**Supporting Information for:**

# Iron(II)-Induced Cycloisomerization of Alkynes via "Non-Vinylidene" Pathways for Iron(II)−Indolizine and −Indolizinone Complexes

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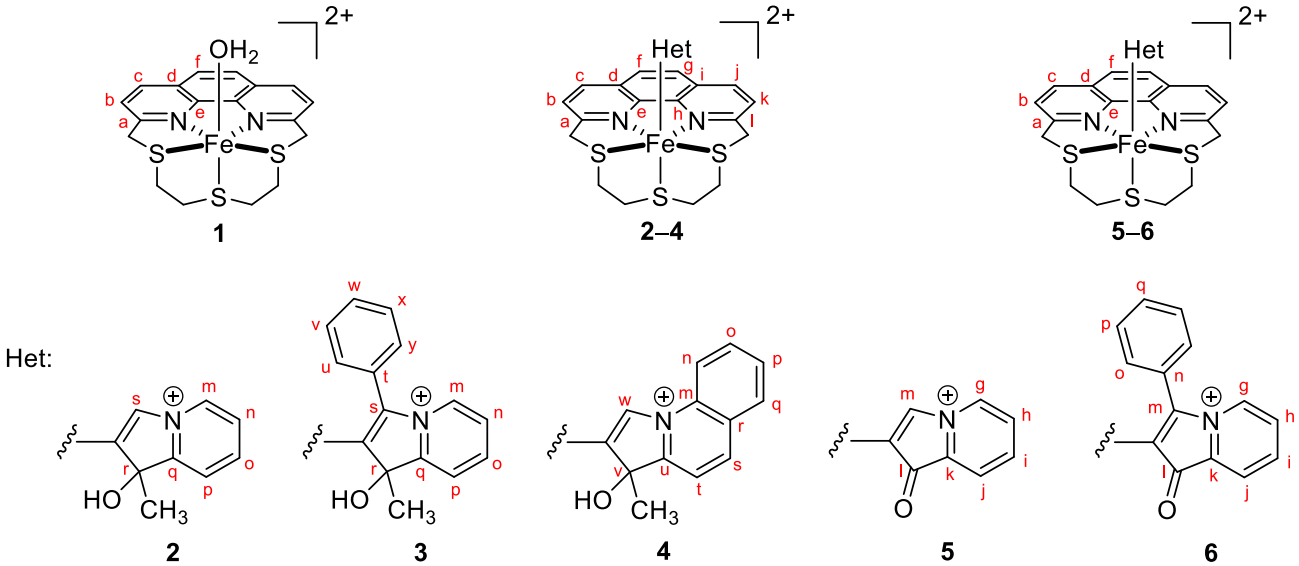
## General Procedures

All reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise stated. All reagents were used as received, and solvents for reactions were purified by a PureSolv MD5 solvent purification system. The [15]ane(phen$N_2$)$S_3$[1], Fe($CH_3CN$)$_2$($OTf$)$_2$[2] and propargylic pyridines[3]/pyridyl ynones[4] were prepared in accordance with literature methods. $^1$H, $^{13}$C{$^1$H}, $^{19}$F{$^1$H}, $^1$H–$^1$H COSY, $^1$H–$^1$H ROESY, $^1$H–$^{13}$C HSQC and $^1$H–$^{13}$C HMBC NMR spectra were recorded on Bruker 600 AVANCE III FT-NMR spectrometers. Peak positions of $^1$H and $^{13}$C{$^1$H} NMR spectra were calibrated with solvent residue peaks as internal standard, and those of $^{19}$F{$^1$H} NMR spectra were calibrated with hexafluorobenzene as external standard. Labeling scheme for H and C atoms in the NMR assignments is shown in Scheme S1. Electrospray ionization mass spectrometry was performed on a PE-SCIEX API 3200 triple quadrupole mass spectrometer. Elemental analyses were done on an Elementar Vario Micro Cube carbon-hydrogen-nitrogen elemental microanalyzer. Infrared spectra were recorded as KBr plates on a Perkin-Elmer Spectrum 100 FTIR spectrometer.

Evans NMR measurements were performed to confirm the diamagnetic nature of complexes **1**–**6**.[5-8] Briefly, the procedure involves placement of a coaxial insert containing a solution of the Fe complex into a standard 5 mm NMR tube with solvent only. Both the inner and outer solvents ($CD_3OD$) contain 5% of benzene, and the chemical shift differences between the inner and outer benzene were used to determine the magnetic susceptibility of the complex. Since no differences in the benzene chemical shift were observed for **1**–**6**, the Fe complexes in this work were confirmed to be diamagnetic.

**Scheme S1.** Labeling scheme for H and C atoms of the complexes in this work.




### Synthesis of [Fe($CH_3CN$)$_2$($OTf$)$_2$]

The metal precursor was synthesized from a modified literature procedure[2]. To a solution of $FeCl_2$ (0.50 g, 3.94 mmol) in anhydrous $CH_3CN$ (20 mL) was added $(CH_3)_3SiOTf$ (4 mL in 10 mL anhydrous $CH_3CN$, 22.09 mmol) in dropwise manner. The reaction mixture was stirred under argon for 16 h, during which

the color of the reaction mixture changed from pale yellow to colorless. The colorless solution was concentrated to about 5 mL by reduced pressure, and then added to $Et_2O$ (150 mL) to give white precipitates. The solids were collected by suction filtration, washed with $Et_2O$ (10 mL × 3) and dried by reduced pressure to give $[Fe(CH_3CN)_2(OTf)_2]$ (yield: 1.20 g, 70 %).

**Synthesis of 1(OTf)$_2$**

A mixture of $[Fe(CH_3CN)_2(OTf)_2]$ (0.39 g, 0.89 mmol) and [15]ane(phen$N_2$)$S_3$ (0.32 g, 0.89 mmol) was stirred in $CH_3CN$ (30 mL) under ambient condition for 16 h, during which the color of the reaction mixture changed from red to deep red with pale yellow precipitates. Upon centrifugation for removal of these precipitates, the supernatant was collected and concentrated to give deep red precipitates. The solids were collected by suction filtration and washed with $Et_2O$ (10 mL × 3). Recrystallization by slow diffusion of $Et_2O$ solution into a $(CH_3)_2CO$ solution of the deep red solids under argon gave analytically pure **1**$(OTf)_2$ as orange crystals.

Complex **1**$(OTf)_2$. Yield: 0.46 g, 71 %. Anal. Calcd for $C_{20}H_{20}F_6FeN_2O_7S_5$: C, 32.88; H, 2.76; N, 3.83. Found: C, 32.98; H, 2.74; N, 3.74. $^1$H NMR (600 MHz, $CD_3CN$): δ 2.27–2.37 (m, 2H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 2.89–2.91 (m, 2H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 2.95–3.04 (m, 2H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 3.14–3.22 (m, 2H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 4.77 (d, *J* = 18.0 Hz, 2H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 5.06 (d, *J* = 18.0 Hz, 2H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 8.13 (d, *J* = 6.0 Hz, 2H, $H_b$), 8.27 (s, 2H, $H_f$), 8.66 (d, *J* = 6.0 Hz, 2H, $H_c$). $^{13}$C{$^1$H} NMR (150 MHz, $CD_3CN$): δ 36.40, 39.65, 49.38 (*C*$H_2$ on [15]ane(phen$N_2$)$S_3$), 123.82 ($C_b$), 127.99 ($C_f$), 129.85 ($C_d$), 136.81 ($C_c$), 150.01 ($C_e$), 167.41 ($C_a$). $^{19}$F{$^1$H} NMR (564 MHz, $CD_3CN$): δ −79.31. ESI-MS found (calcd): m/z 563.30 (563.46) $[C_{19}H_{18}F_3FeN_2O_3S_4]^+$. IR (KBr, cm$^{-1}$): $\nu_{O\text{-}H}$ 3380 (broad).

**Synthesis of 2–6(OTf)$_2$**

A mixture of **1**$(OTf)_2$ (0.10 g, 0.14 mmol) and pyridine-tethered alkynes (0.03 g for 2-(pyridine-2-yl)but-3-yn-2-ol, 0.03 g for 4-phenyl-2-(pyridine-2-yl)but-3-yn-2-ol, 0.04 g for 2-(quinoline-2-yl)but-3-yn-2-ol, 0.03 g for 1-(2-pyridinyl)-2-propyn-1-one, 0.04 g for 3-phenyl-1-(2-pyridinyl)-2-propyn-1-one, 0.21 mmol) was stirred in MeOH (30 mL) under ambient condition for 16 h, during which the color of reaction mixture changed from brown to deep purple with white precipitates. Upon centrifugation for removal of these precipitates, the supernatant was collected and concentrated to give deep purple precipitates. The solids were collected by suction filtration and washed with $Et_2O$ (10 mL × 3). Recrystallization by slow diffusion of $Et_2O$ solution into a MeOH solution of the deep purple solids gave analytically pure **2**–**6**$(OTf)_2$ as purple crystals.

Complex **2**$(OTf)_2$. Yield: 0.09 g, 73 %. Anal. Calcd for $C_{29}H_{27}F_6FeN_3O_7S_5$: C, 40.52; H, 3.17; N, 4.89. Found: C, 40.54; H, 3.15; N, 4.91. $^1$H NMR (600 MHz, $CD_3OD$): δ 1.32 (s, 3H, *C*$H_3$), 2.35–2.50 (m, 2H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 2.98–3.12 (m, 4H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 3.15–3.25 (m, 2H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 4.65–4.81 (m, 4H, C$H_2$ on [15]ane(phen$N_2$)$S_3$), 5.63 (s, 1H, $H_s$), 7.61 (t, *J* = 6.0 Hz, 1H, $H_n$), 7.87 (d, *J* = 6.0 Hz, 1H, $H_p$), 7.93 (d, *J* = 6.0 Hz, 1H, $H_k$), 8.01 (t, *J* = 6.0 Hz, 1H, $H_o$), 8.05 (d, *J* = 6.0 Hz, 1H, $H_b$), 8.18–8.20 (m, 2H, $H_g$ + $H_m$), 8.23 (d, *J* = 6.0 Hz, 1H, $H_f$), 8.46 (d, *J* = 6.0 Hz, 1H, $H_j$), 8.56 (d, *J* = 6.0

Hz, 1H, $H_c$). $^{13}C\{^1H\}$ NMR (150 MHz, $CD_3OD$): δ 24.74 (*C*$H_3$), 34.20, 34.56, 42.13, 42.61, 50.36 (*C*$H_2$ on [15]ane(phen$N_2$)$S_3$), 90.60 ($C_r$), 121.77 ($C_p$), 121.94 ($C_k$), 122.15 ($C_b$), 127.11 ($C_n$), 127.91 ($C_g$), 129.97 ($C_f$), 130.13 ($C_i$), 130.38 ($C_d$), 130.94 ($C_s$), 132.28 ($C_m$), 133.80 ($C_j$), 134.04 ($C_c$), 139.81 ($C_o$), 149.48 ($C_h$), 149.79 ($C_e$), 165.65 ($C_l$), 165.93 ($C_a$), 167.85 ($C_q$), 189.74 (Fe–C). $^{19}F\{^1H\}$ NMR (564 MHz, $CD_3OD$): δ –80.02. ESI-MS found (calcd): m/z 710.30 (710.64) $[C_{28}H_{27}F_3FeN_3O_4S_4]^+$. IR (KBr, $cm^{-1}$): $\nu_{O\text{-}H}$ 3457 (broad).

Complex **3**$(OTf)_2$. Yield: 0.08 g, 61 %. Anal. Calcd for $C_{35}H_{31}F_6FeN_3O_7S_5$: C, 44.92; H, 3.34; N, 4.49. Found: C, 44.95; H, 3.37; N, 4.52. $^1H$ NMR (600 MHz, $CD_3OD$): δ 1.95–2.03 (m, 1H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 2.055 (s, 3H, C*H*$_3$), 2.35–2.43 (m, 1H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 2.46–2.52 (m, 1H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 2.52–2.59 (m, 1H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 2.91–2.99 (m, 1H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 3.12–3.17 (m, 2H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 3.30–3.40 (overlapped with $CD_3OD$; 1H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 4.65 (m, 1H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 4.73–4.79 (m, 3H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 5.54 (d, *J* = 6.0 Hz, 1H, $H_u$), 6.44 (d, *J* = 6.0 Hz, 1H, $H_v$), 6.68 (d, *J* = 6.0 Hz, 1H, $H_y$), 6.90 (d, *J* = 6.0 Hz, 1H, $H_x$), 6.96 (d, *J* = 6.0 Hz, 1H, $H_w$), 7.08 (d, *J* = 6.0 Hz, 1H, $H_m$), 7.52 (m, 1H, $H_n$), 7.83 (d, *J* = 6.0 Hz, 1H, $H_k$), 7.88 (d, *J* = 6.0 Hz, 1H, $H_g$), 8.06 (d, *J* = 6.0 Hz, 1H, $H_b$), 8.08 (d, *J* = 6.0 Hz, 1H, $H_f$), 8.15–8.10 (m, 3H, $H_p$ + $H_j$ + $H_o$), 8.52 (d, *J* = 6.0 Hz, 1H, $H_c$). $^{13}C\{^1H\}$ NMR (150 MHz, $CD_3OD$): δ 25.89 (*C*$H_3$), 32.61, 33.12, 38.35, 40.36, 49.52, 51.06 (*C*$H_2$ on [15]ane(phen$N_2$)$S_3$), 90.43 ($C_r$), 121.45 ($C_p$), 121.66 ($C_k$), 122.39 ($C_b$), 127.01 ($C_n$), 127.47 ($C_f$), 128.00 ($C_g$), 128.92 ($C_v$), 129.39 ($C_i$), 129.66 ($C_x$), 130.00 ($C_d$ + $C_m$ + $C_w$), 130.10 ($C_t$), 130.51 ($C_y$), 130.56 ($C_u$), 133.72 ($C_c$), 134.12 ($C_j$), 140.34 ($C_o$), 143.39 ($C_s$), 150.06 ($C_h$), 150.45 ($C_e$), 166.00 ($C_a$), 166.36 ($C_l$), 167.30 ($C_q$), 177.33 (Fe–C). $^{19}F\{^1H\}$ NMR (564 MHz, $CD_3OD$): δ –79.98. ESI-MS found (calcd): m/z 786.40 (786.73) $[C_{34}H_{31}F_3FeN_3O_4S_4]^+$. IR (KBr, $cm^{-1}$): $\nu_{O\text{-}H}$ 3412 (broad).

Complex **4**$(OTf)_2$. Yield: 0.08 g, 61 %. Anal. Calcd for $C_{33}H_{29}F_6FeN_3O_7S_5$: C, 43.57; H, 3.21; N, 4.62. Found: C, 43.67; H, 3.24; N, 4.64. $^1H$ NMR (600 MHz, $CD_3NO_2$): δ 1.23 (s, 3H, C*H*$_3$), 2.48–2.61 (m, 2H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 3.05–3.28 (m, 6H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 3.59 (s, 1H, *OH*), 4.62–4.90 (m, 4H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 6.53 (s, 1H, $H_w$), 7.83 (t, *J* = 7.7 Hz, 1H, $H_p$), 7.88 (d, *J* = 8.9 Hz, 1H, $H_n$), 7.93–7.98 (m, 3H, $H_k$+$H_o$+$H_s$/$H_t$), 8.08 (d, *J* = 8.4 Hz, 1H, $H_b$), 8.18 (d, 1H, *J* = 8.0 Hz, $H_q$), 8.21–8.27 (m, 2H, $H_g$+$H_f$), 8.47 (d, *J* = 8.3 Hz, 1H, $H_j$), 8.58–8.68 (m, 2H, $H_t$/$H_s$+$H_c$). $^{13}C\{^1H\}$ NMR (150 MHz, $CD_3NO_2$): δ 24.55 (*C*$H_3$), 34.52, 34.98, 42.35, 42.46, 50.03, 50.77 (*C*$H_2$ on [15]ane(phen$N_2$)$S_3$), 92.70 ($C_v$), 117.62 ($C_s$/$C_t$), 118.84 ($C_n$), 122.05 ($C_k$), 122.35 ($C_b$), 127.79 ($C_w$), 128.14 ($C_g$), 128.21 ($C_f$), 130.32 ($C_d$), 130.48 ($C_m$), 130.54 ($C_i$), 130.79 ($C_p$), 131.04 ($C_q$), 131.49 ($C_r$), 134.20 ($C_j$), 134.37 ($C_c$), 135.69 ($C_o$), 141.22 ($C_t$/$C_s$), 149.85 ($C_h$), 150.21 ($C_e$), 165.48 ($C_l$), 165.77 ($C_a$), 170.84 ($C_u$), 187.63 (Fe–C). $^{19}F\{^1H\}$ NMR (564 MHz, $CD_3OD$): δ –80.07. ESI-MS found (calcd): m/z 760.30 (760.69) $[C_{32}H_{29}F_3FeN_3O_4S_4]^+$. IR (KBr, $cm^{-1}$): $\nu_{O\text{-}H}$ 3422 (broad).

Complex **5**$(OTf)_2$. Yield: 0.07 g, 59 %. Anal. Calcd for $C_{28}H_{23}F_6FeN_3O_7S_5$: C, 39.86; H, 2.75; N, 4.98. Found: C, 39.95; H, 2.77; N, 5.02. $^1H$ NMR (600 MHz, $CD_3NO_2$): δ 2.60–2.65 (m, 2H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 3.07–3.14 (m, 4H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 3.17–3.22 (m, 2H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 4.57–4.64 (m, 4H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 7.47 (s, 1H, $H_m$), 7.72 (d, *J* = 7.5 Hz, 1H, $H_j$), 7.85 (t, *J* = 6.8 Hz, 1H, $H_h$), 7.98 (d, *J* = 8.4 Hz, 2H, $H_c$), 8.15 (d, *J* = 5.7 Hz, 1H, $H_g$), 8.22 (t, *J* = 7.8 Hz, 1H, $H_i$), 8.24 (s, 2H, $H_f$), 8.52 (d, *J* = 8.4 Hz, 2H, $H_b$). $^{13}C\{^1H\}$ NMR (150 MHz, $CD_3NO_2$): δ 35.06, 41.76, 50.23 (*C*$H_2$ on [15]ane(phen$N_2$)$S_3$),

122.19 ($C_j$), 122.36 ($C_c$), 128.01 ($C_f$), 130.18 ($C_e$), 131.86 ($C_h$), 134.18 ($C_g$), 134.67 ($C_b$), 140.90 ($C_k$), 144.85 ($C_i$), 150.03 ($C_d$), 154.32 ($C_m$), 164.80 ($C_a$), 167.19 ($C_l$), 192.34 (Fe–C). $^{19}F\{^1H\}$ NMR (564 MHz, $CD_3OD$): δ –79.65. ESI-MS found (calcd): m/z 694.40 (694.59) $[C_{27}H_{23}F_3FeN_3O_4S_4]^+$. IR (KBr, $cm^{-1}$): $\nu_{C=O}$ 1704.

Complex **6**$(OTf)_2$. Yield: 0.09 g, 75%. Anal. Calcd for $C_{34}H_{27}F_6FeN_3O_7S_5$: C, 44.40; H, 2.96; N, 4.57. Found: C, 44.48; H, 2.98; N, 4.60. $^1H$ NMR (600 MHz, $CD_3NO_2$): δ 2.45–2.50 (m, 2H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 2.78–2.82 (m, 2H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 2.89–2.93 (m, 2H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 3.36–3.40 (m, 2H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 4.51–4.59 (m, 4H, C*H*$_2$ on [15]ane(phen$N_2$)$S_3$), 5.95 (d, *J* = 7.0 Hz, 2H, $H_o$), 6.54 (t, *J* = 7.7 Hz, 2H, $H_p$), 6.88 (t, *J* = 7.5 Hz, 1H, $H_q$), 7.31 (d, *J* = 5.8 Hz, 1H, $H_g$), 7.72 (t, *J* = 6.6 Hz, 1H, $H_h$), 7.92 (s, 2H, $H_f$), 7.98 (d, *J* = 8.3 Hz, 2H, $H_c$), 8.14 (d, *J* = 7.5 Hz, 2H, $H_j$), 8.33 (t, *J* = 8.3 Hz, 1H, $H_i$), 8.34 (d, *J* = 8.3 Hz, 2H, $H_b$). $^{13}C\{^1H\}$ NMR (150 MHz, $CD_3NO_2$): δ 34.15, 39.84, 50.28 (*C*$H_2$ on [15]ane(phen$N_2$)$S_3$), 122.06 ($C_j$), 122.47 ($C_c$), 128.08 ($C_f$), 128.10 ($C_n$), 128.63 ($C_o$), 129.41 ($C_p$), 130.13 ($C_e$), 131.12 ($C_q$), 131.54 ($C_h$), 131.88 ($C_g$), 134.64 ($C_b$), 141.81 ($C_k$), 144.83 ($C_i$), 149.68 ($C_d$), 160.44 ($C_m$), 164.99 ($C_a$), 165.34 ($C_l$), 192.36 (Fe–C). $^{19}F\{^1H\}$ NMR (564 MHz, $CD_3OD$): δ –80.07. ESI-MS found (calcd): m/z 770.50 (770.69) $[C_{33}H_{27}F_3FeN_3O_4S_4]^+$. IR (KBr, $cm^{-1}$): $\nu_{C=O}$ 1704.

**X-Ray Crystallography**

Complex **1**$(OTf)_2$ (CCDC 2017986): A specimen of $C_{20}H_{20}F_6FeN_2O_7S_5$ was used for the X-ray crystallographic analysis. A total of 1193 frames were collected. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 24565 reflections to a maximum θ angle of 74.47° (0.80 Å resolution), of which 5543 were independent (average redundancy 4.432, completeness = 99.5%, $R_{int}$ = 6.62%, $R_{sig}$ = 5.47%) and 4312 (77.79%) were greater than $2\sigma(F^2)$. The final cell constants of a = 24.4848(7) Å, b = 11.4726(3) Å, c = 20.4806(6) Å, β = 108.7380(10)°, volume = 5448.2(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 8828 reflections above 20 σ(I) with 8.599° < 2θ < 148.8°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.534.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C2/c, with Z = 8 for the formula unit, $C_{20}H_{20}F_6FeN_2O_7S_5$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 442 variables converged at R1 = 5.95%, for the observed data and wR2 = 18.71% for all data. The goodness-of-fit was 1.178. The largest peak in the final difference electron density synthesis was 0.604 $e^-/Å^3$ and the largest hole was -0.671 $e^-/Å^3$ with an RMS deviation of 0.092 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.781 $g/cm^3$ and F(000), 2960 $e^-$.

Complex **3**$(OTf)_2$ (CCDC 2017987): A specimen of $C_{35}H_{31}F_6FeN_3O_7S_5$ was used for the X-ray crystallographic analysis. A total of 196 frames were collected. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 54076 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 7689 were independent (average redundancy 7.033, completeness = 99.9%, $R_{int}$ = 11.15%, $R_{sig}$ = 6.82%) and 5467 (71.10%) were greater than $2\sigma(F^2)$. The final cell constants of a = 14.2635(4) Å, b = 17.4695(6) Å, c = 30.1975(10) Å, volume = 7524.5(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 8513 reflections above 20 σ(I) with 4.663° < 2θ < 52.65°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.812.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Pbca, with Z = 8 for the formula unit, $C_{35}H_{31}F_6FeN_3O_7S_5$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 516 variables converged at R1 = 5.04%, for the observed data and wR2 = 12.24% for all data. The goodness-of-fit was 1.026. The largest peak in the final difference electron density synthesis was 0.742 $e^-/Å^3$ and the largest hole was -0.529 $e^-/Å^3$ with an RMS deviation of 0.087 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.652 $g/cm^3$ and F(000), 3824 $e^-$.

Complex **4**$(OTf)_2$ (CCDC 2017988): A specimen of $C_{33}H_{29}F_6FeN_3O_7S_5$ was used for the X-ray crystallographic analysis. A total of 919 frames were collected. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 53395 reflections to a maximum θ angle of 26.44° (0.80 Å resolution), of which 14806 were independent (average redundancy 3.606, completeness = 99.4%, $R_{int}$ = 7.72%, $R_{sig}$

= 7.10%) and 11317 (76.44%) were greater than 2σ($F^2$). The final cell constants of a = 13.0248(8) Å, b = 13.4754(9) Å, c = 21.3868(13) Å, α = 86.090(2)°, β = 76.878(2)°, γ = 81.685(2)°, volume = 3614.8(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9964 reflections above 20 σ(I) with 4.740° < 2θ < 52.60°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.723. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5374 and 0.7454.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 4 for the formula unit, $C_{33}H_{29}F_6FeN_3O_7S_5$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 1139 variables converged at R1 = 9.37%, for the observed data and wR2 = 27.45% for all data. The goodness-of-fit was 1.018. The largest peak in the final difference electron density synthesis was 1.786 $e^-/Å^3$ and the largest hole was -1.215 $e^-/Å^3$ with an RMS deviation of 0.124 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.672 $g/cm^3$ and F(000), 1856 $e^-$.

Complex **6**$(OTf)_2$ (CCDC 2017989): A specimen of $C_{40}H_{42}F_6FeN_3O_{8.5}S_5$ was used for the X-ray crystallographic analysis. A total of 936 frames were collected. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 68716 reflections to a maximum θ angle of 26.42° (0.80 Å resolution), of which 9071 were independent (average redundancy 7.575, completeness = 99.7%, $R_{int}$ = 14.34%, $R_{sig}$ = 8.90%) and 6005 (66.20%) were greater than 2σ($F^2$). The final cell constants of a = 10.2770(5) Å, b = 14.2819(8) Å, c = 15.9309(9) Å, α = 88.000(2)°, β = 71.475(2)°, γ = 89.017(2)°, volume = 2215.7(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9488 reflections above 20 σ(I) with 5.011° < 2θ < 51.75°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.677.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, $C_{40}H_{42}F_6FeN_3O_{8.50}S_5$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 599 variables converged at R1 = 7.56%, for the observed data and wR2 = 23.04% for all data. The goodness-of-fit was 1.031. The largest peak in the final difference electron density synthesis was 1.039 $e^-/Å^3$ and the largest hole was -0.629 $e^-/Å^3$ with an RMS deviation of 0.107 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.545 $g/cm^3$ and F(000), 1062 $e^-$.

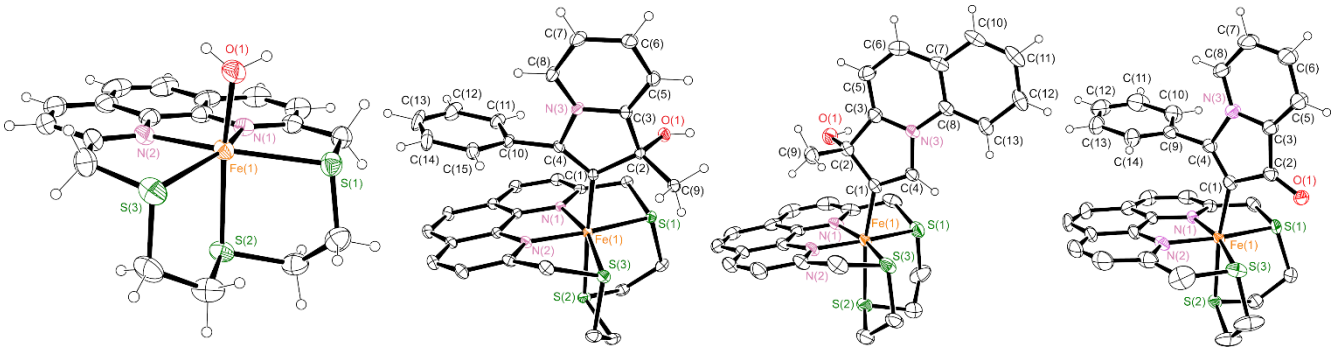



**Figure S1.** Perspective views of **1**, **3**, **4** and **6** (from left to right) as represented by 30 % probability ellipsoids (hydrogen atoms on [15]ane(phen$N_2$)$S_3$ of **3**, **4** and **6** are omitted for clarity).

**Table S1**. Selected bond lengths (Å) and bond angles (deg) for **1**$(OTf)_2$, **3**$(OTf)_2$, **4**$(OTf)_2$ and **6**$(OTf)_2$.

| Complex | **1**$(OTf)_2$ | **3**$(OTf)_2$ | **4**$(OTf)_2$[a] | **6**$(OTf)_2$ |
|---|---|---|---|---|
| Fe–N(1) | 2.145(3) | 1.920(3) | 1.910(5), 1.918(5) | 1.908(4) |
| Fe–N(2) | 2.141(3) | 1.914(3) | 1.910(5), 1.908(5) | 1.921(4) |
| Fe–S(1) | 2.536 (1) | 2.285(1) | 2.248(2), 2.266(2) | 2.250 (1) |
| Fe–S(2) | 2.569(1) | 2.310(1) | 2.315 (2), 2.310(2) | 2.310(1) |
| Fe–S(3) | 2.549(1) | 2.292(1) | 2.271(2), 2.267 (2) | 2.249(1) |
| Fe–O(1) | 2.050(3) | – | – | – |
| Fe–C(1) | – | 2.005(3) | 1.976(5), 1.982(6) | 1.977(5) |
| C(1)–C(2) | – | 1.555(5) | 1.530(8), 1.527(9) | 1.493(7) |
| C(2)–C(3) | – | 1.501(5) | 1.515(8), 1.522(9) | 1.498(7) |
| C(3)–N(3) | – | 1.352(4) | 1.339(8), 1.323(8) | 1.359(7) |
| N(3)–C(4) | – | 1.477(4) | 1.437(7), 1.437(7) | 1.482(6) |
| C(4)–C(1) | – | 1.346(5) | 1.352(7), 1.342(8) | 1.340(7) |
| C(2)–C(9) | – | 1.509(5) | 1.503(8), 1.470(8) | – |
| C(2)–O(1) | – | 1.441(4) | 1.450(7), 1.457(8) | 1.216(6) |
| N(1)–Fe–N(2) | 76.95(13) | 82.78(12) | 82.4(2), 82.6(2) | 82.38(18) |
| N(2)–Fe–S(3) | 78.29(10) | 82.65(9) | 84.57(15), 83.31(17) | 84.37(15) |
| S(1)–Fe–S(3) | 124.61(5) | 110.09(4) | 108.59(7), 109.60(7) | 108.37(6) |
| N(1)–Fe–S(1) | 78.64(9) | 84.01(9) | 84.40(17), 84.53(16) | 84.83(12) |
| O(1)–Fe–S(2) | 168.07(11) | – | – | – |
| Fe–C(1)–C(2) | – | 124.9(2) | 131.4(4), 131.5(4) | 121.2(3) |
| Fe–C(1)–C(4) | – | 128.6(3) | 121.9(4), 122.2(5) | 133.4(4) |
| C(2)–C(1)–C(4) | – | 106.5(3) | 106.7(5), 106.3(5) | 105.3(4) |

[a] The crystal contains two crystallographically independent cations in the asymmetric unit; structural data are listed in the order of Fe(1) moiety and then Fe(2) moiety.

## Computational Methodology

Three reaction pathways were modelled by Density Functional Theory (DFT) calculations using the ORCA software package (version 4.2.1):[9] (a) cycloisomerizations of alkynes **L2** and **L5** to give zwitterions **2'** and **5'** respectively; (b) {[Fe([15]ane(phen$N_2$)$S_3$)]$^{2+}$–**L2**} and {[Fe([15]ane(phen$N_2$)$S_3$)]$^{2+}$–**L5**} Fe–alkyne π-complexes (denoted as **2-π** and **5-π** respectively) to give Fe–indolizine and –indolizinone complexes **2** and **5** respectively, and (c) **2-π** and **5-π** to give Fe–vinylidene complexes **2v** and **5v** respectively. All the calculated structures were optimized in the gas phase using the PBE0 functional.[10] The def2-SVP basis sets were used for all atoms.[11] The combination of the resolution of the identity and the "chain of spheres exchange" algorithms (RIJCOSX)[12] was used to accelerate the calculations with the use of appropriate auxiliary basis sets. Dispersion effects were accounted for using the semiempirical van der Waals corrections by Grimme.[13] Tight SCF convergence criteria were used throughout. The nature of all the optimized stationary points was characterized by frequency calculations; that is, local minima were confirmed by the absence of imaginary vibrational frequencies, and only one imaginary frequency was found for each transition state. The effect of solvent (methanol) on the energies of the optimized structures was treated by the employment of the conductor-like polarizable continuum model (CPCM).[14] The energies depicted in Figures 2 and S2 are zero-point and thermal energy corrected (temperature = 298.15 K).

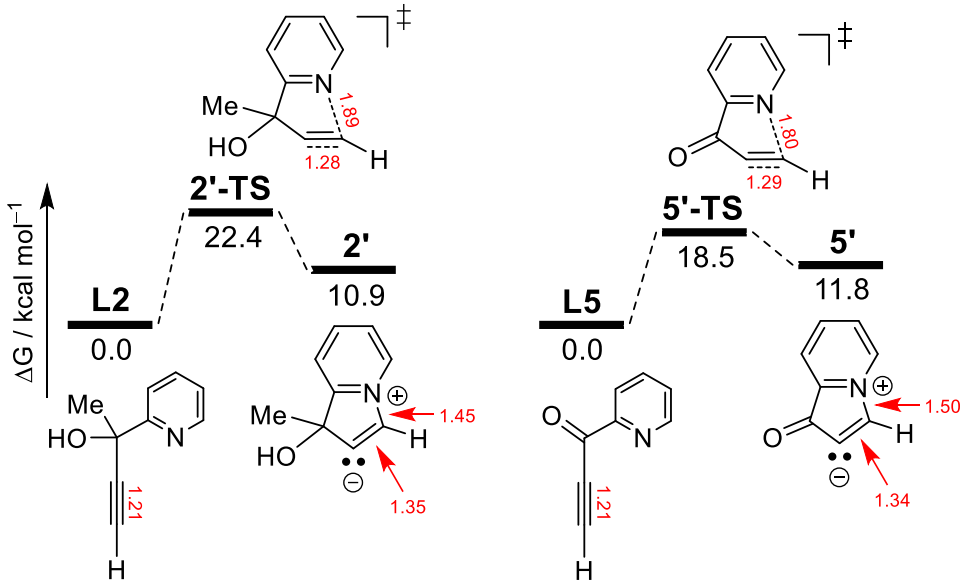



**Figure S2**. Potential energy surfaces calculated at the DFT level (functional = PBE0; solvent = MeOH; 298.15 K) for the *5-endo-dig* cycloisomerizations of alkynes **L2** and **L5** to give zwitterions **2'** and **5'** respectively. Important bond distances (Å) are depicted in red.

