Transition metal-mediated Regioselective B(4)-H Hydroxylation/ Halogenation of *o*-carboranes Bearing a 2-pyridylsulfenyl Ligand

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Contents

Experimental details：

Materials:

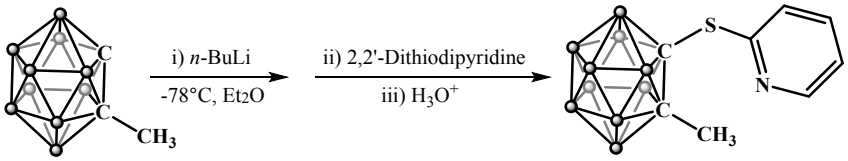
All reagents and solvents were purchased from commercial sources (Sigma Aldrich and Adamas-beta) and used as supplied unless otherwise mentioned. Nondeuterated solvents were dried and distilled under N_2 from appropriate drying agents. The materials $[Cp^*MCl_2]_2$ (M = Ir and Rh),[1] and 1-(2'-C_5H_4N)S-1,2-*o*-$C_2B_{10}H_{10}$[2] were prepared according to literature methods.

Methods:

NMR spectra were recorded on Bruker AVANCE I 400 and VANCE-DMX 500 Spectrometers. ^1H NMR spectra and ^{13}C NMR spectra were recorded on Bruker AVANCE I 400 and AVANCE NEO 400 Spectrometers. Spectra were recorded at room temperature and referenced to the residual protonated solvent for NMR spectra. Proton chemical shift (δ H = 7.26 ($CDCl_3$)) and (δ C = 77.16 ($CDCl_3$)) are reported relative to the solvent residual peak. Coupling constants are expressed in Hertz. $^{11}B\{H\}$ NMR (160 MHz) spectra were recorded with a Bruker AVANCE III HD spectrometer. Elemental analyses were performed on an Elementar Vario EL III analyzer. IR spectra of the solid samples (KBr tablets) in the range 400-4000 cm^{-1} were recorded on a Nicolet AVATAR360IR spectrometer. Mass spectra were obtained with a Micro TOF II mass spectrometer using electrospray ionization.

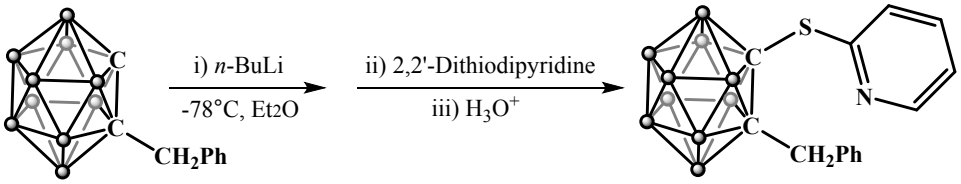
Experimental Section:

Synthesis of compound 1b



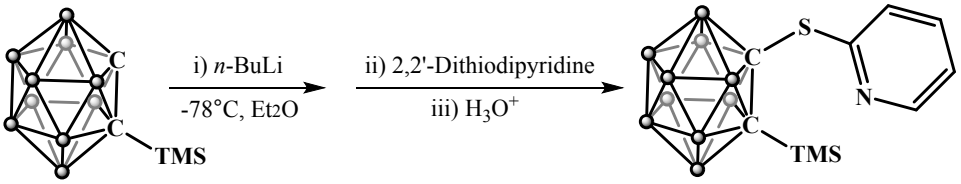
A suspension of *n*-BuLi (1.6 mol/L in *n*-hexane, 0.65 ml, 1.0 mmol) was added to a solution of *o*-CH_3-carborane (158.2 mg, 1 mmol) in diethyl ether 6 ml at -78 °C over a period of 3 h, then 2,2'-Dithiodipyridine (440.62 mg, 2 mmol) was added at room temperature and the resulting mixture was stirred for 12h. The reaction mixture was quenched with dilute HCl and the organic phase was separated and the water phase extracted with diethyl ether (3 × 10 mL). The solvent was then removed under vacuo and the residue was purified by column chromatography on silica gel (CH_2Cl_2/*n*-hexane= 1:4). A white solid was obtained and dried under vacuum to give the compound **1b** (yield: 201.2 mg, 75%). ^1H NMR (400 MHz; $CDCl_3$, ppm): δ = 2.293 (s, 3H, CH_3-H), 7.420 (ddd, J = 7.6, 3.2, 0.4 Hz, 1H, Py-H), 7.697 (dt, J = 8, 0.8 Hz, 1H, Py-H), 7.784 (td, J = 7.6, 1.6 Hz, 1H, Py-H), 8.664 (ddd, J = 4.4, 1.6, 0.8 Hz, 1H, Py-H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$, ppm): δ = 23.84 (CH_3-C), 79.60, 88.66 (cage C), 125.40, 132.50, 138.03, 151.00, 152.59 (Py-C). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, ppm): δ = -9.89 (6B), -8.67 (2B), -4.79 (1B), -3.47 (1B). IR (KBr, disk): *v* (B–H) = 2587 cm^{-1}. Anal. calcd for compound **1b** ($C_8H_{17}B_{10}SN$): C, 35.82; H, 6.39; N, 5.22. Found: C, 35.98; H, 6.81; N, 4.99. ESI-MS: m/z = 268.219 (calcd for $[M+H]^+$ 268.219).

Synthesis of compound 1c



A suspension of *n*-BuLi (1.6 mol/L in *n*-hexane, 0.65 ml, 1.0 mmol) was added to a solution of *o*-CH_2Ph-carborane (237.2 mg, 1 mmol) in ether 6 ml at -78 °C over a period of 3 h, then 2,2'-Dithiodipyridine (440.62 mg, 2 mmol) was added at room temperature and the resulting mixture was stirred for 12h. The reaction mixture was quenched with dilute HCl and the organic phase was separated and the water phase extracted with diethyl ether (3 × 10 mL). The solvent was then removed under vacuo and the residue was purified by column chromatography on silica gel (CH_2Cl_2/*n*-hexane= 1:4). A white solid was obtained and dried under vacuum to give the compound **1c** (yield: 276.2 mg, 80%). ^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 3.958 (s, 2H, CH_2-H), 7.325 (m, 5H, Ph-H), 7.439 (dd, J = 6.4 Hz, 1.6H, Py-H), 7.808 (m, 2H, Py-H), 8.731 (dd, J = 5.2, 1.2 Hz, 1H, Py-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, ppm): δ = 40.83 (CH_2-C), 83.35, 84.33 (cage C), 125.55, 132.43, 138.11, 150.94, 152.41 (Py-C), 127.83, 128.52, 130.55, 136.10 (Ph-C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, ppm): δ = -10.89 (4B), -9.87 (2B), -9.08 (2B), -3.97 (2B). Anal. calcd for compound **1c** ($C_{14}H_{23}B_{10}SN$): C, 48.67; H, 6.71; N, 4.05. Found: C, 48.93; H, 7.21; N, 3.95. ESI-MS: m/z = 334.24 (calcd for $[M+H]^+$ 334.24).

Synthesis of compound 1d



A suspension of *n*-BuLi (1.6 mol/L in *n*-hexane, 0.65 ml, 1.0 mmol) was added to a solution of *o*-TMS-carborane (216.4 mg, 1 mmol) in ether 6 ml at -78 °C over a period of 3 h, then 2,2'-Dithiodipyridine (440.62 mg, 2 mmol) was added at room temperature and the resulting mixture was stirred for 12h. The reaction mixture was quenched with dilute HCl and the organic phase was separated and the water phase extracted with diethyl ether (3 × 10 mL). The solvent was then removed under vacuo and the residue was purified by column chromatography on silica gel (CH_2Cl_2/*n*-hexane= 1:4). A white solid was obtained and dried under vacuum to give the compound **1d** (yield: 250.6 mg, 77%). ^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 0.444 (s, 9H, TMS-H), 7.368 (ddd, J = 6, 4.8, 1.2 Hz, 1H, Py-H), 7.626 (d, J = 8 Hz, 1H, Py-H), 7.745 (td, J = 7.6, 2 Hz, 1H, Py-H), 8.668 (d, J = 4.4, 2 Hz, 1H, Py-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, ppm): δ = 0.79 (TMS-C), 79.15, 79.56 (cage C), 125.01, 131.73, 137.64, 150.87, 152.60 (Py-C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, ppm): δ = –10.48 (4B), -7.37 (4B), -2.84 (1B), -0.05 (1B). IR (KBr, disk): *v* (B–H) = 2599 cm^{-1}. Anal. calcd for compound **1d** ($C_{10}H_{23}B_{10}SNSi$): C, 36.89; H, 7.12; N, 4.30. Found: C, 36.93; H, 7.51; N, 4.99.

Synthesis of *o*-carborane complex 2

To a solution of ligand **1a** (25.3 mg, 0.1 mmol) in CH_2Cl_2 (6 mL), AgOTf (51.4 mg, 0.2 mmol), $[Cp^*IrCl_2]_2$ (40.0 mg, 0.05 mmol), and CH_3COOK (0.1mmol, 10mg) were added and

the mixture was stirred for an additional 3 days. The obtained suspension was filtered. The filtrate was concentrated under vacuum and purified by column chromatography using silica gel (CH_2Cl_2/EA/*n*-hexane= 1:1:4). An orange solution was obtained, and evaporation of the volatiles under vacuum gave the complex **2** (yield: 40.6 mg, 68%). ^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 1.505 (s, 15H, Cp*-H), 3.595 (s, 1H, Cage C-H), 7.241 (t, J = 1.6 Hz, 1H, Py-H), 7.573 (dd, J = 8, 1.2 Hz, 1H, Py-H), 7.689 (td, J = 7.6, 1.2 Hz, 1H, Py-H), 9.529 (dd, J = 6, 1.6 Hz, 1H, Py-H). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, ppm): δ = -11.84 (2B), -9.87 (1B), -7.33 (2B), -6.24 (1B), -5.12 (2B), -3.83 (1B), -2.56 (1B). IR (KBr, disk): *υ* (B–H) = 2596 cm^{-1}. Anal. calcd for complex **2** ($C_{17}H_{29}B_{10}IrNClS$): C, 33.19; H, 4.75; N, 2.28. Found: C, 33.62; H, 5.20; N, 2.60.

Synthesis of *o*-carborane complex 3

To a solution of compound **1b** (26.8 mg, 0.1 mmol) in CH_2Cl_2 (6 mL), AgOTf (51.4 mg, 0.2 mmol), [Cp*$IrCl_2$]$_2$ (40.0 mg, 0.05 mmol), and CH_3COOK (0.1mmol, 10mg) were added and the mixture was stirred for an additional 3 days. The obtained suspension was filtered. The filtrate was concentrated under vacuum and purified by column chromatography using silica gel (CH_2Cl_2/EA/*n*-hexane= 1:1:2). An orange solution was obtained, and evaporation of the volatiles under vacuum gave the complex **3** (yield: 45.9 mg, 73%). ^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 1.514 (s, 15H, Cp*-H), 1.951 (s, 1H, CH_3-H), 7.199 (td, J = 6.0, 1.2 Hz, 1H, Py-H), 7.461 (d, J = 6.8 Hz, 1H, Py-H), 7.620 (td, J = 7.6, 1.2 Hz, 1H, Py-H), 9.607 (dd, J = 5.6, 1.2 Hz, 1H, Py-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, ppm): δ = 8.96 (Cp*-C), 15.52 (CH_3-C), 23.84, 29.85 (cage C), 90.37 (Cp*-C), 125.16, 128.55, 137.12, 157.13, 160.46 (Py-C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, ppm): δ = -10.63 (4B), -8.95 (1B), -7.83 (1B), -6.59 (1B), -5.05 (1B), -3.54 (2B). IR (KBr, disk): *υ* (B–H) = 2565 cm^{-1}. Anal. calcd for complex **3** ($C_{18}H_{31}B_{10}IrNClS$): C, 43.35; H, 4.97; N, 2.22. Found: C, 43.72; H, 5.42; N, 2.41.

Synthesis of *o*-carborane complex 4

To a solution of compound **1a** (25.3 mg, 0.1 mmol) in CH_2Cl_2 (6 mL), AgOTf (51.4 mg, 0.2 mmol), [Cp*$RhCl_2$]$_2$ (30.9 mg, 0.05 mmol), and CH_3COOK (0.1mmol, 10mg) were added and the mixture was stirred in N_2 atmosphere for an additional 3 days. The obtained suspension was filtered. The filtrate was concentrated under vacuum and purified by column chromatography using silica gel (CH_2Cl_2/EA/*n*-hexane= 1:1:2). An orange solution was obtained, and evaporation of the volatiles under vacuum gave the complex **4** (yield: 18.8 mg, 39%). ^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 2.090 (s, 15H, Cp*-H), 7.385 (ddd, J = 6, 5.2, 1.2 Hz, 1H, py-H), 7.433 (d, J = 7.6 Hz, 1H, Py-H), 7.769 (td, J = 8, 2 Hz, 1H, Py-H), 8.624 (dd, J = 4.8, 1.2 Hz, 1H, Py-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, ppm): δ = 9.83 (Cp*-C), 63.10, 63.22 (cage C), 104.62 (Cp*-C), 124.58, 133.07, 137.17, 150.27, 154.97 (Py-C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, ppm): δ = -21.19 (1B), -18.16 (1B), -16.59 (1B), -10.62

(1B), -7.68 (1B), -3.02 (1B), -1.00 (1B), 0.31 (1B), 9.40 (1B). Anal. calcd for complex **4** ($C_{17}H_{29}B_9SNRh$): C, 42.57; H, 6.09; N, 2.92. Found: C, 43.03; H, 6.55; N, 3,18.

Synthesis of *o*-carborane complex 5

To a solution of compound **1b** (26.8 mg, 0.1 mmol) in CH_2Cl_2 (6 mL), AgOTf (51.4 mg, 0.2 mmol), [Cp*$RhCl_2$]$_2$ (30.9 mg, 0.05 mmol), and CH_3COOK (0.1mmol, 10mg) were added and the mixture was stirred for an additional 3 days. The obtained suspension was filtered. The filtrate was concentrated under vacuum and purified by column chromatography using silica gel (CH_2Cl_2/EA/*n*-hexane= 1:1:2). An orange solution was obtained, and evaporation of the volatiles under vacuum gave the complex **5** (yield: 23.2 mg, 43%). ^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 1.489 (s, 15H, Cp*-H), 1.29-3.24 (br, 9H, B-H), 1.955 (s, 1H, CH_3-H), 5.19 (s, 1H, CH), 9.772 (dd, J = 5.6, 1.6 Hz, 1H, Py-H), 7.660 (td, J = 7.6, 2 Hz, 1H, Py-H), 7.441 (d, J = 6.4 Hz, 1H, Py-H), 7.292 (td, J = 7.2, 1.2 Hz, 1H, Py-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, ppm): δ = 9.36 (Cp*-C), 23.70 (CH_3-C), 52.47, 82.03 (cage C), 97.34 (Cp*-C), 124.24, 128.21, 137.47, 157.33, 159.56 (Py-C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, ppm): δ =-11.33 (1B), -10.23 (3B), -8.75 (1B), -7.26 (1B), -5.56 (1B), -3.22 (2B), 2.99 (1B). IR (KBr, disk): υ (B–H) = 2597 cm^{-1}. Anal. calcd for complex **5** ($C_{18}H_{31}B_{10}RhNClS$): C, 40.03; H, 5.79; N, 2.59. Found: C, 40.50; H, 6.19; N, 2.92.

Synthesis of *o*-carborane complex 6

Method 1: NBS (10.7 mg, 0.06 mmol) and AgOTf (12.9 mg, 0.05 mmol) were added to the complex **5** (27 mg, 0.05 mmol) in DCE (Dichloroethane). The reaction mixture was stirred for 24h at 65 ℃ then filtered. The filtrate was concentrated and further purified via silica gel chromatography (CH_2Cl_2/*n*-hexane= 2：5). White solids were obtained and dried under vacuo to give the complex **6**: (yield:15.8 mg, 91%).

Method 2: To a solution of ligand **1b** (26.8 mg, 0.1 mmol) in DCE (6 mL), AgOTf (51.4 mg, 0.2 mmol), [Cp*$RhCl_2$]$_2$ (30.9 mg, 0.05 mmol), NBS (17.8 mg, 0.1mmol) and CH_3COONa (0.1mmol, 9mg) were added and the mixture was stirred for 12h at 65 ℃. The obtained suspension was filtered. The filtrate was concentrated under vacuum and purified by column chromatography using silica gel (CH_2Cl_2/*n*-hexane= 2：3). A colorless solution was obtained, and evaporation of the volatiles under vacuum gave the complex **6** (yield: 32.9 mg, 95%).

^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 2.366 (s, H, CH_3-H), 7.415 (m, 1H, Py-H), 7.801 (m, J = 1.6 Hz, 1H, Py-H), 8.672 (d, J = 5.2 Hz, 1H, Py-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, ppm): δ = 24.03 (CH_3-C), 81.00, 81.36 (cage C), 125.57, 133.15, 138.01, 151.01, 152.02 (Py-C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, ppm): δ =-13.27 (1B), -10.62 (3B), -9.01 (3B), -5.29 (1B), -3.91 (1B), -3.09 (1B). ESI-MS: m/z = 347.12 (calcd for $[M+H]^+$ 347.12).

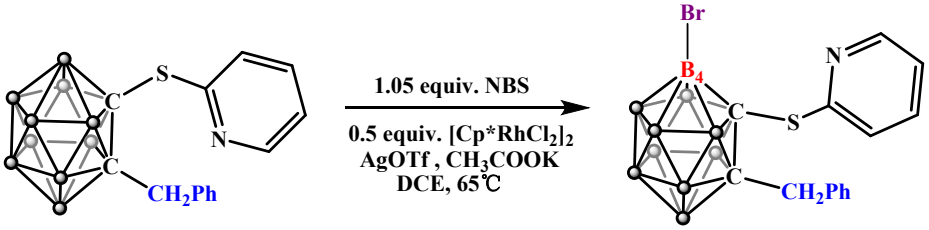
Synthesis of *o*-carborane complex 7

Method 1: NIS (13.5 mg, 0.06 mmol) and AgOTf (12.9 mg, 0.05 mmol) were added to the complex **5** (27 mg, 0.05 mmol) in DCE. The reaction mixture was stirred for 24h at 65 ℃ then filtered. The filtrate was concentrated and further purified via silica gel chromatography (CH_2Cl_2/*n*-hexane= 2：5). White oil were obtained and dried under vacuo to give the complex **7**: (yield:16.4 mg, 83%).

Method 2: To a solution of ligand **1b** (26.8 mg, 0.1 mmol) in DCE (Dichloroethane) (6 mL), AgOTf (51.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol), NIS (22.5mg, 0.1mmol) and CH_3COONa (0.1mmol, 9mg) were added and the mixture was stirred for 12h at 65 ℃. The obtained suspension was filtered. The filtrate was concentrated under vacuum and purified by column chromatography using silica gel (CH_2Cl_2/*n*-hexane= 2：3). A colorless solution was obtained, and evaporation of the volatiles under vacuum gave the complex **7** (yield: 33.8 mg, 86%).

^1H NMR (400 MHz; $CDCl_3$, ppm): δ = 2.360 (s, H, CH_3-H), 7.420 (m, 1H, Py-H), 7.809 (m, 1H, Py-H), 8.668 (ddd, J = 4.8, 2, 1.2 Hz, 1H, Py-H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$, ppm): δ = 23.34 (CH_3-C), 80.75, 81.34 (cage C), 125.59, 133.06, 138.02, 151.05, 152.32 (Py-C). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, ppm): δ =-19.74 (1B), -11.28 (1B), -9.58 (2B), -8.03 (2B), -2.81 (1B), -2.32 (1B). ESI-MS: m/z = 394.11 (calcd for $[M+H]^+$ 394.11).

Synthesis of *o*-carborane complex 6c



1c **6c, 84%**

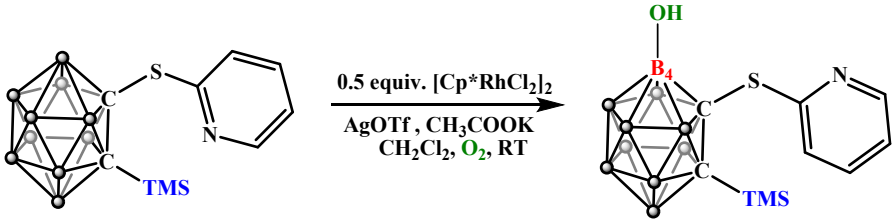
To a solution of ligand **1c** (26.8 mg, 0.1 mmol) in DCE (Dichloroethane) (6 mL), AgOTf (51.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol), NBS (17.8mg, 0.1mmol) and CH_3COONa (0.1mmol, 9mg) were added and the mixture was stirred for 12h at 65 ℃. The obtained suspension was filtered. The filtrate was concentrated under vacuum and purified by column chromatography using silica gel (CH_2Cl_2/*n*-hexane= 1：3). A colorless solution was obtained, and evaporation of the volatiles under vacuum gave the complex **6c** (yield: 35.6 mg, 84%). ^1H NMR (400 MHz; $CDCl_3$, ppm): δ = 2.366 (s, H, CH_3-H), 7.415 (m, 1H, Py-H), 7.801 (m, J = 1.6 Hz, 1H, Py-H), 8.672 (d, J = 5.2 Hz, 1H, Py-H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$, ppm): δ = 41.00 (CH_2-C), 84.02, 86.04 (cage C), 125.73, 133.15, 138.10, 151.02, 152.04 (Py-C), 128.04, 128.66, 130.60, 135.85 (Ph-C). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, ppm): δ =-14.33 (1B), -11.84 (2B), -10.34 (2B), -8.81 (2B), -5.63 (1B), -3.84 (1B), -2.98 (1B). ESI-MS: m/z = 424.15 (calcd for $[M+H]^+$ 424.16).

Synthesis of *o*-carborane complex 8

Compound **1b** (26.8mg, 0.10 mmol), $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol), AgOTf (51.4 mg, 0.2 mmol), and CH_3COOK (0.1mmol, 10mg) were mixed in CH_2Cl_2 (5 mL). After the reaction mixture was cooled to –78 °C, the reaction tube was evacuated and back-filled with O_2 (3

times, balloon). The reaction tube was then closed after the reaction temperature was warmed to room temperature. The resulting mixture was stirred at 35 ℃ for 26 h. The obtained suspension was filtered. The filtrate was concentrated under vacuum and purified by column chromatography using silica gel (CH_2Cl_2/EA/*n*-hexane= 1:1:3). An white solution was obtained, and evaporation of the volatiles under vacuum gave the complex **8** (yield: 21.0 mg, 74%). ^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 2.077 (s, 1H, CH_3-H), 6.922 (s, 1H, OH-H), 7.420 (ddd, J = 7.2, 3.2, 0.4 Hz, 1H, Py-H), 7.578 (d, J = 7.6 Hz, 1H, Py-H), 7.791 (td, J = 7.6, 2 Hz, 1H, Py-H), 8.653 (dd, J = 4.8, 1.2 Hz, 1H, Py-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, ppm): δ = 23.40 (CH_3-C), 76.57, 78.02 (cage C), 125.01, 129.07, 139.10, 150.68, 152.93 (Py-C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, ppm): δ = -19.21 (1B), -13.26 (2B), -11.06 (3B), -17.50 (2B), -6.68 (1B), 5.96 (1B). IR (KBr, disk): *v* (B–H) = 2565 cm^{-1}. Anal. calcd for complex **8** ($C_8H_{17}B_{10}SNO$): C, 33.80; H, 6.03; N, 4.93. Found: C, 34.23; H, 6.48; N, 4.45. ESI-MS: m/z = 284.21 (calcd for $[M+H]^+$ 284.21).

