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Supporting Information

Nucleophilic Iodonium Interactions (NIIs) in 2-coordinate Iodine(I) and Silver(I) Complexes

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Synthesis

General Considerations

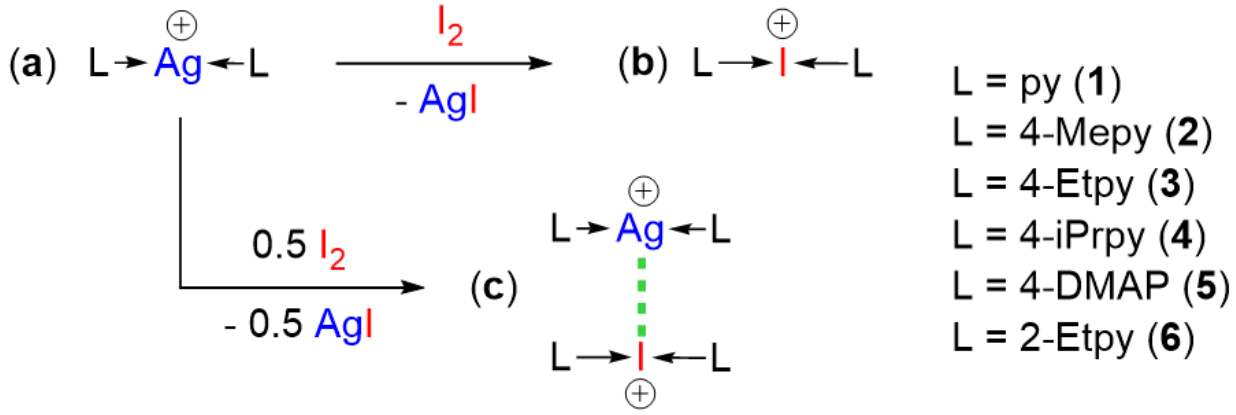
All reagents and solvents were obtained from commercial suppliers and used without further purification. For structural NMR assignments, ^{1}H NMR and ^{1}H-^{15}N NMR correlation spectra were recorded on a Bruker Avance III 500 MHz spectrometer at 25ºC in CD_2Cl_2. Chemical shifts are reported on the δ scale in ppm using the residual solvent signal as internal standard (CD_2Cl_2; δ_H 5.32), or for ^{1}H-^{15}N NMR spectroscopy, to an external d_3-$MeNO_2$ standard. For ^{1}H NMR spectroscopy, each resonance was assigned according to the following conventions: chemical shift (δ) measured in ppm, observed multiplicity, number of hydrogens, observed coupling constant (*J* Hz), and assignment. For the ^{1}H-^{15}N HMBC spectroscopy, spectral windows of 4 ppm (^{1}H) and 600 ppm (^{15}N) were used, with 1024 points in the direct dimension and 512 increments used in the indirect dimension (resolution ≈ 0.3 ppm/point). Multiplicities are denoted as: s (singlet), d (doublet), t (triplet), q (quartet) m (multiplet) and br (broad). The conversion of all silver(I) (**1a**-**6a**), iodonium (**1b**-**6b**), and 1:1 Ag^+:I^+ NII-complexes (**1c**-**6c**) were confirmed to be quantitative by ^{1}H NMR spectroscopy.

The single crystal X-ray data for **2a**, **2b**, and **6a** were collected at 170 K using Bruker-Nonius Kappa CCD diffractometer with an APEX-II detector with graphite-monochromatised Mo-Kα (λ = 0.71073 Å) radiation. The program COLLECT[1] was used for the data collection and DENZO/SCALEPACK[2] for the data reduction. The single crystal X-ray data for **2c**, **4a**, **4b**, **6b**, and **6c_Mixed** 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 program CrysAlisPro[3] was used

for the data collection and reduction on the SuperNova diffractometer, and the intensities were absorption corrected using a gaussian face index absorption correction method. All structures were solved by intrinsic phasing (SHELXT)[4] and refined by full-matrix least squares on F^2 using the OLEX2,[5] utilizing the SHELXL-2015 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) or 1.5 U_{eq} (alkyl) of their respective parent atoms. The X-ray single crystal data and CCDC numbers of all new structures are included below.

The ^{1}H and ^{15}N NMR data of **1a**, **1b**, **3a**, **3b**, **5a**, and **5b** have been previously reported,[7,8] and similarly the solid-state structures (where applicable) were also obtained from these same literature sources.

The following abbreviations are used: py = pyridine, 4-Mepy = 4-methylpyridine, 4-Etpy = 4-ethylpyridine, 4-^{i}Prpy = 4-isopropylpyridine, 4-DMAP = N,N-dimethylpyridin-4-amine, 2-Etpy = 2-ethylpyridine, DCM = dichloromethane, MeCN = acetonitrile, TBME = ^{t}butylmethylether.



General Procedure for Synthesis of Silver(I) Complexes (**1a**-**6a**)

All silver(I) complexes (**1a**-**6a**) were prepared using the same general method, which is given below using pyridine as an example.

Neat pyridine (3.2 μL, 0.04 mmol) was added to a suspension of $AgPF_6$ (5.1 mg, 0.02 mmol) in CD_2Cl_2 (0.5 mL), thoroughly mixed and left for 1 hour to ensure complete formation of the product.

For the preparation of crystallographic samples, the same general procedure was followed but using the scaled-up values of: pyridine (0.1 mmol), $AgPF_6$ (0.05 mmol), and DCM (3 mL).

General Procedure for Synthesis of Iodonium Complexes (**1b**-**6b**)

All iodonium complexes (**1a**-**6a**) were prepared using the same general method of cation exchange, which is given below using pyridine as an example.

Neat pyridine (3.2 μL, 0.04 mmol) was added to a suspension of $AgPF_6$ (5.1 mg, 0.02 mmol) in CD_2Cl_2 (0.5 mL), thoroughly mixed and left for 1 hour to ensure complete formation of the product. I_2 (5.1 mg, 0.02 mmol) was added to immediately give a yellow

precipitate and a colourless (occasionally a hint of pink) solution. Samples were prepared immediately prior to the collection of NMR data.

For the preparation of crystallographic samples, the same general procedure was followed but using the scaled-up values of: pyridine (0.1 mmol), $AgPF_6$ (0.05 mmol), DCM (3 mL), and I_2 (0.05 mmol).

General Procedure for Synthesis of 1:1 Ag^+:I^+ NII-complexes (**1c**-**6c**)

All NII-complexes were prepared using the same general method of partial cation exchange, which is given below using pyridine as an example.

Neat pyridine (3.2 µL, 0.04 mmol) was added to a suspension of $AgPF_6$ (5.1 mg, 0.02 mmol) in CD_2Cl_2 (0.5 mL), thoroughly mixed and left for 1 hour to ensure complete formation of silver(I) salt. I_2 (2.5 mg, 0.01 mmol) was added to give a yellow precipitate and a colourless solution. Samples were prepared immediately prior to the collection of NMR data.

For the preparation of crystallographic samples, the same general procedure was followed but using the scaled-up values of: pyridine (0.1 mmol), $AgPF_6$ (0.05 mmol), DCM (3 mL), and I_2 (0.025 mmol).

Characterisation Data

Complexes **1c**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.75 (d, J = 5.0 Hz, 4H, I^+), 8.64 (d, J = 4.6 Hz, 4H, Ag^+), 8.22 (t, J = 7.7 Hz, 2H, I^+), 7.98 (t, J = 7.8 Hz, 2H, Ag^+), 7.65 – 7.60 (m, 4H, I^+), 7.59 – 7.55 (m, 4H, Ag^+). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -119.2, -174.8.

Complex **2a**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.47 (d, J = 6.1 Hz, 4H), 7.41 (d, J = 5.6 Hz, 4H), 2.47 (s, 6H). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -136.0. Analysis Found: C, 31.85; H, 3.33: N, 6.09%. Calculated for $C_{12}H_{14}AgF_6N_2P \cdot 0.25(CH_2Cl_2)$: C, 31.96; H, 3.18: N, 6.09%. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution vapour diffused with TBME. Crystal data for **2a**: CCDC-2064891, $([C_{12}H_{14}AgN_2][PF_6])_2$, M = 878.18, colourless block, 0.12 x 0.22 x 0.46 mm^3, monoclinic, space group *P*2/*c*, a = 9.3876(3) Å, b = 11.0428(3) Å, c = 15.2827(5) Å, β = 102.186(2)°, V = 1548.59(8) $Å^3$, Z = 2, D_{calc} = 1.883 gcm^{-3}, F000 = 864, μ = 1.46 mm^{-1}, T = 170(1) K, θ_{max} = 31.0°, 4716 total reflections, 3812 with $I_o > 2\sigma(I_o)$, R_{int} = 0.037, 4716 data, 203 parameters, no restraints, GooF = 1.04, 0.40 < dΔρ < -0.42 $eÅ^{-3}$, $R[F^2 > 2\sigma(F^2)]$ = 0.035, $wR(F^2)$ = 0.076.

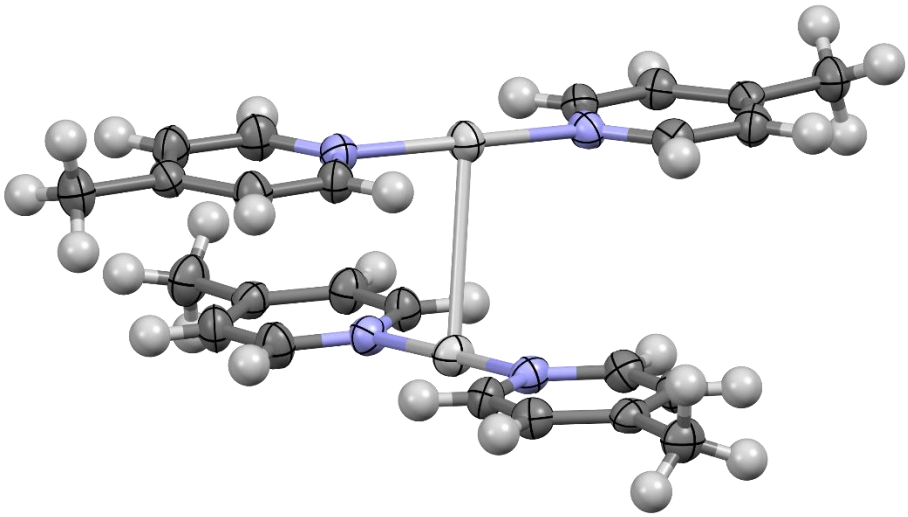


*Figure S1: The X-ray crystal structure of **2a** (PF_6 anions omitted for clarity; thermal ellipsoids at 50% probability).*

Complex **2b**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.54 (d, *J* = 6.3 Hz, 4H), 7.39 (d, *J* = 5.8 Hz, 4H), 2.52 (s, 6H). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -182.2. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution vapour diffused with pentane. Crystal data for **2b**: CCDC-2064895, $[C_{12}H_{14}IN_2][PF_6]$, M = 458.12, colourless block, 0.08 x 0.16 x 0.36 mm^3, orthorhombic, space group *Pbca*, a = 11.6037(5) Å, b = 12.4587(3) Å, c = 22.3220(9) Å, V = 3227.0(2) Å^3, Z = 8, D_{calc} = 1.886 gcm^{-3}, F000 = 1776, μ = 2.14 mm^{-1}, T = 170(1) K, θ_{max} = 27.9°, 3542 total reflections, 2665 with $I_o > 2\sigma(I_o)$, R_{int} = 0.054, 3542 data, 201 parameters, no restraints, GooF = 1.13, 0.66 < dΔρ < -0.80 eÅ^{-3}, $R[F^2 > 2\sigma(F^2)]$ = 0.040, $wR(F^2)$ = 0.122.

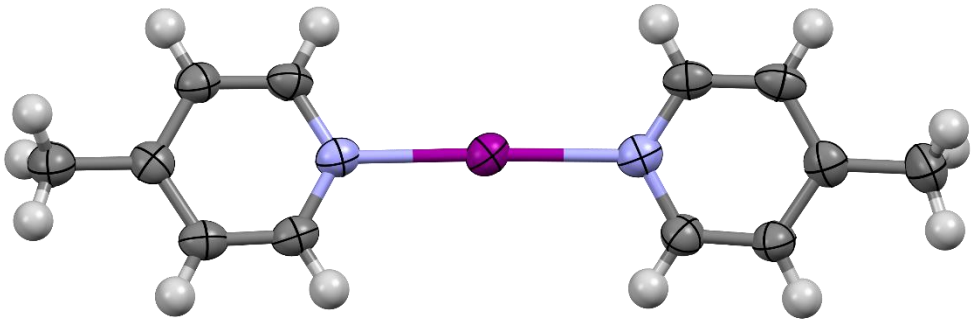


*Figure S2: The X-ray crystal structure of **2b** (PF_6 anion omitted for clarity; thermal ellipsoids at 50% probability).*

Complexes **2c**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.54 (d, *J* = 6.3 Hz, 4H, I^+), 8.47 (d, *J* = 6.2 Hz, 4H, Ag^+), 7.41 (d, *J* = 5.6 Hz, 4H, I^+), 7.39 (d, *J* = 5.8 Hz, 4H, Ag^+), 2.52 (s, 6H, I^+), 2.47 (s, 6H, Ag^+). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -120.4, -182.2. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution vapour diffused with pentane. Crystal data for **2c**: CCDC-2064898, $[C_{12}H_{14}IN_2][PF_6]\cdot[C_{12}H_{14}AgN_2][PF_6]$, M = 897.21, colourless block, 0.05 x 0.08 x 0.13 mm^3, monoclinic, space group $P2_1/n$, a = 6.9897(1) Å, b = 43.9504(4) Å, c = 20.8689(3) Å, β = 94.294(1)°, V = 6392.93(14) Å^3, Z = 8, D_{calc} = 1.864 gcm^{-3}, F000 = 3504, μ = 14.45 mm^{-1}, T = 120.0(1) K, θ_{max} = 76.6°, 12588

total reflections, 11321 with $I_o > 2\sigma(I_o)$, R_{int} = 0.063, 12588 data, 804 parameters, 144 restraints, GooF = 1.04, 1.69 < dΔρ < -1.16 eÅ^{-3}, $R[F^2 > 2\sigma(F^2)]$ = 0.056, $wR(F^2)$ = 0.151.

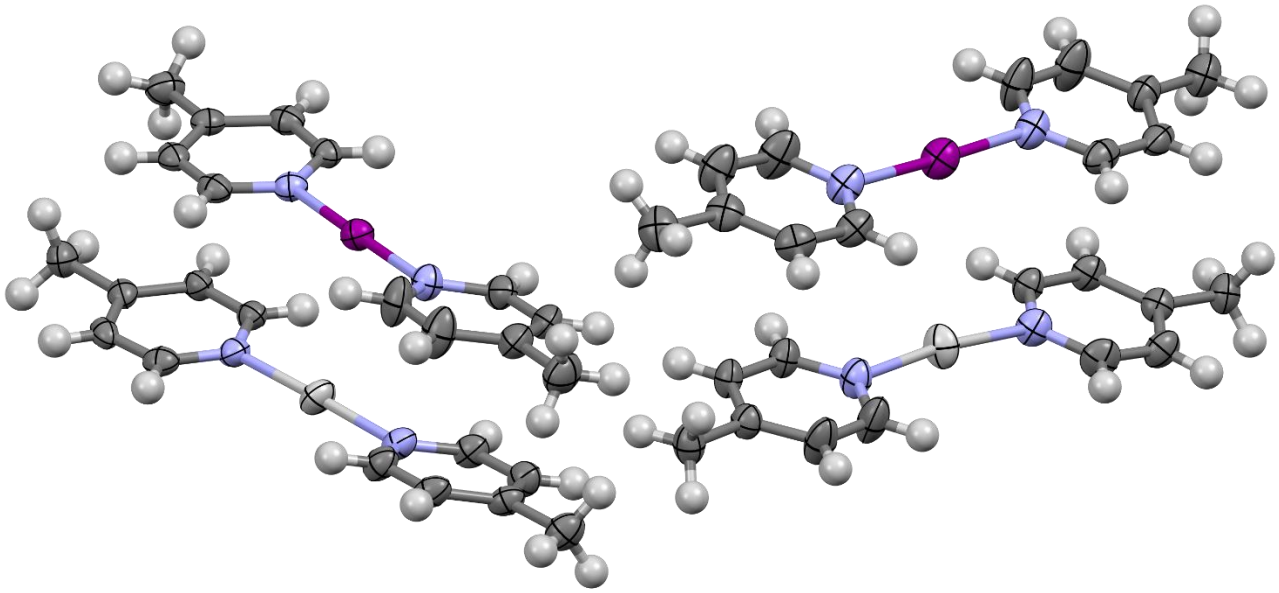


*Figure S3: The X-ray crystal structure of **2c** (PF_6 anions omitted for clarity; thermal ellipsoids at 50% probability).*

Complexes **3c**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.57 (d, *J* = 6.5 Hz, 4H, I^+), 8.48 (d, *J* = 6.3 Hz, 4H, Ag^+), 7.42 – 7.38 (m, *J* = 6.9 Hz, 8H, Ag^+ and I^+), 2.82 (q, *J* = 7.6 Hz, 4H, I^+), 2.76 (q, *J* = 7.6 Hz, 4H, Ag^+), 1.294 (t, *J* = 7.6 Hz, 6H, I^+), 1.289 (t, *J* = 7.6 Hz, 6H, Ag^+). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -126.4, -181.5.

Complex **4a**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.49 (d, *J* = 6.1 Hz, 4H), 7.46 (d, *J* = 5.7 Hz, 4H), 3.01 (septet, *J* = 6.8 Hz, 2H), 1.30 (d, *J* = 6.9 Hz, 12H). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -135.2. Analysis Found: C, 38.40; H, 4.18: N, 5.56%. Calculated for $C_{16}H_{22}AgF_6N_2P$: C, 38.81; H, 4.48: N, 5.66%. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution vapour diffused with pentane. Crystal data for **4a**: CCDC-2064896, $[C_{16}H_{22}AgN_2][PF_6]$, M = 495.19, colourless plate, 0.06 x 0.18 x 0.27 mm^3, triclinic, space group *P*-1 (No. 2), a = 10.2094(2) Å, b = 10.2353(3) Å, c = 19.2604(4) Å,

α = 100.476(2)°, β = 102.846(2)°, γ = 91.053(2)°, V = 1925.92(8) Å^3, Z = 4, D_{calc} = 1.708 gcm^{-3}, F000 = 992, μ = 9.73 mm^{-1}, T = 120.0(1) K, θ_{max} = 76.5°, 7553 total reflections, 6999 with $I_o > 2\sigma(I_o)$, R_{int} = 0.026, 7553 data, 483 parameters, no restraints, GooF = 1.03, 0.50 < dΔρ < -0.54 eÅ^{-3}, $R[F^2 > 2\sigma(F^2)]$ = 0.024, $wR(F^2)$ = 0.064.

