Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for:

Aromaticity transfer in an annulated 1,4,2-diazaborole: Facile access to C_s symmetric 1,4,2,5-diazadiborinines

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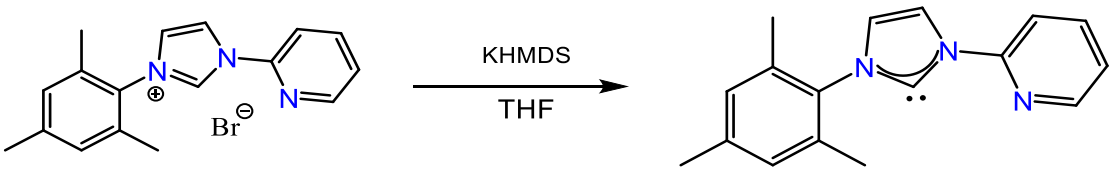
1.) Experimental Details

General experimental considerations

All syntheses were carried out in a nitrogen or argon-filled glovebox or with standard Schlenk techniques[1] unless otherwise stated. Reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. N-mesityl-N'-(2-pyridyl)imidazolium bromide,[2] $MesBBr_2$,[3] $PhBCl_2$,[3] $Na_2[Fe(CO)_4]$,[4] and 9-borabicyclo[3.3.1]nonane (9-BBN)[5] were synthesized according to literature procedures. All solvents were dried by passage through a Grubbs-style solvent purification system and stored over activated 4Å molecular sieves. All solution NMR spectra were acquired on a Varian Mercury Vx 400 MHz NMR spectrometer equipped with an ATB probe at 298 K (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, ^{11}B: 128.4 MHz, ^{19}F: 376.5 MHz). ^{1}H and ^{13}C spectra were referenced to residual solvent signals. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br.s = broad signal, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet. UV-Vis spectra were acquired on a SHIMADZU UV-2550 spectrophotometer and fluorescence spectra were acquired on a PerkinElmer LS45 fluorimeter. Electrospray ionization (ESI) mass spectra were obtained using a high-resolution Agilent 6530 Quadrupole Time of Flight (QToF) mass spectrometer. Melting points were measured using Fisherbrand™ digital melting point apparatus.

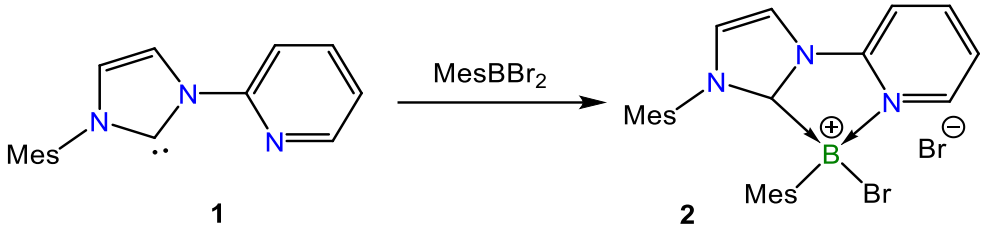
Synthesis of 1:



Potassium hexamethyldisilylamide (KHMDS) (5.80 g, 29.1 mmol) was added to a stirred suspension of N-mesityl-N'-(2-pyridyl)imidazolium bromide (10.0 g, 29.1 mmol) in 200 mL THF. After stirring for 2 hours at room temperature, the light brown suspension was filtered over celite through a glass frit and the solvent was removed under vacuum. The residue was extracted with

hexane (3x 80 mL), the extracts combined, filtered, and concentrated *in vacuo* causing the crystallization of pure carbene. All volatiles were removed under vacuum to obtain **1** as a golden brown solid (6.31 g, 83%). NMR data matched literature values.[6]

Synthesis of 2:



A solution of **1** (2.03 g, 7.71 mmol) in 60 mL hexane was added dropwise to a stirred solution of $MesBBr_2$ (3.35 g, 11.56 mmol) in 40 mL hexane. The precipitate formed was collected, washed with hexane (3x 10 mL), ether (2x 10 mL), and dried under vacuum to afford **2** as an off-white solid (4.01 g, 94%).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 10.64 (d, 1H, ^{3}J = 1.8 Hz, CH_{Imidaz}), 10.33 (d, 1H, ^{3}J = 8.0 Hz, CH_{Py}), 8.69 (t, 1H, ^{3}J = 7.8 Hz, CH_{Py}), 8.49 (d, 1H, ^{3}J = 5.6 Hz, CH_{Py}), 7.82 (t, 1H, ^{3}J = 6.5 Hz, CH_{Py}), 7.28 (d, 1H, ^{3}J = 1.8 Hz, CH_{Imidaz}), 7.07 (s, 1H, CH_{Mes}), 6.79 (s, 1H, CH_{Mes}), 6.71 (s, 1H, CH_{Mes}), 6.61 (s, 1H, CH_{Mes}), 2.35 (s, 3H, $CH_{3\text{-}Mes}$), 2.25 (s, 3H, $CH_{3\text{-}Mes}$), 2.21 (s, 3H, $CH_{3\text{-}Mes}$), 1.82 (s, 3H, $CH_{3\text{-}Mes}$), 1.27 (s, 3H, $CH_{3\text{-}Mes}$), 1.17 (s, 3H, $CH_{3\text{-}Mes}$) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 161.93 (NCN_{Imidaz}), 148.17 (CH_{Py}), 145.98 (CH_{Imidaz}), 144.92 (*q*-Mes), 144.03 (CH_{Py}), 141.64 (*q*-Mes), 139.89 (*q*-Mes), 138.51 (*q*-Mes), 134.71 (*q*-Mes), 134.41 (*q*-Mes), 131.13 (CH_{Mes}), 130.63 (CH_{Mes}), 130.09 (CH_{Mes}), 129.94 (CH_{Mes}), 129.42 (*q*-Mes), 127.87 (CH_{Imidaz}), 125.88 (CH_{Py}), 120.89 (*q*-Mes), 120.86 (*q*-Py), 117.71 (CH_{Py}), 25.65 ($CH_{3\text{-}Mes}$), 23.02 ($CH_{3\text{-}Mes}$), 21.15 ($CH_{3\text{-}Mes}$), 20.72 ($CH_{3\text{-}Mes}$), 18.28 ($CH_{3\text{-}Mes}$), 15.95 ($CH_{3\text{-}Mes}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$): δ = 1.1 ppm.

HRMS (ESI): $C_{26}H_{28}BBr_2N_3$ Calculated for $[M\text{-}Br]^+$ 474.1534, observed 474.1521

MP: 186 ºC (decomp)

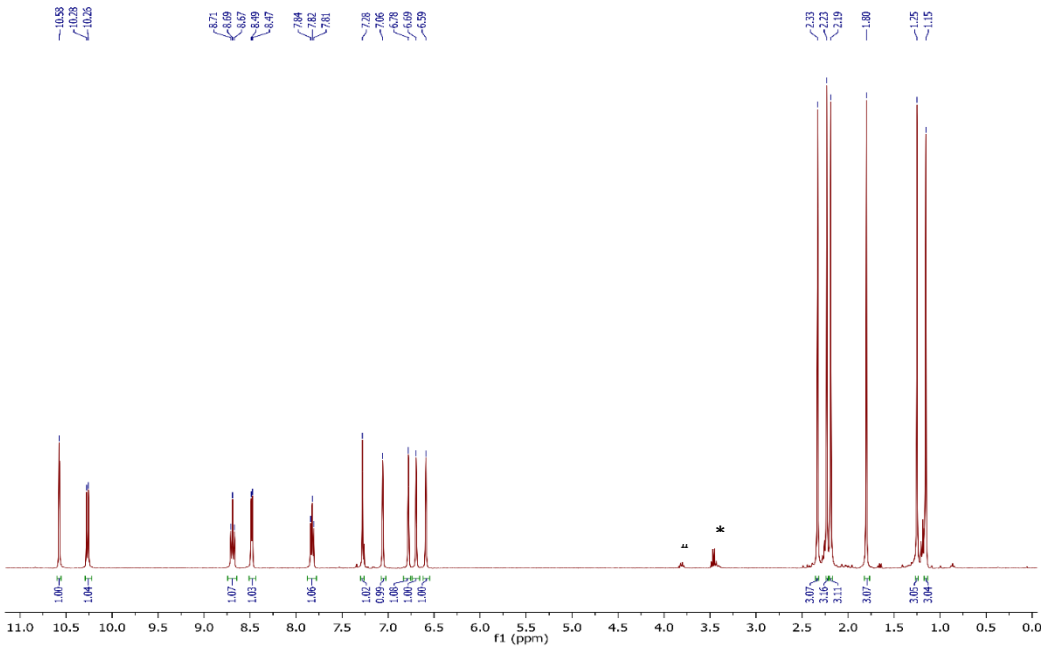


Figure S1: ^{1}H NMR spectrum of **2** in $CDCl_3$ (residual solvent: *ether, #tetrahydrofuran)

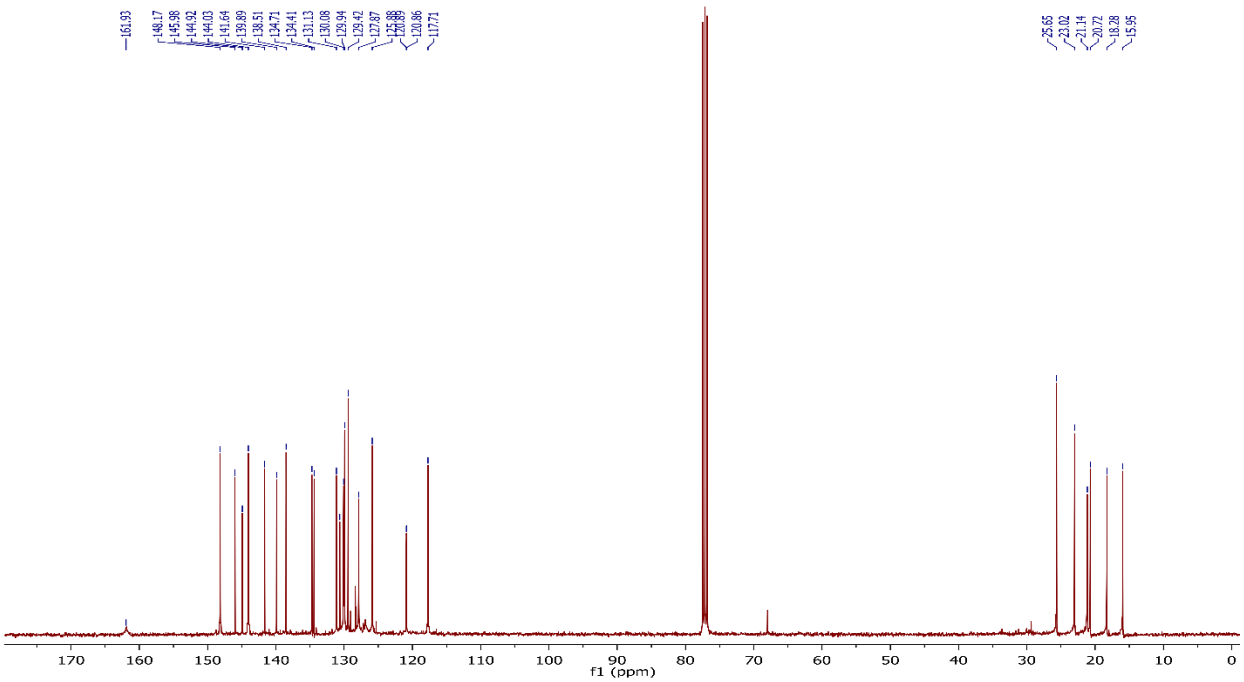


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$

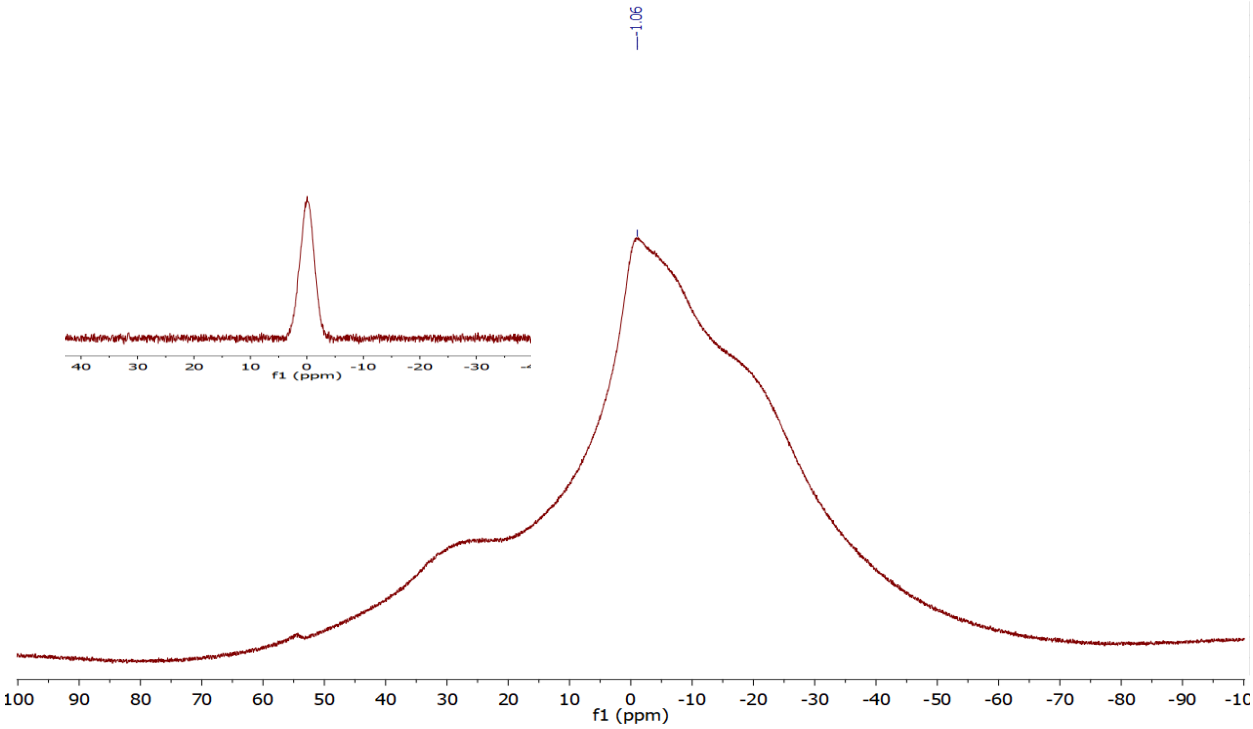
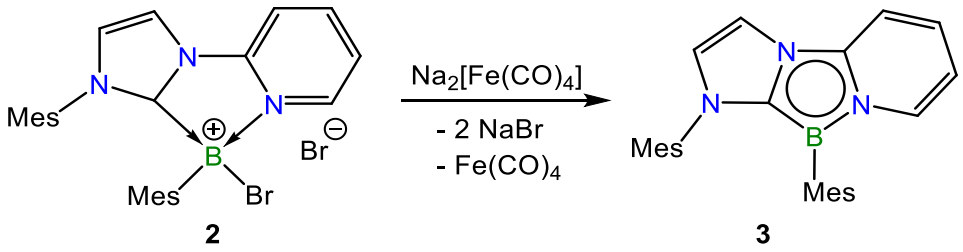


Figure S3: $^{11}B\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$. Inset is the $^{11}B\{^{1}H\}$ spectrum with glass peak subtracted. (* is excess $MesBBr_2$)

Synthesis of 3:



Solid **2** (1.02 g, 1.84 mmol) was slowly added to a stirred suspension of $Na_2[Fe(CO)_4]$ (0.87g, 4.06 mmol) in 60 mL THF at room temperature over the course of 15 minutes. The solution immediately became dark red and was allowed to stir for an additional 15 minutes. The solution was then filtered, the solvent removed, and the residue was extracted with 200 mL hexane. The solvent was removed, and the residue dried under vacuum to obtain **3** as a dark red solid (0.58 g, 80 %). Crystals suitable for single crystal X-ray diffraction were grown from hexane at −35ºC.

^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.56 (dt, 1H, ^{3}J = 7.0 Hz, ^{4}J = 1.0 Hz, CH_{Py}), 6.94 (dt, 1H, ^{3}J = 8.5 Hz, ^{4}J = 1.0 Hz, CH_{Py}), 6.85 (m, 3H, CH_{Mes} + CH_{Imidaz}), 6.57 (s, 2H, CH_{Mes}), 6.30 (m, 2H, CH_{Py} + CH_{Imidaz}), 6.19 (m, 1H, CH_{Py}), 2.24 (s, 6H, *o*-$CH_{3\text{-}Mes}$), 2.14 (s, 3H, *p*-$CH_{3\text{-}Mes}$), 2.01 (s, 6H, *o*-$CH_{3\text{-}Mes}$), 1.93 (s, 3H, *p*-$CH_{3\text{-}Mes}$) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 142.43 (*q*-Mes), 137.46 (*q*-Mes), 136.38 (*q*-Mes), 136.22 (*q*-Mes), 135.42 (*q*-Mes), 129.29 (CH_{Mes}), 127.94 (CH_{Py}), 127.76 (CH_{Mes}), 127.59 (CH_{Imidaz}), 125.18 (CH_{Imidaz}), 118.26 (*q*-NCN), 112.61 (CH_{Py}), 109.79 (CH_{Py}), 107.20 (CH_{Py}), 102.92 (*q*-Py), 22.95 (*o*-$CH_{3\text{-}Mes}$), 21.36 (*p*-$CH_{3\text{-}Mes}$), 20.92 (*p*-$CH_{3\text{-}Mes}$), 18.03 (*o*-$CH_{3\text{-}Mes}$) ppm. Note: The signal for the carbene could not be identified due to broadening.

^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ = 12.2 ppm.

HRMS (ESI): $C_{26}H_{28}BN_3$ Calculated for $[M+H]^+$ 394.2450, observed 394.2479

MP: 120 ºC (decomp)