Synthesis of *o*-carborane complex 8d



1d **8d, 50%**

Compound **1d** (26.8mg, 0.10 mmol), $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol), AgOTf (51.4 mg, 0.2 mmol), and CH_3COOK (0.1mmol, 10mg) were mixed in CH_2Cl_2 (5 mL). After the reaction mixture was cooled to –78 °C, the reaction tube was evacuated and back-filled with O_2 (3 times, balloon). The reaction tube was then closed after the reaction temperature was warmed to room temperature. The resulting mixture was stirred at room temperature for 72 h. The obtained suspension was filtered. The filtrate was concentrated under vacuum and purified by column chromatography using silica gel (CH_2Cl_2/EA/*n*-hexane= 1:1:6). An white solution was obtained, and evaporation of the volatiles under vacuum gave the complex **8d** (yield: 17.16 mg, 50%). ^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 0.296 (s, 9H, TMS-H), 7.385 (ddd, J = 6, 5.2, 1.2 Hz, 1H, Py-H), 7.433 (d, J = 7.6 Hz, 1H, Py-H), 7.769 (td, J = 8, 2 Hz, 1H, Py-H), 8.624 (dd, J = 4.8, 1.2 Hz, 1H, Py-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, ppm): δ = 1.16 (TMS-C), 31.37, 38.30 (cage C), 124.43, 127.36, 138.80, 150.27, 153.66 (Py-C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, ppm): δ = -19.91 (1B), -13.97 (1B), -12.77 (1B), -11.68 (1B), -10.86 (1B), -8.96 (1B), -6.99 (1B), -5.61 (1B), -1.82 (1B), 7.07 (1B). Anal. calcd for complex **8d** ($C_{10}H_{23}B_{10}SNOSi$): C, 35.17; H, 6.79; N, 4.10. Found: C, 34.77; H, 7.45; N, 4.45.

Synthesis of *o*-carborane complex 9

Compound **8** (42.6 mg, 0.15 mmol), anhydrous potassium carbonate (52.50 mg, 0.37 mmol) and benzyl bromide (75 μL, 0.60 mmol) were mixed in acetonitrile (5 mL). The resultant mixture was heated at 90 ℃ for 12 h. After filtration, the filtrate was concentrated to dryness in vacuo. The residue was subjected to column chromatography, giving **9** as colorless oil (46.5 mg, 83%). ^{1}H NMR (400 MHz; $CDCl_3$, ppm): δ = 2.305 (s, 1H, CH_3-H), 4.852 (d, J = 12.4Hz, 1H, CH_2-H), 4.958 (d,

1H, CH_2-H), 7.302 (m, 2H, Ph-H), 7.378 (t, J = 7.2 Hz, 2H, Py-H), 7.445 (s, 1H, Ph-H) 7.463 (s, 1H, Ph-H), 7.653 (m, 2H, Ph-H), 7.578 (dt, J = 5.2, 1.2 Hz, 1H, Py-H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$, ppm): δ = 23.25 (CH_3-C), 31.64, 80.11 (cage C), 72.38 (CH_2-C), 125.18, 128.45, 137.76, 150.71, 152.39 (Py-C), 127.31, 127.61, 132.96, 139.50 (Ph-C). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, ppm): δ = -18.57 (1B), -13.55 (1B), -12.68 (3B), -10.92 (2B), -7.32 (1B), -5.88 (1B), 6.72 (1B).

NMR spectra:

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **1b.**

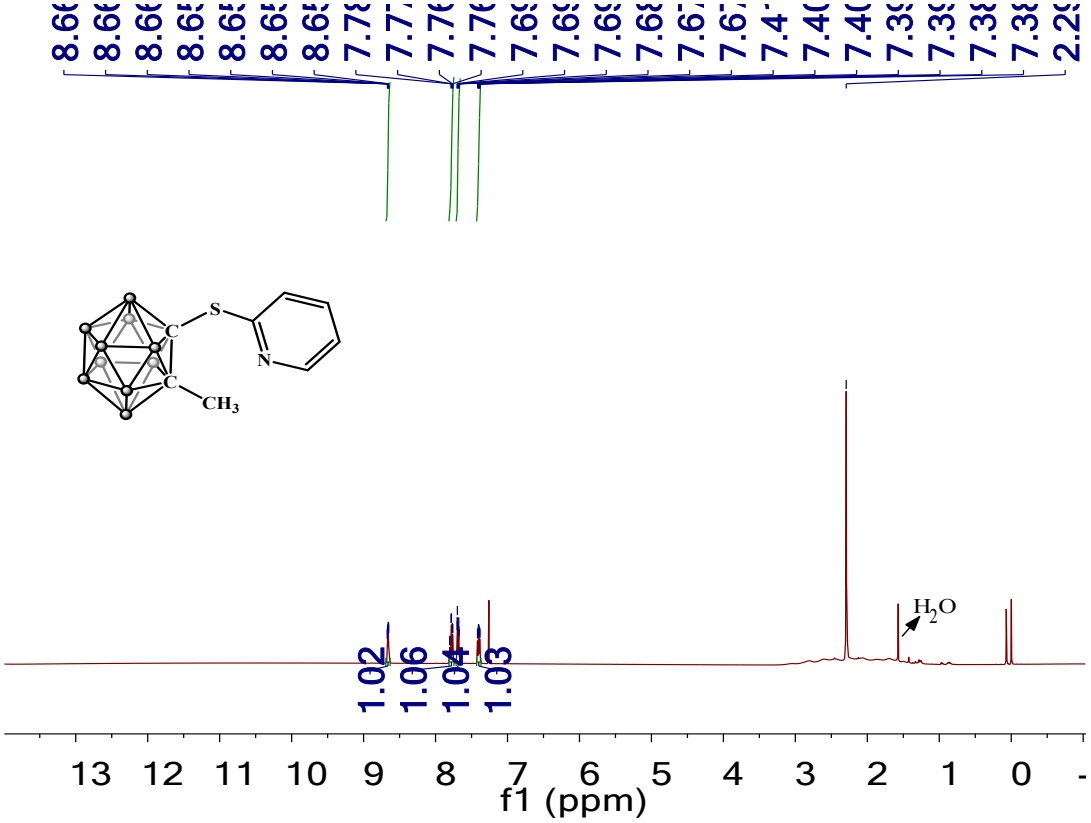


Figure S2. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **1b**.

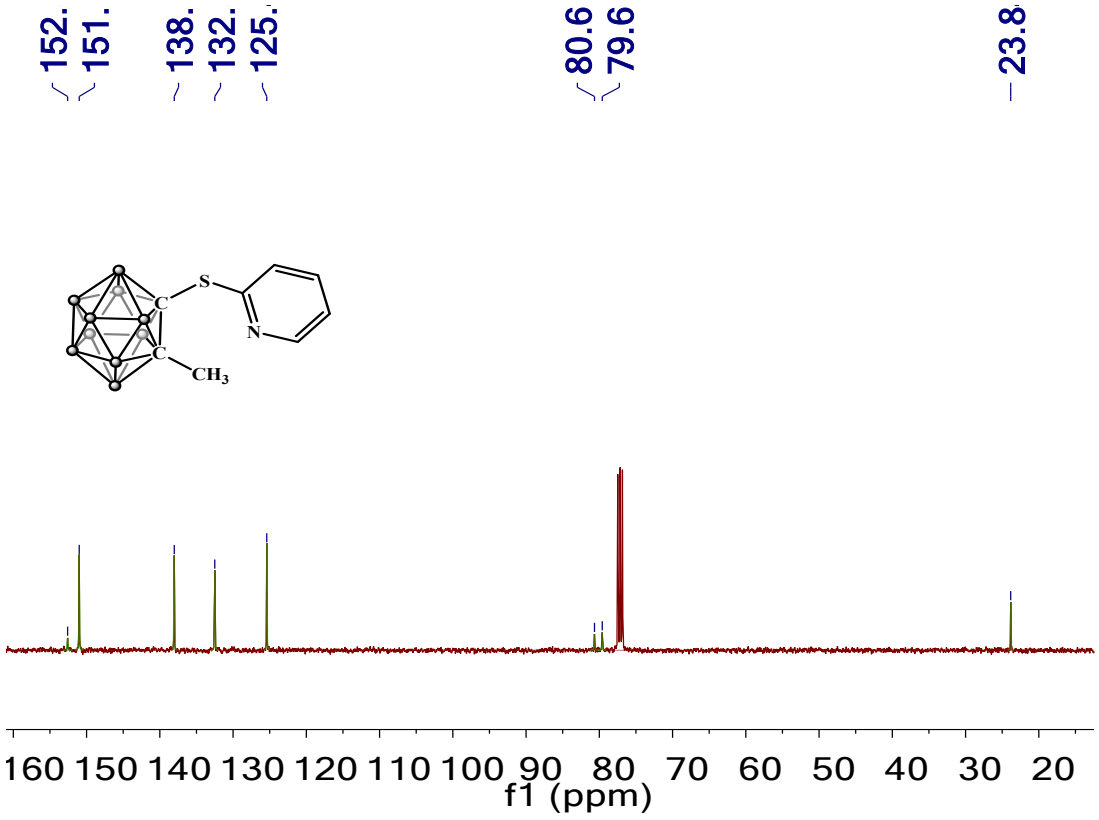


Figure S3. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **1b**.

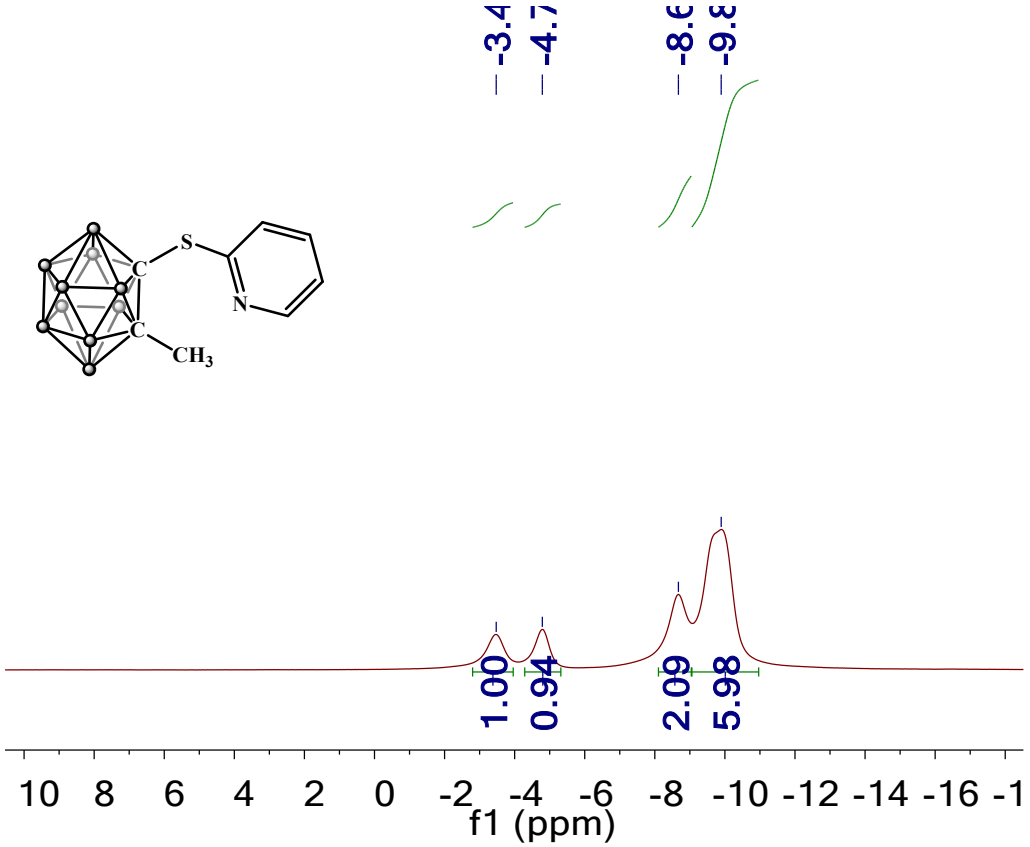


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **1c.**

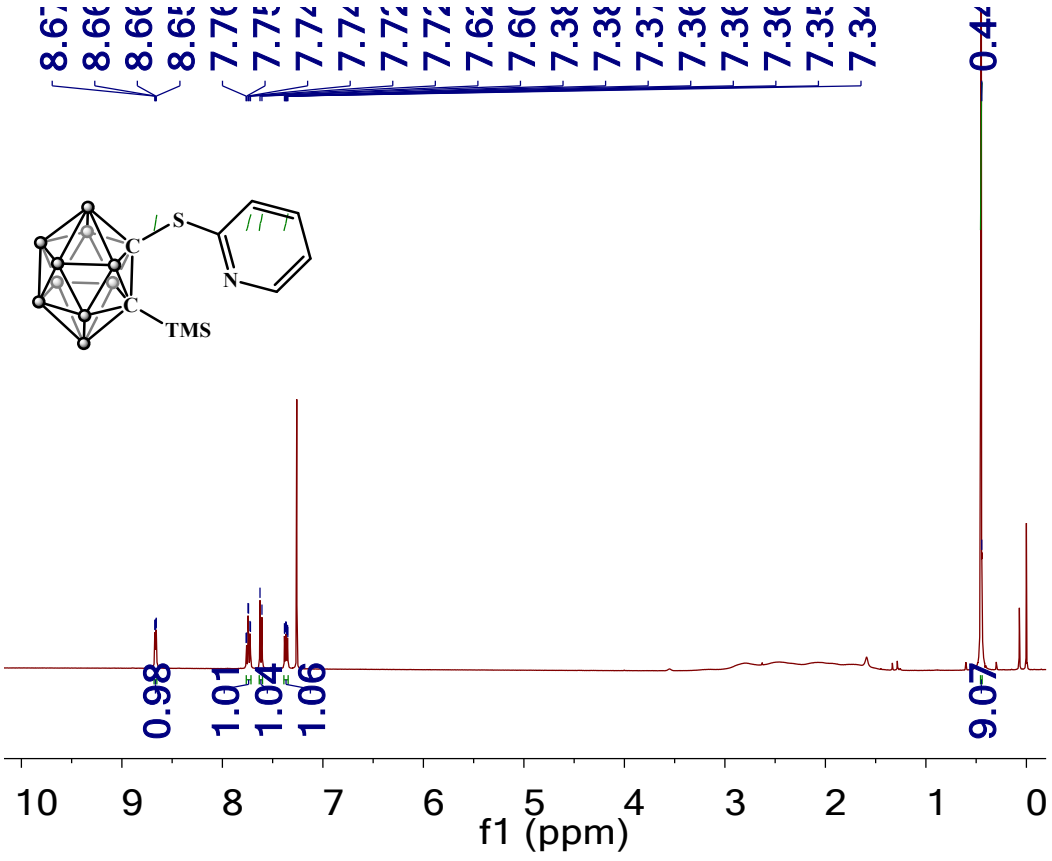


Figure S5. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **1c**.

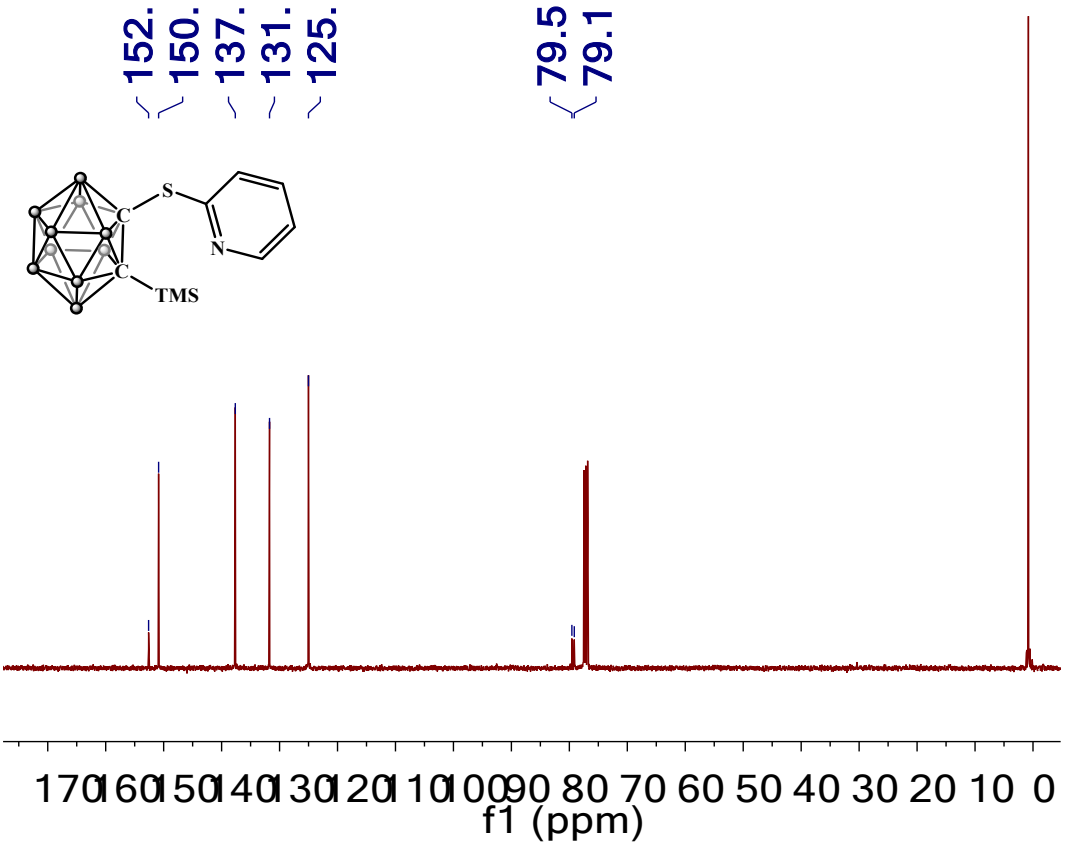


Figure S6. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **1c**.

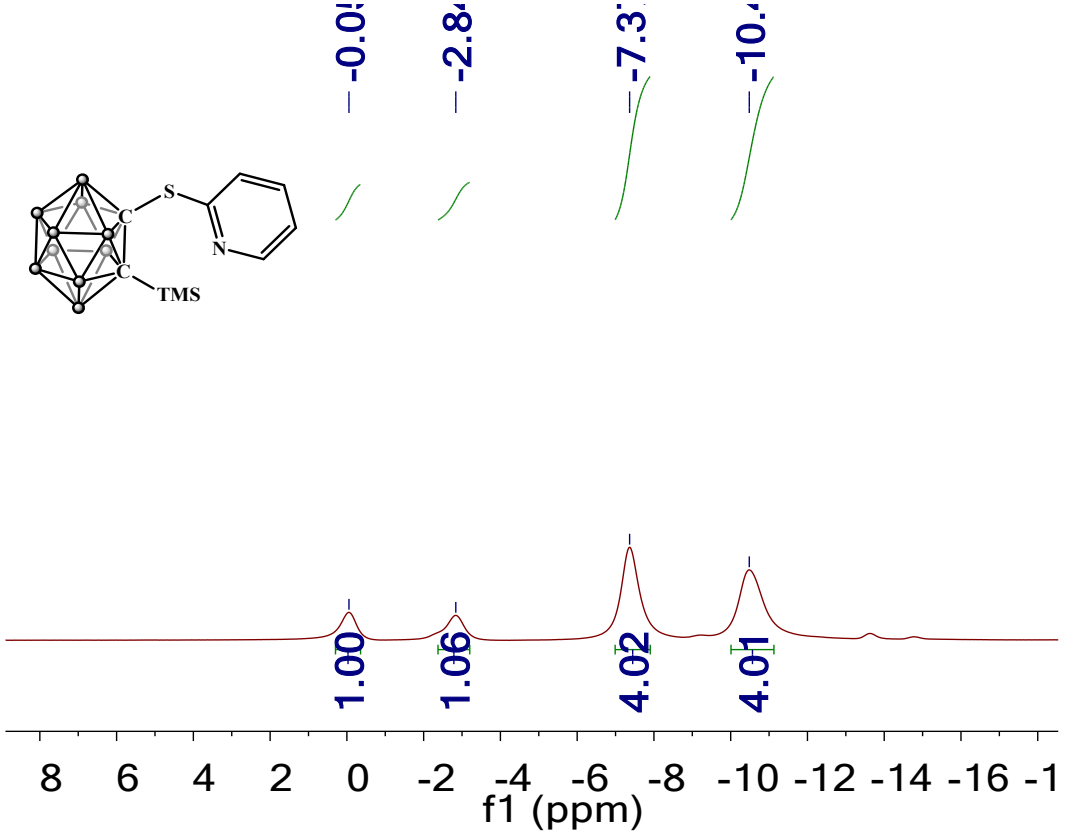


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **1d.**

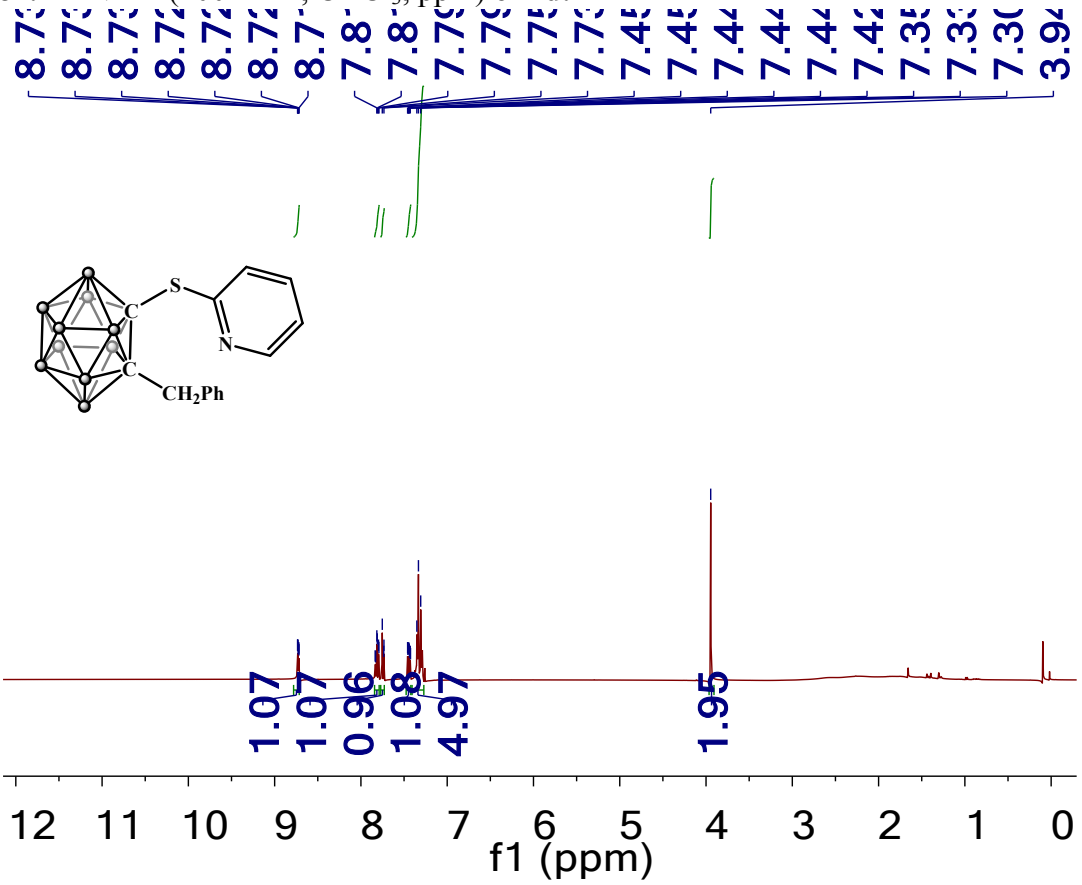


Figure S8. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **1d**.