**Table S2.** Characterization of the DFT-optimized geometries (by frequency calculations, only the first 10 frequencies are listed for each geometry).

| Structure | Vibrational Frequencies[α] | | | |
|---|---|---|---|---|
| L**2** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 42.53 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 94.83 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 165.55 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 177.12 cm**-1 |
| **2'-TS** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | -340.80 cm**-1 ***imaginary mode*** |
| | 2: | 0.00 cm**-1 | 7: | 130.63 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 154.24 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 261.67 cm**-1 |
| **2'** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 80.21 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 127.01 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 239.77 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 257.34 cm**-1 |
| **L5** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 56.01 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 124.84 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 146.11 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 242.46 cm**-1 |
| **5'-TS** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | -310.57 cm**-1 ***imaginary mode*** |
| | 2: | 0.00 cm**-1 | 7: | 100.01 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 139.32 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 292.33 cm**-1 |
| **5'** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 90.28 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 151.05 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 248.54 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 295.21 cm**-1 |
| **2-π** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 4.47 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 32.92 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 43.95 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 54.46 cm**-1 |
| **2-TS** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | -205.97 cm**-1 ***imaginary mode*** |

| | | | | |
|---|---|---|---|---|
| | 2: | 0.00 cm**-1 | 7: | 17.18 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 36.37 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 48.43 cm**-1 |
| **2** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 26.70 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 35.41 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 51.01 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 60.92 cm**-1 |
| **2v-TS** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | -494.66 cm**-1 ***imaginary mode*** |
| | 2: | 0.00 cm**-1 | 7: | 9.83 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 17.15 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 23.47 cm**-1 |
| **2v** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 8.56 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 19.00 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 25.38 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 34.94 cm**-1 |
| **5-π** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 12.75 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 30.81 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 39.91 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 45.40 cm**-1 |
| **5-TS** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | -74.12 cm**-1 ***imaginary mode*** |
| | 2: | 0.00 cm**-1 | 7: | 50.13 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 76.22 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 81.83 cm**-1 |
| **5** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 25.50 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 30.56 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 46.47 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 57.22 cm**-1 |
| **5v-TS1** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | -72.87 cm**-1 ***imaginary mode*** |
| | 2: | 0.00 cm**-1 | 7: | 19.10 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 33.93 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 35.31 cm**-1 |
| **5v-INT** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 28.44 cm**-1 |

| | | | | |
|---|---|---|---|---|
| | 2: | 0.00 cm**-1 | 7: | 28.64 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 43.46 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 49.51 cm**-1 |
| **5v-TS2** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | -521.34 cm**-1 ***imaginary mode*** |
| | 2: | 0.00 cm**-1 | 7: | 12.04 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 15.24 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 21.09 cm**-1 |
| **5v** | 0: | 0.00 cm**-1 | 5: | 0.00 cm**-1 |
| | 1: | 0.00 cm**-1 | 6: | 4.45 cm**-1 |
| | 2: | 0.00 cm**-1 | 7: | 12.77 cm**-1 |
| | 3: | 0.00 cm**-1 | 8: | 22.35 cm**-1 |
| | 4: | 0.00 cm**-1 | 9: | 43.45 cm**-1 |

[α] The first six frequencies correspond to the rotations and translations of the molecule.

**Table S3.** Cartesian coordinates of **L2** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| N | 6.78992598556942 | 12.09079860693826 | 6.22805680539528 |
| C | 5.36873613911340 | 9.67778832125617 | 5.49691167746119 |
| C | 5.84536978933481 | 9.94500585806346 | 6.86443154639802 |
| C | 5.96510563503899 | 11.46067653042484 | 7.06103194171425 |
| C | 5.27270196246811 | 12.11126056830530 | 8.08333120878244 |
| H | 4.62312851565797 | 11.53719313861385 | 8.74387879055245 |
| C | 5.46334212545580 | 13.48198106614620 | 8.24026684630167 |
| H | 4.94205056001672 | 14.02740492778132 | 9.03083996843310 |
| C | 6.33253876149245 | 14.14249944013088 | 7.37710555924218 |
| H | 6.52878484971833 | 15.21237705434918 | 7.47449908421723 |
| C | 6.96812495975411 | 13.39670194554612 | 6.38332797097413 |
| H | 7.65729087496873 | 13.88191906350447 | 5.68223255417962 |
| C | 4.93557005632421 | 9.44412656785650 | 4.39095230394401 |
| H | 4.56174451792935 | 9.23181085856170 | 3.40657597858004 |
| O | 4.96195536688522 | 9.37948207550606 | 7.81033920137213 |
| H | 4.06719394248164 | 9.45565866502568 | 7.45995083629817 |
| C | 7.21824008843398 | 9.31320373308353 | 7.08185806603288 |
| H | 7.50854846842765 | 9.45384637992313 | 8.13314442776385 |
| H | 7.17334077302045 | 8.23849901948289 | 6.85739915931815 |
| H | 7.95231041790870 | 9.80209241950031 | 6.43028053303922 |

**Table S4.** Cartesian coordinates of **2'-TS** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| N | 6.03722282970659 | 11.92909799110468 | 5.91232146893728 |
| C | 5.50756546893520 | 9.51836142064352 | 5.44080708444115 |
| C | 5.66026088195639 | 9.76894644727035 | 6.90366366222595 |
| C | 5.84345966258557 | 11.29507836090178 | 7.06173005340365 |
| C | 5.81654728227379 | 11.99568893652195 | 8.26404929817742 |
| H | 5.62955268531766 | 11.45699690549979 | 9.19458082657602 |
| C | 5.99793185149616 | 13.37640645402838 | 8.23546586662650 |
| H | 5.97248973476612 | 13.95667381631201 | 9.16102382869556 |
| C | 6.20372773822833 | 14.01733648995796 | 7.01199626055255 |
| H | 6.35273563564032 | 15.09714111441017 | 6.95164590093603 |
| C | 6.21834746295933 | 13.24518516910084 | 5.85617736265383 |
| H | 6.37758309271312 | 13.68348610920935 | 4.86584015710550 |
| C | 5.74028498129042 | 10.52479382039679 | 4.69068910711421 |
| H | 5.85706065674475 | 10.95153552871693 | 3.70160998173614 |
| O | 4.57066112288999 | 9.34475489569073 | 7.69141192007458 |
| H | 3.80338030374929 | 9.33399032328656 | 7.10902350225535 |
| C | 6.91172804568709 | 9.07950918029439 | 7.44598715242435 |
| H | 7.01656668739373 | 9.28112707216710 | 8.52367972771948 |
| H | 6.80894215411822 | 7.99668416965535 | 7.29455105429859 |
| H | 7.80995551154793 | 9.43153203483128 | 6.92016024404586 |

**Table S5.** Cartesian coordinates of **2'** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| N | 5.94906304567363 | 11.85426250563332 | 5.95558240568100 |
| C | 5.53113897988756 | 9.61727428877219 | 5.42730407463004 |
| C | 5.61844145133779 | 9.78722400981041 | 6.92953440058438 |
| C | 5.80002386044541 | 11.27810615474920 | 7.17297906650840 |
| C | 5.86306857863390 | 12.05114434276394 | 8.31537515887776 |
| H | 5.73495298515811 | 11.57175569564113 | 9.28708109032775 |
| C | 6.06759618553472 | 13.42858209759529 | 8.19548348425813 |
| H | 6.10963768659729 | 14.06128041502584 | 9.08427857721290 |
| C | 6.21859753281440 | 13.98883761928476 | 6.92664926743775 |
| H | 6.39178733294550 | 15.05818549726448 | 6.79502627169964 |
| C | 6.16004313887971 | 13.17254199902465 | 5.80831706542362 |
| H | 6.27689112869107 | 13.53724634795942 | 4.78647641561436 |
| C | 5.79408393600819 | 10.84445256961392 | 4.92870641863029 |
| H | 5.86086925724560 | 11.22711882521116 | 3.90660732454850 |
| O | 4.44553763188804 | 9.34023797964399 | 7.57234096250025 |
| H | 4.01020654771683 | 8.80787909333080 | 6.89134152405147 |
| C | 6.85309497840319 | 9.05775200825004 | 7.46766895103926 |
| H | 6.90622183318246 | 9.15281356088106 | 8.56406507535210 |
| H | 6.76615391762108 | 7.99567028801697 | 7.20110493176556 |
| H | 7.77859378133549 | 9.45196094152743 | 7.02049199385685 |

**Table S6.** Cartesian coordinates of **L5** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| O | 5.72743003103140 | 8.89536096756190 | 8.28105670035871 |
| N | 5.87651361575996 | 12.03595583483611 | 6.67105152288069 |
| C | 5.62731011671964 | 9.37167019268828 | 5.99581762751510 |
| C | 5.73931515811767 | 9.72778343071073 | 7.40026624457718 |
| C | 5.86685112247282 | 11.19047730608902 | 7.70079363507003 |
| C | 5.96582376944296 | 11.59147385542884 | 9.03573162465905 |
| H | 5.95420931638328 | 10.83024595246906 | 9.81762178243915 |
| C | 6.07195941438277 | 12.95075915504285 | 9.30498485469314 |
| H | 6.15065711664235 | 13.31456483234238 | 10.33248035780700 |
| C | 6.07910060760642 | 13.84117392231654 | 8.23413990120166 |
| H | 6.16244763720886 | 14.91789940712994 | 8.39889037093383 |
| C | 5.98213806119982 | 13.33186625186572 | 6.93634160204576 |
| H | 5.98992078808099 | 14.00970325374078 | 6.07541479233208 |
| C | 5.52756648044007 | 9.04695831490334 | 4.83281592152998 |
| H | 5.43663247935104 | 8.75481916803188 | 3.80222616075164 |

**Table S7.** Cartesian coordinates of **5'-TS** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| O | 5.61684068802061 | 9.24341552655893 | 7.95209101718149 |
| N | 5.88067609853268 | 12.00594508847035 | 5.87227085273445 |
| C | 5.61370837590421 | 9.52550254472740 | 5.52589872111420 |
| C | 5.68512878107189 | 9.90451114676638 | 6.94718334523876 |
| C | 5.86302711986659 | 11.43399164044098 | 7.06628216981915 |
| C | 5.97537879312045 | 12.17904678591976 | 8.22658588069729 |
| H | 5.96300238949528 | 11.66427659573503 | 9.18934306358313 |
| C | 6.09659949144648 | 13.56544780249810 | 8.10254526399284 |
| H | 6.18725418557025 | 14.19356924186119 | 8.99156527893372 |
| C | 6.10373491160829 | 14.14479719996172 | 6.83424214624957 |
| H | 6.19601166258341 | 15.22477648288678 | 6.70265614645330 |
| C | 5.99711486499010 | 13.31641707723173 | 5.71688277745491 |
| H | 6.00209430897360 | 13.70580560961036 | 4.69396027175843 |
| C | 5.70234608274841 | 10.57983209997578 | 4.78649904497700 |
| H | 5.71448684261593 | 10.95977357311363 | 3.76865079741009 |

**Table S8.** Cartesian coordinates of **5'** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| O | 5.62790678552080 | 9.14489374104444 | 7.89016172040870 |
| N | 5.86751455498170 | 11.92637735167848 | 5.90392834737959 |
| C | 5.61474604356801 | 9.58587823266735 | 5.46769206413304 |
| C | 5.68465698466964 | 9.86744639741391 | 6.92711086843897 |
| C | 5.85503774472148 | 11.39212044949694 | 7.13553711971833 |
| C | 5.96817189502748 | 12.18307880870941 | 8.25289897011940 |
| H | 5.95647487111635 | 11.70727975400241 | 9.23566640644628 |
| C | 6.09407986944253 | 13.56909404306765 | 8.07503864461928 |
| H | 6.18915725373316 | 14.23070056532596 | 8.93861053828343 |
| C | 6.10220304033932 | 14.09546988242277 | 6.78665933777320 |
| H | 6.20155930945735 | 15.16839960508233 | 6.61265895502460 |
| C | 5.98873641133649 | 13.23605224633110 | 5.69471454858674 |
| H | 5.99040673758901 | 13.57573969566304 | 4.65619926909803 |
| C | 5.72472606454778 | 10.80393354326701 | 4.91711248439153 |
| H | 5.73202703049720 | 11.16064409958553 | 3.88266750317732 |

**Table S9.** Cartesian coordinates of **2-π** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.63315974560747 | 7.26456924232953 | 5.35933292718258 |
| S | 7.38291526970667 | 6.75798115855020 | 6.78842543479091 |
| S | 5.28393761906858 | 5.00928369409688 | 5.04821279437264 |
| S | 3.72565596506530 | 7.37452007381342 | 6.63333663509000 |
| N | 6.97966792701495 | 7.11677036775765 | 3.97796435357367 |
| N | 4.41997112380543 | 7.41172599317703 | 3.85505631207515 |
| N | 4.58524825541618 | 11.33527426125640 | 7.55279404836286 |
| C | 6.00779731794030 | 9.27554606560520 | 6.18890304011851 |
| C | 6.42568066900085 | 9.76708007841965 | 7.53347048649124 |
| C | 5.91114066605898 | 11.21450753033474 | 7.54577235826021 |
| C | 6.78771643331426 | 12.29391707095408 | 7.55180762045763 |
| H | 7.86568556814842 | 12.12909645621220 | 7.52134530756258 |
| C | 6.23873061926365 | 13.57616296603606 | 7.59441658472622 |
| H | 6.88828524876057 | 14.45402802232701 | 7.60977119141003 |
| C | 4.85530429894327 | 13.71487503588971 | 7.61765260590747 |
| H | 4.38320511277494 | 14.69827870604904 | 7.65615547985800 |
| C | 4.07101226835454 | 12.55979544436214 | 7.59216793067633 |
| H | 2.97816521348693 | 12.63325864528352 | 7.60787524946874 |
| C | 5.76504620846492 | 9.35064847145707 | 4.98201685434995 |
| C | 8.74270131815051 | 6.97735731338472 | 5.59012445810670 |
| H | 9.13315210582161 | 7.97779786841182 | 5.84949661371850 |
| H | 9.54367477200349 | 6.25107549181327 | 5.79502871264152 |
| C | 8.28233098947323 | 6.96312916968037 | 4.16229354350576 |
| C | 9.14253618643088 | 6.85208804519637 | 3.04789431632318 |
| H | 10.21560476517089 | 6.72436850189711 | 3.20601116228655 |
| C | 8.62782602549893 | 6.90842154098813 | 1.76355802289246 |
| H | 9.29593331317855 | 6.82301322782487 | 0.90299499999249 |
| C | 7.23549947620557 | 7.06919812743940 | 1.56429801017127 |
| C | 6.54952134171717 | 7.13370239265759 | 0.30403887623153 |
| H | 7.13370310665875 | 7.06656255896460 | -0.61641311375192 |
| C | 5.18815887611553 | 7.27067264334379 | 0.23904235348250 |
| H | 4.69120792011331 | 7.31368534545236 | -0.73278304971186 |
| C | 4.38803768519052 | 7.36299605466076 | 1.42833145182487 |
| C | 2.97999376863444 | 7.49730917110568 | 1.49334696744794 |
| H | 2.39340000704986 | 7.54097453587133 | 0.57244395038830 |
| C | 2.34739273902253 | 7.57684620002962 | 2.72223494864188 |
| H | 1.26250179810294 | 7.68787235853532 | 2.77650493214502 |

| | | | |
|---|---|---|---|
| C | 3.10278165319401 | 7.53703327432250 | 3.91561132367846 |
| C | 2.51578782009120 | 7.68602246357027 | 5.29110203463894 |
| H | 1.62590924293605 | 7.05758031593696 | 5.44488245762063 |
| H | 2.19259375020457 | 8.72890235142055 | 5.44916515926743 |
| C | 5.05165904535290 | 7.31646825310711 | 2.66276869559812 |
| C | 6.46153849953653 | 7.16508524220688 | 2.73059396710375 |
| C | 7.24685201234916 | 4.96226478535240 | 7.03724663043353 |
| H | 8.23584417241951 | 4.57725683906633 | 7.33162318869439 |
| H | 6.60270051927614 | 4.87852836836714 | 7.92586243497812 |
| C | 6.68096175928546 | 4.19484022186322 | 5.86709060664373 |
| H | 6.38195472180803 | 3.17293511941944 | 6.14869790536330 |
| H | 7.41736333719465 | 4.09390491634560 | 5.05395139535837 |
| C | 3.77144355482458 | 4.64778382961422 | 5.99843492361472 |
| H | 2.98585566142355 | 4.65393778629100 | 5.22633009615929 |
| H | 3.82771562977310 | 3.61686271748949 | 6.38250914527091 |
| C | 3.45921983064057 | 5.63946663746278 | 7.09518377468482 |
| H | 4.11562987646983 | 5.51356664940481 | 7.96924679600826 |
| H | 2.42551694515407 | 5.51850062920395 | 7.45603165031230 |
| H | 5.57608874316725 | 9.74805711969486 | 3.99634480857902 |
| O | 7.83306649414313 | 9.69293565758328 | 7.51983051730212 |
| H | 8.14948847883549 | 9.76955729309649 | 8.42931966203841 |
| C | 5.82946429805206 | 9.03503701306340 | 8.73029956383921 |
| H | 4.73756570858070 | 9.13379873707803 | 8.72525760891615 |
| H | 6.12681840987544 | 7.97804305349951 | 8.74875279109760 |
| H | 6.20238720067660 | 9.51435271437052 | 9.64876958172665 |

**Table S10.** Cartesian coordinates of **2-TS** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.47525184177440 | 7.14861361338198 | 5.50987857221344 |
| S | 7.24961439365087 | 6.68814110822062 | 6.91791415153103 |
| S | 5.40260120753598 | 4.92002873437663 | 4.94368215745317 |
| S | 3.57187065602580 | 6.88769558637897 | 6.76242290792266 |
| N | 6.83179930610890 | 7.31165194166523 | 4.14925586645517 |
| N | 4.26131136158831 | 7.30019045772646 | 4.00847489634679 |
| N | 5.28074821976089 | 11.69490804953761 | 6.35254392667456 |
| C | 5.71289654956785 | 9.09469456889672 | 6.29561688902073 |
| C | 6.30513266958117 | 9.76335755004159 | 7.49711163938502 |
| C | 6.15083574848602 | 11.28078394915512 | 7.26219248619144 |
| C | 6.90662348341136 | 12.16632626492589 | 8.03173441021910 |
| H | 7.63538892011218 | 11.79803030099902 | 8.75573067153033 |
| C | 6.71851949121094 | 13.53261730824128 | 7.83999640453636 |
| H | 7.29583091431616 | 14.25338880022534 | 8.42269556103143 |
| C | 5.78994375114334 | 13.96259590531812 | 6.89382915730177 |
| H | 5.60979792401718 | 15.02379148490950 | 6.71117935231010 |
| C | 5.09495356297686 | 12.99993722860499 | 6.16799781375297 |
| H | 4.36580321320835 | 13.29316427860361 | 5.40599227196659 |
| C | 5.03820140832434 | 9.45091399987785 | 5.31638956065158 |
| C | 8.59413117516365 | 7.15065623807085 | 5.76457624804856 |
| H | 8.89230091828097 | 8.14840144321482 | 6.13047917589608 |
| H | 9.44914888547830 | 6.47118325453750 | 5.89975121583239 |
| C | 8.14195500802142 | 7.24689968842944 | 4.33769256540111 |
| C | 9.01553521002768 | 7.30113908161804 | 3.22937443593882 |
| H | 10.09471935639341 | 7.25889346460017 | 3.39277659563306 |
| C | 8.50739579400902 | 7.40421153764861 | 1.94511815503908 |
| H | 9.18627236697198 | 7.44013674500370 | 1.08952192278919 |
| C | 7.10747389857861 | 7.44789062832767 | 1.73965803092981 |
| C | 6.42481020538800 | 7.50652650668992 | 0.47693479129982 |
| H | 7.01795140926404 | 7.55465716565737 | -0.43894636778734 |
| C | 5.05712482482011 | 7.49410525606442 | 0.40235941827120 |
| H | 4.56434777048153 | 7.53336618674893 | -0.57168322356886 |
| C | 4.24492691910010 | 7.42167108663438 | 1.58472873518567 |
| C | 2.83156011904270 | 7.36352348710880 | 1.64014600579723 |
| H | 2.24805753049558 | 7.38977309321326 | 0.71666261176449 |
| C | 2.18882519967200 | 7.26705746484764 | 2.86370993268490 |
| H | 1.09877167015095 | 7.22061728544736 | 2.91099298617402 |

| | | | |
|---|---|---|---|
| C | 2.93856167037628 | 7.23203760306549 | 4.05958781231938 |
| C | 2.33601789083280 | 7.18276197261184 | 5.43627465958462 |
| H | 1.52376099579563 | 6.44454392448963 | 5.52248319919406 |
| H | 1.88777835636465 | 8.16003341266924 | 5.68381502183844 |
| C | 4.90446261914856 | 7.38479317664526 | 2.82190777993536 |
| C | 6.32171666590683 | 7.40062546870453 | 2.90076361636321 |
| C | 7.31269150432237 | 4.87146508927722 | 6.97364574732721 |
| H | 8.33109314324429 | 4.56887840239368 | 7.26442305944823 |
| H | 6.65808718562924 | 4.61641453645491 | 7.82096613233821 |
| C | 6.87476804145762 | 4.18458990233158 | 5.70377360590232 |
| H | 6.69970948005771 | 3.10664199034555 | 5.84868357719374 |
| H | 7.63529074665650 | 4.27559400841886 | 4.91124692365527 |
| C | 3.93977686066746 | 4.27656868059621 | 5.81470853899944 |
| H | 3.16028393909156 | 4.28044301172191 | 5.03611397248522 |
| H | 4.11748113097870 | 3.22168355591035 | 6.07744460320121 |
| C | 3.51274412859111 | 5.08847734754062 | 7.01747337281337 |
| H | 4.18014089701388 | 4.93340805991242 | 7.87839927069329 |
| H | 2.50032406714078 | 4.80627551684209 | 7.34676767111132 |
| H | 4.47862100033095 | 9.76171206013511 | 4.45175600257166 |
| O | 7.67477509195257 | 9.44419971861352 | 7.60217512173528 |
| H | 7.87015282831152 | 9.18368897336439 | 8.50911241291875 |
| C | 5.55678253683543 | 9.35826163435838 | 8.76579087559605 |
| H | 4.49102173517088 | 9.61366219945451 | 8.69445421336172 |
| H | 5.65385213782586 | 8.27600395982228 | 8.94341553903757 |
| H | 5.97538155215547 | 9.90280686937049 | 9.62615642855124 |

**Table S11.** Cartesian coordinates of **2** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.18814121127023 | 7.72045643067907 | 4.82100635945887 |
| S | 6.90206293170014 | 6.87378849568498 | 6.08912490707605 |
| S | 4.96104740255259 | 5.66359526631486 | 3.77115497924548 |
| S | 3.29475975469869 | 7.33220272153433 | 6.00518417053110 |
| N | 6.56197095953330 | 8.07836272916004 | 3.52339344092992 |
| N | 4.01597211714978 | 8.37805166452596 | 3.45325254194184 |
| N | 5.15194893118460 | 11.80199721890069 | 5.80014989457804 |
| C | 5.31917791356013 | 9.50654001608025 | 5.58579904759575 |
| C | 6.09253566317400 | 9.94625762950260 | 6.84008621241693 |
| C | 5.99389718304344 | 11.46390393802897 | 6.80397999185306 |
| C | 6.58344800994958 | 12.44701275427514 | 7.57051872410413 |
| H | 7.27718219357511 | 12.17497612857178 | 8.36828804043657 |
| C | 6.28047070776525 | 13.78478428548188 | 7.29569172683522 |
| H | 6.74316613372657 | 14.58153640409223 | 7.88126137356315 |
| C | 5.38161033867344 | 14.09707885313668 | 6.27352171803686 |
| H | 5.11621359579330 | 15.13015811950346 | 6.04277426604092 |
| C | 4.81953746897429 | 13.07526954711763 | 5.52643860008911 |
| H | 4.12310907416866 | 13.24142262090313 | 4.70307811948369 |
| C | 4.75155246543619 | 10.62794125851294 | 5.08787689488971 |
| C | 8.30001782191670 | 7.29602342022129 | 4.98666370531142 |
| H | 8.84700291669932 | 8.08688092776036 | 5.52106356499877 |
| H | 8.97200302854671 | 6.42835165564650 | 4.89902275329210 |
| C | 7.85531836847704 | 7.81836084654718 | 3.65158757833770 |
| C | 8.73498942409235 | 8.06022374664292 | 2.57380594881712 |
| H | 9.79890350456317 | 7.84356852500446 | 2.69143037229262 |
| C | 8.25014151400911 | 8.55783391040872 | 1.37647991040248 |
| H | 8.93208191486234 | 8.73918986747046 | 0.54229525814471 |
| C | 6.86658891978078 | 8.81747138954755 | 1.22980966827336 |
| C | 6.19995241347455 | 9.29381963979373 | 0.04908492222127 |
| H | 6.79801613470199 | 9.51710248719075 | -0.83729676486678 |
| C | 4.84072816088380 | 9.46441873278087 | 0.01437766762246 |
| H | 4.36032026154413 | 9.82295010851335 | -0.89876405326512 |
| C | 4.01948056543257 | 9.17448780810361 | 1.15740031950339 |
| C | 2.61052035272858 | 9.28222705872038 | 1.24202432176688 |
| H | 2.03624321884981 | 9.63456824136722 | 0.38174270687926 |
| C | 1.95962995071277 | 8.93470029291068 | 2.41530717352100 |
| H | 0.87341034362512 | 9.02198511076636 | 2.48702101118420 |

| | | | |
|---|---|---|---|
| C | 2.69492328021912 | 8.46159309152313 | 3.52416798180182 |
| C | 2.07944287524512 | 8.06501916681755 | 4.83776449088908 |
| H | 1.23494663891932 | 7.36965716427480 | 4.71151262137257 |
| H | 1.67498190216477 | 8.95139273454747 | 5.35212813009961 |
| C | 4.66524374056335 | 8.72222009044134 | 2.31836088817005 |
| C | 6.07445480655065 | 8.55363955073872 | 2.35665619997342 |
| C | 6.74237204415294 | 5.07648181725701 | 5.85105441542054 |
| H | 7.69685351354202 | 4.60065928530859 | 6.12730082724006 |
| H | 6.01279414159623 | 4.77616832970088 | 6.61814763512191 |
| C | 6.30399261135223 | 4.66032229960855 | 4.46441247866773 |
| H | 6.01752910018391 | 3.59762145944432 | 4.41842227636191 |
| H | 7.11866029865827 | 4.79423781619378 | 3.73456099968214 |
| C | 3.39640020890224 | 5.02040782285108 | 4.42954465556355 |
| H | 2.65921788114507 | 5.33679656368916 | 3.67449940410569 |
| H | 3.41703054509735 | 3.91939970655284 | 4.39752229270215 |
| C | 3.02355608494083 | 5.54223527735820 | 5.80041160505334 |
| H | 3.64221141251781 | 5.09446401933522 | 6.59255650659791 |
| H | 1.97643411913042 | 5.30743251709839 | 6.04878952388128 |
| H | 4.10149383048236 | 10.78777094224304 | 4.22912562847616 |
| O | 7.43348289262402 | 9.53129115133321 | 6.77926197005026 |
| H | 7.76061871324025 | 9.38099328794499 | 7.67456691790470 |
| C | 5.40836234293597 | 9.42716385335314 | 8.10651514415558 |
| H | 4.36272564527854 | 9.75953702884197 | 8.16859387690738 |
| H | 5.42424346858731 | 8.32862140443769 | 8.10681568425923 |
| H | 5.93501717113960 | 9.79485862770157 | 9.00256544199857 |

**Table S12.** Cartesian coordinates of **2v-TS** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.25275078727917 | 6.72825238893465 | 5.49330757426379 |
| S | 6.80190318252306 | 6.10045827112101 | 7.05038332126728 |
| S | 5.23818470958443 | 4.60217402475852 | 4.62440496624728 |
| S | 3.23618963090861 | 6.37947201974017 | 6.46928140620244 |
| N | 6.76684324421676 | 7.05757060770017 | 4.35358860771771 |
| N | 4.24324472033924 | 7.22262472307599 | 3.92921597921802 |
| N | 5.08423552668246 | 12.07764271114855 | 8.17655627147830 |
| C | 5.94813380047823 | 9.35975058106794 | 7.01817706993484 |
| C | 6.74103223474408 | 10.34445015315023 | 7.75551884362010 |
| C | 6.14719833389628 | 11.73506410596930 | 7.45995573145417 |
| C | 6.71930012999588 | 12.54550441852626 | 6.47974665781584 |
| H | 7.59225008935517 | 12.20842138380997 | 5.91947989474419 |
| C | 6.14990423434069 | 13.80092073023674 | 6.26530401196581 |
| H | 6.56927976754365 | 14.47952634869502 | 5.51898849656907 |
| C | 5.04801657484071 | 14.17741154799699 | 7.02643555640405 |
| H | 4.57777732467070 | 15.15352984313598 | 6.89516861915380 |
| C | 4.54974165425143 | 13.27777723133969 | 7.97165280625283 |
| H | 3.68371569561807 | 13.54096480819408 | 8.58810895452004 |
| C | 5.44560834345210 | 8.47861483854365 | 6.27937621747406 |
| C | 8.29541310571754 | 6.68823532815185 | 6.15696419693903 |
| H | 8.54233952231351 | 7.64575787433300 | 6.65257944894481 |
| H | 9.13364658666954 | 6.00042255099125 | 6.34254064622932 |
| C | 8.04103364412286 | 6.94529846016461 | 4.69987554171242 |
| C | 9.04890188748724 | 7.11968523990409 | 3.72744640987417 |
| H | 10.09791824219458 | 7.02966397442339 | 4.01824437584606 |
| C | 8.70766342779263 | 7.39654984126915 | 2.41349387219537 |
| H | 9.49093498545522 | 7.51829204544897 | 1.66130555122940 |
| C | 7.34629187772024 | 7.52157213050417 | 2.04440060191934 |
| C | 6.82391445622325 | 7.77984148648408 | 0.73057712512531 |
| H | 7.52333452146550 | 7.91639238721217 | -0.09699150180406 |
| C | 5.47536483682116 | 7.85120417741026 | 0.49891891583840 |
| H | 5.10643717832474 | 8.04500702513467 | -0.51078054091233 |
| C | 4.52081947202814 | 7.67596841261274 | 1.55869607068294 |
| C | 3.10958989376080 | 7.69515059825322 | 1.44750137047012 |
| H | 2.63964765228653 | 7.88060594014254 | 0.47850186995044 |
| C | 2.32232949296696 | 7.47196314961205 | 2.56516001916501 |
| H | 1.23355694293949 | 7.48449136746954 | 2.47993854006768 |

| | | | |
|---|---|---|---|
| C | 2.92277259305012 | 7.21794359663286 | 3.81895659185921 |
| C | 2.16128656131571 | 6.94871929842947 | 5.08761733944097 |
| H | 1.34155945159211 | 6.22848558371498 | 4.94005993824182 |
| H | 1.69309902024271 | 7.87639219128186 | 5.45767840587968 |
| C | 5.02274529529579 | 7.43586400929121 | 2.84576594545379 |
| C | 6.41984804130699 | 7.35059459058485 | 3.08255439450329 |
| C | 6.85380475603262 | 4.28979309691977 | 6.90183942999140 |
| H | 7.81943432515025 | 3.92791331563094 | 7.28834619144413 |
| H | 6.08695877179260 | 3.95624809223493 | 7.61751827832453 |
| C | 6.58797419029517 | 3.77041701803995 | 5.50543662276410 |
| H | 6.40171677653471 | 2.68457380989624 | 5.49746202385509 |
| H | 7.45334842073265 | 3.94214920421843 | 4.84549417324287 |
| C | 3.66168932137748 | 3.90340447958578 | 5.20251871885361 |
| H | 2.99601816305923 | 4.03824407603335 | 4.33514384331776 |
| H | 3.77869297416772 | 2.81660567186095 | 5.33849210525085 |
| C | 3.08994196528916 | 4.56495056364762 | 6.43731392312636 |
| H | 3.62237304920625 | 4.25803356752887 | 7.35045442566777 |
| H | 2.03308627853836 | 4.29056892162945 | 6.58186179285794 |
| H | 5.33383910014109 | 9.50186656401123 | 5.68880000341624 |
| O | 8.05040176112137 | 10.20242920292897 | 7.24808941885374 |
| H | 8.63305343916644 | 10.77217836718086 | 7.76945255305452 |
| C | 6.67267302259269 | 10.00994021253271 | 9.24762881285432 |
| H | 5.64765497192173 | 10.11602035597344 | 9.62020501405562 |
| H | 7.05554986694893 | 8.99612426904105 | 9.43081146383019 |
| H | 7.30373926211133 | 10.73141903449528 | 9.78730618007757 |

**Table S13.** Cartesian coordinates of **2v** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.19110845139703 | 6.90045376735977 | 5.43851180073561 |
| S | 6.69435707982005 | 6.36615379783138 | 7.06109749943126 |
| S | 5.23194693731383 | 4.66842988246629 | 4.70035052123932 |
| S | 3.14516299636015 | 6.56124297564659 | 6.37417021414043 |
| N | 6.73596209307090 | 7.15900359057183 | 4.32412452435950 |
| N | 4.22396450335342 | 7.18560517320773 | 3.79298331552177 |
| N | 4.73840142690311 | 11.83077250469938 | 8.89686123667930 |
| C | 5.37208479430816 | 9.77388464087358 | 6.45400385335662 |
| C | 6.12298572182052 | 10.21758695260736 | 7.72699511744161 |
| C | 5.73714549950077 | 11.66346551804871 | 8.03613543667726 |
| C | 6.40904989271776 | 12.72693585848903 | 7.42800524684998 |
| H | 7.22014809188209 | 12.53999780142137 | 6.72145086772491 |
| C | 6.02060409767528 | 14.02385790607425 | 7.76110547838087 |
| H | 6.52612218161984 | 14.88197940219769 | 7.31254416280390 |
| C | 4.98638396996827 | 14.20260554023517 | 8.67624327018784 |
| H | 4.65319798785163 | 15.19859212444165 | 8.97489477684876 |
| C | 4.37323840554275 | 13.06972632071077 | 9.21358509873766 |
| H | 3.55171873282540 | 13.17088288392035 | 9.93119894829382 |
| C | 5.23148360670438 | 8.56258036540820 | 6.01500826169651 |
| C | 8.18153265235289 | 7.02011021107522 | 6.21286818271697 |
| H | 8.26772599151307 | 8.04155876158157 | 6.63736588674355 |
| H | 9.06679792192687 | 6.44341427993775 | 6.51712890853732 |
| C | 7.99624800987059 | 7.11974629547671 | 4.72848551607569 |
| C | 9.03608605670038 | 7.21776282402062 | 3.77943321804838 |
| H | 10.07505296525962 | 7.18726373963326 | 4.11425697770723 |
| C | 8.73745785057704 | 7.34822503848187 | 2.43221628759487 |
| H | 9.54671787395950 | 7.41198223394849 | 1.70056882438690 |
| C | 7.38842779291705 | 7.39593168202816 | 2.00268962083447 |
| C | 6.90852192483799 | 7.50314978759484 | 0.65211975973430 |
| H | 7.63482612569262 | 7.57281898157804 | -0.16055370175423 |
| C | 5.56799301620513 | 7.51257671479192 | 0.36724246085209 |
| H | 5.23309755098797 | 7.59022968745118 | -0.66970427819202 |
| C | 4.57920550684143 | 7.41664065924763 | 1.40555108087180 |
| C | 3.17255103435801 | 7.38236895255457 | 1.24641499234649 |
| H | 2.73344822703332 | 7.45739490993926 | 0.24832780881258 |
| C | 2.34968977675983 | 7.24550547566399 | 2.35262766480562 |
| H | 1.26494361677656 | 7.21735984177171 | 2.22922488731049 |

| | | | |
|---|---|---|---|
| C | 2.90931519509148 | 7.13174671194946 | 3.64484436904969 |
| C | 2.11242190026318 | 6.97706890881374 | 4.91017016194521 |
| H | 1.29928799311118 | 6.24141796831223 | 4.80964364740358 |
| H | 1.63075441769639 | 7.93446565913012 | 5.17289726377398 |
| C | 5.04010775131679 | 7.31970227260127 | 2.72523405699062 |
| C | 6.42819152519424 | 7.30637059499798 | 3.01957961265142 |
| C | 6.83096733016606 | 4.55192554830955 | 6.99434136535007 |
| H | 7.80971880361020 | 4.26632317466385 | 7.41148845515264 |
| H | 6.07461928052946 | 4.22110708171102 | 7.72285942769045 |
| C | 6.60530616989000 | 3.94199782727549 | 5.63153133660741 |
| H | 6.45872817430774 | 2.85151838279269 | 5.68970134226116 |
| H | 7.46748270437581 | 4.10681161001845 | 4.96637930721177 |
| C | 3.67097073229807 | 3.98923438954181 | 5.33814408928948 |
| H | 3.00858567748802 | 4.01482326352408 | 4.45803769578951 |
| H | 3.81568988264929 | 2.92567284401972 | 5.58620834441534 |
| C | 3.06582083004671 | 4.74767293684646 | 6.49992090535709 |
| H | 3.59632200722369 | 4.54666536241419 | 7.44345919672212 |
| H | 2.01687046197559 | 4.45196339223993 | 6.66107515771045 |
| H | 4.97971336325913 | 10.56124914978268 | 5.79170703318721 |
| O | 7.49268795364360 | 10.12540101641564 | 7.36584860732211 |
| H | 8.00287029983767 | 10.59643074780052 | 8.03961008172653 |
| C | 5.81914923113759 | 9.31635390476153 | 8.91221598881246 |
| H | 4.75132257790657 | 9.32929986259301 | 9.15627154798042 |
| H | 6.15635730154851 | 8.29307337799352 | 8.70095292137810 |
| H | 6.35893606022749 | 9.68843727850272 | 9.79479658568141 |

