Formation and Reactivity of a Unique M···C-H Interaction Stabilized by Carborane Cages

Xin-Ran Liu[†a], Peng-Fei Cui[†a], Yago García-Rodeja[b], Miquel Solà[b], and Guo-Xin Jin*[a]

a. State Key Laboratory of Molecular Engineering of Polymers, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai, 200433 (P. R. China).

b. Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, C/Maria Aurèlia Capmany, 69, 17003 Girona, Spain.

Corresponding author: Guo-Xin Jin E-mail: gxjin@fudan.edu.cn

Table of Contents

S1. Materials and Methods Experimental Procedures

Materials

All reagents and solvents were purchased from commercial sources (Sigma Aldrich, Chem-extension, Leyan and Energy Chemical) and used as supplied unless otherwise mentioned. The starting material $[Cp^*IrCl_2]_2$[1] and $[Cp^*RhCl_2]_2$[1] were prepared by literature method.

Methods

NMR spectra were recorded on Bruker AVANCE I 400 Spectrometers. Spectra were recorded at room temperature and referenced to the residual protonated solvent for NMR spectra. Proton chemical shifts (δ H = 7.26 ($CDCl_3$)); (δ C = 77.16 ($CDCl_3$)); (δ H = 3.31 (CD_3OD)) and (δ C = 49.00 (CD_3OD)) are reported relative to the solvent residual peak. Coupling constants are expressed in hertz.

Infrared (IR) spectra of solid samples (KBr tablets) were measured using a Nicolet AVATAR-360IR spectrometer in the wavelength range of 400–4000 cm^{-1}.

UV–vis absorbance of samples was measured using an Agilent Cary 100 UV spectrophotometer with 0.1 mM solutions in dichloromethane.

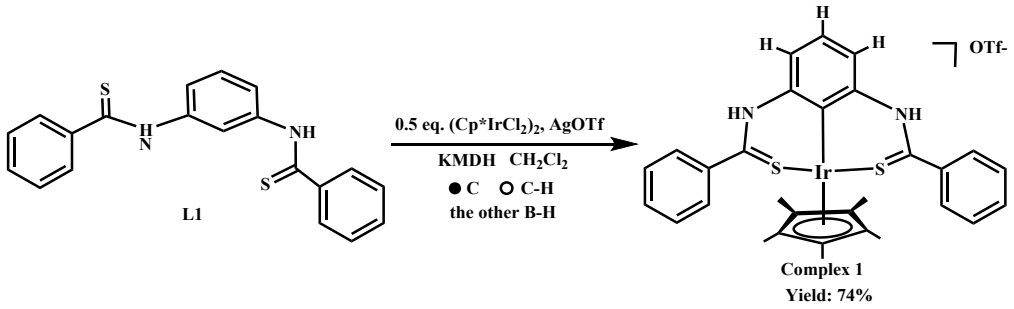
ESI-MS of samples were measured using a Water G2-xs time-of-flight mass spectrometer using ESI.

Single crystals of **L3**, **L4**, complex **3a**, complex **3b**, complex **4**, complex **5a**, complex **5b** and complex **6** suitable for X-ray diffraction study were obtained at suitable temperature. X-ray intensity data of **L3** and complex **6** were collected on a Bruker D8 Venture system ($Cu_{K\alpha}$, λ = 1.54178 Å). X-ray intensity data of the others were collected on a CCD-Bruker SMART APEX system ($Ga_{K\alpha}$, λ = 1.34138 Å).

CCDC number: 2303640 (**L3**); 2303643 (**L4**); 2303637 (complex **3a**); 2303636 (complex **3b**); 2303641 (complex **4**); 2303638 (complex **5a**); 2303644 (complex **5b**); 2303639 (complex **6**).

S2. Synthesis and Characterization

S2.1 Synthesis and Characterization of complex 1.



Scheme S1. Synthesis of complex **1**.

Ligand **1** (34.85 mg, 0.10 mmol), $[Cp^*IrCl_2]_2$ (40.40 mg, 0.05 mmol), AgOTf (51.20 mg, 0.20 mmol) and KMDH (0.05 mL) were added to the CH_2Cl_2 solution (10 mL) at room temperature. The reaction mixture was stirred in the dark for 8 h. Then the mixture was filtrated and the filtrate was concentrated and further purified via silica gel column chromatography (CH_2Cl_2 : MeOH, 30 : 1). Orange solids were obtained and dried under vacuo to give the complex **1**: 60.98 mg 74%. ^1H NMR (400 MHz; $CDCl_3$, 298K, ppm): δ = 1.64 (s, 15H, Cp*-H); 6.65 (t, 1H, Ar-H); 7.45 (d, 2H, Ar-H); 7.48 (t, 4H, Ar-H); 7.62 (t, 2H, Ar-H); 8.00 (d, 4H, Ar-H). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$, 298K, ppm): δ =8.17, 93.75 (Cp*-C), 107.98, 119.20, 126.05, 128.95, 129.13, 133.74, 136.33, 143.40 (Ar-C); 190.19 (N-C=S). IR (KBr disk, cm^{-1}): v = 3213.38, 3059.26, 2959.48, 2920.72, 1593.74, 1529.12, 1452.09, 1424.20, 1382.08, 1285.65, 1245.43, 1158.25, 1029.63, 916.53, 880.68, 691.69, 637.18, 516.68. ESI-MS: m/z = 675.1479 (calcd for $[M - OTf]^+$ = 675.1456).

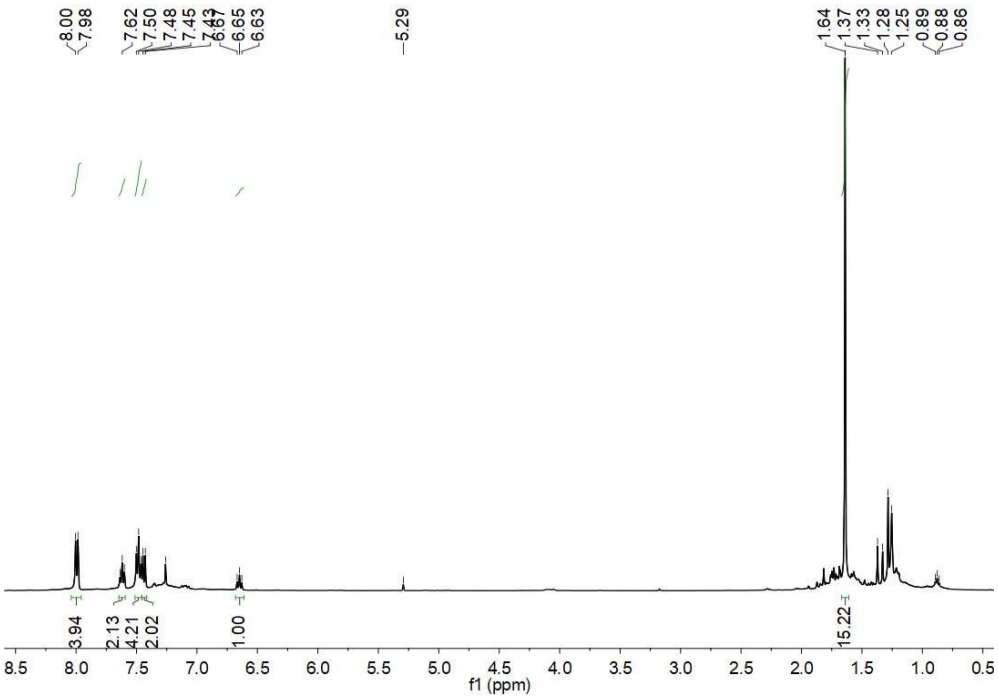


Figure S1. ^1H NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **1**.

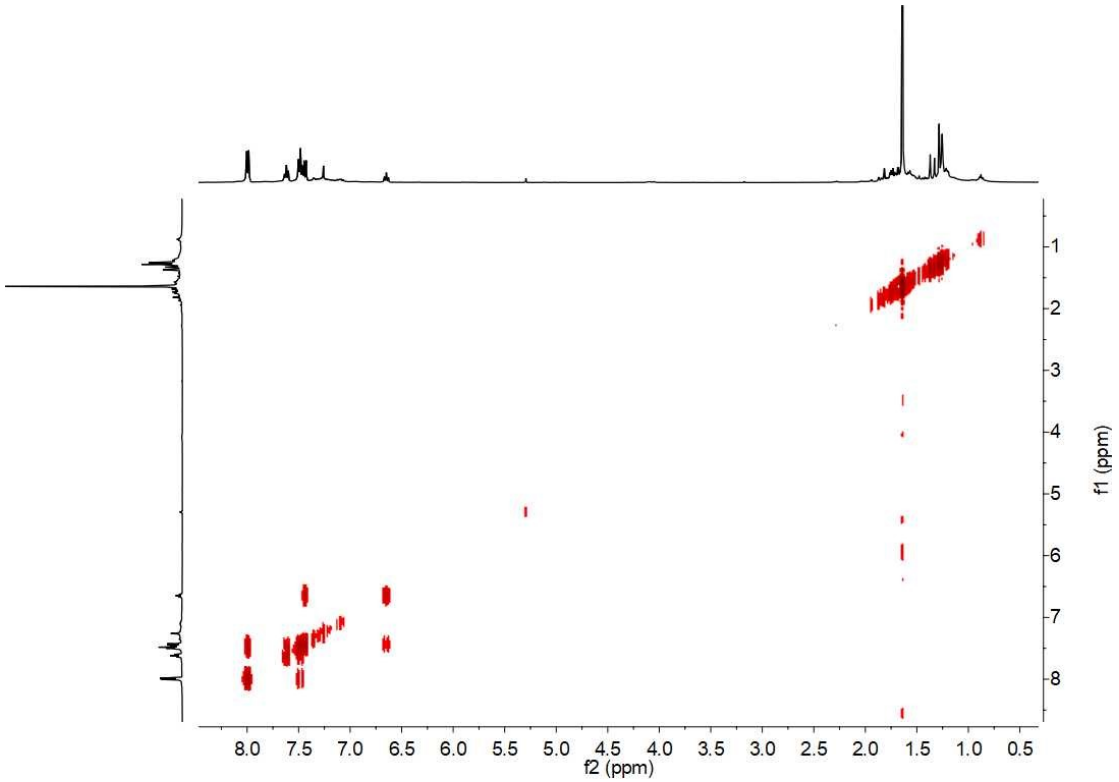


Figure S2.^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **1**.

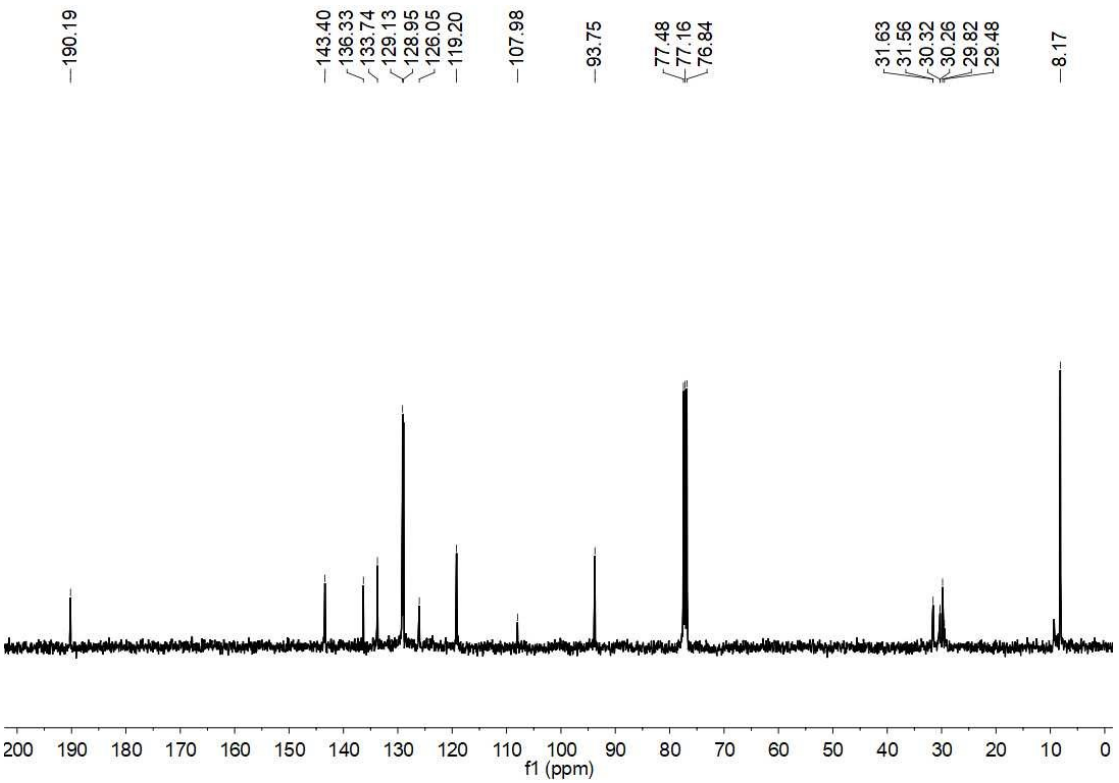


Figure S3. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298K, ppm) of complex **1**.

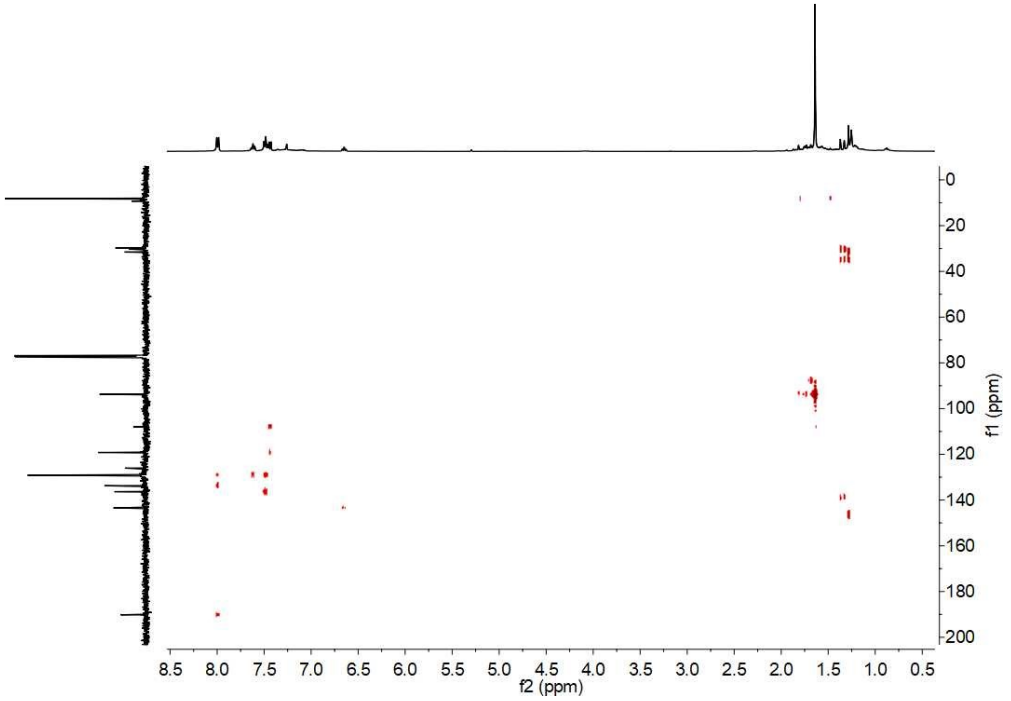


Figure S4. ^{13}C-^{1}H HMBC NMR (400 MHz, $CDCl_3$, 298K) of complex **1**.

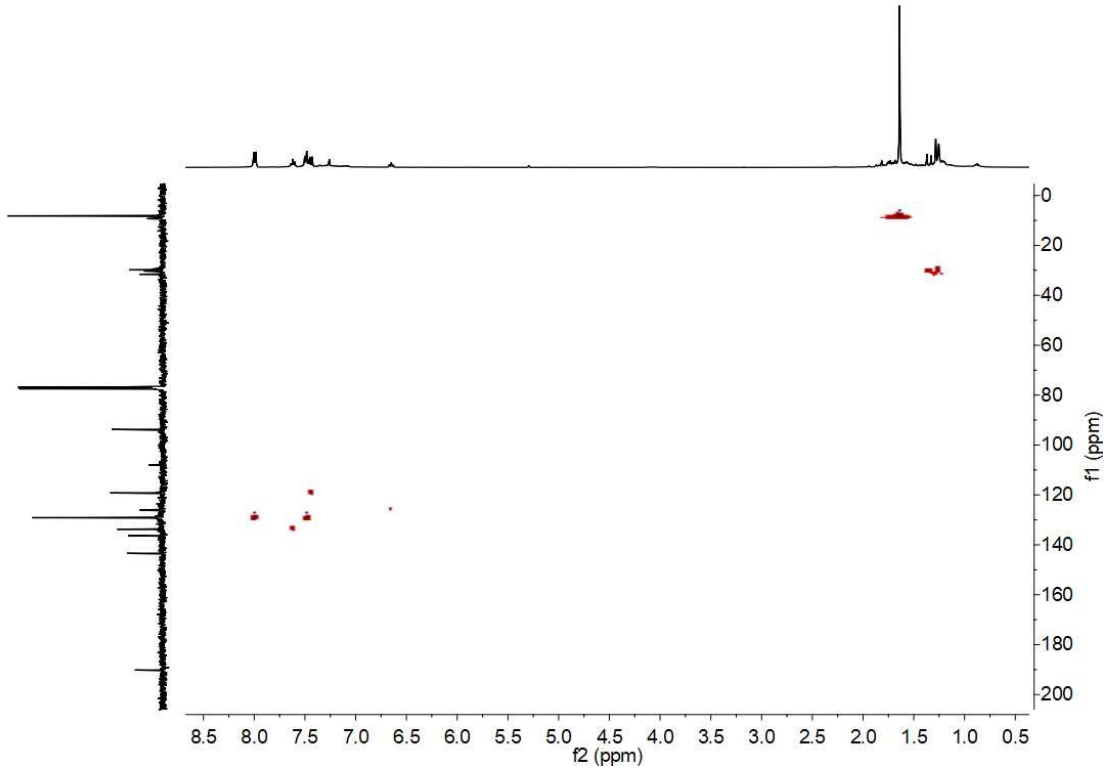


Figure S5. ^{13}C-^{1}H HSQC NMR (400 MHz, $CDCl_3$, 298K) of complex **1**.

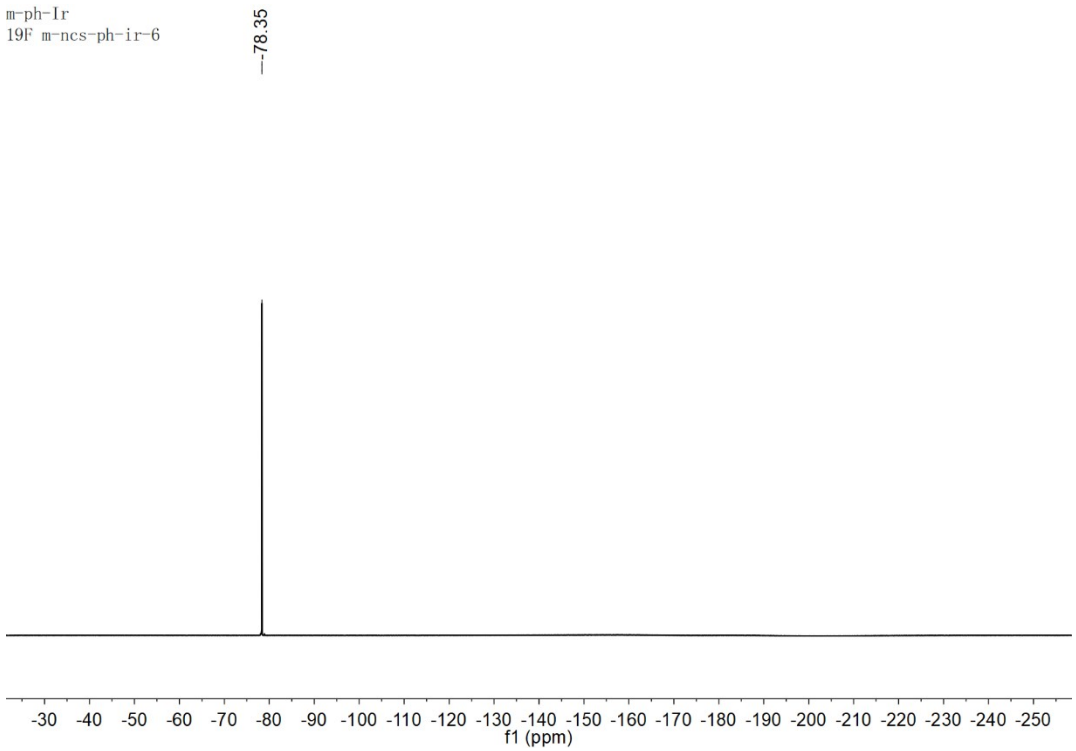


Figure S6. ^{19}F NMR (378 MHz, $CDCl_3$, 298K) of complex **1**.

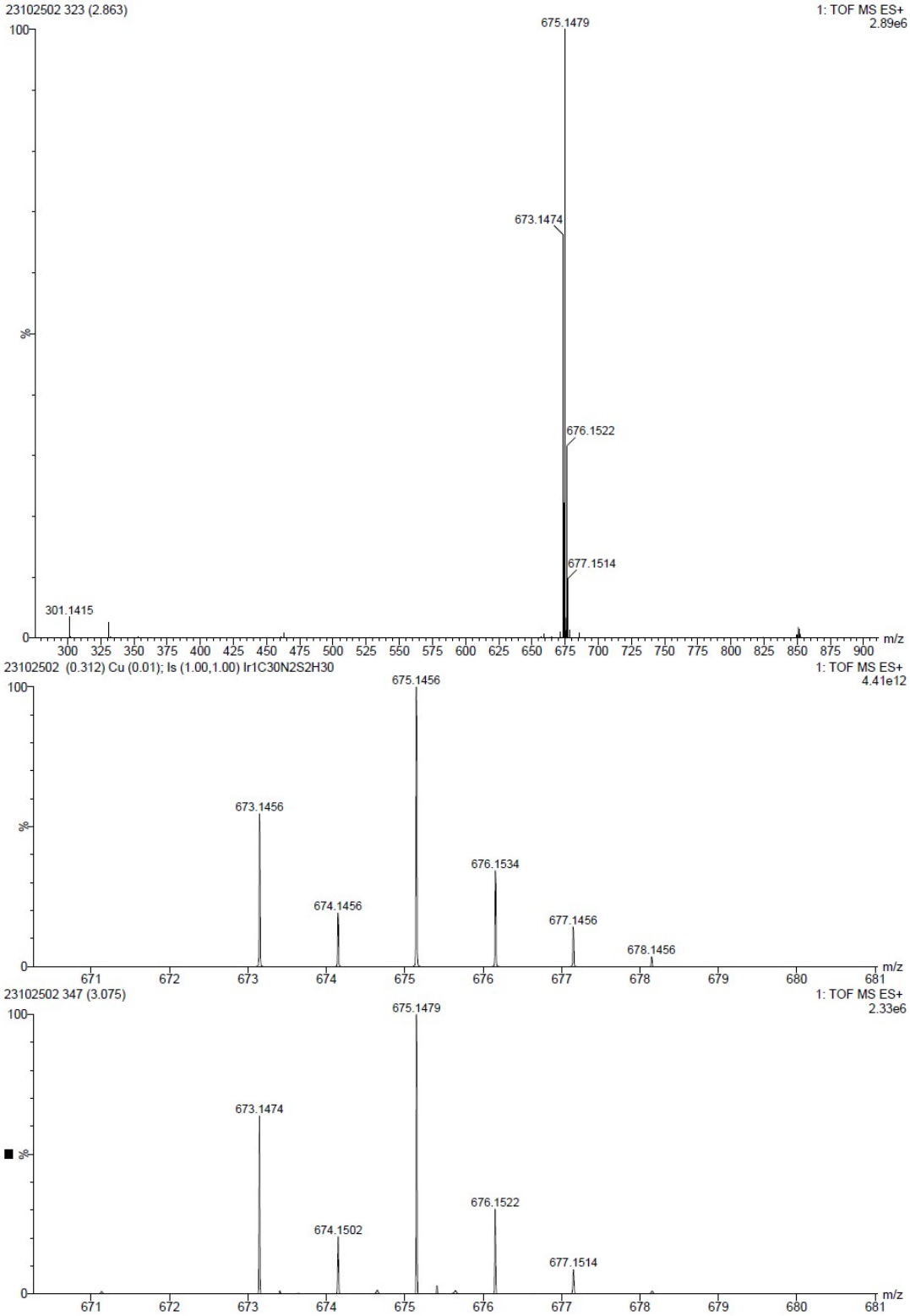
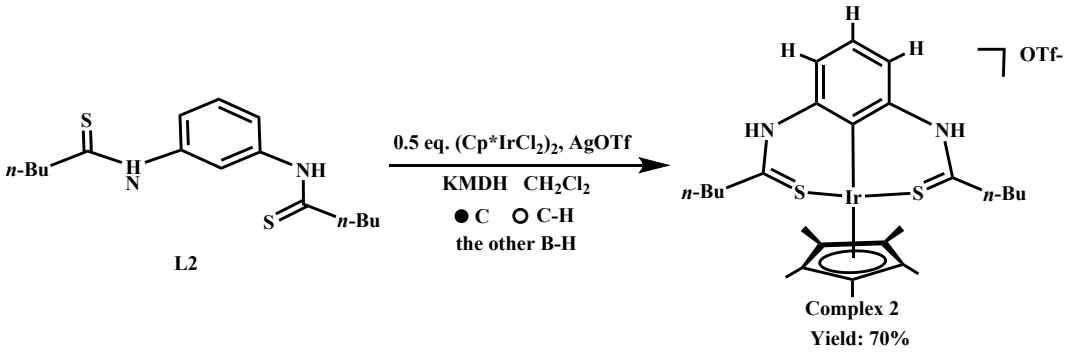


Figure S7. Experimental (bottom) and theoretical (top) ESI-MS of complex **1.**

S2.2 Synthesis and Characterization of complex 2.



Scheme S2. Synthesis of complex **2**.

Ligand **2** (30.85 mg, 0.10 mmol), $[Cp^*IrCl_2]_2$ (40.40 mg, 0.05 mmol), AgOTf (51.20 mg, 0.20 mmol) and KMDH (0.05 mL) were added to the CH_2Cl_2 solution (10 mL) at room temperature. The reaction mixture was stirred in the dark for 8 h. Then the mixture was filtrated and the filtrate was concentrated and further purified via silica gel column chromatography (CH_2Cl_2 : MeOH, 10 : 1). Orange solids were obtained and dried under vacuo to give the complex **2**: 54.88 mg 70%. ^{1}H NMR (400 MHz; $CDCl_3$, 298K, ppm): δ = 1.52 (s, 15H, Cp*-H); 0.94 (t, 6H, Bu-H); 1.43 (m, 4H, Bu-H); 1.77 (t, 4H, Bu-H); 2.85 (m, 4H, Bu-H); 6.52 (t, 1H, Ar-H); 7.01 (d, 2H, Ar-H); 10.94 (s, 2H, N-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, 298K, ppm): δ = 7.84, 93.32 (Cp*-C), 13.79, 22.35, 31.65, 42.51 (Bu-C); 102.37, 117.80, 125.41, 142.41 (Ar-C); 196.61 (N-C=S). IR (KBr disk, cm^{-1}): v = 3235.20, 2962.96, 2924.42, 2852.87, 2360.30, 1600.41, 1449.93, 1382.42, 1261.69, 1097.10, 1028.25, 864.48, 802.32, 637.20. ESI-MS: m/z = 635.2096 (calcd for $[M - OTf]^+$ = 635.2083).

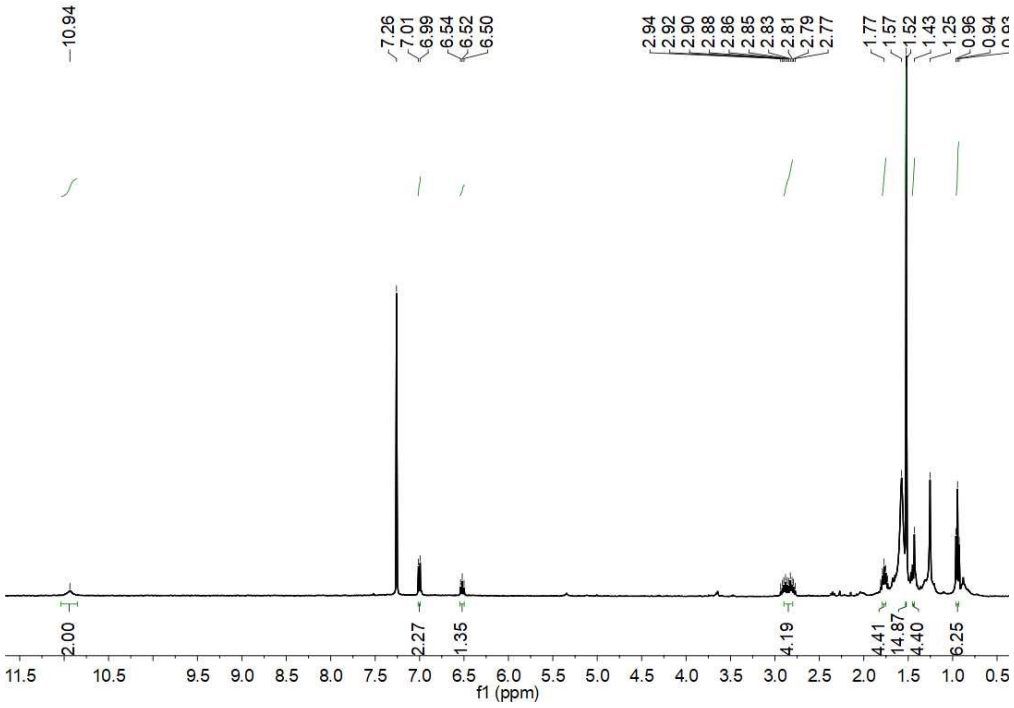


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **2**.

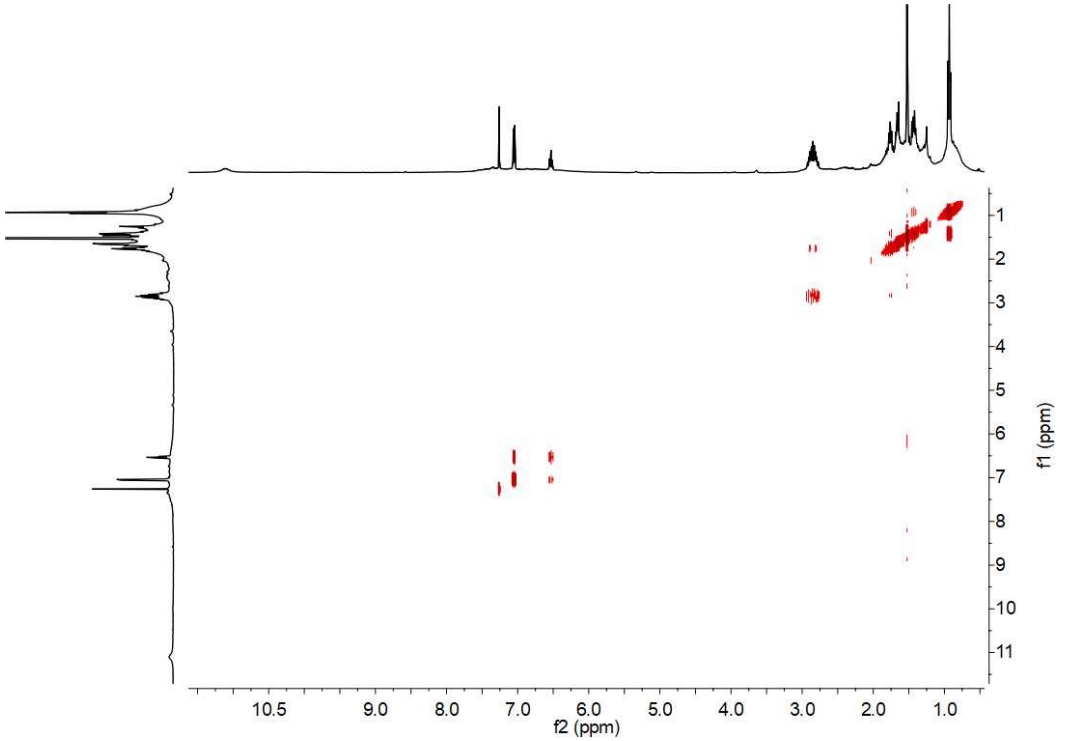


Figure S9.^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **2**.

