Supporting Information

From Citronellal to Iridoids. Asymmetric Syntheses of Iridoids and Their Analogs Via Organocatalytic Intramolecular Michael Reactions.

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SUPPORTING INFORMATION:

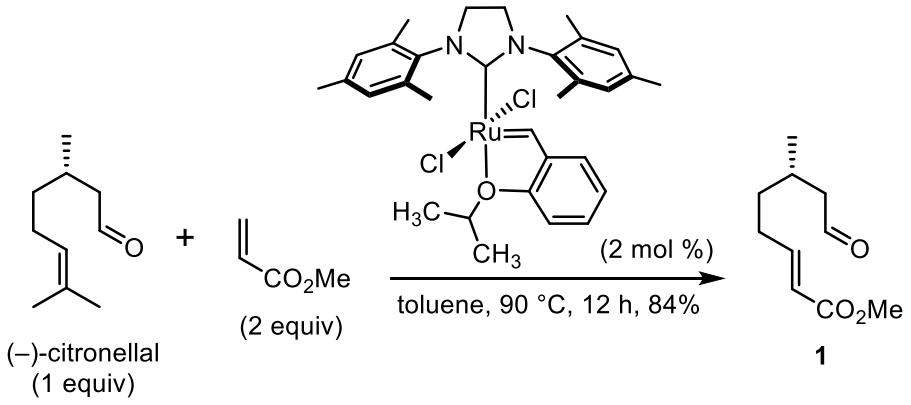
Contents:

General Procedure.

All solvents were reagent grade. Reactions were normally carried out under a nitrogen atmosphere in glassware or vial. Merck silica gel 60 (particle size 0.04-0.063 mm) was employed for flash chromatography. ^{1}H NMR spectra were obtained in $CDCl_3$ unless otherwise noted at 400 MHz (Bruker DPX-400, Bruker Ascend^{TM} 400**)** or 500 MHz (Varian-Unity INOVA-500). ^{13}C NMR spectra were obtained at 125 MHz or 100 MHz. *E.e.* values were measured by HPLC on a chiral column (CHIRALPAK IA, 0.46 cm x 15 cm, 5 μm) by elution with 1% ^{i}PrOH-hexane. The flow rate of the indicated elution solvent is maintained at 1.0 mL/min, and the retention time of a compound is recorded accordingly. HPLC was equipped with ultraviolet detectors. The melting point was recorded on a melting point apparatus (MPA100–Automated melting point system, Stanford Research Systems, Inc.) and is uncorrected. IR spectra were recorded on Bruker Alpha FT-IR spectrometer. The optical rotation values were recorded with a Jasco-P-2000 digital polarimeter. ESI ionization time-of-flight mass (ESI-TOF HRMS) spectral data were collected on a JMS-T100LP 4G(JEOL) mass spectrometer equipped with the ESI source, detecting positive and negative ions. Typical measurement conditions are as follows: needle voltage: 2000 kV, orifice 1 voltage: 30 V, ring lens voltage: 10 V, spray temperature: 250 ℃. EI-TOF mass spectral data were collected on a JMS-T200GC AccuTOF GCx-plus (JEOL) mass spectrometer. EI ionization time-of-flight mass (EI-TOF HRMS) spectral data were collected on a JMS-T200GC AccuTOF GCx-plus (JEOL) mass spectrometer equipped with the EI ion source and DIP sampling device. Typical measurement conditions are as follows: ionizing voltage: 70 eV, ionizing current: 300 μA, ion chamber temperature: 250 ℃, DIP temperature: 50 to 200 ℃ in 2 minutes. The single-crystal

X-ray diffraction data of crystals were individually collected in-house on a Bruker D8 Venture diffractometer equipped with a Cu-target (Kα =1.54178 Å) or Mo-target (Kα = 0.71073 Å) microfocus X-ray generators and a PHOTON-II CMOS detector. The temperature was adjusted with a nitrogen flow (Oxford Cryosystems). After collection, the data were integrated with the Bruker SAINT software package using a narrow-frame algorithm and were corrected for absorption effects using the Multi-Scan method (SADABS). Then, the molecular structure was solved and refined by the Bruker SHELXTL Software Package and the final anisotropic full-matrix least-squares method was used to refine on F2 with variables parameters to determine crystal structure.

Preparation of aldehyde ester 1:



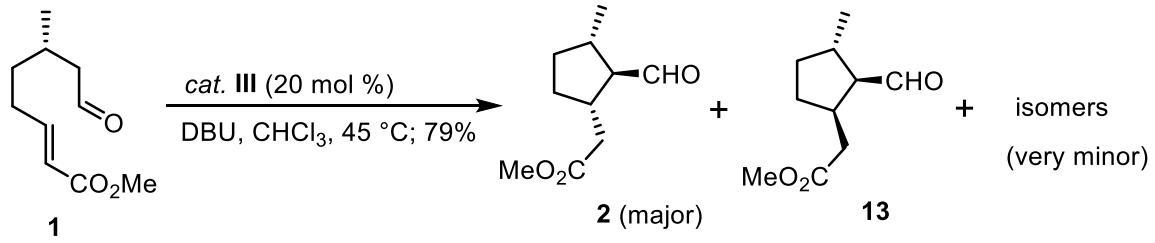
To a solution of (–)-citronellal (500 mg, 3.24 mmol) and methyl acrylate (558 mg, 6.48 mmol, 2.0 equiv) in toluene (10 mL), placed in a dry 20-mL sealed tube, was added Hoveyda-Grubbs Catalyst® M720 (Umicore, CAS no. 301224-40-8, 40.6 mg, 0.06 mmol, 2 mol%) at room temperature under nitrogen. The resulting solution was stirred at 90 ℃ for 12 h until the completion of the reaction, as monitored by TLC. The reaction solution was concentrated *in vacuo* to give the crude residue. The *E*-isomer was found to be predominated, as determined by ^{1}H NMR analysis of the crude product. The crude product was purified by flash column chromatography with 5% EtOAc-hexane (R_f = 0.45 in 20% EtOAc-hexane) to afford product **1** (503 mg, 84% yield) as a colorless oil.[1] Chiral HPLC analysis for **1**: Chiralpak IA (elute: 1% ^{i}PrOH−hexane), flow rate 1.0 mL/min, detector 225 nm, t_1 = 14.9 min, t_2 = 19.2 min, 98.4:1.6 er.

Selected data for **1**: $[\alpha]_D^{26}$ –32.8 (c 1, $CHCl_3$); IR (neat): 2923, 2854, 1705, 1462, 1166, 915, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.73 (s, 1 H), 6.96 – 6.88 (m, 1 H), 5.81 (d, J = 15.6 Hz, 1 H), 3.70 (s, 3 H), 2.39 (dd, J = 16.4, 5.6 Hz, 1 H), 2.29 – 2.14 (m, 3 H), 2.11 – 2.02

[1] (a) Bilel, H.; Hamdi, N.; Zagrouba, F.; Fischmeister, C.; Bruneau, C. *Green Chem.* **2011**, *13*, 1448 – 1452. (b) Yoshikai, K.; Hayama, T.; Nishimura, K.; Yamada, K.-I.; Tomioka, K. *J. Org. Chem.* **2005**, *70*, 681 – 683.

(m, 1 H), 1.53 – 1.44 (m, 1 H), 1.41 – 1.31 (m, 1 H), 0.96 (d, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 202.3 (CH), 167.0 (C), 148.8 (CH), 121.2 (CH), 51.4 (CH_3), 50.8 (CH_2), 34.9 (CH_2), 29.6 (CH_2), 27.5 (CH), 19.6 (CH_3); HRMS (GC-EI-TOF) *m/z*: $[M]^+$ Calcd for $C_{10}H_{16}O_3$ 184.1099; found: 184.1092.

Preparation of aldehyde 2:

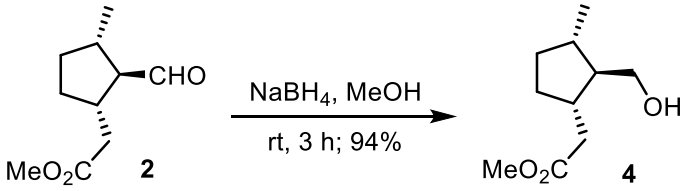


To a solution of catalyst **III** (176.7 mg, 0.54 mmol, 0.2 equiv) and **1** (500 mg, 2.71 mmol) in $CHCl_3$ (9 mL) was added DBU (82.6 mg, 0.54 mmol, 0.2 equiv) at ambient temperature. The resulting solution was stirred at 45 ℃ for 48 h until the completion of the reaction, as monitored by TLC. The reaction solution was diluted with EtOAc, and washed with water and brine. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The dr ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 83:17. The crude product was purified by flash column chromatography with 5% EtOAc-hexane (R_f = 0.51 in 20% EtOAc-hexane) to afford products **2** and **13** (396.7 mg, 79% yield) as a colorless oil. Purification of the mixture using prolonged flash column chromatography resulted in the isolation of pure samples of **2** (351 mg; 70%; R_f = 0.51 in 20% EtOAc-hexane) and **13** (7.3 mg; R_f = 0.52 in 20% EtOAc-hexane) for analysis.

Selected data for **2**: $[\alpha]_D^{26}$ –10.3 (*c* 1, $CHCl_3$); IR (neat): 3483, 2959, 2874, 1724, 1457, 1381, 1285, 1208, 1167 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.55 (d, J = 3.9 Hz, 1 H), 3.63 (s, 3 H), 2.67 – 2.56 (m, 1 H), 2.38 (d, J = 7.4 Hz, 2 H), 2.26 – 2.13 (m, 1 H), 2.01 – 1.84 (m, 3 H), 1.47 – 1.39 (m, 1 H), 1.38 – 1.29 (m, 1 H), 1.04 (d, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 203.3 (CH), 172.8 (C), 65.8 (CH), 51.6 (CH_3), 39.3 (CH_2), 37.6 (CH), 36.8 (CH), 33.3 (CH_2), 31.3 (CH_2), 19.5 (CH_3); HRMS (GC-EI-TOF) *m/z*: $[M]^+$ Calcd for $C_{10}H_{16}O_3$ 184.1099; found: 184.1090.

Selected data for **13**: $[\alpha]_D^{20}$ –7.9 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.73 (d, J = 3.0 Hz, 1 H), 3.64 (s, 3 H), 2.79 – 2.70 (m, 1 H), 2.53 – 2.46 (m, 2 H), 2.41 – 2.31 (m, 2 H), 2.01 – 1.89 (m, 2 H), 1.42 – 1.32 (m, 1 H), 1.28 – 1.18 (m, 1 H), 1.03 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.2 (CH), 173.1 (C), 61.2 (CH), 51.6 (CH_3), 38.3 (CH), 35.7 (CH_2), 34.5 (CH), 33.4 (CH_2), 32.4 (CH_2), 20.4 (CH_3).

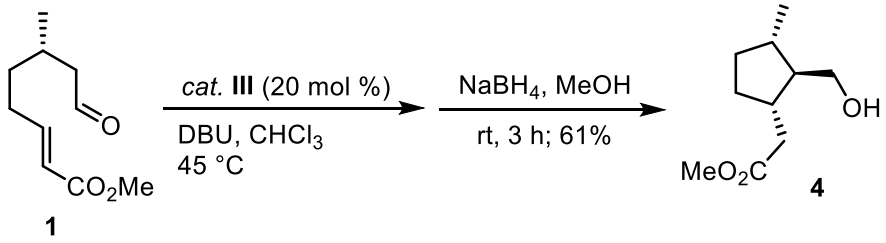
Preparation of 4:



To a solution of **2** (200 mg, 1.09 mmol) in MeOH (10 mL) was added $NaBH_4$ (82.1 mg, 2.17 mmol, 2.0 equiv) at ambient temperature. The resulting solution was stirred at room temperature for 3 h until the completion of the reaction, as monitored by TLC. The reaction was quenched by the addition of an aqueous solution of 2N HCl (0.5 mL). The reaction mixture was diluted with EtOAc, and washed with water and brine. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 0 to 30 % EtOAc-hexane (R_f = 0.47 in 40 % EtOAc-hexane) to afford product **4** (191 mg, 94% yield) as a colorless oil.[2]

Selected data for **4**: $[\alpha]_D^{27}$ 13.7 (*c* 1, $CHCl_3$); IR (neat): 3429, 2949, 2869, 1734, 1440, 1161, 1018, 874 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.65 (s, 3 H), 3.61 (dd, *J* = 11.0, 4.5 Hz, 1 H), 3.52 (dd, *J* = 11.0, 6.5 Hz, 1 H), 2.45 (dd, *J* = 15.9, 7.7 Hz, 1 H), 2.33 (dd, *J* = 15.9, 6.7 Hz, 1 H), 2.22 – 2.11 (m, 1 H), 1.85 – 1.64 (m, 4 H), 1.40 – 1.29 (m, 1 H), 1.29 – 1.12 (m, 2 H), 0.99 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.5 (C), 64.4 (CH_2), 55.8 (CH), 51.6 (CH_3), 40.0 (CH_2), 38.6 (CH), 37.0 (CH), 32.9 (CH_2), 31.2 (CH_2), 20.1 (CH_3); HRMS (HPLC-ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_{18}NaO_3$: 209.1154; found: 209.1153.

Preparation of 4:



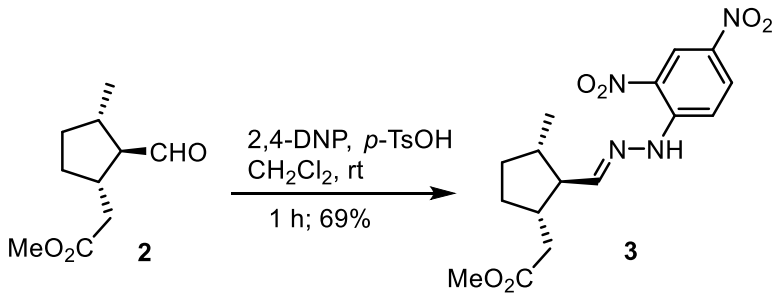
To a solution of catalyst **III** (17.7 mg, 0.05 mmol, 0.2 equiv) and DBU (8.3 mg, 0.05 mmol, 0.2 equiv) in $CHCl_3$ (1 mL) was added a solution of **1** (50 mg 0.27 mmol) in $CHCl_3$ (1.1 mL) at ambient temperature. The resulting solution was stirred at 45 °C for 48 h until the completion of the reaction, as monitored by TLC. The reaction solution was diluted with EtOAc (15 mL), and washed with water (7 mL) and brine (7 mL). The combined organic

[2] Bonini, C.; Fabio, R. D. *J. Org. Chem.* **1982**, *47*, 1343 – 1345.

solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was directly used for the next step reaction without further purification.

To a solution of the above crude product in MeOH (1 mL) was added $NaBH_4$ (20.5 mg, 0.54 mmol, 2 equiv) at ambient temperature. The resulting solution was stirred at room temperature for 3 h until the completion of the reaction, as monitored by TLC. The reaction was quenched by the addition of water (0.5 mL). The reaction mixture was diluted with EtOAc (15 mL), and washed with water (5 mL) and brine (5 mL). The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 10 % EtOAc-hexane (R_f = 0.45 for **4** in 15 % EtOAc-hexane, after developing twice) to afford products **4** (31 mg, 61 %) as a colorless oil.

Preparation of 3:

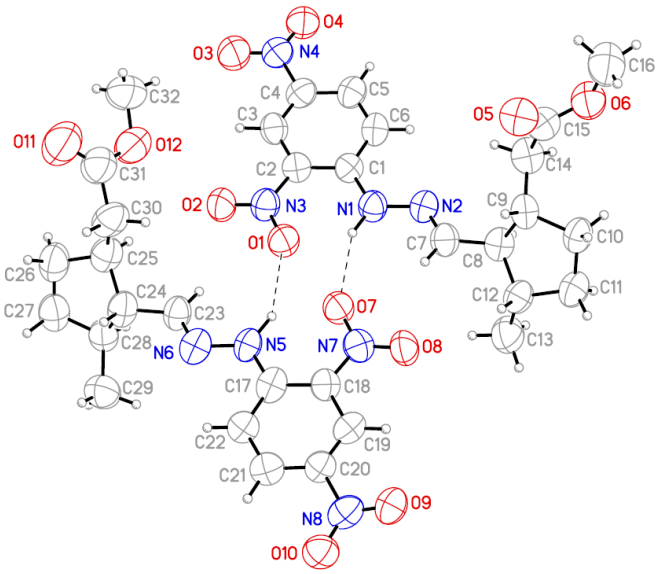


To a solution of **2** (90.0 mg, 0.49 mmol) in CH_2Cl_2 (6 mL) was added 2,4-dinitrophenylhydrazine (96.8 mg, 0.45 mmol, 1.08 equiv) and *p*-TsOH (4.6 mg, 0.03 mmol, 0.05 equiv) at room temperature. The resulting solution was stirred at room temperature for 1 h until the completion of the reaction, as monitored by TLC. The reaction mixture was diluted with EtOAc, and the solution was washed with saturated aqueous $NaHCO_3$ solution, followed by brine. The organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 10 % EtOAc-hexane (R_f = 0.48 in 30% EtOAc-hexane) to afford product **3** (123 mg, 69% yield) as yellow color solids.

Selected data for **3**: mp. 106-107 ℃; $[\alpha]_D^{26}$ 10.2 (*c* 1, $CHCl_3$); IR (KBr): 3293, 2949, 2867, 1738, 1617, 1511, 1428, 1337, 1310, 1266, 1138, 1071, 739, 605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 11.01 (s, 1 H), 9.10 (d, J = 2.6 Hz, 1 H), 8.28 (dd, J = 9.6, 2.5 Hz, 1 H), 7.90 (d, J = 9.6 Hz, 1 H), 7.38 (d, J = 6.2 Hz, 1 H), 3.59 (s, 3 H), 2.53 – 2.27 (m, 3 H), 2.09 – 1.90 (m, 4 H), 1.51 – 1.30 (m, 2 H), 1.04 (d, J = 5.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0 (C), 154.3 (CH), 145.0 (C), 137.9 (C), 130.0 (CH), 128.9 (C), 123.5 (CH), 116.5 (CH), 56.9 (CH), 51.6 (CH_3), 40.7 (CH), 39.6 (CH), 38.9 (CH_2), 32.8 (CH_2), 30.8 (CH_2), 19.0 (CH_3); HRMS (GC-EI-TOF) *m/z*: $[M]^+$ Calcd for $C_{16}H_{20}N_4O_6$ 364.1383; found: 364.1389.

Recrystallization of 3 was performed as follows:

Compound **3** (~3 mg) in a screw cap vial (4 mL vial) was dissolved in $CHCl_3$ (~0.5 mL) and then diluted with *n*-hexane (~2.5 mL). The vial was covered with aluminum foil (with 4-5 holes in it) and placed in another vial (20 mL vial), which was filled with *n*-hexane (~8 mL). The 20-mL vial was closed gently with a screw cap and let stand for 4-5 days until the solvent in the inner vial has completely evaporated. The crystals formed were subjected to single-crystal X-ray analysis.



Thermal ellipsoids draw at the 50% probability level

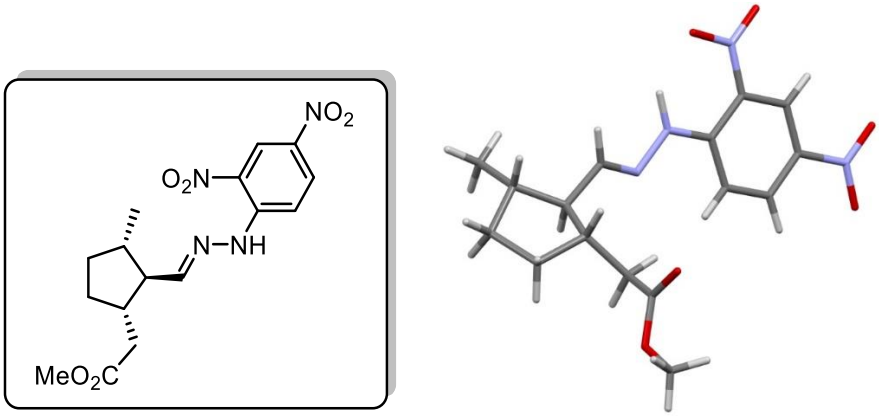


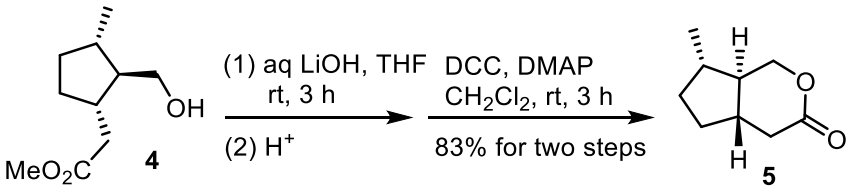
Figure S1. ORTEP and Stereo plots for X-ray crystal structures of **3** (**ic21707**).

CCDC 2235981 contains the supplementary crystallographic data for **3 (ic21707)**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk

Table S1. Crystal data and structure refinement for **3** (**ic21707**).

Identification code	ic21707	
Empirical formula	C32 H40 N8 O12	
Formula weight	728.72	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 4.8265(7) Å	α= 74.980(12)°.
	b = 11.8034(18) Å	β= 85.102(12)°.
	c = 16.146(2) Å	γ = 79.447(12)°.
Volume	872.7(2) $Å^3$	
Z	1	
Density (calculated)	1.387 Mg/m^3	
Absorption coefficient	0.909 mm^{-1}	
F(000)	384	
Crystal size	0.600 x 0.163 x 0.159 mm^3	
Theta range for data collection	3.933 to 67.980°.	
Index ranges	-4<=h<=5, -14<=k<=14, -19<=l<=19	
Reflections collected	10899	
Independent reflections	5724 [R(int) = 0.1226]	
Completeness to theta = 67.679°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.41539	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5724 / 16 / 482	
Goodness-of-fit on F^2	1.376	
Final R indices [I>2sigma(I)]	R1 = 0.1206, wR2 = 0.2821	
R indices (all data)	R1 = 0.1726, wR2 = 0.3346	
Absolute structure parameter	0.3(9)	
Extinction coefficient	0.010(3)	
Largest diff. peak and hole	0.480 and -0.447 $e.Å^{-3}$	

Preparation of 5:

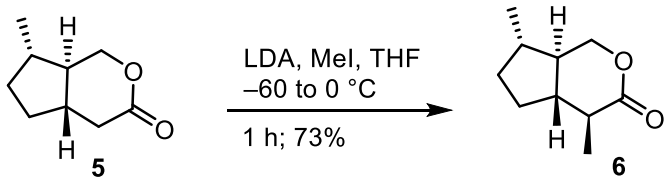


To a solution of **4** (100 mg, 0.54 mmol) in THF (3 mL) was added an aqueous solution of LiOH (19.4 mg, 0.81 mmol, 1.5 equiv) in water (1.5 mL) at room temperature. The resulting solution was stirred at room temperature for 3 h until the completion of the reaction, as monitored by TLC. The pH of the solution was adjusted to 2-3 by adding 3M aqueous HCl at 0 ℃. The reaction mixture was diluted and extracted with EtOAc. The solution was washed with water and brine. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give the crude product as an oil. This residue was proceeded to the next step without further purification.

To a solution of the above crude product in dry CH_2Cl_2 (10 mL) was added DCC (111.4 mg, 0.54, mmol 1.0 equiv) and DMAP (13.2 mg, 0.11 mmol, 0.2 equiv) at room temperature. The resulting solution was stirred at room temperature for 3 h until the completion of the reaction, as monitored by TLC. The reaction mixture was diluted with EtOAc, followed by washing with brine and water. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 5 % EtOAc-hexane (R_f = 0.46 in 30% EtOAc-hexane) to afford product **5** (69 mg, 83% yield) as a colorless oil.

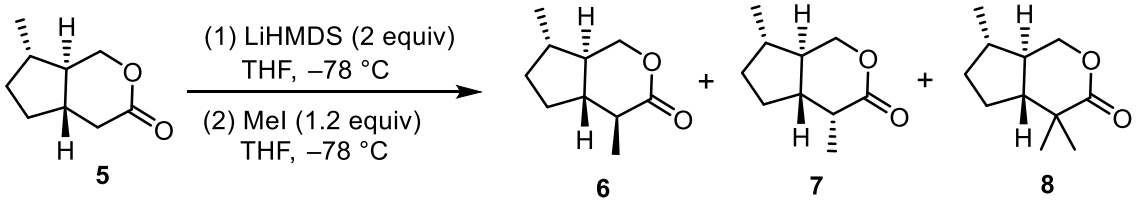
Select data for **5:** $[\alpha]_D^{27}$ 95 (*c* 1, $CHCl_3$); IR (neat): 2953, 2871, 1732, 1404, 1310, 1195, 1132, 1018, 799, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 4.55 (dd, *J* = 10.5, 5.0 Hz, 1 H), 4.05 (dd, *J* = 11.7, 10.5 Hz, 1 H), 2.84 (dd, *J* = 17.7, 5.0 Hz, 1 H), 2.23 (dd, *J* = 17.7, 12.6 Hz, 1 H), 2.10 – 2.00 (m, 1 H), 1.94 – 1.78 (m, 2 H), 1.73 – 1.62 (m, 1 H), 1.46 – 1.21 (m, 3 H), 1.03 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.5 (C), 74.3 (CH_2), 48.6 (CH), 41.5 (CH), 38.1 (CH_2), 36.0 (CH), 33.0 (CH_2), 29.7 (CH_2), 19.0 (CH_3); HRMS (GC-EI-TOF) *m/z*: $[M]^+$ Calcd for $C_9H_{14}O_2$ 154.0994; found: 154.0991.

Preparation of 6 with LDA:



To a solution of **5** (20 mg, 0.13 mmol) in dry THF (3 mL) was added LDA (0.08 mL, 2 M in hexane, 1.5 equiv) at –60 ℃. The resulting solution was stirred at –60 ℃ for 30 min, followed by the addition of iodomethane (10 μL, 0.16 mmol, 1.2 equiv), and the solution was gradually warmed up to 0 ℃ over 1 h. The reaction was quenched by the addition of an aqueous saturated solution of NH_4Cl (5 mL). The resulting solution was extracted with EtOAc (10 mL x 2), washed with brine (5 mL), and the combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 5 % EtOAc-hexane (R_f = 0.52 in 30% in EtOAc-hexane) to afford product **6** (16 mg, 73%) as a colorless oil.

Preparation of 6 and 7 with LiHMDS:

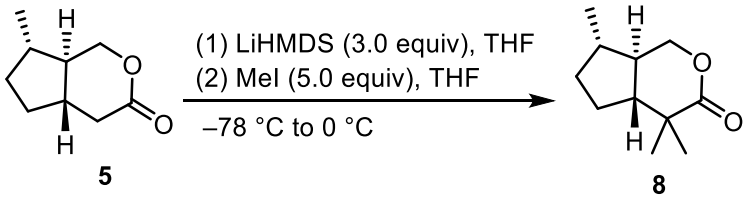


To a solution of **5** (40.0 mg, 0.26 mmol) in dry THF (3.2 mL) was added lithium bis(trimethylsilyl)amide (0.52 mL, 1.0 M in THF, 0.52 mmol, 2.0 equiv) at –78 ℃. The resulting solution was stirred at –78 ℃ for 30 min, followed by the addition of iodomethane (20 μL, 0.32 mmol, 1.2 equiv), and the solution was stirred at –78 ℃ for 30 min. The reaction was quenched by the addition of an aqueous saturated solution of NH_4Cl (20 mL), and the solution was gradually warmed up to room temperature. The resulting mixture was extracted with EtOAc, washed with brine, and the combined organic solution was dried over $MgSO_4$ and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 0 to 10 % EtOAc-hexane to afford product **6** (R_f = 0.52 in 30% in EtOAc-hexane, 19.5 mg, 45% yield) as a colorless oil, product **7** (R_f = 0.50 in 30% in EtOAc-hexane, 11.6 mg, 27% yield) as a colorless oil, **8** (R_f = 0.54 in 30% in EtOAc-hexane, 2.3 mg, 5% yield), and recovered **5** (3.5 mg, 9% yield).

Select data for **6**: $[\alpha]_D^{27}$ 36.9 (*c* 1, $CHCl_3$);[3] IR (neat): 2954, 2872, 1731, 1459, 1312, 1174, 1133, 1010, 797 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 4.52 (dd, *J* = 10.4, 5.1 Hz, 1 H), 4.03 (dd, *J* = 11.7, 10.4 Hz, 1 H), 2.25 (dq, *J* = 11.9, 7.0 Hz, 1H), 2.10 – 2.00 (m, 1 H), 1.98 – 1.89 (m, 1 H), 1.75 – 1.55 (m, 2 H), 1.51 – 1.35 (m, 2 H), 1.30 – 1.22 (m, 1 H), 1.25 (d, *J* = 7.0 Hz, 3 H), 1.01 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.0 (C), 74.3 (CH_2), 48.7 (CH), 48.3 (CH), 44.1 (CH), 36.7 (CH), 33.0 (CH_2), 28.9 (CH_2), 19.0 (CH_3), 15.4 (CH_3);[4] HRMS (HPLC-ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{16}NaO_2$: 191.1048; found: 191.1050.

Select data for **7**: $[\alpha]_D^{23}$ 113.9 (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 4.51 (dd, *J* = 10.5, 5.1 Hz, 1 H), 3.99 (dd, *J* = 11.4, 10.5 Hz, 1 H), 2.89 (qd, *J* = 7.6, 5.9 Hz, 1 H), 2.08 – 1.97 (m, 2 H), 1.70 – 1.46 (m, 4 H), 1.42 – 1.33 (m, 1 H), 1.22 (d, *J* = 7.6 Hz, 3 H), 1.03 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 175.0 (C), 74.6 (CH_2), 44.7 (CH), 42.2 (CH), 38.9 (CH), 36.4 (CH), 33.2 (CH_2), 24.5 (CH_2), 19.2 (CH_3), 13.0 (CH_3); HRMS (HPLC-ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{16}NaO_2$: 191.1048; found: 191.1044.

Preparation of 8:



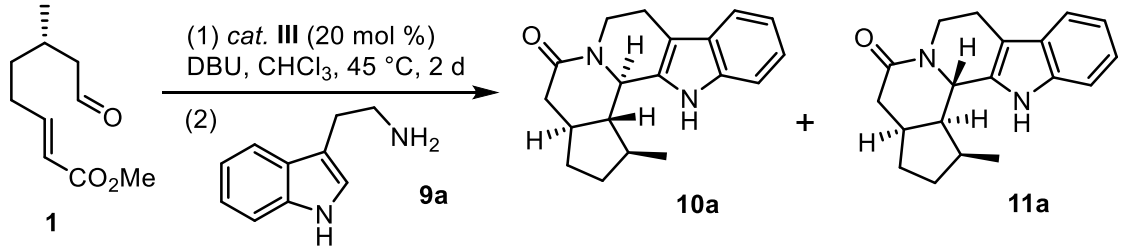
To a stirred solution of **5** (45.0 mg, 0.29 mmol) in anhydrous THF (3.6 mL) at -78 ℃ was added lithium bis(trimethylsilyl)amide (0.90 mL, 1.0 M in THF, 0.90 mmol, 3.1 equiv). The resulting solution was stirred at -78 ℃ for 30 min, followed by the addition of iodomethane (50 μL, 1.46 mmol, 5.0 equiv), and the solution was stirred at -78 ℃ for 30 min, then slowly warmed to 0 ℃ over 1 h. Saturated aqueous NH_4Cl (30 mL) was added to quench the reaction, and the solution was gradually warmed to room temperature. The resulting mixture was extracted with EtOAc and washed with brine, the combined organic solutions were dried over $MgSO_4$ and concentrated *in vacuo* to give a residue. The crude product was purified by flash column chromatography with 0 to 10 % EtOAc-hexane to afford product **8** (R_f = 0.54 in 30% in EtOAc-hexane, 37.3 mg, 70% yield) as a white solid.

Select data for **8**: mp. 66-67 ℃; $[\alpha]_D^{22}$ –7.7 (*c* 1, $CHCl_3$); IR (neat): 2957, 2870, 1727, 1464, 1378, 1232, 1130, 1010, 800, 650 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 4.50 (dd, *J* = 10.5, 5.0 Hz, 1 H), 4.00 (dd, *J* = 11.0, 10.5 Hz, 1 H), 2.08 – 1.98 (m, 1 H), 1.86 – 1.77 (m, 1 H), 1.71 – 1.59 (m, 3 H), 1.51 – 1.41 (m, 1 H), 1.41 – 1.32 (m, 1 H), 1.26 (s, 3 H), 1.18 (s, 3

[3] Trave, R.; Garanti, Marchesini, A.; Garanti, L. *Gazz. Chim. Ital.* **1970**, *100*, 1061–1075.
[4] R. Hilgraf, N. Zimmermann, L. Lehmann, A. Tröger, W. Francke *Beilstein J. Org. Chem.* **2012**, *8*, 1256–1264.

H), 1.01 (d, J = 6.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 177.6 (C), 74.6 (CH_2), 51.4 (CH), 43.7 (CH), 42.8 (C), 37.0 (CH), 33.1 (CH_2), 26.1 (CH_3), 23.1 (CH_2), 21.1 (CH_3), 19.1 (CH_3); HRMS (HPLC-ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{18}NaO_2$: 205.1204; found: 205.1205.

One Pot Organocatalytic asymmetric Michael-Pictet-Spengler-Lactamization Reaction. **Preparation of indoleamide 10a and 11a:**



To a mixture of **1** (25 mg 0.14 mmol) and catalyst **III** (9 mg, 0.03 mmol, 0.2 equiv), and $CHCl_3$ (0.5 mL) in a 25-mL pear-shaped flask was added DBU (4.2 mg, 0.03 mmol, 0.2 equiv) at ambient temperature. The resulting solution was stirred at 45 ℃ for 48 h until the completion of the reaction, as monitored by TLC. The reaction solution was concentrated *in vacuo* to give the residue, which was then employed directly in the subsequent process without further purification.

To a solution of the above crude product in toluene (14 mL) was added tryptamine (32.6 mg, 0.20 mmol, 1.5 equiv) and TFA (23.2 mg, 0.20 mmol, 1.5 equiv) at ambient temperature. The resulting solution was heated to reflux with the Dean-Stark trap for 6 h until the completion of the reaction, as monitored by TLC. The solution was neutralized by the addition of an aqueous $NaHCO_3$ solution, monitored by pH paper. The mixture was extracted with EtOAc (20 mL x 2). The combined organic solution was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 84:16. The crude product was purified by flash column chromatography with 0 to 35 % EtOAc-hexane as eluent (R_f = 0.41 for **11a**, R_f = 0.40 for **10a** in 70 % EtOAc-hexane) to afford products **10a** and **11a** (20.8 mg, 52 % yield). Purification of the mixture using prolonged flash column chromatography resulted in the isolation of pure samples **10a** and **11a** for analysis.

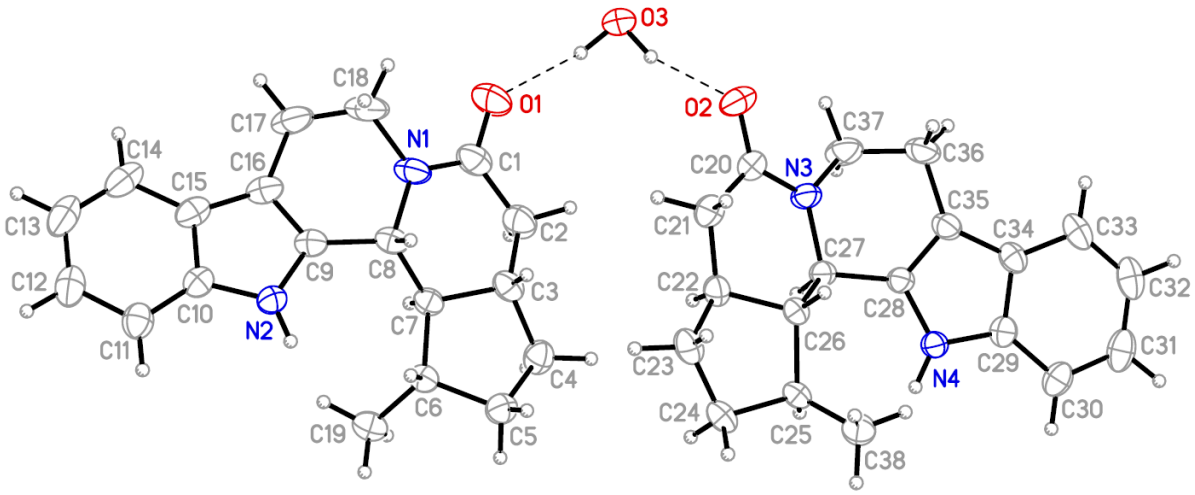
Selected data for **10a**: white solid, mp: 200-201 ℃; $[\alpha]_D^{26}$ 109.4 (*c* 1, $CHCl_3$); IR (neat): IR (neat): 3352, 2946, 2867, 1625, 1409, 1351, 1307, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.83 (brs, 1 H), 7.49 (d, J = 7.8 Hz, 1 H), 7.32 (d, J = 8.1 Hz, 1 H), 7.19 – 7.15 (m, 1 H), 7.12 – 7.09 (m, 1 H), 5.09 (ddd, J = 12.0, 4.4, 1.2 Hz, 1 H), 4.66 (d, J = 10.0 Hz, 1 H), 2.90 – 2.67 (m, 4 H), 2.38 – 2.02 (m, 3 H), 2.00 – 1.82 (m, 2 H), 1.61 – 1.51 (m, 1 H), 1.27 (d, J = 6.8 Hz,

3 H), 1.38 – 1.15 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.9 (C), 135.9 (C), 133.1 (C), 126.7 (C), 122.2 (CH), 119.9 (CH), 118.4 (CH), 110.9 (C), 110.8 (CH), 60.1 (CH), 55.0 (CH), 42.4 (CH), 41.5 (CH_2), 38.8 (CH_2), 35.8 (CH), 34.9 (CH_2), 29.6 (CH_2), 23.0 (CH_3), 21.3 (CH_2); MS (*m/z*, relative intensity): 294 (M^+, 100), 279 (15), 237 (11), 211 (11), 170 (33), 169 (35), 143 (11), 97 (11), 83 (10), 69 (11), 57 (16); HRMS (GC-EI-TOF) *m/z*: $[M]^+$ Calcd for $C_{19}H_{22}N_2O$ (M^+): 294.1732; found: 294.1728.

Selected data for **11a**: white solid, mp: 149-150 ℃ (decomposed); $[\alpha]_D^{27}$ –30.4 (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (brs, 1 H), 7.49 (d, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 1 H), 7.19 – 7.15 (m, 1 H), 7.13 – 7.09 (m, 1 H), 5.15 – 5.12 (m, 1 H), 4.71 (d, J = 11.0 Hz, 1 H), 2.92 – 2.66 (m, 5 H), 2.26 – 1.98 (m, 4 H), 1.74 – 1.66 (m, 1 H), 1.54 – 1.45 (m, 1 H), 1.30 – 1.14 (m, 1 H), 1.19 (d, *J* = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.0 (C), 136.0 (C), 133.7 (C), 126.6 (C), 122.3 (CH), 119.9 (CH), 118.4 (CH), 110.9 (CH), 110.1 (C), 55.8 (CH), 49.6 (CH), 41.1 (CH_2), 39.3 (CH_2), 35.5 (CH), 34.1 (CH), 33.2 (CH_2), 29.7 (CH_2), 21.2 (CH_2), 17.7 (CH_3).

Recrystallization of 10a (major isomer) for single-crystal X-ray analysis:

Compound **10a** (~3 mg) was placed in a screw cap vial (4 mL vial) and dissolved in ethyl acetate (3 mL). Cover the vial with aluminum foil (with 4-5 holes on it) and place in another 20-mL vial. The 20-mL was closed gently with a screw cap and let stand for 7-8 days until the complete evaporation of the solvent in the inner vial. The crystals formed were subjected to single-crystal X-ray analysis.



Thermal ellipsoids draw at the 50% probability level

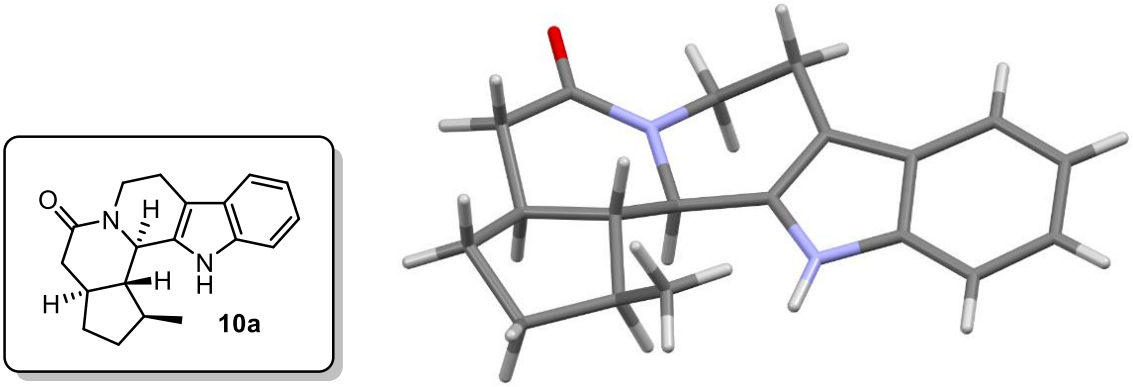
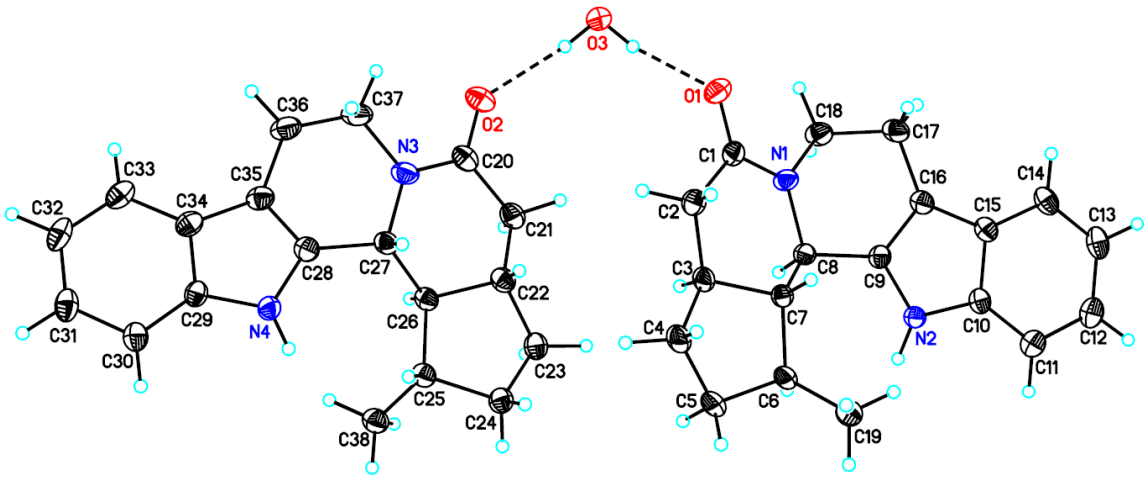


Figure S2. ORTEP and Stereo plots for X-ray crystal structures of **10a** (ic21774).

CCDC 2235983 contains the supplementary crystallographic data for **10a** (ic21774). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk

Table S2. Crystal data and structure refinement for **10a** (ic21774).

Identification code	ic21774	
Empirical formula	C38 H46 N4 O3	
Formula weight	606.79	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.6926(4) Å	α= 73.2229(17)°.
	b = 10.2171(5) Å	β= 86.5859(18)°.
	c = 10.4436(5) Å	γ = 65.2493(15)°.
Volume	804.46(7) $Å^3$	
Z	1	
Density (calculated)	1.252 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	326	
Crystal size	0.229 x 0.169 x 0.064 mm^3	
Theta range for data collection	2.294 to 30.000°.	
Index ranges	-12<=h<=12, -14<=k<=14, -14<=l<=14	
Reflections collected	25318	
Independent reflections	9341 [R(int) = 0.0351]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9604 and 0.8889	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9341 / 6 / 415	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.0920	
R indices (all data)	R1 = 0.0649, wR2 = 0.1051	
Absolute structure parameter	-0.5(5)	
Extinction coefficient	0.047(6)	
Largest diff. peak and hole	0.195 and -0.183 $e.Å^{-3}$	



Thermal ellipsoids draw at the 50% probability level

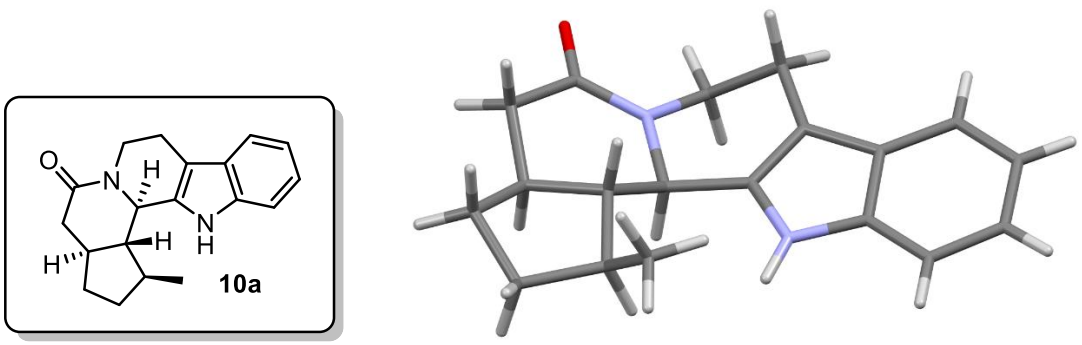


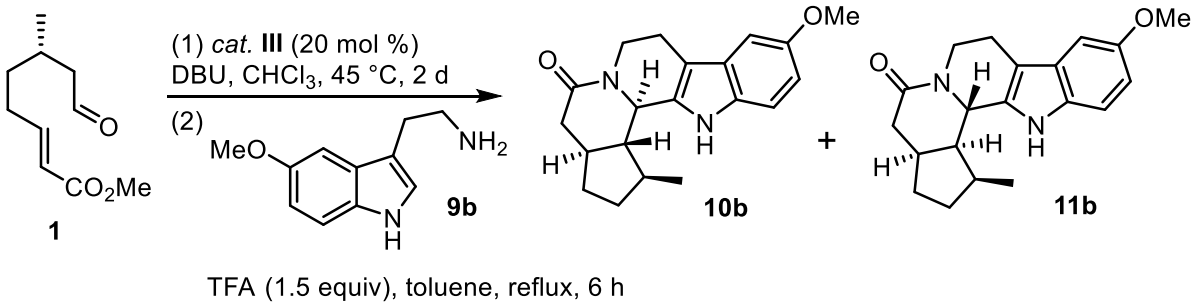
Figure S3. ORTEP and Stereo plots for X-ray crystal structures of **10a**, **another crystal** (ic21796).

CCDC 2236742 contains the supplementary crystallographic data for **10a**, **another crystal** (ic21796). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk

Table S3. Crystal data and structure refinement for **10a**, another crystal (ic21796).

Identification code	ic21796	
Empirical formula	C19 H23 N2 O1.50	
Formula weight	303.39	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.6495(4) Å	α= 72.9361(19)°.
	b = 10.1461(5) Å	β= 86.3302(18)°.
	c = 10.4409(5) Å	γ = 65.6886(17)°.
Volume	796.57(7) $Å^3$	
Z	2	
F(000)	326	
Density (calculated)	1.265 Mg/m^3	
Wavelength	1.54178 Å	
Cell parameters reflections used	9847	
Theta range for Cell parameters	4.44 to 78.11°.	
Absorption coefficient	0.634 mm^{-1}	
Temperature	100(2) K	
Crystal size	0.200 x 0.100 x 0.050 mm^3	
Data collection		
Diffractometer	Bruker AXS D8 VENTURE, PhotonIII_C28	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8635	
No. of measured reflections	25517	
No. of independent reflections	6039 [R(int) = 0.0355]	
No. of observed [I>2_igma(I)]	5925	
Completeness to theta = 67.679°	99.3 %	
Theta range for data collection	4.439 to 78.353°.	
Refinement		
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.1019	
R indices (all data)	R1 = 0.0401, wR2 = 0.1031	
Goodness-of-fit on F^2	1.021	
No. of reflections	6039	
No. of parameters	412	
No. of restraints	3	
Absolute structure parameter	0.12(17)	
Largest diff. peak and hole	0.266 and -0.166 e.$Å^{-3}$	

Preparation of indoleamide 10b.



To a mixture of **1** (25 mg 0.14 mmol) and catalyst **III** (9 mg, 0.03 mmol, 0.2 equiv), and $CHCl_3$ (0.5 mL) in a 25-mL pear-shaped flask was added DBU (4.2 mg, 0.03 mmol, 0.2 equiv) at ambient temperature. The resulting solution was stirred at 45 ℃ for 48 h until the completion of the reaction, as monitored by TLC. The reaction solution was concentrated *in vacuo* to give the residue, which was then employed directly in the subsequent process without further purification.

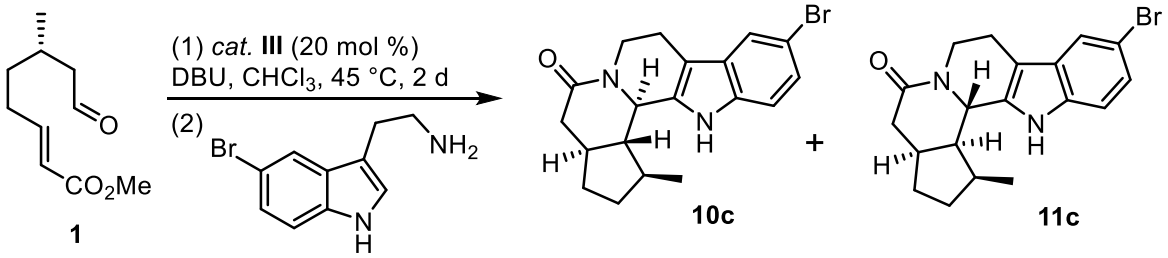
To a solution of the above crude product in toluene (14 mL) was added 5-methoxytryptamine (38.7 mg, 0.20 mmol, 1.5 equiv) and TFA (23.2 mg, 0.20 mmol, 1.5 equiv) at ambient temperature. The resulting solution was heated to reflux with the Dean-Stark trap for 6 h until the completion of the reaction, as monitored by TLC. The solution was neutralized by the addition of an aqueous $NaHCO_3$ solution, monitored by pH paper. The mixture was extracted with EtOAc (20 mL x 2). The combined organic solution was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 84:16. The crude product was purified by flash column chromatography with 0 to 35 % EtOAc-hexane as eluent (R_f = 0.45 for **10b** and **11b** in 70 % EtOAc-hexane) to afford products **10b** and **11b** (25.7 mg, 58% yield). Purification of the mixture using prolonged flash column chromatography resulted in the isolation of pure samples of **10b** for analysis.

Selected data for **10b**: white solid; mp 219–220 ℃; $[\alpha]_D^{25}$ 93.5 (*c* 1, $CHCl_3$); IR (neat): 3371, 2929, 2878, 1622, 1462, 1411, 1265, 1211, 1031, 916, 797, 626 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.70 (brs, 1 H), 7.20 (d, J = 8.7 Hz, 1 H), 6.93 (d, J = 2.5 Hz, 1 H), 6.82 (dd, J = 8.7, 2.5 Hz, 1 H), 5.10 – 5.05 (m, 1 H), 4.64 (d, J = 10.0 Hz, 1 H), 3.84 (s, 3 H), 2.86 – 2.64 (m, 4 H), 2.30 – 2.22 (m, 1 H), 2.21 (dd, J = 17.0, 12.6 Hz, 1 H), 2.13 – 2.02 (m, 1 H), 1.99 – 1.81 (m, 2 H), 1.58 – 1.51 (m, 1 H), 1.35 – 1.22 (m, 2 H), 1.26 (d, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.9 (C), 154.4 (C), 134.0 (C), 130.9 (C), 127.1 (C), 112.2 (CH), 111.5 (CH), 110.7 (C), 100.4 (CH), 60.1 (CH), 55.9 (CH_3), 55.0 (CH), 42.3 (CH), 41.5 (CH_2), 38.8 (CH_2), 35.8 (CH), 34.9 (CH_2), 29.6 (CH_2), 23.0 (CH_3), 21.3 (CH_2); HRMS (HPLC-ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{25}N_2O_2$: 325.1916; found: 325.1912.

Selected data for **11b** from the mixture of **10b** and **11b**: 169.9 (C),[§] 154.4 (C),[§] 134.0 (C),[§]

130.9 (C),[§] 127.1 (C),[§] 112.22 (CH),* 111.6, (CH),* 109.9 (C),* 100.4 (CH),[§] 55.90 (CH_3),* 55.8 (CH),* 49.6 (CH),* 41.1 (CH_2),* 39.3 (CH_2),* 35.5 (CH),* 34.0 (CH),* 33.2 (CH_2),* 29.7 (CH_2),* 21.2 (CH_2),* 17.7 (CH_3).* [§]Overlap with major isomer **10b**; *peaks of **11b**.

Preparation of indoleamide 10c



To a mixture of **1** (25 mg 0.14 mmol) and catalyst **III** (9 mg, 0.03 mmol, 0.2 equiv), and $CHCl_3$ (0.5 mL) in a 25-mL pear-shaped flask was added DBU (4.2 mg, 0.03 mmol, 0.2 equiv) at ambient temperature. The resulting solution was stirred at 45 ℃ for 48 h until the completion of the reaction, as monitored by TLC. The reaction solution was concentrated *in vacuo* to give the residue, which was then employed directly in the subsequent process without further purification.

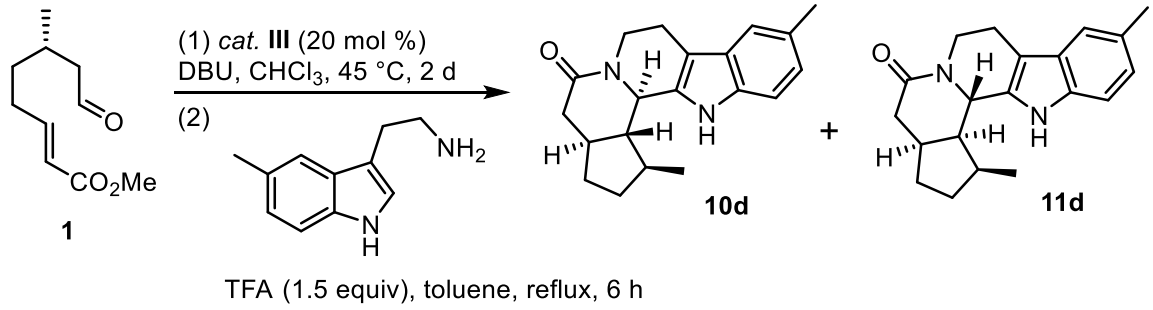
To a solution of the above crude product in toluene (14 mL) was added 5-bromotryptamine (48.6 mg, 0.20 mmol, 1.5 equiv) and TFA (23.2 mg, 0.20 mmol, 1.5 equiv) at ambient temperature. The resulting solution was heated to reflux with the Dean-Stark trap for 6 h until the completion of the reaction, as monitored by TLC. The solution was neutralized by the addition of an aqueous $NaHCO_3$ solution, monitored by pH paper. The mixture was extracted with EtOAc (20 mL x 2). The combined organic solution was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 82:18. The crude product was purified by flash column chromatography with 0 to 35 % EtOAc-hexane as eluent (R_f = 0.51 for **10c** and R_f = 0.52 **11c** in 70 % EtOAc-hexane) to afford products **10c** and **11c** (31.2 mg, 62% yield). Purification of the mixture using prolonged flash column chromatography resulted in the isolation of pure samples of **10c** and **11c** for analysis.

Selected data for **10c:** mp: 226-227 ℃ (decomposed); $[\alpha]_D^{27}$ 128.8 (*c* 1, $CHCl_3$); IR (neat): 3289, 2947, 2865, 1619, 1408, 1306, 799, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87 (brs, 1 H), 7.61 (d, *J* = 1.9 Hz, 1 H), 7.24 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.18 (dd, *J* = 8.5 Hz, 1 H), 5.10 – 5.05 (m, 1 H), 4.64 (d, *J* = 10.0 Hz, 1 H), 2.85 – 2.72 (m, 3 H), 2.68 – 2.63 (m, 1 H), 2.30 – 2.24 (m, 1 H), 2.21 (dd, *J* = 17.1, 12.6 Hz, 1 H), 2.14 – 2.01 (m, 1 H), 2.00 – 1.81 (m, 2 H), 1.60 – 1.52 (m, 1 H), 1.36 – 1.21 (m, 2 H), 1.26 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR

($CDCl_3$, 125 MHz): δ 169.8 (C), 134.5 (C), 134.5 (C), 128.5 (C), 125.0 (CH), 121.1 (CH), 113.1 (C), 112.2 (CH), 110.6 (C), 59.9 (CH), 54.8 (CH), 42.4 (CH), 41.4 (CH_2), 38.8 (CH_2), 35.8 (CH), 34.9 (CH_2), 29.6 (CH_2), 23.0 (CH_3), 21.1 (CH_2); HRMS (HPLC-ESI-TOF) *m/z*: $[M–H]^+$ Calcd for $C_{19}H_{20}BrN_2O$: 371.0759; found: 371.0759.

Selected data for **11c**: white solid, 275-276 ℃; $[\alpha]_D^{22}$ –52.1 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (brs, 1 H), 7.60 (d, *J* = 1.9 Hz, 1 H), 7.24 (dd, *J* = 8.6, 1.9 Hz, 1 H), 7.19 (d, *J* = 8.6 Hz, 1 H), 5.16 – 5.09 (m, 1 H), 4.68 (d, *J* = 11.0 Hz, 1 H), 2.88 – 2.74 (m, 3 H), 2.73 – 2.63 (m, 2 H), 2.26 – 2.16 (m, 1 H), 2.15 – 1.98 (m, 3 H), 1.72 – 1.63 (m, 1 H), 1.55 – 1.46 (m, 1 H), 1.25 – 1.15 (m, 1 H), 1.18 (d, *J* = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.9 (C), 135.1 (C), 134.6 (C), 128.4 (C), 125.0 (CH), 121.1 (CH), 113.1 (C), 112.3 (CH), 109.8 (C), 55.7 (CH), 49.4 (CH), 41.0 (CH_2), 39.2 (CH_2), 35.6 (CH), 34.0 (CH), 33.1 (CH_2), 29.7 (CH_2), 21.0 (CH_2), 17.7 (CH_3).

Preparation of indoleamide 10d.



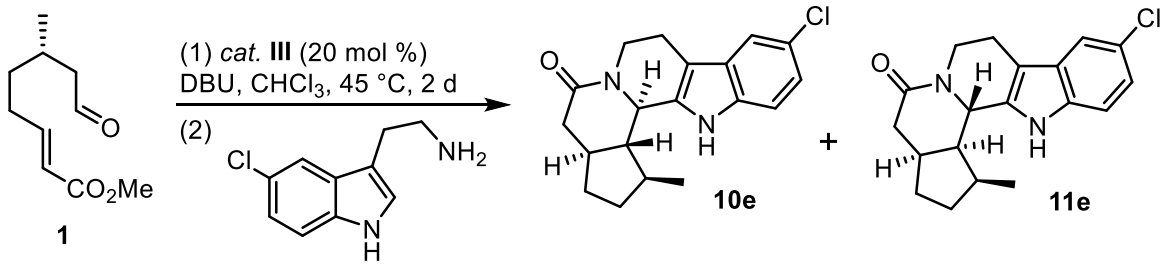
To a mixture of **1** (25 mg 0.14 mmol) and catalyst **III** (9 mg, 0.03 mmol, 0.2 equiv), and $CHCl_3$ (0.5 mL) in a 25-mL pear-shaped flask was added DBU (4.2 mg, 0.03 mmol, 0.2 equiv) at ambient temperature. The resulting solution was stirred at 45 ℃ for 48 h until the completion of the reaction, as monitored by TLC. The reaction solution was concentrated *in vacuo* to give the residue, which was then employed directly in the subsequent process without further purification.

To a solution of the above crude product in toluene (14 mL) was added 5-methyltryptamine (35.4 mg, 0.20 mmol, 1.5 equiv) and TFA (23.2 mg, 0.20 mmol, 1.5 equiv) at ambient temperature. The resulting solution was heated to reflux with the Dean-Stark trap for 6 h until the completion of the reaction, as monitored by TLC. The solution was neutralized by the addition of an aqueous $NaHCO_3$ solution, monitored by pH paper. The mixture was extracted with EtOAc (20 mL x 2). The combined organic solution was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil. The diastereomeric ratio, as determined by ^{1}H NMR analysis of the crude mixture, was found to be 88:12. The crude product was purified by flash column chromatography with 0 to 35 % EtOAc-hexane as eluent

(R_f = 0.43 for **10d** and **10d** in 70 % EtOAc-hexane) to afford products **10d** and **11d** (23.2 mg, 55 % yield). Purification of the mixture using prolonged flash column chromatography resulted in the isolation of pure samples of **10d** for analysis.

Selected data for **10d**: mp 218–219 °C; $[\alpha]_D^{27}$ 107.0 (*c* 1, $CHCl_3$); IR (neat): 3303, 2945, 2862, 1625, 1406, 1310, 1232, 795 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.71 (brs, 1 H), 7.27 (s, 1 H), 7.20 (d, *J* = 8.0 Hz, 1 H), 6.99 (dd, *J* = 8.0 Hz, 1 H), 5.10 – 5.04 (m, 1 H), 4.64 (d, *J* = 10.0 Hz, 1 H), 2.90 – 2.64 (m, 4 H), 2.42 (s, 3 H), 2.32 – 2.25 (m, 1 H), 2.21 (dd, *J* = 17.1, 12.6 Hz, 1 H), 2.13 – 2.00 (m, 1 H), 1.99 – 1.79 (m, 2 H), 1.56 – 1.50 (m, 1 H), 1.35 – 1.26 (m, 2 H), 1.25 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.9 (C), 134.2 (C), 133.2 (C), 129.2 (C), 126.9 (C), 123.7 (CH), 118.2 (CH), 110.44 (CH), 110.40 (C), 60.1 (CH), 55.1 (CH), 42.4 (CH), 41.5 (CH_2), 38.8 (CH_2), 35.8 (CH), 34.9 (CH_2), 29.6 (CH_2), 23.0 (CH_3), 21.4 (CH_3), 21.3 (CH_2); HRMS (HPLC-ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{25}N_2O$: 309.1967; found: 309.1959.

Preparation of indoleamide 10e.



To a mixture of **1** (25 mg 0.14 mmol) and catalyst **III** (9 mg, 0.03 mmol, 0.2 equiv), and $CHCl_3$ (0.5 mL) in a 25-mL pear-shaped flask was added DBU (4.2 mg, 0.03 mmol, 0.2 equiv) at ambient temperature. The resulting solution was stirred at 45 °C for 48 h until the completion of the reaction, as monitored by TLC. The reaction solution was concentrated *in vacuo* to give the residue, which was then employed directly in the subsequent process without further purification.

To a solution of the above crude product in toluene (14 mL) was added 5-chlorotryptamine (39.7 mg, 0.20 mmol, 1.5 equiv) and TFA (23.2 mg, 0.20 mmol, 1.5 equiv) at ambient temperature. The resulting solution was heated to reflux with the Dean-Stark trap for 6 h until the completion of the reaction, as monitored by TLC. The solution was neutralized by the addition of an aqueous $NaHCO_3$ solution, monitored by pH paper. The mixture was extracted with EtOAc (20 mL x 2). The combined organic solution was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil. The diastereomeric ratio, as determined by ^1H NMR analysis of the crude mixture, was found to be 83:17. The crude product was

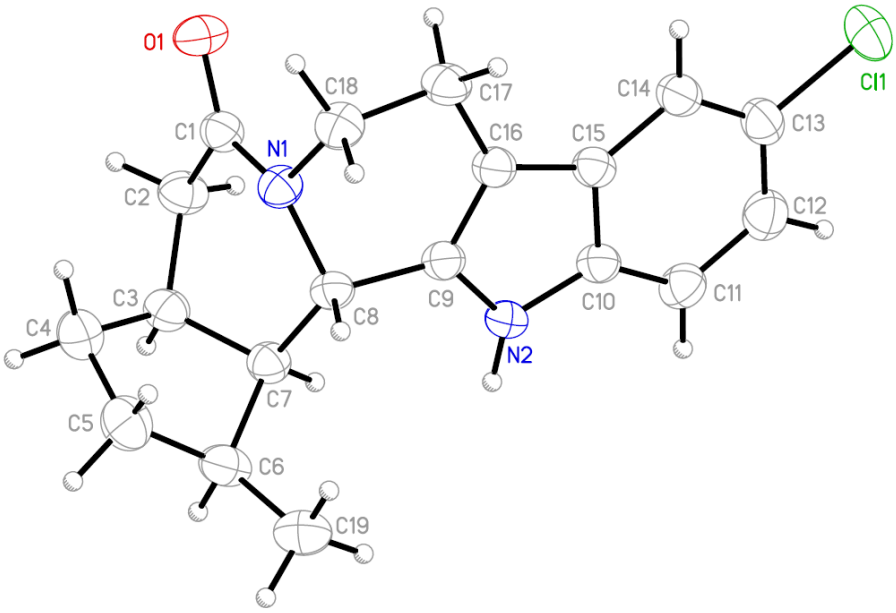
purified by flash column chromatography with 0 to 35 % EtOAc-hexane as eluent (R_f = 0.47 for **10e** and R_f = 0.48 **11e** in 70 % EtOAc-hexane) to afford products **10e** and **11e** (28.3 mg, 63% yield). Purification of the mixture using prolonged flash column chromatography resulted in the isolation of pure samples of **10e** and **11e** for analysis.

Selected data for **10e**: white solid; mp 241–242 ºC; $[\alpha]_D^{27}$ 100.6 (*c* 1, $CHCl_3$); IR (neat): 3300, 2947, 2867, 1619, 1464, 1406, 1306, 1051, 800, 755, 660 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.86 (s, 1 H), 7.45 (d, *J* = 2.0 Hz, 1 H), 7.23 (d, *J* = 8.6 Hz, 1 H), 7.11 (dd, *J* = 8.6, 2.0 Hz, 1 H), 5.10 – 5.05 (m, 1 H), 4.64 (d, *J* = 10.0 Hz, 1 H), 2.86 – 2.72 (m, 3 H), 2.69 – 2.63 (m, 1 H), 2.31 – 2.24 (m, 1 H), 2.21 (dd, *J* = 17.0, 12.6 Hz, 1 H), 2.16 – 2.02 (m, 1 H), 2.01 – 1.90 (m, 1 H), 1.89 – 1.82 (m, 1 H), 1.60 – 1.51 (m, 1 H), 1.35 – 1.22 (m, 2 H) 1.26 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.8 (C), 134.6 (C), 134.2 (C), 127.8 (C), 125.6 (C), 122.5 (CH), 118.0 (CH), 111.8 (CH), 110.7 (C), 59.9 (CH), 54.8 (CH), 42.4 (CH), 41.4 (CH_2), 38.8 (CH_2), 35.9 (CH), 34.9 (CH_2), 29.6 (CH_2), 23.0 (CH_3), 21.2 (CH_2); HRMS (HPLC-ESI-TOF) *m/z*: $[M–H]^+$ Calcd for $C_{19}H_{20}ClN_2O$: 327.1264; found: 327.1262.

Selected data for **11e**: white solid; mp 188-189 ℃ (decomposed); $[\alpha]_D^{27}$ –39.9 (c 1, $CHCl_3$); IR (neat): 3350, 2957, 2860, 1623, 1456, 1261, 1099, 1018, 803, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.79 (brs, 1 H), 7.44 (d, *J* = 2.0 Hz, 1 H), 7.23 (d, *J* = 8.5 Hz, 1 H), 7.11 (dd, *J* = 8.5, 2.0 Hz, 1 H), 5.17 – 5.08 (m, 1 H), 4.68 (d, *J* = 11.0 Hz, 1 H), 2.88 – 2.75 (m, 3 H), 2.73 – 2.64 (m, 2 H), 2.25 – 2.17 (m, 1 H), 2.15 – 1.99 (m, 4 H), 1.73 – 1.64 (m, 1 H), 1.61 – 1.46 (m, 1 H), 1.18 (d, *J* = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.9 (C), 135.3 (C), 134.3 (C), 127.8 (C), 125.6 (C), 122.5 (CH), 118.1 (CH), 111.9 (CH), 109.9 (C), 55.7 (CH), 49.4 (CH), 41.0 (CH_2), 39.2 (CH_2), 35.6 (CH), 34.0 (CH), 33.2 (CH_2), 29.7 (CH_2), 21.0 (CH_2), 17.7 (CH_3).

Recrystallization of 11e (minor isomer) for single-crystal X-ray analysis:

Compound **11e** (~2.5 mg) in a screw-capped vial (4 mL vial) was dissolved in $CHCl_3$ (~0.5 mL), and diluted with hexane (~2.5 mL). The vial was covered with aluminum foil (with 4-5 holes on it) and placed in another 20-mL vial filled with n-hexane (~8 mL). The 20-mL was closed gently with a screw cap and let stand for 6-7 days until the solvent in the inner vial has completely evaporated. The crystals formed were subjected to single-crystal X-ray analysis.



Thermal ellipsoids draw at the 50% probability level

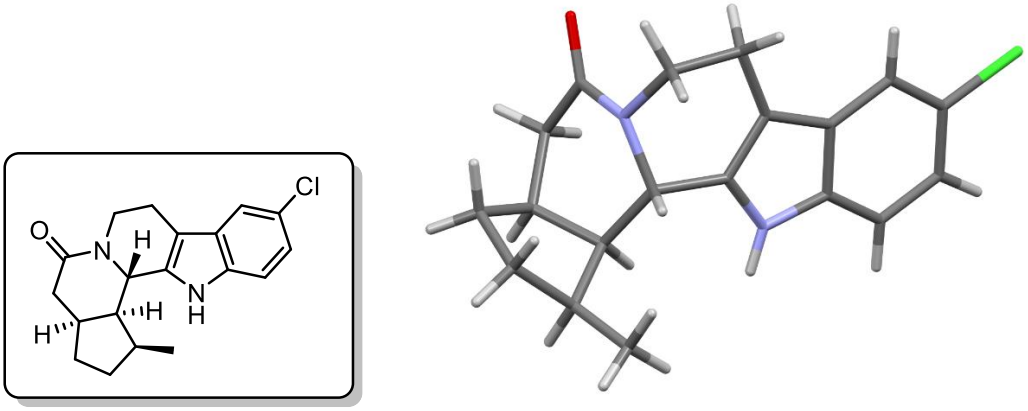


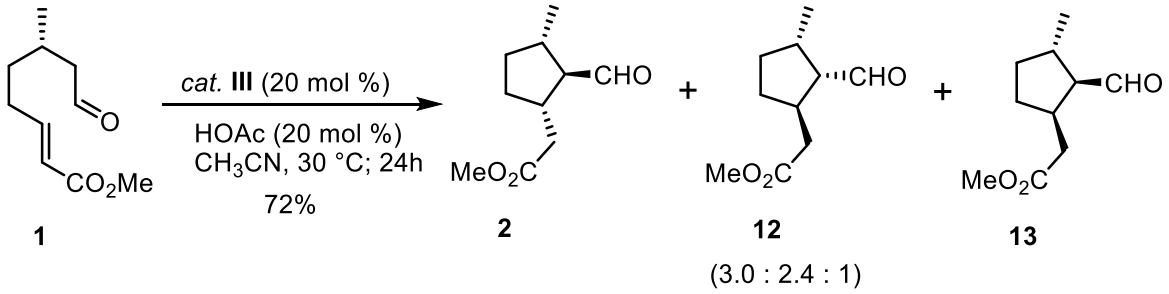
Figure S4. ORTEP and Stereo plots for X-ray crystal structures of **11e** (ic21750).

CCDC 2235984 contains the supplementary crystallographic data for **11e** (ic21750). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk

Table S4. Crystal data and structure refinement for **11e** (ic21750).

Identification code	ic21750	
Empirical formula	C19 H21 Cl N2 O	
Formula weight	328.83	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.2485(2) Å	α= 90°.
	b = 10.0179(3) Å	β= 90°.
	c = 22.3054(7) Å	γ = 90°.
Volume	1619.70(8) Å^3	
Z	4	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.242 mm^{-1}	
F(000)	696	
Crystal size	0.540 x 0.418 x 0.034 mm^3	
Theta range for data collection	2.229 to 27.497°.	
Index ranges	-9<=h<=9, -13<=k<=12, -28<=l<=24	
Reflections collected	24516	
Independent reflections	3712 [R(int) = 0.0361]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9604 and 0.8231	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3712 / 0 / 213	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.0890	
R indices (all data)	R1 = 0.0519, wR2 = 0.0975	
Absolute structure parameter	0.02(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.261 and -0.230 e.Å^{-3}	

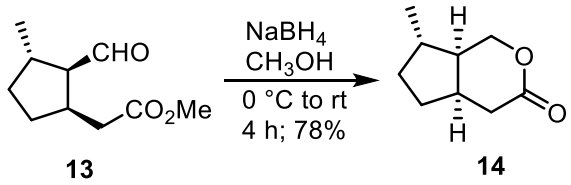
Reaction of aldehyde 1 with cat. III–HOAc (0.2 equiv) in CH_3CN:



To a solution of catalyst **III** (188.9 mg, 0.58 mmol, 0.20 equiv) and **1** (535.0 mg, 2.90 mmol) in CH_3CN (9.6 mL) was added acetic acid (33 μL, 0.58 mmol, 0.20 equiv) at ambient temperature. The resulting solution was stirred at 30 ℃ for 24 h until the completion of the reaction, as monitored by TLC. The reaction solution was diluted with EtOAc, and washed with water and brine. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 5% EtOAc-hexane (R_f = 0.51 in 20% EtOAc-hexane) to afford products **2** and **12** (ratio 1:1; 349.8 mg, 65% yield; R_f = 0.51 in 20% EtOAc-hexane) as a colorless oil and **13** (37.8 mg; 7% yield, R_f = 0.52 in 20% EtOAc-hexane) for analysis.

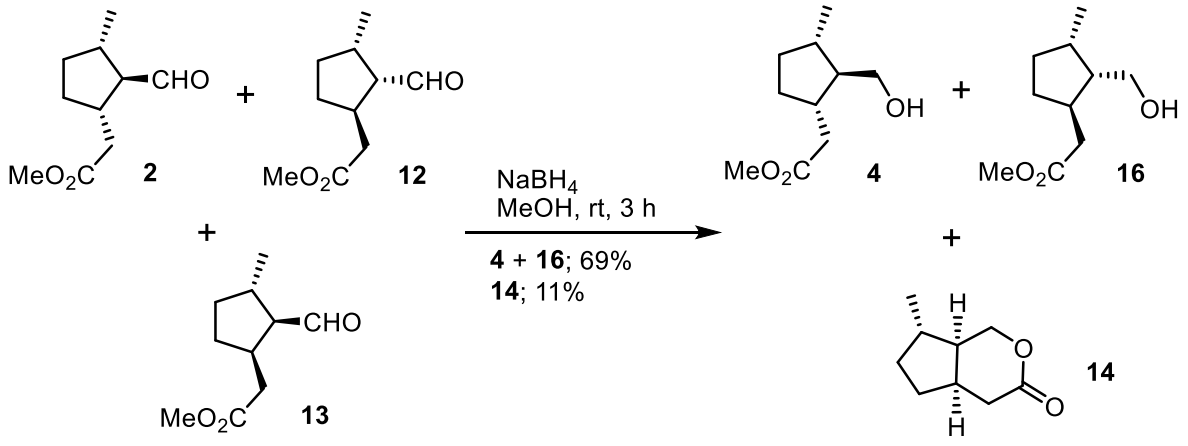
Selected data for **12** (**12** denoted by an asterisk, identified from the mixture with **2**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.73 (d, J = 3.0 Hz, 1 H*), 9.54 (d, J = 3.9 Hz, 1 H), 3.62 (s, 3 H), 3.61 (s, 3 H*), 2.81 – 2.72 (m, 1 H*), 2.66 – 2.55 (m, 1 H), 2.54 – 2.43 (m, 1 H*), 2.37 (d, J = 7.4 Hz, 2 H), 2.34 (dd, J = 7.2, 5.7 Hz, 2 H*), 2.24 – 2.14 (m, 1 H), 2.09 – 2.00 (m, 1 H*), 2.00 – 1.83 (m, 3 H and 2 H*), 1.48 – 1.39 (m, 1 H), 1.38 – 1.25 (m, 1 H and 2 H*), 1.03 (d, J = 6.7 Hz, 3 H), 1.00 (d, J = 6.9 Hz, 3 H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.5 (CH),* 203.2 (CH), 172.88 (C),* 172.74 (C), 65.8 (CH), 60.3 (CH),* 51.53 (CH_3), 51.50 (CH_3),* 39.28 (CH_2),* 39.25 (CH_2), 37.5 (CH), 37.1 (CH),* 36.8 (CH), 35.2 (CH),* 34.3 (CH_2),* 33.3 (CH_2), 31.5 (CH_2),* 31.3 (CH_2), 19.5 (CH_3), 16.5 (CH_3).*

Preparation of (+)-7-*epi*-boschnialactone 14



To a stirred solution of **13** (50.0 mg, 0.27 mmol) in MeOH (5 mL) was added $NaBH_4$ (20.5 mg, 0.54 mmol, 2.0 equiv) at 0 ℃. The resulting solution was stirred at room temperature for 4 h until the completion of the reaction, as monitored by TLC. The reaction was quenched by the addition of an aqueous solution of 2N HCl (0.5 mL). The reaction mixture was diluted with EtOAc, and washed with water and brine. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 0 to % EtOAc-hexane (R_f = 0.45 in 30 % EtOAc-hexane) to afford product **14** (32.8 mg, 78% yield) as a white solid. Selected data for **14**: m.p. 56–57 ℃; $[\alpha]_D^{22}$ 94.2 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.25 (dd, *J* = 11.5, 4.5 Hz, 1 H), 4.08 (dd, *J* = 11.5, 4.5 Hz, 1 H), 2.63 – 2.53 (m, 2 H), 2.35 – 2.29 (m, 1 H), 2.02 – 1.95 (m, 1 H), 1.89 – 1.74 (m, 3 H), 1.26 – 1.08 (m, 2 H), 1.04 (d, *J* = 6.0 Hz, 3 H);[5] ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.7 (C), 69.0 (CH_2), 44.6 (CH), 37.5 (CH), 34.82 (CH), 34.81 (CH_2), 34.6 (CH_2), 33.4 (CH_2), 18.7 (CH_3); HRMS (HPLC-ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_9H_{14}NaO_2$: 177.08915; found: 177.08918.

Reduction of the mixture of 2, 12, and 13

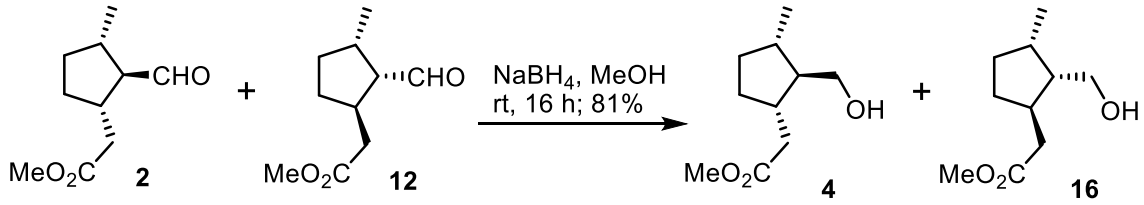


To a stirred solution of the mixture of **2, 12**, and **13** (50.0 mg, 0.27 mmol) in MeOH (5 mL) was added $NaBH_4$ (20.5 mg, 0.54 mmol, 2.0 equiv) at 0 ℃. The resulting solution was

[5] Tanaka, D.; Yoshino, T.; Kouno, I.; Miyashita, M.; Irie, H. *Tetrahedron*, **1993**, *49*, 10253 – 10262. (b) Inoue, T.; Kitagawa, O.; Saito, A.; Taguchi, T. *J. Org. Chem.* **1997**, *62*, 7384 – 7389.

stirred at room temperature for 3 h, and the reaction was quenched by the addition of an aqueous solution of 2N HCl (0.5 mL). The reaction mixture was diluted with EtOAc, and washed with water and brine. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 0 to 30 % EtOAc-hexane to afford the inseparable **4** and **16** mixtures as a colorless oil (34.8 mg, 69% yield; R_f = 0.47 in 40% EtOAc–hexane) and **14** as a white solid (4.5 mg, 11% yield; R_f = 0.48 in 40% EtOAc–hexane).