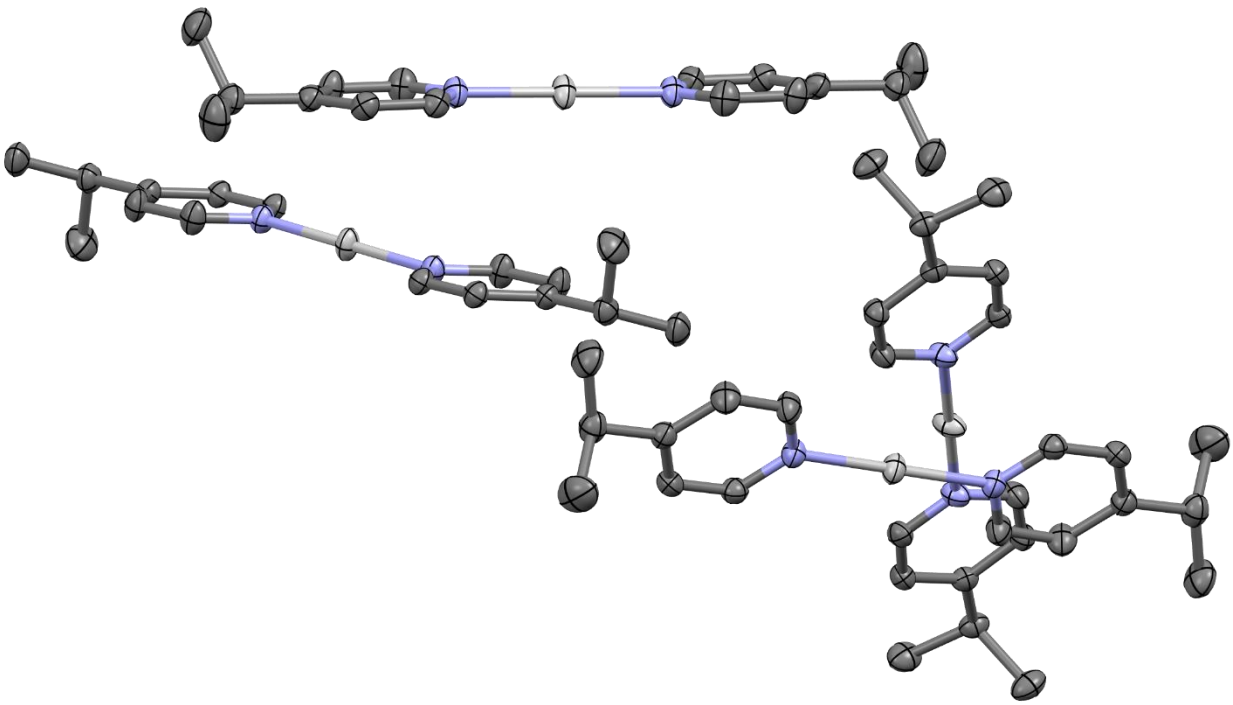


*Figure S4: The X-ray crystal structure of **4a** (PF_6 anions and hydrogen atoms omitted for clarity; thermal ellipsoids at 50% probability).*

Complex **4b**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.58 (d, *J* = 6.5 Hz, 4H), 7.42 (d, *J* = 6.3 Hz, 4H), 3.06 (septet, *J* = 6.8 Hz, 2H), 1.29 (d, *J* = 6.9 Hz, 12H). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -181.2. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution vapour diffused with pentane. Crystal data for **4b**: CCDC-2064897, $[C_{16}H_{22}IN_2][PF_6]$, M = 514.22, colourless plate, 0.03 x 0.05 x 0.17 mm^3, triclinic, space

group *P*-1 (No. 2), a = 17.9543(10) Å, b = 20.8051(10) Å, c = 26.6647(10) Å, α = 100.468(4)°, β = 94.508(4)°, γ = 106.703(5)°, V = 9290.4(8) Å^3, Z = 18, D_{calc} = 1.654 gcm^{-3}, F000 = 4572, μ = 13.44 mm^{-1}, T = 120.0(1) K, θ_{max} = 73.4°, 36261 total reflections, 19164 with $I_o > 2\sigma(I_o)$, R_{int} = 0.088, 36261 data, 2329 parameters, 1204 restraints, GooF = 1.02, 2.77 < dΔρ < -1.95 eÅ^{-3}, $R[F^2 > 2\sigma(F^2)]$ = 0.116, $wR(F^2)$ = 0.345.

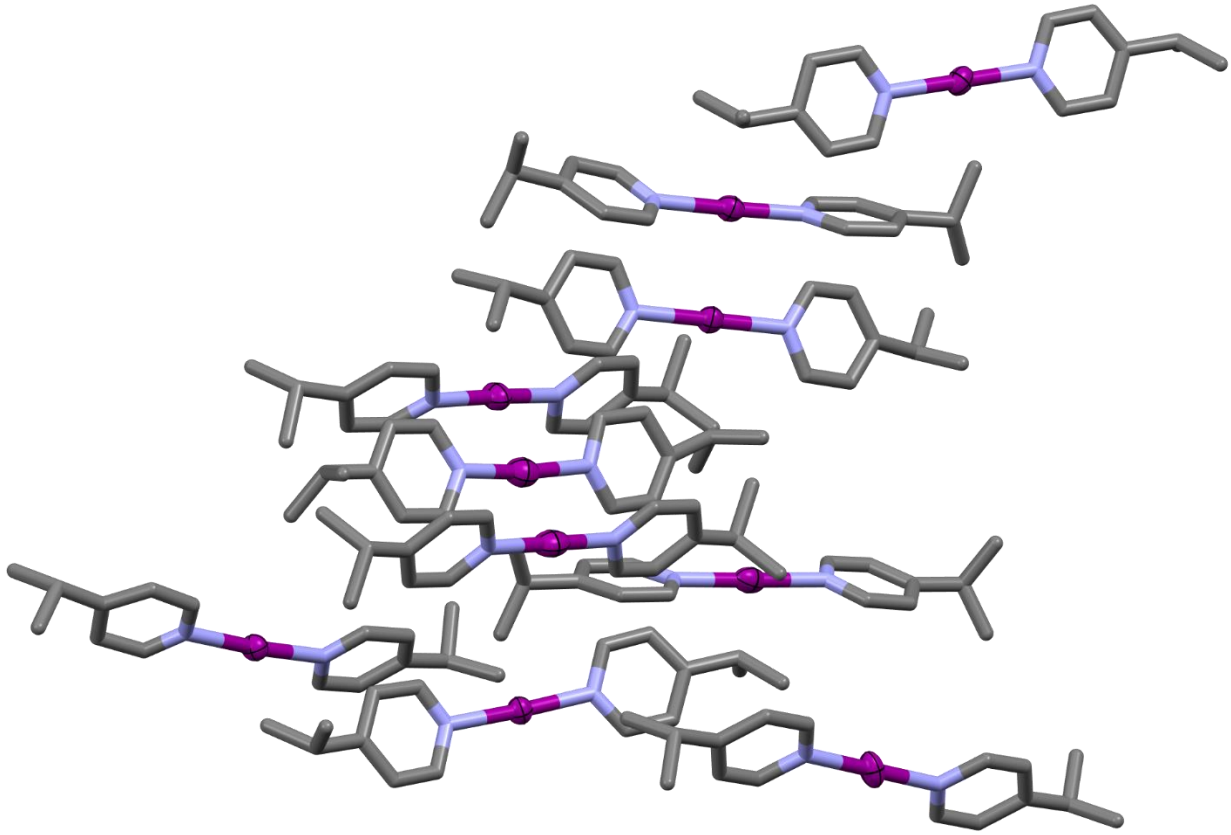


*Figure S5: The X-ray crystal structure of **4b** (4-iPrpy ligands simplified; PF_6 anions and hydrogen atoms omitted for clarity; thermal ellipsoids at 50% probability).*

Complexes **4c**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.59 (d, *J* = 6.5 Hz, 4H, I$^+$), 8.50 (d, *J* = 6.3 Hz, 4H, Ag$^+$), 7.46 – 7.39 (m, 8H, Ag$^+$ and I$^+$), 3.06 (septet, *J* = 7.0 Hz, 2H, I$^+$), 3.00 (septet, *J* = 7.0 Hz, 2H, Ag$^+$), 1.30 (s, 12H, I$^+$), 1.29 (s, 12H, Ag$^+$). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -127.5, -181.2.

Complexes **5c**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.07 – 8.04 (m, 8H, Ag^+ and I^+), 6.63 (d, *J* = 7.1 Hz, 4H, Ag^+), 6.50 (d, *J* = 7.3 Hz, 4H, I^+), 3.10 (s, 12H, I^+), 3.08 (s, 12H, Ag^+). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -170.3, -216.0.

Complex **6a**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.56 (d, *J* = 5.3 Hz, 2H), 7.89 (td, *J* = 7.8, 1.7 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.35 (m, 2H), 2.98 (q, *J* = 7.6 Hz, 4H), 1.37 (t, *J* = 7.7 Hz, 6H). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -112.2. Analysis Found: C, 36.47; H, 3.95: N, 6.04%. Calculated for $C_{14}H_{18}AgF_6N_2P$: C, 36.00; H, 3.88: N, 6.00%. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution vapour diffused with pentane. Crystal data for **6a**: CCDC-2064893, $[C_{14}H_{18}AgN_2][PF_6]$, M = 467.14, colourless plate, 0.04 x 0.24 x 0.28 mm^3, monoclinic, space group $P2_1/n$, a = 10.8641(3) Å, b = 11.1767(2) Å, c = 15.0419(4) Å, β = 108.620(1)°, V = 1730.86(7) $Å^3$, Z = 4, D_{calc} = 1.793 gcm^{-3}, F000 = 928, μ = 1.32 mm^{-1}, T = 170(1) K, θ_{max} = 30.5°, 4856 total reflections, 3778 with $I_o > 2\sigma(I_o)$, R_{int} = 0.037, 4856 data, 256 parameters, 87 restraints, GooF = 1.05, 0.93 < dΔρ < -0.51 $eÅ^{-3}$, $R[F^2 > 2\sigma(F^2)]$ = 0.044, $wR(F^2)$ = 0.104.

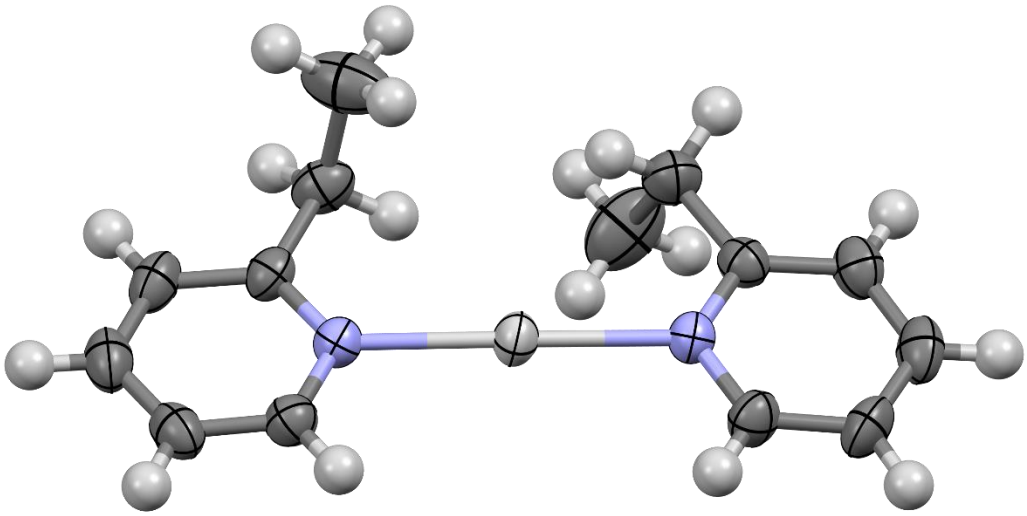


*Figure S6: The X-ray crystal structure of **6a** (PF_6 anion omitted for clarity; thermal ellipsoids at 50% probability).*

Complex **6b**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.89 (d, *J* = 5.6 Hz, 2H), 8.11 (t, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 6.6 Hz, 2H), 3.10 (q, *J* = 7.6 Hz, 4H), 1.41 (t, *J* = 7.6 Hz, 6H). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -167.9. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution vapour diffused with pentane. Crystal data for **6b**: CCDC-2064892, $[C_{14}H_{18}IN_2][PF_6]$, M = 486.17, colourless block, 0.12 x 0.20 x 0.25 mm^3, monoclinic, space group *C*2/*c*, a = 11.7938(3) Å, b = 10.2841(2) Å, c = 15.1354(3) Å, β = 109.149(2)°, V = 1734.18(7) Å^3, Z = 4, D_{calc} = 1.862 gcm^{-3}, F000 = 941, μ = 15.96 mm^{-1}, T = 120.0(1) K, θ_{max} = 76.5°, 1712 total reflections, 1686 with $I_o > 2\sigma(I_o)$, R_{int} = 0.019, 1712 data, 111 parameters, no restraints, GooF = 1.09, 0.39 < dΔρ < -0.70 eÅ^{-3}, $R[F^2 > 2\sigma(F^2)]$ = 0.021, $wR(F^2)$ = 0.054.

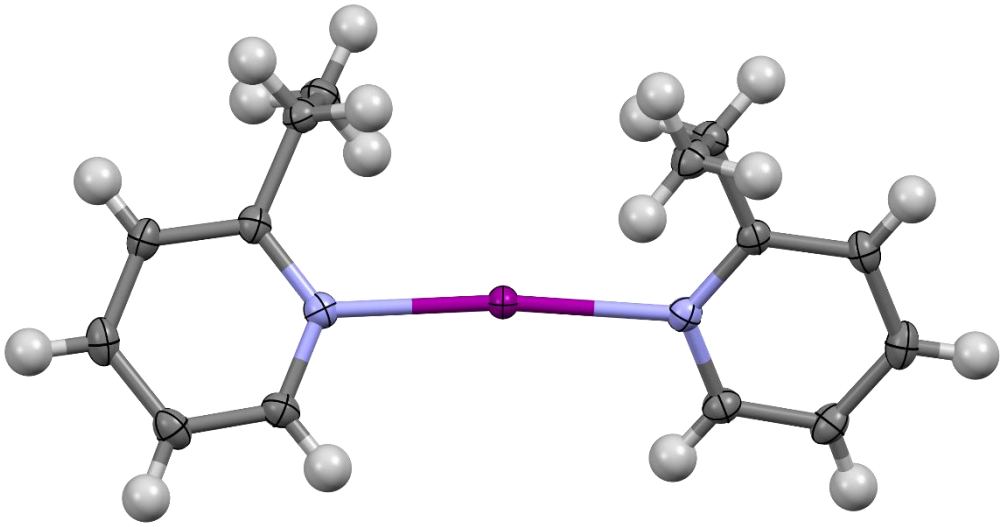


*Figure S7: The X-ray crystal structure of **6b** (PF_6 anion omitted for clarity; thermal ellipsoids at 50% probability).*

Complexes **6c**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.89 (d, *J* = 5.6 Hz, 2H, I$^+$), 8.54 (d, *J* = 5.0 Hz, 2H, Ag$^+$), 8.11 (t, *J* = 7.7 Hz, 2H, I$^+$), 7.81 (t, *J* = 7.7 Hz, 2H, Ag$^+$), 7.58 (d, *J* = 7.9 Hz, 2H, I$^+$), 7.38 (d, *J* = 7.4 Hz, 2H, Ag$^+$), 7.35 (t, *J* = 7.0 Hz, 2H, I$^+$), 7.30 (t, *J* = 6.5 Hz, 2H, Ag$^+$), 3.10 (q, *J* = 7.6 Hz, 4H, I$^+$), 2.93 (q, *J* = 7.6 Hz, 4H, Ag$^+$), 1.41 (t, *J* = 7.6 Hz, 6H,

I^+), 1.34 (t, *J* = 7.6 Hz, 6H, Ag^+). ^{15}N NMR (500 MHz, CD_2Cl_2) δ -101.6, -168.0. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution vapour diffused with TBME. Crystal data for **6c_Mixed**: CCDC-2064894, $[C_{14}H_{18}Ag_{0.26}I_{0.74}N_2][PF_6]$, M = 481.23, colourless block, 0.05 x 0.18 x 0.29 mm^3, monoclinic, space group *C*2/*c*, a = 11.8384(6) Å, b = 10.2312(4) Å, c = 15.1646(6) Å, β = 109.654(5)°, V = 1729.74(14) $Å^3$, Z = 4, D_{calc} = 1.848 gcm^{-3}, F000 = 946, μ = 14.65 mm^{-1}, T = 120.0(1) K, θ_{max} = 76.5°, 1704 total reflections, 1670 with $I_o > 2\sigma(I_o)$, R_{int} = 0.027, 1704 data, 113 parameters, no restraints, GooF = 1.10, 2.18 < dΔρ < -0.74 $eÅ^{-3}$, $R[F^2 > 2\sigma(F^2)]$ = 0.038, $wR(F^2)$ = 0.103.

