Supporting Information

for

Versatile chemistry of six-membered NHC with boranes: bromination at sp^3 borane, activation of B–H bond of HBpin, and ring expansion of NHC

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S1. General procedures and instrumentation

All manipulations were carried out in an inert atmosphere of argon using standard Schlenk techniques and in argon filled glove box. The solvents, especially toluene, tetrahydrofuran, dichloromethane and *n*-hexane were purified by MBRAUN solvent purification system MB SPS-800. Benzene-d_6 was dried and distilled over Na/benzophenone mixture prior to use. Other chemicals were purchased from Sigma Aldrich and TCI Chemicals and were used without further purification. The starting material, 6-SIDipp was synthesized by using literature procedure.[1] The ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded in C_6D_6 and $CDCl_3$, using a Bruker Advance DPX 200, Bruker Avance DPX 400, or a Bruker Avance DPX 500 spectrometer. Chemical shifts (δ) are given in ppm. NMR spectra were referenced to external $SiMe_4$ (^{1}H and ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), $CFCl_3$ (^{19}F) respectively. High resolution mass spectra (HRMS) were obtained using a Q Exactive Thermo Scientific at the CSIR-National Chemical Laboratory, Pune. Elemental analyses were performed at the CSIR-National Chemical Laboratory, Pune, India.

S2. Synthetic procedure and spectroscopic characterization of 1-8

1 & **2**: 1.2 equivalent of N-bromosuccinamide (NBS) (0.102 g, 0.58 mmol) and 6-SIDipp-BH_3 (0.2 g, 0.48 mmol) were taken in a Schlenk flask and 5 ml of toluene was added to the reaction mixture. The reaction was continued for 12 h at 70 ˚C temperature. Colorless crystals of **1** and **2** were isolated after keeping the solution at 4 ˚C for a day, where **1** was observed to be the major product with 40% NMR yield along with 20% NMR yield for **2**. As both **1** and **2** were crystallized in similar reaction condition it's very difficult to separate both the products. Hence the NMRs spectra are given for mixture of products.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of **2**: δ = 1.29 (d, J = 6.63 Hz, 12 H, $CH(CH_3)_2$), 1.48 (d, J = 6.63 Hz, 12 H, $CH(CH_3)_2$), 2.37 (quintet, 2 H, $NCH_2CH_2CH_2N$), 2.76 (s, 4 H, NCH_2CH_2N, NBS),

3.22 (m, 4 H, C*H*(CH_3)$_2$), 3.68 (m, *J* = 5.62 Hz, 4 H, NC*H*$_2$C*H*$_2$C*H*$_2$N), 7.23 (m, 4 H, Ar-*H*), 7.36 (t, *J* = 7.75 Hz, 2 H, Ar-*H*) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) of **2**: δ = 19.7 ($CH_2CH_2CH_2$), 23.9 ($CH(CH_3)_2$), 26.2 ($CH(CH_3)_2$), 29.5 (N-CH_2CH_2N, NBS) , 28.9 ($CH(CH_3)_2$), 52.3 (NCH_2), 124.6 (Ar-*C*), 129.1 (Ar-*C*), 140.3 (Ar-*C*), 144.8 (Ar-*C*) ppm, N*C*N signal not observed.

^{11}B{^{1}H} NMR (128 MHz, 298 K, $CDCl_3$) **1** and **2**: δ = -14.3 (bs, 1 B, *B*HBr_2), -20.1 (bs, 1 B, *B*H_2Br) ppm.

HRMS (CH_3CN) of **2**: m/z Calcd. for $C_{28}H_{41}N_2BBr_2$ $[M+H]^+$ 575.1802, found 575.1605.

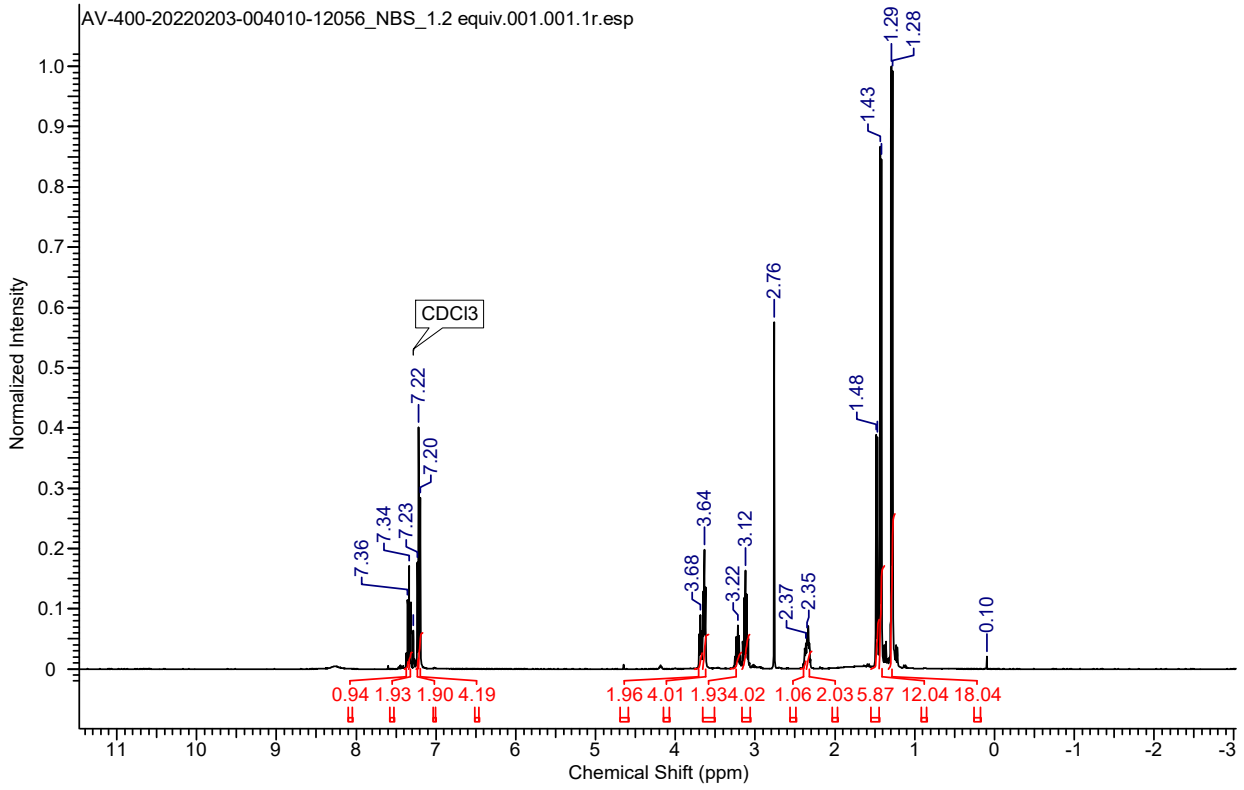

Figure S1. ^{1}H NMR spectrum for mixture of **1** and **2**.

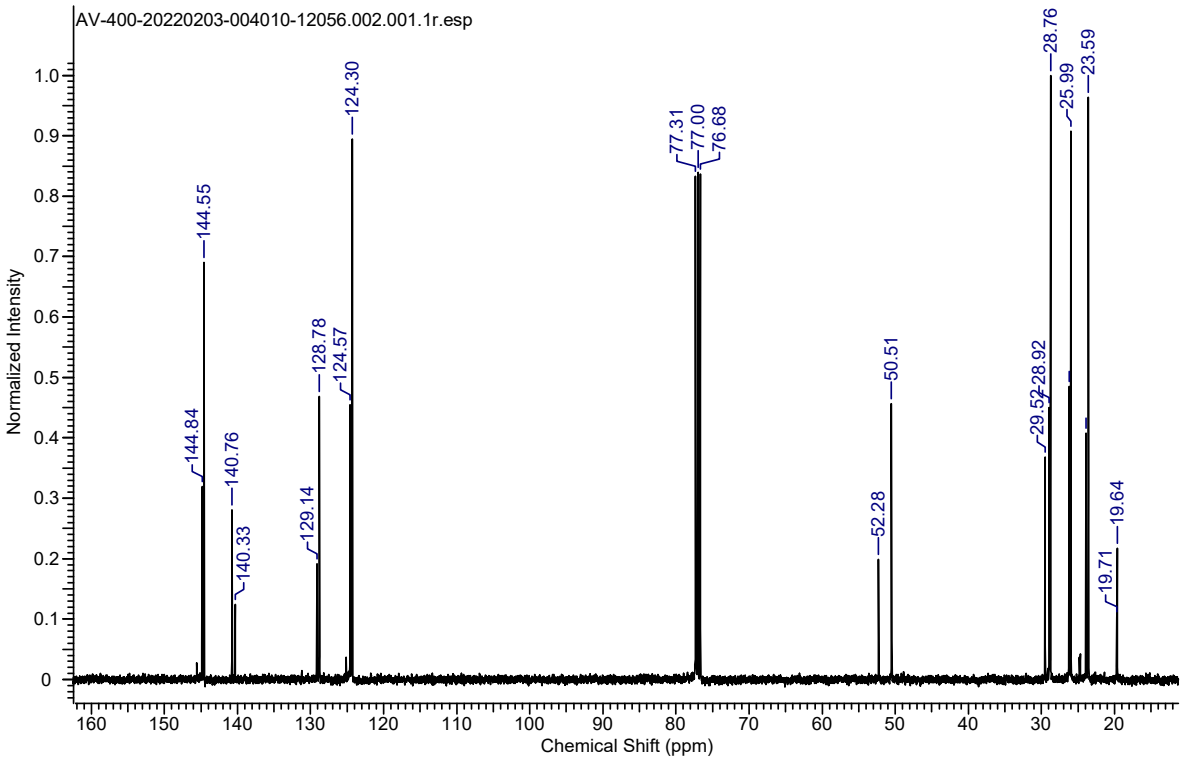

Figure S2. ^{13}C NMR spectrum for mixture of **1** and **2**.

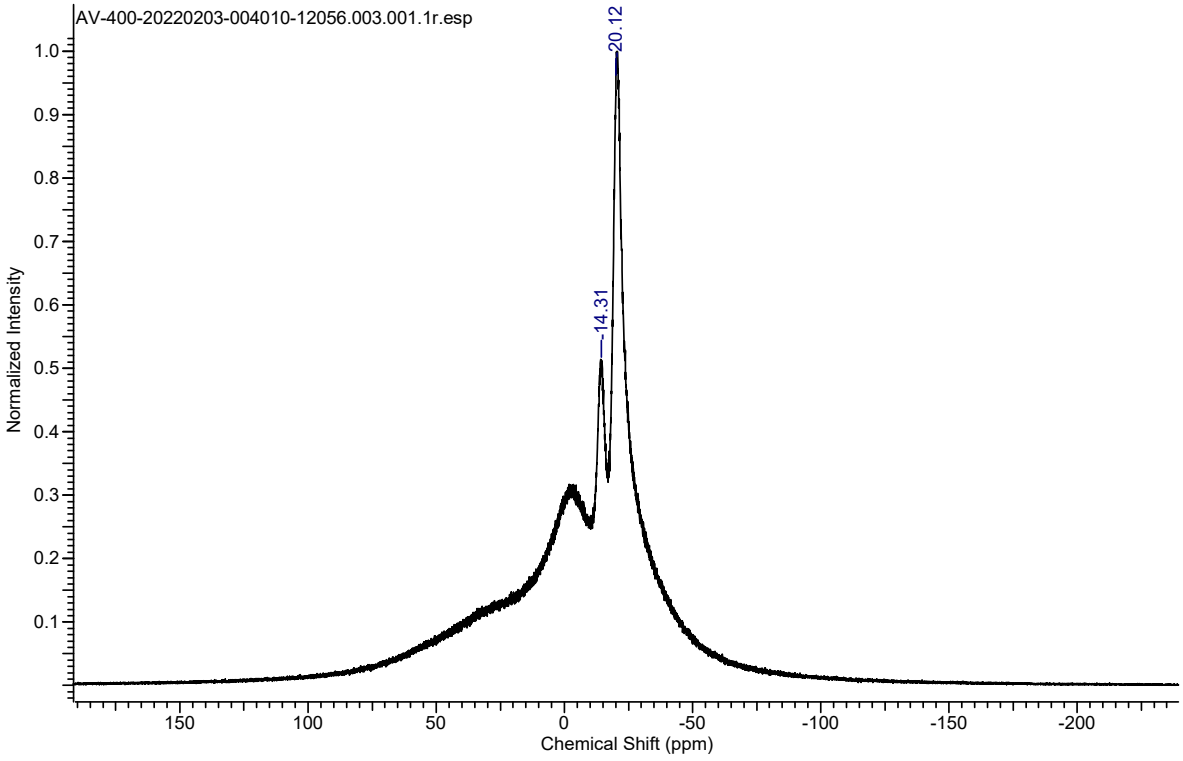

Figure S3. ^{11}B NMR spectrum for mixture of **1** and **2**.

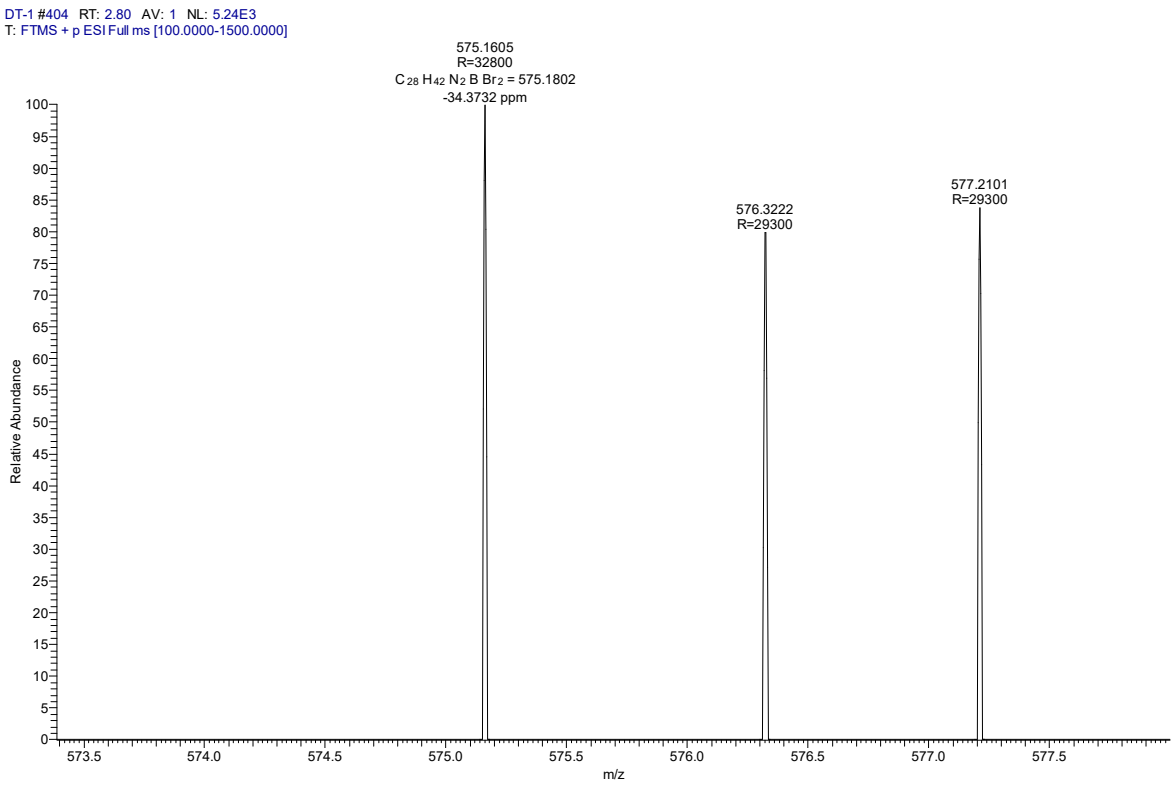

Figure S4. HRMS spectrum of **2**.

1. Two equivalents of carbon tetrabromide (CBr_4) (0.32 g, 0.96 mmol) and 6-SIDipp-BH_3 (0.2 g, 0.48 mmol) were taken in a Schlenk flask and 5 ml of toluene was added to it. The reaction mixture was then heated to 105 ˚C for 24 h. Colorless crystals of **1** were isolated from the flask after keeping the solution at room temperature for a day with a yield of 0.17 g (70%).

Alternatively, 1.5 equivalents of *n*-octyl bromide (0.14 g, 0.72 mmol) or *n*-decyl bromide (0.16 g, 0.72 mmol) or *n*-dodecyl bromide (0.18 g, 0.72 mmol) were added to 6-SIDipp-BH_3 (0.2 g, 0.48 mmol) in 5 ml *o*-xylene solvent and at 145 °C for a fixed time period of 48 h. The reaction mixtures were dried completely and 3 ml toluene solvent were added to it. colorless crystal of **1** came after keeping the toluene solution for one day at room temperature with a yield of 65%-70%.

Table S1: Formation of 6-SIDipp·BH_2Br from the reduction of CBr_4 and alkyl halides

Entry	R-Br	Equivalent	Solvent	Temperature (°C)	Time	Yield (%)
1	$C_8H_{17}Br$	1.5	*o*-Xylene	145	48 h	68
2	$C_{10}H_{21}Br$	1.5	*o*-Xylene	145	48 h	70
3	$C_{12}H_{25}Br$	1.5	*o*-Xylene	145	48 h	65
4	CBr_4	1.2	Toluene	95	48 h	36
5	CBr_4	2	Toluene	105	24 h	70

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 1.27 (d, J = 6.88 Hz, 12 H, CH(CH_3)$_2$), 1.43 (d, J = 6.63 Hz, 12 H, CH(CH_3)$_2$), 1.56, (s, 2 H, BH_2Br), 2.35 (quintet, J = 5.38 Hz, 2 H, NCH$_2$CH_2CH$_2$N), 3.12 (sept, J = 6.75 Hz, 4 H, CH(CH$_3$)$_2$), 3.65 (t, J = 5.88 Hz, 4 H, NCH_2CH$_2$CH_2N), 7.20) (d, J = 7.75 Hz, 4 H, Ar-*H*), 7.33 (t, J = 7.75 Hz, 2 H, Ar-*H*) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ = 19.7 (CH$_2$*C*H$_2$CH$_2$), 23.7 (CH(*C*H$_3$)$_2$), 26.0 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 50.5 (N*C*H$_2$), 124.4 (Ar-*C*), 128.9 (Ar-*C*), 140.8 (Ar-*C*), 144.6 (Ar-*C*) ppm, N*C*N signal not observed.

^{11}B{^{1}H} NMR (128 MHz, 298 K, $CDCl_3$): δ = -20.1 (bs, 1 B, *B*H$_2$Br) ppm.

HRMS (CH_3CN): m/z Calcd. for $C_{28}H_{42}N_2BBr$ $[M-H]^+$ 495.2534, found 497.2541.

Elemental Analysis: Calcd. C, 67.62; H, 8.51; N, 5.63; found C, 67.58; H, 8.43; N, 5.41.

