

Supporting Information

Carbonyl Hypoiodites from Pivalic and Trimesic Acid and their Silver(I) Intermediates

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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, ^1H NMR and ^1H - ^{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 $(\text{CD}_3)_2\text{SO}$ (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 : δ_{H} 5.32, δ_{C} 53.84; $(\text{CH}_3)_2\text{SO}$ in $(\text{CD}_3)_2\text{SO}$: δ_{H} 2.50, δ_{C} 39.52), or for ^1H - ^{15}N NMR spectroscopy, to an external CD_3NO_2 standard. For the ^1H 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), m (multiplet), and br (broad). For the ^1H - ^{15}N HMBC spectroscopy, spectral windows of 4 ppm (^1H) 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 NMR data for pyridine and DMAP in CD_2Cl_2 have been previously reported.¹

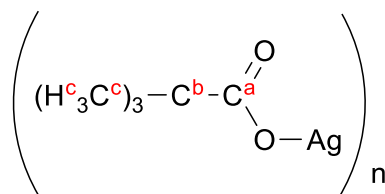
The single crystal X-ray data for **1**, **1b**, **2c**, **2e**, **4a**, and **4b** were collected at 120 K using an Agilent SuperNova dual wavelength diffractometer with an Atlas detector using mirror-monochromated Cu-K α ($\lambda = 1.54184 \text{ \AA}$) radiation. The single crystal X-ray data for **(1c)**₂, **2b** and **3a**·(**py**)₄ were collected at 120 K using an Agilent SuperNova diffractometer with an Eos detector using mirror-monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation. The program CrysAlisPro² was used for the data collection and reduction on the SuperNova diffractometers. All structures were solved by intrinsic phasing (SHELXT)³ and refined by full-matrix least squares on F^2 using Olex2,⁴ utilising the ShelXL-2015 module.⁵ 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 $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (aromatic; cyclic alkyl) or $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$ (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: 4-Mepy = 4-methylpyridine, 4-morpy = 4-morpholinopyridine, DCM = dichloromethane, DIPE = diisopropylether, DMAP = 4-dimethylaminopyridine, DMSO = dimethylsulfoxide, py = pyridine, TBME = ^tbutylmethylether.

Nomenclature Key

Ligand (L)	Ag(pivalate)(L)	(pivalyl-OI)(L)	Ag ₃ (trimesate)(L) ₃	(trimesyl-OI)(L) ₃
No ligand	1	(not observed)	3	(not observed)
Pyridine (a)	1a	2a	3a	4a
4-Mepy (b)	1b	2b	3b	4b
DMAP (c)	1c	2c		
4-morpy (d)	1d	2d		

Synthesis of Silver(I) Precursors



Ag(pivalate) (1): Prepared in the absence of light. Pivalic acid (1.02 g, 10 mmol) was added to a H₂O (15 mL) solution of NaOH (0.40 g, 10.05 mmol), and after stirring the colourless solution for 15 minutes, a H₂O (20 mL) solution of AgNO₃ (1.71 g 10.05 mmol) was added dropwise to immediately give a precipitate. The resulting brown-ish suspension was stirred for 1 hour, then the precipitate was isolated by filtration. The solid was washed with H₂O (3 × 15 mL), MeOH (3 × 15 mL), and Et₂O (3 × 15 mL) to give an off-white solid that was dried under reduced pressure. Recovered yield = 1.90 g (91%). ¹H NMR (500 MHz, (CD₃)₂SO) δ 1.10 (s, 9H, H^c); ¹³C NMR (126 MHz, (CD₃)₂SO) δ 181.8 (C^a), 28.8 (C^c) (C^b at ~39 ppm is obscured by the residual DMSO peak at 39.5 ppm). Crystals suitable for single crystal X-ray diffraction were obtained from a DCM/DMSO solution of **1** vapour diffused with DIPE. Crystal data for **1**: CCDC-2173463, (C₁₀H₉Ag₂O₄)_n, M = 417.98, colourless needle, 0.01 × 0.06 × 0.22 mm³, triclinic, space group *P*-1 (No. 2), a = 5.7752(4) Å, b = 13.483(1) Å, c = 16.9347(12) Å, α = 108.220(7)°, β = 90.240(5)°, γ = 94.770(6)°, V = 1247.57(16) Å³, Z = 4, D_{calc} = 2.225 gcm⁻³, F₀₀₀ = 816, μ = 25.18 mm⁻¹, T = 120.0(1) K, θ_{max} = 76.6°, 4849 total reflections, 3314 with I_o > 2σ(I_o), R_{int} = 0.047, 4849 data, 301 parameters, no restraints, GooF = 0.98, 1.26 < dΔρ < -1.04 eÅ⁻³, R[F² > 2σ(F²)] = 0.037, wR(F²) = 0.086.

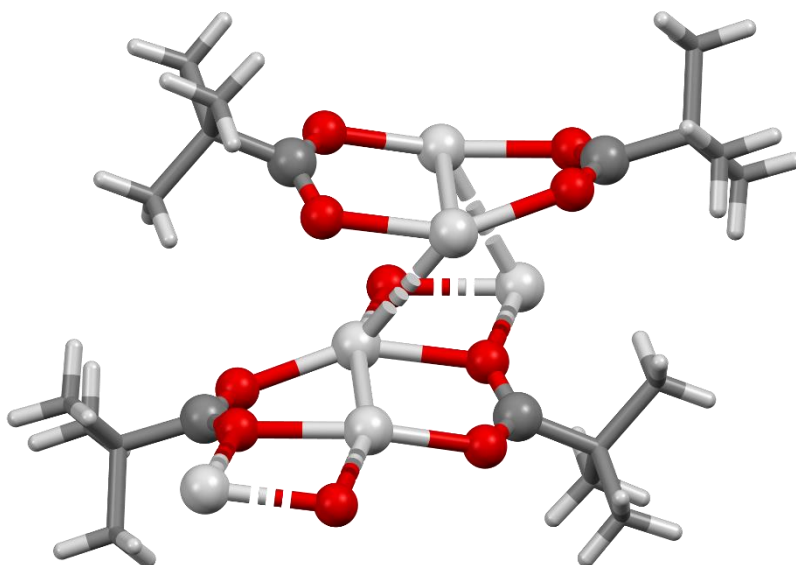


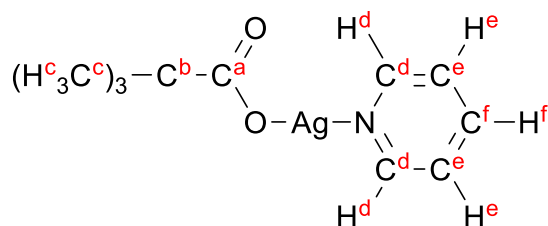
Figure S1: The X-ray crystal structure of polymer **1** (alkyl groups simplified for clarity). Colour key: light grey = silver, red = oxygen, dark grey = carbon, white = hydrogen.

Pivalic acid: ¹H NMR (500 MHz, CD₂Cl₂) δ 1.22 (s, 9H, H^c) (hydroxyl hydrogen atom not observed); ¹³C NMR (126 MHz, CD₂Cl₂) δ 184.8 (C^a), 38.8 (C^b), 27.1 (C^c).

^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 1.11 (s, 9H, H^c) (hydroxyl hydrogen atom not observed); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{SO}$) δ 179.3 (C^a), 37.7 (C^b), 27.0 (C^c).

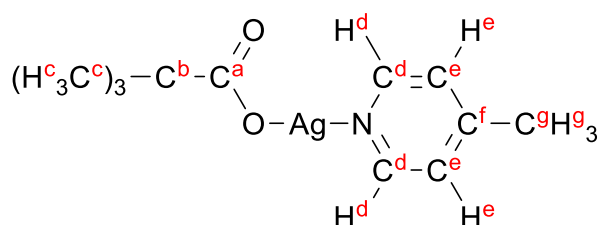
$\text{Ag}_3(\text{trimesate})$ (3): Prepared in the absence of light. Trimesic acid (1.00 g, 4.76 mmol) was added to a H_2O (20 mL) solution of NaOH (0.57 g, 14.28 mmol), and after stirring the colourless solution for 15 minutes, a H_2O (20 mL) solution of AgNO_3 (2.43 g 14.28 mmol) was added dropwise to immediately give a precipitate. The resulting off-white suspension was stirred for 1 hour, then the precipitate was isolated by filtration. The solid was washed with H_2O (3×15 mL), MeOH (3×15 mL), and hexane (3×15 mL) to give a white solid that was dried under reduced pressure. Recovered yield = 2.44 g (97%).

Synthesis of Silver(I) Compounds



Ag(pivalate)(py) (1a): Ag(pivalate) (**1**; 10.5 mg, 0.05 mmol) was dissolved in DMSO (4 mL), followed by addition of py (4.04 μ L, 0.05 mmol) to give a pale beige solution. ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 8.58 (s, 2H, H^{d}), 7.82 (s, 1H, H^{f}), 7.42 (s, 2H, H^{e}), 1.10 (s, 9H, H^{c}).

Pyridine: ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 8.57 (d, $J = 4.1$ Hz, 2H, H^{d}), 7.78 (tt, $J = 7.6, 1.6$ Hz, 1H, H^{f}), 7.41 – 7.35 (m, 2H, H^{e}); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{SO}$) δ 149.6 (C^{d}), 136.1 (C^{f}), 123.9 (C^{e}); ^{15}N NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ -64.1.



Ag(pivalate)(4-Mepy) (1b): Ag(pivalate) (**1**; 10.5 mg, 0.05 mmol) was dissolved in DMSO (4 mL), followed by addition of 4-Mepy (4.87 μ L, 0.05 mmol) to give a pale beige solution. ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 8.43 (s.br, 2H, H^{d}), 7.27 (s.br, 2H, H^{e}), 2.33 (s, 3H, H^{f}), 1.10 (s, 9H, H^{c}). Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution (doped with several drops of DMSO to complete dissolution) of **1a** vapour diffused with pentane. Crystal data for **1a** (connectivity only): $\text{C}_{11}\text{H}_{16}\text{AgNO}_2$, $M = 302.12$, colourless plate, $0.01 \times 0.10 \times 0.13$ mm^3 , triclinic, space group $P-1$ (No. 2), $a = 5.688(2)$ \AA , $b = 8.659(3)$ \AA , $c = 13.226(6)$ \AA , $\alpha = 76.65(4)^\circ$, $\beta = 78.93(4)^\circ$, $\gamma = 85.96(3)^\circ$, $V = 621.8(5)$ \AA^3 , $Z = 2$, $D_{\text{calc}} = 1.614$ gcm^{-3} , $F000 = 304$, $\mu = 12.86$ mm^{-1} , $T = 120.0(1)$ K, $\theta_{\text{max}} = 71.9^\circ$, 2175 total reflections, 341 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.201$, 2175 data, 53 parameters, 3 restraints, $\text{Goof} = 1.02$, $0.69 < d\Delta\rho < -1.29$ $\text{e}\text{\AA}^{-3}$, $R[F^2 > 2\sigma(F^2)] = 0.261$, $wR(F^2) = 0.666$.

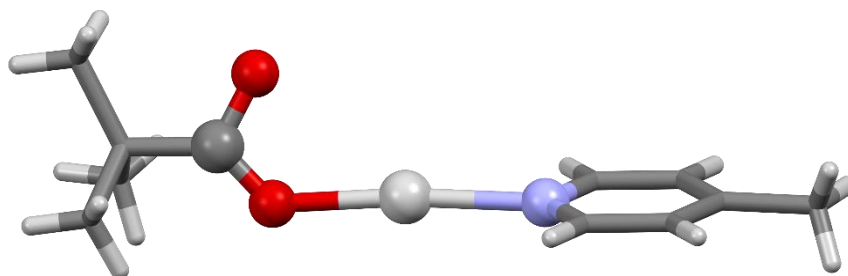
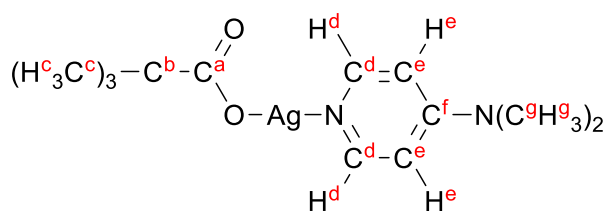


Figure S2: The X-ray determined connectivity (isotropic) model of **1b** (alkyl and aryl groups simplified for clarity). Colour key: light grey = silver, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

4-Mepy: ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 8.42 (d, $J = 6.1$ Hz, 2H, H^{d}), 7.18 (d, $J = 5.3$ Hz, 2H, H^{e}), 2.29 (s, 3H, H^{f}); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{SO}$) δ 149.3 (C^{d}), 146.6 (C^{f}), 124.6 (C^{e}), 20.3 (C^{g}); ^{15}N NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ -72.3.



Ag(pivalate)(DMAP) (1c): Ag(pivalate) (**1**; 10.5 mg, 0.05 mmol) was dissolved in DMSO (4 mL), followed by addition of DMAP (6.1 mg, 0.05 mmol) to give a pale beige solution. ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 8.11 (d, $J = 5.7$ Hz, 2H, H^{d}), 6.68 (d, $J = 5.7$ Hz, 2H, H^{e}), 2.99 (s, 6H, H^{f}), 1.08 (s, 9H, H^{g}); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{SO}$) δ 182.2 (C^{a}), 154.3 (C^{f}), 150.4 (C^{d}), 107.0 (C^{e}), 38.6 (C^{b}), 38.3 (C^{g}), 28.9 (C^{c}); ^{15}N NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ -144.6 (pyridinic), -318.1 (NMe_2). Crystals suitable for single crystal X-ray diffraction were obtained by evaporation of an acetone solution (doped with several drops of DMSO to complete dissolution) of **1c**. Crystal data for **(1c)**₂: CCDC-2173464, $\text{C}_{24}\text{H}_{38}\text{Ag}_2\text{N}_4\text{O}_4$, $M = 662.32$, colourless block, $0.05 \times 0.10 \times 0.27 \text{ mm}^3$, triclinic, space group $P-1$ (No. 2), $a = 6.8349(11) \text{ \AA}$, $b = 9.4356(18) \text{ \AA}$, $c = 11.4549(19) \text{ \AA}$, $\alpha = 82.991(14)^\circ$, $\beta = 72.900(14)^\circ$, $\gamma = 73.381(15)^\circ$, $V = 676.0(2) \text{ \AA}^3$, $Z = 1$, $D_{\text{calc}} = 1.627 \text{ g cm}^{-3}$, $F000 = 336$, $\mu = 1.48 \text{ mm}^{-1}$, $T = 120.0(1) \text{ K}$, $\theta_{\text{max}} = 26.4^\circ$, 2745 total reflections, 1914 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.065$, 2745 data, 159 parameters, no restraints, $\text{Goof} = 0.90$, $1.65 < d\Delta\rho < -1.61 \text{ e\AA}^{-3}$, $R[F^2 > 2\sigma(F^2)] = 0.054$, $wR(F^2) = 0.112$.

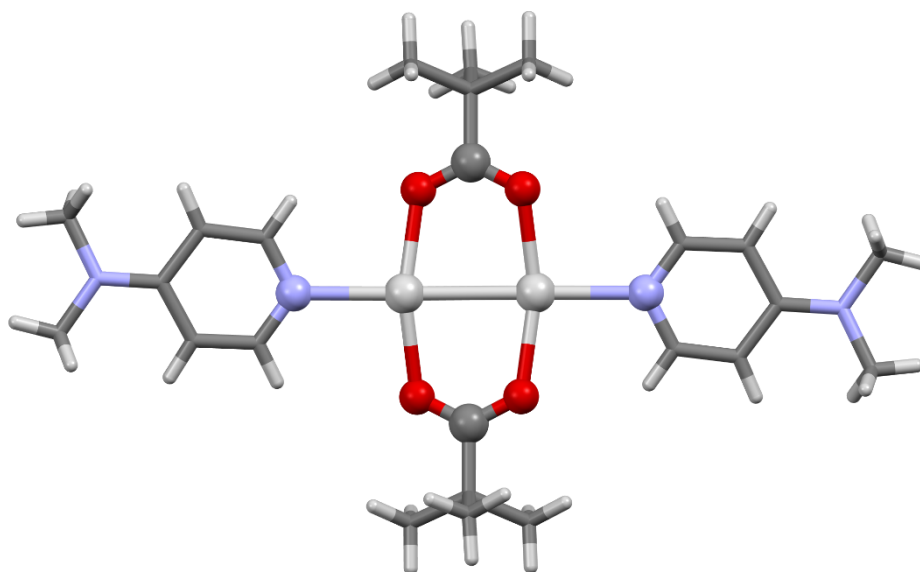
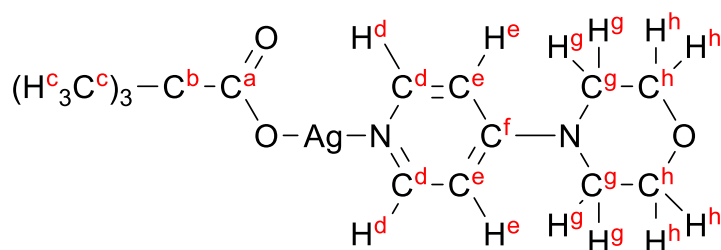


Figure S3: The X-ray crystal structure of **(1c)**₂ (alkyl and aryl groups simplified for clarity). Colour key: light grey = silver, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

DMAP: ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 8.09 (dd, $J = 5.0, 1.5$ Hz, 2H, H^{d}), 6.57 (dd, $J = 5.0, 1.4$ Hz, 2H, H^{e}), 2.94 (s, 6H, H^{g}); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{SO}$) δ 153.9 (C^{f}), 149.3 (C^{d}), 106.7 (C^{e}), 38.6 (C^{g}); ^{15}N NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ -105.3 (pyridinic), -325.0 (NMe_2).



Ag(pivalate)(4-morpy) (1d): Ag(pivalate) (**1**; 10.5 mg, 0.05 mmol) was dissolved in DMSO (4 mL), followed by addition of 4-morphy (8.2 mg, 0.05 mmol) to give a pale beige solution. ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 8.18 (d, $J = 5.2$ Hz, 2H, H^{d}), 6.90 (d, $J = 5.2$ Hz, 2H, H^{e}), 3.71 (unresolved t.br, 4H, H^{h}), 3.34 (unresolved t.br, 4H, H^{g}), 1.09 (s, 9H, H^{c}); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{SO}$) δ 182.1 (C^{a}), 155.0 (C^{f}), 150.8 (C^{d}), 108.2 (C^{e}), 65.6 (C^{h}), 45.3 (C^{g}), 38.5 (C^{b}), 28.9 (C^{c}); ^{15}N NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ -132.3 (pyridinic), -304.6 (morpholino).

4-morphy: ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 8.18 (dd, $J = 5.0, 1.5$ Hz, 2H, H^{d}), 6.82 (dd, $J = 5.0, 1.4$ Hz, 2H, H^{e}), 3.71 (t, $J = 4.9$ Hz, 4H, H^{h}), 3.26 (t, $J = 4.9$ Hz, 4H, H^{g}); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{SO}$) δ 154.8 (C^{f}), 149.8 (C^{d}), 108.2 (C^{e}), 65.7 (C^{h}), 45.6 (C^{g}); ^{15}N NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ -94.7 (pyridinic), -306.5 (morpholino).

[Ag₃(trimesate)(py)₇]_n (3a·(py)₄): Crystals suitable for single crystal X-ray diffraction were obtained from a pyridine solution (doped with several drops of DMSO to complete dissolution) of **3** vapour diffused with TBME. Crystal data for **3a·(py)₄**: CCDC- 2173468, $\text{C}_{44}\text{H}_{38}\text{Ag}_3\text{N}_7\text{O}_6$, $M = 1084.42$, colourless plate, $0.01 \times 0.09 \times 0.13 \text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 20.8504(9) \text{ \AA}$, $b = 10.5290(3) \text{ \AA}$, $c = 19.2520(4) \text{ \AA}$, $\beta = 91.048(3)^\circ$, $V = 4225.8(2) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.705 \text{ g cm}^{-3}$, $F000 = 2160$, $\mu = 1.43 \text{ mm}^{-1}$, $T = 120.0(1) \text{ K}$, $\theta_{\text{max}} = 27.3^\circ$, 8637 total reflections, 6802 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.085$, 8637 data, 541 parameters, 36 restraints, $\text{Goof} = 1.21$, $2.16 < d\Delta\rho < -0.84 \text{ e\AA}^{-3}$, $R[F^2 > 2\sigma(F^2)] = 0.079$, $wR(F^2) = 0.132$.

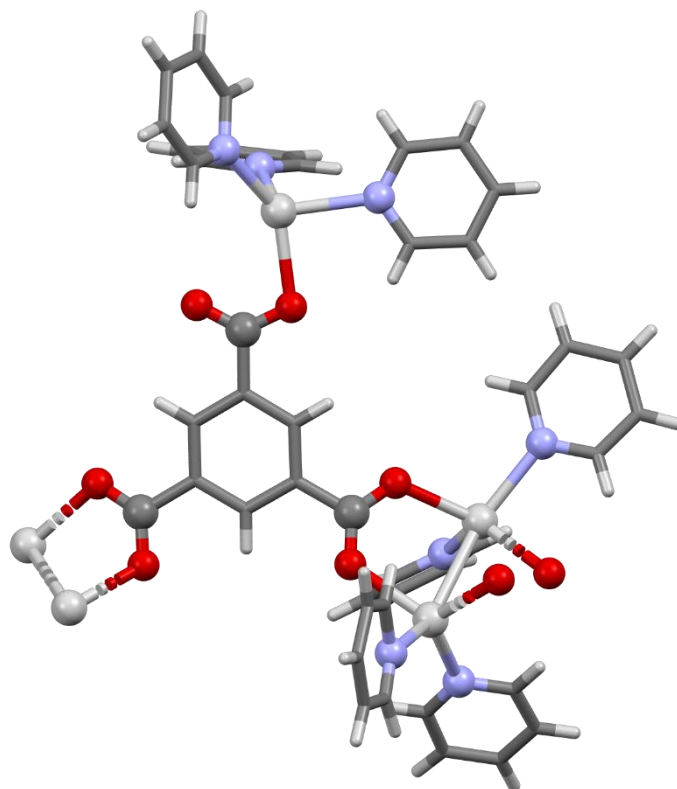
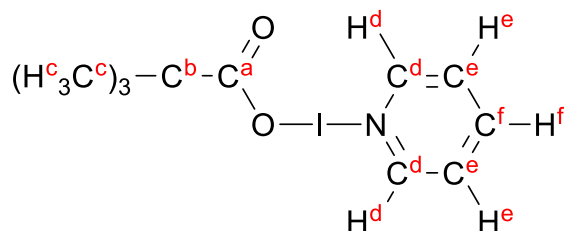


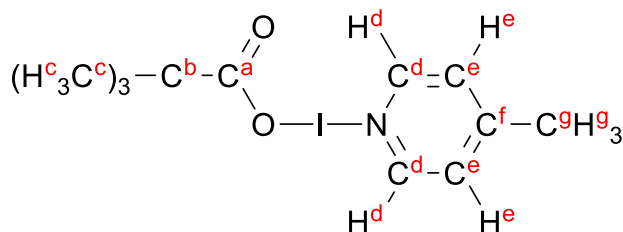
Figure S4: The X-ray crystal structure of **3a·(py)₄** (alkyl and aryl groups simplified for clarity). Colour key: light grey = silver, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

Synthesis of O–I–N Compounds

All stabilised hypoiodite compounds were prepared using the same quantitative general methods, which are given below using (pivalyl-OI)(4-Mepy) (**2b**) and (trimesyl-OI)(py)₃ (**4a**) as examples.



(pivalyl-OI)(py) (2a): Synthesis the same as for **2b** with pyridine (4.0 μL , 0.05 mmol) instead of 4-Mepy. ¹H NMR (500 MHz, CD₂Cl₂) δ 8.64 (d, J = 4.7 Hz, 2H, H^d), 7.94 (t, J = 7.5 Hz, 1H, H^f), 7.40 (dd, J = 7.2, 6.3 Hz, 2H, H^e), 1.13 (s, 9H, H^c).



(pivalyl-OI)(4-Mepy) (2b): Ag(pivalate) (**1**; 10.5 mg, 0.05 mmol) was suspended in DCM (4 mL) and 4-Mepy (4.87 μL , 0.05 mmol) added to give a colloidal suspension. Stirred for 10 minutes, then I₂ (12.7 mg, 0.05 mmol) was added as a solid and left to stir for approximately 5 minutes (until all the I₂ had dissolved). The filtrate of the resulting pale red solution and yellow precipitate was isolated by filtration. The compound's high solubility in most organic solvents prevented isolation of the bulk sample by precipitation, and concentration under reduced pressure resulted in rapid decomposition of the compound (strong purple colour generated upon decomposition). ¹H NMR (500 MHz, CD₂Cl₂) δ 8.47 (d, J = 6.3 Hz, 2H, H^d), 7.20 (d, J = 5.6 Hz, 2H, H^e), 2.42 (s, 3H, H^g), 1.13 (s, 9H, H^c); ¹³C NMR (126 MHz, CD₂Cl₂) δ 183.1 (C^a), 152.7 (C^d), 149.0 (C^f), 127.5 (C^e), 38.4 (C^b), 28.4 (C^c), 21.6 (C^g); ¹⁵N NMR (500 MHz, CD₂Cl₂) δ -154.4. Crystals suitable for single crystal X-ray diffraction were obtained from a toluene solution of **2b** vapour diffused with pentane. Crystal data for **2b**: CCDC-2173465, C₁₁H₁₆INO₂, M = 321.15, colourless plate, 0.03 x 0.14 x 0.21 mm³, triclinic, space group $P\bar{1}$ (No. 2), a = 5.6777(3) Å, b = 8.6359(5) Å, c = 13.1369(8) Å, α = 76.766(5)°, β = 78.689(5)°, γ = 86.009(4)°, V = 614.64(6) Å³, Z = 2, D_{calc} = 1.735 gcm⁻³, $F(000)$ = 316, μ = 2.59 mm⁻¹, T = 120.0(1) K, θ_{max} = 28.5°, 2509 total reflections, 2254 with $I_o > 2\sigma(I_o)$, R_{int} = 0.035, 2509 data, 140 parameters, no restraints, Goof = 1.02, $0.88 < d\Delta\rho < -0.81 \text{ e}\text{\AA}^{-3}$, $R[F^2 > 2\sigma(F^2)]$ = 0.036, $wR(F^2)$ = 0.066.

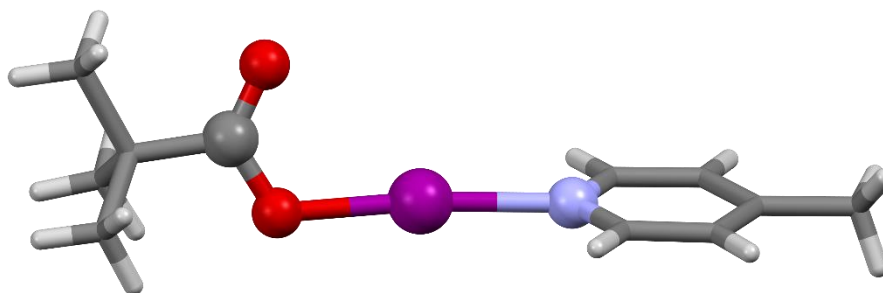
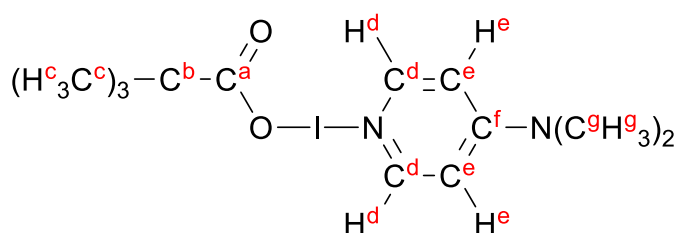


Figure S5: The X-ray crystal structure of **2b** (alkyl and aryl groups simplified for clarity). Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

4-Mepy: ^1H NMR (500 MHz, CD_2Cl_2) δ 8.42 (d, $J = 5.9$ Hz, 2H, H^d), 7.10 (d, $J = 5.3$ Hz, 2H, H^e), 2.33 (s, 3H, H^g); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 149.9 (C^d), 147.4 (C^f), 124.9 (C^e), 21.1 (C^g); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -75.1.



