Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Ruthenium–Indolizinone Complexes as a New Class of Metalated Heterocyclic Compound: Insight into Unconventional Alkyne Activation Pathway, Revelation of Unexpected Electronic Properties and Exploration of Medicinal Application

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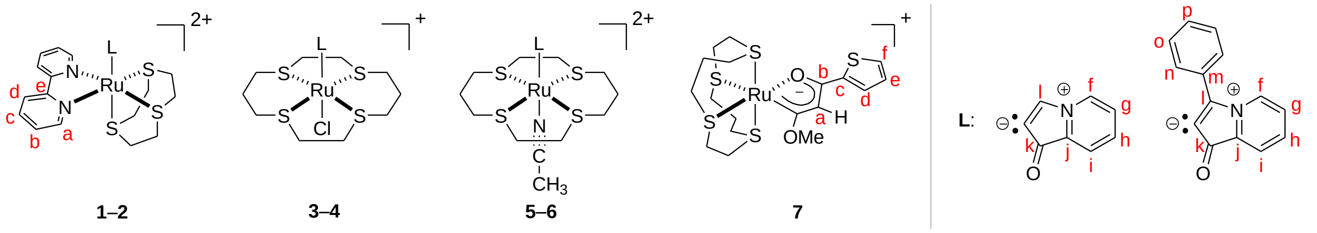
General Procedures

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. $[Ru([9]aneS3)(bpy)(OH_2)](ClO_4)_2$ and *cis*-$[Ru([14]aneS4)Cl_2]$ ([9]aneS3 = 1,4,7-trithiacyclononane, bpy = 2,2′-bipyridine, [14]aneS4 = 1,4,8,11-tetrathiacyclotetradecane) were prepared in accordance with literature methods.[1,2] ^1H, $^{13}C\{^1H\}$, 1H–1H COSY, ^1H–^1H NOESY, ^1H–^{13}C HSQC and ^1H–^{13}C HMBC NMR spectra were recorded on Bruker 600 AVANCE III FT-NMR spectrometer. Peak positions were calibrated with solvent residue peaks as internal standard. Labeling scheme for H and C atoms in the NMR assignments is shown in Scheme S1. Electrospray mass spectrometry was performed on a PE-SCIEX API 2000 triple quadrupole mass spectrometer. Elemental analyses were done on an Elementar Vario Micro Cube carbon-hydrogen-nitrogen elemental microanalyzer. UV–visible spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry was performed with a CH Instrument model 600C series electrochemical analyzer/workstation. All the electrochemical measurements were performed in CH_3CN solution with $[n\text{-}Bu_4N]PF_6$ (0.1 M) as supporting electrolyte at room temperature. The glassy-carbon working electrode was polished with 0.05μm alumina on a microcloth, sonicated for 5 min in deionized water, and rinsed with CH_3CN before use. An Ag/AgCl (CH_3CN) electrode was used as reference electrode, with a platinum wire as the counter electrode. All solutions were degassed with argon before experiments. The $E_{1/2}$ value of the ferrocenium/ferrocene couple ($Cp_2Fe^{+/0}$) measured in the same solution was used as an internal reference. Cell lines A549 (human lung adenocarcinoma), HepG2 (human hepatocarcinoma), HT1080 (human fibrosarcoma), MCF-7 (human breast adenocarcinoma) and HeLa (human cervical carcinoma) were preserved by our laboratory. Fetal bovine serum (FBS), phosphate-buffered saline (PBS), penicillin-streptomycin (PS), trypsin-EDTA, Minimum Essential Medium (MEM), Dulbecco's modified Eagle's medium (DMEM) and N-(2-Hydroxyethyl)piperazine-N′-(2-ethanesulfonic acid) (HEPES) were purchased from Gibco BRL (Gaithersburg, MD, USA). Dimethyl sulfoxide (DMSO, >99.8%) was obtained from Acros Organics and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was purchased from Invitrogen.



Scheme S1 Labeling scheme for H and C atoms in this work.

Synthesis of 1-(2-pyridinyl)-2-propyn-1-one

This ligand was synthesized from a modified literature procedure:[3a] To a solution of 2-pyridinecarboxaldehyde (0.95 mL, 9.99 mmol) in THF (10 mL) at –10 °C was added ethynylmagnesium bromide (22 mL of a 0.5 M solution in THF, 11.00 mmol) in dropwise manner. The reaction mixture was stirred for 2 hr at 0 °C and then gradually warmed to room temperature over a period of 30 min. Upon addition of a saturated aqueous NH_4Cl solution (5 mL), the reaction mixture was extracted with Et_2O (50 mL × 2) and CH_2Cl_2 (50 mL × 2). The organic phases were combined, washed with brine (50 mL × 2), dried over anhydrous $MgSO_4$, and concentrated to give a brown oil. 1-(2-pyridinyl)-2-propyn-1-ol was obtained after silica gel column chromatography (hexane/EtOAc: 9:1 to 7:3 (v/v); yield: 1.13 g, 85%). The 1-(2-pyridinyl)-2-propyn-1-ol (0.30 g, 2.25 mmol) was then stirred with MnO_2 (5 equiv., 0.98 g, 11.25 mmol) in CH_2Cl_2 (125 mL) at room temperature for 16 hr, and the resultant purple suspension was filtered to remove purple solids. The filtrate was concentrated to give a purple paste. 1-(2-pyridinyl)-2-propyn-1-one was obtained as brown solids (yield: 0.14 g, 48% based on 1-(2-pyridinyl)-2-propyn-1-ol) after silica gel column chromatography (hexane/CH_2Cl_2: 9:1 to 3:7 (v/v)).

Synthesis of 3-phenyl-1-(2-pyridinyl)-2-propyn-1-one

This ligand was synthesized from a modified literature procedure:[3a] To a solution of phenylacetylene (1.46 mL, 13.25 mmol) in THF (20 mL) at –40 °C was added *n*-butyllithium (8.30 mL of a 1.6 M solution in hexane, 13.28 mmol) in dropwise manner. The reaction mixture was stirred at –40 °C for 10 min, gradually warmed to –15 °C over a period of 15 min and further cooled to –78 °C for 10 min. Weinreb amide (*N*-methoxy-*N*-methylpicolinamide) (2.00 g, 12.05 mmol) in THF (10 mL) was added to the reaction mixture in dropwise manner at –78 °C for 10 min. The reaction mixture was warmed to room temperature, during which the color of the reaction mixture changed from yellow to red. Upon addition of a saturated aqueous $NaHCO_3$ solution (5 mL), the reaction mixture was extracted with EtOAc (50 mL × 2). The organic phases were combined, washed with brine (50 mL × 2), dried over anhydrous $MgSO_4$, and concentrated to give a reddish brown oil. 3-phenyl-1-(2-pyridinyl)-2-propyn-1-

one was obtained as greyish blue solids (yield: 1.25 g, 50%) after silica gel column chromatography (petroleum ether/diethyl ether: 9:1 to 7:3 (v/v)).

Synthesis of 1-(2-thienyl)-2-propyn-1-one

This ligand was synthesized from a modified literature procedure:[3b] To a solution of 2-thiophenecarboxaldehyde (0.93 mL, 9.99 mmol) in THF (10 mL) at –10 °C was added ethynylmagnesium bromide (22 mL of a 0.5 M solution in THF, 11.00 mmol) in dropwise manner. The reaction mixture was stirred for 2 hr at 0 °C and then gradually warmed to room temperature over a period of 30 min. Upon addition of a saturated aqueous NH_4Cl solution (5 mL), the reaction mixture was extracted with Et_2O (50 mL × 2) and CH_2Cl_2 (50 mL × 2). The organic phases were combined, washed with brine (50 mL × 2), dried over anhydrous $MgSO_4$, and concentrated to give a brown oil. 1-(2-thienyl)-2-propyn-1-ol was obtained after silica gel column chromatography (hexane/EtOAc: 20:0 to 19:1 (v/v); yield: 1.24 g, 90%). The 1-(2-thienyl)-2-propyn-1-ol (1.24 g, 9 mmol) was then stirred with MnO_2 (5 equiv., 3.92 g, 11.25 mmol) in CH_2Cl_2 (150 mL) at room temperature for 16 hr, and the resultant purple suspension was filtered to remove purple solids. The filtrate was concentrated to give a brown paste. 1-(2-thienyl)-2-propyn-1-one was obtained as orange solids (yield: 0.92 g, 75% based on 1-(2-thienyl)-2-propyn-1-ol) after silica gel column chromatography (hexane/EtOAc: 100:0 to 98:2 (v/v)).

Synthesis of **1**(ClO_4)$_2$ and **2**(ClO_4)$_2$

A mixture of ynone (1-(2-pyridinyl)-2-propyn-1-one for **1**, 3-phenyl-1-(2-pyridinyl)-2-propyn-1-one for **2**; 0.041 g for **1**, 0.064 g for **2**, 0.31 mmol) and [Ru([9]aneS3)(bpy)(OH_2)](ClO_4)$_2$ (0.051 g, 0.08 mmol) in anhydrous THF (10 mL) was heated in a 30 mL heavy-wall glass pressure vessel (sealed with fluoropolymer resin bushing) at evaluated temperature (120 °C for **1**, 80 °C for **2**) under argon for 16 hr, during which the color of the reaction mixture changed from yellow-brown to purple with deep green precipitates. Upon cooling to room temperature, the precipitates were collected by suction filtration and washed with Et_2O (10 mL × 3). Recrystallization by slow diffusion of Et_2O into a CH_3CN solution of the deep green solids gave analytically pure **1**(ClO_4)$_2$ or **2**(ClO_4)$_2$ as deep green crystals.

Complex **1**(ClO_4)$_2$. Yield: 0.052 g, 85%. Anal. Calcd for $C_{24}H_{25}N_3S_3RuCl_2O_9$: C, 37.55; H, 3.28, N, 5.47. Found: C, 37.46; H, 3.50, N, 5.44. ^1H NMR (600 MHz, CD_3CN): δ 2.46–2.66 (m, 8H, [9]aneS3), 2.69–2.79 (m, 2H, [9]aneS3), 2.94–3.05 (m, 2H, [9]aneS3), 7.58 (t, *J* = 6.0 Hz, 2H, H_c), 7.68 (s, 1H, H_l), 7.74 (d, *J* = 6.0 Hz, 1H, H_i), 7.78 (t, *J* = 6.0 Hz, 1H, H_g), 8.03 (t, *J* = 6.0 Hz, 2H, H_b), 8.17 (t, *J* = 6.0 Hz, 1H, H_h), 8.21 (d, *J* = 6.0 Hz, 1H, H$_f$), 8.29 (d, *J* = 6.0 Hz, 2H, H$_a$), 9.07 (d, *J* = 6.0 Hz, 2H, H$_d$). ^{13}C NMR (150 MHz, CD$_3$CN): δ 32.03, 32.68, 36.67 (C on [9]aneS3), 121.56 (C$_i$), 124.09 (C$_a$), 127.80 (C$_c$), 131.45 (C$_g$), 135.21 (C$_f$), 138.46 (C$_b$), 139.01 (C$_j$), 144.96 (C$_h$), 149.16 (C$_l$), 154.31 (C$_d$), 156.86 (C$_e$), 158.95 (C$_k$), 194.21 (Ru–C). IR (KBr, cm^{-1}): $\nu_{C=O}$ = 1705. ESI-MS: m/z 667.9 [**1**+ClO$_4$]$^+$.

Complex **2**(ClO$_4$)$_2$. Yield: 0.051 g, 75%. Anal. Calcd for $C_{30}H_{29}N_3S_3RuCl_2O_9$: C, 42.65; H, 3.46, N, 4.97. Found: C, 42.90; H, 3.67, N, 6.33. ^{1}H NMR (600 MHz, CD$_3$CN): δ 2.30–2.41 (m, 2H, [9]aneS3), 2.41–2.53 (m, 2H, [9]aneS3), 2.53–2.62 (m, 2H, [9]aneS3), 2.62–2.70 (m, 2H, [9]aneS3), 2.70–2.81 (m, 2H, [9]aneS3), 2.87–2.98 (m, 2H, [9]aneS3), 6.89 (d, *J* = 6.0 Hz, 2H, H$_n$), 7.25 (t, *J* = 6.0 Hz, 2H, H$_b$), 7.33 (t, *J* = 6.0 Hz, 2H, H$_o$), 7.38 (d, *J* = 6.0 Hz, 1H, H$_f$), 7.54 (t, *J* = 6.0 Hz, 1H, H$_p$), 7.63 (t, *J* = 6.0 Hz, 1H, H$_g$), 7.87 (d, *J* = 6.0 Hz, 1H, H$_i$), 7.91 (t, *J* = 6.0 Hz, 2H, H$_c$), 8.15 (d, *J* = 6.0 Hz, 2H, H$_d$), 8.20 (t, *J* = 6.0 Hz, 1H, H$_h$), 8.51 (d, *J* = 6.0 Hz, 2H, H$_a$). ^{13}C NMR (150 MHz, CD$_3$CN): δ 31.94, 33.41, 37.29 (C on [9]aneS3), 121.04 (C$_i$), 123.94 (C$_d$), 127.25 (C$_b$), 129.78 (C$_m$), 130.05 (C$_o$), 131.17 (C$_g$ + C$_n$ + C$_p$), 133.28 (C$_f$), 138.16 (C$_c$), 138.86 (C$_j$), 145.05 (C$_h$), 152.06 (C$_k$), 154.68 (C$_a$), 156.90 (C$_e$), 162.26 (C$_l$), 194.80 (Ru–C). IR (KBr, cm^{-1}): $\nu_{C=O}$ = 1710. ESI-MS: m/z 746.4 [**2**+ClO$_4$]$^+$.

Synthesis of **3**(ClO$_4$) and **4**(ClO$_4$)

A mixture of ynone (1-(2-pyridinyl)-2-propyn-1-one for **3**, 3-phenyl-1-(2-pyridinyl)-2-propyn-1-one for **4**; 0.035 g for **3**, 0.056 g for **4**, 0.27 mmol) and *cis*-[Ru([14]aneS4)Cl$_2$] (0.14 mmol) were refluxed in MeOH (50 mL) under argon for 16 hr, during which the color of the reaction mixture changed from orange-brown to deep green. Upon cooling to room temperature, all the solvent was removed by reduced pressure, and the residue was added saturated NaClO$_4$ solution (5 mL) to give deep green precipitates. These precipitates, collected by suction filtration, were dissolved in CH$_2$Cl$_2$ (20 mL) and washed with deionized water (20 mL × 3). The CH$_2$Cl$_2$ portion was dried over anhydrous MgSO$_4$ and concentrated to give deep green precipitates. The solids were collected by suction filtration and washed with Et$_2$O (10 mL × 3). Recrystallization by slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of the deep green solids under argon gave analytically pure **3**(ClO$_4$) or **4**(ClO$_4$) as deep green crystals.

Complex **3**(ClO$_4$). Yield: 0.057 g, 64%. Anal. Calcd for $C_{18}H_{25}N_1S_4RuCl_2O_5$: C, 34.01; H, 3.96, N, 2.20. Found: C, 34.01; H, 4.27, N, 2.43. ^{1}H NMR (600 MHz, CD$_2$Cl$_2$): δ 1.47–1.68 (m, 2H, [14]aneS4), 2.39–2.49 (m, 2H, [14]aneS4), 2.92–3.02 (m, 4H, [14]aneS4), 3.13–3.29 (m, 8H, [14]aneS4), 3.79–3.93 (m, 4H, [14]aneS4), 7.67 (d, *J* = 6.0 Hz, 1H, H$_i$), 7.71 (t, *J* = 6.0 Hz, 1H, H$_g$), 7.79 (s, 1H, H$_l$), 8.01 (t, *J* = 6.0 Hz, 1H, H$_h$), 8.56 (d, *J* = 6.0 Hz, 1H, H$_f$). ^{13}C NMR (150 MHz, CD$_2$Cl$_2$): δ 26.56, 32.94, 36.80 (C on

[14]aneS4), 121.46 (C_i), 131.63 ($C_f + C_g$), 137.63 (C_j), 139.77 (C_h), 148.32 (C_l), 171.40 (C_k), 188.28 (Ru–C). IR (KBr, cm^{-1}): $\nu_{C=O}$ = 1705. ESI-MS: m/z 538.4 [**3**]$^+$.

Complex **4**(ClO_4). Yield: 0.073 g, 73%. Anal. Calcd for $C_{24}H_{29}N_1S_4RuCl_2O_5$: C, 40.50; H, 4.11, N, 1.97. Found: C, 40.51; H, 4.12, N, 2.08. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 1.32–1.47 (m, 2H, [14]aneS4), 2.25–2.39 (m, 2H, [14]aneS4), 2.41–2.76 (m, 4H, [14]aneS4), 2.76–2.93 (m, 4H, [14]aneS4), 2.93–3.15 (m, 4H, [14]aneS4), 3.62–3.82 (m, 4H, [14]aneS4), 7.43 (d, J = 6.0 Hz, 1H, H_f), 7.55 (t, J = 6.0 Hz, 2H, H_o), 7.58–7.66 (m, 2H, $H_g + H_p$), 7.68–7.73 (d, J = 6.0 Hz, 2H, H_n), 7.86 (d, J = 6.0 Hz, 1H, H_i), 8.15 (t, J = 6.0 Hz, 1H, H_h). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 26.24, 32.88, 36.56 (C on [14]aneS4), 121.61 (C_i), 128.58 (C_o), 128.73 (C_f), 129.01 (C_m), 131.20 (C_g), 131.24 (C_p), 134.11 (C_n), 137.79 (C_j), 140.58 (C_h), 159.30 (C_l), 164.24 (C_k), 187.62 (Ru–C). IR (KBr, cm^{-1}): $\nu_{C=O}$ = 1705. ESI-MS: m/z 614.3 [**4**]$^+$.

Synthesis of **5**(ClO_4)$_2$ and **6**(ClO_4)$_2$

A 25 mL CH_3CN solution of **3**(ClO_4) or **4**(ClO_4) (0.051 g for **3**, 0.057 g for **4**, 0.08 mmol) was added $AgClO_4$ (0.017 g, 0.08 mmol), and this mixture was stirred at room temperature under argon for 16 hr, during which the color of the reaction mixture turned from deep green to deep blue. Upon centrifugation for removal of AgCl, the supernatant was collected and concentrated to give deep blue precipitates. The solids were collected by suction filtration and washed with Et_2O (10 mL × 3). Recrystallization by slow diffusion of Et_2O into a CH_3CN solution of the deep blue solids gave analytically pure **5**(ClO_4)$_2$ or **6**(ClO_4)$_2$ as deep blue crystals.

Complex **5**(ClO_4)$_2$. Yield: 0.057 g, 94%. Anal. Calcd for $C_{20}H_{28}N_2S_4RuCl_2O_9$: C, 32.43; H, 3.81, N, 3.78. Found: C, 31.72; H, 4.04, N, 3.87. ^{1}H NMR (600 MHz, CD_3CN): δ 1.60–1.73 (m, 2H, [14]aneS4), 2.56–2.65 (m, 2H, [14]aneS4), 2.77–2.94 (m, 8H, [14]aneS4), 3.11–3.22 (m, 4H, [14]aneS4), 3.30–3.39 (m, 4H, [14]aneS4), 7.58 (s, 1H, H_l), 7.80–7.88 (m, 2H, $H_h + H_i$), 8.20 (t, J = 6.0 Hz, 1H, H_g), 8.28 (d, J = 6.0 Hz, 1H, H_f). ^{13}C NMR (150 MHz, CD_3CN): δ 26.95, 34.55, 37.39 (C on [14]aneS4), 122.04 (C_i), 131.90 (C_g), 134.21 (C_f), 138.56 (C_j), 144.15 (C_h), 150.68 (C_l), 161.57 (C_k), 192.60 (Ru–C). IR (KBr, cm^{-1}): $\nu_{C=O}$ = 1705. ESI-MS: m/z 599.9 [**5**–CH_3CN+ClO_4]$^+$.

Complex **6**(ClO_4)$_2$. Yield: 0.062 g, 95%. Anal. Calcd for $C_{26}H_{32}N_2S_4RuCl_2O_9$: C, 38.23; H, 3.95, N, 3.43. Found: C, 38.25; H, 4.13, N, 4.04. ^{1}H NMR (600 MHz, CD_3CN): δ 1.28–1.44 (m, 2H, [14]aneS4), 2.40–2.52 (m, 2H, [14]aneS4), 2.57–2.72 (m, 8H, [14]aneS4), 2.72–2.84 (m, 4H, [14]aneS4), 3.14–3.27 (m, 4H, [14]aneS4), 7.50 (d, J = 6.0 Hz, 1H, H_f), 7.55 (t, J = 6.0 Hz, 2H, H_o), 7.60–7.72 (m, 4H, $H_g + H_n +$

H_p), 7.94 (d, *J* = 6.0 Hz, 1H, H_i), 8.21 (t, *J* = 6.0 Hz, 1H, H_h). ^{13}C NMR (150 MHz, CD_3CN): δ 26.55, 34.53, 37.20 (C on [14]aneS4), 121.47 (C_i), 128.88 (C_o), 131.52 (C_g), 131.74 (C_p), 132.59 (C_f), 134.60 (C_n), 138.53 (C_j), 144.20 (C_h), 154.13 (C_m), 162.38 (C_l), 192.98 (C_k), 207.78 (Ru–C). IR (KBr, cm^{-1}): $\nu_{C=O}$ = 1701. ESI-MS: m/z 678.3 [**6**–CH_3CN+ClO_4]$^+$.

Synthesis of **7**(ClO_4)

A mixture of 2-thienyl ynone (0.063 g, 0.46 mmol) and *cis*-[Ru([14]aneS4)Cl_2] (0.10 g, 0.23 mmol) were refluxed in MeOH (50 mL) under argon for 16 hr. Upon cooling to room temperature, a saturated aqueous $NaClO_4$ solution (5 mL) was added, and the MeOH was removed by reduced pressure. The yellow solids were collected by suction filtration and washed with water (5 mL × 2), EtOH (5 mL × 2), and finally Et_2O (10 mL × 3). Recrystallization by slow diffusion of Et_2O into a CH_3CN solution of the yellow solids gave analytically pure **7**(ClO_4) as bright orange crystals.

Complex **7**(ClO_4). Yield: 0.12 g, 83%. Anal. Calcd for $C_{18}H_{27}S_5RuClO_6$: C, 33.98; H, 4.28, N, 0.00. Found: C, 34.01; H, 4.34, N, 0.03. ^1H NMR (600 MHz, CD_3CN): δ 1.67–1.78 (m, 1H, [14]aneS4), 1.78–1.86 (m, 1H, [14]aneS4), 2.06–2.15 (m, 1H, [14]aneS4), 2.18–2.27 (m, 1H, [14]aneS4), 2.27–2.46 (m, 4H, [14]aneS4), 2.50–2.60 (m, 1H, [14]aneS4), 2.68–2.79 (m, 1H, [14]aneS4), 2.80–2.89 (m, 1H, [14]aneS4), 2.89–2.97 (m, 1H, [14]aneS4), 2.98–3.06 (m, 1H, [14]aneS4), 3.06–3.16 (m, 2H, [14]aneS4), 3.16–3.25 (m, 2H, [14]aneS4), 3.33–3.39 (m, 1H, [14]aneS4), 3.41–3.49 (m, 1H, [14]aneS4), 3.57–3.65 (m, 1H, [14]aneS4), 4.05 (s, 3H, CH_3), 6.76 (s, 1H, H_a), 7.12–7.16 (m, 1H, H_e), 7.61–7.65 (m, 1H, H_d), 7.69–7.71 (m, 1H, H_f). ^{13}C NMR (150 MHz, CD_3CN): δ 24.89, 25.39, 31.60, 32.32, 32.75, 32.81, 34.12, 35.24, 35.30, 39.22 (C on [14]aneS4), 59.00 (C on CH_3), 107.40 (C_a), 129.23 (C_e), 130.51 (C_f), 132.42 (C_d), 143.24 (C_c), 193.46 (C_b), 260.25 (Ru–C). IR (KBr, cm^{-1}): $\nu_{C=O}$ = 1639. ESI-MS: m/z 537.2 [**7**]$^+$.

UV-Visible Spectroscopy

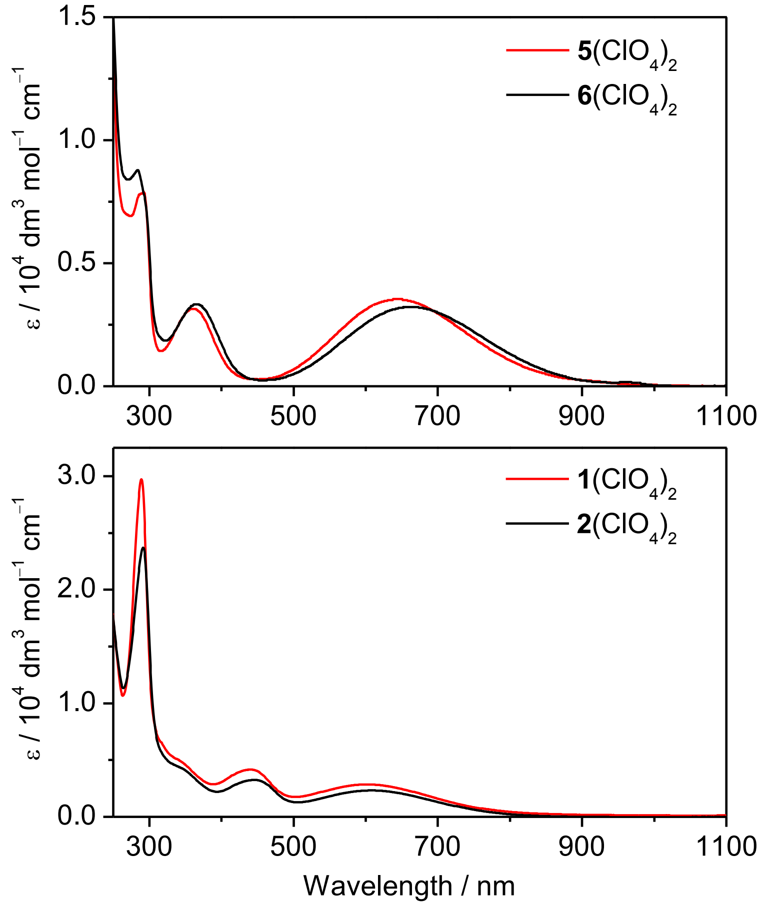


Fig. S1 UV-Visible absorption spectra of selected complexes in CH_3CN at 298 K.

Table S1 UV-Visible absorption data for **1**(ClO_4)$_2$, **2**(ClO_4)$_2$, **5**(ClO_4)$_2$, and **6**(ClO_4)$_2$ in CH_3CN at 298 K.

	λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})
1(ClO_4)$_2$	289 (29710), 351 (sh, 4450), 440 (4100), 602 (2810)
2(ClO_4)$_2$	291 (23710), 341 (sh, 4100), 446 (3130), 608 (2260)
5(ClO_4)$_2$	293 (7660), 362 (3100), 643 (3460)
6(ClO_4)$_2$	284 (8320), 365 (3130), 663 (3120)

Electrochemistry

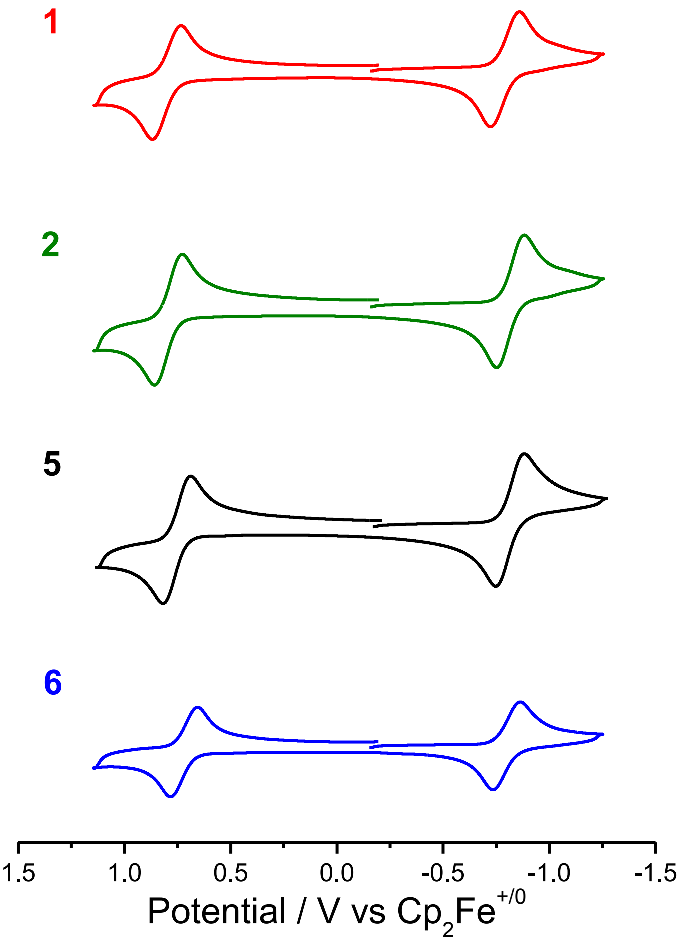


Fig. S2 Cyclic voltammograms for **1**$(ClO_4)_2$, **2**$(ClO_4)_2$, **5**$(ClO_4)_2$, and **6**$(ClO_4)_2$ (supporting electrolyte: 0.1M $[Bu_4N]PF_6$ in CH_3CN; 298 K; scan rate = 100 mV s^{-1}).