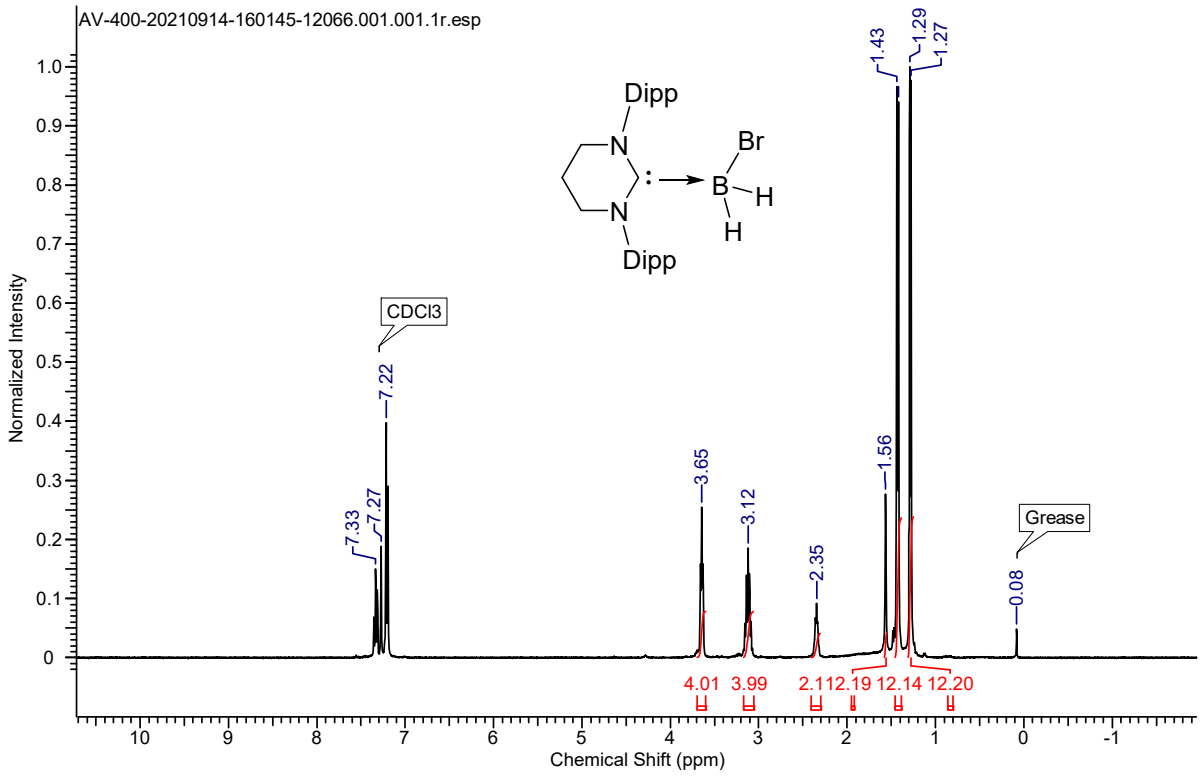

Figure S5. ^{1}H NMR spectrum of **1**.

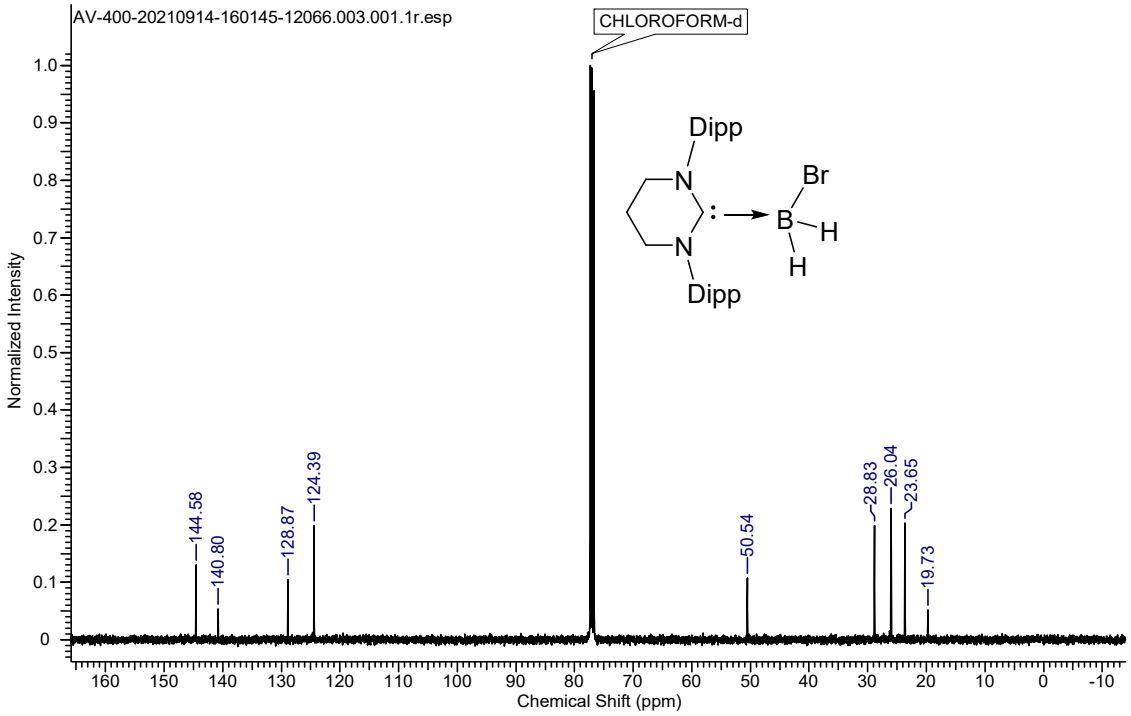

Figure S6. ^{13}C NMR spectrum of **1**.

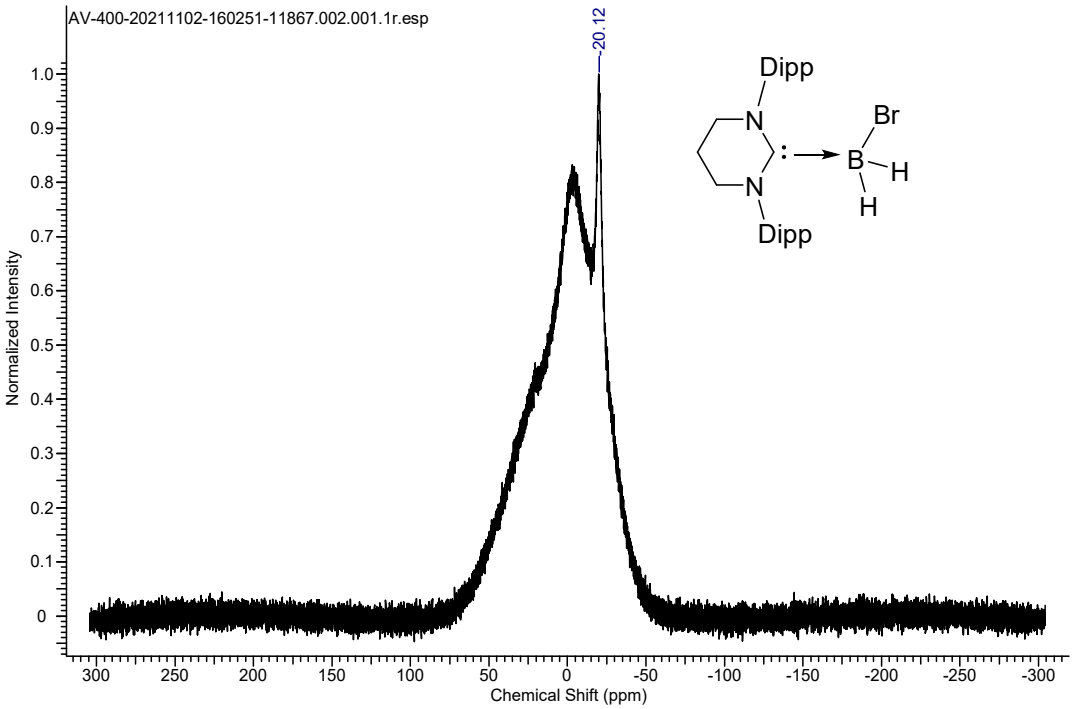

Figure S7. ^{11}B NMR spectrum of **1**.

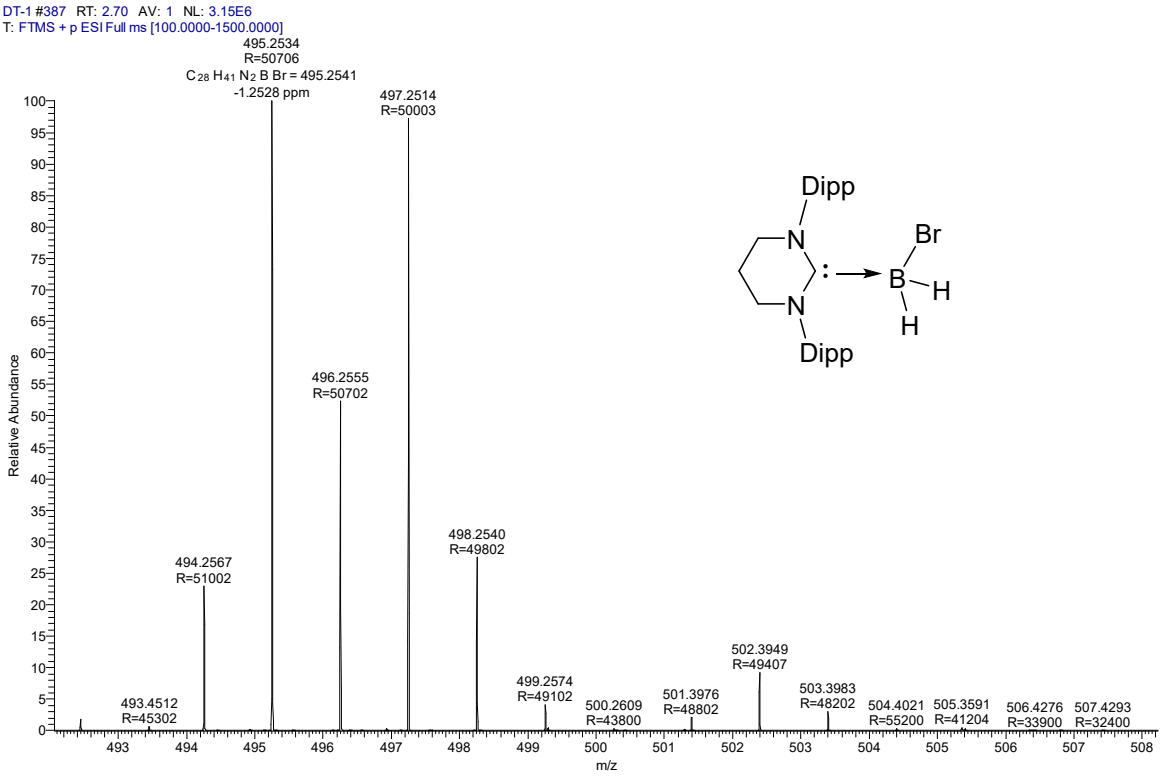

Figure S8. HRMS spectrum of **1**.

3: A slightly excess of $BHCl_2$·dioxane (0.05 ml, 0.70 mmol) was added to a 5 ml toluene and 3 ml hexane solution of 6-SIDipp (0.20 g, 0.50 mmol) at room temperature in a flask. Stirring the resulted reaction mixture for further 2 hours at room temperature accessed a white precipitate. Colorless crystals of **3** were isolated after keeping the white powder in the mixture of 1 ml dichloromethane and 2 ml toluene solution for overnight. Yield 0.17 g (68%).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 1.27 (d, J = 6.85 Hz, 12 H, $CH(CH_3)_2$), 1.43 (d, J = 6.60 Hz, 12 H, $CH(CH_3)_2$, 2.35 (q, J = 4.52 Hz, 2 H, $NCH_2CH_2CH_2N$), 3.16 (sept, J = 6.72 Hz, 4 H, $CH(CH_3)_2$), 3.65 (t, J = 5.87 Hz, 4 H, $NCH_2CH_2CH_2N$), 7.20 (d, J = 7.70 Hz, 4 H, Ar-*H*), 7.34 (t, J = 7.70 Hz, 2 H, Ar-*H*) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ = 19.7 ($CH_2CH_2CH_2$), 23.6 ($CH(CH_3)_2$), 26.2 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 51.9 (NCH_2), 124.3 (Ar-*C*), 129.1(Ar-*C*), 140.1(Ar-*C*), 144.9 (Ar-*C*) ppm, N*C*N signal not observed.

^{11}B{^{1}H} NMR (128 MHz, 298 K, $CDCl_3$): δ = -7.4 (s, 1 B, $BHCl_2$) ppm.

HRMS (CH_3CN): m/z Calcd. for $C_{28}H_{41}BCl_2N_2$ $[M+Na]^+$ 509. 2632, found 509.2636.

Elemental Analysis: Calcd. C, 68.45; H, 8.48; N, 5.75; found: C, 68.88; H, 8.53; N, 5.48.

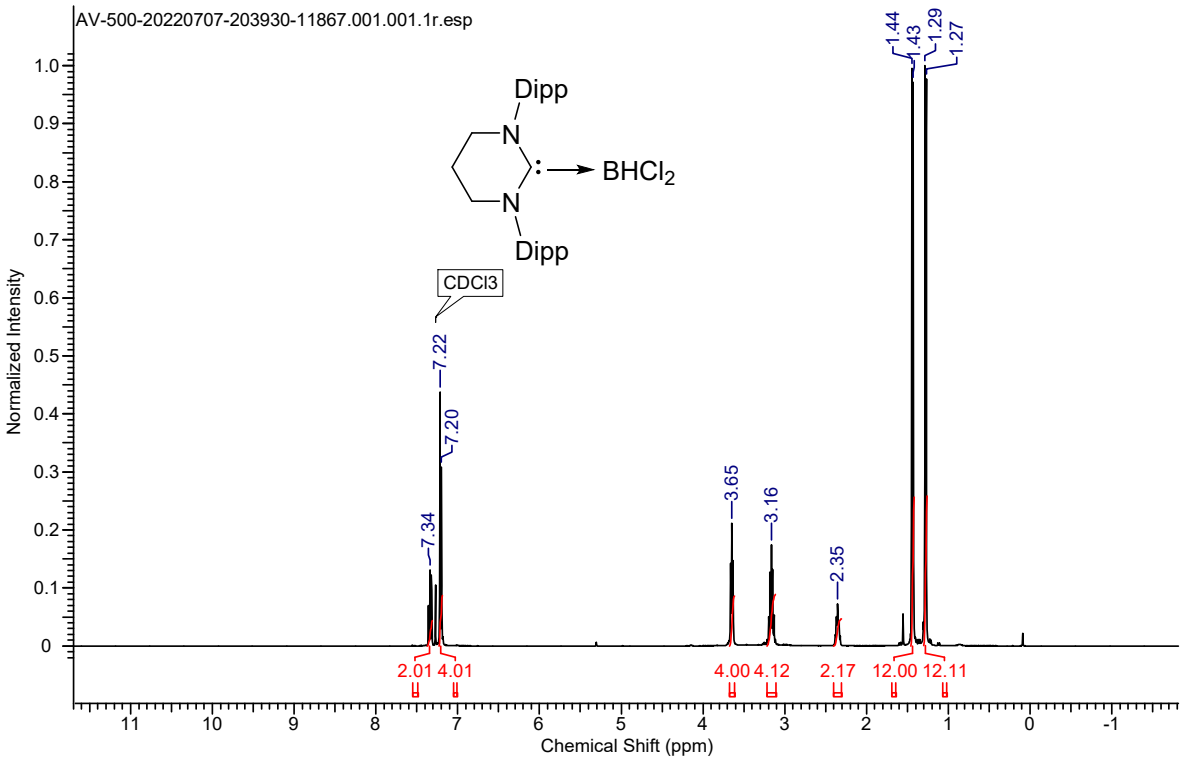

Figure S9. ^{1}H NMR spectrum of **3**.

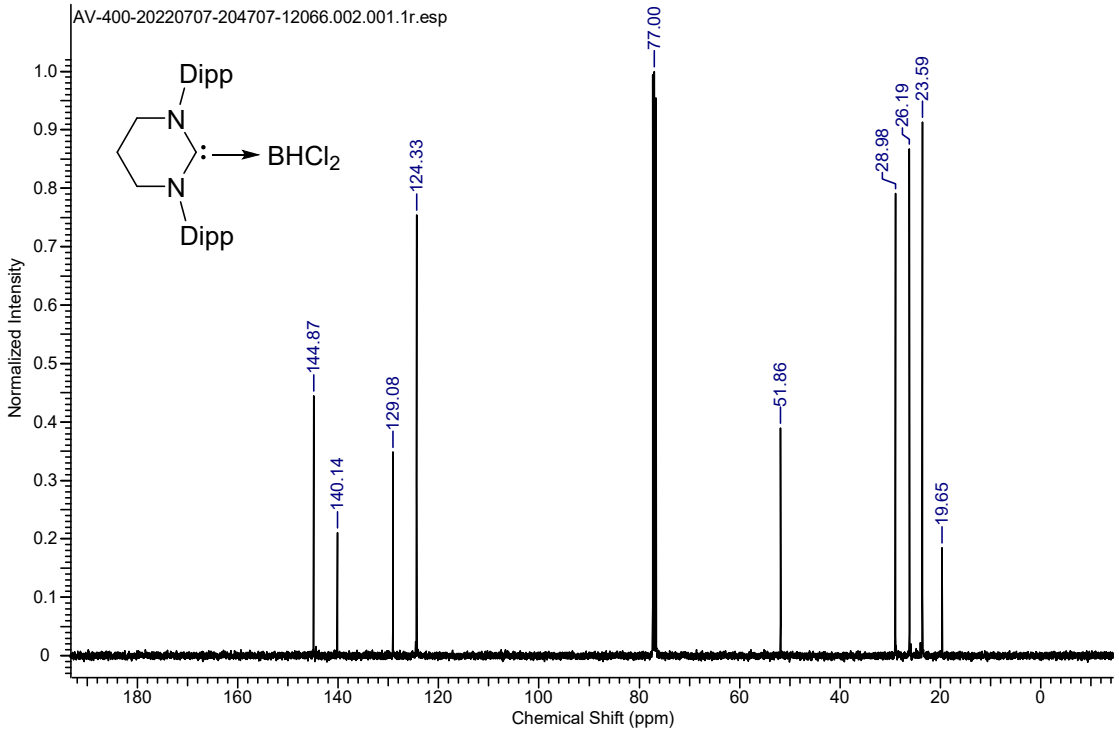

Figure S10. ^{13}C NMR spectrum of **3**.

