

## Supporting Information

# The Solid-state Hierarchy and Iodination Potential of [*bis*(3-acetaminopyridine)iodine(I)]PF<sub>6</sub>

Jas S. Ward<sup>a\*</sup>

<sup>a</sup> University of Jyväskylä, Department of Chemistry, Jyväskylä 40014, Finland.

E-mail: [james.s.ward@ju.fi](mailto:james.s.ward@ju.fi)

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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,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and  $^1\text{H}$ - $^{15}\text{N}$  NMR correlation spectra were recorded on a Bruker Avance III 500 MHz spectrometer at 25°C in  $\text{CD}_3\text{CN}$  or  $\text{CD}_2\text{Cl}_2$ . Chemical shifts are reported on the  $\delta$  scale in ppm using the residual solvent signal as internal standard ( $\text{CH}_3\text{CN}$  in  $\text{CD}_3\text{CN}$ :  $\delta_{\text{H}}$  1.94,  $\delta_{\text{C}}$  1.32/118.26;  $\text{CH}_2\text{Cl}_2$  in  $\text{CD}_2\text{Cl}_2$ :  $\delta_{\text{H}}$  5.32,  $\delta_{\text{C}}$  53.84), or for  $^1\text{H}$ - $^{15}\text{N}$  NMR spectroscopy, to an external  $\text{CD}_3\text{NO}_2$  standard. For the  $^1\text{H}$  NMR spectroscopy, each resonance was assigned according to the following conventions: chemical shift ( $\delta$ ) 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  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectroscopy, spectral windows of 8 ppm ( $^1\text{H}$ ) and 300 ppm ( $^{15}\text{N}$ ) 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  $^{15}\text{N}$  NMR resonances.

The single crystal X-ray data for **2·2(MeCN)**, **3\_1**, **3\_2**, and **4** were collected at 120 K using an Agilent SuperNova dual wavelength diffractometer with an Atlas detector using mirror-monochromated Cu-K $\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) radiation. The program CrysAlisPro was used for the data collection and reduction on the SuperNova diffractometers.<sup>1</sup> All structures were solved by intrinsic phasing (SHELXT)<sup>2</sup> and refined by full-matrix least squares on  $F^2$  using Olex2,<sup>3</sup> utilising the SHELXL module.<sup>4</sup> 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) or  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$  (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, MeCN = acetonitrile, TBME = <sup>t</sup>butylmethylether.

## Preparation and Characterisation Details

**3-acetaminopyridine (1):** Ligand **1** was synthesised as previously reported in the literature.<sup>5</sup> <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  8.65 (d,  $J$  = 2.2 Hz, 1H), 8.45 (s.br, 1H), 8.26 (dd,  $J$  = 4.5, 1.0 Hz, 1H), 8.02 (d,  $J$  = 8.2 Hz, 1H), 7.27 (dd,  $J$  = 8.2, 4.7 Hz, 1H), 2.08 (s, 3H); <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN)  $\delta$  170.0, 145.4, 141.9, 136.7, 127.1, 124.4, 24.14; <sup>15</sup>N NMR (<sup>1</sup>H-<sup>15</sup>N HMBC, CD<sub>3</sub>CN)  $\delta$  -63.7 (pyridinic), -254.4 (amido).

**[Ag(3-acetaminopyridine)<sub>2</sub>]PF<sub>6</sub> (2):** A solution (DCM or MeCN; 3.5 mL) of **1** (10.9 mg, 0.08 mmol) was added to an MeCN (0.5 mL) solution of AgPF<sub>6</sub> (10.1 mg, 0.04 mmol), and stirred for 15 minutes to give a colourless solution. All volatiles removed under reduced pressure to leave a white solid. Yield is quantitative. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  8.78 (d,  $J$  = 2.1 Hz, 2H), 8.59 (s.br, 2H), 8.23 (dd,  $J$  = 4.8, 1.2 Hz, 2H), 8.02 (d,  $J$  = 8.3 Hz, 2H), 7.37 (dd,  $J$  = 8.3, 4.9 Hz, 2H), 2.09 (s, 6H); <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN)  $\delta$  170.2, 146.0, 142.5, 137.4, 128.1, 125.2, 24.1; <sup>15</sup>N NMR (<sup>1</sup>H-<sup>15</sup>N HMBC, CD<sub>3</sub>CN)  $\delta$  -85.8 (pyridinic), -254.2 (amido). Crystals suitable for single crystal X-ray diffraction were obtained from a DCM:MeCN (7:1) solution of **2** vapour diffused with pentane. Crystal data for **2**: CCDC2193903, [C<sub>18</sub>H<sub>22</sub>AgN<sub>6</sub>O<sub>2</sub>]PF<sub>6</sub>, M = 607.25, colourless block, 0.10 × 0.26 × 0.38 mm<sup>3</sup>, triclinic, space group *P*-1 (No. 2), a = 7.2685(3) Å, b = 12.4304(6) Å, c = 14.1913(6) Å,  $\alpha$  = 108.995(4)°,  $\beta$  = 101.944(4)°,  $\gamma$  = 92.083(4)°, V = 1178.64(10) Å<sup>3</sup>, Z = 2, D<sub>calc</sub> = 1.711 gcm<sup>-3</sup>, F<sub>000</sub> = 608,  $\mu$  = 8.20 mm<sup>-1</sup>, T = 120.0(1) K,  $\theta_{\max}$  = 76.5°, 4755 total reflections, 4505 with  $I_o > 2\sigma(I_o)$ , R<sub>int</sub> = 0.027, 4755 data, 317 parameters, no restraints, GooF = 1.03, 0.54 < d $\Delta\rho$  < -0.55 eÅ<sup>-3</sup>, R[F<sup>2</sup> > 2 $\sigma$ (F<sup>2</sup>)] = 0.028, wR(F<sup>2</sup>) = 0.078.

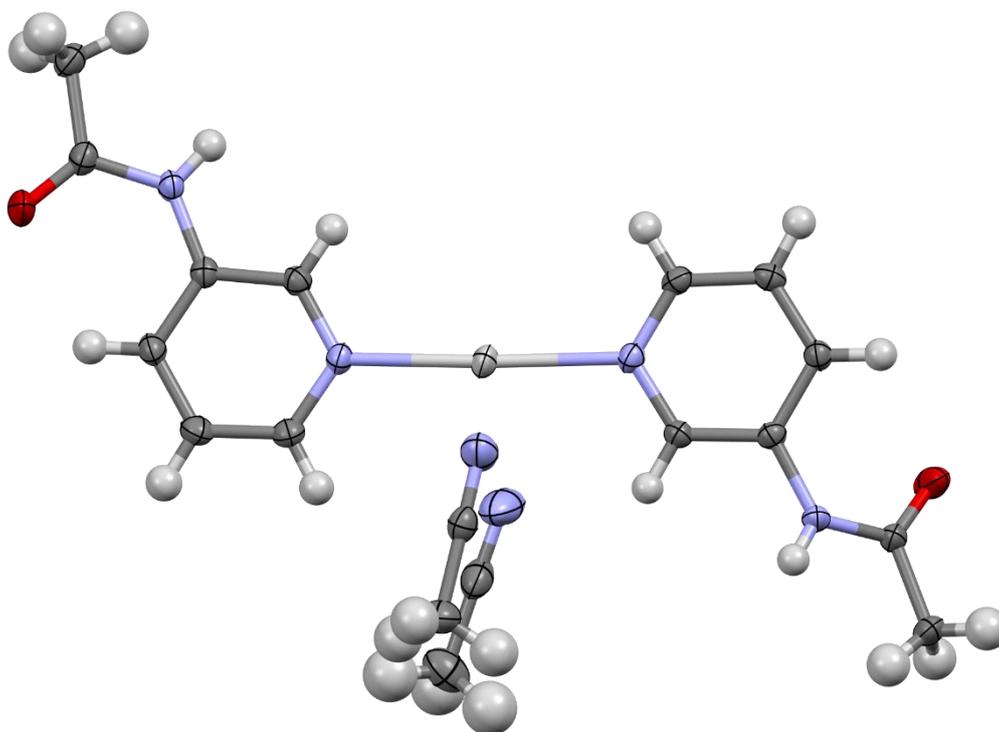


Figure S1: The X-ray crystal structure of **2·2(MeCN)** (PF<sub>6</sub> anion omitted for clarity). Colour key: light grey = silver, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

**[(3-acetaminopyridine)<sub>2</sub>]PF<sub>6</sub> (3):** Elemental iodine (10.2 mg, 0.04 mmol) was added as a solid to a solution (either 7:1 DCM:MeCN or neat MeCN; 4 mL) of **2** (21.0 mg, 0.04 mmol) to give a pale orange solution and yellow precipitate (AgI) once all the I<sub>2</sub> had dissolved (~5 minutes). The yellow precipitate was removed by filtration. Yield is quantitative. The pure complex can be isolated by precipitation with petroleum ether, with a minor loss of yield, to give a white solid. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN) δ 9.30 (s, 2H), 8.91 (s.br, 2H), 8.45 (d, *J* = 5.2 Hz, 2H), 8.12 (dd, *J* = 8.5, 0.7 Hz, 2H), 7.51 (dd, *J* = 8.3, 5.5 Hz, 2H), 2.13 (s, 6H); <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN) δ 170.6, 144.9, 141.0, 140.1, 131.9, 128.7, 24.1; <sup>15</sup>N NMR (<sup>1</sup>H-<sup>15</sup>N HMBC, CD<sub>3</sub>CN) δ -174.5 (pyridinic), -253.5 (amido).

Two crystallographic polymorphs were identified for **3**.