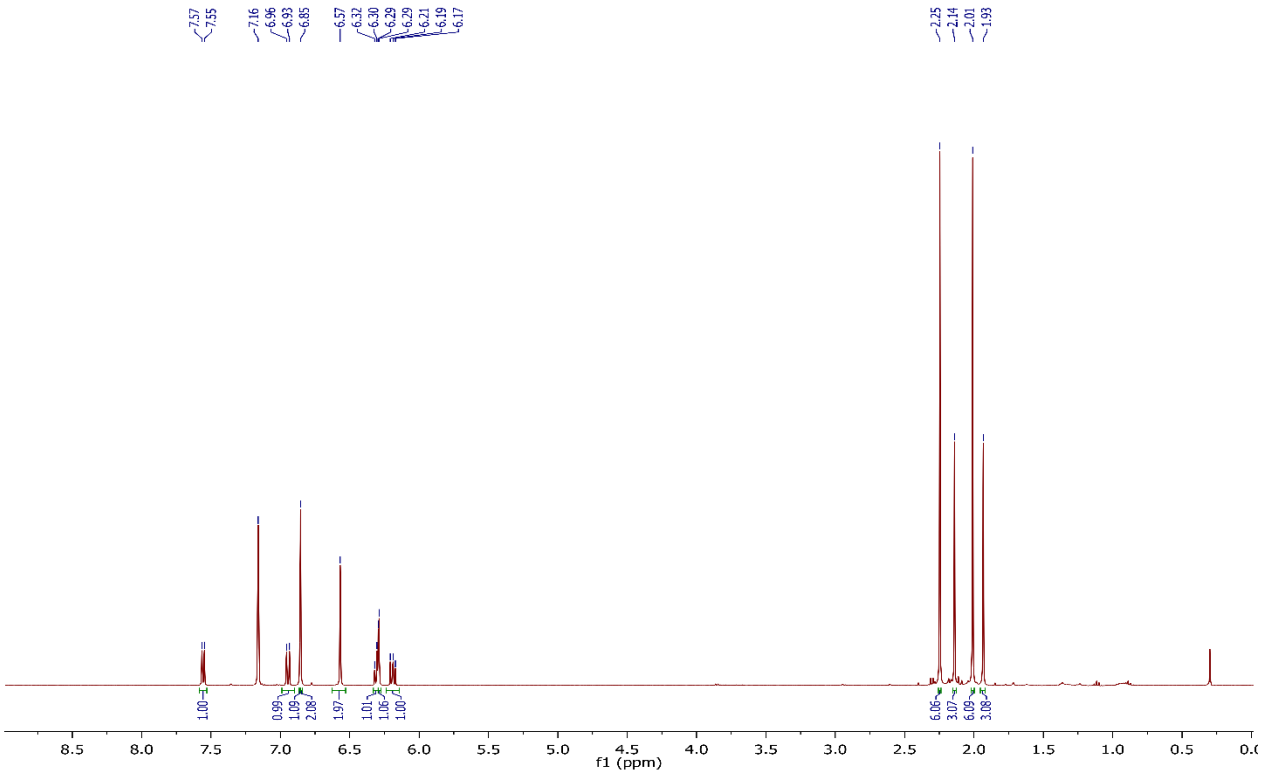


Figure S4: ^{1}H NMR spectrum of **3** in C_6D_6

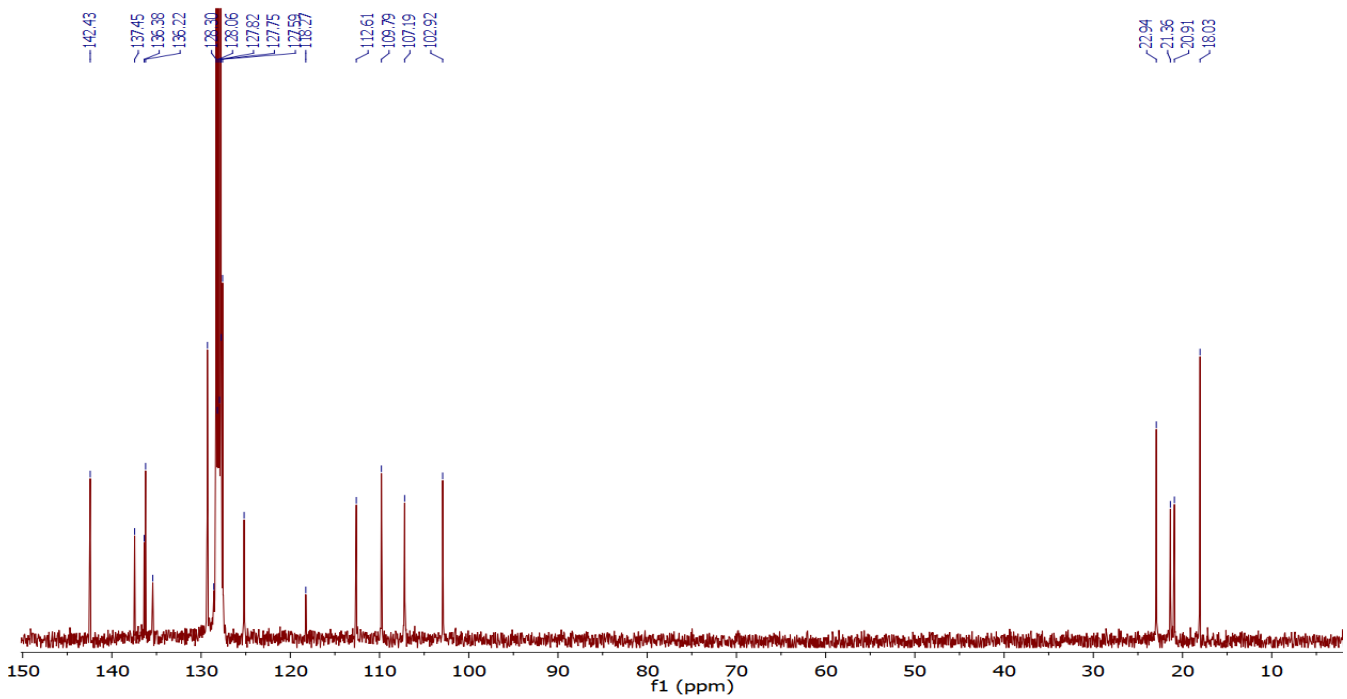


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

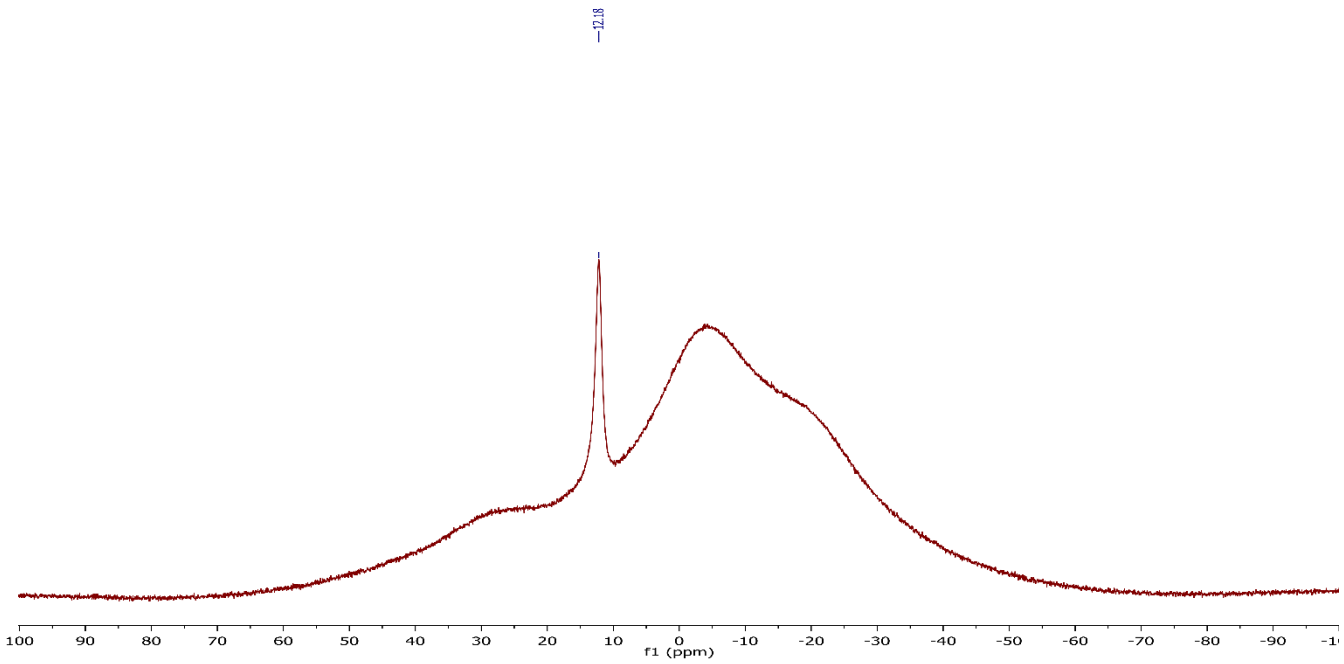
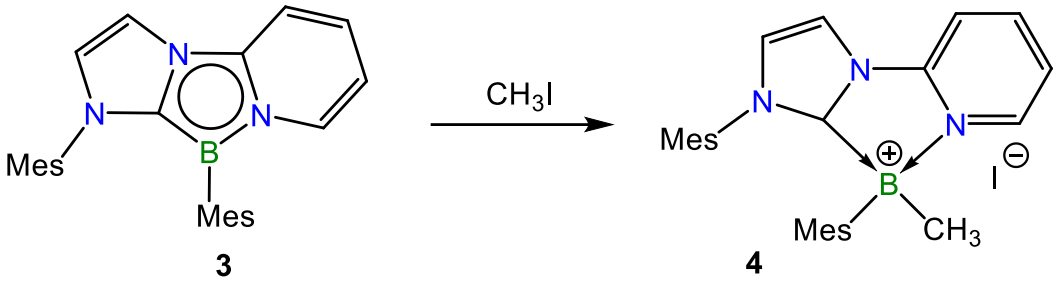


Figure S6: $^{11}B\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

Synthesis of 4:



3 **4**

A solution of **3** (100 mg, 0.25 mmol) in benzene (5 ml) was combined with iodomethane (40 mg, 0.28 mmol) and stirred at 60ºC for 6 hours, resulting in the formation of a blue solution and the formation of a precipitate. The precipitate was collected by filtration, washed with benzene (3 x 5 mL), and dried under vacuum affording **4** as a white solid (88 mg, 65%). Crystals suitable for single crystal X-ray diffraction were grown from a DCM solution layered with ether.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 10.06 (d, 1H, ^{3}J = 2.0 Hz, CH_{Imidaz}), 9.92 (dt, 1H, ^{3}J = 8.4 Hz, ^{4}J = 0.8 Hz, CH_{Py}), 8.63 (ddd, 1H, ^{3}J = 8.4 Hz, 7.6 Hz, ^{4}J = 1.5 Hz, CH_{Py}), 8.23 (ddd, 1H, ^{3}J = 5.8 Hz, ^{4}J = 1.5 Hz, ^{5}J = 0.8 Hz, CH_{Py}), 7.79 (ddd, 1H, ^{3}J = 7.6 Hz, 5.8 Hz, ^{4}J = 0.8 Hz, CH_{Py}), 7.27 (d, 1H, ^{3}J = 1.8 Hz, CH_{Imidaz}), 7.05 (s, 1H, CH_{Mes}), 6.79 (s, 1H, CH_{Mes}), 6.66 (s, 1H, CH_{Mes}), 6.57 (s, 1H, CH_{Mes}), 2.34 (s, 3H, $CH_{3\text{-}Mes}$), 2.18 (s, 3H, $CH_{3\text{-}Mes}$), 2.08 (s, 3H, $CH_{3\text{-}Mes}$), 1.74 (s, 3H, $CH_{3\text{-}Mes}$), 1.30 (s, 3H, $CH_{3\text{-}Mes}$), 1.08 (s, 3H, $CH_{3\text{-}Mes}$), 0.39 (s, 3H, B-CH_3) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): 169.73 (NCN_{Imidaz}), 144.73 (CH_{Py}), 144.52 (*q*-Mes), 143.98 (*q*-Mes), 141.48 (*q*-Py), 140.15 (*q*-Mes), 136.10 (*q*-Mes), 133.82 (*q*-Mes), 133.15 (CH_{Py}), 129.94 (*q*-Mes), 129.67 (CH_{Mes}), 128.98 (CH_{Mes}), 128.55 (CH_{Mes}), 128.46 (CH_{Mes}), 127.30 (*q*-Mes), 126.08 (CH_{Imidaz}), 123.89 (CH_{Py}), 118.80 (CH_{Imidaz}), 116.15 (CH_{Py}), 23.60 ($CH_{3\text{-}Mes}$), 21.54 ($CH_{3\text{-}Mes}$), 20.07 ($CH_{3\text{-}Mes}$), 19.59 ($CH_{3\text{-}Mes}$), 16.67 ($CH_{3\text{-}Mes}$), 14.96 ($CH_{3\text{-}Mes}$), 10.30 (B-CH_3) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$): δ −0.2 ppm.

HRMS (ESI): $C_{27}H_{31}BN_3I$ Calculated for $[2M]^+$ 1070.3302, observed 1070.3334

MP: 192 ºC (decomp)

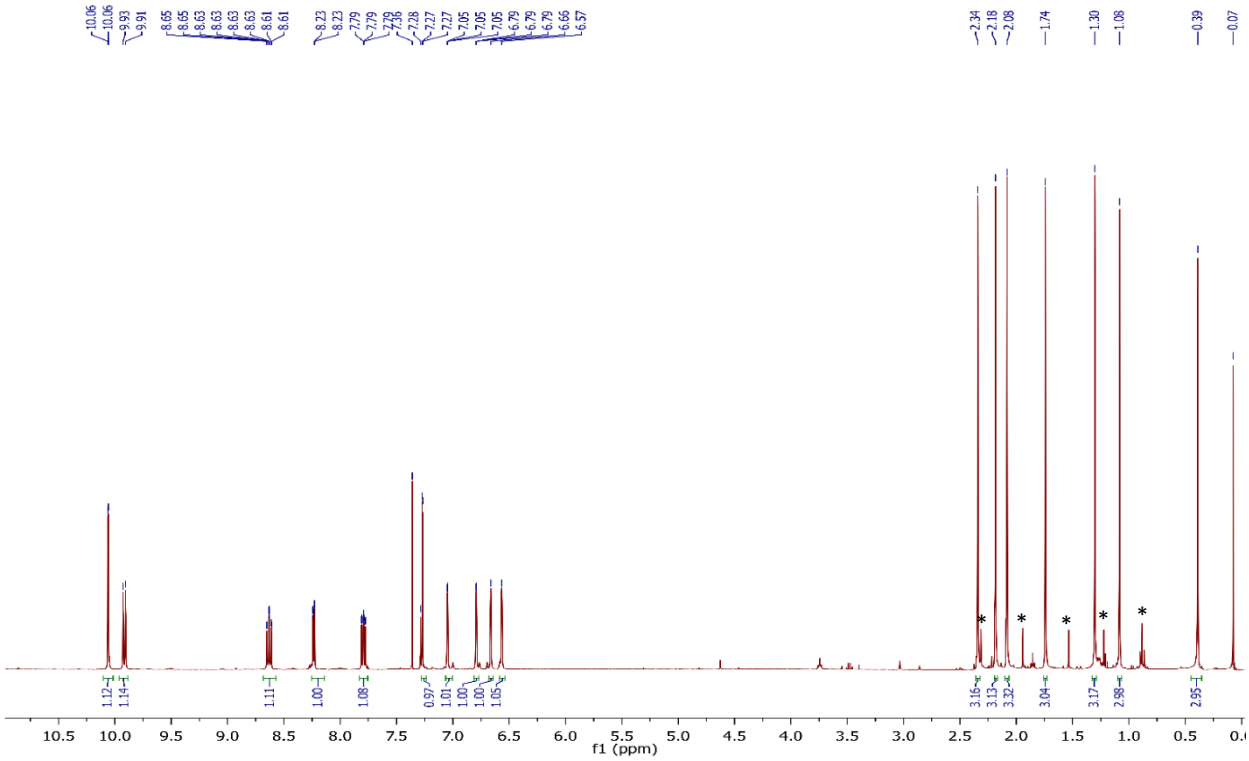


Figure S7: ^{1}H NMR spectrum of **4** in $CDCl_3$ (*unidentifiable minor impurity)

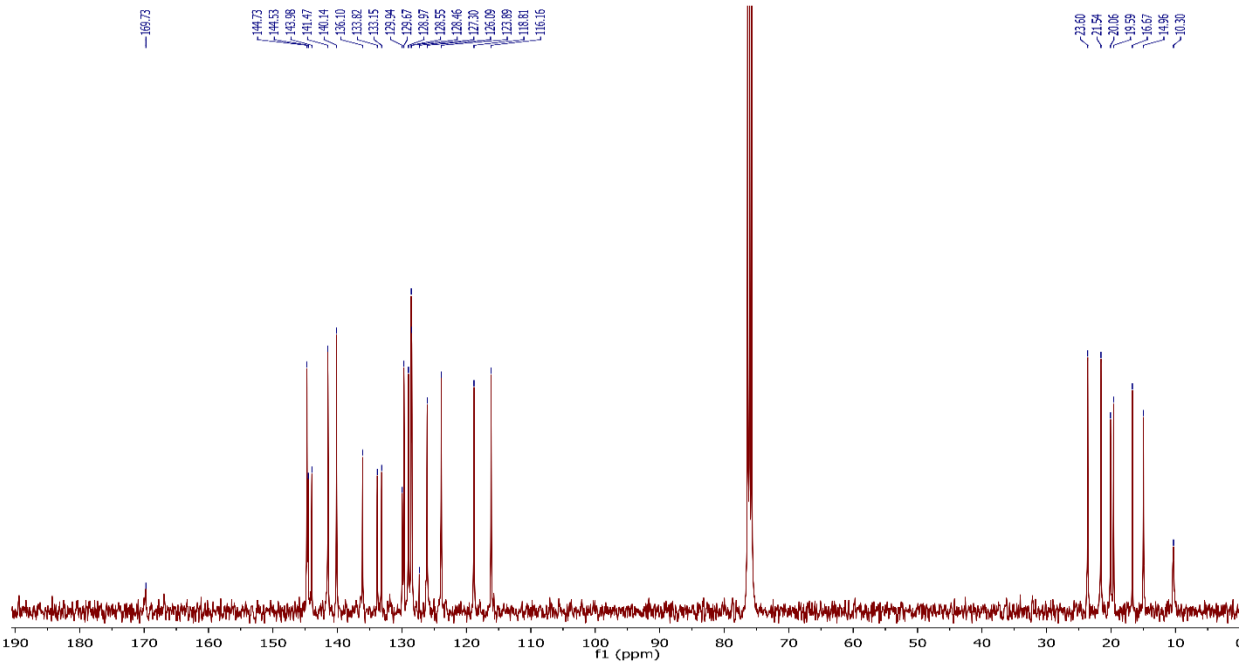


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$

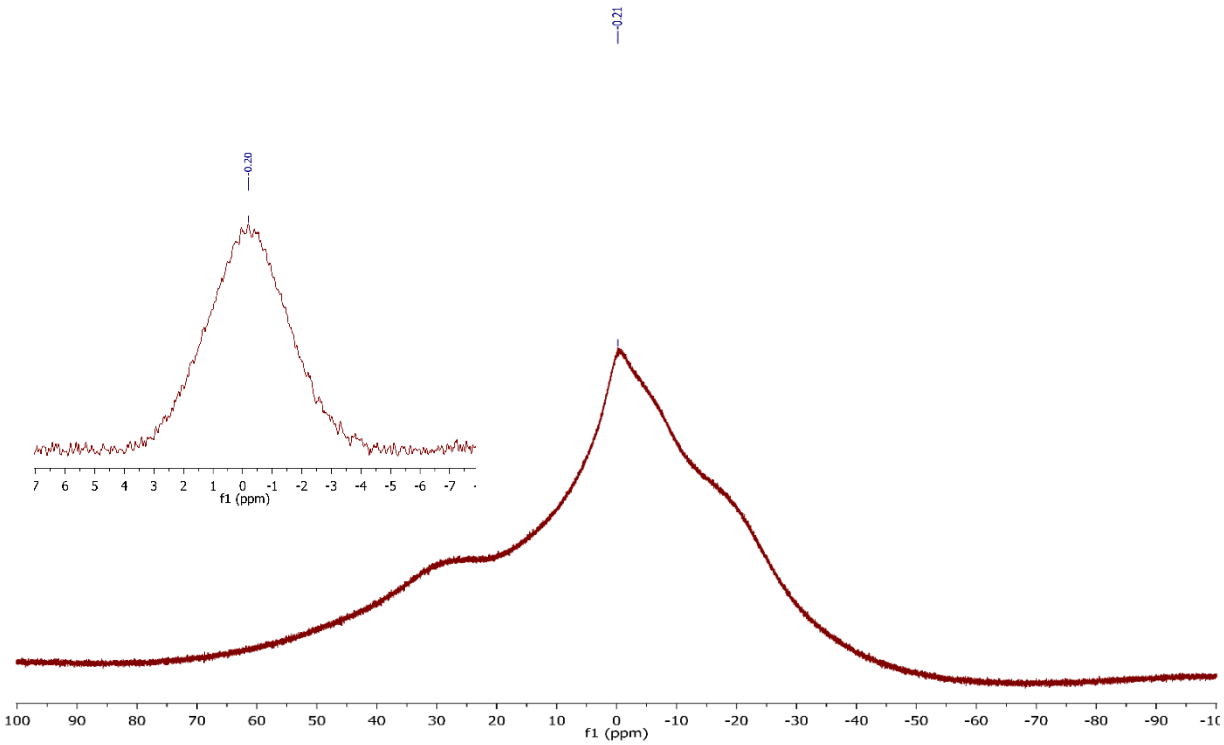
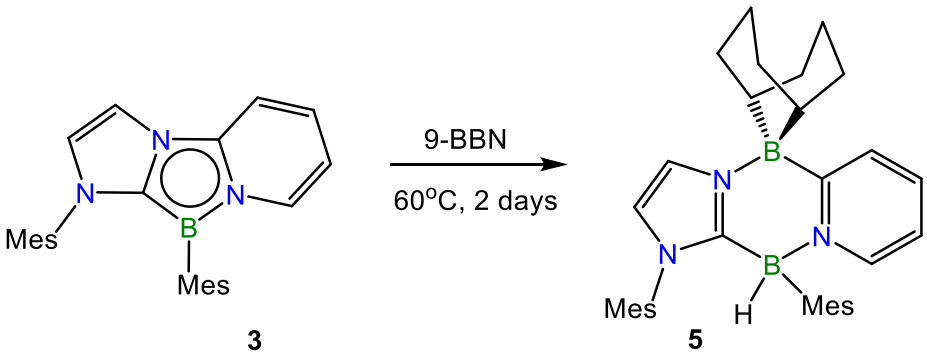


Figure S9: $^{11}B\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$. Inset is the $^{11}B\{^{1}H\}$ spectrum with glass peak subtracted.

Synthesis of 5:



3 **5**

Compound **3** (100 mg, 0.25 mmol) was combined with 9-borabicyclo[3.3.1]nonane (9-BBN) (30 mg, 0.25 mmol) in 8 mL toluene and stirred at 60ºC for 48 hrs. The solution was then filtered, concentrated, and cooled to −35ºC overnight resulting in the formation of colorless crystals. The crystals were then collected, washed with pentane (2 x 3 mL) and dried under vacuum to obtain **5** as a colorless solid (77 mg, 58%). Crystals suitable for X-ray diffraction were grown from hexane at −35ºC.

^{1}H NMR (400.1 MHz, C_6D_6): δ = 8.03 (dd, 1H, ^{3}J = 8.0 Hz, ^{4}J = 1.0 Hz, CH_{Py}), 7.92 (dd, 1H, ^{3}J = 6.2 Hz, ^{4}J = 1.0 Hz, CH_{Py}), 7.60 (d, 1H, ^{3}J = 1.7 Hz, CH_{Imidaz}), 6.89 (dt, 1H, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, CH_{Py}), 6.59 – 6.56 (m, 1H, CH_{Mes}), 6.54 (br.s, 1H, CH_{Mes}), 6.41 (br.s, 1H, CH_{Mes}), 6.30 – 6.26 (m, 1H, CH_{Mes}), 6.25 (d, 1H, ^{3}J = 1.8 Hz, CH_{Imidaz}), 6.08 (ddd, 1H, ^{3}J = 7.5 Hz, 5.8 Hz, ^{4}J = 1.7 Hz, CH_{Py}), 4.95 (br.s, 1H, B-H), 3.00 – 2.80 (m, 2H, 9-BBN), 2.41 (s, 3H, $CH_{3\text{-}Mes}$), 2.38 – 2.32 (m, 1H, 9-BBN), 2.32 – 2.20 (m, 3H, 9-BBN), 2.13 (s, 6H, $CH_{3\text{-}Mes}$), 2.03 (s, 3H, $CH_{3\text{-}Mes}$), 2.02 - 1.97 (m, 3H, $CH_{3\text{-}Mes}$), 1.97 – 1.86 (m, 2H, 9-BBN), 1.85 – 1.70 (m, 1H, 9-BBN), 1.70 – 1.61 (m, 1H, CH-9-BBN), 1.60 (s, 3H, $CH_{3\text{-}Mes}$), 1.38 – 1.20 (m, 1H, CH-9-BBN), 0.92 – 0.80 (m, 3H, 9-BBN) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): 182.20 (BC_{Py}), 166.97 (BC_{Imidaz}), 146.18 (CH_{Py}), 143.07 (*q*-Mes), 140.61 (*q*-Mes), 137.02 (*q*-Mes), 134.64 (CH_{Py}), 134.62 (*q*-Mes), 134.44 (*q*-Mes), 134.37 (*q*-Mes), 133.31 (*q*-Mes), 130.03 (CH_{Py}), 128.85 (CH_{Mes}), 128.52 (*q*-Mes), 128.22 (CH_{Mes}), 128.19 (CH_{Mes}), 127.51 (CH_{Mes}), 123.52 (CH_{Imidaz}), 119.73 (CH_{Imidaz}),119.67 (CH_{Py}), 35.82 (CH_2-9-BBN), 34.09 (CH_2-9-BBN), 32.75 ($CH_{3\text{-}Mes}$), 30.71 (CH_2-9-BBN), 24.91 (CH-9-BBN), 24.35 (CH_2-9-BBN), 24.19 ($CH_{3\text{-}Mes}$), 23.62 (CH_2-9-BBN), 21.68 (CH-9-BBN), 21.35 (CH_2-9-BBN), 20.64 ($CH_{3\text{-}Mes}$), 20.42 ($CH_{3\text{-}Mes}$), 18.01 ($CH_{3\text{-}Mes}$), 17.61 ($CH_{3\text{-}Mes}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ = −5.6 (9-BBN), −8.5 ppm (B-Mes) ppm.

