Supporting Information

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Iodination of Antipyrine with [N-I-N]$^+$ and Carbonyl Hypoiodite Iodine(I) Complexes

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General Considerations

All reagents and solvents were obtained from commercial suppliers and used without further purification, except for CH_2Cl_2 used for the reactivity studies which was dried by passing degassed solvent through activated alumina columns (MBraun SPS-800 Series solvent purification system), and PhC(O)OAg which was prepared according to a literature procedure.[1] For structural NMR assignments, ^{1}H NMR and ^{1}H-^{15}N HMBC correlation spectra were recorded on a Bruker Avance III 500 MHz spectrometer at 25°C in CD_2Cl_2. 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), or for ^{1}H-^{15}N NMR spectroscopy, to an external CD_3NO_2 standard. For the ^{1}H NMR spectroscopy, each resonance was assigned according to the following conventions: chemical shift (δ) measured in ppm, observed multiplicity, observed coupling constant (*J* Hz), and number of hydrogens. Multiplicities are denoted as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad).

The single crystal X-ray data for [**2**-I-**2**]SbF_6, [**4**-I-**4**]PF_6, and iodo-antipyrine were collected at 120 K using an Agilent SuperNova dual wavelength diffractometer with an Atlas detector using mirror-monochromated Cu-Kα (λ = 1.54184 Å) radiation. The single crystal X-ray data for [**3**-I-**3**]PF_6 was 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[2] was used for the data collection and DENZO/SCALEPACK[3] for the data reduction. All structures were solved by intrinsic phasing (SHELXT)[4] and refined by full-matrix least squares on F^2 using Olex2,[5] utilising the SHELXL module.[6] Anisotropic displacement parameters were assigned to non-H atoms and isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with U_{iso}(H) = 1.2 U_{eq}(aromatic) or U_{iso}(H) = 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 following abbreviations are used: DCM = dichloromethane, DIPE = diisopropylether, DMAP = 4-dimethylaminopyridine, MeCN = acetonitrile, 4-Mepy = 4-methylpyridine, OTf = trifluoromethanesulfonate (triflate) anion, py = pyridine.

Nomenclature Key

pyridine (py)	**1**
4-dimethylaminopyridine (DMAP)	**2**
4-methylpyridine (4-Mepy)	**3**
methyl pyridine-4-carboxylate (4-nico)	**4**
4-cyanopyridine (4-CNpy)	**5**

Synthesis of Iodine(I) Species

All iodine(I) complexes were prepared using the same quantitative general methods, which are given below using [**1**-I-**1**]BF_4 as an example.

[I(pyridine)$_2$]BF_4 ([**1**-I-**1**]BF_4): A solution of pyridine (**1**; 0.121 mL, 1.5 mmol) in DCM (7 mL) was added to a solution of $AgBF_4$ (146 mg, 0.75 mmol) in MeCN (2.5 mL) to give a colourless solution that was stirred for 15 minutes. I_2 (190 mg, 0.75 mmol) was added as a DCM (2 mL) solution to give a peach-coloured solution with a yellow precipitate once all the I_2 had been introduced. After being stirred for 60 minutes, the reaction was filtered to remove the yellow precipitate and the product was precipitated from the filtrate with petroleum ether (40-60°C) to give a white solid. The solid was sonicated in pentane (3 × 10 mL) to remove excess I_2, and further repeated as necessary until the filtrate was colourless. The product was dried under reduced pressure to give a white solid (189.1 mg, 0.51 mmol, 68%). The NMR spectra for this complex matched those previously reported.[7]

Old sample (~2 years) of [I(pyridine)$_2$]BF_4 ([**1**-I-**1**]BF_4): Found by ^{1}H NMR integration to contain a 70% impurity. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.78 (dd, *J* = 6.2, 1.3 Hz, 4H, [**1**-I-**1**]BF_4), 8.60 (dd, *J* = 5.9, 1.4 Hz, 2.8H, impurity), 8.22 (tt, *J* = 7.8, 1.3 Hz, 2H, [**1**-I-**1**]BF_4), 7.97 – 7.89 (m, 1.4H, impurity), 7.63 (dd, *J* = 7.6, 6.4 Hz, 4H, [**1**-I-**1**]BF_4), 7.51 – 7.42 (m, 2.8H, impurity); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -174.5 ([**1**-I-**1**]BF_4), -103.2 (impurity).

[I(pyridine)$_2$]PF_6 ([**1**-I-**1**]PF_6): Prepared the same as [**1**-I-**1**]BF_4 using $AgPF_6$ (316 mg, 1.25 mmol) instead of $AgBF_4$. The product was precipitated as a white solid (409.9 mg, 0.95 mmol, 76%). The NMR spectra for this complex matched those previously reported.[8]

[I(DMAP)$_2$]BF_4 ([**2**-I-**2**]BF_4): Prepared the same as [**1**-I-**1**]BF_4 using $AgBF_4$ (117 mg, 0.6 mmol) and DMAP (**2**; 147 mg, 1.2 mmol) instead of pyridine. The product was precipitated as a white solid (168.6 mg, 0.37 mmol, 61%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.05 (d, *J* = 6.3 Hz, 4H), 6.50 (d, *J* = 7.2 Hz, 4H), 3.09 (s, 12H); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -215.9 (pyridinic), -306.4 (NMe_2).

[I(DMAP)$_2$]PF_6 ([**2**-I-**2**]PF_6): Prepared the same as [**1**-I-**1**]BF_4 using $AgPF_6$ (316 mg, 1.25 mmol) and DMAP (**2**; 305 mg, 2.5 mmol) instead of $AgBF_4$ and pyridine, respectively. The product was precipitated as a white solid (574.9 mg, 1.1 mmol, 89%). The NMR spectra for this complex matched those previously reported.[8]

[I(DMAP)$_2$]SbF_6 ([**2**-I-**2**]SbF_6): Prepared the same as [**1**-I-**1**]BF_4 using $AgSbF_6$ (206 mg, 0.6 mmol) and DMAP (**2**; 147 mg, 1.2 mmol) instead of $AgBF_4$ and pyridine, respectively. The product was precipitated as a white solid (182.8 mg, 0.3 mmol, 50%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.05 (d, *J* = 6.9 Hz,4), 6.49 (d, *J* = 6.9 Hz, 4H), 3.10 (s, 12H); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -215.8 (pyridinic), -306.6 (NMe_2). Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution of the complex vapour diffused with DIPE. Crystal data for [**2**-I-**2**]SbF_6: CCDC-2208422, $[C_{14}H_{20}IN_4]SbF_6$, M = 606.99, colourless block, 0.05 x 0.08 x 0.10 mm, monoclinic, space group *C*2/*m*, a =

25.9324(15) Å, b = 10.7459(7) Å, c = 8.4481(5) Å, β = 92.962(6)°, V = 2351.1(2) Å^3, Z = 4, D_{calc} = 1.715 gcm^{-3}, F000 = 1160, μ = 20.10 mm^{-1}, T = 120.0(1) K, θ_{max} = 76.6°, 2435 total reflections, 2176 with $I_o > 2\sigma(I_o)$, R_{int} = 0.031, 5294 data, 159 parameters, no restraints, GooF = 1.03, 0.50 < dΔρ < -1.07 eÅ^{-3}, $R[F^2 > 2\sigma(F^2)]$ = 0.031, $wR(F^2)$ = 0.083.

[I(DMAP)$_2$]OTf ([**2**-I-**2**]OTf): Prepared the same as [**1**-I-**1**]BF_4 using AgOTf (321 mg, 1.25 mmol) and DMAP (**2**; 306 mg, 2.5 mmol) instead of $AgBF_4$ and pyridine, respectively. The product was precipitated as a white solid (333.4 mg, 0.64 mmol, 51%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.06 (d, *J* = 7.2 Hz, 4H), 6.51 (d, *J* = 7.0 Hz, 4H), 3.10 (s, 12H); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -215.8 (pyridinic), -306.5 (NMe_2).

[I(4-Mepy)$_2$]PF_6 ([**3**-I-**3**]PF_6): Prepared the same as [**1**-I-**1**]BF_4 using $AgPF_6$ (190 mg, 0.75 mmol) and 4-Mepy (**3**; 146 μl, 1.50 mmol) instead of $AgBF_4$ and pyridine, respectively. The product was precipitated as a white solid (195.0 mg, 0.42 mmol, 57%). ^{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 [**3**-I-**3**]PF_6: 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.

[I(4-nico)$_2$]PF_6 ([**4**-I-**4**]PF_6): A solution of methyl pyridine-4-carboxylate (**4**; 1.16 μl, 2.00 mmol) in DCM (10 mL) was added to a solution of $AgPF_6$ (253 mg, 1.00 mmol) in MeCN (3.0 mL) to give a colourless solution that was stirred for 15 minutes. I_2 (254 mg, 1.0 mmol) was added as a DCM (16 mL) solution to give an orange-coloured solution with a yellow precipitate once all the I_2 had been introduced. After being stirred for 60 minutes, the reaction was filtered to remove the yellow precipitate and the product was precipitated from the ruby red filtrate with petroleum ether (40-60°C) to give an off-white solid. The solid was sonicated in pentane (3 × 10 mL) to remove excess I_2, and further repeated as necessary until the filtrate was colourless. The product was dried under reduced pressure to give an off-white solid (430.9 mg, 0.79 mmol, 79%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.94 (d, *J* = 5.7 Hz, 4H), 8.11 (d, *J* = 5.5 Hz, 4H), 4.02 (s, 6H); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -167.4. Crystals suitable for single crystal X-ray diffraction were obtained from a DCM solution vapour diffused with DIPE. Crystal data for [**4**-I-**4**]PF_6: CCDC-2208423, $[C_{14}H_{14}IN_2O_4]PF_6$, M = 546.14, colourless block, 0.11 x 0.12 x 0.16 mm^3, monoclinic, space group $P2_1/c$, a = 15.7548(5) Å, b = 9.8035(3) Å, c = 30.8925(8) Å, β = 92.272(2)°, V = 4767.7(2) Å^3, Z = 10, D_{calc} = 1.902 gcm^{-3}, F000 = 2660, μ = 14.77 mm^{-1}, T = 120.0(1) K, θ_{max} = 76.4°, 9730 total reflections, 6316 with $I_o > 2\sigma(I_o)$, R_{int} = 0.037, 9730 data, 639 parameters, 133 restraints, GooF = 1.09, 2.30 < dΔρ < -2.02 eÅ^{-3}, $R[F^2 > 2\sigma(F^2)]$ = 0.067, $wR(F^2)$ = 0.210.

