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Supporting Information

Oxidative Trimerization of indoles via Water-Assisted Visible-Light Photoredox Catalysis and the Study of Their Anti-Cancer Activities.

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SUPPORTING INFORMATION:

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General Procedure. All solvents were reagent grade. Reactions were normally carried out in pear-shaped flasks or glass vials with screw cap. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} glass plates. ^{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. IR spectra were recorded on Bruker Alpha FT-IR spectrometer or PerkinElmer Spectrum Two FT-IR Spectrometer L160000A with Universal ATR (UATR) sampling accessory. The melting point was recorded on a melting point apparatus (MPA100–Automated melting point system, Stanford Research Systems, Inc.) and is uncorrected. ESI ionization time-of-flight mass (ESI-TOF MS) spectral data were obtained 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: 40 V, ring lens voltage: 10 V, spray temperature: 250°C. LEDs were purchased from shop.cpu.com.tw. 12V DC, 180 mA, LED type: SMD5050 (5x5 mm), 18 LED in each trip, size of a trip: 300 (L) x 10 (W) x 3.3 (D) mm. For blue LED, product no: 4105-18B (λ_{max} = 465-467.5 nm); for green LED, product no: 4105-18G (λ_{max} = 514.7 nm); for white LED, product no: 4105-18W. For CFL: 24 W Philips Tornado daylight compact fluorescence light.

Cell culture

Human breast carcinoma MDA-MB-231 cell, lung carcinoma A549 cell, and cervical epithelioid carcinoma HELA cell were purchased from Bioresource Collection and Research Center (BCRC 60425, 60074, and 60005 respectively). Cells maintained in Dulbecco's modified Eagle's medium (DMEM; HyClone) with 10% fetal bovine serum (FBS; Biological industries), 2 mM L-glutamine and antibiotics (containing 100 mg/L Streptomycin and 100 U/mL Penicillin G). All of cancer cell lines were maintained in a humidified incubator with 5% CO_2 at 37 °C.

MTT assay

Cancer cells were seeded at a density of 1.5×10^4 per well in 96-well culture dishes. After 24 h incubation, the cells were treated with different concentration of 3-indolones **1a**–**1j** or DMSO as vehicle control for 48 h. Following cells were incubated with 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (1 mg/mL, Sigma) at 37 °C for 4 h and then with DMSO at room temperature for 30 min. The spectrophotometric absorbance of the samples was determined by Molecular Devices SPECTRAmax PLUS384 at 540 nm.

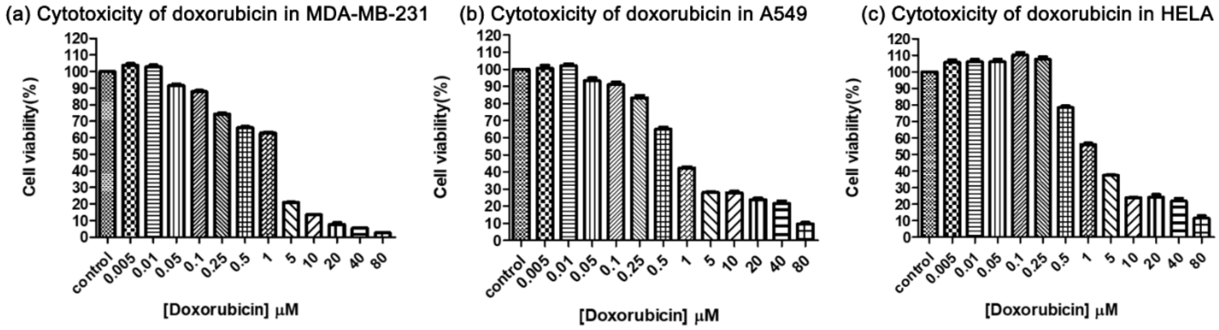
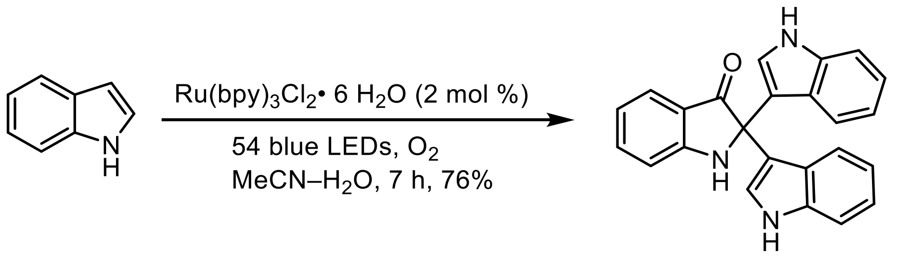