(pivalyl-OI)(DMAP) (2c): Synthesis the same as for **2b** with DMAP (6.1 mg, 0.05 mmol) instead of 4-Mepy. ^1H NMR (500 MHz, CD_2Cl_2) δ 8.08 (d, $J = 6.5$ Hz, 2H, H^d), 6.41 (d, $J = 6.4$ Hz, 2H, H^e), 3.05 (s, 6H, H^g), 1.10 (s, 9H, H^c); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 183.3 (C^a), 155.5 (C^f), 148.6 (C^d), 108.3 (C^e), 39.7 (C^g), 38.5 (C^b), 28.6 (C^c); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -201.8 (pyridinic), -311.4 (NMe_2). Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution of **2c** vapour diffused with pentane. Crystal data for **2c**: CCDC-2173466, $\text{C}_{12}\text{H}_{19}\text{IN}_2\text{O}_2$, $M = 350.19$, colourless plate, $0.04 \times 0.20 \times 0.26 \text{ mm}^3$, triclinic, space group $P-1$ (No. 2), $a = 10.4936(5) \text{ \AA}$, $b = 14.6196(7) \text{ \AA}$, $c = 14.9627(7) \text{ \AA}$, $\alpha = 95.341(4)^\circ$, $\beta = 91.077(4)^\circ$, $\gamma = 107.447(4)^\circ$, $V = 2177.71(19) \text{ \AA}^3$, $Z = 6$, $D_{\text{calc}} = 1.602 \text{ gcm}^{-3}$, $F_000 = 1044$, $\mu = 17.29 \text{ mm}^{-1}$, $T = 120.0(1) \text{ K}$, $\theta_{\text{max}} = 76.6^\circ$, 8483 total reflections, 7561 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.043$, 8483 data, 475 parameters, no restraints, $\text{Goof} = 1.03$, $0.94 < d\Delta\rho < -0.95 \text{ e\AA}^{-3}$, $R[F^2 > 2\sigma(F^2)] = 0.036$, $wR(F^2) = 0.097$.

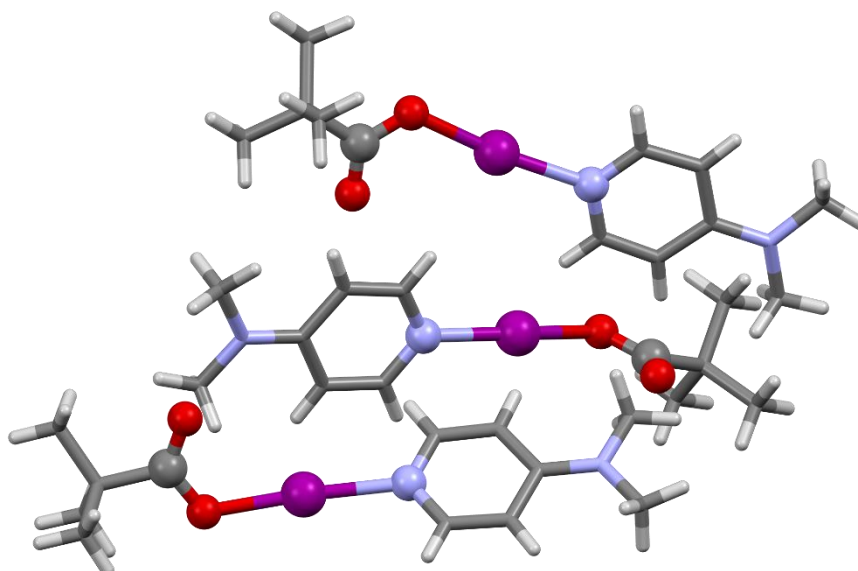
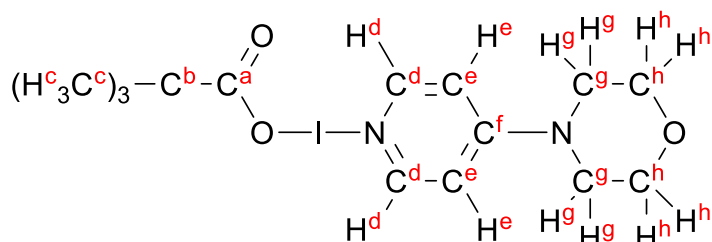


Figure S6: The X-ray crystal structure of **2c** (asymmetric unit cell; alkyl and aryl groups simplified for clarity). Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.



(pivalyl-OI)(4-morpy) (2d): Synthesis the same as for **2b** with 4-morpy (8.2 g, 0.05 mmol) instead of 4-Mepy. ^1H NMR (500 MHz, CD_2Cl_2) δ 8.15 (d, $J = 6.8$ Hz, 2H, H^d), 6.58 (d, $J = 6.8$ Hz, 2H, H^e), 3.79 (t, $J = 5.0$ Hz, 4H, H^h), 3.38 (t, $J = 5.0$ Hz, 4H, H^g), 1.10 (s, 9H, H^c); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 183.3 (C^a), 156.1 (C^f), 149.3 (C^d), 109.2 (C^e), 66.3 (C^h), 46.0 (C^g), 38.4 (C^b), 28.5 (C^c); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -193.3 (pyridinic), -298.7 (morpholino). Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution of **2d** vapour diffused with DIPE. Crystal data for **2d**: CCDC-2173467, $\text{C}_{14}\text{H}_{21}\text{IN}_2\text{O}_3$, $M = 392.23$, colourless block, $0.07 \times 0.15 \times 0.43 \text{ mm}^3$, triclinic, space group $P-1$ (No. 2), $a = 10.6593(3) \text{ \AA}$, $b = 12.9198(4) \text{ \AA}$, $c = 13.3925(5) \text{ \AA}$, $\alpha = 83.712(3)^\circ$, $\beta = 71.291(3)^\circ$, $\gamma = 65.959(3)^\circ$, $V = 1594.89(10) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.633 \text{ g cm}^{-3}$, $F_000 = 784$, $\mu = 15.86 \text{ mm}^{-1}$, $T = 120.0(1) \text{ K}$, $\theta_{\text{max}} = 76.6^\circ$, 6221 total reflections, 5820 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.027$, 6221 data, 367 parameters, no restraints, $\text{GooF} = 1.03$, $1.20 < d\Delta\rho < -1.42 \text{ e\AA}^{-3}$, $R[F^2 > 2\sigma(F^2)] = 0.030$, $wR(F^2) = 0.082$.

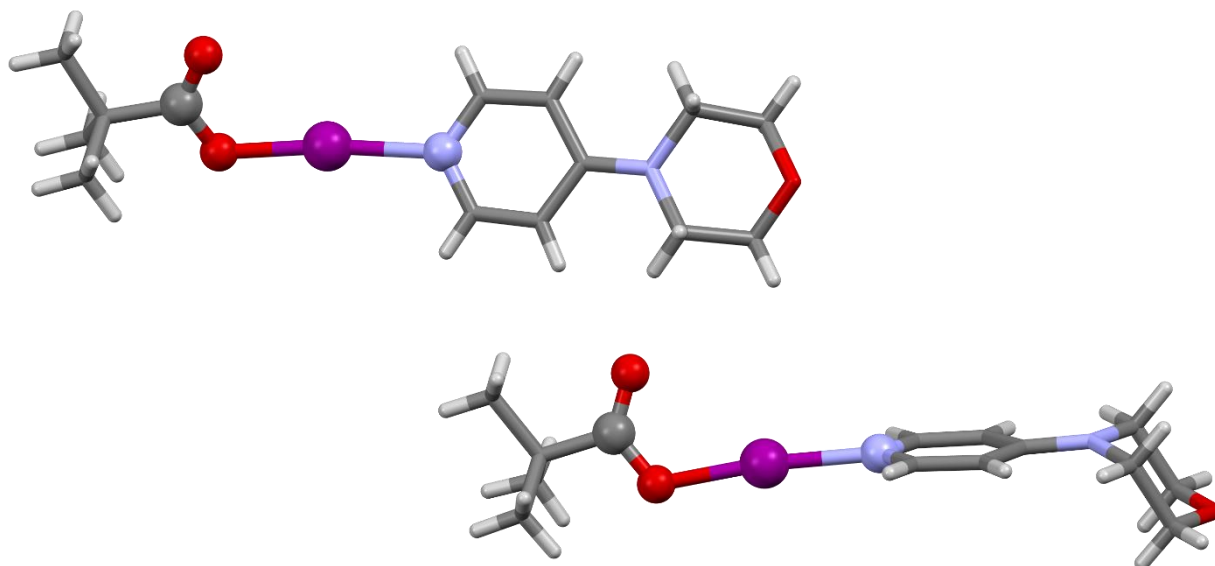


Figure S7: The X-ray crystal structure of **2d** (asymmetric unit cell; alkyl and aryl groups simplified for clarity). Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

4-morpy: ^1H NMR (500 MHz, CD_2Cl_2) δ 8.25 (dd, $J = 5.0, 1.5$ Hz, 2H, H^d), 6.67 (dd, $J = 5.0, 1.5$ Hz, 2H, H^e), 3.80 (t, $J = 5.0$ Hz, 4H, H^h), 3.25 (t, $J = 5.0$ Hz, 4H, H^g); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 155.6 (C^f), 150.6 (C^d), 108.5 (C^e), 66.7 (C^h), 46.6 (C^g); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -99.1 (pyridinic), -311.1 (morpholino).

(trimesyl-OI)(py)₃ (4a): $\text{Ag}_3(\text{trimesate})$ (**3**, 8.0 mg, 0.015 mmol) was suspended in DCM (4 mL), followed by addition of pyridine (3.63 μL , 0.045 mmol). Stirred for 10 minutes, then I_2 (11.4 mg, 0.045 mmol) was added as a solid and left to stir for approximately 5 minutes (until all the I_2 had dissolved). The filtrate of the resulting pale orange solution and yellow precipitate was isolated by filtration. The compound could be isolated in very low yields from the filtrate by precipitation with petroleum ether, however, the isolated white solid was observed to undergo partial decomposition within minutes of being precipitated out of solution. ^1H NMR (500 MHz, CD_2Cl_2) δ 8.74 (d, $J = 4.8$ Hz, 6H), 8.55 (s, 3H), 8.01 (s, 3H), 7.51 – 7.40 (m, 6H); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -151.6. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution of **4a** vapour diffused with pentane. Crystal data for **4a**: CCDC-2173469, $\text{C}_{24}\text{H}_{18}\text{I}_3\text{N}_3\text{O}_6 \cdot \text{H}_2\text{O}$, $M = 843.13$, colourless needle, $0.03 \times 0.03 \times 0.19 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 9.7621(2) \text{ \AA}$, $b = 24.2101(5) \text{ \AA}$, $c = 11.4785(2) \text{ \AA}$, $\beta = 91.437(2)^\circ$, $V = 2711.99(9) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 2.065 \text{ gcm}^{-3}$, $F000 = 1600$, $\mu = 27.57 \text{ mm}^{-1}$, $T = 120.0(1) \text{ K}$, $\theta_{\text{max}} = 75.5^\circ$, 5294 total reflections, 4622 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.030$, 5294 data, 337 parameters, no restraints, $\text{Goof} = 1.01$, $0.49 < d\Delta\rho < -0.74 \text{ e\AA}^{-3}$, $R[F^2 > 2\sigma(F^2)] = 0.026$, $wR(F^2) = 0.066$.

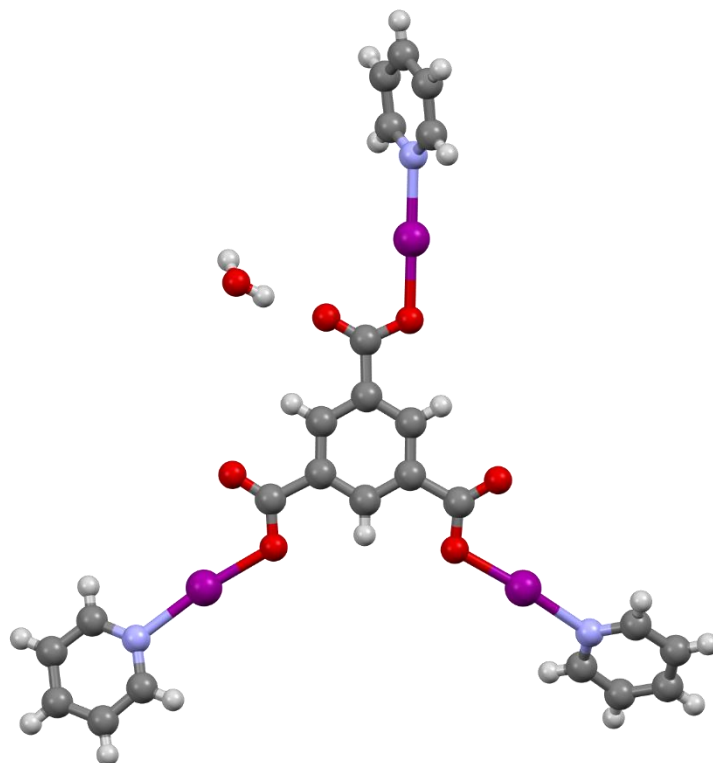


Figure S8: The X-ray crystal structure of **4a**. Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

(trimesyl-OI)(4-Mepy)₃ (4b): Synthesis the same as for **4a** with 4-Mepy (4.4 μL , 0.045 mmol) instead of pyridine. ^1H NMR (500 MHz, CD_2Cl_2) δ 8.55 (s.br, 6H), 8.53 (s, 3H), 7.24 (s.br, 6H), 2.44 (s, 9H). Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution of **4b** vapour diffused with TBME. Crystal data for **4b**: CCDC-2173470, $\text{C}_{27}\text{H}_{24}\text{I}_3\text{N}_3\text{O}_6$, $M = 867.19$, yellow block, $0.06 \times 0.08 \times 0.15 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 15.6502(4) \text{ \AA}$, $b = 9.9201(2) \text{ \AA}$, $c = 19.5464(5) \text{ \AA}$, $\beta = 109.522(3)^\circ$, $V = 2860.16(13) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 2.014 \text{ gcm}^{-3}$, $F000 = 1656$, $\mu = 26.14 \text{ mm}^{-1}$, $T = 120.0(1) \text{ K}$, $\theta_{\text{max}} = 76.4^\circ$, 5592 total reflections, 4760 with $I_o > 2\sigma(I_o)$, $R_{\text{int}} = 0.031$, 5592 data, 355 parameters, no restraints, $\text{Goof} = 1.05$, $1.71 < d\Delta\rho < -1.30 \text{ e\AA}^{-3}$, $R[F^2 > 2\sigma(F^2)] = 0.035$, $wR(F^2) = 0.100$.

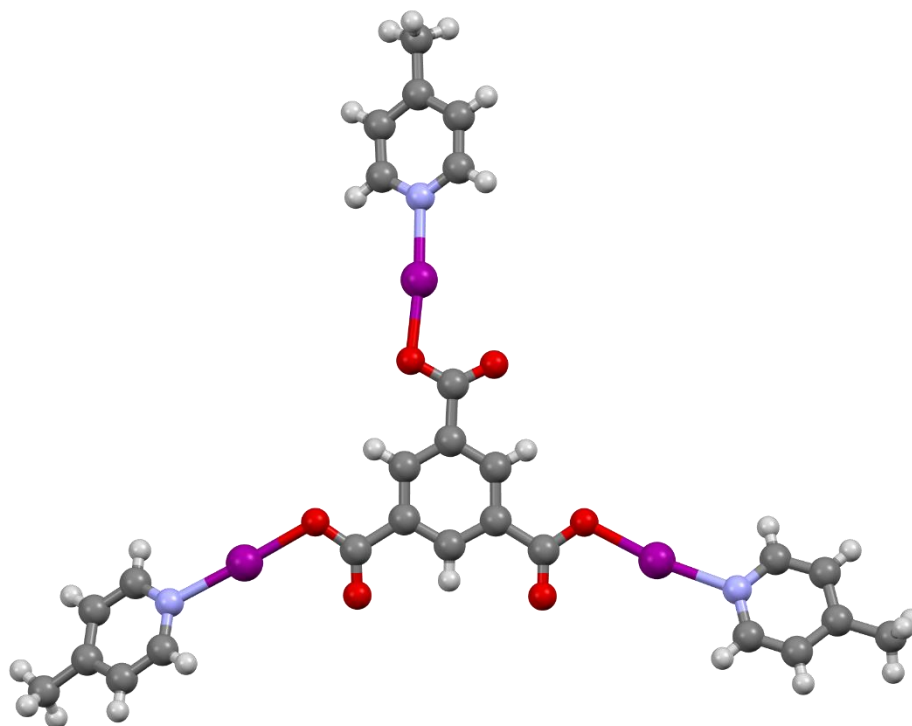


Figure S9: The X-ray crystal structure of **4b**. Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

Comparison Tables of Chemical Shifts

Table S1: Comparison of the carboxylic ^{13}C and pyridinic ^{15}N NMR chemical shifts (in $(\text{CD}_3)_2\text{SO}$) of the silver(I) compounds **1-1b** and their precursors (in ppm).

Compound	Carboxylic carbon (δ_{C})	Pyridinic nitrogen (δ_{N})
1	181.8	-
Pivalic acid	179.3	-
1c	182.2	-144.6
DMAP	-	-105.3
1d	182.1	-132.3
4-morpy	-	-94.7

Table S2: Comparison of the carboxylic ^{13}C and pyridinic ^{15}N NMR chemical shifts (in CD_2Cl_2) of the iodine(I) compounds **2a-2d** and their precursors (in ppm).

Compound	Carboxylic carbon (δ_{C})	Pyridinic nitrogen (δ_{N})
Pivalic acid	184.8	-
2a	(unable to observe)*	(unable to observe)*
Pyridine	-	-67.7
2b	183.1	-154.4
4-Mepy	-	-75.1
2c	183.3	-201.8
DMAP	-	-108.9
2d	183.3	-193.3
4-morpy	-	-99.1

*Compound **2a** was observed to decompose during NMR analysis with the initial peaks having completely diminished after approximately 30 minutes, which was an insufficient timeframe to accurately determine the ^{13}C or ^{15}N NMR chemical shifts.

NMR Spectra

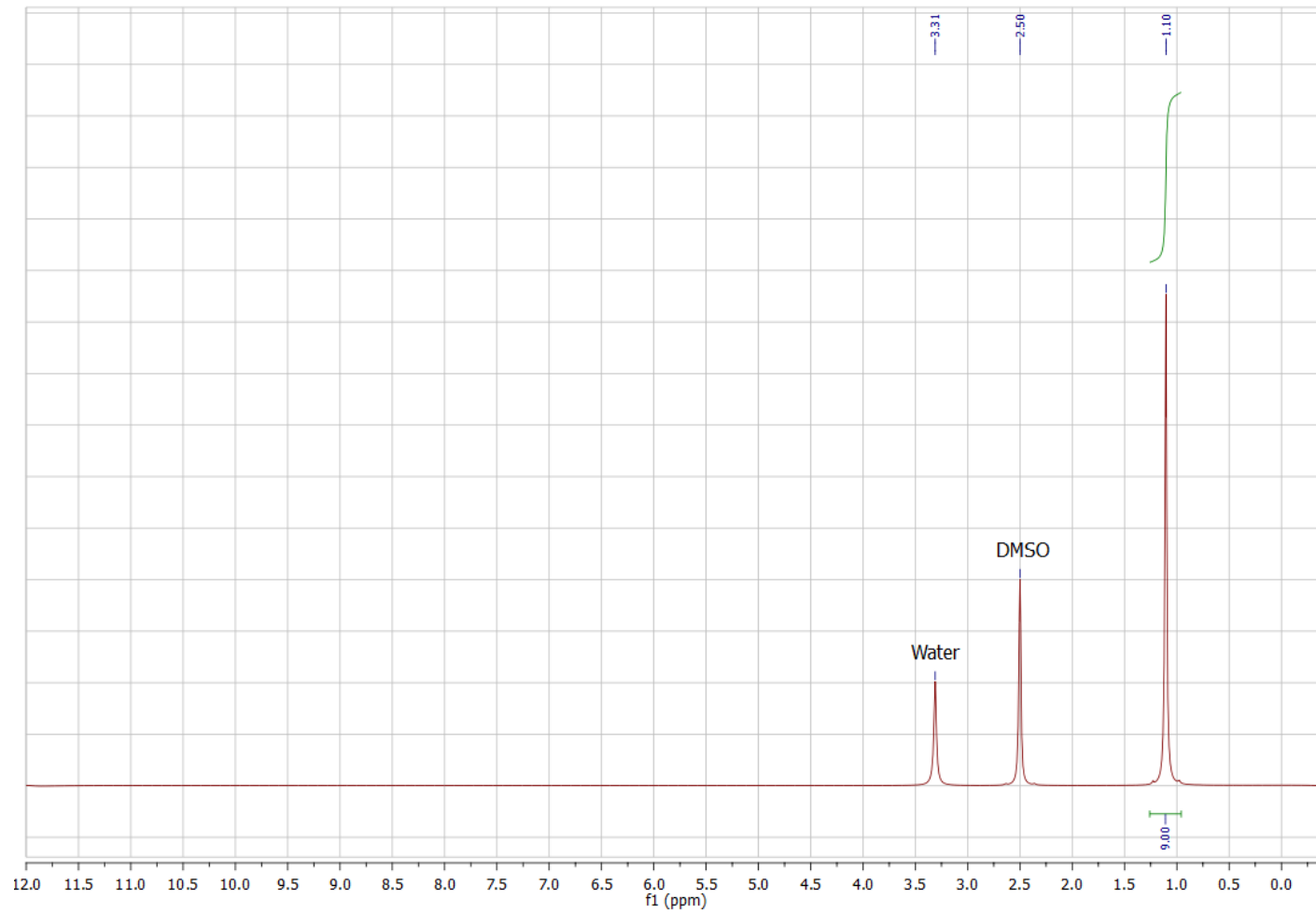


Figure S10: The ^1H NMR spectrum of compound **1** in $(\text{CD}_3)_2\text{SO}$.

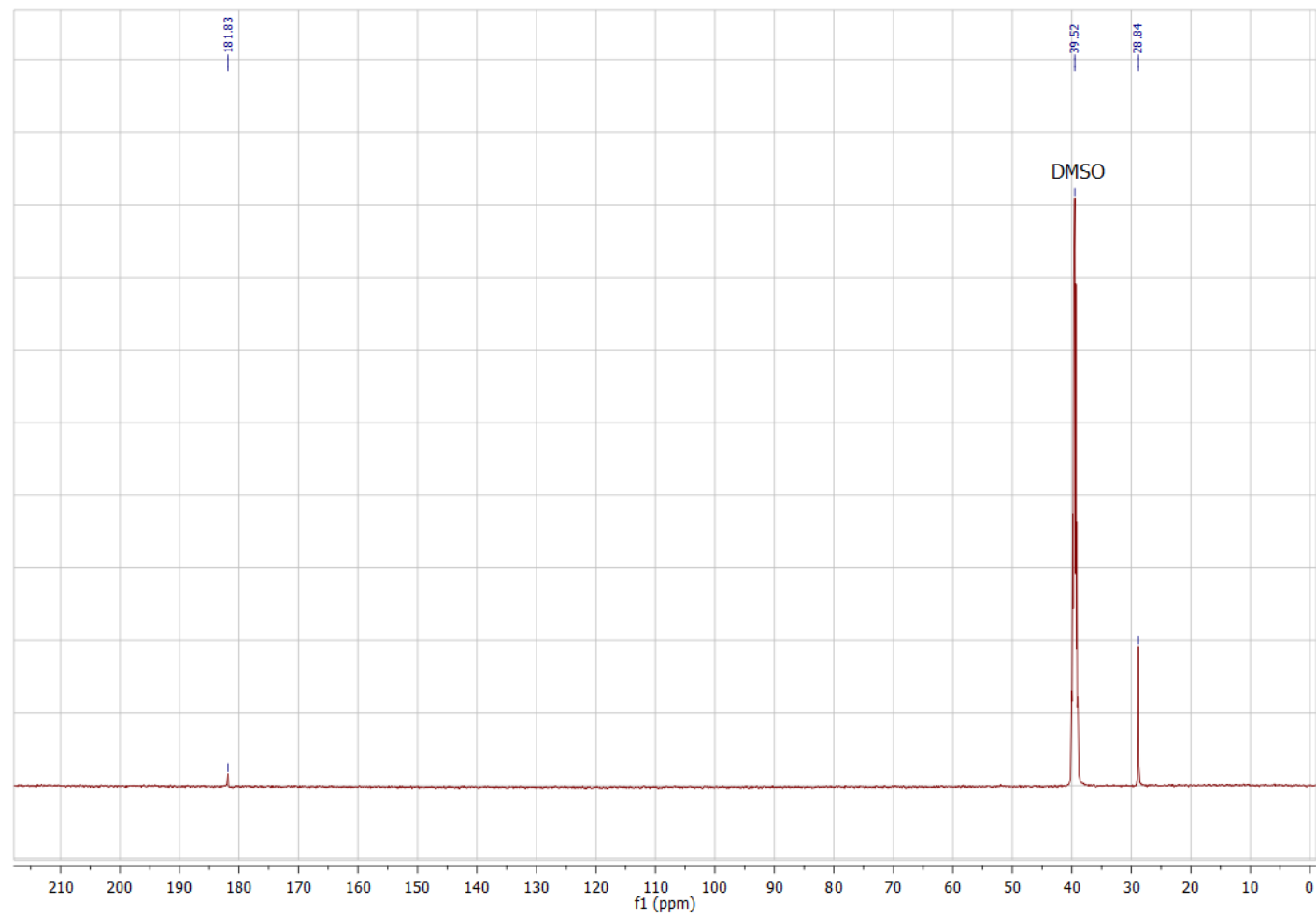


Figure S11: The ^{13}C NMR spectrum of compound **1** in $(\text{CD}_3)_2\text{SO}$.

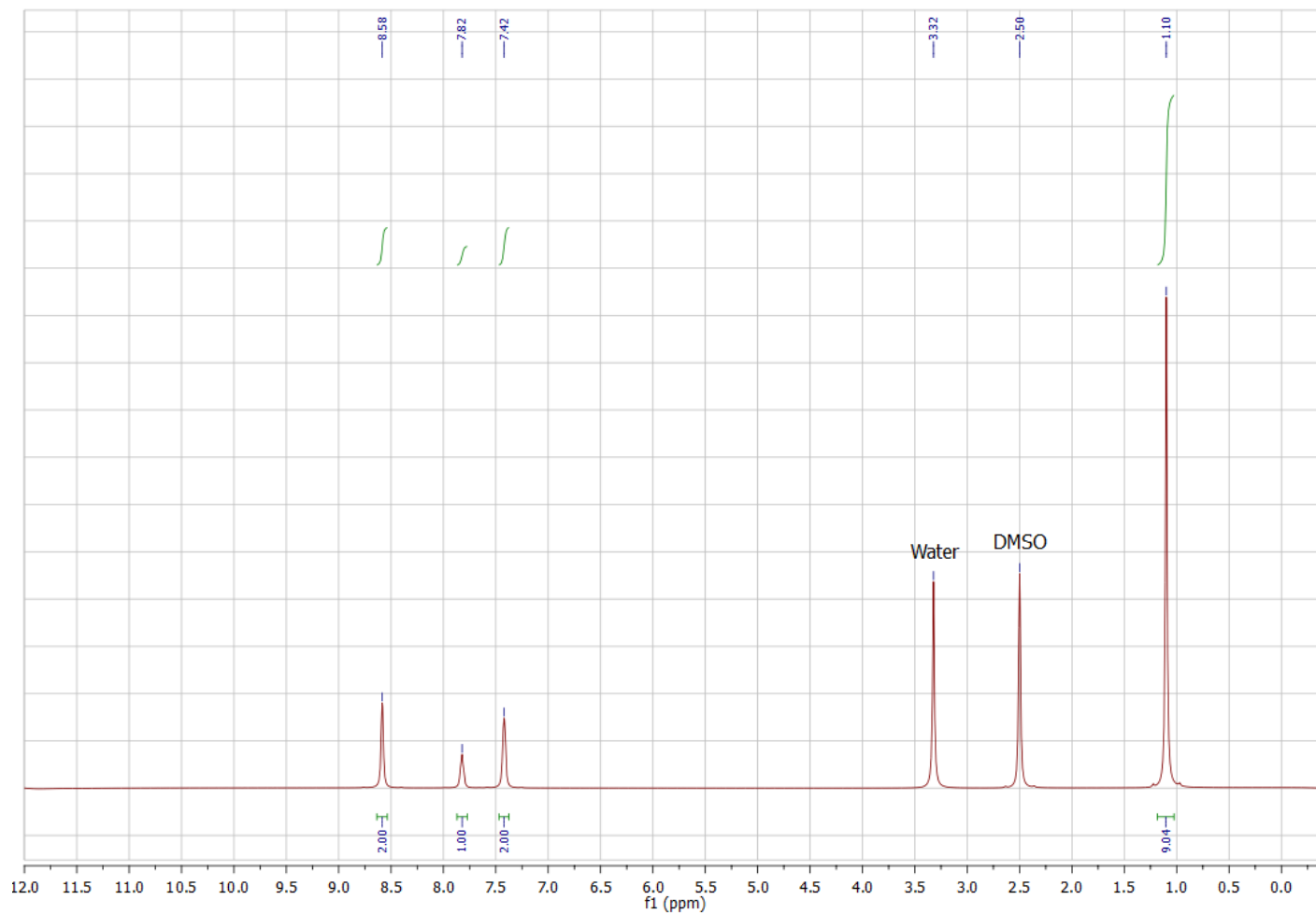


Figure S12: The ^1H NMR spectrum of compound **1a** in $(\text{CD}_3)_2\text{SO}$.

