Supporting information for:

C=O and C=S bond activation by an annulated 1,4,2-diazaborole

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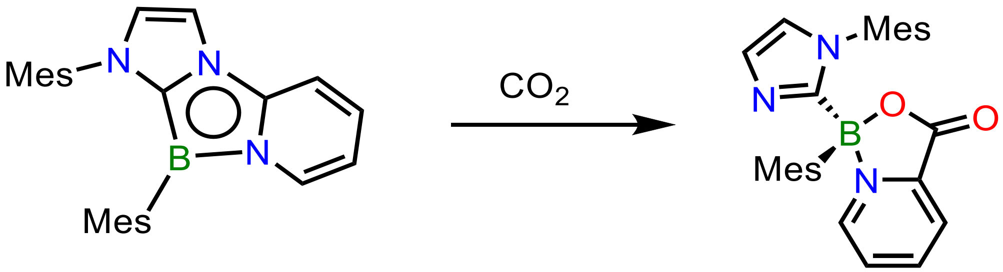
1.) Experimental Details

General experimental considerations

All syntheses were carried out in an inert atmosphere glovebox under purified nitrogen or with standard Schlenk techniques[1] under high purity argon (99.999). Solvents (hexane, tetrahydrofuran, diethyl ether, and toluene) were dried by passage through a Grubbs-style solvent purification system, degassed, and stored over activated 4Å molecular sieves. Other solvents, including benzene and deuterated solvents, were distilled from appropriate drying agents, degassed and stored over activated 4Å molecular sieves. Compound **1** was synthesized according to a literature procedure.[2] CS_2 (99.9%) was purchased from Fischer and used as received. Benzophenone (99%), acetophenone (99%), phenylisothiocyanate (99%), and methylisothiocyanate (97%) were purchased from Sigma Aldrich and used as received. CO_2 (99.5%) was purchased from Linde Gas & Equipment Inc. All reagents were used without further purification unless stated otherwise. All solution NMR spectra were acquired on a Varian Mercury Vx 400 MHz NMR spectrometer equipped with an ATB probe at 298 K (^1H: 400.1 MHz, ^{13}C: 100.6 MHz, ^{11}B: 128.4 MHz). ^1H NMR spectra were referenced to residual solvent signals.$^{13}C\{^1H\}$ spectra were referenced to the solvent itself. ^{11}B spectra were reference to external $BF_3{\cdot}OEt_2$. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br.s = broad signal, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets. Electrospray ionization (ESI) mass spectra were obtained using a high-resolution Agilent 6530 Quadrupole Time of Flight (QToF) mass spectrometer. Infrared spectra were measured on a Perkin Elmer, Spectrum Two FT-IR Spectrometer.

Synthesis of 2:



Compound **1** (80 mg, 0.20 mmol) was dissolved in benzene (2 mL) and CO_2 was bubbled through the solution for 15 mins. The reaction flask was then sealed under CO_2 atmosphere and heated at 80°C overnight to obtain a clear brown solution. The flask was slowly cooled to room temperature, causing the product to crystallize from solution. The crystals were collected, washed with hexane (2 mL x 3) and dried under vacuum to afford **2** as an off-white solid (69 mg, 78%). Crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution of **2** in benzene.

^{1}H NMR (400.1 MHz, THF-*d*^{8}): δ = 9.30 (d, 1H, $^3J_{H\text{-}H}$ = 6 Hz, CH_{Py}), 8.42 (t, 1H, $^3J_{H\text{-}H}$ = 8 Hz, CH_{Py}), 8.21 (d, 1H, $^3J_{H\text{-}H}$ = 8 Hz, CH_{Py}), 8.01 (t, 1H, $^3J_{H\text{-}H}$ = 6 Hz, CH_{Py}), 6.93 (s, 1H, $CH_{Imidazole}$), 6.88 (s, 1H, CH_{Mes}), 6.74 (s, 1H, $CH_{Imidazole}$), 6.63 (s, 1H, CH_{Mes}), 6.55 (s, 2H, CH_{Mes}), 2.24 (s, 3H, $CH_{3\text{-}Mes}$), 2.09 (s, 3H, $CH_{3\text{-}Mes}$), 2.05 (s, 6H, $CH_{3\text{-}Mes}$), 1.73 (s, 3H, $CH_{3\text{-}Mes}$), 1.59 (s, 3H, $CH_{3\text{-}Mes}$) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, THF-*d*^{8}): δ = 163.37 (C=O), 146.38 (*q*-Py), 144.44 (CH_{Py}), 144.27 (*q*-Mes), 143.62 (*q*-Mes), 138.36 (*q*-Mes), 138.03 (CH_{Py}), 136.66 (CH_{Py}), 136.63 (*q*-Mes), 136.37 (*q*-Mes), 130.95 (CH_{Mes}), 129.51 (CH_{Py}), 129.24 (CH_{Imidaz}), 129.19 (CH_{Mes}), 129.17 (CH_{Mes}), 128.90 (CH_{Mes}), 128.89 (*q*-Mes), 123.79 (*q*-Mes), 122.02 (CH_{Imidaz}), 25.48 ($CH_{3\text{-}Mes}$), 25.21 ($CH_{3\text{-}Mes}$), 21.21 ($CH_{3\text{-}Mes}$), 20.98 ($CH_{3\text{-}Mes}$), 17.77 ($CH_{3\text{-}Mes}$), 17.68 ($CH_{3\text{-}Mes}$) ppm.

Due to coupling with quadrupolar ^{11}B, the boron-bound C atoms were not observed.

^{11}B{^{1}H} NMR (128.4 MHz, THF-*d*^{8}): δ = 7.0 ppm.

IR (KBr): 1748 cm^{-1} (νC=O)

HRMS (ESI): $C_{27}H_{28}BN_3O_2$ Calculated for $[M]^+$: 437.2275, observed 437.2256

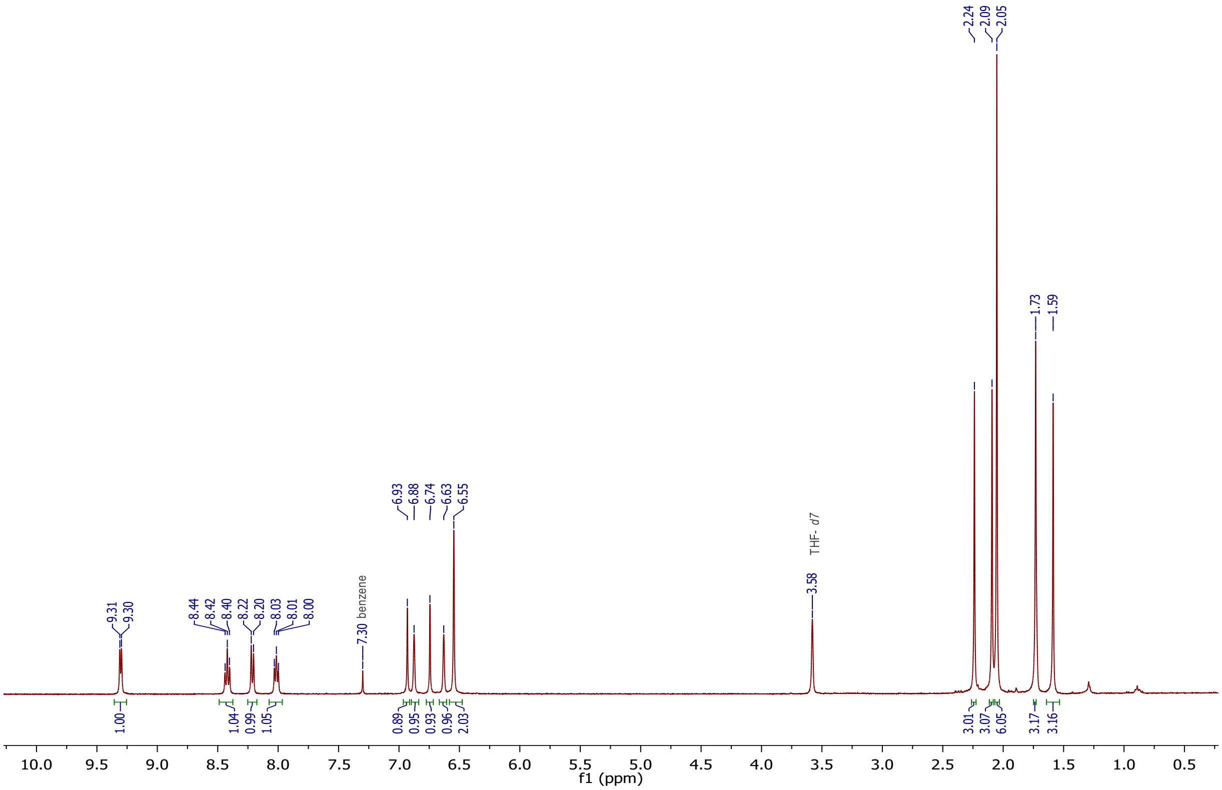


Figure S1: ^{1}H NMR spectrum of **2** in THF-*d*^{8}.

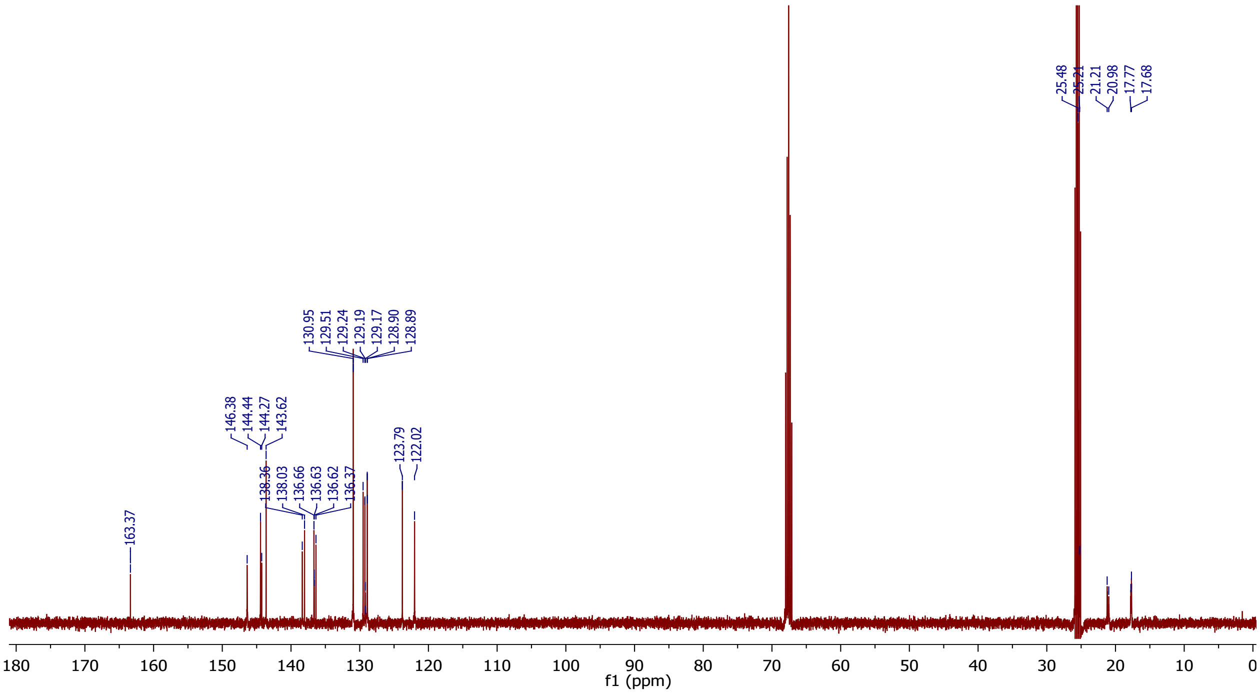


Figure S2: ^{13}C{^{1}H} NMR spectrum of **2** in THF-*d*^{8}.