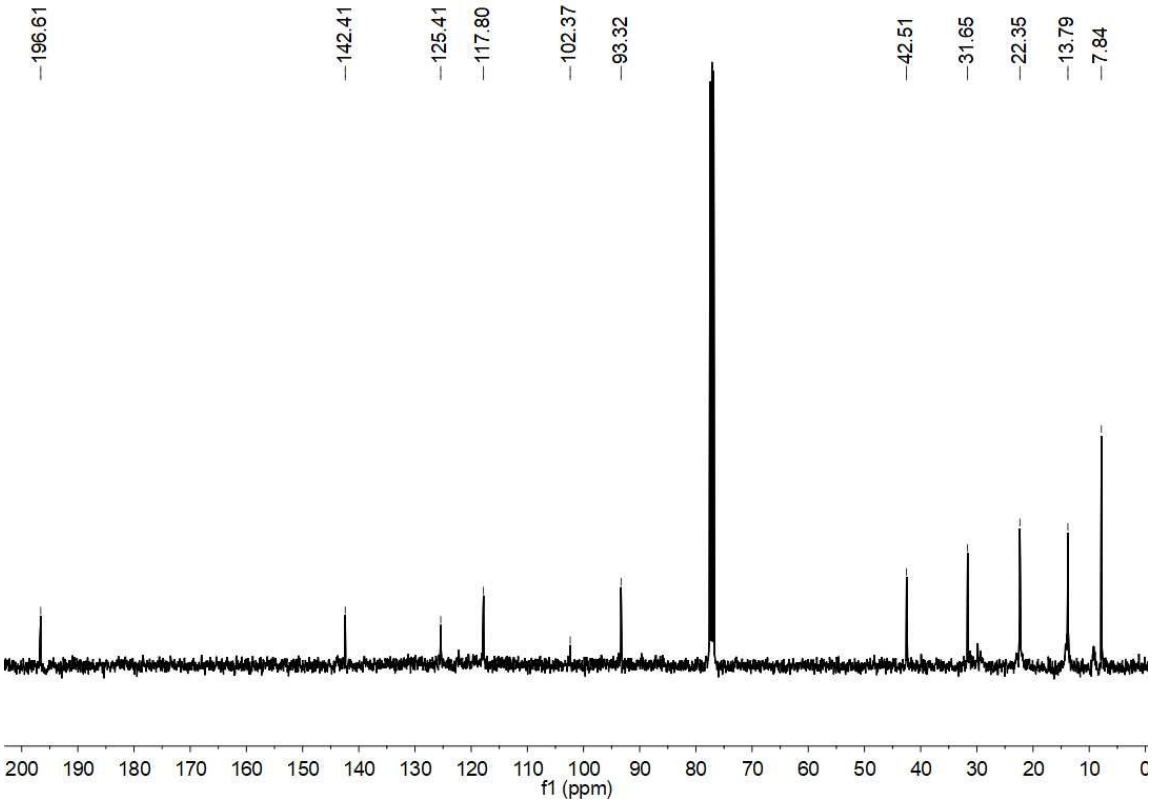


Figure S10. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298K, ppm) of complex **2**.

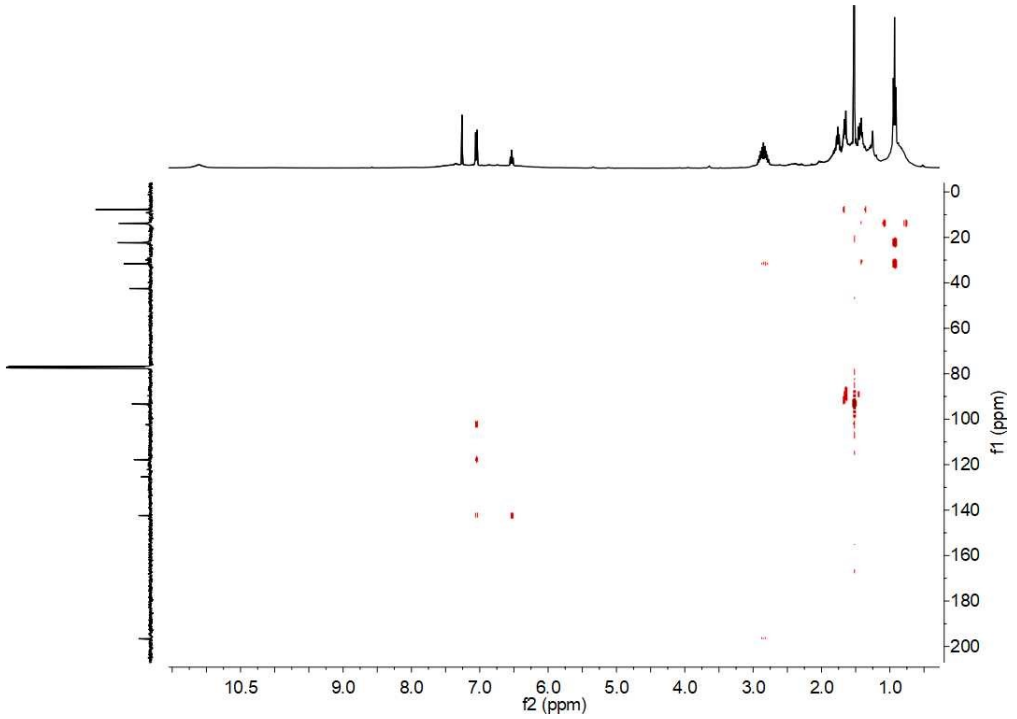


Figure S11. ^{13}C-^{1}H HMBC NMR (400 MHz, $CDCl_3$, 298K) of complex **2**.

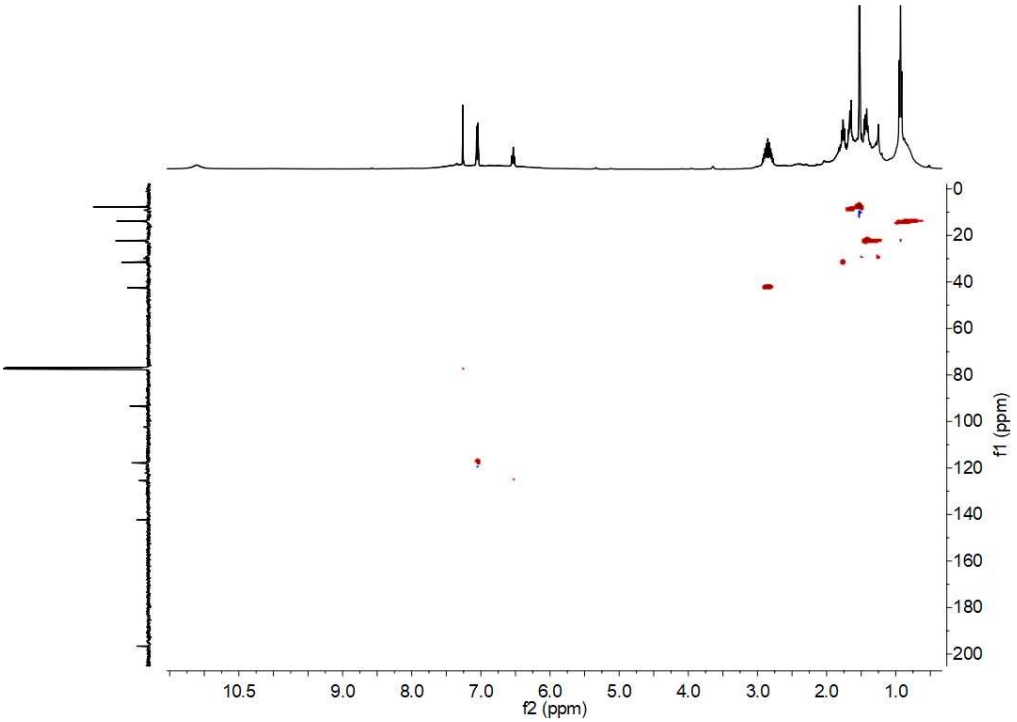


Figure S12. ^{13}C-^{1}H HSQC NMR (400 MHz, $CDCl_3$, 298K) of complex **2**.

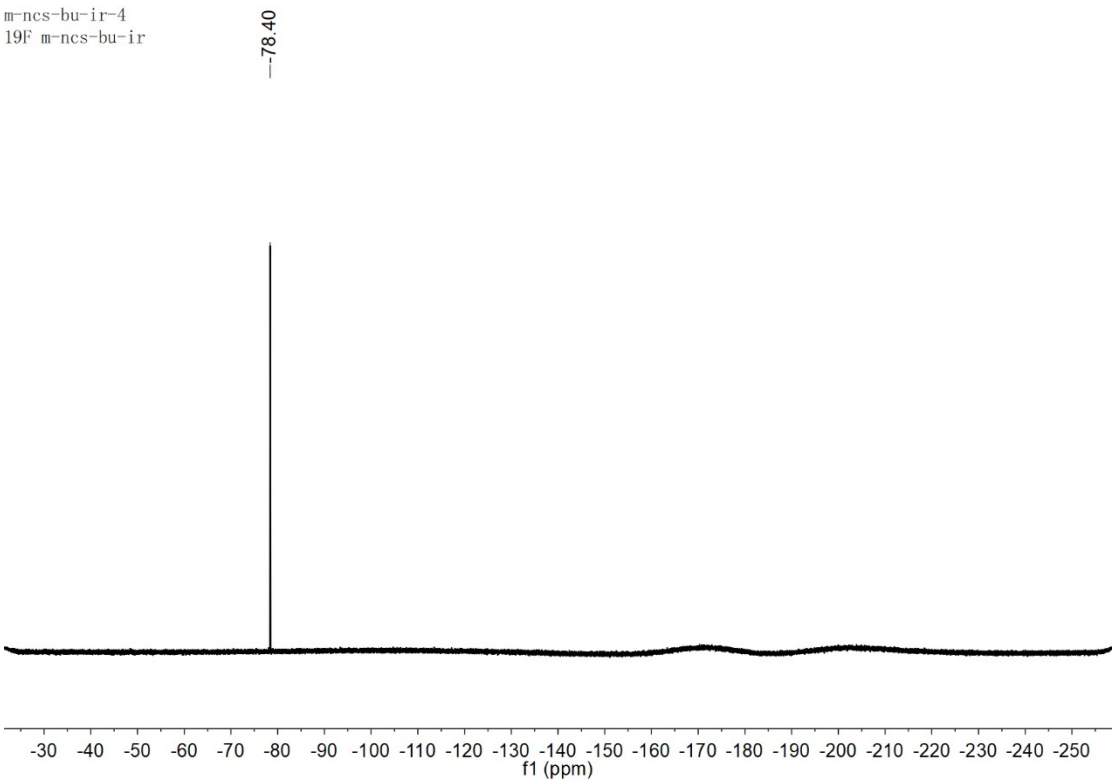


Figure S13. ^{19}F NMR (378 MHz, $CDCl_3$, 298K) of complex **2**.

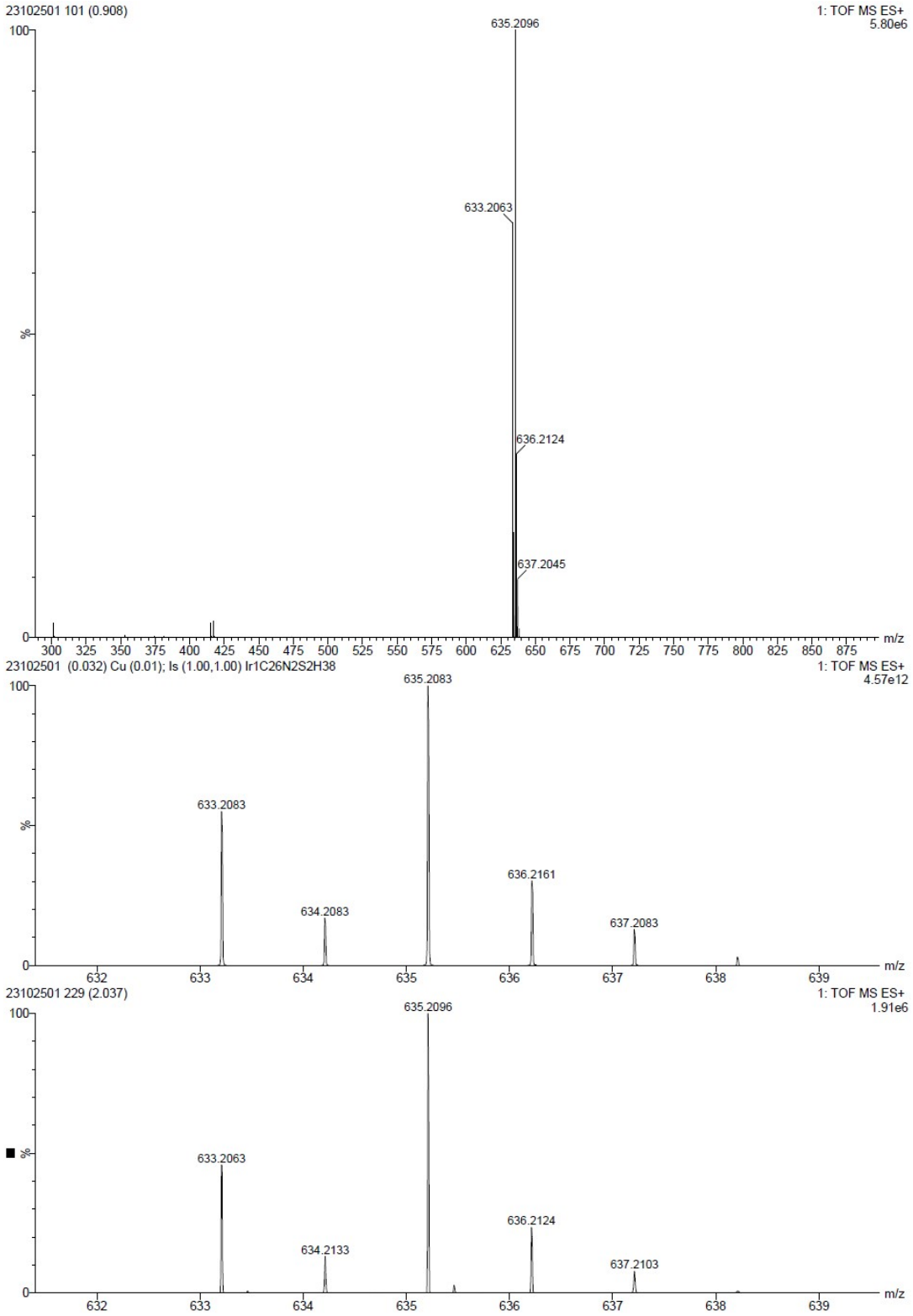
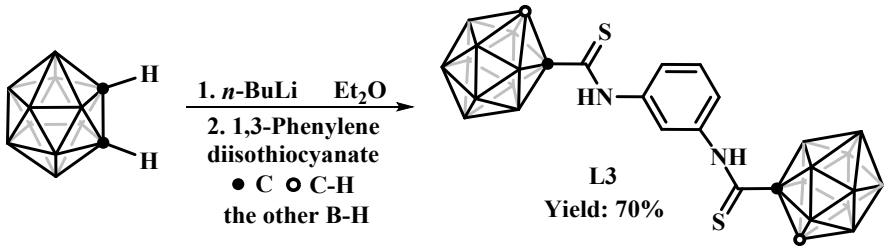


Figure S14. Experimental (bottom) and theoretical (top) ESI-MS of complex **2.**

S2.3 Synthesis and Characterization of Ligand 3.



Scheme S3. Synthesis of Ligand **3**.

A suspension of n-BuLi (1.60 mol/L in n-hexane, 1.30 mL, 2.00 mmol) was added to a solution of *o*-carborane (288.00 mg, 2.00 mmol) in ether 10 mL at -78 °C over a period of 2 h, then 1,3-Phenylene di-isothiocyanate (192.20 mg, 1.00 mmol) was added at room temperature and the resulting mixture was stirred for 24 h. 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 (petroleum ether : CH_2Cl_2, 4 : 1). Elution with petroleum ether gave Ligand **3** as a yellow solid (yield: 338.80 mg, 70.0%). ^{1}H NMR (400 MHz; $CDCl_3$, 298K, ppm): δ = 1.79-2.90 (br, 20H, B-H); 4.92 (s, 2H, C_{cage}-H); 7.51 (s, 3H, Ar-H); 8.15 (s, 1H, Ar-H); 9.09 (s, 2H, N-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, 298K, ppm): δ = 60.76, 78.75 (cage C); 119.04, 123.32, 130.16, 138.56 (Ar-C); 186.62 (N-C=S). ^{11}B NMR (160 MHz, $CDCl_3$, 298K, ppm): δ = -2.95, -4.10, -8.39, -9.61, -11.37, -12.55, -13.81. IR (KBr disk, cm^{-1}): v = 3275.83, 3043.45, 2962.24, 2573.55, 1601.41, 1541.56, 1440.57, 1388.87, 1261.21, 1193.67, 1010.66, 787.07. ESI-MS: m/z = 482.3756 (calcd for $[M + H]^+$ = 482.3754).

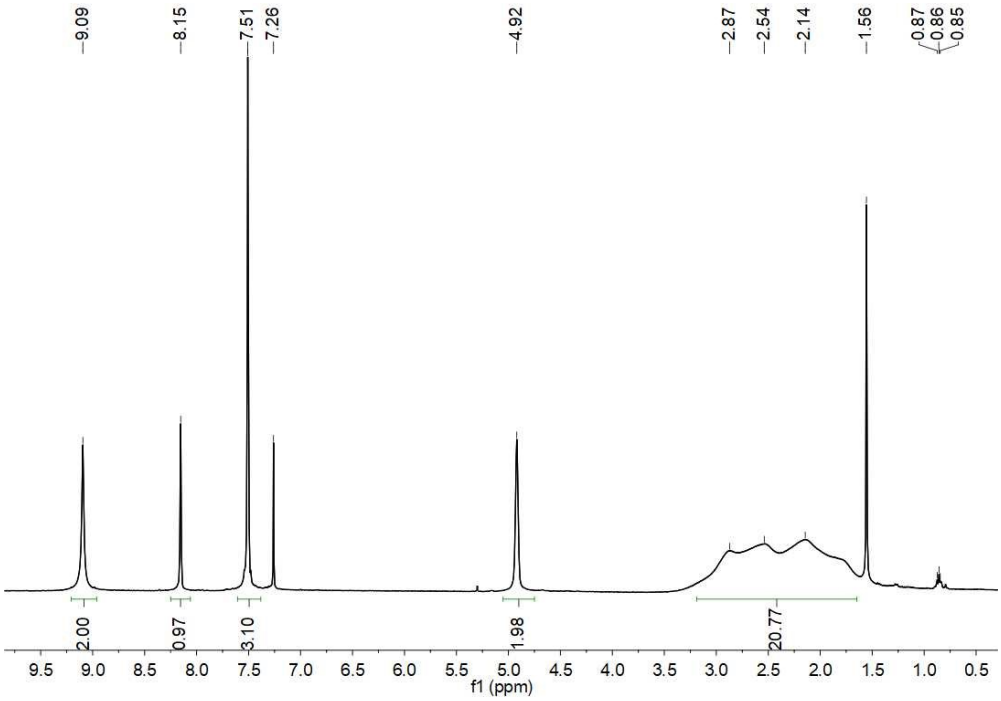


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) of Ligand **3**.

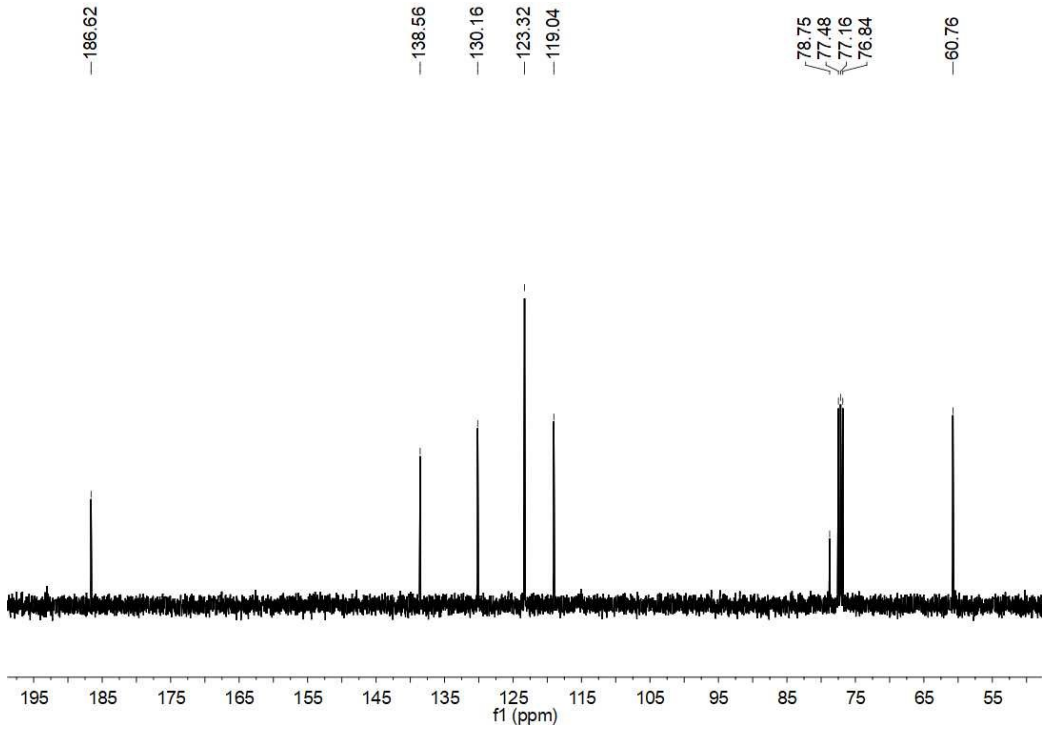


Figure S16. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298K, ppm) of Ligand **3**.

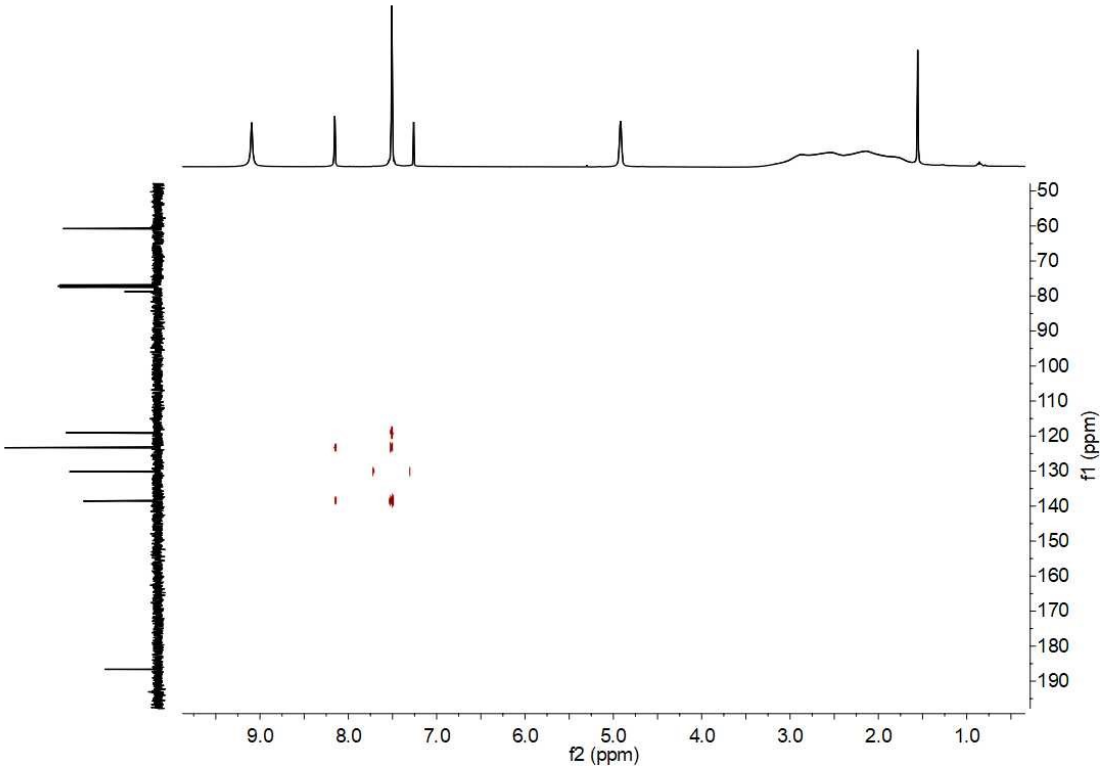


Figure S17. ^{13}C-^{1}H HMBC NMR (400 MHz, $CDCl_3$, 298K) of Ligand **3**.

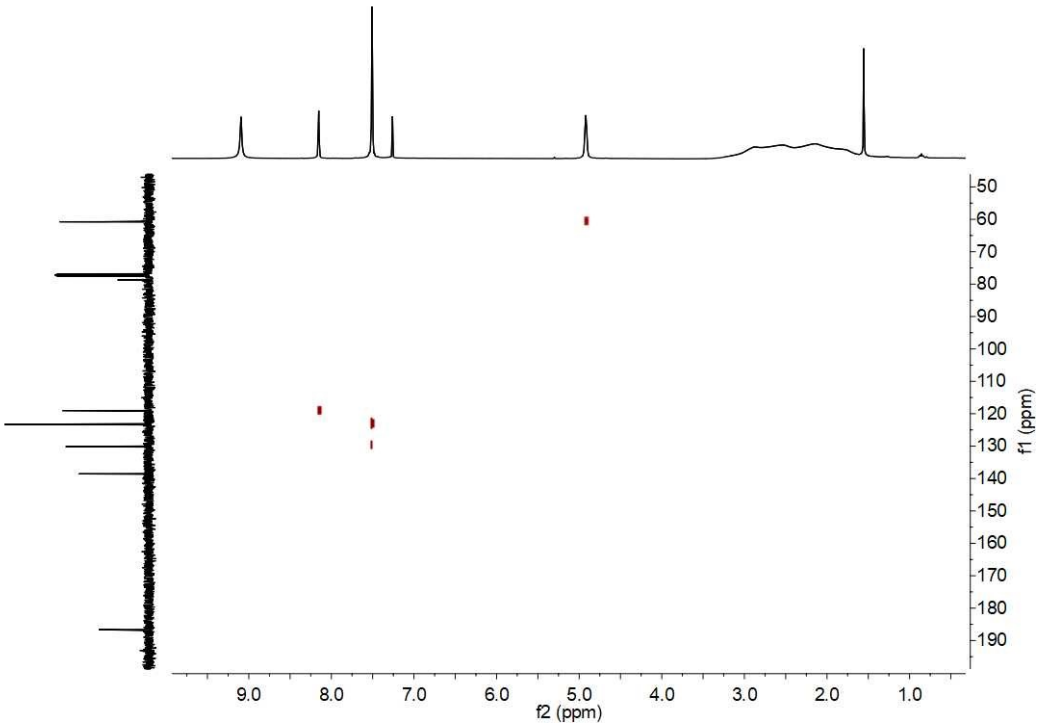


Figure S18. ^{13}C-^{1}H HSQC NMR (400 MHz, $CDCl_3$, 298K) of Ligand **3**.

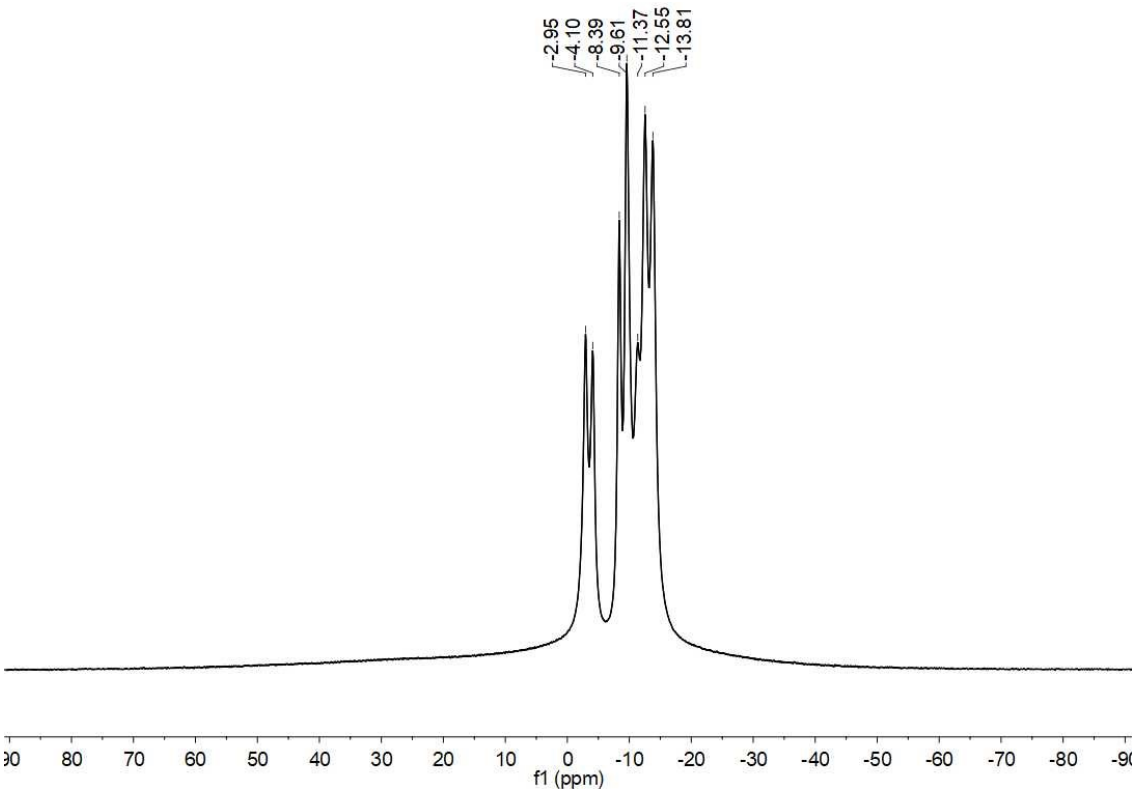


Figure S19. ^{11}B NMR (160 MHz, $CDCl_3$, 298 K, ppm) of Ligand **3**.

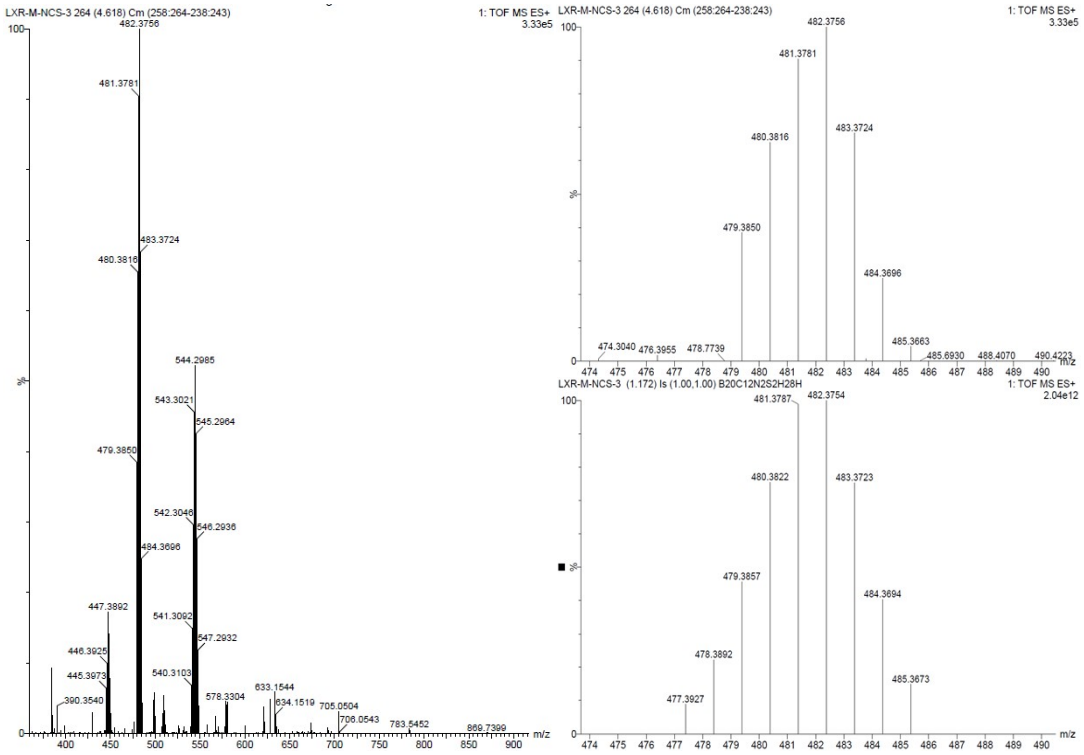
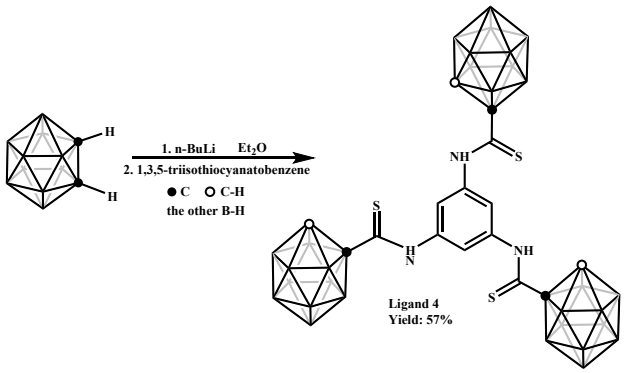


Figure S20. Experimental (top) and theoretical (bottom) ESI-MS of Ligand **3.**

S2.4 Synthesis and Characterization of Ligand 4.