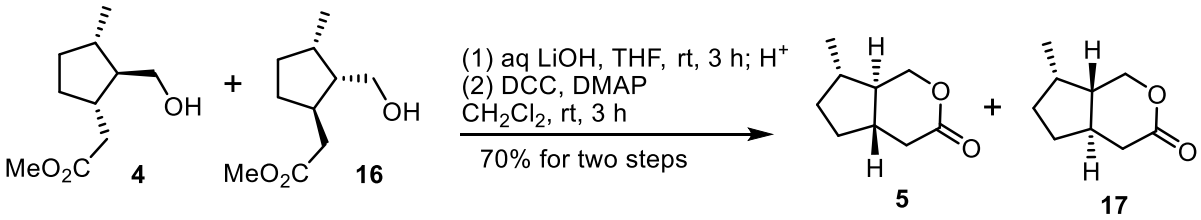
Preparation of 4 and 16



To a stirred solution of the mixture of **2** and **12** (100.0 mg, 0.54 mmol) in MeOH (10 mL) was added $NaBH_4$ (41.0 mg, 1.08 mmol, 2.0 equiv) at 0 ℃. The resulting solution was stirred at room temperature for 3 h until the completion of the reaction, as monitored by TLC. The reaction was further stirred at room temperature for an additional 16 h, but no lactone product was produced, and the reaction was unchanged for a prolonged reaction. The reaction was quenched by the addition of an aqueous solution of 2N HCl (0.5 mL). The reaction mixture was diluted with EtOAc, and washed with water and brine. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 0 to 20 % EtOAc-hexane (R_f = 0.47 in 40 % EtOAc-hexane) to afford products of the inseparable **4** and **16** mixtures (82.1 mg, 81% yield) as a colorless oil. The two isomers were unable to be separated by silica gel chromatography.

Selected data for **16** (**16** denoted by an asterisk, identified from the mixture with **4**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.68 (dd, J = 11.0, 6.5 Hz, 1 H*), 3.655 (s, 3 H), 3.649 (s, 3 H*), 3.61 (dd, J = 11.0, 4.5 Hz, 1 H), 3.52 (dd, J = 11.0, 6.5 Hz, 1 H), 3.50 (dd, J = 11.0, 7.0 Hz, 1 H*), 2.45 – 2.40 (m, 1 H* and 1 H), 2.37 – 2.28 (m, 1 H* and 1 H), 2.21 – 2.10 (m, 1 H* and 1 H), 2.00 – 1.65 (m, 4 H* and 4 H), 1.40 – 1.12 (m, 3 H* and 3 H), 0.99 (d, J = 6.6 Hz, 3 H), 0.91 (d, J = 7.0 Hz, 3 H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.5 (C), 174.3 (C),* 64.4 (CH_2), 63.2 (CH_2),* 55.8 (CH), 51.62 (CH_3), 51.56 (CH_3),* 50.4 (CH),* 40.4 (CH_2),* 40.0 (CH_2), 38.6 (CH), 37.4 (CH),* 37.1 (CH), 35.6 (CH),* 33.2 (CH_2),* 32.9 (CH_2), 31.3 (CH_2),* 31.2 (CH_2), 20.1 (CH_3), 15.2 (CH_3).*

Preparation of Lactone 5 and 17

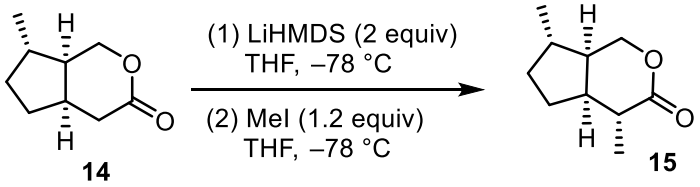


To a solution of the mixture of **4** and **16** (210.0 mg, 1.13 mmol) in THF (4.2 mL) was added an aqueous solution of LiOH (54.3 mg, 2.27 mmol, 2.0 equiv) in water (2.1 mL) at room temperature. The resulting solution was stirred at room temperature for 3 h until the completion of the reaction, as monitored by TLC. The pH of the solution was adjusted to 2-3 by adding 2M aqueous HCl at 0 ℃. The reaction mixture was diluted and extracted with EtOAc. The solution was washed with water and brine. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give the crude product as an oil. This residue was proceeded to the next step without further purification.

To a solution of the above crude product in dry CH_2Cl_2 (21 mL) was added DCC (233.9 mg, 1.13 mmol, 1.0 equiv) and DMAP (27.2 mg, 0.20 mmol, 0.2 equiv) at room temperature. The resulting solution was stirred at room temperature for 3 h until the completion of the reaction, as monitored by TLC. The reaction mixture was diluted with EtOAc, followed by washing with brine and water. The combined organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 10-15 % EtOAc-hexane (R_f = 0.48 in 40% EtOAc-hexane) to afford the mixture of products **5** and **17** (121.2 mg, 70% yield) as a colorless oil.

Selected data for **17** (**17** denoted by an asterisk, identified from the mixture with **5**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.55 (dd, J = 10.5, 5.0 Hz, 1 H), 4.51 (dd, J = 10.5, 5.0 Hz, 1 H*), 4.21 (dd, J = 12.0, 10.5 Hz, 1 H*), 4.05 (dd, J = 11.7, 10.5 Hz, 1 H), 2.90 (dd, J = 17.8, 5.0 Hz, 1 H*), 2.84 (dd, J = 17.7, 5.0 Hz, 1 H), 2.39 – 1.61 (m, 5 H and 5 H*), 1.47 – 1.08 (m, 3 H and 3 H*), 1.03 (d, J = 6.6 Hz, 3 H), 0.84 (d, J = 7.3 Hz, 3 H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.5 (C and C*), 74.3 (CH_2), 72.3 (CH_2),* 48.6 (CH), 44.0 (CH),* 41.5 (CH), 38.2 (CH_2),* 38.1 (CH_2), 37.6 (CH),* 36.0 (CH), 33.7(CH_2),* 33.0 (CH_2), 31.9 (CH),* 31.2 (CH_2),* 29.7 (CH_2), 19.1 (CH_3), 17.3 (CH_3).*

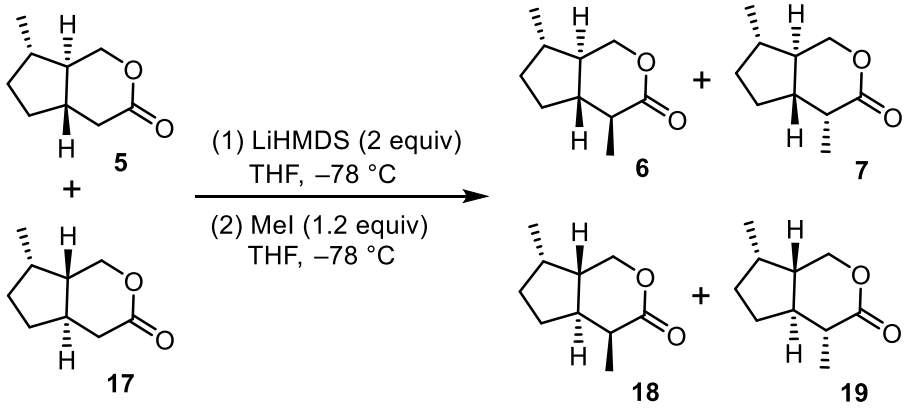
Preparation of (–)-isoiridomyrmecin 15



To a solution of **14** (20.0 mg, 0.13 mmol) in dry THF (1.6 mL) was added lithium bis(trimethylsilyl)amide (0.26 mL, 1.0 M in THF, 0.26 mmol, 2.0 equiv) at –78 ℃. The resulting solution was stirred at –78 ℃ for 30 min, followed by the addition of iodomethane (10 μL, 0.16 mmol, 1.2 equiv), and the solution was stirred at –78 ℃ for 30 min. The reaction was quenched by the addition of an aqueous saturated solution of NH_4Cl (5 mL), and the solution was gradually warmed up to room temperature. The resulting mixture was extracted with EtOAc, washed with brine, and the combined organic solution was dried over $MgSO_4$ and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 0 to 10 % EtOAc-hexane to afford product isoiridomyrmecin (**15**, R_f = 0.52 in 30% in EtOAc-hexane, 16.1 mg, 74% yield) as a white solid.

Selected data for **15**: mp. 53–54 °C; $[\alpha]_D^{23}$ –57.4 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.36 – 4.30 (m, 1 H), 3.93 (t, *J* = 11.2 Hz, 1 H), 2.34 – 2.24 (m, 1 H), 2.14 – 2.07 (m, 1 H), 2.06 – 1.96 (m, 2 H), 1.91 – 1.83 (m, 1 H), 1.68 – 1.59 (m, 1 H), 1.36 – 1.23 (m, 2 H), 1.18 (d, *J* = 6.6 Hz, 3 H), 1.03 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 176.4 (C), 69.4 (CH_2), 45.3 (CH), 43.1 (CH), 39.1 (CH), 38.3 (CH), 35.7 (CH_2), 33.1 (CH_2), 19.1 (CH_3), 13.9 (CH_3);[4] HRMS (HPLC-ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_{16}NaO_2$: 191.10480; found: 191.10483.

Preparation of 6, 7, 18, and 19 with LiHMDS:



To a solution of **5** and **17** mixtures (110.0 mg, 0.71 mmol) in dry THF (8.9 mL) was added lithium bis(trimethylsilyl)amide (1.42 mL, 1.0 M in THF, 1.42 mmol, 2.0 equiv) at –78

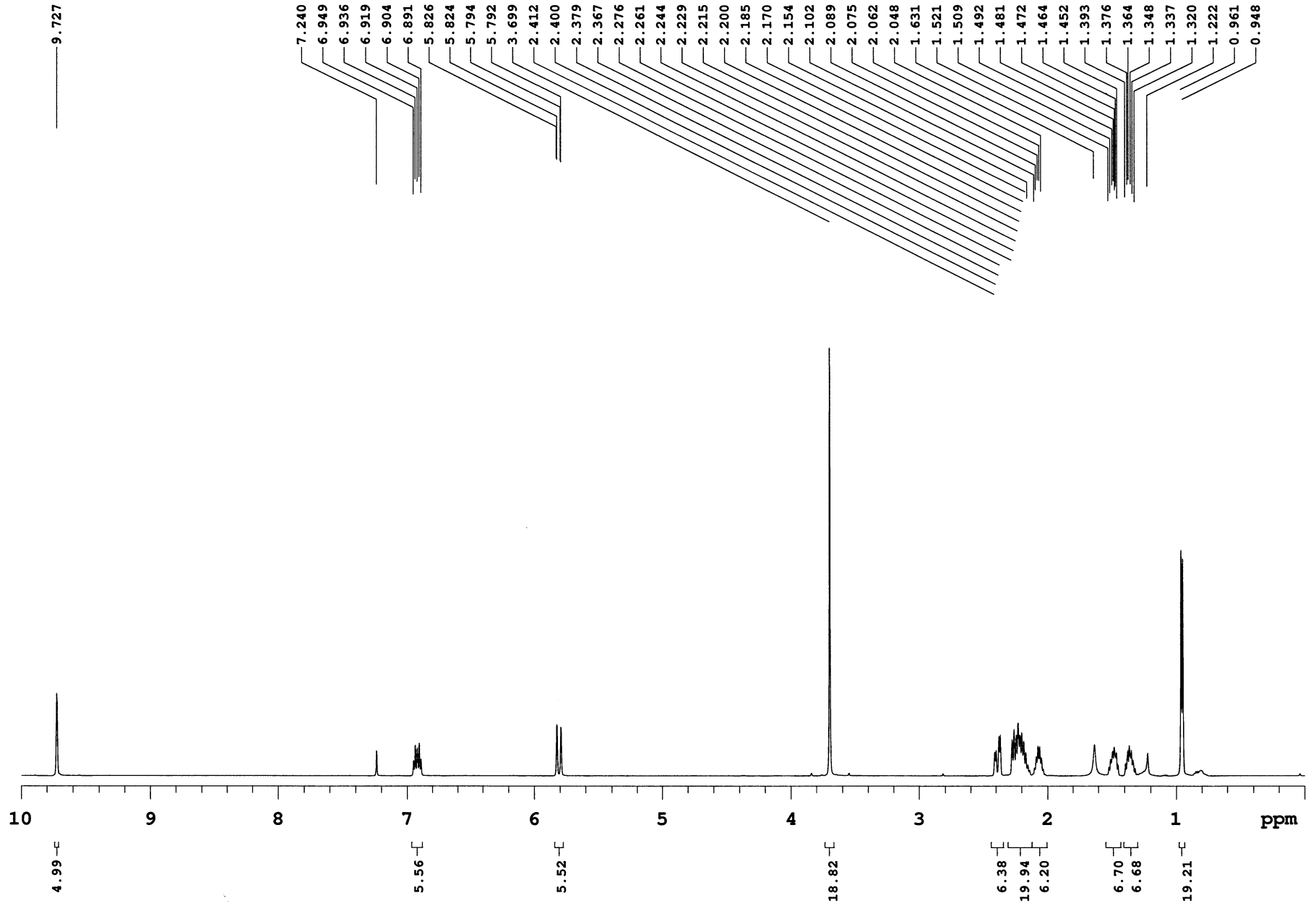
℃. The resulting solution was stirred at –78 ℃ for 30 min, followed by the addition of iodomethane (55 μL, 0.88 mmol, 1.2 equiv), and the solution was stirred at –78 ℃ for 30 min. The reaction was quenched by the addition of an aqueous saturated solution of NH_4Cl (20 mL), and the solution was gradually warmed up to room temperature. The resulting mixture was extracted with EtOAc, washed with brine, and the combined organic solution was dried over $MgSO_4$ and concentrated *in vacuo* to give a crude oil. The crude product was purified by flash column chromatography with 10 to 25 % EtOAc-hexane to afford the product mixtures of **6**, **7**, **18**, and **19** in several fractions (R_f = 0.50-0.52 in 30% in EtOA–hexane, total collecting weight: 80.5 mg; 67% yield). The properties of these isomers are very similar and individual pure substances cannot be completely separated from the mixture of these isomers. However, in addition to compounds **6** and **7**, compounds **18** and **19** can also be identified from some fractions, where the ^{13}C NMR chemical shift values were in good agreement with the literature data.[4]

Select data from the spectra of isomers: For **18** (iridomyrmecin C'): ^{13}C NMR ($CDCl_3$, 125 MHz): δ 175.0, 72.4, 41.0, 38.9, 37.3, 34.1, 31.8, 26.1, 17.1, 13.2. For **19** (iridomyrmecin D'): ^{13}C NMR ($CDCl_3$, 125 MHz): 173.9, 72.2, 44.5, 44.4, 44.1, 33.7, 32.6, 30.3, 17.2, 15.7.[6]

[6] Ref. 4; lit. data, for **18** (iridomyrmecin C): ^{13}C NMR ($CDCl_3$, 125 MHz): δ 175.1, 72.5, 41.0, 38.9, 37.3, 34.1, 31.8, 26.1, 17.1, 13.2. For **19** (iridomyrmecin D): ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.0, 72.2, 44.6, 44.5, 44.2, 33.7, 32.6, 30.3, 17.2, 15.7.

PDC-02-374-f1

Sample Name **PDC-02-374-f1**	Pulse sequence **PROTON**	Temperature **20**	Study owner **vnmr2**
Date collected **2015-12-07**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



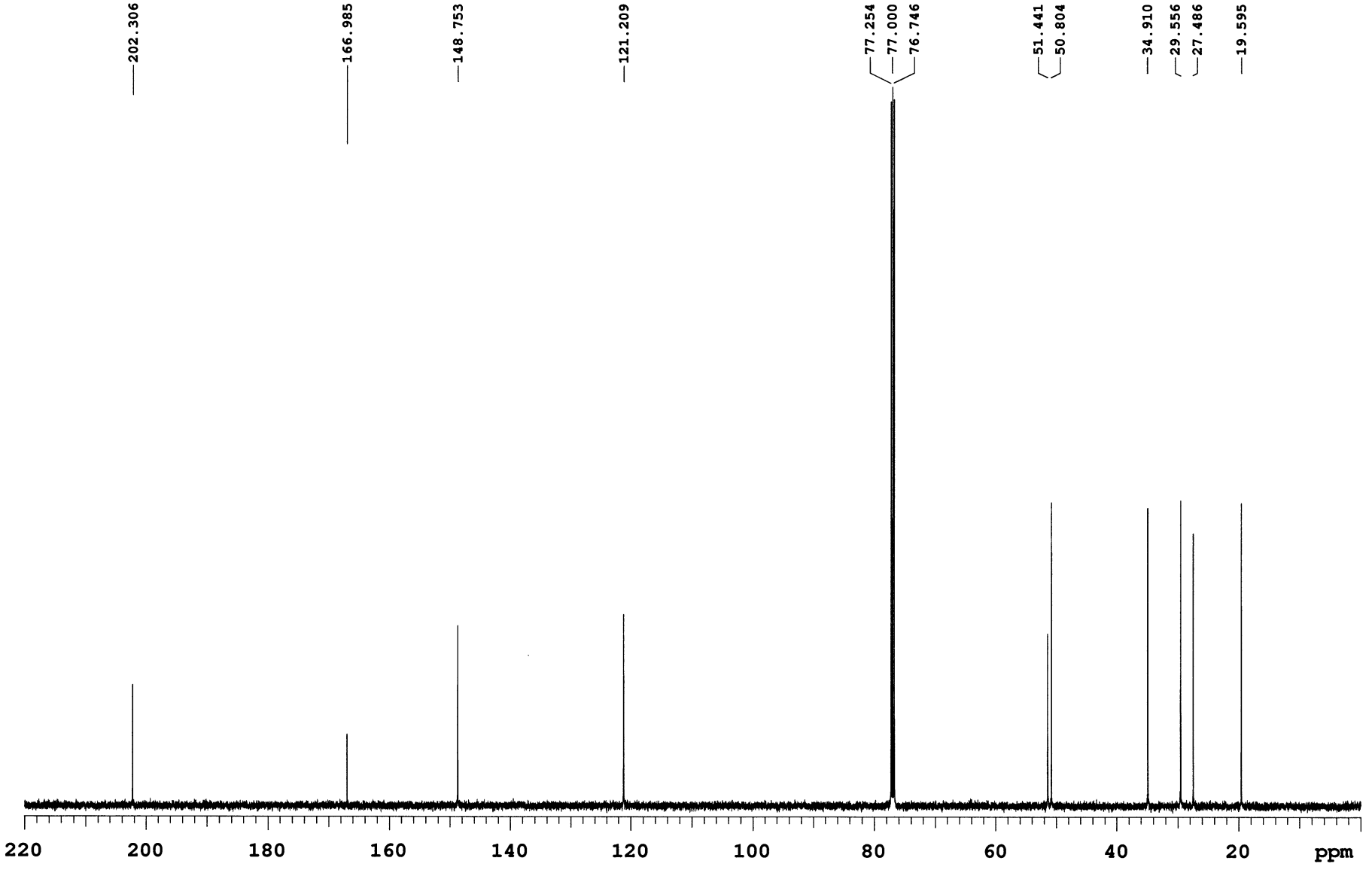
Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-374-f1/PROTON_02

1H NMR (500 MHz, CDCl3) of compound 1

Plot date 2015-12-09

PDC-02-374-f1

Sample Name **PDC-02-374-f1**	Pulse sequence **CARBON**	Temperature **20**	Study owner **vnmr2**
Date collected **2015-12-07**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



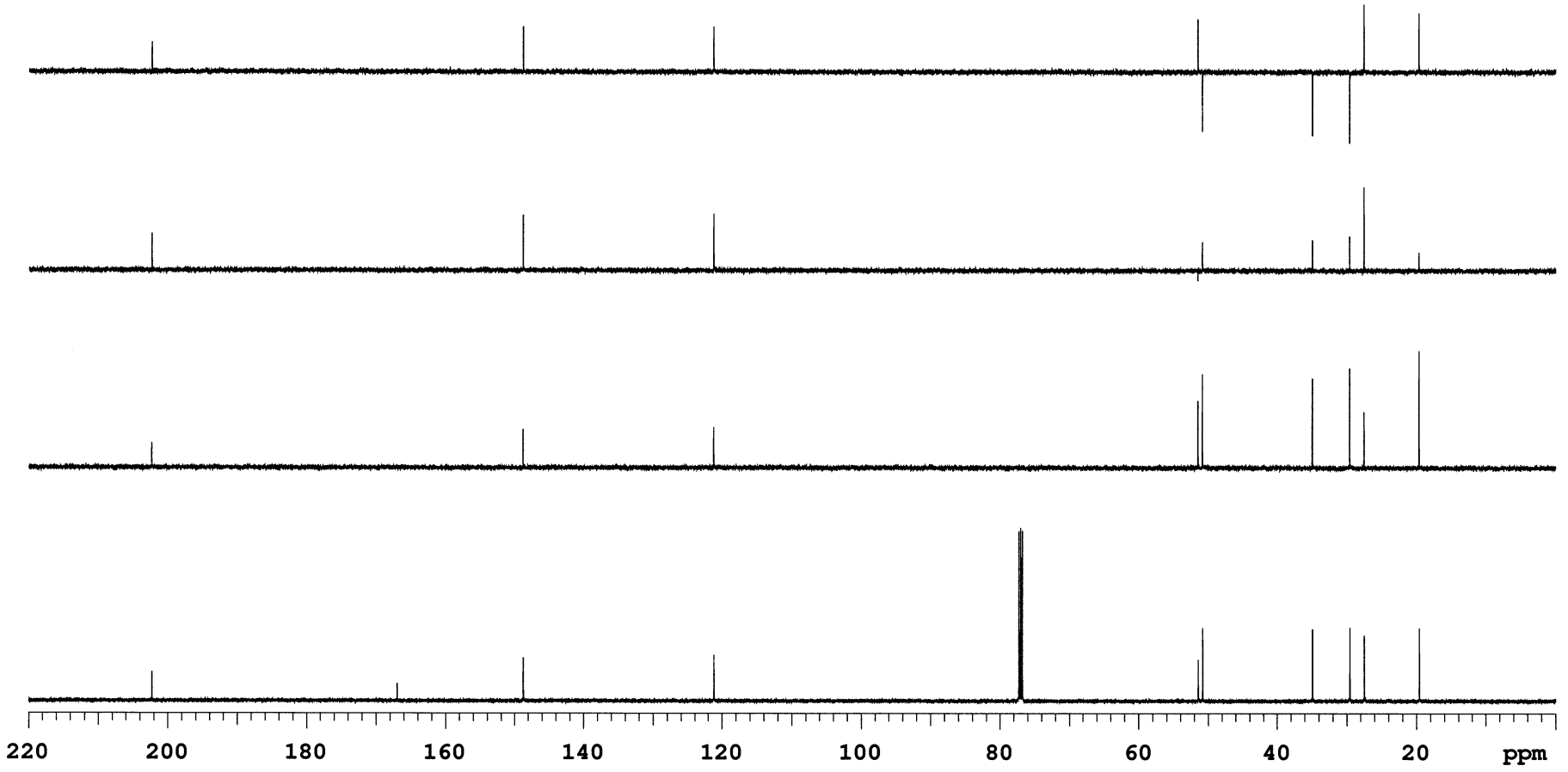
13C NMR (125 MHz, CDCl3) of compound 1

Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-374-f1/CARBON_01

Plot date 2015-12-09

PDC-02-374-f1

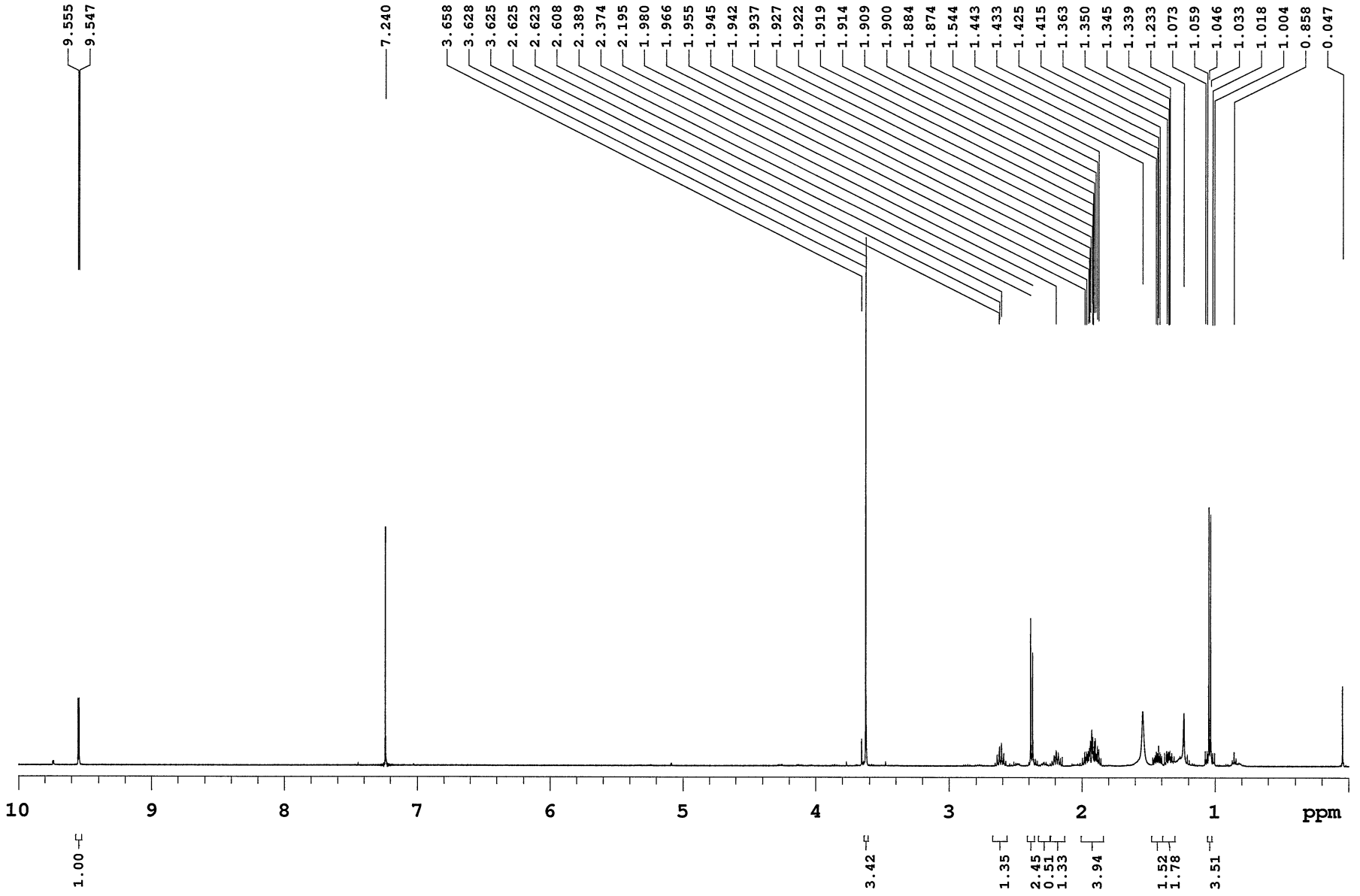
Sample Name **PDC-02-374-f1**	Pulse sequence **DEPT**	Temperature **20**	Study owner **vnmr2**
Date collected **2015-12-07**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 1

PDC-02-428-f2

Sample Name	**PDC-02-428-f2**	Pulse sequence	**PROTON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-04-07**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



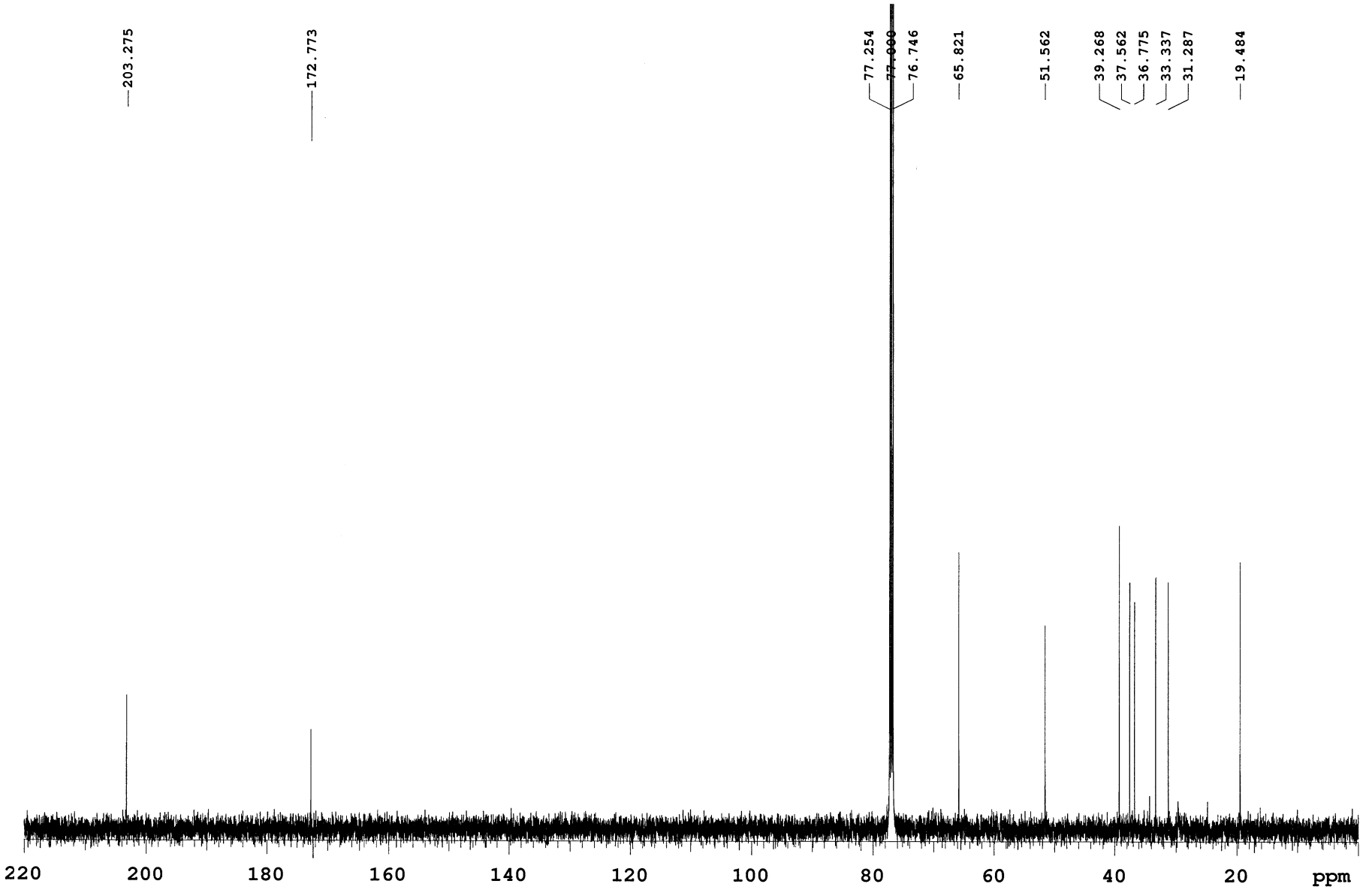
Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-428-f2/PROTON_04

1H NMR (500 MHz, CDCl3) of compound 2

Plot date 2020-06-15

PDC-02-428-f2

Sample Name **PDC-02-428-f2** | Pulse sequence **CARBON** | Temperature **25** | Study owner **vnmr2**
Date collected **2016-04-07** | Solvent **cdcl3** | Spectrometer **Agilent-NMR-inova500** | Operator **vnmr2**



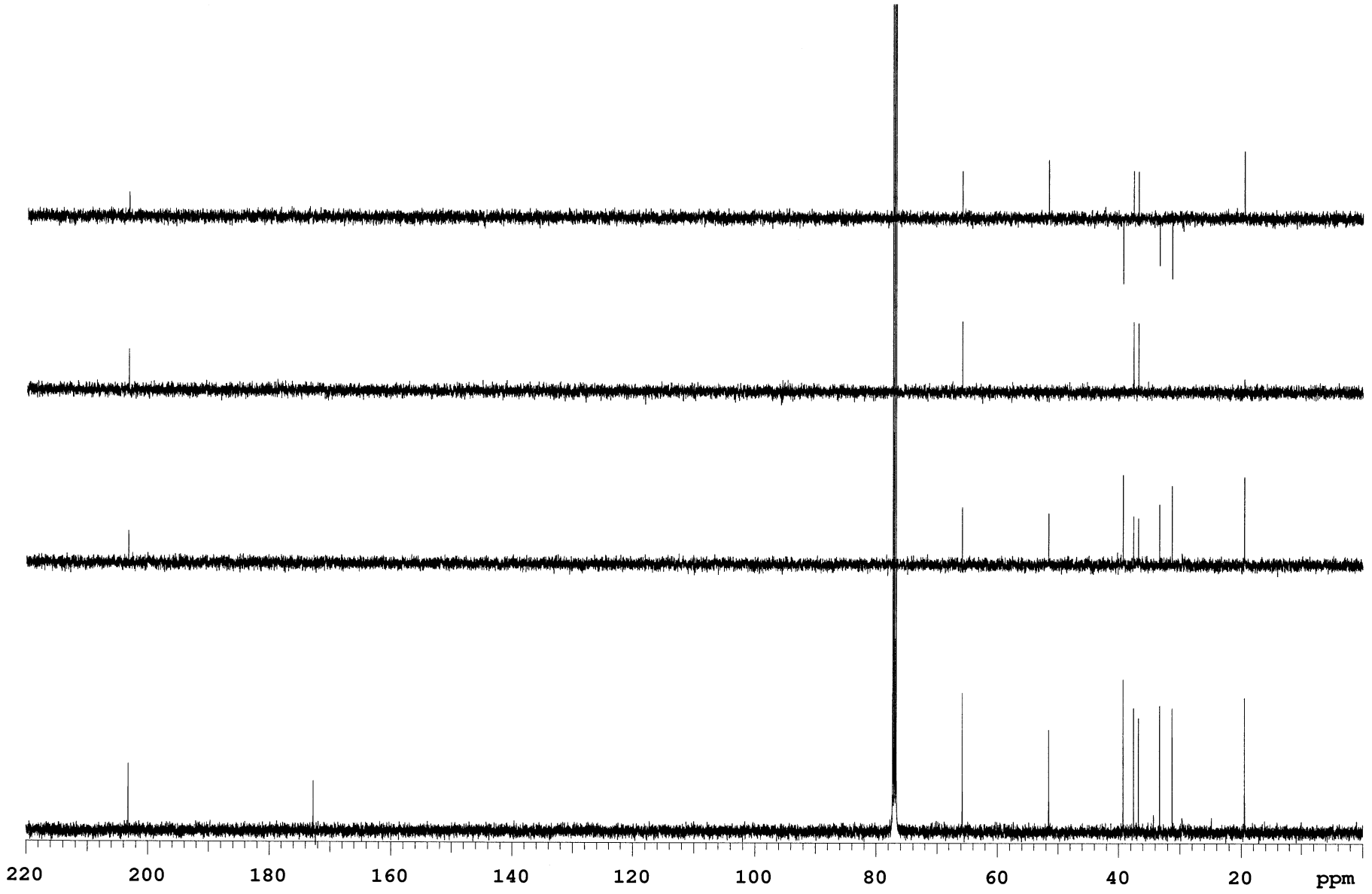
13C NMR (125 MHz, CDCl3) of compound 2

Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-428-f2/CARBON_01.fid

Plot date 2016-04-08

PDC-02-428-f2

Sample Name	**PDC-02-428-f2**	Pulse sequence	**DEPT**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-04-07**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



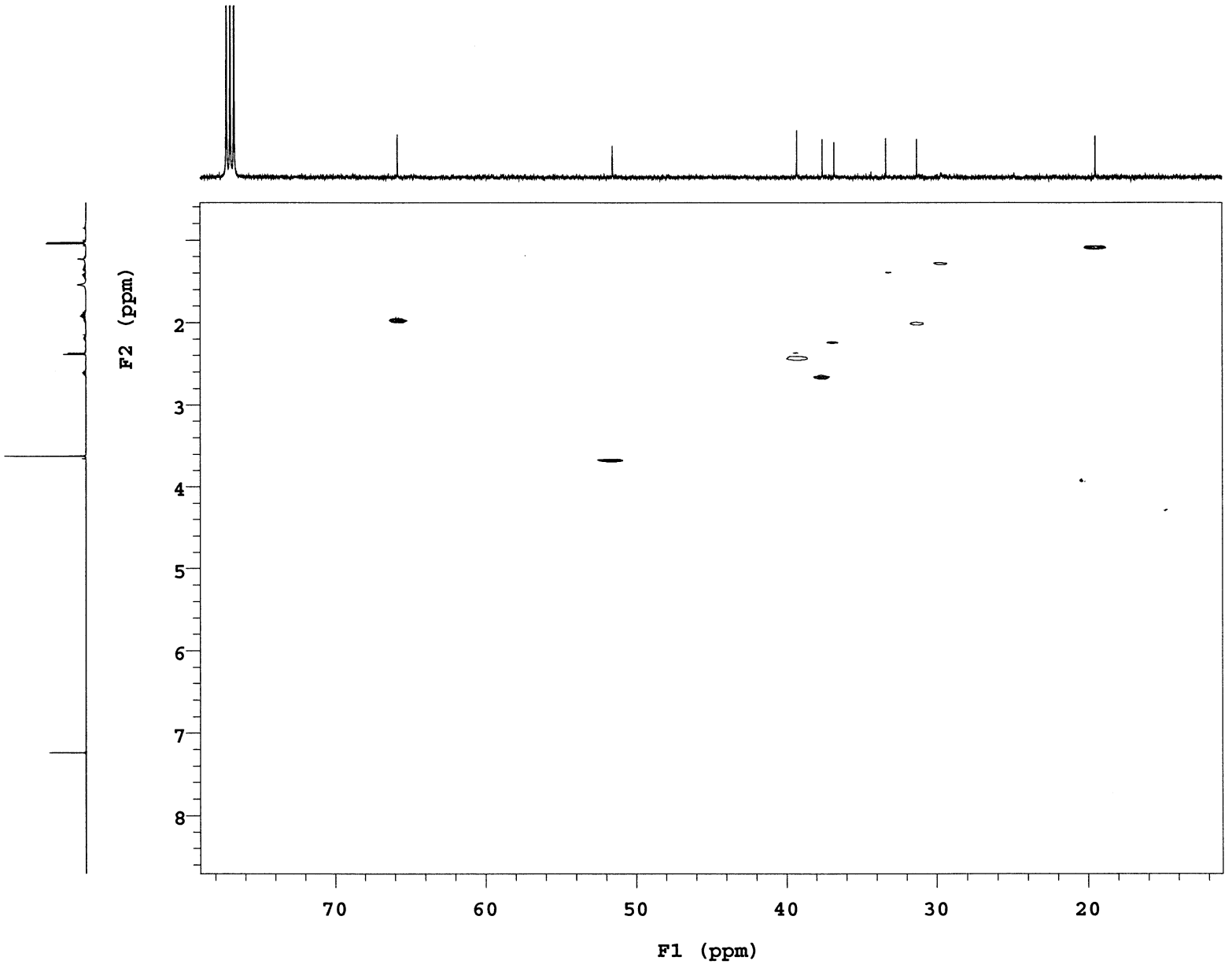
DEPT of compound 2

Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-428-f2/DEPT_01.fid

Plot date 2016-04-08

PDC-02-428-F2-2D

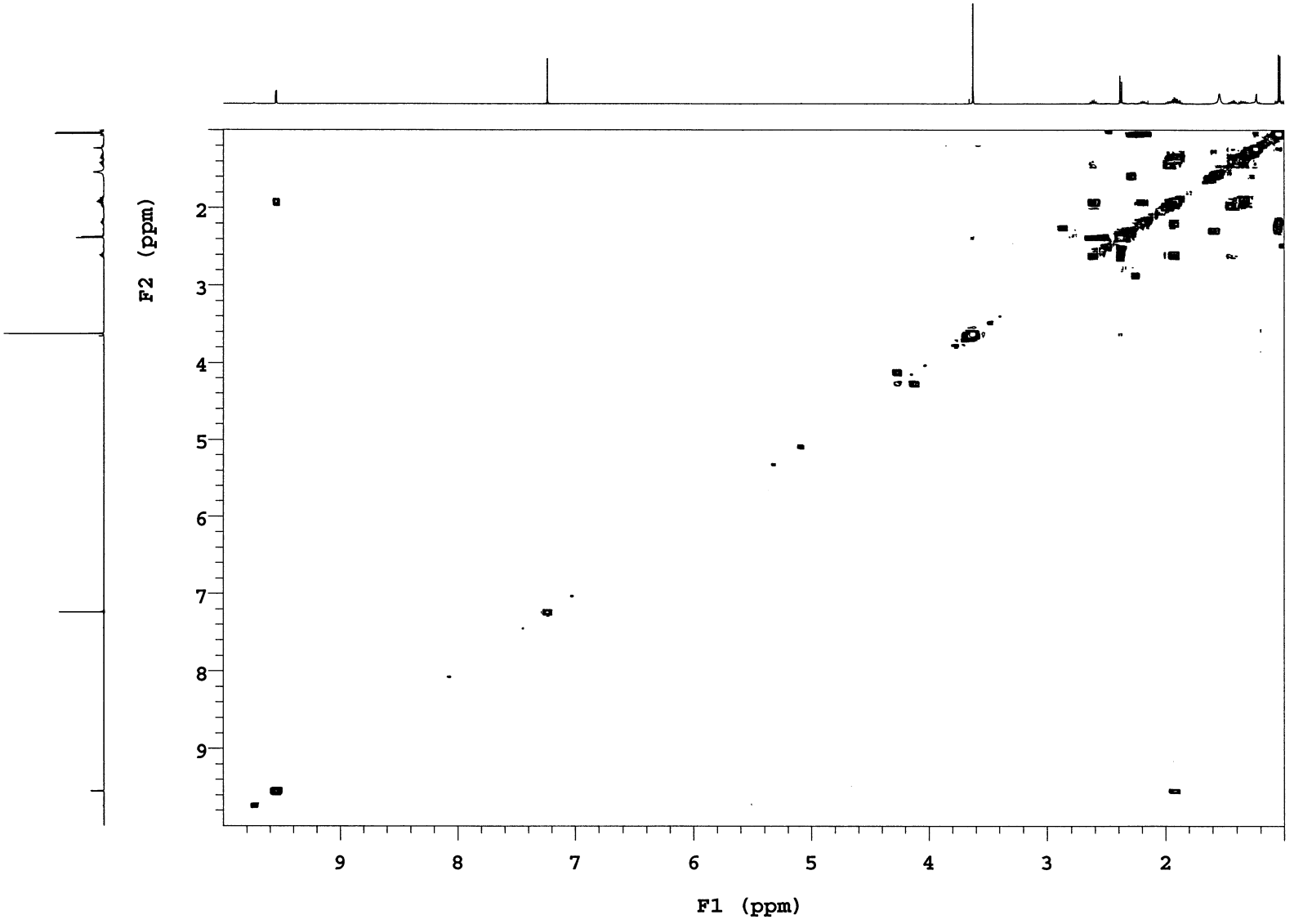
Sample Name **PDC-02-428-F2-2D**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2016-04-09**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



HSQC of compound 2

PDC-02-428-F2-2D

Sample Name	**PDC-02-428-F2-2D**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-04-08**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



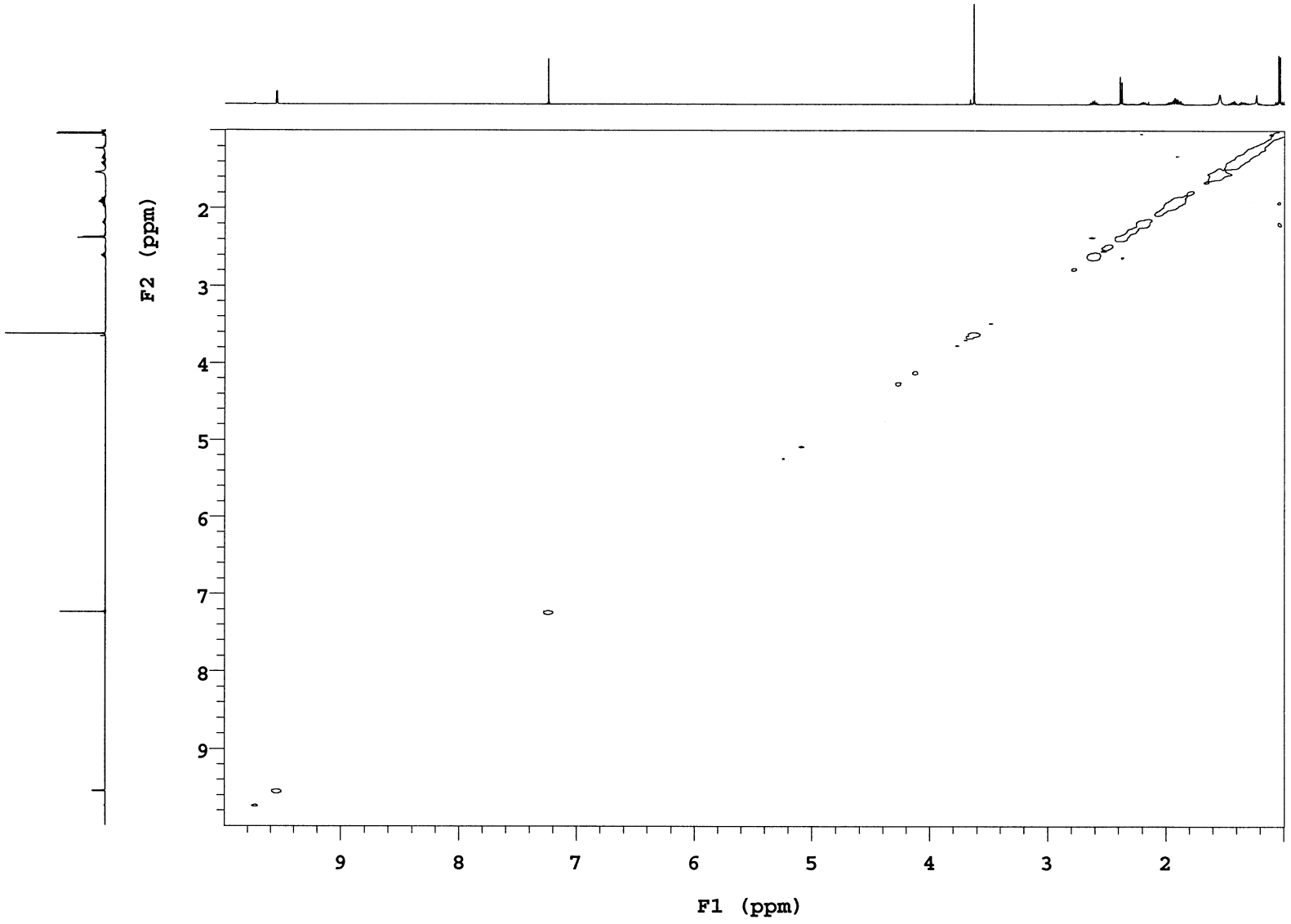
COSY of compound 2

Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-428-F2-2D/gCOSY_01

Plot date 2016-04-09

PDC-02-428-F2-2D

Sample Name	**PDC-02-428-F2-2D**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-04-09**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**

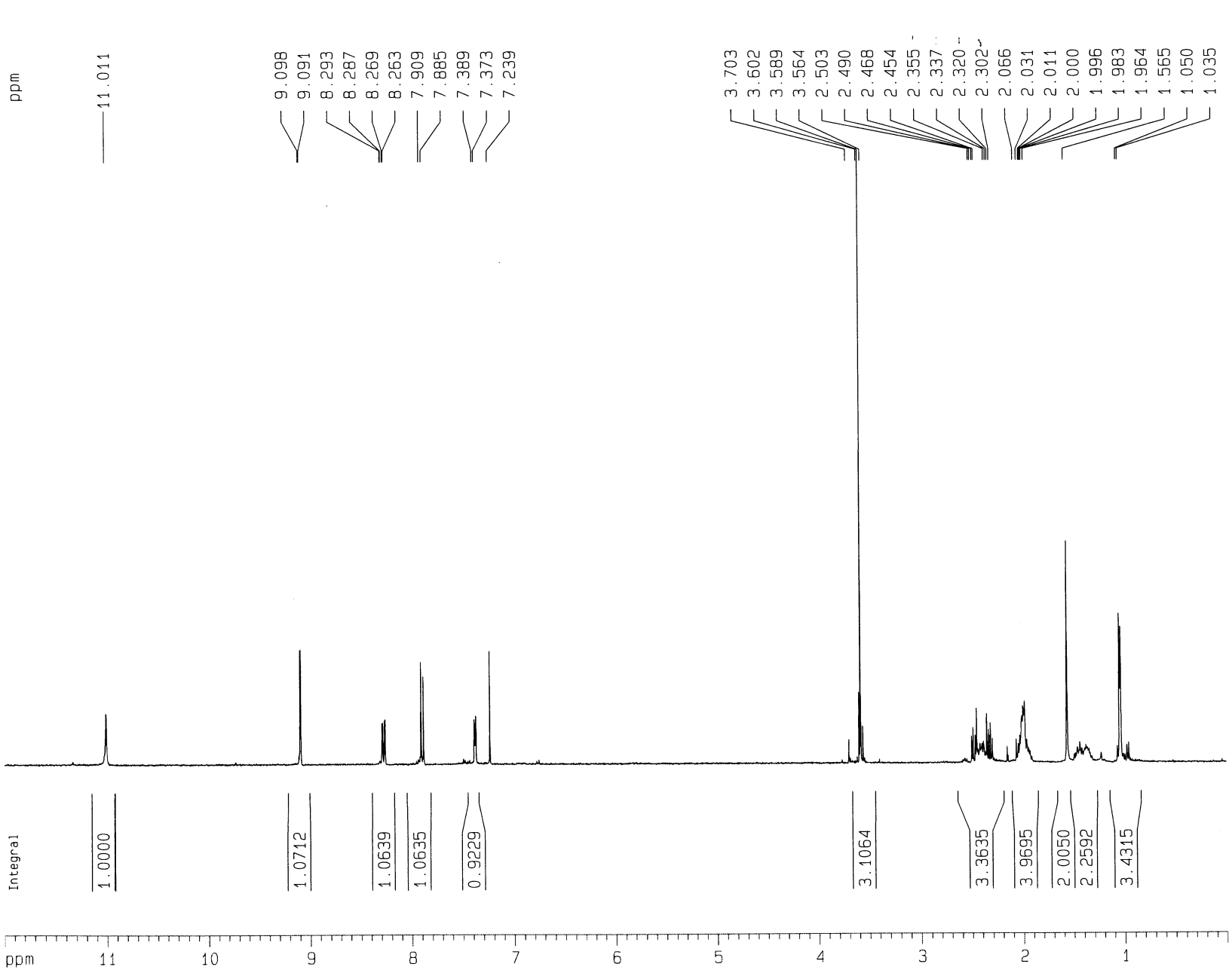


NOESY of compound 2

Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-428-F2-2D/NOESY_01

Plot date 2016-04-09

1H NMR (400 MHz, CDCl3) of compound 3

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PROCNO                   1

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TD                  16384
SOLVENT             CDCl3
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SWH             5995.204 Hz
FIDRES          0.365918 Hz
AQ              1.3664756 sec
RG                 5792.6
DW                83.400 usec
DE                 6.50 usec
TE                300.0 K
D1             1.50000000 sec

============ CHANNEL f1 =============
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P1                  11.90 usec
PL1                 -3.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
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SF           400.1300179 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  21.50 cm
F1P                12.000 ppm
F1                4801.56 Hz
F2P               -0.000 ppm
F2                 -0.00 Hz
PPMCM           0.55814 ppm/cm
HZCM          223.32837 Hz/cm
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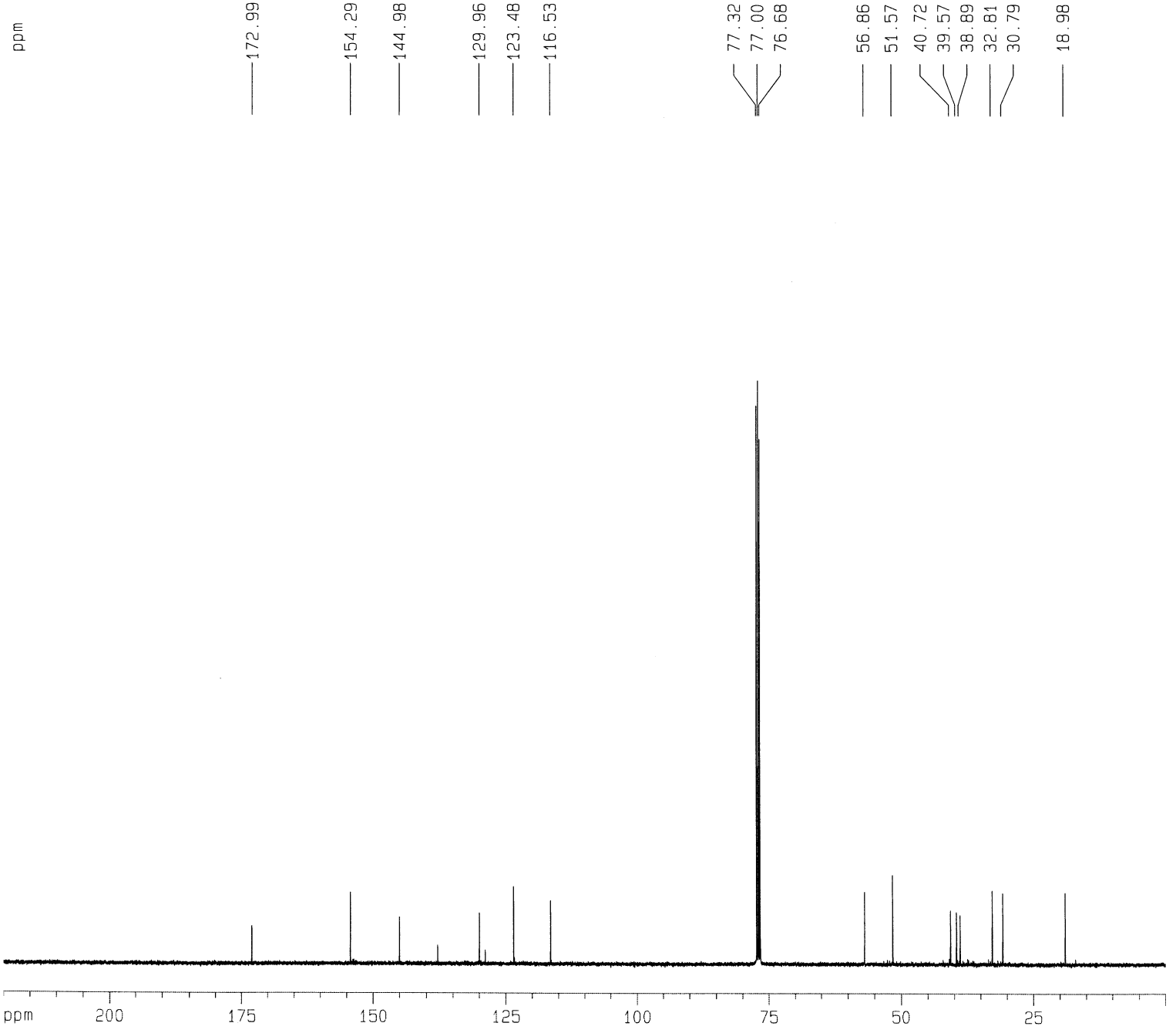
13C NMR (100 MHz, CDCl3) of compound 3

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EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
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INSTRUM            spect
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 4096
DS                    4
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG                  256
DW               19.900 usec
DE                6.50 usec
TE               300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                10.20 usec
PL1                0.00 dB
SF01         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2          waltz16
NUC2                1H
PCPD2             90.00 usec
PL2               -3.00 dB
PL12              14.50 dB
PL13              17.50 dB
SF02         400.1326008 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127708 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               220.000 ppm
F1              22134.81 Hz
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F2                 0.00 Hz
PPMCM          11.00000 ppm/cm
HZCM         1106.74048 Hz/cm
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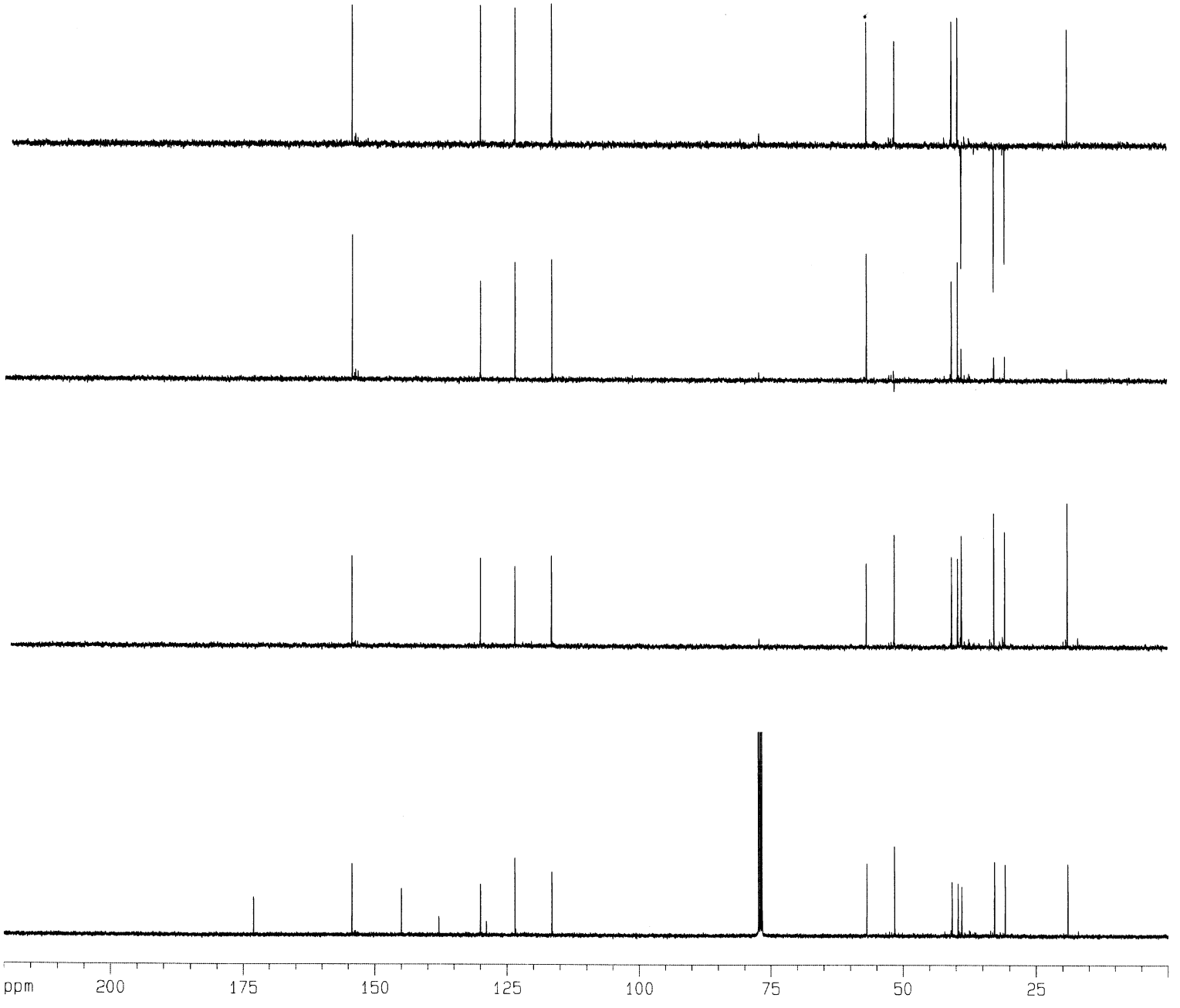
DEPT of compound 3

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Current Data Parameters
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EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150408
Time                3.20
INSTRUM            spect
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 4096
DS                    4
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG                  256
DW               19.900 usec
DE                6.50 usec
TE               300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

============ CHANNEL f1 =============
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P1               10.20 usec
PL1               0.00 dB
SFO1        100.6237959 MHz