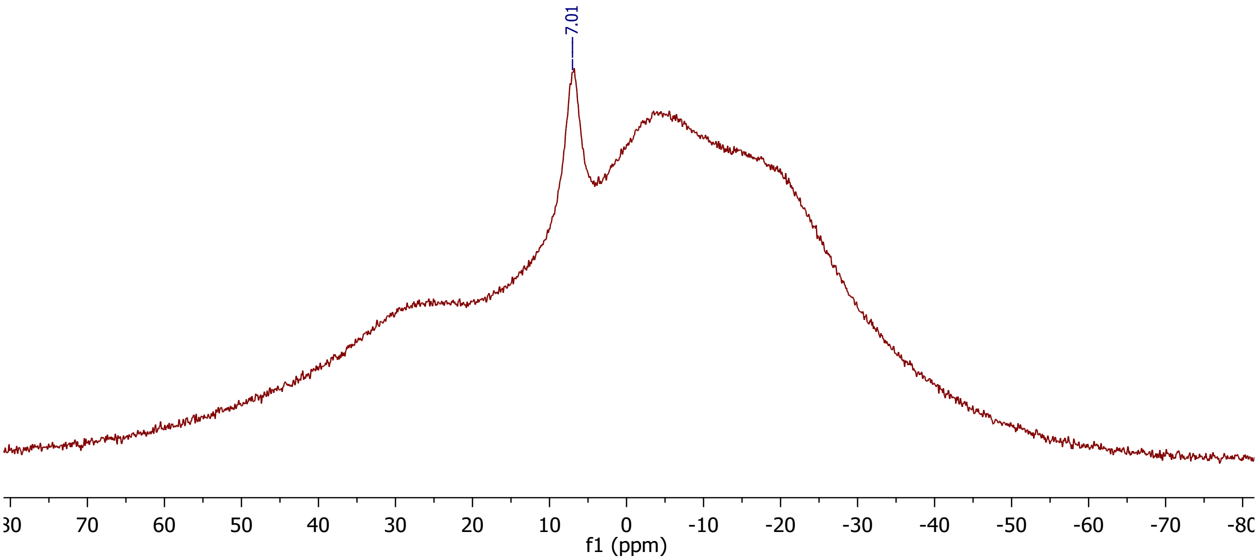


Figure S3: $^{11}B\{^{1}H\}$ NMR spectrum of **2** in THF-*d*^{8}.

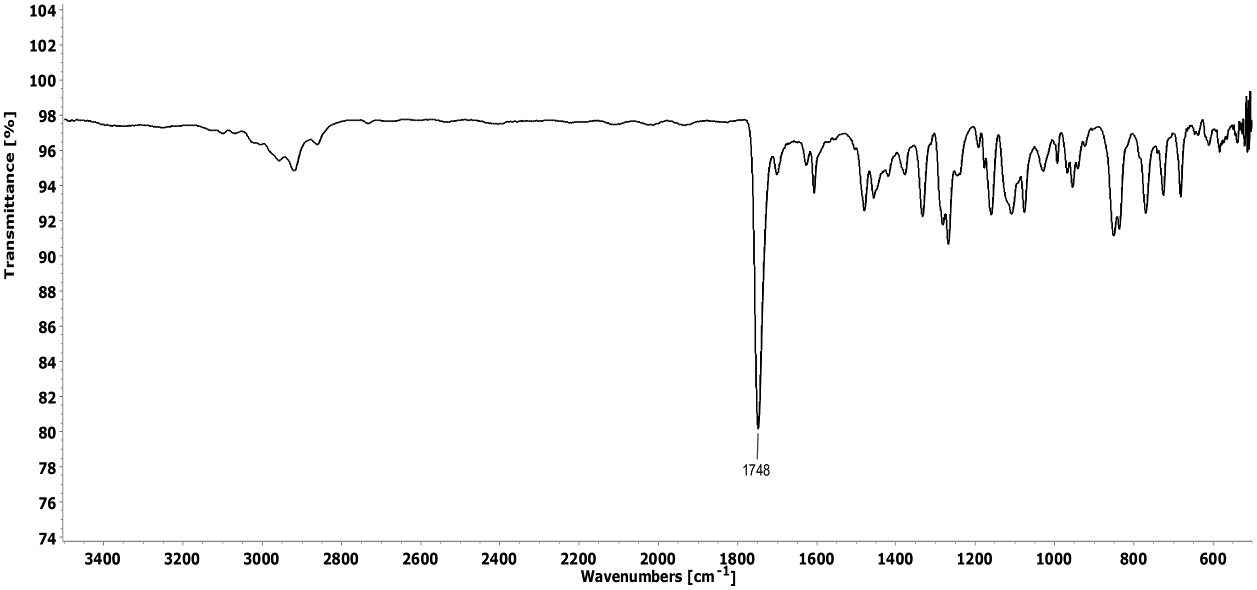
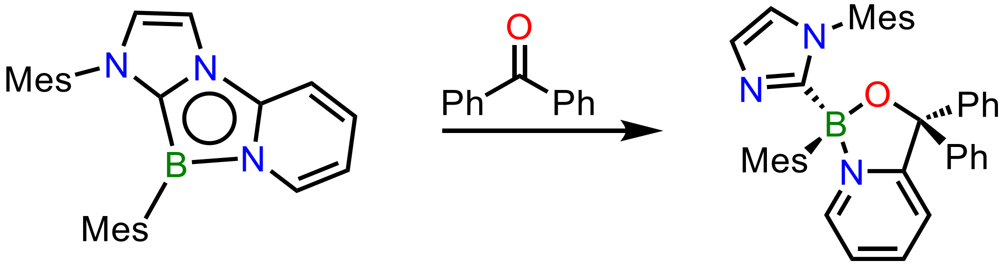


Figure S4: IR spectrum (KBr) of **2**.

Synthesis of 3:



Benzophenone (23 mg, 0.12 mmol) was added to a stirred solution of **1** (50 mg, 0.12 mmol) in benzene (5 mL) and was heated at 75°C for 24 hrs. It was then allowed to cool to room temperature causing the crystallization of product as colourless crystals. The crystals were isolated, washed with hexane (2 mL x 3) and dried under vacuum to afford **3** as a white solid (62 mg, 84 %). Single crystals suitable for X-ray diffraction were obtained from a saturated solution of **3** in benzene.

^{1}H NMR (400.1 MHz, C_6D_6): δ = 9.02 (d, 1H, ^3J = 6 Hz, CH_{Py}), 7.53 (d, 1H, ^3J = 1 Hz, CH_{Imidaz}), 7.10 – 6.94 (m, 7H, CH_{Phenyl}), 6.90 – 6.77 (m, 1H CH_{Py} + 3H CH_{Phenyl}), 6.77 – 6.69 (m, 1H CH_{Py} + 1H CH_{Mes}), 6.65 (d, 1H, ^3J = 1 Hz, CH_{Imidaz}), 6.55 (s, 3H, CH_{Mes}), 6.33 (ddd, 1H, ^3J = 8 Hz, ^3J = 6 Hz, ^4J = 1 Hz, CH_{Py}), 2.19 (s, 3H, $CH_{3\text{-}Mes}$), 2.16 (s, 3H, $CH_{3\text{-}Mes}$), 2.14 (s, 9H, $CH_{3\text{-}Mes}$), 1.33 (s, 3H, $CH_{3\text{-}Mes}$) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 163.31 (CH_{Py}), 146.41 (*q*-Py), 145.80 (CH_{Py}), 143.84 (*q*-Mes), 140.81 (*q*-Mes), 139.97 (*q*-Mes), 137.82 (*q*-Mes), 136.86 (CH_{Py}), 136.75 (*q*-Mes), 135.91 (*q*-Mes), 133.73 (CH_{Imidaz}), 129.72 (CH_{Mes}), 129.34 (CH_{Mes}), 127.94 (CH_{Phenyl}), 127.75 (CH_{Phenyl}), 127.40 (CH_{Mes}), 127.11 (CH_{Mes}), 122.71 (CH_{Py}), 122.23 (*q*-Mes), 121.81 (CH_{Imidaz}), 89.63 (C-O), 25.28 ($CH_{3\text{-}Mes}$), 22.75 ($CH_{3\text{-}Mes}$), 21.16 ($CH_{3\text{-}Mes}$), 20.93 ($CH_{3\text{-}Mes}$), 18.63 ($CH_{3\text{-}Mes}$), 17.53 ($CH_{3\text{-}Mes}$) ppm.

Due to overlap with the C_6D_5H solvent signal, not all aryl signals could be identified. Due to coupling with quadrupolar ^{11}B, the boron-bound C atoms were not observed.

^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ = 9.2 ppm.

IR (KBr): 840 cm^{-1} (νB-O)

HRMS (ESI): $C_{39}H_{38}BN_3O$ Calculated for $[M]^+$ 575.3108, observed 575.3092

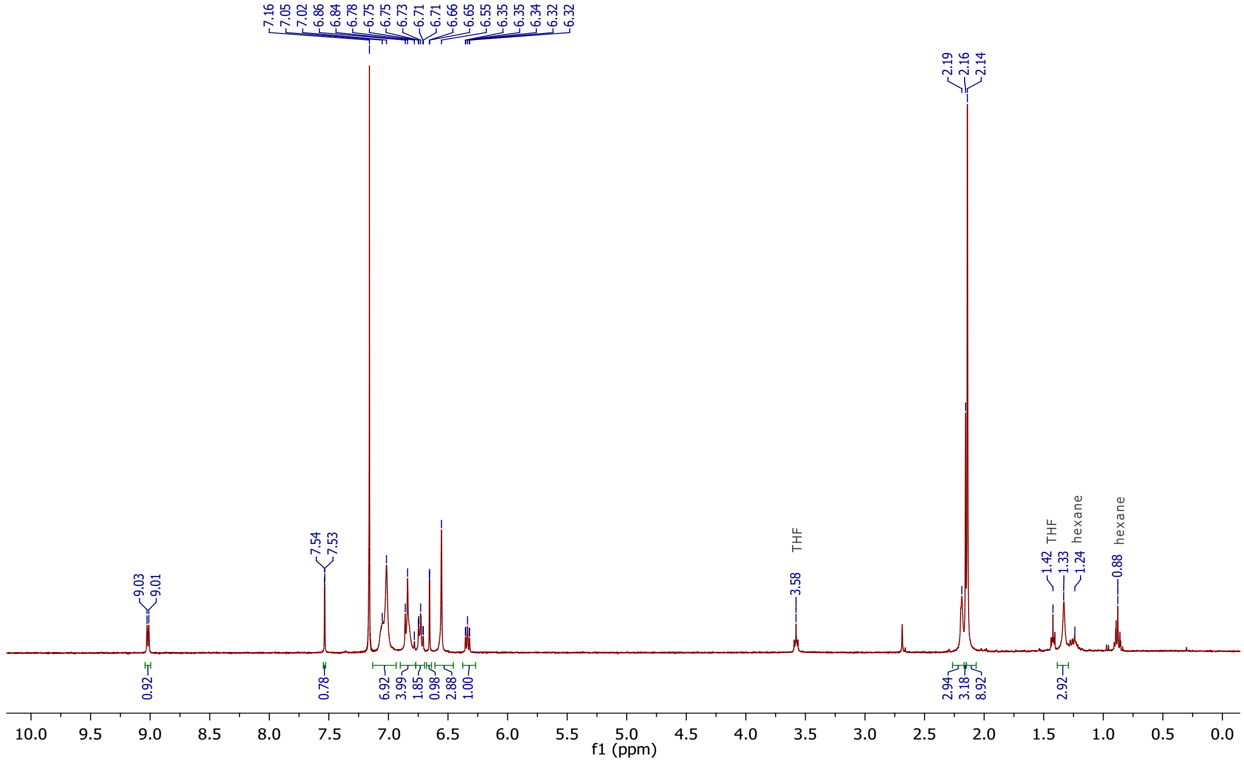


Figure S5: ^{1}H NMR spectrum of **3** in C_6D_6.