**Table S14.** Cartesian coordinates of **5-π** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.33206384258777 | 7.21001494266633 | 5.46034870020182 |
| S | 7.30085442759029 | 6.98525207425778 | 6.65233327026278 |
| S | 5.07742083607601 | 4.92030653073887 | 5.54153379427721 |
| S | 3.57750491439063 | 7.40963295890072 | 6.96408736593854 |
| O | 5.76698214320321 | 8.78507010054108 | 8.41485277241939 |
| N | 6.47662852230215 | 6.90583833360206 | 3.92103720532548 |
| N | 3.91514125462056 | 7.21049645622042 | 4.12898955735089 |
| N | 5.88716484323854 | 11.85549499038255 | 6.67505212118110 |
| C | 5.61385826098088 | 9.24972594295070 | 6.11388499036618 |
| C | 5.76178635390026 | 9.62396001297906 | 7.54047307379761 |
| C | 5.88000923504413 | 11.08343950408668 | 7.76555722668896 |
| C | 5.96543765550326 | 11.57167963949587 | 9.07226256677433 |
| H | 5.95692207023065 | 10.87851419311578 | 9.91506897141661 |
| C | 6.05364433375882 | 12.95055269585538 | 9.24240191041579 |
| H | 6.11794032394361 | 13.38826252211780 | 10.24104990081764 |
| C | 6.06086670376497 | 13.76120499468925 | 8.11118801397246 |
| H | 6.13067838900277 | 14.84764891600005 | 8.20034495680824 |
| C | 5.98030365822987 | 13.16537567117009 | 6.84603662875975 |
| H | 5.98994513597933 | 13.78379986744447 | 5.94249716809332 |
| C | 5.51759119076362 | 9.26545372748823 | 4.88301295464522 |
| C | 8.46045534638299 | 6.67579222237888 | 5.26389986713101 |
| H | 9.22490939099937 | 7.46698139659750 | 5.32596258862556 |
| H | 8.99141156442330 | 5.72458659815396 | 5.43065757905087 |
| C | 7.78585312088398 | 6.70118282301703 | 3.92447836230281 |
| C | 8.48069285175314 | 6.52939641955305 | 2.70636898303266 |
| H | 9.56082456915900 | 6.37153324419619 | 2.72361827639416 |
| C | 7.79745859097194 | 6.55525645300850 | 1.50517536988074 |
| H | 8.33691646359047 | 6.42546960090840 | 0.56376623209585 |
| C | 6.39302940392142 | 6.73219959189116 | 1.49697929479770 |
| C | 5.54734943206062 | 6.74726316905207 | 0.33764803185751 |
| H | 6.00555617660684 | 6.63056255992748 | -0.64707240335712 |
| C | 4.19046822540782 | 6.89126853598642 | 0.44901190671975 |
| H | 3.56642257198530 | 6.89115507941035 | -0.44736841367771 |
| C | 3.56095869068889 | 7.04069460295215 | 1.73010698176554 |
| C | 2.17270712086699 | 7.17731743869224 | 1.97042723114843 |
| H | 1.47057310026323 | 7.17358415625996 | 1.13301767180683 |
| C | 1.70725156532062 | 7.31415589484464 | 3.26557437371216 |

| | | | |
|---|---|---|---|
| H | 0.63771946953229 | 7.42194136759870 | 3.45960734541958 |
| C | 2.61401452296758 | 7.33325632788965 | 4.34801075689106 |
| C | 2.19236092019539 | 7.53488004202552 | 5.77250467648638 |
| H | 1.38687537289107 | 6.84616154770179 | 6.07130315880412 |
| H | 1.78617293036150 | 8.55206870975838 | 5.90209068138667 |
| C | 4.38361125964301 | 7.05507691350178 | 2.86799027243486 |
| C | 5.78922173241698 | 6.89761640620944 | 2.75335381275215 |
| C | 7.09939390470186 | 5.36114779913765 | 7.43199311199445 |
| H | 8.07100674079476 | 5.02602359167543 | 7.82884393703436 |
| H | 6.46411374262678 | 5.59231841043837 | 8.30054114831189 |
| C | 6.49059873173243 | 4.32120073812546 | 6.52053005482329 |
| H | 6.17388062207681 | 3.42359673891203 | 7.07411485691424 |
| H | 7.21083698389577 | 3.97951062595611 | 5.76174442099233 |
| C | 3.61098798451079 | 4.66167446503032 | 6.58492349247722 |
| H | 2.78244313259958 | 4.63388594869698 | 5.85898835468232 |
| H | 3.67046602110398 | 3.65669844166372 | 7.03228322789787 |
| C | 3.39114310201961 | 5.73312032133794 | 7.62420078220108 |
| H | 4.12554129472903 | 5.68966450402579 | 8.44232066205431 |
| H | 2.39579020350709 | 5.64558501194097 | 8.08787235100303 |
| H | 5.47474541729620 | 9.60052906684049 | 3.85594984263843 |

**Table S15.** Cartesian coordinates of **5-TS** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.32662599215567 | 8.02617438736446 | 4.50311458509804 |
| S | 7.20212533659804 | 7.42445432118020 | 5.71179599644915 |
| S | 4.98827973493014 | 5.82738308376891 | 3.95285544109430 |
| S | 3.53318540099267 | 7.92550108361672 | 5.93724371644482 |
| O | 5.70583100404031 | 9.18977404436525 | 7.76263289617547 |
| N | 6.54748220103948 | 8.11247856184895 | 3.00782937869533 |
| N | 3.99394568494126 | 8.41879463548632 | 3.15599730941996 |
| N | 5.96252735333953 | 12.34665802898497 | 6.19382705720620 |
| C | 5.63868752032734 | 9.81550042109064 | 5.46354421127533 |
| C | 5.75257634533622 | 10.05542074025503 | 6.92904644507809 |
| C | 5.91911387401851 | 11.51222502557880 | 7.23008600097107 |
| C | 6.00586567843997 | 11.93169164776752 | 8.55686205063784 |
| H | 5.96673432328852 | 11.19305023664496 | 9.35968223706727 |
| C | 6.13121343779915 | 13.29775201136266 | 8.80126292237168 |
| H | 6.19662817667262 | 13.67743069675264 | 9.82354194348605 |
| C | 6.17101819869778 | 14.16897154972076 | 7.71790604399484 |
| H | 6.26861297854376 | 15.24647145680865 | 7.86653947072631 |
| C | 6.08821153781604 | 13.64567129296949 | 6.42154425771810 |
| H | 6.12361240897494 | 14.30612558482619 | 5.54995332960158 |
| C | 5.67101184815486 | 10.58635610268944 | 4.48492831713166 |
| C | 8.45358769154445 | 7.65574450587481 | 4.39456625319206 |
| H | 9.03512349781696 | 8.54077847168789 | 4.70393277255875 |
| H | 9.15704193983706 | 6.80827057635507 | 4.40784622526311 |
| C | 7.85364628667608 | 7.88271696815897 | 3.03827776640400 |
| C | 8.60185735517647 | 7.87693649597684 | 1.84120718148311 |
| H | 9.67778359555814 | 7.69569657137450 | 1.88260182375914 |
| C | 7.97230475232058 | 8.07501240881645 | 0.62488150973054 |
| H | 8.54982988042028 | 8.05022301509372 | -0.30238740255520 |
| C | 6.57367842936451 | 8.28712510124770 | 0.58282729220189 |
| C | 5.77098160684234 | 8.44321533818134 | -0.59694100443135 |
| H | 6.26460790130641 | 8.43704508202997 | 1.57135624237683 |
| C | 4.41069481665309 | 8.57765740369226 | 0.52000193987373 |
| H | 3.82115410034649 | 8.67790731158296 | 1.43377448960335 |
| C | 3.73048773243808 | 8.57933344434246 | 0.74424561175105 |
| C | 2.33187733009644 | 8.65547722300060 | 0.94586761775000 |
| H | 1.66093729995932 | 8.74890698013408 | 0.08857113416776 |
| C | 1.81582760868733 | 8.59353208249279 | 2.22839597588939 |

| | | | |
|---|---|---|---|
| H | 0.73698921136572 | 8.64106261430301 | 2.39231404554671 |
| C | 2.68038760634494 | 8.45966875794686 | 3.33590639890424 |
| C | 2.20271775943271 | 8.36631933508837 | 4.75498741946975 |
| H | 1.36263444624576 | 7.66337862692443 | 4.86915804791838 |
| H | 1.82836250306675 | 9.34567157354725 | 5.09683169615534 |
| C | 4.51051503622911 | 8.46256523293547 | 1.90517804728850 |
| C | 5.91873657025042 | 8.30509933464320 | 1.82400644474404 |
| C | 7.05794489607528 | 5.61866672068514 | 5.82712797856482 |
| H | 8.04964097113252 | 5.19787407684113 | 6.05657761222399 |
| H | 6.43408674324164 | 5.46375700980956 | 6.72018584004810 |
| C | 6.45832927511401 | 4.97951468474686 | 4.59685101968315 |
| H | 6.21162746594369 | 3.91789541585542 | 4.75760012335441 |
| H | 7.15868952485822 | 5.01435193853928 | 3.74615423578044 |
| C | 3.57428234163986 | 5.29530653553120 | 4.97314353781087 |
| H | 2.72383379689051 | 5.34197257907633 | 4.27502033090772 |
| H | 3.70835089624743 | 4.23323421275256 | 5.23377317972246 |
| C | 3.32713738135601 | 6.14227119687657 | 6.20123470418085 |
| H | 4.05097887222696 | 5.93278613507538 | 7.00362777075971 |
| H | 2.32606321954652 | 5.95354906710662 | 6.62069148833666 |
| H | 5.67878062164103 | 11.11099105859018 | 3.54177638264617 |

**Table S16.** Cartesian coordinates of **5** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.35310242101401 | 7.88646399237546 | 4.72211579707898 |
| S | 7.18226153211986 | 7.16090833889152 | 5.87050445176449 |
| S | 5.05719236306145 | 5.76605072927532 | 3.82865575728149 |
| S | 3.56743121395403 | 7.53872430566527 | 6.11066349130365 |
| O | 5.65397221228059 | 9.10718255038112 | 7.87644094773522 |
| N | 6.58039727104077 | 8.16722405610592 | 3.26972144604277 |
| N | 4.03707805962218 | 8.45072274788082 | 3.43795636220531 |
| N | 5.87099199411340 | 11.90999917469697 | 5.90003280076466 |
| C | 5.59892657395063 | 9.63573183271241 | 5.48187093690426 |
| C | 5.69305755634881 | 9.88851073749520 | 6.96451518831362 |
| C | 5.85596312720807 | 11.37951083585006 | 7.14588173906609 |
| C | 5.96384331805778 | 12.17439729665505 | 8.25894331024933 |
| H | 5.94783107617660 | 11.71440923657148 | 9.24934304398592 |
| C | 6.08774789985934 | 13.56150942122625 | 8.06880117667032 |
| H | 6.17317500168883 | 14.22821175919274 | 8.92944803324067 |
| C | 6.10466504578026 | 14.08025302048128 | 6.77782612861373 |
| H | 6.20553504077529 | 15.15247244514582 | 6.59945589131990 |
| C | 5.99654333723460 | 13.22252157362538 | 5.68517949656992 |
| H | 6.00494260339177 | 13.56338698398496 | 4.64793339416788 |
| C | 5.72131425424115 | 10.85802673995828 | 4.91785526914893 |
| C | 8.46218732966437 | 7.54270727729012 | 4.61347509913137 |
| H | 9.01953208936373 | 8.39950592463539 | 5.02806708337019 |
| H | 9.18100001906062 | 6.71074912927191 | 4.55171899752518 |
| C | 7.88087180713741 | 7.90649771536638 | 3.27806790231909 |
| C | 8.62925971960738 | 7.98746924531037 | 2.08391911535265 |
| H | 9.69847103317469 | 7.76755621066070 | 2.10514255778025 |
| C | 8.00746121737950 | 8.31431355230171 | 0.89059933090393 |
| H | 8.58482893470784 | 8.35380502544931 | -0.03631985822743 |
| C | 6.61644618155114 | 8.57255282264747 | 0.87162590891698 |
| C | 5.81446380404062 | 8.85713456811349 | -0.28556489186417 |
| H | 6.30634129986900 | 8.93102504212468 | -1.25816149836932 |
| C | 4.45784117588138 | 9.01835657818168 | -0.19305039969598 |
| H | 3.87204541306802 | 9.22149129549824 | -1.09199100107765 |
| C | 3.77508152478758 | 8.90749559691516 | 1.06593670994792 |
| C | 2.37893037542826 | 8.99094855240978 | 1.28068318103824 |
| H | 1.70863625135859 | 9.19695570451528 | 0.44286774392195 |
| C | 1.86392440283602 | 8.79505845712408 | 2.55153573055258 |

| | | | |
|---|---|---|---|
| H | 0.78727448809463 | 8.85538751285178 | 2.72477021139741 |
| C | 2.72586553148774 | 8.50004227942512 | 3.62914464701177 |
| C | 2.25763975676823 | 8.23905612942728 | 5.03273795149996 |
| H | 1.36700284204046 | 7.59302226397932 | 5.06666073121561 |
| H | 1.96822487056990 | 9.18689748770765 | 5.51615322139264 |
| C | 4.55388593649809 | 8.64954075890672 | 2.20442535358673 |
| C | 5.96141588090573 | 8.48797518591806 | 2.11015205364232 |
| C | 7.03132168053840 | 5.35078122394114 | 5.78808043793683 |
| H | 8.01262448891145 | 4.90084161449781 | 6.00652929403395 |
| H | 6.37937843801340 | 5.11430245290799 | 6.64231972510158 |
| C | 6.46770423557488 | 4.82808035702873 | 4.48473948357370 |
| H | 6.19109253099126 | 3.76385244266041 | 4.55236788203283 |
| H | 7.21056164569084 | 4.90491998911740 | 3.67401317564806 |
| C | 3.54462567685226 | 5.16113620883211 | 4.62814504529872 |
| H | 2.75840356034458 | 5.45101156831596 | 3.91270350049405 |
| H | 3.55895985518132 | 4.05982430594015 | 4.64231070309921 |
| C | 3.27558257784848 | 5.74475778667799 | 5.99769727595922 |
| H | 3.94429590870130 | 5.32545645594439 | 6.76460799284441 |
| H | 2.24675005871009 | 5.53168869215127 | 6.32871551942980 |
| H | 5.71889555544119 | 11.17098480778138 | 3.87312942084807 |

**Table S17.** Cartesian coordinates of **5v-TS1** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.30127546027103 | 7.19559948720365 | 5.65996576348602 |
| S | 7.22862797104149 | 6.85510672276470 | 6.87215107921079 |
| S | 5.02661394044410 | 4.91786868558354 | 5.50907337448383 |
| S | 3.52155250682562 | 7.29536512011357 | 7.11841040750355 |
| O | 5.59582153597151 | 8.24368926095157 | 8.95188461506838 |
| N | 6.48422862444168 | 7.09866379996234 | 4.12596154154020 |
| N | 3.92908417677151 | 7.39086855248808 | 4.29771952034165 |
| N | 5.95674949682824 | 11.45174050270499 | 7.86063308251584 |
| C | 5.66408704944374 | 9.52732910811796 | 6.92556790397024 |
| C | 5.70988886470058 | 9.30702252685472 | 8.40078294795739 |
| C | 5.90638128938831 | 10.66232355228092 | 8.93783662871320 |
| C | 6.01409813129134 | 11.11560864016457 | 10.24425467410654 |
| H | 5.96897539665448 | 10.42107921831118 | 11.08507068693012 |
| C | 6.17451055639966 | 12.49233513157037 | 10.41193488083262 |
| H | 6.26376796249153 | 12.92319009553970 | 11.41191096235984 |
| C | 6.22226798311396 | 13.31744316623463 | 9.28901235876184 |
| H | 6.34980876153631 | 14.39667040590101 | 9.39812592116873 |
| C | 6.11315530614313 | 12.75747245340460 | 8.00881183264342 |
| H | 6.15302954858123 | 13.37528633526539 | 7.10734225588764 |
| C | 5.55916170189113 | 9.23599503645098 | 5.69870538560194 |
| C | 8.43410855134432 | 6.75321465603577 | 5.49233640054528 |
| H | 9.16128850197512 | 7.56296797208289 | 5.66495552193912 |
| H | 9.00041449857016 | 5.81155694207876 | 5.57128044486903 |
| C | 7.79511481887310 | 6.90426273582118 | 4.14271468469694 |
| C | 8.52563706516623 | 6.86172496877147 | 2.93479999924066 |
| H | 9.60655751266138 | 6.71166596253861 | 2.96732835232741 |
| C | 7.87448079519871 | 6.99544725729935 | 1.72235529549789 |
| H | 8.43823343302859 | 6.95371671624766 | 0.78725553719891 |
| C | 6.47118271585202 | 7.17310070255497 | 1.69504625236463 |
| C | 5.65341156825043 | 7.28902580393436 | 0.52137675298262 |
| H | 6.13524506407417 | 7.26068512462945 | -0.45855500059932 |
| C | 4.29418503327551 | 7.42100556370516 | 0.61199611670664 |
| H | 3.69197466686627 | 7.49829741061490 | -0.29581273464968 |
| C | 3.63223921220480 | 7.45837999233217 | 1.88472359442416 |
| C | 2.23802481102489 | 7.56417405919125 | 2.09977334018891 |
| H | 1.55765531748681 | 7.63774539318655 | 1.24795484040913 |
| C | 1.74073263343809 | 7.57077897586912 | 3.38999323601317 |

| | | | |
|---|---|---|---|
| H | 0.66618069794481 | 7.65285201564761 | 3.56776921157174 |
| C | 2.62052902414420 | 7.47856275068737 | 4.49024422957914 |
| C | 2.15619704999666 | 7.50361175575677 | 5.91583836129611 |
| H | 1.37348264830267 | 6.75399479163745 | 6.11146698957058 |
| H | 1.70319335443383 | 8.48181939020455 | 6.14760880407596 |
| C | 4.42640377333224 | 7.37130215931056 | 3.03949399052428 |
| C | 5.83419481117425 | 7.22092758512627 | 2.94507503548204 |
| C | 7.06231297556449 | 5.13635797281744 | 7.42985145510128 |
| H | 8.04396398110683 | 4.76735617123883 | 7.76609555113315 |
| H | 6.43294510232695 | 5.23076276735123 | 8.32746292000918 |
| C | 6.45565562218426 | 4.21819015767480 | 6.39320692993636 |
| H | 6.15725527215008 | 3.25099426770262 | 6.82671531946651 |
| H | 7.17202187928515 | 3.99096361192017 | 5.58894527845187 |
| C | 3.57613415717844 | 4.57529065994817 | 6.55577169049471 |
| H | 2.74046089082757 | 4.57723287094381 | 5.83749357620818 |
| H | 3.65469615307426 | 3.54732312425797 | 6.94380385946629 |
| C | 3.34153096379246 | 5.57710812910259 | 7.66117678788531 |
| H | 4.07668782289756 | 5.49053720877663 | 8.47509736996124 |
| H | 2.34630269257827 | 5.44431295013174 | 8.11418681859234 |
| H | 5.58582482418384 | 9.80688275100141 | 4.77170943395448 |

**Table S18.** Cartesian coordinates of **5v-INT** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.33596438929104 | 7.13158770844779 | 5.46912380587077 |
| S | 7.25876646009000 | 6.88121893911393 | 6.66467556306759 |
| S | 5.06880847494263 | 4.81374803609890 | 5.47099623593608 |
| S | 3.62575054599335 | 7.29717918884064 | 6.97432230813204 |
| O | 5.77599101193172 | 8.45387131022701 | 8.86245030907310 |
| N | 6.48115440452251 | 6.96359020644217 | 3.92861379666794 |
| N | 3.94411134969394 | 7.27226688312079 | 4.14058755661133 |
| N | 5.82221936115057 | 11.14737112739557 | 7.05879485155927 |
| C | 5.70404649800557 | 9.71649321433126 | 6.70090917010362 |
| C | 5.78676486486862 | 9.42056309951253 | 8.16733125096975 |
| C | 5.88867893652941 | 10.93314322036588 | 8.40385772145579 |
| C | 5.98468211675063 | 11.97690958019812 | 9.28697768774484 |
| H | 6.03634923929286 | 11.80772735396844 | 10.36445123995795 |
| C | 6.01327974936669 | 13.26861254597280 | 8.72232874717806 |
| H | 6.08759141438852 | 14.14173665832844 | 9.37459622226511 |
| C | 5.95164591085278 | 13.44868211170207 | 7.34195903669208 |
| H | 5.97834577511089 | 14.45005697147462 | 6.90812529604564 |
| C | 5.85422795430542 | 12.34273855952954 | 6.48980717653537 |
| H | 5.79895086620591 | 12.40965393623026 | 5.40091463599825 |
| C | 5.54756028529951 | 9.04470746844933 | 5.55101365128254 |
| C | 8.44214730731451 | 6.62870566919899 | 5.28050668068321 |
| H | 9.23373104895803 | 7.38401948735694 | 5.40404327531927 |
| H | 8.93397851715969 | 5.64926306227655 | 5.39502100076928 |
| C | 7.79036129325993 | 6.75752153379454 | 3.93279252328236 |
| C | 8.49975319128956 | 6.67178261933152 | 2.71481660143368 |
| H | 9.57980673018486 | 6.51355849266289 | 2.73368750595994 |
| C | 7.82971775302096 | 6.77151887122712 | 1.50827711094662 |
| H | 8.37917218997628 | 6.69682836283474 | 0.56685907943622 |
| C | 6.42689874486121 | 6.95356563649485 | 1.49743254638510 |
| C | 5.58363428509432 | 7.03665089759457 | 0.33789510074179 |
| H | 6.04426734927932 | 6.97280474768814 | -0.65054472900431 |
| C | 4.22676452894949 | 7.17940680462018 | 0.45118161527252 |
| H | 3.60815143692819 | 7.23019620568399 | -0.44740125859642 |
| C | 3.58872980341232 | 7.26196630508208 | 1.73518066171011 |
| C | 2.20170584557105 | 7.38968240047850 | 1.98214470067849 |
| H | 1.49916290122337 | 7.43778421051993 | 1.14670750619753 |
| C | 1.73780873977909 | 7.45465125431367 | 3.28480430036623 |

| | | | |
|---|---|---|---|
| H | 0.66915418478557 | 7.55970919135917 | 3.48511209511025 |
| C | 2.64394924370382 | 7.39591230069880 | 4.36535641929478 |
| C | 2.23043217236077 | 7.51342346352679 | 5.80376400107741 |
| H | 1.42208550094037 | 6.81334772154903 | 6.06532196543252 |
| H | 1.83331096888952 | 8.52341657923723 | 5.99804801157133 |
| C | 4.40855502495201 | 7.20469687528969 | 2.87296004769468 |
| C | 5.81329604408504 | 7.04554729437859 | 2.75565694643637 |
| C | 7.08027850782761 | 5.22836806803593 | 7.39400258269277 |
| H | 8.05449557834083 | 4.88669181972868 | 7.77840367015682 |
| H | 6.44538619892642 | 5.42719341995404 | 8.27076451394650 |
| C | 6.47264906913835 | 4.20590517763844 | 6.45838147927875 |
| H | 6.15611888434420 | 3.29990532999986 | 6.99809345097774 |
| H | 7.20039829875277 | 3.87674915633096 | 5.70140239124329 |
| C | 3.59429571018860 | 4.55930750734261 | 6.50486705170460 |
| H | 2.76967298144513 | 4.57326251664842 | 5.77390535352433 |
| H | 3.62498109612014 | 3.54220502958607 | 6.92676139119544 |
| C | 3.38427227228222 | 5.60339354209934 | 7.57549166040555 |
| H | 4.10925218610940 | 5.51399203335668 | 8.39827927754258 |
| H | 2.38242402051561 | 5.52052355760338 | 8.02576374567071 |
| H | 5.52081715143565 | 9.66076557472512 | 4.63585549031331 |

**Table S19.** Cartesian coordinates of **5v-TS2** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.37540288090661 | 7.23661614546457 | 5.50044445446956 |
| S | 7.29195865612749 | 6.99556553222751 | 6.70984145241712 |
| S | 5.06591437807914 | 4.95657711094361 | 5.52364662085444 |
| S | 3.70161839020391 | 7.47601704548697 | 7.03492363642469 |
| O | 5.83858343038660 | 11.16662380878186 | 8.27499320411643 |
| N | 6.50798079061470 | 7.00942891601307 | 3.96351500401685 |
| N | 3.97383852557454 | 7.36239737518210 | 4.18823726001050 |
| N | 5.80897313790174 | 12.56988994313334 | 5.06649660218866 |
| C | 5.72088735917417 | 10.25141185848312 | 6.19813159351582 |
| C | 5.81736645611889 | 11.41642917104651 | 7.09702332365189 |
| C | 5.85754087006932 | 12.70721383040527 | 6.39613740878430 |
| C | 5.92974889254586 | 13.92558431103942 | 7.06478526283509 |
| H | 5.96779198659209 | 13.95149217594945 | 8.15622740972480 |
| C | 5.95125965213328 | 15.07985162783476 | 6.28449509691920 |
| H | 6.00686612061843 | 16.06514007785971 | 6.75259249221520 |
| C | 5.90422728181516 | 14.95082128755749 | 4.89850358069176 |
| H | 5.92163678908948 | 15.83141693547104 | 4.25340499028913 |
| C | 5.83456173527634 | 13.67190741688388 | 4.33031208798802 |
| H | 5.79741442443278 | 13.54678253927017 | 3.24316487916173 |
| C | 5.60568753235220 | 9.14621574384695 | 5.60396894301437 |
| C | 8.48123735355734 | 6.79520711915564 | 5.31957918425962 |
| H | 9.18646156986433 | 7.63783305243733 | 5.40663965719034 |
| H | 9.07375935012485 | 5.88053363149359 | 5.48162140460230 |
| C | 7.81668596519312 | 6.80754891686441 | 3.97093596908442 |
| C | 8.51217207389841 | 6.65397650317543 | 2.75078100056821 |
| H | 9.59144071408309 | 6.48971154923274 | 2.76429761858142 |
| C | 7.82917299584280 | 6.70510236162161 | 1.54784324596890 |
| H | 8.37068339407894 | 6.58403489294774 | 0.60649989537305 |
| C | 6.42722426620615 | 6.90338086647015 | 1.53819379937684 |
| C | 5.57366771694171 | 6.96511210854633 | 0.38414131294521 |
| H | 6.02292760388780 | 6.86007178398861 | -0.60605967964477 |
| C | 4.22083182891252 | 7.14388463169698 | 0.50440424167313 |
| H | 3.59682117896091 | 7.18365180058306 | -0.39106359616552 |
| C | 3.59601561504302 | 7.28266459479706 | 1.79097128981502 |
| C | 2.21673887752177 | 7.46709092823371 | 2.05216079636950 |
| H | 1.50519117336921 | 7.51333847169329 | 1.22404195648423 |
| C | 1.76879038354117 | 7.59540054825603 | 3.35668893931063 |

| | | | |
|---|---|---|---|
| H | 0.70702976818685 | 7.74986833572586 | 3.56149217370369 |
| C | 2.68482819520472 | 7.54379955959245 | 4.43038520449959 |
| C | 2.30519381192918 | 7.74191577431888 | 5.87130282516159 |
| H | 1.45652640453053 | 7.11047407860315 | 6.17625509272698 |
| H | 1.98365911809090 | 8.78424807785693 | 6.03479523351813 |
| C | 4.42508866317845 | 7.23510546902239 | 2.92115397892312 |
| C | 5.82617326442513 | 7.04572867155164 | 2.79684876230958 |
| C | 7.12335387914377 | 5.32232713617529 | 7.40191926033694 |
| H | 8.10767498252361 | 4.97491480228562 | 7.75391513026131 |
| H | 6.51256376391978 | 5.49121626101162 | 8.30200034696201 |
| C | 6.49040489372943 | 4.32060184371048 | 6.46274043781405 |
| H | 6.18354283859866 | 3.40442916053511 | 6.99103076552734 |
| H | 7.19462843993965 | 4.00581583828055 | 5.67742015701798 |
| C | 3.60045980737987 | 4.73095666282275 | 6.57768222466485 |
| H | 2.76981607681286 | 4.75006150911935 | 5.85379724571558 |
| H | 3.62166427431432 | 3.71673427342465 | 7.00729471581312 |
| C | 3.41805790376482 | 5.78744706129434 | 7.64004627059357 |
| H | 4.13728481907563 | 5.67951058729332 | 8.46567983042250 |
| H | 2.41407490196900 | 5.73596495160931 | 8.09037012209090 |
| H | 5.63657553224235 | 9.90732515169089 | 4.70911988285446 |

**Table S20.** Cartesian coordinates of **5v** at the PBE0 optimized geometry.

| | Coordinates in Å | | |
|---|---|---|---|
| | X | Y | Z |
| Fe | 5.36475008045202 | 7.36530334116288 | 5.42617014606331 |
| S | 7.28502708385692 | 7.19273726041718 | 6.64621987796458 |
| S | 5.06813809377343 | 5.04216848950113 | 5.56798029588702 |
| S | 3.68633363010841 | 7.65789580374387 | 6.94679942110394 |
| O | 5.88861901142995 | 10.32165539086070 | 8.06984377579911 |
| N | 6.49736075648877 | 7.03014399090688 | 3.90514270073989 |
| N | 3.95497942742860 | 7.37615955264548 | 4.11233560971935 |
| N | 5.97157364572224 | 13.00341583613434 | 5.78271374413348 |
| C | 5.74293770452292 | 10.36644558792653 | 5.66338864870261 |
| C | 5.87478731258675 | 10.96072997239402 | 7.05125457094791 |
| C | 5.97970051582348 | 12.45085952955550 | 6.99257983924119 |
| C | 6.07541425304887 | 13.18586901488598 | 8.17490894658625 |
| H | 6.08021944433578 | 12.66734677260053 | 9.13501704532746 |
| C | 6.16227631435899 | 14.57144833644372 | 8.06732804867321 |
| H | 6.23760699586710 | 15.19288105849889 | 8.96196079981512 |
| C | 6.15700212194491 | 15.14980556714192 | 6.80066412951107 |
| H | 6.22872213744690 | 16.23196130177792 | 6.67170925007605 |
| C | 6.06370704247982 | 14.32143646776749 | 5.67840064162691 |
| H | 6.06292345795078 | 14.74361946887868 | 4.66867769697912 |
| C | 5.58217129253545 | 9.10597223070936 | 5.44219506954389 |
| C | 8.47336180952772 | 6.93774544701316 | 5.26652384548414 |
| H | 9.14972872879070 | 7.80770298255474 | 5.29640630227484 |
| H | 9.09464614553257 | 6.05488753522840 | 5.48676906121830 |
| C | 7.80801587309207 | 6.84668592546143 | 3.92301247199108 |
| C | 8.50245274485616 | 6.62876108558451 | 2.71214517343889 |
| H | 9.58289470991094 | 6.47299113697599 | 2.73217313334191 |
| C | 7.81800146322927 | 6.61544346255395 | 1.50922705601207 |
| H | 8.36031586379926 | 6.45309220316962 | 0.57451168526994 |
| C | 6.41481954459420 | 6.80468201436049 | 1.48962320472601 |
| C | 5.56376367267218 | 6.81597368075610 | 0.33228407676218 |
| H | 6.01554268945723 | 6.67258821352877 | -0.65189708594546 |
| C | 4.21023556662632 | 6.99609904421902 | 0.44288297777845 |
| H | 3.58744314736862 | 6.99918852588417 | -0.45437066615342 |
| C | 3.58353632624007 | 7.18415361691832 | 1.72214062208211 |
| C | 2.20352037971182 | 7.37811436044293 | 1.97297532841291 |
| H | 1.49377985698603 | 7.38851782290203 | 1.14201984395164 |
| C | 1.75211196400862 | 7.56154760430004 | 3.26939951732552 |

| | | | |
|---|---|---|---|
| H | 0.68961848543870 | 7.72234418638484 | 3.46508075071459 |
| C | 2.66630985446164 | 7.56452389191971 | 4.34591465211316 |
| C | 2.28492426518026 | 7.83211998786007 | 5.77340198484085 |
| H | 1.45022391590948 | 7.20072360462181 | 6.11509787857865 |
| H | 1.94545248107565 | 8.87592883584300 | 5.88121757713519 |
| C | 4.41061440506437 | 7.18729594708931 | 2.85460378088184 |
| C | 5.81196332760159 | 6.99940041166849 | 2.74042296268796 |
| C | 7.12696018067755 | 5.55139033010184 | 7.41308913188182 |
| H | 8.11513627903531 | 5.23691606413250 | 7.78587784855664 |
| H | 6.51167265739426 | 5.75581873116414 | 8.30266435176251 |
| C | 6.51641021319589 | 4.49367219670440 | 6.52241338203384 |
| H | 6.24385480033453 | 3.59146871169896 | 7.09232743226926 |
| H | 7.22320597611260 | 4.16608579566314 | 5.74426924964905 |
| C | 3.61875328361829 | 4.87670045535501 | 6.65226743120080 |
| H | 2.77838598025729 | 4.83624303875470 | 5.94049939870137 |
| H | 3.65522138219616 | 3.89390131799024 | 7.14927046722765 |
| C | 3.43992644261285 | 5.99843012235333 | 7.64652458675349 |
| H | 4.16870520058851 | 5.95132220634646 | 8.46966967313116 |
| H | 2.44225517205520 | 5.96563295714545 | 8.11280723679204 |
| H | 5.78921840862369 | 11.16767939139547 | 4.89405262667532 |