Table S2. Electrochemical data for **1**$(ClO_4)_2$, **2**$(ClO_4)_2$, **5**$(ClO_4)_2$, and **6**$(ClO_4)_2$ (supporting electrolyte: 0.1M $[Bu_4N]PF_6$ in CH_3CN; 298 K; scan rate = 100 mV s^{-1}).

	$E_{1/2}{}^{a}$ / V vs $Cp_2Fe^{+/0}$	
	Reduction	Oxidation
1$(ClO_4)_2$	–0.79	0.80
2$(ClO_4)_2$	–0.82	0.79
5$(ClO_4)_2$	–0.82	0.75
6$(ClO_4)_2$	–0.80	0.72

[a] $E_{1/2} = (E_{pc} + E_{pa})/2$ at 298 K for reversible couples.

Cytotoxicity activity in vitro by MTT assay

The cytotoxicity of all indolizinone complexes and cisplatin in this work against A549, HepG2, HT1080, MCF-7, and HeLa cancer cells was evaluated using the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay.[4] Briefly, cells (A549, HepG2, HT1080, MCF-7 and HeLa) were seeded at a specific amount (14000 cells per well for A549; 20000 cells per well for HepG2; 5000 cells per well for HT1080; 10000 cells per well for MCF-7; 4000 cells per well for HeLa) in a 96-well culture microplate using 100 μL 10% Fetal Bovine Serum (FBS) and 1% Penicillin Streptomycin (PS) Minimum Essential Medium (MEM) supplemented with 10 mM N-(2-Hydroxyethyl)piperazine-N'-(2-ethanesulfonic acid) (HEPES, for A549 cells) or 100 μL 10% FBS and 1% PS Dulbecco's Modified Eagle's Medium (DMEM, for HepG2, HT1080, MCF-7 and HeLa cells) as culture solution and incubated for 24 hr at 37 °C, 5% CO_2, 95% air in a humidified incubator. Stock solutions of all indolizinone complexes (20 mM) and cisplatin (5 mM) were prepared using DMSO and 0.9% (w/v) saline solution as solvent respectively. Serial dilutions (1.53 nM–400 μM) of indolizinone complexes and (0.95 nM–250 μM) of cisplatin in 100 μL 1% FBS and 1% PS MEM supplemented with HEPES or DMEM were then added to each well and the microplate was incubated at 37 °C, 5% CO_2, 95% air in a humidified incubator for 48 hr. Afterwards, the complex-containing culture medium was replaced by MTT reagent (5 mg/mL in Phosphate Buffered Saline (PBS)) and the microplate was incubated at 37 °C, 5% CO_2, 95% air in a humidified incubator for 4 hr. Upon incubation, the PBS medium was replaced by 100 μL of DMSO and the microplate was shaken at room temperature for 150 s. The absorbance values of supernatant were measured at 570 nm using a microplate reader. The cytotoxicity of each complex and cisplatin, expressed as IC_{50}, was determined by the surviving cells curve after exposure to complexes for 48 hr (Fig. S3–S7). Each experiment was repeated three times to obtain the mean values.

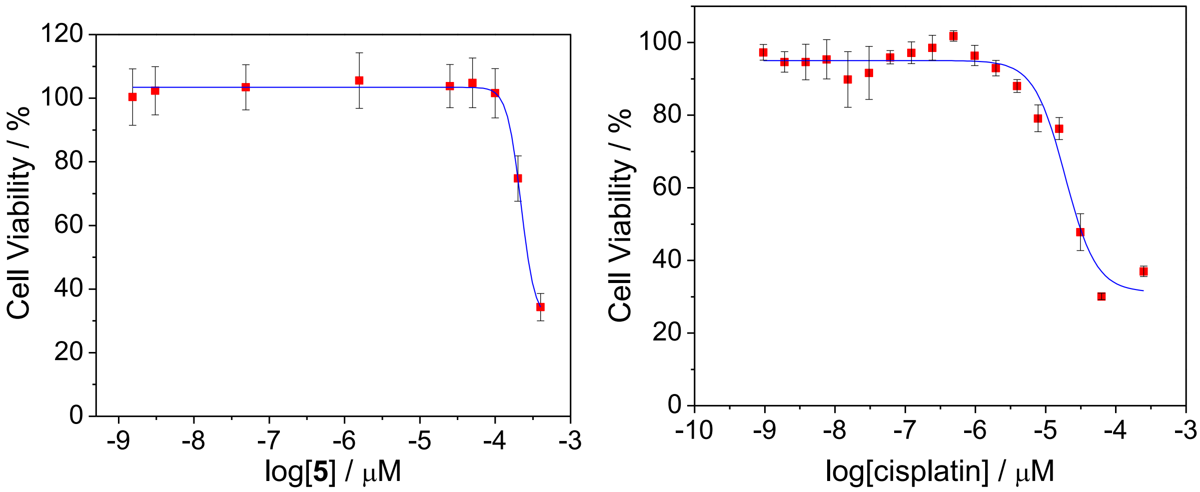


Fig. S3 Dose response analysis of cell viability of **5**($(ClO_4)_2$) and cisplatin against A549 cells. Data are expressed as the mean±SD in triplicate.

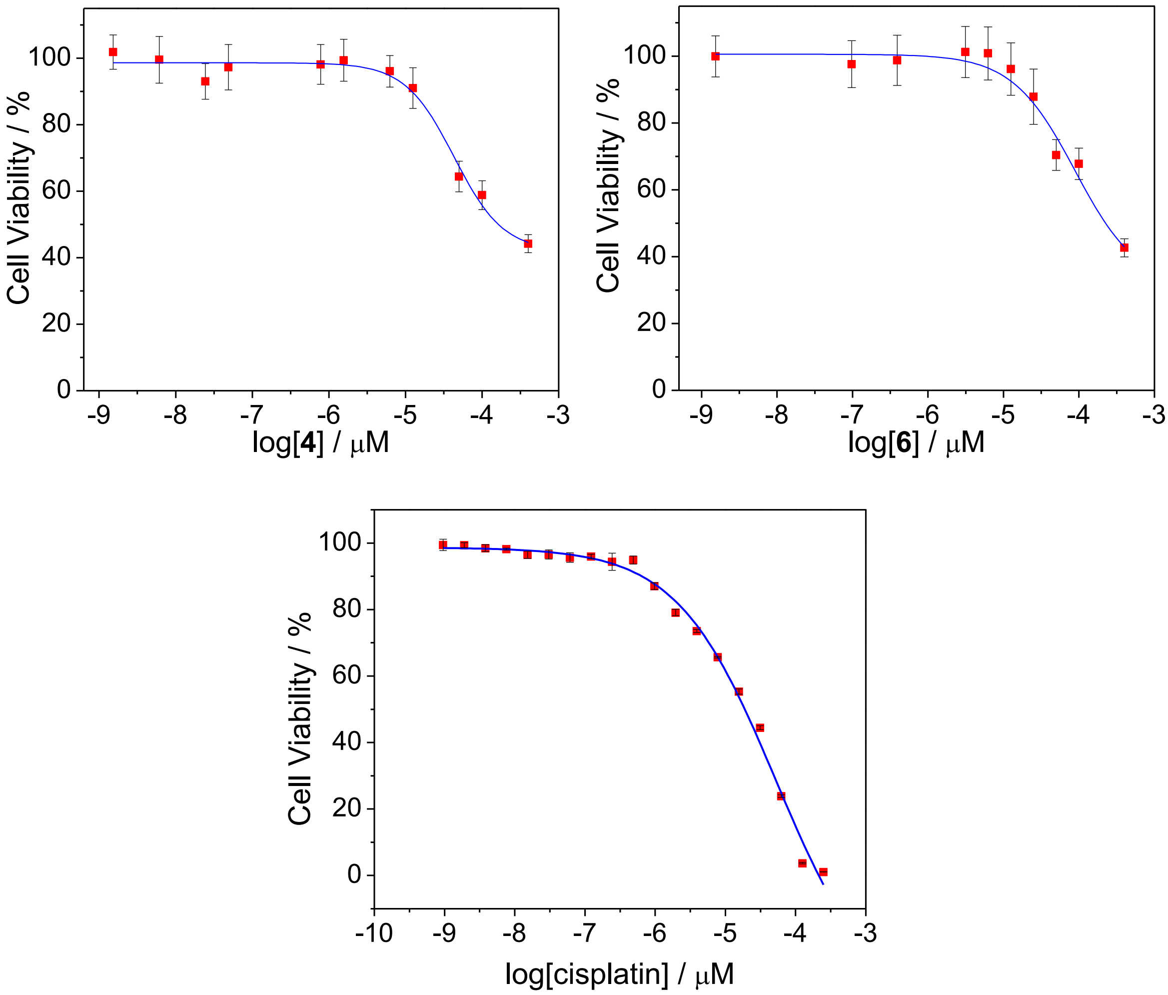


Fig. S4 Dose response analysis of cell viability of **4**((ClO_4)), **6**($(ClO_4)_2$) and cisplatin against HepG2 cells. Data are expressed as the mean±SD in triplicate.

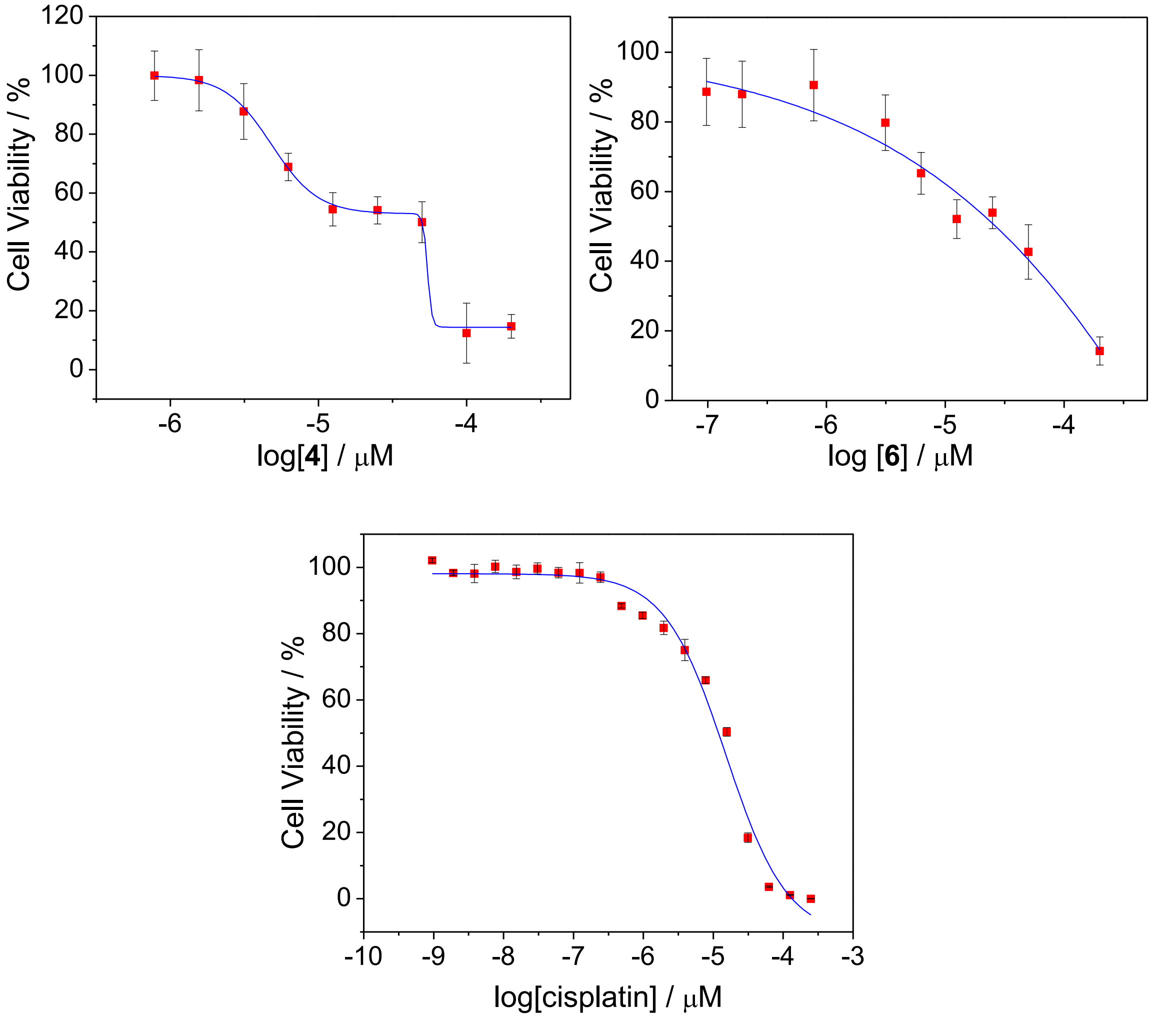


Fig. S5 Dose response analysis of cell viability of **4**(ClO_4), **6**(ClO_4)$_2$ and cisplatin against HT1080 cells. Data are expressed as the mean±SD in triplicate.

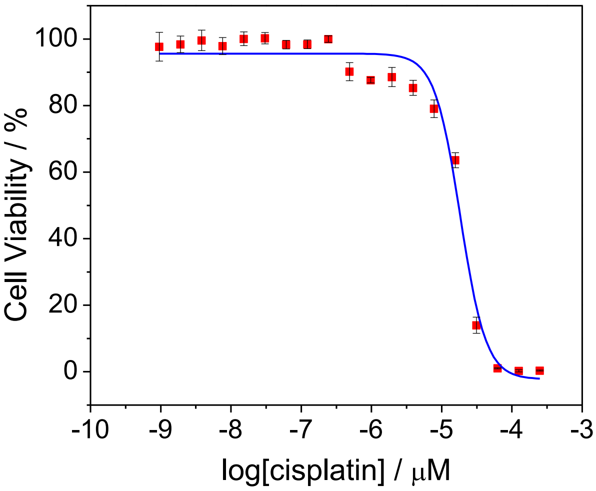


Fig. S6 Dose response analysis of cell viability of cisplatin against HeLa cells. Data are expressed as the mean±SD in triplicate.

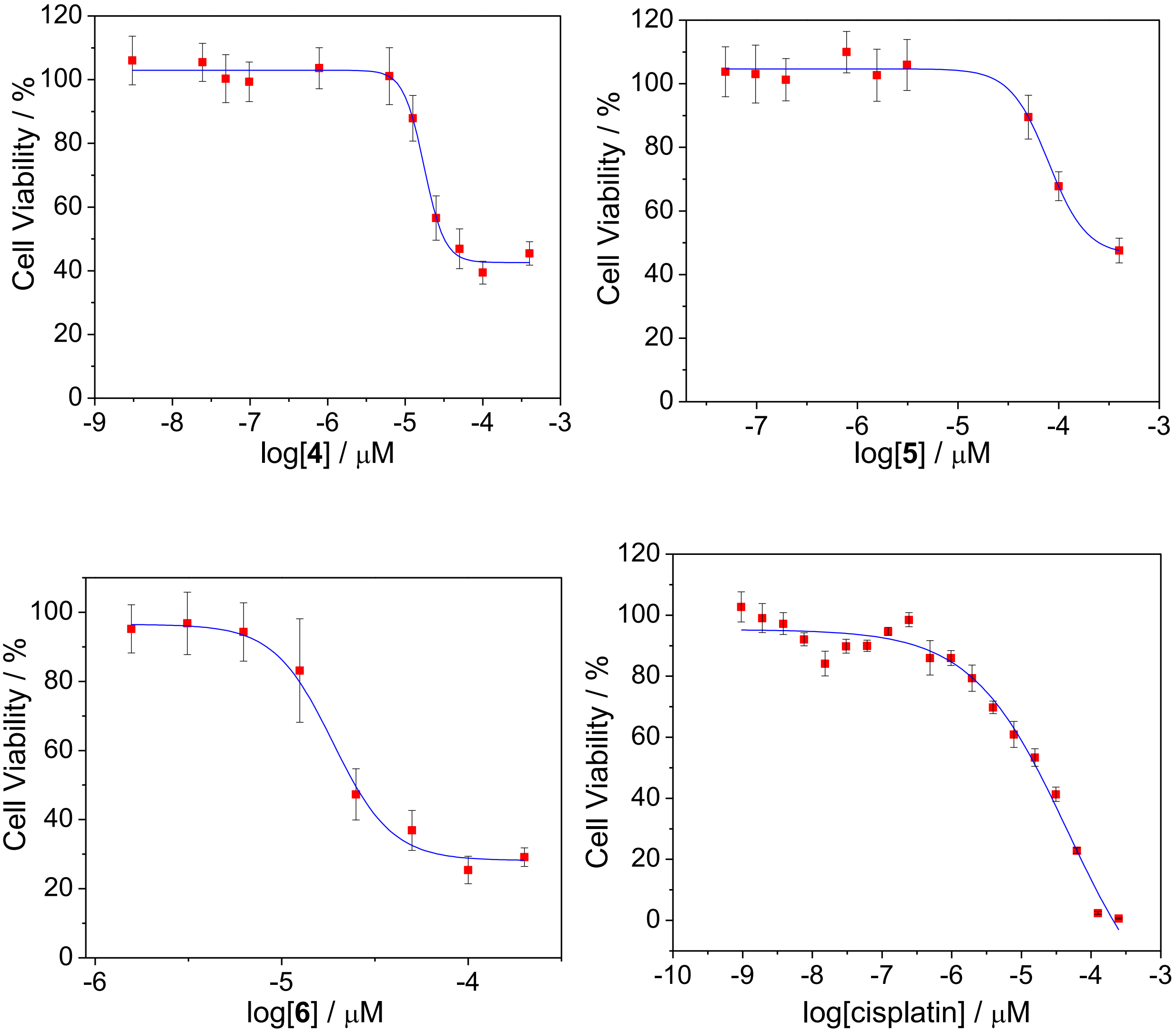


Fig. S7 Dose response analysis of cell viability of **4**(ClO_4), **5**(ClO_4)$_2$, **6**(ClO_4)$_2$ and cisplatin against MCF-7 cells. Data are expressed as the mean±SD in triplicate.

X-Ray Crystallography

X-ray diffraction data were collected on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer with Mo or Cu Kα radiations. Using Olex2,[5] the structure was solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the ShelXL[7] refinement package using Least Squares minimization. CCDC 1832533–1832537 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

1(ClO_4)$_2$: Single crystals of **1**(ClO_4)$_2$ were obtained by slow diffusion of Et_2O into a CH_3CN solution of **1**(ClO_4)$_2$.

Cyrstal Data for **1**(ClO_4)$_2$ ($C_{24}H_{25}Cl_2N_3O_9RuS_3$; M = 767.62 g/mol): triclinic, space group *P-1* (no. 2), a = 12.9174(7) Å, b = 13.5973(8) Å, c = 21.5012(10) Å, α = 76.549(4)°, β = 78.742(4)°, γ = 65.660(5)°, V = 3325.4(3) Å^3, Z = 4, T = 173(2) K, μ(Mo Kα) = 0.870 mm^{-1}, $Dcalc$ = 1.533 g/cm^3, 31577 reflections measured (6.062° ≤ 2Θ ≤ 58.274°), 15321 unique (R_{int} = 0.0316, R_{sigma} = 0.0512) which were used in all calculations. The final R_1 was 0.0449 ($I > 2\sigma(I)$) and wR_2 was 0.1127 (all data).

(CCDC 1832534)

2(ClO_4)$_2$·(CH_3CN)$_2$: Single crystals of **2**(ClO_4)$_2$·(CH_3CN)$_2$ were obtained by slow diffusion of Et_2O into a CH_3CN solution of **2**(ClO_4)$_2$.

Cyrstal Data for **2**(ClO_4)$_2$·(CH_3CN)$_2$ ($C_{34}H_{35}Cl_2N_5O_9RuS_3$; M =925.82 g/mol): monoclinic, space group *P2₁/c* (no. 14), a = 14.0052(2) Å, b = 14.0258(2) Å, c = 20.0904(3) Å, β = 106.910(2)°, V = 3775.81(10) Å^3, Z = 4, T = 133(2) K, μ(CuKα) = 6.735 mm^{-1}, $Dcalc$ = 1.629 g/cm^3, 14616 reflections measured (6.596° ≤ 2Θ ≤ 143.544°), 7179 unique (R_{int} = 0.0191, R_{sigma} = 0.0214) which were used in all calculations. The final R_1 was 0.0344 (I > 2σ(I)) and wR_2 was 0.0875 (all data).

(CCDC 1832536)

4(ClO_4): Single crystals of **4**(ClO_4) were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **4**(ClO_4) under argon.

Cyrstal Data for **4**(ClO_4)·($C_{24}H_{29}Cl_2NO_5RuS_4$; M =711.69 g/mol): monoclinic, space group *P2₁/c* (no. 14), a = 10.07100(10) Å, b = 19.7495(2) Å, c = 13.70510(10) Å, β = 92.1070(10)°, V = 2724.06(4) Å^3, Z = 4, T = 193(2) K, μ(CuKα) = 9.652 mm^{-1}, $Dcalc$ = 1.735 g/cm^3, 11905 reflections measured (7.856° ≤ 2Θ ≤

143.596°), 5230 unique (R_{int} = 0.0293, R_{sigma} = 0.0321) which were used in all calculations. The final R_1 was 0.0319 ($I > 2\sigma(I)$) and wR_2 was 0.0867 (all data).

(CCDC 1832535)

6$(ClO_4)_2 \cdot (CH_3CN)_2$: Single crystals of **6**$(ClO_4)_2 \cdot (CH_3CN)_2$ were obtained by slow diffusion of Et_2O into a CH_3CN solution of **6**$(ClO_4)_2$.

Crystal Data for **6**$(ClO_4)_2 \cdot (CH_3CN)_2$ ($C_{30}H_{38}Cl_2N_4O_9RuS_4$; M =898.85 g/mol): triclinic, space group *P-1* (no. 2), a = 9.5445(4) Å, b = 15.1103(6) Å, c = 15.3485(5) Å, α = 100.172(3)°, β = 106.850(3)°, γ = 108.038(4)°, V = 1926.19(14) Å^3, Z = 2, T = 193.00(14) K, $\mu(CuK\alpha)$ = 7.062 mm^{-1}, $Dcalc$ = 1.550 g/cm^3, 13754 reflections measured (6.434° ≤ 2Θ ≤ 143.31°), 7320 unique (R_{int} = 0.0598, R_{sigma} = 0.0562) which were used in all calculations. The final R_1 was 0.0571 ($I > 2\sigma(I)$) and wR_2 was 0.1656 (all data).

(CCDC 1832537)

7(ClO_4): Single crystals of **7**(ClO_4) were obtained by slow diffusion of Et_2O into a CH_3CN solution of **7**(ClO_4).

Crystal Data for **7**$(ClO_4)_2 \cdot (C_{18}H_{27}ClO_6RuS_5$; M =636.21 g/mol): triclinic, space group *P-1* (no. 2), a = 8.9651(4) Å, b = 11.5193(6) Å, c = 13.0076(7) Å, α = 76.314(4)°, β = 73.637(5)°, γ = 80.380(4)°, V = 1245.02(12) Å^3, Z = 2, T = 193(2) K, $\mu(CuK\alpha)$ = 10.289 mm^{-1}, $Dcalc$ = 1.697 g/cm^3, 7842 reflections measured (7.23° ≤ 2Θ ≤ 143.474°), 4572 unique (R_{int} = 0.0418, R_{sigma} = 0.0365) which were used in all calculations. The final R_1 was 0.0528 ($I > 2\sigma(I)$) and wR_2 was 0.1485 (all data).

(CCDC 1832533)

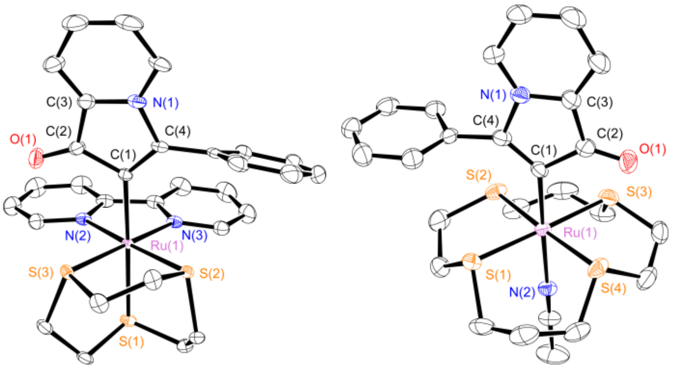
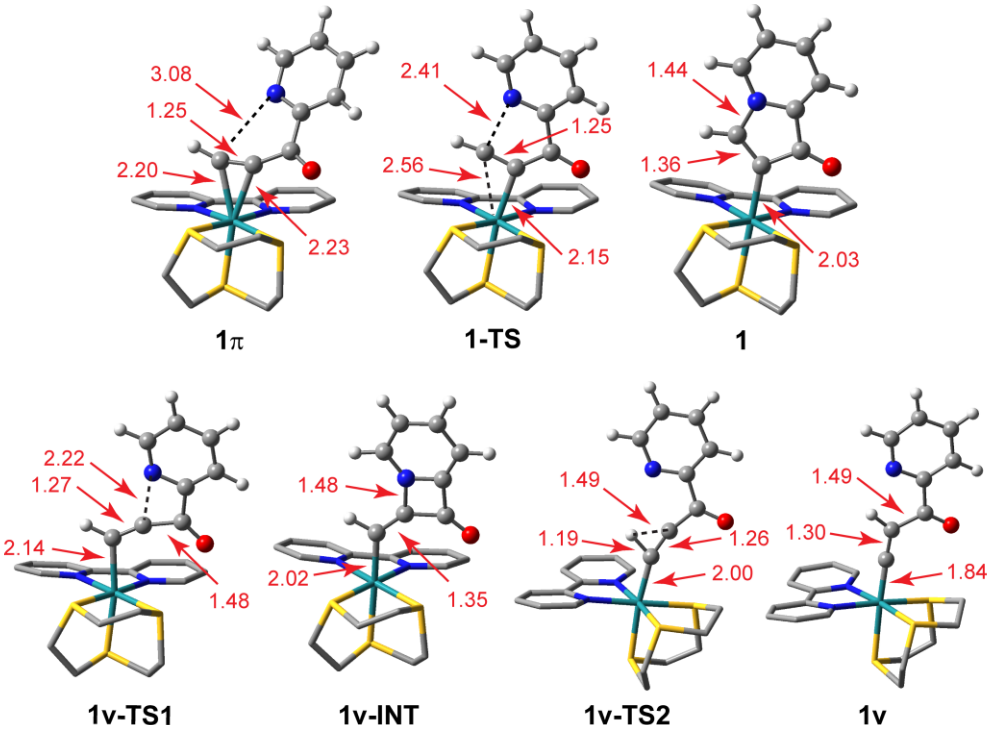


Fig. S8 Perspective view of cations **2** (left) and **6** (right) as represented by 50% probability ellipsoids; hydrogen atoms are omitted for clarity.

Computational Methodology

The reaction pathways for the {[Ru([9]aneS3)(bpy)]$^{2+}$ + HC≡C(C=O)(2-py)} system, together with the UV-visible absorption spectrum of **5** (the first 80th vertical transitions), were modelled by Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) calculations respectively using the ORCA software package (versions 3.0.2 and 3.0.3)[8]. All the calculated structures were optimized in the gas phase using the PBE0 functional.[9] The def2-SVP basis sets were used for the H, C, N, and O atoms, while the def2-TZVP(-f) basis sets were used for the S and Ru atoms.[10] Relativistic effects were treated using the zeroth-order regular approximation (ZORA).[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 on the reaction pathway calculations were accounted for using the semiempirical van der Waals corrections by Grimme.[13] Tight SCF convergence criteria (1×10^{-8} E_h in energy, 1×10^{-7} E_h in the density change, and 5×10^{-7} in the DIIS error) 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 (THF or CH_3CN) on the energies of the optimized structures and vertical transitions was treated by the employment of the conductor-like screening model (COSMO).[14]



1π **1-TS** **1**

1v-TS1 **1v-INT** **1v-TS2** **1v**

Fig. S9 Selected bond lengths (Å) for DFT-optimized intermediates and transition states; hydrogen atoms on [9]aneS3 and bpy are omitted for clarity.