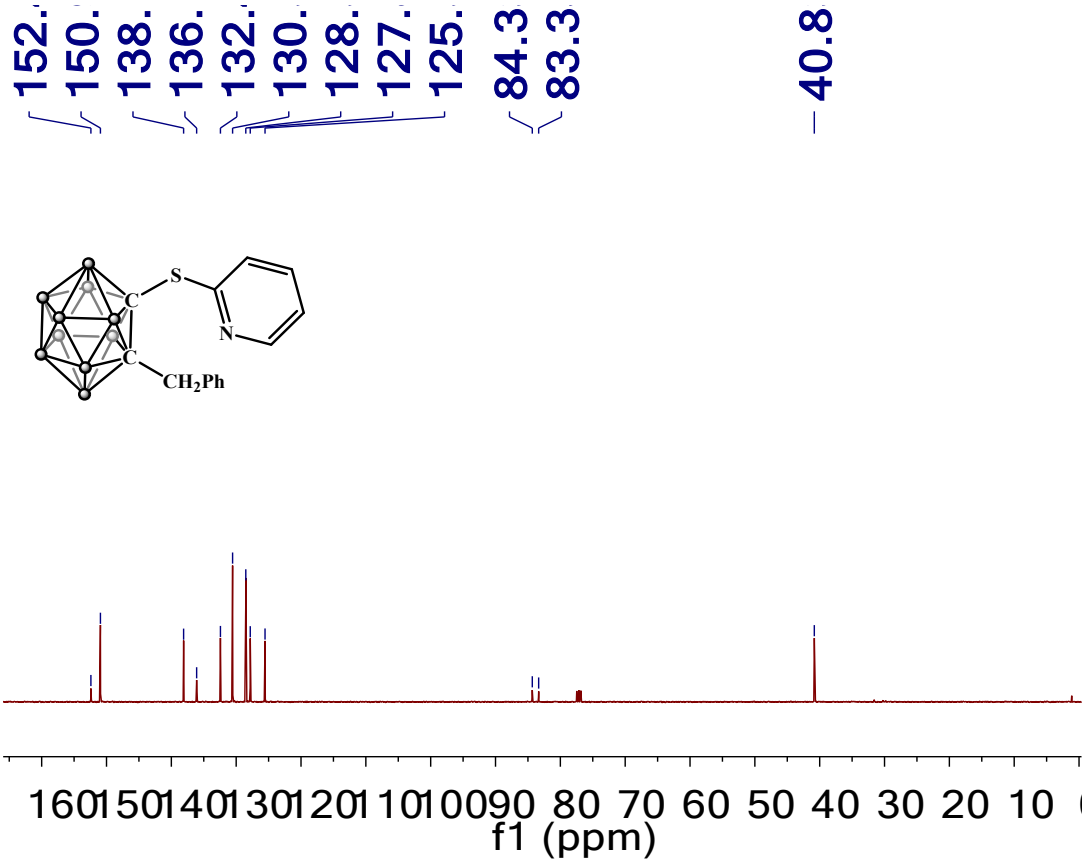


Figure S9. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **1d**.

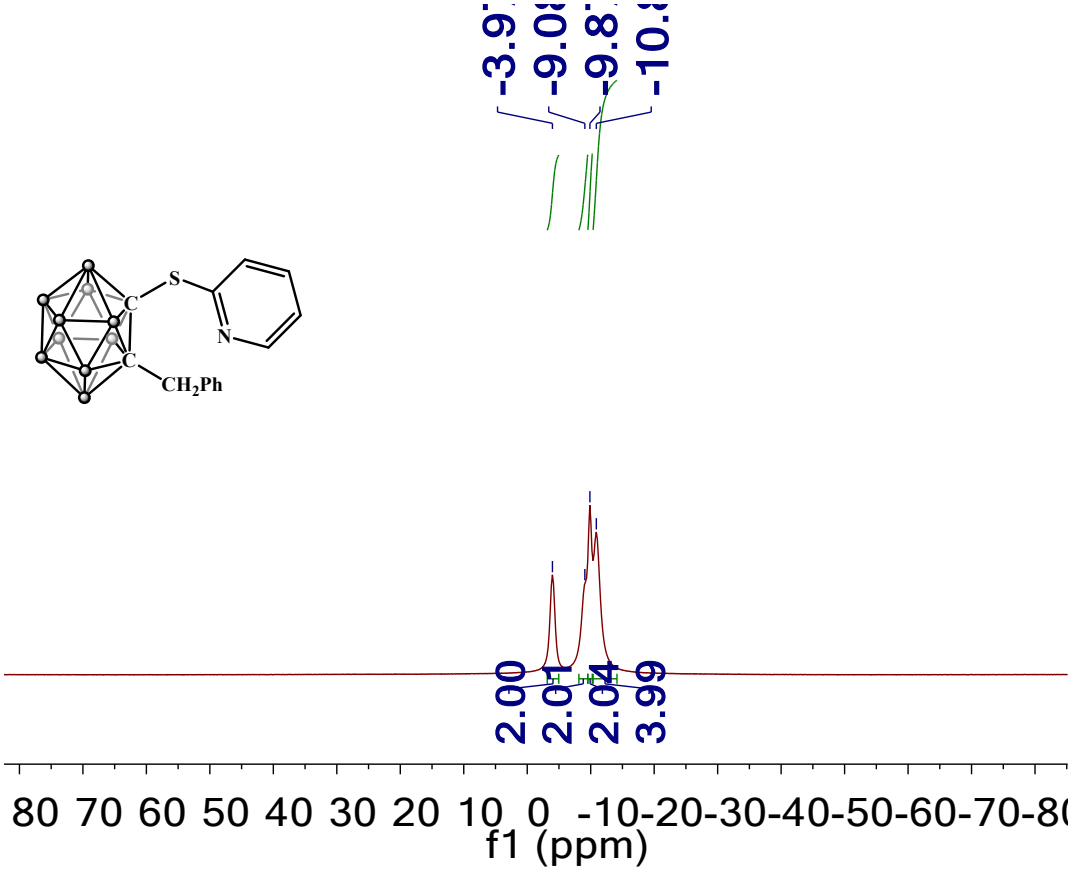


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **2.**

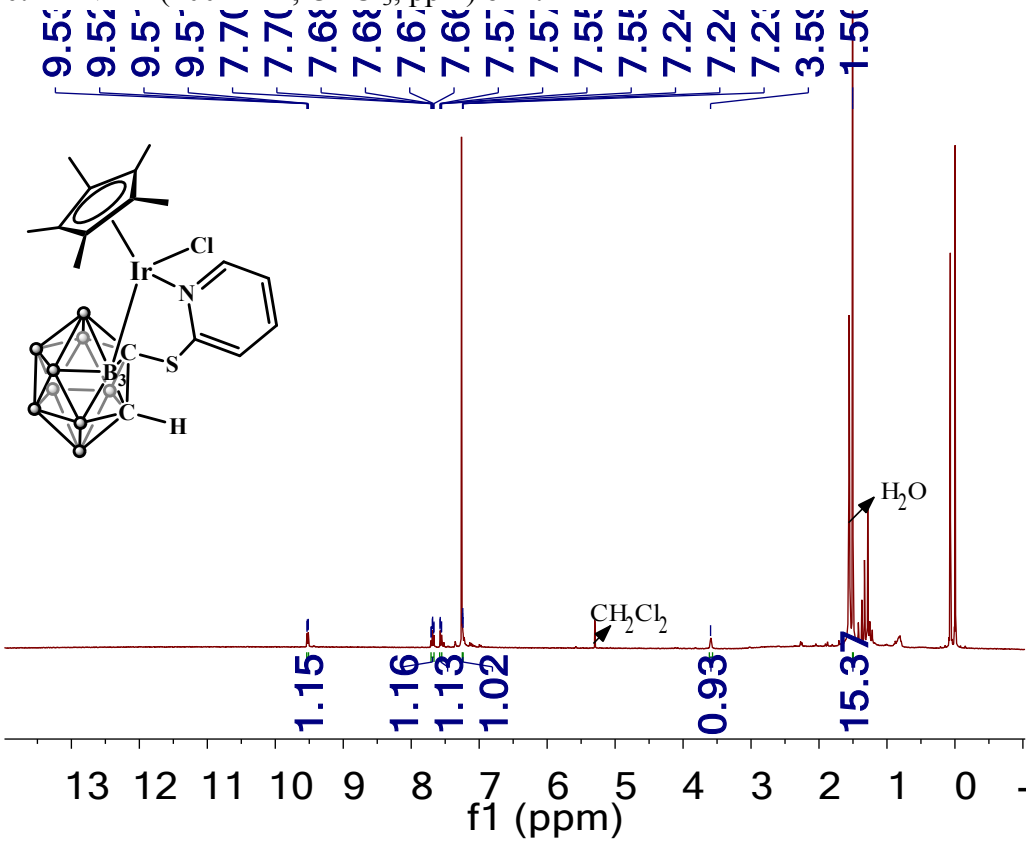


Figure S11. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **2**.

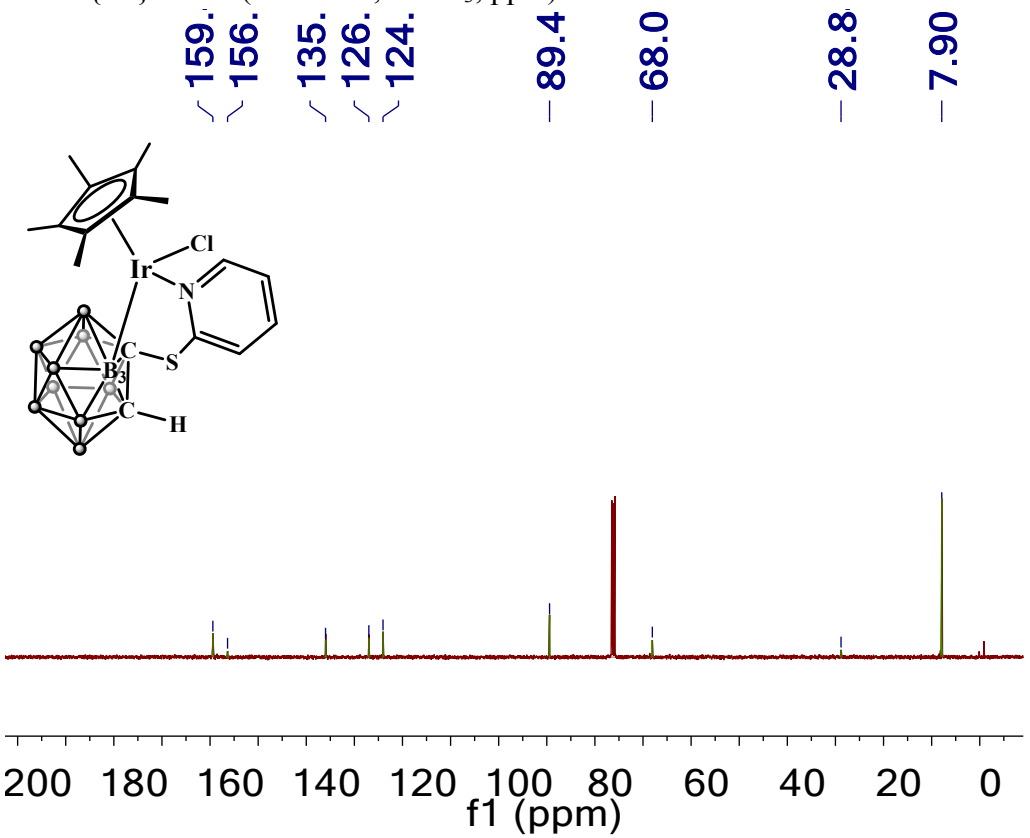


Figure S12. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **2**.

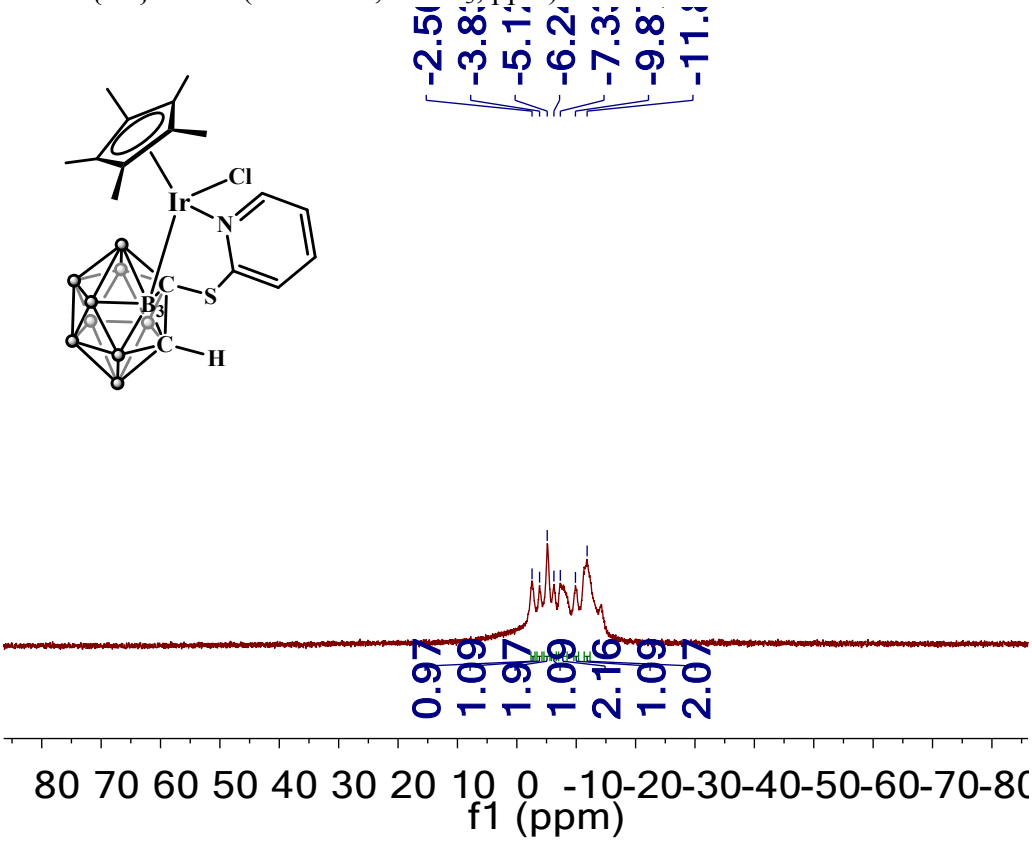


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **3.**

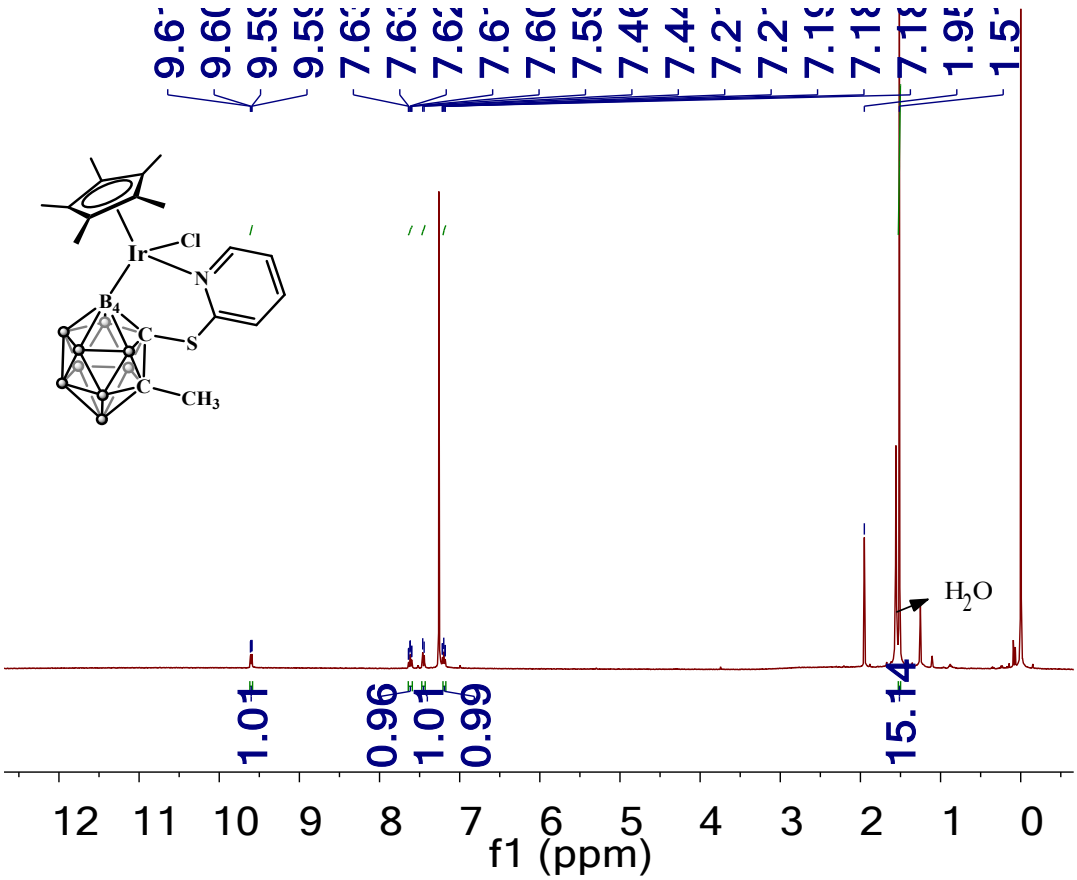


Figure S14. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **3**.

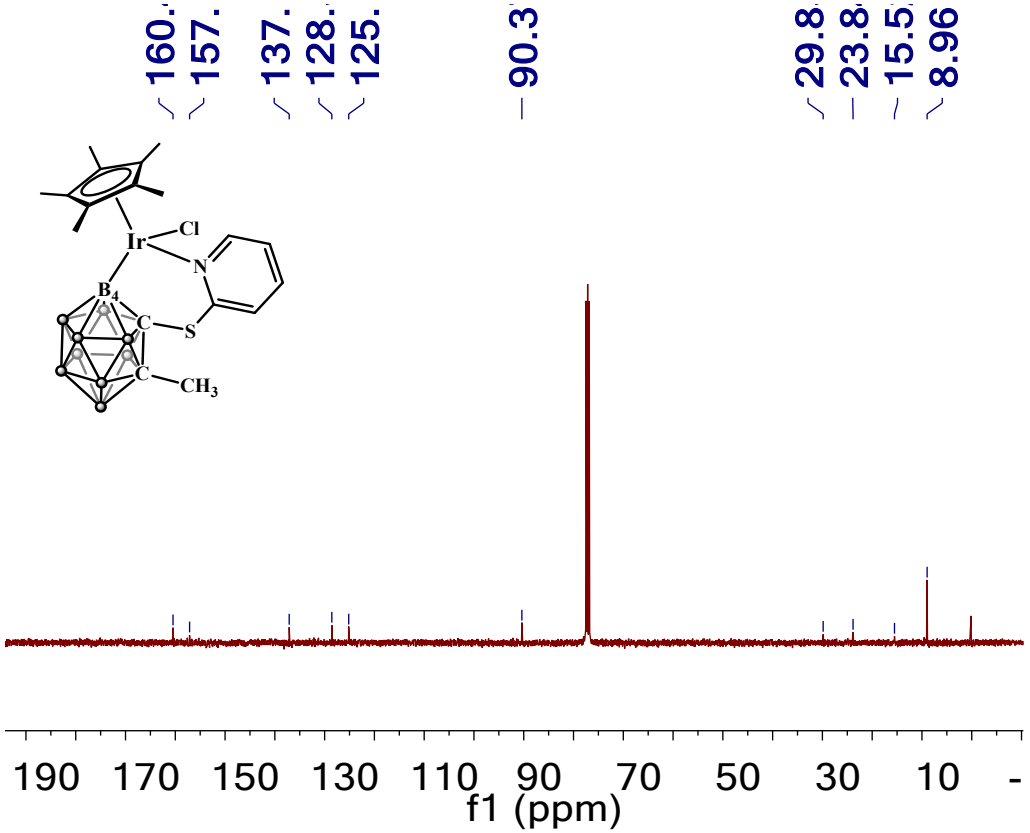


Figure S15. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **3**.