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**NMR Spectra**

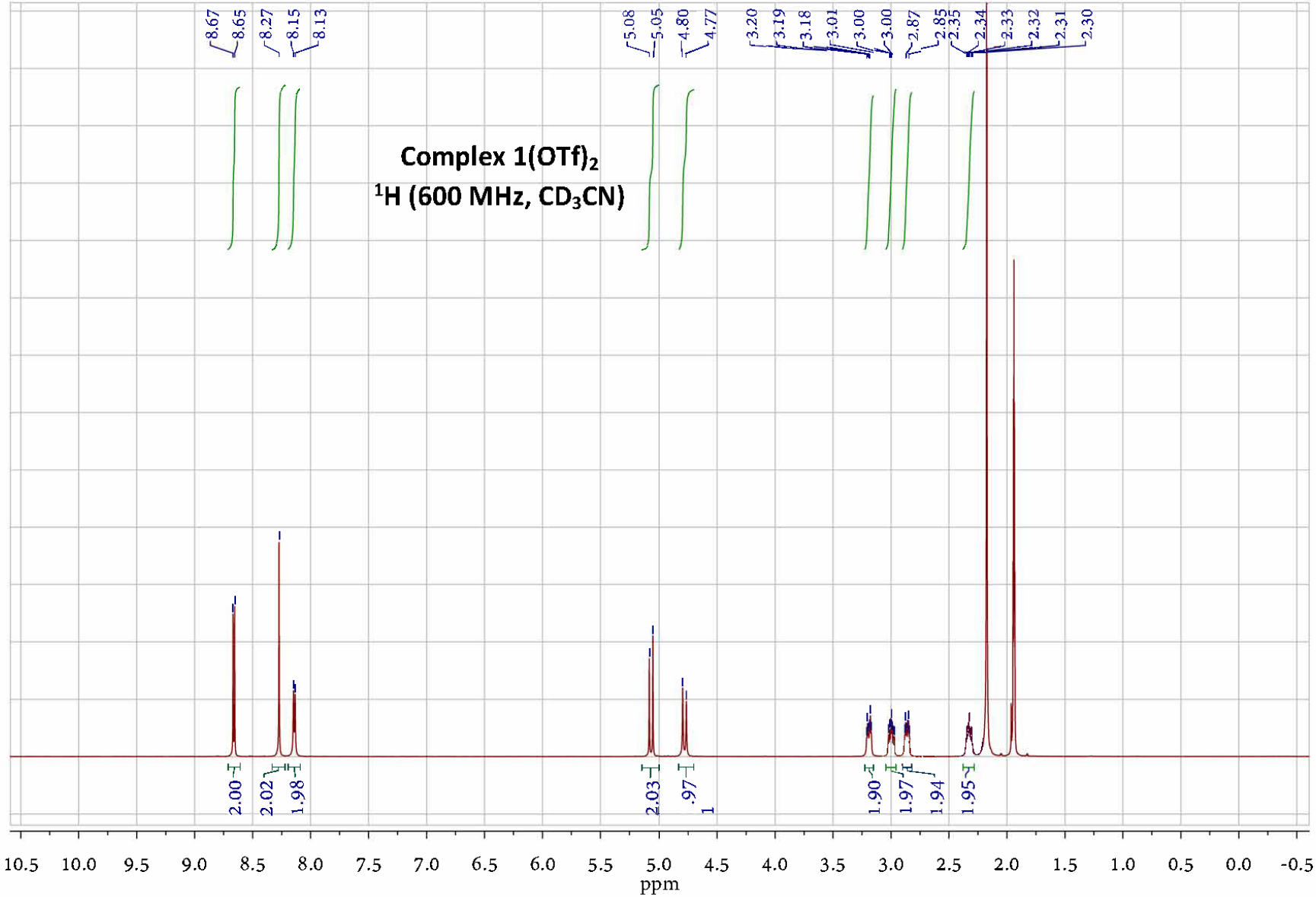


**Figure S3**. $^{1}H$ NMR of **1** in $CD_3CN$ at 298 K.

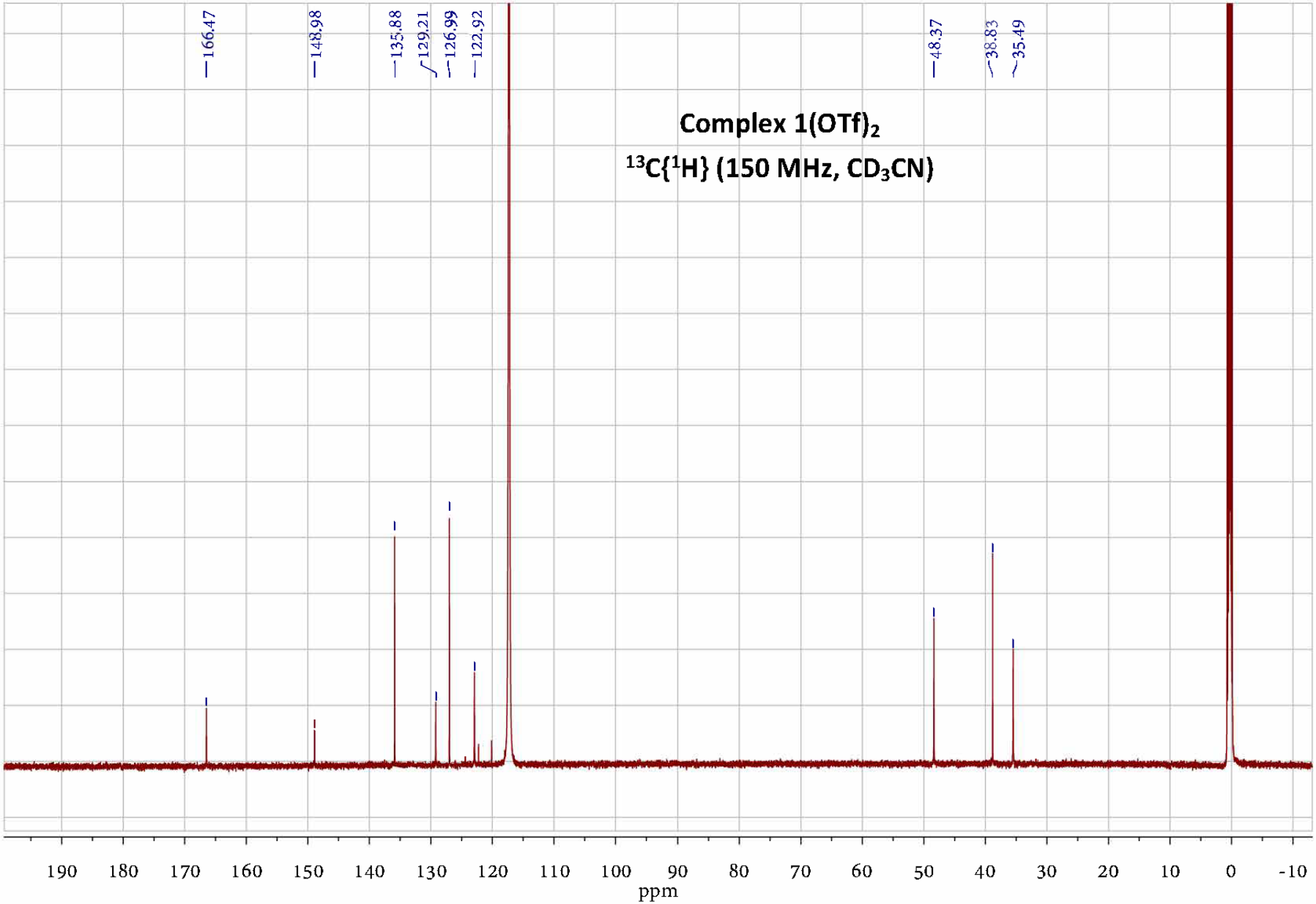


**Figure S4**. $^{13}C\{^{1}H\}$ NMR of **1** in $CD_3CN$ at 298 K.

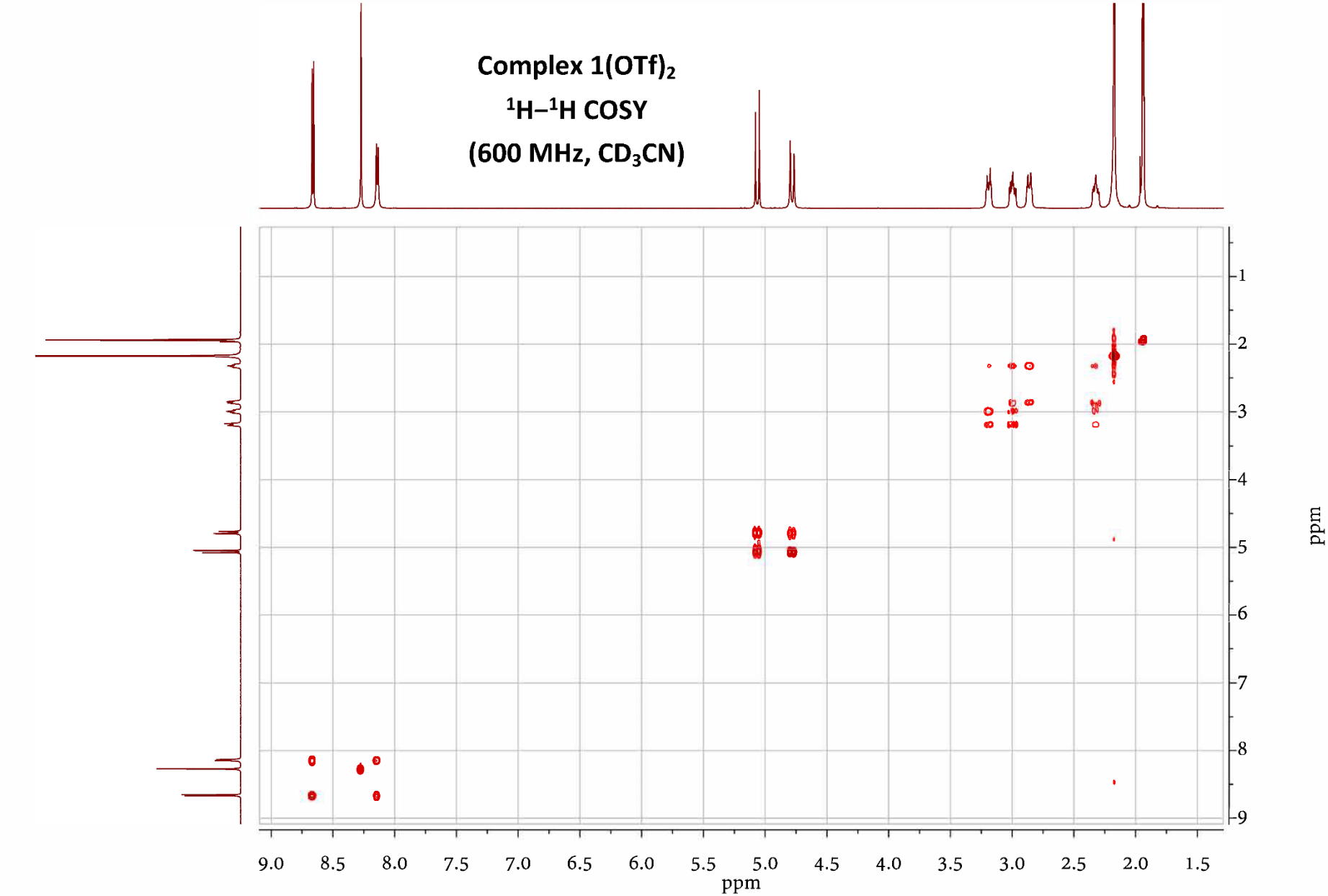


**Figure S5**. $^{1}H$-$^{1}H$ COSY NMR of **1** in $CD_3CN$ at 298 K.

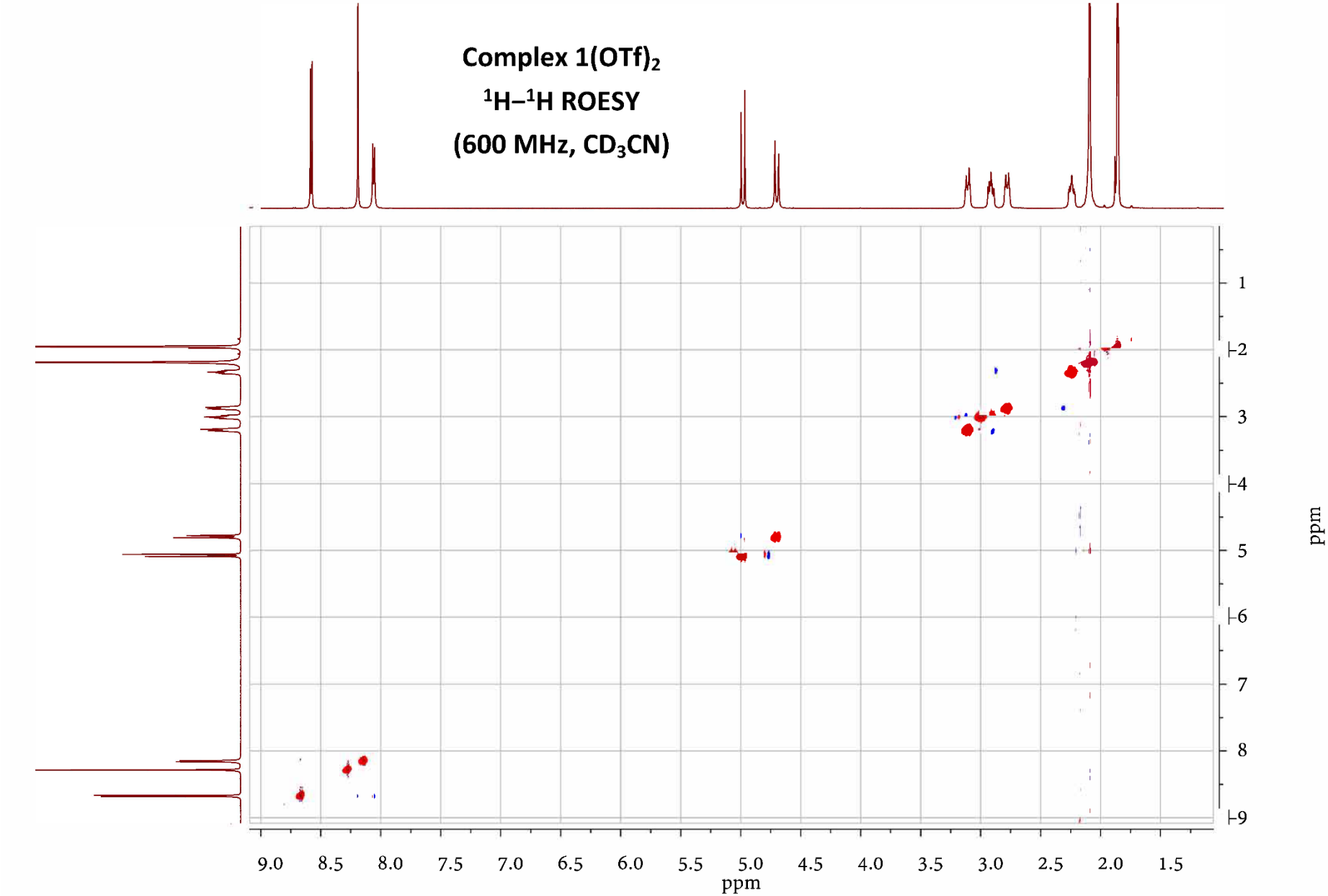


**Figure S6**. $^{1}$H-$^{1}$H ROESY NMR of **1** in $CD_3CN$ at 298 K.

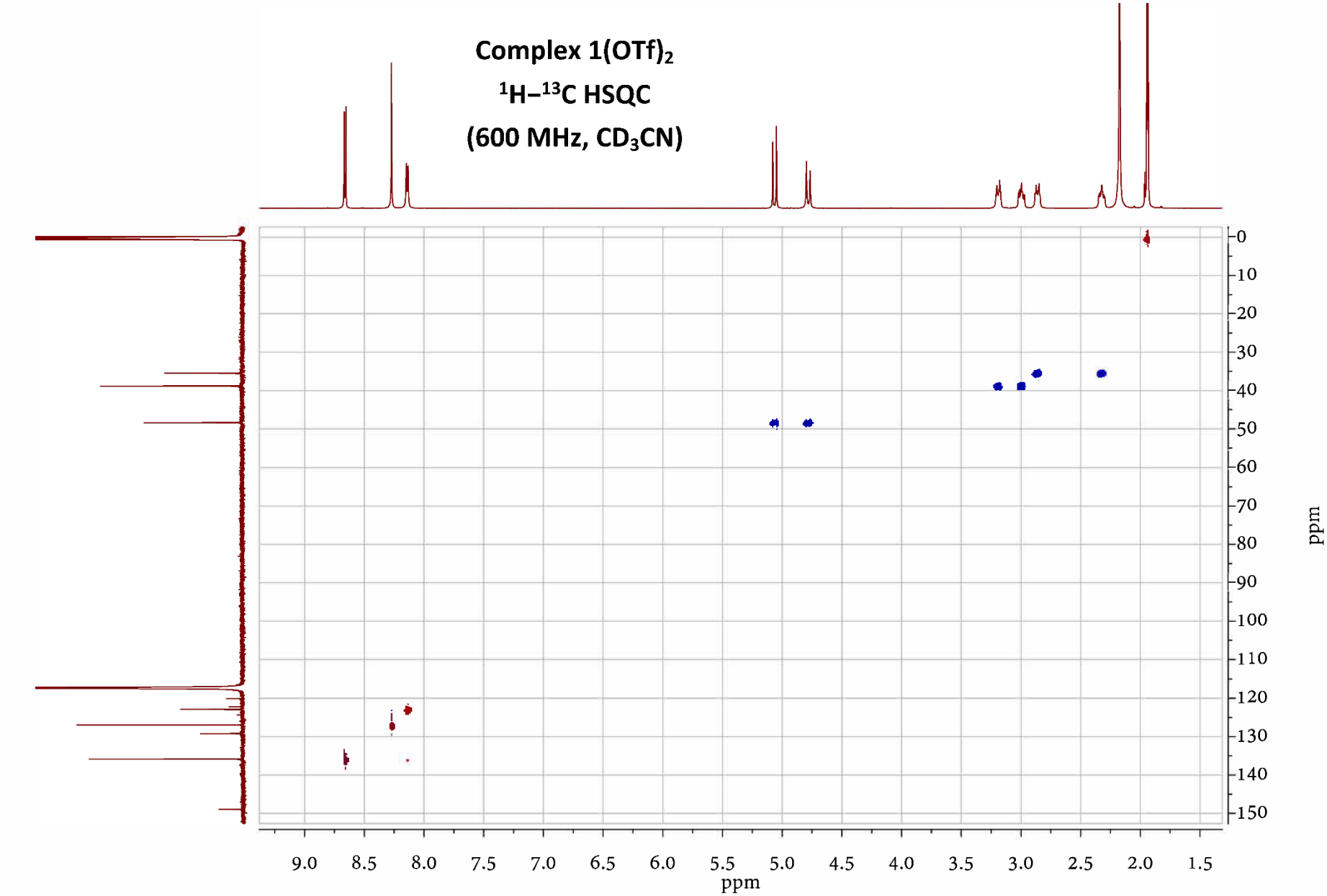


**Figure S7**. $^{1}H$-$^{13}C$ HSQC NMR of **1** in $CD_3CN$ at 298 K.

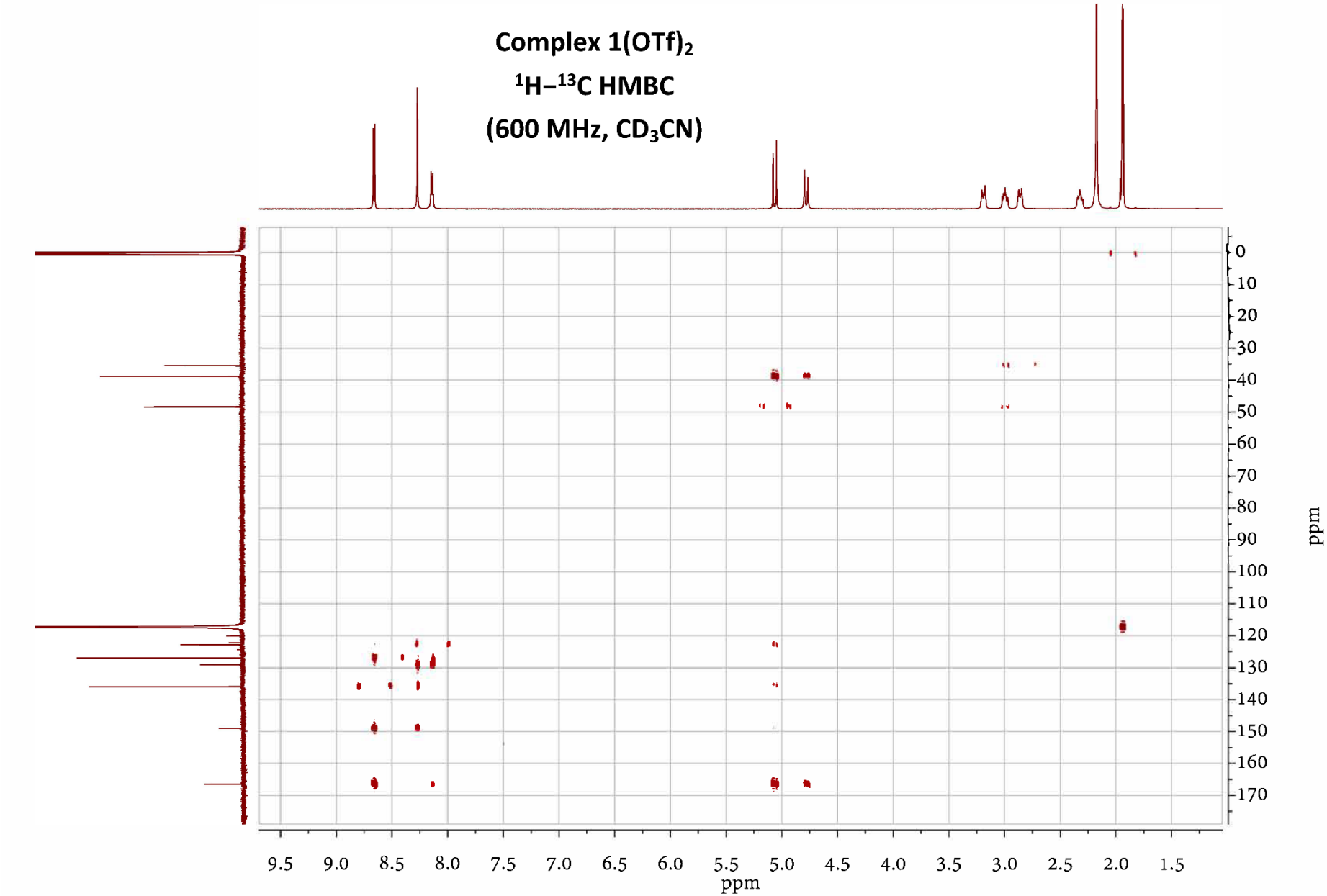


**Figure S8**. $^{1}H$-$^{13}C$ HMBC NMR of **1** in $CD_3CN$ at 298 K.

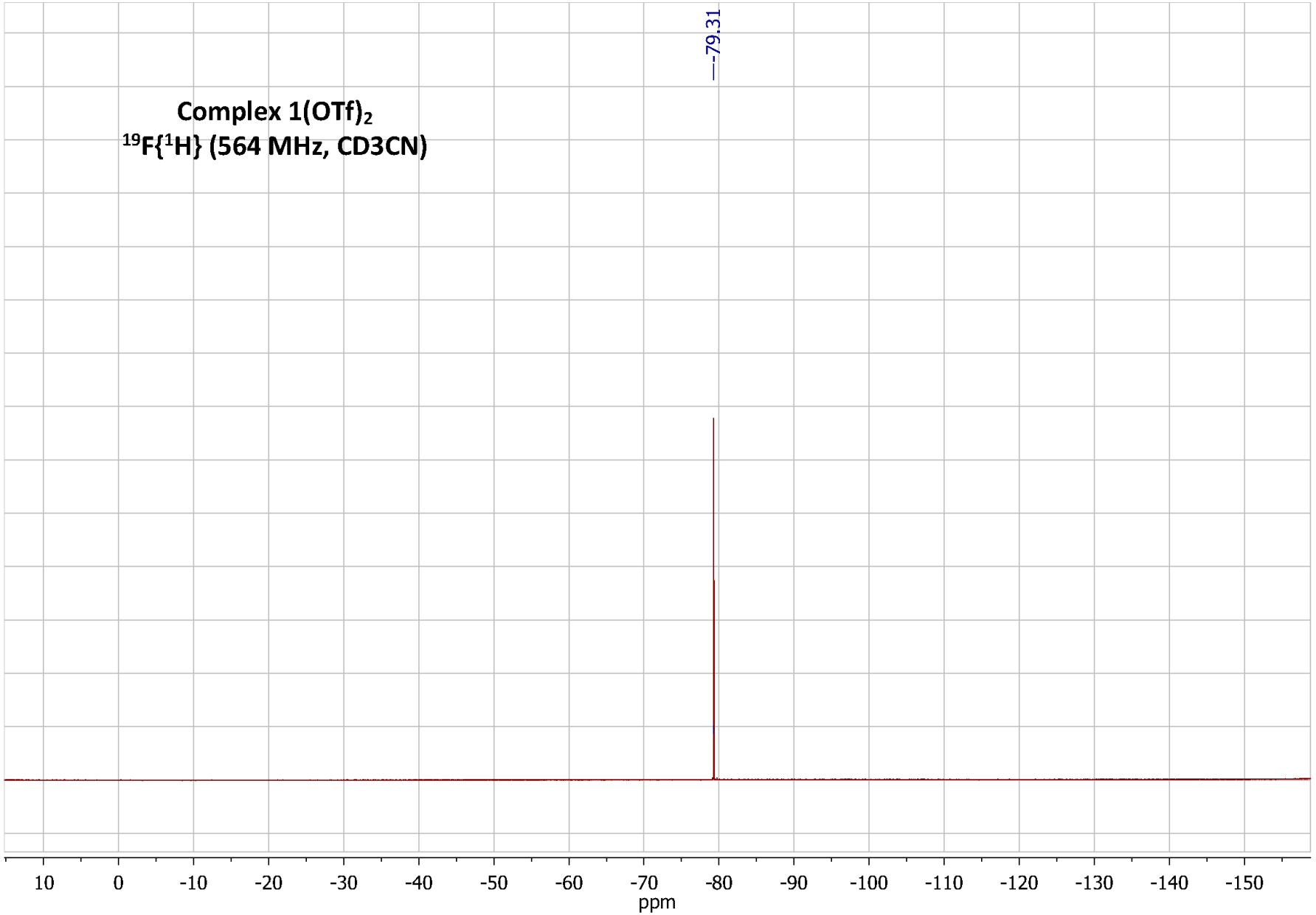


**Figure S9**. $^{19}F\{^{1}H\}$ NMR of **1** in $CD_3CN$ at 298 K.

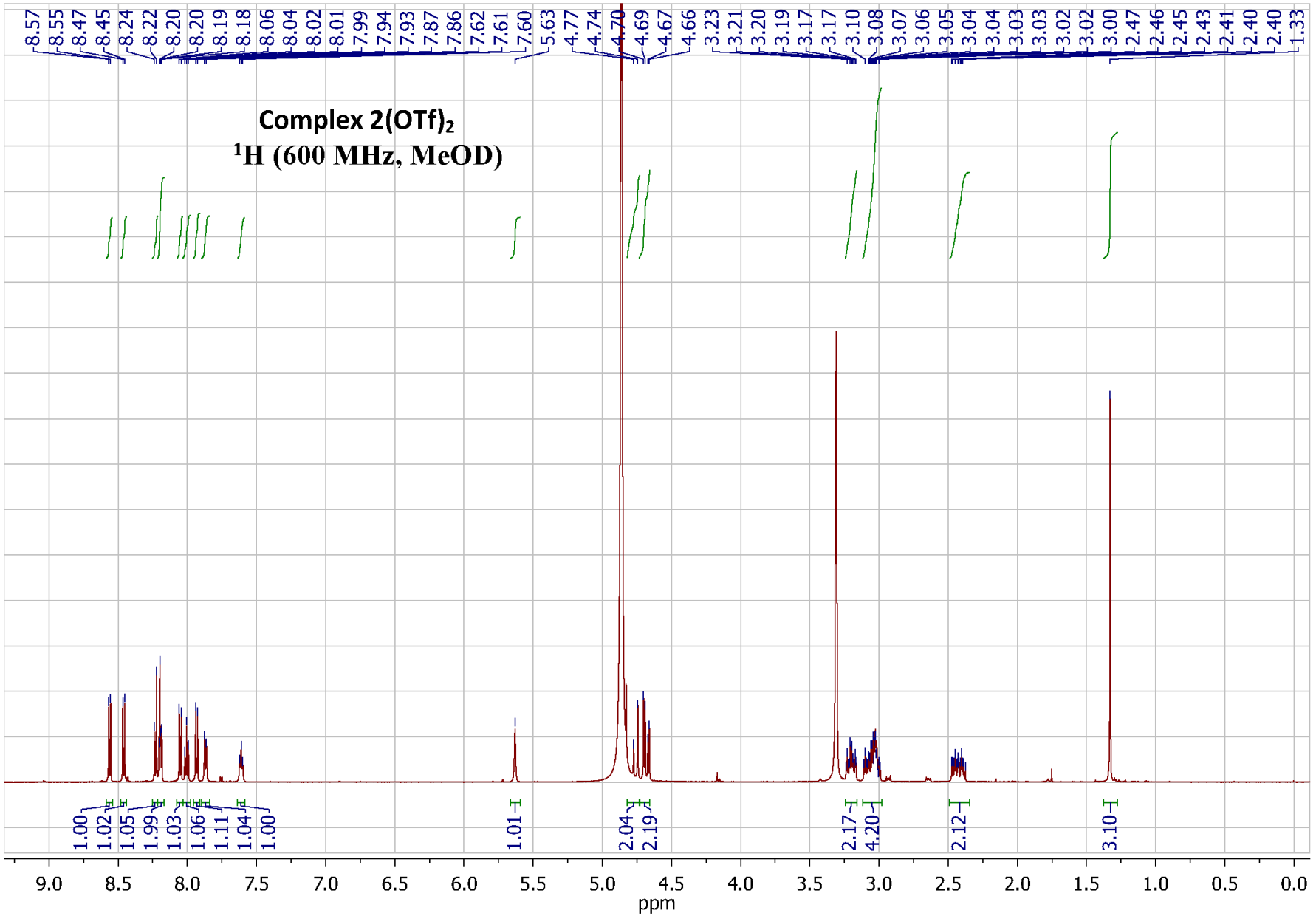


**Figure S10**. $^{1}H$ NMR of **2** in $CD_3OD$ at 298 K.

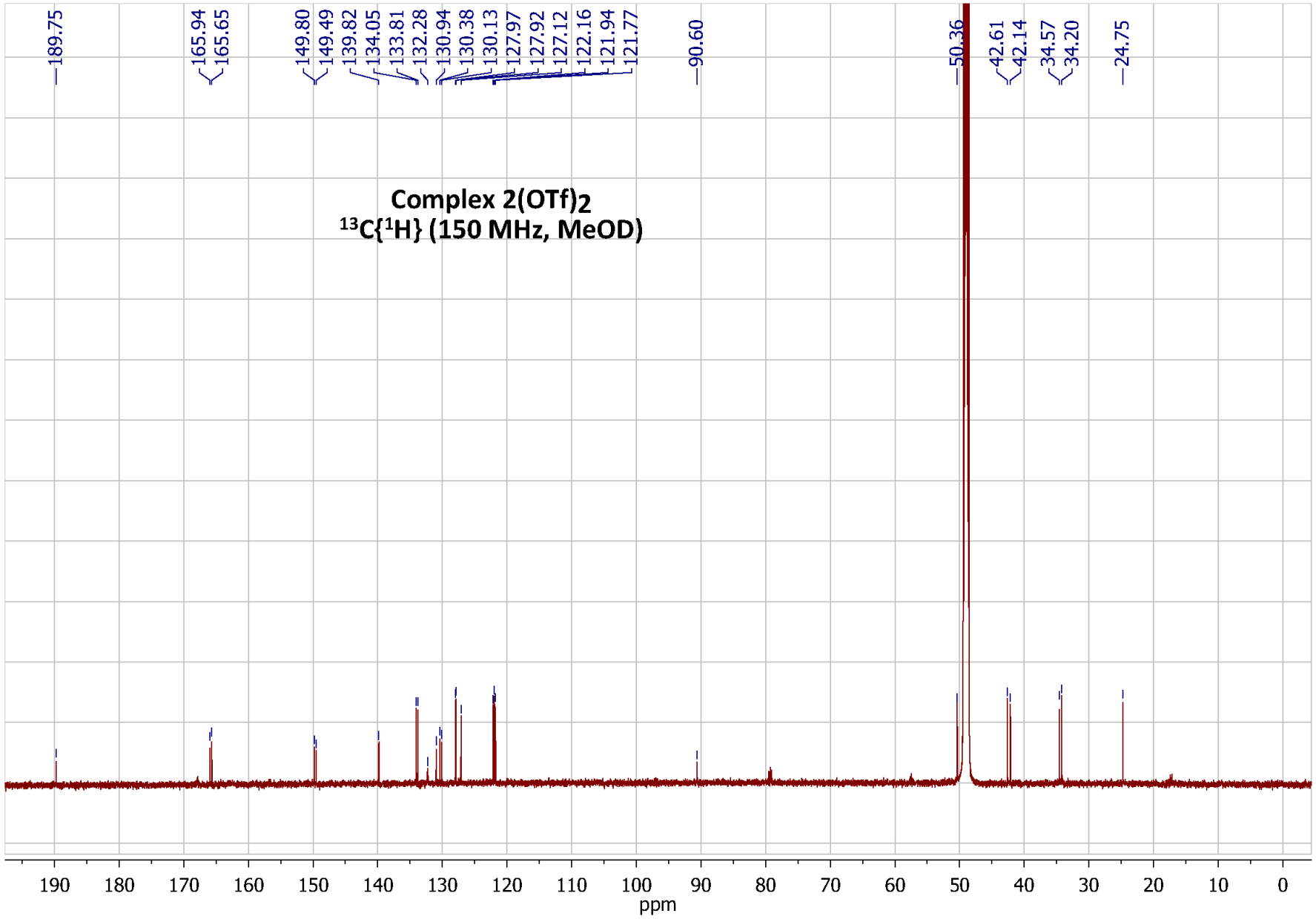


**Figure S11**. $^{13}C\{^{1}H\}$ NMR of **2** in $CD_3OD$ at 298 K.

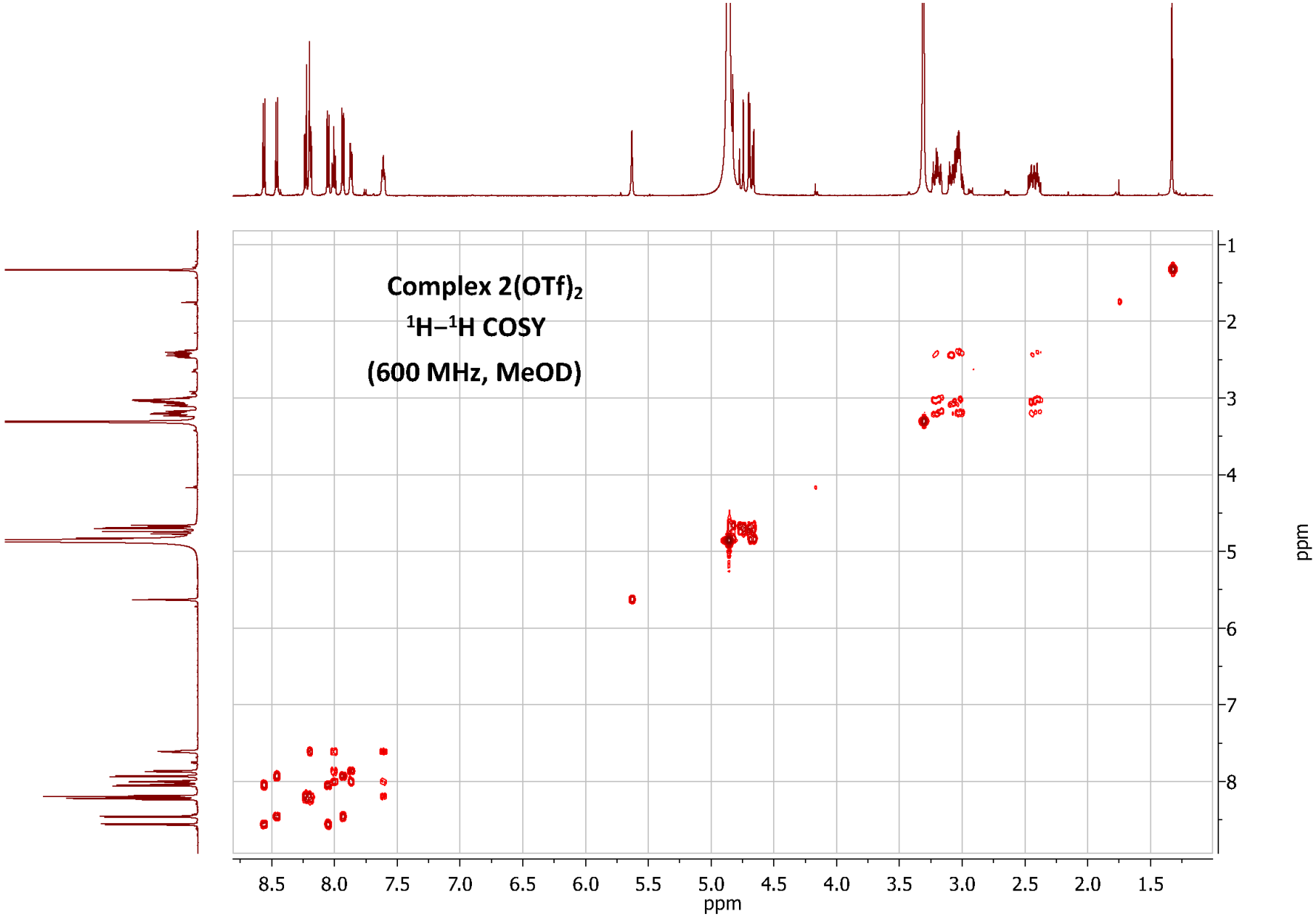