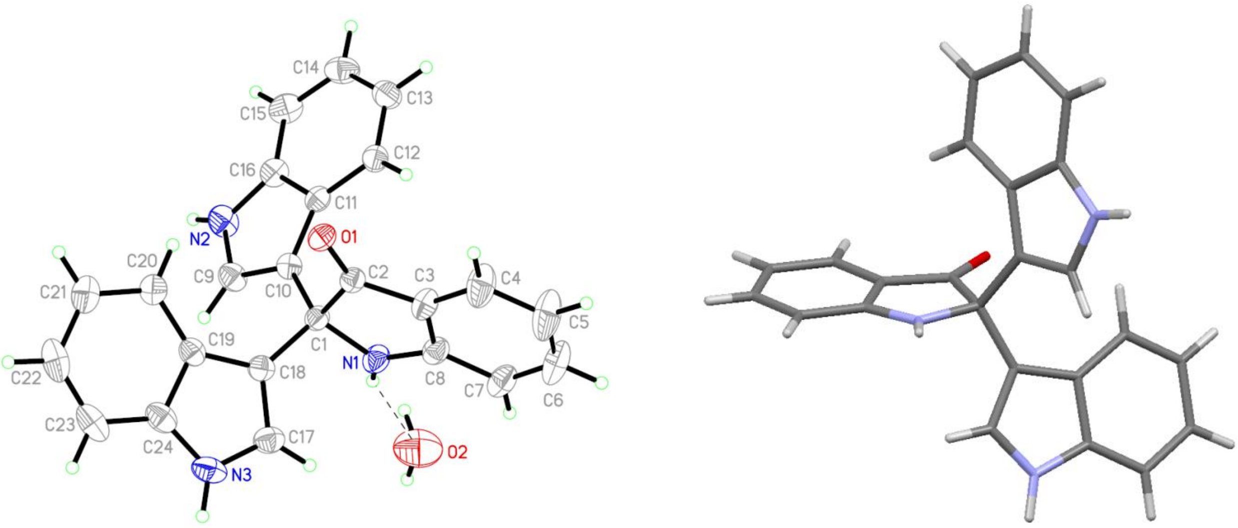
Fig. S1 Growth inhibition activity of doxorubicin (reference drug) against three cultured human tumor cell lines. Concentration of doxorubicin necessary to inhibit the growth of a panel of human cancer cells by 50% after 48 h exposure. Data are representative of three individual experiments, performed in three replicates (IC_{50}, mean ± SEM, n = 3).

Preparation of [3,2':2',3''-terindolin]-3'-one (1a)



1a

A magnetic stirring bar and indole (46.8 mg, 0.40 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of $Ru(bpy)_3Cl_2$•$6H_2O$ (6.0 mg, 0.01 mmol, 0.02 equiv), CH_3CN (2.4 mL) and H_2O (1.6 mL). The Schlenk tube was equipped with a balloon of oxygen. With careful sealing, a single balloon of oxygen can last for the duration of the reaction without the need to refill the oxygen gas. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 7 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **1a** (R_f = 0.39 in 50% EtOAc–hexane; 36.8 mg, 76% yield) as pale yellow solids. Selected data for **1a**:[1] m.p 234–235 °C (decomp.); IR (KBr): 3346, 3059, 2924, 1663, 1614, 1489, 1457, 1329, 1149, 1105, 743 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 10.97 (brs, 2 H), 8.13 (s, 1 H), 7.52 – 7.45 (m, 2 H), 7.35 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 8.0 Hz, 2 H) 7.09 (d, J = 2.5 Hz, 2 H), 7.03 (dd, J = 8.0, 8.0 Hz, 2 H), 6.94 (d, J = 8.0 Hz, 1 H), 6.83 (dd, J = 8.0, 8.0 Hz, 2 H), 6.72 (dd, J = 8.0, 8.0 Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 200.8 (C), 160.5 (C), 137.4 (CH), 136.9 (two C), 125.6 (two C), 124.4 (CH), 124.0 (two CH), 121.0 (two CH), 120.5 (two CH), 118.3 (two CH), 117.7 (C), 117.0 (CH), 114.0 (two C), 111.8 (CH), 111.6 (two CH), 67.6 (C);[2] EI-MS (*m/z*, relative intensity): 364 (M^++1, 7), 363 (M^+, 28), 335 (26), 334 (100), 332 (6), 219 (6), 218 (7), 217 (7), 190 (8), 166 (4), 117 (3); exact mass calculated for $C_{24}H_{17}N_3O$ (M^+): 363.1372; found: 363.1365.



