Electronic Supplementary Information

Ring-Opening and Ring-Expansion Reactions of Carborane-Fused Borirane

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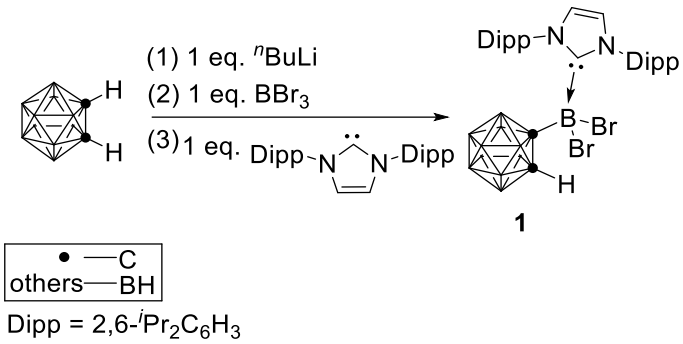
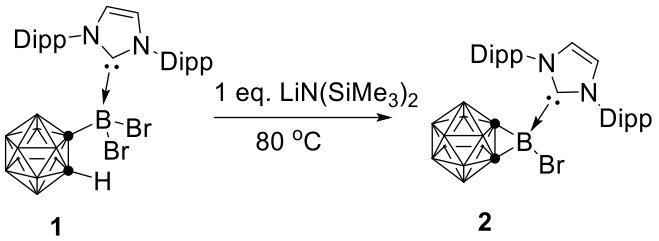
Experimental Section

General Procedures. All operations were carried out under a dry argon atmosphere using standard Schlenk and glovebox techniques. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker DPX 400/500 spectrometer at 400/500 MHz, 100/125 MHz and 128/160 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Elemental analyses were performed by MEDAC Ltd, U.K., or the Shanghai Institute of Organic Chemistry, CAS, China. Mass spectrum were obtained on solariX XR spectrometer. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Compound 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Idipp) was prepared according to the literature procedure.[1] All other chemicals were purchased from either Aldrich, J&K or Acros Chemical Co. and used as received unless otherwise specified.



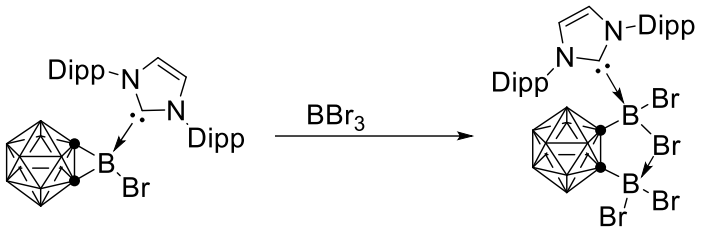
Preparation of 1-BBr_2Idipp-1,2-$C_2B_{10}H_{11}$ (1). To a toluene solution (30 mL) of *o*-$C_2B_{10}H_{12}$ (1.152 g, 8.0 mmol) was slowly added via syringe a hexane solution of n-BuLi (1.6 M, 5.0 mL, 8.0 mmol) at 0 °C with stirring. The reaction mixture was then allowed to warm to room temperature and stirred overnight, to which was added via syringe a dichloromethane solution of BBr_3 (1.0 M, 8.0 mL, 8.0 mmol) at -78 °C. The reaction mixture was allowed to slowly warm to room temperature within 4 h and stirred at room temperature for another 12 h. Removal of the inorganic salts by filtration, and the volatiles by vacuum, gave a brownish liquid. The brownish liquid was then suspended in toluene (20 mL), to which was slowly added a toluene solution (20 mL) of 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (Idipp; 3.104 g, 8.0 mmol) at 0 °C via syringe. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. After removal of the solvent under vacuum, the residue was washed with a mixed solvent of hexane and toluene (V/V = 2/1) and then recrystallized from toluene (15 mL) at room temperature via slow evaporation to give compound **1** as colorless crystals (3.033 g, 54 %). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.52 (t, *J* = 7.7 Hz, 2H; aromatic C*H*), 7.32 (s, 2H; NC*H*), 7.30 (m, 4H; aromatic C*H*), 4.24 (s, 1H; Cage *H*), 2.83 (m, 4H; C*H*Me_2), 1.49 (d, *J* = 6.6 Hz, 12H; CH*Me*$_2$), 1.10 (d, *J* = 6.6 Hz, 12H; CH*Me*$_2$). ^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_2): δ 146.57 (N*C*N), 137.2, 131.5, 127.7, 124.2 (N*CC*N, aromatic *C*), 67.6 (Cage *C*), 30.2 (*C*HMe$_2$), 27.1, 22.6 (CH*Me*$_2$). ^{11}B NMR (160 MHz, CD_2Cl_2): δ -3.0 (br, J_{BH}

unresolved; 2B), -7.4 (br, J_{BH} unresolved; 1B), -8.0 (br, J_{BH} unresolved; 2B), -10.6 (br, J_{BH} unresolved; 2B), -12.6 (br, J_{BH} unresolved; 4B). M.p.: 204.0 °C (dec.); HRMS: m/z calcd for $C_{29}H_{47}B_{11}Br_2N_2^-(M)^-$: 702.3203. Found: 702.3237. Anal. Calcd for $C_{29}H_{47}B_{11}Br_2N_2$ (M): C 49.59, H 6.74, N 3.99. Found: C 49.57, H 6.80, N 3.91.



1 2

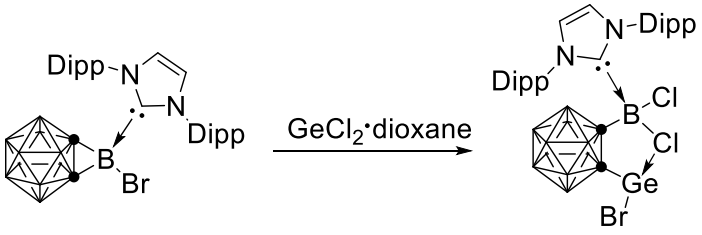
Preparation of 1,2-BBr(Idipp)-1,2-$C_2B_{10}H_{10}$ (2).To a mixture of **1** (3.510 g, 5.0 mmol) and lithium bis(trimethylsilyl)amide (835 mg, 5.0 mmol) was added toluene (30 mL) at room temperature. The reaction mixture was allowed to stir at 80 °C overnight. After removal of the volatiles under reduced pressure, the residue was extracted with toluene (3 x 15 mL). The resultant light red toluene solution was concentrated to about 10 mL. Slow evaporation of the solvent gave compound **2** as colorless crystals (2.174 g, 70 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.56 (t, *J* = 7.8 Hz, 2H; aromatic C*H*), 7.41-7.36 (m, 4H; aromatic C*H*), 7.25 (s, 2H; NC*H*), 2.77, 2.69 (m, 4H; C*H*Me$_2$), 1.43 (d, *J* = 6.7 Hz, 6H; CH*Me$_2$*), 1.33 (d, *J* = 6.6 Hz, 6H; CH*Me$_2$*), 1.13 (d, *J* = 6.8 Hz, 6H; CH*Me$_2$*),1.08 (d, *J* = 6.8 Hz, 6H; CH*Me$_2$*). ^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_2): δ 146.7 (N*C*N), 145.2, 133.7, 131.8, 125.3, 125.2, 125.1 (N*CC*N, aromatic *C*), 68.2 (Cage *C*), 29.5, 29.4 (*C*HMe$_2$), 26.2, 26.1 (CH*Me$_2$*), 22.9, 22.6 (CH*Me$_2$*). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 1.2 (d, J_{BH} = 142 Hz, 2B), -2.9 (br, J_{BH} unresolved; 1B), -7.7 (br, J_{BH} unresolved; 2B), -9.2 (br, J_{BH} unresolved; 5B), -13.5 (s, 1B). M.p.: 126.8 °C (dec.); HRMS: m/z calcd for $C_{29}H_{47}B_{11}BrN_2^+(M+H)^+$: 622.4017. Found: 622.4029. Anal. Calcd for $C_{29}H_{46}B_{11}BrN_2$ (M): C 56.04, H 7.46, N 4.51. Found: C 56.42, H 7.41, N 4.55.



2 3

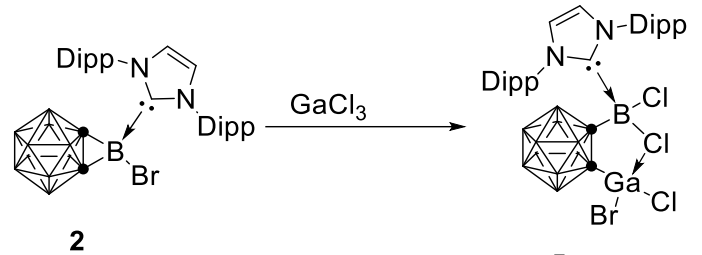
Preparation of 1-[BBr_2(Idipp)]-2-BBr_2-1,2-$C_2B_{10}H_{10}$ (3). To a toluene solution (10 mL) of **2** (311 mg, 0.5 mmol) was added via syringe a dichloromethane solution of BBr_3 (1.0 M, 0.5 mL, 0.5 mmol) at room temperature. The reaction mixture was allowed to stir at room temperature overnight. The colorless solution was concentrated to about 3 mL and stand at -30 °C, which gave compound **3** as colorless crystals (327 mg, 75 %). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.59 (t, *J*=7.9 Hz, 2H; aromatic C*H*), 7.41 (s, 2H; NC*H*), 7.38 (d, *J*=7.6 Hz, 2H; aromatic C*H*), 7.34 (d, *J*=7.7 Hz, 2H; aromatic C*H*), 2.68 (m, 4H; C*H*Me$_2$), 1.53 (d, *J*=6.3 Hz, 6H; CH*Me$_2$*), 1.43 (d, *J*=6.4 Hz, 6H; CH*Me$_2$*), 1.14 (d, *J*=6.4 Hz, 6H; CH*Me$_2$*), 1.08 (d, *J*=6.5 Hz, 6H; CH*Me$_2$*).

^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_2): δ 146.8, 145.9 (N*C*N), 135.4, 132.4, 128.4, 124.9, 124.7 (N*CC*N, aromatic *C*), 30.4, 30.1 (*C*HMe$_2$), 27.1 (CH*Me*$_2$), 22.5, 22.3 (CH*Me*$_2$). ^{11}B NMR (160 MHz, CD_2Cl_2): δ 3.9 (s, 1B), -0.1 (s, 1B), -3.1 (br, J_{BH} unresolved; 2B), -5.1 (br, J_{BH} unresolved; 1B), -7.1 (br, J_{BH} unresolved; 1B), -8.3 (br, J_{BH} unresolved; 2B), -12.5 (br, J_{BH} unresolved; 4B). M.p.: 221.4 °C (dec.); HRMS: m/z calcd for $C_{29}H_{46}N_2B_{12}Br_4^-$ $(M)^-$: 872.1569. Found: 872.1569. Anal. Calcd for $C_{32.5}H_{50}B_{12}Br_4N_2$ (M+0.5C_7H_8): C 42.52, H 5.49, N 3.05. Found: C 42.35, H 5.57, N 3.02.



2 **4**

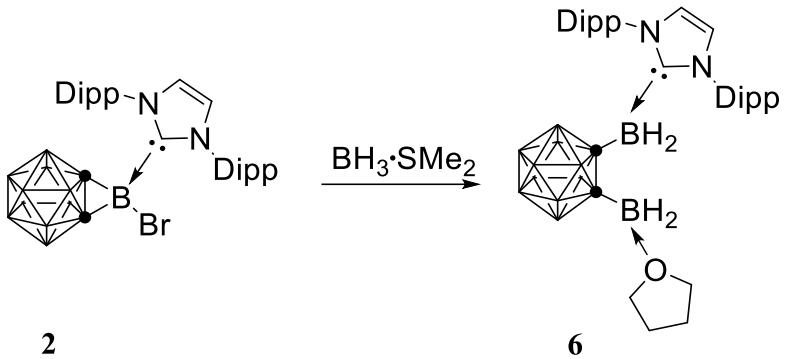
Preparation of 1-[BCl$_2$(Idipp)]-2-GeBr-1,2-$C_2B_{10}H_{10}$ (4). To a toluene solution (10 mL) of **2** (311 mg, 0.5 mmol) and was added germanium chloride dioxane complex (116 mg, 0.5 mmol) at room temperature. The reaction mixture was allowed to stir at room temperature overnight. After filtration, the resulting solution was concentrated to about 3 mL. Slow evaporation of the solvent at room temperature over 3 days gave compound **4** as colorless crystals (260 mg, 68%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.56 (t, *J* = 7.6 Hz, 2H; aromatic C*H*), 7.36-7.32 (m, 6H; NC*H*, aromatic C*H*), 2.72 (m, 4H; C*H*Me$_2$), 1.47 (d, *J* = 5.4 Hz, 12H; CH*Me*$_2$), 1.11 (d, *J* = 6.0 Hz, 12H; CH*Me*$_2$). ^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_2): δ 146.4 (N*C*N), 135.5, 131.9, 127.9, 124.4 (N*CC*N, aromatic *C*), 30.2 (*C*HMe$_2$), 27.1, 22.3 (CH*Me*$_2$). ^{11}B NMR (160 MHz, CD_2Cl_2): δ 5.2 (s, 1B), -2.3 (d, J_{BH} =127 Hz, 2B), -4.9 (br, J_{BH} unresolved; 2B), -9.8 (br, J_{BH} unresolved; 2B), -11.4 (br, J_{BH} unresolved; 4B). M.p.: 167.7 °C (dec.); HRMS: m/z calcd for $C_{29}H_{46}N_2B_{11}BrGeCl_2^-$ $(M)^-$: 765.2527. Found: 765.2524. Anal. Calcd for $C_{39.5}H_{58}B_{11}BrCl_2GeN_2$ (M+1.5C_7H_8): C 52.52, H 6.47, N 3.10. Found: C 52.74, H 6.68, N 2.94.



2 **5**

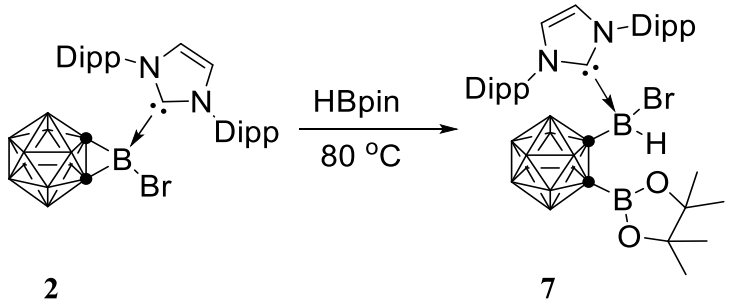
Preparation of 1-[BCl$_2$(Idipp)]-2-GaClBr-1,2-$C_2B_{10}H_{10}$ (5). To a toluene solution (10 mL) of **2** (311 mg, 0.5 mmol) was added gallium trichloride (88 mg, 0.5 mmol) at room temperature. The reaction mixture was allowed to stir at room temperature overnight. After removal of the solvent under reduced pressure, the resulting white solid was washed with toluene (2 x 2 mL) and dried under vacuum to give **5** as a white powder (255 mg, 64%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.57 (t, *J* = 7.7 Hz, 2H; aromatic C*H*), 7.39-7.34 (m, 6H; NC*H*, aromatic C*H*), 2.68

(m, 4H; C*H*Me$_2$), 1.47 (d, *J* = 6.6 Hz, 12H; CH*Me$_2$*), 1.11 (d, *J* = 6.7 Hz, 12H; CH*Me$_2$*). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 146.2 (N*C*N), 132.2, 128.2, 124.6 (N*CC*N, aromatic *C*), 30.2 (*C*HMe$_2$), 27.1, 22.3 (CH*Me$_2$*). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 5.3 (s, 1B), -1.4 (d, J_{BH} = 104 Hz, 2B), -4.9 (d, J_{BH} = 141 Hz, 2B), -10.9 (br, J_{BH} unresolved; 6B). M.p.: 275.0 °C (dec.); HRMS: m/z calcd for $C_{29}H_{46}N_2B_{11}BrGaCl_3^-$ (M)$^-$: 797.2241. Found: 797.2252. Anal. Calcd for $C_{32.5}H_{50}B_{11}Br\,Cl_3GaN_2$ (M+0.5C_7H_8): C 46.27, H 5.97, N 3.32. Found: C 46.37, H 6.02, N 3.06.



