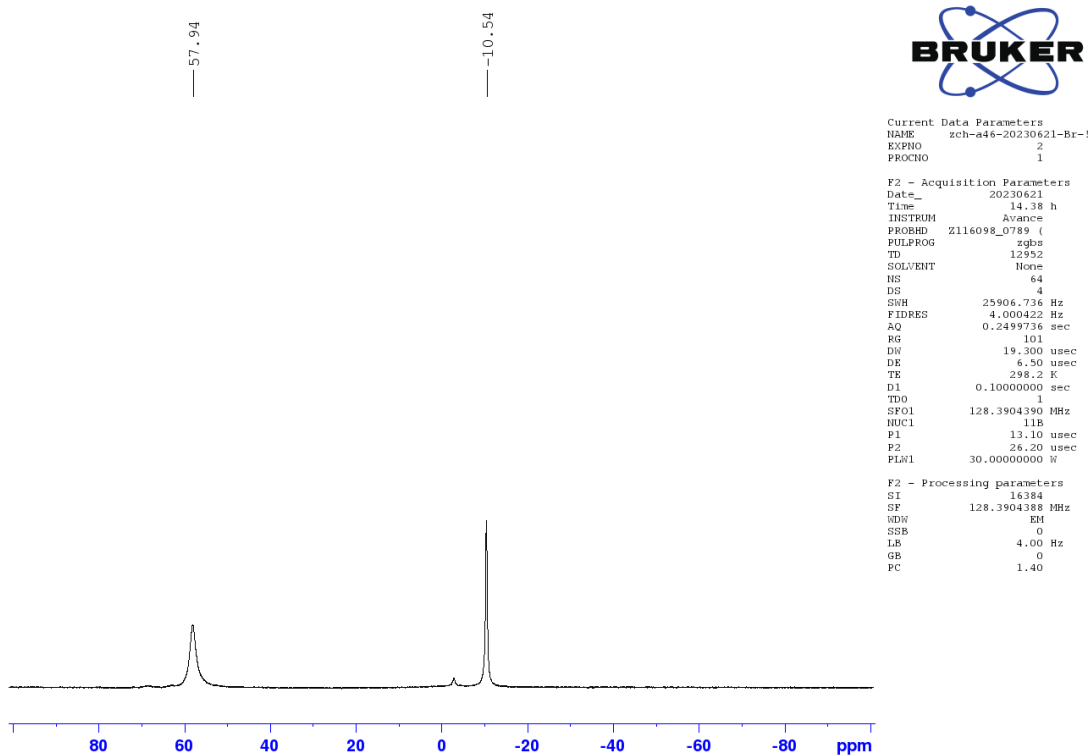


Figure S49. ^{11}B NMR spectrum of 10^{Br} mixed with 2^{Br} in C_6D_6 .

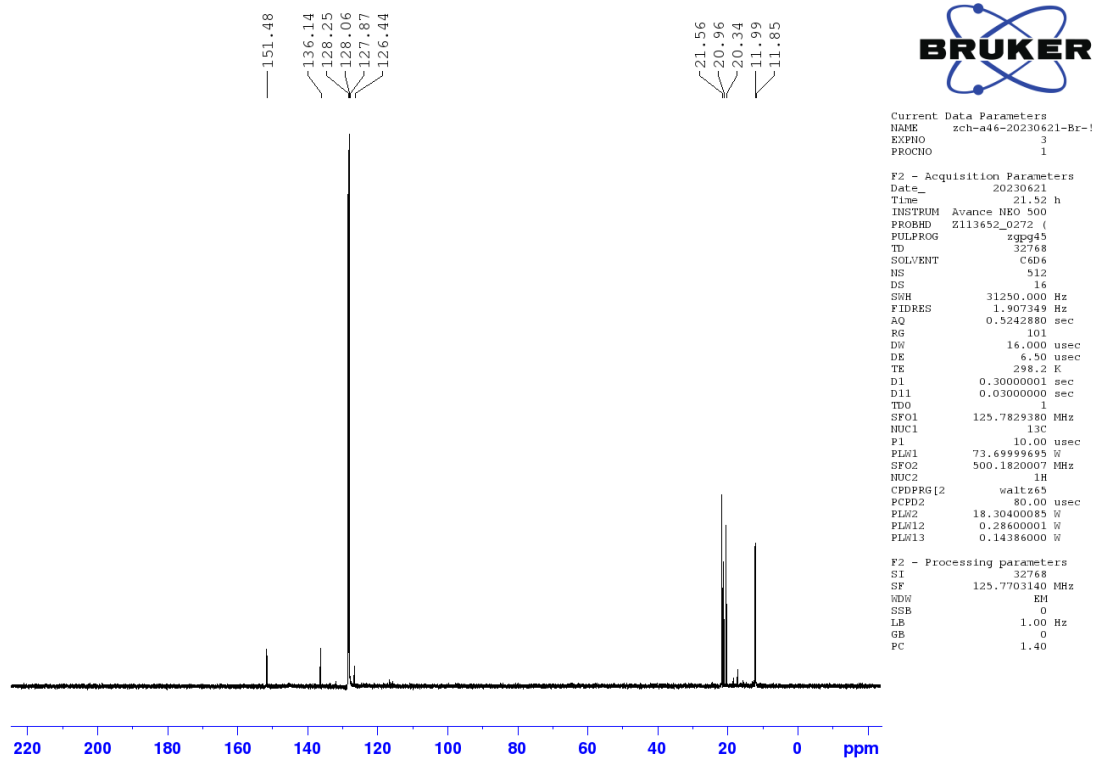


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 10^{Br} mixed with 2^{Br} in C_6D_6 .

