# Supporting Information

# Chiral Carbonyl Hypoiodites

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# Synthesis

## General Considerations

All reagents and solvents were obtained from commercial suppliers and used without further purification. For structural NMR assignments, $^{1}$H NMR and $^{1}$H-$^{15}$N NMR correlation spectra were recorded on a Bruker Avance III 500 MHz spectrometer at 25°C in $CD_2Cl_2$, or at 30°C in $(CD_3)_2SO$ (DMSO melting point = 19°C). Chemical shifts are reported on the δ scale in ppm using the residual solvent signal as internal standard ($CH_2Cl_2$ in $CD_2Cl_2$: $\delta_H$ 5.32, $\delta_C$ 53.84; $CHCl_3$ in $CDCl_3$: $\delta_H$ 7.26, $\delta_C$ 77.16; $(CH_3)_2SO$ in $(CD_3)_2SO$: $\delta_H$ 2.50, $\delta_C$ 39.52), or for $^{1}$H-$^{15}$N NMR spectroscopy, to an external $CD_3NO_2$ standard. For the $^{1}$H NMR spectroscopy, each resonance was assigned according to the following conventions: chemical shift (δ) measured in ppm, observed multiplicity, observed coupling constant (*J* Hz), and number of hydrogens. Multiplicities are denoted as: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), m (multiplet), and br (broad). For the $^{1}$H-$^{15}$N HMBC spectroscopy, spectral windows of 6 ppm ($^{1}$H; 10 and 7 ppm for **1** and **3b**, respectively) and 300 ppm ($^{15}$N) were used, with 1024 points in the direct dimension and 512 increments used in the indirect dimension, with subsequent peak shape analysis being performed to give the reported $^{15}$N NMR resonances. The $^{1}$H and $^{15}$N NMR data for uncoordinated DMAP have been previously reported.[1]

The single crystal X-ray data for **3b** and **3c** were collected at 120 K using an Agilent SuperNova dual wavelength diffractometer with an Atlas detector using mirror-monochromated Cu-Kα (λ = 1.54184 Å) radiation. The single crystal X-ray data for **4-morpy** was collected at 120 K using a Rigaku XtaLAB Synergy R diffractometer with a HyPix-Arc 100 detector using mirror-monochromated Cu-Kα (λ = 1.54184 Å) radiation. The single crystal X-ray data for **3a** was collected at 170 K using Bruker-Nonius Kappa CCD diffractometer with an APEX-II detector with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. The program COLLECT was used for the data collection and DENZO/SCALEPACK for the data reduction.[2,3] All structures were solved by intrinsic phasing (SHELXT)[4] and refined by full-matrix least squares on $F^2$ using Olex2,[5] utilising the SHELXL module.[6] Anisotropic displacement parameters were assigned to non-H atoms and isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with $U_{iso}$(H) = 1.2 $U_{eq}$(aromatic; cyclic alkyl) or $U_{iso}$(H) = 1.5 $U_{eq}$(acyclic alkyl) of their respective parent atoms. The X-ray single crystal data and CCDC numbers of all new structures are included below.

The following abbreviations are used: DCM = dichloromethane, DMAP = 4-dimethylaminopyridine, 4-morpy = 4-morpholinopyridine, 4-pyrpy = 4-pyrrolidinopyridine, TBME = $^{t}$butylmethyl ether.

## Precursor Species (**1**)

**(*S*)-*N*-phthaloylvaline** (**1**): Prepared as previously described.[7] $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.4, 3.0 Hz, 2H), 4.62 (d, *J* = 8.5 Hz, 1H), 2.75 (sep, *J* = 6.8 Hz, 1H), 1.16 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), *N.B. carboxylic acid hydrogen atom was not observed*; $^{13}$C NMR (126 MHz, $CDCl_3$) δ 174.3, 167.9, 134.4, 131.8, 123.8, 57.7, 28.6, 21.0, 19.6; $^{15}$N NMR (500 MHz, $CDCl_3$) δ -219.4.

**4-pyrpy**: $^{1}$H NMR (500 MHz, $CD_2Cl_2$) δ 8.12 (dd, *J* = 5.0, 1.4 Hz, 2H), 6.36 (dd, *J* = 5.0, 1.4 Hz, 2H), 3.28 (t, *J* = 6.6 Hz, 4H), 2.00 (t, *J* = 6.7 Hz, 4H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ 152.0, 149.9, 107.2, 47.2, 25.7; $^{15}$N NMR (500 MHz, $CD_2Cl_2$) δ -136.8 (pyridinic), -290.4 (pyrrolidino). The solid-state structure is known.[8]

**4-morpholinopyridine** (**4-morpy**): The NMR ($^{1}$H and $^{1}$H-$^{15}$N HMBC) spectra in $CD_2Cl_2$ and $(CD_3)_2SO$ have already been reported for this compound.[9] Crystals suitable for single crystal X-ray diffraction were obtained by evaporation of a DCM:pentane (1:4) solution of the compound. Crystal data for **4-morpy**: CCDC-2245212, $C_9H_{12}N_2O$, M = 164.21, colourless plate, 0.03 × 0.09 × 0.15 mm, monoclinic, space group $P2_1/c$, a = 9.7571(4) Å, b = 7.3863(2) Å, c = 12.0704(5) Å, β = 111.521(4)°, V = 809.25(6) Å$^3$, Z = 4, $D_{calc}$ = 1.348 gcm$^{-3}$, F(000) = 352, μ = 0.73 mm$^{-1}$, T = 120.0(1) K, $\theta_{max}$ = 74.5°, 3052 total reflections, 2900 with $I_o > 2\sigma(I_o)$, $R_{int}$ = N/A (twin data refinement), 3052 data, 109 parameters, no restraints, GooF = 1.08, 0.24 < dΔρ < -0.31 eÅ$^{-3}$, $R[F^2 > 2\sigma(F^2)]$ = 0.047, $wR(F^2)$ = 0.142.

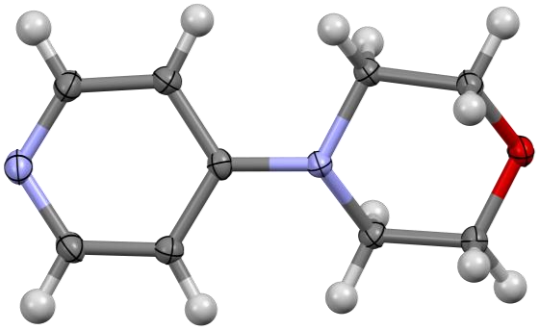

Figure S1: The asymmetric unit cell of **4-morpy**. Colour key: red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

## Silver(I) Complex (**2**)

**Ag[(*S*)-*N*-phthaloylvalinate]** (**2**): (*S*)-N-phthaloylvaline (**1**; 1.00 g, 4.04 mmol) was dissolved in $H_2O$ (30 mL), followed by the addition of a $H_2O$ (5 mL) solution of NaOH (0.17 g, 4.25 mmol), and stirred for 15 minutes. In the absence of light, a $H_2O$ (3.5 mL) solution of $AgNO_3$ (0.72 g, 4.25 mmol) was added to give a white precipitate, and the resulting mixture stirred in the dark for 1.5 hours. The white precipitate was isolated by filtration and washed with $H_2O$ (3 × 4 mL), MeOH (2 × 2mL), and $Et_2O$ (3 × 2 mL), then further air dried on the sinter to give a white solid. Yield = 0.61 g (1.72 mmol, 43%). $^{1}$H NMR (500 MHz, $(CD_3)_2SO$) δ 7.88 – 7.83 (m, 4H), 4.22 (d, *J* = 8.6 Hz, 1H), 2.62 (sep, *J* = 6.7 Hz, 1H), 1.12 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (126 MHz, $(CD_3)_2SO$) δ 171.3, 168.0, 134.5, 131.4, 123.0, 59.9, 28.3, 21.9, 20.2; $^{15}$N NMR (500 MHz, $(CD_3)_2SO$) δ -212.9.

## Iodine(I) Compounds (**3a-3c**)

All iodine(I) complexes were prepared using the same quantitative general method, which is given below using **3a** as an example.

**DMAP (*S*)-*N*-phthaloylvalinoyl hypoiodite** (**3a**): Ag[(*S*)-*N*-phthaloylvalinate] (**2**; 14.2 mg, 0.04 mmol) was suspended in DCM (2 mL) and to it was added a DCM (2 mL) solution of DMAP (4.9 mg, 0.04 mmol), causing nearly all of the solid to dissolve. After 10 minutes stirring, $I_2$ (10.2 mg, 0.04 mmol) was added as a solid to give a yellow precipitate and a pale red solution (once all the $I_2$ had been consumed with stirring over 10-15 minutes). Removed the yellow precipitate by filtration and vapour diffused the filtrate with TBME (16 mL) over 72 hours at ambient temperature to give the product as large colourless crystals, which were isolated by filtration, washed with pentane (2 × 4 mL), and briefly air dried. Yield = 12.8 mg (0.026 mmol, 65%). $^{1}$H NMR (500 MHz, $CD_2Cl_2$) δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.39 (d, *J* = 7.2 Hz, 2H), 4.39 (d, *J* = 8.5 Hz, 1H), 3.04 (s, 6H), 2.65 (sep, *J* = 6.8 Hz, 1H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ 173.1, 168.5, 155.5, 148.8, 134.2, 132.5, 123.4, 108.4, 57.9, 39.7, 29.4, 21.5, 19.9; $^{15}$N NMR (500 MHz, $CD_2Cl_2$) δ -212.5 (pyridinic), -309.7 ($NMe_2$), N.B. *phthalimide nitrogen atom was not observed*.

Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution of the complex vapour diffused with TBME. Crystal data for **3a**: CCDC-2225069, $C_{20}H_{22}IN_3O_4$, M = 495.30, colourless plate, 0.02 × 0.20 × 0.20 mm, monoclinic, space group $P2_1$, a = 11.0497(6) Å, b = 10.5607(8) Å, c = 18.3987(13) Å, β = 106.167(4)°, V = 2062.1(2) Å$^3$, Z = 4, $D_{calc}$ = 1.595 gcm$^{-3}$, F(000) = 992, μ = 1.58 mm$^{-1}$, T = 170(1) K, $\theta_{max}$ = 25.2°, 6319 total reflections, 4185 with $I_o > 2\sigma(I_o)$, $R_{int}$ = 0.064, 6319 data, 602 parameters, 337 restraints, GooF = 1.04, 0.68 < dΔρ < -0.64 eÅ$^{-3}$, $R[F^2 > 2\sigma(F^2)]$ = 0.054, $wR(F^2)$ = 0.103, Flack = 0.05(3).