2 **6**

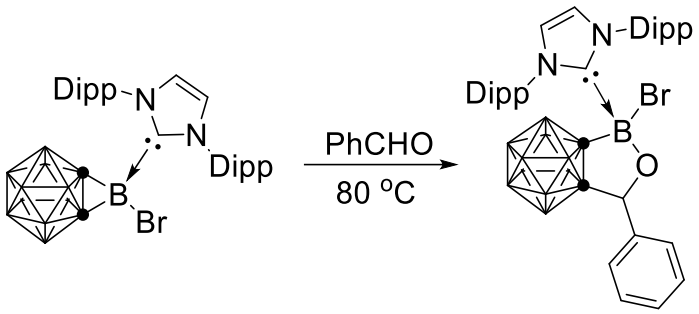
Preparation of 1-[BH$_2$(Idipp)]-2-BH$_2$THF-1,2-C$_2$B$_{10}$H$_{10}$ (6).To a toluene solution (10 mL) of **2** (311 mg, 0.5 mmol) was slowly added via syringe a dichloromethane of BH_3·SMe_2 (1.0 M, 1.0 mL, 1.0 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature for 2 h and stirred overnight. The ^{11}B NMR showed the presence of H_2BBr·SMe_2 at −19.2 ppm. After removal of the solvent under reduced pressure, the resulting white solid was washed with THF (2 x 2 mL). The residue was recrystallized from THF to give compound **6** as colorless crystals (286 mg, 91%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.51 (m, 2H; aromatic C*H*), 7.34 (d, *J* = 2.5 Hz, 2H; aromatic C*H*), 7.32 (d, *J*=2.5 Hz, 2H; aromatic C*H*), 7.14 (d, *J* = 3.0 Hz, 2H; NC*H*), 3.84 (m, 4H; OC*H*$_2$CH$_2$), 2.64 (m, 4H; C*H*Me$_2$), 1.87 (m, 4H; OCH$_2$C*H*$_2$), 1.40 (m, 12H; CH*Me$_2$*), 1.10 (m, 12H; CH*Me$_2$*). ^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_2): δ 146.4 (N*C*N), 135.1, 130.7, 124.2 (N*CC*N, aromatic *C*), 78.7 (O*C*H$_2$CH$_2$), 29.4 (*C*HMe$_2$), 26.5 (CH*Me$_2$*), 25.4 (OCH$_2$*C*H$_2$), 22.1 (CH*Me$_2$*). ^{11}B NMR (160 MHz, CD_2Cl_2): δ 4.0 (br, J_{BH} unresolved; 1B), -3.5 (br, J_{BH} unresolved; 2B), -4.6 (br, J_{BH} unresolved; 2B), -9.4 (br, J_{BH} unresolved; 6B), -23.0 (t, J_{BH} = 75 Hz, 1B). M.p.: 255.9 °C (dec.); HRMS: m/z calcd for $C_{29}H_{50}B_{12}N_2^-$ (M-THF)$^-$: 556.5186. Found: 556.5189.



2 **7**

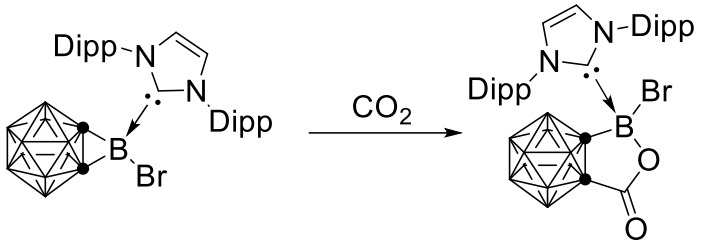
Preparation of 1-[BHBr(Idipp)]-2-Bpin-1,2-C$_2$B$_{10}$H$_{10}$ (7). To a toluene solution (10 mL) of **2** (311 mg, 0.5 mmol) was slowly added a toluene solution of HBpin (64 mg, 0.5 mmol) at room

temperature. The reaction mixture was stirred for 3 days. After removal of the solvent under reduced pressure, the resulting white solid was washed with toluene (2 x 2 mL). The residue was recrystallized from toluene to give compound **7** as colorless crystals (307 mg, 82%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.53 (t, *J* = 7.2 Hz, 2H; aromatic C*H*), 7.42-7.27 (m, 4H; aromatic C*H*), 7.22 (s, 2H; NC*H*), 2.94-2.72 (m, 4H; C*H*Me$_2$), 1.58-1.29 (m, 12H; CH*Me$_2$*), 1.17-0.95 (m, 24H; CH*Me$_2$*, CMe$_2$). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 147.8, 146.8, 146.0, 145.3 (N*C*N), 134.8, 131.6, 130.9, 127.3, 124.4 (N*CC*N, aromatic *C*), 85.6 (O*C*), 30.3, 29.5 (*C*HMe$_2$), 27.6, 27.2, 26.6, 26.0 (C*Me$_2$*), 24.7, 24.7, 22.4 (CH*Me$_2$*). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 30.2 (s, 1B), 0.3 (d, J_{BH} = 137 Hz, 1B), -3.3 (d, J_{BH} = 127 Hz, 1B), -6.9 (br, J_{BH} unresolved; 2B), -8.9 (br, J_{BH} unresolved; 3B), -10.8 (br, J_{BH} unresolved; 2B), -13.1 (br, J_{BH} unresolved; 2B). M.p.: 283.5 ^{o}C (dec.); HRMS: m/z calcd for $C_{35}H_{59}B_{12}BrN_2O_2^-$ $(M)^-$: 749.4966. Found: 749.4997.



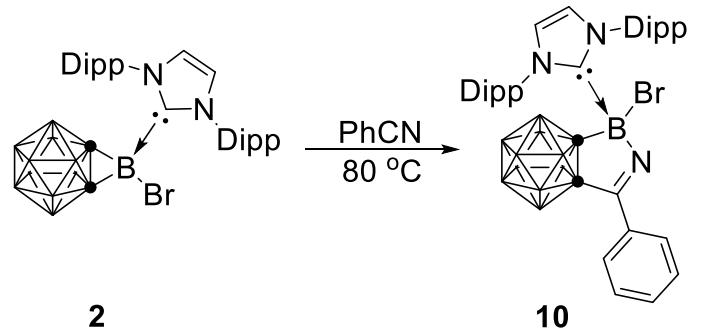
2 **8**

Preparation of 1,2-[BBr(Idipp)OCHPh]-1,2-$C_2B_{10}H_{10}$ (8). To a toluene solution (10 mL) of **2** (311 mg, 0.5 mmol) was added benzaldehyde (53 mg, 0.5 mmol) at room temperature. The reaction mixture was allowed to stir at 80 ^{o}C overnight. Volatiles were removed under reduced pressure, the resulting white solid was washed with toluene (2 x 2 mL). And the residue was recrystallized from toluene, affording compound **8** as colorless crystals (258 mg, 71 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.60-7.11 (m, 11H; aromatic C*H*), 7.01 (d, *J* = 4.8 Hz, 2H; NC*H*), 4.79 (s, 1H; OC*H*), 3.61-3.42 (m, 1H; C*H*Me$_2$), 3.33-3.09 (m, 1H; C*H*Me$_2$), 2.87-2.58 (m, 2H; C*H*Me$_2$), 1.54-1.38 (m, 12H; CH*Me$_2$*), 1.16 (d, *J* = 6.8 Hz, 6H; CH*Me$_2$*), 1.13-1.03 (m, 6H; CH*Me$_2$*). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 138.8, 128.1, 127.6, 126.7, 124.9 ((N*CC*N, aromatic *C*), 87.3 (O*C*), 82.8 (Cage *C*), 29.6, 29.4 (*C*HMe$_2$), 26.7, 22.9 (CH*Me$_2$*). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 3.3 (s, 1B), -4.7 (br, J_{BH} unresolved; 2B), -7.1 (br, J_{BH} unresolved; 2B), -10.7 (br, J_{BH} unresolved; 2B), -12.6 (br, J_{BH} unresolved; 4B). M.p.: 286.0 ^{o}C (dec.); HRMS: m/z calcd for $C_{36}H_{52}B_{11}BrN_2O^-$ $(M)^-$: 727.4372. Found: 727.4380.



2 **9**

Preparation of 1,2-[BBr(Idipp)OCO]-1,2-$C_2B_{10}H_{10}$ (9). A dichloromethane solution (10 mL) of **2** (311 mg, 0.5 mmol) was subjected to three freeze-pump-thaw cycles before backfilling with CO_2 (ca. 1 atm), and the reaction mixture was allowed to stir at room temperature overnight. Volatiles were removed under reduced pressure, the resulting white solid was washed with toluene (2 x 2 mL). And the residue was recrystallized from toluene, affording compound **9** as colorless crystals (289 mg, 87 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.57 (s, 2H; aromatic C*H*), 7.38 (d, *J* = 7.7 Hz, 4H; aromatic C*H*), 7.19 (s, 2H; NC*H*), 3.41(m, 1H; C*H*Me$_2$), 2.96(m, 1H; C*H*Me$_2$), 2.19 (m, 2H; C*H*Me$_2$), 1.54-1.36 (m, 12H; CH*Me*$_2$), 1.19 (d, *J* = 7.7 Hz, 6H; CH*Me*$_2$), 1.13-1.00 (m, 6H; CH*Me*$_2$). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 162.2 (*C*OOB), 147.7, 146.9 (N*C*N), 132.6, 131.0, 126.7 (aromatic *C*), 125.4 (N*CC*N), 74.1 (Cage *C*), 29.7, 29.6 (*C*HMe$_2$), 27.3, 26.4, 23.7, 22.7 (CH*Me*$_2$). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 0.1 (s, 1B), -4.0 (br, J_{BH} unresolved; 2B), -6.8 (br, J_{BH} unresolved; 1B), -7.6 (br, J_{BH} unresolved; 2B), -11.9 (br, J_{BH} unresolved; 5B). M.p.: 283.1 °C (dec.); HRMS: m/z calcd for $C_{30}H_{46}B_{11}N_2O_2^-$ $(M\text{-}Br)^+$: 585.4666. Found: 585.4668.



2 **10**

Preparation of 1,2-[BBr(Idipp)NCPh]-1,2-$C_2B_{10}H_{10}$ (10). A toluene solution of **2** (311 mg, 0.5 mmol) was added benzonitrile (62 mg, 0.6 mmol) at room temperature. The reaction mixture was allowed to stir at 80 °C overnight. Volatiles were removed under reduced pressure, the resulting white solid was washed with THF (2 x 2 mL). and the residue was recrystallized from THF, affording compound **10** as colorless crystals (300 mg, 83 %). ^{1}H NMR (400 MHz, THF-d_8): δ 7.69 (s, 1H; aromatic C*H*), 7.60 (m, 2H; aromatic C*H*), 7.48-7.39 (br, 4H; NC*H*, aromatic C*H*), 7.31-7.25 (br, 3H; NC*H*, aromatic C*H*), 7.10 (t, *J* = 7.6 Hz, 2H; aromatic C*H*), 6.89 (br, 1H; aromatic C*H*), 3.84 (br, 1H; C*H*Me$_2$), 3.37 (br, 1H; C*H*Me$_2$), 2.29 (br, 1H; C*H*Me$_2$), 2.18 (br, 1H; C*H*Me$_2$), 1.46 (br, 9H; CH*Me*$_2$), 1.25-1.15 (m, 9H; CH*Me*$_2$), 0.91 (br, 3H; CH*Me*$_2$), 0.69 (br, 3H; CH*Me*$_2$). ^{13}C NMR (100 MHz, THF-d_8): δ 161.0 (*C*NB), 148.5, 147.2, 145.2,

143.8 (N*C*N), 139.5, 135.5, 133.4, 132.4, 131.2, 129.7, 128.4, 128.0, 127.4, 125.9, 125.4, 124.2 (aromatic *C*, N*CC*N), 90.9, 86.0 (Cage *C*), 29.6 (*C*HMe$_2$), 27.0, 26.2, 26.0, 22.8, 22.6, 22.1, 21.6 (CH*Me*$_2$). ^{11}B NMR (128 MHz, THF-d$_8$): δ -0.6 (br, J_{BH} unresolved; 2B), -6.5 (br, J_{BH} unresolved; 2B), -9.6 (br, br, J_{BH} unresolved; 2B), -14.0 (br, J_{BH} unresolved; 5B). M.p.: 258.1 ^{o}C (dec.); HRMS: m/z calcd for $C_{36}H_{52}B_{11}BrN_3^+$ $(M+H)^+$: 725.4443. Found: 725.4443.

Crystal Data and Summary of Data Collection and Refinement

X-ray Structure Determination. Single crystals were immersed in Paraton-N oil and sealed under argon in thin-walled glass capillaries. All data were collected at 296 K or 173 K on a Bruker Kappa ApexII Duo Diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[2] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[3] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and refinement are given in Tables S1-S3. Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC 2102172-2102180 for **1**·THF, **2**·THF, **3**, **4**·Toluene, **6**, **7**·Toluene, **8**, **9** and **10**·0.5THF, respectively.

Table S1. Crystal Data and Summary of Data Collection and Refinement for **1**·THF, **2**·THF and **3**,

Compound	**1**·THF	**2**·THF	**3**
Formula	$C_{33}H_{55}B_{11}Br_2N_2O$	$C_{33}H_{54}B_{11}BrN_2O$	$C_{29}H_{46}B_{12}Br_4N_2$
MW	774.52	693.60	872.04
Crystal size (mm^3)	0.40x0.30x0.20	0.40x0.30x0.20	0.40x0.30x0.20
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	12.426 (1)	12.581(1)	12.467(1)
b, Å	16.465(1)	15.361(2)	16.621(1)
c, Å	23.205(2)	19.888(3)	21.012(1)
β, deg	99.00(1)	90.94(1)	105.63(1)
V, Å^3	4689.3(4)	3842.9(6)	4192.89(18)
Z	4	4	4
D_{calcd} Mg/m^3	1.097	1.199	1.381
Radiation (Å)	0.71073	0.71073	0.71073
2θ range, deg	4.14 to 55.96	5.68 to 50.50	4.52 to 50.50
μ, mm^{-1}	1.754	1.099	3.862
F(000)	1600	1456	1736
No. of obsd reflns	11264	6938	7560
No. of params refnd	487	433	424
Goodness of fit	1.063	1.069	1.046

R1	0.0773	0.0529	0.0359
wR2	0.2280	0.1410	0.1068

Table S2. Crystal Data and Summary of Data Collection and Refinement for **4**·toluene, **6** and **7**·toluene

Compound	**4**·toluene	**6**	**7**·toluene
Formula	$C_{36}H_{54}B_{11}BrCl_2GeN_2$	$C_{33}H_{58}B_{12}N_2O$	$C_{42}H_{67}B_{12}BrN_2O_2$
MW	857.12	628.53	841.60
Crystal size (mm^3)	0.40x0.30x0.20	0.40x0.30x0.20	0.50x0.40x0.30
Crystal system	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	19.855(2)	10.042(2)	12.000(1)
b, Å	11.675(1)	19.622(2)	17.275(1)
c, Å	20.906(1)	20.134(3)	24.869(2)
β, deg	106.20(1)	90.34(1)	97.24(1)
V, $Å^3$	4653.8(3)	3967.3(9)	5114.2(3)
Z	4	4	4
D_{calcd} Mg/m^3	1.223	1.052	1.093
Radiation (Å)	0.71073	0.71073	0.71073
2θrange, deg	4.82 to 50.50	4.54 to 50.62	4.62 to 50.50
μ, mm^{-1}	1.658	0.057	0.838
F(000)	1760	1352	1776
No. of obsd reflns	8411	7173	9255
No. of params refnd	505	434	536
Goodness of fit	1.060	1.061	1.029
R1	0.0588	0.0979	0.0410
wR2	0.1759	0.2429	0.1070

Table S3. Crystal Data and Summary of Data Collection and Refinement for **8**, **9** and **10**·0.5THF

Compound	**8**	**9**	**10**·0.5THF
Formula	$C_{36}H_{52}B_{11}BrN_2O$	$C_{37}H_{54}B_{11}BrN_2O_2$	$C_{42}H_{64}B_{11}BrN_3O_{1.5}$
MW	727.61	757.64	833.78
Crystal size (mm^3)	0.40x0.30x0.20	0.10x0.03x0.02	0.40x0.30x0.30
Crystal system	trigonal	monoclinic	triclinic
Space Group	R-3	$P2_1/c$	P-1
a, Å	48.431(2)	10.269(1)	11.771(1)
b, Å	48.431(2)	17.629(2)	11.911(1)

c, Å	10.583(2)	24.803(2)	18.323(1)
α, deg	90	90	93.830(1)
β, deg	90	99.17(1)	94.618(1)
γ, deg	120	90	105.727(1)
V, $Å^3$	21499(2)	4433.2(2)	2454.2(2)
Z	222	4	2
D_{calcd} Mg/m^3	1.012	1.135	1.128
Radiation (Å)	0.71073	1.34139	0.71073
2θ range, deg	4.46 to 50.50	6.28 to 110.04	4.84 to 50.50
μ, mm^{-1}	0.887	1.017	0.872
F(000)	6840	1584	878
No. of obsd reflns	8660	8410	8872
No. of params refnd	460	487	550
Goodness of fit	1.081	1.026	1.083
R1	0.0430	0.0593	0.0711
wR2	0.1055	0.1537	0.2145

Computational detail: All of the calculations were carried out using the Gaussian 09 program.[4] Optimization of the ground state structures were performed at B3LYP[5] /6-31+G(d,p) level of theory. Frequency calculations were made to determine the characteristics of all stationary points as energy minima or saddle point. Intrinsic reaction coordinates (IRC) [6] were calculated to confirm that transition states lead to relevant intermediates.