Crystals suitable for single crystal X-ray diffraction were obtained from a DCM:MeCN (7:1) solution of **3** vapour diffused with pentane at -20°C. Crystal data for **3\_1**: CCDC2193904, [C<sub>14</sub>H<sub>16</sub>I<sub>N<sub>4</sub>O<sub>2</sub>)]PF<sub>6</sub>, *M* = 544.18, colourless plate, 0.03 × 0.31 × 0.38 mm<sup>3</sup>, triclinic, space group *P*-1 (No. 2), *a* = 8.1008(4) Å, *b* = 10.1196(7) Å, *c* = 12.4667(6) Å, α = 98.710(5)°, β = 92.055(4)°, γ = 105.936(5)°, *V* = 968.14(10) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc</sub> = 1.867 gcm<sup>-3</sup>, *F*<sub>000</sub> = 532, μ = 14.49 mm<sup>-1</sup>, *T* = 200.0(1) K (crystals found to catastrophically shatter at temperatures below 200 K), θ<sub>max</sub> = 76.8°, 3914 total reflections, 3523 with *I*<sub>o</sub> > 2σ(*I*<sub>o</sub>), *R*<sub>int</sub> = 0.055, 3914 data, 289 parameters, 126 restraints, *Goof* = 1.03, 2.33 < Δρ < -1.45 eÅ<sup>-3</sup>, *R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.061, *wR*(*F*<sup>2</sup>) = 0.174.</sub>

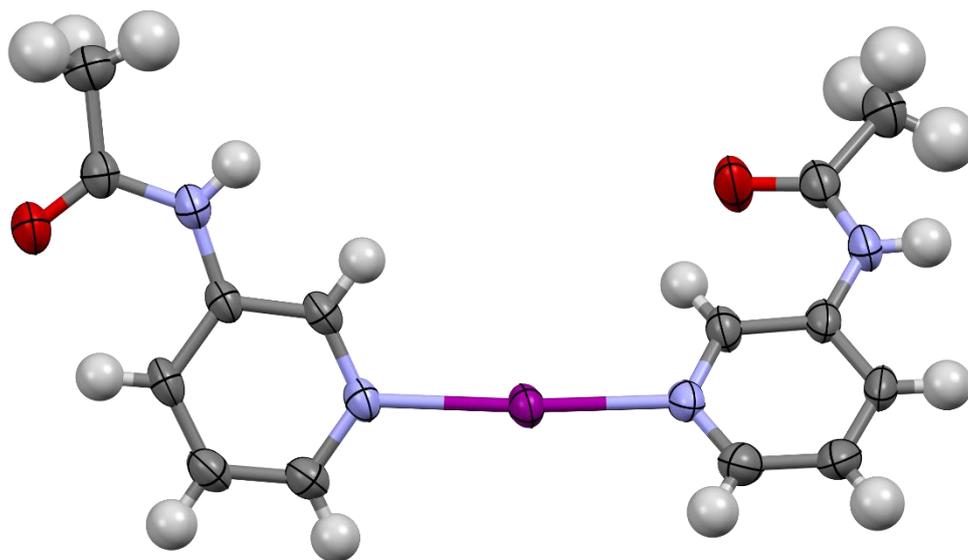


Figure S2: The X-ray crystal structure of **3\_1** (PF<sub>6</sub> anion omitted for clarity). Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

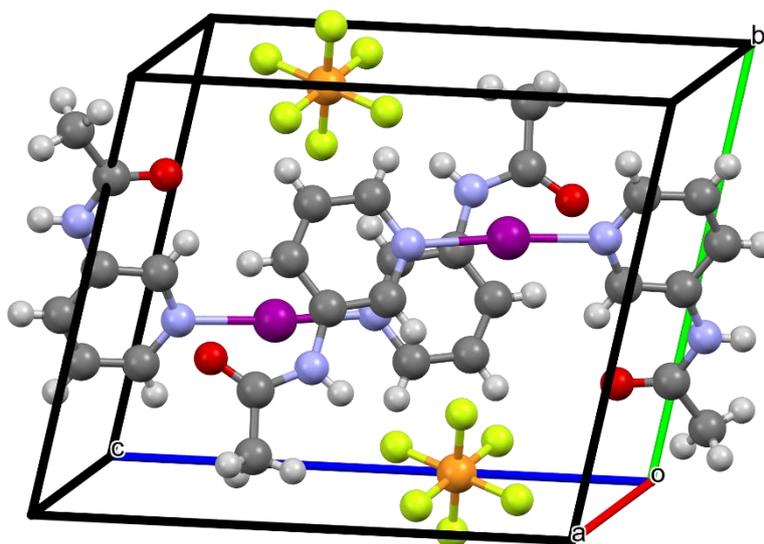


Figure S3: The unit cell packing of **3\_1** (disordered PF<sub>6</sub> anion positions omitted for clarity).

Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of an MeCN solution of **3**. Crystal data for **3\_2**: CCDC2193905, [C<sub>14</sub>H<sub>16</sub>IN<sub>4</sub>O<sub>2</sub>]PF<sub>6</sub>, M = 544.18, colourless plate, 0.01 × 0.16 × 0.17 mm<sup>3</sup>, triclinic, space group *P*-1 (No. 2), a = 9.9264(3) Å, b = 13.3351(4) Å, c = 14.6878(5) Å, α = 103.504(3)°, β = 99.401(2)°, γ = 90.172(2)°, V = 1863.36(10) Å<sup>3</sup>, Z = 4, D<sub>calc</sub> = 1.940 gcm<sup>-3</sup>, F<sub>000</sub> = 1064, μ = 15.06 mm<sup>-1</sup>, T = 120.0(1) K, θ<sub>max</sub> = 76.6°, 7610 total reflections, 6527 with I<sub>o</sub> > 2σ(I<sub>o</sub>), R<sub>int</sub> = 0.054, 7610 data, 509 parameters, no restraints, GooF = 1.08, 6.17 < dΔρ < -1.35 eÅ<sup>-3</sup>, R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.056, wR(F<sup>2</sup>) = 0.151.

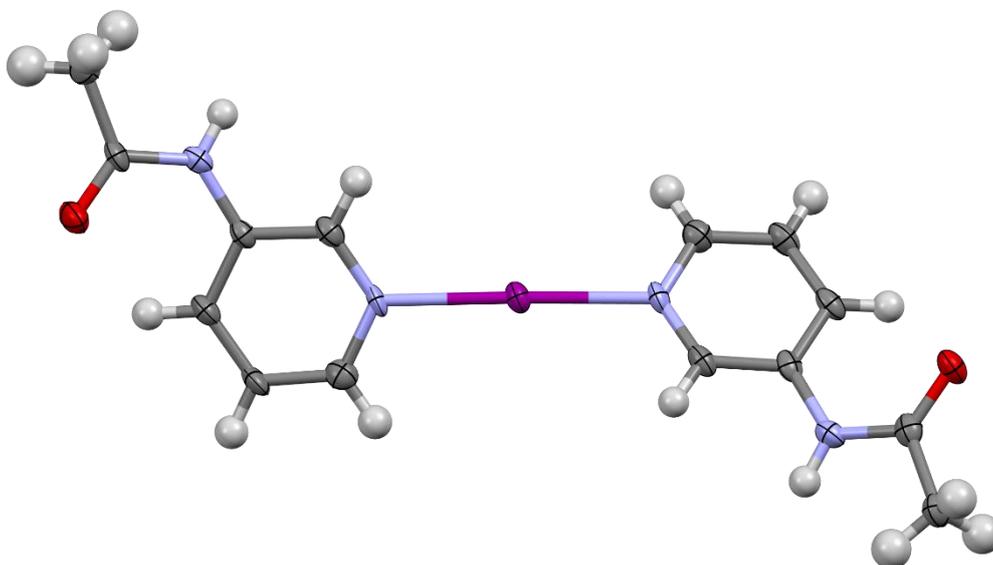


Figure S4: The X-ray crystal structure of **3\_2** (2<sup>nd</sup> crystallographically independent cation and PF<sub>6</sub> anions omitted for clarity). Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

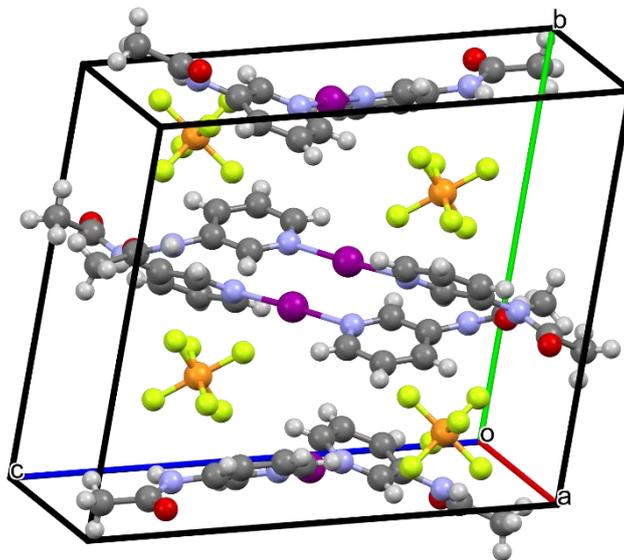


Figure S5: The unit cell packing of **3\_1**.

**[3-acetamido-1-(1-iodo-2-methylpropan-2-yl)pyridin-1-ium]PF<sub>6</sub> (4)**: A solution (either 7:1 DCM:MeCN or neat MeCN; 4 mL) of **3** (21.8 mg, 0.04 mmol) was vapour diffused with TBME (16 mL) over 48 hours to give the product as colourless crystals, which were decanted and dried to give a colourless crystalline solid. Yield = 12.0 mg (0.026 mmol, 65%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN) δ 9.48 (s, 1H), 9.15 (s.br, 1H), 8.53 (d, *J* = 6.2 Hz, 1H), 8.36 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.97 (dd, *J* = 8.2, 6.6 Hz, 1H), 3.82 (s, 2H), 2.19 (s, 3H), 1.94 (s, 6H; overlapping with CH<sub>3</sub>CN at 1.94 ppm); <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN) δ 171.1, 140.6, 136.9, 135.2, 132.7, 129.1, 71.8, 27.2, 24.2, 17.1; <sup>15</sup>N NMR (<sup>1</sup>H-<sup>15</sup>N HMBC, CD<sub>3</sub>CN) δ -154.5 (pyridinic), -252.9 (amido).

*NMR analyses also performed in CD<sub>2</sub>Cl<sub>2</sub> due to the overlap of the residual CH<sub>3</sub>CN and water peaks with some of the alkyl resonances when performed in CD<sub>3</sub>CN.* <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 9.32 (s, 1H), 8.96 (dd, *J* = 8.6, 1.1 Hz, 1H), 8.92 (s, 1H), 8.27 (d, *J* = 6.2 Hz, 1H), 7.95 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.76 (s, 2H), 2.29 (s, 3H), 2.02 (s, 6H); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 171.1, 141.2, 135.4, 134.3, 131.9, 128.5, 71.4, 27.7, 27.1, 24.4, 15.8; <sup>15</sup>N NMR (<sup>1</sup>H-<sup>15</sup>N HMBC, CD<sub>2</sub>Cl<sub>2</sub>) δ -154.6 (pyridinic), -254.0 (amido).