Thermal ellipsoids draw at the 50% probability level

Figure S2. ORTEP and Stereo plots for X-ray crystal structures of **1a** (**ic19115**).

CCDC 2005723 contains the supplementary crystallographic data for **1a** (**ic19115**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk

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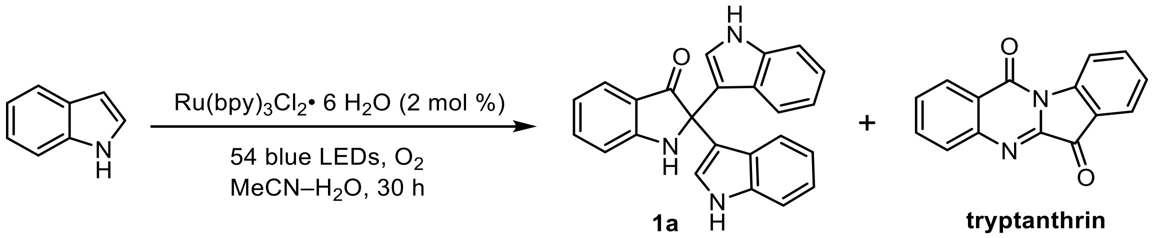
[1] (a) Kothandapani, J.; Reddy, S. M. K.; Thamotharan, S.; Kumar, S. M.; Byrappa, K.; Ganesan, S. S. *Eur. J. Org. Chem*. **2018**, 2762–2767. (b) Azimi, M.; Nafissi-Varcheh, N.; Mogharabi, M.; Faramarzi, M. Ali; Aboofazeli, R. *J. Mol. Catal. B: Enzym.* **2016**, *126*, 69 – 75. (c) Qin, W.-B.; Chang, Q.; Bao, Y.-H.; Wang, N.; Chen, Z.-W.; Liu, L.-X. *Org. Biomol. Chem.* **2012**, *10*, 8814 – 8821.

[2] (a) Kothandapani, J.; Reddy, S. M. K.; Thamotharan, S.; Kumar, S. M.; Byrappa, K.; Ganesan, S. S. *Eur. J. Org. Chem*. **2018**, 2762–2767. (b) Azimi, M.; Nafissi-Varcheh, N.; Mogharabi, M.; Faramarzi, M. Ali; Aboofazeli, R. *J. Mol. Catal. B: Enzym.* **2016**, *126*, 69 – 75. (c) Qin, W.-B.; Chang, Q.; Bao, Y.-H.; Wang, N.; Chen, Z.-W.; Liu, L.-X. *Org. Biomol. Chem.* **2012**, *10*, 8814 – 8821.

Table S1. Crystal data and structure refinement for **1a** (**ic19115**).

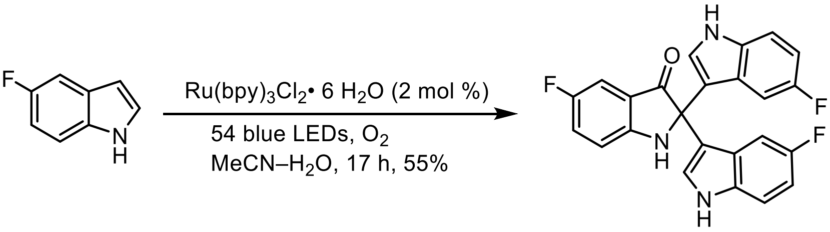
Identification code	ic19115	
Empirical formula	C24 H17.19 N3 O1.10	
Formula weight	365.12	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.5627(3) Å	α= 90°.
	b = 8.8564(3) Å	β= 98.7088(9)°.
	c = 19.8868(7) Å	γ = 90°.
Volume	1838.91(10) Å^3	
Z	4	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	0.657 mm^{-1}	
F(000)	764	
Crystal size	0.232 x 0.162 x 0.048 mm^3	
Theta range for data collection	4.484 to 74.982°.	
Index ranges	-12<=h<=13, -11<=k<=11, -24<=l<=24	
Reflections collected	12050	
Independent reflections	3770 [R(int) = 0.0169]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7539 and 0.6813	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3770 / 0 / 275	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0919	
R indices (all data)	R1 = 0.0399, wR2 = 0.0964	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.251 and -0.187 e.Å^{-3}	