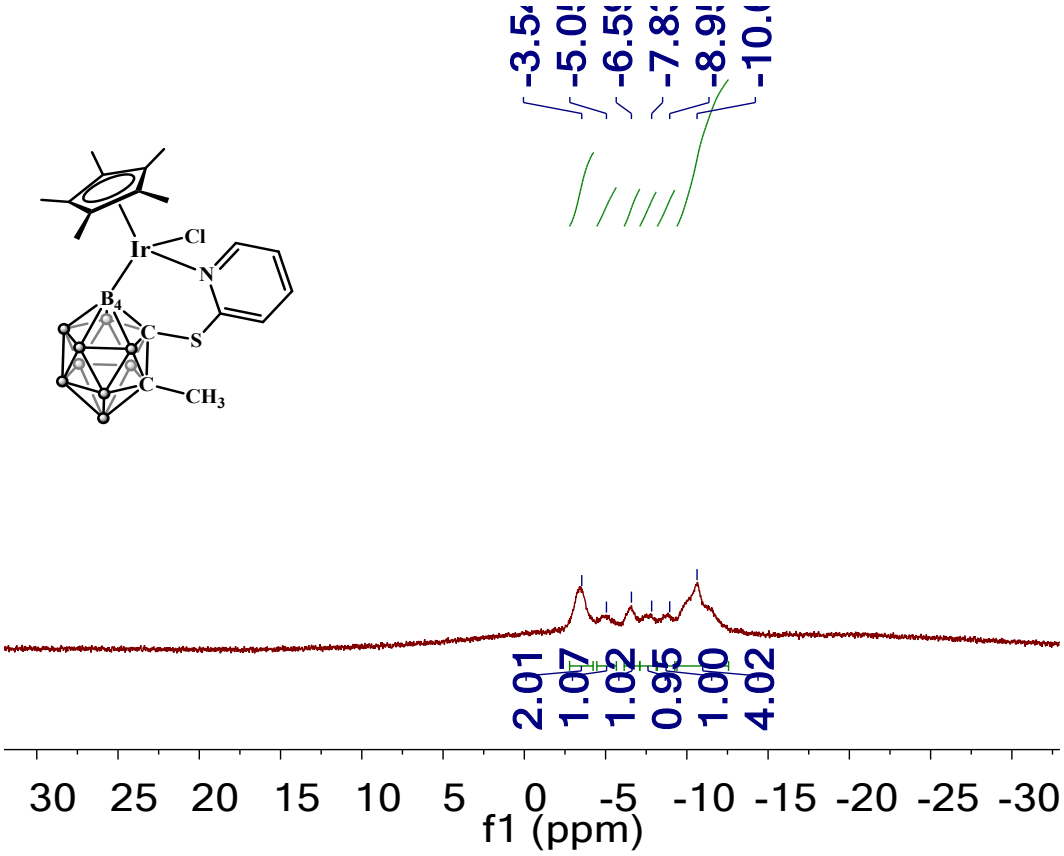


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **4.**

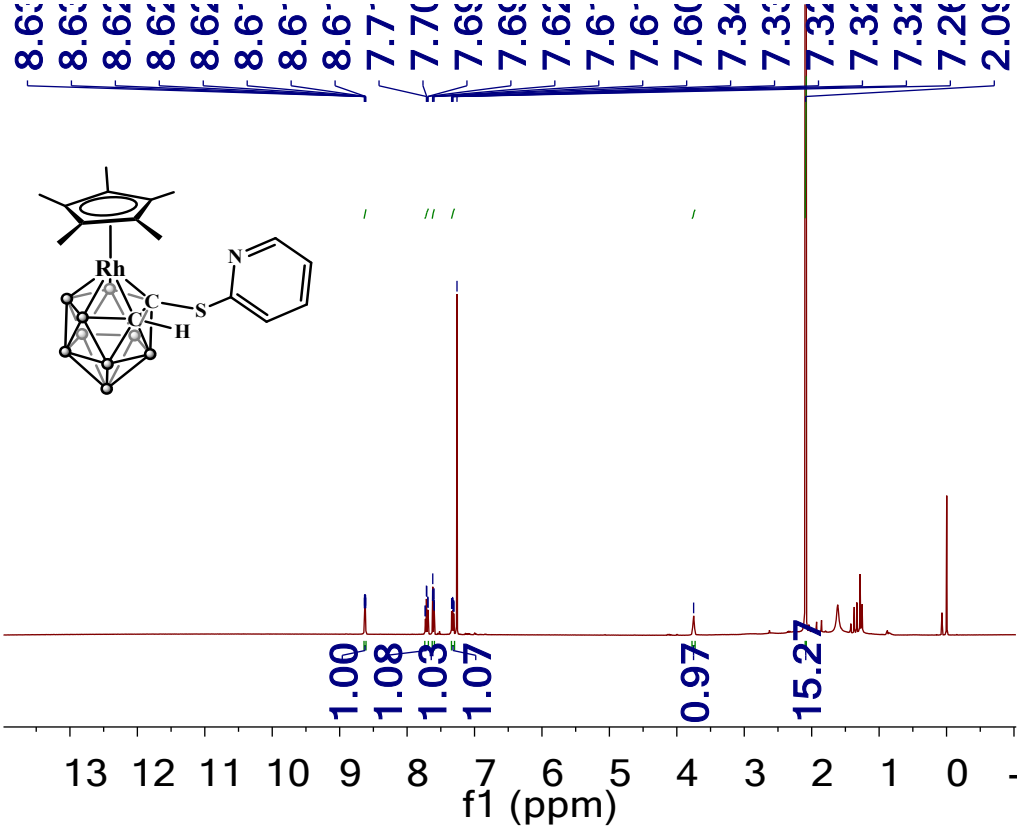


Figure S17. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **4**.

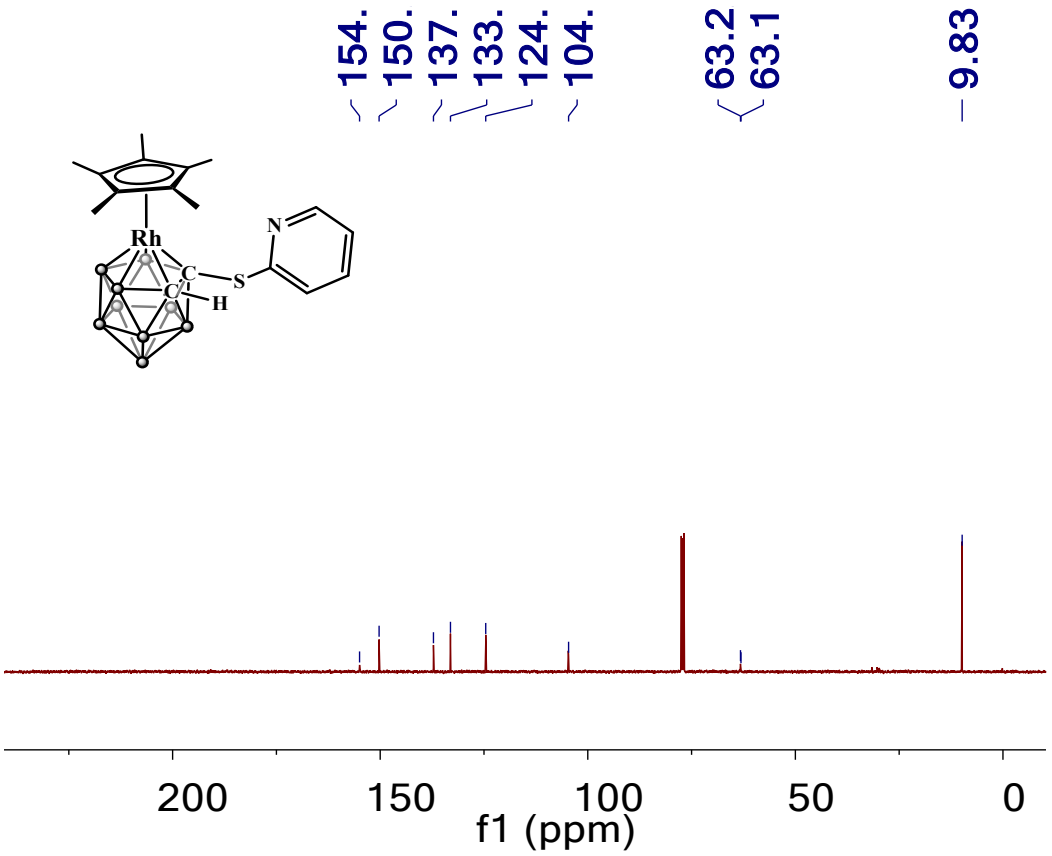


Figure S18. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **4**.

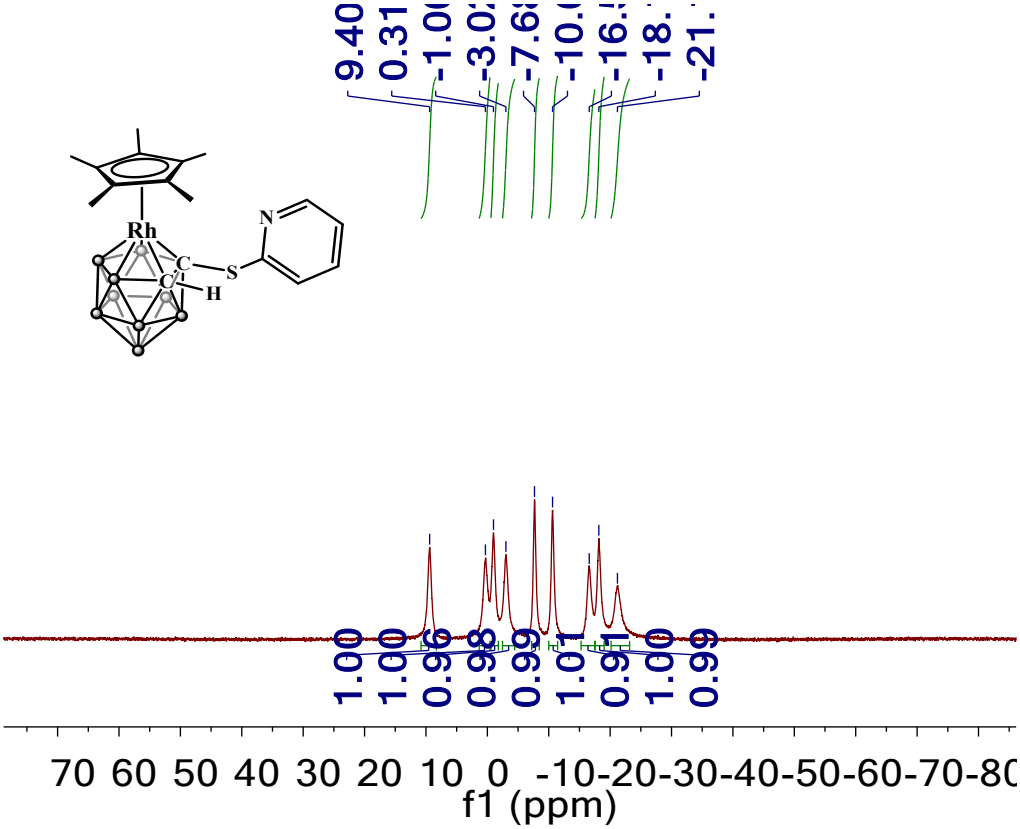


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **5.**

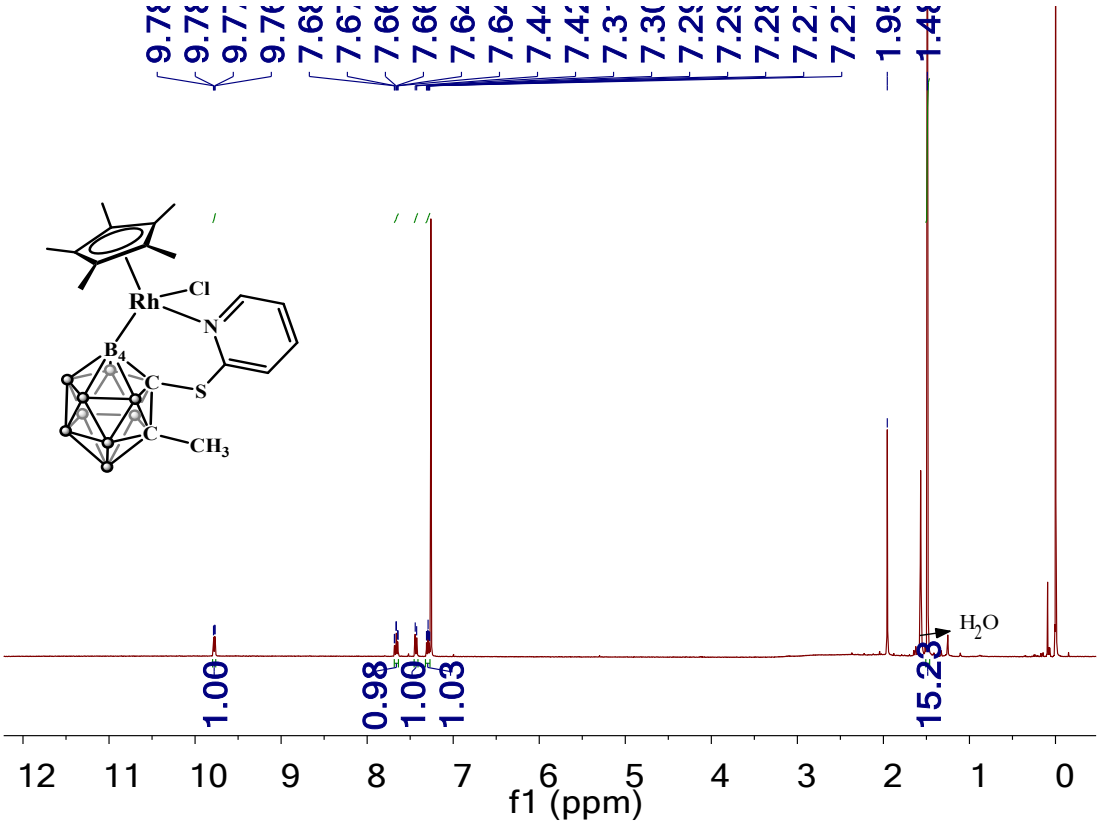


Figure S20. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **5**.

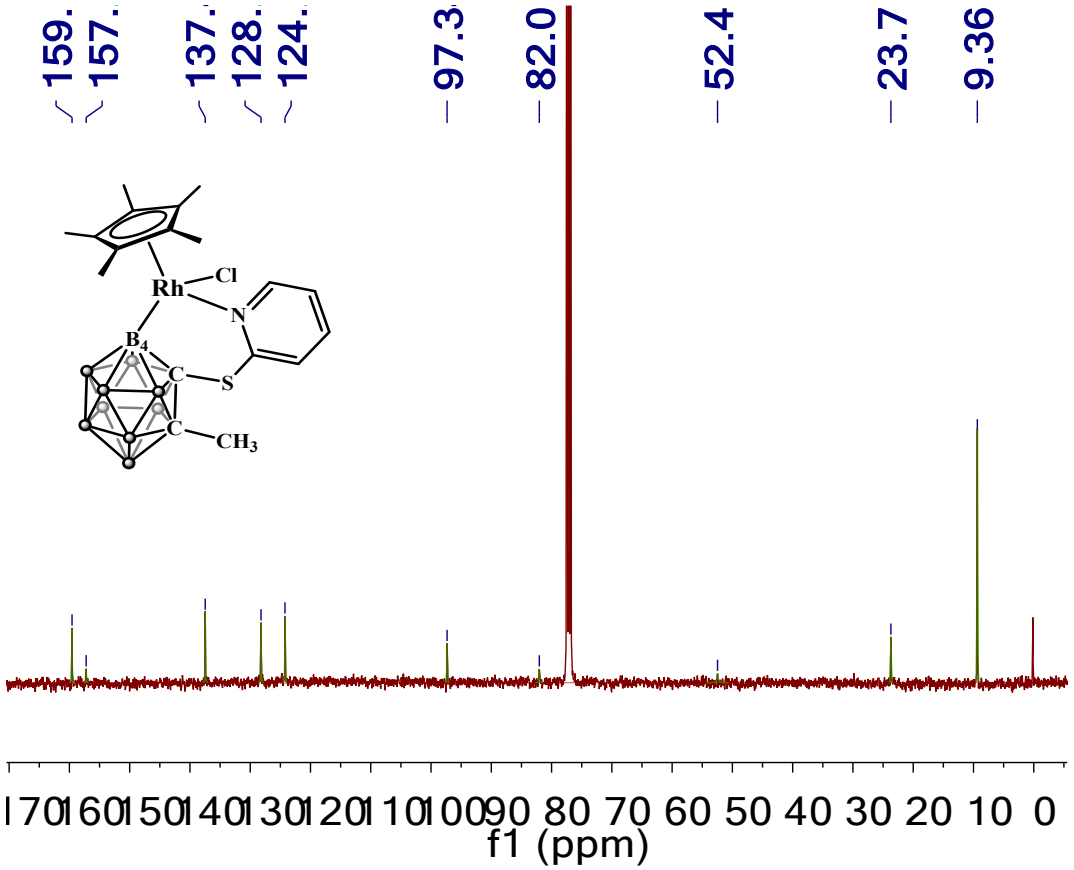


Figure S21. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **5**.

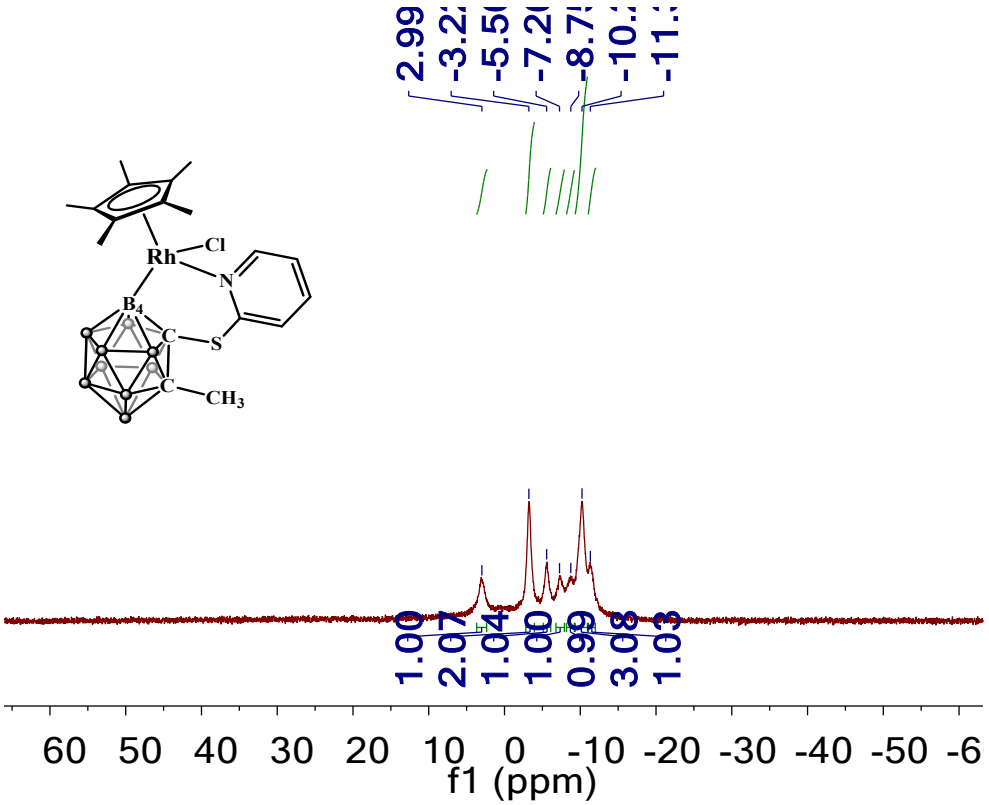


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **6.**

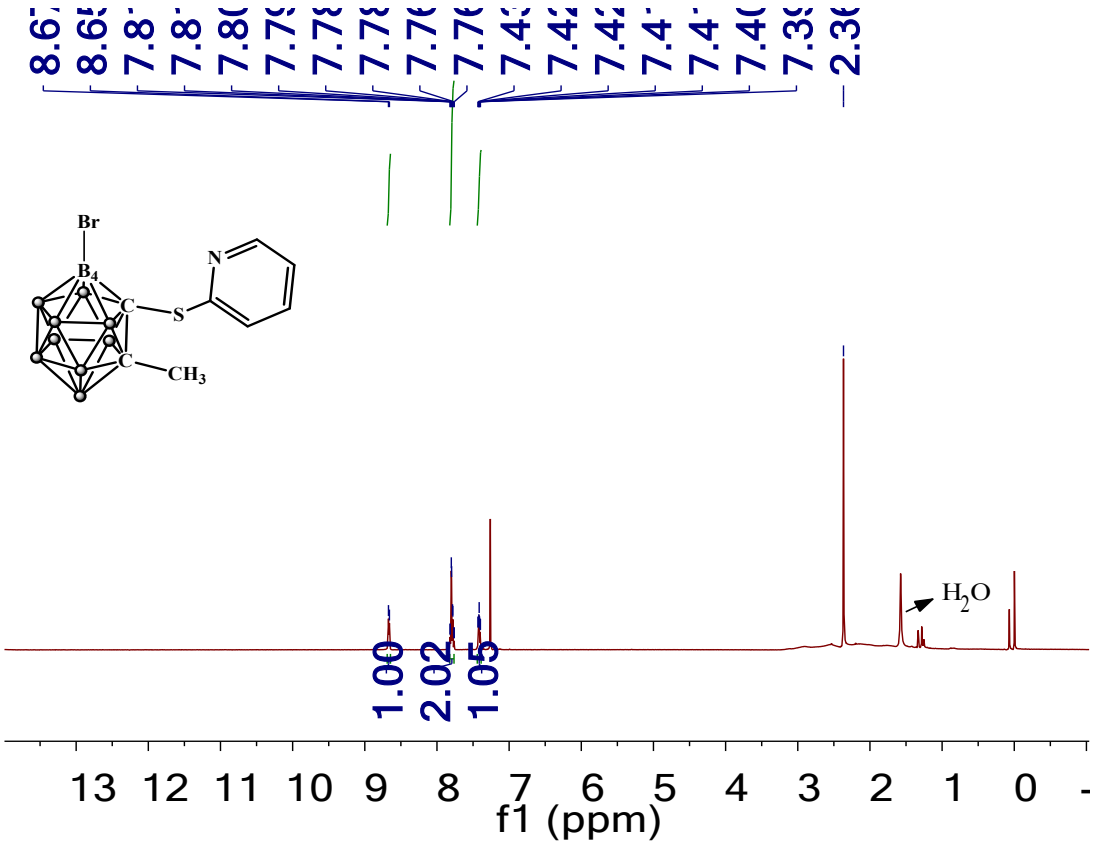


Figure S23. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **6**.

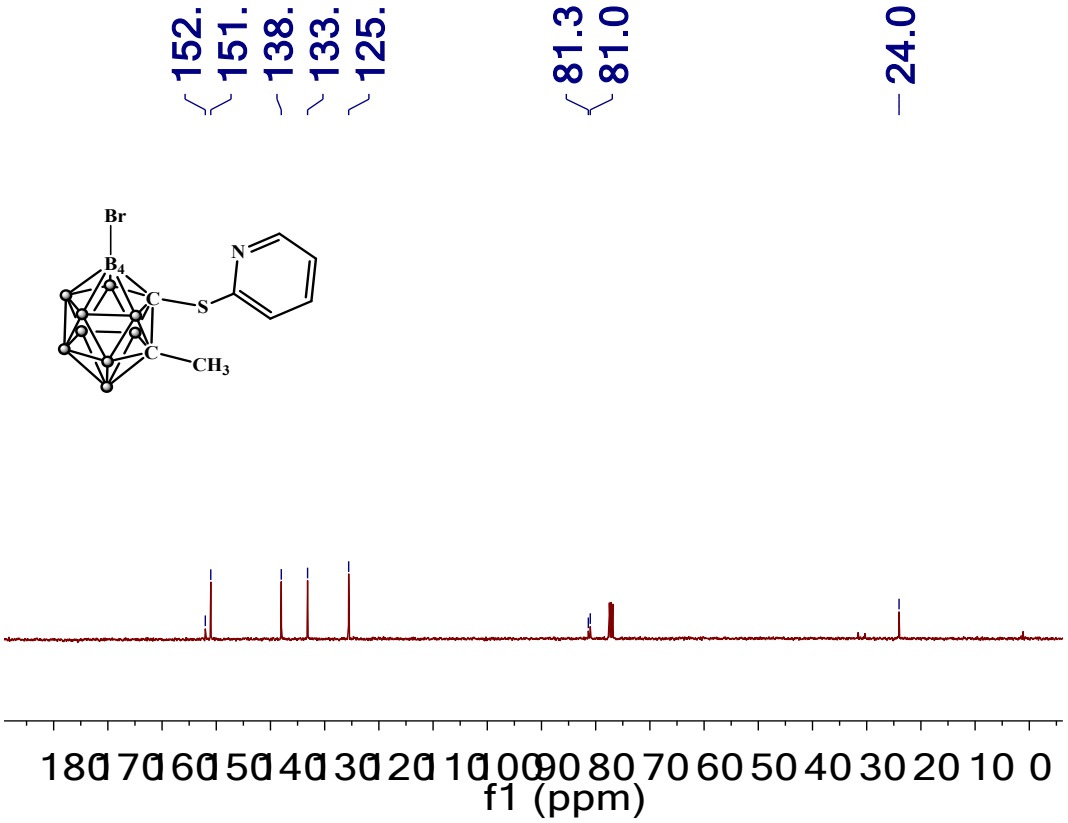


Figure S24. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **6**.