[I(4-CNpy)$_2$]PF_6 ([**5**-I-**5**]PF_6): A solution of 4-cyanopyridine (**5**; 156 mg, 1.5 mmol) in DCM (7 mL) was added to a solution of $AgPF_6$ (190 mg, 0.75 mmol) in MeCN (2.5 mL) and was stirred for 15 minutes. I_2 (190 mg, 0.75 mmol)

was added as a DCM (10 mL) solution to give an orange-coloured solution with a yellow precipitate once all the I_2 had been introduced. After being stirred for 60 minutes, the reaction was filtered to remove the yellow precipitate and the product was precipitated from the ruby red filtrate with petroleum ether (40-60°C) to give an off-white solid. The solid was sonicated in pentane (3 × 10 mL) to remove any excess I_2, and further repeated as necessary until the filtrate was colourless. The product was dried under reduced pressure to give an off-white solid (173.3 mg, 0.36 mmol, 48%). ^{1}H NMR (500 MHz, CD_3CN) δ 8.94 (s.br, 4H), 7.91 (s.br, 4H); no peaks observed in the ^{1}H-^{15}N HMBC NMR studies due to the broad ^{1}H NMR resonances. Crystals suitable for single crystal X-ray diffraction were obtained by evaporation of a DCM solution of [**5**-I-**5**]PF_6. Crystal data for [**5**-I-**5**]PF_6: CCDC-2208424, 3[$C_{12}H_8IN_4$-]PF_6·CH_2Cl_2, M = 1525.21, colourless block, 0.40 x 0.50 x 0.50 mm^3, triclinic, space group *P*-1 (No. 2), a = 10.6696(3) Å, b = 13.9953(3) Å, c = 18.4479(4) Å, α = 81.771(1)°, β = 75.316(1)°, γ = 78.793(1)°, V = 2601.11(11) Å^3, Z = 2, D_{calc} = 1.947 gcm^{-3}, F000 = 1464, μ = 2.11 mm^{-1}, T = 170(1) K, θ_{max} = 28.3°, 11442 total reflections, 9156 with $I_o > 2\sigma(I_o)$, R_{int} = 0.037, 11442 data, 743 parameters, 171 restraints, GooF = 1.02, 1.19 < dΔρ < -0.93 eÅ^{-3}, $R[F^2 > 2\sigma(F^2)]$ = 0.043, $wR(F^2)$ = 0.100.

PhC(O)O–I–DMAP (PhC(O)OI–**2**): A solution of DMAP (**2**; 122 mg, 1.0 mmol) in DCM (2 mL) was added to a suspension of PhC(O)OAg (229 mg, 1.0 mmol) in DCM (7 mL) and was stirred for 15 minutes. I_2 (254 mg, 1.0 mmol) was added as a DCM (5 mL) solution to give a peach-coloured solution with a yellow precipitate once all the I_2 had been introduced. After being stirred for 20 minutes, the reaction was filtered to remove the yellow precipitate and the product was precipitated from the filtrate with diethyl ether to give a white solid. The solid was sonicated in pentane (3 × 10 mL) to remove excess I_2, and further repeated as necessary until the filtrate was colourless. The product was dried under reduced pressure to give a white solid (244.9 mg, 0.66 mmol, 66%). The NMR spectra for this compound matched those previously reported.[1]

Antipyrine: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.46 (td, *J* = 7.6, 1.7 Hz, 2H), 7.36 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 5.29 (s, 1H), 3.03 (s, 3H), 2.21 (s, 3H); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -246.2, -197.7.

Iodo-antipyrine: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.48-7.34 (m, 5H), 3.12 (s, 3H), 2.32 (s, 3H); ^{15}N NMR (500 MHz, CD_2Cl_2) δ -241.5, -201.5. Crystals suitable for single crystal X-ray diffraction were obtained by sublimation of the compound under reduced pressure. Crystal data for iodo-antipyrine: CCDC-2208425, $C_{11}H_{11}IN_2O$, M = 314.12, colourless plate, 0.03 x 0.08 x 0.15 mm, trigonal, space group *R*-3, a = 27.1958(6) Å, c = 7.8944(2) Å, V = 5056.5(3) Å^3, Z = 18, D_{calc} = 1.857 gcm^{-3}, F000 = 2736, μ = 22.19 mm^{-1}, T = 120.0(1) K, θ_{max} = 76.6°, 2223 total reflections, 2147 with $I_o > 2\sigma(I_o)$, R_{int} = 0.038, 2223 data, 138 parameters, no restraints, GooF = 1.05, 0.33 < dΔρ < -0.43 eÅ^{-3}, $R[F^2 > 2\sigma(F^2)]$ = 0.016, $wR(F^2)$ = 0.041.

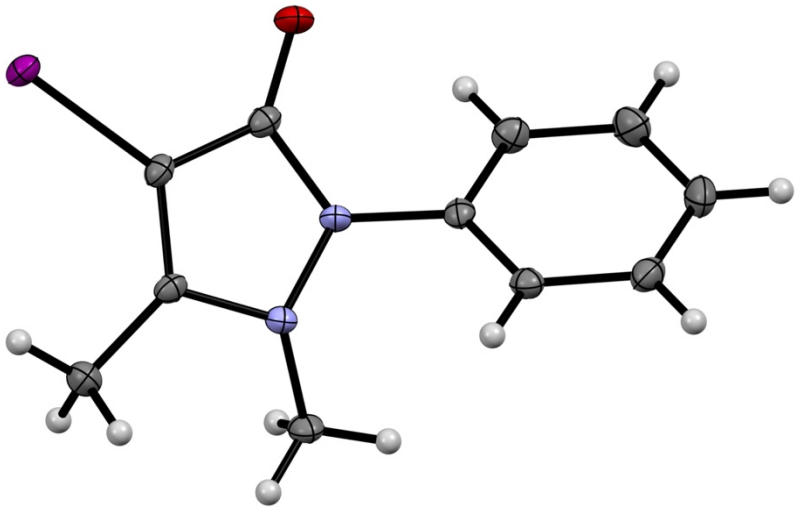

Figure S1: The X-ray crystal structure of iodo-antipyrine (thermal ellipsoids at 50% probability). Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

The ^{15}N Chemical Shift table

Table S1: The ^{15}N NMR chemical shifts (in CD_2Cl_2), determined by ^{1}H-^{15}N HMBC studies, of all iodine(I) complexes (in ppm).

Complex	**Pyridinic nitrogen (δ_N)**
[**1**-I-**1**]BF_4	-175.1[7]
[**1**-I-**1**]PF_6	-174.8[8]
[**2**-I-**2**]BF_4	-215.9
[**2**-I-**2**]PF_6	-216.1[8]
[**2**-I-**2**]SbF_6	-215.8
[**2**-I-**2**]OTf	-215.8
[**3**-I-**3**]PF_6	-182.2
[**4**-I-**4**]PF_6	-167.4
[**5**-I-**5**]PF_6	(not observed)
PhC(O)OI-**2**	-209.5[1]

Reactivity Studies

The general procedure for testing the reactivity of the iodine(I) complexes, following prior studies and performed in triplicate,[9] was as follows:

Antipyrine (18.8 mg, 0.1 mmol) was added to a CH_2Cl_2 (5 mL) solution of the iodine(I) complex (0.1 mmol) being tested and stirred for 2 hours or 22 hours, followed by an aqueous work-up consisting of washing with a saturated $NaHCO_3$ solution (4 × 25 mL). The iodo-antipyrine product was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, filtered, then isolated under reduced pressure as a white solid and the yield calculated.

Table S2: The average percentage conversion of antipyrine to iodo-antipyrine (after 2 hours unless otherwise stated).

Complex	**Average Antipyrine to Iodo-antipyrine Conversion (%)**
I_2	55
I_2 (22 hours)	90
[**1**-I-**1**]BF_4	93
[**1**-I-**1**]PF_6	76
[**2**-I-**2**]BF_4	50
[**2**-I-**2**]BF_4 (22 hours)	78
[**2**-I-**2**]PF_6	58
[**2**-I-**2**]PF_6 (22 hours)	79
[**2**-I-**2**]SbF_6	49
[**2**-I-**2**]OTf	63
[**3**-I-**3**]PF_6	77
[**4**-I-**4**]PF_6	85
[**5**-I-**5**]PF_6	89
PhC(O)OI-**2**	37
PhC(O)OI-**2** (22 hours)	68

NMR Spectra

Photo and NMR spectra of an old sample of [**1**-I-**1**]BF_4 (Barluenga's reagent)

Figure S2: Photographic comparison of a freshly prepared sample of [**1**-I-**1**]BF_4 (Barluenga's reagent; left) and an old sample after approximately two years stored under dry conditions in a desiccator (right).

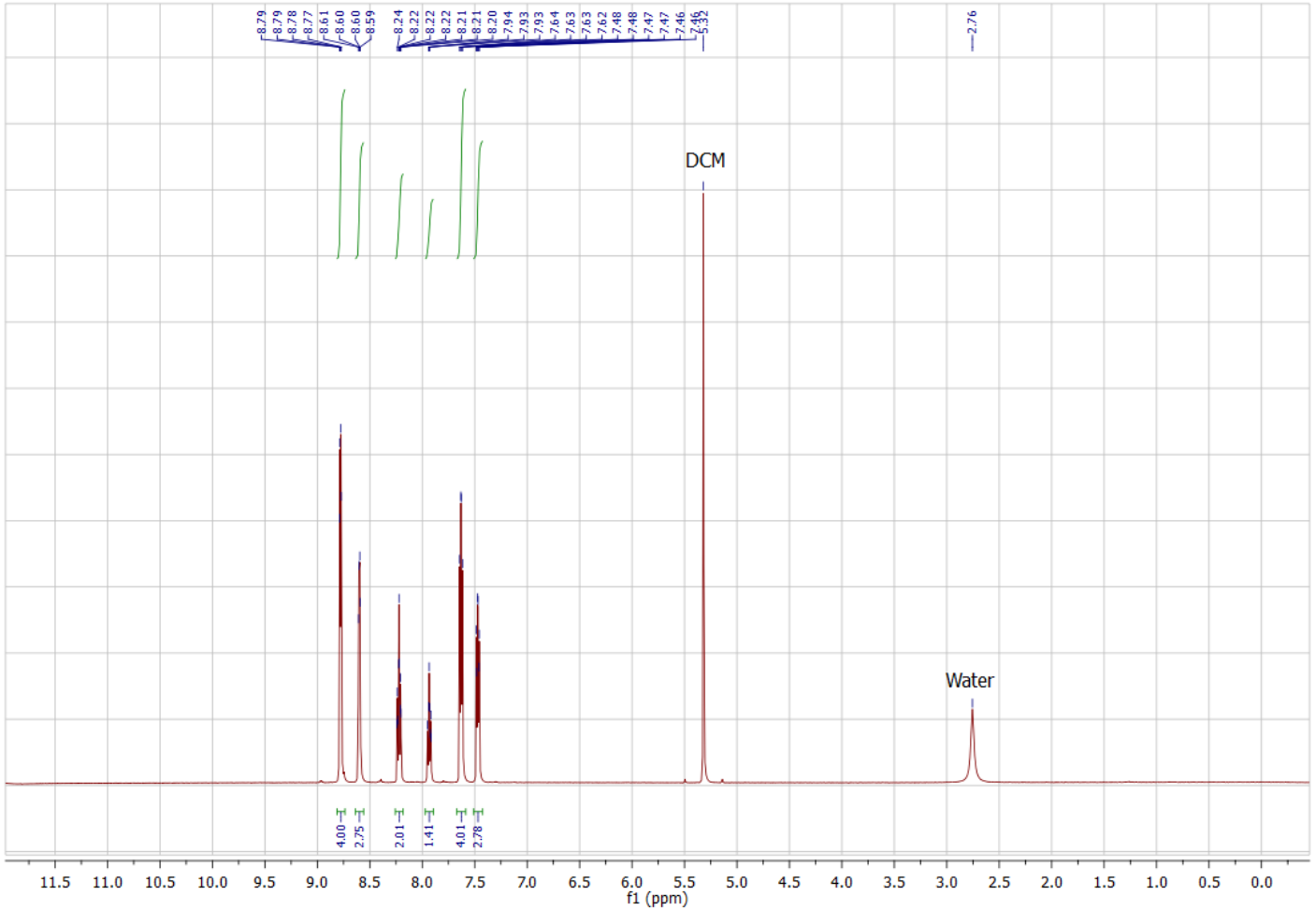

Figure S3: The ^{1}H NMR spectrum of an old sample of [**1**-I-**1**]BF_4 (~2 years) in CD_2Cl_2.