Preparation of 1a and tryptanthrin



A magnetic stirring bar and indole (46.8 mg, 0.40 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of Ru(bpy)$_3$Cl$_2$•6H$_2$O (6.0 mg, 0.01 mmol, 0.02 equiv), CH$_3$CN (3.6 mL) and H$_2$O (0.4 mL). The Schlenk tube was equipped with a balloon of oxygen. With careful sealing, a single balloon of oxygen can last for the duration of the reaction without the need to refill the oxygen gas. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 30 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over MgSO$_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **1a** (R_f = 0.37 in 40% EtOAc–hexane; 11.1 mg, 23% yield) as pale yellow solids and tryptanthrin (R_f = 0.65 in 40% EtOAc–hexane; 13.4 mg, 27% yield) as pale yellow solids. Selected data for tryptanthrin:[3] m.p. 265–266 °C (decomp); lit 261–262 °C.[4] lit. 266–267 °C;[5] lit. 265–267 °C;[6] ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.62 (d, J = 8.0 Hz, 1 H), 8.43 (d, J = 8.0, 1 H), 8.02 (d, J = 8.0, 1.0 Hz, 1 H), 7.90 (d, J = 7.5 Hz, 1 H), 7.84 (dd, J = 8.0, 8.0 Hz, 1 H), 7.77 (dd, J = 8.0, 7.5 Hz, 1 H), 7.66 (dd, J = 8.0, 8.0 Hz, 1 H), 7.41 (dd, J = 7.5, 7.5 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 182.6 (C), 158.1 (C), 146.6 (C), 146.4 (C), 138.3 (CH), 135.1 (CH), 130.7 (CH), 130.3 (CH), 127.6 (CH), 127.2 (CH), 125.4 (CH), 123.8 (C), 121.9 (C), 118.0 (CH).

Preparation of 5,5',5''-trifluoro-[3,2':2',3''-terindolin]-3'-one (1b), method 1.



1b

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[3] (a) Liu, M.; Shu, M.; Yao, C.; Yin, G.; Wang, D.; Huang, J. *Org. Lett.* **2016**, *18*, 824–827. (b) Cai, Z. J.; Wang, S. Y.; Ji, S.-J. Org. Lett. **2013**, *15*, 5226–5229.

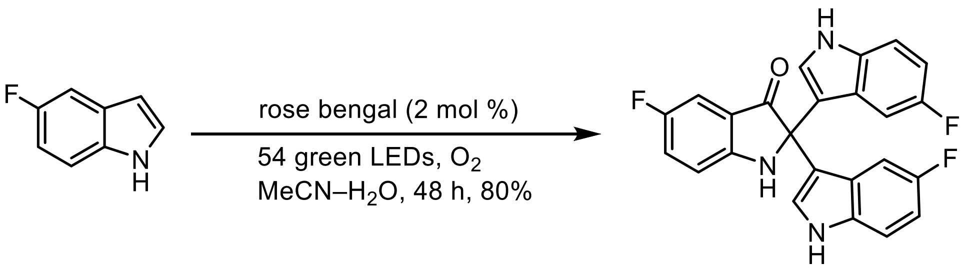
[4] Lygin, A. V.; De Meijere, A. *Org. Lett.* **2009**, *11*, 389 – 392.

[5] Jahng, K. C.; Kim, Seung I.; Kim, D. H.; Seo, C. S.; Son, J.-K.; Lee, S. H.; Lee, E. S.; Jahng, Y. *Chem. Pharm. Bull.* **2008**, *56*, 607 – 609.

