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ELECTRONIC SUPPLEMENTARY INFORMATION

Cooperative Bimetallic Reactivity of a Heterodinuclear Molybdenum-Copper Model of Mo-Cu CODH

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1. General Experimental Details

All reactions involving air-sensitive materials were carried out in a nitrogen-filled glovebox. 2,7-Di-*tert*-butyl-9,9-dimethyl-4,5-diaminoxanthene, tetrakis(acetonitrile)copper(I) tetrakis(pentafluorophenyl)borate, tetraethylammonium tungstate, and tetraethylammonium molybdate were synthesized using previously published procedures.[1] 2,3-Dihydroxybenzaldehyde, sodium borohydride, 2-pyridine carboxaldehyde, and 2,6-dimethylphenyl isocyanide were purchased from Sigma and used as received. Tetrakis(acetonitrile)copper(I) hexafluorophosphate was purchased from Strem and used as received. All non-deuterated solvents were purchased from Aldrich and were of HPLC grade. The non-deuterated solvents were purified using an MBraun solvent purification system. Dichloromethane-d_2 and acetonitrile-d_3 were purchased from Cambridge Isotope Laboratories. All solvents were stored over 3 Å molecular sieves. Compounds were generally characterized by ^{1}H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. Selected compounds were characterized by X-ray crystallography, IR spectroscopy, and UV-vis spectroscopy. NMR spectra of the ligands and metal complexes were recorded at the Lumigen Instrument Centre (Wayne State University) on an Agilent DD2-600 MHz Spectrometer, a Varian VNMRS-500 MHz Spectrometer and an Agilent 400 MHz Spectrometer in CD_2Cl_2 at room temperature or CD_3CN at various temperatures (room temperature to 50 °C). Chemical shifts and coupling constants (J) were reported in parts per million (δ) and Hertz respectively. Detailed assignments of the signals in ^{1}H NMR are given in the ESI. X-ray structures were collected using Bruker Apex2 at the Lumigen Instrument Centre (Wayne State University). Full details on data collection, structure solution and refinement are given below. High resolution mass spectra of the metal complexes (unless otherwise stated) were collected at the Lumigen Instrument Centre (Wayne State University) on a Thermofisher Scientific LTQ Orbittrap XL mass spectrometer. The MS survey scan was set from 200 – 2000. The resolution was set to 60000. In all cases, only one microscan was used in the analysis. HRMS for ligands and **4**$(NEt_4)_2$ were run using a LCT Premier XE with a range of 200 – 2000 scans. Leucine Enkephalin was used as a lockmass. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR Spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. UV-visible spectra were obtained on a Shimadzu UV-1800 spectrometer. Elemental analysis was performed under ambient air-free conditions by Midwest Microlab LLC.

2. Synthetic procedures

Preparation of L1

A 200 mL solution of 2,3-dihydroxybenzaldehyde (0.391 g, 2.83 mmol, 1.0 equiv.) in ethanol was added slowly to a stirring 800 mL solution of 2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene-4,5-diamine (1.00 g, 2.83 mmol, 1.0 equiv.) in ethanol. The reaction mixture was stirred for 24 hours, after which it was cooled to 0 °C. Sodium borohydride (0.118 g, 3.12 mmol, 1.1 equiv.) was then added portionwise and the reaction was stirred for 40 minutes at 0 °C. The solvent was evaporated and the residue taken up in diethyl ether (15 mL) and saturated brine solution (15 mL). The organic layer was separated and the aqueous layer extracted with diethyl ether (2 x 15 mL). The combined organic extracts were dried with $NaSO_4$, filtered and evaporated. The compound was purified by recrystallization from a minimal amount of cyclohexane (approximately 3-4 mL). The obtained pale orange precipitate was washed with cyclohexane until washings were colorless. L1 was obtained in 63% yield. (0.849 g, 1.79 mmol). ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 9.4 (v br s, 2H, catechol-O***H***), 7.03 (d, $^4J_{HH}$ = 2.2 Hz, 1H, para-***H*** on *N*-substituted xanthene side), 6.86 (d, $^4J_{HH}$ = 2.2 Hz, 1H, ortho-***H*** on *N*-substituted xanthene side), 6.85 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, 6-***H*** on catechol), 6.83 (d, $^4J_{HH}$ = 2.2 Hz, 1H, para-***H*** on unsubstituted xanthene side), 6.80 (t, $^3J_{HH}$ = 7.7 Hz, 1H, 5-***H*** on catechol), 6.76 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, 4-***H*** on catechol), 6.69 (d, $^4J_{HH}$ = 2.2 Hz, 1H, ortho-***H*** on unsubstituted xanthene side), 5.63 (br s, 1H, amine-***H*** on *N*-substituted xanthene side), 4.52 (s, 2H, benzyl-***H***), 3.89 (br s, 2H, amine-***H*** on unsubstituted xanthene side), 1.61 (s, 6H, methyl-***H***), 1.29 (s, 9H, *tert*-butyl-***H*** on *N*-substituted xanthene side), 1.25 (s, 9H, *tert*-butyl-***H*** on unsubstituted xanthene side); ^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz) δ 146.62, 146.25, 145.57, 144.53, 138.92, 136.54, 134.71, 134.52, 129.99, 129.94, 124.05, 120.74, 119.98, 115.74, 114.53, 112.65, 112.10, 111.53, 49.93, 35.12, 35.08, 34.86, 32.57, 31.77, 31.71. ESI-MS Calcd for $[L1+H]^+$: 475.2955; Found: 475.2961.

Preparation of LH_2

A 2 mL solution of 2-pyridine carboxaldehyde (0.2 mL, 2.10 mmol, 1.0 equiv.) in methanol was added dropwise to a stirring 40 mL solution of L1 (1 g, 2.11 mmol, 1.0 equiv.) in methanol. The reaction mixture was stirred for 30 minutes. The solvent was evaporated. The resulting solid was dissolved in a minimum amount of hexanes and left in the freezer (- 4 ^{O}C) for 48 hours to afford LH_2 as bright yellow beads (0.974 g, 1.73 mmol, 82%). ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 9.05 (br s, 1H, catechol-O***H***), 8.70 (s, 1H, imine-***H***), 8.64 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, α-***H*** on pyridine), 7.98 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, β'-***H*** on pyridine), 7.68 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, γ-***H*** on pyridine), 7.36 (d, $^{4}J_{HH}$ = 1.8 Hz, 1H, ortho-***H*** on pyridinyl xanthene side), 7.36 (t, $^{3}J_{HH}$ = 4.8 Hz, 1H, β-***H*** on pyridine), 7.07 (d, $^{4}J_{HH}$ = 1.8 Hz, 1H, para-***H*** on pyridinyl xanthene side), 6.97 (d, $^{4}J_{HH}$ = 1.8 Hz, 1H, para-***H*** on catechol xanthene side), 6.87 (d, $^{4}J_{HH}$ = 1.8 Hz, 1H, ortho-***H*** on catechol xanthene side), 6.85 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, 6-***H*** on catechol), 6.75 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, 5-***H*** on catechol), 6.71 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, 4-***H*** on catechol), 6.09 (br s, 1H, catechol-O***H***), 4.87 (br s, 1H, amine-***H***), 4.45 (s, 2H, benzyl-***H***), 1.65 (s, 6H, methyl-***H***), 1.36 (s, 9H, *tert*-butyl-***H*** on pyridinyl xanthene side), 1.29 (s, 9H, *tert*-butyl-***H*** on catechol xanthene side); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 150 MHz) δ 162.46, 154.97, 150.04, 146.68, 146.65, 145.92, 144.14, 141.79, 139.05, 138.69, 137.57, 135.71, 131.62, 129.91, 125.86, 124.99, 122.04, 121.31, 120.69, 120.44, 115.82, 114.80, 113.79, 110.78, 48.89, 35.59, 35.20, 35.19, 31.87, 31.82, 31.80. Anal. Calcd for $C_{36}H_{41}N_3O_3$: C, 76.70; H, 7.33; N, 7.45. Found: C, 76.25; H, 7.57; N, 6.78. ESI-MS Calcd for $[LH_2+H]^+$: 564.3221; Found: 564.3226.

Preparation of 1(PF_6)

A 2 mL solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate $[Cu(NCMe)_4](PF_6)$ (20 mg, 0.054 mmol, 1.0 equiv.) in acetonitrile and a 2 mL solution of **LH_2** (30.25 mg, 0.054 mmol, 1.0 equiv.) in THF were prepared and cooled to -33 °C. The solution of cold **LH_2** was then added dropwise to a stirring solution of cold $[Cu(NCMe)_4](PF_6)$, producing a red brown solution. The reaction mixture was stirred for 30 minutes, upon which the volatiles were removed *in vacuo*. The product was obtained as a red brown solid. This solid was purified by recrystallization from THF/diethyl ether, which yielded red-brown crystals of **1(PF_6)** (39.4 mg, 0.051 mmol, 94%). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 8.92 (s, 1H, imine-***H***), 8.04 (t, $^{3}J_{HH}$ = 6.6 Hz, 1H, γ-***H*** on pyridine), 7.77 (d, $^{3}J_{HH}$ = 6.6 Hz, 1H, β'-***H*** on pyridine) 7.61 (br s, 1H, β-***H*** on pyridine), 7.54 (m, 2H, α-***H*** on pyridine and ortho-***H*** on pyridinyl xanthene side), 7.45 (s, 1H, para-***H*** on pyridinyl xanthene side), 7.42 (s, 1H, para-***H*** on catechol xanthene side), 7.33 (s, 1H, ortho-***H*** on catechol xanthene side), 6.97 (d, $^{3}J_{HH}$ = 6.4 Hz, 1H, 6-***H*** on catechol), 6.80 (d, $^{3}J_{HH}$ =

6.4 Hz, 1H, 4-***H*** on catechol), 6.58 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, 5-***H*** on catechol), 6.23 (br s, 2H, catechol-O***H***), 5.87 (br s, 1H, amine-***H***), 4.44 (s, 2H, benzyl-***H***), 1.75 (s, 6H, methyl-***H***), 1.39 (s, 9H, *tert*-butyl-***H*** on pyridinyl xanthene side), 1.36 (s, 9H, *tert*-butyl-***H*** on catechol xanthene side); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125 MHz) δ 154.93, 151.63, 150.49, 148.81, 147.80, 147.46, 146.38, 144.24, 140.35, 137.48, 136.76, 136.30, 134.00, 133.31, 129.48, 128.16, 123.67, 123.22, 122.92, 121.36, 120.36, 119.43, 117.35, 113.10, 57.35, 38.14, 35.66, 35.47, 31.78, 31.67, 27.45. Anal. Calcd for $C_{36}H_{41}CuF_6N_3O_3P$: C, 55.99; H, 5.35; N, 5.44. Found: C, 55.42, 5.23; N, 5.24. ESI-MS Calcd for [**1**]$^{+}$: 626.2438; Found: 626.2446.

Preparation of 1(B(C_6F_5)$_4$)

A 2 mL solution of tetrakis(acetonitrile)copper(I) tetrakis(pentafluorophenyl)borate [Cu(NCMe)$_4$][B(C_6F_5)$_4$] (32.1 mg, 0.035 mmol, 1.0 equiv.) in diethyl ether and a 2 mL solution of **LH$_2$** (20 mg, 0.035 mmol, 1.0 equiv.) in THF were prepared and cooled to -33 °C. The solution of cold **LH$_2$** was then added dropwise to a stirring solution of cold [Cu(NCMe)$_4$][B(C_6F_5)$_4$] producing a red brown solution. The reaction mixture was stirred for 30 minutes, upon which the volatiles were removed *in vacuo*. The product was obtained as a red-brown solid (44.2 mg, 0.033 mmol, 94%). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.91 (s, 1H, imine-***H***), 8.06 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, γ-***H*** on pyridine), 7.78 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, β'-***H*** on pyridine), 7.59 (d, $^{4}J_{HH}$ = 2.0 Hz, 1H, ortho-***H*** on pyridinyl xanthene side), 7.59 (br s, 1H, α-***H*** on pyridine), 7.52 (t, $^{3}J_{HH}$ = 6.2 Hz, 1H, β-***H*** on pyridine), 7.45 (s, 1H, para-***H*** on pyridinyl xanthene side), 7.44 (s, 1H, para-***H*** on catechol xanthene side), 7.29 (s, 1H, ortho-***H*** on catechol xanthene side), 6.92 (dd, $^{3}J_{HH}$ = 7.8, $^{4}J_{HH}$ = 1.0 Hz, 1H, 6-***H*** on catechol), 6.83 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, 4-***H*** on catechol), 6.65 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, 5-***H*** on catechol), 6.31 (br s, 1H, catechol-O***H***), 6.01 (br s, 1H, amine-***H***), 5.75 (br s, 1H, catechol-O***H***), 4.49 (s, 2H, benzyl-***H***), 1.76 (s, 6H, methyl-***H***), 1.40 (s, 9H, *tert*-butyl-***H*** on pyridinyl xanthene side), 1.36 (s, 9H, *tert*-butyl-***H*** on catechol xanthene side). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz) δ 151.37, 150.81, 149.89, 148.88, 147.50, 144.28, 143.69, 140.45, 138.08, 135.62, 133.71, 133.26, 128.99, 128.20, 123.75, 123.60, 123.36, 121.34, 120.37, 119.03, 116.62, 113.24, 112.02, 56.91, 38.02, 35.62, 35.44, 31.74, 31.71, 27.67. Anal. Calcd for $C_{61}H_{44}BCuF_{20}N_3O_3$: C,55.17; H, 3.16; N, 3.22. Found: C, 54.86; H, 3.72; N, 3.03. ESI-MS Calcd for [1]$^{+}$: 626.2438; Found: 626.2438.

Preparation of $2(B(C_6F_5)_4)$

A 1 mL solution of 2,6-dimethylphenyl isocyanide (2.48 mg, 0.019 mmol, 1.0 equiv.) in THF was added dropwise to a stirring 2 mL solution of complex **$1(B(C_6F_5)_4)$** (25 mg, 0.019 mmol, 1.0 equiv.) in diethyl ether producing an orange-red solution. The reaction mixture was stirred for 30 minutes, upon which the volatiles were removed *in vacuo*. The product was obtained as a red orange solid (26.2 mg, 0.018 mmol, 95 %). ^1H NMR (CD_2Cl_2, 600 MHz) δ 8.81 (s, 1H, imine-***H***), 8.59 (br s, 1H, α-***H*** on pyridine), 8.10 (t, $^3J_{HH}$ = 7.6 Hz, 1H, γ-***H*** on pyridine), 7.73 (br s, 2H, β-***H*** on pyridine and β'-***H*** on pyridine), 7.57 (d, $^4J_{HH}$ = 2.2 Hz, 1H, ortho-***H*** on pyridinyl xanthene side), 7.30 (t, $^3J_{HH}$ = 7.5 Hz, 2H, para-***H*** on isocyanide and para-***H*** on pyridinyl xanthene side), 7.14 (d, $^3J_{HH}$ = 7.7 Hz, 3H, meta-***H*** on isocyanide and para-***H*** on catechol xanthene side), 6.90 (s, 1H, ortho-***H*** on catechol xanthene side), 6.80 (d, $^3J_{HH}$ = 8.1 Hz, 1H, 6-***H*** on catechol), 6.69 (t, $^3J_{HH}$ = 7.9 Hz, 1H, 5-***H*** on catechol), 6.66 (d, $^3J_{HH}$ = 7.7 Hz, 1H, 4-***H*** on catechol), 4.37 (s, 2H, benzyl-***H***), 2.27 (s, 6H, methyl-***H*** on isocyanide), 1.71 (s, 6H, methyl-***H***), 1.36 (s, 9H, *tert*-butyl-***H*** on pyridinyl xanthene side), 1.31 (s, 9H, *tert*-butyl-***H*** on catechol xanthene side); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150 MHz) δ 162.82, 151.98, 150.51, 149.57, 148.09, 148.00, 147.73, 145.01, 143.79, 141.59, 139.67, 138.45, 138.04, 137.73, 136.31, 135.12, 134.47, 132.61, 131.24, 130.11, 128.91, 128.36, 125.62, 124.81, 123.89, 121.20, 120.92, 118.57, 115.98, 115.50, 112.39, 49.14, 35.67, 35.35, 35.33, 32.51, 31.76, 31.65, 18.86. IR (cm^{-1}, selected peaks): 2360.87 (m), 2337.32 (w), 2144.84 (w). Anal. Calcd for $C_{69}H_{50}BCuF_{20}N_4O_3*H_2O$: C, 56.94; H, 3.60; N, 3.85. Found: C, 56.70; H, 3.61; N, 3.68.

Preparation of $3(NEt_4)_2$

A 3 mL solution of tetraethylammonium molybdate $[MoO_4](Et_4N)_2$ (20 mg, 0.048 mmol, 1.0 equiv.) in acetonitrile and a 3 mL solution of **LH_2** (26.5 mg, 0.047 mmol, 1.0 equiv.) in THF were prepared and cooled to -33 °C. The solution of cold **LH_2** was then added dropwise to a stirring solution of cold $[MoO_4](NEt_4)_2$ over 30 minutes producing a yellow solution. The reaction mixture was stirred for 15 minutes, after which the volatiles were removed *in vacuo*. The resulting yellow solid was washed with diethyl ether, extracted with THF and filtered. The crude product precipitates from THF solution at room temperature as a dark yellow solid. The crude product was purified by recrystallization (vapor diffusion) from THF/CH_3CN mixture

(4:1) and diethyl ether, which yielded dark yellow needle-like crystals of **3(NEt$_4$)$_2$** (30.9 mg, 0.032 mmol, 68%). ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 8.61 (m, 2H, imine-***H*** and α-***H*** on pyridine), 7.84 (m, 2H, β'-***H*** and γ-***H*** on pyridine), 7.37 (m, 2H, β-***H*** on pyridine and ortho-***H*** on pyridinyl xanthene side), 7.05 (s, 1H, para-***H*** on pyridinyl xanthene side), 6.78 (s, 1H, para-***H*** on catechol xanthene side), 6.75 (s, 1H, ortho-***H*** on catechol xanthene side), 6.47 (m, 2H, 4-***H*** and 6-***H*** on catechol), 6.26 (t, $^3J_{HH}$ = 7.3 Hz, 1H, 5-***H*** on catechol), 4.49 (br s, 1H, amine-***H***), 4.30 (d, $^3J_{HH}$ = 4.0 Hz, 2H, benzyl-***H***), 3.12 (q, $^3J_{HH}$ = 6.8 Hz, 16H, methylene-***H*** on tetraethylammonium), 1.63 (s, 6H, methyl-***H***), 1.35 (s, 9H, *tert*-butyl-***H*** on pyridinyl xanthene side), 1.34 (s, 9H, *tert*-butyl-***H*** on catechol xanthene side), 1.07 (t, $^3J_{HH}$ = 6.4 Hz, 24H, methyl-***H*** on tetraethylammonium); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150 MHz) δ 161.69, 159.84, 158.06, 155.03, 149.81, 146.98, 146.31, 142.54, 138.96, 138.48, 137.78, 136.05, 131.43, 128.58, 125.68, 122.07, 121.56, 120.50, 115.10, 114.82, 114.38, 110.80, 109.35, 106.47, 52.86, 42.97, 35.31, 35.25, 35.18, 32.13, 32.00, 31.78, 7.89. Anal. Calcd for $C_{52}H_{79}MoN_5O_6{}^*H_2O$: C, 63.46; H, 8.30; N, 7.12. Found: C, 63.25; H, 8.19; N, 7.11. ESI-MS Calcd for [**3**+H]$^-$: 708.1977; Found: 708.1967.

Preparation of 4(NEt$_4$)$_2$

A 3 mL solution of tetraethylammonium tungstate $[WO_4](Et_4N)_2$ (20 mg, 0.039 mmol, 1.0 equiv.) in acetonitrile and a 3 mL solution of **LH$_2$** (22 mg, 0.0039 mmol, 1.0 equiv.) in THF were prepared and cooled to -33 °C. The solution of cold **LH$_2$** was then added slowly dropwise to a stirred solution of cold $[WO_4](NEt_4)_2$ over 30 minutes producing a yellow solution. The reaction mixture was stirred for 15 minutes, after which the volatiles were removed *in vacuo*. The resulting yellow solid was washed with diethyl ether, extracted with THF and filtered. The crude product precipitates from THF solution at room temperature as a light yellow solid. The crude product was purified by recrystallization (vapor diffusion) from THF/CH_3CN mixture (4:1) and diethyl ether, which yielded light yellow needle-like crystals of **4(NEt$_4$)$_2$** (26.7 mg, 0.025 mmol, 64%). ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 8.62 (m, 2H, imine-***H*** and α-***H*** on pyridine), 7.82 (m, 2H, β'-***H*** and γ-***H*** on pyridine), 7.37 (m, 2H, β-***H*** on pyridine and ortho-***H*** on pyridinyl xanthene side), 7.06 (d, $^4J_{HH}$ = 2.2 Hz, 1H, para-***H*** on pyridinyl xanthene side), 6.78 (d, $^4J_{HH}$ = 2.2 Hz, 1H, para-***H*** on catechol xanthene side), 6.76 (d, $^4J_{HH}$ = 2.2 Hz, 1H, ortho-***H*** on catechol xanthene side), 6.52 (m, 2H, 4-***H*** and 6-***H*** on catechol), 6.32 (t, $^3J_{HH}$ = 7.6 Hz, 1H, 5-***H*** on catechol), 4.49 (t, $^{3}J_{HH}$ = 4.8 Hz, 1H, amine-***H***), 4.32 (d, $^{3}J_{HH}$ = 4.8 Hz, 2H, benzyl-***H***), 3.22 (q, $^{3}J_{HH}$ = 7.3 Hz, 16H, methylene-***H*** on tetraethylammonium), 1.64 (s, 6H, methyl-***H***), 1.36 (s, 9H, *tert*-butyl-***H*** on pyridinyl xanthene side), 1.34 (s, 9H, *tert*-butyl-***H*** on catechol xanthene side), 1.14 (t, $^{3}J_{HH}$ = 7.3 Hz, 24H, methyl-***H*** on tetraethylammonium); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 150 MHz) δ 161.72, 159.46, 157.82, 155.05, 149.82, 146.99, 146.34, 142.49, 138.97, 138.37, 137.70, 136.08, 131.43, 128.64, 125.66, 121.98, 121.90, 121.54, 116.07, 115.70, 114.41, 112.12, 109.51, 106.48, 52.97, 42.86, 35.33, 35.25, 35.16, 32.14, 31.99, 31.78, 7.96. Anal. Calcd for $C_{52}H_{79}WN_5O_6{}^*H_2O$: C, 58.26; H, 7.62; N, 6.53. Found: C, 57.68; H, 7.43; N, 6.60. ESI-MS Calcd for [**4**+H]$^-$: 794.2432; Found: 794.2399.

Preparation of Complex 5(NEt$_4$)$_2$

A 1.5 mL solution of tetraethyl ammonium molybdate $[MoO_4](NEt_4)_2$ (10 mg, 0.024 mmol, 1.0 equiv.) in acetonitrile was added dropwise to a stirring 1 mL solution of **LH$_2$** (26.5mg, 0.047 mmol, 2.0 equiv.) in THF producing a deep orange solution. The reaction mixture was stirred for 1 hour, upon which the volatiles were removed *in vacuo*. The product was obtained as an orange solid. This solid was purified by recrystallization from acetonitrile at room temperature (25.7 mg, 0.017 mmol, 71%). ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 8.60 (m, 2H, imine-***H*** and α-***H*** on pyridine), 7.83 (m, 2H, β'-***H*** and γ-***H*** on pyridine), 7.34 (m, 2H, β-***H*** on pyridine and ortho-***H*** on pyridinyl xanthene side), 7.05 (s, 1H, para-***H*** on pyridinyl xanthene side), 6.70 (m, 2H, para-***H*** and ortho-***H*** on catechol xanthene side), 6.46 (br s, 1H, 6-***H*** on catechol), 6.32 (m, 2H, 4-***H*** and 5-***H*** on catechol), 4.51 (br s, 1H, amine-***H***), 4.25 (br s, 2H, benzyl-***H***), 2.94 (q, $^{3}J_{HH}$ = 7.2 Hz, 8H, methylene-***H*** on tetraethylammonium), 1.61 (s, 6H, methyl-***H***), 1.34 (s, 9H, *tert*-butyl-***H*** on pyridinyl xanthene side), 1.28 (s, 9H, *tert*-butyl-***H*** on catechol xanthene side), 0.93 (t, $^{3}J_{HH}$ = 7.2 Hz, 12H, methyl-***H*** on tetraethylammonium); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 150 MHz) δ 161.73, 155.04, 149.74, 146.96, 146.30, 142.54, 139.02, 138.60, 137.71, 136.07, 131.37, 128.60, 125.70, 122.17, 121.38, 114.40, 111.43, 109.27, 106.33, 52.96, 43.10, 35.35, 35.23, 35.19, 32.36, 32.00, 31.81, 7.80. Anal. Calcd for $C_{88}H11_{118}N_8O_8Mo$: C, 69.91; H, 7.87; N, 7.41. Found: C, 69.75; H, 7.89; N, 7.47. ESI-MS Calcd for [**5**+H]$^-$: 1253.5019; Found: 1253.5016.

Preparation of Complex 6(NEt$_4$)$_2$

A 1.5 mL solution of tetraethyl ammonium tungstate $[WO_4](NEt_4)_2$ (10 mg, 0.019 mmol, 1.0 equiv.) in acetonitrile was added dropwise to a stirring 1 mL solution of **LH$_2$** (22 mg, 0.039 mmol, 2.0 equiv.) in THF producing yellow solution. The reaction mixture was stirred for 1 hour, upon which the volatiles were removed *in vacuo*. The product was obtained as a yellow solid This solid was purified by recrystallization from acetonitrile at room temperature (22 mg, 0.013 mmol, 70 %). ^{1}H NMR (CD_3CN, 500 MHz, 50 °C) δ 8.61 (br s, 2H, imine-***H*** and α-***H*** on pyridine), 7.94 br s, 2H, β'-***H*** and γ-***H*** on pyridine), 7.43 (s, 1H, ortho-***H*** on pyridinyl xanthene side), 7.37 (br s, 1H, β-***H*** on pyridine), 7.11 (s, 1H, para-***H*** on pyridinyl xanthene side), 6.78 (br s, 2H, para-***H*** and ortho-***H*** on catechol xanthene side), 6.38 (br s, 1H, 6-***H*** on catechol), 6.23 (br s, 1H, 4-***H*** on catechol), 6.12 (br s, 1H, 5-***H*** on catechol), 4.46 (br s, 1H, amine-***H***), 4.23 (br s, 2H, benzyl-***H***), 3.10 (q, $^3J_{HH}$ = 7.1 Hz, 8H, methylene-***H*** on tetraethylammonium), 1.65 (s, 6H, methyl-***H***), 1.37 (s, 9H, *tert*-butyl-***H*** on pyridinyl xanthene side), 1.32 (br s, 9H, *tert*-butyl-***H*** on catechol xanthene side), 1.10 (tt, $^3J_{HH}$ = 7.2 Hz, $^2J_{HH}$ = 1.5 Hz, 12H, methyl-***H*** on tetraethylammonium). ESI-MS Calcd for $[\mathbf{6}+H]^-$: 1339.5474; Found: 1339.5453.

Preparation of Complex 7(NEt$_4$)

A 0.5 mL solution of **1(PF$_6$)** (18.4 mg, 0.024 mmol, 1.0 equiv.) in dichloromethane and a 1 mL solution of tetraethyl ammonium molybdate $[MoO_4](NEt_4)_2$ (10 mg, 0.024 mmol, 1.0 equiv.) in dichloromethane were prepared and cooled to -33 °C. The solution of cold **1(PF$_6$)** was then added dropwise to a stirring solution of chilled $[MoO_4](NEt_4)_2$ producing a red brown solution. The reaction mixture was stirred at room temperature and monitored by NMR spectroscopy. After 45 h, the reaction mixture was concentrated in vacuo to about half of the volume and left at -33 °C for 2 weeks. After 2 weeks, no by-products were observed by ^{1}H NMR. The volatiles were removed *in vacuo*. The product was washed with diethyl ether, extracted with THF, filtered and dried in vacuo, to obtain spectroscopically pure **7(NEt$_4$)** as a dark brown yellow solid (18.9 mg, 0.22 mmol, 95%). X-ray quality crystals were obtained by recrystallization from dichloromethane at -33 °C, which yielded dark yellow crystals of **7(NEt$_4$)**. ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 8.56 (d, $^3J_{HH}$ = 5.1 Hz, 1H, α-***H*** on pyridine), 7.85 (t, $^3J_{HH}$ = 7.3 Hz, 1H, γ-***H*** on pyridine), 7.70 (d, $^3J_{HH}$ = 7.7 Hz, 1H, β'-***H*** on pyridine), 7.37 (t, $^3J_{HH}$ = 6.4 Hz, 1H, β-***H*** on pyridine), 7.16 (d, $^{3}J_{HH}$ = 11.4 Hz, 1H, benzyl-***H*** on pyridinyl xanthene side), 7.11 (s, 1H, para-***H*** on pyridinyl xanthene side), 6.89 (d, $^{4}J_{HH}$ = 1.1 Hz, 1H, ortho-***H*** on pyridinyl xanthene side), 6.82 (d, $^{4}J_{HH}$ = 1.8 Hz, 1H, para-***H*** on catechol xanthene side), 6.70 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, 6-***H*** on catechol), 6.67 (d, $^{4}J_{HH}$ = 1.1 Hz, 1H, ortho-***H*** on catechol xanthene side), 6.50 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H, 4-***H*** on catechol), 6.40 (m, 2H, 5-***H*** on catechol and benzyl-***H*** on catechol xanthene side), 5.73 (d, $^{3}J_{HH}$ = 11.7 Hz, 1H, aniline-***H*** on pyridinyl xanthene side), 4.23 (m, 1H, aniline-***H*** on catechol xanthene side), 4.10 (d, $^{3}J_{HH}$ = 12.8 Hz, 1H, benzyl-***H*** on catechol xanthene side), 3.04 (q, $^{3}J_{HH}$ = 7.0 Hz, 8H, methylene-***H*** on tetraethylammonium), 1.74 (s, 3H, methyl-***H***), 1.41 (s, 3H, methyl-***H***), 1.37 (s, 9H, *tert*-butyl-***H*** on pyridinyl xanthene side), 1.33 (s, 9H, *tert*-butyl-***H*** on catechol xanthene side), 1.12 (t, $^{3}J_{HH}$ = 7.0 Hz, 12H, methyl-***H*** on tetraethylammonium); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 150 MHz) δ 161.99, 158.66, 158.49, 147.03, 146.79, 146.60, 139.33, 138.23, 138.03, 134.81, 130.90, 130.15, 124.82, 122.39, 120.76, 120.25, 114.82, 112.50, 111.48, 110.45, 108.47, 107.55, 88.83, 52.83, 50.65, 35.77, 35.33, 35.25, 34.17, 32.07, 31.99, 7.69. ESI-MS Calcd for $[7]^{-}$: 708.1977; Found: 708.1968.

3. X-ray crystallographic details

Structures of complexes **1(PF_6)**, **6(NEt_4)$_2$**, and **7(NEt_4)** were confirmed by X-ray structure determination. The crystals were mounted on a Bruker APEXII/Kappa three circle goniometer platform diffractometer equipped with an APEX-2 detector. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and refined using the APEX2 software. Structures were solved by direct methods in SHELXS and refined by standard difference Fourier techniques in the SHELXTL program suite (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically; all other atoms were refined anisotropically. The structure of **1**(PF_6) co-crystallized with two ether molecules, one of which occupies a special position, which results in half occupancy per asymmetric unit. Both molecules were fully refined. The structure of **7**(NEt_4) co-crystallized with two dichloromethane molecules which were also fully refined. In the structure of **6**(NEt_4)$_2$, the complex itself occupies a special position, resulting in half of the complex and one tetraethylammonium counter-ion comprising the asymmetric unit. Tetraethylammonium was found to be disordered over two (nearly overlapping) conformations. Our attempts to refine disordered tetraethylammonium anisotropically (with attached hydrogens) met with only limited success, resulting in larger than usual Atomic Displacement Parameter (ADP) values (B-level alerts in a cif file), and short contacts between hydrogen atoms (A-level alerts). Detailed crystal and structure refinement data are given in **Table S1**.

Table S1. X-ray crystallographic details for complexes **1**(PF_6), **6**(NEt_4)$_2$, and **7**(NEt_4).

complex	**1**(PF_6)×1.5$C_4H_{10}O$	**6**(NEt_4)$_2$	**7**(NEt_4)×2CH_2Cl_2
formula	$C_{36}H_{41}CuF_6PN_3O_3$ ×1.5$C_4H_{10}O$	$C_{44}H_{57}N_4O_4W_{0.50}$	$C_{44}H_{42}MoN_4O_6$ ×2CH_2Cl_2
Fw, g/mol	883.41	797.86	1006.75
temperature	100(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/c	*C*2/c	*P*2_1/c
color	red	yellow	yellow
Z	8	8	4
a, Å	23.123(2)	46.586(5)	16.1435(6)
b, Å	20.901(2	9.6827(7)	18.7693(7)
c, Å	17.9704(17)	17.8776(13)	15.6833(6)
α, deg	90.00	90.00	90.00
β, deg	102.919(4)	90.110(6)	90.121(2)
γ, deg	90.00	90.00	90.00
V, A^3	8465.0(14)	8064.2(12)	4752.1(3)
d_{calcd}, g/cm^3	1.386	1.314	1.407
μ, mm^{-1}	0.626	1.493	0.552
2θ, deg	50.30	55.32	54.46
R_1^{α} (all data)	0.0979	0.1183	0.0995
wR_2^b (all data)	0.1103	0.1655	0.0870
R_1^a [(I>2σ)]	0.0461	0.0632	0.0421
wR_2^b [(I>2σ)]	0.0965	0.1358	0.0766
GOF (F^2)	0.976	1.143	0.886

4. NMR spectra

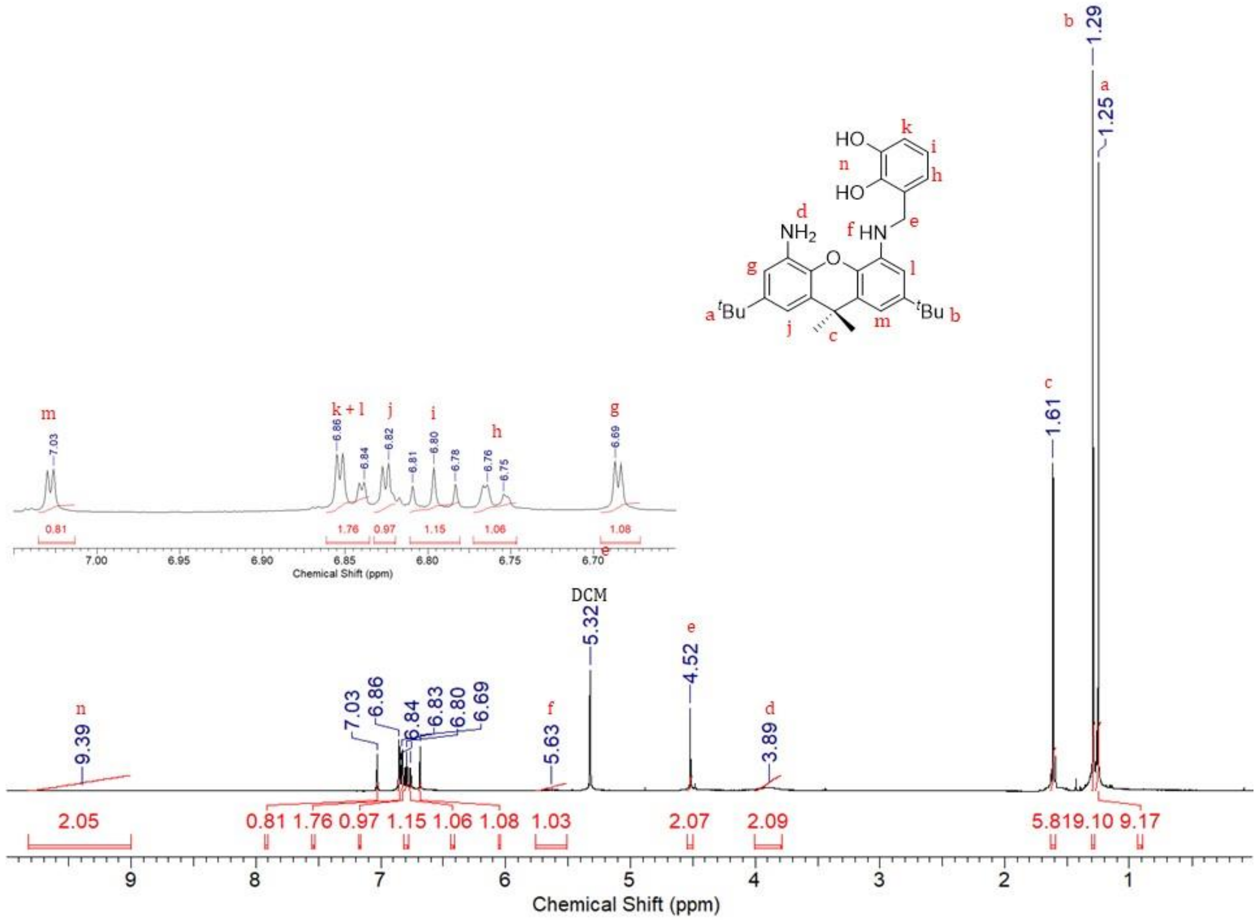

Figure S1. ^{1}H NMR spectrum of **L1** (CD_2Cl_2, 600 MHz).