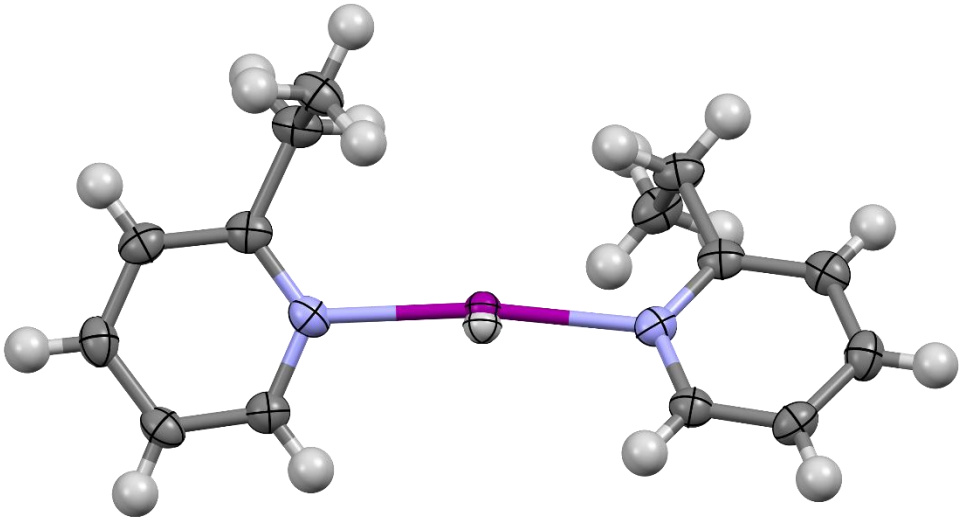


*Figure S8: The X-ray crystal structure of **6c_Mixed** (Minor Ag^+ component drawn without bonds; PF_6 anion omitted for clarity; thermal ellipsoids at 50% probability).*

Comparison Table of ^{15}N NMR Resonances for Ag^{+}–N and I^{+}–N

Pure Complexes	^{15}N (ppm)	NII-complexes	^{15}N (ppm)
$[Ag(py)_2]PF_6$ (**1a**)	-121.6	$[Ag(py)_2]PF_6$	-119.2
$[I(py)_2]PF_6$ (**1b**)	-174.8	$[I(py)_2]PF_6$ (**1c**)	-174.8
$[Ag(4\text{-}Mepy)_2]PF_6$ (**2a**)	-136.0	$[Ag(4\text{-}Mepy)_2]PF_6$	-135.1
$[I(4\text{-}Mepy)_2]PF_6$ (**2b**)	-182.2	$[I(4\text{-}Mepy)_2]PF_6$ (**2c**)	-182.1
$[Ag(4\text{-}Etpy)_2]PF_6$ (**3a**)	-118.6	$[Ag(4\text{-}Etpy)_2]PF_6$	-126.4
$[I(4\text{-}Etpy)_2]PF_6$ (**3b**)	-181.9	$[I(4\text{-}Etpy)_2]PF_6$ (**3c**)	-181.5
$[Ag(4\text{-}^{i}Prpy)_2]PF_6$ (**4a**)	-135.2	$[Ag(4\text{-}^{i}Prpy)_2]PF_6$	-127.5
$[I(4\text{-}^{i}Prpy)_2]PF_6$ (**4b**)	-181.2	$[I(4\text{-}^{i}Prpy)_2]PF_6$ (**4c**)	-181.2
$[Ag(4\text{-}DMAP)_2]PF_6$ (**5a**)	-168.7	$[Ag(4\text{-}DMAP)_2]PF_6$	-170.3
$[I(4\text{-}DMAP)_2]PF_6$ (**5b**)	-216.1	$[I(4\text{-}DMAP)_2]PF_6$ (**5c**)	-216.0
$[Ag(2\text{-}Etpy)_2]PF_6$ (**6a**)	-112.2	$[Ag(2\text{-}Etpy)_2]PF_6$	-101.4
$[I(2\text{-}Etpy)_2]PF_6$ (**6b**)	-167.9	$[I(2\text{-}Etpy)_2]PF_6$ (**6c**)	-168.0

Table S1: The ^{15}N NMR resonances (determined by ^{1}H-^{15}N HMBC experiments) of the coordinating nitrogen atoms for all pure compounds and their respective NII-complexes.