Cartesian coordinates:

2-Me

Br	-1.29111600	2.22075500	-0.00019300
N	-2.24274500	-1.04110400	-1.08148600
N	-2.24283600	-1.04084500	1.08160500
C	1.02245900	0.05990400	-0.78833600
C	1.02245200	0.06006300	0.78830800
C	-1.57938600	-0.58638400	0.00003000
C	-3.33398500	-1.79268100	-0.68137600
H	-4.00335900	-2.25575800	-1.38820300
C	-3.33398000	-1.79260700	0.68157800
H	-4.00337400	-2.25557900	1.38845500
B	1.92112400	1.34019000	-0.00011700
H	1.45113200	2.41776400	-0.00018500
B	2.52447700	0.56018200	-1.45514200
H	2.55920600	1.16658100	-2.47229400
B	2.03909400	-1.16325100	-1.45426000
H	1.74268500	-1.70392300	-2.46851400
B	1.11976800	-1.49581900	0.00007800
H	0.15763200	-2.18538400	0.00008900
B	2.52438600	0.56043700	1.45512600
H	2.55900000	1.16699500	2.47218600
B	3.57058800	0.83599500	0.00000200
H	4.43051700	1.65487800	-0.00004000
B	3.67230100	-0.69812100	-0.90470800
H	4.63479000	-0.97025200	-1.54611500
B	2.78176100	-1.94852700	0.00021500
H	3.07023300	-3.10116200	0.00030700
B	2.03893600	-1.16298000	1.45445200
H	1.74252500	-1.70350300	2.46878800
B	3.67222600	-0.69798600	0.90498700
H	4.63470500	-0.97000000	1.54645800
B	-0.35221900	0.41457300	-0.00002900
C	-1.85015200	-0.73758600	2.45961400
H	-1.80026800	0.34580800	2.58764100
H	-2.59643400	-1.15676100	3.13447600
H	-0.87148000	-1.17343300	2.66872100
C	-1.84983000	-0.73831900	-2.45952800
H	-1.79920500	0.34502300	-2.58767600
H	-0.87144700	-1.17485200	-2.66857800
H	-2.59640500	-1.15704300	-3.13434700

CO_2

C	0.00000000	0.00000000	-0.00002300
O	0.00000000	0.00000000	-1.16945300
O	0.00000000	0.00000000	1.16947000

TS

Br	1.02774300	1.58373600	-1.55764600
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N	2.70596900	-1.49142400	-0.28959600
C	-1.70481000	0.42835200	0.50580000
C	-0.71299900	-0.63347800	-0.30908500
C	1.95016400	-0.50556900	0.23680800
C	3.70774200	-0.83762500	1.56309600
H	4.34164800	-0.68670900	2.42212600
C	3.80522600	-1.70982600	0.52077100
H	4.54463900	-2.46016600	0.29126400
B	-2.02782000	0.03334700	-1.13685000
H	-1.83684500	0.84183500	-1.97831600
B	-3.32676400	0.06672100	0.03619400
H	-4.11047300	0.95483100	-0.01034500
B	-2.68175000	-0.50003500	1.57700500
H	-3.01481500	-0.01071200	2.60623900
B	-1.00193700	-0.90826500	1.34528500
H	-0.13350100	-0.71103600	2.13107700
B	-1.52476600	-1.68625500	-1.37754100
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B	-3.23705100	-1.26856500	-1.14838800
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B	-2.19386400	-2.21947900	1.38708600
H	-2.21485100	-2.98648200	2.29578200
B	-0.88907600	-2.26561300	0.18731000
H	0.08651400	-2.94787100	0.22505600
B	-2.52869900	-2.69657800	-0.31095600
H	-2.80330300	-3.81417600	-0.61325200
B	0.64795400	0.06994200	-0.45758100
C	2.42808100	-2.15140800	-1.57185900
H	2.56695200	-1.43787900	-2.38744600
H	3.12038100	-2.98450600	-1.68908000
H	1.40421600	-2.52858700	-1.57428300
C	2.07326600	0.96450000	2.25810500
H	2.84815300	1.72732800	2.35595100
H	1.17163800	1.41141700	1.84405300
H	1.83602500	0.53311300	3.23219800
C	-1.29210400	2.97967200	0.84612300
O	-2.14063500	3.30386000	0.10712100

O	-0.39910100	2.92194600	1.61665800

9-Me

Br	1.28110200	-1.94716200	-1.28908700
N	2.49931700	1.59503300	0.20169600
N	2.37949900	-0.17290500	1.44461800
C	-1.77786600	0.70693900	-0.62709000
C	-0.80848200	-0.25922700	0.25260900
C	1.82867000	0.42793100	0.36275900
C	3.47015400	1.72094000	1.17971900
H	4.11705500	2.58136900	1.23579500
C	3.39497600	0.60983600	1.95927400
H	3.96562500	0.31025100	2.82355500
B	-2.04012600	-0.98618300	-0.72870400
H	-1.69492500	-1.52842400	-1.71552100
B	-3.39464300	0.17497800	-0.67643900
H	-4.01296200	0.34292600	-1.66971300
B	-2.90612300	1.57463400	0.31524800
H	-3.19546600	2.67000000	-0.02285200
B	-1.24513400	1.29289300	0.89206600
H	-0.40558200	2.12690400	0.88967000
B	-1.69370700	-1.54829200	0.91609600
H	-1.14577400	-2.59021600	1.04506500
B	-3.38110700	-1.28213200	0.36398500
H	-4.11592000	-2.19103200	0.16143200
B	-3.92507500	0.29639200	1.01996200
H	-5.06199000	0.50197400	1.29033600
B	-2.58527400	0.99829500	1.98019700
H	-2.74768700	1.70285000	2.92147500
B	-1.21518100	-0.15192500	1.90498300
H	-0.35167500	-0.24379500	2.71071900
B	-2.87609100	-0.77259500	2.00503700
H	-3.26367700	-1.32710500	2.98044800
B	0.61870700	-0.15001900	-0.54317900
C	2.07442300	-1.51340300	1.95827900
H	2.80135400	-2.22498700	1.56179600
H	2.11689900	-1.48212500	3.04809500
H	1.08298600	-1.82120000	1.64410000
C	2.26989900	2.61169100	-0.83662500
H	3.02740600	3.38596500	-0.71431300
H	2.34689200	2.16171700	-1.82429000
H	1.27740900	3.04759300	-0.72291000
C	-0.92181500	1.24438200	-1.76383100
O	-1.29354300	2.01095300	-2.61484900
O	0.33213900	0.77009100	-1.66088200

NMR spectrum

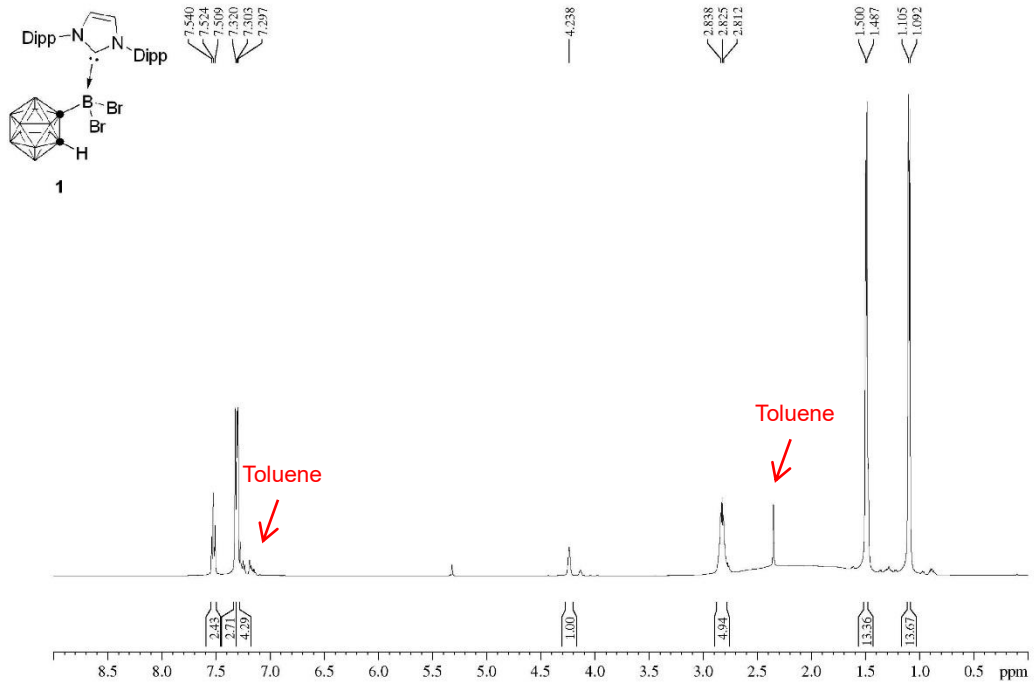

Figure S1. ^{1}H NMR spectrum of compound **1** in CD_2Cl_2.

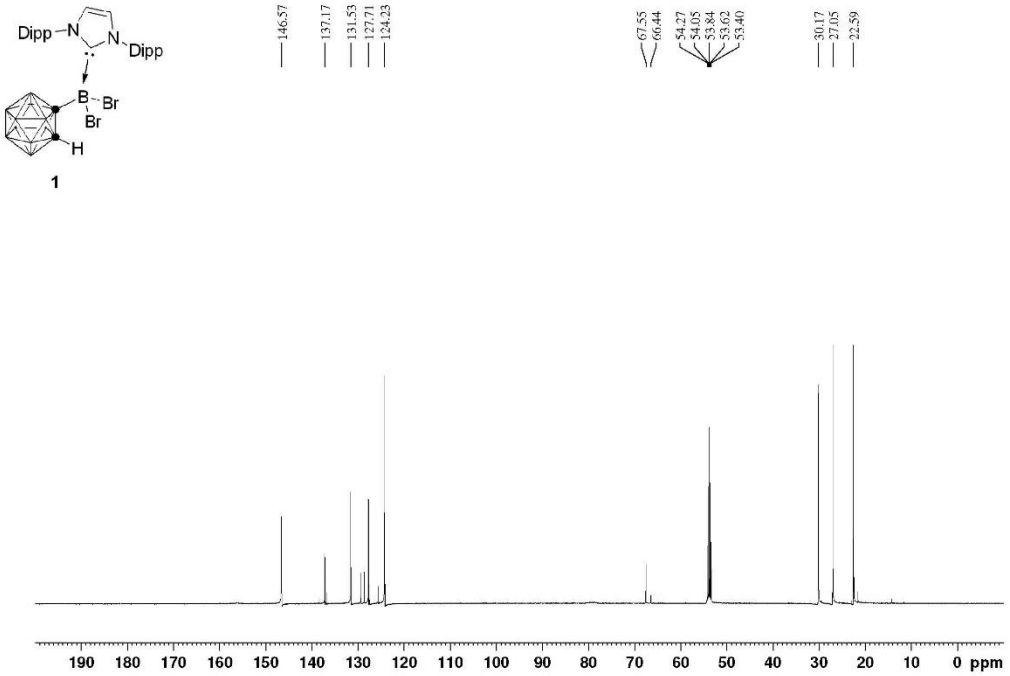

Figure S2. ^{13}C NMR spectrum of compound **1** in CD_2Cl_2.

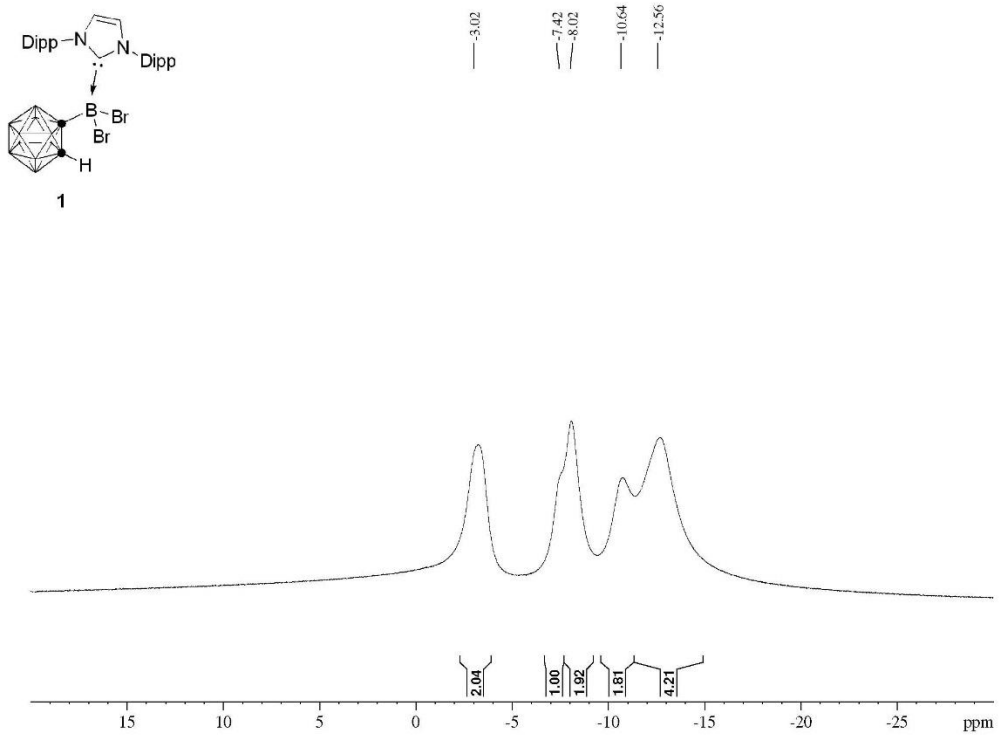

Figure S3. ^{11}B {^{1}H} NMR spectrum of compound **1** in CD_2Cl_2.

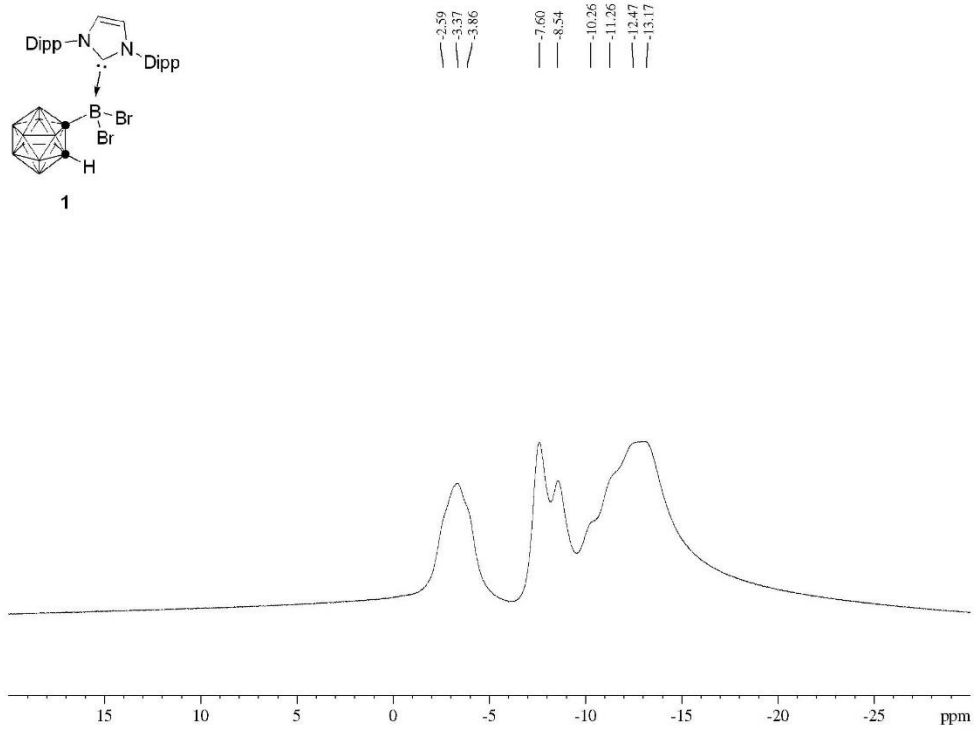

Figure S4. ^{11}B NMR spectrum of compound **1** in CD_2Cl_2.