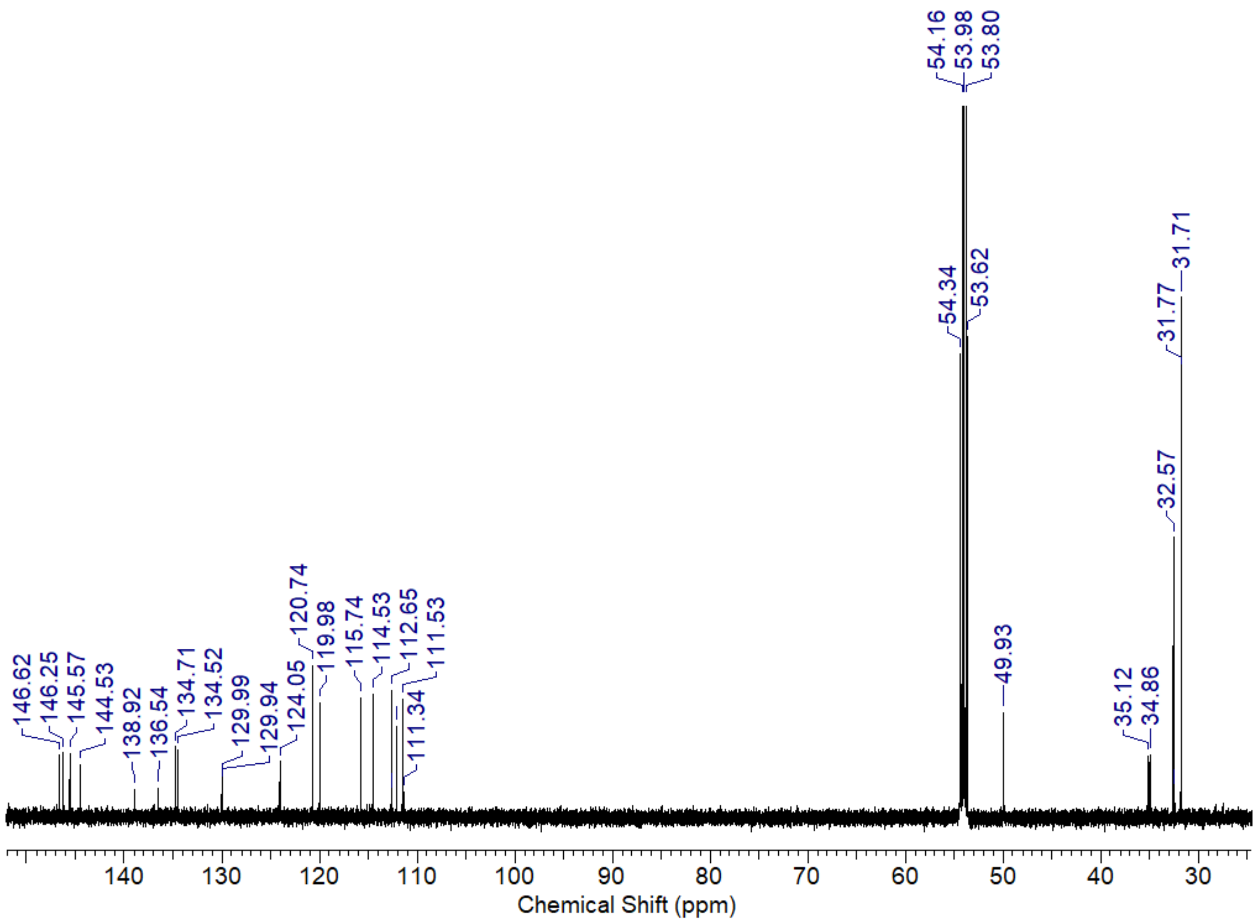

Figure S2. ^{13}C NMR spectrum of **L1** (CD_2Cl_2, 150 MHz).

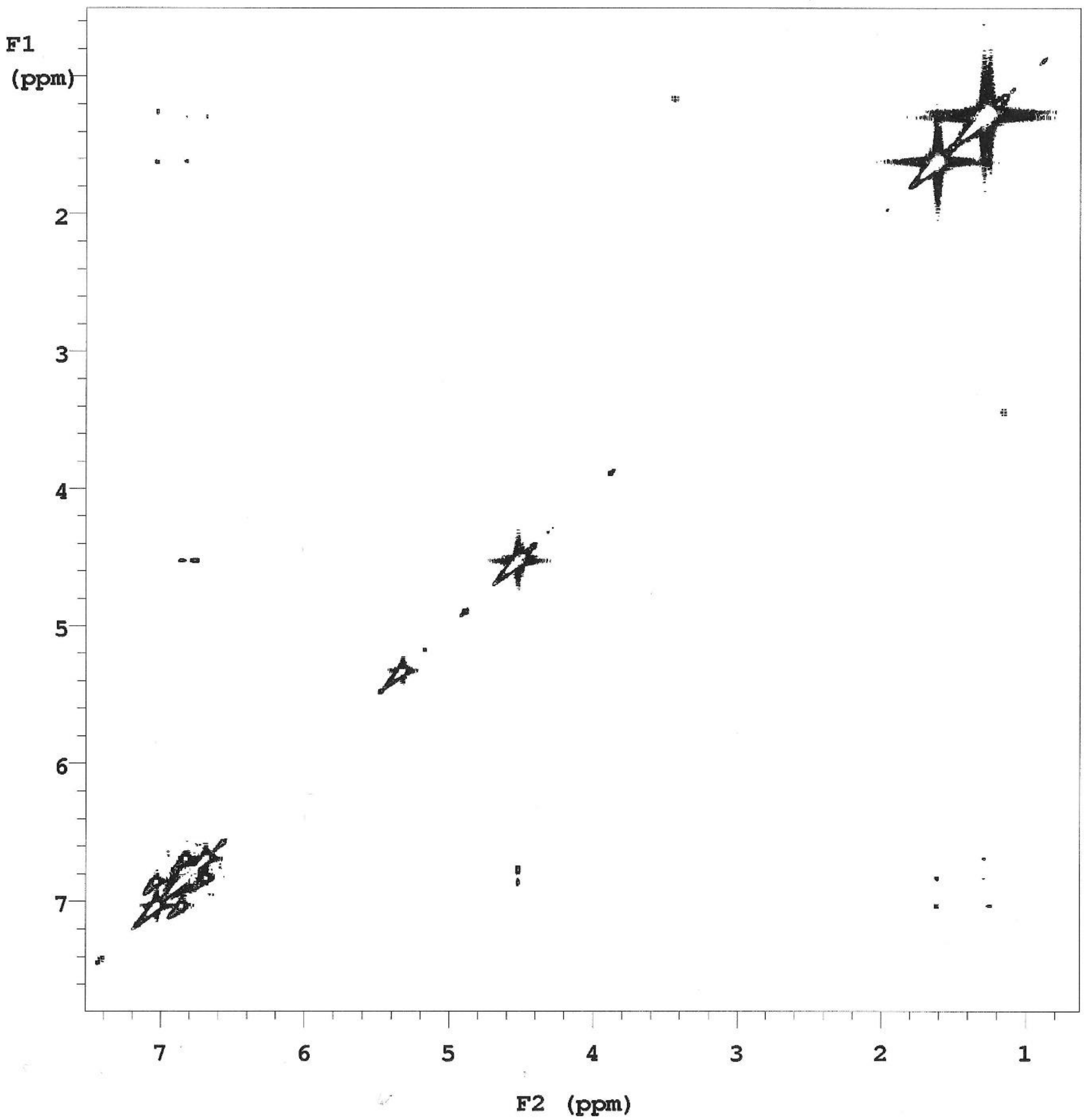

Figure S3. COSY NMR spectrum of **L1** (CD_2Cl_2, 600 MHz).

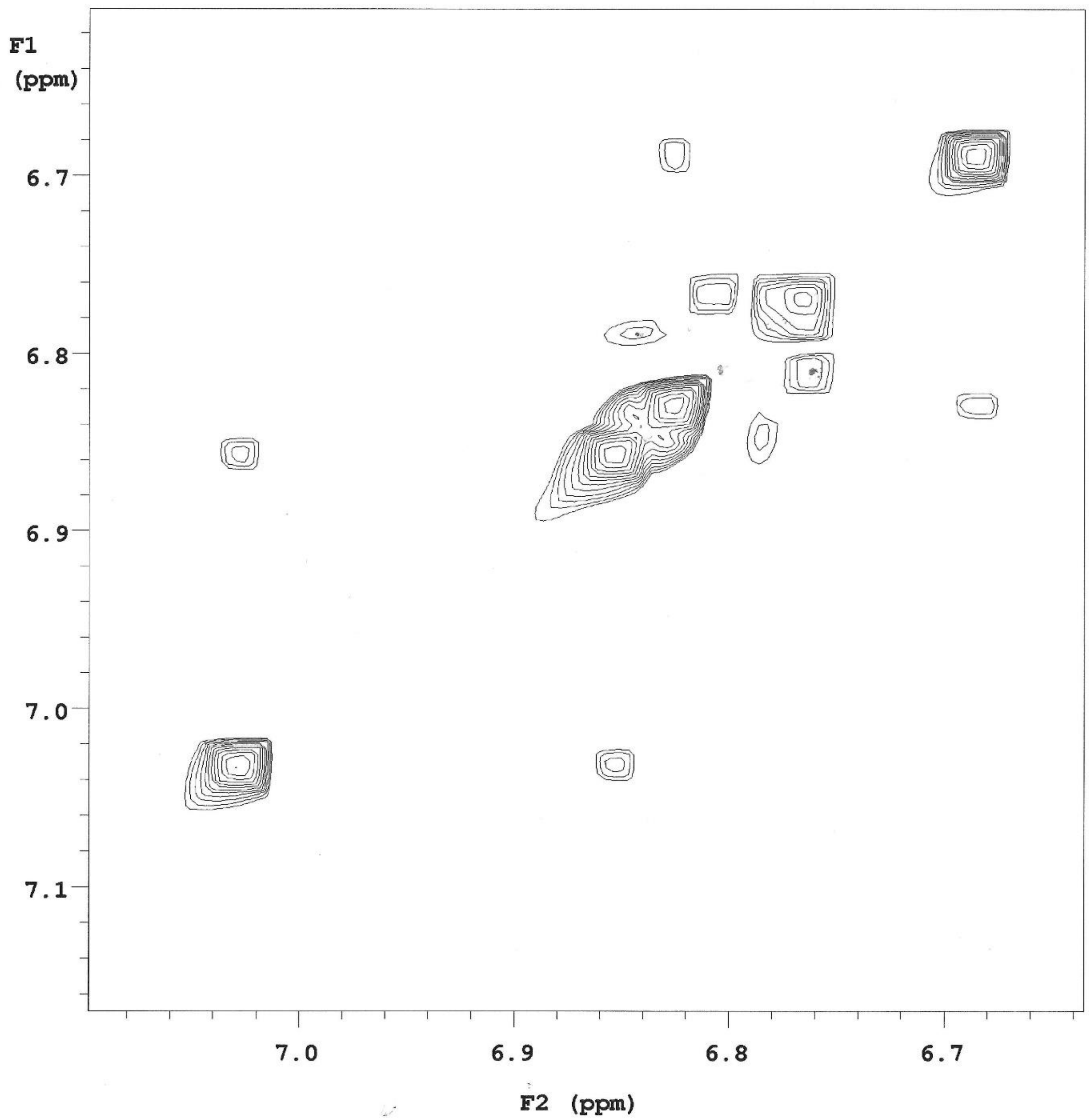

Figure S4. COSY spectrum of **L1** (CD_2Cl_2, 600 MHz) – aromatic region.

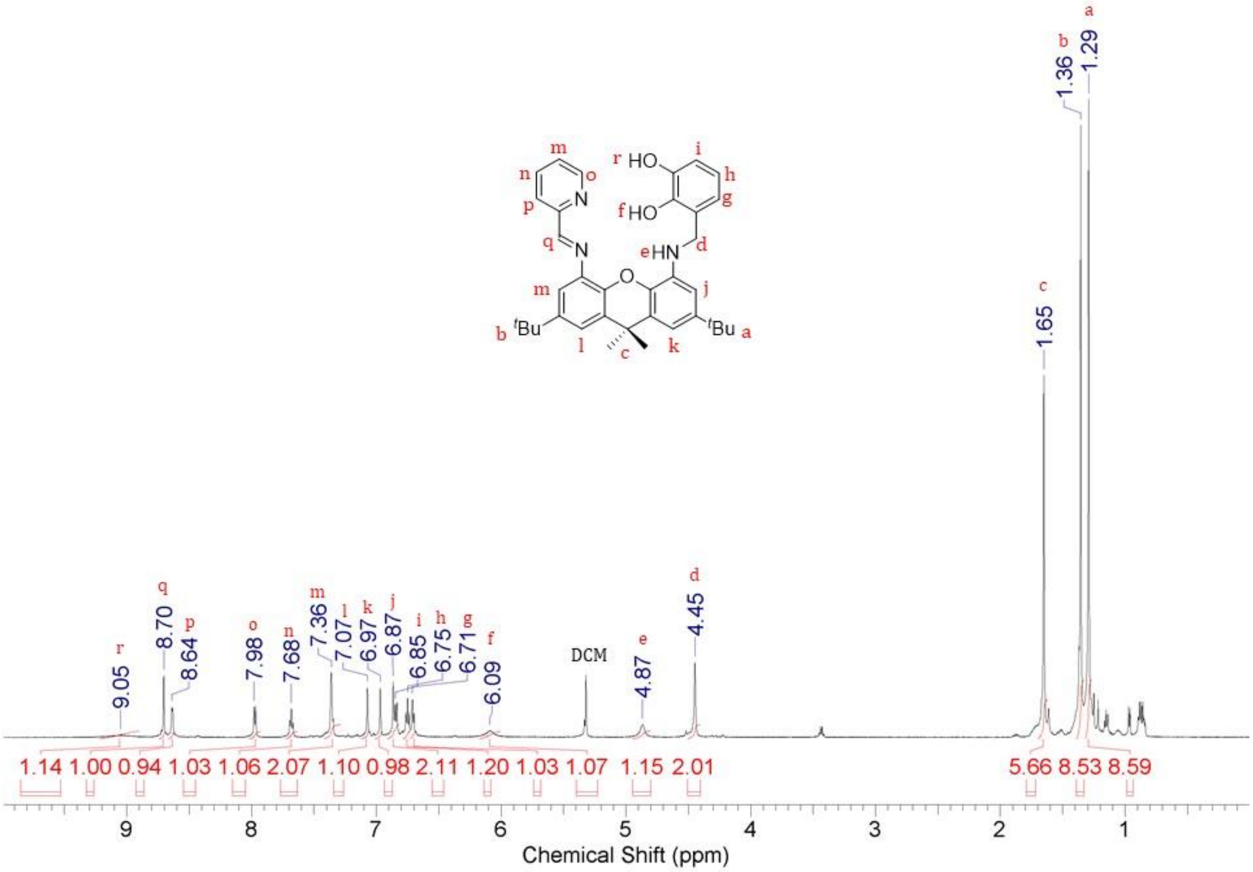

Figure S5. ^{1}H NMR spectrum of **LH₂** (CD_2Cl_2, 600 MHz).

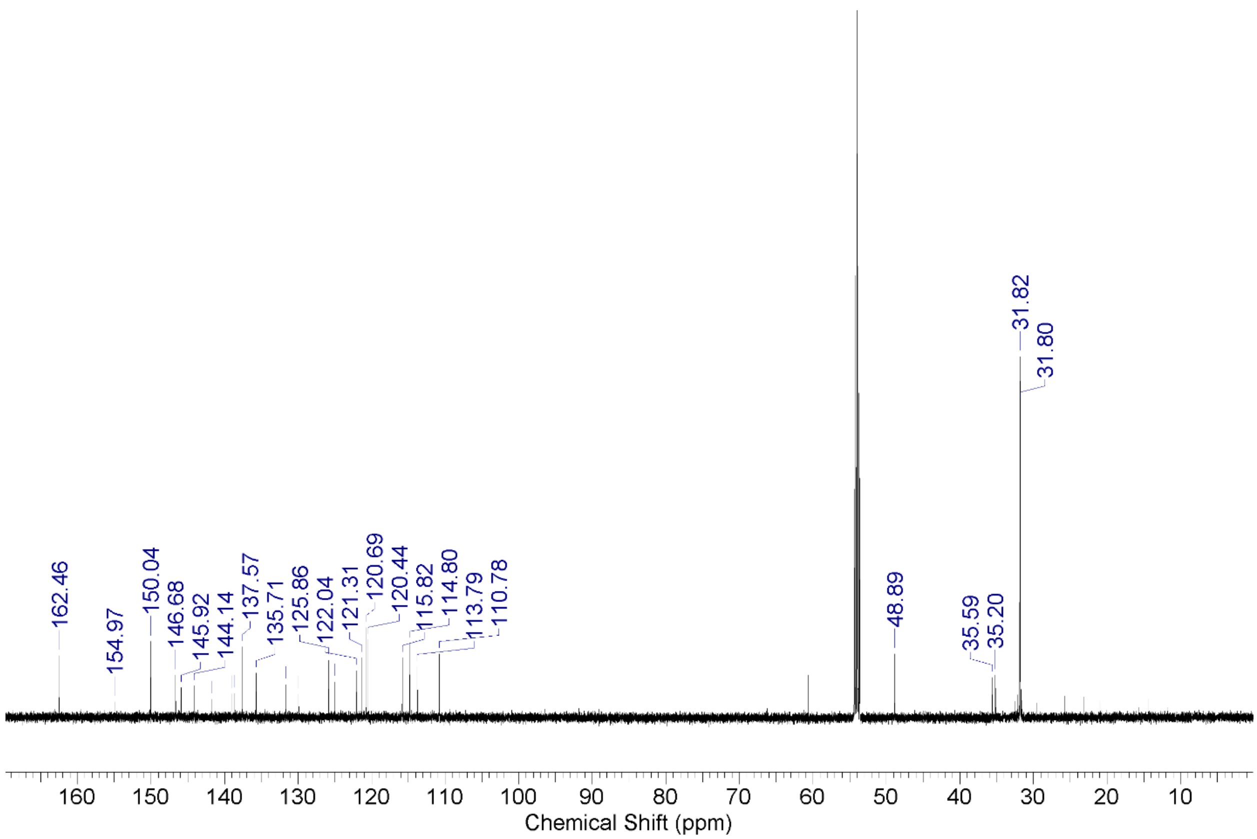

Figure S6. ^{13}C NMR spectrum of $\mathbf{LH_2}$ (CD_2Cl_2, 150 MHz).

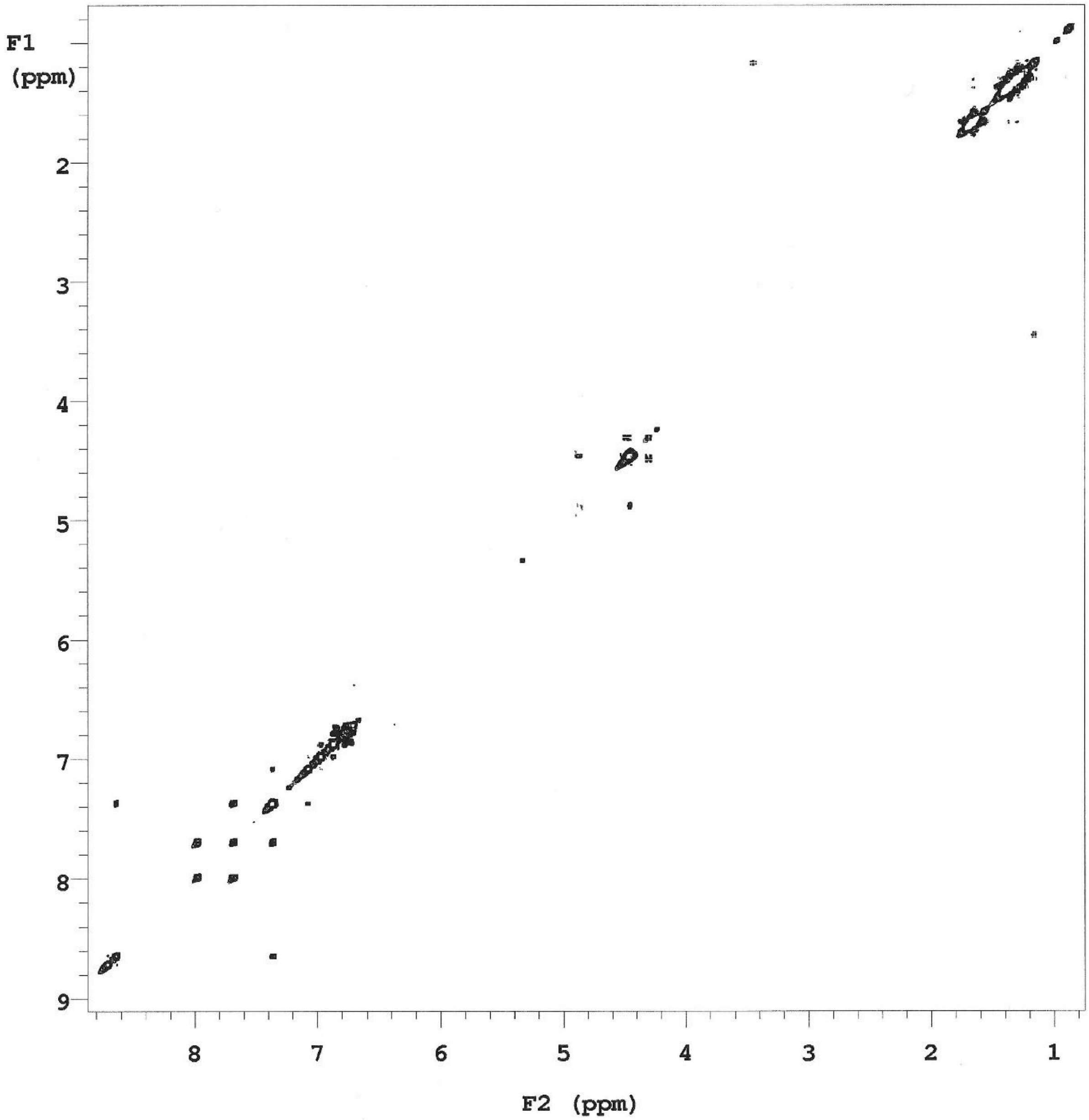

Figure S7. COSY NMR spectrum of $\mathbf{LH_2}$ (CD_2Cl_2, 600 MHz).

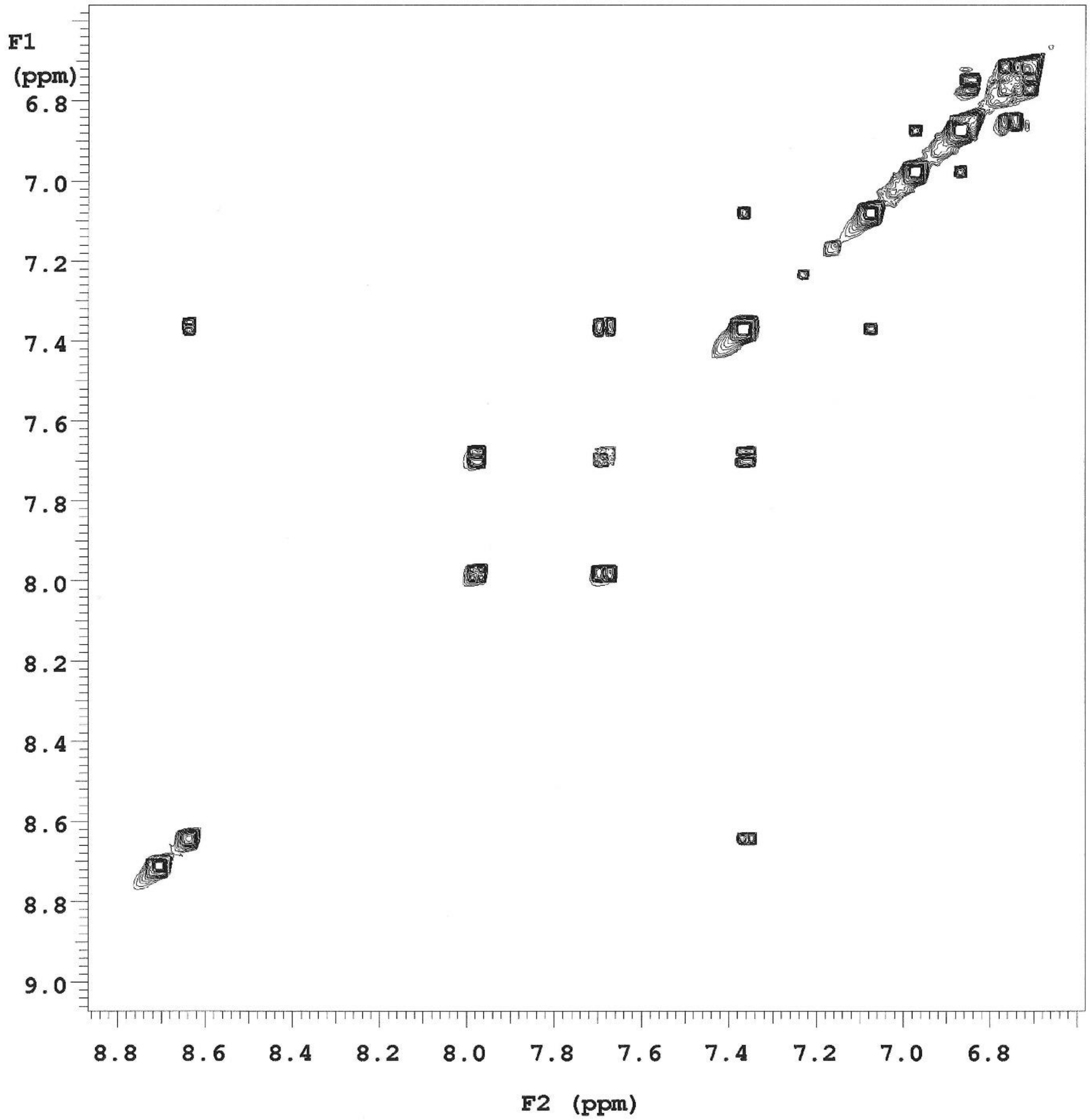

Figure S8. COSY NMR spectrum of **LH_2** (CD_2Cl_2, 600 MHz) – aromatic region.

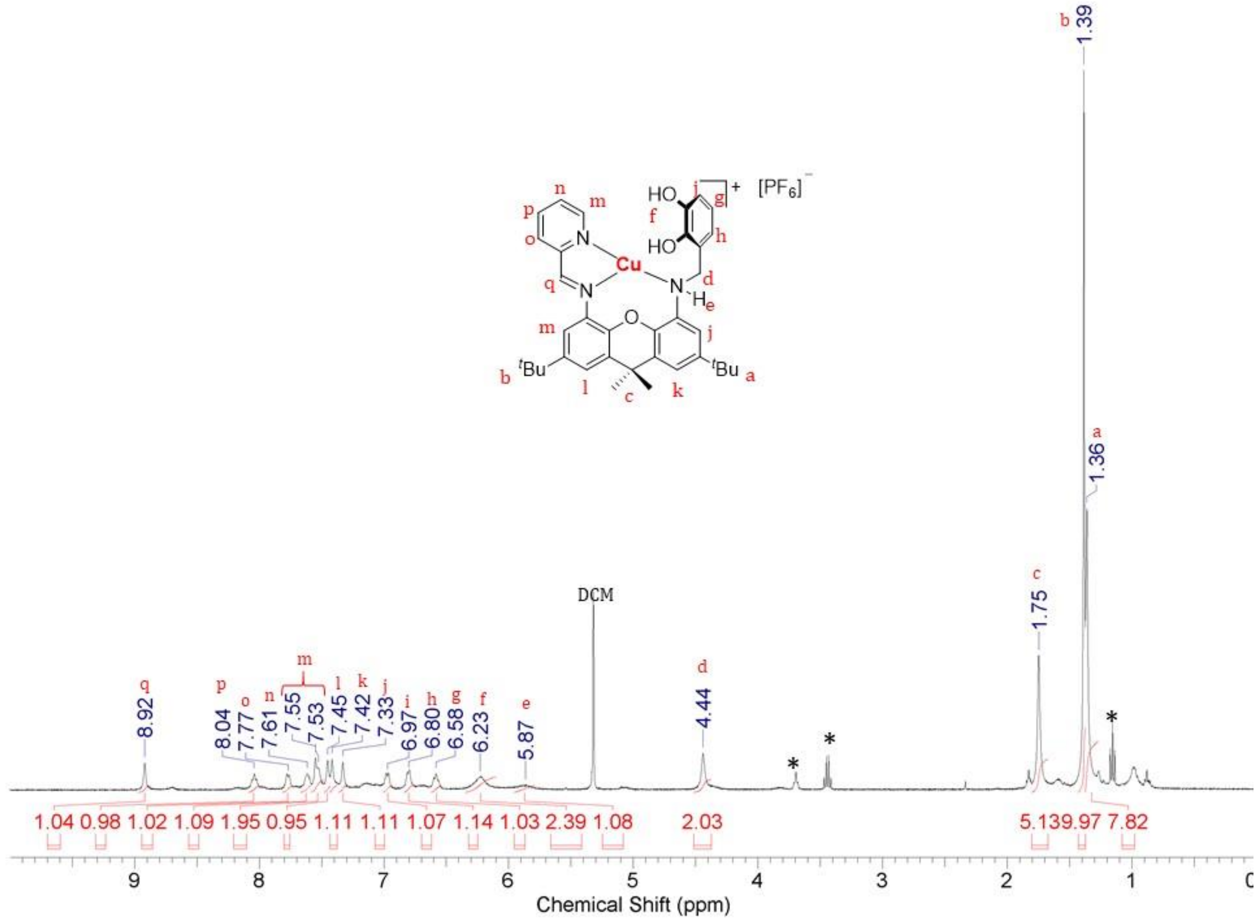

Figure S9. [1]H NMR spectrum of **1(PF$_6$)** (CD_2Cl_2, 500 MHz); * indicates residual THF and diethyl ether.

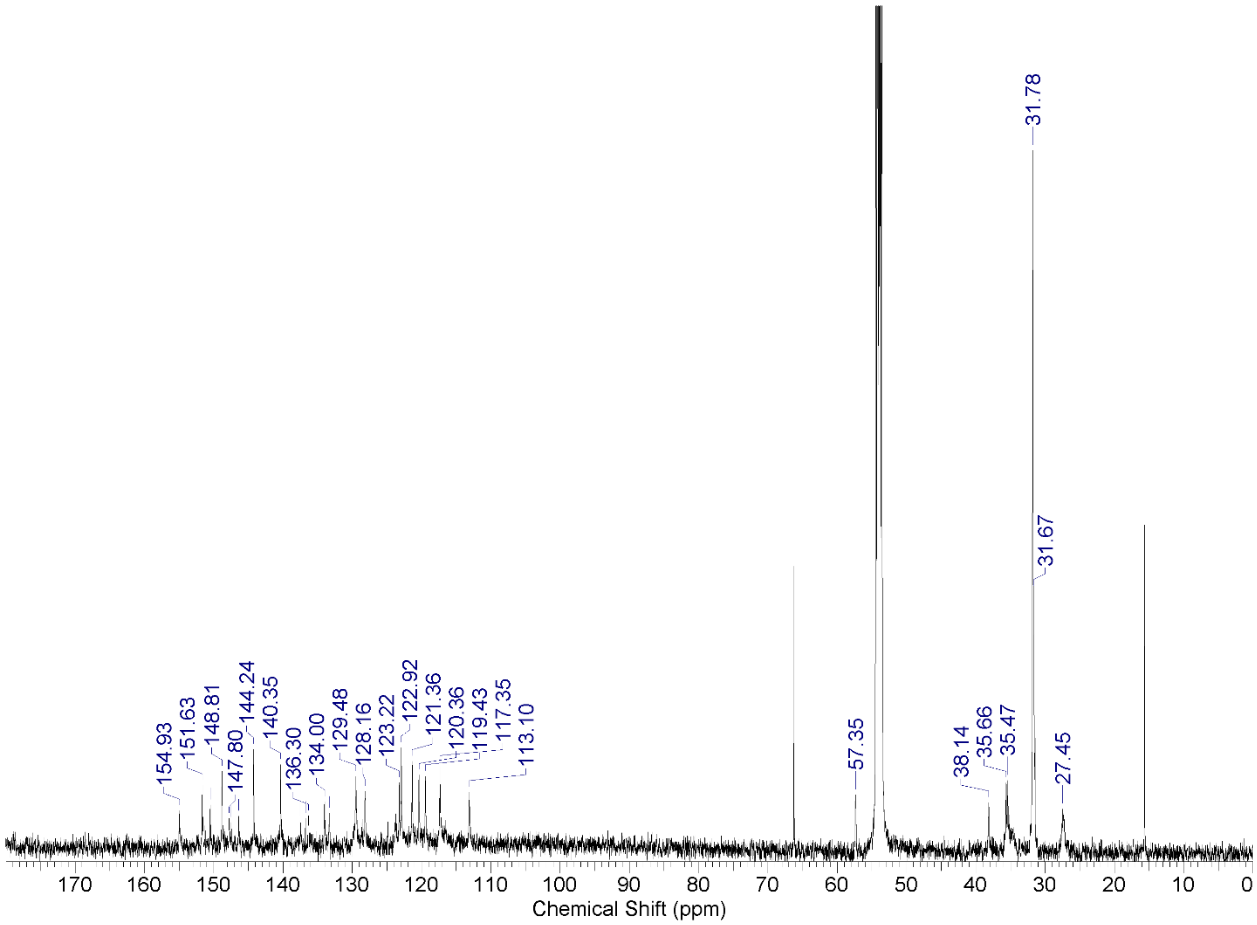

Figure S10. ^{13}C NMR spectrum of **1(PF$_6$)** (CD_2Cl_2, 125 MHz).

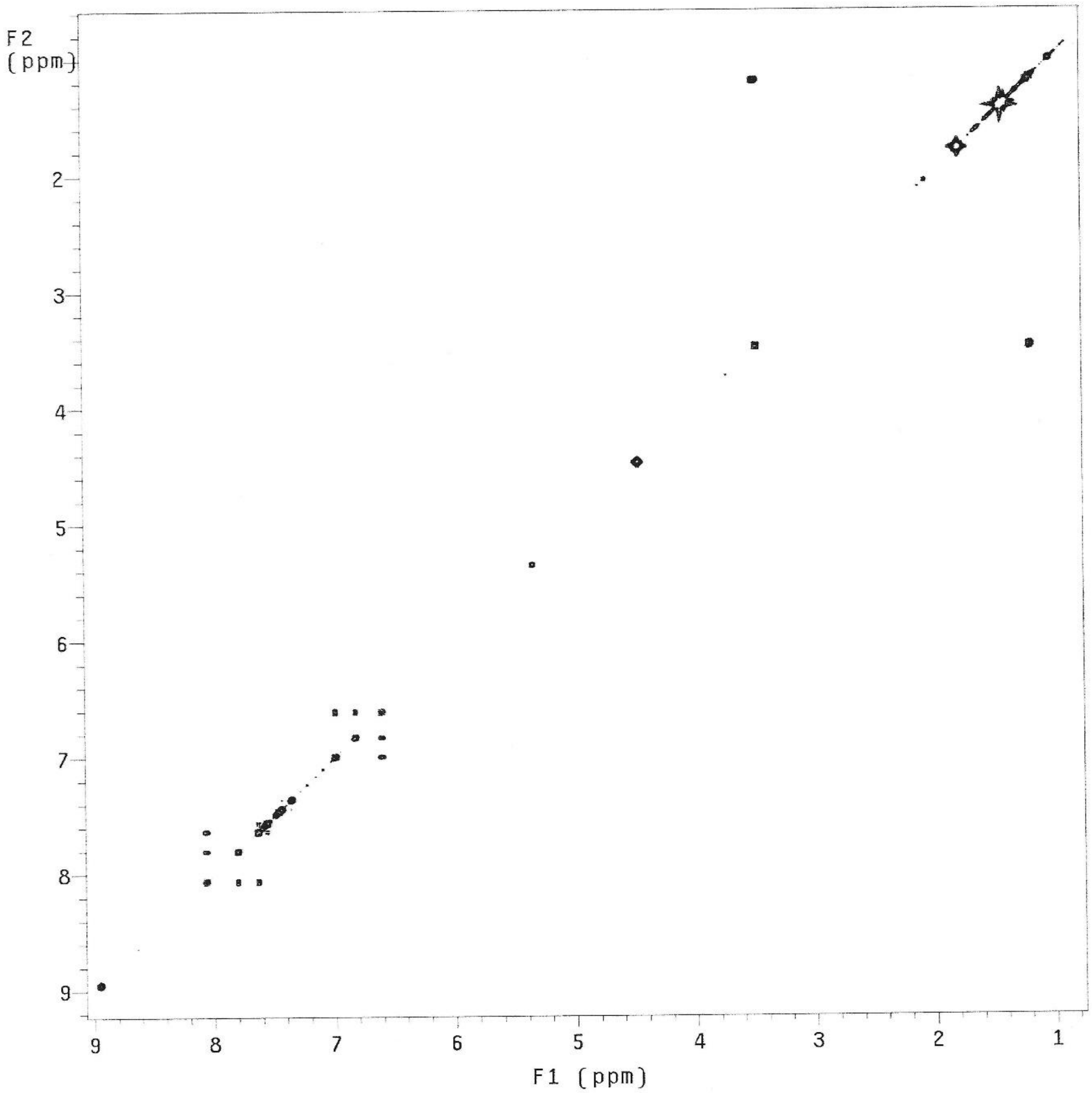

Figure S11. COSY NMR spectrum of **1(PF$_6$)** (CD_2Cl_2, 500 MHz).

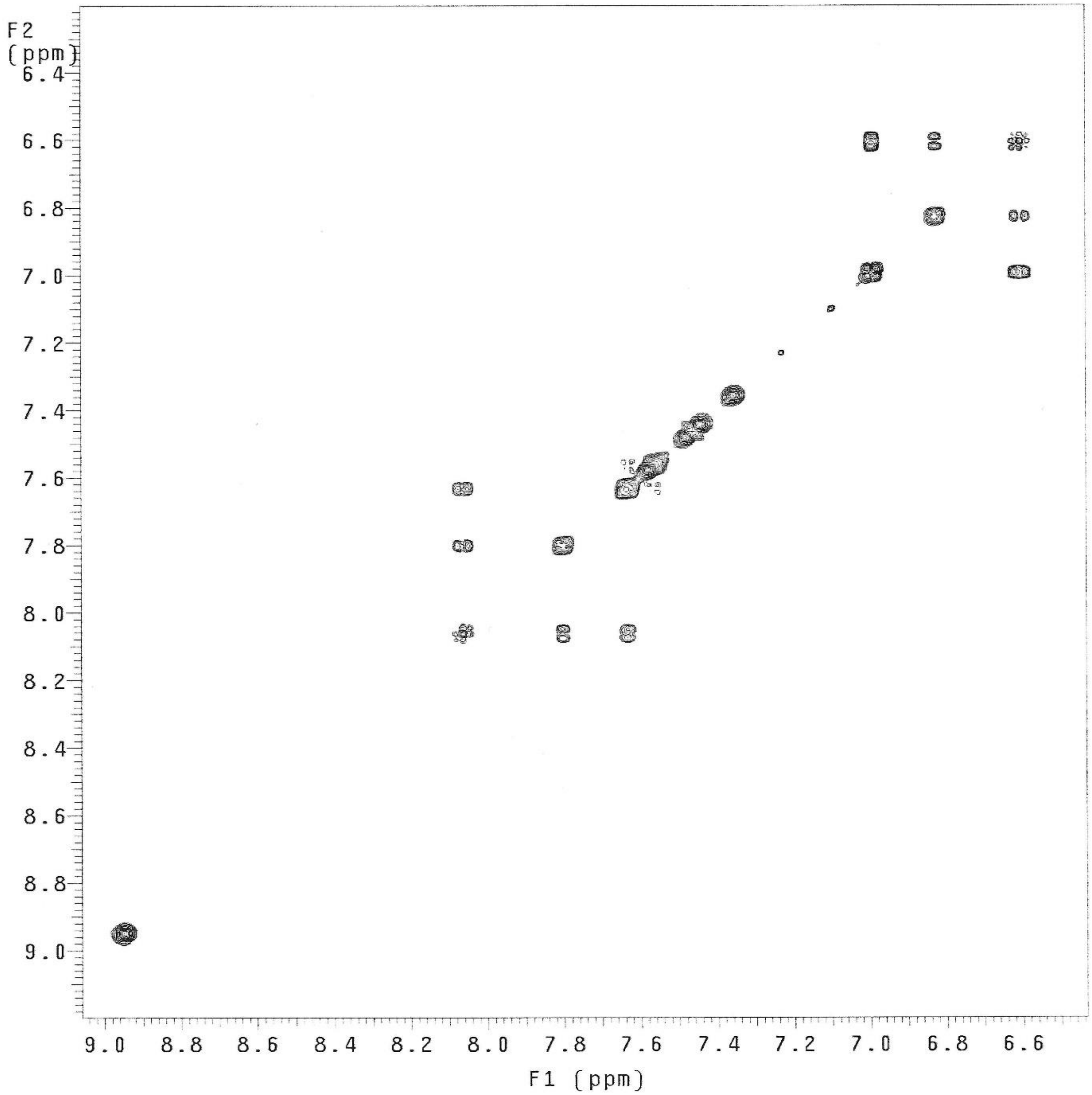

Figure S12. COSY NMR spectrum of **1(PF$_6$)** (CD_2Cl_2, 500 MHz) – aromatic region.