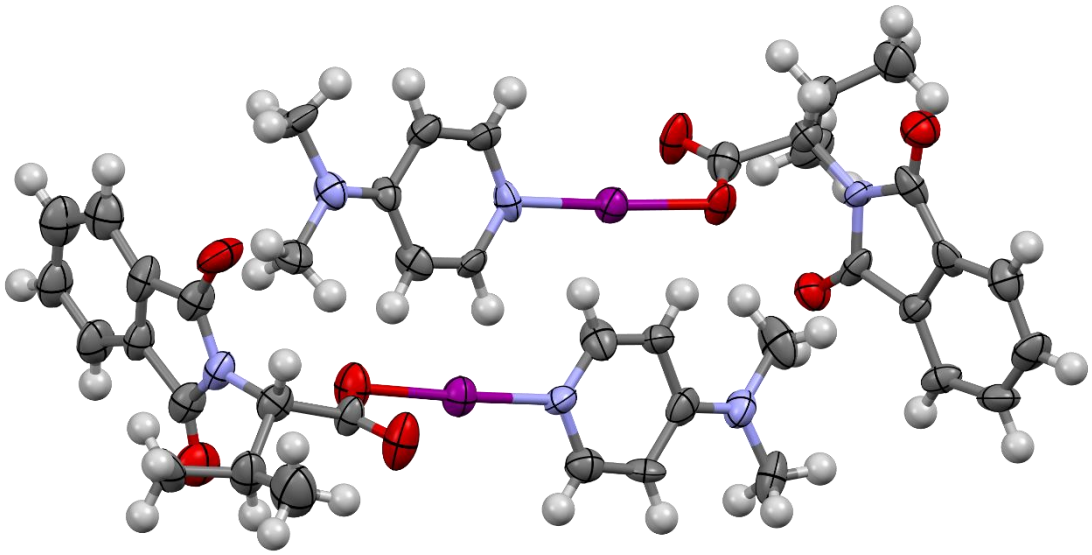

Figure S2: The asymmetric unit cell of **3a** (minor disordered atom positions omitted). Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

**4-pyrpy (*S*)-*N*-phthaloylvalinoyl hypoiodite** (**3b**): Prepared as described for **3a**, but with 4-pyrpy (5.9 mg, 0.04 mmol) instead of DMAP. Vapour diffusion was performed at ambient temperature using pentane (16 mL) instead of TBME. Product was recovered as an off-white crystalline solid. Yield = 17.7 mg (0.033 mmol, 85%). $^{1}$H NMR (500 MHz, $CD_2Cl_2$) δ 8.03 (d, *J* = 6.9 Hz, 2H), 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.28 (d, *J* = 7.0 Hz, 2H), 4.39 (d, *J* = 8.5 Hz, 1H), 3.33 (t, *J* = 6.5 Hz, 4H), 2.64 (sep, *J* = 6.5 Hz, 1H), 2.04 (t, *J* = 6.6 Hz, 4H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ 173.1, 168.5, 152.9, 148.7, 134.1, 132.5, 123.4, 109.0, 57.9, 48.0, 29.4, 25.6, 21.5, 19.9; $^{15}$N NMR (500 MHz, $CD_2Cl_2$) δ -214.7 (pyridinic), -280.8 (pyrrolidino), N.B. *phthalimide nitrogen atom was not observed*.

Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution of the complex vapour diffused with pentane. Crystal data for **3b**: CCDC-2225070, $(C_{22}H_{24}IN_3O_4)_{0.8}\cdot(C_{22}H_{22}IN_3O_5)_{0.2}$, M = 524.14, colourless plate, 0.06 × 0.19 × 0.20 mm, triclinic, space group *P*1, a = 7.8221(2) Å, b = 8.3335(2) Å, c = 16.8477(3) Å, α = 88.532(2)°, β = 83.279(2)°, γ = 84.899(2)°, V = 1086.23(4) Å$^3$, Z = 2, $D_{calc}$ = 1.603 gcm$^{-3}$, F000 = 526, μ = 11.87 mm$^{-1}$, T = 120.0(1) K, $\theta_{max}$ = 74.5°, 8298 total reflections, 8132 with $I_o > 2\sigma(I_o)$, $R_{int}$ = 0.025, 8298 data, 563 parameters, 18 restraints, GooF = 1.05, 0.44 < dΔρ < -0.50 eÅ$^{-3}$, $R[F^2 > 2\sigma(F^2)]$ = 0.024, $wR(F^2)$ = 0.061, Flack = -0.017(4).

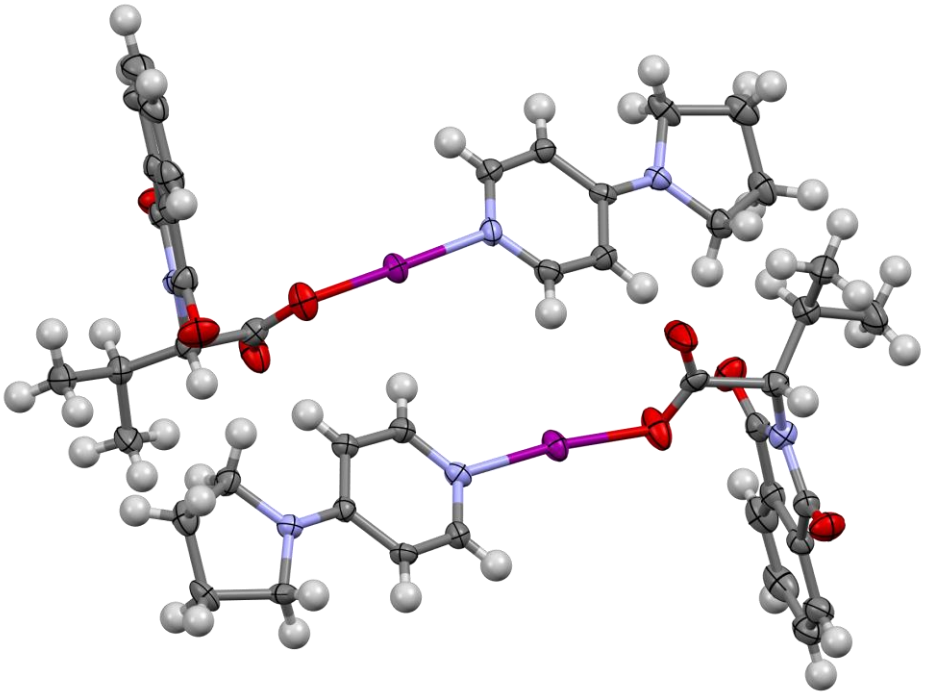

Figure S3: The asymmetric unit cell of **3b** (minor disordered positions omitted for clarity). Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

**4-morpy (*S*)-*N*-phthaloylvalinoyl hypoiodite** (**3c**): Prepared as described for **3a**, but with 4-morpy (6.6 mg, 0.04 mmol) instead of DMAP. Vapour diffusion was also performed using pentane (16 mL) instead of TBME. Product was recovered as a beige solid. Yield = 19.5 mg (0.036 mmol, 91%). $^{1}$H NMR (500 MHz, $CD_2Cl_2$) δ 8.13 (d, *J* = 7.1 Hz, 2H), 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.55 (d, *J* = 7.1 Hz, 2H), 4.41 (d, *J* = 8.5 Hz, 1H), 3.78 (t, *J* = 5.0 Hz, 4H), 3.38 (t, *J* = 5.0 Hz, 4H), 2.64 (sep, *J* = 6.8 Hz, 1H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ 173.1, 168.5, 156.1, 149.5, 134.2, 132.5, 123.4, 109.3, 66.3, 57.7, 45.9, 29.4, 21.5, 19.9; $^{15}$N NMR (500 MHz, $CD_2Cl_2$) δ -204.2 (pyridinic), -297.2 (morpholino), N.B. *phthalimide nitrogen atom was not observed*.

Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution of the complex vapour diffused with pentane. Crystal data for **3c**: CCDC-2225071, $C_{22}H_{24}IN_3O_5$, M = 537.34, colourless plate, 0.02 × 0.16 × 0.35 mm, monoclinic, space group *I*2, a = 15.4356(3) Å, b = 7.9667(2) Å, c = 36.8918(9) Å, β = 101.429(2)°, V = 4446.66(18) Å$^3$, Z = 4, $D_{calc}$ = 1.605 gcm$^{-3}$, F(000) = 2160, μ = 11.65 mm$^{-1}$, T = 120.0(1) K, $\theta_{max}$ = 75.9°, 8930 total reflections, 8281 with $I_o > 2\sigma(I_o)$, $R_{int}$ = 0.063, 8930 data, 557 parameters, 12 restraints, GooF = 1.05, 3.62 < dΔρ < -1.64 eÅ$^{-3}$, $R[F^2 > 2\sigma(F^2)]$ = 0.071, $wR(F^2)$ = 0.196, Flack = -0.023(7).

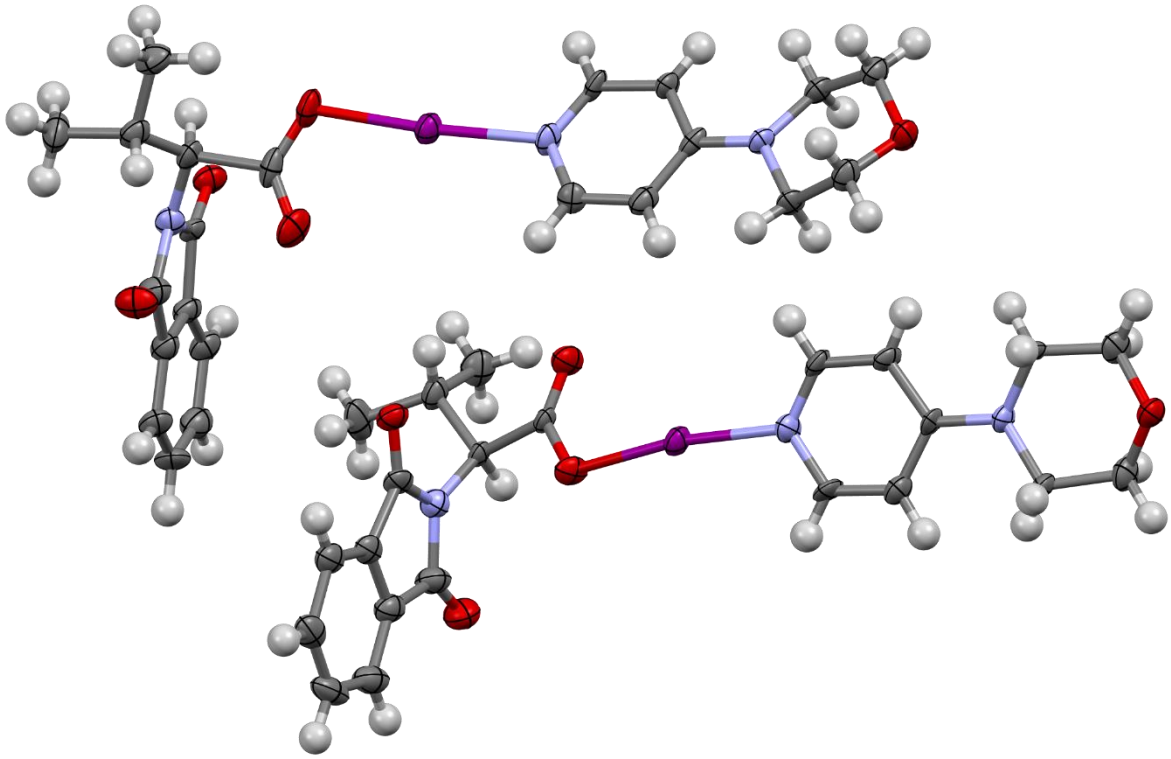

Figure S4: The asymmetric unit cell of **3c**. Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

## Comparison Table of Chemical Shifts

Table S1: Comparison of the carboxylic $^{13}C$ and $^{15}N$ NMR chemical shifts (in $CD_2Cl_2$ unless otherwise noted) of the complexes reported herein (in ppm).

| Compound | Carboxylic carbon ($\delta_C$) | $^{15}N$ NMR Chemical Shift(s) ($\delta_N$) |
|---|---|---|
| **1** | 174.3 | -219.4‡ |
| **2** | 171.3 | -212.9† |
| **3a** | 173.1 | -212.5<br>-309.7 |
| **3b** | 173.1 | -214.7<br>-280.8 |
| **3c** | 173.1 | -204.2<br>-297.2 |

‡ Recorded in $CDCl_3$.

† Recorded in $(CD_3)_2SO$.