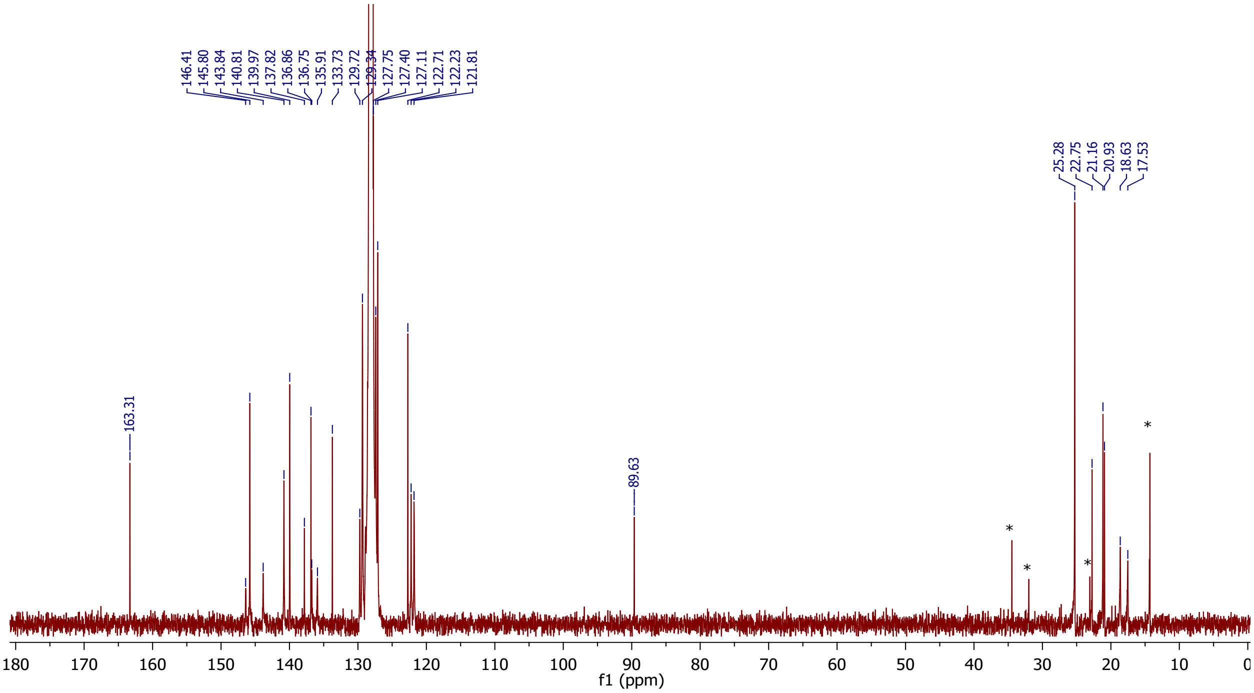


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6. (* residual hexane/pentane)

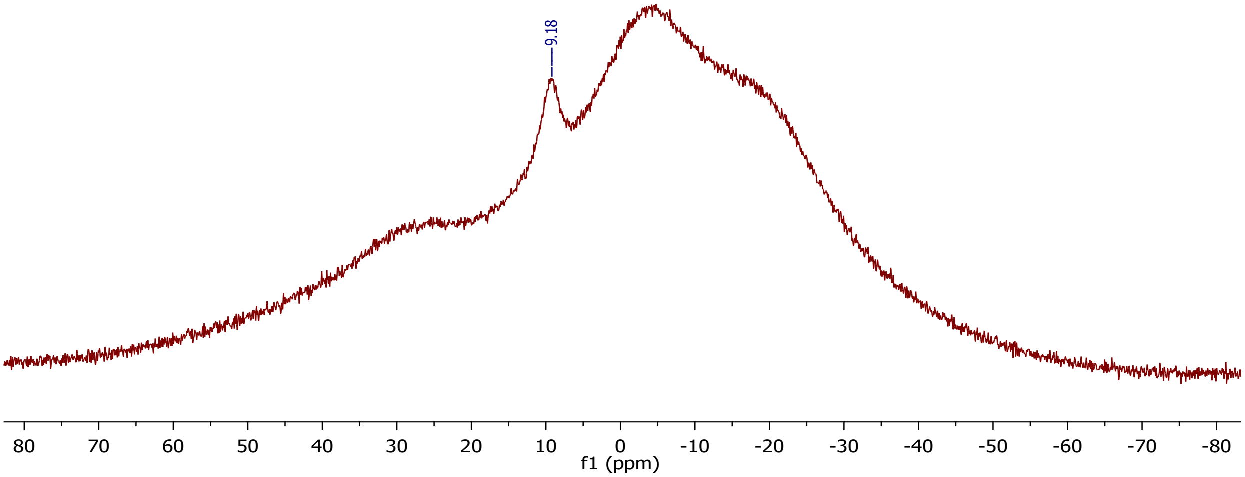


Figure S7: $^{11}B\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

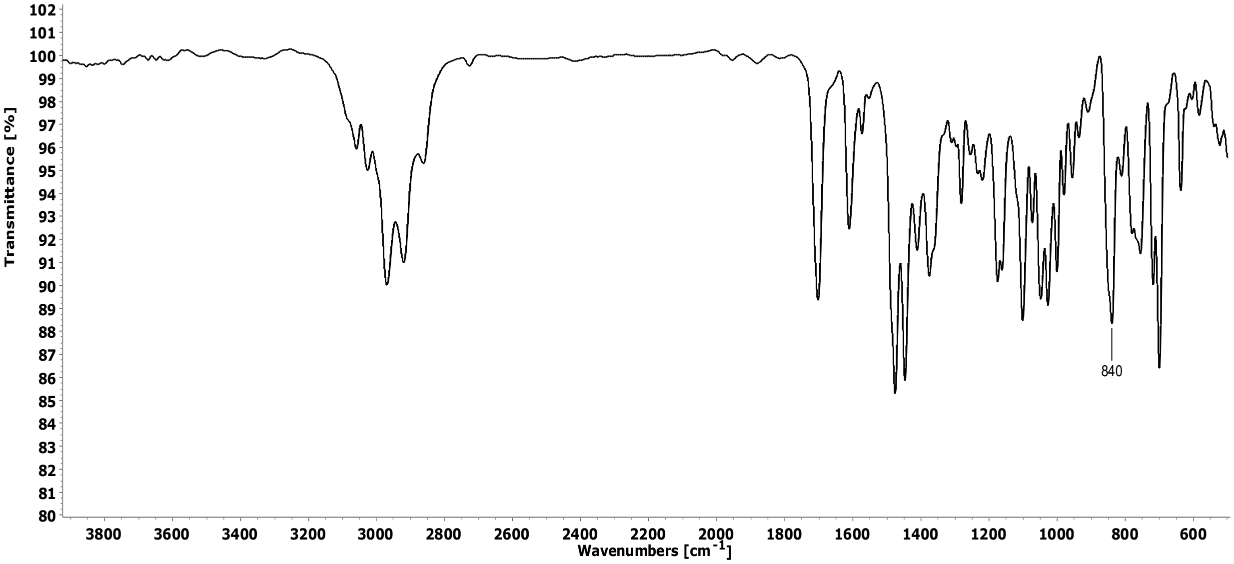
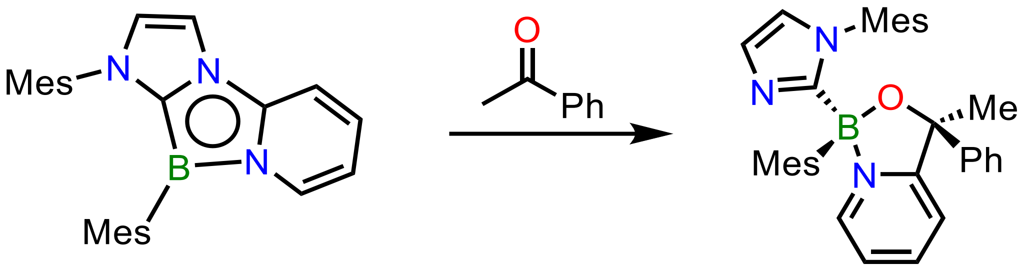


Figure S8: IR spectrum (KBr) of **3**.

Synthesis of 4:



Acetophenone (15 mg, 0.12 mmol) was added to a stirred solution of **1** (50 mg, 0.12 mmol) in benzene (5 mL) and was heated at 60°C for 24 hrs. It was then allowed to cool to room temperature causing the crystallization of product as colourless crystals. The crystals were isolated, washed with hexane (3 mL x 3) and dried under vacuum to afford **4** as a light-brown solid (57 mg, 87 %). Single crystals suitable for X-ray diffraction were obtained from a saturated solution of **4** in benzene.

^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 8.78 (br s, 1H, CH$_{Py}$), 8.01 (t, 1H, ^3J = 8 Hz, CH$_{Py}$), 7.57 (br s, 1H, CH$_{Py}$), 7.46 (t, 1H, ^3J = 7 Hz, CH$_{Py}$), 7.21 (s, 1H, CH$_{Imidaz}$), 7.16 – 7.08 (m, 2H, CH$_{Phenyl}$), 7.07 – 6.90 (m, 3H, CH$_{Phenyl}$), 6.79 (s, 1H, CH$_{Mes}$), 6.67 (s, 1H, CH$_{Imidaz}$), 6.62 (s, 1H, CH$_{Mes}$), 6.48 (s, 2H, CH$_{Mes}$), 2.24 (s, 3H, CH$_{3\text{-}Mes}$), 2.12 (s, 3H, CH$_{3\text{-}Mes}$), 1.74 (br s, 6H, CH$_{3\text{-}Mes}$), 1.14 (s, 6H, CH$_{3\text{-}Mes}$) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ = 144.43 (CH$_{Py}$), 141.30 (*q*-Py), 140.69 (CH$_{Py}$), 137.13 (*q*-Mes), 137.06 (*q*-Phen), 135.25 (*q*-Mes), 134.39 (CH$_{Phenyl}$), 129.42 (CH$_{Py}$), 128.96 (CH$_{Py}$), 128.74 (CH$_{Phenyl}$), 128.48 (CH$_{Phenyl}$), 127.89 (*q*-Mes), 127.79 (CH$_{Imidaz}$), 127.58 (CH$_{Mes}$), 126.78 (CH$_{Mes}$), 125.75 (*q*-Mes), 123.43 (CH$_{Mes}$), 121.55 (CH$_{Imidaz}$), 121.04 (CH$_{Mes}$), 84.18 (C-O), 34.28 (CH$_{3\text{-}Me}$), 24.50 (CH$_{3\text{-}Mes}$), 22.49 (CH$_{3\text{-}Mes}$), 20.99 (CH$_{3\text{-}Mes}$), 20.89 (CH$_{3\text{-}Mes}$), 17.00 (CH$_{3\text{-}Mes}$), 14.22 (CH$_{3\text{-}Mes}$) ppm.

Due to coupling with quadrupolar ^{11}B, the boron-bound C atoms were not observed.

^{11}B{^{1}H} NMR (128.4 MHz, CDCl$_3$): δ = 8.2 ppm.

IR (KBr): 851 cm^{-1} (νB-O)

HRMS (ESI): $C_{34}H_{36}BN_3O$ Calculated for $[M+H]^+$ 514.2951, observed 514.2990

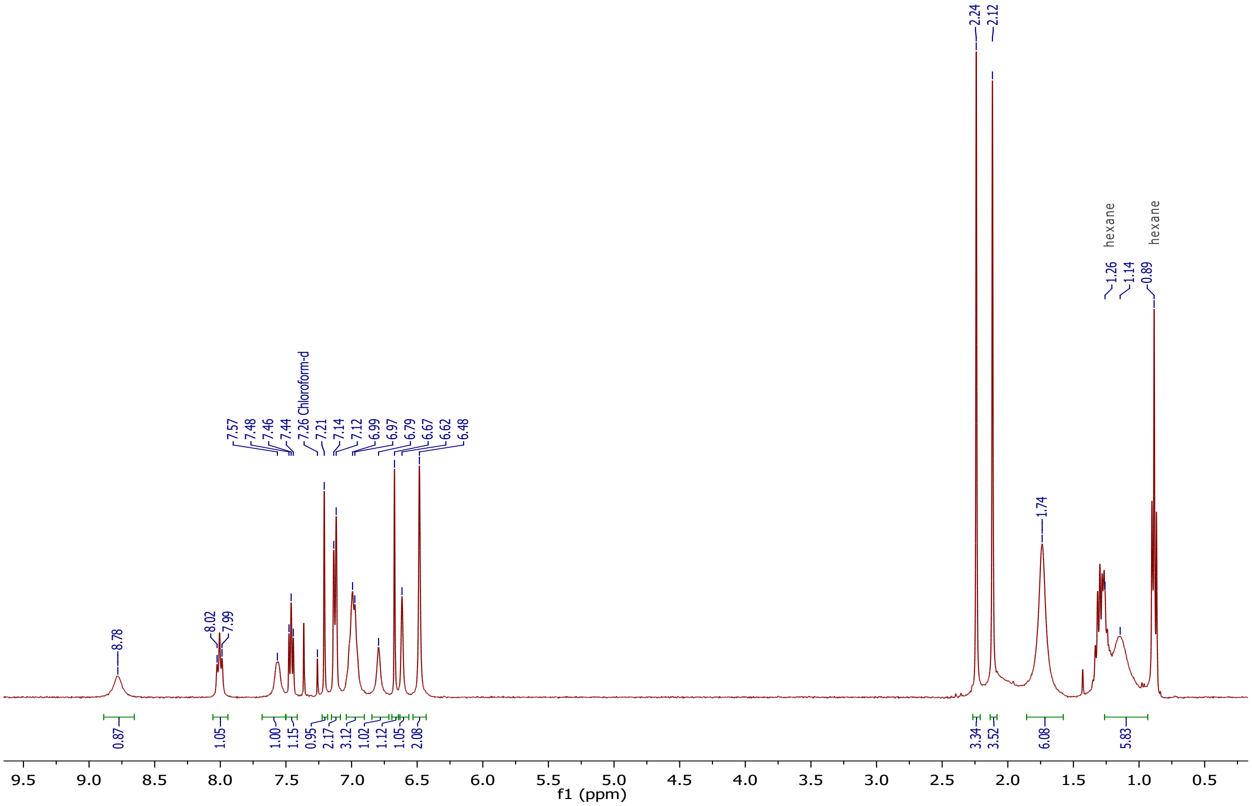


Figure S9: ^{1}H NMR spectrum of **4** in $CDCl_3$.