Crystals suitable for single crystal X-ray diffraction were obtained from a DCM:MeCN (7:1) solution of **3** vapour diffused with TBME. Crystal data for **4**: CCDC2193906, [C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O]PF<sub>6</sub>, *M* = 464.13, colourless needle, 0.05 × 0.08 × 0.24 mm<sup>3</sup>, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 10.4701(1) Å, *b* = 14.7904(1) Å, *c* = 10.5256(1) Å, β = 100.659(1)°, *V* = 1601.84(2) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.925 gcm<sup>-3</sup>, *F*<sub>000</sub> = 904, μ = 17.28 mm<sup>-1</sup>, *T* = 120.0(1) K, θ<sub>max</sub> = 76.2°, 3333 total reflections, 3248 with *I*<sub>o</sub> > 2σ(*I*<sub>o</sub>), *R*<sub>int</sub> = 0.021, 3333 data, 202 parameters, no restraints, *Goof* = 1.04, 1.19 < *d*Δ*p* < -0.66 eÅ<sup>-3</sup>, *R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.023, *wR*(*F*<sup>2</sup>) = 0.058.



## Reaction of Complex **3** with <sup>t</sup>BuOMe

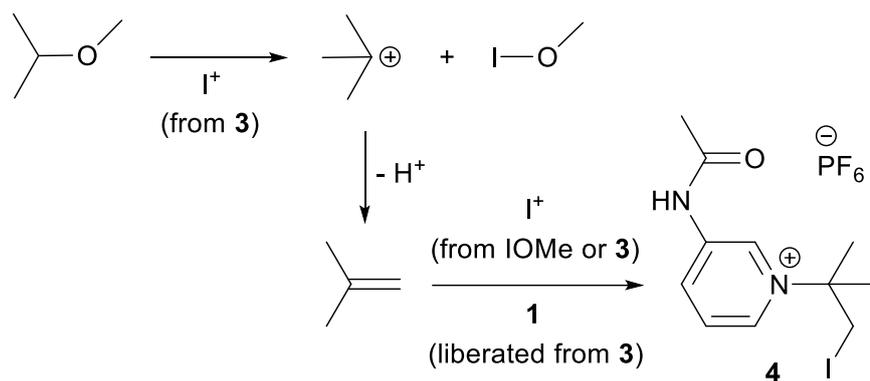


Figure S7: A proposed mechanism to explain the observation of complex **4** as the major product upon reaction of complex **3** with <sup>t</sup>BuOMe, which relies upon the <sup>t</sup>BuOMe initially reacting with a source of " $I^+$ " to form 2-methylpropene. The 2-methylpropene goes on to react with a source of  $I^+$  and a molecule of **1** to form complex **4**.

# NMR Spectra

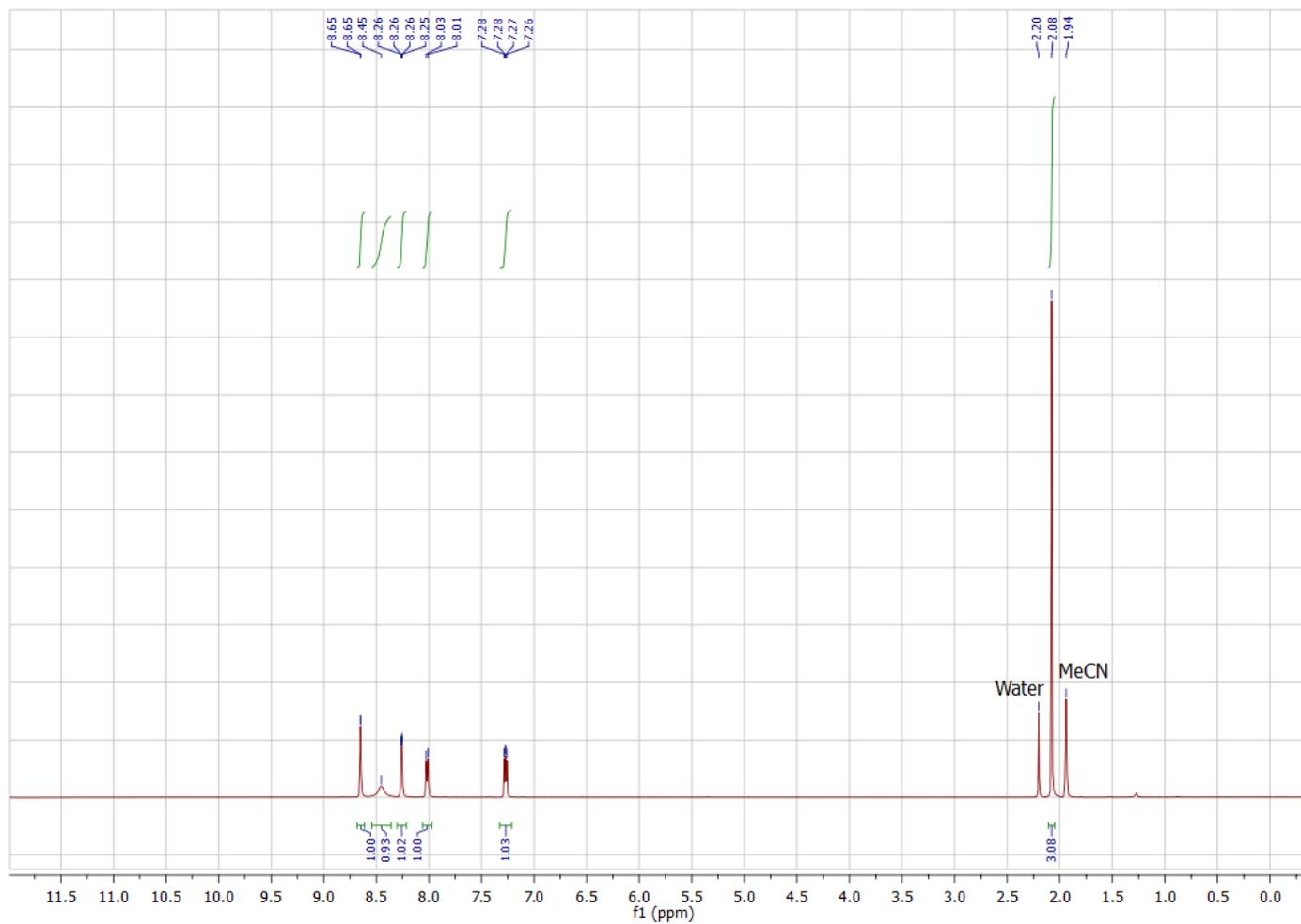


Figure S8: The  $^1\text{H}$  NMR spectrum of ligand **1** in  $\text{CD}_3\text{CN}$ .

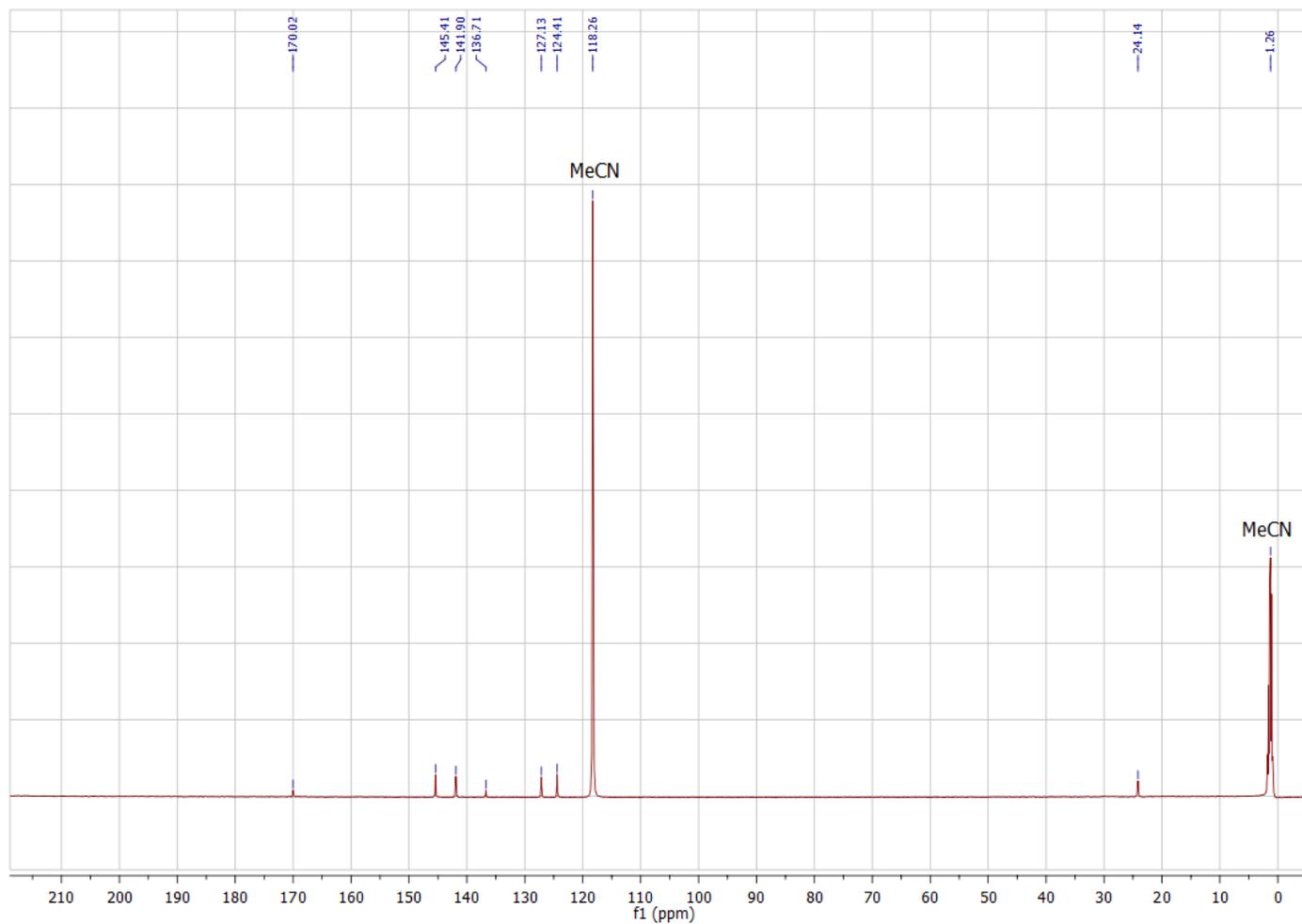


Figure S9: The  $^{13}\text{C}$  NMR spectrum of ligand 1 in  $\text{CD}_3\text{CN}$ .