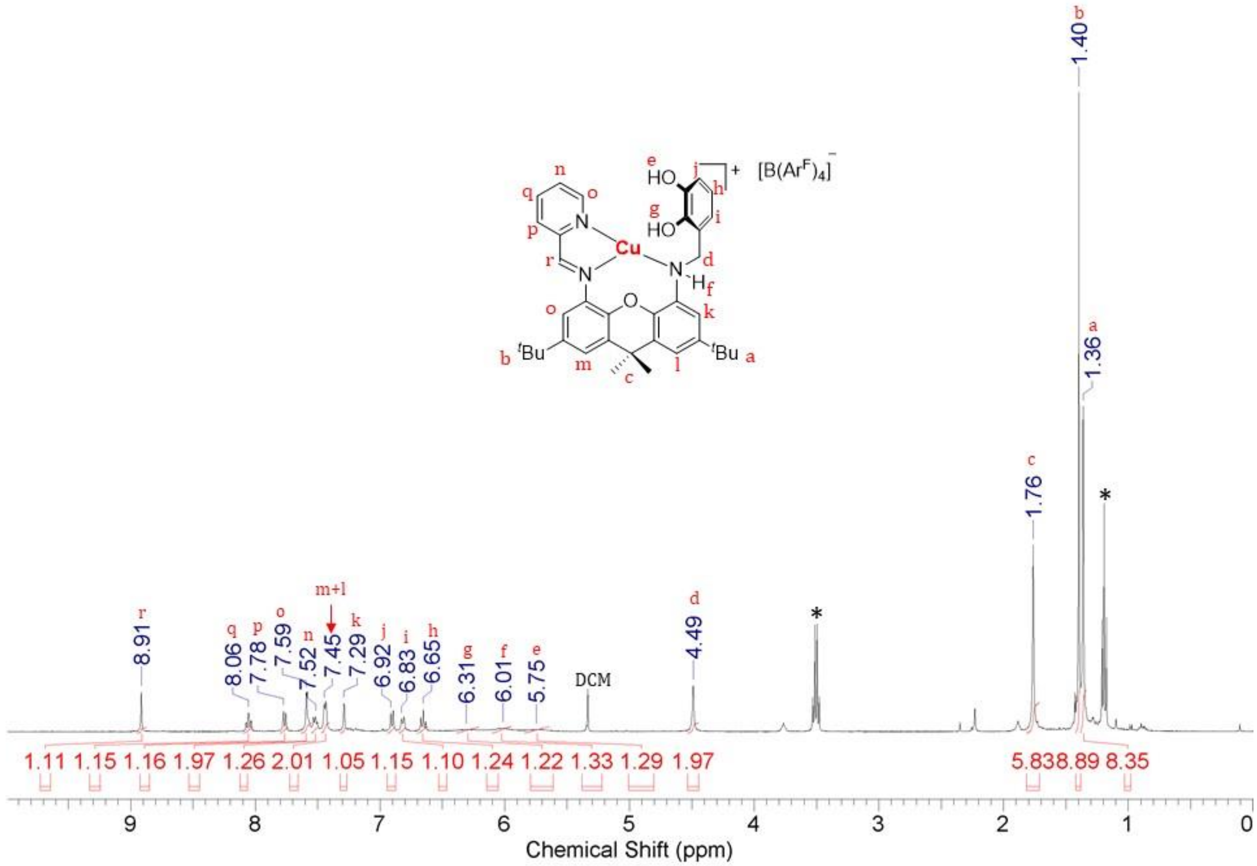

Figure S13. [1]H NMR spectrum of **1(B(C_6F_5)$_4$)** (CD_2Cl_2, 400 MHz); * indicates residual diethyl ether.

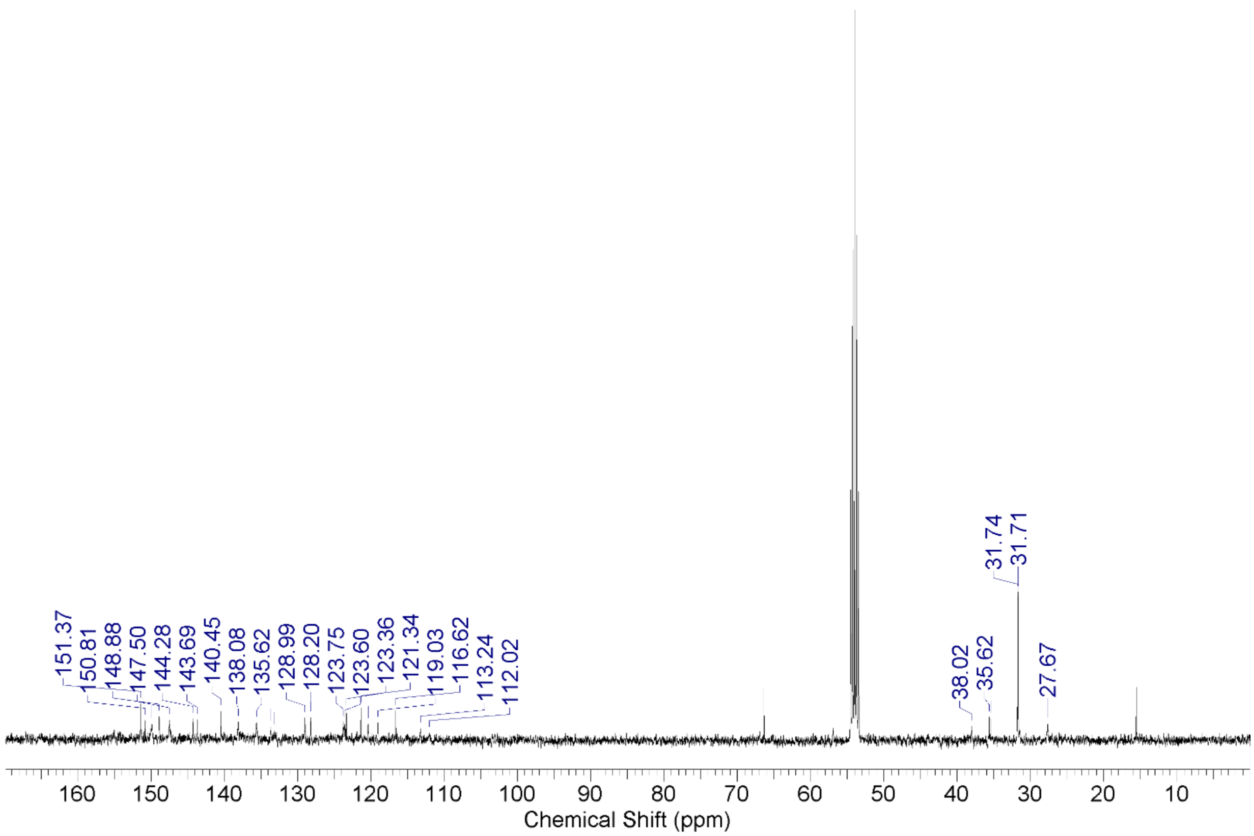

Figure S14. ^{13}C NMR spectrum of **1(B(C$_6$F$_5$)$_4$)** (CD$_2$Cl$_2$, 100 MHz).

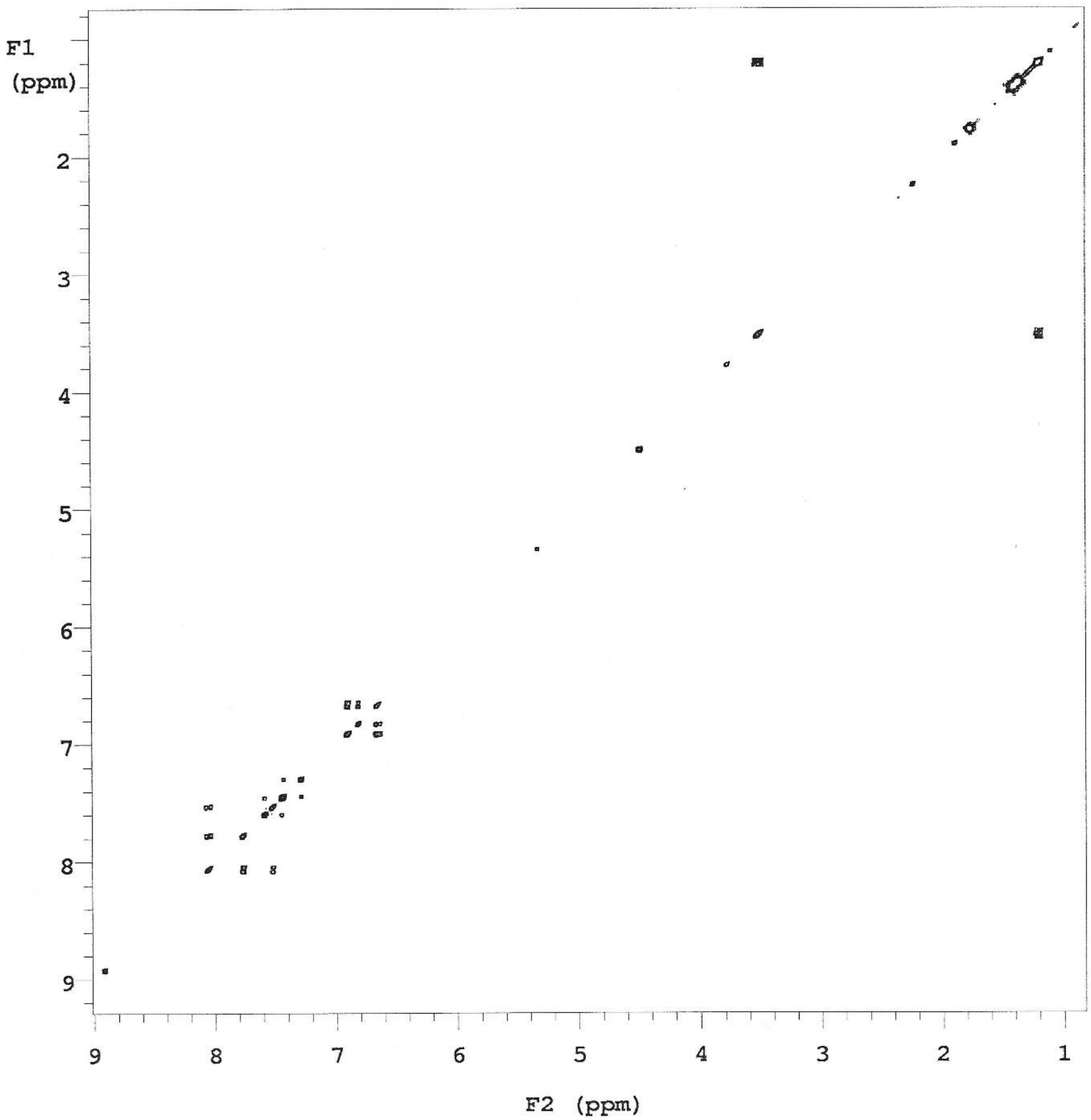

Figure S15. COSY NMR spectrum of **1(B(C_6F_5)$_4$)** (CD_2Cl_2, 400 MHz).

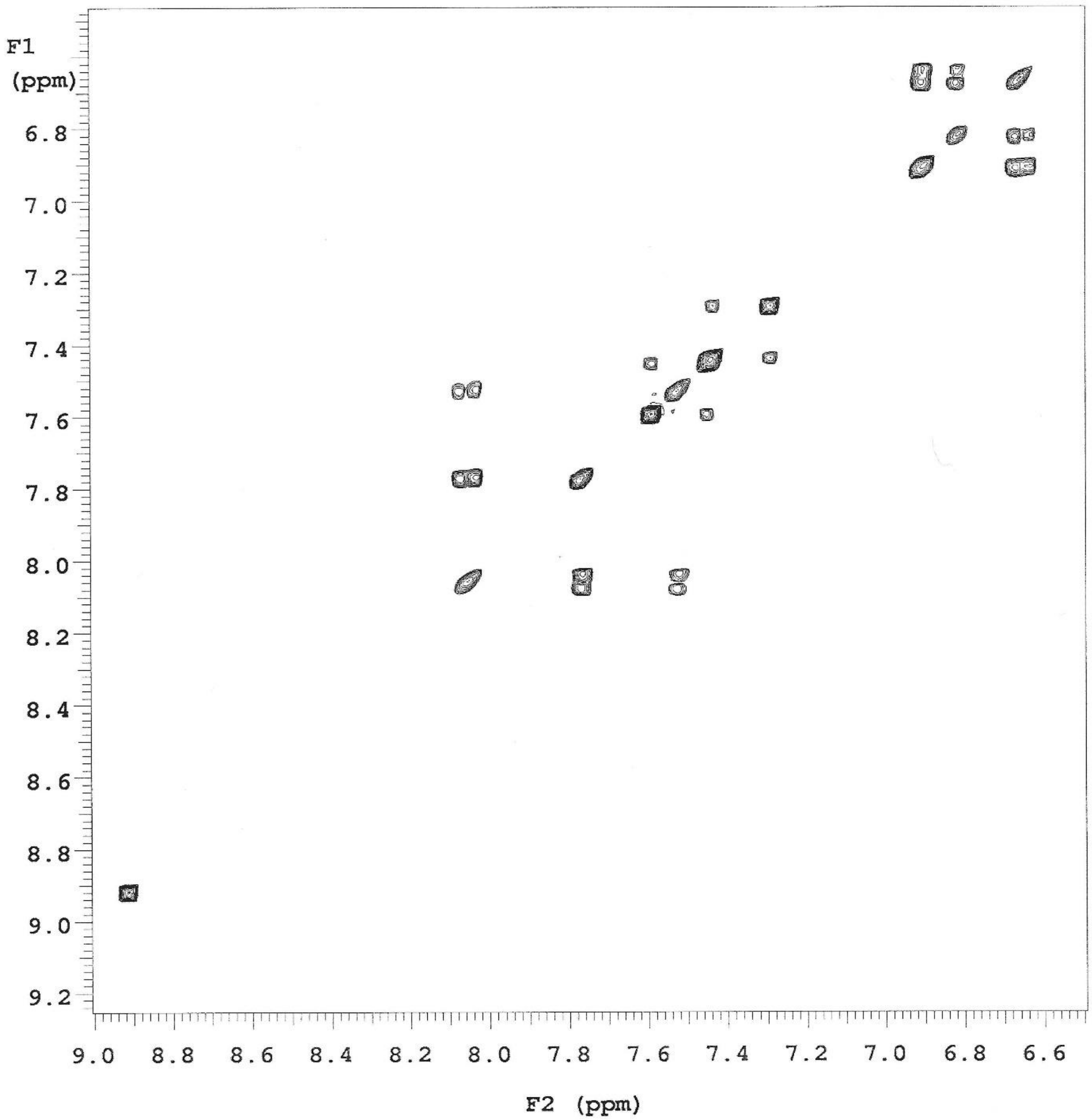

Figure S16. COSY NMR spectrum of **1(B(C_6F_5)$_4$)** (CD_2Cl_2, 400 MHz) – aromatic region.

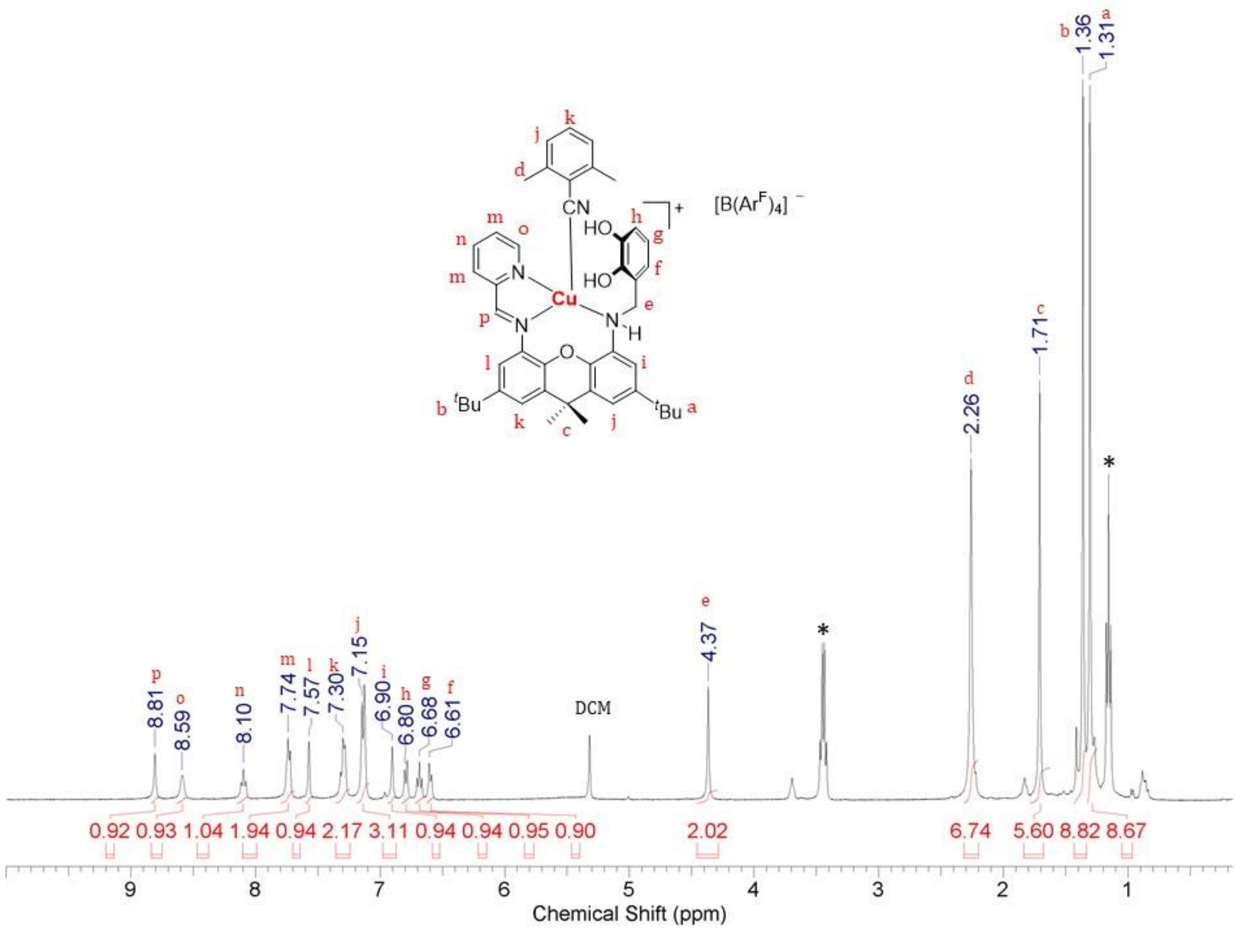

Figure S17. ^{1}H NMR spectrum of **2(B(C$_6$F$_5$)$_4$)**(CD$_2$Cl$_2$, 600 MHz); * indicates residual diethyl ether.

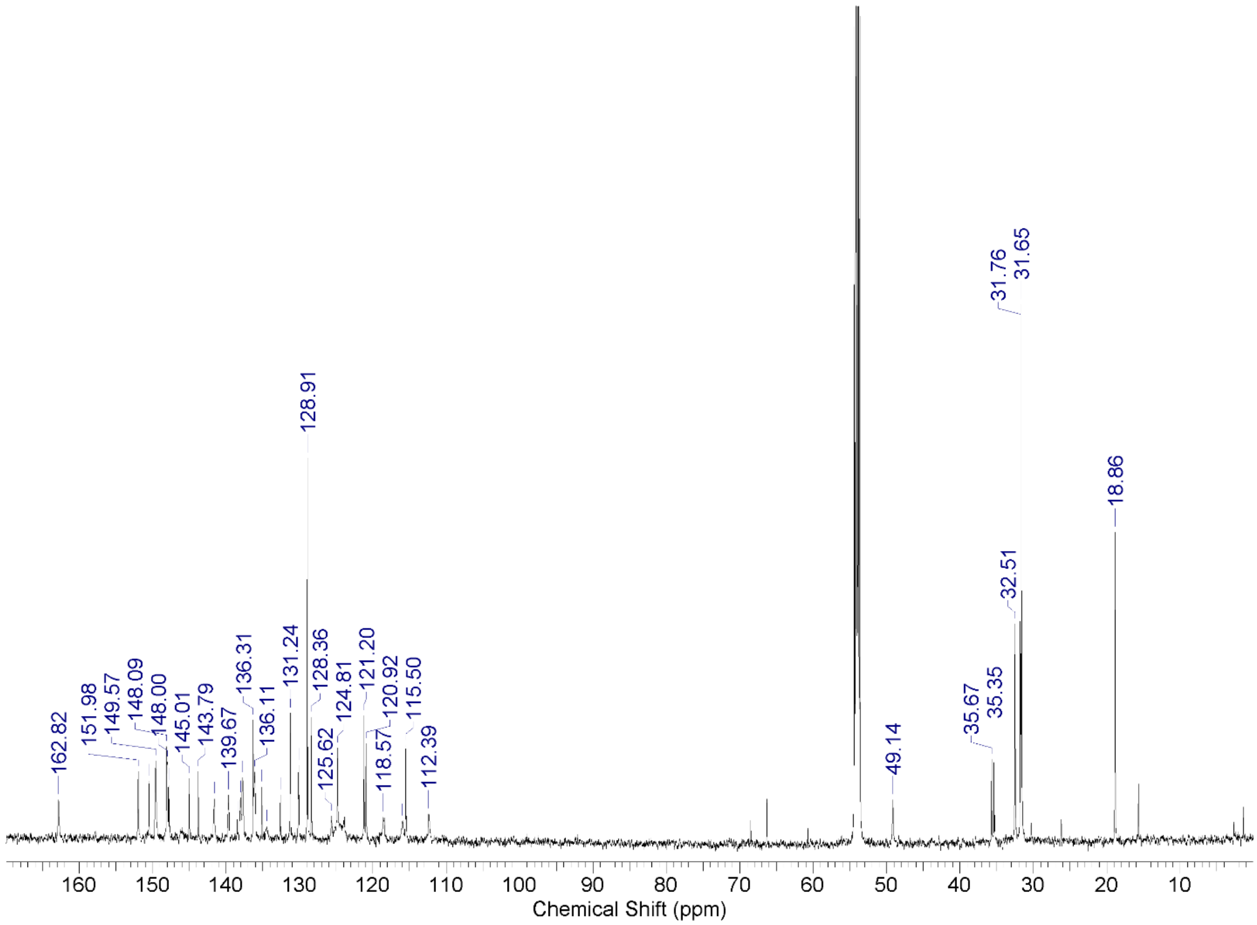

Figure S18. ^{13}C NMR spectrum of **$2(B(C_6F_5)_4)$** (CD_2Cl_2, 150 MHz).

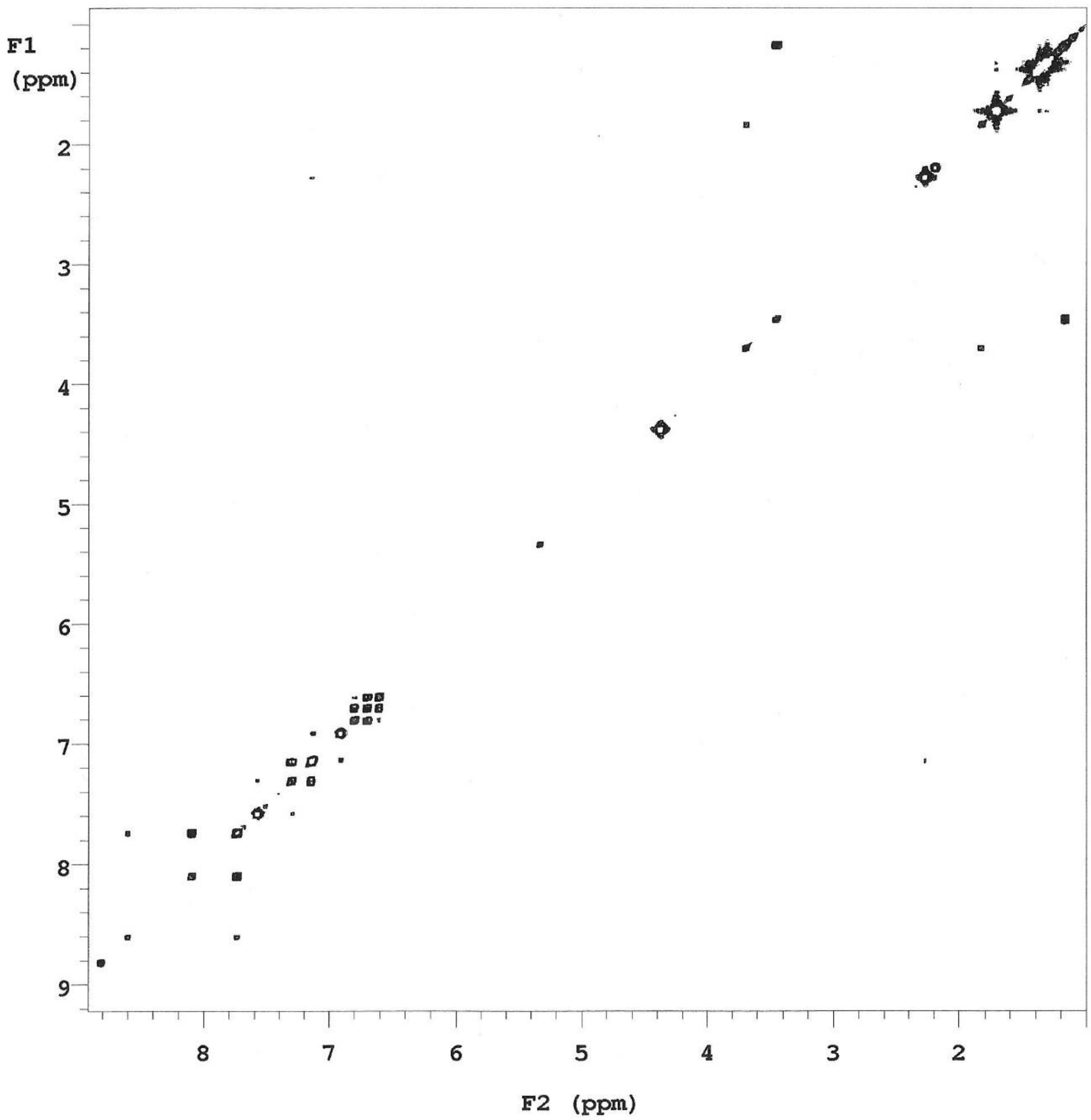

Figure S19. COSY NMR spectrum of **2(B(C_6F_5)$_4$)** (CD_2Cl_2, 600 MHz).

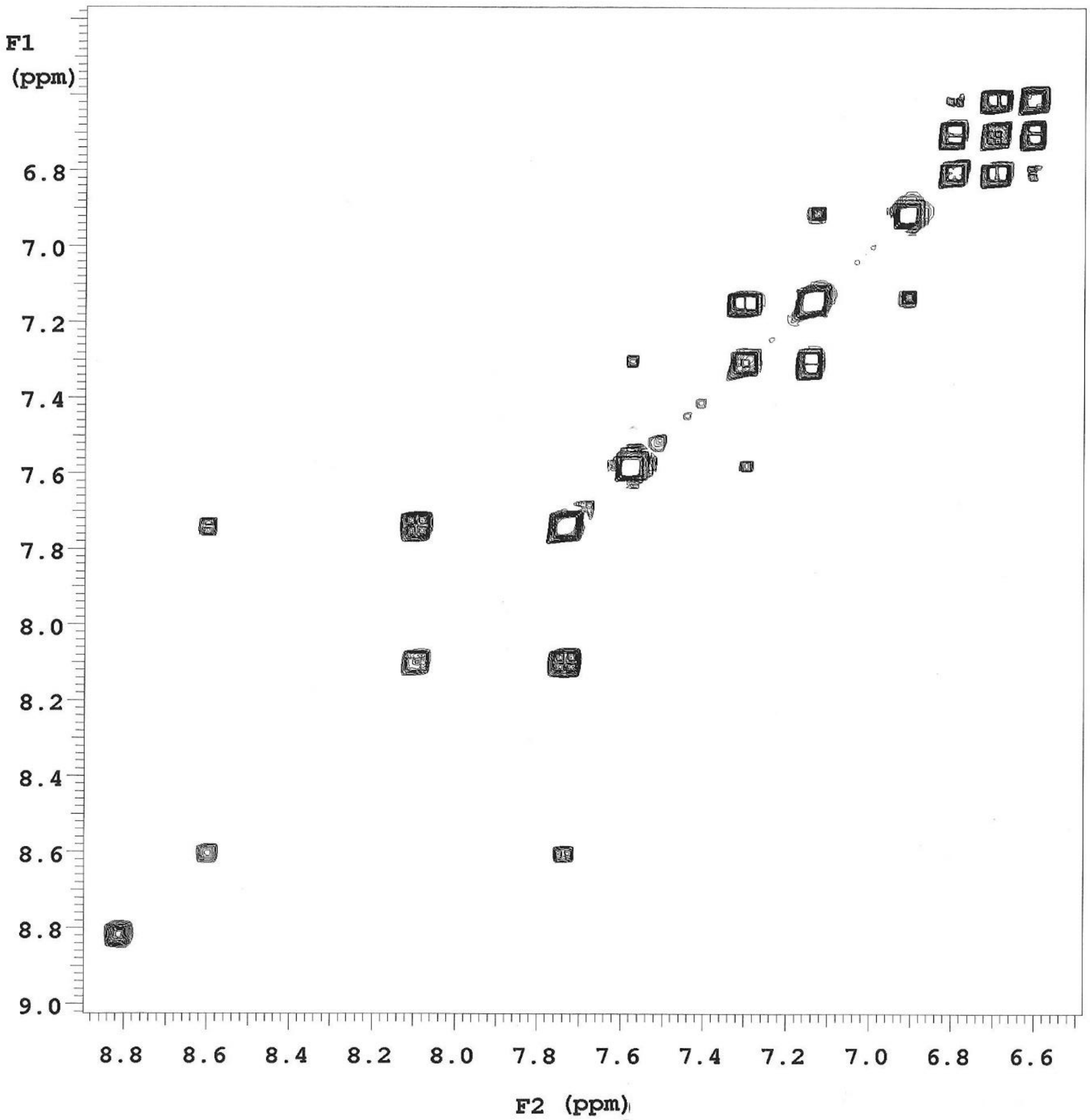

Figure S20. COSY NMR spectrum of complex **2(B(C_6F_5)$_4$)** (CD_2Cl_2, 600 MHz) – aromatic region.

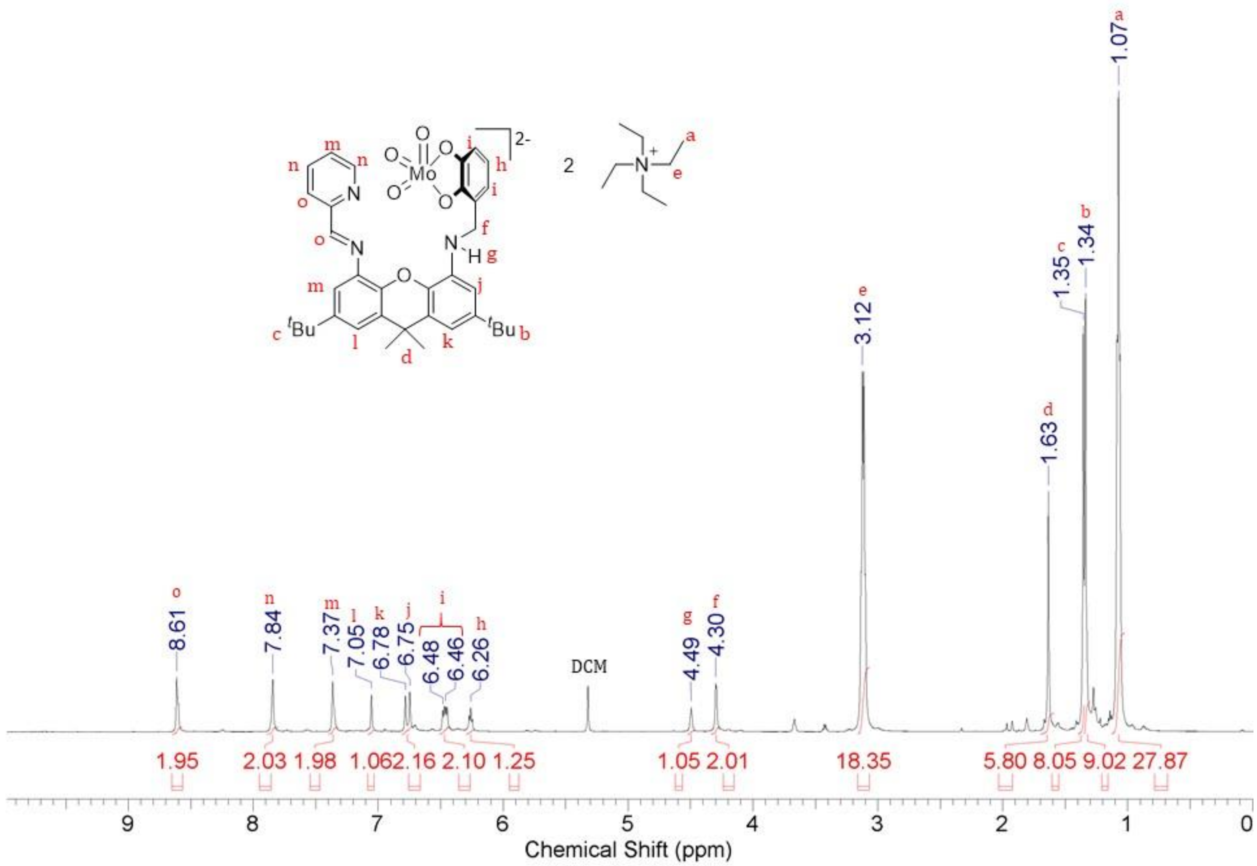

Figure S21. ^{1}H NMR spectrum of complex **$3(NEt_4)_2$** (CD_2Cl_2, 600 MHz).

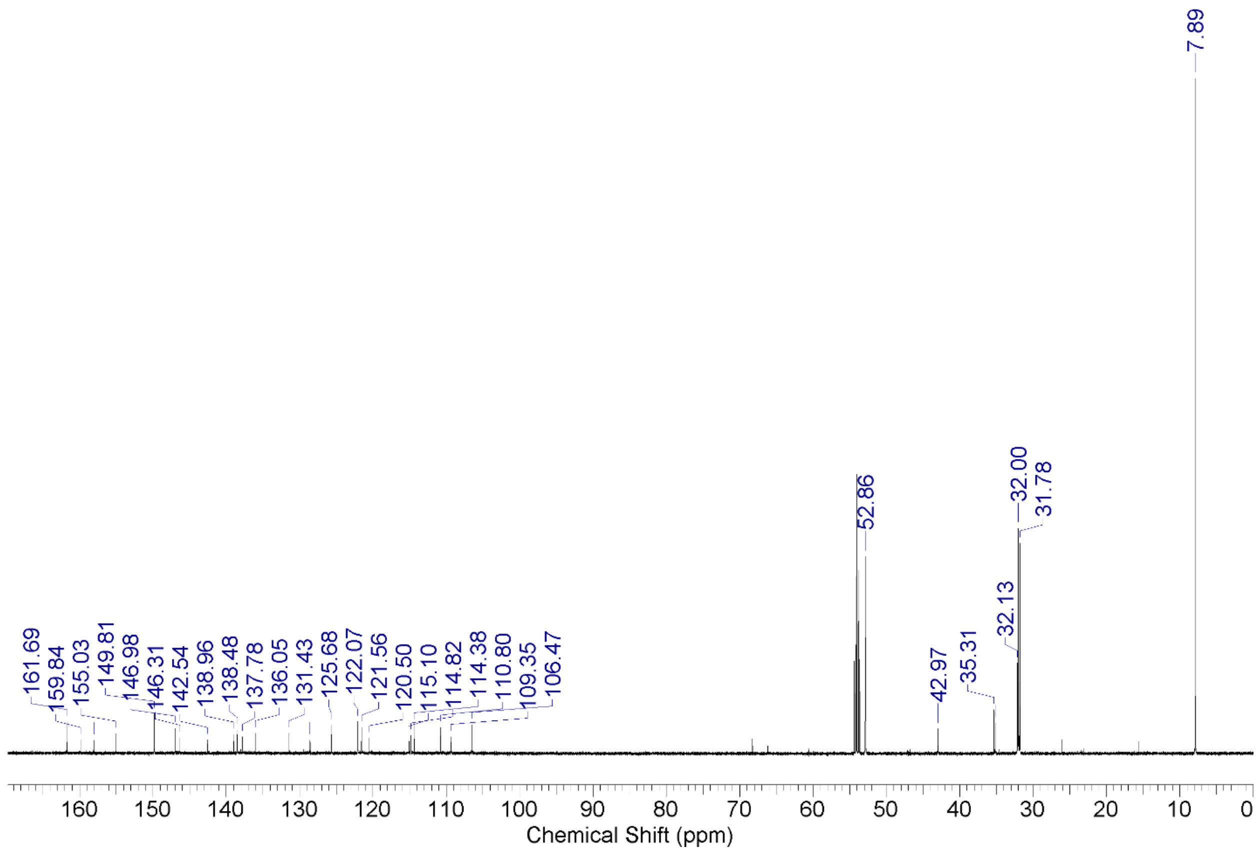

Figure S22. ^{13}C NMR spectrum of complex **3(NEt$_4$)$_2$** (CD_2Cl_2, 150 MHz).