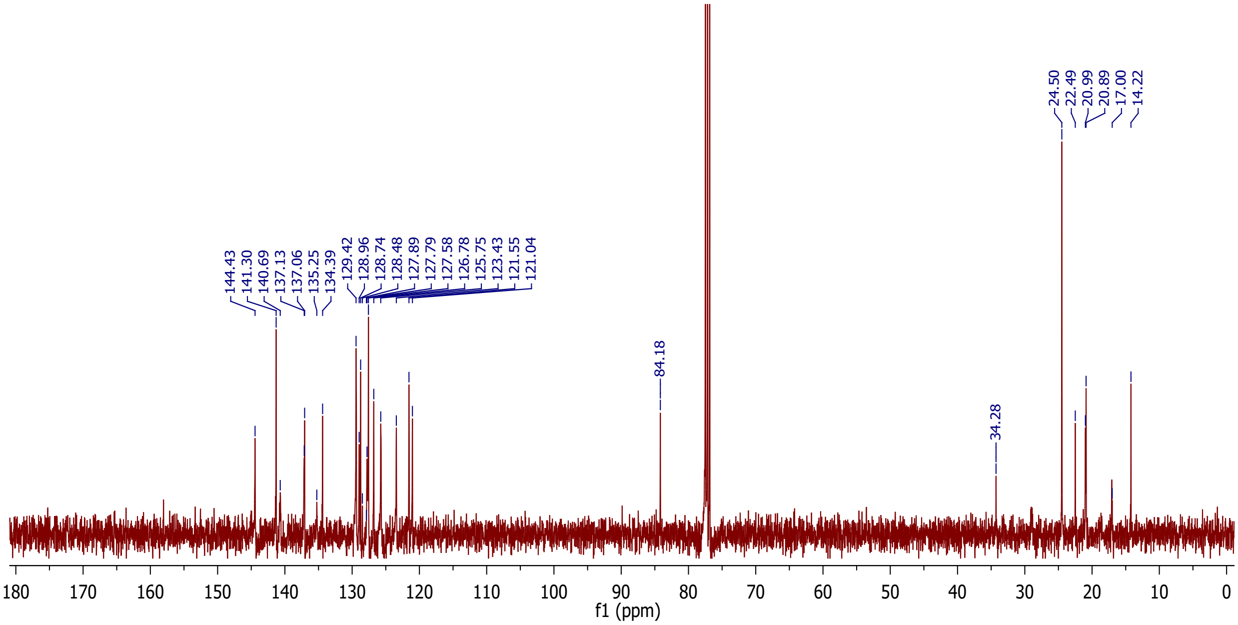


Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

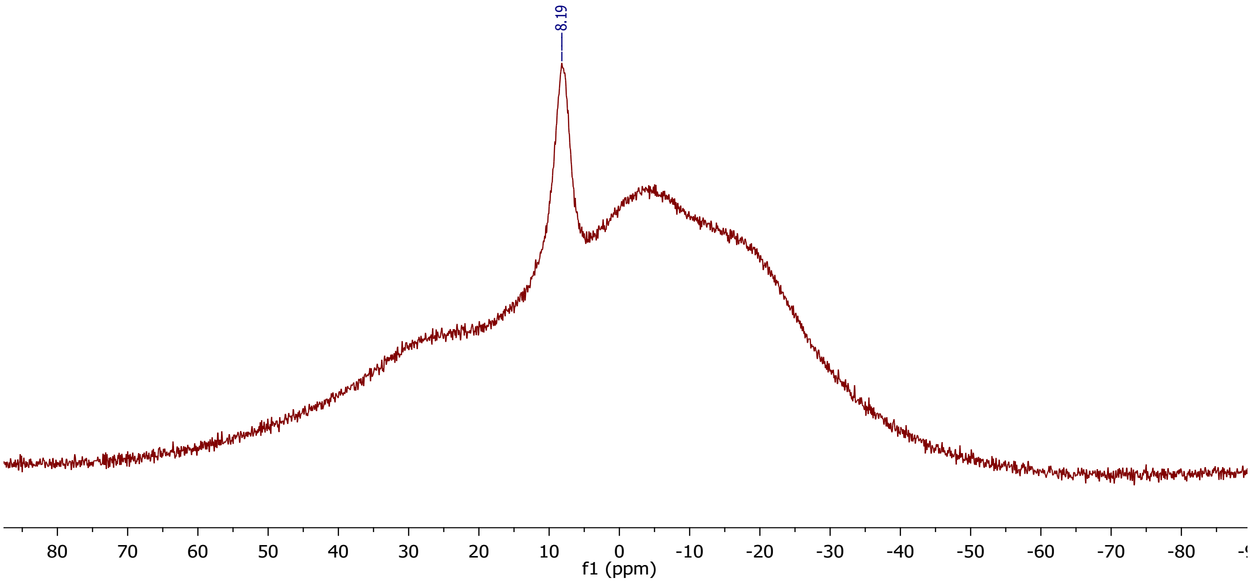


Figure S11: $^{11}B\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

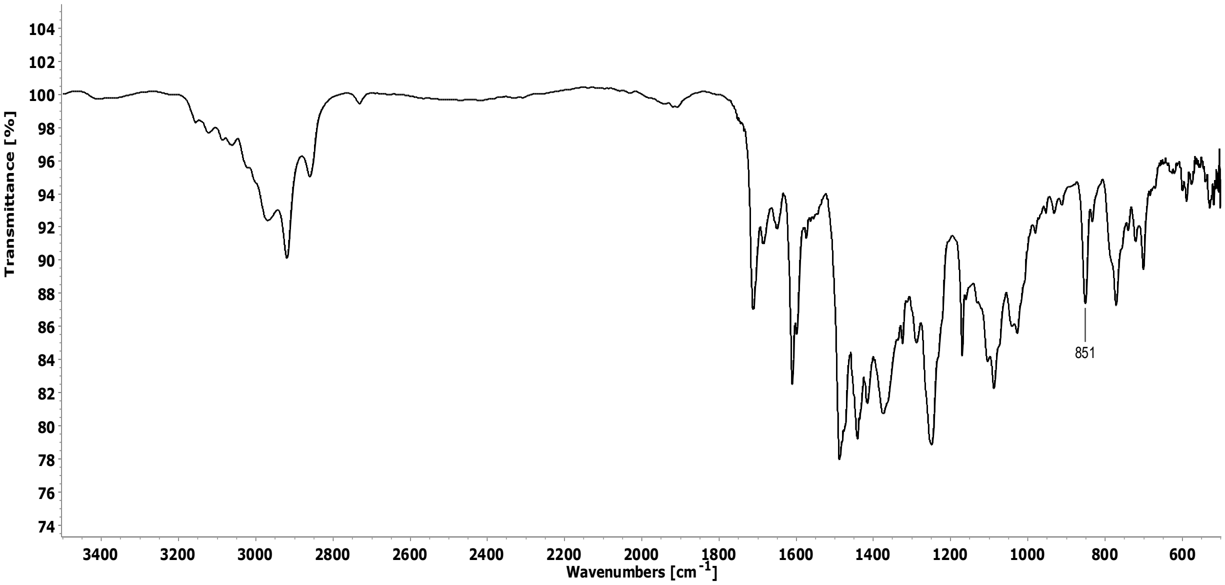
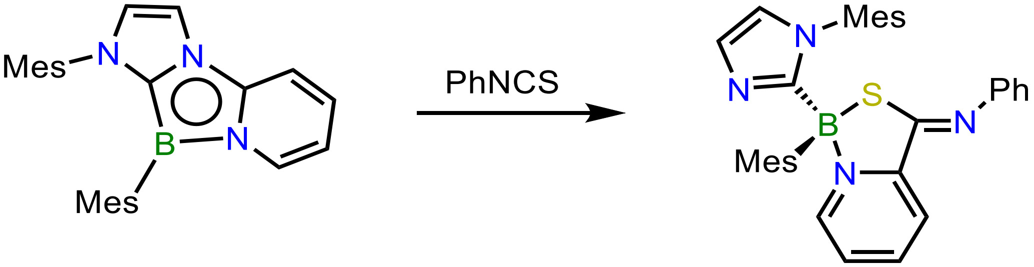


Figure S12: IR spectrum (KBr) of **4**.

Synthesis of 5:



Phenyliosthiocyanate (14 mg, 0.10 mmol) was added to a stirred solution of **1** (40 mg, 0.10 mmol) in benzene (4 mL). A colour change was observed from red to brown within 10 mins and the reaction mixture was allowed to stir for another 1 hr at room temperature. Hexane (5 mL) was added to the solution causing the product to precipitate. The precipitate was then collected, washed with hexane (3 mL x 3) and dried under vacuum to afford **5** as a light brown solid (41 mg, 75%). Single crystals suitable for X-ray diffraction were obtained from a saturated solution of **5** in benzene.

^{1}H NMR (400.1 MHz, C_6D_6): δ = 9.16 (d, 1H, ^3J = 6 Hz, CH_{Py}), 8.03 (d, 1H, ^3J = 7 Hz, CH_{Py}), 7.44 (s, 1H, CH_{Imidaz}), 7.33 – 7.23 (m, 4H, CH_{Phenyl}), 7.02 (tt, 1H, ^3J = 7 Hz, ^4J = 2 Hz, CH_{Phenyl}), 6.85 (s, 2H, CH_{Mes}), 6.75 – 6.69 (m, 2H, CH_{Py} + CH_{Imidaz}), 6.49 (s, 2H, CH_{Mes}), 6.23 (t, 1H, ^3J = 6.0 Hz, CH_{Py}), 2.24 (s, 3H, $CH_{3\text{-}Mes}$), 2.15 (s, 3H, $CH_{3\text{-}Mes}$), 2.08 (s, 3H, $CH_{3\text{-}Mes}$), 1.85 (br s, 6H, $CH_{3\text{-}Mes}$), 0.82 (s, 3H, $CH_{3\text{-}Mes}$) ppm.

$^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 163.52 (CH_{Py}), 154.80 (*q*-Mes), 150.80 (*q*-Mes), 146.41 (CH_{Imidaz}), 140.90 (CH_{Imidaz}), 137.64 (*q*-Mes), 137.56 (*q*-Py), 136.14 (*q*-Mes), 135.40 (*q*-Mes), 135.11 (CH_{Py}), 130.54 (CH_{Mes}), 130.36 (*q*-Mes), 129.36 (CH_{Py}), 128.90 (CH_{Mes}), 128.58 (CH_{Phenyl}), 128.18 (CH_{Phenyl}), 128.14 (CH_{Phenyl}), 127.94 (CH_{Phenyl}), 125.73 (CH_{Mes}), 125.28 (CH_{Phenyl}), 122.46 (*q*-Mes), 121.83 (CH_{Mes}), 121.02 (CH_{Py}), 24.13 (br, $CH_{3\text{-}Mes}$), 21.08 ($CH_{3\text{-}Mes}$), 20.95 ($CH_{3\text{-}Mes}$), 19.08 ($CH_{3\text{-}Mes}$), 15.87 ($CH_{3\text{-}Mes}$) ppm.

Due to coupling with quadrupolar ^{11}B, the boron-bound C atoms were not observed.

$^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): δ = 3.7 ppm.

IR (KBr): 1570 cm^{-1} (νC=N), 694 cm^{-1} (νB-S)

HRMS (ESI): $C_{33}H_{33}BN_4S$ Calculated for $[M]^+$ 528.2519, observed 528.2466

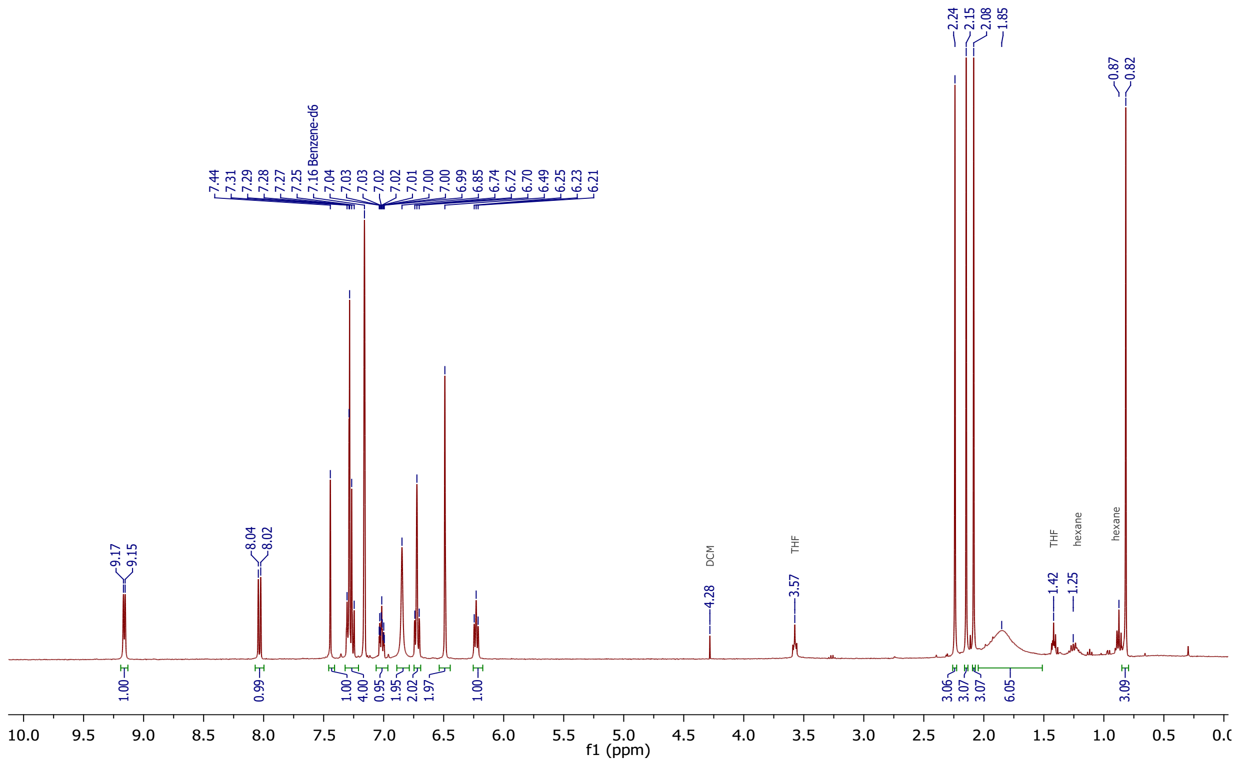


Figure S13: ^{1}H NMR spectrum of **5** in C_6D_6.