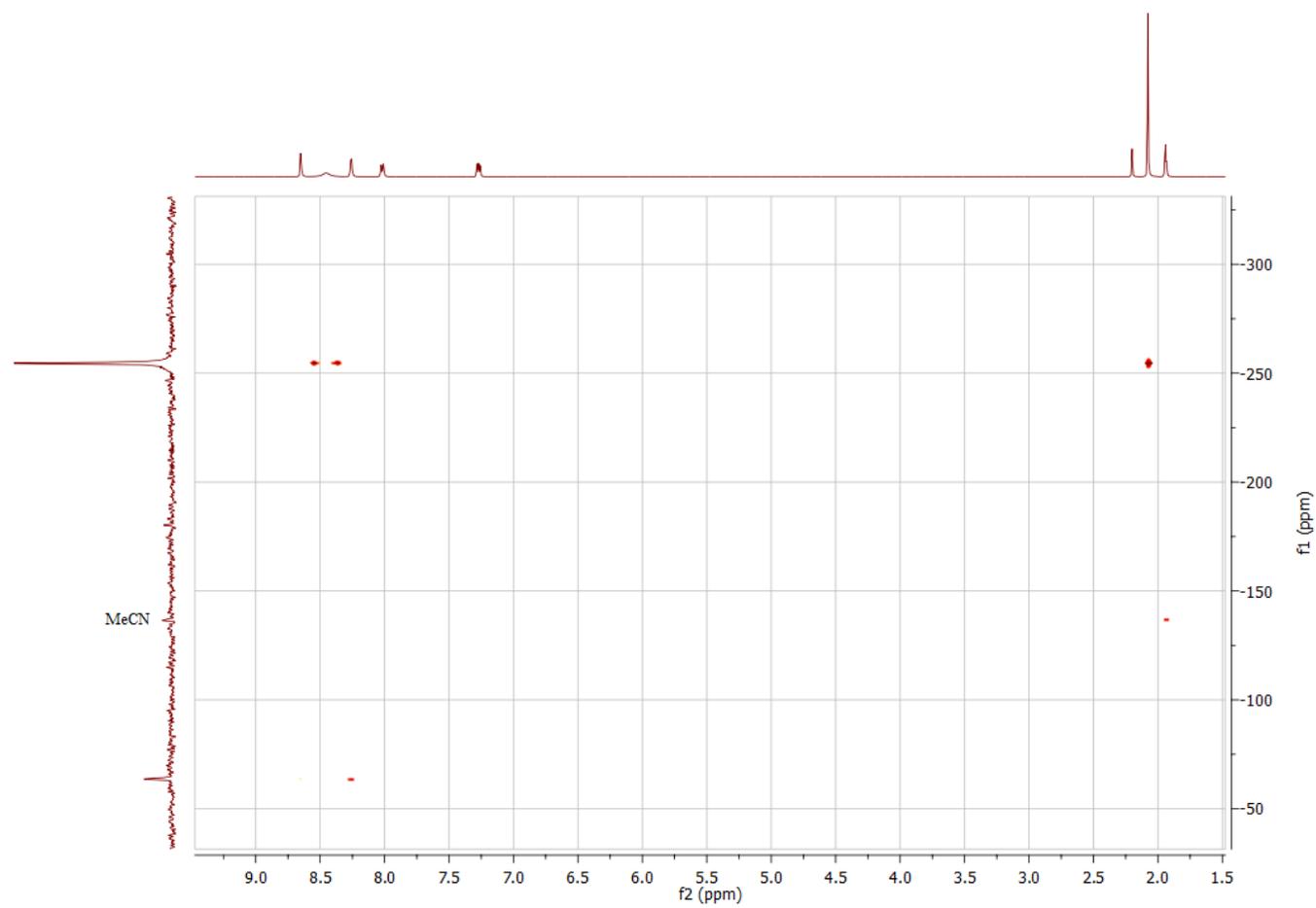


Figure S10: The  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectrum of ligand **1** in  $\text{CD}_3\text{CN}$ .

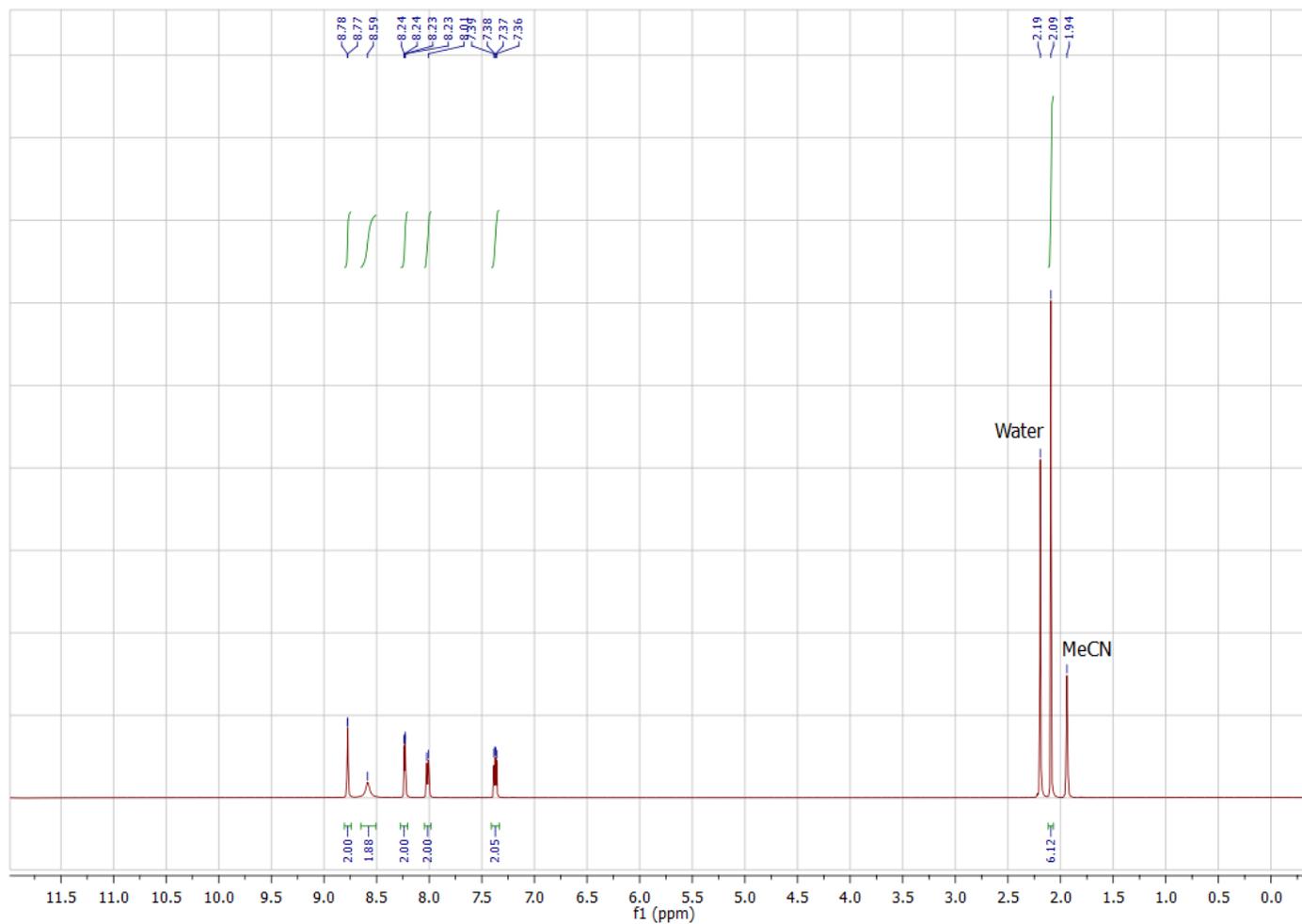


Figure S11: The  $^1\text{H}$  NMR spectrum of complex 2 in  $\text{CD}_3\text{CN}$ .