HRMS (ESI): $C_{34}H_{43}B_2N_3$ Calculated for $[M+H]^+$ 516.3721, observed 516.3727

MP: 230 ºC (decomp)

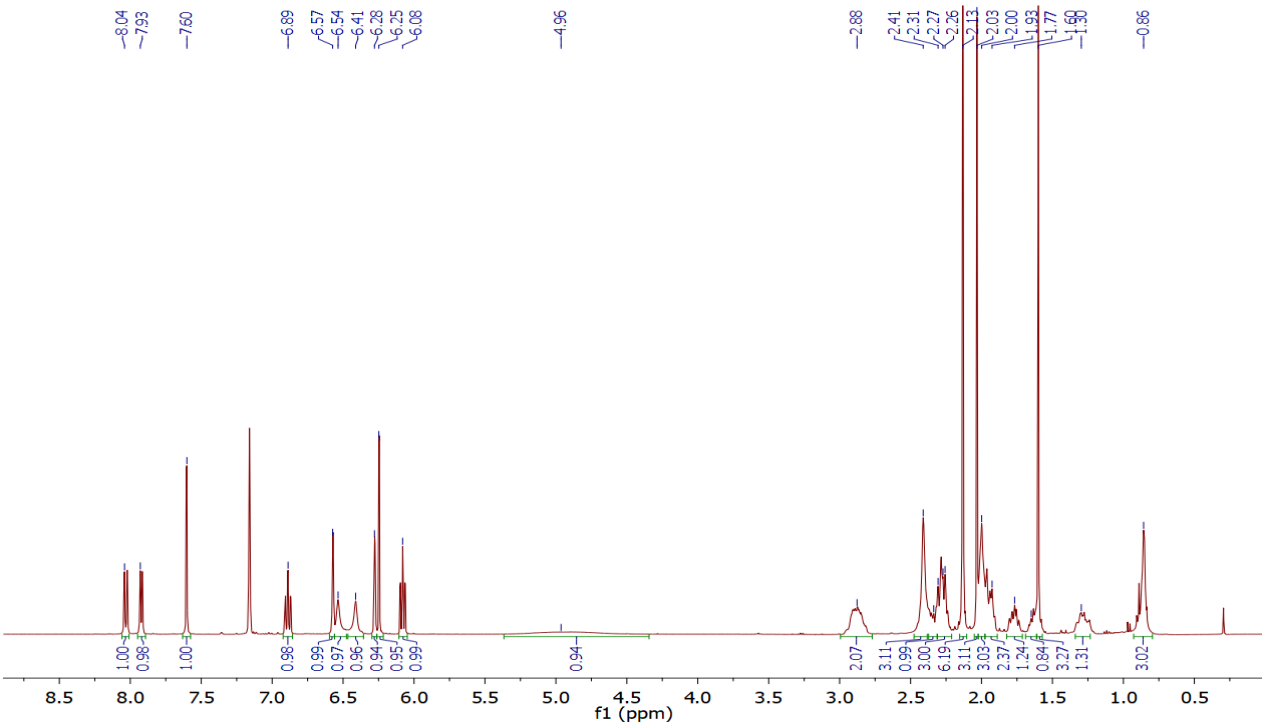


Figure S10: ^{1}H NMR spectrum of **5** in C_6D_6

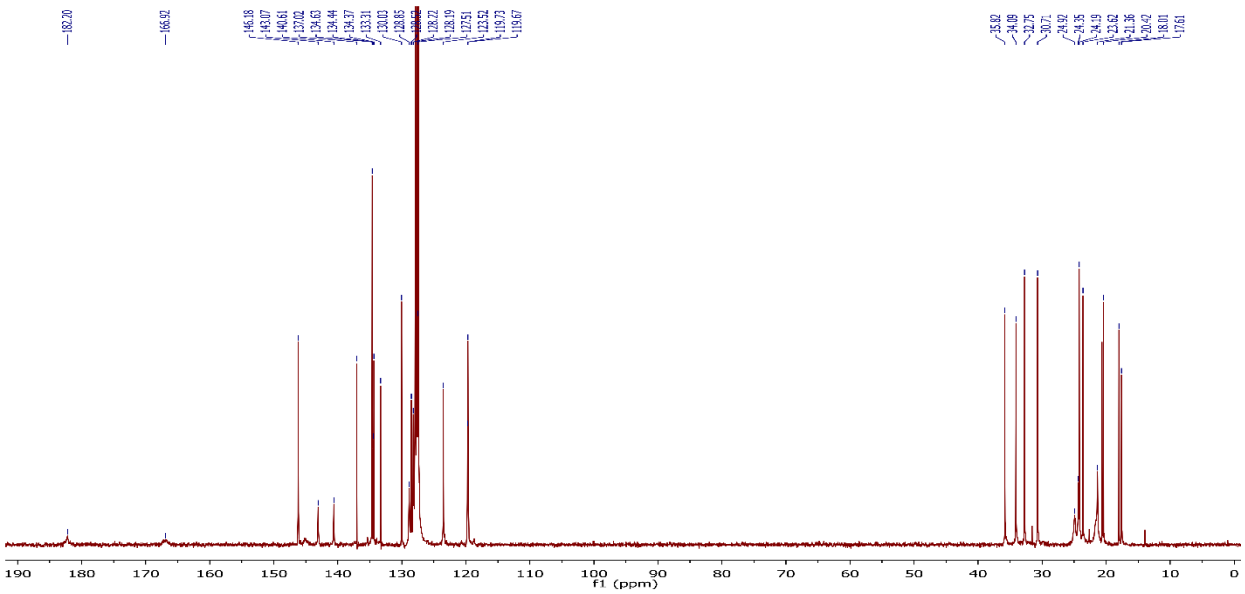


Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6

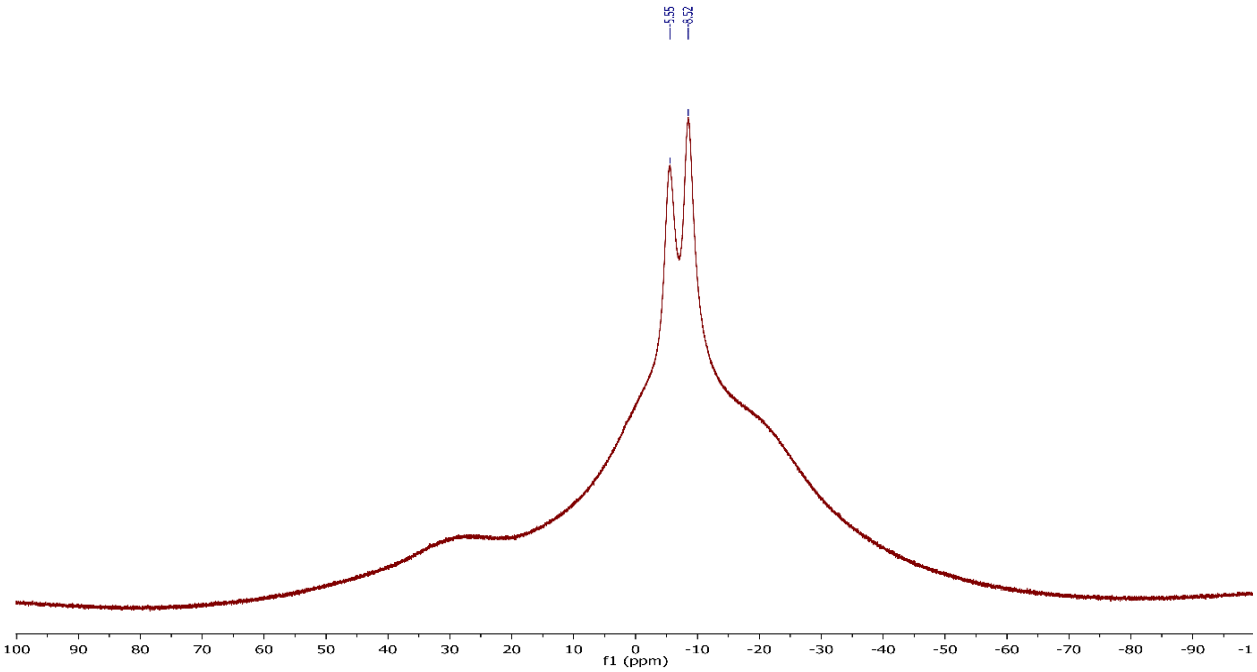
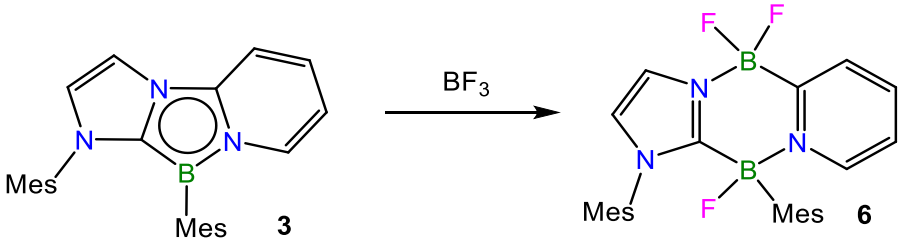


Figure S12: $^{11}B\{^{1}H\}$ NMR spectrum of **5** in C_6D_6

Synthesis of 6:



To a 5 mL of toluene solution of **3** (100 mg, 0.25 mmol) was added $BF_3{\cdot}OEt_2$ (40 mg, 0.28 mmol) and the mixture was stirred for 30 mins at room temperature. All volatiles were removed and the residue was washed with hexane (3 x 3 mL) and dried under vacuum affording **6** as an off-white solid (52 mg, 44%). Crystals suitable for X-ray diffraction were obtained from a benzene solution layered with hexane.

^{1}H NMR (400.1 MHz, C_6D_6): δ = 8.06 (d, 1H, ^{3}J = 7.8 Hz, CH_{Py}), 7.96 (d, 1H, ^{3}J = 6.2 Hz, CH_{Py}), 7.47 (s, 1H, CH_{Imidaz}), 6.81 (t, 1H, ^{3}J = 7.8 Hz, CH_{Py}), 6.67 (s, 1H, CH_{Mes}), 6.60 (br.s, 2H, CH_{Mes}), 6.43 (s, 1H, CH_{Mes}), 6.12 (t, 1H, ^{3}J = 6.2 Hz, CH_{Py}), 5.93 (s, 1H, CH_{Imidaz}), 2.12 (s, 3H, $CH_{3\text{-}Mes}$), 2.06 (s, 3H, $CH_{3\text{-}Mes}$), 1.95 (br.s, 9H, $CH_{3\text{-}Mes}$), 1.21 (s, 3H, $CH_{3\text{-}Mes}$) ppm.

$^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6): 154.66 (BC_{Py}), 146.34 (BC_{Imidaz}), 144.23 (CH_{Py}), 139.23 (*q*-Mes), 139.13 (*q*-Mes), 137.16 (*q*-Mes), 136.46 (*q*-Mes), 136.04 (*q*-Mes), 133.30 (*q*-Mes), 129.69 (CH_{Mes}), 129.58 (CH_{Mes}), 129.11 (CH_{Py}), 128.57 (CH_{Mes}), 128.39 (CH_{Py}), 128.16 (CH_{Mes}), 127.92 (*q*-Mes), 127.89 (*q*-Mes), 123.39 (CH_{Imidaz}), 122.56 (CH_{Py}), 120.90 (CH_{Imidaz}), 22.98 ($CH_{3\text{-}Mes}$), 22.91 ($CH_{3\text{-}Mes}$), 20.91 ($CH_{3\text{-}Mes}$), 17.49 ($CH_{3\text{-}Mes}$), 17.43 ($CH_{3\text{-}Mes}$), 16.46 ($CH_{3\text{-}Mes}$) ppm.

$^{11}B\{^{1}H\}$ NMR (128.4 MHz, C_6D_6): δ 4.1, 1.4 ppm.

^{19}F NMR (376.5 MHz, C_6D_6): δ = −143.5 to −144.4 (m, 1F, C-BF_2-N), −147.9 to −148.9 (m, 1F, C-BF_2-N), −158.9 to −160.1 (m, 1F, Mes-B-F) ppm.

HRMS (ESI): $C_{26}H_{28}B_2N_3F_3$ Calculated for $[3M]^+$ 1382.7300, observed 1382.7305

MP: 262 ºC (decomp)

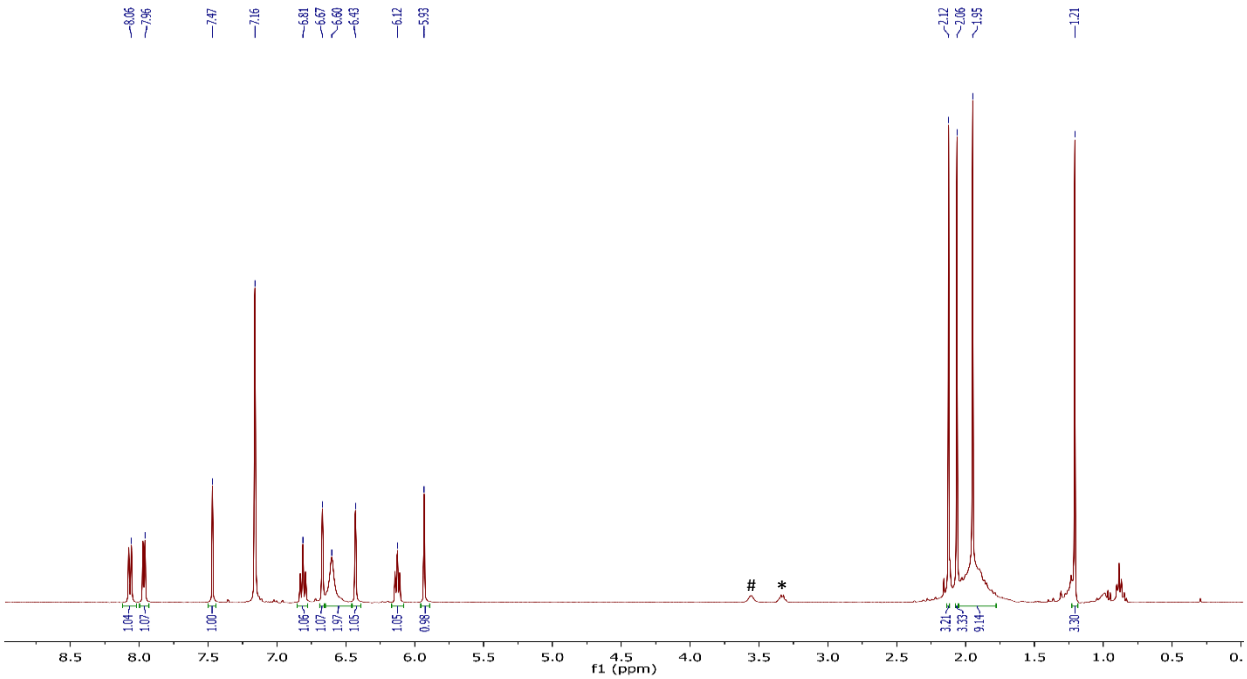


Figure S13: ^{1}H NMR spectrum of **6** in C_6D_6 (*diethylether, $^{\#}BF_3.OEt_2$)

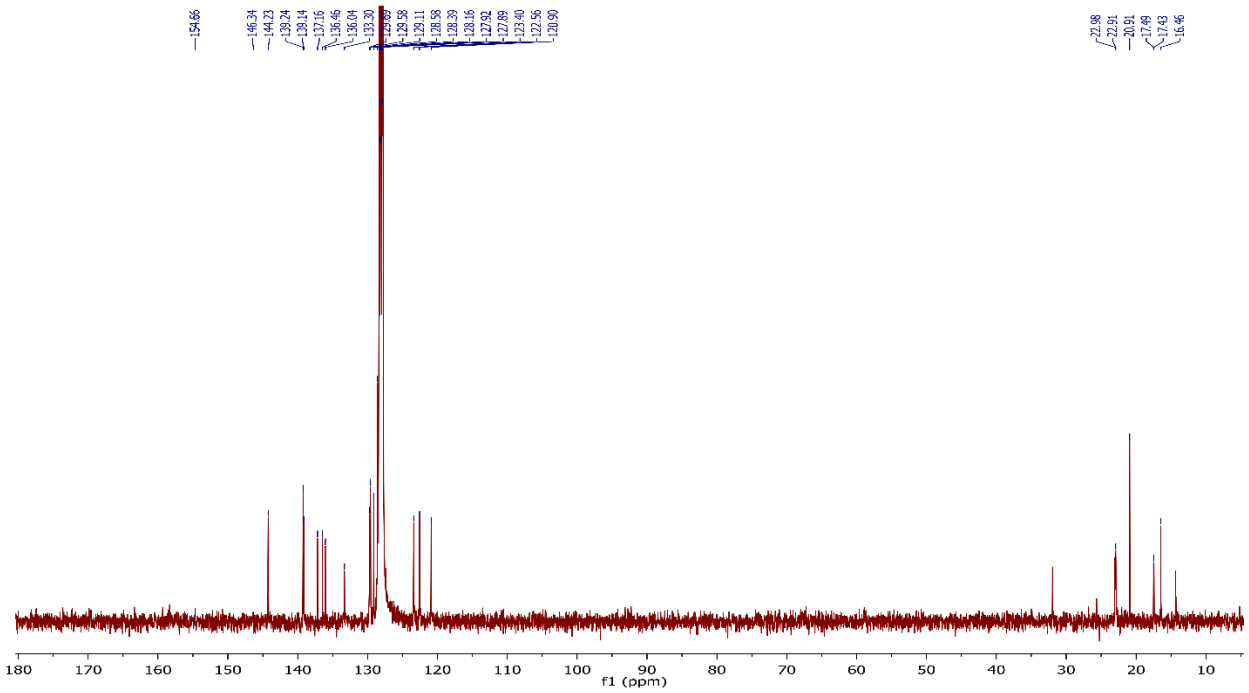


Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6

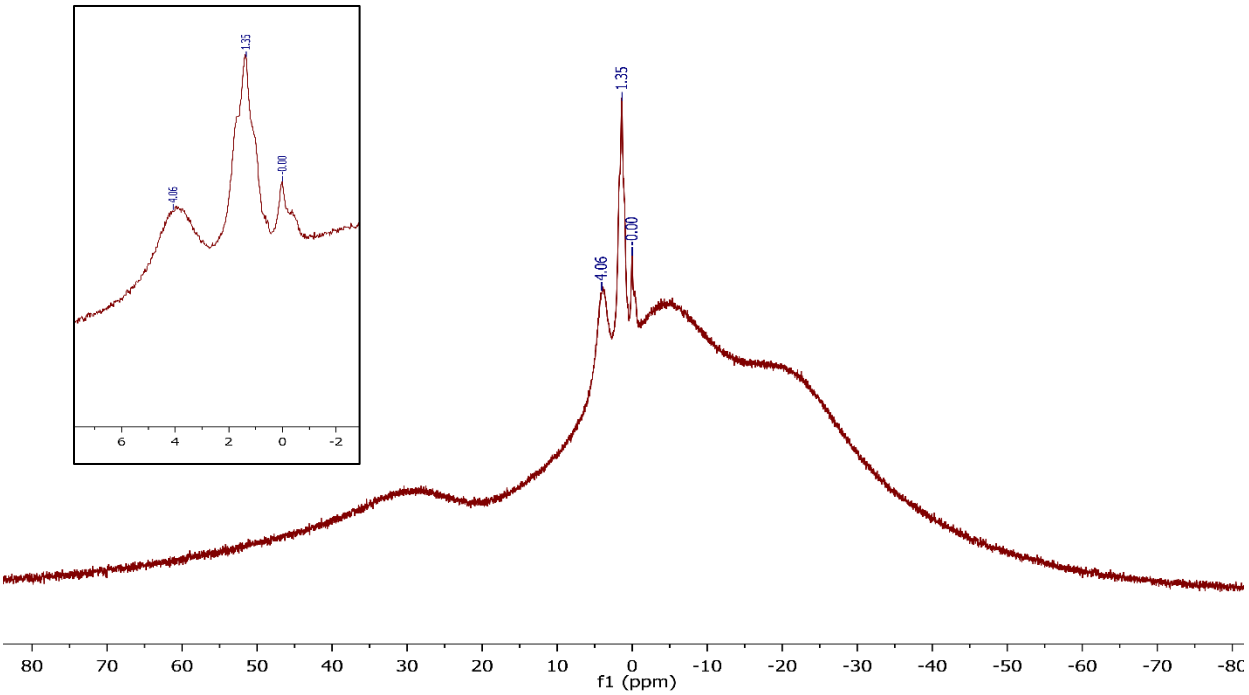


Figure S15: $^{11}B\{^{1}H\}$ NMR spectrum of **6** in C_6D_6. $BF_3{\cdot}OEt_2$ is identifiable as a minor impurity at 0 ppm.

