Tetra-coordinate boron appended Zinc(II)-salen: A highly selective fluorescence based sensor for Sm^{3+} ion via sensitization

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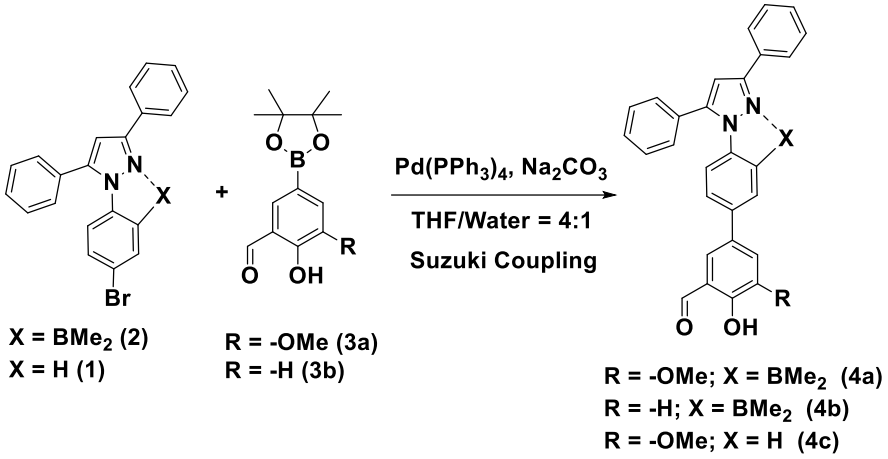
Supplementary Information

Experimental Section:

General Information:

All reagents were used as received from Spectrochem, Alfa-aesar and Sigma-Aldrich unless otherwise noted. Dichloromethane and toluene were dried using calcium hydride and Na/benzophenone respectively. The substrates and complexes were characterized by multinuclear NMR data. All ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR were recorded at room temperature on Bruker ARX 400 MHz spectrometer. Residual protonated solvents were used as internal standards for ^{1}H and ^{13}C NMR. ^{11}B NMR spectra were referenced externally to $BF_3{\cdot}Et_2O$ in $CDCl_3$ (δ = 0 ppm). ESI mass spectra were recorded with Bruker micro TOF-QII mass spectrometer. MALDI was recorded on Bruker UltrafleXtreme MALDI TOF/TOF analyzer equipped with a nitrogen UV laser. Matrix and target mixed solution (v/v: 1/1) was dropped onto the MALDI plate and analyzed in positive ion reflection mode with the mass range of m/z 400–2500 Da. Each point was collected using 1000 laser shots and results were analyzed by Bruker flexAnalysis software. Elemental analyses of the compounds were performed using a Euro Vector EA instrument (EuroEA3000). Rigaku Oxford X-ray diffractometer having Cu-Kα radiation (1.54184 Å) and Mo-Kα radiation (0.71073 Å) was used for collecting single crystal X-ray diffraction data. SADABS absorption corrections were applied. Olex were used for structure solving and refinement. Anisotropic refinements were used for non-hydrogen atoms. The H atoms were placed at calculated positions and were refined as riding atoms (CCDC no. 2152949-

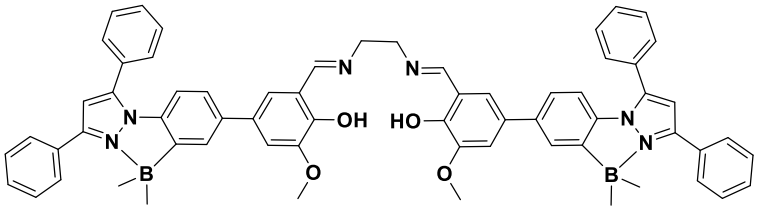
2152950). UV-Visible spectra were recorded on JASCO V-730 UV/Visible spectrometer. The fluorescence spectra were recorded with a Edinburgh Instruments FS5 Spectrofluorometer. DFT calculations were performed with the Gaussian 16 program.[1] The structures were optimized using B3LYP with LANL2DZ basis set for Zn and 6-31G basis set for other atoms. Frequency calculations confirmed the optimized structures to be local minimum structures. Excitation data were determined using TD-DFT (CAM-B3LYP/631g)–calculations. Compound **6d**, synthesized following the literature reported method.[2]



Scheme S1: Synthesis of compounds **4a**-**4c**

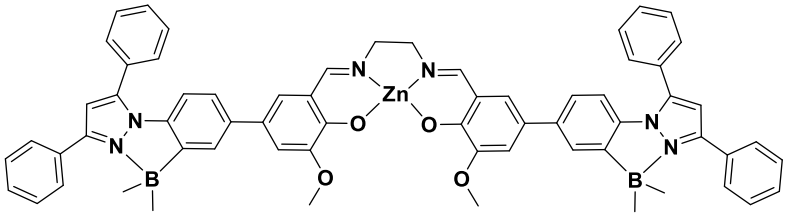
Synthesis of compound 4a: To an oven dried two neck 250ml RB, compound **2a** (2.41 mmol, 1.00 g, 1.0 equiv.), compound **3a**, (2.65 mmol, 0.737 g, 1.1 equiv.), Na_2CO_3 (7.23 mmol, 0.765 g, 3.0 equiv.) and $Pd(PPh_3)_4$ (0.072 mmol, 0.083 g, 3 mol%) were loaded under nitrogen atmosphere. To this mixture, degassed THF (40 mL) and water (10 mL) in 4:1 ratio was added and the reaction mixture was refluxed for 24 h. The progress of the reaction was monitored through TLC. After completion of the reaction, the whole mixture is cooled to room temperature. Dichloromethane (50 mL) and water (50 mL) were added to the reaction mixture; organic layer was separated and the aqueous layer was extracted using CH_2Cl_2 (3x20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (1:20 of EtOAc : *n*-hexane) on silica gel to afford the corresponding coupled product **4a.** Yield: 61% (0.715 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.00 (s, 1H), 9.97 (s, 1H), 7.87 – 7.77 (m, 2H), 7.70 – 7.65 (m, 2H), 7.64 – 7.56 (m, 4H), 7.55 – 7.46 (m, 3H), 7.38 (s, 1H), 7.34

(s, 1H), 7.12 (d, *J* = 8.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.61 (s, 1H), 3.98 (s, 3H), 0.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 150.9, 148.8, 148.6, 140.2, 138.0, 138.0, 133.8, 130.5, 129.8, 129.7, 129.6, 129.2, 129.1, 128.7, 128.5, 127.9, 123.7, 122.9, 120.9, 117.3, 112.2, 110.9, 56.6, 9.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ -1.95. HRMS (ESI+, m/z) calcd for $C_{31}H_{27}BN_2O_3Na$, $[M+Na]^+$ m/z = 509.2012, found 509.1989.



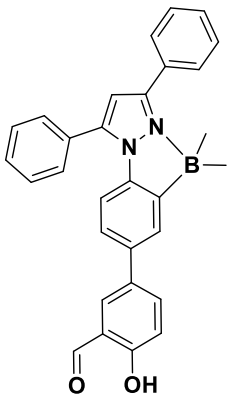
Synthesis of compound 5a: To 100 mL one neck RB, compound **4a** (1.0 mmol, 0.50 g, 2.0 equiv.) and ethylene diamine (0.51 mmol, 34 μL, 1.0 equiv.) were added to dry methanol and refluxed overnight. The reaction mixture was filtered and the resultant yellow precipitate of compound **5a** was collected. Yield: 92% (0.467 g) ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.61 (s, 2H), 8.65 (s, 2H), 7.93 – 7.86 (m, 4H), 7.82 – 7.73 (m, 4H), 7.71 – 7.65 (m, 6H), 7.62 – 7.53 (m, 8H), 7.29 (d, *J* = 2.2 Hz, 2H), 7.26 (d, *J* = 2.1 Hz, 2H), 7.24 (d, *J* = 1.86 Hz, 2H), 7.20 (d, *J* = 2.1 Hz, 2H), 7.13 (s, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 4H), 3.81 (s, 6H), 0.08 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 9.7, 55.7, 58.1, 111.3, 111.5, 113.1, 118.1, 121.0, 123.4, 126.7, 128.0, 128.6, 128.6, 128.9, 129.2, 129.7, 129.9, 130.6, 136.8, 137.9, 140.1, 148.0, 148.4, 151.6, 167.4. ^{11}B NMR (128 MHz, DMSO-d_6) δ 0.45. HRMS (ESI+, m/z) calcd for $C_{64}H_{59}B_2N_6O_4$, $[M+H]^+$ m/z = 997.4736, found 997.4716.

Synthesis of complex 6a: To 100 mL one neck RB, compound **5a** (0.200 g, 0.2 mmol, 1.0 equiv.) was dissolved in 10 mL of CH_2Cl_2 and a solution of $Zn(OAc)_2.2H_2O$ (0.049 g, 0.22 mmol, 1.1 equiv.) in 10 mL dry methanol was added dropwise. The greenish-yellow solution was refluxed for 12 h. Light green color crystals of complex **6a** with a coordinated solvent molecule were collected after 1 week. Yield: 73% (155 mg) ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.56 (s, 2H), 7.93 – 7.88 (m, 4H), 7.82 – 7.75 (m, 4H), 7.71 – 7.66 (m, 6H), 7.62 – 7.53 (m, 8H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.11 (m, 4H), 7.06 (s, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 3.80 (s, 6H), 3.75 (s, 4H), 1.80 (s, 6H), 0.09 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.7, 168.5, 155.5, 152.7, 147.8, 139.9, 138.9, 136.0, 130.5, 129.7, 129.2, 129.0, 128.6, 128.1, 125.9, 123.9, 123.3,

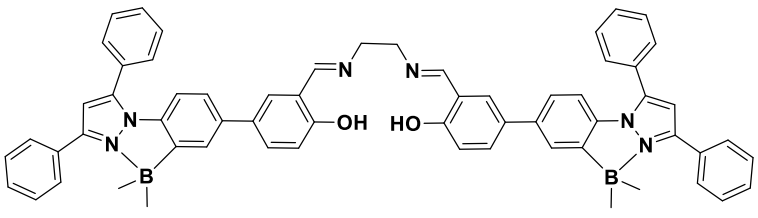


122.5, 118.4, 111.5, 111.1, 55.9, 55.2, 22.4, 9.8. ^{11}B NMR (128 MHz, DMSO-d_6) δ -3.12. MALDI-MS calcd for $C_{64}H_{59}B_2N_6O_5Zn$, $[M+H_2O+H]^+$ m/z = 1079.2, found 1079.2. Anal. Calcd for $C_{64}H_{58}B_2N_6O_5Zn$: C, 71.29; H, 5.42; N, 7.79. Found: C, 71.00; H, 5.05; N, 8.21.

Synthesis of compound 4b: To an oven dried two neck 250ml RB, compound **2a** (2.41 mmol, 1.00 g, 1.0 equiv.), compound **3b**, (2.65 mmol, 0.659 g, 1.1 equiv.), Na_2CO_3 (7.23 mmol, 0.766 g, 3.0 equiv.) and $Pd(PPh_3)_4$ (0.072 mmol, 0.083 g, 3 mol%) were loaded under nitrogen atmosphere. To this mixture, degassed THF (40 mL) and water (10 mL) in 4:1 ratio was added and the reaction mixture was refluxed for 24 h. The progress of the reaction was monitored through TLC. After completion of the reaction, the whole mixture is cooled to room temperature. Dichloromethane (50 mL) and water (50 mL) were added to the reaction mixture; organic layer was separated and the aqueous layer was extracted using CH_2Cl_2 (3x20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (1:20 of EtOAc : *n*-hexane) on silica gel to afford the corresponding coupled product **4b.** Yield: 58% (0.637 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 9.96 (s, 1H), 7.85 – 7.80 (m, 2H), 7.79 – 7.75 (m, 2H), 7.70 -7.64 (m, 2H), 7.65 – 7.58 (m, 4H), 7.54 -7.48 (m, 3H), 7.12 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.08 – 7.02 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.61 (s, 1H), 0.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 160.9, 148.8, 140.1, 137.9, 137.6, 135.9, 133.8, 131.9, 130.5, 129.8, 129.7, 129.6, 129.2, 129.1, 128.7, 128.5, 127.8, 123.5, 120.8, 118.1, 112.2, 110.9, 9.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ 0.54. HRMS (ESI+, m/z) calcd for $C_{30}H_{26}BN_2O_2$, $[M+H]^+$ m/z = 457.2045, found 457.2073

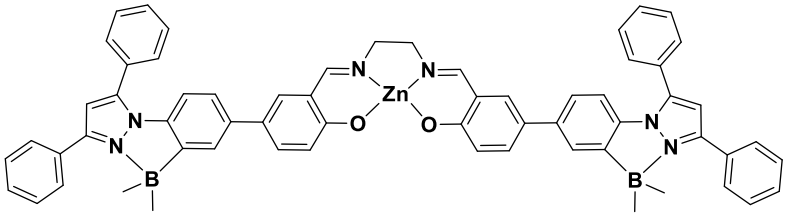


Synthesis of compound 5b: To 100 mL one neck RB, compound **4b** (1.0 mmol, 0.50 g, 2.0 equiv.) and ethylene diamine (0.51 mmol, 34 μL, 1.0 equiv.) were added to dry methanol and refluxed overnight. The reaction mixture was filtered and the resultant yellow precipitate of compound **5b** was collected. Yield: 88% (0.421 g) ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.45 (s, 2H), 8.69 (s, 2H), 7.89 (d, *J* = 7.2 Hz, 4H), 7.81 – 7.72 (m, 6H),



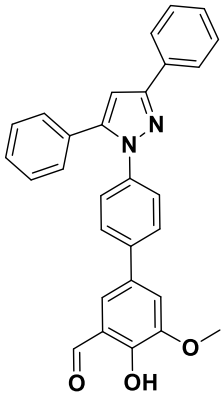
7.71 – 7.63 (m, 7H), 7.62 – 7.47 (m, 11H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.14 (s, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 4H), 0.08 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.2, 160.2, 148.0, 140.2, 137.6, 136.9, 130.7, 129.7, 129.2, 128.9, 128.6, 128.6, 128.0, 126.7, 123.2, 118.7, 117.1, 111.7, 111.4, 58.8, 9.8. ^{11}B NMR (128 MHz, DMSO-d_6) δ 0.84. HRMS (ESI+, m/z) calcd for $C_{62}H_{55}B_2N_6O_2$, $[M+H]^+$ m/z = 937.4586, found 937.4457

Synthesis of complex 6b: To 100 mL one neck RB, compound **5b** (0.187 g, 0.20 mmol, 1.0 equiv.)



was dissolved in 10 mL of CH_2Cl_2 and a solution of $Zn(OAc)_2.2H_2O$ (0.049 g, 0.22 mmol, 1.1 equiv.) in 10 mL dry methanol was added dropwise. The greenish-yellow solution was refluxed for 12 h. Light green color precipitate of complex **6b** was collected after the reaction. Yield: 78% (156 mg) ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.56 (s, 2H), 7.91 – 7.86 (m, 4H), 7.79 – 7.75 (m, 4H), 7.70 – 7.64 (m, 6H), 7.61 – 7.49 (m, 10H), 7.46 (d, *J* = 8 Hz, 2H), 7.19 (dd, *J* = 8.0, 1.8 Hz, 2 Hz), 7.10 (s, 2H), 6.70 (d, 8.0 Hz, 2 Hz), 6.68 (d, 8.0 Hz, 2 Hz), 3.71 (s, 4H), 0.08 (s, 12 H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.1, 168.7, 156.3, 148.3, 140.2, 139.0, 136.6, 133.0, 131.7, 130.9, 130.0, 129.6, 129.5, 129.1, 128.9, 128.6, 126.4, 125.0, 123.9, 122.6, 119.7, 112.1, 111.5, 56.4, 10.2. ^{11}B NMR (128 MHz, DMSO-d_6) δ -2.86. MALDI-MS calcd for $C_{64}H_{59}B_2N_6O_3SZn$, $[M+(CH_3)_2SO+H]^+$ m/z = 1079.2, found 1079.2. Anal. Calcd for $C_{62}H_{52}B_2N_6O_2Zn$: C, 74.46; H, 5.24; N, 8.40. Found: C, 74.76; H, 4.77; N, 8.68.