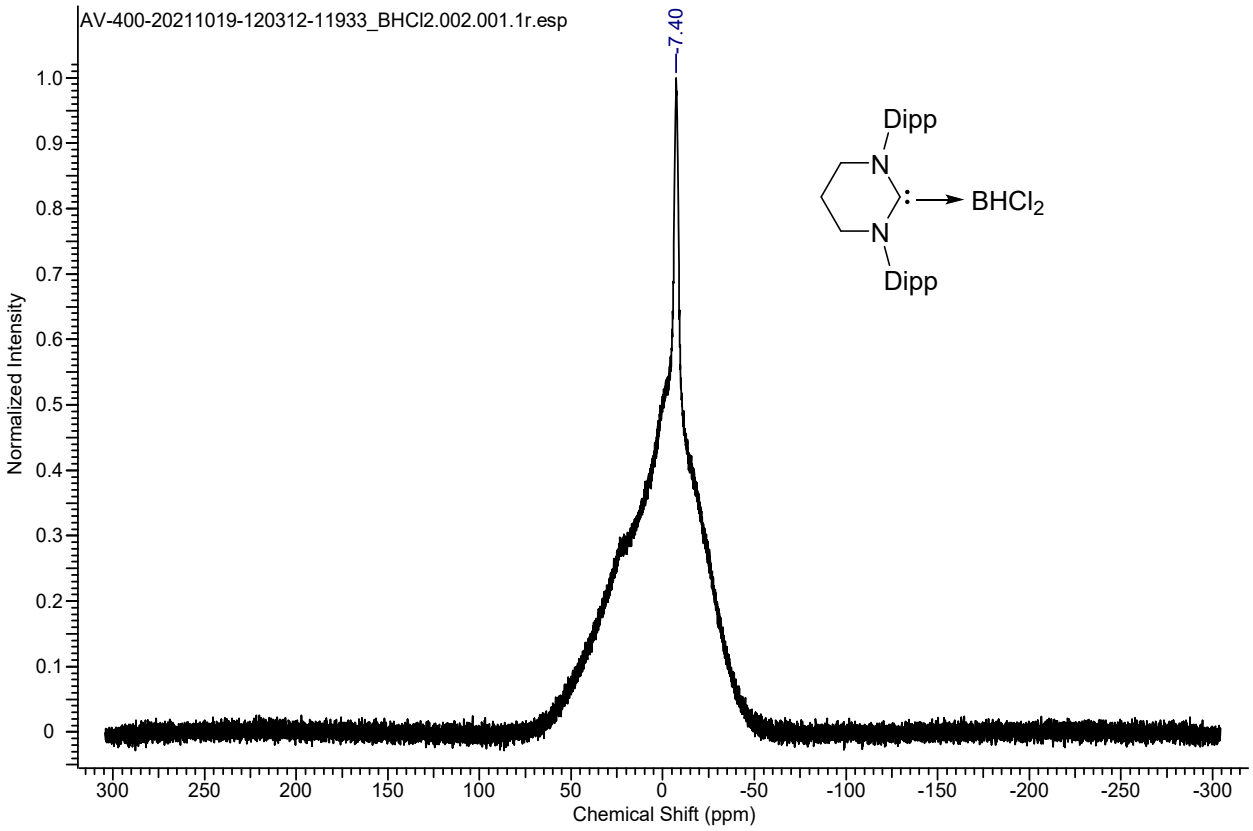

Figure S11. ^{11}B NMR spectrum of **3**.

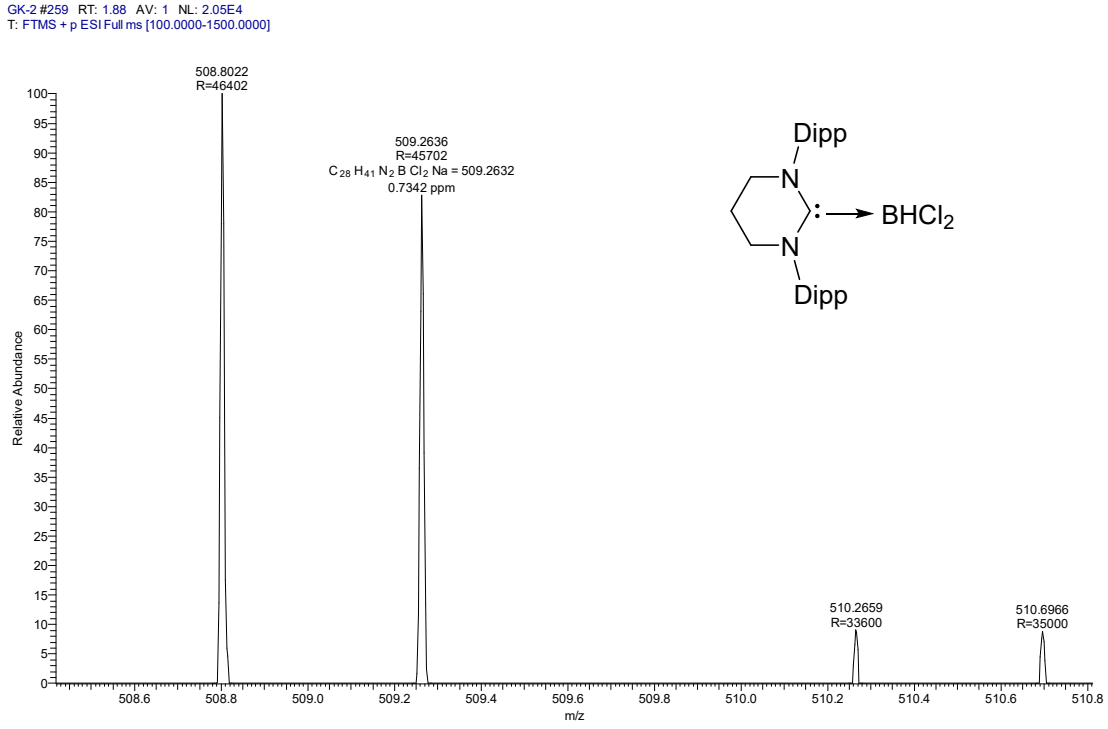

Figure S12. HRMS spectrum of **3**.

4: Two equivalents of triflic acid (0.150 g, 1.0 mmol) were added to the DCM solution of **3** (0.3 g, 0.5 mmol) at low temperature. The reaction was run for 12 h at room temperature. The reaction mixture was dried completely and washed with hexane for 2 times. Then 5 ml of toluene was added to the reaction mixture and filtered through frit. The reaction mixture was concentrated and colorless crystals of **4** were isolated after keeping the solution at room temperature for a day with a yield of 0.11 g (35%).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 1.27 (d, J = 6.88 Hz, 12 H, $CH(CH_3)_2$), 1.32 (d, J = 6.75 Hz, 12 H, $CH(CH_3)_2$), 2.48 (quintet, J = 5.63 Hz, 2 H, $NCH_2CH_2CH_2N$), 2.97 (sept, J = 6.75 Hz, 4 H, $CH(CH_3)_2$), 3.69 (t, J = 5.75 Hz, 4 H, $NCH_2CH_2CH_2N$), 7.21 (m, J = 7.88 Hz, 4 H, Ar-*H*), 7.43 (t, J = 7.75 Hz, 2 H, Ar-*H*) 7.64 (bs, 2 H, $B(OH)_2$) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ = 18.7 ($CH_2CH_2CH_2$), 22.5 ($CH(CH_3)_2$), 26.3 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 48.2 (NCH_2), 124.9 (Ar-*C*), 128.2 (Ar-*C*), 129.0 (Ar-*C*), 131.1 (Ar-*C*), 136.1(Ar-*C*), 146.1(Ar-*C*) ppm, N*C*N signal not observed.

^{11}B{^{1}H} NMR (128 MHz, 298 K, $CDCl_3$): δ = 24.6 (q, 1 B, $B(OH)_2$) ppm.

^{19}F{^{1}H} NMR (377 MHz, 298 K, $CDCl_3$): δ = -78.9 (s, 3 F, CF_3) ppm.

HRMS (CH_3CN): m/z Calcd. for $C_{29}H_{42}BF_3O_5N_2S$ $[M+H]^+$ 599.2932, found 599.3036.

Elemental Analysis: Calcd. C, 58.20; H, 7.07; N, 4.68; found C, 58.60; H, 7.21; N, 4.53

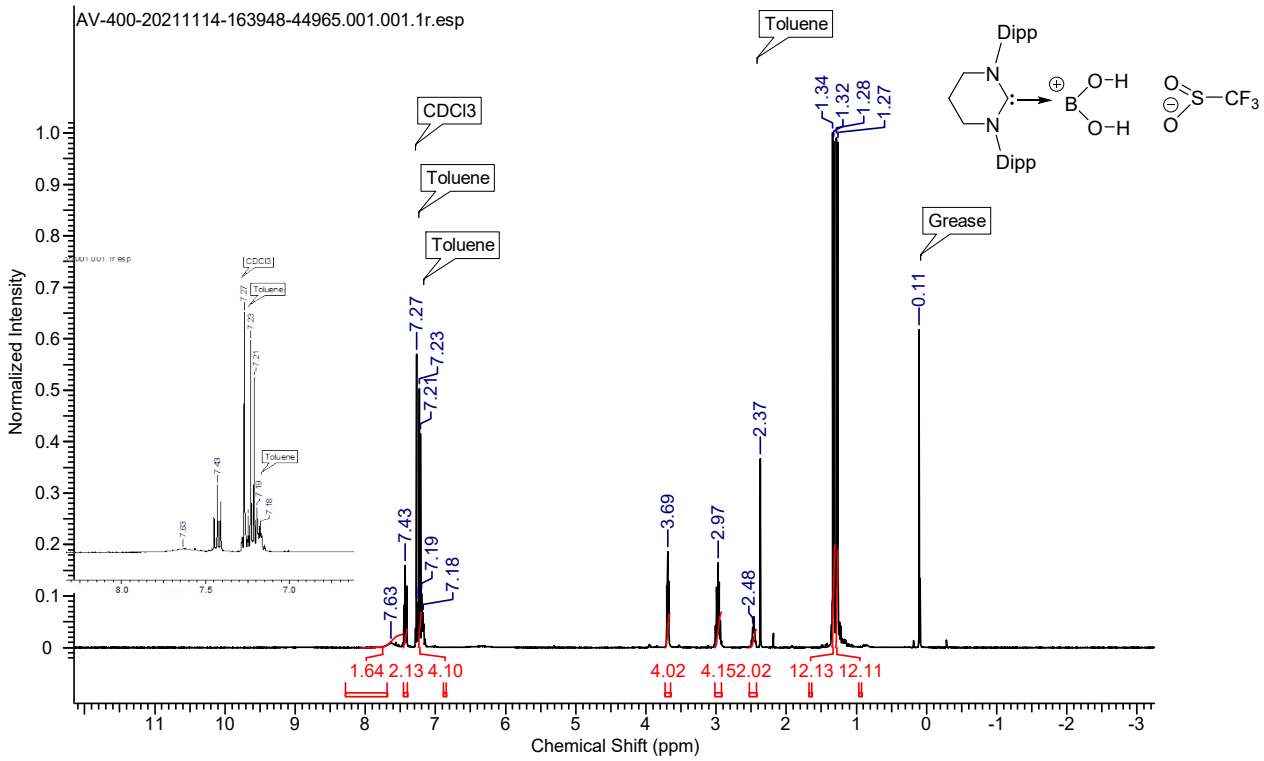

Figure S13. ^{1}H NMR spectrum of **4**.

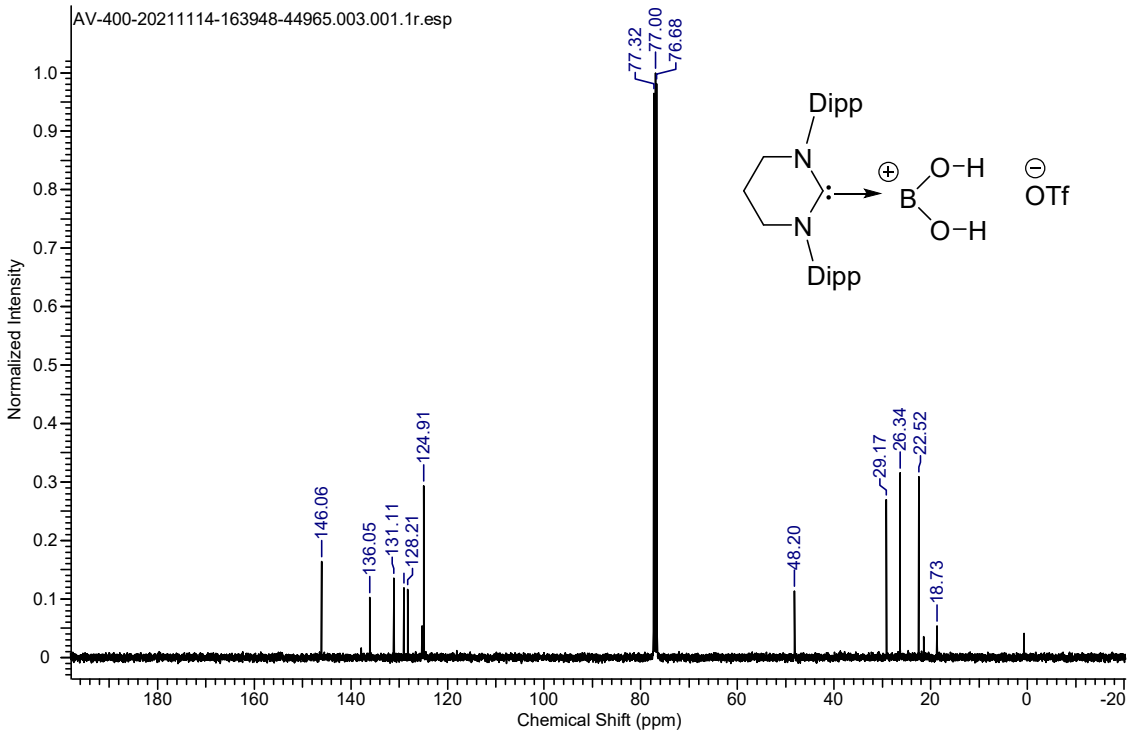

Figure S14. ^{13}C NMR spectrum of **4**.

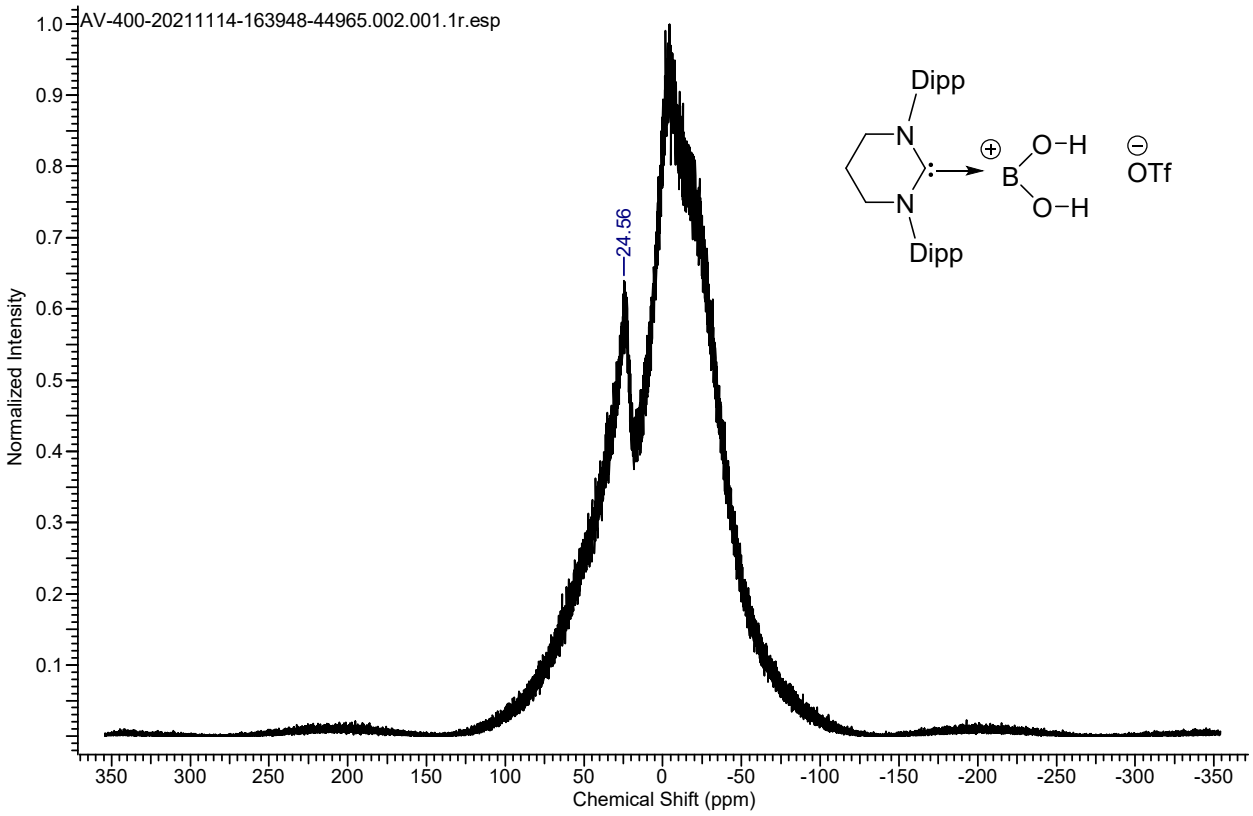

Figure S15. ^{11}B NMR spectrum of **4**.

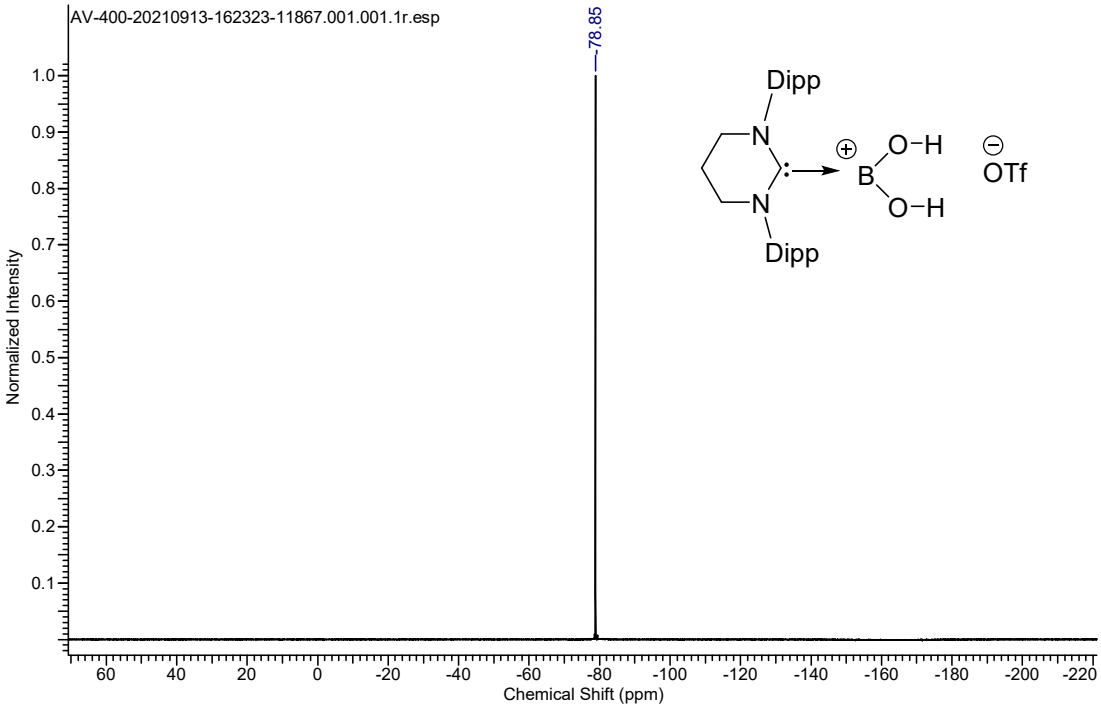

Figure S16. ^{19}F NMR spectrum of **4**.