**Figure S12**. $^{1}$H-$^{1}$H COSY NMR of **2** in $CD_3OD$ at 298 K.

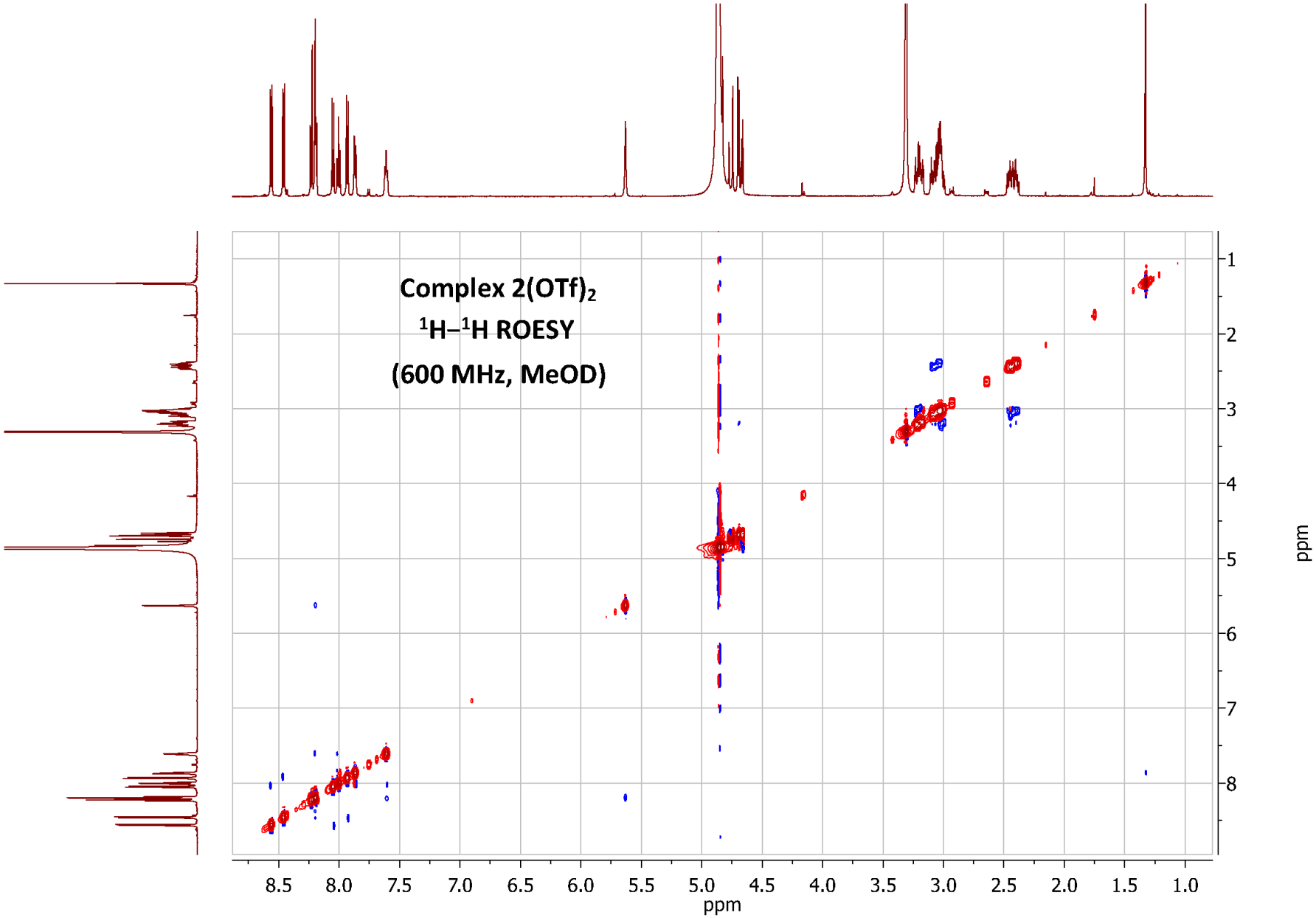


**Figure S13**. $^{1}$H-$^{1}$H ROESY NMR of **2** in $CD_3OD$ at 298 K.

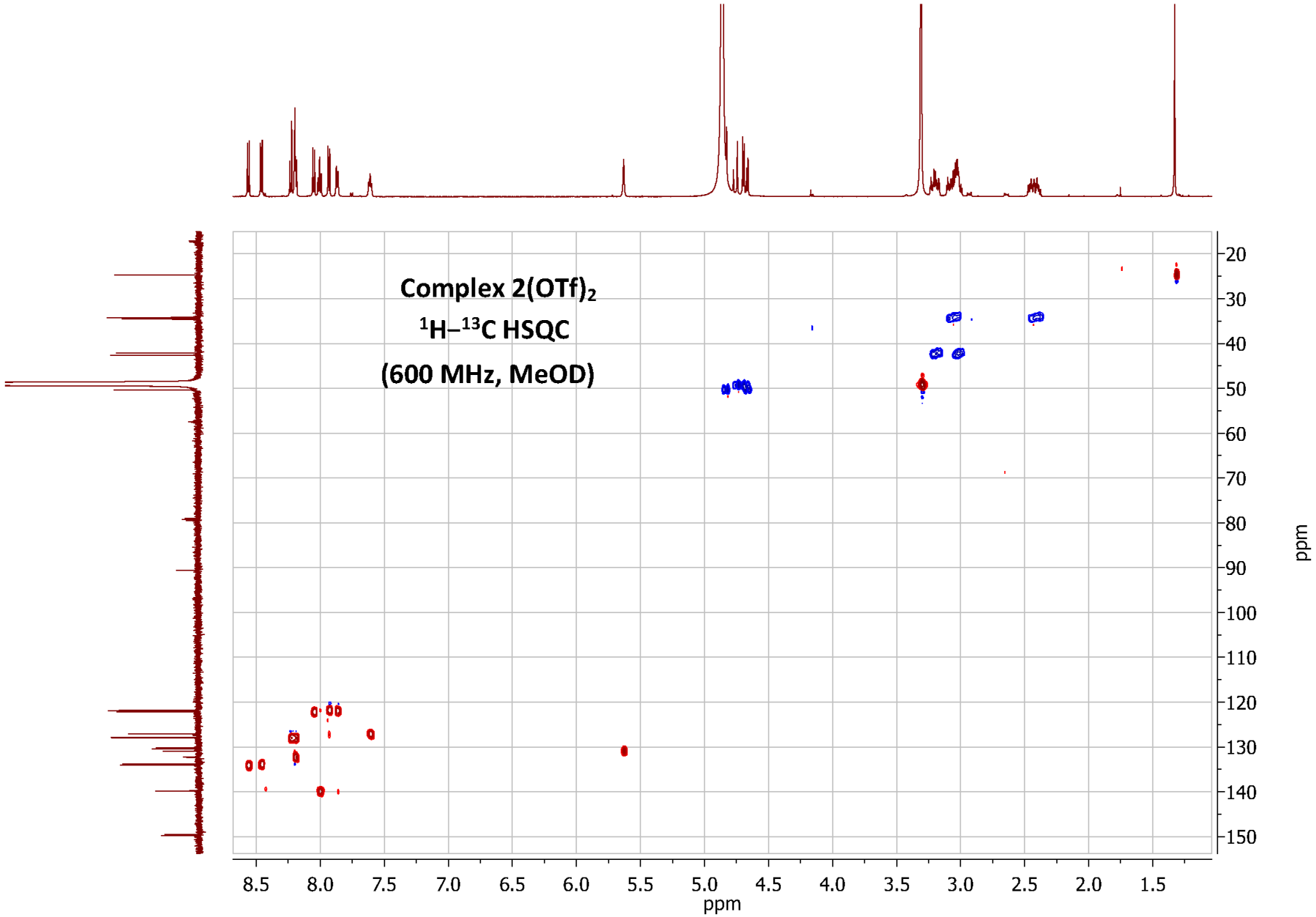


**Figure S14**. $^{1}H$-$^{13}C$ HSQC NMR of **2** in $CD_3OD$ at 298 K.

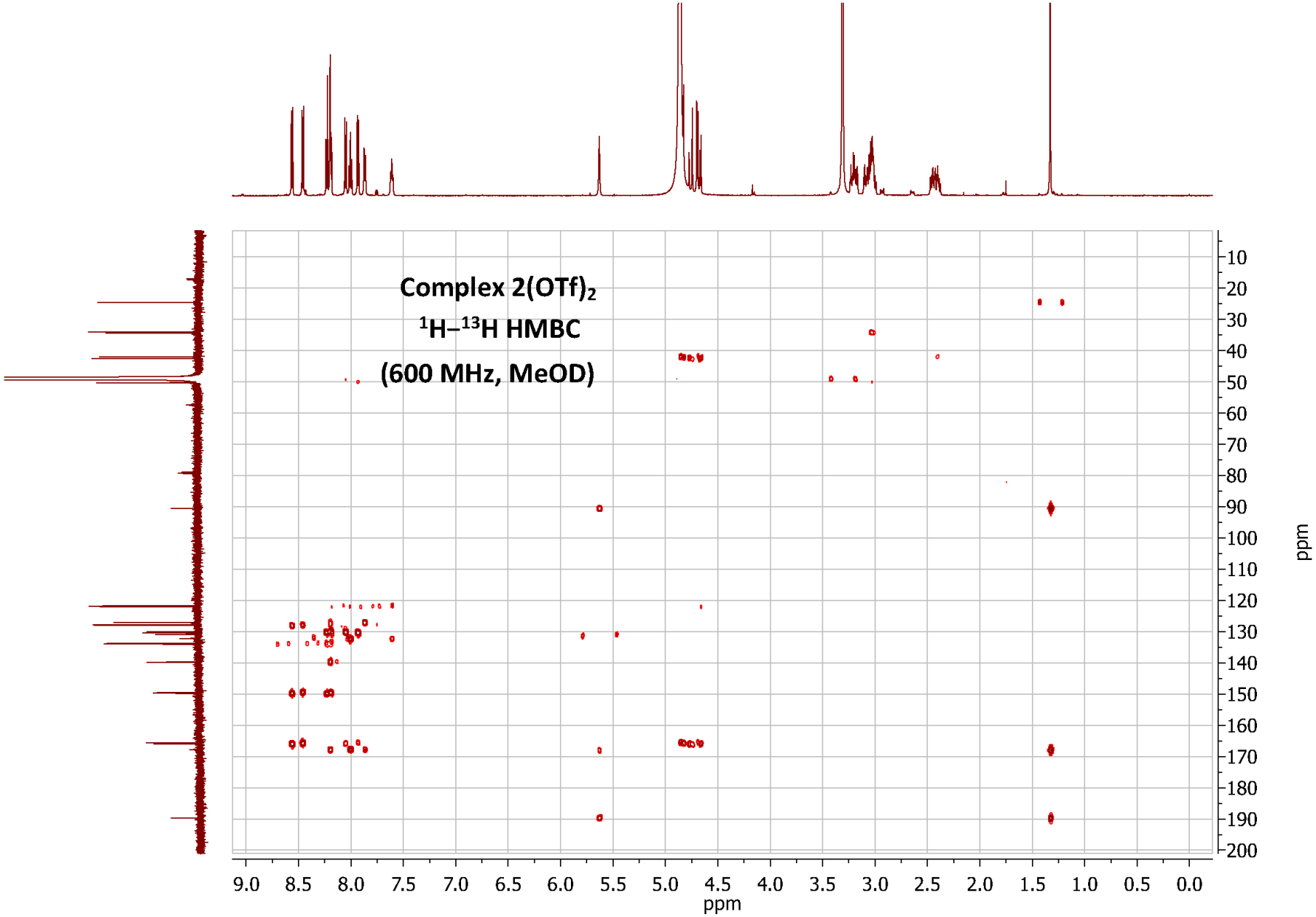


**Figure S15**. $^{1}H$-$^{13}C$ HMBC NMR of **2** in $CD_3OD$ at 298 K.

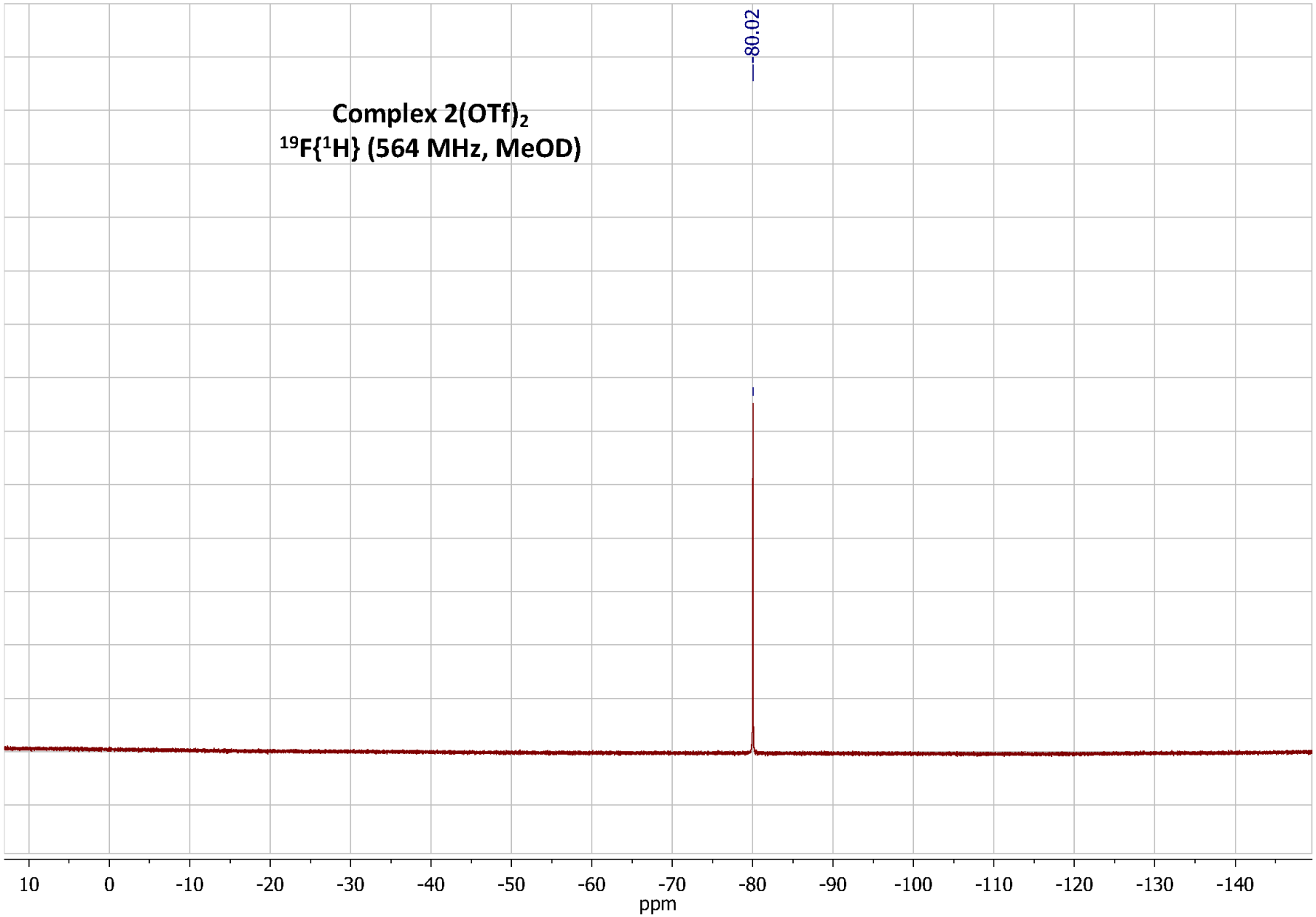


**Figure S16**. $^{19}F\{^{1}H\}$ NMR of **2** in $CD_3OD$ at 298 K.

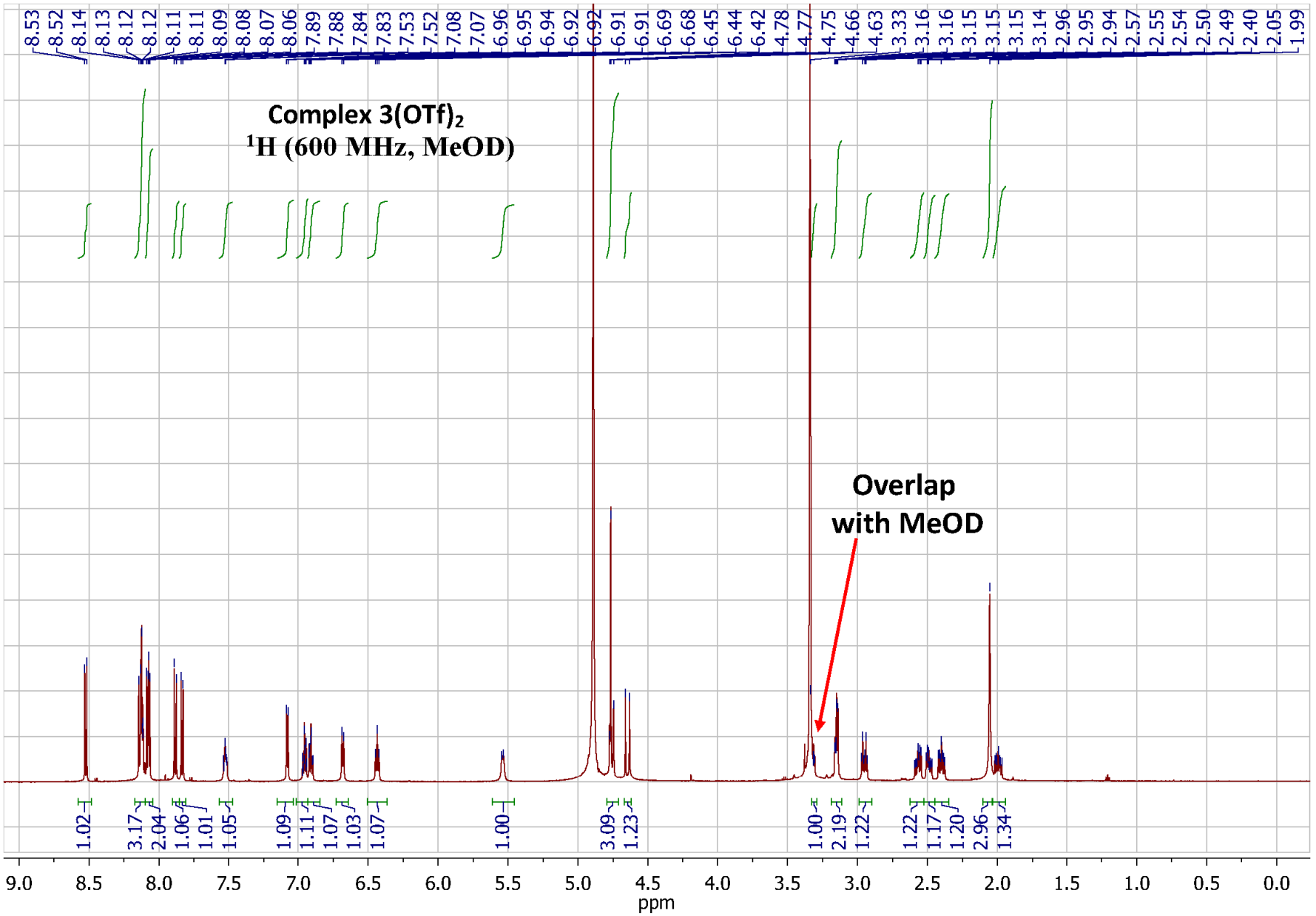


**Figure S17**. $^{1}H$ NMR of **3** in $CD_3OD$ at 298 K.

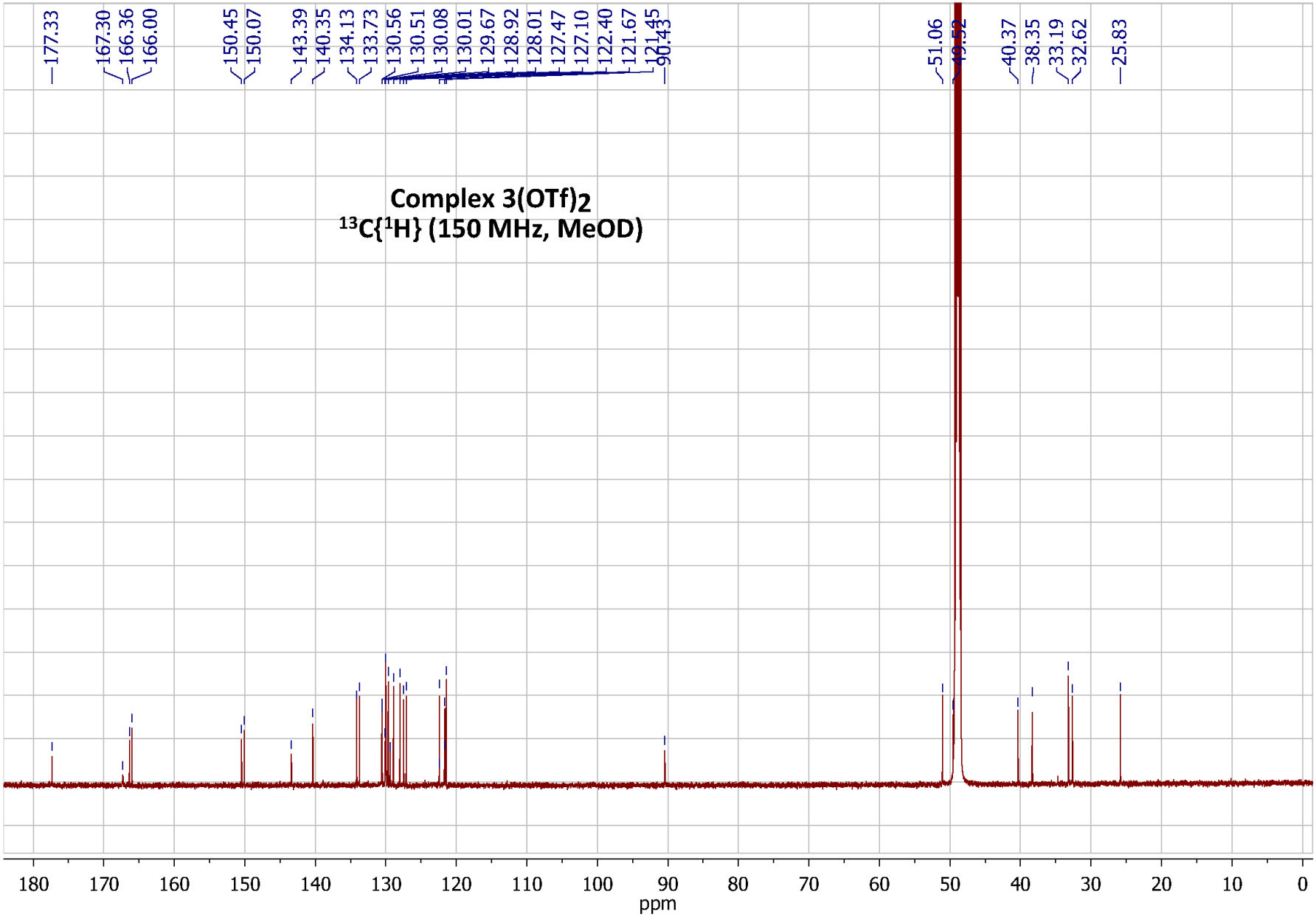


**Figure S18**. $^{13}C\{^{1}H\}$ NMR of **3** in $CD_3OD$ at 298 K.

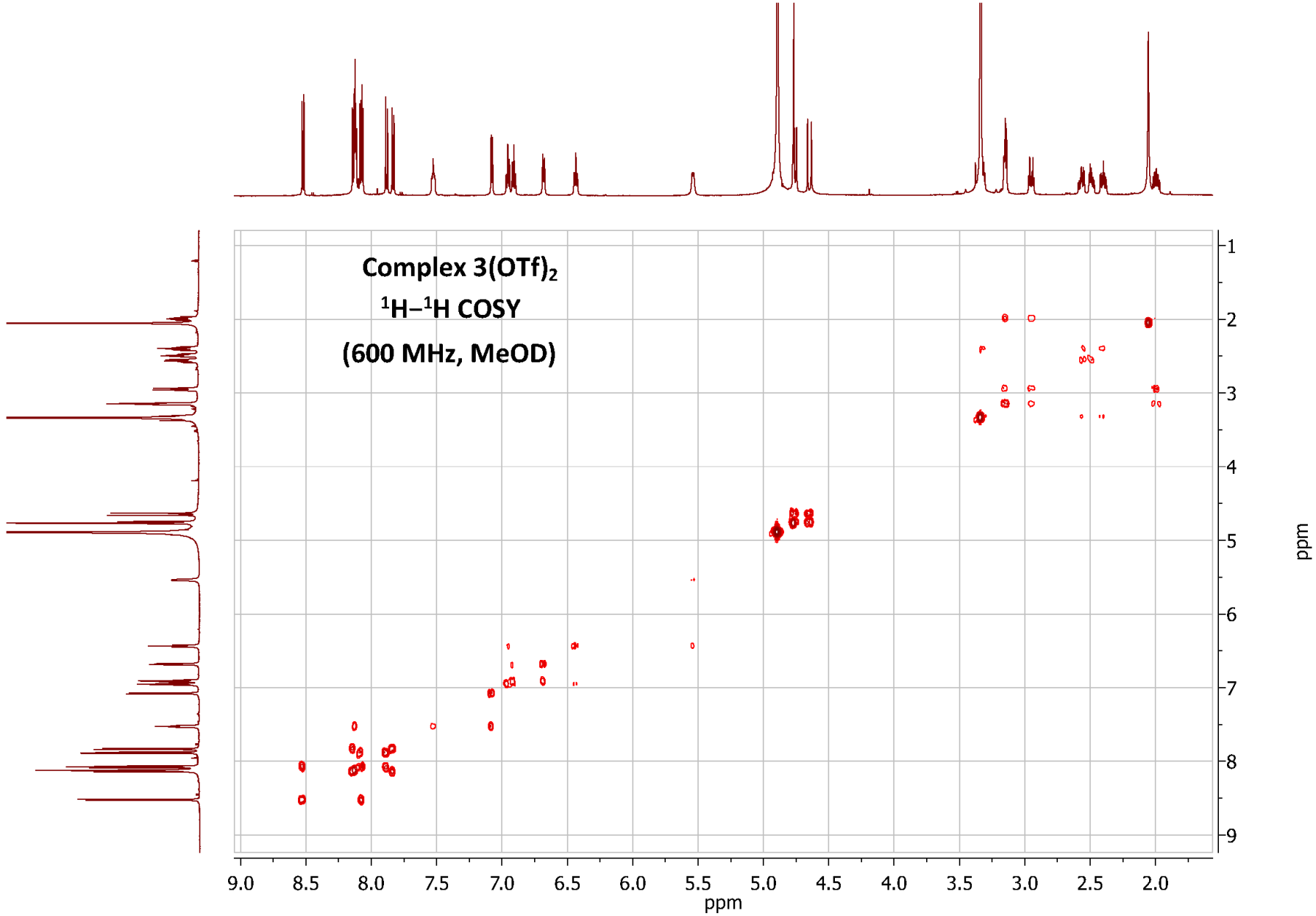


**Figure S19**. $^{1}$H-$^{1}$H COSY NMR of **3** in $CD_3OD$ at 298 K.

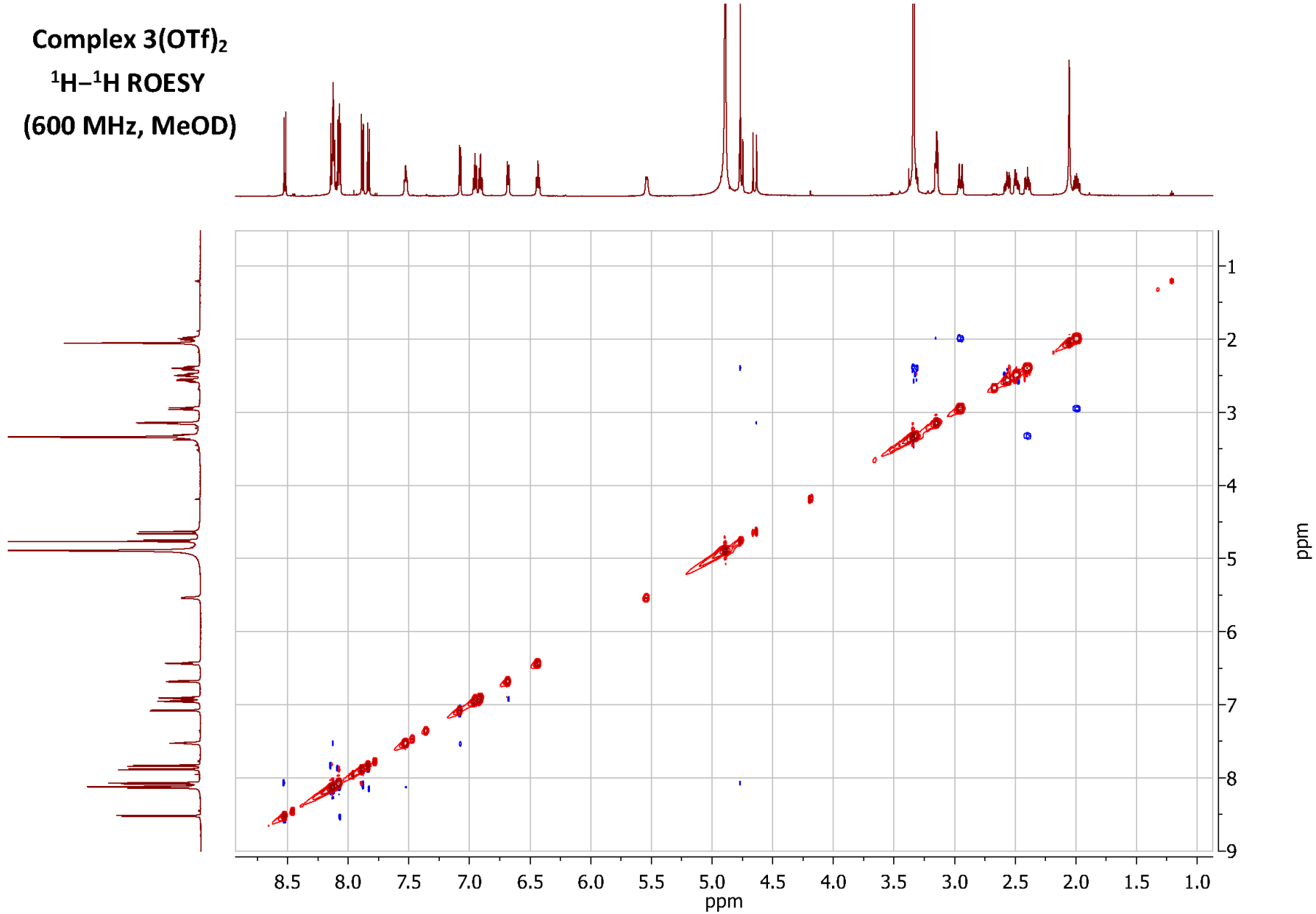


**Figure S20**. $^{1}$H-$^{1}$H ROESY NMR of **3** in $CD_3OD$ at 298 K.

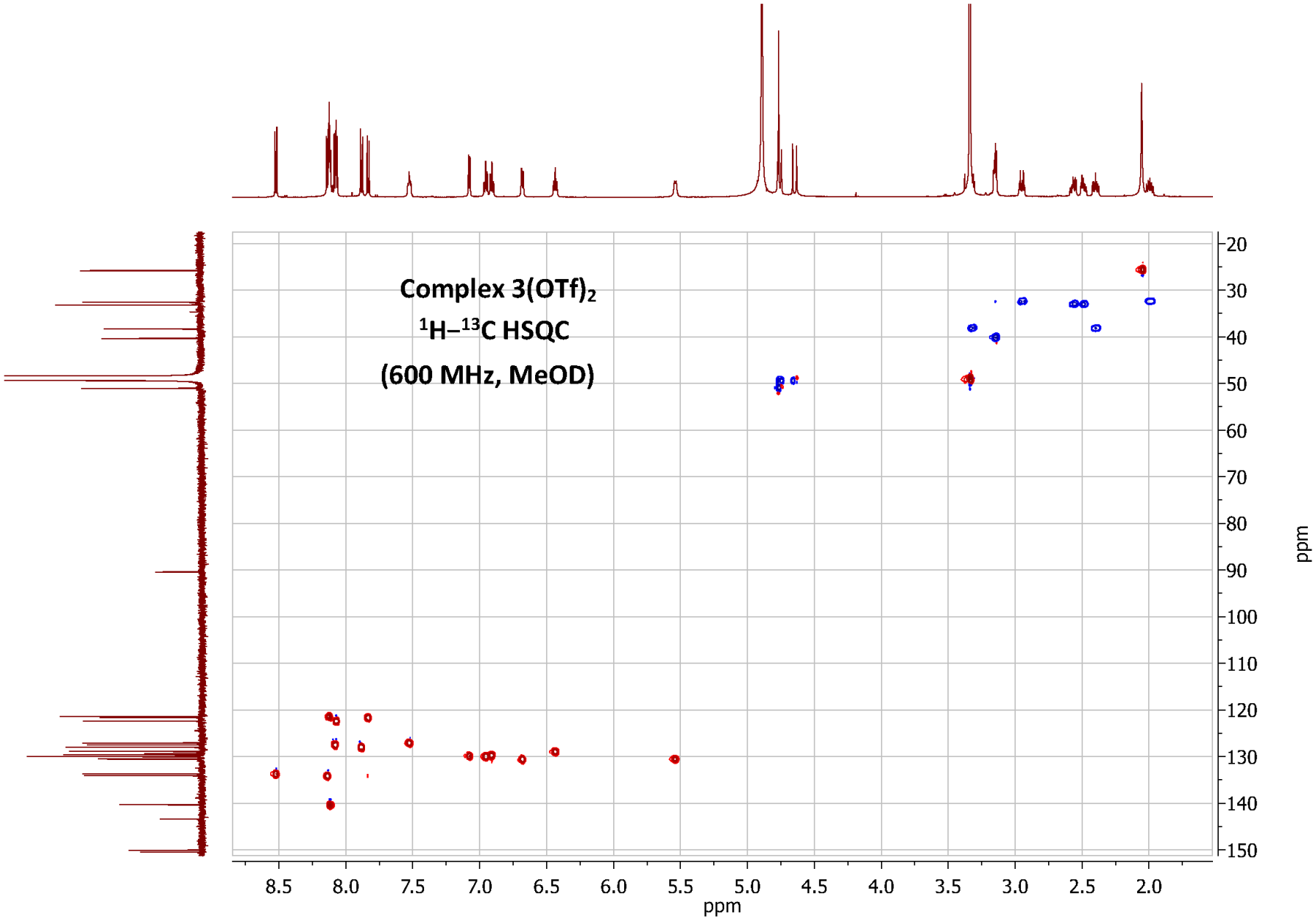