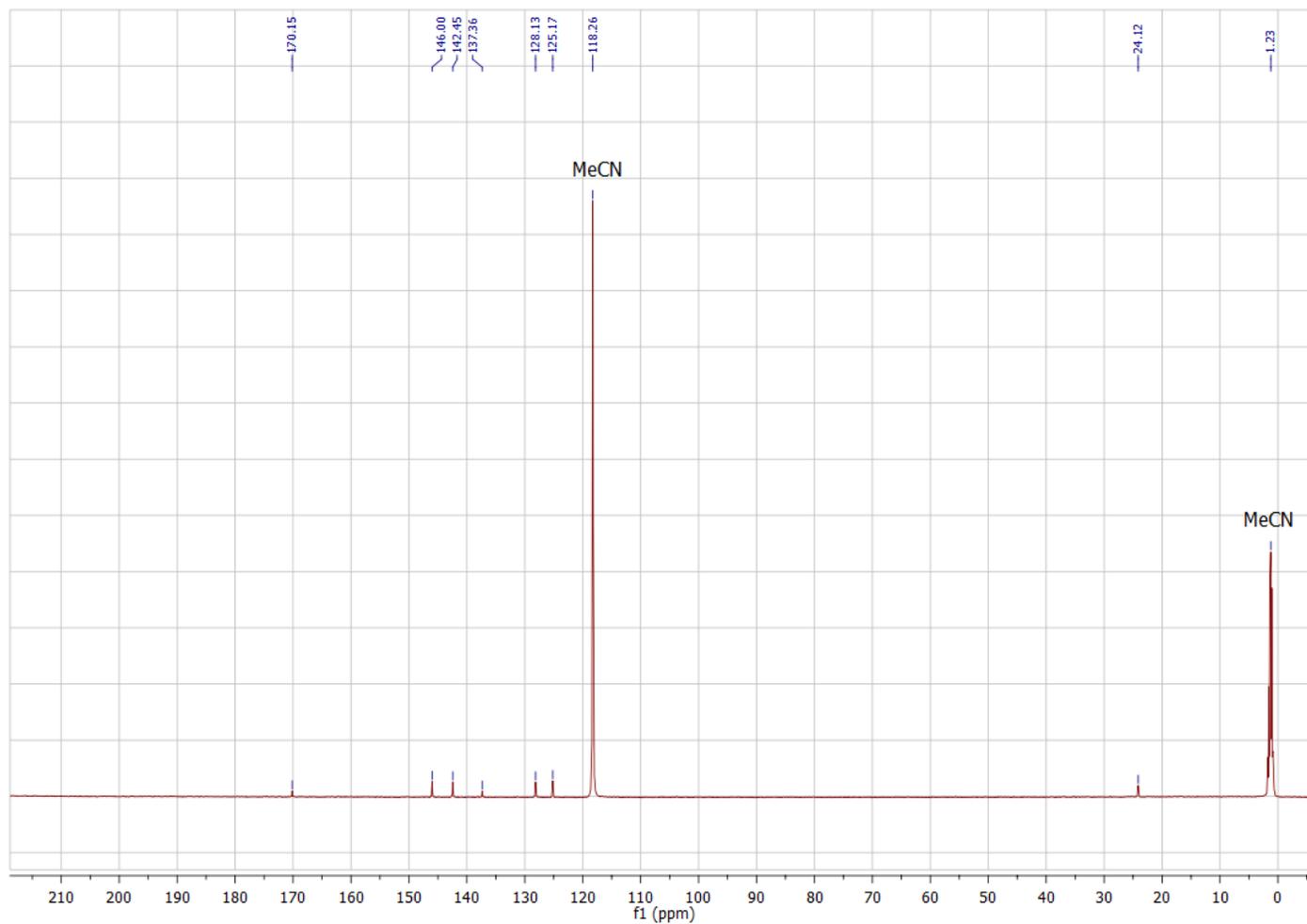


Figure S12: The  $^{13}\text{C}$  NMR spectrum of complex 2 in  $\text{CD}_3\text{CN}$ .

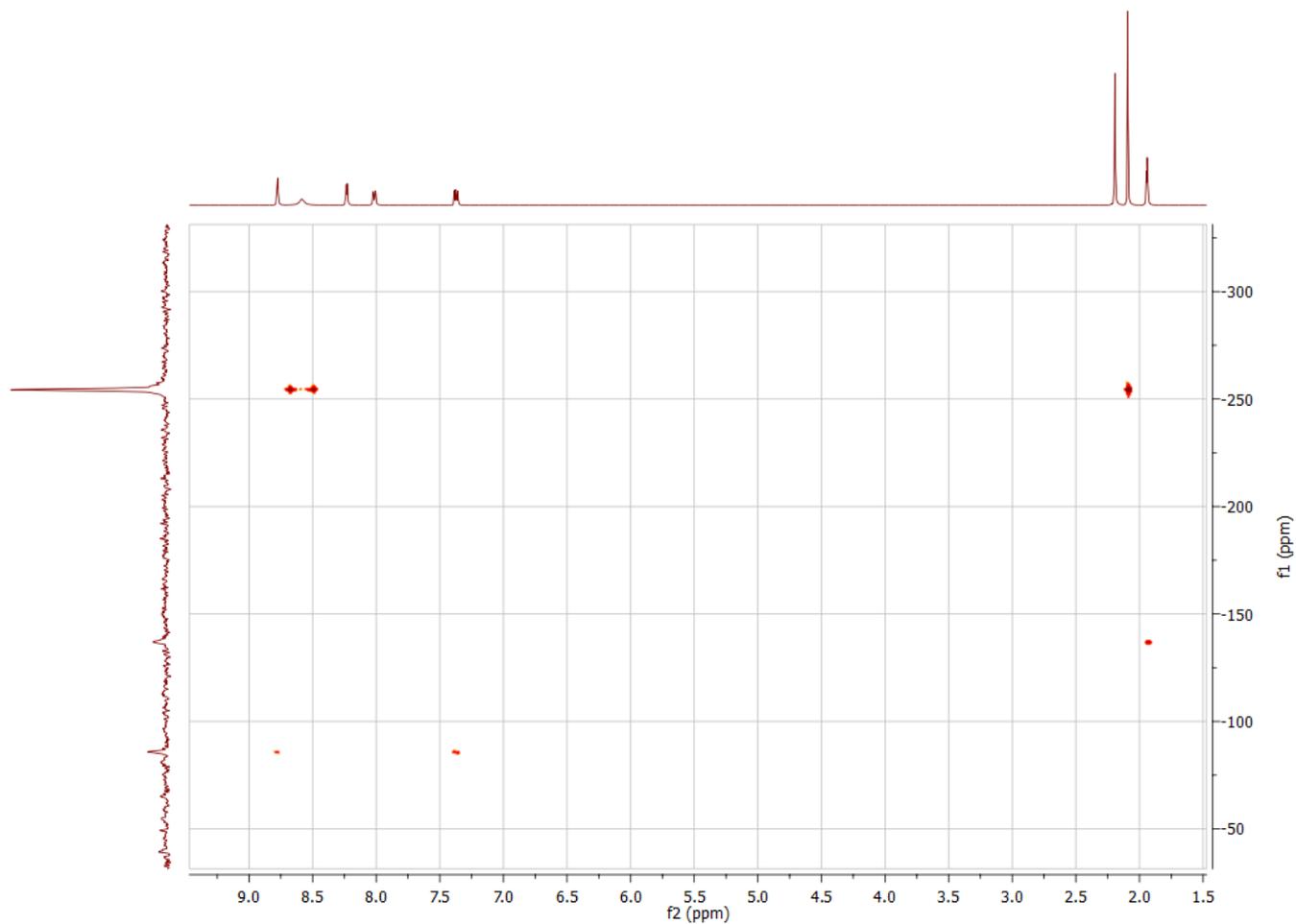


Figure S13: The  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectrum of complex **2** in  $\text{CD}_3\text{CN}$ .

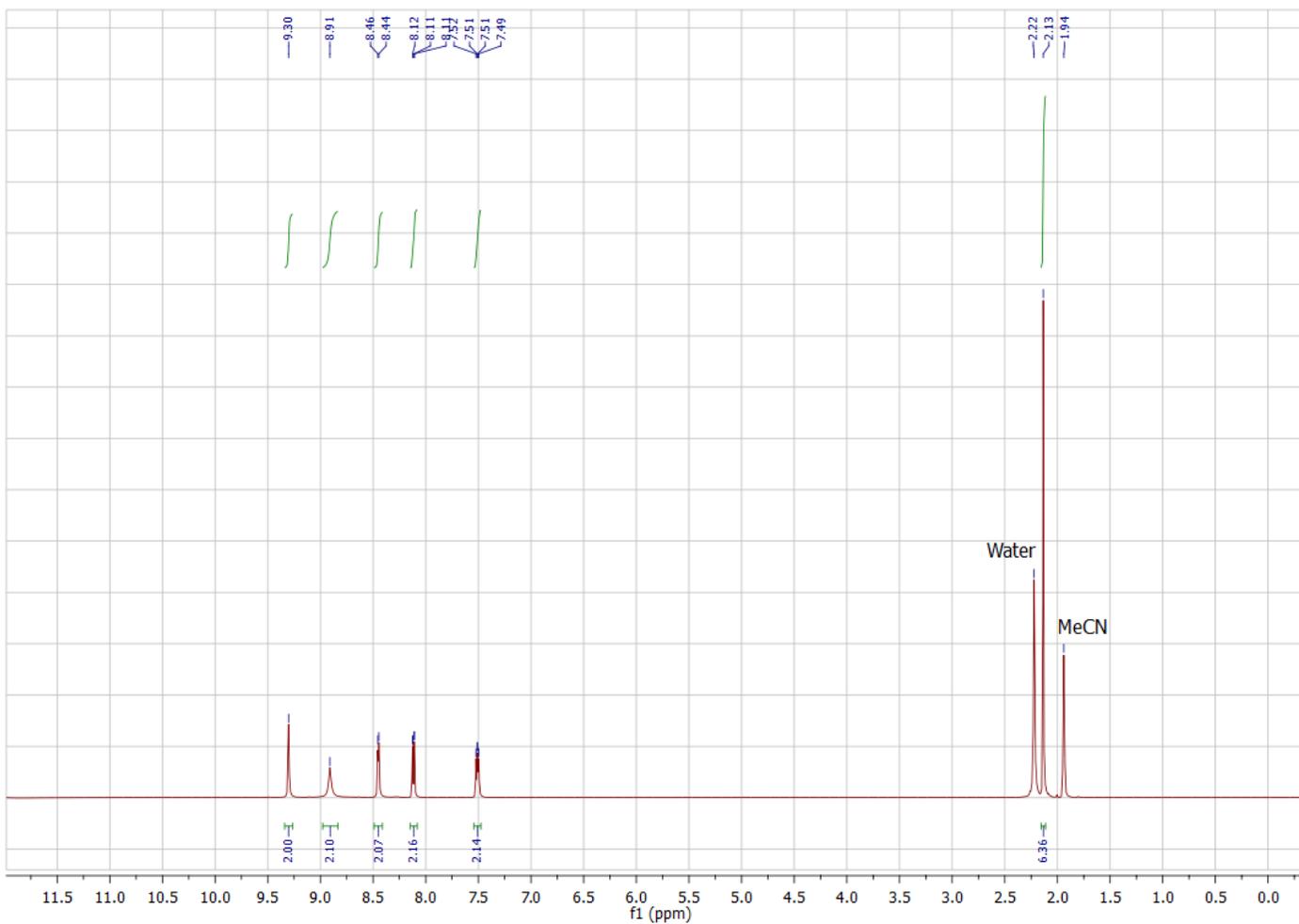


Figure S14: The  $^1\text{H}$  NMR spectrum of complex 3 in  $\text{CD}_3\text{CN}$ .