# NMR Spectra

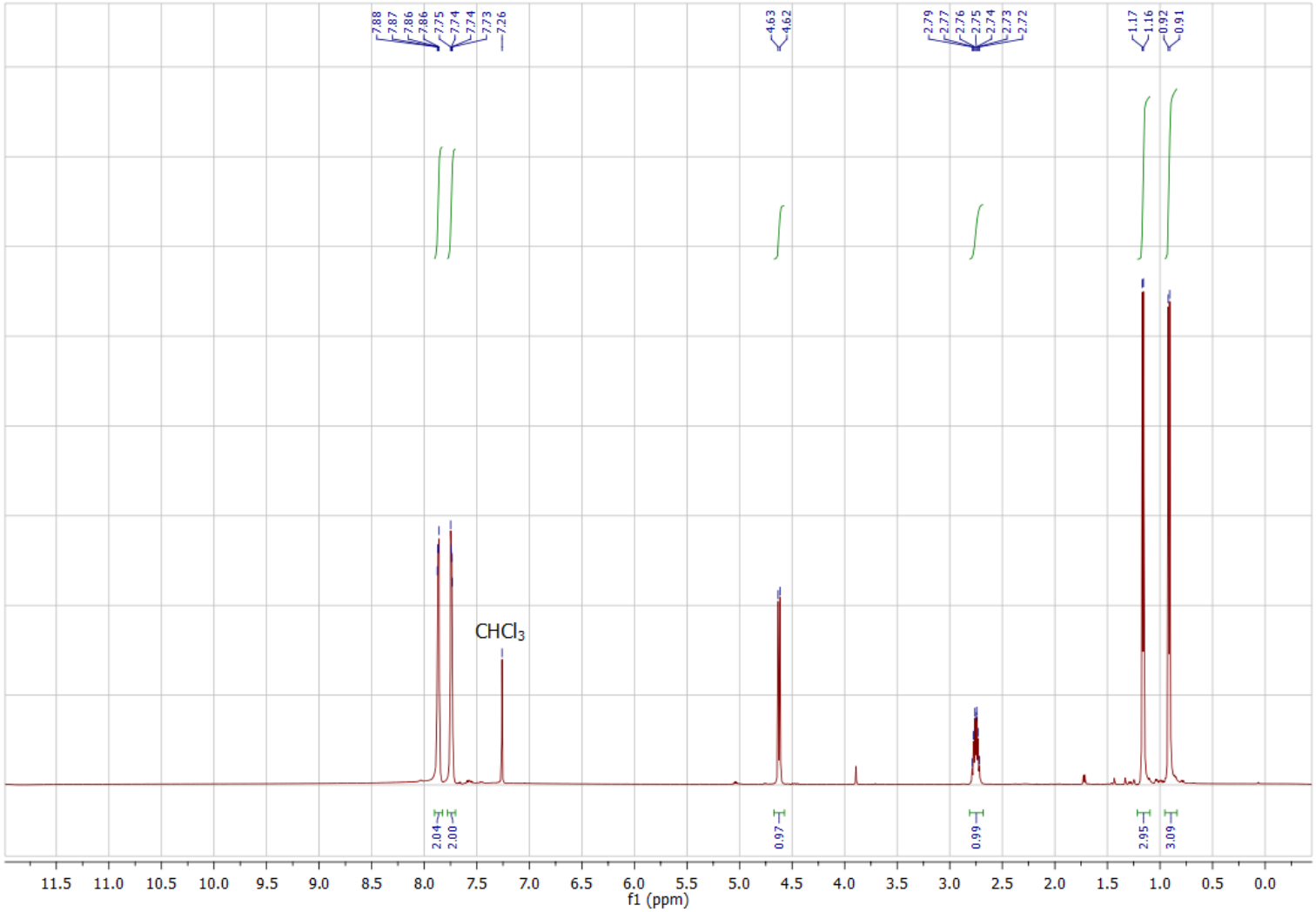


Figure S5: The $^{1}H$ NMR spectrum of compound **1** in $CDCl_3$.

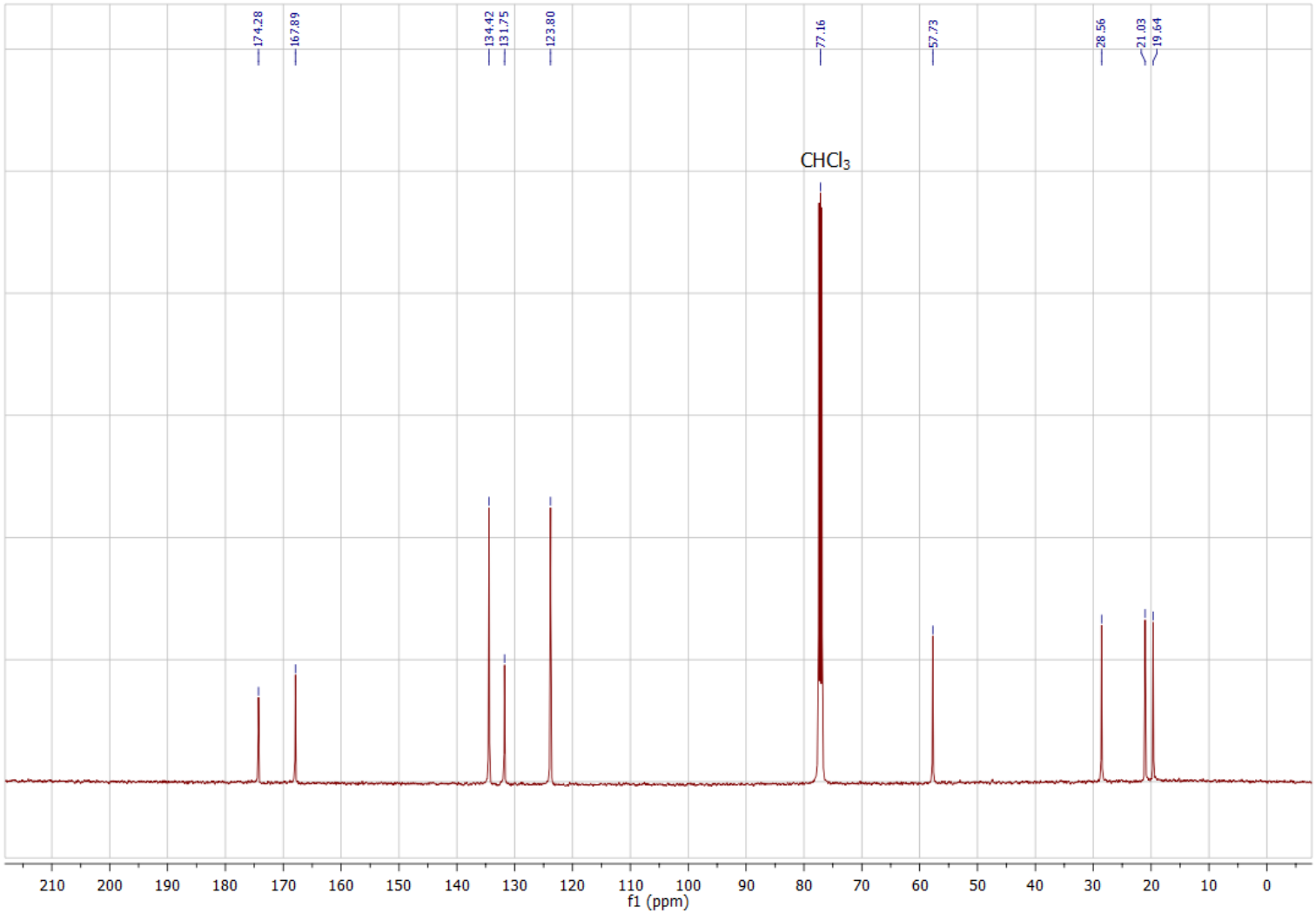


Figure S6: The $^{13}C$ NMR spectrum of compound **1** in $CDCl_3$.

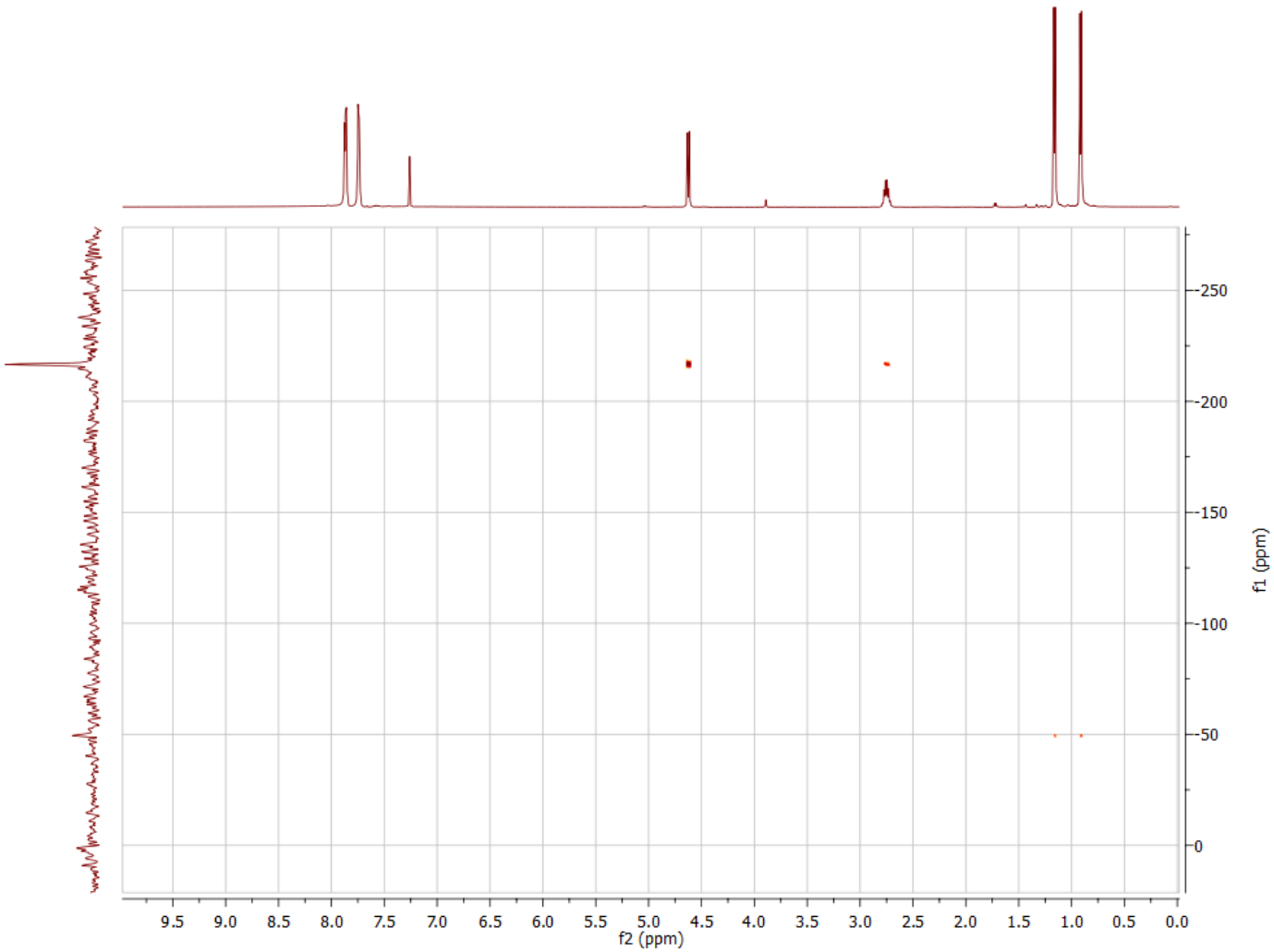


Figure S7: The $^{1}H$-$^{15}N$ HMBC spectrum of compound **1** in $CDCl_3$.