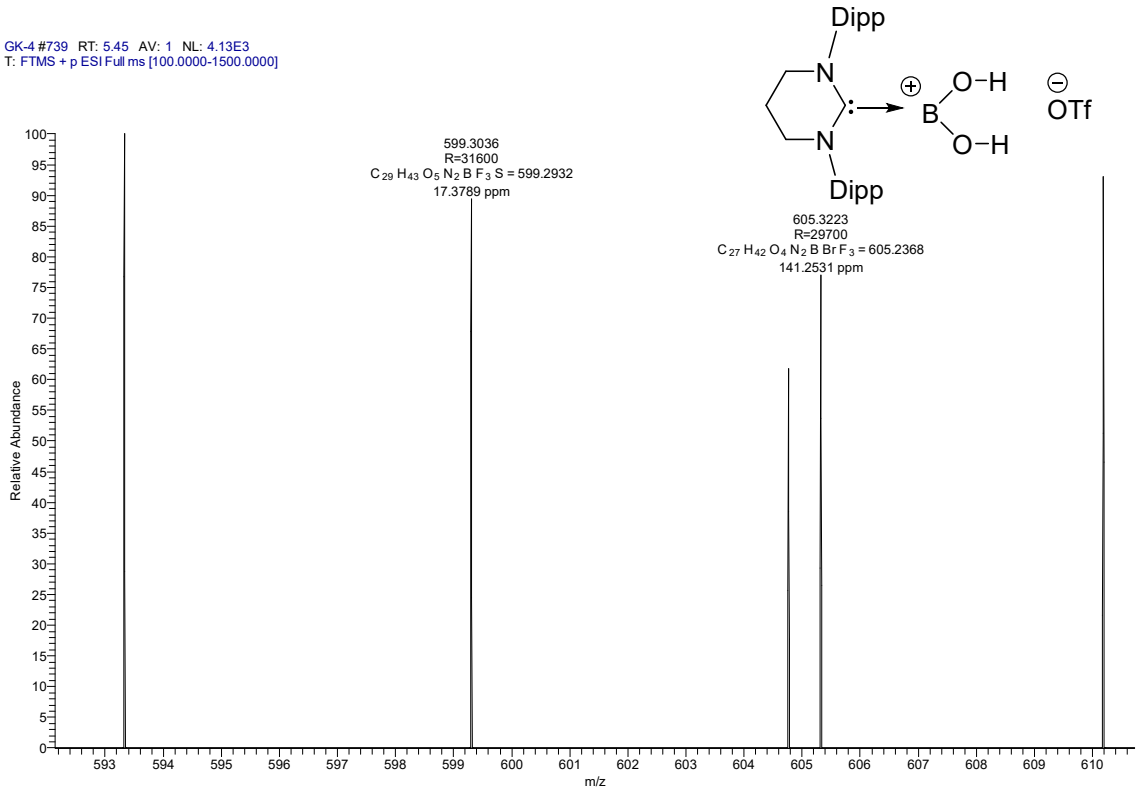

Figure S17. HRMS spectrum of **4**.

5: one equivalent silver hexafluoroantimonate ($AgSbF_6$) (0.171 g, 0.50 mmol) was added to the toluene solution of **3** (0.3 g, 0.50 mmol) at low temperature. The reaction was run for 4 h at room temperature. The reaction mixture was dried completely and washed with hexane. Then 5 ml of toluene was added to the reaction mixture and filtered through frit. The reaction mixture was concentrated and colorless crystals of **5** were isolated after keeping the solution at -36 ˚C temperature for a day with a yield of 0.14 g (42%).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 1.32 (d, J = 6.88 Hz, 12 H, CH(CH_3)$_2$), 1.38 (d, J = 6.75 Hz, 12 H, CH(CH_3)$_2$), 2.33 (q, J = 5.63 Hz, 2 H, NCH$_2$CH_2CH$_2$N), 3.06 (sept, J = 6.75 Hz, 4 H, CH(CH$_3$)$_2$), 3.55 (t, J = 5.75 Hz, 4 H, NCH_2CH$_2$CH_2N), 7.21 (d, J = 7.63 Hz, 4 H, Ar-H), 7.36 (t, J = 7.75 Hz, 2 H, Ar-H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$): δ = 19.6 ($CH_2CH_2CH_2$), 23.3 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 50.5 (NCH_2), 123.9 (Ar-*C*), 128.8 (Ar-*C*), 140.4 (Ar-*C*), 144.7 (Ar-*C*) ppm, N*C*N signal not observed.

$^{11}B\{^{1}H\}$ NMR (127 MHz, 298 K, $CDCl_3$): δ = 24.5 (m, 1 B, $B(OH)_2$) and -0.03 (doublet, unknown tetraborate anion fragment due to the decomposition of the **6** with time) ppm.

$^{19}F\{^{1}H\}$ NMR (377 MHz, 298 K, $CDCl_3$): δ = -130.7 (s, 6 F, SbF_6) ppm.

HRMS (CH_3CN): m/z Calcd. for $C_{28}H_{42}N_2O_2B$ $[M+H]^+$ 450.3412, found 450.3474.

Elemental Analysis: Calcd. C, 49.08; H, 6.18; N, 4.09; found C, 49.12; H, 6.68; N, 4.18.

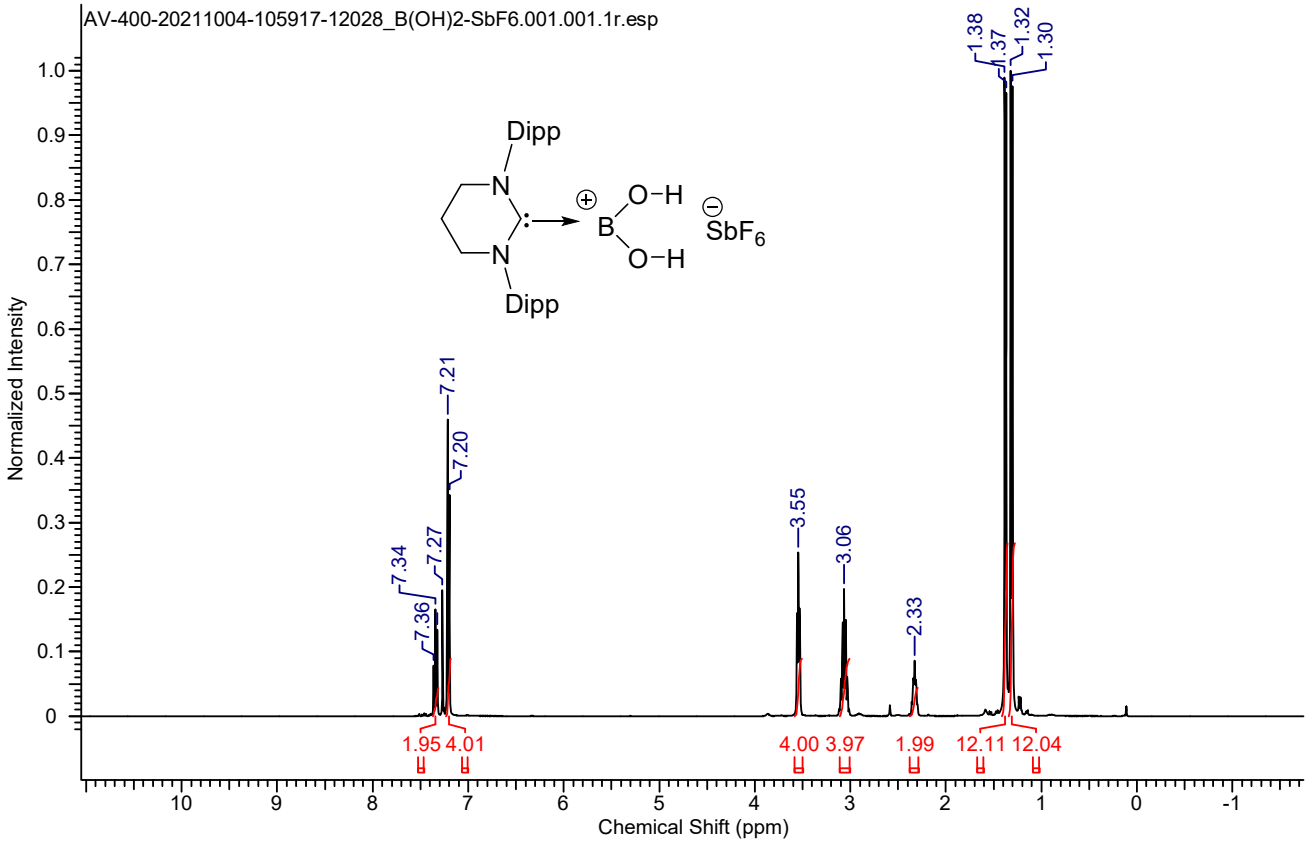

Figure S18. ^{1}H NMR spectrum of **5**.

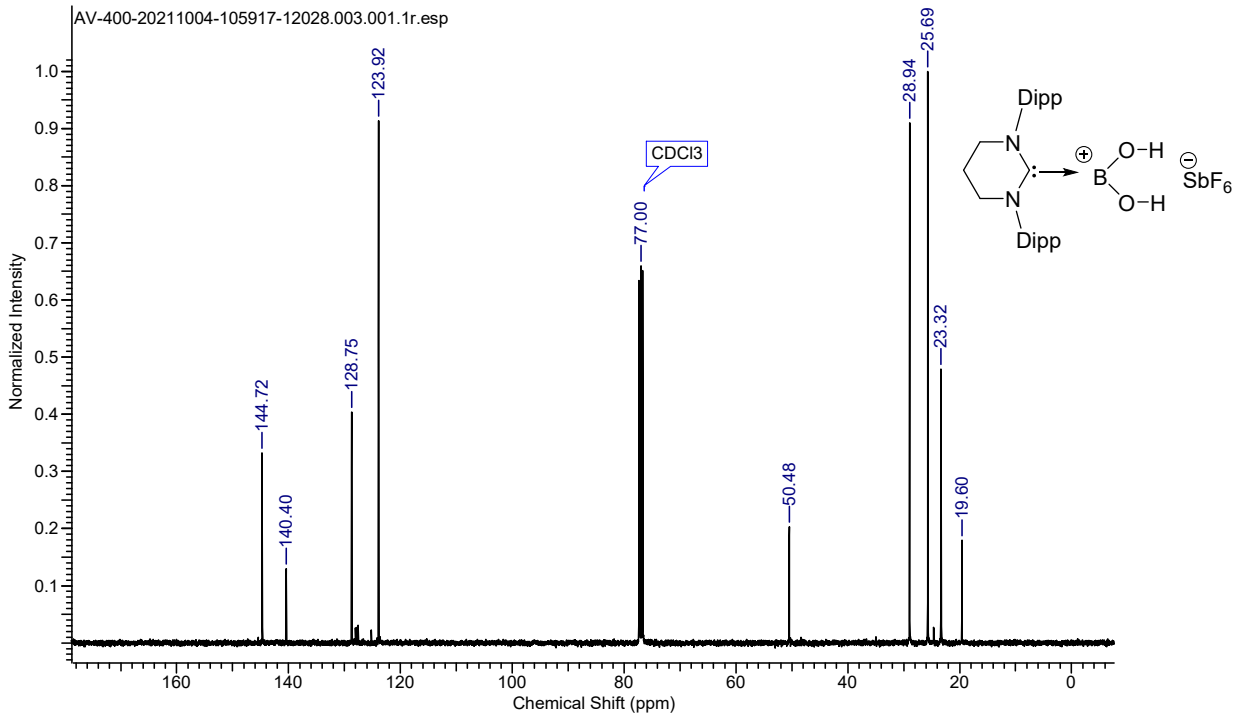

Figure S19. ^{13}C NMR spectrum of **5**.

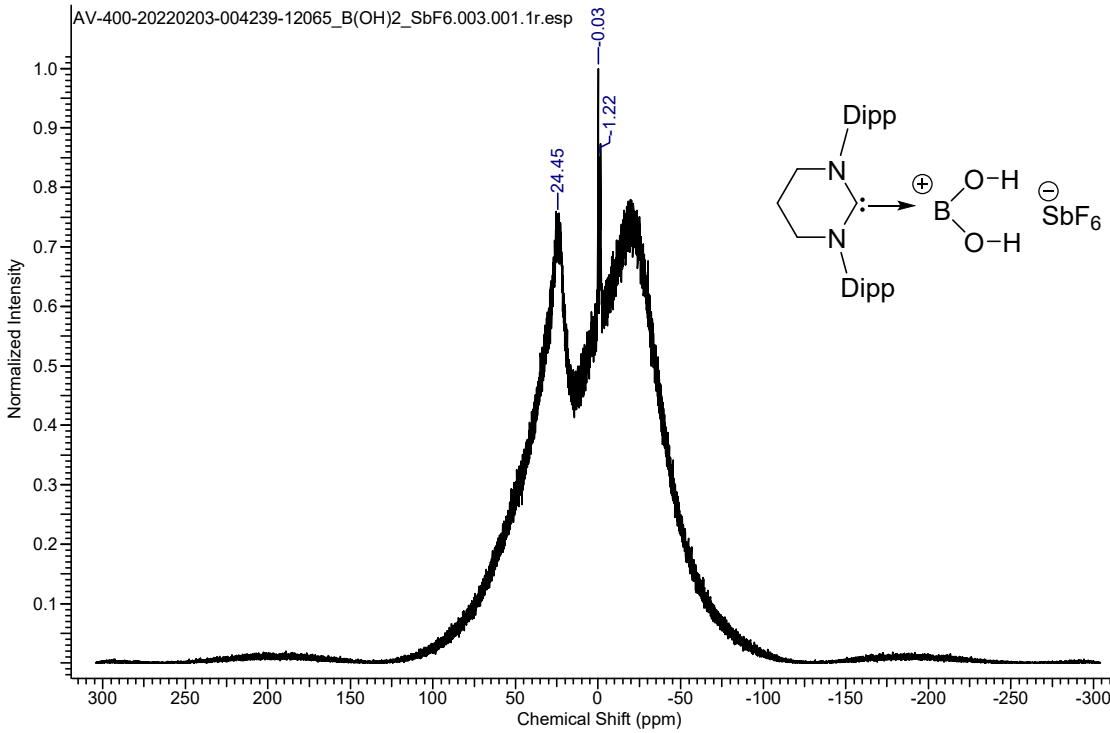

Figure S20. ^{11}B NMR spectrum of **5**.

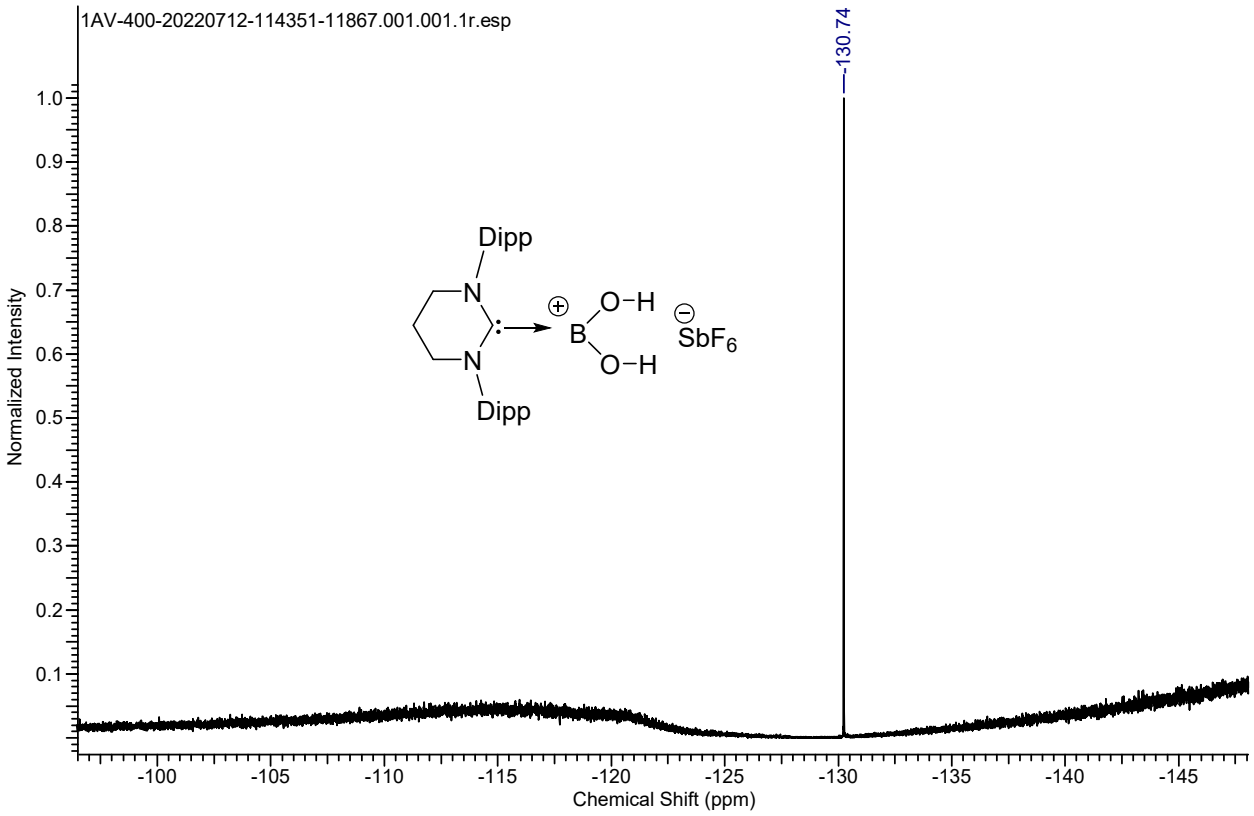

Figure S21. ^{19}F NMR spectrum of **5**.

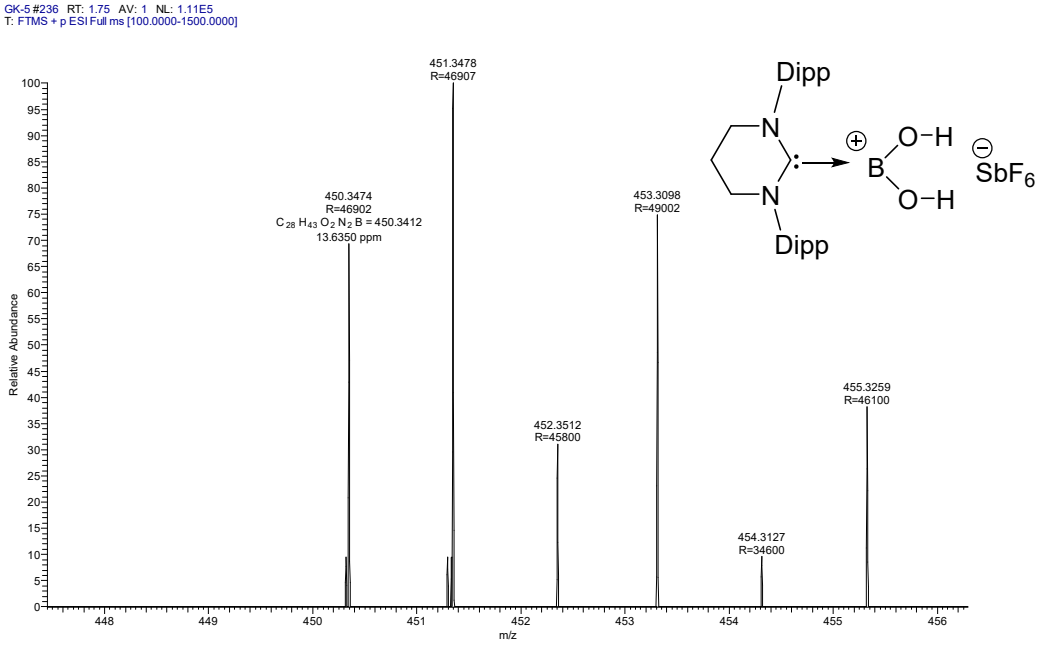

Figure S22. HRMS spectrum of **5**.