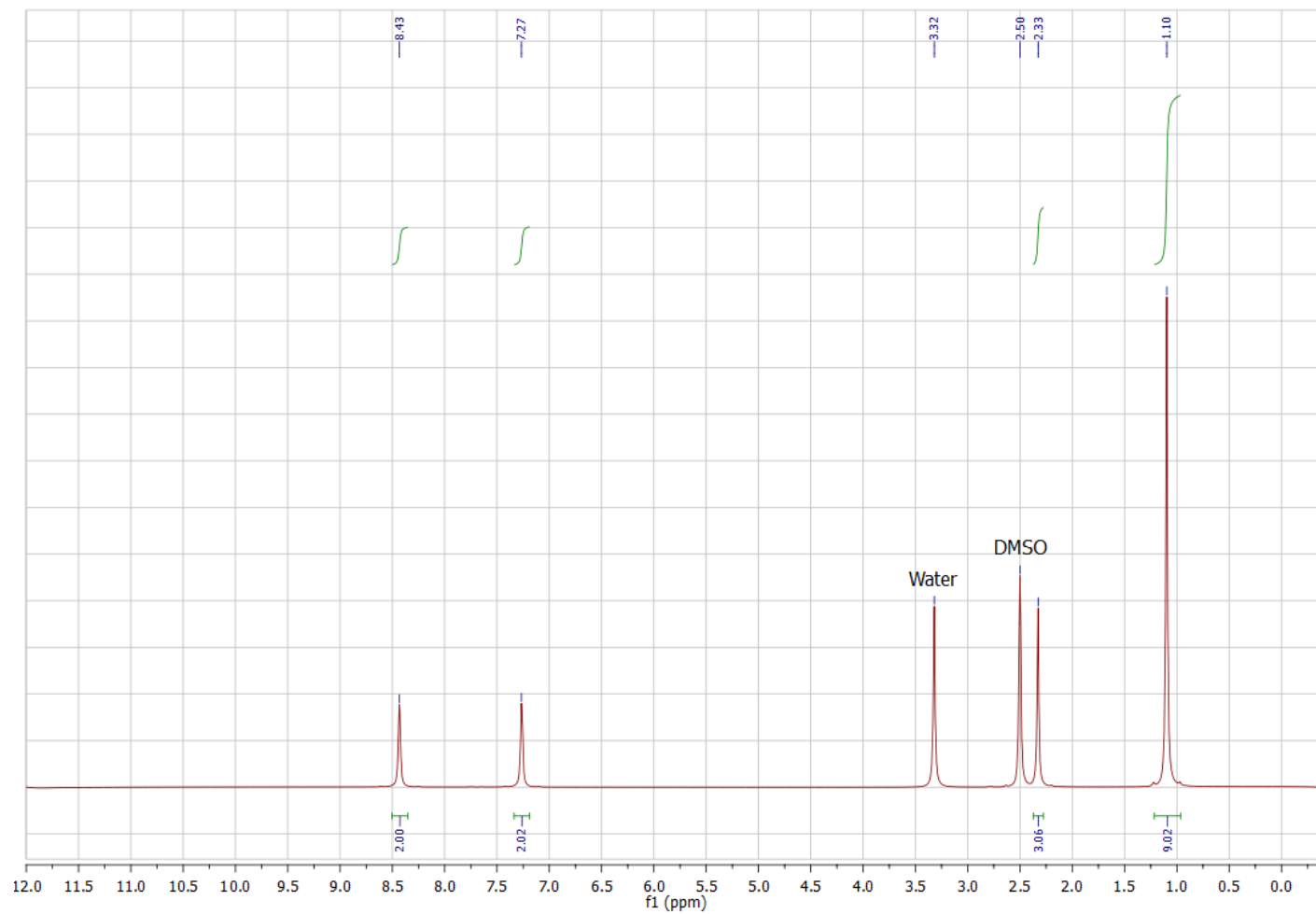


Figure S13: The ^1H NMR spectrum of compound **1b** in $(\text{CD}_3)_2\text{SO}$.

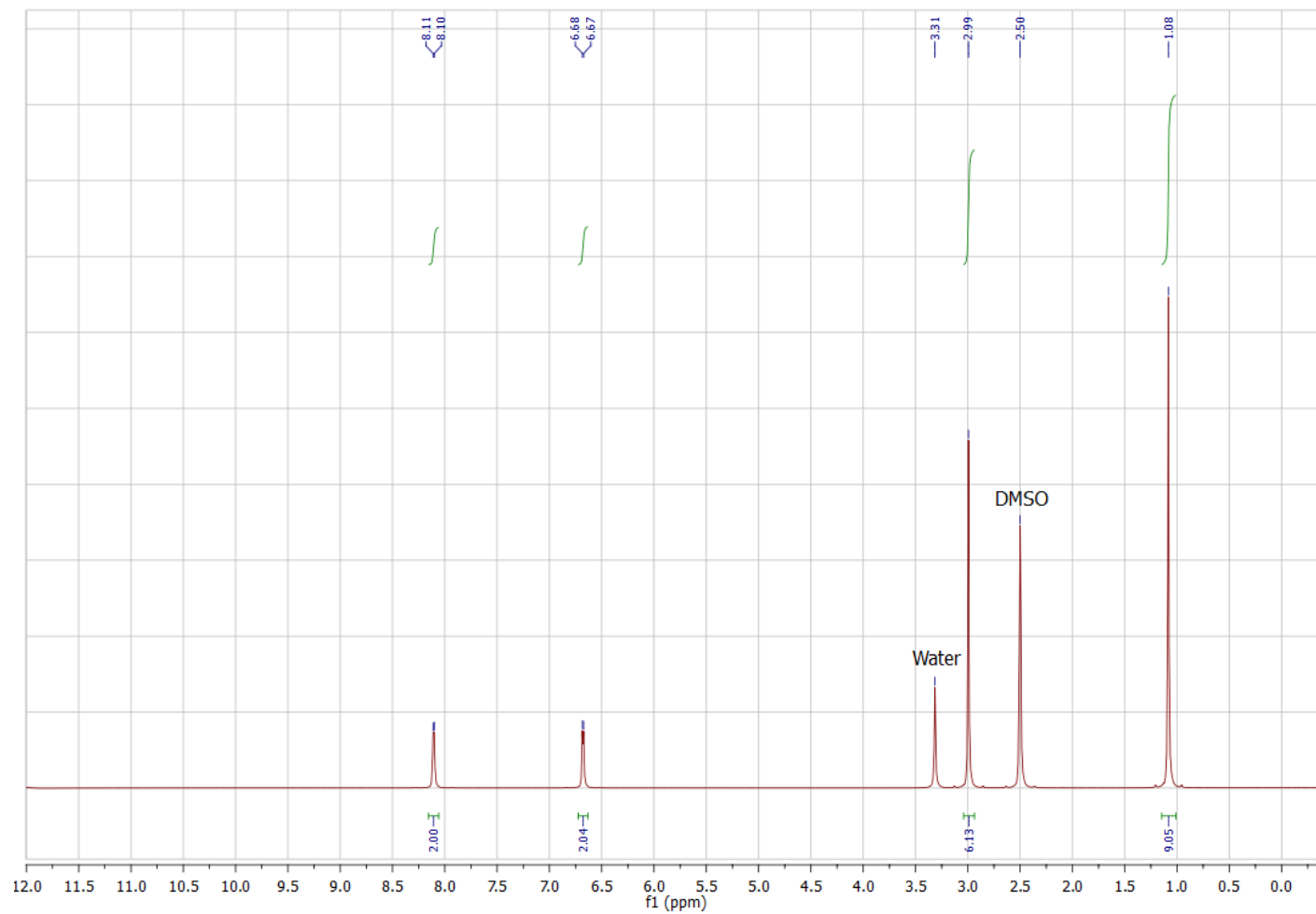


Figure S14: The ^1H NMR spectrum of compound **1c** in $(\text{CD}_3)_2\text{SO}$.

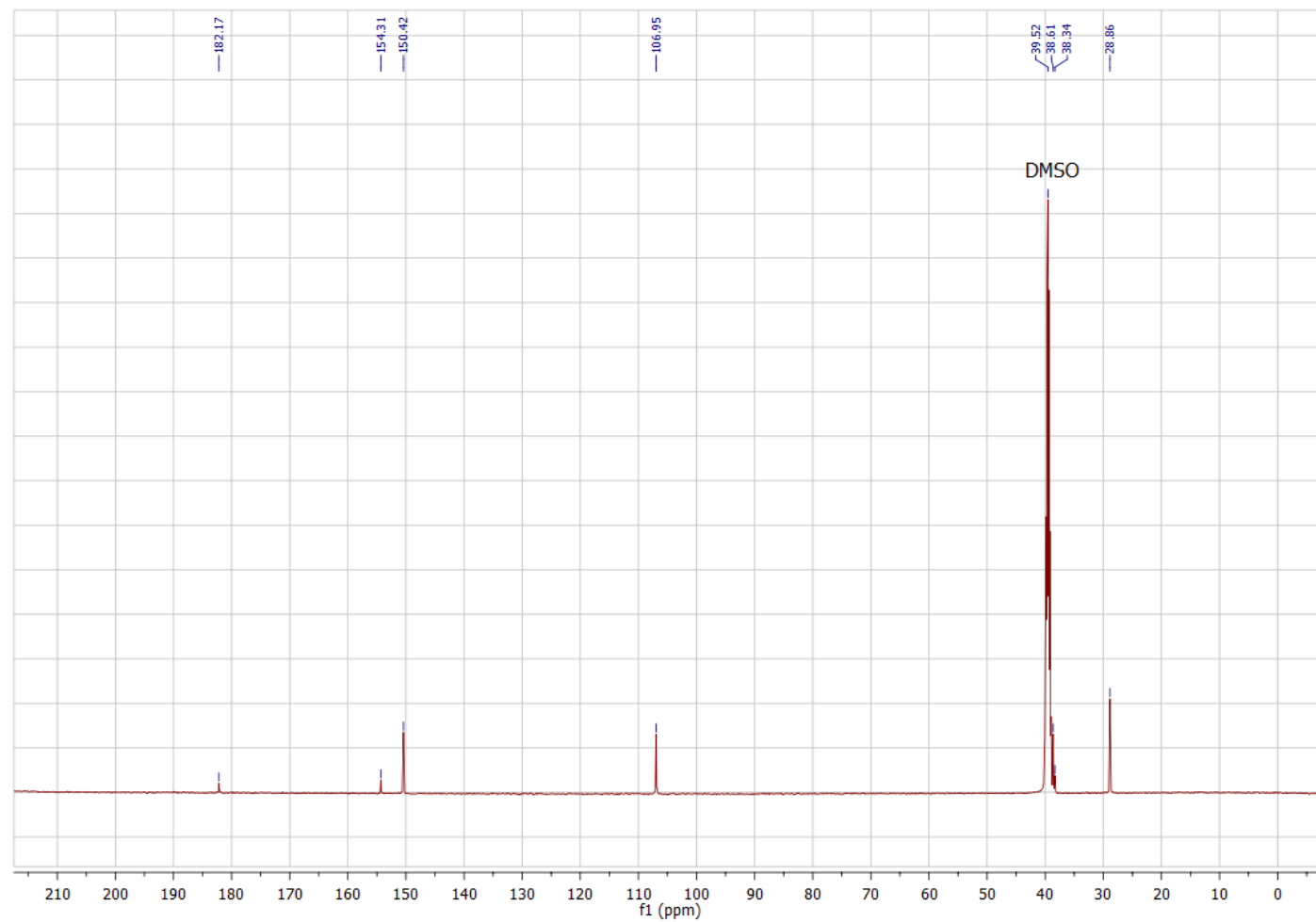


Figure S15: The ^{13}C NMR spectrum of compound **1c** in $(\text{CD}_3)_2\text{SO}$.

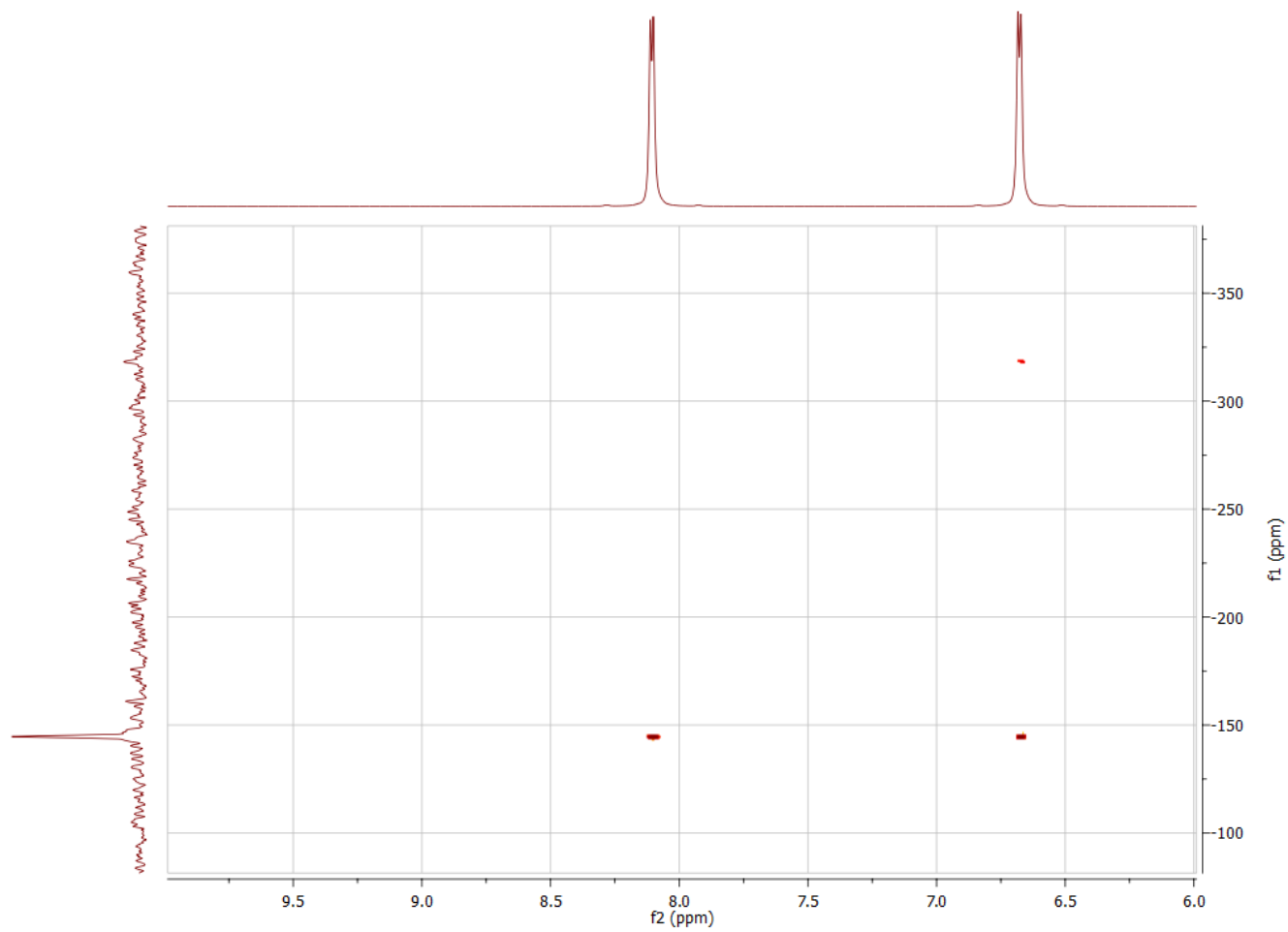


Figure S16: The ^1H - ^{15}N HMBC spectrum of compound **1c** in $(\text{CD}_3)_2\text{SO}$.

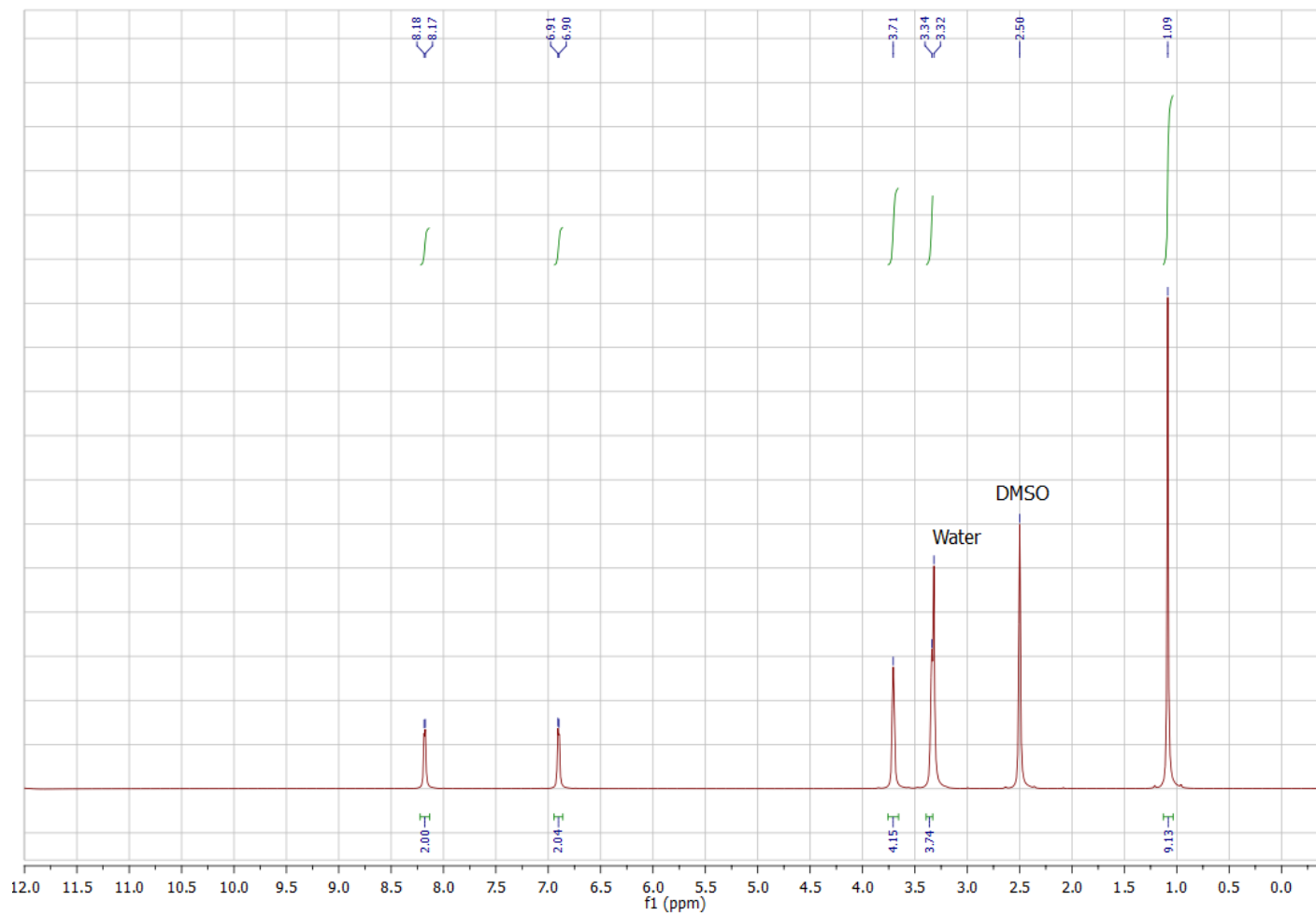


Figure S17: The ^1H NMR spectrum of compound **1d** in $(\text{CD}_3)_2\text{SO}$.

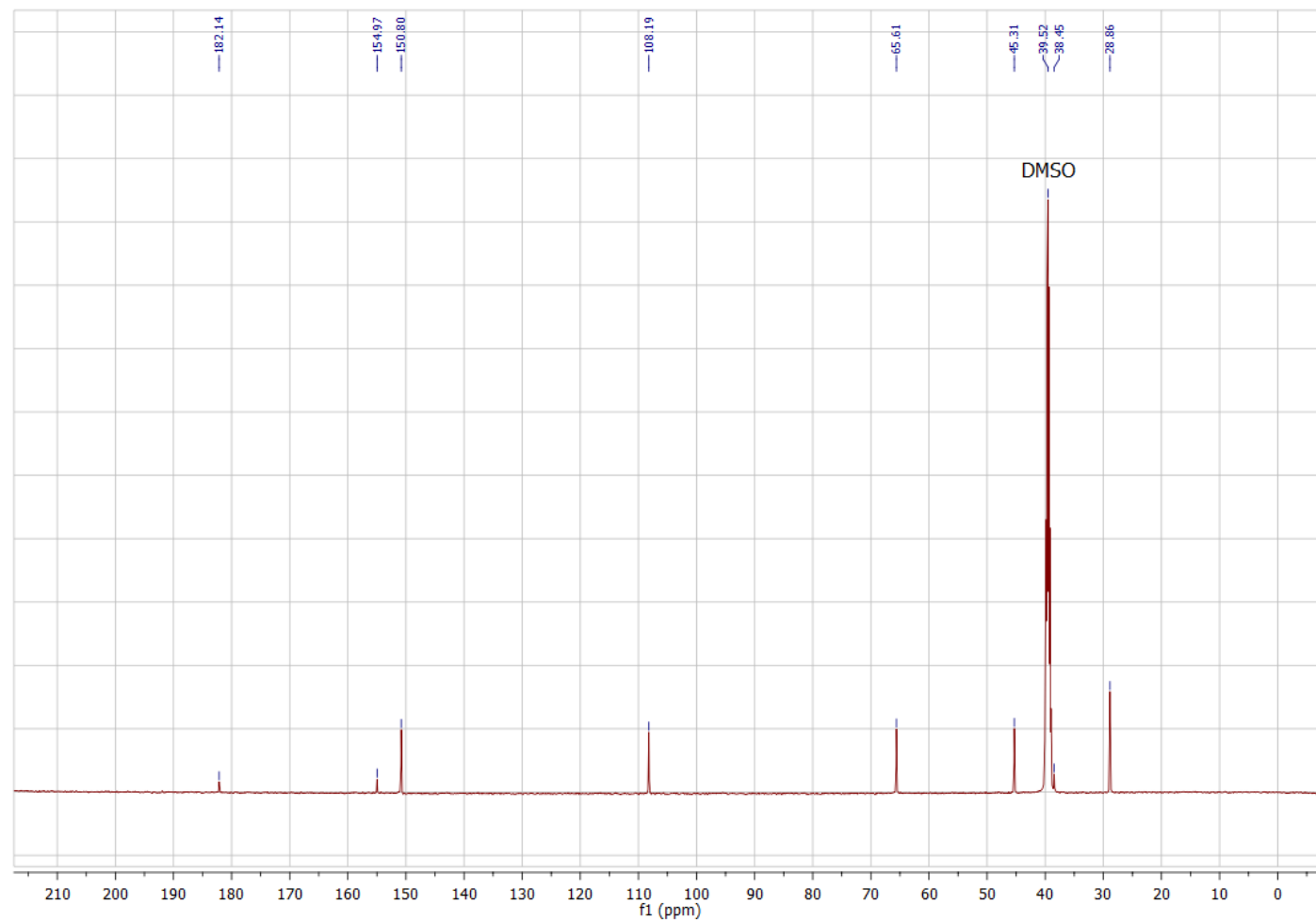


Figure S18: The ^{13}C NMR spectrum of compound **1d** in $(\text{CD}_3)_2\text{SO}$.

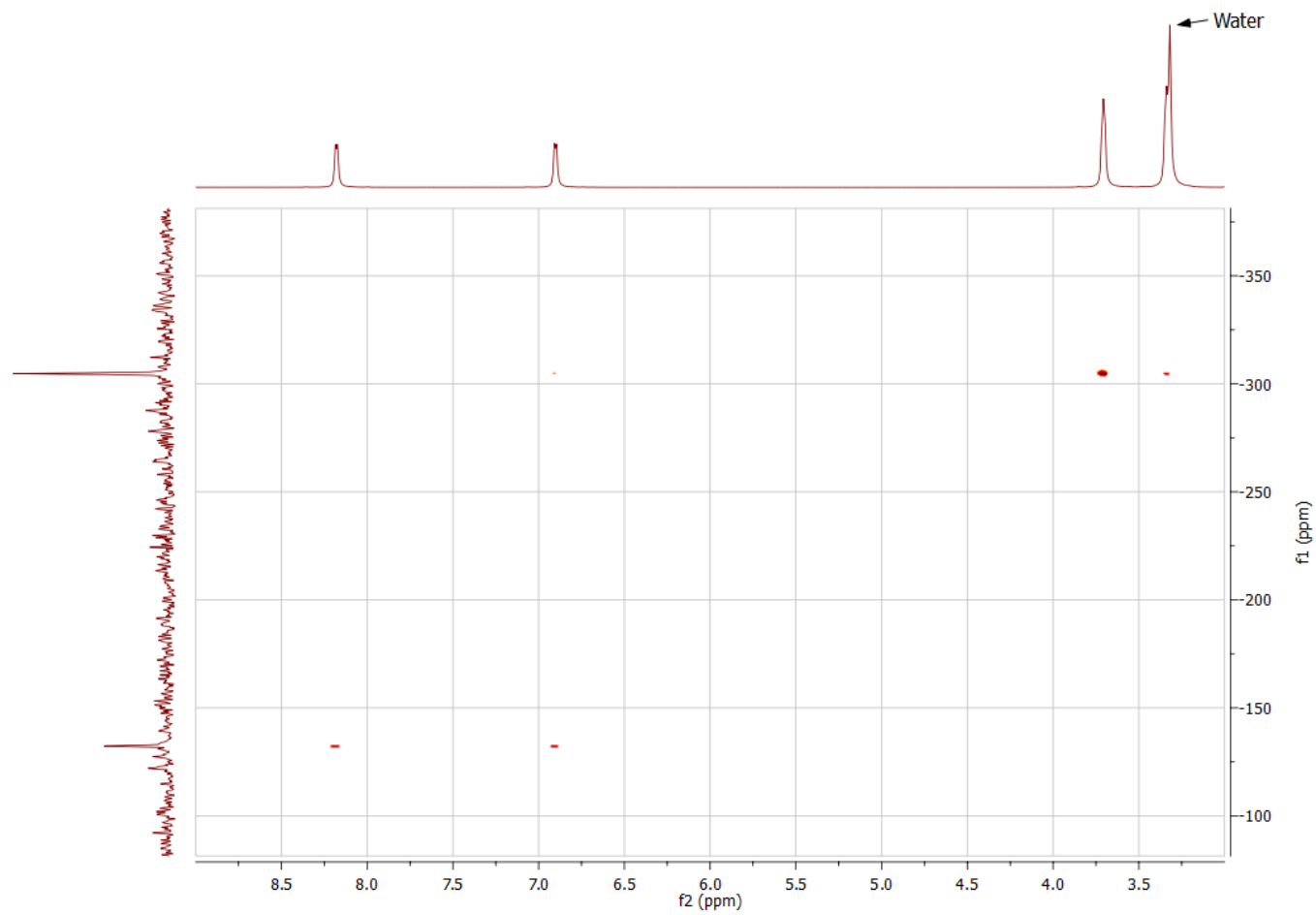


Figure S19: The ^1H - ^{15}N HMBC spectrum of compound **1d** in $(\text{CD}_3)_2\text{SO}$.

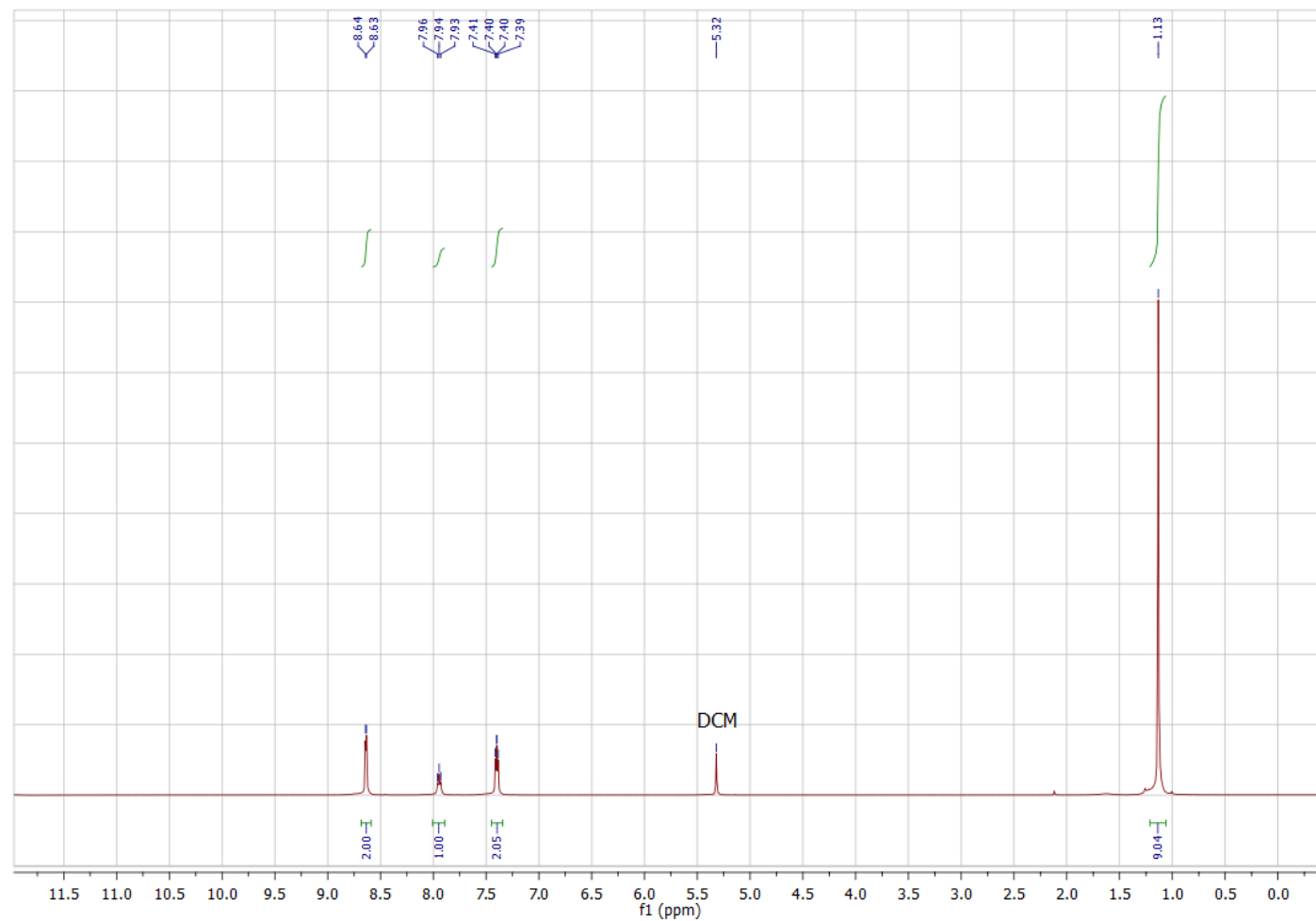


Figure S20: The ^1H NMR spectrum of compound **2a** in CD_2Cl_2 .