[6] Al-Jalal, N.; Al-Awadi, N. A.; Ibrahim, M. R.; Elnagdi, M. H. *ARKIVOC*, **2011**, 288 – 297.

A magnetic stirring bar and 5-fluoro-1*H*-indole (54.0 mg, 0.40 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of Ru(bpy)$_3$Cl$_2$•6H$_2$O (6.3 mg, 0.01 mmol, 0.02 equiv), CH$_3$CN (2.4 mL) and H$_2$O (1.6 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 17 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over MgSO$_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **1b** (R_f = 0.58 in 50% EtOAc–hexane; 30.6 mg, 55% yield) as pale yellow solids. Selected data for **1b**:[7] m.p 154–155°C (decomp); IR (ATR) $\nu_{\max}$: 3463, 3399, 3345, 1684, 1482, 1454, 1253, 1175, 801, 775 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.19 (brs, 2 H), 7.35 (dd, J = 7.0, 2.5 Hz, 1 H), 7.28 (ddd, J = 8.5, 8.5, 2.5 Hz, 1 H), 7.22 (dd, J = 8.5, 4.0 Hz, 2 H), 7.14 (d, J = 2.5 Hz, 2 H), 7.00 (dd, J = 10.0, 2.5 Hz, 2 H), 6.92 – 6.84 (m, 3 H), 5.25 (s, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 200.8 (d, J = 3.1 Hz, C), 157.7 (d, J = 234.8 Hz, two C), 157.0 (d, J = 240.3 Hz, C), 156.9 (C), 133.5 (two C), 125.9 (d, J = 25.4 Hz, CH), 125.8 (d, J = 10.0 Hz, two C), 125.5 (two CH), 120.4 (d, J = 7.2 Hz, C), 114.7 (d, J = 4.5 Hz, two C), 114.3 (d, J = 7.4 Hz, CH), 112.2 (d, J = 9.5 Hz, two CH), 110.9 (d, J = 26.6 Hz, two CH), 110.2 (d, J = 22.2 , CH), 105.3 (d, J = 24.5 Hz, two CH), 69.0 (C); MS (*m/z*, relative intensity): 419 (M$^+$+2, 0.5), 418 (M$^+$1, 7), 417 (M$^+$, 28), 416 (5), 401 (7), 389 (27), 388 (100), 282 (4), 271 (4), 255 (9), 254 (13), 253 (7), 226 (8), 135 (9), 86 (9), 84 (16); exact mass calculated for C$_{24}$H$_{14}$F$_3$N$_3$O(M$^+$): 417.1089; found: 417.1085.

Preparation of 5,5',5''-trifluoro-[3,2':2',3''-terindolin]-3'-one (1b), method 2.



1b

A magnetic stirring bar and 5-fluoro-1*H*-indole (54.0 mg, 0.40 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of rose bengal (7.8 mg, 0.01 mmol, 0.02 equiv), CH$_3$CN (2.4 mL) and H$_2$O (1.6 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 green LEDs, located 2-5 cm away from the reaction vial, for 17 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over MgSO$_4$, and concentrated *in vacuo* to give a crude residue. The crude product was

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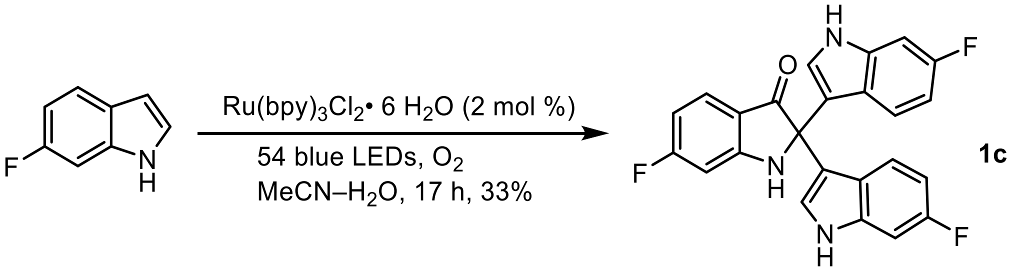
[7] Qin, W.-B.; Chang, Q.; Bao, Y.-H.; Wang, N.; Chen, Z.-W.; Liu, L.-X. *Org. Biomol. Chem.* **2012**, *10*, 8814 – 8821.

purified by flash column chromatography with 30% EtOAc–hexane to afford **1b** (R_f = 0.58 in 50% EtOAc–hexane; 44.5 mg, 80% yield) as pale yellow solids.