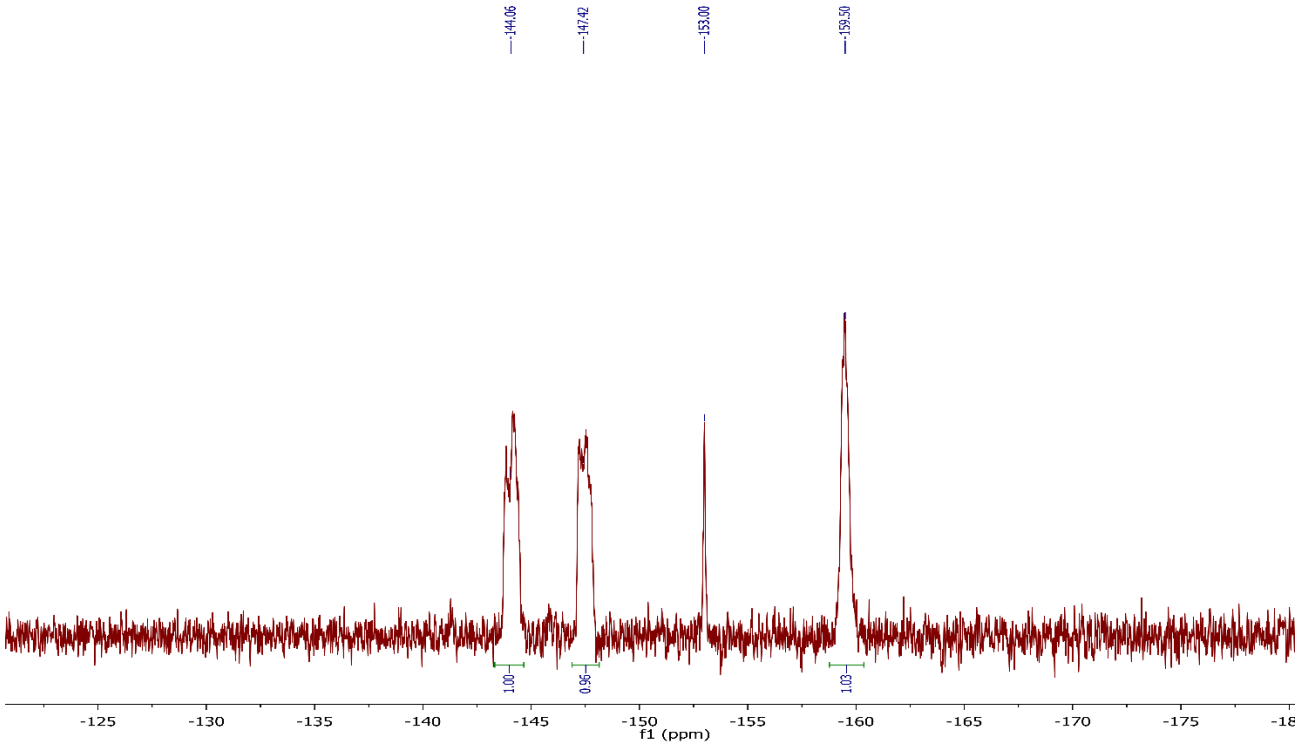
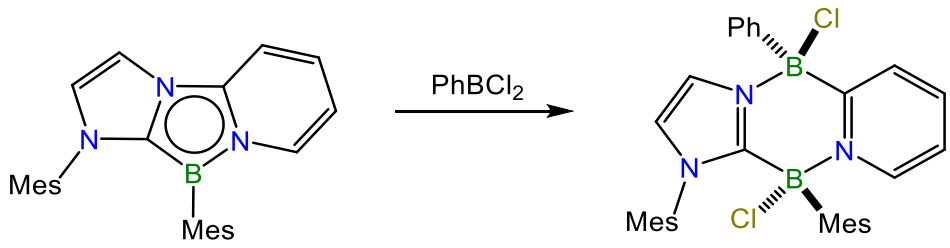


Figure S16: ^{19}F NMR spectrum of **6** in C_6D_6. $BF_3{\cdot}OEt_2$ is identifiable as a minor impurity at −153.0 ppm.

Synthesis of 7



3 **7**

To a 5 mL benzene solution of **3** (100 mg, 0.25 mmol) was added $PhBCl_2$ in 3 mL hexane (40 mg, 0.28 mmol) with vigorous stirring. The reaction mixture was left undisturbed overnight resulting in the formation of colourless crystals. The crystals were collected, washed with hexane (3x 3 mL) and dried under vacuum to afford **7** as a colourless solid (73 mg, 52%). Crystals suitable for X-ray diffraction were grown from slow evaporation of a benzene solution**.**

^{1}H NMR (400.1 MHz, C_6D_6): δ = 8.32 − 8.22 (m, 2H, CH_{phenyl}), 7.98 (d, 1H, ^{3}J = 6.3 Hz, CH_{Py}), 7.85 (d, 1H, ^{3}J = 8.0 Hz, CH_{Py}), 7.46 − 7.34 (m, 3H, CH_{phenyl}), 7.16 (s, 1H, CH_{Imidaz}), 6.72 (s, 1H, CH_{Mes}), 6.65 (s, 1H, CH_{Mes}), 6.57 (t, 1H, ^{3}J = 8.0 Hz, CH_{Py}), 6.55 (s, 1H, CH_{Mes}), 6.42 (s, 1H, CH_{Mes}), 5.96 (t, 1H, ^{3}J = 6.3 Hz, CH_{Py}), 5.78 (s, 1H, CH_{Imidaz}), 2.31 (s, 3H, $CH_{3\text{-}Mes}$), 2.12 (s, 6H, $CH_{3\text{-}Mes}$), 2.07 (s, 3H, $CH_{3\text{-}Mes}$), 1.77 (s, 3H, $CH_{3\text{-}Mes}$), 1.15 (s, 3H, $CH_{3\text{-}Mes}$) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 173.15 (BC_{Py}), 155.51 (BC_{Imidaz}), 148.49 (q-CH_{phenyl}), 145.43 (q-Mes), 143.70 (CH_{Py}), 142.59 (q-Mes), 138.94 (q-Mes), 137.48 (CH_{Py}), 136.48 (q-Mes), 136.35 (q-Mes), 136.31 (q-Mes), 135.55 (CH_{phenyl}), 133.84 (q-Mes), 132.73 (q-Mes), 132.64 (CH_{Py}), 132.56 (CH_{phenyl}), 130.45 (CH_{Mes}), 129.86 (CH_{Mes}), 128.91 (CH_{Mes}), 128.25 (CH_{Mes}), 1268.21 (CH_{phenyl}), 128.01 (CH_{phenyl}), 126.83 (CH_{phenyl}), 123.55 (CH_{Imidaz}), 122.93 (CH_{Imidaz}), 121.86 (CH_{Py}), 25.08 ($CH_{3\text{-}Mes}$), 23.86 ($CH_{3\text{-}Mes}$), 20.47 ($CH_{3\text{-}Mes}$), 20.38 ($CH_{3\text{-}Mes}$), 18.57 ($CH_{3\text{-}Mes}$), 16.13 ($CH_{3\text{-}Mes}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ = 0.7 ppm.

HRMS (ESI): $C_{32}H_{33}B_2N_3Cl_2$ Calculated for $[M\text{-}Cl]^-$ 514.2622, observed 514.2670

MP: 220 ºC (decomp)

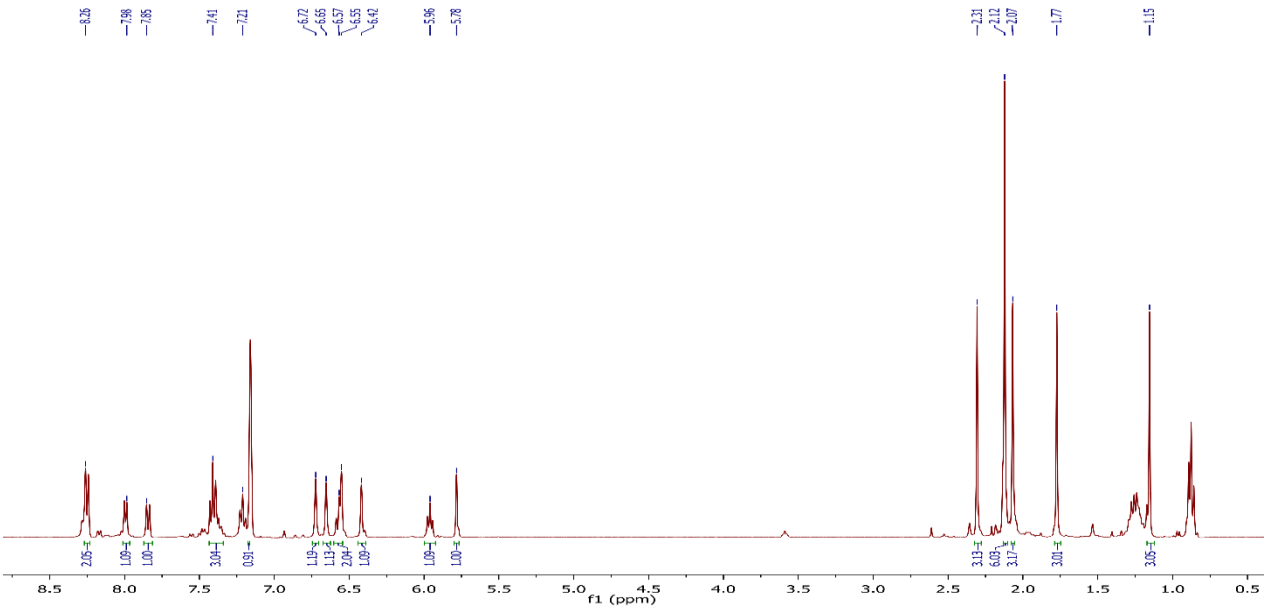


Figure S17: ^{1}H NMR spectrum of **7** in C_6D_6. Peak at 7.21 ppm corresponds to excess $PhBCl_2$. Peaks at 0.89 and 1.24 ppm correspond to residual solvent hexane.

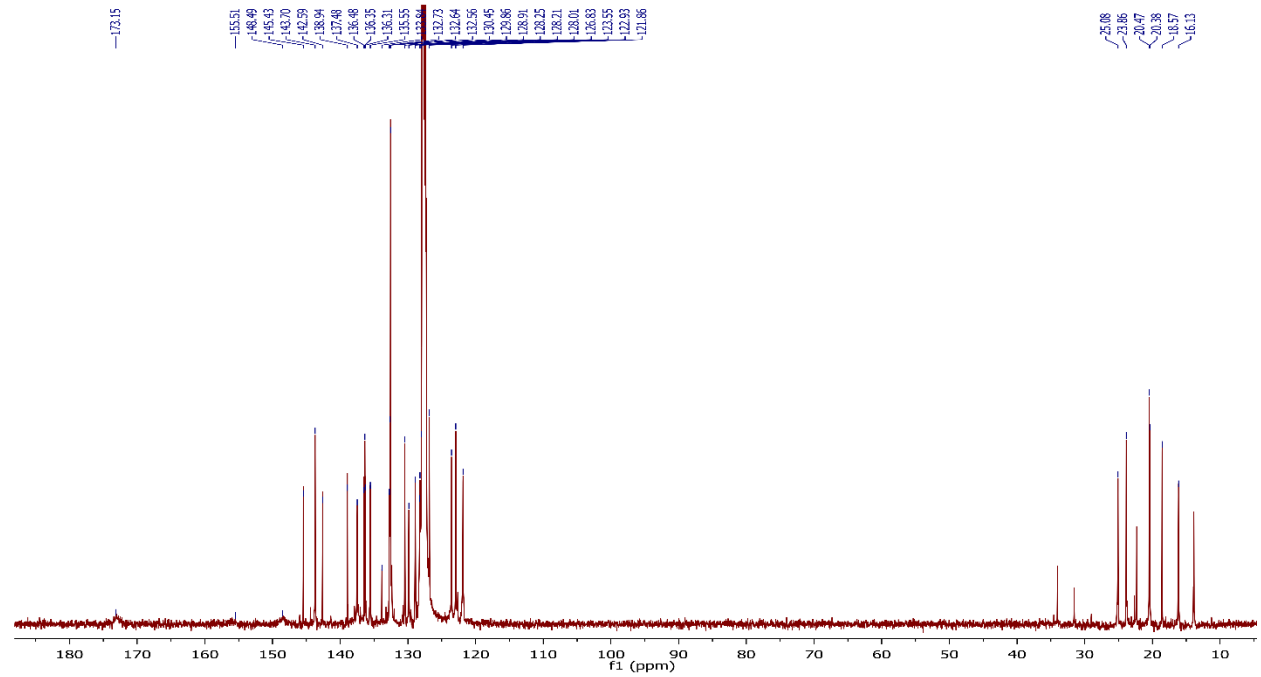


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6

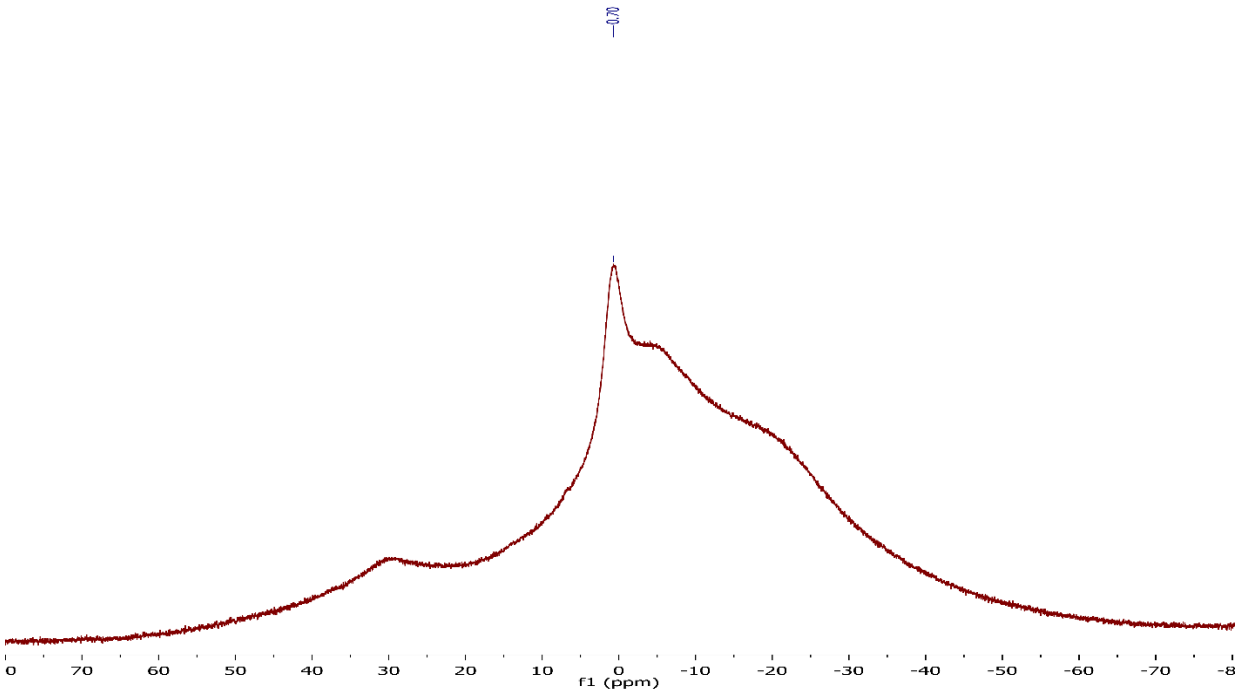
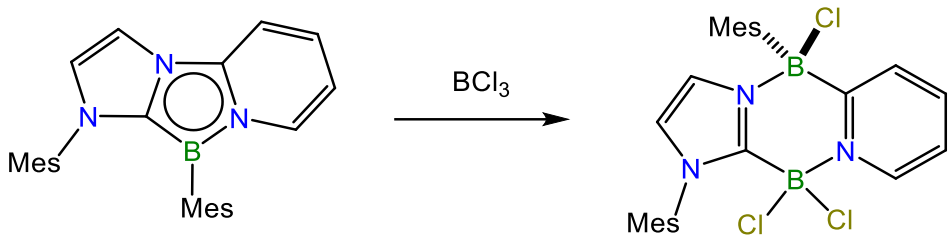


Figure S19: $^{11}B\{^{1}H\}$ NMR spectrum of **7** in C_6D_6

Synthesis of 8



3 **8**

To a 5 mL of a benzene solution of **3** (100 mg, 0.25 mmol) was added BCl_3 in hexane (30 mg, 0.28 mmol) under stirring. The reaction mixture was left undisturbed overnight resulting in the formation of colourless crystals. Crystals were collected, washed with hexane (3x 3 mL) and dried under vacuum to afford **8** as a colourless solid (82 mg, 63%). Crystals suitable for single crystal X-ray diffraction were grown from slow evaporation of a benzene solution.

^{1}H NMR (400.1 MHz, C_6D_6): δ = 8.84 (d, 1H, ^{3}J = 6.3 Hz, CH_{Py}), 7.38 (d, 1H, ^{3}J = 8.0 Hz, CH_{Py}), 6.94 (s, 2H, CH_{Mes}), 6.77 (s, 1H, CH_{Imidaz}), 6.73 (s, 2H, CH_{Mes}), 6.55 (t, 1H, ^{3}J = 7.7 Hz, CH_{Py}), 6.16 (t, 1H, ^{3}J = 6.9 Hz, CH_{Py}), 5.82 (s, 1H, CH_{Imidaz}), 2.52 (s, 6H, *o*-$CH_{3\text{-}Mes}$), 2.24 (s, 3H, *p*-$CH_{3\text{-}Mes}$), 2.13 (s, 3H, *p*-$CH_{3\text{-}Mes}$), 2.04 (s, 6H, *o*-$CH_{3\text{-}Mes}$) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 144.11, 143.29, 140.11, 139.79, 136.76, 136.66, 135.89, 133.56, 131.02 (CH_{Mes}), 130.13 (CH_{Mes}), 129.49 (CH_{Mes}), 129.03 (CH_{Mes}), 128.58, 128.14, 127.94, 124.07, 123.16, 122.24, 60.06, 38.61, 31.71, 30.23 ($CH_{3\text{-}Mes}$), 25.49 ($CH_{3\text{-}Mes}$), 21.06 ($CH_{3\text{-}Mes}$), 20.92 ($CH_{3\text{-}Mes}$), 18.73 ($CH_{3\text{-}Mes}$) ppm. Note: The signals for B-bound C atoms could not be identified due to quadrupolar broadening.

^{11}B{^{1}H } NMR (128.4 MHz, C_6D_6): δ 1.4, −0.2 ppm.

HRMS (ESI): $C_{26}H_{28}B_2N_3Cl_3$ Calculated for $[M\text{-}2Cl]^-$ 240.6425, observed 240.6459

MP: 195ºC (decomp)

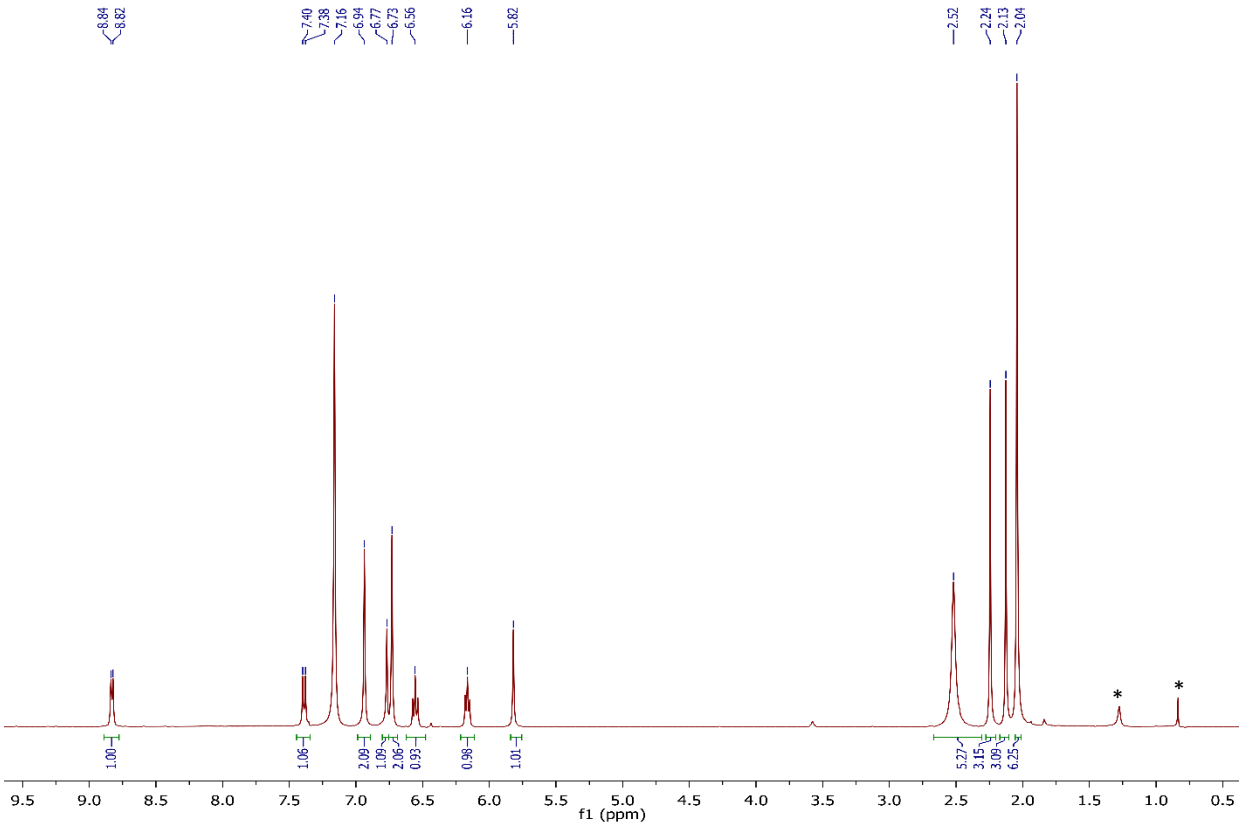


Figure S20: ^{1}H NMR spectrum of **8** in C_6D_6.