Scheme S4. Synthesis of Ligand **4**.

A suspension of *n*-BuLi (1.60 mol/L in n-hexane, 2.10 mL, 3.00 mmol) was added to a solution of *o*-carborane (432.00 mg, 3.00 mmol) in ether 10 mL at -78 °C over a period of 2 h, then 1,3,5-triisothiocyanatobenzene (249.30 mg, 1.00 mmol) was added at room temperature and the resulting mixture was stirred for 24 h. 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 (petroleum ether: CH_2Cl_2, 2 : 1). Elution with petroleum ether gave Ligand **4** as a yellow solid (yield: 391.60 mg, 57.0%). ^{1}H NMR (400 MHz; $CDCl_3$, 298K, ppm): δ = 1.76-2.95 (br, 30H, B-H); 4.88 (s, 3H, C_{cage}-H); 7.95 (s, 3H, Ar-H); 9.10 (s, 3H, N-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, 298K, ppm): δ = 60.74, 78.65 (cage C); 118.18, 139.12 (Ar-C); 187.07 (N-C=S). ^{11}B NMR (160 MHz, $CDCl_3$, 298K, ppm): δ = -2.87, -4.03, -8.33, -9.55, -12.54, -13.72. IR (KBr disk, cm^{-1}): v = 3355.73, 3048.21, 2961.08, 2587.27, 1608.55, 1545.24, 1376.49, 1260.61, 1013.75, 799.44. ESI-MS: m/z = 683.5391 (calcd for $[M + H]^+$ = 683.5373).

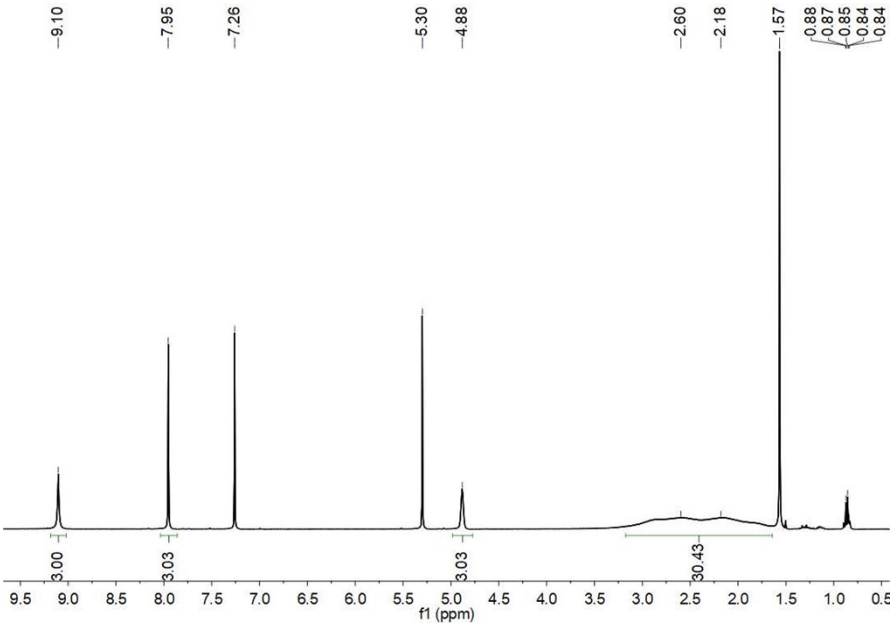


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) of Ligand **4**.

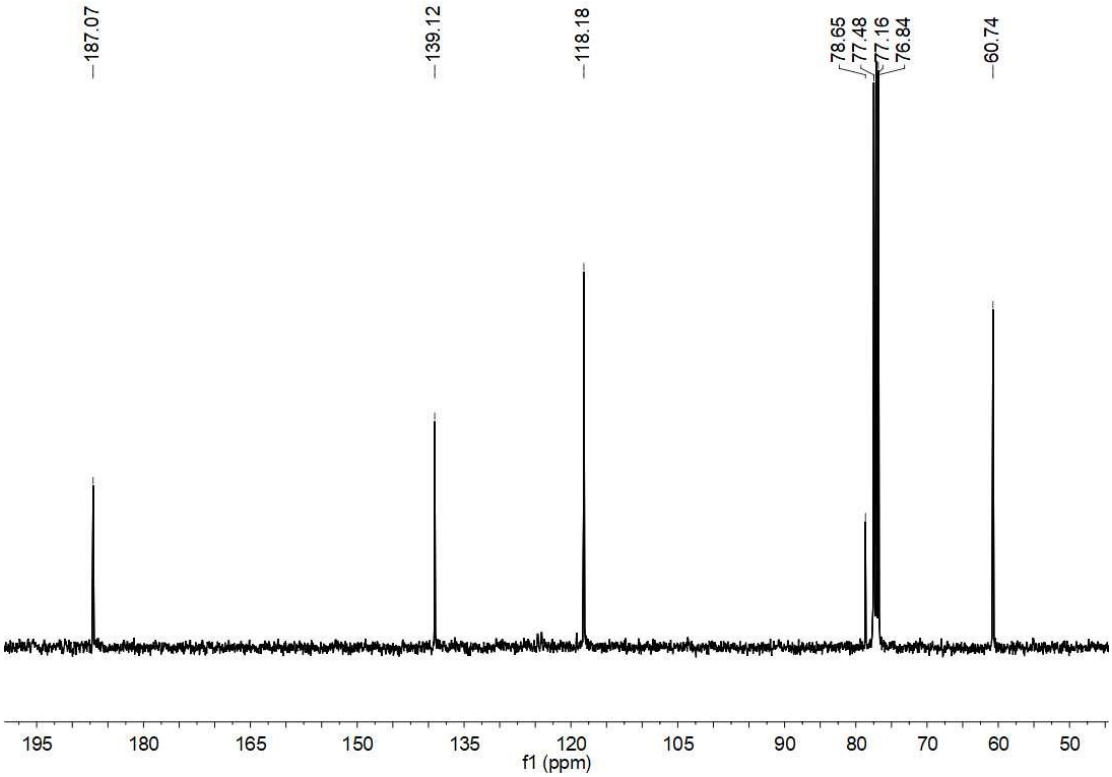


Figure S22. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298K, ppm) of Ligand **4**.

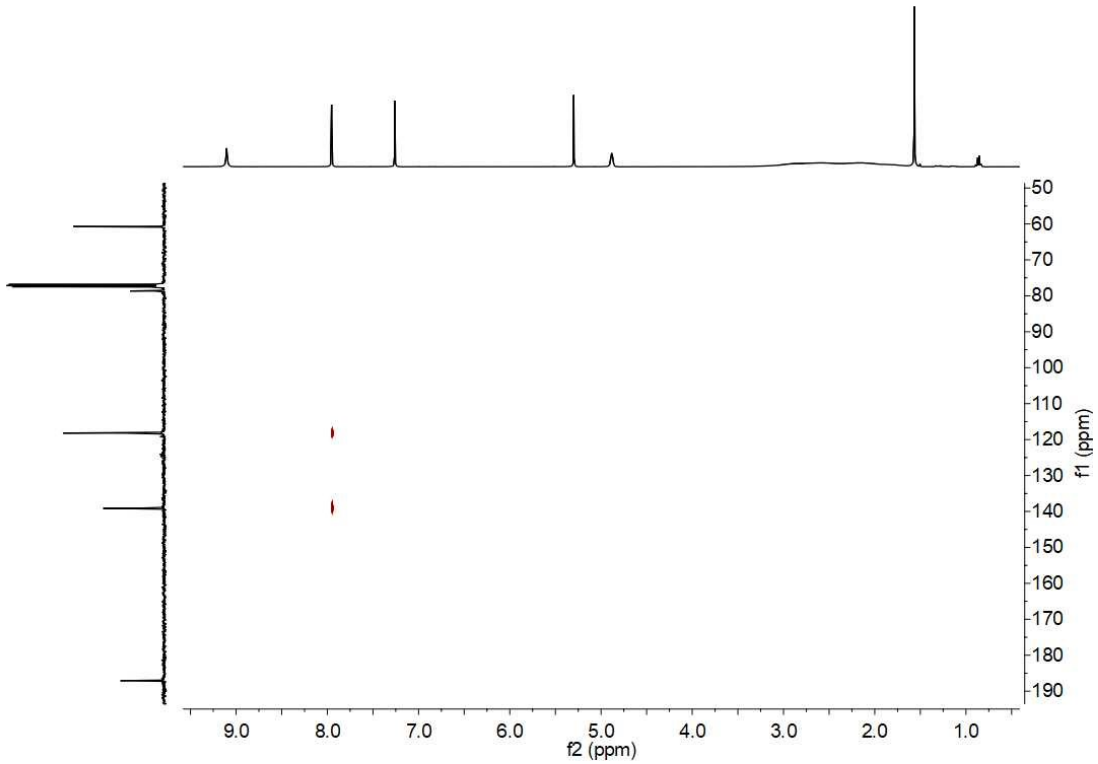


Figure S23. ^{13}C-^{1}H HMBC NMR (400 MHz, $CDCl_3$, 298K) of Ligand **4**.

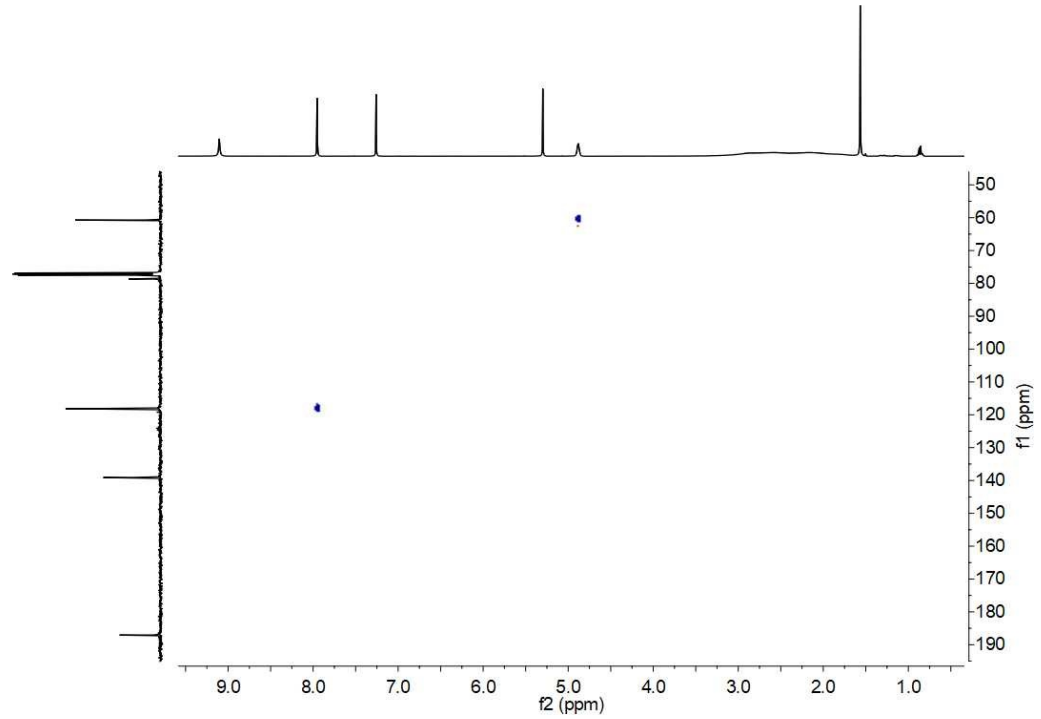


Figure S24. ^{13}C-^{1}H HSQC NMR (400 MHz, $CDCl_3$, 298K) of Ligand **4**.

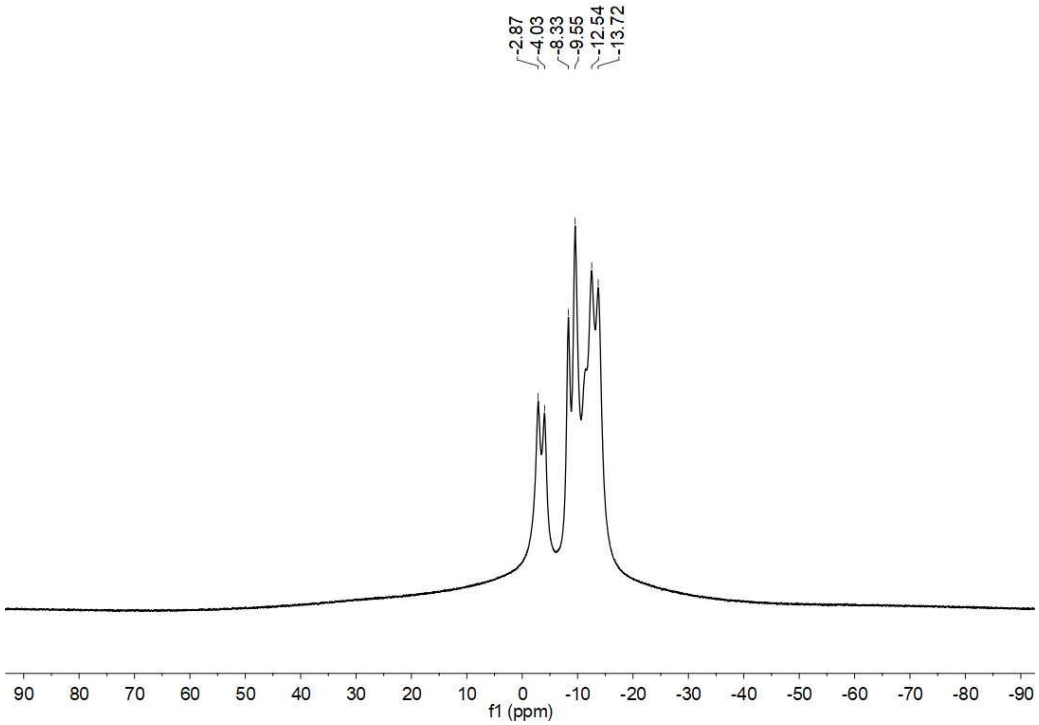


Figure S25. ^{11}B NMR (160 MHz, $CDCl_3$, 298 K, ppm) of Ligand **4**.

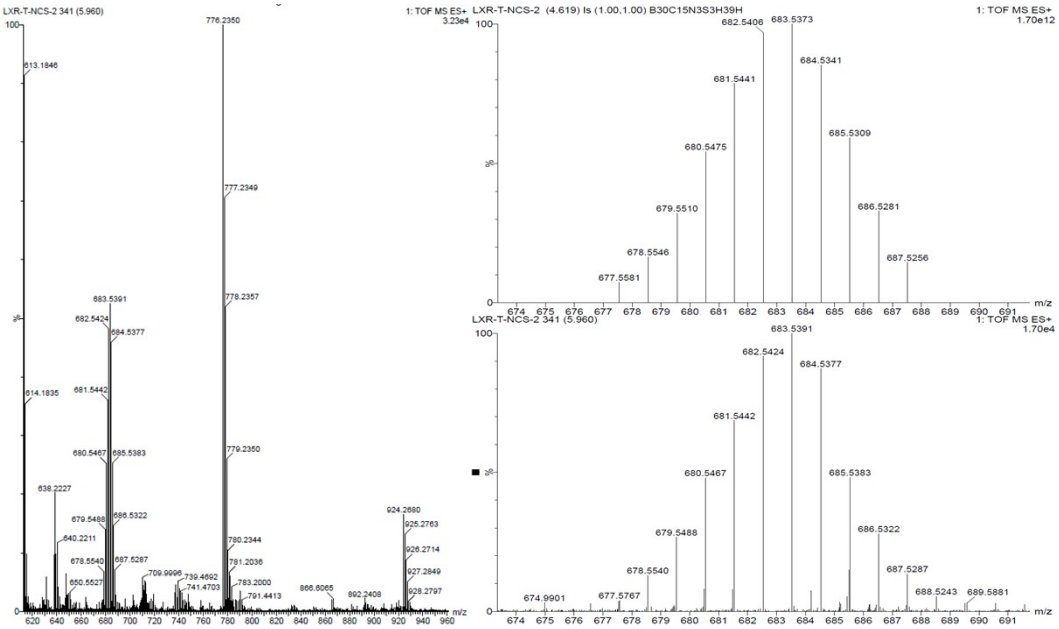
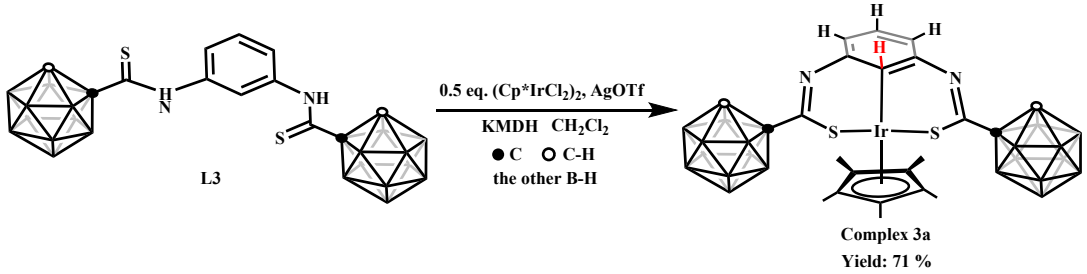


Figure S26. Experimental (bottom) and theoretical (top) ESI-MS of Ligand **4.**

S2.5 Synthesis and Characterization of complex 3a.



Scheme S5. Synthesis of complex **3a**.

Ligand **3** (48.40 mg, 0.10 mmol), $[Cp^*IrCl_2]_2$ (40.40 mg, 0.05 mmol), AgOTf (51.20 mg, 0.20 mmol) and KMDH (0.05 mL) were added to the CH_2Cl_2 solution (10 mL) at room temperature. The reaction mixture was stirred in the dark for 12 h. Then the mixture was filtrated and the filtrate was concentrated and further purified via silica gel column chromatography (*n*-Hexane : CH_2Cl_2, 4 : 1). Pink solids were obtained and dried under vacuo to give the complex **3a**: 57.20 mg 71%. ^{1}H NMR (400 MHz; $CDCl_3$, 298K, ppm): δ = 2.01-2.58 (br, 20H, B-H); 1.10 (s, 15H, Cp*-H); 4.78 (s, 2H, C_{cage}-H); 5.66 (s, 1H, Ar-H); 6.59 (d, 2H, Ar-H); 8.11 (t, 1H, Ar-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, 298K, ppm): δ = 6.89, 93.08 (Cp*-C), 58.46 (cage C); 41.71, 118.83, 138.10, 159.92 (Ar-C); 168.03 (N=C-S). ^{11}B NMR (160 MHz, $CDCl_3$, 298K, ppm): δ = -3.20, -4.05, -8.93, -10.00. IR (KBr disk, cm^{-1}): v = 3080.19, 3069.26, 2962.02, 2627.04, 2590.28, 2556.87, 1574.55, 1506.80, 1460.71, 1376.47, 1310.92, 1261.77, 1139.39, 1013.86, 809.33. ESI-MS: m/z = 807.4387 (calcd for $[M + H]^+$ = 807.4412).

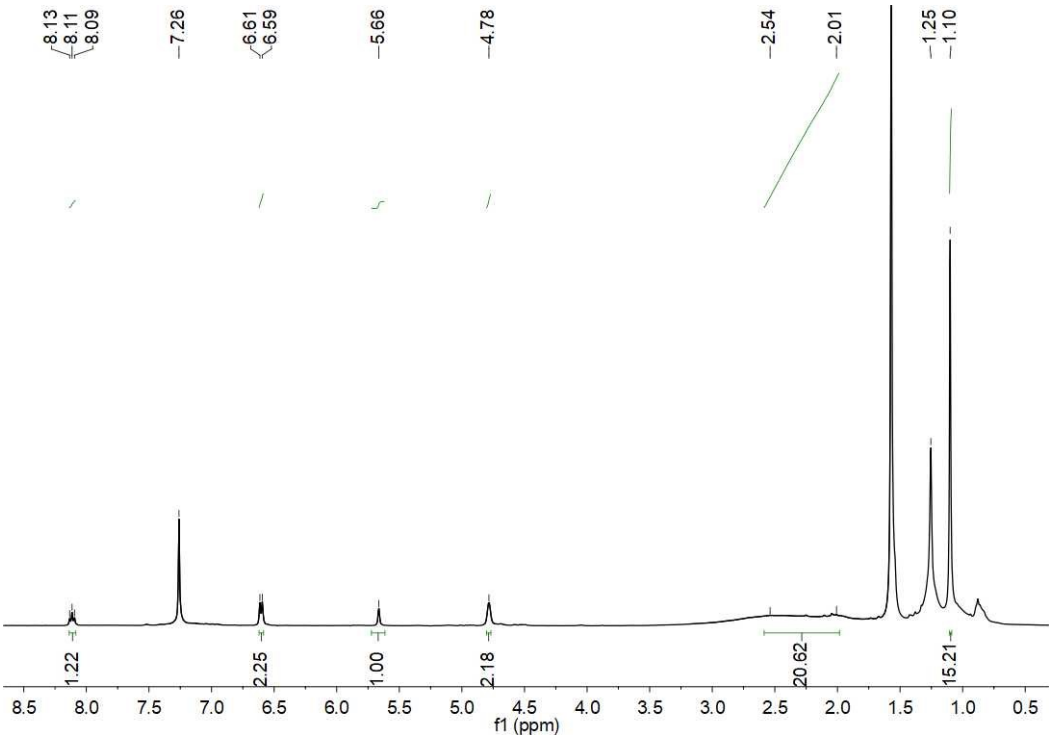


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **3a**.

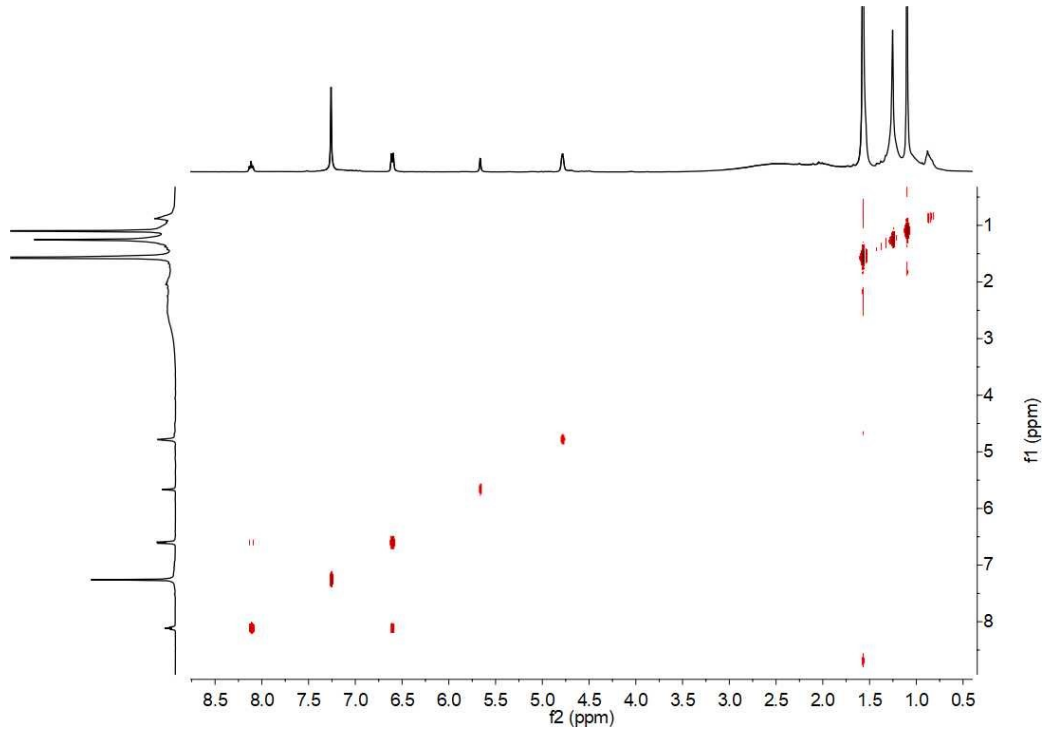


Figure S28. ^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **3a**.

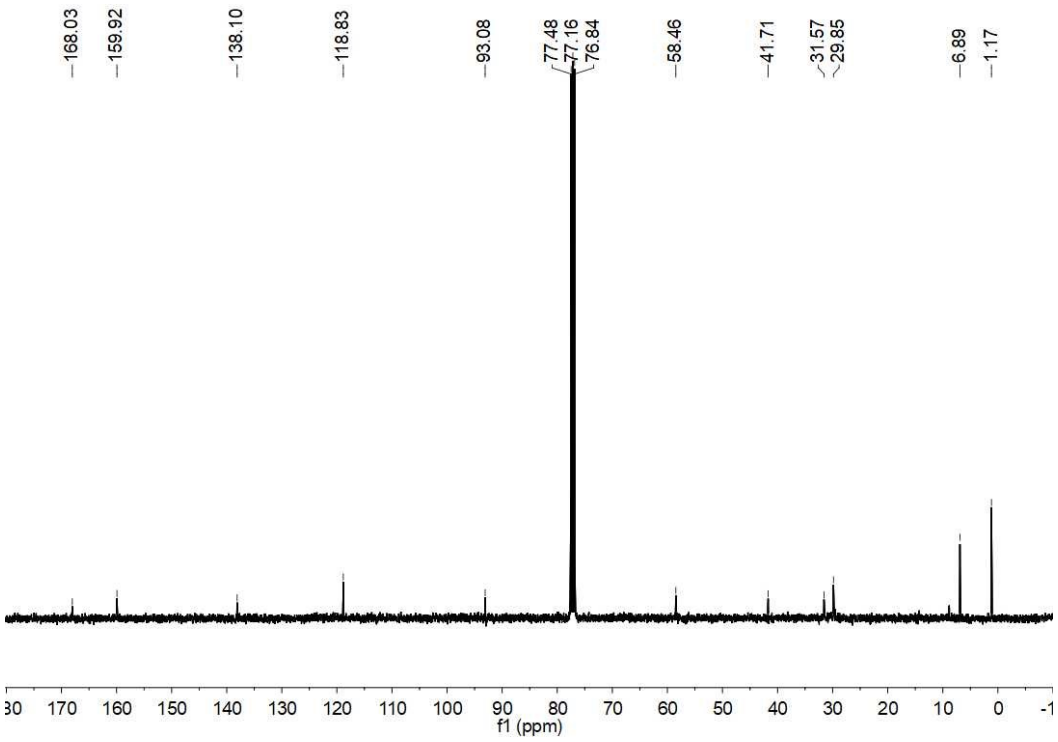


Figure S29. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298K, ppm) of complex **3a**.

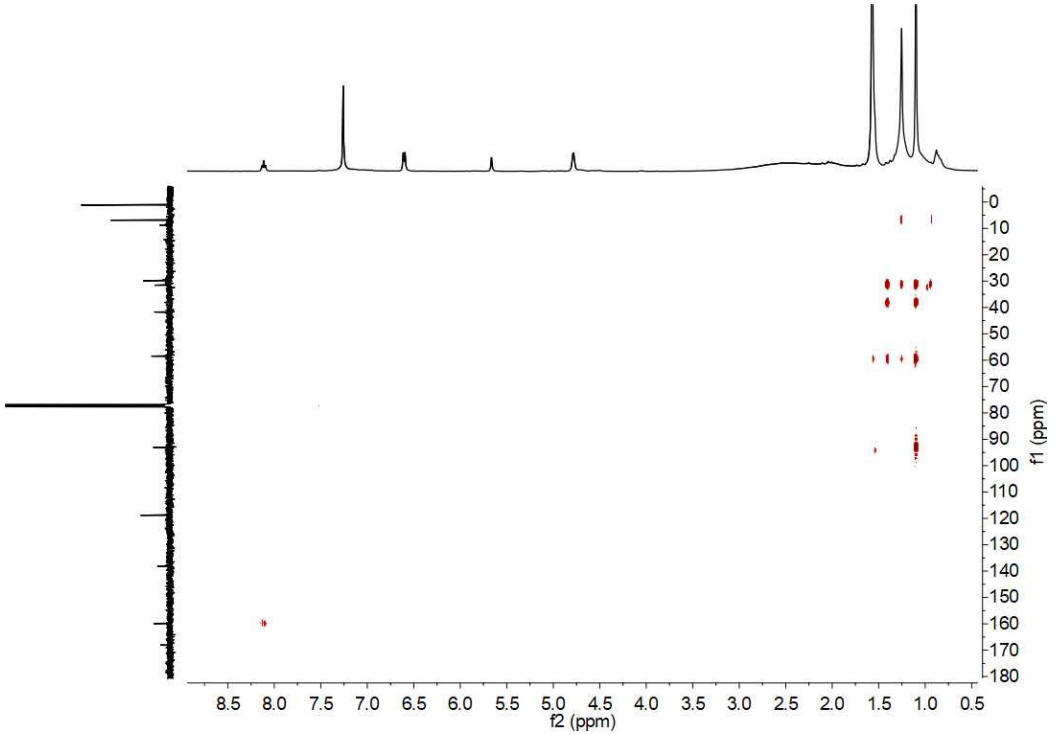


Figure S30. ^{13}C-^{1}H HMBC NMR (400 MHz, $CDCl_3$, 298K) of complex **3a**.

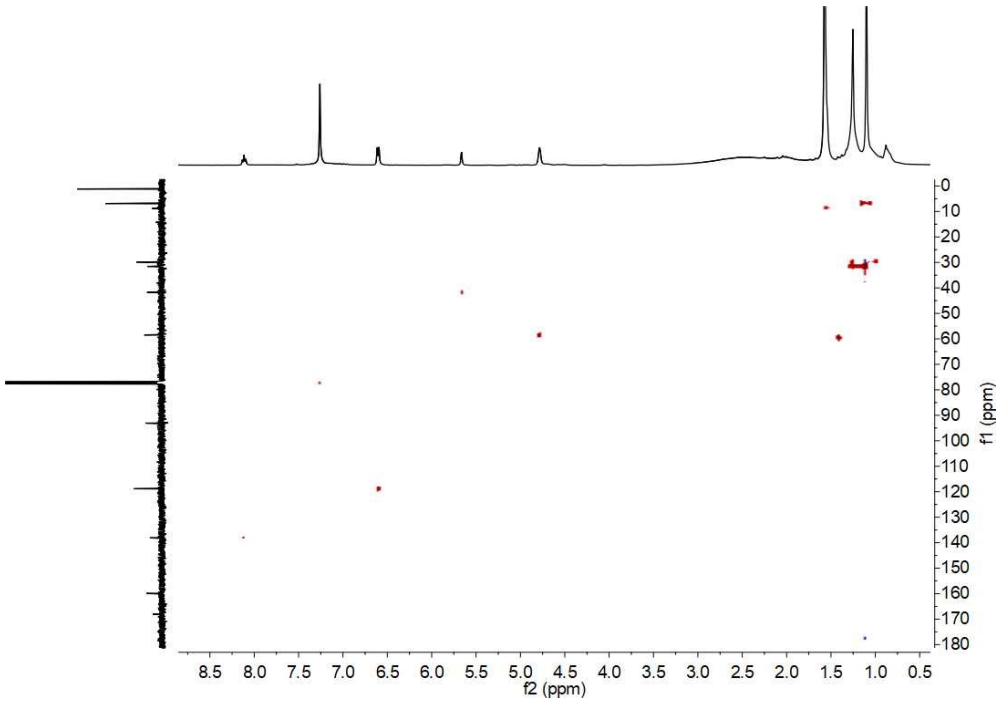


Figure S31. ^{13}C-^{1}H HSQC NMR (400 MHz, $CDCl_3$, 298K) of complex **3a**.