Crystal structure

Low-temperature (100 K) diffraction data were collected on a Bruker-AXS X8 Kappa Duo diffractometer with I μ S micro-sources, coupled to a Photon 3 CPAD detector for all structures. Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) was used for all the structures. Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.38A, 2013). The structure was solved with the XT structure solution program using the Intrinsic Phasing solution method¹⁰ and by using Olex2¹¹ as the graphical interface. The model was refined with the ShelXL program¹² using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data as supplementary publication nos. CCDC-2297451 (**1^{Cl}**), 2297452 (**2^{Ph}**), 2297453 (**3**), 2297454 (**4**), 2297455 (**5^{Cl}**), 2297456 (**5^{Br}**), 2297457 (**6**), 2297458 (**7**), 2297459 (**8**), 2297460 (**9**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via Data <https://www.ccdc.cam.ac.uk>.

Table S1 Crystal data and structure refinement for **1^{Cl}**.

Identification code	2297451
Empirical formula	C ₁₆ H ₂₄ B ₂ Cl ₂
Formula weight	308.87
Temperature/K	100.00
Crystal system	monoclinic
Space group	P21
a/ \AA	8.5963(5)
b/ \AA	14.7551(8)
c/ \AA	13.3230(7)
α / $^{\circ}$	90
β / $^{\circ}$	94.308(2)
γ / $^{\circ}$	90
Volume/ \AA^3	1685.11(16)
Z	4
ρ calcg/cm ³	1.217
μ /mm ⁻¹	0.372
F(000)	656.0
Crystal size/mm ³	0.087 \times 0.067 \times 0.012
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^{\circ}$	3.066 to 55.136
Index ranges	-12 \leq h \leq 12, -21 \leq k \leq 21, -19 \leq l \leq 19
Reflections collected	4036
Independent reflections	4036 [Rint = 0.0408, Rsigma = 0.0304]

Data/restraints/parameters	4036/1/377
Goodness-of-fit on F2	1.082
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0545, wR2 = 0.1415
Final R indexes [all data]	R1 = 0.0675, wR2 = 0.1558
Largest diff. peak/hole / e Å ⁻³	0.83/-0.59

Table S2 Crystal data and structure refinement for **2^{Ph}**.

Identification code	2297452
Empirical formula	C18H23B
Formula weight	250.17
Temperature/K	100.00
Crystal system	monoclinic
Space group	P21/c
a/Å	8.7528(3)
b/Å	10.9747(3)
c/Å	15.4186(6)
$\alpha/^\circ$	90
$\beta/^\circ$	91.674(2)
$\gamma/^\circ$	90
Volume/Å ³	1480.47(9)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.122
μ/mm^{-1}	0.062
F(000)	544.0
Crystal size/mm ³	0.067 × 0.045 × 0.023
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	4.556 to 55.2
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	36806
Independent reflections	3433 [Rint = 0.1677, Rsigma = 0.0539]
Data/restraints/parameters	3433/0/178
Goodness-of-fit on F2	1.066
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0611, wR2 = 0.1507
Final R indexes [all data]	R1 = 0.0663, wR2 = 0.1565
Largest diff. peak/hole / e Å ⁻³	0.48/-0.31

Table S3 Crystal data and structure refinement for **3**.

Identification code	2297453
Empirical formula	C22H36BCIN
Formula weight	360.78

Temperature/K	100.00
Crystal system	monoclinic
Space group	P21
a/Å	9.2417(5)
b/Å	10.0889(6)
c/Å	11.8541(8)
α /°	90
β /°	110.192(3)
γ /°	90
Volume/Å ³	1037.33(11)
Z	2
ρ calcg/cm ³	1.155
μ /mm ⁻¹	0.189
F(000)	394.0
Crystal size/mm ³	0.065 × 0.056 × 0.012
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.66 to 62.282
Index ranges	-12 ≤ h ≤ 13, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	59900
Independent reflections	6660 [Rint = 0.0395, Rsigma = 0.0278]
Data/restraints/parameters	6660/1/233
Goodness-of-fit on F ²	1.053
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0482, wR2 = 0.1274
Final R indexes [all data]	R1 = 0.0533, wR2 = 0.1303
Largest diff. peak/hole / e Å ⁻³	1.50/-0.52

Table S4 Crystal data and structure refinement for **4**.

Identification code	2297454
Empirical formula	C ₄₄ H ₇₀ BCIN ₂
Formula weight	673.28
Temperature/K	100.00
Crystal system	monoclinic
Space group	P21/c
a/Å	11.6102(4)
b/Å	20.6129(8)
c/Å	16.4977(5)
α /°	90
β /°	95.3990(10)
γ /°	90
Volume/Å ³	3930.7(2)

Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.138
μ/mm^{-1}	0.130
F(000)	1480.0
Crystal size/mm ³	0.054 × 0.036 × 0.028
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	3.17 to 62.22
Index ranges	-16 ≤ h ≤ 16, -29 ≤ k ≤ 29, -23 ≤ l ≤ 20
Reflections collected	333778
Independent reflections	12596 [Rint = 0.1014, Rsigma = 0.0292]
Data/restraints/parameters	12596/0/448
Goodness-of-fit on F ²	1.070
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0371, wR2 = 0.1012
Final R indexes [all data]	R1 = 0.0478, wR2 = 0.1047
Largest diff. peak/hole / e \AA^{-3}	0.46/-0.27

Table S5 Crystal data and structure refinement for **5^{Cl}**.

Identification code	2297455
Empirical formula	C ₂₃ H ₃₅ BCIN
Formula weight	371.78
Temperature/K	100.00
Crystal system	orthorhombic
Space group	Pbca
a/ \AA	13.334
b/ \AA	12.104
c/ \AA	25.993
$\alpha/^\circ$	90
$\beta/^\circ$	90.02
$\gamma/^\circ$	90
Volume/ \AA^3	4195.0
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.177
μ/mm^{-1}	0.189
F(000)	1616.0
Crystal size/mm ³	0.119 × 0.111 × 0.039
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	3.134 to 68.742
Index ranges	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -37 ≤ l ≤ 37
Reflections collected	276364
Independent reflections	6699 [Rint = 0.0396, Rsigma = 0.0100]

Data/restraints/parameters	6699/0/240
Goodness-of-fit on F2	1.092
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0438, wR2 = 0.1292
Final R indexes [all data]	R1 = 0.0470, wR2 = 0.1316
Largest diff. peak/hole / e Å ⁻³	0.73/-0.43

Table S6 Crystal data and structure refinement for **5^{Br}**.