Preparation of 6,6',6''-trifluoro-[3,2':2',3''-terindolin]-3'-one (1c), method 1.



A magnetic stirring bar and 6-fluoro-1*H*-indole (58.3 mg, 0.43 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of $Ru(bpy)_3Cl_2•6H_2O$ (6.5 mg, 0.01 mmol, 0.02 equiv), CH_3CN (2.0 mL) and H_2O (1.3 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 17 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **1c** (R_f = 0.32 in 40% EtOAc–hexane; 19.8 mg, 33% yield) as pale yellow solids. Selected data for **1c**:[8] m.p. 180–181°C (decomp); IR (ATR) ν_{max}: 3402, 3334, 1684, 1622, 1591, 1453, 1297, 1142, 1090, 951, 835, 801 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d$_6$): δ 11.09 (brs, 2 H), 8.51 (s, 1 H), 7.55 (dd, J = 8.5, 6.0 Hz, 1 H), 7.24 (dd, J = 8.5, 6.0 Hz, 2 H), 7.14 (dd, J = 10.0, 2.5 Hz, 2 H), 7.12 (d, J = 2.5 Hz, 2 H), 6.76 – 6.71 (m, 2 H), 6.64 (dd, J = 10.5 2.5 Hz, 1 H), 6.57 – 6.51 (m, 1 H); ^{13}C NMR (125 MHz, DMSO-d$_6$): δ 198.6 (C), 168.9 (d, J = 251.4 Hz, C), 161.8 (d, J = 14.8 Hz, C), 158.7 (d, J = 234.3 Hz, two C), 136.8 (d, J = 12.4 Hz, two C), 127.4 (d, J = 12.7 Hz, CH), 124.6 (d, J = 2.9 Hz, two CH), 122.2 (two C), 121.3 (d, J = 10.0 Hz, two CH), 114.4 (C), 113.8 (two C), 107.1 (d, J = 24.2 Hz, two CH), 105.7 (d, J = 25.0 Hz, CH), 97.5 (d, J = 25.7 Hz, two CH), 97.3 (d, J = 26.1 Hz, CH), 68.0 (C); MS (*m/z*, relative intensity): 419 (M^++2, 1), 418 (M^++1, 5), 417 (M^+, 20), 389 (19), 388 (72), 254 (14), 226 (14), 223 (13), 181 (14), 167 (17), 165 (60), 149 (100), 147 (21), 137 (19), 135 (14), 121 (23), 105 (99), 91 (29), 84 (34), 77 (70); exact mass calculated for $C_{24}H_{14}F_3N_3O$ (M^+): 417.1089; found: 417.1092.

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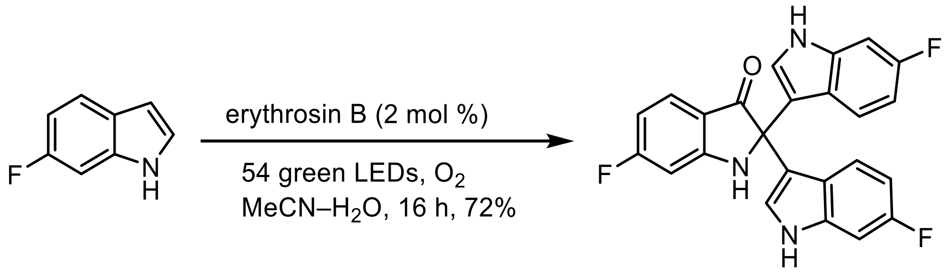
[8] Qin, W.-B.; Chang, Q.; Bao, Y.-H.; Wang, N.; Chen, Z.-W.; Liu, L.-X. *Org. Biomol. Chem.* **2012**, *10*, 8814 – 8821.