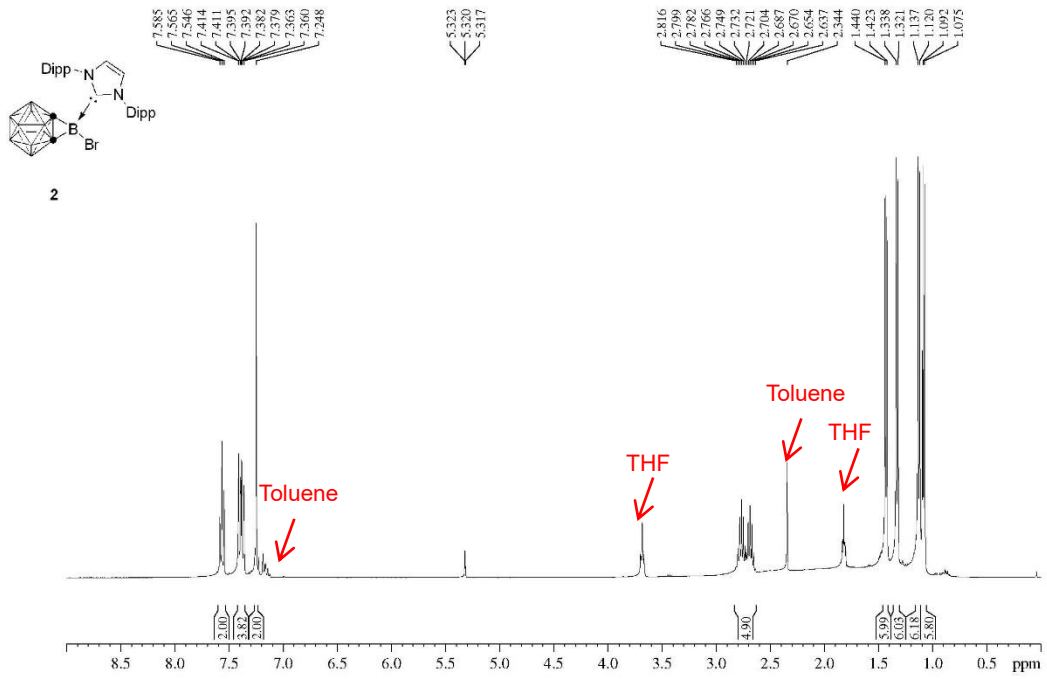

Figure S5. ^{1}H NMR spectrum of compound **2** in CD_2Cl_2.

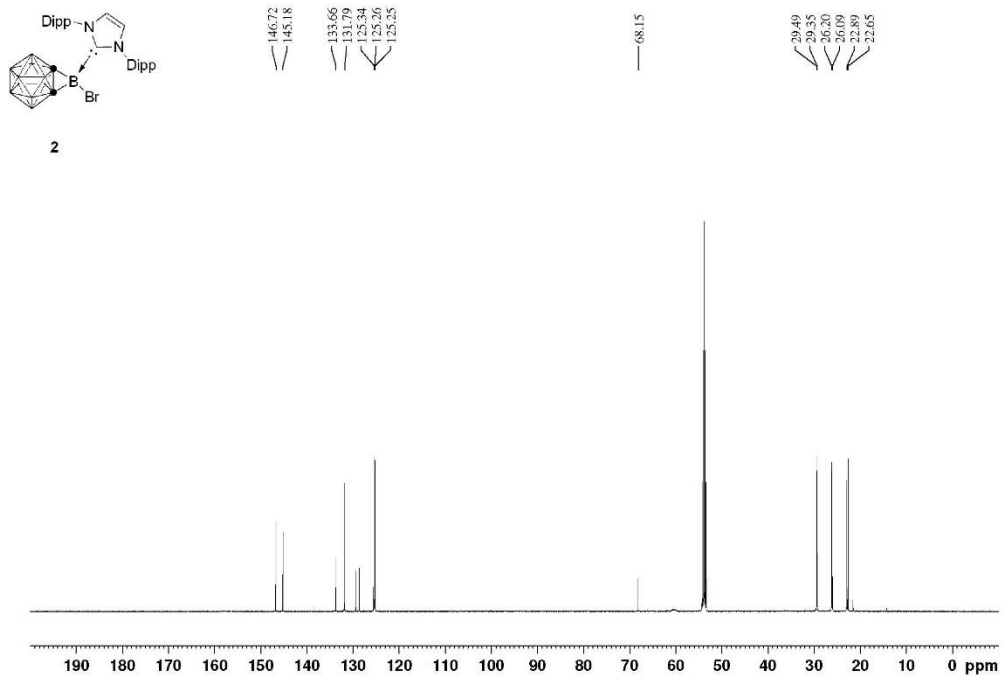

Figure S6. ^{13}C NMR spectrum of compound **2** in CD_2Cl_2.

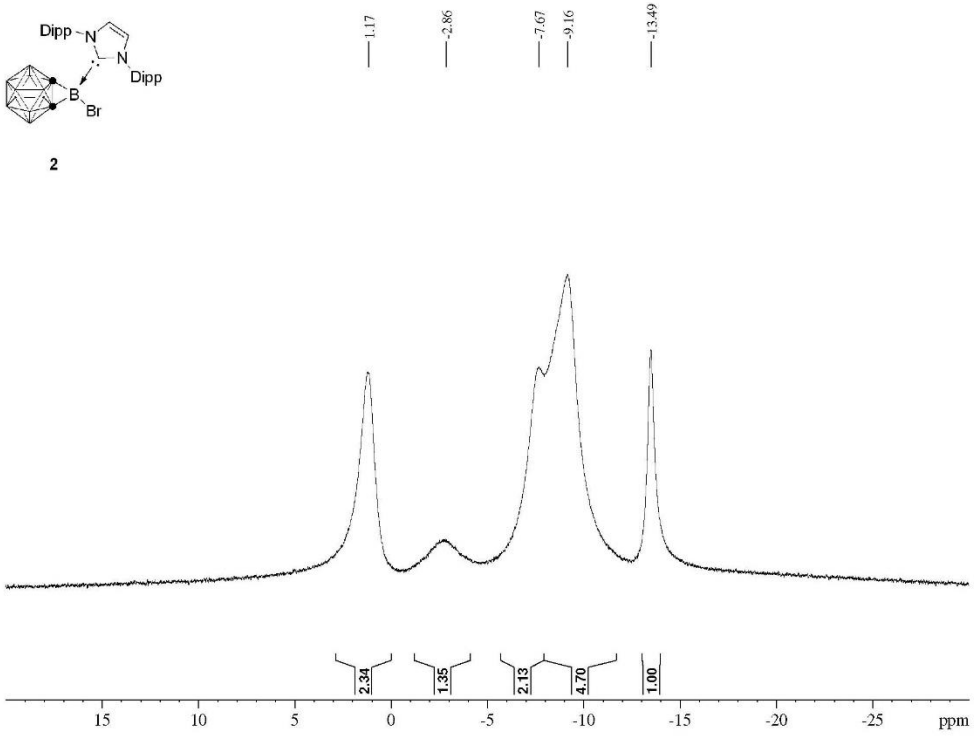

Figure S7. ^{11}B {^{1}H} NMR spectrum of compound **2** in CD_2Cl_2.

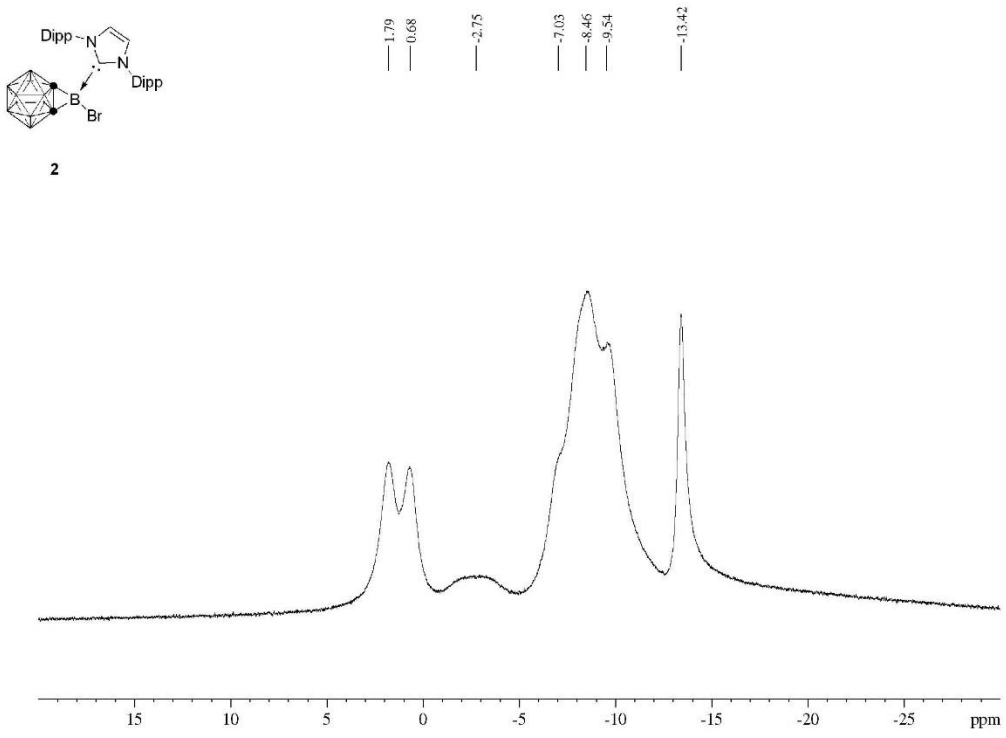

Figure S8. ^{11}B NMR spectrum of compound **2** in CD_2Cl_2.

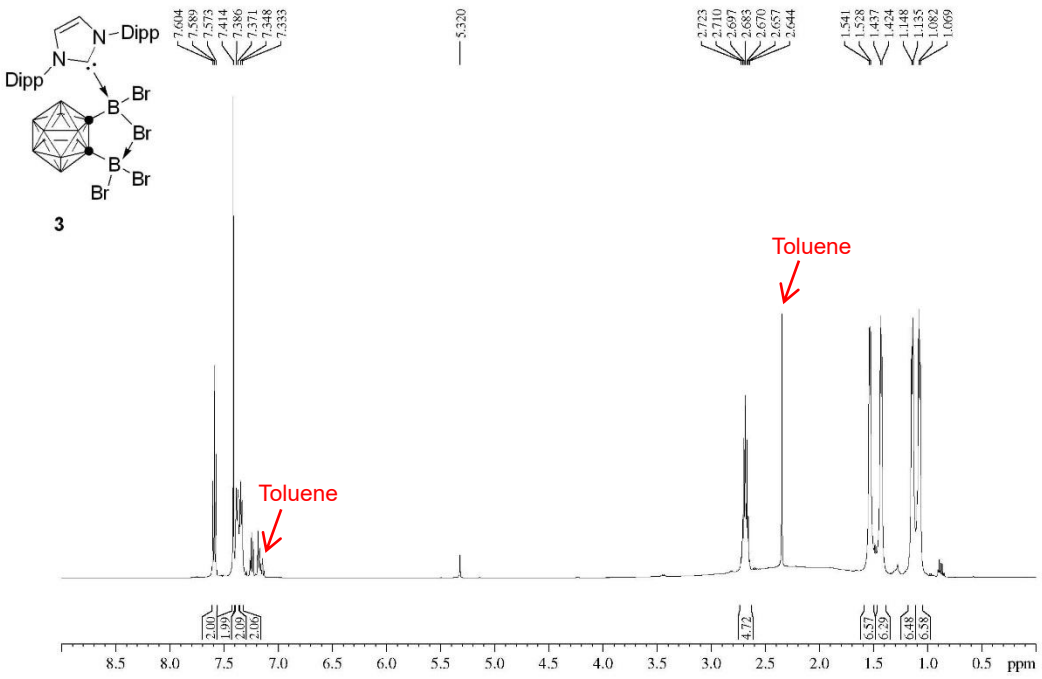

Figure S9. ^{1}H NMR spectrum of compound **3** in CD_2Cl_2.

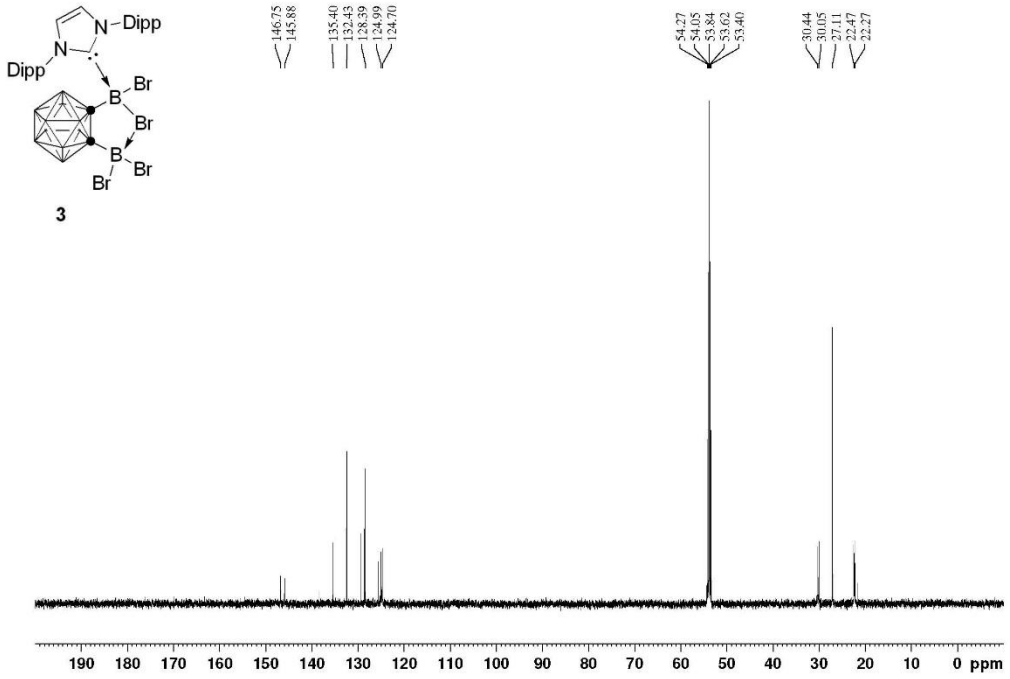

Figure S10. ^{13}C NMR spectrum of compound **3** in CD_2Cl_2.

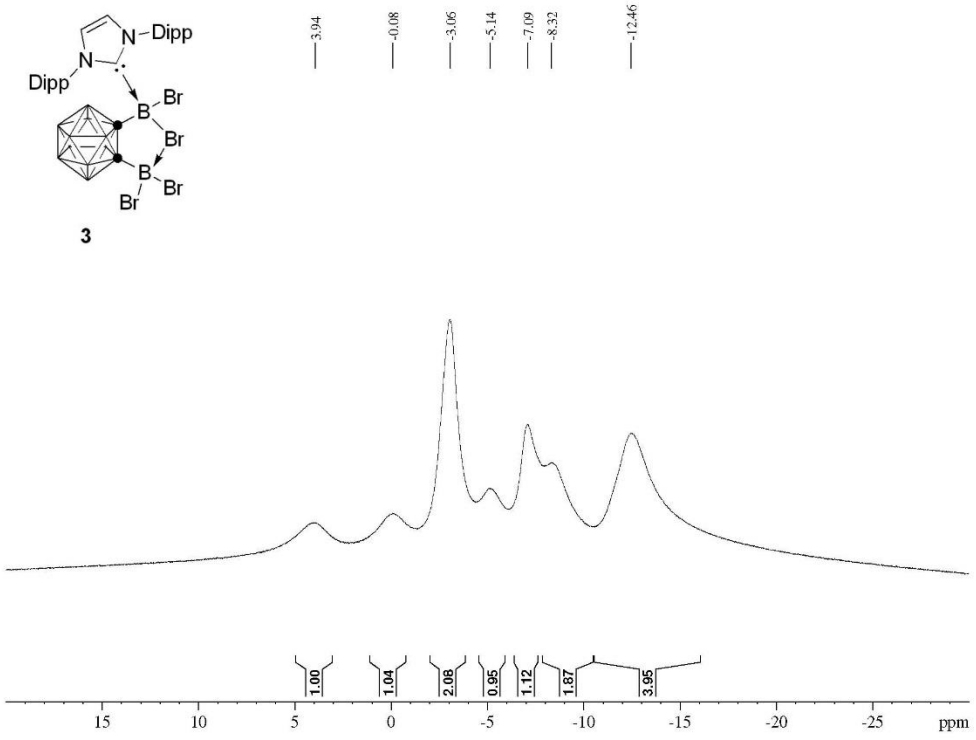

Figure S11. ^{11}B {^{1}H} NMR spectrum of compound **3** in CD_2Cl_2.