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NMR Spectra

*Figure S9: The ^{1}H NMR spectrum of complex **1c** in CD_2Cl_2.*

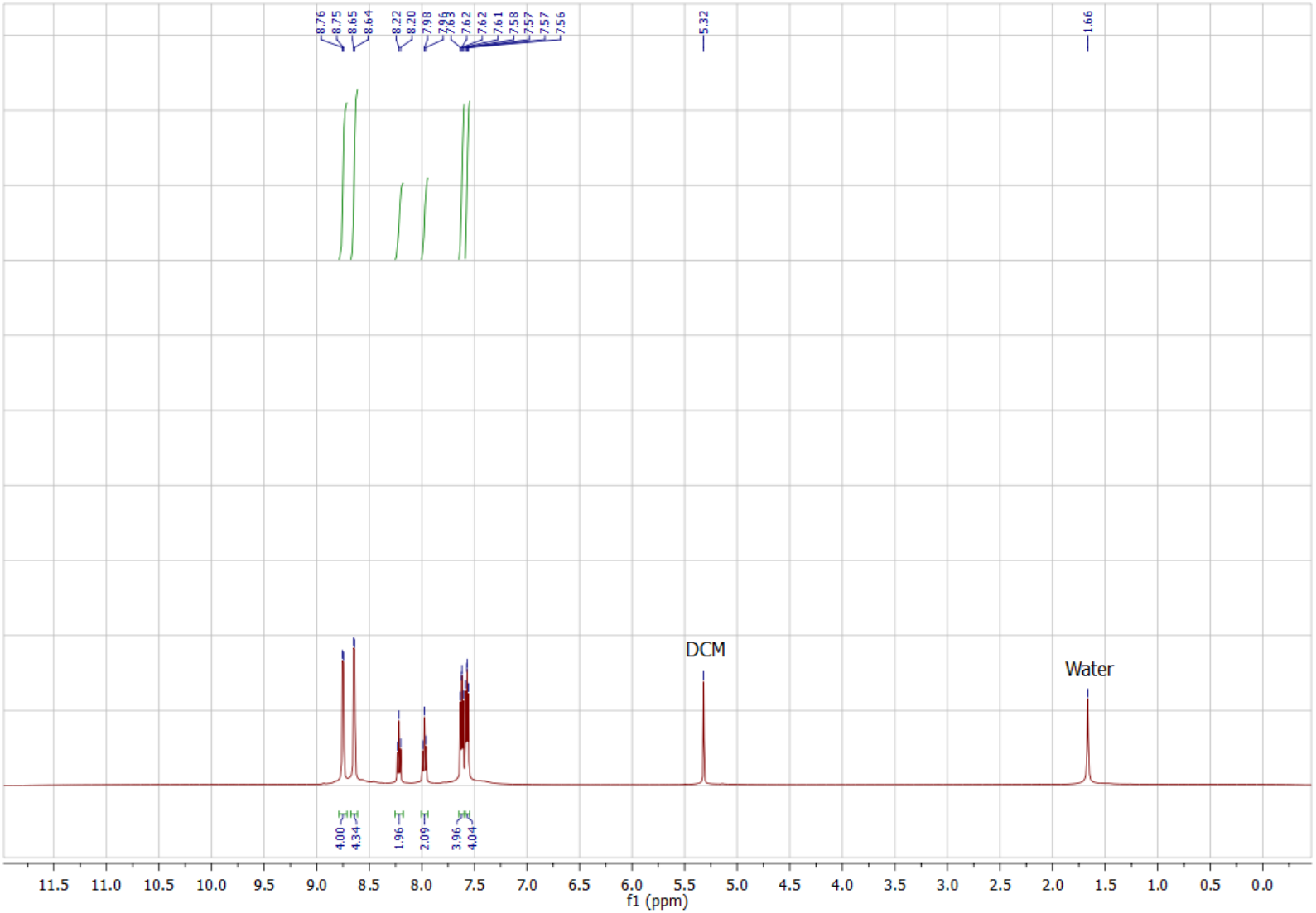


*Figure S10: The ^{1}H-^{15}N HMBC spectrum of complex **1c** in CD_2Cl_2.*

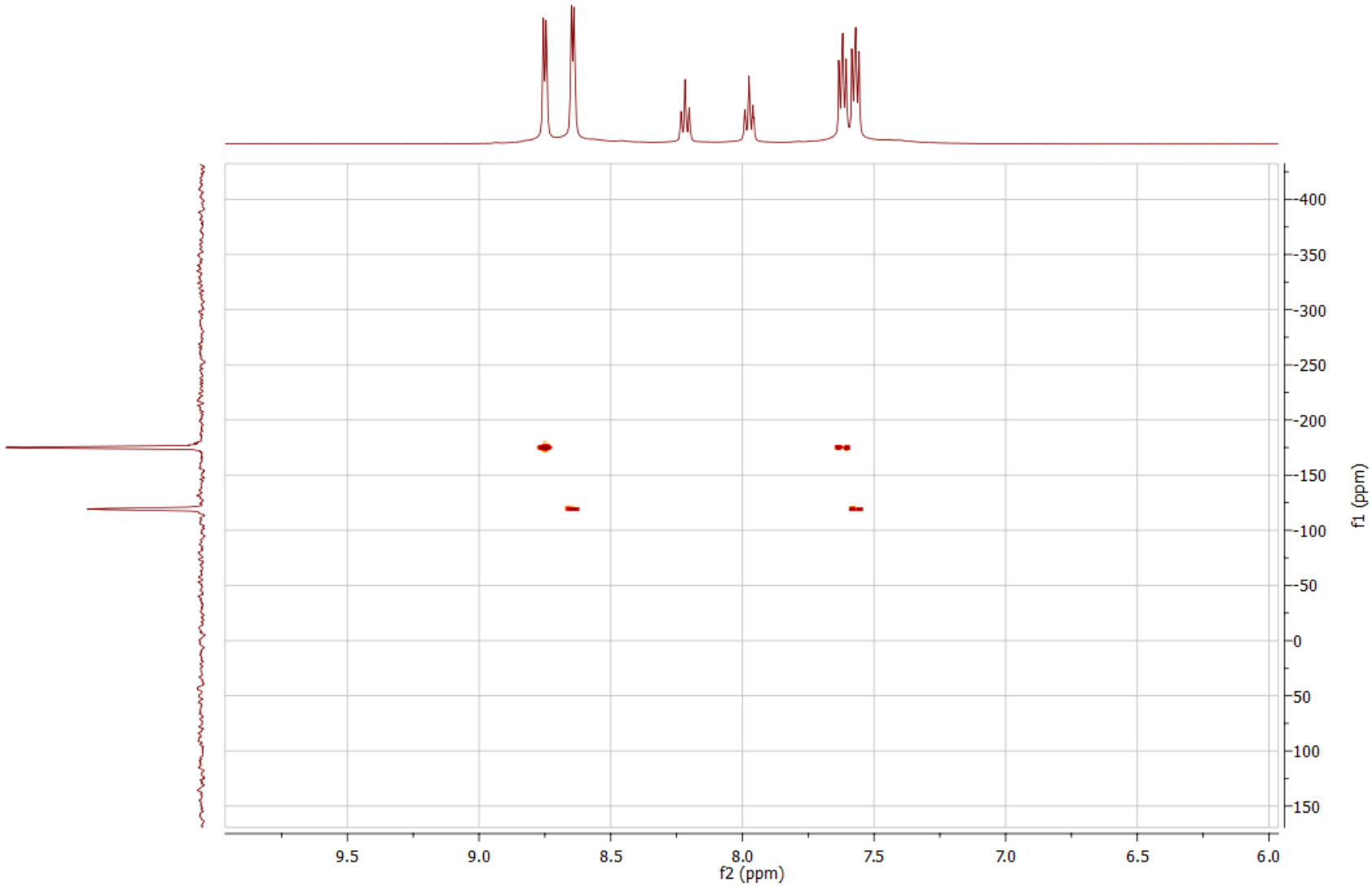


*Figure S11: The ^{1}H NMR spectrum of complex **2a** in CD_2Cl_2.*

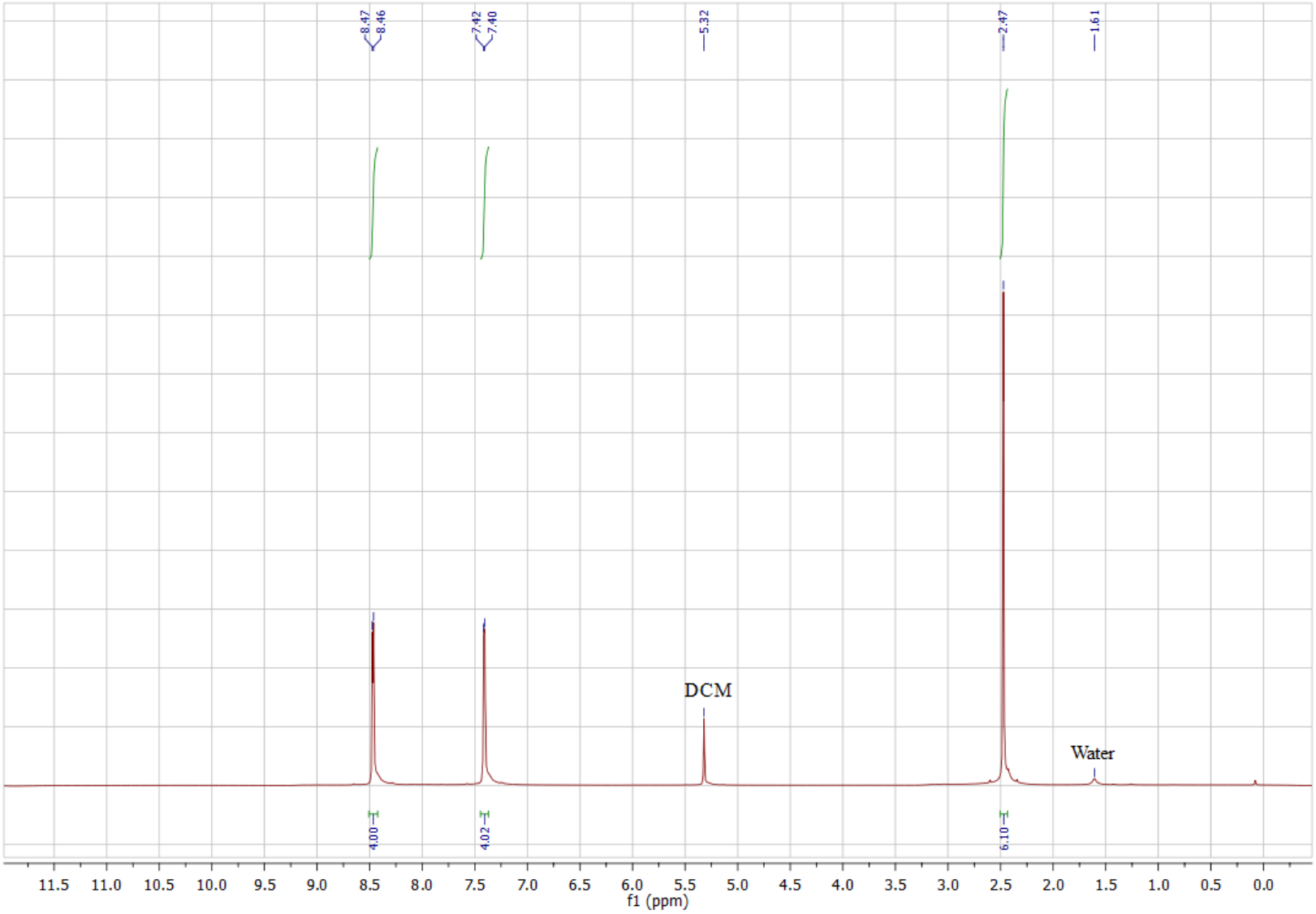


*Figure S12: The ^{1}H-^{15}N HMBC spectrum of complex **2a** in CD_2Cl_2.*

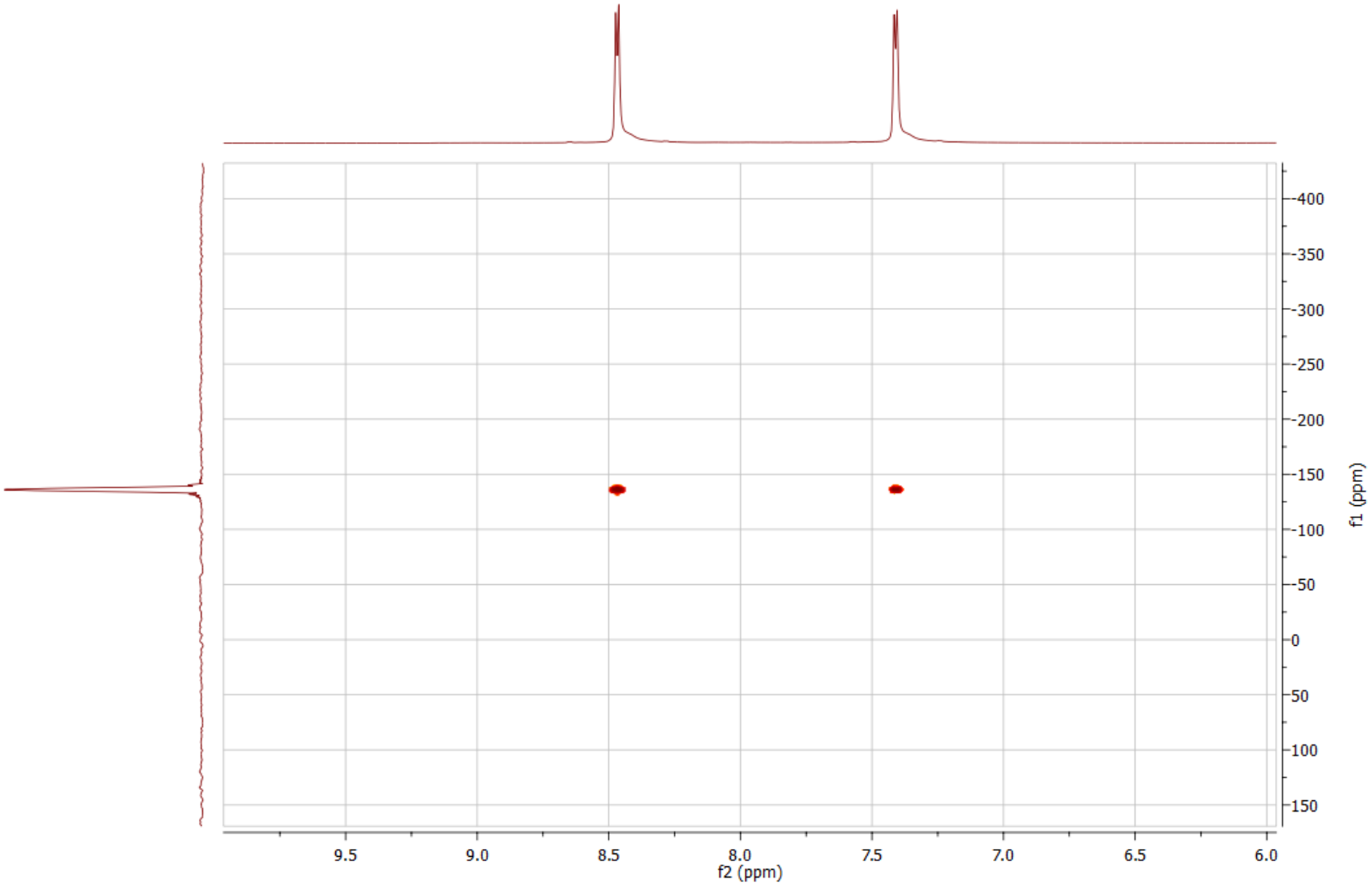


*Figure S13: The ^{1}H NMR spectrum of complex **2b** in CD_2Cl_2.*

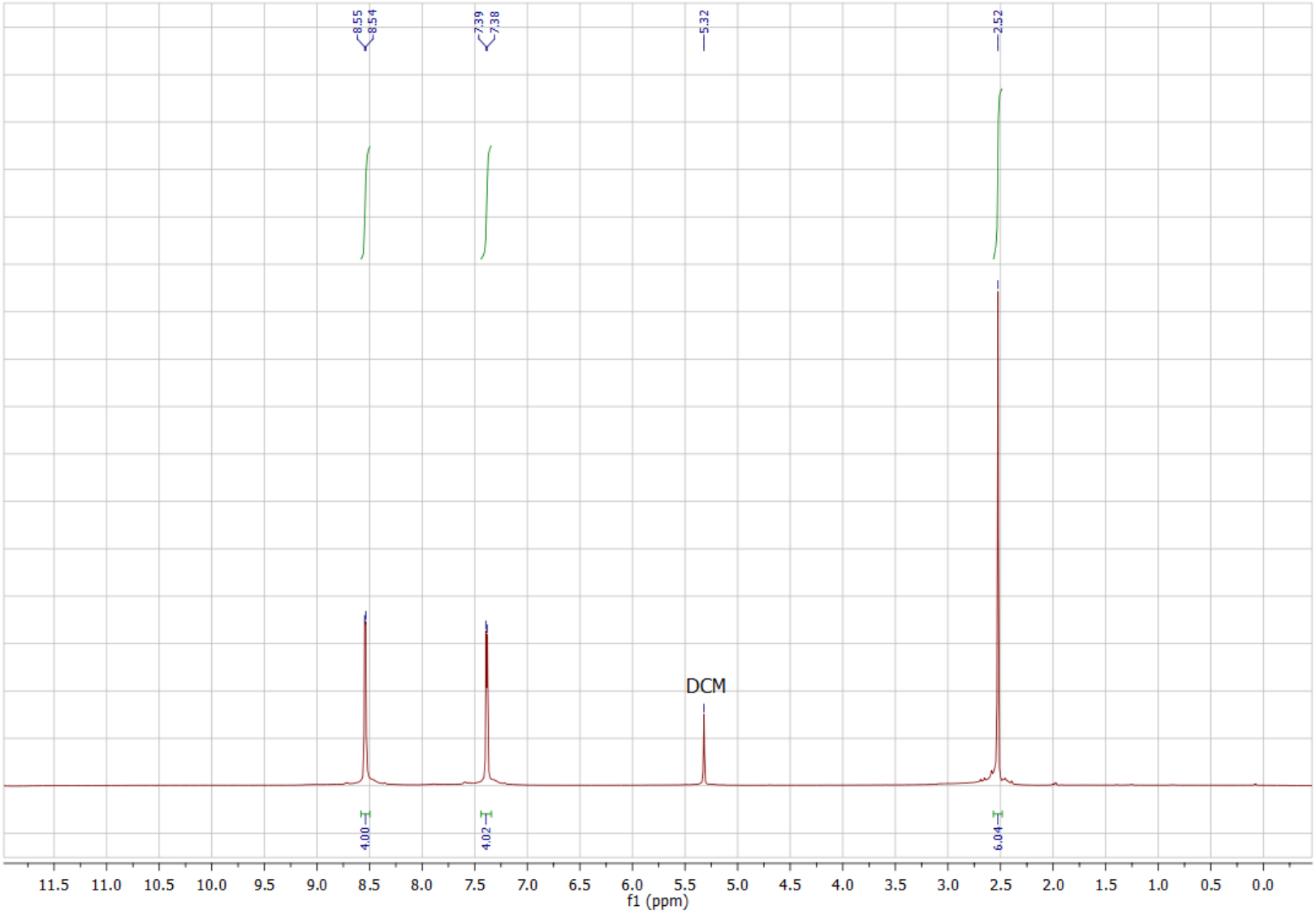