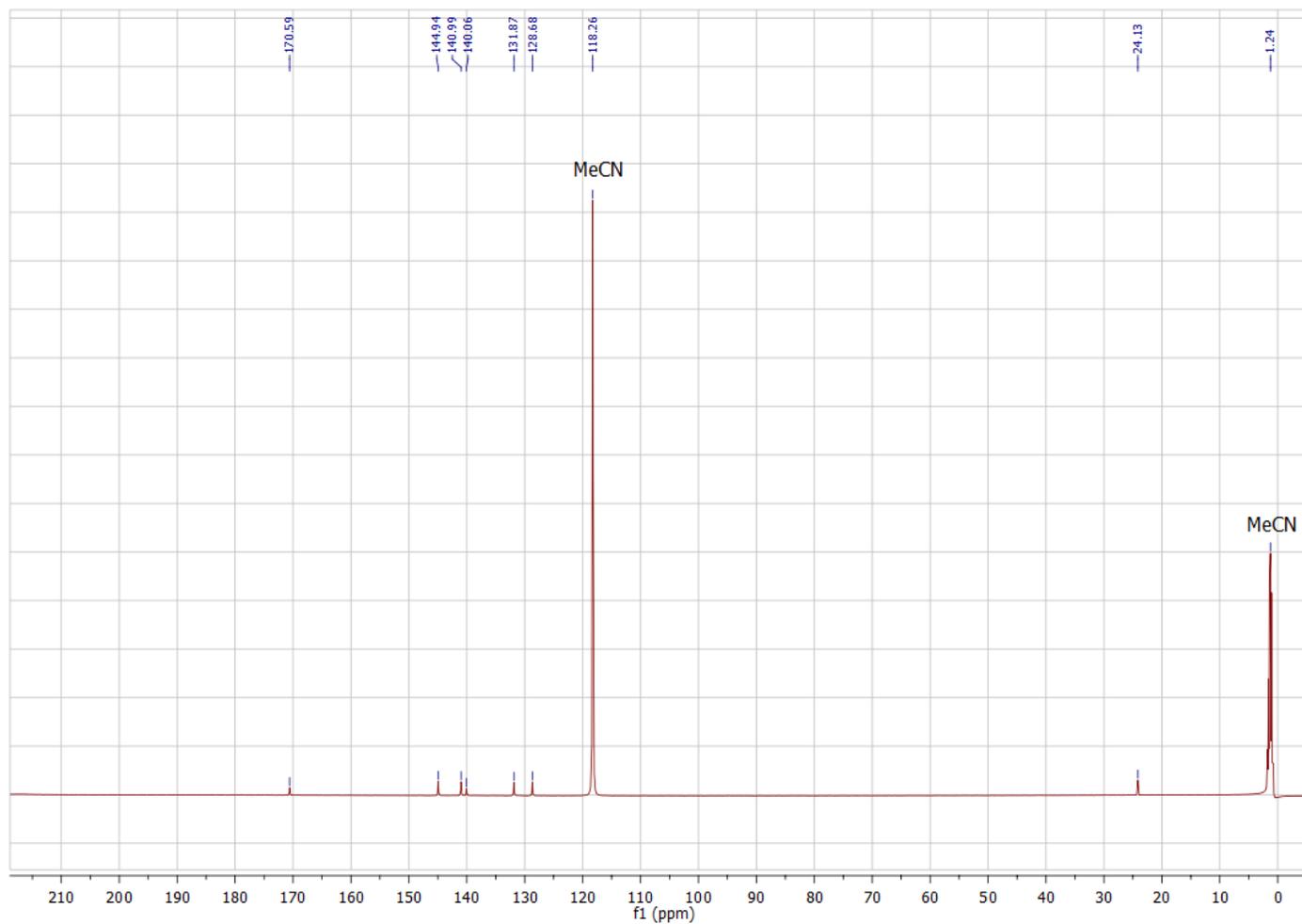


Figure S15: The  $^{13}\text{C}$  NMR spectrum of complex 3 in  $\text{CD}_3\text{CN}$ .

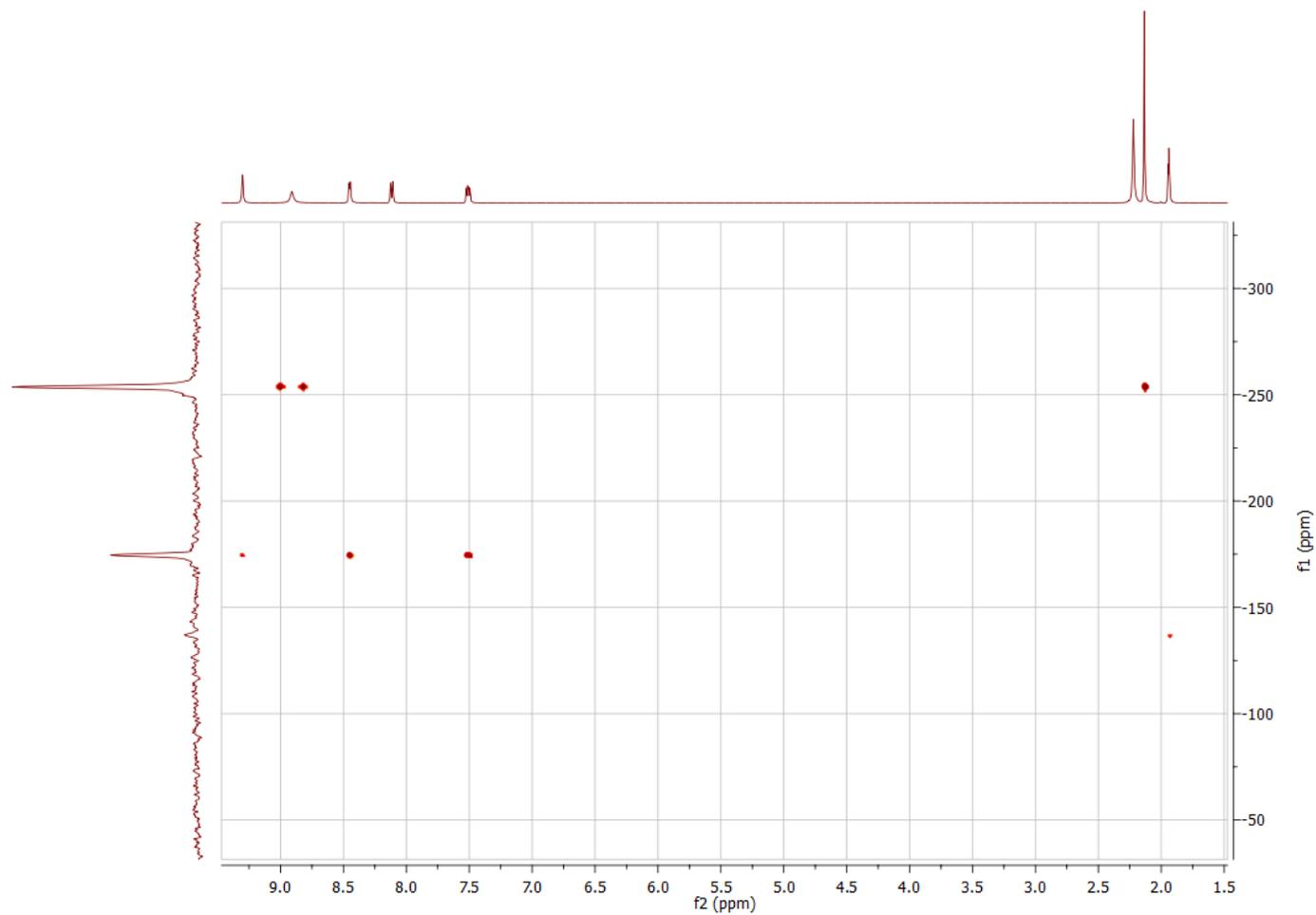


Figure S16: The  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectrum of complex **3** in  $\text{CD}_3\text{CN}$ .

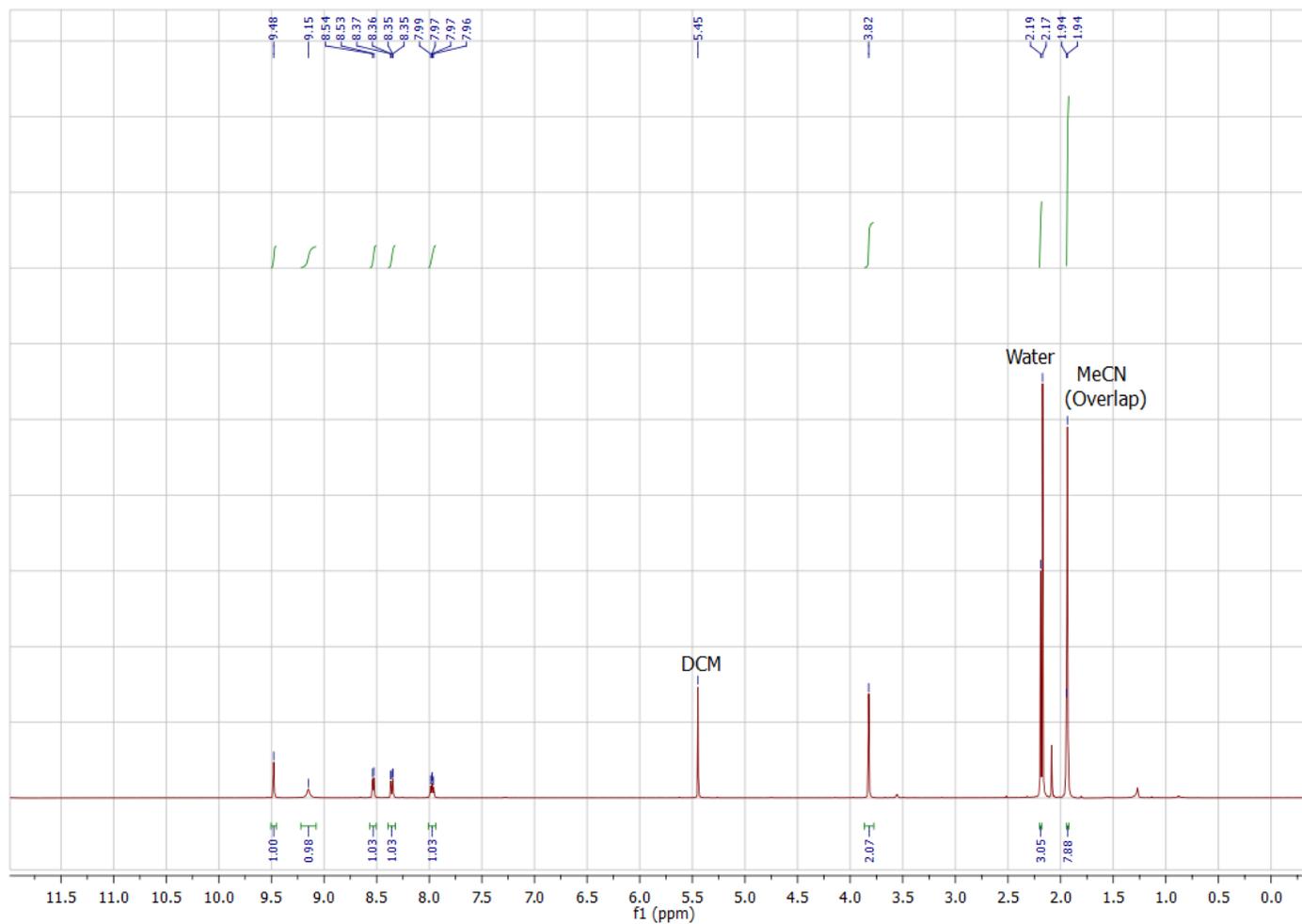


Figure S17: The  $^1\text{H}$  NMR spectrum of complex 4 in  $\text{CD}_3\text{CN}$ .