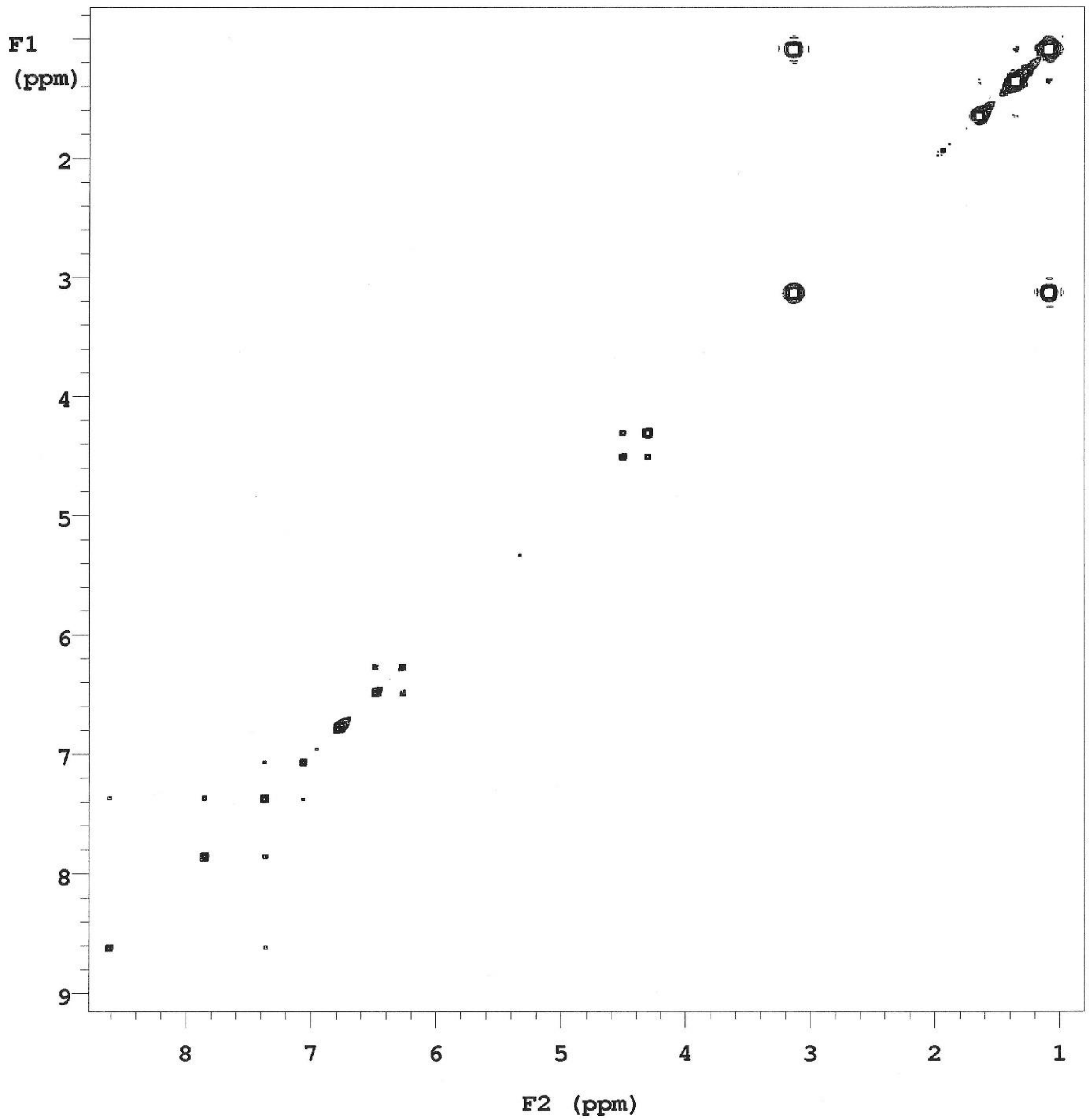

Figure S23. COSY NMR spectrum of **3(NEt$_4$)$_2$** (CD_2Cl_2, 600 MHz).

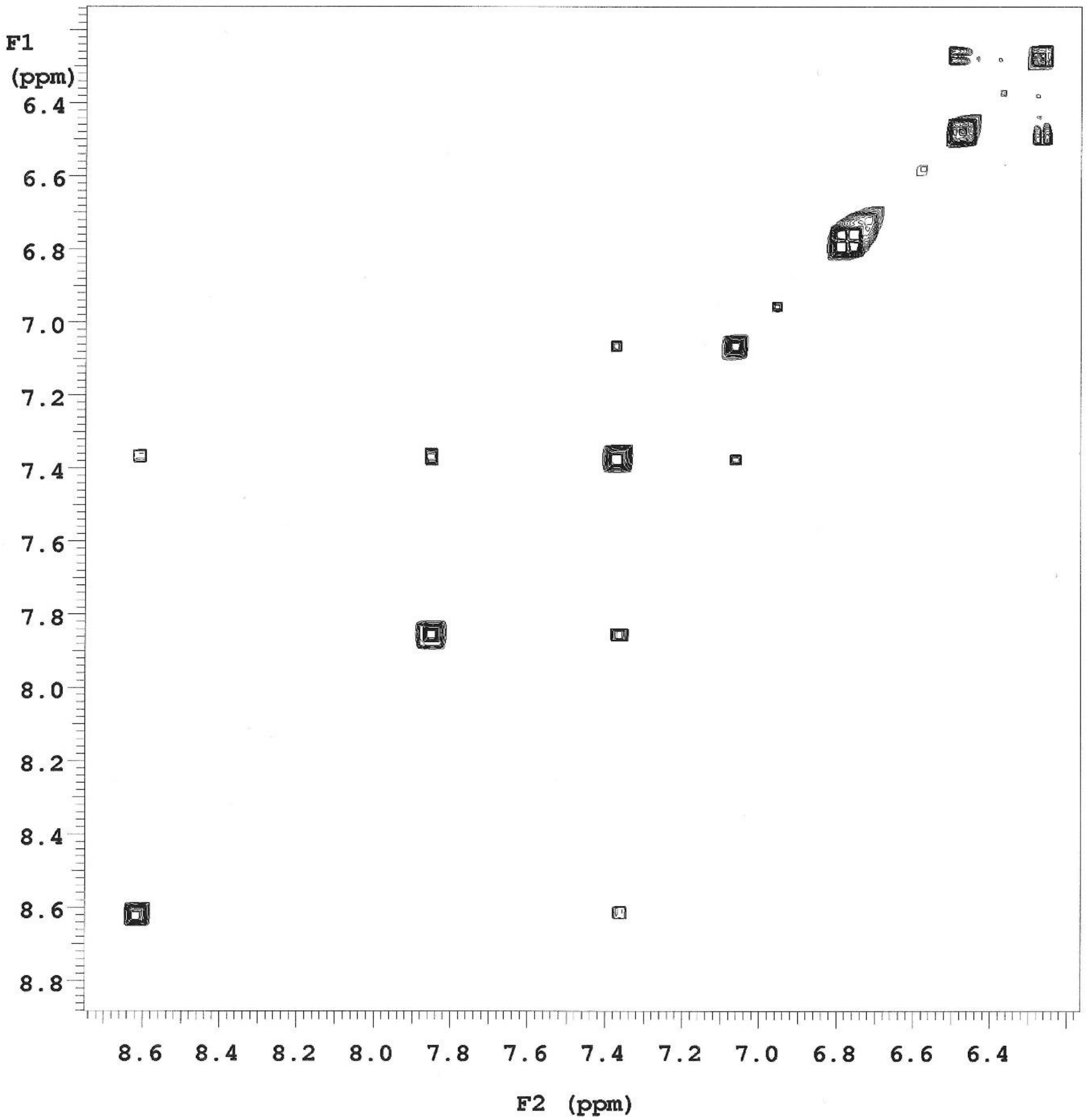

Figure S24. COSY NMR spectrum of complex **3(NEt$_4$)$_2$** (CD_2Cl_2, 600 MHz) – aromatic region.

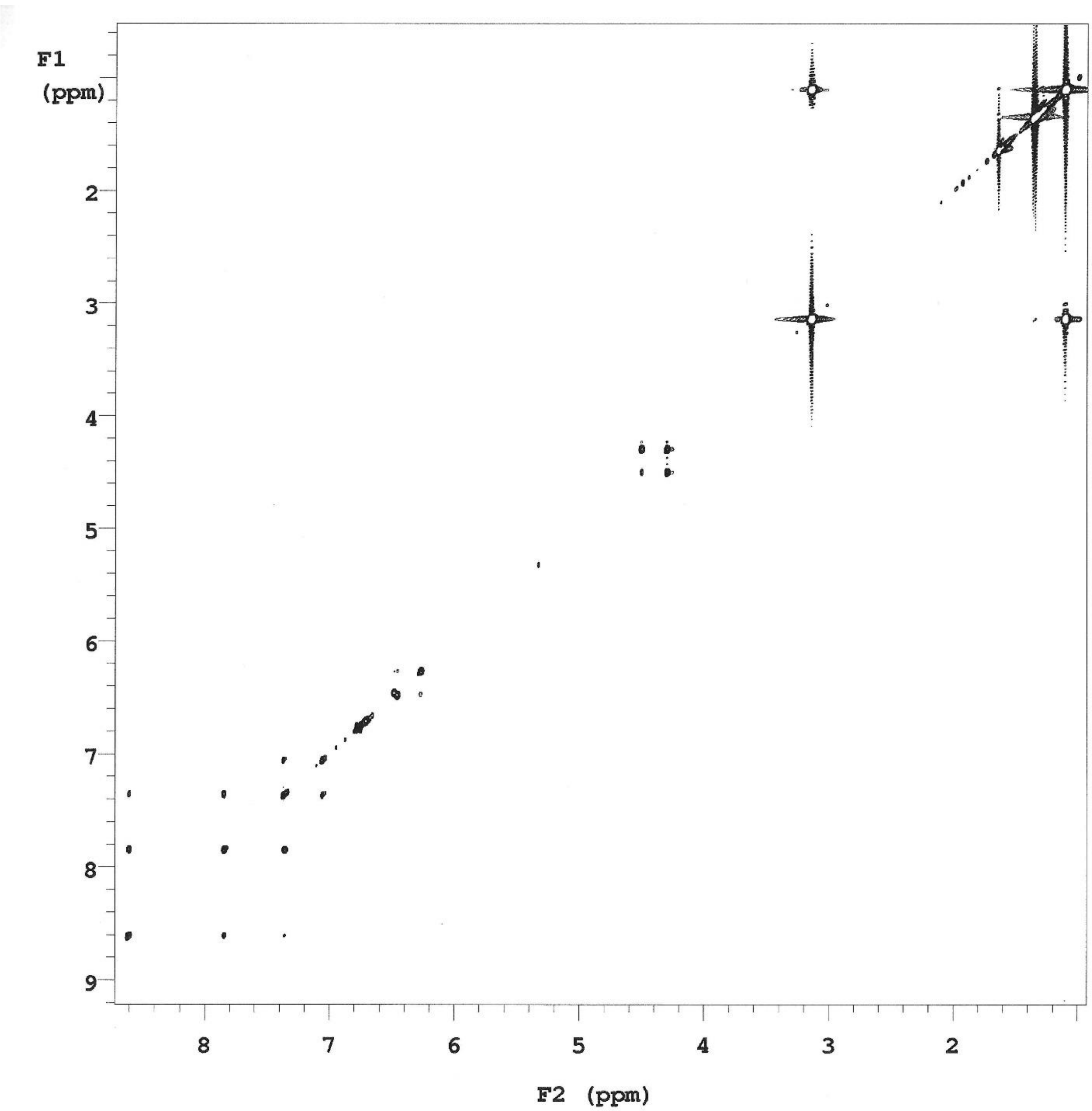

Figure S25. TOCSY NMR spectrum of complex **$3(NEt_4)_2$** (CD_2Cl_2, 600 MHz).

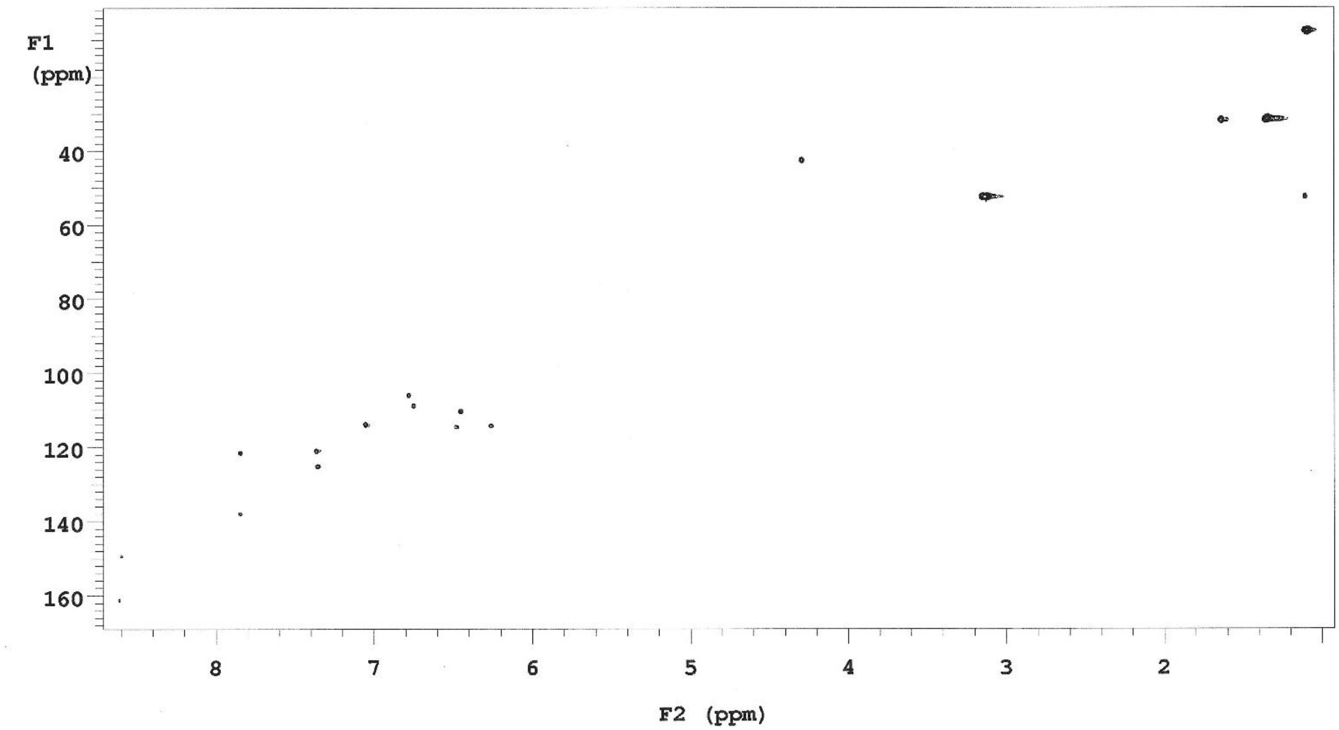

Figure S26. HSQC NMR spectrum of complex **3(NEt$_4$)$_2$** (CD_2Cl_2, 600 MHz).

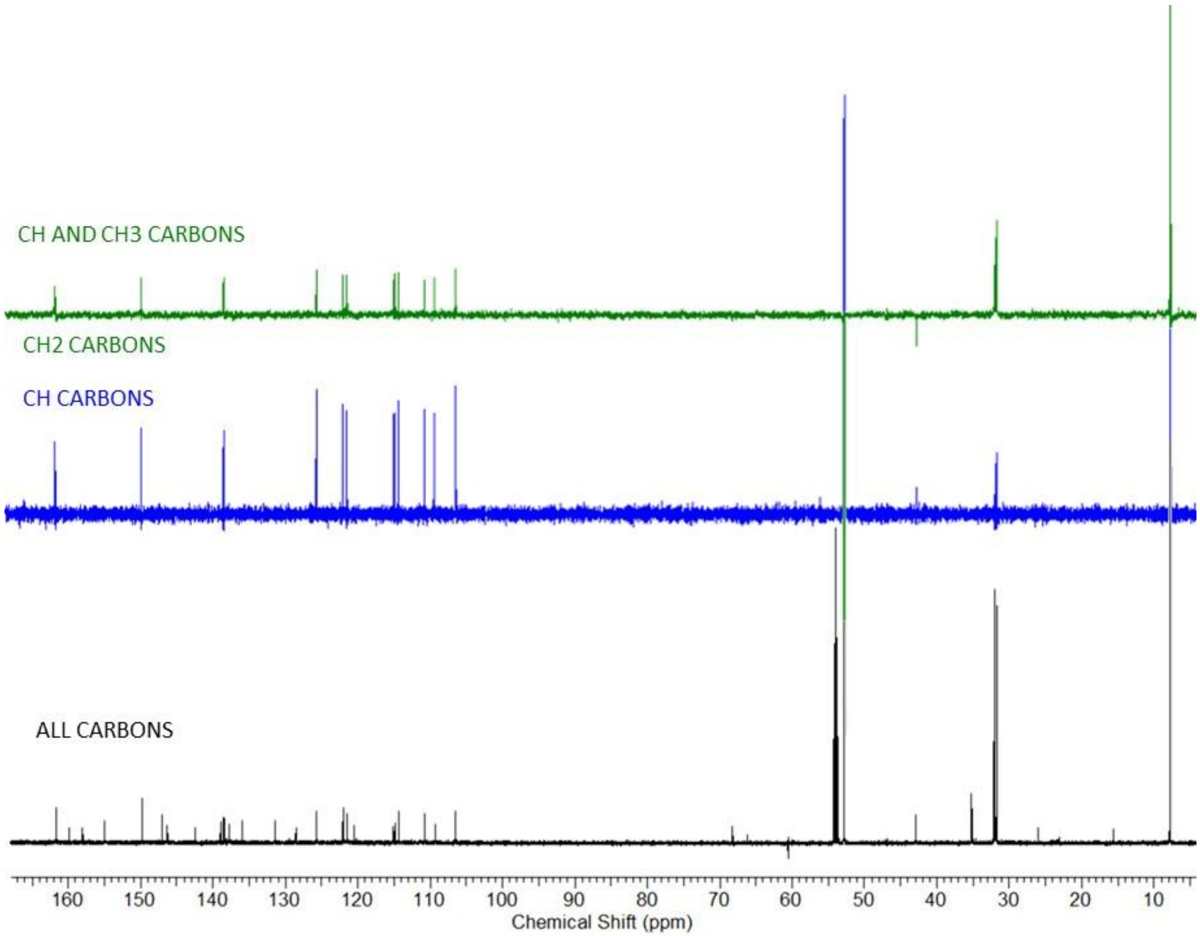

Figure S27. ^{13}C DEPT NMR spectrum of complex **3(NEt$_4$)$_2$** (CD_2Cl_2, 150 MHz).

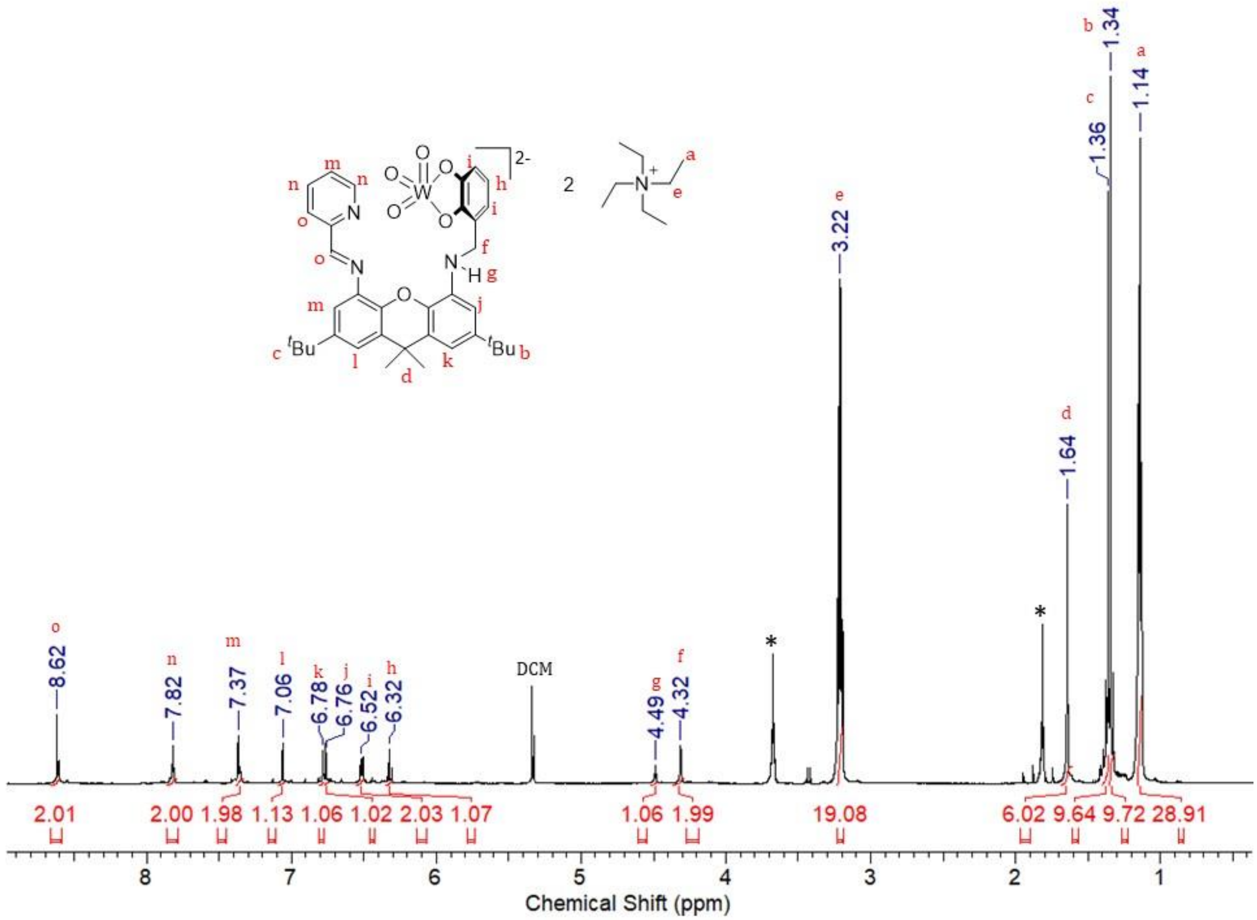

Figure S28. [1]H NMR spectrum of complex **$4(NEt_4)_2$** (CD_2Cl_2, 600 MHz); * indicates residual THF.

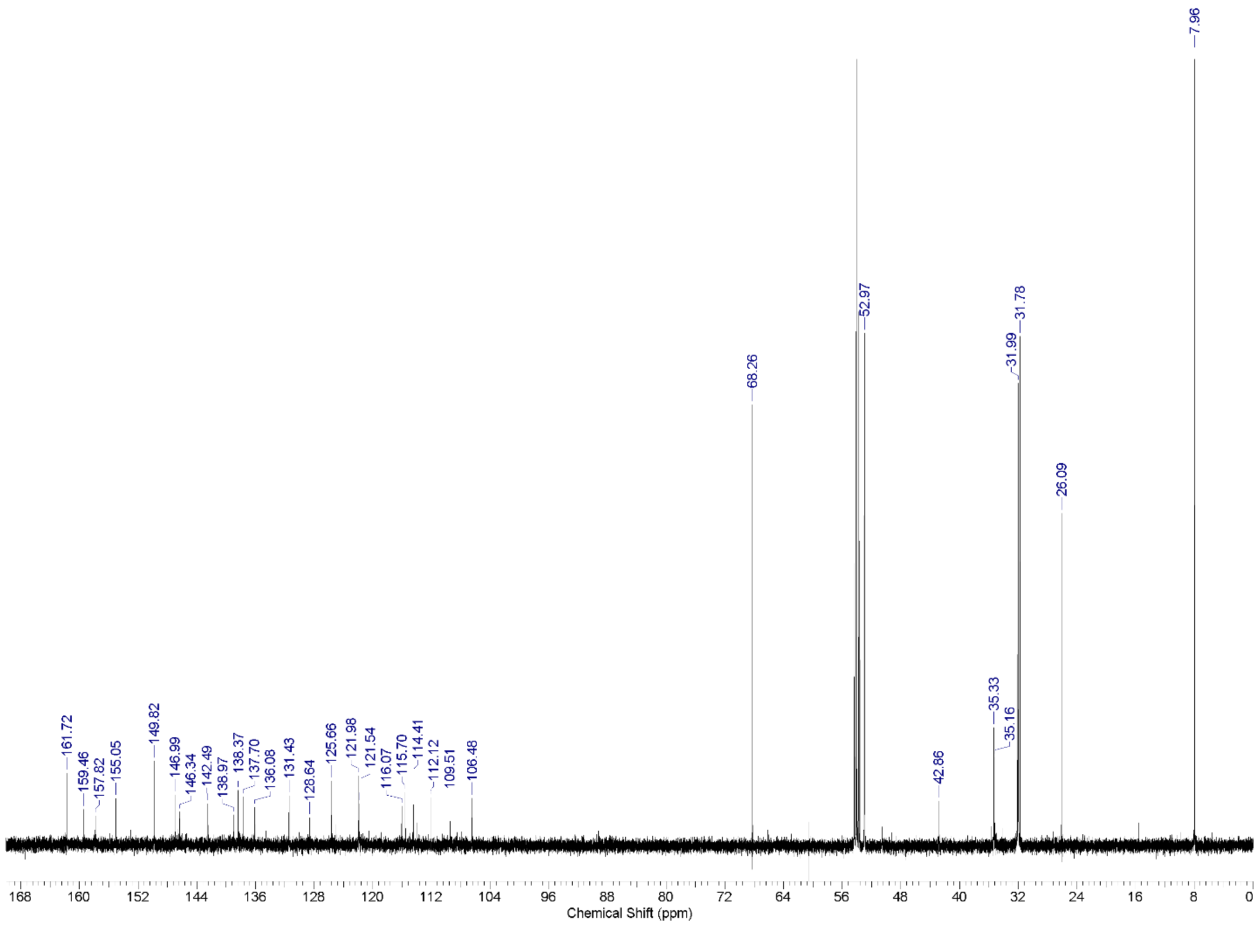

Figure S29. ^{13}C NMR spectrum of complex **4(NEt$_4$)$_2$** (CD_2Cl_2, 150 MHz).

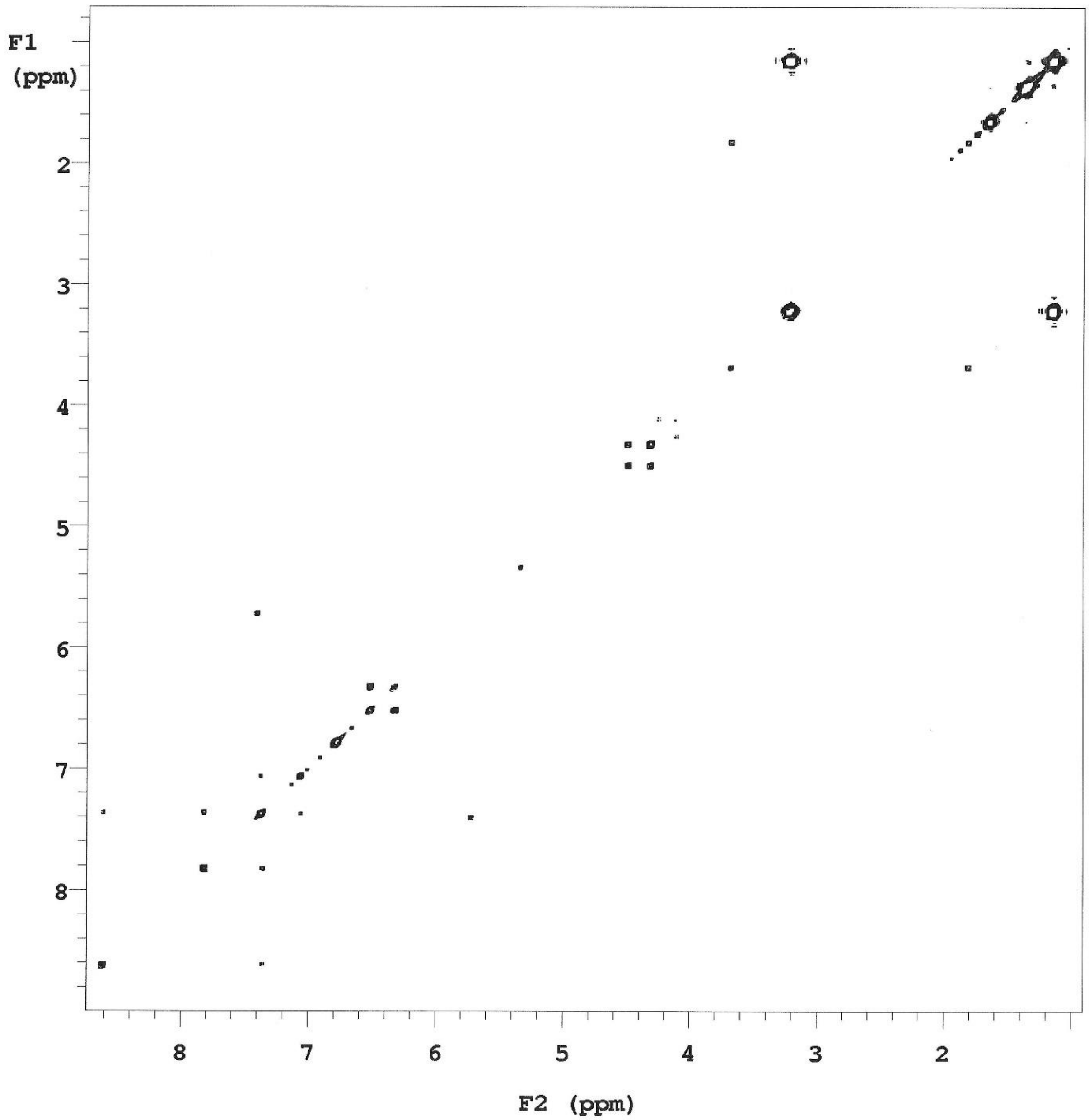

Figure S30. COSY NMR spectrum of complex **4(NEt$_4$)$_2$** (CD_2Cl_2, 600 MHz).

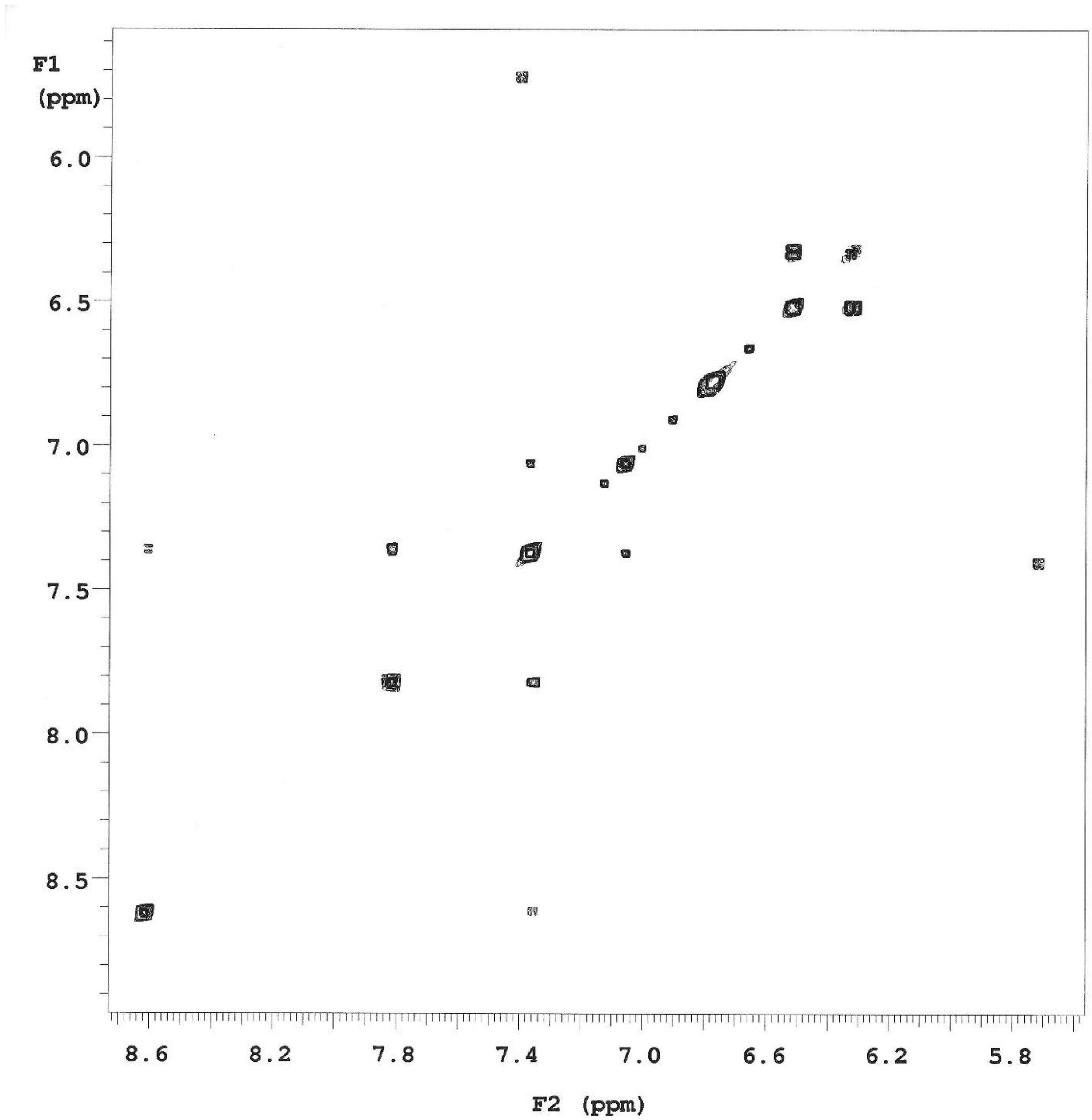

Figure S31. COSY NMR spectrum of complex **4(NEt$_4$)$_2$** (CD_2Cl_2, 600 MHz) – aromatic region.

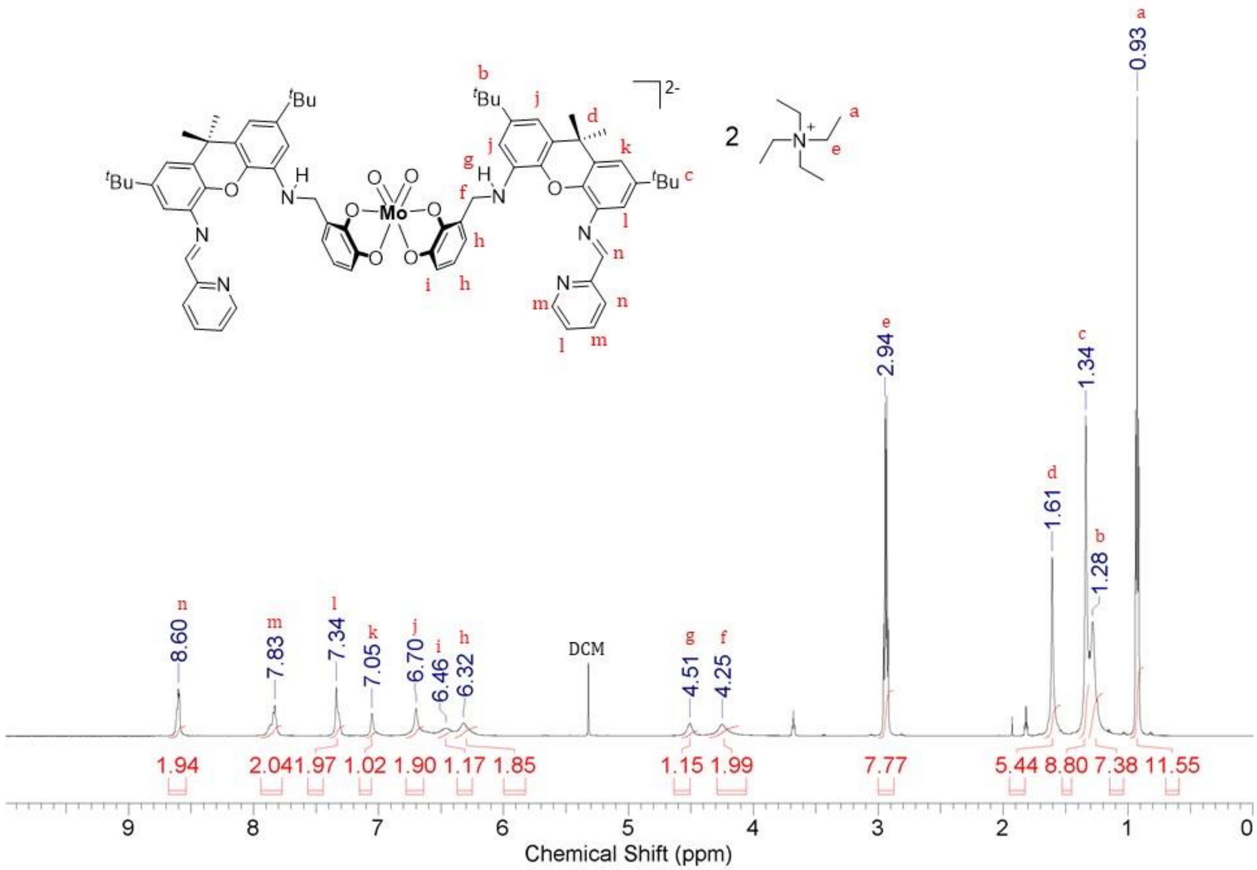

Figure S32. ^{1}H NMR spectrum of **$5(NEt_4)_2$** (CD_2Cl_2, 600 MHz).

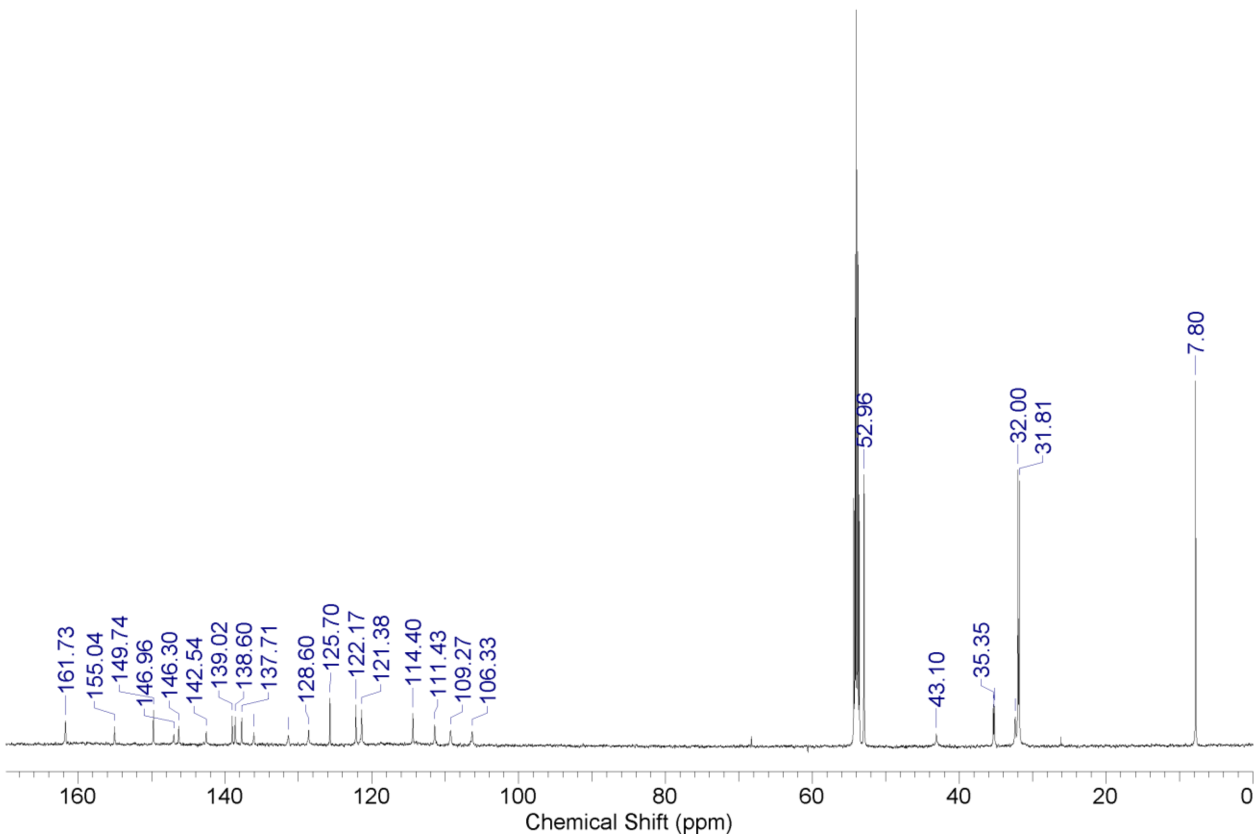

Figure S33. ^{13}C NMR spectrum of complex **5(NEt$_4$)$_2$** (CD_2Cl_2, 150 Hz).