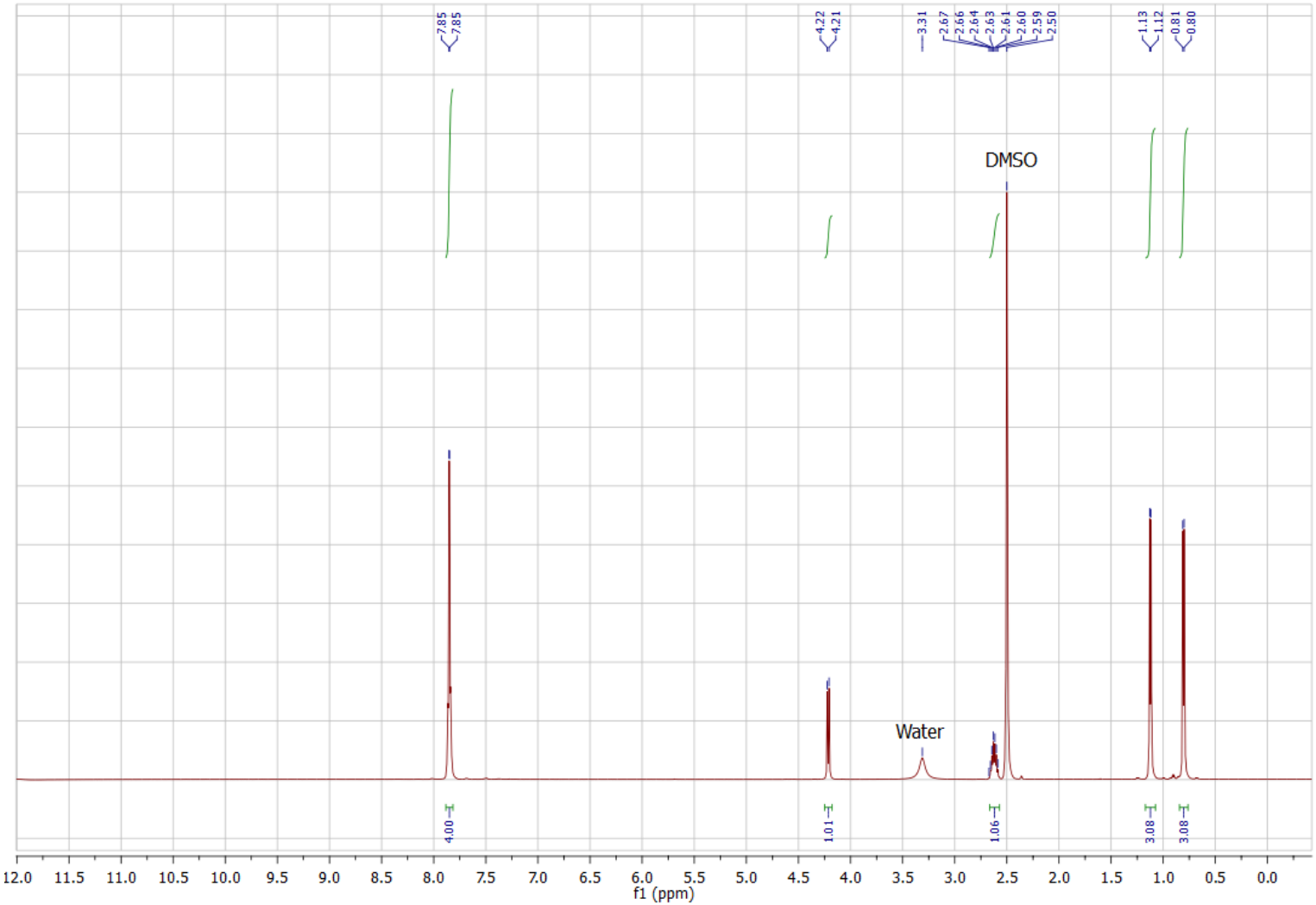


Figure S8: The $^{1}H$ NMR spectrum of complex **2** in $(CD_3)_2SO$.

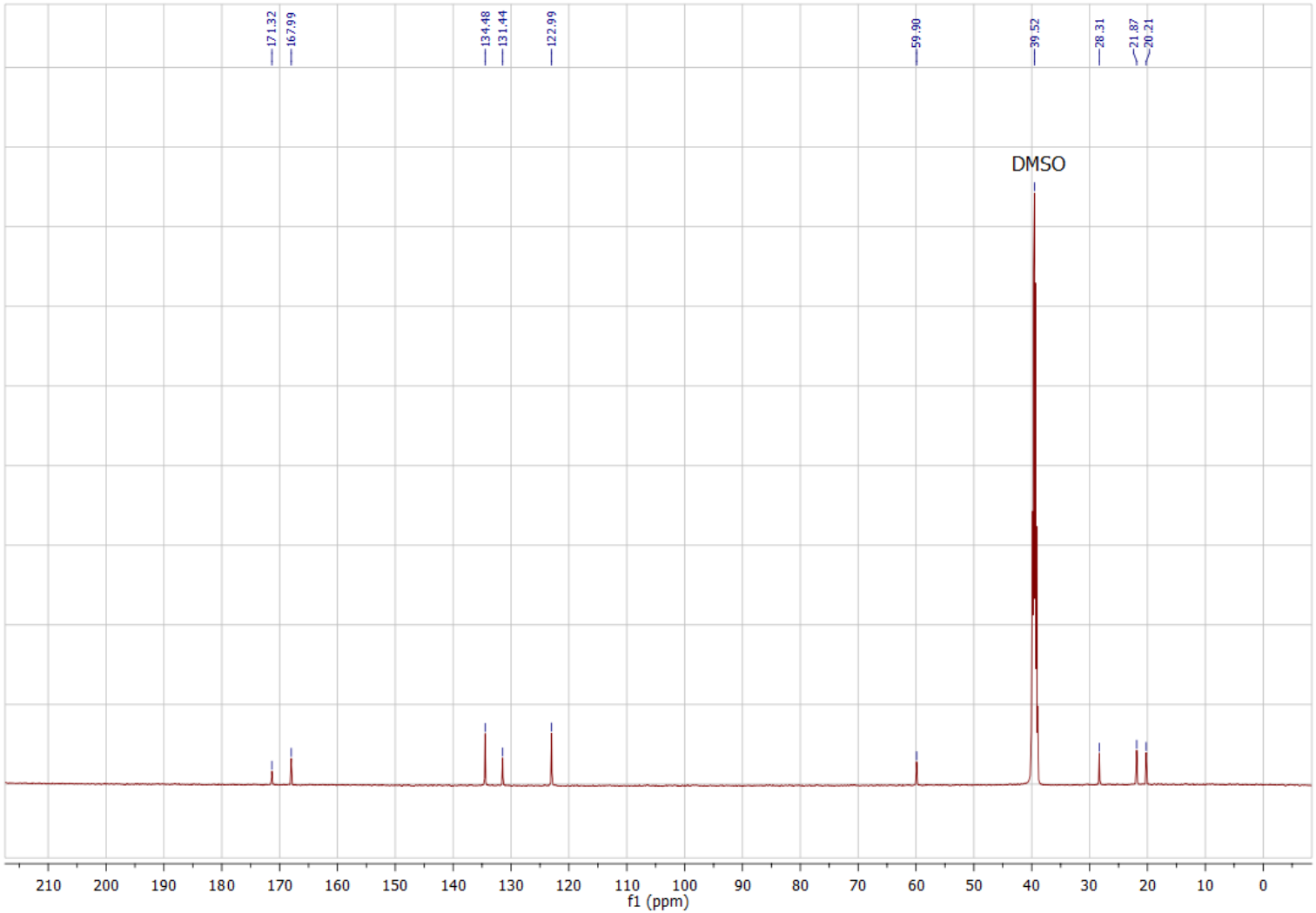


Figure S9: The $^{13}C$ NMR spectrum of complex **2** in $(CD_3)_2SO$.

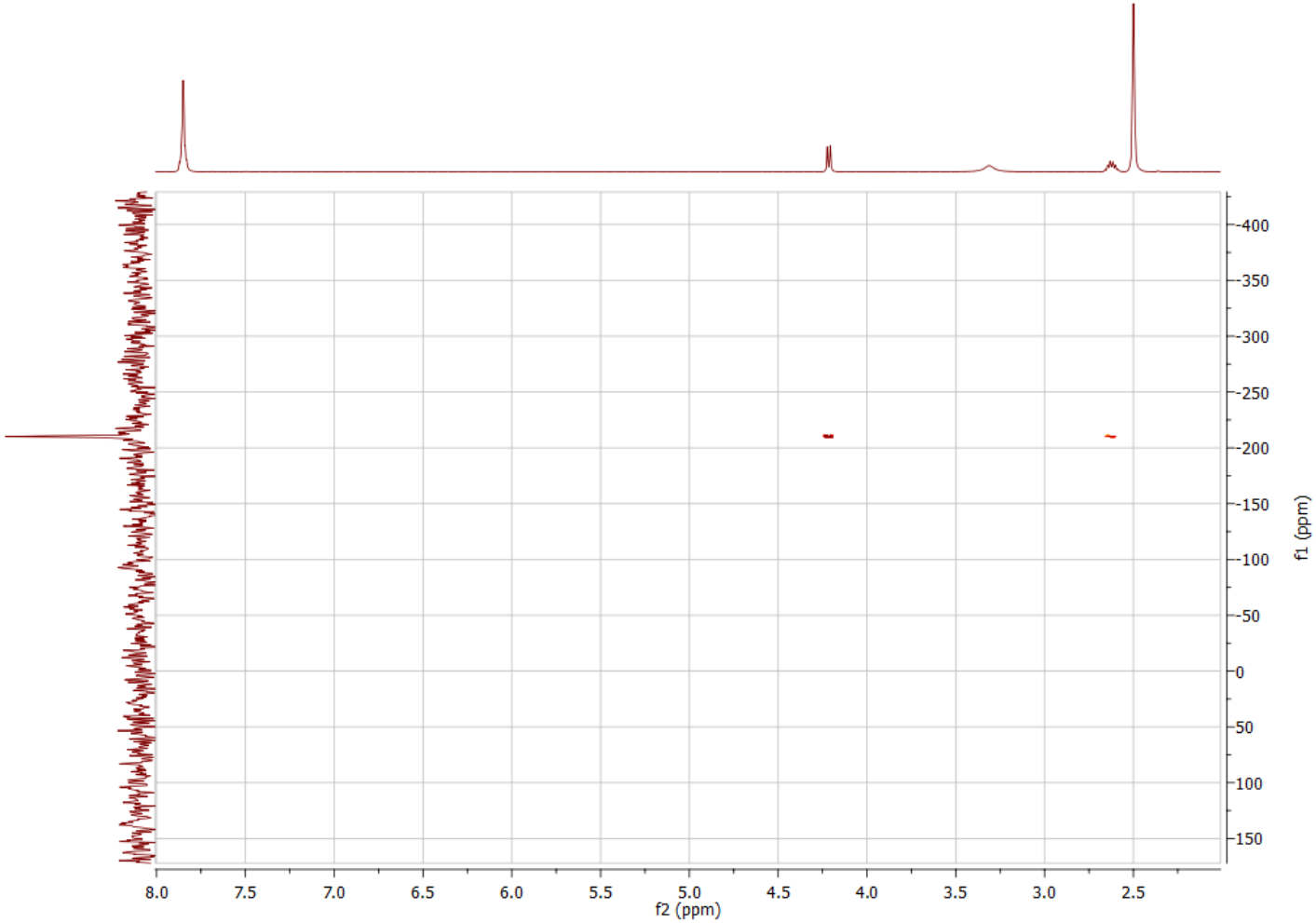


Figure S10: The $^{1}H$-$^{15}N$ HMBC spectrum of complex **2** in $(CD_3)_2SO$.