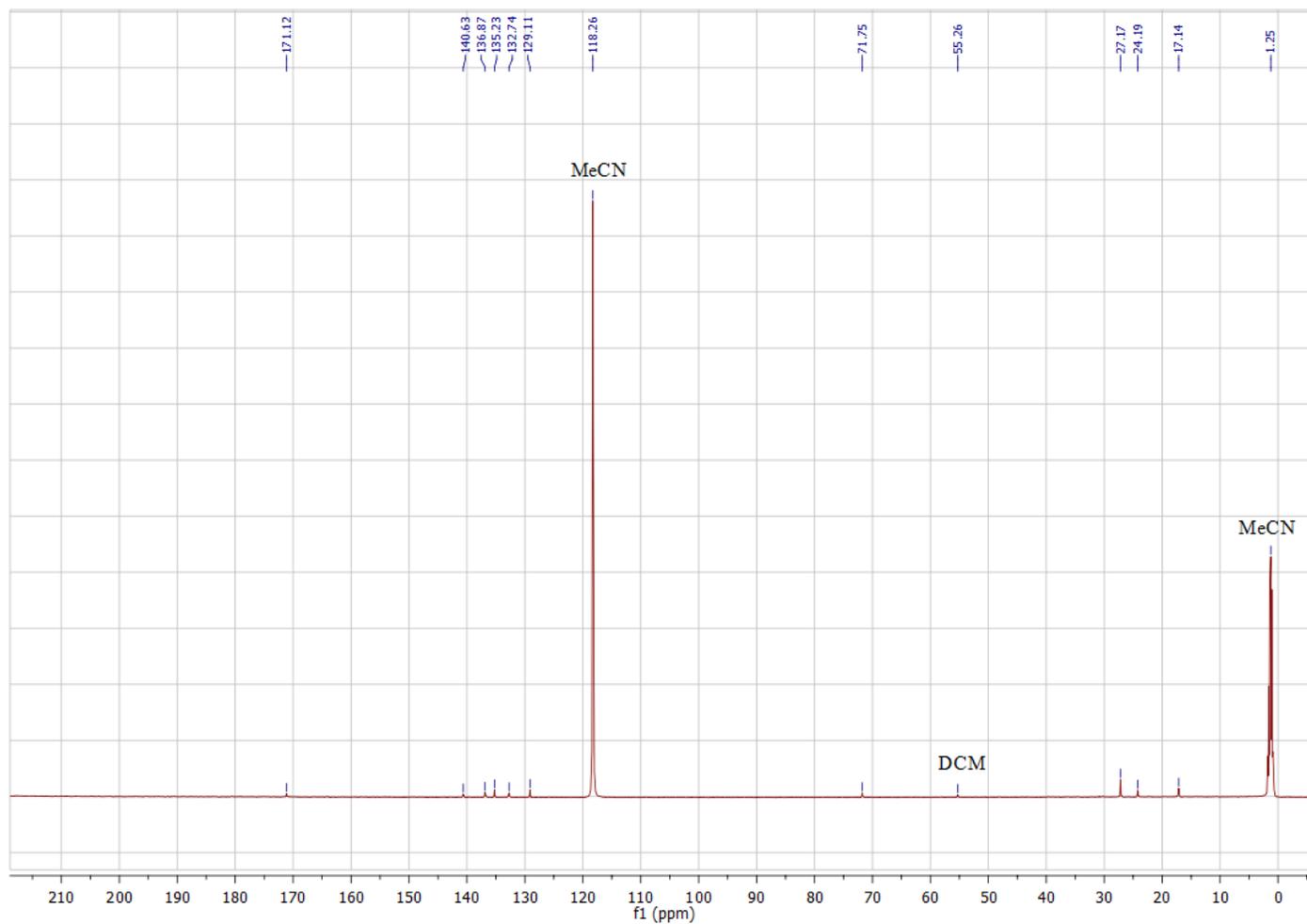


Figure S18: The  $^{13}\text{C}$  NMR spectrum of complex 4 in  $\text{CD}_3\text{CN}$ .

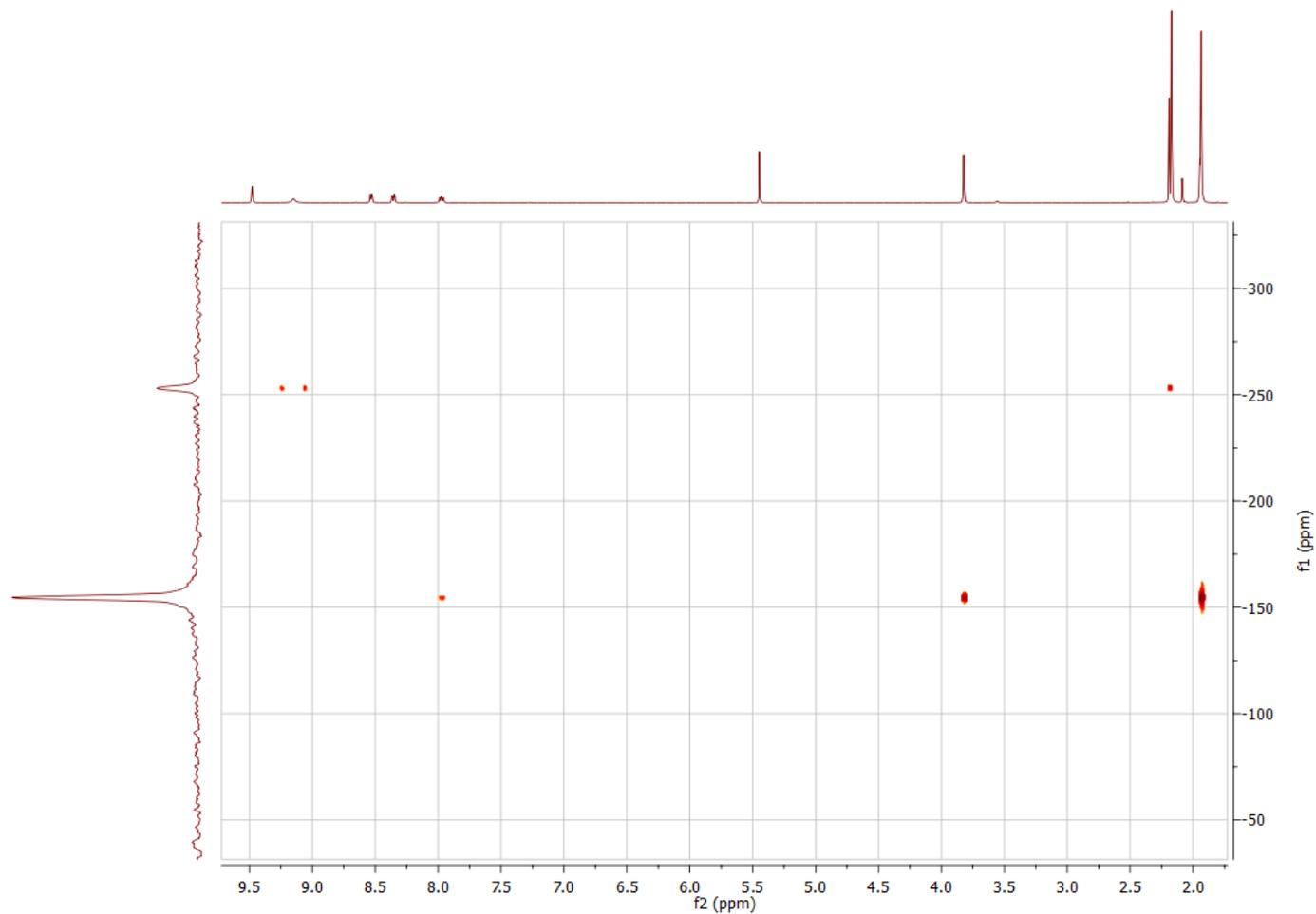


Figure S19: The  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectrum of complex **4** in  $\text{CD}_3\text{CN}$ .