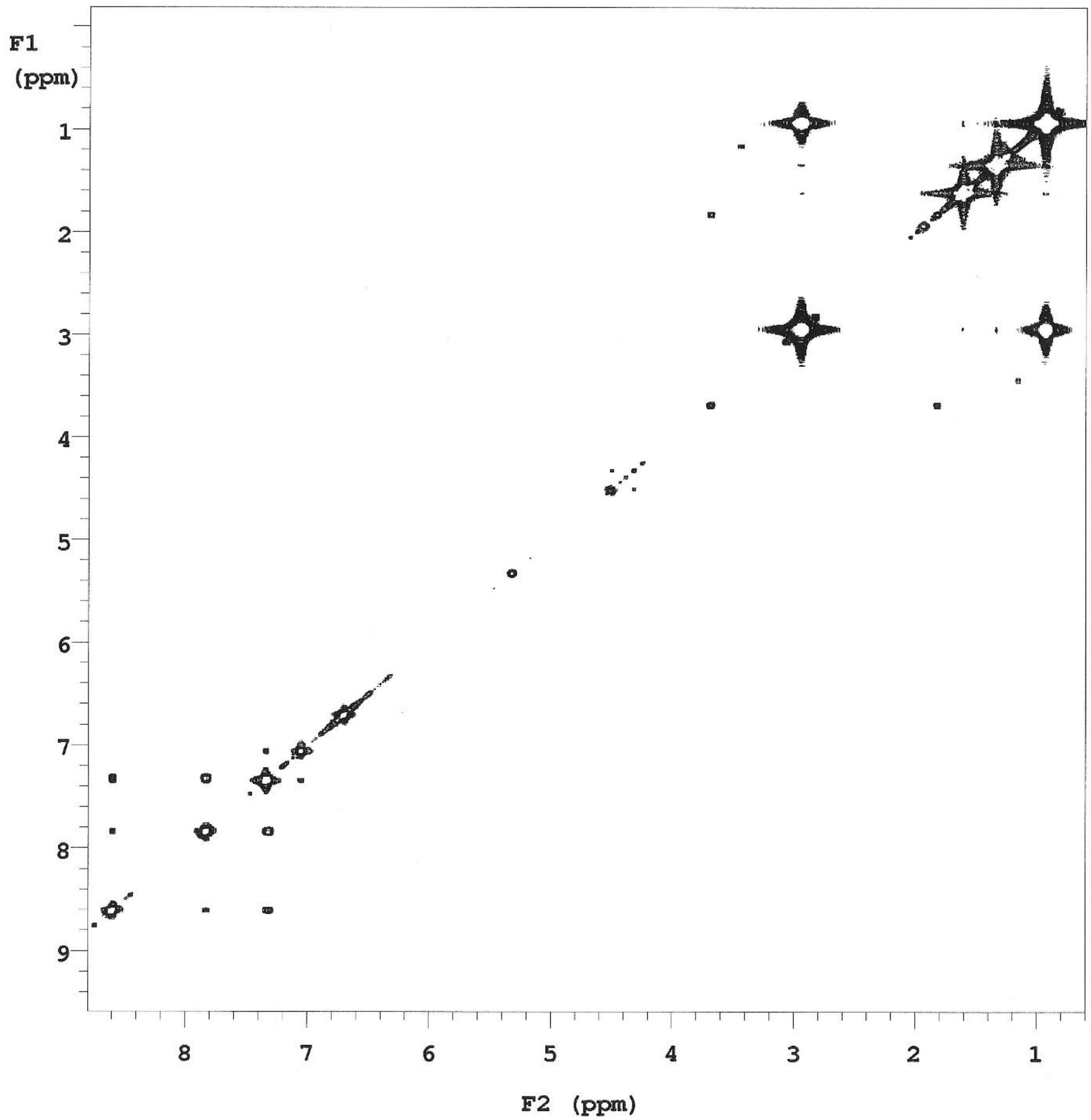

Figure S34. COSY NMR spectrum of **$5(NEt_4)_2$** (CD_2Cl_2, 600 MHz).

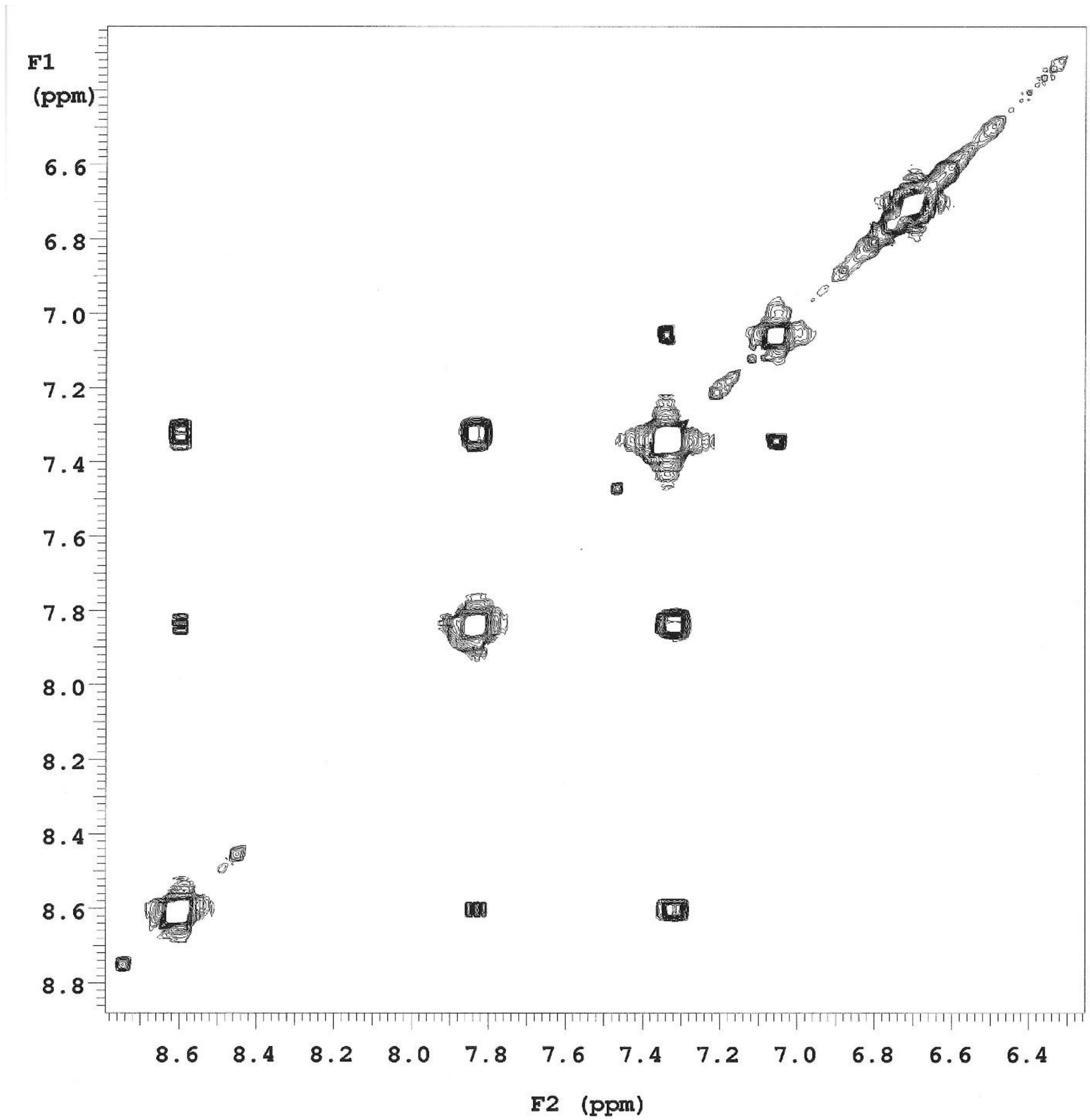

Figure S35. COSY NMR spectrum of **5(NEt$_4$)$_2$** CD_2Cl_2, 600 MHz) – aromatic region.

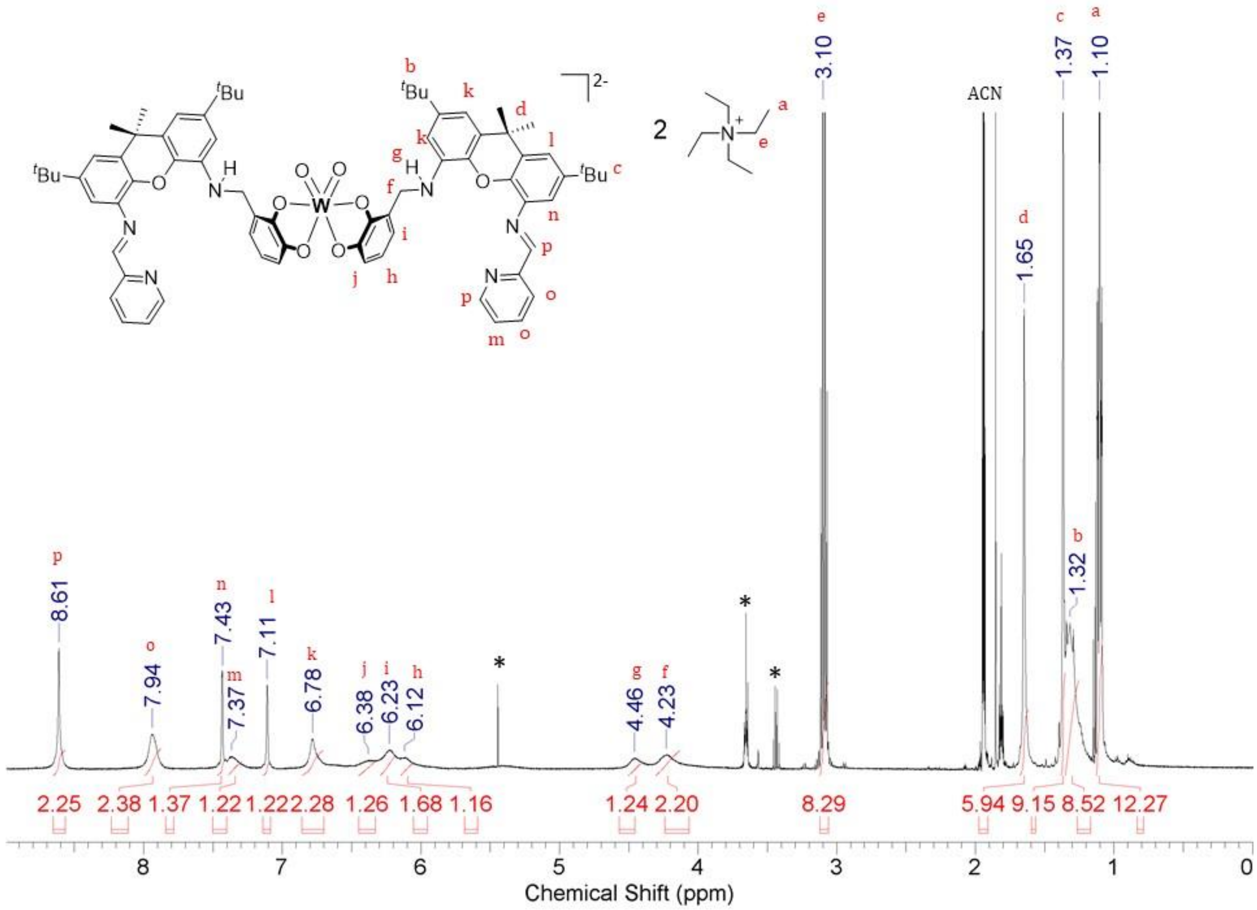

Figure S36. ^{1}H spectrum of **$6(NEt_4)_2$** (CD_3CN, 500 MHz, 50 °C); *indicates residual diethyl ether, THF and DCM.

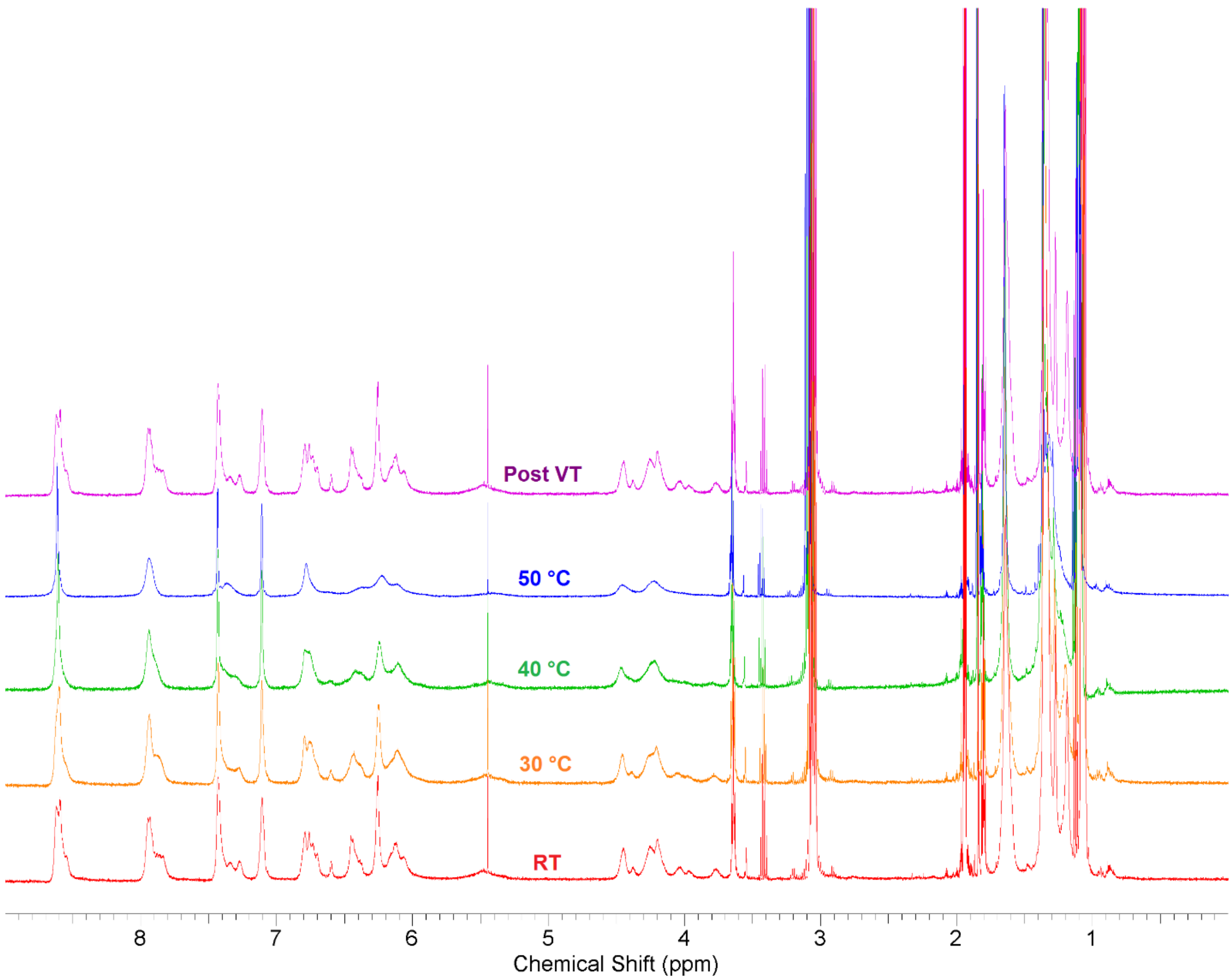

Figure S37. [1]H spectrum of **6(NEt$_4$)$_2$** at variable temperatures (CD_3CN, 500 MHz).

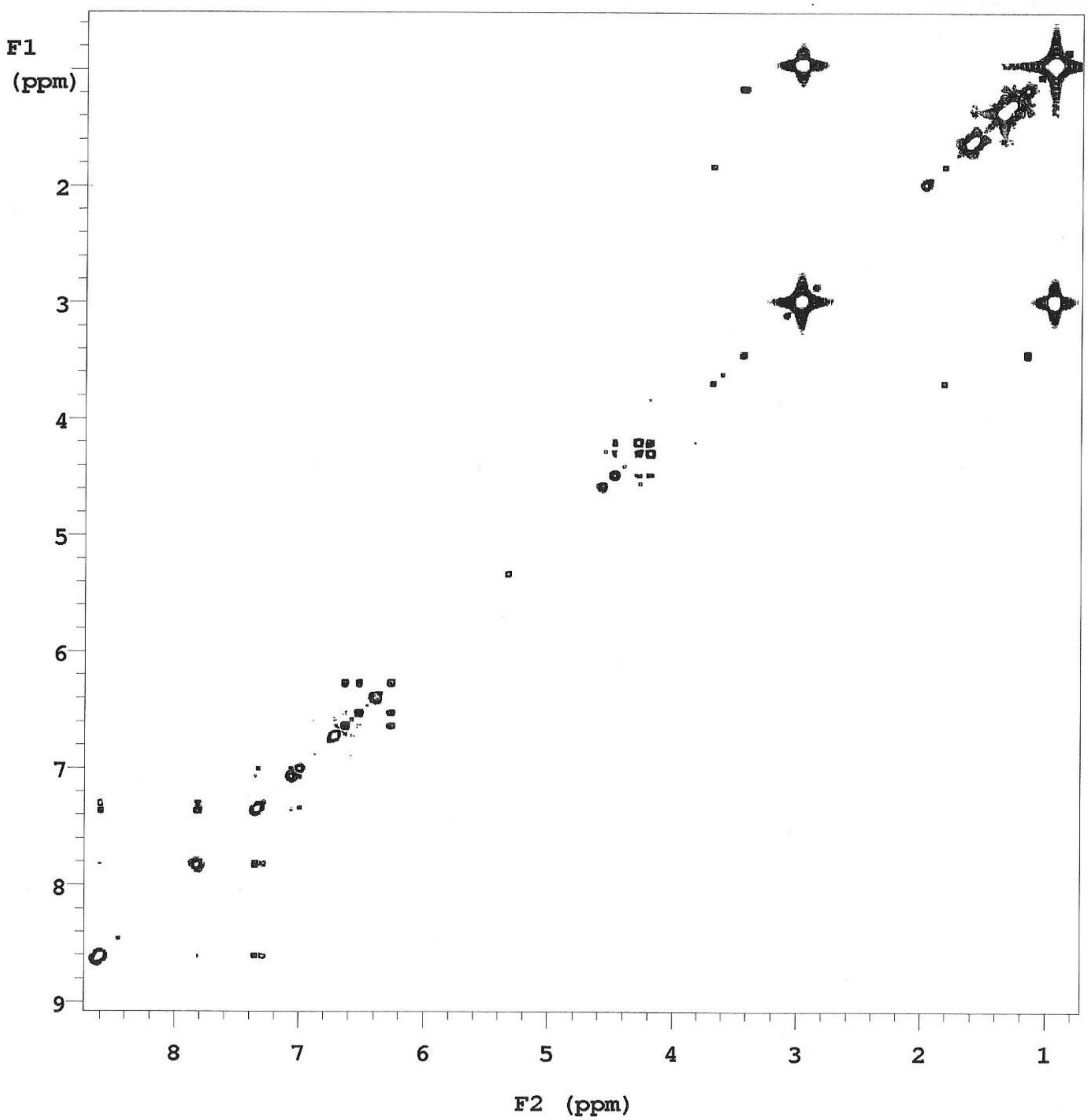

Figure S38. COSY NMR spectrum of **6(NEt$_4$)$_2$** (CD_2Cl_2, 600 MHz).

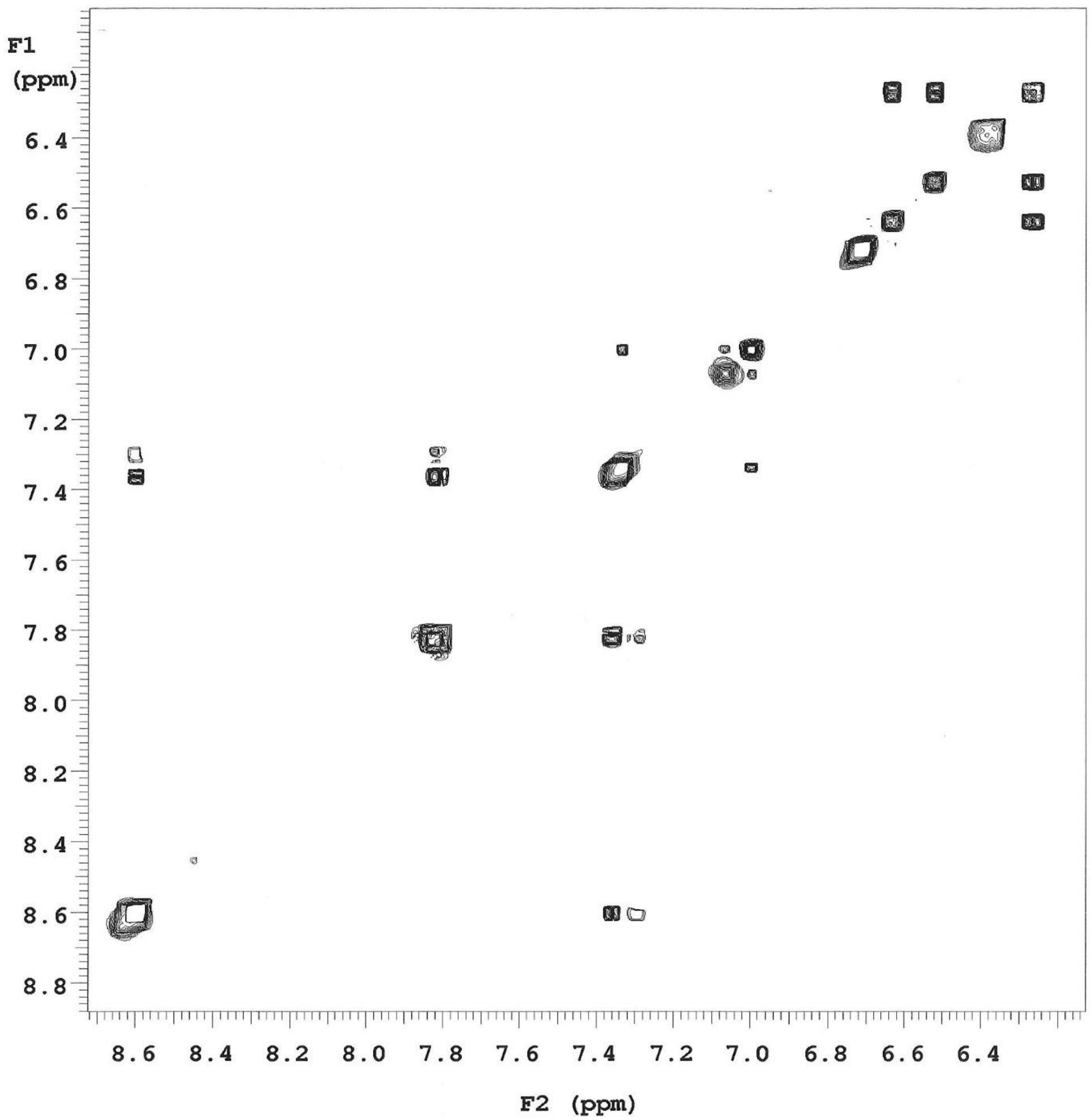

Figure S39. NMR spectrum of **6(NEt$_4$)$_2$** (CD_2Cl_2, 600 MHz) – aromatic region.

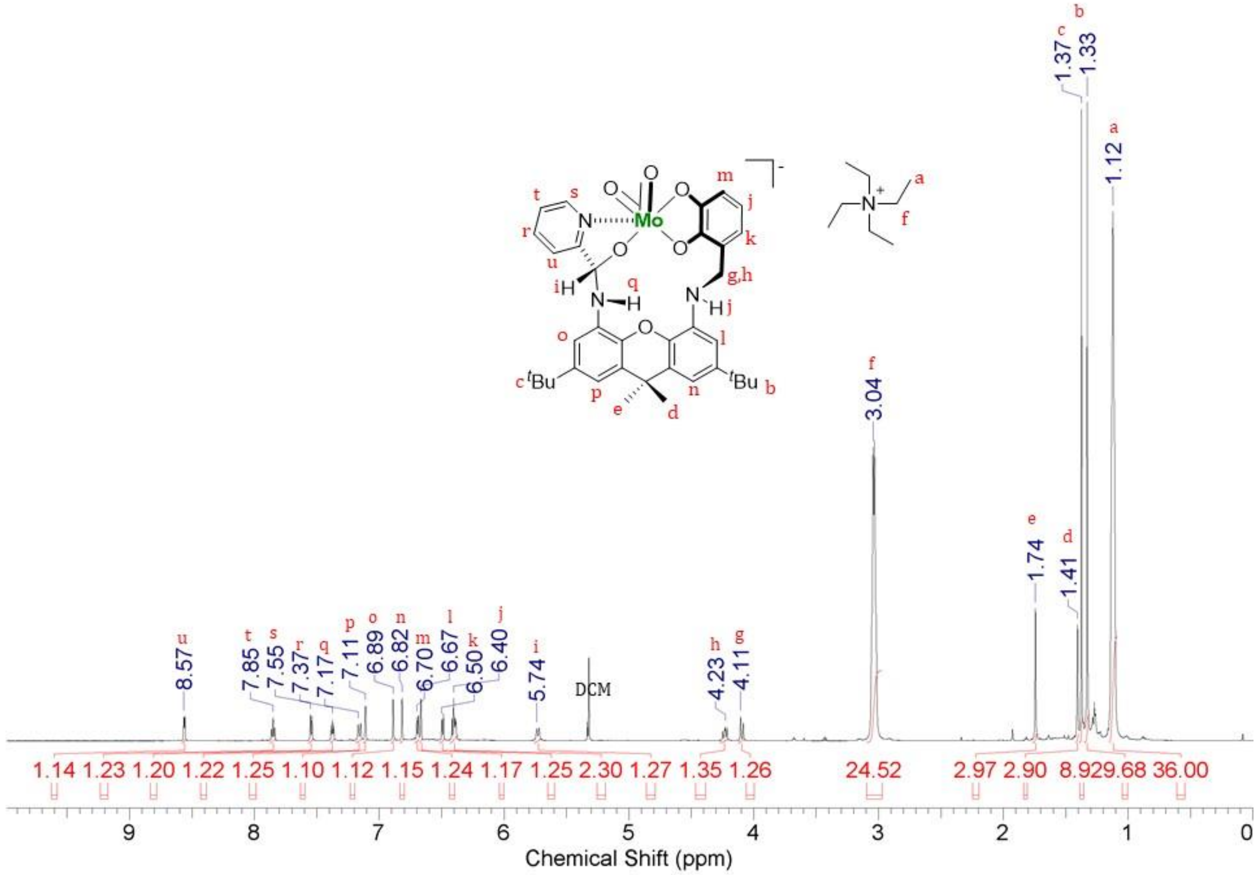

Figure S40. ^{1}H NMR spectrum of **7(NEt$_4$)** (CD_2Cl_2, 600 MHz).

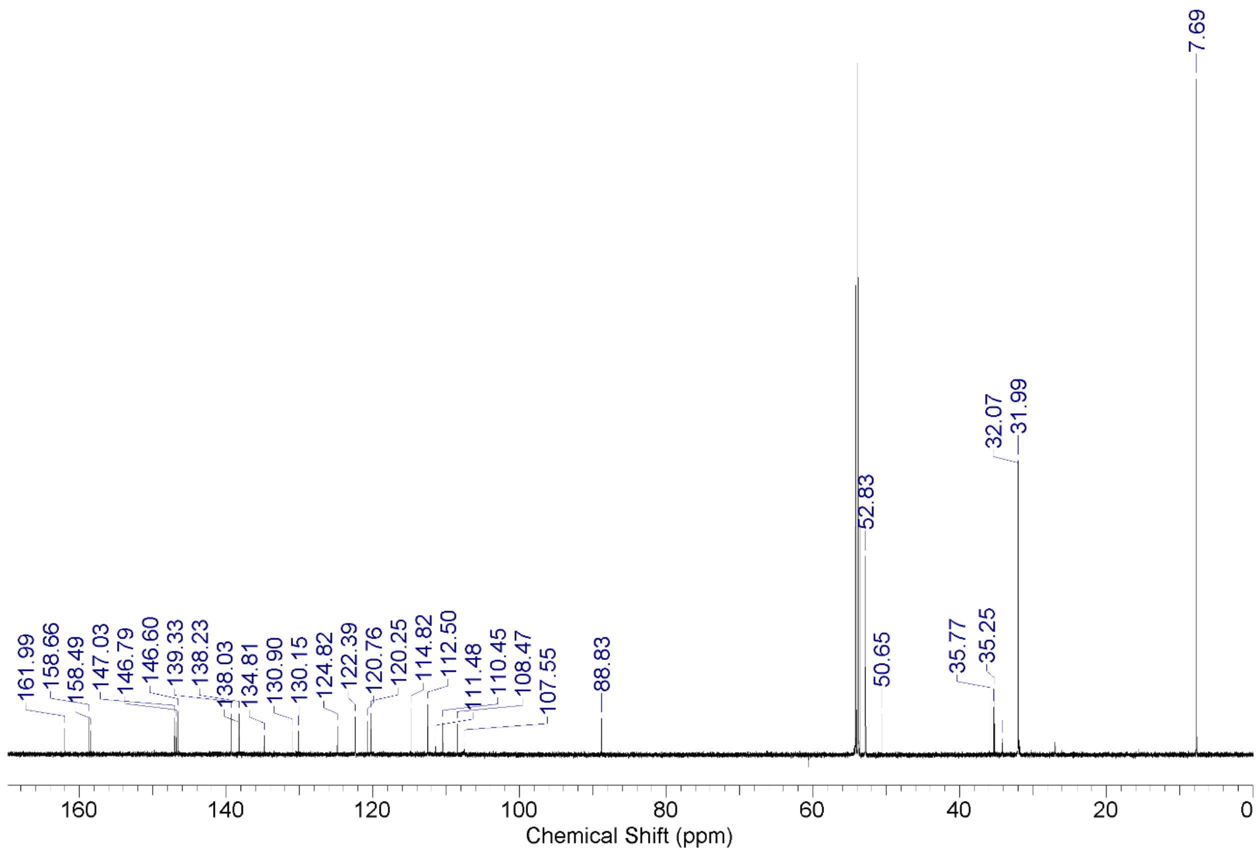

Figure S41. ^{13}C NMR spectrum of **7(NEt$_4$)** (CD_2Cl_2, 150 MHz).

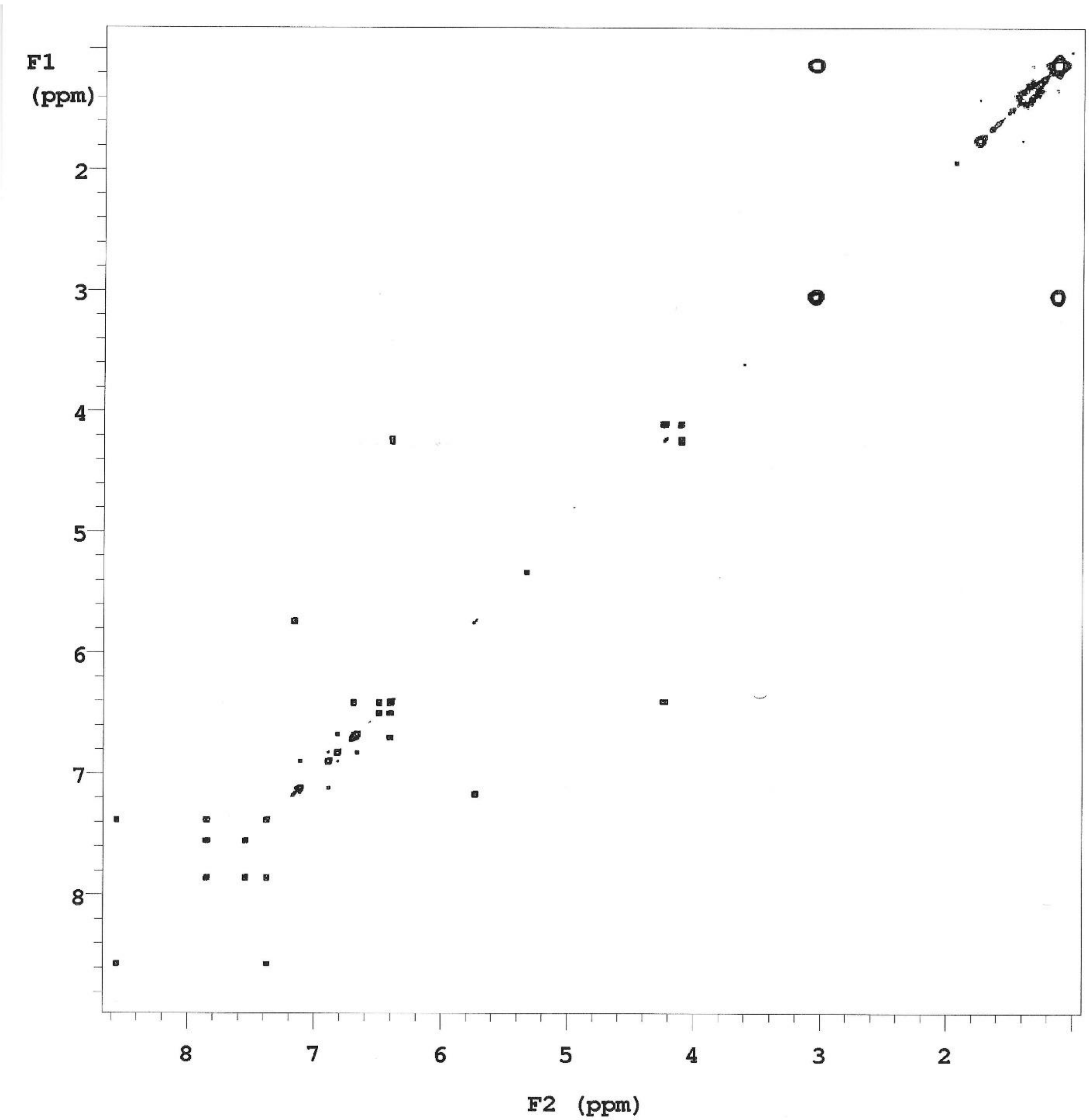

Figure S42. COSY NMR spectrum of **7(NEt$_4$)** (CD_2Cl_2, 600 MHz).

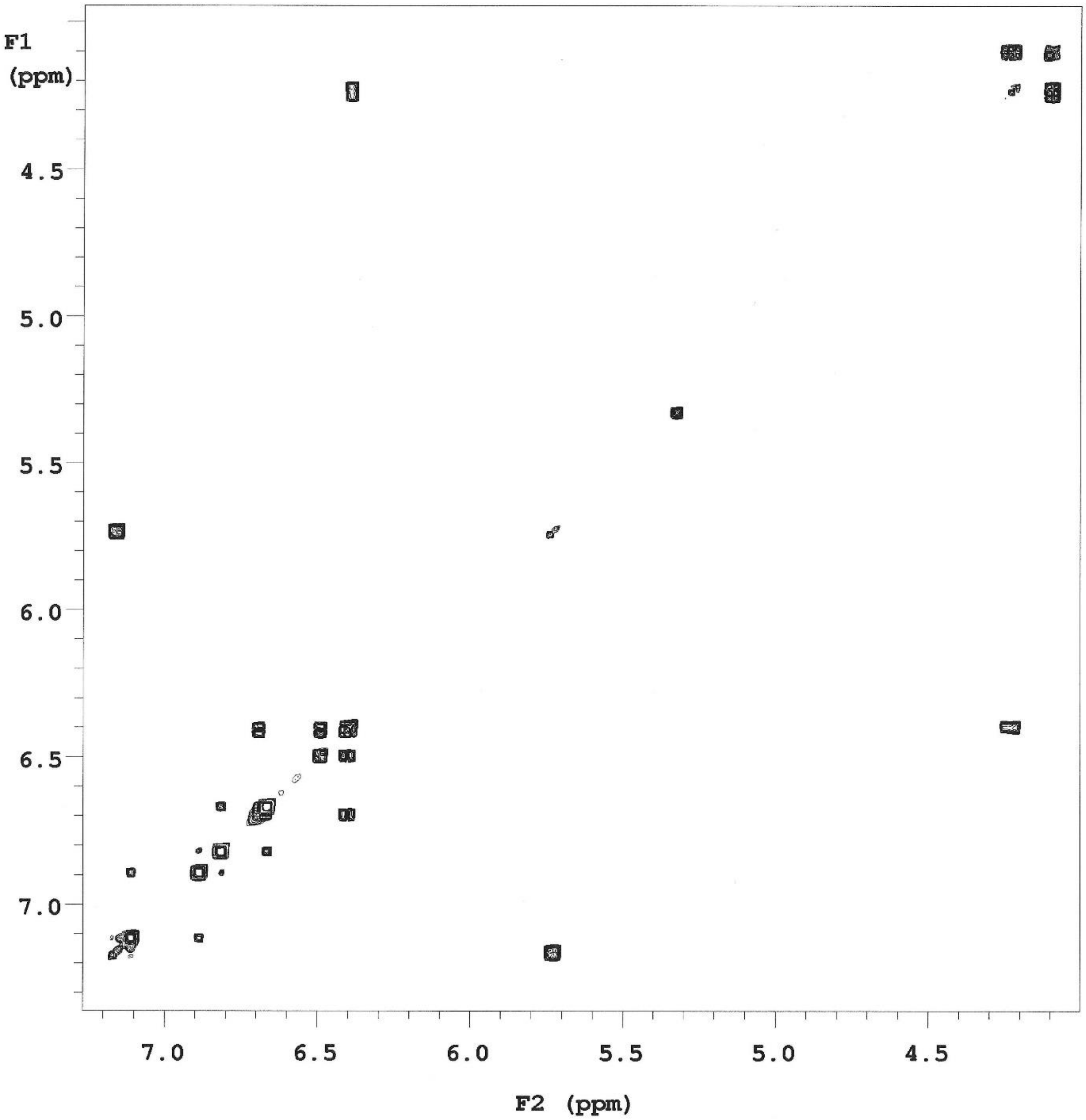

Figure S43. COSY NMR spectrum of **7(NEt$_4$)** (CD_2Cl_2, 600 MHz) – aromatic region.