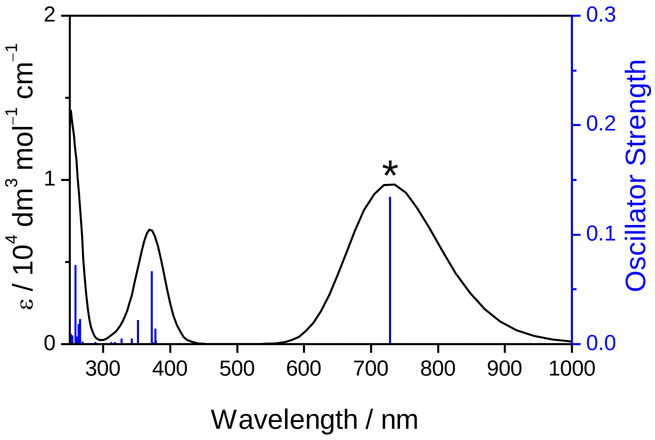


Fig. S10 Calculated absorption spectrum for **5** from TD-DFT/COSMO calculations. Excitation energies and oscillator strengths are shown by the blue vertical lines; spectra (in black) are convoluted with Gaussian function having full width half maximum of 3000 cm^{-1}. See Fig. 4 for the electronic difference density plot for the labelled vertical transitions.

Table S3 Calculated vertical transition energies (λ > 300 nm) for **5** (gas phase optimized geometries with COMSO to model solvation in CH_3CN).[a]

Calculated λ / nm	Experimental λ / nm	Oscillator Strength	Major Contribution[b]
372.8	362	6.645e-02	56.4% HOMO => L+1, 25.8% H-4 => LUMO
728.1	643	1.346e-01	96.0% HOMO => LUMO

[a] Only excitations with oscillator strengths > 5 × 10^{-2} are listed. [b] Only contributions > 10% are listed.

Table S4 Compositions of HOMO and LUMO for **5** (gas phase optimized geometries with COMSO to model solvation in CH_3CN).

Molecular Orbital	Ru	Indolizinone	[14]aneS4	CH_3CN
HOMO	51.83	21.53	22.85	3.80
LUMO	2.95	91.67	5.03	0.35

Table S5 Characterization of the DFT-optimized geometries (by frequency calculations, only the first 10 frequencies are listed for each geometry).

Structure	Vibrational Frequencies[a]			
1-π	0:	0.00 cm**-1	5:	0.00 cm**-1
	1:	0.00 cm**-1	6:	8.71 cm**-1
	2:	0.00 cm**-1	7:	32.81 cm**-1
	3:	0.00 cm**-1	8:	41.89 cm**-1
	4:	0.00 cm**-1	9:	56.47 cm**-1
1-TS	0:	0.00 cm**-1	5:	0.00 cm**-1
	1:	0.00 cm**-1	6:	-284.00 cm**-1 ***imaginary mode***
	2:	0.00 cm**-1	7:	14.04 cm**-1
	3:	0.00 cm**-1	8:	18.74 cm**-1
	4:	0.00 cm**-1	9:	39.63 cm**-1
1	0:	0.00 cm**-1	5:	0.00 cm**-1
	1:	0.00 cm**-1	6:	24.82 cm**-1
	2:	0.00 cm**-1	7:	28.48 cm**-1
	3:	0.00 cm**-1	8:	39.80 cm**-1
	4:	0.00 cm**-1	9:	45.52 cm**-1
1v-TS1	0:	0.00 cm**-1	5:	0.00 cm**-1
	1:	0.00 cm**-1	6:	-159.09 cm**-1 ***imaginary mode***
	2:	0.00 cm**-1	7:	19.10 cm**-1
	3:	0.00 cm**-1	8:	27.36 cm**-1
	4:	0.00 cm**-1	9:	38.83 cm**-1
1v-INT	0:	0.00 cm**-1	5:	0.00 cm**-1
	1:	0.00 cm**-1	6:	25.30 cm**-1
	2:	0.00 cm**-1	7:	34.69 cm**-1
	3:	0.00 cm**-1	8:	42.96 cm**-1
	4:	0.00 cm**-1	9:	47.58 cm**-1
1v-TS2	0:	0.00 cm**-1	5:	0.00 cm**-1
	1:	0.00 cm**-1	6:	-664.23 cm**-1 ***imaginary mode***
	2:	0.00 cm**-1	7:	20.30 cm**-1
	3:	0.00 cm**-1	8:	33.17 cm**-1
	4:	0.00 cm**-1	9:	42.18 cm**-1
1v	0:	0.00 cm**-1	5:	0.00 cm**-1
	1:	0.00 cm**-1	6:	12.30 cm**-1
	2:	0.00 cm**-1	7:	23.61 cm**-1
	3:	0.00 cm**-1	8:	32.78 cm**-1
	4:	0.00 cm**-1	9:	41.82 cm**-1
5	0:	0.00 cm**-1	5:	0.00 cm**-1
	1:	0.00 cm**-1	6:	25.79 cm**-1
	2:	0.00 cm**-1	7:	33.09 cm**-1
	3:	0.00 cm**-1	8:	42.25 cm**-1
	4:	0.00 cm**-1	9:	51.52 cm**-1

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

Table S6 Cartesian coordinates of **1-π** at the PBE0 optimized geometry.

	Coordinates in Å		
	X	Y	Z
C	10.075878	11.209293	19.640155
C	10.512888	11.258996	21.043104
C	9.734086	12.194694	21.905172
N	8.735323	12.883139	21.335325
C	9.255180	11.351925	18.714198
H	8.311691	11.523667	18.220439
C	8.028424	13.706510	22.100551
H	7.208344	14.250825	21.621395
C	8.299662	13.896035	23.461554
H	7.692113	14.588468	24.045300
C	9.350322	13.183955	24.046565
H	9.593502	13.313368	25.100168
C	10.084891	12.300287	23.254967
H	10.905050	11.698256	23.651563
C	9.225492	11.958013	15.492522
H	8.971934	10.900374	15.467858
C	8.604903	12.845470	14.625155
H	7.880244	12.478244	13.901202
C	8.931834	14.198073	14.713752
H	8.475720	14.927572	14.047490
C	9.843315	14.604456	15.680977
H	10.108429	15.654450	15.770309
C	10.420250	13.660077	16.533533
C	11.347439	14.010558	17.619856
C	11.652791	15.324660	17.982100
H	11.204290	16.159909	17.451860
C	12.521276	15.562102	19.042752
H	12.770215	16.579710	19.339793
C	13.055521	14.473291	19.726276
H	13.728262	14.606378	20.570746
C	12.697328	13.192515	19.325352
H	13.066712	12.321763	19.862613
C	14.313311	10.514304	16.854348
H	15.079564	10.225671	16.123984
H	14.612838	11.481817	17.275381
C	14.143170	9.463005	17.922144
H	15.042673	9.411725	18.547556
H	13.990621	8.465842	17.498016
C	11.937068	8.264472	19.261736
H	12.664934	7.560388	19.683083
H	11.191021	8.464412	20.039157
C	11.327582	7.714834	17.991518
H	10.642992	6.892033	18.226298
H	12.087704	7.320260	17.308448

C	11.007404	8.763407	15.378885
H	10.876716	7.715233	15.081661
H	10.341750	9.351809	14.738244
C	12.447099	9.195702	15.220280
H	12.712364	9.256770	14.157663
H	13.134893	8.483787	15.684386
N	10.123533	12.345076	16.410010
N	11.873076	12.962490	18.293455
O	11.441478	10.584139	21.451424
Ru	11.190723	11.074221	17.713469
S	12.765952	10.860700	15.950559
S	12.751291	9.878464	19.049669
S	10.339644	8.973903	17.067214

Table S7 Cartesian coordinates of **1-TS** at the PBE0 optimized geometry.

	Coordinates in Å		
	X	Y	Z
C	10.431334	11.801858	19.634125
C	10.873459	11.955662	21.041398
C	9.705977	12.131504	21.964524
N	8.499457	12.183577	21.406695
C	9.280705	11.901583	19.145107
H	8.351419	11.954498	18.606278
C	7.430283	12.287613	22.180589
H	6.458571	12.328639	21.687807
C	7.529055	12.338134	23.576352
H	6.627949	12.411390	24.181329
C	8.790360	12.296663	24.163145
H	8.902782	12.339633	25.245375
C	9.911843	12.197303	23.340822
H	10.924799	12.158990	23.736065
C	9.195164	12.179005	15.705061
H	8.805364	11.179853	15.887662
C	8.623561	12.988136	14.734073
H	7.791155	12.616631	14.140399
C	9.142813	14.268096	14.544334
H	8.736346	14.928311	13.780462
C	10.184712	14.692305	15.359784
H	10.606119	15.685456	15.231118
C	10.700285	13.831037	16.332453
C	11.763267	14.210043	17.275096
C	12.188925	15.525169	17.468464
H	11.743377	16.335287	16.897903
C	13.164418	15.796960	18.423206
H	13.501036	16.817355	18.596931
C	13.693752	14.741082	19.159457
H	14.452966	14.903164	19.921351
C	13.217765	13.456779	18.925134
H	13.565606	12.617774	19.522069
C	14.243968	10.279272	16.646150
H	14.866058	9.791881	15.885078
H	14.718094	11.237305	16.890856
C	14.081347	9.398393	17.861881
H	15.036771	9.292383	18.388312
H	13.748845	8.391871	17.589989
C	11.912068	8.678075	19.567061
H	12.584845	7.939132	20.018547
H	11.274394	9.066827	20.369265
C	11.096959	8.058823	18.455397
H	10.345172	7.376968	18.869686
H	11.720712	7.476885	17.768685

C	10.615915	8.820014	15.756929
H	10.336730	7.767155	15.624077
H	9.940664	9.403248	15.120948
C	12.060837	9.054061	15.385918
H	12.192241	8.972383	14.300281
H	12.718429	8.312046	15.847606
N	10.223793	12.571923	16.470196
N	12.277355	13.194922	18.006705
O	12.021539	11.912909	21.408416
Ru	11.353218	11.338206	17.745908
S	12.652479	10.733411	15.877189
S	12.889494	10.129598	19.056851
S	10.185451	9.324217	17.462002

Table S8 Cartesian coordinates of **1** at the PBE0 optimized geometry.

		Coordinates in Å	
	X	Y	Z
C	10.354629	11.744666	19.503958
C	9.014656	11.802406	19.712089
H	8.180937	11.677358	19.027293
C	9.814399	12.170062	21.827100
C	10.956719	12.006531	20.857898
C	7.466817	12.135583	21.651290
H	6.603803	12.034948	20.996825
C	7.363626	12.332942	23.029002
H	6.376537	12.395906	23.481918
C	8.513564	12.442430	23.802981
H	8.437682	12.591908	24.878732
C	9.774289	12.365789	23.183959
H	10.706540	12.452591	23.739272
C	9.093616	12.212035	16.055921
H	8.732006	11.205409	16.255808
C	8.404503	13.048736	15.189425
H	7.504847	12.692404	14.693115
C	8.896961	14.334513	14.974542
H	8.397903	15.017700	14.290090
C	10.034208	14.736167	15.664142
H	10.430501	15.736905	15.517522
C	10.669734	13.846757	16.534442
C	11.838681	14.203129	17.354058
C	12.318931	15.507833	17.484391
H	11.850576	16.323528	16.941135
C	13.385704	15.765217	18.339335
H	13.761953	16.778727	18.465437
C	13.961811	14.703004	19.029597
H	14.800240	14.852656	19.705875
C	13.439135	13.427940	18.851179
H	13.838998	12.580737	19.400841
C	14.293451	10.231902	16.605153
H	14.898459	9.730892	15.839409
H	14.789984	11.181402	16.839528
C	14.146439	9.356211	17.828240
H	15.113968	9.230291	18.327217
H	13.786289	8.356977	17.564689
C	12.022337	8.645116	19.577105
H	12.703009	7.887514	19.982886
H	11.421675	9.023520	20.411981
C	11.151224	8.061000	18.487760
H	10.401423	7.388235	18.919601
H	11.738795	7.475607	17.772665
C	10.607458	8.866425	15.818014

H	10.290183	7.825692	15.675720
H	9.937066	9.484821	15.210363
C	12.049062	9.059179	15.407531
H	12.144485	8.955863	14.320177
H	12.697813	8.302721	15.859166
N	8.679217	12.050237	21.094645
N	10.212897	12.581650	16.692376
N	12.400429	13.180810	18.041612
O	12.116061	12.060231	21.179566
Ru	11.436097	11.339463	17.828888
S	12.699585	10.720520	15.866150
S	12.994667	10.099126	19.057801
S	10.235419	9.359878	17.541189

Table S9 Cartesian coordinates of **1v-TS1** at the PBE0 optimized geometry.

	Coordinates in Å		
	X	Y	Z
C	8.950656	12.138635	19.484466
C	9.368109	12.315038	20.896924
C	8.106819	12.438746	21.644433
N	7.132329	12.409480	20.731293
C	8.974849	11.907201	18.237077
H	8.161234	11.904090	17.515132
C	5.870213	12.491607	21.123588
H	5.095337	12.469855	20.357914
C	5.547519	12.593582	22.484042
H	4.504109	12.648189	22.789544
C	6.567256	12.619353	23.434222
H	6.326163	12.696115	24.493349
C	7.896448	12.546459	23.011512
H	8.735850	12.567499	23.703905
C	9.644218	12.181771	14.781246
H	9.164974	11.209800	14.875245
C	9.488502	12.934965	13.625354
H	8.895223	12.545324	12.801289
C	10.113430	14.178277	13.553376
H	10.038538	14.791249	12.657242
C	10.822964	14.633793	14.658176
H	11.302955	15.607455	14.631022
C	10.930780	13.827610	15.794003
C	11.630178	14.235809	17.021769
C	12.108462	15.528448	17.240892
H	11.995536	16.292575	16.476686
C	12.710525	15.842264	18.455280
H	13.082975	16.847155	18.645139
C	12.822420	14.848129	19.421589
H	13.279845	15.045251	20.388328
C	12.330177	13.579258	19.138657
H	12.363407	12.792003	19.886884
C	13.993431	10.322746	17.711229
H	14.857720	9.792430	17.292418
H	14.360720	11.282733	18.092370
C	13.325618	9.506685	18.793713
H	13.967227	9.460603	19.681520
H	13.141739	8.476866	18.469952
C	10.667822	8.752616	19.378518
H	11.132226	8.024704	20.054570
H	9.742773	9.095927	19.856533
C	10.402519	8.138064	18.022330
H	9.561679	7.437979	18.079459
H	11.268657	7.578308	17.653142

C	11.043705	8.899247	15.374830
H	10.827924	7.850845	15.134894
H	10.703670	9.496771	14.521725
C	12.515056	9.102531	15.645375
H	13.088618	9.010163	14.716342
H	12.904379	8.355308	16.343092
N	10.370808	12.596701	15.827698
N	11.744475	13.277706	17.971909
O	10.508360	12.339925	21.282731
Ru	10.918270	11.420749	17.472778
S	12.876044	10.775856	16.337976
S	11.723008	10.243386	19.329457
S	9.957605	9.405864	16.756233

Table S10 Cartesian coordinates of **1v-INT** at the PBE0 optimized geometry.

	Coordinates in Å		
	X	Y	Z
C	10.138050	12.195267	20.866821
C	11.252984	12.420898	21.843726
C	10.189296	12.567681	22.933844
N	9.209270	12.409361	22.001438
C	9.904307	11.884859	19.577719
H	8.832021	11.837375	19.331633
C	7.912694	12.439967	22.278264
H	7.198842	12.307252	21.467487
C	7.550234	12.622815	23.619875
H	6.495247	12.643075	23.886907
C	8.528297	12.764928	24.600676
H	8.230563	12.896973	25.640227
C	9.897579	12.750556	24.260378
H	10.683536	12.868253	25.003183
C	8.816234	12.180685	16.211252
H	8.452822	11.205337	16.532952
C	8.131905	12.908801	15.249005
H	7.226757	12.502256	14.802566
C	8.640583	14.148448	14.871557
H	8.142718	14.747307	14.111553
C	9.795353	14.617426	15.492673
H	10.197486	15.586722	15.217445
C	10.432083	13.832835	16.458605
C	11.625926	14.254584	17.214823
C	12.259048	15.484644	17.037534
H	11.928350	16.169945	16.262578
C	13.321560	15.833328	17.864003
H	13.825726	16.787869	17.734701
C	13.719310	14.943485	18.860842
H	14.531139	15.181201	19.544065
C	13.066096	13.722276	18.968382
H	13.342406	13.000239	19.736007
C	14.201619	10.612832	17.068333
H	14.904376	10.148810	16.365001
H	14.589123	11.611644	17.300033
C	14.055397	9.770851	18.314974
H	14.983650	9.789399	18.897321
H	13.848852	8.723905	18.065744
C	11.849935	8.844119	19.842080
H	12.560374	8.147484	20.304220
H	11.142807	9.156595	20.619721
C	11.134572	8.195276	18.681967
H	10.442564	7.425031	19.043522
H	11.833711	7.704736	17.996368

C	10.669545	8.971839	16.011588
H	10.410223	7.920716	15.827302
H	10.020831	9.574122	15.365235
C	12.128292	9.232729	15.716812
H	12.317740	9.122456	14.642383
H	12.778099	8.517833	16.232170
N	9.943202	12.616839	16.788824
N	12.061194	13.375932	18.152576
O	12.442344	12.486725	21.833013
Ru	11.167809	11.500387	18.051534
S	12.628356	10.936037	16.203654
S	12.714432	10.393126	19.417540
S	10.146724	9.415921	17.707702

Table S11 Cartesian coordinates of **1v-TS2** at the PBE0 optimized geometry.

		Coordinates in Å	
	X	Y	Z
C	9.726654	11.533186	20.574155
C	9.393113	11.045670	21.918008
C	8.317097	11.778011	22.595075
N	7.838092	12.791718	21.850908
C	10.128945	11.626619	19.381588
H	9.182528	12.342945	19.453159
C	6.868420	13.541220	22.362368
H	6.486254	14.366499	21.747747
C	6.342733	13.301251	23.641205
H	5.548725	13.943695	24.025478
C	6.842923	12.235136	24.402129
H	6.443208	12.024995	25.393535
C	7.864925	11.443988	23.870670
H	8.305363	10.599007	24.411808
C	8.950958	11.891746	15.868258
H	8.645044	10.895498	16.182452
C	8.232668	12.583761	14.901613
H	7.368719	12.119189	14.432198
C	8.648454	13.867512	14.555349
H	8.121186	14.438188	13.792903
C	9.737406	14.421189	15.219477
H	10.060233	15.429925	14.977879
C	10.406992	13.674324	16.192684
C	11.501605	14.200286	17.023914
C	11.944087	15.523453	16.970497
H	11.534964	16.213446	16.237592
C	12.900997	15.964144	17.878251
H	13.252757	16.993597	17.850253
C	13.388752	15.070661	18.829260
H	14.121677	15.376291	19.572921
C	12.922671	13.761619	18.813557
H	13.277462	13.032683	19.539550
C	14.386872	10.648313	16.962883
H	15.133248	10.211935	16.287349
H	14.723686	11.664416	17.200980
C	14.228770	9.805686	18.206875
H	15.135758	9.861831	18.819788
H	14.066250	8.751044	17.962348
C	12.007436	8.818002	19.699148
H	12.737186	8.175596	20.206483
H	11.270241	9.116071	20.455513
C	11.374543	8.100290	18.528032
H	10.684758	7.328451	18.888153
H	12.119978	7.603130	17.898405

C	11.008959	8.804636	15.781288
H	10.830515	7.736368	15.605183
H	10.342958	9.350878	15.102815
C	12.456741	9.161809	15.534857
H	12.695663	9.061519	14.469188
H	13.133427	8.497731	16.080472
N	10.027005	12.406886	16.479072
N	12.017457	13.329398	17.924815
O	10.046930	10.087525	22.287015
Ru	11.293405	11.372167	17.780866
S	12.840009	10.897238	16.023612
S	12.827879	10.385703	19.251169
S	10.390622	9.235490	17.447719

Table S12 Cartesian coordinates of **1v** at the PBE0 optimized geometry.

	Coordinates in Å		
	X	Y	Z
C	9.173238	12.027232	20.102273
C	9.078280	11.223454	21.358358
C	7.973402	11.681433	22.247068
N	7.261669	12.726493	21.828130
C	10.041793	11.822909	19.155359
H	8.398436	12.812427	20.041985
C	6.274087	13.171480	22.591195
H	5.715351	14.033932	22.226951
C	5.948661	12.573851	23.814263
H	5.131736	12.971057	24.413047
C	6.687394	11.474522	24.245744
H	6.452548	10.986628	25.189804
C	7.733763	11.013892	23.450088
H	8.357653	10.168340	23.732137
C	9.067974	12.178886	15.746149
H	8.652614	11.214683	16.031360
C	8.459327	12.956819	14.770662
H	7.567300	12.592386	14.266665
C	9.011373	14.200490	14.473373
H	8.565724	14.840484	13.713931
C	10.129155	14.628090	15.181960
H	10.551818	15.607741	14.979813
C	10.686870	13.801850	16.159614
C	11.801946	14.205143	17.036630
C	12.413364	15.458923	16.983913
H	12.127480	16.182712	16.225884
C	13.385008	15.789938	17.923438
H	13.862703	16.767189	17.898042
C	13.722955	14.857645	18.901076
H	14.461214	15.080869	19.668241
C	13.091960	13.619447	18.886041
H	13.321891	12.864889	19.635834
C	14.285976	10.444526	16.963712
H	15.017132	9.944982	16.315901
H	14.686419	11.440685	17.187927
C	14.052520	9.636397	18.219229
H	14.957034	9.643835	18.838964
H	13.827924	8.589687	17.989436
C	11.749220	8.785654	19.666660
H	12.430730	8.076091	20.151382
H	11.037956	9.142223	20.426462
C	11.059469	8.145786	18.484309
H	10.313468	7.424614	18.838306
H	11.755917	7.603415	17.836026

C	10.751069	8.895471	15.764444
H	10.458733	7.853937	15.578328
H	10.155785	9.512205	15.081210
C	12.232522	9.090901	15.531772
H	12.465068	8.943491	14.470292
H	12.830174	8.367851	16.094856
N	10.164688	12.576789	16.401335
N	12.172535	13.294227	17.968023
O	9.803841	10.292764	21.637075
Ru	11.226011	11.437028	17.799174
S	12.786537	10.781794	15.989102
S	12.689430	10.292437	19.267350
S	10.156406	9.363174	17.427888

Table S13 Cartesian coordinates of **5** at the PBE0 optimized geometry.

	Coordinates in Å		
	X	Y	Z
Ru	0.850651	0.666649	9.956930
S	3.020760	0.672813	10.822987
S	0.332588	2.314428	11.545104
S	-1.382939	0.720502	9.179763
S	1.232006	-0.951701	8.293278
O	-0.041308	1.557373	6.734905
N	2.256520	3.978462	7.545809
N	0.364684	-0.912994	11.302409
C	1.363113	2.131111	8.651496
C	0.771298	2.262241	7.276444
C	1.386540	3.478190	6.634985
C	2.229273	3.173338	8.740411
C	1.211452	4.072057	5.410654
H	0.501134	3.647278	4.703635
C	1.972452	5.219773	5.120973
H	1.861304	5.723519	4.162628
C	2.865993	5.708997	6.068297
H	3.465726	6.594550	5.870108
C	2.996129	5.064555	7.299626
H	3.670454	5.402095	8.084233
C	2.626943	1.011883	12.585575
H	2.105831	0.141506	12.999295
H	3.565759	1.152708	13.135434
C	1.781927	2.268800	12.681817
H	2.365507	3.157081	12.411327
H	1.423154	2.426909	13.705766
C	-1.055428	1.635205	12.523632
H	-0.753999	0.685903	12.978061
H	-1.248381	2.356027	13.326596
C	-2.323406	1.485340	11.676423
H	-3.143770	1.316987	12.387130
H	-2.559798	2.441975	11.187696
C	-2.400415	0.350447	10.651320
H	-3.433414	0.266364	10.292497
H	-2.110754	-0.609977	11.087938
C	-1.526981	-0.782086	8.129310
H	-2.497020	-1.252216	8.330479
H	-1.552326	-0.379075	7.112337
C	-0.402024	-1.788715	8.291385
H	-0.421425	-2.502366	7.457778
H	-0.491546	-2.347737	9.228645
C	2.296141	-2.260715	8.998205
H	1.750217	-2.773339	9.799276
H	2.473925	-2.981907	8.192370

C	3.632066	-1.719765	9.504495
H	4.309573	-2.581003	9.579640
H	4.095449	-1.062686	8.754364
C	3.628423	-1.052415	10.880146
H	4.649703	-1.009492	11.276114
H	3.012993	-1.617462	11.589662
C	0.075145	-1.787569	12.006544
C	-0.321260	-2.878520	12.877134
H	-0.853484	-3.645735	12.301411
H	-0.986239	-2.508736	13.666889
H	0.555602	-3.339256	13.347459
H	2.891220	3.486735	9.542261