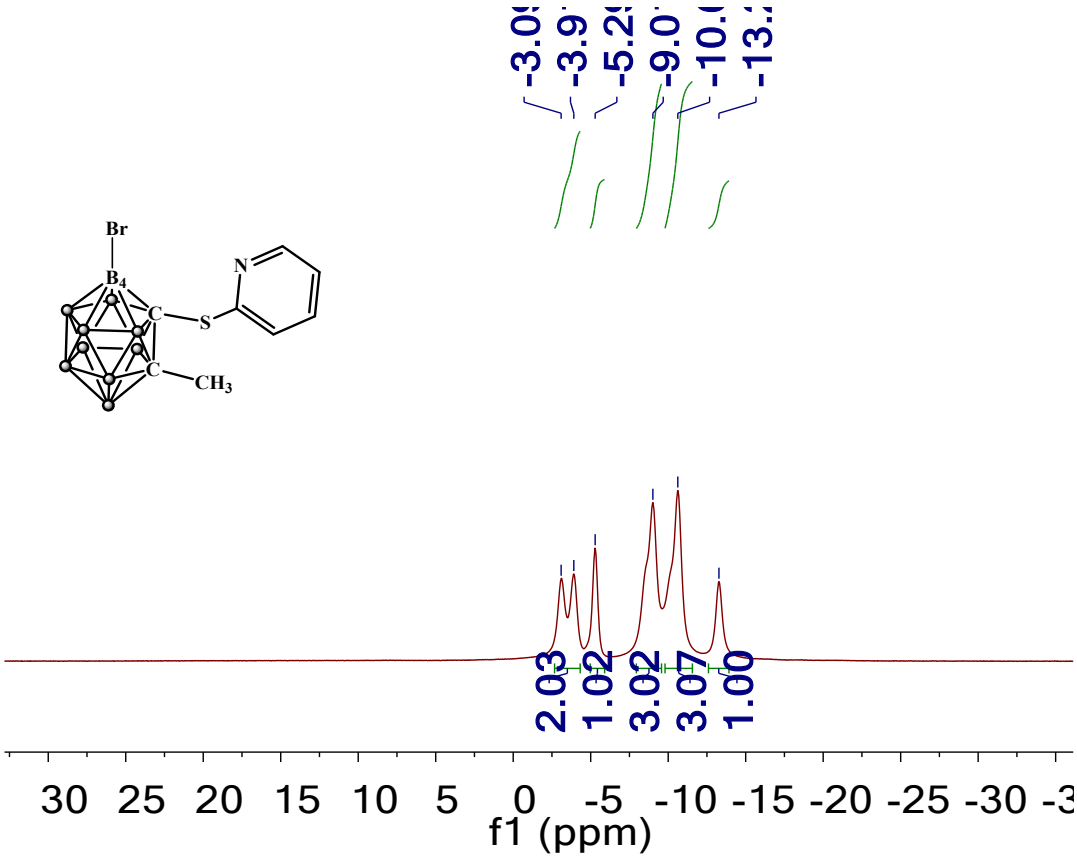


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **7.**

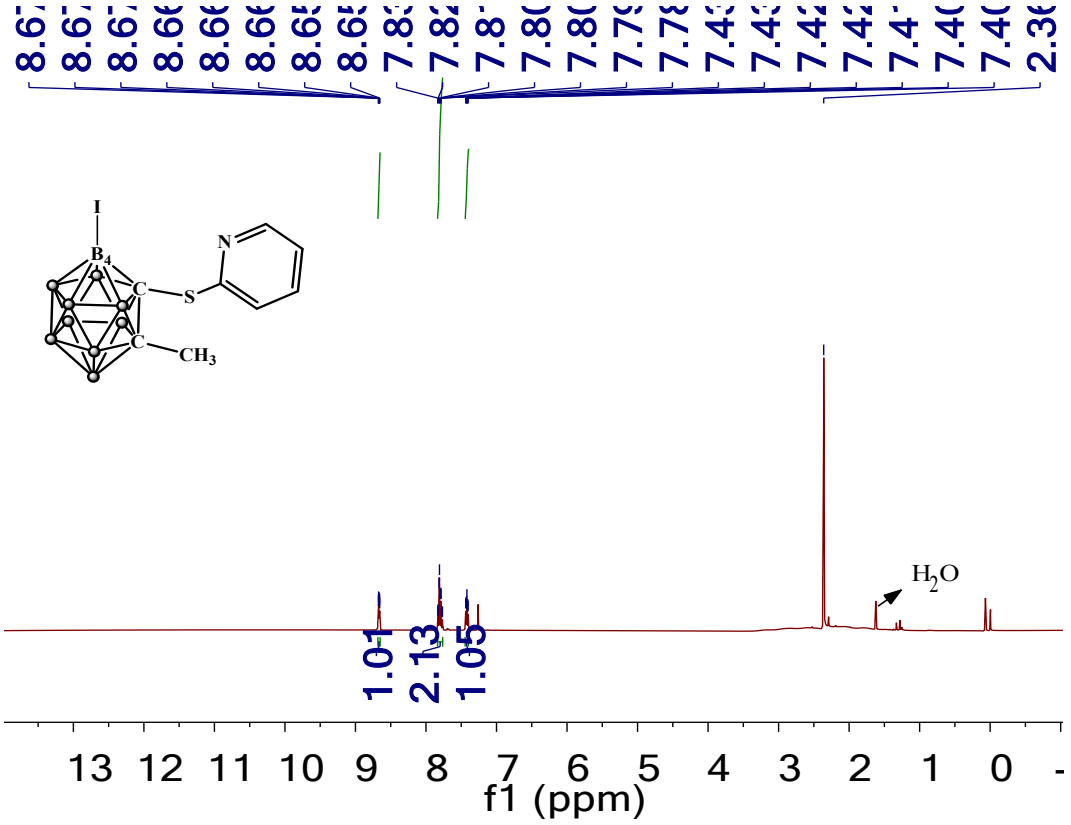


Figure S26. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **7**.

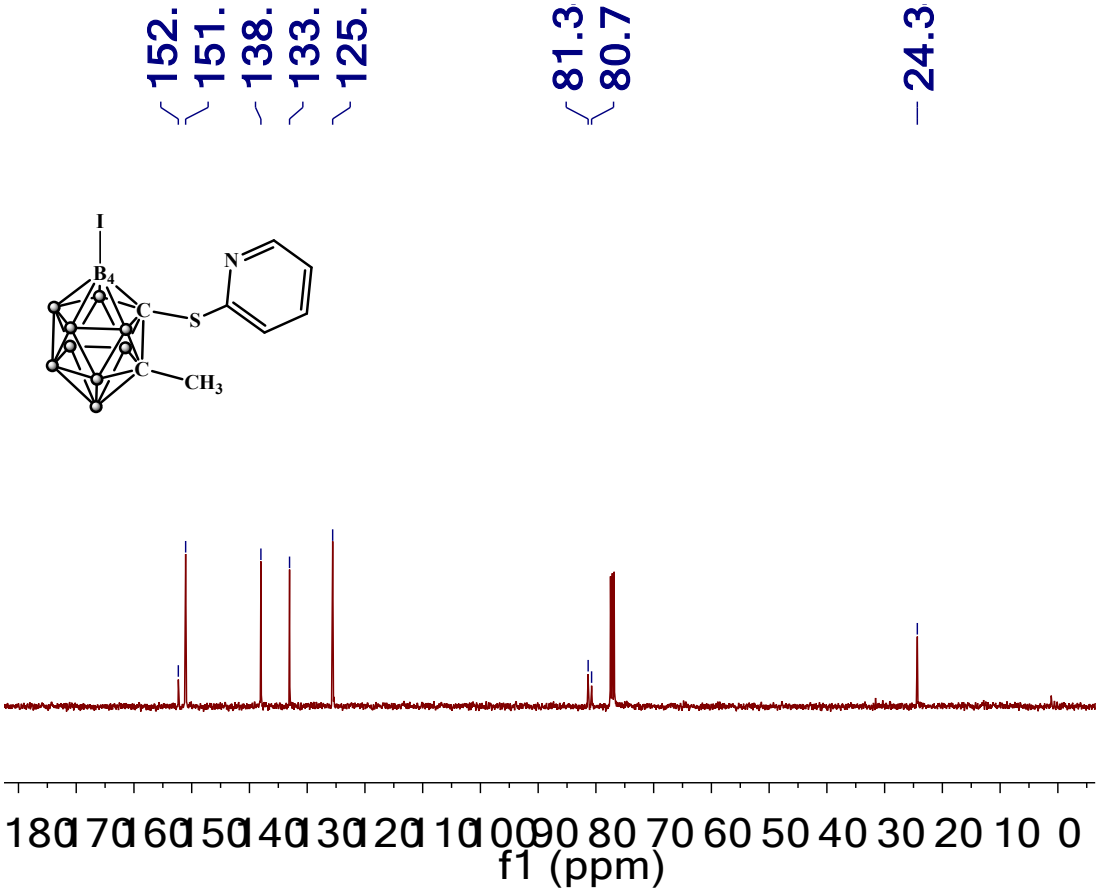


Figure S27. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **7**.

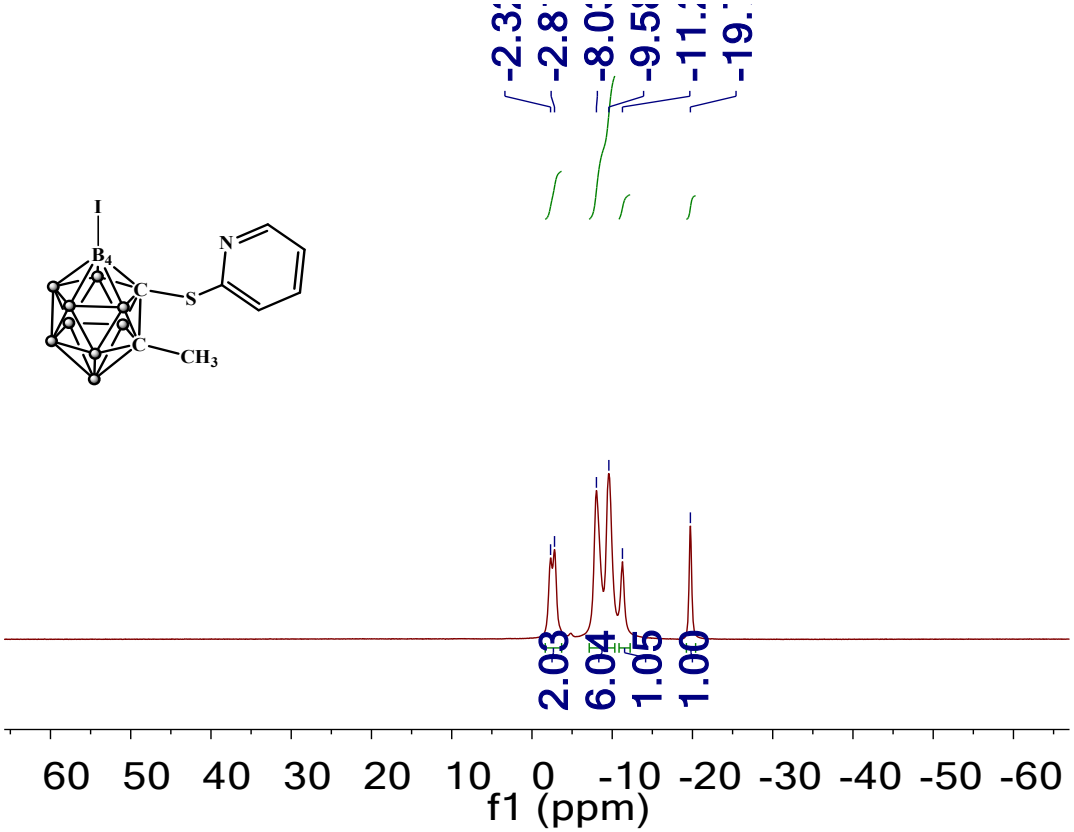


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **6c.**

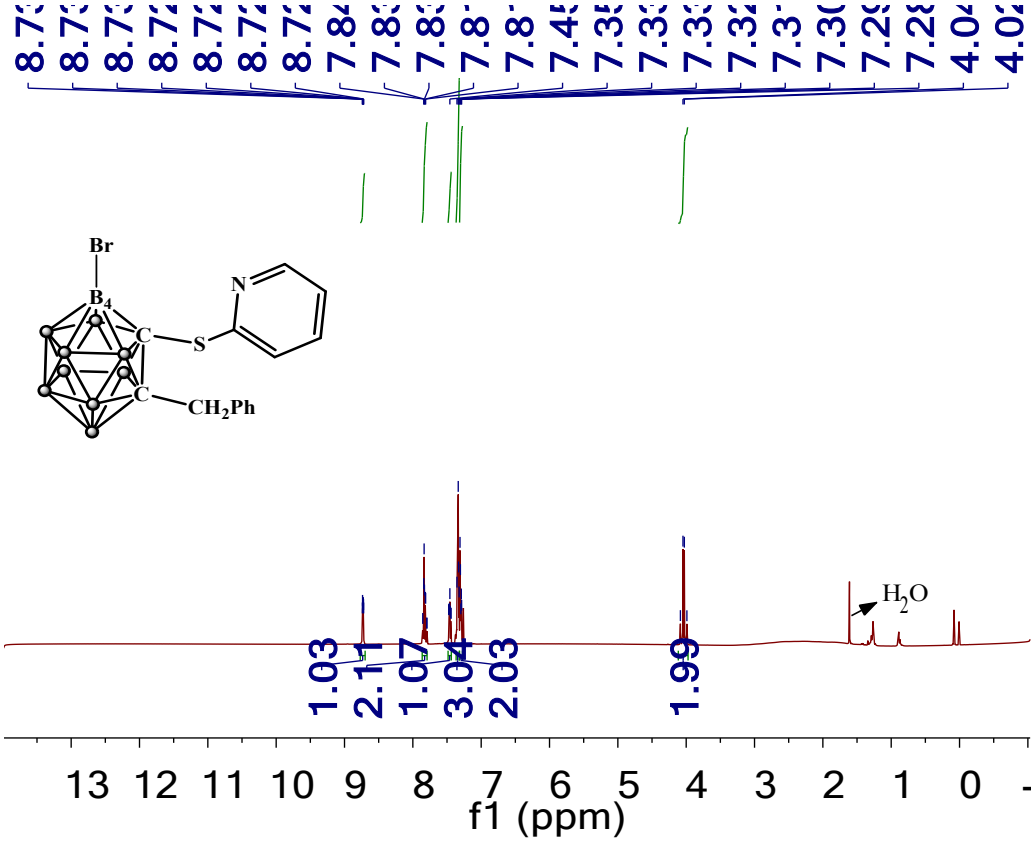


Figure S29. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **6c**.

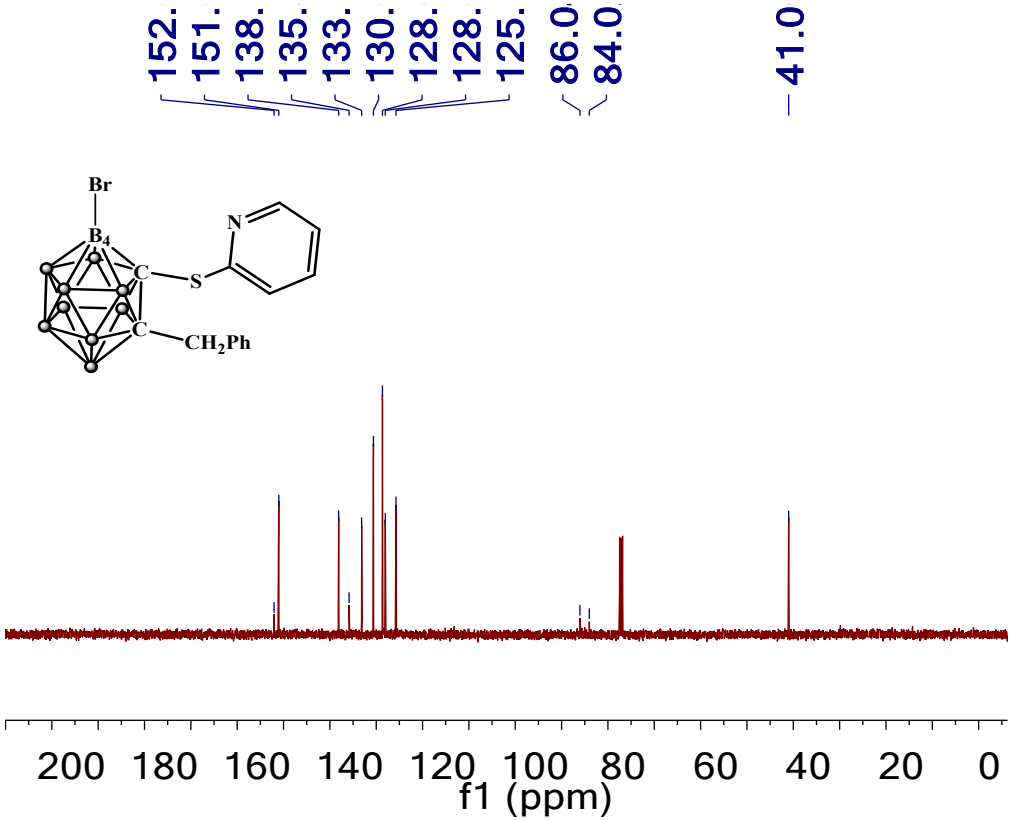


Figure S30. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **6c**.

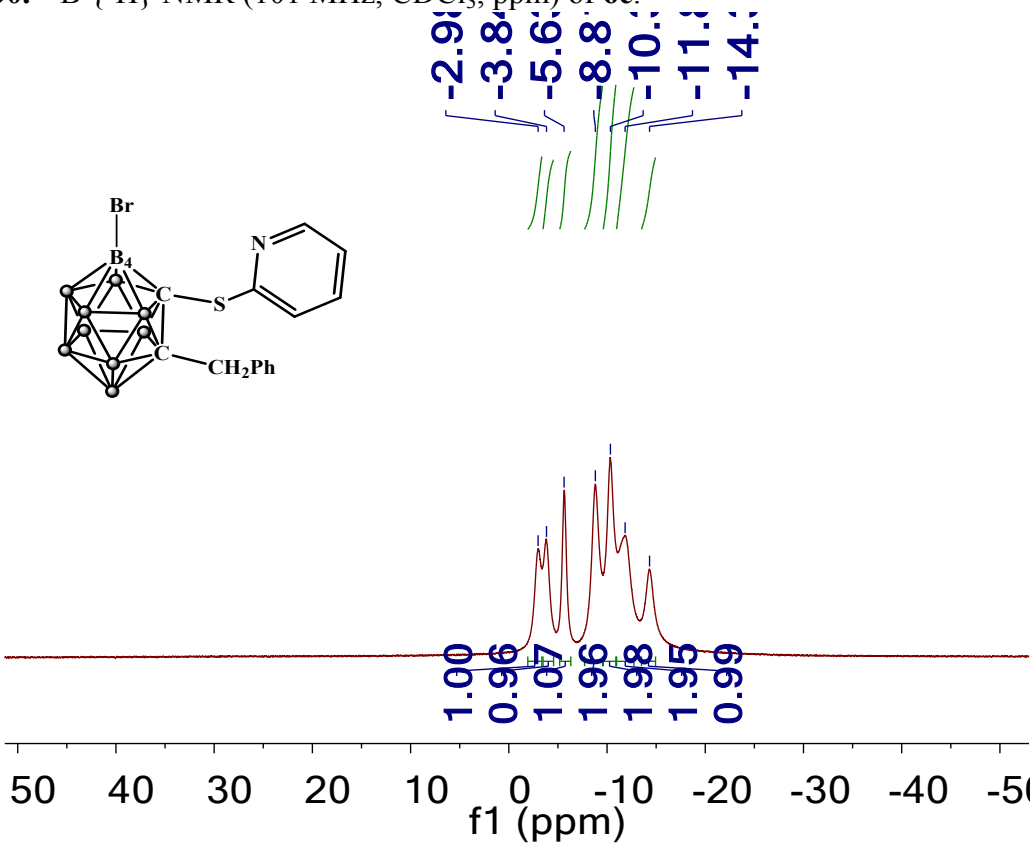


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **8.**

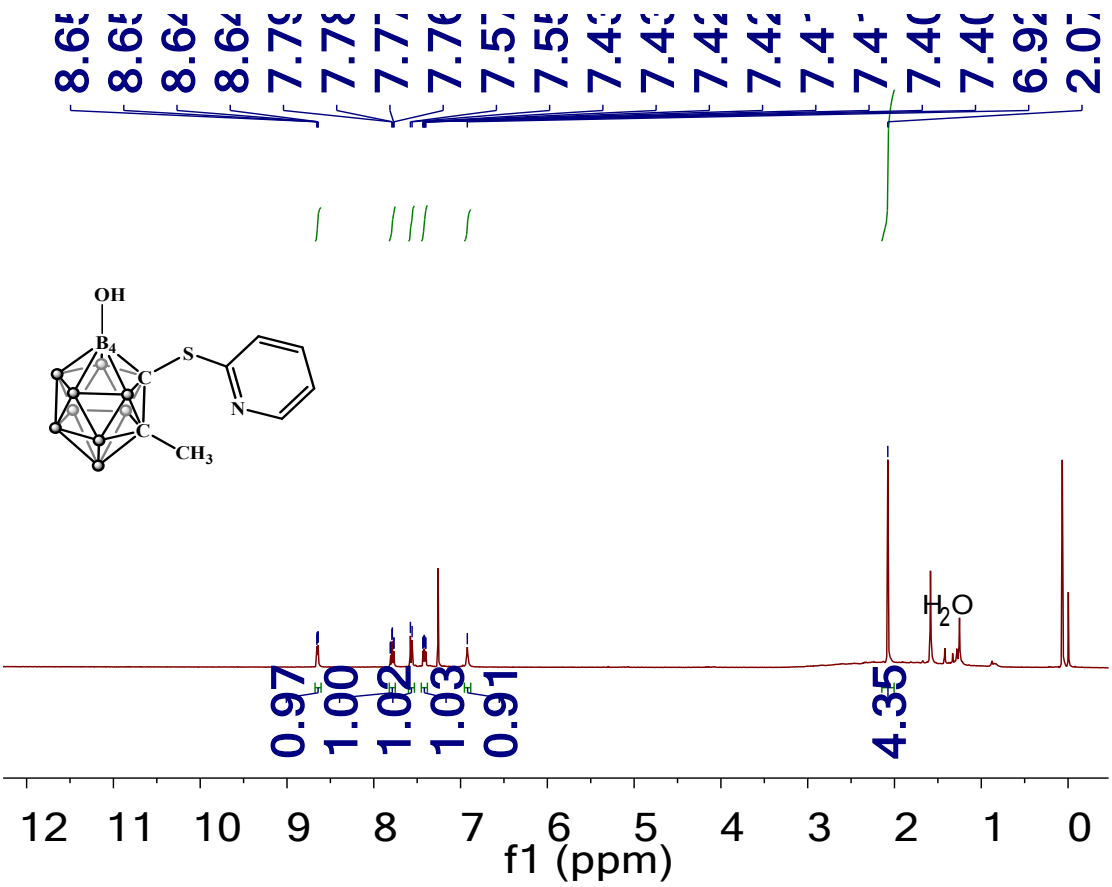


Figure S32. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **8**.