**Figure S21**. $^{1}H$-$^{13}C$ HSQC NMR of **3** in $CD_3OD$ at 298 K.

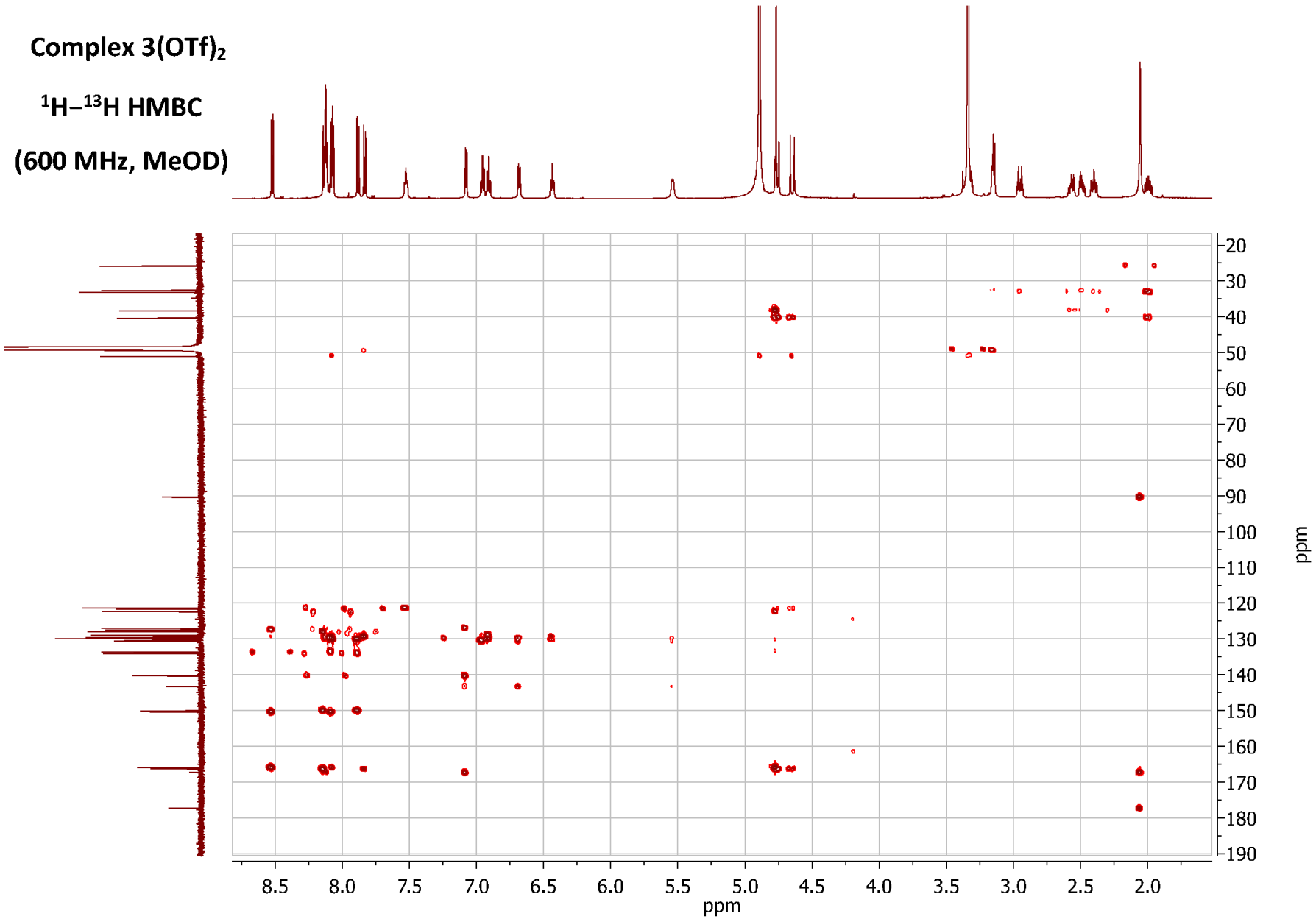


**Figure S22**. $^{1}H$-$^{13}C$ HMBC NMR of **3** in $CD_3OD$ at 298 K.

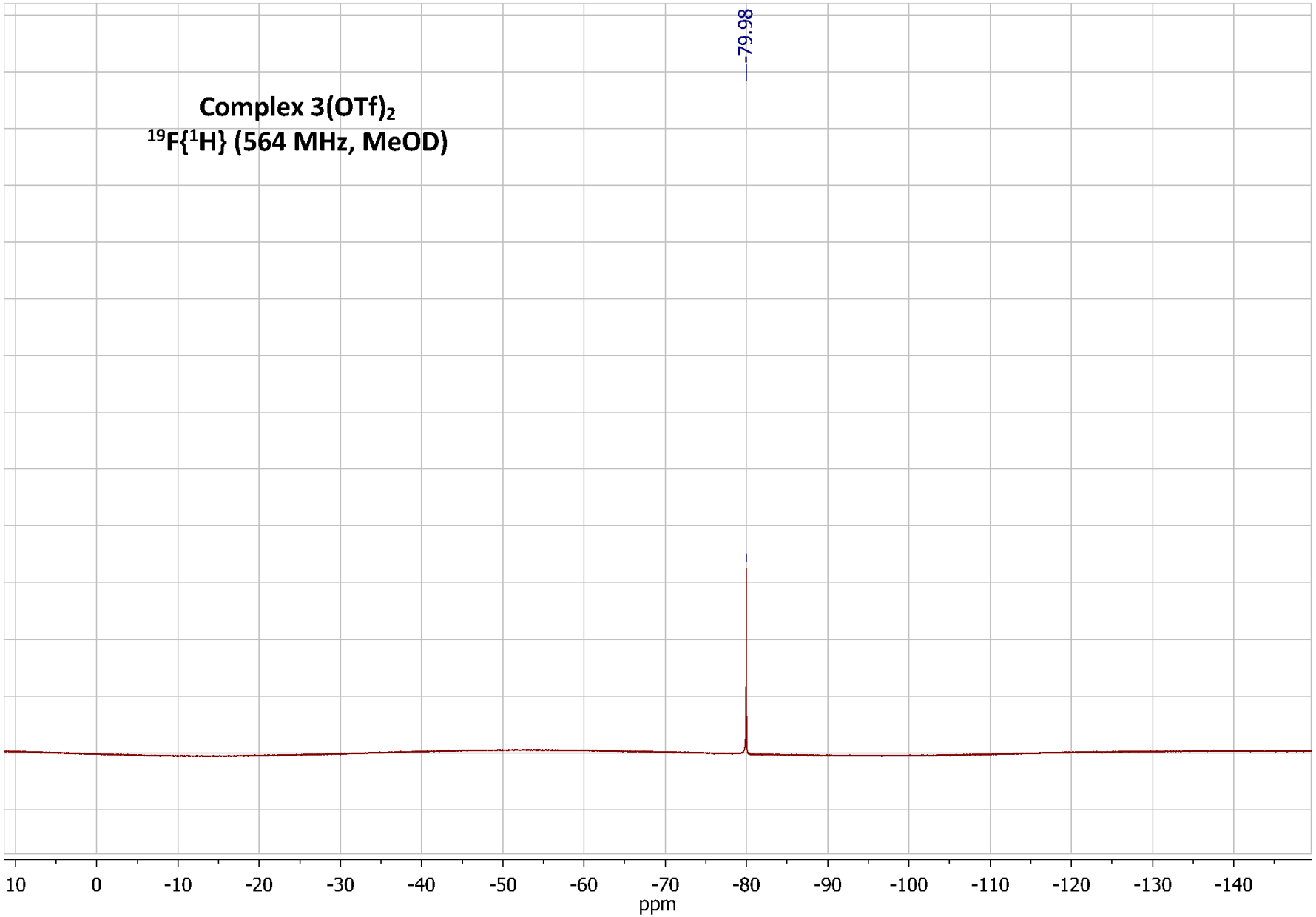


**Figure S23**. $^{19}F\{^{1}H\}$ NMR of **3** in $CD_3OD$ at 298 K.

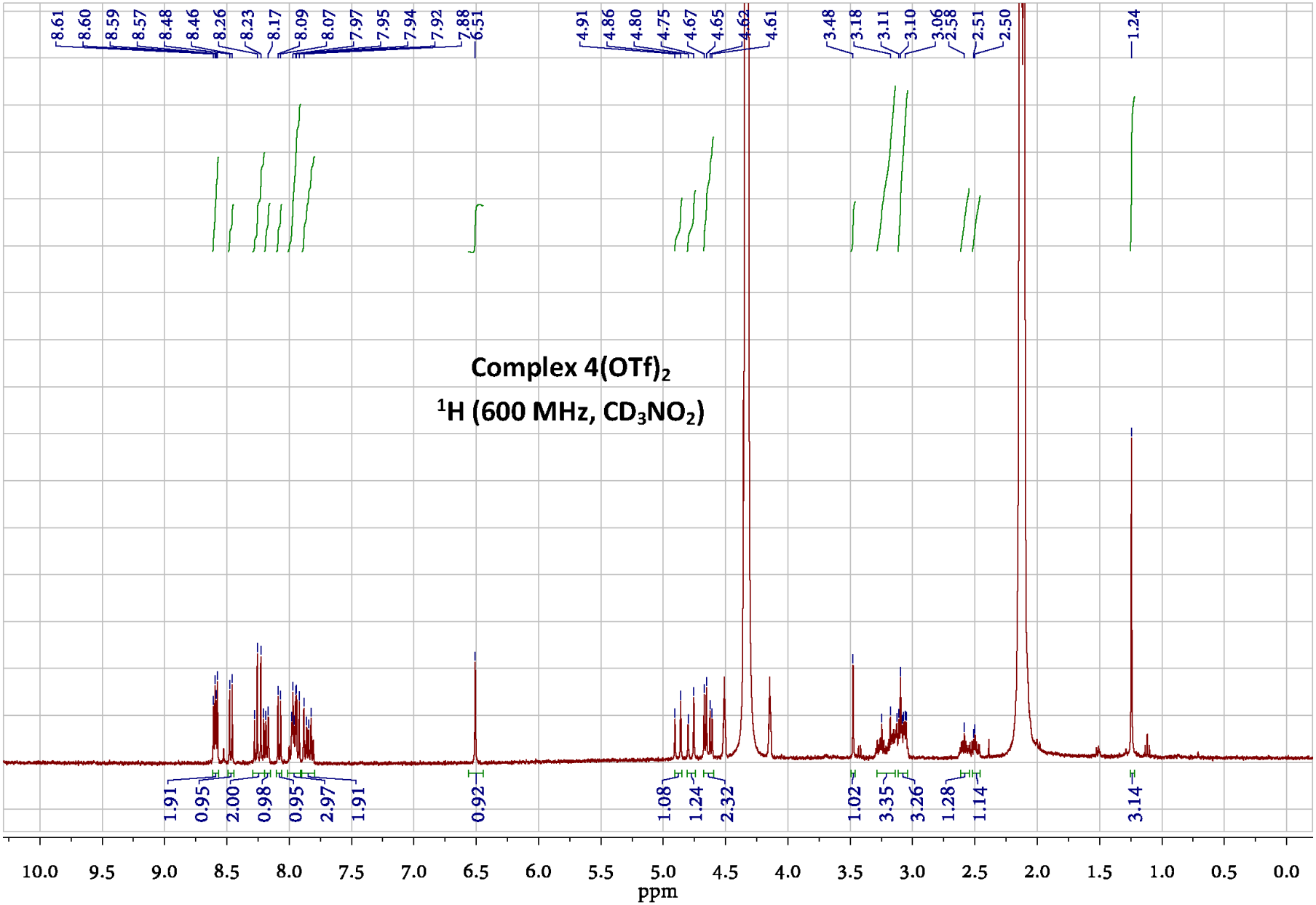


**Figure S24**. $^{1}H$ NMR of **4** in $CD_3NO_2$ at 298 K.

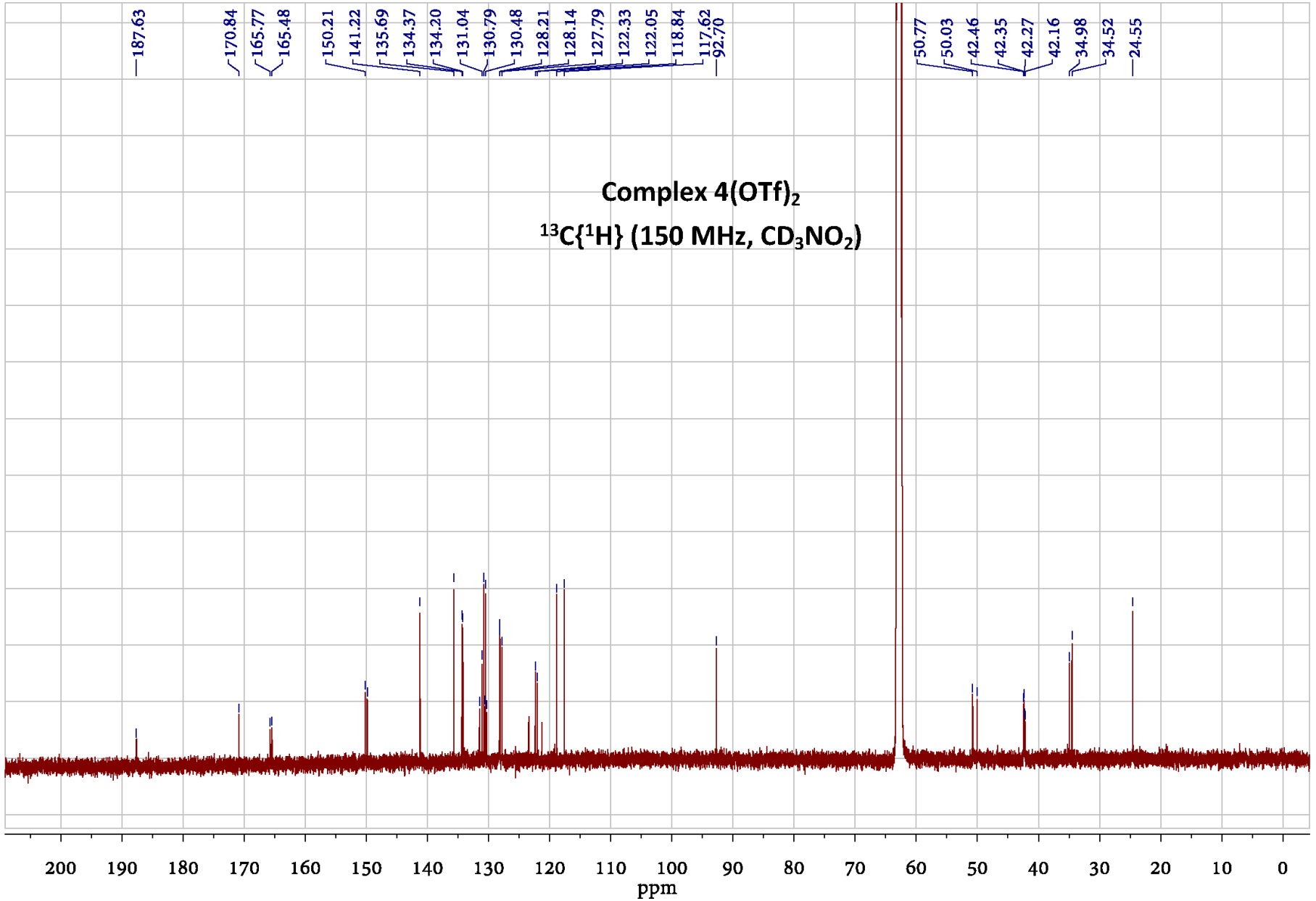


**Figure S25**. $^{13}C\{^{1}H\}$ NMR of **4** in $CD_3NO_2$ at 298 K.

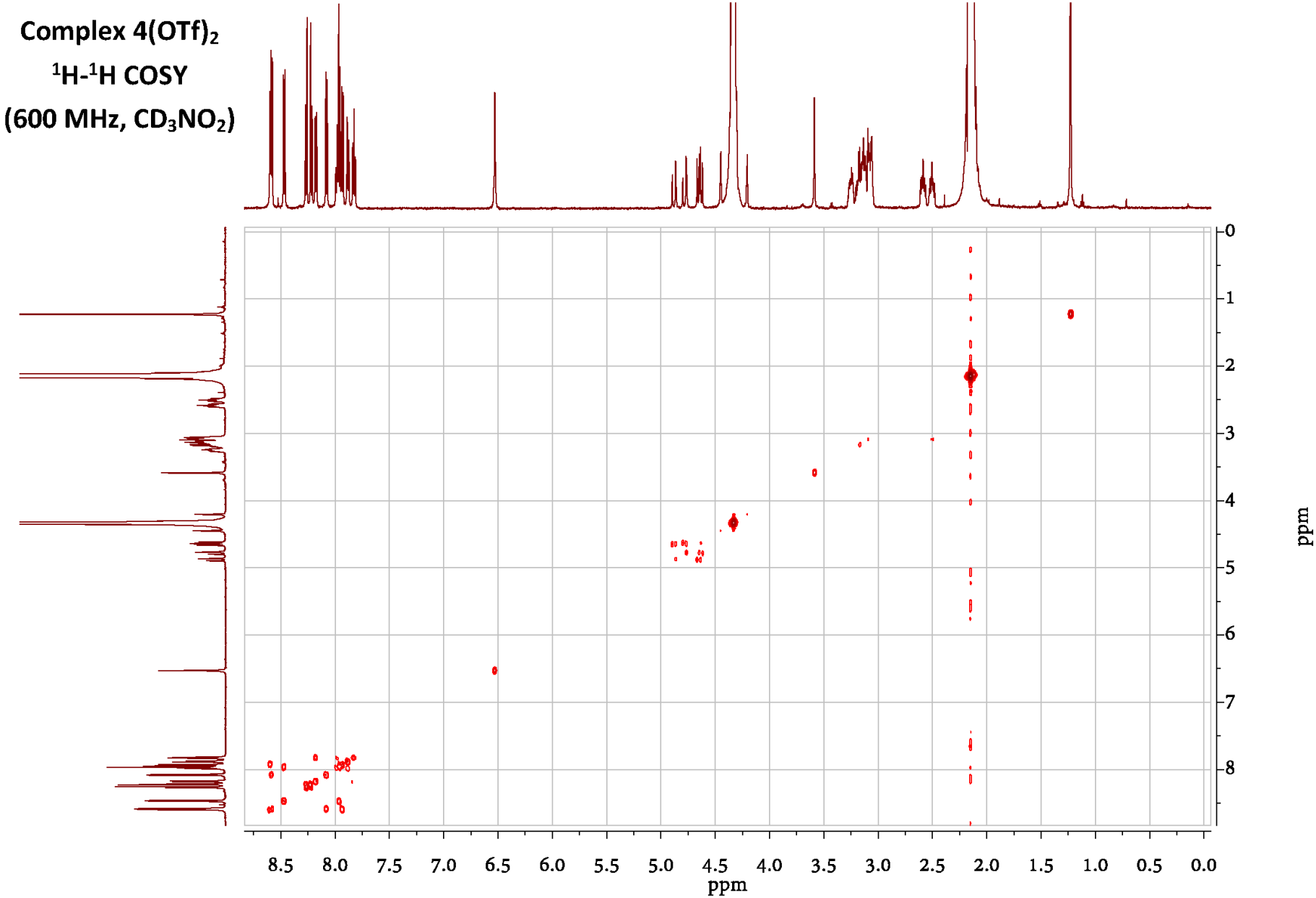


**Figure S26**. $^{1}H$-$^{1}H$ COSY NMR of **4** in $CD_3NO_2$ at 298 K.

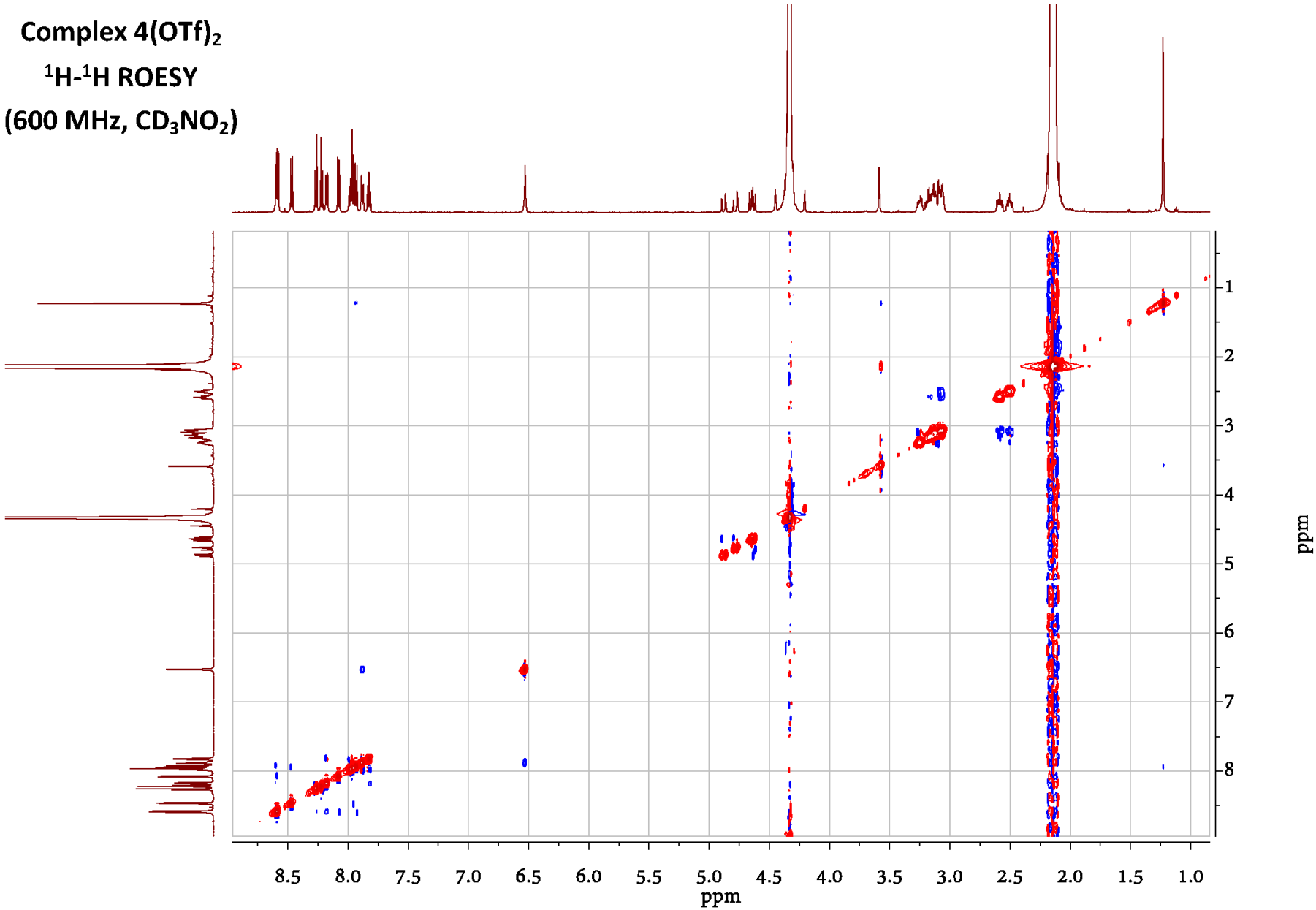


**Figure S27**. $^{1}$H-$^{1}$H ROESY NMR of **4** in $CD_3NO_2$ at 298 K.

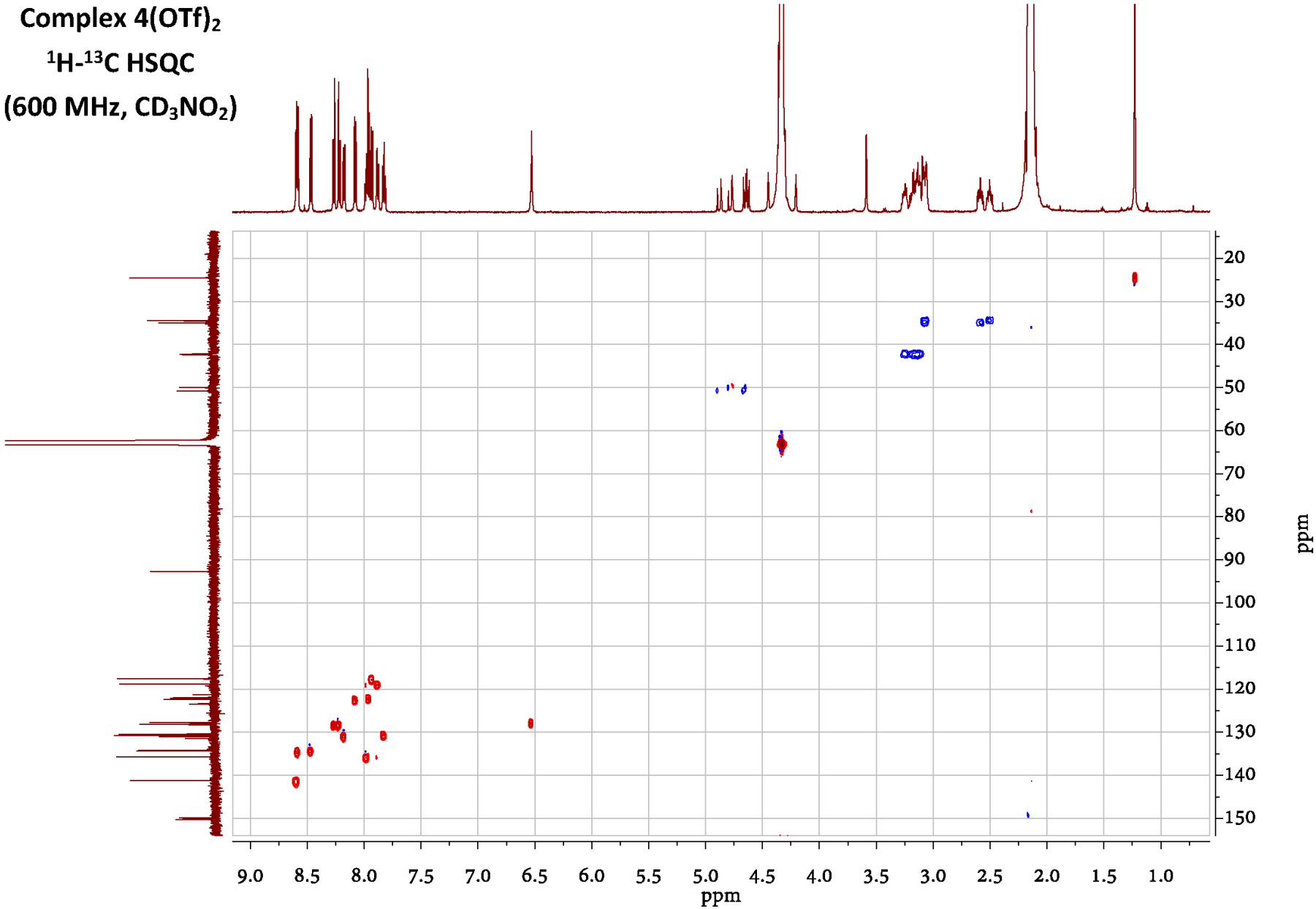


**Figure S28**. $^{1}H$-$^{13}C$ HSQC NMR of **4** in $CD_3NO_2$ at 298 K.

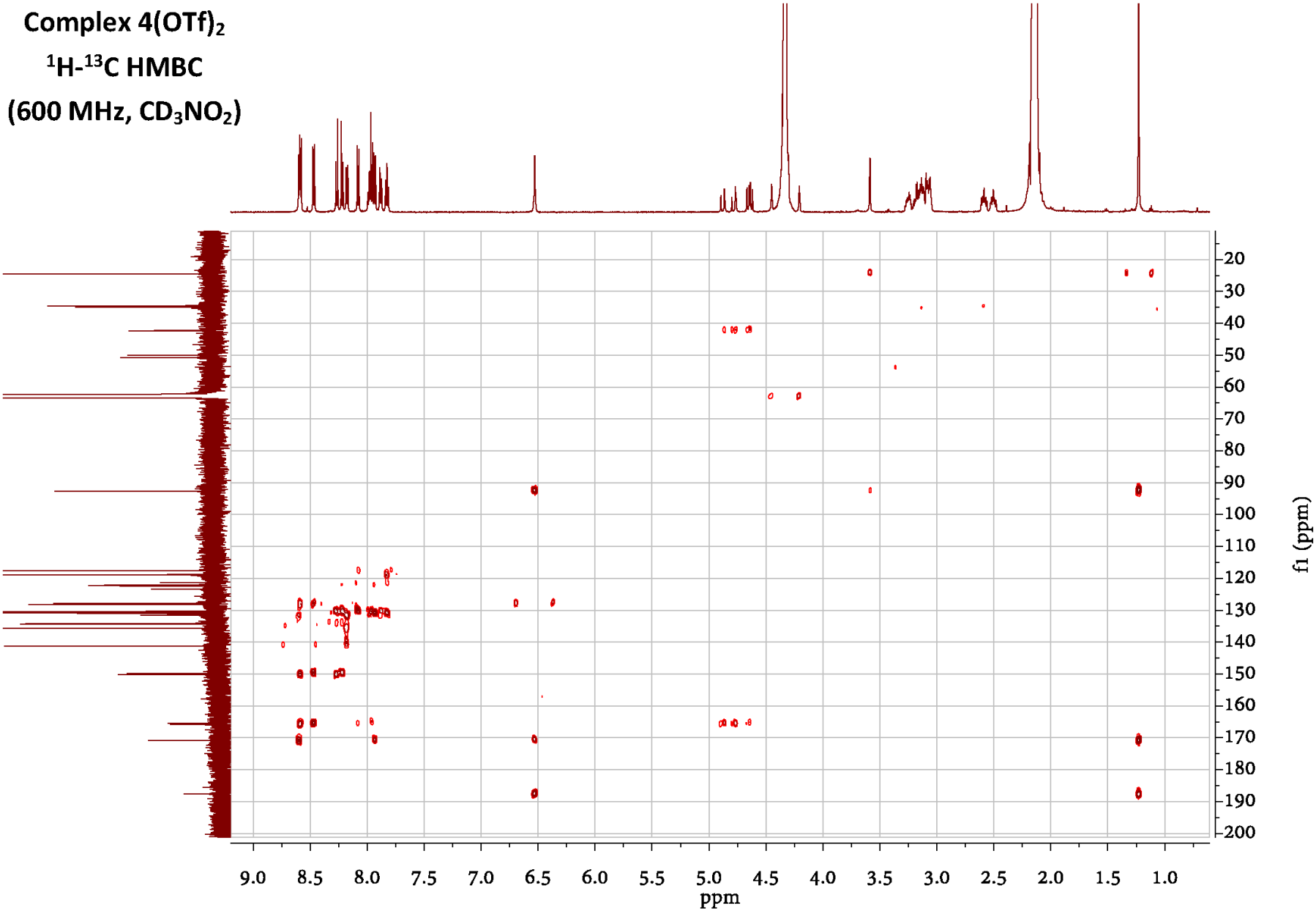


**Figure S29**. $^{1}H$-$^{13}C$ HMBC NMR of **4** in $CD_3NO_2$ at 298 K.

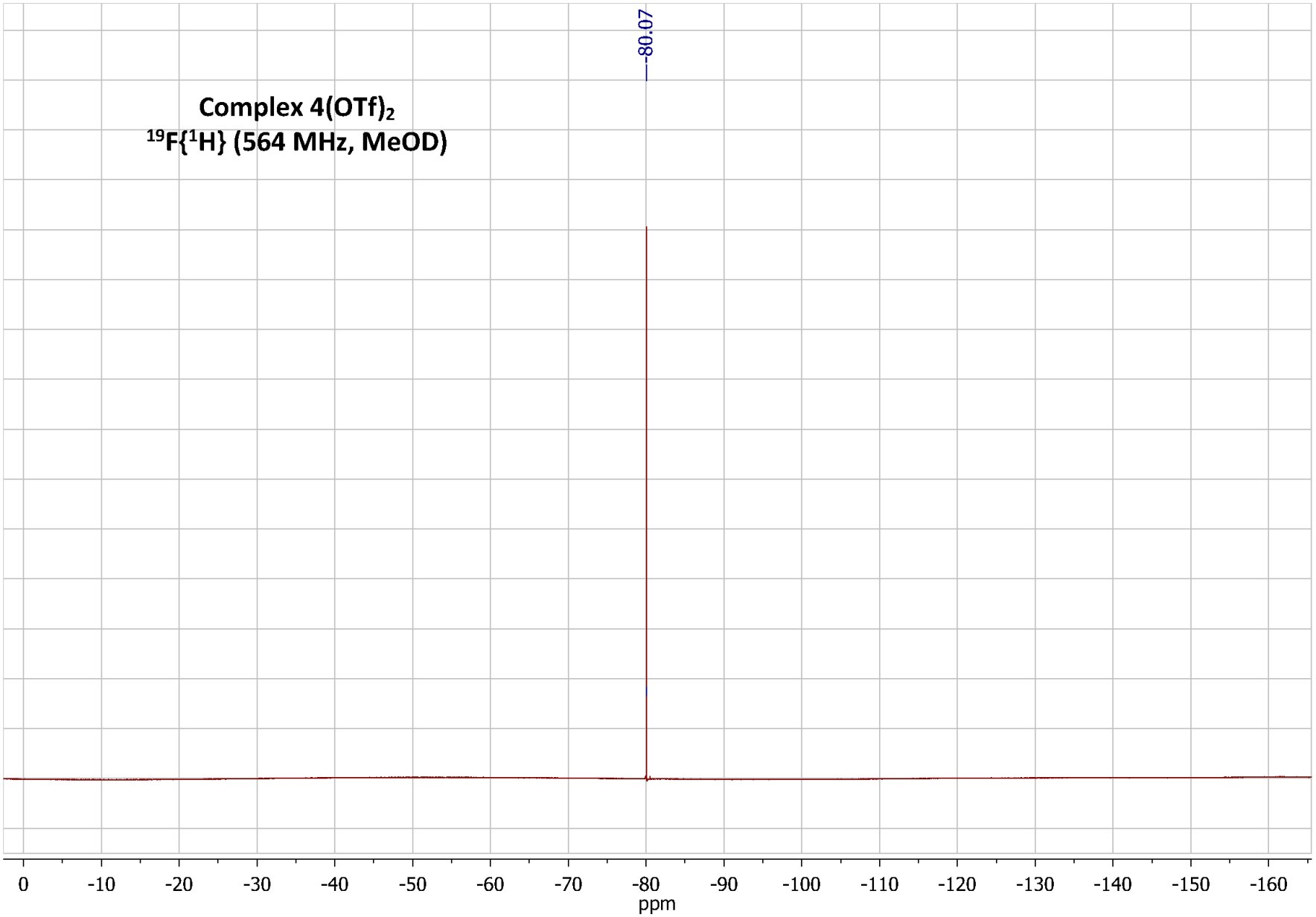


**Figure S30**. $^{19}F\{^{1}H\}$ NMR of **4** in $CD_3OD$ at 298 K.

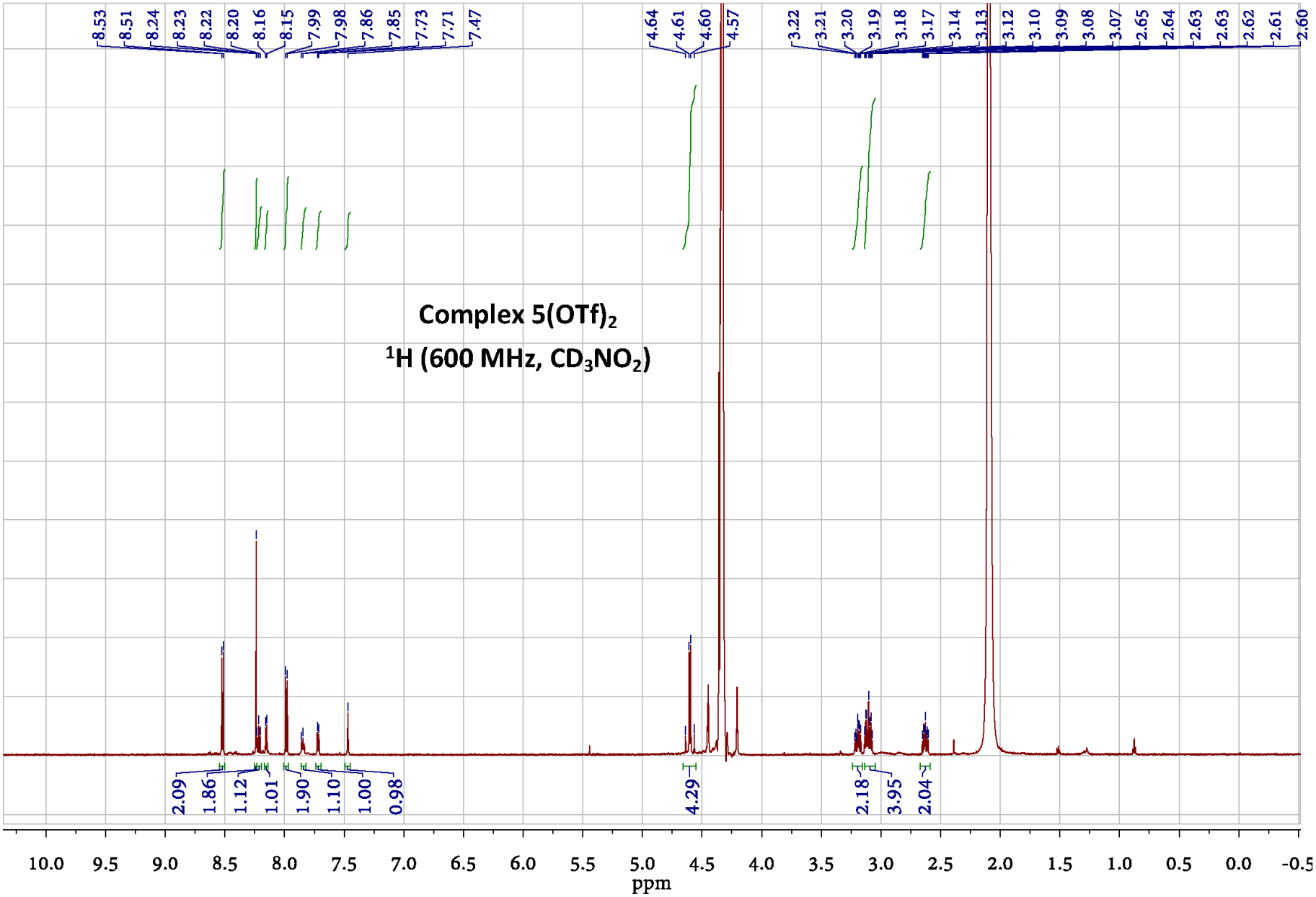