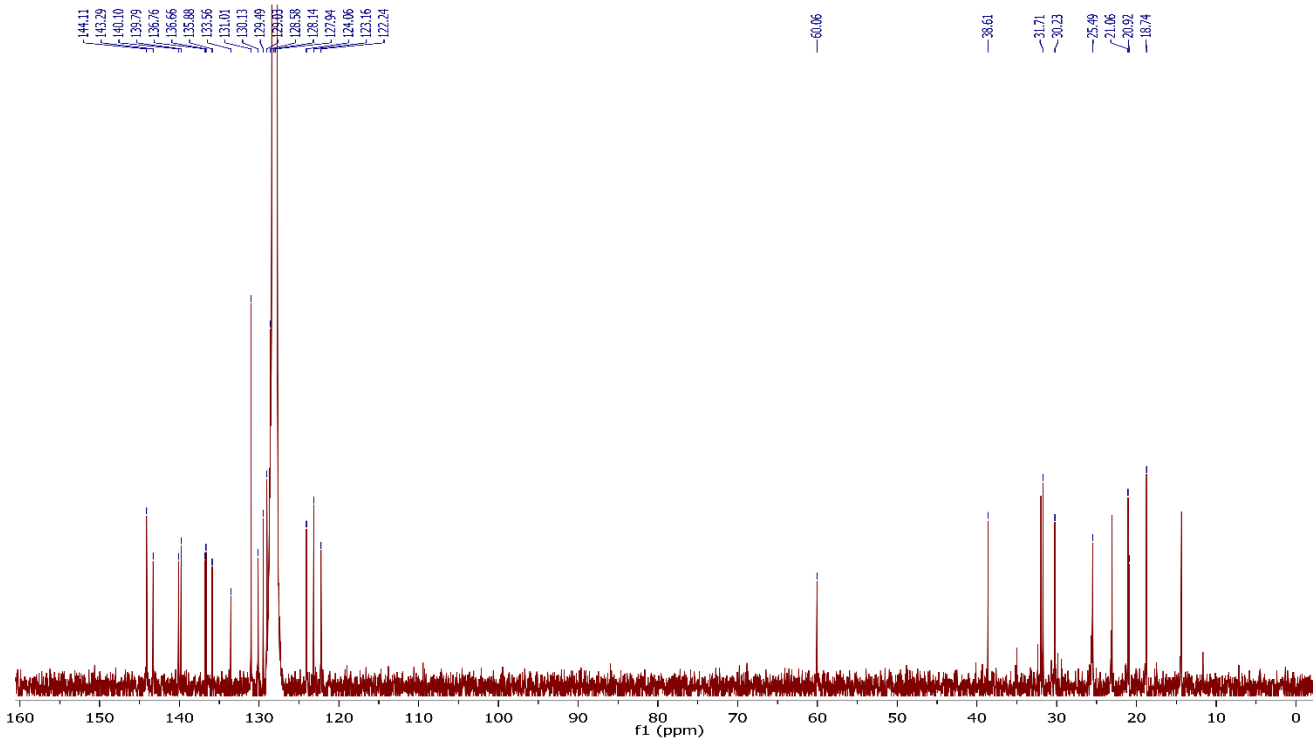


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of **8** in C_6D_6

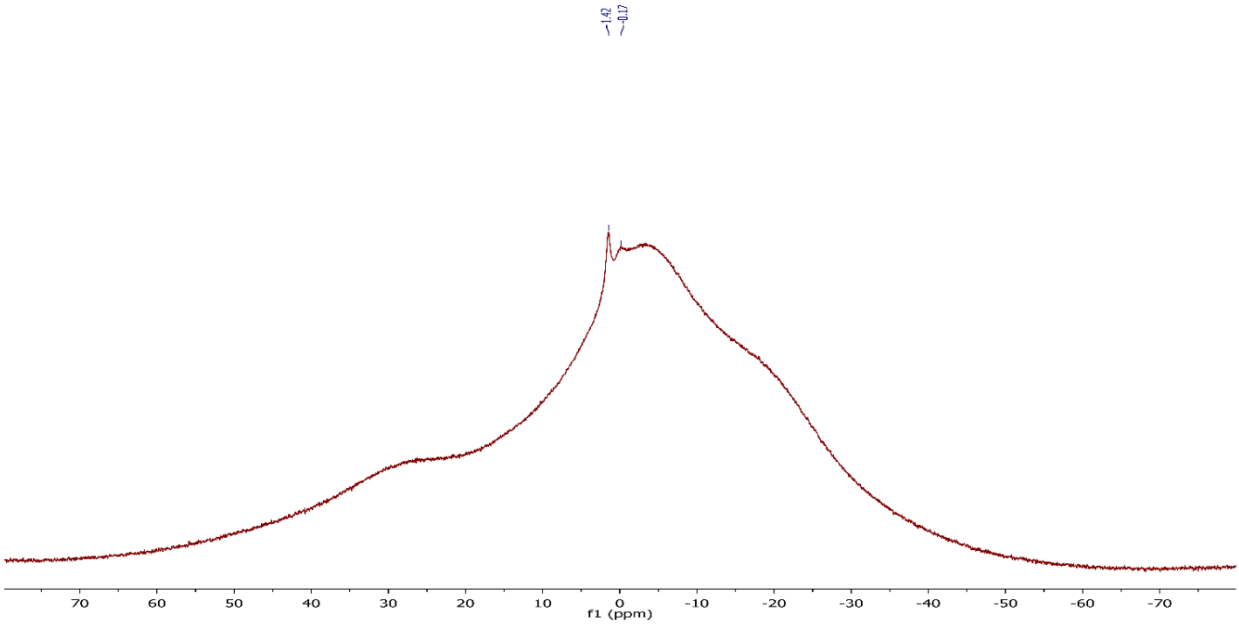
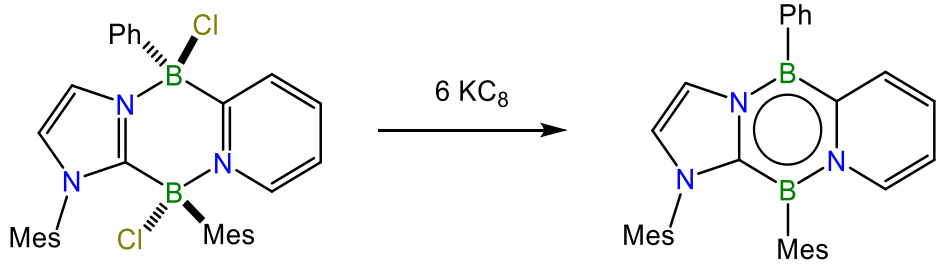


Figure S22: $^{11}B\{^{1}H\}$ NMR spectrum of **8** in C_6D_6

Synthesis of 9



7 **9**

Potassium graphite (74 mg, 0.54 mmol) was added to a solution of **7** (50 mg, 0.09 mmol) 5 mL benzene and stirred overnight at 50ºC. Once cooled, the reaction mixture was then filtered and dried under vacuum to afford **9** as a red powder (33 mg, 75%). Crystals suitable for single crystal X-ray diffraction were grown from slow evaporation of a benzene solution.

^{1}H NMR (400.1 MHz, C_6D_6): δ = 8.11 – 8.04 (m, 1H, CH_{Py}), 7.89 (d, 2H, ^{3}J = 7.2 Hz, CH_{Ph}), 7.78 – 7.73 (m, 1H, CH_{Py}), 7.69 (d, 1H, ^{3}J = 1.6 Hz, CH_{Imidaz}), 7.44 (t, 2H, ^{3}J = 7.3 Hz, CH_{Ph}), 7.34 (t, 2H, ^{3}J = 7.3 Hz, CH_{Ph}), 6.57 (s, 2H, CH_{Mes}), 6.38 (s, 2H, CH_{Mes}), 6.22 (d, 1H, ^{3}J = 1.6 Hz,

CH_{Imidaz}), 6.14 – 6.08 (m, 2H, CH_{Py}), 2.20 (s, 3H, *p*-$CH_{3\text{-}Mes}$), 2.03 (s, 3H, *p*-$CH_{3\text{-}Mes}$), 1.97 (s, 6H, *o*-$CH_{3\text{-}Mes}$), 1.66 (s, 6H, *o*-$CH_{3\text{-}Mes}$) ppm.

$^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 141.17 (*q*-Mes), 138.02 (*q*-Mes), 136.57 (*q*-Phenyl), 136.16 (*q*-Mes), 135.85 (CH_{phenyl}), 135.20 (CH_{phenyl}), 134.60 (CH_{Py}), 131.92 (CH_{Py}), 128.58 (CH_{phenyl}), 128.50 (*q*-Mes), 128.41 (CH_{phenyl}), 127.35 (CH_{Mes}), 127.02 (CH_{Mes}), 126.99 (CH_{Mes}), 126.97 (CH_{Mes}), 124.42 (*q*-Mes), 124.35 (CH_{Imidaz}), 117.22 (CH_{Py}), 117.19 (CH_{Imidaz}), 111.98 (CH_{Py}), 22.85 ($CH_{3\text{-}Mes}$), 21.33 ($CH_{3\text{-}Mes}$), 20.91 ($CH_{3\text{-}Mes}$), 18.07 ($CH_{3\text{-}Mes}$) ppm. Note: The signals for B-bound C atoms could not be identified due to quadrupolar broadening.

$^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): δ = 27.4, 24.0 ppm.

HRMS (ESI): $C_{32}H_{33}B_2N_3$ Calculated for $[M]^{+2}$ 437.2231, observed 437.2275

MP: 242 ºC (decomp)

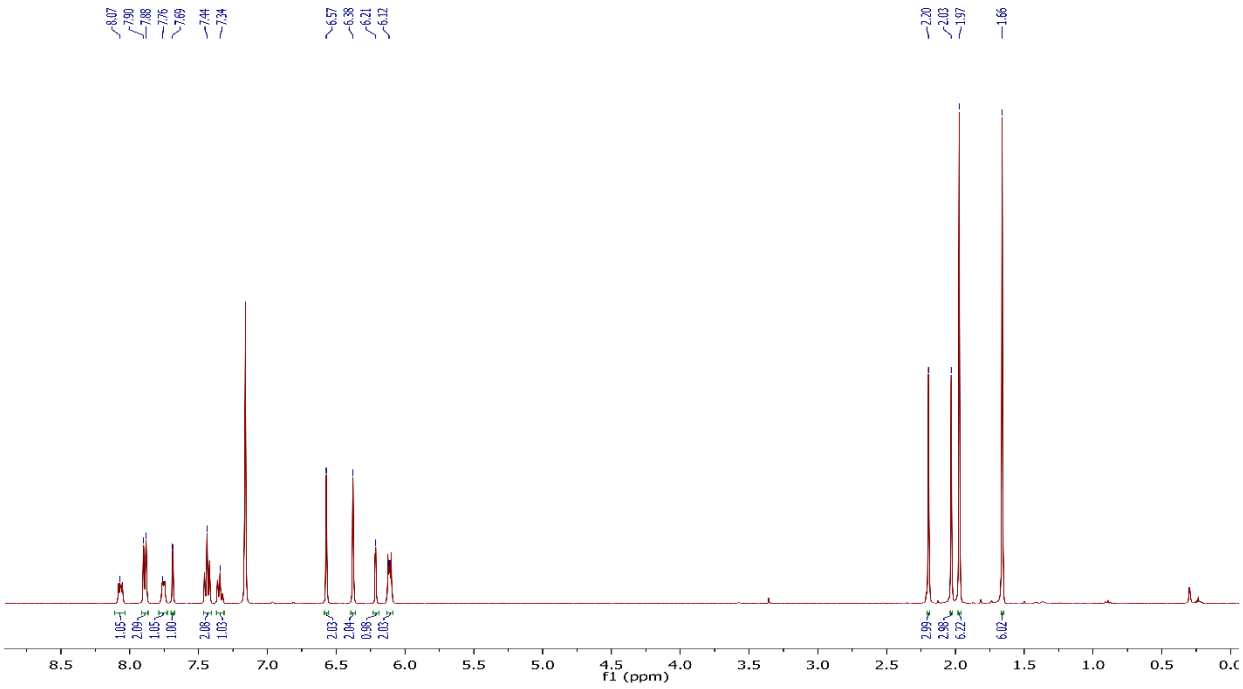


Figure S23: ^1H NMR spectrum of **9** in C_6D_6

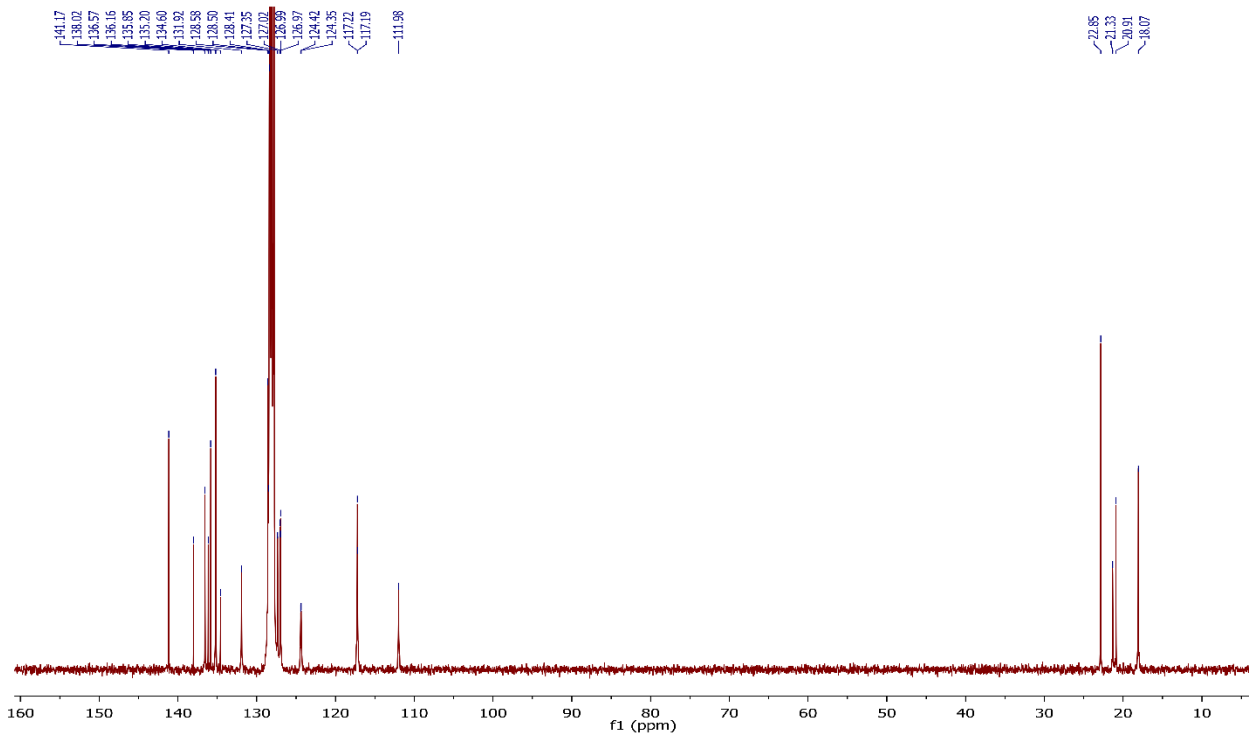


Figure S24: $^{13}C\{^{1}H\}$ NMR spectrum of **9** in C_6D_6

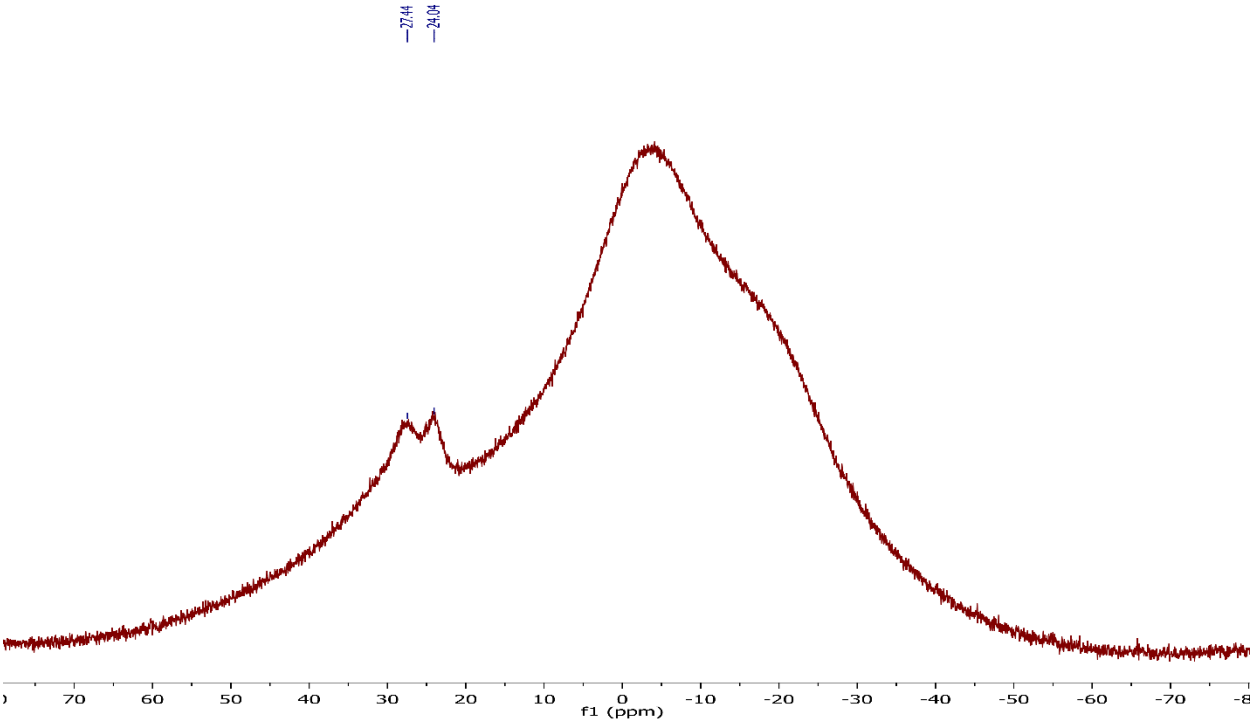
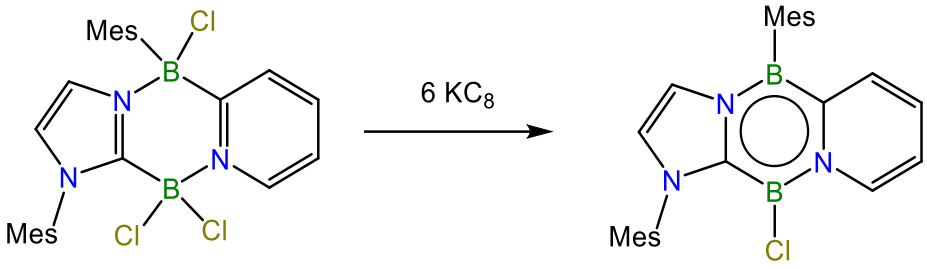


Figure S25: $^{11}B\{^{1}H\}$ NMR spectrum of **9** in C_6D_6

Synthesis of 10



8 **10**

Potassium graphite (79 mg, 0.59 mmol) was added to a solution of **8** (50 mg, 0.1 mmol) 5 mL benzene and stirred for 30 mins. The reaction mixture was then filtered and dried under vacuum to afford **10** as a red powder (23 mg, 54%).

^{1}H NMR (400.1 MHz, C_6D_6): δ = 8.48 (d, 1H, ^{3}J = 7.5 Hz, CH_{Py}), 7.6 (d, 1H, ^{3}J = 8.5 Hz, CH_{Py}), 7.07 (d, 1H, ^{3}J = 1.8 Hz, CH_{Imidaz}), 7.0 (s, 2H, CH_{Mes}), 6.7 (s, 2H, CH_{Mes}), 6.3 (ddd, 1H, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, CH_{Py}), 6.18 (d, 1H, ^{3}J = 1.8 Hz, CH_{Imidaz}), 6.07 – 6.01 (m, 1H, CH_{Py}), 2.37 (s, 3H, $CH_{3\text{-}Mes}$), 2.21 (s, 6H, $CH_{3\text{-}Mes}$), 2.12 (s, 3H, $CH_{3\text{-}Mes}$), 1.76 (s, 6H, $CH_{3\text{-}Mes}$) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 141.88 (*q*-Mes), 138.86 (*q*-Mes), 137.36 (*q*-Mes), 136.49 (*q*-Mes), 136.07 (CH_{Py}), 135.13 (*q*-Mes), 129.41 (CH_{Py}), 128.94 (CH_{Mes}), 127.91 (CH_{Mes}), 124.66 (CH_{Mes}), 124.62 (CH_{Mes}), 118.10 (CH_{Py}), 117.07(CH_{Imidaz}), 111.39 (CH_{Py}), 34.95 ($CH_{3\text{-}Mes}$), 25.61 ($CH_{3\text{-}Mes}$), 22.69 ($CH_{3\text{-}Mes}$), 21.47 ($CH_{3\text{-}Mes}$), 21.10 ($CH_{3\text{-}Mes}$), 17.30 ($CH_{3\text{-}Mes}$) ppm. Note: The signals for B-bound C atoms could not be identified due to quadrupolar broadening.

^{11}B{^{1}H } NMR (128.4 MHz, C_6D_6): δ = 27.9, 18.8 ppm.