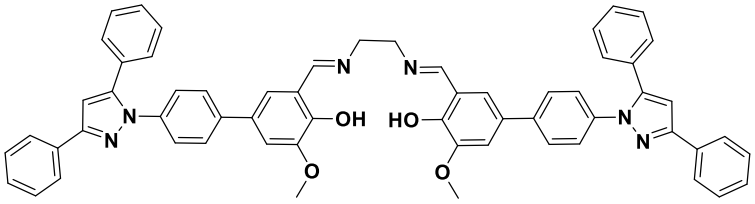
Synthesis of compound 4c: To an oven dried two neck 250 mL RB, compound **2b** (2.66 mmol,



1.00 g, 1.0 equiv.), compound **3a**, (2.93 mmol, 0.815 g, 1.1 equiv.), Na_2CO_3 (7.98 mmol, 0.845 g, 3.0 equiv.) and $Pd(PPh_3)_4$ (0.0798 mmol, 0.092 g, 3.00 mol%) were loaded under nitrogen atmosphere. To this mixture, degassed THF (40 mL) and water (10 mL) in 3:1 ratio was added and the reaction mixture was refluxed for 24 h. The progress of the reaction was monitored through TLC. After completion of the reaction, the whole mixture is cooled to room temperature. Dichloromethane (50 mL) and water (50 mL) were added to the reaction mixture; organic layer was separated and the aqueous layer was extracted using CH_2Cl_2 (3x20 mL). The combined organic layer was washed with brine, dried over

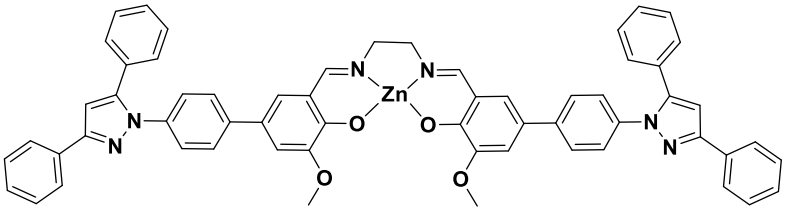
Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (1:20 of EtOAc: *n*-hexane) on silica gel to afford the corresponding coupled product **4c.** Yield: 69% (0.819 g) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 9.99 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.43 (m, 4H), 7.41 – 7.30 (m, 8H), 6.86 (s, 1H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 152.2, 151.4, 148.8, 144.6, 139.4, 138.7, 132.8, 132.2, 130.6, 128.9, 128.8, 128.8, 128.7, 128.6, 128.3, 127.2, 125.9, 125.7, 122.7, 120.9, 116.8, 105.7, 56.6. HRMS (ESI+, m/z) calcd for $C_{29}H_{23}N_2O_3$, $[M+H]^+$ m/z = 447.1703, found 447.1729.

Synthesis of compound 5c: To 100 mL one neck RB, compound **4c** (1.11 mmol, 0.50 g, 2.0



equiv.) and ethylene diamine (0.56 mmol, 37 μL, 1.0 equiv.) were added to dry methanol and refluxed overnight. The reaction mixture was filtered and the resultant orange precipitate of compound **5c** was collected. Yield: 88% (0.447 g) ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.75 (s, 2H), 8.65 (s, 2H), 7.94 (d, *J* = 8 Hz, 4H), 7.72 (d, *J* = 8.0 Hz, 4H), 7.47 (t, *J* = 8.0 Hz, 4H), 7.42 – 7.28 (m, 20H), 7.18 (s, 2H), 3.98 (s, 4H), 3.85 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.9, 152.1, 151.2, 148.5, 144.3, 138.7, 138.3, 128.4, 128.4, 127.8, 126.4, 125.3, 125.1, 121.2, 112.6, 105.2, 58.7, 55.7. HRMS (ESI+, m/z) calcd for $C_{60}H_{49}N_6O_4$, $[M+H]^+$ m/z = 917.3815, found 917.3878.

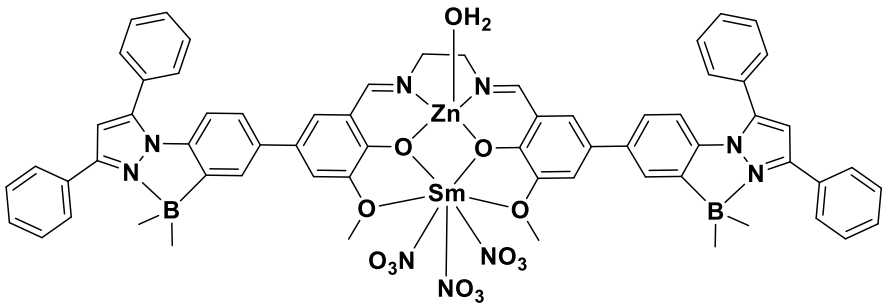
Synthesis of complex 6c: To 100 mL one neck RB, compound **5c** (0.200 g, 0.22 mmol, 1.0 equiv.)



was dissolved in 10 mL of CH_2Cl_2 and a solution of $Zn(OAc)_2.2H_2O$ (0.053 g, 0.24 mmol, 1.1 equiv.) in 10 mL methanol was added dropwise. The greenish-yellow solution was refluxed for 12 h. Light green powder was collected and washed with methanol multiple times before drying the remaining solvent completely. Yield: 71% (153 mg) ^{1}H NMR (400 MHz, DMSO) δ 8.65 (s, 2H), 7.94 (d, J = 8.0 Hz, 4H), 7.70 (d, *J* = 8.2 Hz, 4H), 7.47 (t, *J* = 8.0 Hz, 5H), 7.43 – 7.32 (m, 14H), 7.24 (s, 2H), 7.18 (s, 4H), 3.84 (s, 6H), 3.77 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 168.3, 162.1, 152.9, 150.9, 144.1, 139.8, 137.4, 132.7, 130.1, 128.8, 128.7, 128.6, 128.1, 125.6, 125.5, 125.4, 121.6, 118.4, 111.1, 105.3, 56.1,

55.3. MALDI-MS Calcd for $C_{60}H_{49}N_6O_5Zn$, $[M+H_3O]^+$ m/z = 999.4, found 999.4. Anal. Calcd for $C_{60}H_{46}N_6O_4Zn$: C, 73.50; H, 4.73; N, 8.57. Found: C, 73.34; H, 4.93; N, 8.39

Synthesis of Complex **6a.Sm^{3+}:**



To 50 mL one neck RB, complex **6a** (0.05 g, 0.046 mmol, 1.0 equiv.) was dissolved in 5 mL of $CHCl_3$ and a solution of $Sm(NO_3)_3.6H_2O$ (0.031 g, 0.069 mmol, 1.5 equiv.) in 5 mL dry ethanol was added dropwise. The green solution was stirred for 6 h at room temperature. The solution was kept undisturbed for few days. Light green crystals of **6a.Sm^{3+}** were collected after one week. Yield: 53% (0.034 g). Anal. Calcd for $C_{64}H_{58}B_2N_9O_{14}SmZn$: C, 54.34; H, 4.13; N, 8.91. Found: C, 54.06; H, 4.18; N, 8.91

Measurement of Binding Constant

Benesi Hildebrand (B-H) plot [3] was used to estimate the binding constant of both **5a** with Zn^{2+}. The binding constant was calculated using the Eq. (i) from the fluorescence titration data for **5a** with Zn^{2+} complex.

$$1/\Delta I = 1/\Delta I_{max} + 1/(K\Delta I_{max})(1/[Zn^{2+}]) \quad \text{.....(i)}$$

Here $\Delta I = I - I_{min}$ and $\Delta I_{max} = I_{max} - I_{min}$, where I_{min}, I, and I_{max} are the emission intensities of receptor considered in the absence of Zn^{2+} , at an intermediate Zn^{2+} concentration, and at a concentration of complete saturation where K is the binding constant and $[Zn^{2+}]$ is the Zn^{2+} concentration respectively. From the plot of $[1 / (I - I_{min})]$ against $1/[Zn^{2+}]$ for **5a**, the value of K has been determined from the slope (Fig S3). The binding constant (K) was found to be 1.9×10^4 M^{-1} for **5a**-Zn^{2+}.

A calibration curve representing emission intensity vs concentration of zinc ions showed an excellent linearity with high coefficient ($R^2 = 0.98$) in the range from 0 to 24 μM (Fig 2). The

detection limit of **5a** for Zn^{2+} is 72 nM which was calculated using the calibration curve. These results showed the valuable applicability of sensor **5a** in quantitative determination of Zn^{2+} with high sensitivity.

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3. H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.* 1949, **71**, 2703–2707.

Table S1: Crystal data and structure refinement for complex **6a** and compounds **6a.Sm^{3+}**

Identification code	Complex **6a**	Complex **6a.Sm^{3+}**
Empirical formula	$C_{70}H_{72}B_2N_8O_7Zn$	$C_{64}H_{70}B_2N_9O_{20}SmZn$
Formula weight	1224.34	1522.63
Temperature/K	100.0	100.00(10)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	11.8935(3)	24.2907(6)
b/Å	13.7058(3)	12.6115(4)
c/Å	23.2005(5)	22.4062(7)
α/°	79.5340(10)	90
β/°	76.7020(10)	92.615(2)
γ/°	77.6310(10)	90
Volume/Å^3	3560.05(14)	6856.8(3)
Z	2	4
ρ_{calc}g/cm^3	1.142	1.475
μ/mm^{-1}	0.912	1.276
F(000)	1288.0	3116.0
Crystal size/mm^3	0.28 × 0.25 × 0.23	0.19 × 0.17 × 0.15
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.668 to 136.61	6.626 to 49.998
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -27 ≤ l ≤ 27	-28 ≤ h ≤ 26, -13 ≤ k ≤ 14, -26 ≤ l ≤ 26
Reflections collected	118979	41152
Independent reflections	13012 [R_{int} = 0.0674, R_{sigma} = 0.0335]	11843 [R_{int} = 0.0513, R_{sigma} = 0.0480]
Data/restraints/parameters	13012/0/824	11843/0/899
Goodness-of-fit on F^2	1.046	1.073

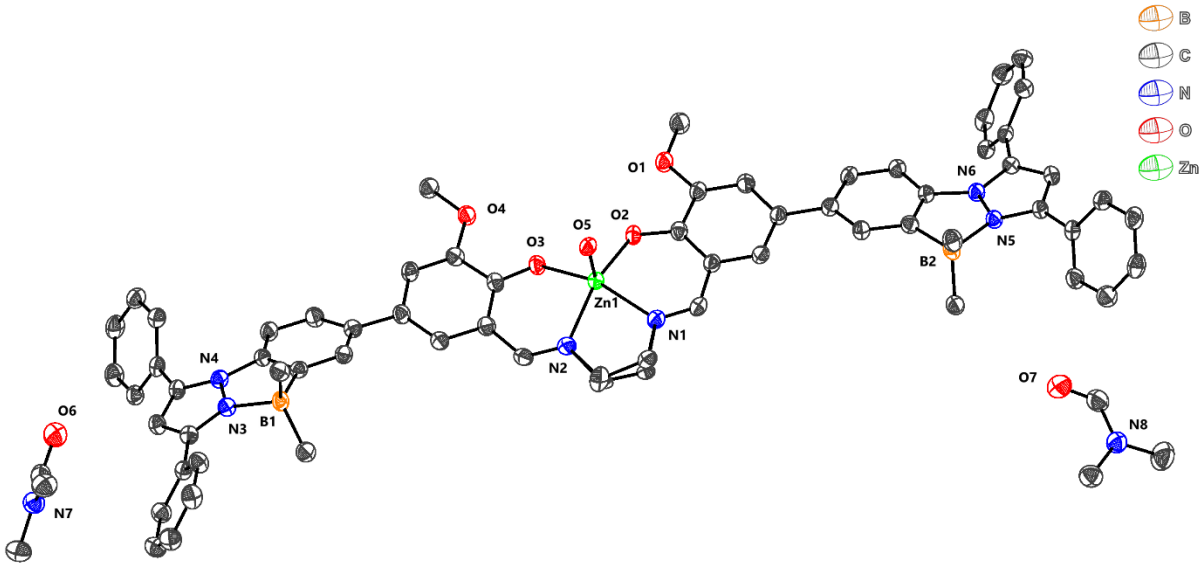


Figure S1: Crystal Structure of complex **6a**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and water molecules are removed for clarity.

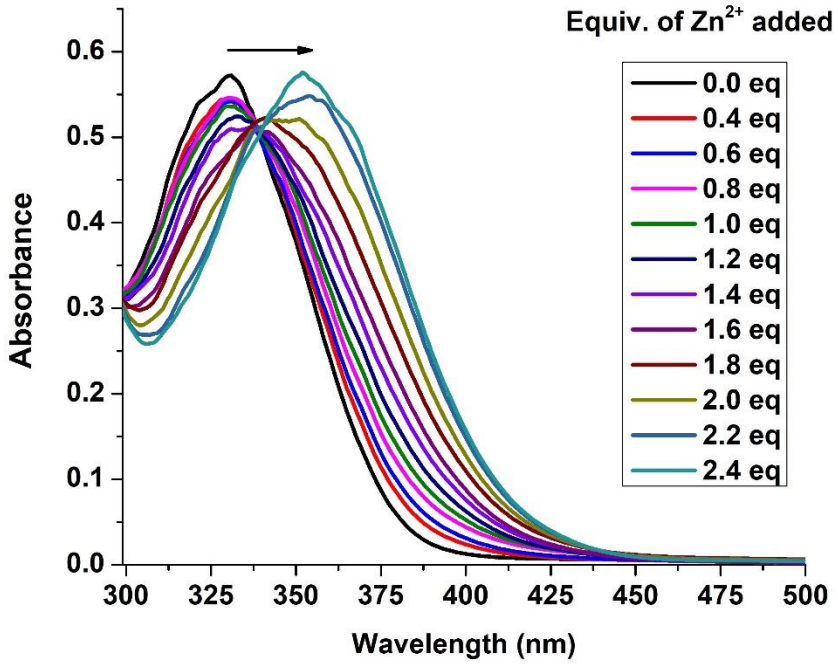


Figure S2: Absorbance spectra of **5a** (10 μM) with addition of 2.2 equiv. of NaOAc and subsequently upon addition of 0 – 2.4 equiv of Zn^{2+} in (10:90) Methanol/THF.