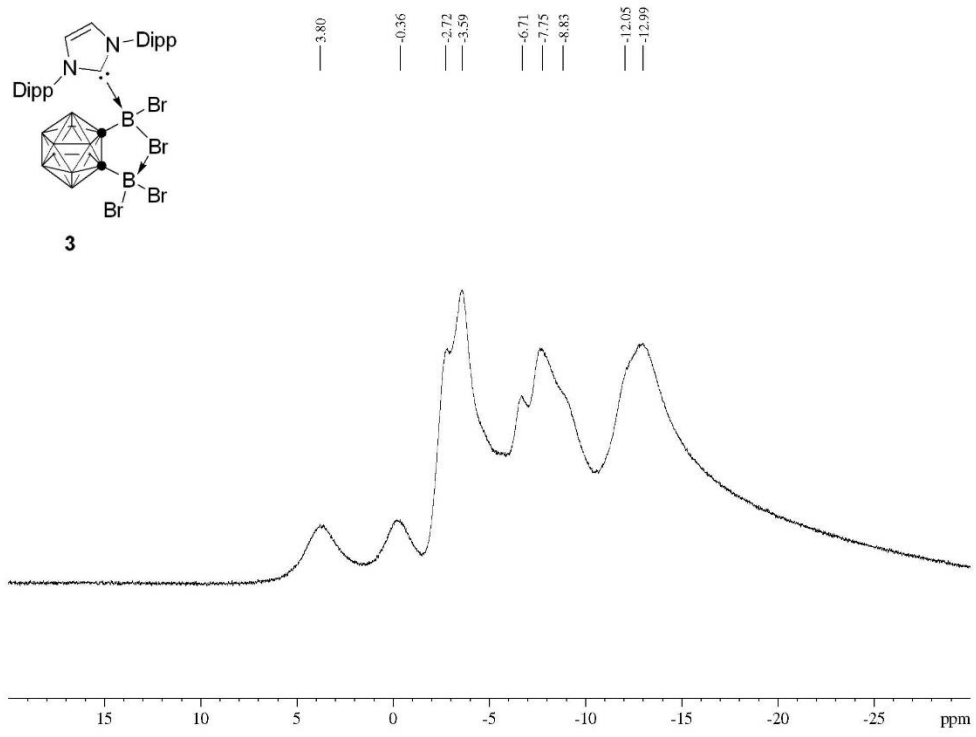

Figure S12. ^{11}B NMR spectrum of compound **3** in CD_2Cl_2.

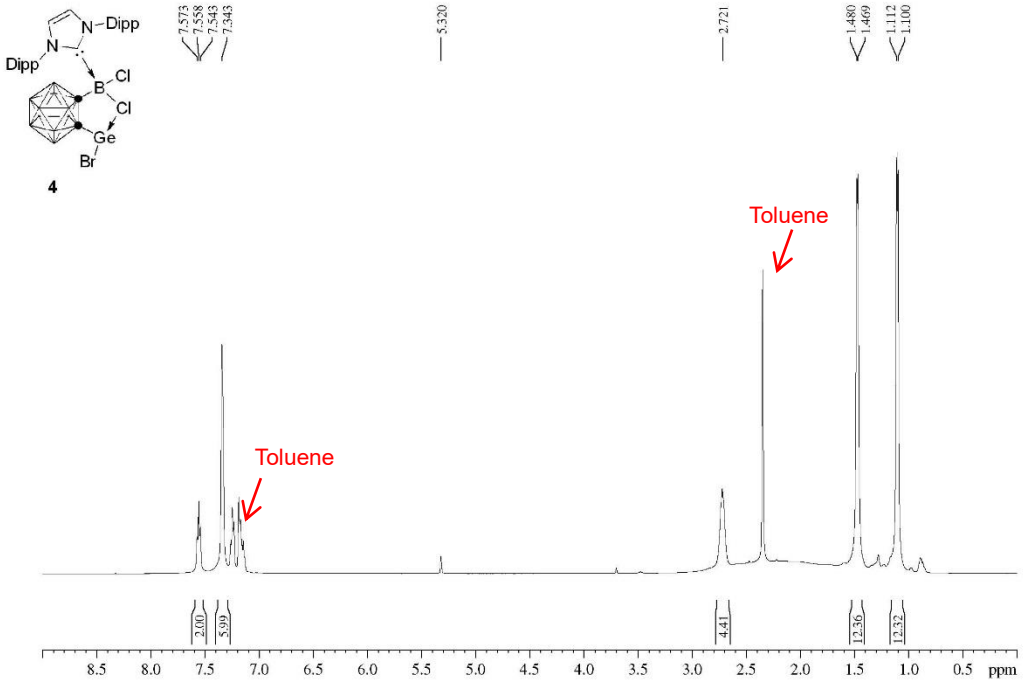

Figure S13. ^{1}H NMR spectrum of compound **4** in CD_2Cl_2.

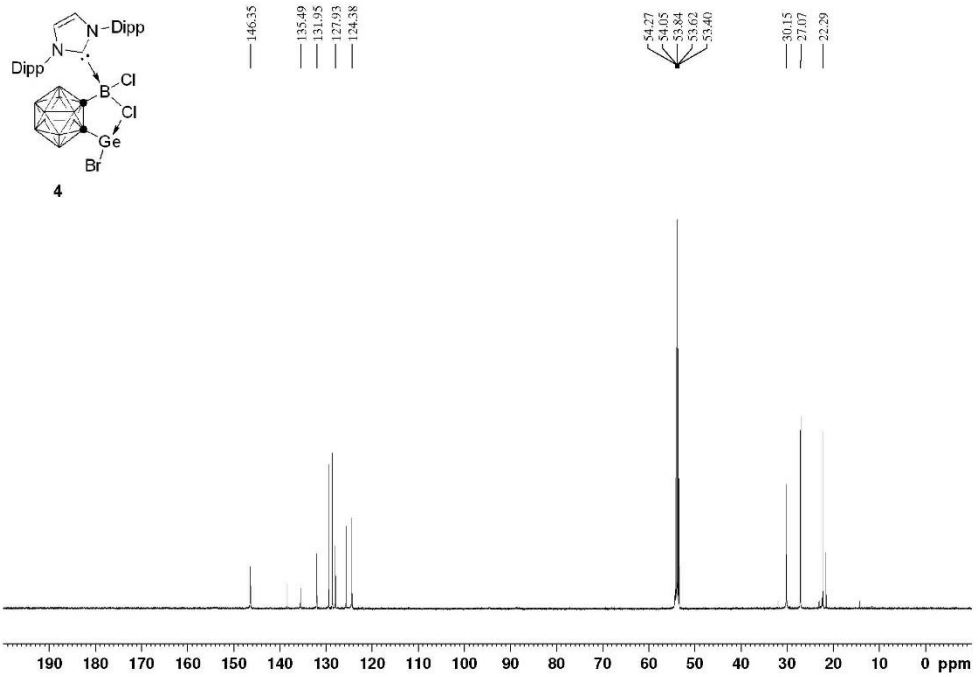

Figure S14. ^{13}C NMR spectrum of compound **4** in CD_2Cl_2.

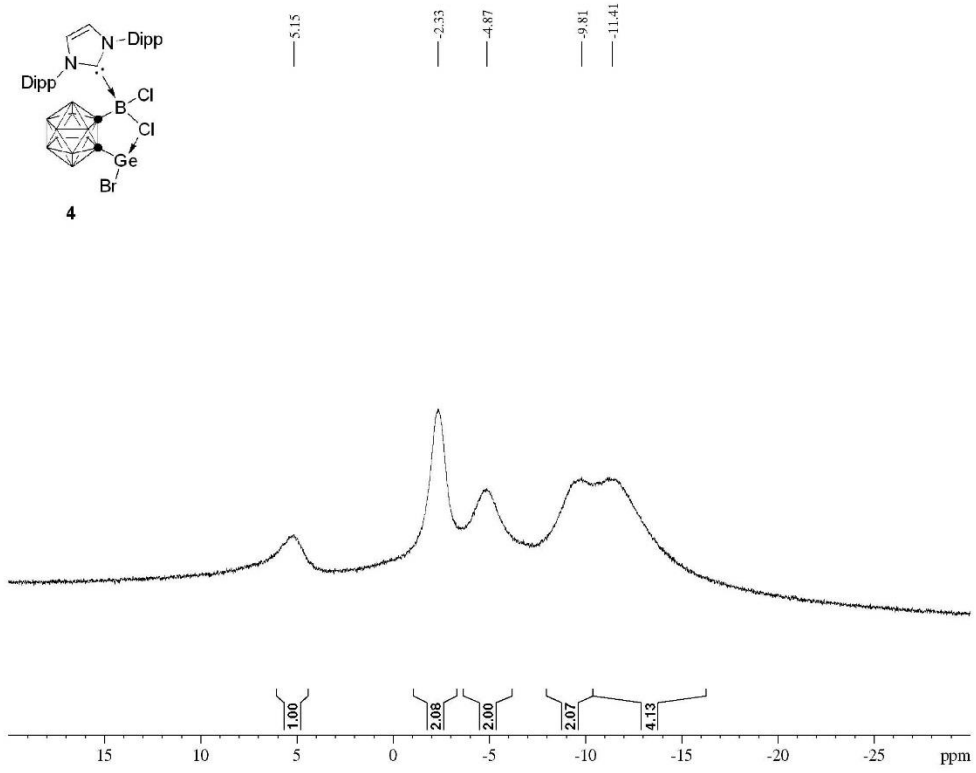

Figure S15. ^{11}B {^{1}H} NMR spectrum of compound **4** in CD_2Cl_2.

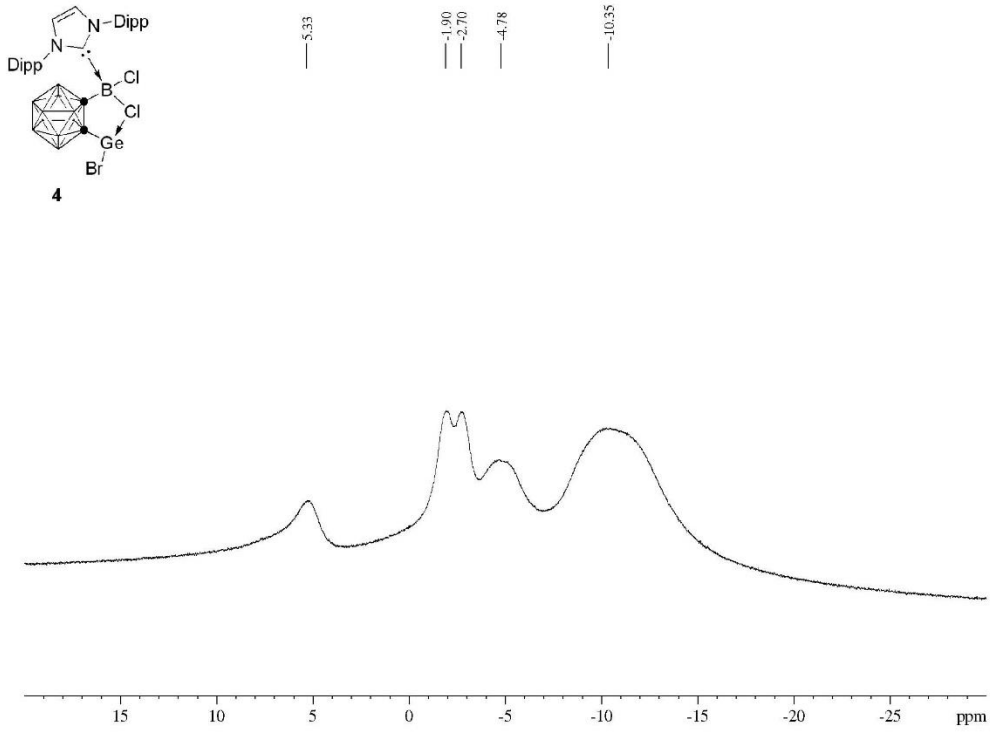

Figure S16. ^{11}B NMR spectrum of compound **4** in CD_2Cl_2.

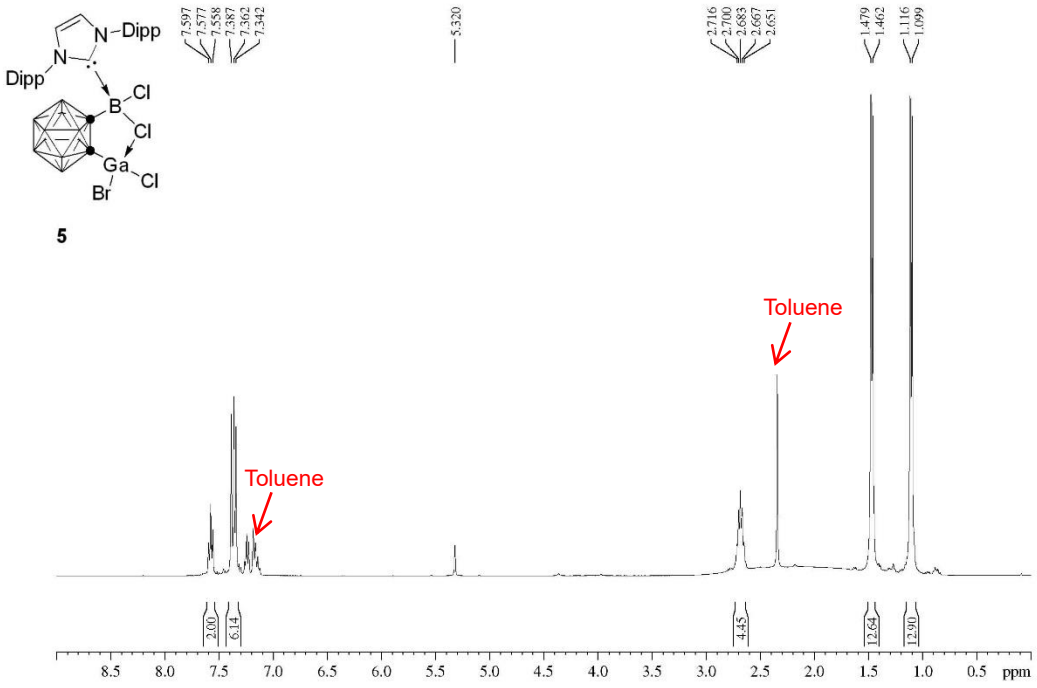

Figure S17. ^{1}H NMR spectrum of compound **5** in CD_2Cl_2.

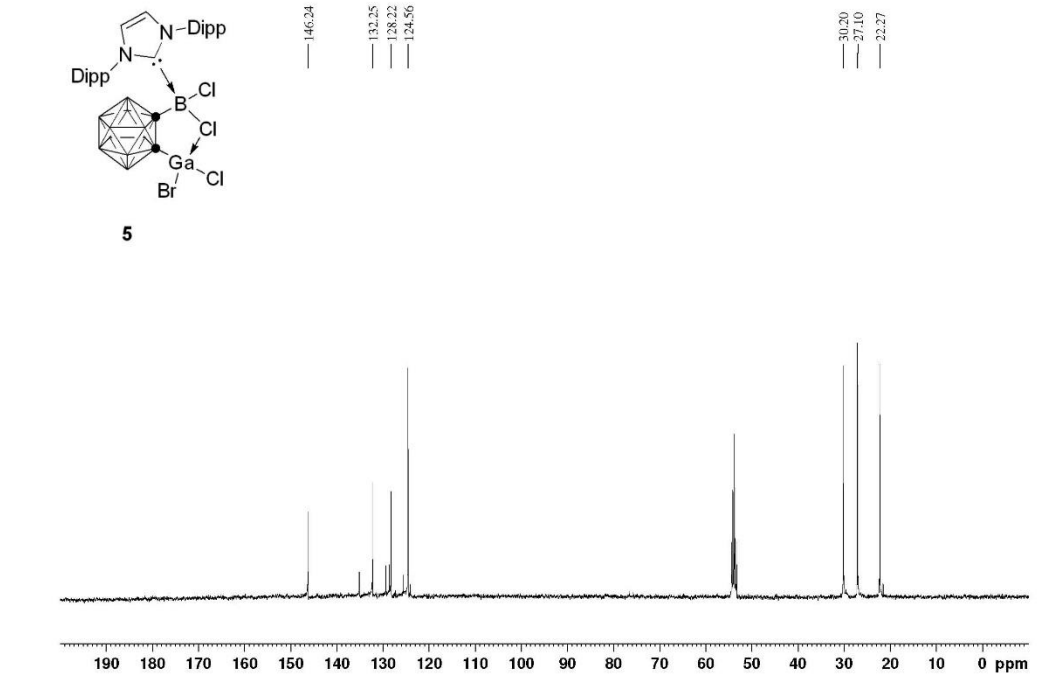

Figure S18. ^{13}C NMR spectrum of compound **5** in CD_2Cl_2.

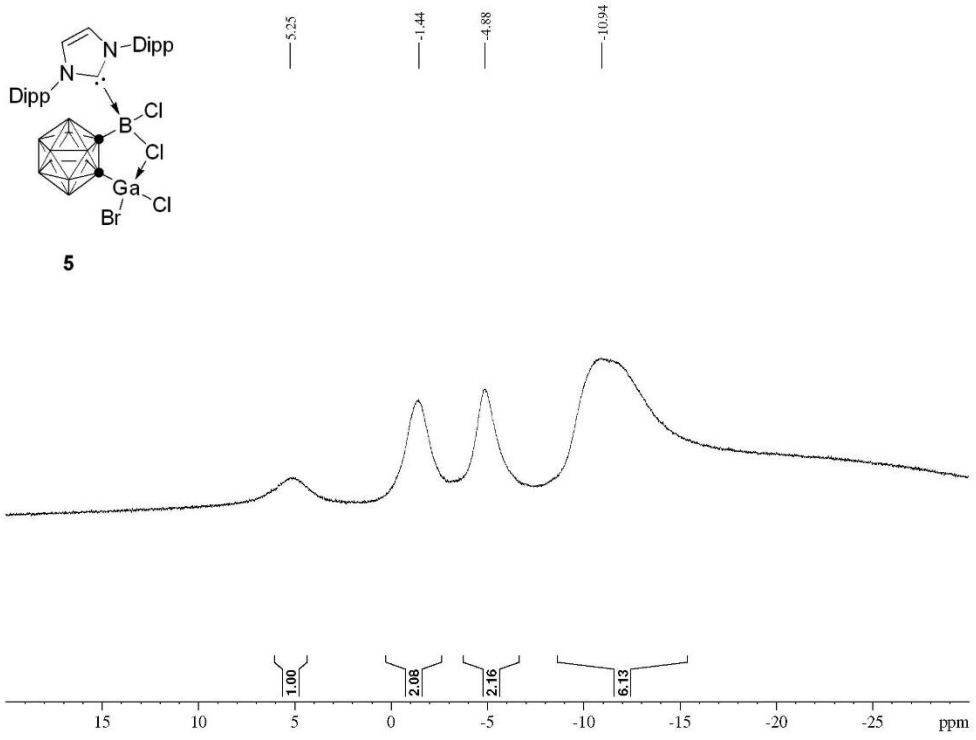

Figure S19. ^{11}B {^{1}H} NMR spectrum of compound **5** in CD_2Cl_2.