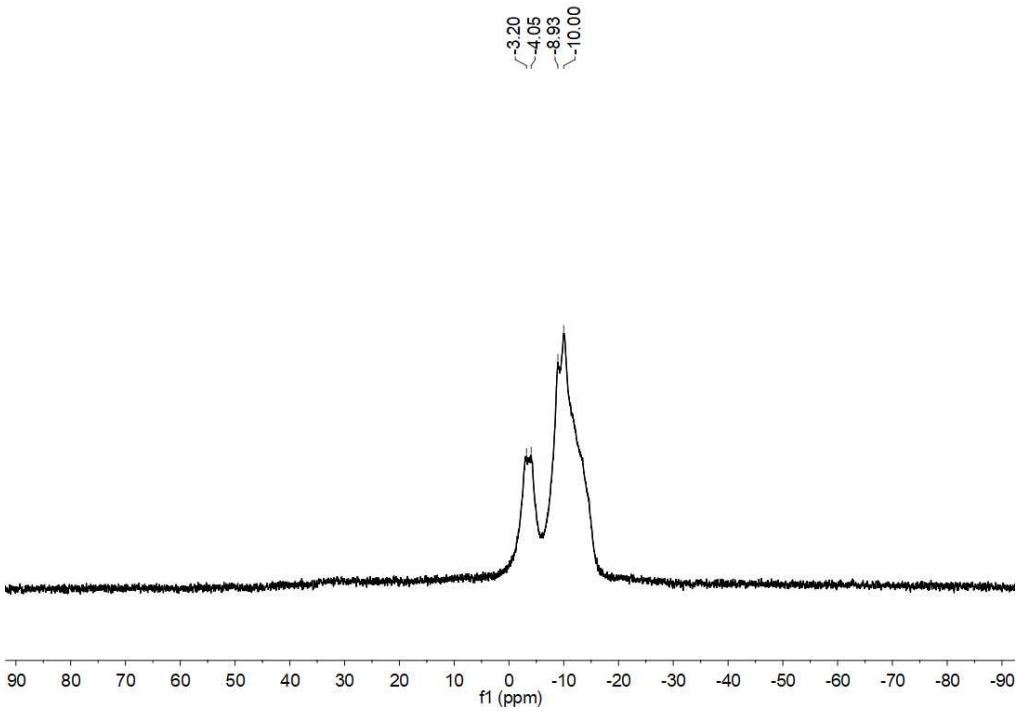


Figure S32. ^{11}B NMR (160 MHz, $CDCl_3$, 298 K, ppm) of complex **3a**.

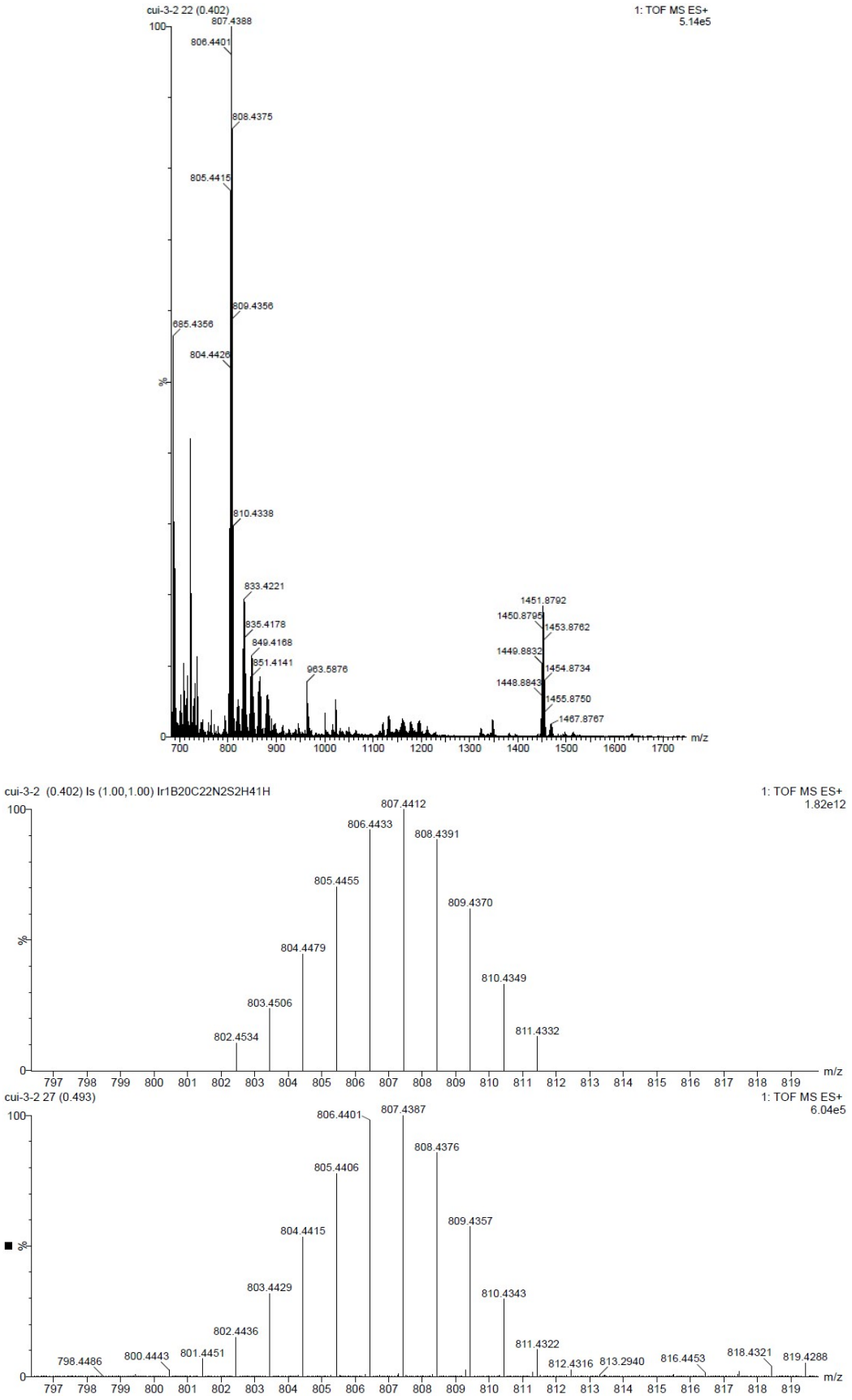


Figure S33. Experimental (bottom) and theoretical (top) ESI-MS of complex **3a**.

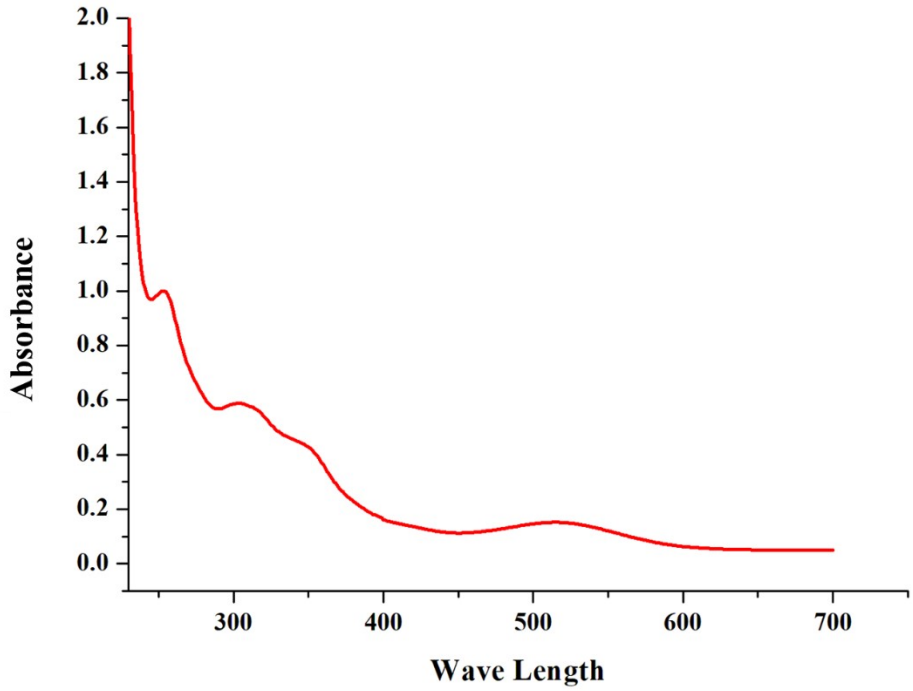
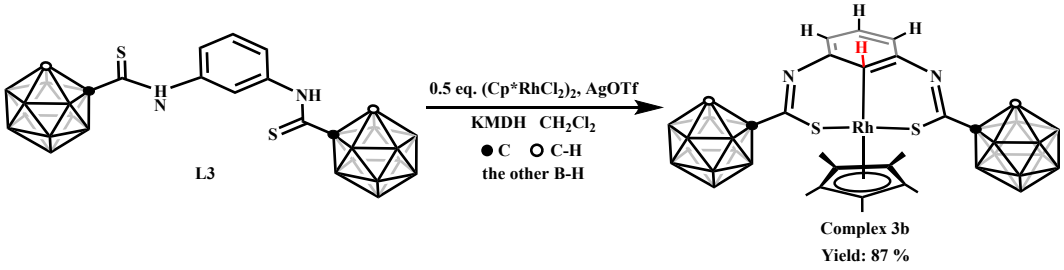


Figure S34. UV-visible absorption spectra of complex **3a** in dichloromethane.

S2.6 Synthesis and Characterization of complex 3b.



Scheme S6. Synthesis of complex **3b**.

Ligand **3** (48.40 mg, 0.10 mmol), $[Cp^*RhCl_2]_2$ (30.90 mg, 0.05 mmol), AgOTf (51.20 mg, 0.20 mmol) and KMDH (0.05 mL) were added to the CH_2Cl_2 solution (10 mL) at room temperature. The reaction mixture was stirred in the dark for 12 h. Then the mixture was filtrated and the filtrate was concentrated and further purified via silica gel column chromatography (*n*-Hexane : CH_2Cl_2, 3 : 1). Red solids were obtained and dried under vacuo to give the complex **3b**: 62.30 mg 87%. ^{1}H NMR (400 MHz; $CDCl_3$, 298K, ppm): δ = 1.96-2.54 (br, 20H, B-H); 1.12 (s, 15H, Cp*-H); 4.75 (s, 2H, C_{cage}-H); 5.91 (s, 1H, Ar-H); 6.65 (d, 2H, Ar-H); 7.92 (t, 1H, Ar-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, 298K, ppm): δ = 7.69, 98.70 (Cp*-C), 58.48 (cage C); 56.57, 119.21, 137.23, 159.91 (Ar-C); 170.79 (N=C-S). ^{11}B NMR (160 MHz, $CDCl_3$, 298K, ppm): δ = -3.25, -4.12, -10.26, -13.05. IR (KBr disk, cm^{-1}): v = 3071.45, 2961.92, 2924.04, 2855.10, 2576.54, 1515.58, 1465.80, 1261.73, 1139.59, 1110.58, 1016.61, 803.55. ESI-MS: m/z = 718.3834 (calcd for $[M + H]^+$ = 718.3834).

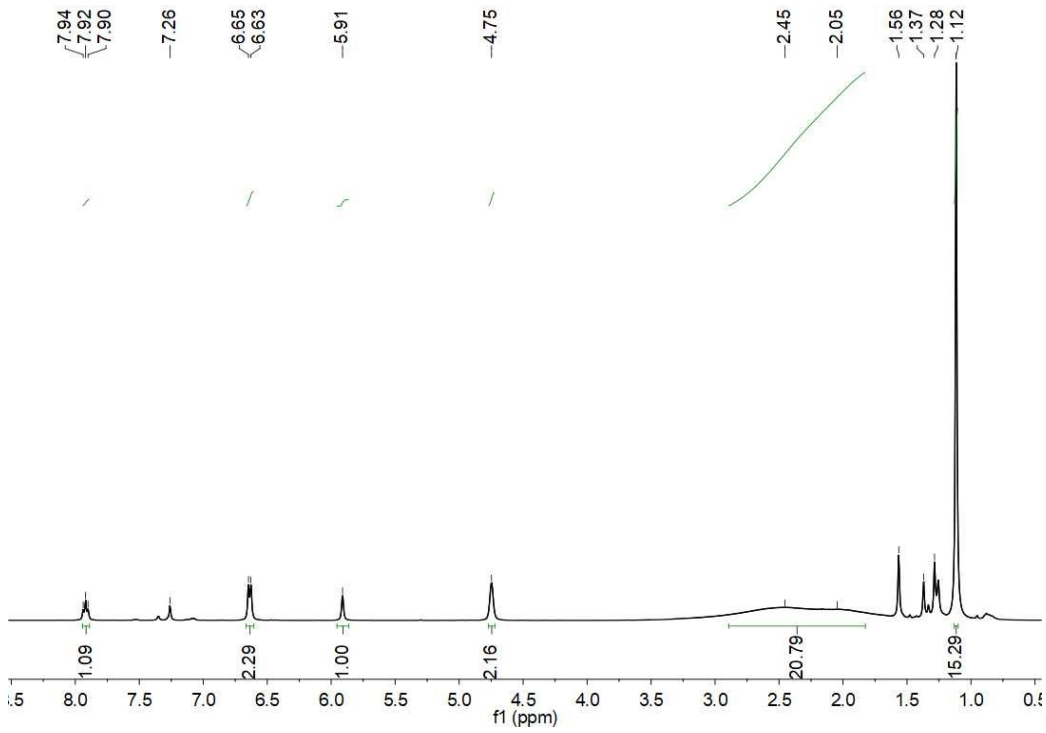


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **3b**.

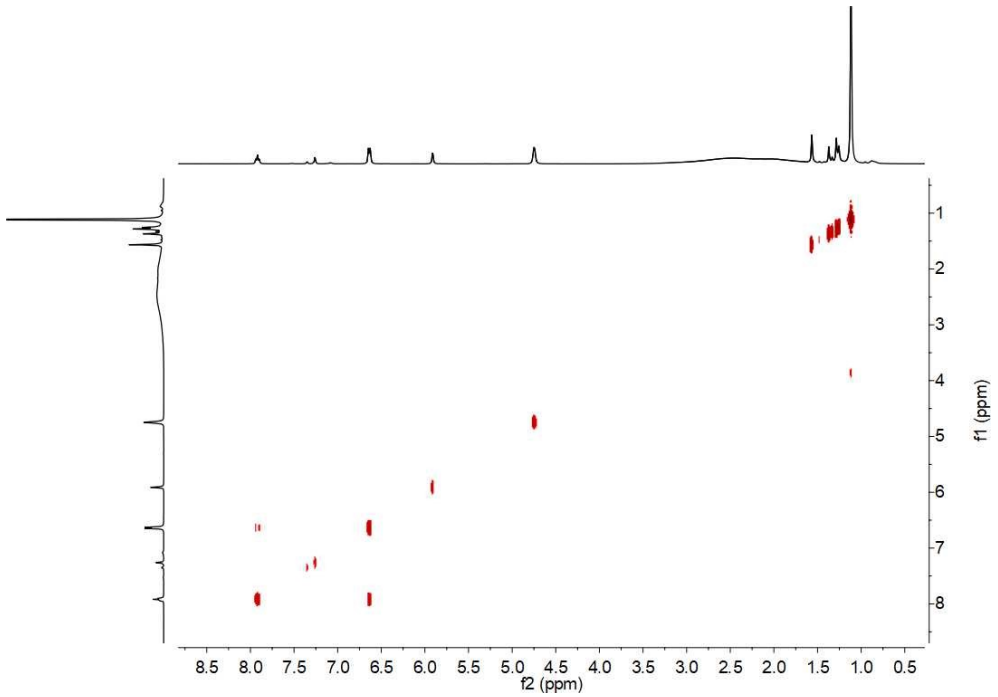


Figure S36.[1]H-[1]H COSY NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **3b**.

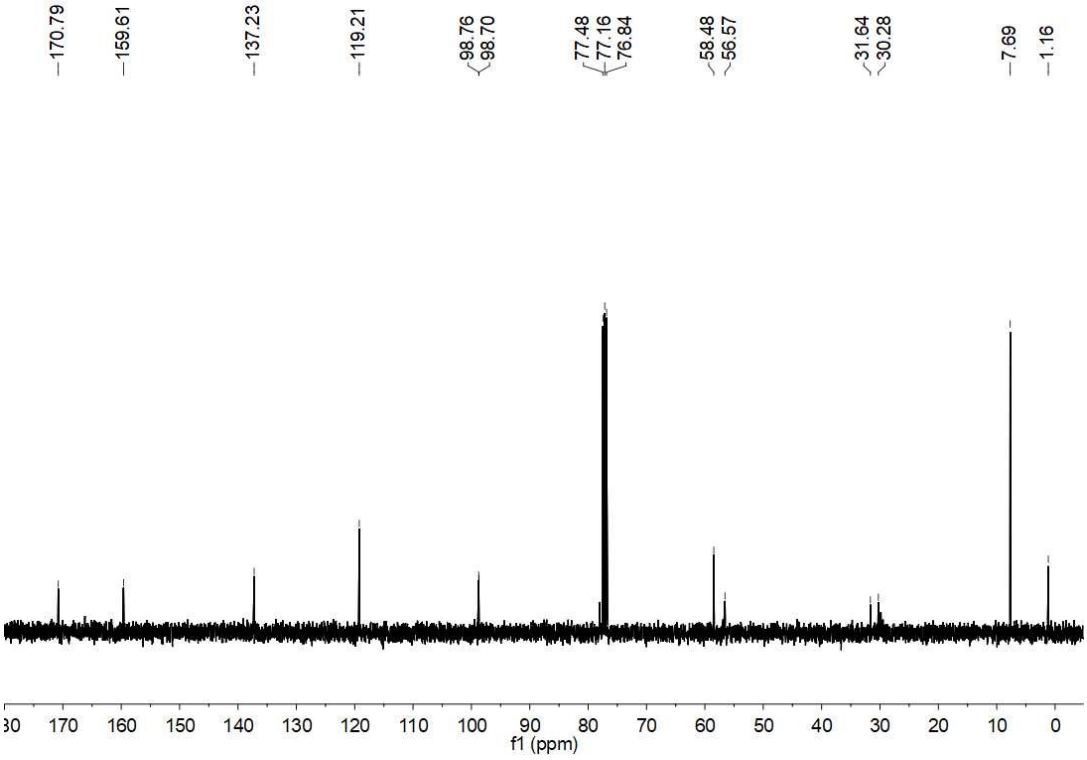


Figure S37. [13]C{[1]H} NMR (101 MHz, $CDCl_3$, 298K, ppm) of complex **3b**.

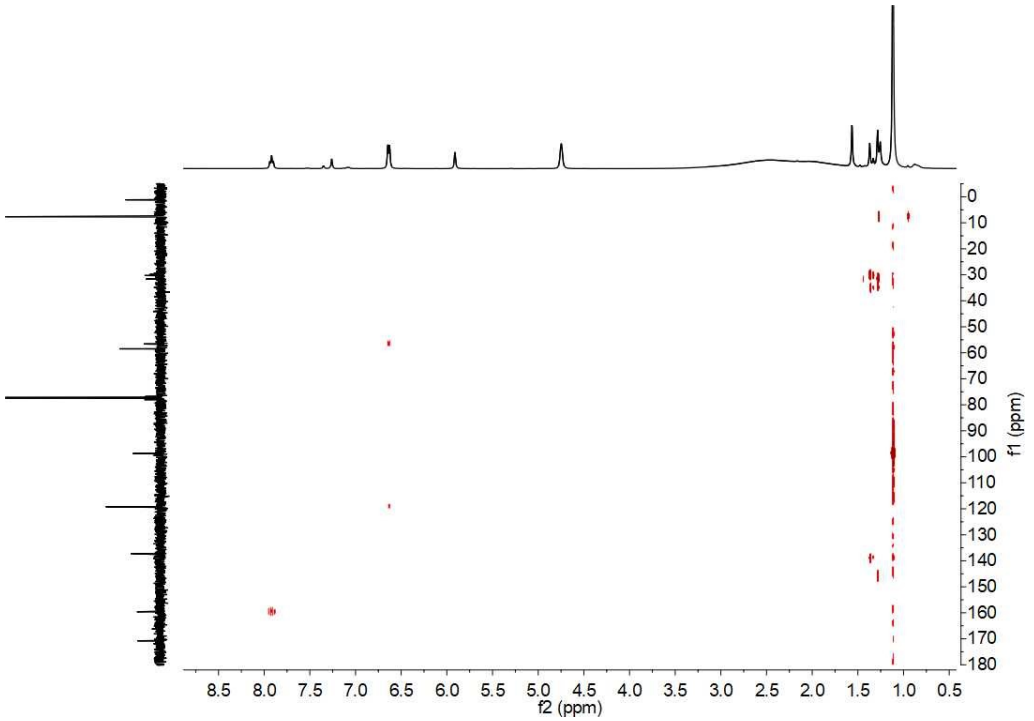


Figure S38. ^{13}C-^{1}H HMBC NMR (400 MHz, $CDCl_3$, 298K) of complex **3b**.

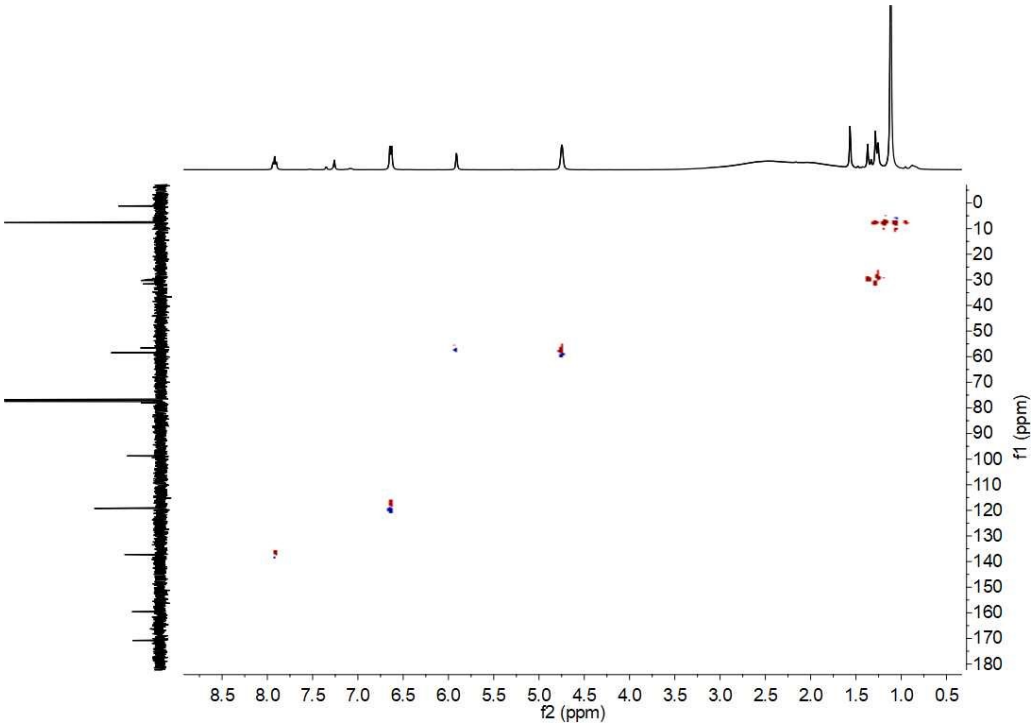


Figure S39. ^{13}C-^{1}H HSQC NMR (400 MHz, $CDCl_3$, 298K) of complex **3b**.

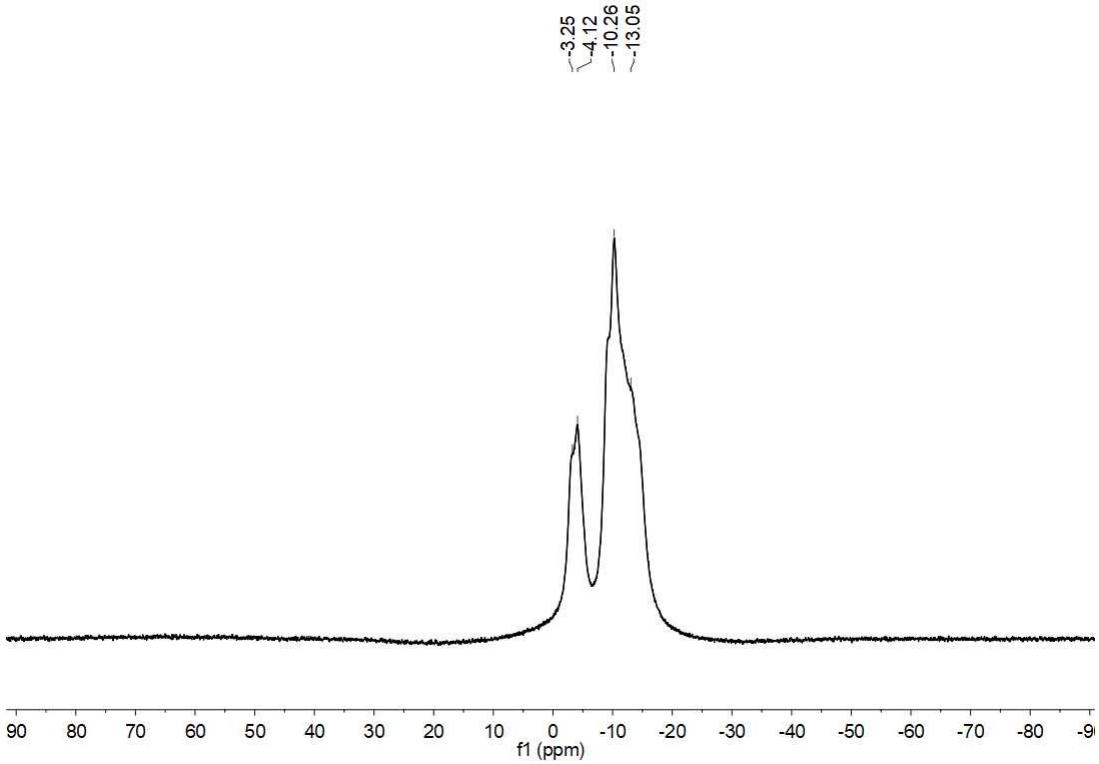


Figure S40. ^{11}B NMR (160 MHz, $CDCl_3$, 298 K, ppm) of complex **3b**.

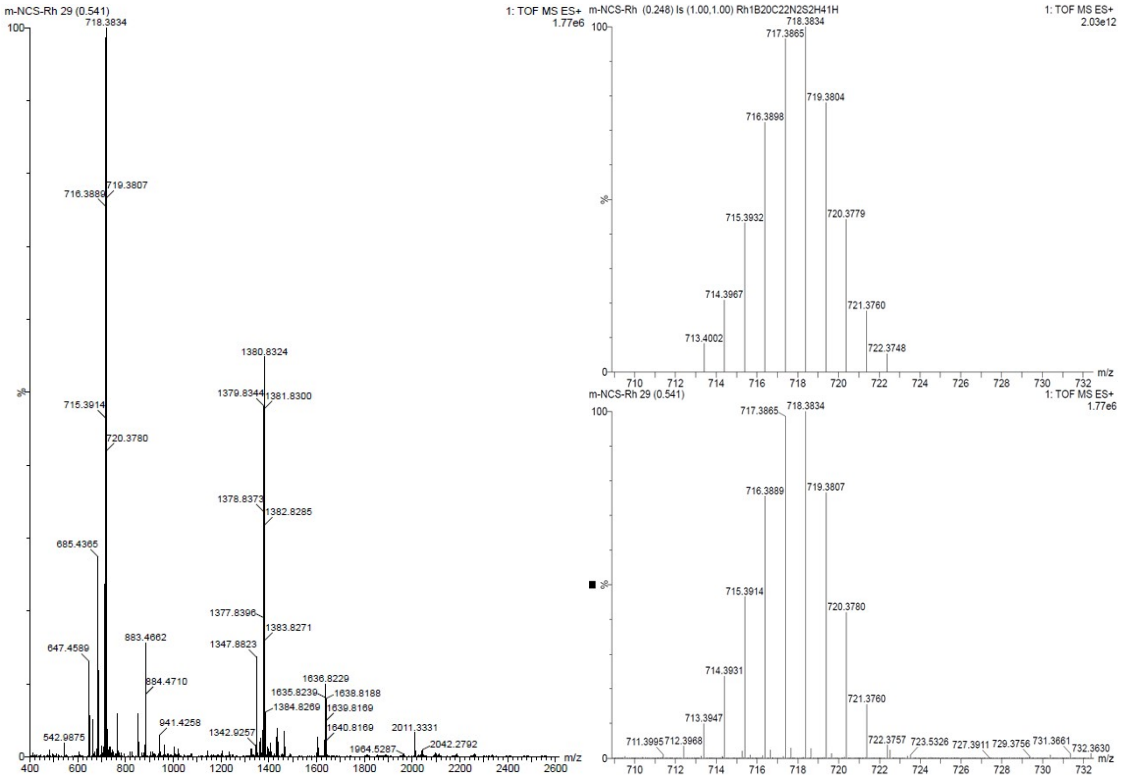


Figure S41. Experimental (bottom) and theoretical (top) ESI-MS of complex **3b.**

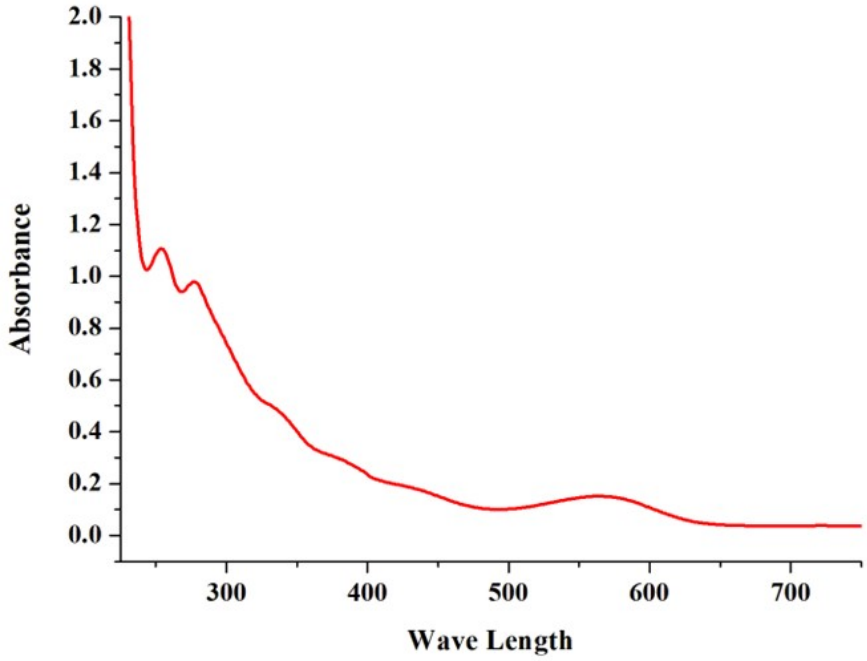
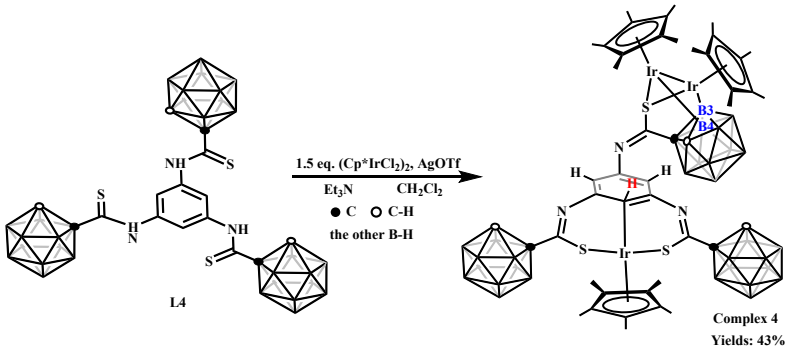


Figure S42. UV-visible absorption spectra of complex **3b** in dichloromethane.

S2.7 Synthesis and Characterization of complex 4.



Scheme S7. Synthesis of complex **4**.