Identification code	2297456
Empirical formula	C ₂₃ H ₃₅ BBrN
Formula weight	416.24
Temperature/K	100.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.1571(5)
b/Å	13.5618(7)
c/Å	25.8390(13)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	4260.1(4)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.298
μ/mm^{-1}	1.937
F(000)	1760.0
Crystal size/mm ³	0.042 × 0.033 × 0.023
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	3.152 to 49.996
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -30 ≤ l ≤ 30
Reflections collected	217441
Independent reflections	3751 [Rint = 0.0404, Rsigma = 0.0084]
Data/restraints/parameters	3751/1/244
Goodness-of-fit on F2	1.093
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0421, wR2 = 0.1000
Final R indexes [all data]	R1 = 0.0435, wR2 = 0.1006
Largest diff. peak/hole / e Å ⁻³	1.87/-0.75

Table S7 Crystal data and structure refinement for **6**.

Identification code	2297457
Empirical formula	C ₃₆ H ₄₈ BCl ₇ N ₂
Formula weight	767.72

Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	11.7206(8)
b/Å	12.0045(8)
c/Å	15.0853(10)
α /°	108.946(3)
β /°	93.723(2)
γ /°	95.092(3)
Volume/Å ³	1989.7(2)
Z	2
ρ calcd/cm ³	1.281
μ /mm ⁻¹	0.526
F(000)	804.0
Crystal size/mm ³	0.122 × 0.083 × 0.023
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	2.868 to 62.14
Index ranges	-17 ≤ h ≤ 16, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21
Reflections collected	28466
Independent reflections	12481 [Rint = 0.0225, Rsigma = 0.0293]
Data/restraints/parameters	12481/0/427
Goodness-of-fit on F ²	1.032
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0400, wR2 = 0.0982
Final R indexes [all data]	R1 = 0.0462, wR2 = 0.1031
Largest diff. peak/hole / e Å ⁻³	1.70/-1.45

Table S8 Crystal data and structure refinement for **7**.

Identification code	2297458
Empirical formula	C ₃₅ H ₅₃ BBrN
Formula weight	578.50
Temperature/K	100.00
Crystal system	monoclinic
Space group	P21/c
a/Å	10.810(11)
b/Å	12.282(8)
c/Å	23.47(3)
α /°	90
β /°	93.75(5)
γ /°	90
Volume/Å ³	3110(5)

Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.236
μ/mm^{-1}	1.346
F(000)	1240.0
Crystal size/ mm^3	0.091 × 0.054 × 0.023
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.478 to 62.138
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -34 ≤ l ≤ 33
Reflections collected	207305
Independent reflections	9960 [Rint = 0.0401, Rsigma = 0.0154]
Data/restraints/parameters	9960/0/355
Goodness-of-fit on F ²	1.100
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0289, wR2 = 0.0800
Final R indexes [all data]	R1 = 0.0345, wR2 = 0.0822
Largest diff. peak/hole / e \AA^{-3}	0.95/-0.29

Table S9 Crystal data and structure refinement for **8**.

Identification code	2297459
Empirical formula	C ₂₃ H ₃₅ BBrN
Formula weight	416.24
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/ \AA	8.7428(7)
b/ \AA	9.4037(8)
c/ \AA	13.3258(11)
$\alpha/^\circ$	80.686(3)
$\beta/^\circ$	87.975(3)
$\gamma/^\circ$	80.672(3)
Volume/ \AA^3	1066.79(15)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.296
μ/mm^{-1}	1.933
F(000)	440.0
Crystal size/ mm^3	0.102 × 0.098 × 0.021
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.098 to 62.768
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -19 ≤ l ≤ 19
Reflections collected	70071
Independent reflections	6941 [Rint = 0.0428, Rsigma = 0.0207]

Data/restraints/parameters	6941/0/241
Goodness-of-fit on F2	1.073
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0242, wR2 = 0.0646
Final R indexes [all data]	R1 = 0.0283, wR2 = 0.0660
Largest diff. peak/hole / e \AA^{-3}	0.68/-0.46

Table S10 Crystal data and structure refinement for **9**.

Identification code	2297460
Empirical formula	C ₃₆ H ₅₅ BBrCl ₂ N
Formula weight	663.43
Temperature/K	100.00
Crystal system	monoclinic
Space group	P21/c
a/ \AA	14.0779(6)
b/ \AA	12.7663(6)
c/ \AA	20.0966(10)
$\alpha/^\circ$	90
$\beta/^\circ$	91.539(2)
$\gamma/^\circ$	90
Volume/ \AA^3	3610.5(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.220
μ/mm^{-1}	1.311
F(000)	1408.0
Crystal size/mm ³	0.12 × 0.09 × 0.03
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	2.894 to 64.25
Index ranges	-19 ≤ h ≤ 21, -19 ≤ k ≤ 19, -30 ≤ l ≤ 30
Reflections collected	299895
Independent reflections	12617 [R _{int} = 0.0347, R _{sigma} = 0.0118]
Data/restraints/parameters	12617/4/391
Goodness-of-fit on F2	1.064
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0616, wR2 = 0.2118
Final R indexes [all data]	R1 = 0.0679, wR2 = 0.2195
Largest diff. peak/hole / e \AA^{-3}	1.49/-2.43

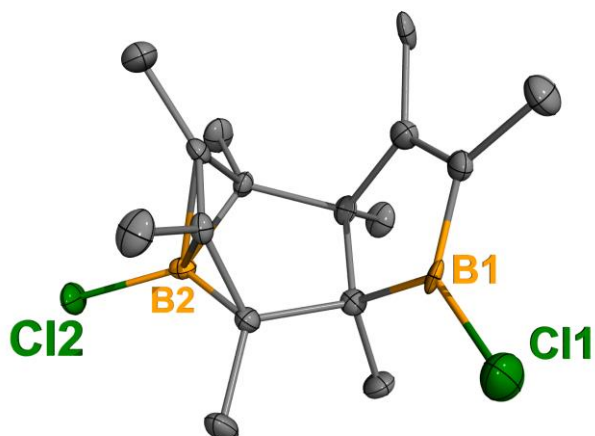


Figure S51. Single crystal structure of **1^{Cl}**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level.