*Figure S14: The ^{1}H-^{15}N HMBC spectrum of complex **2b** in CD_2Cl_2.*

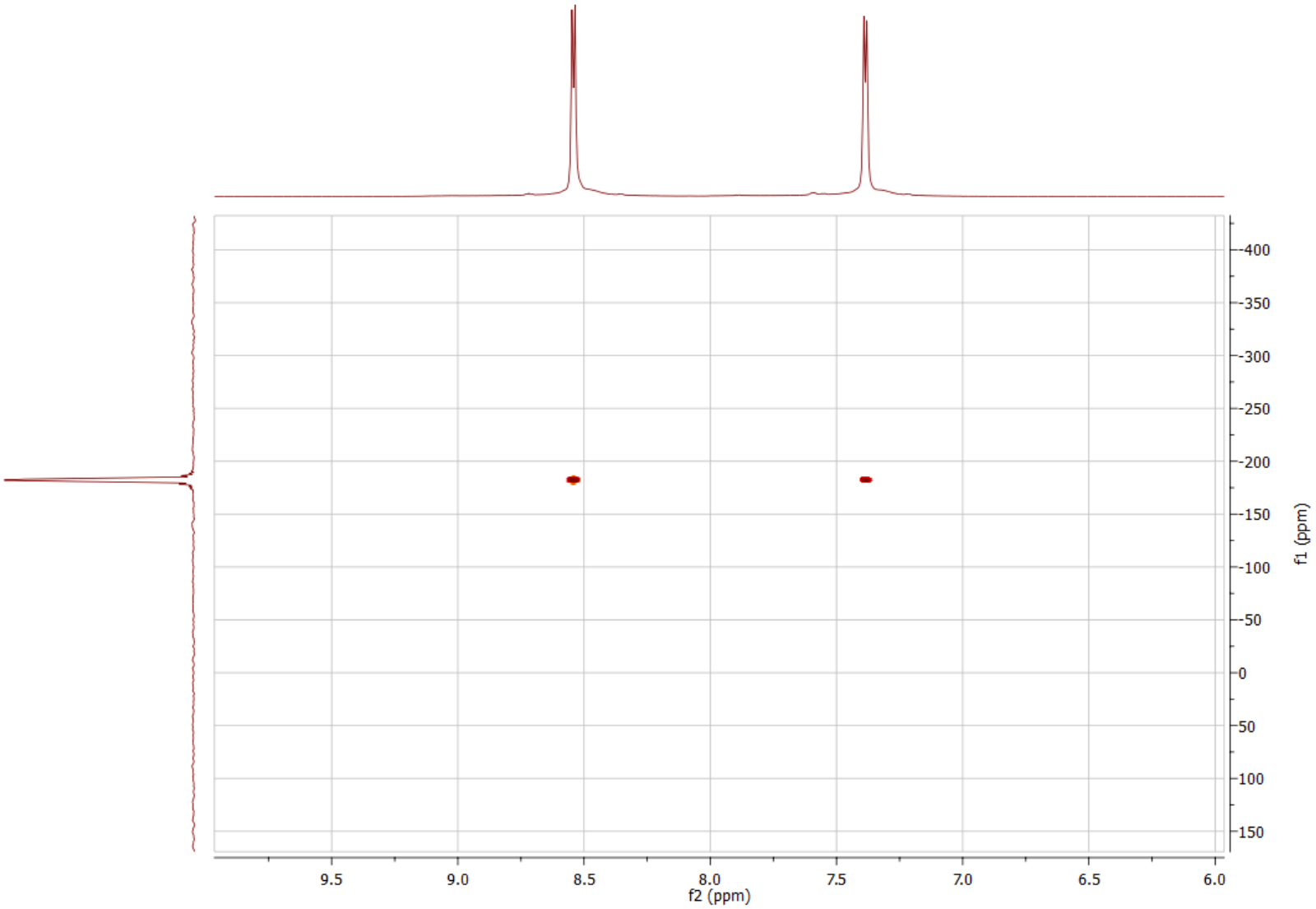


*Figure S15: The ^{1}H NMR spectrum of complex **2c** in CD_2Cl_2.*

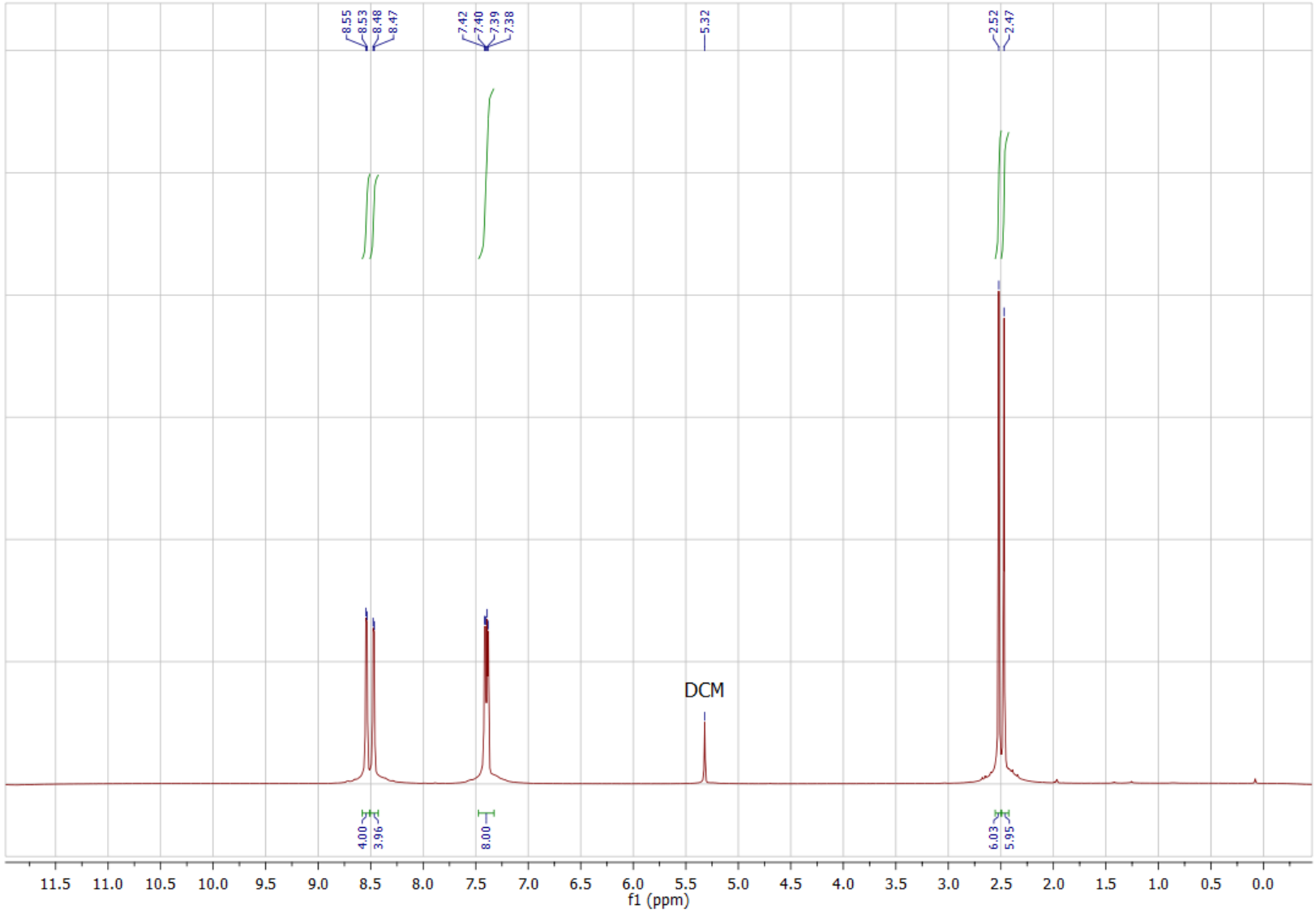


*Figure S16: The ^{1}H-^{15}N HMBC spectrum of complex **2c** in CD_2Cl_2.*

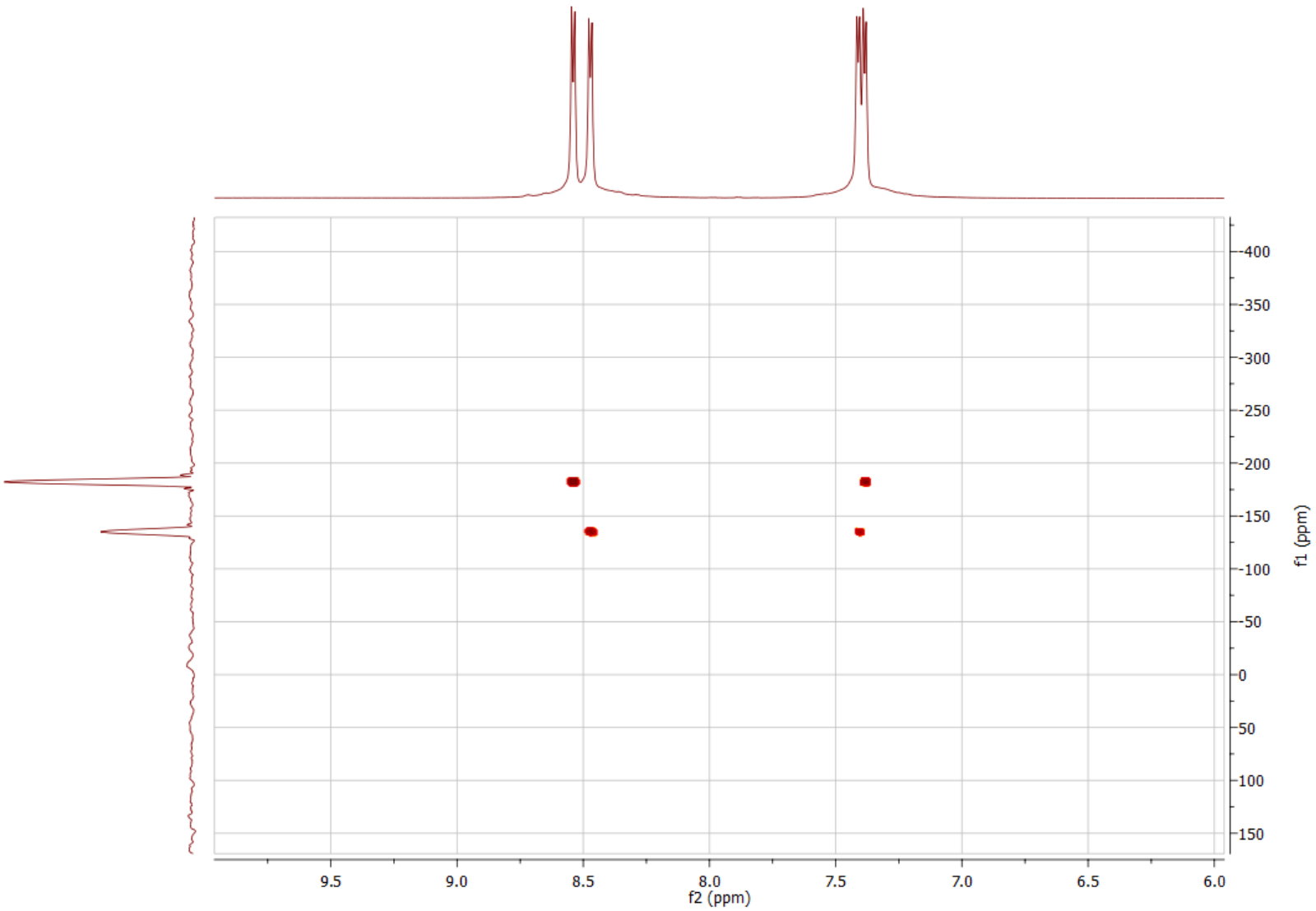


*Figure S17: The ^{1}H NMR spectrum of complex **3c** in CD_2Cl_2.*

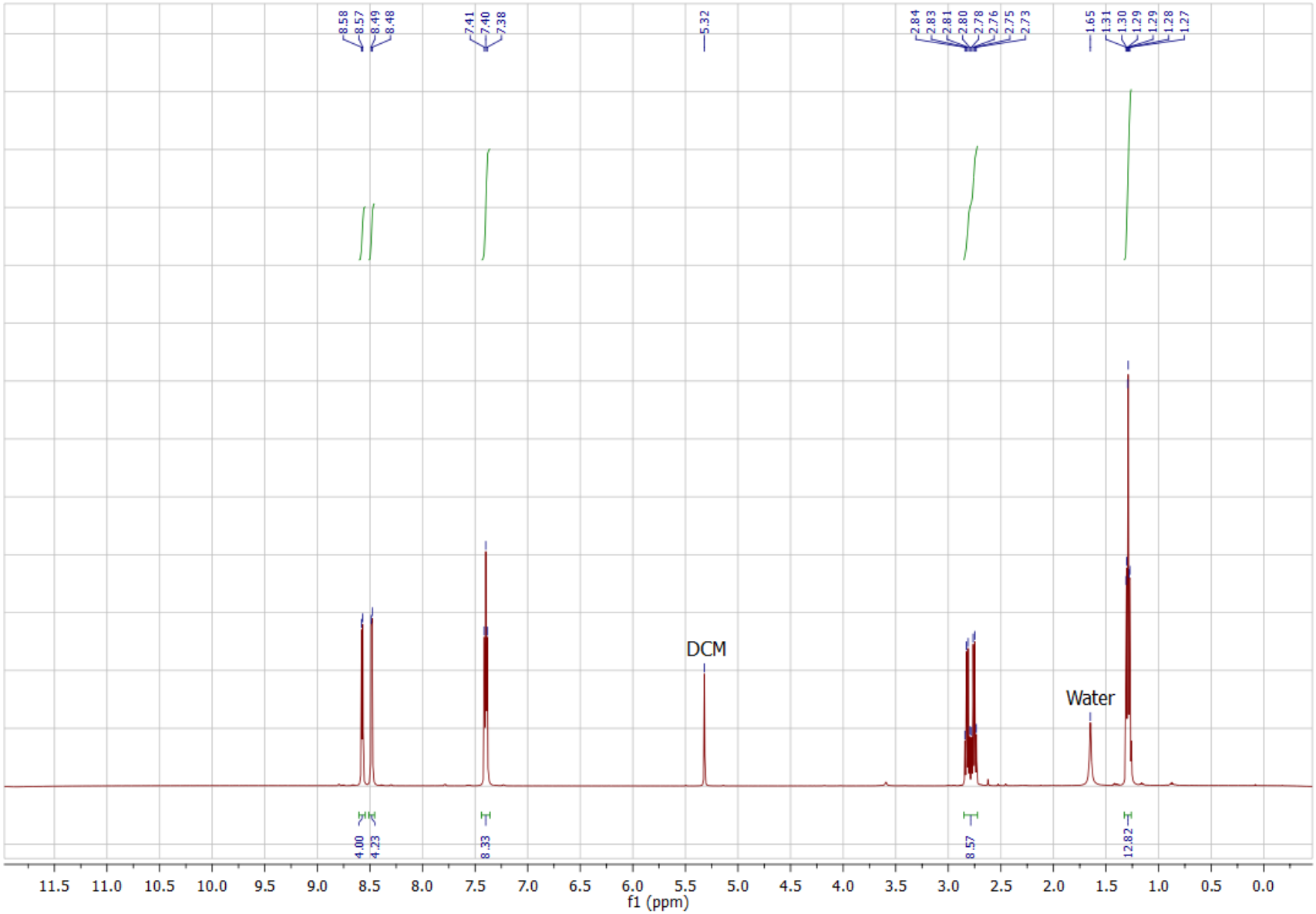


*Figure S18: The ^{1}H-^{15}N HMBC spectrum of complex **3c** in CD_2Cl_2.*

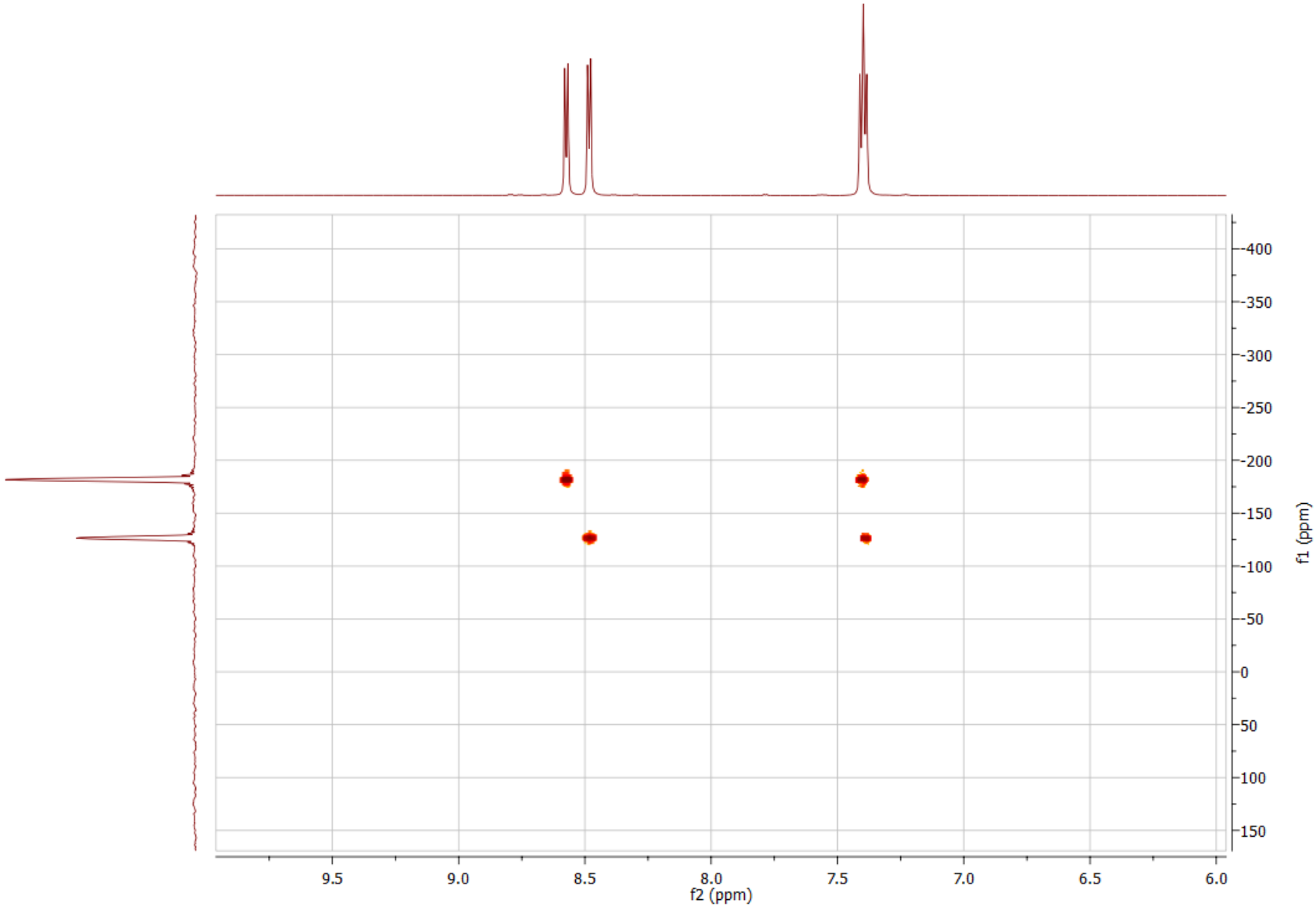


*Figure S19: The ^{1}H NMR spectrum of complex **4a** in CD_2Cl_2.*

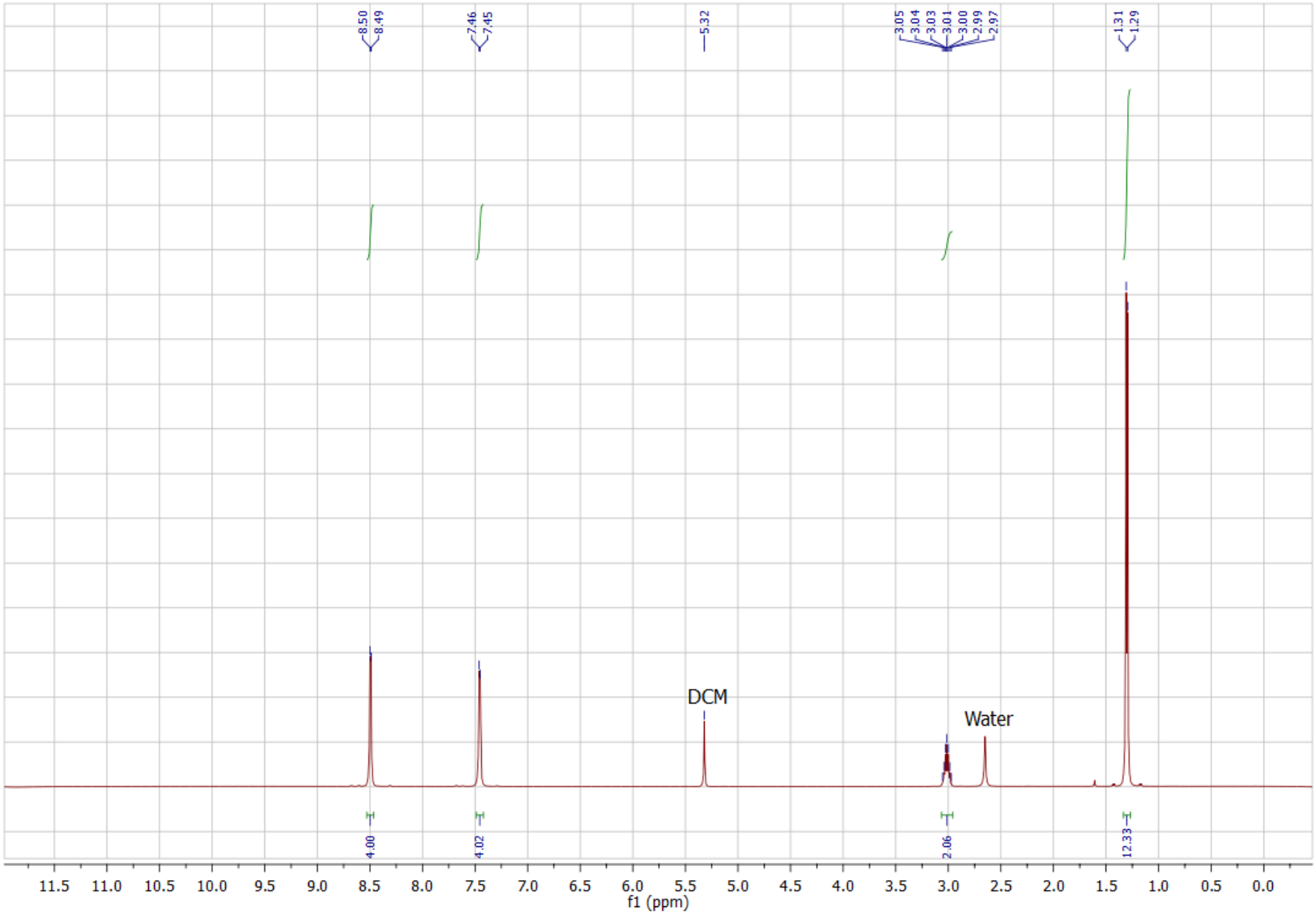