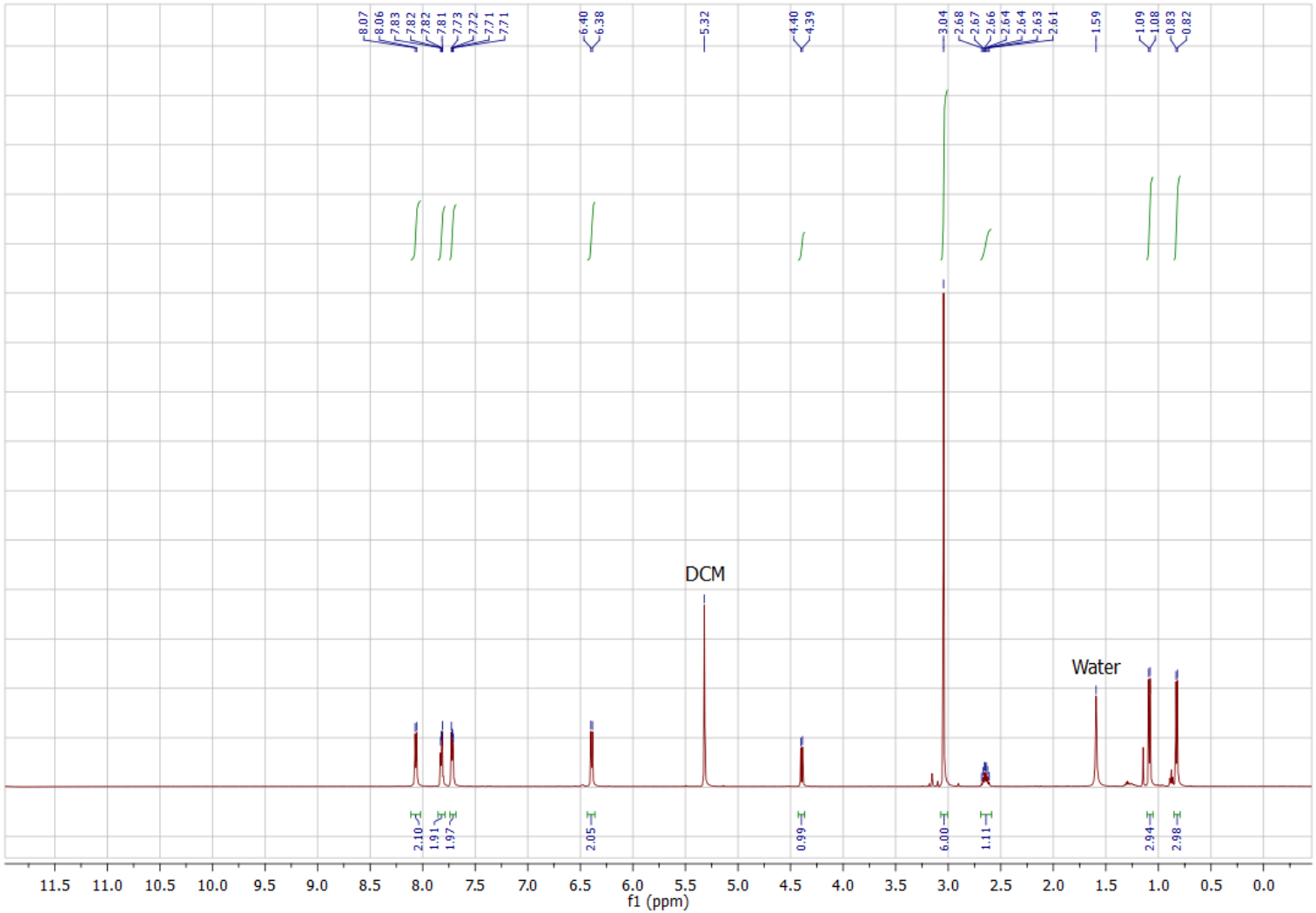


Figure S11: The $^{1}H$ NMR spectrum of complex **3a** in $CD_2Cl_2$.

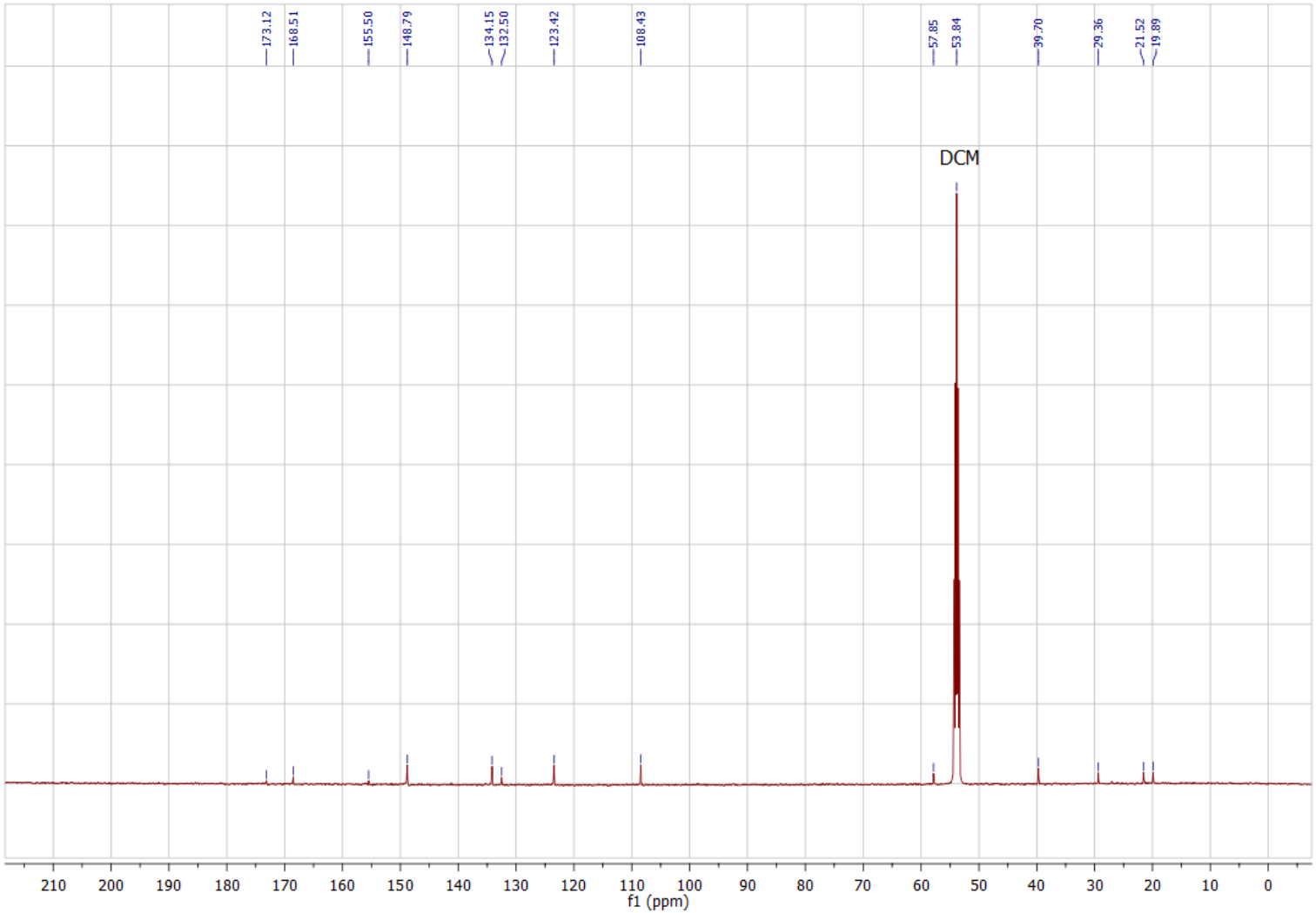


Figure S12: The $^{13}C$ NMR spectrum of complex **3a** in $CD_2Cl_2$.

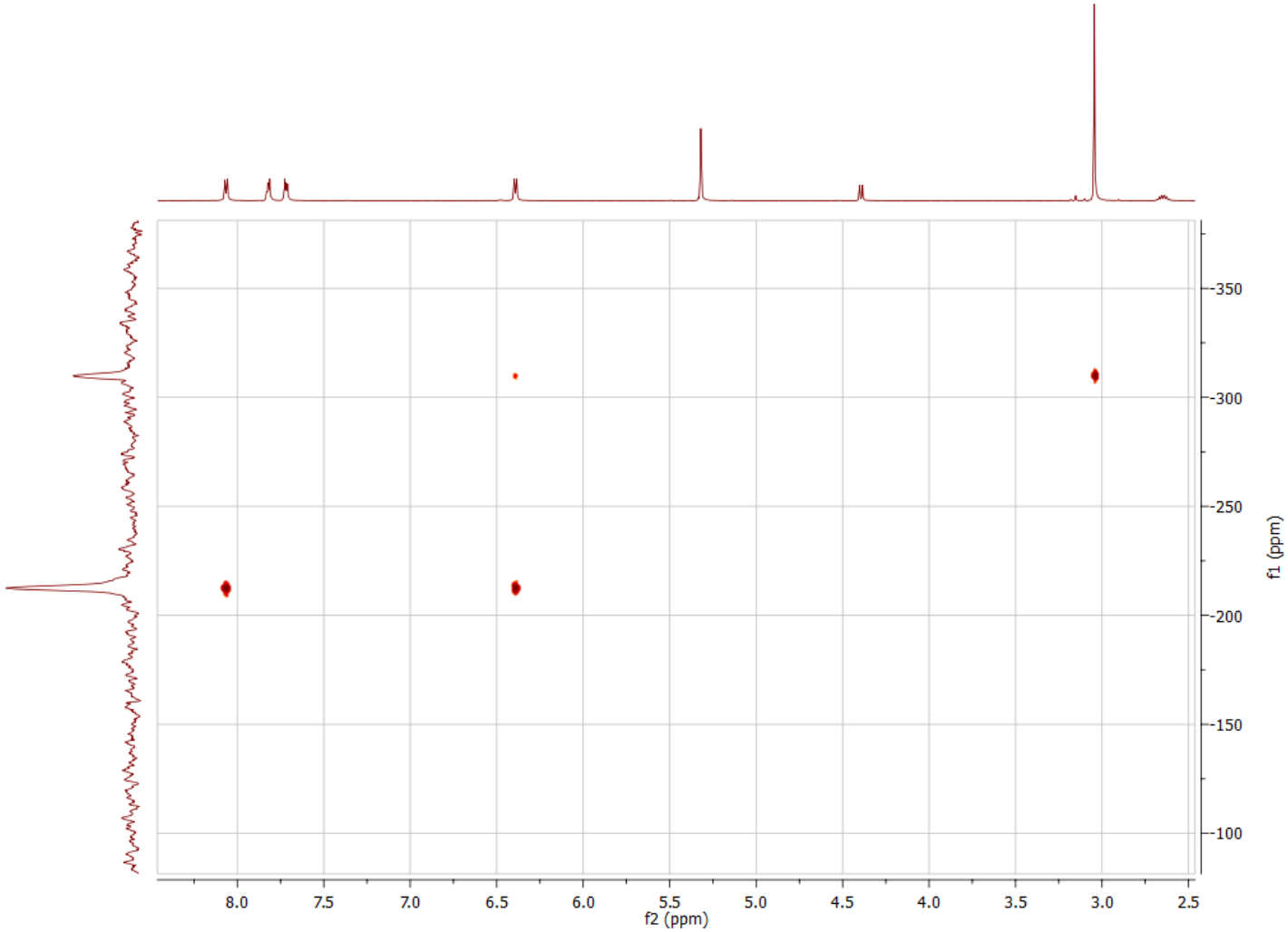


Figure S13: The $^{1}H$-$^{15}N$ HMBC spectrum of complex **3a** in $CD_2Cl_2$.