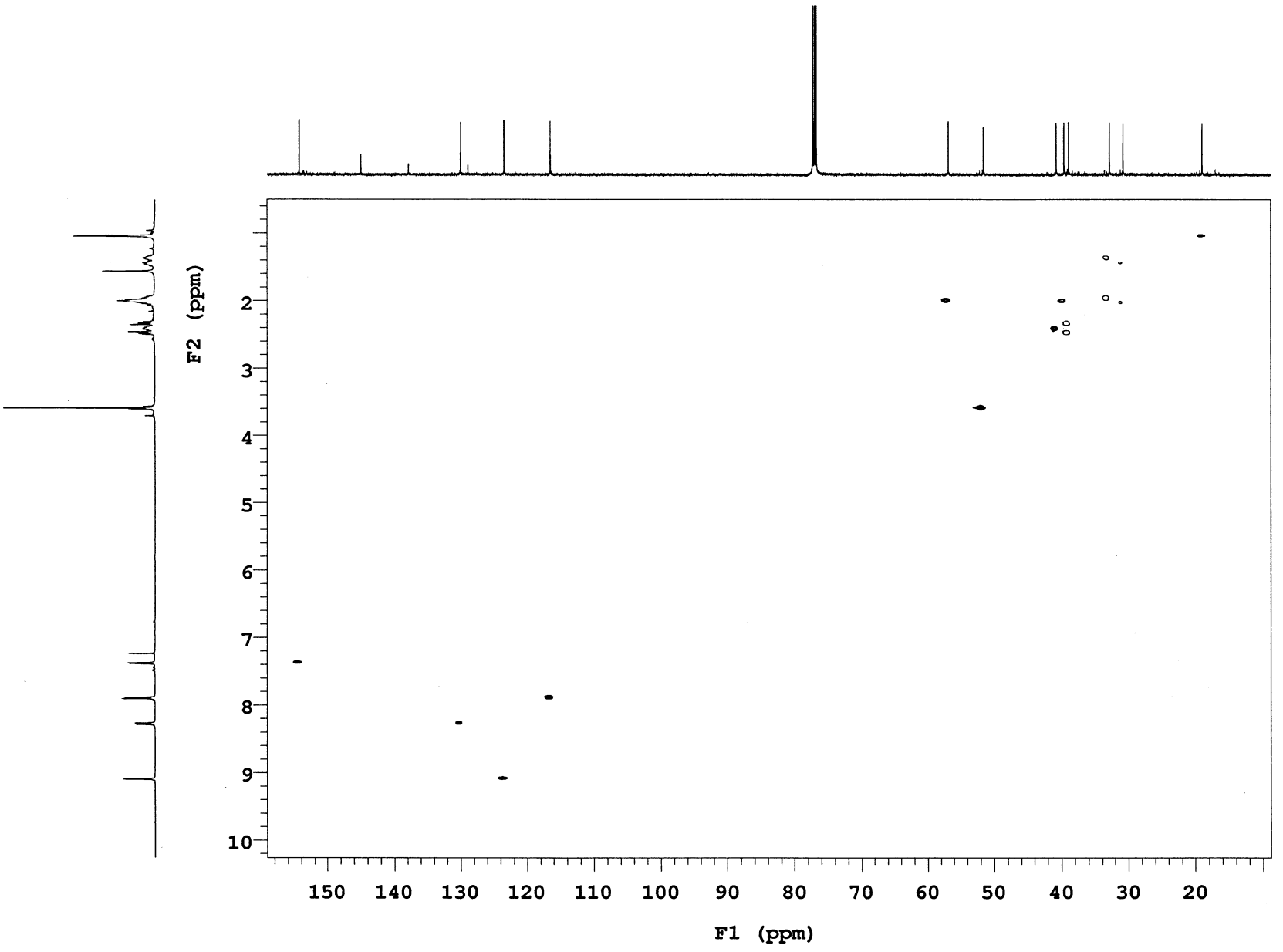
============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2              -3.00 dB
PL12             14.50 dB
PL13             17.50 dB
SFO2        400.1326008 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127708 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              220.000 ppm
F1             22134.81 Hz
F2P              0.000 ppm
F2               0.00 Hz
PPMCM          11.00000 ppm/cm
HZCM         1106.74048 Hz/cm
```

PDC-02-433-f2-2D

Sample Name **PDC-02-433-f2-2D**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2016-04-12**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



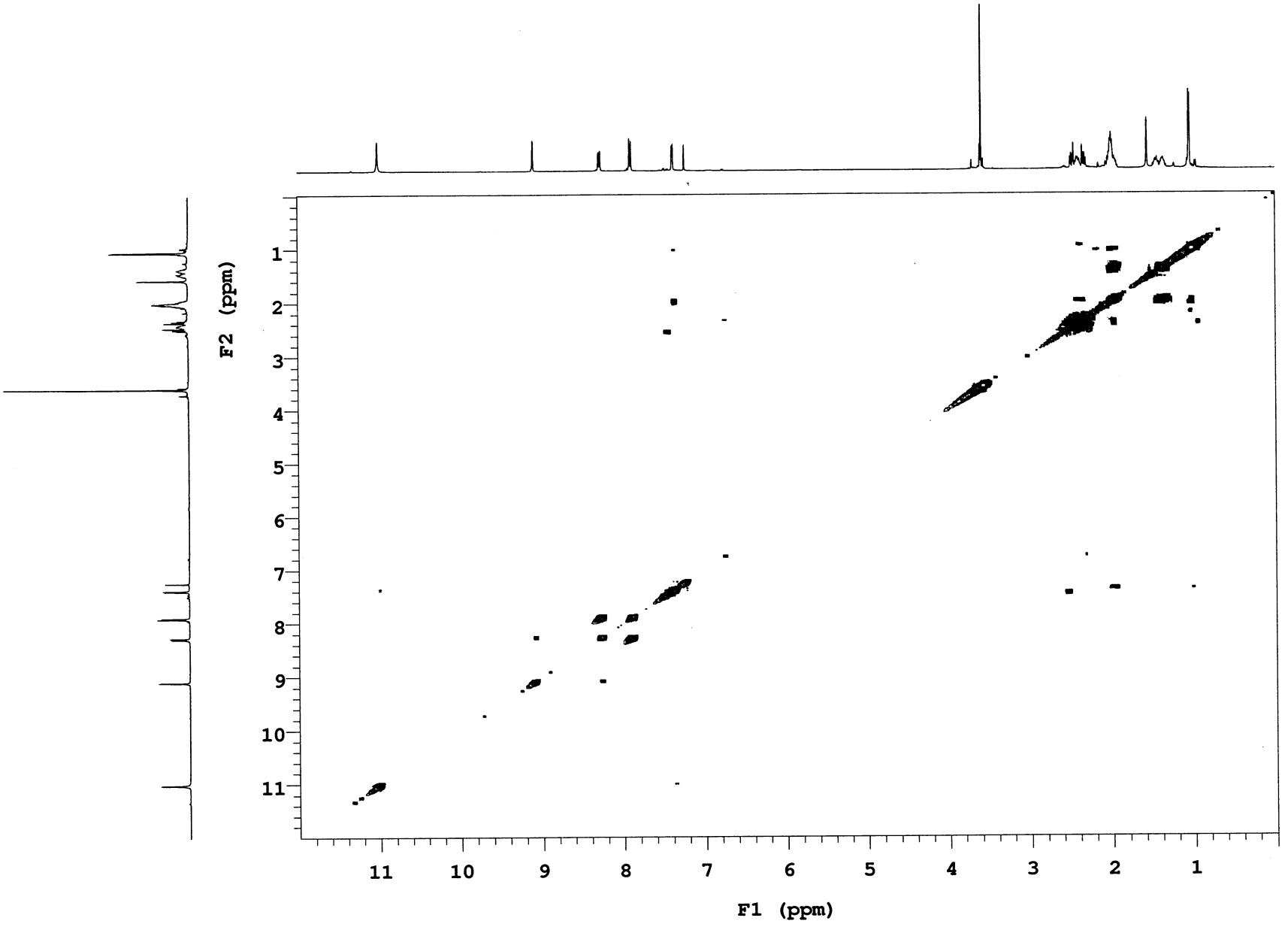
Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-433-f2-2D/gHSQC_01.fid

HSQC of compound 3

Plot date 2016-04-18

PDC-02-433-f2-2D

Sample Name **PDC-02-433-f2-2D**	Pulse sequence **gCOSY**	Temperature **25**	Study owner **vnmr2**
Date collected **2016-04-12**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



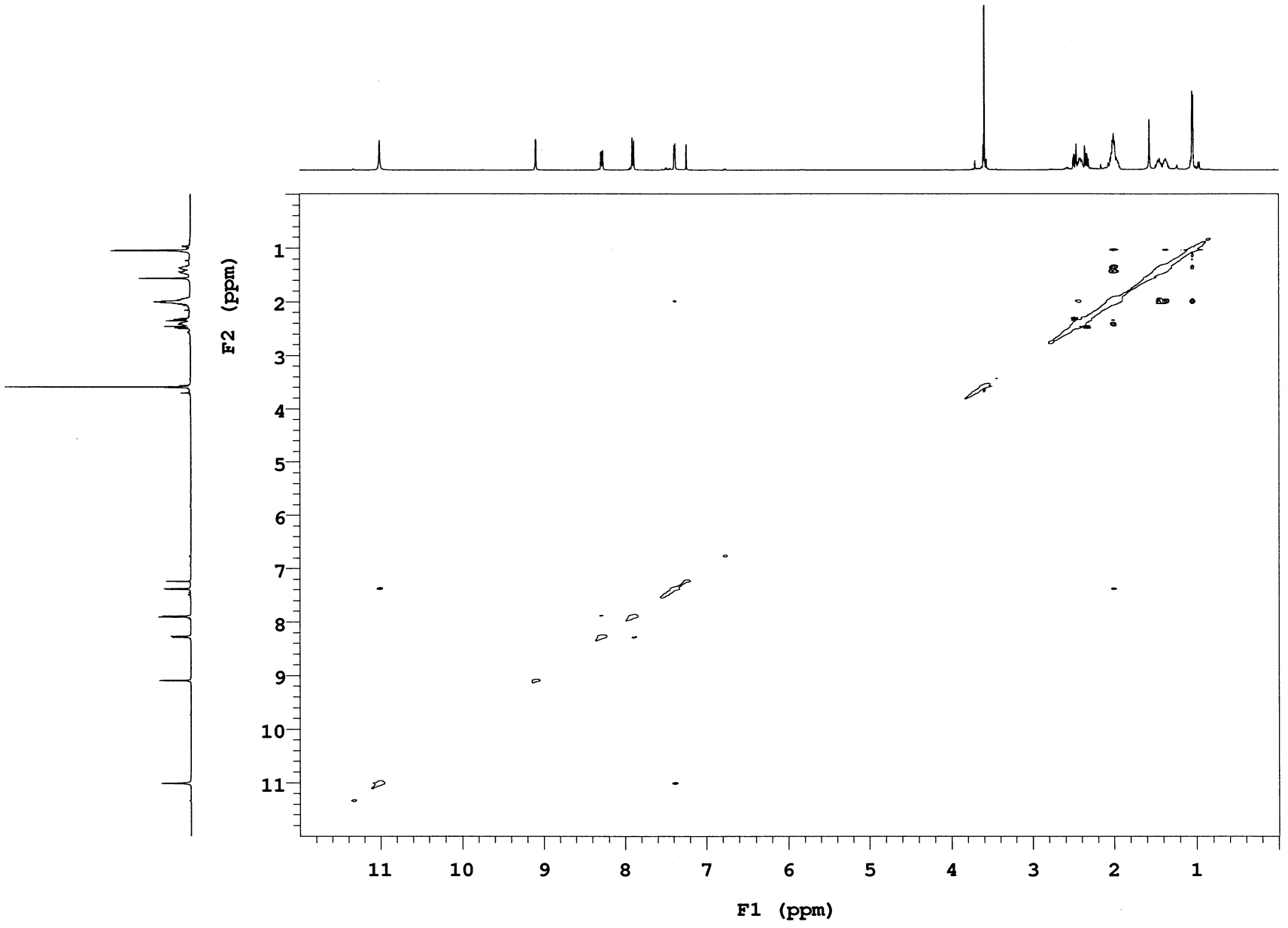
COSY of compound 3

Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-433-f2-2D/gCOSY_01.fid

Plot date 2016-04-18

PDC-02-433-f2-2D

Sample Name	**PDC-02-433-f2-2D**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-04-12**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



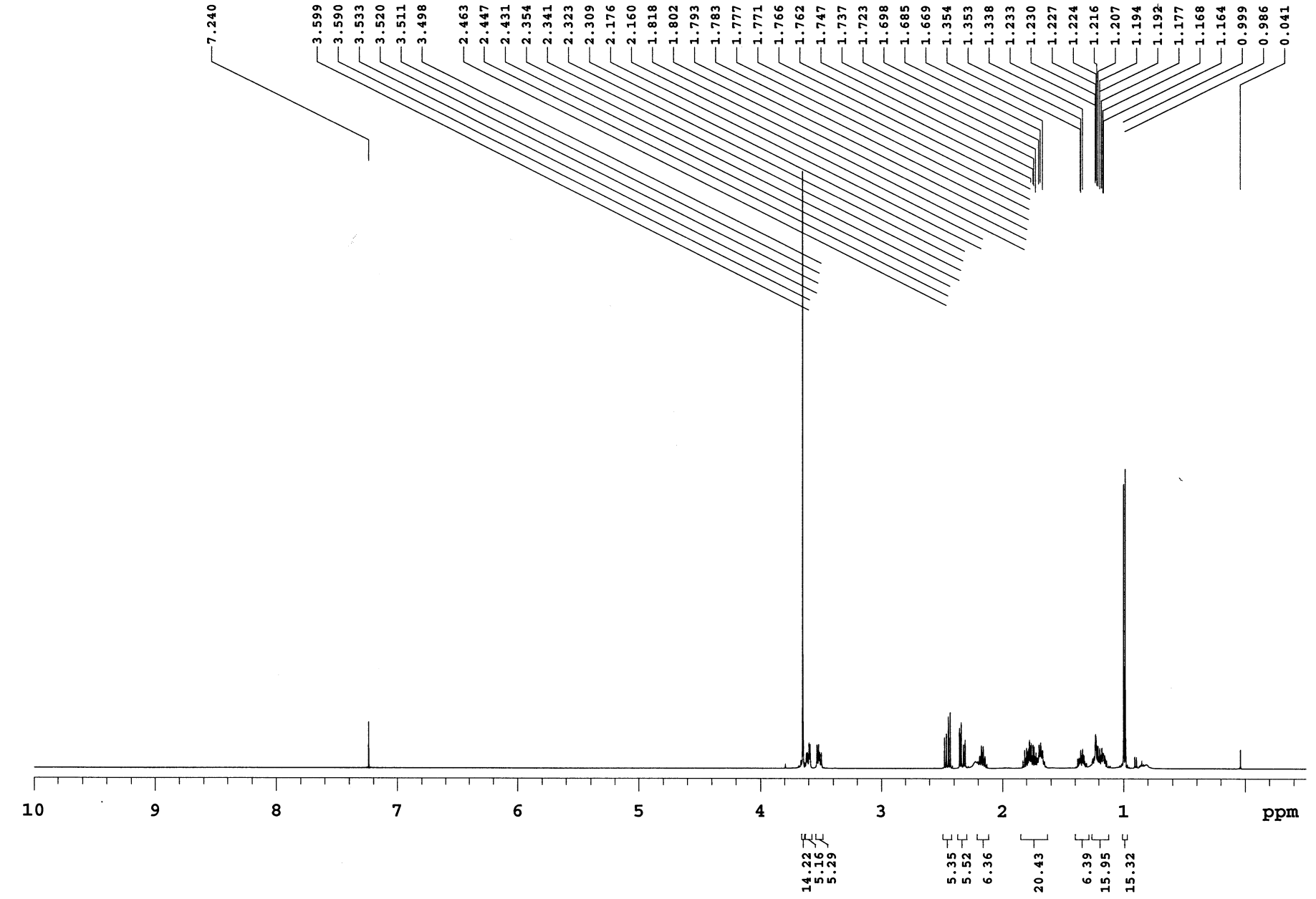
Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-433-f2-2D/NOESY_01.fid

NOESY of compound 3

Plot date 2016-04-18

PDC-02-425-F1

Sample Name	**PDC-02-425-F1**	Pulse sequence	**PROTON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-04-28**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



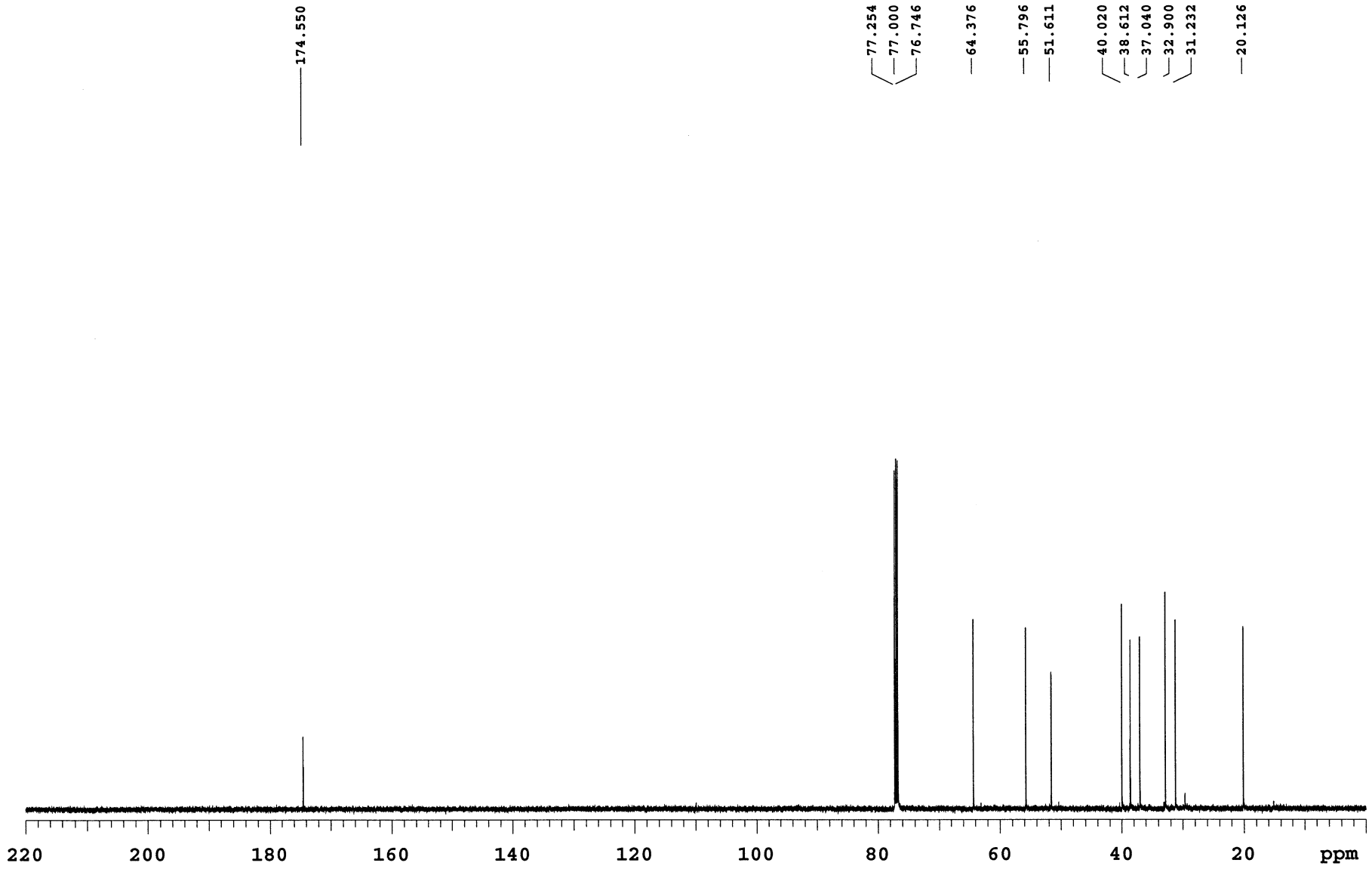
Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-425-F1/PROTON_06

1H NMR (500 MHz, CDCl3) of compound 4

Plot date 2016-04-29

PDC-02-425-F1

Sample Name	**PDC-02-425-F1**	Pulse sequence	**CARBON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-04-28**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



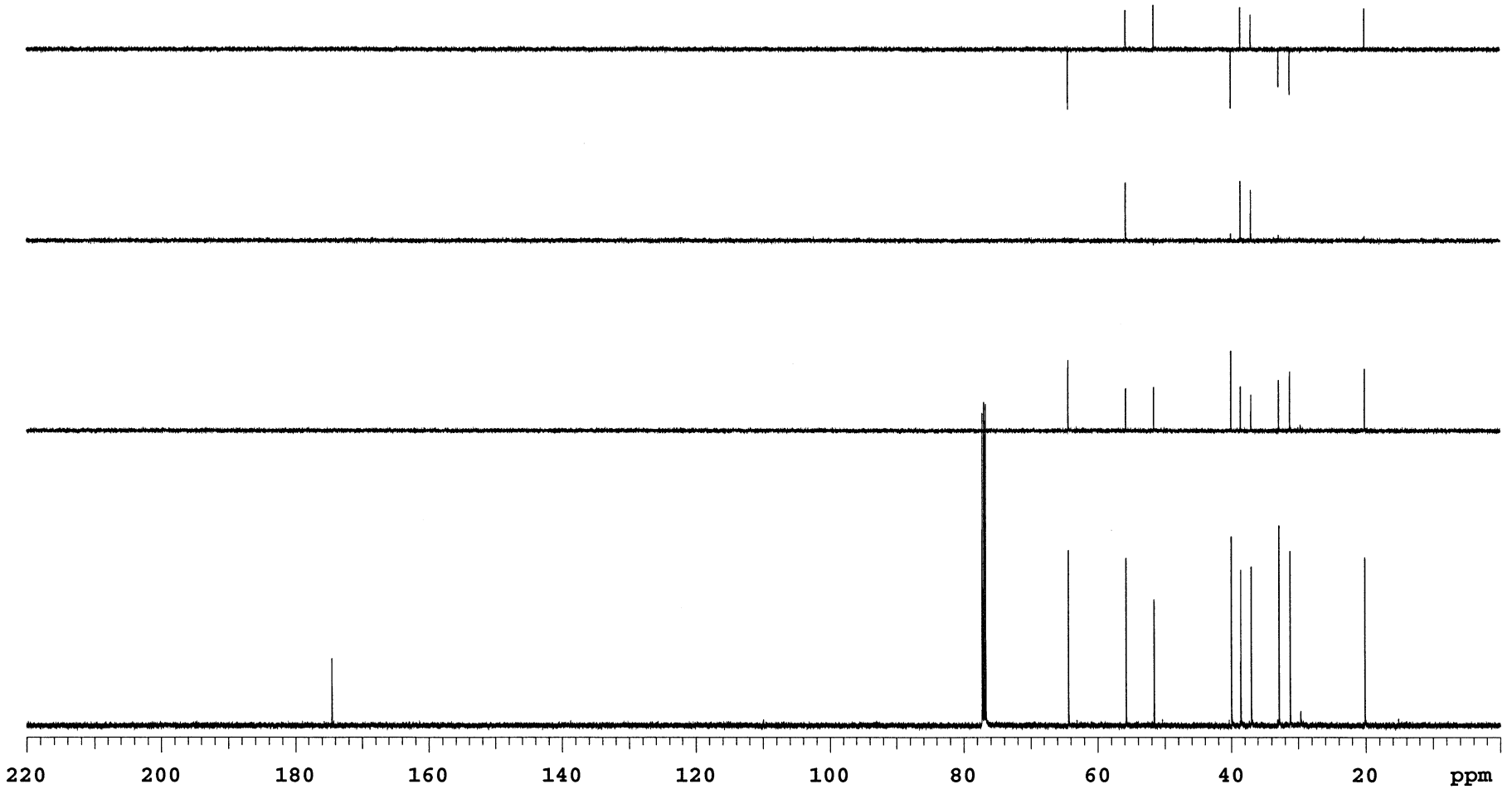
13C NMR (125 MHz, CDCl3) of compound 4

Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-425-F1/CARBON_02

Plot date 2016-04-29

PDC-02-425-F1

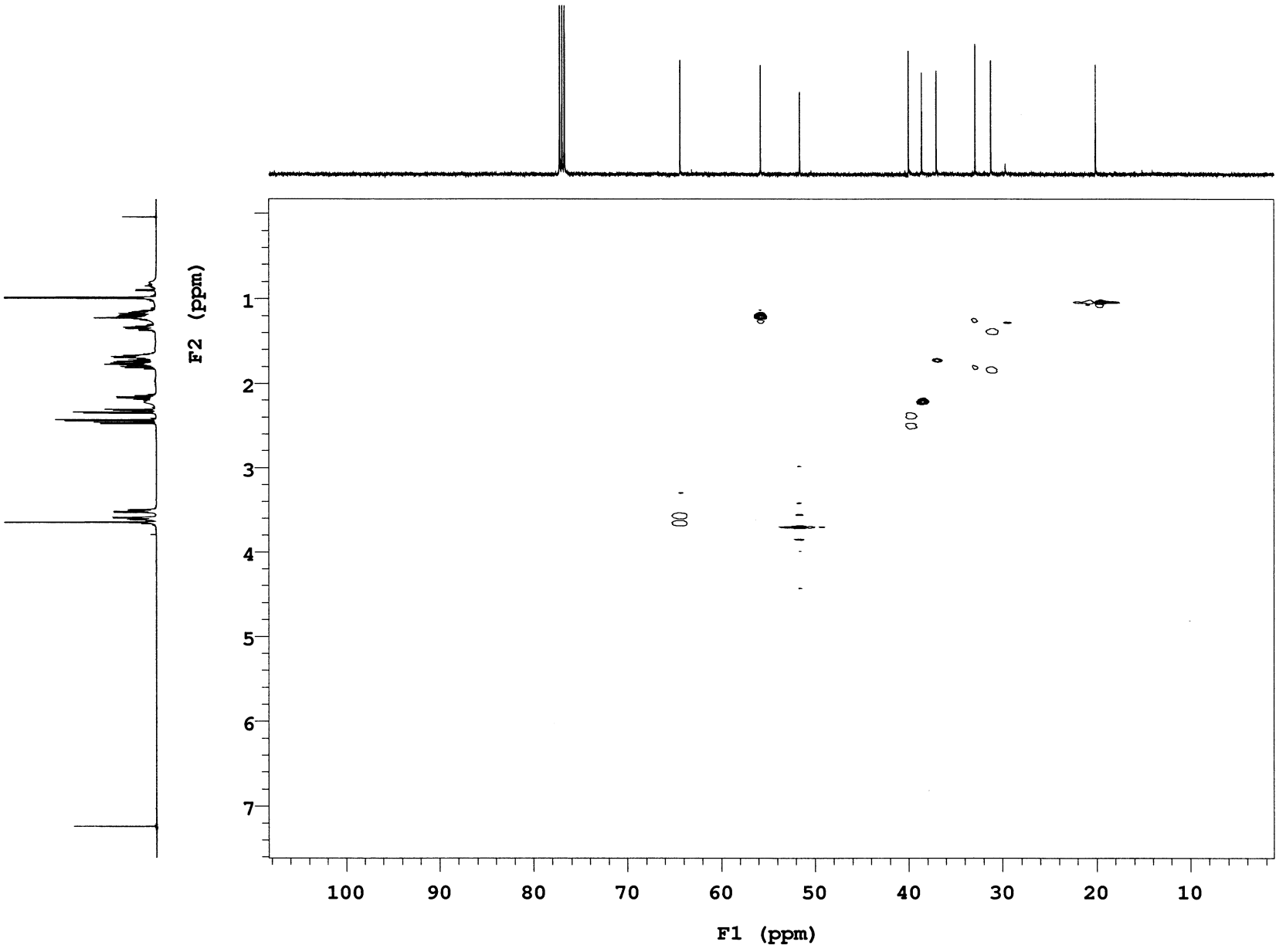
Sample Name **PDC-02-425-F1**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2016-04-28**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 4

PDC-02-425-F1

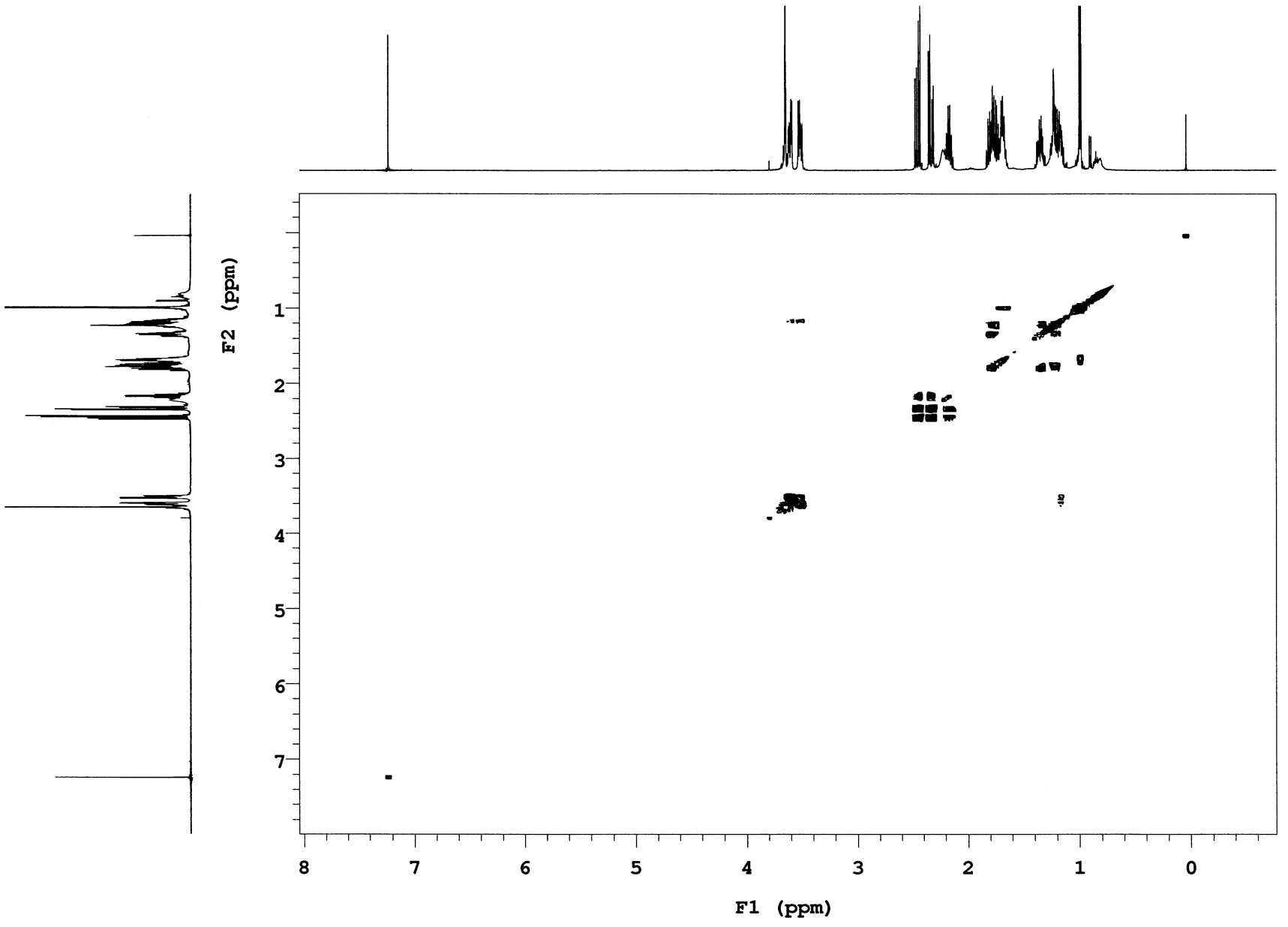
Sample Name	**PDC-02-425-F1**	Pulse sequence	**gHSQC**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-05-09**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



HSQC of compound 4

PDC-02-425-F1

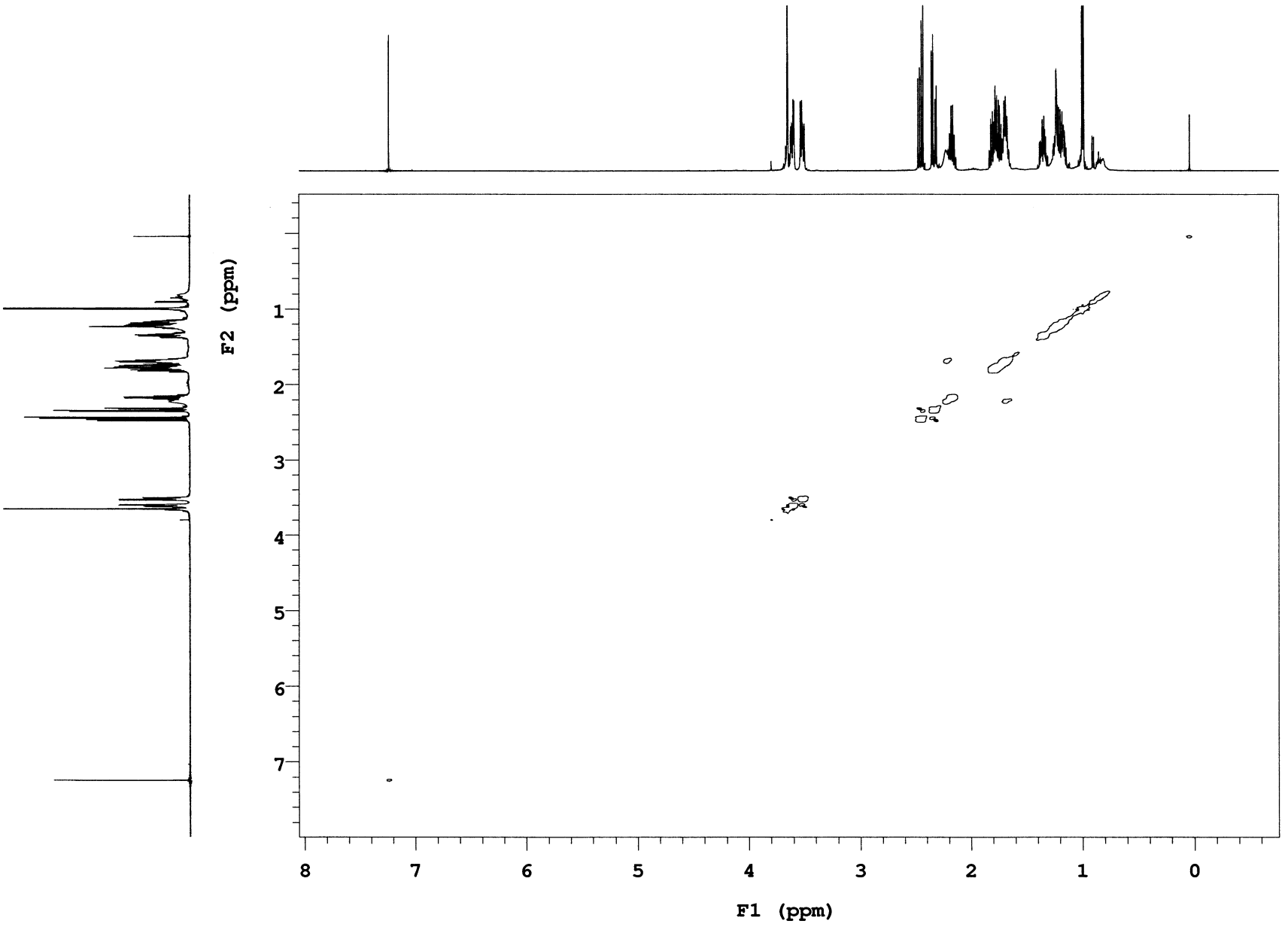
Sample Name **PDC-02-425-F1** | Pulse sequence **gCOSY** | Temperature **25** | Study owner **vnmr2**
Date collected **2016-05-09** | Solvent **cdcl3** | Spectrometer **Agilent-NMR-inova500** | Operator **vnmr2**



COSY of compound 4

PDC-02-425-F1

Sample Name **PDC-02-425-F1** | Pulse sequence **NOESY** | Temperature **25** | Study owner **vnmr2**
Date collected **2016-05-09** | Solvent **cdcl3** | Spectrometer **Agilent-NMR-inova500** | Operator **vnmr2**



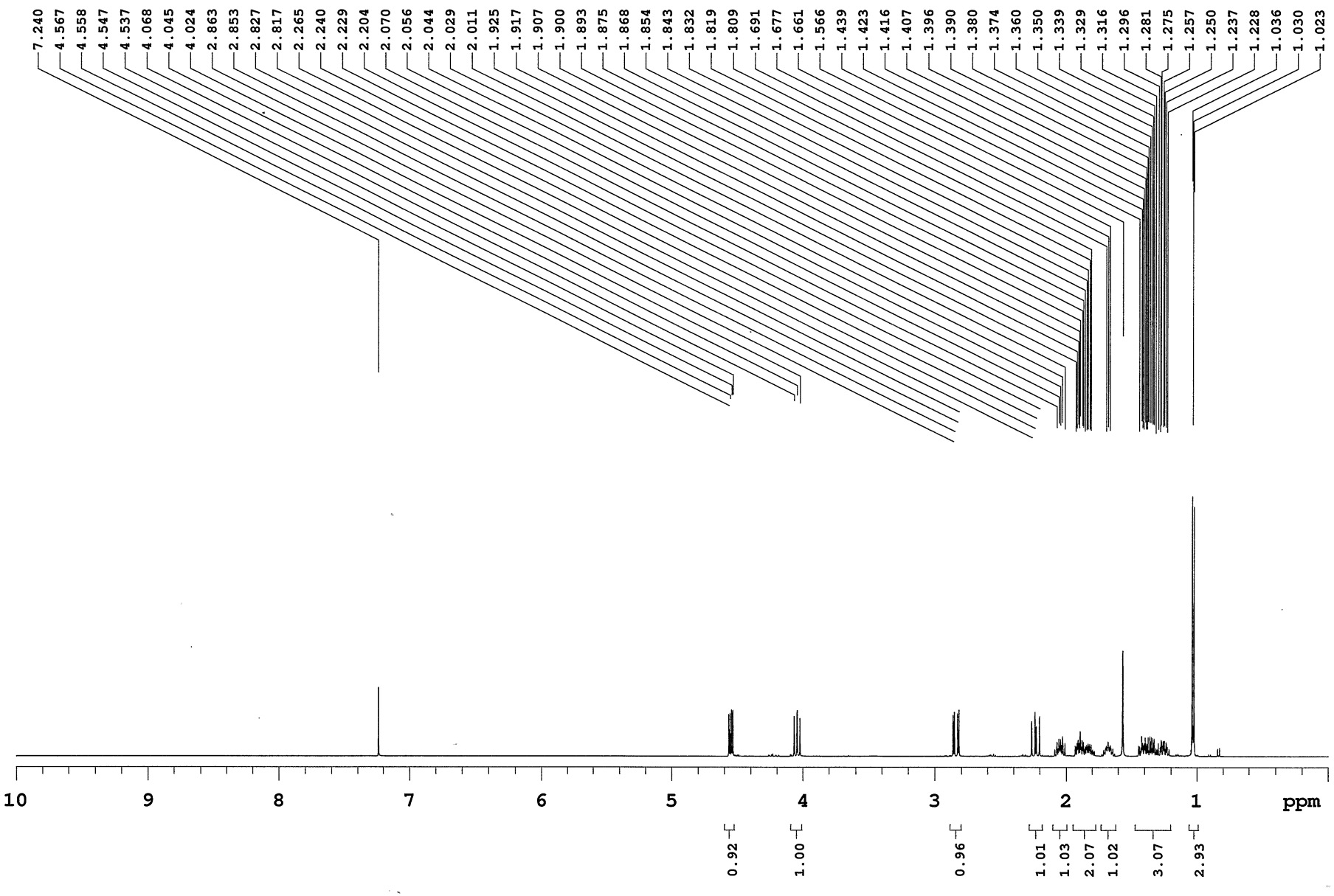
NOESY of compound 4

Data file /home/vnmr2/vnmrsys/data/511/PDC/PDC-02-425-F1/NOESY_01

Plot date 2016-05-10

RRT-244-F1

Sample Name	**RRT-244-F1**	Pulse sequence	**PROTON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-12-16**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



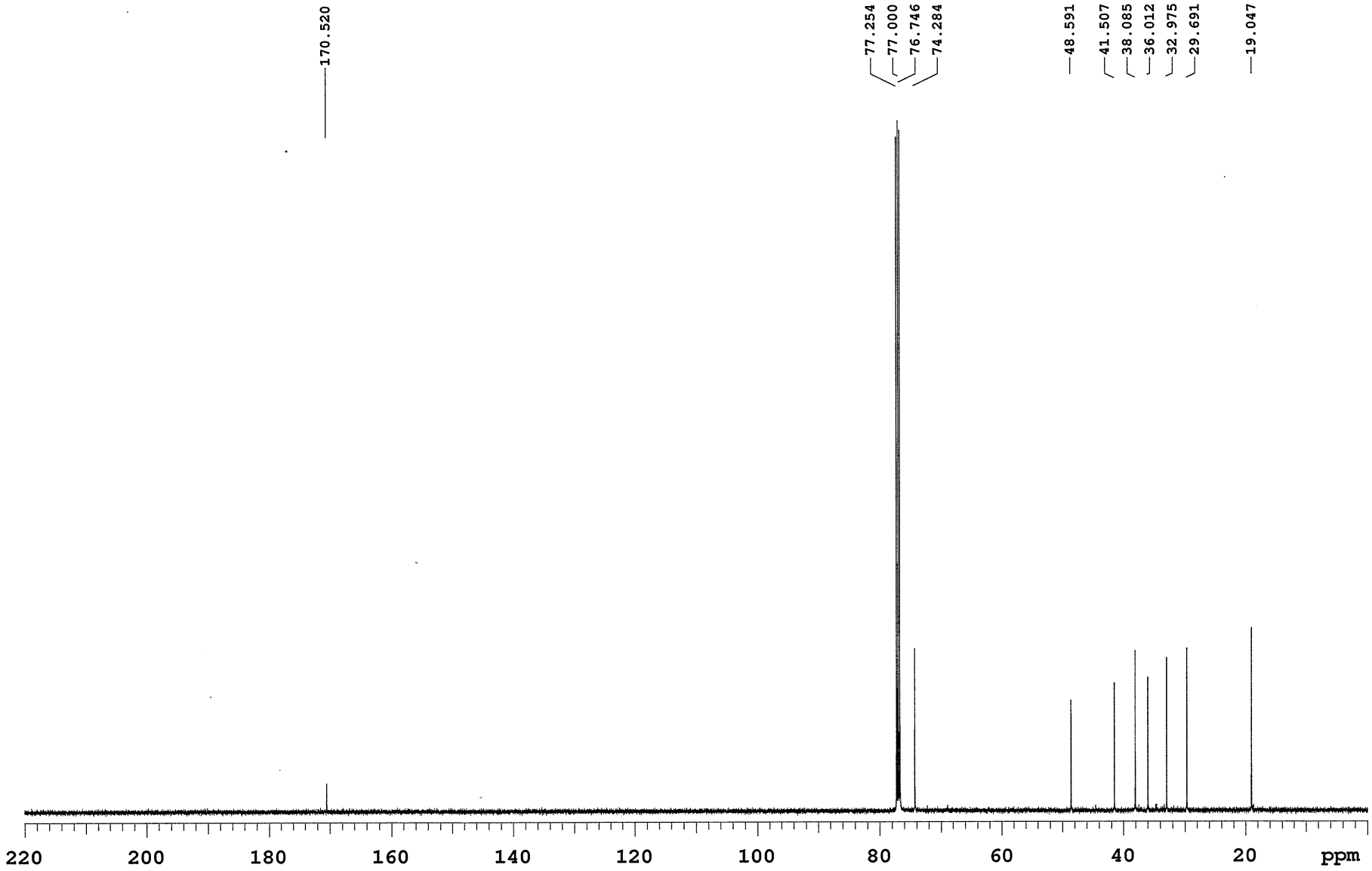
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-244-F1/PROTON_03.fid

1H NMR (500 MHz, CDCl3) of compound 5

Plot date 2022-12-20

RRT-244-F1

Sample Name	RRT-244-F1	Pulse sequence	CARBON	Temperature	25	Study owner	vnmr2
Date collected	2022-12-16	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



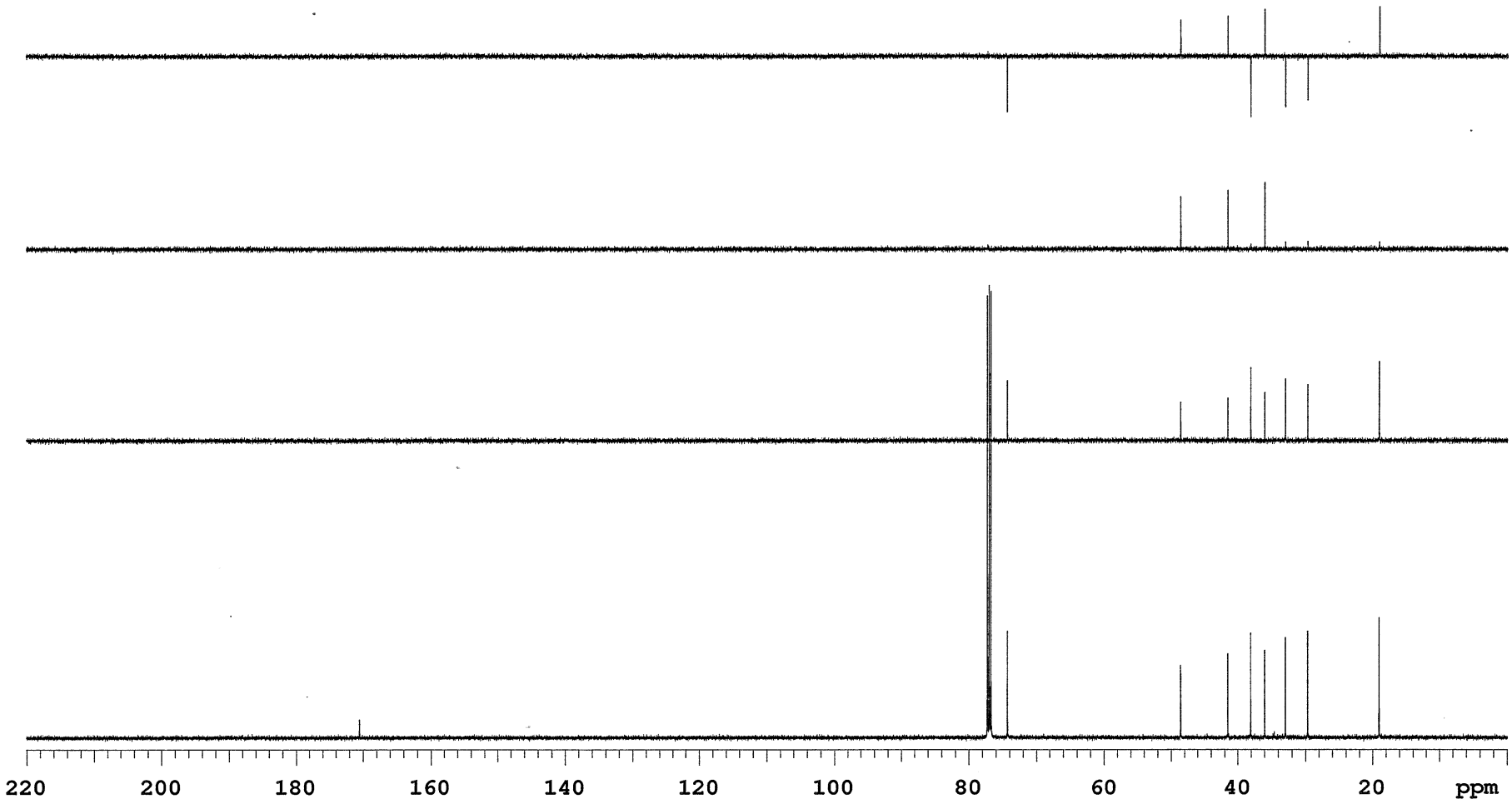
13C NMR (125 MHz, CDCl3) of compound 5

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-244-F1/CARBON_02

Plot date 2022-12-17

RRT-244-F1

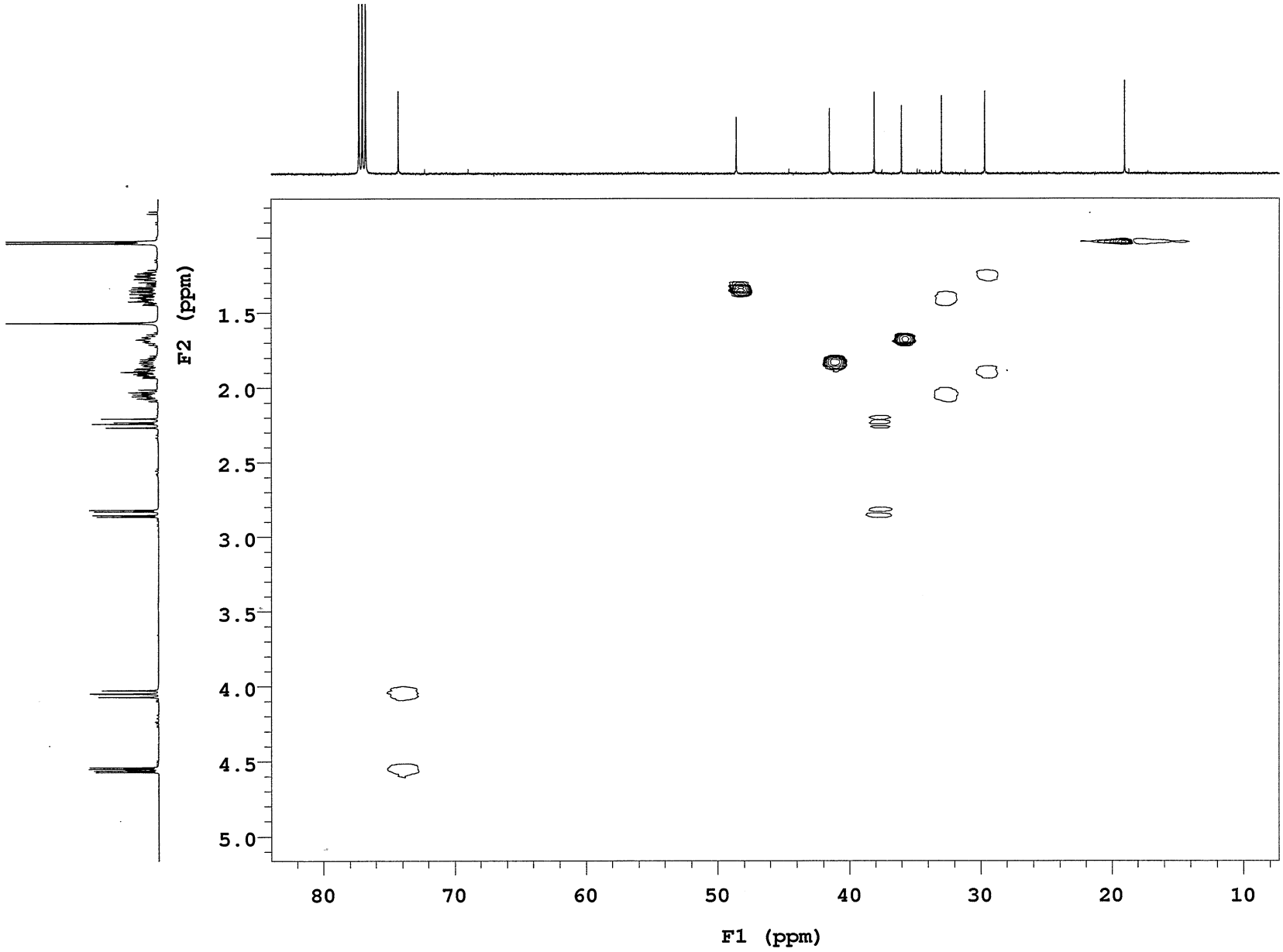
Sample Name **RRT-244-F1**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-16**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 5

RRT-244-F1

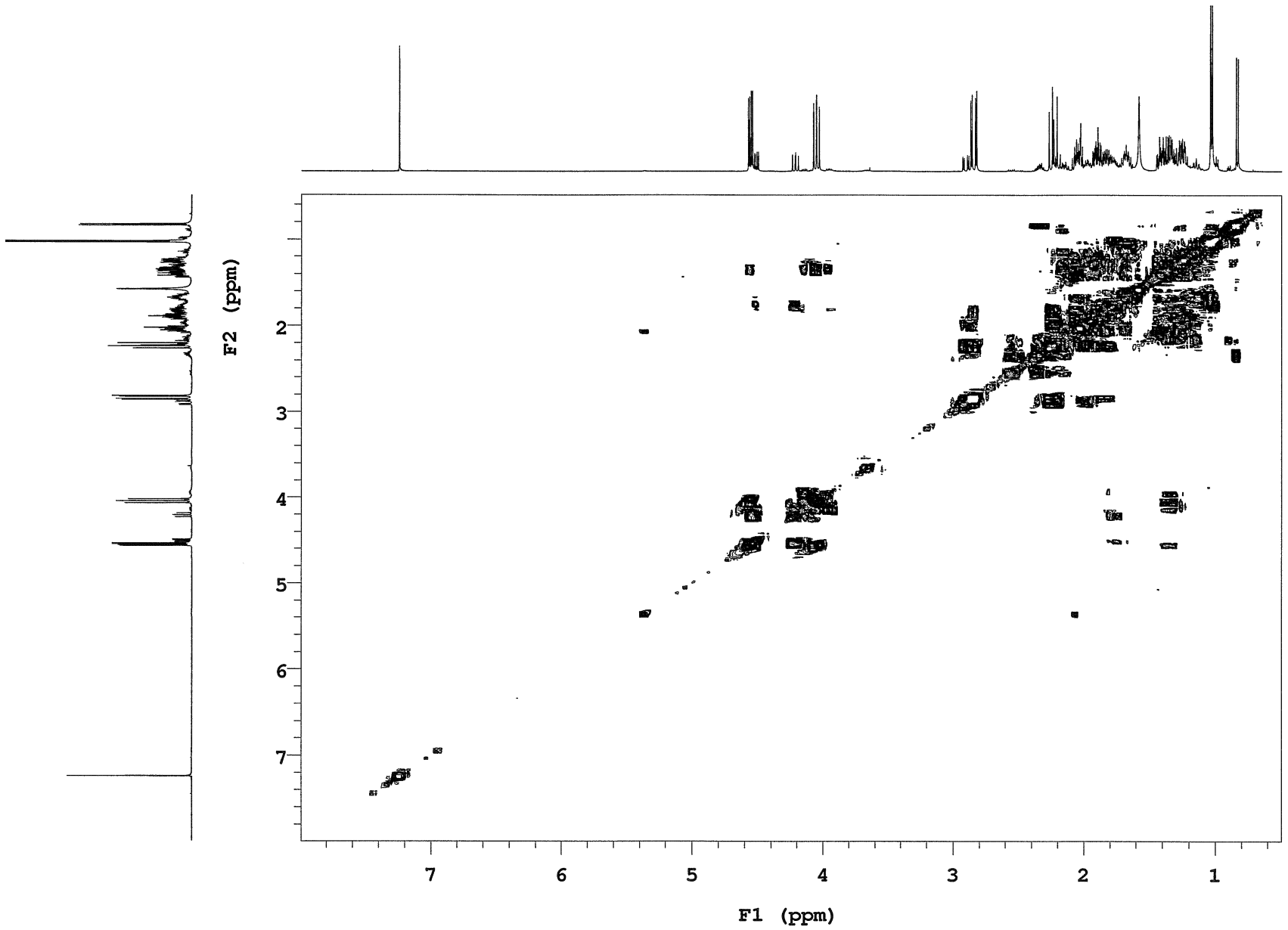
Sample Name **RRT-244-F1**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-17**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



HSQC of compound 5

RRT-04-071

Sample Name **RRT-04-071**	Pulse sequence **gCOSY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-11-01**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



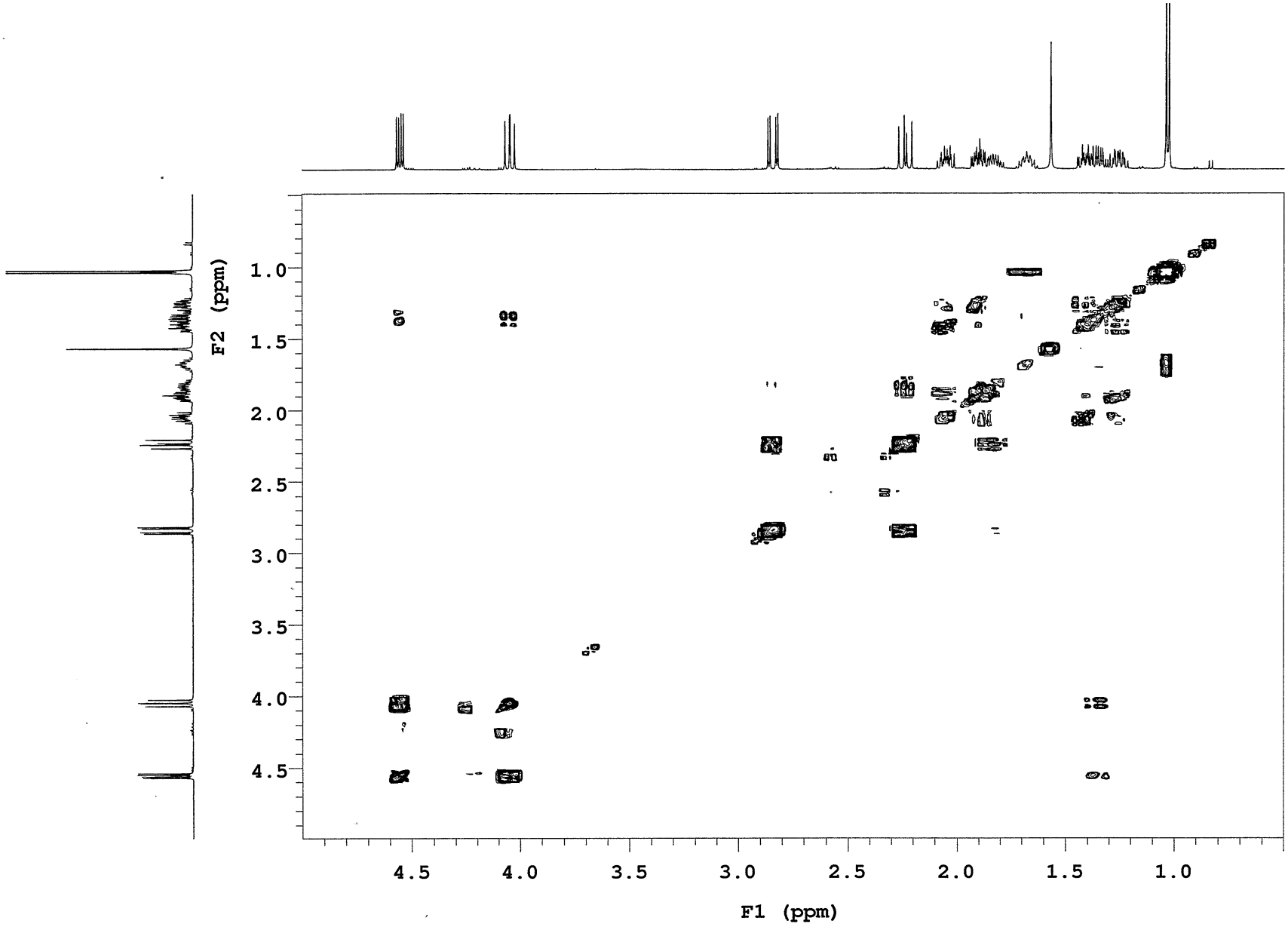
COSY of compound 5

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-071/gCOSY_01

Plot date 2022-12-07

RRT-244-F1

Sample Name **RRT-244-F1**	Pulse sequence **gCOSY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-17**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



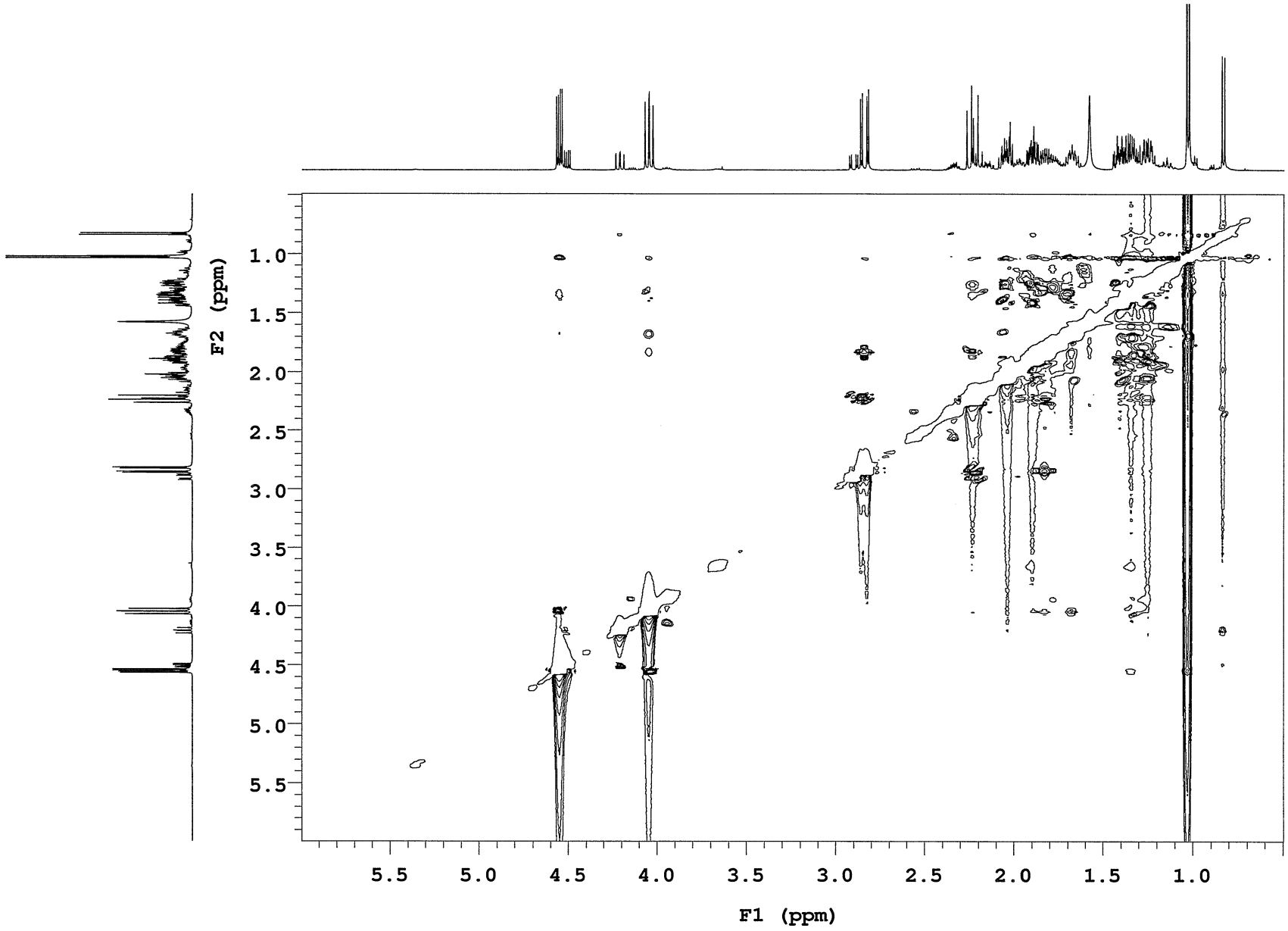
COSY of compound 5, expanded

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-244-F1/gCOSY_01

Plot date 2022-12-17

RRT-04-071

Sample Name	RRT-04-071	Pulse sequence	NOESY	Temperature	25	Study owner	vnmr2
Date collected	2022-11-01	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



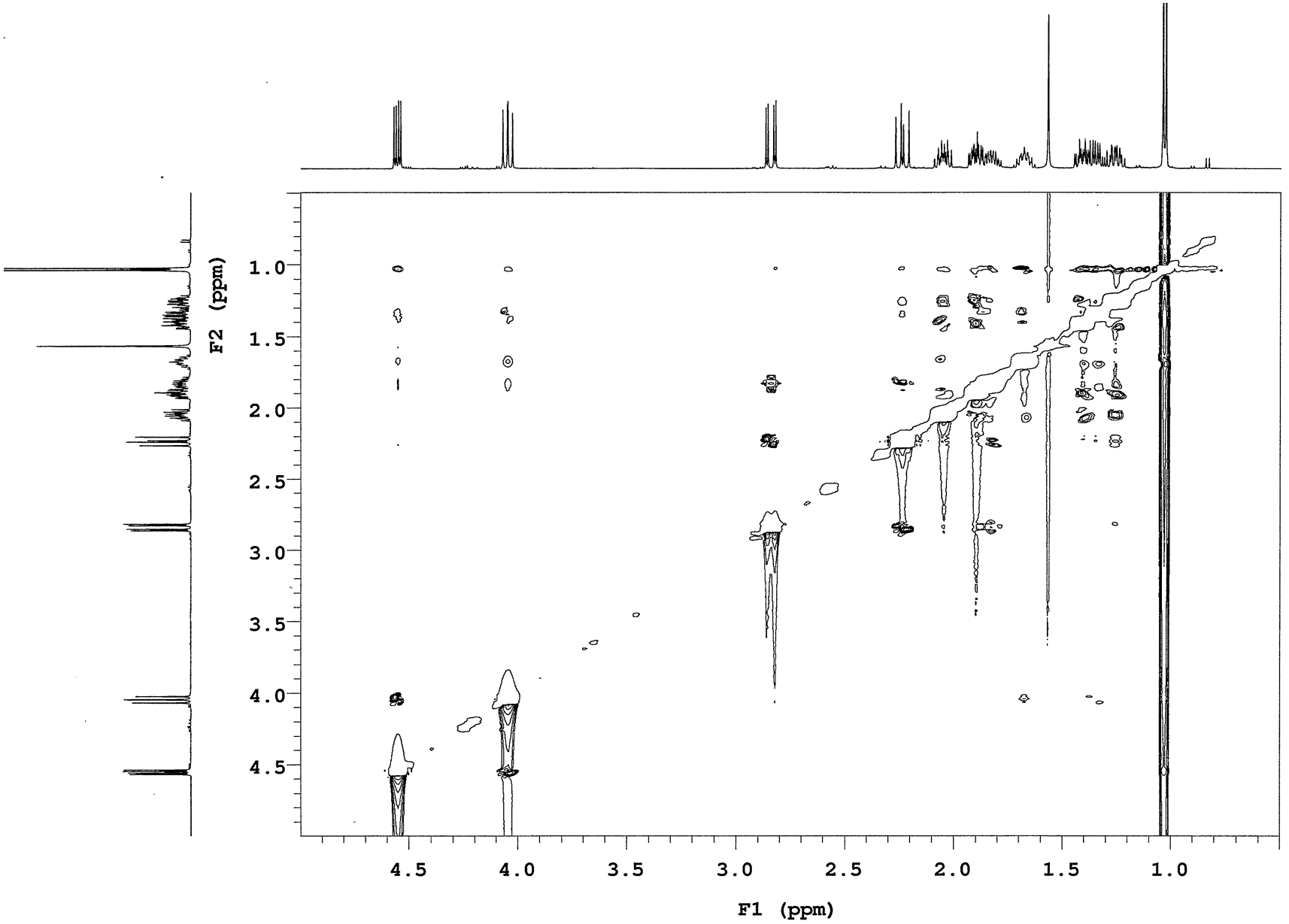
NOESY of compound 5

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-071/NOESY_01

Plot date 2022-12-07

RRT-244-F1

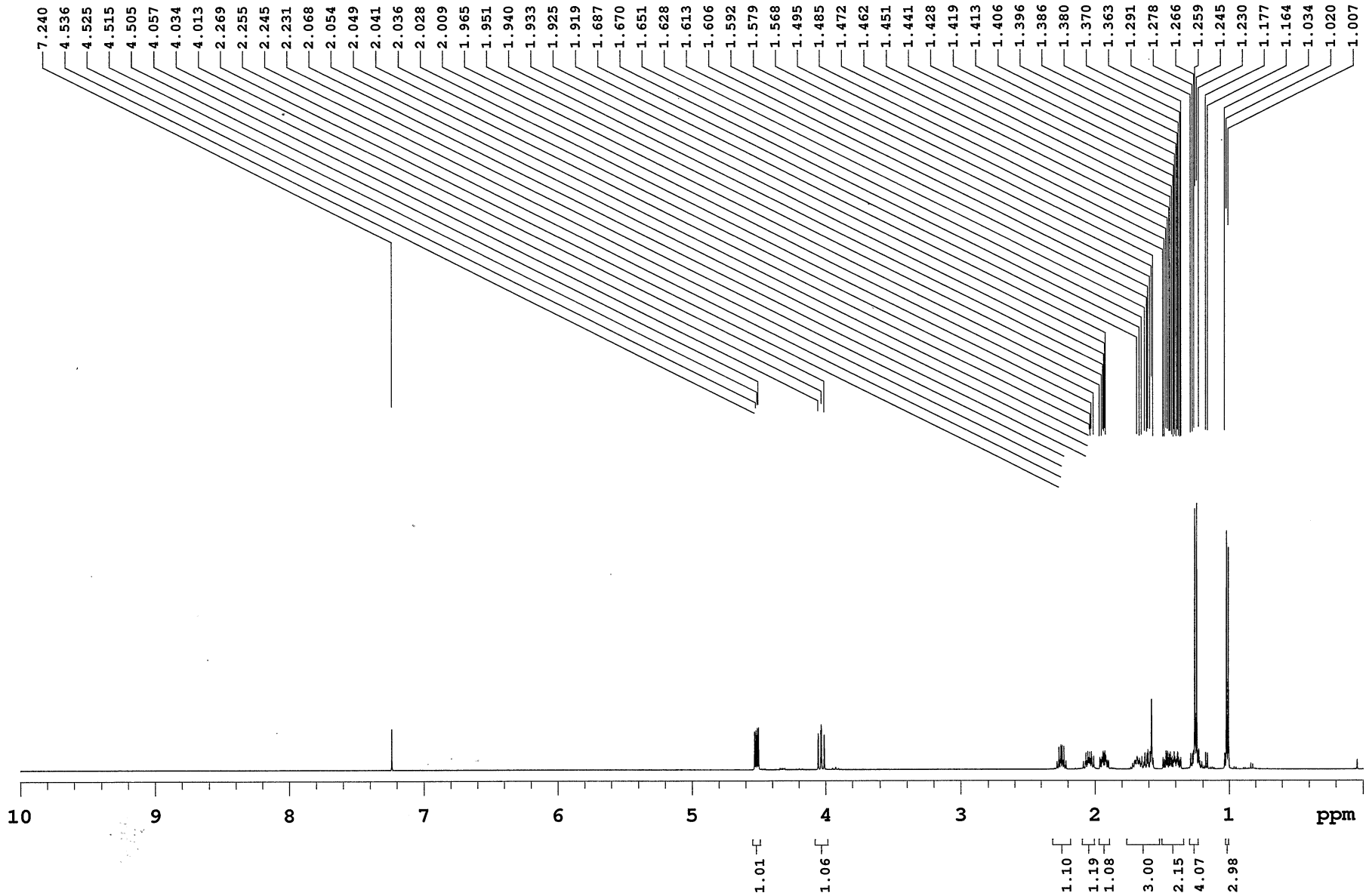
Sample Name **RRT-244-F1**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-17**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



NOESY of compound 5, expanded

RRT-04-087-I

Sample Name	**RRT-04-087-I**	Pulse sequence	**PROTON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-12-23**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



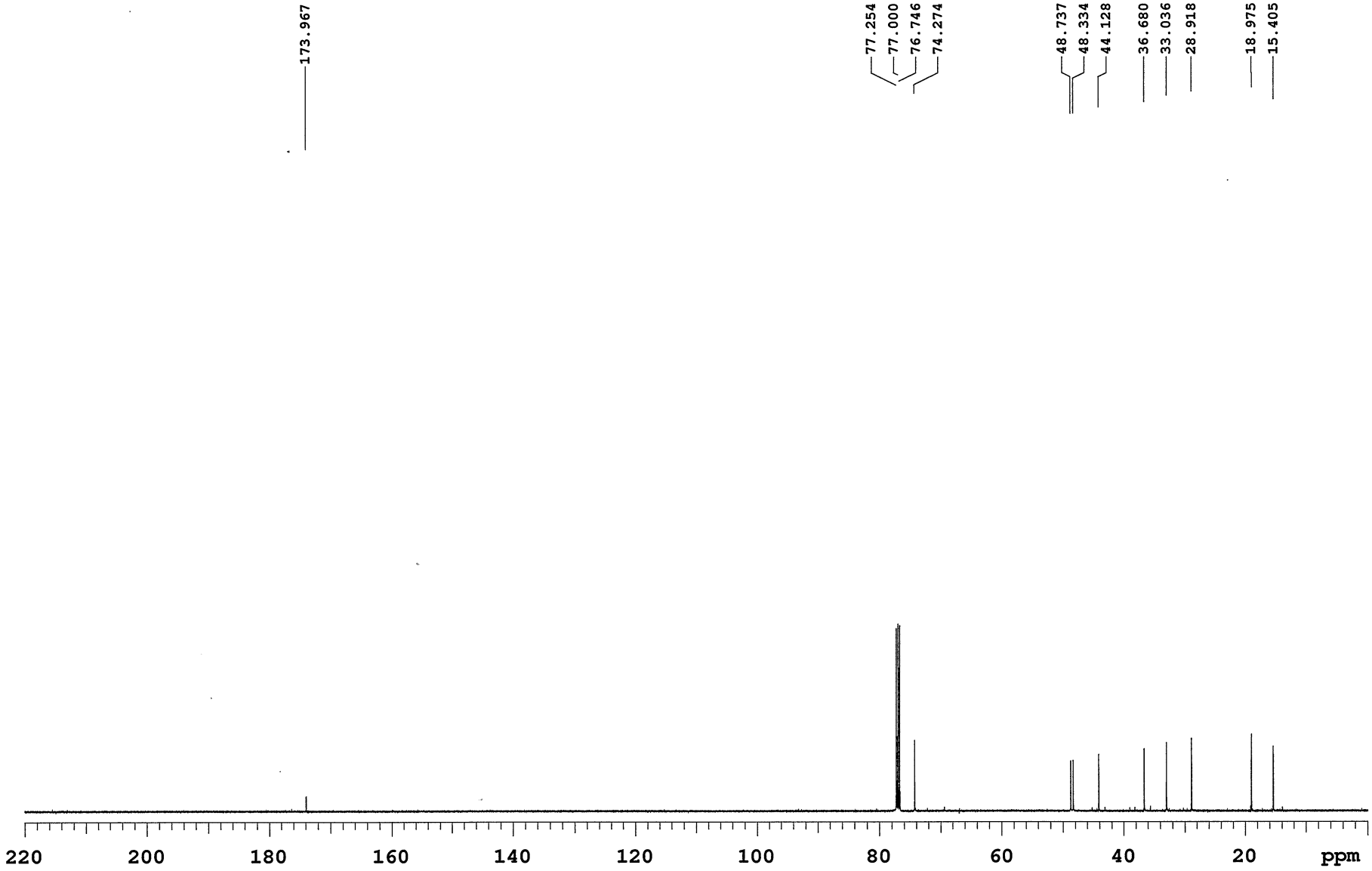
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-081-I/PROTON_03

1H NMR (500 MHz, CDCl3) of compound 6

Plot date 2022-12-26

RRT-04-087-I

Sample Name	**RRT-04-087-I**	Pulse sequence	**CARBON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-12-23**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



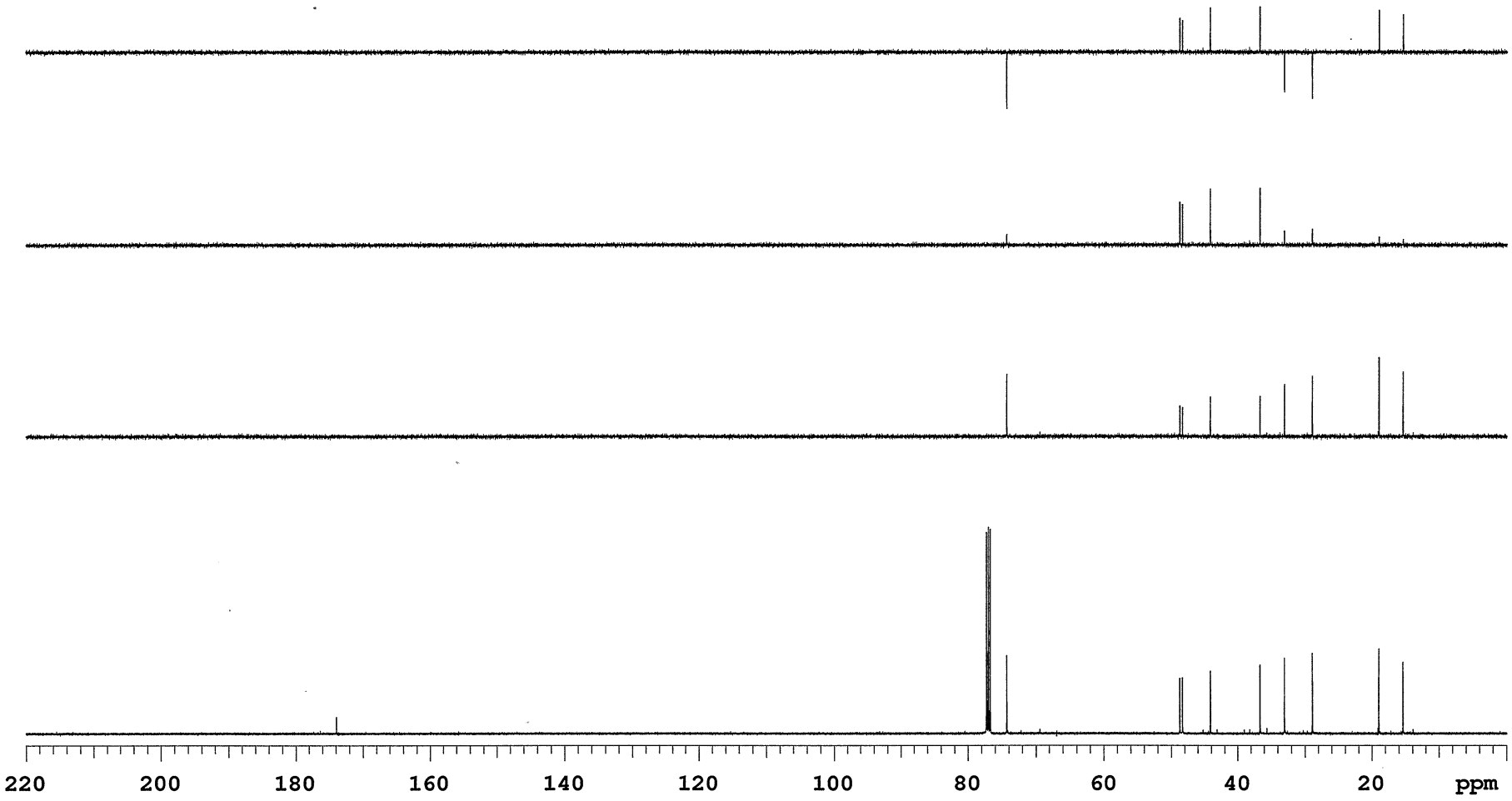
13C NMR (125 MHz, CDCl3) of compound 6

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-081-I/CARBON_02

Plot date 2022-12-26

RRT-04-087-I

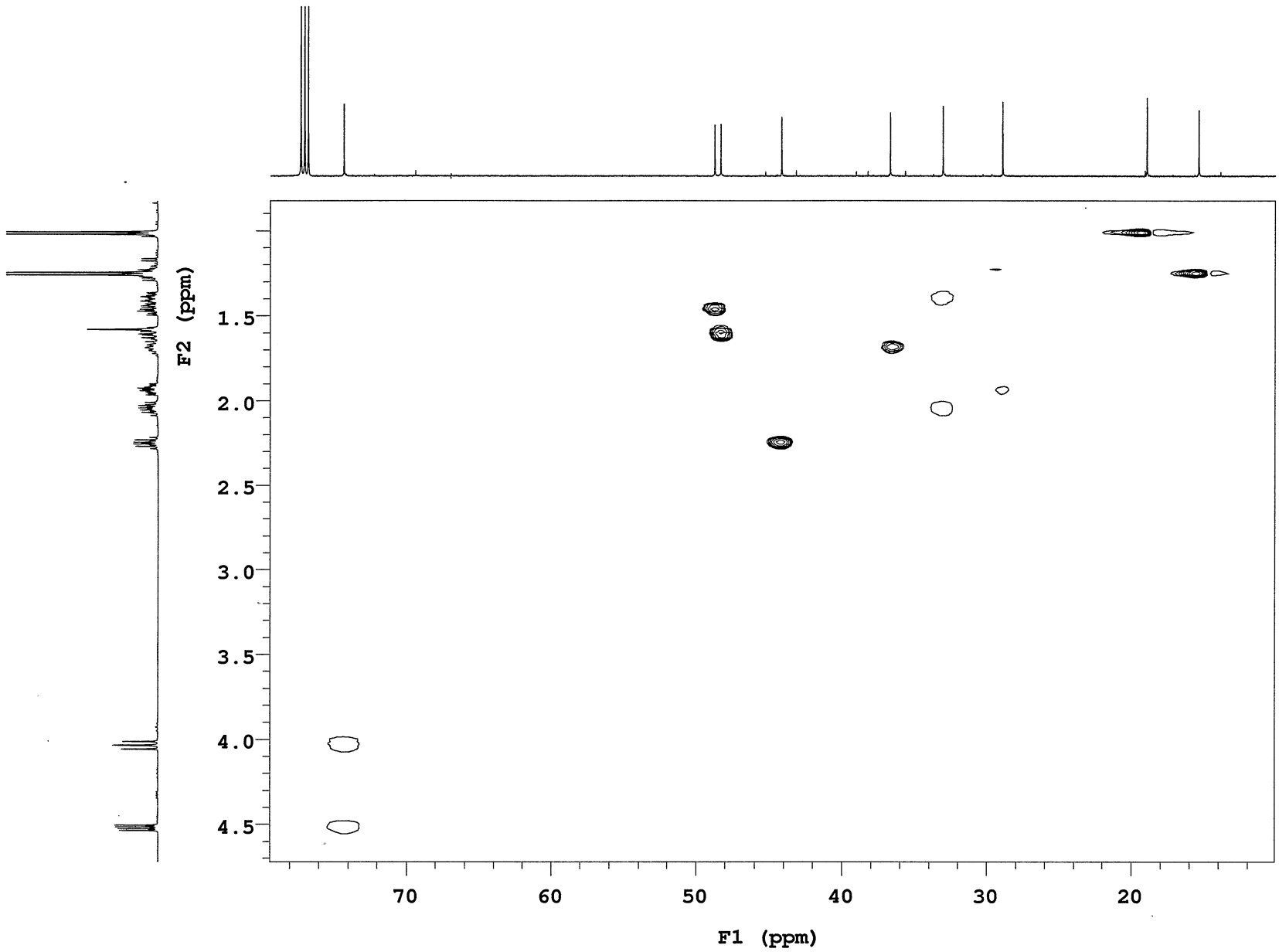
Sample Name **RRT-04-087-I**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-23**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 6

RRT-04-087-I

Sample Name **RRT-04-087-I**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-24**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



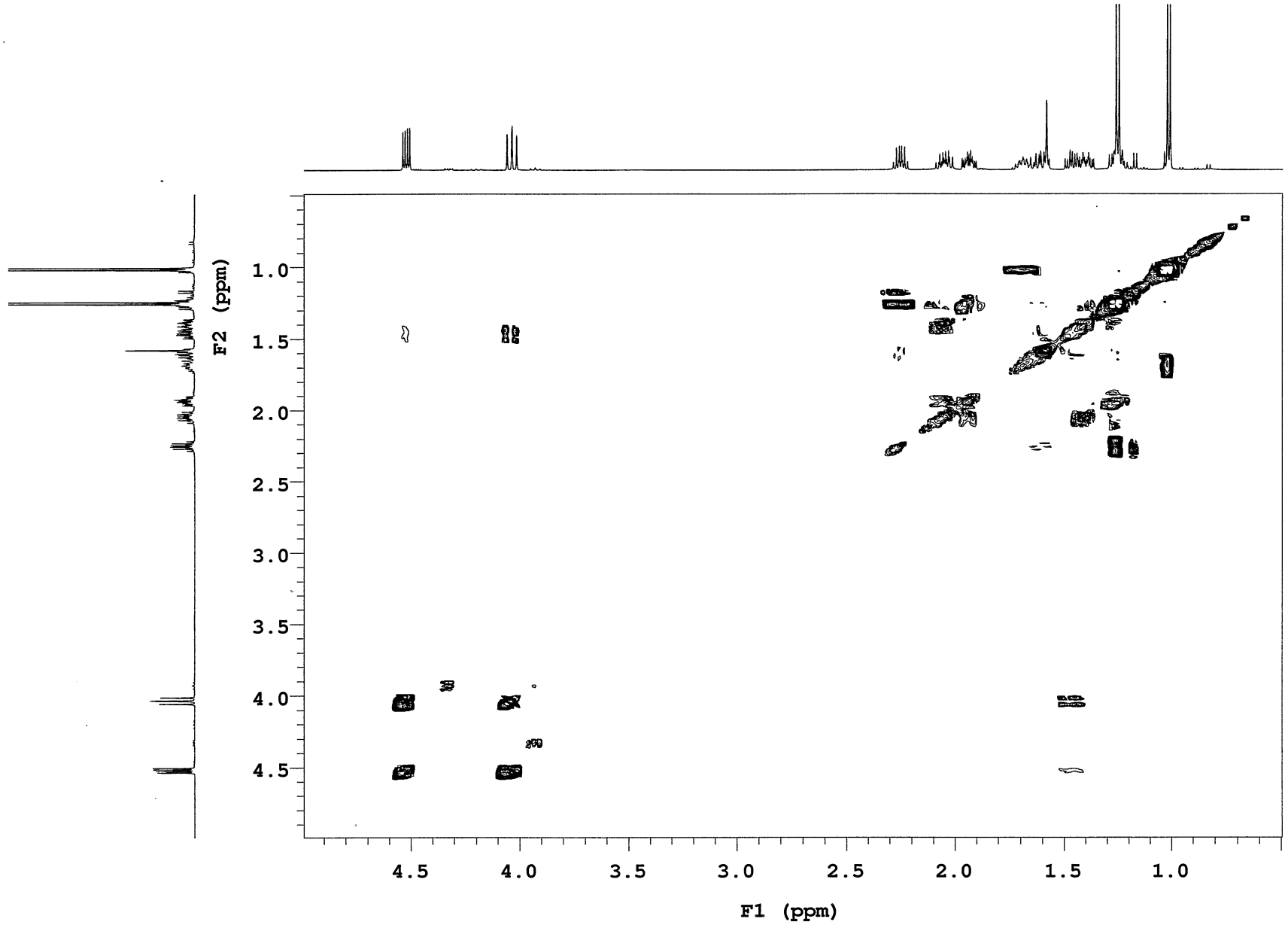
HSQC of compound 6

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-081-I/gHSQC_01

Plot date 2022-12-26

RRT-04-087-I