*Figure S20: The ^{1}H-^{15}N HMBC spectrum of complex **4a** in CD_2Cl_2.*

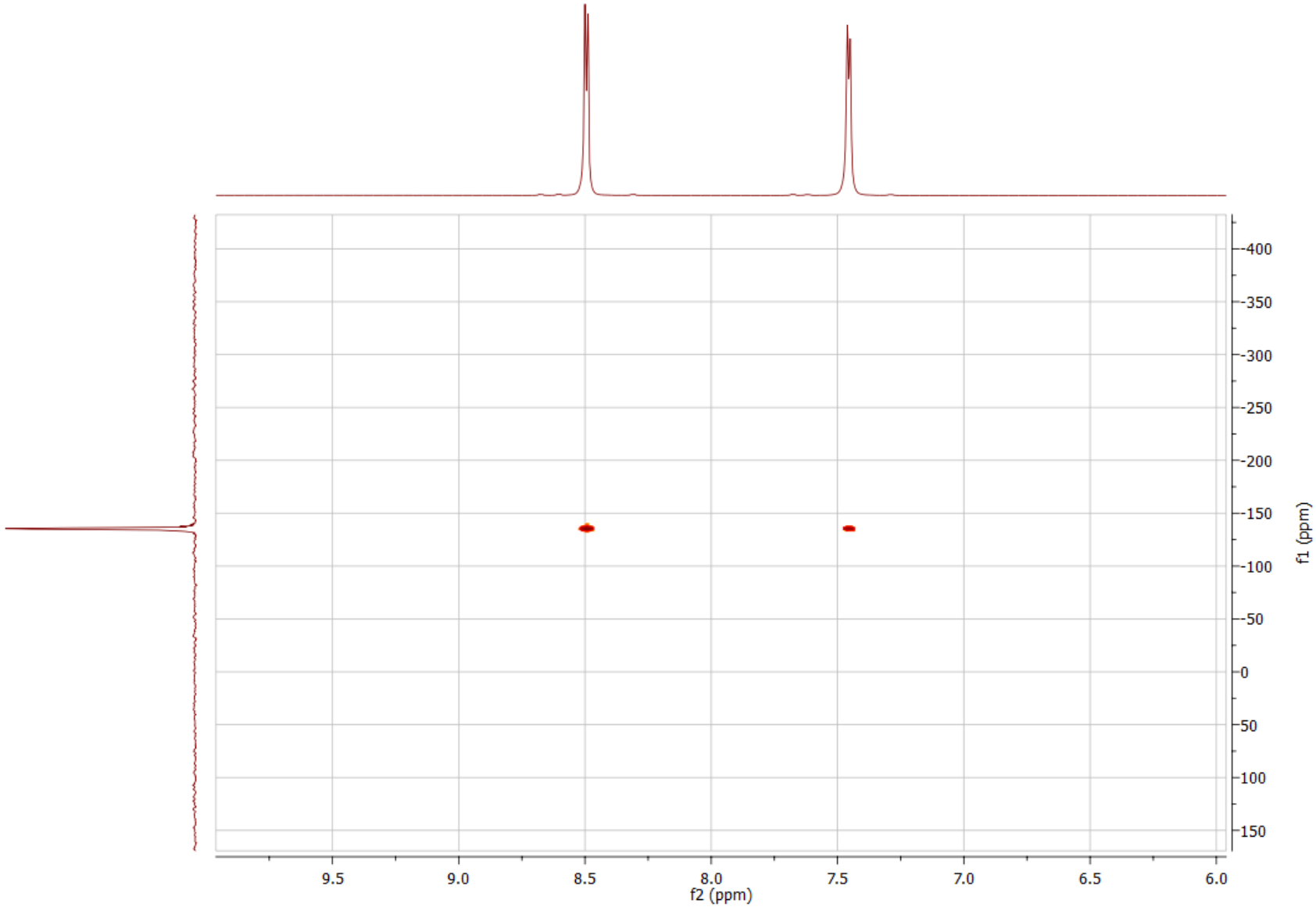


*Figure S21: The ^{1}H NMR spectrum of complex **4b** in CD_2Cl_2.*

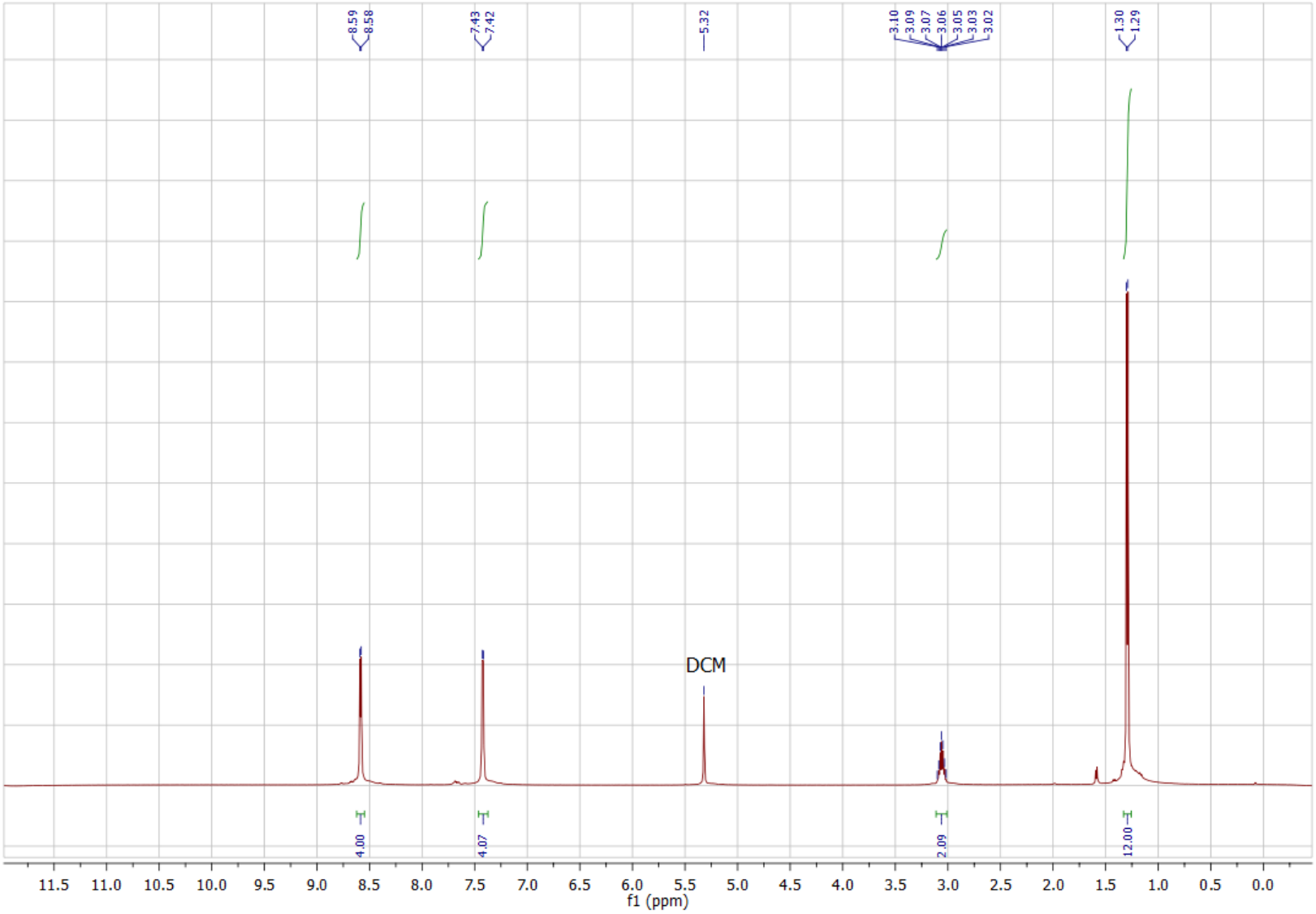


*Figure S22: The ^{1}H-^{15}N HMBC spectrum of complex **4b** in CD_2Cl_2.*

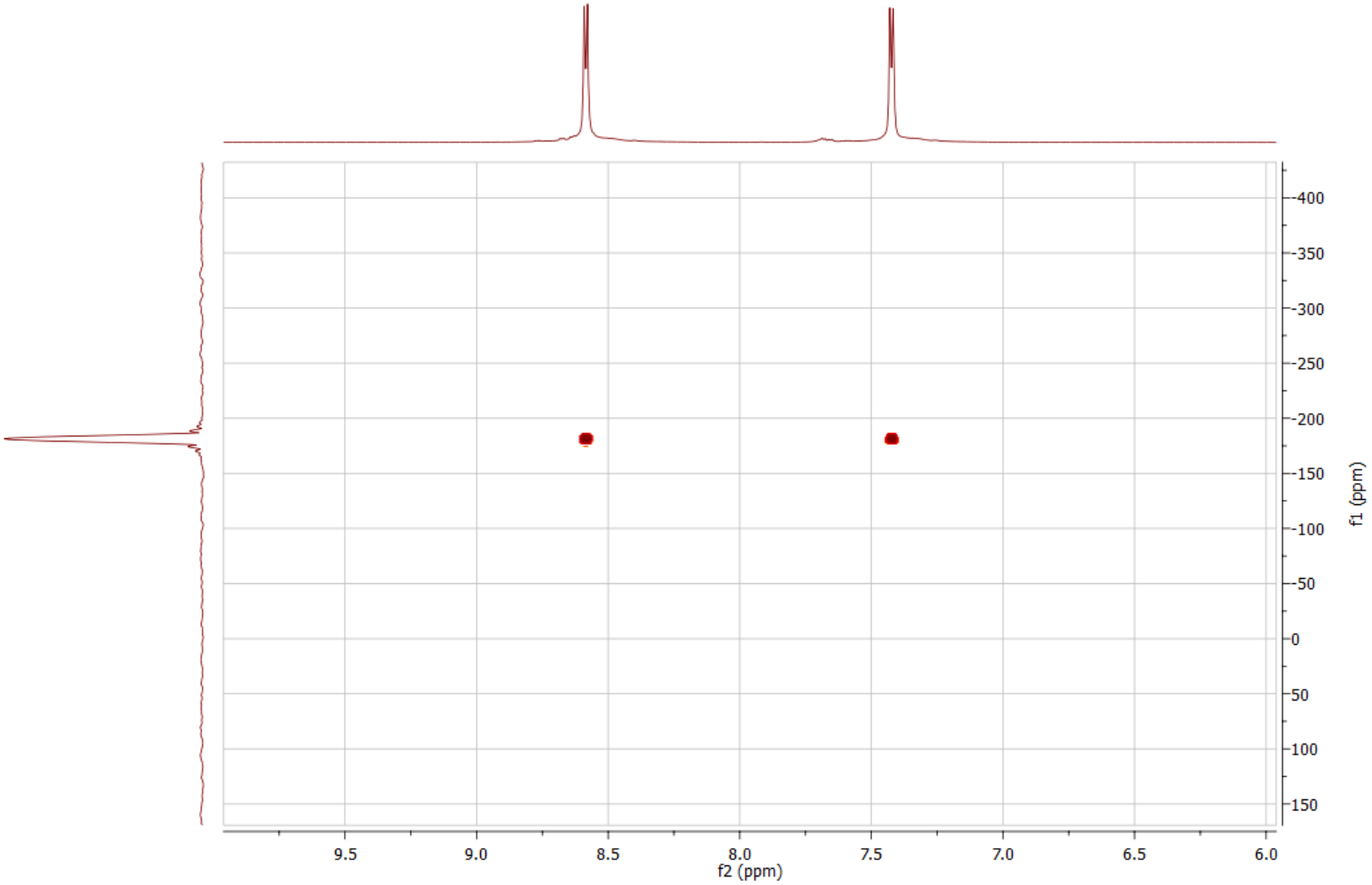


*Figure S23: The ^{1}H NMR spectrum of complex **4c** in CD_2Cl_2.*

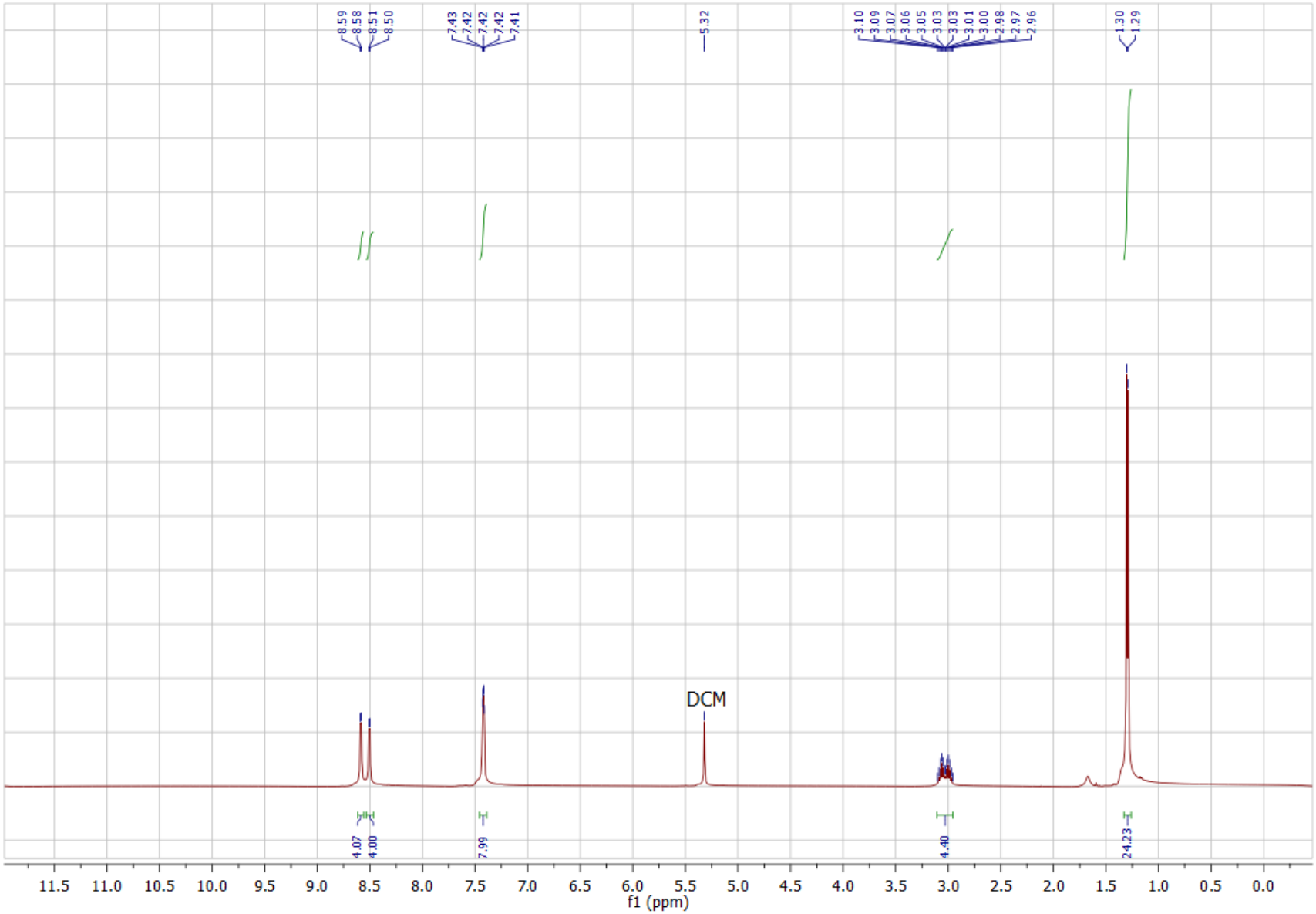


*Figure S24: The ^{1}H-^{15}N HMBC spectrum of complex **4c** in CD_2Cl_2.*

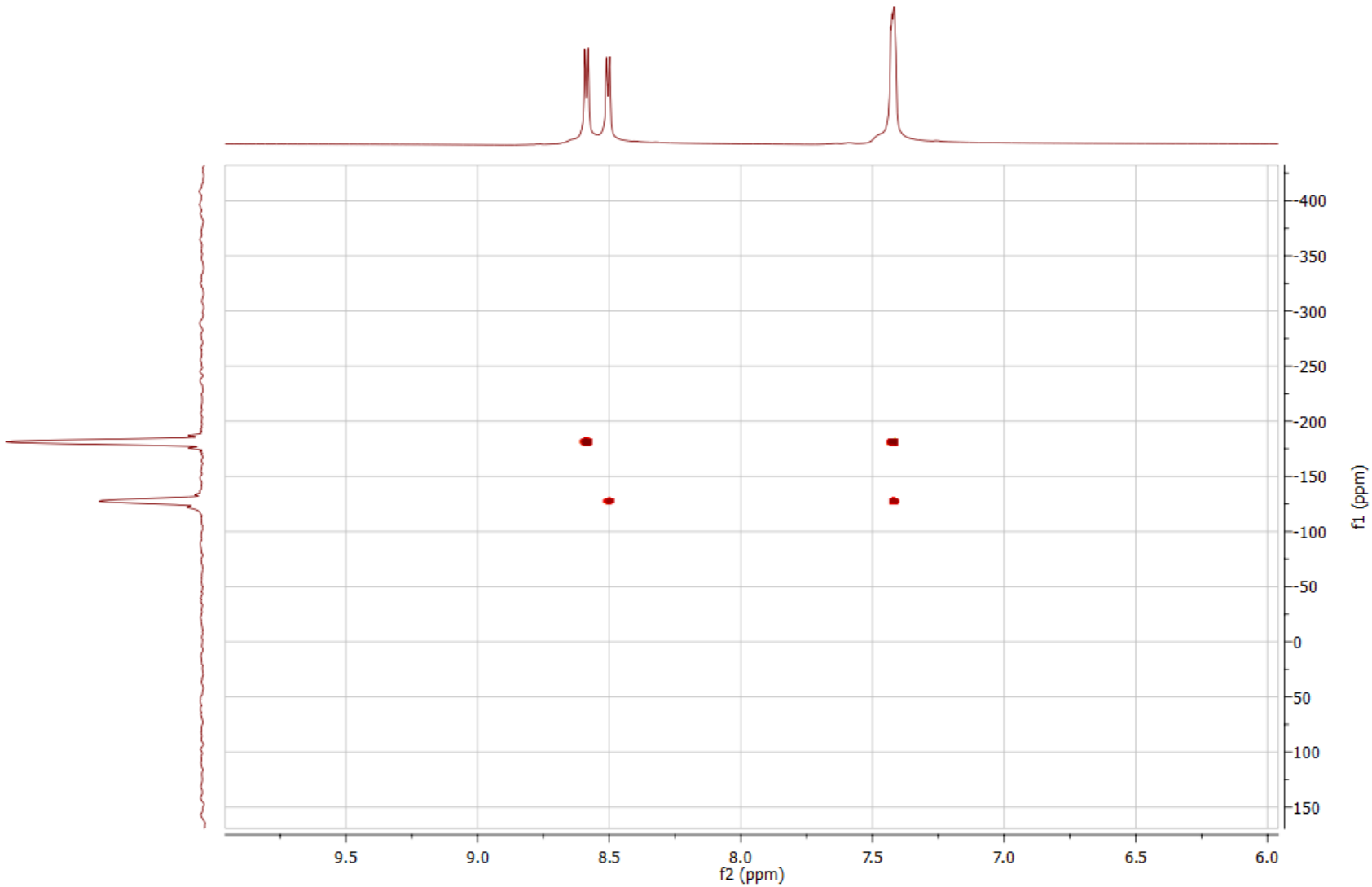


*Figure S25: The ^{1}H NMR spectrum of complex **5c** in CD_2Cl_2.*