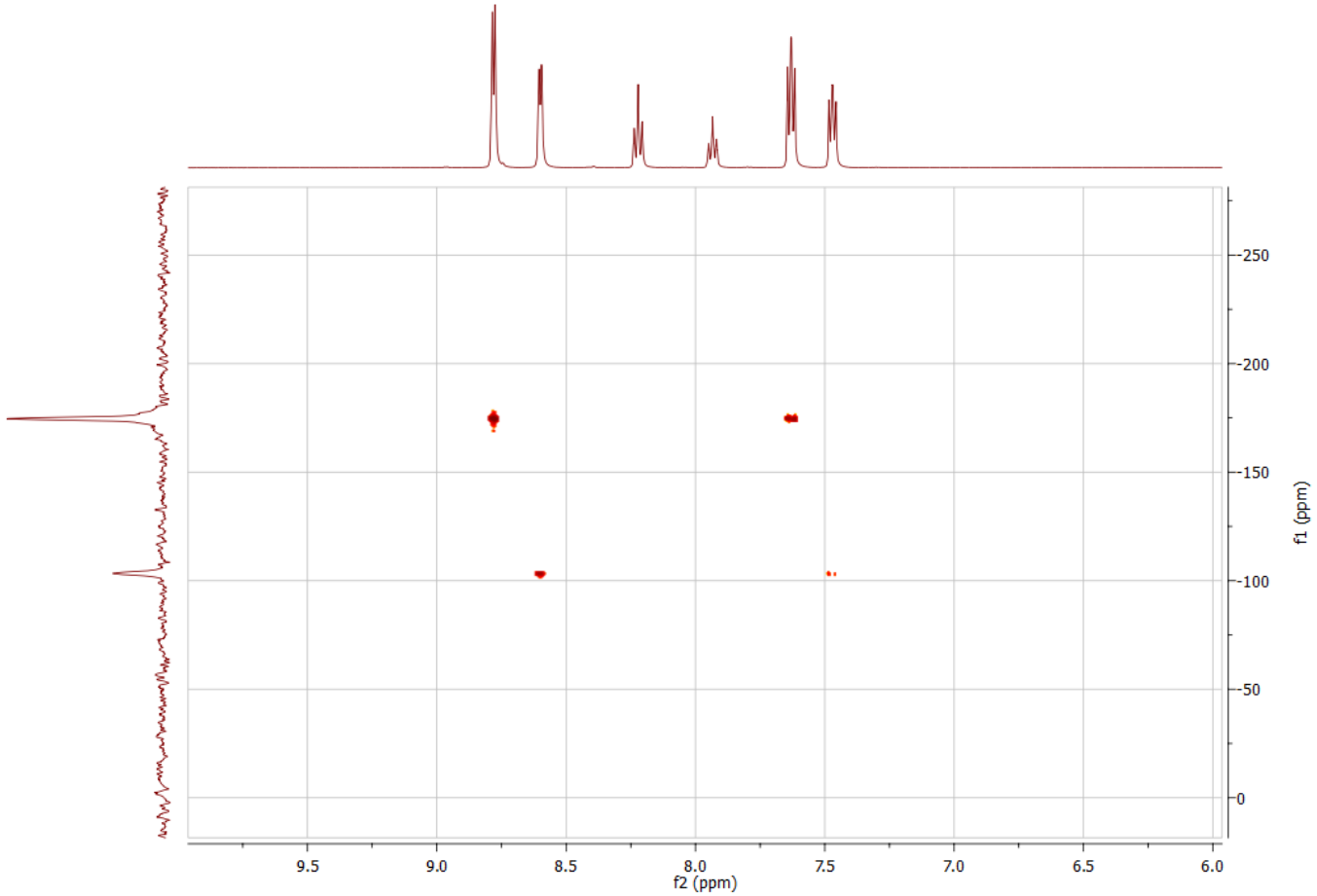

Figure S4: The ^{1}H-^{15}N HMBC spectrum of an old sample of complex [**2**-I-**2**]BF_4 (~2 years) in CD_2Cl_2.

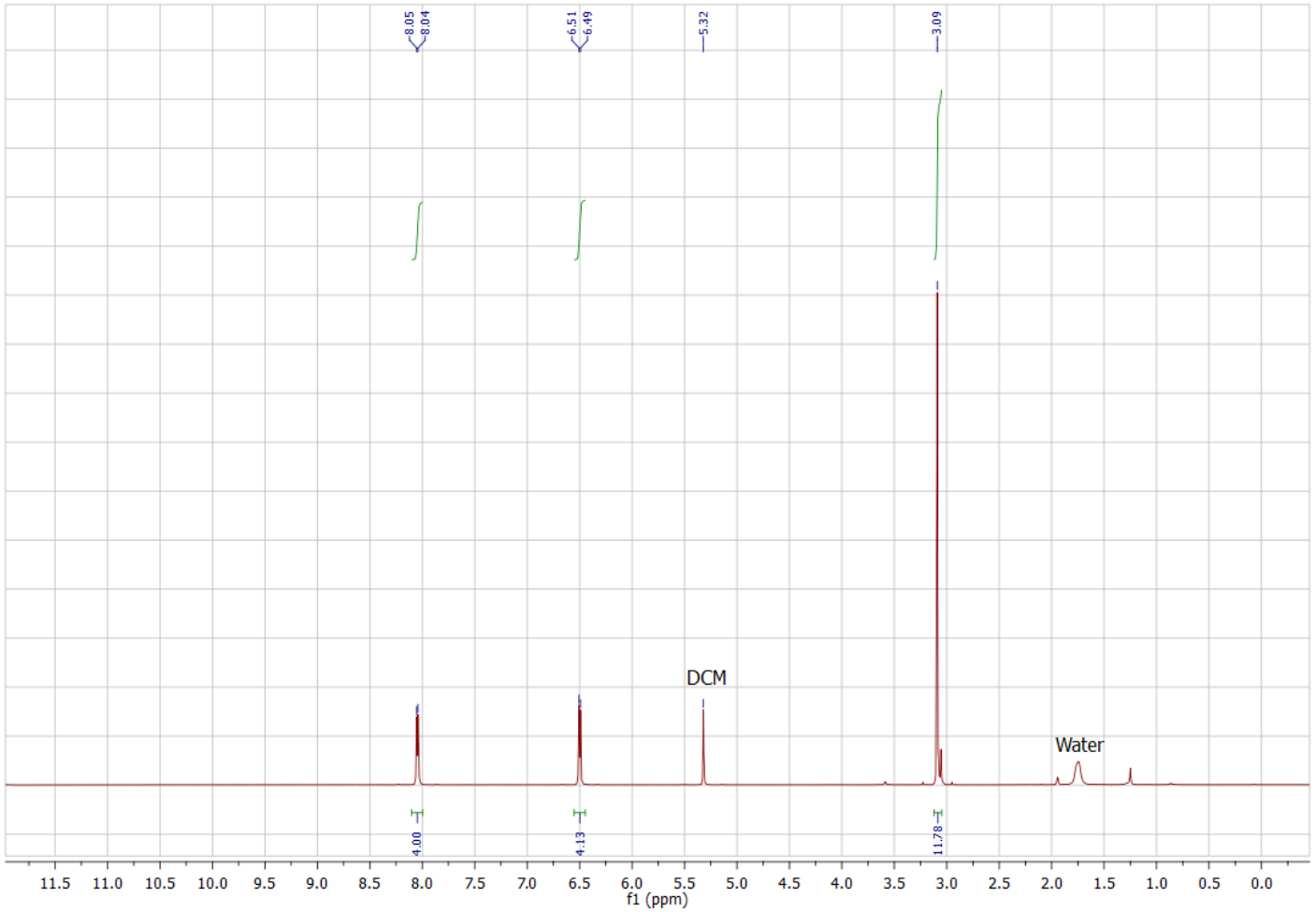

Figure S5: The ^{1}H NMR spectrum of complex [**2**-I-**2**]BF_4 in CD_2Cl_2.