Sample Name **RRT-04-087-I**	Pulse sequence **gCOSY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-24**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



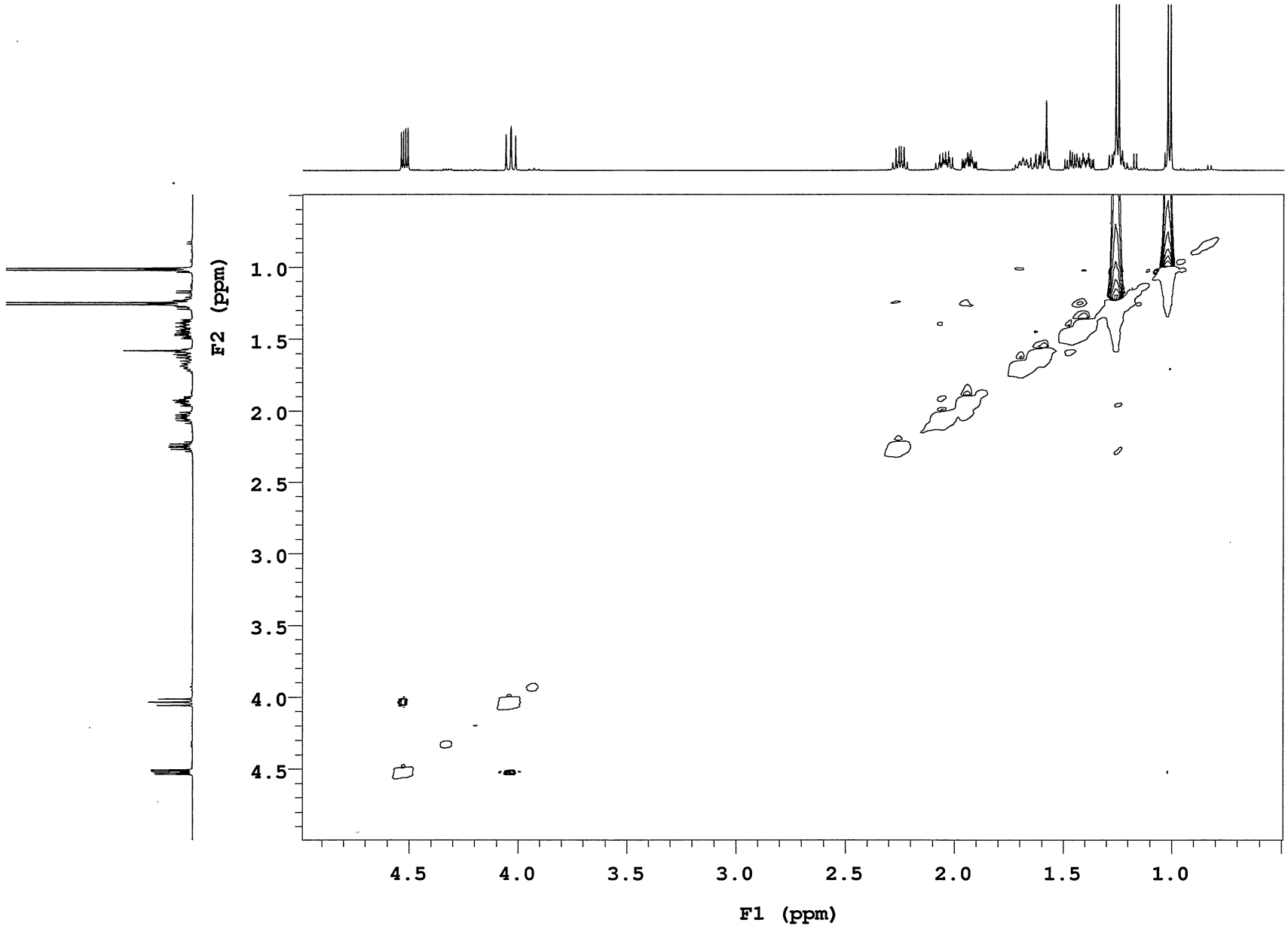
COSY of compound 6

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-081-I/gCOSY_01

Plot date 2022-12-26

RRT-04-087-I

Sample Name	RRT-04-087-I	Pulse sequence	NOESY	Temperature	25	Study owner	vnmr2
Date collected	2022-12-24	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



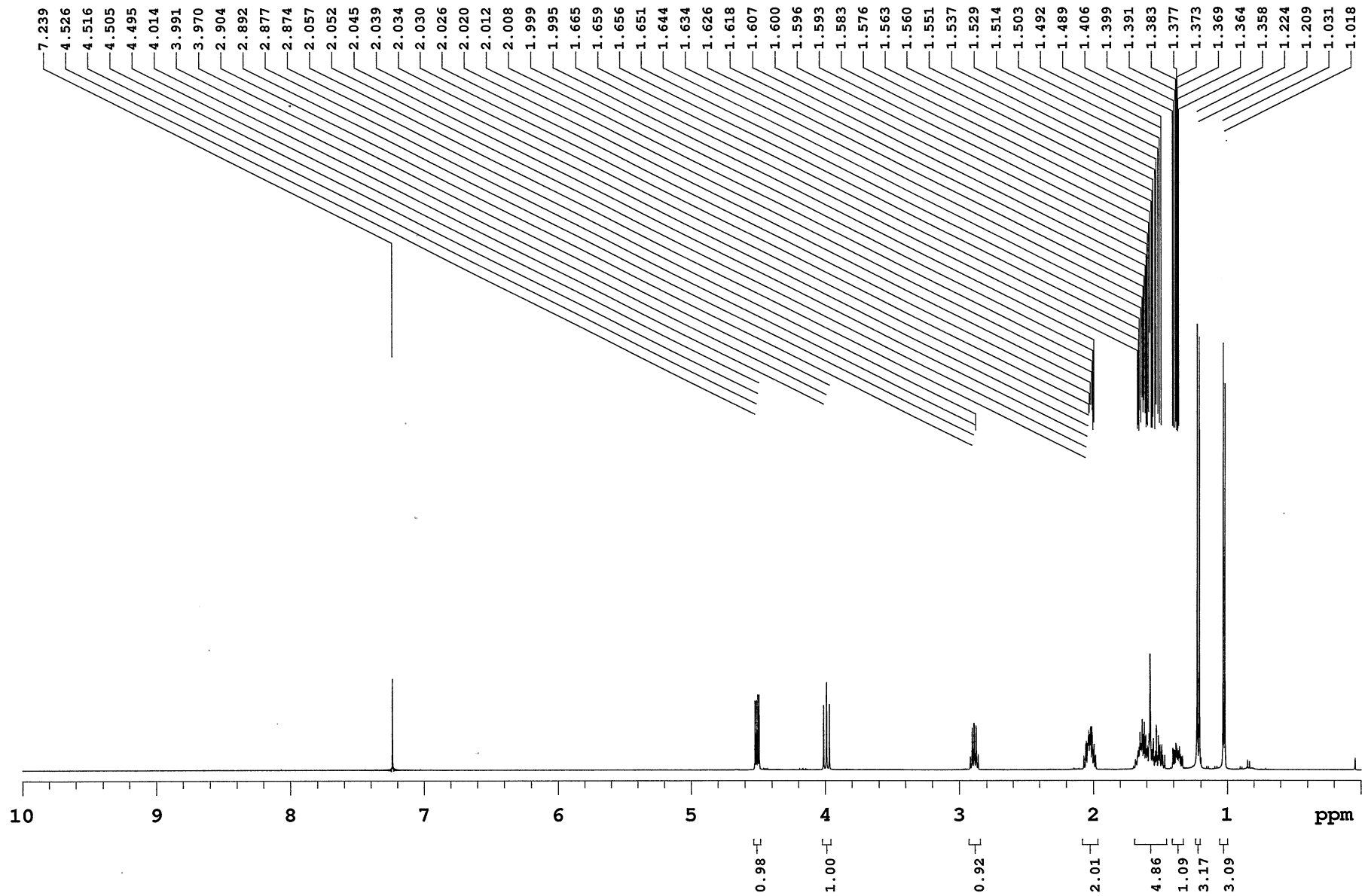
NOESY of compound 6

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-081-I/NOESY_01

Plot date 2022-12-26

RRT-04-087-II

Sample Name	**RRT-04-087-II**	Pulse sequence	**PROTON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-12-24**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



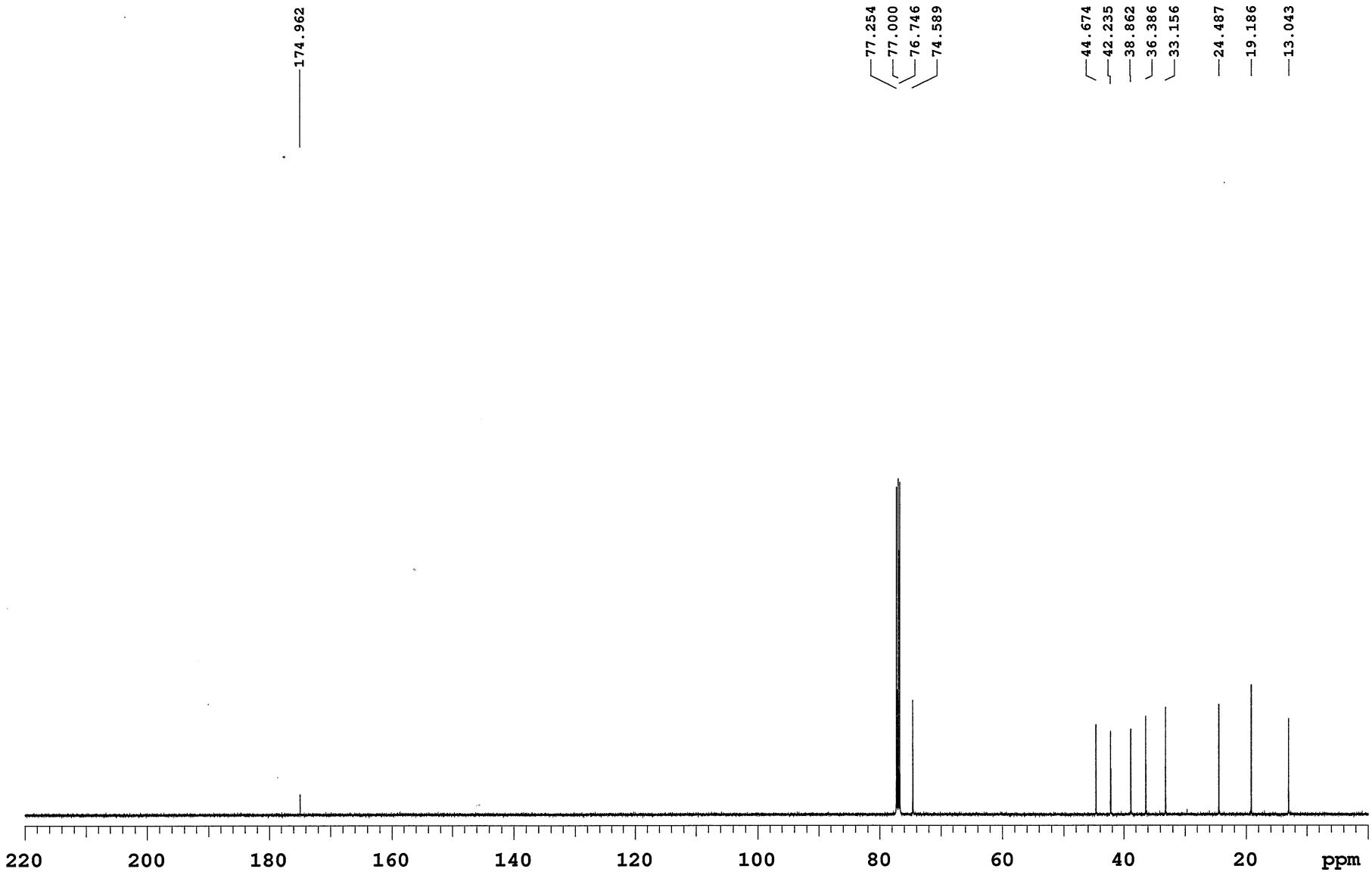
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-087-II/PROTON_03

1H NMR (500 MHz, CDCl3) of compound 7

Plot date 2022-12-26

RRT-04-087-II

Sample Name	**RRT-04-087-II**	Pulse sequence	**CARBON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-12-24**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



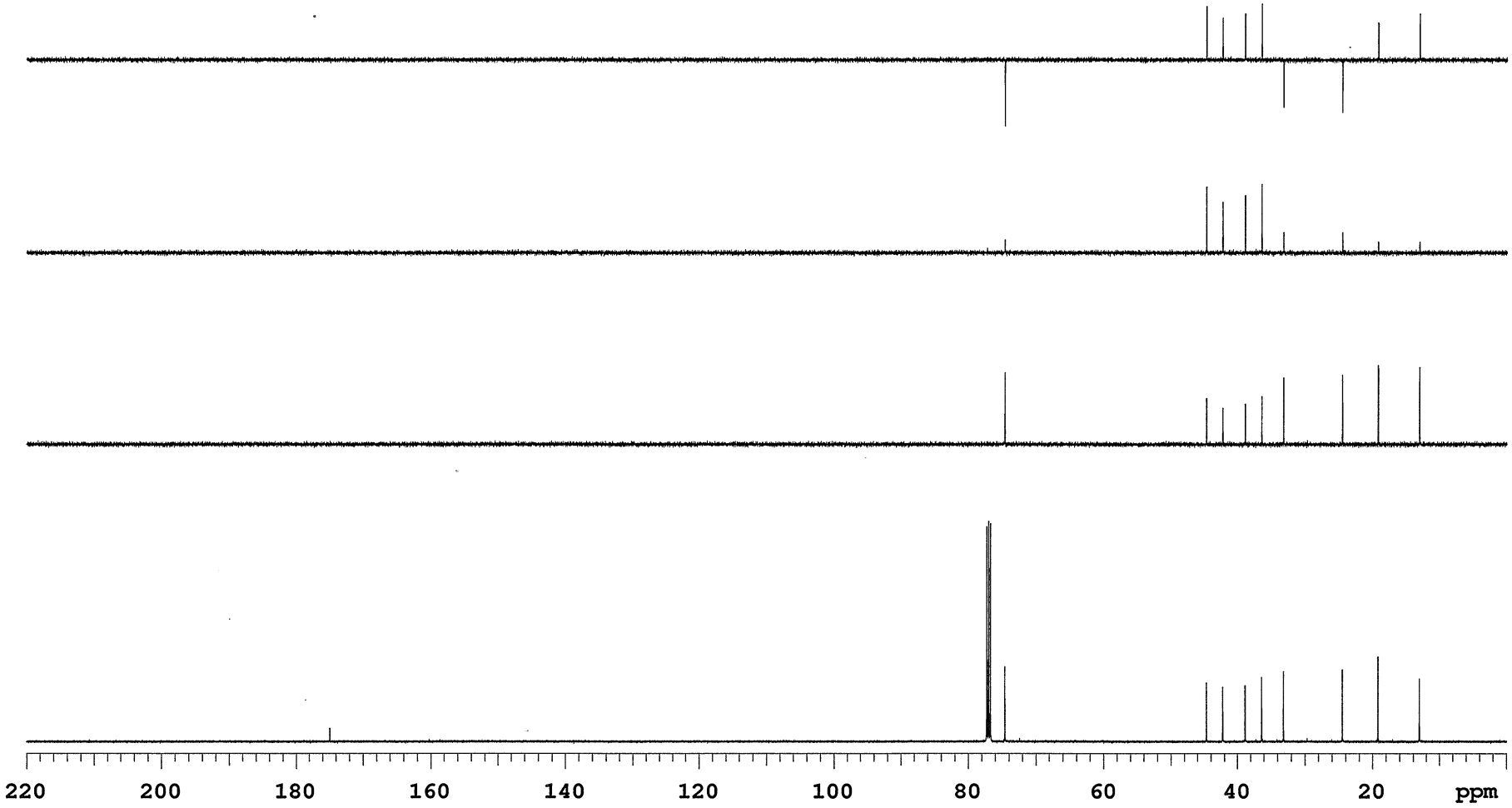
13C NMR (125 MHz, CDCl3) of compound 7

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-087-II/CARBON_02

Plot date 2022-12-26

RRT-04-087-II

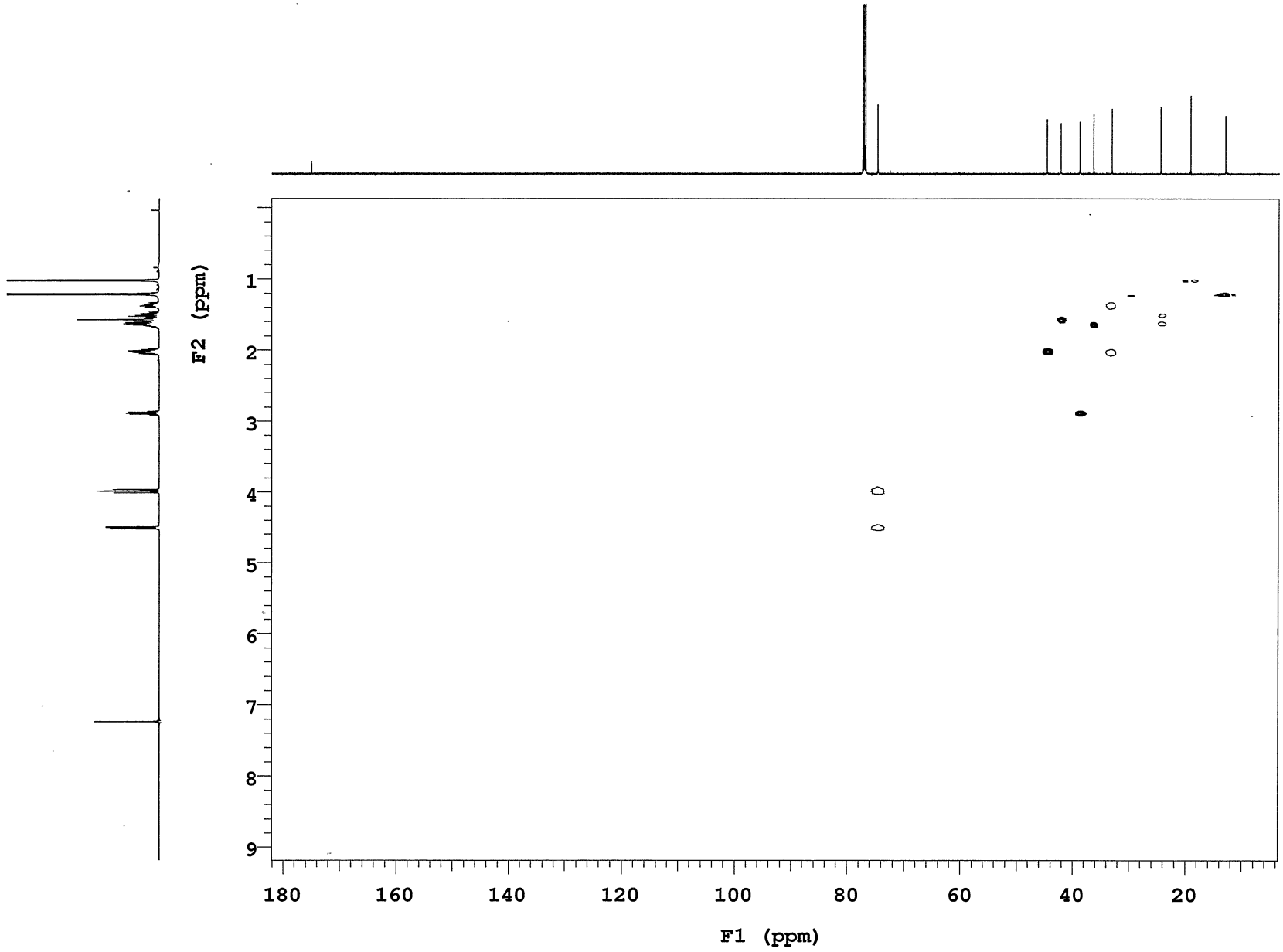
Sample Name **RRT-04-087-II**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-24**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 7

RRT-04-087-II

Sample Name	RRT-04-087-II	Pulse sequence	gHSQC	Temperature	25	Study owner	vnmr2
Date collected	2022-12-26	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



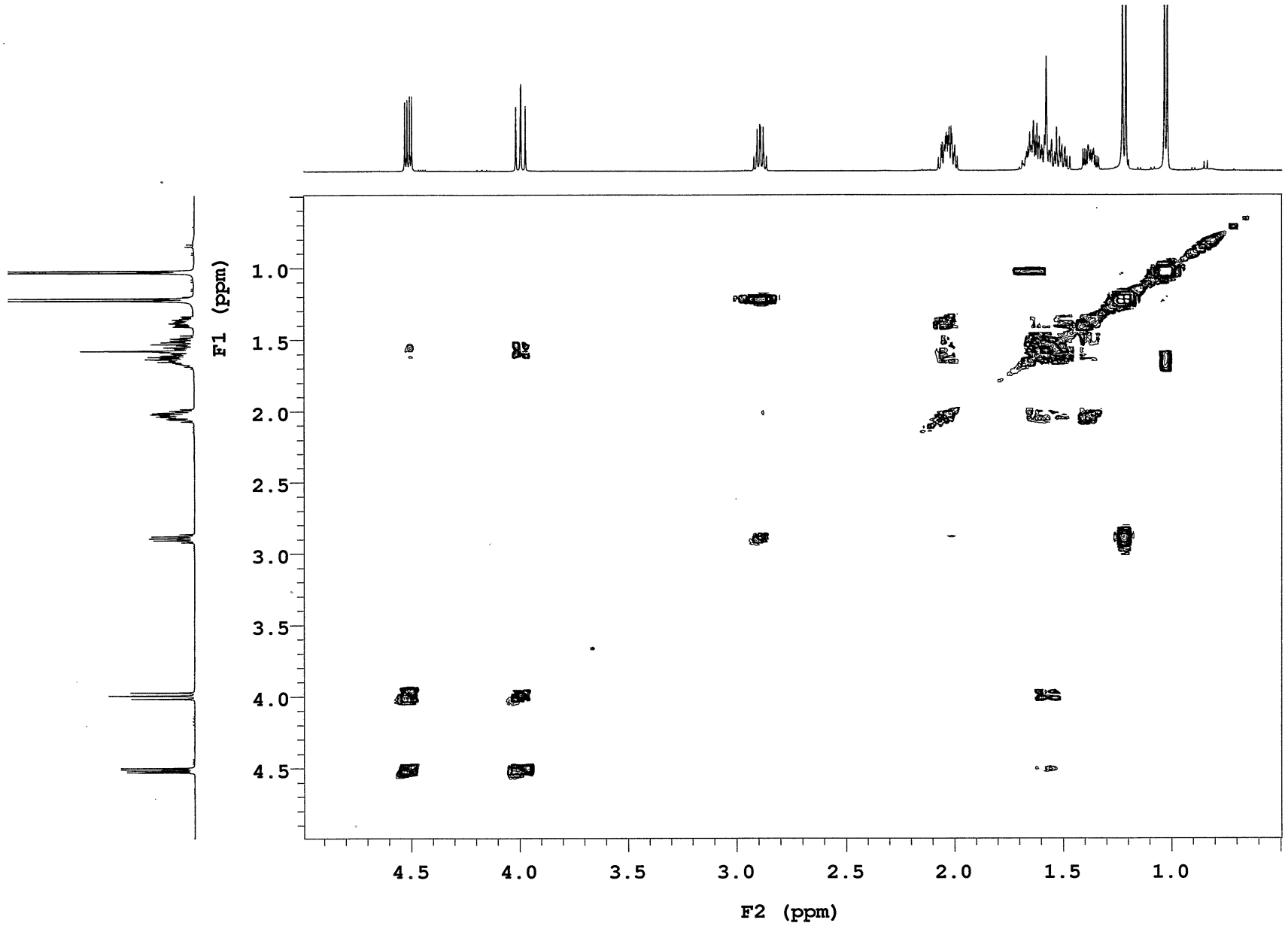
HSQC of compound 7

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-087-II/gHSQC_01

Plot date 2022-12-27

RRT-04-087-II

Sample Name	RRT-04-087-II	Pulse sequence	gCOSY	Temperature	25	Study owner	vnmr2
Date collected	2022-12-25	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



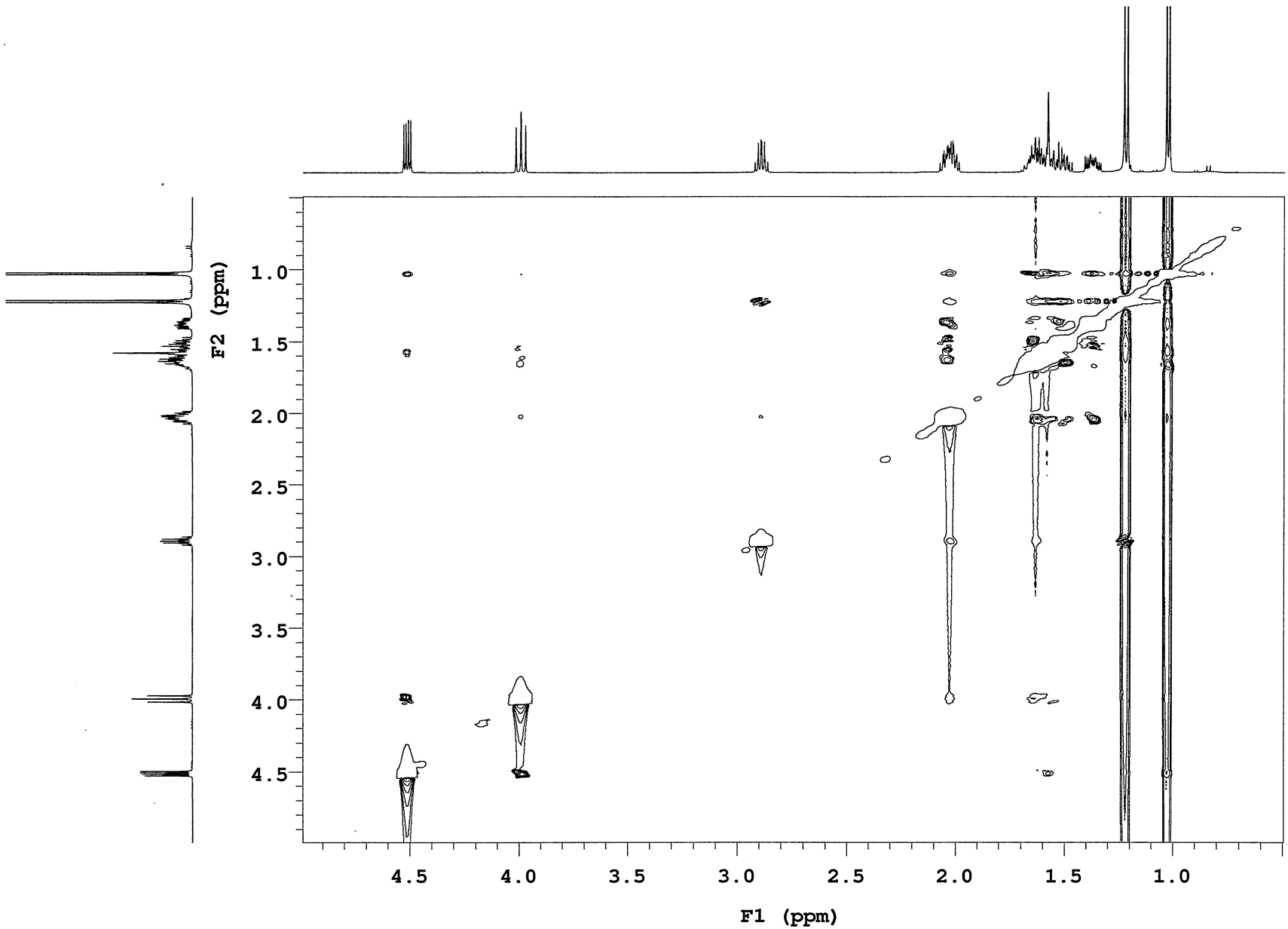
COSY of compound 7

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-087-II/gCOSY_01

Plot date 2022-12-26

RRT-04-087-II

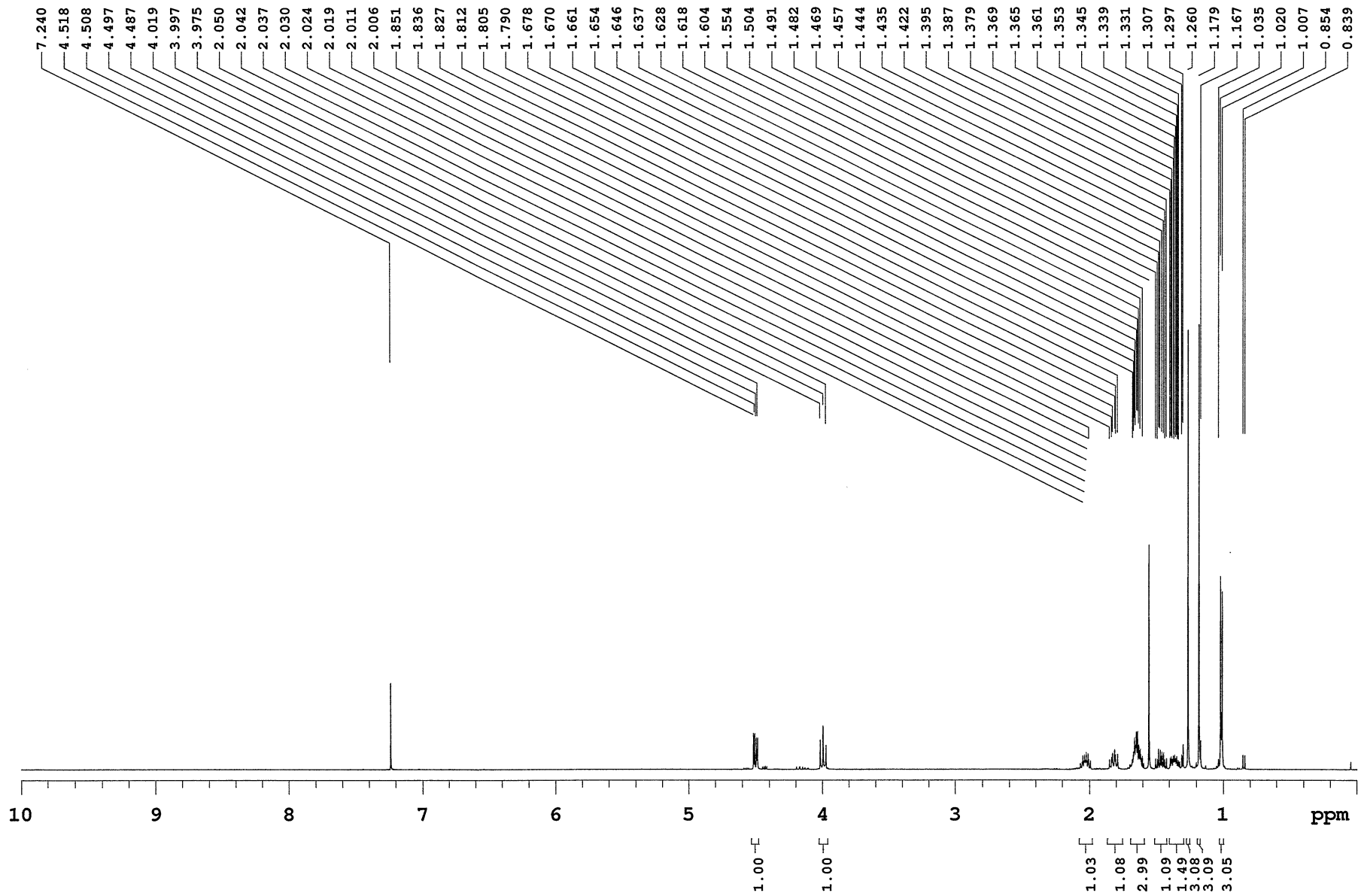
Sample Name **RRT-04-087-II**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-26**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



NOESY of compound 7

RRT-04-084-F-I

Sample Name **RRT-04-084-F-I**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-09**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



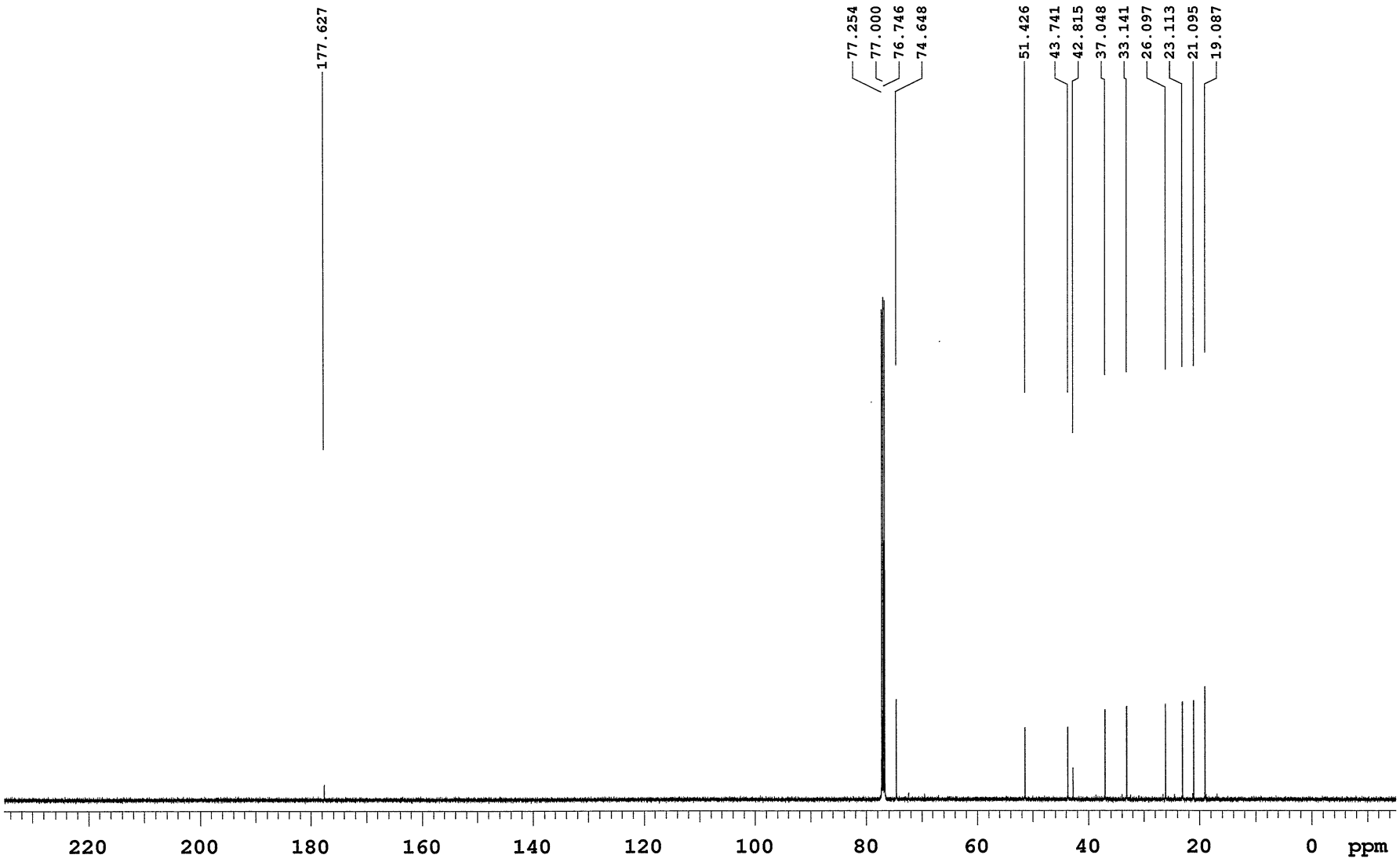
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-084-F-I/PROTON_03

1H NMR (500 MHz, CDCl3) of compound 8

Plot date 2022-12-11

RRT-04-084-F-I

Sample Name **RRT-04-084-F-I**	Pulse sequence **CARBON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-09**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



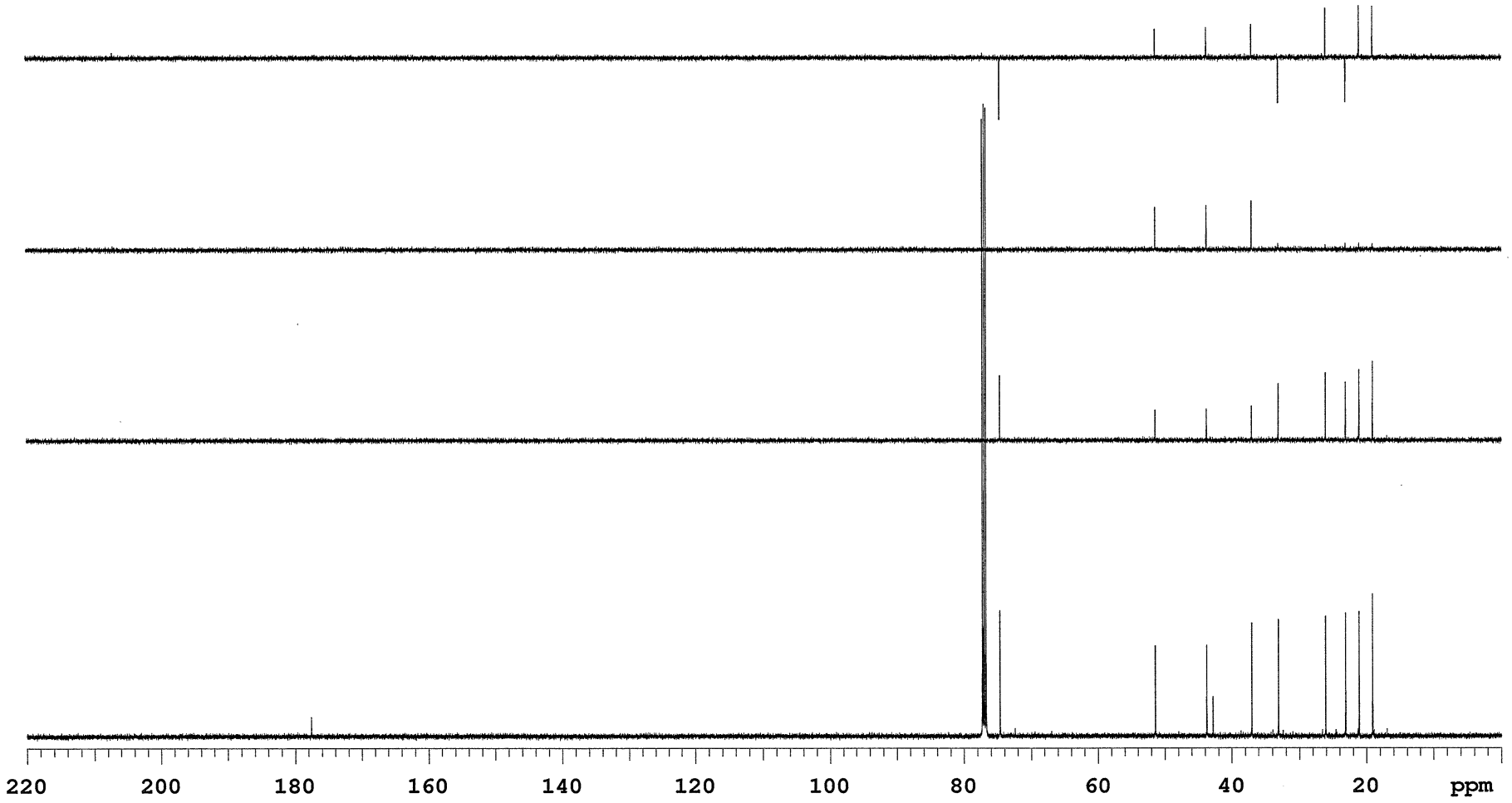
13C NMR (125 MHz, CDCl3) of compound 8

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-084-F-I/CARBON_02

Plot date 2022-12-11

RRT-04-084-F-I

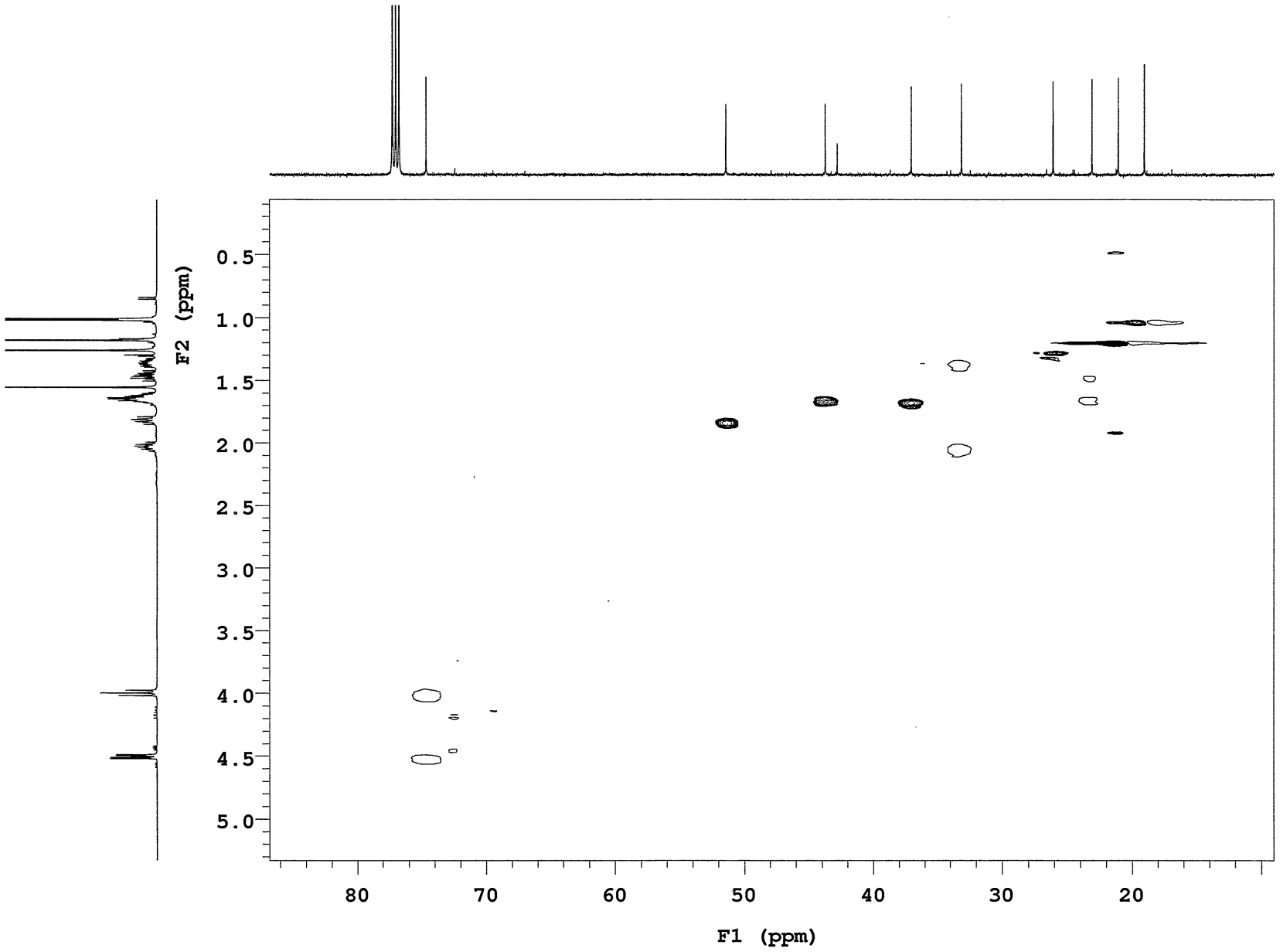
Sample Name **RRT-04-084-F-I**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-09**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 8

RRT-04-084-F-I

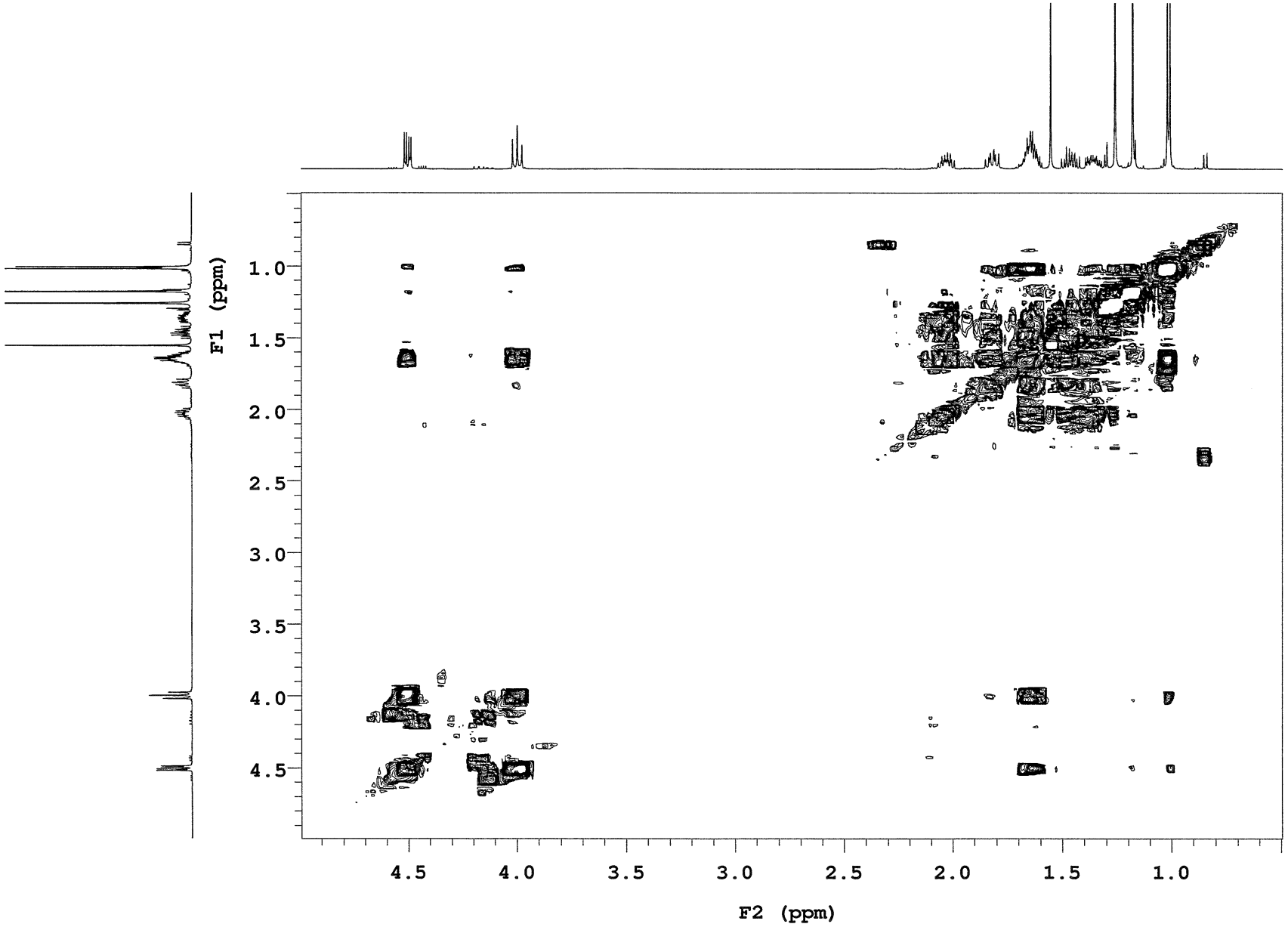
Sample Name **RRT-04-084-F-I**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-10**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



HSQC of compound 8

RRT-04-084-F-I

Sample Name **RRT-04-084-F-I**	Pulse sequence **gCOSY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-10**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



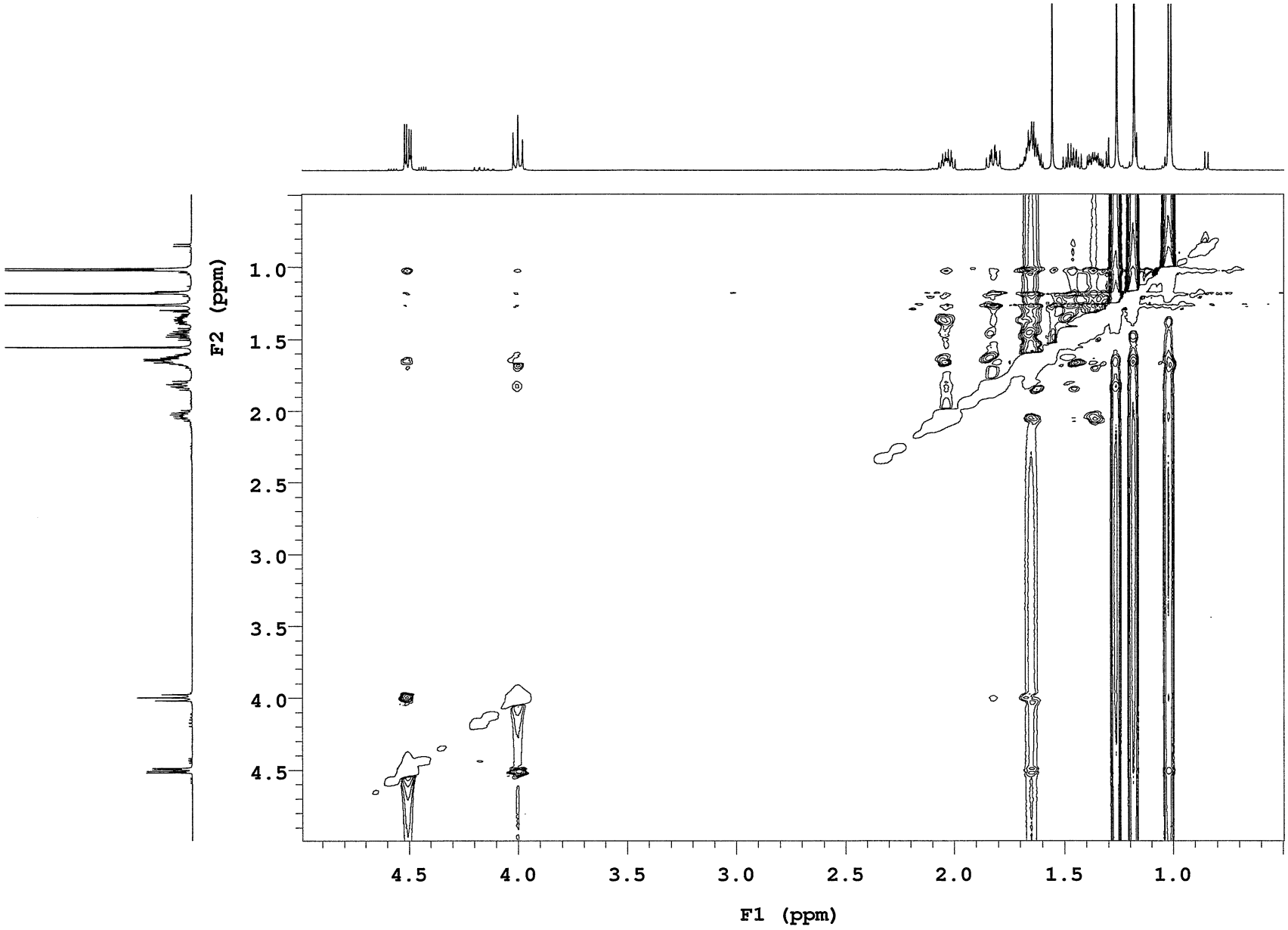
COSY of compound 8

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-084-F-I/gCOSY_01

Plot date 2022-12-11

RRT-04-084-F-I

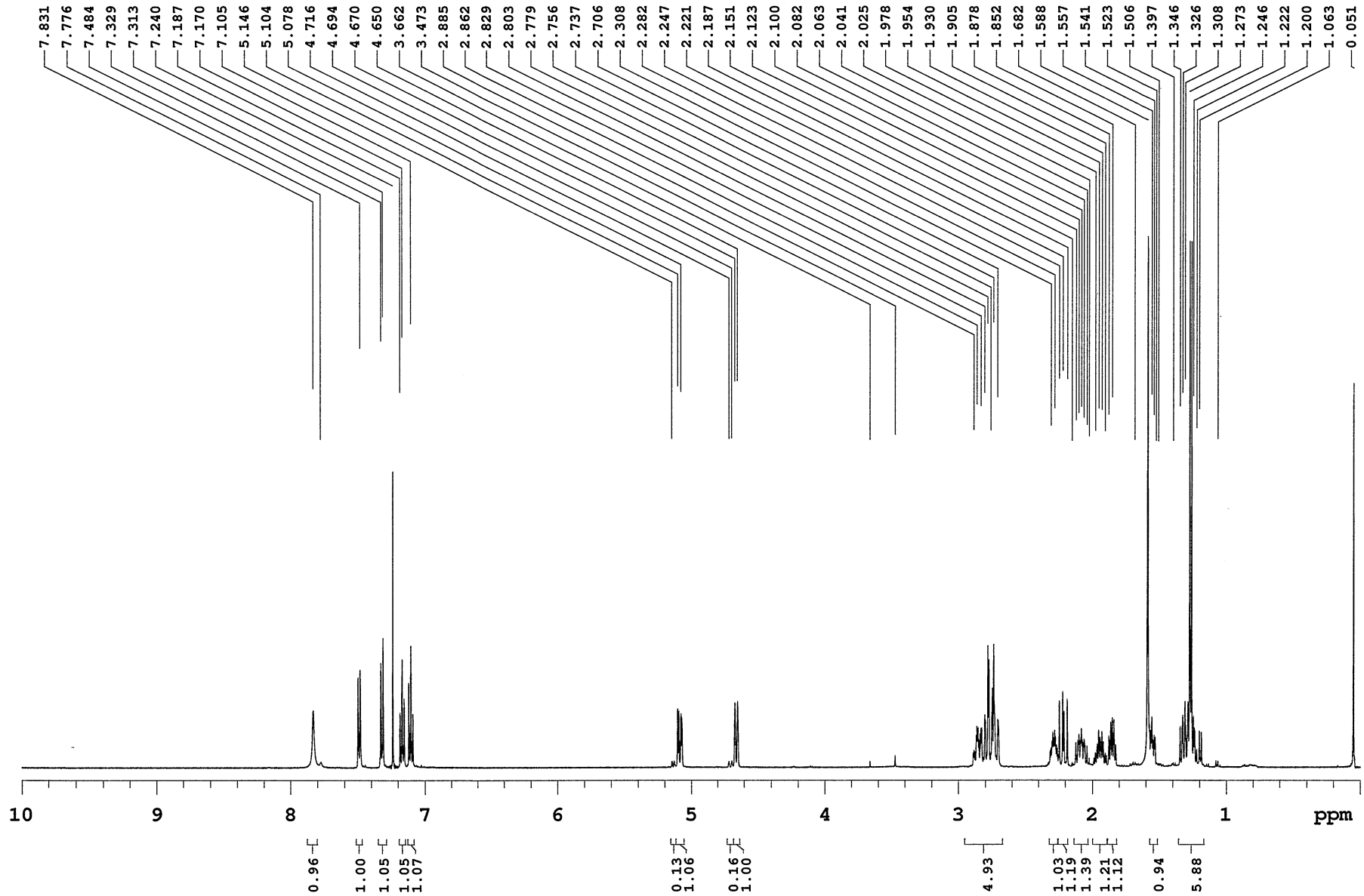
Sample Name	RRT-04-084-F-I	Pulse sequence	NOESY	Temperature	25	Study owner	vnmr2
Date collected	2022-12-10	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



NOESY of compound 8

RRT-04-064-II-B

Sample Name **RRT-04-064-II-B**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-17**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



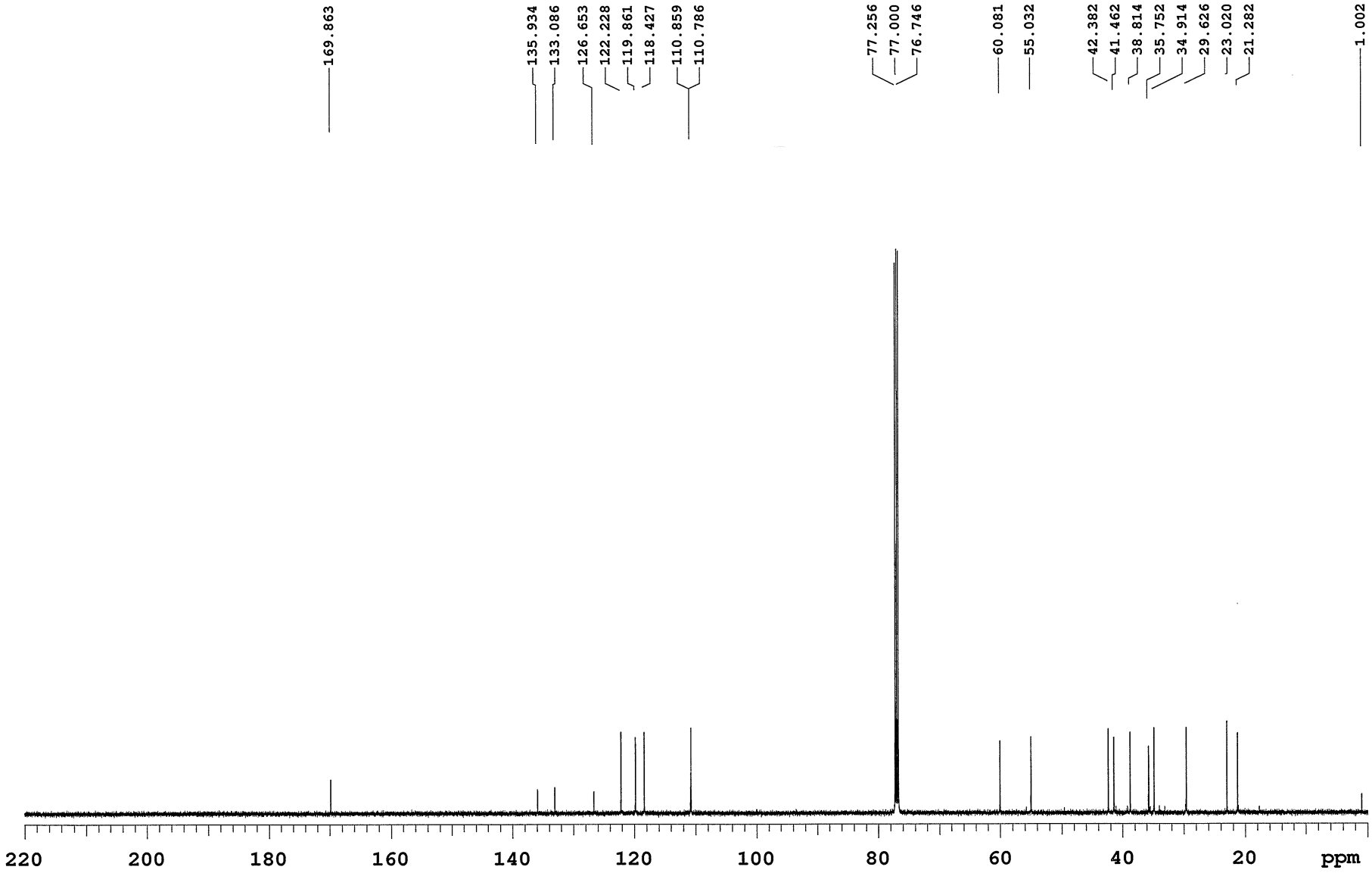
Data file /home/vnmr2/vnmrsys/data/511/RTT/RRT-04-064-II-B/PROTON_03

1H NMR (500 MHz, CDCl3) of compound 10a

Plot date 2022-10-18

RRT-04-064-II-B

Sample Name **RRT-04-064-II-B**	Pulse sequence **CARBON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-17**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



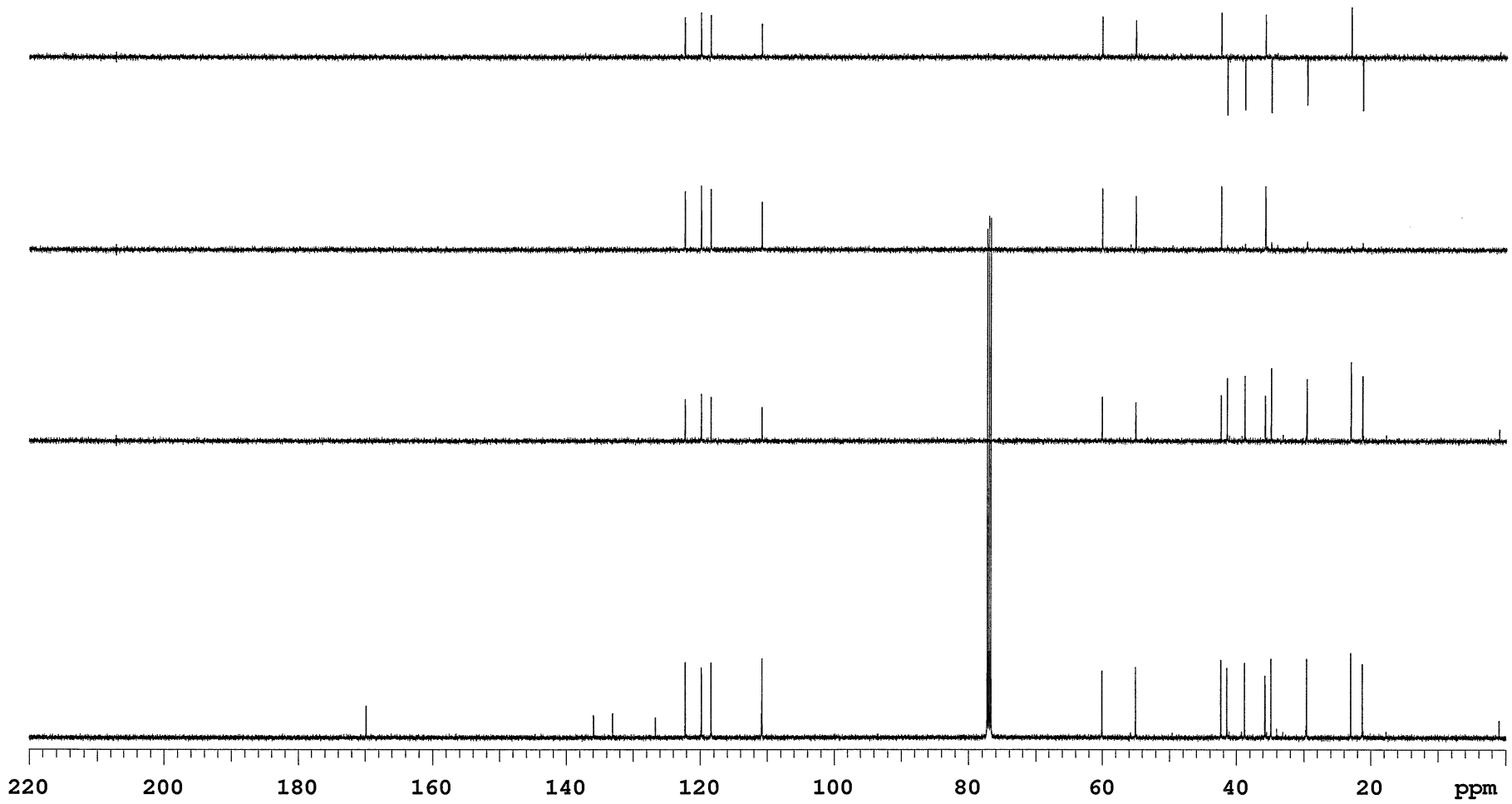
13C NMR (125 MHz, CDCl3) of compound 10a

Data file /home/vnmr2/vnmrsys/data/511/RTT/RRT-04-064-II-B/CARBON_02

Plot date 2022-10-18

RRT-04-064-II-B

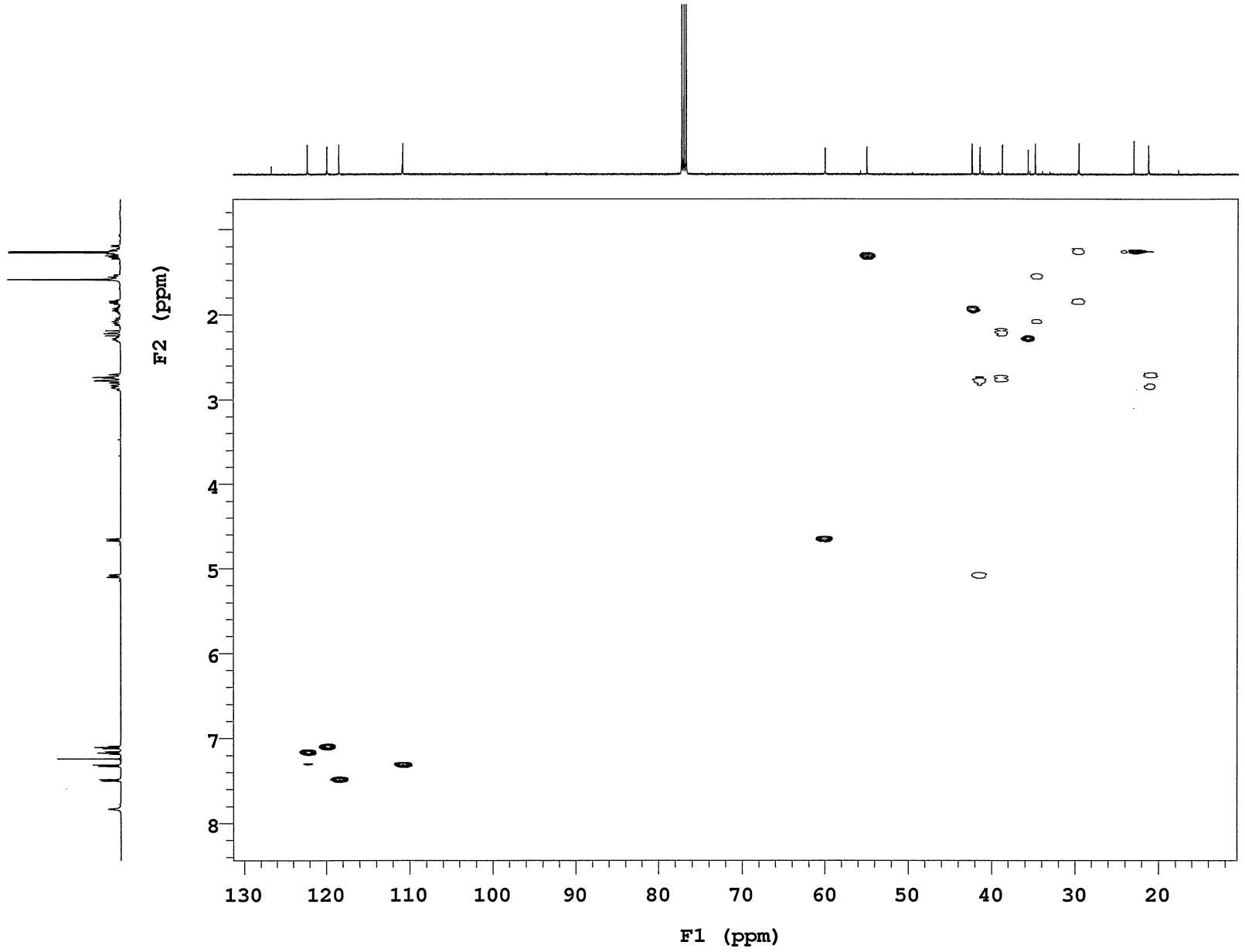
Sample Name **RRT-04-064-II-B**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-18**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 10a

RRT-04-064-II-B

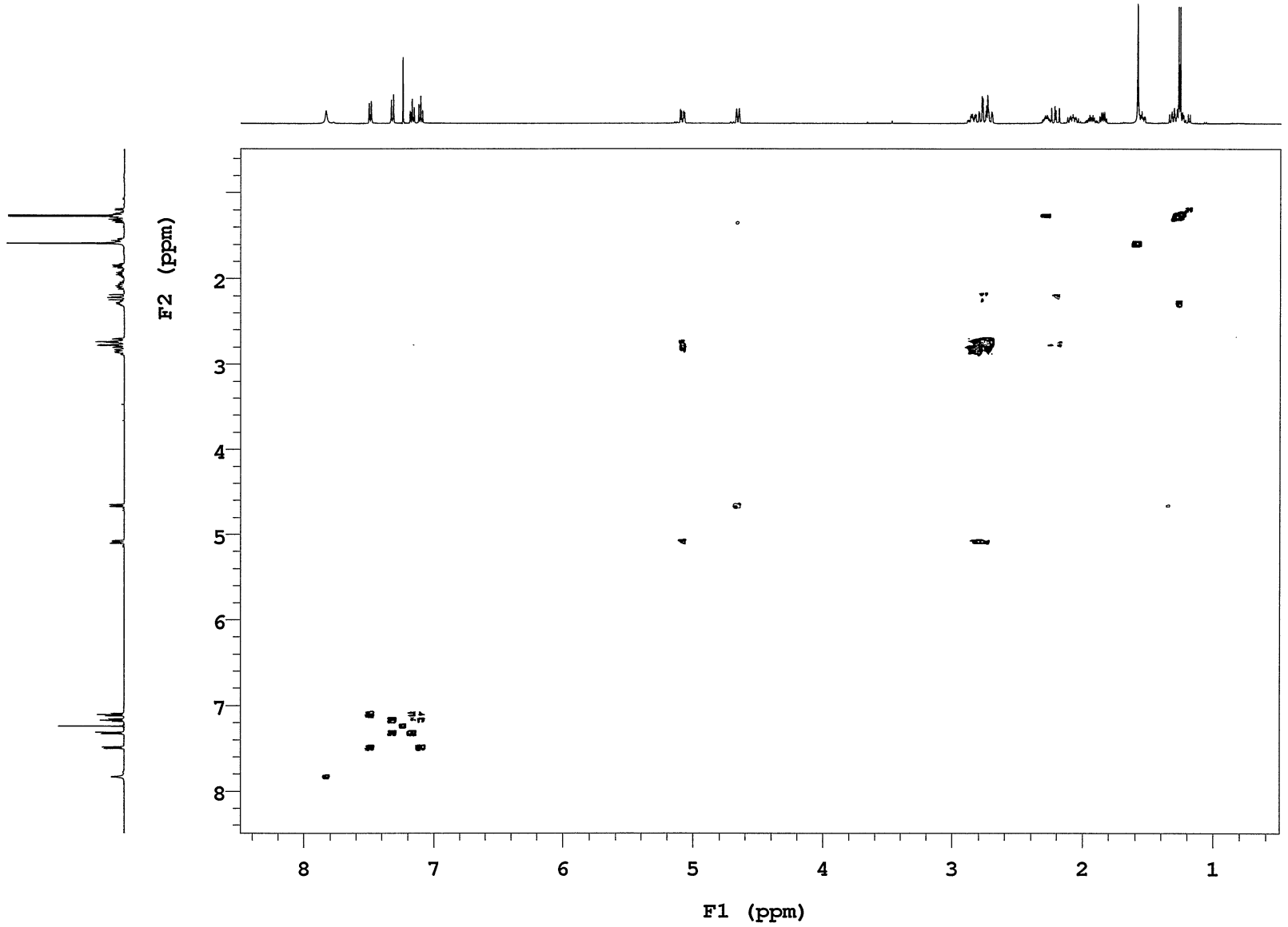
Sample Name **RRT-04-064-II-B**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-18**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



HSQC of compound 10a

RRT-04-064-II-B

Sample Name	**RRT-04-064-II-B**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-10-18**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



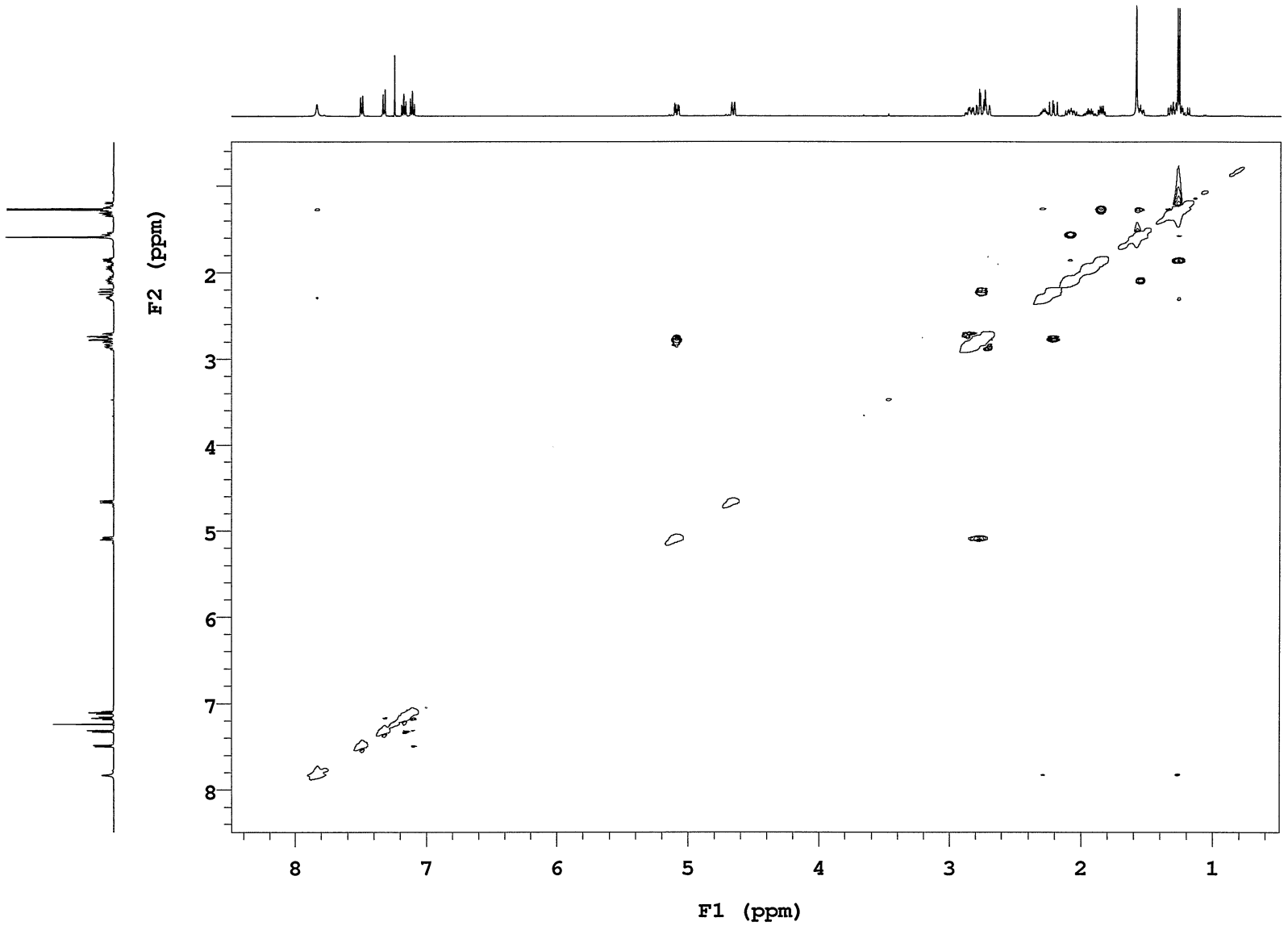
COSY of compound 10a

Data file /home/vnmr2/vnmrsys/data/511/RTT/RRT-04-064-II-B/gCOSY_01

Plot date 2022-10-18

RRT-04-064-II-B

Sample Name **RRT-04-064-II-B**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-18**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



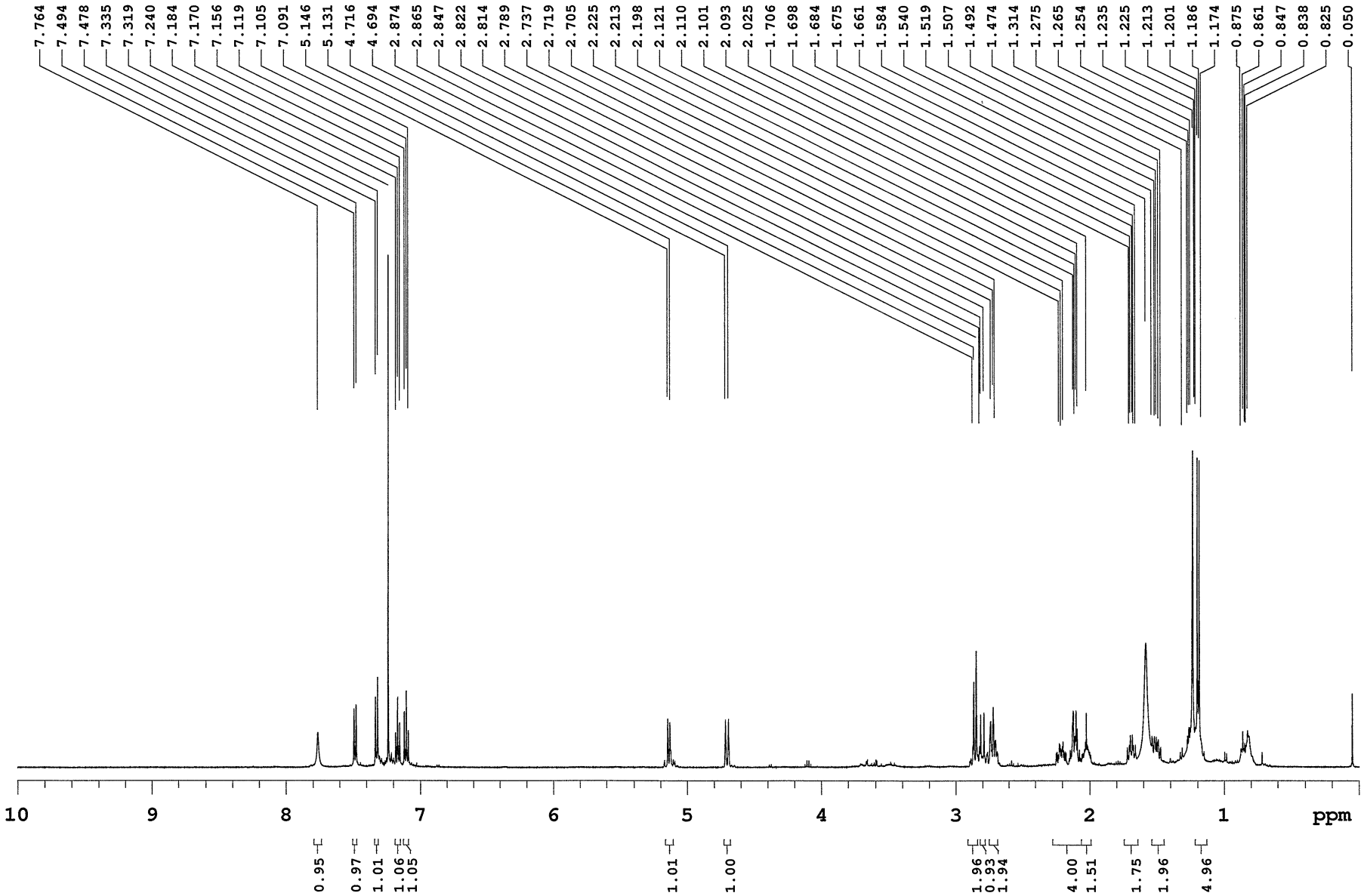
Data file /home/vnmr2/vnmrsys/data/511/RTT/RRT-04-064-II-B/NOESY_01

NOESY of compound 10a

Plot date 2022-10-18

RRT-04-064-I

Sample Name **RRT-04-064-I**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-13**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



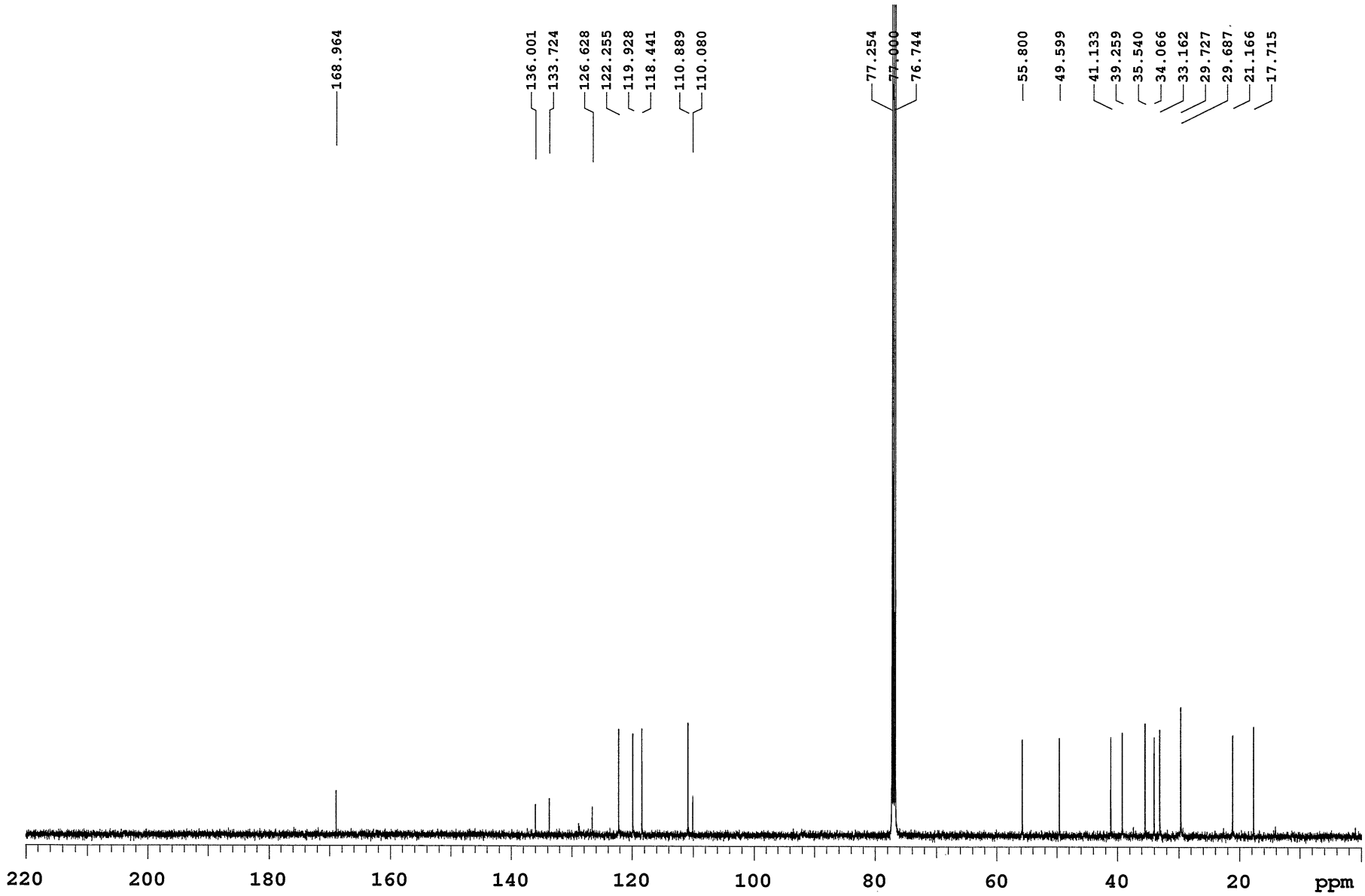
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-064-I/PROTON_03

1H NMR (500 MHz, CDCl3) of compound 11a

Plot date 2022-11-30

RRT-04-064-I

Sample Name **RRT-04-064-I** | Pulse sequence **CARBON** | Temperature **25** | Study owner **vnmr2**
Date collected **2022-10-13** | Solvent **cdcl3** | Spectrometer **Agilent-NMR-inova500** | Operator **vnmr2**



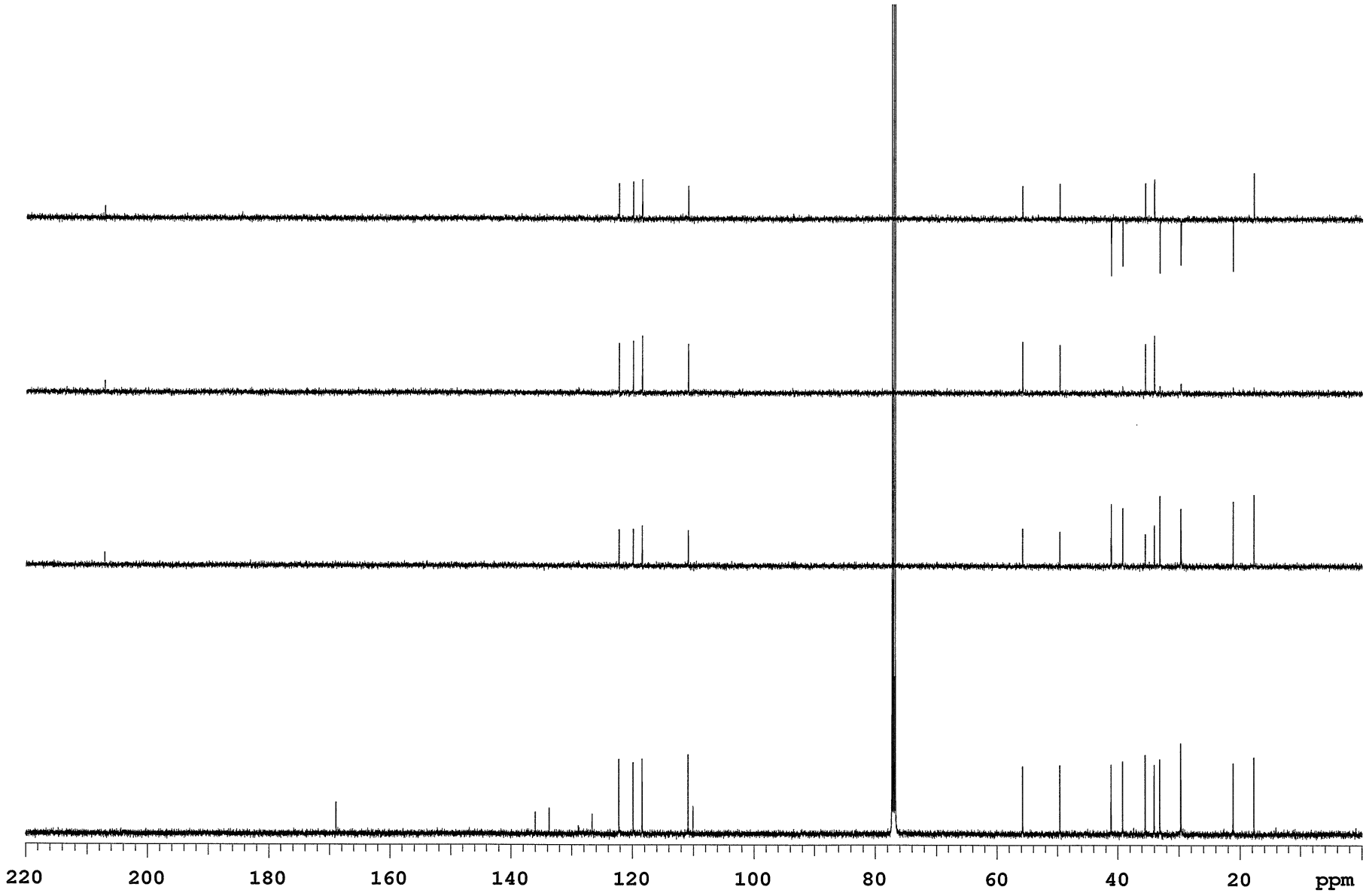
13C NMR (125 MHz, CDCl3) of compound 11a

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-064-I/CARBON_02

Plot date 2022-10-14

RRT-04-064-I

Sample Name **RRT-04-064-I**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-13**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



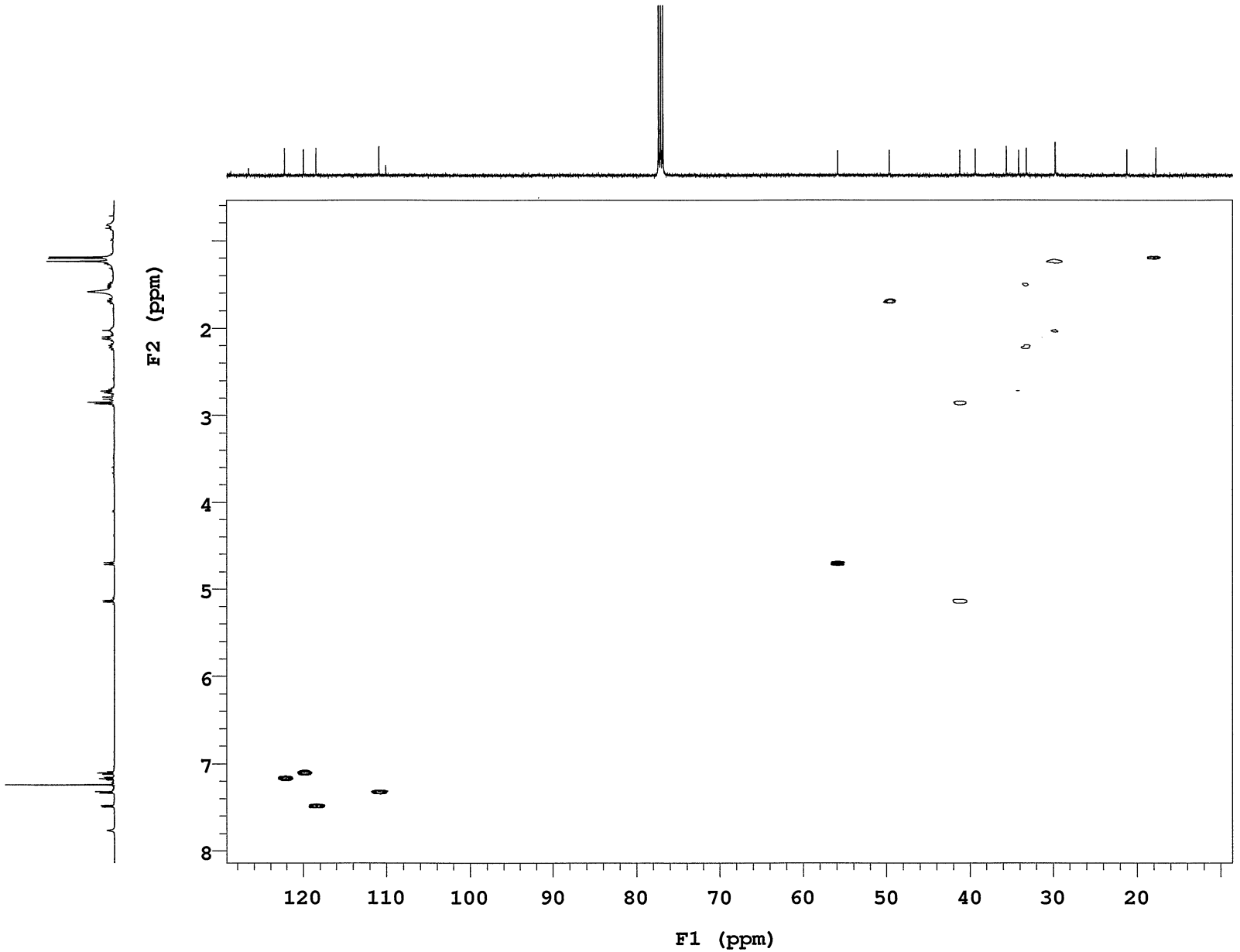
DEPT of compound 11a

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-064-I/DEPT_01

Plot date 2022-10-14

RRT-04-064-I

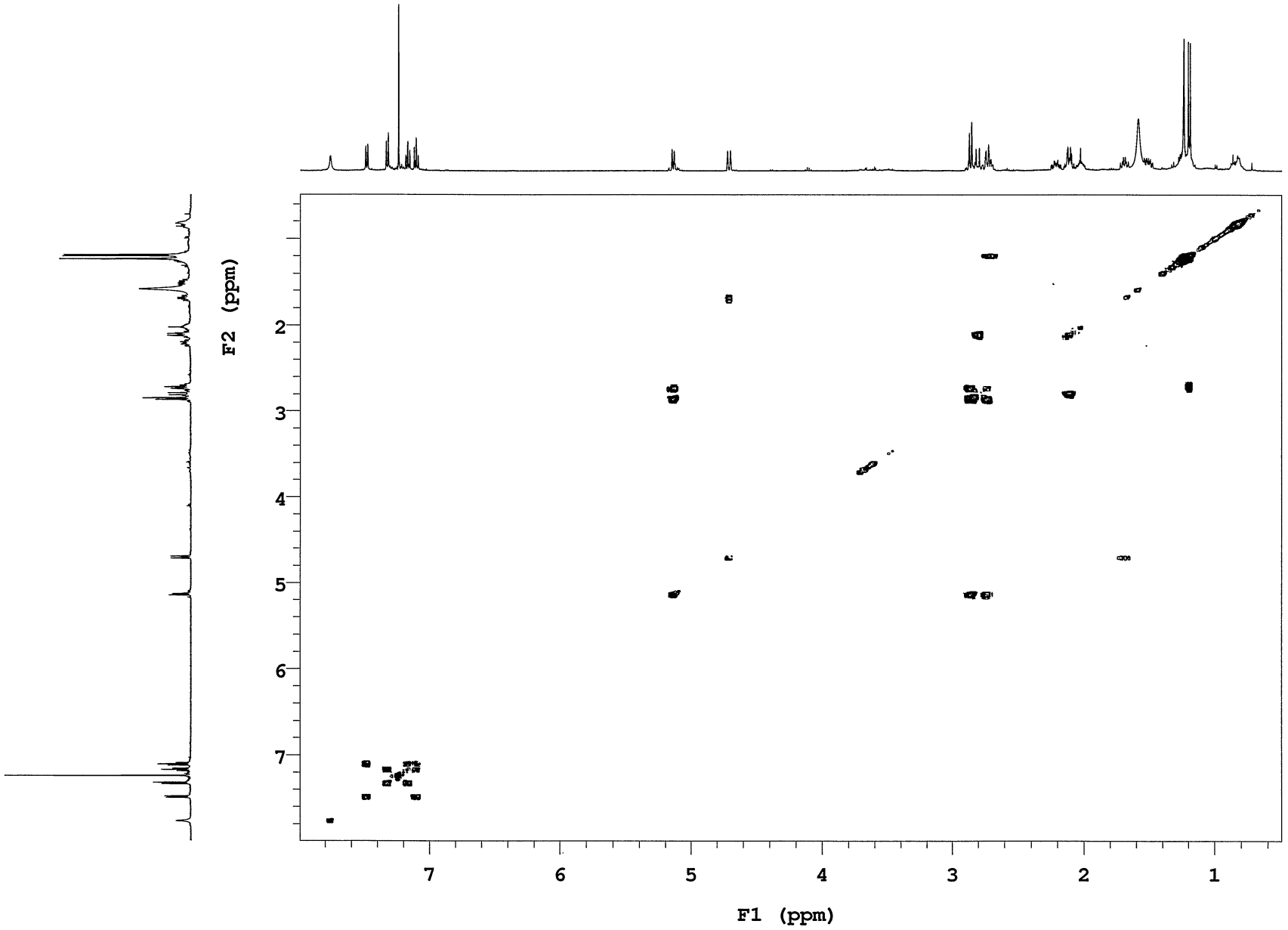