Ligand **4** (27.40 mg, 0.04 mmol), $[Cp^*IrCl_2]_2$ (48.48 mg, 0.06 mmol), AgOTf (61.00 mg, 0.24 mmol) and Et_3N (0.05 mL) were added to the CH_2Cl_2 solution (10 mL) at room temperature. The reaction mixture was stirred in the dark for 18 h. Then the mixture was filtrated and the filtrate was concentrated and further purified via silica gel column chromatography (*n*-Hexane : CH_2Cl_2, 4 : 1). Orange solids were obtained and dried under vacuo to give the complex **4**: 28.54 mg 43%. ^{1}H NMR (400 MHz; $CDCl_3$, 298K, ppm): δ = 2.31-2.96 (br, 28H, B-H); 1.20 (s, 15H, Cp*-H); 2.11 (d, 30H, Cp*-H); 4.67 (s, 3H, C_{cage}-H); 5.57 (s, 1H, Ar-H); 5.98 (s, 1H, Ar-H); 6.04 (s, 1H, Ar-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, 298K, ppm): δ = 7.18, 10.41, 10.66, 91.80, 92.20, 93.49 (Cp*-C), 58.48 (cage C); 35.04, 109.91, 128.99, 131.07 (Ar-C); 161.76, 168.12 (N=C-S). ^{11}B NMR (160 MHz, $CDCl_3$, 298K, ppm): δ = -3.56, -9.67. IR (KBr disk, cm^{-1}): v = 3057.39, 2963.00, 2884.42, 2579.67, 1614.33, 1450.23, 1383.79, 1261.40, 1194.33, 1097.51, 1025.35, 803.59. ESI-MS: m/z = 1659.7423 (calcd for $[M + H]^+$ = 1659.7402).

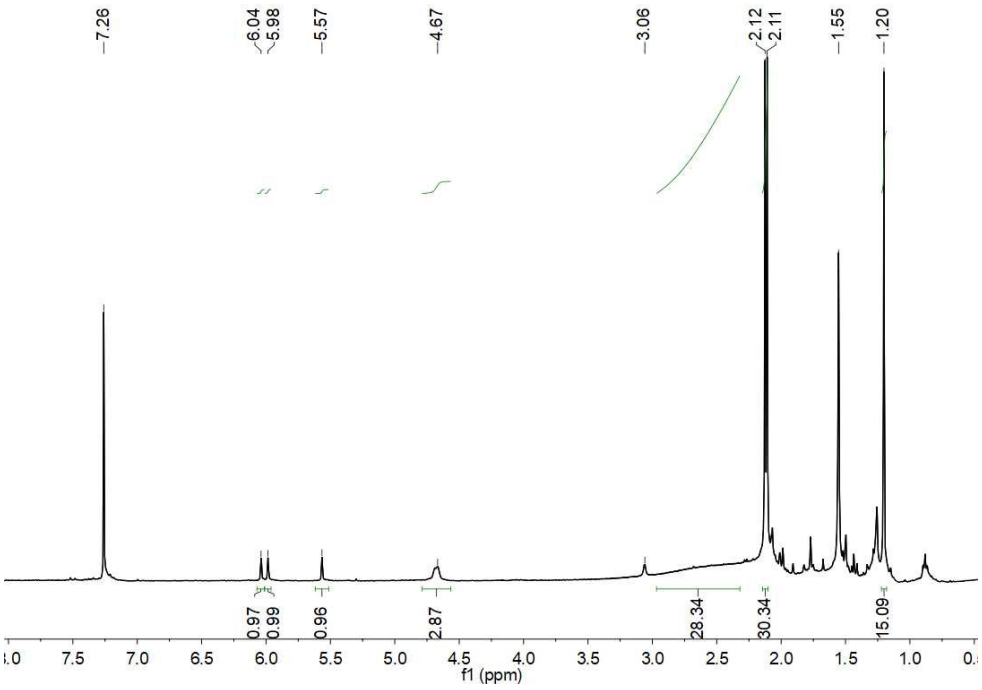


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **4**.

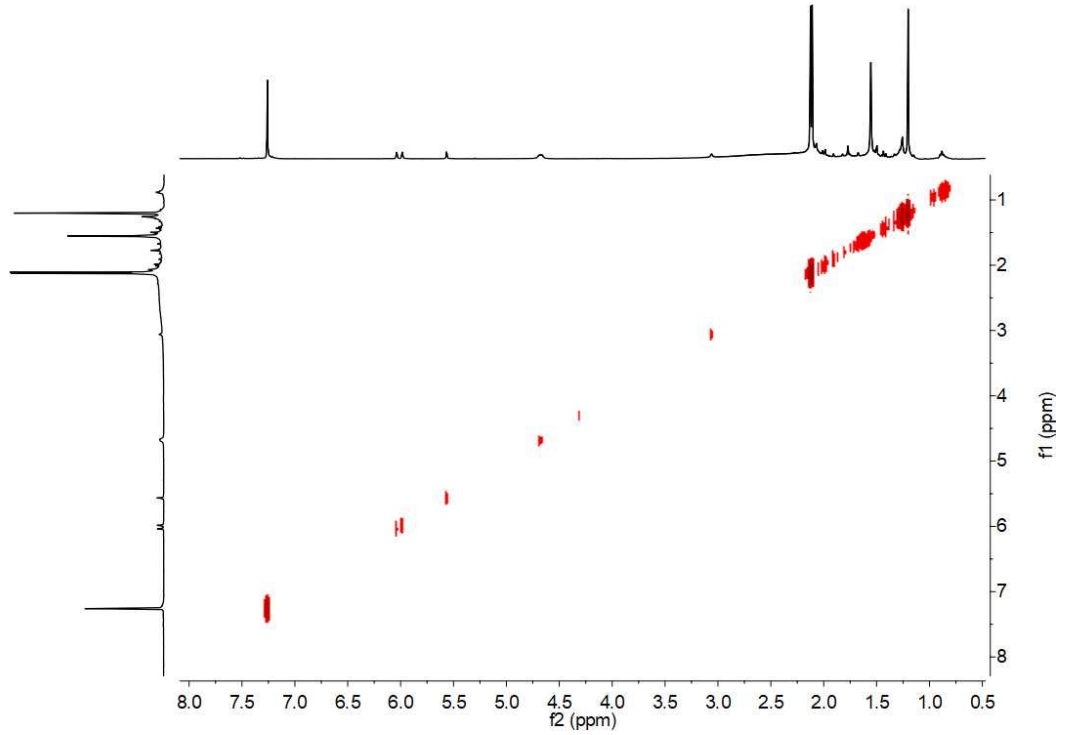


Figure S44. ^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **4**.

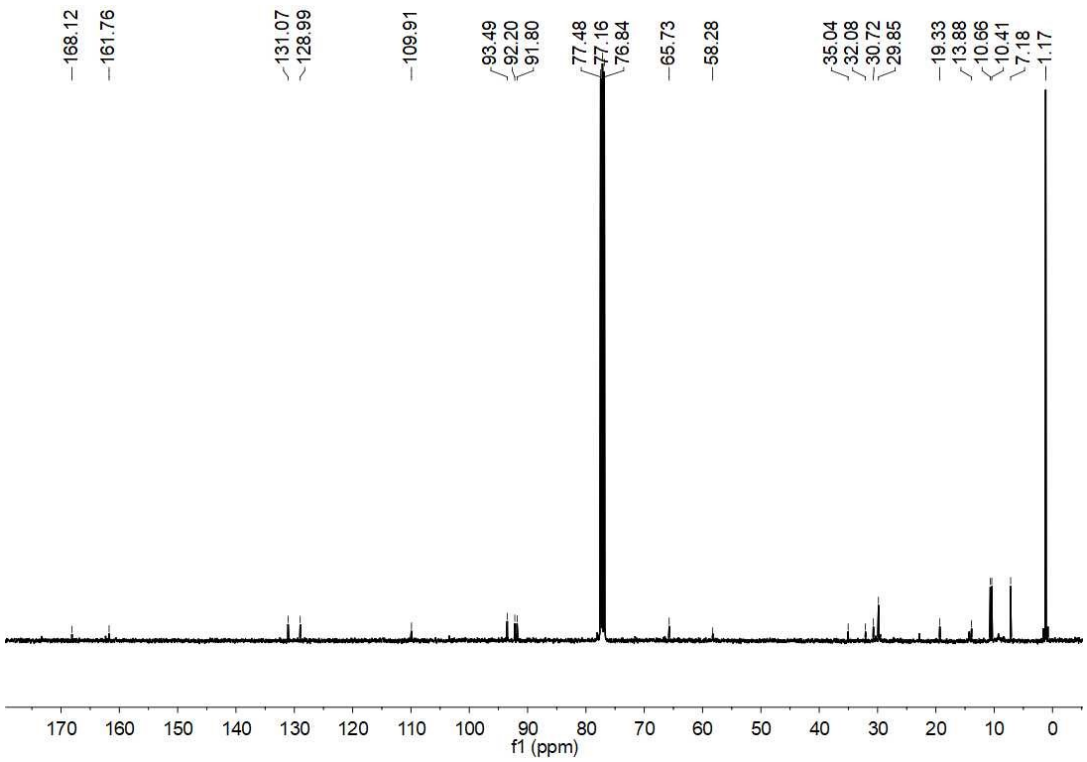


Figure S45. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298K, ppm) of complex **4**.

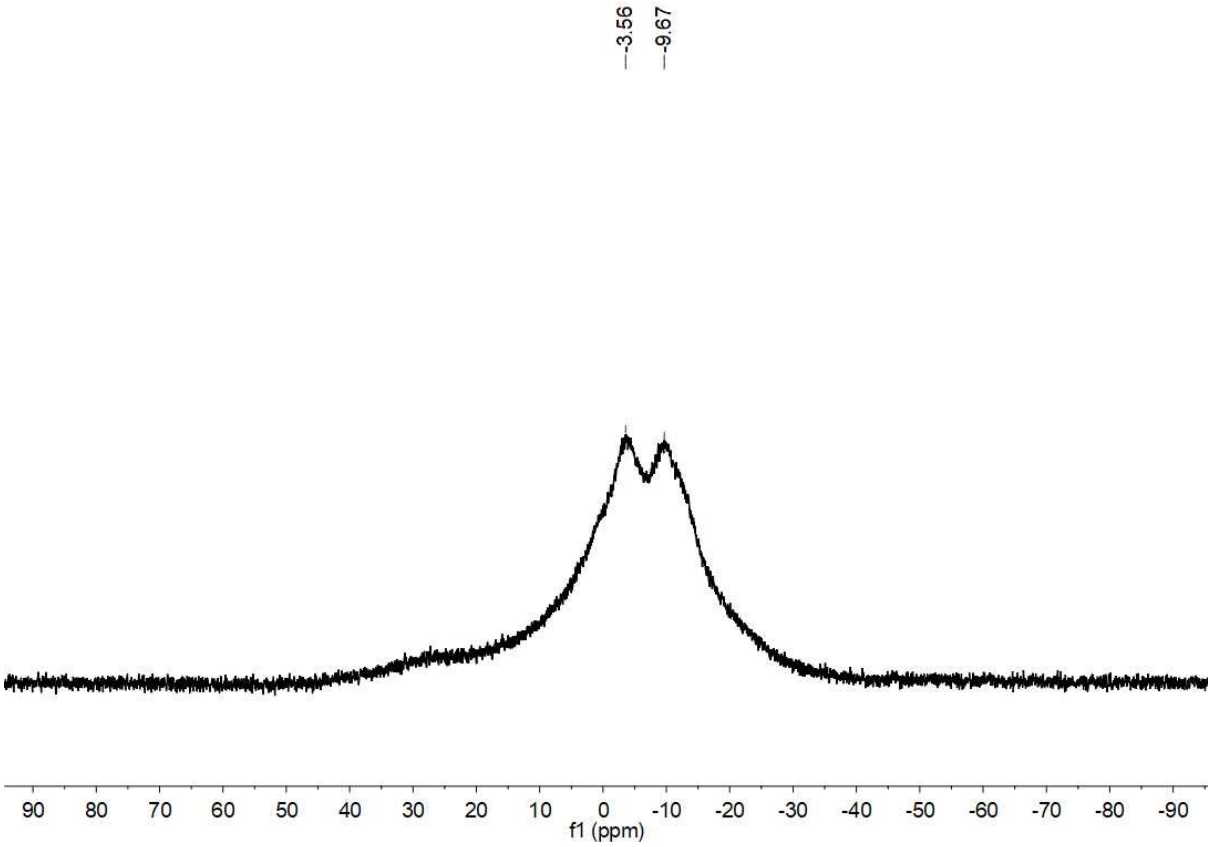


Figure S46. ^{11}B NMR (160 MHz, $CDCl_3$, 298 K, ppm) of complex **4**.

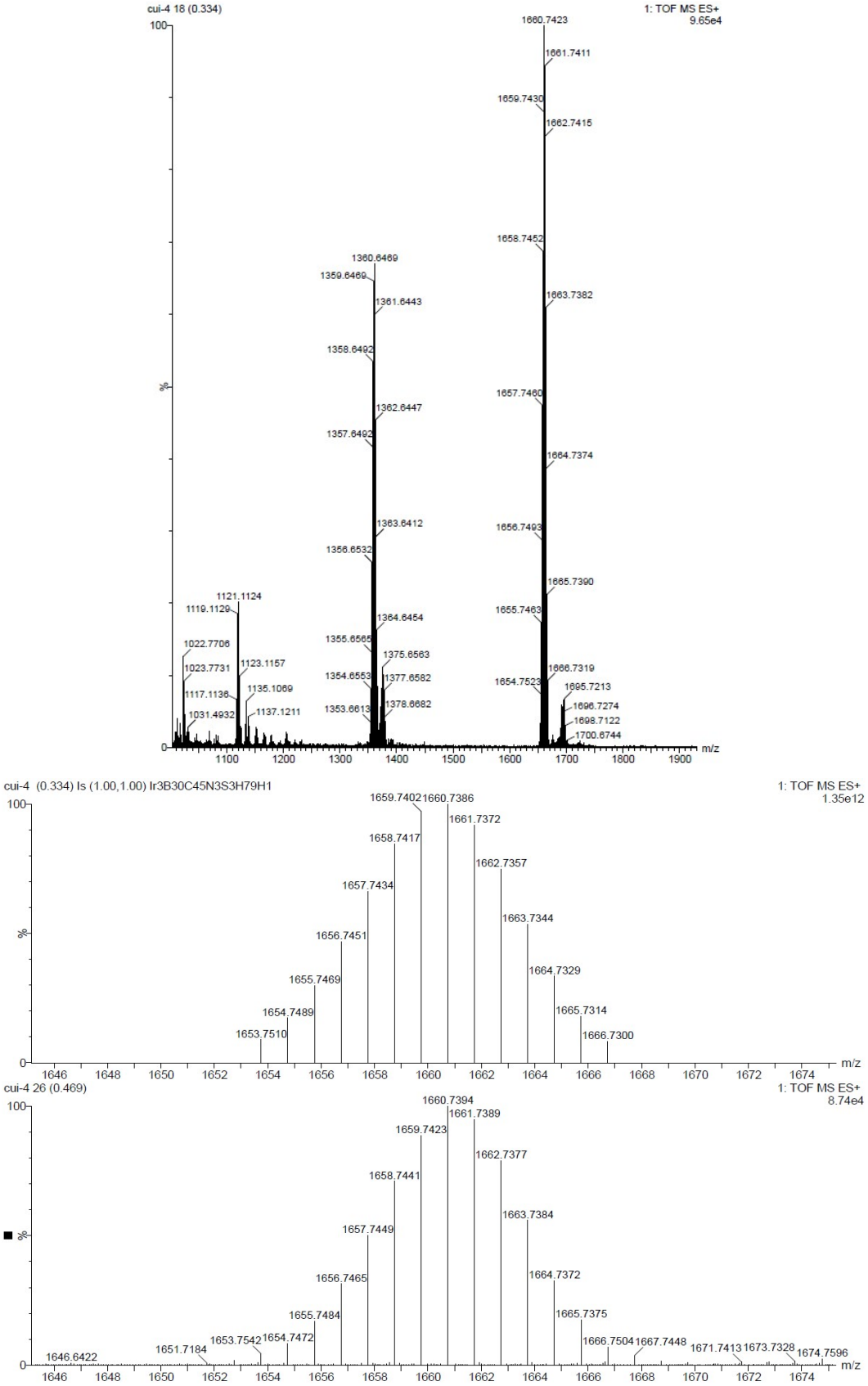
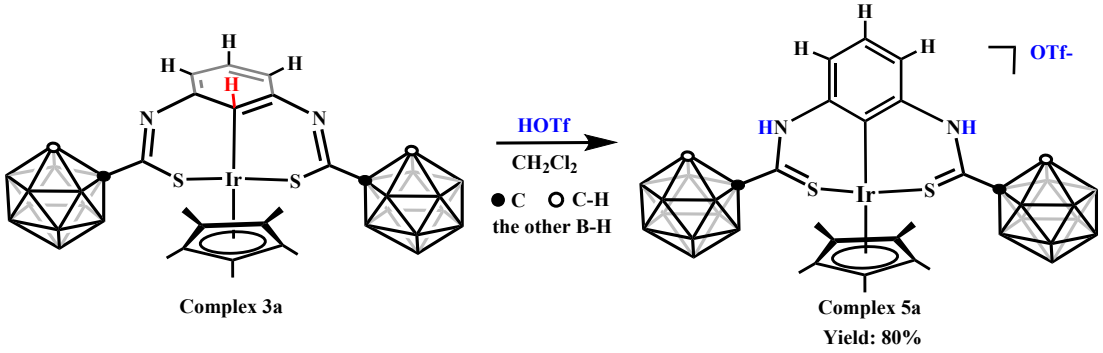


Figure S47. Experimental (bottom) and theoretical (top) ESI-MS of complex **4**.

S2.8 Synthesis and Characterization of complex 5a.



Scheme S8. Synthesis of complex **5a**.

The complex **3a** (40.31 mg, 0.05 mmol) was dissolved in the CH_2Cl_2 solution. And HOTf (0.05 mL) was added to the solution at room temperature. The reaction mixture was stirred 10 h. Then the mixture was filtered and the precipitate was washed by Et_2O. Orange solid was obtained and dried under vacuo to give the complex **5a**: 38.25 mg 80%. ^{1}H NMR (400 MHz; CD_3OD, 298K, ppm): 1.53, 1.58, 1.59 (s, 15H, Cp*-H); 2.89 (s, 2H, C_{cage}-H); 6.78 (s, 3H, Ar-H). $^{13}C\{^1H\}$ NMR (101 MHz; CD_3OD, 298K, ppm): δ = 8.14, 94.24 (Cp*-C); 108.35, 117.48, 125.84, 144.52 (Ar-C); 199.14 (N-C=S). ^{11}B NMR (160 MHz, CD_3OD, 298K, ppm): δ = 18.33, -9.07, -16.49, -21.65, -31.21, -32.25, -34.46, -35.42. IR (KBr disk, cm^{-1}): v = 3448.31, 3063.61, 2874.62, 2588.29, 2346.60, 1613.09, 1424.81, 1357.23, 1284.95, 1243.76, 1170.70, 1029.78, 639.90. ESI-MS: m/z = 807.4139 (calcd for $[M - OTf]^+$ = 807.4511).

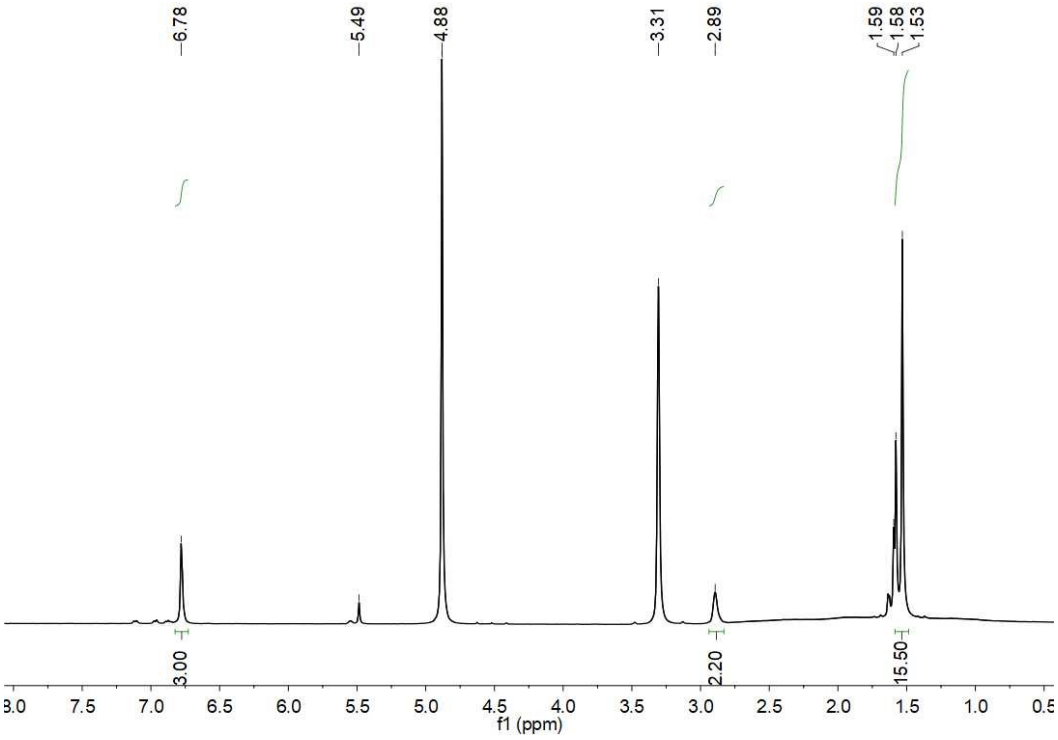


Figure S48. ^{1}H NMR (400 MHz, CD_3OD, 298K, ppm) of complex **5a**.

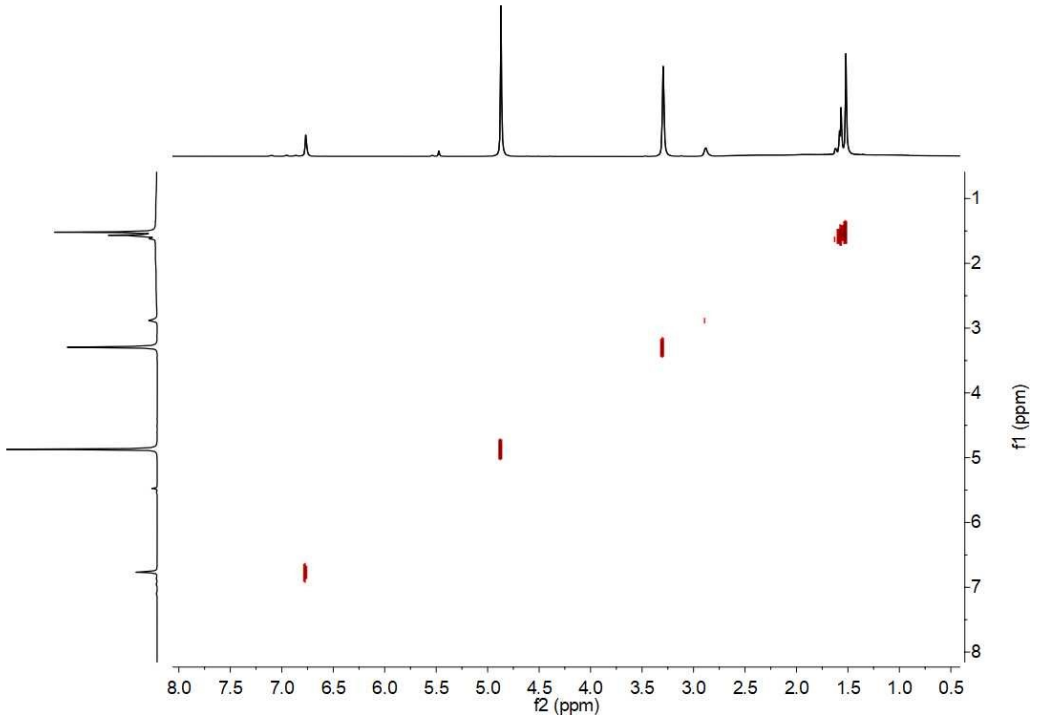


Figure S49. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3OD, 298K, ppm) of complex **5a**.

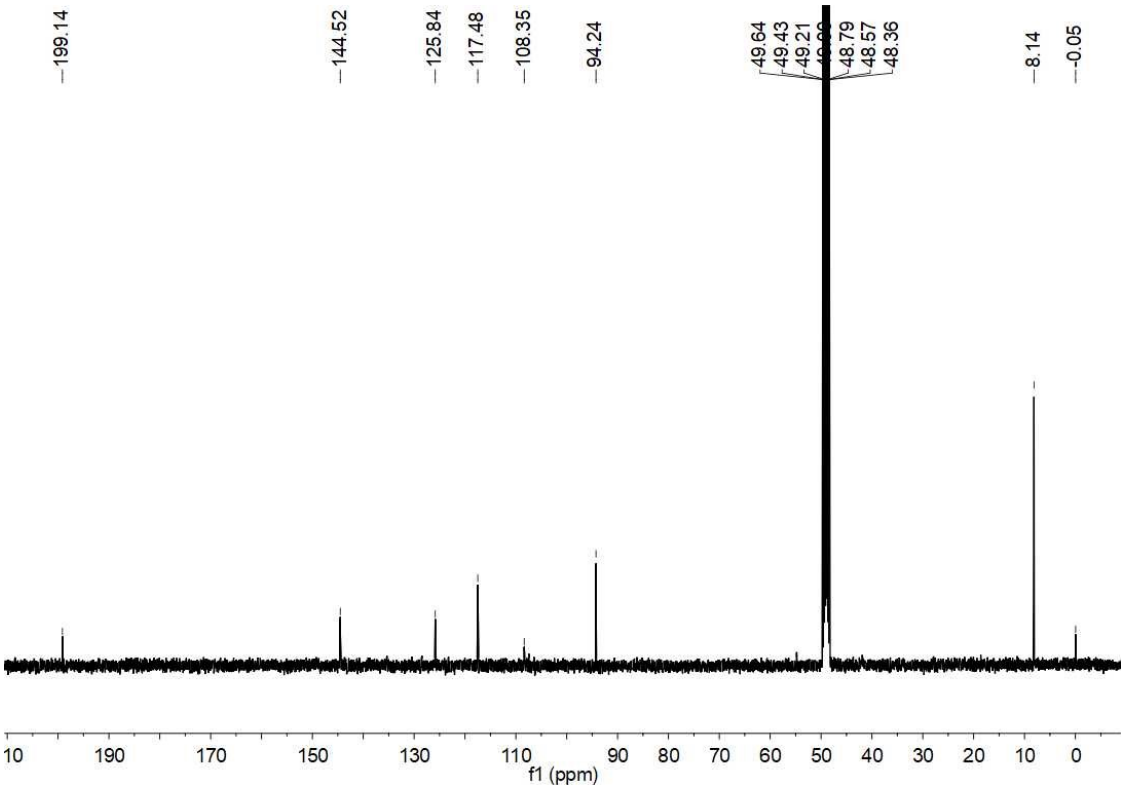


Figure S50. ^{13}C{^{1}H} NMR (101 MHz, CD_3OD, 298K, ppm) of complex **5a**.

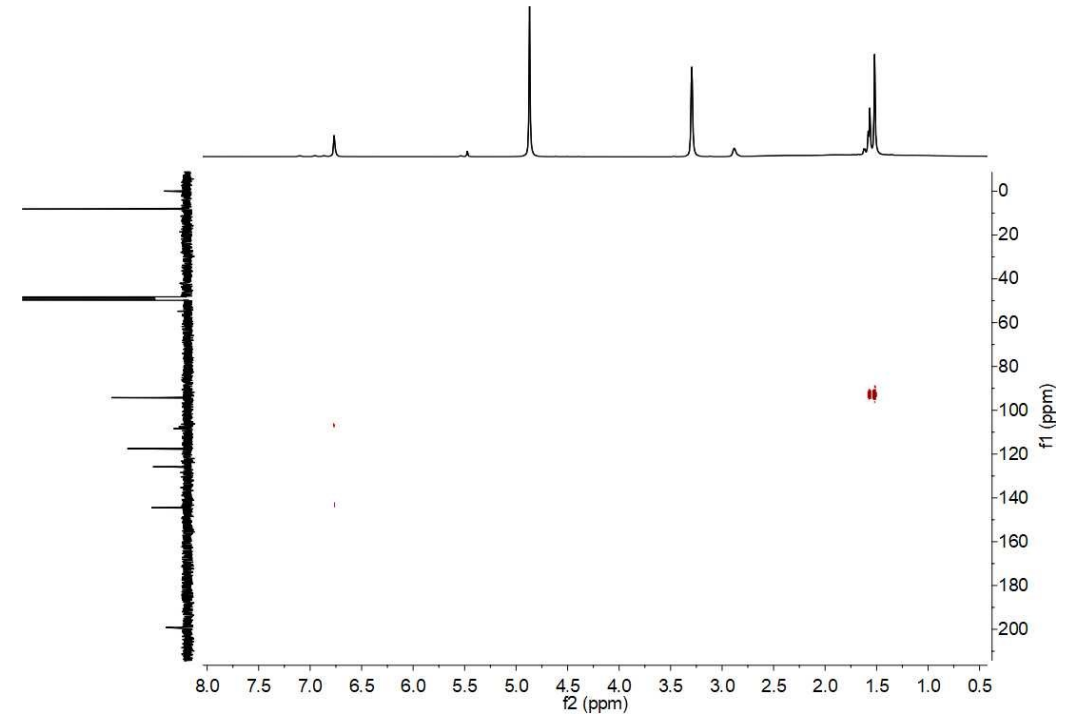


Figure S51. ^{13}C-^{1}H HMBC NMR (400 MHz, CD_3OD, 298K) of complex **5a**.

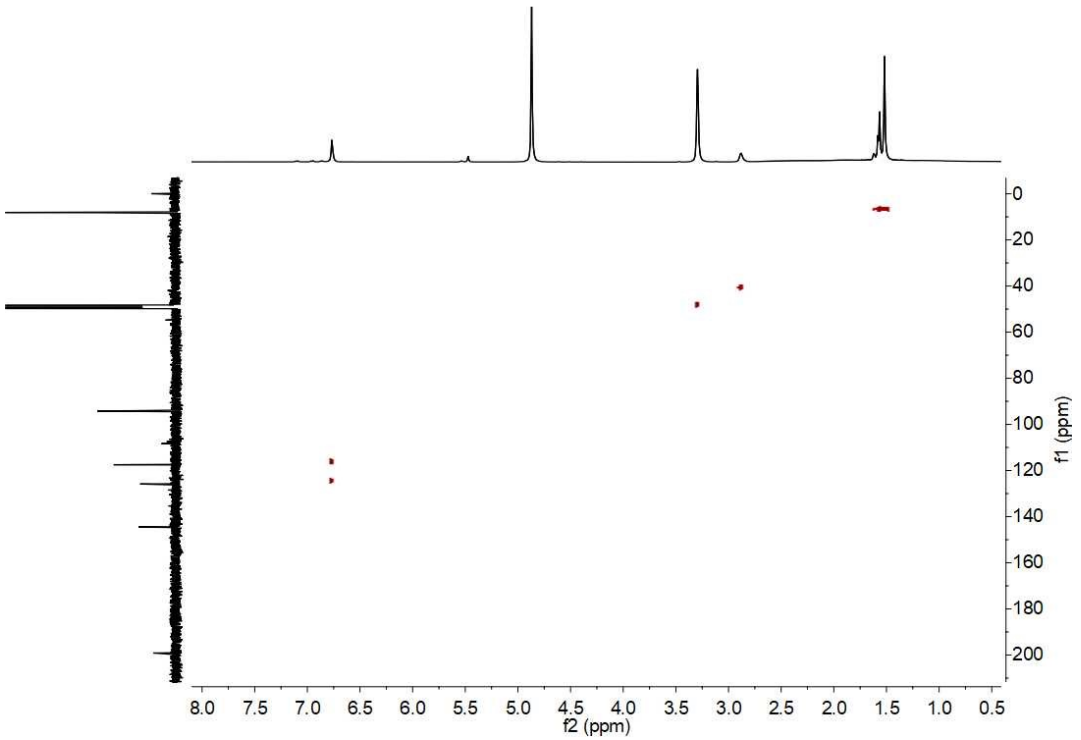


Figure S52. ^{13}C-^{1}H HSQC NMR (400 MHz, CD_3OD, 298K) of complex **5a**.