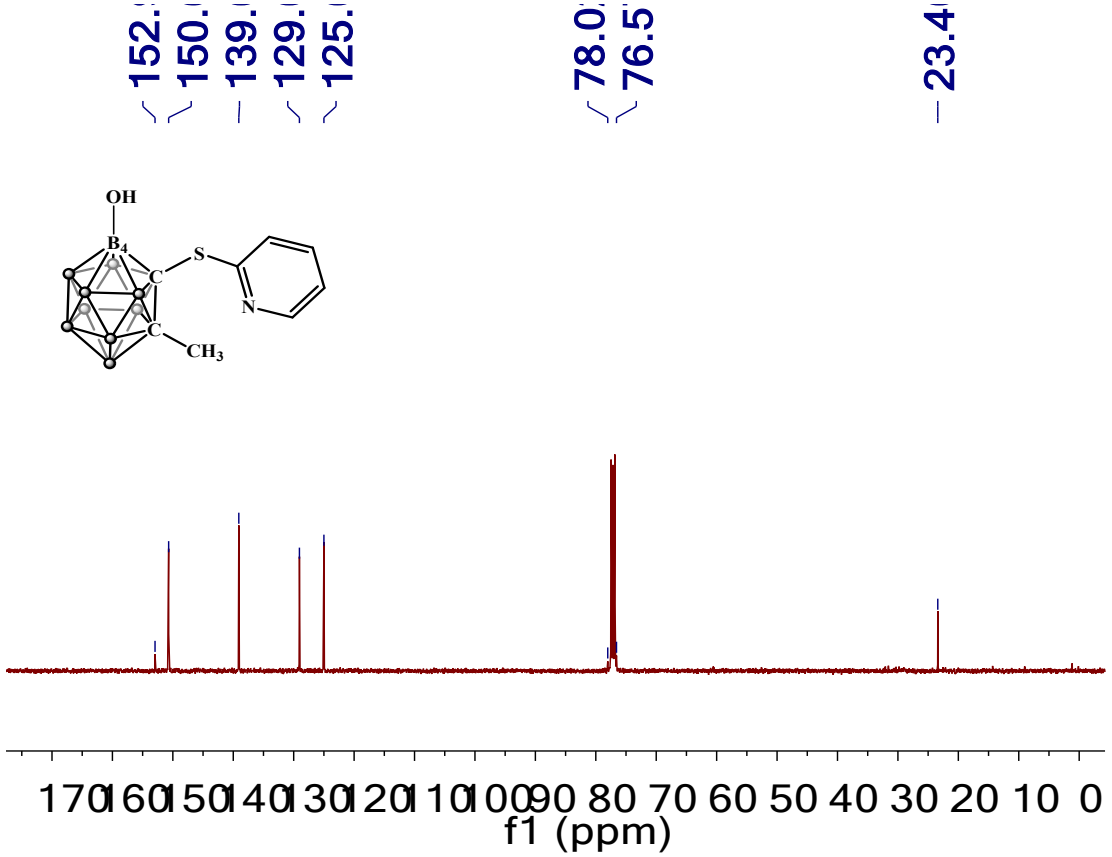


Figure S33. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **8**.

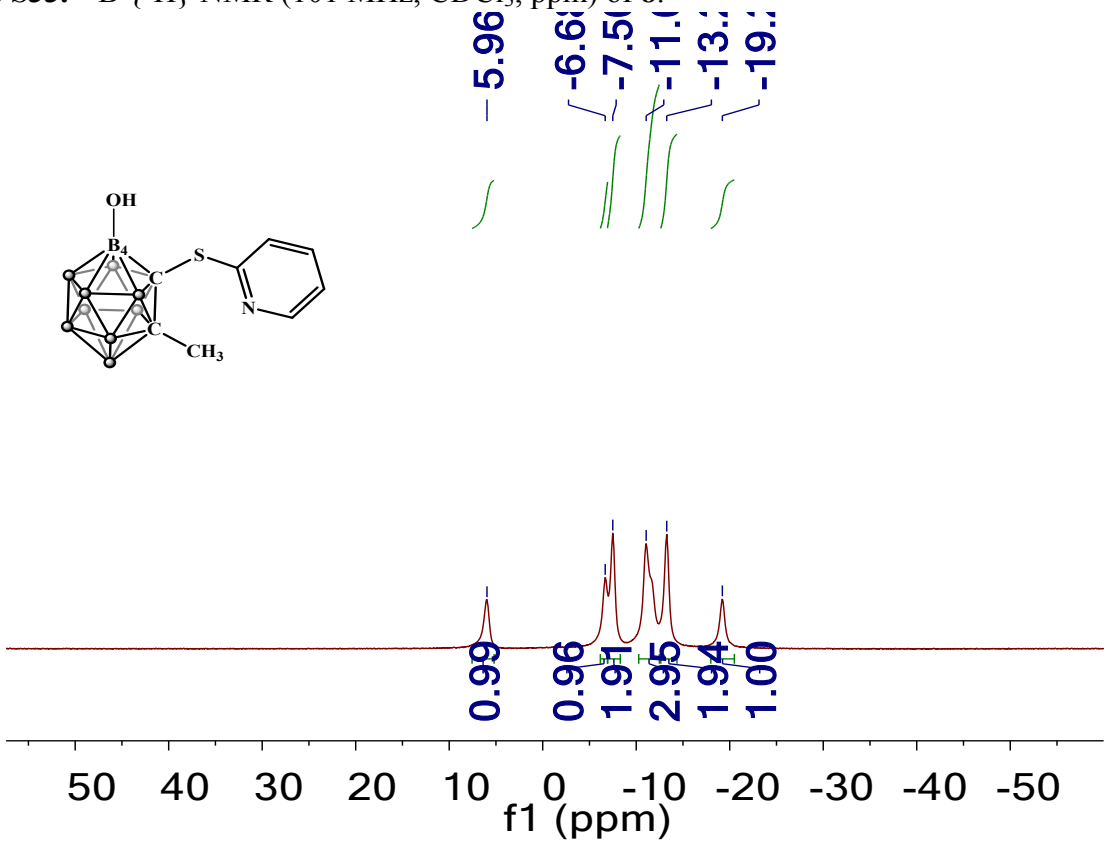


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **8d.**

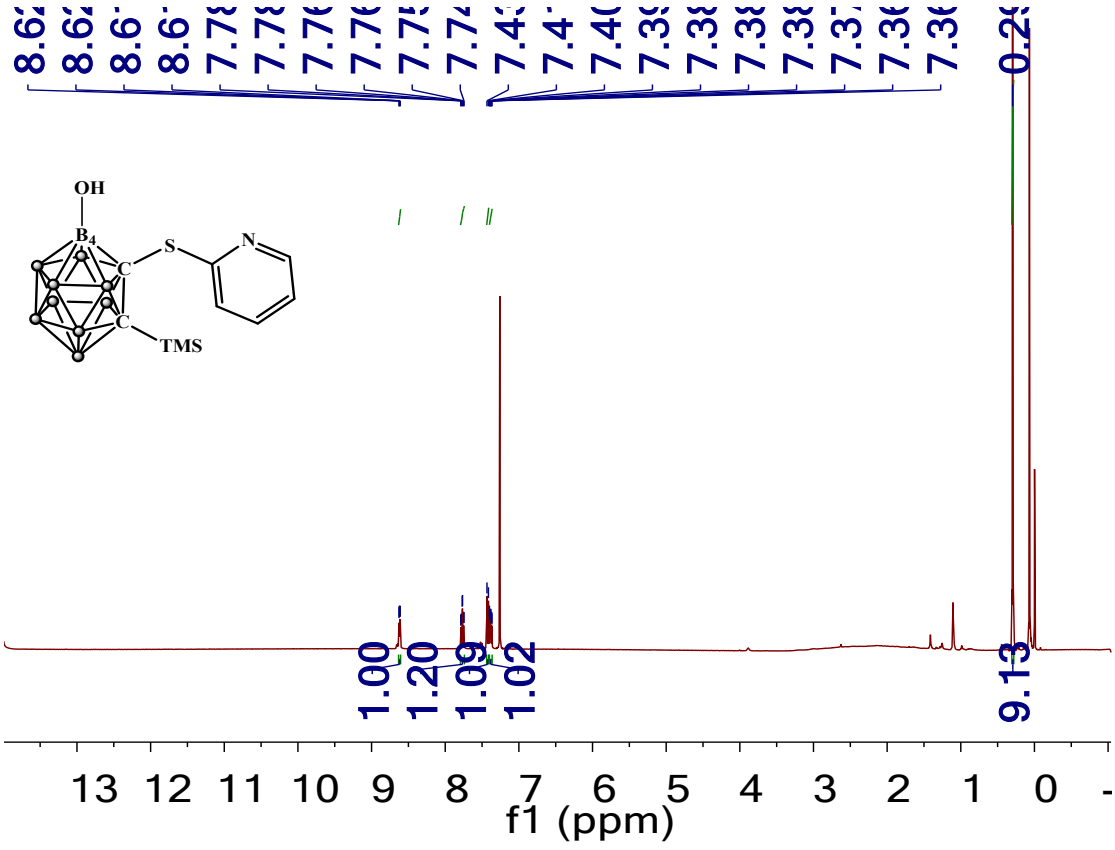


Figure S35. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **8d**.

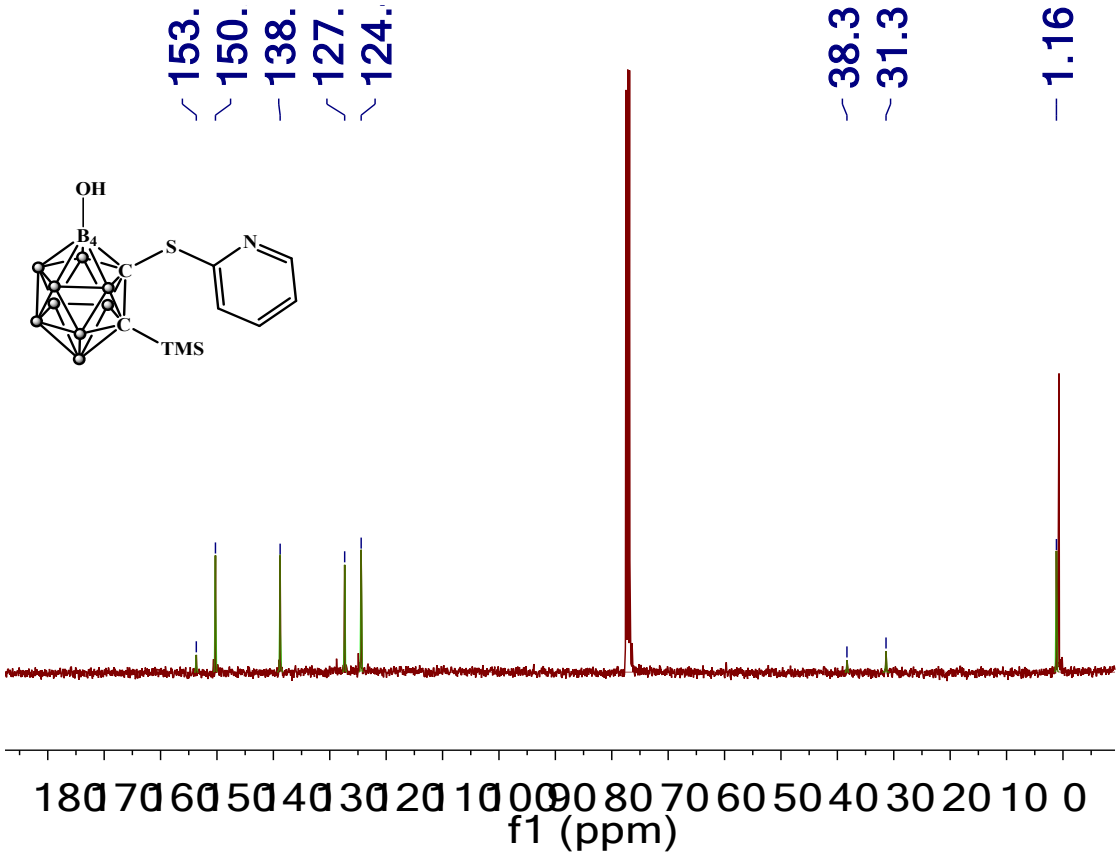


Figure S36. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **8d**.

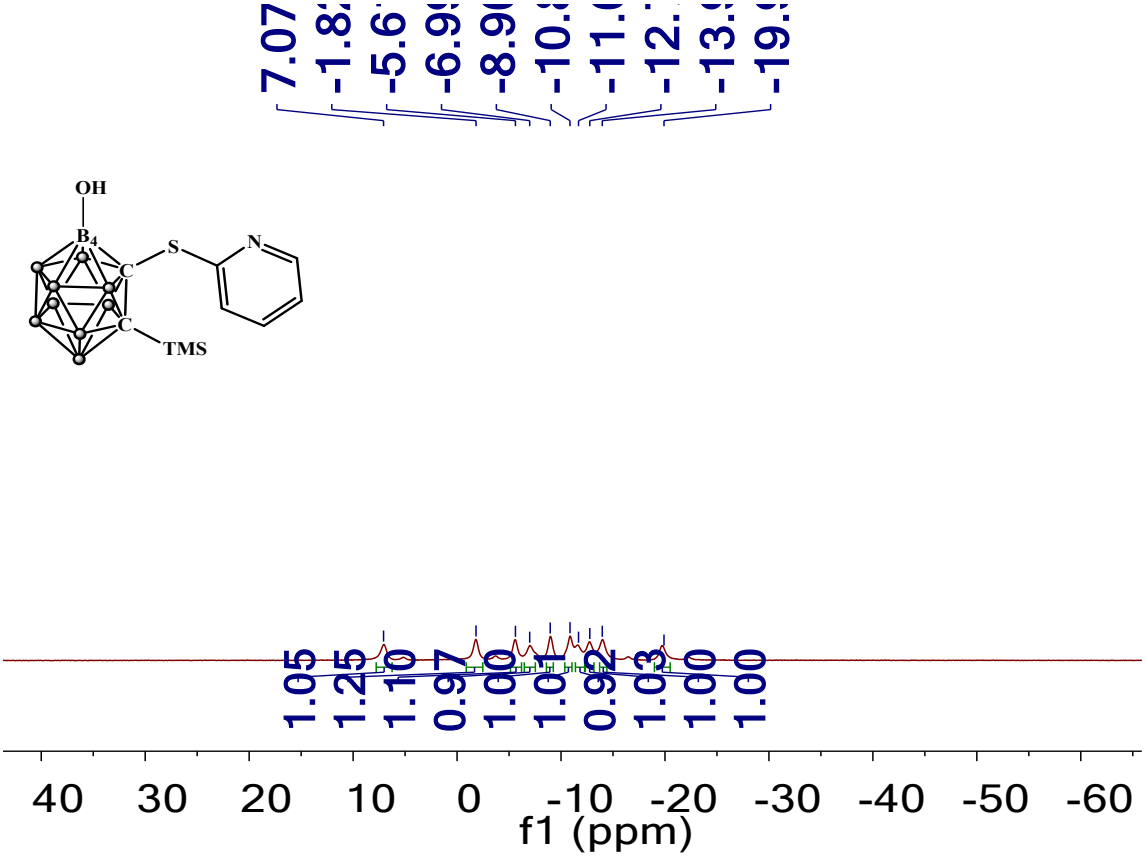


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **9.**

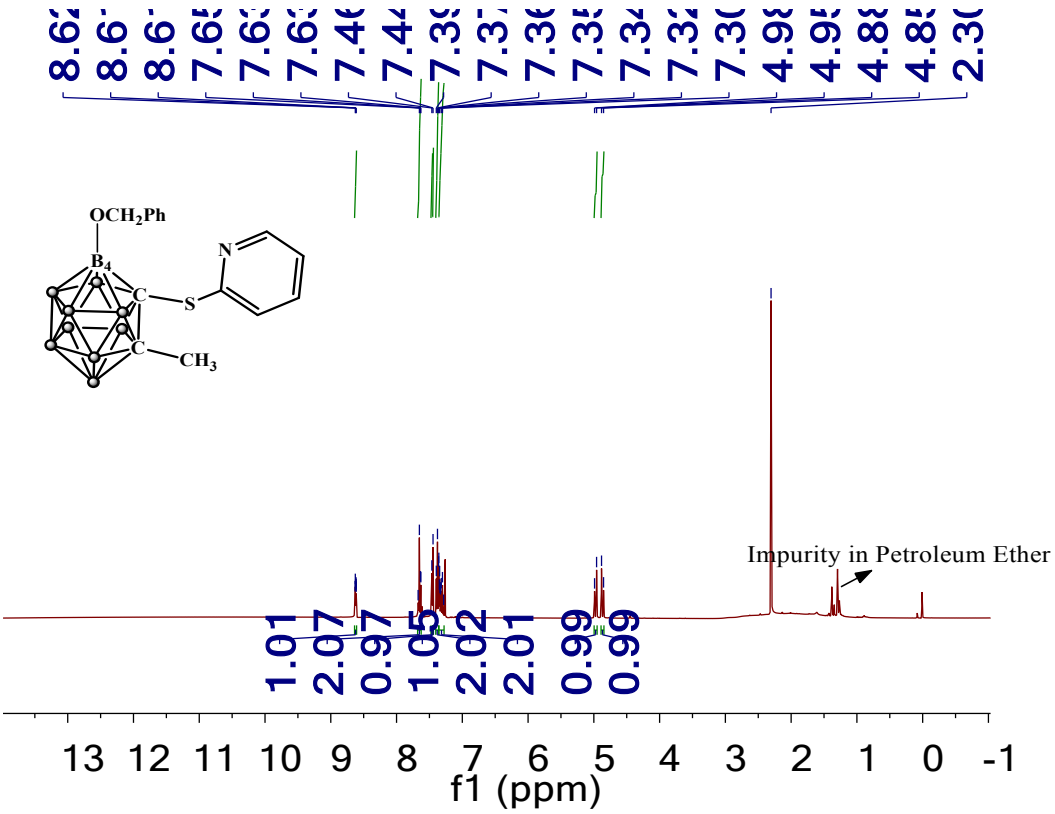


Figure S38. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **9**.

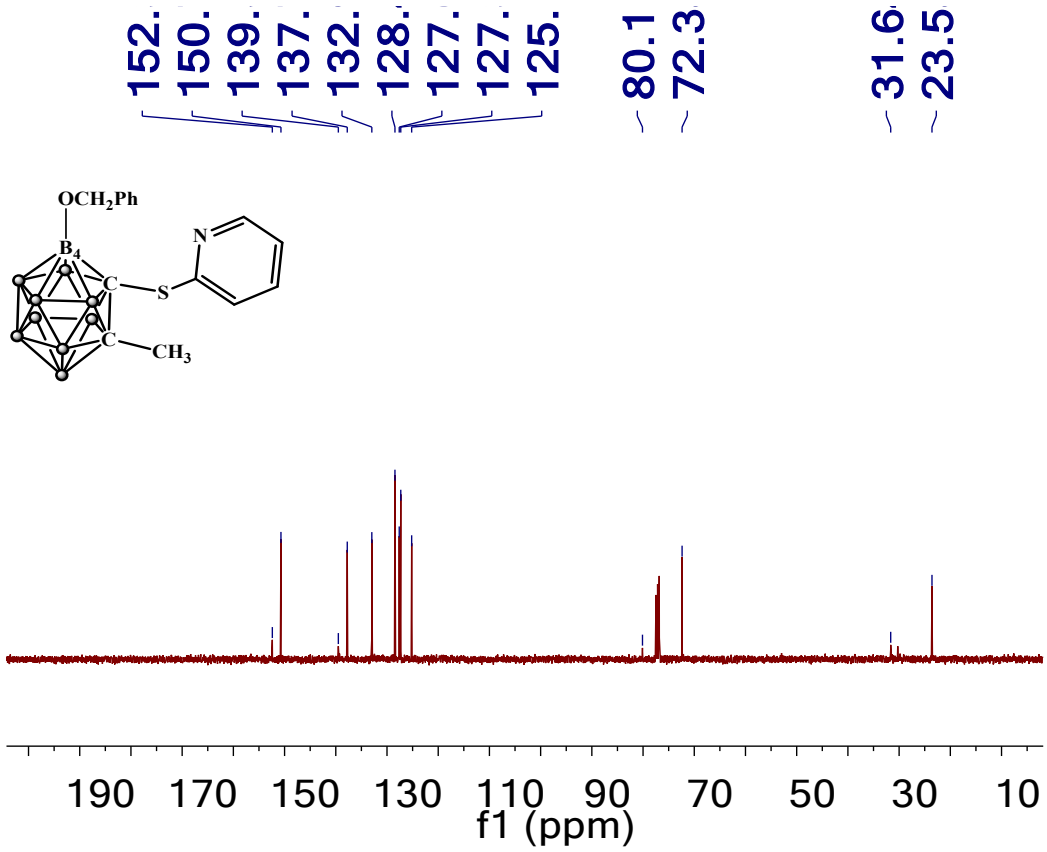
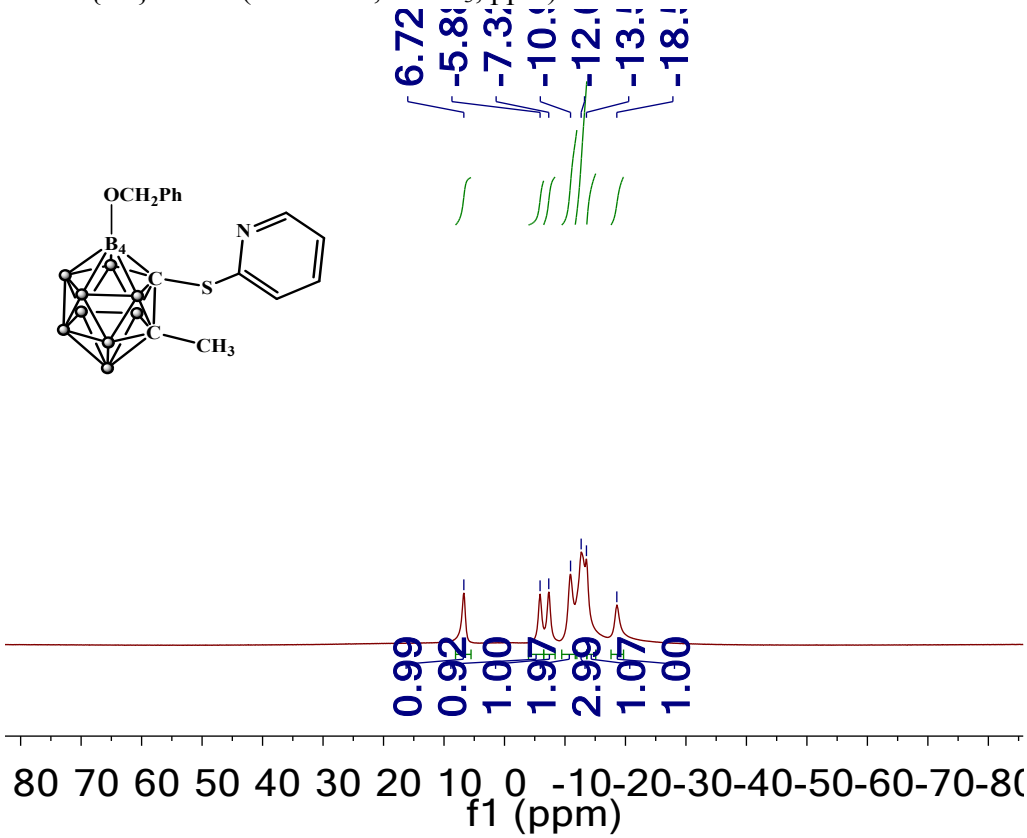


Figure S39. ^{11}B {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **9**.