Sample Name	**RRT-04-064-I**	Pulse sequence	**gHSQC**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-10-14**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



HSQC of compound 11a

RRT-04-064-I

Sample Name	RRT-04-064-I	Pulse sequence	gCOSY	Temperature	25	Study owner	vnmr2
Date collected	2022-10-14	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



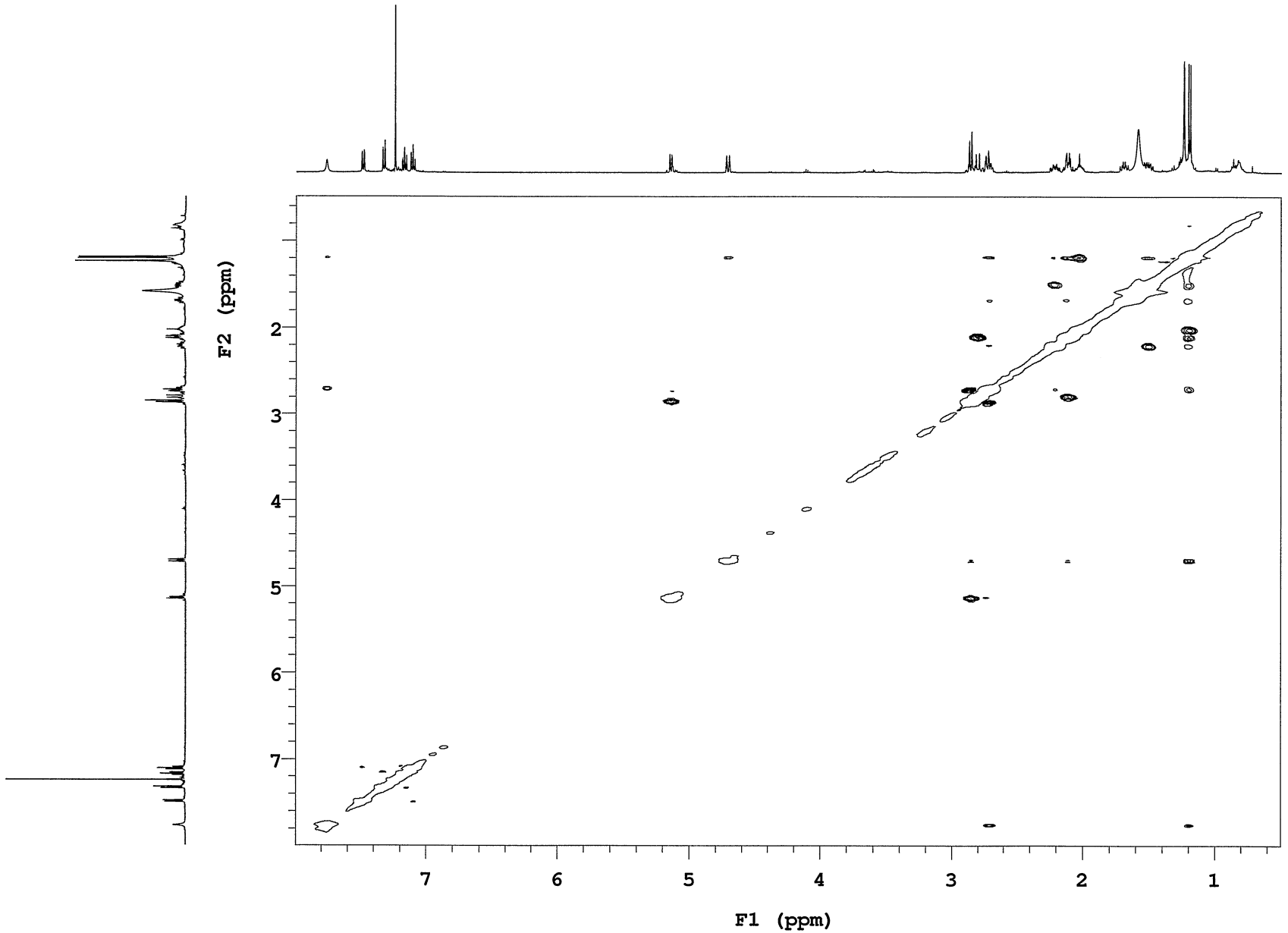
COSY of compound 11a

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-064-I/gCOSY_01

Plot date 2022-10-14

RRT-04-064-I

Sample Name	**RRT-04-064-I**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-10-14**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



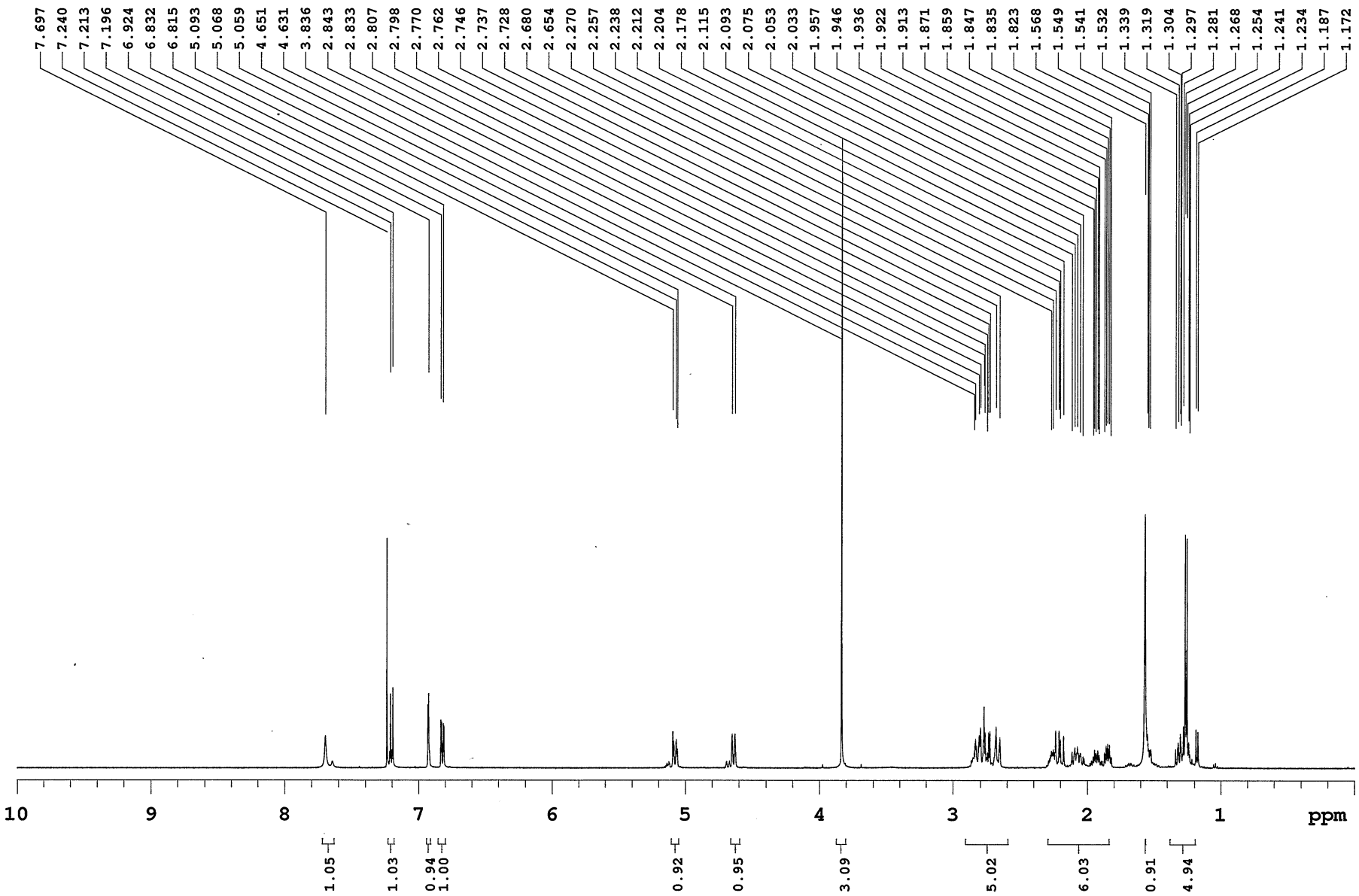
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-064-I/NOESY_01

NOESY of compound 11a

Plot date 2022-10-14

RTT-252

Sample Name **RTT-252**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-18**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



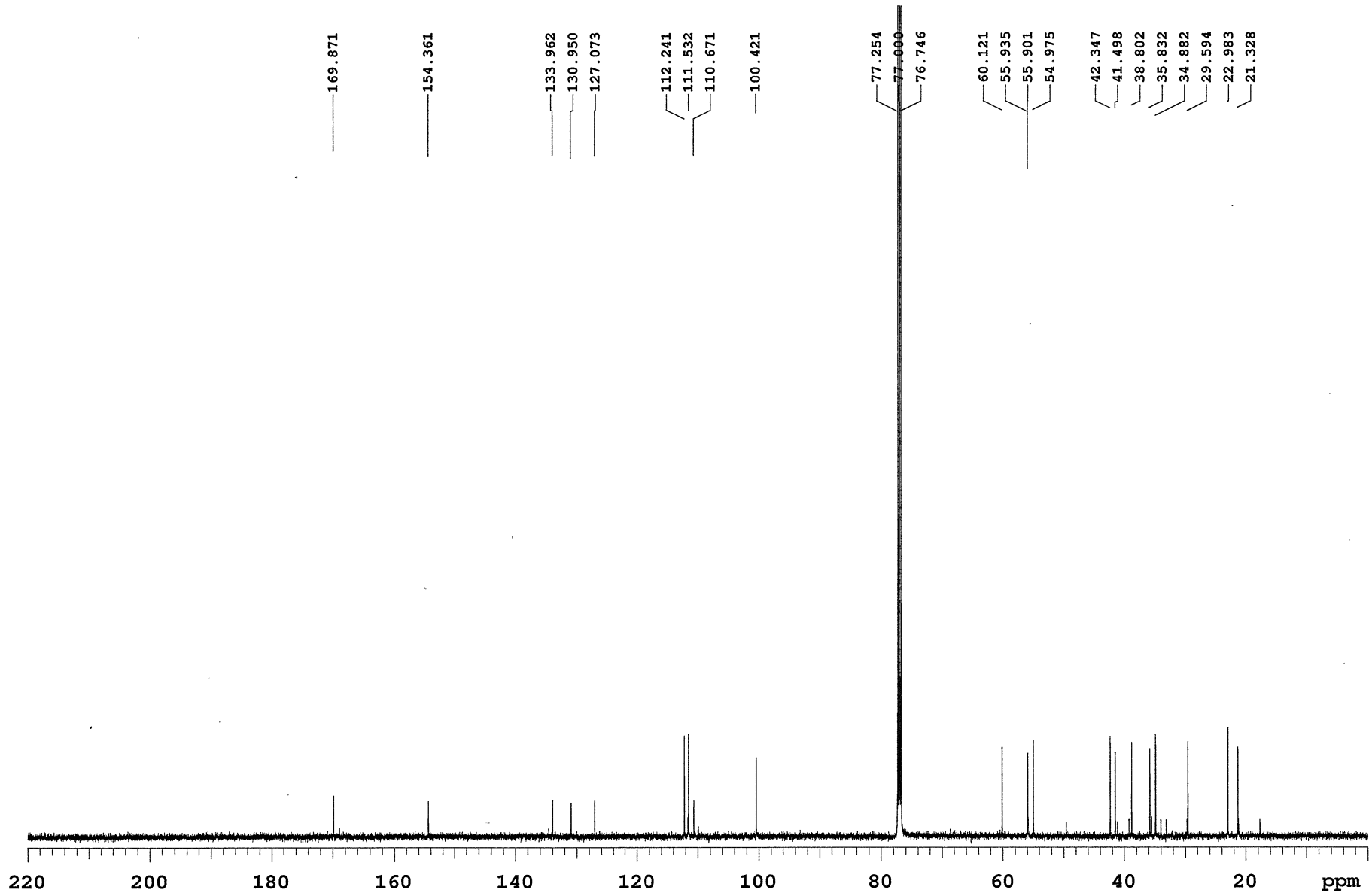
Data file /home/vnmr2/vnmrsys/data/511/RRT/RTT-252/PROTON_03.fid

Plot date 2022-12-20

1H NMR (500 MHz, CDCl3) of compound 10b

RTT-252

Sample Name **RTT-252** | Pulse sequence **CARBON** | Temperature **25** | Study owner **vnmr2**
Date collected **2022-12-18** | Solvent **cdcl3** | Spectrometer **Agilent-NMR-inova500** | Operator **vnmr2**



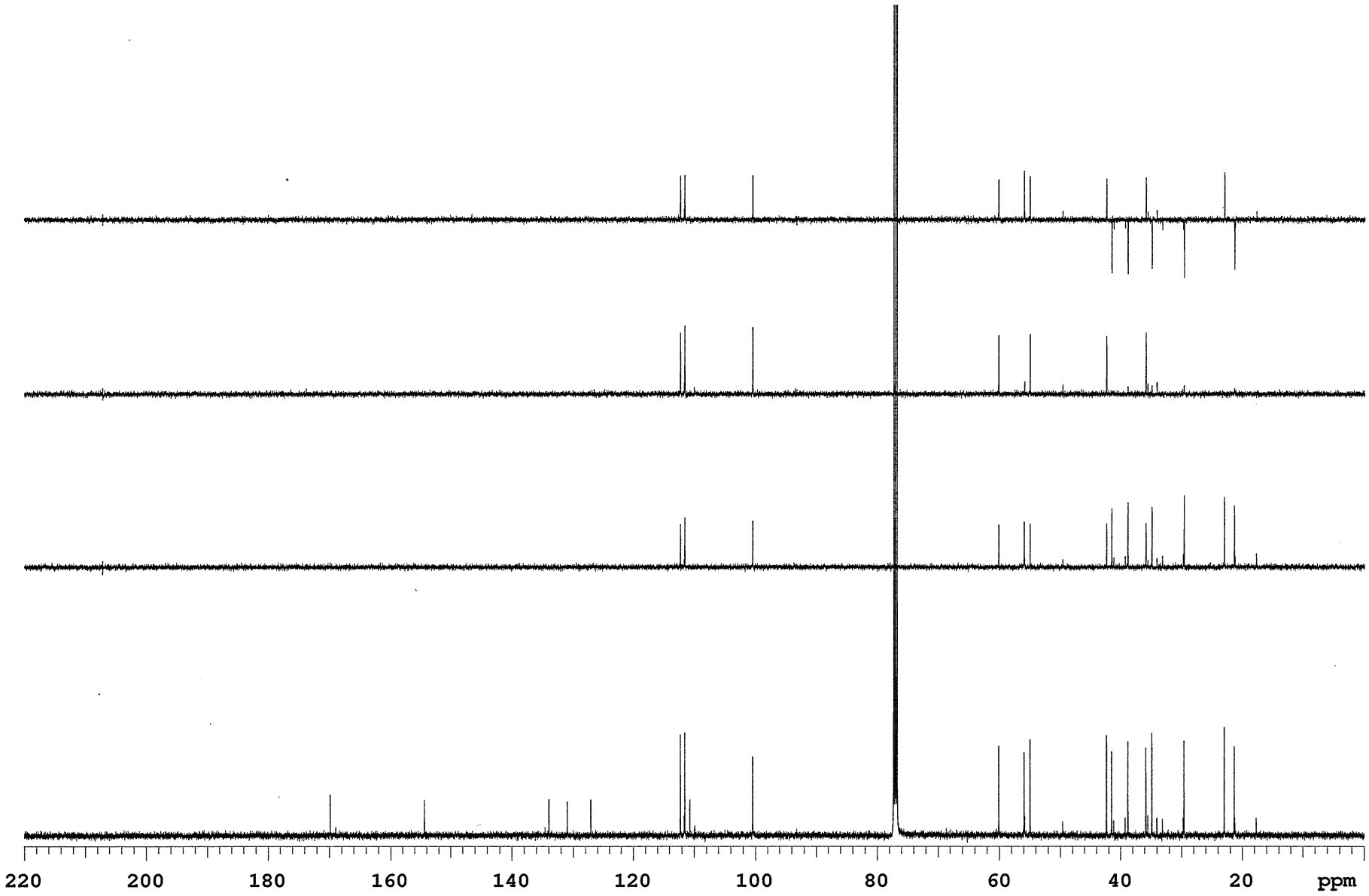
13C NMR (125 MHz, CDCl3) of compound 10b

Data file /home/vnmr2/vnmrsys/data/511/RRT/RTT-252/CARBON_02

Plot date 2022-12-19

RTT-252

Sample Name **RTT-252**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-19**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



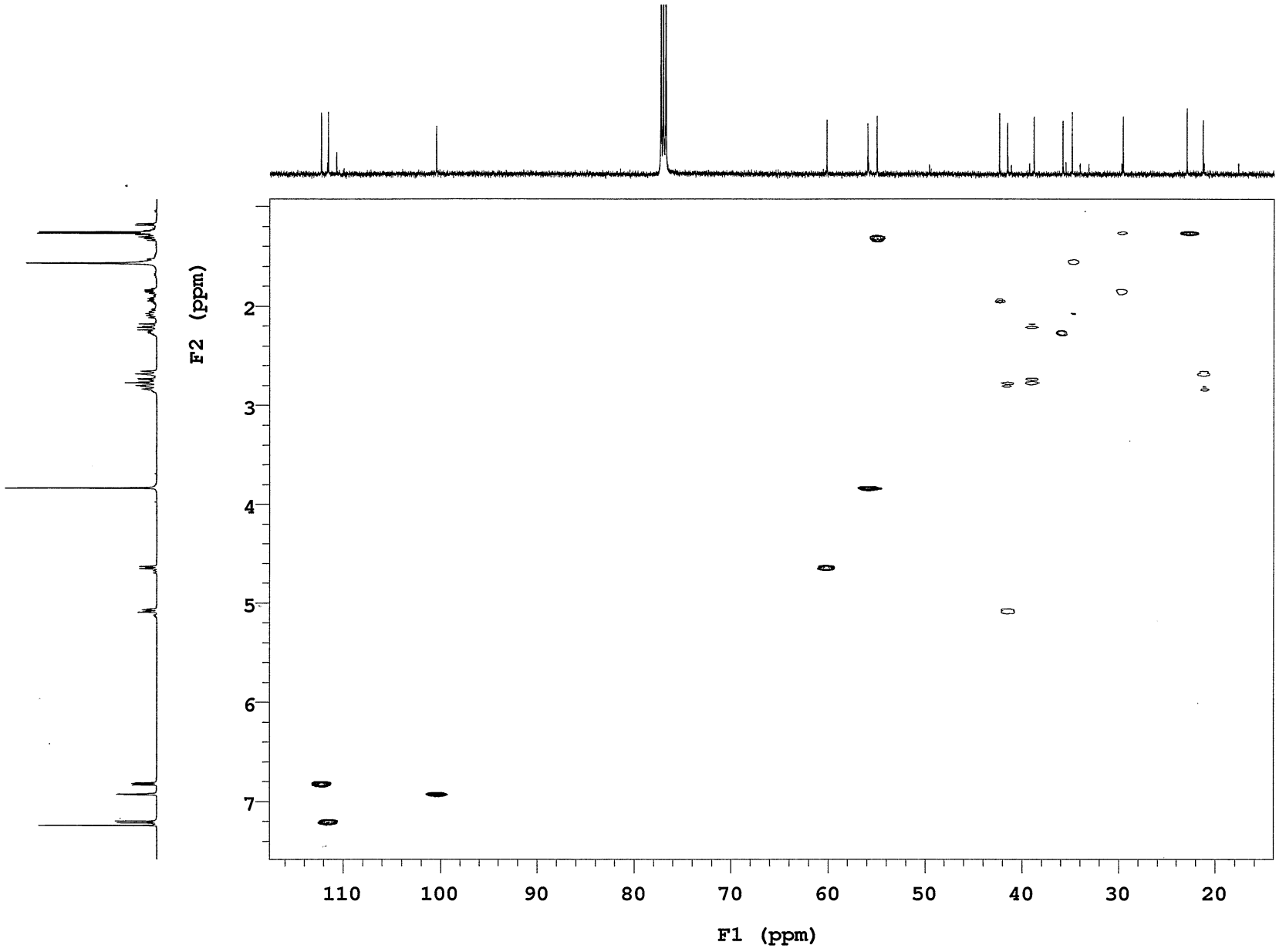
DEPT of compound 10b

Data file /home/vnmr2/vnmrsys/data/511/RRT/RTT-252/DEPT_01

Plot date 2022-12-19

RTT-252

Sample Name **RTT-252**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-19**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



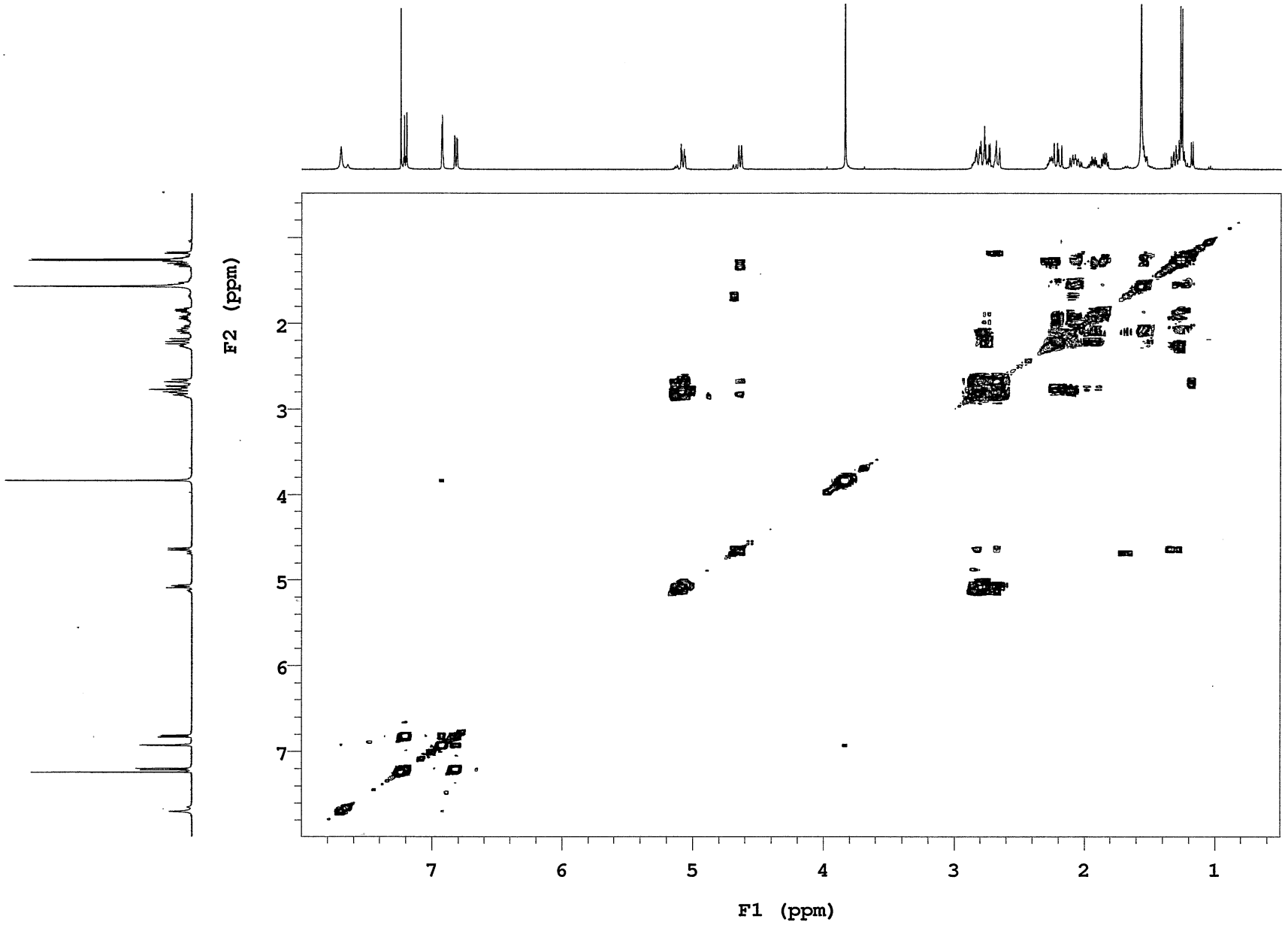
Data file /home/vnmr2/vnmrsys/data/511/RRT/RTT-252/gHSQC_01

HSQC of compound 10b

Plot date 2022-12-19

RTT-252

Sample Name	RTT-252	Pulse sequence	gCOSY	Temperature	25	Study owner	vnmr2
Date collected	2022-12-19	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



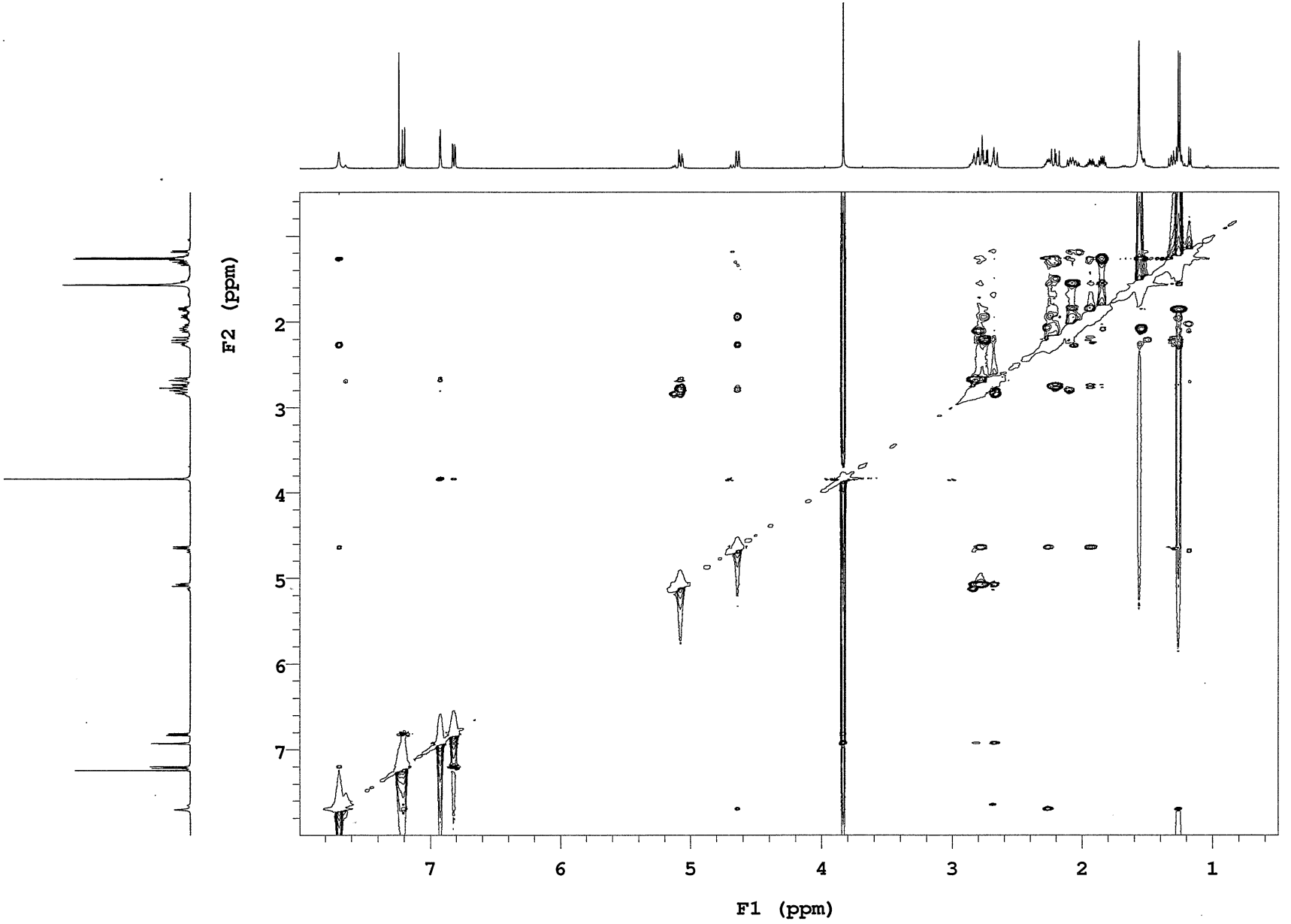
COSY of compound 10b

Data file /home/vnmr2/vnmrsys/data/511/RRT/RTT-252/gCOSY_01

Plot date 2022-12-19

RTT-252

Sample Name **RTT-252**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-12-19**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



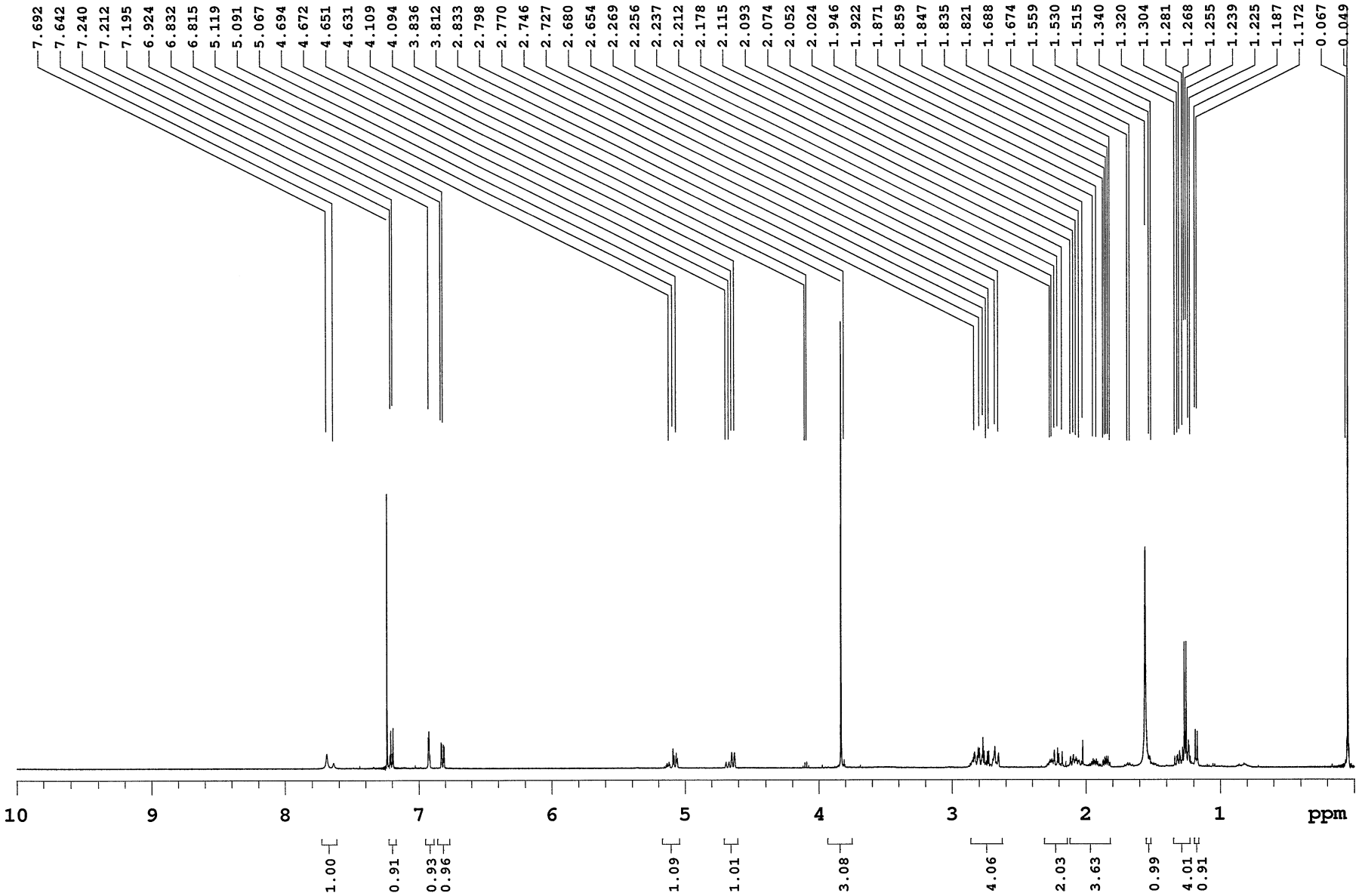
Data file /home/vnmr2/vnmrsys/data/511/RRT/RTT-252/NOESY_01

NOESY of compound 10b

Plot date 2022-12-19

RRT-04-067

Sample Name **RRT-04-067**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-27**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



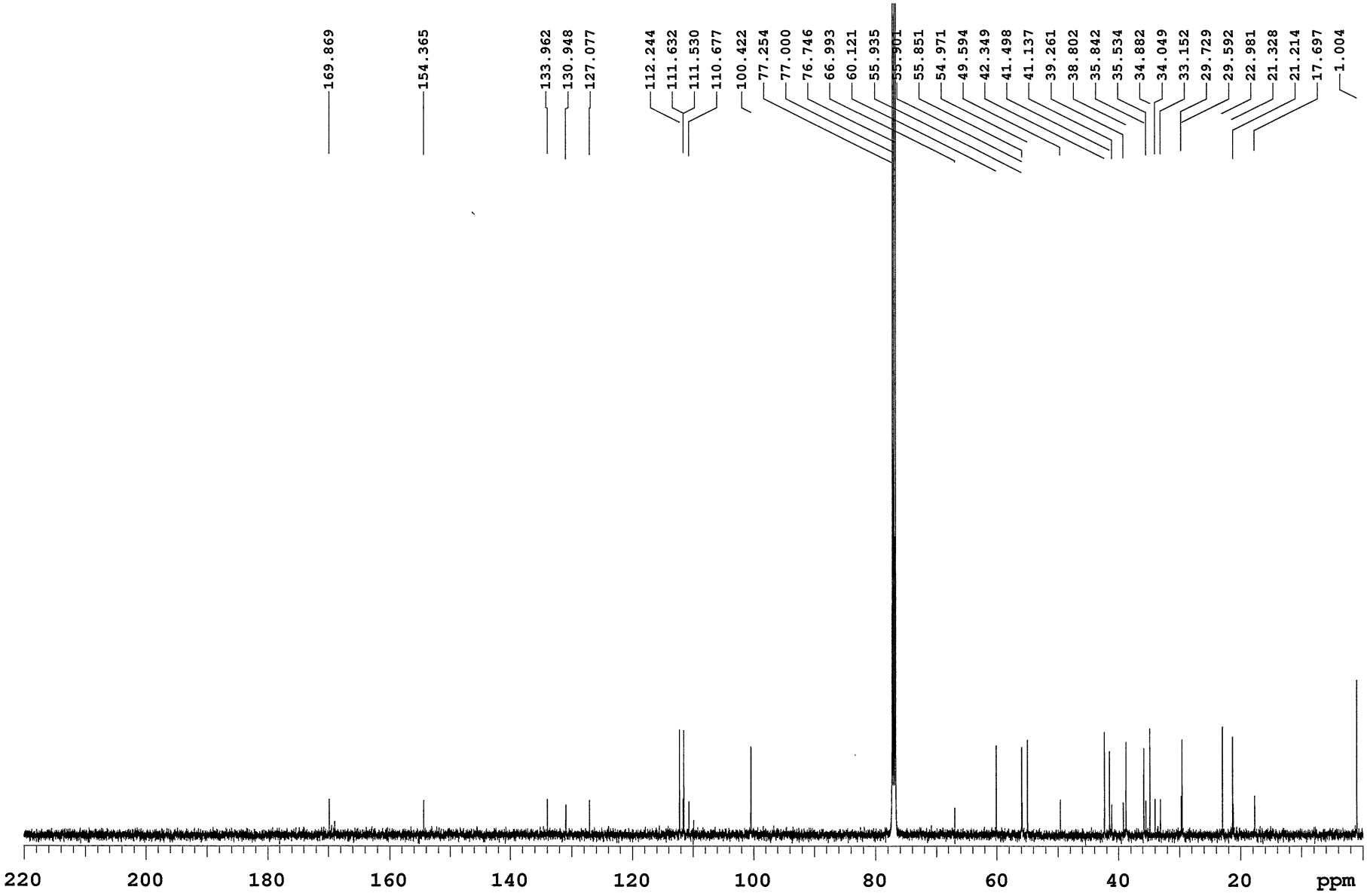
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-067/PROTON_03

Plot date 2022-11-01

1H NMR (500 MHz, CDCl3) of the mixture of **10b** and **11b**

RRT-04-067

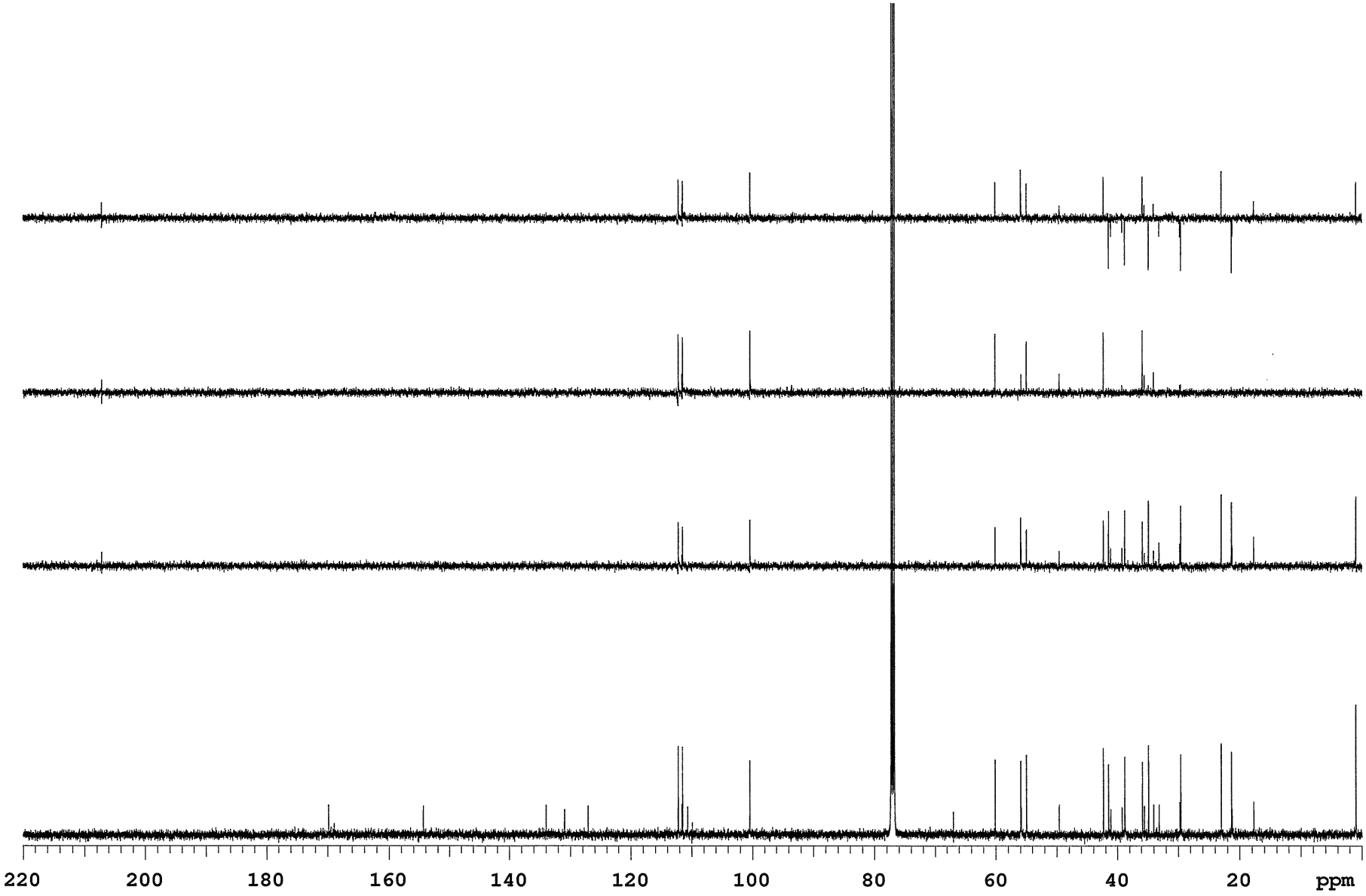
Sample Name **RRT-04-067**	Pulse sequence **CARBON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-27**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



13C NMR (500 MHz, CDCl3) of the mixture of **10b** and **11b**

RRT-04-067

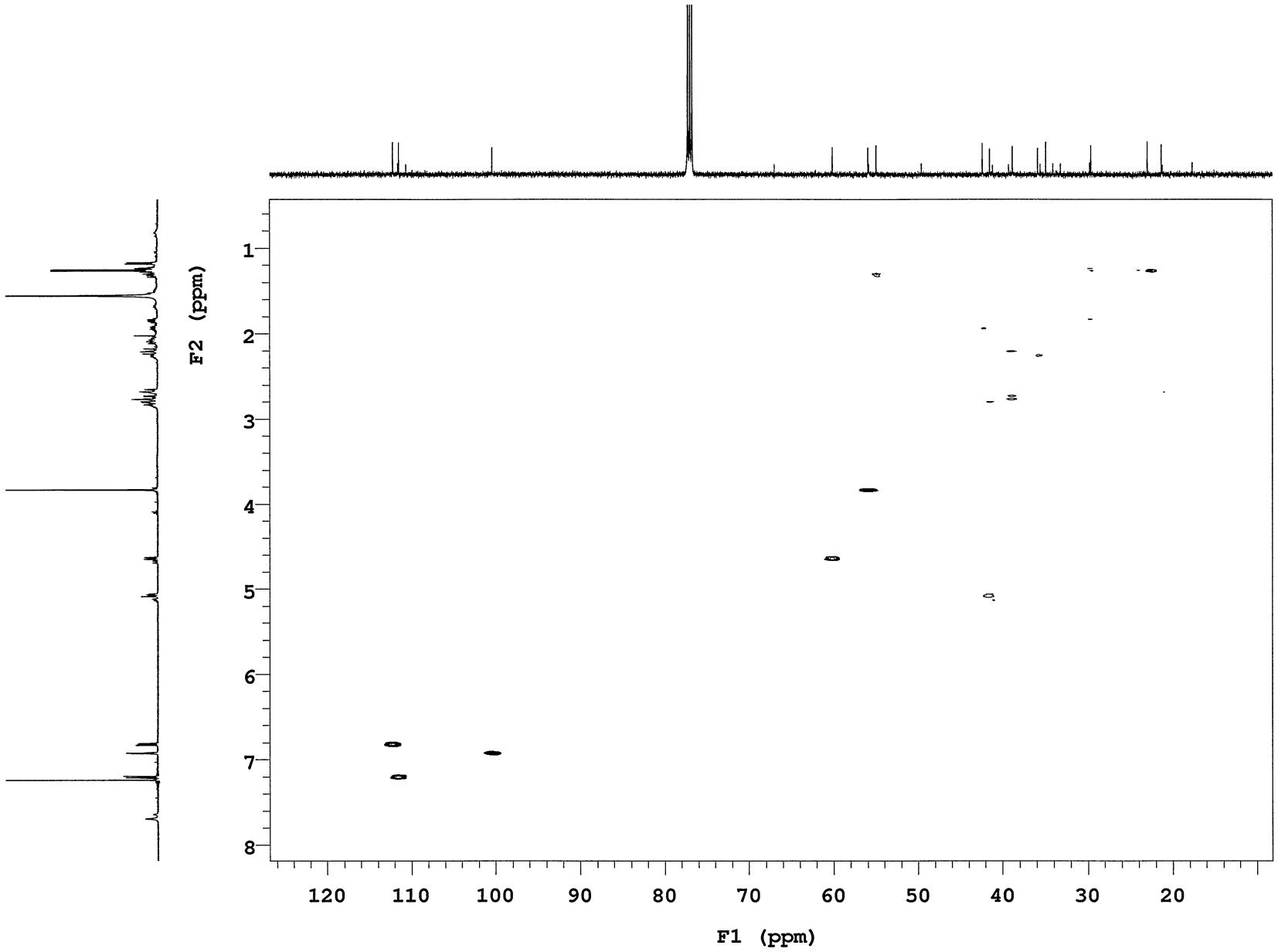
Sample Name **RRT-04-067**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-27**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of the mixture of **10b** and **11b**

RRT-04-067

Sample Name **RRT-04-067**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-28**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



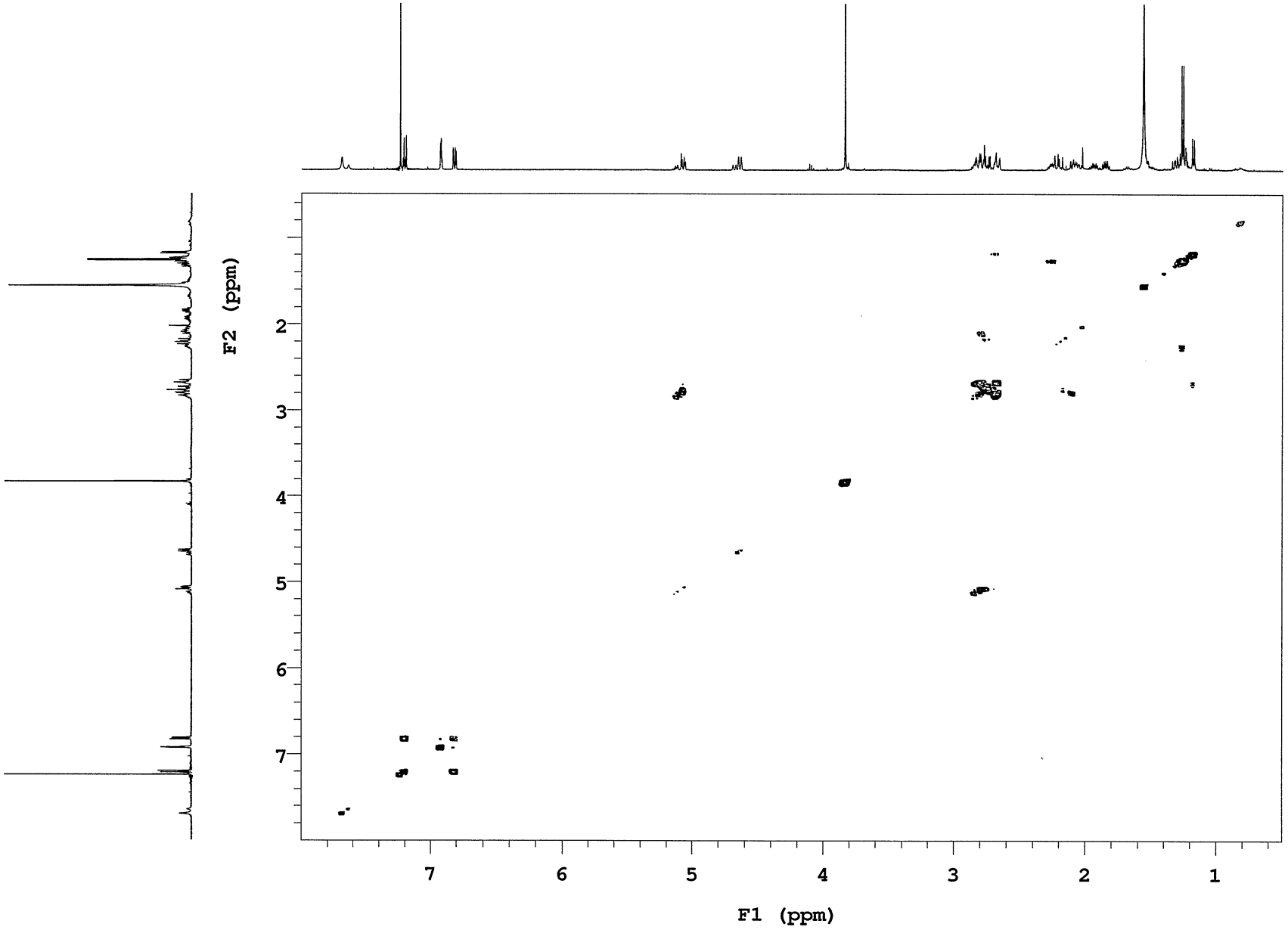
HSQC of the mixture of **10b** and **11b**

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-067/gHSQC_01

Plot date 2022-10-28

RRT-04-067

Sample Name	RRT-04-067	Pulse sequence	gCOSY	Temperature	25	Study owner	vnmr2
Date collected	2022-10-28	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



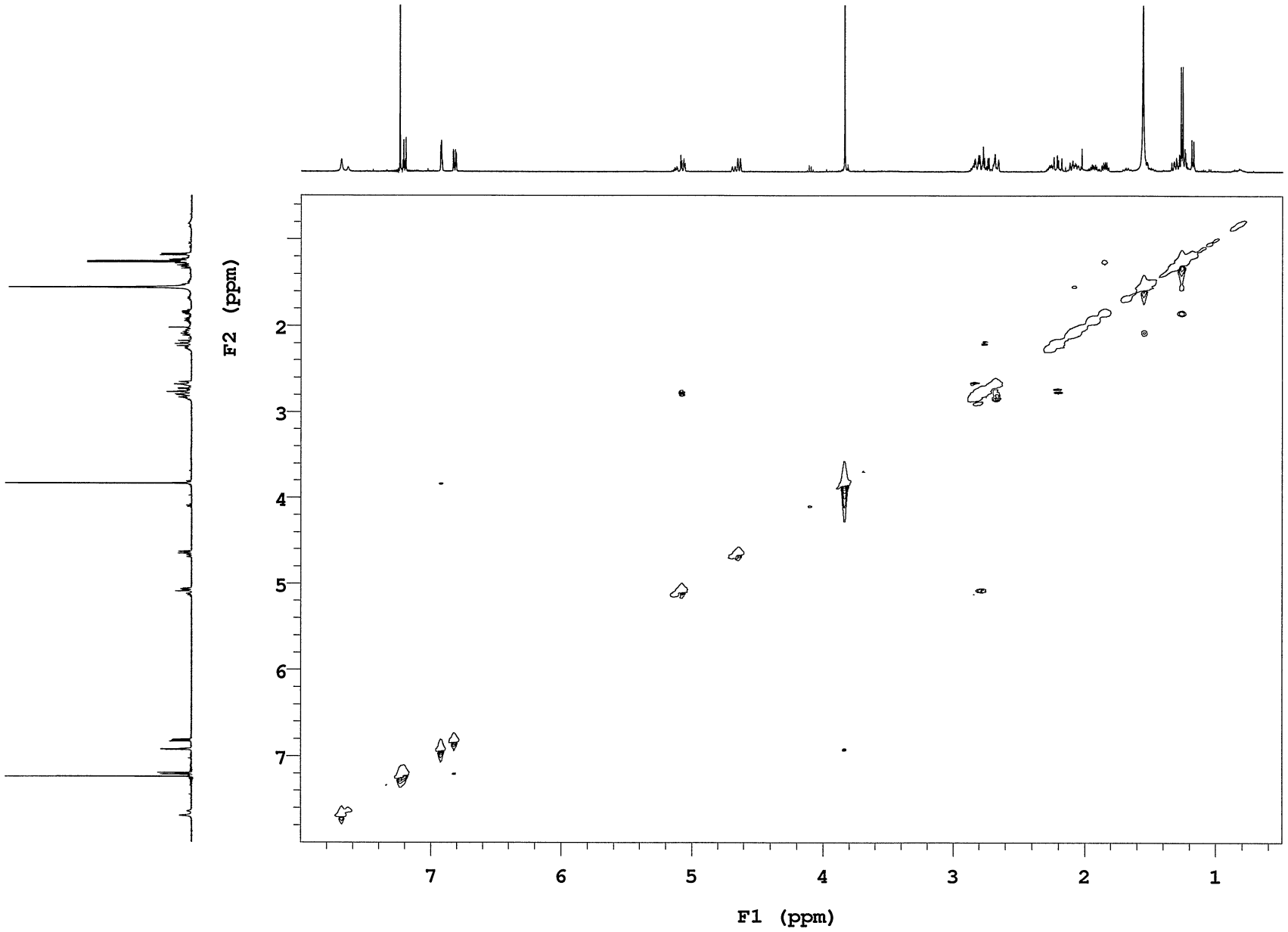
COSY of the mixture of **10b** and **11b**

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-067/gCOSY_01

Plot date 2022-10-28

RRT-04-067

Sample Name **RRT-04-067**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-28**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



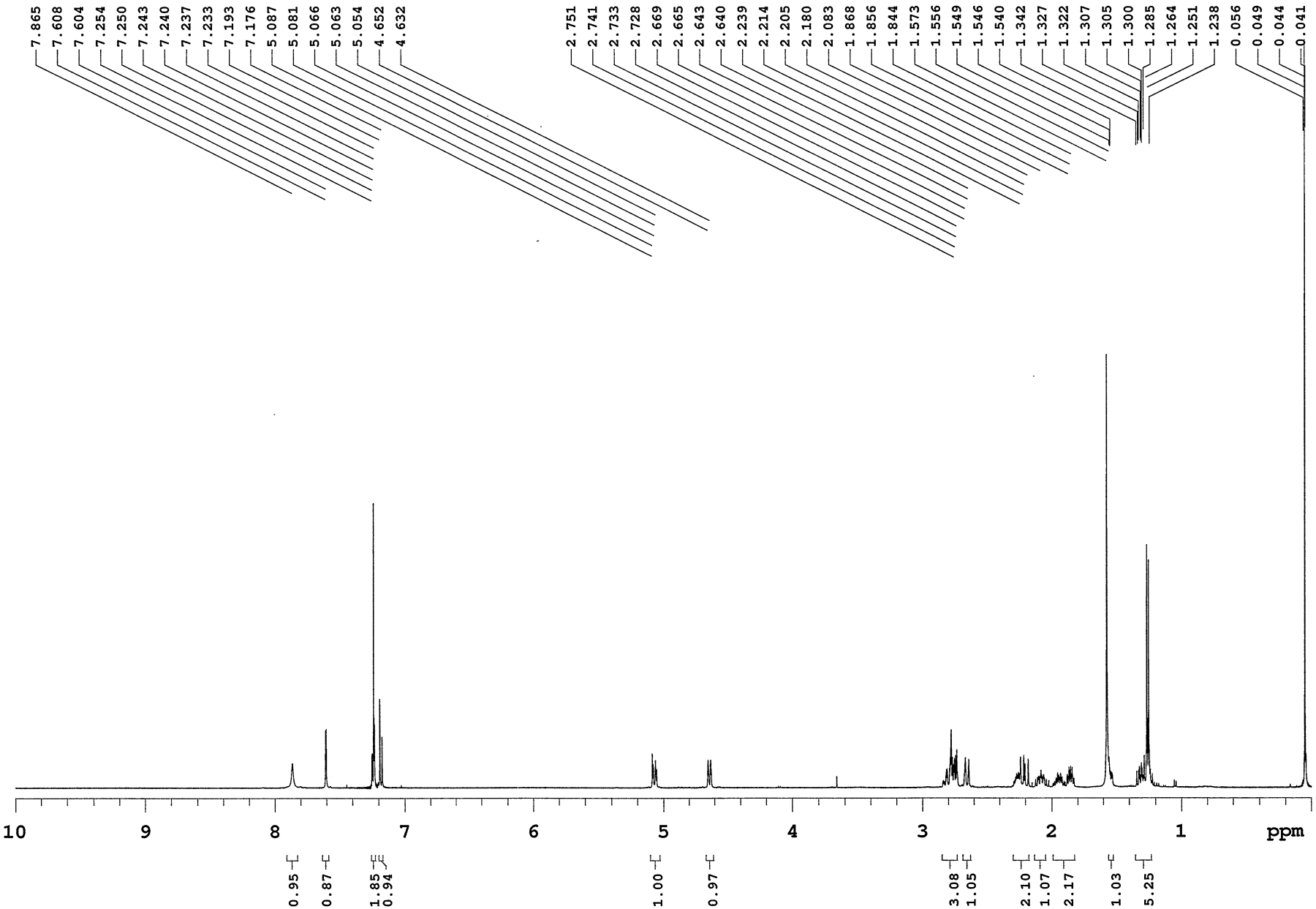
NOESY of the mixture of **10b** and **11b**

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-067/NOESY_01

Plot date 2022-10-28

RRT-04-075-F-II

Sample Name	RRT-04-075-F-II	Pulse sequence	PROTON	Temperature	25	Study owner	vnmr2
Date collected	2022-11-11	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



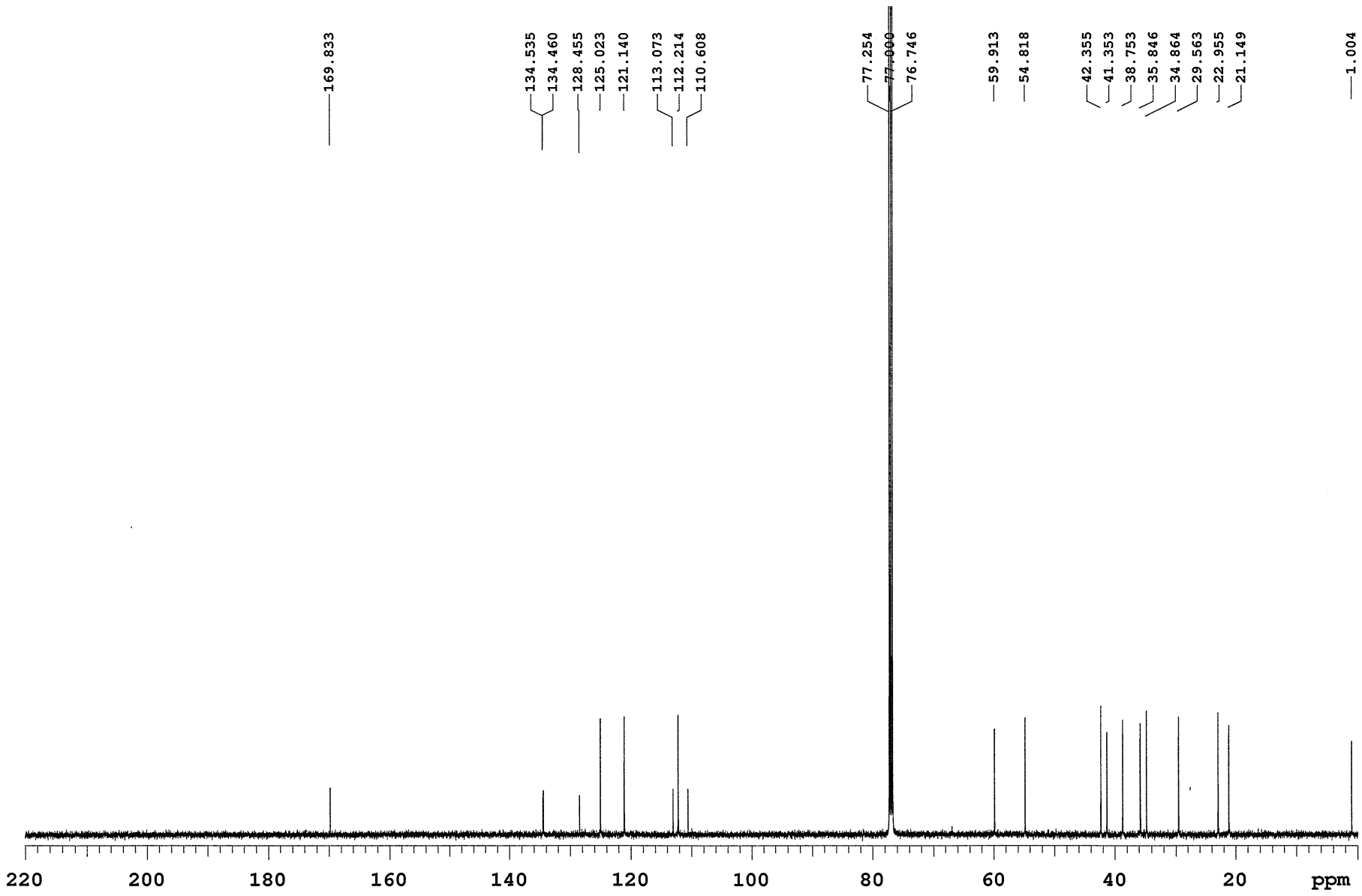
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-075-F-II/PROTON_03

Plot date 2022-11-12

1H NMR (500 MHz, CDCl3) of compound 10c

RRT-04-075-F-II

Sample Name **RRT-04-075-F-II**	Pulse sequence **CARBON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-11-11**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



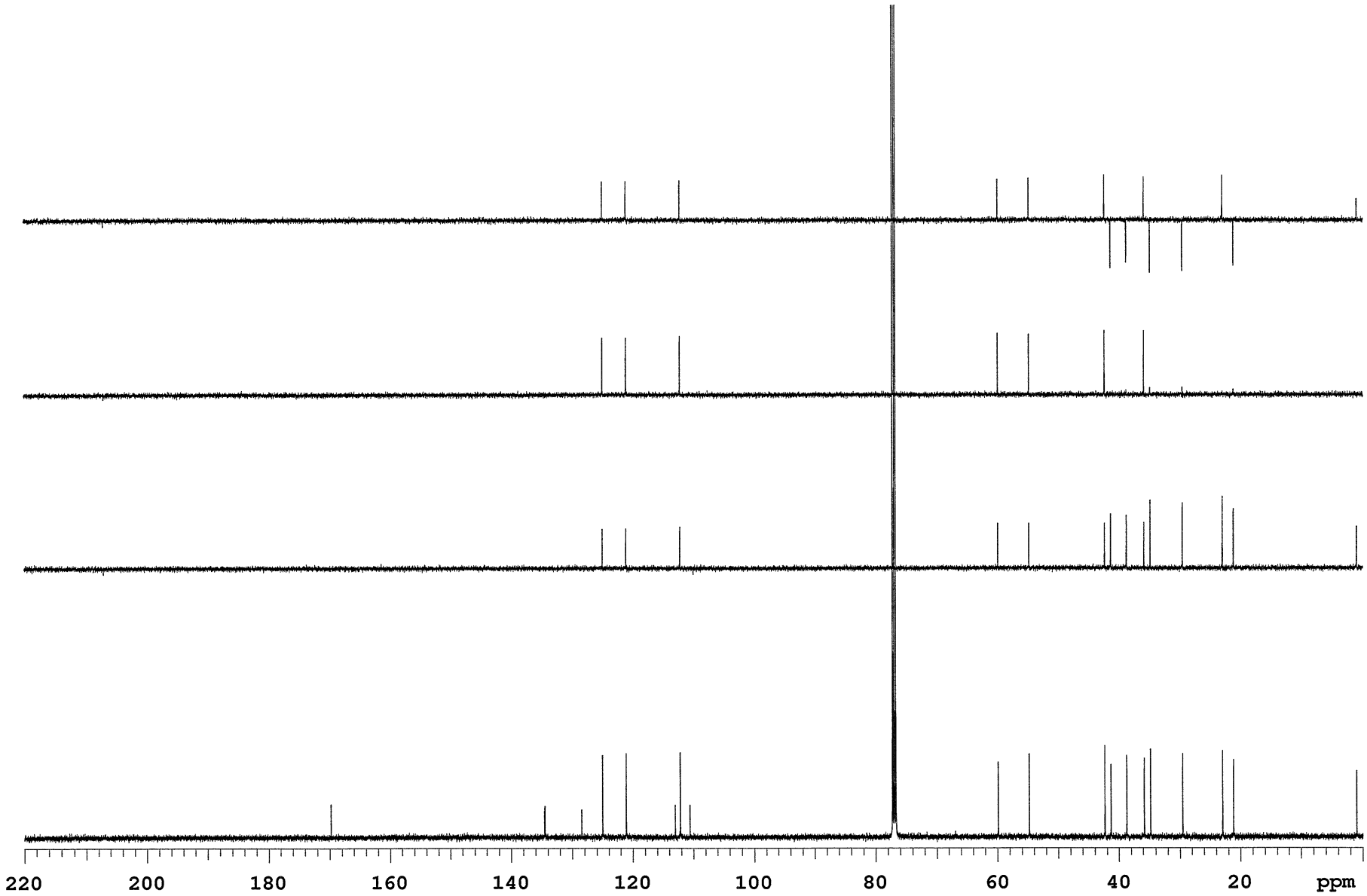
13C NMR (125 MHz, CDCl3) of compound 10c

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-075-F-II/CARBON_02

Plot date 2022-11-12

RRT-04-075-F-II

Sample Name	RRT-04-075-F-II	Pulse sequence	DEPT	Temperature	25	Study owner	vnmr2
Date collected	2022-11-11	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



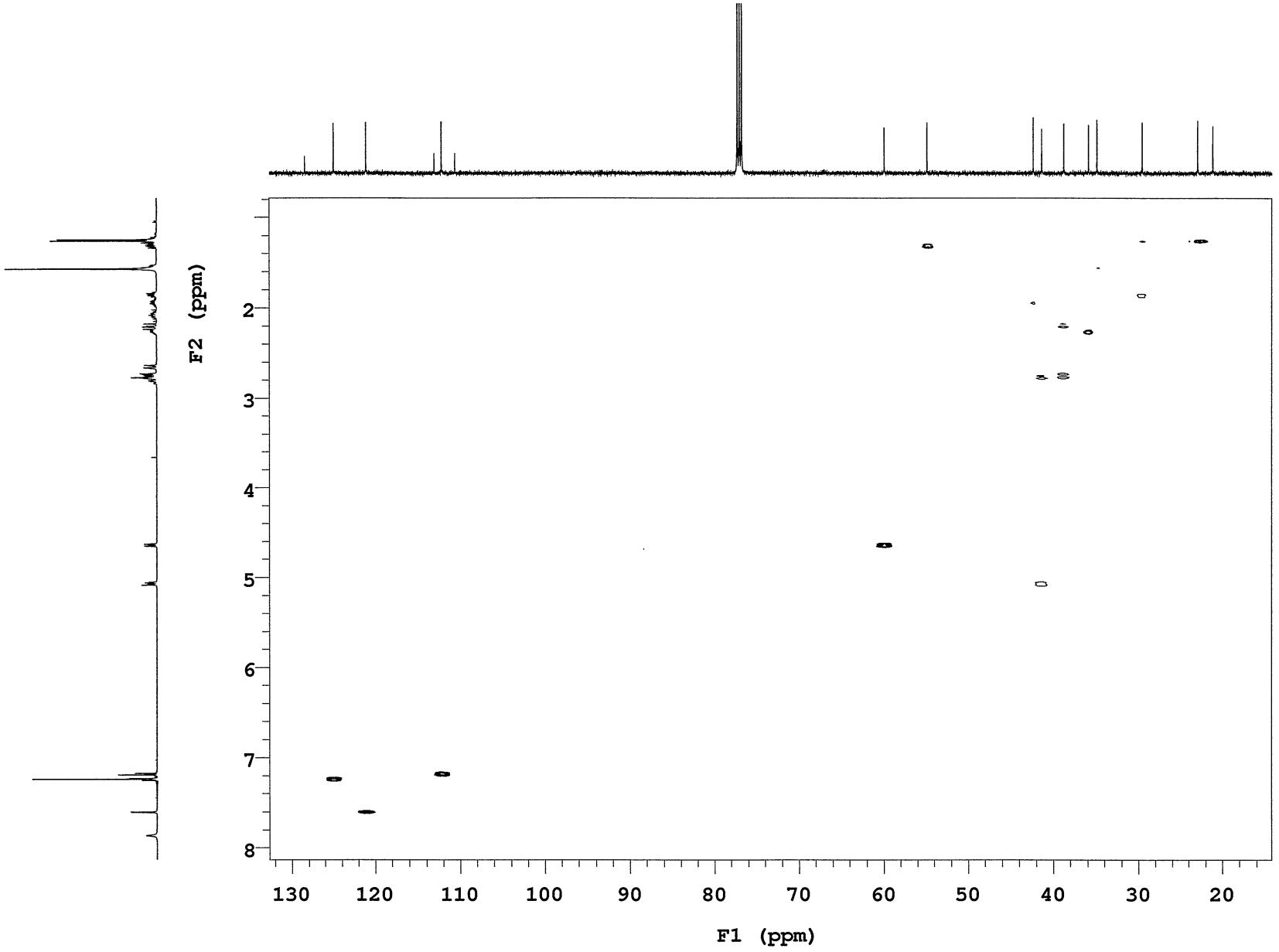
DEPT of compound 10c

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-075-F-II/DEPT_01

Plot date 2022-11-12

RRT-04-075-F-II

Sample Name **RRT-04-075-F-II**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-11-12**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



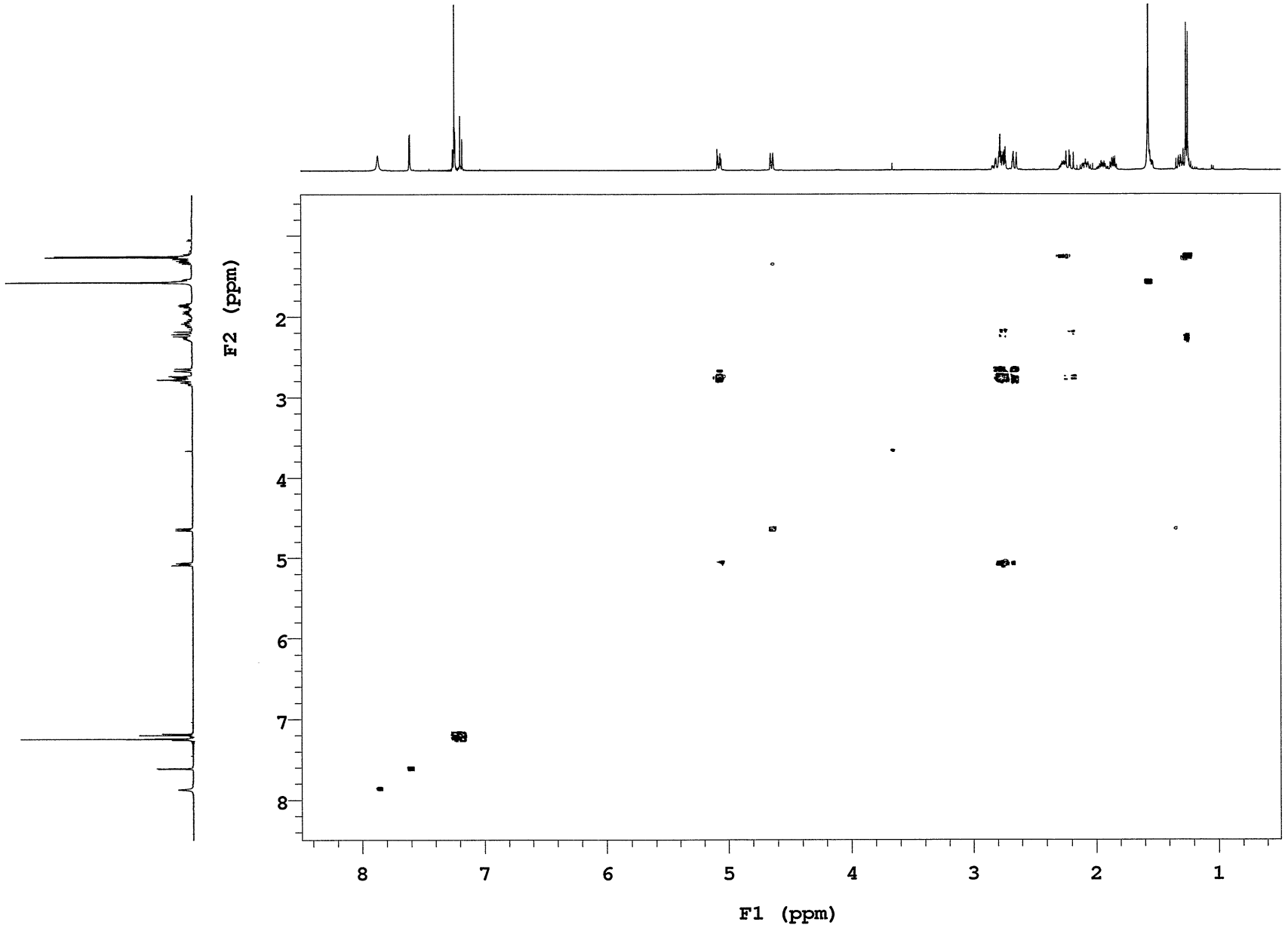
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-075-F-II/gHSQC_01

HSQC of compound 10c

Plot date 2022-11-12

RRT-04-075-F-II

Sample Name	RRT-04-075-F-II	Pulse sequence	gCOSY	Temperature	25	Study owner	vnmr2
Date collected	2022-11-12	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



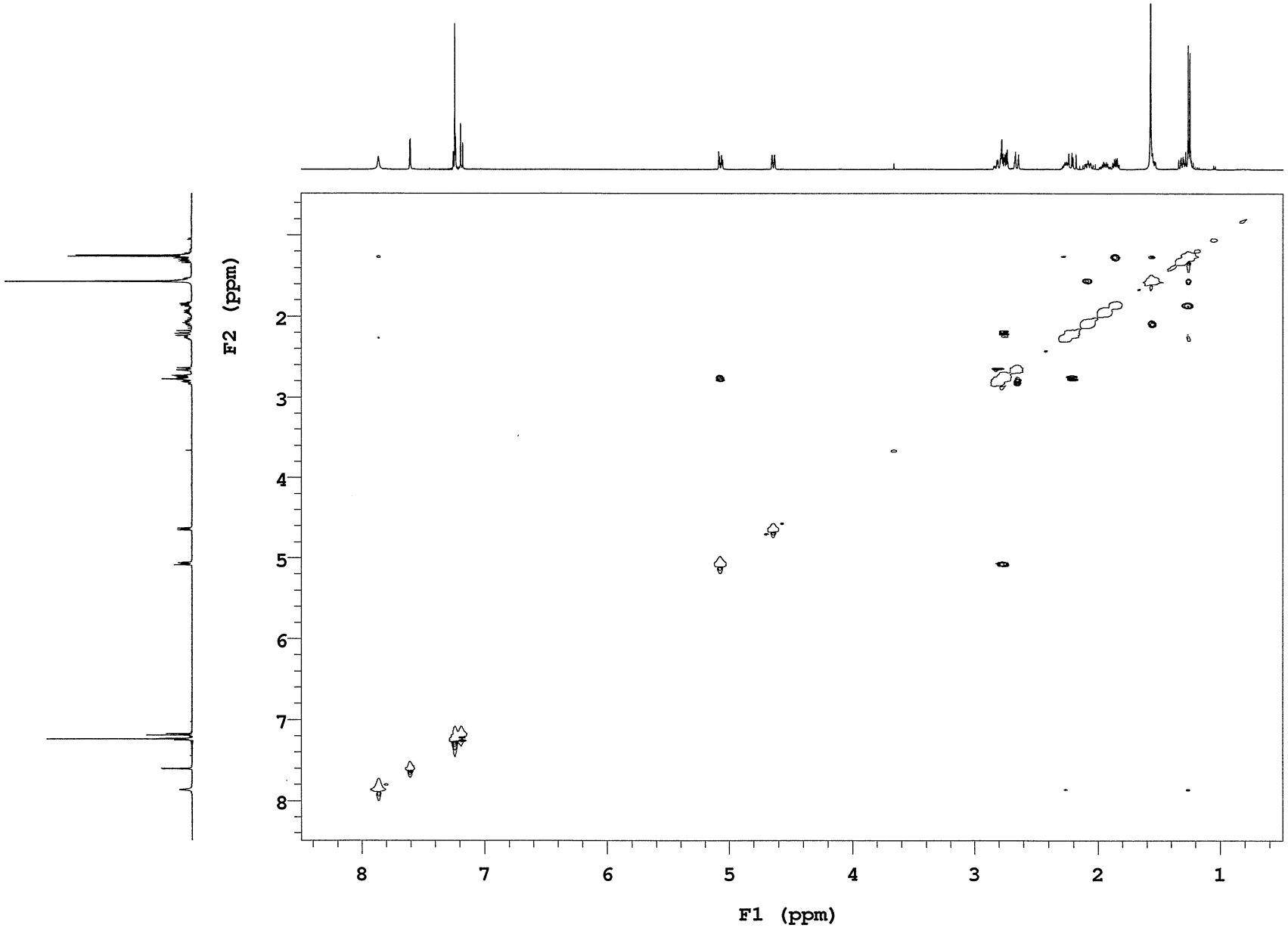
COSY of compound 10c

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-075-F-II/gCOSY_01

Plot date 2022-11-12

RRT-04-075-F-II

Sample Name	**RRT-04-075-F-II**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-11-12**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



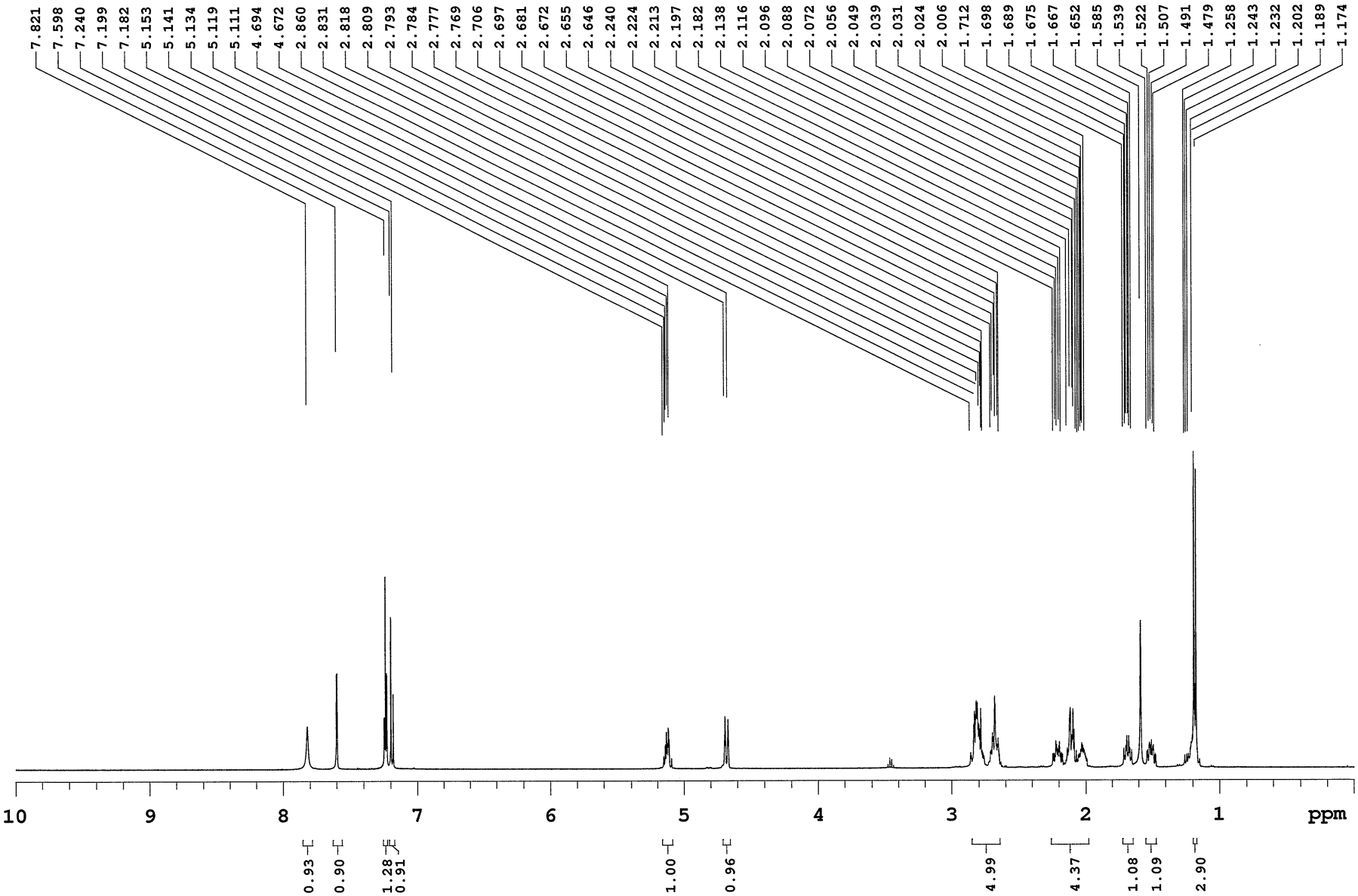
NOESY of compound 10c

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-075-F-II/NOESY_01

Plot date 2022-11-12

RRT-04-089-F-I

Sample Name **RRT-04-089-F-I**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-07**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



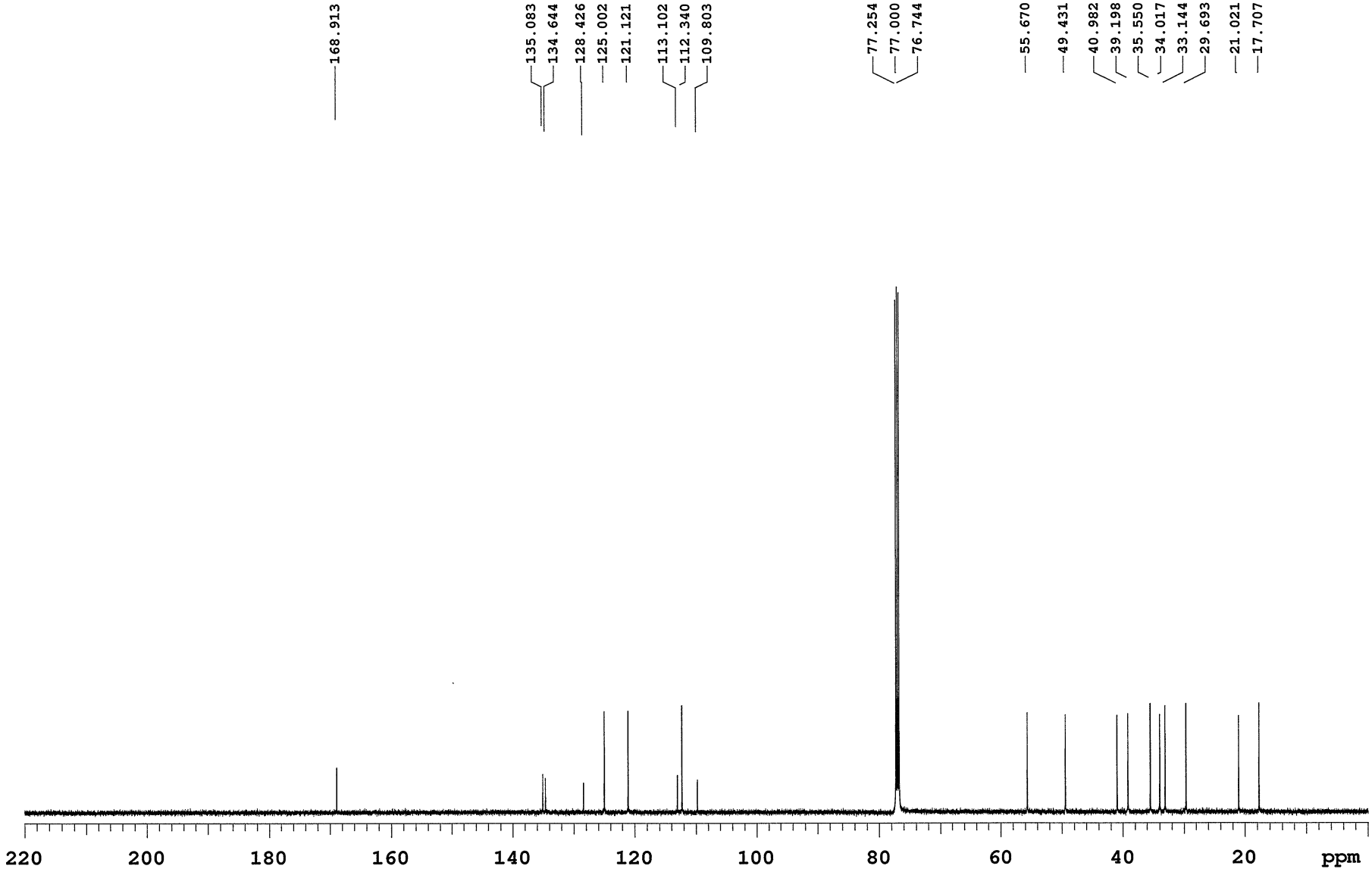
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-089-F-I/PROTON_03

1H NMR (500 MHz, CDCl3) of compound 11c

Plot date 2023-01-09

RRT-04-089-F-I