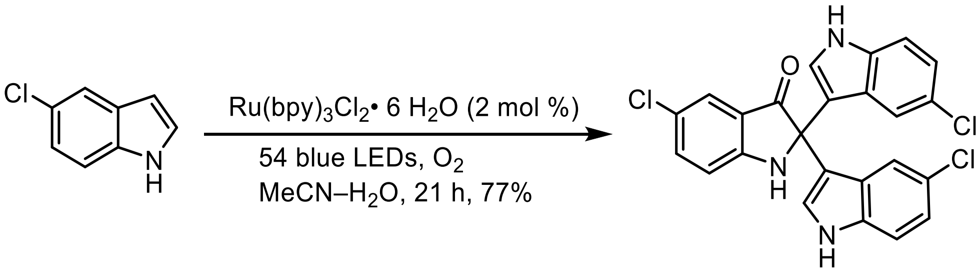
Preparation of 6,6',6''-trifluoro-[3,2':2',3''-terindolin]-3'-one (1c), method 2.



1c

A magnetic stirring bar and 6-fluoro-1*H*-indole (58.3 mg, 0.43 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of erythrosine B (7.8 mg, 0.01 mmol, 0.02 equiv), CH_3CN (2.4 mL) and H_2O (1.6 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 green LEDs, located 2-5 cm away from the reaction vial, for 17 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **1c** (R_f = 0.32 in 40% EtOAc–hexane; 40.1 mg, 72% yield) as pale yellow solids.

Preparation of 5,5',5''-trichloro-[3,2':2',3''-terindolin]-3'-one (1d)



1d

A magnetic stirring bar and 5-chloro-1*H*-indole (61.5 mg, 0.406 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of $Ru(bpy)_3Cl_2{\bullet}6H_2O$ (7.4 mg, 0.01 mmol, 0.02 equiv), CH_3CN (2.0 mL) and H_2O (1.3 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 21 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **1d** (R_f = 0.30 in 40% EtOAc–hexane; 48.6 mg, 77% yield) as pale yellow solids. Selected data for **1d**:[9] m.p. 214–216 °C (decomp); IR (ATR) ν_{max}: 3407, 3337, 1689, 1614, 1464, 1254, 1170, 1103, 894, 799, 685 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 11.29 (brs, 1 H), 11.28 (brs, 1 H), 8.51 (s, 1 H), 7.55 (dd, J = 8.6, 2.3

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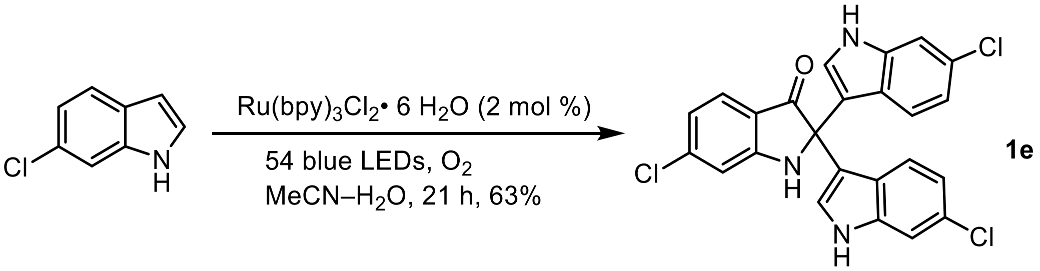
[9] Liao, H.; Peng, X.; Hu, D.; Xu, X.; Huang, P.; Liu, Q.; Liu, L. *Org. Biomol. Chem.* **2018**, *16*, 5699 – 5706.

Hz, 1 H), 7.50 (d, $J = 2.3$ Hz, 1 H), 7.40 (d, $J = 8.6$ Hz, 2 H), 7.25 – 7.21 (m, 4 H), 7.05 (dd, $J = 8.6$, 2.3 Hz, 2 H), 7.00 (d, $J = 8.6$ Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d$_6$): δ 199.3 (C), 159.0 (C), 137.6 (CH), 135.5 (two C), 126.5 (two C), 125.6 (two CH), 123.6 (CH), 123.2 (two C), 121.3 (two CH), 121.2 (C), 119.3 (two CH), 118.3 (C), 113.7 (CH), 113.5 (two CH), 113.0 (two C), 67.9 (C);[10] MS (*m/z*, relative intensity): 468 (M^++3, 10), 467 (M^++2, 32), 466 (M^++1, 14), 465 (M^+, 34), 451 (14), 441 (9), 440 (34), 439 (29), 438 (98), 437 (31), 436 (100), 402 (11), 401 (11), 400 (11), 365 (9), 316 (13), 314 (12), 288 (18), 287 (20), 286 (23), 252 (11), 251 (10), 216 (10), 176 (10), 151 (33), 89 (11); exact mass calculated for $C_{24}H_{14}{}^{35}Cl_3N_3O$ (M^+): 465.0202; found: 465.0212.