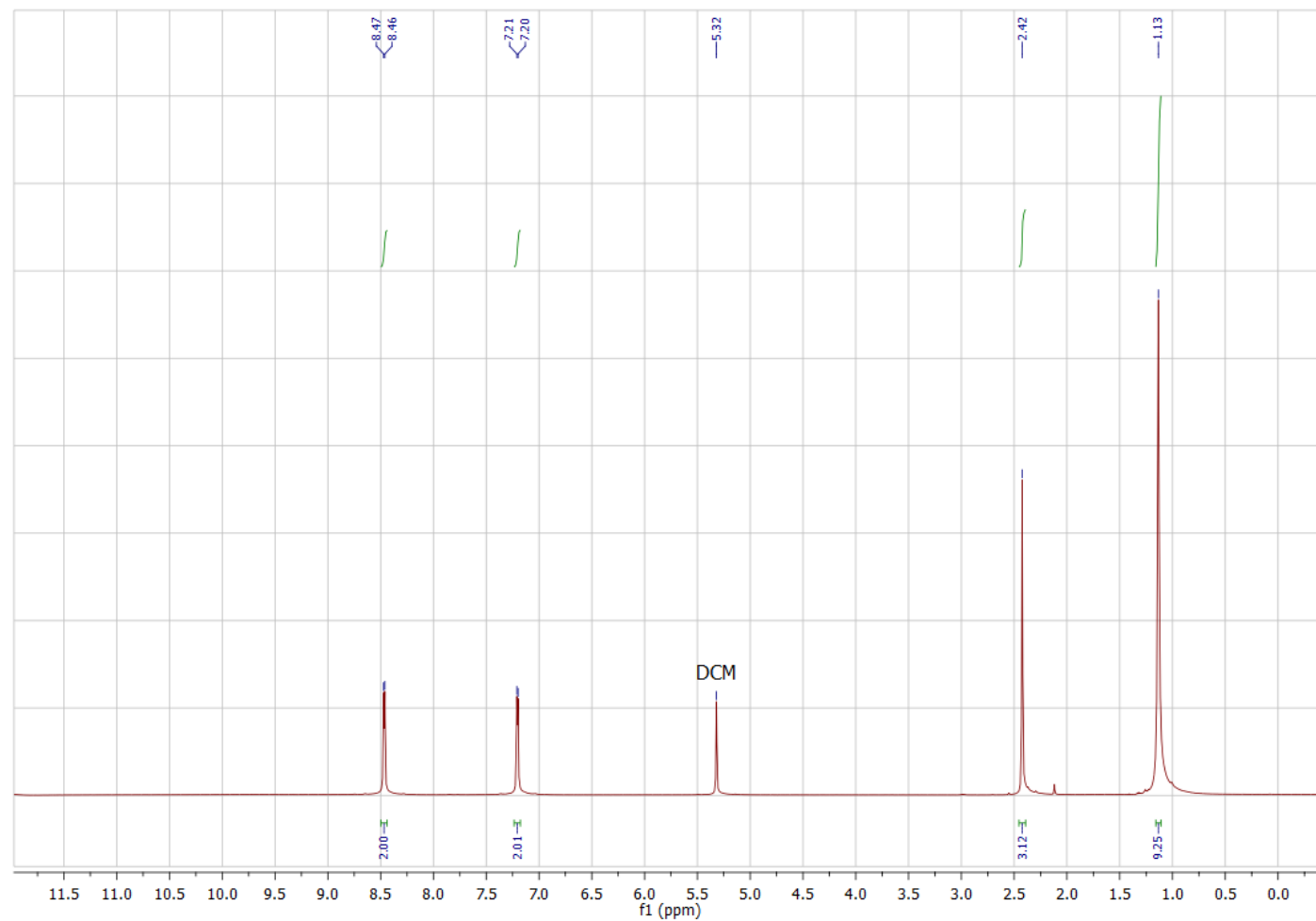


Figure S21: The ^1H NMR spectrum of compound **2b** in CD_2Cl_2 .

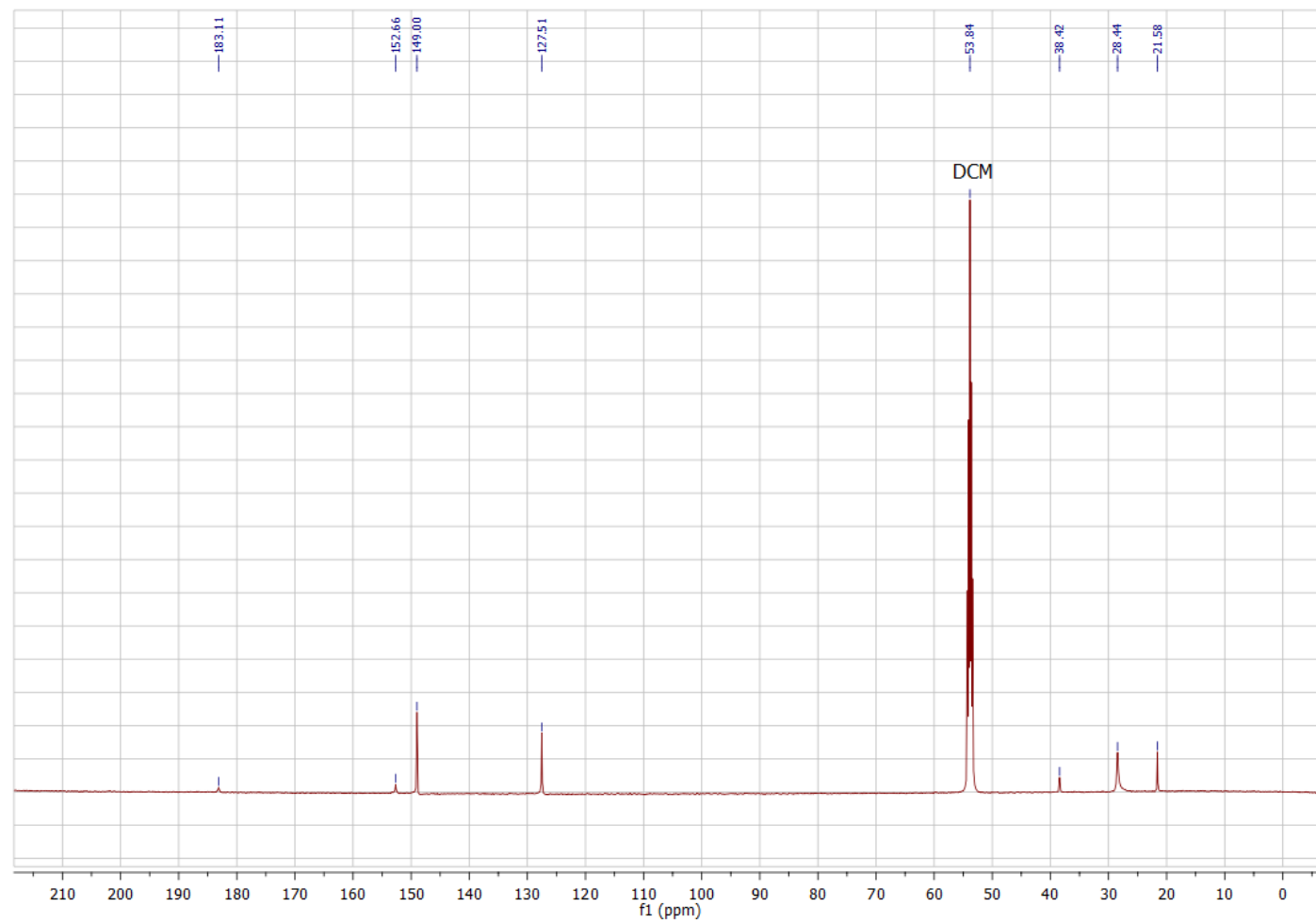


Figure S22: The ^{13}C NMR spectrum of compound **2b** in CD_2Cl_2 .

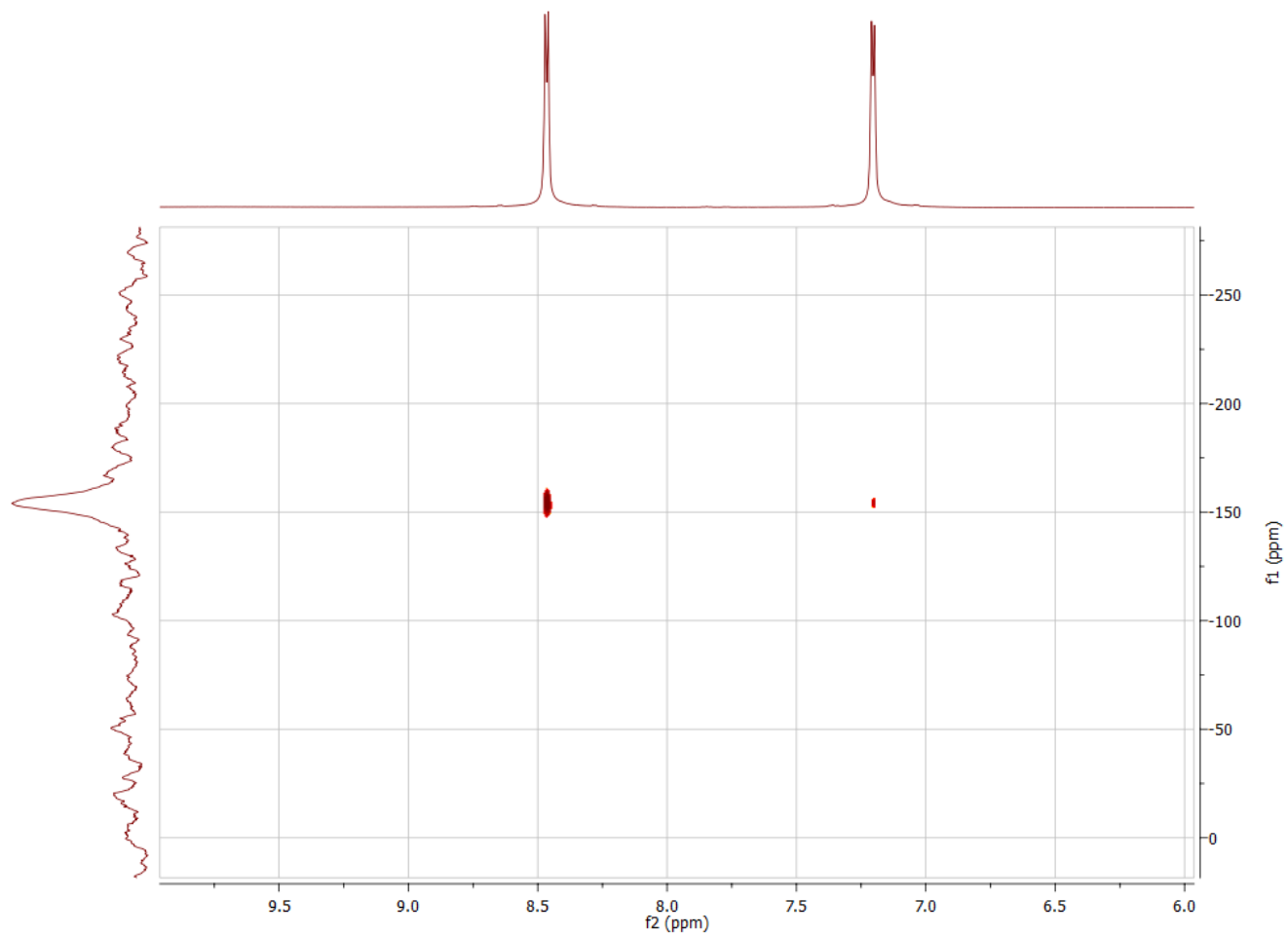


Figure S23: The ^1H - ^{15}N HMBC spectrum of compound **2b** in CD_2Cl_2 .

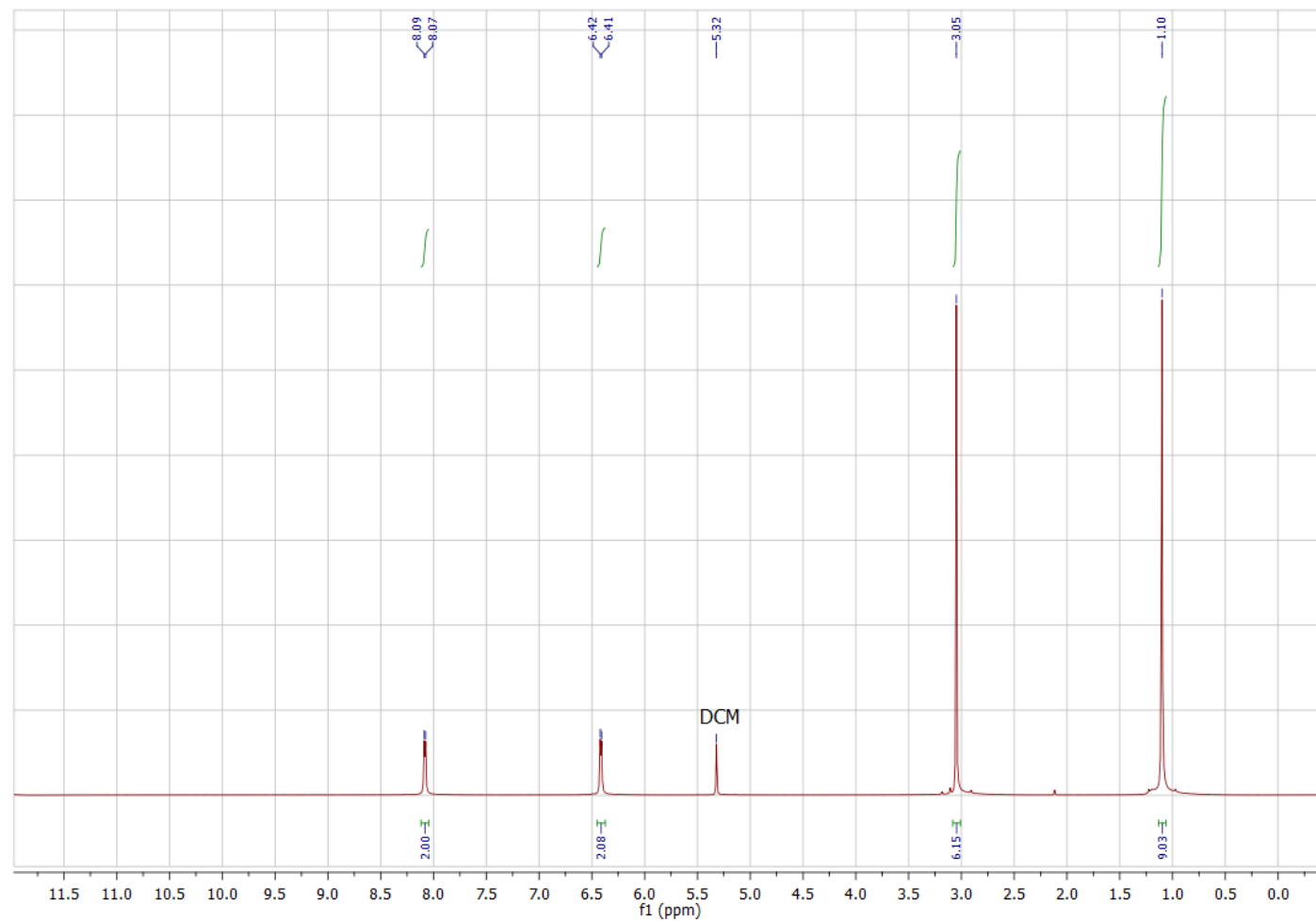


Figure S24: The ^1H NMR spectrum of compound **2c** in CD_2Cl_2 .

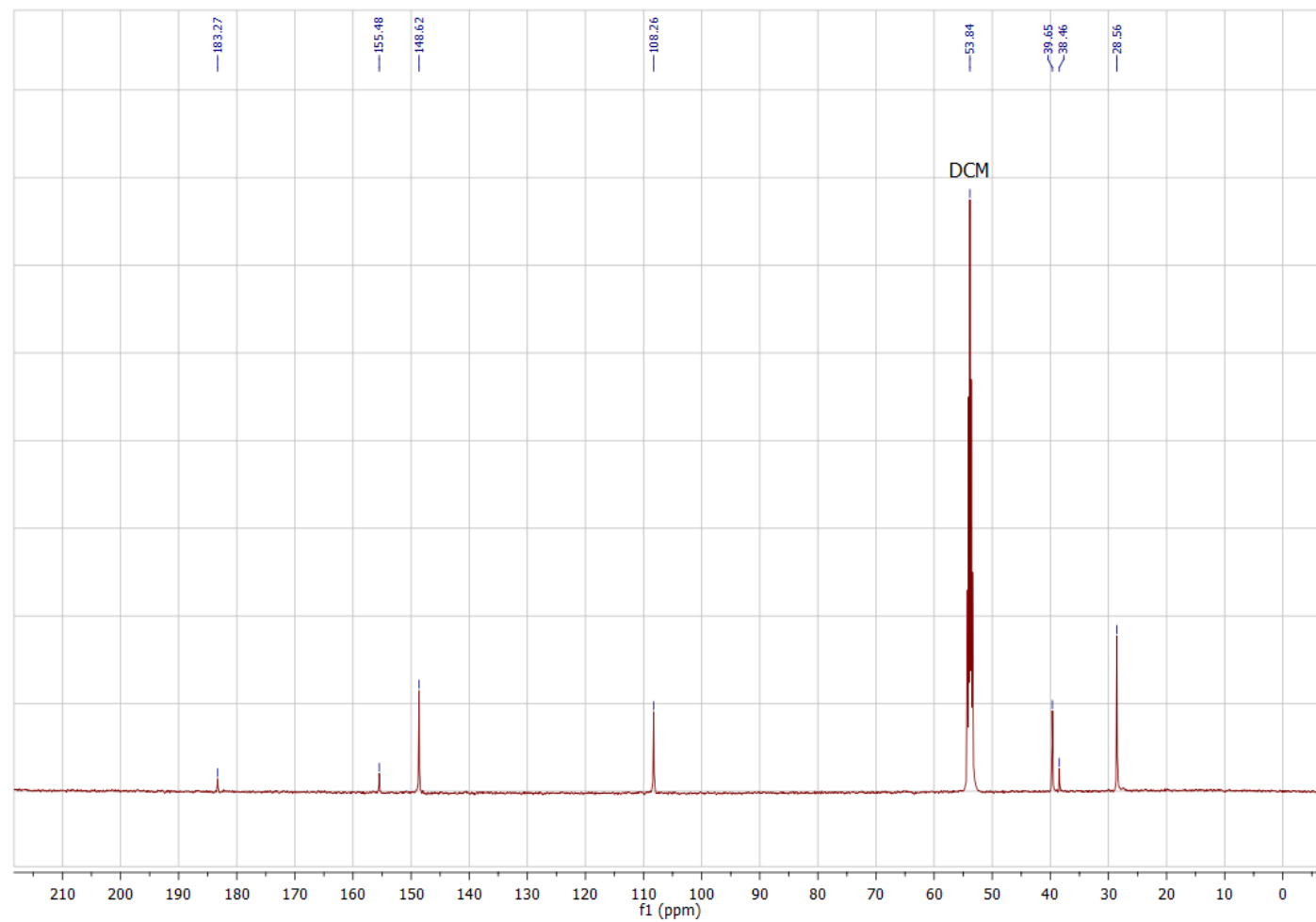


Figure S25: The ^{13}C NMR spectrum of compound **2c** in CD_2Cl_2 .

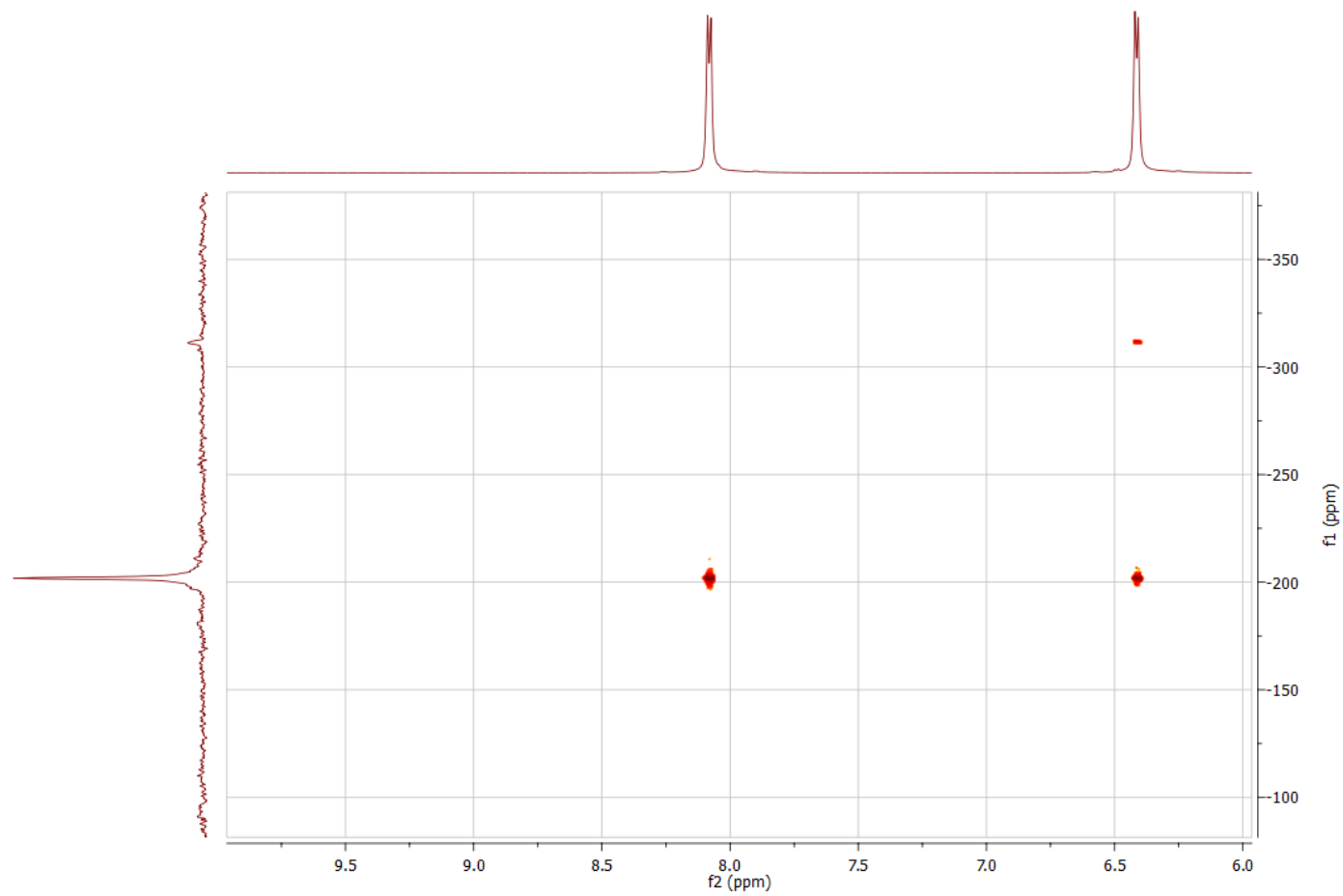


Figure S26: The ^1H - ^{15}N HMBC spectrum of compound **2c** in CD_2Cl_2 .

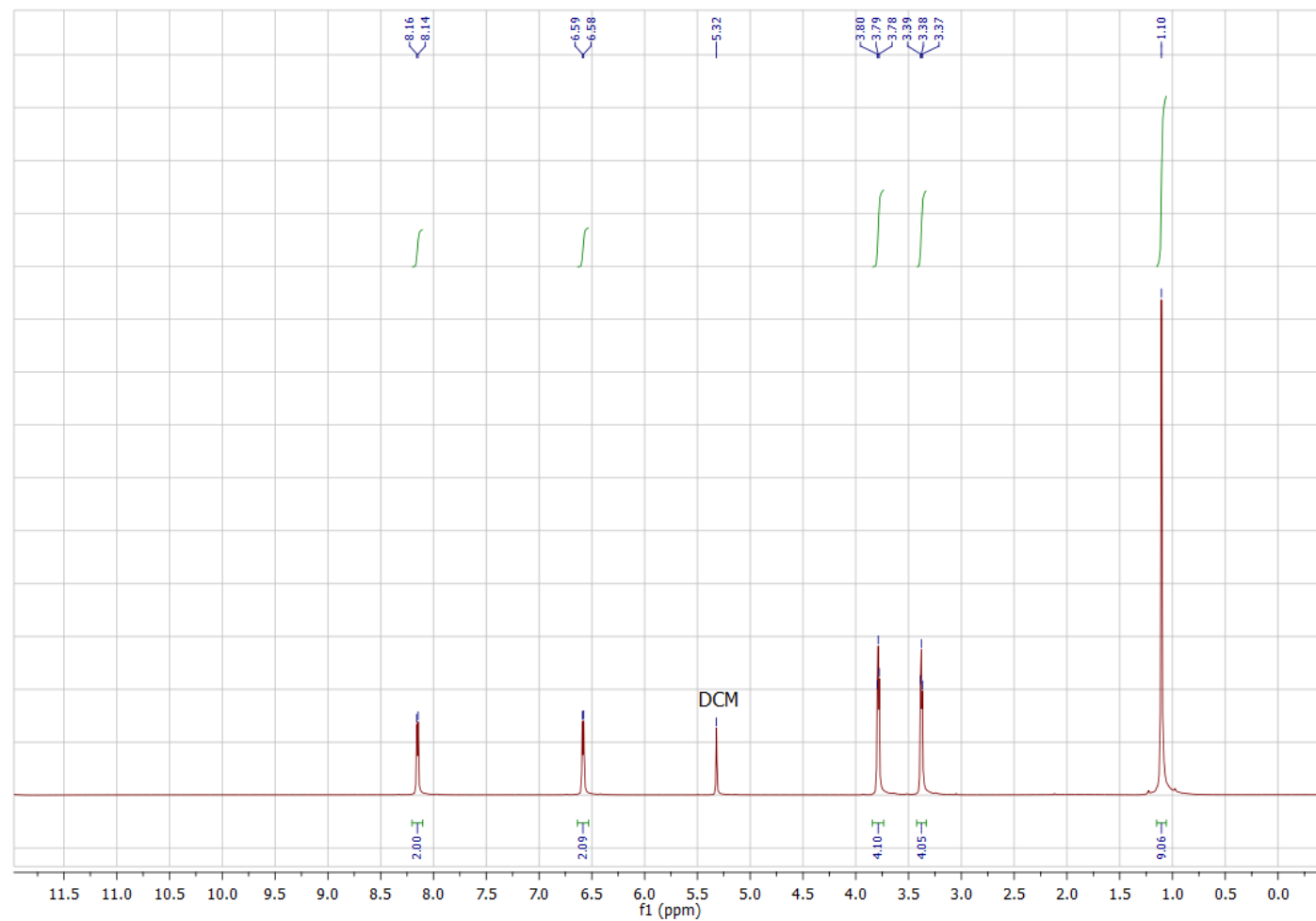


Figure S27: The ^1H NMR spectrum of compound **2d** in CD_2Cl_2 .