ESI-MS spectra:

Figure S40. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **1b.**

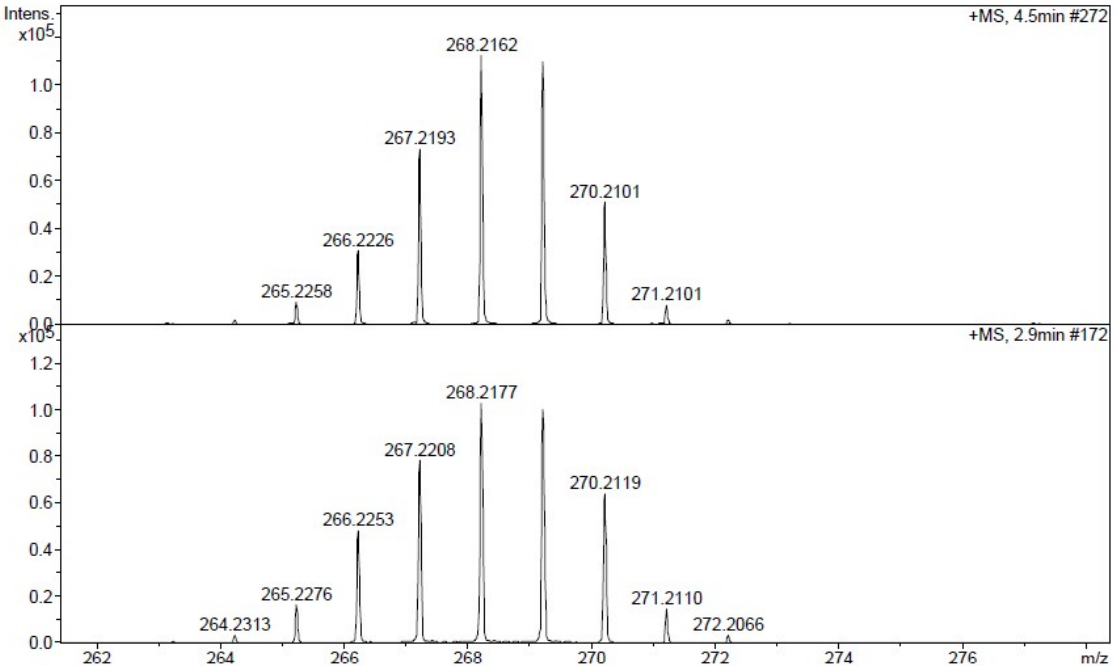


Figure S41. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **1c.**

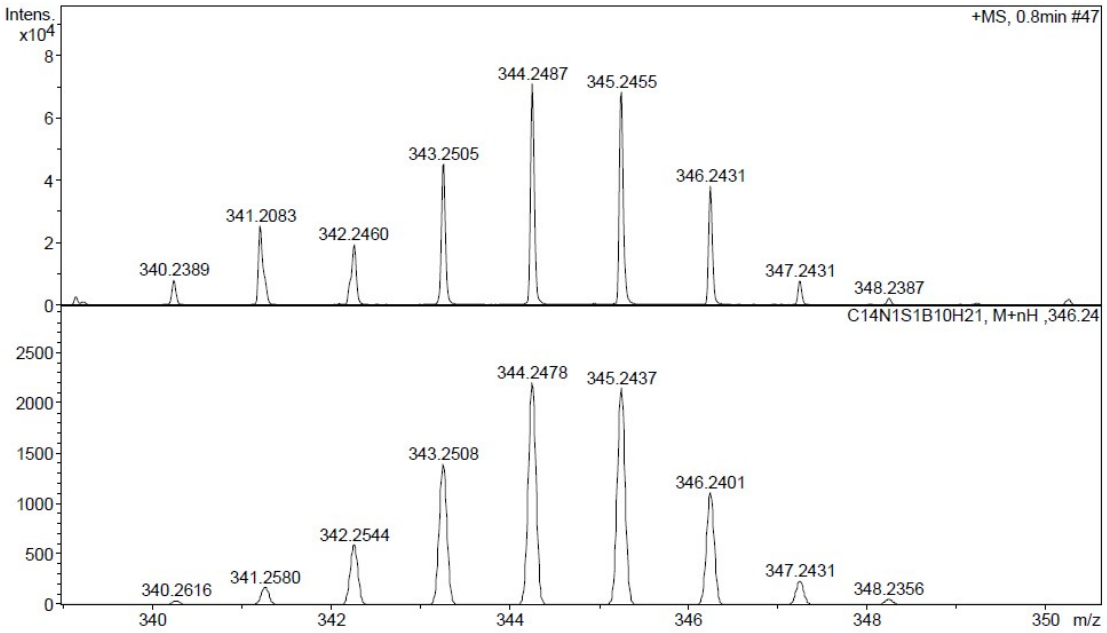


Figure S42. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **6.**

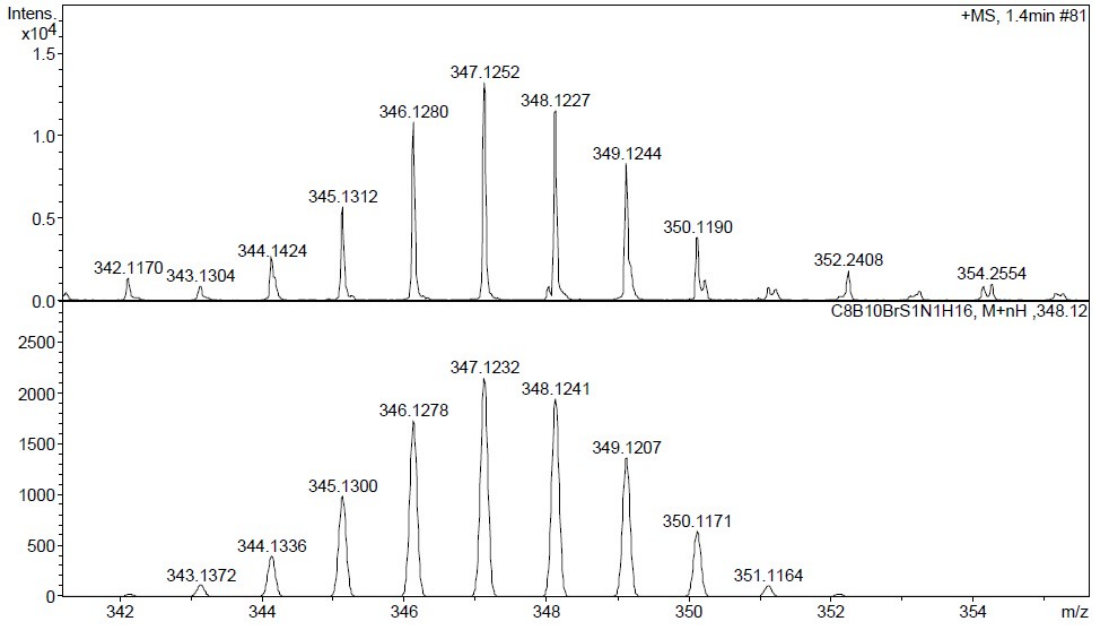


Figure S43. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **7.**

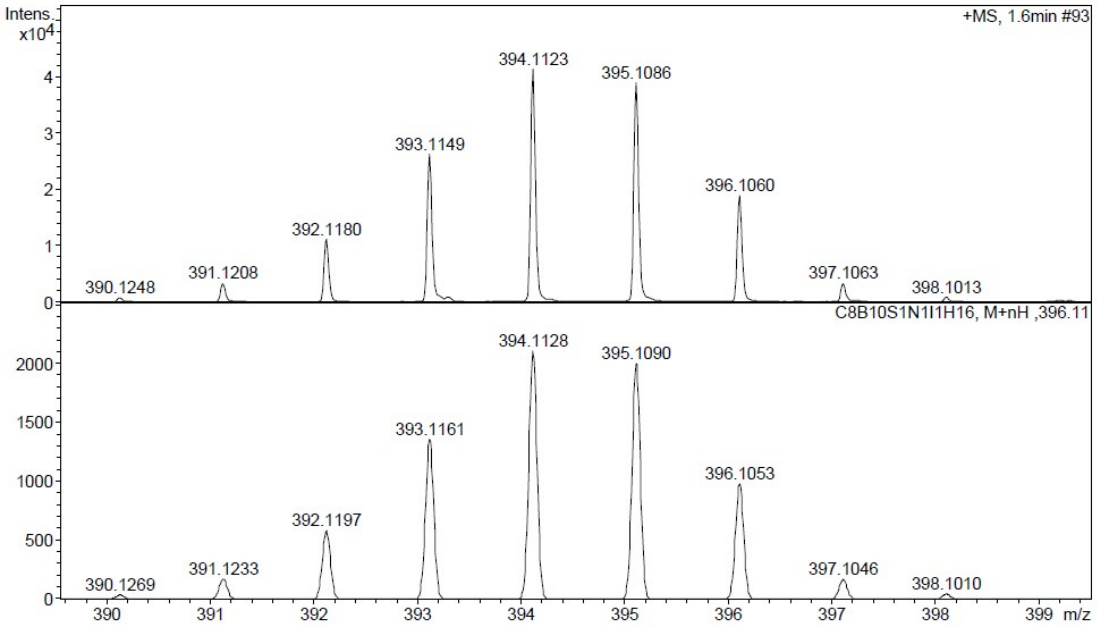


Figure S44. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **6c.**

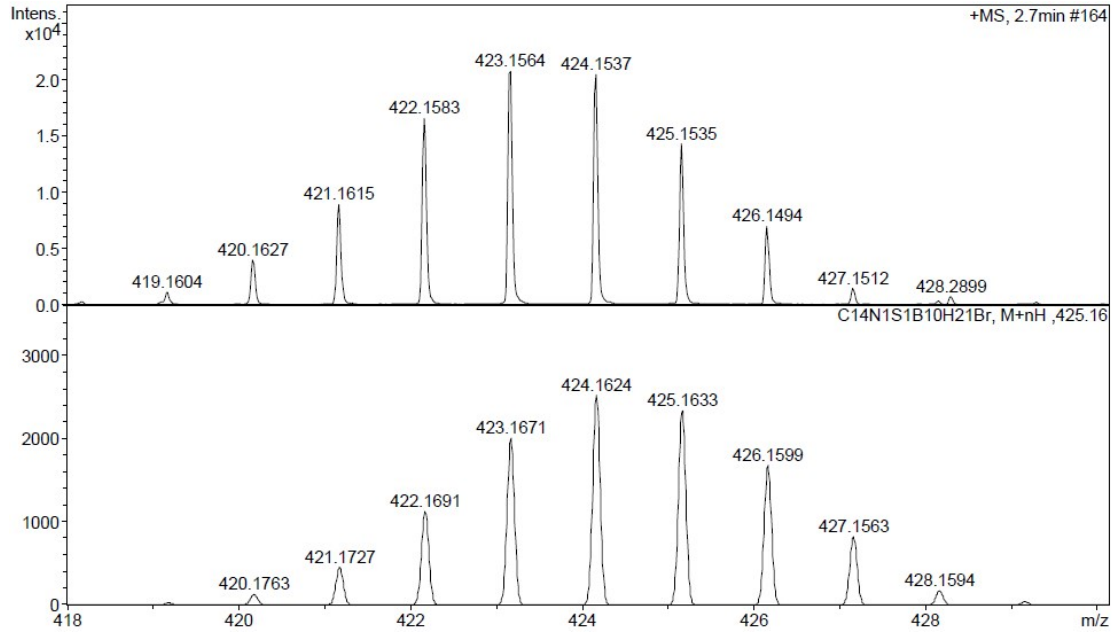


Figure S45. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **8.**

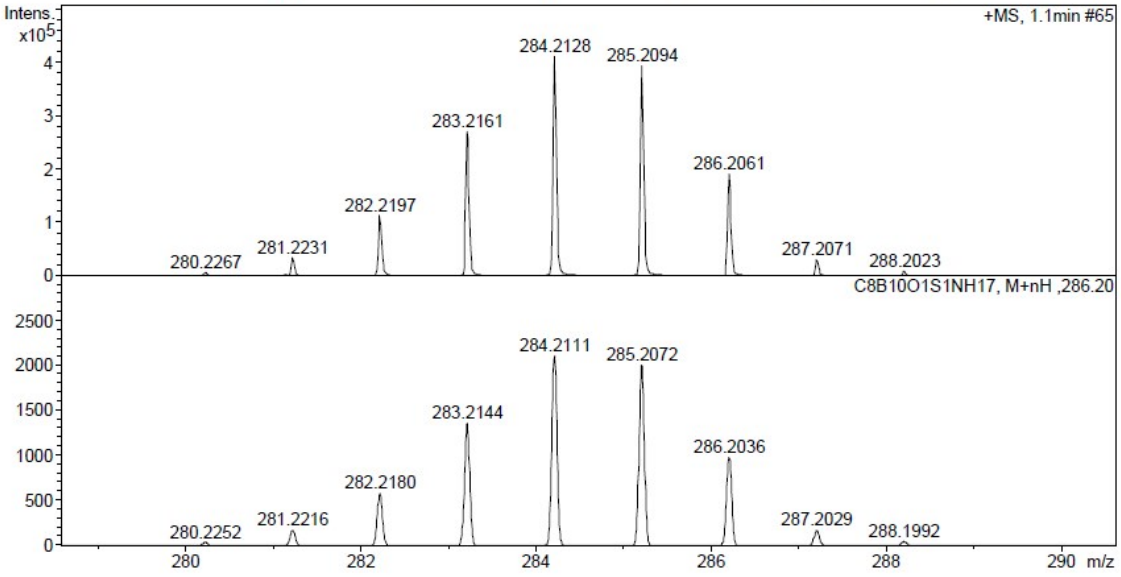
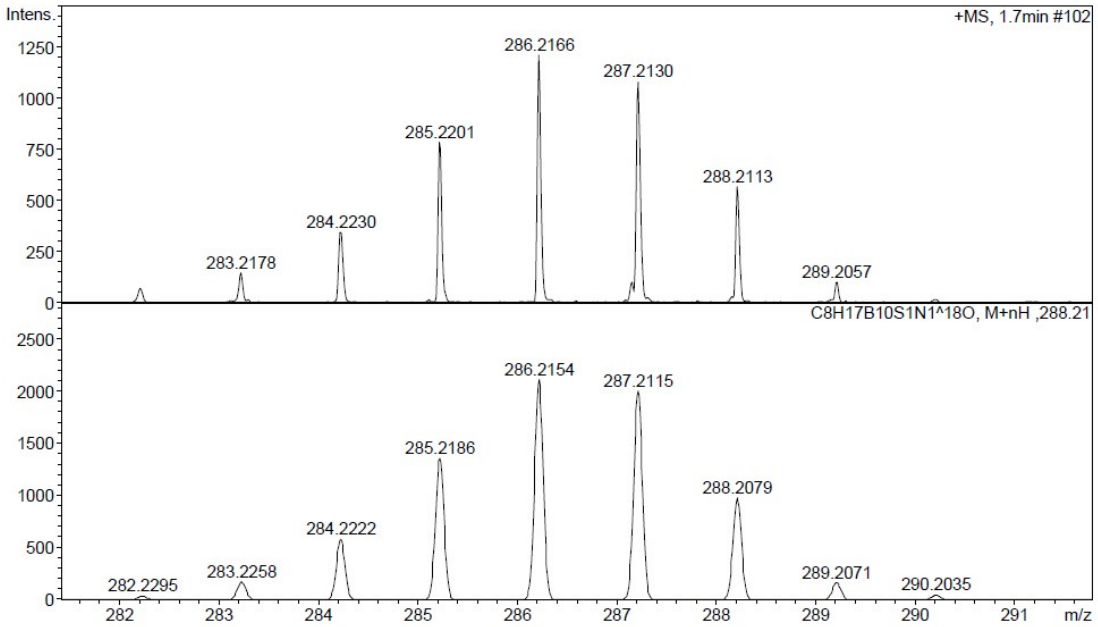


Figure S46. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **8′. (Using $^{18}O_2$)**



Monitoring the reaction for complex 8 by EI-mass:

Compound **1b** (26.8mg, 0.10 mmol), $[Cp^*RhCl_2]_2$ (30.9 mg, 0.05 mmol), AgOTf (51.4 mg, 0.2 mmol), and CH_3COOK (0.1mmol, 10mg) were mixed in CH_2Cl_2 (5 mL). After the reaction mixture was cooled to –78 °C, the reaction tube was evacuated and back-filled with O_2 (3 times, balloon). The reaction tube was then closed after the reaction temperature was warmed to room temperature. The solution detected by EI-MS at 10min, 25min, 55min, 3h and 15 h.

Proposed reaction mechanism.

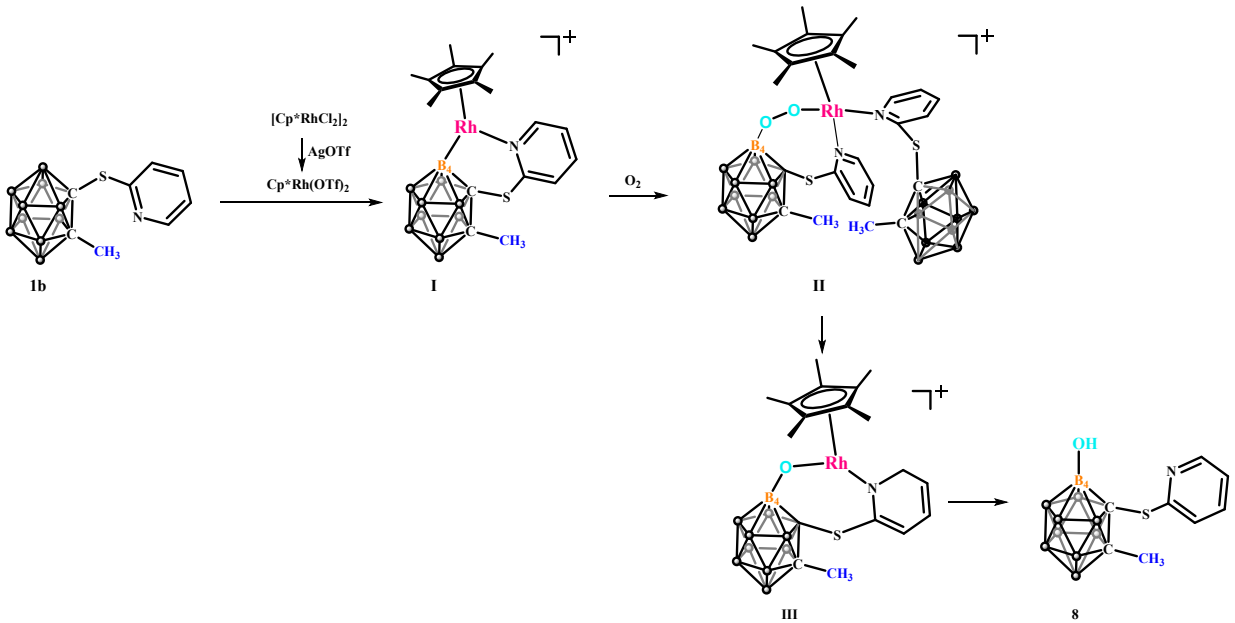


Figure S47. MS data of reaction: (1) 10 min.

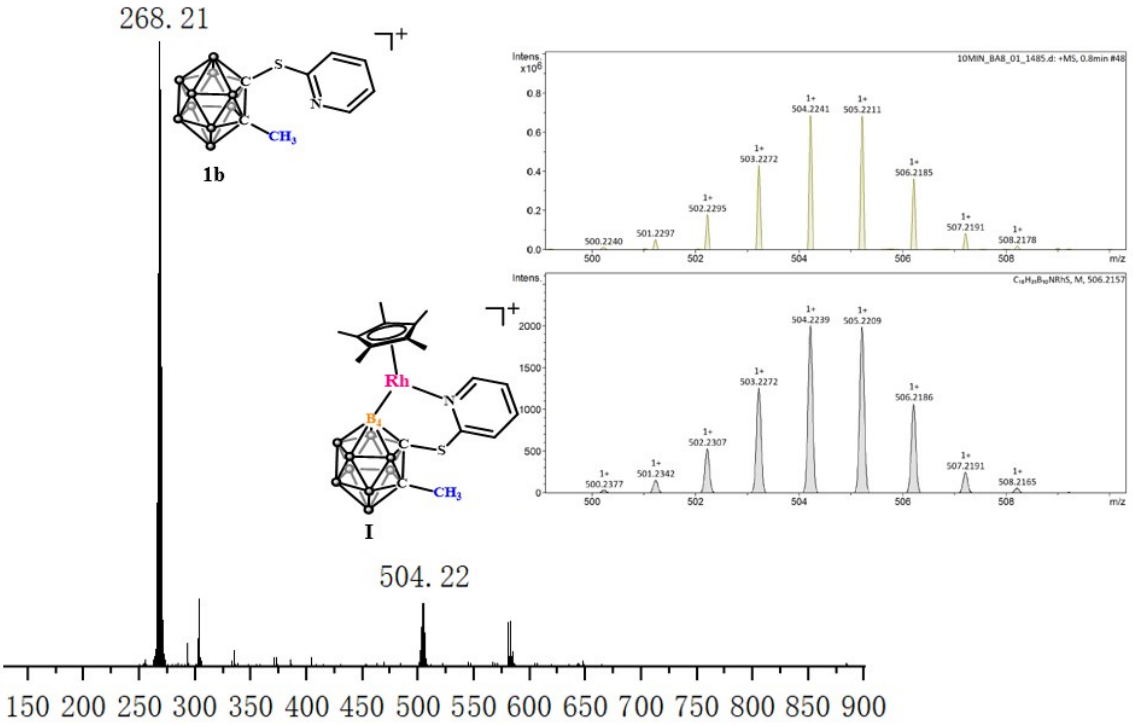


Figure S48. MS data of reaction: (2) 25 min.