Sample Name **RRT-04-089-F-I**	Pulse sequence **CARBON**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-07**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



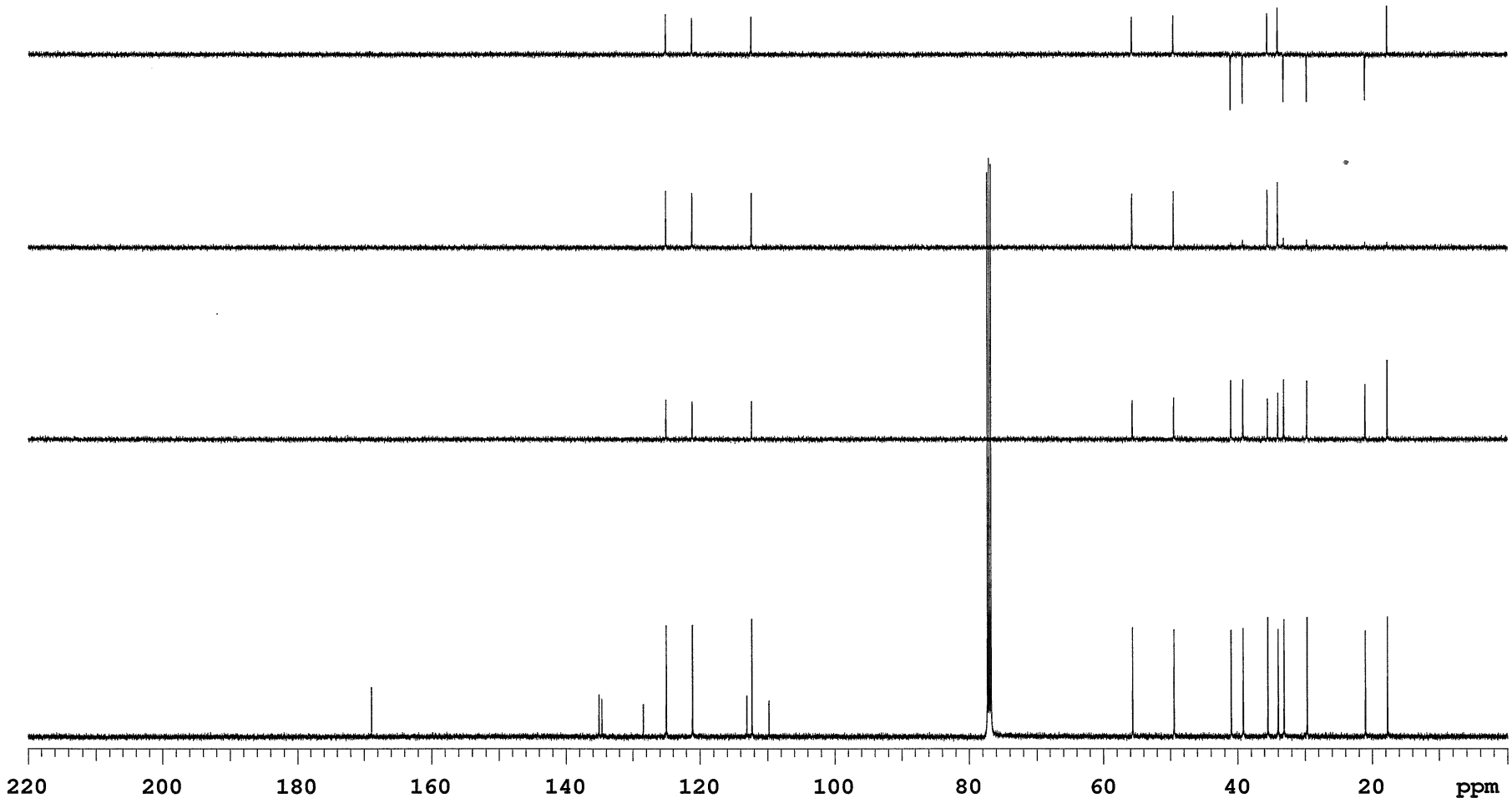
13C NMR (125 MHz, CDCl3) of compound 11c

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-089-F-I/CARBON_02

Plot date 2023-01-09

RRT-04-089-F-I

Sample Name **RRT-04-089-F-I**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-07**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



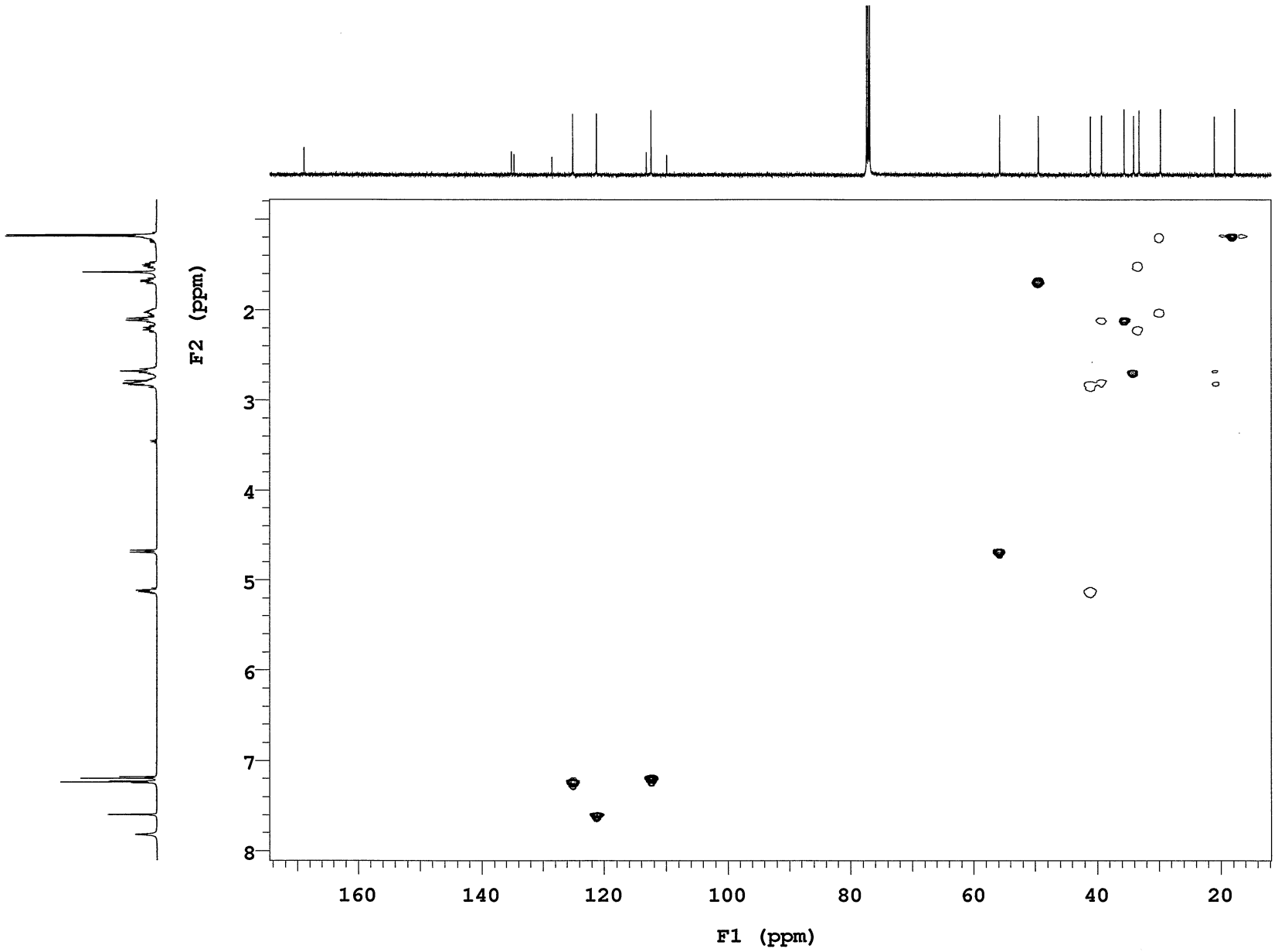
DEPT of compound 11c

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-089-F-I/DEPT_01

Plot date 2023-01-09

RRT-04-089-F-I

Sample Name **RRT-04-089-F-I**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-08**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



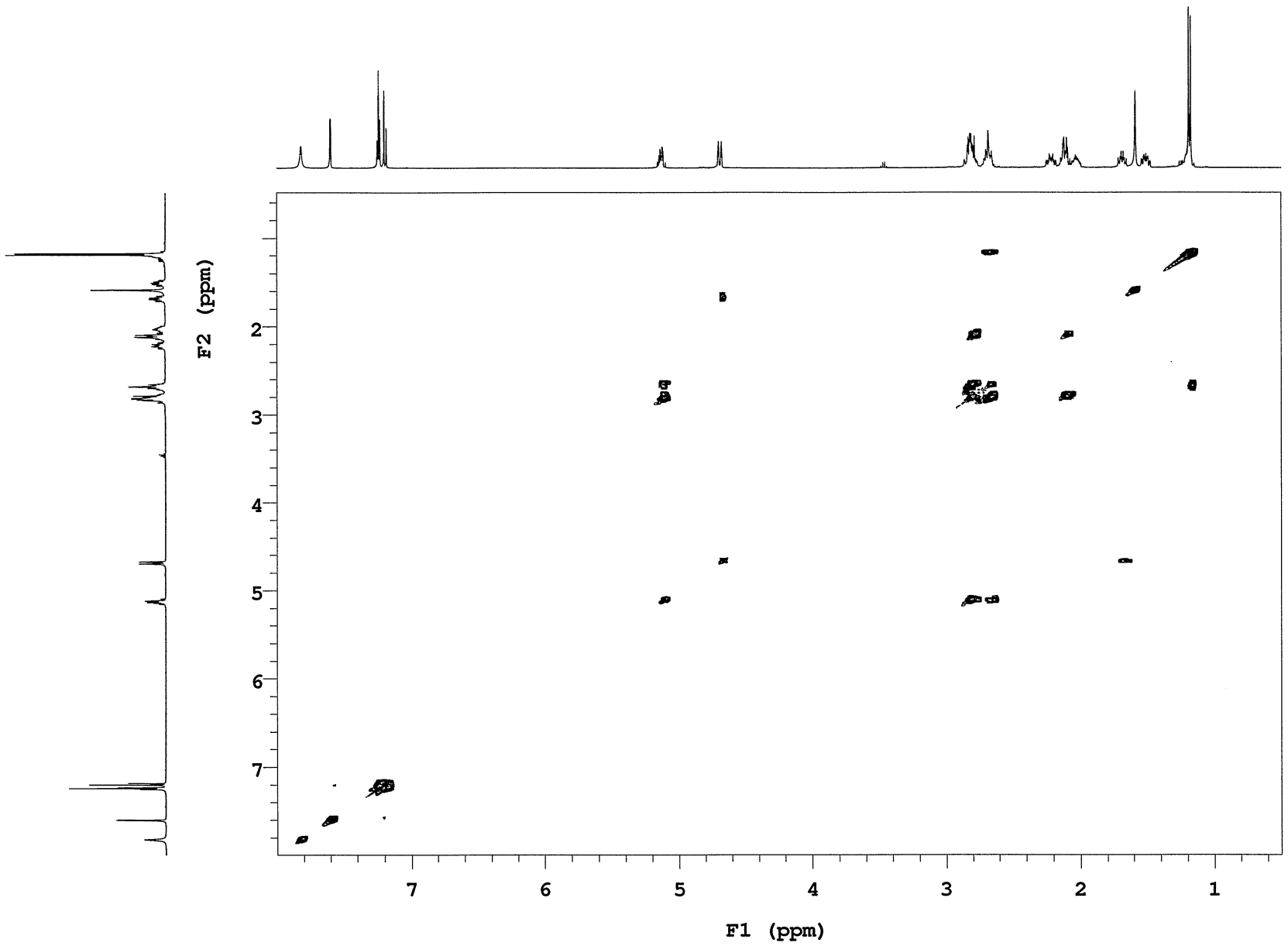
HSQC of compound 11c

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-089-F-I/gHSQC_01

Plot date 2023-01-09

RRT-04-089-F-I

Sample Name	**RRT-04-089-F-I**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2023-01-08**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



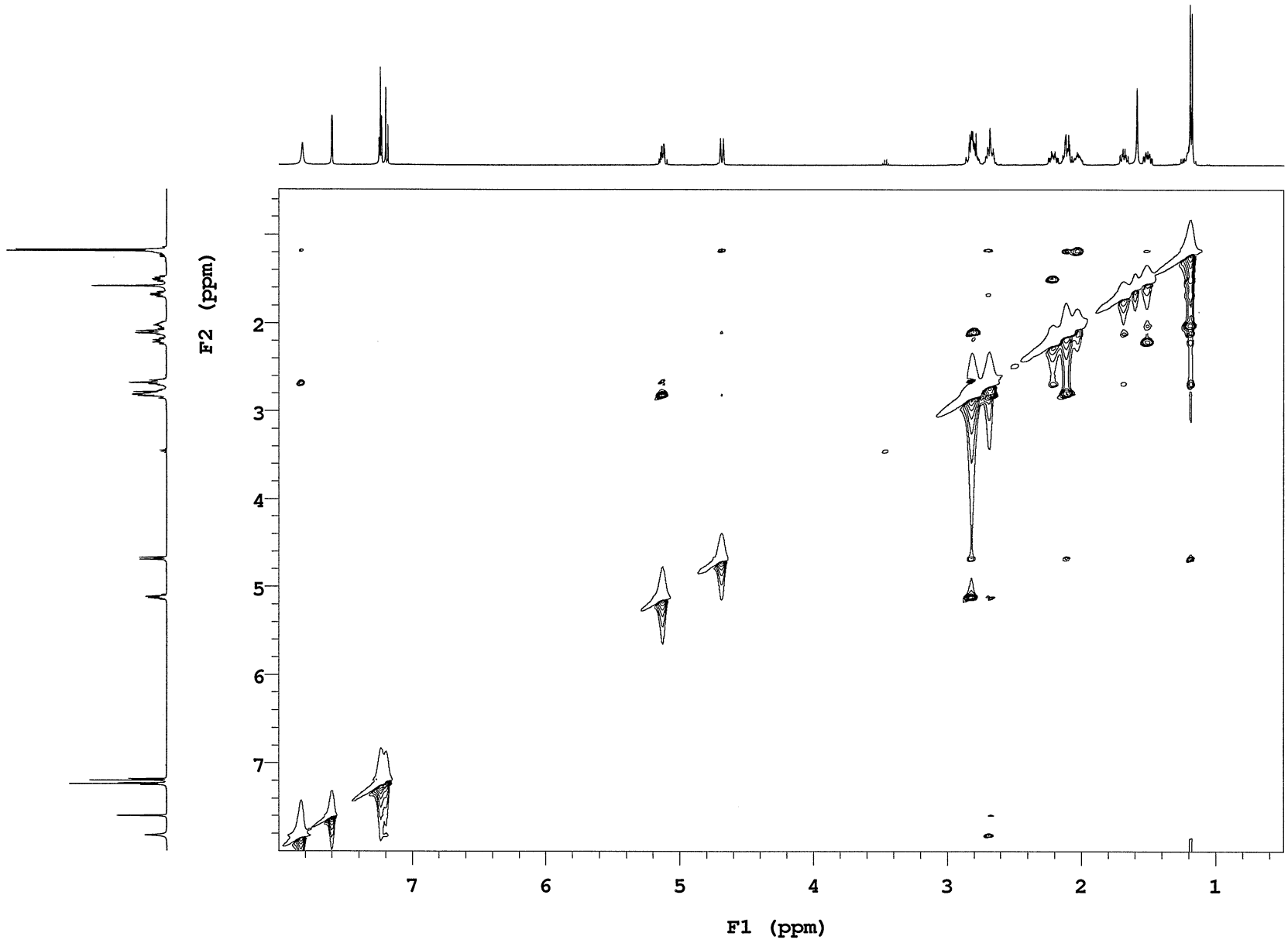
COSY of compound 11c

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-089-F-I/gCOSY_01

Plot date 2023-01-09

RRT-04-089-F-I

Sample Name **RRT-04-089-F-I**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-08**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



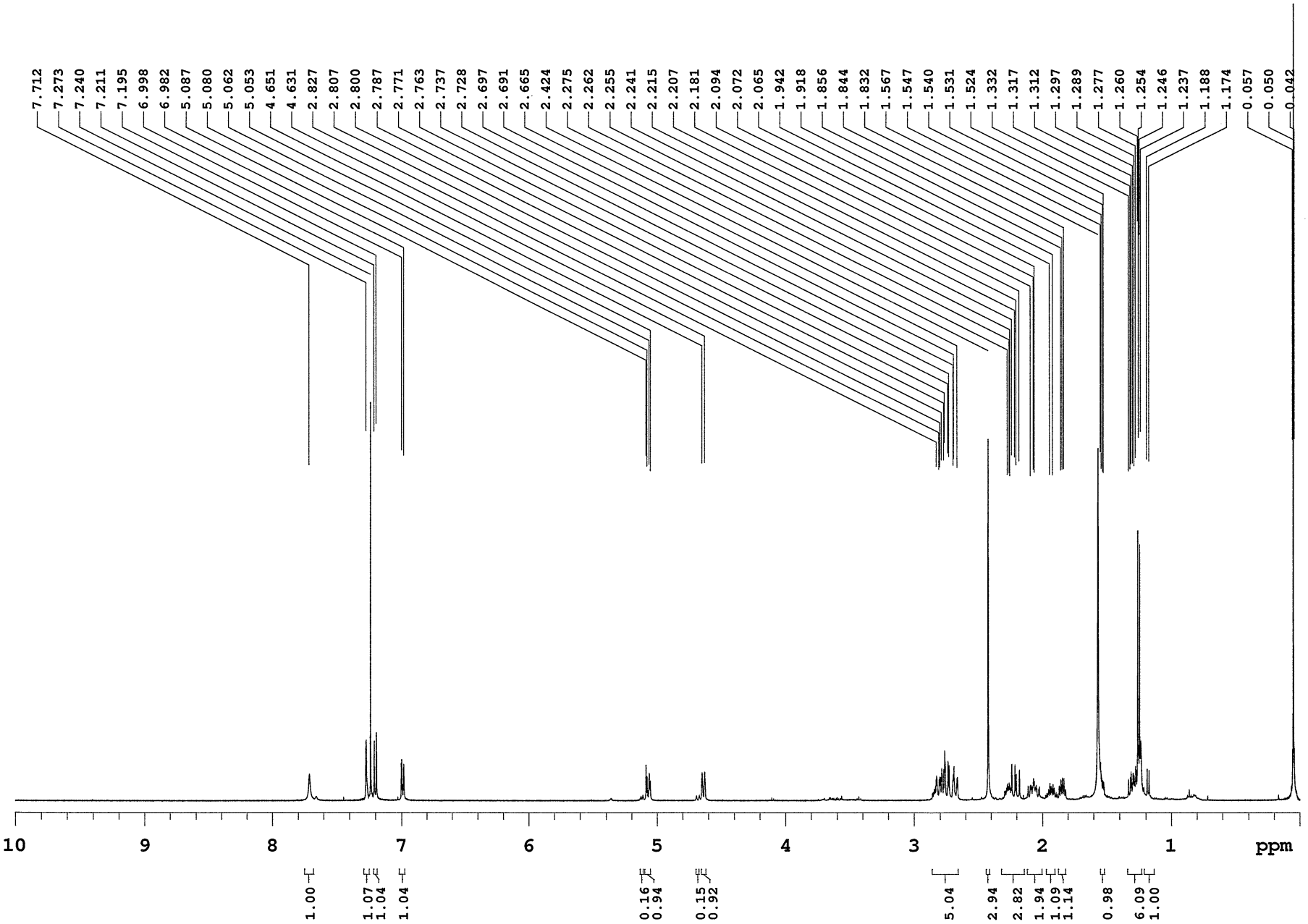
NOESY of compound 11c

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-089-F-I/NOESY_01

Plot date 2023-01-09

RRT-04-069

Sample Name	RRT-04-069	Pulse sequence	PROTON	Temperature	25	Study owner	vnmr2
Date collected	2022-10-28	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



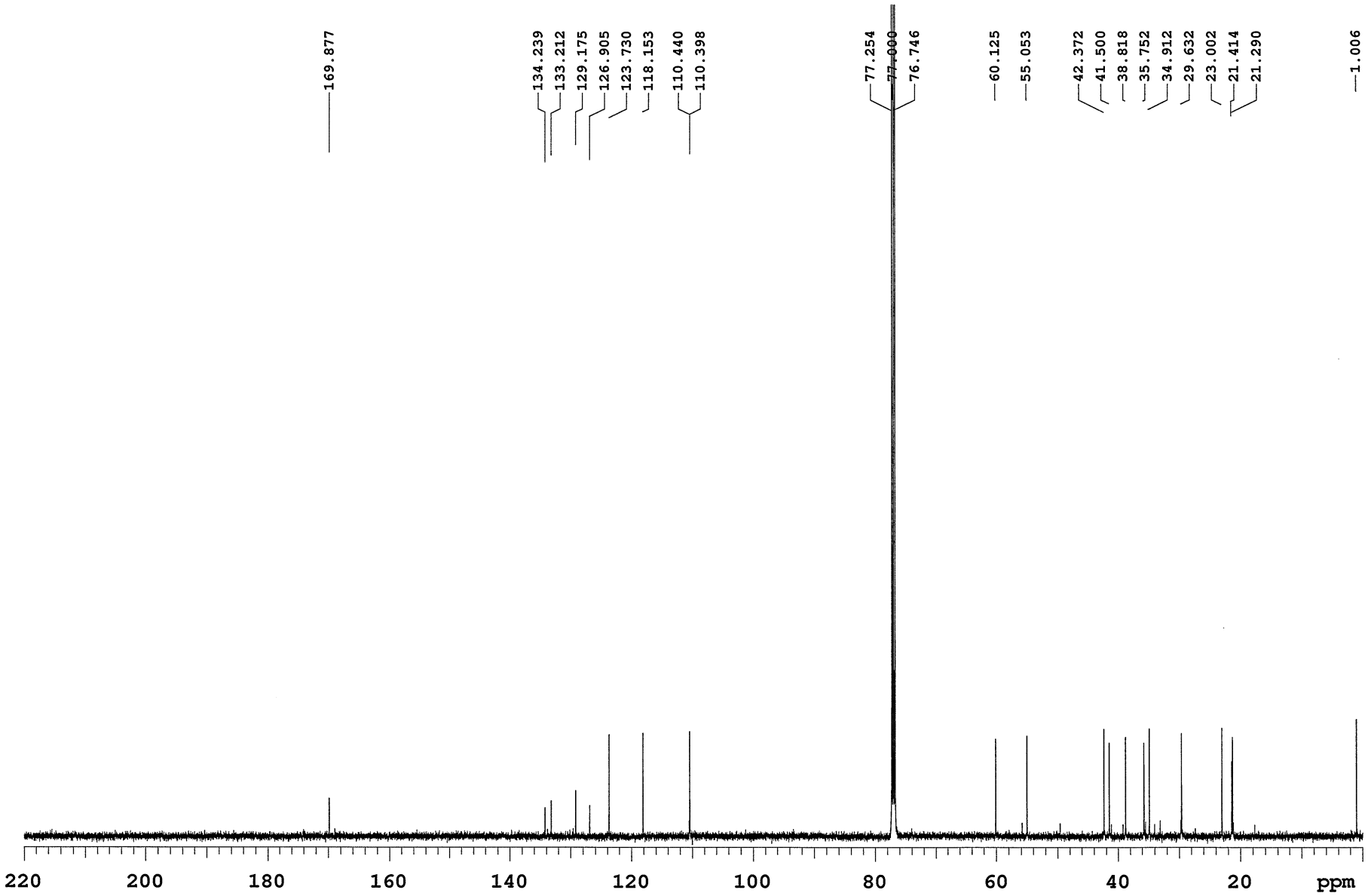
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-069/PROTON_03

Plot date 2022-11-05

1H NMR (500 MHz, CDCl3) of compound 10d

RRT-04-069

Sample Name **RRT-04-069** | Pulse sequence **CARBON** | Temperature **25** | Study owner **vnmr2**
Date collected **2022-10-28** | Solvent **cdcl3** | Spectrometer **Agilent-NMR-inova500** | Operator **vnmr2**



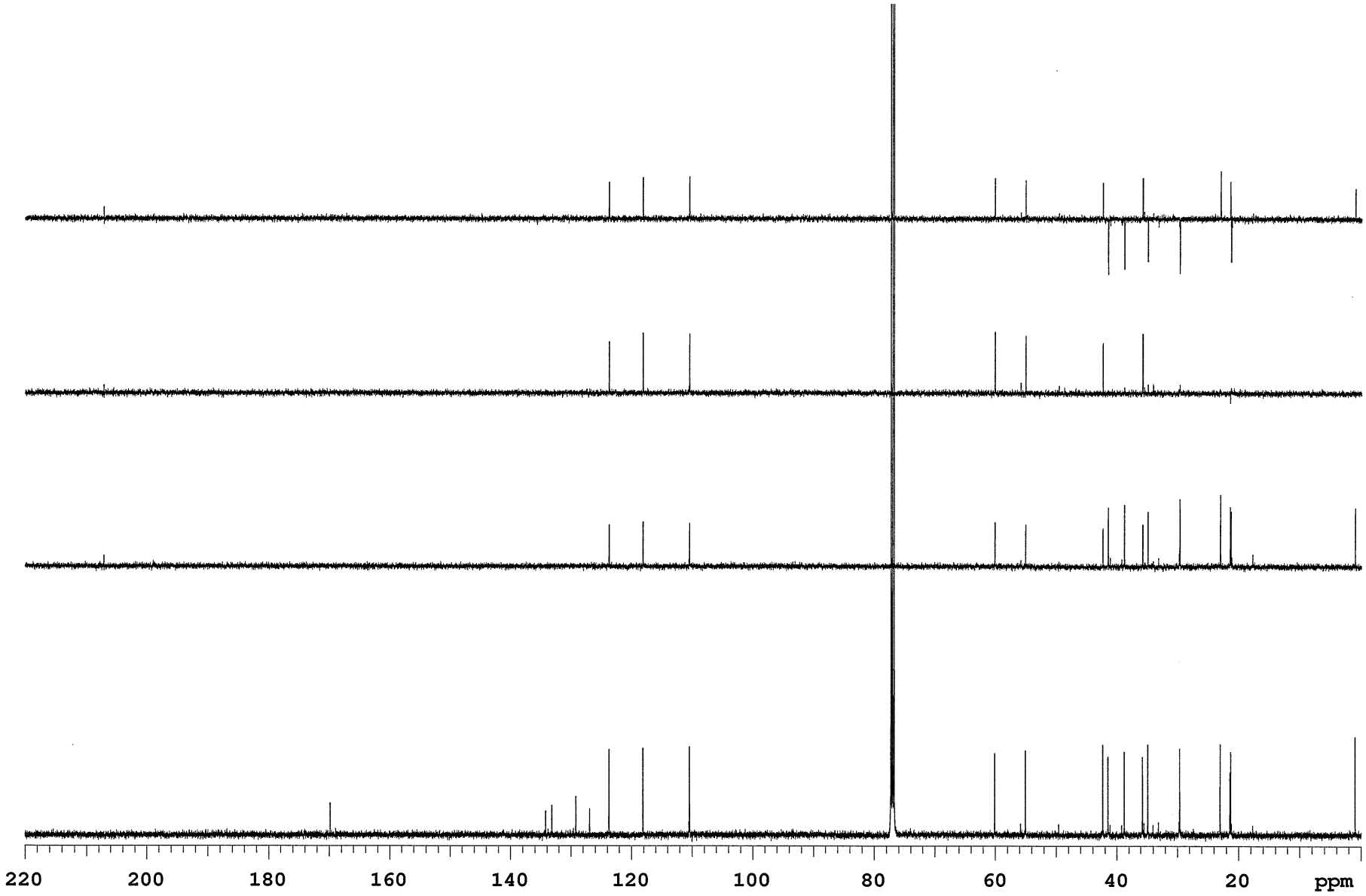
13C NMR (125 MHz, CDCl3) of compound 10d

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-069/CARBON_02

Plot date 2022-10-29

RRT-04-069

Sample Name **RRT-04-069**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-28**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



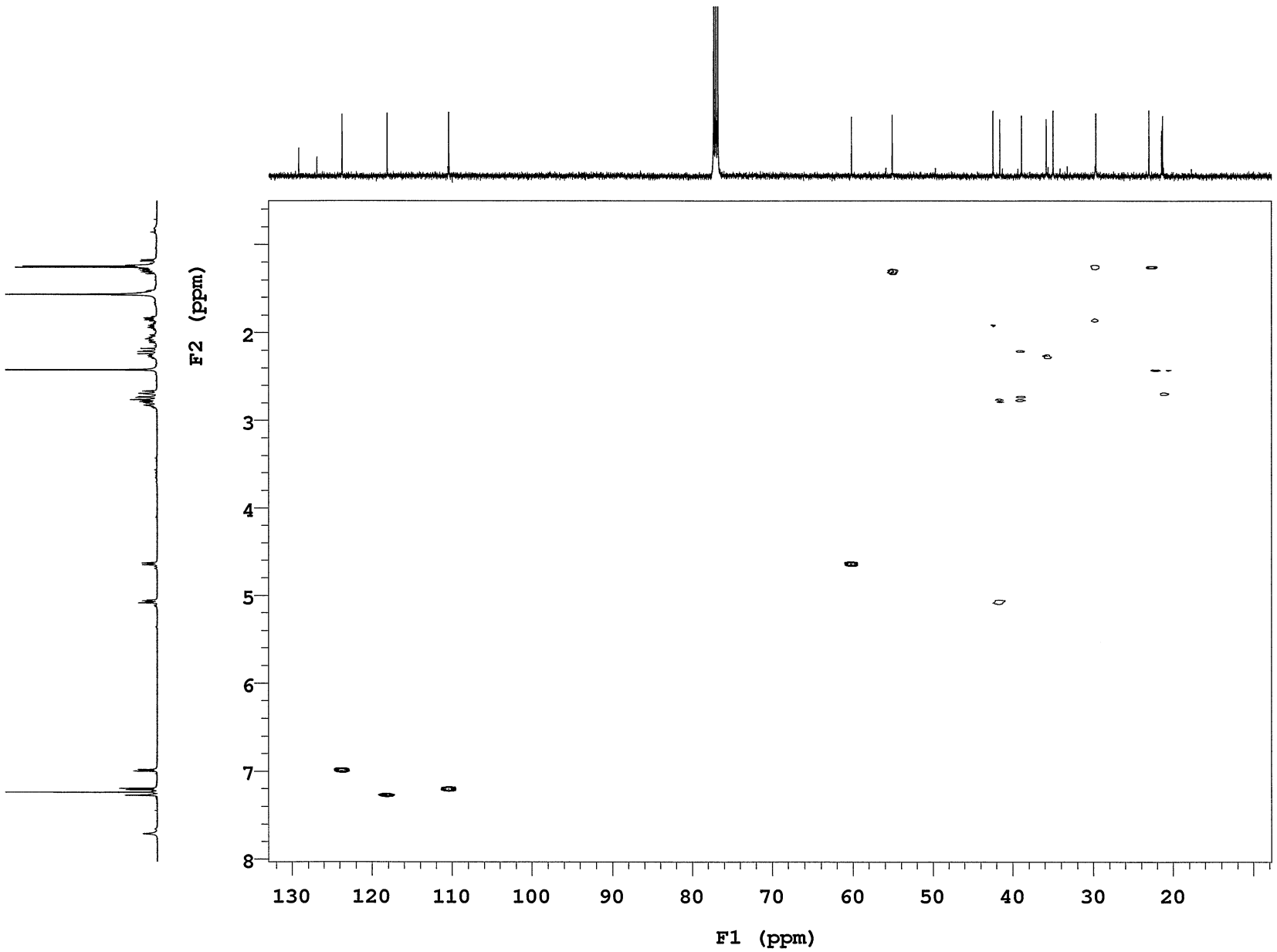
DEPT of compound 10d

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-069/DEPT_01

Plot date 2022-10-29

RRT-04-069

Sample Name **RRT-04-069**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-29**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



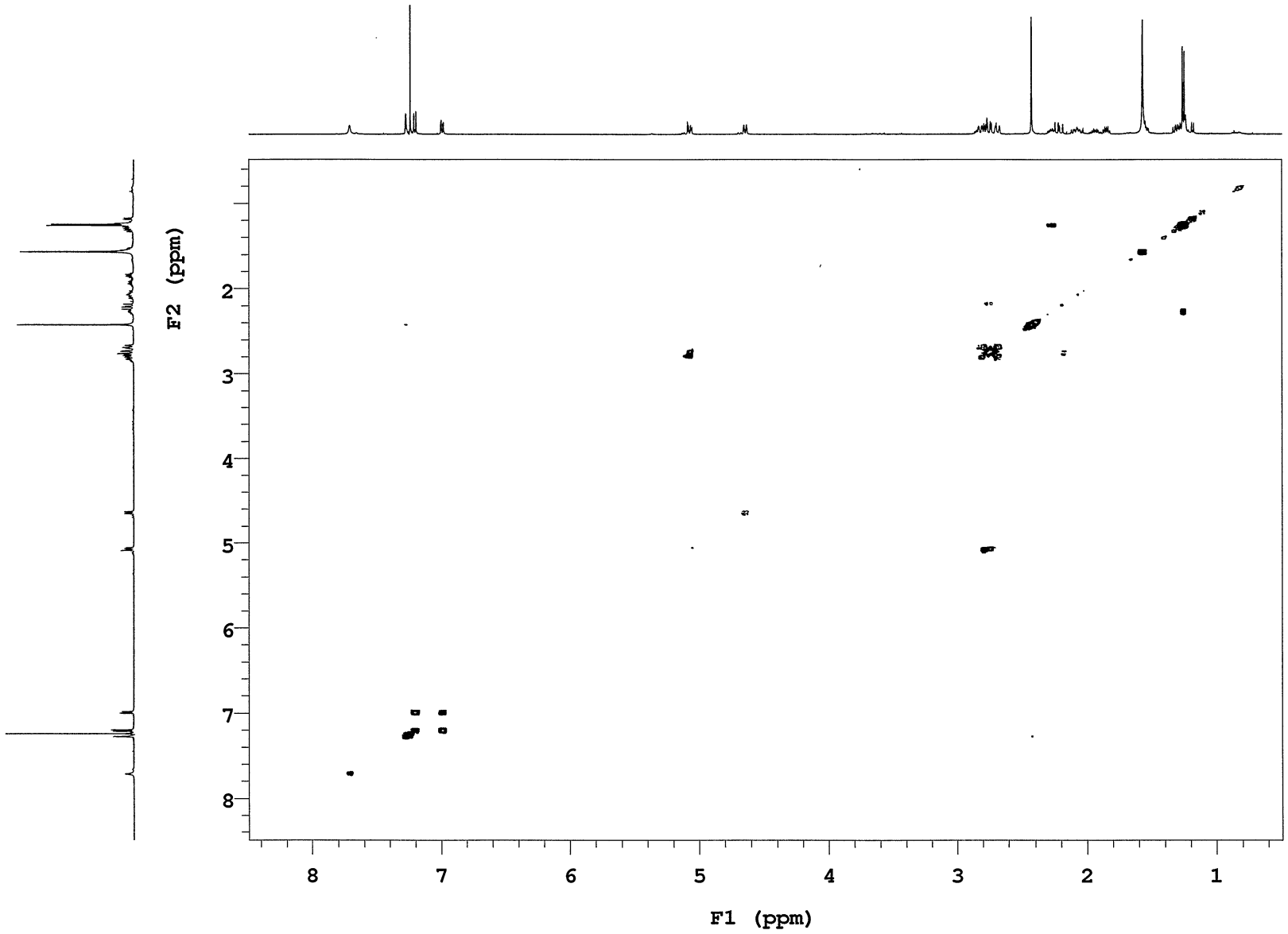
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-069/gHSQC_01

HSQC of compound 10d

Plot date 2022-10-29

RRT-04-069

Sample Name	**RRT-04-069**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-10-29**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



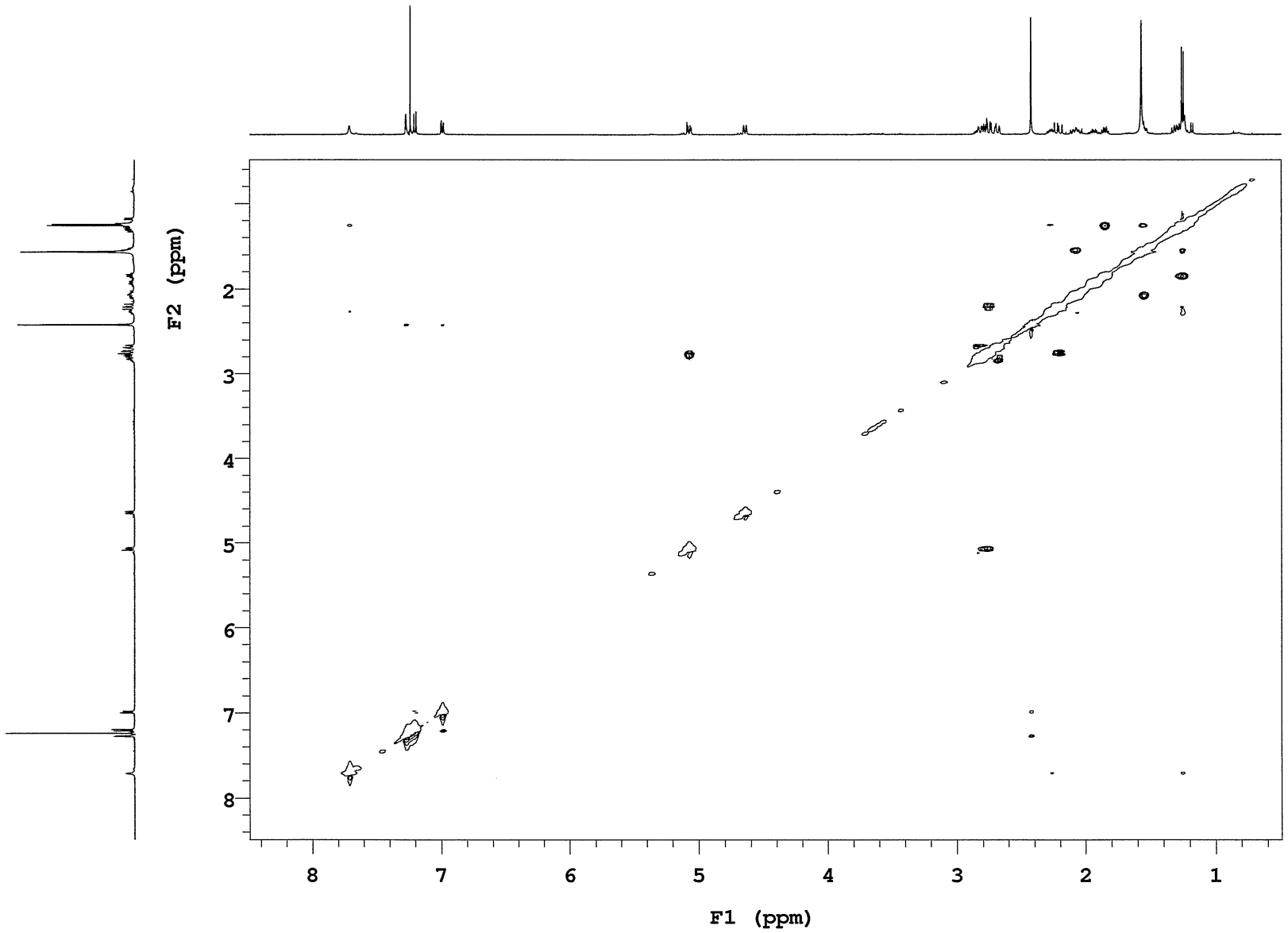
COSY of compound 10d

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-069/gCOSY_01

Plot date 2022-10-29

RRT-04-069

Sample Name	**RRT-04-069**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-10-29**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



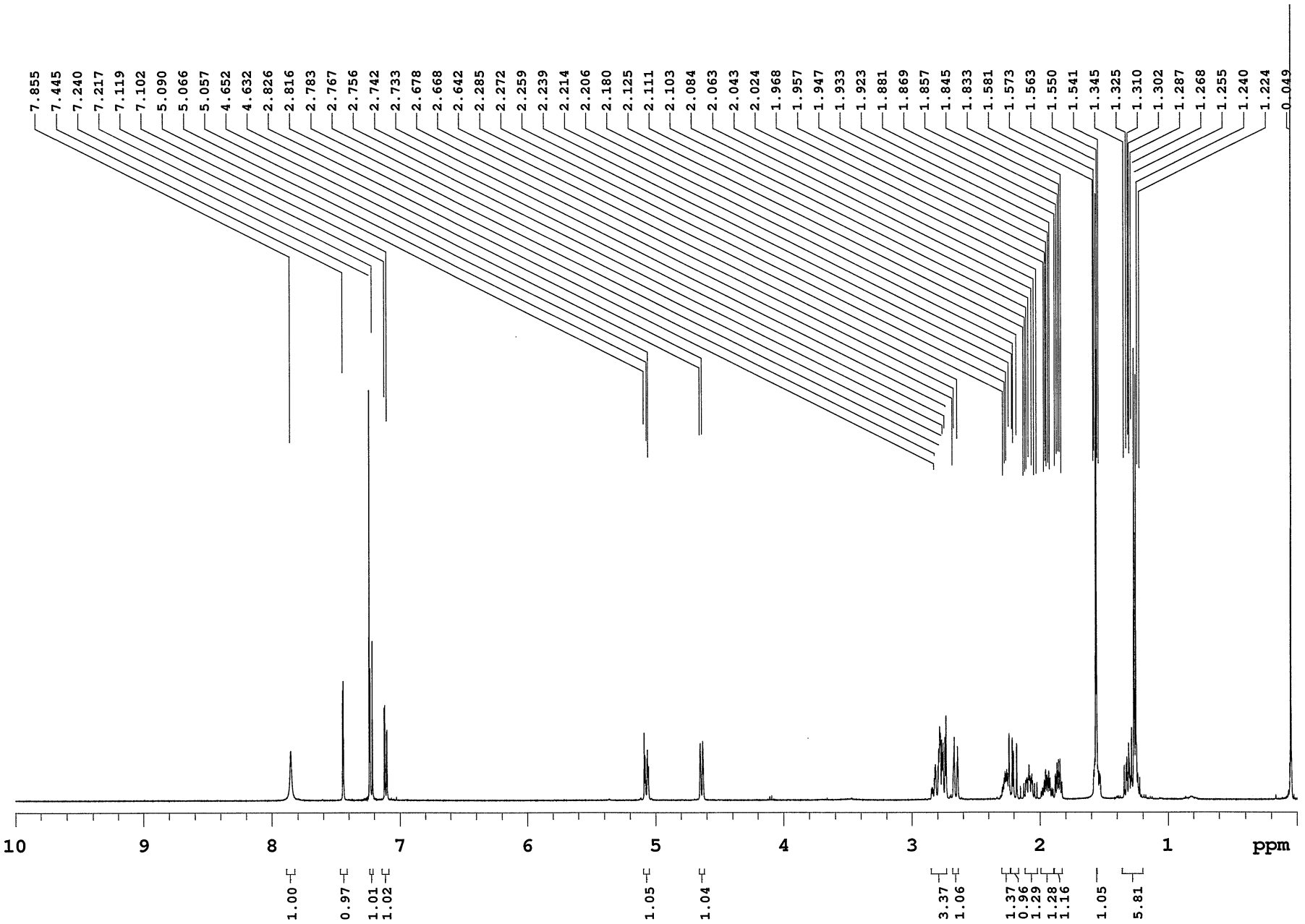
NOESY of compound 10d

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-069/NOESY_01

Plot date 2022-10-29

RRT-04-070

Sample Name	**RRT-04-070**	Pulse sequence	**PROTON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-10-29**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



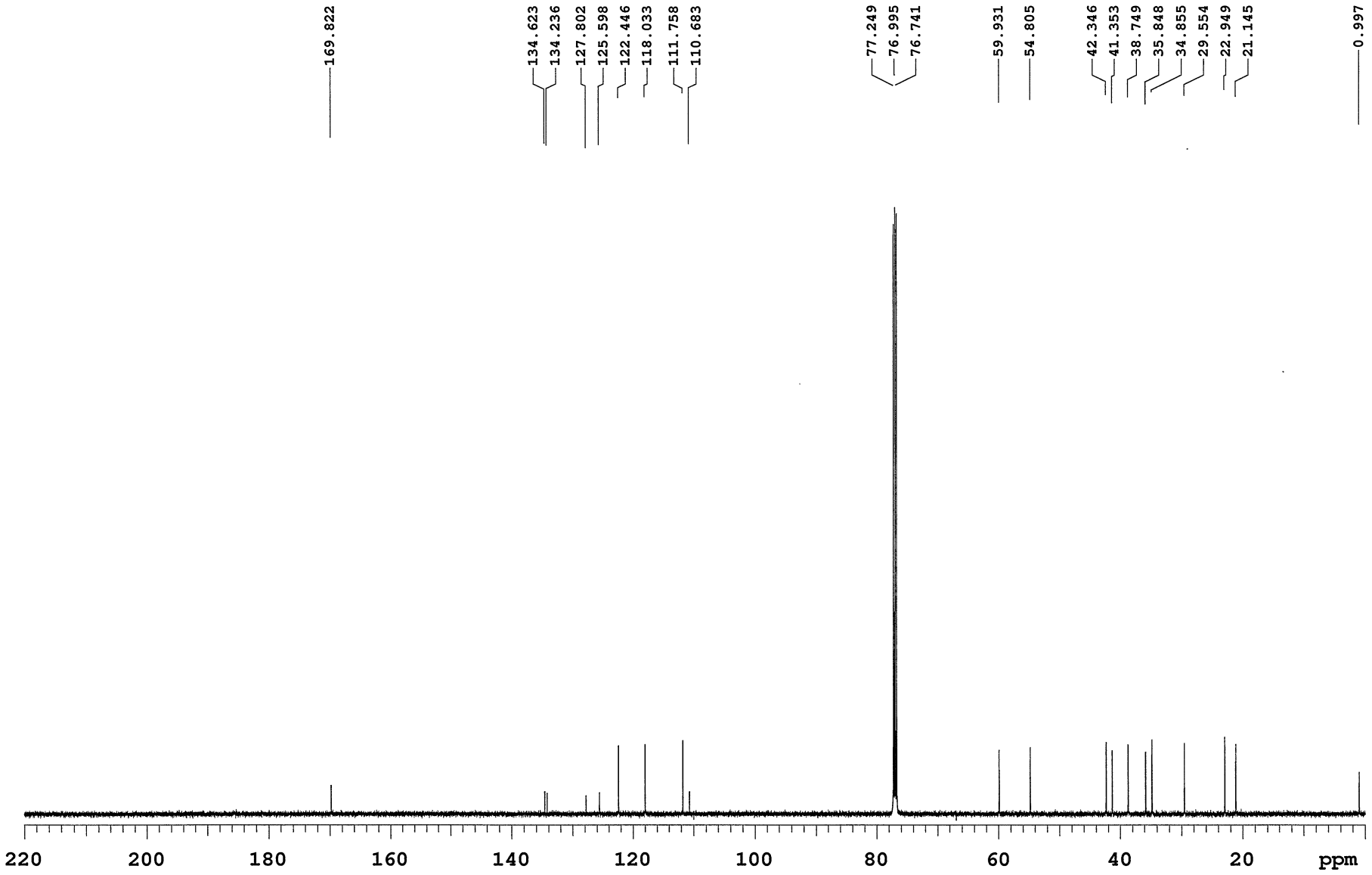
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070/PROTON_03

Plot date 2022-11-01

1H NMR (500 MHz, CDCl3) of compound 10e

RRT-04-070

Sample Name **RRT-04-070**	Pulse sequence **CARBON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-29**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**

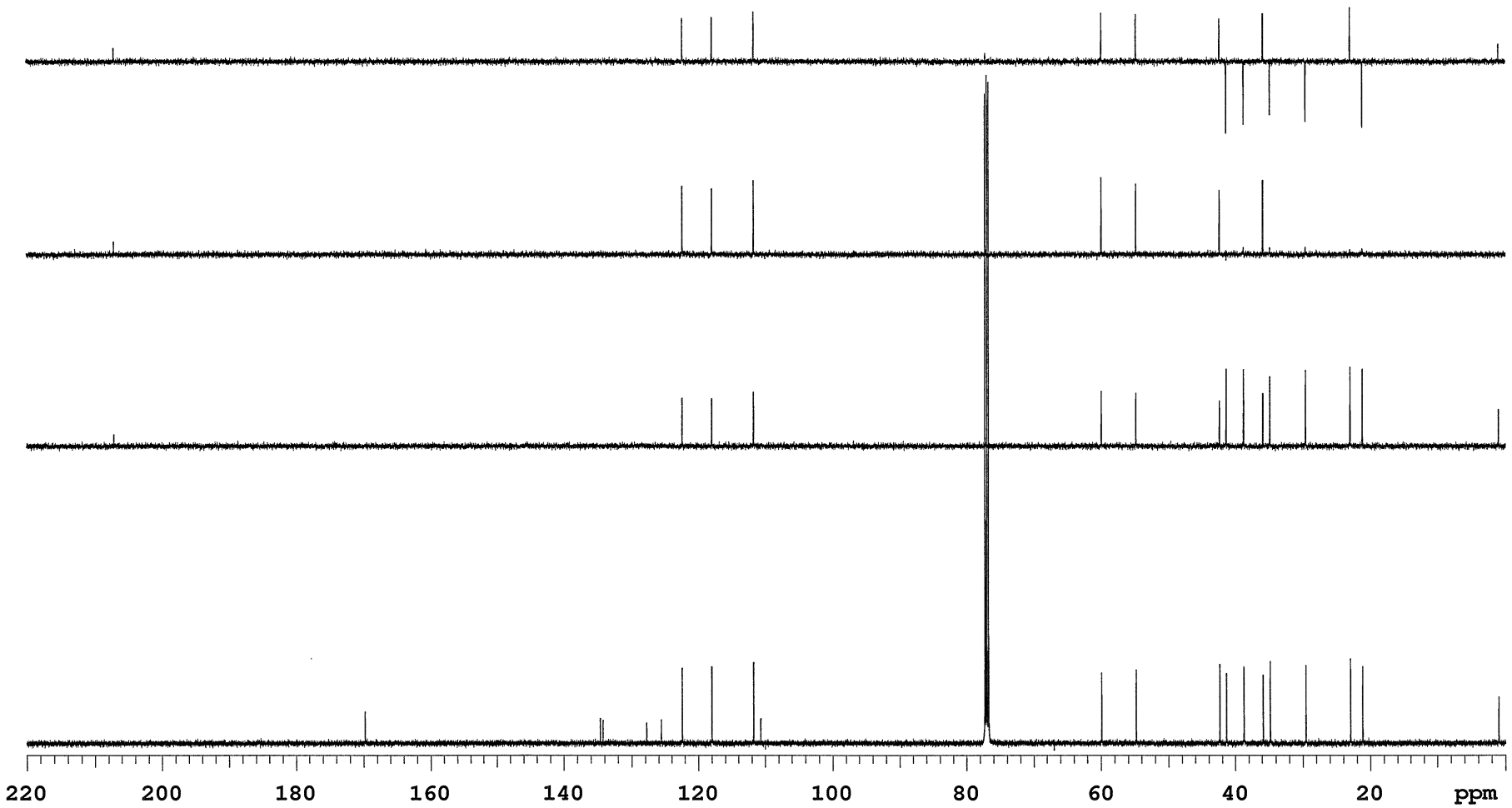


13C NMR (125 MHz, CDCl3) of compound 10e

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070/CARBON_02

Plot date 2022-10-31

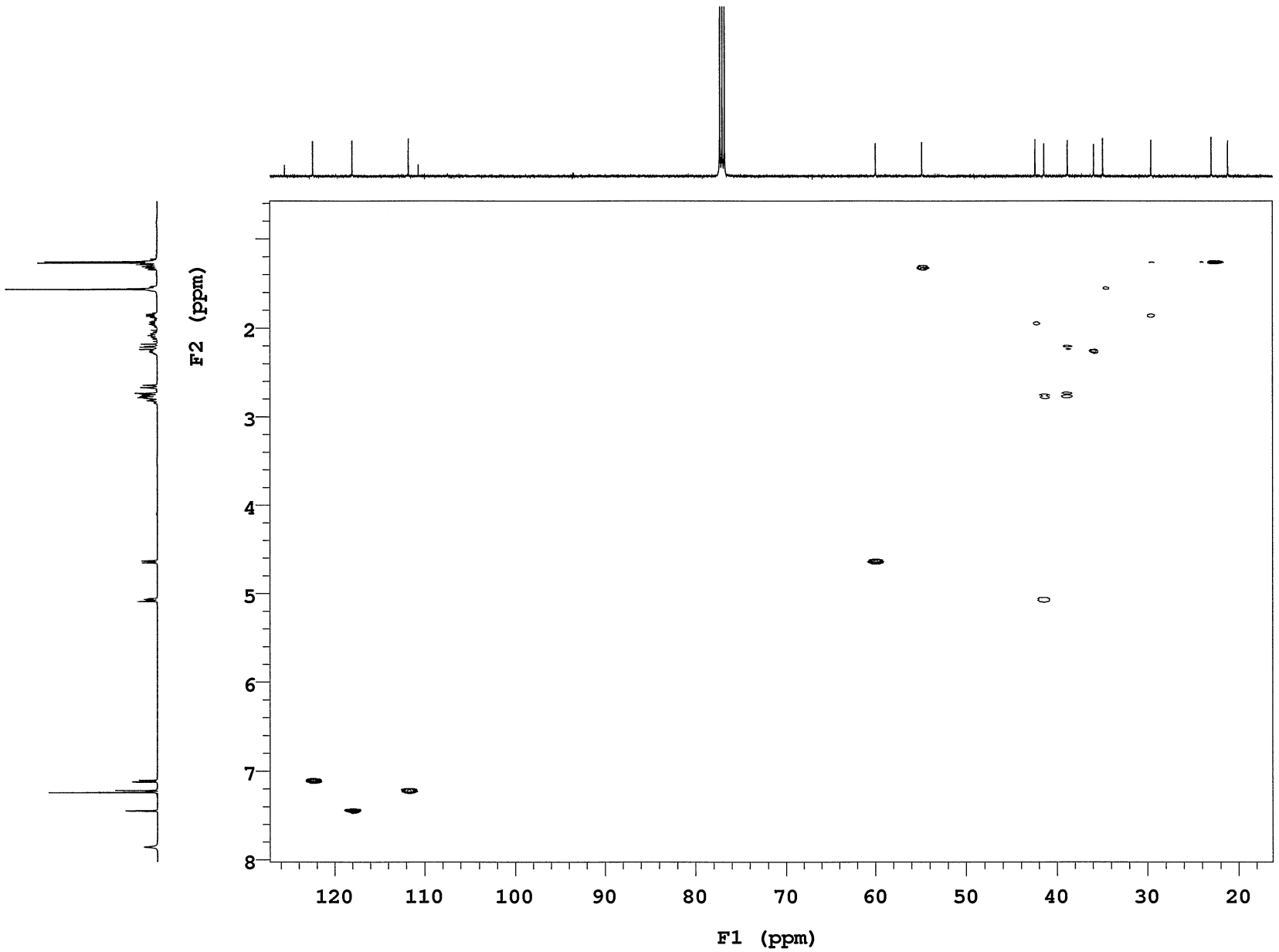
Sample Name **RRT-04-070**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-29**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 10e

RRT-04-070

Sample Name **RRT-04-070**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-30**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



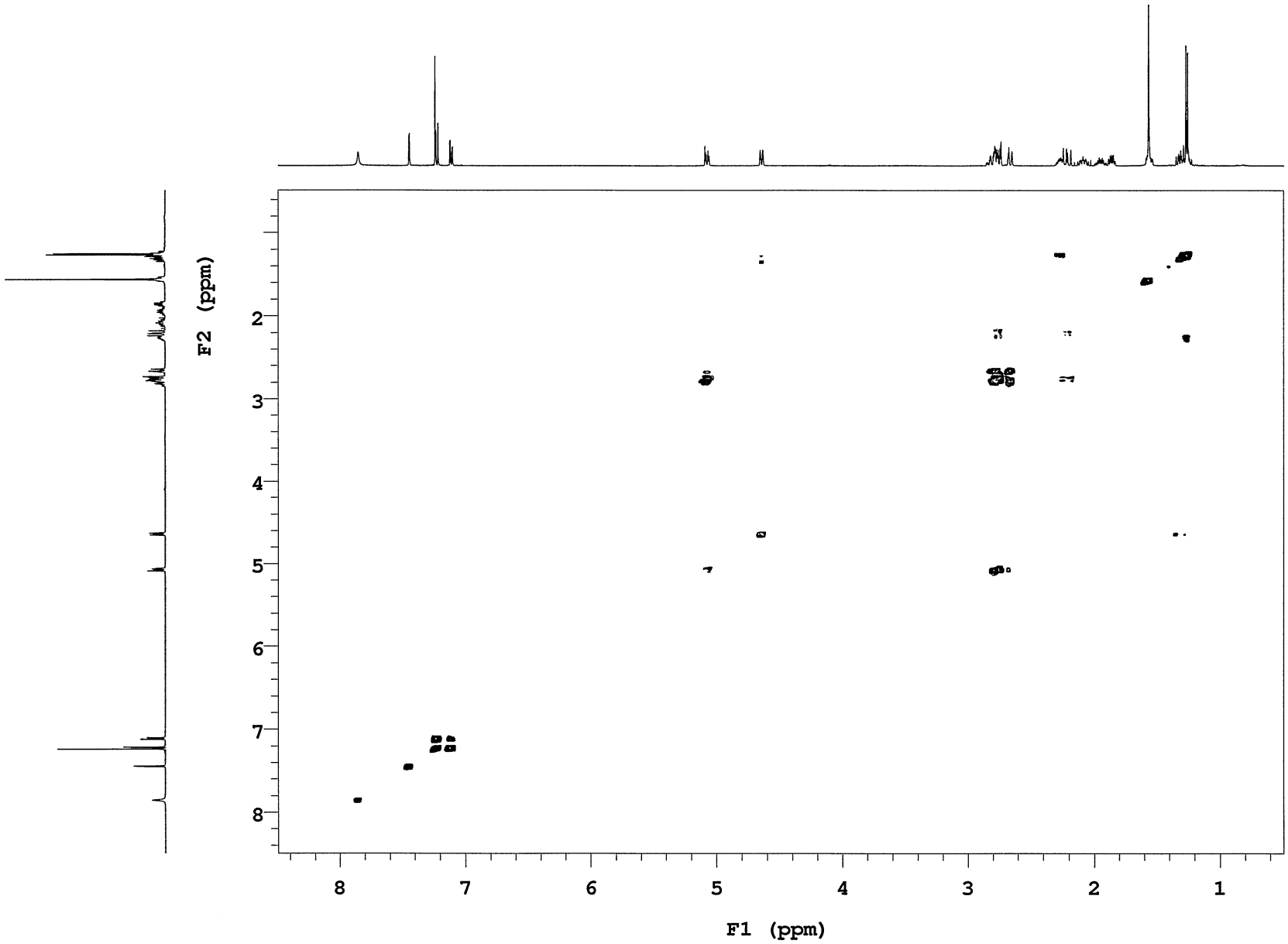
HSQC of compound 10e

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070/gHSQC_01

Plot date 2022-10-31

RRT-04-070

Sample Name **RRT-04-070**	Pulse sequence **gCOSY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-30**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



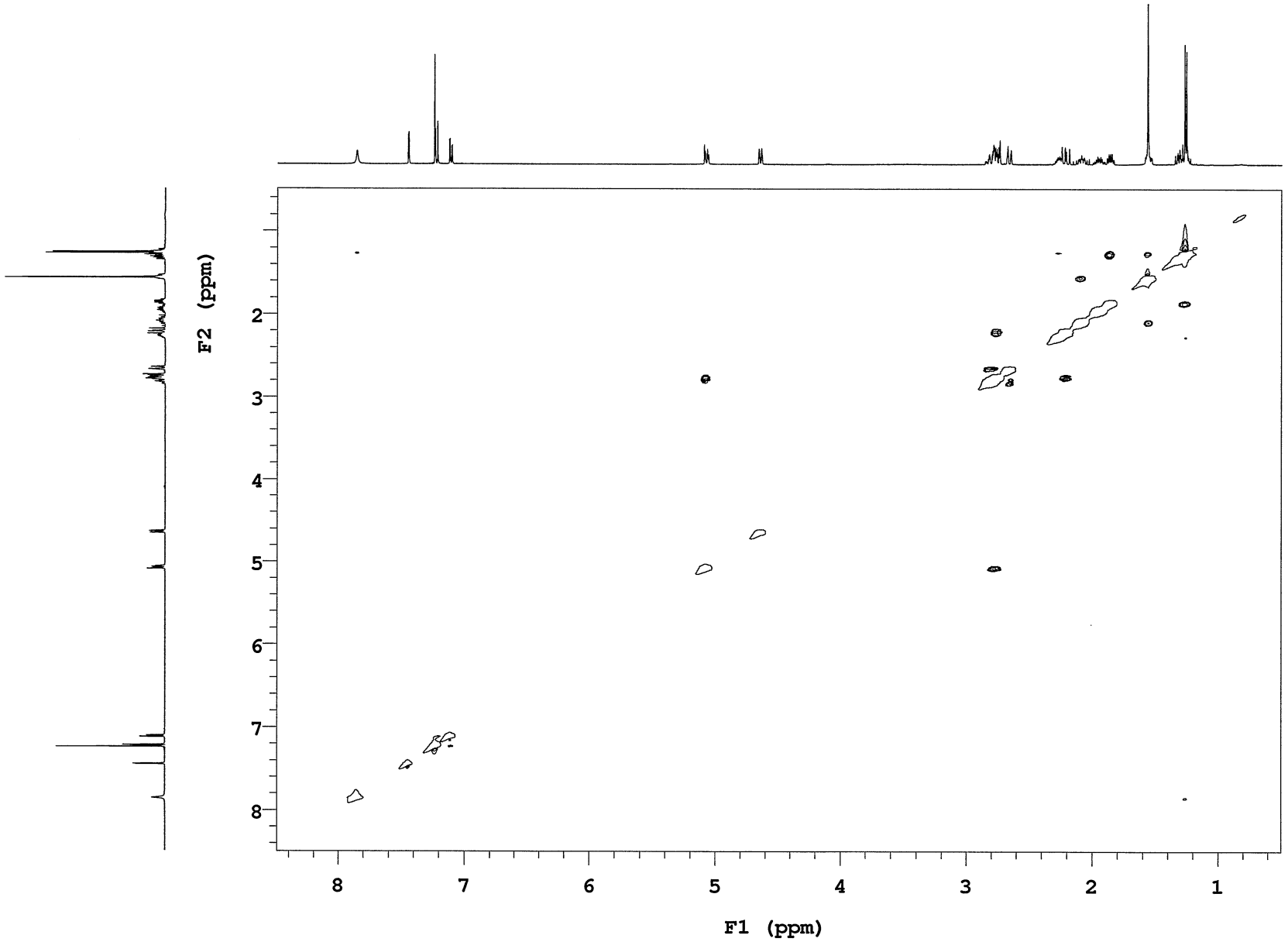
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070/gCOSY_01

COSY of compound 10e

Plot date 2022-10-31

RRT-04-070

Sample Name	**RRT-04-070**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-10-30**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



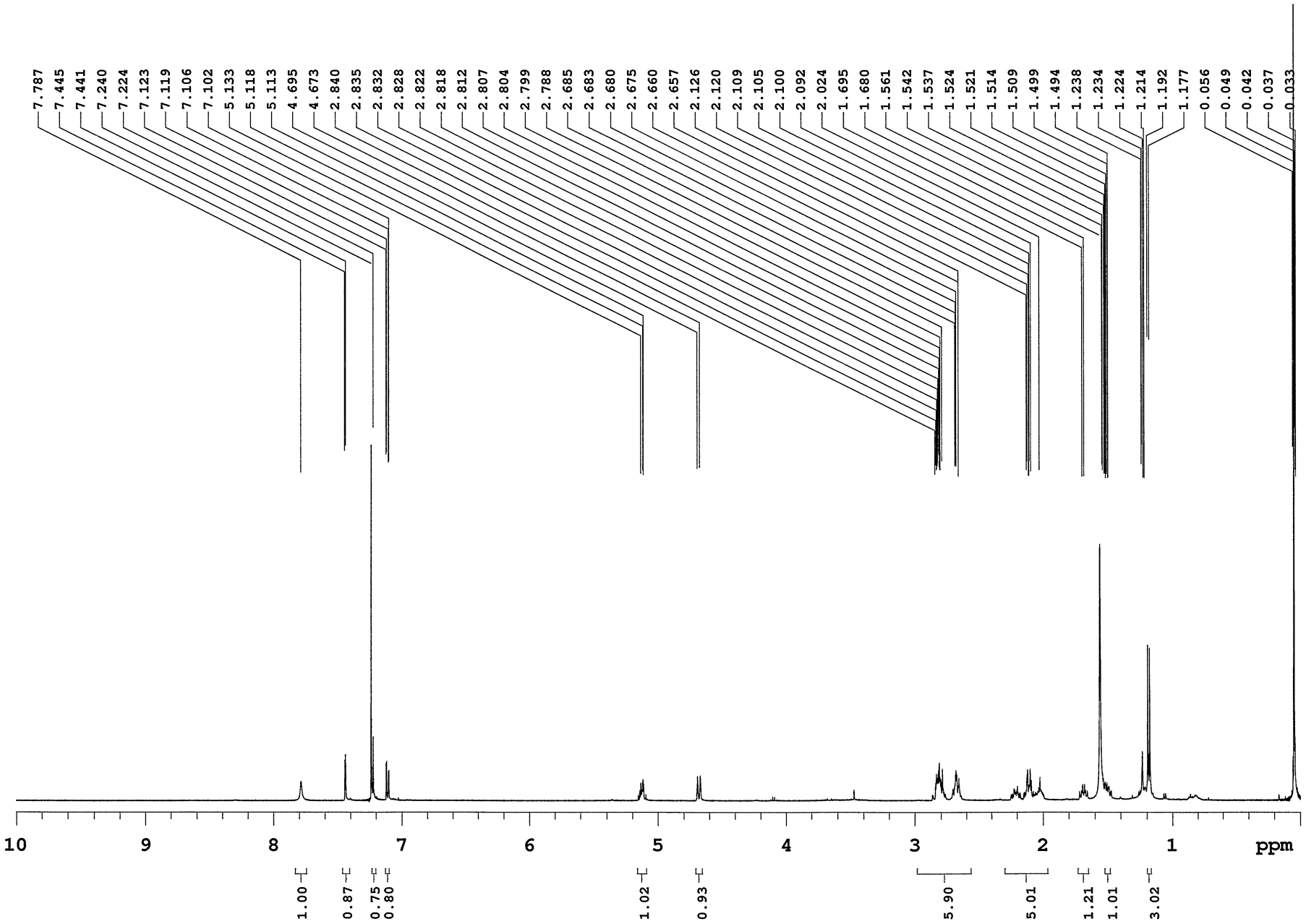
NOESY of compound 10e

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070/NOESY_01

Plot date 2022-10-31

RRT-04-070-F-I

Sample Name **RRT-04-070-F-I**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-11-12**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



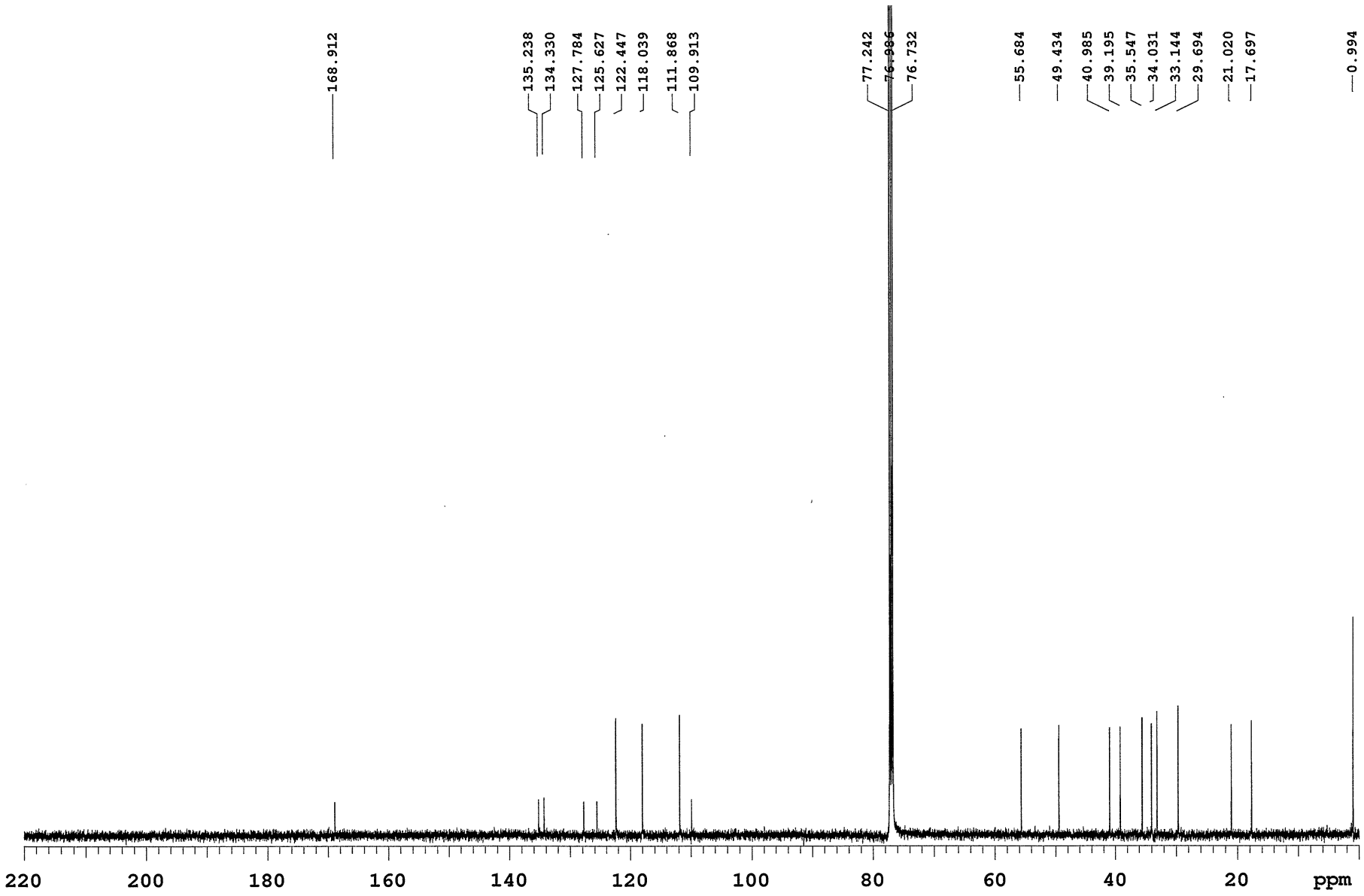
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070-F-I/PROTON_03.fid

1H NMR (500 MHz, CDCl3) of compound 11e

Plot date 2022-11-30

RRT-04-070-F-I

Sample Name	RRT-04-070-F-I	Pulse sequence	CARBON	Temperature	25	Study owner	vnmr2
Date collected	2022-11-12	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



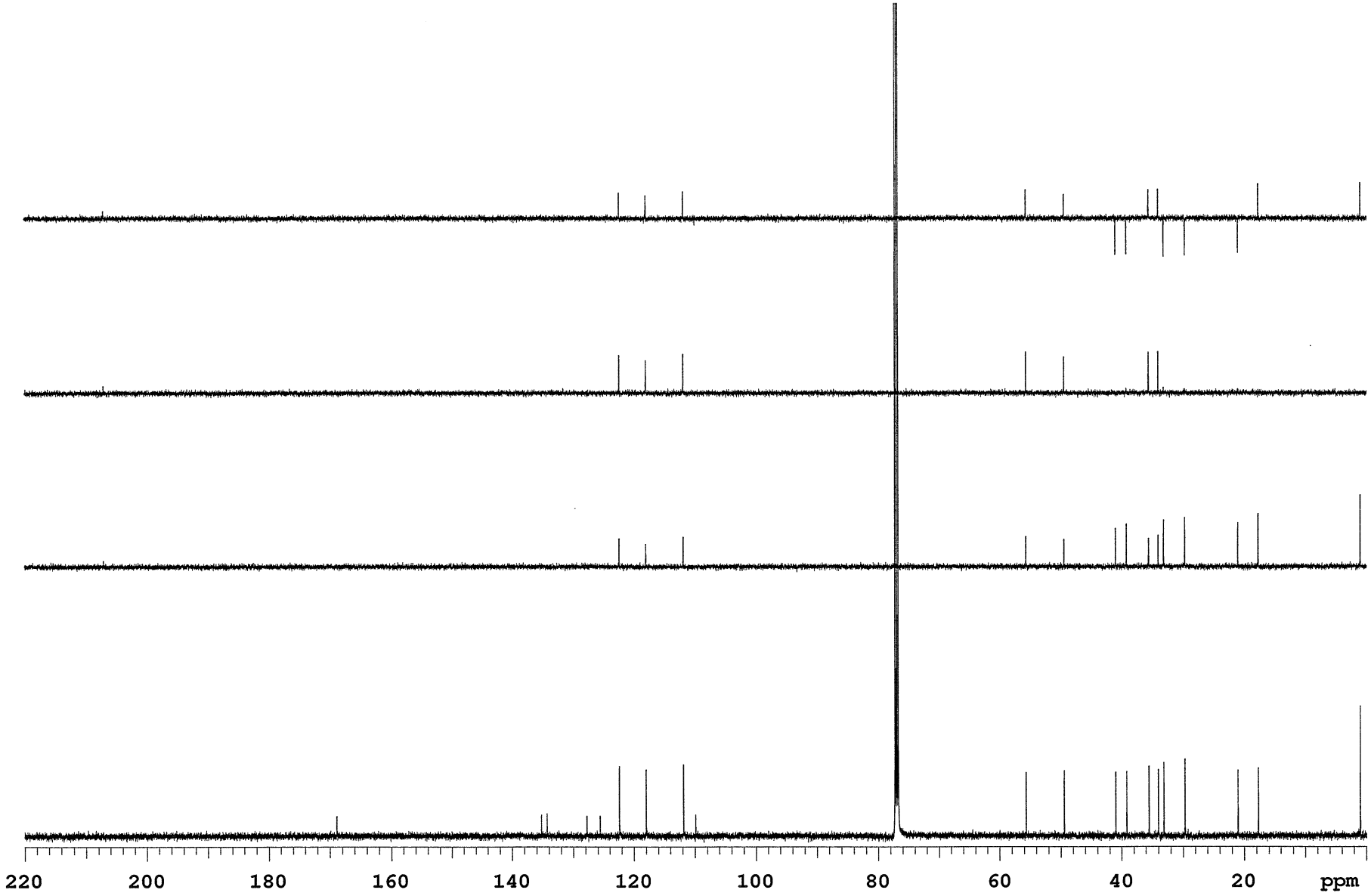
13C NMR (125 MHz, CDCl3) of compound 11e

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070-F-I/CARBON_02

Plot date 2022-11-14

RRT-04-070-F-I

Sample Name **RRT-04-070-F-I**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-11-12**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



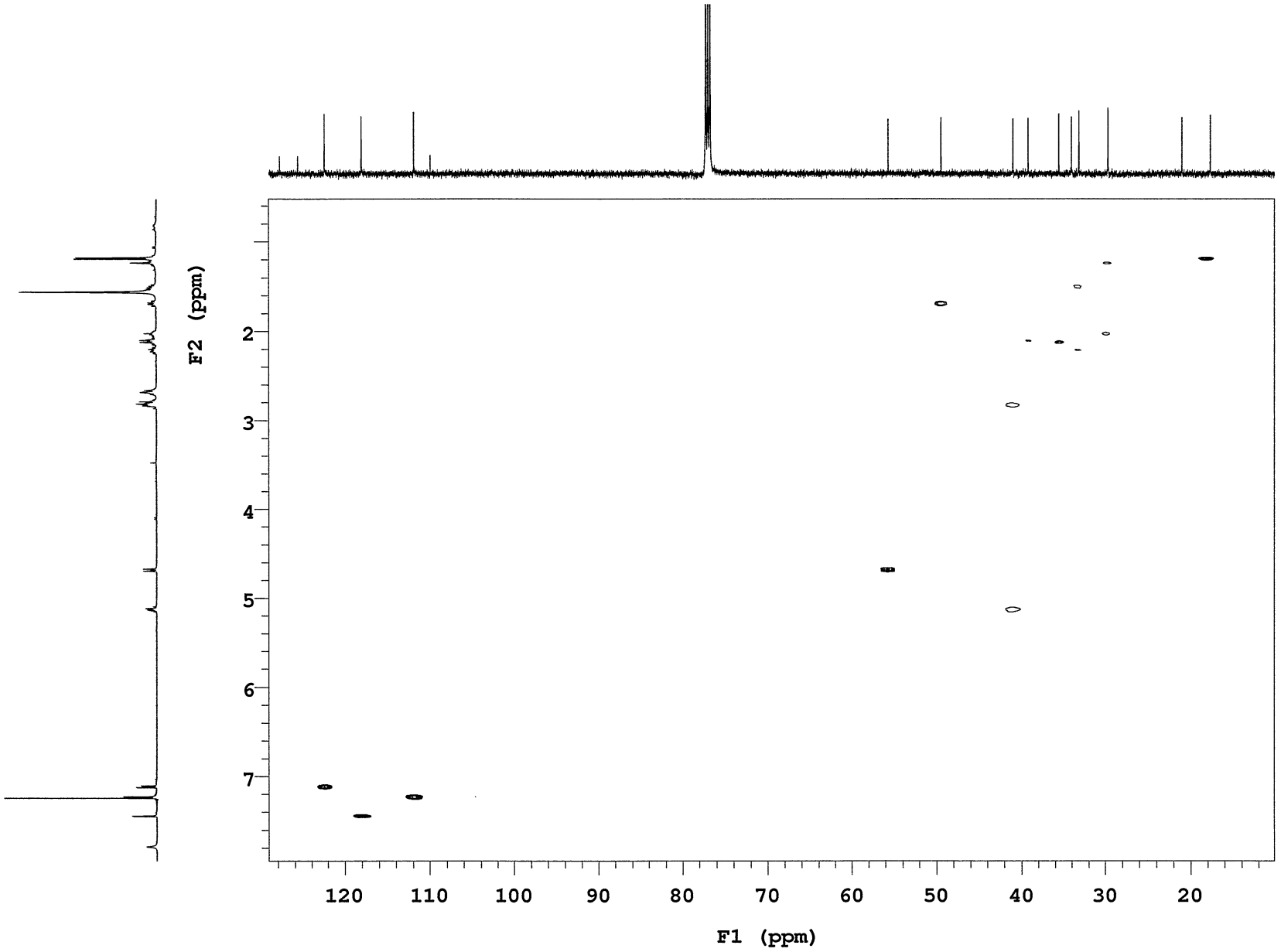
DEPT of compound 11e

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070-F-I/DEPT_01

Plot date 2022-11-14

RRT-04-070-F-I

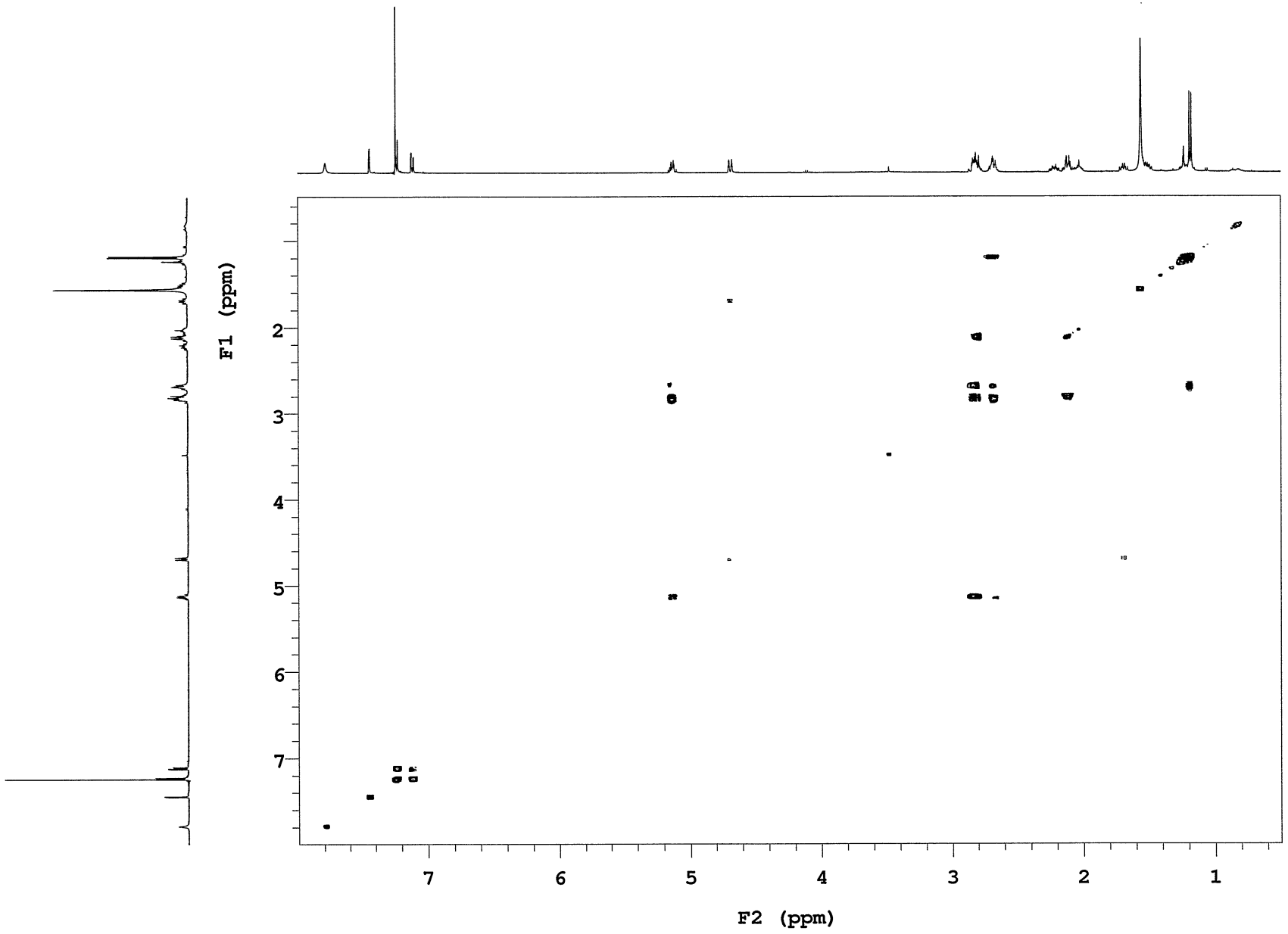
Sample Name	RRT-04-070-F-I	Pulse sequence	gHSQC	Temperature	25	Study owner	vnmr2
Date collected	2022-11-13	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



HSQC of compound 11e

RRT-04-070-F-I

Sample Name	RRT-04-070-F-I	Pulse sequence	gCOSY	Temperature	25	Study owner	vnmr2
Date collected	2022-11-13	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



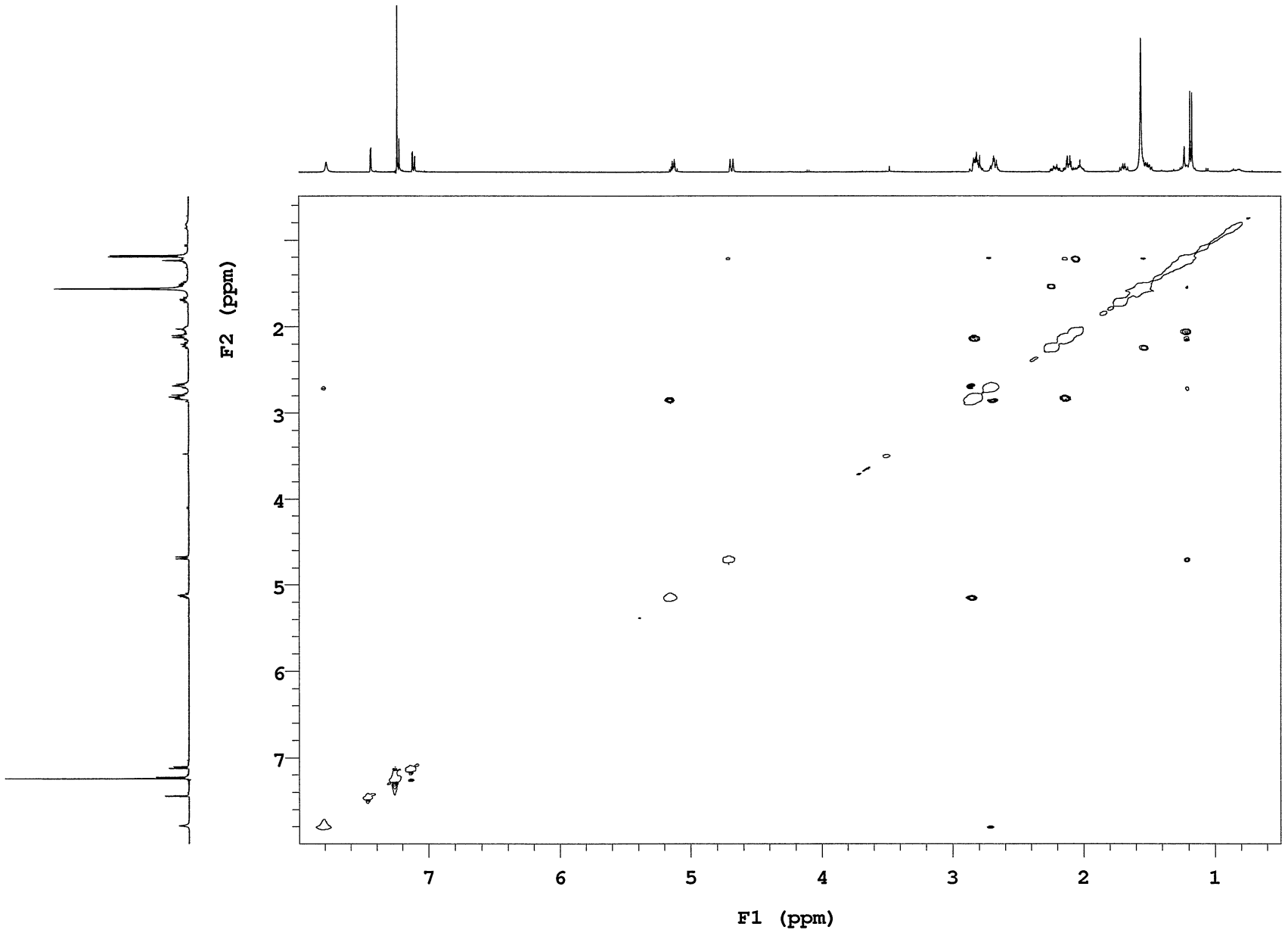
COSY of compound 11e

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070-F-I/gCOSY_01