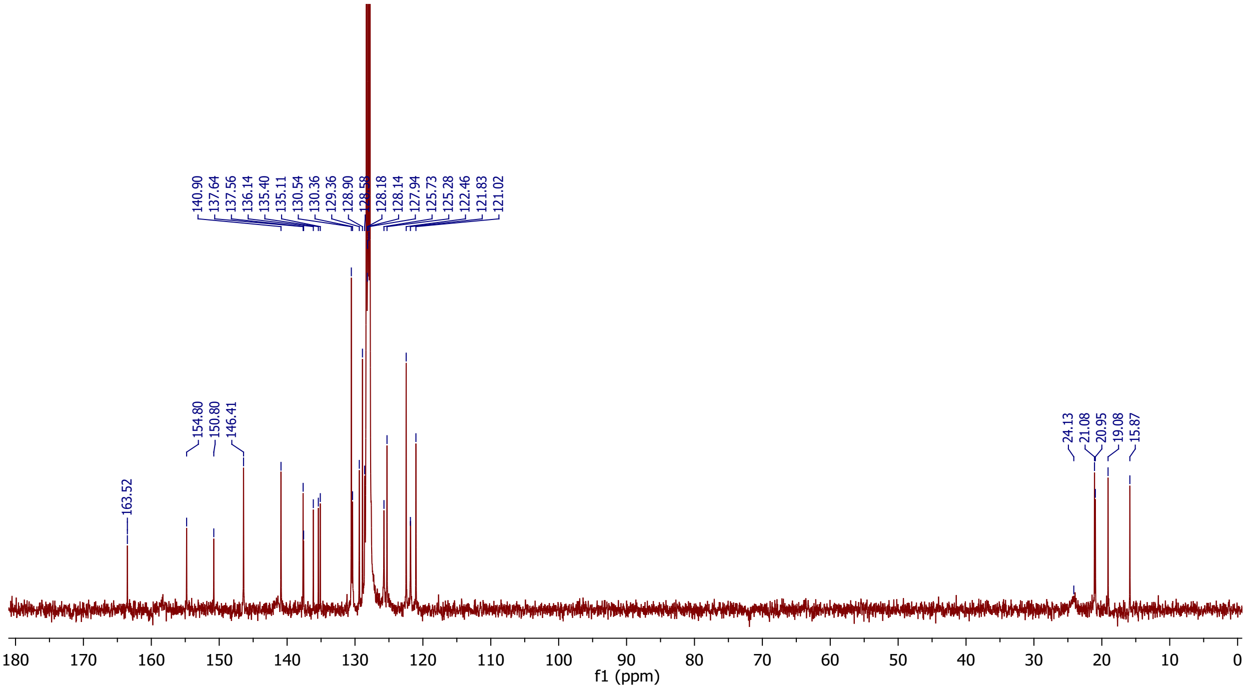


Figure S14: $^{13}C\{^1H\}$ NMR spectrum of **5** in C_6D_6.

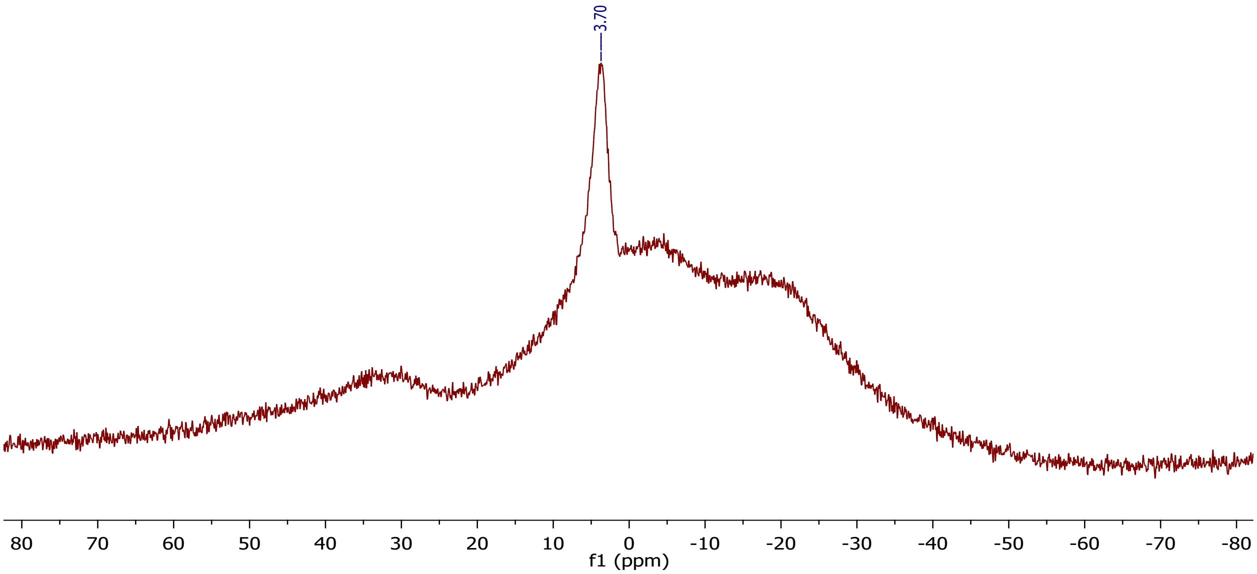


Figure S15: $^{11}B\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

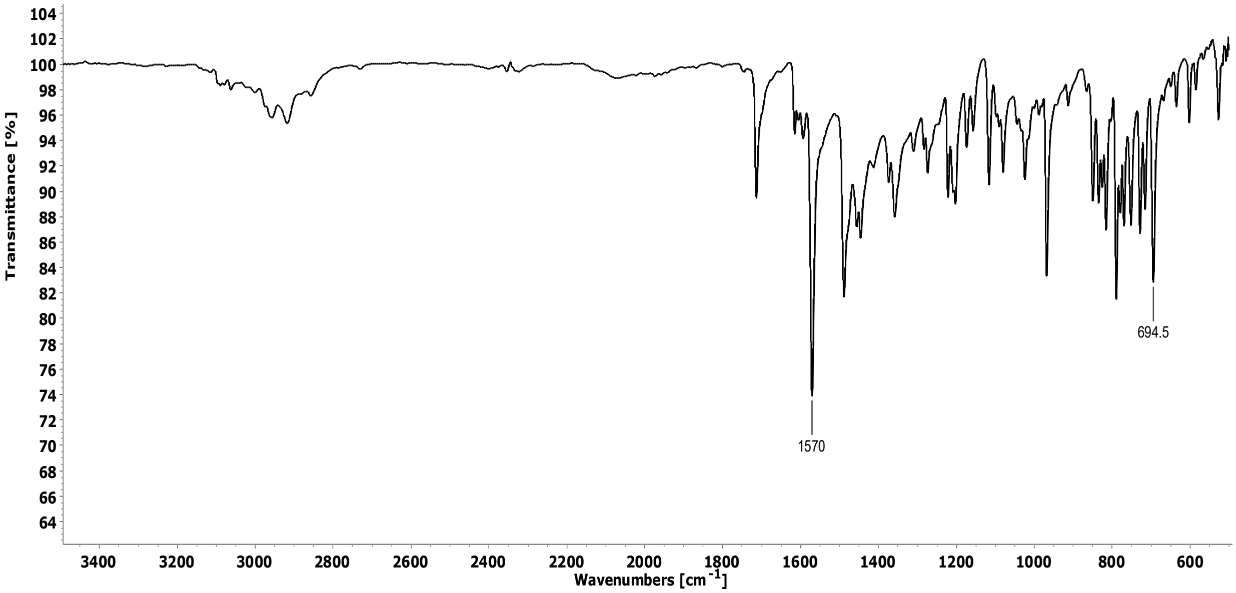
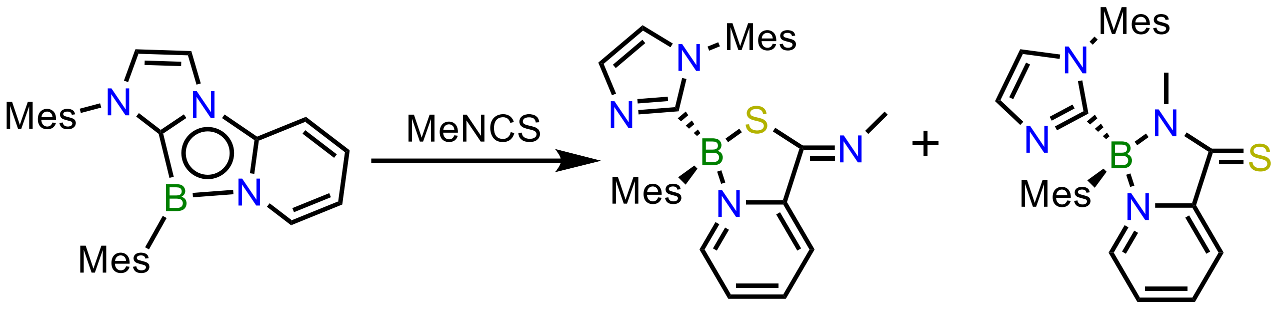


Figure S16: IR spectrum (KBr) of **5**.

Synthesis of 6, 7:



6 (major) **7** (minor)

Methylisothiocyanate (7.4 mg, 0.10 mmol) was added to a stirred solution of **1** (40 mg, 0.10 mmol) in benzene (4 mL). The reaction mixture was allowed to stir overnight at room temperature. The solvent was removed under vacuum, causing the formation of single crystals of [MeNCS·**6**·(**7**/**6**)] suitable for X-ray diffraction, along with some amorphous material. The obtained product was washed with hexane (3 mL x 3) and dried under vacuum to afford an approximate 9:1 mixture of **6:7** as a light brown solid (35 mg, 73%). Single crystals of **6** were obtained from a saturated solution in benzene. Unfortunately, attempts to cleanly isolate **7** from the reaction mixture were unsuccessful.

^{1}H NMR (400.1 MHz, C_6D_6): Major product 6: δ = 9.09 (d, 1H, ^3J = 6 Hz, CH_{Py}), 7.92 (d, 1H, ^3J = 8 Hz, CH_{Py}), 7.43 (s, 1H, CH_{Imidaz}), 6.86 (s, 2H, CH_{Mes}), 6.76 (s, 1H, CH_{Imidaz}), 6.71 (t, 1H, ^3J = 8 Hz, CH_{Py}), 6.50 (s, 2H, CH_{Mes}), 6.26 (t, 1H, ^3J = 6 Hz, CH_{Py}), 3.19 (s, 3H, NCH_3), 2.29 (s, 3H, $CH_{3\text{-}Mes}$), 2.25 (s, 3H, $CH_{3\text{-}Mes}$), 2.15 (s, 3H, $CH_{3\text{-}Mes}$), 1.90 (br s, 6H, $CH_{3\text{-}Mes}$), 0.76 (s, 3H, $CH_{3\text{-}Mes}$) ppm. **Minor product 7:** δ = 8.99 (br.s, 1H), 8.18 (d, 1H, 8 Hz), 7.41 (s, 1H), 6.97 (s, 1H), 6.64 (s, 1H), 2.66 (s, 3H), 2.55 (s, 3H), 2.34 (s, 3H), 2.18 (s, 6H) ppm. Due to signal overlap with **6**, only partial resonances of **7** could be identified.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): Major product 6: δ = 165.64 (CH_{Py}), 153.86 (*q*-Mes), 146.33 (*q*-Mes), 141.20 (*q*-Py), 140.81 (CH_{Py}), 137.67 (*q*-Mes), 137.25 (*q*-Mes), 136.37 (CH_{Imidaz}), 135.30 (*q*-Mes), 135.15 (CH_{Py}), 130.46 (CH_{Mes}), 129.17 (CH_{Imidaz}), 128.56 (CH_{Mes}), 125.54 (*q*-Mes), 125.46 (CH_{Mes}), 121.69 (CH_{Mes}), 121.59 (*q*-Mes), 120.34 (CH_{Py}), 43.17 (NCH_3), 25.93 ($CH_{3\text{-}Mes}$), 24.18 ($CH_{3\text{-}Mes}$), 20.96 ($CH_{3\text{-}Mes}$), 19.30 ($CH_{3\text{-}Mes}$), 19.27 ($CH_{3\text{-}Mes}$), 15.89 ($CH_{3\text{-}Mes}$) ppm.