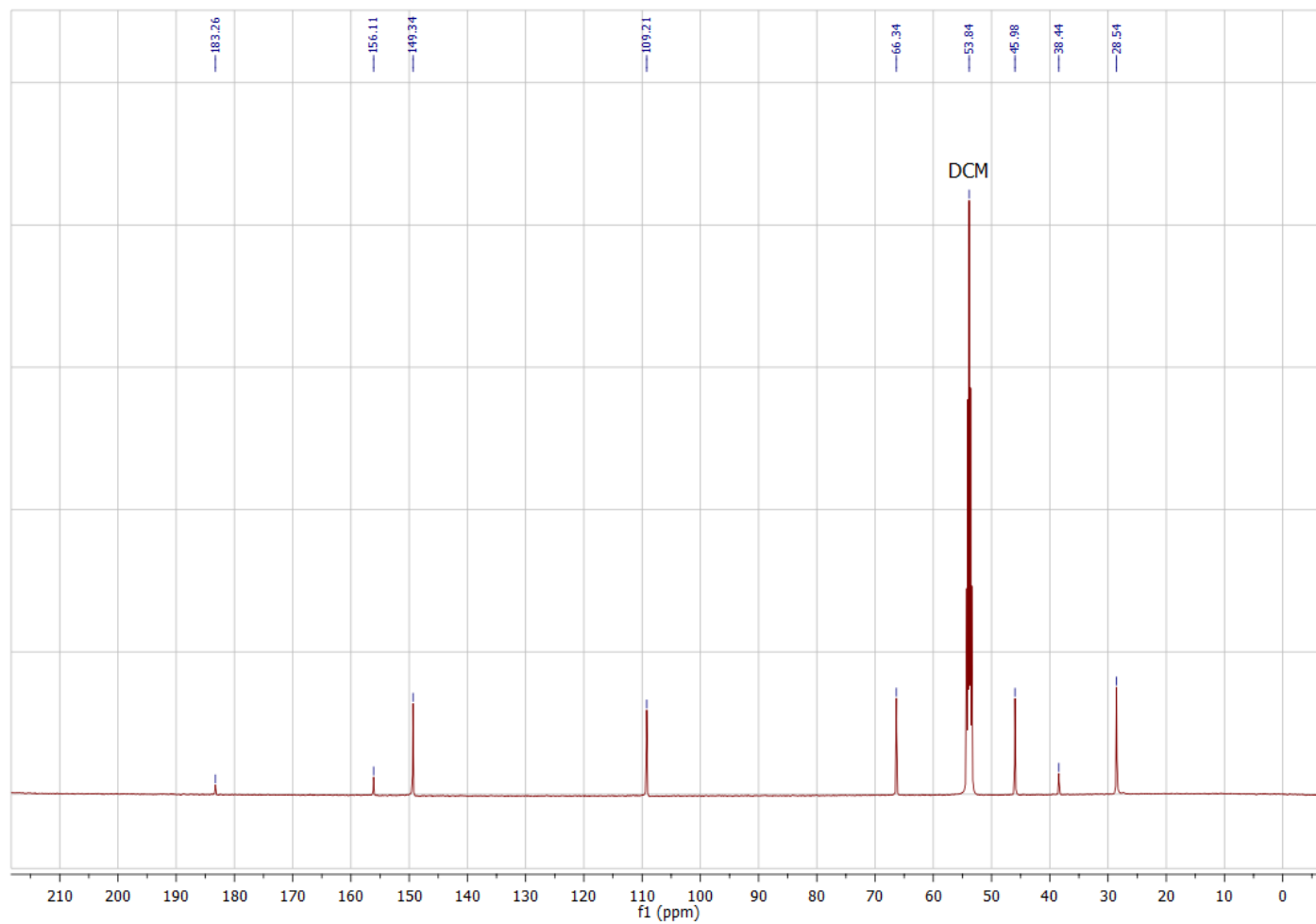


Figure S28: The ^{13}C NMR spectrum of compound **2d** in CD_2Cl_2 .

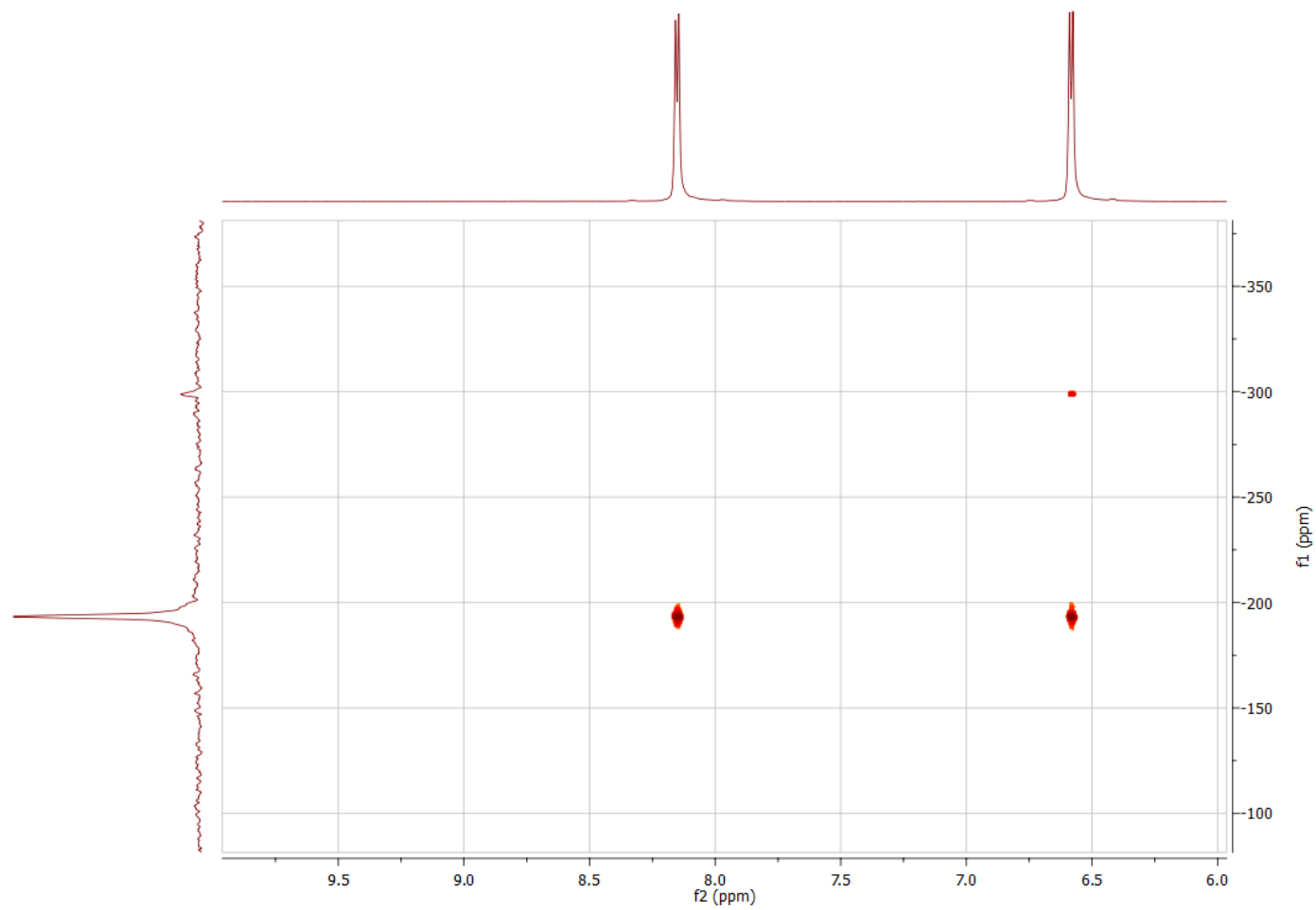


Figure S29: The ^1H - ^{15}N HMBC spectrum of compound **2d** in CD_2Cl_2 .

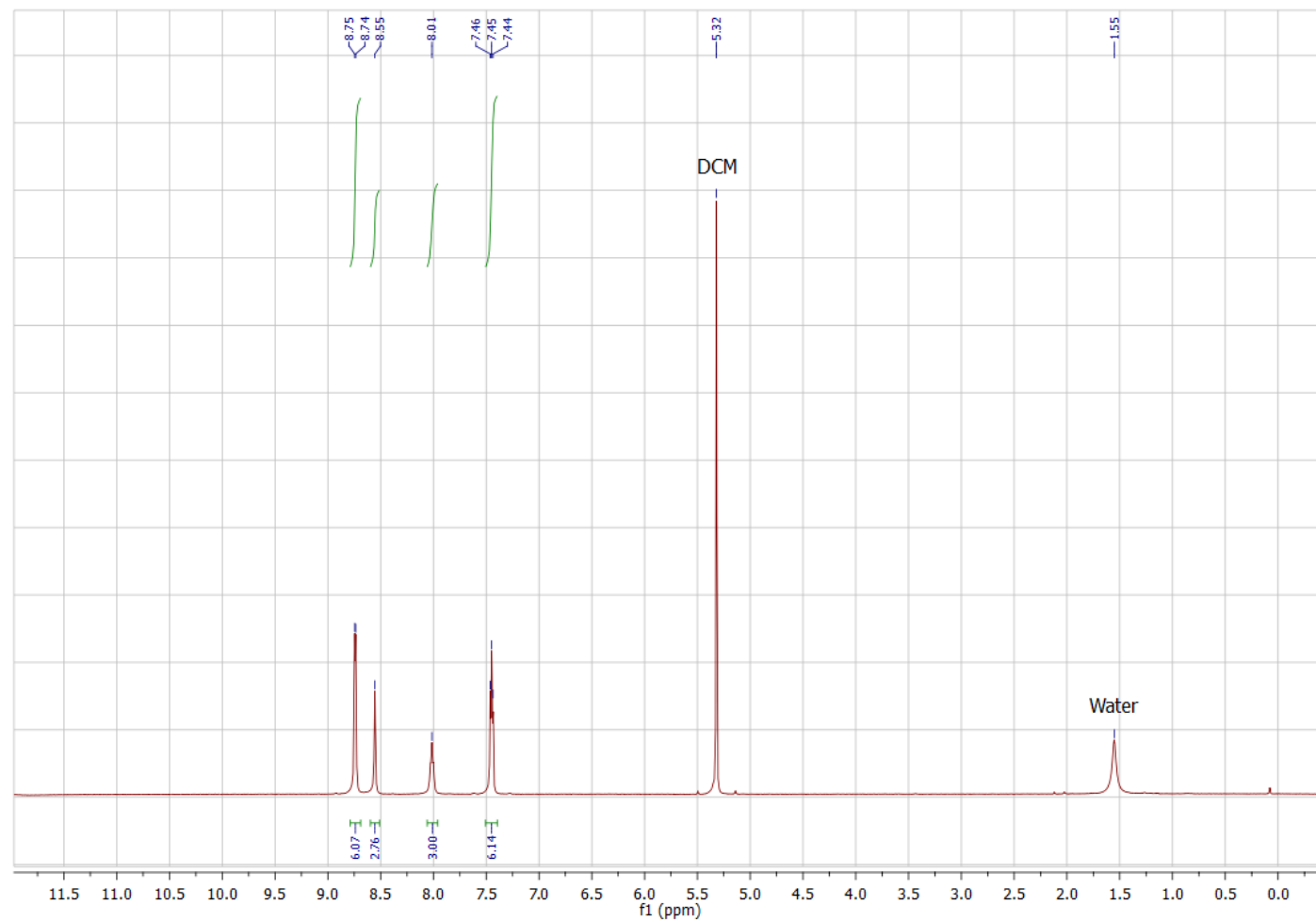


Figure S30: The ^1H NMR spectrum of compound **4a** in CD_2Cl_2 .

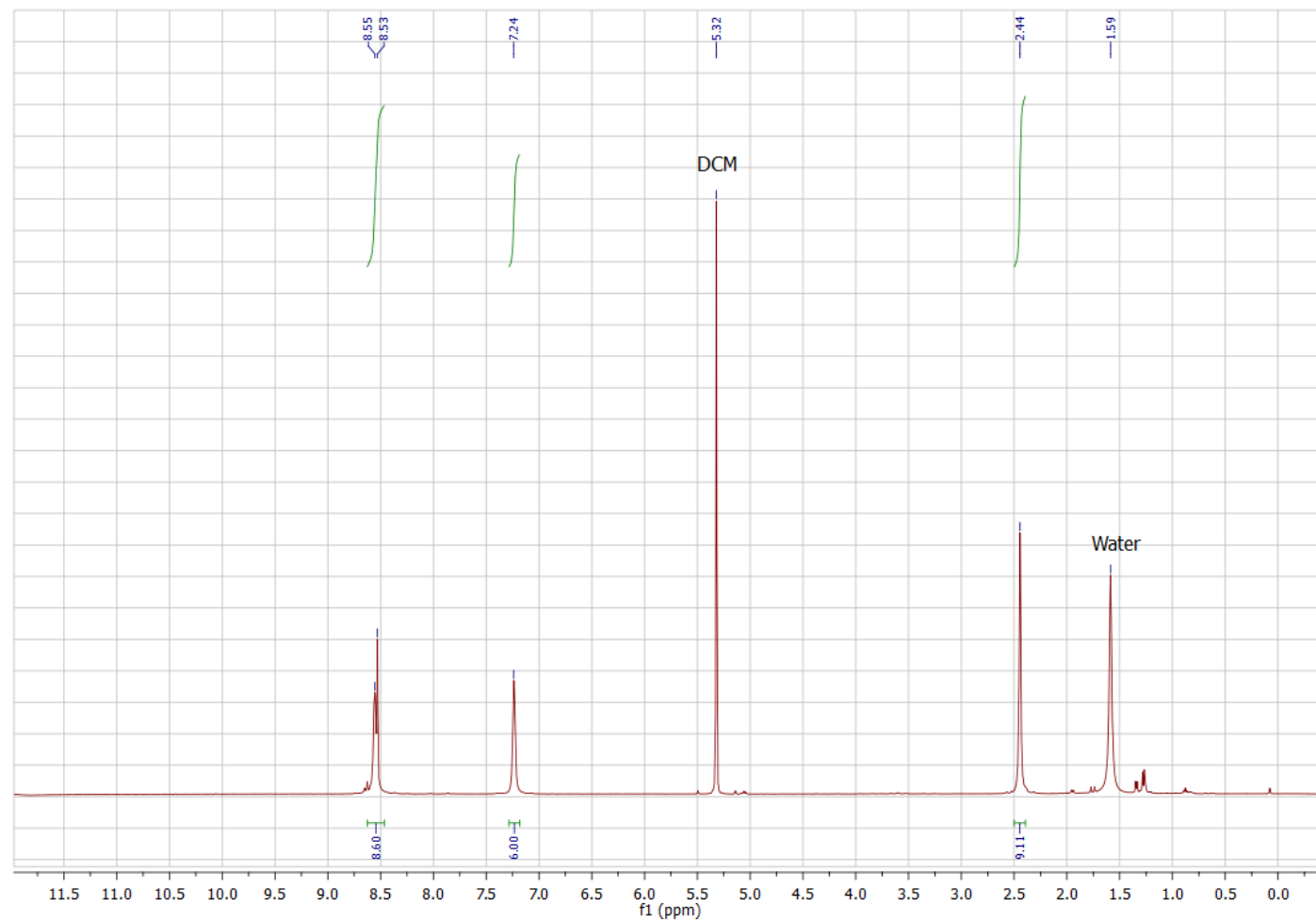


Figure S31: The ^1H NMR spectrum of compound **4b** in CD_2Cl_2 .

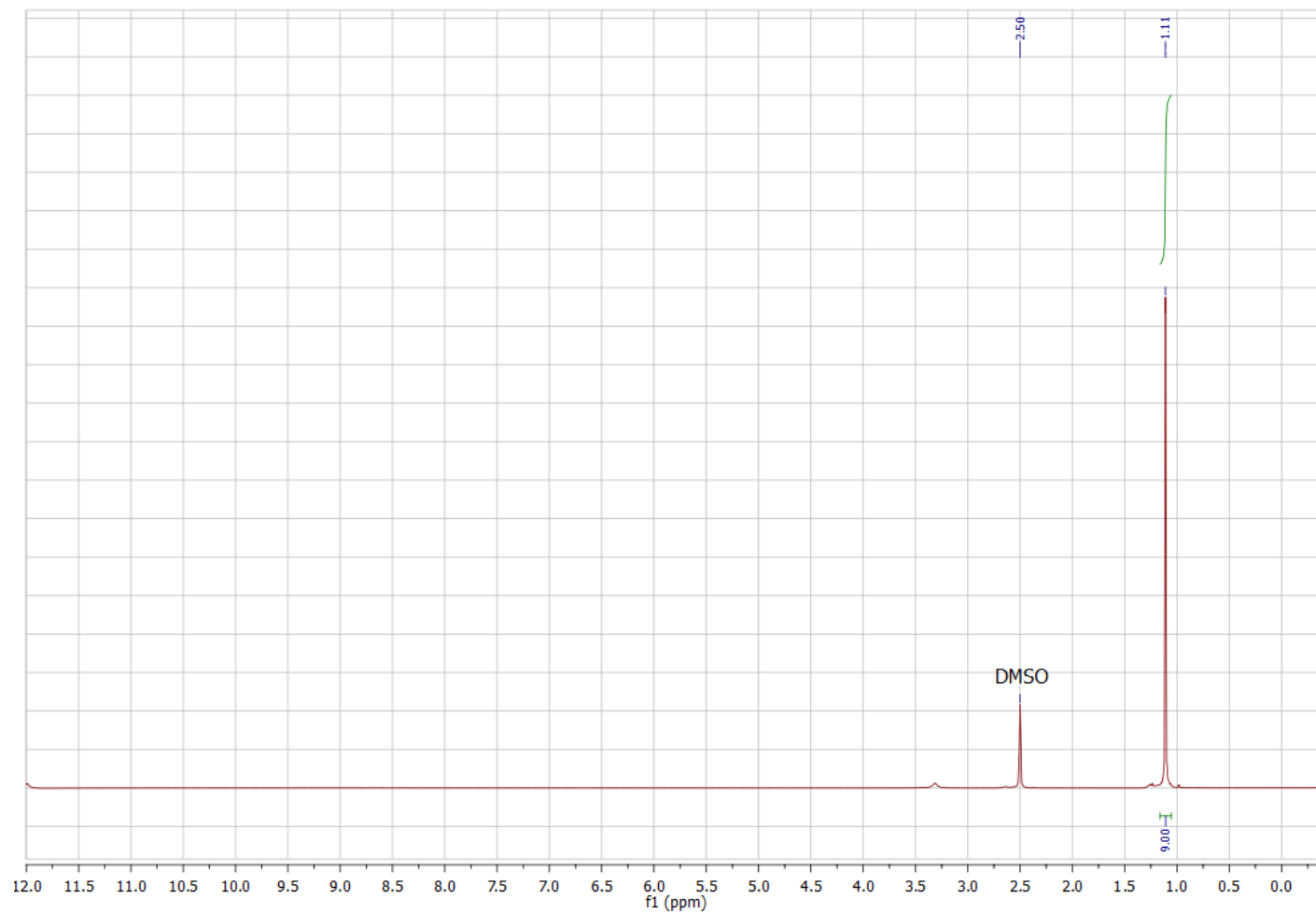


Figure S32: The ^1H NMR spectrum of pivalic acid in $(\text{CD}_3)_2\text{SO}$.

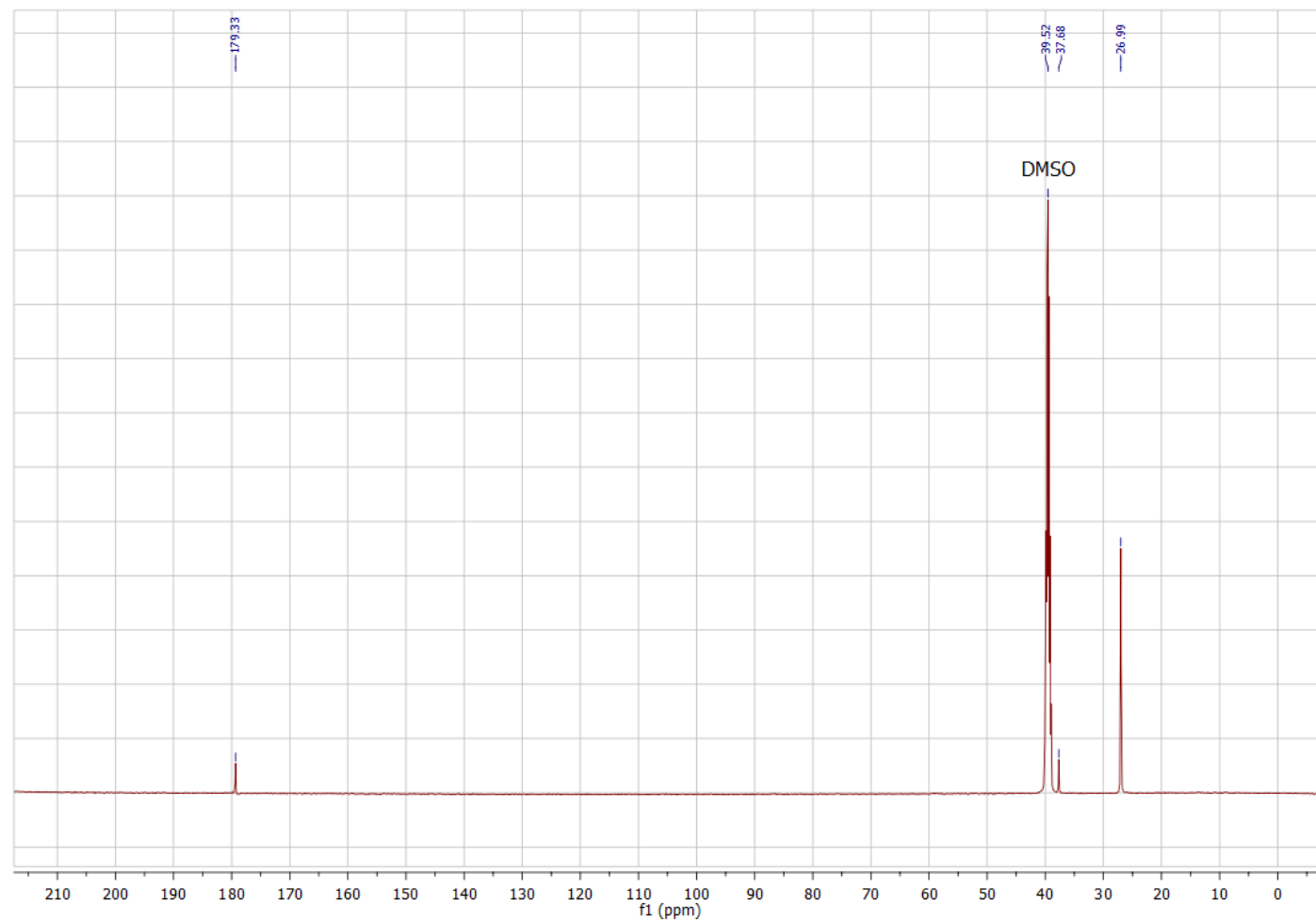


Figure S33: The ^{13}C NMR spectrum of pivalic acid in $(\text{CD}_3)_2\text{SO}$.

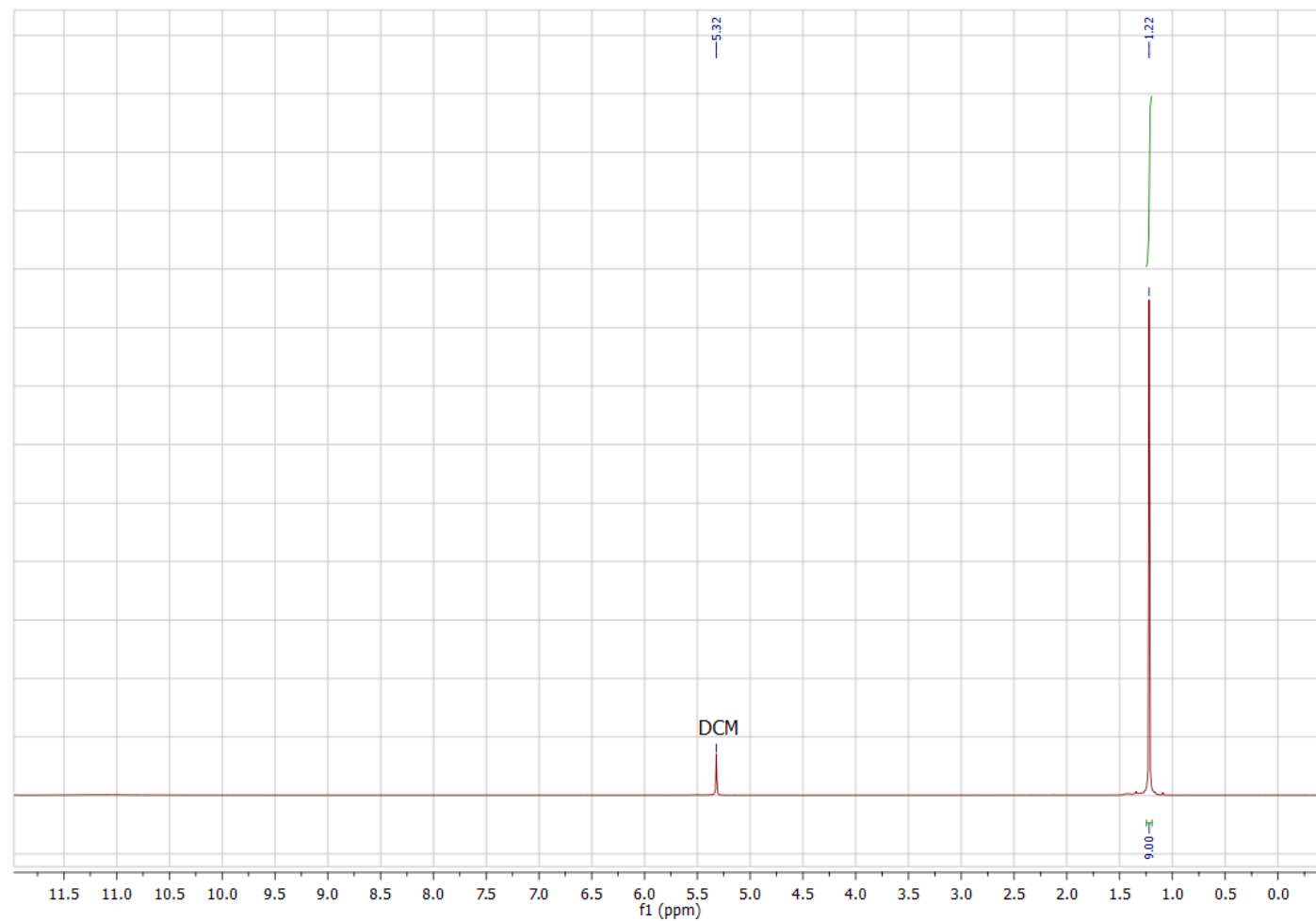


Figure S34: The ^1H NMR spectrum of pivalic acid in CD_2Cl_2 .

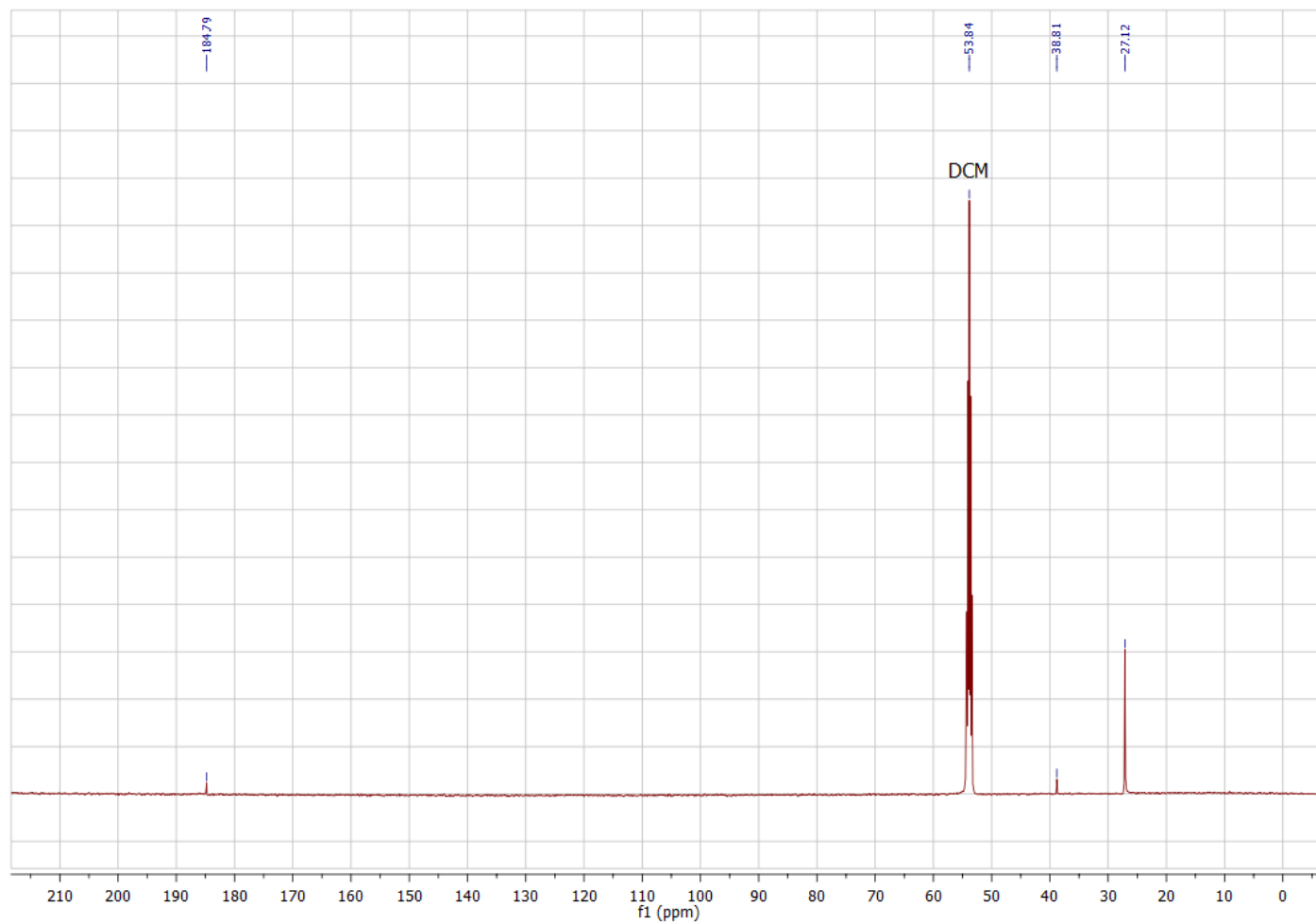


Figure S35: The ^{13}C NMR spectrum of pivalic acid in CD_2Cl_2 .