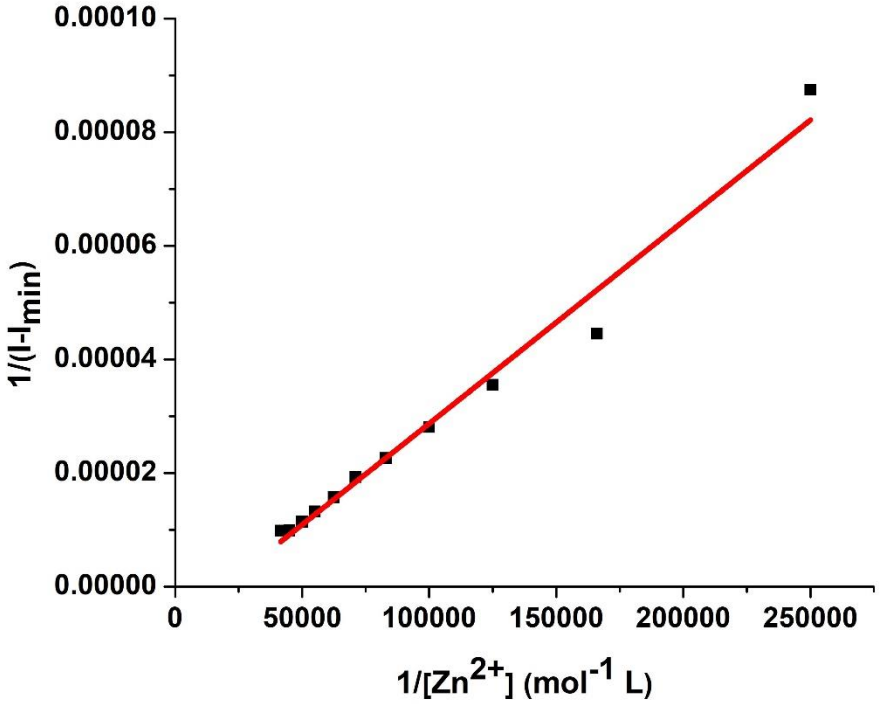


Figure S3: B-H plot assuming 1:1 stoichiometry for complexation between **5a** and Zn^{2+}

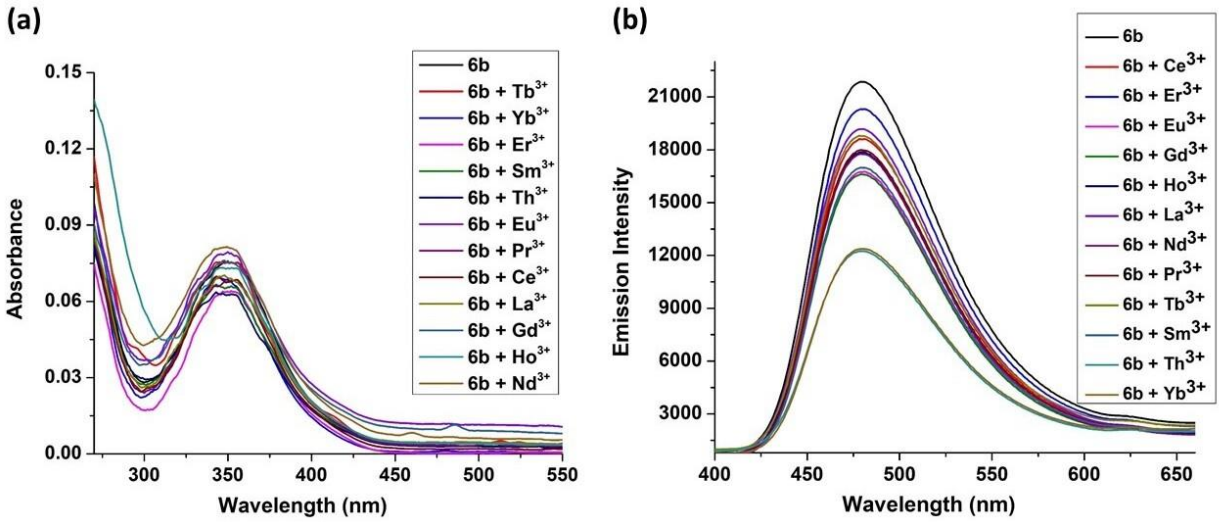


Figure S4: (a) Absorbance and (b) Fluorescence Spectra of **6b** (1×10^{-5} M) upon the addition of different lanthanide ions (1.2 equiv) excitation wavelength, 350 nm in (10:90) Methanol/THF.

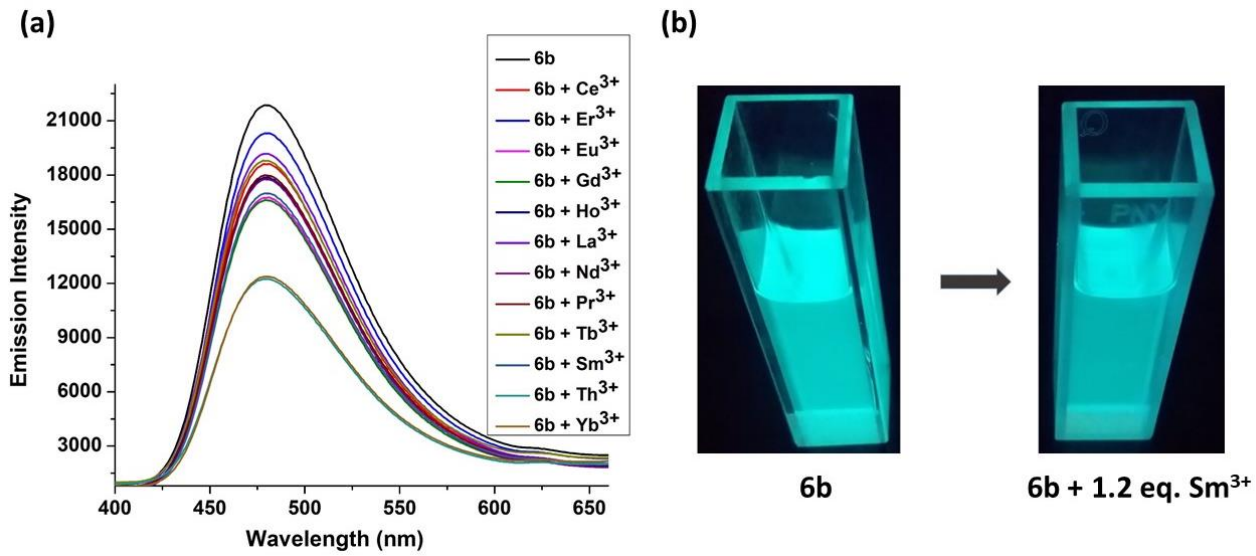


Figure S5: (a) Fluorescence spectra of **6b** (1 x 10^{-5} M) upon the addition of different lanthanide ions (1 equiv) excitation wavelength, 350 nm in 10% Methanol/THF; (b) Color change under a UV lamp of **6b** and **6b** + 1.2 eq Sm^{3+} at 10^{-5} M concentration in (10:90) Methanol/THF.

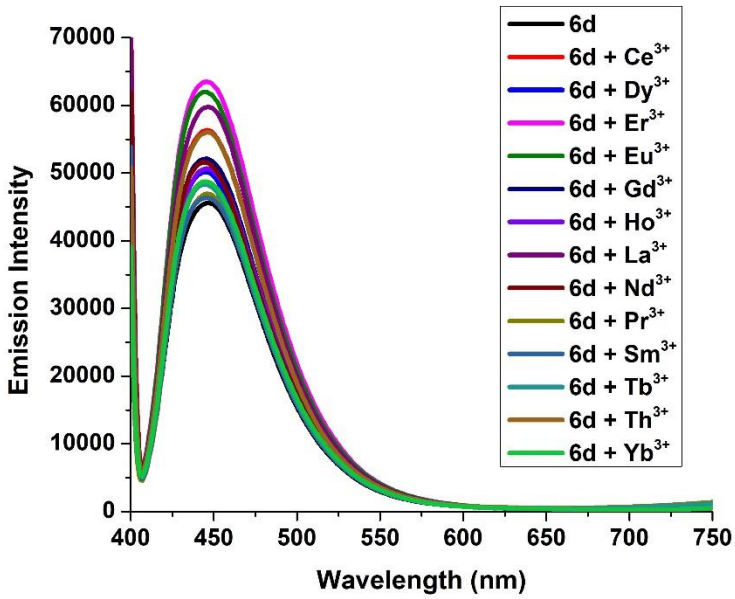


Figure S6: Fluorescence Spectra of **6d** (1 x 10^{-5} M) upon the addition of different lanthanide ions (1.2 equiv) excitation wavelength, 390 nm in degassed in (10:90) Methanol/THF.

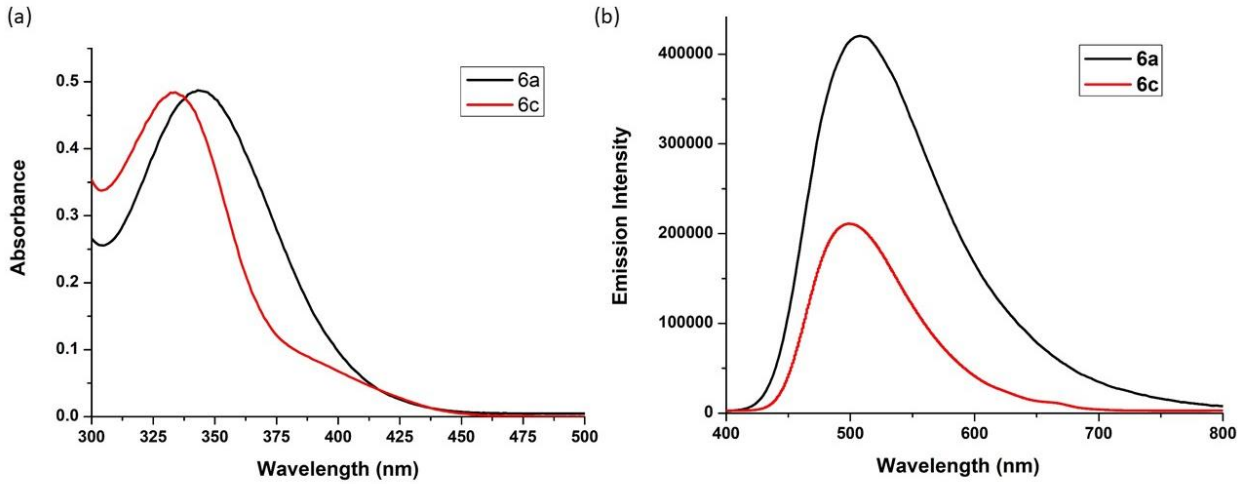


Figure S7: (a) Absorbance and (b) emission spectra of complexes **6a** and **6c** at 1 x 10^{-5} M concentration in THF

Table S2: Photophysical data of complexes **6a** and **6c**

	Complex	**λ_{max} (nm)**	**λ_{ems} (nm)**	**ε (mol^{-1} L cm^{-1})**	**ΔE (cm^{-1}) Stokes Shift**	**ϕ^{a}**
THF	**6a**	344	527	48670	10094	3.68
	6c	334	500	48346	9940	3.19

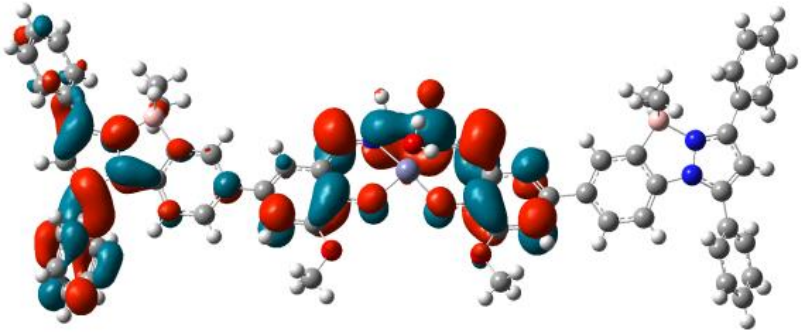
[a] relative quantum yield

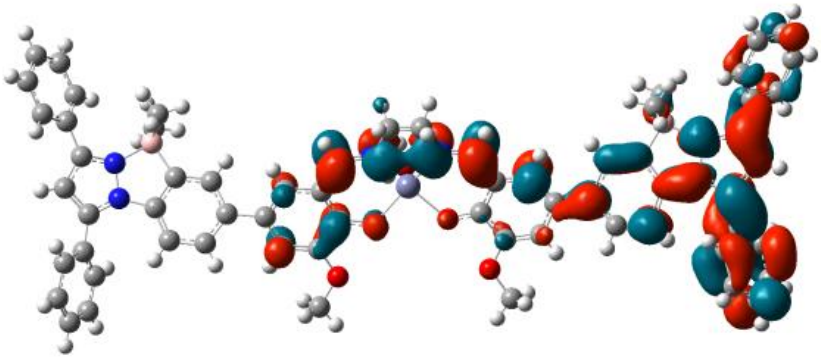
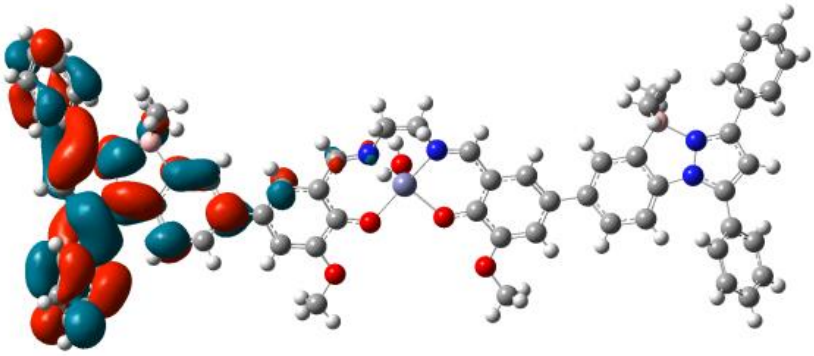
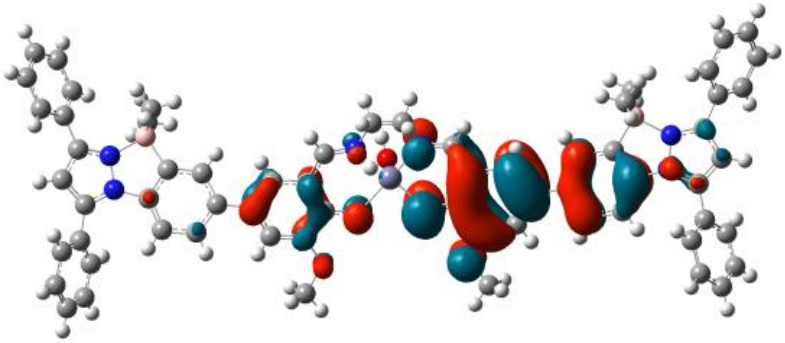
Table S3: Calculated electronic transitions for compound **6a** from TD-DFT (CAM-B3LYP) calculations

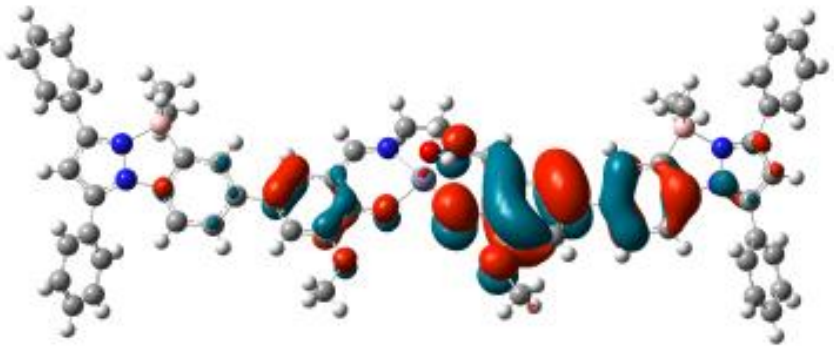
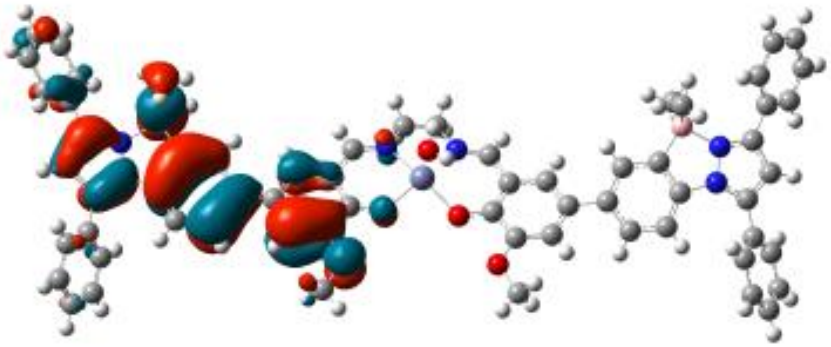
Compound	Transition	MO contributions	Energy gap eV (nm)	Oscillator strength/f
6a	$S_0 \rightarrow S_1$	HOMO-1→LUMO+2(17%) HOMO-1→LUMO+3(26%) HOMO→LUMO+1(37%) HOMO→LUMO+2(40%) HOMO→LUMO+3(25%)	3.19 (388)	0.0647
	$S_0 \rightarrow S_2$	HOMO-1→LUMO(11%) HOMO-1→LUMO+1(31%) HOMO-1→LUMO+2(43%) HOMO-1→LUMO+3(19%) HOMO→LUMO+1(12%) HOMO→LUMO+3(36%)	3.42 (362)	0.1431
	$S_0 \rightarrow S_3$	HOMO-3→LUMO (16%) HOMO-2→LUMO+1(16%) HOMO-1→LUMO(29%) HOMO-1→LUMO+1(14%) HOMO-1→LUMO+11(11%) HOMO→LUMO(14%) HOMO→LUMO+1(35%) HOMO→LUMO+2(32%) HOMO→LUMO+10(15%)	3.75 (330)	1.7614
	$S_0 \rightarrow T_1$	$HOMO_\alpha \rightarrow LUMO_\alpha$(66%)	1.18 (1053)	0.0148