Due to coupling with quadrupolar ^{11}B, the boron-bound C atoms were not observed.

$^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): Major product 6: $\delta = 3.1$ ppm. **Minor product 7:** $\delta = 1.4$ ppm.

IR (KBr): 1595 cm^{-1} (νC=N), 679 cm^{-1} (νB-S)

HRMS (ESI): $C_{39}H_{31}BN_4O$ Calculated for $[M-H]^+$ 465.2399, observed 465.2291

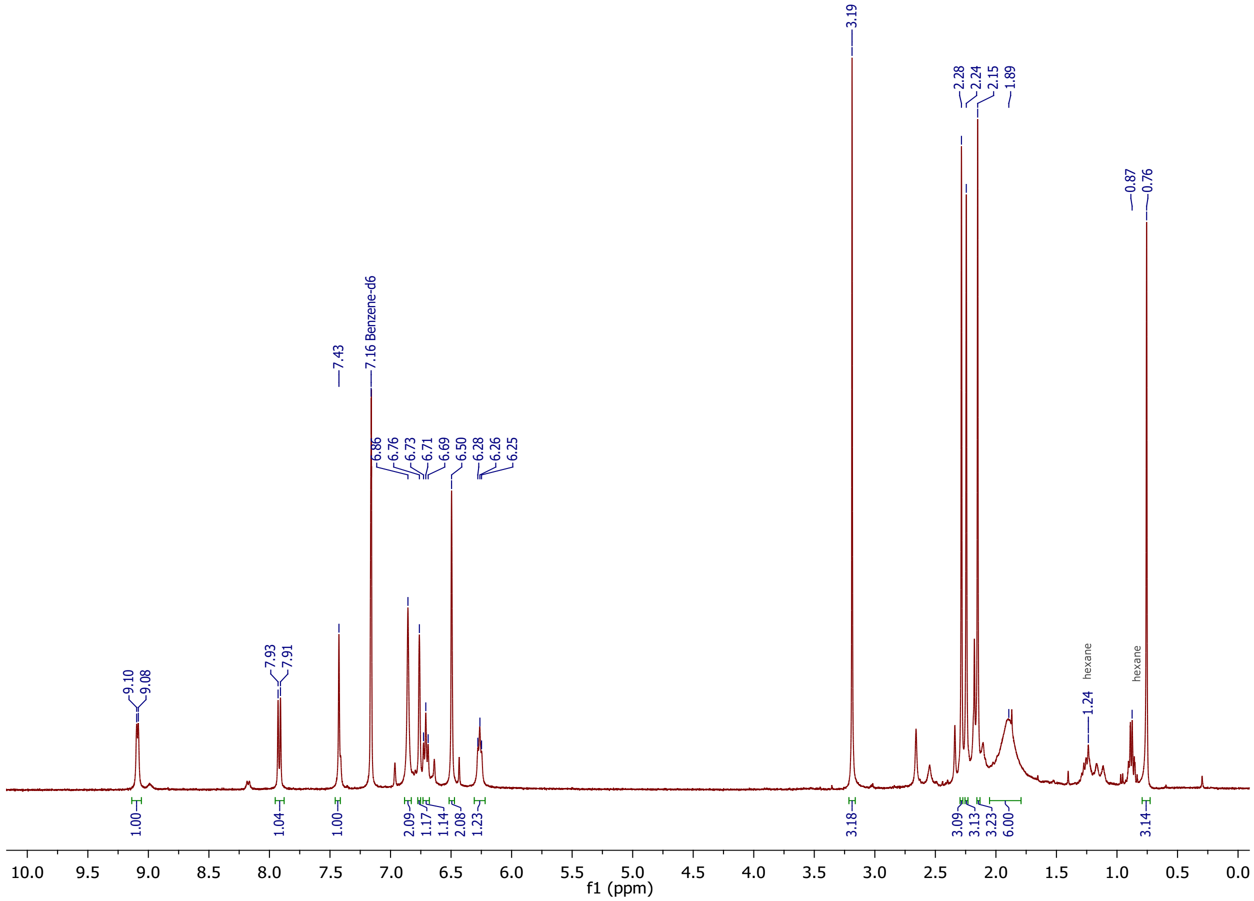


Figure S17: ^1H NMR spectrum of **6/7** in C_6D_6 in an approximate 9:1 ratio. The major product **6** is integrated and peak-picked.

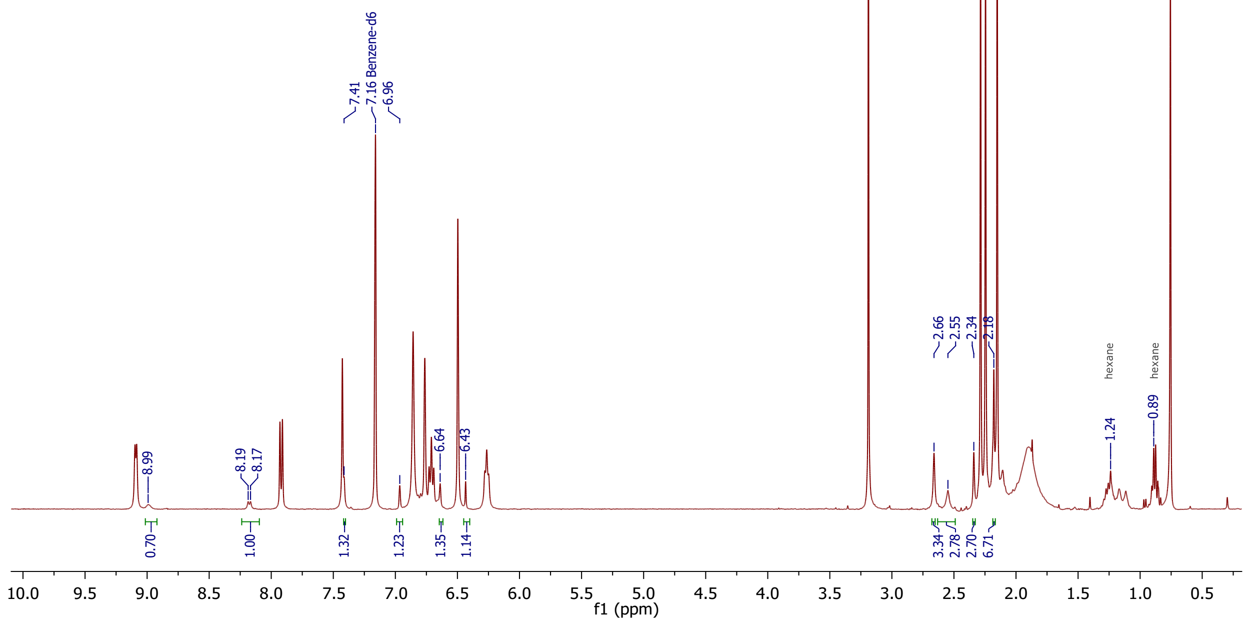


Figure S18: ^{1}H NMR spectrum of **6/7** in C_6D_6 in an approximate 9:1 ratio. The minor product **7** is integrated and peak-picked.

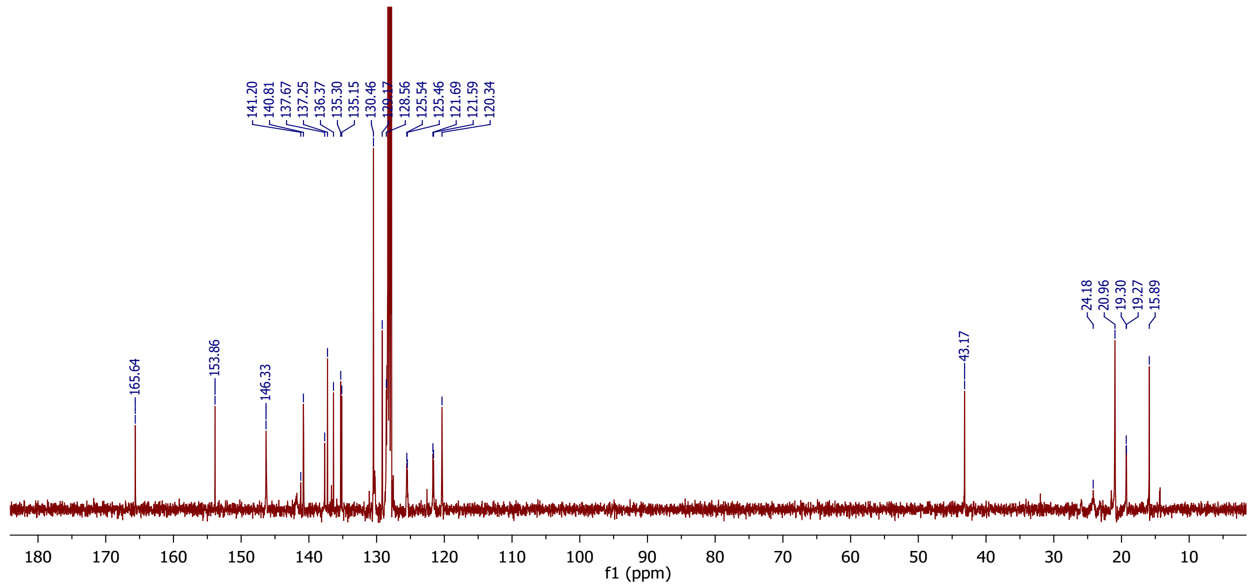


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6.

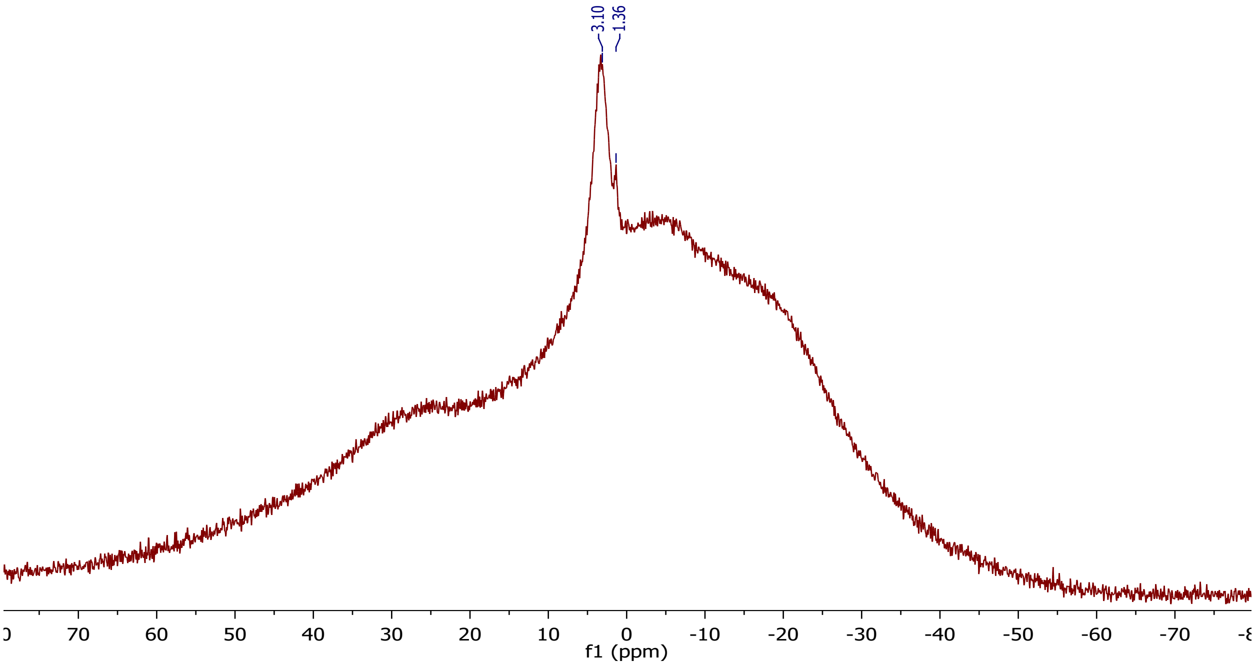


Figure S20: $^{11}B\{^{1}H\}$ NMR of **6/7** in C_6D_6 in an approximate 9:1 ratio.