MP: 155 ºC (decomp)

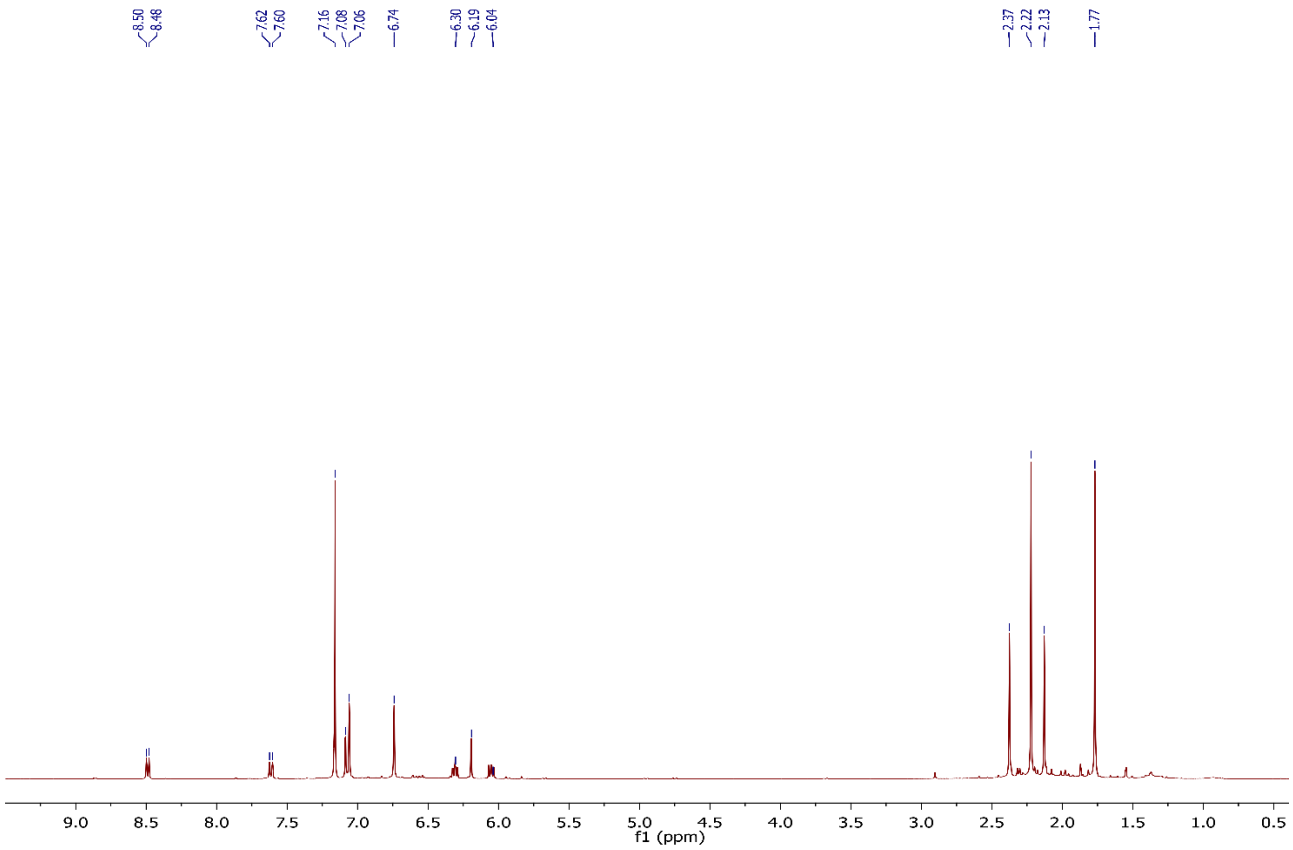


Figure S26: ^{1}H NMR spectrum of **10** in C_6D_6

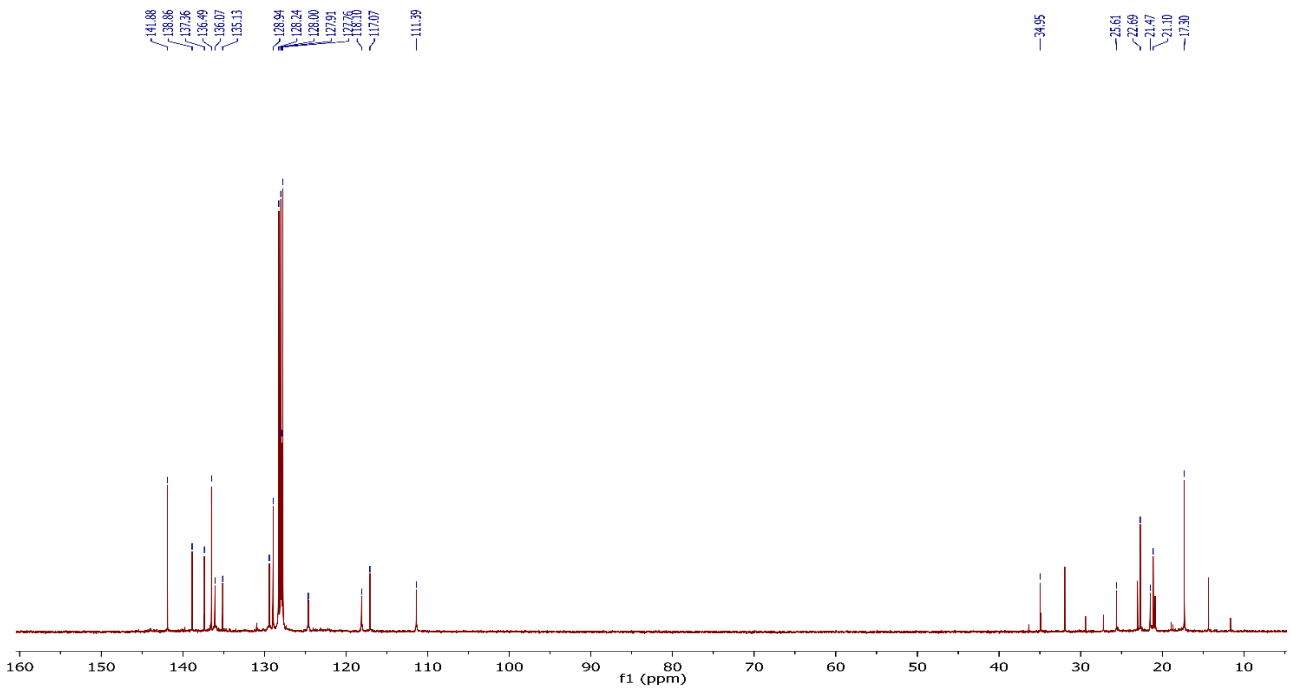


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum of **10** in C_6D_6

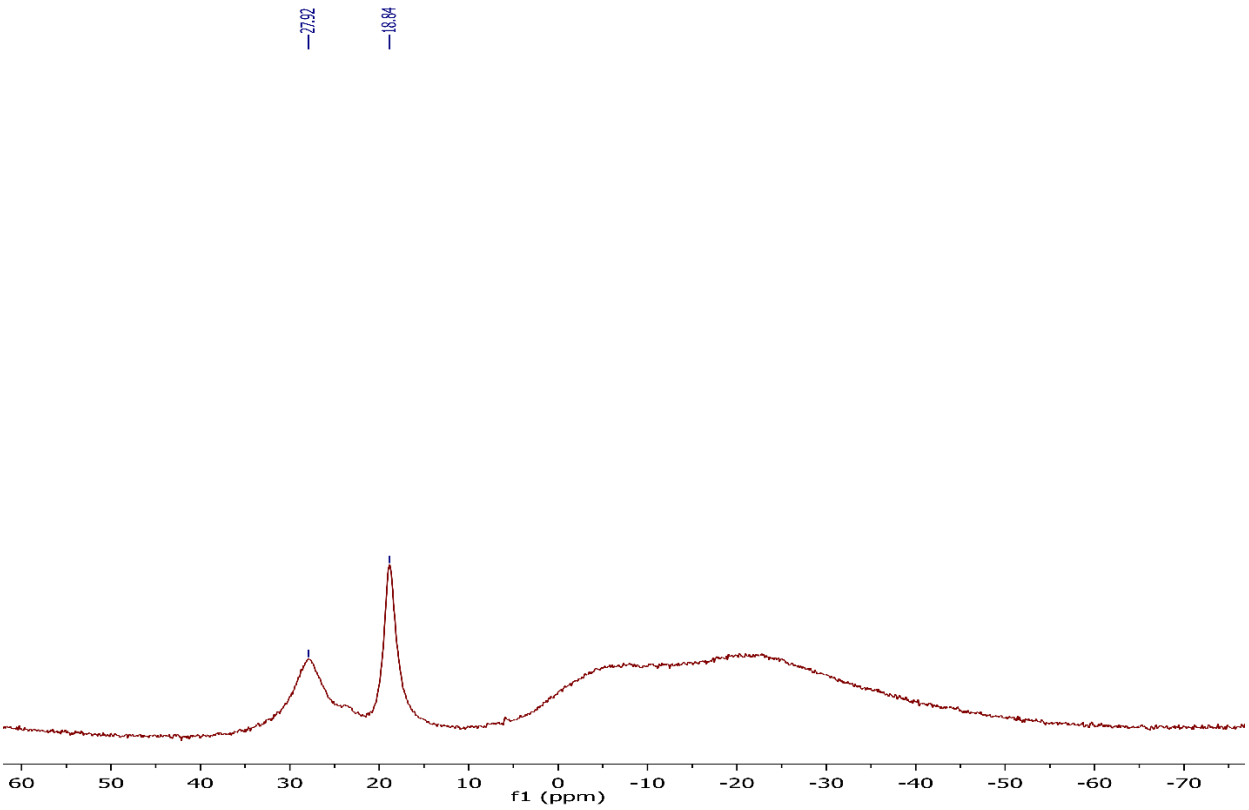


Figure S28: $^{11}B\{^{1}H\}$ NMR spectrum of **10** in C_6D_6

2.) Cyclic Voltammetry

Cyclic voltammetry experiments were performed in a nitrogen filled glovebox using Ossila Potentiostat. A standard 3-electrode cell configuration was employed using a platinum disk working electrode, platinum wire counter electrode and pseudo-reference electrode. Redox potentials were referenced by using ferrocene as an internal standard. The measurements were carried out in dry degassed THF with tetra-*n*-butylammonium tetrafluoroborate ([*n*Bu$_4$N][BF$_4$]) as the supporting electrolyte with a scan rate of 50 mV/s at room temperature.

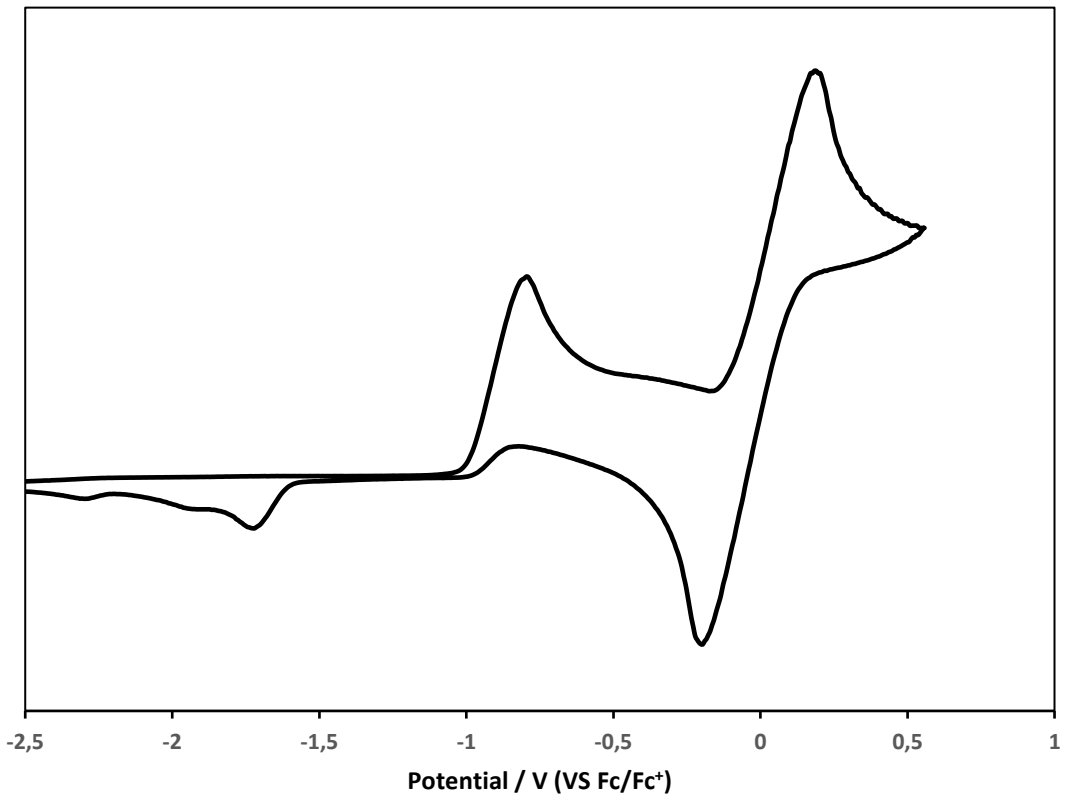


Figure S29: Cyclic voltammogram of **4** in THF/0.1 M [*n*Bu$_4$N][BF$_4$] measured at 50 mV/s. Ferrocene used as the internal standard.

3.) UV-Visible and Fluorescence spectrum

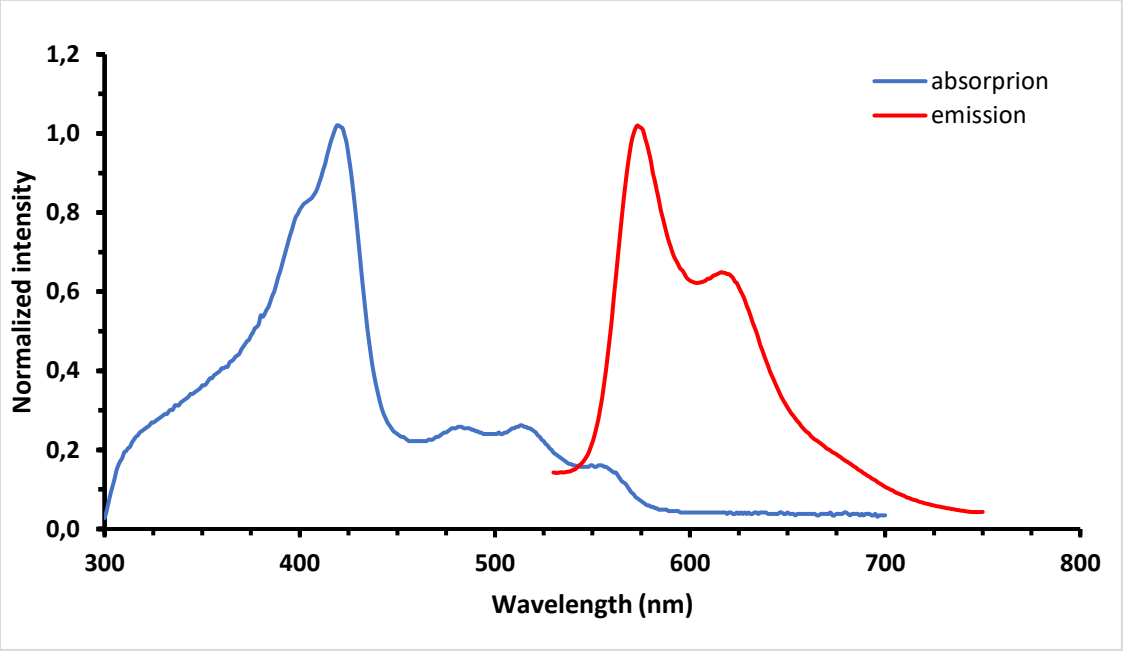


Figure S30: UV-Vis absorption and fluorescent emission spectrum of **3** in toluene. (λ_{ex}= 420 nm)

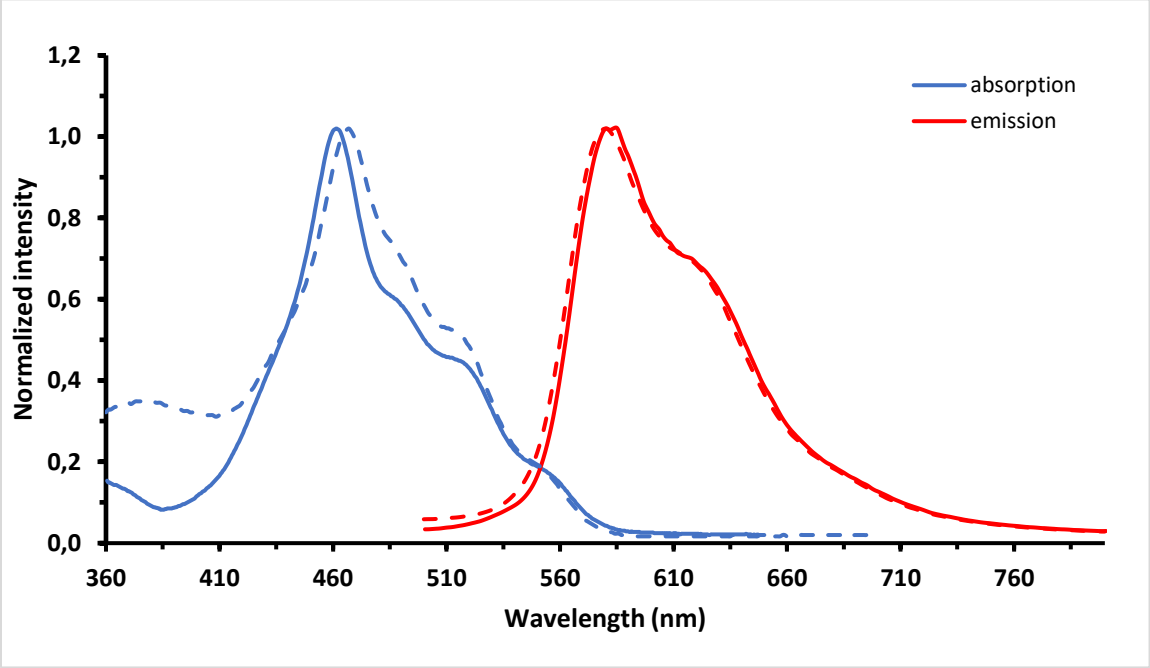
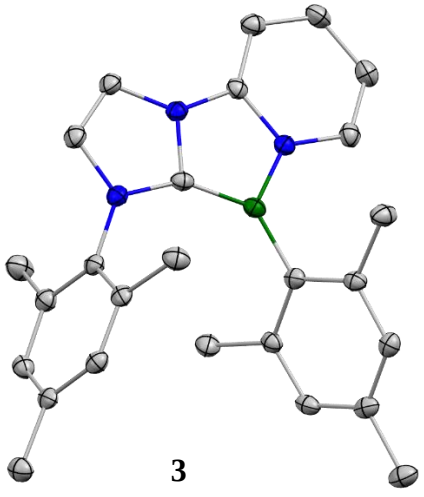


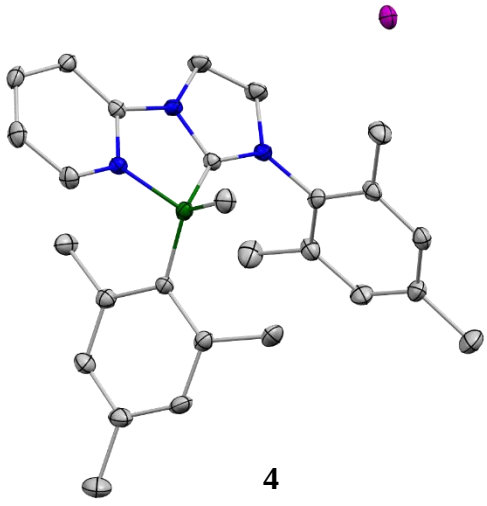
Figure S31: UV-Vis absorption and fluorescent emission spectrum of **9** (dotted line) and **10** (solid line) in benzene. (λ_{ex}= 462 nm for **9**, λ_{ex}= 468 nm for **10**)

4.) Crystallographic Details

Crystals were coated in Paratone-N oil in a glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on Bruker Apex DUO diffractometer except for the structures **7** and **9** which were collected on Bruker D8 QUEST ECO diffractometer using a graphite monochromator with Mo K α (λ = 0.71073 Å) radiation. The data were collected at 100(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method SADABS. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques. In the final cycles of each refinement, all nonhydrogen atoms were assigned anisotropic temperature factors in the absence of positional disordering. C-H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Specific details can be found in the cif files.