5. HRMS data

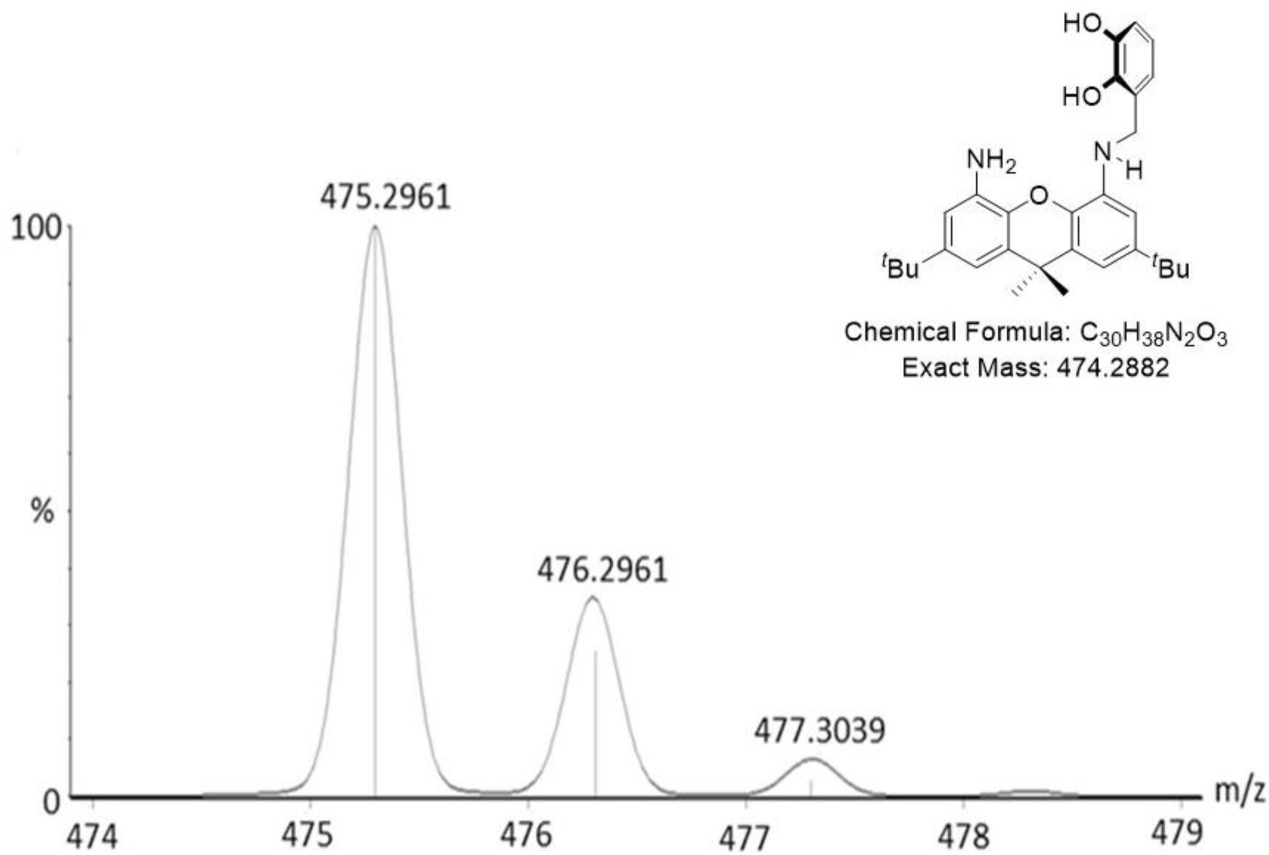

Figure S44. Experimental and calculated high-resolution mass spectrum of LH_2 in the 472–479 (m/z) region, demonstrating the peak attributed to $[L1+H]^+$.

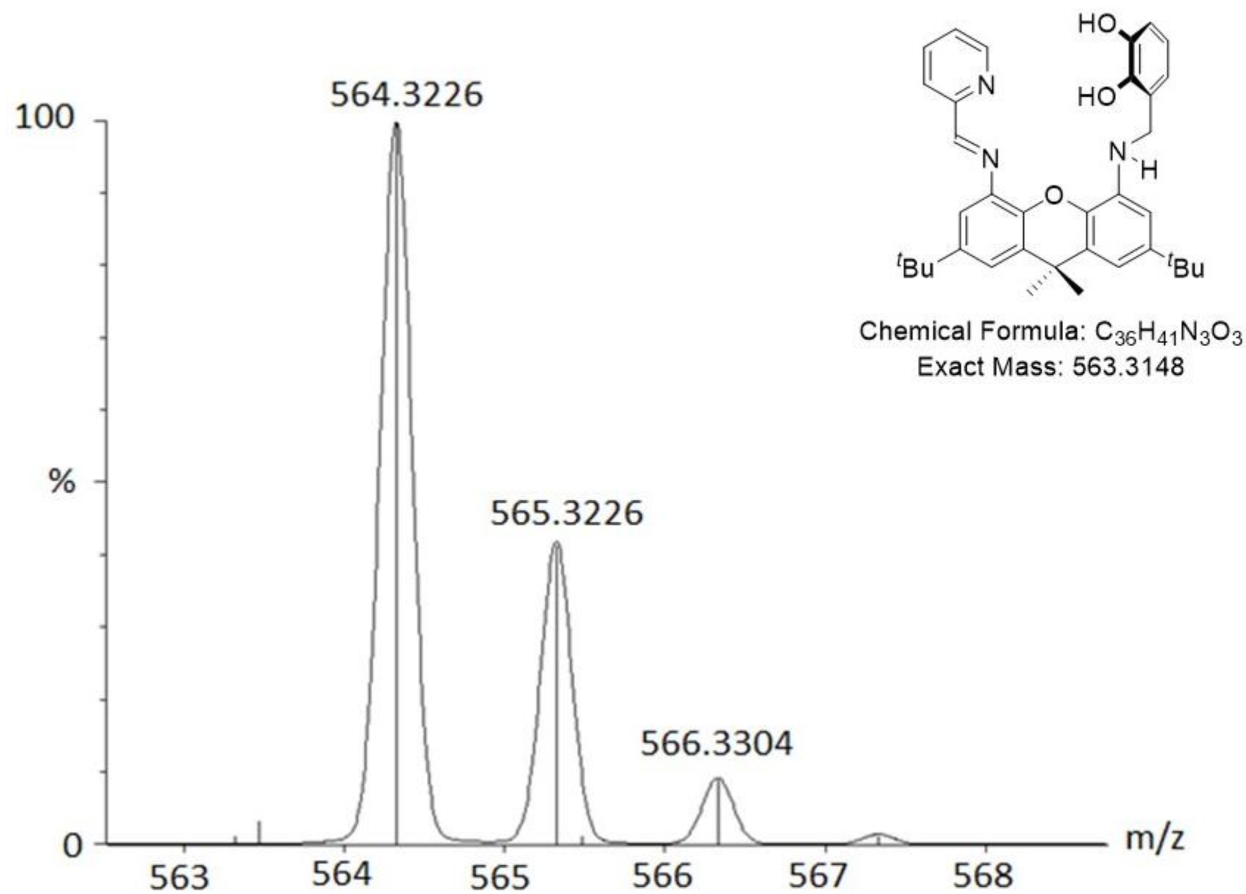

Figure S45. Experimental and calculated high-resolution mass spectrum of LH_2 in the 563–568 (m/z) region, demonstrating the peak attributed to $[LH_2+H]^+$.

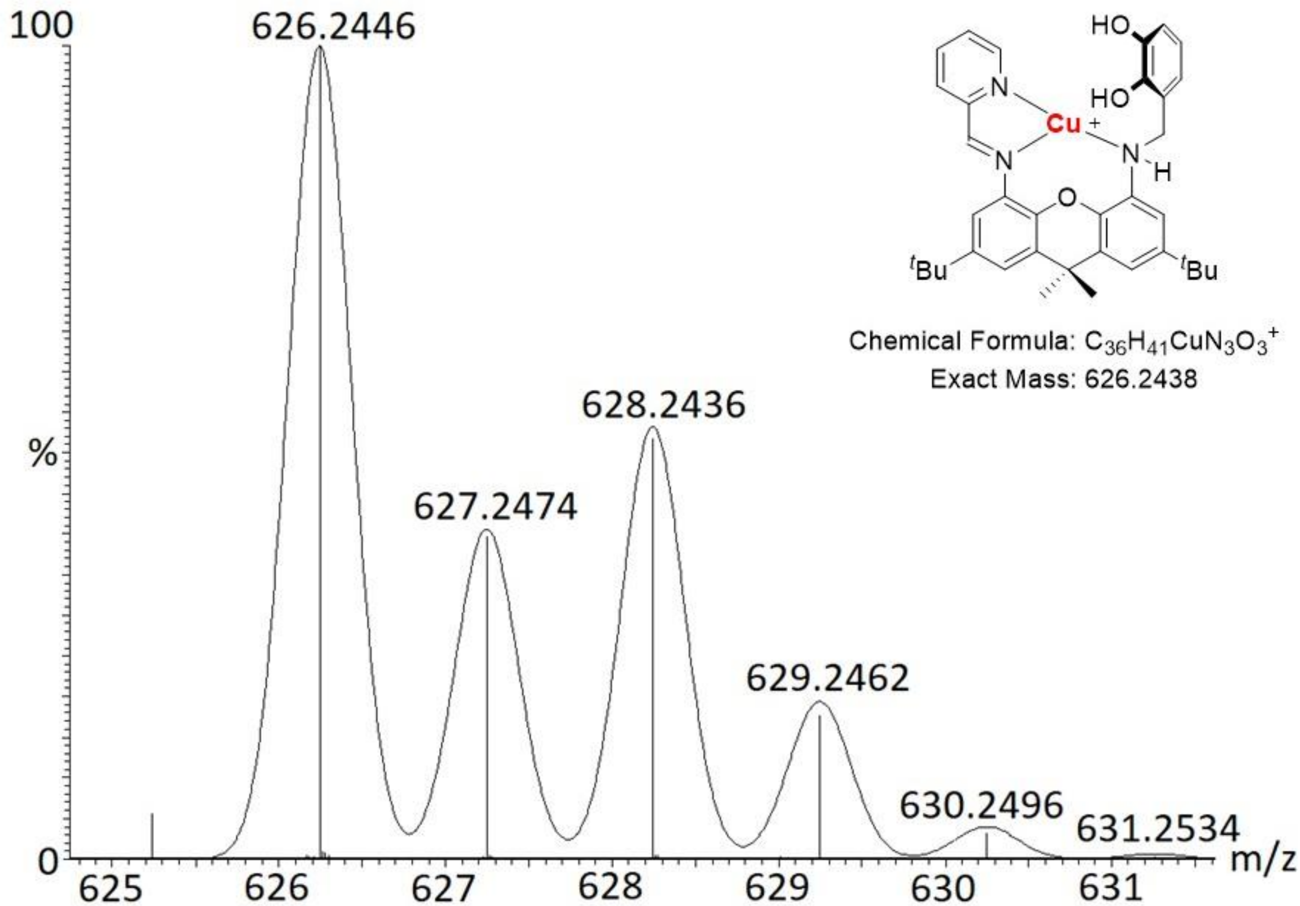

Figure S46. Experimental and calculated high-resolution mass spectrum of **1(PF_6)**, in the 625–632 (m/z) region, demonstrating the peak attributed to [**1**]$^+$.

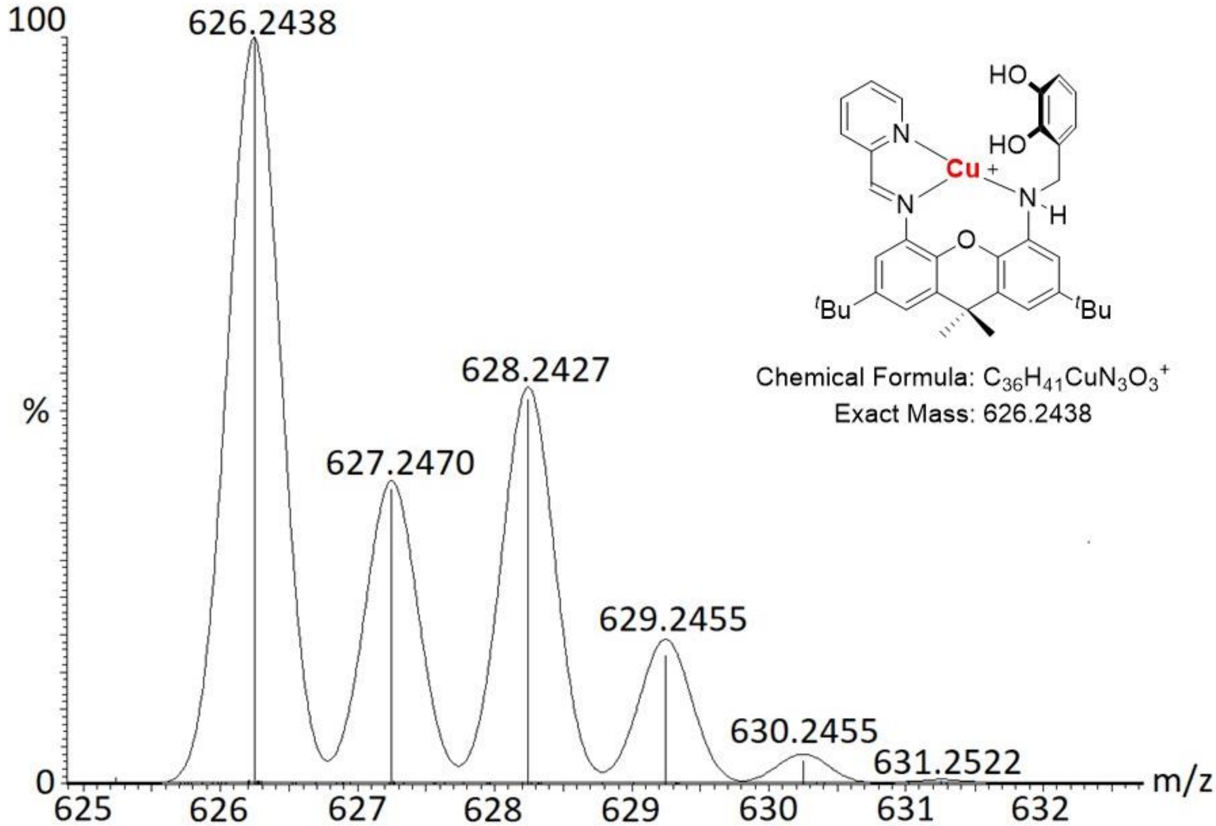

Figure S47. Experimental and calculated high-resolution mass spectrum of **1(B(C_6F_5)$_4$),** in the 625–632 (m/z) region, demonstrating the peak attributed to [**1**]$^+$.

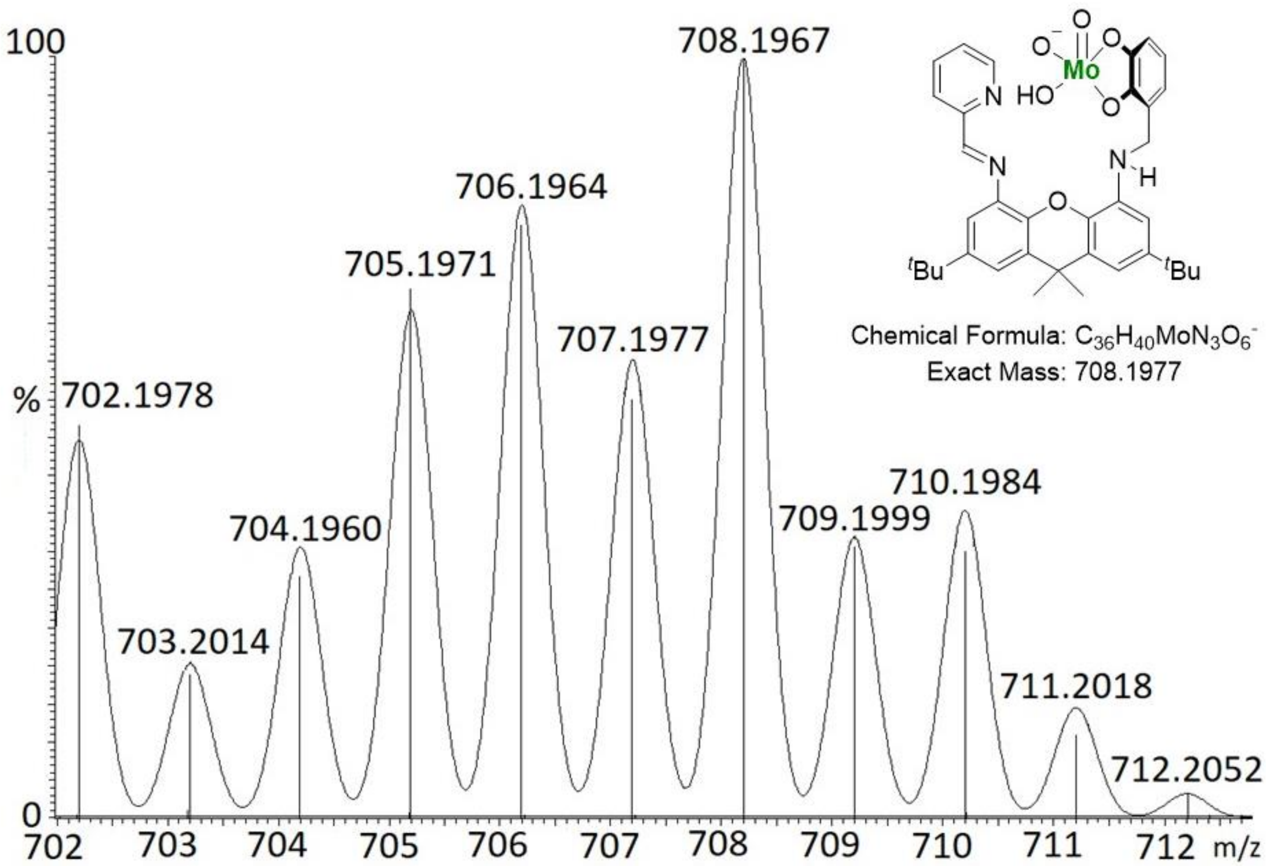

Figure S48. Experimental and calculated high-resolution mass spectrum of **3(NEt$_4$)$_2$**, in the 702–713 (m/z) region, demonstrating the peak attributed to [**3+H**]$^-$.

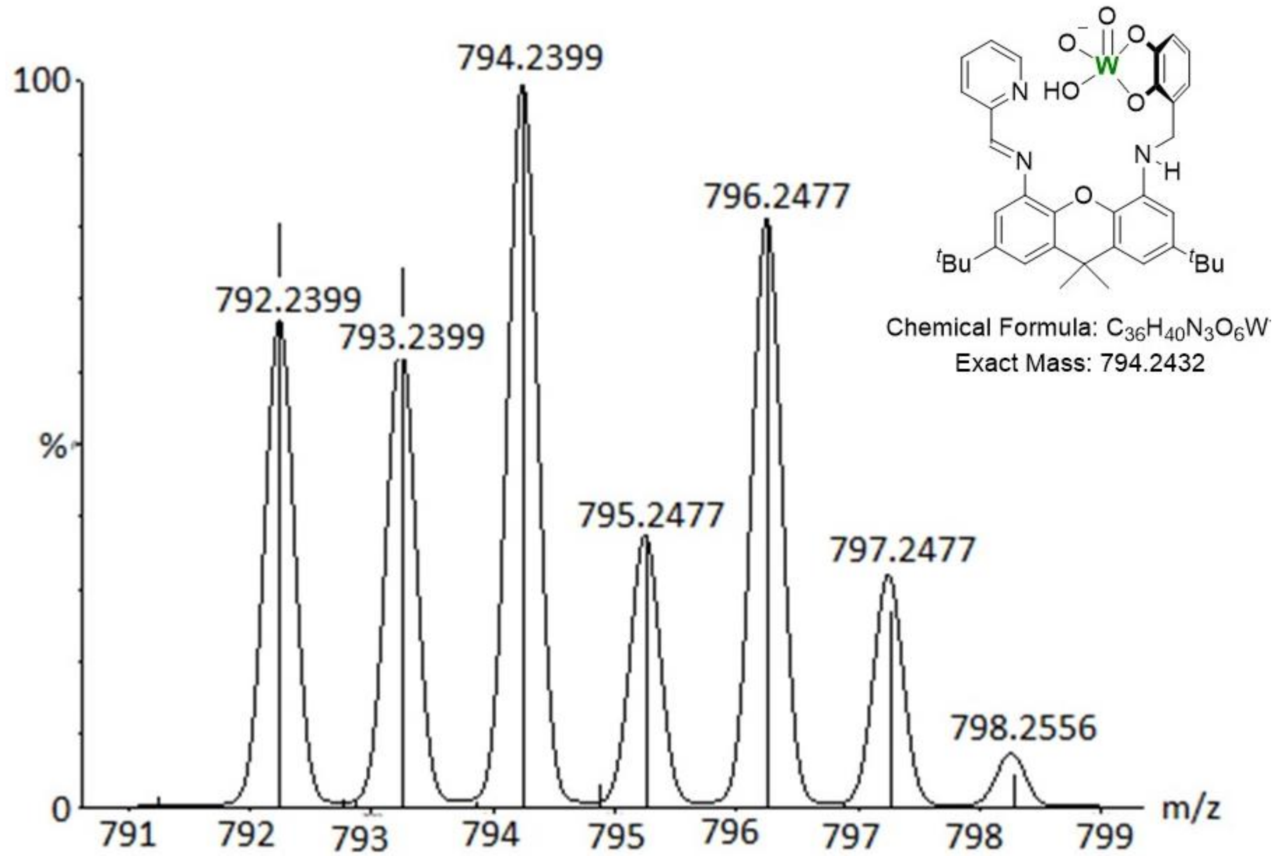

Figure S49. Experimental and calculated high-resolution mass spectrum of **4(NEt$_4$)$_2$,** in the 791–799 (m/z) region, demonstrating the peak attributed to [**4+H**]$^-$.

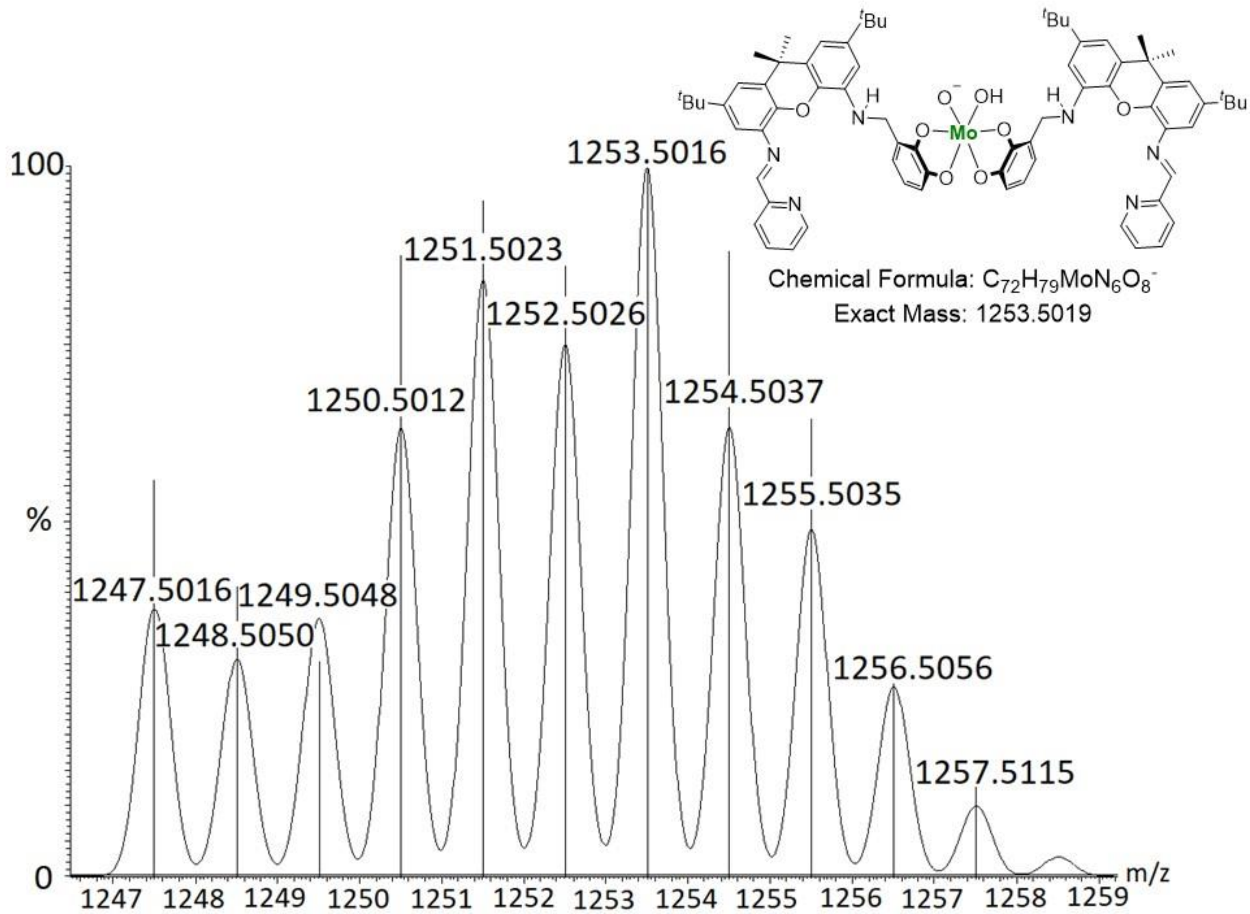

Figure S50. Experimental and calculated high-resolution mass spectrum of **$5(NEt_4)_2$,** in the 1246–1259 (m/z) region, demonstrating the peak attributed to [**5+H**]$^-$.

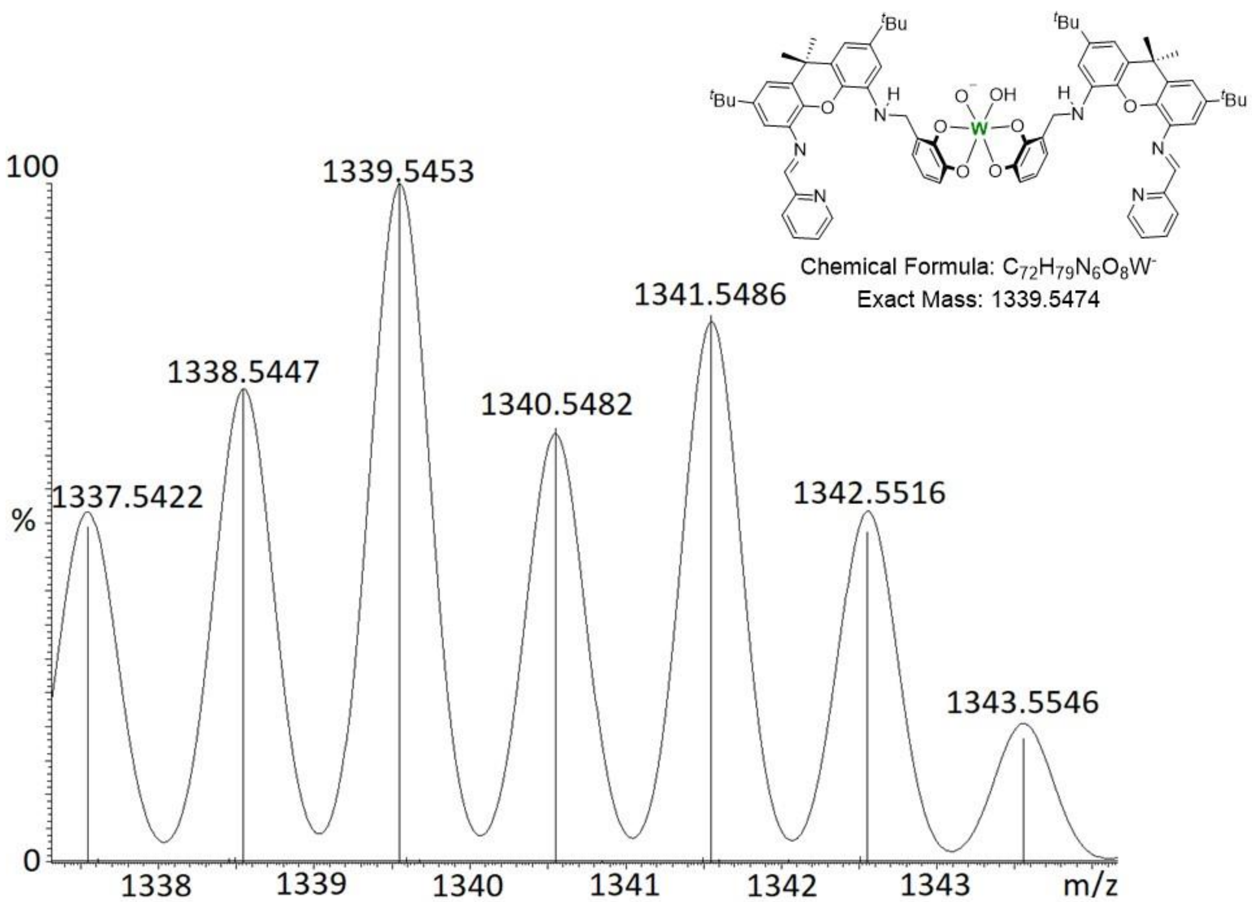

Figure S51. Experimental and calculated high-resolution mass spectrum of **6(NEt$_4$)$_2$,** in the 1337–1344 (m/z) region, demonstrating the peak attributed to [**6+H**]$^-$.

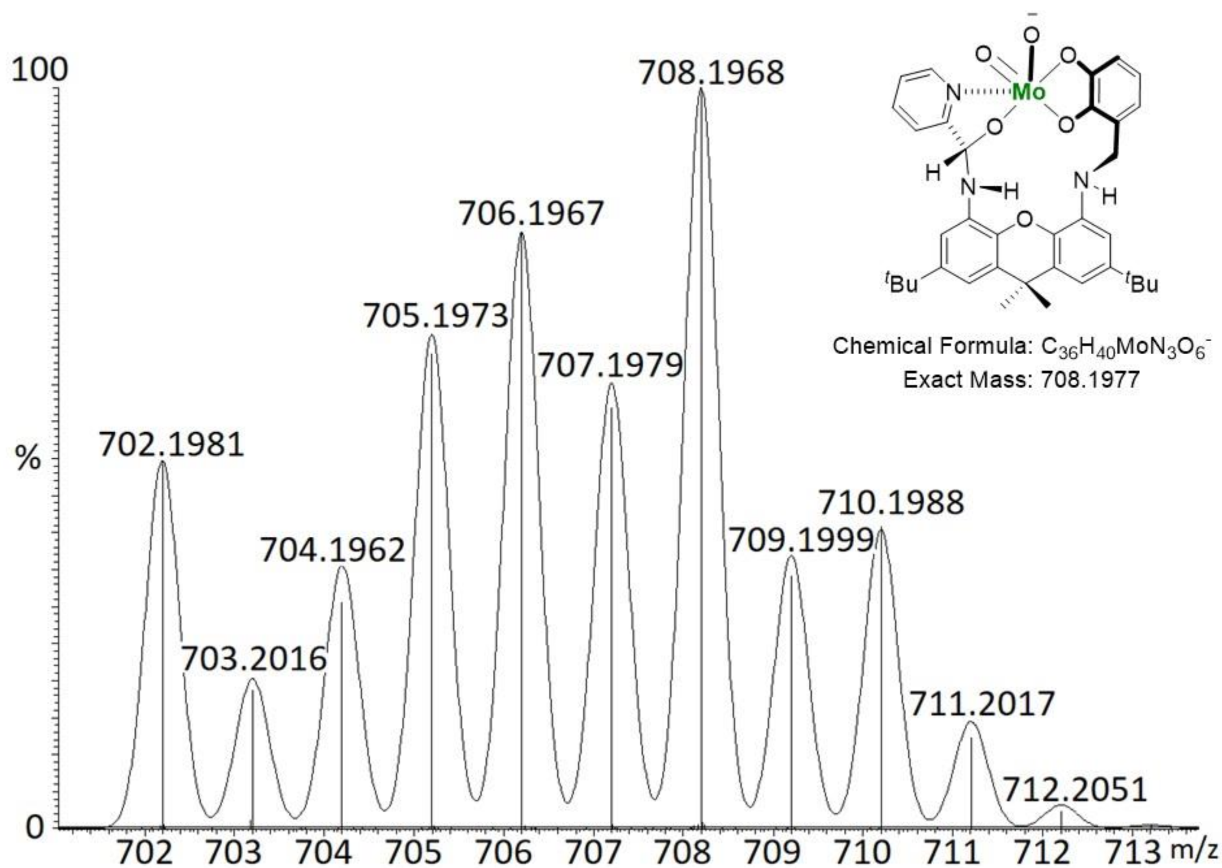

Figure S52. Experimental and calculated high-resolution mass spectrum of **7(NEt$_4$)$_2$,** in the 701–713 (m/z) region, demonstrating the peak attributed to [**7**]$^-$.

6. IR spectrum of compound 2(B(C_6F_5)$_4$)

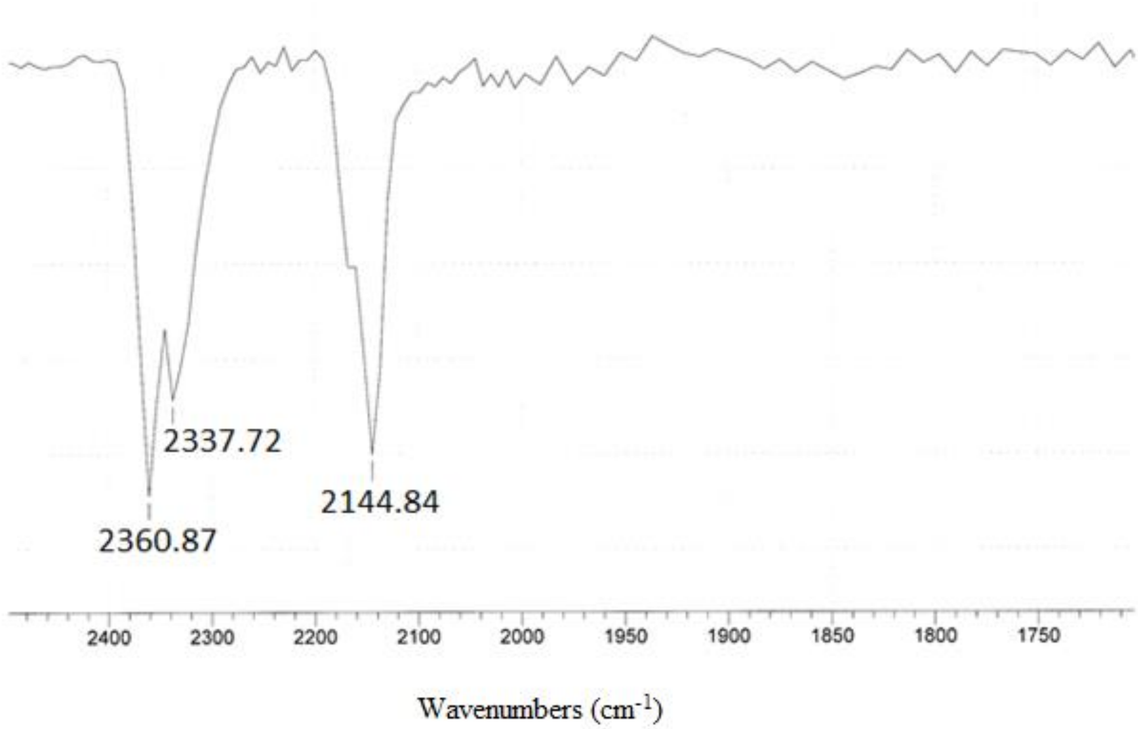

Figure S53. IR spectrum of **2(B(C_6F_5)$_4$)**

Table S2. Selected wavelengths for 2,6-dimethylphenyl isocyanide complexes

Selected Compound	**Wavelength (cm^{-1})** of CN bond
2,6-Dimethylphenyl isocyanide	2119
2,6-Dimethylphenyl isocyanide with backbonding	< 2119
Complex 2 + 2,6-Dimethylphenyl isocyanide	~2145
Carbon Dioxide	~2360

7. UV/VIS Data

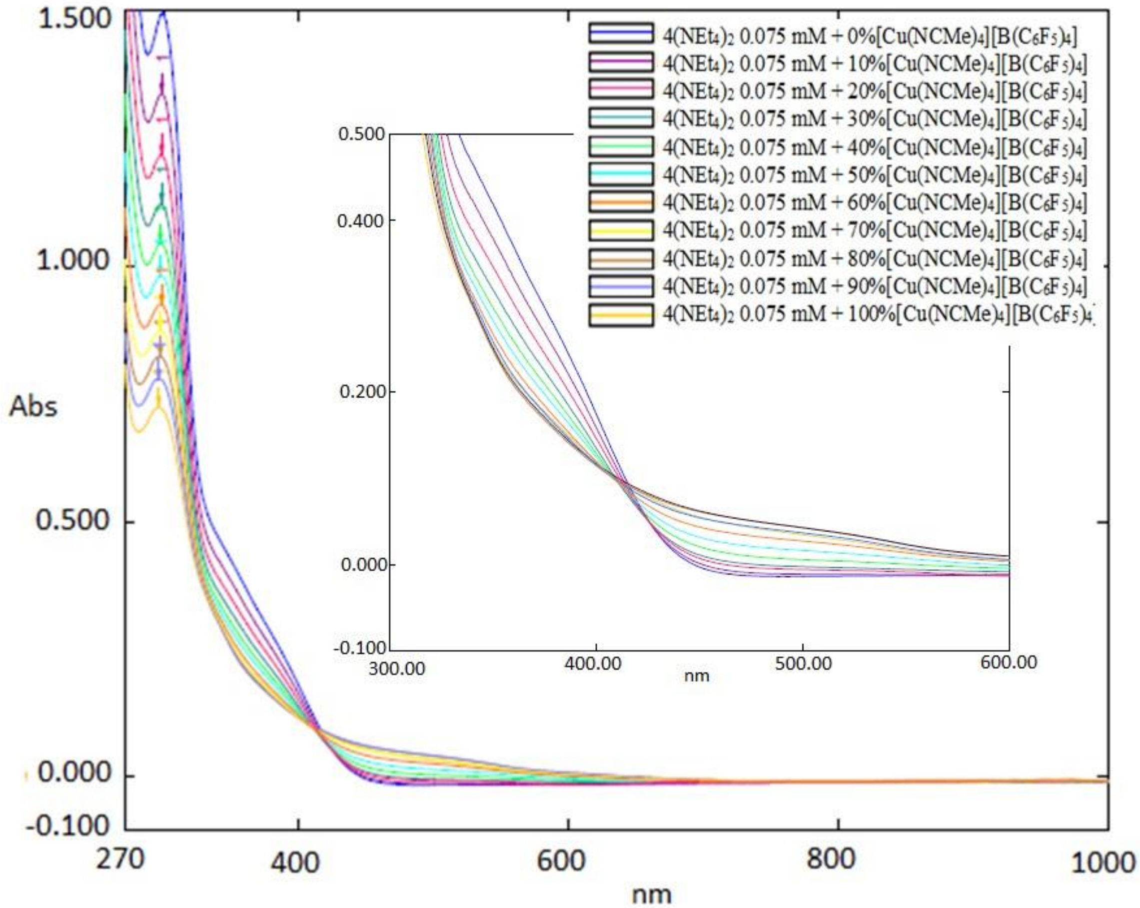

Figure S54. UV/vis spectra for titration of **$4(NEt_4)_2$** with $[Cu(NCMe)_4][B(C_6F_5)_4]$.