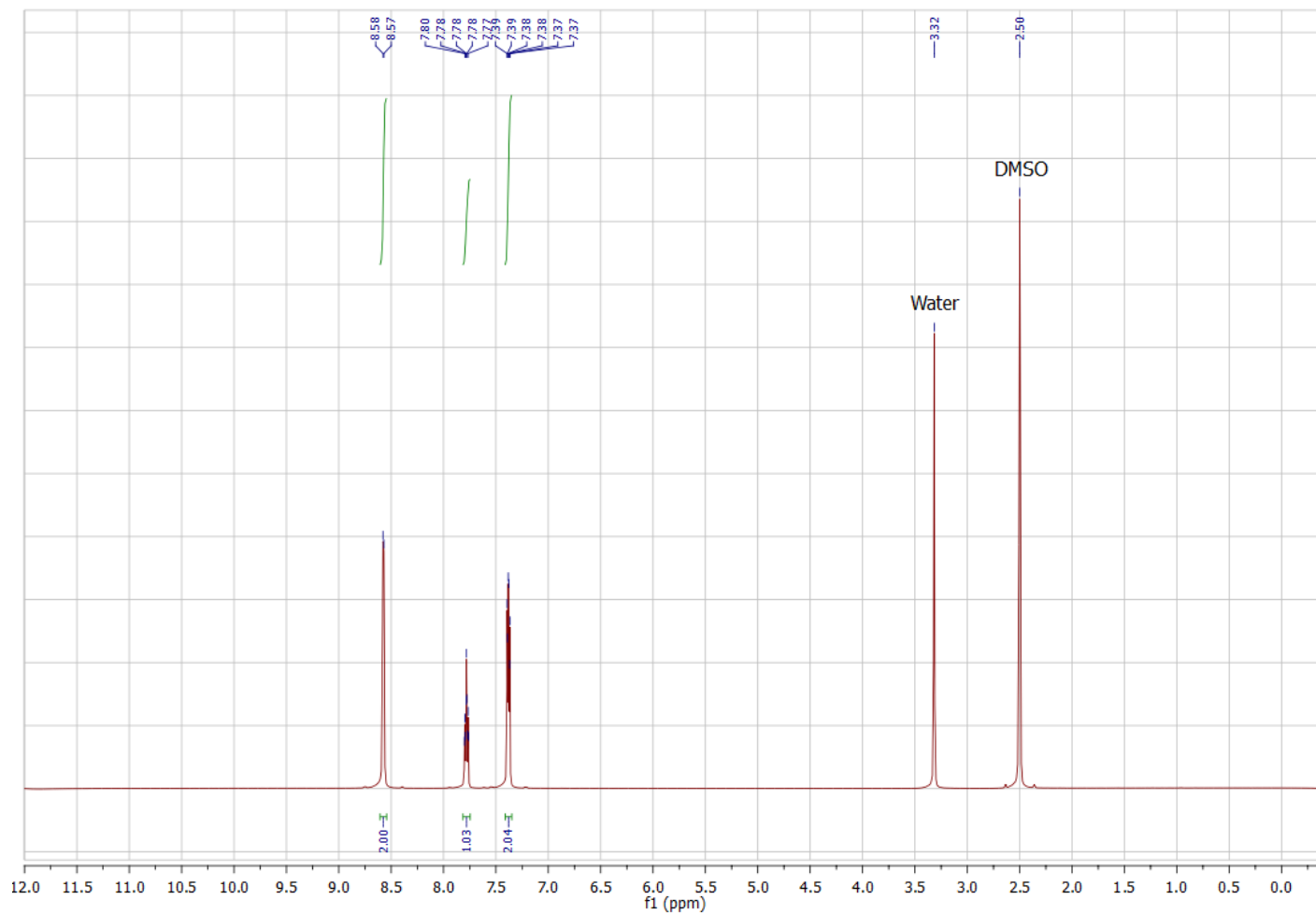


Figure S36: The ^1H NMR spectrum of pyridine in $(\text{CD}_3)_2\text{SO}$.

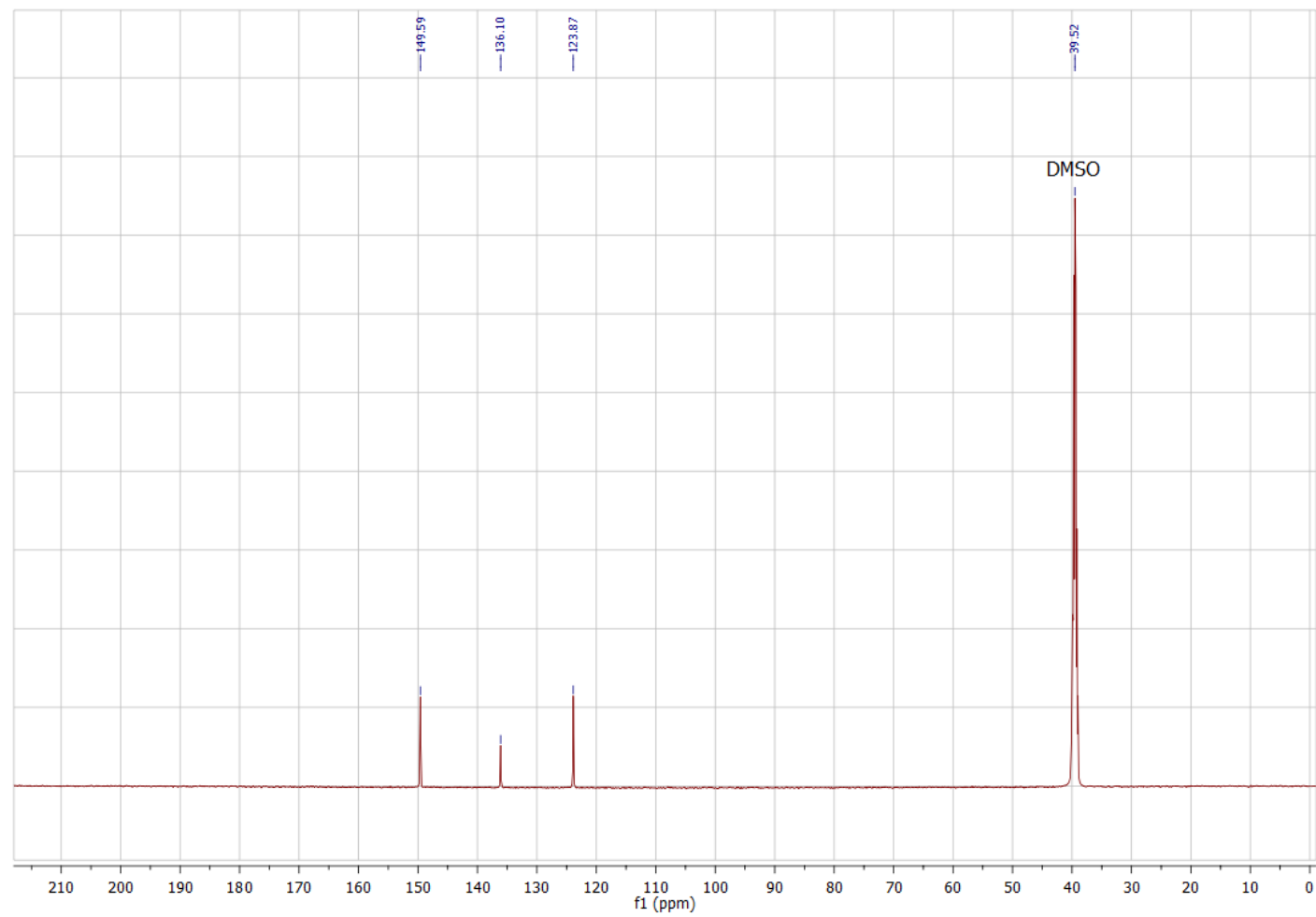


Figure S37: The ^{13}C NMR spectrum of pyridine in $(\text{CD}_3)_2\text{SO}$.

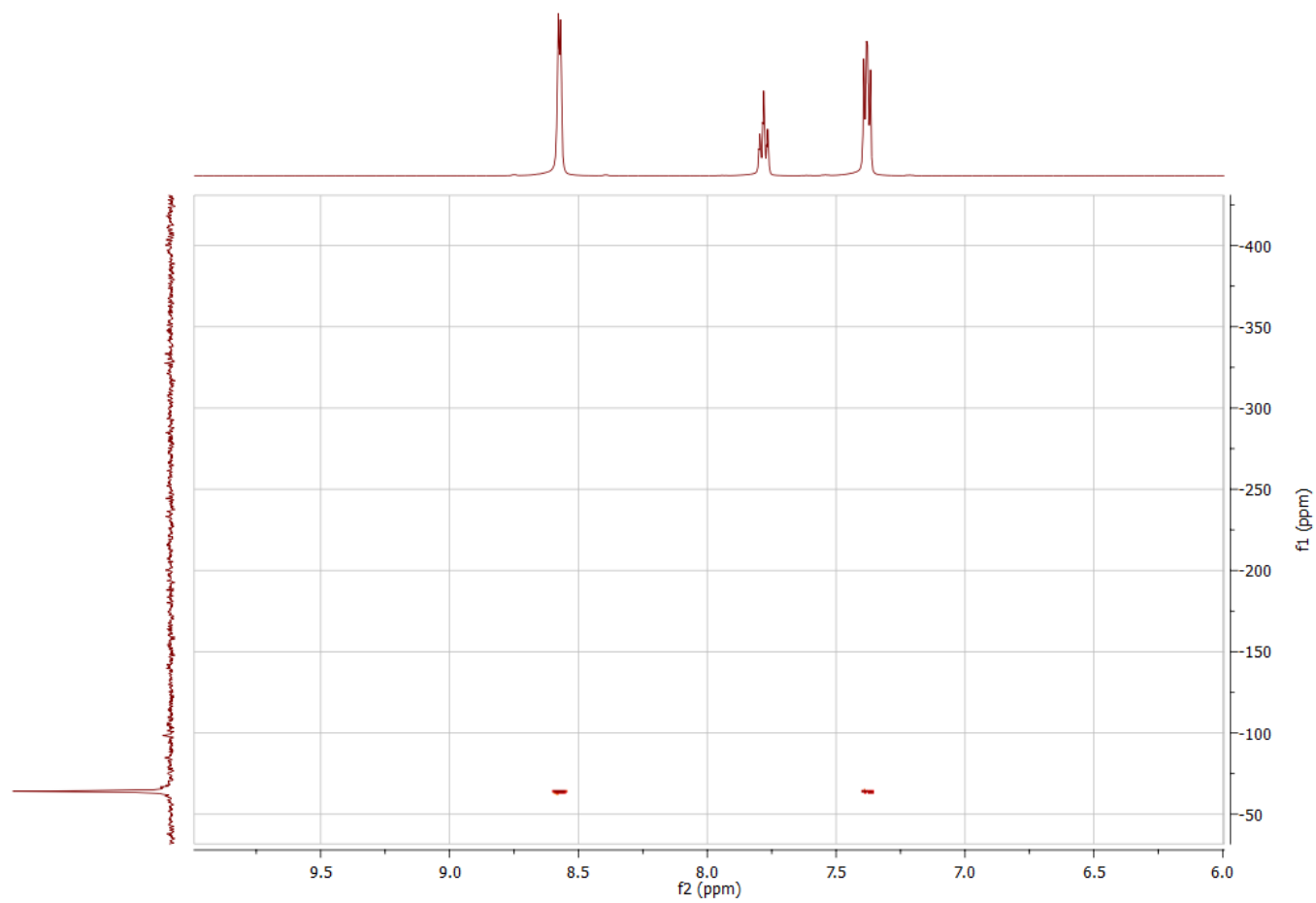


Figure S38: The ^1H - ^{15}N HMBC spectrum of pyridine in $(\text{CD}_3)_2\text{SO}$.

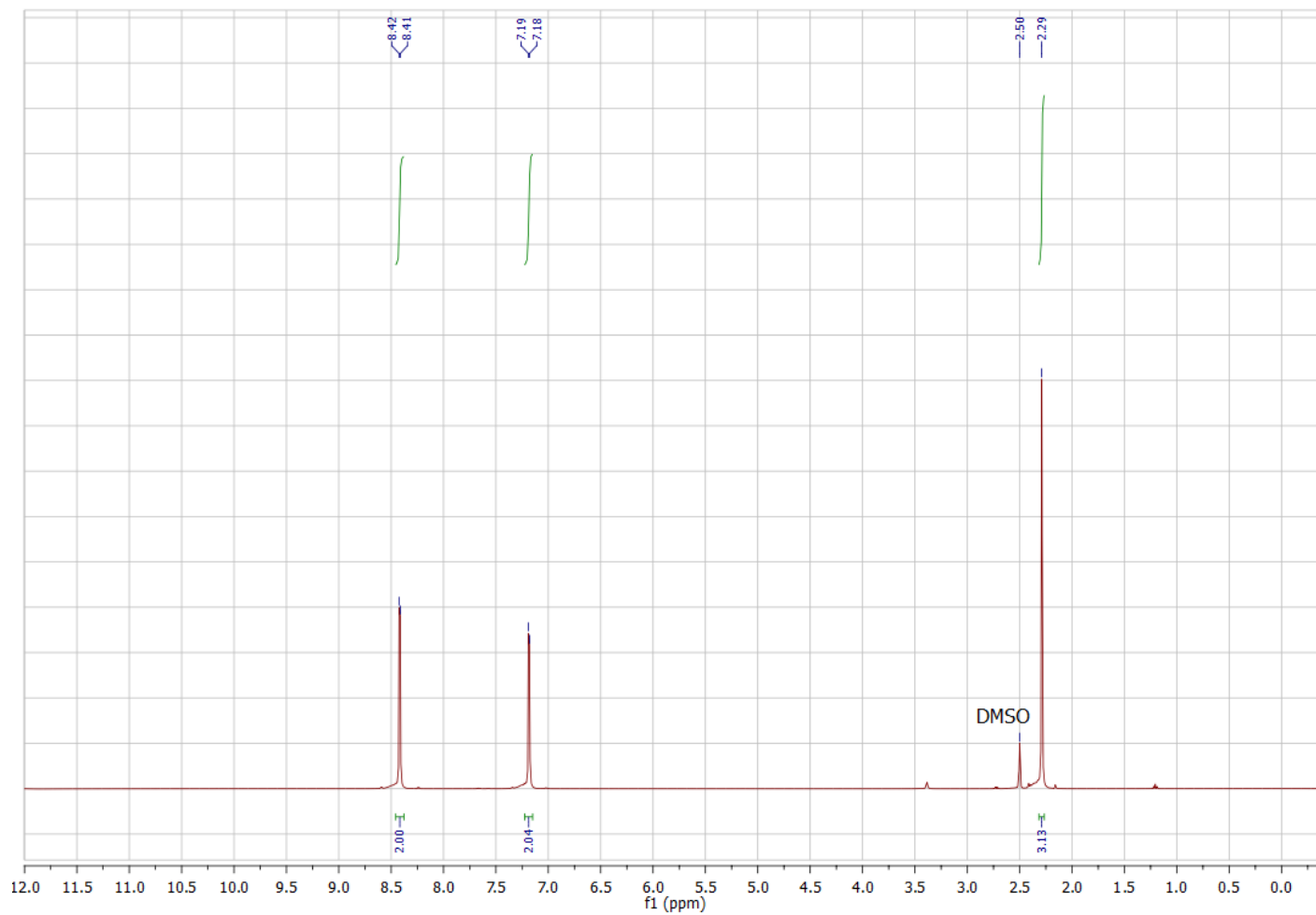


Figure S39: The ^1H NMR spectrum of 4-Mepy in $(\text{CD}_3)_2\text{SO}$.

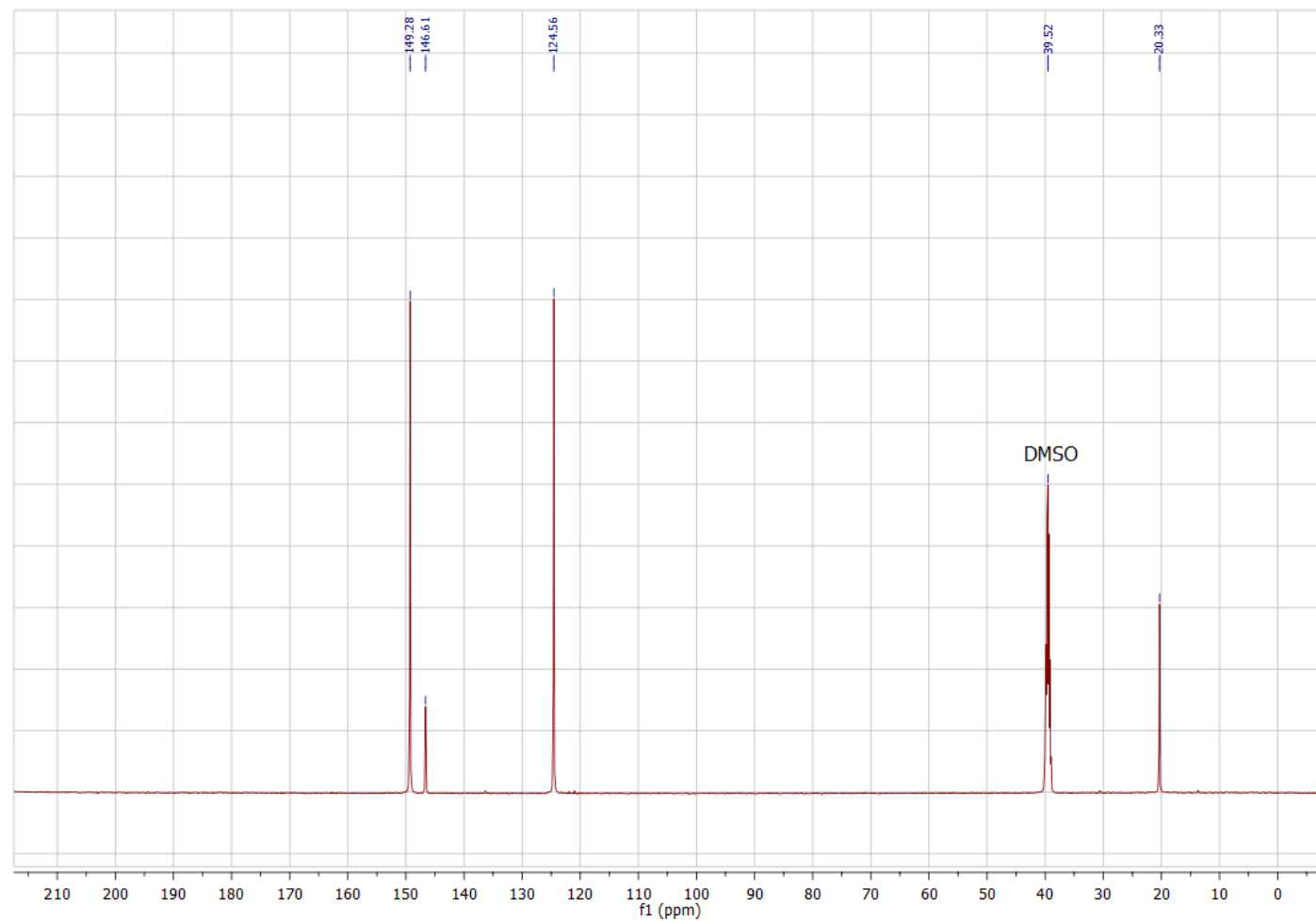


Figure S40: The ^{13}C NMR spectrum of 4-Mepy in $(\text{CD}_3)_2\text{SO}$.

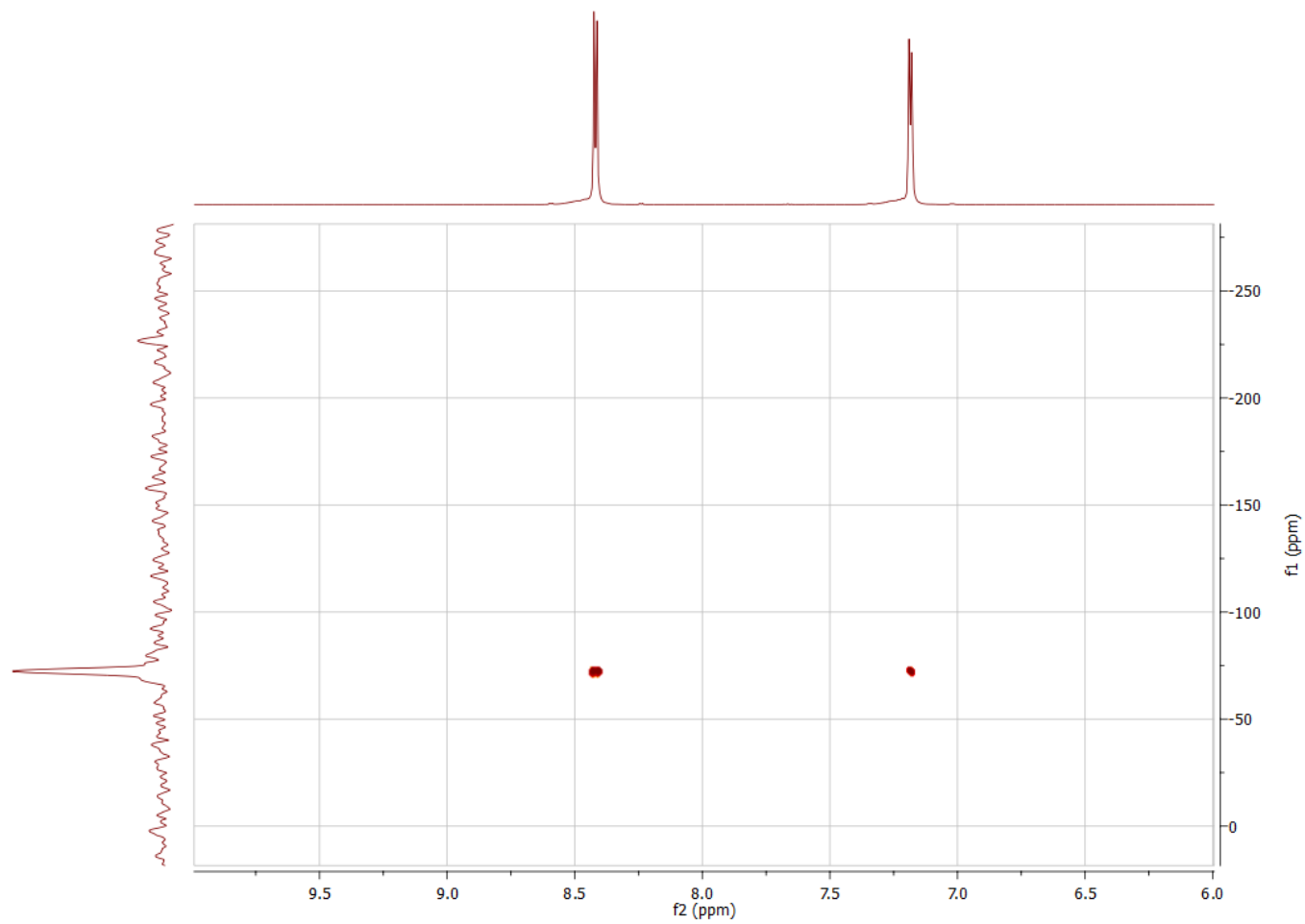


Figure S41: The ^1H - ^{15}N HMBC spectrum of 4-Mepy in $(\text{CD}_3)_2\text{SO}$.

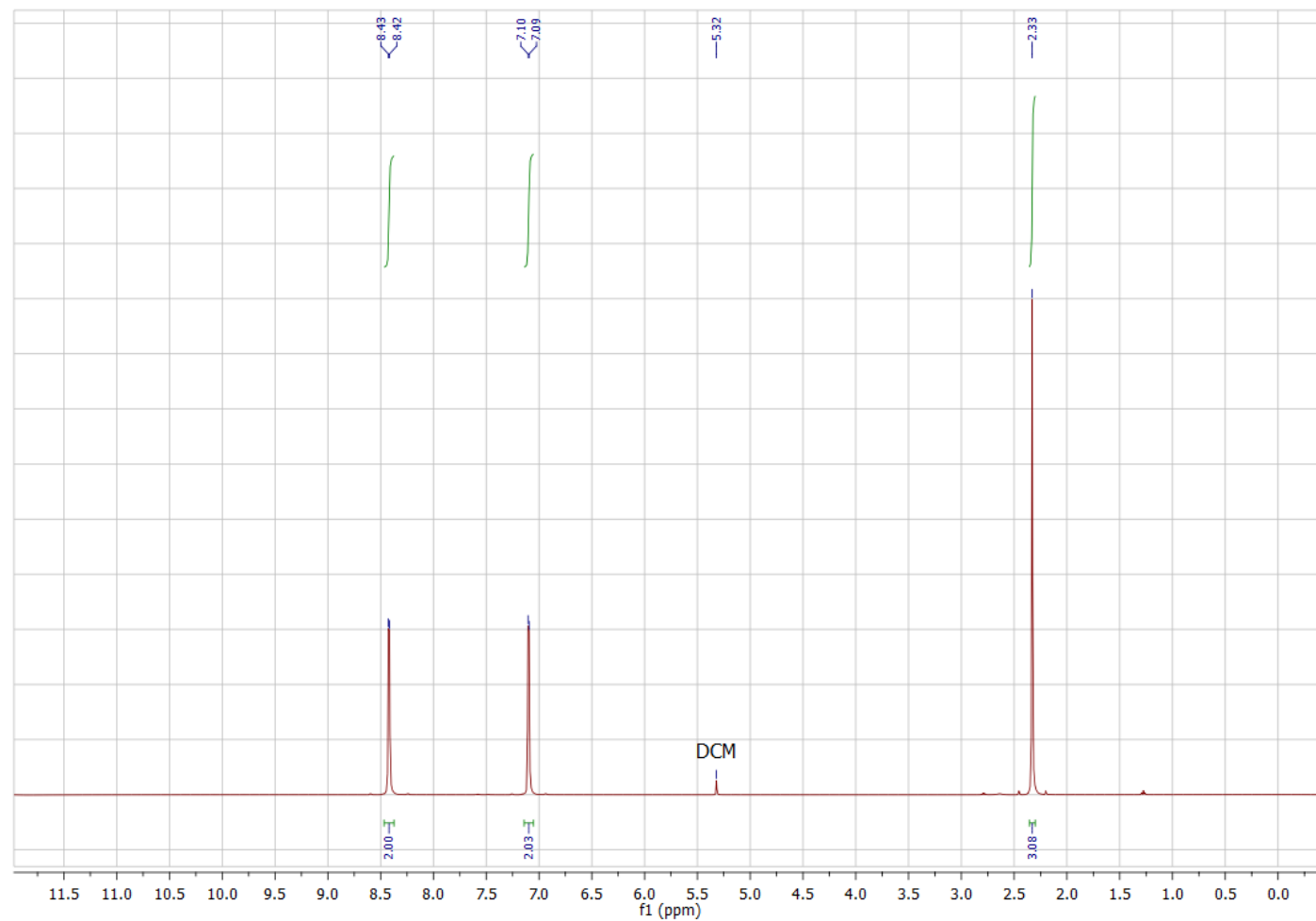


Figure S42: The ^1H NMR spectrum of 4-Mepy in CD_2Cl_2 .