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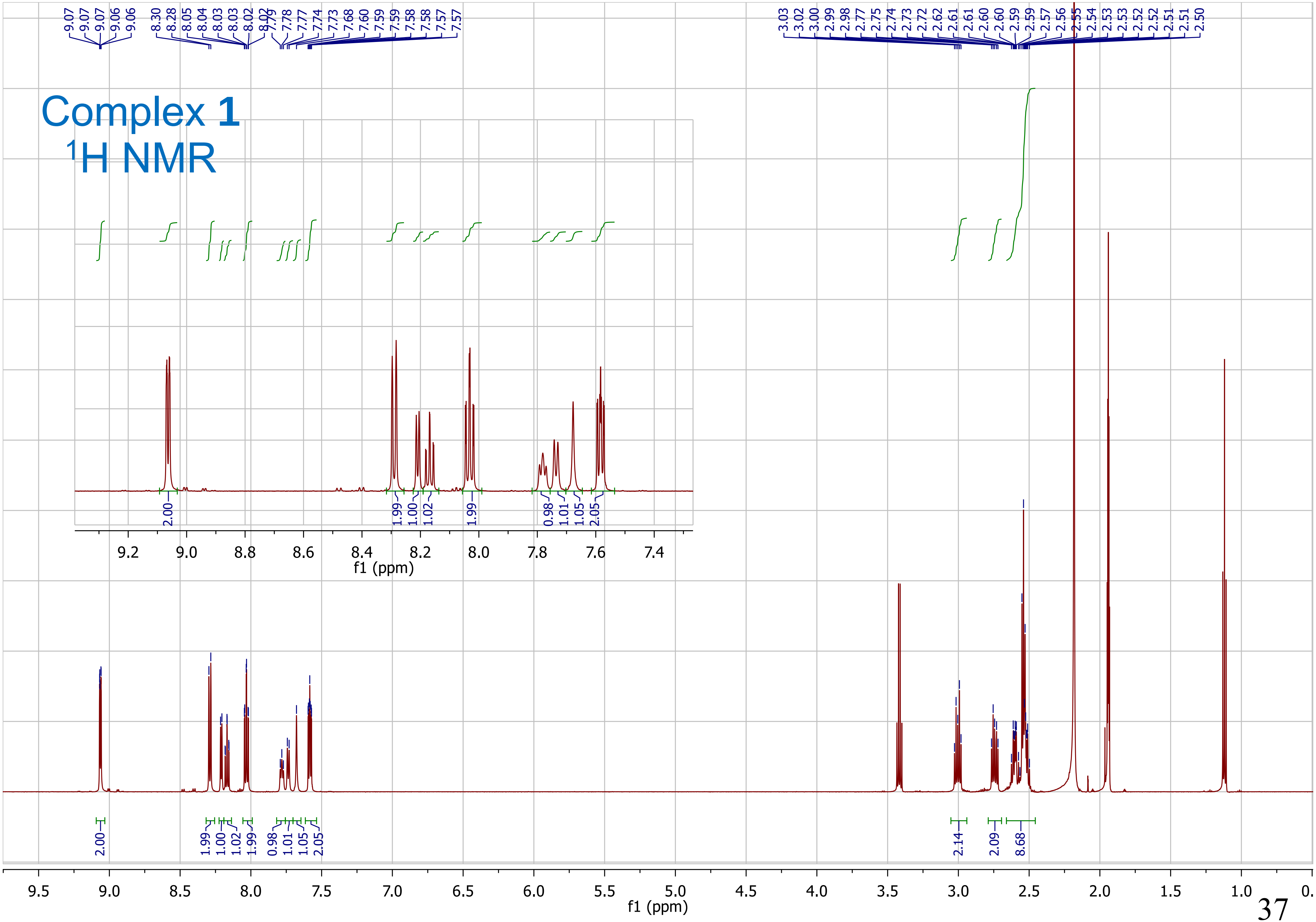
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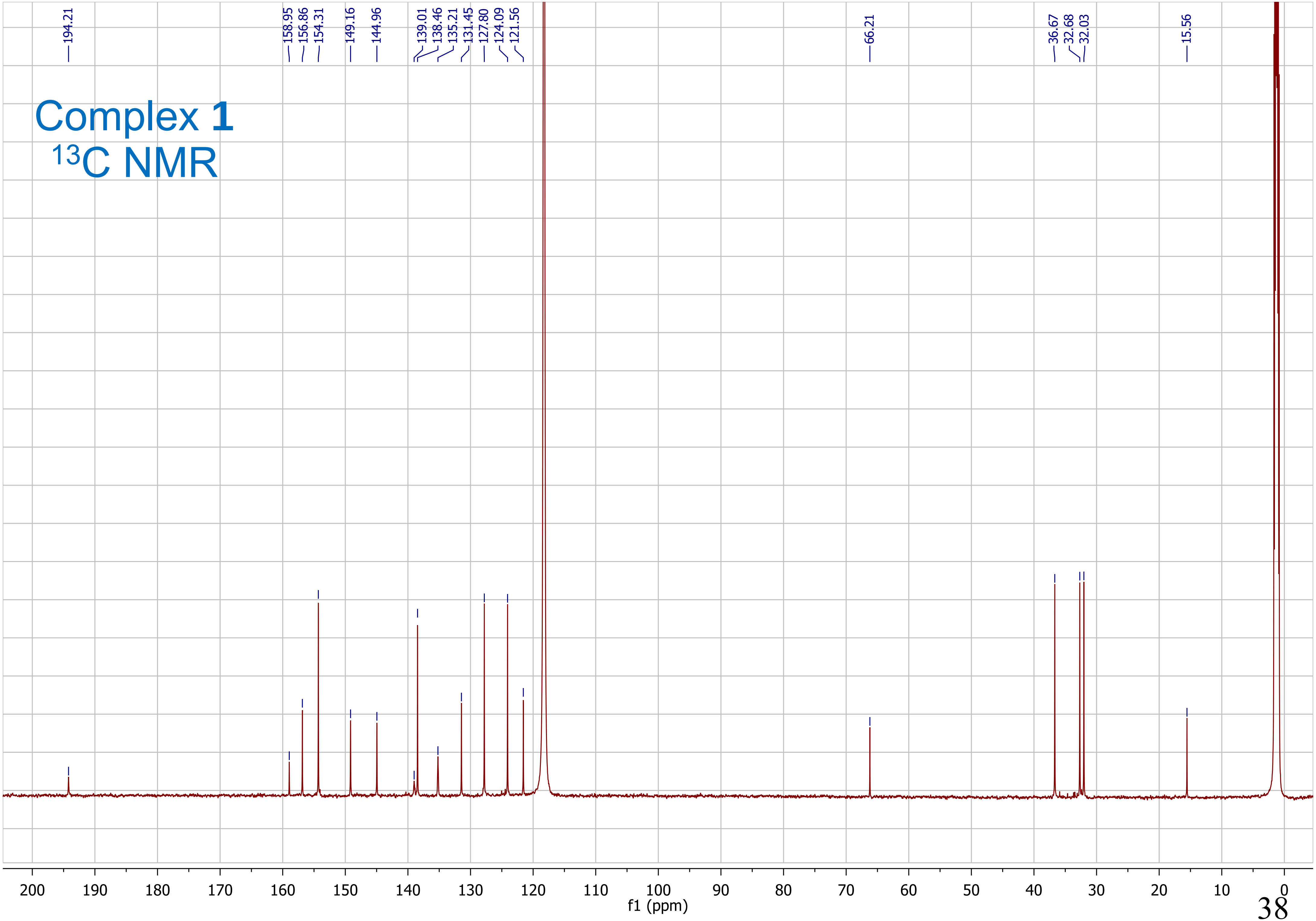
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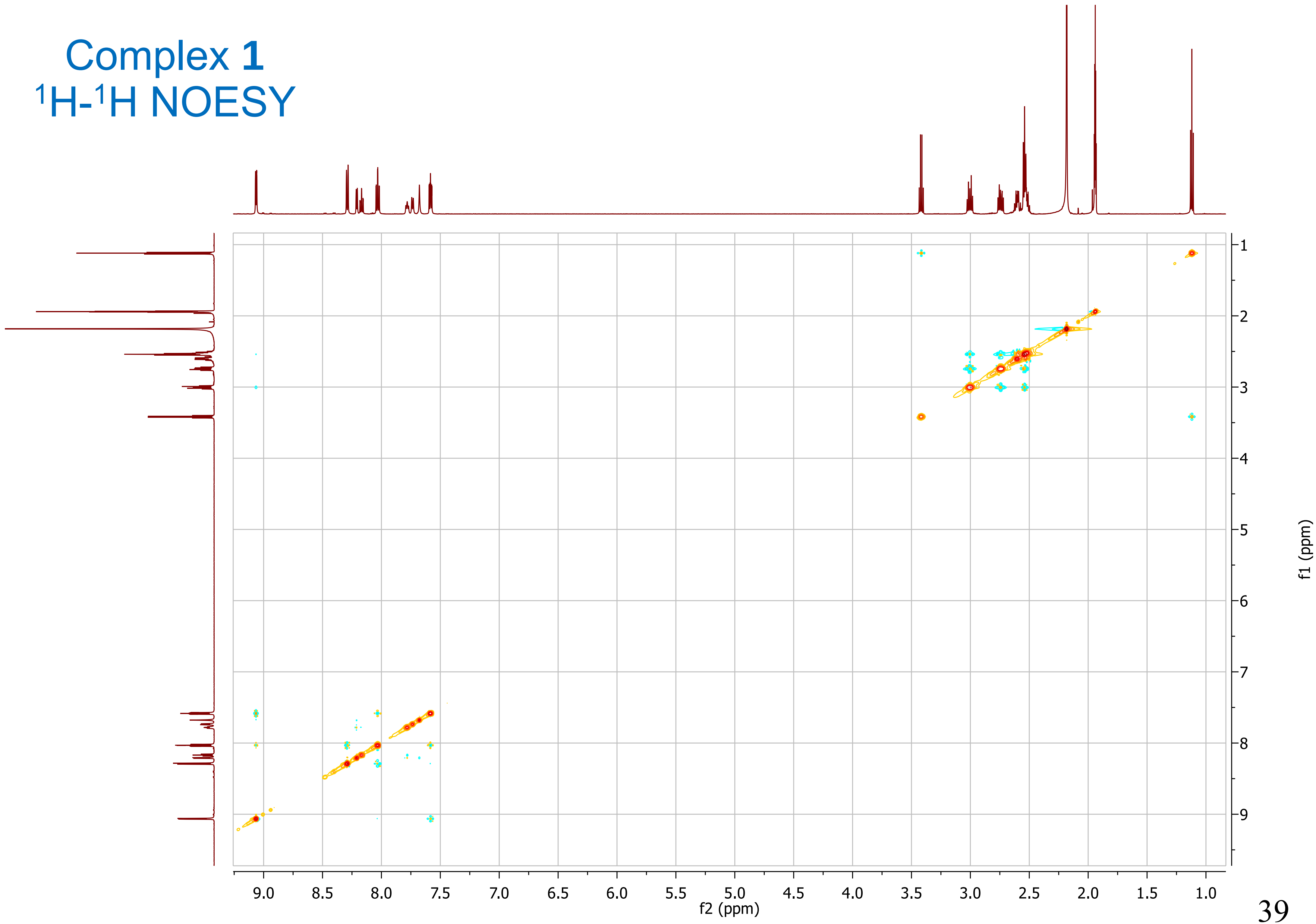
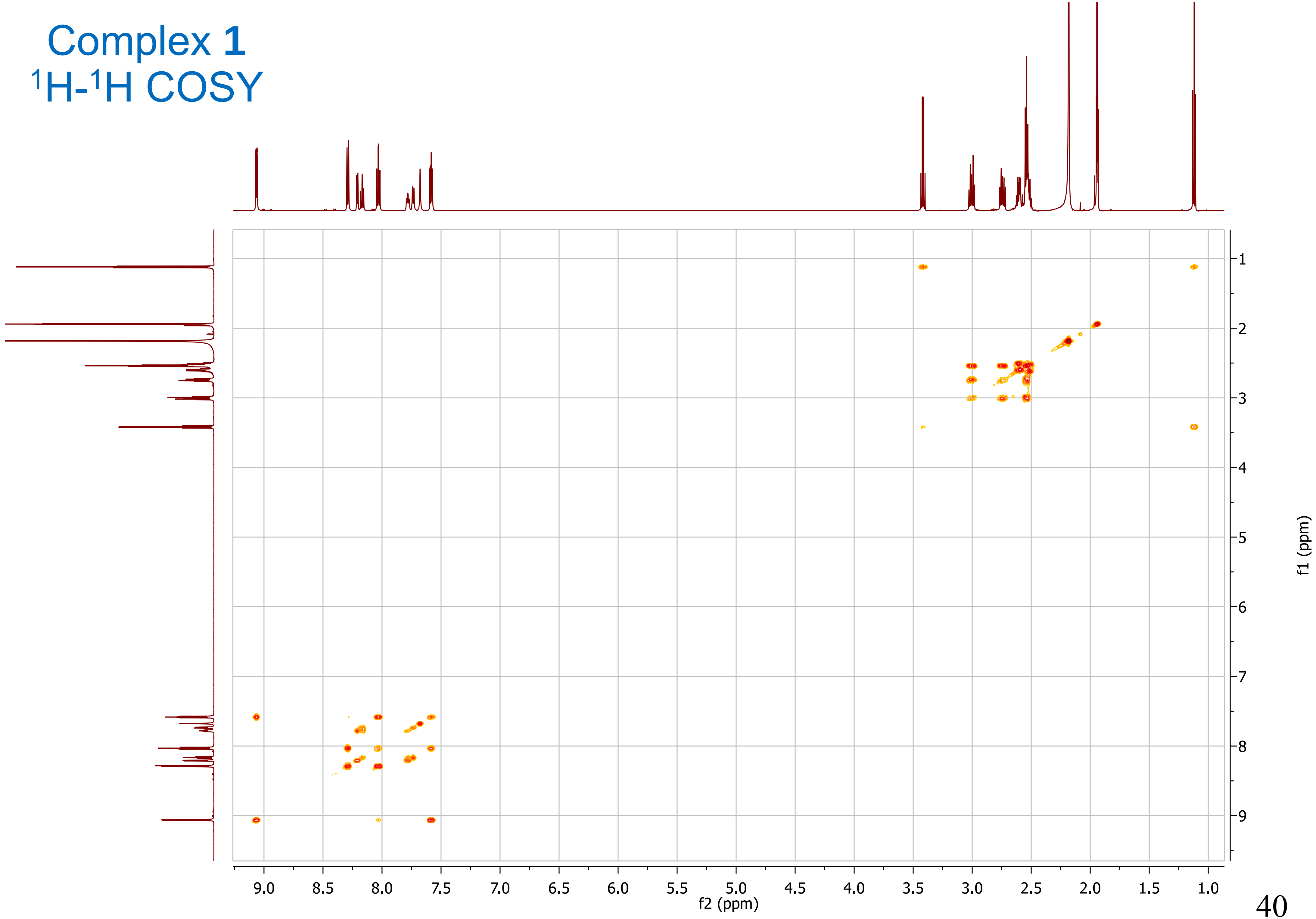
127.80
124.09
121.56
66.21
36.67
32.68
32.03
15.56
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Complex **1**