		$HOMO_{\alpha} \rightarrow LUMO+3_{\alpha}(11\%)$ $HOMO_{\alpha} \rightarrow LUMO+5_{\alpha}(14\%)$ $HOMO_{\alpha} \rightarrow LUMO+7_{\alpha}(57\%)$ $HOMO_{\alpha} \rightarrow LUMO+10_{\alpha}(27\%)$ $HOMO_{\alpha} \rightarrow LUMO+12_{\alpha}(20\%)$ $HOMO\text{-}1_{\beta} \rightarrow LUMO_{\beta}(70\%)$		

Table S4: Computed orbitals from DFT (CAM-B3LYP:6-31G) calculations for complexes **6a** (color red indicates negative and blue indicates positive)

Compound	**6a**
LUMO+2	 0.075 eV

LUMO+1	 0.0029 eV
LUMO	 -0.1499 eV
HOMO	 -4.250 eV

HOMO-1	 -5.680 eV
HOMO-2	 -6.780 eV

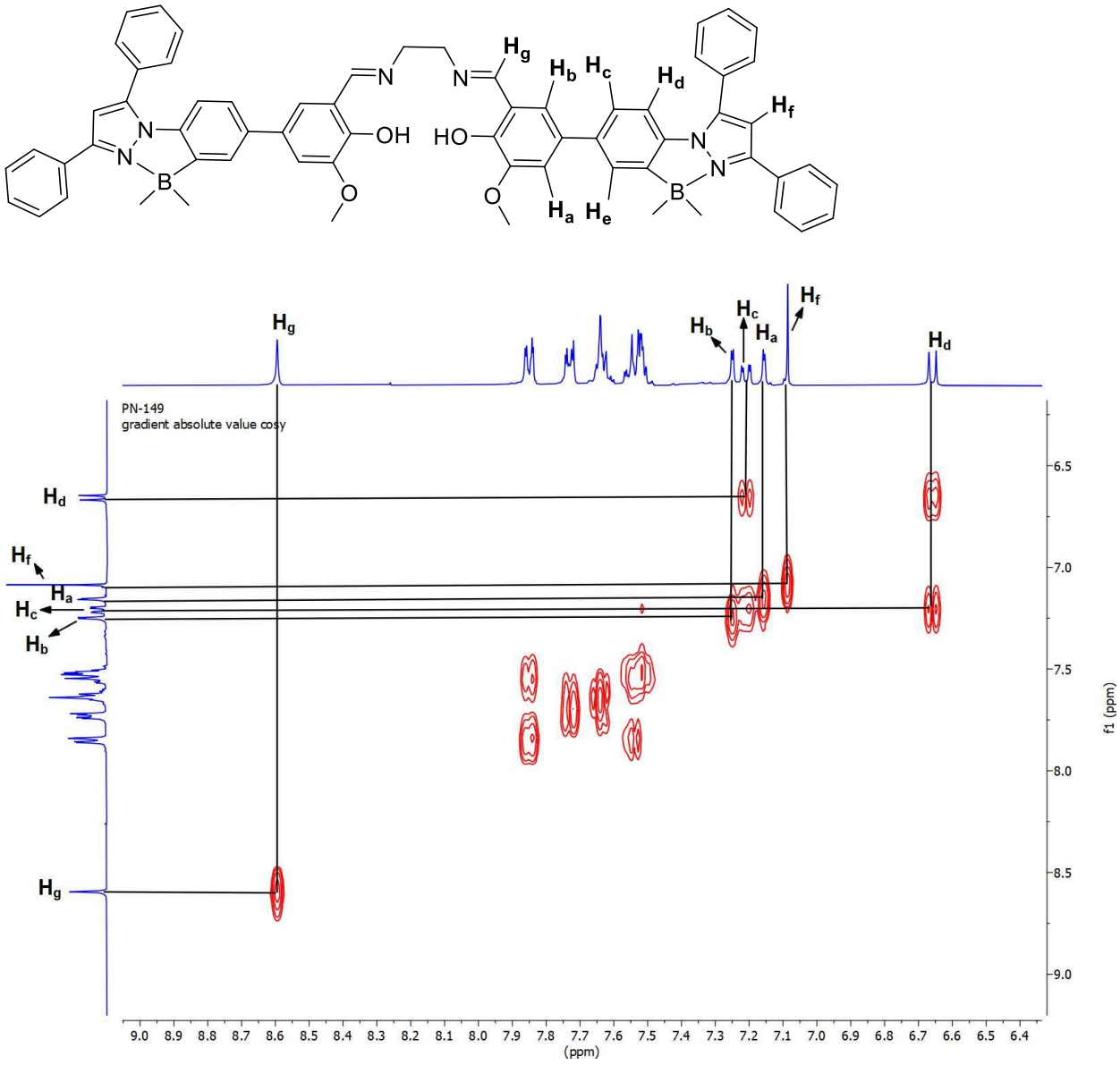


Figure S8: ^{1}H-^{1}H COSY NMR of compound **5a** in DMSO-*d*$_{6}$.

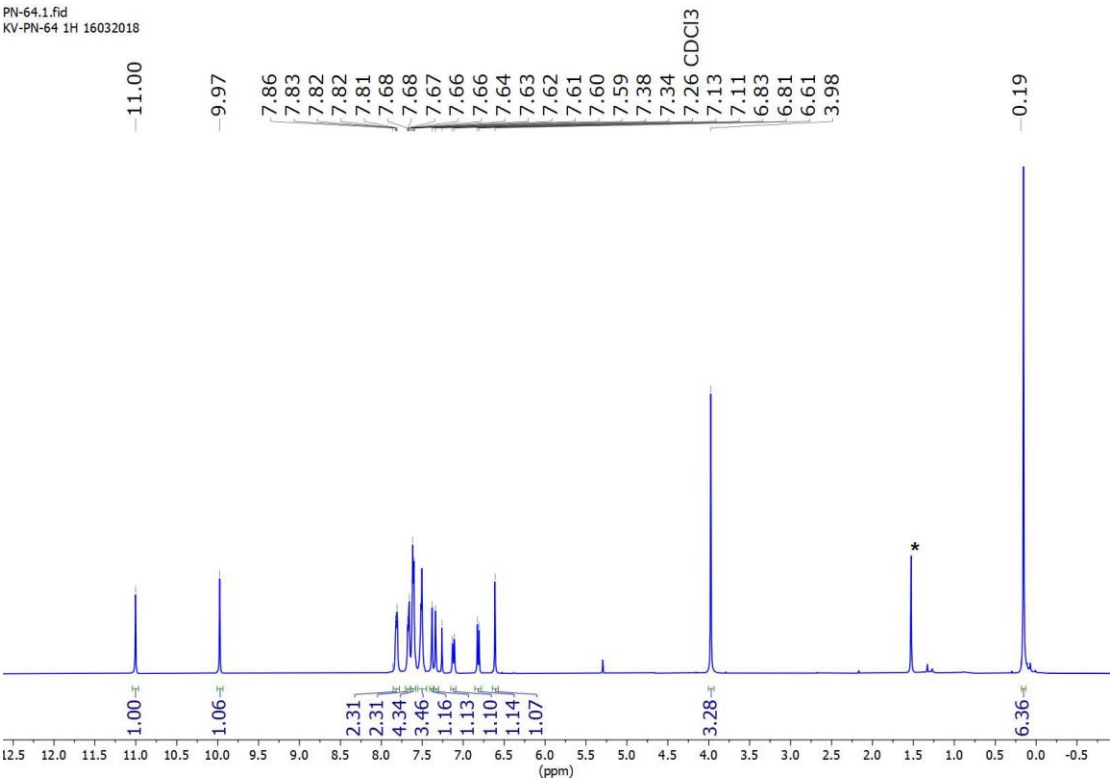


Figure S9: ^{1}H NMR of compound **4a** at 298 K in $CDCl_3$. The asterisks (*) denote residual H_2O