6a and 6b: 6-SIDipp (0.20 g, 0.50 mmol) was dissolved in benzene-d_6 (5 mL) in a vial and 9-BBN (0.061 g, 0.50 mmol) was added to this solution at room temperature. The resulting mixture was directly kept at -4 °C to get the crystals of **6a** after 1 day. When the same resulting mixture was kept at room temperature it gives the colorless crystals of **6b** after 2 days. We have monitored the conversion of **6a** to **6b** via time dependent ^{11}B NMR spectra. **6a** is unstable at room temperature and converts to the ring expansion product within 6 hours which is shown below. We have attempted many times but could not get better ^{1}H and ^{13}C spectrum due to the mixture of product formations.

$^{11}B\{^{1}H\}$ NMR (128 MHz, 298 K, C_6D_6) after 30 min reaction: δ = –13.3 (bs, 1 B, 9-BBN), 27.9 (bs, 1 B, excess 9-BBN) ppm.

$^{11}B\{^{1}H\}$ NMR (128 MHz, 298 K, C_6D_6) after 3 h reaction: δ = –13.3 (bs, 1 B, 9-BBN), 48.9 (bs, 1 B, $NBCNC_3$) ppm

$^{11}B\{^{1}H\}$ NMR (128 MHz, 298 K, $CDCl_3$) after 6 h reaction: δ = 49.1(bs, 1 B, $NBCNC_3$), 31.9 (bs, 1 B, excess 9-BBN), ppm.

HRMS (CH_3CN) of **6b**: m/z Calcd. for $C_{36}H_{55}BN_2$ $[M+H]^+$ 527.4531, found 527.4514.

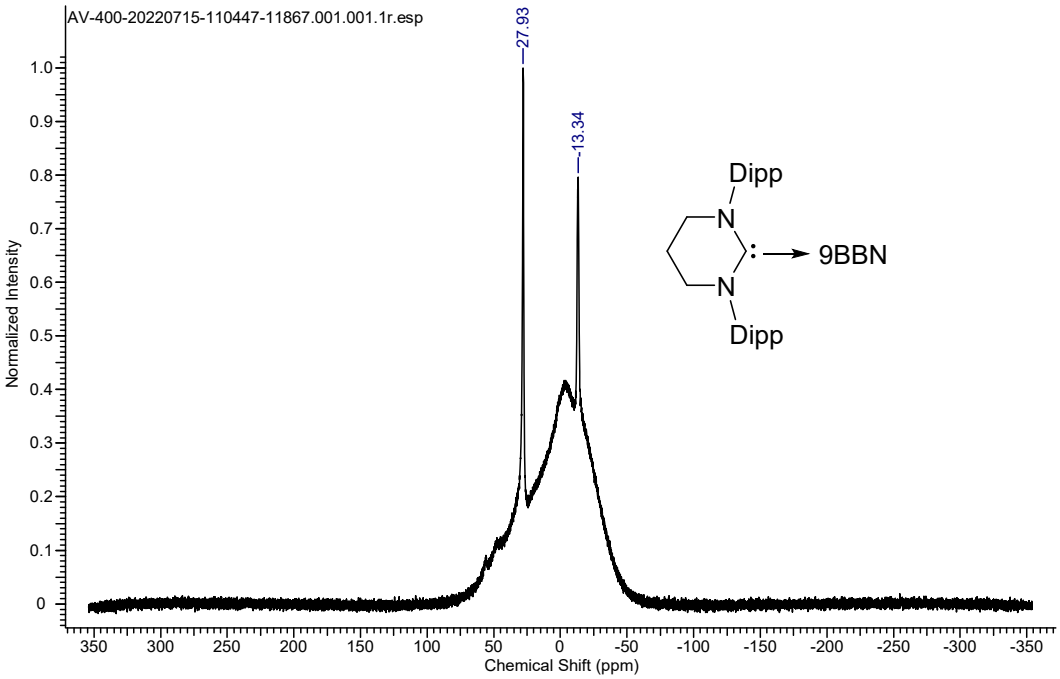

Figure S23. ^{11}B NMR spectrum of **6a** recorded after 30 min reaction time of 9-BBN and 6-SIDipp.

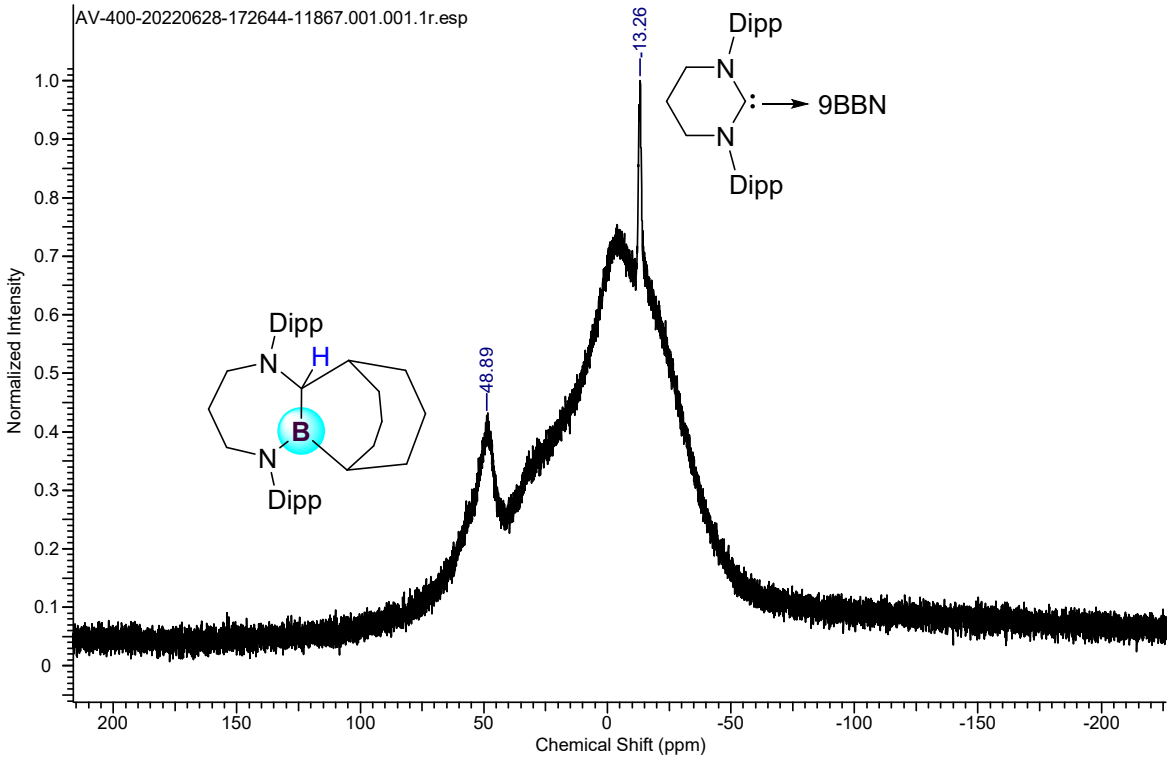

Figure S24. ^{11}B NMR spectrum recorded after 3 h of reaction time of 9-BBN and 6-SIDipp.

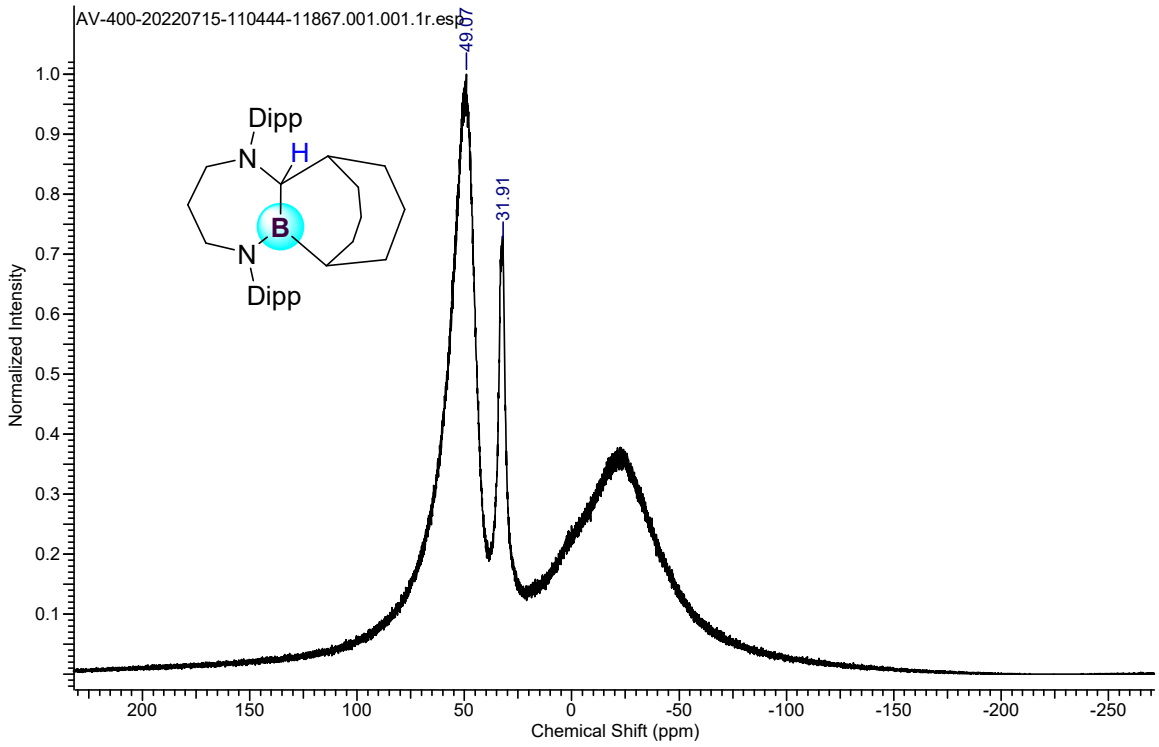

Figure S25. ^{11}B NMR spectrum of **6b** recorded after 6 h of reaction time of 9-BBN and 6-SIDipp.

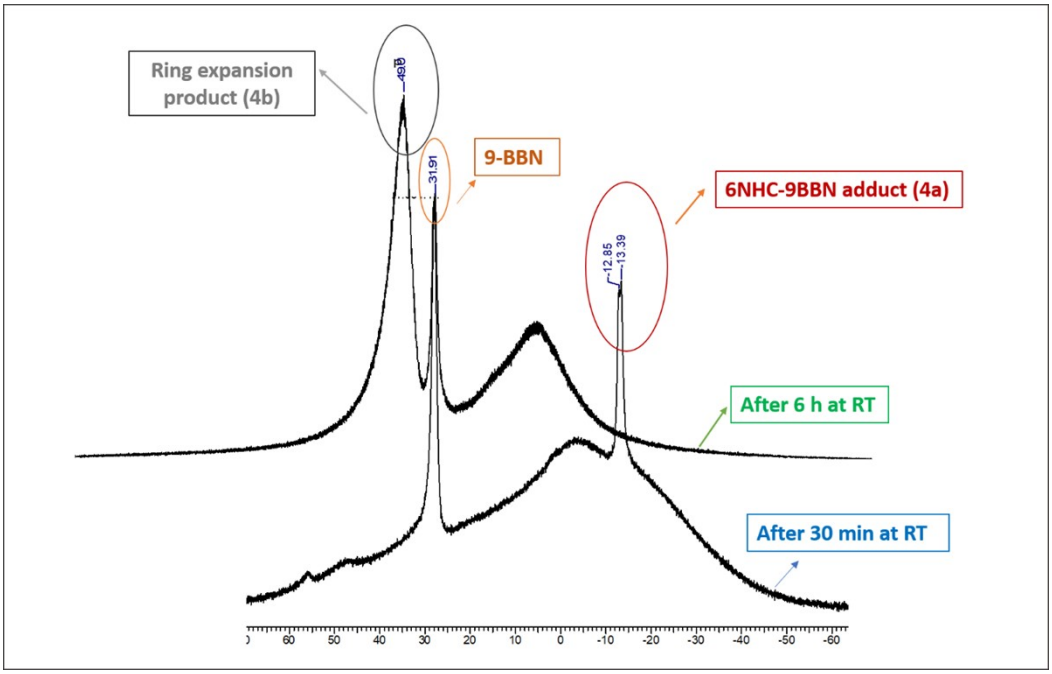

Figure S26. Time dependent ^{11}B NMR spectra to monitor the reaction of 9-BBN and 6-SIDipp.

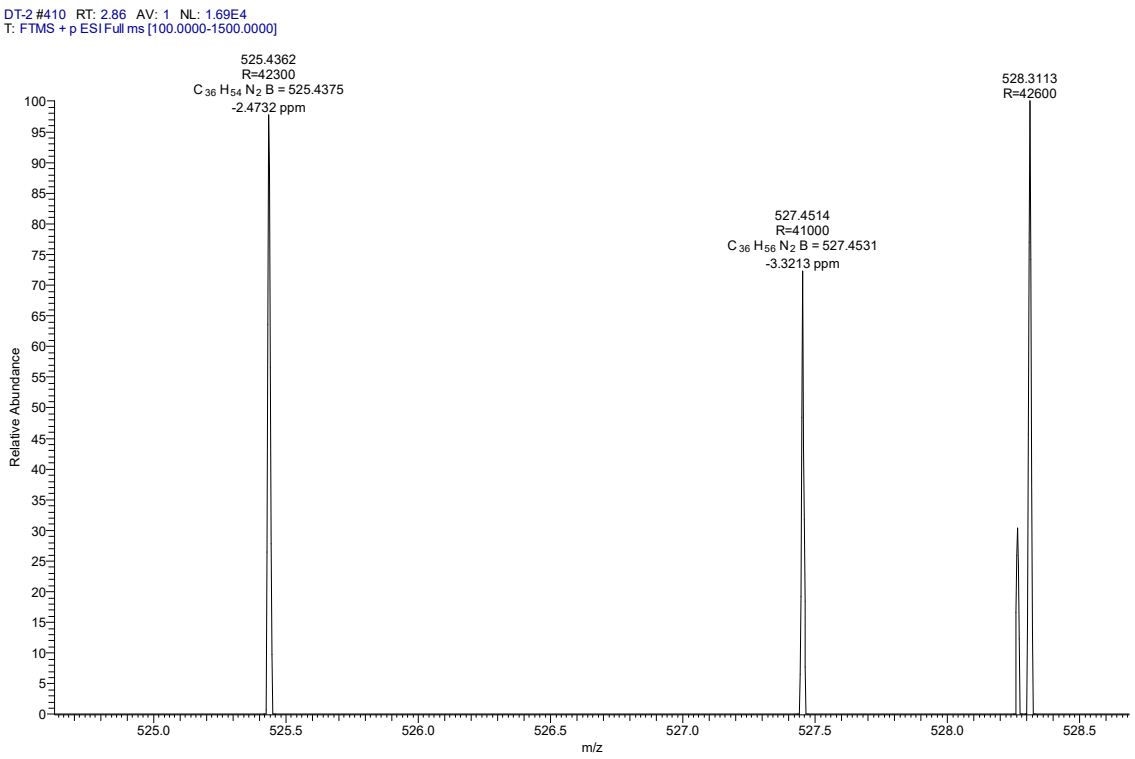

Figure S27. HRMS spectrum of **6b**.

7: To a benzene-d_6 solution (5 mL) of 6-SIDipp (0.2 g, 0.50 mmol) in a Schlenk flask, one equivalent of HBpin (0.06 g, 0.50 mmol) was added at room temperature. Colorless crystals of **7** were isolated from the same flask after keeping the solution at room temperature for a day, with a yield of 0.17 g (65%).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 0.39 (s, 12 H, 2*C(CH_3)$_2$ in Bpin), 1.17 (d, J = 6.88 Hz, 6 H, CH(CH_3)$_2$), 1.24 (d, J = 6.75 Hz, 6 H, CH(CH_3)$_2$), 1.31 (d, 6 H, J = 7.00 Hz, 6 H, CH(CH_3)$_2$), 1.35 (d, 6 H, J = 6.88 Hz, 6 H, CH(CH_3)$_2$), 3.12 (m, 1 H, NCH$_2$CH_2CH$_2$N), 3.15 (m, 1 H, NCH$_2$CH_2CH$_2$N), 3.32 (m, 2 H, CH(CH_3)$_2$), 3.36 (m, 2 H, CH(CH_3)$_2$), 4.41 (m, J = 5.62 Hz, 4 H, NCH_2CH$_2$CH_2N), 4.88 (s, 1 H, N-CH-N), 6.98-7.10 (m, 6 H, Ar-H) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ = 14.1 (C(CH_3)$_2$; Bpin), 22.3 (CH$_2$CH$_2$CH$_2$), 22.7 (CH$_2$CH$_2$CH$_2$), 23.1 (C(CH_3)$_2$; Bpin), 23.6 (C(CH_3)$_2$; Bpin), 25.7 CH(CH_3)$_2$), 26.2 CH(CH_3)$_2$),

27.7 $CH(CH_3)_2$), 28.1 $CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 31.6 $CH(CH_3)_2$), 53.7 (NCH_2), 82.7 (NCN), 122.9 (Ar-*C*), 123.9 (Ar-*C*), 126.4 (Ar-*C*), 145.6 (Ar-*C*), 150.5 (Ar-*C*), 151.5 (Ar-*C*) ppm.

$^{11}B\{^1H\}$ NMR (127 MHz, 298 K, $CDCl_3$): δ = 30.9 (q, 1 B, *B*pin) ppm.

HRMS (CH_3CN): m/z Calcd. for $C_{34}H_{53}BO_2N_2$ $[M+H]^+$ 533.4273, found 533.4267.