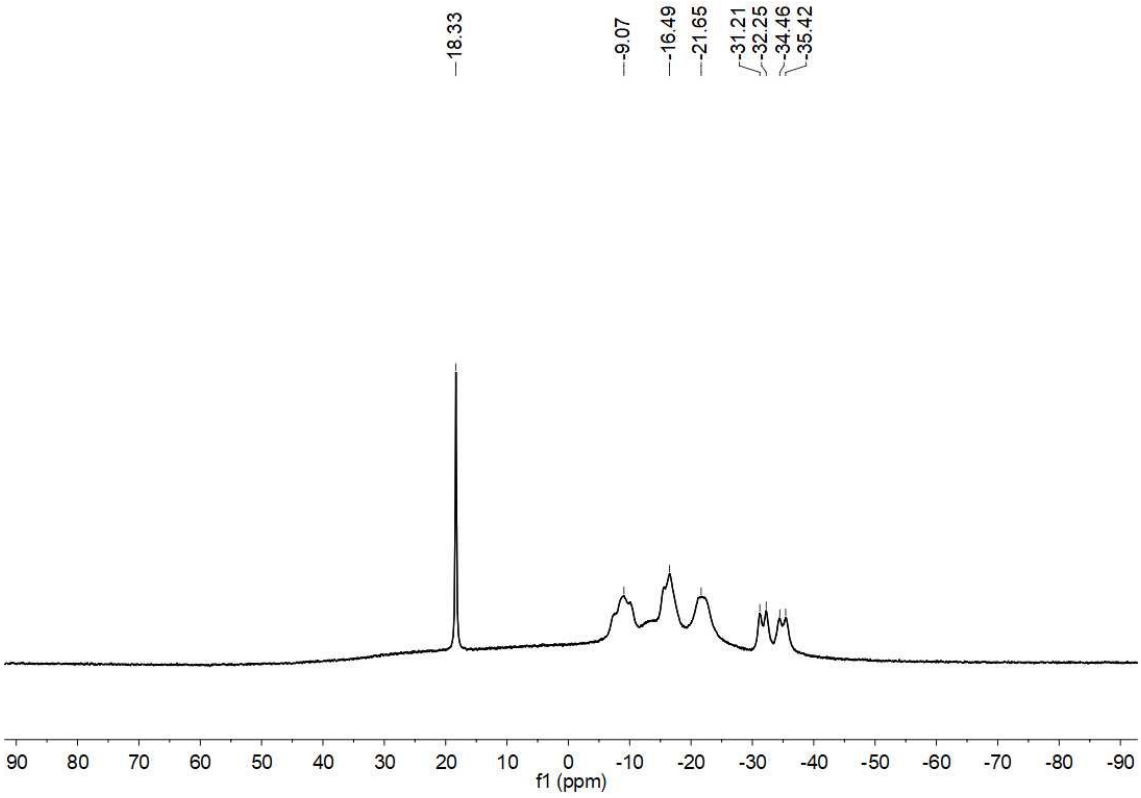


Figure S53. ^{11}B NMR (160 MHz, CD_3OD, 298 K, ppm) of complex **5a**.

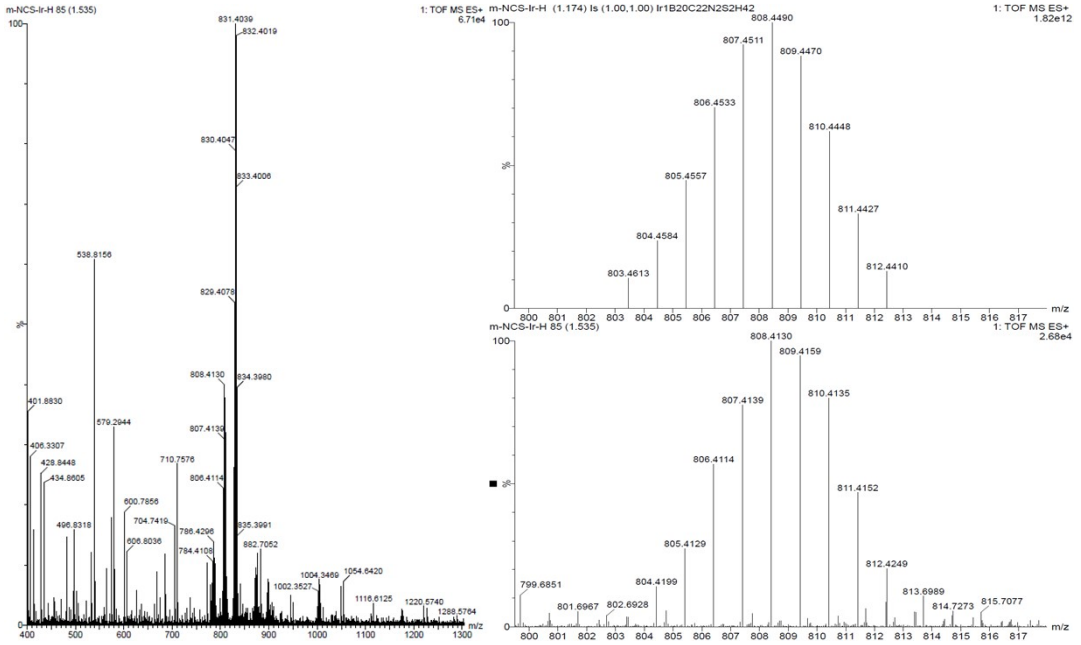
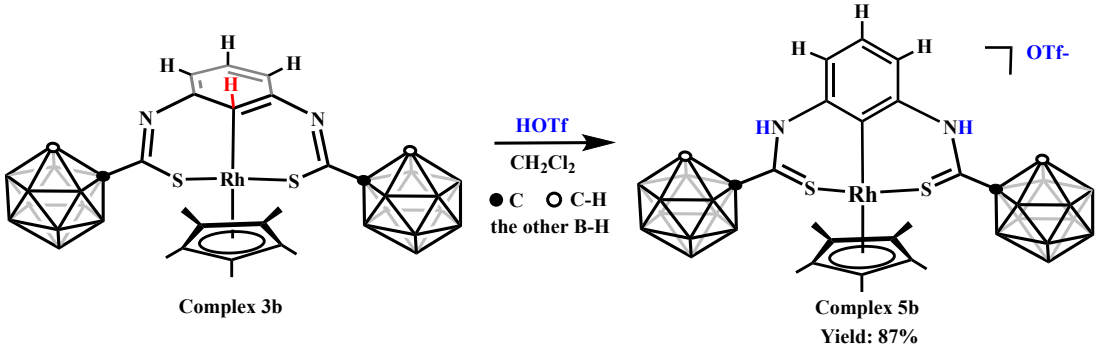


Figure S54. Experimental (bottom) and theoretical (top) ESI-MS of complex **5a.**

S2.9 Synthesis and Characterization of complex 5b.



Scheme S9. Synthesis of complex **5b**.

Complex **3b** (35.84 mg, 0.05 mmol) was dissolved in the CH_2Cl_2 solution. And HOTf (0.05 mL) was added to the solution at room temperature. The reaction mixture was stirred 6 h. Then the mixture was filtered and the precipitate was washed by Et_2O. Orange solid was obtained and dried under vacuo to give the complex **5b**: 37.71 mg 87%. ^{1}H NMR (400 MHz; CD_3OD, 298K, ppm): 1.47, 1.52 (s, 15H, Cp*-H); 2.96 (s, 2H, C_{cage}-H); 6.90, 6.92, 6.95, 6.96 (3H, Ar-H). ^{11}B NMR (160 MHz, CD_3OD, 298K, ppm): δ = 18.33, -7.54, -9.07, -16.43, -21.88, -31.23, -32.19, -34.31, -35.42. IR (KBr disk, cm^{-1}): v = 3448.41, 3222.36, 3060.20, 2916.95, 2586.59, 1554.33, 1421.83, 1283.98, 1243.38, 1170.27, 1029.34, 636.71. ESI-MS: m/z = 718.3762 (calcd for $[M - OTf]^+$ = 718.3943).

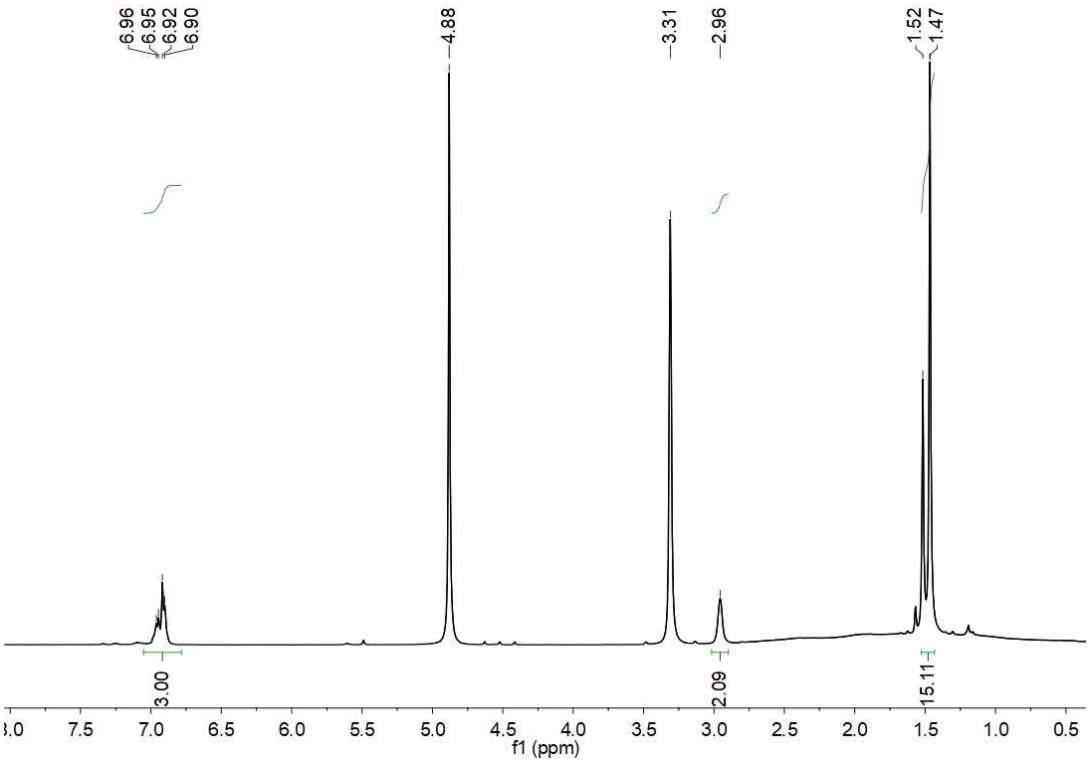


Figure S55. ^{1}H NMR (400 MHz, CD_3OD, 298K, ppm) of complex **5b**.

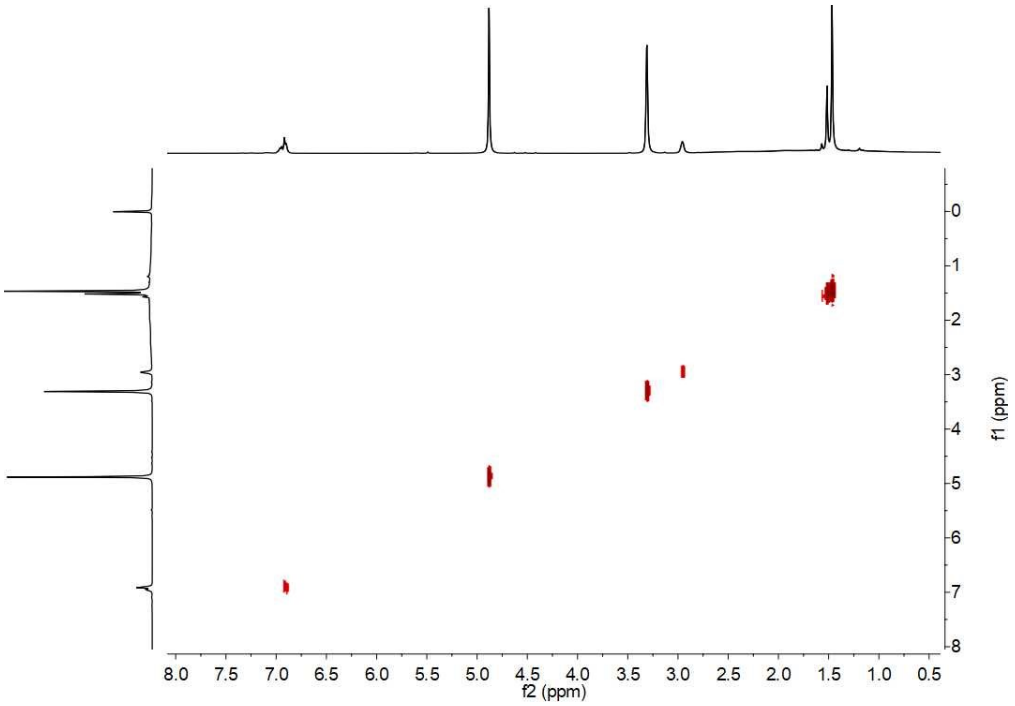


Figure S56. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3OD, 298K, ppm) of complex **5b**.

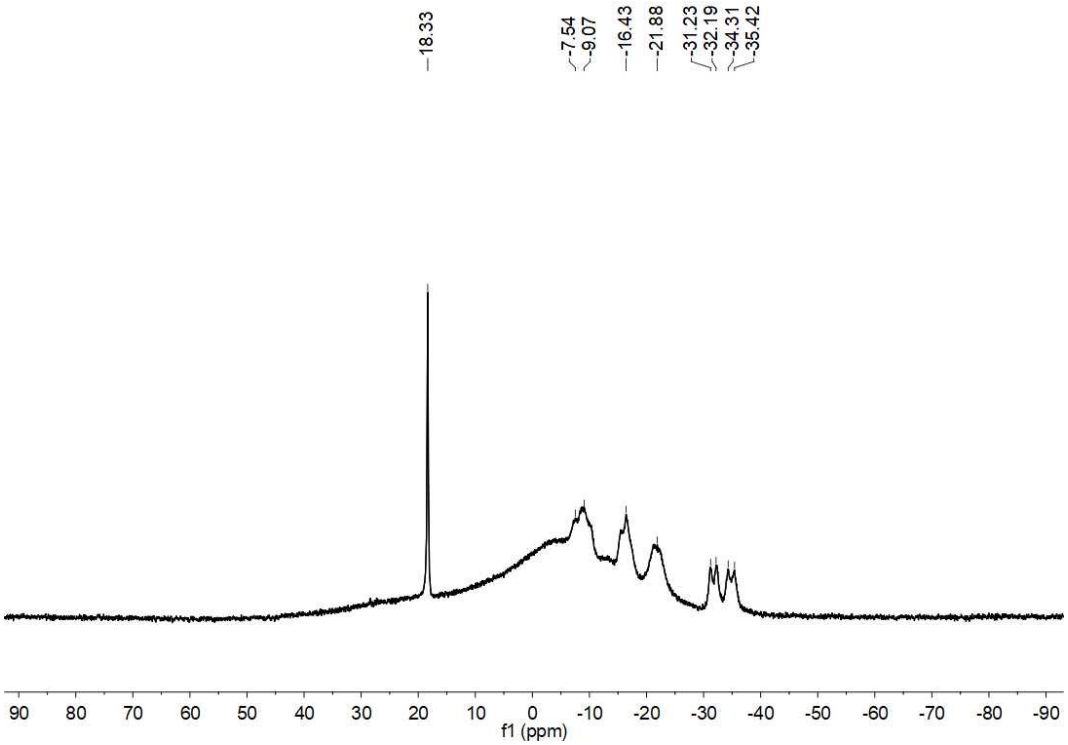


Figure S57. ^{11}B NMR (160 MHz, CD_3OD, 298 K, ppm) of complex **5b**.

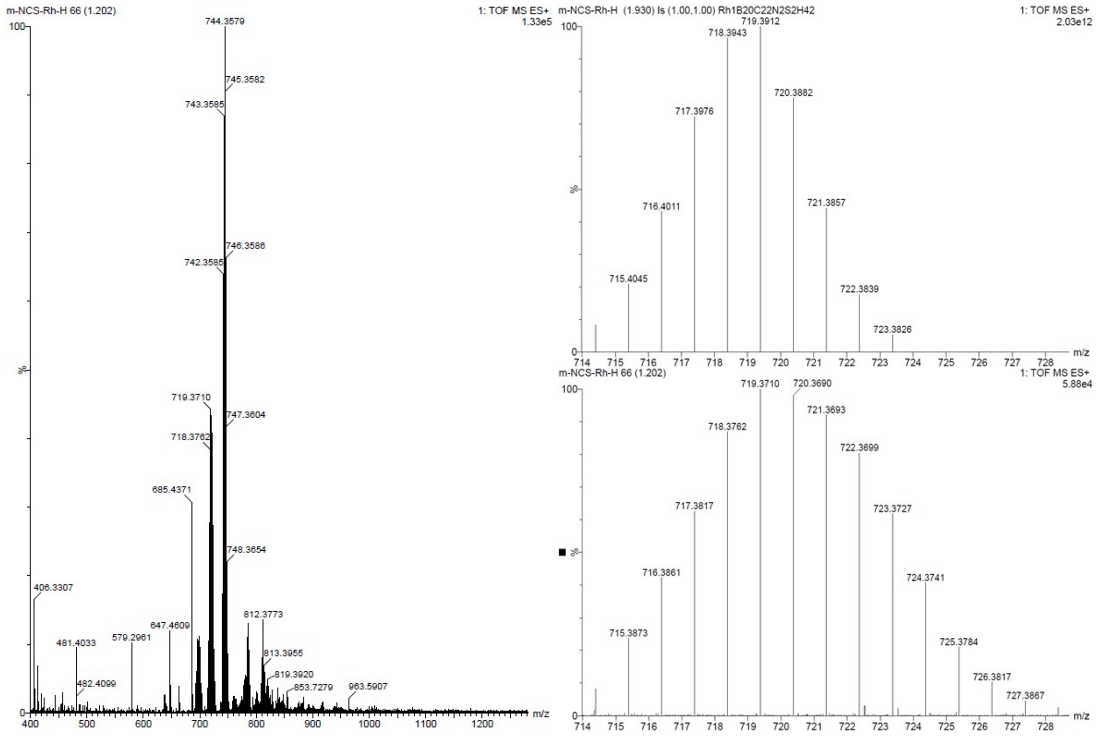
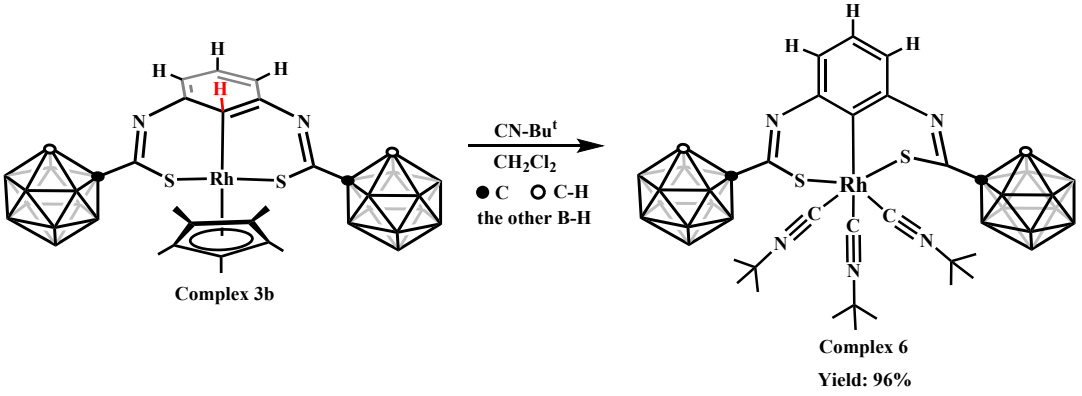


Figure S58. Experimental (bottom) and theoretical (top) ESI-MS of complex **5b.**

S2.10 Synthesis and Characterization of complex 6.



Scheme S10. Synthesis of complex **6**.

Complex **3b** (35.84 mg, 0.05 mmol) was dissolved in the CH_2Cl_2 solution. And tert-Butyl isocyanide (0.05 mL) was added to the solution at room temperature. The reaction mixture was stirred 10 h. Then the mixture was concentrated and further purified via silica gel column chromatography (n-Hexane : CH_2Cl_2, 2 : 1). Yellow solids were obtained and dried under vacuo to give the complex **6**: 39.80 mg 96%. ^{1}H NMR (400 MHz; $CDCl_3$, 298K, ppm): δ = 1.83-2.82 (br, 20H, B-H); 1.39 (s, 18H, CH_3); 1.60 (s, 9H, CH_3); 4.86 (s, 2H, C_{cage}-H); 7.02 (s, 3H, Ar-H). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$, 298K, ppm): δ = 30.22 (CH_3); 58.77 (C-(CH_3)$_3$); 79.97 (CN); 58.00 (cage C); 125.24, 125.88, 149.40 (Ar-C); 157.81 (N=C-S). ^{11}B NMR (160 MHz, $CDCl_3$, 298K, ppm): δ = -3.42, -4.28, -9.66, -10.73. IR (KBr disk, cm^{-1}): v = 2963.44, 2925.99, 2855.17, 2592.56, 2199.45, 2161.92, 1493.50, 1261.85, 1186.51, 1096.74, 1019.22, 800.03. ESI-MS: m/z = 830.4823 (calcd for $[M + H]^+$ = 830.4821).

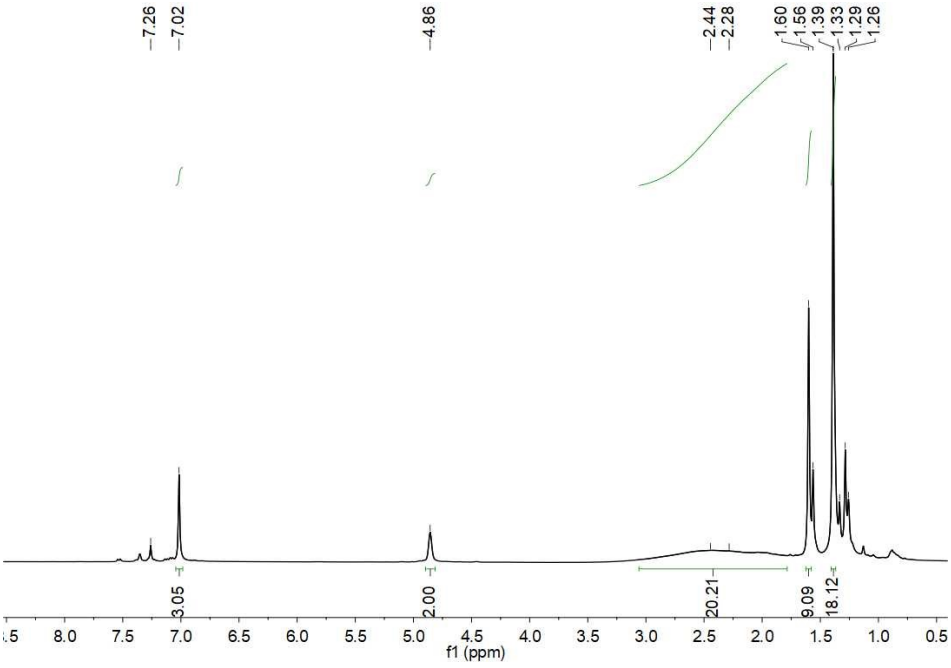


Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **6**.

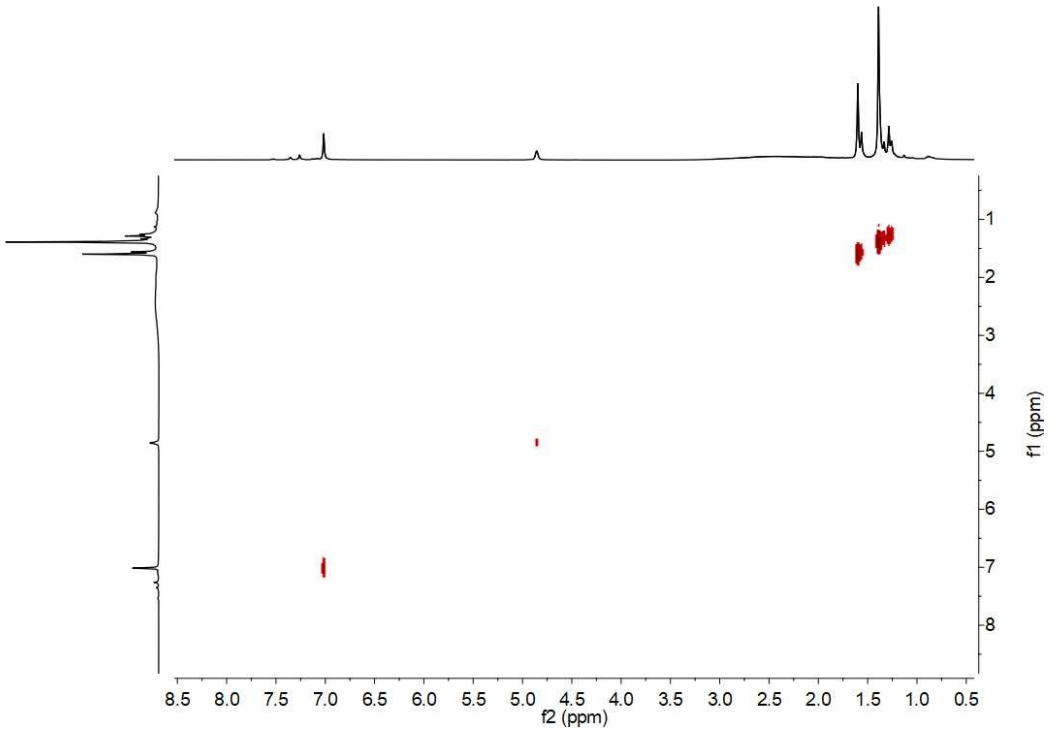


Figure S60.^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$, 298K, ppm) of complex **6**.

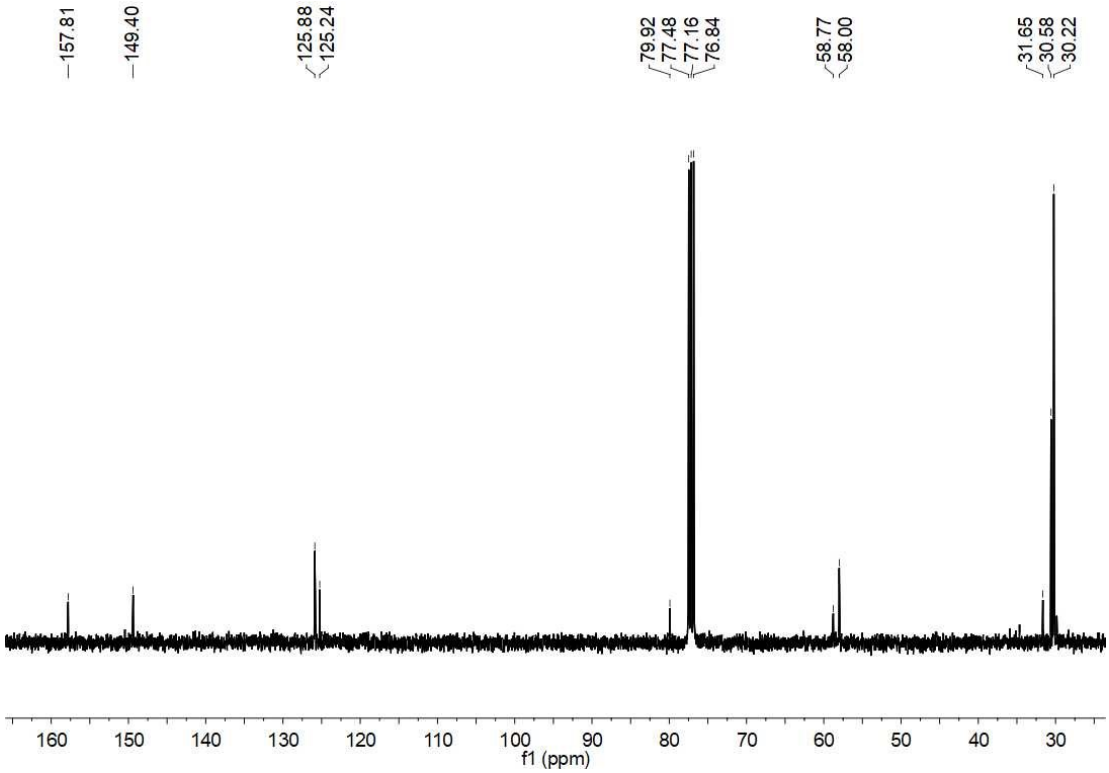


Figure S61. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298K, ppm) of complex **6**.

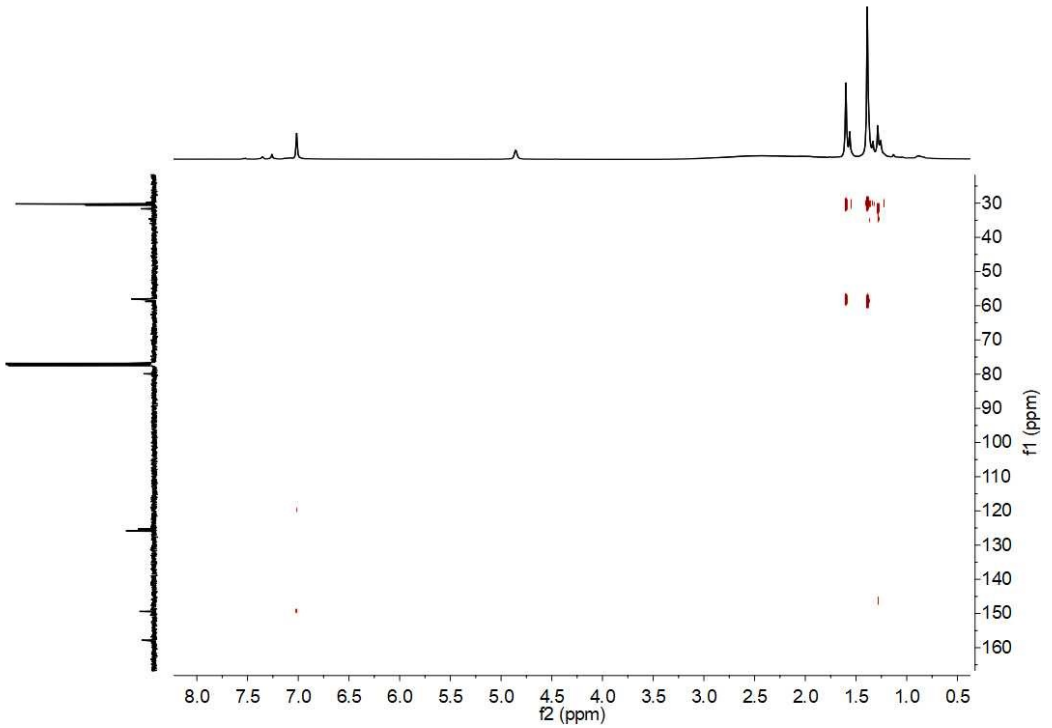


Figure S62. ^{13}C-^{1}H HMBC NMR (400 MHz, $CDCl_3$, 298K) of complex **6**.

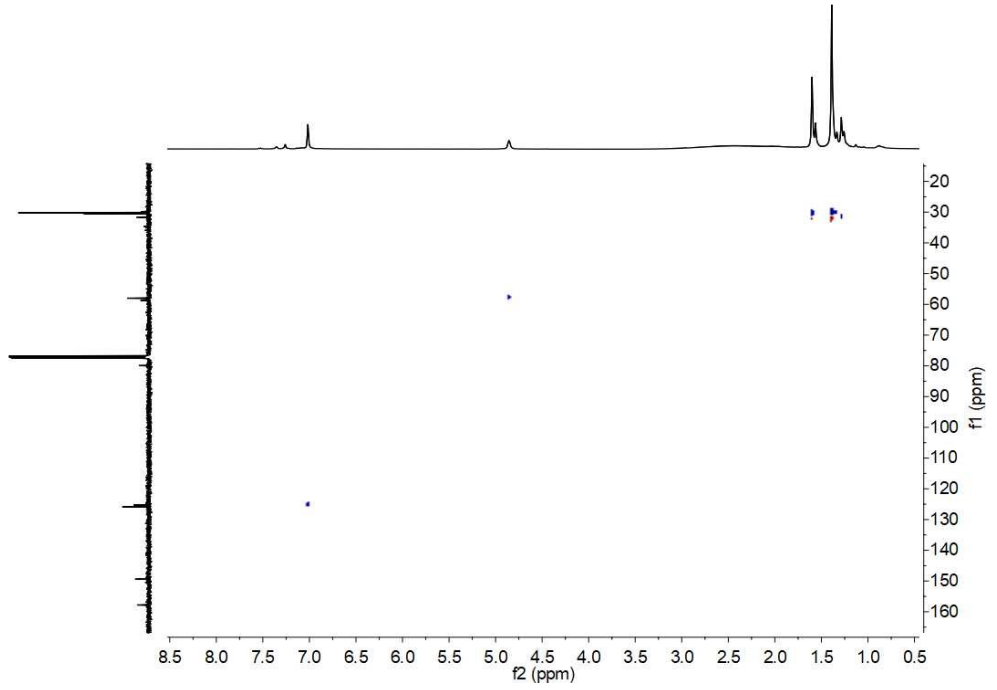


Figure S63. ^{13}C-^{1}H HSQC NMR (400 MHz, $CDCl_3$, 298K) of complex **6**.