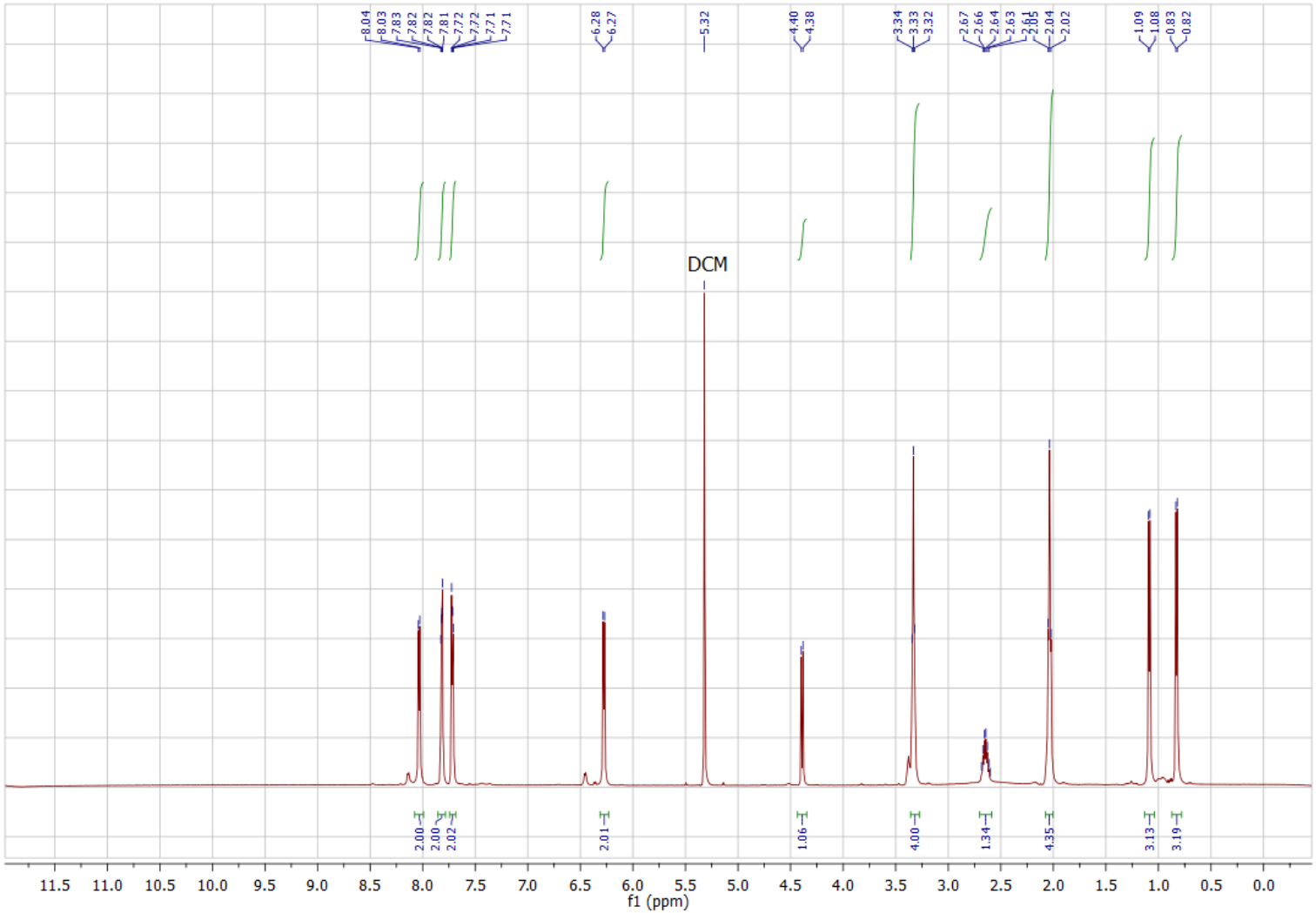


Figure S14: The $^{1}H$ NMR spectrum of complex **3b** in $CD_2Cl_2$.

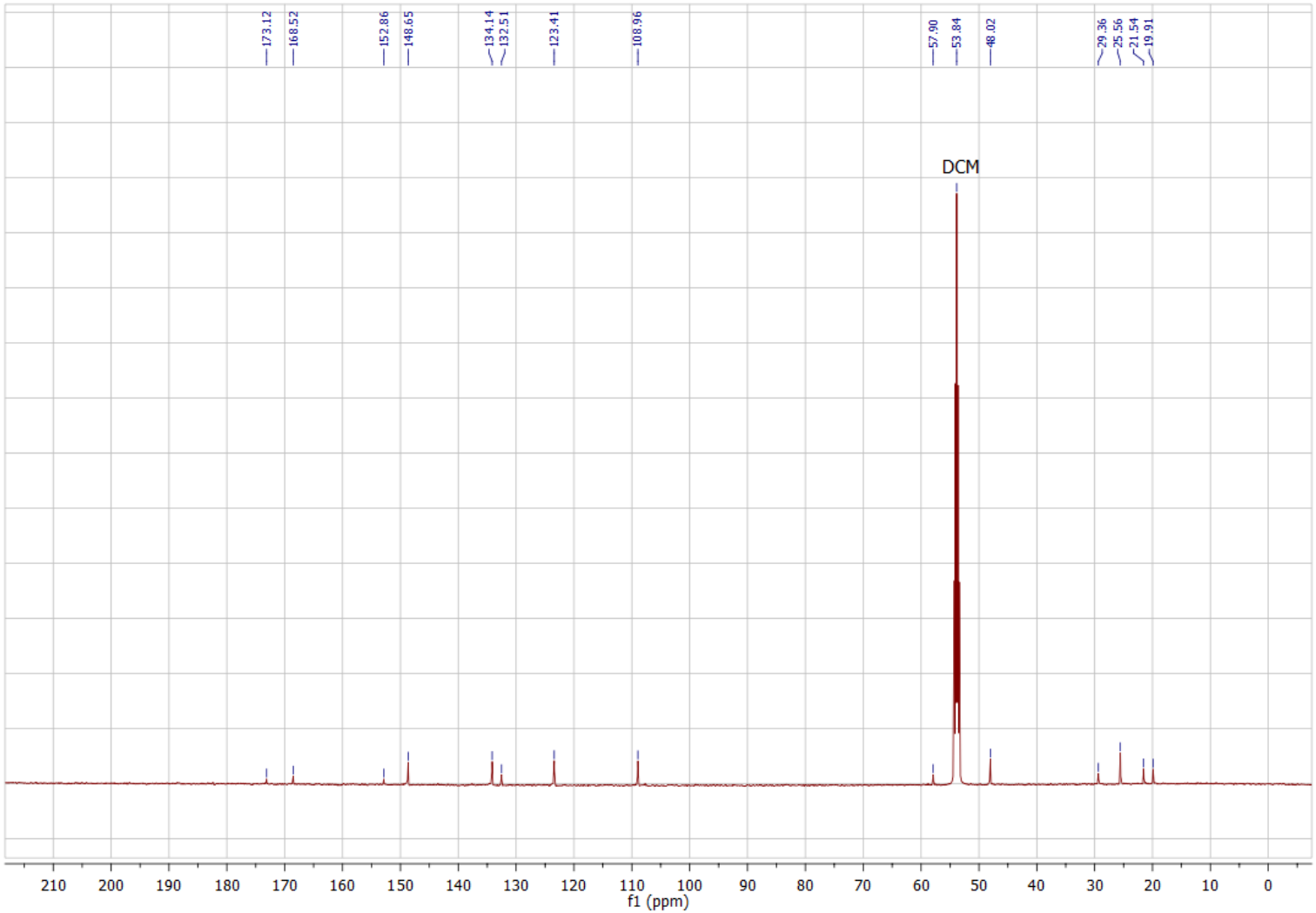


Figure S15: The $^{13}C$ NMR spectrum of complex **3b** in $CD_2Cl_2$.

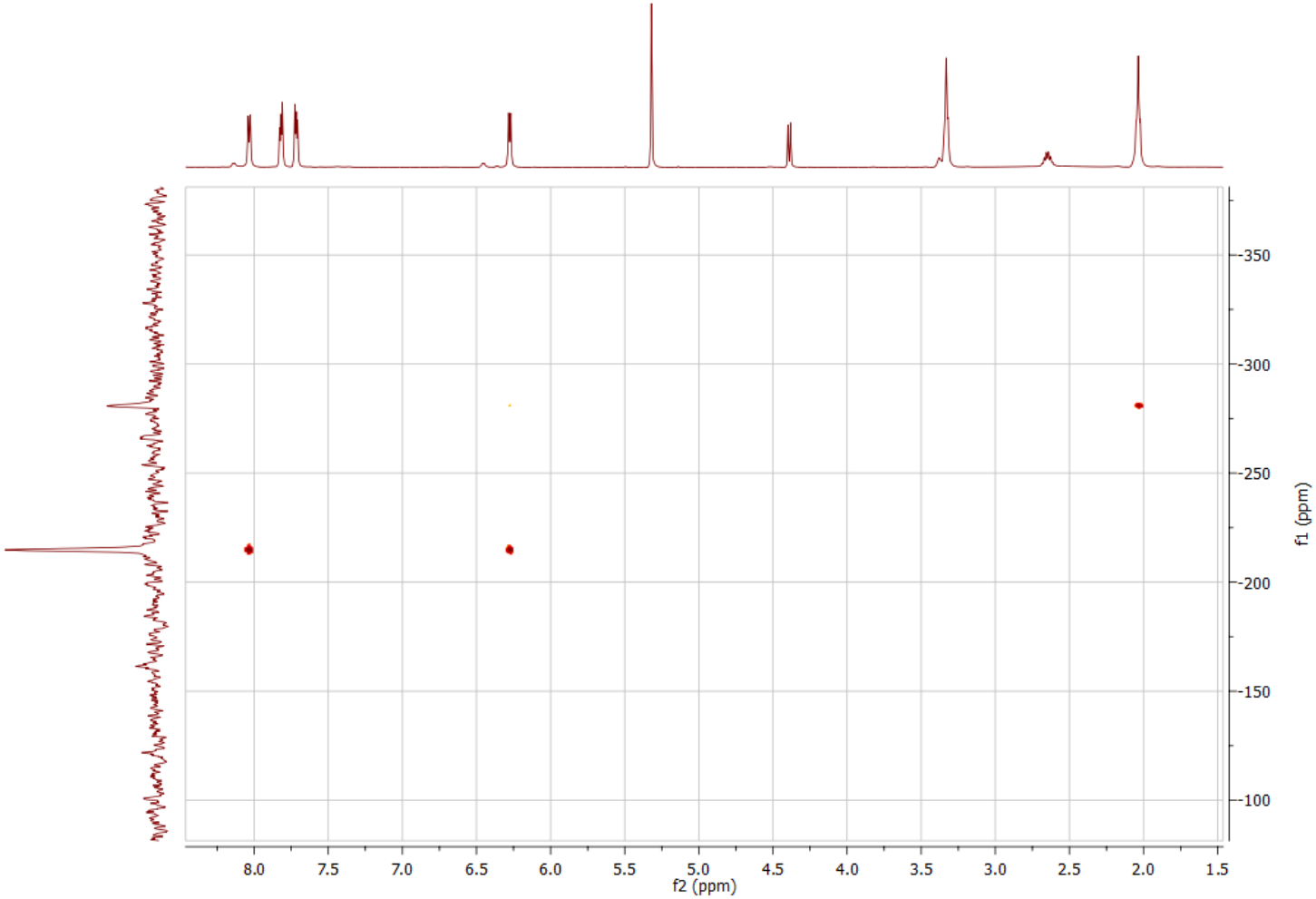


Figure S16: The $^{1}H$-$^{15}N$ HMBC spectrum of complex **3b** in $CD_2Cl_2$.