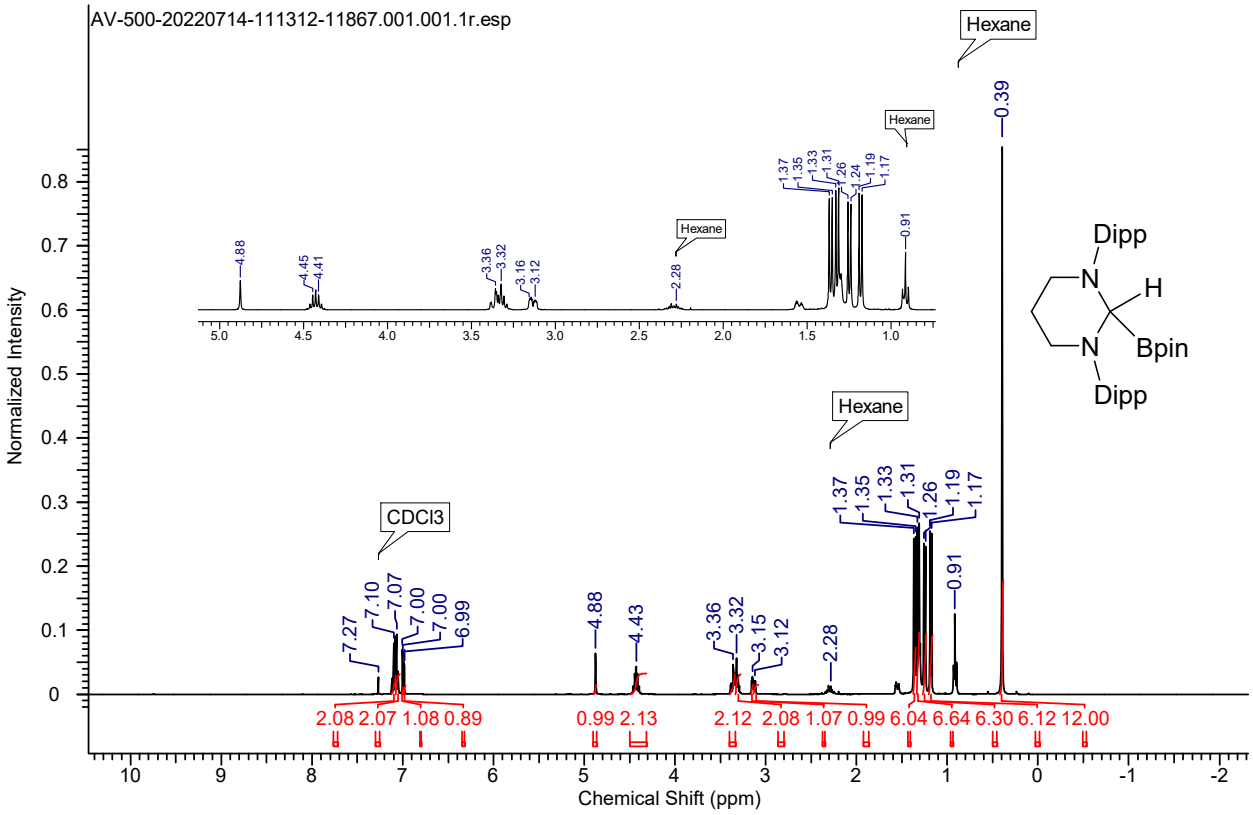

Figure S28. ^1H NMR spectrum of **7**.

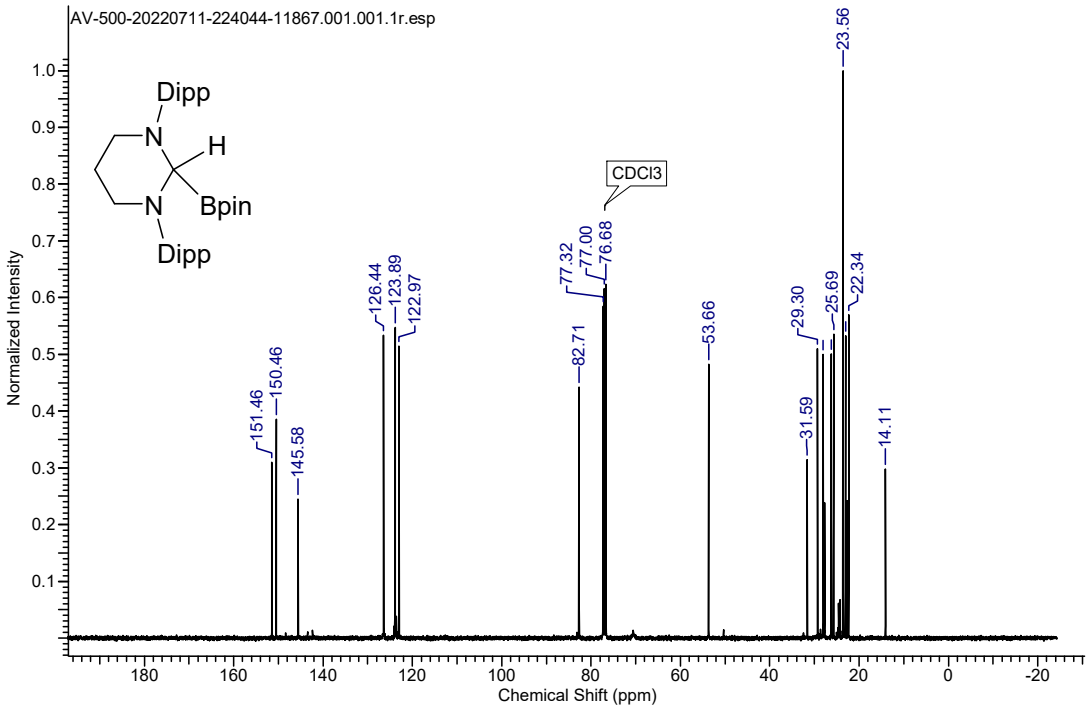

Figure S29. ^{13}C NMR spectrum of **7**.

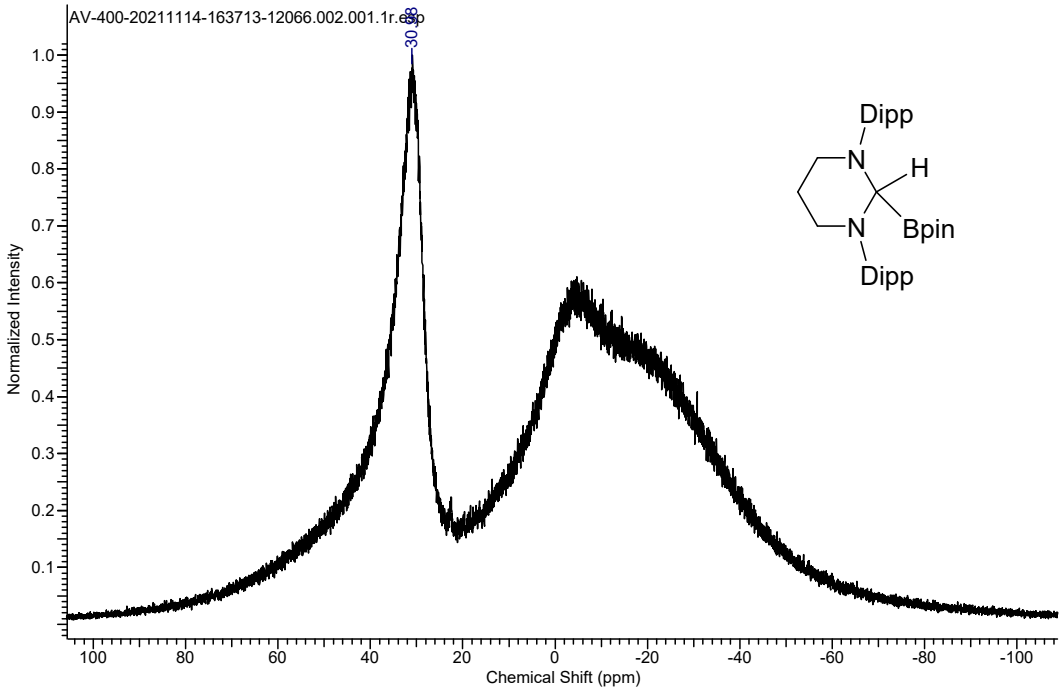

Figure S30. ^{11}B NMR spectrum of **7**.

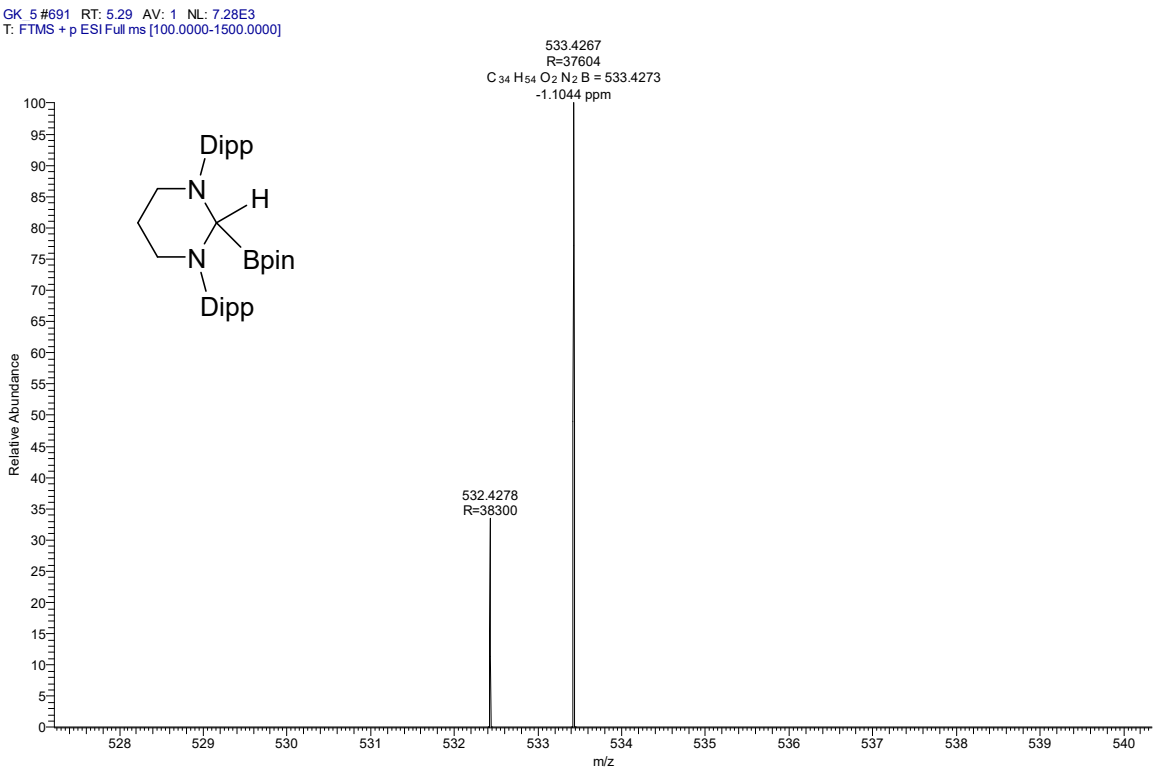

Figure S31. HRMS spectrum of **7**.

8: HBcat (0.072 g, 0.61 mmol) was added to a benzene-d_6 solution (4 mL) of 6-SIDipp (0.2 g, 0.50 mmol) in a Schlenk flask at room temperature. Keeping the reaction mixture for 2-3 hours at room temperature produced the crystals of **8** with a yield of 0.14 g (46%).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 1.22 (d, J = 6.84 Hz, 12 H, CH(CH_3)$_2$), 1.31 (d, J = 6.72 Hz, 12 H, CH(CH_3)$_2$, 2.45 (q, J = 5.14 Hz, 2 H, NCH$_2$CH_2CH$_2$N), 2.83 (sept, J = 6.85 Hz, 4 H, CH(CH$_3$)$_2$), 3.76 (t, J = 5.62 Hz, 4 H, NCH_2CH$_2$CH_2N), 6.58-6.61 (m, 8 H, Ar-H-Bcat), 7.25 (doublet, 4 H, Ar-H), 7.46 (t, 2 H, Ar-H), 7.48 (s, 1 H, NCHN) ppm.

^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$): δ = 18.8 (CH$_2$CH_2CH$_2$), 24.6 (CH(CH_3)$_2$), 28.9 (CH(CH$_3$)$_2$), 48.9 (NCH_2), 67.9 (NCHN), 108.4 (Ar-C), 117.6 (Ar-C), 125.2 (Ar-C), 128.2 (Ar-C), 128.9 (Ar-C), 131.4 (Ar-C), 135.5 (Ar-C), 145.2 (Ar-C), 151.9 (Ar-C), 153.1 (Ar-C) ppm.

^{11}B{^{1}H} NMR (377 MHz, 298 K, $CDCl_3$): δ = 14.3 (s, 1 B, B(cat)$_2$) ppm.

HRMS (CH_3CN): m/z Calcd. for $C_{28}H_{41}N_2$ $[M\text{-}C_{12}H_8BO_4]^+$ 405.3264, found 405.3260 and $C_{12}H_8BO_4$ $[M\text{-}C_{28}H_{41}N_2]^+$ 227.0510, found 226.9510.

Elemental Analysis: Calcd. C, 75.94; H, 7.81; N, 4.43; found Calcd. C, 75.23; H, 7.52; N, 4.21.

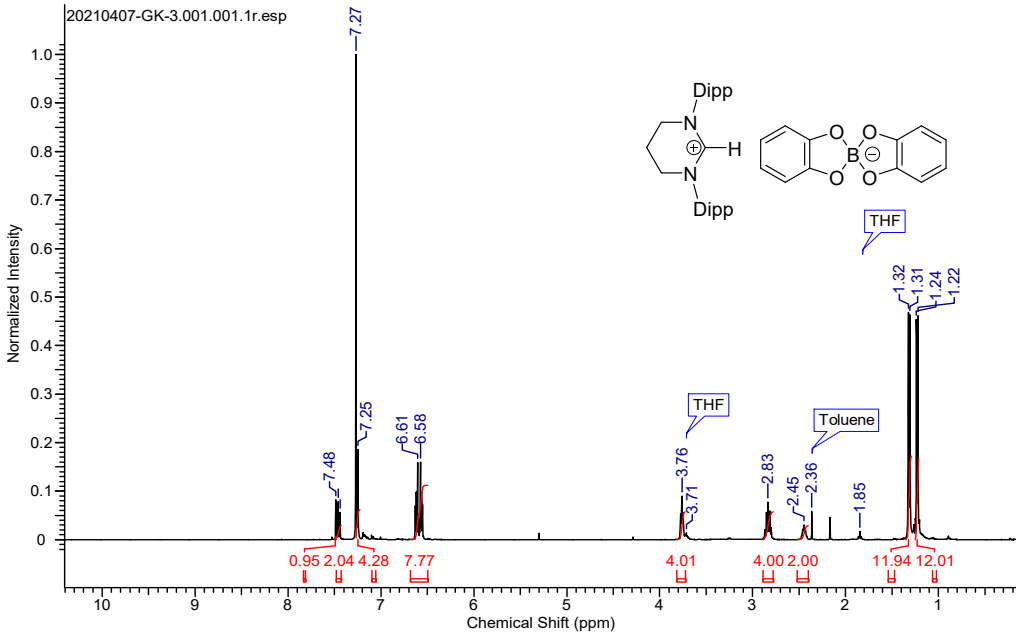

Figure S32. ^1H NMR spectrum of **8**.

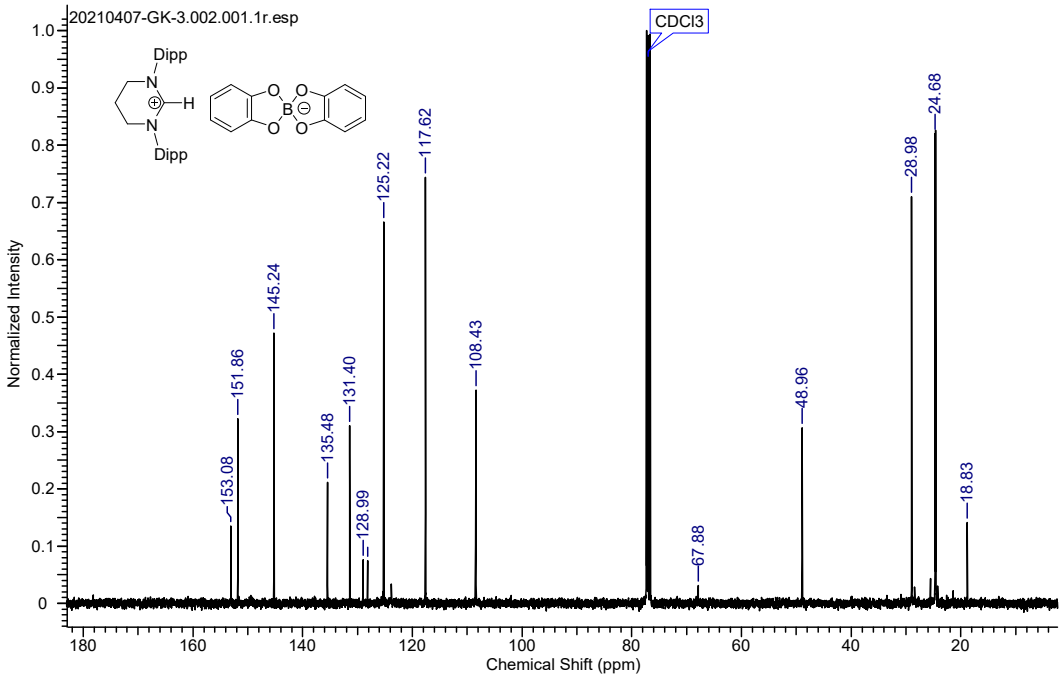

Figure S33. ^{13}C NMR spectrum of **8**.

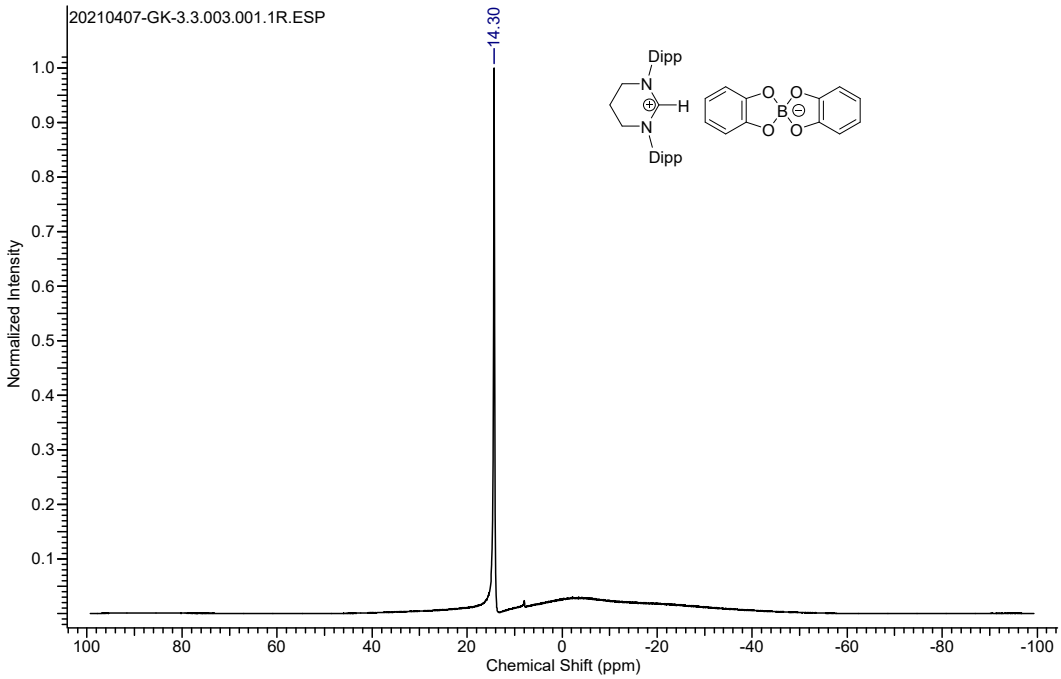

Figure S34. ^{11}B NMR spectrum of **8**.