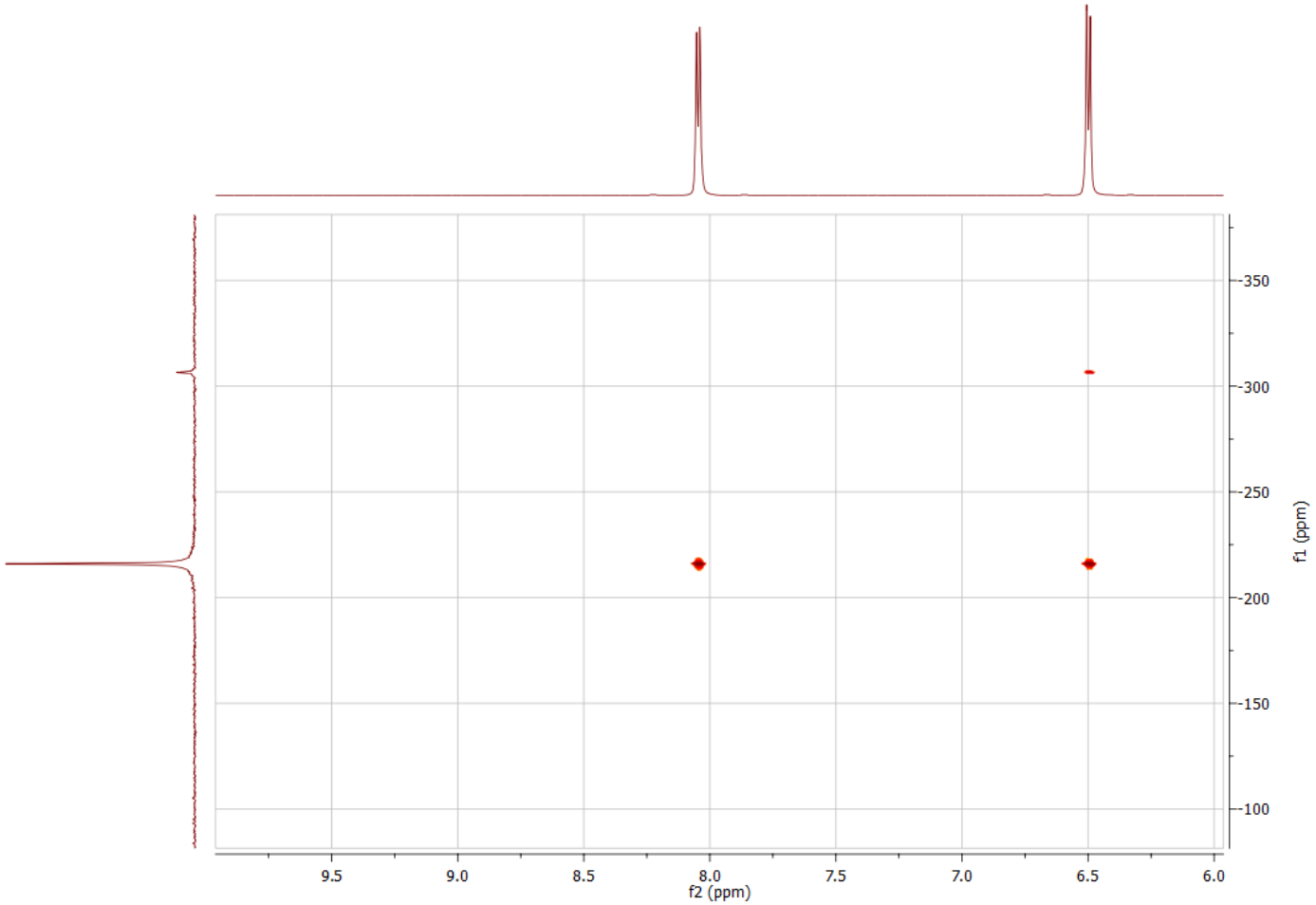

Figure S6: The ^{1}H-^{15}N HMBC spectrum of complex [**2**-I-**2**]BF_4 in CD_2Cl_2.

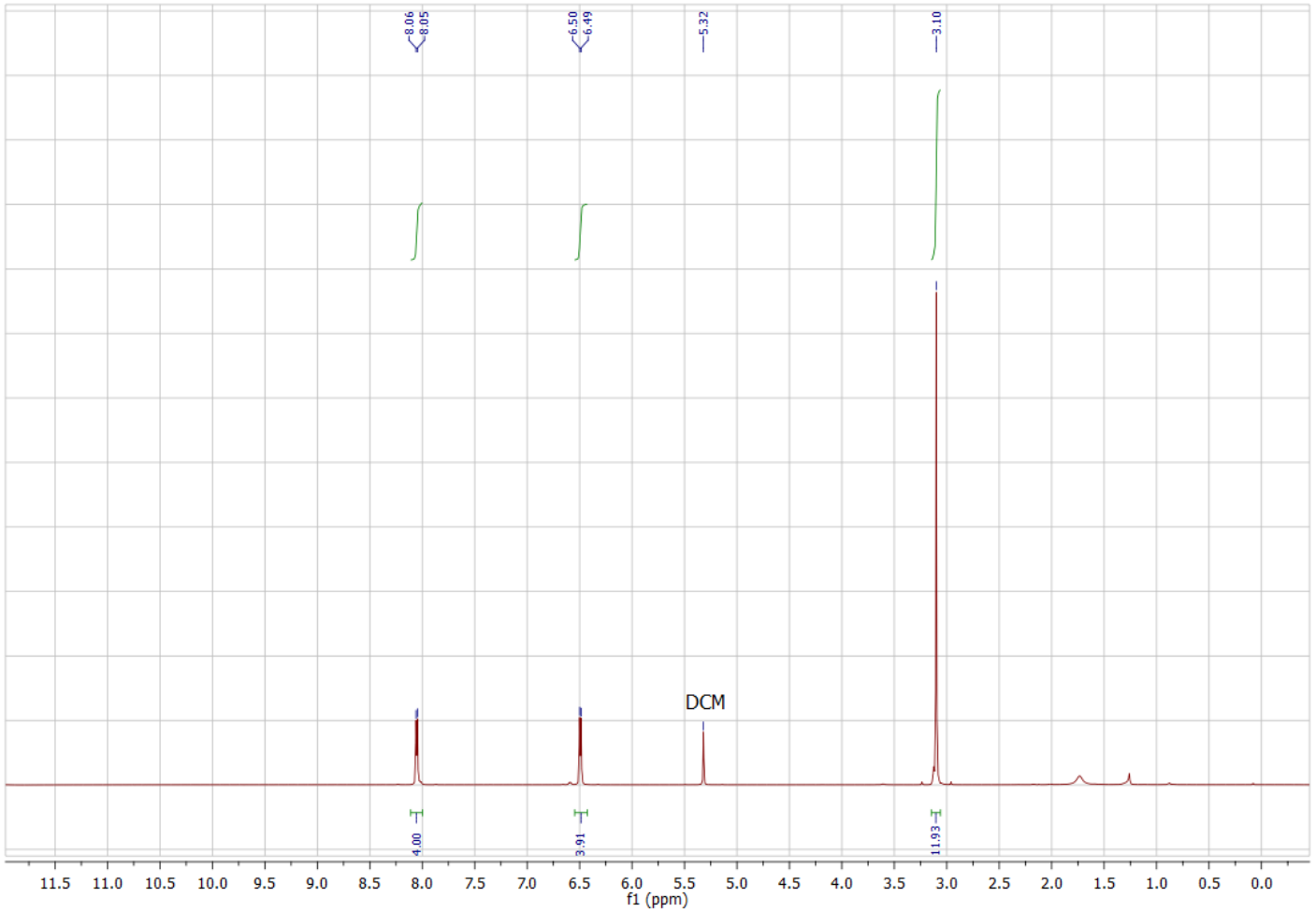

Figure S7: The ^{1}H NMR spectrum of complex [**2**-I-**2**]SbF_6 in CD_2Cl_2

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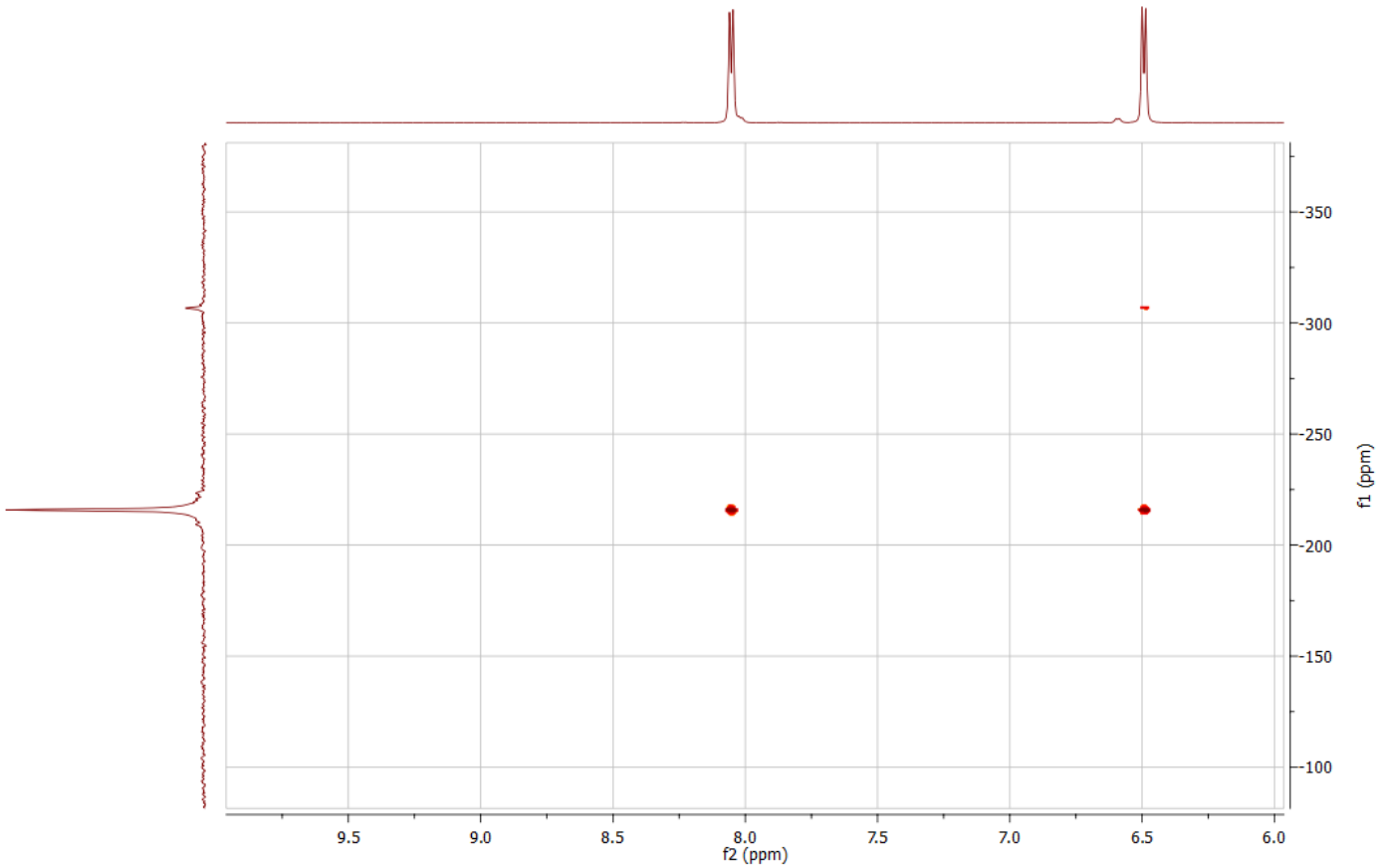

Figure S8: The ^{1}H-^{15}N HMBC spectrum of complex [**2**-I-**2**]SbF_6 in CD_2Cl_2.