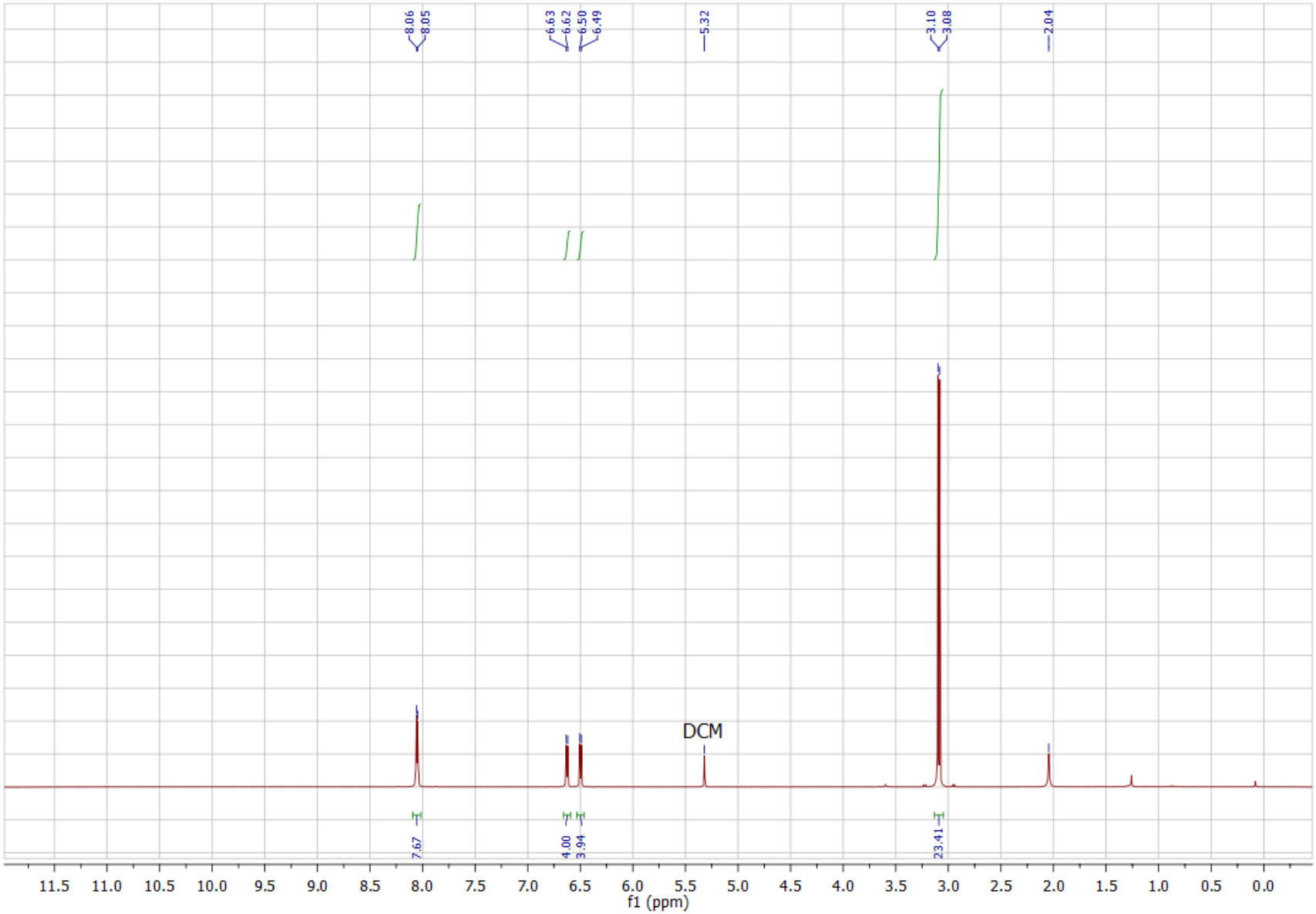


*Figure S26: The ^{1}H-^{15}N HMBC spectrum of complex **5c** in CD_2Cl_2.*

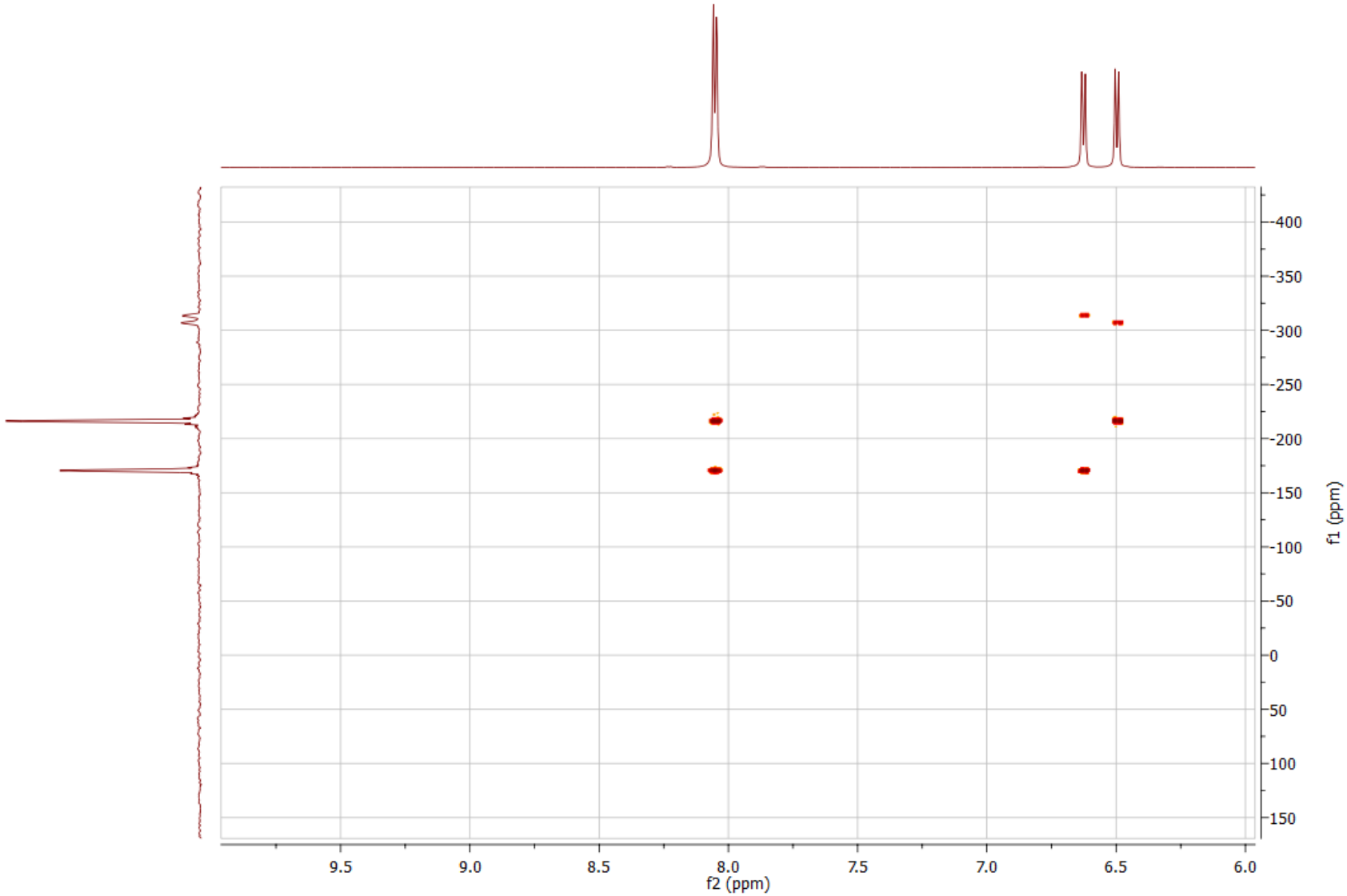


*Figure S27: The ^{1}H NMR spectrum of complex **6a** in CD_2Cl_2.*

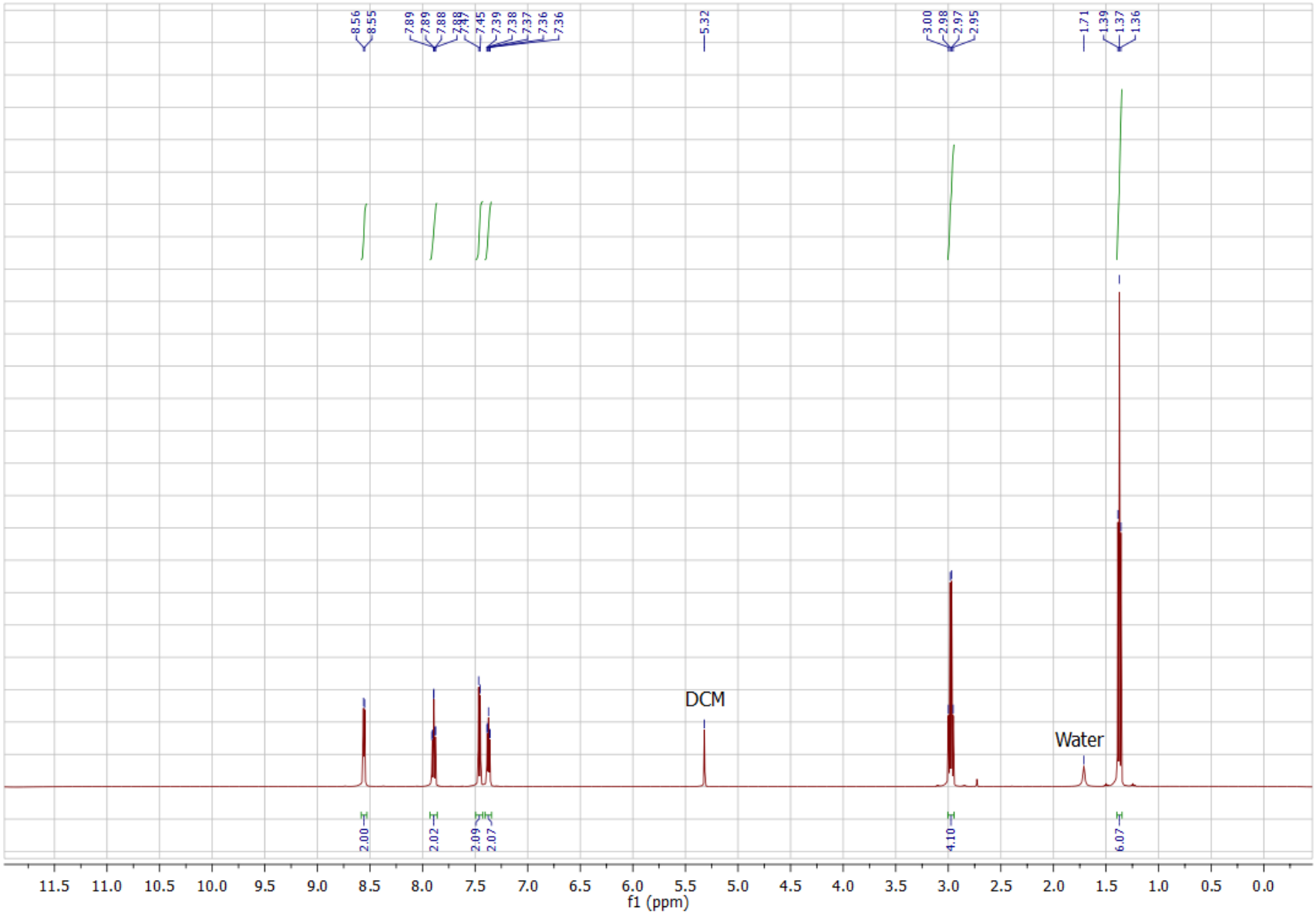


*Figure S28: The ^{1}H-^{15}N HMBC spectrum of complex **6a** in CD_2Cl_2.*

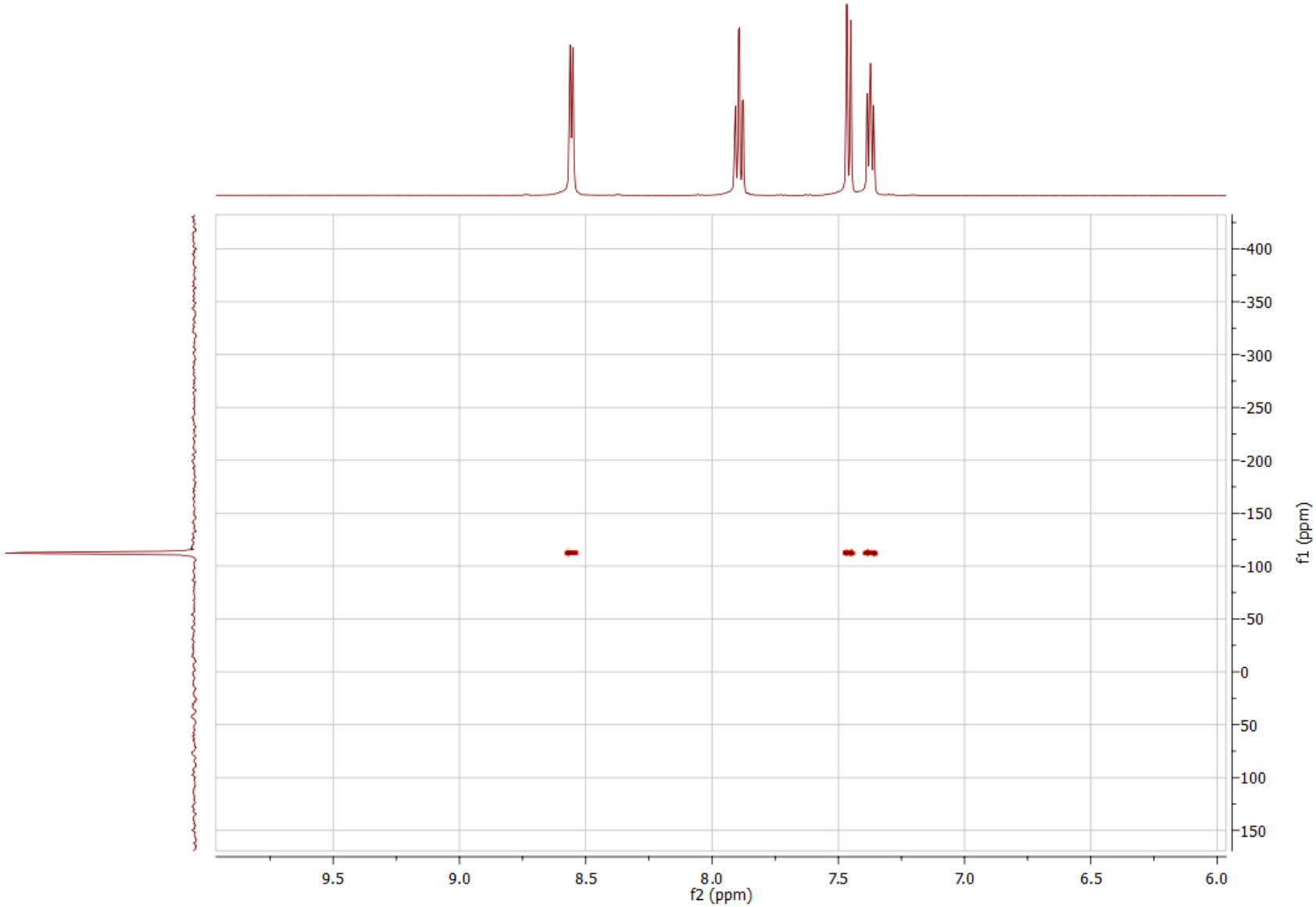


*Figure S29: The ^{1}H NMR spectrum of complex **6b** in CD_2Cl_2 (a minor impurity is labelled with blue circles).*

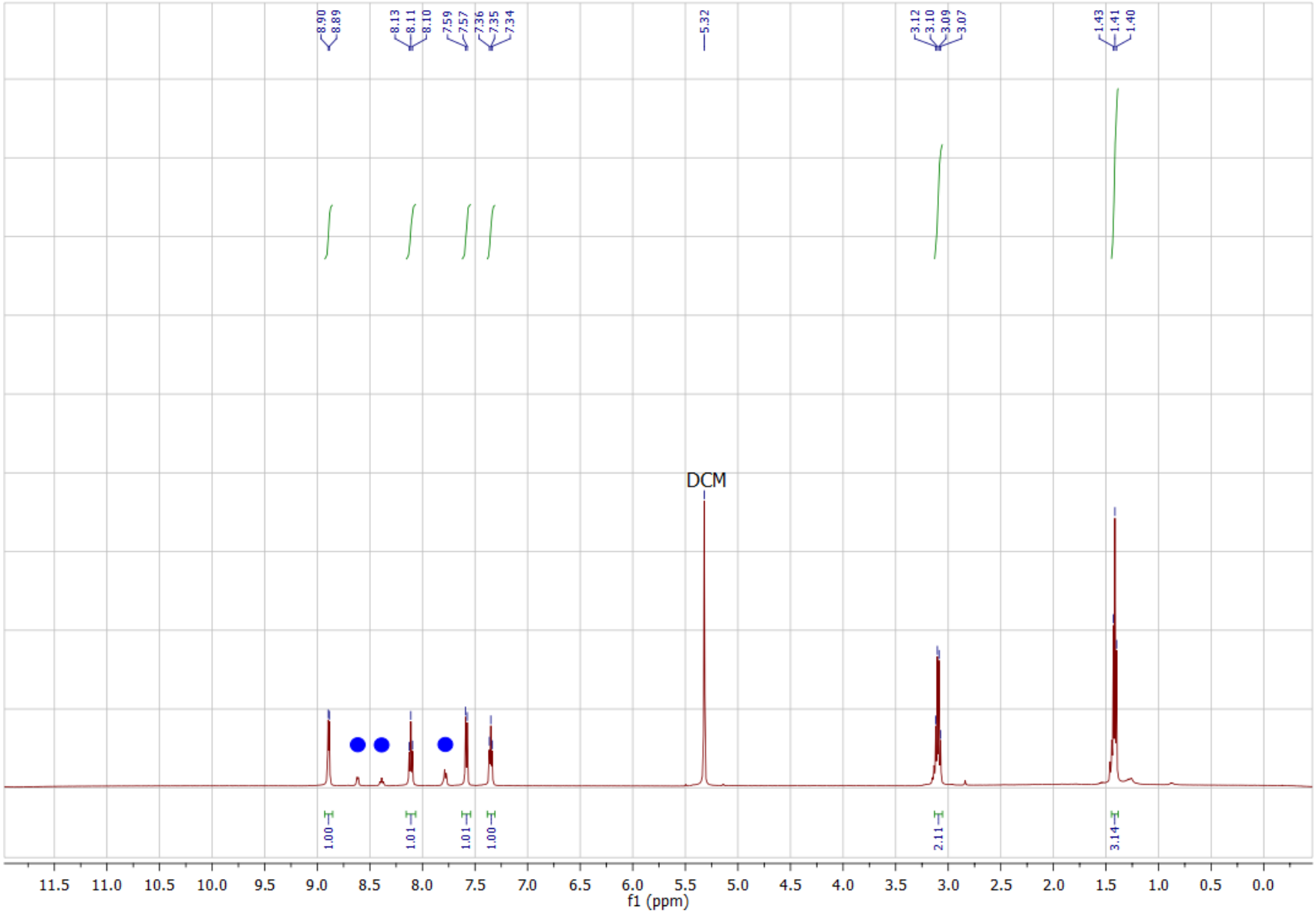


*Figure S30: The ^{1}H-^{15}N HMBC spectrum of complex **6b** in CD_2Cl_2 (a minor impurity is labelled with blue circles)..*