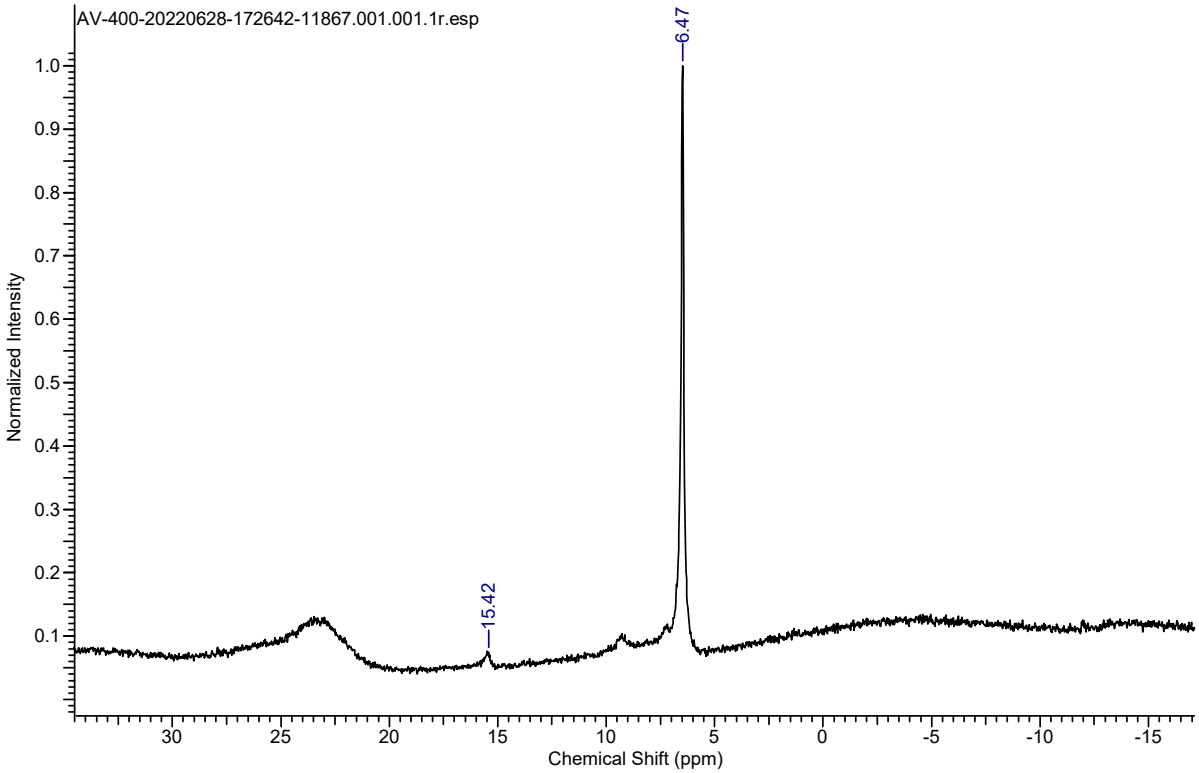

Figure S35: ^{11}B NMR recorded after 10 min reaction between HBcat and 6-SIDipp.

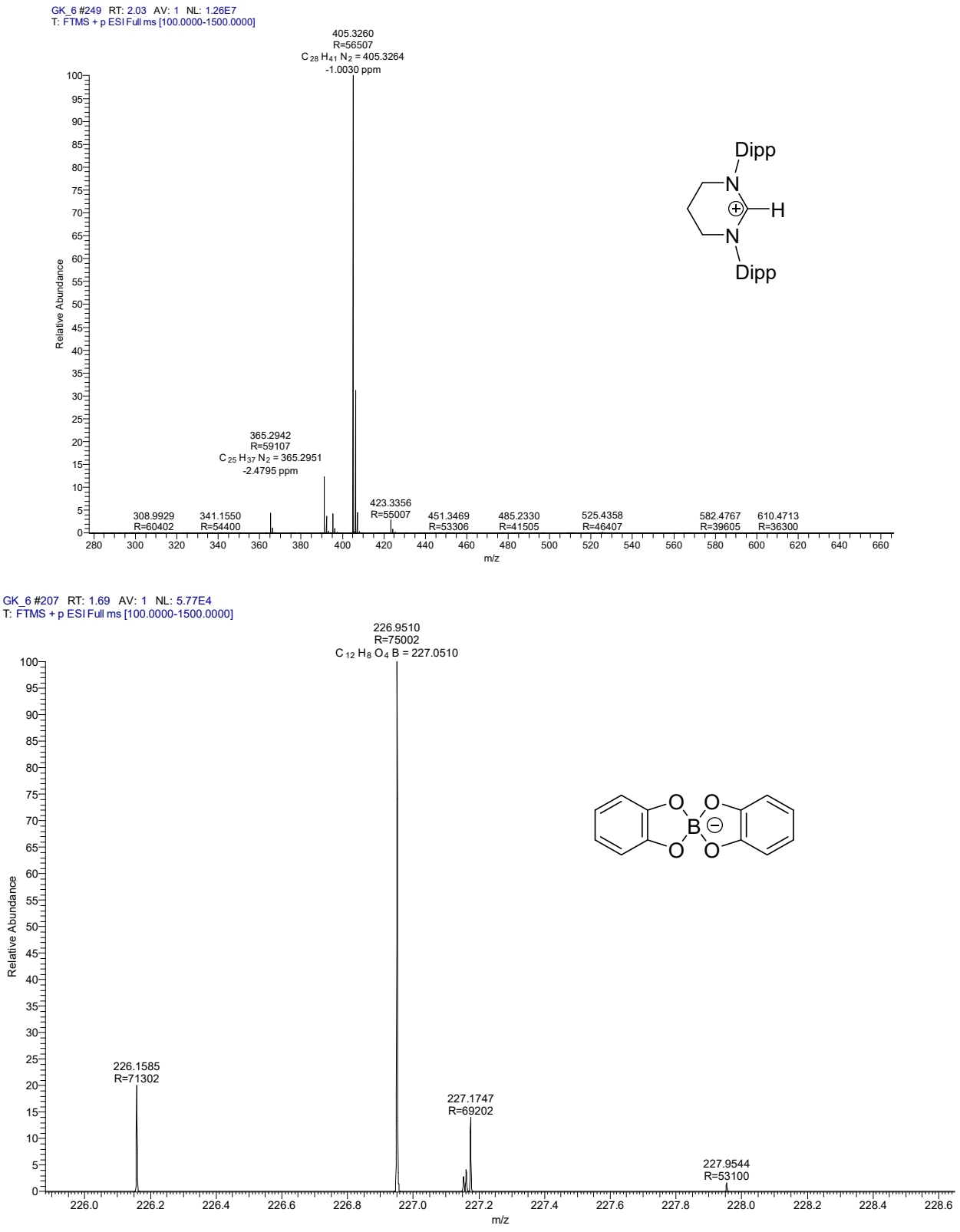

Figure S36. HRMS spectrum of **8**.

S3. Crystallographic data for the structural analysis of compounds 1, 2, 3, 6a, 6b, 7 and 8

Single crystals of **1**, **2**, **3**, **6a**, **6b**, **7** and **8** were mounted on a Bruker SMART APEX II single crystal X-ray CCD diffractometer having graphite monochromatised (Mo-Kα = 0.71073 Å) radiation at low temperature 100 K. The X-ray generator was operated at 50 kV and 30 mA. The X-ray data acquisition was monitored by APEX2 program suit. The data were corrected for Lorentz-polarization and absorption effects using SAINT and SADABS programs which are an integral part of APEX2 package.[2] The structures were solved by direct methods and refined by full matrix least squares, based on F^2, using SHELXL Crystal structures were refined using Olex2-1.0 software. Anisotropic refinement was performed for all non-H atom. The C-H hydrogen atoms were calculated using the riding model.[3] The structures were examined using the ADSYM subroutine of PLATON to assure that no additional symmetry could be applied to the models. The molecular weight of each structure mentioned herein has been calculated considering the solvent molecules trapped in the crystal. For structure **1**, the residual electron density is modelled with another Br atom (disorder), and the first and second site occupancies are obtained at ~97% and 3%, respectively. The second bond distance is B-Br 1.83 Å. The bond length is very unusual and chemically not reasonable. Hence, this current model would be more appropriate and chemically meaningful. Crystallographic information is available at www.ccdc.cam.ac.uk/data or as part of the Supporting Information.

Table S2: Crystal data and structure refinement for DT-1, DT-2 and DT-3

Identification code	DT_1	DT-2	DT_3
Empirical formula	$C_{28}H_{42}BBrN_2$	$C_{56}H_{82}B_2Br_3N_4$	$C_{28}H_{41}BCl_2N_2$
Formula weight	497.35	1072.60	487.34
Temperature/K	100	100	100.0
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	19.3060(17)	10.529(5)	10.3971(15)
b/Å	7.3776(6)	19.135(10)	18.854(3)
c/Å	20.0281(17)	13.705(6)	13.6858(18)
α/°	90	90	90
β/°	106.909(5)	99.104(14)	98.734(4)
γ/°	90	90	90
Volume/Å^3	2729.3(4)	2726(2)	2651.7(6)
Z	4	2	4
ρ_{calc}g/cm^3	1.210	1.307	1.221
μ/mm^{-1}	1.523	2.258	0.264
F(000)	1056.0	1122.0	1048.0
Crystal size/mm^3	0.22 × 0.12 × 0.08	0.2 × 0.12 × 0.1	0.16 × 0.12 × 0.07
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.41 to 60.98	4.458 to 64.634	3.706 to 73.896
Index ranges	-27 ≤ h ≤ 28, -10 ≤ k ≤ 10, -29 ≤ l ≤ 28	-15 ≤ h ≤ 14, -28 ≤ k ≤ 28, -20 ≤ l ≤ 20	-17 ≤ h ≤ 17, -31 ≤ k ≤ 31, -23 ≤ l ≤ 23
Reflections collected	60606	98762	228033
Independent reflections	8813 [R_{int} = 0.0587, R_{sigma} = 0.0470]	9669 [R_{int} = 0.1038, R_{sigma} = 0.0472]	13370 [R_{int} = 0.0569, R_{sigma} = 0.0196]
Data/restraints/parameters	8813/1/305	9669/0/306	13370/0/310
Goodness-of-fit on F^2	1.041	1.072	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, wR_2 = 0.0988	R_1 = 0.0554, wR_2 = 0.1571	R_1 = 0.0309, wR_2 = 0.0899
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.1076	R_1 = 0.0688, wR_2 = 0.1669	R_1 = 0.0355, wR_2 = 0.0943
Largest diff. peak/hole / e Å^{-3}	2.488/ -0.529	2.46/-2.14	0.57/-0.37
CCDC Number	2123564	2176142	2102133

Table S3: Crystal data and structure refinement for DT-6a, DT-6b, DT-7 and DT-8

Identification code	**DT-6a**	**DT-6b**	**DT-7**	**DT-8**
Empirical formula	$C_{36}H_{55}BN_2$	$C_{72}H_{108.5}B_2N_4$	$C_{37}H_{56}BN_2O_2$	$C_{46}H_{55}BN_2O_4$
Formula weight	526.63	1051.75	571.65	710.73
Temperature/K	100.00	100.0	100(2)	100.00
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic
Space group	*P*nma	*P*-1	$P2_1/c$	$P2_1/c$
a/Å	19.1631(19)	9.8912(9)	9.764(2)	18.245(7)
b/Å	19.543(2)	16.5219(14)	17.218(3)	12.362(5)
c/Å	8.3341(9)	20.764(2)	20.843(5)	18.528(7)
α/°	90	71.460(3)	90.00	90.00
β/°	90	86.897(3)	102.176(8)	106.590(10)
γ/°	90	82.860(3)	90.00	90.00
Volume/Å^3	3121.2(6)	3191.8(5)	3425.2(12)	4005(3)
Z	4	2	4	4
ρ_{calc}g/cm^3	1.121	1.094	1.109	1.179
μ/mm^{-1}	0.063	0.062	0.067	0.074
F(000)	1160.0	1157.0	1252.0	1528.0
Crystal size/mm^3	0.12 × 0.09 × 0.05	0.15 × 0.12 × 0.08	0.25 × 0.15 × 0.12	0.12 × 0.11 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.954 to 52	4.14 to 56.6	4.26 to 60.36	4.04 to 56.98
Index ranges	-19 ≤ h ≤ 23, -24 ≤ k ≤ 24, -10 ≤ l ≤ 10	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -27 ≤ l ≤ 27	-11 ≤ h ≤ 13, -20 ≤ k ≤ 24, -21 ≤ l ≤ 29	-24 ≤ h ≤ 24, -16 ≤ k ≤ 16, -20 ≤ l ≤ 24
Reflections collected	39073	143859	22136	80481
Independent reflections	3145 [R_{int} = 0.1044, R_{sigma} = 0.0475]	15829 [R_{int} = 0.0645, R_{sigma} = 0.0339]	9606 [R_{int} = 0.0719, R_{sigma} = 0.0764]	9657 [R_{int} = 0.0826, R_{sigma} = 0.0484]
Data/restraints/parameters	3145/0/224	15829/0/756	9606/0/392	9657/0/487
Goodness-of-fit on F^2	1.094	1.065	1.025	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0649, wR_2 = 0.1609	R_1 = 0.0820, wR_2 = 0.1904	R_1 = 0.0594, wR_2 = 0.1453	R_1 = 0.0544, wR_2 = 0.1205
Final R indexes [all data]	R_1 = 0.0771, wR_2 = 0.1717	R_1 = 0.0980, wR_2 = 0.2004	R_1 = 0.0847, wR_2 = 0.1601	R_1 = 0.0839, wR_2 = 0.1359
Largest diff. peak/hole / e Å^{-3}	0.33/-0.27	0.79/-0.65	0.49/-0.31	0.31/-0.23
CCDC Number	2102135	2191019	2102136	2102137

S4. Details of theoretical calculations for the formation of 7

All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 7.5 suite of programs,[4] using the PBE functional.[5] The TZVP basis set has been employed. The resolution of identity (RI),[6] along with the multipole accelerated resolution of identity (marij)[7] approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations.Dispersion corrections (disp3) and solvent corrections were incorporated with optimization calculations using the COSMO model,[8] with Toluene (ε = 2.38) as the solvent. The values reported are ΔG values, with zero point energy corrections, internal energy and entropic contributions included through frequency calculations on the optimized minima, with the temperature taken to be 298.15 K. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition state structures.

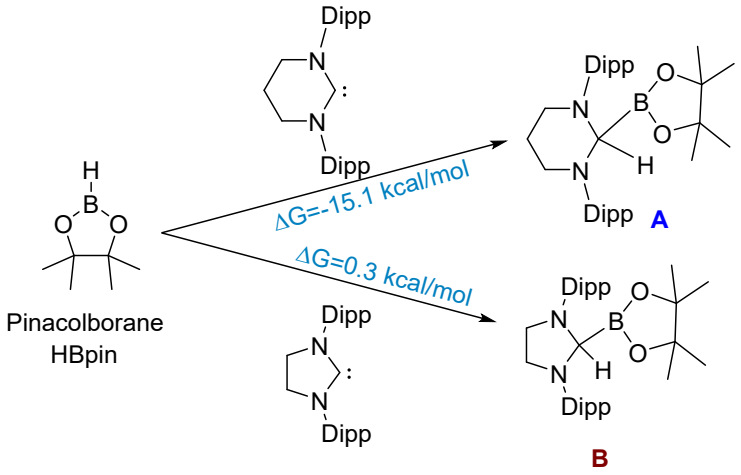

Figure S37. The comparison between six-membered NHC and five-membered NHC after oxidative addition of HBpin. The values (in kcal/mol) have been calculated at the PBE/TZVP level of theory with DFT.

S5. References

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S6. PBE/TZVP optimized geometries for all the compounds and transition state in Figure 5

Ts

92

C	-1.467934	-1.306472	2.986807
C	-1.029537	-0.192978	2.239781
C	-1.755000	1.021579	2.245036
C	-2.887560	1.117656	3.061186
C	-3.301104	0.042269	3.849795
C	-2.600534	-1.159912	3.802567
N	0.203137	-0.256997	1.495314
C	1.424379	-0.400674	2.302015
C	2.631670	0.151379	1.558802
C	2.692823	-0.515991	0.192553
N	1.431894	-0.293167	-0.523393
C	0.219566	-0.517688	0.122844
B	-1.070528	-0.882283	-0.668120
O	-1.112517	-1.011808	-2.076851
C	-2.495467	-0.810668	-2.473047
C	-2.667946	0.678983	-2.793111
C	1.535884	-0.071965	-1.943330
C	1.460108	1.252341	-2.428974
C	1.616107	1.465188	-3.806064
C	1.862820	0.402592	-4.674796
C	1.958471	-0.895428	-4.174748
C	1.792767	-1.157008	-2.808531
C	1.280528	2.434605	-1.490062
C	0.204737	3.421969	-1.963431
C	1.886545	-2.585468	-2.293463
C	3.329372	-3.112950	-2.382337
C	-1.311696	2.194028	1.383049
C	-0.265873	3.052979	2.114892
C	-0.789617	-2.667096	2.895947
C	-1.770185	-3.748706	2.413807
O	-2.371326	-0.827468	-0.123172
C	-3.278440	-1.246000	-1.182876
C	-4.611356	-0.541125	-0.965988
C	-3.457184	-2.764846	-1.089489
C	2.622948	3.155002	-1.266637
C	0.909393	-3.526096	-3.016933
C	-2.476627	3.057133	0.882919
C	-0.134415	-3.071048	4.227496
C	-2.770684	-1.650143	-3.714984
H	0.963432	2.029536	-0.519589

H	-3.459625	2.046555	3.082300
H	2.154479	-1.723158	-4.860674
H	1.587137	-2.573062	-1.234010
H	1.558176	2.480989	-4.204016
H	-2.947957	-2.009753	4.394690
H	3.500038	-0.098323	-0.423385
H	2.893847	-1.600005	0.315041
H	2.543404	1.241757	1.436256
H	3.547298	-0.060001	2.131166
H	1.986426	0.588088	-5.744359
H	0.488611	3.917107	-2.904819
H	0.056377	4.210572	-1.210421
H	-0.757316	2.916085	-2.123923
H	-0.825305	1.766337	0.495249
H	-4.181955	0.139364	4.488498
H	3.389738	2.464046	-0.886329
H	2.507090	3.972723	-0.538006
H	2.998176	3.586797	-2.207516
H	1.619938	-1.460008	2.559011
H	1.254422	0.138494	3.244618
H	3.664590	-3.163456	-3.430190
H	3.398069	-4.126377	-1.957617
H	4.031769	-2.464076	-1.838468
H	-0.113626	-3.135879	-2.942255
H	0.943338	-4.528967	-2.564269
H	1.165293	-3.633688	-4.082554
H	-0.007239	-2.597532	2.125911
H	-0.701859	3.510096	3.016736
H	0.099942	3.862570	1.463534
H	0.598772	2.448852	2.424105
H	-3.244811	2.439401	0.395587
H	-2.111212	3.791747	0.150291
H	-2.956238	3.620180	1.698151
H	-2.582829	-3.912226	3.137577
H	-1.244168	-4.706268	2.277871
H	-2.216924	-3.458871	1.453914
H	0.590213	-2.316751	4.567831
H	0.391320	-4.033040	4.126492
H	-0.892433	-3.184935	5.018008
H	-0.173842	-1.985161	-0.074948
H	-1.917173	0.964973	-3.542801
H	-3.668824	0.899478	-3.191619
H	-2.505420	1.290796	-1.894469
H	-3.827038	-1.572070	-4.012609
H	-2.150320	-1.286095	-4.546553
H	-2.528894	-2.706829	-3.547206
H	-5.309715	-0.763435	-1.786595
H	-5.061395	-0.888827	-0.025210
H	-4.480087	0.545656	-0.896690
H	-3.846223	-3.016065	-0.093227
H	-4.168941	-3.136092	-1.840615