**Figure S31**. $^{1}H$ NMR of **5** in $CD_3NO_2$ at 298 K.

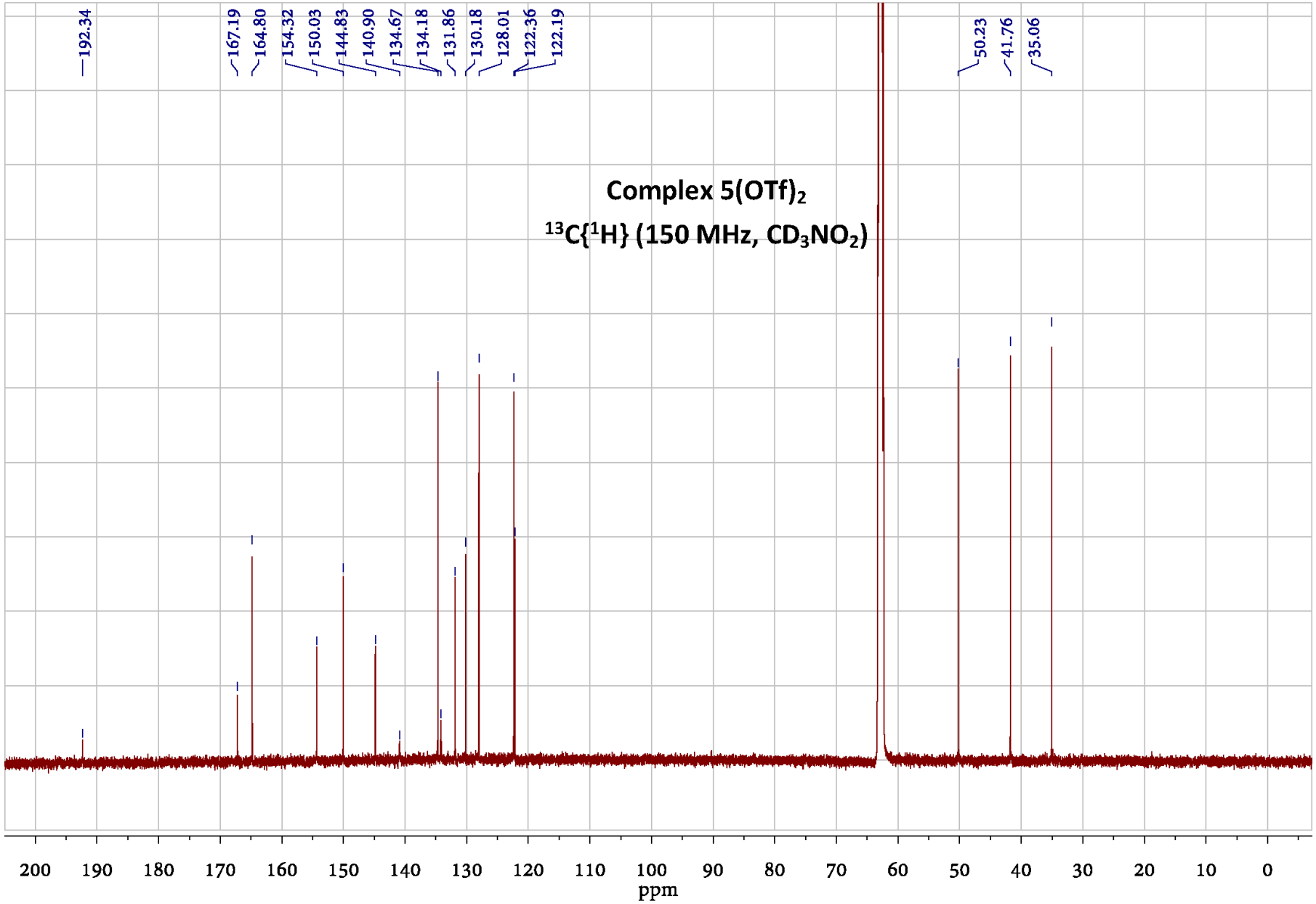


**Figure S32**. $^{13}C\{^{1}H\}$ NMR of **5** in $CD_3NO_2$ at 298 K.

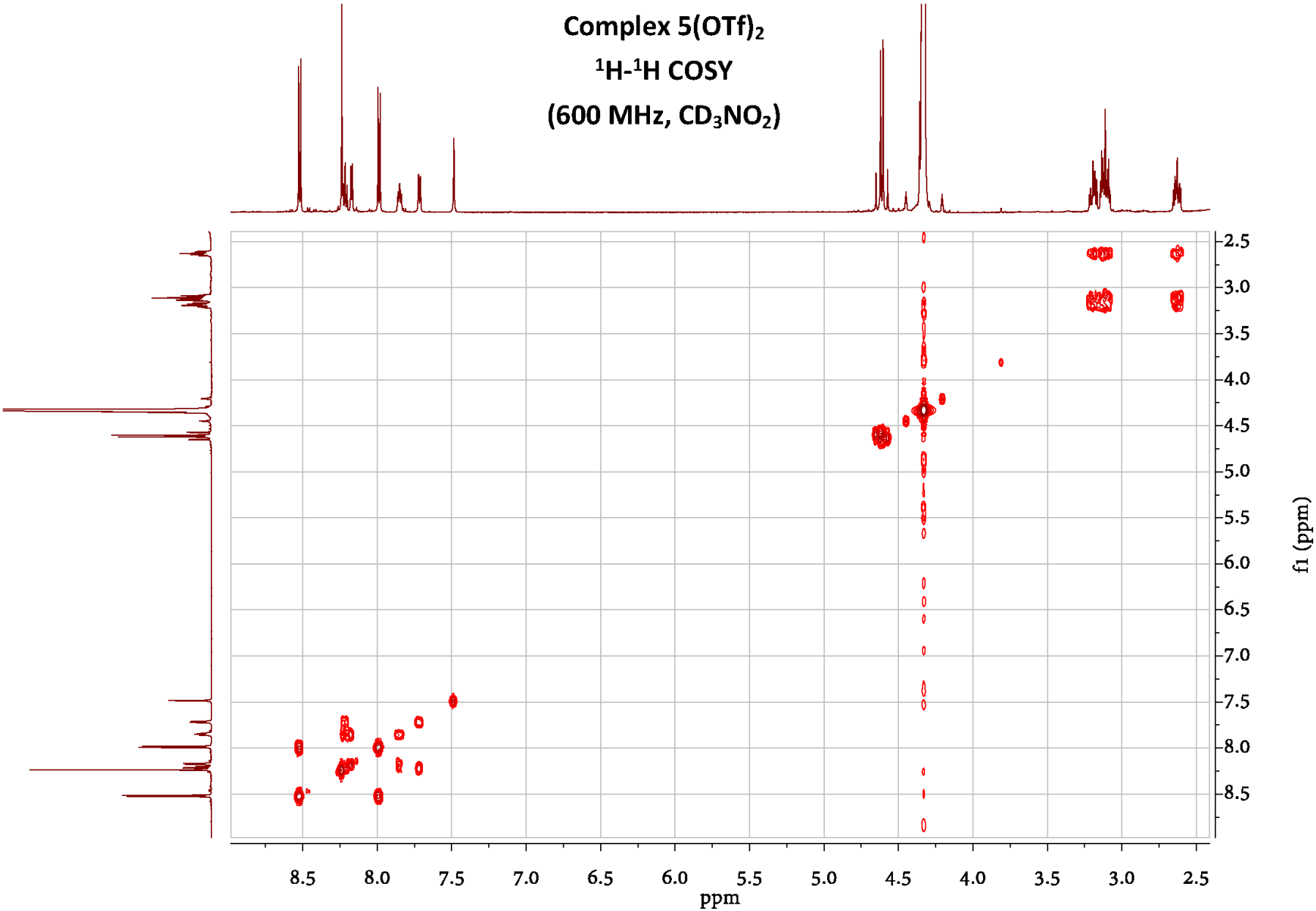


**Figure S33**. $^{1}H$-$^{1}H$ COSY NMR of **5** in $CD_3NO_2$ at 298 K.

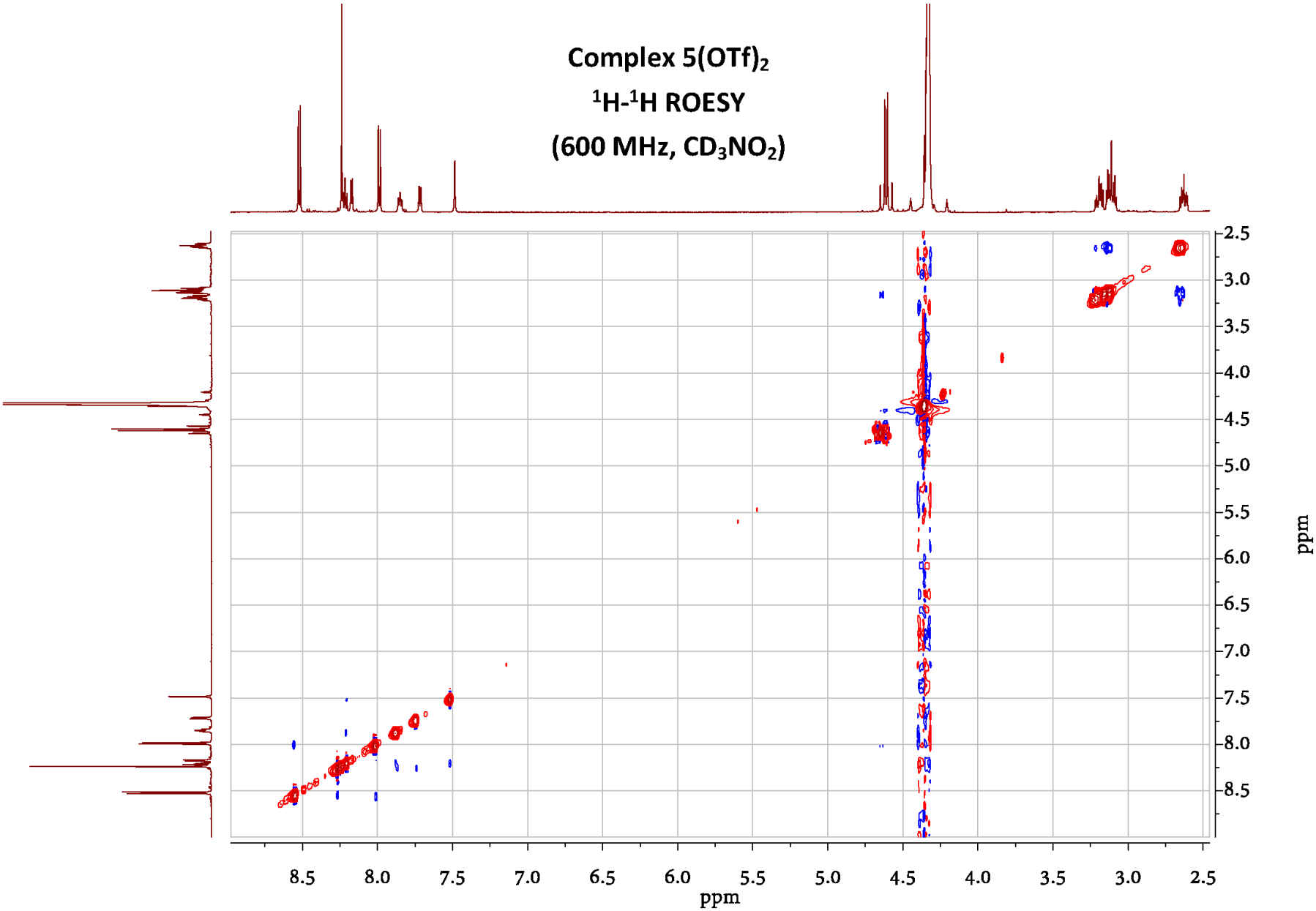


**Figure S34**. $^{1}H$-$^{1}H$ ROESY NMR of **5** in $CD_3NO_2$ at 298 K.

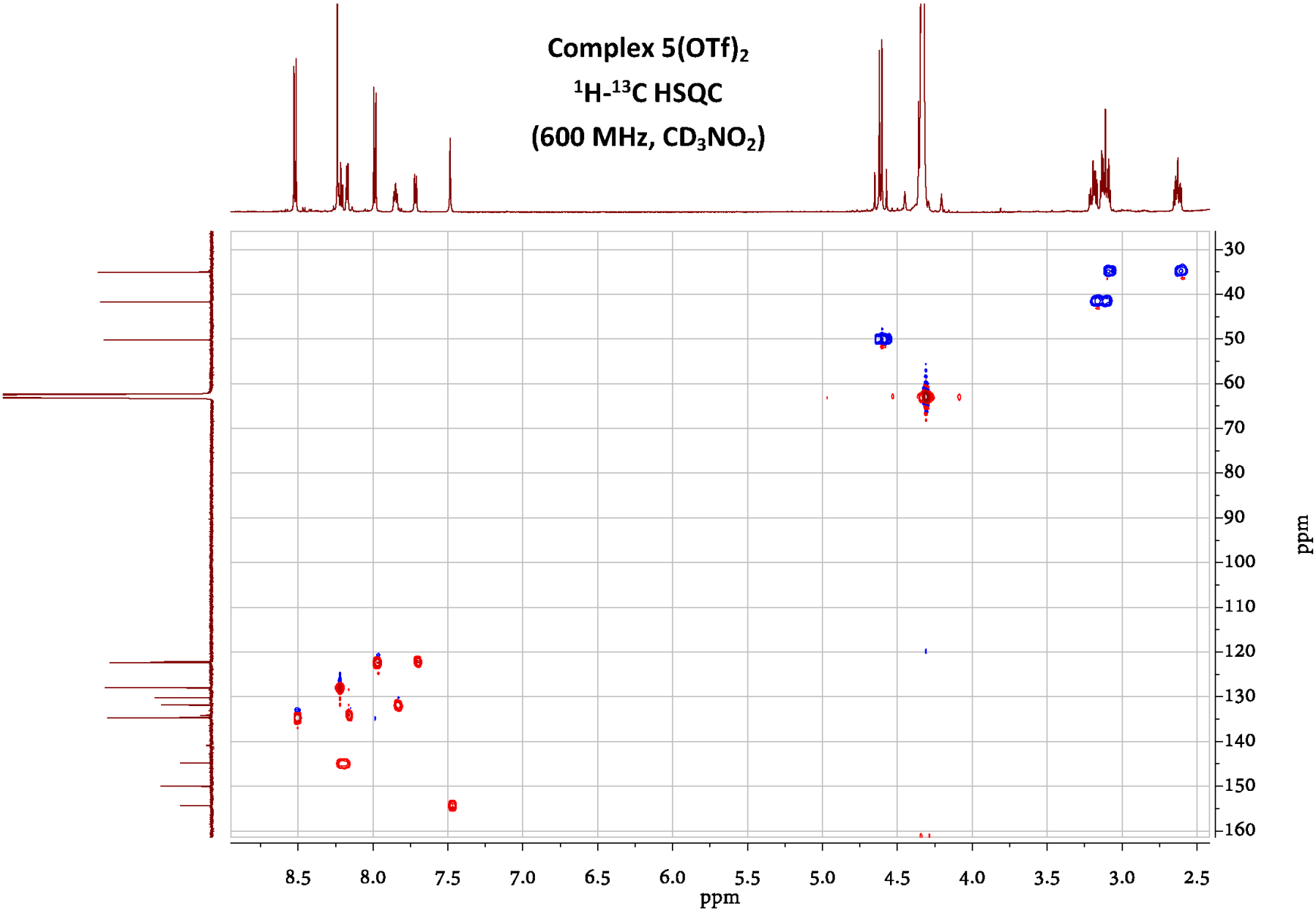


**Figure S35**. $^{1}H$-$^{13}C$ HSQC NMR of **5** in $CD_3NO_2$ at 298 K.

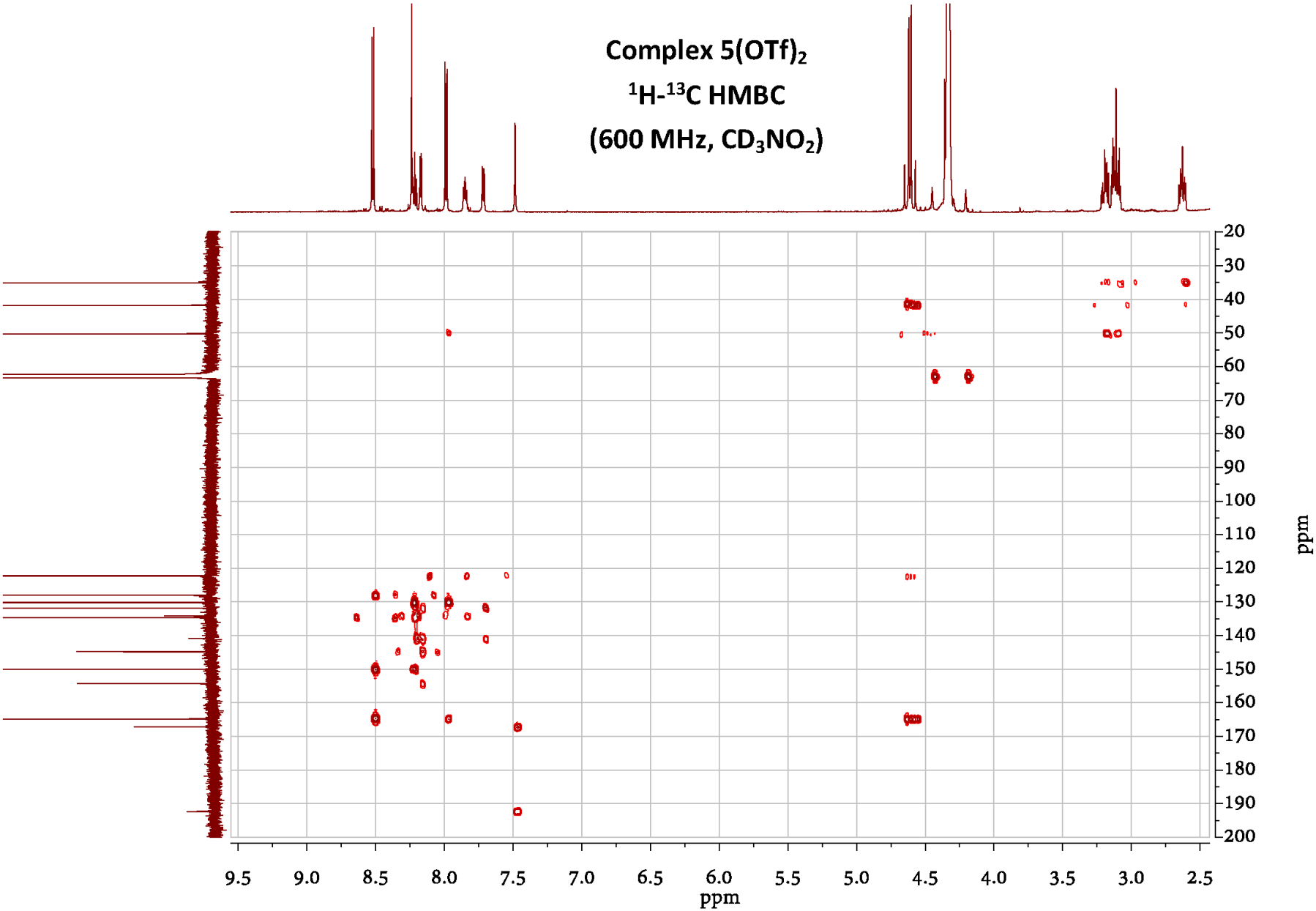


**Figure S36**. $^{1}H$-$^{13}C$ HMBC NMR of **5** in $CD_3NO_2$ at 298 K.

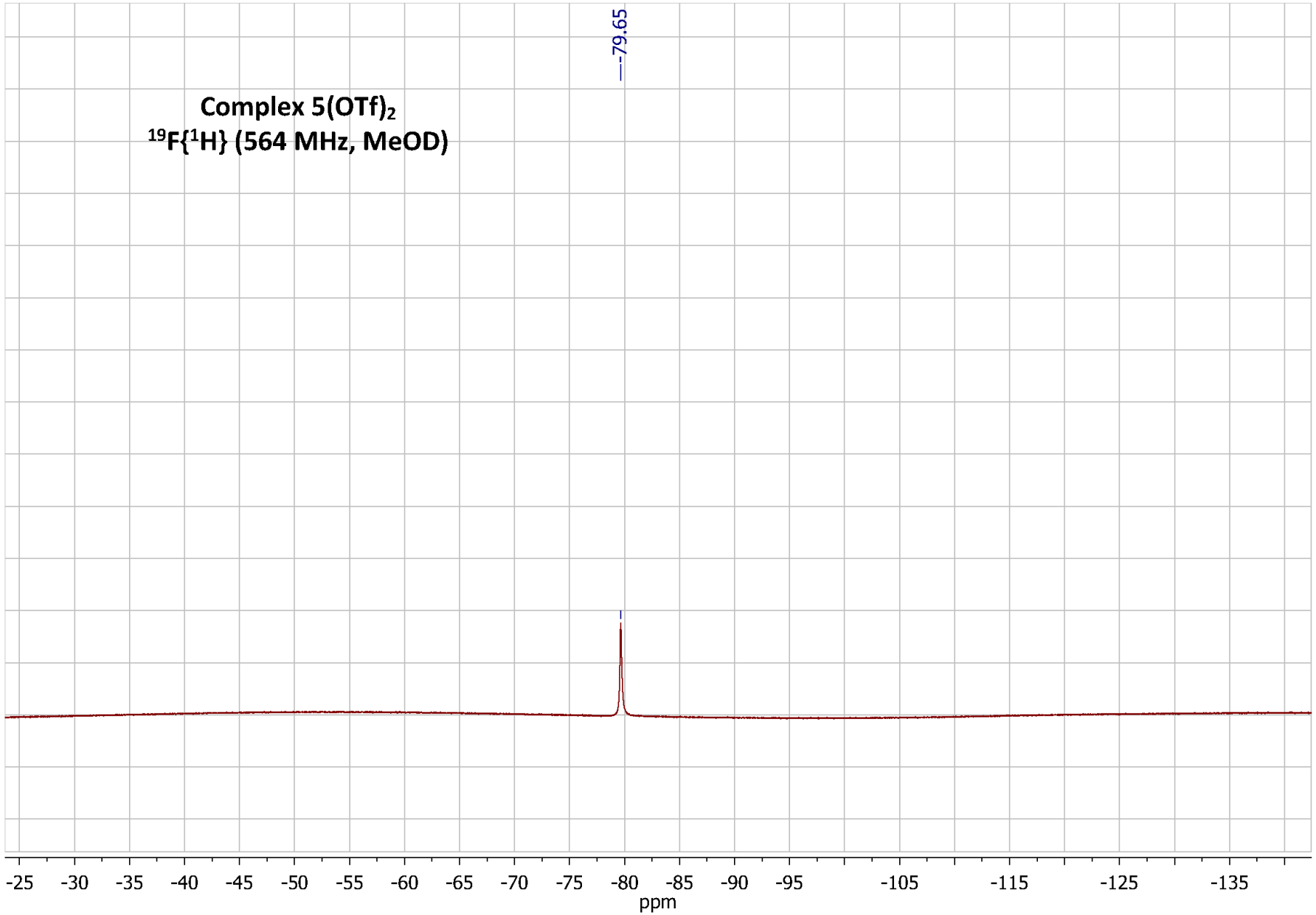


**Figure S37**. $^{19}F\{^{1}H\}$ NMR of **5** in $CD_3OD$ at 298 K.

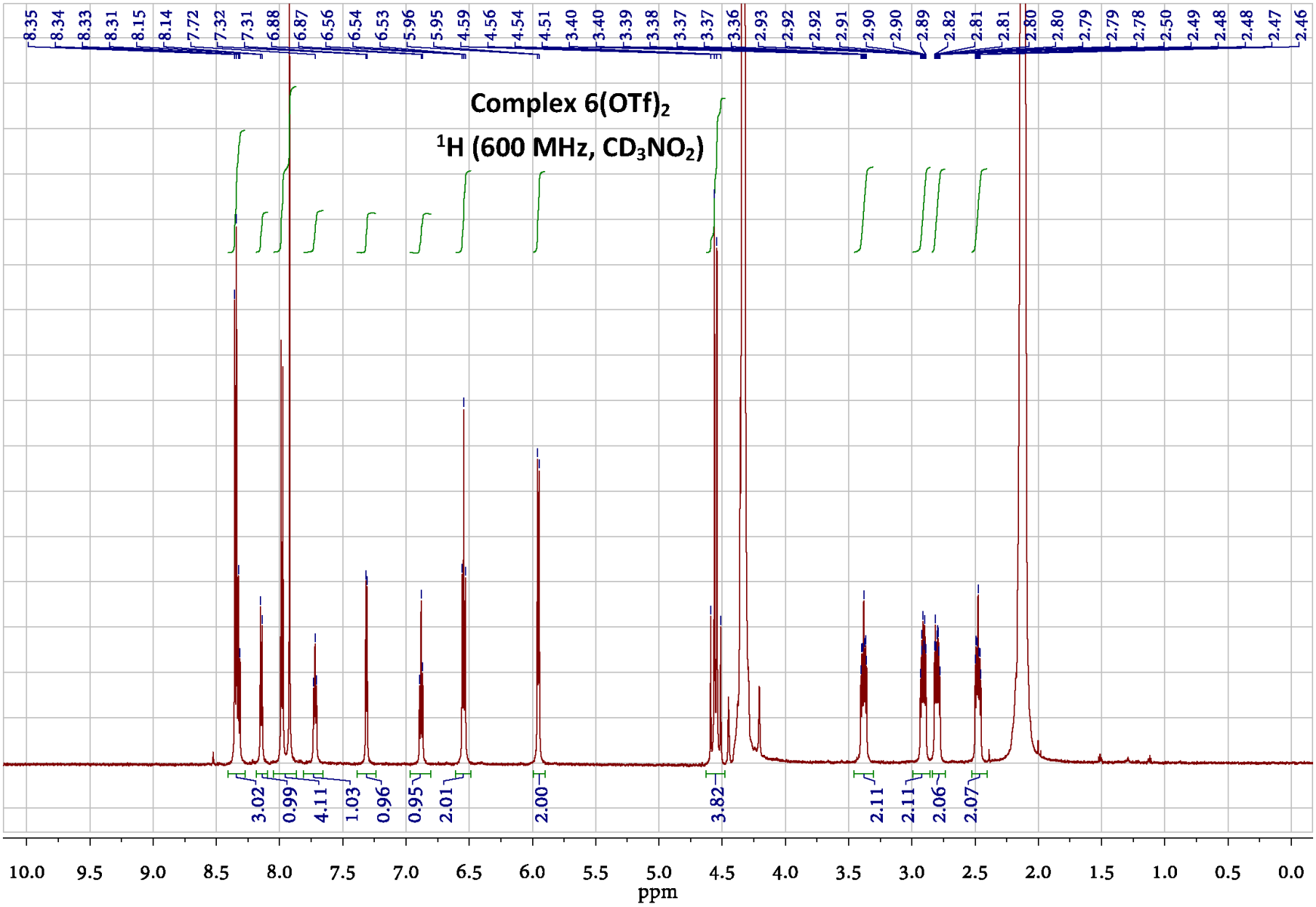


**Figure S38**. $^{1}H$ NMR of **6** in $CD_3NO_2$ at 298 K.

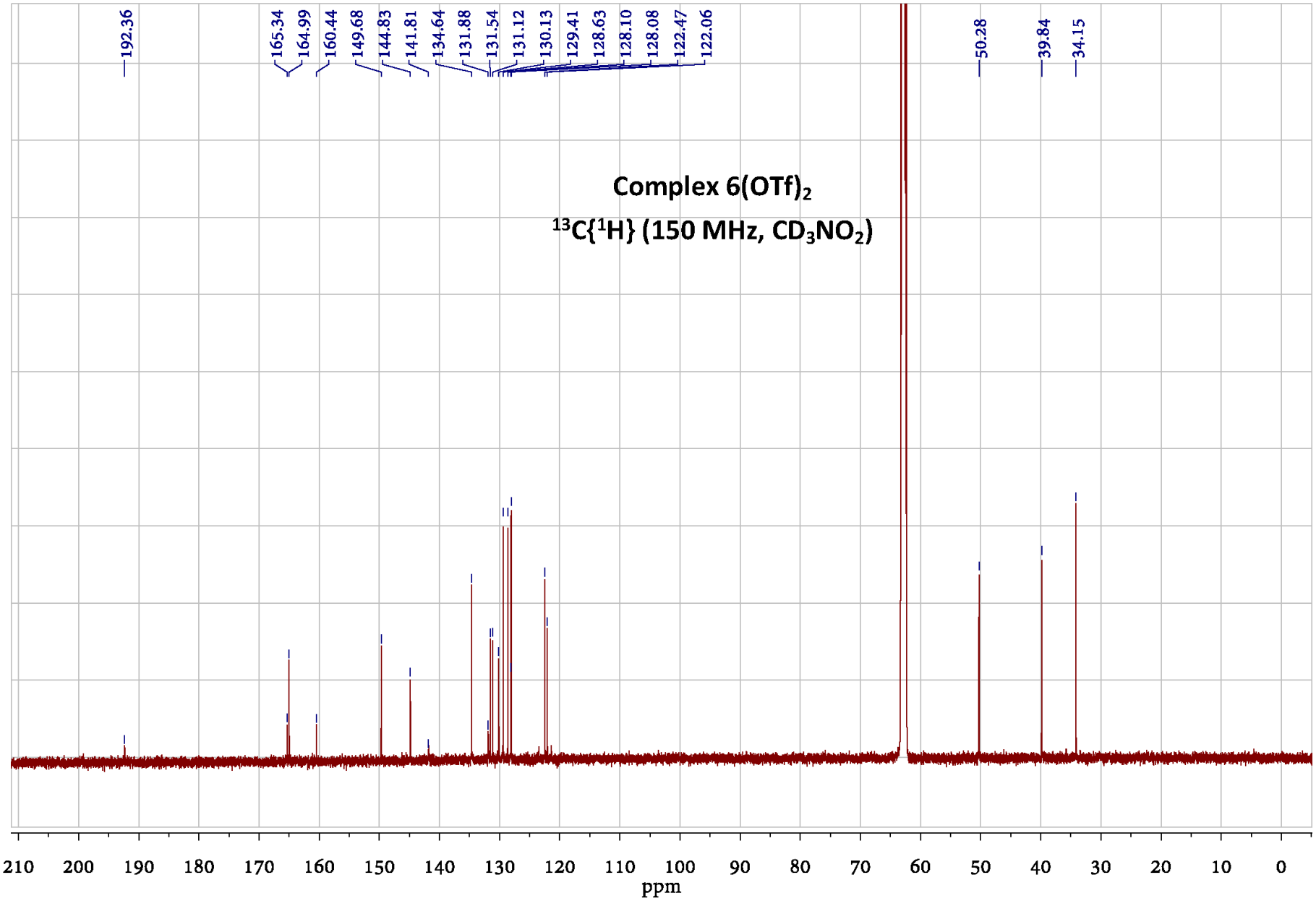


**Figure S39**. $^{13}C\{^{1}H\}$ NMR of **6** in $CD_3NO_2$ at 298 K.

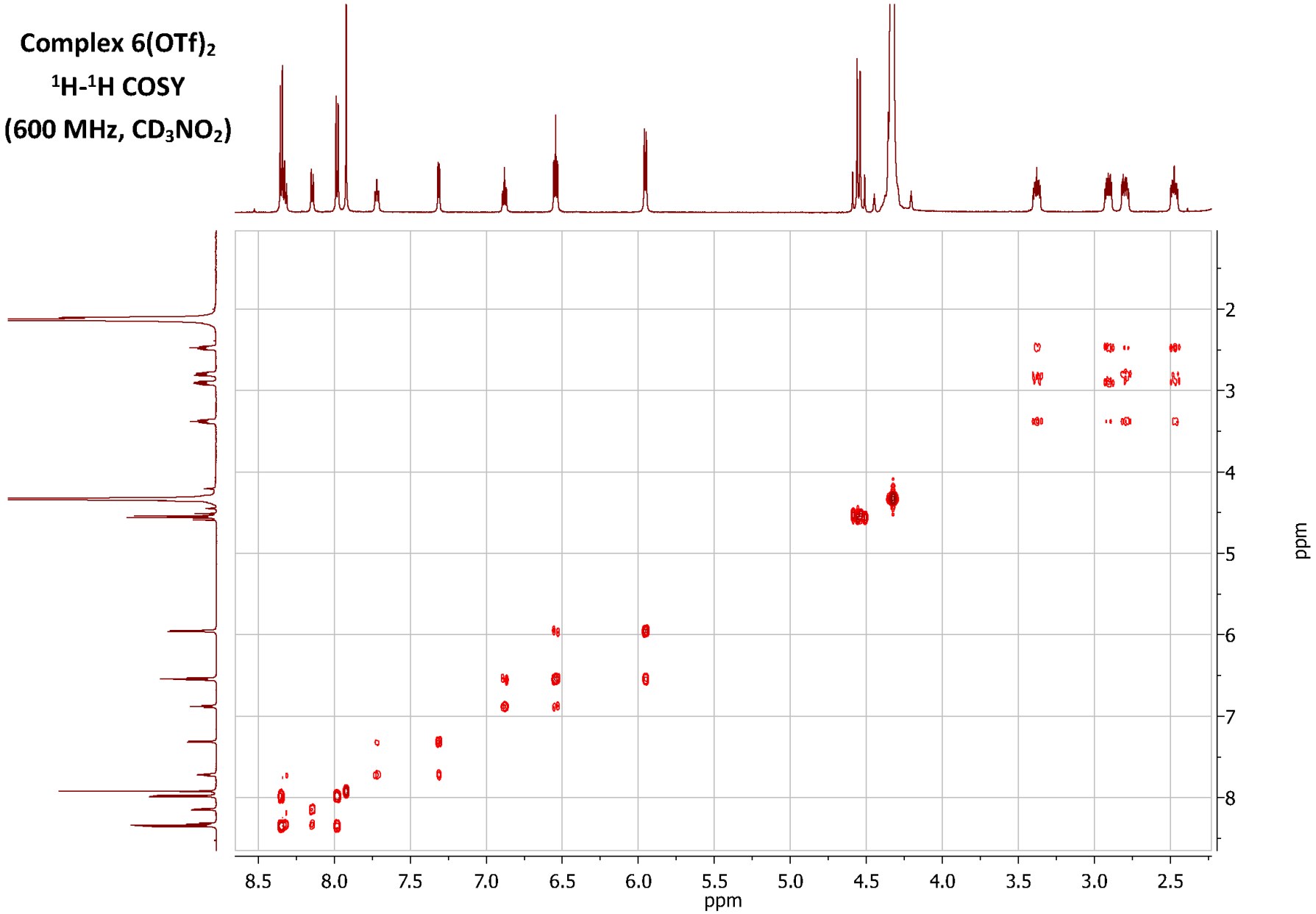


**Figure S40**. $^{1}H$-$^{1}H$ COSY NMR of **6** in $CD_3NO_2$ at 298 K.

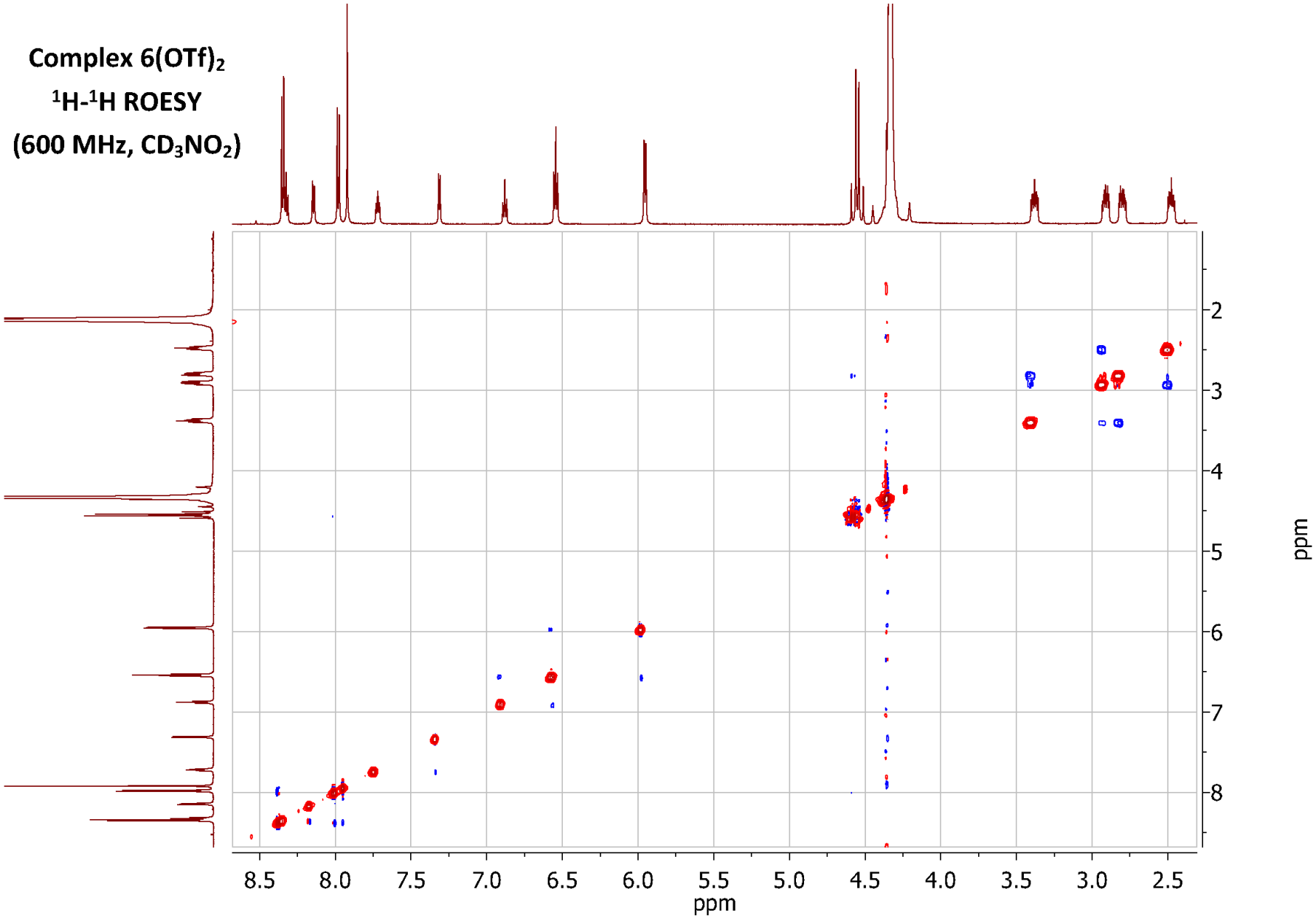