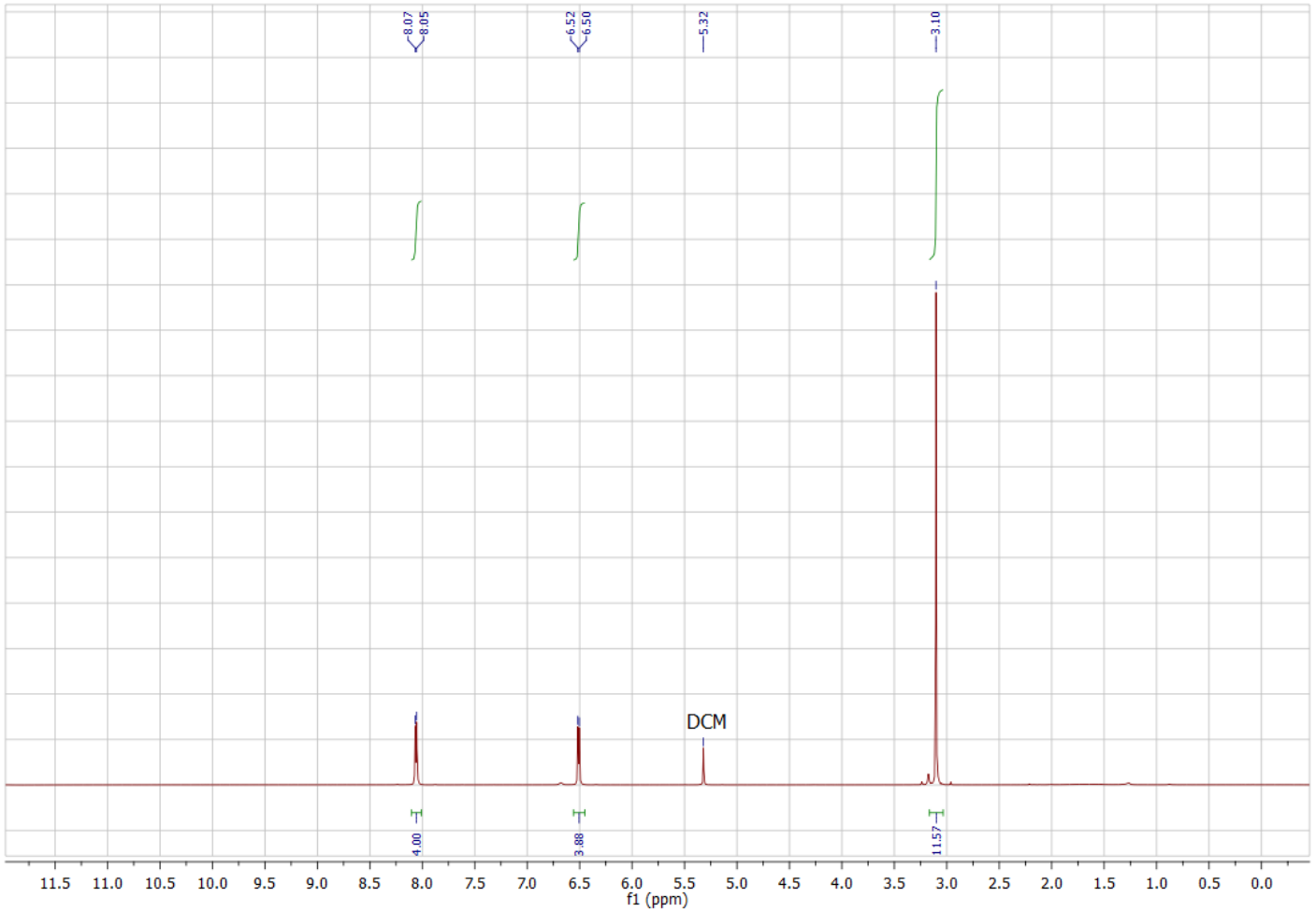

Figure S9: The ^{1}H NMR spectrum of complex [**2**-I-**2**]OTf in CD_2Cl_2.

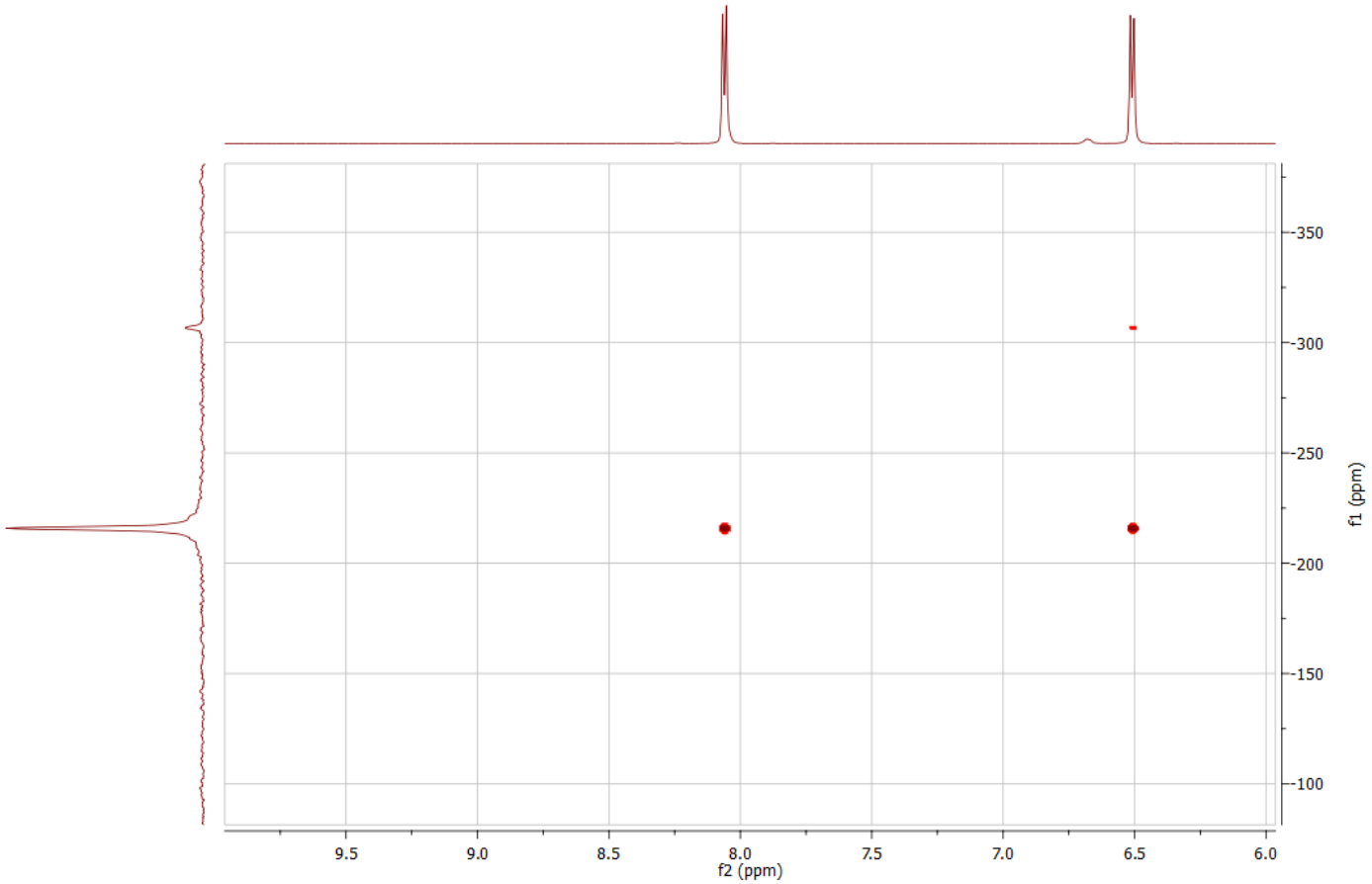

Figure S10: The ^{1}H-^{15}N HMBC spectrum of complex [**2**-I-**2**]OTf in CD_2Cl_2.

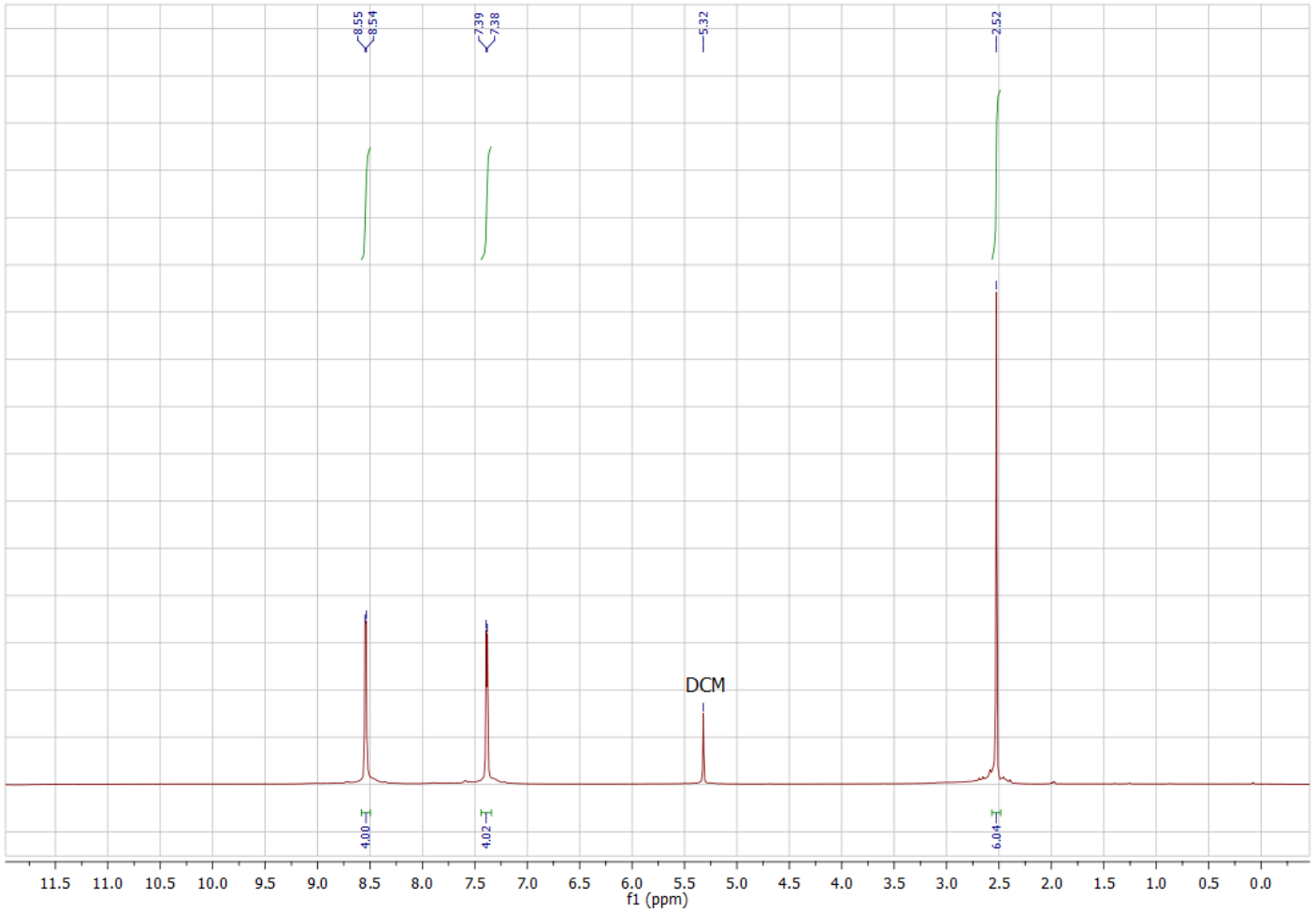

Figure S11: The ^{1}H NMR spectrum of complex [**3**-I-**3**]PF_6 in CD_2Cl_2.