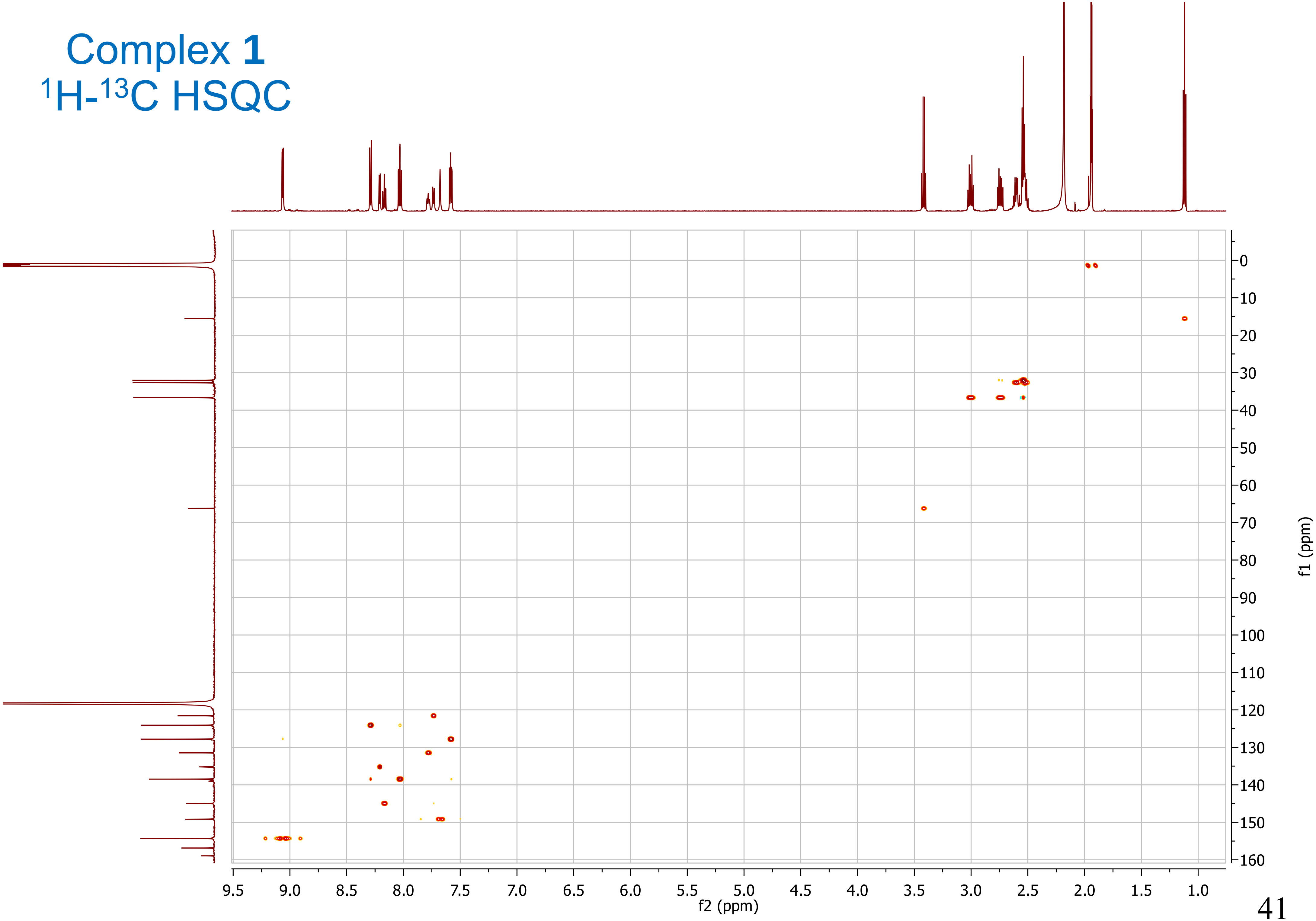
^{1}H-^{1}H NOESY



Complex **1**
^{1}H-^{1}H COSY

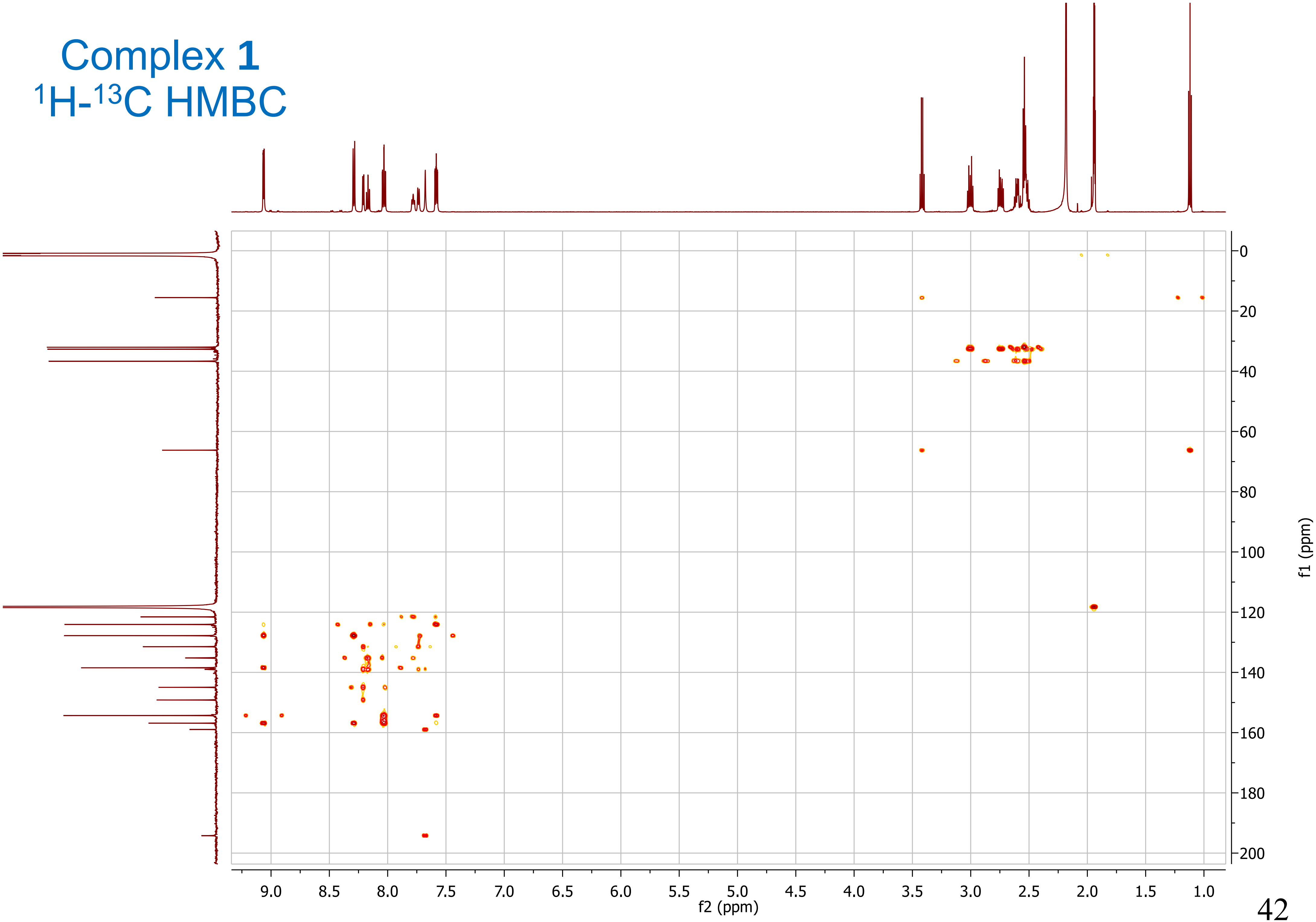


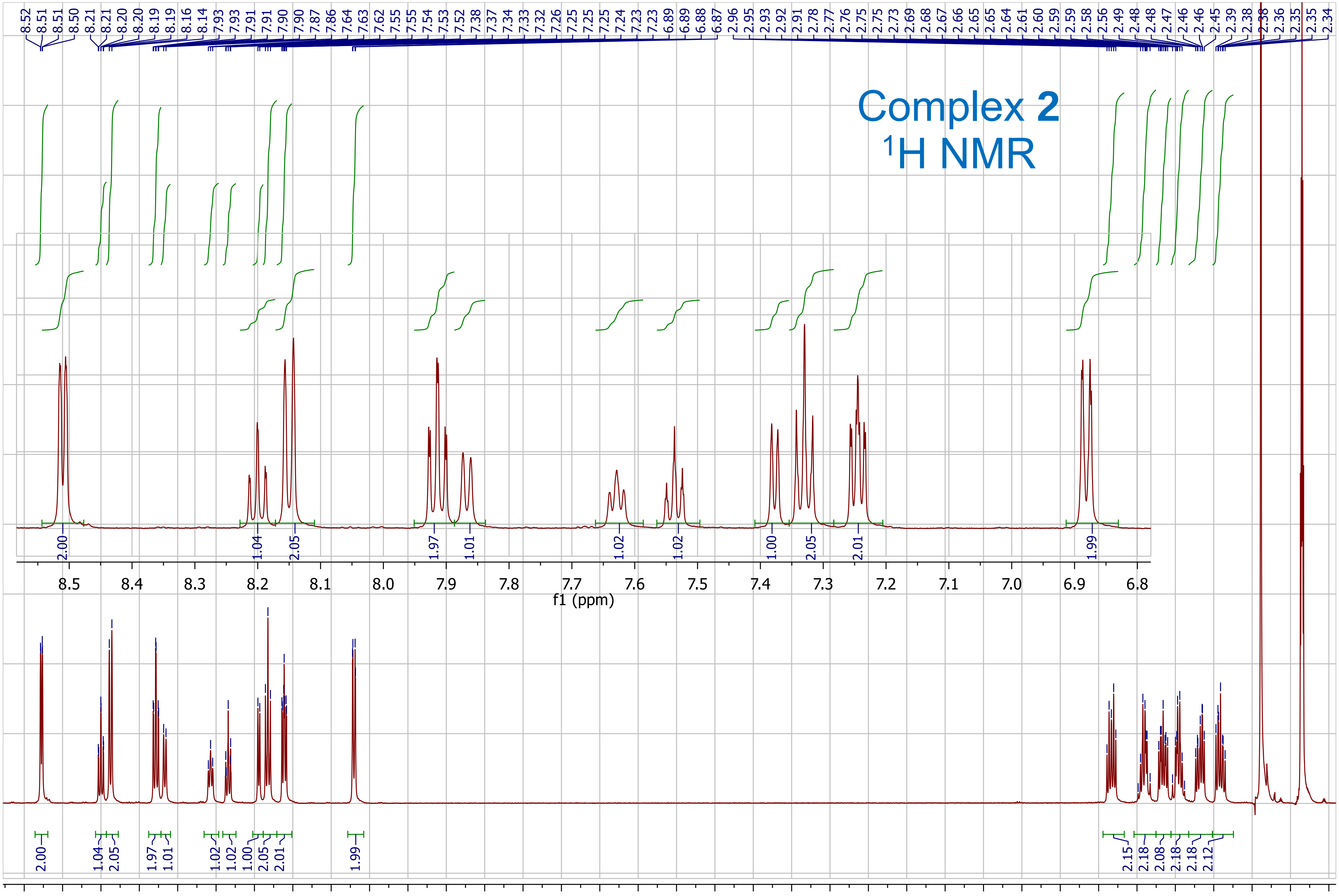
Complex **1**
^{1}H-^{13}C HSQC

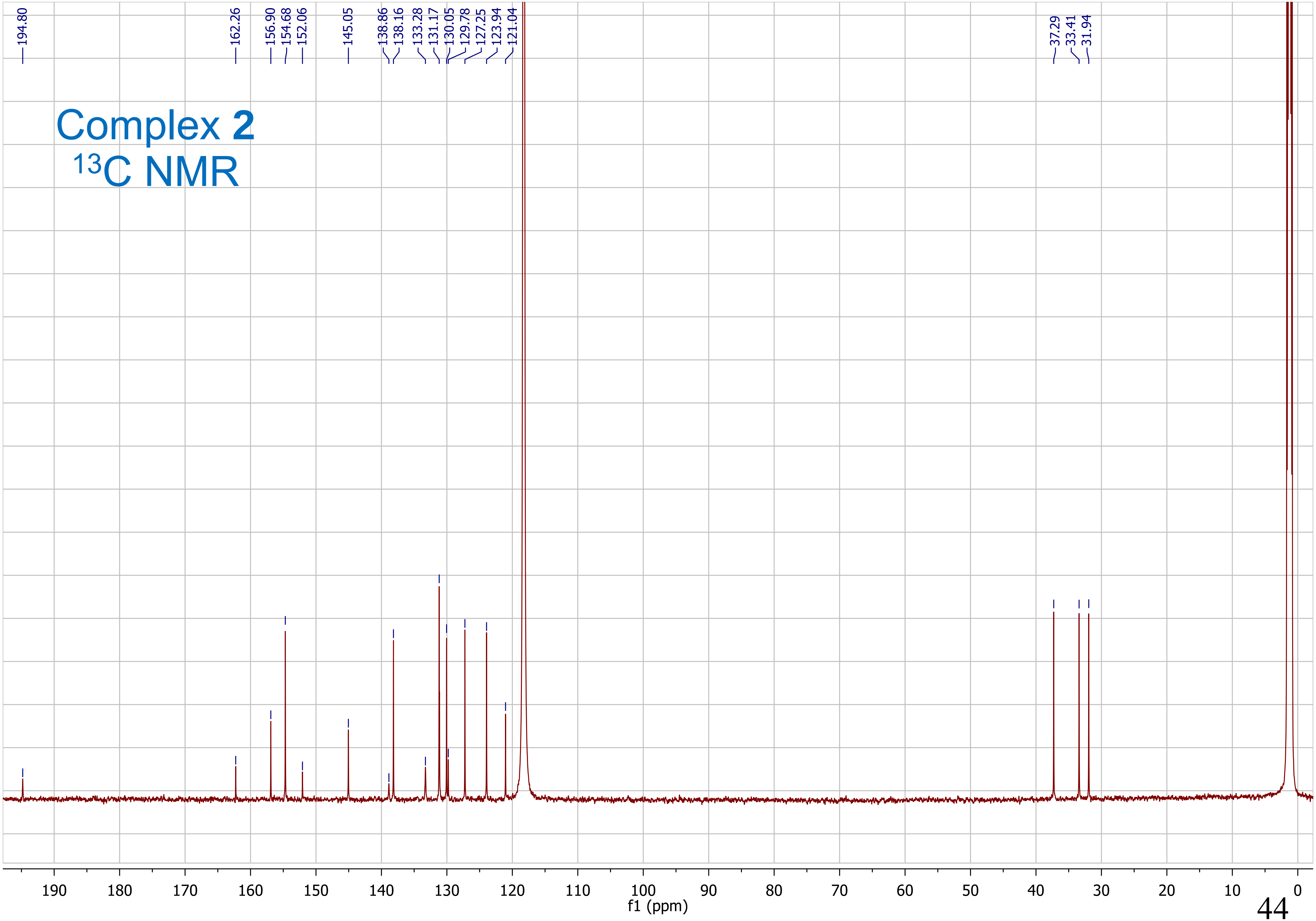


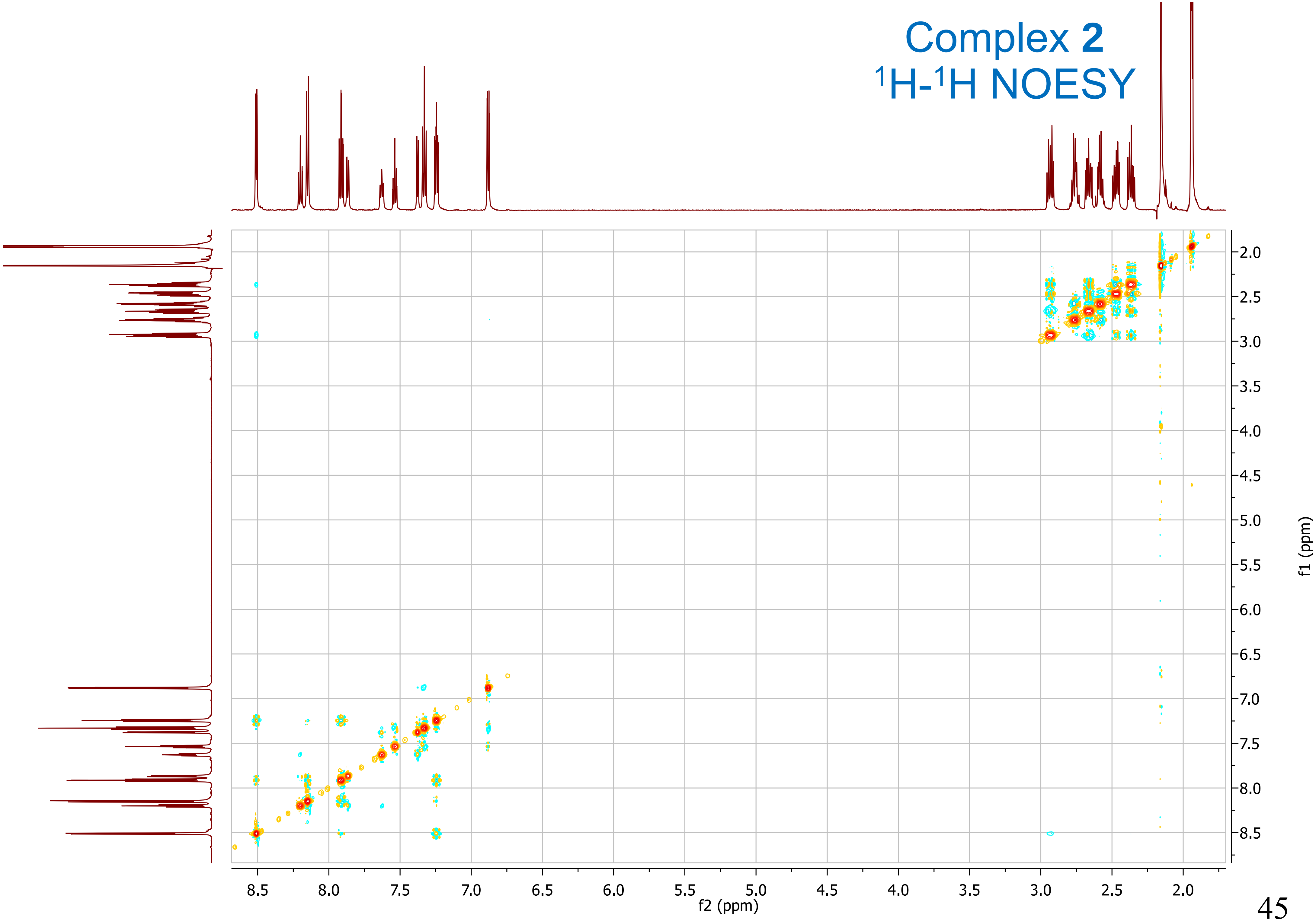
Complex **1**

^{1}H-^{13}C HMBC



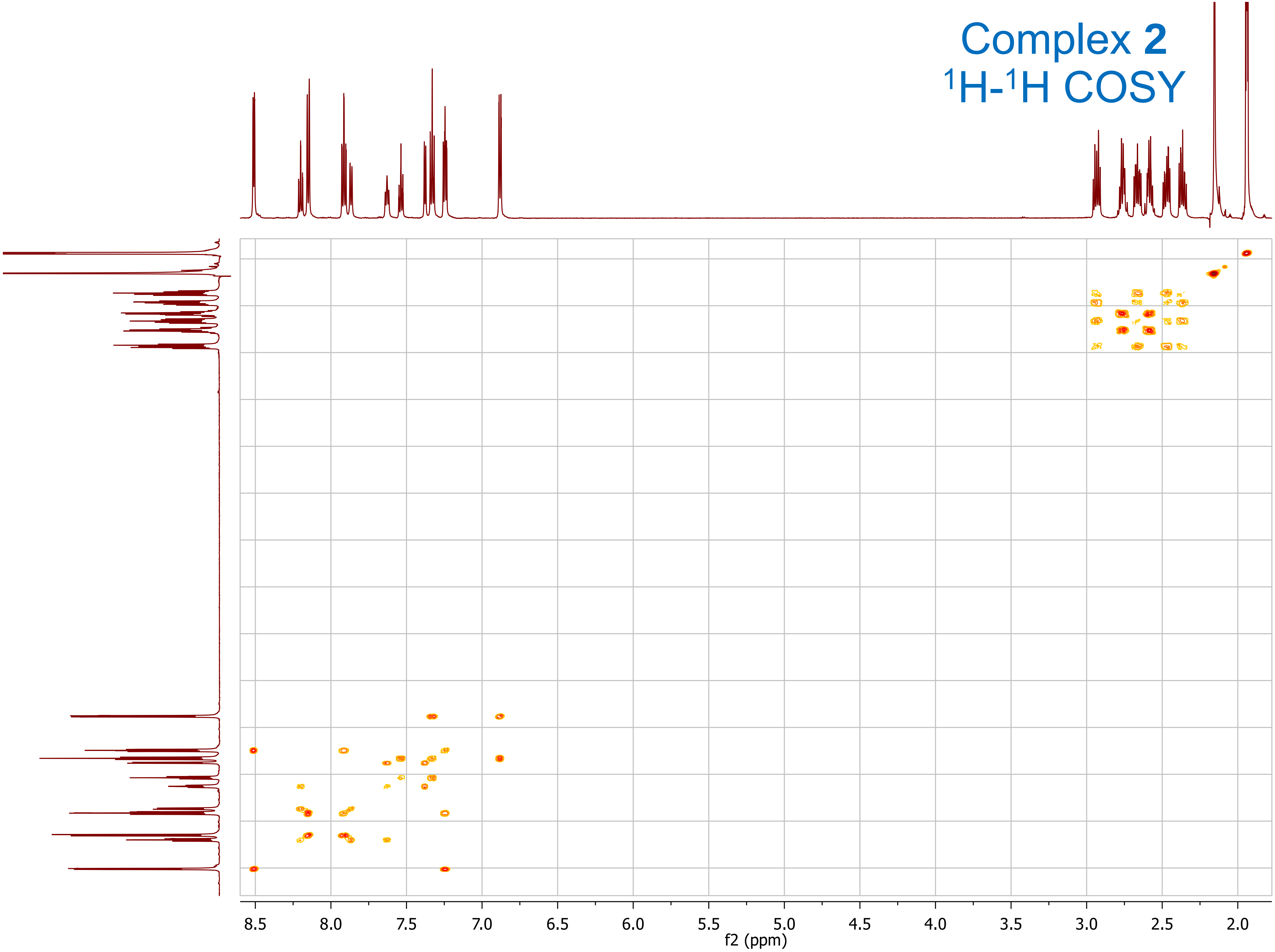

Complex 2
^{1}H NMR
8.52
8.51
8.51
8.50
8.21
8.21
8.20
8.20
8.19
8.19
8.16
8.14
7.93
7.93
7.91
7.91
7.90
7.90
7.87
7.86
7.64
7.63
7.62
7.55
7.54
7.53
7.52
7.38
7.37
7.34
7.33
7.32
7.26
7.25
7.25
7.24
7.23
7.23
6.89
6.89
6.88
6.87
2.96
2.95
2.93
2.92
2.91
2.78
2.77
2.76
2.75
2.75
2.73
2.69
2.68
2.67
2.66
2.65
2.65
2.64
2.61
2.60
2.59
2.59
2.58
2.56
2.49
2.48
2.48
2.47
2.46
2.46
2.45
2.39
2.38
2.38
2.36
2.35
2.35
2.34
2.00
1.04
2.05
1.97
1.01
1.02
1.02
1.00
2.05
2.01
1.99
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
2.00
1.04
2.05
1.97
1.01
1.02
1.02
1.00
2.05
2.01
1.99
2.15
2.18
2.08
2.18
2.18
2.12
8.6
8.2
7.8
7.6
7.4
7.2
7.0
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
f1 (ppm)

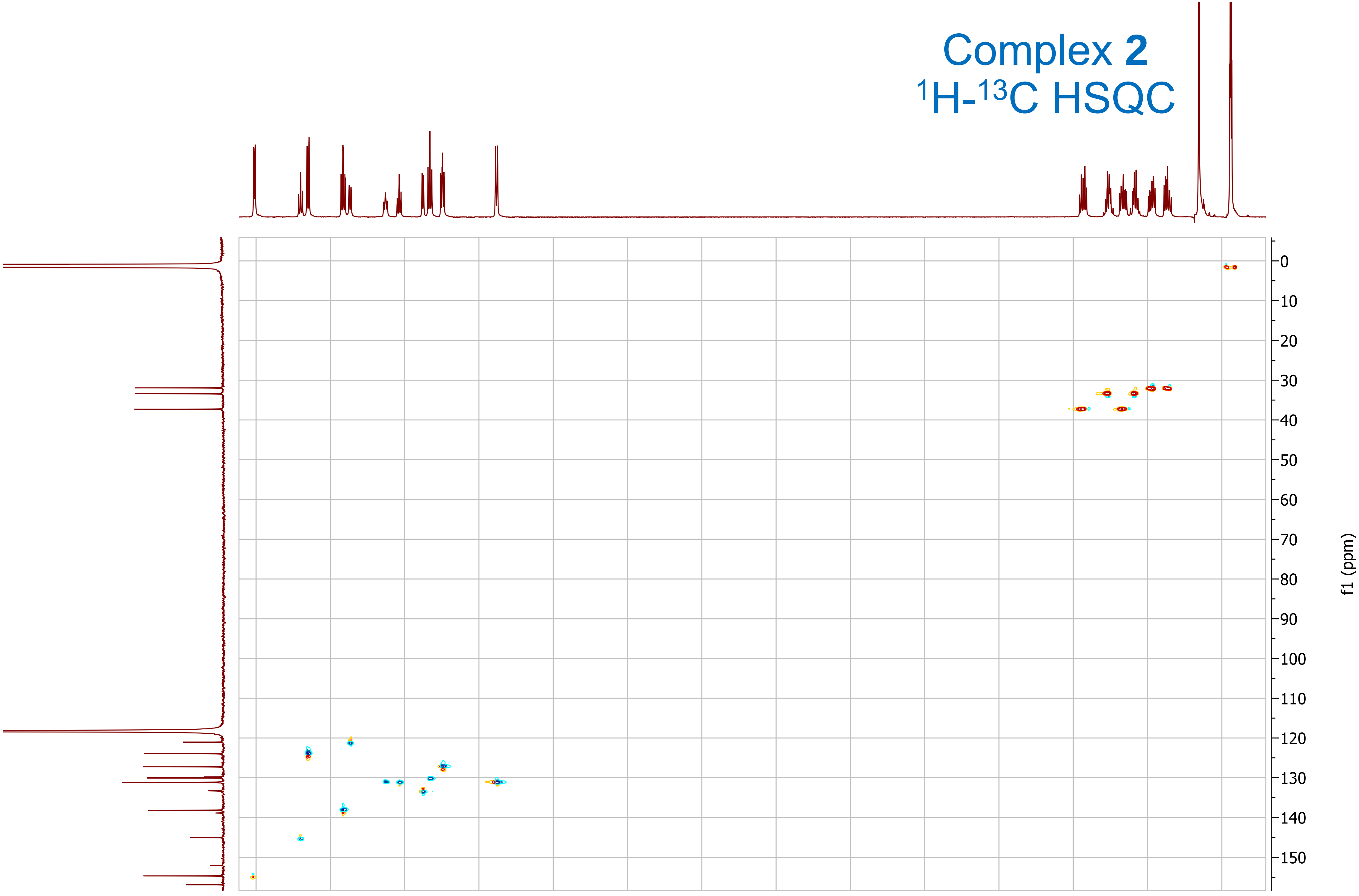

Complex 2
^{13}C NMR
194.80
162.26
156.90
154.68
152.06
145.05
138.86
138.16
133.28
131.17
130.05
129.78
127.25
123.94
121.04
37.29
33.41
31.94
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

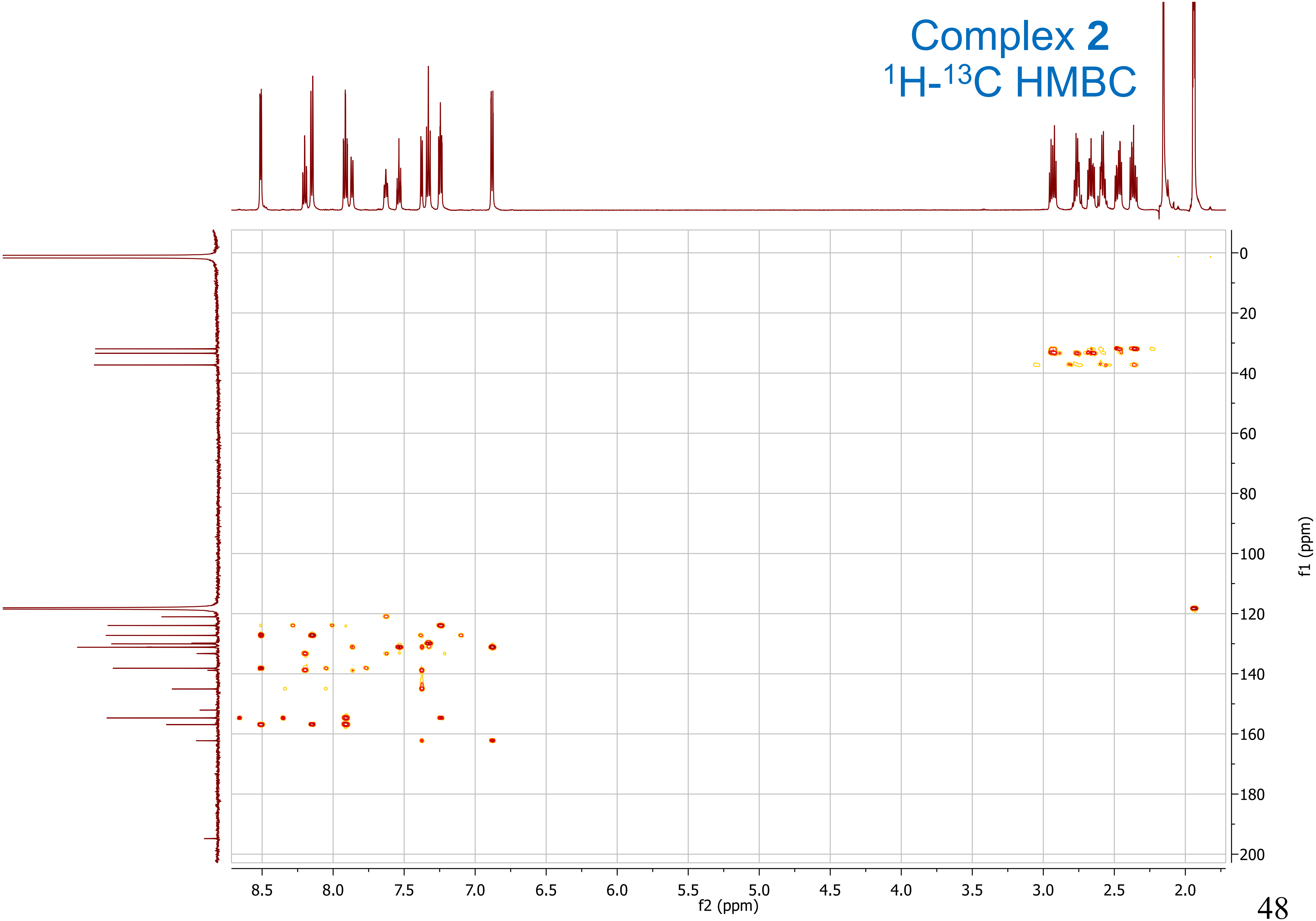

Complex **2**
^{1}H-^{1}H NOESY
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
f1 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5

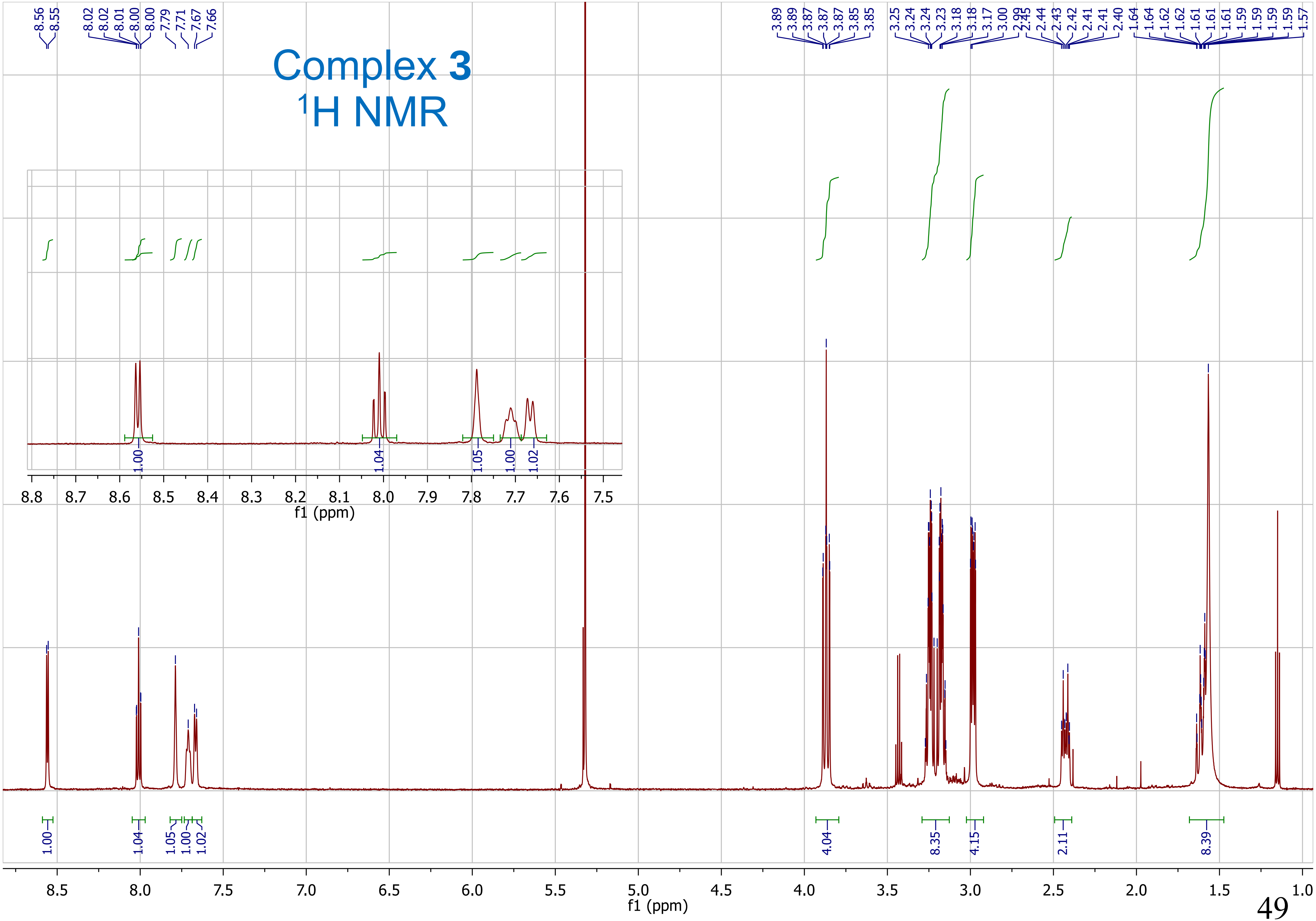
Complex **2**

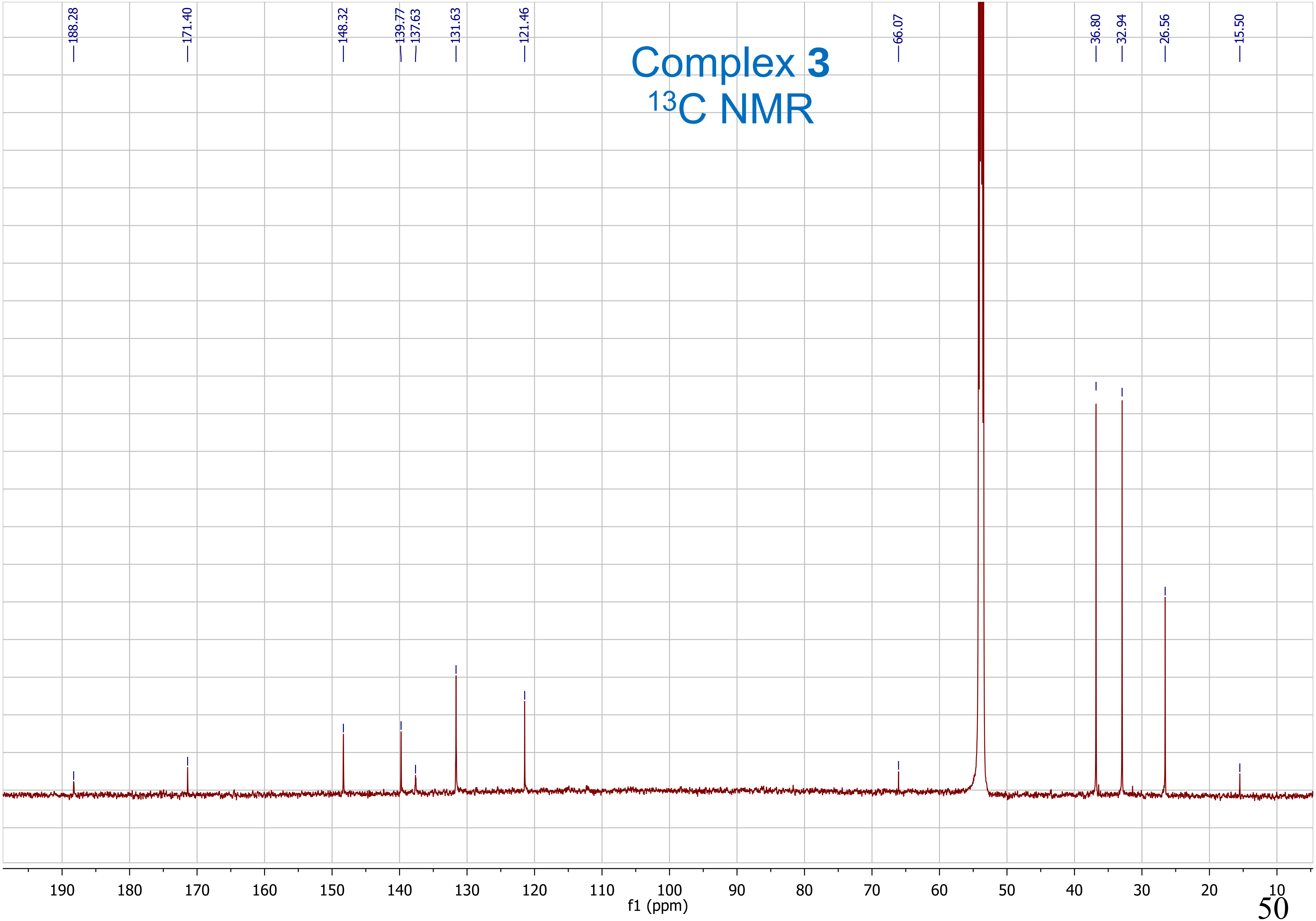
^{1}H-^{1}H COSY




Complex **2**
^{1}H-^{13}C HSQC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

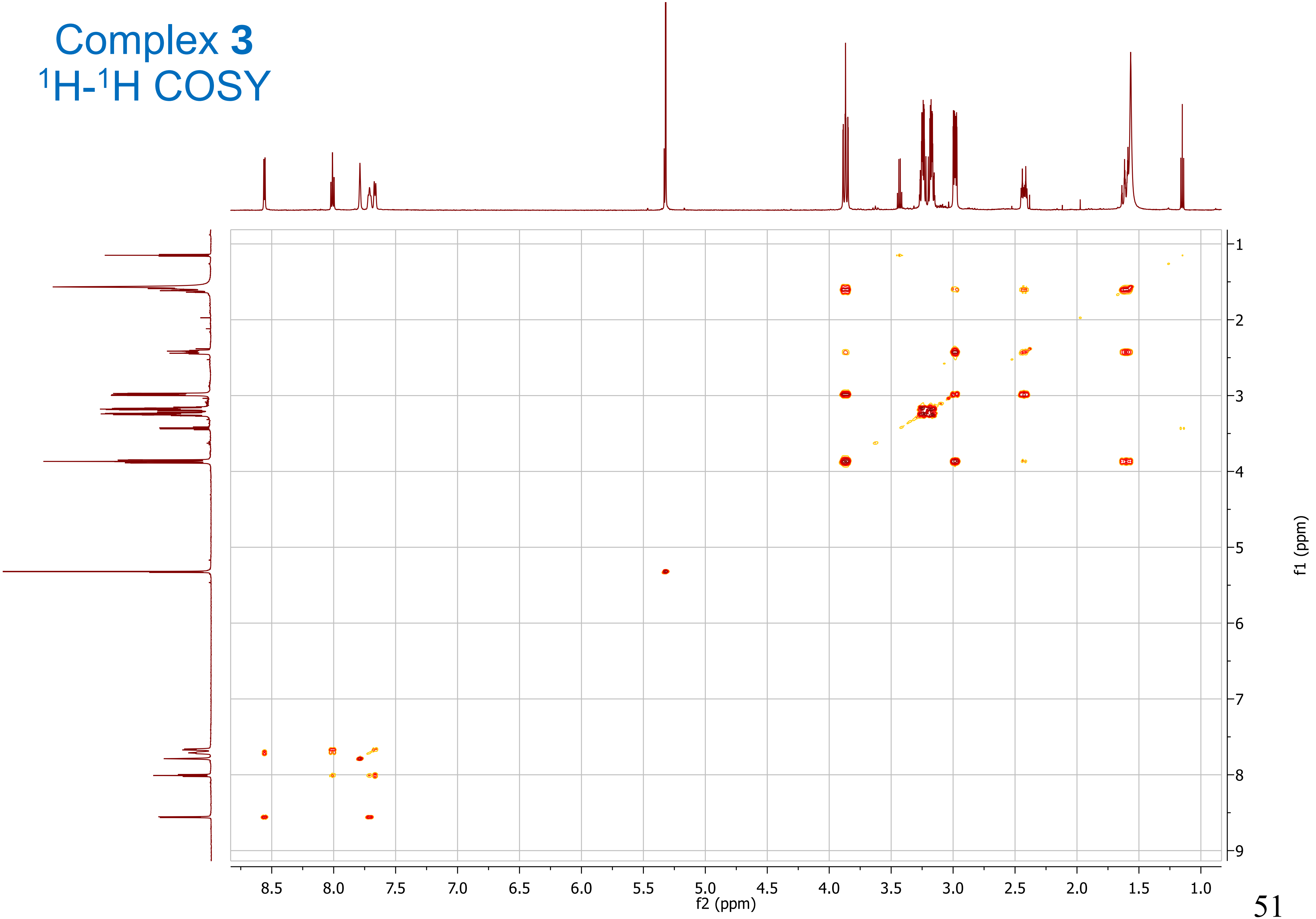

Complex **2**
^{1}H-^{13}C HMBC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)


Complex 3
^{1}H NMR
8.56
8.55
8.02
8.02
8.01
8.00
8.00
7.79
7.71
7.67
7.66
3.89
3.89
3.87
3.87
3.87
3.85
3.85
3.25
3.24
3.24
3.23
3.18
3.18
3.17
3.00
2.99
2.45
2.44
2.43
2.42
2.41
2.41
2.40
1.64
1.64
1.62
1.62
1.61
1.61
1.61
1.59
1.59
1.59
1.59
1.57
1.00
1.04
1.05
1.00
1.02
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
f1 (ppm)
1.00
1.04
1.05
1.00
1.02
4.04
8.35
4.15
2.11
8.39
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

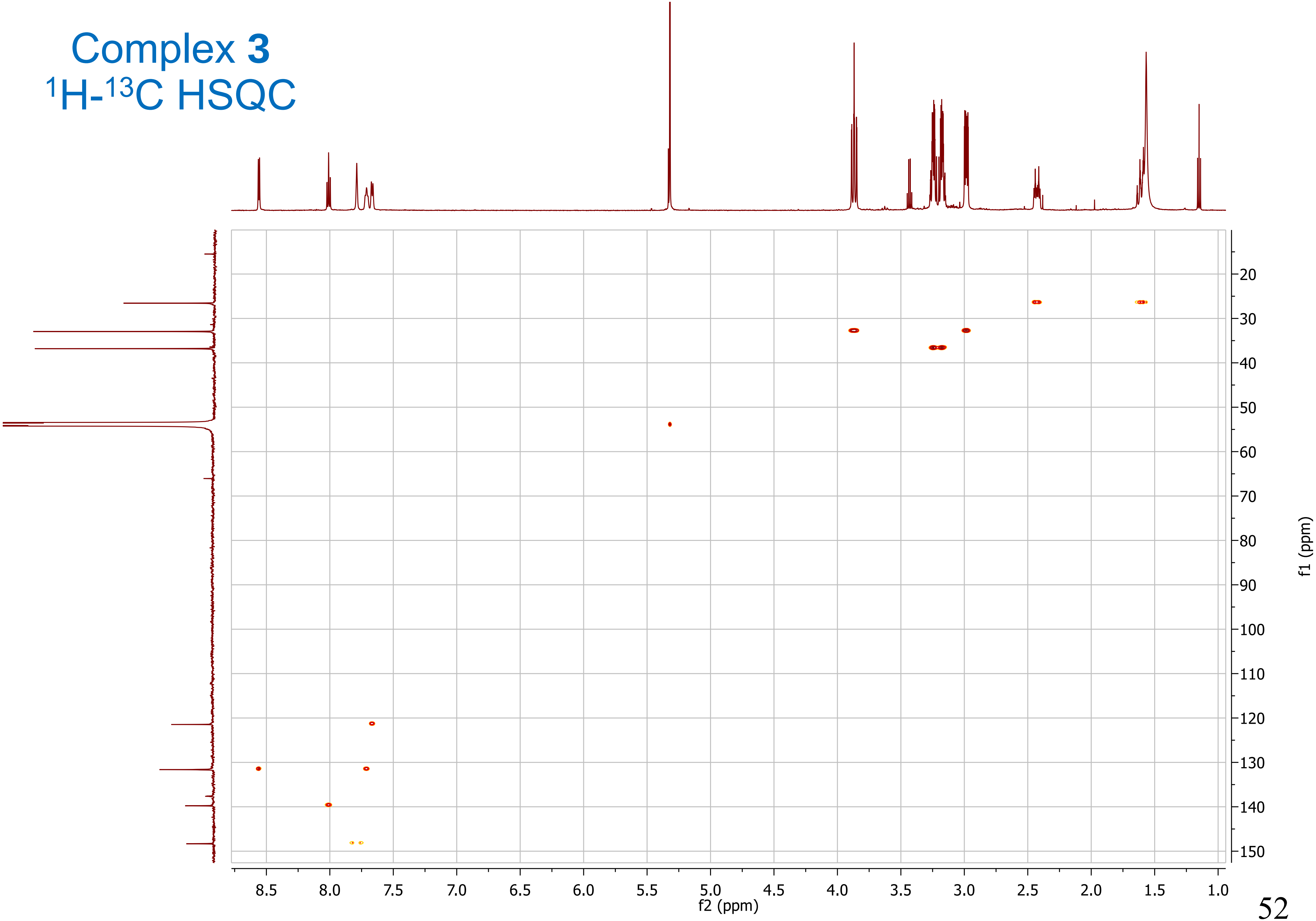

188.28
171.40
148.32
139.77
137.63
131.63
121.46
66.07
36.80
32.94
26.56
15.50
Complex **3**
^{13}C NMR
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Complex **3**