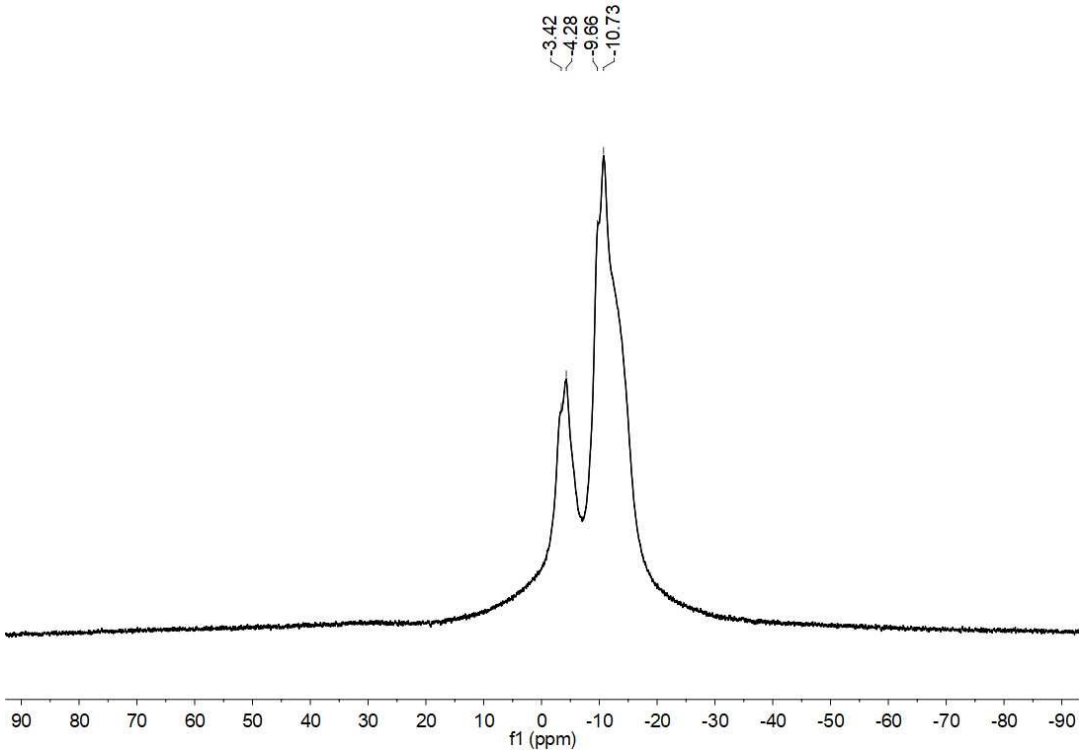


Figure S64. ^{11}B NMR (160 MHz, $CDCl_3$, 298 K, ppm) of complex **6**.

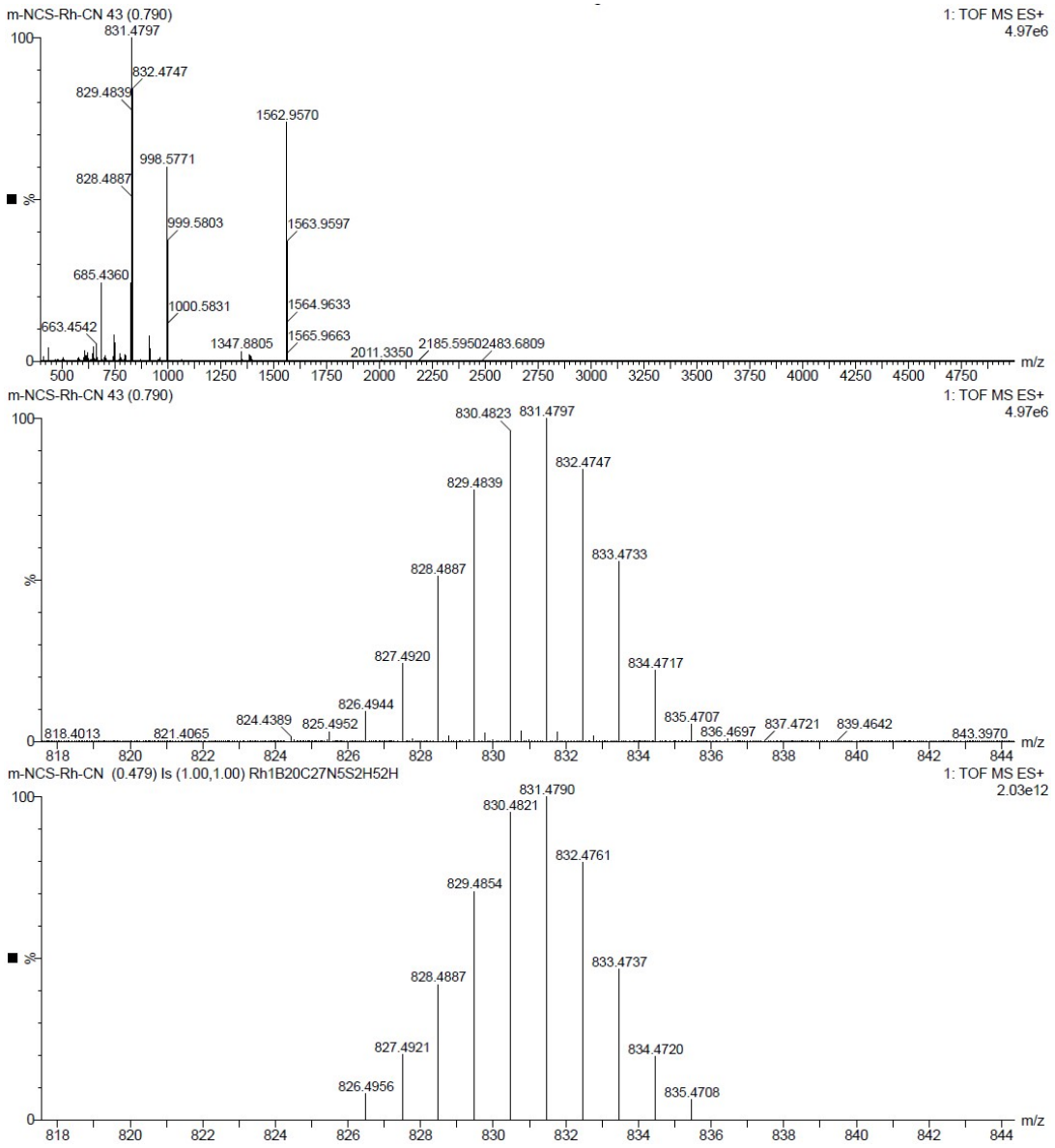
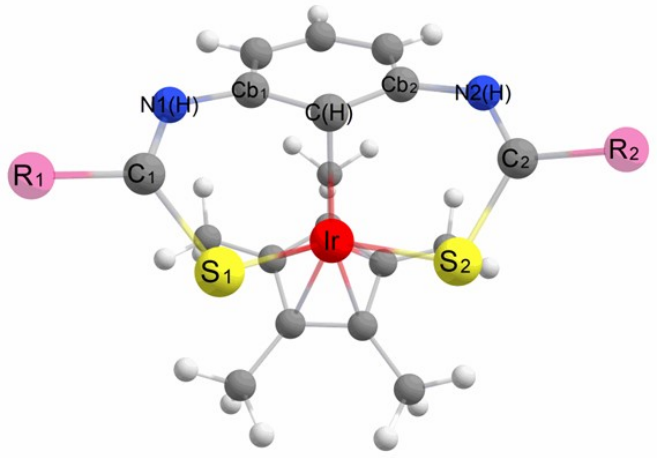


Figure S65. Experimental (top) and theoretical (bottom) ESI-MS of complex **6**.

S3. Density functional theory (DFT) calculations[2-6]

Table S1. NPA charges (*in e*) for Ligands **1-3** and R = CN, OH, H. Level of theory: SMD(CH_2Cl_2)-B3LYP-D3/Def2-TZVPP//SMD(CH_2Cl_2)-B3LYP-D3/Def2-SVP**.**



	Ligand **1**	Ligand **2**	Ligand **3**	R= –CN[a]	R = –OH[a]	R = –H[a]
S1	-0.191	-0.221	-0.089	-0.058	-0.263	-0.201
S2	-0.188	-0.221	-0.121	-0.058	-0.270	-0.201
C1	0.109	0.148	0.112	-0.032	0.391	-0.075
C2	0.108	0.148	0.128	-0.032	0.393	-0.075
N1(H)	-0.528 (0.424)	-0.533 (0.420)	-0.515 (0.435)	-0.473 (0.442)	-0.568 (0.421)	-0.513 (0.428)
N2(H)	-0.515 (0.423)	-0.533 (0.420)	-0.511 (0.440)	-0.473 (0.442)	-0.571 (0.422)	-0.513 (0.428)
C(H)	-0.266 (0.273)	-0.266 (0.273)	-0.263 (0.276)	-0.263 (0.271)	-0.234 (0.263)	-0.277 (0.273)
C1b	0.146	0.142	0.144	0.137	0.140	0.137
C2b	0.143	0.142	0.143	0.137	0.141	0.137
R1	0.022	0.034	-0.124	-0.069	-0.245	0.212
R2	0.022	0.034	-0.123	-0.069	-0.244	0.212

[a] R = R_1 = R_2 in Figure of Table S1.

Table S2. EDDB analysis for the different complexes. Level of theory: SMD(CH_2Cl_2)-B3LYP-D3/Def2-SVP.[a]

	Complex **1**	Complex **2**	Complex **3a**	Complex **5a**	R = –CN[b]	R = –OH[b]	R = –H[b]
Total population of electrons	36.6266e (6.1044 e/atom)	36.6355e (6.1059 e/atom)	36.6625e (6.1104 e/atom)	36.5920e (6.0987 e/atom)	36.6732e (6.1122 e/atom)	36.7256e (6.1209 e/atom)	36.7294e (6.1216 e/atom)
Total population of delocalized electrons	4.8254 e (0.8042 e/atom)	4.8135 e (0.8023 e/atom)	3.5179 e (0.5863 e/atom)	4.7757 e (0.7959 e/atom)	3.477 e (0.5796 e/atom)	3.4678 e (0.5780 e/atom)	3.4568 e (0.5761 e/atom)

[a] For benzene: 37.3361 e (6.2227 e/atom) and 5.5746 e (0.9291 e/atom). [b] R = R_1 = R_2 in Figure of Table S1.

Table S3. NICS(1)zz values for the different complexes. Level of theory: SMD(CH_2Cl_2)-B3LYP-D3/Def2-SVP.[a]

	Complex **1**	Complex **2**	Complex **3a**	Complex **5a**	R = –CN[b]	R = –OH[b]	R = –H[b]
NICS(1)zz (ppm)	-16.7	-18.2	-19.9	-15.3	-22.7	-18.7	-20.7

[a] For benzene: -27.70 ppm. [b] R = R_1 = R_2 in Figure of Table S1.

Table S4. Metal···C–H interaction analysis by Mayer bond orders and three-centre electron sharing indices (3c-ESI). Level of theory: SMD(CH_2Cl_2)-B3LYP-D3/Def2-SVP (Insert: The structures of complexes: $PhCr(CO)_3$; $AuPhCl_3$; H-Bond; Anagostic; $Cp^*Ir(C_2H_4)_2^+$).

System	**Mayer Bond Order**			**3c-ESI**
	M-C	**C-H**	**M-H**	**M···C-H**
Complex 3a	0.500	0.889	0.041	0.017
$PhCr(CO)_3$	0.451	0.988	0.002	0.005
$AuPhCl_3$[a]	0.367	0.914	0.019	0.020
H-Bond[b]	0.001	0.796	0.155	-0.002
Anagostic[c]	0.213	0.804	0.166	0.043
$Cp^*Ir(C_2H_4)_2^+$ [d]	0.299	0.688	0.268	0.098

[a] Zwitterionic Wheland intermediate[6]; [b-d] Complexes possessing H-bond, anagostic and agostic interactions, respectively, obtained from ref. 46 of the main text. CCDC for b and c: ZIYJID and BIXFUJ. 3c-ESI referred to M···H-X (X = C or N) instead of M···C-H.

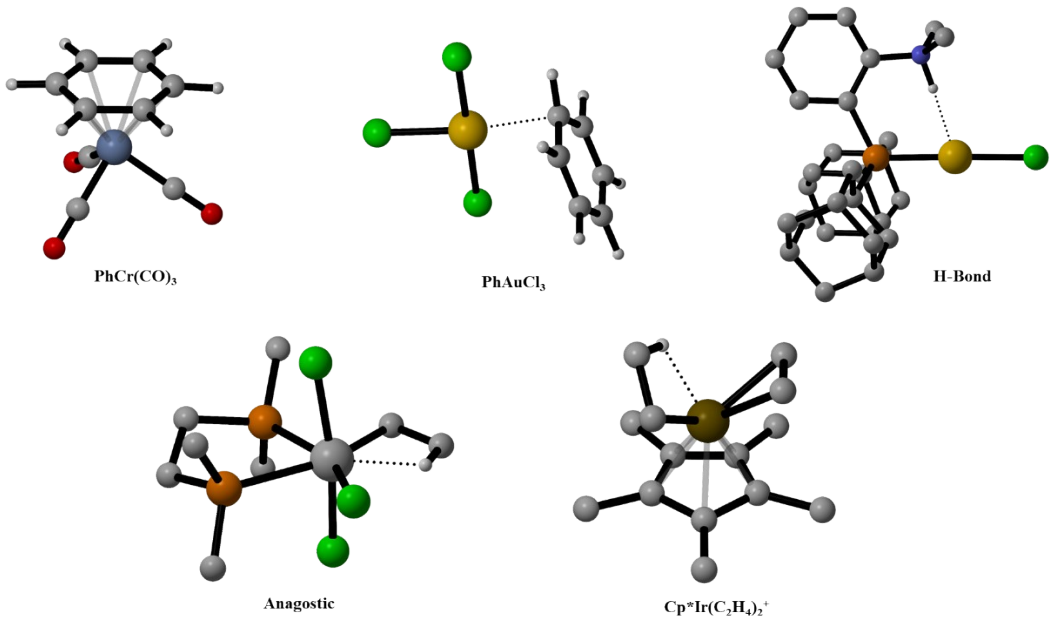
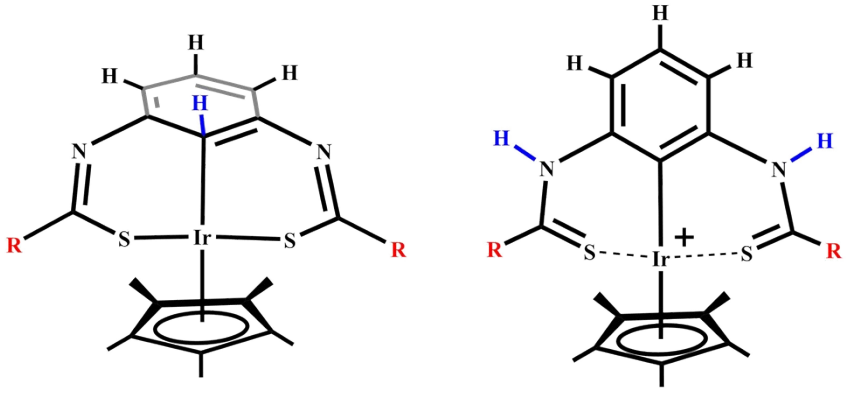


Table S5. Gibbs energies (kcal/mol) for reaction (1).[a]

System	ΔG
Complex 1	-7.01
Complex 2	-6.04
Complex 3a	12.50
R = –CN	11.17
R = –OH	5.01
R = –H	-5.07

[a] Complex n + $NEt_3H^+ \rightarrow$ Complex np + NEt_3 (1). See Figure S66. [b] R = R_1 = R_2 in Figure of Table S1.



Complex n Complex np

Figure S66. Molecular structures of complexes n and np in Equation (1).

Table S6. QTAIM analysis[7] of the bond critical point (BCP) Ir···C. Level of theory: SMD(CH_2Cl_2)-B3LYP-D3/Def2-SVP.

	ρ	**$\nabla\rho^2$**	**ε**	**K**
Complex **3a**	0.079	0.108	0.113	0.026

Table S7. QTAIM analysis[7] of the bond critical point (BCP) C–H. Level of theory: SMD(CH_2Cl_2)-B3LYP-D3/Def2-SVP.

	ρ	**$\nabla\rho^2$**	**ε**	**K**
Complex **3a**	0.279	-1.065	0.027	0.305

S4. Crystallographic Information

Table S8. Crystal data and structure refinement for Ligand **3.**

CCDC number	2303640	
Identification code	cu_230621b_0m_a	
Empirical formula	C12 H28 B20 N2 S2	
Formula weight	480.68	
Temperature	298(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 31.1627(9) Å	α = 90°.
	b = 12.4318(3) Å	β = 107.595(2)°.
	c = 14.5172(4) Å	γ = 90°.
Volume	5361.0(3) $Å^3$	
Z	8	
Density (calculated)	1.191 Mg/m^3	
Absorption coefficient	1.823 mm^{-1}	
F(000)	1968	
Crystal size	0.250 x 0.220 x 0.180 mm^3	
Theta range for data collection	4.712 to 65.153°.	
Index ranges	-35<=h<=36, -13<=k<=14, -15<=l<=17	
Reflections collected	26231	
Independent reflections	4556 [R(int) = 0.0721]	
Completeness to theta = 65.153°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.753 and 0.576	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4556 / 14 / 343	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0633, wR2 = 0.1794	
R indices (all data)	R1 = 0.0797, wR2 = 0.1932	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.522 and -0.338 $e.Å^{-3}$	

$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ (based on reflections with $F_0^2>2\sigma F^2$); $wR_2 = [\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table S9. Crystal data and structure refinement for Ligand **4.**

CCDC number	2303643	
Identification code	platon_sq	
Empirical formula	C17 H43 B30 N3 S3 Cl4	
Formula weight	851.82	
Temperature	193.0 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 10.9098(9)Å	α = 90°.
	b = 25.502(2) Å	β = 90°.
	c = 31.388(3) Å	γ = 90°.
Volume	8732.6(12) $Å^3$	
Z	8	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	2.586 mm^{-1}	
F(000)	3456.0	
Crystal size	0.33 × 0.28 × 0.12 mm^3	
Theta range for data collection	3.255 to 53.499°.	
Index ranges	-13<=h<=12, -30<=k<=30, -37<=l<=37	
Reflections collected	32746	
Independent reflections	7801 [R(int) = 0.1447]	
Completeness to theta = 53.499°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7510 and 0.4735	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7801 / 212 / 639	
Goodness-of-fit on F2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.1440, wR2 = 0.3770	
R indices (all data)	R1 = 0.2144, wR2 = 0.4114	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.386 and -0.570 $e.Å^{-3}$	

$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ (based on reflections with $F_0^2>2\sigma F^2$); $wR_2 = [\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table S10. Crystal data and structure refinement for complex **3a.**

CCDC number	2303637
Identification code	230804b_0ma_a
Empirical formula	C17.60 H32.80 B16 Ir0.80 N1.60 S1.60
Formula weight	644.87
Temperature	174(2) K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 19.1073(6) Å α = 90°.
	b = 13.3046(4) Å β = 99.2970(10)°.
	c = 13.9712(4) Å γ = 90°.
Volume	3505.03(18) $Å^3$
Z	5
Density (calculated)	1.528 Mg/m^3
Absorption coefficient	5.715 mm^{-1}
F(000)	1584
Crystal size	0.260 x 0.250 x 0.200 mm^3
Theta range for data collection	3.537 to 52.187°.
Index ranges	-22<=h<=22, -15<=k<=9, -15<=l<=16
Reflections collected	23569
Independent reflections	5958 [R(int) = 0.0354]
Completeness to theta = 66.004°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.750 and 0.421
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5958 / 8 / 442
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.1137
R indices (all data)	R1 = 0.0380, wR2 = 0.1171
Extinction coefficient	0.00042(8)
Largest diff. peak and hole	1.673 and -1.847 $e.Å^{-3}$

$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ (based on reflections with $F_0^2>2\sigma F^2$); $wR_2 = [\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table S11. Crystal data and structure refinement for complex **3b.**

CCDC number	2303636	
Identification code	230802g_0ma_a	
Empirical formula	C22 H41 B20 N2 Rh S2	
Formula weight	716.80	
Temperature	173(2) K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 19.052(2) Å	α = 90°.
	b = 13.3058(15)) Å	β = 99.388(8)°.
	c = 13.995(2) Å	γ = 90°.
Volume	3500.2(8) $Å^3$	
Z	4	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	3.494 mm^{-1}	
F(000)	1456	
Crystal size	0.250 x 0.220 x 0.180 mm^3	
Theta range for data collection	3.541 to 48.177°.	
Index ranges	-21<=h<=17, -13<=k<=14, -15<=l<=15	
Reflections collected	17259	
Independent reflections	4930 [R(int) = 0.0708]	
Completeness to theta = 48.177°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.750 and 0.512	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4930 / 8 / 441	
Goodness-of-fit on F^2	1.099	
Final R indices [I>2sigma(I)]	R1 = 0.0767, wR2 = 0.1908	
R indices (all data)	R1 = 0.1225, wR2 = 0.2238	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.560 and -1.785 $e.Å^{-3}$	

$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ (based on reflections with $F_0^2>2\sigma F^2$); $wR_2 = [\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table S12. Crystal data and structure refinement for complex **4.**

CCDC number	2303641	
Identification code	230218d_0m_a	
Empirical formula	C90 H158 B60 Ir6 N6 S6	
Formula weight	3318.37	
Temperature	173.0 K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 17.6388(6) Å	α = 91.778(2)°.
	b = 18.5304(7) Å	β = 91.812(2)°.
	c = 24.0367(9) Å	γ = 103.9010(10)°.
Volume	7616.5(5) $Å^3$	
Z	2	
Density (calculated)	1.447 Mg/m^3	
Absorption coefficient	7.552 mm^{-1}	
F(000)	3196	
Crystal size	0.18 x 0.15 x 0.12 mm^3	
Theta range for data collection	3.736 to 52.299°.	
Index ranges	-20<=h<=20, -21<=k<=21, -28<=l<=28	
Reflections collected	125456	
Independent reflections	26018 [R(int) = 0.0460]	
Completeness to theta = 52.299°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.008 and 0.002	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	26018 / 0 / 1549	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.0973	
R indices (all data)	R1 = 0.0472, wR2 = 0.1016	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.618 and -1.691 $e.Å^{-3}$	

$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ (based on reflections with $F_0^2>2\sigma F^2$); $wR_2 = [\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table S13. Crystal data and structure refinement for complex **5a.**

CCDC number	2303638	
Identification code	230806d_0m_a	
Empirical formula	C23 H42 B20 F3 Ir N2 O3 S3	
Formula weight	956.16	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.6139(5) Å	α = 98.948(2)°.
	b = 13.1923(6) Å	β = 101.424(2)°.
	c = 13.5261(6) Å	γ = 91.727(2)°.
Volume	2002.63(15) $Å^3$	
Z	2	
Density (calculated)	1.586Mg/m^3	
Absorption coefficient	5.489 mm^{-1}	
F(000)	940	
Crystal size	0.280 x 0.250 x 0.220 mm^3	
Theta range for data collection	3.811 to 52.000°.	
Index ranges	-13<=h<=13, -15<=k<=15, -15<=l<=15	
Reflections collected	25232	
Independent reflections	6539 [R(int) = 0.0448]	
Completeness to theta = 48.514°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.750 and 0.439	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6539 / 107 / 584	
Goodness-of-fit on F^2	1.100	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0958	
R indices (all data)	R1 = 0.0431, wR2 = 0.1000	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.342 and -2.189 e.$Å^{-3}$	

$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ (based on reflections with $F_0^2>2\sigma F^2$); $wR_2 = [\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table S14. Crystal data and structure refinement for complex **5b**.

CCDC number	2303644	
Identification code	ga_230808f_a	
Empirical formula	C23 H42 B20 F3 N2 O3 Rh S3	
Formula weight	866.87	
Temperature	173.00 K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.6103(11) Å	α = 99.204(4)°.
	b = 13.1824(13) Å	β = 101.430(4)°.
	c = 13.5411(13) Å	γ = 91.527(4)°.
Volume	2001.6(3) $Å^3$	
Z	2	
Density (calculated)	1.438 Mg/m^3	
Absorption coefficient	3.495 mm^{-1}	
F(000)	876	
Crystal size	0.25 x 0.22 x 0.18 mm^3	
Theta range for data collection	2.960 to 51.998°.	
Index ranges	-13<=h<=13, -15<=k<=15, -15<=l<=15	
Reflections collected	13097	
Independent reflections	6632 [R(int) = 0.0284]	
Completeness to theta = 51.998°	97.6%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6146 and 0.4633	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6632 / 135 / 581	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.0906	
R indices (all data)	R1 = 0.0595, wR2 = 0.1036	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.717 and -0.805 e.$Å^{-3}$	

$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ (based on reflections with $F_0^2>2\sigma F^2$); $wR_2 = [\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table S15. Crystal data and structure refinement for complex **6**.

CCDC number	2303639	
Identification code	cu_230824a_a	
Empirical formula	C27 H52 B20 N5 Rh S2	
Formula weight	829.96	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.1157(11) Å	α = 102.935(4)°.
	b = 13.1515(12) Å	β = 95.742(5)°.
	c = 15.8884(14) Å	γ = 111.659(4)°.
Volume	2246.1(4) $Å^3$	
Z	2	
Density (calculated)	1.227 Mg/m^3	
Absorption coefficient	4.131 mm^{-1}	
F(000)	852	
Crystal size	0.180 x 0.120 x 0.110 mm^3	
Theta range for data collection	2.913 to 64.999°.	
Index ranges	-14<=h<=14, -15<=k<=15, -18<=l<=18	
Reflections collected	13869	
Independent reflections	7550 [R(int) = 0.0306]	
Completeness to theta = 64.999°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.644 and 0.523	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7550 / 8 / 513	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0291, wR2 = 0.0685	
R indices (all data)	R1 = 0.0326, wR2 = 0.0704	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.505 and -0.269 $e.Å^{-3}$	

$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ (based on reflections with $F_0^2>2\sigma F^2$); $wR_2 = [\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

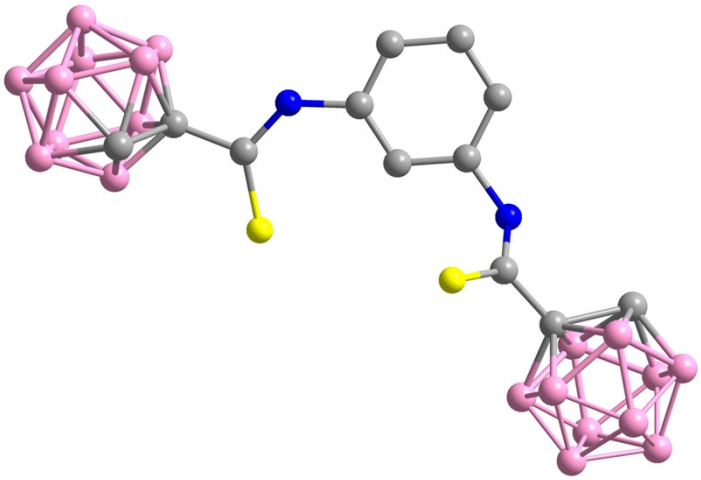


Figure S67. Crystallographically-derived molecular structure of Ligand **3** (the H atoms have been omitted for clarity). Color code: S, yellow; N, blue; C, grey; B, light pink.

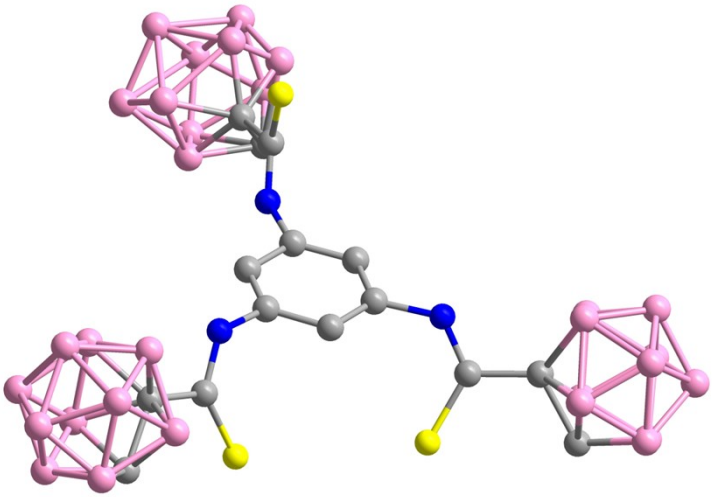


Figure S68. Crystallographically-derived molecular structure of Ligand **4** (the H atoms have been omitted for clarity). Color code: S, yellow; N, blue; C, grey; B, light pink.

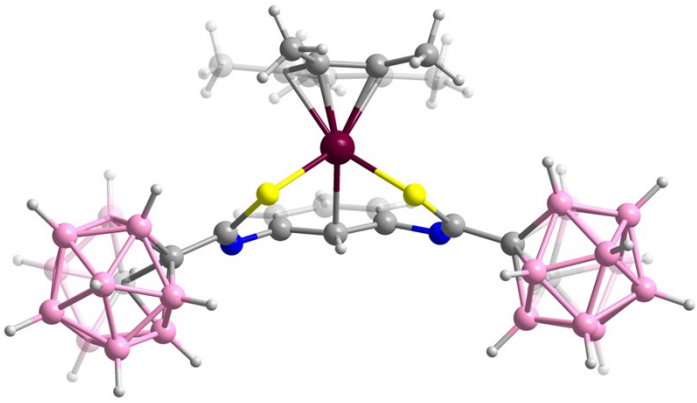


Figure S69. Crystallographically-derived molecular structure of complex **3b**. Color code: Rh, dark red; S, yellow; N, blue; C, grey; B, light pink; H, light grey.

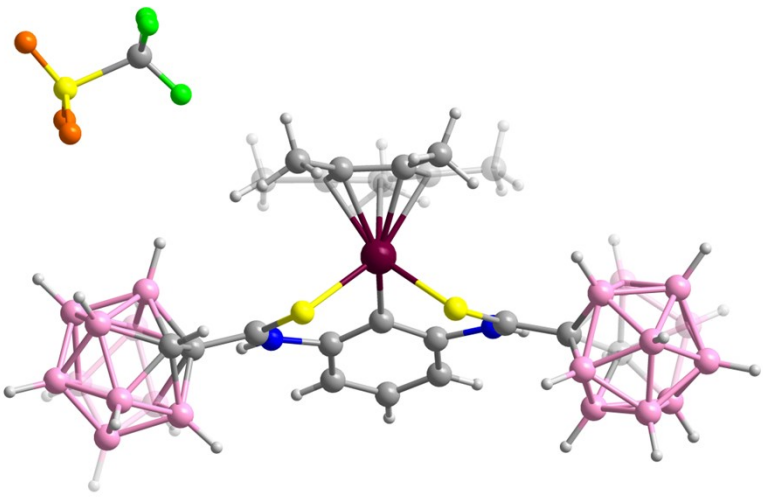


Figure S70. Crystallographically-derived molecular structure of complex **5b**. Color code: Rh, dark red; S, yellow; N, blue; C, grey; B, light pink; H, light grey.

S5. Cartesian coordinates and Gibbs energies of all the computed systems

Table S16. Cartesian coordinates (in Å) ZPE corrected electronic and Gibbs energies (in a.u.) of all the stationary points discussed in the text computed at SMD(CH_2Cl_2)-B3LYP-D3/Def2-SVP level of theory.