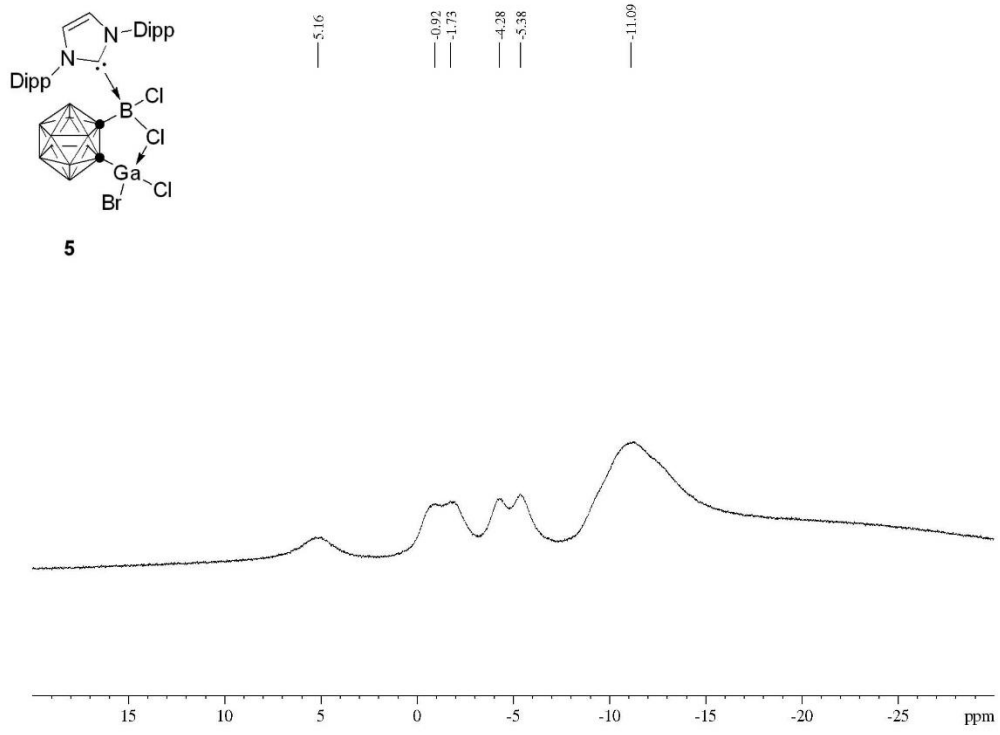

Figure S20. ^{11}B NMR spectrum of compound **5** in CD_2Cl_2.

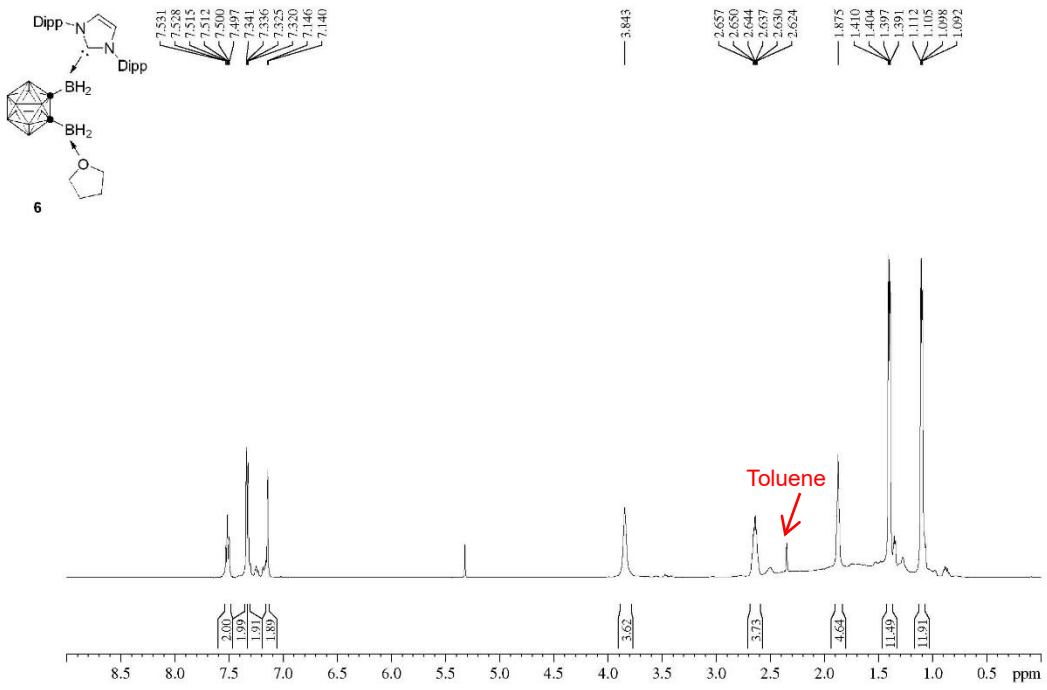

Figure S21. ^{1}H NMR spectrum of compound **6** in CD_2Cl_2.

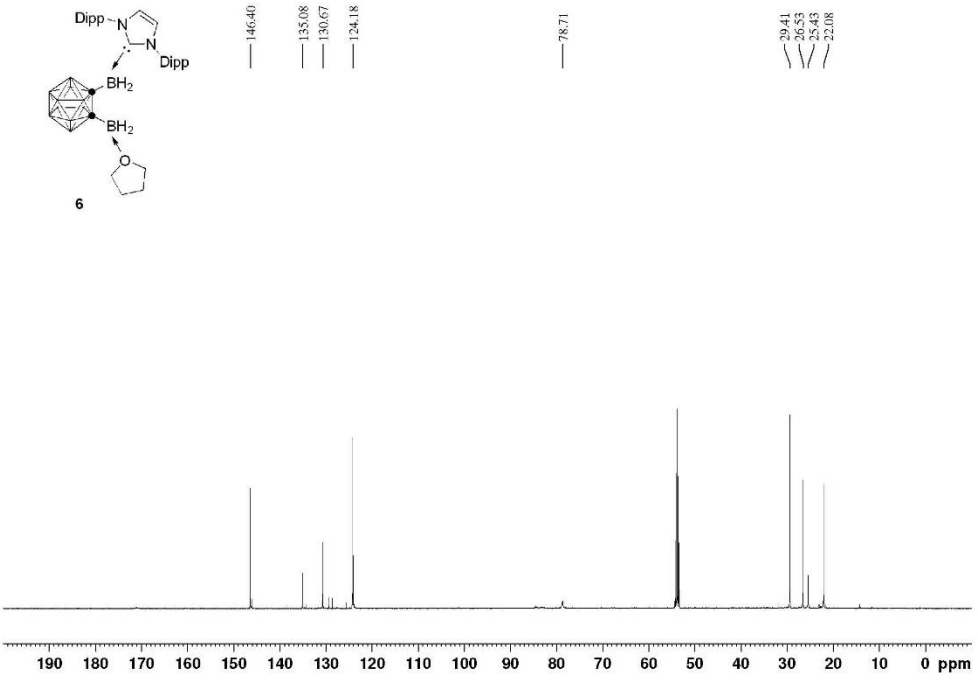

Figure S22. ^{13}C NMR spectrum of compound **6** in CD_2Cl_2.

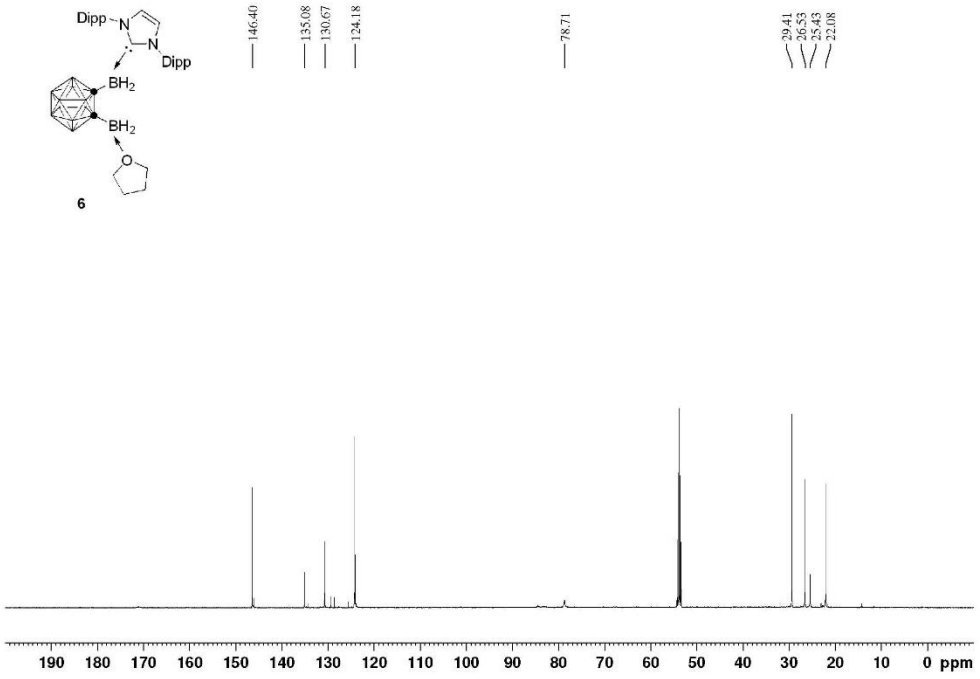

Figure S23. ^{11}B {^{1}H} NMR spectrum of compound **6** in CD_2Cl_2.

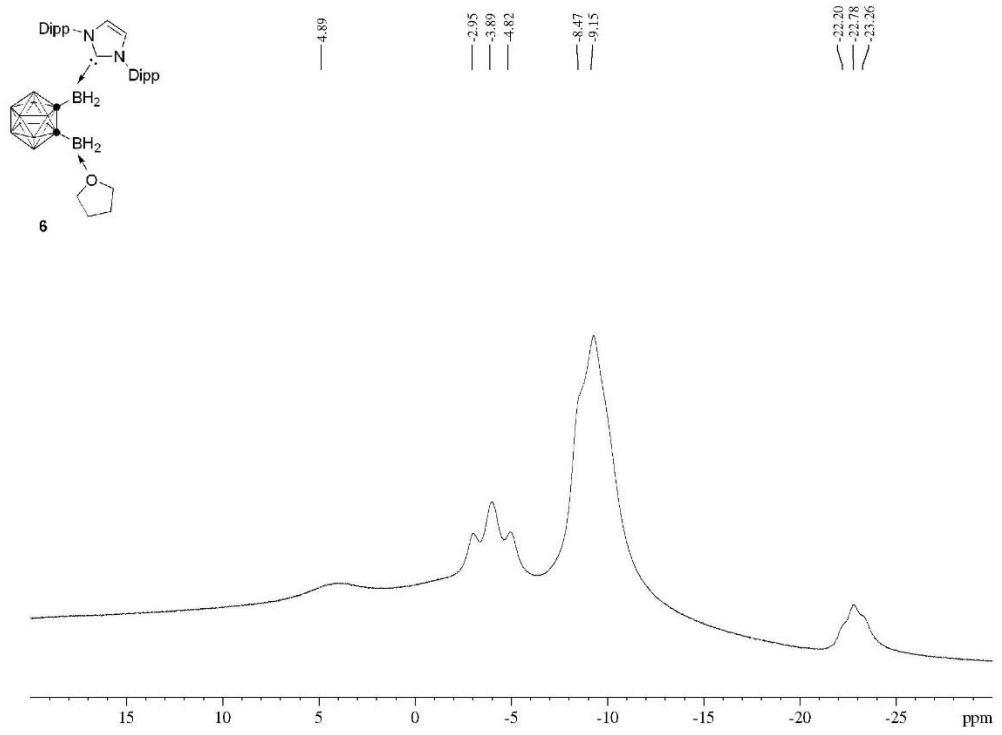

Figure S24. ^{11}B NMR spectrum of compound **6** in CD_2Cl_2.

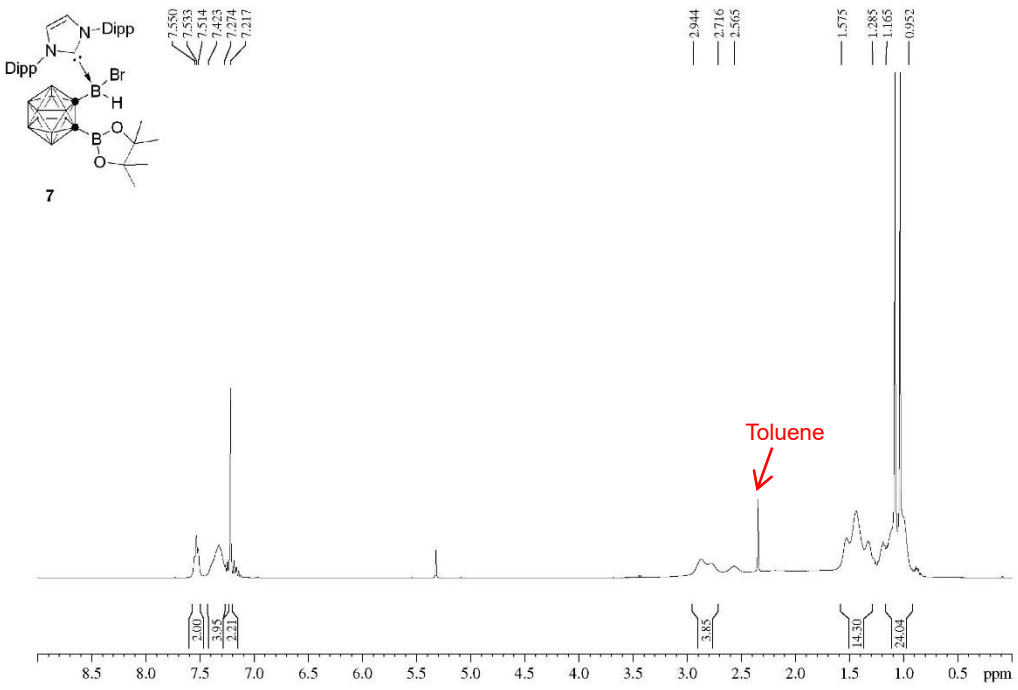

Figure S25. ^{1}H NMR spectrum of compound **7** in CD_2Cl_2.

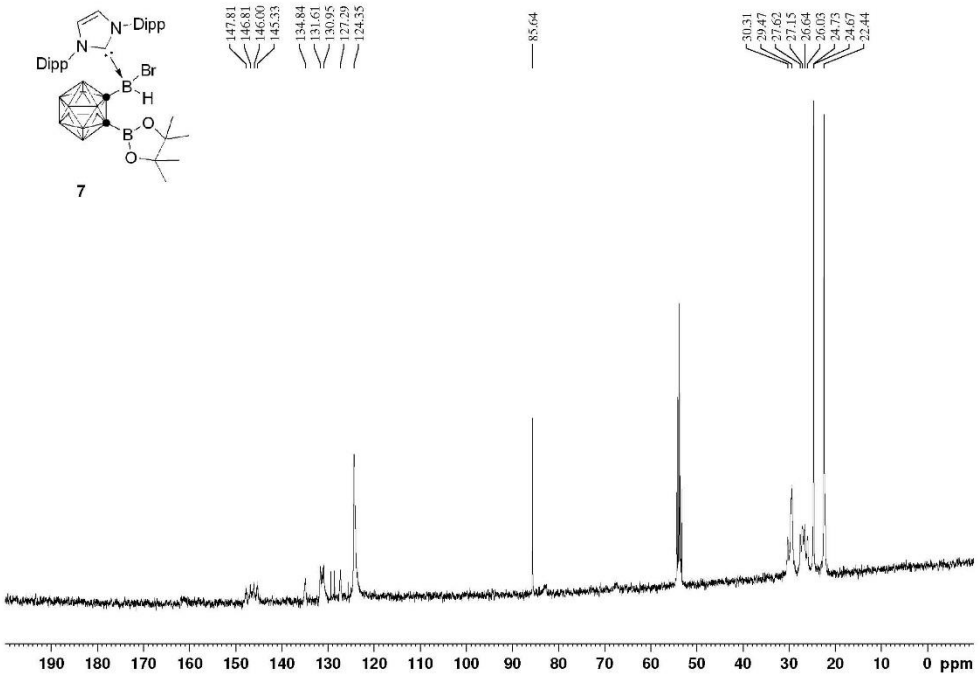

Figure S26. ^{13}C NMR spectrum of compound **7** in CD_2Cl_2.