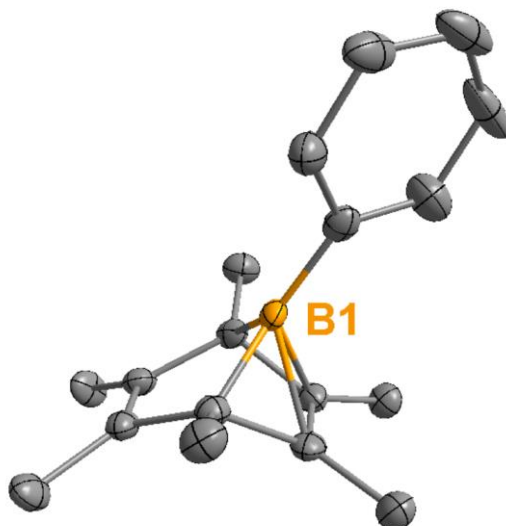


Figure S52. Single crystal structure of **2^{Ph}**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level.

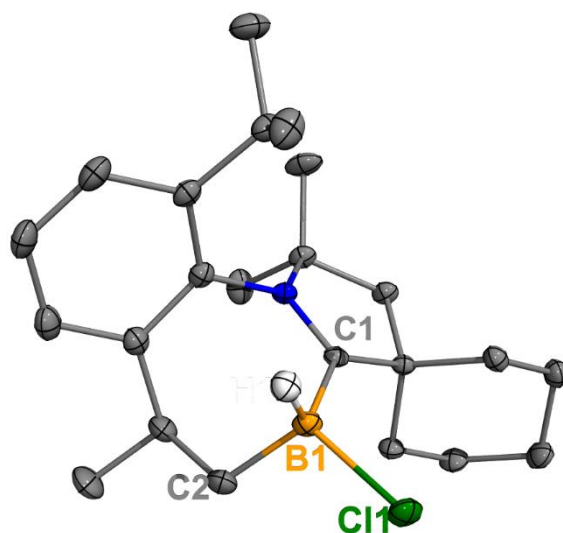


Figure S53. Single crystal structure of **5^{Cl}**. Hydrogen atoms, except for the one connected to B1, have been omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level.

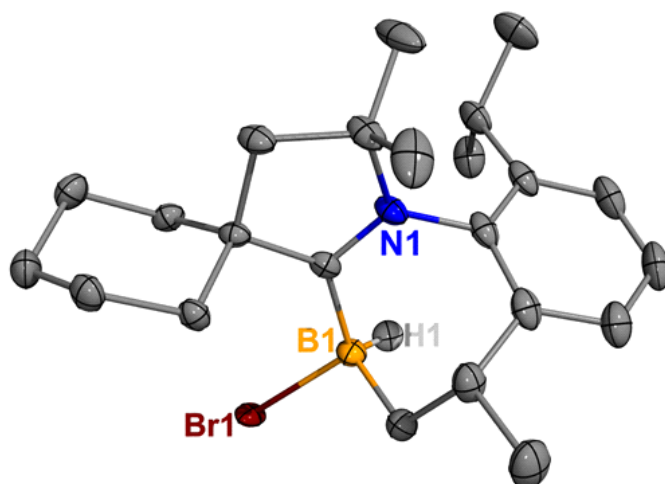


Figure S54. Single crystal structure of **5^{Br}**. Hydrogen atoms, except for the one connected to B1, have been omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level.

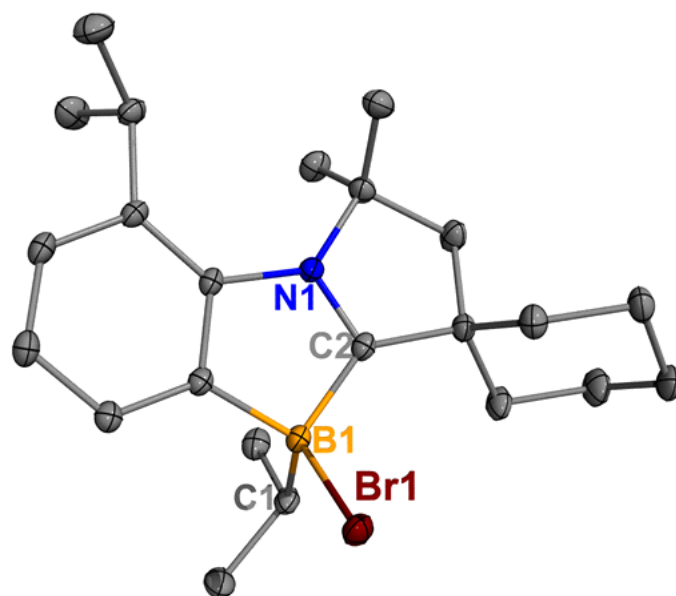


Figure S55. Single crystal structure of **8**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50 % probability level.