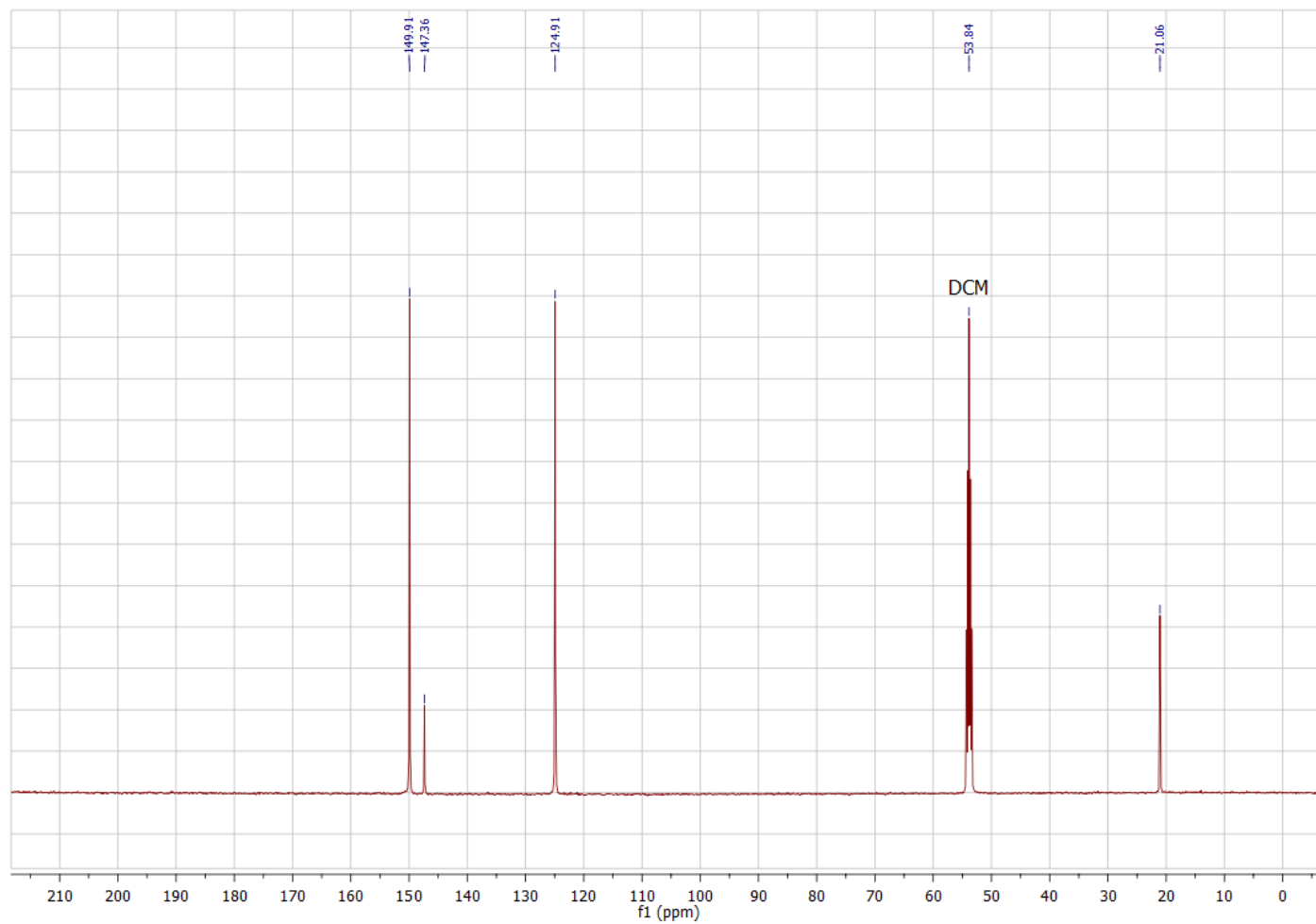


Figure S43: The ^{13}C NMR spectrum of 4-Mepy in CD_2Cl_2 .

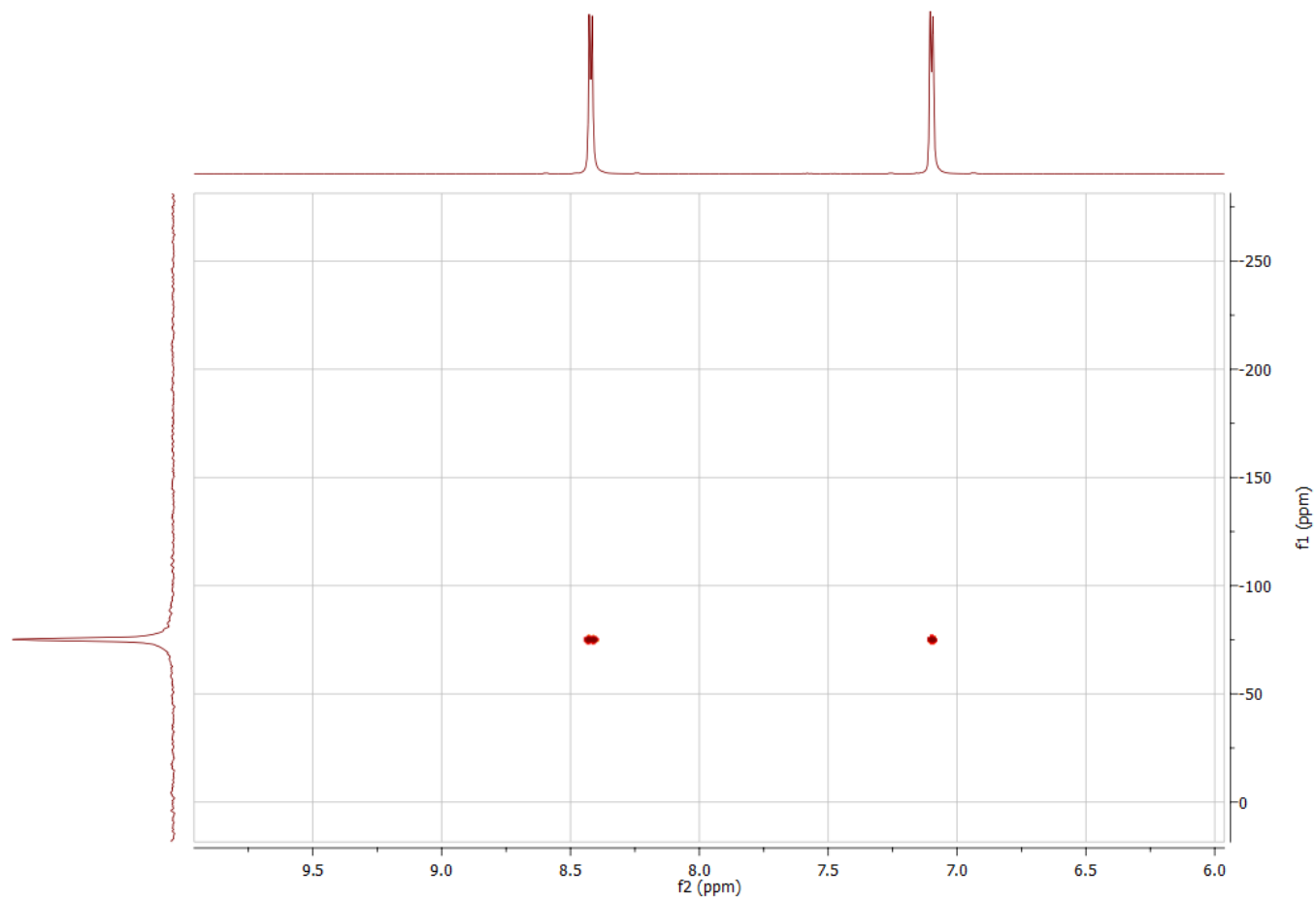


Figure S44: The ^1H - ^{15}N HMBC spectrum of 4-Mepy in CD_2Cl_2 .

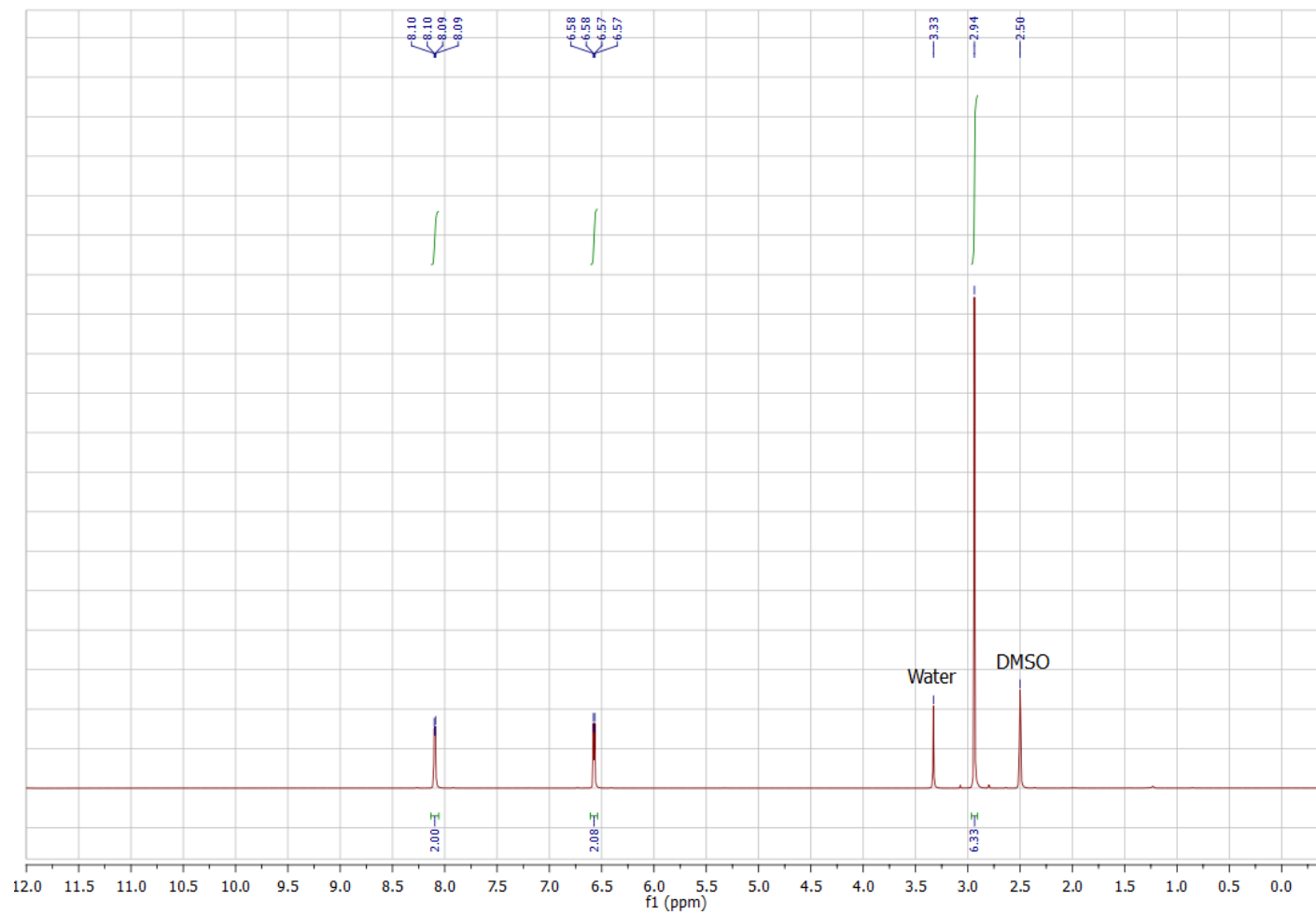


Figure S45: The ^1H NMR spectrum of DMAP in $(\text{CD}_3)_2\text{SO}$.

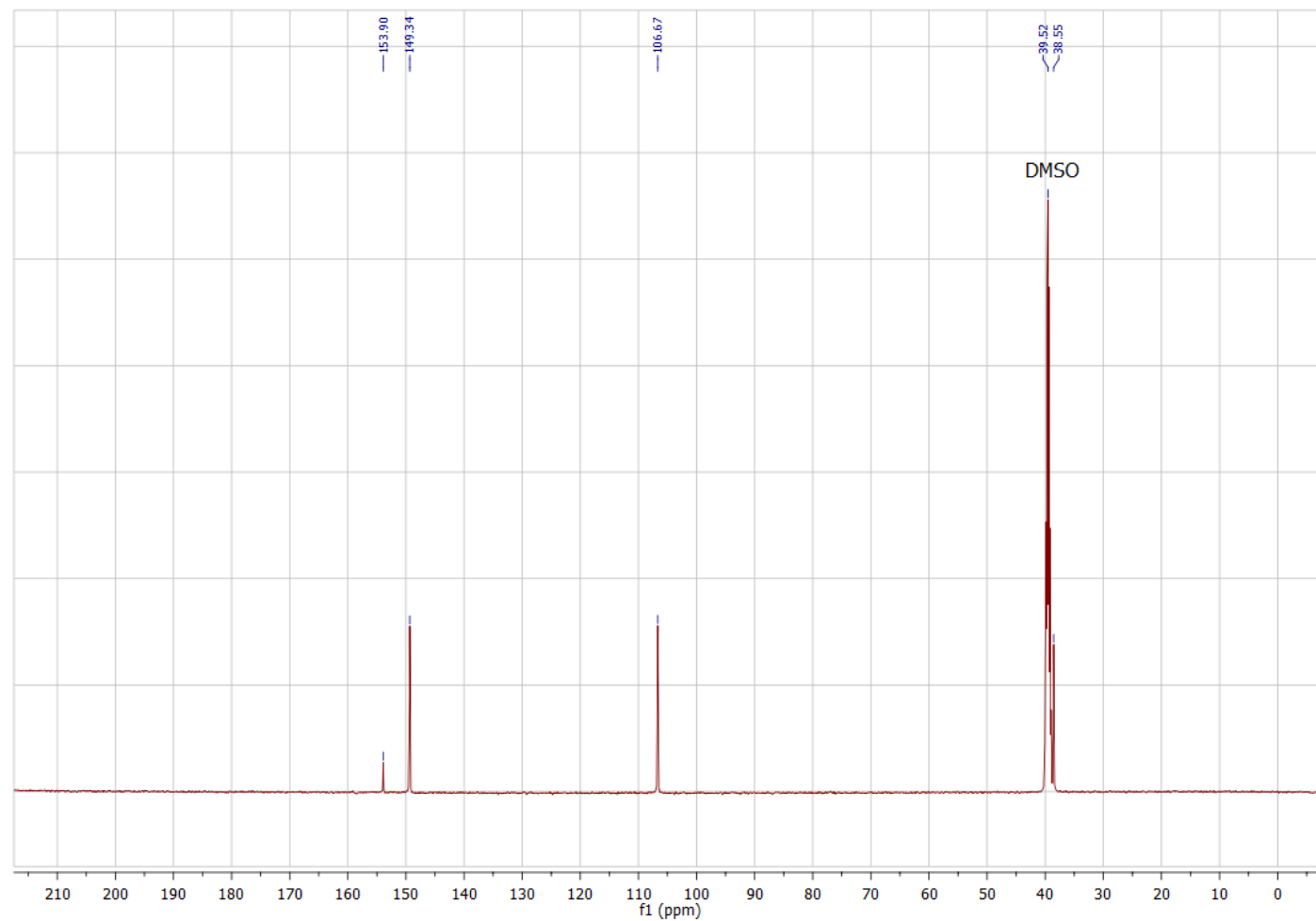


Figure S46: The ^{13}C NMR spectrum of DMAP in $(\text{CD}_3)_2\text{SO}$.

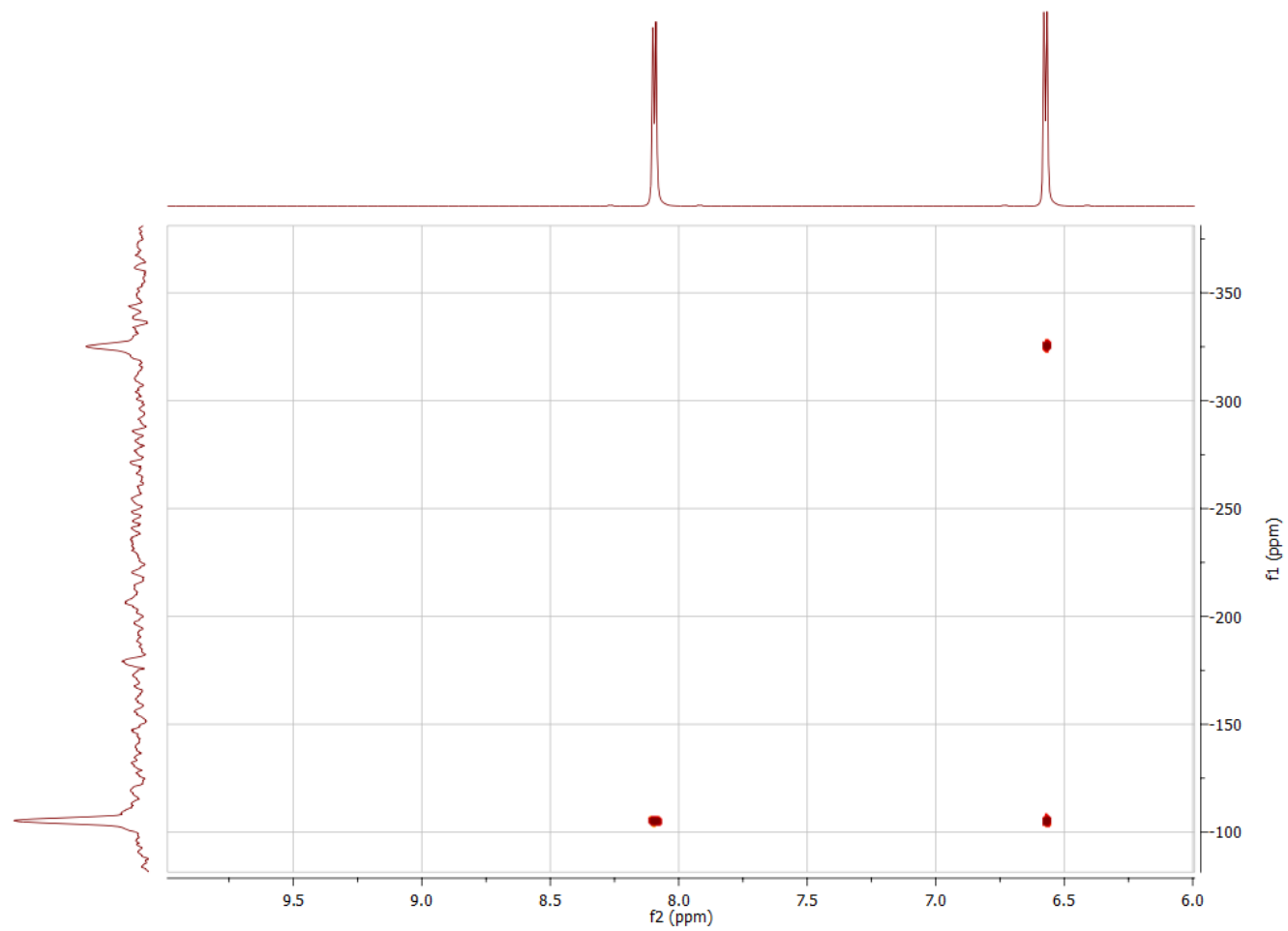


Figure S47: The ^1H - ^{15}N HMBC spectrum of DMAP in $(\text{CD}_3)_2\text{SO}$.

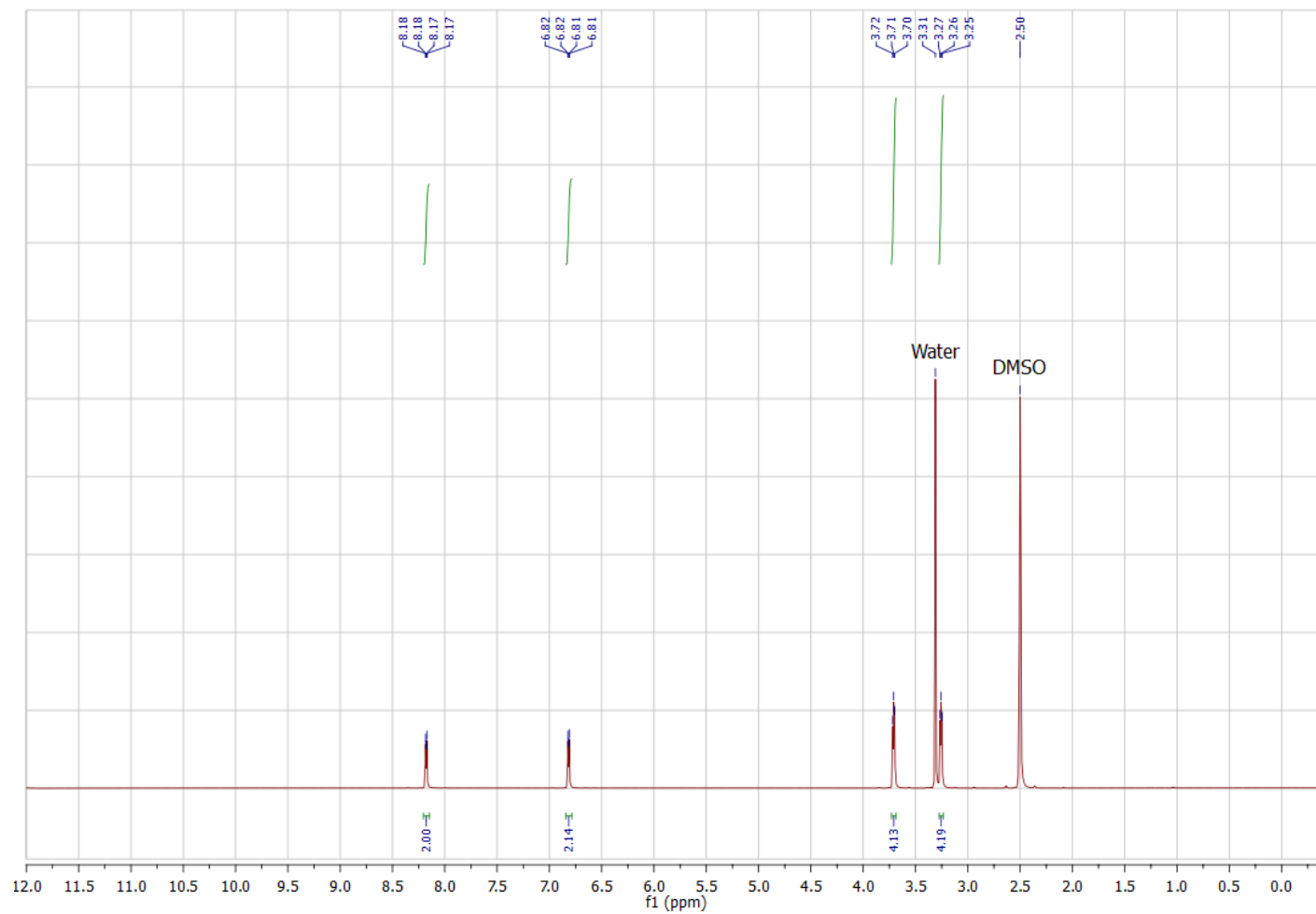


Figure S48: The ^1H NMR spectrum of 4-morphy in $(\text{CD}_3)_2\text{SO}$.

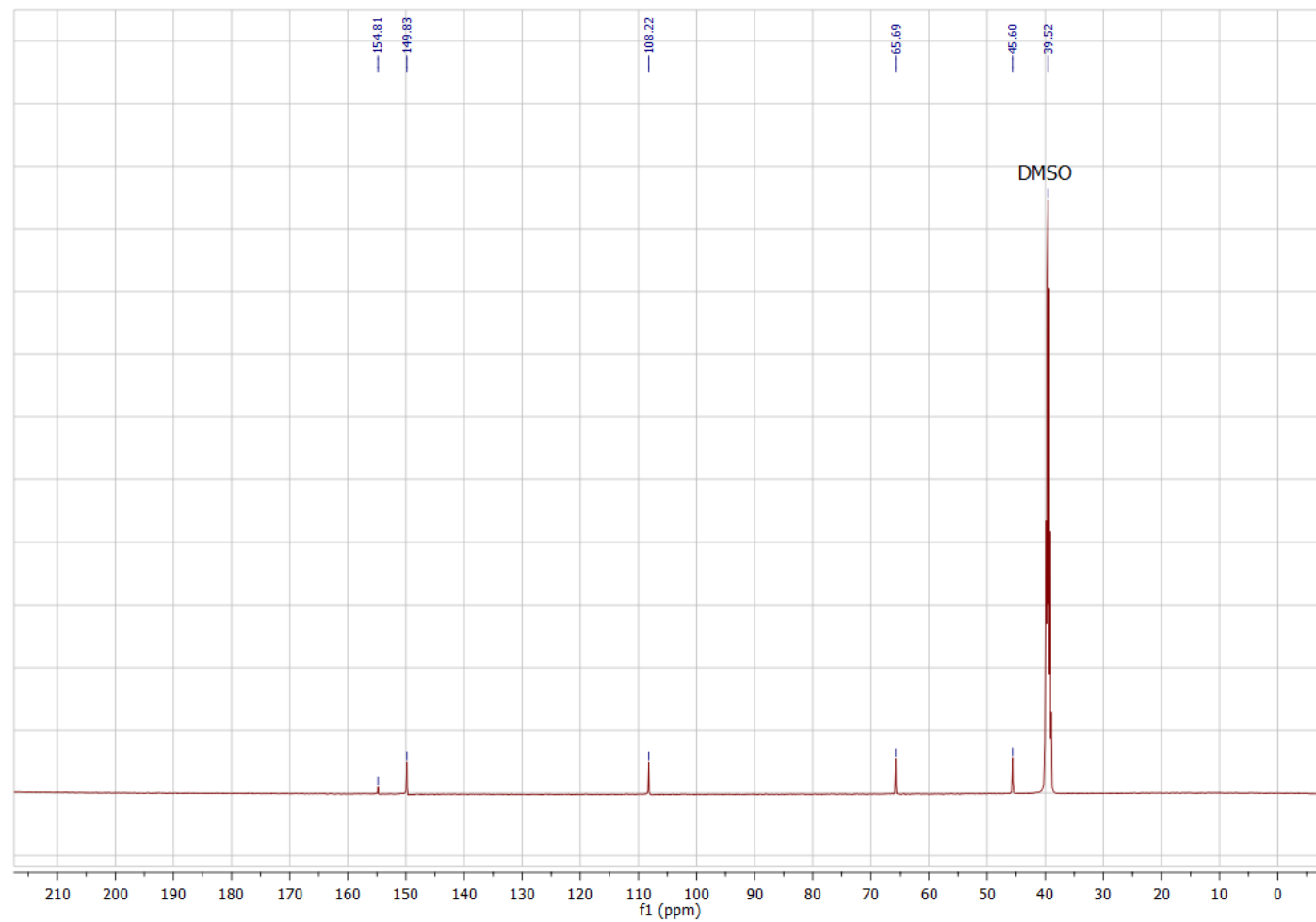


Figure S49: The ^{13}C NMR spectrum of 4-morphy in $(\text{CD}_3)_2\text{SO}$.

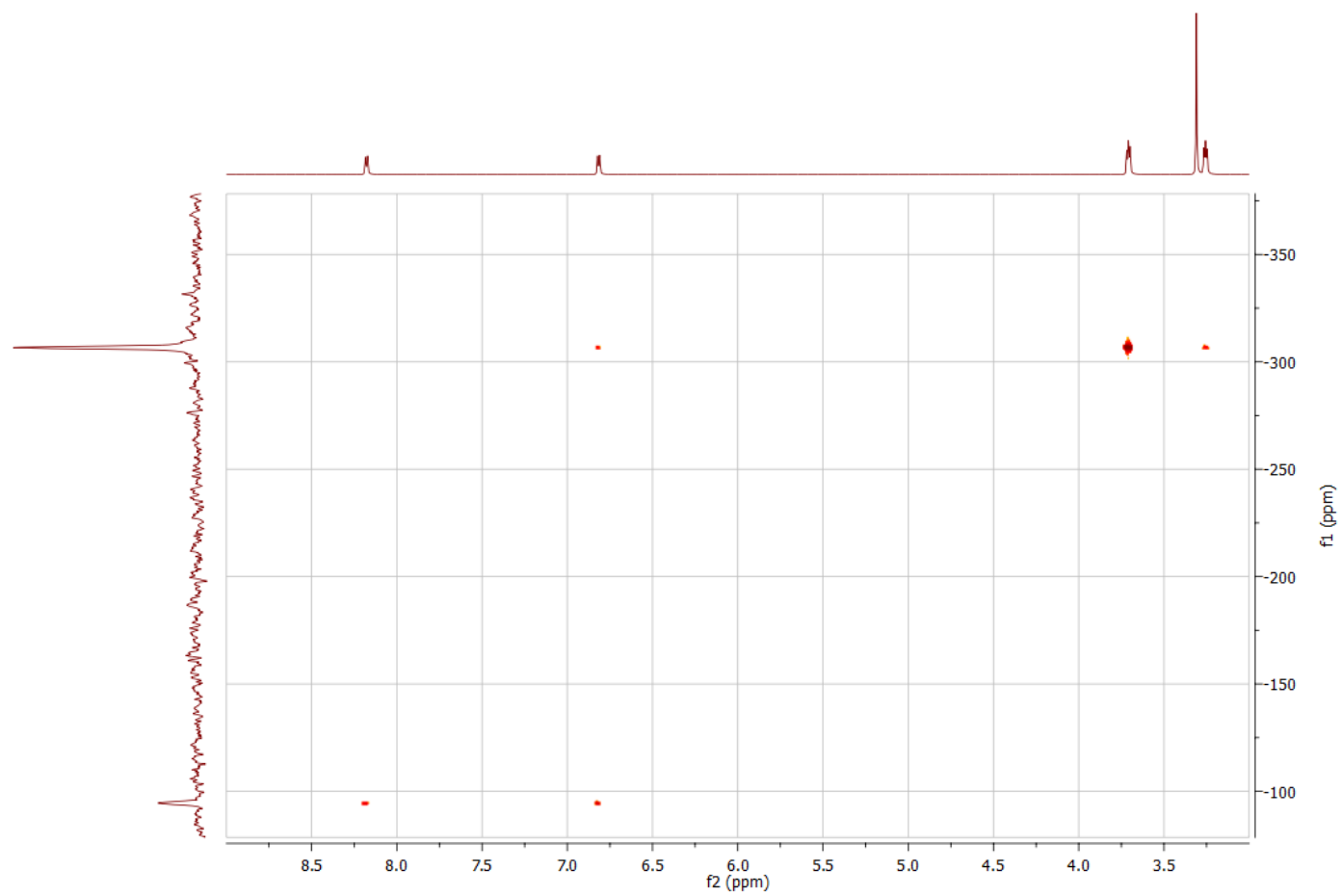


Figure S50: The ^1H - ^{15}N HMBC spectrum of 4-morphy in $(\text{CD}_3)_2\text{SO}$.