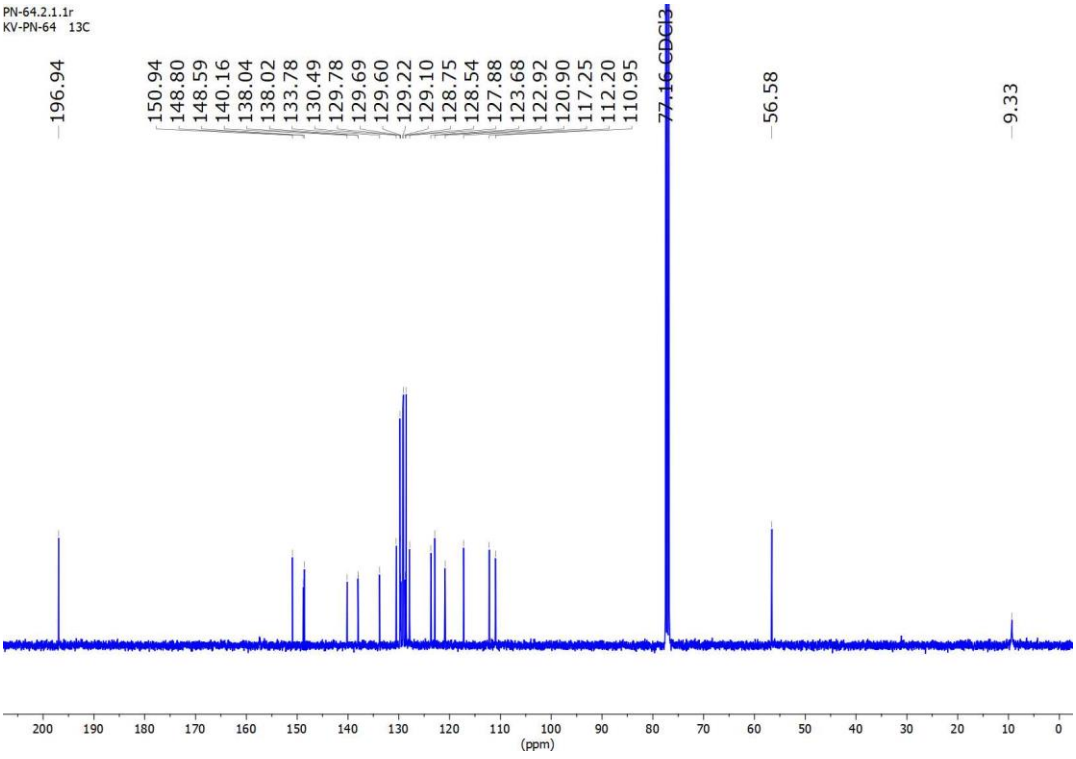


Figure S10: ^{13}C NMR of compound **4a** at 298 K in $CDCl_3$

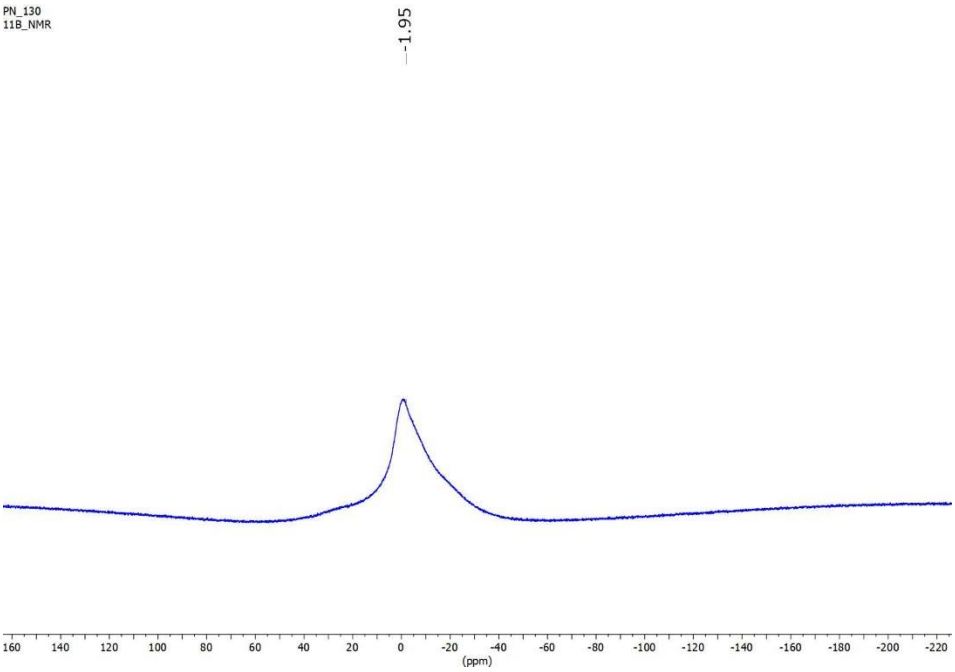


Figure S11: ^{11}B NMR of compound **4a** at 298 K in $CDCl_3$

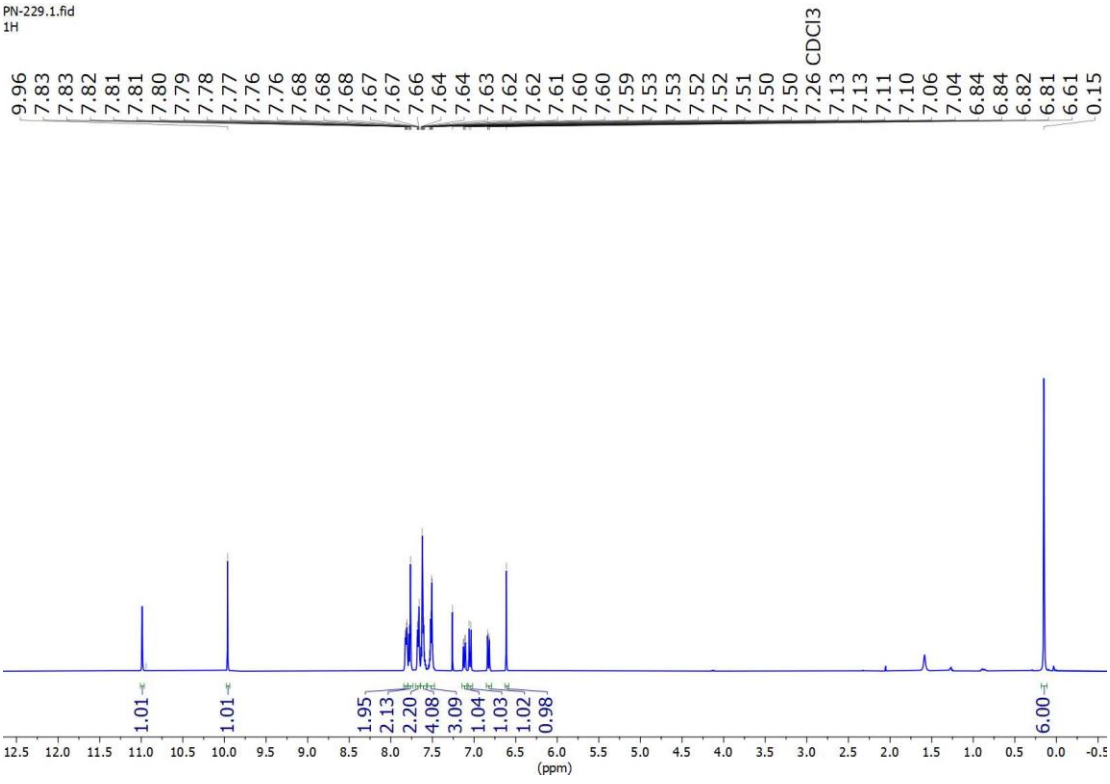


Figure S12: ^{1}H NMR of compound **4b** at 298 K in $CDCl_3$

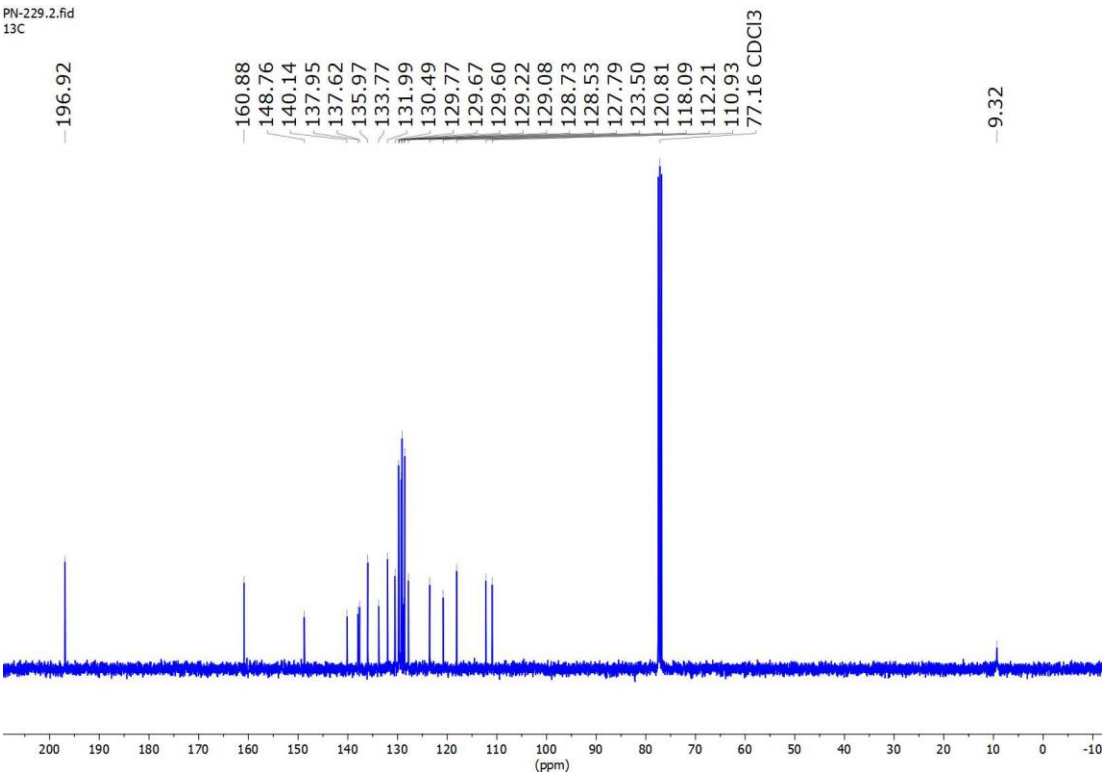


Figure S13: ^{13}C NMR of compound **4b** at 298 K in $CDCl_3$

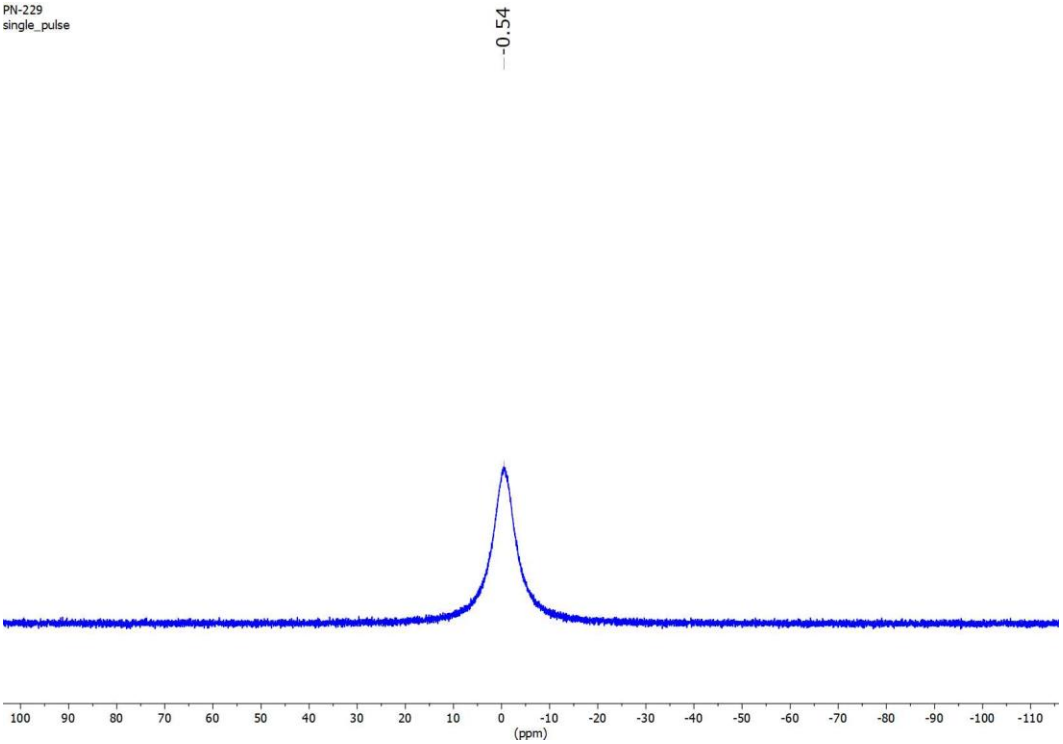


Figure S14: ^{11}B NMR of compound **4b** at 298 K in $CDCl_3$

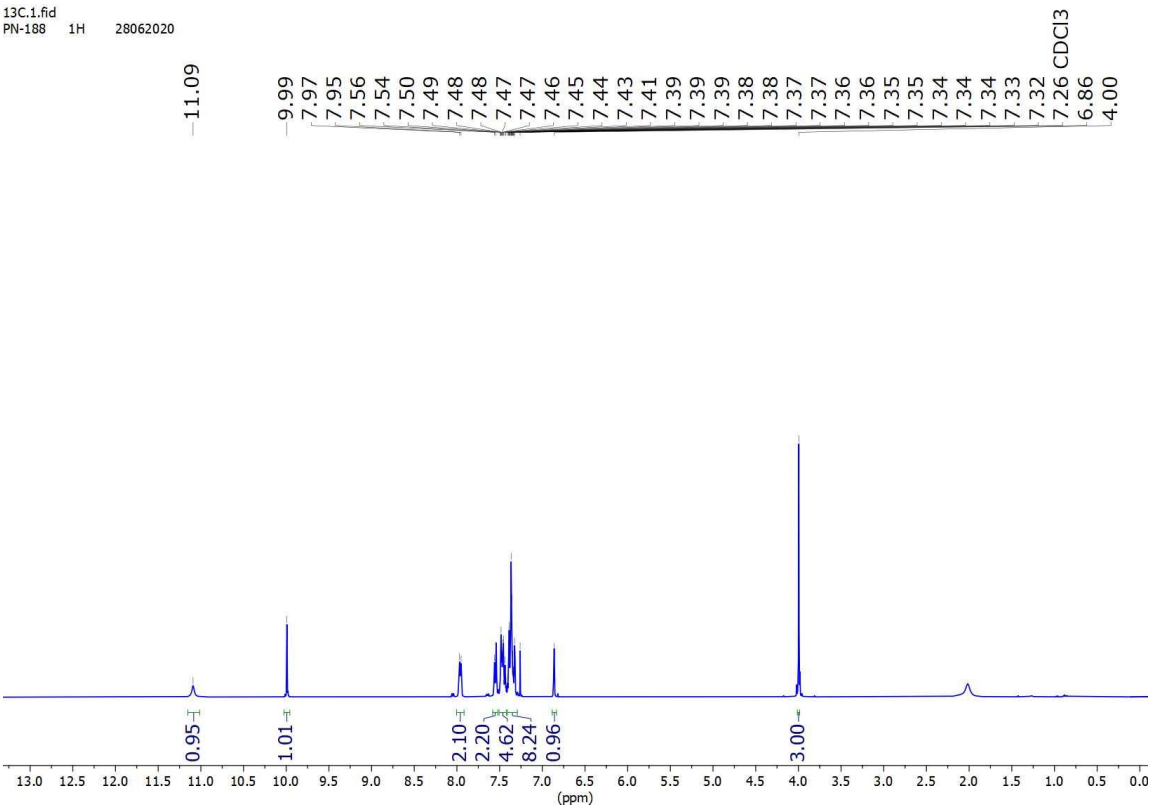


Figure S15: ^{1}H NMR of complex **4c** in $CDCl_3$ at 298 K

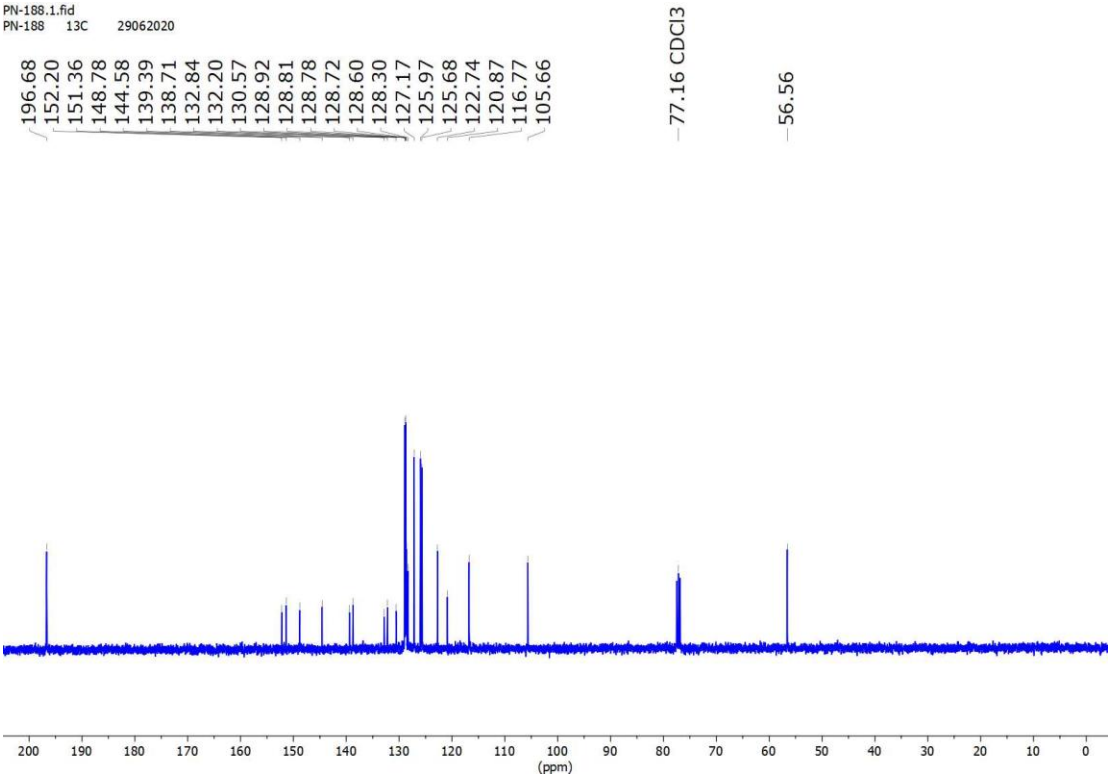