Computational Studies

Unless otherwise indicated, all calculations were performed with Gaussian 09 program¹³ and ORCA 5.0.3 program¹⁴. All geometry optimizations and frequency calculation were performed at ω B97xD/6-311G** level of theory¹⁵⁻¹⁹ with Gaussian 09. Frequency calculations were performed to confirm a transition state has only one imaginary frequency, while a local minimum has no imaginary frequency. Intrinsic reaction coordinate (IRC) calculations^{20, 21} were also carried out to further confirm that transition states can link the relevant local minima. Single point energies were calculated at ω B97M-V/def2-QZVPP level of theory²²⁻²⁴ with ORCA 5.0.3. In all cases, computed electronic energies were corrected for thermal energy to obtain the corresponding free energy (all free energies reported at 298.15 K within this SI). All geometry optimizations, frequency calculations, and electronic energy calculations applied the SMD solvation module.²⁵ Static electron-correlation effects of I to IV and TS_{SM-I} to TS_{III-IV} were measured and their FOD plots are displayed in Figure S56.²⁶ All of the intermediates or transition states suggested either no visible FOD or relatively localized FOD. Cartesian coordinates from all structures are compiled in xyz_all.xyz file which could be found at <https://pubs.acs.org>.

Table S11. Computed energies for singlet and triplet borylenes. Computed single-point energies and total Gibbs free energies (G) (Hartree) at the level of ω B97xD/6-311G**, relative electronic energies (ΔE) (kcal/mol), relative Gibbs free energies (ΔG_T) (kcal/mol).

	E_h	ΔE	G_T	ΔG_T
IV (singlet)	-1437.316571		-1436.828204	
IV (triplet)	-1437.310514	3.81591	-1436.825355	1.79487
IV-Br (singlet)	-3551.28128		-3550.794479	
IV-Br (triplet)	-3551.275085	3.90285	-3550.788872	3.53241

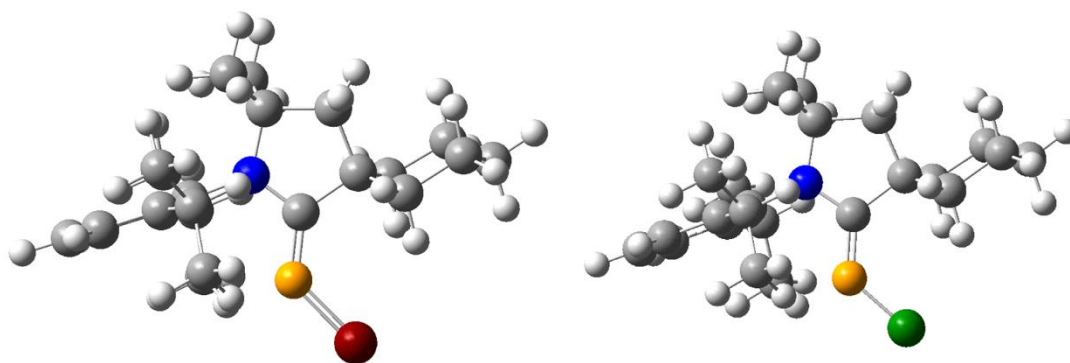


Figure S56. Optimized structure of triplet IV^{Br} (left) and IV (right).

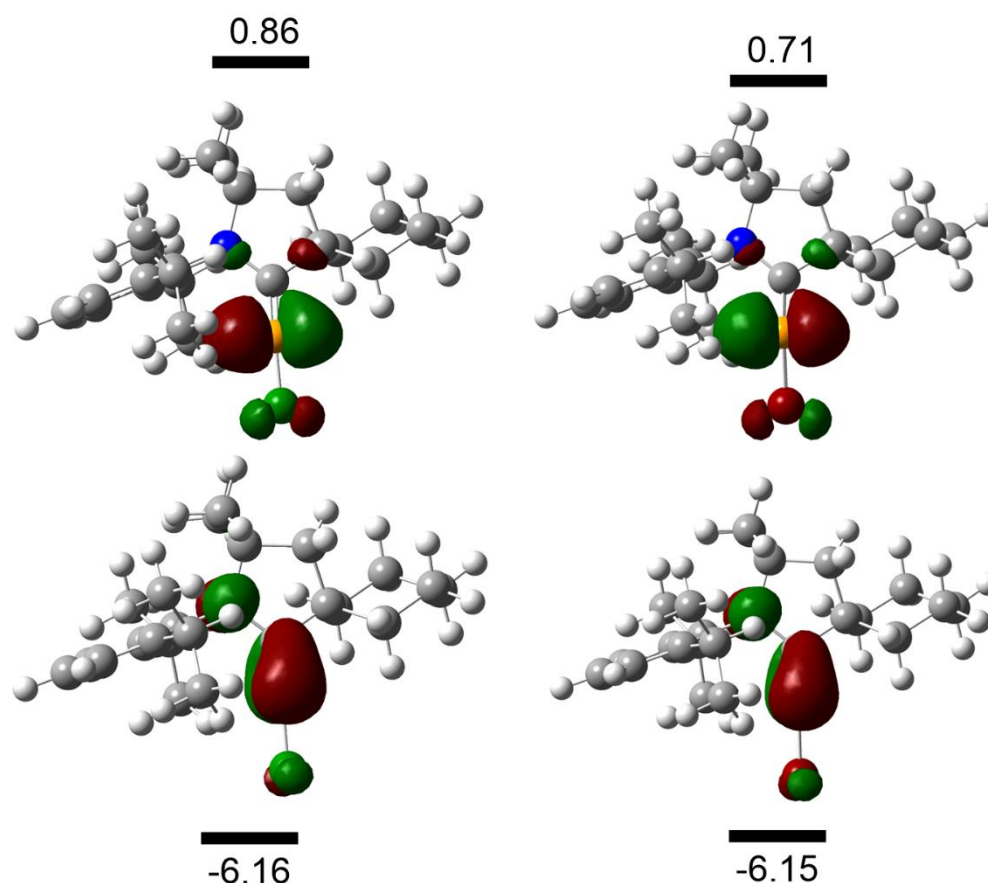


Figure S57. HOMO-LUMO gap of singlet **IV** (left) and **IV^{Br}** (right). The unit of energies is eV and an isovalue of 0.06 ($\text{e}/\text{\AA}^3/2$) was used in the isosurface contour plots.