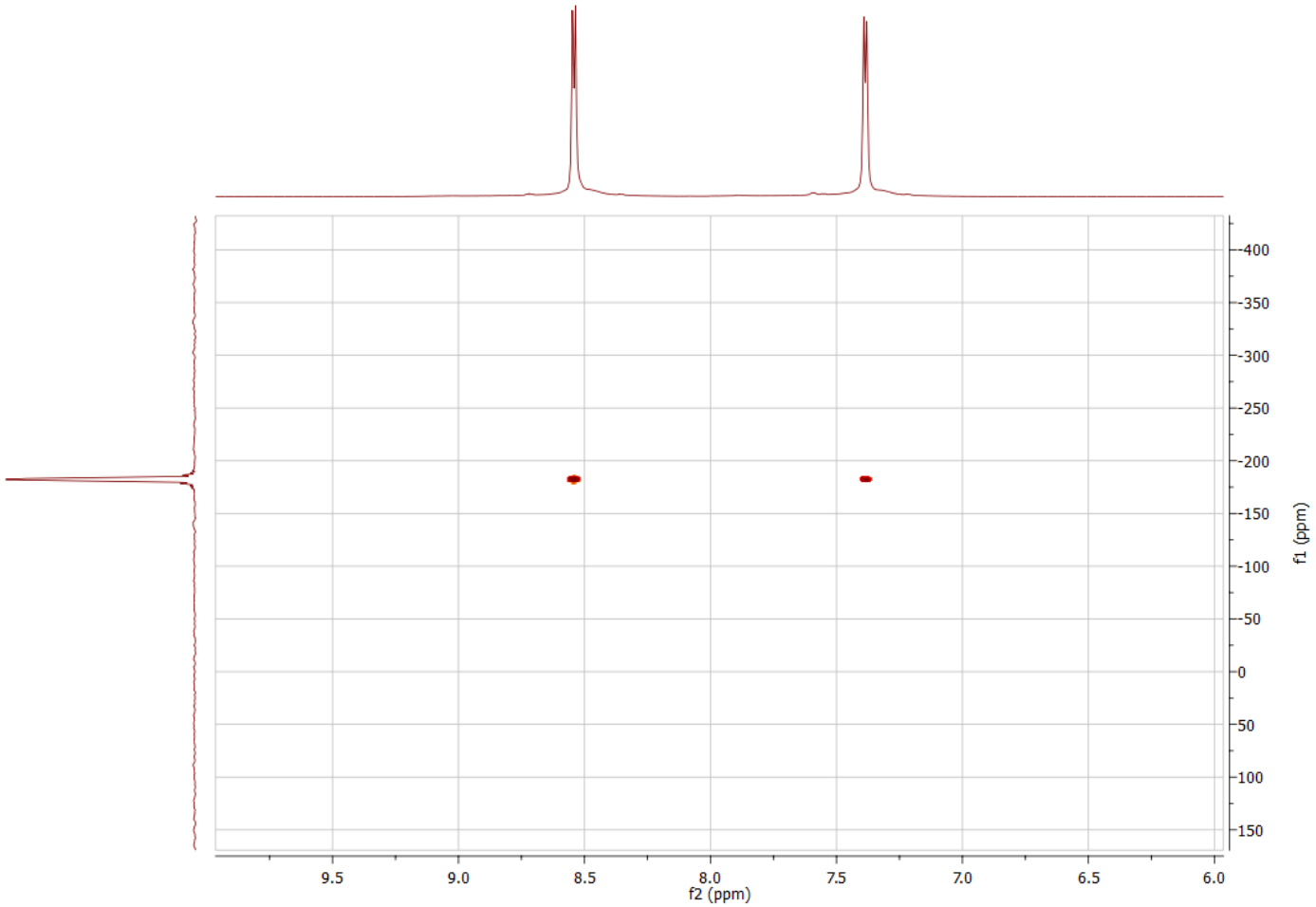

Figure S12: The ^{1}H-^{15}N HMBC spectrum of complex [**3**-I-**3**]PF_6 in CD_2Cl_2.

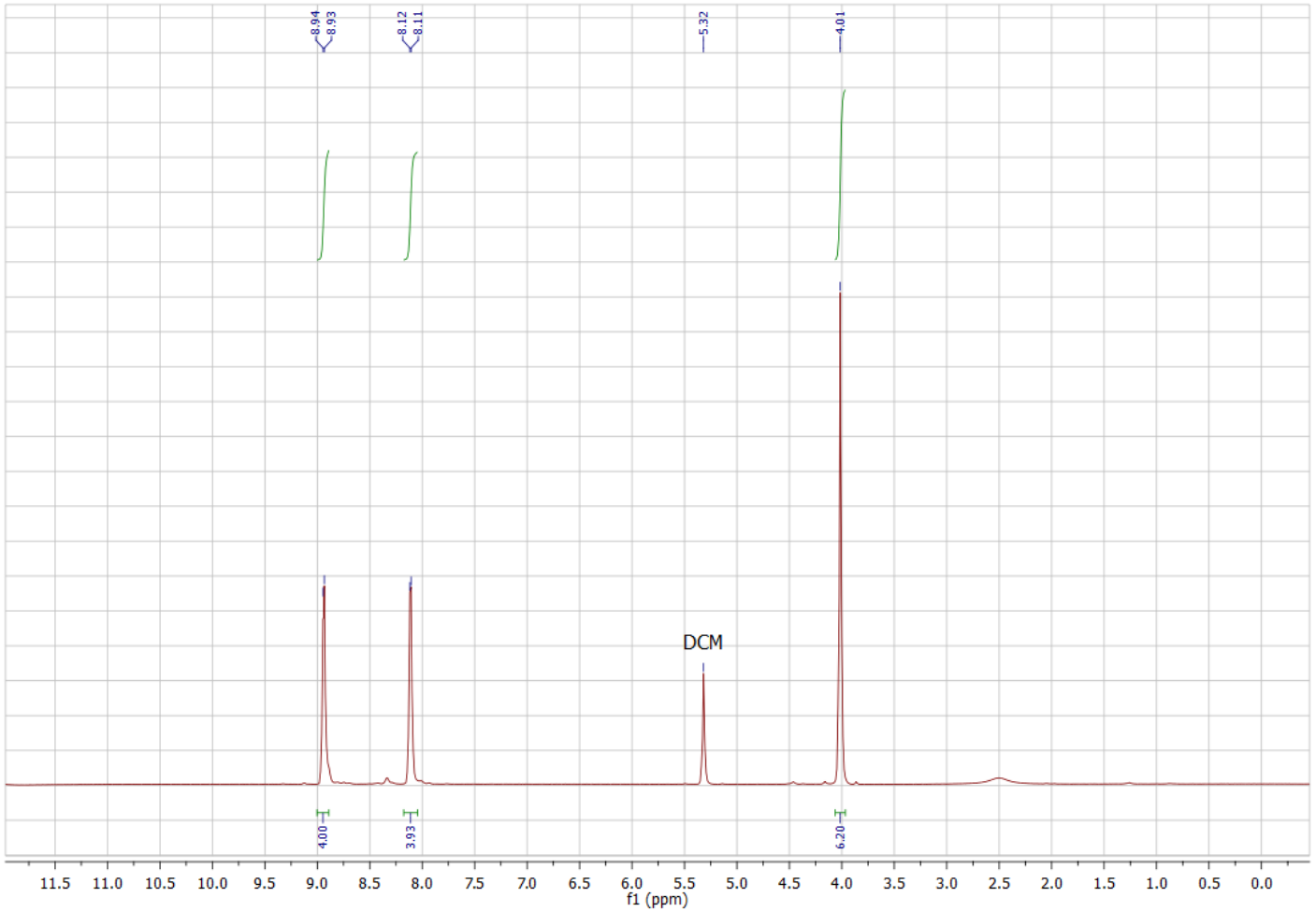

Figure S13: The ^{1}H NMR spectrum of complex [**4**-I-**4**]PF_6 in CD_2Cl_2.