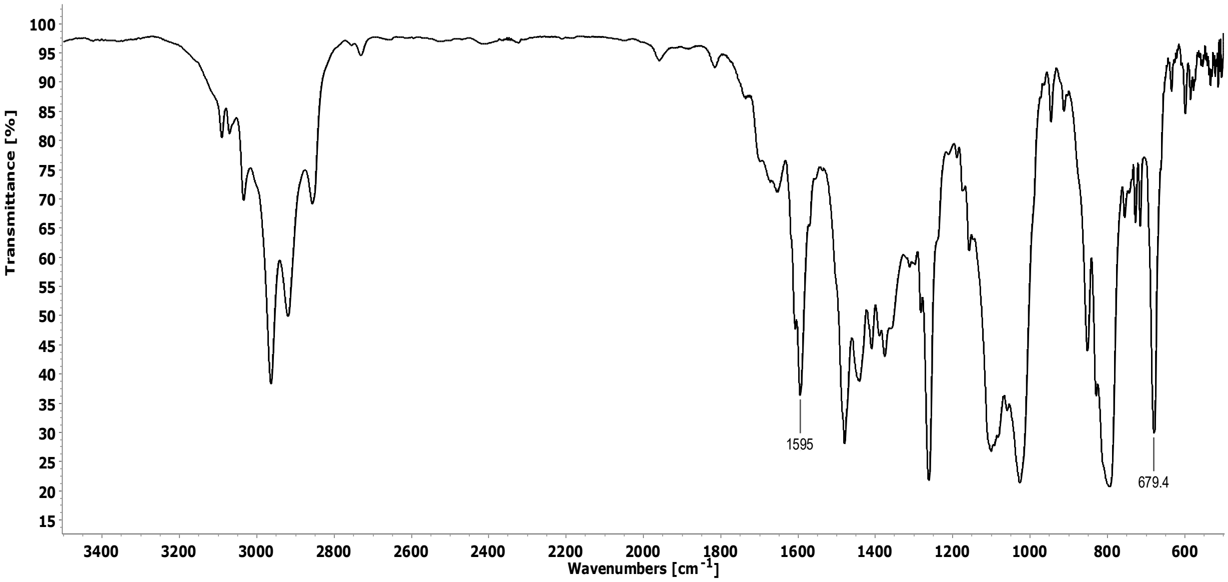
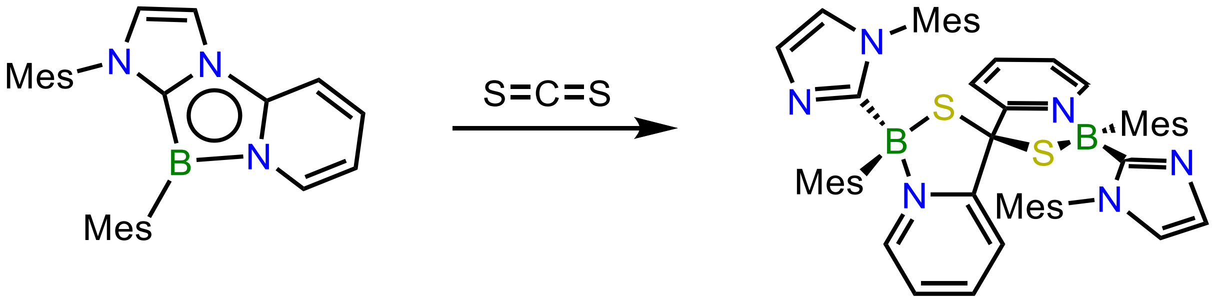


Figure S21: IR spectrum (KBr) of **6**.

Synthesis of 8:



CS_2 (7.7 mg, 0.1 mmol) was added to a stirred solution of **1** (80 mg, 0.20 mmol) in benzene (5 mL). An instantaneous colour change was observed from red to brown and the reaction mixture was allowed to stir for 1 hr at room temperature. Hexane (6 mL) was added to the solution causing the formation of a precipitate. The precipitate was collected, washed with hexane (3 mL x 3) and dried under vacuum to afford **8** as a light brown solid (47 mg, 53.4%). X-ray quality crystals were obtained from a saturated solution of **8** in THF.

^{1}H NMR (400.1 MHz, THF- *d*^{8}): δ = 8.68 (d, 2H, ^3J = 6.0 Hz, CH_{Py}), 7.72 (d, 2H, ^3J = 7.8 Hz, CH_{Py}), 7.66 (t, 2H, ^3J = 7.8 Hz, CH_{Py}), 7.41 (t, 2H, ^3J = 6.0 Hz, CH_{Py}), 6.96 (d, 2H, ^3J = 6.0 Hz, CH_{Imidaz}), 6.88 (s, 2H, CH_{Mes}), 6.76-6.66 (br m, 2H, CH_{Mes}), 6.62 (d, 2H, ^3J = 0.88 Hz, CH_{Imidaz}), 6.60-6.52 (br m, 2H, CH_{Mes}), 6.50 (s, 2H, CH_{Mes}), 2.32 (s, 6H, $CH_{3\text{-}Mes}$), 2.21 (s, 6H, $CH_{3\text{-}Mes}$), 2.11 (s, 6H, $CH_{3\text{-}Mes}$), 1.98 (br s, 6H, $CH_{3\text{-}Mes}$), 1.31 (br s, 6H, $CH_{3\text{-}Mes}$), 0.71 (s, 6H, $CH_{3\text{-}Mes}$) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, THF- *d*^{8}): δ = 166.04, 142.92, 137.86, 137.46, 136.31, 134.81, 134.38, 129.78, 129.70, 129.62, 129.24, 129.19, 128.35, 124.99, 123.14, 30.82 ppm.

Due to the limited solubility of **8** in all solvents, complete ^{13}C{^{1}H} NMR data could not be obtained. The reported spectrum was acquired with 80,000 scans of a saturated solution.

^{11}B{^{1}H} NMR (128.4 MHz, THF- *d*^{8}): δ = 5.7 ppm.

HRMS (ESI): $C_{53}H_{56}B_2N_6S_2$ Calculated for $[2M+H]^+$ 860.4261, observed 860.4270

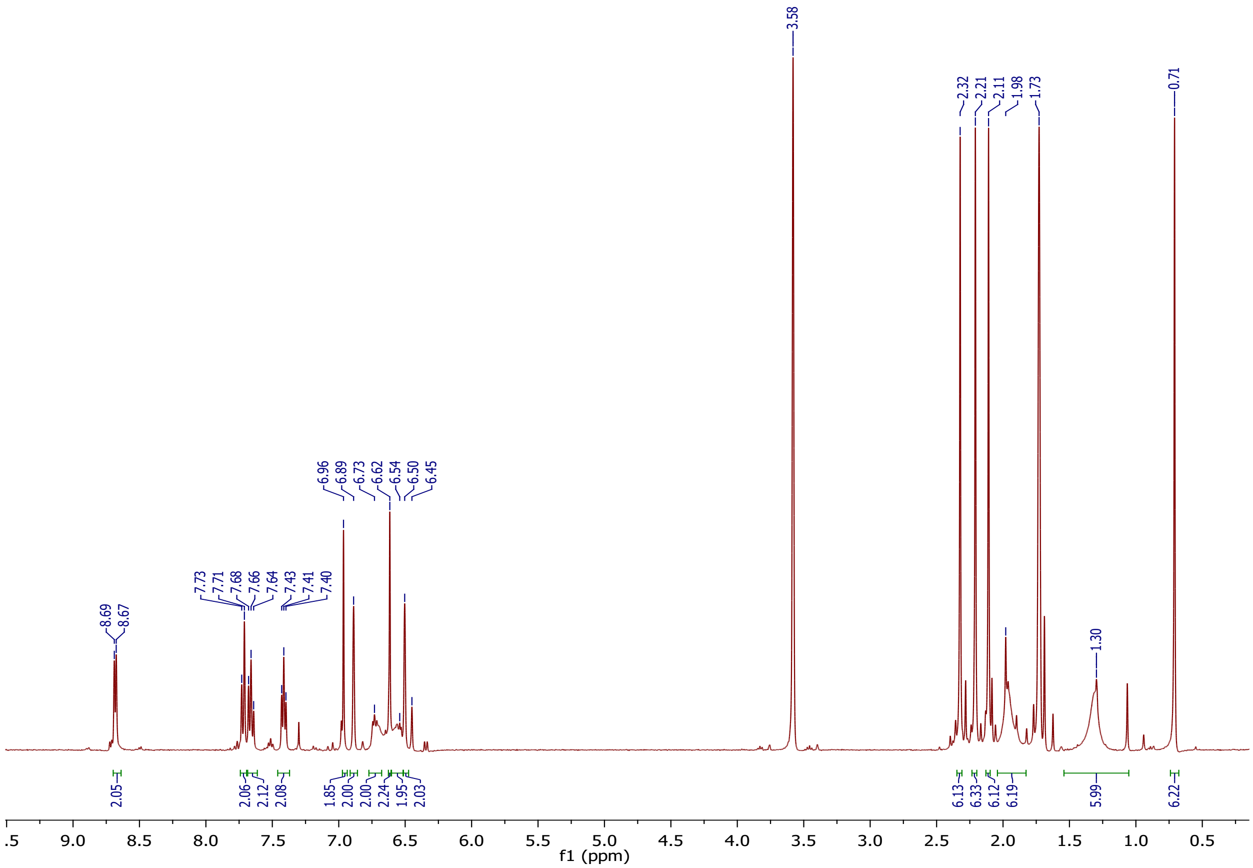


Figure S22: ^{1}H NMR spectrum of **8** in THF- *d*^{8}. Traces of unidentified diamagnetic impurities are present.

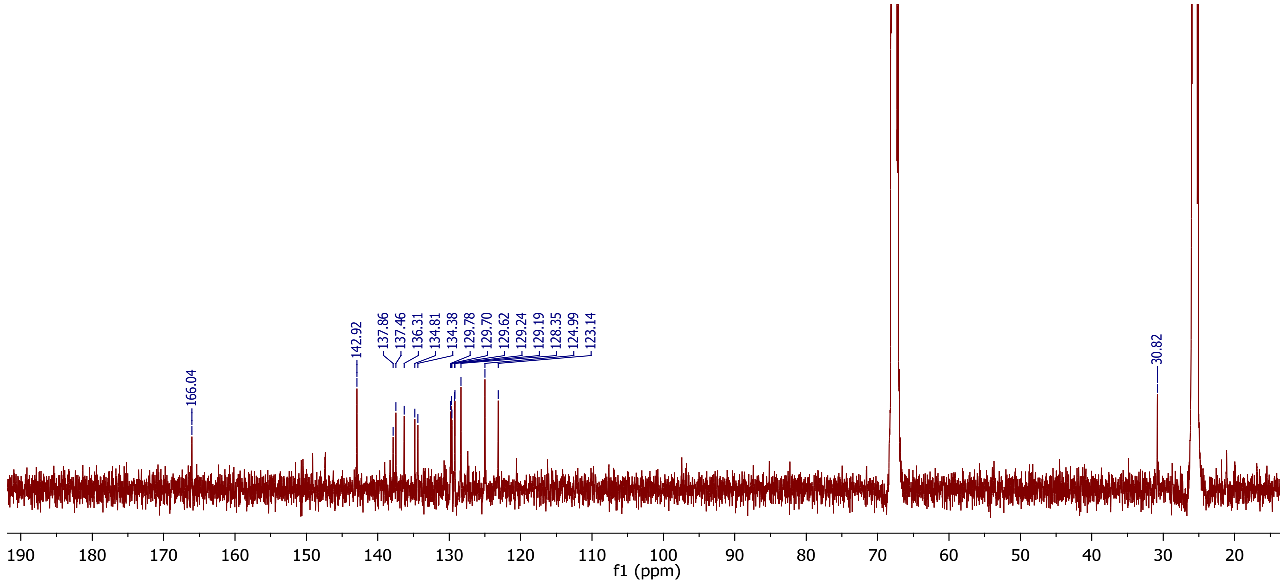


Figure S23: ^{13}C{^{1}H} NMR spectrum of **8** in THF- *d*^{8}.