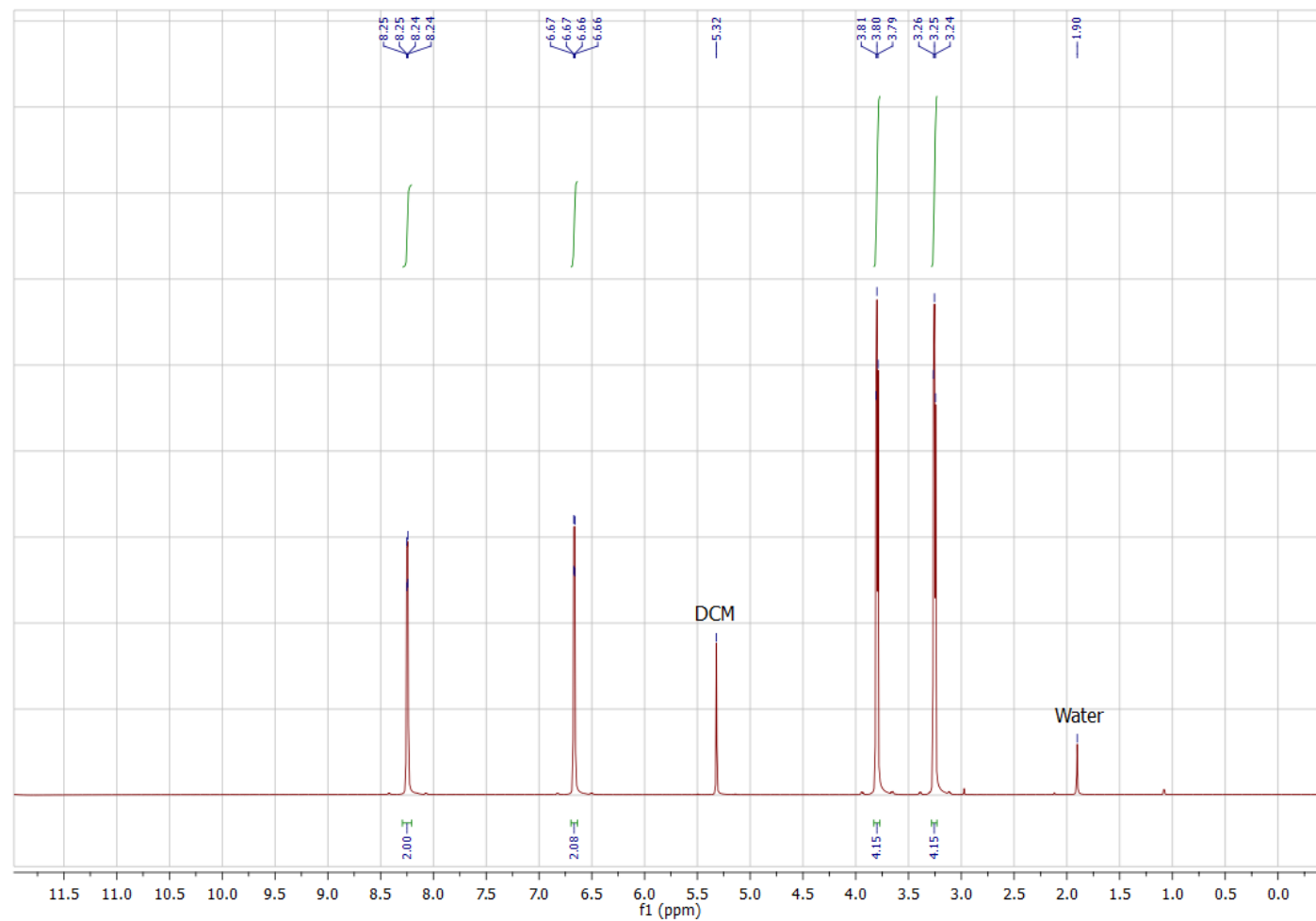


Figure S51: The ^1H NMR spectrum of 4-morphy in CD_2Cl_2 .

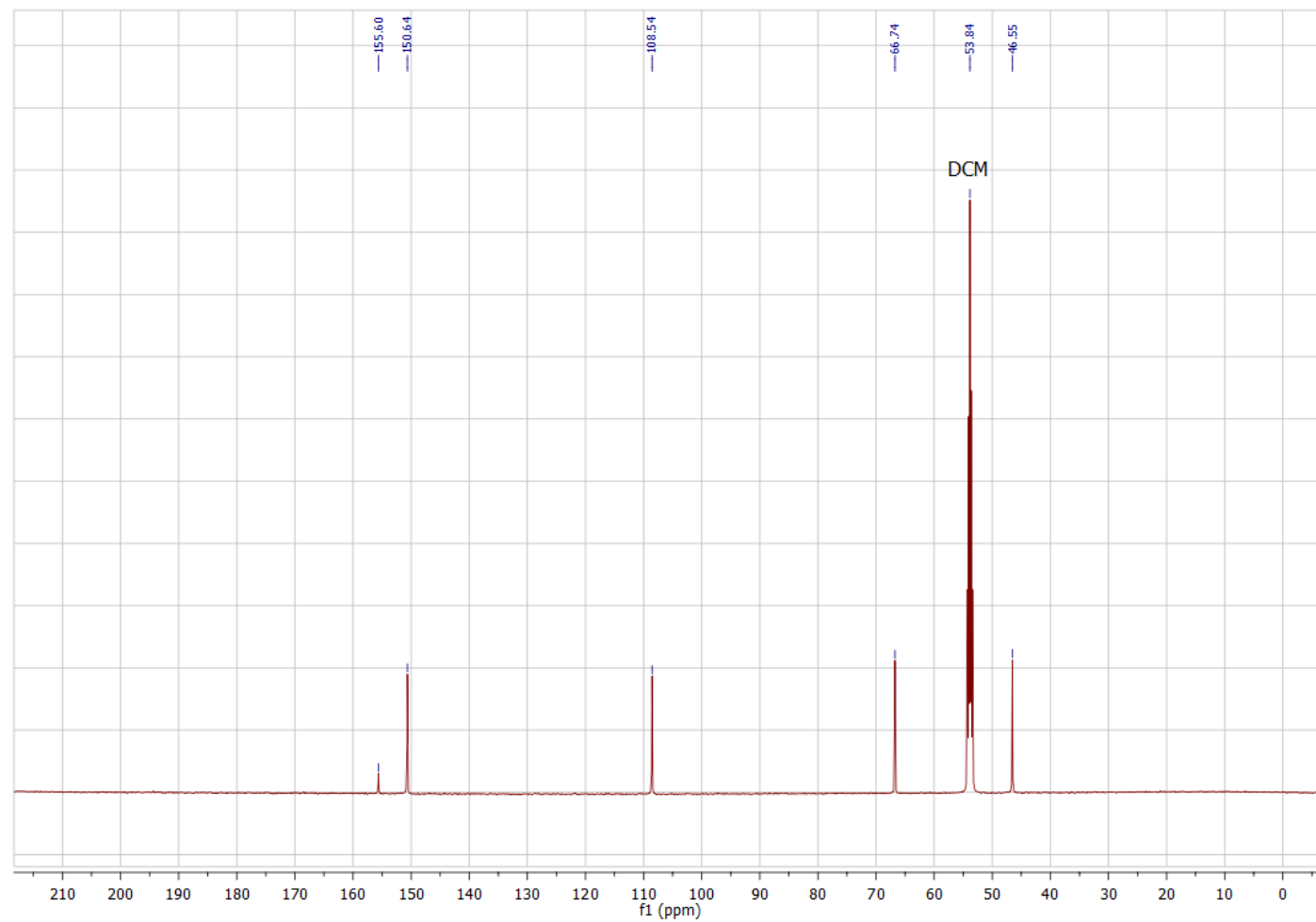


Figure S52: The ^{13}C NMR spectrum of 4-morphy in CD_2Cl_2 .

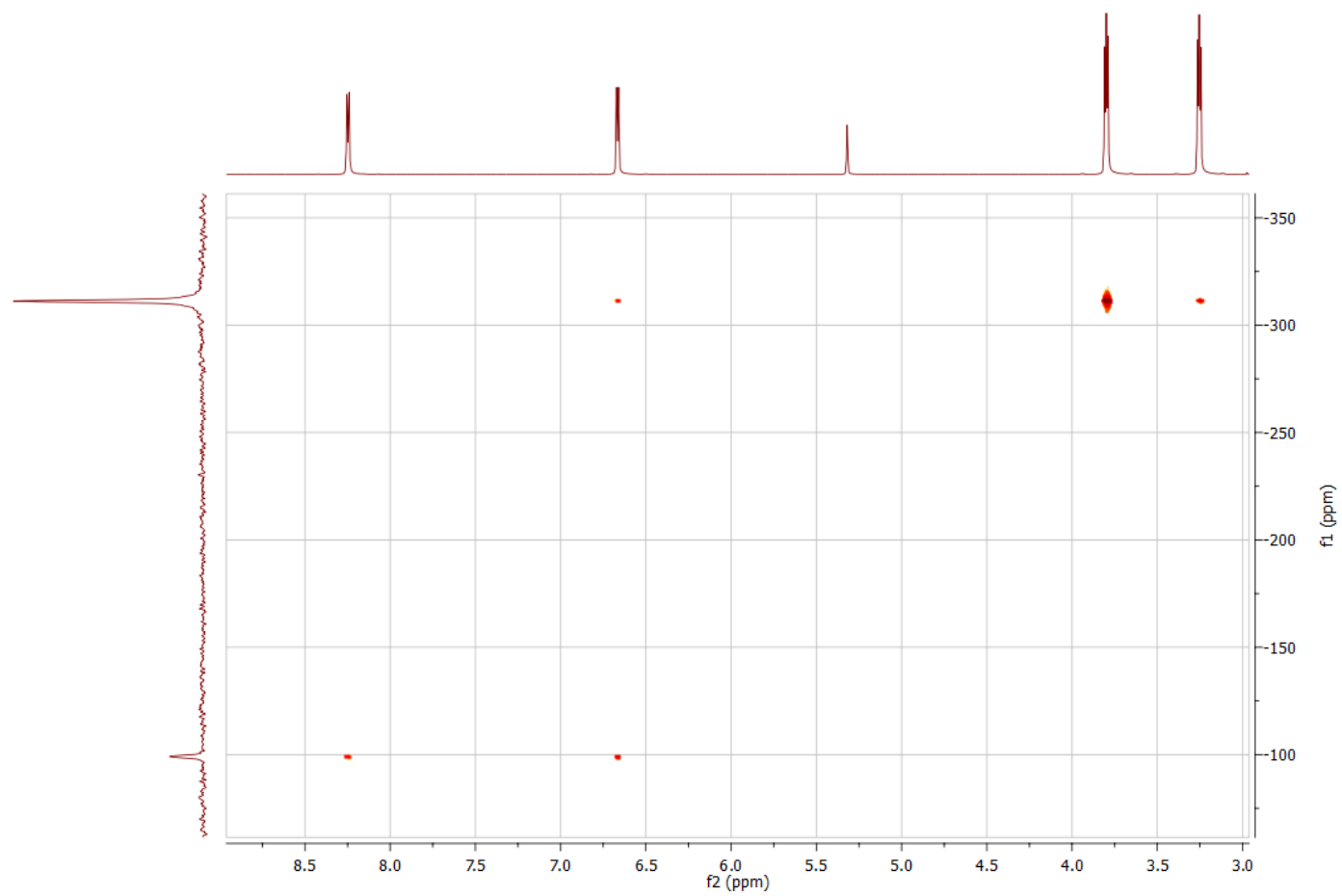


Figure S53: The ^1H - ^{15}N HMBC spectrum of 4-morpy in CD_2Cl_2 .

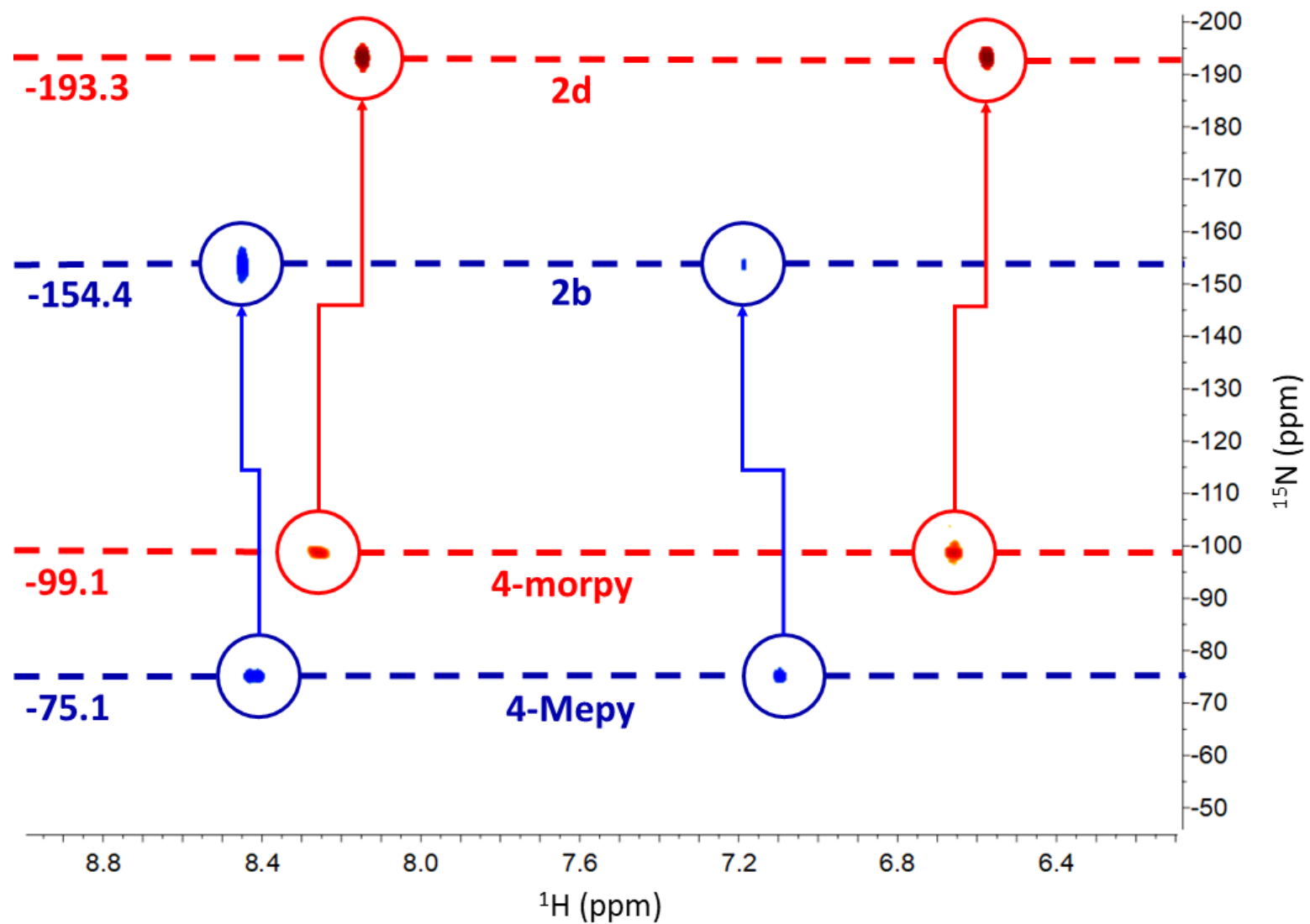


Figure S54: The superimposed ^1H - ^{15}N HMBC spectra of the pyridinic nitrogen atoms of 4-Mepy, **2b**, 4-morpy, and **2d**, showing the large differences induced upon coordination to the iodine(I) atom.

Computational Details

General Considerations

The geometry calculations for the complexes were done at the M06-2X/def2-TZVP level of theory⁶ using the SPARTAN18 program⁷ with dichloromethane (dielectric = 8.82) as the solvent using the conductor like polarizable continuum model (C-PCM).^{8,9} The initial models were built using SPARTAN18 and optimised at the MM-level before the DFT calculations. The hypoiodite complexes **2a**, **2b**, **2c**, and **2d** were built up from the corresponding MM-level optimised carboxyl hypoiodites and their respective pyridine derivatives so that the N...O distance was ca. 4.7 Å and the O-I...N angle ca. 170 - 175°, and then optimised with the given DFT method.

DFT/XRD Comparison Table

Table S3: Comparison of Experimental (XRD) Versus Computational (DFT) Bond Lengths and Angles.

Compound	2a	2b	2c*	2d†
O-I (Å) (XRD)	-	2.166(3)	2.175(3) 2.167(3) 2.169(4)	2.155(3) 2.170(3)
O-I (Å) (DFT)	2.120	2.126	2.157	2.145
I-N (Å) (XRD)	-	2.282(4)	2.254(3) 2.270(4) 2.268(4)	2.292(3) 2.271(4)
I-N (Å) (DFT)	2.318	2.308	2.268	2.282
C=O (Å) (XRD)	-	1.225(4)	1.206(6) 1.204(4) 1.228(7)	1.219(3) 1.224(3)
C=O (Å) (DFT)	1.218	1.217	1.220	1.220
C-O (Å) (XRD)	-	1.318(5)	1.281(7) 1.314(5) 1.297(5)	1.304(4) 1.305(4)
C-O (Å) (DFT)	1.309	1.308	1.303	1.305
O-I-N (°) (XRD)	-	174.7(1)	173.3(1) 172.7(1) 175.8(1)	174.13(9) 174.2(1)
O-I-N (°) (DFT)	176.4	176.2	176.4	176.5

* Three crystallographically independent molecules were observed in the asymmetric unit cell of **2c**.

† Two crystallographically independent molecules were observed in the asymmetric unit cell of **2d**.

Computational Structures

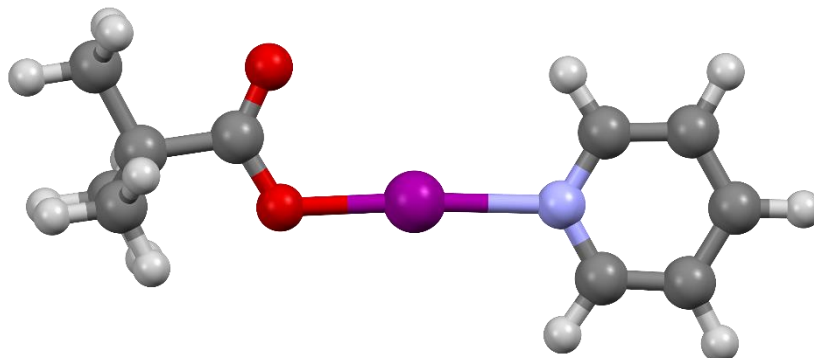


Figure S55: The computationally generated geometry of **2a**.

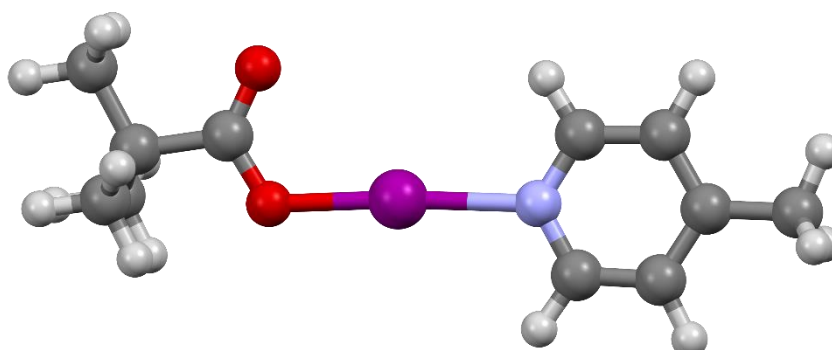


Figure S56: The computationally generated geometry of **2b**.

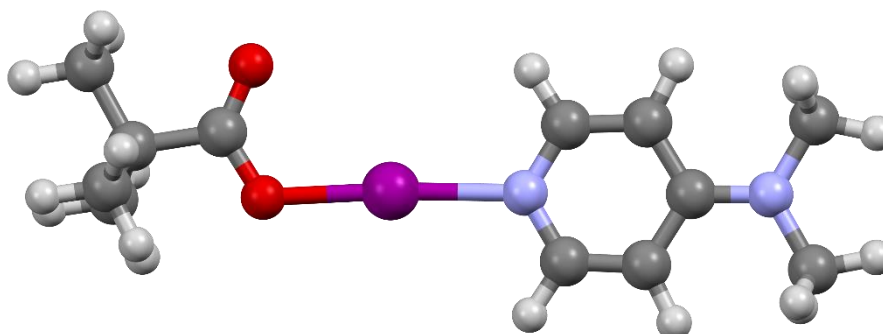


Figure S57: The computationally generated geometry of **2c**.

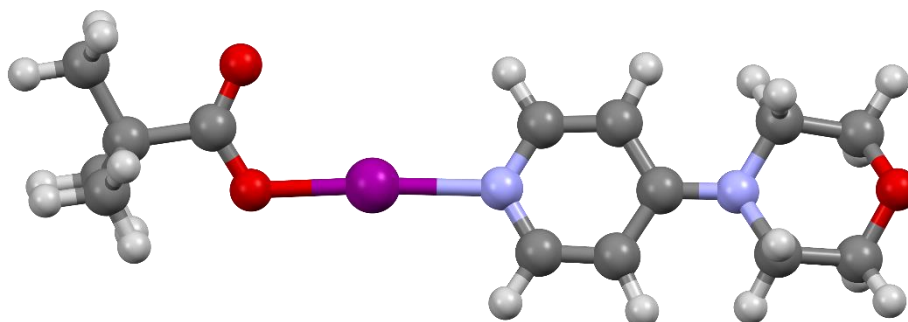


Figure S58: The computationally generated geometry of **2d**.

Cartesian Coordinates

2a

I	-0.266370	-0.000000	-1.036942
C	-0.072944	0.000000	3.352836
C	1.157152	-0.000000	4.253682
H	1.771743	0.883173	4.076850
H	1.771743	-0.883174	4.076850
H	0.840140	-0.000001	5.298249
C	-0.914280	-1.253680	3.615841
H	-0.340457	-2.159629	3.407273
H	-1.812057	-1.259952	2.997466
H	-1.214100	-1.273589	4.666093
C	-0.914280	1.253680	3.615841
H	-0.340456	2.159629	3.407274
H	-1.214099	1.273588	4.666094
H	-1.812056	1.259953	2.997466
C	0.361410	0.000000	1.881831
O	1.529792	0.000001	1.538922
O	-0.647694	-0.000000	1.048088
N	0.005961	-0.000000	-3.339230
C	0.332762	-0.000000	-6.069143
C	-1.062895	-0.000000	-4.138011
C	1.232925	0.000000	-3.863030
C	1.437530	0.000000	-5.230308
C	-0.938674	-0.000000	-5.514868
H	-2.029863	-0.000001	-3.650417
H	2.057173	0.000000	-3.160478
H	2.445167	0.000000	-5.621395
H	-1.825057	-0.000001	-6.133039
H	0.461786	-0.000000	-7.143795

2b

I	-0.312342	0.000000	-0.248846
C	-0.013882	0.000000	4.142186
C	1.236334	0.000000	5.014325
H	1.846723	0.883163	4.823630
H	1.846723	-0.883163	4.823630
H	0.943404	0.000000	6.065908
C	-0.849114	-1.253521	4.424269
H	-0.280643	-2.159434	4.203313
H	-1.759381	-1.259286	3.825561
H	-1.125879	-1.273368	5.480249
C	-0.849114	1.253521	4.424269
H	-0.280643	2.159434	4.203313
H	-1.125879	1.273368	5.480249
H	-1.759381	1.259286	3.825561
C	0.385657	0.000000	2.661006
O	1.546432	0.000000	2.291899
O	-0.640929	0.000000	1.851354
N	-0.107315	0.000000	-2.547730
C	0.137588	0.000000	-5.312456
C	-1.198188	0.000000	-3.320212
C	1.099061	0.000000	-3.114924
C	1.257960	0.000000	-4.487930
C	-1.113349	0.000000	-4.696253
H	-2.152050	0.000000	-2.807643
H	1.948959	0.000000	-2.443584
H	2.255171	0.000000	-4.907535
H	-2.020905	0.000000	-5.285723
C	0.257886	0.000000	-6.805544
H	1.300162	0.000000	-7.117969
H	-0.236533	0.879270	-7.222187
H	-0.236533	-0.879270	-7.222187

2c

I	-0.353775	-0.091335	0.798086
C	0.057388	-0.183037	5.209892
C	1.312492	0.011144	6.053070
H	1.768183	0.983027	5.860201
H	2.053488	-0.759468	5.839003
H	1.049548	-0.044325	7.111397
C	-0.547978	-1.563797	5.485560
H	0.157581	-2.357880	5.231531
H	-1.460946	-1.711900	4.909014
H	-0.788800	-1.648436	6.547352
C	-0.967234	0.906337	5.540802
H	-0.565576	1.898664	5.324441
H	-1.212838	0.862573	6.603912
H	-1.882573	0.768977	4.966034
C	0.409973	-0.099488	3.717773
O	1.557135	0.036885	3.323634
O	-0.627250	-0.195222	2.935343
N	-0.208873	0.004795	-1.462640
C	-0.015032	0.152558	-4.256193
C	-1.301029	-0.093807	-2.233002
C	0.978553	0.174321	-2.060946
C	1.124339	0.251685	-3.420780
C	-1.257405	-0.029033	-3.601113
H	-2.242068	-0.230477	-1.714449
H	1.838088	0.248938	-1.406230
H	2.114038	0.387376	-3.827919
H	-2.180412	-0.116038	-4.153233
N	0.078289	0.226337	-5.593847
C	1.373580	0.427135	-6.223423
H	2.055210	-0.394516	-5.992294
H	1.829051	1.362030	-5.890222
H	1.237597	0.472086	-7.299160
C	-1.115646	0.108685	-6.415297
H	-0.831681	0.182074	-7.460229
H	-1.827482	0.906212	-6.190634
H	-1.607934	-0.853080	-6.255434

2d

I	-0.429000	-0.249000	1.810000
C	-0.140000	-0.312000	6.219000
C	0.962000	0.249000	7.112000
H	1.062000	1.327000	6.982000
H	1.924000	-0.212000	6.883000
H	0.720000	0.045000	8.157000
C	-0.254000	-1.827000	6.419000
H	0.681000	-2.327000	6.157000
H	-1.054000	-2.242000	5.807000
H	-0.472000	-2.038000	7.468000
C	-1.476000	0.356000	6.557000
H	-1.425000	1.436000	6.397000
H	-1.715000	0.178000	7.608000
H	-2.281000	-0.049000	5.944000
C	0.187000	-0.031000	4.746000
O	1.183000	0.582000	4.400000
O	-0.704000	-0.508000	3.921000
N	-0.249000	-0.054000	-0.456000
C	0.027000	0.155000	-3.248000
C	-0.995000	-0.800000	-1.280000
C	0.641000	0.784000	-1.000000
C	0.813000	0.916000	-2.354000
C	-0.891000	-0.738000	-2.646000
H	-1.701000	-1.474000	-0.812000
H	1.242000	1.362000	-0.308000
H	1.571000	1.601000	-2.697000
H	-1.534000	-1.379000	-3.225000
N	0.136000	0.281000	-4.599000
C	1.221000	1.078000	-5.169000
H	2.160000	0.513000	-5.132000
H	1.345000	1.996000	-4.600000
C	-0.325000	-0.794000	-5.478000
H	-1.266000	-1.199000	-5.119000
H	0.419000	-1.599000	-5.490000
C	0.908000	1.476000	-6.599000
H	1.777000	1.962000	-7.038000
H	0.063000	2.175000	-6.609000
C	-0.552000	-0.286000	-6.888000
H	-1.396000	0.415000	-6.898000
H	-0.780000	-1.125000	-7.543000
O	0.599000	0.354000	-7.399000

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