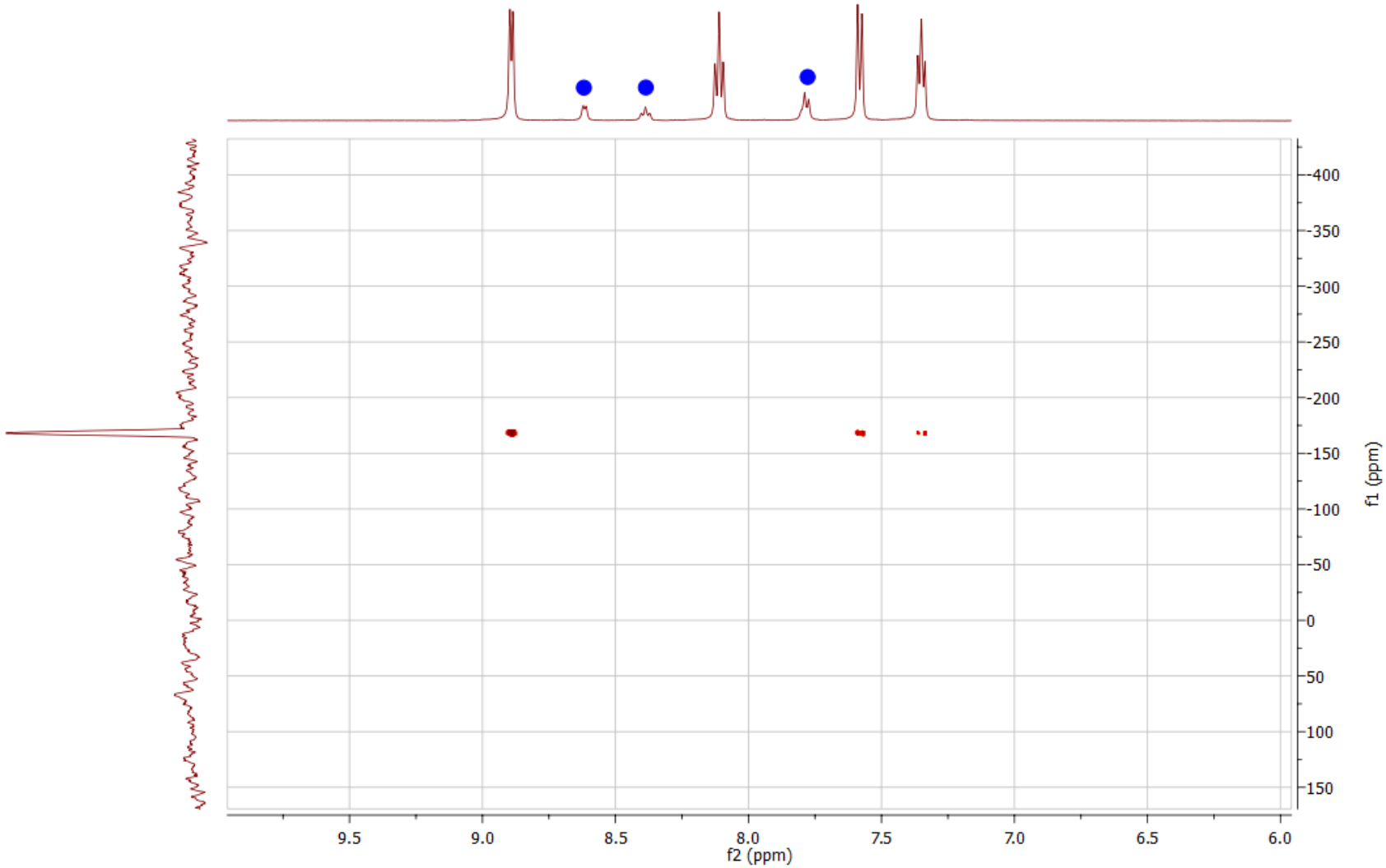


*Figure S31: The ^{1}H NMR spectrum of complex **6c** in CD_2Cl_2.*

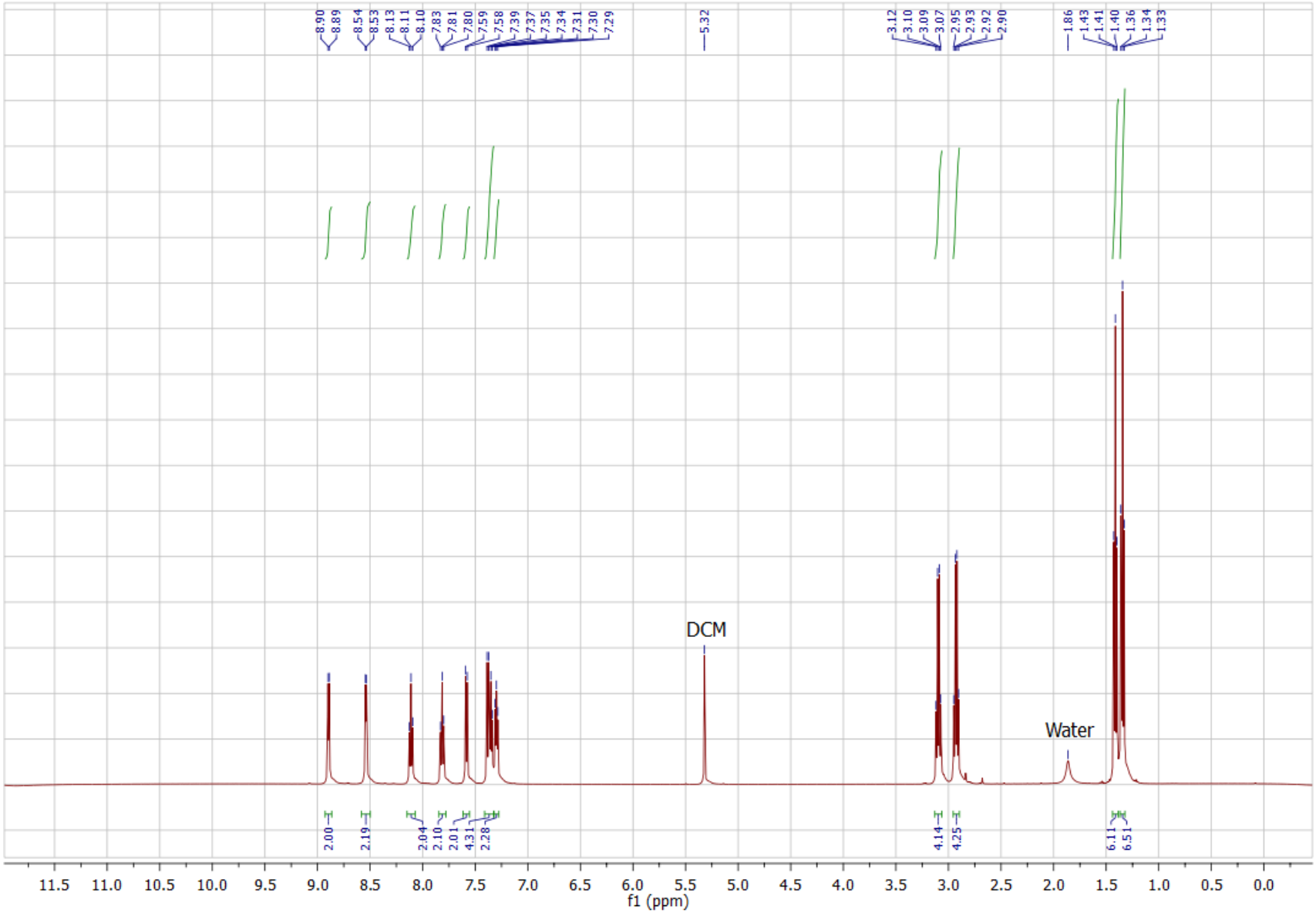


*Figure S32: The ^{1}H-^{15}N HMBC spectrum of complex **6c** in CD_2Cl_2.*

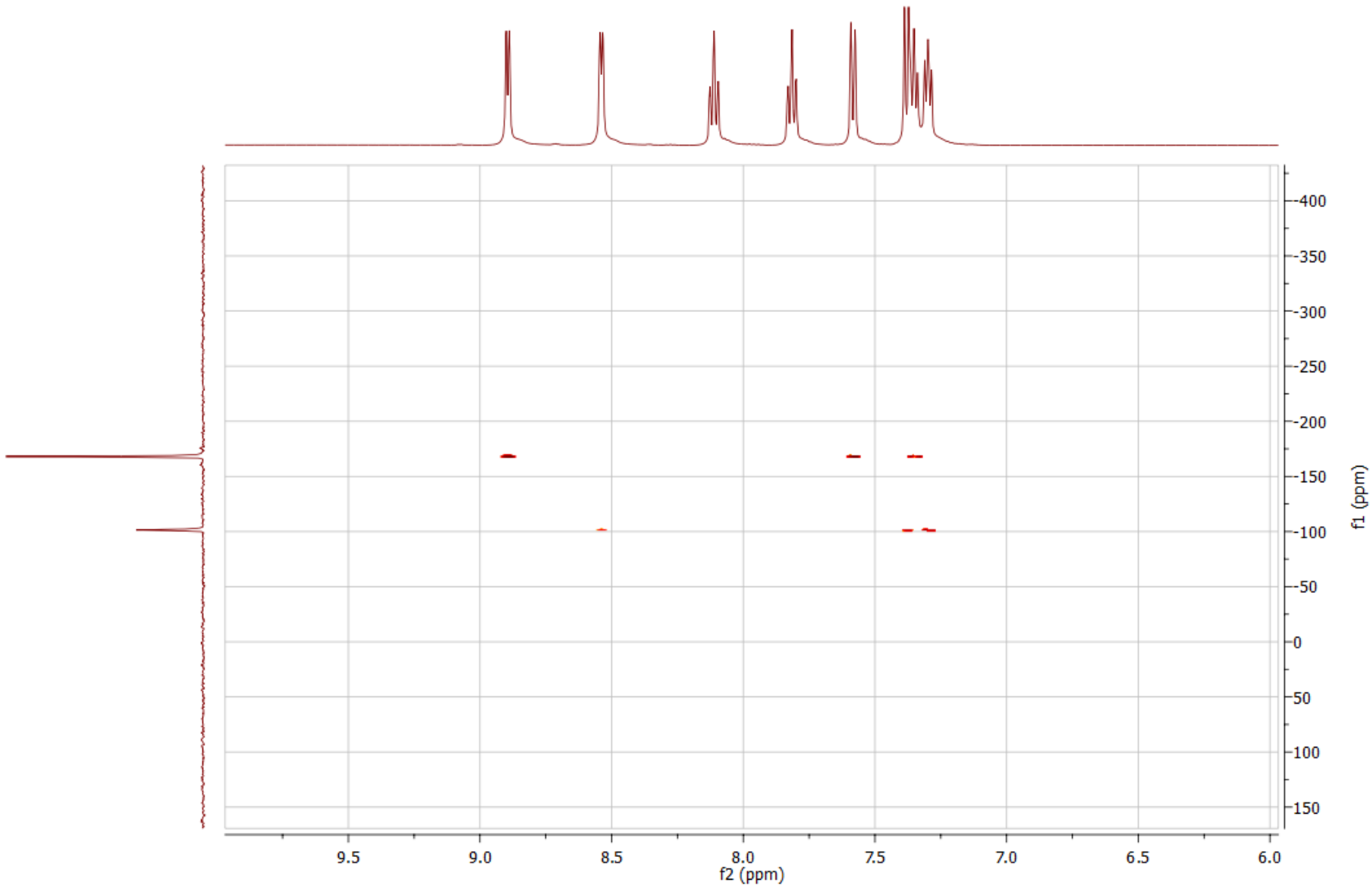


*Figure S33: The ^{1}H NMR spectrum of complex **2a** + 1eq. of $[NBu_4]PF_6$ in CD_2Cl_2*

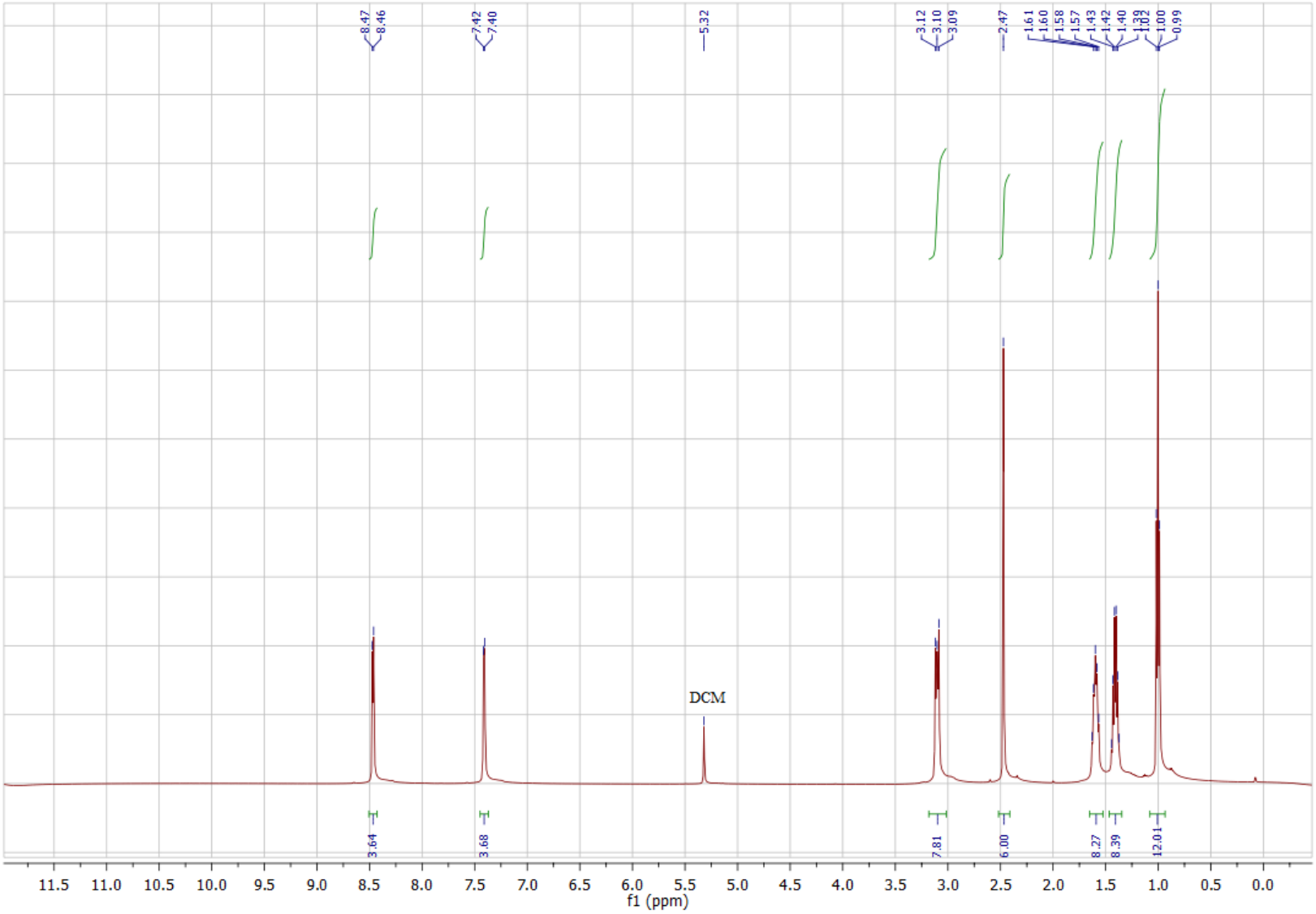
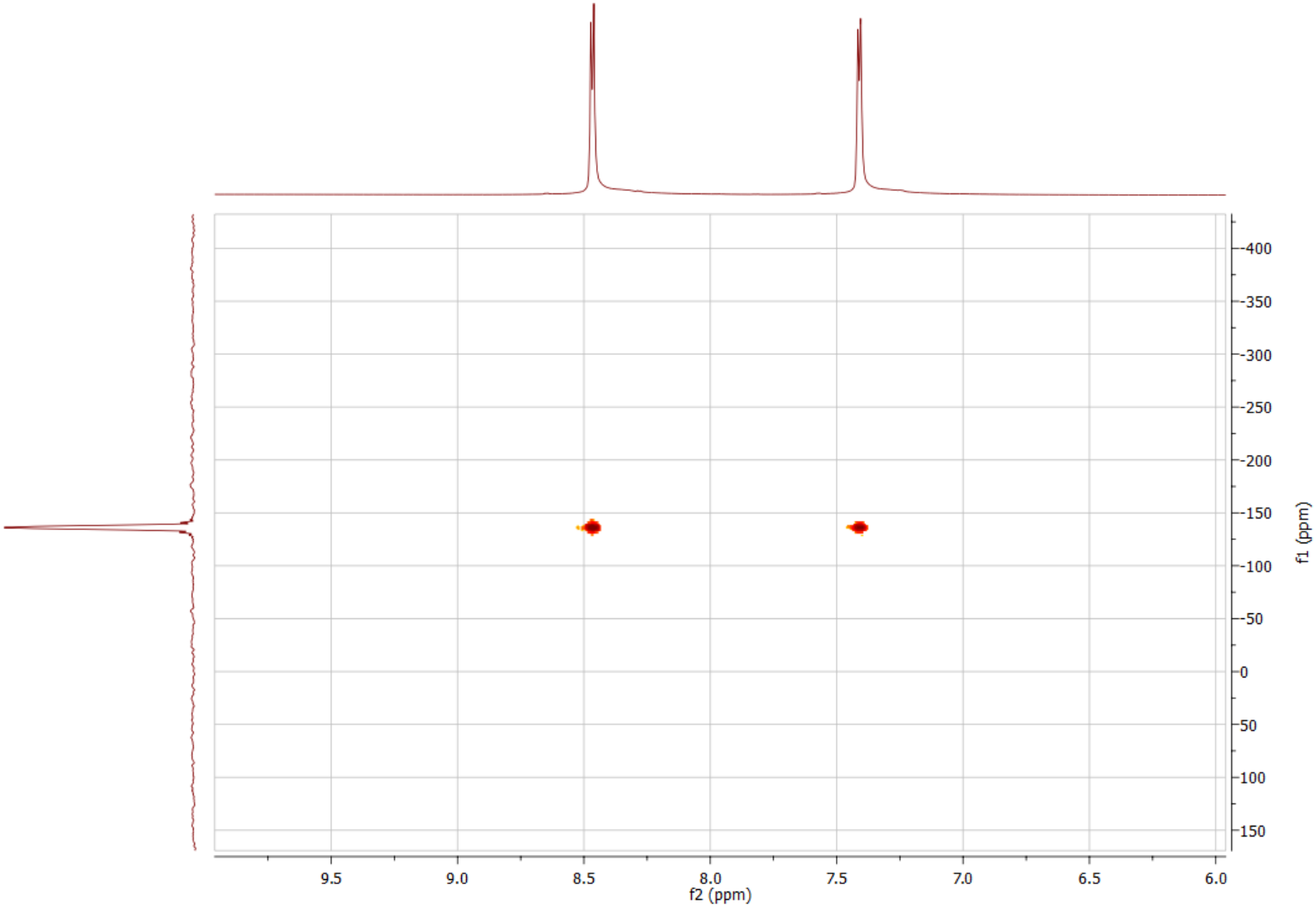


*Figure S34: The ^{1}H-^{15}N HMBC spectrum of complex **2a** + 1eq. of $[NBu_4]PF_6$ in CD_2Cl_2.*



Computational Details

Theoretical methods

For the calculations we have used the M06-2X/def2-TZVP level of theory and the Gaussian-16 program.[8,9] The X-ray coordinates have been used for the calculations. We have used this procedure because we are interested in the analysis of the interactions as they stand in the solid state. The NBO,[10] AIM,[11] and NCIplot calculations have been computed using M06-2X/def2-TZVP level of theory.[12,13] The AIM analysis has been performed using the AIMALL program.[14] The interaction energy of complex **2c** and a model to estimate the π-stacking interaction have been computed taking into consideration the BSSE correction at the M06-2X/def2-TZVP level of theory.[15]

Theoretical analysis of the contribution of π-stacking interactions in **2c**

The binding energy of complex **2c** is repulsive (39.5 kcal/mol) due to the electrostatic cation···cation repulsion (the counterions are not considered in this model). However, the dimerisation energy is significantly smaller than the coulombic repulsion between two positive charges located at 3.5184 Å (I···Ag distance), which is +94.4 kcal/mol. Figure S35b shows a theoretical model used to evaluate the π-stacking interaction in complex **2c**. We have simply used a model where the iodonium atom has been eliminated and the rest of the complex has been kept frozen. The interaction energy is -13.0 kcal/mol, thus evidencing that each π-stacking contributes in approximately -6.5 kcal/mol.

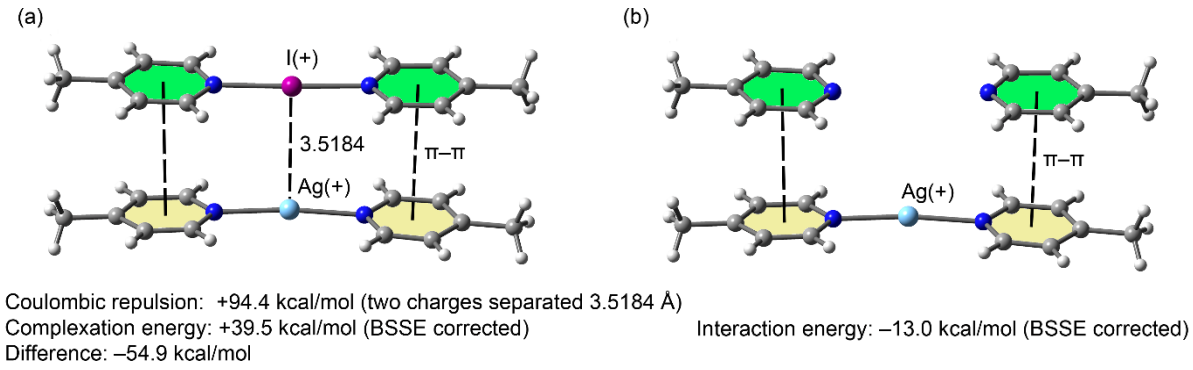


*Figure S35: (a) Interaction energy of complex **2c** with indication of the coulombic repulsion. (b) Theoretical model used to estimate the contribution of the π-stacking interaction.*

NMR calculations

Figure S36 shows the results from the NMR analysis of complex **2c** computed using Gauge-Independent Atomic Orbital (GIAO) method and taking into consideration solvent effects by using the PCM continuum model (DCM solvent). It can be observed an excellent agreement between the experimental and theoretical variation of the ^{15}N NMR chemical shifts upon complexation. The upshift field of the N-atoms coordinated to Ag^+ is well reproduced by the theoretical calculations, thus supporting the formation of **2c** in solution. Moreover, the DFT method also predicts a slight downfield shift of the N-atoms connected to I^+. This is also observed experimentally, although the shift is much more attenuated.

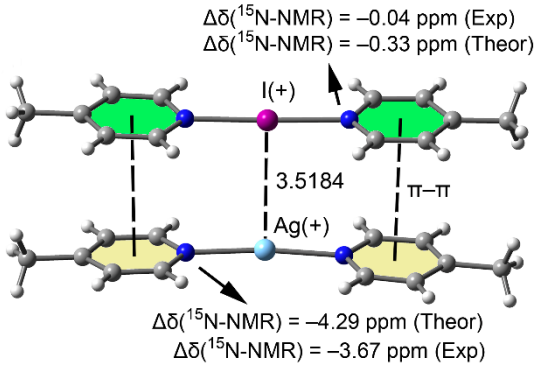


Figure S36: Indication of the ^{15}N NMR chemical shift variations upon complexation at the M06-2X(GIAO)/def2-TZVP level of theory. Solvent = DCM.

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