3



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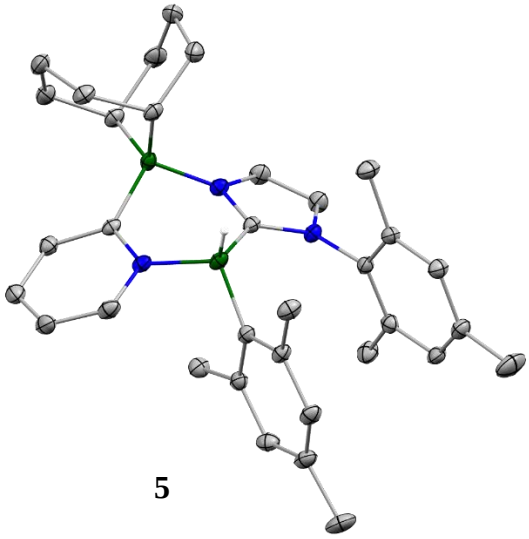

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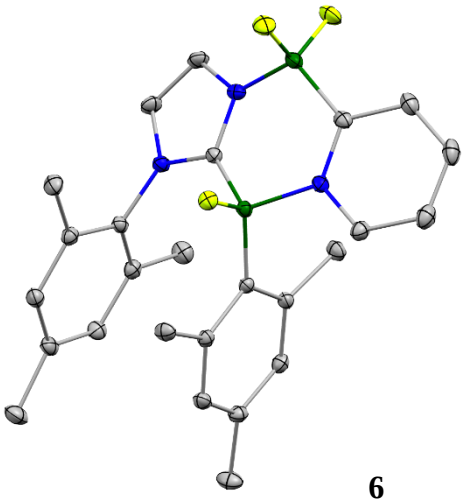

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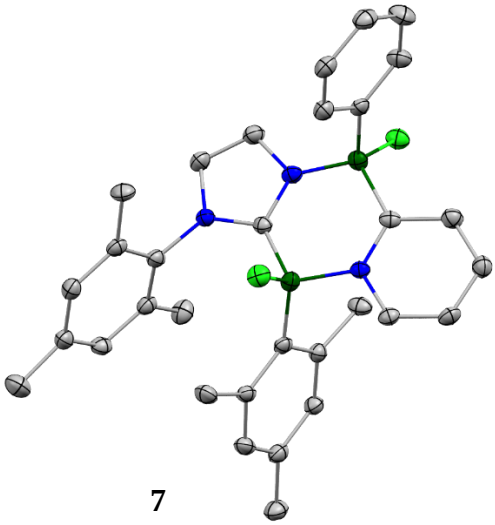

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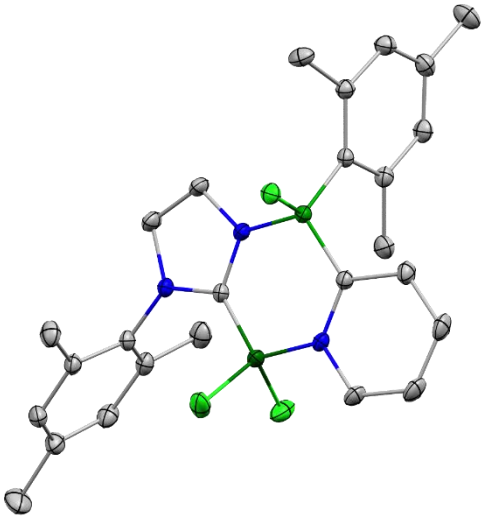
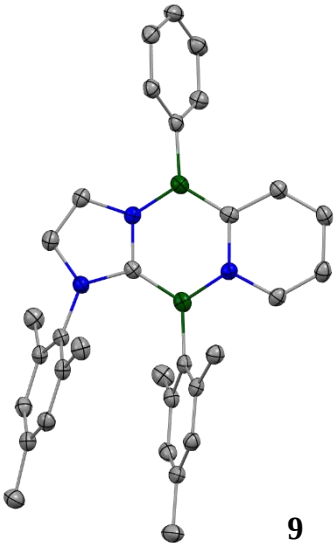


8



9

Figure S32: Molecular structures of compounds **3-9**. Thermal ellipsoids are drawn at 50% probability. Carbon-bound hydrogen atoms are omitted for clarity. Element colors: carbon; grey, nitrogen; blue, boron; forest green, chlorine, light green, fluorine; yellow-green, iodine; purple, hydrogen; white.

Table S1: Crystal data and structure refinement

	3	**4**	**5**
CCDC#	2331652	2331655	2331653
Formula	$C_{26}H_{28}N_3B$	$C_{27}H_{31}N_3BI$	$C_{34}H_{43}N_3B_2$
Wt	393.32	535.26	515.33
Crystal system	Monoclinic	Monoclinic	monoclinic
Space group	P 2_1/c	P 2_1/c	P 2_1/n
a(Å)	8.4111(6)	8.0398(6)	11.6929(6)
b(Å)	15.3474(11)	28.378(2)	17.5821(9)
c(Å)	17.0335(13)	11.9315(9)	14.6284(8)
α(deg)	90	90	90
β(deg)	96.326(2)	108.797(2)	104.319(2)
γ(deg)	90	90	90
V(Å3)	2185.4(3)	2577.1(3)	2914.0(3)
Z	4	4	4
d(calc) gcm^{-1}	1.195	1.380	1.175
R(int)	0.0523	0.0646	0.0676
Total data	36951	82821	44958
μ, mm^{-1}	0.070	1.261	0.067
>2σ(F_O^2)	5213	7912	8946
Parameters	277	296	361
R1 (>2σ)	0.0523	0.0350	0.0550
R_w	0.1208	0.0666	0.1201
GOOF	1.019	1.072	1.009
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.31, -0.23	0.85, -1.34	0.36, -0.26

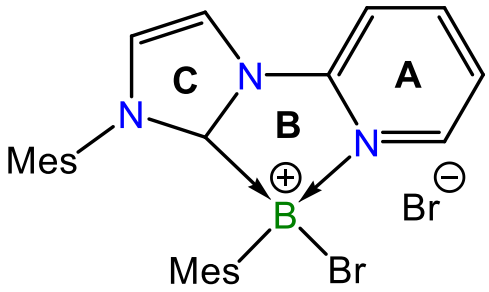
Table S2: Crystal data and structure refinement

	6	**7**	**8**	**9**
CCDC#	2331654	2331660	2331659	2331656
Formula	$C_{26}H_{28}N_3F_3B_2$	$C_{32}H_{33}B_2Cl_2N_3$	$C_{26}H_{28}B_2Cl_3N_3$	$C_{32}H_{33}B_2N_3$
Wt	461.13	552.13	510.48	481.23
Crystal system	orthorhombic	triclinic	monoclinic	triclinic
Space group	P c a 21	P -1	P 2_1/c	P -1
a(Å)	13.4867(18)	8.2484(7)	15.6649(12)	8.9434(6)
b(Å)	12.7379(17)	8.6731(8)	11.3864(9)	12.0020(8)
c(Å)	13.3863(18)	22.3744(19)	15.8645(12)	13.5298(9)
α(deg)	90	81.768(2)	90	105.413(2)
β(deg)	90	85.754(2)	115.787(2)	90.951(2)
γ(deg)	90	62.036(2)	90	109.556(2)
V(Å3)	2299.7(5)	1399.1(2)	2547.9(3)	1310.34(15)
Z	4	2	4	2
d(calc) gcm^{-1}	1.332	1.311	1.331	1.220
R(int)	0.0320	0.0548	0.0284	0.0503
Total data	43912	27539	50528	31471
μ, mm^{-1}	0.094	0.260	0.380	0.070
>2σ(F_O^2)	6817	5714	7706	5543
Parameters	313	358	313	341
R1 (>2σ)	0.0335	0.0667	0.0508	0.0550
R_w	0.0823	0.1542	0.1294	0.1285
GOOF	1.020	1.114	1.057	1.061
$\Delta_{\rho max}$, $\Delta_{\rho min}$ (eÅ^{-3})	0.31, -0.21	0.73, -0.70	1.40, -0.49	0.28, -0.27

5.) Density Functional Theory Calculations

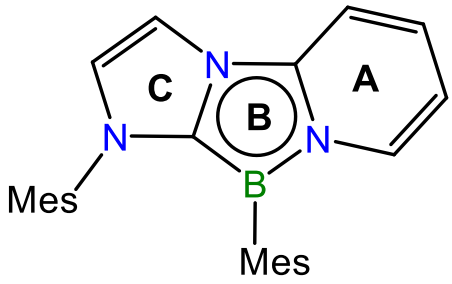
All calculations were performed with Gaussian 16, Revision C.01[7]. Geometry optimization were carried out at PBE0-D3(BJ)[8,9]/6-311+G(d,p)[10,11] level of theory. Solvent effect in benzene was considered by the SMD solvation model.[12] Optimized geometries were characterized as either equilibrium structure (no imaginary frequencies) or transition state (one imaginary frequency) through vibrational frequency calculation at the same level of theory. Transition states were confirmed by intrinsic reaction coordinate (IRC) calculations to connect two corresponding intermediates. Mayer bond order analysis[13] was performed using Multiwfn 3.8[14] at the level of optimization. NICS[15] calculations were performed using the Gauge-Independent Atomic Orbital (GIAO) method at the level of optimization. Anisotropy of Current (Induced) Density (ACID)[16] calculation was performed by using the reported method at the level of optimization. TD-DFT calculation for **9** was performed at PBE0-D3(BJ)/6-311+G(d,p)|SMD(benzene) level of theory. For the reaction mechanism study, the mesityl groups were simplified to phenyl groups. Chemcraft[17] was used for visualizing optimized structures and rendering of molecular orbitals.

Table S3: NICS values for **2** and **3** calculated at PBE0-D3(BJ)/6-311+G(d,p)|SMD(benzene).



2

	NICS(0)	NICS(1)	$NICS_{zz}(1)$
A	-6.9	-8.7	-22.7
B	0.9	-0.6	0.7
C	-10.0	-7.5	-20.2



3

	NICS(0)	NICS(1)	$NICS_{zz}(1)$
A	-4.8	-6.0	-15.6
B	-16.3	-12.3	-35.0
C	-10.4	-6.4	-19.8

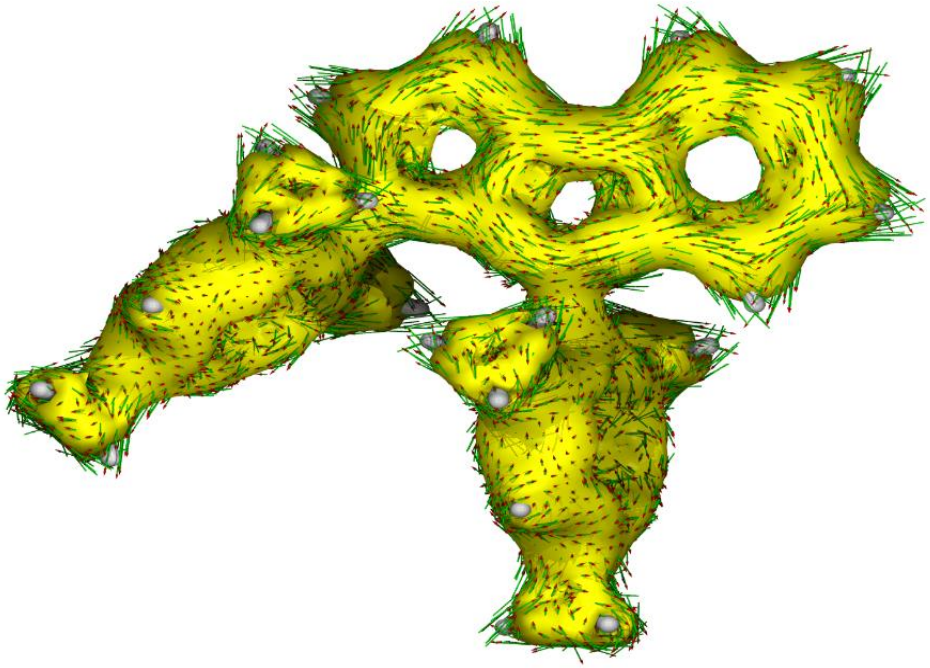
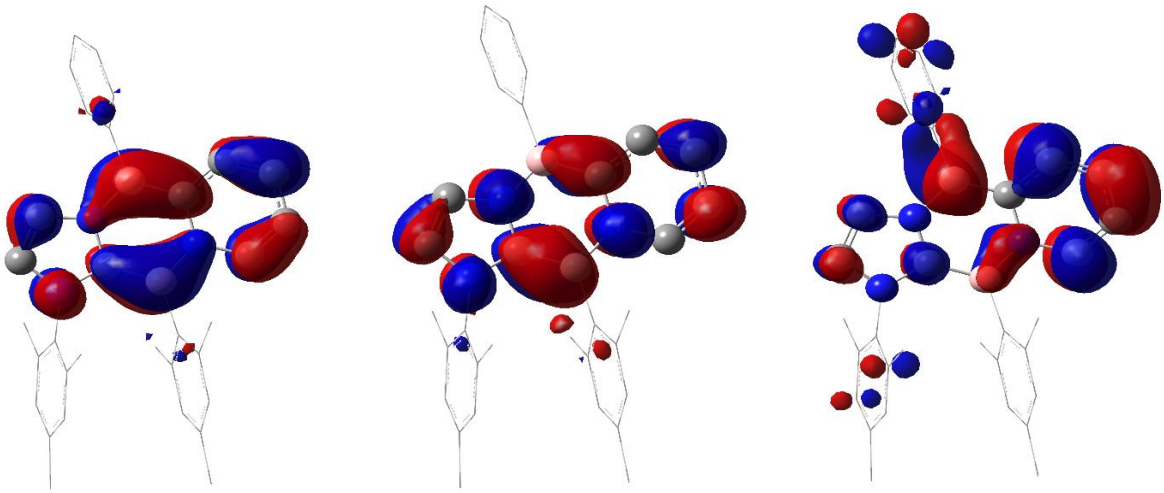
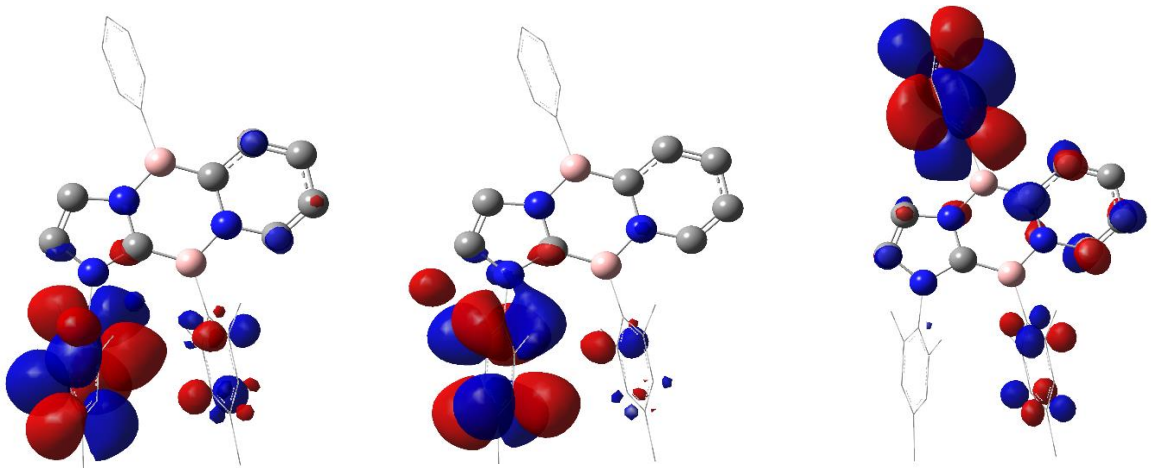


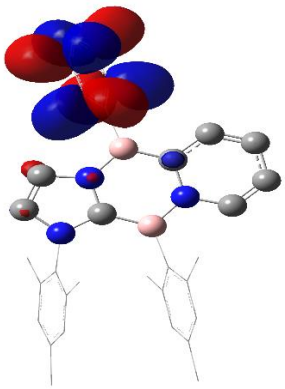
Figure S33: ACID isosurface of **3** plotted at an isosurface value of 0.032. Current density vectors are plotted onto the ACID isosurface indicating diatropic ring current. The magnetic field vector is orthogonal with respect to the ring plane and points toward the viewer. Current densities were calculated at PBE0-D3(BJ)/6-311+G(d,p)|SMD(benzene).



HOMO **LUMO** **LUMO +1**



LUMO +2 **LUMO +3** **LUMO +4**



LUMO +5

Figure S34: Plots of molecular orbitals of **9**. Hydrogen atoms are omitted for clarity.

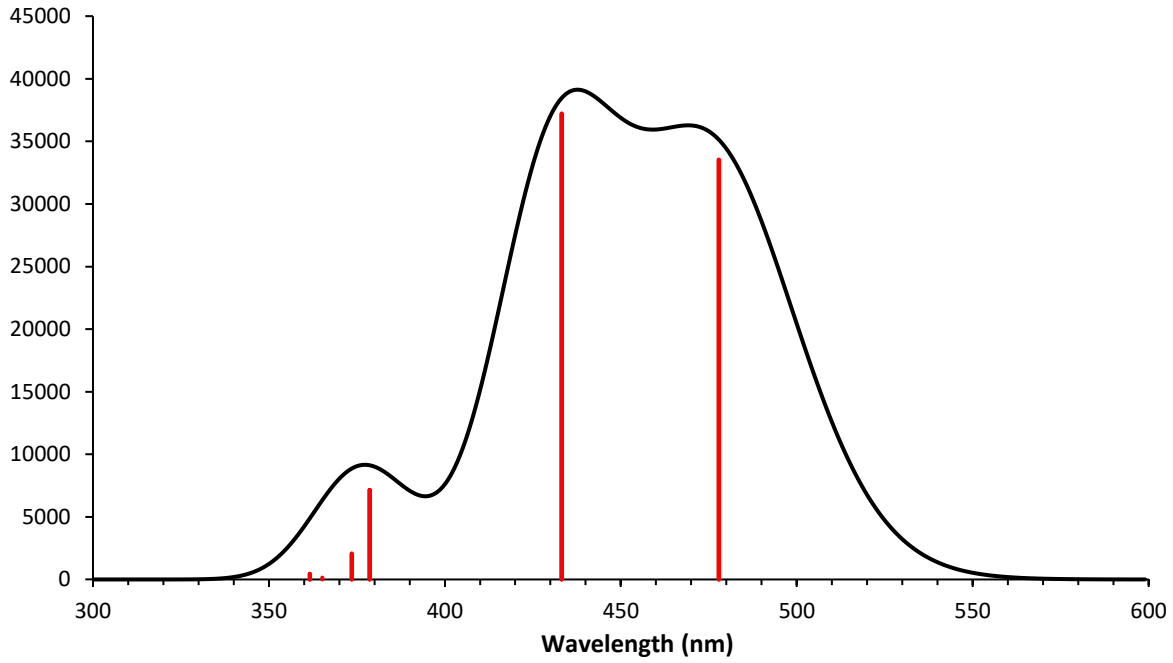


Figure S35: UV-Vis spectrum calculated at PBE0-D3(BJ)/6-311+G(d,p)|SMD(benzene).

Table S4: TD-DFT excitation energies calculated for **9**.

Energy (eV)	**Wavelength (nm)**	**Oscillator strength (f)**	**Contribution**
2.6	478	0.34	HOMO → LUMO (70.8%) HOMO → LUMO+1 (28.0%)
2.9	433	0.37	HOMO → LUMO (28.2%) HOMO → LUMO+1 (66.4%) HOMO → LUMO+4 (2.5%)
3.3	378	0.07	HOMO → LUMO+1 (3.7%) HOMO → LUMO+2 (51.7%) HOMO → LUMO+4 (39.5%) HOMO → LUMO+5 (2.8%)
3.3	374	0.02	HOMO → LUMO+2 (46.0%) HOMO → LUMO+4 (50.0%) HOMO → LUMO+5 (2.2%)

Table S5: Cartesian coordinates of optimized structures (PBE0-D3(BJ)/6-311+G(d,p)| SMD(benzene))

Compound 2

Br	-6.314225000	0.324337000	2.948407000
N	0.000000000	0.000000000	-1.000000000
C	1.146262000	0.014941000	-1.678461000
H	1.054077000	0.023860000	-2.755888000
B	-1.498654000	0.056978000	-1.628748000
N	-1.303979000	-0.009321000	0.802693000
C	2.351861000	0.011348000	-1.016531000
H	3.273298000	0.016878000	-1.579079000
N	-3.399835000	-0.024420000	0.373511000
C	2.354545000	0.002896000	0.374108000
H	3.292497000	0.001591000	0.913402000
C	1.163520000	0.000000000	1.077473000
H	1.131559000	-0.000006000	2.156876000
C	0.000000000	0.000000000	0.338896000
C	-2.212352000	0.012254000	-0.194744000
C	-1.944800000	-0.055261000	2.033366000
H	-1.422064000	-0.072490000	2.971792000
C	-3.266552000	-0.062769000	1.759569000
H	-4.174491000	-0.051929000	2.387567000
Br	-1.518671000	1.994727000	-2.289373000
C	-1.826278000	-1.137838000	-2.656488000
C	-2.755194000	-0.997801000	-3.711580000
C	-2.956600000	-2.046689000	-4.602569000
H	-3.672787000	-1.908855000	-5.405424000
C	-2.303162000	-3.260648000	-4.490811000
C	-1.476680000	-3.432565000	-3.394531000
H	-1.017664000	-4.401334000	-3.228015000
C	-1.249049000	-2.416617000	-2.473875000
C	-4.634257000	-0.003190000	-0.372580000
C	-5.120907000	-1.203928000	-0.871564000
C	-6.270598000	-1.147488000	-1.644075000
H	-6.674187000	-2.068980000	-2.047659000
C	-6.924052000	0.051895000	-1.892986000

C	-6.412424000	1.218732000	-1.342204000
H	-6.931070000	2.156463000	-1.503762000
C	-5.266008000	1.219264000	-0.562772000
C	-3.626483000	0.215149000	-3.924535000
H	-4.494829000	-0.065856000	-4.519667000
H	-3.098466000	1.007980000	-4.454206000
H	-3.996768000	0.631215000	-2.989885000
C	-2.506979000	-4.354322000	-5.498945000
H	-3.520249000	-4.337662000	-5.901595000
H	-2.327105000	-5.337062000	-5.062075000
H	-1.818186000	-4.234730000	-6.339038000
C	-0.453404000	-2.823858000	-1.250821000
H	-0.904233000	-2.455932000	-0.327486000
H	0.588370000	-2.498575000	-1.276875000
H	-0.440032000	-3.909865000	-1.172893000
C	-4.457672000	-2.512433000	-0.556503000
H	-4.397108000	-2.660021000	0.524002000
H	-3.449361000	-2.563701000	-0.971495000
H	-5.028810000	-3.338385000	-0.976513000
C	-8.193931000	0.080680000	-2.694734000
H	-9.059273000	0.018981000	-2.030671000
H	-8.246535000	-0.759059000	-3.388193000
H	-8.281644000	1.005680000	-3.265505000
C	-4.773720000	2.466091000	0.104278000
H	-5.283778000	3.341629000	-0.293715000
H	-3.699713000	2.609129000	-0.031565000
H	-4.993435000	2.395060000	1.174749000

Compound 3

7	-2.706971000	0.019379000	-0.211470000
6	-3.112965000	-1.306615000	-0.027346000
5	-1.252314000	0.181779000	-0.127962000
7	-1.988555000	-2.028834000	0.167171000
6	-4.446542000	-1.694164000	-0.067154000
1	-4.701790000	-2.737281000	0.083622000
7	0.207364000	-2.100994000	0.334918000
6	-5.410442000	-0.738119000	-0.299250000