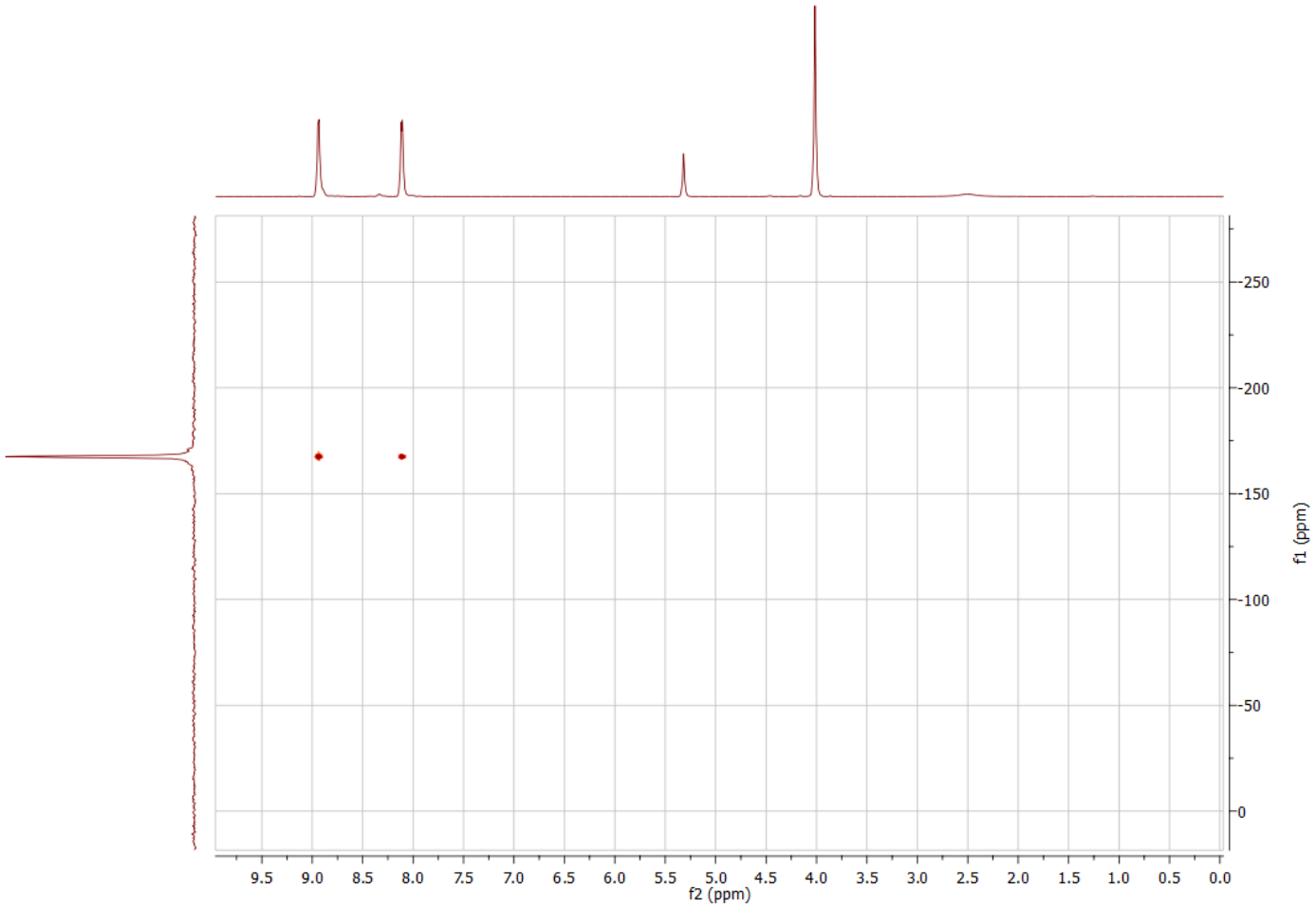

Figure S14: The ^{1}H-^{15}N HMBC spectrum of complex [**4**-I-**4**]PF_6 in CD_2Cl_2.

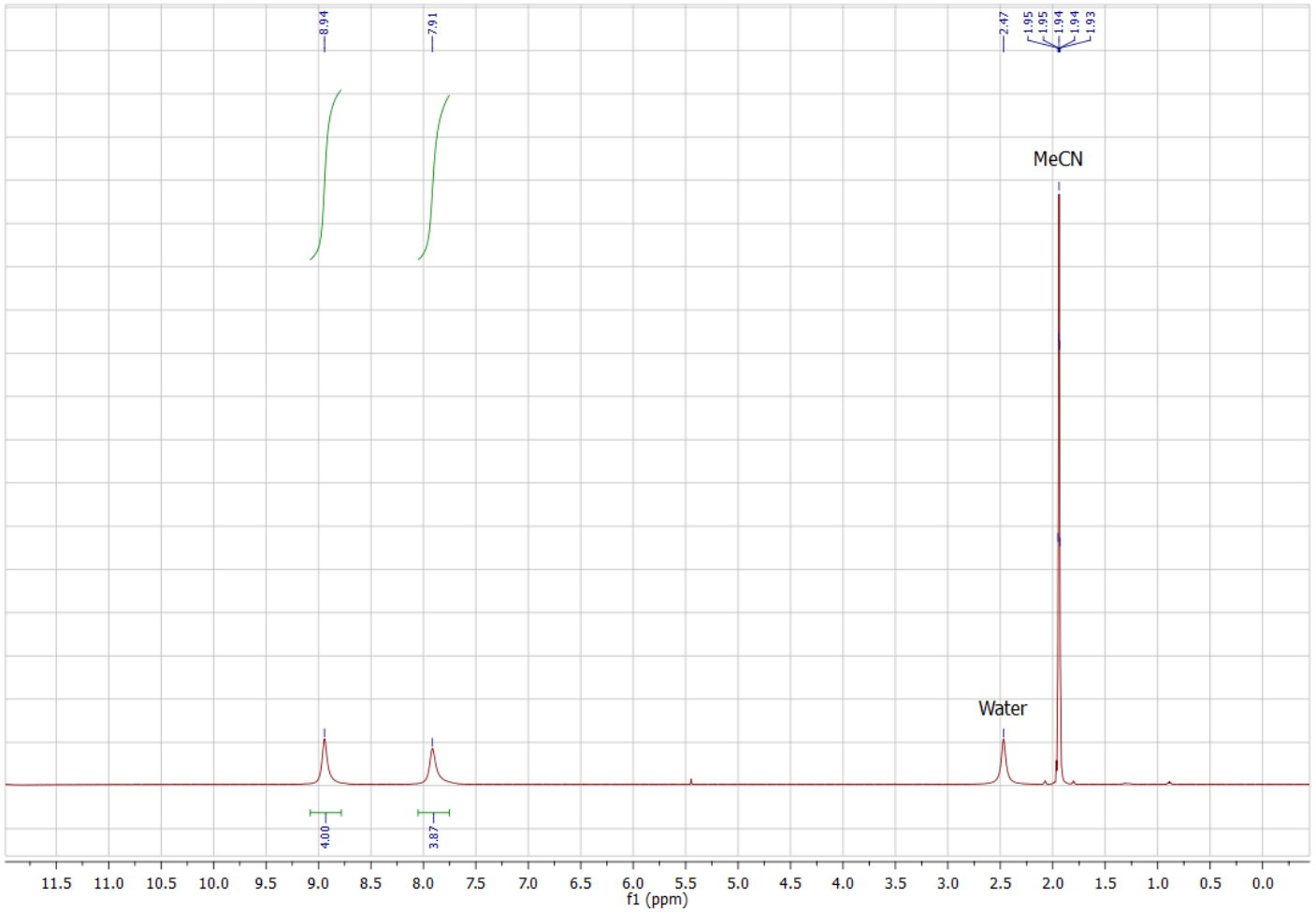

Figure S15: The ^{1}H NMR spectrum of complex [**5**-I-**5**]PF_6 in CD_2Cl_2.

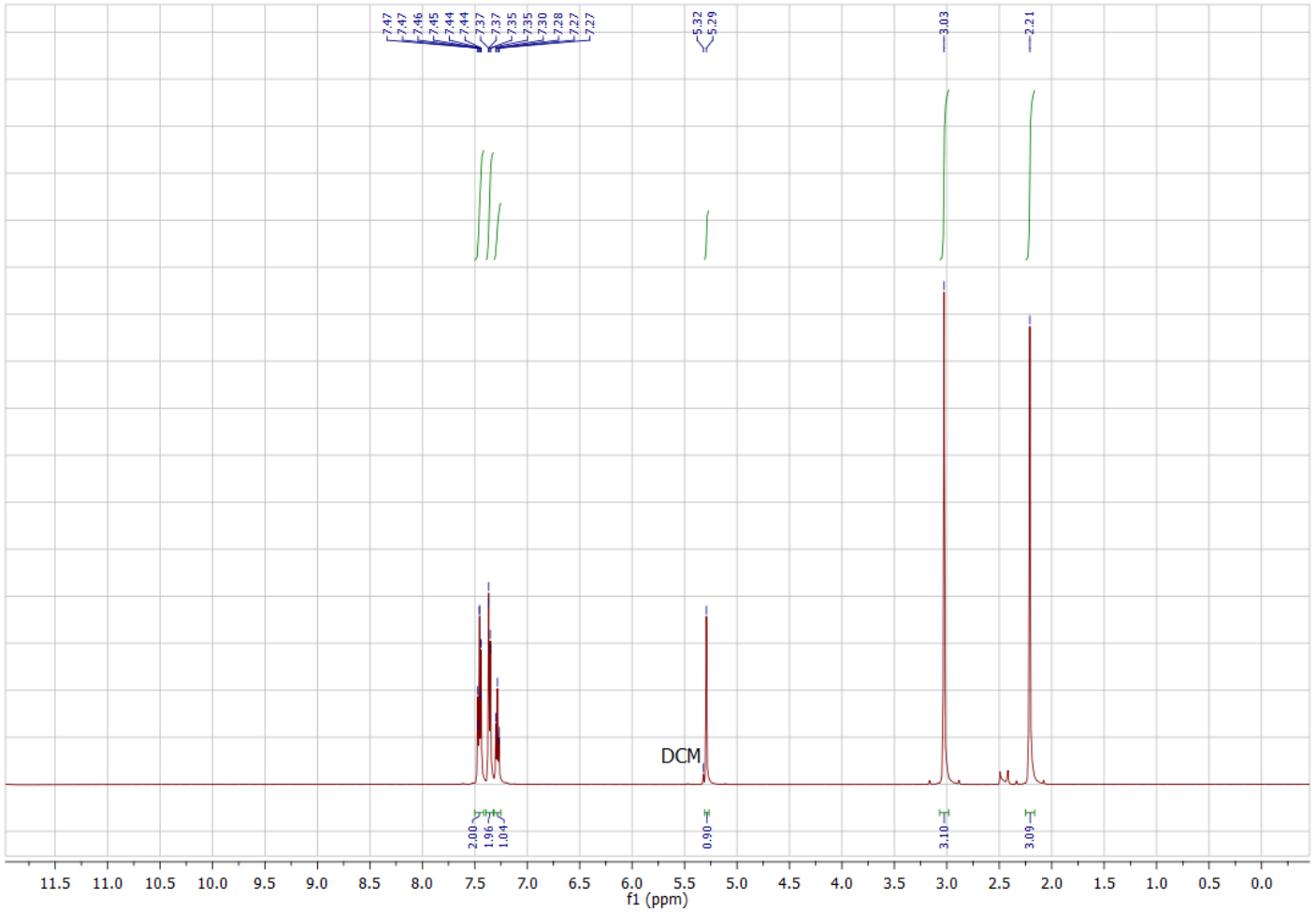

Figure S16: The ^{1}H NMR spectrum of antipyrine in CD_2Cl_2.