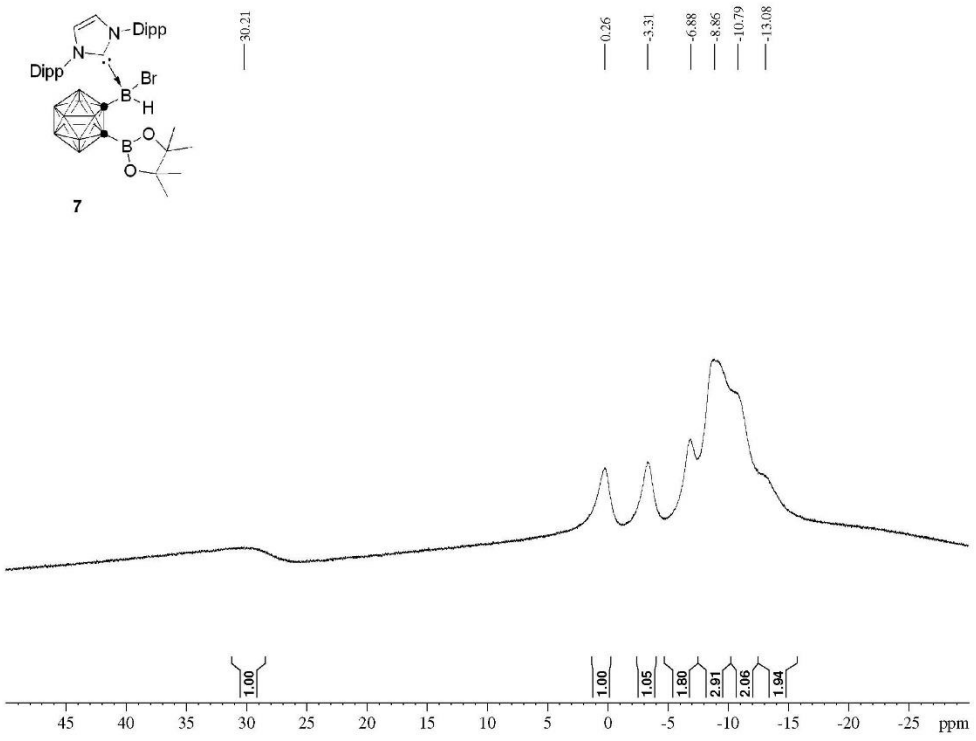

Figure S27. ^{11}B {^{1}H} NMR spectrum of compound **7** in CD_2Cl_2.

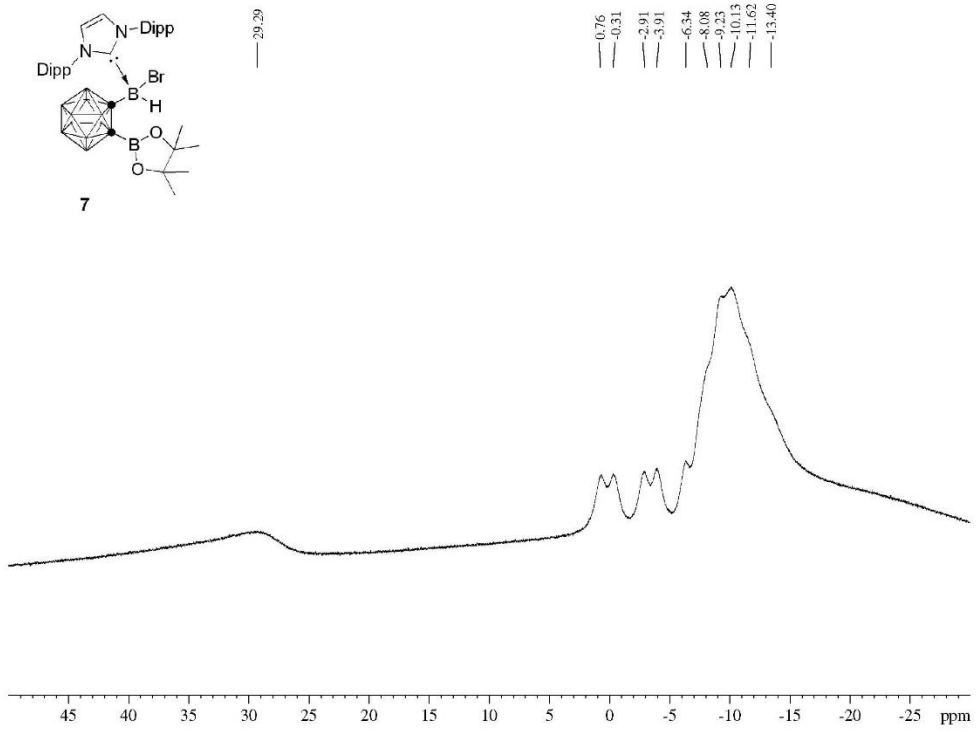

Figure S28. ^{11}B NMR spectrum of compound **7** in CD2Cl2

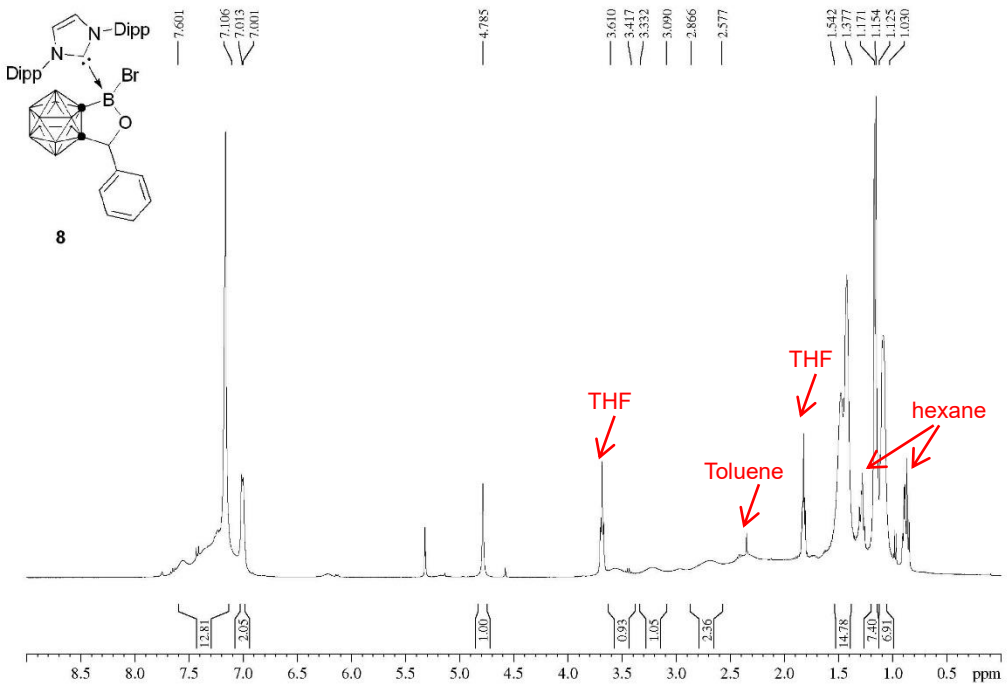

Figure S29. ^{1}H NMR spectrum of compound **8** in CD_2Cl_2.

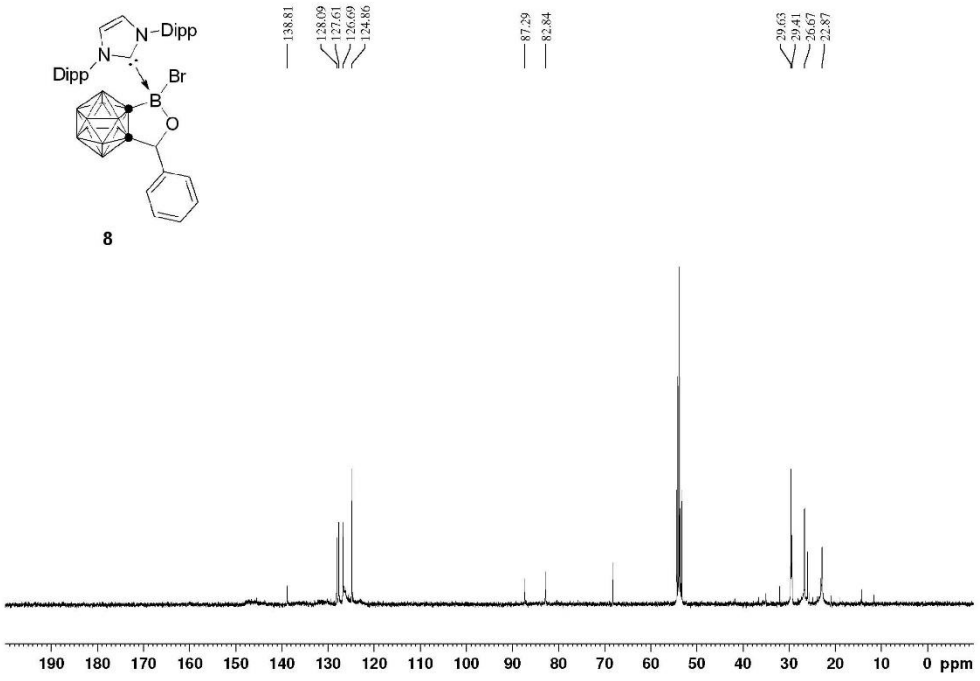

Figure S30. ^{13}C NMR spectrum of compound **8** in CD_2Cl_2.

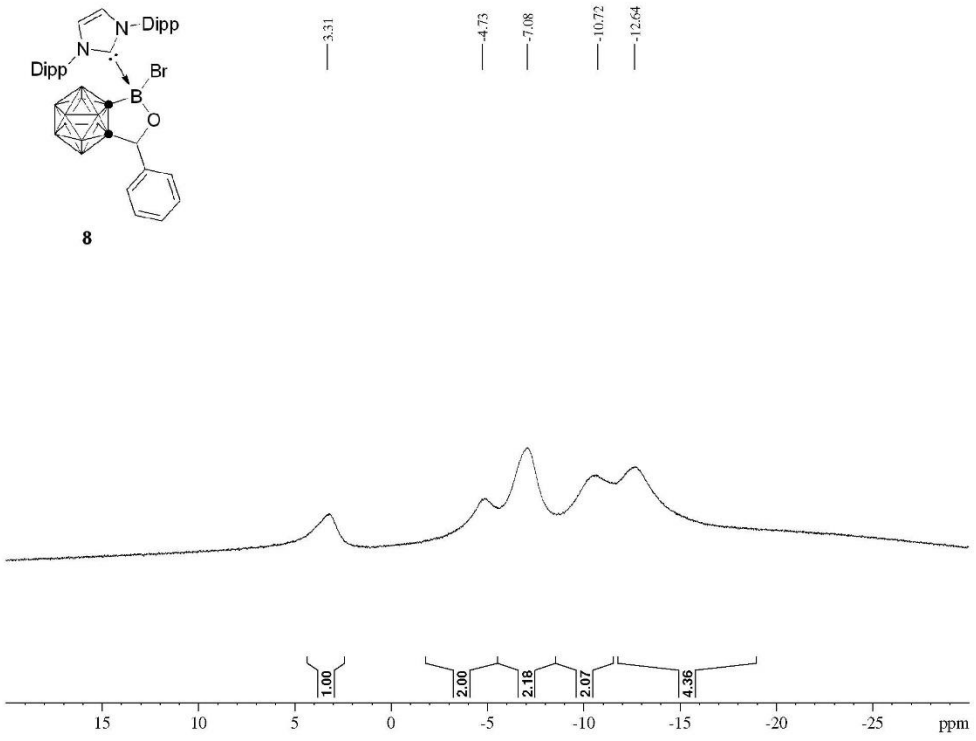

Figure S31. ^{11}B {^{1}H} NMR spectrum of compound **8** in CD_2Cl_2.

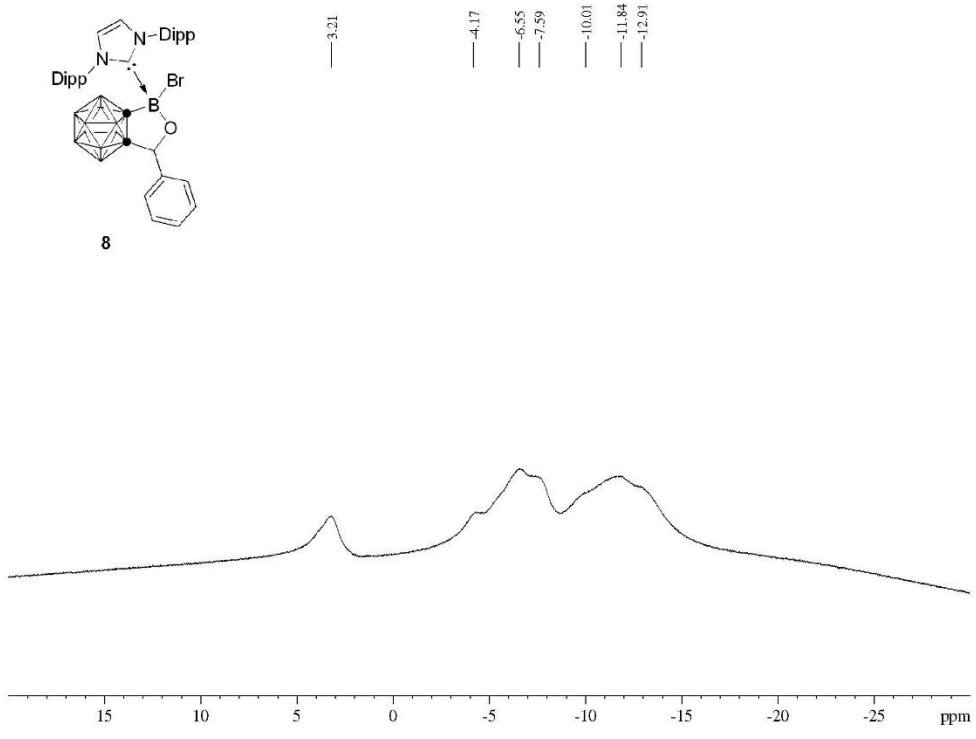

Figure S32. ^{11}B NMR spectrum of compound **8** in CD2Cl2

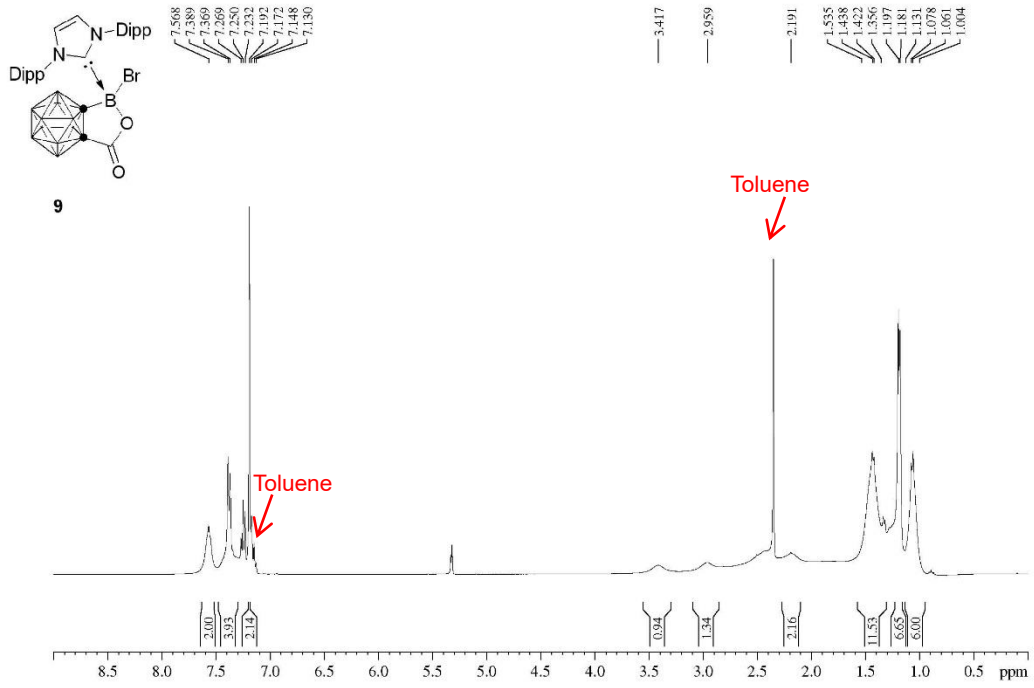

Figure S33. ^{1}H NMR spectrum of compound **9** in CD_2Cl_2.