Table S12. Computed energies for the release of CAAC–chloroborylene in toluene solution. Computed Single-point energies ($E_{\text{n}1}$, $\omega\text{B97xD}/6\text{-}311\text{G}^{**}$; $E_{\text{n}2}$ $\omega\text{B97M-V}/\text{def2-QZVPP}$), Gibbs free-energy corrections (G_{c} , $\omega\text{B97xD}/6\text{-}311\text{G}^{**}$) (Hartree), total Gibbs free energies ($G_{\text{T}} = E_{\text{n}2} + G_{\text{c}}$) (Hartree), relative electronic energies (ΔE) (kcal/mol), relative Gibbs free energies (ΔG_{T}) (kcal/mol).

	$E_{\text{n}1}$	G_{c}	$E_{\text{n}2}$	G_{T}	ΔG_{T}	ΔE
2^{O}	-953.191335	0.233547	-953.183658	-952.950111		
CAAC	-952.227229	0.485641	-952.222040	-951.736399	0.000000	0.000000
$\text{TS}_{\text{SM-I}}$	-1905.420707	0.745392	-1905.402031	-1904.656639	18.818251	2.309731
I	-1905.449456	0.749715	-1905.430241	-1904.680526	3.769510	-15.462499
$\text{TS}_{\text{I-II}}$	-1905.423063	0.748385	-1905.401741	-1904.653356	20.886900	2.492790
II	-1905.463108	0.747583	-1905.434677	-1904.687094	-0.367996	-18.256846
$\text{TS}_{\text{II-III}}$	-1905.417885	0.750183	-1905.394023	-1904.643840	26.882125	7.355275
III	-1905.453023	0.753546	-1905.434459	-1904.680913	3.526167	-18.119373
$\text{TS}_{\text{III-IV}}$	-1905.41271	0.74725	-1905.396934	-1904.649684	23.200374	5.521314
IV	-1437.316571	0.48837	-1437.307478			
C_6Me_6	-468.112472	0.230473	-468.105126	-1904.693763	-4.569907	-4.350667
$\text{TS}_{\text{I-IV}}$	-1905.382373	0.747226	-1905.364224	-1904.616998	43.792420	26.128480

Table S13. Computed energies for the release of CAAC–bromoborylene, C–H activation, and the conversion from **7** to **9** in toluene solution. Computed Single-point energies (E_{h1} , ω B97xD/6-311G**; E_{h2} ω B97M-V/def2-QZVPP), Gibbs free-energy corrections (G_c , ω B97xD/6-311G**) (Hartree), total Gibbs free energies ($G_T = E_{h2} + G_c$) (Hartree), relative electronic energies (ΔE) (kcal/mol), relative Gibbs free energies (ΔG_T) (kcal/mol).

	E_{h1}	G_c	E_{h2}	G_T	ΔG_T	ΔE
9	-4019.484272	0.745854	-4019.358549	-4018.612695	-40.268901	-38.165961
TS _{IV-9} ^{Br}	-4019.394271	0.744142	-4019.267937	-4018.523795	15.737879	18.919379
IV ^{Br} + C ₆ Me ₆	-4019.393752	0.717274	-4019.268151	-4018.550877	-1.323756	18.784584
TS _{III-IV} ^{Br}	-4019.371489	0.744712	-4019.248644	-4018.503932	28.252035	31.074435
III ^{Br}	-4019.415646	0.749503	-4019.290004	-4018.540501	5.213521	5.017591
TS _{7-III} ^{Br}	-4019.384842	0.748748	-4019.255770	-4018.507022	26.305070	26.584790
7	-4019.430646	0.749192	-4019.297968	-4018.548776	0.000000	0.000000
TS ₇₋₉ ^{Br}	-4019.370316	0.747196	-4019.239857	-4018.492661	35.352771	36.610251
9	-4019.484272	0.745854	-4019.358549	-4018.612695	-40.268901	-38.165961
C-H activation						
IV ^{Br}	-3551.281280	0.486801	-3551.163025	-3550.676224	0.000000	0.000000
TS _{IV-5} ^{Br}	-3551.267754	0.487579	-3551.153324	-3550.665745	6.602299	6.112159
5 ^{Br}	-3551.361558	0.491492	-3551.247131	-3550.755639	-50.031078	-52.986408

Table S14. Computed energies for the release of CAAC–bromoborylene and the conversion from II^{Br} to V^{Br} in DCM solution. Computed Single-point energies (E_{h1} , ω B97xD/6-311G**; E_{h2} ω B97M-V/def2-QZVPP), Gibbs free-energy corrections (G_c , ω B97xD/6-311G**) (Hartree), total Gibbs free energies ($G_T = E_{h2} + G_c$) (Hartree), relative electronic energies (ΔE) (kcal/mol), relative Gibbs free energies (ΔG_T) (kcal/mol).

	E_{h1}	G_c	E_{h2}	G_T	ΔG_T	ΔE
C ₆ Me ₆	-468.114814	0.230080	-468.106702			
IV ^{Br}	-3551.284817	0.486610	-3551.165629	-4018.555641	5.405211	25.456851
TS _{III-IV} ^{Br}	-4019.377965	0.744807	-4019.253601	-4018.508794	34.918563	37.256493
III ^{Br}	-4019.423730	0.750017	-4019.296721	-4018.546704	11.035483	10.091113
TS _{7-III} ^{Br}	-4019.394593	0.746647	-4019.264035	-4018.517388	29.504853	30.683583
7	-4019.446859	0.748518	-4019.312739	-4018.564221	0.000000	0.000000
TS ₇₋₉ ^{Br}	-4019.384695	0.741824	-4019.254550	-4018.512726	32.441932	36.659152
9	-4019.493778	0.744713	-4019.366246	-4018.621533	-36.106610	-33.709460

Table S15. Computed energies for the conversion from borepin VII^{Br} to boranorbornadiene II^{Br} in toluene solution. Computed Single-point energies (E_{h1} , ω B97xD/6-311G**; E_{h2} ω B97M-V/def2-QZVPP), Gibbs free-energy corrections (G_c , ω B97xD/6-311G**) (Hartree), total Gibbs free energies ($G_T = E_{h2} + G_c$) (Hartree), relative electronic energies (ΔE) (kcal/mol), relative Gibbs free energies (ΔG_T) (kcal/mol).