Complex 3a

Ir	-0.002066	-1.161492	-0.276623
S	1.765088	0.223331	-1.136716
S	-1.722765	0.282591	-1.133539
N	2.463218	0.554252	1.496840
N	-2.441819	0.565468	1.498803
C	4.031105	1.368907	-0.099929
C	4.891169	1.917709	1.170752
H	4.410599	1.750655	2.132703
B	5.431597	0.494103	0.391574
H	5.259599	-0.551030	0.935936
B	5.075582	0.794992	-1.323819
H	4.714181	-0.124894	-1.991322
B	4.266479	2.372877	-1.458193
H	3.359329	2.521460	-2.217691
B	4.114994	3.068077	0.172007
H	3.132191	3.601504	0.582694
B	6.557386	1.749762	0.948546
H	7.238814	1.506296	1.899990
B	6.713596	1.058486	-0.682552
H	7.617873	0.325335	-0.971386
B	5.996089	2.224710	-1.830890
H	6.390900	2.330414	-2.959500
B	5.396679	3.630582	-0.903997
H	5.356668	4.742032	-1.352453
B	5.750786	3.328224	0.812812
H	5.889484	4.146174	1.673277
B	6.916542	2.817004	-0.426796
H	7.984714	3.354671	-0.529610
B	-4.104276	3.091072	0.191425
H	-3.128978	3.629064	0.613833
B	-4.238896	2.410713	-1.446591
H	-3.328197	2.574931	-2.198642
B	-5.034878	0.824395	-1.333572
H	-4.660550	-0.085715	-2.007277
B	-5.399172	0.503228	0.376283
H	-5.221330	-0.545628	0.911385
B	-5.746608	3.329829	0.823947
H	-5.898431	4.137839	1.691540
B	-5.383979	3.652613	-0.887472
H	-5.351236	4.768795	-1.324584
B	-5.964682	2.250831	-1.832430
H	-6.353032	2.364418	-2.962516
B	-6.679117	1.066815	-0.700554
H	-7.574783	0.328387	-1.002515
B	-6.539709	1.742929	0.938404
H	-7.225152	1.483713	1.882774
B	-6.899523	2.820721	-0.428456
H	-7.971803	3.349823	-0.532874
C	2.702159	0.712923	0.237012
C	1.256902	0.145902	2.013298
C	0.011892	0.451873	1.348916
H	0.015552	1.328764	0.697933
C	-1.236055	0.150680	2.012250

C	-1.213782	-0.508713	3.250263
H	-2.160579	-0.740998	3.741267
C	0.008146	-0.827575	3.849656
H	0.007088	-1.335245	4.817943
C	1.231304	-0.511343	3.252328
H	2.176768	-0.748646	3.743492
C	-2.672593	0.744965	0.240289
C	-4.003409	1.395808	-0.097107
C	-4.876341	1.923573	1.173429
H	-4.400652	1.750739	2.136826
C	-1.171823	-3.031632	-0.011789
C	-0.840788	-2.870912	-1.412480
C	0.592574	-2.873517	-1.540925
C	1.161546	-3.058339	-0.218276
C	0.069705	-3.198726	0.703604
C	-2.547738	-3.151409	0.560184
H	-2.890142	-4.200997	0.538262
H	-3.268578	-2.551369	-0.012979
H	-2.575380	-2.808793	1.603889
C	-1.824442	-2.782802	-2.528782
H	-1.407447	-2.253336	-3.396516
H	-2.740720	-2.264369	-2.215008
H	-2.103247	-3.801241	-2.851048
C	1.371813	-2.794529	-2.809873
H	1.652559	-3.810355	-3.138342
H	2.298661	-2.219388	-2.671446
H	0.788840	-2.324318	-3.613810
C	2.615636	-3.201640	0.095617
H	2.832215	-2.899857	1.129870
H	3.228669	-2.582968	-0.574515
H	2.936727	-4.251053	-0.026511
C	0.191935	-3.576286	2.137048
H	0.155905	-4.678400	2.207336
H	-0.634440	-3.179736	2.738994
H	1.141534	-3.243906	2.573836

Sum of electronic and zero-point Energies = -2369.178520
Sum of electronic and thermal Free Energies = -2369.249408

Complex 1

Ir	-0.001431	-0.645160	0.062750
S	1.758249	-0.106361	-1.467465
S	-1.738013	-0.077481	-1.483087
N	2.481412	1.550442	0.517898
H	3.253288	1.989711	1.017851
N	-2.464548	1.573564	0.504854
H	-3.235995	2.012496	1.005875
C	2.838317	0.814475	-0.535771
C	1.199215	2.030874	0.898867
C	0.006959	1.347217	0.584715
C	-1.180421	2.042644	0.892112
C	-1.187603	3.254988	1.602034
H	-2.141412	3.733499	1.841116
C	0.014996	3.843385	1.985115
H	0.018033	4.780446	2.545690
C	1.213880	3.243198	1.608703
H	2.170848	3.712712	1.853095
C	-2.820644	0.838265	-0.548655
C	1.159419	-1.911153	1.466033
C	0.035866	-1.358725	2.172553
C	-1.166104	-1.822217	1.528873

C	-0.772682	-2.759594	0.476908
C	0.642178	-2.814187	0.437665
C	2.602963	-1.761066	1.826906
H	2.920124	-2.579110	2.497697
H	2.791526	-0.810302	2.344325
H	3.244589	-1.799343	0.935083
C	0.099553	-0.462929	3.366055
H	-0.766753	0.211701	3.408039
H	1.012500	0.148265	3.363507
H	0.100699	-1.068038	4.289279
C	-2.569118	-1.570971	1.982324
H	-2.886561	-2.341726	2.706919
H	-3.274516	-1.600821	1.139884
H	-2.662088	-0.591562	2.471860
C	-1.735331	-3.519624	-0.375977
H	-2.171978	-4.358175	0.193433
H	-1.245934	-3.930277	-1.269873
H	-2.565463	-2.877178	-0.706908
C	1.499246	-3.649458	-0.457195
H	2.343464	-3.066419	-0.855528
H	0.928981	-4.048971	-1.307399
H	1.921804	-4.501732	0.102614
C	4.268104	0.848288	-0.912317
C	5.014887	2.034365	-0.760493
C	4.896402	-0.298243	-1.434372
C	6.362586	2.066389	-1.118389
C	6.245983	-0.261558	-1.784218
C	6.981490	0.918716	-1.627049
H	4.533130	2.945267	-0.397178
H	4.321955	-1.218884	-1.546919
H	6.929386	2.994371	-1.010365
H	6.727753	-1.160012	-2.177560
H	8.038350	0.945643	-1.904678
C	-4.251204	0.865307	-0.921867
C	-4.876230	-0.288013	-1.432770
C	-5.002472	2.048870	-0.773838
C	-6.227663	-0.259891	-1.776446
C	-6.351816	2.072282	-1.126092
C	-6.967569	0.918267	-1.624339
H	-4.298001	-1.207111	-1.539415
H	-4.522703	2.963588	-0.417398
H	-6.707341	-1.163345	-2.160777
H	-6.922666	2.998182	-1.021601
H	-8.025785	0.938475	-1.897331

Sum of electronic and zero-point Energies = -2170.144530
Sum of electronic and thermal Free Energies = -2170.209033

Complex 2

Ir	0.024212	-0.370517	0.021362
S	1.861680	-0.085634	-1.495030
S	-1.624039	-0.251220	-1.711998
N	2.401550	1.984615	0.122368
H	3.126886	2.590174	0.505909
N	-2.525750	1.819118	-0.258168
H	-3.336182	2.391147	-0.023062
C	2.841441	1.071307	-0.737860
C	1.079580	2.462184	0.353307
C	-0.068632	1.682090	0.105341
C	-1.291829	2.380493	0.174800
C	-1.382435	3.704333	0.636465

H	-2.360373	4.189341	0.701043
C	-0.228245	4.399057	0.988686
H	-0.291303	5.424593	1.358324
C	1.010301	3.787214	0.814172
H	1.933380	4.336067	1.018440
C	-2.764939	0.865827	-1.153025
C	1.139087	-1.201444	1.750794
C	-0.066718	-0.590566	2.238259
C	-1.184802	-1.271720	1.641681
C	-0.657392	-2.388304	0.855918
C	0.757242	-2.344439	0.920775
C	2.534183	-0.879690	2.181951
H	2.801432	-1.460408	3.082580
H	2.648033	0.186003	2.424561
H	3.261445	-1.133365	1.398892
C	-0.146889	0.548344	3.201117
H	-1.044649	1.157961	3.029455
H	0.732214	1.202989	3.126305
H	-0.193910	0.161977	4.234110
C	-2.629844	-1.031629	1.940604
H	-2.949747	-1.631818	2.810965
H	-3.264005	-1.316099	1.091219
H	-2.822237	0.025172	2.173841
C	-1.503714	-3.393785	0.144523
H	-1.918792	-4.121482	0.863260
H	-0.926372	-3.948741	-0.608305
H	-2.352120	-2.911541	-0.363766
C	1.728806	-3.292046	0.295985
H	2.571969	-2.752981	-0.161505
H	1.252220	-3.904446	-0.481837
H	2.145649	-3.972040	1.059072
C	-4.174112	0.773490	-1.677345
H	-4.624571	1.780240	-1.681767
H	-4.128573	0.423800	-2.719885
C	-5.055446	-0.187311	-0.859127
H	-5.079515	0.145286	0.192519
H	-4.591359	-1.187574	-0.862397
C	-6.480957	-0.275285	-1.406068
H	-6.443283	-0.604030	-2.459911
H	-6.929661	0.734189	-1.416290
C	4.312073	1.124773	-1.071328
H	4.388776	1.500961	-2.107764
H	4.791272	1.882927	-0.430228
C	5.060527	-0.208523	-0.960951
H	4.600503	-0.941905	-1.642550
H	4.936831	-0.610225	0.059329
C	6.549016	-0.068311	-1.282673
H	7.002142	0.674462	-0.601487
H	6.662090	0.343744	-2.301609
C	7.302361	-1.392944	-1.174233
H	7.229032	-1.811940	-0.155892
H	6.891889	-2.143763	-1.870869
H	8.372415	-1.269205	-1.408238
C	-7.363453	-1.225123	-0.598246
H	-6.952236	-2.249068	-0.597622
H	-7.443450	-0.899737	0.453173
H	-8.384337	-1.275298	-1.010982

Sum of electronic and zero-point Energies = -2022.565060
Sum of electronic and thermal Free Energies = -2022.632424

Complex 5a

Ir	0.010241	0.857628	0.052441
S	-1.738869	-0.088001	-1.279820
S	1.777112	-0.108765	-1.251408
N	-2.488110	-1.106531	1.082804
H	-3.252447	-1.354122	1.707892
N	2.457133	-1.198304	1.107036
H	3.215745	-1.561205	1.685187
C	-4.269325	-0.833575	-0.535619
C	-5.195774	-1.953327	0.219277
H	-4.708899	-2.571713	0.971169
B	-5.437544	-0.300516	0.623489
H	-5.026142	0.092640	1.669369
B	-5.203056	0.543722	-0.929353
H	-4.655921	1.601875	-0.919825
B	-4.771282	-0.662176	-2.164495
H	-3.952341	-0.406281	-2.988675
B	-4.719460	-2.269041	-1.396276
H	-3.863632	-3.075637	-1.581192
B	-6.790317	-1.434106	0.436382
H	-7.364092	-1.774897	1.426822
B	-6.837935	0.171315	-0.333679
H	-7.562613	1.037150	0.066777
B	-6.433057	-0.053436	-2.059773
H	-6.869827	0.665590	-2.914011
B	-6.127789	-1.791063	-2.348105
H	-6.342961	-2.328636	-3.396699
B	-6.356511	-2.636628	-0.801488
H	-6.638055	-3.785823	-0.639480
B	-7.416720	-1.273236	-1.218517
H	-8.578719	-1.449423	-1.455230
B	5.131204	0.510954	-0.882804
H	4.502675	1.514468	-0.972672
B	5.480043	-0.322496	0.652897
H	5.107841	0.188252	1.665526
B	5.245260	-2.072685	0.408881
H	4.732065	-2.728002	1.265517
B	4.733422	-2.353839	-1.271910
H	3.851350	-3.086984	-1.590466
B	6.291360	-0.064124	-2.092592
H	6.503446	0.641606	-3.032054
B	6.801824	0.208526	-0.409405
H	7.505384	1.129713	-0.106746
B	6.877487	-1.388502	0.391910
H	7.642478	-1.617829	1.286211
B	6.411293	-2.640651	-0.799093
H	6.834367	-3.760942	-0.772148
B	6.048903	-1.810476	-2.331458
H	6.098186	-2.272685	-3.431276
B	7.381490	-1.227290	-1.307257
H	8.522199	-1.336407	-1.659609
C	-2.814401	-0.712776	-0.143225
C	-1.210511	-1.455915	1.607544
C	-0.010958	-0.908364	1.115405
C	1.164544	-1.498852	1.618621
C	1.154612	-2.452356	2.650888
H	2.099091	-2.857549	3.025747
C	-0.057128	-2.887812	3.180944
H	-0.074160	-3.621006	3.989573
C	-1.246870	-2.408684	2.638678
H	-2.210680	-2.775931	3.002621

C	2.811889	-0.774300	-0.097357
C	4.282037	-0.923517	-0.410721
C	4.761444	-0.776039	-1.954476
H	3.974178	-0.568413	-2.677858
C	-1.153495	2.451463	1.053804
C	-0.018030	2.132878	1.877609
C	1.171436	2.410325	1.118371
C	0.760343	3.006084	-0.154738
C	-0.655070	3.033427	-0.193843
C	-2.587947	2.402114	1.469805
H	-2.876876	3.352965	1.950772
H	-2.770049	1.593510	2.190465
H	-3.250684	2.254973	0.607699
C	-0.065885	1.610289	3.275385
H	0.767210	0.923777	3.480183
H	-1.007138	1.080118	3.474368
H	0.005662	2.450079	3.987939
C	2.578418	2.304788	1.610644
H	2.888647	3.250529	2.088491
H	3.275973	2.108309	0.786918
H	2.685691	1.503242	2.354089
C	1.708041	3.501012	-1.197594
H	2.127433	4.476527	-0.897138
H	1.208871	3.626193	-2.168103
H	2.551538	2.807205	-1.331446
C	-1.528597	3.573386	-1.279058
H	-2.372552	2.898235	-1.487227
H	-0.968879	3.722755	-2.212722
H	-1.952686	4.545729	-0.974793

Sum of electronic and zero-point Energies = -2369.611286
Sum of electronic and thermal Free Energies = -2369.677655

Ligand 1

S	2.085435	-1.436835	-1.133546
S	-1.889418	-1.723870	0.283410
N	2.479419	1.008967	-0.072316
H	3.191724	1.676838	0.214524
N	-2.469271	0.880242	-0.182002
H	-3.234288	1.529606	-0.350741
C	2.946514	-0.230981	-0.367511
C	1.205049	1.592224	-0.227982
C	0.016478	0.850130	-0.145771
C	-1.214301	1.512246	-0.265599
C	-1.249515	2.905574	-0.476755
H	-2.212705	3.412793	-0.579540
C	-0.062369	3.628720	-0.545980
H	-0.094626	4.709521	-0.703657
C	1.168065	2.982918	-0.419736
H	2.101887	3.548347	-0.476190
C	-2.870545	-0.389720	0.069399
H	0.040092	-0.222689	0.007157
C	4.363338	-0.441085	0.061098
C	5.222549	-1.253739	-0.699851
C	4.856175	0.151468	1.239224
C	6.544486	-1.453050	-0.303376
C	6.177318	-0.061470	1.642127
C	7.026834	-0.858935	0.869740
H	4.834666	-1.722463	-1.606076
H	4.196160	0.755730	1.866512
H	7.203849	-2.076738	-0.912777

H	6.539811	0.391944	2.568429
H	8.061457	-1.022581	1.182833
C	-4.358576	-0.519932	0.169371
C	-5.002484	-1.672753	-0.314150
C	-5.134990	0.490440	0.768216
C	-6.387675	-1.803233	-0.218192
C	-6.521202	0.350270	0.877048
C	-7.152323	-0.793439	0.379285
H	-4.399097	-2.461141	-0.767661
H	-4.653815	1.378817	1.185638
H	-6.874821	-2.699306	-0.611680
H	-7.107415	1.135782	1.361101
H	-8.237144	-0.901557	0.460907

Sum of electronic and zero-point Energies = -1676.691617
Sum of electronic and thermal Free Energies = -1676.743914

Ligand 2

S	1.676150	-1.349303	-1.443096
S	-1.676149	-1.349539	1.442723
N	2.410805	1.097382	-0.553740
H	3.206229	1.721787	-0.434566
N	-2.410711	1.097363	0.553851
H	-3.206110	1.721827	0.434818
C	2.733469	-0.132411	-1.017650
C	1.177704	1.724823	-0.279927
C	0.000053	1.016041	0.000035
C	-1.177613	1.724793	0.280004
C	-1.180261	3.131164	0.267489
H	-2.105680	3.674674	0.476741
C	0.000028	3.822860	0.000036
H	0.000012	4.915681	0.000032
C	1.180334	3.131190	-0.267418
H	2.105748	3.674706	-0.476669
C	-2.733412	-0.132488	1.017573
H	0.000064	-0.067558	0.000030
C	4.231027	-0.357817	-1.084748
H	4.438003	-1.047098	-1.915125
H	4.748226	0.594379	-1.299793
C	4.774509	-0.953900	0.225253
H	4.235447	-1.894010	0.432242
H	4.541287	-0.270034	1.060900
C	6.280432	-1.217379	0.178969
H	6.809525	-0.272904	-0.043412
H	6.502016	-1.896408	-0.664013
C	-4.230979	-0.357803	1.084774
H	-4.437945	-1.047032	1.915198
H	-4.748104	0.594434	1.299818
C	-4.774583	-0.953906	-0.225167
H	-4.235644	-1.894096	-0.432107
H	-4.541294	-0.270122	-1.060863
C	-6.280538	-1.217179	-0.178834
H	-6.809505	-0.272604	0.043424
H	-6.502213	-1.896071	0.664235
C	6.818546	-1.815432	1.478051
H	6.639655	-1.141008	2.333145
H	6.327721	-2.776619	1.707988
H	7.904053	-1.999828	1.419520
C	-6.818735	-1.815327	-1.477840
H	-6.639735	-1.141043	-2.333022
H	-6.328052	-2.776617	-1.707645

H	-7.904270	-1.999550	-1.419293

Sum of electronic and zero-point Energies = -1529.114516
Sum of electronic and thermal Free Energies = -1529.171448

Ligand 3

S	-1.956663	-1.533402	0.408179
S	2.032435	-1.448198	-0.682336
N	-2.474849	1.063968	-0.079794
H	-3.218454	1.736432	-0.262535
N	2.488542	1.115508	0.035003
H	3.218586	1.794470	0.245123
C	-4.420856	-0.343413	-0.004709
C	-5.376284	0.312039	1.166413
H	-4.847495	0.841457	1.958764
B	-5.375014	1.061446	-0.363565
H	-4.852319	2.124591	-0.485690
B	-5.225924	-0.281332	-1.513597
H	-4.554328	-0.122493	-2.488527
B	-5.113612	-1.794549	-0.581450
H	-4.381967	-2.660832	-0.945097
B	-5.165657	-1.388503	1.148945
H	-4.477109	-1.876473	1.984645
B	-6.865242	0.865671	0.563615
H	-7.345231	1.844064	1.053373
B	-6.812697	0.459784	-1.171103
H	-7.364463	1.142556	-1.987248
B	-6.660949	-1.312883	-1.302996
H	-7.114300	-1.923531	-2.230960
B	-6.615677	-1.995307	0.346785
H	-7.033466	-3.085181	0.619516
B	-6.739214	-0.640973	1.492340
H	-7.139900	-0.691135	2.616851
B	-7.672642	-0.602995	-0.021177
H	-8.869143	-0.689637	-0.009861
B	5.365724	-0.379684	-1.499687
H	4.762085	-0.422893	-2.524677
B	5.484782	1.063866	-0.467567
H	4.992573	2.079075	-0.861124
B	5.259327	0.572216	1.225797
H	4.609516	1.254619	1.959744
B	4.998739	-1.186755	1.273504
H	4.172276	-1.723679	1.940640
B	6.686509	-1.474969	-1.049192
H	7.044572	-2.276401	-1.859508
B	6.951428	0.283966	-1.091067
H	7.615781	0.802190	-1.943551
B	6.890463	0.874571	0.596360
H	7.516783	1.832133	0.957179
B	6.585557	-0.520737	1.672273
H	6.988315	-0.580248	2.799604
B	6.462179	-1.968230	0.644482
H	6.670023	-3.099548	0.966991
B	7.637993	-0.699184	0.236536
H	8.817307	-0.895749	0.335237
C	-2.893535	-0.202069	0.103686
C	-1.206672	1.678269	-0.046052
C	0.010113	0.980354	-0.025596
C	1.208654	1.708752	-0.003053
C	1.193651	3.114382	0.008700
H	2.135439	3.668230	0.032690

C	-0.023145	3.792218	-0.019496
H	-0.036270	4.884488	-0.017343
C	-1.222369	3.085455	-0.050892
H	-2.176153	3.618572	-0.072807
C	2.926330	-0.129450	-0.220849
C	4.441999	-0.226922	-0.048811
C	5.146329	-1.648402	-0.369707
H	4.453613	-2.427648	-0.687370
H	0.019856	-0.102545	-0.027990

Sum of electronic and zero-point Energies = -1876.173868
Sum of electronic and thermal Free Energies = -1876.231069

NEt_3H

N	0.000920	-0.000241	-0.916755
C	1.424641	-0.401480	-0.577618
H	1.478187	-1.483593	-0.761514
H	2.046691	0.097680	-1.334018
C	1.921509	-0.047174	0.812280
H	1.324935	-0.498781	1.614882
H	1.968895	1.039750	0.970395
H	2.948659	-0.435098	0.899033
C	-0.363612	1.433013	-0.577973
H	0.547688	2.019376	-0.760898
H	-1.106399	1.722513	-1.334466
C	-0.920735	1.685329	0.811075
H	-0.232378	1.394122	1.614476
H	-1.886504	1.182912	0.966941
H	-1.098420	2.768777	0.897964
C	-1.059541	-1.031401	-0.578619
H	-2.022017	-0.534690	-0.762662
H	-0.939957	-1.819679	-1.334888
C	-1.002698	-1.638409	0.811219
H	-1.089863	-0.894101	1.613051
H	-0.088148	-2.227922	0.967832
H	-1.855992	-2.328989	0.900309
H	0.000802	0.000133	-1.941341

Sum of electronic and zero-point Energies = -292.493122
Sum of electronic and thermal Free Energies = -292.525398

NEt_3

N	-0.000754	0.000269	-0.789819
C	0.511369	-1.344230	-0.632257
H	-0.285622	-2.040695	-0.947593
H	1.345830	-1.493495	-1.346337
C	1.012145	-1.758907	0.761541
H	0.231924	-1.645454	1.530079
H	1.881108	-1.155360	1.069964
H	1.332137	-2.815588	0.752803
C	0.908391	1.115547	-0.632294
H	1.909298	0.773070	-0.949244
H	0.620349	1.914014	-1.345068
C	1.019633	1.754045	0.762346
H	1.312090	1.019656	1.528791
H	0.063335	2.205001	1.073177
H	1.775364	2.558930	0.754265
C	-1.421008	0.229635	-0.631329
H	-1.624939	1.268337	-0.946210
H	-1.968616	-0.417514	-1.345457

C	-2.030184	0.003778	0.762568
H	-1.540783	0.622223	1.530898
H	-1.943311	-1.050621	1.070910
H	-3.104961	0.256407	0.754312

Sum of electronic and zero-point Energies = -292.043595
Sum of electronic and thermal Free Energies = -292.077466

BIXFUJ

Ti	-0.212640	0.909961	-0.011806
Cl	-2.560305	1.392333	-0.198974
Cl	0.039792	0.717961	-2.321276
Cl	-0.230527	0.764264	2.306453
P	1.855682	-0.618622	0.013615
P	-1.182923	-1.481504	0.025409
C	1.436393	2.249453	0.089245
C	0.400107	3.351283	0.141934
C	1.398148	-2.357277	-0.439948
C	0.117913	-2.770908	0.287600
H	2.061446	2.179137	0.986331
H	2.043008	2.264685	-0.821702
H	0.487524	4.067562	-0.690050
H	0.383575	3.886867	1.102844
H	-0.661189	2.983011	0.035905
H	1.249018	-2.368078	-1.531936
H	2.237483	-3.034364	-0.212267
H	0.290652	-2.836260	1.374269
H	-0.247095	-3.754753	-0.048973
C	3.231476	-0.238341	-1.131724
H	3.942431	-1.078857	-1.163743
H	2.822272	-0.057717	-2.135760
H	3.759201	0.664202	-0.791108
C	2.687892	-0.801804	1.635614
H	1.972956	-1.185077	2.376239
H	3.545920	-1.487373	1.551052
H	3.039435	0.182673	1.977761
C	-2.435360	-1.815127	1.313145
H	-3.289033	-1.142117	1.149064
H	-2.769476	-2.863894	1.271037
H	-2.000961	-1.596841	2.298933
C	-2.004088	-1.962868	-1.537963
H	-1.270620	-1.948812	-2.356065
H	-2.452852	-2.965007	-1.450766
H	-2.784234	-1.220191	-1.759554

Sum of electronic and zero-point Energies = - 3229.521586
Sum of electronic and thermal Free Energies = - 3229.571213

$PhCr(CO)_3$

C	1.618282	0.442437	1.338851
C	1.632622	-0.941897	1.061040
C	1.631103	1.390671	0.285460
H	1.602248	-1.666819	1.875141
H	1.600034	2.457936	0.506745
C	1.619788	-1.380075	-0.286819
C	1.618473	0.939004	-1.052271
H	1.578673	-2.448337	-0.506999
H	1.576377	1.663530	-1.867695
C	1.632286	-0.447389	-1.346782
H	1.602719	-0.789775	-2.381701
H	1.575483	0.786126	2.373992

Cr	-0.117480	-0.000242	-0.000417
C	-1.177882	0.605869	1.362046
O	-1.833456	0.993690	2.236105
C	-1.178196	-1.483172	-0.156244
O	-1.833850	-2.434053	-0.256526
C	-1.178859	0.876342	-1.205817
O	-1.835408	1.439413	-1.977858

Sum of electronic and zero-point Energies = -1616.184076
Sum of electronic and thermal Free Energies = -1616.223470

$Cp^*Ir(C_2H_4)_2^+$

Ir	0.517506	-0.061658	-0.170937
C	-1.126512	1.366224	0.413360
C	-1.695527	0.656773	-0.720645
C	-1.736511	-0.724443	-0.415177
C	-1.158107	-0.900880	0.913427
C	-0.862864	0.412112	1.458831
C	2.066127	1.233161	0.356338
H	1.685407	2.168350	0.782553
H	2.883804	0.816585	0.952739
C	2.277164	1.249482	-1.125360
H	2.104846	2.222283	-1.606940
H	1.485701	0.593382	-1.700375
H	3.214254	0.782611	-1.459918
C	1.952528	-1.643577	0.265919
H	2.985014	-1.283045	0.245459
H	1.668154	-2.155380	1.190023
C	1.297726	-1.944951	-0.950002
H	1.821574	-1.799305	-1.900019
H	0.488343	-2.680023	-0.978220
C	-0.456643	0.713584	2.864626
H	-1.355403	0.833102	3.494923
H	0.147478	-0.098867	3.291676
H	0.123015	1.644949	2.925649
C	-1.022590	2.854261	0.519237
H	-0.644101	3.299120	-0.413286
H	-2.016845	3.292127	0.713808
H	-0.359072	3.155087	1.341263
C	-2.157434	1.305448	-1.982535
H	-1.514108	2.153955	-2.257636
H	-2.182154	0.594774	-2.820337
H	-3.178951	1.702016	-1.846128
C	-2.306967	-1.816889	-1.259021
H	-3.381694	-1.940099	-1.036671
H	-2.211319	-1.597928	-2.332244
H	-1.821189	-2.781906	-1.057071
C	-1.132102	-2.191182	1.666970
H	-2.145683	-2.421006	2.038163
H	-0.816493	-3.027516	1.026345
H	-0.458245	-2.140315	2.532552

Sum of electronic and zero-point Energies = -651.582713
Sum of electronic and thermal Free Energies = -651.627844

$PhAuCl_3$

C	3.467555	-0.257704	0.507900
C	3.225674	-0.212315	-0.881698
C	2.689367	0.474165	1.407891
H	3.857635	-0.790237	-1.559335
H	2.897496	0.432958	2.478760

C	2.190985	0.558203	-1.376084
C	1.652562	1.272828	0.925140
H	1.990398	0.613314	-2.448195
H	1.066941	1.901762	1.599440
C	1.366563	1.298397	-0.476540
H	0.752220	2.108138	-0.875912
H	4.286890	-0.874993	0.885735
Au	-0.523121	-0.017953	-0.043438
Cl	0.633042	-2.050407	0.014478
Cl	-2.533376	-1.195498	0.161849
Cl	-1.692679	2.023899	-0.016830

Sum of electronic and zero-point Energies = -1748.097808
Sum of electronic and thermal Free Energies = -1748.138561

ZIYJID

C	0.243511	-0.161690	2.058133
C	-0.255438	0.727906	3.031853
H	-0.841235	1.589698	2.721913
C	-0.028264	0.542181	4.394505
H	-0.438928	1.256995	5.111123
C	0.721102	-0.550343	4.833803
H	0.907571	-0.709092	5.898247
C	1.238982	-1.443415	3.898284
H	1.831285	-2.298793	4.228700
C	1.005542	-1.247885	2.535742
C	3.095281	-2.264654	1.667412
H	3.422504	-2.653934	2.638522
H	3.444751	-2.918399	0.858142
H	3.464425	-1.243003	1.519601
C	0.992726	-3.598013	1.750537
H	-0.093621	-3.499135	1.637072
H	1.401630	-4.228530	0.950844
H	1.241015	-4.014872	2.733967
C	-1.982052	0.500683	0.118451
C	-2.688917	-0.587636	0.963911
H	-2.335608	-1.585472	0.651762
H	-2.439181	-0.468250	2.028017
C	-4.214589	-0.484916	0.785806
H	-4.691169	-1.262881	1.404662
C	-2.375492	0.287292	-1.369784
H	-2.039994	-0.706321	-1.705563
H	-1.877492	1.031192	-2.007346
C	-4.008847	1.986503	0.382444
H	-4.335100	2.985885	0.714297
C	-4.381074	1.778988	-1.093021
H	-5.472745	1.864554	-1.225197
H	-3.913204	2.561115	-1.714863
C	-3.901539	0.390326	-1.541016
H	-4.139655	0.235864	-2.606147
C	-2.477725	1.900591	0.544544
H	-2.000079	2.672949	-0.075267
H	-2.221416	2.110825	1.590882
C	-4.581860	-0.694177	-0.691464
H	-5.676224	-0.645954	-0.819701
H	-4.256584	-1.694493	-1.024428
C	-4.682975	0.906384	1.244903
H	-4.430936	1.058373	2.308431
H	-5.779451	0.983639	1.155260
C	0.988733	1.655929	-0.140781
C	3.100861	2.660072	-1.956123

H	3.812650	3.434556	-2.287599
H	3.207575	1.802151	-2.641473
C	1.854087	3.969988	0.367917
H	1.745538	4.825754	1.054380
C	0.675690	2.107498	-1.585832
H	-0.351407	2.496485	-1.643230
H	0.741258	1.243435	-2.267997
C	3.425803	2.228605	-0.516381
H	4.450641	1.825006	-0.468902
C	0.875545	2.864362	0.813060
H	1.123694	2.558983	1.839577
H	-0.149290	3.258622	0.820190
C	1.664717	3.205391	-2.015348
H	1.423146	3.510352	-3.046667
C	3.293049	3.433743	0.428370
H	3.542566	3.135368	1.460965
H	4.004464	4.223879	0.135139
C	2.444731	1.124353	-0.084917
H	2.548419	0.252836	-0.751332
H	2.681678	0.789421	0.938234
C	1.525754	4.408959	-1.068466
H	2.208131	5.217204	-1.380813
H	0.499293	4.810927	-1.116717
Au	0.416922	-1.503947	-1.189834
Cl	0.980206	-3.192049	-2.722798
N	1.601567	-2.237251	1.619680
P	-0.119241	0.198736	0.276150
H	1.354368	-1.932752	0.648459

Sum of electronic and zero-point Energies = -2082.353943
Sum of electronic and thermal Free Energies = -2082.412967

S6. References

1. C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.*, 1992, **29**, 228-234.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Montgomery, J. A. Montgomery, Jr. J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT, 2019.
3. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis and F. Weinhold, NBO 7.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2018.
4. E. Matito, ESI-3D: Electron Sharing Indices Program for 3D Molecular Space Partitioning;

Institute of Computational chemistry and Catalysis (IQCC), University of Girona, Catalonia, Spain, 2006; http://iqc.udg.es/ eduard/ESI, 2014.

5. E. Matito, M. Solà, P. Salvador and M. Duran*, Faraday Discuss*., 2007, **135**, 325-345.
6. (a) L. Rocchigiani, J. Fernadez-Cestau, P. H. M. Budzelaar and M. Bochmann, *Chem. Commun.* 2017, 53, 4358–4361; (b) M. S. Kharasch and H. S. Isbell, *J. Am. Chem. Soc*., 1931, **53**, 3053–3059; (c) Y. Fuchita, Y. Utsunomiys and M. Yasutake, *J. Chem. Soc., Dalton Trans*., 2001, 2330–2334.
7. AIMAll (Version 19.10.12), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2019 (aim.tkgristmill.com)