Figure S16: ^{13}C NMR of complex **4c** in $CDCl_3$ at 298 K

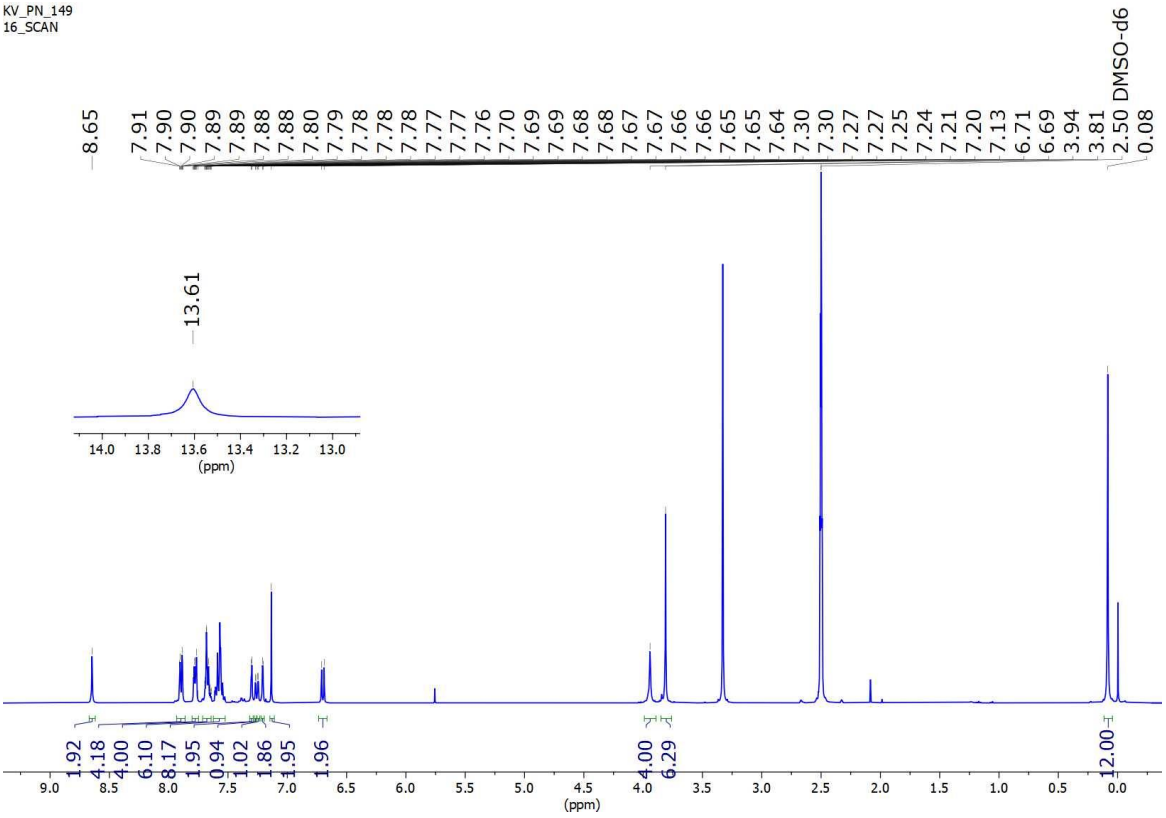


Figure S17: ^{1}H-NMR of compound **5a** at 298 K in DMSO-d_6

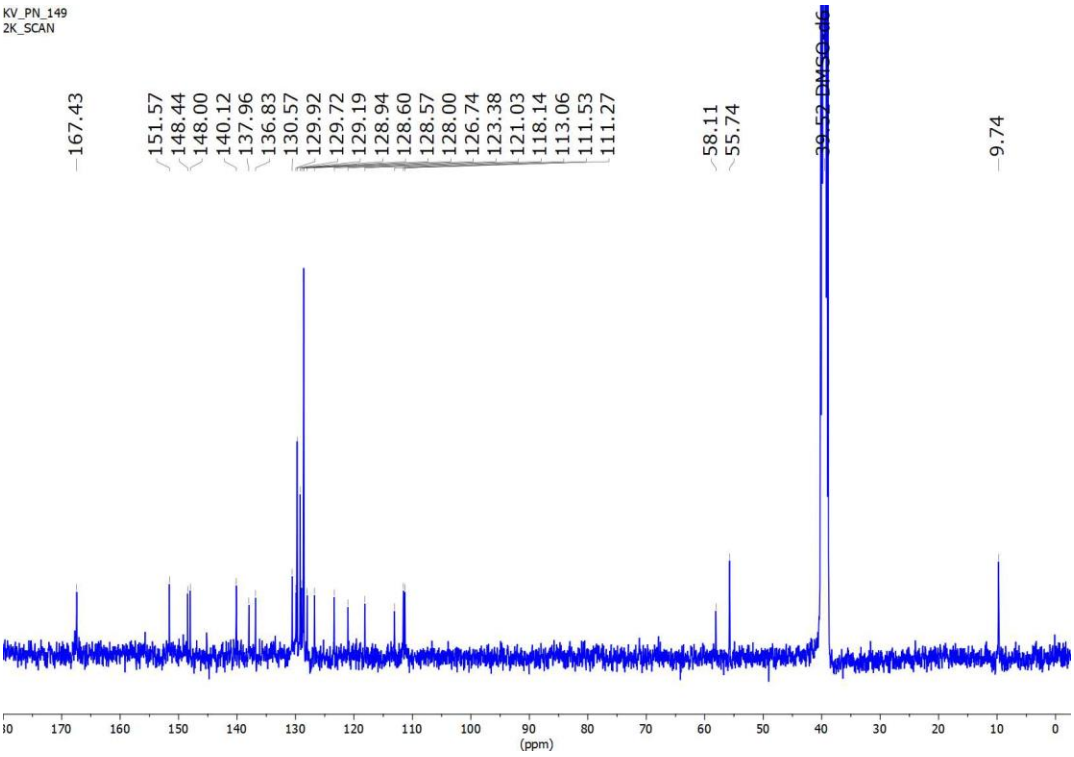


Figure S18: ^{13}C-NMR of compound **5a** at 298 K in DMSO-d_6

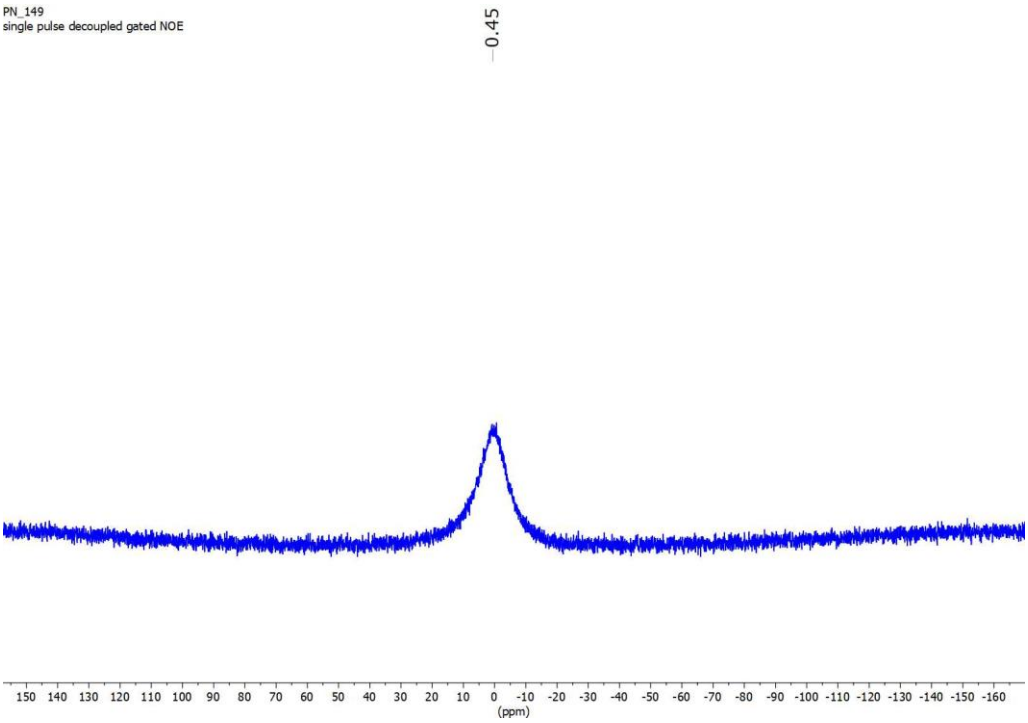


Figure S19: ^{11}B NMR of compound **5a** at 298 K in DMSO-d_6.

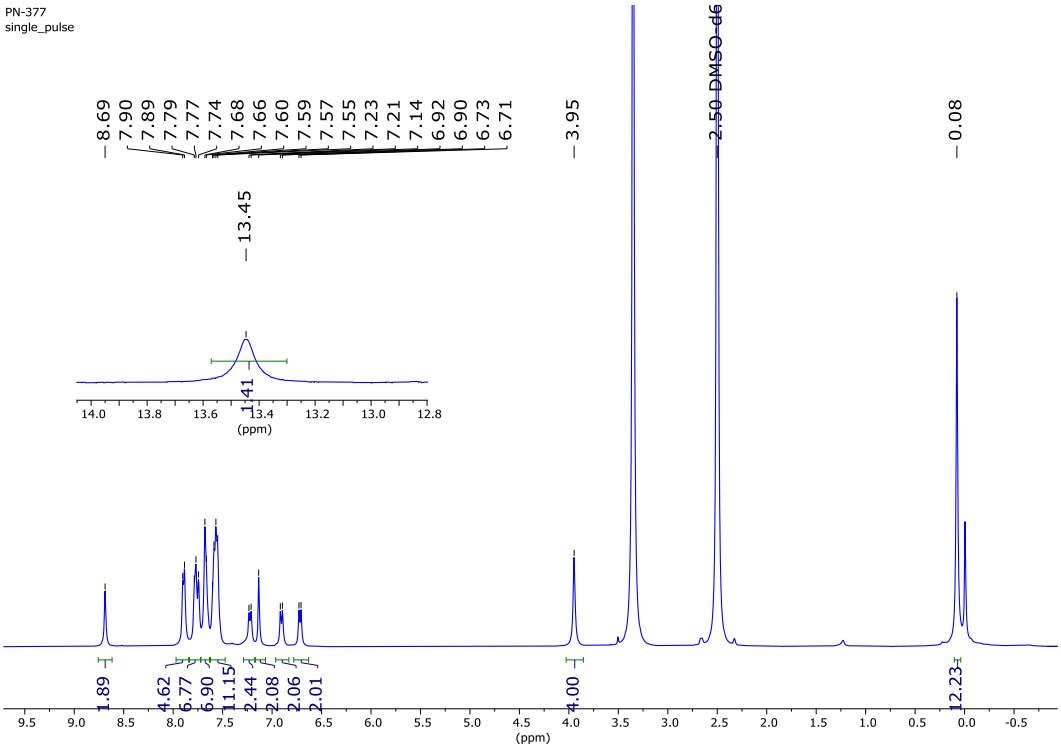


Figure S20: ^{1}H NMR of ligand **5b** at 298 K in DMSO-d_6.

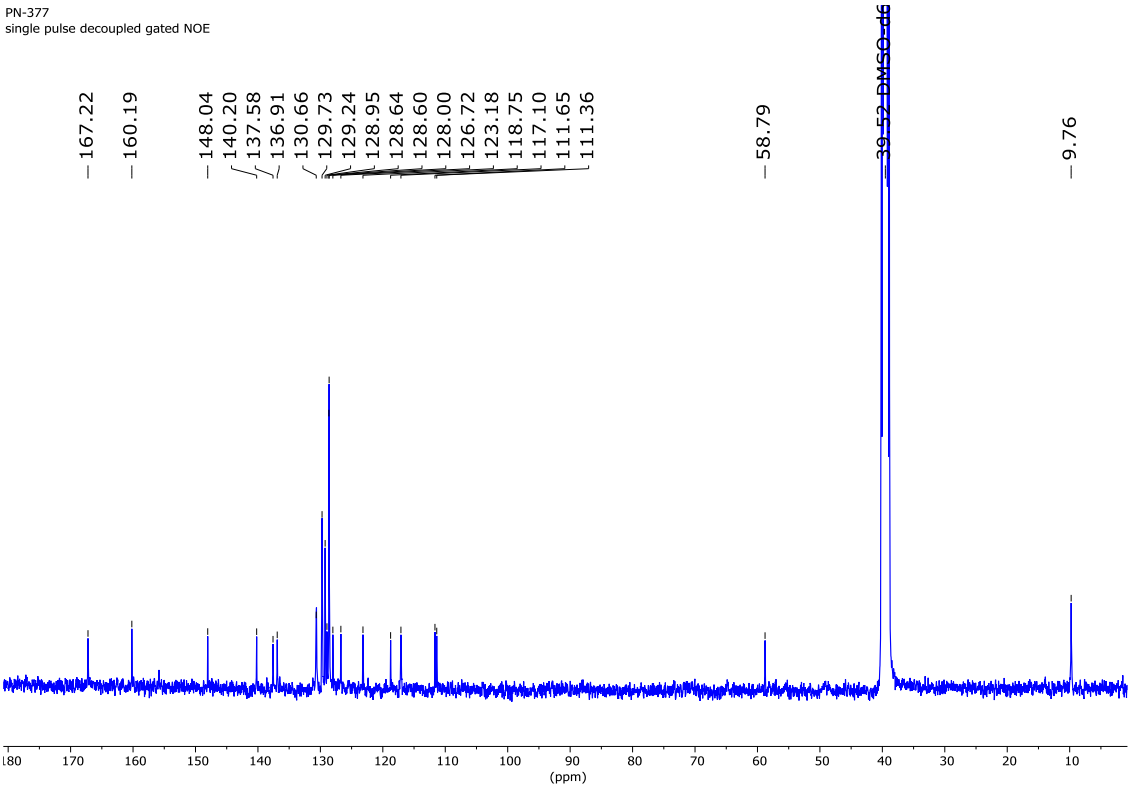


Figure S21: ^{13}C NMR of ligand **5b** at 298 K in DMSO-d_6.

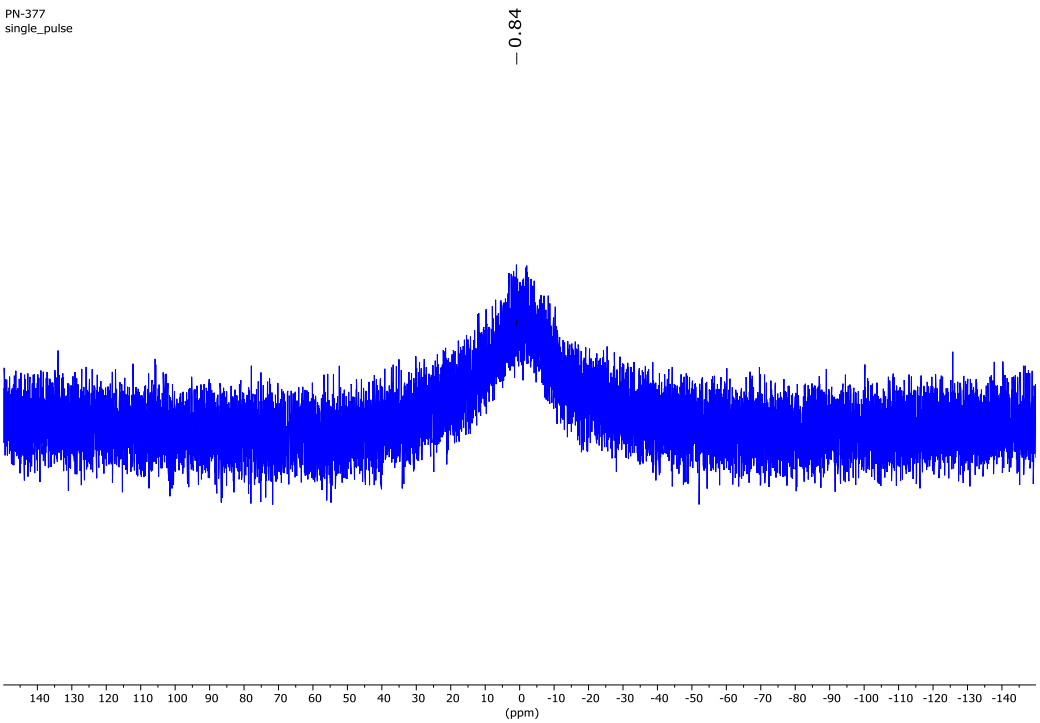


Figure S22: ^{11}B NMR of ligand **5b** at 298 K in DMSO-d_6.