Plot date 2022-11-14

RRT-04-070-F-I

Sample Name	RRT-04-070-F-I	Pulse sequence	NOESY	Temperature	25	Study owner	vnmr2
Date collected	2022-11-13	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



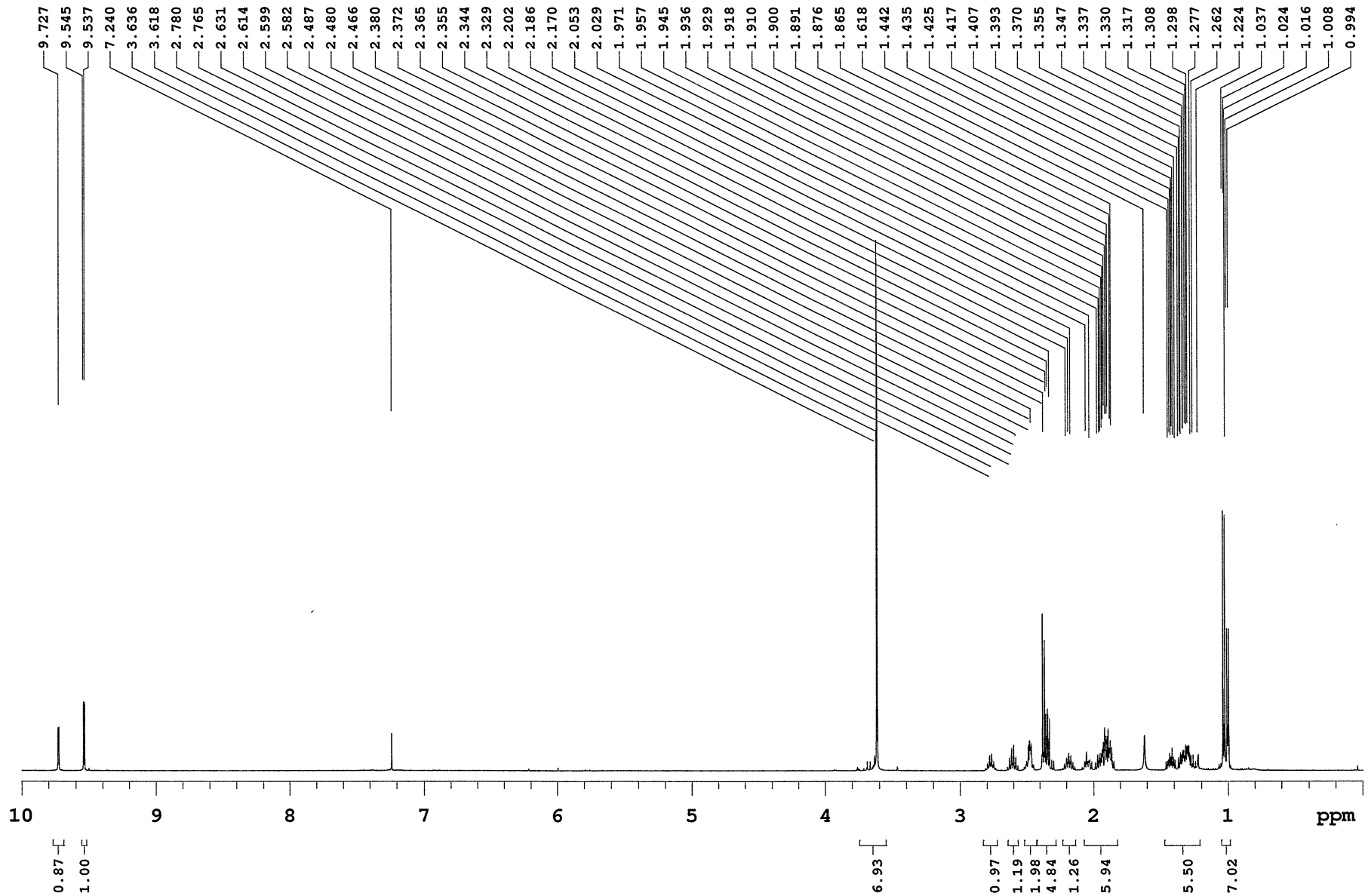
NOESY of compound 11e

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-070-F-I/NOESY_01

Plot date 2022-11-14

RRT-231_and_RRT-263

Sample Name **RRT-231_and_RRT-263**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-02-13**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



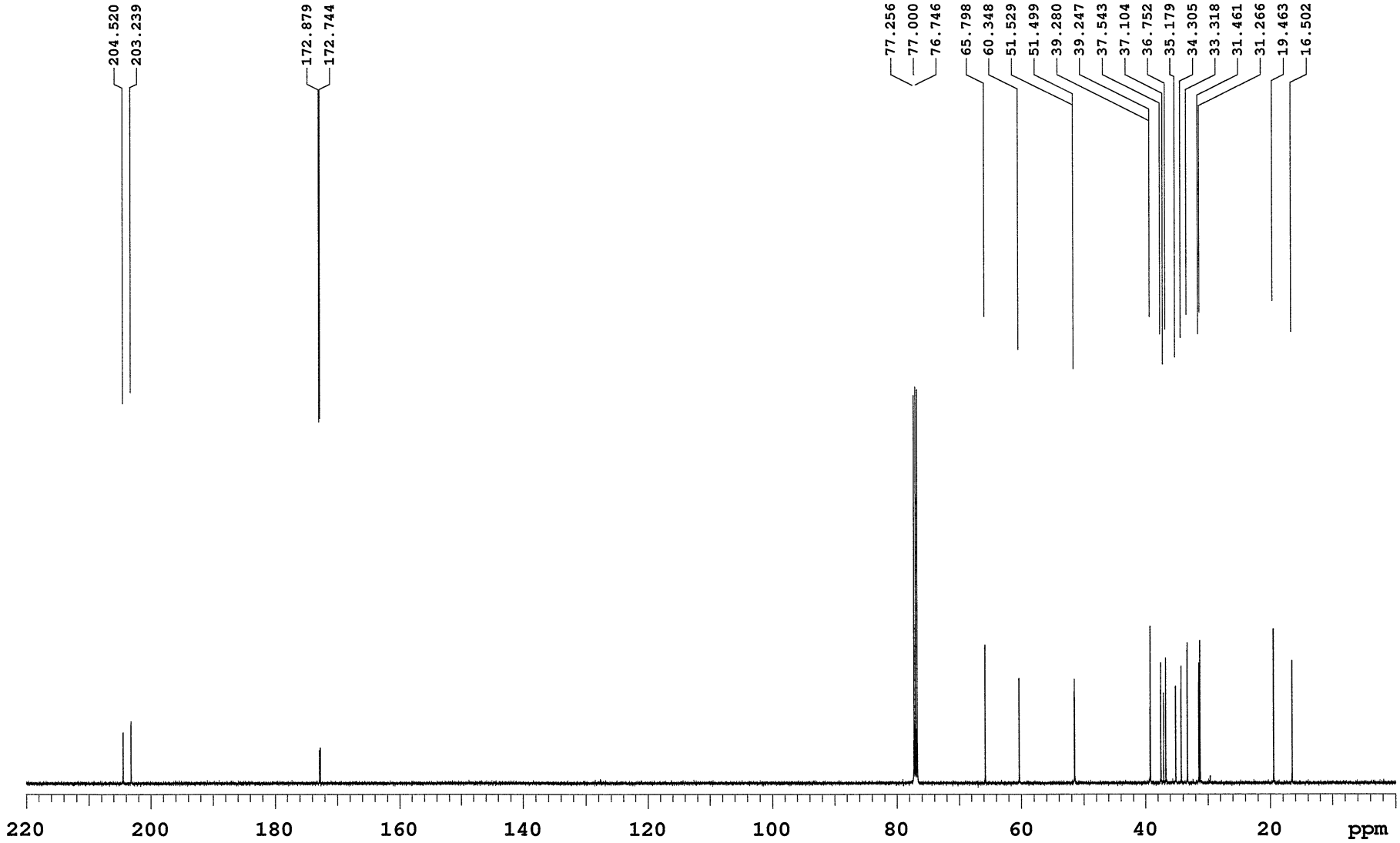
Data file /home/vnmr2/vnmrsys/data/511-1/RRT/RRT-231_and_RRT-263/PROTON_03

1H NMR (500 MHz, CDCl3) of the mixture of **2** and **12** (Scheme 3)

Plot date 2023-02-14

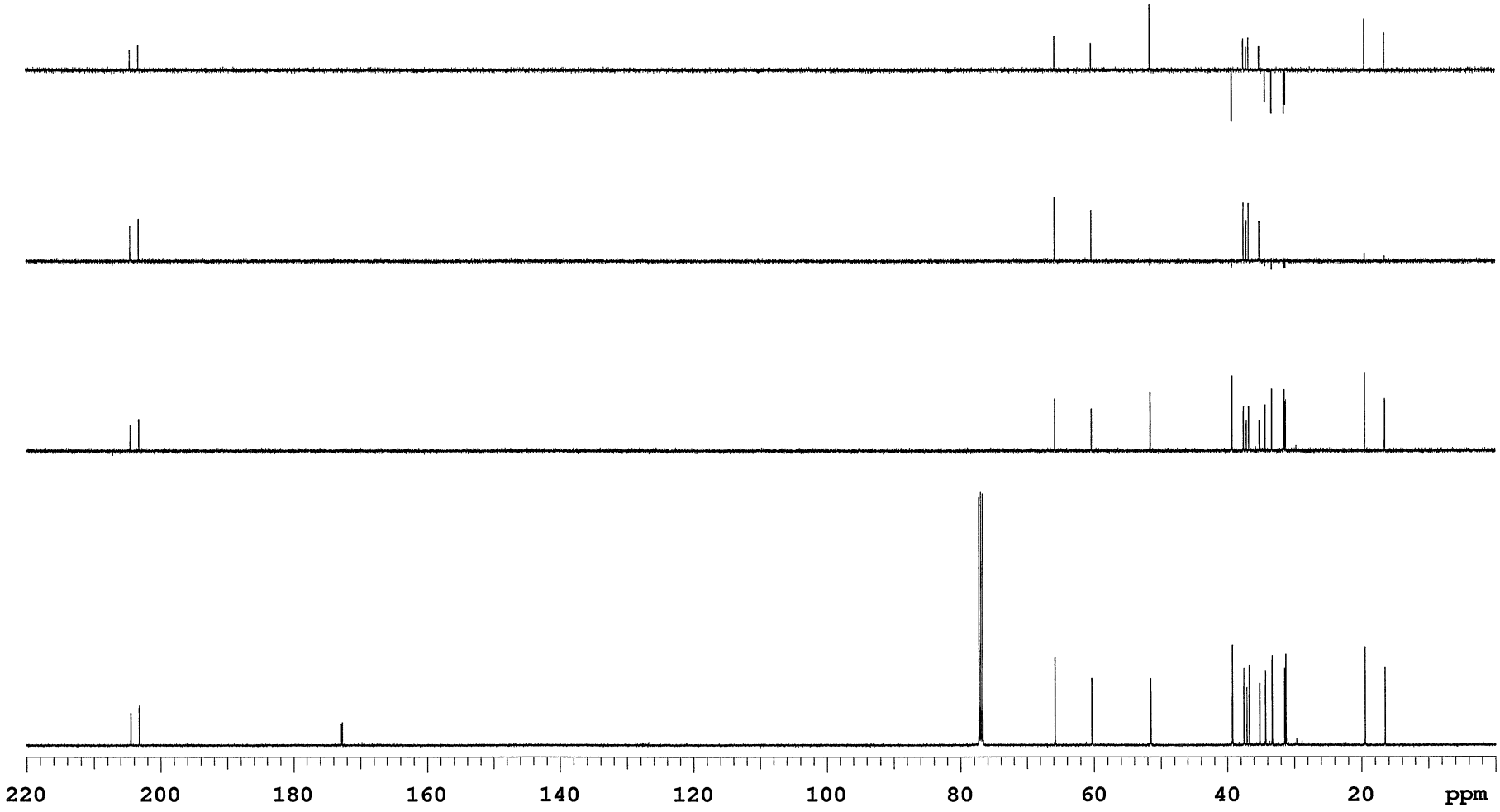
RRT-231_and_RRT-263

Sample Name	**RRT-231_and_RRT-263**	Pulse sequence	**CARBON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2023-02-13**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



13C NMR (125 MHz, CDCl3) of the mixture of of **2** and **12** (Scheme 3)

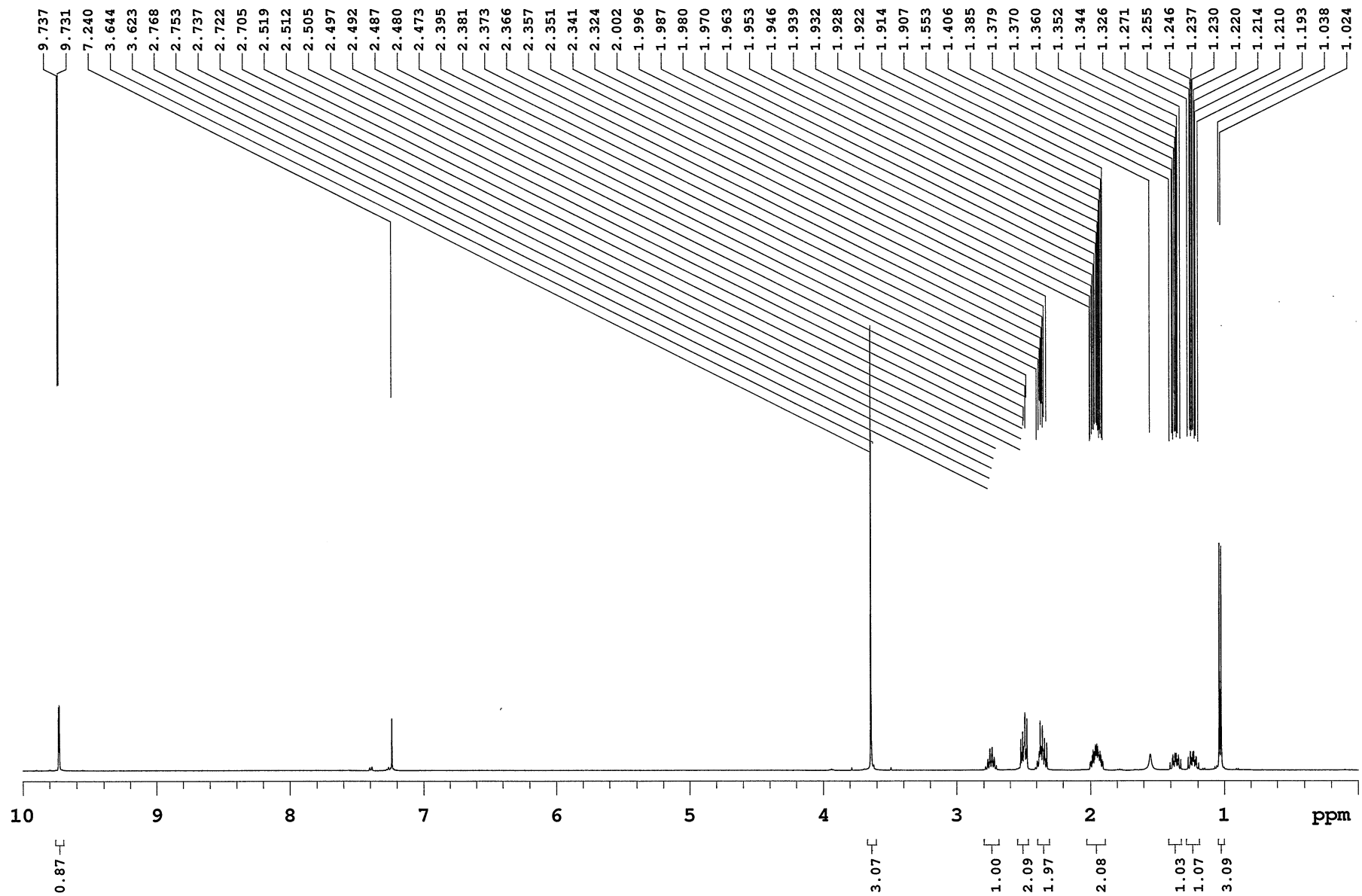
Sample Name **RRT-231_and_RRT-263**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-02-13**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of the mixture of of **2** and **12** (Scheme 3)

RRT-04-090-I

Sample Name	**RRT-04-090-I**	Pulse sequence	**PROTON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2023-01-06**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



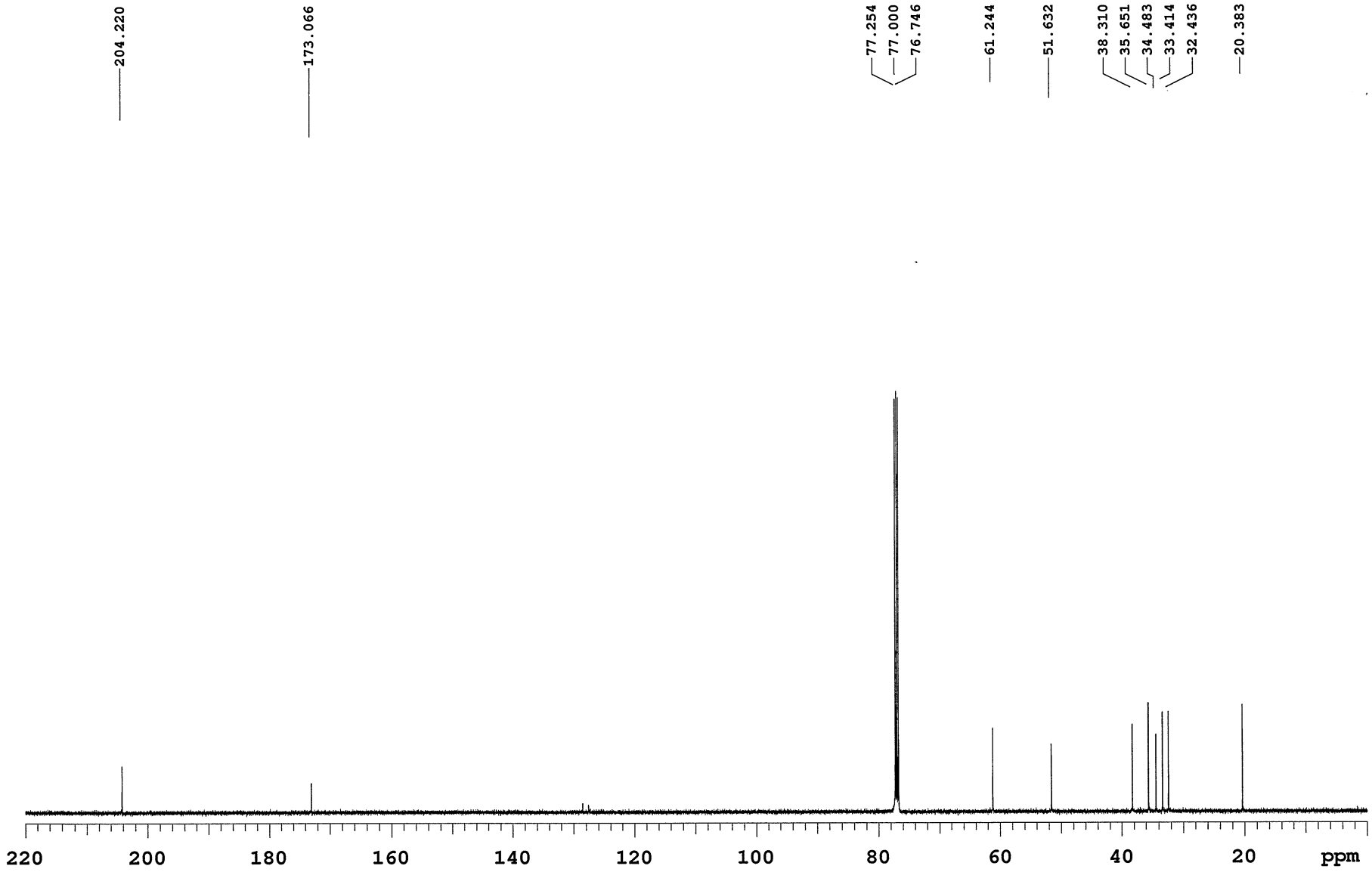
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-090-I/PROTON_03

1H NMR (500 MHz, CDCl3) of compound 13

Plot date 2023-01-07

RRT-04-090-I

Sample Name	RRT-04-090-I	Pulse sequence	CARBON	Temperature	25	Study owner	vnmr2
Date collected	2023-01-06	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



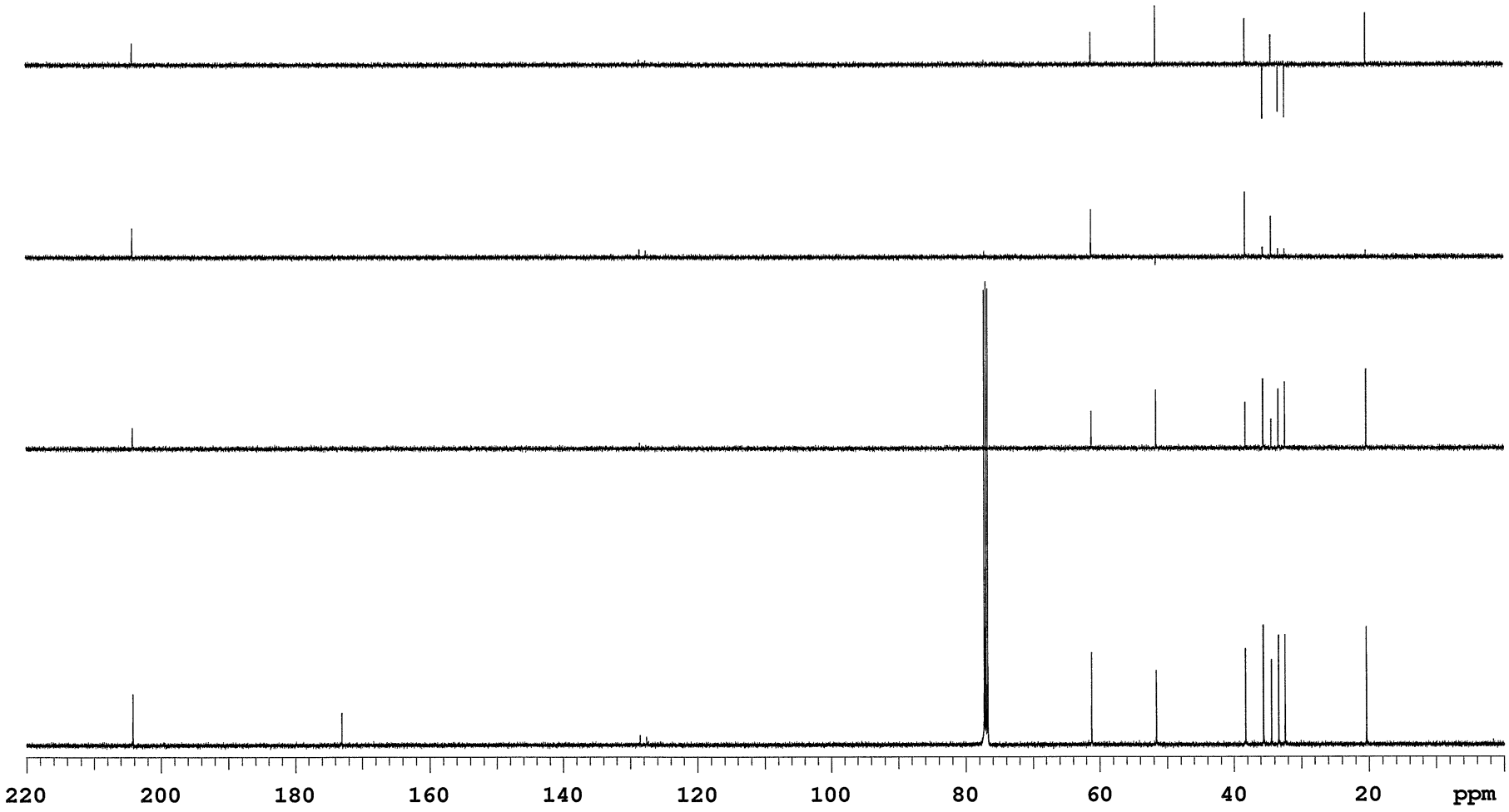
13C NMR (125 MHz, CDCl3) of compound 13

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-090-I/CARBON_02

Plot date 2023-01-07

RRT-04-090-I

Sample Name	**RRT-04-090-I**	Pulse sequence	**DEPT**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2023-01-06**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



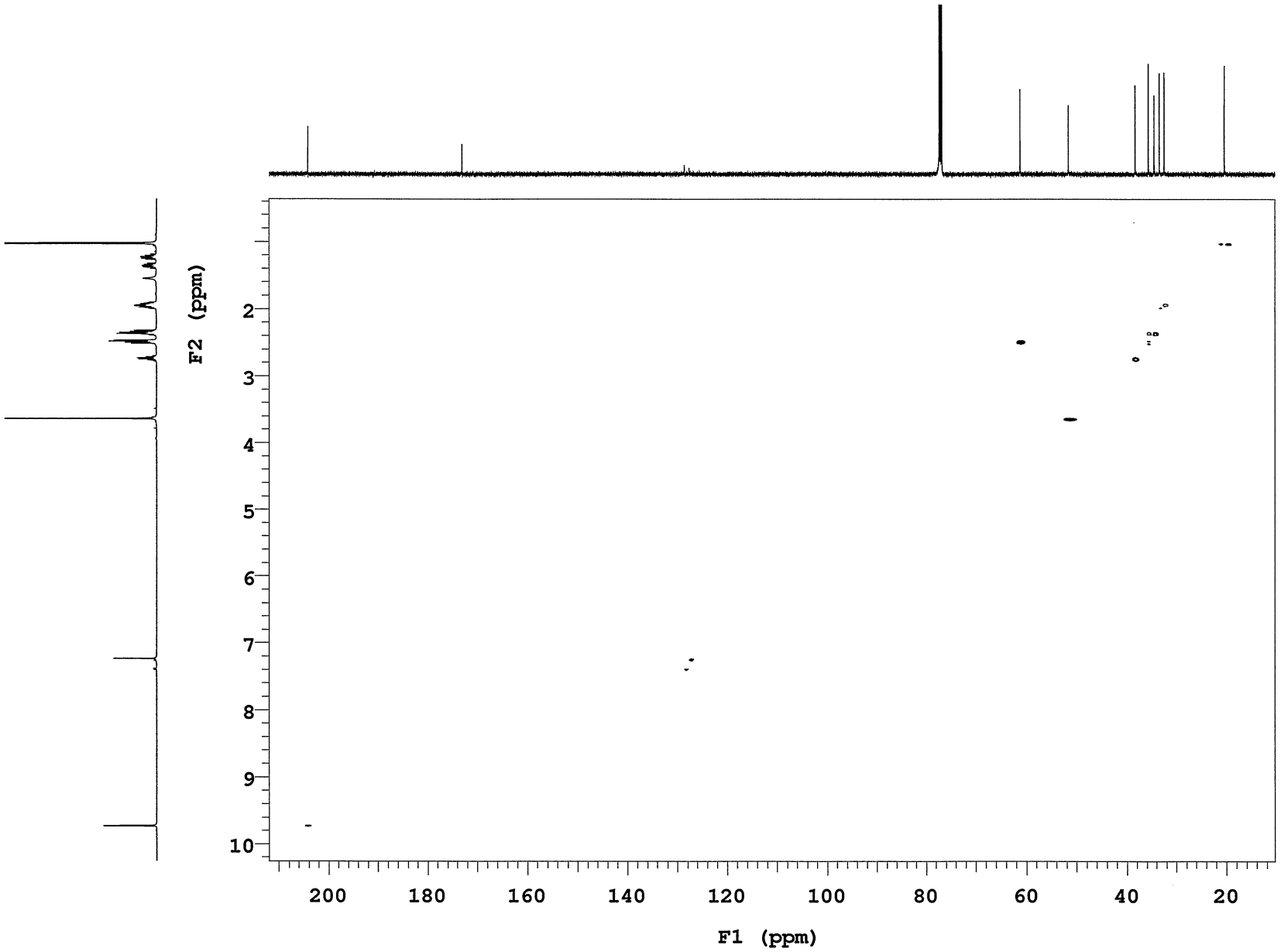
DEPT of compound 13

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-090-I/DEPT_01

Plot date 2023-01-07

RRT-04-090-I

Sample Name **RRT-04-090-I**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-07**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



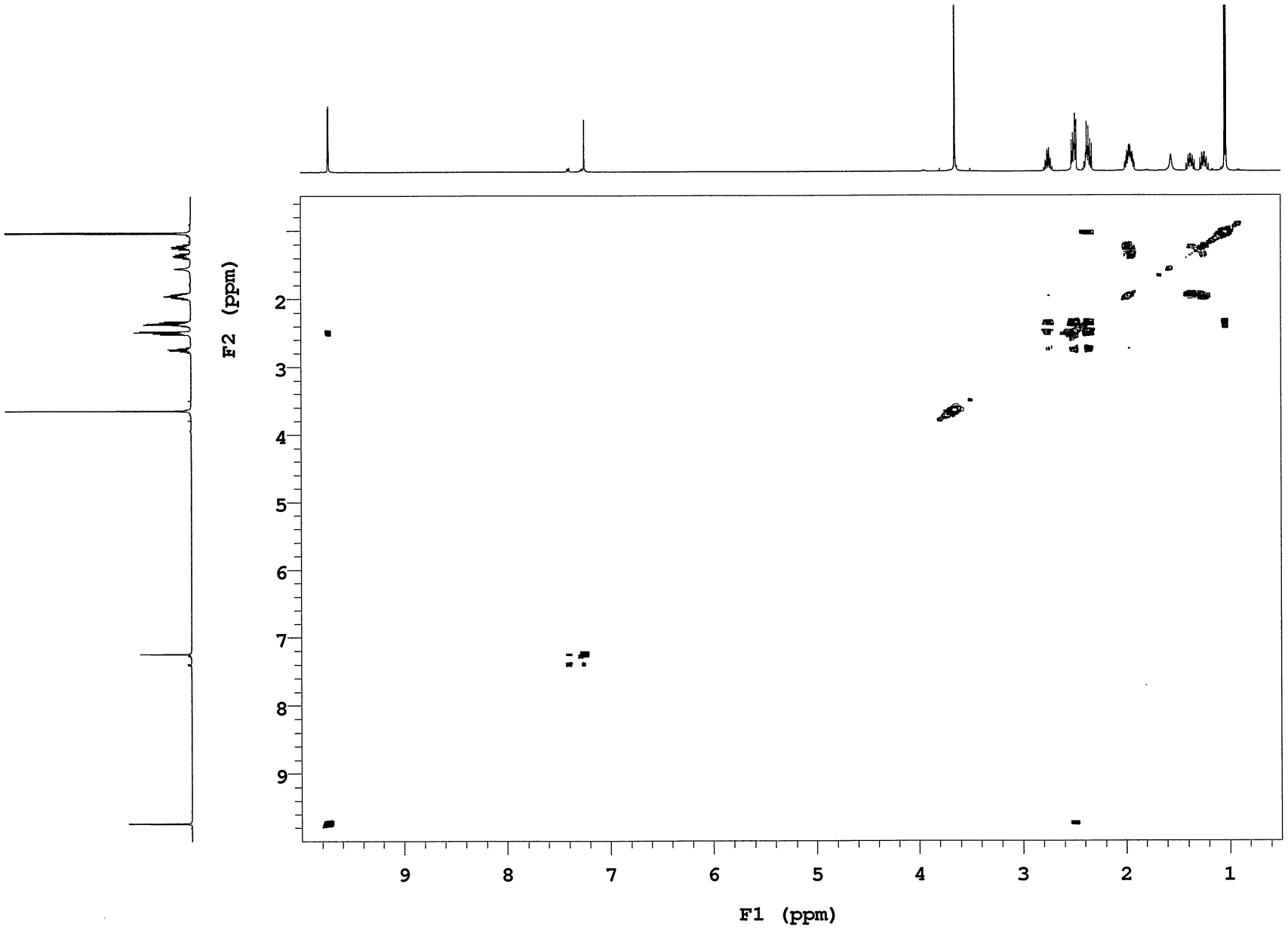
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-090-I/gHSQC_01

HSQC of compound 13

Plot date 2023-01-07

RRT-04-090-I

Sample Name	RRT-04-090-I	Pulse sequence	gCOSY	Temperature	25	Study owner	vnmr2
Date collected	2023-01-07	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



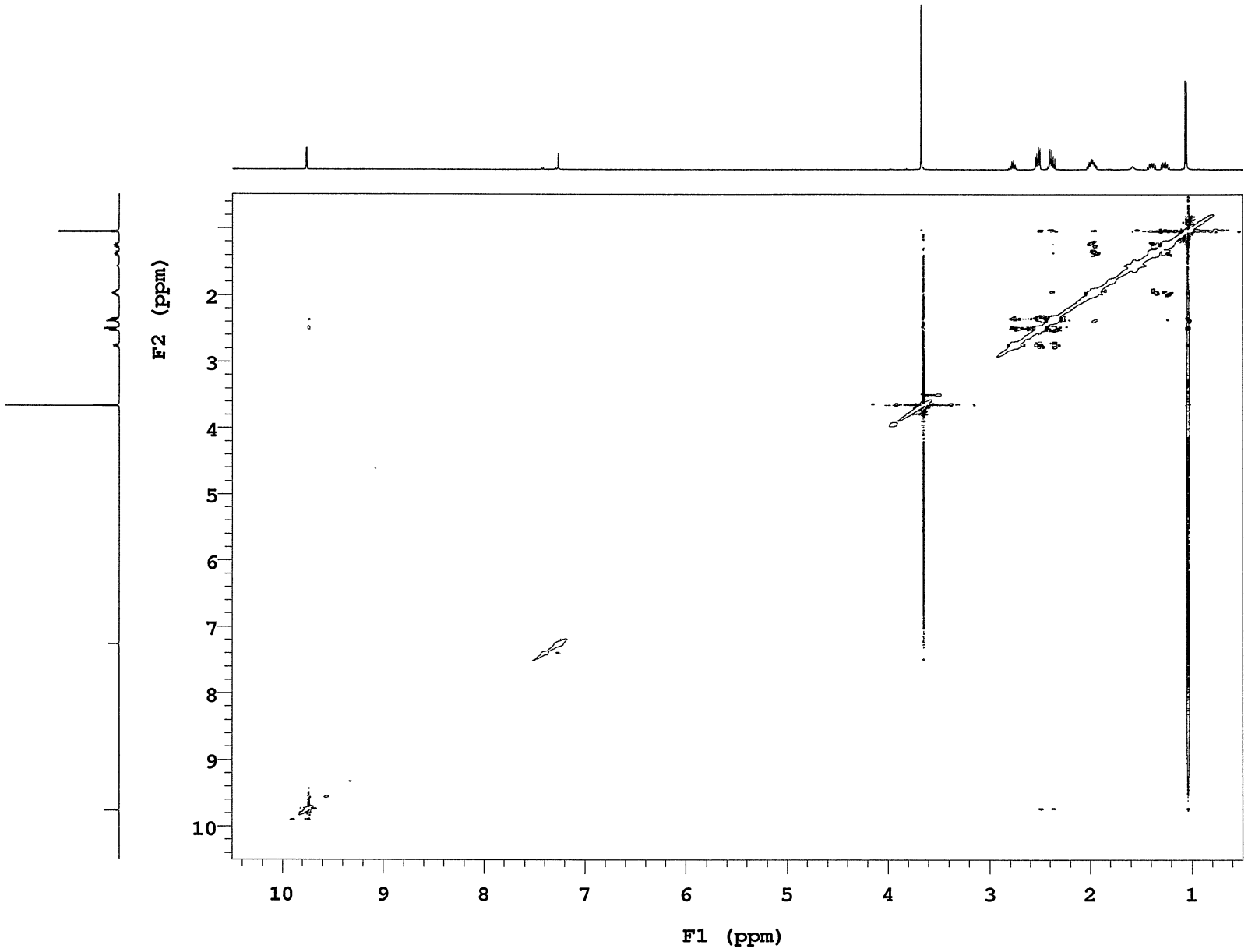
COSY of compound 13

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-090-I/gCOSY_01

Plot date 2023-01-07

RRT-04-090-I

Sample Name	RRT-04-090-I	Pulse sequence	NOESY	Temperature	25	Study owner	vnmr2
Date collected	2023-01-07	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



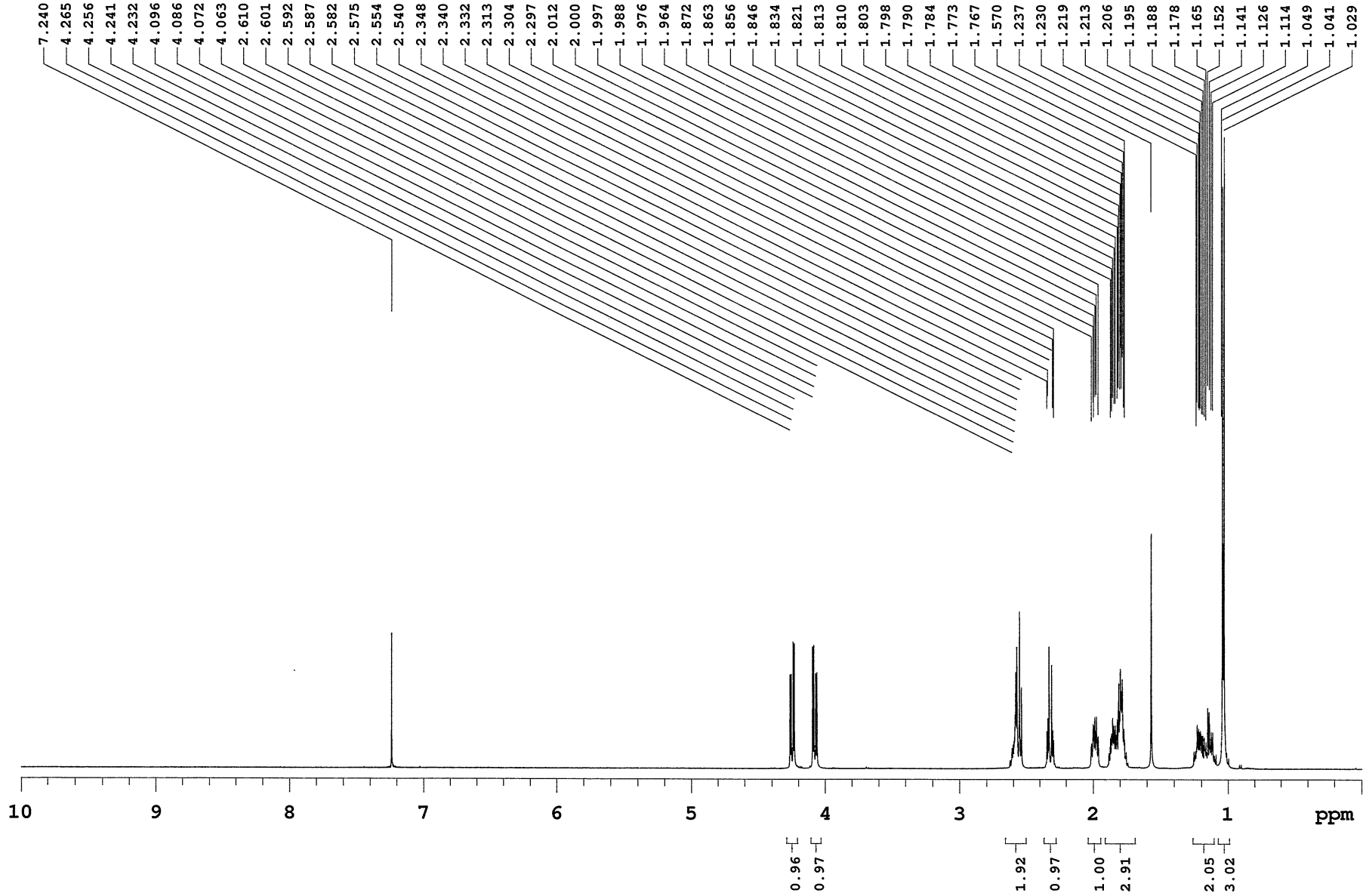
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-090-I/NOESY_01

NOESY of compound 13

Plot date 2023-01-30

RRT-262-solid

Sample Name **RRT-262-solid**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-10**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



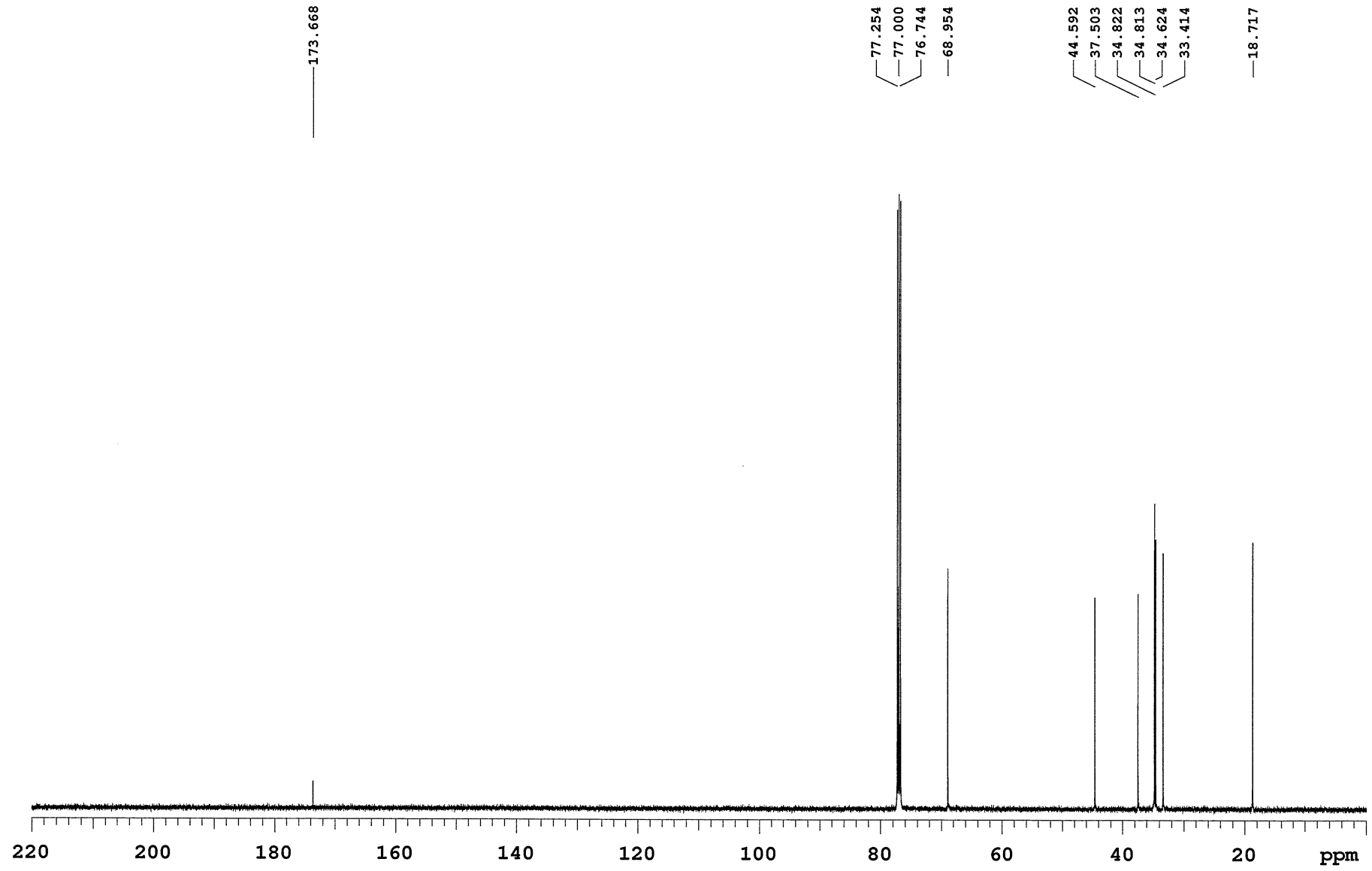
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-262-solid/PROTON_03

1H NMR (500 MHz, CDCl3) of compound 14

Plot date 2023-01-11

RRT-262-solid

Sample Name	RRT-262-solid	Pulse sequence	CARBON	Temperature	25	Study owner	vnmr2
Date collected	2023-01-10	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



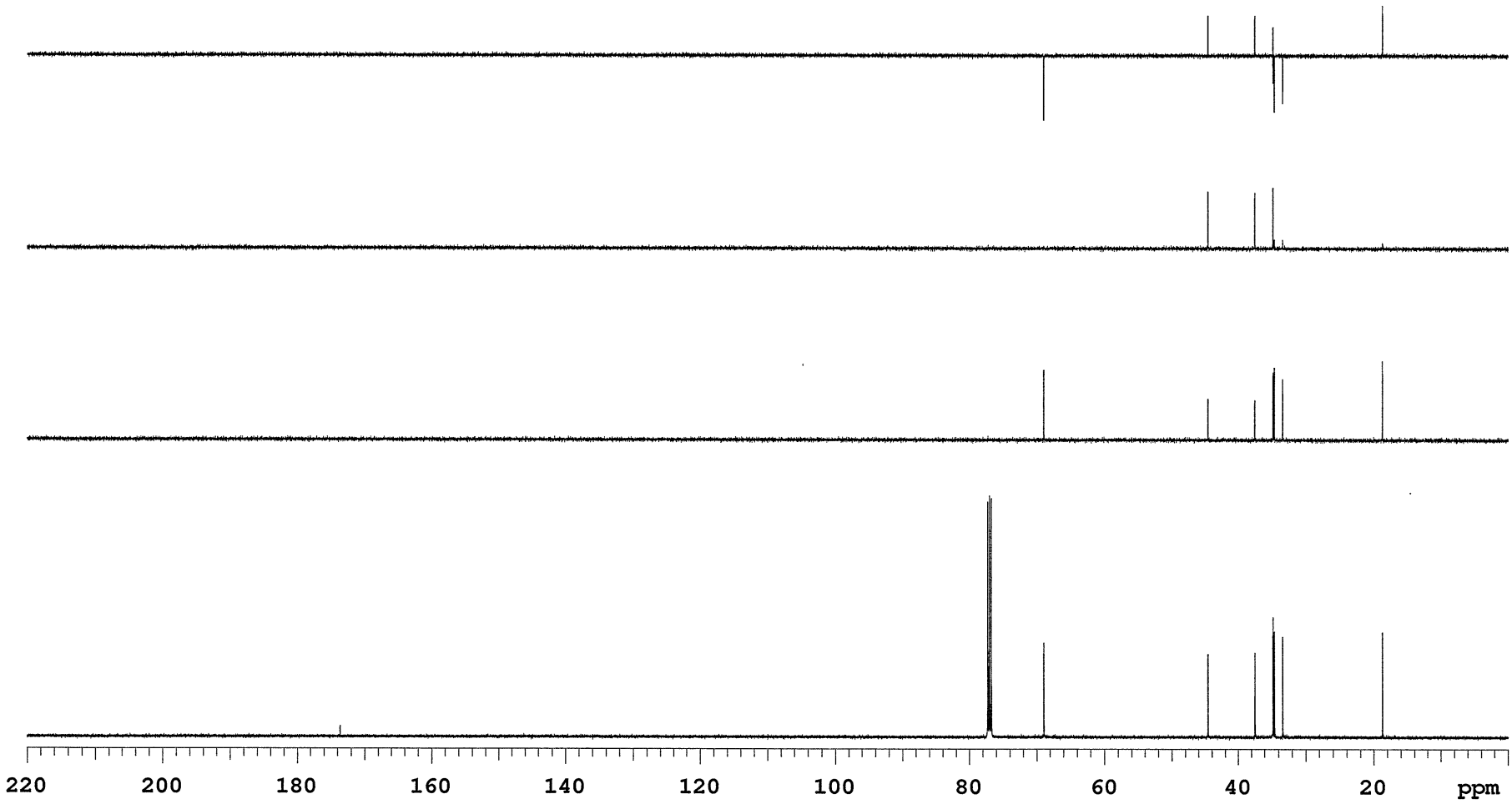
13C NMR (125 MHz, CDCl3) of compound 14

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-262-solid/CARBON_02

Plot date 2023-01-11

RRT-262-solid

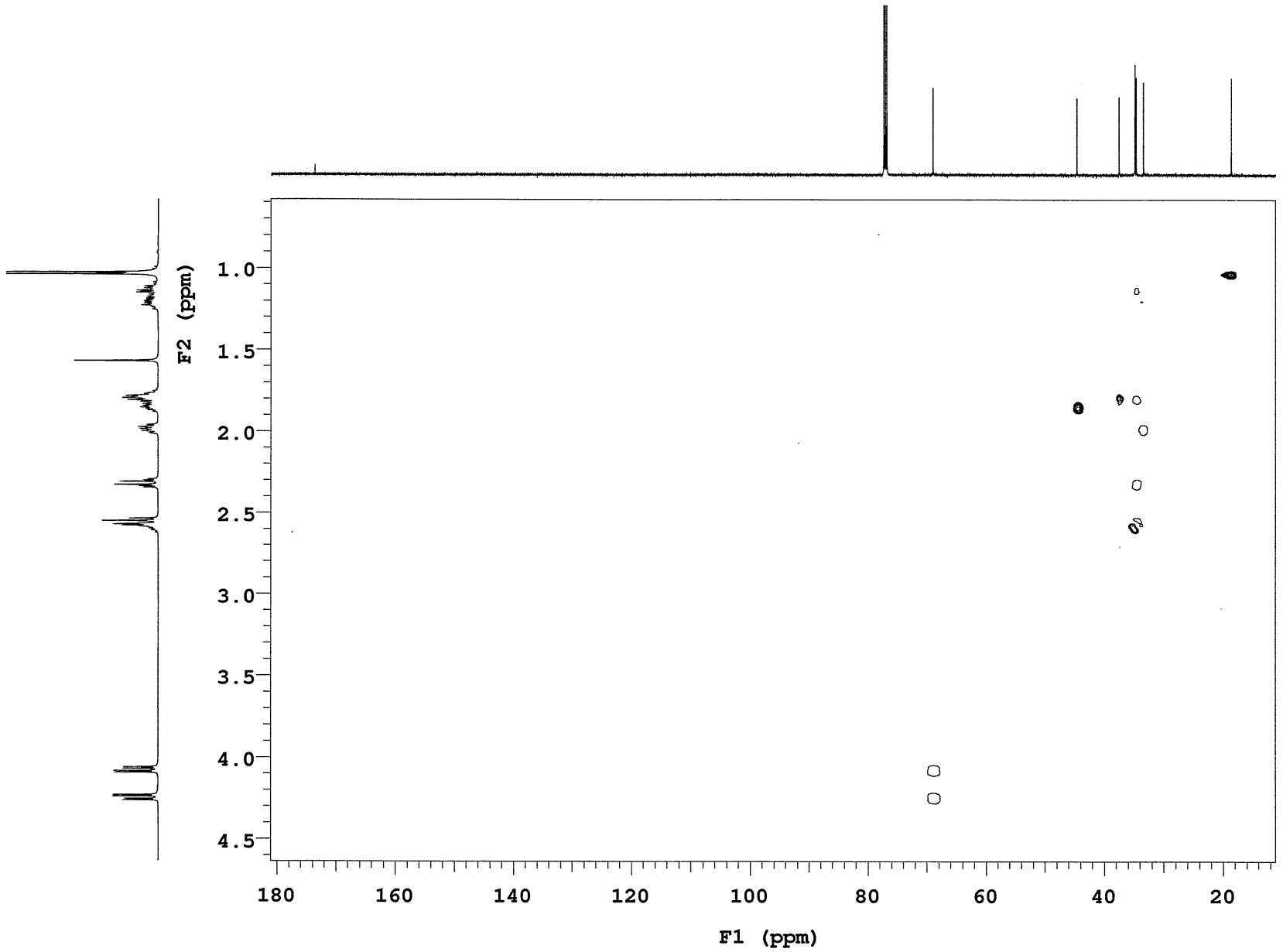
Sample Name **RRT-262-solid**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-10**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 14

RRT-262-solid

Sample Name	**RRT-262-solid**	Pulse sequence	**gHSQC**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2023-01-11**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



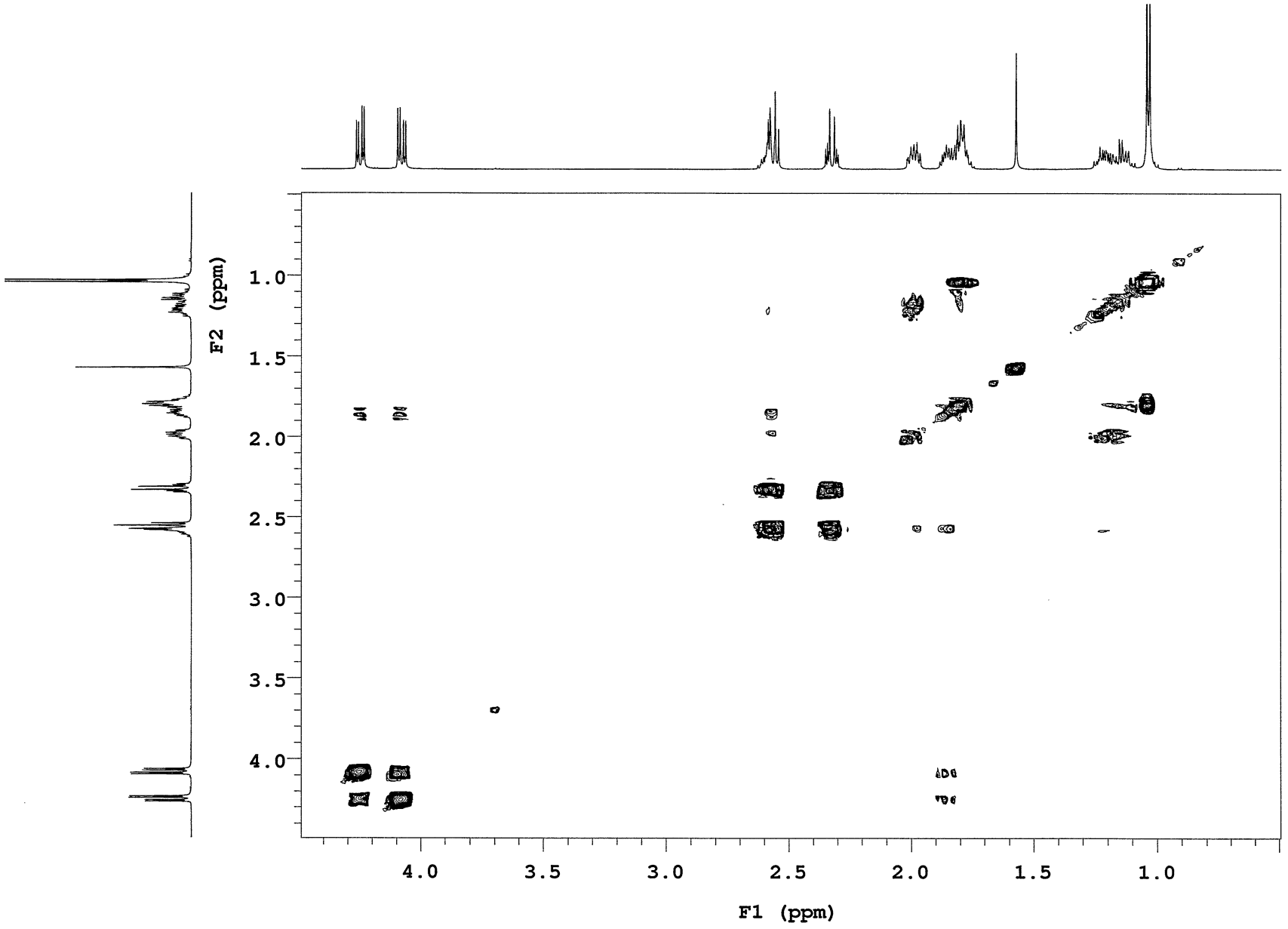
HSQC of compound 14

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-262-solid/gHSQC_01

Plot date 2023-01-11

RRT-262-solid

Sample Name	**RRT-262-solid**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2023-01-11**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



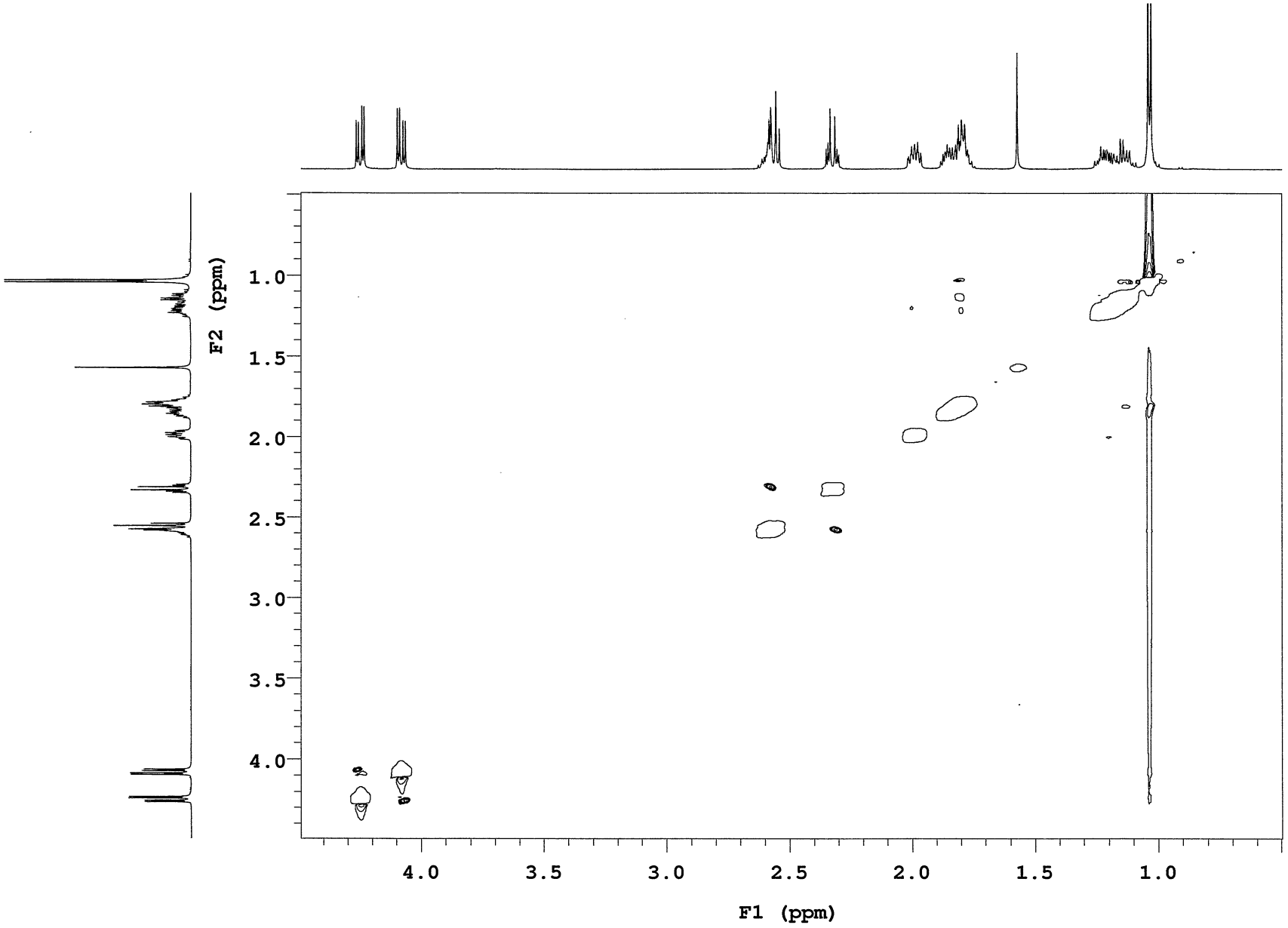
COSY of compound 14

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-262-solid/gCOSY_01

Plot date 2023-01-11

RRT-262-solid

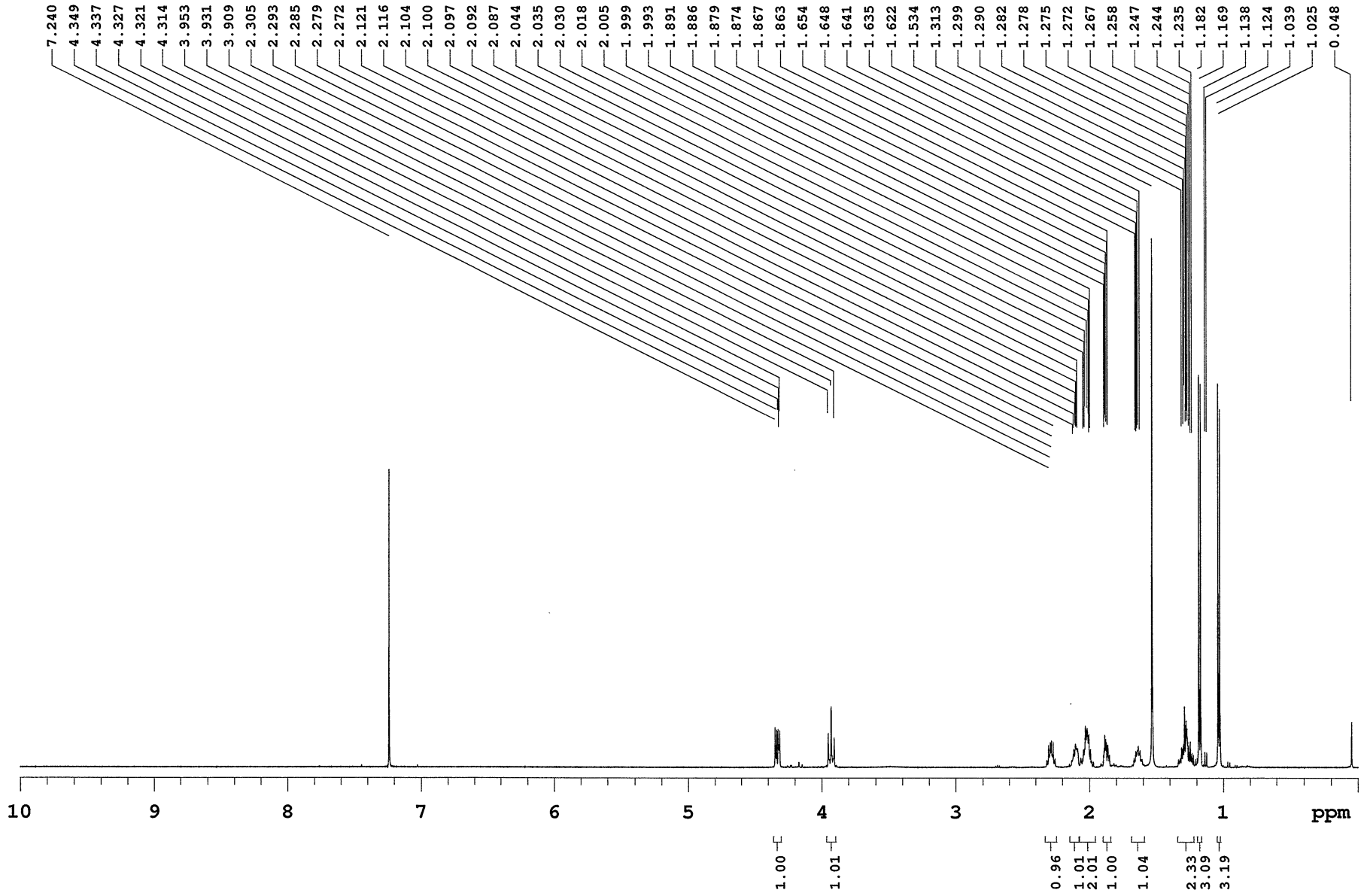
Sample Name	**RRT-262-solid**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2023-01-11**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



NOESY of compound 14

RRT-265

Sample Name	**RRT-265**	Pulse sequence	**PROTON**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2023-01-13**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



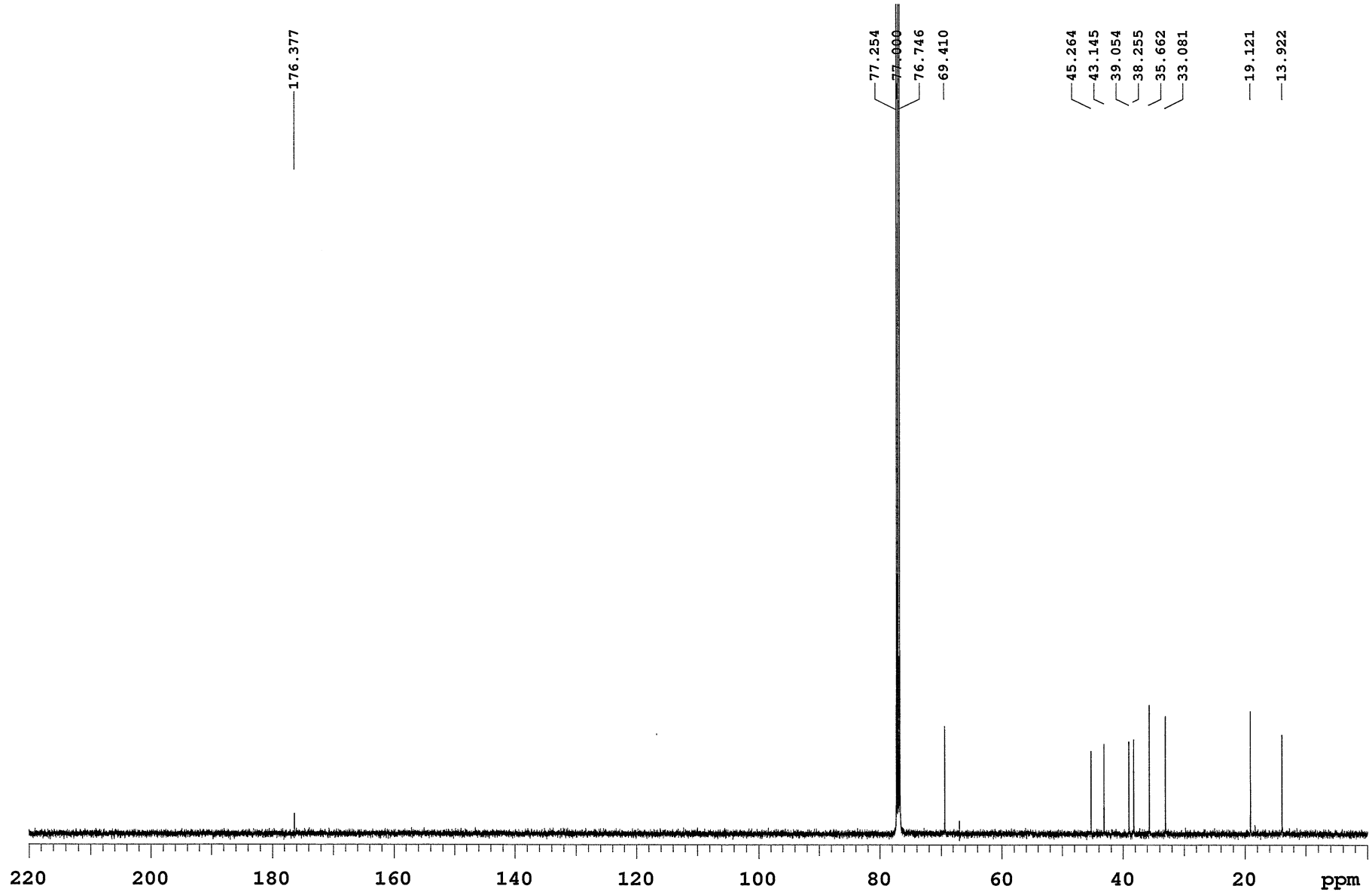
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-265/PROTON_03

1H NMR (500 MHz, CDCl3) of compound 15

Plot date 2023-01-14

RRT-265

Sample Name	RRT-265	Pulse sequence	CARBON	Temperature	25	Study owner	vnmr2
Date collected	2023-01-13	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



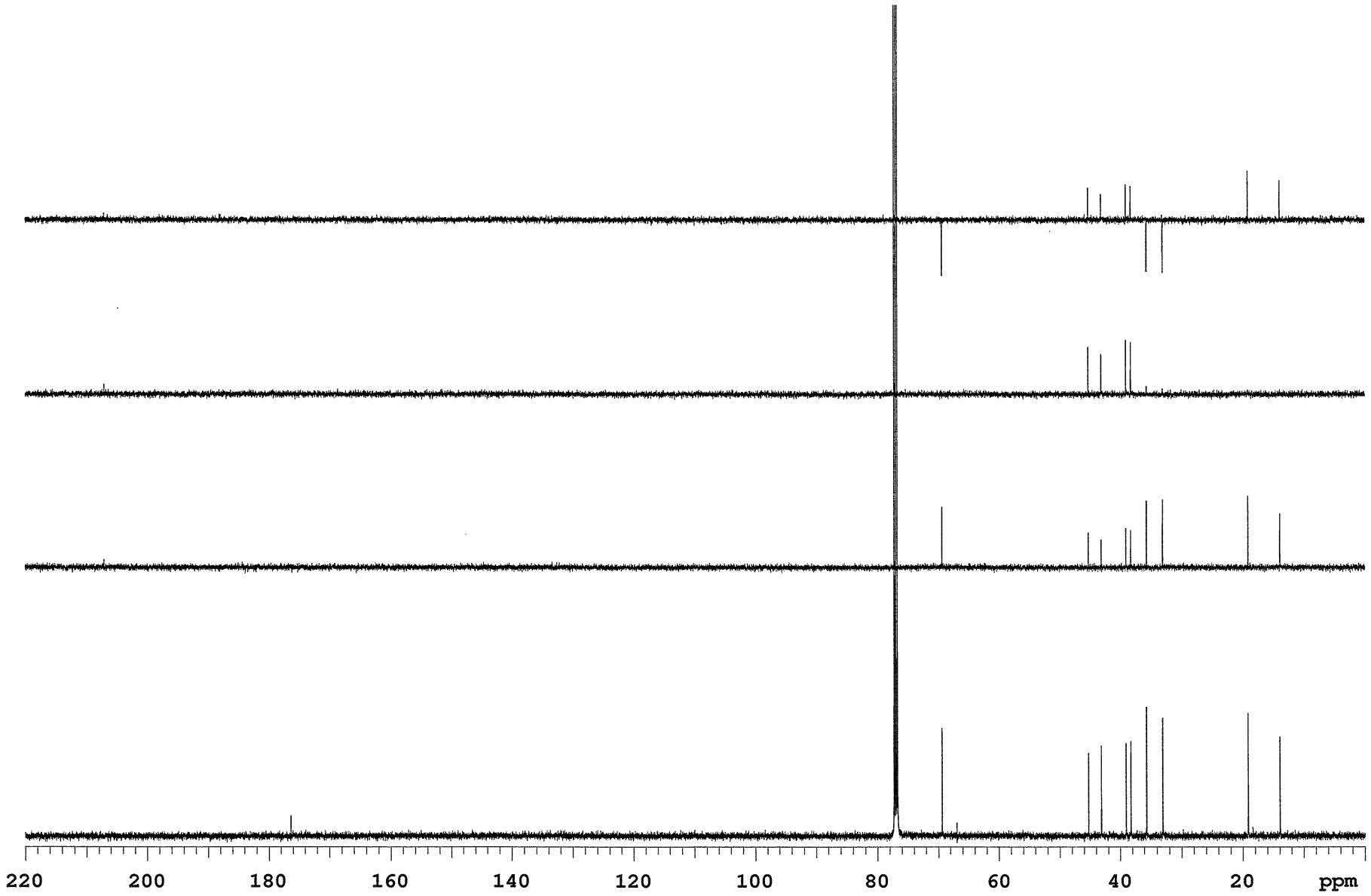
13C NMR (125 MHz, CDCl3) of compound 15

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-265/CARBON_02

Plot date 2023-01-14

RRT-265

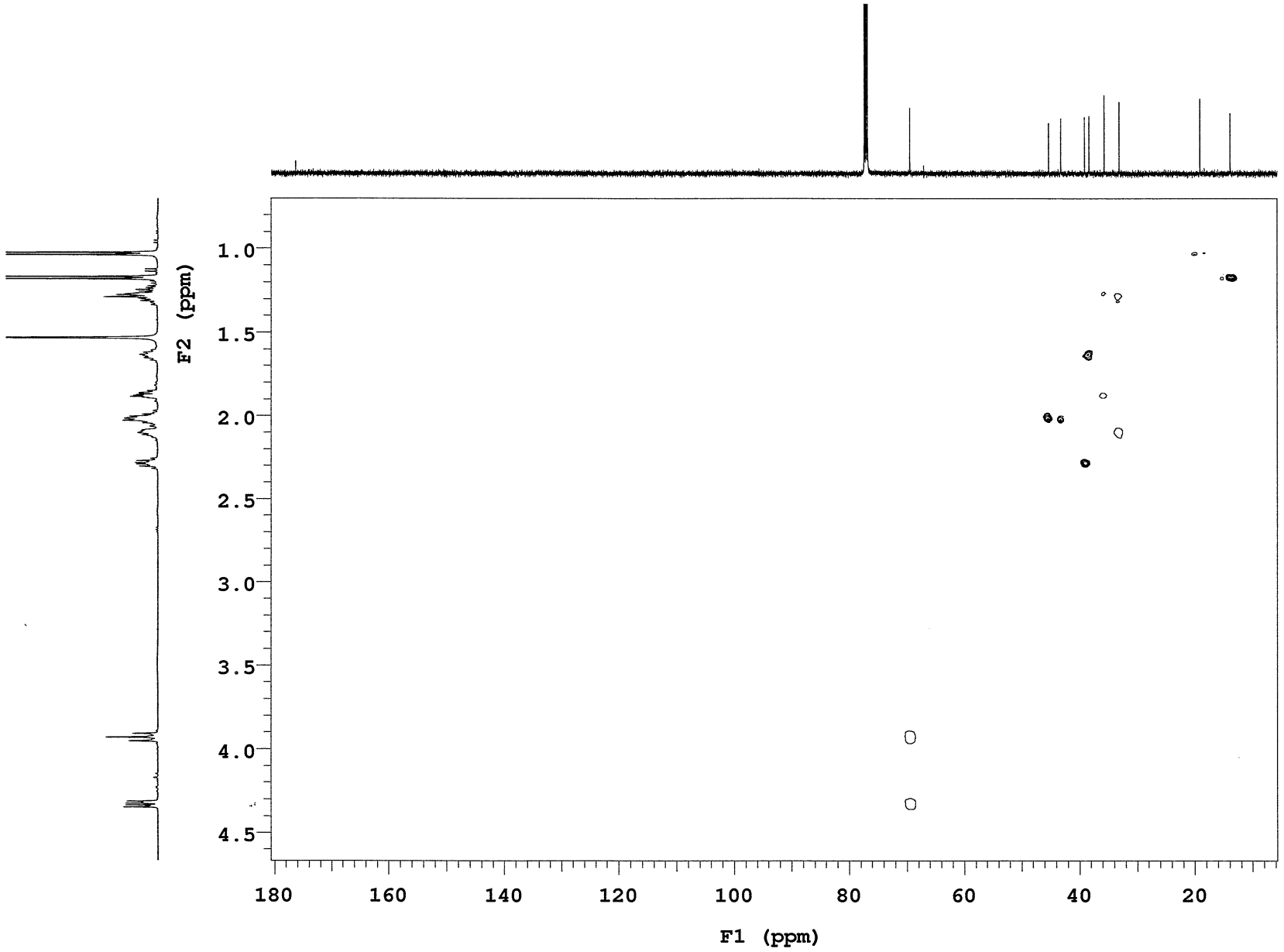
Sample Name **RRT-265**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-13**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of compound 15

RRT-265

Sample Name **RRT-265**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-14**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



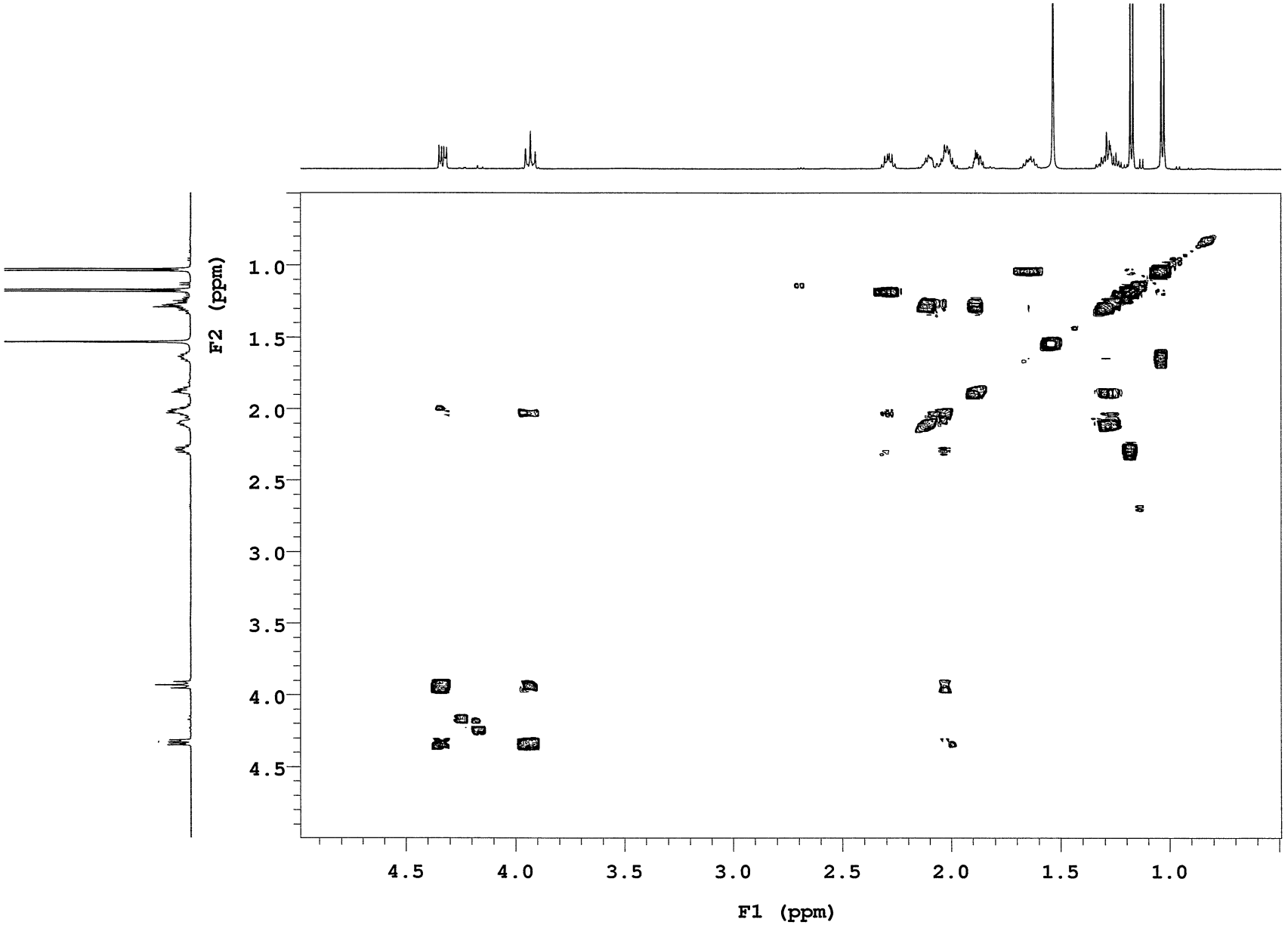
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-265/gHSQC_01

HSQC of compound 15

Plot date 2023-01-31

RRT-265

Sample Name **RRT-265**	Pulse sequence **gCOSY**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-14**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



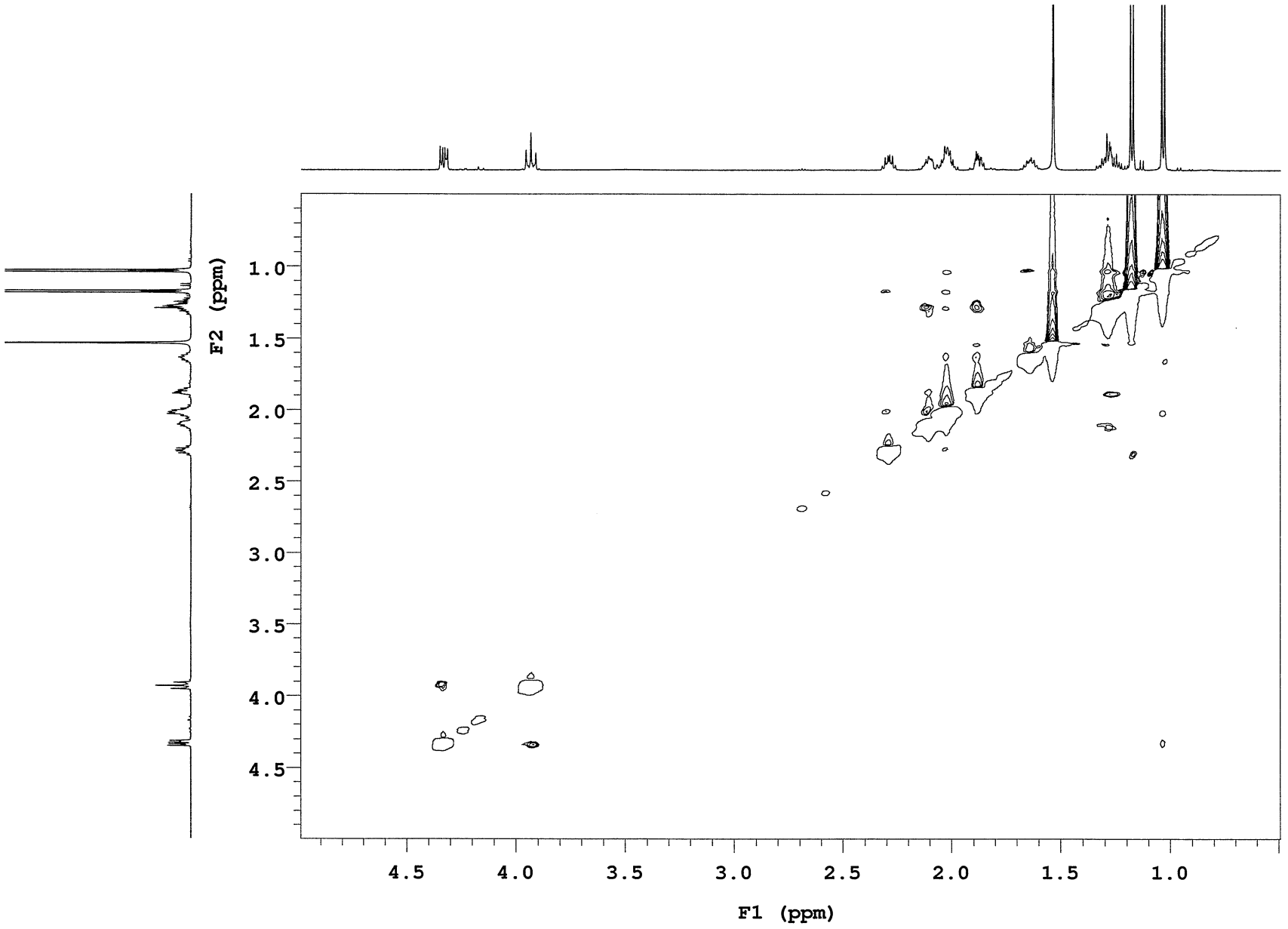
COSY of compound 15

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-265/gCOSY_01

Plot date 2023-01-14

RRT-265

Sample Name **RRT-265**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-14**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



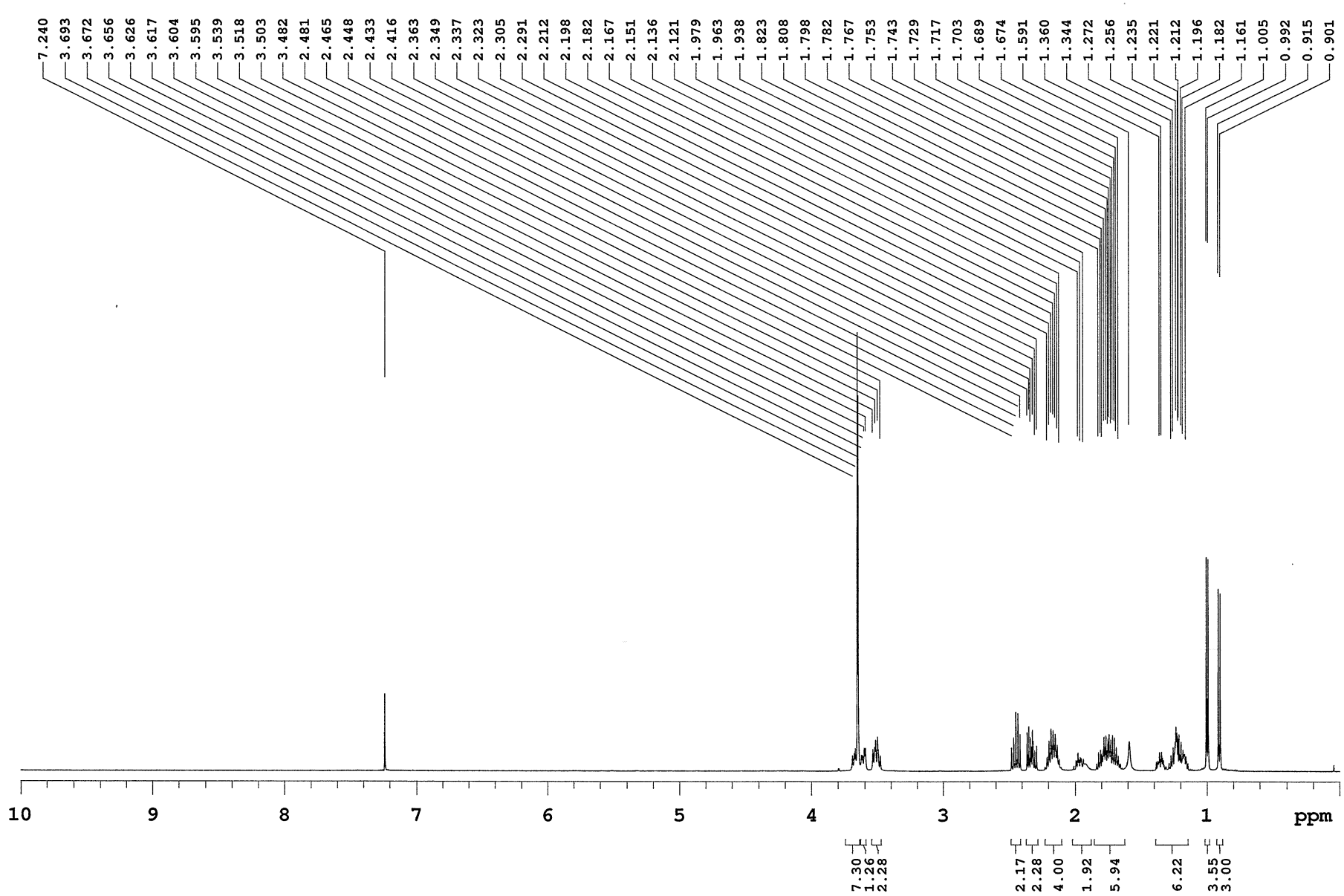
NOESY of compound 15

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-265/NOESY_01

Plot date 2023-01-14

RRT-241_and_RRT-264