1	-6.458414000	-1.009284000	-0.334468000
6	-5.004674000	0.606992000	-0.501536000
1	-5.738426000	1.379315000	-0.700834000
6	-3.689113000	0.952506000	-0.459079000
1	-3.334712000	1.961333000	-0.628405000
6	-0.847707000	-1.231854000	0.112297000
6	-0.288660000	-3.374846000	0.508721000
1	0.367667000	-4.208224000	0.703110000
6	-1.640614000	-3.353819000	0.412459000
1	-2.362412000	-4.147091000	0.506753000
6	-0.498507000	1.549911000	-0.209708000
6	0.423388000	1.820487000	-1.244104000
6	1.097277000	3.037405000	-1.280817000
1	1.800712000	3.228074000	-2.088963000
6	0.893777000	4.019074000	-0.311451000
6	-0.012042000	3.749533000	0.707838000
1	-0.179970000	4.496980000	1.480403000
6	-0.706362000	2.539579000	0.771563000
6	1.579911000	-1.734171000	0.317569000
6	2.083300000	-0.918333000	1.338122000
6	3.423085000	-0.545032000	1.277785000
1	3.822036000	0.091077000	2.063626000
6	4.260437000	-0.965548000	0.247144000
6	3.727780000	-1.786416000	-0.743704000
1	4.363503000	-2.118619000	-1.560404000
6	2.390302000	-2.176180000	-0.734872000
6	0.704601000	0.799580000	-2.309601000
1	-0.208426000	0.280817000	-2.615611000
1	1.401766000	0.037903000	-1.944365000
1	1.154997000	1.263006000	-3.191846000
6	1.633808000	5.323172000	-0.375097000
1	2.717501000	5.165341000	-0.383752000
1	1.393837000	5.959689000	0.480220000
1	1.381924000	5.877561000	-1.285811000
6	-1.664754000	2.315856000	1.908081000
1	-2.687833000	2.602435000	1.636354000
1	-1.384712000	2.909634000	2.782568000

1	-1.699982000	1.262005000	2.199728000
6	1.212074000	-0.449501000	2.461437000
1	0.562880000	0.367507000	2.131826000
1	1.820168000	-0.084766000	3.291934000
1	0.563918000	-1.250051000	2.828264000
6	5.689615000	-0.514080000	0.188388000
1	6.306705000	-1.211152000	-0.383927000
1	6.119494000	-0.418172000	1.189034000
1	5.765933000	0.467008000	-0.294346000
6	1.837901000	-3.019930000	-1.845091000
1	1.734011000	-4.068925000	-1.546926000
1	2.500757000	-2.990343000	-2.712493000
1	0.848333000	-2.674475000	-2.155374000

Compound 9

7	-1.165772000	1.774993000	-0.299470000
7	-1.876492000	-0.940614000	0.160935000
7	0.161914000	-1.754137000	0.278535000
6	-2.535385000	1.424845000	-0.251749000
6	-0.552849000	-0.590627000	0.100002000
6	1.415455000	1.288753000	-0.035667000
6	1.575833000	-1.890587000	0.134991000
6	-4.444745000	-0.494941000	0.082812000
6	-0.840121000	3.112825000	-0.527753000
1	0.218687000	3.318356000	-0.571323000
6	-4.941769000	-1.090716000	1.246467000
1	-4.292344000	-1.195594000	2.109656000
6	2.412061000	-1.601937000	1.208328000
6	1.919249000	1.795195000	1.175978000
6	3.274030000	2.058951000	1.310859000
1	3.650368000	2.429502000	2.259590000
6	-1.965086000	-2.310862000	0.371141000
1	-2.913865000	-2.809078000	0.448325000
6	-1.762738000	4.077323000	-0.686165000
1	-1.427971000	5.091017000	-0.860402000
6	2.295815000	1.152101000	-1.113714000
6	-3.148894000	3.760682000	-0.623386000

1	-3.898449000	4.531336000	-0.737748000
6	-3.489876000	2.467117000	-0.412242000
1	-4.531783000	2.181347000	-0.349810000
6	4.163830000	1.851001000	0.263083000
6	-5.325343000	-0.372731000	-0.995245000
1	-4.974743000	0.083360000	-1.914545000
6	0.990985000	2.085252000	2.326272000
1	1.543079000	2.250541000	3.251977000
1	0.280169000	1.273929000	2.490145000
1	0.399137000	2.982642000	2.125084000
6	3.454543000	-2.318654000	-1.269618000
1	3.860691000	-2.597871000	-2.235878000
6	-0.711314000	-2.796480000	0.438408000
1	-0.358171000	-3.802815000	0.581823000
6	3.782945000	-1.641524000	0.992940000
1	4.445591000	-1.380659000	1.810971000
6	3.650863000	1.422522000	-0.948858000
1	4.322157000	1.282326000	-1.790859000
6	2.078645000	-2.281663000	-1.106094000
6	-6.636106000	-0.820806000	-0.918787000
1	-7.294133000	-0.713168000	-1.772619000
6	1.803589000	0.752796000	-2.478846000
1	2.480464000	0.040187000	-2.952811000
1	1.738650000	1.629373000	-3.128911000
1	0.809888000	0.307735000	-2.436766000
6	-6.250324000	-1.540885000	1.332895000
1	-6.607907000	-1.991177000	2.251090000
6	4.320979000	-1.973038000	-0.240166000
6	1.159612000	-2.648281000	-2.236890000
1	1.696457000	-2.646405000	-3.184638000
1	0.321584000	-1.955739000	-2.317242000
1	0.739156000	-3.646350000	-2.092179000
6	1.878349000	-1.266366000	2.570144000
1	2.448415000	-0.448665000	3.010604000
1	1.964316000	-2.131370000	3.232346000
1	0.831564000	-0.973614000	2.539953000
6	-7.103276000	-1.407435000	0.247196000

1	-8.126273000	-1.757090000	0.310755000
6	5.639992000	2.058028000	0.454707000
1	6.087961000	1.193227000	0.952612000
1	5.844151000	2.932160000	1.075012000
1	6.150770000	2.190517000	-0.499790000
6	5.802548000	-1.903110000	-0.473793000
1	6.361288000	-2.107394000	0.440038000
1	6.078636000	-0.900639000	-0.812523000
1	6.122572000	-2.611459000	-1.238495000
5	-0.098490000	0.833135000	-0.112651000
5	-2.956839000	0.016736000	-0.006741000

3_ph

7	2.268162000	0.057053000	0.022629000
6	2.514336000	-1.316510000	-0.013219000
5	0.827480000	0.366367000	0.038659000
7	1.312078000	-1.928386000	-0.029088000
6	3.800401000	-1.855266000	-0.013822000
1	3.928702000	-2.932540000	-0.046847000
7	-0.893875000	-1.805415000	-0.015309000
6	4.878422000	-0.998225000	0.030376000
1	5.891393000	-1.384648000	0.026912000
6	4.637398000	0.401413000	0.090832000
1	5.463691000	1.101819000	0.146003000
6	3.364098000	0.890207000	0.089936000
1	3.138374000	1.947772000	0.152633000
6	0.255688000	-1.015592000	-0.002157000
6	-0.518942000	-3.136026000	-0.041571000
1	-1.251542000	-3.925966000	-0.093854000
6	0.832311000	-3.231497000	-0.050389000
1	1.471627000	-4.098382000	-0.086221000
6	0.249982000	1.817456000	0.099581000
6	-0.763418000	2.165474000	1.011429000
6	-1.285452000	3.455979000	1.069525000
1	-2.067712000	3.690082000	1.787248000
6	-0.803674000	4.446223000	0.214951000
6	0.198839000	4.130080000	-0.701141000

1	0.575561000	4.890991000	-1.380161000
6	0.712471000	2.836048000	-0.755420000
6	-2.220540000	-1.349189000	-0.087366000
6	-2.515579000	-0.142389000	-0.728546000
6	-3.835075000	0.291826000	-0.807514000
1	-4.051209000	1.232380000	-1.306068000
6	-4.869637000	-0.467003000	-0.264093000
6	-4.570146000	-1.668960000	0.376401000
1	-5.363736000	-2.264151000	0.819300000
6	-3.254374000	-2.107307000	0.476792000
1	1.475544000	2.606319000	-1.496841000
1	-1.206899000	5.454348000	0.260534000
1	-1.146736000	1.408780000	1.691636000
1	-1.715651000	0.444575000	-1.165695000
1	-5.897307000	-0.123236000	-0.331743000
1	-3.028702000	-3.023205000	1.014737000

Int 1

N	-1.597532000	0.840097000	-0.420404000
C	-2.317819000	-0.432709000	-0.335074000
B	-0.190944000	0.719016000	-0.286013000
N	-1.231176000	-1.384300000	-0.452452000
C	-3.415938000	-0.542124000	-1.327275000
H	-3.767092000	-1.530954000	-1.600109000
N	0.871452000	-1.830158000	-0.253150000
C	-4.033959000	0.576299000	-1.731588000
H	-4.904735000	0.519770000	-2.375836000
C	-3.530661000	1.875818000	-1.336107000
H	-4.076721000	2.776148000	-1.587997000
C	-2.335830000	1.975494000	-0.729355000
H	-1.848647000	2.920883000	-0.528004000
C	-0.020372000	-0.819486000	-0.330059000
C	0.193983000	-3.028483000	-0.337896000
H	0.709929000	-3.973395000	-0.292137000
C	-1.135122000	-2.747489000	-0.447230000
H	-1.990450000	-3.399242000	-0.498142000
C	0.846884000	1.858585000	-0.147819000

C	2.033728000	1.853841000	-0.892666000
C	2.971574000	2.868685000	-0.753353000
H	3.881631000	2.850205000	-1.344616000
C	2.748081000	3.902528000	0.150357000
C	1.581713000	3.919513000	0.908126000
H	1.407437000	4.719321000	1.620923000
C	0.638933000	2.910253000	0.755145000
C	2.276031000	-1.683285000	-0.070298000
C	2.747043000	-0.866555000	0.949766000
C	4.117379000	-0.715268000	1.112784000
H	4.491651000	-0.074801000	1.903794000
C	5.001641000	-1.384404000	0.274028000
C	4.515935000	-2.206555000	-0.737226000
H	5.203296000	-2.725721000	-1.396382000
C	3.147104000	-2.355827000	-0.919070000
H	-0.262384000	2.925481000	1.361640000
H	3.483690000	4.692286000	0.266588000
H	2.228172000	1.046432000	-1.592727000
H	2.047805000	-0.360374000	1.605448000
H	6.071449000	-1.265634000	0.408646000
H	2.755149000	-2.973353000	-1.720354000
B	-2.913716000	-0.653097000	1.244104000
F	-1.828679000	-0.516215000	2.121796000
F	-3.434136000	-1.956417000	1.308919000
F	-3.891412000	0.293842000	1.517031000

Int 2

N	1.992955000	-0.322522000	0.178691000
C	2.303869000	-1.220487000	-0.775479000
B	0.500704000	0.175286000	0.190719000
N	0.368727000	-0.687902000	2.612023000
C	3.596304000	-1.718370000	-0.843487000
H	3.847348000	-2.437309000	-1.614492000
N	-1.573413000	-0.718920000	1.565089000
C	4.544231000	-1.289450000	0.074013000
H	5.558709000	-1.671513000	0.032401000
C	4.185883000	-0.363481000	1.047582000

H	4.898828000	-0.006300000	1.779977000
C	2.890323000	0.107572000	1.074972000
H	2.538359000	0.827058000	1.802056000
C	-0.236358000	-0.431476000	1.463295000
C	-1.803477000	-1.192260000	2.835546000
H	-2.788929000	-1.492813000	3.155165000
C	-0.592239000	-1.154109000	3.468023000
H	-0.363059000	-1.437893000	4.485231000
C	0.397424000	1.741744000	-0.054021000
C	0.209311000	2.618440000	1.019193000
C	0.156947000	3.995393000	0.825023000
H	0.008902000	4.657817000	1.672480000
C	0.283168000	4.520342000	-0.456090000
C	0.467246000	3.663222000	-1.536984000
H	0.561795000	4.067474000	-2.540269000
C	0.529197000	2.289544000	-1.334924000
C	-2.557135000	-0.614082000	0.541981000
C	-3.207545000	-1.762339000	0.103304000
C	-4.161980000	-1.665931000	-0.900711000
H	-4.666058000	-2.561227000	-1.249164000
C	-4.455935000	-0.431340000	-1.470071000
C	-3.798433000	0.710613000	-1.027157000
H	-4.023786000	1.676322000	-1.467223000
C	-2.852665000	0.625298000	-0.013168000
H	0.666140000	1.633683000	-2.190008000
H	0.235016000	5.593379000	-0.613504000
H	0.092839000	2.216370000	2.022749000
H	-2.945842000	-2.722469000	0.534969000
H	-5.194577000	-0.360696000	-2.261709000
H	-2.339575000	1.510659000	0.343757000
B	1.068317000	-1.580209000	-1.726342000
F	0.002429000	-0.553452000	-1.070654000
F	0.514758000	-2.812212000	-1.565177000
F	1.167489000	-1.182734000	-3.025276000

6_Ph

F	0.121250000	0.464959000	2.027773000

N	-1.856595000	0.744972000	0.689550000
C	-2.841386000	-0.035207000	0.200285000
B	-0.301851000	0.371774000	0.674632000
F	-2.866679000	-1.332911000	-1.911826000
N	-1.103545000	-1.896855000	-0.392286000
C	-4.159874000	0.412799000	0.298472000
H	-4.946111000	-0.220977000	-0.094738000
B	-2.582204000	-1.456207000	-0.536119000
F	-3.404656000	-2.450680000	0.017988000
N	1.018919000	-1.808214000	-0.023931000
C	-4.455106000	1.628855000	0.884057000
H	-5.481831000	1.972199000	0.956780000
C	-3.413201000	2.408594000	1.378580000
H	-3.589107000	3.369939000	1.845222000
C	-2.129171000	1.934002000	1.262133000
H	-1.271578000	2.488714000	1.621711000
C	-0.142093000	-1.134122000	0.125646000
C	0.773067000	-3.016263000	-0.647155000
H	1.564335000	-3.719220000	-0.848872000
C	-0.562176000	-3.065962000	-0.875033000
H	-1.169542000	-3.830135000	-1.331589000
C	0.490424000	1.396017000	-0.276299000
C	0.150912000	1.545160000	-1.625823000
C	0.864108000	2.398430000	-2.459496000
H	0.582542000	2.498580000	-3.503566000
C	1.940379000	3.123783000	-1.955391000
C	2.292642000	2.989687000	-0.617369000
H	3.133405000	3.549387000	-0.218077000
C	1.573144000	2.132264000	0.210201000
C	2.318262000	-1.317556000	0.310682000
C	2.672961000	-1.141661000	1.640587000
C	3.935885000	-0.646718000	1.941294000
H	4.219598000	-0.499939000	2.977943000
C	4.829894000	-0.341207000	0.921241000
C	4.463490000	-0.528772000	-0.407231000
H	5.154195000	-0.280036000	-1.205566000
C	3.201577000	-1.016117000	-0.718503000

H	1.961467000	-1.376183000	2.422825000
H	2.886768000	-1.137839000	-1.749241000
H	5.813907000	0.047465000	1.161878000
H	1.862601000	2.020707000	1.250821000
H	-0.684624000	0.982291000	-2.037710000
H	2.501135000	3.789553000	-2.604394000

TS 1

N	-1.607321000	0.781430000	-0.621128000
C	-2.200176000	-0.495103000	-0.696044000
B	-0.166176000	0.720791000	-0.440824000
N	-1.165818000	-1.387123000	-0.651411000
C	-3.505609000	-0.673945000	-1.198439000
H	-3.876607000	-1.680233000	-1.355793000
N	0.970785000	-1.793449000	-0.383636000
C	-4.284934000	0.426594000	-1.408063000
H	-5.310186000	0.320544000	-1.740317000
C	-3.730383000	1.722048000	-1.177675000
H	-4.334145000	2.610008000	-1.321845000
C	-2.436593000	1.871135000	-0.803781000
H	-1.966622000	2.837732000	-0.679826000
C	0.053798000	-0.767880000	-0.478097000
C	0.312141000	-2.996646000	-0.534205000
H	0.836881000	-3.936426000	-0.480310000
C	-1.011969000	-2.762467000	-0.701164000
H	-1.835404000	-3.445524000	-0.818978000
C	0.764202000	1.948482000	-0.237917000
C	1.980242000	2.064687000	-0.927671000
C	2.827836000	3.147392000	-0.726307000
H	3.762879000	3.210644000	-1.274688000
C	2.480036000	4.148297000	0.174970000
C	1.280118000	4.055360000	0.873199000
H	1.004626000	4.827303000	1.585476000
C	0.436788000	2.969832000	0.667457000
C	2.345367000	-1.647074000	-0.106298000
C	2.772398000	-0.659213000	0.777792000
C	4.127708000	-0.517806000	1.042143000

H	4.454871000	0.256826000	1.727588000
C	5.056485000	-1.362220000	0.444144000
C	4.621581000	-2.350564000	-0.433071000
H	5.338970000	-3.008251000	-0.912764000
C	3.270659000	-2.490849000	-0.719430000
H	-0.485165000	2.902276000	1.239230000
H	3.140913000	4.994656000	0.334268000
H	2.267357000	1.292825000	-1.635654000
H	2.046019000	-0.013171000	1.255820000
H	6.114085000	-1.249316000	0.657237000
H	2.935443000	-3.238104000	-1.430790000
B	-2.835891000	-0.830584000	1.614195000
F	-1.618678000	-0.576920000	2.083852000
F	-3.218262000	-2.103068000	1.485687000
F	-3.765867000	0.111187000	1.718067000

TS 2

N	-1.850009000	0.808973000	-0.460360000
C	-2.589861000	-0.304367000	0.011080000
B	-0.475259000	0.643136000	0.180658000
N	-1.420269000	-1.511182000	-0.366776000
C	-3.874214000	-0.524579000	-0.642868000
H	-4.595022000	-1.181935000	-0.170114000
N	0.701213000	-1.881920000	-0.239573000
C	-4.129676000	0.084154000	-1.824622000
H	-5.078346000	-0.089705000	-2.324580000
C	-3.195541000	0.996030000	-2.407197000
H	-3.394374000	1.472734000	-3.358018000
C	-2.089737000	1.329757000	-1.691984000
H	-1.365286000	2.061198000	-2.035100000
C	-0.244062000	-0.922090000	-0.193155000
C	0.082522000	-3.103249000	-0.441413000
H	0.648212000	-4.018066000	-0.519604000
C	-1.258782000	-2.860305000	-0.496159000
H	-2.082942000	-3.541970000	-0.634056000
C	0.618588000	1.756972000	0.022912000
C	1.568255000	1.696707000	-1.002276000

C	2.518232000	2.698407000	-1.165206000
H	3.247192000	2.630002000	-1.966797000
C	2.539891000	3.781240000	-0.292778000
C	1.604194000	3.859194000	0.733713000
H	1.616486000	4.703032000	1.416784000
C	0.650835000	2.858479000	0.884507000
C	2.100509000	-1.679133000	-0.072582000
C	2.554284000	-0.904806000	0.987754000
C	3.917482000	-0.685005000	1.129710000
H	4.275563000	-0.073511000	1.950650000
C	4.816063000	-1.247895000	0.230374000
C	4.350014000	-2.030842000	-0.820205000
H	5.047617000	-2.466970000	-1.527193000
C	2.986968000	-2.244957000	-0.981137000
H	-0.077218000	2.929291000	1.687290000
H	3.284648000	4.562137000	-0.411841000
H	1.573747000	0.848435000	-1.682029000
H	1.845981000	-0.479997000	1.689676000
H	5.880661000	-1.075411000	0.347414000
H	2.610620000	-2.829521000	-1.814045000
B	-2.458492000	-0.257473000	1.620877000
F	-0.949961000	0.494113000	1.670351000
F	-2.266908000	-1.417229000	2.302426000
F	-3.265478000	0.632957000	2.249449000

TS 3

N	1.965375000	-0.372461000	-0.374116000
C	1.980302000	-1.707090000	-0.578270000
B	0.509951000	0.349264000	-0.226331000
N	0.545929000	-0.820125000	2.093058000
C	3.187333000	-2.381257000	-0.683446000
H	3.188588000	-3.453963000	-0.842602000
N	-1.483039000	-0.652631000	1.241418000
C	4.383666000	-1.681846000	-0.576121000
H	5.331706000	-2.203319000	-0.651124000
C	4.342086000	-0.314643000	-0.367926000
H	5.244863000	0.276123000	-0.274998000

C	3.108843000	0.306394000	-0.270617000
H	3.009936000	1.371131000	-0.101324000
C	-0.146729000	-0.390757000	1.045060000
C	-1.616599000	-1.273549000	2.460124000
H	-2.581518000	-1.569432000	2.840758000
C	-0.350707000	-1.359070000	2.970927000
H	-0.043574000	-1.783659000	3.916271000
C	0.673796000	1.935812000	-0.061422000
C	0.928743000	2.533464000	1.178627000
C	1.058743000	3.912977000	1.304557000
H	1.254293000	4.353363000	2.277876000
C	0.927392000	4.729378000	0.185467000
C	0.666091000	4.156940000	-1.055275000
H	0.554976000	4.788861000	-1.931679000
C	0.542139000	2.775897000	-1.172654000
C	-2.565265000	-0.340699000	0.376206000
C	-3.440178000	-1.349611000	-0.012877000
C	-4.507999000	-1.046002000	-0.847826000
H	-5.188535000	-1.833196000	-1.155269000
C	-4.693323000	0.255464000	-1.301120000
C	-3.810066000	1.256306000	-0.910528000
H	-3.948921000	2.273939000	-1.260355000
C	-2.748880000	0.964669000	-0.064418000
H	0.326285000	2.336976000	-2.142543000
H	1.021800000	5.806801000	0.281197000
H	1.023012000	1.903783000	2.060126000
H	-3.269003000	-2.366291000	0.325198000
H	-5.523219000	0.488756000	-1.960007000
H	-2.060113000	1.739820000	0.251575000
B	0.647283000	-2.544812000	-0.713329000
F	-0.152412000	0.008527000	-1.435090000
F	0.240551000	-3.329687000	0.269074000
F	0.040647000	-2.693518000	-1.874888000

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