^{1}H-^{1}H COSY

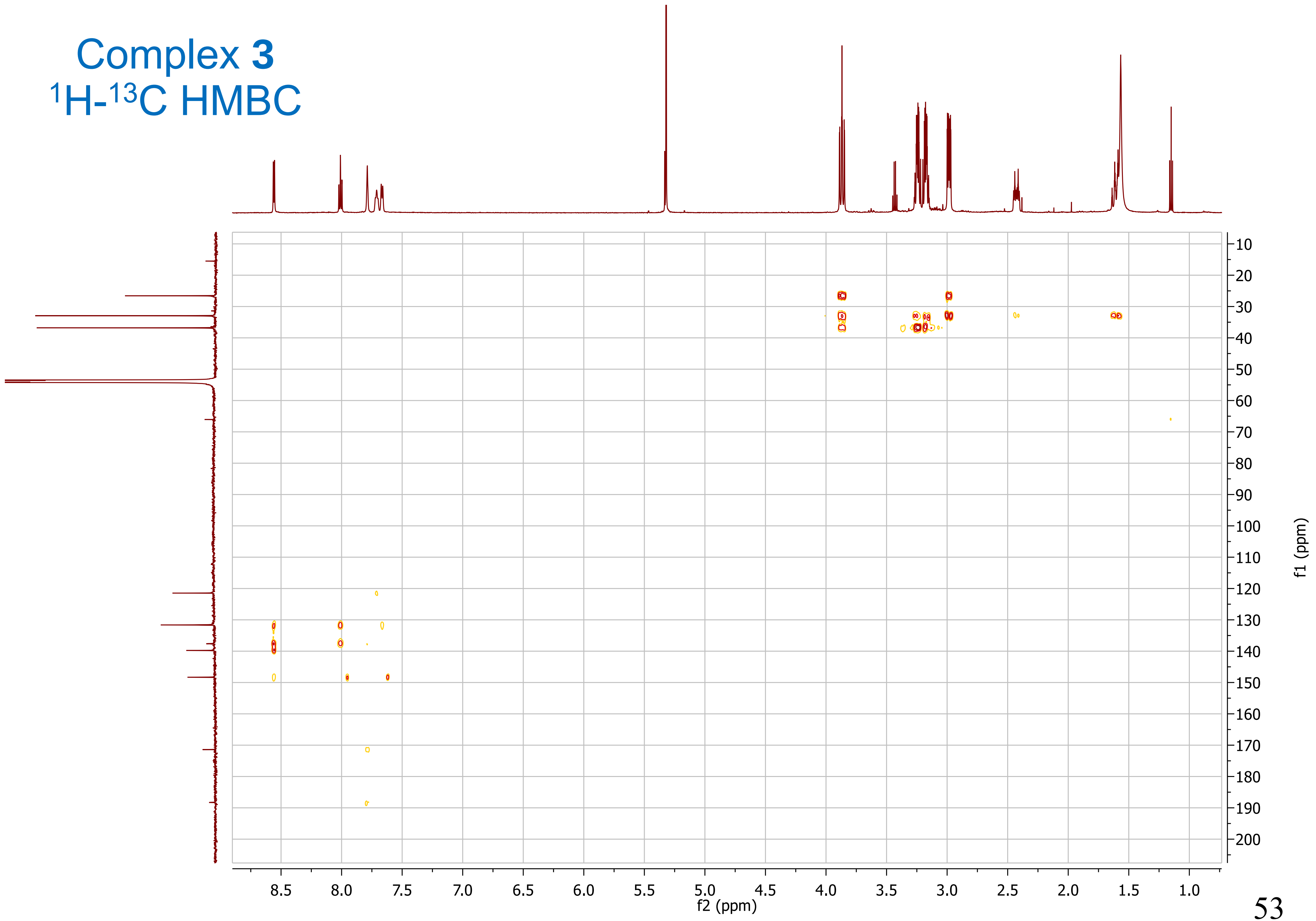


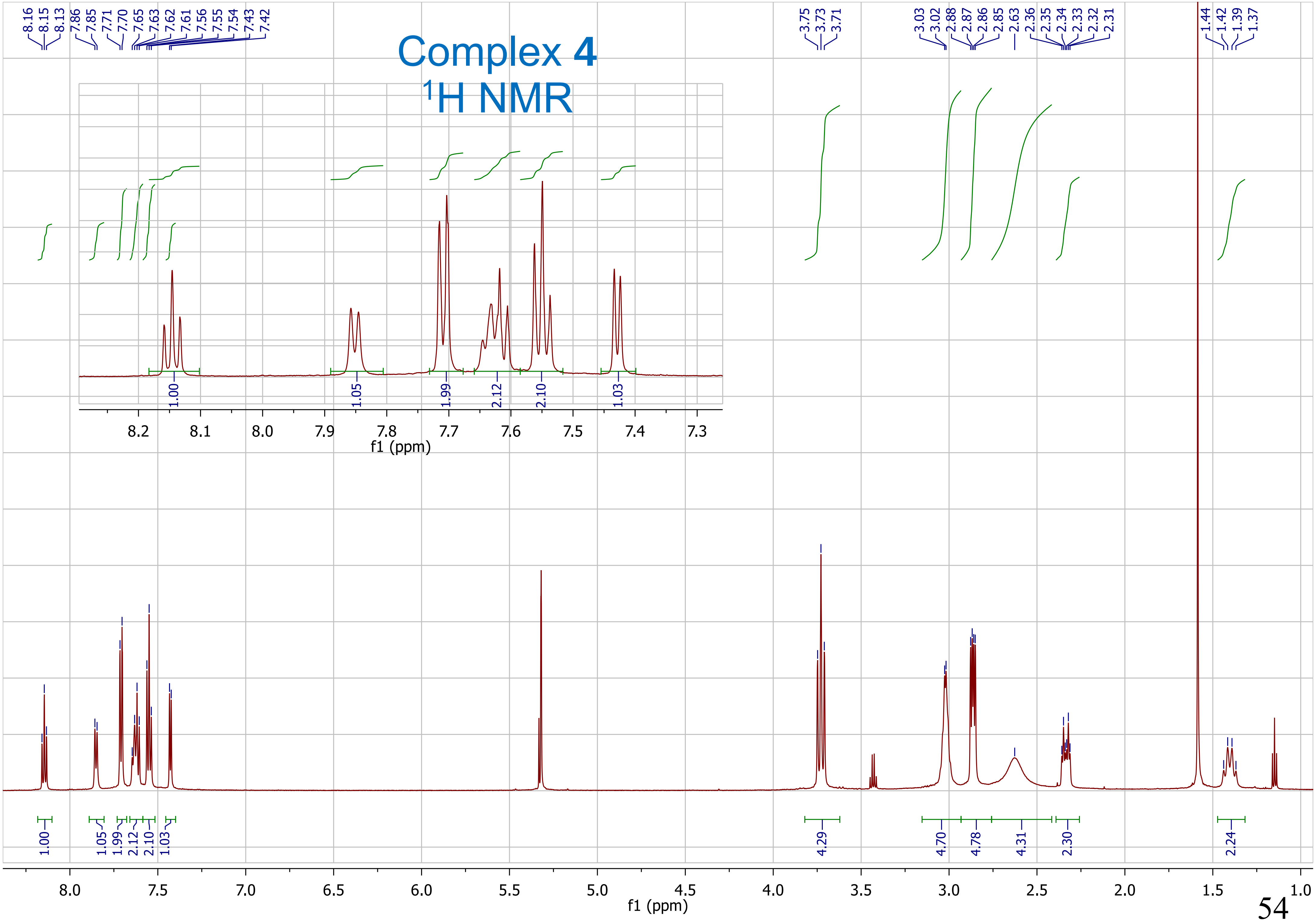
Complex **3**
^{1}H-^{13}C HSQC



Complex **3**

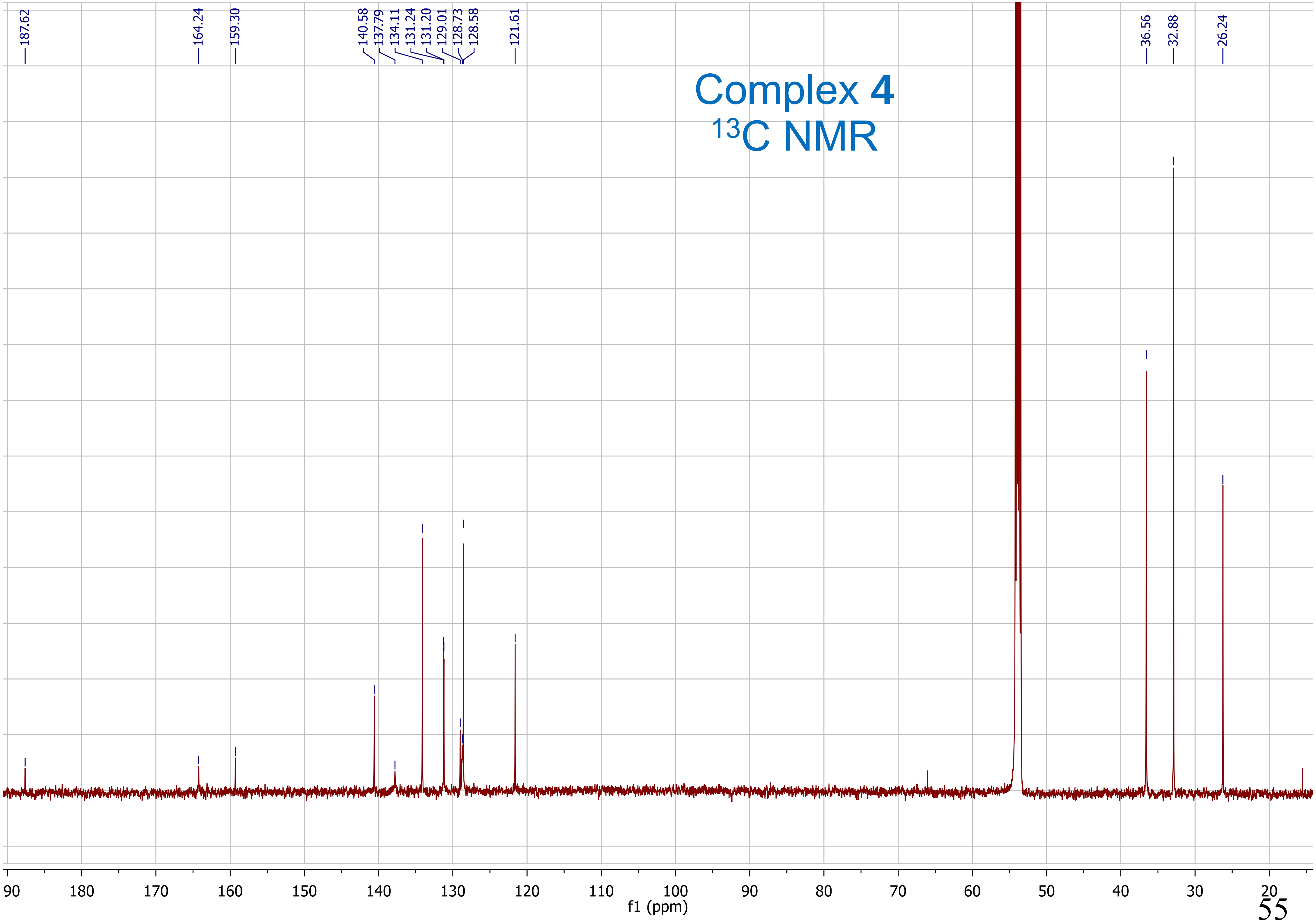
^{1}H-^{13}C HMBC



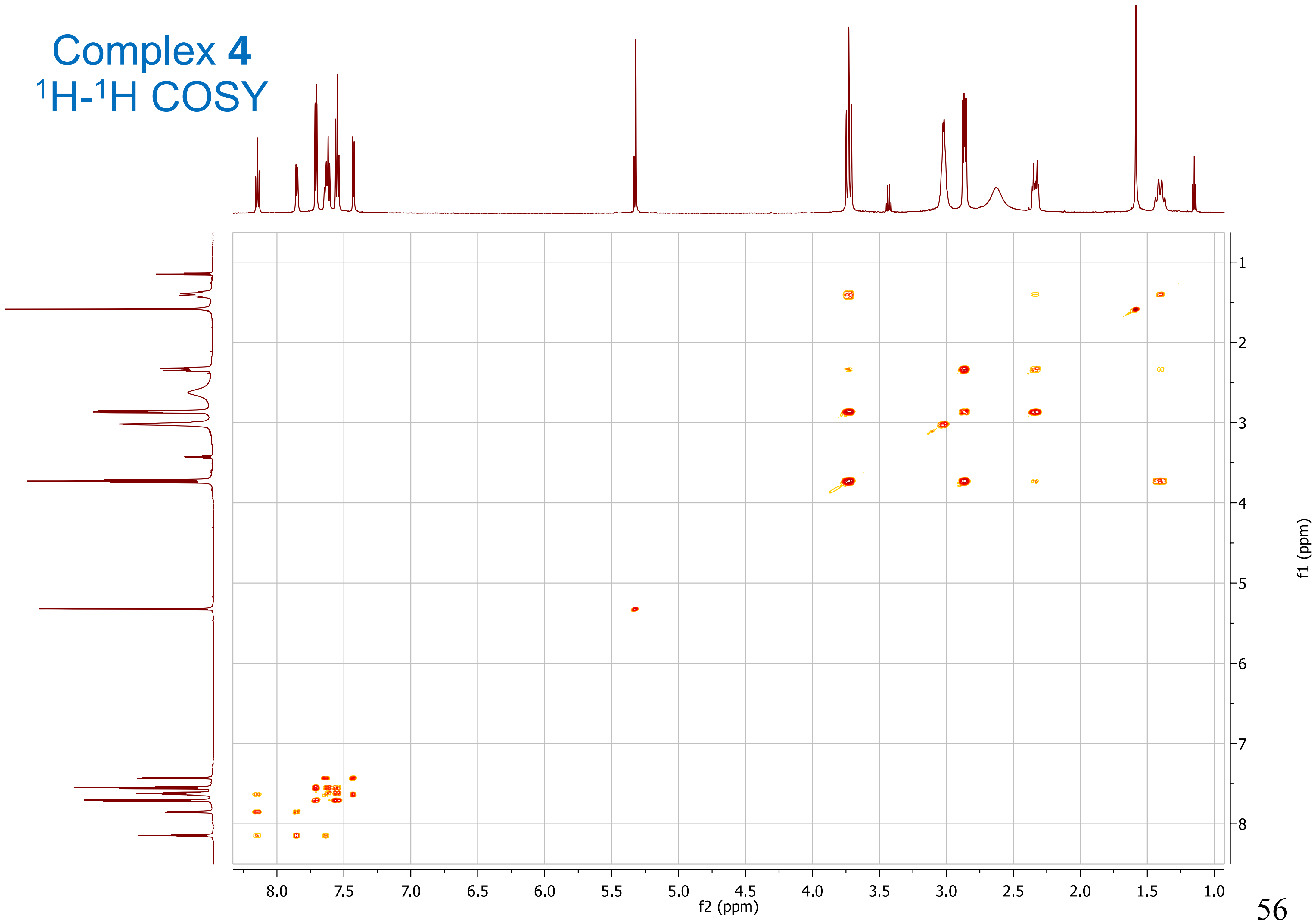


Complex **4**

^{1}H NMR

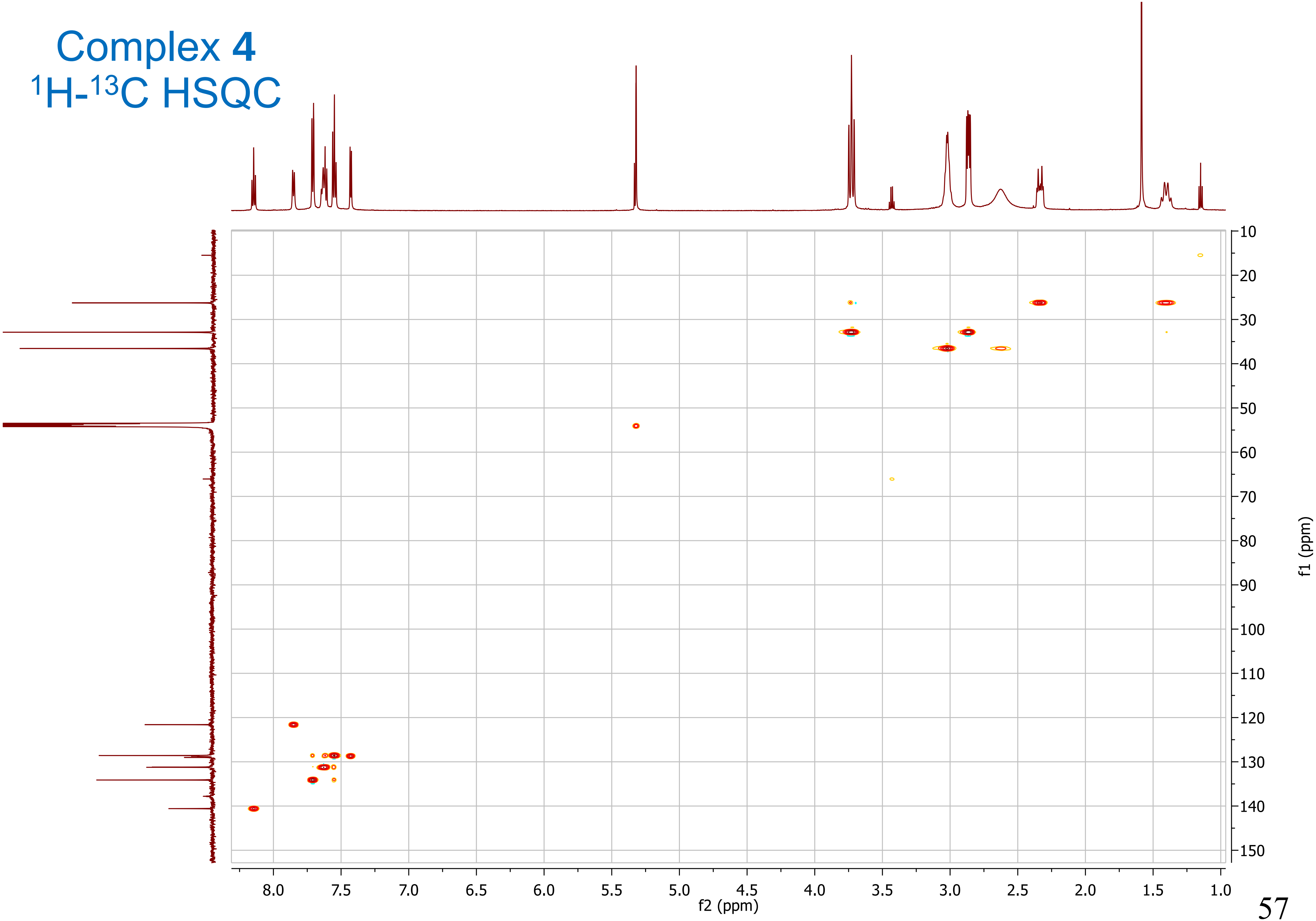

187.62
164.24
159.30
140.58
137.79
134.11
131.24
131.20
129.01
128.73
128.58
121.61
36.56
32.88
26.24
Complex **4**
^{13}C NMR
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