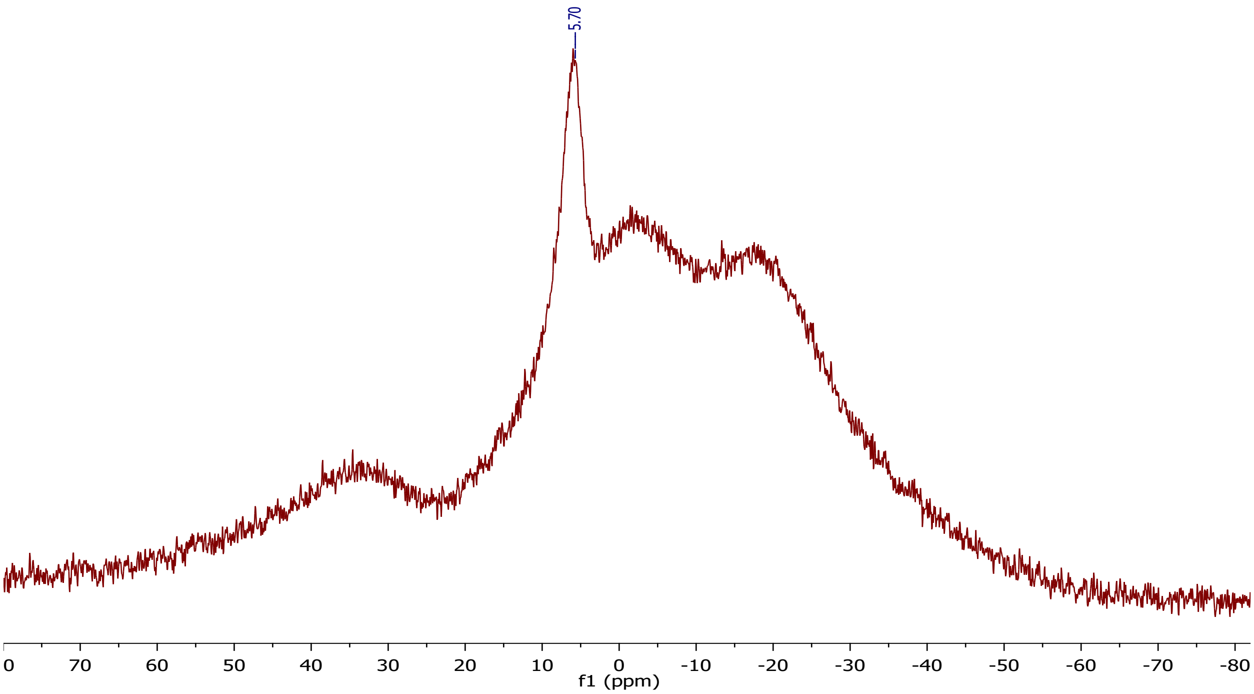


Figure S24: $^{11}B\{^{1}H\}$ NMR spectrum of **8** in THF-d^{8}.

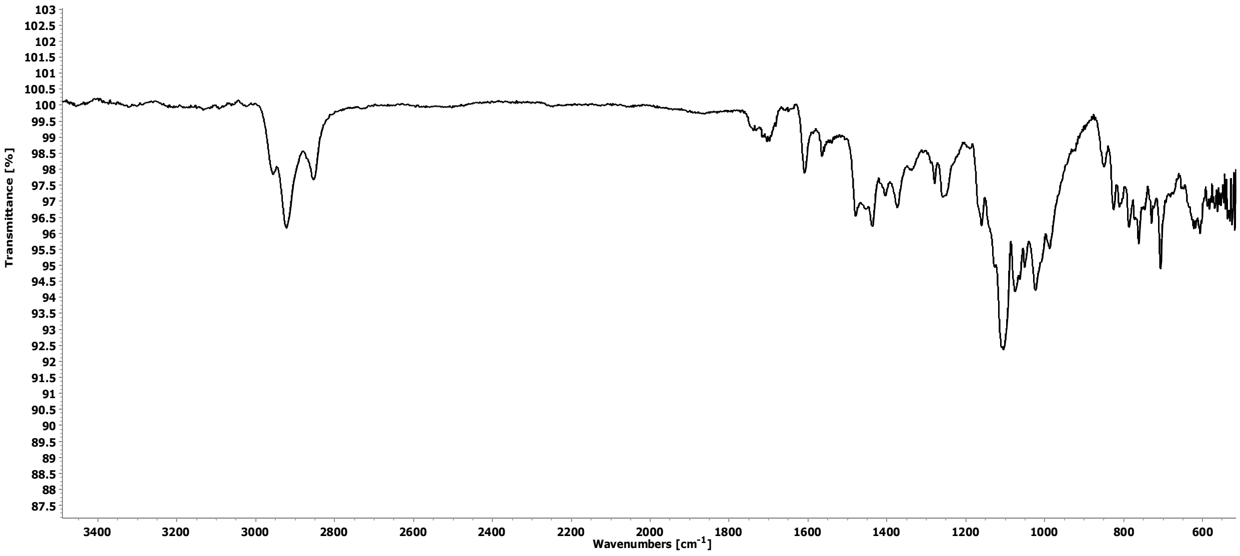


Figure S25: IR spectrum (KBr) of **8**.

2.) 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 a Bruker D8 QUEST ECO diffractometer using a graphite monochromator with Mo Kα (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 multi-scan 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. All non-hydrogen atoms were assigned anisotropic temperature factors in the absence of positional disordering. 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.

Table S1: Crystal data and structure refinement.

	2	**3**	**4**
CCDC#	2431184	2431182	2431179
Formula	$C_{27}H_{28}BN_3O_2$	$2(C_{39}H_{38}BN_3O),3(C_6H_6)$	$C_{34}H_{36}BN_3O$
Wt	437.33	1385.39	513.47
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	P 21/c	P 21/c	P c a 21
a(Å)	17.6177(11)	14.7375(7)	16.2727(6)
b(Å)	8.6944(5)	22.0921(11)	8.0712(3)
c(Å)	15.4216(9)	24.4726(13)	21.5149(9)
α(deg)	90	90	90
β(deg)	107.003(2)	101.945(2)	90
γ(deg)	90	90	90
V(Å^3)	2259.0(2)	7795.3(7)	2825.77(19)
Z	4	4	4
Theta(max)	25.060	25.250	25.362
d(calc) gcm^{-3}	1.286	1.18	1.207
R(int)	0.0874	0.0708	0.0834
Total data	17999	95442	64219
μ, mm^{-1}	0.081	0.07	0.072
>2σ(Fo^2)	3899	14095	5170
Parameters	305	999	360
R_1 (>2σ)	0.0615	0.0495	0.0406
R_w	0.1646	0.1147	0.0858
GOOF	1.051	1.024	1.061
$\Delta_{\rho max}$,$\Delta_{\rho min}$(eÅ^{-3})	0.28,−0.31	0.28,−0.21	0.18,−0.21

Table S1 continued: Crystal data and structure refinement.

	5	**6**	**6·6/7**	**8**
CCDC#	2431181	2431190	2431186	2431178
Formula	$C_{33}H_{33}BN_4S$	$C_{28}H_{31}BN_4S$	$2(C_{28}H_{31}BN_4S)$, C_2H_3NS	$C_{53}H_{56}B_2N_6S_2$, $2(C_4H_8O)$
Wt	528.50	466.44	1005.99	1006.99
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	P -1	P -1	P -1	C 2/c
a(Å)	7.5630(6)	9.4822(4)	10.7986(6)	17.886(3)
b(Å)	11.6778(9)	11.9253(5)	11.9758(6)	15.680(3)
c(Å)	16.8015(12)	12.6868(5)	21.0996(11)	20.640(3)
α(deg)	79.421(3)	62.2530(10)	102.707(2)	90
β(deg)	89.102(3)	75.2810(10)	90.477(2)	110.403(8)
γ(deg)	72.302(2)	83.1210(10)	99.590(2)	90
V($Å^3$)	1388.36(18)	1227.97(9)	2621.7(2)	5425.6(16)
Z	2	2	2	4
Theta(max)	25.343	25.680	25.352	24.953
d(calc) gcm^{-1}	1.264	1.261	1.274	1.233
R(int)	0.106	0.0590	0.0934	0.1728
Total data	31204	34732	53787	55807
μ, mm^{-1}	0.147	0.156	0.19	0.147
>2σ(F_O^2)	5079	4676	9585	4711
Parameters	359	314	662	399
R_1 (>2σ)	0.0555	0.0510	0.0820	0.0761
R_w	0.1199	0.1371	0.1763	0.1852
GOOF	1.041	1.043	1.089	1.121
$\Delta_{\rho max}$,$\Delta_{\rho min}$(e$Å^{-3}$)	0.29,−0.34	0.45,−0.37	0.42,−0.45	0.57,−0.60

3.) Density Functional Theory Calculations

All calculations were performed with Gaussian 16, Revision C.01[3]. Geometry optimizations were carried out at M062X-D3[4,5]/Def2SVP[6,7] level of theory. 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. Chemcraft[8] and GaussView[9] were used for visualizing optimized structures. xyz coordinates of all structures can be found in the additional computational information.

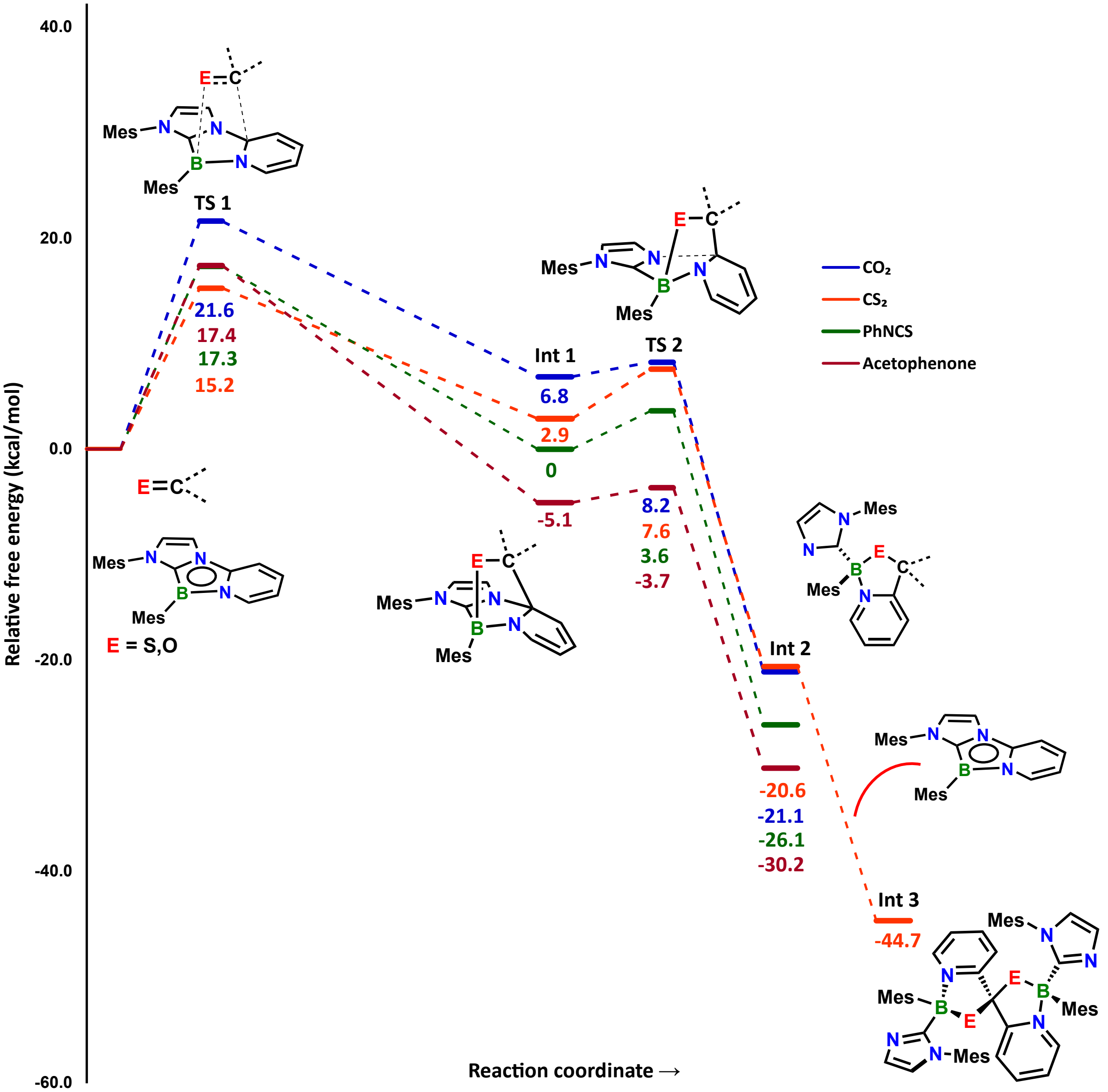


Figure S26: Computed reaction pathway for the formation of **2, 4, 5** and **8**. (M062X-D3/Def2SVP)

4.) Supplementary References

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