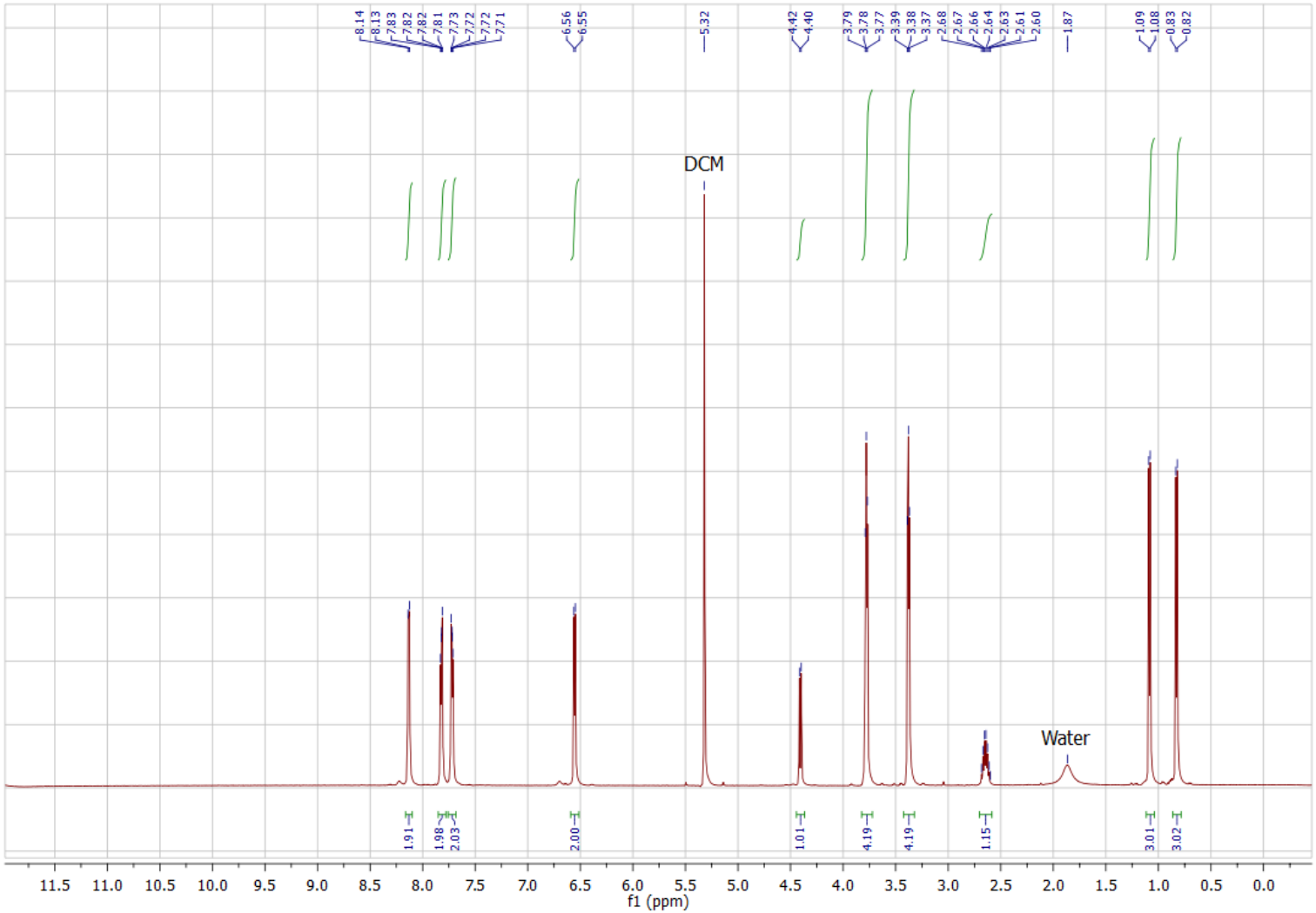


Figure S17: The $^{1}H$ NMR spectrum of complex **3c** in $CD_2Cl_2$.

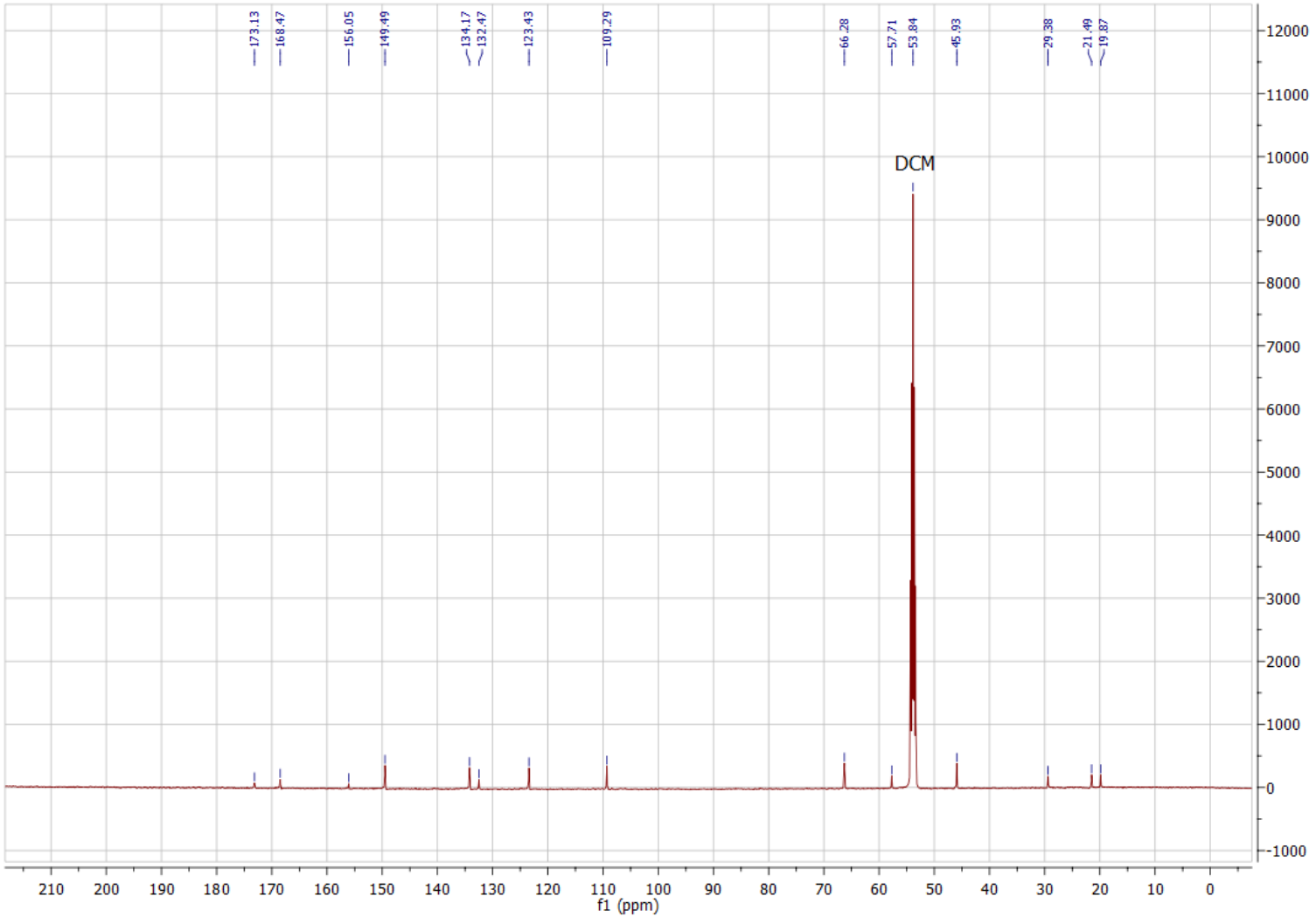


Figure S18: The $^{13}C$ NMR spectrum of complex **3c** in $CD_2Cl_2$.

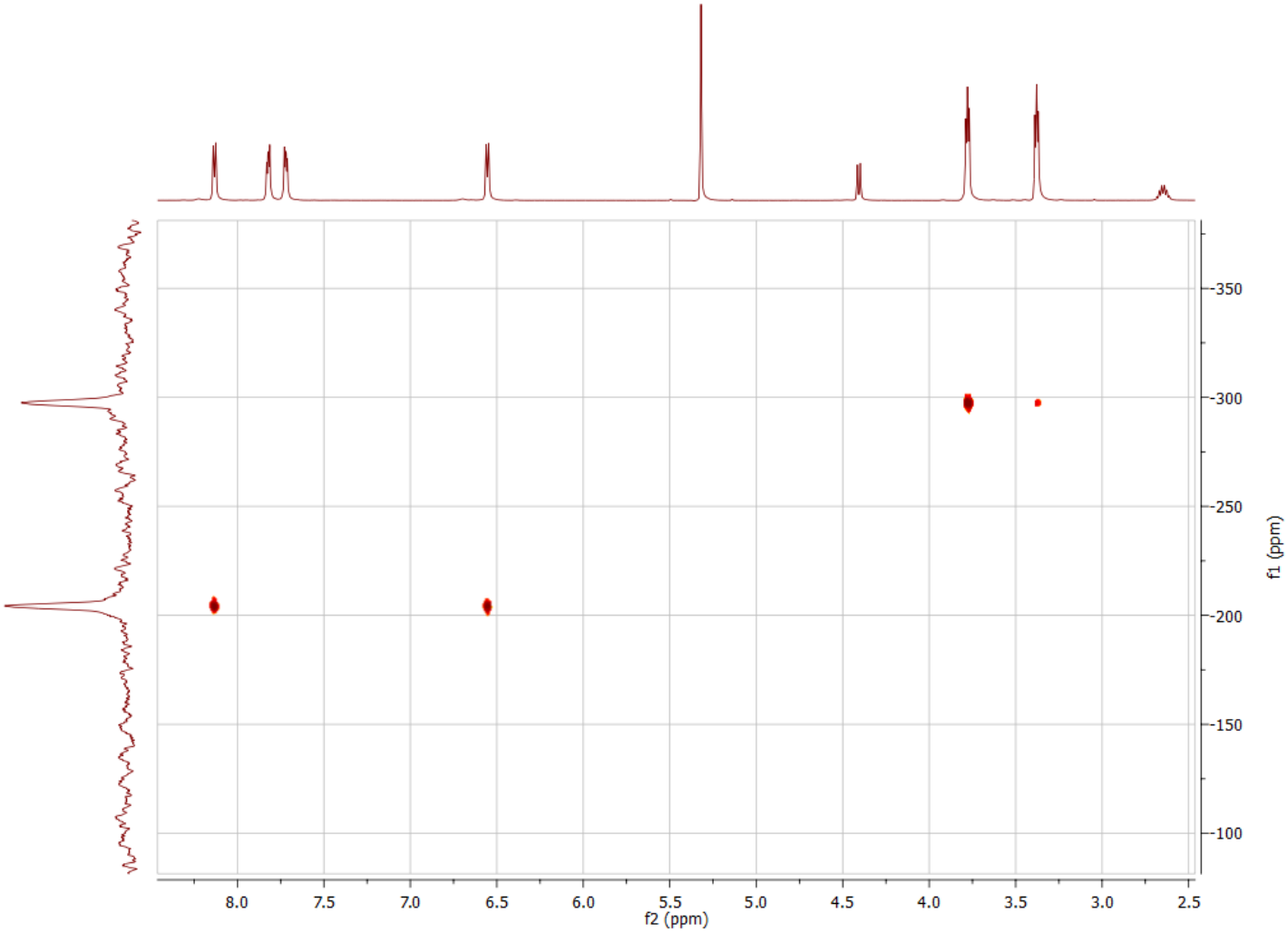


Figure S19: The $^{1}H$-$^{15}N$ HMBC spectrum of complex **3c** in $CD_2Cl_2$.