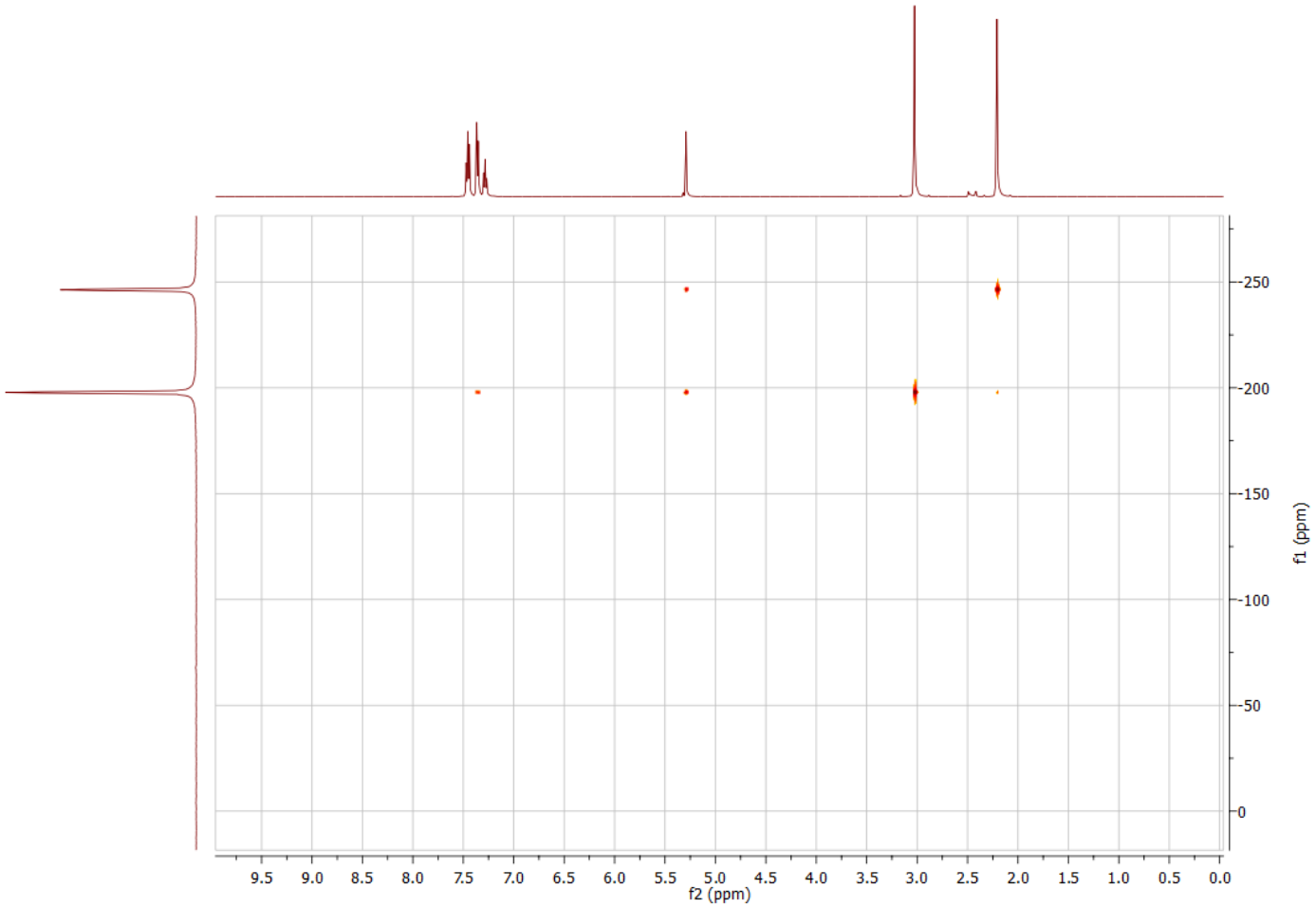

Figure S17: The ^{1}H-^{15}N HMBC spectrum of antipyrine in CD_2Cl_2.

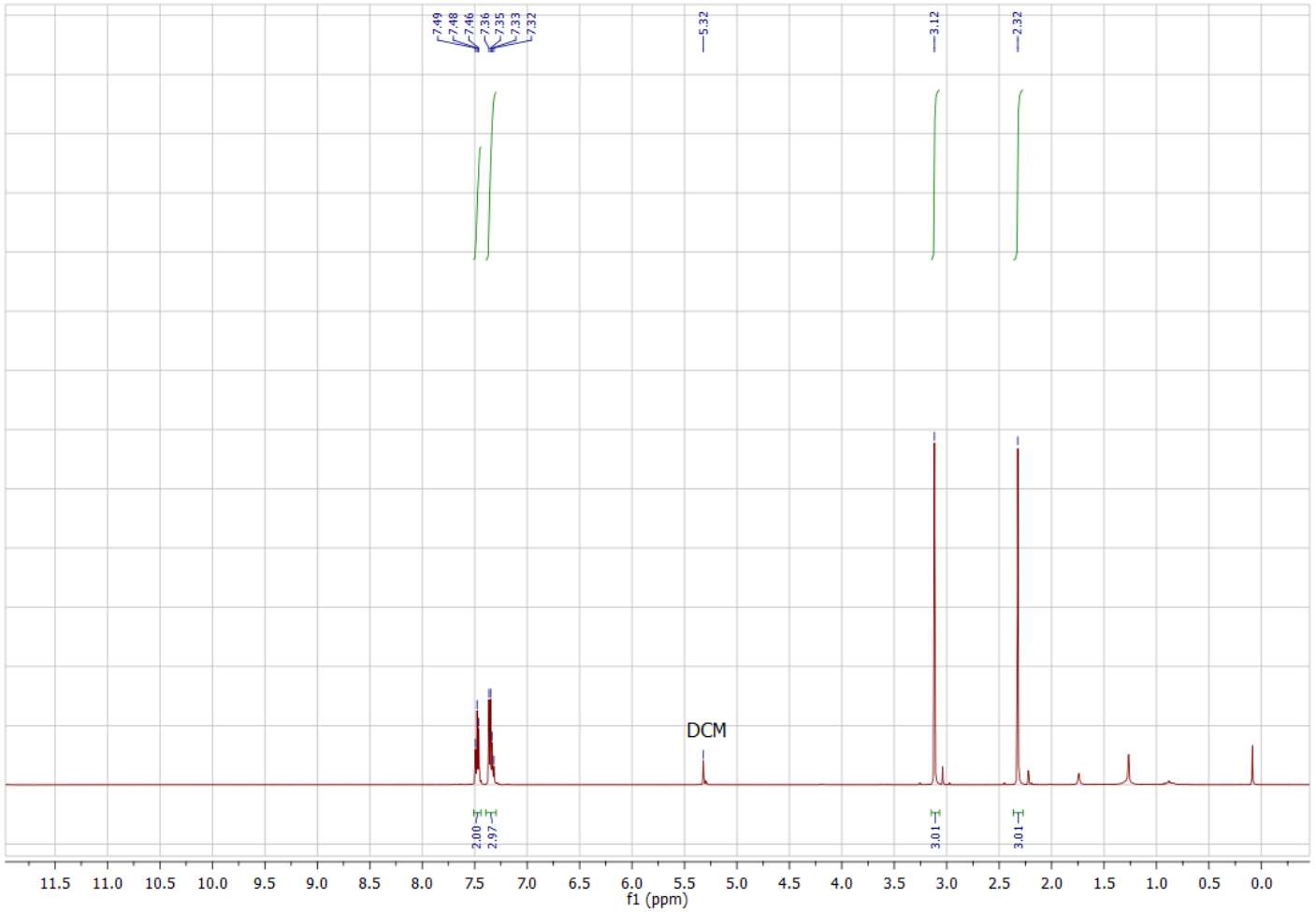

Figure S18: The ^{1}H NMR spectrum of iodo-antipyrine in CD_2Cl_2.

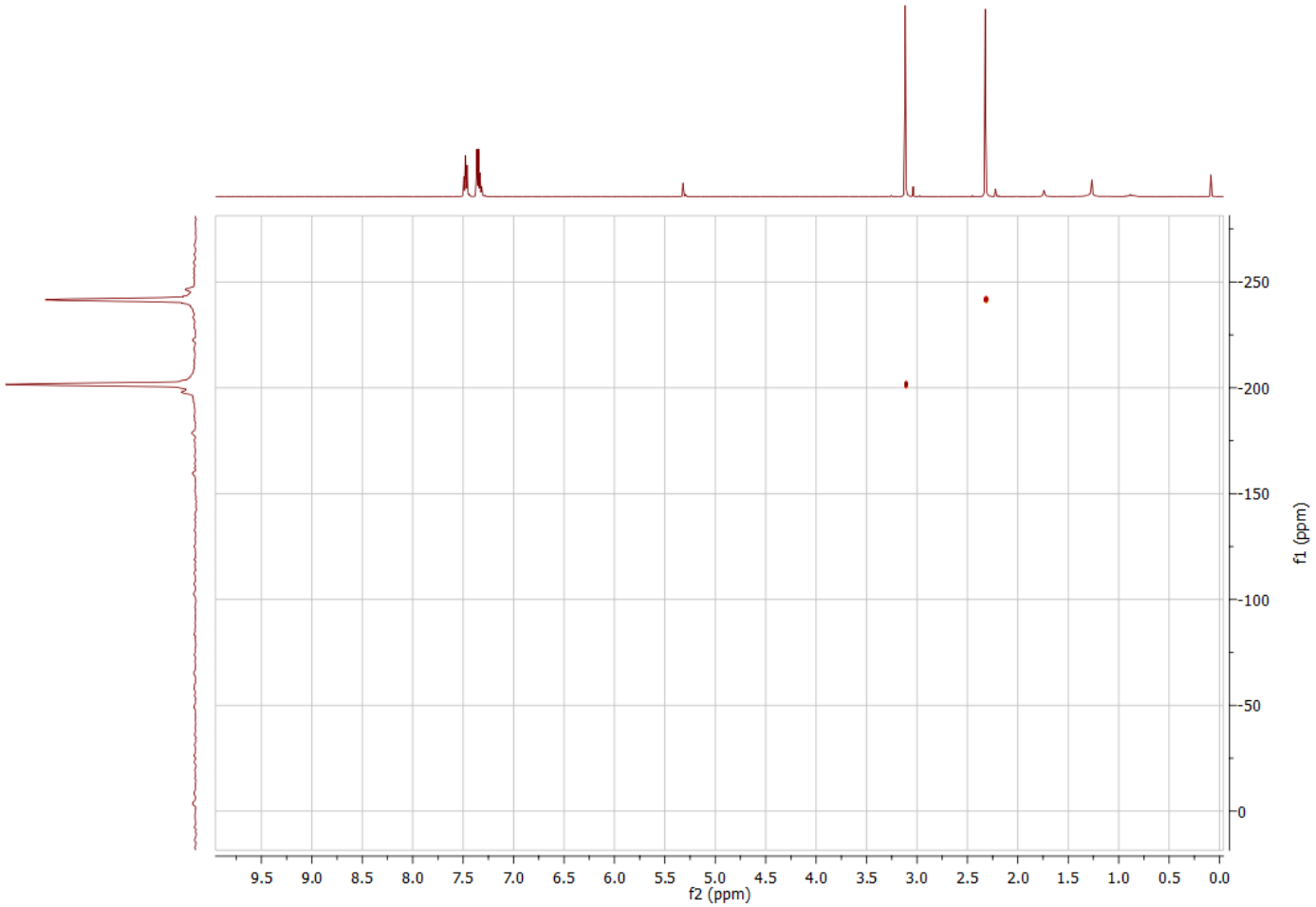

Figure S19: The ^{1}H-^{15}N HMBC spectrum of iodo-antipyrine in CD_2Cl_2.

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