Sample Name **RRT-241_and_RRT-264**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-14**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



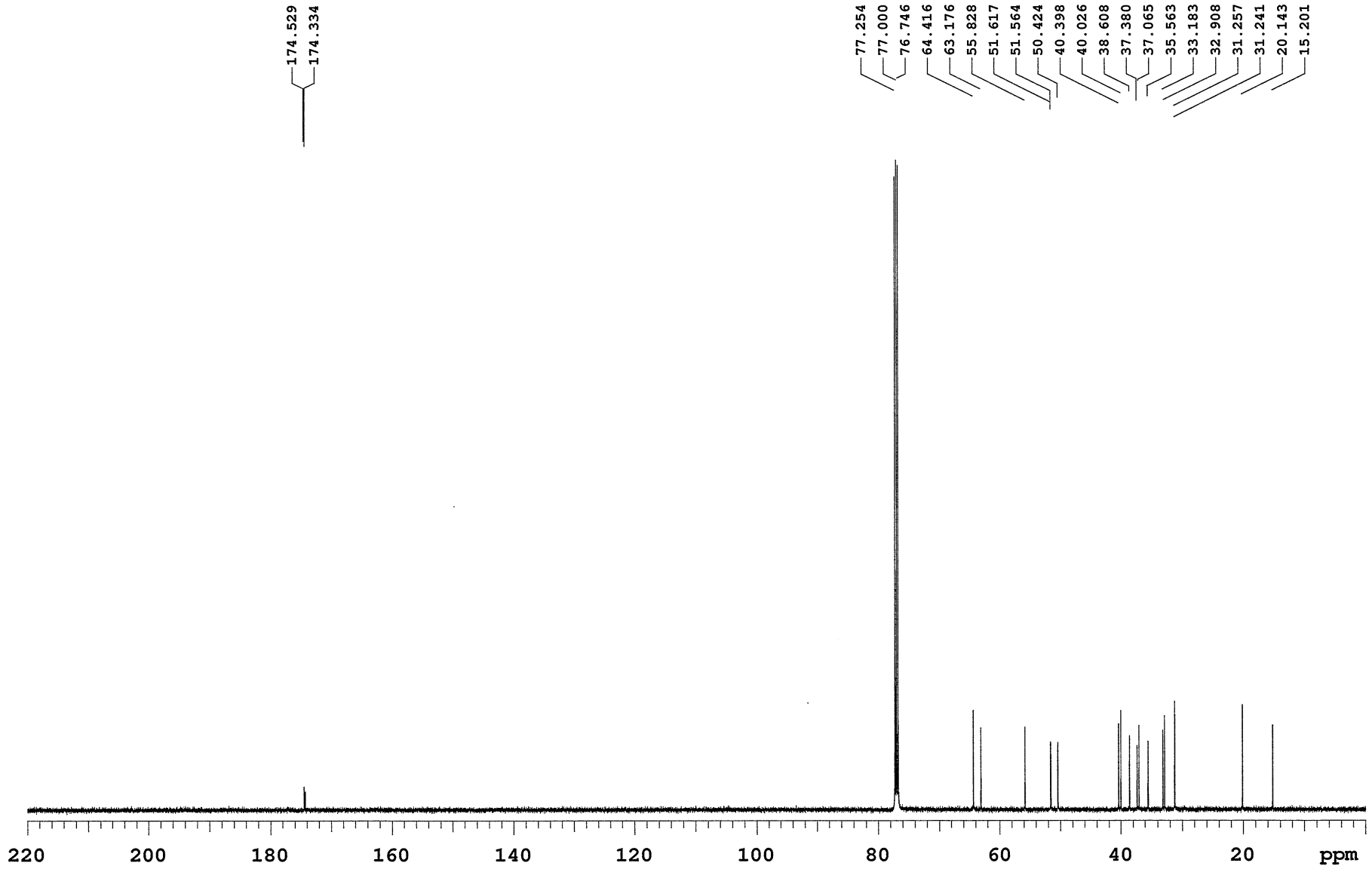
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-241_and_RRT-264/PROTON_03

1H NMR (500 MHz, CDCl3) of the mixture of **4** and **16** (Scheme 3)

Plot date 2023-01-16

RRT-241_and_RRT-264

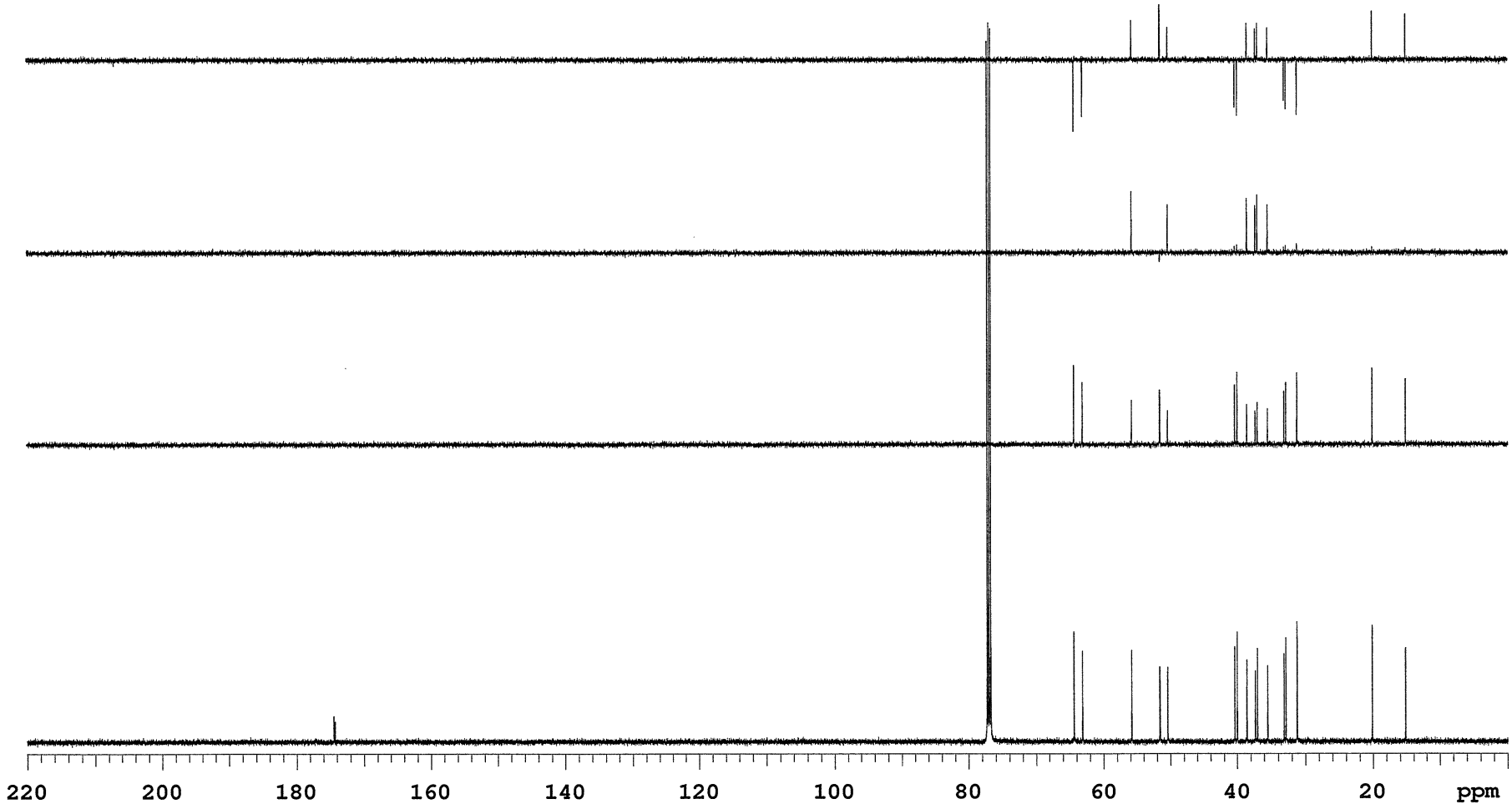
Sample Name **RRT-241_and_RRT-264**	Pulse sequence **CARBON**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-14**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



13C NMR (125 MHz, CDCl3) of the mixture of **4** and **16** (Scheme 3)

RRT-241_and_RRT-264

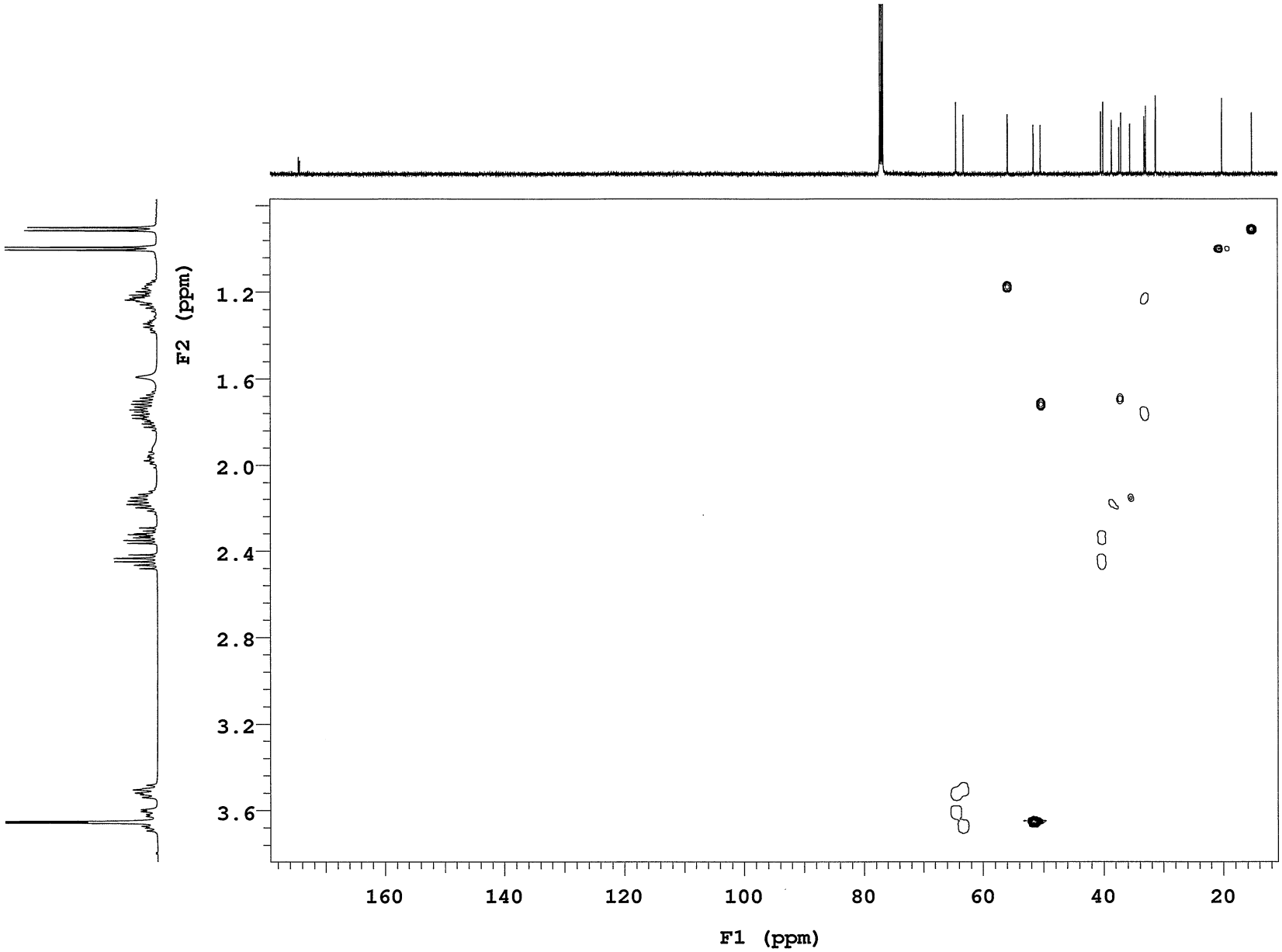
Sample Name **RRT-241_and_RRT-264**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-14**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of the mixture of **4** and **16** (Scheme 3)

RRT-241_and_RRT-264

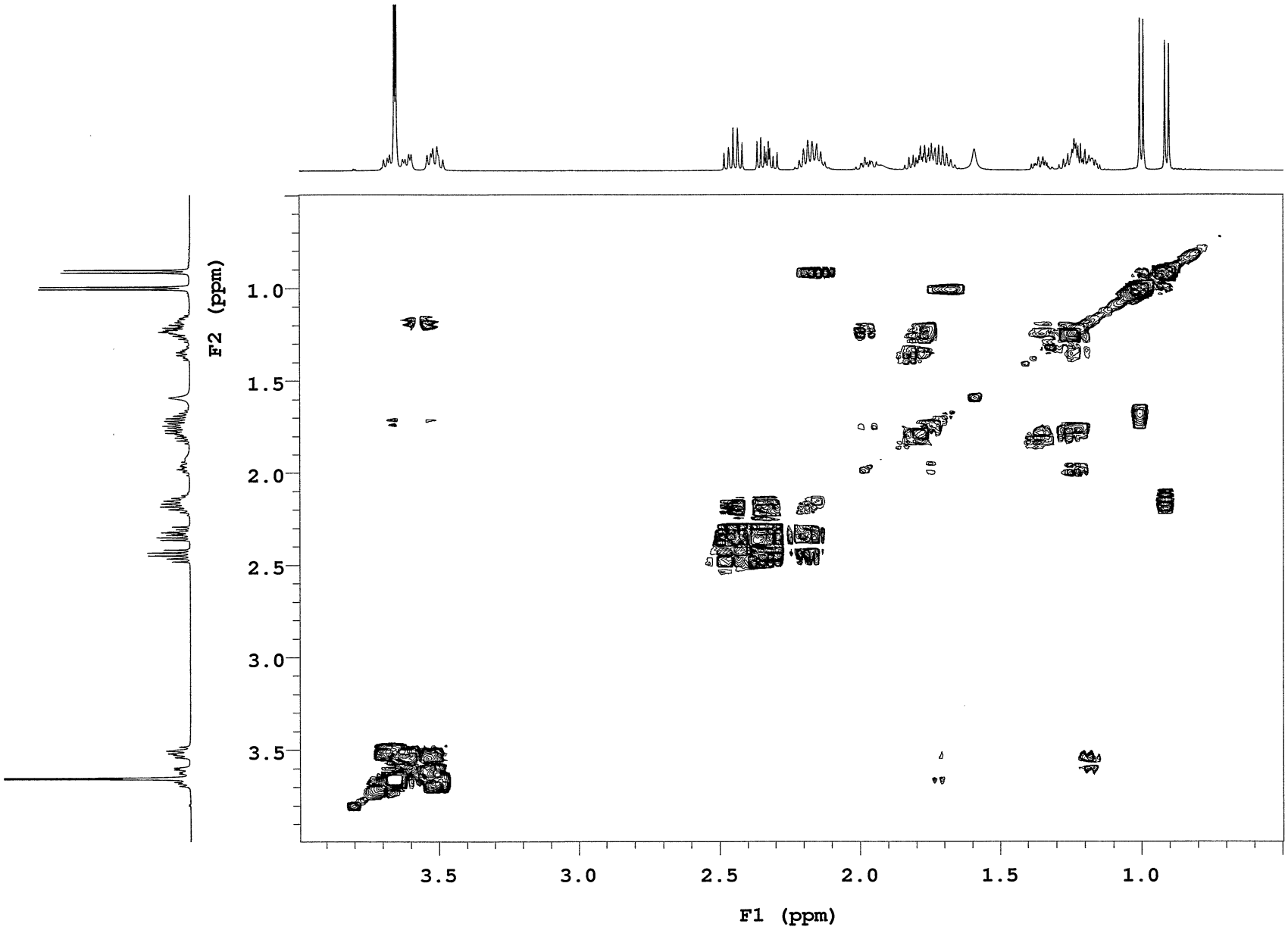
Sample Name **RRT-241_and_RRT-264**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-15**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



HSQC of the mixture of **4** and **16** (Scheme 3)

RRT-241_and_RRT-264

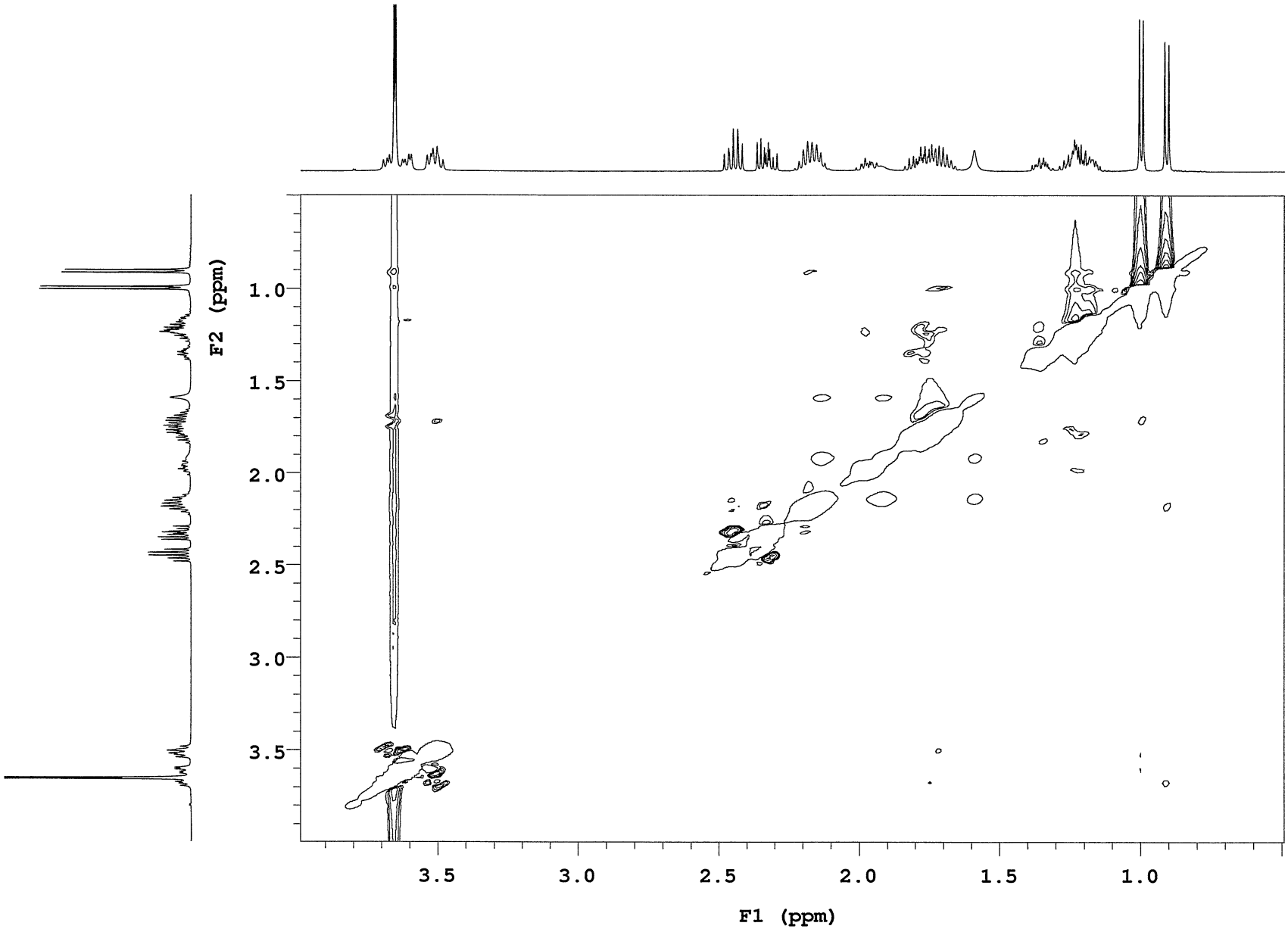
Sample Name	RRT-241_and_RRT-264	Pulse sequence	gCOSY	Temperature	25	Study owner	vnmr2
Date collected	2023-01-15	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



COSY of the mixture of **4** and **16** (Scheme 3)

RRT-241_and_RRT-264

Sample Name **RRT-241_and_RRT-264**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2023-01-15**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



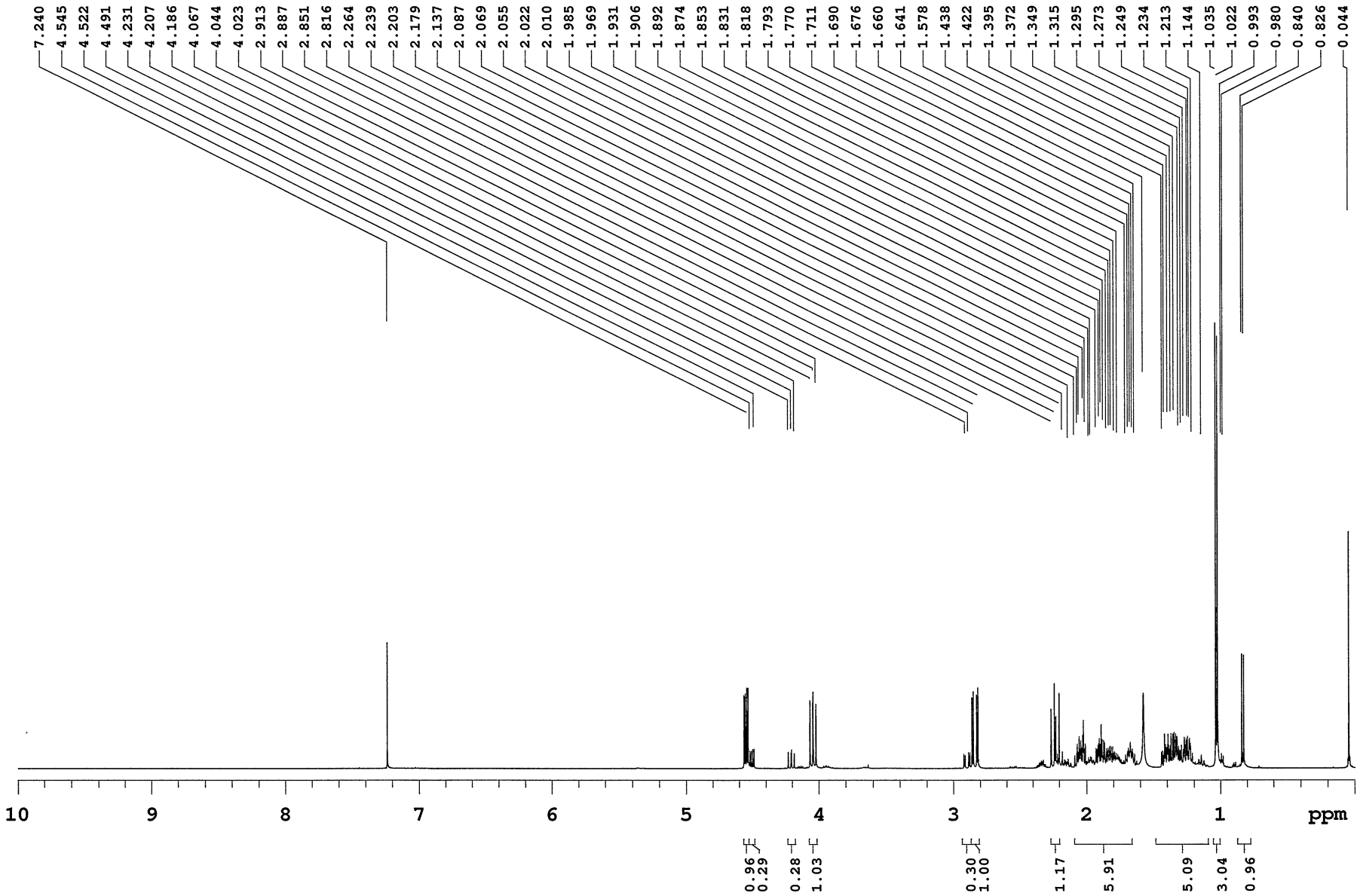
NOESY of the mixture of **4** and **16** (Scheme 3)

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-241_and_RRT-264/NOESY_01

Plot date 2023-01-16

RRT-04-071

Sample Name	RRT-04-071	Pulse sequence	PROTON	Temperature	25	Study owner	vnmr2
Date collected	2022-10-31	Solvent	cdcl3	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2



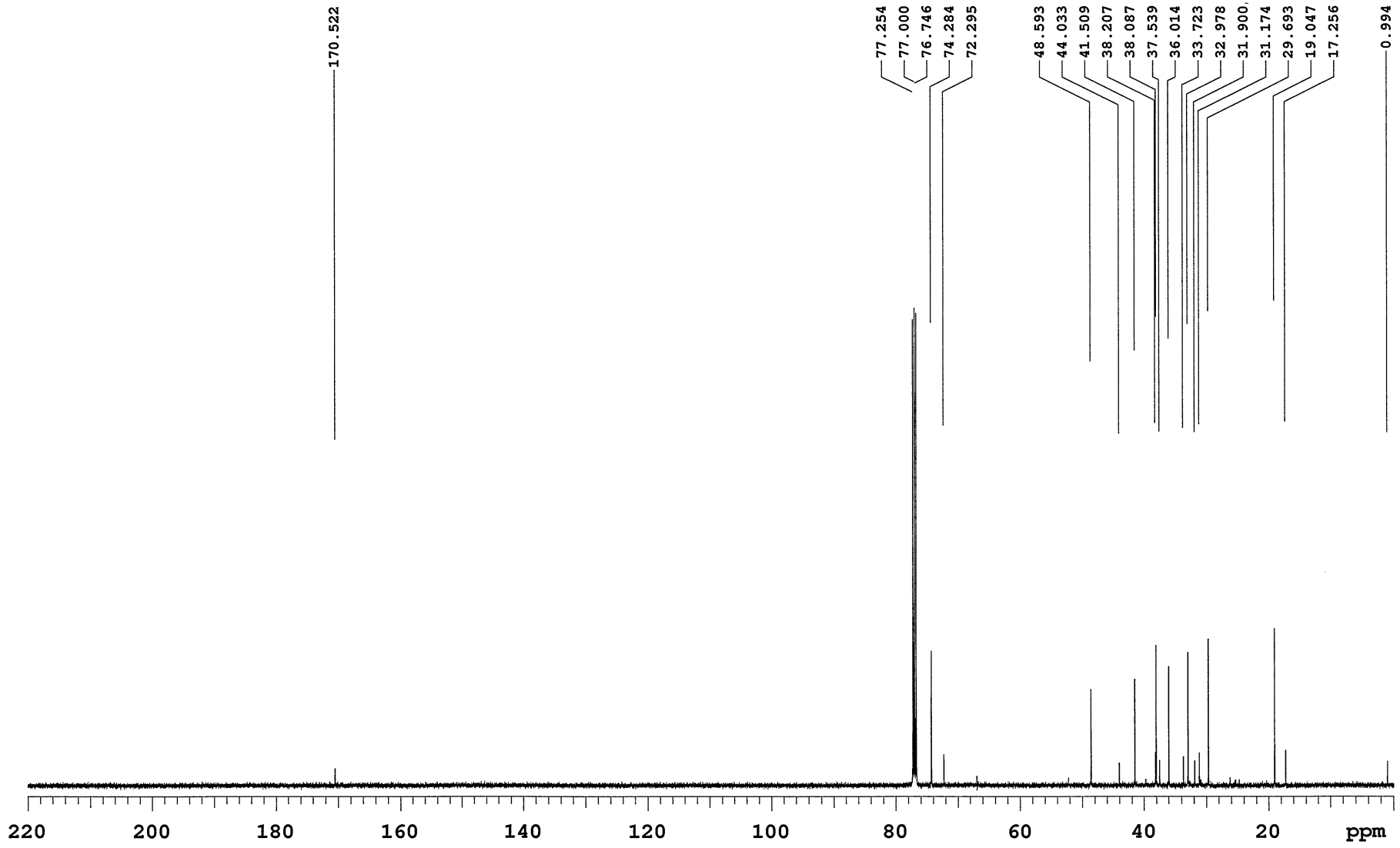
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-071/PROTON_03.fid

1H NMR (500 MHz, CDCl3) of the mixture of **5** and **17** (Scheme 3)

Plot date 2022-11-30

RRT-04-071

Sample Name **RRT-04-071**	Pulse sequence **CARBON**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-31**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



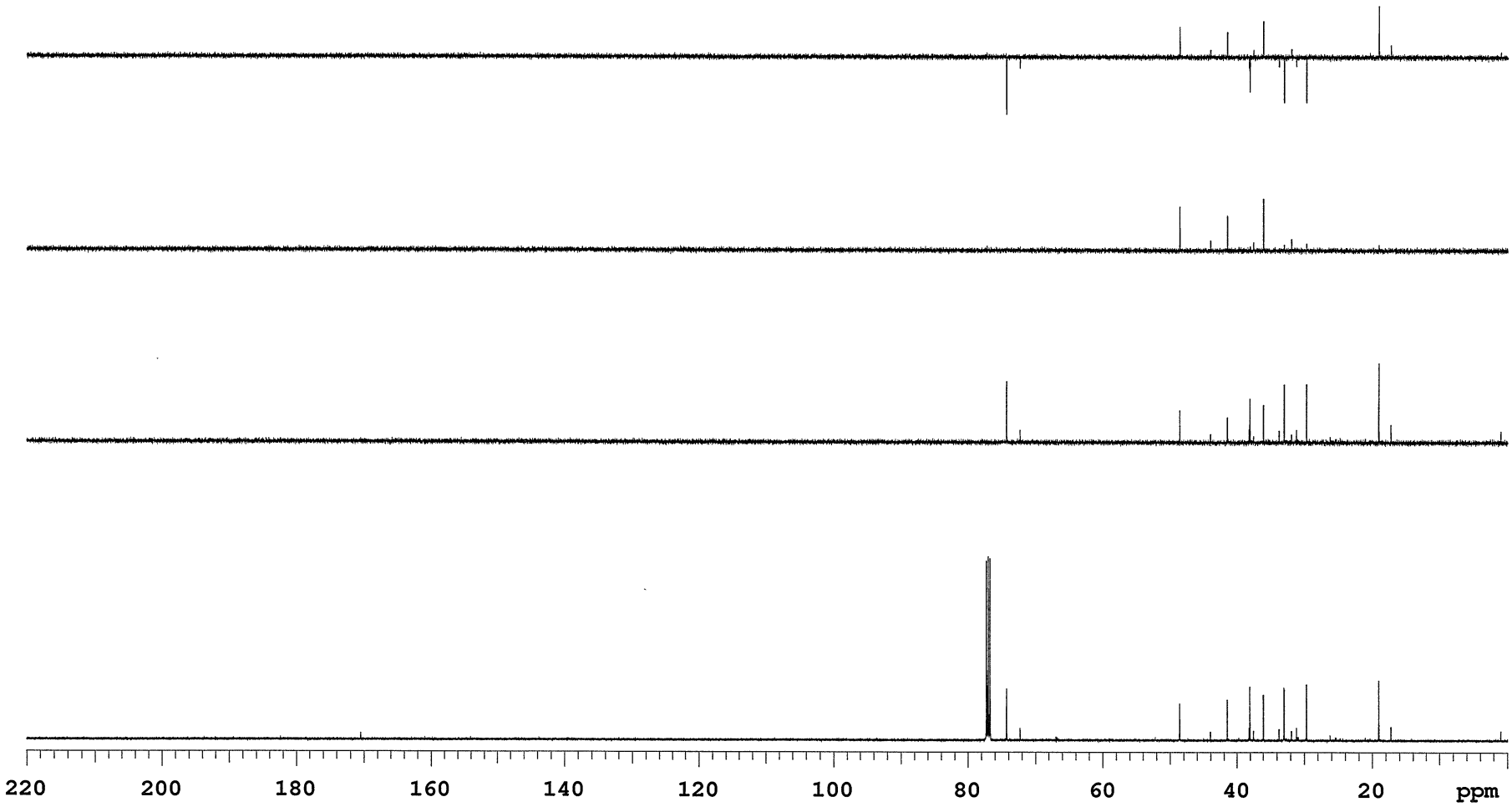
13C NMR (125 MHz, CDCl3) of the mixture of **5** and **17** (Scheme 3)

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-071/CARBON_02

Plot date 2022-11-01

RRT-04-071

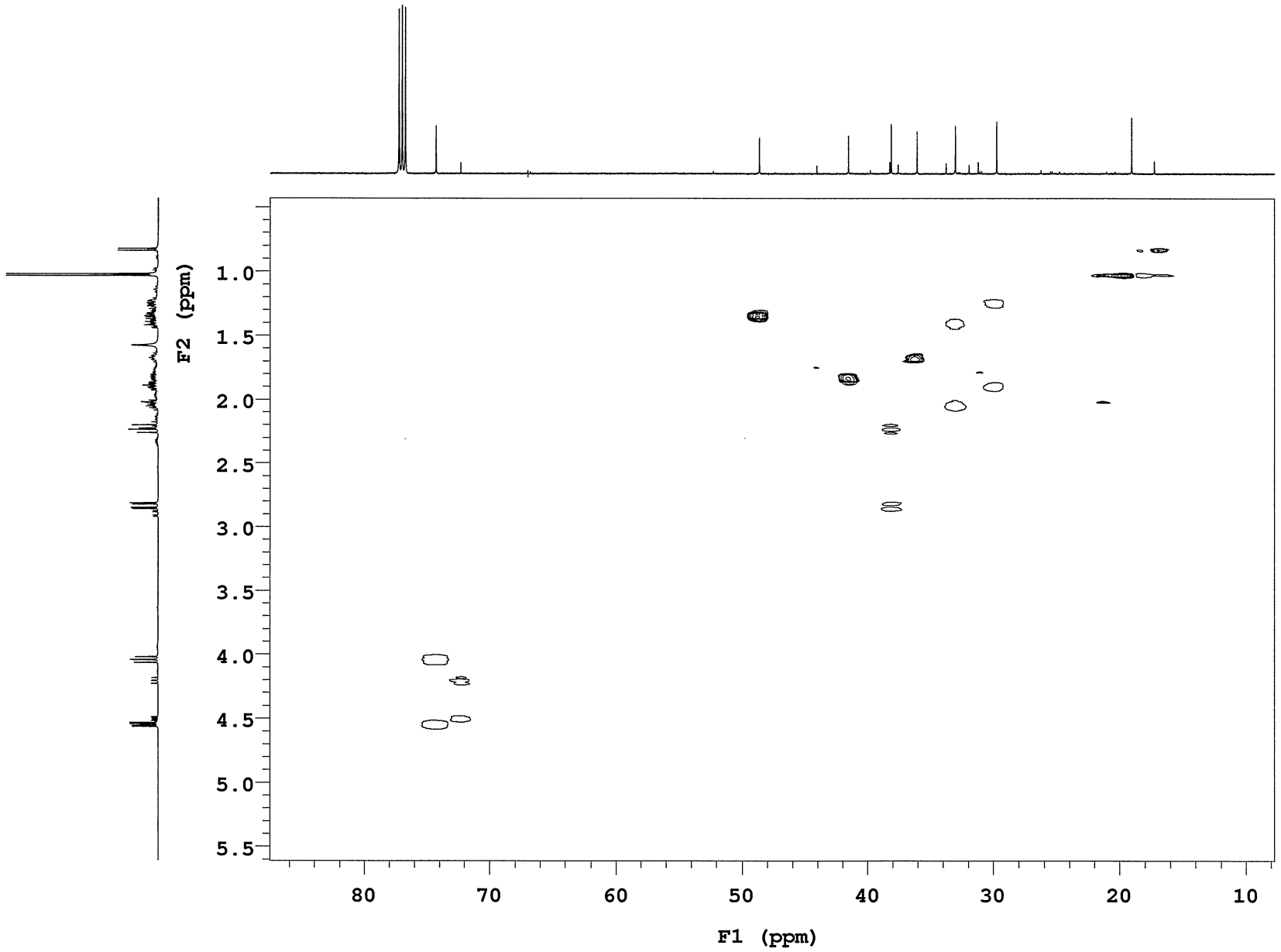
Sample Name **RRT-04-071**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-10-31**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



DEPT of the mixture of **5** and **17** (Scheme 3)

RRT-04-071

Sample Name **RRT-04-071**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-11-01**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



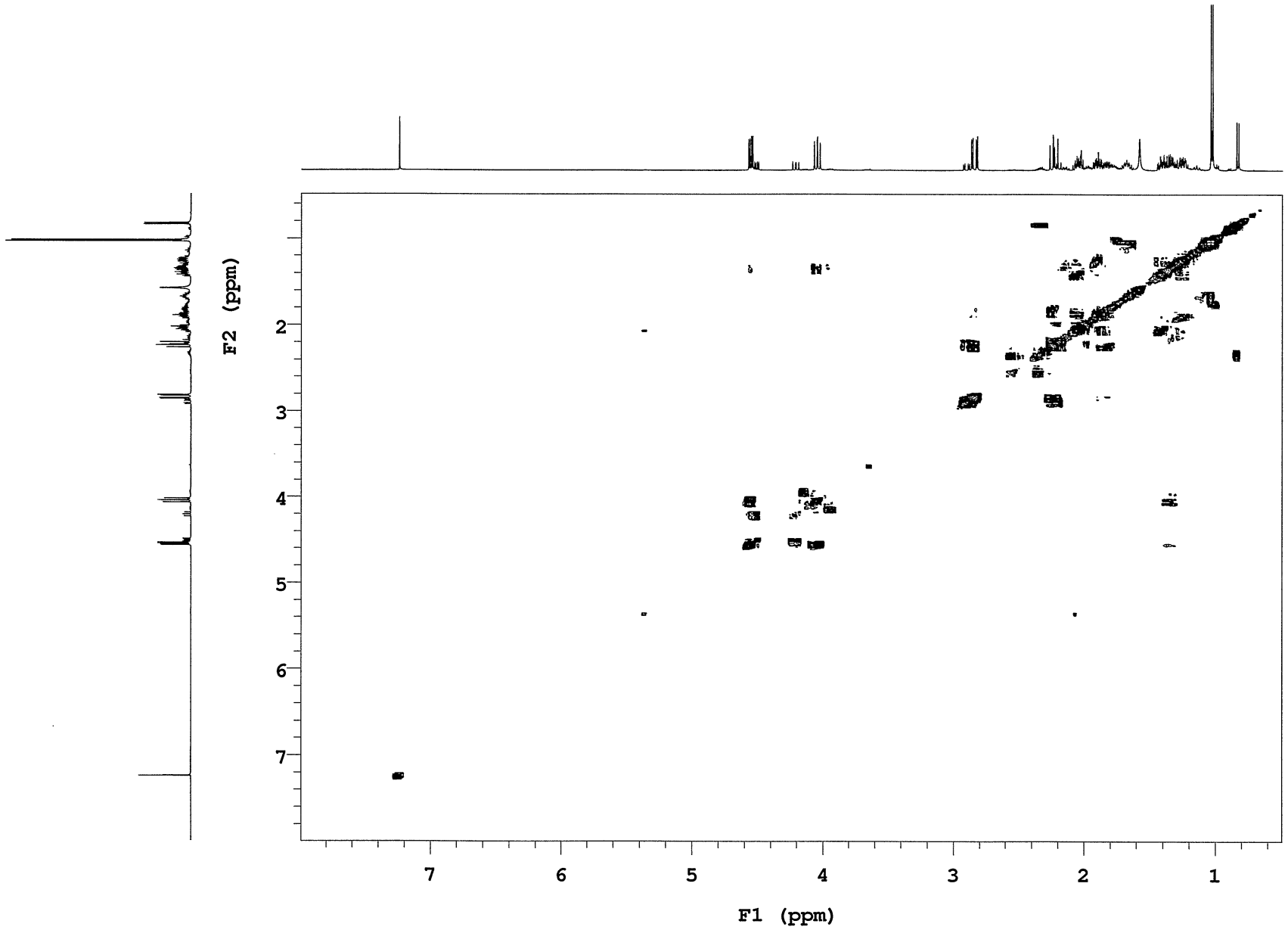
Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-071/gHSQC_01

HSQC of the mixture of **5** and **17** (Scheme 3)

Plot date 2022-11-01

RRT-04-071

Sample Name **RRT-04-071**	Pulse sequence **gCOSY**	Temperature **25**	Study owner **vnmr2**
Date collected **2022-11-01**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



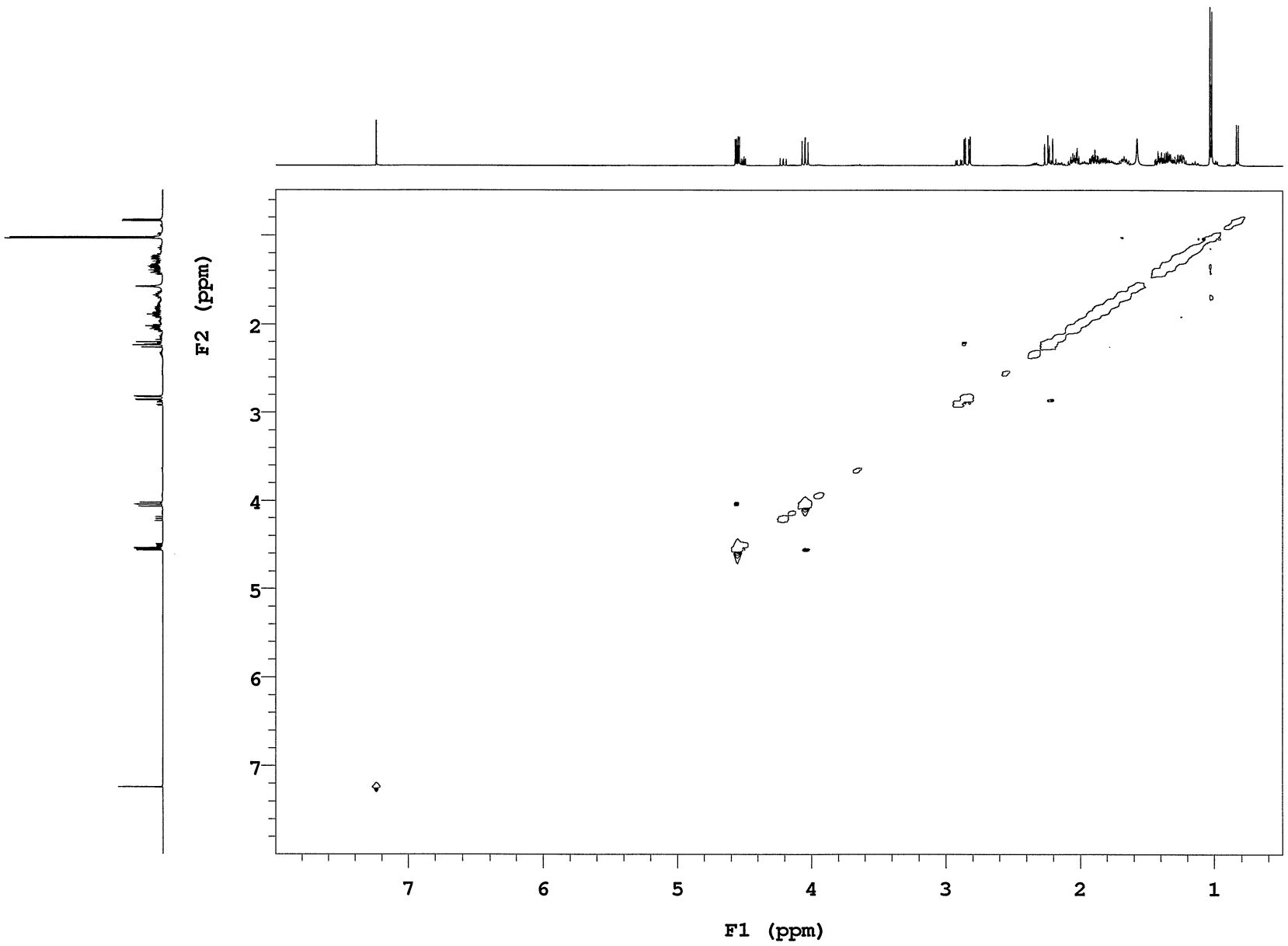
COSY of the mixture of **5** and **17** (Scheme 3)

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-071/gCOSY_01

Plot date 2022-11-01

RRT-04-071

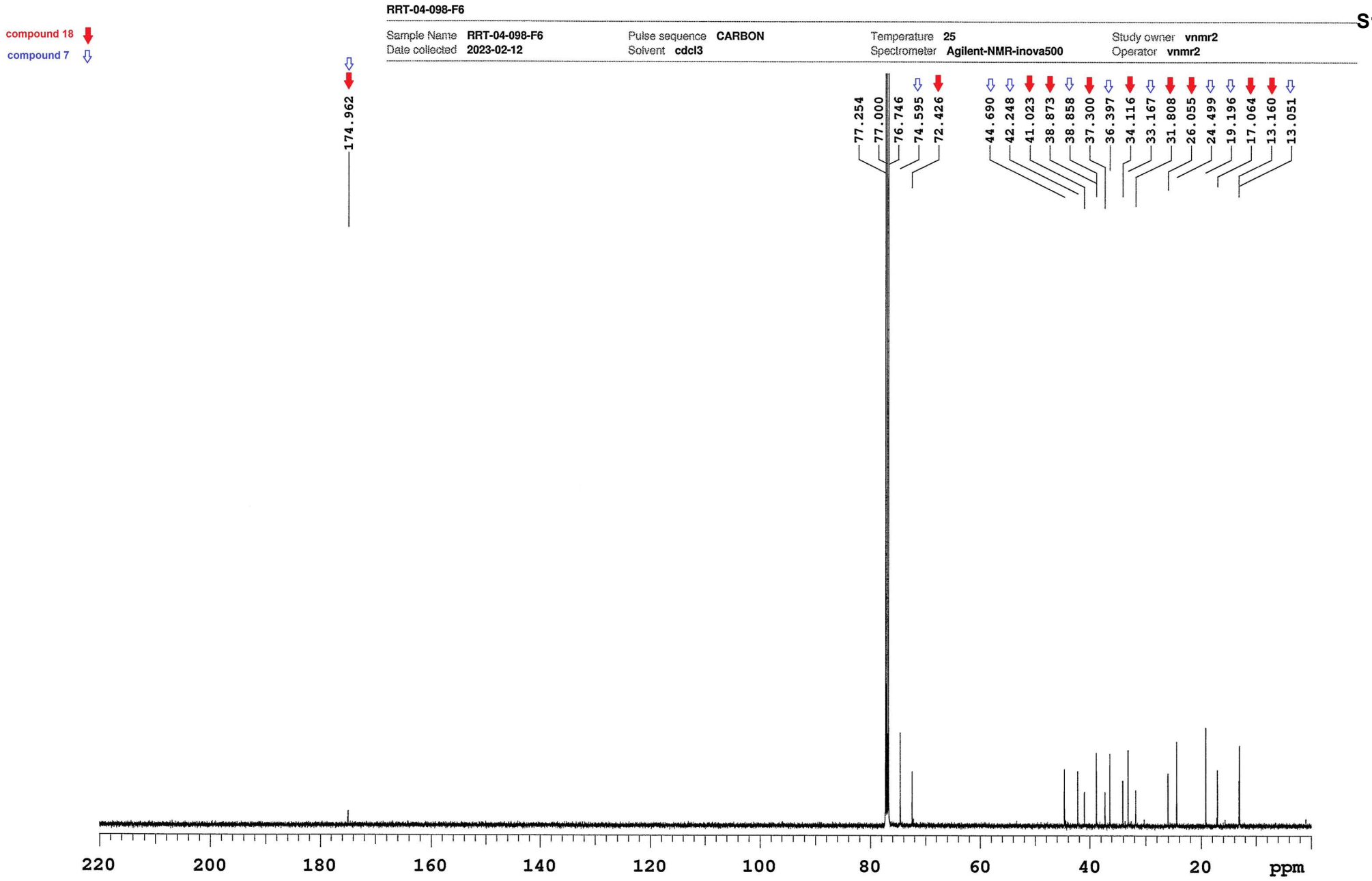
Sample Name	**RRT-04-071**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2022-11-01**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-071/NOESY_01

NOESY of the mixture of **5** and **17** (Scheme 3)

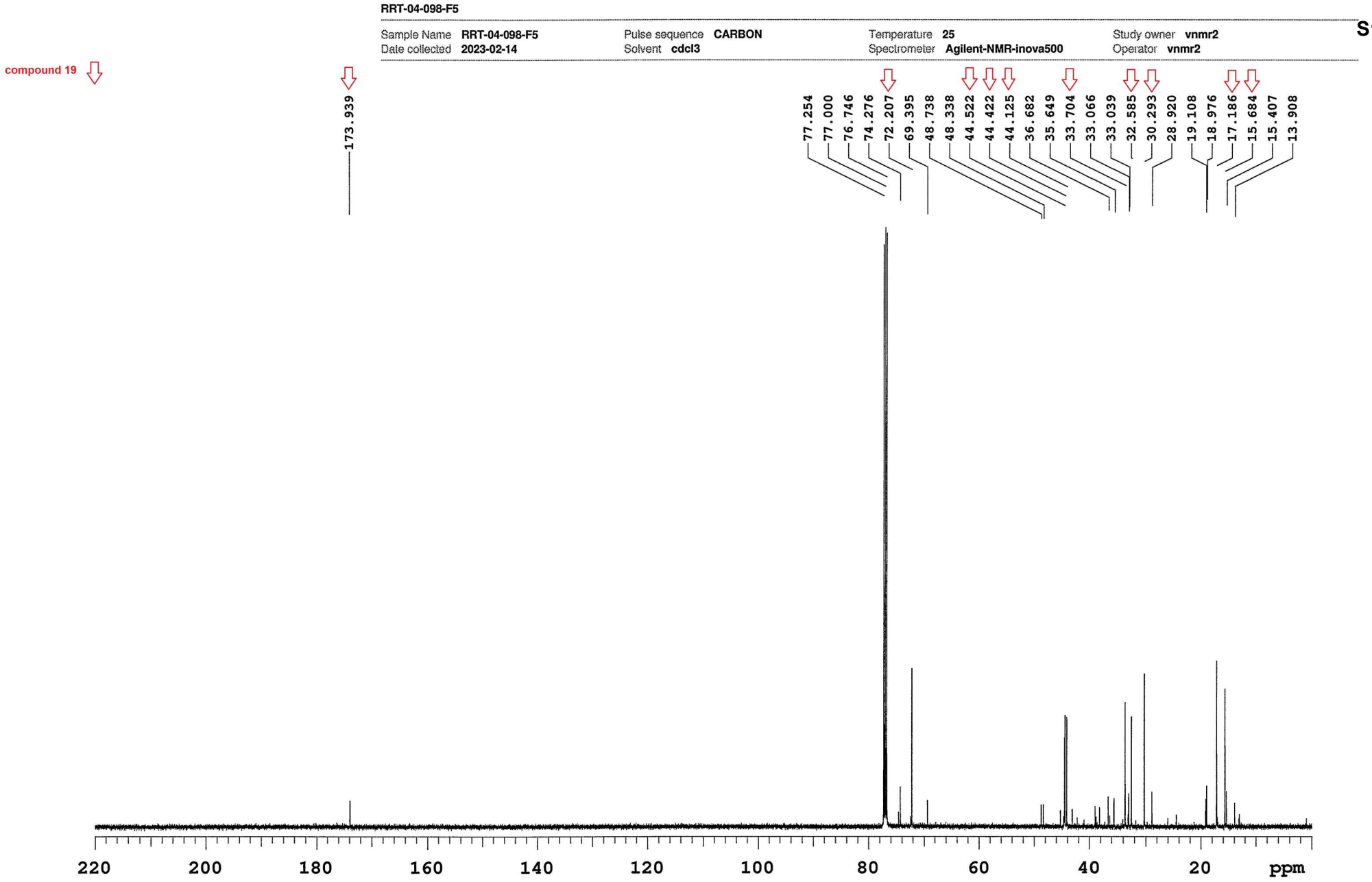
Plot date 2022-11-01



13C NMR (125 MHz, CDCl3) of the mixture of **7** (major) and **18** (minor), Scheme 3

Data file /home/vnmr2/vnmrsys/data/511-1/RRT/RRT-04-098-F6/CARBON_02

Plot date 2023-02-13



13C NMR (125 MHz, CDCl3) of the mixture of **19** (major) and other isomers (minor), Scheme 3

Data file /home/vnmr2/vnmrsys/data/511/RRT/RRT-04-098-F5/CARBON_02

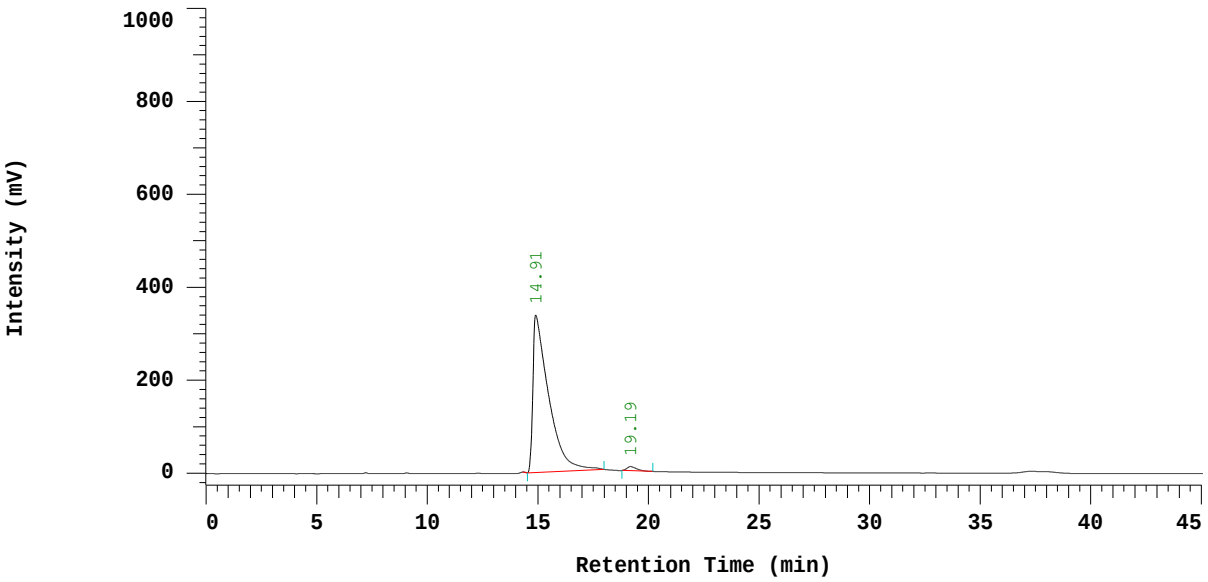
Plot date 2023-02-15

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 02/01/2016 07:20 PM
Reported Date and Time: 02/01/2016 08:41 PM
Processed Date and Time: 02/01/2016 08:40 PM
Data Path: D:\Prakash\DATA\0059\
Processing Method: test-IPA/Hx

System (acquisition): Sys 1
Series: 0059
Application(data): Prakash Chaudari
Vial Number: 1
Sample Name: PDC-02-412F1 (Chiral))
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 1%IPA+HX 1mL/MIN COL-IA

Chrom Type: Fixed WL Chromatogram, 225 nm



Processing Method: test-IPA/Hx
Column Type: IA
Method Developer: Prakash
Method Description:

Chrom Type: Fixed WL Chromatogram, 225 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	14.91	16613945	338847	98.418
2	19.19	267081	8932	1.582
		16881026	347779	100.000

Peak rejection level: 200000

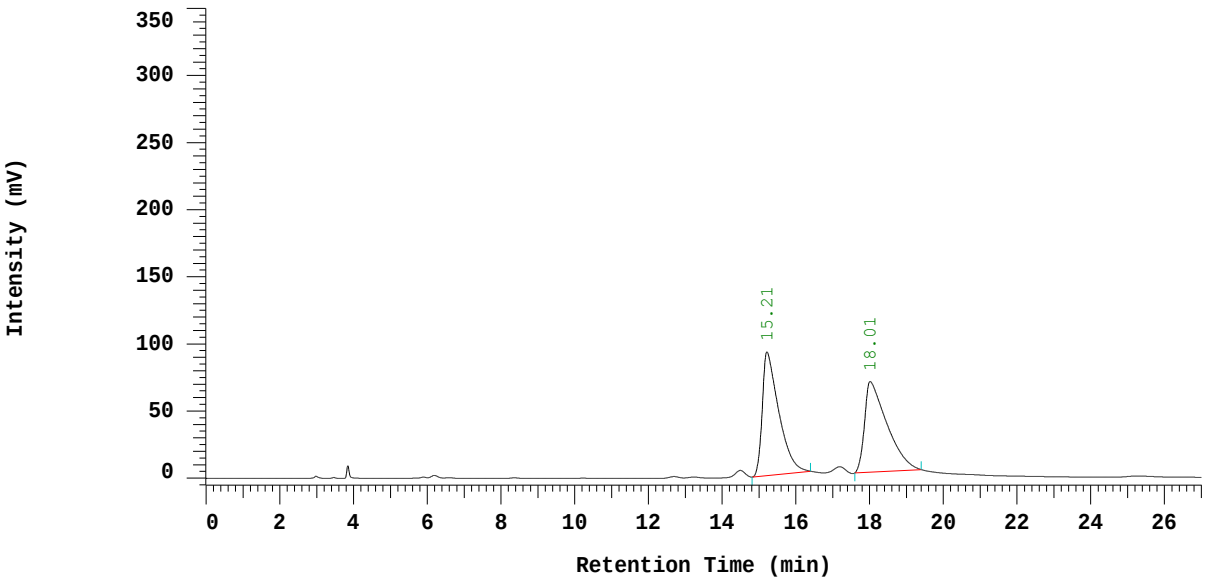
HPLC analysis of (–)-**1**, obtained from the metathesis reaction of (–)-citronellal.

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 02/19/2016 06:18 PM
Reported Date and Time: 02/19/2016 07:15 PM
Processed Date and Time: 02/19/2016 07:12 PM
Data Path: D:\Prakash\DATA\0075\
Processing Method: test-IPA/Hx

System (acquisition): Sys 1
Series: 0075
Application(data): Prakash Chaudari
Vial Number: 1
Sample Name: PDC-02-409-F2 (Racemic)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 1%IPA+HX 1.00mL/MIN COL-IA

Chrom Type: Fixed WL Chromatogram, 225 nm



Processing Method: test-IPA/Hx
Column Type: IA
Method Developer: Prakash
Method Description:

Chrom Type: Fixed WL Chromatogram, 225 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	15.21	2852853	92120	50.198
2	18.01	2830365	67429	49.802
		5683218	159549	100.000

Peak rejection level: 200

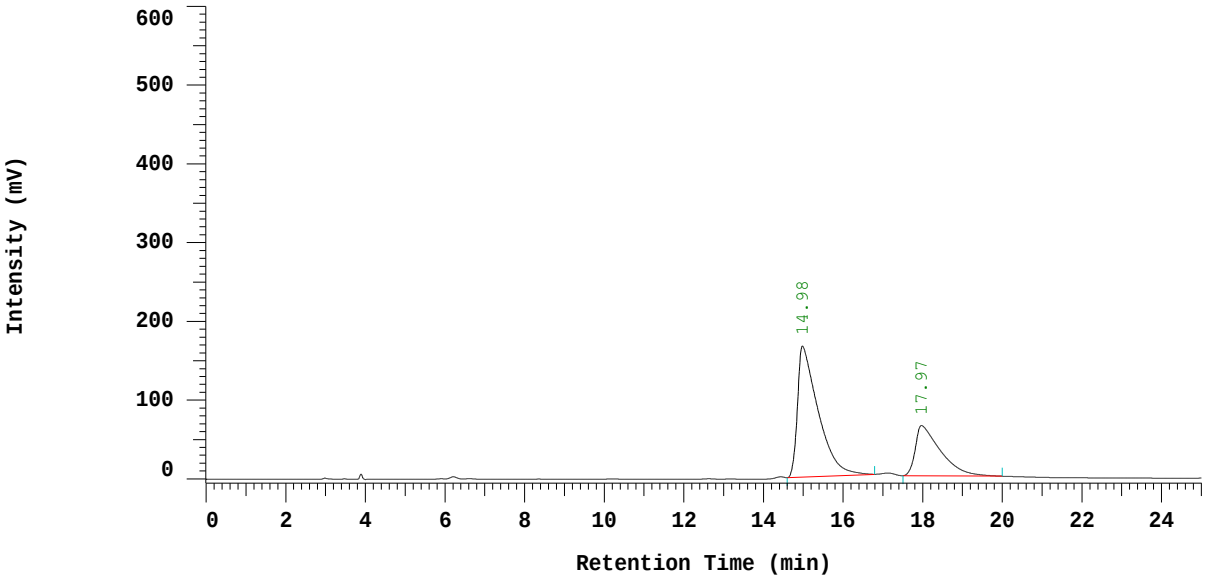
HPLC analysis of (±)-**1**, obtained from the metathesis reaction of (±)-citronellal
For comparison.

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 02/20/2016 12:46 AM
Reported Date and Time: 02/20/2016 03:22 PM
Processed Date and Time: 02/20/2016 03:18 PM
Data Path: D:\Prakash\DATA\0077\
Processing Method: test-IPA/Hx

System (acquisition): Sys 1
Series: 0077
Application(data): Prakash Chaudari
Vial Number: 1
Sample Name: PDC-02-409 & 410 CO
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 1%IPA+HX 1.00mL/MIN COL-IA

Chrom Type: Fixed WL Chromatogram, 225 nm



Processing Method: test-IPA/Hx
Column Type: IA
Method Developer: Prakash
Method Description:

Chrom Type: Fixed WL Chromatogram, 225 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	14.98	5994592	166447	68.276
2	17.97	2785342	63763	31.724
		8779934	230210	100.000

Peak rejection level: 200

HPLC analysis with the co-injection of (–)-**1** and (±)-**1**, for comparison.