Complex **4**
^{1}H-^{1}H COSY

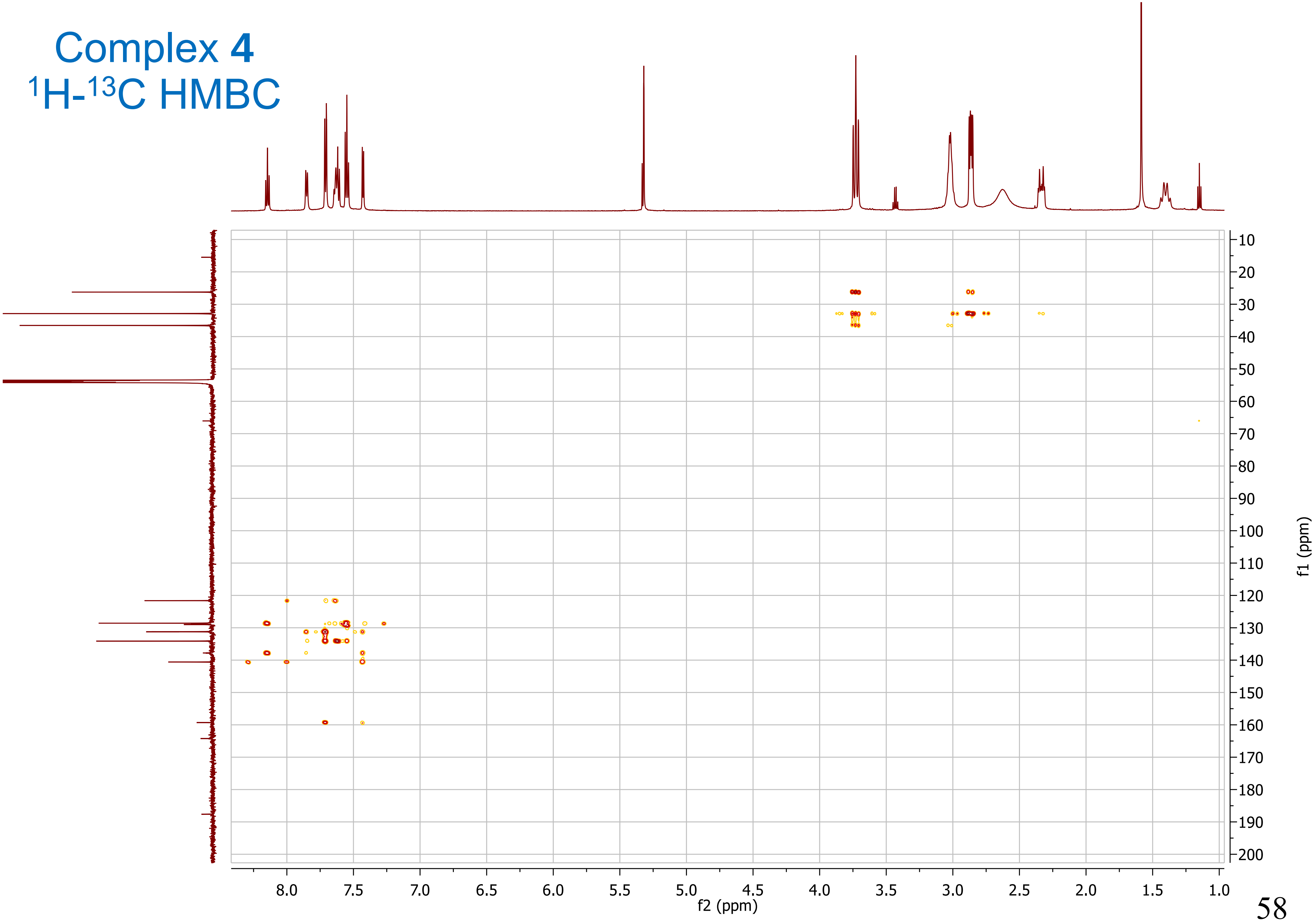


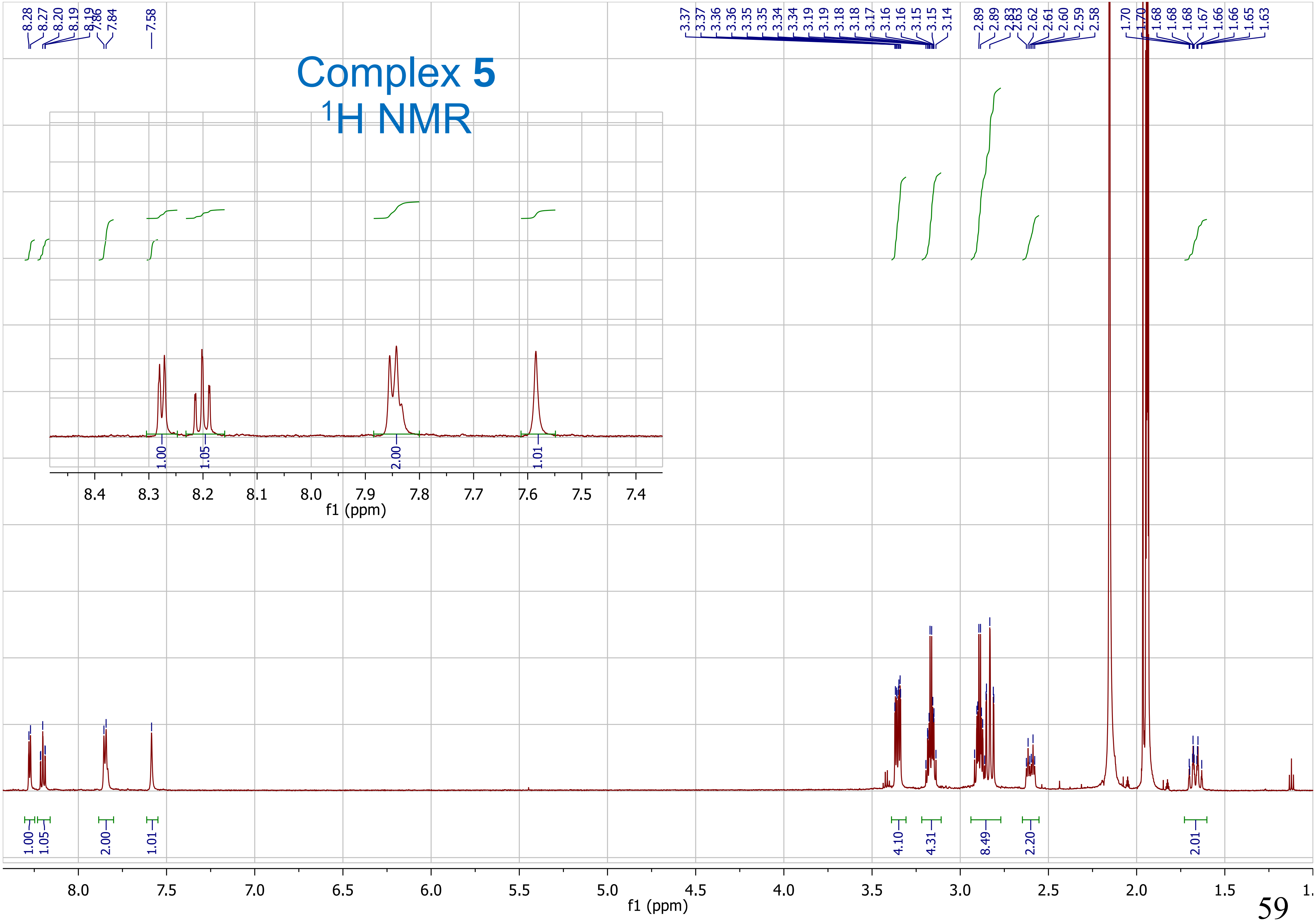
Complex **4**

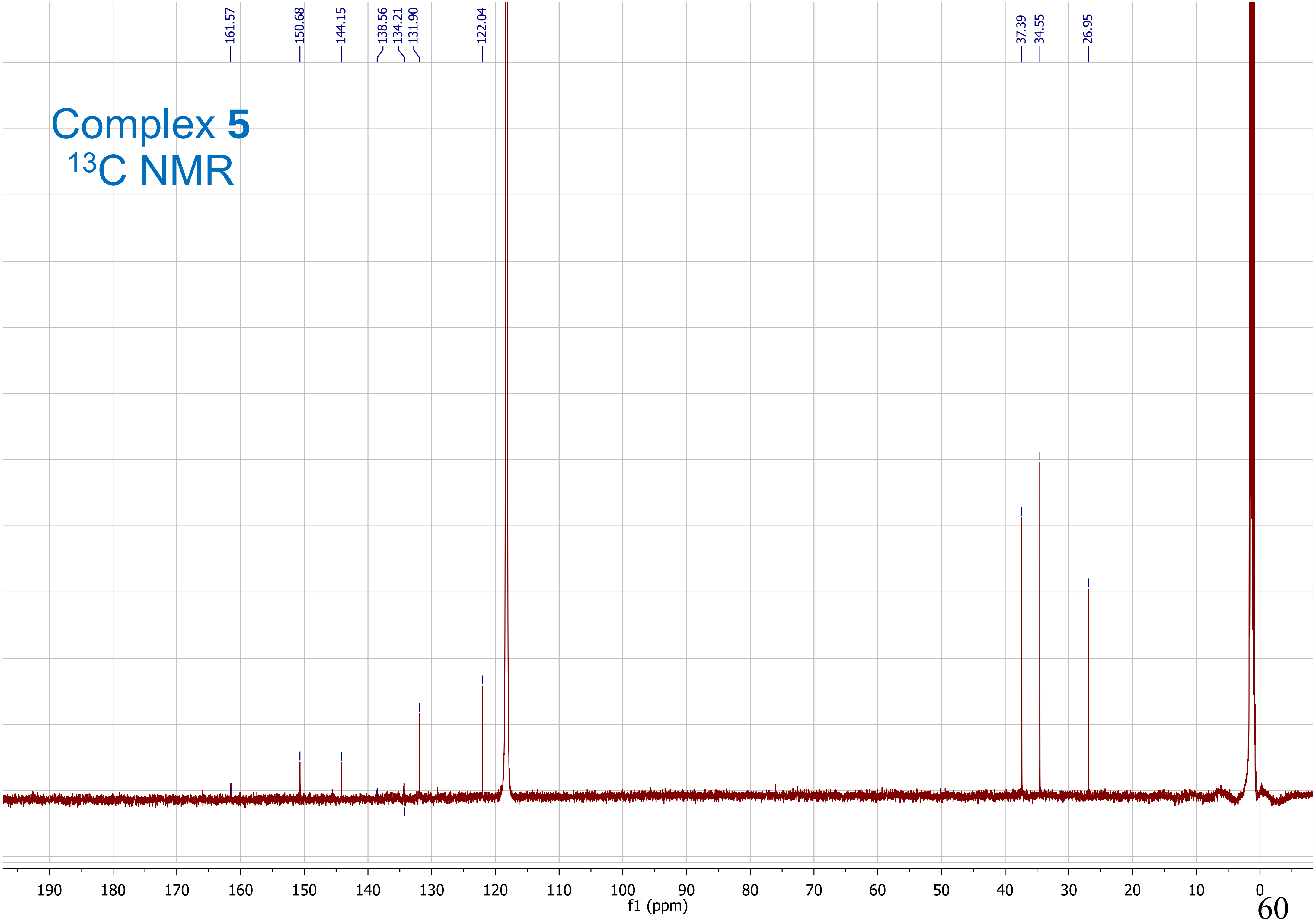
^{1}H-^{13}C HSQC



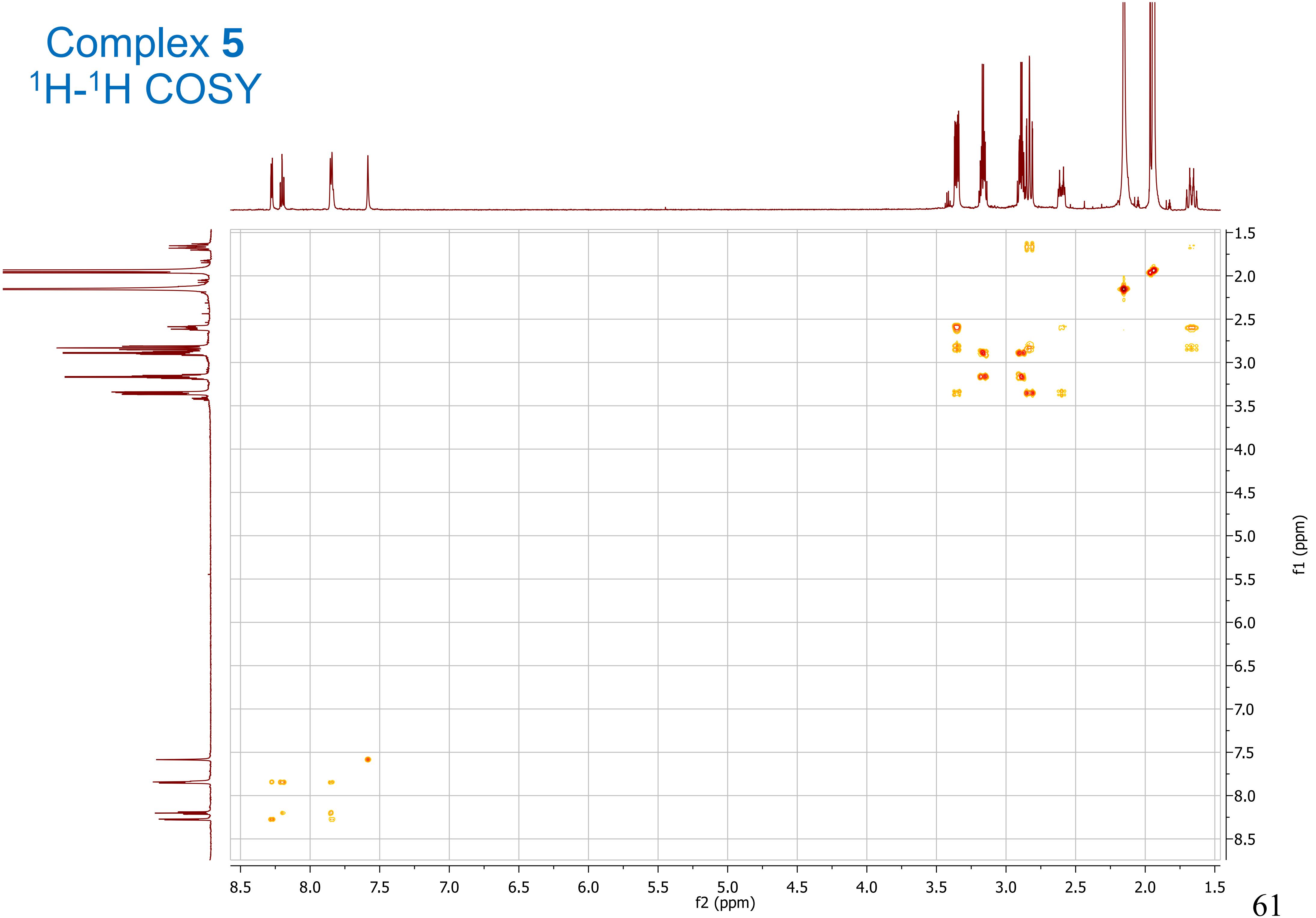
Complex **4**
^{1}H-^{13}C HMBC



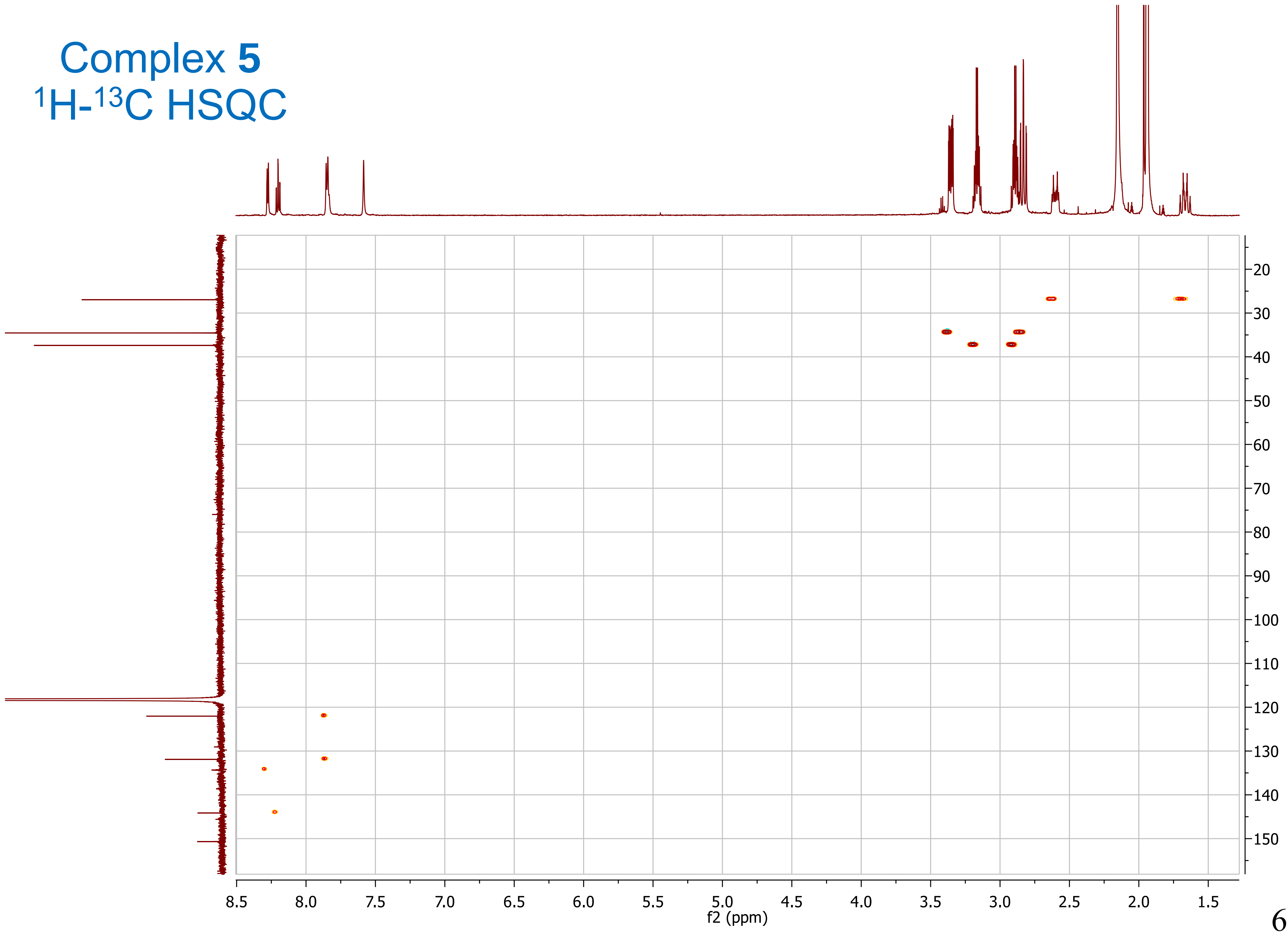

Complex 5
^{1}H NMR
8.28
8.27
8.20
8.19
8.19
7.86
7.84
7.58
3.37
3.37
3.36
3.36
3.35
3.35
3.34
3.34
3.19
3.19
3.18
3.18
3.17
3.16
3.16
3.15
3.15
3.14
2.89
2.89
2.83
2.63
2.62
2.61
2.60
2.59
2.58
1.70
1.70
1.68
1.68
1.68
1.67
1.66
1.65
1.63
1.00
1.05
2.00
1.01
4.10
4.31
8.49
2.20
2.01
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.
f1 (ppm)


Complex 5
^{13}C NMR
161.57
150.68
144.15
138.56
134.21
131.90
122.04
37.39
34.55
26.95
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

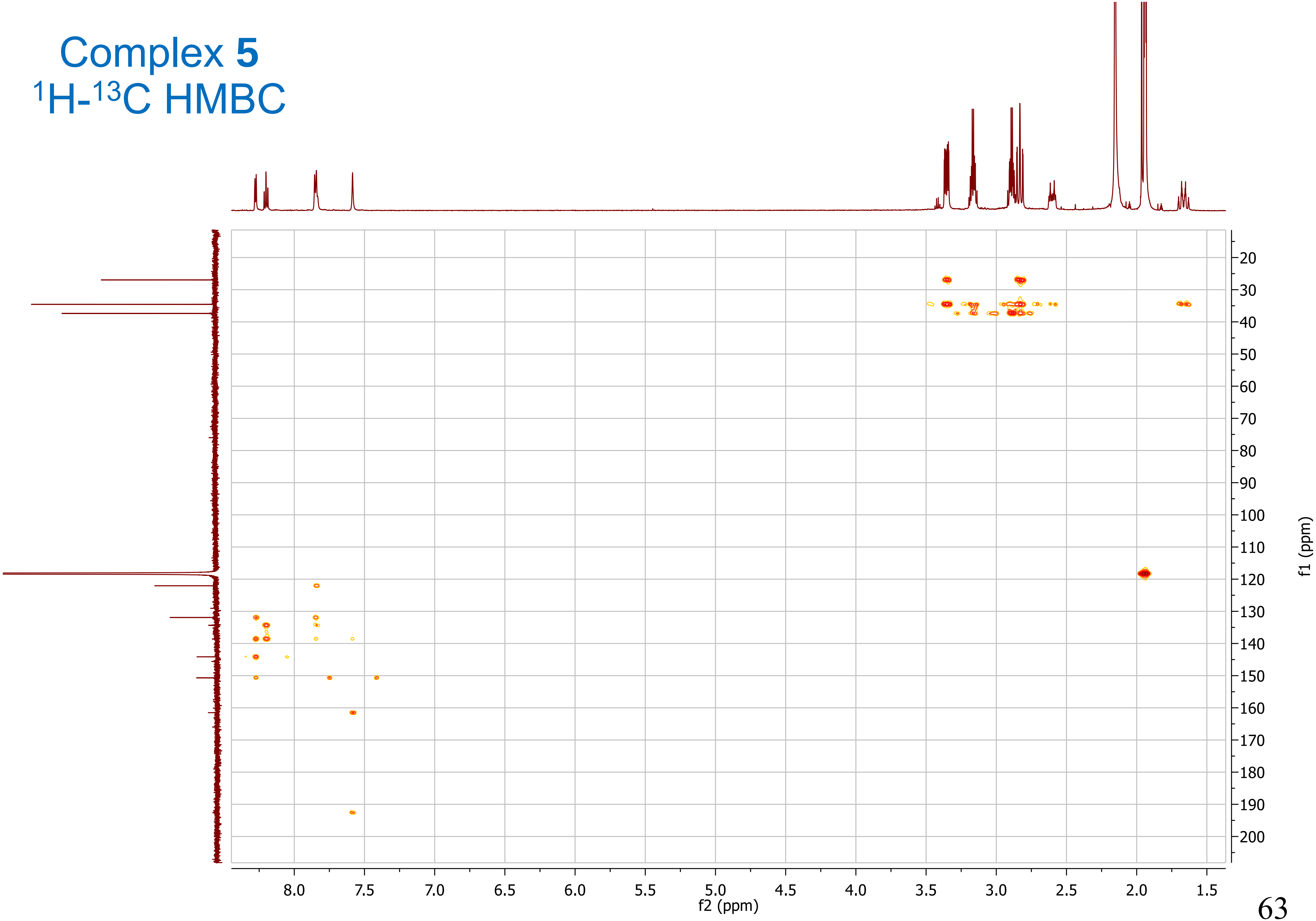
Complex **5**
^{1}H-^{1}H COSY

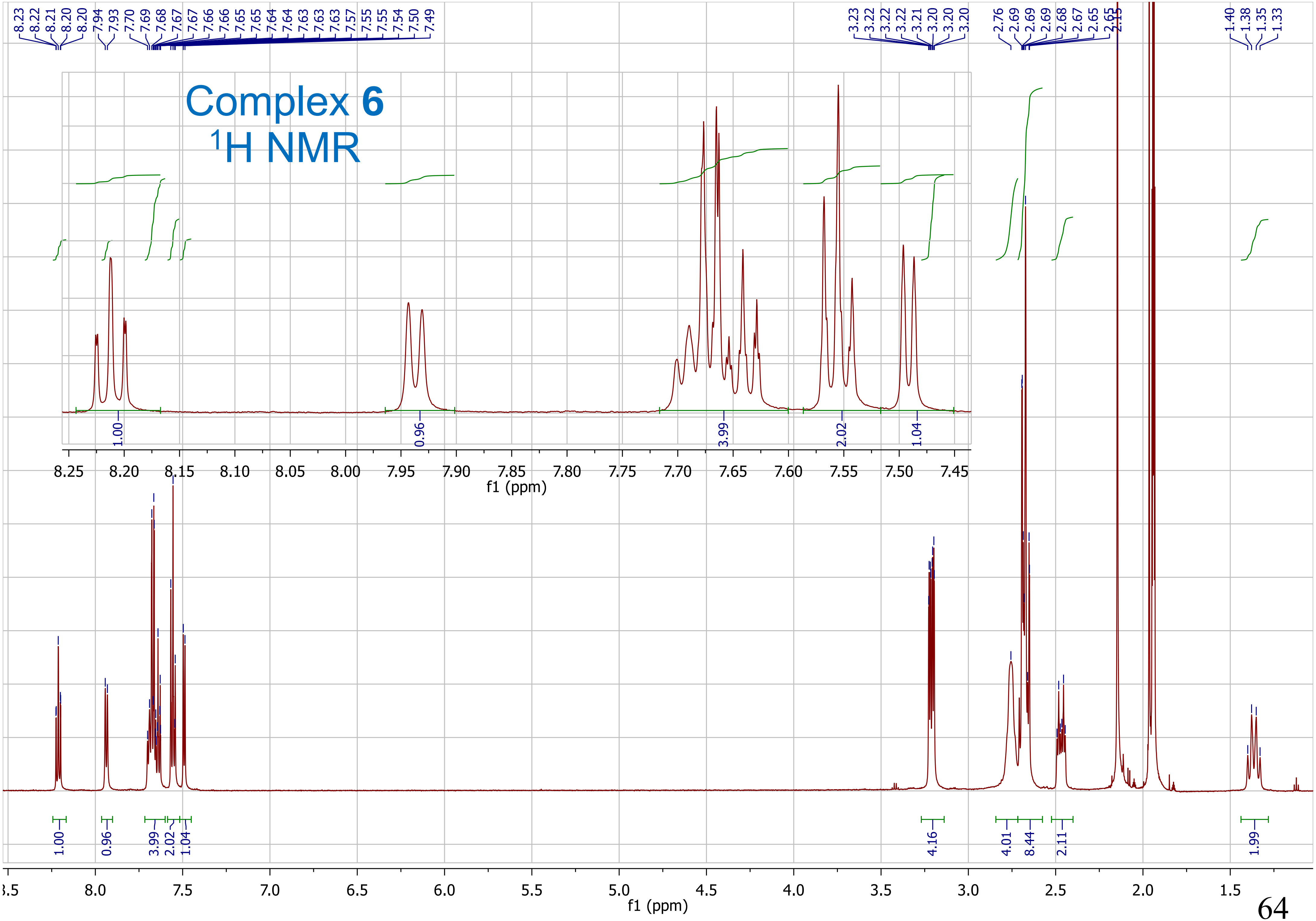


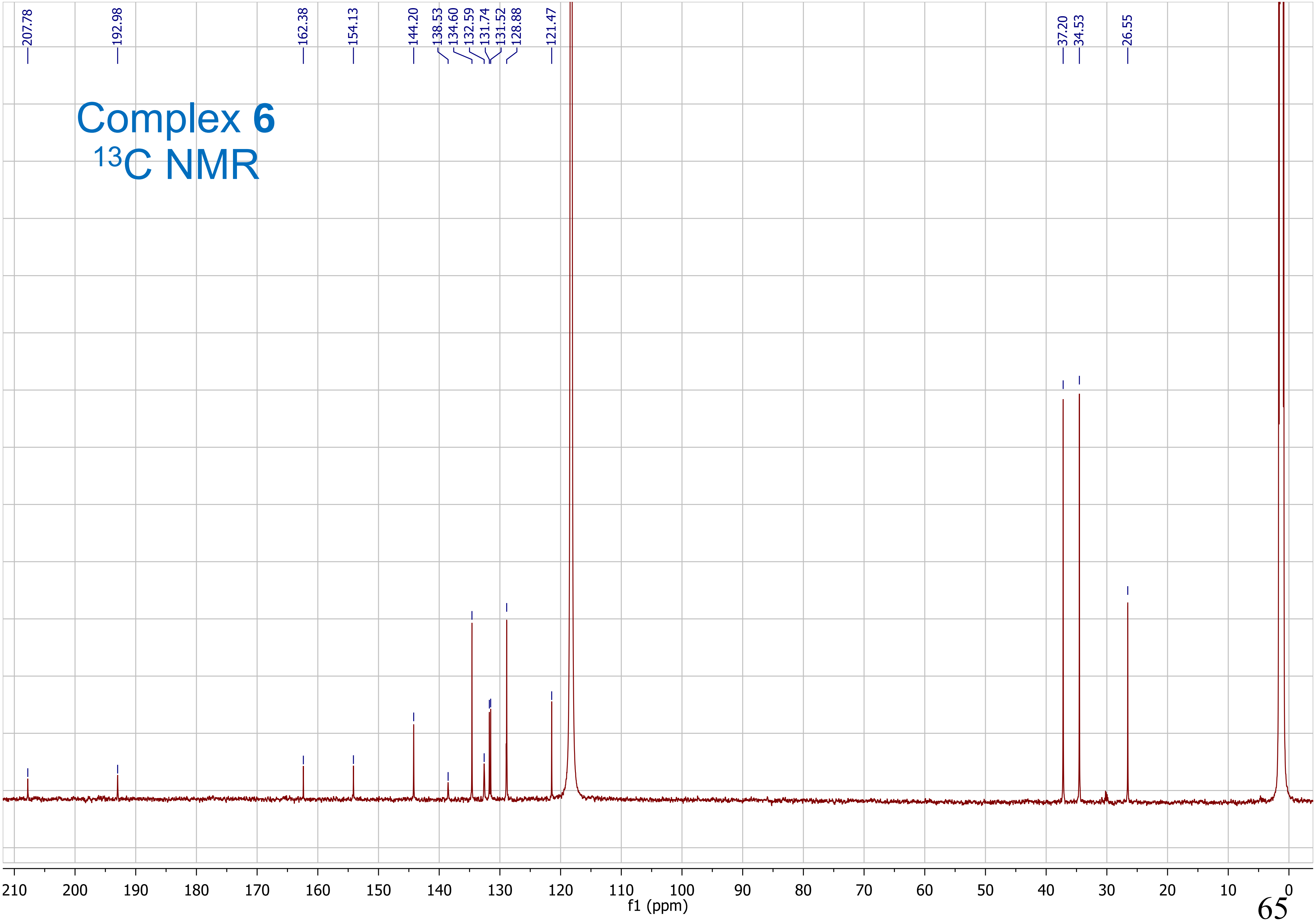
Complex **5**
^1H-^{13}C HSQC



Complex **5**
^{1}H-^{13}C HMBC

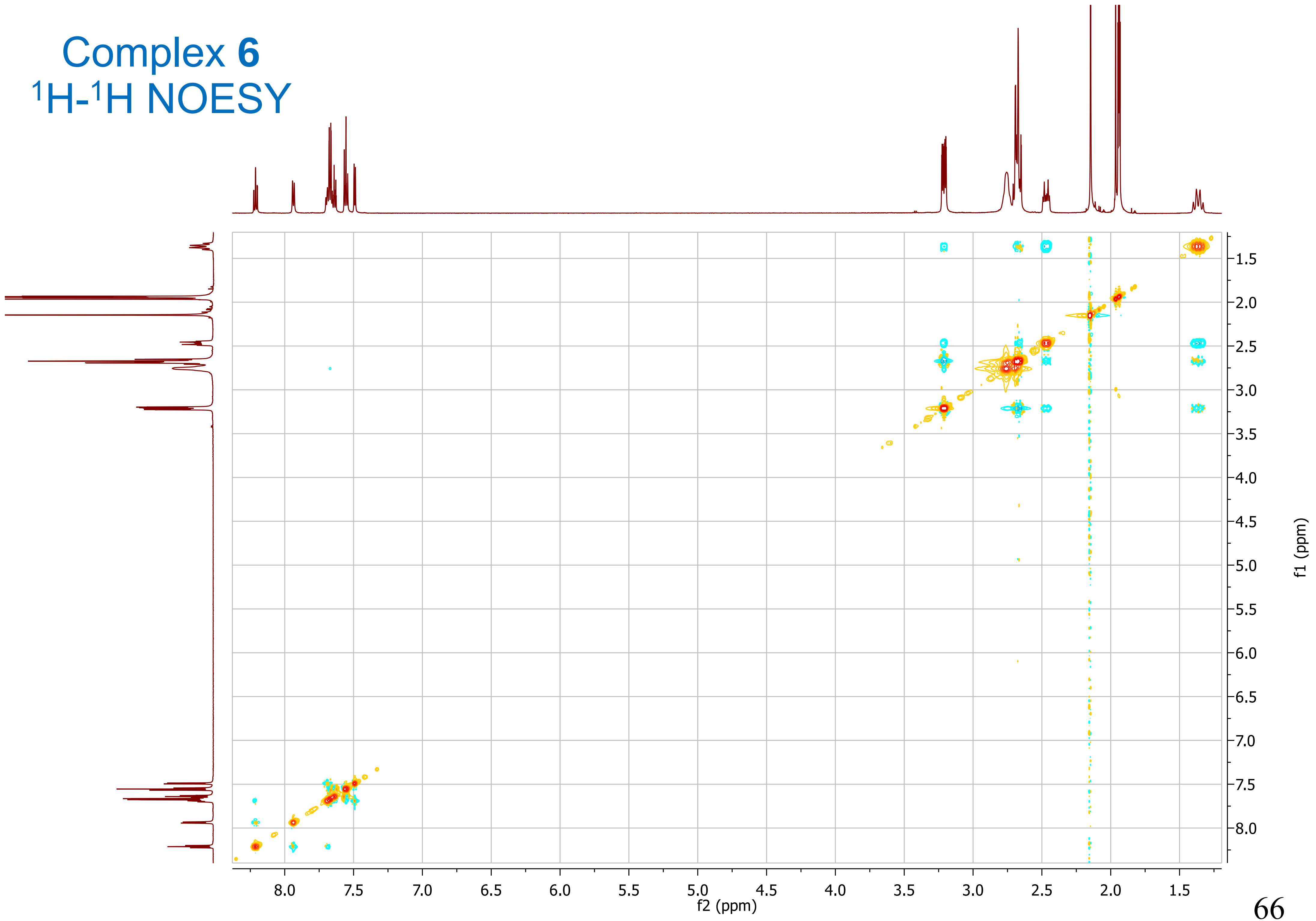



Complex 6
1H NMR
8.23 8.22 8.21 8.20 8.20 7.94 7.93 7.70 7.69 7.68 7.67 7.67 7.66 7.66 7.65 7.65 7.64 7.64 7.63 7.63 7.63 7.57 7.55 7.55 7.54 7.50 7.49
3.23 3.22 3.22 3.22 3.21 3.20 3.20 3.20 3.20
2.76 2.69 2.69 2.69 2.68 2.67 2.65 2.65 2.15
1.40 1.38 1.35 1.33
1.00 0.96 3.99 2.02 1.04
8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45
f1 (ppm)
1.00 0.96 3.99 2.02 1.04 4.16 4.01 8.44 2.11 1.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)


Complex **6**
^{13}C NMR
207.78
192.98
162.38
154.13
144.20
138.53
134.60
132.59
131.74
131.52
128.88
121.47
37.20
34.53
26.55
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