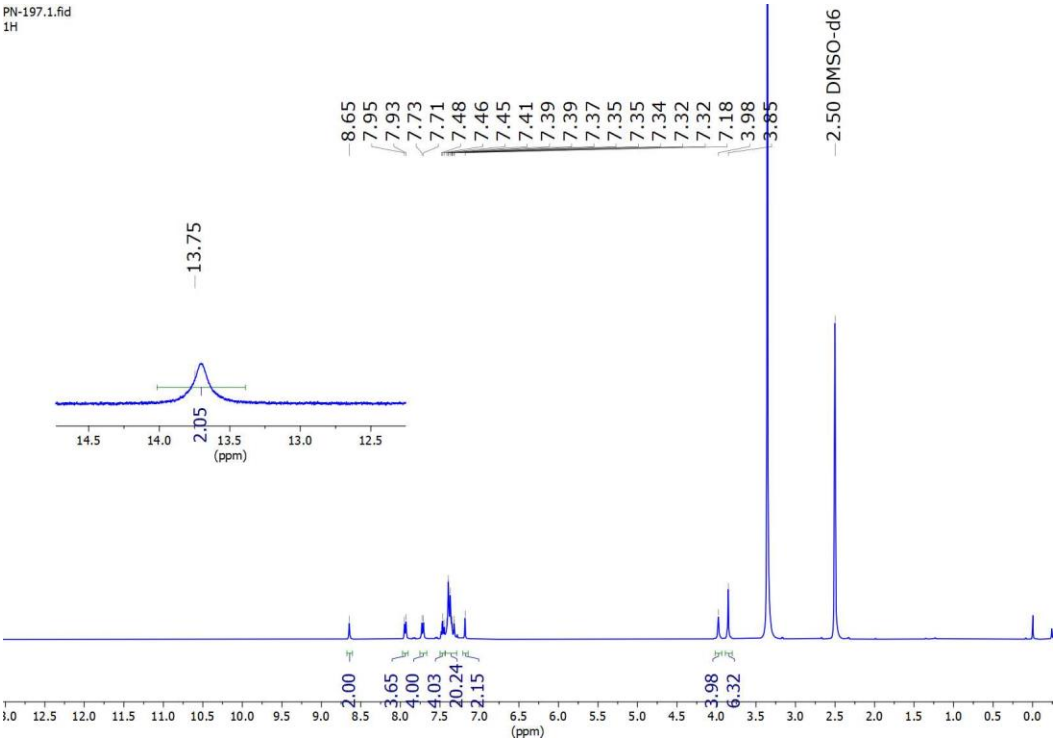


Figure S23: ^{1}H NMR of complex **5c** in DMSO-d_6 at 298 K

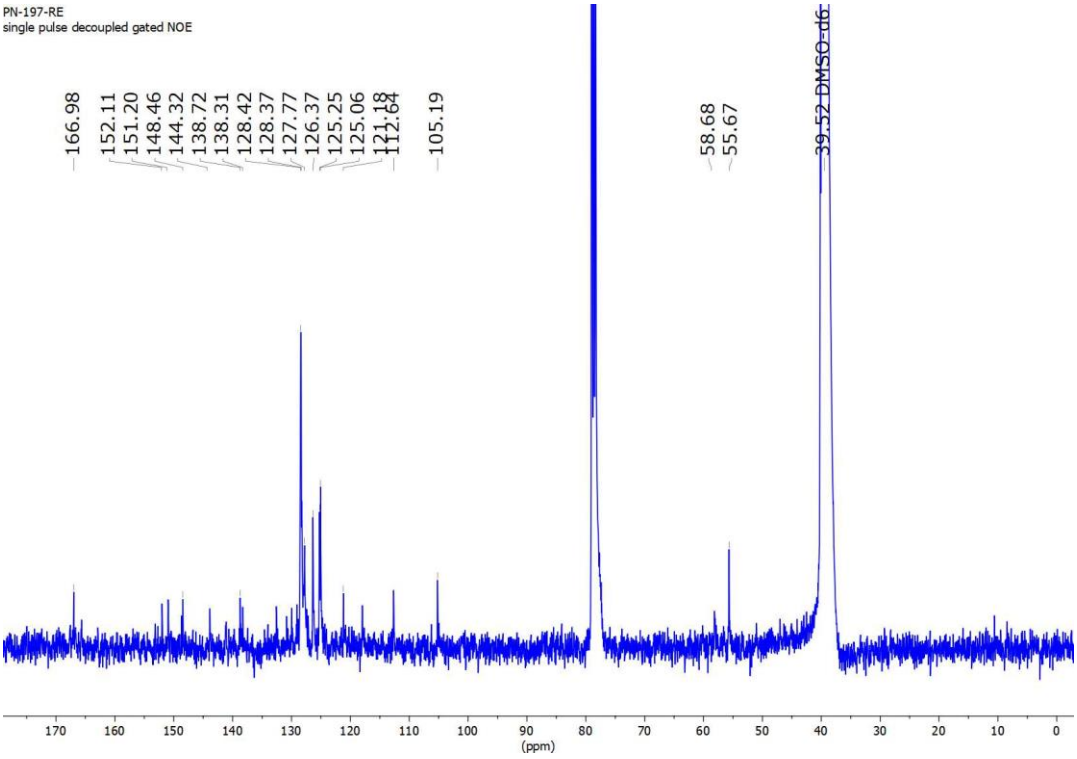


Figure S24: ^{13}C NMR of complex **5c** in $CDCl_3$ at 298 K

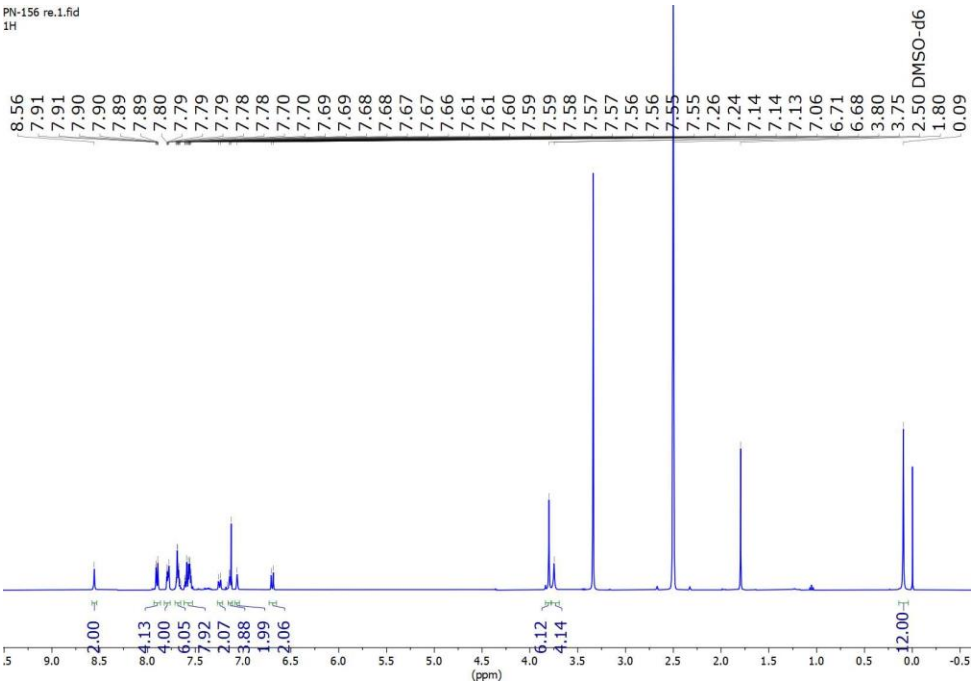


Figure S25: ^{1}H NMR of complex **6a** at 298 K in DMSO-d_6.

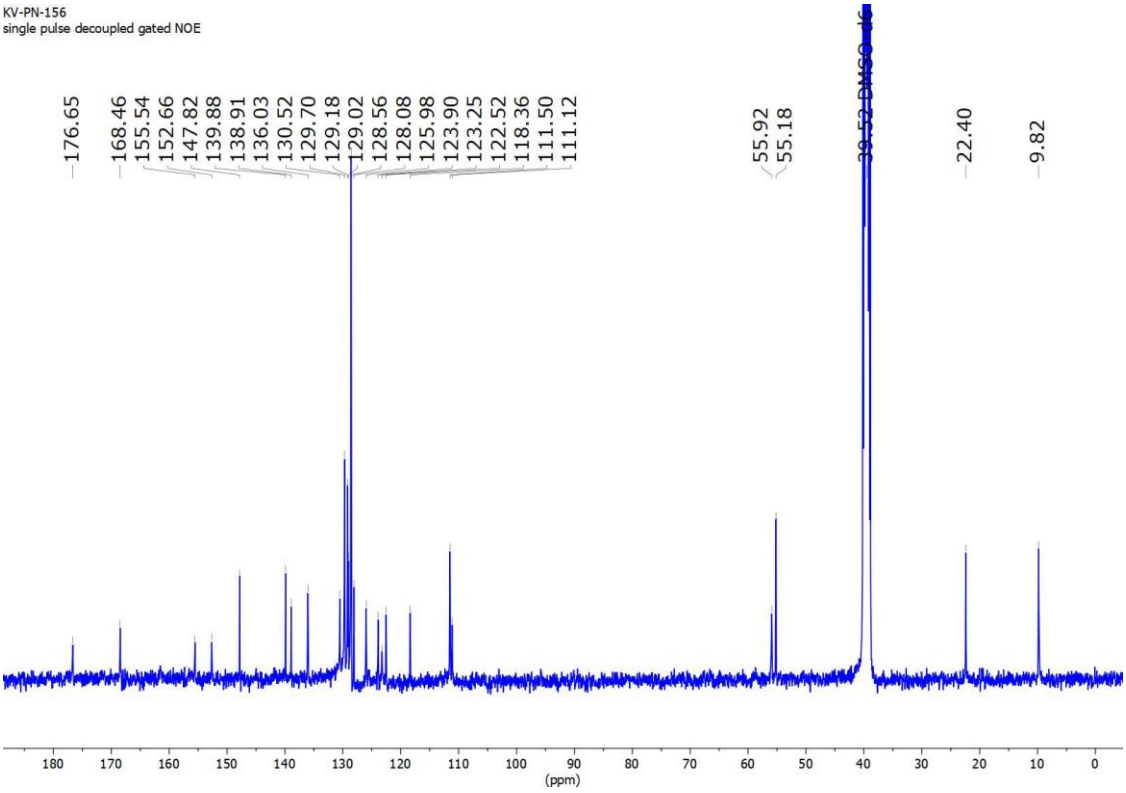


Figure S26: ^{13}C NMR of complex **6a** at 298 K in DMSO-d_6.

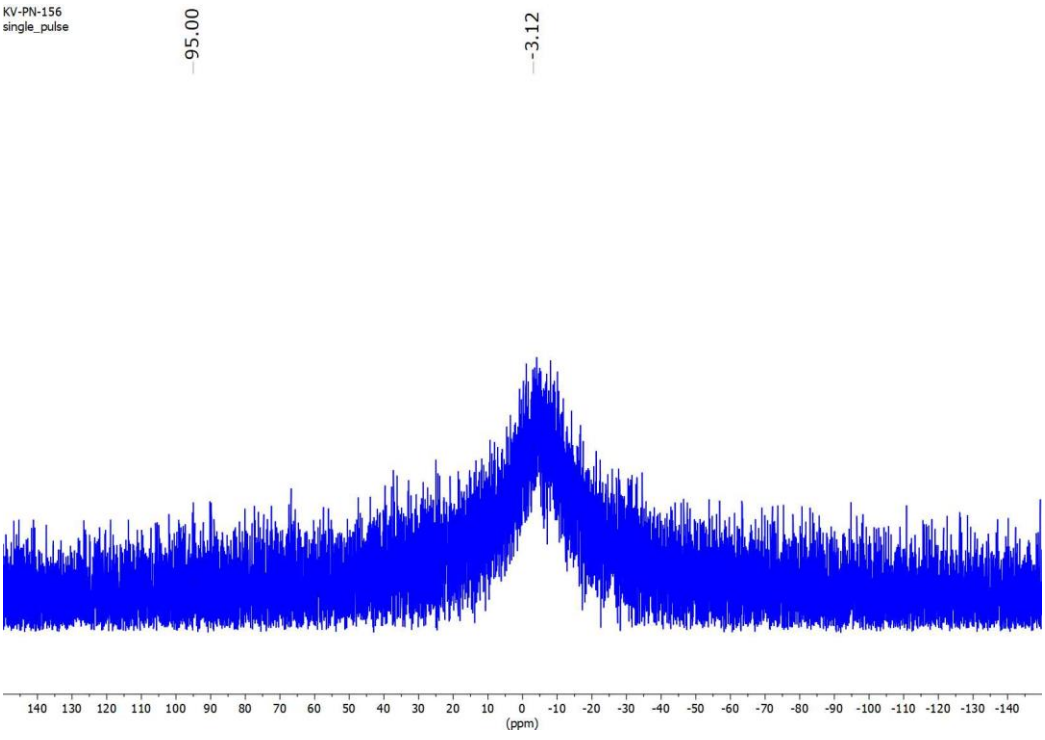


Figure S27: ^{11}B NMR of complex **6a** at 298 K in DMSO-d_6.

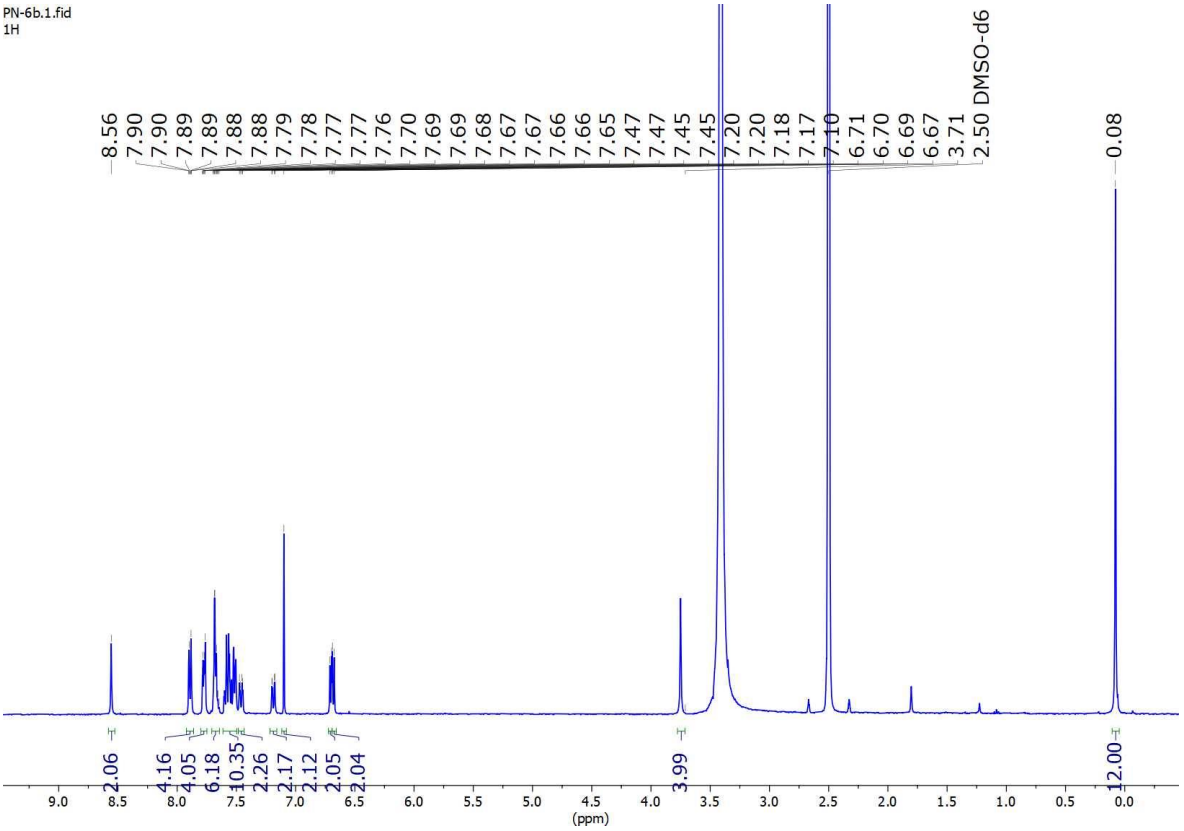


Figure S28: ^{1}H NMR of ligand **6b** at 298 K in $CDCl_3$/DMSO-d_6 in 1:9 ratio.

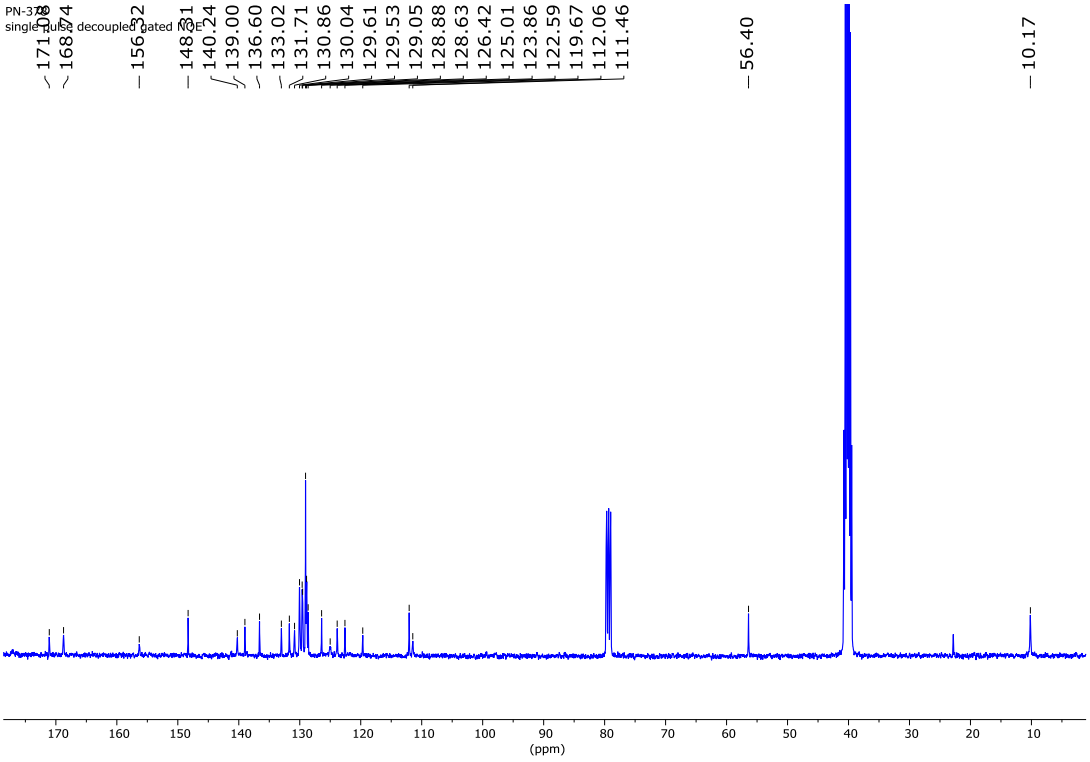


Figure S29: ^{13}C NMR of ligand **6b** at 298 K in $CDCl_3$/DMSO-d_6 in 1:9 ratio.