**Figure S41**. $^{1}H$-$^{1}H$ ROESY NMR of **6** in $CD_3NO_2$ at 298 K.

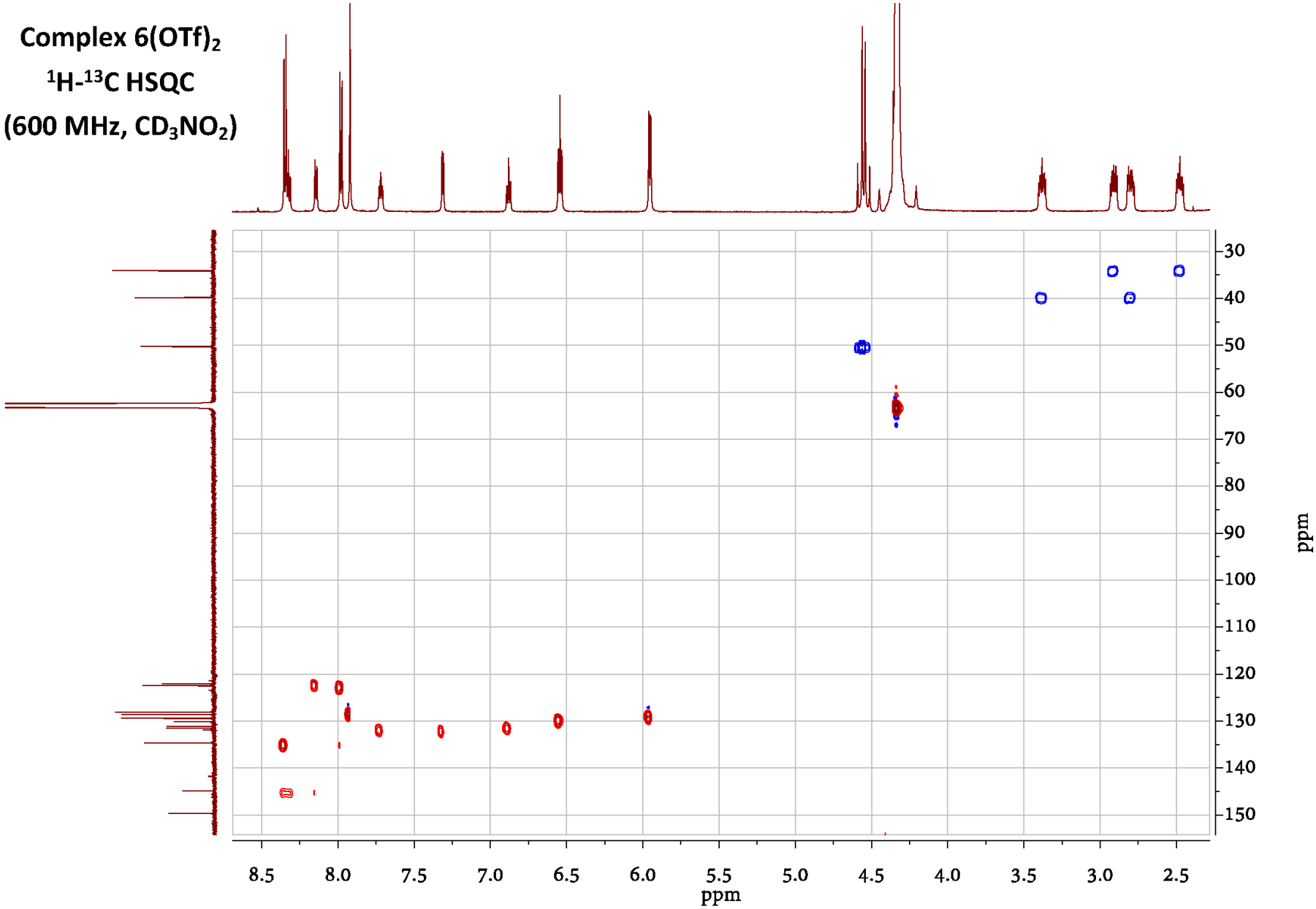


**Figure S42**. $^{1}H$-$^{13}C$ HSQC NMR of **6** in $CD_3NO_2$ at 298 K.

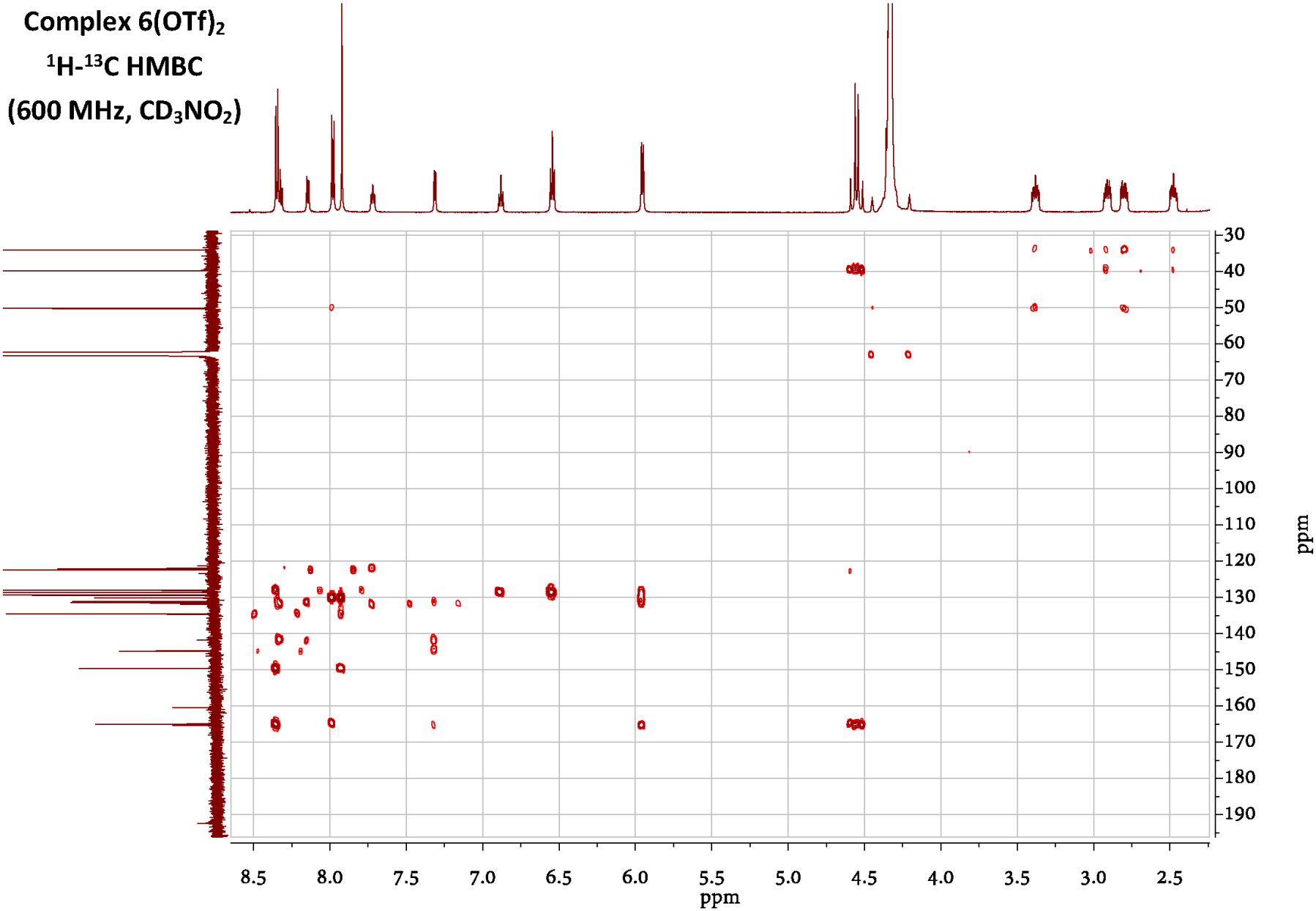


**Figure S43**. $^{1}H$-$^{13}C$ HMBC NMR of **6** in $CD_3NO_2$ at 298 K.

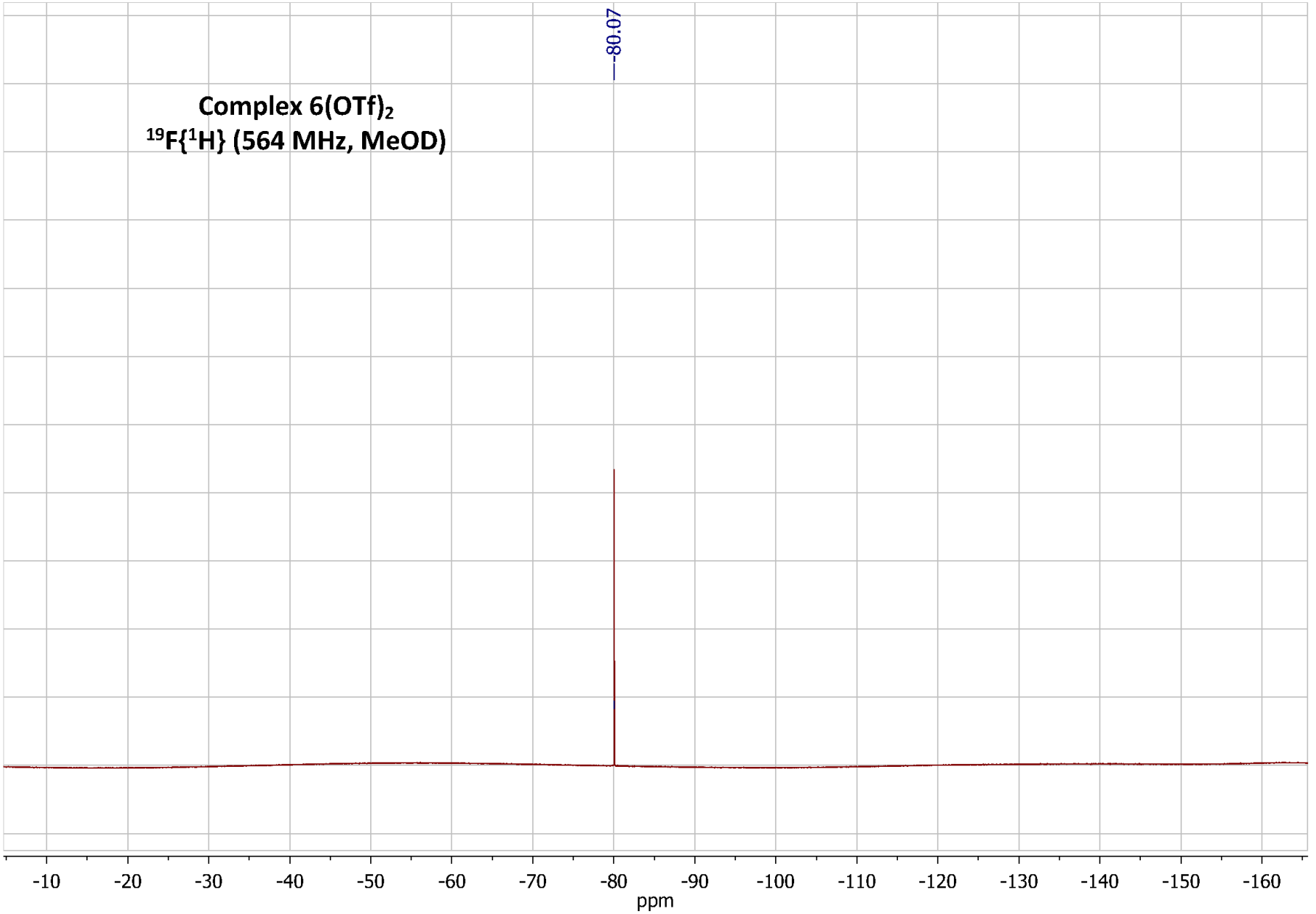


**Figure S44**. $^{19}F\{^{1}H\}$ NMR of **6** in $CD_3OD$ at 298 K.

**IR Spectra**

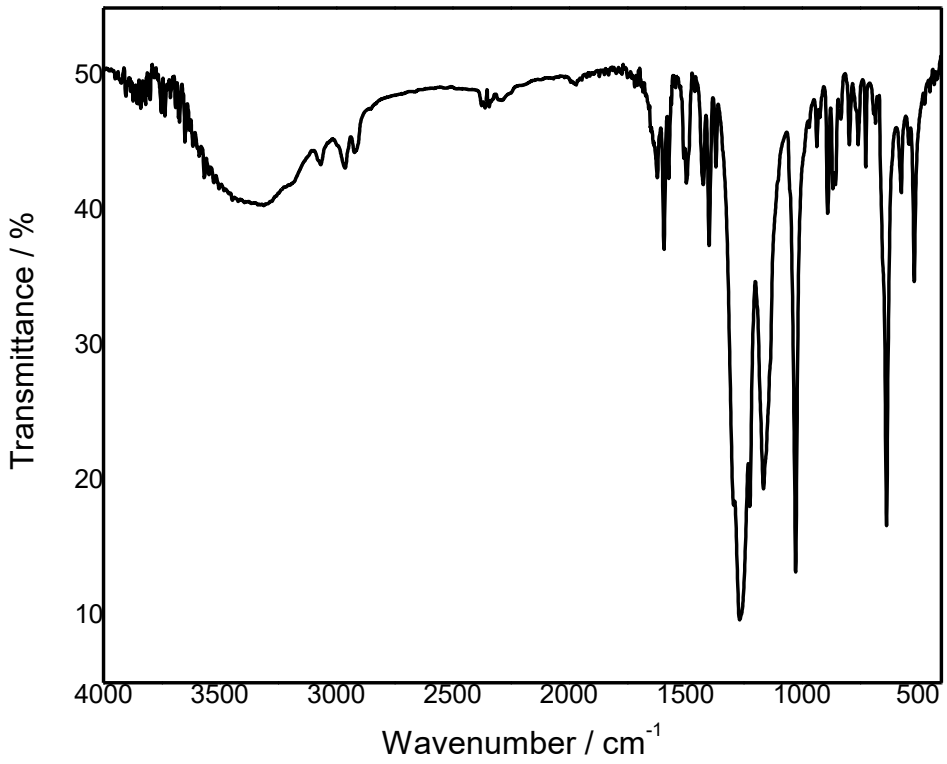


**Figure S45**. Infrared spectra of **1** on KBr plate.

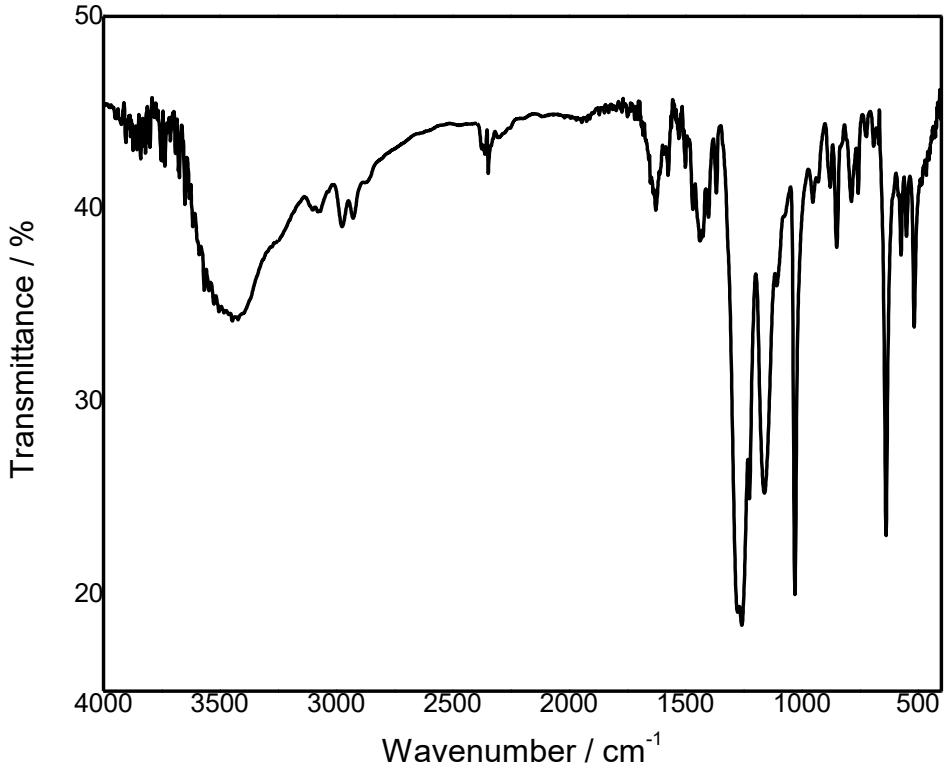


**Figure S46**. Infrared spectra of **2** on KBr plate.

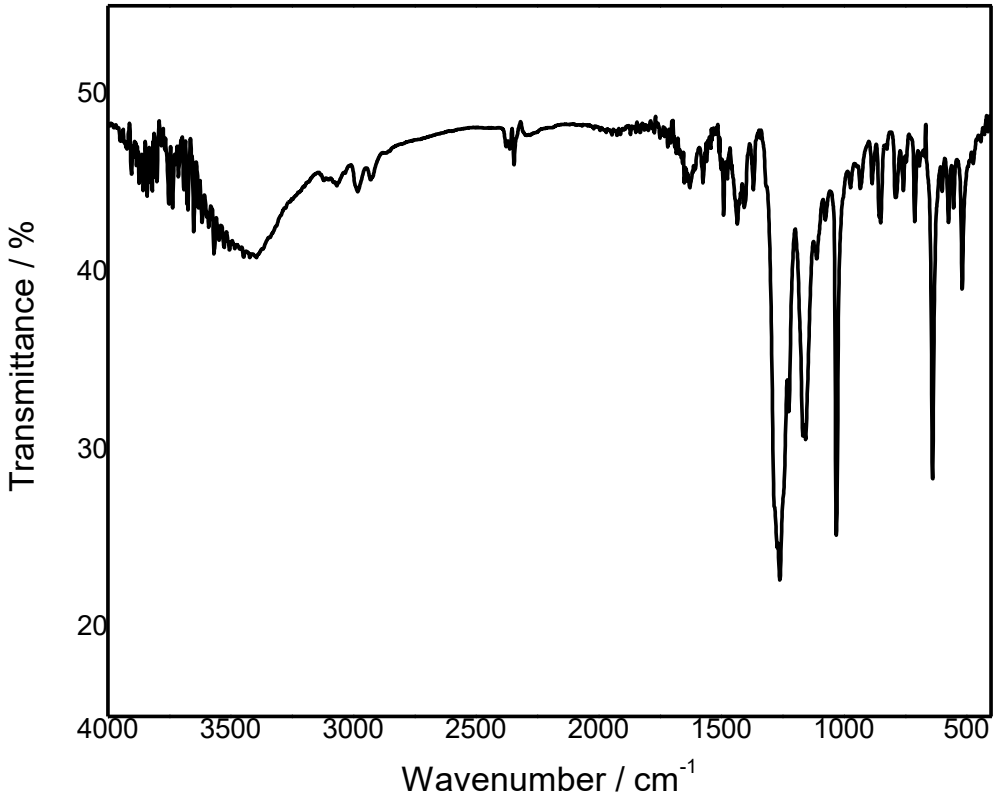


**Figure S47**. Infrared spectra of **3** on KBr plate.

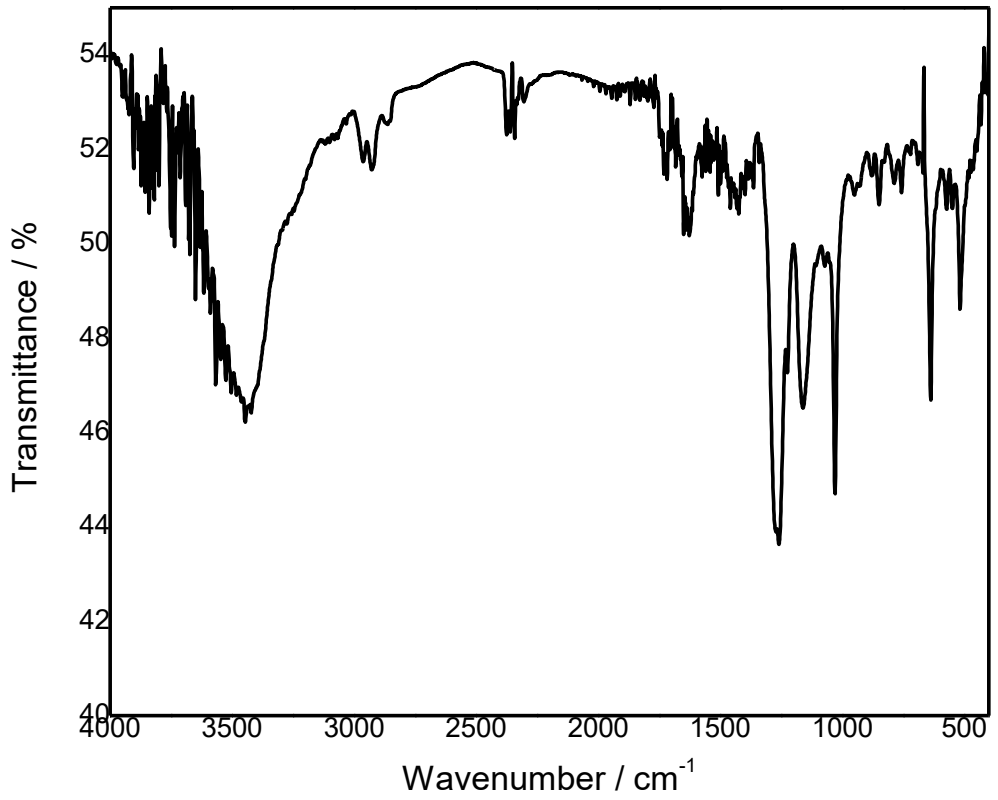


**Figure S48**. Infrared spectra of **4** on KBr plate.

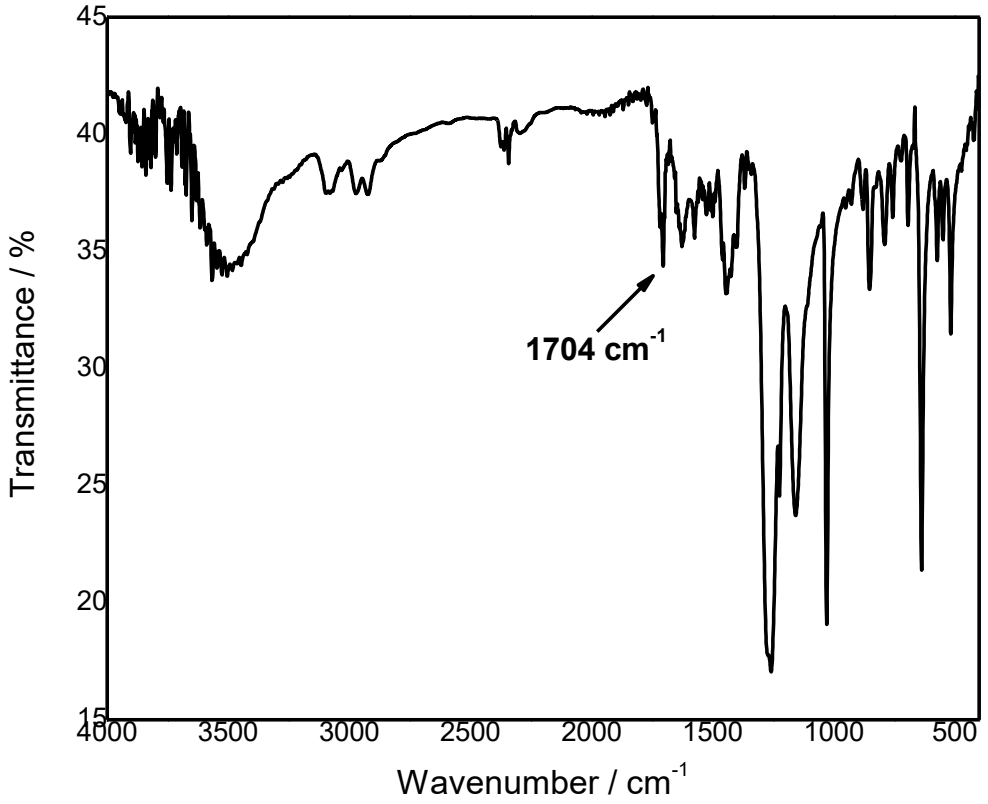


**Figure S49**. Infrared spectra of **5** on KBr plate.

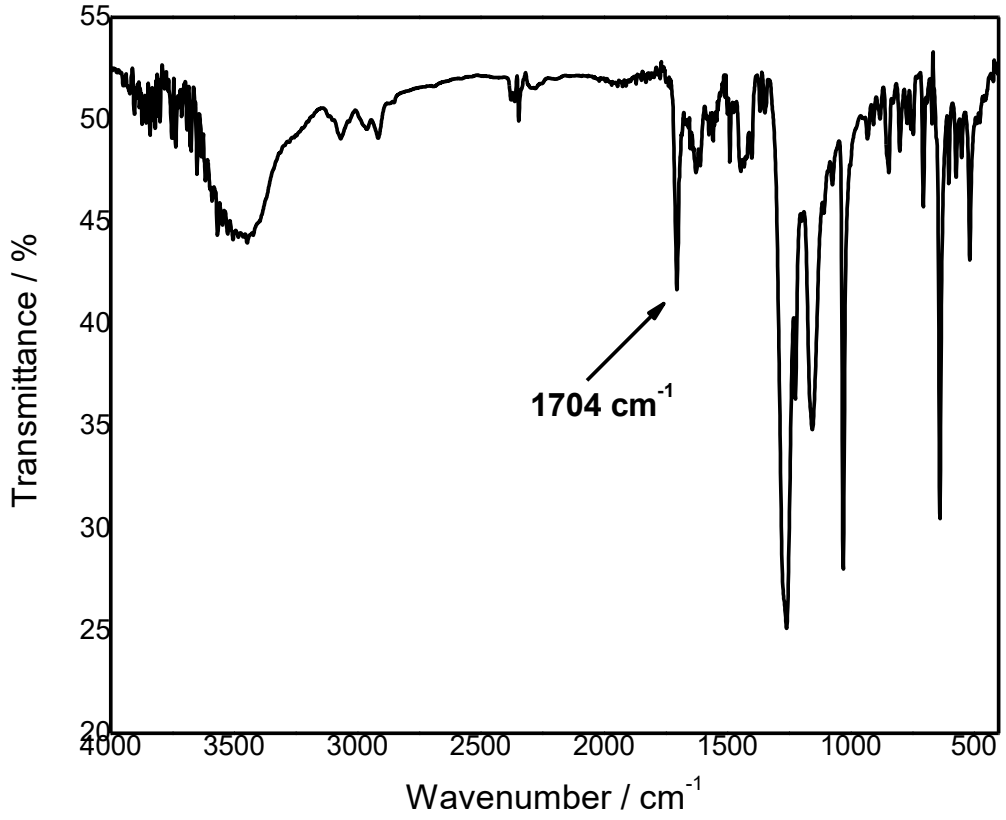


**Figure S50**. Infrared spectra of **6** on KBr plate.