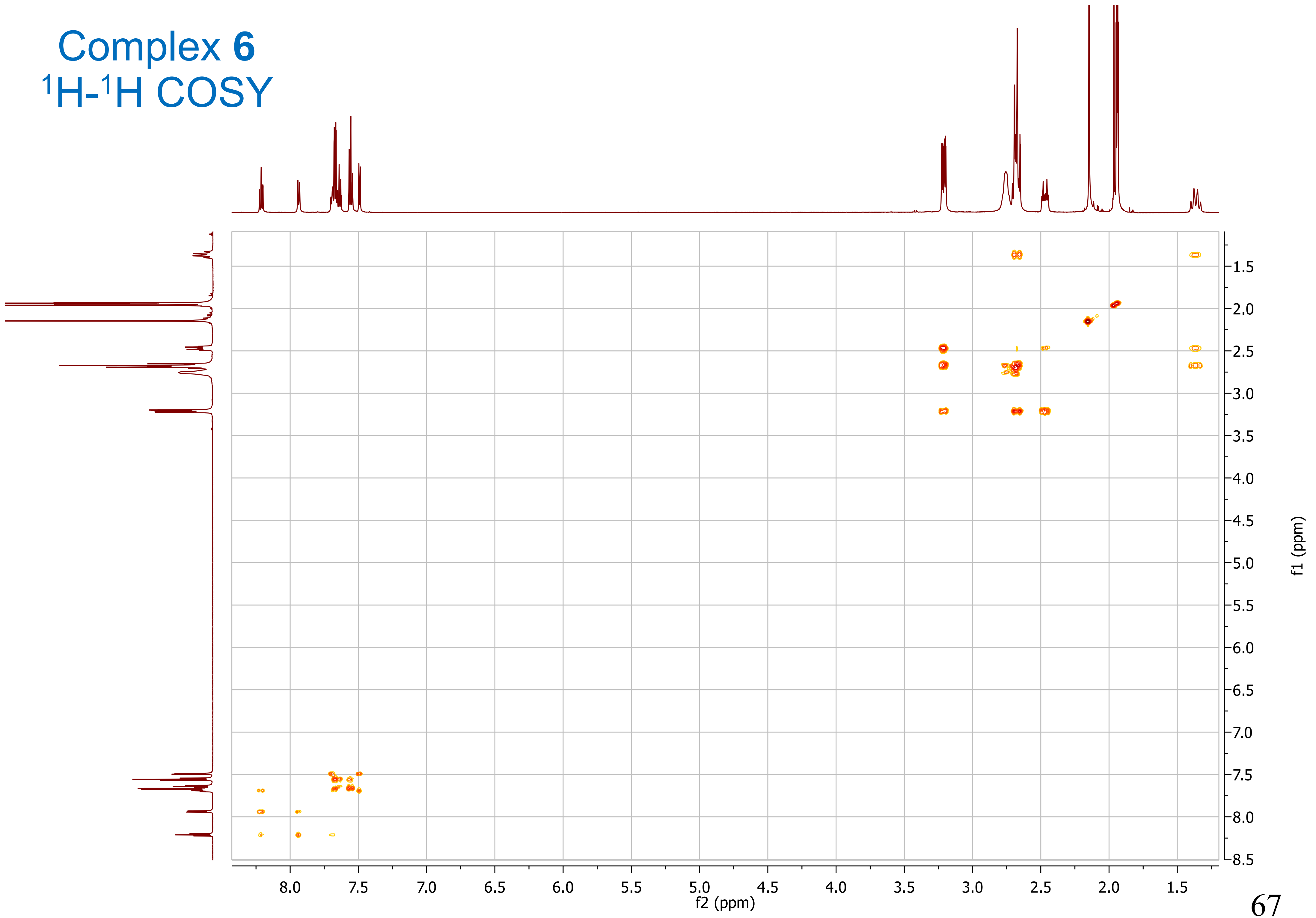
Complex **6**

^{1}H-^{1}H NOESY

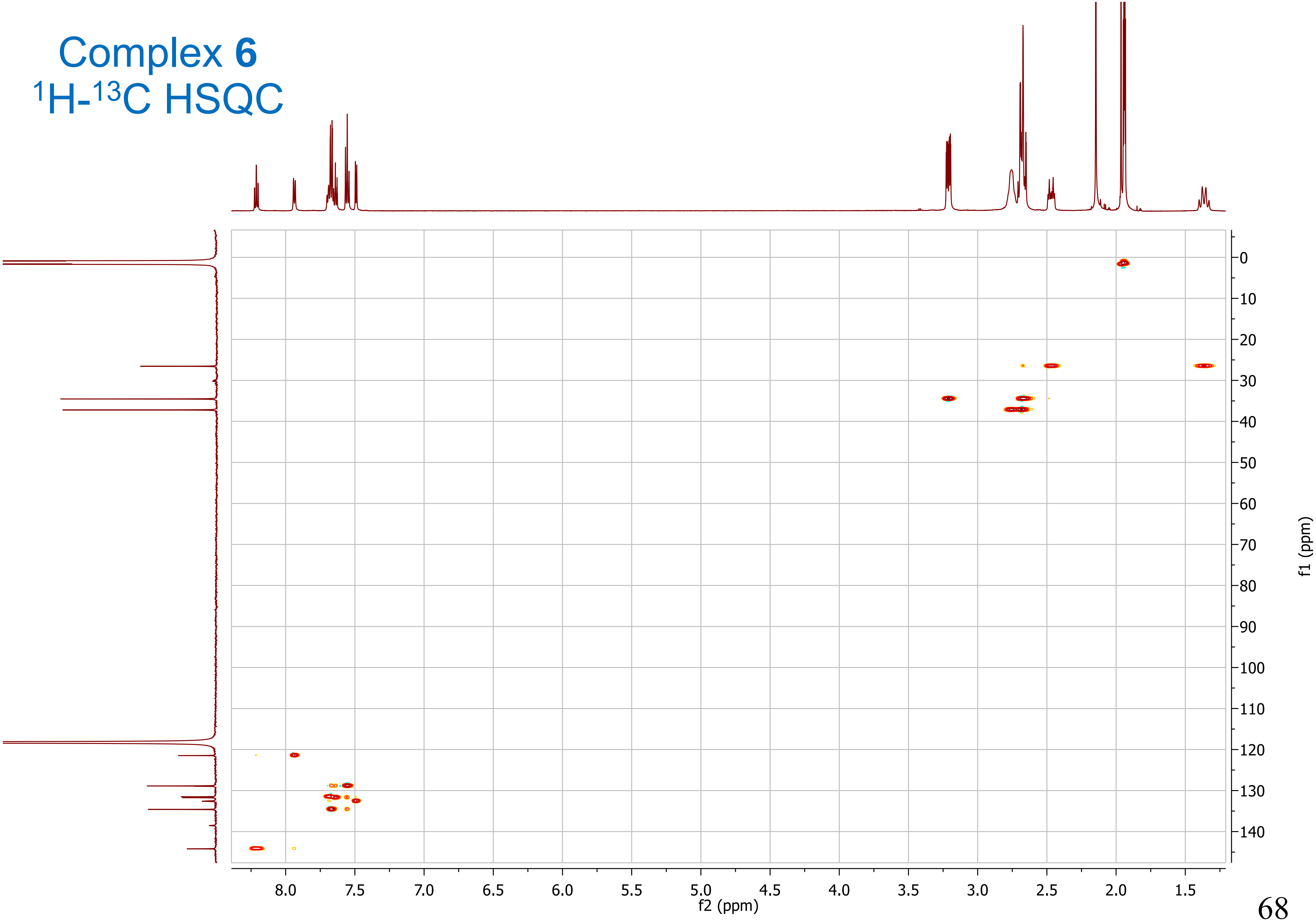


Complex **6**

^{1}H-^{1}H COSY

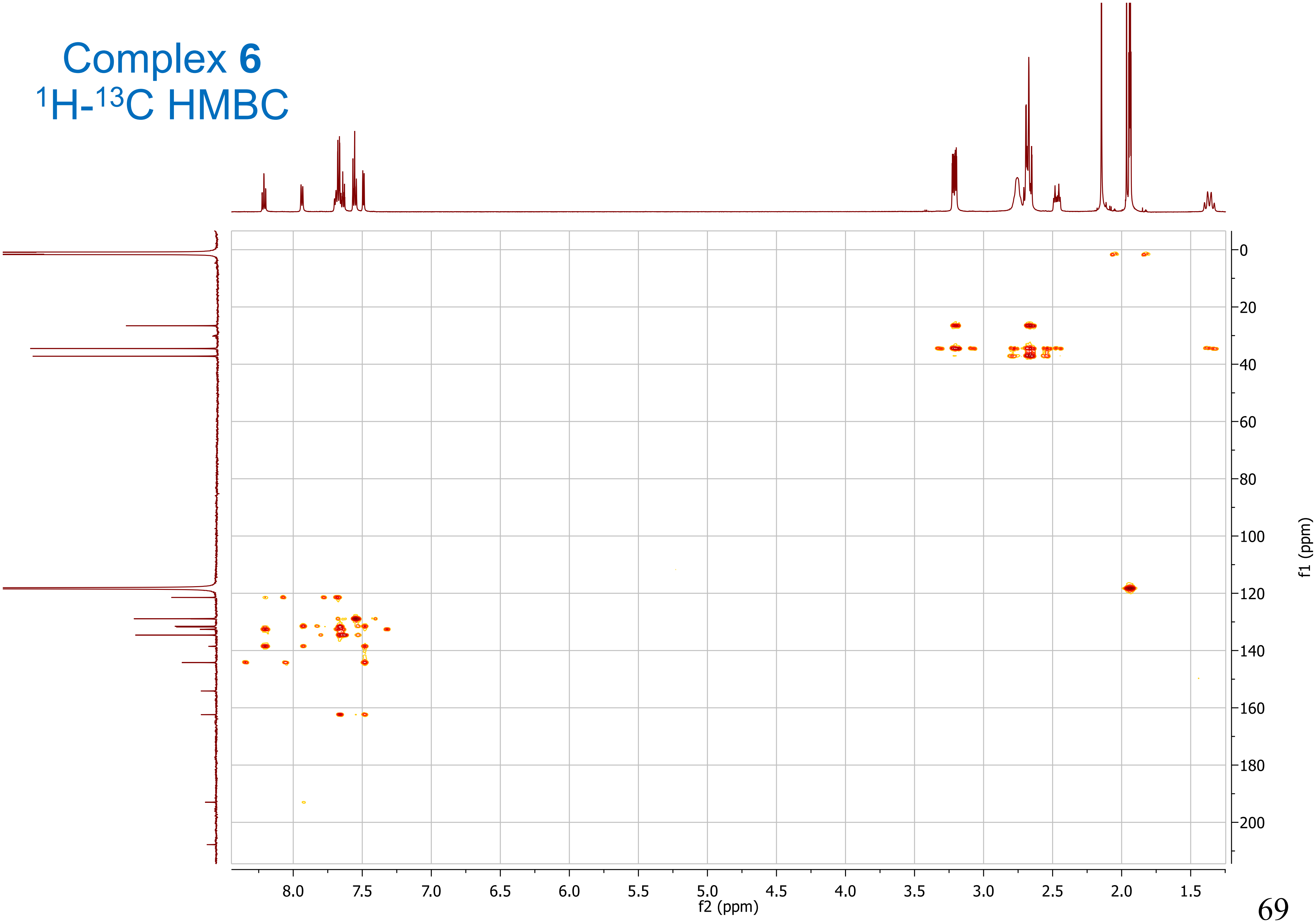


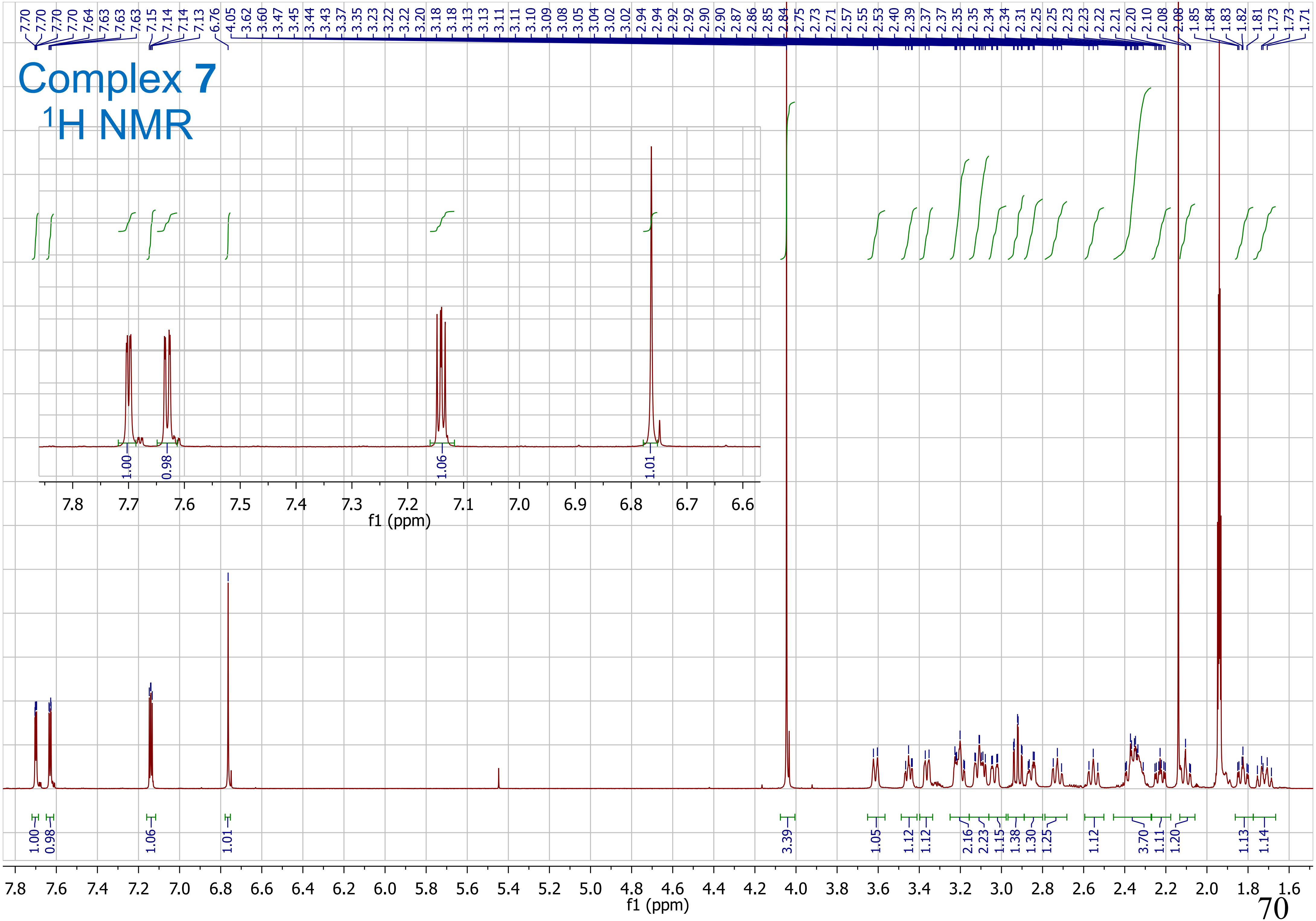
Complex **6**
^{1}H-^{13}C HSQC

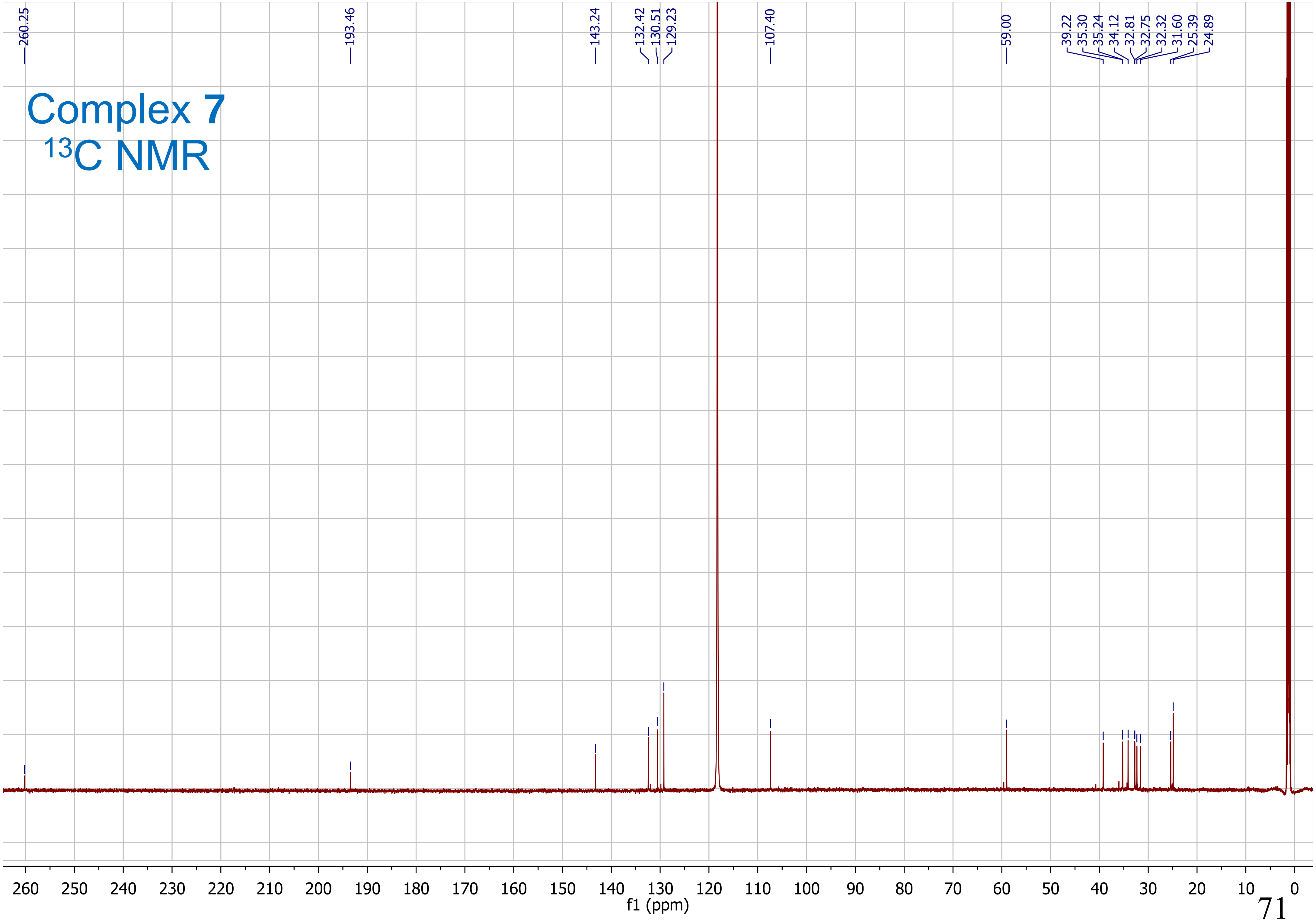


Complex **6**

^{1}H-^{13}C HMBC

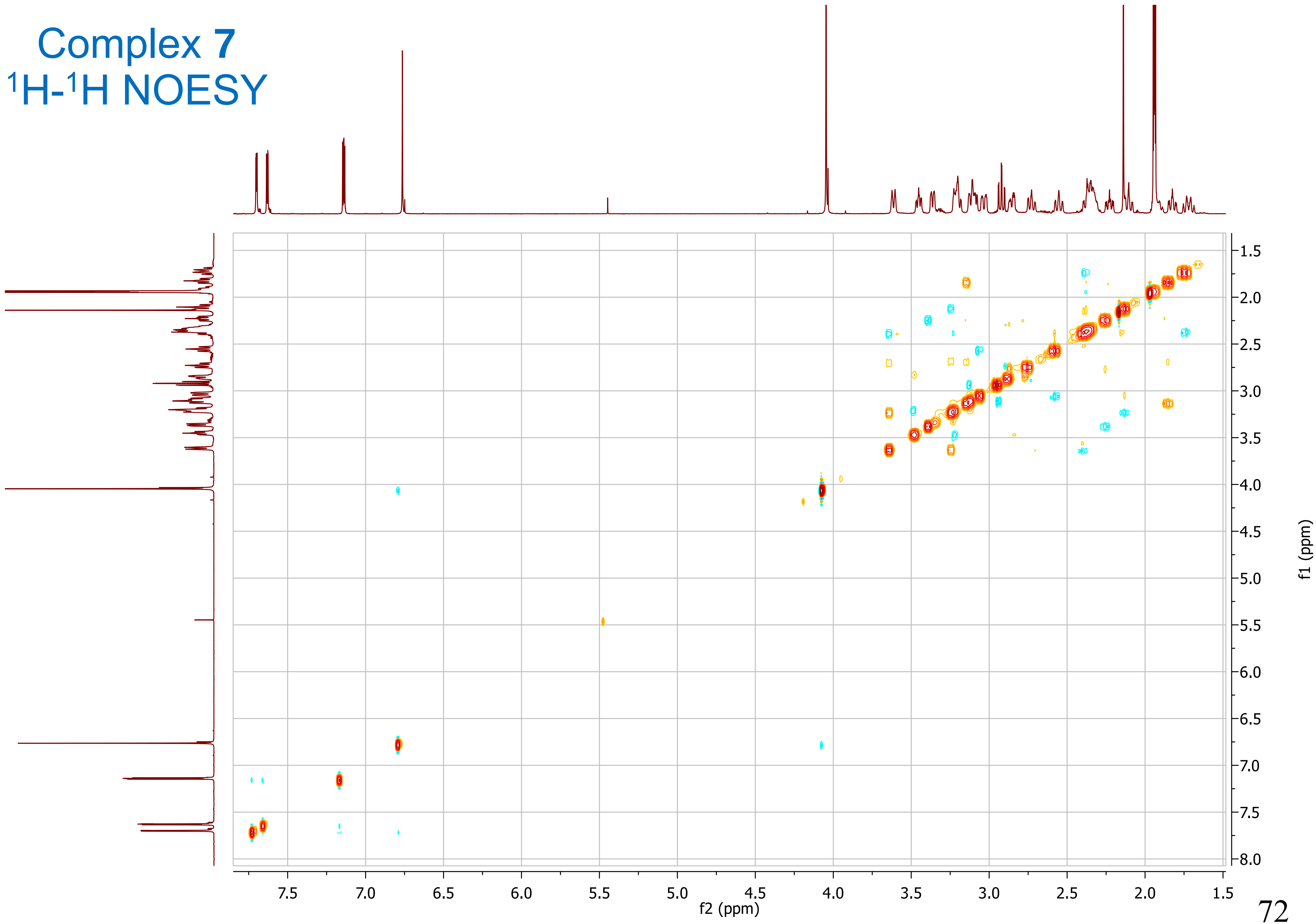



Complex 7
^{1}H NMR
7.70 7.70 7.70 7.70 7.64 7.63 7.63 7.63 7.15 7.14 7.14 7.13 6.76 4.05 3.62 3.60 3.47 3.45 3.44 3.43 3.37 3.35 3.23 3.22 3.22 3.20 3.18 3.18 3.13 3.13 3.11 3.11 3.10 3.09 3.08 3.05 3.04 3.02 3.02 2.94 2.94 2.92 2.92 2.90 2.90 2.87 2.86 2.85 2.84 2.75 2.73 2.71 2.57 2.55 2.53 2.40 2.39 2.37 2.37 2.35 2.35 2.34 2.34 2.31 2.25 2.25 2.23 2.23 2.22 2.21 2.20 2.10 2.08 2.08 1.85 1.84 1.83 1.82 1.81 1.73 1.73 1.71
1.00 0.98 1.06 1.01
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
1.00 0.98 1.06 1.01 3.39 1.05 1.12 1.12 2.16 2.23 1.15 1.38 1.30 1.25 1.12 3.70 1.11 1.20 1.13 1.14
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)

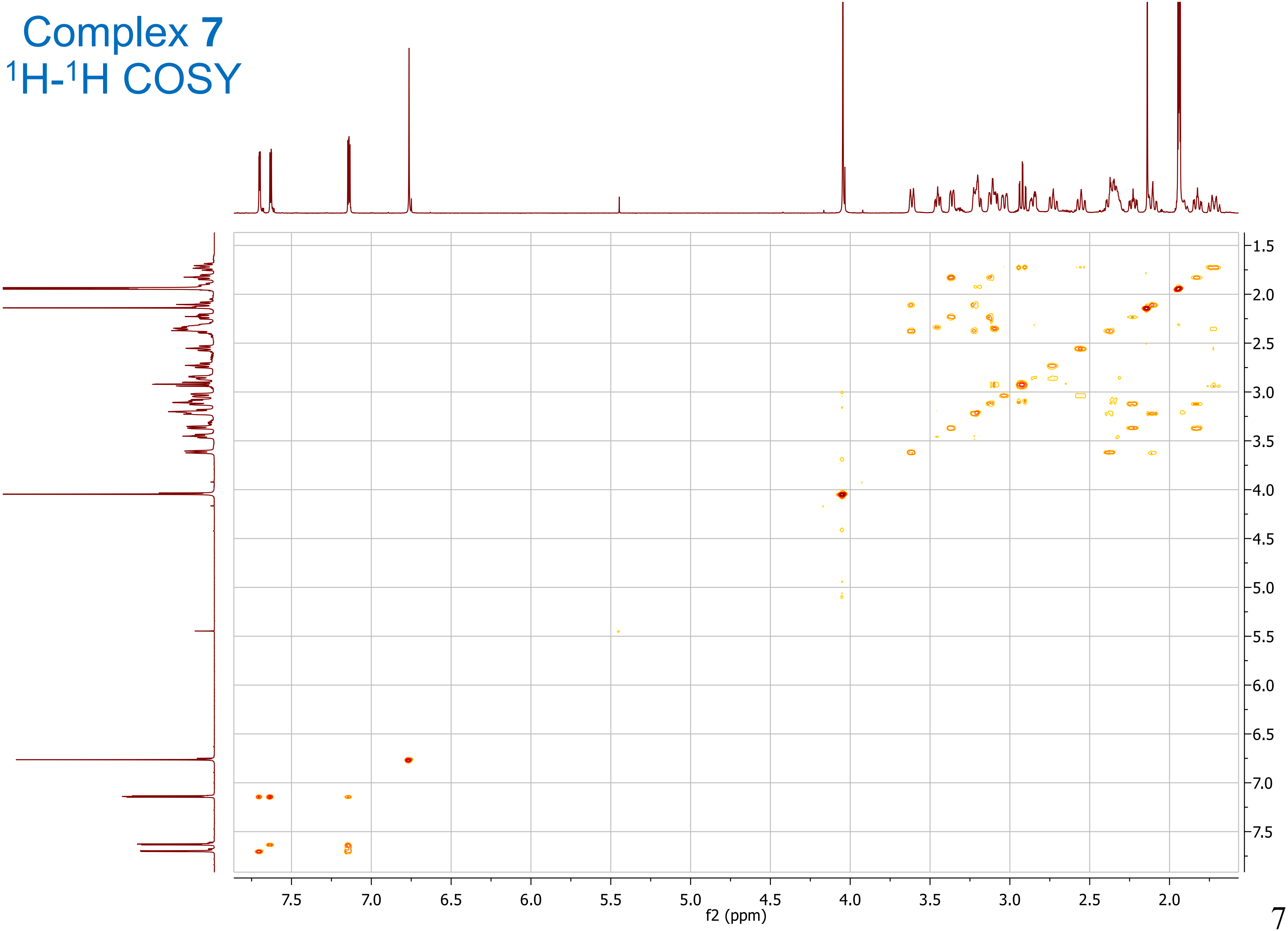

Complex 7
^{13}C NMR
260.25
193.46
143.24
132.42
130.51
129.23
107.40
59.00
39.22
35.30
35.24
34.12
32.81
32.75
32.32
31.60
25.39
24.89
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Complex **7**

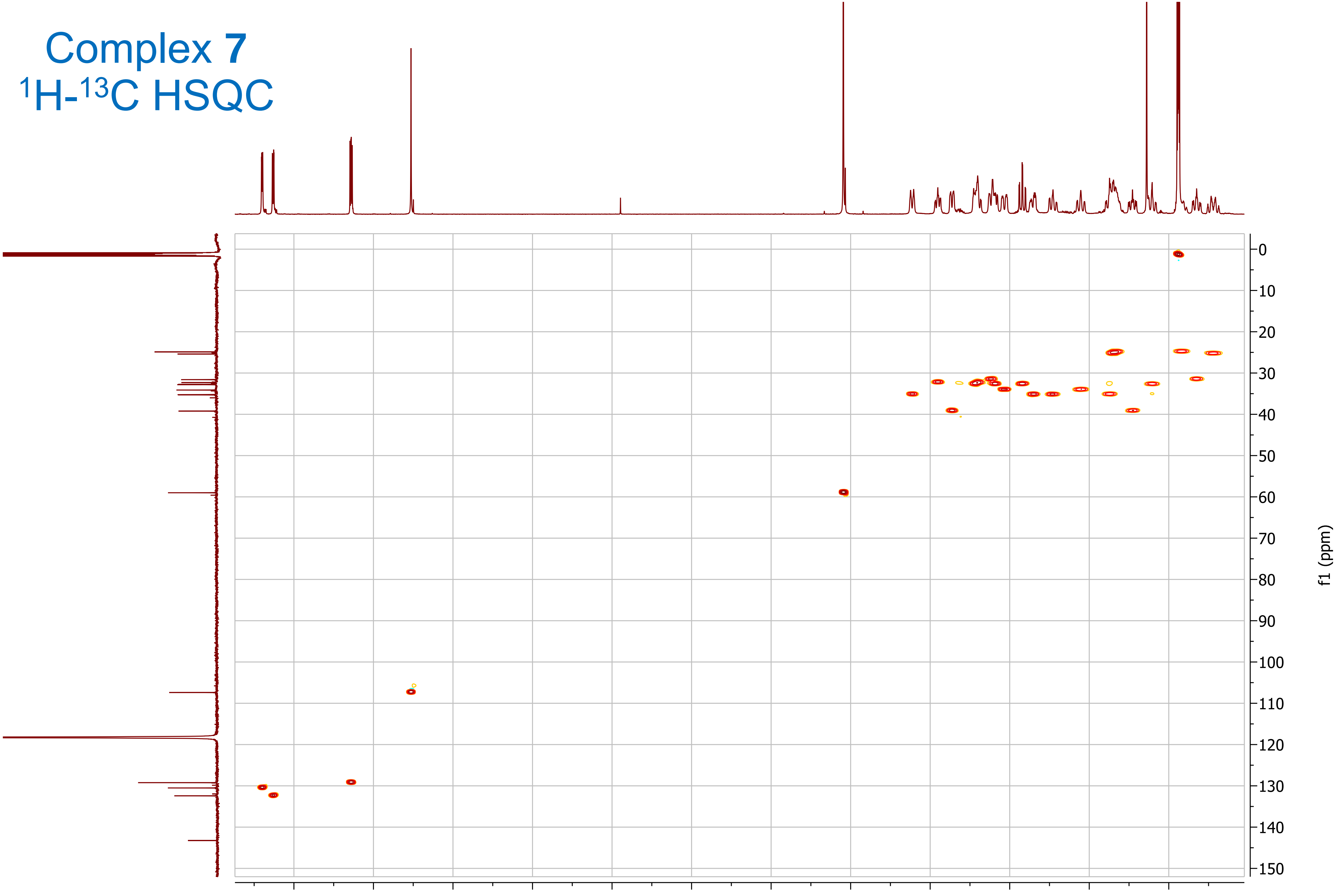
^{1}H-^{1}H NOESY



Complex **7**
^{1}H-^{1}H COSY



Complex **7**
^{1}H-^{13}C HSQC



Complex **7**

^{1}H-^{13}C HMBC