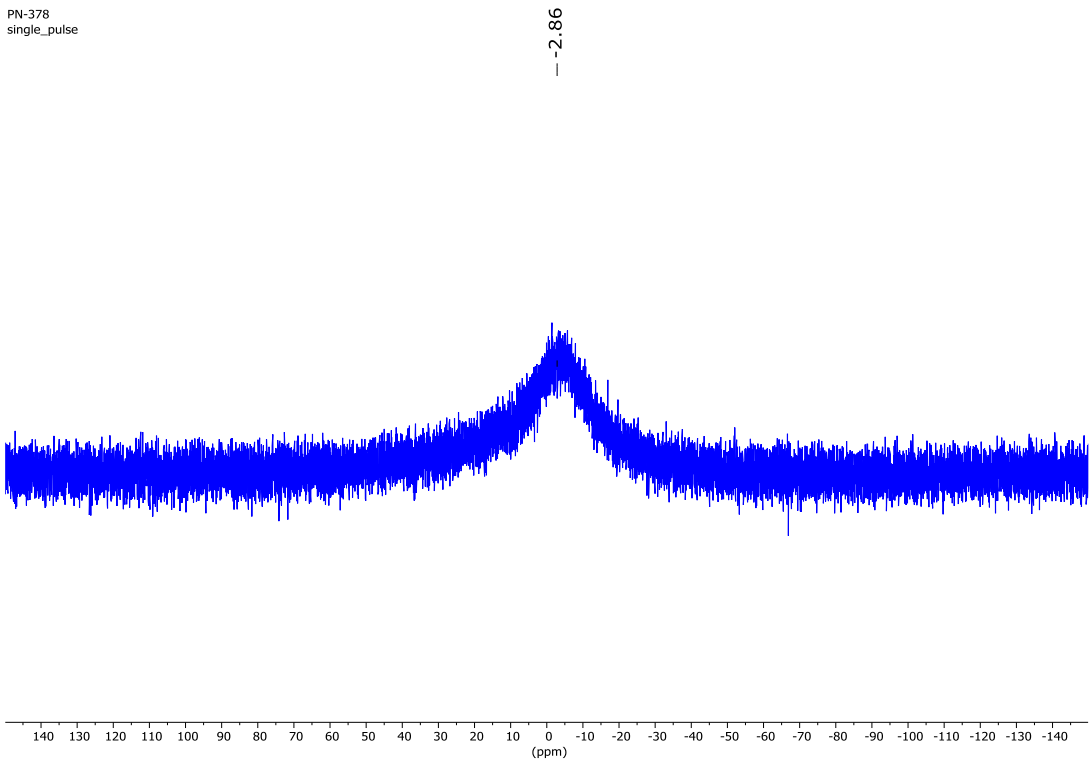


Figure S30: ^{11}B NMR of ligand **6b** at 298 K in $CDCl_3$/DMSO-d_6 in 1:9 ratio.

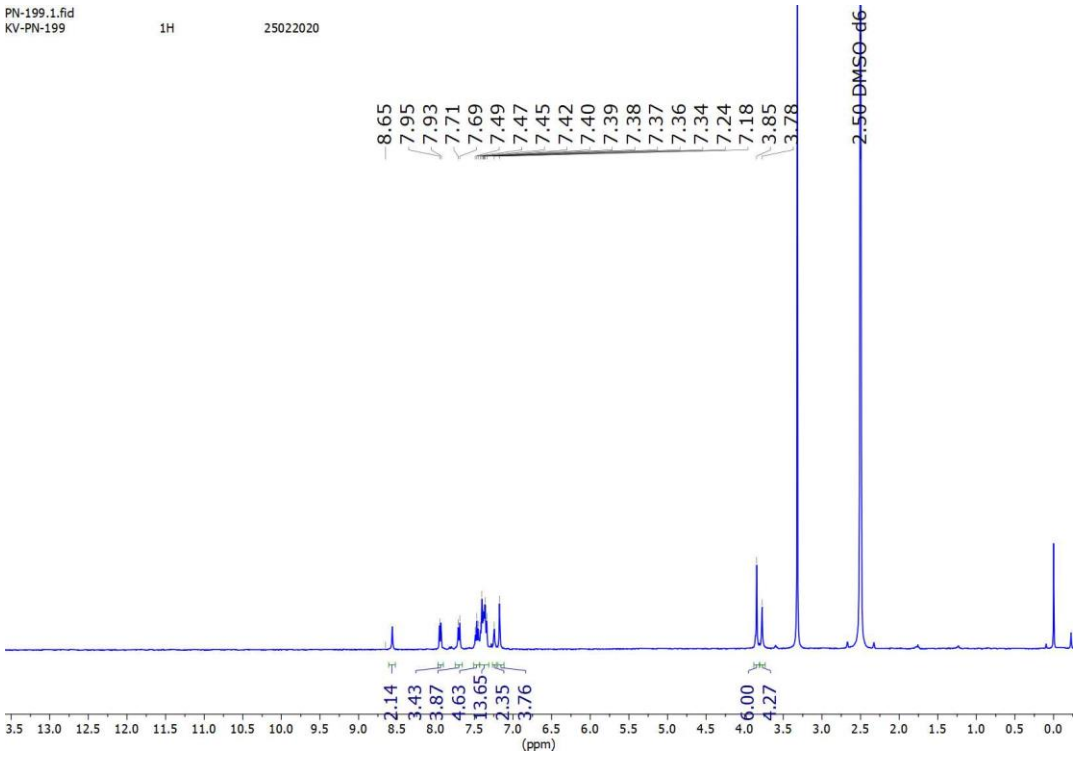


Figure S31: ^{1}H NMR of complex **6c** in DMSO-d_6

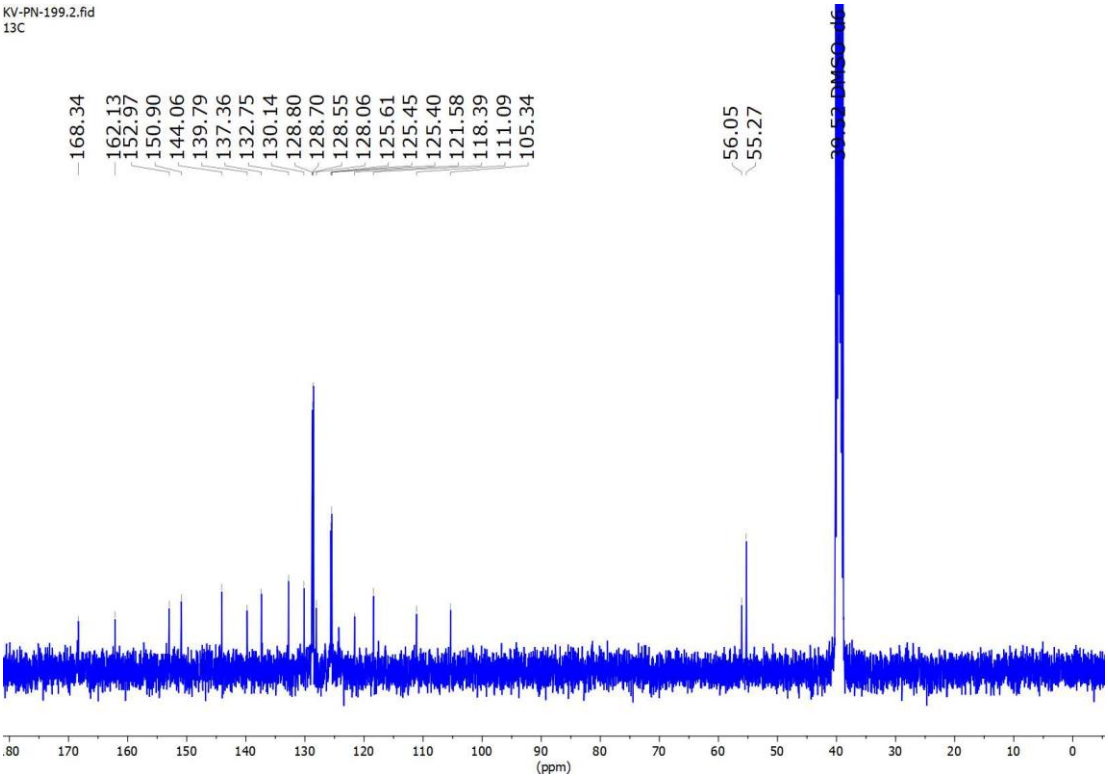


Figure S32: ^{13}C NMR of complex **6c** in DMSO-d_6

Optimized x,y,z coordinates for complex **6a** calculated on Gaussian 16 at B3LYP with LANL2DZ basis set for Zn and 6-31G basis set for other atoms.

Complex **6a (**Energy = -3293.765286 Hartree)

Center Type	Atomic	Atomic Coordinates (Angstroms) X	Y	Z
Zn		-0.025125	-0.040776	-1.190708
O		-0.100491	-0.393890	-3.391365
H		-0.831060	-1.035690	-3.303897
H		0.713854	-0.934044	-3.290774
O		-1.574342	-1.306118	-1.165645
O		1.642638	-1.123701	-1.551962
O		-3.146202	-3.373396	-1.440073
O		3.347640	-2.838044	-2.544051
N		-11.513737	1.130032	0.149169
N		11.174969	-0.084545	0.737948
N		-11.217371	-0.140592	0.557478

N	11.417275	1.259914	0.679313
N	-1.377569	1.511615	-0.653924
N	1.236707	1.259599	-0.040002
C	-12.360031	-2.076380	1.720404
C	-2.833107	-1.095837	-0.938738
C	11.772550	-2.900422	2.111716
H	11.084157	-2.346640	2.743477
C	-9.183349	0.630221	-0.240700
C	-9.835955	-0.455731	0.356165
C	3.867826	-1.874852	-1.727300
C	12.470018	-2.231413	1.091949
C	7.751020	0.663977	-0.134926
H	7.173503	1.558629	-0.356228
C	12.341105	-0.774618	0.898508
C	9.811562	-0.392434	0.428662
C	12.747887	1.435837	0.785513
C	-7.116976	-0.688298	-0.169322
C	-3.746193	-2.208320	-1.056755
C	13.357644	0.175711	0.916273
H	14.406154	-0.017227	1.087493
C	5.204068	-1.751464	-1.401578
H	5.926317	-2.448866	-1.810811
C	-12.766566	1.404169	0.559697
C	-13.479714	2.671617	0.316595
C	13.432689	2.741830	0.777653
C	2.883747	-0.947624	-1.225181
C	-5.098121	-2.061739	-0.816157
H	-5.762292	-2.909029	-0.943951
C	-7.823048	0.482735	-0.507529
H	-7.290631	1.290579	-1.004328
C	7.120081	-0.591513	-0.233040
C	-13.271800	0.281035	1.238553
H	-14.270953	0.160828	1.629913
C	-5.664105	-0.811987	-0.438060
C	7.895809	-1.744151	-0.004891
H	7.429104	-2.723511	-0.058812
C	4.755260	0.214683	-0.097969
H	5.082604	1.021248	0.553486
C	-12.739752	-2.301647	3.052474
H	-12.900948	-1.452438	3.710270
C	-2.638073	1.362489	-0.397744
H	-3.192460	2.222709	0.004159
C	2.517896	1.148210	0.124708
H	3.033787	1.913243	0.722111
C	-3.955801	-4.525365	-1.564296
H	-4.444390	-4.783386	-0.613867

H	-3.283844	-5.335600	-1.854918
H	-4.728076	-4.400732	-2.336976
C	9.100311	0.790683	0.191154
C	-12.278420	-0.693017	1.213311
C	-12.153496	-3.178753	0.874203
H	-11.880387	-3.013745	-0.164037
C	-7.827432	-1.736511	0.447132
H	-7.298965	-2.635014	0.752175
C	5.680104	-0.698312	-0.570651
C	-3.415400	0.163591	-0.575899
C	9.248249	-1.663153	0.324508
H	9.819832	-2.566752	0.493397
C	-10.374672	2.173355	-2.096466
H	-10.833661	1.342706	-2.651434
H	-9.386930	2.338122	-2.550191
H	-10.958566	3.080121	-2.301411
C	-13.526397	3.271580	-0.950930
H	-13.007137	2.808158	-1.781119
C	3.372464	0.120152	-0.406334
C	-9.191754	-1.638267	0.716044
H	-9.707945	-2.453700	1.206382
C	9.573773	3.071268	1.542431
H	9.643225	2.597173	2.532002
H	8.517342	3.342438	1.403503
H	10.128562	4.017588	1.581715
C	14.581464	2.898797	-0.015674
H	14.908525	2.078038	-0.647965
C	13.378904	-2.952881	0.302464
H	13.920863	-2.440358	-0.487149
C	-14.188752	3.263027	1.375550
H	-14.151335	2.808250	2.361533
C	10.263902	2.887053	-1.092786
H	11.003329	3.694988	-1.007348
H	9.322358	3.355859	-1.412433
H	10.584671	2.230098	-1.912855
C	11.968201	-4.264736	2.321182
H	11.423140	-4.769878	3.113725
C	15.284279	4.102534	-0.015114
H	16.165229	4.212117	-0.641727
C	13.013468	3.810042	1.585076
H	12.146712	3.689772	2.223815
C	14.853011	5.164864	0.782219
H	15.399386	6.104108	0.782106
C	-12.306062	-4.476910	1.358851
H	-12.144596	-5.321041	0.694179
C	-14.913975	4.436329	1.175119

H	-15.449405	4.887115	2.006315
C	13.574937	-4.317225	0.517338
H	14.276435	-4.864676	-0.106055
C	-4.808869	0.268856	-0.325173
H	-5.201598	1.232751	-0.010896
C	-9.838869	3.198110	0.376877
H	-10.605451	3.978483	0.276856
H	-8.894875	3.640232	0.027390
H	-9.714919	2.991686	1.448847
C	-12.894385	-3.602113	3.533276
H	-13.181535	-3.762487	4.568762
C	13.718450	5.013369	1.581931
H	13.382770	5.832057	2.212524
C	-12.675687	-4.692202	2.689184
H	-12.795158	-5.704892	3.064160
C	4.236447	-3.794851	-3.086849
H	4.737331	-4.376153	-2.299886
H	5.000611	-3.325910	-3.722824
H	3.624107	-4.464948	-3.693807
C	12.868694	-4.976968	1.524694
H	13.020553	-6.039799	1.691158
C	-14.945768	5.033125	-0.087113
H	-15.509829	5.948552	-0.243763
C	-14.251936	4.446292	-1.147292
H	-14.279753	4.899514	-2.134397
B	-10.178778	1.876287	-0.506139
B	10.033614	2.104927	0.313386
C	-0.686071	2.742269	-0.303892
H	-0.323483	3.220086	-1.224235
H	-1.338090	3.456588	0.219813
C	0.521536	2.371992	0.580215
H	0.146169	2.052170	1.562945
H	1.170437	3.246119	0.734160