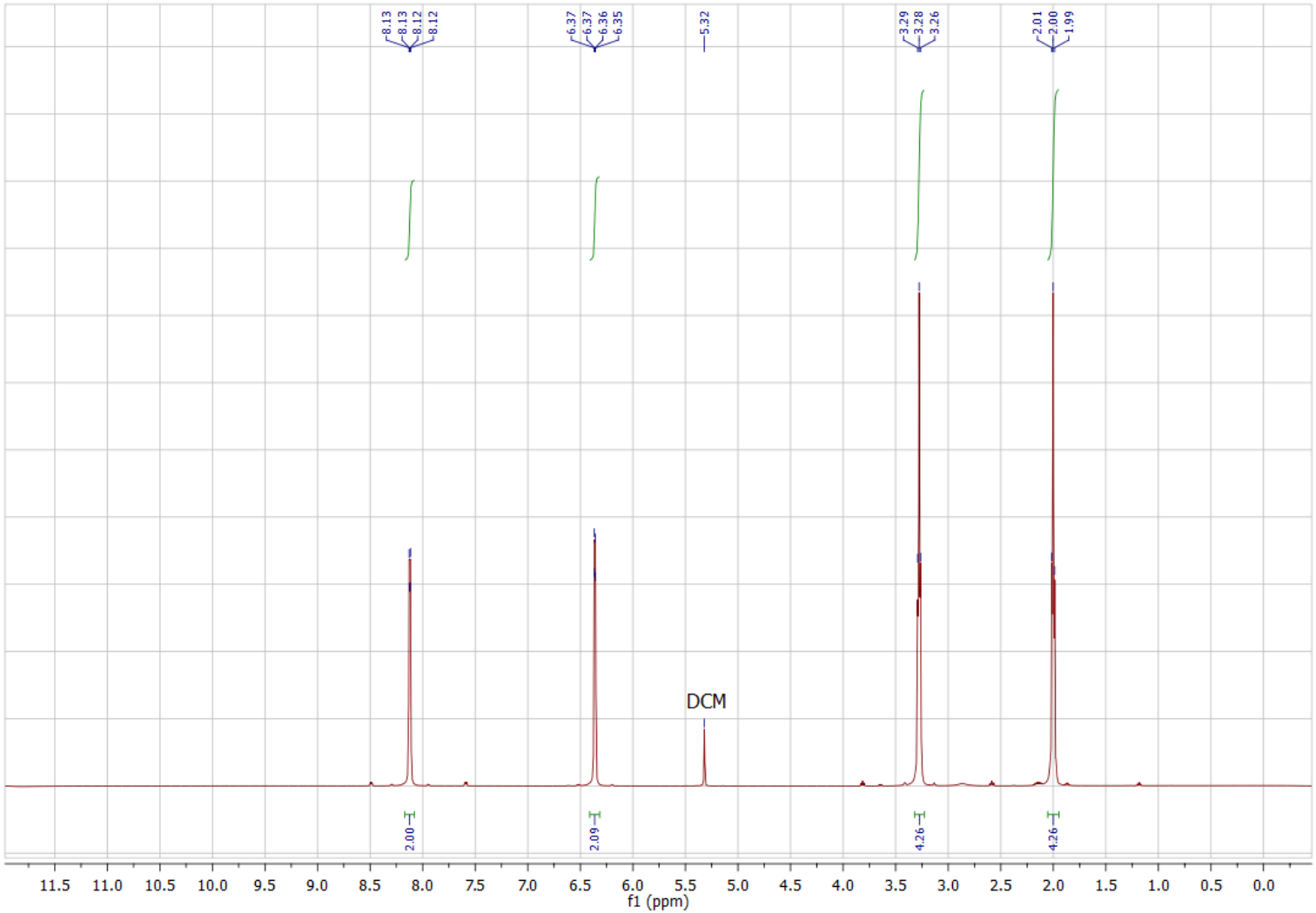


Figure S20: The $^{1}H$ NMR spectrum of complex **4-pyrpy** in $CD_2Cl_2$.

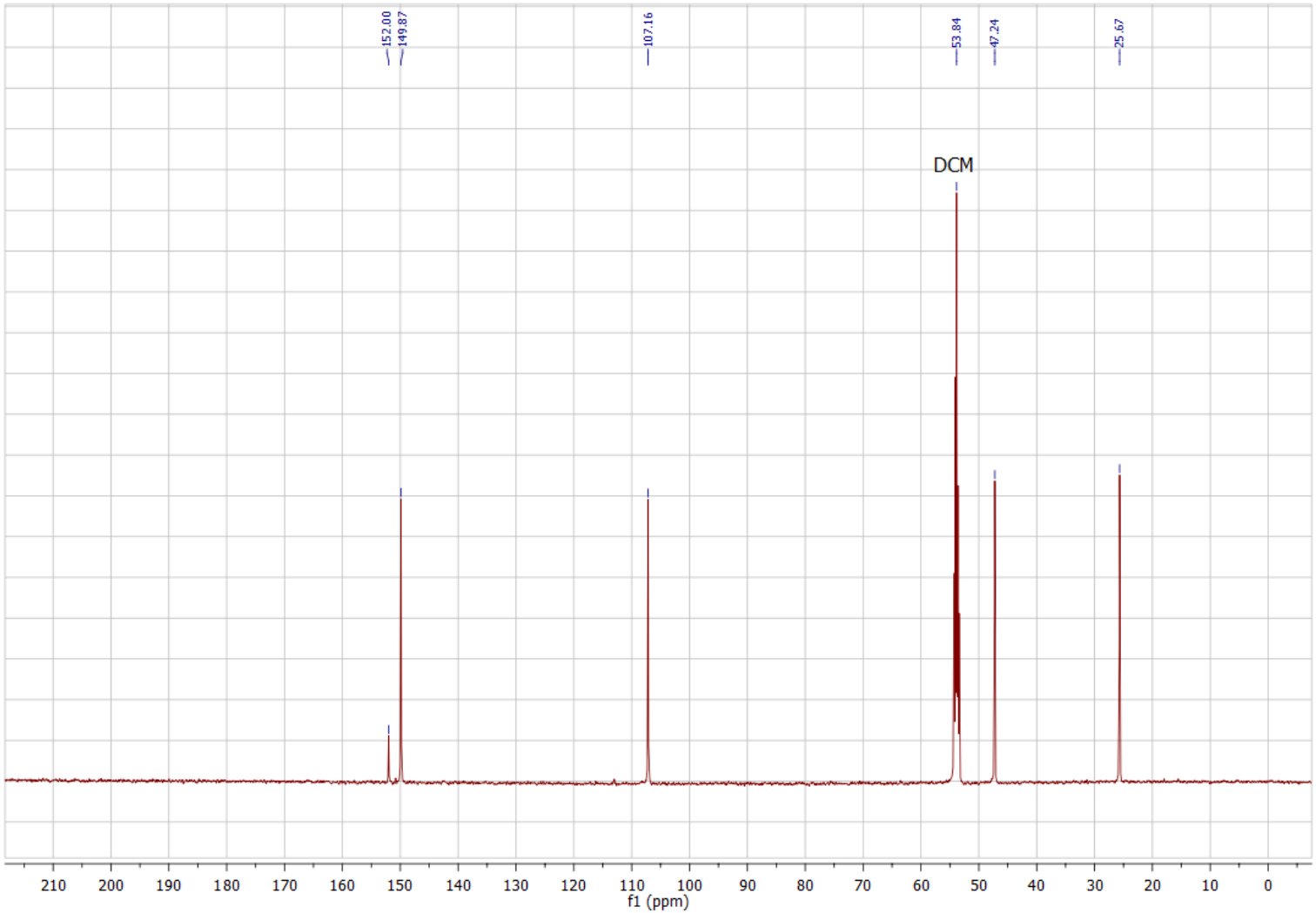


Figure S21: The $^{13}C$ NMR spectrum of complex **4-pyrpy** in $CD_2Cl_2$.

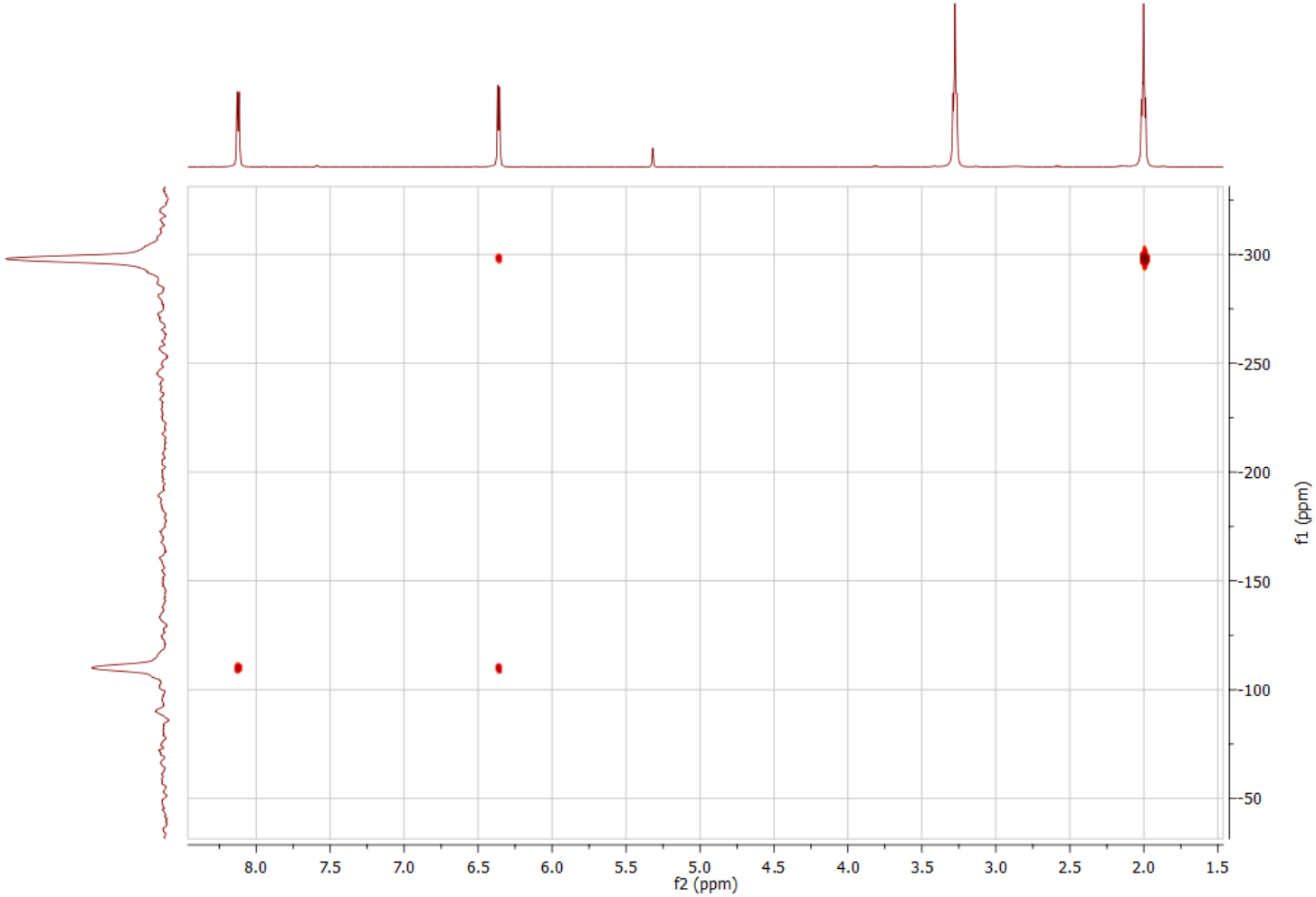


Figure S22: The $^{1}H$-$^{15}N$ HMBC spectrum of complex **4-pyrpy** in $CD_2Cl_2$.

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