H -2.496894 -3.283291 -1.226080

Five-membered NHC_pdt

87

C 3.125682 -0.462452 -0.989468
C 2.538896 0.727932 -0.484690
C 3.292824 1.629213 0.304593
C 4.617786 1.292448 0.625274
C 5.191596 0.109630 0.165991
C 4.451588 -0.752977 -0.644712
N 1.168093 0.985254 -0.808912
C 0.760238 2.002989 -1.702550
C -0.563522 2.230618 -1.558566
N -1.071870 1.452186 -0.487182
C 0.111738 0.922912 0.235921
C -2.315248 0.743888 -0.570950
C -3.310788 1.072133 0.382927
C -4.552045 0.426395 0.311595
C -4.810856 -0.521982 -0.678063
C -3.821754 -0.845084 -1.606803
C -2.558917 -0.234134 -1.568447
C -3.065278 2.145699 1.432782
C -3.417176 1.681714 2.853366
C -1.501666 -0.630221 -2.589255
C -1.845673 -0.076185 -3.983358
C 2.727060 2.956988 0.792846
C 3.552533 4.144235 0.267294
C 2.349586 -1.361344 -1.939138
C 2.728876 -2.842806 -1.846847
C -3.820292 3.434573 1.061378
C -1.288260 -2.151775 -2.645422
C 2.615699 2.995662 2.326545
C 2.487992 -0.852059 -3.385736
H -1.990077 2.375290 1.407800
H 5.209763 1.974651 1.240463
H -4.031354 -1.594585 -2.373683
H -0.551263 -0.177773 -2.276387
H -5.331018 0.674249 1.036200
H 4.917971 -1.665696 -1.019662
H -1.222142 2.863498 -2.144690
H -5.785761 -1.012808 -0.724939
H -4.489241 1.451733 2.957438
H -3.178227 2.473047 3.580268
H -2.840045 0.785539 3.120384
H 1.715391 3.068982 0.377965
H 6.222650 -0.137148 0.429511
H -3.525739 3.790735 0.063287
H -3.605694 4.233085 1.788421
H -4.908715 3.265642 1.052295

H	1.462760	2.442940	-2.403735
H	-2.786662	-0.508252	-4.359040
H	-1.047988	-0.321789	-4.701318
H	-1.957529	1.017049	-3.958642
H	-1.004681	-2.543380	-1.659317
H	-0.477026	-2.391149	-3.349741
H	-2.190188	-2.681292	-2.988632
H	1.294278	-1.273359	-1.656493
H	4.580087	4.129856	0.660900
H	3.089595	5.095033	0.572426
H	3.611629	4.128742	-0.830992
H	1.993237	2.169654	2.702251
H	2.162551	3.942856	2.656710
H	3.606263	2.911913	2.799630
H	3.743209	-3.042158	-2.226935
H	2.030763	-3.442353	-2.450428
H	2.673892	-3.203540	-0.809829
H	2.123756	0.180938	-3.479958
H	1.900947	-1.481139	-4.073654
H	3.539259	-0.876314	-3.714178
H	0.362787	1.658039	1.045287
B	-0.119108	-0.477283	0.950857
O	0.294914	-1.696144	0.470916
C	0.128438	-2.659401	1.574587
C	-0.982894	-1.970395	2.448905
O	-0.742239	-0.540253	2.178641
C	1.484181	-2.746079	2.278816
C	-0.261417	-4.007283	0.986632
C	-0.857209	-2.203420	3.947201
C	-2.401359	-2.279832	1.966121
H	-0.453118	-4.734271	1.789292
H	-1.158620	-3.932222	0.360849
H	0.560769	-4.390394	0.366350
H	1.469561	-3.495987	3.082370
H	2.249919	-3.034639	1.546457
H	1.774862	-1.776011	2.705769
H	-1.664812	-1.673734	4.471572
H	-0.946460	-3.275245	4.177435
H	0.102012	-1.838286	4.333896
H	-3.108330	-1.614593	2.479272
H	-2.507374	-2.106908	0.885673
H	-2.676804	-3.319741	2.190145

six-membered NHC_pdt

92

N	1.282322	-0.033982	-0.613447
N	0.053598	0.007072	1.425043
C	0.091862	-0.555222	0.065161
C	1.306153	0.099303	-2.039960

C	-1.215792	0.133937	2.082259
C	1.366374	1.417194	-2.568643
C	1.404199	2.624015	-1.645778
H	1.112840	2.251060	-0.653658
C	-2.990176	1.611561	2.840575
H	-3.413230	2.612765	2.944855
C	1.322666	-0.797358	-4.296474
H	1.311849	-1.652984	-4.976204
C	1.299089	-1.019235	-2.909729
C	-1.746675	1.447309	2.217371
C	-1.927398	-0.981207	2.588711
C	1.320847	-2.453438	-2.396609
H	1.265222	-2.419793	-1.300046
C	1.413204	1.588308	-3.957519
H	1.463103	2.596994	-4.374516
C	-3.165475	-0.765918	3.214811
H	-3.723041	-1.619548	3.607971
C	2.525259	-0.378074	0.067580
H	3.364597	0.058669	-0.492580
H	2.688406	-1.481988	0.095087
C	2.491048	0.154116	1.503235
H	2.492351	1.255510	1.483116
H	3.385651	-0.185343	2.050144
C	1.382411	0.491929	-4.820147
H	1.408863	0.643692	-5.901781
C	0.413613	3.722568	-2.052335
H	0.654374	4.157944	-3.035071
H	0.435171	4.542009	-1.317162
H	-0.609437	3.324344	-2.085095
C	-0.951838	2.650273	1.733832
H	-0.287299	2.277706	0.942223
C	-3.698292	0.514976	3.336489
H	-4.667644	0.661875	3.818791
C	2.834630	3.181485	-1.536004
H	3.538482	2.411582	-1.186738
H	2.868679	4.021752	-0.824760
H	3.192997	3.546353	-2.511590
C	1.229138	-0.339033	2.217295
H	1.321000	-1.439094	2.377360
H	1.132382	0.123576	3.210055
C	2.645832	-3.145449	-2.764338
H	2.760044	-3.232430	-3.855992
H	2.680400	-4.160305	-2.339180
H	3.509083	-2.581799	-2.380217
C	0.113687	-3.267468	-2.890610
H	-0.829347	-2.802021	-2.572723
H	0.148320	-4.288423	-2.480769
H	0.108286	-3.349508	-3.988434
C	-1.384314	-2.402879	2.501156
H	-0.448282	-2.368784	1.928937
C	-0.059701	3.189512	2.867107

H	-0.671086	3.557056	3.706815
H	0.561897	4.023979	2.505714
H	0.611502	2.409960	3.254163
C	-1.814954	3.770560	1.146117
H	-2.447856	3.393440	0.331985
H	-1.168322	4.559414	0.733541
H	-2.461230	4.242733	1.902562
C	-2.336134	-3.345953	1.746836
H	-3.301066	-3.446614	2.267018
H	-1.892902	-4.350842	1.670504
H	-2.526154	-2.972518	0.731316
C	-1.050842	-2.950843	3.900011
H	-0.341684	-2.295332	4.427019
H	-0.602376	-3.953357	3.824754
H	-1.957510	-3.032931	4.519203
H	0.177280	-1.671939	0.147645
C	-2.805727	0.795716	-2.052799
C	-3.340281	-0.617047	-1.607387
B	-1.254379	-0.247750	-0.737160
O	-1.659453	0.999501	-1.150702
O	-2.123305	-1.261156	-1.084404
C	-3.790825	1.937874	-1.849420
H	-3.332216	2.882920	-2.171997
H	-4.696967	1.776161	-2.451953
H	-4.080617	2.035605	-0.796445
C	-2.251217	0.809271	-3.478473
H	-3.058530	0.714679	-4.218234
H	-1.729167	1.759474	-3.651251
H	-1.524997	0.000311	-3.636099
C	-4.332926	-0.547746	-0.445889
H	-5.291119	-0.118429	-0.770037
H	-4.518464	-1.563776	-0.071798
H	-3.937258	0.050583	0.386722
C	-3.890039	-1.476879	-2.737284
H	-4.217537	-2.446404	-2.336552
H	-4.758976	-0.989017	-3.202680
H	-3.134054	-1.660808	-3.510215

Five-membered NHC
65

C	0.101920	-0.200450	0.123225
N	1.006485	-0.261570	1.186332
C	0.398612	-0.305910	2.419158
N	-0.929386	-0.268818	2.066492
C	-1.137297	-0.205057	0.687121
C	-1.997896	-0.291705	3.028207
C	-2.479951	0.932023	3.532794
C	-3.535138	0.883543	4.455176
C	-4.081465	-0.334769	4.858879
C	-3.576730	-1.531758	4.351009

C	-2.522996	-1.536861	3.425760
C	2.435807	-0.272734	1.017724
C	3.121193	0.958680	1.000024
C	4.515783	0.920176	0.858767
C	5.190664	-0.294898	0.737209
C	4.485180	-1.498493	0.749952
C	3.089892	-1.514359	0.888720
C	-1.888568	2.268945	3.110793
C	-2.918373	3.115969	2.343633
C	-1.976517	-2.852476	2.890701
C	-1.402861	-3.720649	4.023286
C	2.380343	2.275681	1.188598
C	2.345228	2.653066	2.682174
C	2.315883	-2.824164	0.960157
C	2.862873	-3.905734	0.018473
C	-1.317314	3.035525	4.315665
C	-3.042153	-3.612976	2.083593
C	2.949181	3.420728	0.339114
C	2.262179	-3.327648	2.415731
H	-1.049746	2.064837	2.430459
H	5.082324	1.852500	0.845290
H	-4.006073	-2.480338	4.681398
H	-1.145703	-2.618771	2.210026
H	-3.932091	1.814330	4.866671
H	5.028122	-2.439869	0.652775
H	-2.126515	-0.169706	0.243312
H	-4.902506	-0.351795	5.578806
H	-2.107108	3.306295	5.032719
H	-0.834479	3.965973	3.980059
H	-0.566375	2.431748	4.844563
H	1.338473	2.117272	0.868040
H	6.277394	-0.303906	0.629490
H	-3.292489	2.582181	1.457241
H	-2.465336	4.061428	2.008509
H	-3.783484	3.362843	2.978319
H	0.417330	-0.159880	-0.913671
H	-3.899902	-3.889911	2.715783
H	-2.618945	-4.539139	1.666103
H	-3.421466	-3.003031	1.250066
H	-0.624000	-3.177437	4.576817
H	-0.954069	-4.637302	3.611005
H	-2.185711	-4.020032	4.736600
H	1.280165	-2.612784	0.649922
H	3.956246	3.716688	0.669764
H	2.304318	4.307604	0.429044
H	3.007167	3.145787	-0.724496
H	1.874991	1.853068	3.272210
H	1.770086	3.580155	2.830389
H	3.365106	2.816217	3.064580
H	3.275680	-3.548517	2.785758
H	1.663916	-4.249514	2.481454

H	1.808049	-2.570263	3.071044
H	2.937995	-3.541361	-1.016709
H	2.195432	-4.780305	0.026809
H	3.858925	-4.255122	0.329794

Six-membered NHC

70

C	3.568958	4.596383	14.674061
C	2.225484	4.369712	15.048965
C	1.883643	3.473293	16.080935
C	2.921967	2.789823	16.733380
C	4.252917	2.997404	16.376772
C	4.571835	3.892406	15.353112
N	1.184298	5.111203	14.381710
C	0.553677	4.532867	13.335328
N	-0.451009	5.257800	12.795008
C	-0.899846	6.600465	13.236323
C	0.255148	7.334577	13.904438
C	0.878533	6.438654	14.966882
C	-1.192216	4.692173	11.695417
C	-0.769464	4.952934	10.373634
C	-1.545170	4.450309	9.318954
C	-2.704116	3.714213	9.564579
C	-3.097291	3.454822	10.876956
C	-2.352540	3.935663	11.964219
C	0.492998	5.746907	10.074579
C	0.165848	7.088140	9.395530
C	-2.799127	3.624400	13.384841
C	-2.855184	2.108099	13.632762
C	0.437404	3.210186	16.473090
C	0.179697	3.507496	17.959493
C	3.904213	5.516597	13.508499
C	3.913933	4.707933	12.197805
C	1.485302	4.927937	9.232861
C	-4.146472	4.291043	13.711163
C	0.029772	1.772324	16.109326
C	5.211696	6.297363	13.693276
H	1.815480	6.868983	15.350144
H	0.197874	6.315997	15.828727
H	1.013728	7.592383	13.148280
H	-0.098972	8.272411	14.354977
H	-1.752056	6.496512	13.931720
H	-1.262640	7.148748	12.355054
H	-1.235496	4.637052	8.287943
H	-3.297648	3.334173	8.730193
H	-3.999071	2.866344	11.061735
H	0.982811	5.961817	11.035645
H	1.730664	3.978491	9.729113
H	2.419925	5.490698	9.087845

H	1.075139	4.697695	8.237604
H	-0.309585	6.930873	8.414662
H	1.084054	7.673486	9.234388
H	-0.522007	7.691691	10.006490
H	-2.040549	4.035785	14.067311
H	-4.950625	3.894938	13.071823
H	-4.103057	5.379522	13.557306
H	-4.426265	4.102669	14.758983
H	-3.112307	1.900279	14.682469
H	-1.884214	1.640102	13.418135
H	-3.615607	1.625049	13.000116
H	2.681964	2.083379	17.531250
H	5.048046	2.457408	16.895523
H	5.617655	4.039507	15.077352
H	-0.195801	3.885535	15.878934
H	-1.029650	1.597239	16.351746
H	0.630826	1.037418	16.666666
H	0.172844	1.591316	15.034679
H	0.460463	4.540034	18.215214
H	0.754959	2.831945	18.611072
H	-0.886282	3.371308	18.197392
H	3.088998	6.252456	13.423086
H	5.221073	6.852808	14.642886
H	5.336461	7.019016	12.872076
H	6.090966	5.635535	13.678467
H	2.950582	4.196227	12.056287
H	4.710823	3.947705	12.219814
H	4.092162	5.368394	11.335104

Int_1

92

N	1.516196	-0.285256	-0.432974
N	0.327143	-0.249870	1.557390
C	0.327263	-0.349772	0.208706
C	1.619623	-0.114969	-1.868701
C	-0.901869	-0.182917	2.321180
C	1.657701	1.198581	-2.384143
C	1.595448	2.428213	-1.485961
H	1.240128	2.101048	-0.498414
C	-2.678141	1.134000	3.268618
H	-3.224039	2.074582	3.357075
C	1.948696	-1.043447	-4.062505
H	2.062243	-1.906039	-4.722879
C	1.782568	-1.248486	-2.686968
C	-1.577795	1.054173	2.407945
C	-1.335337	-1.324933	3.017371
C	1.771401	-2.659408	-2.120340
H	1.487946	-2.587893	-1.059384
C	1.816161	1.350211	-3.768578

H	1.837220	2.353123	-4.200563
C	-2.444387	-1.194375	3.867124
H	-2.801880	-2.066305	4.419378
C	2.810369	-0.333032	0.278924
H	3.565690	0.113585	-0.378622
H	3.093111	-1.388472	0.438239
C	2.711036	0.401140	1.605026
H	2.554267	1.475640	1.426119
H	3.642547	0.287015	2.176293
C	1.956641	0.241331	-4.602795
H	2.078026	0.381247	-5.679322
C	0.617409	3.502145	-1.984859
H	0.945028	3.938301	-2.940521
H	0.556080	4.323052	-1.253949
H	-0.390281	3.091808	-2.125707
C	-1.145541	2.256268	1.578954
H	-0.660790	1.860552	0.674864
C	-3.101697	0.025289	4.004193
H	-3.961533	0.111385	4.672355
C	2.999595	3.036639	-1.300484
H	3.719183	2.302173	-0.910475
H	2.964217	3.885466	-0.599933
H	3.390563	3.405166	-2.261122
C	1.548412	-0.180302	2.388817
H	1.797239	-1.192832	2.750420
H	1.309890	0.430200	3.270108
C	3.169343	-3.297998	-2.205531
H	3.488357	-3.408169	-3.253741
H	3.163520	-4.299192	-1.748037
H	3.926809	-2.688573	-1.689640
C	0.712129	-3.541766	-2.799720
H	-0.270774	-3.056193	-2.735605
H	0.663432	-4.522602	-2.302628
H	0.953121	-3.717102	-3.860117
C	-0.677828	-2.684483	2.834224
H	0.108681	-2.573432	2.072537
C	-0.119503	3.125504	2.327550
H	-0.566875	3.554333	3.237570
H	0.221364	3.956804	1.690272
H	0.765886	2.549226	2.631378
C	-2.325737	3.111992	1.101577
H	-3.085373	2.487728	0.613080
H	-1.974508	3.861135	0.376063
H	-2.803495	3.657248	1.929857
C	-1.682169	-3.708165	2.278710
H	-2.494543	-3.903330	2.995305
H	-1.177069	-4.664774	2.074084
H	-2.121444	-3.339585	1.342321
C	-0.029900	-3.188328	4.134888
H	0.707579	-2.470693	4.525859
H	0.481224	-4.148422	3.965140

H	-0.787078	-3.345948	4.918212
H	-0.701224	-2.164342	-0.229953
C	-2.375746	-0.394937	-2.383491
C	-3.237542	-0.757745	-1.118681
B	-1.008487	-0.981599	-0.560549
O	-1.073972	-0.882780	-2.022644
O	-2.305171	-0.530342	-0.050694
C	-2.288460	1.121760	-2.604345
H	-1.486803	1.320995	-3.329370
H	-3.228229	1.544156	-2.991482
H	-2.036992	1.626417	-1.660760
C	-2.807669	-1.079670	-3.679379
H	-3.836048	-0.799071	-3.954631
H	-2.136679	-0.773914	-4.495823
H	-2.751101	-2.171720	-3.586385
C	-4.462943	0.123924	-0.897149
H	-5.176306	0.021634	-1.729094
H	-4.968954	-0.176449	0.032216
H	-4.183292	1.180668	-0.803543
C	-3.662033	-2.236447	-1.111487
H	-4.072051	-2.476396	-0.119702
H	-4.431653	-2.448417	-1.868082
H	-2.798252	-2.891467	-1.293066