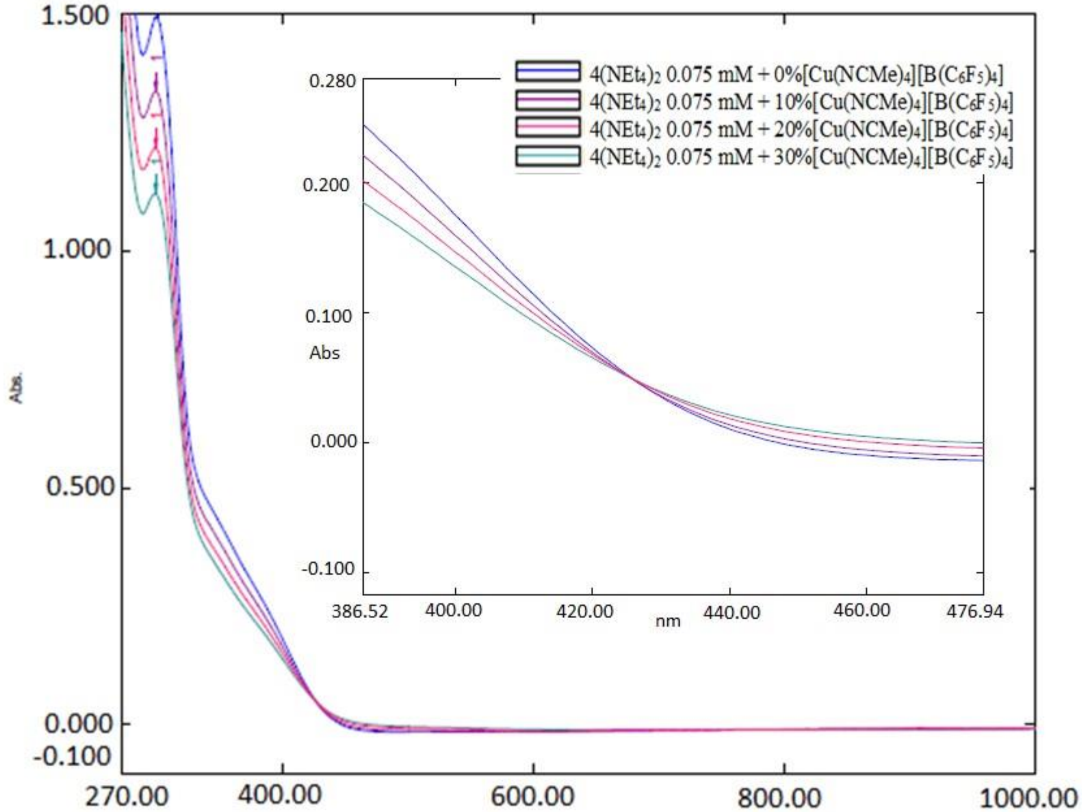

Figure S55. UV/vis spectra for titration of of **$4(NEt_4)_2$** with 0% -30% $[Cu(NCMe)_4][B(C_6F_5)_4]$.

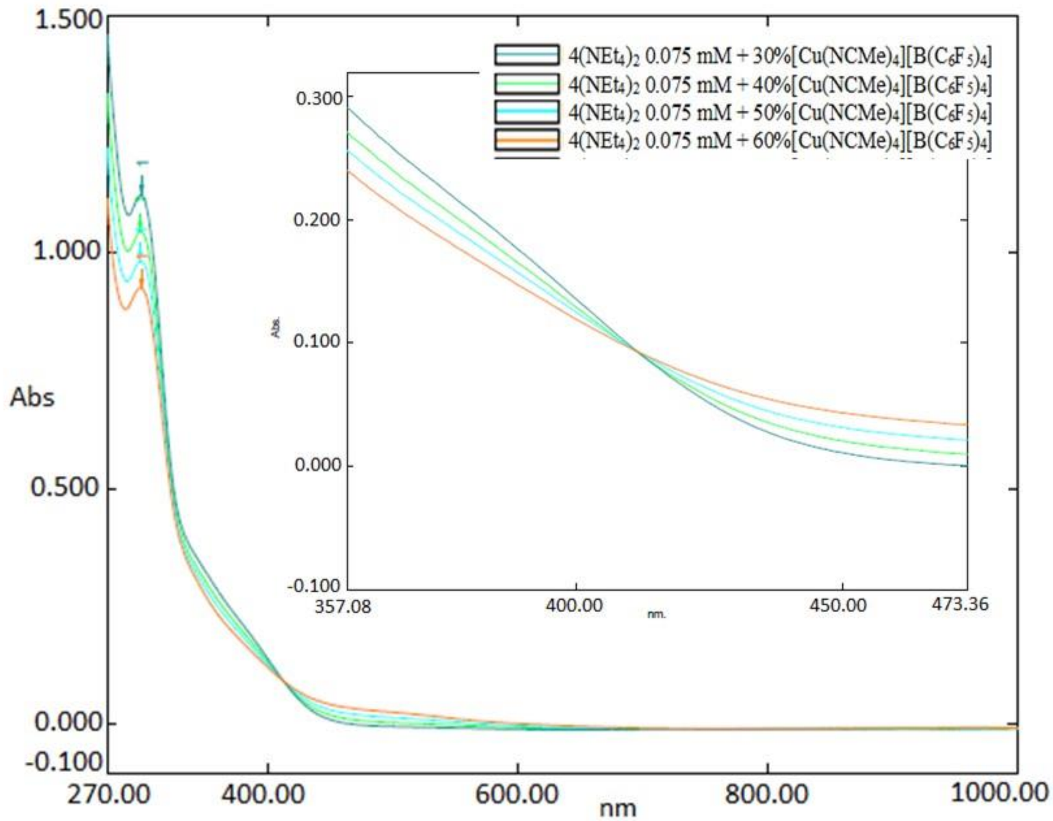

Figure S56. UV/vis spectra for titration of **$4(NEt_4)_2$** with 30% -60% $[Cu(NCMe)_4][B(C_6F_5)_4]$.

8. Computational methods and results

DFT calculations were performed with Gaussian 09.[2] Geometry optimizations were done at the OPBE/SDD/6-31G(d) level of theory[3,4] (SDD for Cu/Mo/W, 6-31G(d) for all other atoms)[5,6] with implicit solvation included (SMD model for THF).[7,8] The tBu groups on the xanthene backbone were replaced by H but otherwise full model calculations were performed. The pure functional OPBE was chosen so we could employ density fitting to speed up the electronic structure calculations during these optimizations. All optimized structures were verified to be minima or first-order saddle points by analyzing the harmonic frequencies,[9] and all wavefunctions were tested for stability.[10,11] Subsequent follow-up single point energies at the OPBE/def2TZVP,[12] B3LYP/def2TZVP,[13-17] and B3LYP-D3/def2TZVP[18] levels of theory were evaluated again with implicit solvation. The triple-zeta OPBE and B3LYP results were similar (see Table S5), but inclusion of the empirical dispersion corrections made these reactions more energetically feasible. The D3 correction was not available in the version of Gaussian employed. Therefore, approximate triple-zeta free energies at B3LYP-D3/def2TZVP//OPBE/SDD/6-31G(d) using $G(TZ) \approx G(DZ) - E(DZ) + E(TZ)$, where DZ and TZ represent double- and triple-zeta, respectively, are presented herein and throughout the manuscript. The free energy corrections to the electronic energies assume standard approximations.[19]

Transition states for **9** -> **10** and **3** -> **11** are shown in Figure S57. The forming C–O bond lengths are 1.843 and 1.726 Å, respectively. The pyridine in **3** has not started coordinating to Mo(VI) in the transition state, however, no analogue of **11** with pyridine rotated away from the metal was able to be optimized (each attempt optimized to the structure with pyridine coordinated).

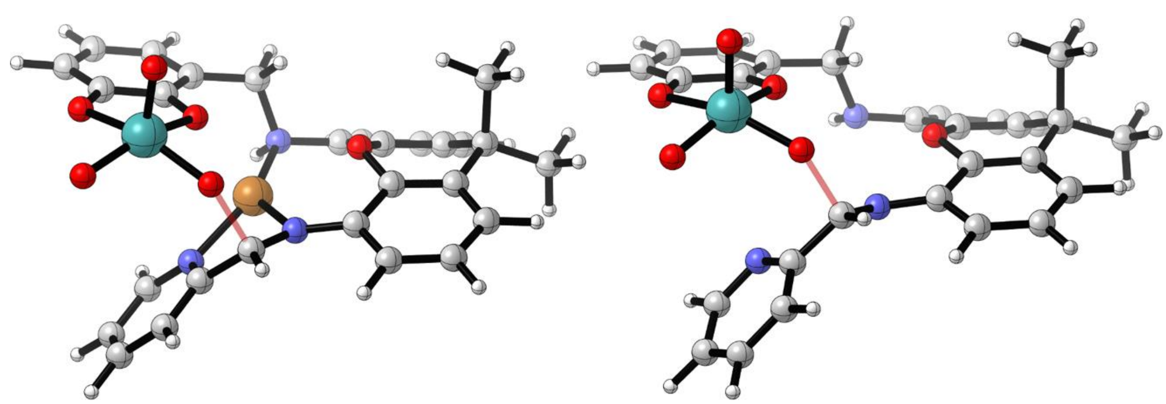

Figure S57. Optimized structures of **9–10–TS** (left) and **3–11–TS** (right). The forming bond is highlighted in transparent red.

Analogous calculations were performed for W(VI) vs. Mo(VI) containing species (Figure S58). While the W(VI) version of **3** is defined as **4** in the manuscript, the hypothetical intermediates and transition states were not discussed. Therefore, **12**, **13**, and **14** are the W versions of **9**, **10**, and **11**, respectively. The energetics of these species are slightly different with the Cu(I) reaction free energy of 0.6 kcal/mol and a barrier of 2.3 kcal/mol (vs. 2.5 and 4.6 kcal/mol for Mo), while the Cu-free version has a reaction free energy of 8.9 kcal/mol and a barrier of 21.9 kcal/mol (vs. 16.3 and 25.7 kcal/mol). A similar orbital stabilization upon Cu-binding to that in the Mo species was found: the LUMO lowers by 0.73 eV and the HOMO–2 lowers by 0.35 eV, giving rise to a better energy matching when Cu is bound (ΔE_{orb} = 0.88 eV) vs. not (ΔE_{orb} = 1.53 eV)

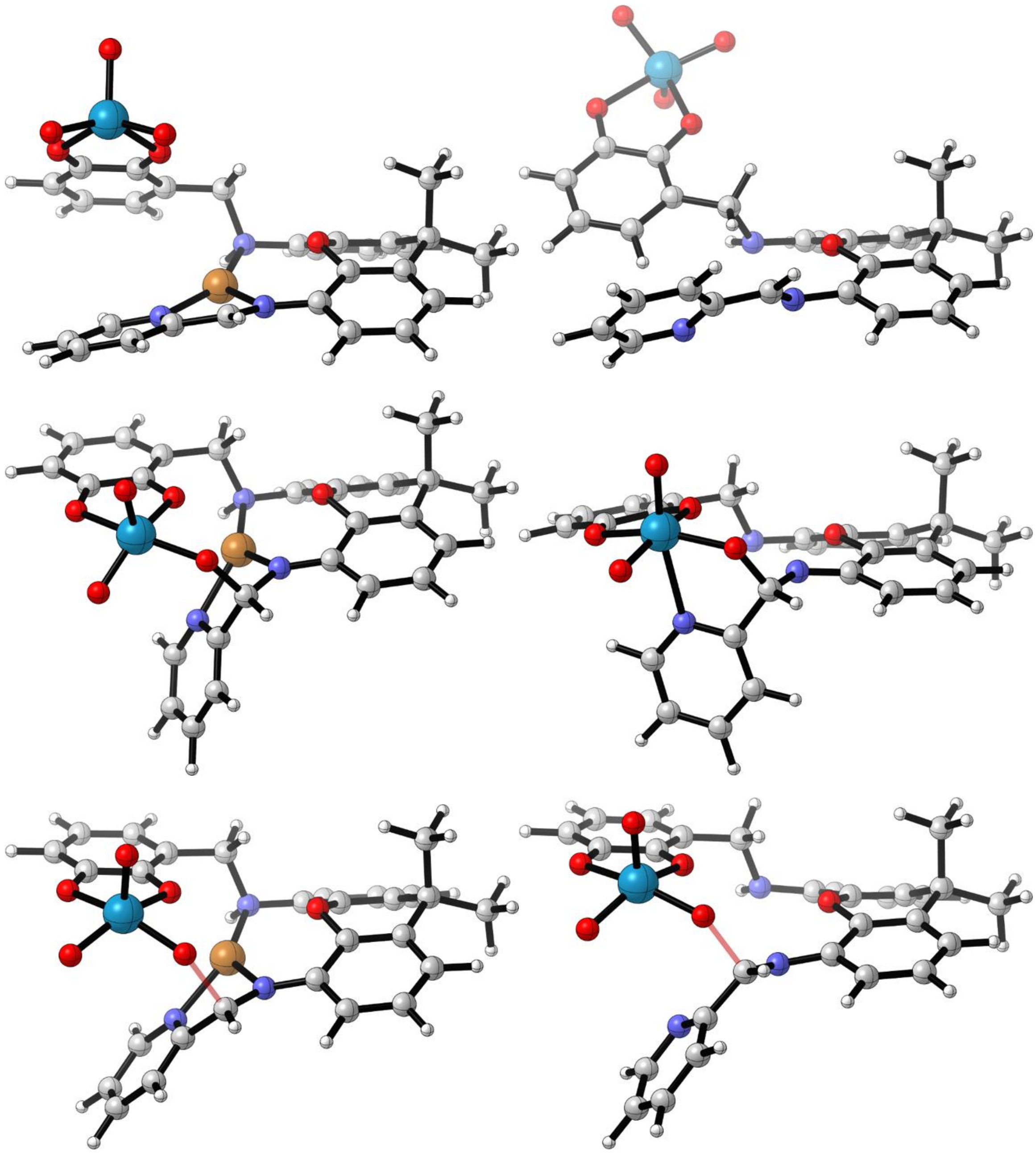

Figure S58. Optimized structures of the W(VI) species: **12** (top left), **4** (top right), **13** (middle left), **14** (middle right), **12–13–TS** (bottom left), **4–14–TS** (bottom right). The forming bond in the TSs is highlighted in transpared red.

Table S3. Cartesian coordinates (Å) for all optimized species.

9

C	-4.344316	-3.469264	-0.987778
C	-5.080052	-2.612958	-0.161166
C	-4.493527	-1.461098	0.383558
C	-3.152955	-1.211250	0.054693
C	-2.386613	-2.055091	-0.764669
C	-3.004782	-3.201555	-1.281271
C	-5.184084	-0.463430	1.325148
C	-3.353676	1.037329	0.504720
C	-4.686011	0.929422	0.916938
C	-5.446271	2.109309	0.923732
H	-6.489289	2.088345	1.236261
C	-4.884589	3.329583	0.524542
C	-3.564296	3.404433	0.083078
C	-2.771684	2.240345	0.046281
H	-4.819182	-4.359700	-1.402502
H	-6.119652	-2.853770	0.056124
H	-2.435367	-3.876674	-1.923021
H	-5.498794	4.231409	0.533717
H	-3.163530	4.345764	-0.293148
O	-2.537679	-0.063852	0.490414
N	-1.006217	-1.734398	-1.046020
N	-1.513035	2.137589	-0.541409
C	-0.054385	-2.399593	-0.059079
H	-0.454121	-3.406642	0.146642
C	-0.658593	3.107139	-0.568248
H	-0.809529	4.065409	-0.056113
C	1.345617	-2.477635	-0.595767
C	2.387924	-1.716443	-0.008868
C	3.720753	-1.796176	-0.558133
C	2.936887	-3.419407	-2.204011
C	3.975508	-2.640745	-1.651039
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H	4.989563	-2.695155	-2.057322
C	0.581229	2.921709	-1.319061
C	1.477408	3.980732	-1.517932
N	0.805904	1.679780	-1.824798
C	2.628245	3.764416	-2.277112
H	1.264461	4.957147	-1.081756
C	1.914051	1.483782	-2.556634
C	2.846505	2.493790	-2.812785
H	3.342674	4.571549	-2.442117
H	2.070782	0.473133	-2.931725
H	3.734351	2.269891	-3.403851
Cu	-0.519662	0.245725	-1.306694
C	1.645759	-3.340938	-1.682661
H	0.854240	-3.970829	-2.100793
H	-0.082999	-1.821713	0.870731
O	2.252006	-0.903725	1.008766
O	4.612843	-1.023055	0.019188
H	-0.788649	-2.167200	-1.947611
Mo	4.053874	0.123873	1.777268
O	5.441442	1.112319	1.361857
O	2.897448	1.306250	2.362526
O	4.518104	-0.886128	3.128106
C	-6.712307	-0.569623	1.262516
H	-7.177515	0.138689	1.959848
H	-7.099756	-0.368958	0.254128
H	-7.043548	-1.570332	1.568330
C	-4.723787	-0.752976	2.777662
H	-5.173593	-0.026884	3.470044
H	-5.039015	-1.761468	3.081802
H	-3.633196	-0.692116	2.884901

9-10-TS

C	-4.600375	2.863752	1.469347
C	-5.206549	1.840935	0.730017
C	-4.431024	0.905100	0.026818
C	-3.038119	1.041141	0.112497
C	-2.400694	2.068941	0.832243
C	-3.207824	2.990625	1.511270
C	-4.967052	-0.231083	-0.860179
C	-2.682286	-1.172651	-0.433910
C	-4.037011	-1.437377	-0.648858
C	-4.434748	-2.785924	-0.647015
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C	-3.489305	-3.793317	-0.417472
C	-2.158264	-3.491767	-0.120792
C	-1.716440	-2.149166	-0.073192
H	-5.222010	3.579220	2.010382
H	-6.294160	1.784090	0.705535
H	-2.742389	3.796275	2.083508
H	-3.806997	-4.838326	-0.432439
H	-1.471357	-4.298124	0.139251
O	-2.220223	0.125585	-0.484475
N	-0.960429	2.129068	0.844213
N	-0.517815	-1.695319	0.444346
C	-0.422685	2.859892	-0.362536
H	-0.919170	3.841285	-0.430867
C	0.609229	-2.403120	0.436876
H	0.618404	-3.460029	0.149748
C	1.067909	3.029458	-0.319442
C	1.904052	1.929525	-0.604533
C	3.321605	2.076542	-0.621338
C	3.058152	4.424521	-0.054987
C	3.892453	3.327728	-0.342677
H	3.505032	5.399676	0.152304
H	4.979456	3.439576	-0.355947
C	1.537514	-2.054703	1.551907
C	2.420943	-2.989977	2.105273
N	1.439847	-0.791549	2.031558
C	3.219351	-2.616185	3.187300
H	2.476357	-3.995789	1.687307
C	2.222289	-0.436249	3.064539
C	3.119983	-1.311134	3.679405
H	3.910135	-3.331128	3.637288
H	2.122713	0.595787	3.405879
H	3.728873	-0.969486	4.516917
Cu	-0.028132	0.271545	0.996511
C	1.668309	4.279093	-0.044498
H	1.030419	5.143715	0.157279
H	-0.717905	2.267385	-1.237725
O	1.463439	0.706363	-0.864078
O	4.000097	0.970297	-0.889118
H	-0.687522	2.686993	1.656504
Mo	2.947249	-0.760492	-1.466169
O	4.386107	-1.618782	-1.004284
O	1.632834	-1.953226	-1.028401
O	2.943701	-0.672426	-3.194728
C	-6.427187	-0.571132	-0.535786
H	-6.794897	-1.368449	-1.194322
H	-6.554102	-0.897629	0.505656
H	-7.075707	0.297664	-0.708720
C	-4.881898	0.222098	-2.340647
H	-5.229282	-0.583067	-3.004203
H	-5.516127	1.105106	-2.507990
H	-3.855067	0.479498	-2.630638

10

C	-4.404406	2.811150	1.783277
C	-5.080543	1.878924	0.986603
C	-4.375439	1.019120	0.128412

C	-2.977653	1.135967	0.118269
C	-2.271583	2.069195	0.902418
C	-3.009875	2.917958	1.737075
C	-4.990555	-0.018171	-0.825934
C	-2.695978	-1.012388	-0.695305
C	-4.061979	-1.247134	-0.819863
C	-4.480289	-2.588733	-0.945257
H	-5.532966	-2.842260	-1.060321
C	-3.516352	-3.605279	-0.932310
C	-2.157898	-3.345742	-0.728908
C	-1.685563	-2.016225	-0.529147
H	-4.972026	3.468231	2.444524
H	-6.167668	1.831571	1.041329
H	-2.489695	3.645825	2.364211
H	-3.837793	-4.642911	-1.057789
H	-1.464862	-4.185604	-0.663273
O	-2.227835	0.291973	-0.639651
N	-0.829832	2.092287	0.844047
N	-0.457592	-1.592981	-0.133473
C	-0.307225	2.909936	-0.309972
H	-0.802556	3.894018	-0.305927
C	0.704697	-2.392059	-0.132915
H	0.550616	-3.448289	-0.411947
C	1.184611	3.085087	-0.246302
C	2.046216	2.009511	-0.534129
C	3.456193	2.156054	-0.458471
C	3.157712	4.481079	0.141967
C	4.013675	3.398606	-0.127913
H	3.586109	5.452845	0.396633
H	5.098726	3.512436	-0.078679
C	1.289848	-2.328480	1.271177
C	1.646670	-3.462348	2.006848
N	1.390040	-1.077583	1.782817
C	2.094628	-3.308207	3.323463
H	1.568088	-4.451818	1.553722
C	1.848138	-0.937830	3.039311
C	2.196484	-2.018883	3.853576
H	2.363945	-4.180490	3.921876
H	1.940884	0.088553	3.401968
H	2.549037	-1.846730	4.871263
Cu	-0.025310	0.178860	0.724220
C	1.769427	4.326053	0.090621
H	1.119002	5.178725	0.300211
H	-0.603281	2.385299	-1.227366
O	1.640053	0.786714	-0.876504
O	4.142452	1.042986	-0.693963
H	-0.500926	2.558024	1.692979
Mo	3.116868	-0.676522	-1.212883
O	4.333222	-1.544926	-0.346447
O	1.663187	-1.913658	-1.104823
O	3.511864	-0.743031	-2.885842
C	-6.425116	-0.383632	-0.422953
H	-6.852915	-1.106052	-1.129784
H	-6.472830	-0.818717	0.584918
H	-7.076756	0.500188	-0.448307
C	-5.018807	0.585959	-2.253834
H	-5.431053	-0.144674	-2.965138
H	-5.648107	1.488209	-2.282642
H	-4.013522	0.861153	-2.598490

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C	0.095713	-3.989629	1.327901
C	1.382748	-4.232275	0.841553
C	2.165504	-3.169933	0.358220
C	1.630022	-1.873932	0.407137
C	0.301620	-1.598849	0.835047
C	-0.442181	-2.704352	1.303626
C	3.544255	-3.355735	-0.287338
C	3.750694	-0.893827	0.173596
C	4.396093	-2.136155	0.073506
C	5.792154	-2.161219	0.229437
H	6.329169	-3.107785	0.183992
C	6.519391	-0.985217	0.436193
C	5.867611	0.247886	0.478296
C	4.466888	0.318477	0.356589
H	-0.510431	-4.818013	1.700210
H	1.765887	-5.250957	0.830530
H	-1.462532	-2.531235	1.652167
H	7.602329	-1.031675	0.564758
H	6.426558	1.165053	0.669770
O	2.397430	-0.777309	0.061362
N	-0.226826	-0.317231	0.919929
N	3.745210	1.500740	0.514196
C	-0.250189	0.623789	-0.217413
H	0.749175	0.687398	-0.656261
C	4.131412	2.568178	-0.093602
H	4.966937	2.563245	-0.814154
C	-1.286470	0.297731	-1.270341
C	-2.648330	0.209091	-0.885375
C	-3.646058	-0.107561	-1.866694
C	-1.915643	-0.213025	-3.580217
C	-3.271594	-0.310693	-3.204002
H	-1.629923	-0.374677	-4.623213
H	-4.040070	-0.551022	-3.944945
C	3.473227	3.874062	0.096622
C	3.891403	4.960457	-0.694905
N	2.490129	3.977661	1.017330
C	3.261233	6.196121	-0.535330
H	4.691851	4.832804	-1.425834
C	1.900780	5.167301	1.153993
C	2.239663	6.306875	0.408748
H	3.561383	7.053668	-1.140021
H	1.105919	5.221193	1.904389
H	1.712851	7.248351	0.570218
C	-0.939898	0.080100	-2.622142
H	0.111589	0.146760	-2.918350
H	-0.461780	1.609644	0.228458
O	-3.088199	0.376822	0.338224
O	-4.891607	-0.194357	-1.413720
H	-1.178327	-0.351389	1.287491
Mo	-5.318038	0.147686	0.635045
O	-4.916646	-0.871947	2.004147
O	-5.483045	1.812327	1.157278
O	-6.946017	-0.357734	0.215679
C	4.214468	-4.671214	0.132312
H	5.181673	-4.795554	-0.371488
H	4.379449	-4.723534	1.217442
H	3.602953	-5.532002	-0.166325
C	3.357069	-3.371695	-1.828108
H	4.328549	-3.473465	-2.334863
H	2.720330	-4.217829	-2.125131
H	2.879604	-2.450942	-2.188553

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C	-5.075380	3.189916	0.919192
C	-5.522264	1.983079	0.376631
C	-4.606018	1.006236	-0.050485
C	-3.233667	1.253618	0.132398
C	-2.749982	2.518807	0.569264
C	-3.706810	3.465669	0.977192
C	-4.998200	-0.278732	-0.785915
C	-2.714539	-1.033059	-0.037500
C	-4.039229	-1.384424	-0.331647
C	-4.407229	-2.742482	-0.265538
H	-5.428316	-3.051848	-0.483450
C	-3.454913	-3.706176	0.075398
C	-2.143071	-3.338952	0.372264
C	-1.708951	-1.983530	0.352428

H	-5.795683	3.938324	1.256031
H	-6.593270	1.811379	0.278560
H	-3.357240	4.433565	1.345650
H	-3.745198	-4.759101	0.128635
H	-1.438374	-4.106781	0.695956
O	-2.301005	0.283464	-0.100156
N	-1.373021	2.790848	0.642274
N	-0.491028	-1.547971	0.793554
C	-0.653838	2.894787	-0.649107
H	-1.115177	3.680731	-1.280682
C	0.606077	-2.302089	0.632109
H	0.505356	-3.314954	0.204555
C	0.814832	3.180872	-0.462305
C	1.748485	2.133389	-0.600156
C	3.144536	2.355555	-0.387909
C	2.670915	4.701703	0.026828
C	3.599699	3.646700	-0.079667
H	3.027016	5.709159	0.257548
H	4.667673	3.824002	0.074024
C	1.558651	-2.310435	1.797354
C	2.040788	-3.537510	2.290763
N	1.887409	-1.135295	2.368051
C	2.869546	-3.546522	3.413805
H	1.762889	-4.472638	1.801112
C	2.686871	-1.161094	3.440370
C	3.203426	-2.329073	4.013152
H	3.249484	-4.489716	3.813008
H	2.936394	-0.184016	3.867556
H	3.849554	-2.280282	4.891052
C	1.304104	4.472429	-0.159788
H	0.599624	5.305604	-0.078017
H	-0.763569	1.938038	-1.168233
O	1.439028	0.895948	-0.925342
O	3.898377	1.271698	-0.489129
H	-1.235292	3.661660	1.153009
Mo	2.948240	-0.560623	-1.026338
O	4.313451	-1.284972	-0.226835
O	1.597836	-1.762434	-0.673838
O	3.247359	-0.693100	-2.729515
C	-6.469268	-0.651059	-0.555546
H	-6.739779	-1.549544	-1.124581
H	-6.688246	-0.836733	0.505322
H	-7.134617	0.146536	-0.911739
C	-4.790238	-0.045077	-2.306108
H	-5.039786	-0.956362	-2.870133
H	-5.433327	0.772248	-2.666533
H	-3.748372	0.215726	-2.534726

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C	-4.880153	2.966630	1.308917
C	-5.394158	1.805132	0.728169
C	-4.538654	0.882550	0.099483
C	-3.155253	1.137789	0.107338
C	-2.610598	2.346158	0.631093
C	-3.512802	3.244499	1.233300
C	-5.016524	-0.360813	-0.659589
C	-2.644222	-1.114051	-0.341292
C	-3.986977	-1.476830	-0.428752
C	-4.321246	-2.850633	-0.373663
H	-5.356831	-3.181689	-0.432121
C	-3.294252	-3.793081	-0.252624
C	-1.952470	-3.417367	-0.173774
C	-1.533998	-2.043135	-0.208235
H	-5.550669	3.676765	1.797798
H	-6.468210	1.626562	0.761561
H	-3.118561	4.169867	1.661643
H	-3.549135	-4.857287	-0.213711
H	-1.202162	-4.201483	-0.059172
O	-2.271938	0.219383	-0.369513
N	-1.232073	2.601632	0.658638
N	-0.301437	-1.519597	-0.111598
C	-0.466779	2.692123	-0.602334
H	-0.886840	3.487630	-1.251333
C	0.850939	-2.339117	-0.043418
H	0.677971	-3.432238	-0.146077
C	0.997343	2.956914	-0.335128
C	1.943571	1.928940	-0.545664
C	3.320508	2.120670	-0.210051
C	2.822602	4.404295	0.430534
C	3.758739	3.363373	0.264890
H	3.161009	5.377582	0.794643
H	4.814096	3.514449	0.506875
C	1.491514	-2.069502	1.309104
C	1.123412	-2.737152	2.490265
N	2.410794	-1.088655	1.309404
C	1.707081	-2.351523	3.694510
H	0.387732	-3.541685	2.457219
C	2.954927	-0.706408	2.474418
C	2.634621	-1.299622	3.695017
H	1.445170	-2.861717	4.624102
H	3.690556	0.097954	2.415716
H	3.109958	-0.958529	4.615549
C	1.469098	4.201051	0.140721
H	0.761095	5.023008	0.283417
H	-0.562930	1.737933	-1.126868
O	1.672988	0.749130	-1.047910
O	4.087194	1.044421	-0.370652
H	-1.060936	3.443458	1.204453
Mo	3.200243	-0.699036	-1.092025
O	4.599472	-1.526228	-0.472839
O	1.799426	-2.033442	-1.068959
O	3.483987	-0.627915	-2.798086
C	-6.432758	-0.781237	-0.242253
H	-6.766456	-1.652933	-0.819824
H	-6.491422	-1.034619	0.825607
H	-7.156504	0.018833	-0.448344
C	-5.041393	-0.017624	-2.172761
H	-5.349893	-0.895143	-2.760720
H	-5.749472	0.800509	-2.377059
H	-4.050496	0.293639	-2.529059

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C	4.871784	-3.357407	0.758310
C	5.457955	-2.444385	-0.125527
C	4.745662	-1.323677	-0.578359
C	3.437524	-1.164851	-0.098993
C	2.816891	-2.071755	0.775604
C	3.556874	-3.183076	1.198940
C	5.261174	-0.274977	-1.575749
C	3.449490	1.097741	-0.523658
C	4.726512	1.080396	-1.093809
C	5.399028	2.309558	-1.177674
H	6.395188	2.360842	-1.614900
C	4.808823	3.487542	-0.699668
C	3.552195	3.470411	-0.095457
C	2.852572	2.253990	0.025571
H	5.444018	-4.221135	1.100187
H	6.479607	-2.616793	-0.461003
H	3.101857	-3.903744	1.881475
H	5.354540	4.429342	-0.776085
H	3.138515	4.380750	0.338917
O	2.708578	-0.051380	-0.435110
N	1.454957	-1.841708	1.197543
N	1.692362	2.059276	0.771644
C	0.458646	-2.488317	0.249079
H	0.822622	-3.508961	0.043034
C	0.781777	2.964631	0.918163
H	0.794350	3.928560	0.395141

C	-0.932417	-2.513203	0.813068
C	-1.948933	-1.713730	0.238838
C	-3.279558	-1.742585	0.785634
C	-2.549381	-3.385509	2.432442
C	-3.562897	-2.573866	1.880748
H	-2.784965	-4.050838	3.267189
H	-4.576750	-2.593475	2.290095
C	-0.331753	2.693725	1.825631
C	-1.278622	3.681058	2.129929
N	-0.389188	1.446270	2.363320
C	-2.304834	3.385294	3.028379
H	-1.202561	4.663245	1.662615
C	-1.376110	1.174974	3.231761
C	-2.349102	2.110677	3.596522
H	-3.057472	4.134715	3.275315
H	-1.400513	0.161398	3.630822
H	-3.134454	1.826539	4.296630
Cu	0.925492	0.099618	1.620738
C	-1.258474	-3.360115	1.904335
H	-0.489211	-4.017653	2.321012
H	0.480820	-1.919532	-0.686073
O	-1.786193	-0.901133	-0.781862
O	-4.140516	-0.937982	0.197512
H	1.337166	-2.337453	2.085222
W	-3.525422	0.141351	-1.583433
O	-4.869201	1.229671	-1.193136
O	-2.321738	1.259307	-2.251675
O	-4.062923	-0.889999	-2.913919
C	6.790114	-0.284047	-1.687910
H	7.128104	0.457118	-2.423336
H	7.277831	-0.067227	-0.727572
H	7.144500	-1.259589	-2.044731
C	4.657926	-0.583123	-2.971023
H	4.987387	0.170749	-3.700374
H	4.992637	-1.570996	-3.318732
H	3.560559	-0.581771	-2.955053

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C	-5.028999	2.812280	1.253965
C	-5.562238	1.745648	0.520366
C	-4.720789	0.813840	-0.108575
C	-3.339661	0.999931	0.045778
C	-2.774387	2.073843	0.757905
C	-3.645377	2.989191	1.362060
C	-5.169081	-0.369672	-0.981961
C	-2.884875	-1.219328	-0.393565
C	-4.216562	-1.536677	-0.671856
C	-4.572203	-2.896378	-0.637064
H	-5.591094	-3.211371	-0.857845
C	-3.611000	-3.862498	-0.314477
C	-2.308187	-3.506073	0.041141
C	-1.911123	-2.149151	0.056625
H	-5.701153	3.523255	1.737355
H	-6.644652	1.650767	0.442341
H	-3.237609	3.829837	1.927861
H	-3.895436	-4.917087	-0.304188
H	-1.611867	-4.278462	0.370164
O	-2.461604	0.090698	-0.469699
N	-1.339074	2.184707	0.836673
N	-0.756393	-1.635958	0.618544
C	-0.769738	2.883496	-0.374173
H	-1.294249	3.843368	-0.506714
C	0.391686	-2.302628	0.691996
H	0.452834	-3.367287	0.444478
C	0.711220	3.108733	-0.275251
C	1.599953	2.036149	-0.490022
C	3.008124	2.239274	-0.464542
C	2.637252	4.587910	0.014207
C	3.523523	3.517201	-0.208888
H	3.037933	5.585865	0.206181
H	4.604983	3.671378	-0.188830
C	1.256514	-1.876123	1.829946
C	2.139115	-2.758160	2.465955
N	1.098812	-0.596830	2.247980
C	2.873301	-2.312971	3.566340
H	2.244143	-3.778898	2.096783
C	1.820377	-0.172721	3.299204
C	2.712810	-0.991396	3.994044
H	3.561994	-2.986038	4.079677
H	1.674424	0.869604	3.588831
H	3.270533	-0.594358	4.842716
Cu	-0.366533	0.365875	1.119769
C	1.254611	4.388366	-0.020472
H	0.577803	5.233429	0.130283
H	-1.003893	2.246031	-1.235974
O	1.220809	0.783755	-0.719015
O	3.734575	1.146800	-0.675926
H	-1.124535	2.784265	1.636831
W	2.774061	-0.644259	-1.183848
O	4.222646	-1.449330	-0.597063
O	1.474007	-1.869794	-0.749878
O	2.855718	-0.670299	-2.931814
C	-6.634957	-0.745370	-0.731835
H	-6.938824	-1.573614	-1.384635
H	-6.813710	-1.043682	0.310512
H	-7.297729	0.097103	-0.969536
C	-5.010088	0.032080	-2.471306
H	-5.290079	-0.809326	-3.121659
H	-5.662072	0.885055	-2.710471
H	-3.976747	0.314116	-2.711241

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C	-4.860307	2.763963	1.609558
C	-5.469273	1.780470	0.820333
C	-4.699306	0.917662	0.023130
C	-3.307228	1.085132	0.066497
C	-2.667800	2.069356	0.845119
C	-3.469530	2.919911	1.616762
C	-5.237529	-0.169597	-0.922666
C	-2.915295	-1.073394	-0.671254
C	-4.265440	-1.361938	-0.845716
C	-4.628591	-2.721091	-0.952926
H	-5.665452	-3.017265	-1.104101
C	-3.629687	-3.700219	-0.874002
C	-2.291349	-3.384566	-0.622728
C	-1.876658	-2.033871	-0.440270
H	-5.478088	3.422630	2.222492
H	-6.555558	1.696537	0.832036
H	-3.002267	3.687839	2.237602
H	-3.907700	-4.751984	-0.984640
H	-1.571312	-4.195911	-0.507724
O	-2.495738	0.247612	-0.631653
N	-1.226031	2.140253	0.845484
N	-0.681171	-1.555156	-0.008411
C	-0.682666	2.933587	-0.315826
H	-1.211652	3.898349	-0.369919
C	0.507282	-2.309950	0.047567
H	0.403097	-3.376107	-0.213527
C	0.798173	3.166780	-0.197288
C	1.710893	2.120815	-0.424387
C	3.108466	2.322901	-0.297589
C	2.702125	4.642945	0.240569
C	3.608659	3.588859	0.027972
H	3.083012	5.634933	0.492290
H	4.685768	3.744631	0.117504
C	1.045410	-2.192894	1.465805
C	1.419634	-3.296455	2.237648
N	1.084770	-0.927576	1.950977

C	1.824090	-3.097154	3.562045
H	1.389868	-4.297663	1.805024
C	1.500898	-0.743831	3.216599
C	1.864537	-1.793392	4.064604
H	2.107980	-3.945524	4.187412
H	1.545926	0.292792	3.558309
H	2.182096	-1.585875	5.087161
Cu	-0.351317	0.250085	0.837079
C	1.323857	4.434971	0.136273
H	0.635027	5.266741	0.302555
H	-0.919131	2.365154	-1.223980
O	1.366763	0.872229	-0.751215
O	3.842901	1.226326	-0.486434
H	-0.950251	2.648664	1.688872
W	2.909651	-0.540282	-0.972134
O	4.103230	-1.360805	0.004764
O	1.481919	-1.813750	-0.907065
O	3.408231	-0.673579	-2.633880
C	-6.671736	-0.579007	-0.563409
H	-7.044824	-1.335809	-1.265216
H	-6.741423	-0.988969	0.453657
H	-7.354631	0.277796	-0.637802
C	-5.232925	0.393867	-2.367159
H	-5.591423	-0.370053	-3.072612
H	-5.892900	1.270942	-2.444515
H	-4.225788	0.696490	-2.682326