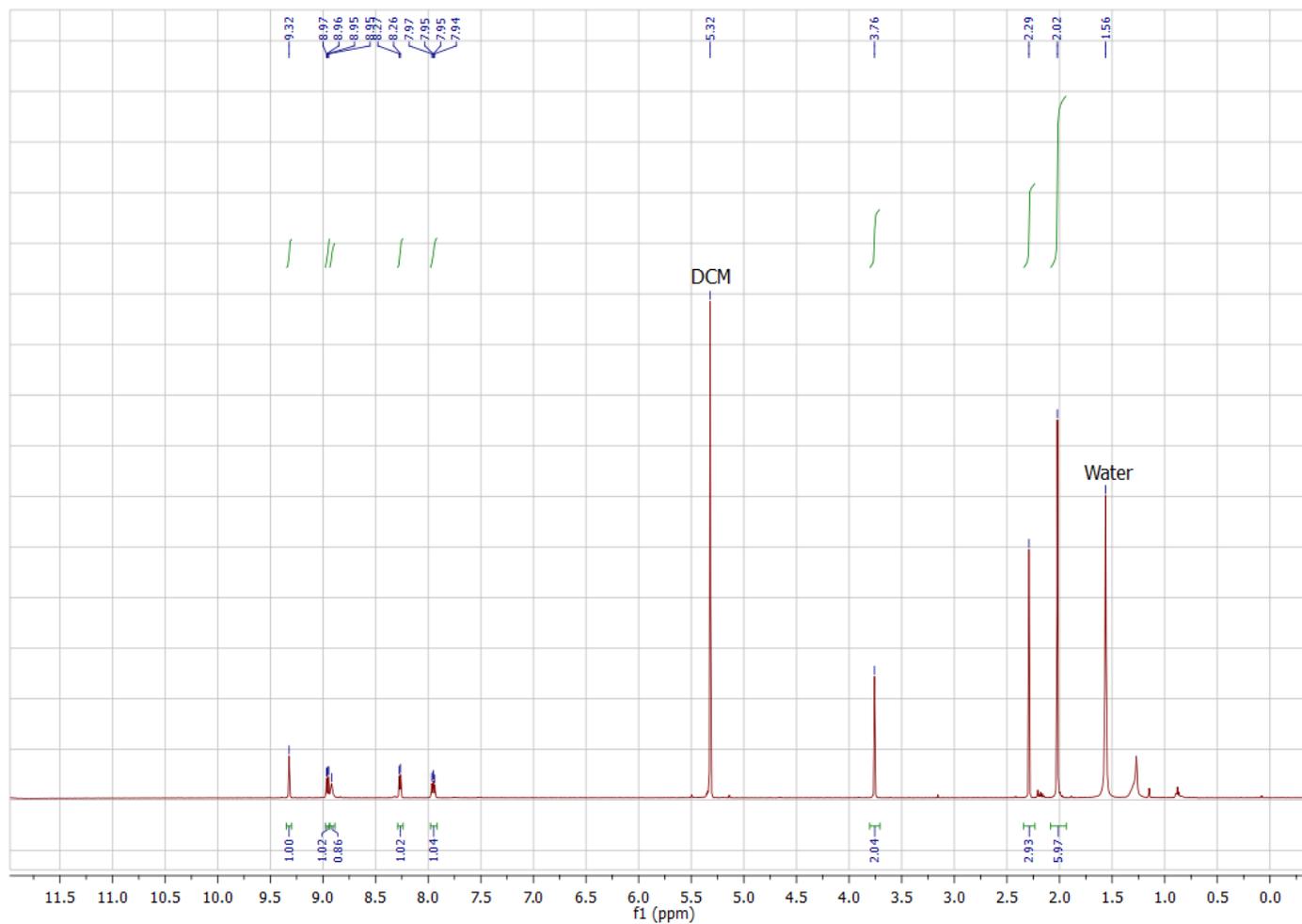


Figure S20: The  $^1\text{H}$  NMR spectrum of complex 4 in  $\text{CD}_2\text{Cl}_2$ .

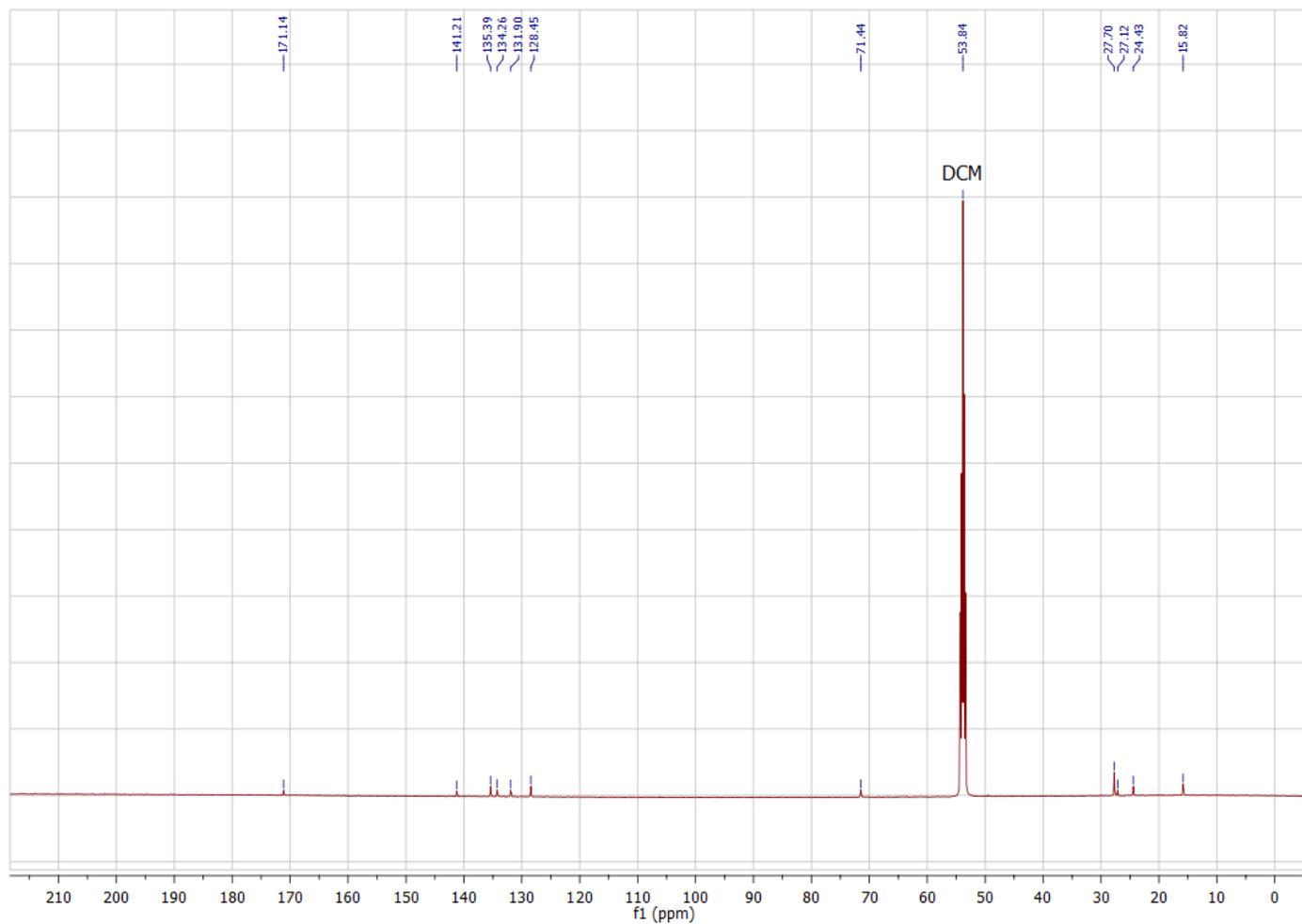


Figure S21: The  $^{13}\text{C}$  NMR spectrum of complex 4 in  $\text{CD}_2\text{Cl}_2$ .

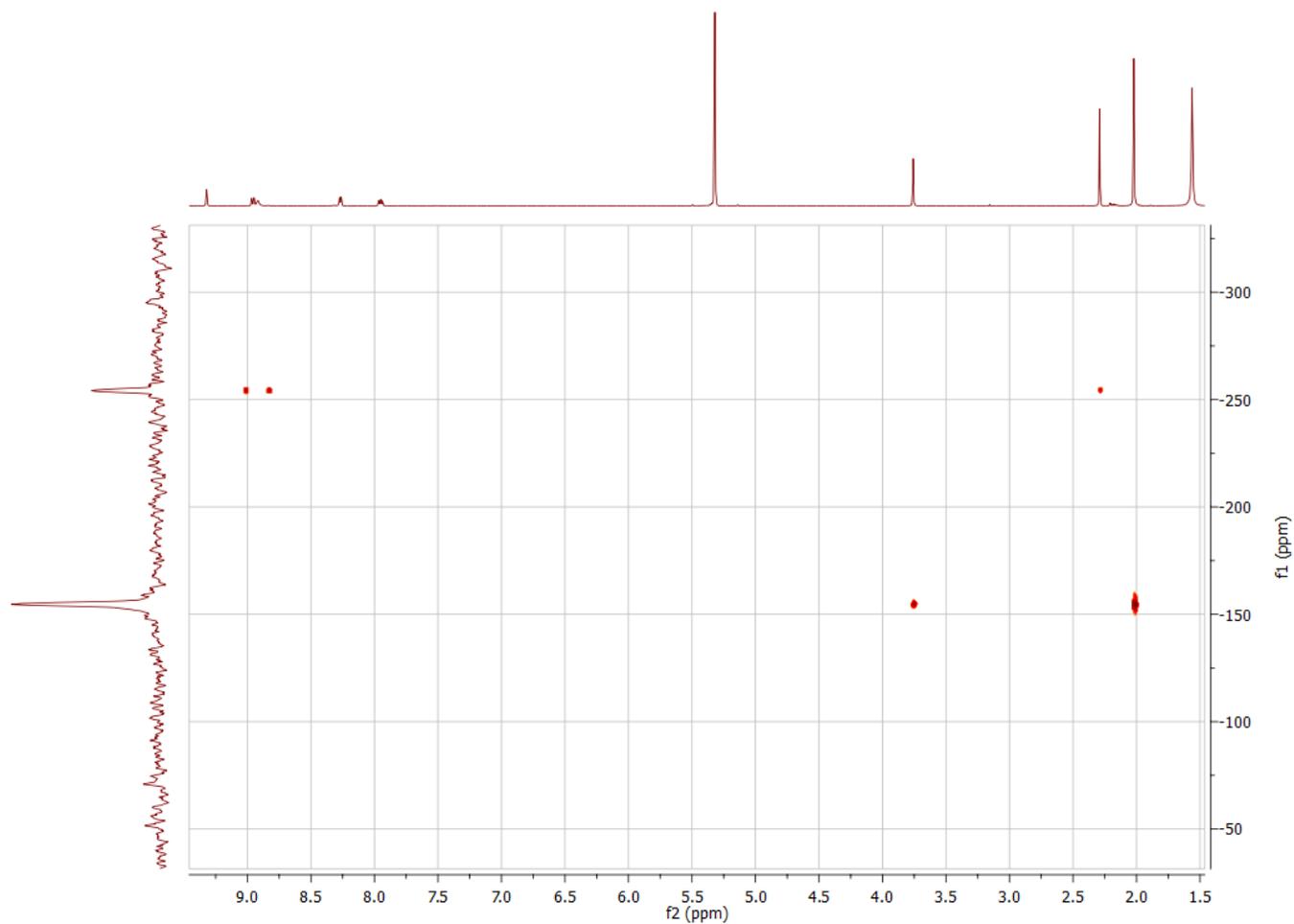


Figure S22: The  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectrum of complex 4 in  $\text{CD}_2\text{Cl}_2$ .

## References

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