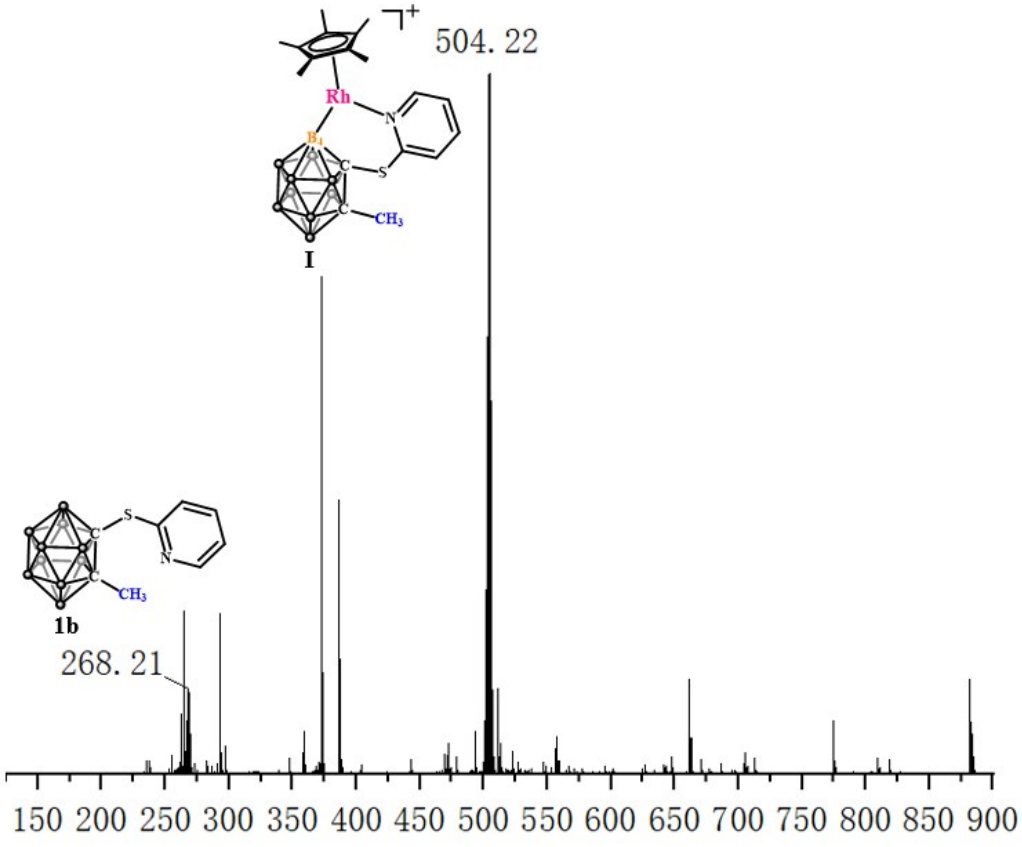


Figure S49. MS data of reaction: (3) 55 min.

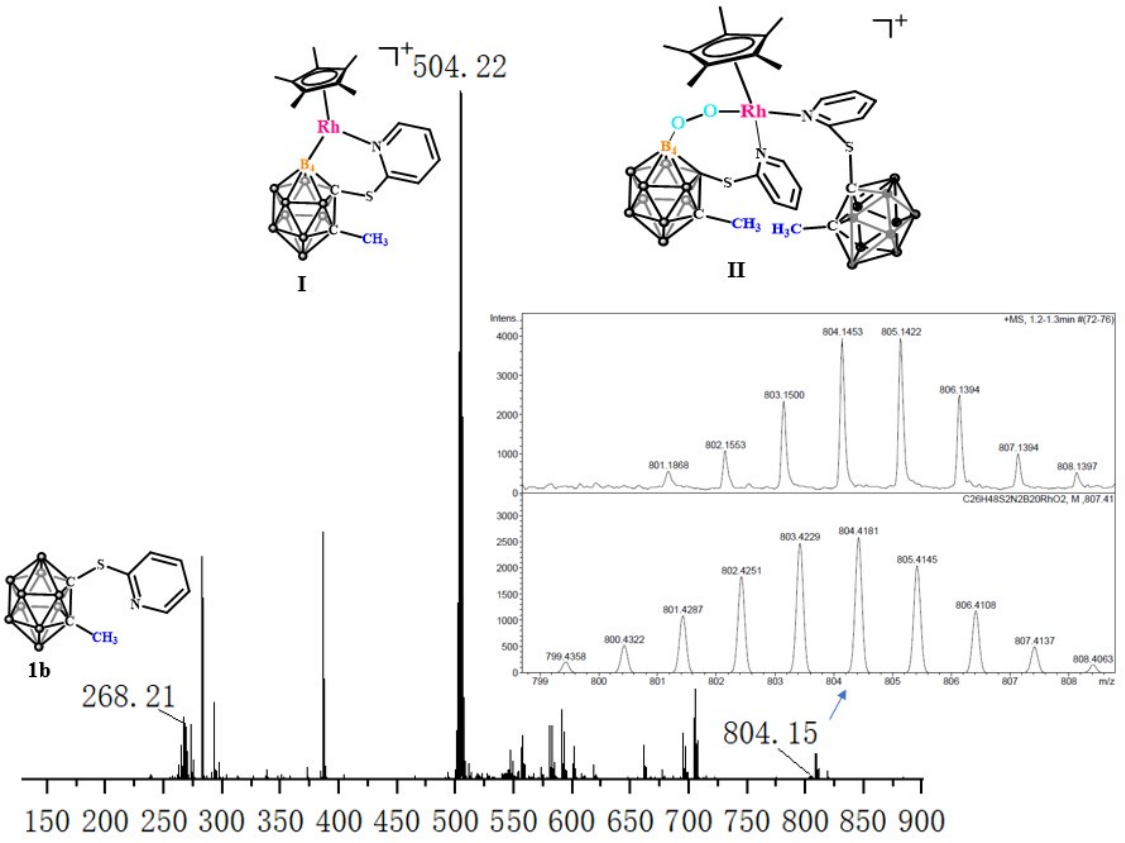


Figure S50. MS data of reaction: (4) 3h.

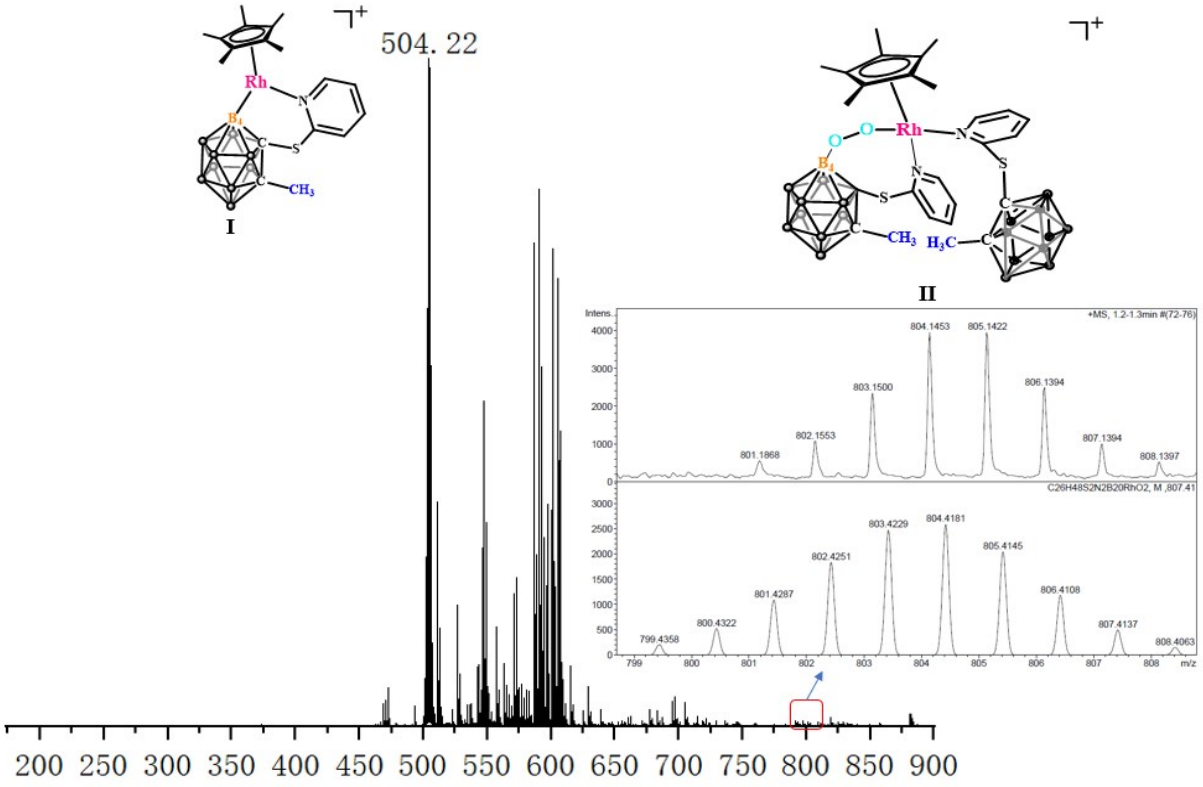
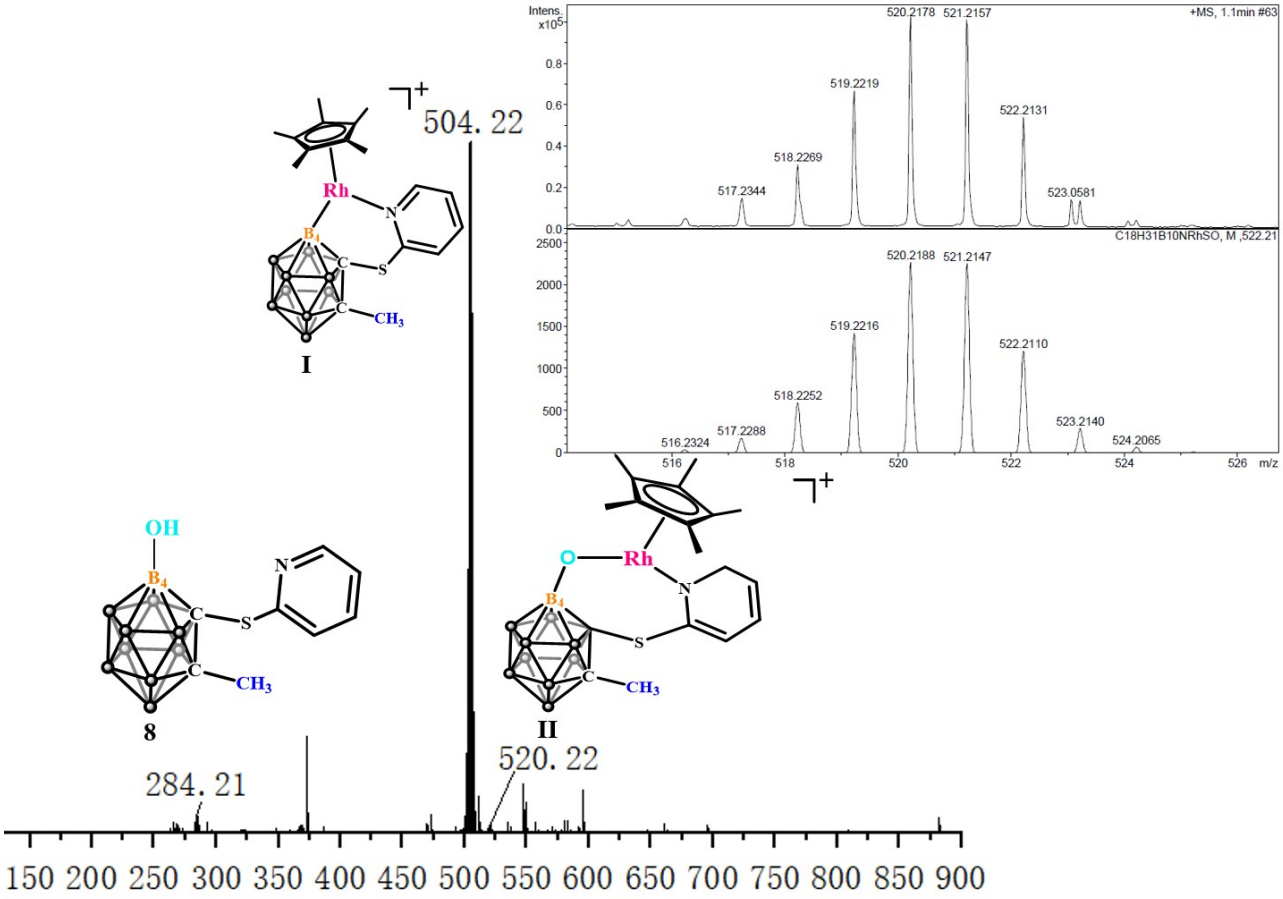


Figure S51. MS data of reaction: (5) 15h.



X-ray crystallography details

X-ray diffraction data of **1b** and **2** were collected on a Bruker D8 Venture system ($Mo_{K\alpha}$, λ = 0.71073 Å). X-ray diffraction data of **3** were collected on a CCD-Bruker APEX DUO system ($Mo_{K\alpha}$, λ = 0.71073 Å). X-ray diffraction data of **4, 5, 6** and **8** were collected on a Bruker D8 Venture system ($Ga_{K\alpha}$, λ = 1.34138 Å). X-ray diffraction data of **8d** were collected on a Bruker D8 Venture system ($Cu_{K\alpha}$, λ = 1.54178 Å). Diffraction data were collected over the full sphere and corrected for absorption. Structure solutions were found with the SHELXS package using direct methods and were refined with the SHELXL program against F^2 using first isotropic and then anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. All calculations were performed using the Bruker Smart program.

In asymmetric unit of **4**, the chloroform molecule was disordered and it was divided into two parts (53:47).

The metallacarborane has mirror symmetry which has a symmetry operator x, 1-y, z. In asymmetric unit of **8** and **8d**, hydrogen atoms of hydroxy group were found in difference map and others were put in calculated positions.

Figure S52. Crystal data and structure refinement for compound 1b.

Empirical formula	C8H17B10NS
Formula weight	267.38
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
a	7.1017(5) Å
b	8.7972(6) Å
c	23.5265(17) Å
Volume	1462.15(18) $Å^3$
α	90°
β	95.855(3)°
γ	90°
Z	4
Density	1.215 Mg/m^3
Absorption coefficient	0.197 mm^{-1}
F(000)	552
Crystal size	0.180 x 0.140 x 0.060 mm^3
Theta range for data collection	2.473 to 27.139°
Index ranges	-9<=h<=9, -11<=k<=11, -30<=l<=30
Reflections collected	25994
Independent reflections	3235 [R(int) = 0.0995]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.453
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3235 / 3 / 193
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1026
R indices (all data)	R1 = 0.0536, wR2 = 0.1112
Extinction coefficient	n/a
Largest diff. peak and hole	0.279 and -0.272 $e.Å^{-3}$

Figure S53. Crystal data and structure refinement for complex 2.

Empirical formula	C17H29B10ClIrNS
Formula weight	615.22
Temperature	173K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a	8.7616(3)
b	14.8923(7)
c	18.1794(8)
Volume	2372.06(17)
α	90
β	90
γ	90
Z	4
Density	1.723
Absorption coefficient	5.836 mm^{-1}
F(000)	1192
Crystal size	0.21×0.18×0.15
Theta range for data collection	2.581 to 26.396°
Index ranges	-10<=h<=10, -17<=k<=18, -22<=l<=22
Reflections collected	25220
Independent reflections	4855 [R(int) = 0.0731]
Completeness to theta = 25.242°	99.90
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.500
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4855 / 2 / 290
Absolute structure parameter	0.471(9)
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0256, wR2 = 0.0495
R indices (all data)	R1 = 0.0290, wR2 = 0.0505
Extinction coefficient	n/a
Largest diff. peak and hole	0.578 and -1.209 $e.Å^{-3}$

Figure S54. Crystal data and structure refinement for complex 3.

Empirical formula	C18H31B10ClIrNS
Formula weight	629.25
Temperature	296.15
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pbca
a	16.183(2)
b	15.932(2)
c	19.224(3)
Volume	4956.5(12)
α	90
β	90
γ	90
Z	8
Density	1.687g/cm^3
Absorption coefficient	5.588 mm^{-1}
F(000)	2448.0
Crystal size	0.18 × 0.14 × 0.08
Theta range for data collection	4.166 to 53.54
Index ranges	-18 ≤ h ≤ 20, -20 ≤ k ≤ 19, -24 ≤ l ≤ 21
Reflections collected	26427
Independent reflections	5285 [R_{int} = 0.0696, R_{sigma} = 0.0533]
Completeness to theta = 26.770°	99.9
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.472
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5285/0/295
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0786
R indices (all data)	R1 = 0.0637, wR2 = 0.0948
Extinction coefficient	n/a
Largest diff. peak and hole	1.46/-0.81 e.Å^{-3}

Figure S55. Crystal data and structure refinement for complex 4.

Empirical formula	C17H29B9NRhS•CHCl3
Formula weight	599.04
Temperature	173.02K
Wavelength	1.34138 Å
Crystal system	monoclinic
Space group	C2/m
a	17.1460(7) Å
b	9.4000(4) Å
c	16.8416(7) Å
Volume	2690.41(19) $Å^3$
α	90°
β	97.623(2)°
γ	90°
Z	4
Density	1.479 Mg/m^3
Absorption coefficient	5.724 mm^{-1}
F(000)	1208.0
Crystal size	0.2 × 0.14 × 0.03 mm^3
Theta range for data collection	9.054 to 116.908°.
Index ranges	$-18 \leq h \leq 21$, $-10 \leq k \leq 11$, $-21 \leq l \leq 21$
Reflections collected	14358
Independent reflections	3069 [Rint = 0.0650, Rsigma = 0.0512]
Completeness to theta = 53.594°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7516 and 0.4531
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3069/62/240
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0905
R indices (all data)	R1 = 0.0360, wR2 = 0.0921
Extinction coefficient	n/a
Largest diff. peak and hole	1.64 and -0.89 $e.Å^{-3}$

Figure S56. Crystal data and structure refinement for complex 5.

Empirical formula	C18H31B10ClNRhS
Formula weight	539.96
Temperature	173(2) K
Wavelength	1.34138 Å
Crystal system	Orthorhombic
Space group	Pbca
a	15.9981(6) Å
b	15.7969(5) Å
c	19.0542(7) Å
Volume	4815.4(3) $Å^3$
α	90
β	90
γ	90
Z	8
Density	1.490 Mg/m^3
Absorption coefficient	5.122 mm^{-1}
F(000)	2192
Crystal size	0.140 x 0.120 x 0.080 mm^3
Theta range for data collection	3.972 to 55.962°.
Index ranges	-19<=h<=19, -15<=k<=19, -23<=l<=23
Reflections collected	35086
Independent reflections	4755 [R(int) = 0.1197]
Completeness to theta = 53.594°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.751 and 0.312
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4755 / 60 / 295
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1219
R indices (all data)	R1 = 0.0627, wR2 = 0.1323
Extinction coefficient	n/a
Largest diff. peak and hole	1.145 and -1.515 $e.Å^{-3}$

Figure S57. Crystal data and structure refinement for complex 6.

Empirical formula	C8H16B10BrNS
Formula weight	346.29
Temperature	200.01 K
Wavelength	1.54178 Å
Crystal system	orthorhombic
Space group	P212121
a	8.880(3) Å
b	12.558(3) Å
c	14.122(3) Å
a	90°
b	90°
g	90°
Volume	1574.7(7) $Å^3$
Z	4
Density (calculated)	1.461 Mg/m^3
Absorption coefficient	3.121 mm^{-1}
F(000)	688.0
Crystal size	0.12 × 0.11 × 0.08 mm^3
Theta range for data collection	10.238 to 111.896°.
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 12$, $-14 \leq l \leq 17$
Reflections collected	10415
Independent reflections	3089 [Rint = 0.0606, Rsigma = 0.0582]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7512 and 0.4961
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3089/0/192
Absolute structure parameter	0.51(5)
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.1030
R indices (all data)	R1 = 0.0550, wR2 = 0.1088
Extinction coefficient	n/a
Largest diff. peak and hole	1.05 and -0.36 $e.Å^{-3}$

Figure S57. Crystal data and structure refinement for complex 8.

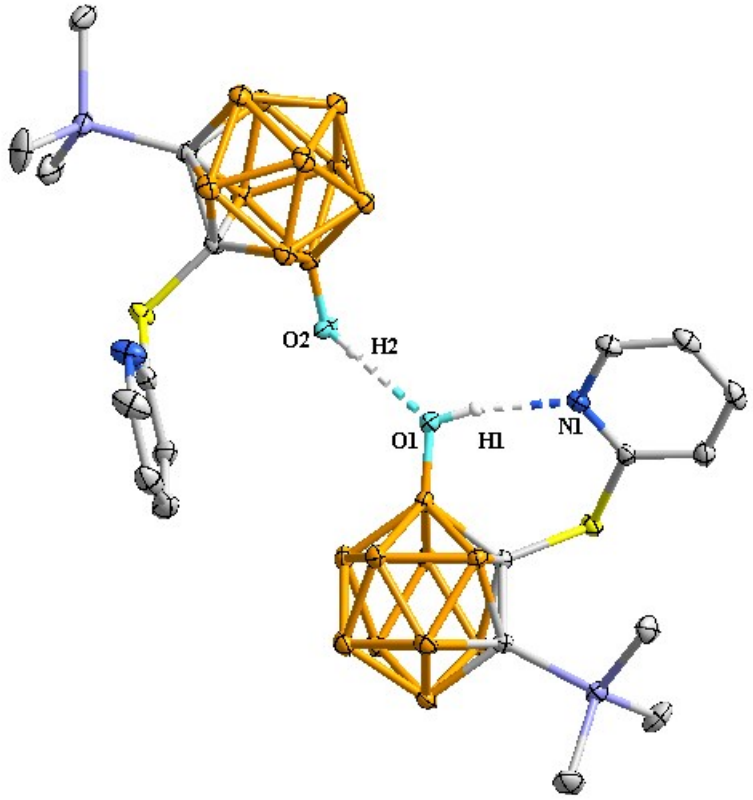
Empirical formula	C8H17B10NOS
Formula weight	283.38
Temperature	296(2) K
Wavelength	1.34138 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
a	13.0313(7) Å
b	12.7774(7) Å
c	9.0470(4) Å
Volume	1506.38(13) $Å^3$
α	90°
β	90°
γ	90°
Z	4
Density	1.250 Mg/m^3
Absorption coefficient	1.150 mm^{-1}
F(000)	584
Crystal size	0.370 x 0.140 x 0.120 mm^3
Theta range for data collection	5.212 to 57.051°.
Index ranges	-15<=h<=16, -15<=k<=15, -9<=l<=11
Reflections collected	10291
Independent reflections	2745 [R(int) = 0.0795]
Completeness to theta = 53.594°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.751 and 0.590
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2745 / 2 / 195
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0397, wR2 = 0.0941
R indices (all data)	R1 = 0.0653, wR2 = 0.1042
Absolute structure parameter	0.00(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.252 and -0.295 $e.Å^{-3}$

Figure S58. Crystal data and structure refinement for complex 8d.

Empirical formula	C10H23B10NOSSi
Formula weight	341.54
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
a	9.6689(5) Å
b	13.6644(8) Å
c	15.5496(8) Å
a	103.901(3)°
b	93.292(3)°.
g	106.301(3)°.
Volume	1896.81(18) $Å^3$
Z	4
Density (calculated)	1.196 Mg/m^3
Absorption coefficient	2.055 mm^{-1}
F(000)	712
Crystal size	0.180 x 0.090 x 0.030 mm^3
Theta range for data collection	2.954 to 71.498°.
Index ranges	-11<=h<=11, -16<=k<=16, -19<=l<=19
Reflections collected	73951
Independent reflections	7396 [R(int) = 0.0821]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.754 and 0.554
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7396 / 2 / 447
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.1059
R indices (all data)	R1 = 0.0497, wR2 = 0.1124
Extinction coefficient	n/a
Largest diff. peak and hole	0.297 and -0.425 $e.Å^{-3}$

α : $R_1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2=[\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2F_c^2]/3(F_0^2>2\sigma F^2)$.

Figure S59. Molecular structure of complex **8d**.



Ellipsoids are set at 30% probability. Color code: O, cyan; S, yellow; N, blue; C, grey; B, orange; Si, light purple; H, white. Some of H atoms have been omitted. The distance of O1-H1···N1 hydrogen bond is 1.858(17) Å. The distance of O2-H2···O1 hydrogen bond is 1.940(17) Å.

Reference

1. C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.*, 1992, **29**, 228.
2. O. Crespo, M. C. Gimeno and A. Laguna, *Polyhedron,* 1999, **18**, 1279–1283.