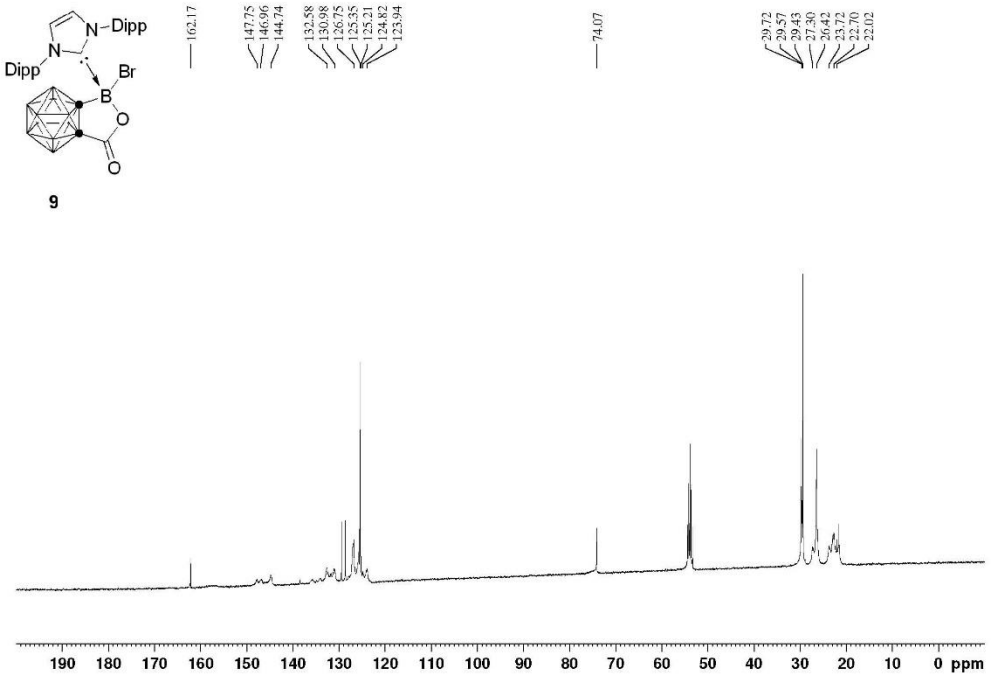

Figure S34. ^{13}C NMR spectrum of compound **9** in CD_2Cl_2.

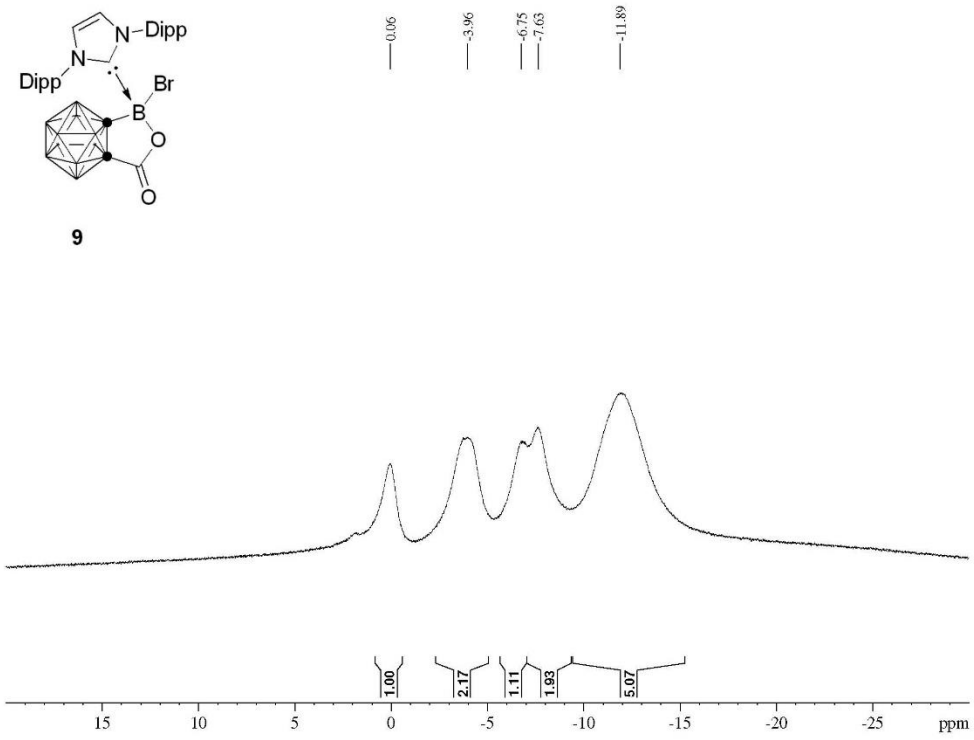

Figure S35. ^{11}B {^{1}H} NMR spectrum of compound **9** in CD_2Cl_2.

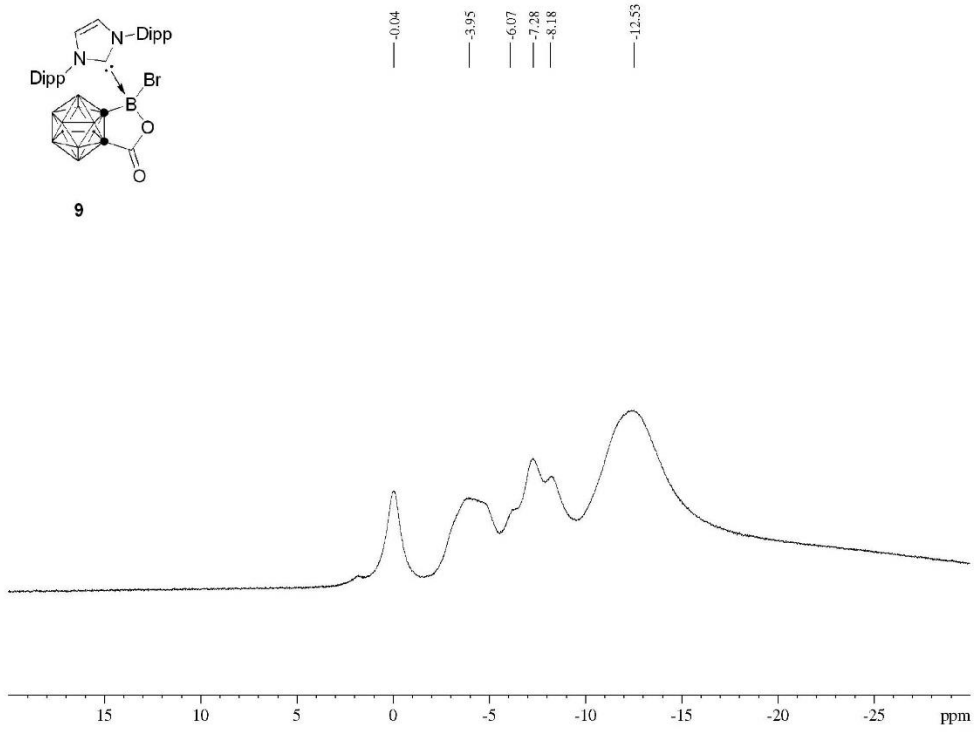

Figure S36. ^{11}B NMR spectrum of compound **9** in CD2Cl2

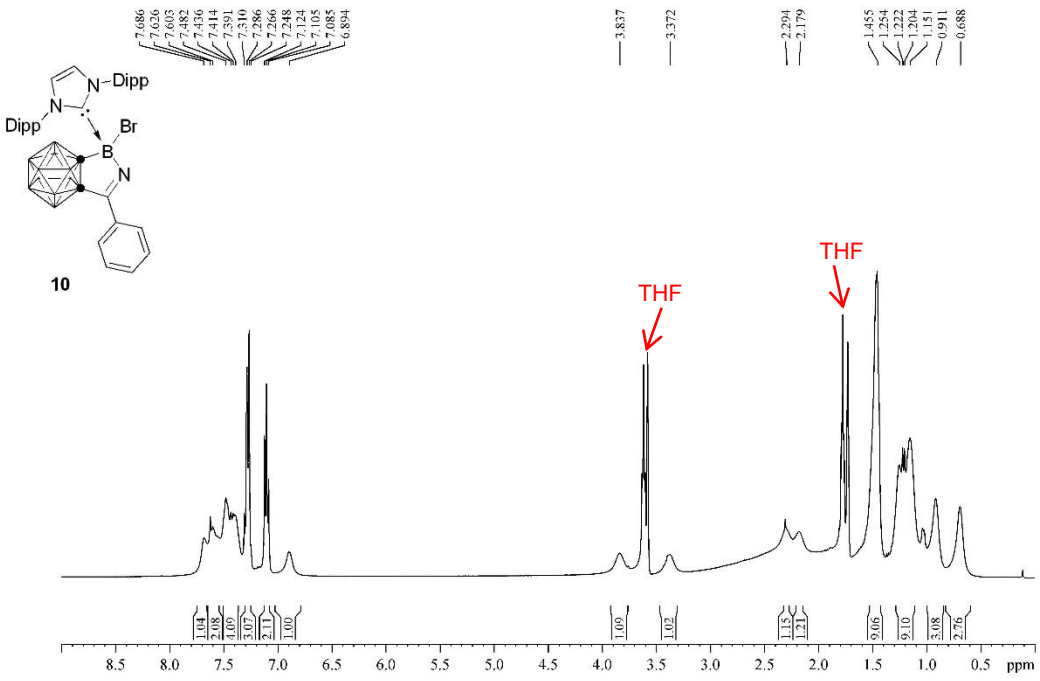

Figure S37. ^{1}H NMR spectrum of compound **10** in CD_2Cl_2.

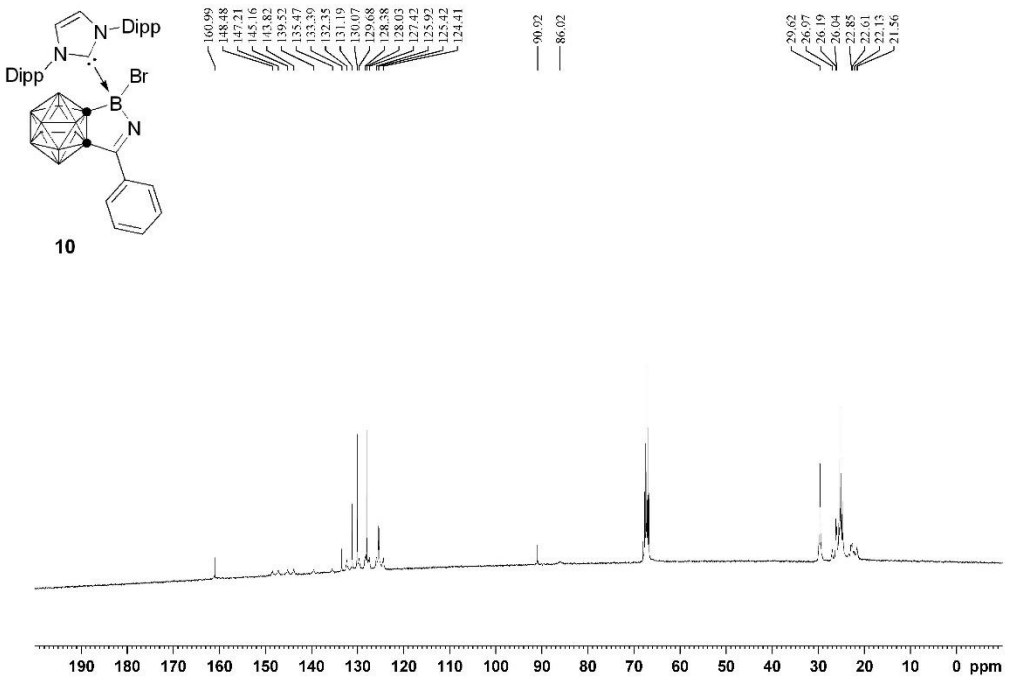

Figure S38. ^{13}C NMR spectrum of compound **10** in CD_2Cl_2.

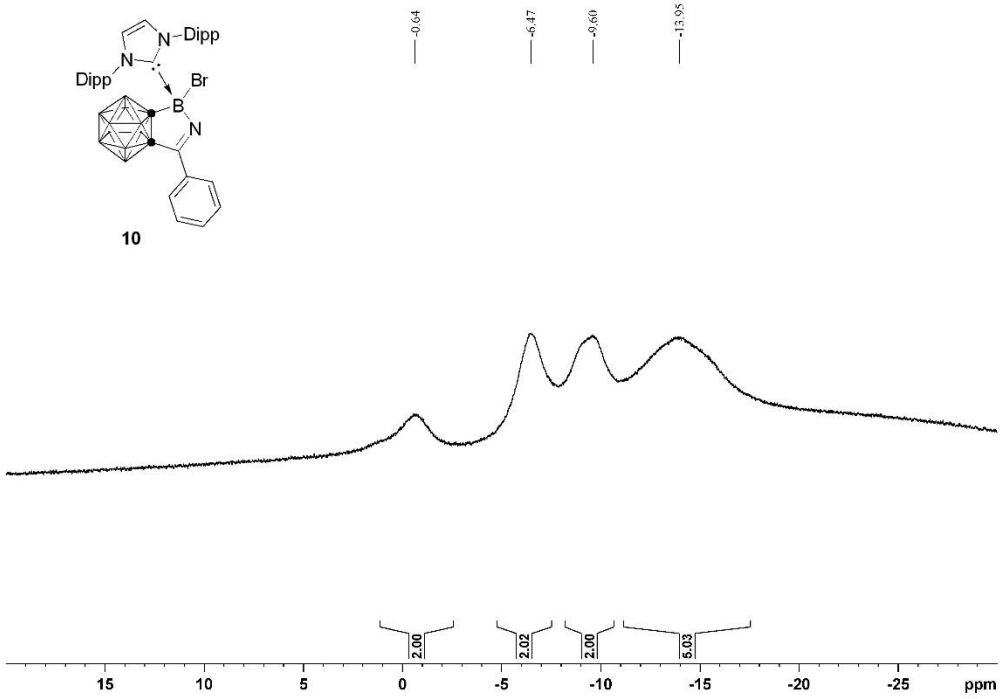

Figure S39. ^{11}B {^{1}H} NMR spectrum of compound **10** in CD_2Cl_2.

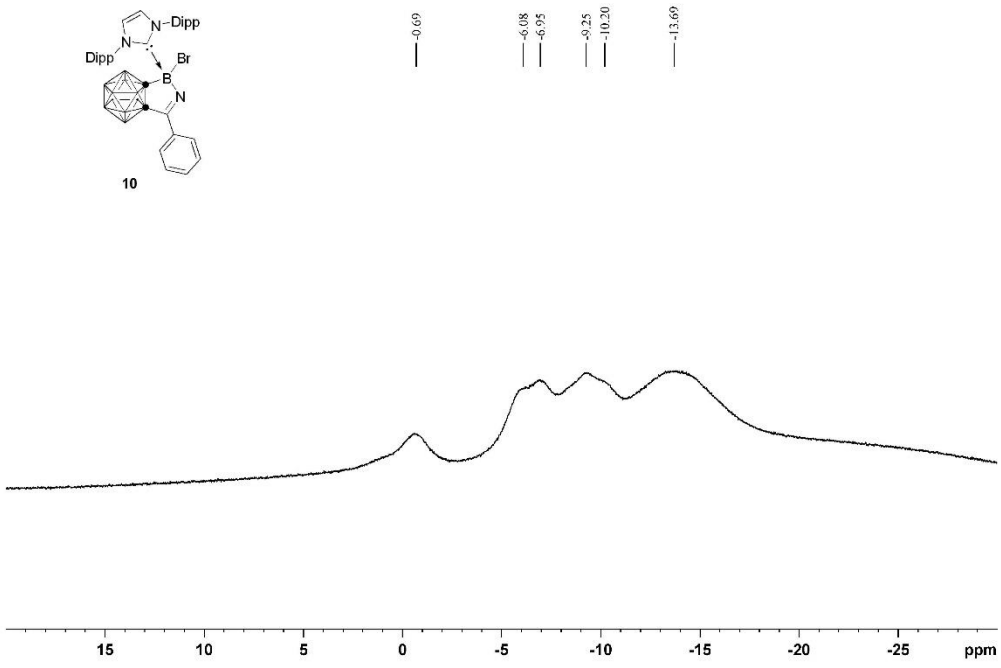

Figure S40. ^{11}B NMR spectrum of compound **10** in CD_2Cl_2.

References

1 Kuhn, N.; Kratz, T. *Synthesis* **1993**, *25*, 561-562.

2 G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen: Germany, **1996**.

3 G. M. Sheldrick, SHELXTL 5.10 for Windows NT: Structure Determination Software Programs. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, **1997**.

4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O.Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin,K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J.Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01; Gaussian, Inc.: Pittsburgh, PA, **2009**.

5 a) A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648-5652; b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, **1988**, *37*, 785-789.

6 a) K. Fukui, *J. Phys. Chem*. **1970**, *74*, 4161-4163; b) K. Fukui, *Acc. Chem. Res*. **1981**, *14*, 363-368.