	E_{h1}	G_c	E_{h2}	G_T	ΔG_T	ΔE
7	-4019.415646	0.749503	-4019.290004	-4018.540501	0.000000	0.000000

TS _{7-VII} ^{Br}	-4019.398008	0.749931	-4019.272734	-4018.522803	11.149431	10.879791
VII ^{Br}	-4019.404125	0.746333	-4019.279926	-4018.533593	4.351706	6.348806

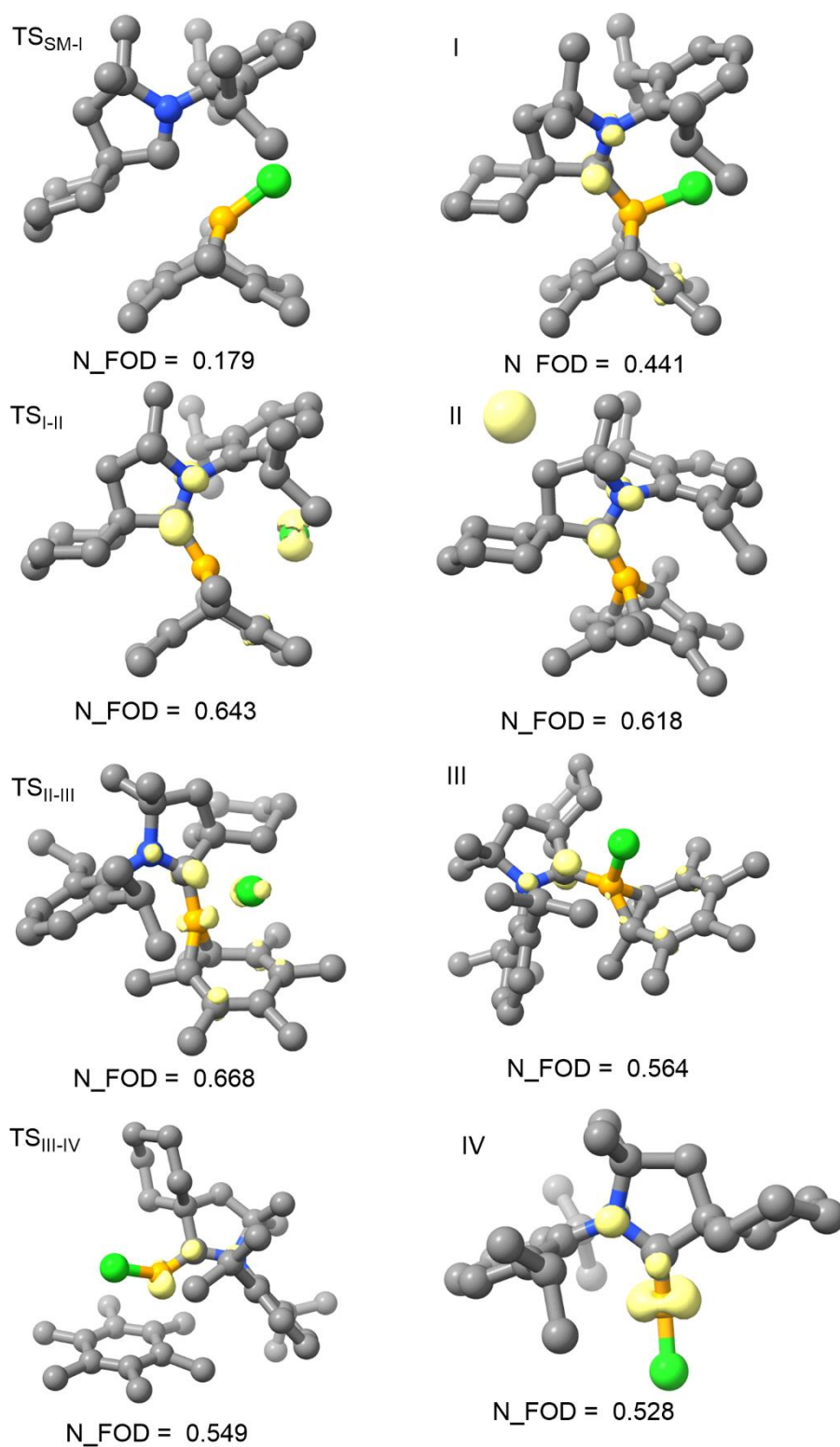


Figure S58. FOD plots at $\sigma=0.005$ e Bohr⁻³ for intermediates I, II, III, and IV and transition states TS_{SM-I}, TS_{I-II}, TS_{II-III}, and TS_{III-IV} (FOD in yellow).