4

C	-2.693137	-4.249618	0.210784
C	-3.722939	-3.346816	0.489860
C	-3.453468	-1.970302	0.559415
C	-2.144674	-1.532262	0.303313
C	-1.060954	-2.428216	0.097705
C	-1.384491	-3.802068	0.045913
C	-4.488504	-0.920306	0.976978
C	-2.875143	0.653050	-0.135218
C	-4.213149	0.343514	0.160451
C	-5.206293	1.247072	-0.251617
H	-6.255306	1.027702	-0.058544
C	-4.874917	2.438209	-0.902735
C	-3.538863	2.753853	-1.148130
C	-2.510049	1.865978	-0.777322
H	-2.905494	-5.319440	0.161750
H	-4.728660	-3.723096	0.667286
H	-0.577298	-4.518337	-0.123415
H	-5.663013	3.121596	-1.223950
H	-3.275480	3.663103	-1.690468
O	-1.853696	-0.182655	0.211736
N	0.246436	-2.013553	-0.116625
N	-1.177269	2.085178	-1.129704
C	0.912619	-1.020469	0.760815
H	0.503037	-1.089712	1.780994
C	-0.666050	3.251014	-0.931341
H	-1.208339	4.038752	-0.382145
C	2.401583	-1.255774	0.796490
C	2.972156	-2.135167	1.744793
C	4.392532	-2.350004	1.770721
C	4.630738	-0.840394	-0.128396
C	5.207929	-1.699371	0.828592
H	5.270326	-0.339864	-0.860786
H	6.288742	-1.866424	0.850056
C	0.673836	3.634486	-1.410094
C	1.185883	4.889350	-1.030256
N	1.350105	2.781170	-2.210162
C	2.447731	5.273303	-1.487721
H	0.603259	5.547593	-0.383308
C	2.553709	3.169247	-2.638710
C	3.151988	4.395821	-2.313197
H	2.870677	6.238356	-1.203328
H	3.079867	2.459682	-3.284811
H	4.140828	4.647118	-2.699141
C	3.251910	-0.623396	-0.143670
H	2.808254	0.047924	-0.882989
H	0.701178	-0.013509	0.379331
O	2.294470	-2.793300	2.670440
O	4.816316	-3.158332	2.719359
H	0.852756	-2.822401	-0.222047
W	3.328990	-4.188860	3.942094
O	4.579916	-4.193326	5.200498
O	1.835671	-4.137012	4.899987
O	3.342455	-5.771052	3.150923
C	-5.929630	-1.419614	0.807262
H	-6.647910	-0.662698	1.147521
H	-6.161839	-1.673937	-0.236260
H	-6.105256	-2.306991	1.428385
C	-4.262809	-0.589490	2.476590
H	-4.968236	0.186668	2.809308
H	-4.421099	-1.487697	3.091108
H	-3.243621	-0.227859	2.665612

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C	-5.476913	3.147432	0.747430
C	-5.873813	1.901145	0.257498
C	-4.917704	0.941026	-0.117098
C	-3.557494	1.246017	0.069526
C	-3.125695	2.550390	0.440981
C	-4.120486	3.478479	0.798401
C	-5.253230	-0.384225	-0.807200
C	-2.957908	-1.027766	0.010770
C	-4.261614	-1.437132	-0.300626
C	-4.583130	-2.804716	-0.195833
H	-5.587235	-3.158443	-0.424564
C	-3.605620	-3.720204	0.201578
C	-2.318325	-3.294480	0.525582
C	-1.932558	-1.924291	0.474236
H	-6.227246	3.882831	1.045236
H	-6.936812	1.685808	0.158282
H	-3.810784	4.476908	1.117697
H	-3.859163	-4.780798	0.283675
H	-1.599228	-4.024293	0.900905
O	-2.587846	0.299011	-0.100524
N	-1.762891	2.885134	0.494316
N	-0.755615	-1.429153	0.957327
C	-1.039877	2.894282	-0.798208
H	-1.542241	3.576702	-1.512640
C	0.370150	-2.156357	0.907852
H	0.330142	-3.173119	0.480858
C	0.405869	3.296005	-0.649717
C	1.405262	2.306365	-0.604905
C	2.783566	2.648933	-0.472026
C	2.161102	4.993808	-0.461311
C	3.157497	3.998685	-0.401285
H	2.451391	6.046661	-0.416801
H	4.213028	4.267352	-0.307908
C	1.214144	-2.150246	2.156694
C	1.746402	-3.367185	2.624703
N	1.386188	-0.995026	2.829694
C	2.460930	-3.389969	3.823094
H	1.594314	-4.285153	2.053956
C	2.083389	-1.032151	3.970717
C	2.637534	-2.193137	4.522546
H	2.874450	-4.326881	4.203204
H	2.207755	-0.070953	4.480701
H	3.189895	-2.154063	5.462670
C	0.811603	4.648917	-0.582809
H	0.054280	5.436351	-0.640100
H	-1.085899	1.881836	-1.209952
O	1.174786	1.006549	-0.693496

O	3.603563	1.608403	−0.414434
H	−1.663311	3.803569	0.923920
W	2.773260	−0.332701	−0.645181
O	4.087471	−0.864234	0.395591
O	1.470730	−1.606081	−0.306110
O	3.255972	−0.662342	−2.297571
C	−6.712722	−0.801594	−0.579440
H	−6.944400	−1.728664	−1.119000
H	−6.937342	−0.957518	0.484984
H	−7.401983	−0.042048	−0.971362
C	−5.035422	−0.197382	−2.332273
H	−5.239236	−1.137960	−2.865749
H	−5.706599	0.578951	−2.730427
H	−4.002195	0.098414	−2.557535

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C	−5.314839	2.983238	0.995959
C	−5.773135	1.769707	0.478980
C	−4.868403	0.815342	−0.020442
C	−3.492408	1.099818	0.049276
C	−2.999540	2.353014	0.516705
C	−3.948742	3.279004	0.987396
C	−5.288642	−0.489286	−0.708171
C	−2.909902	−1.162371	−0.253847
C	−4.238777	−1.561997	−0.380439
C	−4.540451	−2.941535	−0.282941
H	−5.564407	−3.300700	−0.370491
C	−3.498689	−3.853840	−0.082271
C	−2.169450	−3.443195	0.027419
C	−1.784360	−2.061942	−0.053421
H	−6.026152	3.717711	1.379667
H	−6.844700	1.575036	0.458520
H	−3.595294	4.242240	1.364746
H	−3.731571	−4.921181	−0.008394
H	−1.402792	−4.201347	0.196997
O	−2.562527	0.177068	−0.310111
N	−1.624552	2.628327	0.605748
N	−0.569413	−1.503767	0.047514
C	−0.821398	2.689445	−0.636034
H	−1.244039	3.443771	−1.330668
C	0.609301	−2.265067	0.218428
H	0.489700	−3.369986	0.215547
C	0.627148	3.006822	−0.344032
C	1.605991	2.000689	−0.493219
C	2.965375	2.242696	−0.128623
C	2.393330	4.531435	0.412238
C	3.361020	3.510573	0.309973
H	2.696080	5.526602	0.746958
H	4.405152	3.697745	0.574060
C	1.183482	−1.830893	1.559298
C	0.759901	−2.352627	2.793617
N	2.087349	−0.836631	1.487943
C	1.265359	−1.805006	3.969569
H	0.037115	−3.168799	2.821576
C	2.557117	−0.296442	2.624519
C	2.175173	−0.740100	3.888579
H	0.955442	−2.198116	4.940278
H	3.279614	0.511627	2.504600
H	2.589066	−0.273844	4.783377
C	1.054051	4.279913	0.096949
H	0.320752	5.086442	0.192123
H	−0.876594	1.711437	−1.121399
O	1.381833	0.792414	−0.955340
O	3.763736	1.175284	−0.226395
H	−1.497201	3.501350	1.114108
W	2.944763	−0.622994	−0.850056
O	4.353483	−1.407416	−0.143393
O	1.576911	−2.000408	−0.803869
O	3.283639	−0.657342	−2.567955
C	−6.705135	−0.920900	−0.300257
H	−7.000316	−1.838371	−0.825247
H	−6.786369	−1.101961	0.780696
H	−7.444144	−0.158086	−0.579681
C	−5.280273	−0.247300	−2.241457
H	−5.546840	−1.170895	−2.777182
H	−6.005022	0.534012	−2.518539
H	−4.288882	0.069372	−2.591966

Table S4. Harmonic frequencies (cm^{-1}) for all optimized species. One of the minima, **4**, has a small imaginary frequency (< 30 cm^{-1}) corresponding to a torsional motion in the aminocatechol arm. All other imaginary frequencies correspond to the transition state motion forming the new C–O bond upon nucleophilic attack of the imine.

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9
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     7.1032    17.5599    25.7205
    35.3892    43.0910    52.0884
    58.8321    67.4335    73.0321
    85.8063    89.4529    96.6095
   107.7707   117.5272   131.9803
   136.6251   140.4165   166.3339
   179.3825   191.6322   200.3968
   207.7144   211.9480   229.1424
   232.7158   235.4230   247.8128
   258.5141   274.3728   279.5519
   288.8151   293.2551   299.1705
   309.1447   328.7907   332.7439
   342.5347   346.5794   359.4514
   370.1353   378.2583   382.6747
   407.6678   413.0617   423.2865
   478.9521   490.2005   493.0755
   505.5613   510.2055   521.7655
   529.7241   535.5974   545.9893
   550.8888   559.4831   575.5730
   582.3093   592.2959   605.4066
   620.1781   628.9273   640.1648
   657.7311   686.2976   692.9226
   717.4352   729.4439   731.4594
   733.2747   742.5972   756.1756
   763.5500   778.2241   782.9423
   805.2220   814.8937   841.1286
   861.9741   862.9544   867.7478
   869.1655   872.6840   874.4435
   877.8589   878.8610   896.7119
   896.9389   905.2746   935.4017
   936.8674   938.4355   939.3401
   940.6801   944.5606   951.8554
   985.1482   992.3889  1004.1356
  1008.8582  1031.0769  1060.1040
  1067.3177  1086.1700  1091.9563
  1095.3396  1117.7631  1125.7493
  1141.6007  1152.2828  1159.1504
  1165.6598  1182.9458  1189.5744
  1222.1410  1227.5223  1236.2768
  1237.9922  1243.1268  1260.0184
  1269.6994  1274.5494  1281.8944
  1309.2523  1311.0742  1337.6754
  1341.9570  1353.7872  1375.5361
  1376.6254  1384.9019  1392.0551
  1397.4850  1401.5449  1415.9924
  1448.4306  1462.1303  1464.4577
  1472.0833  1475.3979  1476.4110
  1478.6029  1483.2441  1489.4923
  1492.9219  1498.2193  1505.4403
  1529.5959  1578.9823  1589.3451
  1598.9451  1601.3631  1619.2284
  1623.1840  1629.2562  1645.1726
  1656.6852  3016.0312  3034.6461
  3043.7370  3116.3247  3126.9046
  3128.6989  3139.4263  3140.1238
  3141.1742  3142.7369  3143.5550
  3161.4975  3174.4108  3182.7380
  3189.8509  3193.9844  3201.8849
  3204.4777  3209.3828  3210.0290
  3213.0062  3222.2304  3469.8973
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  -238.0624    29.8612    34.7233
    44.9277    50.2932    51.7696
    59.6945    68.6470    81.4018
    96.8474    99.8073   104.8556
   110.4340   116.7443   128.9134
   156.4218   158.4331   175.6129
   183.5044   203.5102   211.2745
   216.2817   218.1736   227.5929
   236.9026   237.7516   247.4719
   265.9296   271.1652   279.7029
   285.7852   295.6909   314.7799
   324.4696   330.6364   333.7850
   336.1300   357.9636   367.0084
   375.9262   380.2757   396.9986
   406.0227   410.6893   445.3040
   485.4390   494.2470   501.4672
   515.4198   523.3884   525.4307
   531.3181   542.9391   551.4261
   557.3898   564.3086   581.8830
   587.0210   598.2157   605.0071
   617.8347   624.8111   639.6833
   657.9862   660.6680   688.5270
   709.4575   711.4222   727.8308
   728.3185   735.7414   745.5849
   754.1019   763.2586   765.6433
   782.9509   815.0301   827.7425
   837.1182   847.4364   864.1229
   867.3391   871.4716   873.1138
   887.1856   894.6382   898.1348
   907.6649   921.0821   922.8939
   929.8566   933.2984   934.9292
   938.7192   958.6812   973.8770
   993.0553   996.3053  1003.9126
  1040.4160  1060.9043  1063.5960
  1083.1791  1087.1085  1090.4388
  1105.7135  1113.9235  1123.5957
  1140.7115  1153.6340  1158.4011
  1165.5473  1182.5907  1187.8895
  1222.6708  1224.9346  1229.0610
  1241.8640  1248.7880  1256.0406
  1267.6347  1270.9248  1279.8753
  1295.4440  1310.7589  1330.9437
  1333.3835  1350.2077  1372.3077
  1373.1464  1381.0749  1388.6123
  1394.9219  1398.7252  1422.6203
  1435.9278  1459.3668  1465.0204
  1468.5444  1472.8754  1475.7257
  1479.9295  1482.3608  1484.1281
  1488.5052  1494.6154  1503.0796
  1516.2281  1526.6532  1591.3771
  1592.4151  1603.2563  1609.5505
  1613.9787  1625.4296  1629.0969
  1641.9397  3029.3110  3030.6864
  3040.9717  3113.3068  3117.6286
  3121.6133  3134.8331  3137.8825
  3140.6185  3146.6334  3157.5863
  3166.5385  3167.1233  3173.9177
  3177.4556  3183.4777  3185.1223
  3186.9243  3196.7776  3202.9348
  3204.5924  3207.3206  3489.5840
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10

16.3456	26.3890	38.8834
44.1403	45.7385	59.3039
71.6727	82.1390	92.3435
94.4756	101.6272	112.4754
115.6319	132.6922	149.3761
161.5854	171.2807	189.7916
195.1242	204.6592	214.9518
224.6729	233.8061	241.1335
243.7127	246.8609	264.0725
272.6288	280.5188	289.3124
296.1271	299.6653	320.8109
331.5205	337.6496	351.9391
354.3031	366.2574	376.6419
378.7744	383.2525	394.8441
409.1346	432.0444	480.9093
488.4033	500.0760	512.2107
520.8871	527.2344	538.0070
549.0680	554.4563	560.8659
565.7588	582.6410	589.0484
599.0165	602.9033	614.0920
622.4879	633.8539	643.1102
660.1820	694.0313	697.2033
709.3302	721.0164	730.1863
732.4893	734.8214	745.9771
761.1365	773.4126	783.9380
790.7475	812.2648	832.5406
847.4196	853.6467	864.4414
866.4467	869.4923	873.6664
894.4316	897.1470	903.0526
911.2117	917.8605	927.6919
928.9802	933.8158	937.4084
944.5140	962.0044	968.0405
986.3265	991.2762	1007.3577
1040.8654	1060.3378	1060.6058
1082.1433	1087.6323	1089.7172
1101.4466	1111.7857	1135.9450
1148.7874	1152.2050	1160.0293
1166.3541	1180.0714	1194.3480
1204.5145	1212.3785	1226.0581
1244.7052	1248.7017	1255.2559
1266.1157	1275.4880	1281.5131
1298.3918	1318.0464	1325.3044
1330.0579	1348.5974	1364.6065
1374.3979	1374.8414	1384.7315
1388.6299	1396.4358	1400.7798
1430.6597	1444.8307	1465.3583
1468.4957	1474.5072	1478.6748
1479.3421	1480.3858	1482.8443
1489.1088	1497.0152	1503.5441
1504.2306	1511.5661	1574.4584
1595.8700	1596.3355	1608.1864
1615.6622	1617.5384	1626.1798
1638.6448	3008.9051	3027.0700
3031.2394	3039.7351	3115.7606
3118.3565	3130.1424	3136.4996
3139.6281	3147.6841	3153.8378
3162.5311	3165.8189	3166.4677
3179.6868	3180.7715	3180.9451
3182.4519	3191.0150	3200.8378
3202.1573	3202.2879	3484.1630

3

16.5579	20.3809	23.9484
26.6614	35.4442	44.8431
52.4722	54.2945	58.2034
70.5909	87.4609	96.5163
111.3537	125.0967	148.5915
159.5494	165.3303	184.5170
188.7250	199.8788	224.4275
229.3034	232.9679	239.4006
243.1869	252.4280	267.5620
286.4165	292.5187	300.9387
308.4957	322.9478	323.4733
345.6470	348.6308	357.4076
365.9175	368.0921	390.9253
395.6203	397.1276	433.2057
459.9970	471.9973	478.7474
502.5056	511.1334	523.3819
526.7568	540.2360	543.1473
548.9445	554.8424	568.6028
582.3948	586.0844	600.2749
612.8591	613.0725	626.9583
660.1120	678.3975	690.3721
707.3579	716.8969	720.4650
734.3792	735.0879	740.3683
756.8572	764.6564	783.5362
786.0164	810.7909	812.4140
842.7959	847.9316	858.8880
861.5670	864.2281	865.6975
869.5886	872.2970	889.5344
893.9465	895.1425	912.2936
921.7479	924.8899	935.8030
955.1809	963.1731	975.4359
985.1720	985.9260	1002.8541
1005.7069	1042.3429	1059.5961
1063.7703	1079.6729	1096.2178
1106.8682	1111.2832	1127.4079
1139.8086	1154.3057	1157.4544
1164.4125	1183.7055	1194.3638
1213.1163	1220.7878	1232.1401
1248.0886	1251.1742	1263.0649
1279.9467	1283.0488	1306.2816
1318.0893	1320.4247	1335.0649
1347.6829	1357.2118	1373.9980
1385.3200	1391.1956	1393.7862
1398.9359	1401.8952	1442.3991
1451.1400	1458.0361	1464.8278
1466.2716	1476.2567	1478.1492
1481.3160	1487.6174	1494.7713
1503.2615	1504.5080	1522.1598
1535.6399	1581.9580	1599.4849
1602.6075	1602.8655	1612.8687
1617.1207	1621.5347	1641.2963
1673.9835	3023.3799	3026.4747
3033.2718	3042.5428	3118.8775
3128.4949	3135.2344	3136.8003
3138.2811	3140.3604	3152.9634
3155.1865	3157.9460	3164.6048
3174.7264	3180.1733	3181.0399
3190.9549	3192.6625	3204.0701
3205.8889	3207.8266	3485.7193

3-11-TS

-239.5234	27.1076	33.6533
42.1759	50.7097	62.3623
78.4923	82.9217	94.5639
102.0990	118.4046	123.1029
135.3061	154.7091	159.8483
164.4618	178.8029	199.4971
212.0015	216.9344	226.5548
234.5264	239.5063	244.7796
253.5268	258.8806	276.9620
279.4984	288.6010	306.0887
317.6098	334.1407	339.8963
345.3422	356.7095	358.4344

370.3476	379.0822	388.7927
397.2449	417.9030	443.9050
479.8244	488.4331	493.7983
520.3741	524.5738	529.7187
541.8165	545.3957	549.7475
551.9235	562.5868	575.4541
584.6723	606.3410	612.6034
616.8853	627.3195	641.5574
651.4581	662.8748	691.7353
704.5108	705.3992	715.8458
731.2198	734.2166	740.9119
750.5023	758.3989	776.8842
780.6242	785.0521	810.6775
815.0227	817.0370	845.6194
852.9338	861.0083	870.5425
873.1663	875.4863	888.5922
896.0544	905.4513	910.4271
913.6558	925.8454	931.9597
943.8697	961.8541	972.6120
989.1902	1002.1940	1007.7462
1023.1164	1061.4062	1063.3877
1078.8566	1095.5722	1099.8190
1103.7491	1123.2178	1137.6363
1152.1134	1155.2481	1162.6337
1169.3522	1180.0305	1187.6302
1212.5890	1218.3461	1233.6785
1245.0498	1247.2716	1250.5564
1262.6140	1270.2860	1291.8646
1305.6392	1318.4934	1333.0023
1338.5014	1355.8591	1362.0167
1371.3328	1375.3797	1386.4482
1392.8334	1397.6850	1423.7667
1443.7146	1458.4982	1464.3969
1466.7582	1476.3773	1478.8864
1479.9215	1482.0536	1488.6268
1493.3621	1501.8590	1503.9633
1514.0618	1525.9487	1582.7633
1590.3617	1603.4932	1605.9896
1609.1812	1617.4032	1623.3666
1632.6328	2944.7512	2987.7523
3022.4376	3040.0538	3113.3313
3129.7077	3131.8124	3132.9710
3135.4730	3138.1363	3140.9237
3145.7418	3149.7535	3157.4644
3163.8900	3166.6529	3175.1530
3175.5422	3180.7220	3194.2903
3199.9400	3200.5452	3522.9695

11

32.7519	37.0707	42.9893
54.1510	71.6150	85.1519
88.0731	93.9906	96.5452
122.7534	134.6730	147.3109
149.2842	156.6575	174.3669
179.3118	198.6968	207.6752
218.2295	233.1609	235.3567
243.8917	251.5193	263.2372
268.4168	275.7906	282.9161
298.5004	302.3954	312.7911
318.2817	337.8746	355.7474
359.7412	367.7508	368.3586
374.7568	383.4943	413.8608
419.7217	441.4289	474.0621
485.9947	492.3479	505.8960
520.1409	527.0599	543.7059
547.2347	553.1419	554.0107
563.3934	577.8386	585.2905
599.7891	607.6011	616.7300
623.3719	632.3053	641.6021
664.7502	679.8054	691.4247
705.3269	707.6170	717.5868
728.8307	734.3704	739.8534
753.4721	755.4587	758.9472
767.8684	779.9871	812.6355
822.1896	839.1597	851.9058
856.2428	859.7719	869.2888
876.0114	877.9963	890.0535
891.4506	904.4906	905.7647
924.5187	928.9552	929.8856
952.9483	962.8625	975.4722
995.8036	998.5728	1006.4646
1022.2944	1058.2983	1063.4668
1080.3457	1088.1238	1093.7200
1107.3135	1108.6768	1130.4094
1140.5480	1151.2540	1157.2579
1163.2820	1182.0586	1188.3401
1205.6261	1213.8225	1233.0431
1244.3928	1249.3391	1256.8019
1272.2557	1280.4532	1292.3947
1306.2019	1309.8107	1322.4367
1330.6158	1347.4167	1360.0134
1371.6271	1377.4152	1385.1933
1387.4468	1394.0584	1398.7215
1442.1072	1452.4010	1468.1951
1468.7363	1478.9578	1482.1771
1482.6261	1485.0014	1490.3054
1496.3454	1503.7378	1506.5924
1517.4443	1524.8227	1564.2932
1587.6929	1598.6258	1606.0199
1606.4872	1616.6487	1626.5547
1632.3389	2900.9105	2938.7392
3021.0047	3036.2017	3110.2285
3126.6675	3130.5132	3133.7785
3135.4718	3137.1084	3148.5984
3149.5010	3153.2790	3168.5153
3169.2481	3171.2724	3174.4448
3175.8941	3192.7606	3198.1289
3198.4518	3198.7313	3531.2171

12

-28.4088	14.1956	18.7537
27.3382	31.7170	39.8954
55.6843	62.2576	66.7358
72.3917	88.2345	100.9871
103.0347	113.6256	128.1196
135.7314	147.8446	164.2662
173.7137	188.7199	196.6951
204.7386	210.2018	220.1591
233.4222	238.4485	251.2590
260.4594	274.6342	279.4292
292.7271	294.7838	297.8491
311.8725	326.4942	331.2594
338.2374	342.6838	348.4491
363.1806	373.3998	384.1094
403.1472	409.4347	425.6975
482.8276	486.9502	494.4386
506.0679	515.1703	524.0831
532.0221	538.9193	546.6240
552.4784	561.5139	576.6655
584.5274	597.5494	605.6910
620.2248	627.7962	641.6778
658.9842	687.6611	698.2713
720.0783	727.8387	733.0036
735.0805	743.6651	755.7627
761.9714	777.5101	785.1690
812.9098	816.5832	839.3479
846.8140	852.6307	868.3670
869.9527	870.0112	874.3770

877.8420	881.1976	897.0048
902.2143	906.6408	936.8827
937.5838	939.0700	939.7902
941.9523	948.3839	949.2565
982.5962	994.5190	1003.4783
1008.8874	1030.7340	1062.8675
1065.8794	1089.8722	1093.2215
1100.2130	1115.9066	1127.4868
1139.9143	1155.1121	1157.3812
1166.3563	1184.3640	1191.4559
1228.9996	1233.0353	1238.7940
1242.3207	1244.1264	1262.7196
1271.9279	1277.1039	1284.4428
1311.3728	1312.8318	1338.8504
1342.7514	1349.9954	1377.7034
1380.9566	1382.9617	1394.8842
1395.7873	1401.8738	1421.2701
1447.6183	1462.0480	1466.3530
1472.5333	1475.5969	1477.0377
1478.1014	1483.9000	1489.6029
1493.5705	1500.2162	1507.4496
1532.0261	1585.3309	1591.2385
1601.2161	1602.9530	1619.4270
1624.6613	1629.0152	1645.4331
1659.0691	3016.1739	3034.5522
3044.0146	3116.6186	3128.5846
3131.0265	3140.0864	3140.7886
3143.5926	3144.3183	3147.4204
3164.2927	3175.4250	3181.9499
3190.3934	3193.2767	3200.7173
3202.0601	3207.8047	3208.4842
3209.4325	3218.0051	3470.3320

12-13-TS

-213.1822	20.4166	30.5694
42.0755	45.3385	52.3621
58.3505	59.2694	76.2127
90.7051	95.9825	97.3108
107.4443	116.4201	126.9663
150.2468	155.7186	172.7553
181.5688	200.2030	206.4261
212.5717	218.0283	229.4552
237.1109	243.4698	255.7573
265.2419	270.2644	281.8792
294.9233	300.2716	314.4570
321.0296	328.2716	337.6537
344.3218	345.9709	356.2929
374.8664	380.8466	396.6994
407.2266	410.1020	445.8099
486.4393	495.4481	501.8154
515.6719	523.8839	525.9949
533.6019	544.4044	553.7935
558.4045	564.3237	582.3508
587.3683	597.9364	606.0468
619.7128	624.2533	640.6942
657.8800	662.6963	689.7997
710.7737	712.8792	728.5264
728.6928	737.8420	747.0585
755.9214	764.6030	766.4188
784.4718	814.9856	829.6604
839.1375	846.5647	864.3104
868.1565	872.0234	873.5519
881.0210	889.6018	895.8793
909.5914	920.7500	923.4706
930.8908	935.0212	937.2890
942.0604	959.5061	974.5475
993.8183	996.2013	1009.1928
1040.8230	1061.5082	1063.8303
1084.0947	1087.6719	1091.3743
1105.6680	1114.1456	1124.6940
1142.3863	1154.1146	1158.4250
1166.2611	1183.3179	1188.4476
1223.3756	1225.6634	1229.6000
1242.5245	1249.6649	1257.5458
1267.8903	1271.9250	1280.2431
1300.1040	1306.1044	1330.2035
1332.0750	1350.4859	1372.6697
1375.5386	1381.6884	1389.6409
1398.2413	1400.4484	1422.1233
1436.1269	1461.9973	1467.4262
1472.5752	1474.7146	1477.6582
1481.1204	1483.4469	1484.9692
1489.4573	1499.0567	1507.2595
1517.2296	1529.1454	1592.4334
1596.2302	1602.6223	1613.2439
1614.5504	1625.8862	1628.8733
1642.7121	3030.1789	3031.6636
3041.6069	3116.9328	3118.0950
3122.4666	3134.8996	3138.8116
3140.8327	3146.5300	3159.1952
3166.6080	3168.2196	3175.4026
3177.2896	3184.3816	3184.6032
3187.4008	3196.5019	3203.3183
3204.0552	3205.9455	3486.2569

13

20.8857	26.7449	39.7637
49.1204	50.2759	58.0627
77.9878	83.2200	93.1483
95.9255	107.9161	115.4229
119.6764	135.7516	150.7285
162.2015	175.1567	188.4922
192.3393	201.2120	212.1025
225.3730	232.8395	237.4764
243.4681	244.7829	264.9049
268.3459	280.0044	284.2212
290.5891	297.8804	320.2781
329.0972	334.9453	348.0620
356.8726	362.0820	371.8719
379.6809	382.4196	395.7623
408.4495	430.0077	481.9147
490.4679	501.0200	513.7552
521.5078	530.4556	542.7593
549.2985	554.8831	565.7543
570.1973	583.9921	589.9785
601.9397	603.8723	614.6336
623.8088	636.8394	643.6930
660.2742	695.6342	696.6336
712.5310	720.5055	731.8461
732.1326	736.9554	746.4238
762.2652	774.6402	784.7761
790.5613	812.6123	836.4354
847.8686	853.4205	862.8752
865.9278	869.4372	875.0266
896.7007	897.4879	903.0207
904.1955	907.8841	926.1250
930.4984	932.1282	937.1143
945.7577	962.1437	969.5626
986.0000	991.2650	1004.7403
1039.1824	1059.6692	1060.7160
1080.9978	1087.4285	1088.9251
1102.0691	1112.5136	1136.2495
1149.9965	1152.7025	1161.1121
1166.7395	1179.1845	1195.2505
1207.1373	1212.7527	1225.5128
1244.4845	1248.2519	1254.9096
1264.8088	1277.8335	1281.0792
1295.1023	1321.3562	1327.7665

1331.9552	1348.0587	1365.4051
1374.4058	1375.6414	1384.6118
1387.8599	1395.8498	1402.9239
1429.2854	1445.3838	1464.9029
1465.2422	1475.3144	1476.8048
1479.0650	1480.4230	1484.3675
1488.1408	1496.0439	1502.4015
1504.4607	1513.2193	1575.0845
1595.5375	1600.4959	1608.4076
1618.1054	1619.9317	1626.2676
1638.4638	3016.4060	3026.7251
3033.2535	3039.9713	3117.8773
3119.1984	3130.3494	3136.7990
3138.8297	3148.7660	3153.8644
3163.3949	3167.1548	3168.3232
3178.2827	3180.7846	3181.7976
3183.5661	3190.4494	3200.0906
3202.0375	3202.6611	3483.2704

4

12.7447	15.2890	21.6150
27.6516	38.1784	45.4892
49.5615	65.5239	76.1041
82.9878	88.5612	92.5857
112.3290	115.3490	150.7893
159.3048	167.9569	178.6765
189.1855	195.6962	209.2903
223.5106	232.1261	239.1540
242.1703	253.5173	265.8471
270.2189	285.8566	300.1510
310.7803	318.9583	330.8327
336.6993	340.0821	353.2913
357.2164	366.0654	367.6305
392.7391	397.8497	423.8241
462.8724	475.2300	490.1385
502.7025	518.3236	523.8559
533.1615	538.2768	542.6141
549.8262	561.1011	567.3583
580.6040	603.0396	603.9576
611.5148	620.5163	634.7804
654.8171	680.0110	690.0416
704.8580	708.9769	721.9283
731.4360	740.1342	746.7002
754.0675	764.6996	773.5251
778.3875	807.3591	809.7892
835.2069	841.2270	848.8752
851.9489	862.9023	864.2942
874.6253	879.0117	885.9693
898.3802	903.0861	916.7681
925.9072	935.8171	940.4360
953.2602	956.4671	974.5214
984.0373	985.0789	1000.4235
1011.5242	1045.6019	1056.9628
1062.3597	1076.9029	1096.7906
1104.7295	1110.9934	1128.0362
1140.5840	1155.8572	1157.8082
1164.7621	1182.9339	1196.6933
1212.0681	1221.7161	1231.3300
1245.0070	1247.2315	1259.3524
1269.9677	1281.7198	1300.2735
1319.3420	1319.5845	1341.7041
1354.0897	1356.8470	1372.9462
1383.6102	1386.5715	1393.5354
1396.9483	1402.2039	1441.1590
1446.6280	1461.9230	1465.5232
1475.2707	1477.2349	1479.6841
1484.3876	1488.1828	1493.3864
1500.6144	1505.0789	1519.4292
1527.4953	1589.8652	1599.7637
1601.3094	1603.8537	1612.6314
1618.0620	1620.3815	1640.6014
1670.3128	3022.6418	3026.4874
3042.3431	3043.5342	3107.9549
3119.7670	3134.2173	3136.2059
3137.0806	3140.9969	3149.1662
3150.0125	3165.1565	3167.0862
3174.6800	3179.9040	3181.0667
3190.5119	3191.2467	3202.2736
3207.1268	3209.5075	3557.8115

4-14-TS

-217.5706	21.3292	30.7539
36.9538	44.6188	55.9416
68.9767	74.1064	81.9817
95.1050	104.8823	123.1253
127.3448	153.8463	155.0120
163.8978	168.8690	196.2131
201.9855	211.5794	221.5104
225.7707	229.6472	236.8804
249.0461	254.9376	272.5155
276.7744	283.4693	310.5519
316.6162	328.5931	336.3429
347.2078	350.7524	357.3233
362.0553	368.8881	389.1635
402.2203	409.9040	443.1049
478.1187	490.9598	495.1152
517.8540	521.5278	530.5776
540.5540	547.2062	549.2316
555.6533	564.0421	575.8223
585.9920	604.9125	614.8311
619.2783	625.1256	639.4584
649.9198	658.4264	690.9259
699.1414	707.0951	713.6317
730.0320	735.2327	738.8550
749.6815	756.3398	771.4362
780.7883	784.3497	800.0181
805.3491	820.1628	840.9865
855.1022	859.5977	871.8739
876.0451	878.6096	880.7213
887.4254	900.8558	909.2238
917.4880	928.2788	931.9244
943.1780	963.6994	974.5121
985.5556	1001.0378	1008.5884
1026.5894	1063.3352	1064.7513
1080.0624	1095.2382	1099.9852
1105.3943	1122.5600	1137.7649
1154.6135	1159.0340	1162.9499
1175.9294	1182.4697	1188.3357
1211.2534	1219.9312	1234.3778
1246.3853	1249.0626	1255.4520
1266.0072	1269.6105	1292.9922
1305.9626	1314.8156	1334.7970
1341.1742	1359.5854	1362.0653
1370.9643	1376.8574	1387.2289
1392.1472	1401.2307	1424.6339
1443.8359	1457.8211	1462.7033
1465.6955	1477.1091	1479.1832
1480.4783	1485.6872	1488.4688
1493.5557	1501.3959	1503.6056
1512.9365	1527.4083	1581.3300
1598.0040	1603.4243	1608.8736
1613.1726	1617.9705	1623.0611
1632.7389	2950.3721	2991.5633
3021.0298	3039.7760	3112.0985
3130.4924	3134.1644	3137.0658
3137.3177	3138.2362	3144.4260
3147.1489	3149.6750	3156.6808
3167.2440	3168.4613	3173.8219

3178.1252	3181.1521	3194.2913
3198.5961	3200.0314	3520.8170

14

24.9917	30.7492	35.9406
40.0271	69.0703	70.7743
88.4838	94.7059	98.3488
116.1688	127.2625	133.4775
145.1926	155.9624	163.8335
172.5828	192.0126	201.8788
214.9574	226.9052	232.7433
237.7520	249.4693	261.0210
265.6232	274.1620	281.6473
283.2332	291.2929	308.7784
313.2044	331.4458	352.4064
353.8083	356.6990	363.7879
367.9607	377.7837	410.9355
417.5116	437.7235	470.9348
483.8025	492.1311	503.1533
519.1910	524.6346	541.4048
545.7929	550.6523	556.8367
565.9611	578.6242	588.5289
596.6579	607.6408	611.3543
621.2733	634.4184	640.2497
661.2396	679.3200	690.9607
705.3010	708.3948	714.6065
731.5262	736.5852	739.1168
754.0460	756.8397	762.4952
764.2990	780.8172	806.2596
830.8451	840.4179	850.3933
855.5141	860.4562	868.1855
872.6812	880.2376	881.3289
889.8339	899.8225	902.2494
923.9596	926.4134	929.4757
951.5372	966.9272	979.0811
996.4716	1002.6901	1006.4270
1019.5213	1058.0832	1059.6370
1077.7657	1088.5095	1094.0583
1106.1565	1111.0909	1129.7290
1138.4695	1151.6263	1155.3499
1161.6685	1180.3707	1186.4141
1202.4008	1212.6306	1231.3391
1242.1415	1249.2804	1255.8883
1275.1566	1277.0188	1289.4209
1302.0205	1304.3784	1315.8575
1326.2772	1347.1772	1359.2279
1367.3611	1377.2661	1386.4652
1387.4543	1394.6524	1399.2728
1442.6922	1451.9589	1465.5567
1467.8923	1479.4632	1480.9337
1481.6739	1484.6997	1489.5421
1494.2584	1503.1125	1508.9984
1518.1310	1525.1323	1565.7279
1591.9521	1596.6858	1605.5259
1610.7528	1616.8332	1628.3318
1632.1245	2901.7971	2940.8987
3017.6433	3036.5037	3107.9021
3125.9269	3128.4660	3131.3283
3135.7090	3137.0381	3152.0980
3152.3840	3155.3200	3170.7964
3171.8100	3173.6215	3174.4051
3186.5003	3197.3972	3199.1731
3201.1601	3203.4026	3528.0359

Table S5. Absolute thermodynamics summary (E_h) for all optimized species.

Species	E(DZ)	H(DZ)	G(DZ)	$E(TZ)_{OPBE}$	$E(TZ)_{B3LYP}$	$E(TZ)_{B3LYP-D3}$
9	-1962.157546	-1961.663941	-1961.768683	-3406.007581	-3406.276367	-3406.451153
9–10–TS	-1962.143303	-1961.651112	-1961.749247	-3405.991082	-3406.261924	-3406.448944
10	-1962.150476	-1961.657162	-1961.756742	-3405.998329	-3406.264281	-3406.452094
3	-1764.467701	-1763.978006	-1764.080167	-1765.094069	-1765.753533	-1765.907198
3–11–TS	-1764.428316	-1763.940458	-1764.033913	-1765.054059	-1765.710599	-1765.873125
11	-1764.437470	-1763.948275	-1764.040983	-1765.062650	-1765.721746	-1765.890262
12	-1961.094434	-1960.601586	-1960.704271	-3404.932503	-3405.201815	-3405.376636
12–13–TS	-1961.080965	-1960.588565	-1960.688072	-3404.917645	-3405.189183	-3405.375685
13	-1961.088149	-1960.594753	-1960.694009	-3404.925452	-3405.192382	-3405.379710
4	-1763.402939	-1762.913224	-1763.016068	-1764.017676	-1764.676616	-1764.828662
4–14–TS	-1763.366393	-1762.878579	-1762.974008	-1763.981252	-1764.638013	-1764.799356
14	-1763.378639	-1762.889709	-1762.984451	-1763.993121	-1764.653335	-1764.821828

Table S6. Relative thermodynamics summary (kcal/mol) for all reactions.

Reaction	ΔG(DZ)	$\Delta G(TZ)_{OPBE}$	$\Delta G(TZ)_{B3LYP}$	$\Delta G(TZ)_{B3LYP-D3}$
9 → 9–10–TS	12.20	13.61	12.32	4.64
9 → 10	7.49	8.86	10.64	2.47
3 → 3–11–TS	29.02	29.42	31.25	25.69
3 → 11	24.59	25.33	25.57	16.25
12 → 12–13–TS	10.17	11.04	9.64	2.31
12 → 13	6.44	6.92	8.41	0.57
4 → 4–14–TS	26.39	26.32	27.68	21.85
4 → 14	19.84	20.00	19.20	8.88

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