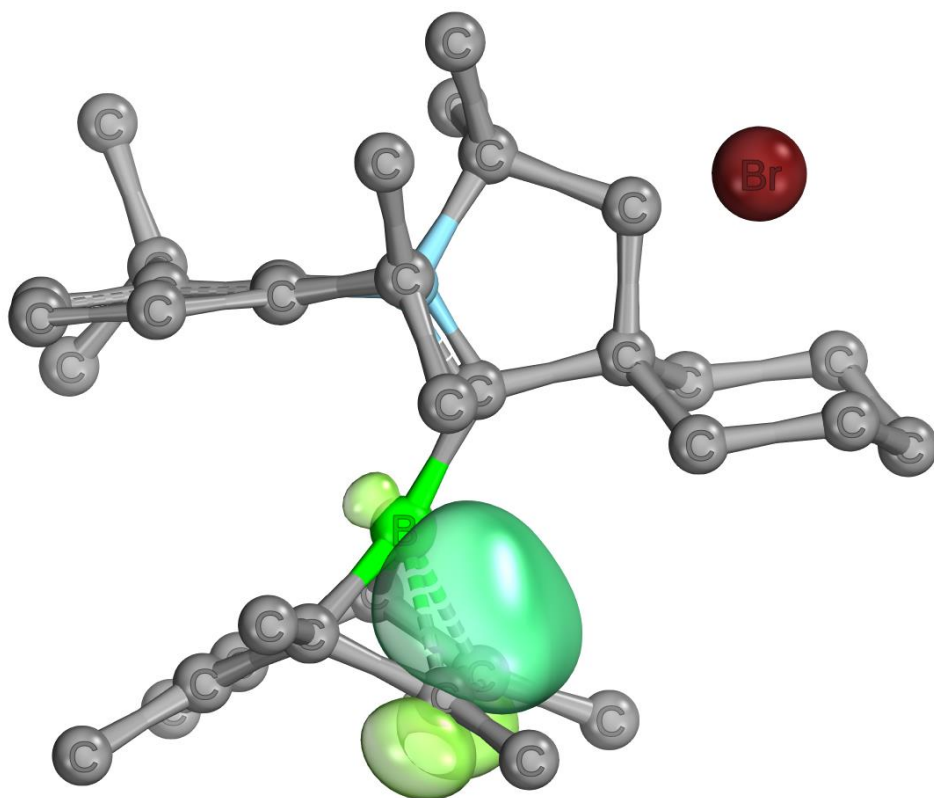


Figure S59. The 3c-2e bond of compound **7** depicted by IBO view.

Discussion on other possible mechanism

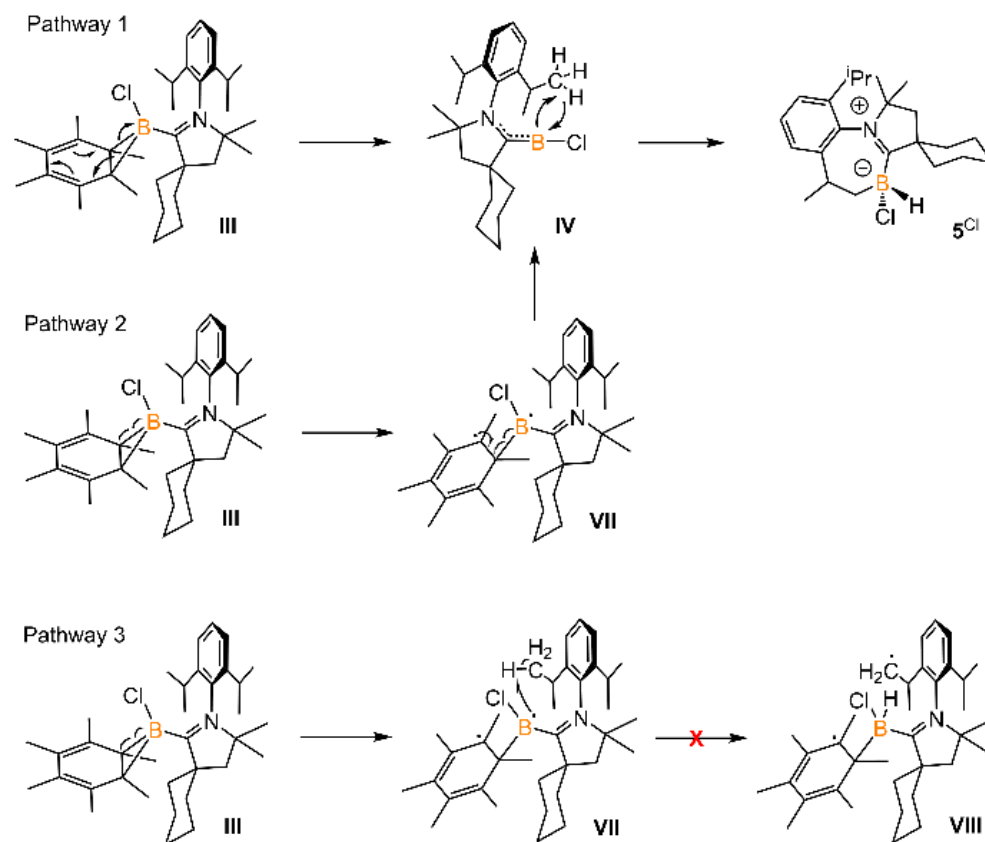


Figure 60. Possible reaction pathways leading to the C–H activation product

In all, there are three possible pathways to the formation of C_6Me_6 and the C–H activation product from boranorcaradiene.

The first pathway is what we proposed and preferred in the manuscript. The borylene-releasing step is a two-electron step. The second pathway still involves the borylene intermediate, while the borylene-releasing step is a stepwise process. The C–B bond undergoes homolysis cleavage, giving a boron radical **VII**. The second C–B bond homolysis occurs and yields the intermediate **IV**. The third pathway does not involve the borylene intermediate. Starting from the boron radical **VII**, it abstracts a hydrogen atom of the isopropyl group and yields a primary carbon radical.

We currently cannot exclude the possibility of the second pathway while we argue that the third pathway is unlikely to be the case. Braunschweig *et al.* isolated a similar chloroborane radical, and the compound showed no reaction to the C–H bond of the CAAC ligand at room temperature.²⁷ Theoretically, it is hard to yield an unstable primary carbon radical from a stable CAAC-stabilized boron radical.

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