Preparation of 6,6',6''-trichloro-[3,2':2',3''-terindolin]-3'-one (1e)



A magnetic stirring bar and 6-chloro-1*H*-indole (61.7 mg, 0.407 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of $Ru(bpy)_3Cl_2{\bullet}6H_2O$ (6.8 mg, 0.01 mmol, 0.02 equiv), CH_3CN (2.0 mL) and H_2O (1.3 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 21 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **1e** ($R_f = 0.32$ in 40% EtOAc–hexane; 39.9 mg, 63% yield) as pale yellow solids. Selected data for **1e**:[11] m.p. 219–220 °C (decomp); IR (ATR) $\nu_{\max}$: 3458, 3329, 3267, 1665, 1601, 1451, 1291, 1064, 848, 809, 799 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d$_6$): δ 11.18 (brs, 2 H), 8.47 (s, 1 H), 7.49 (d, $J = 8.2$ Hz, 1 H), 7.41 (d, $J = 2.0$ Hz, 2 H), 7.21 (d, $J = 8.6$ Hz, 2 H), 7.17 (d, $J = 2.0$ Hz, 2 H), 6.95 (d, $J = 2.0$ Hz, 1 H), 6.89 (dd, $J = 8.6$, 2.0 Hz, 2 H), 6.75 (dd, $J = 8.2$, 2.0 Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d$_6$): δ 199.0 (C), 160.6 (C), 142.4 (C), 137.3 (C), 126.4 (CH), 126.0 (two C), 125.1 (two CH), 124.2 (two C), 121.5 (two CH), 119.0 (two CH and C), 117.7 (CH), 116.3 (C), 113.6 (two C), 111.3 (two CH), 111.0 (CH), 67.7 (C);[12] MS (*m/z*, relative intensity): 469 (M^++4, 11), 468 (M^++3, 10), 467 (M^++2, 31), 466 (M^++1,

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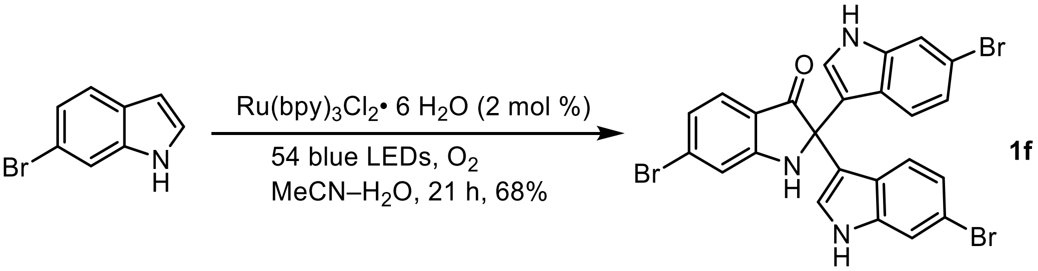
[10] Gohain, S. B.; Basumatary, M.; Boruah, P. K.; Das, M. R.; Thakur, A. J. *Green Chem.* **2020**, *22*, 170 – 179.

[11] (a) Kothandapani, J.; Reddy, S. M. K.; Thamotharan, S.; Kumar, S. M.; Byrappa, K.; Ganesan, S. S. *Eur. J. Org. Chem.* **2018**, 2762 – 2767. (b) Kong, Y.-B.; Zhu, J.-Y.; Chen, Z.-W.; Liu, L.-X. *Can. J. Chem.* **2014**, *92*, 269 – 273. (c) Xue, J.; Bao, Y.; Qin, W.; Zhu, J.; Kong, Y.; Qu, H.; Chen, Z.; Liu, L. *Synth. Commun.* **2014**, *44*, 2215 – 2221.

[12] Kothandapani, J.; Reddy, S. M. K.; Thamotharan, S.; Kumar, S. M.; Byrappa, K.; Ganesan, S. S. *Eur. J. Org. Chem.*

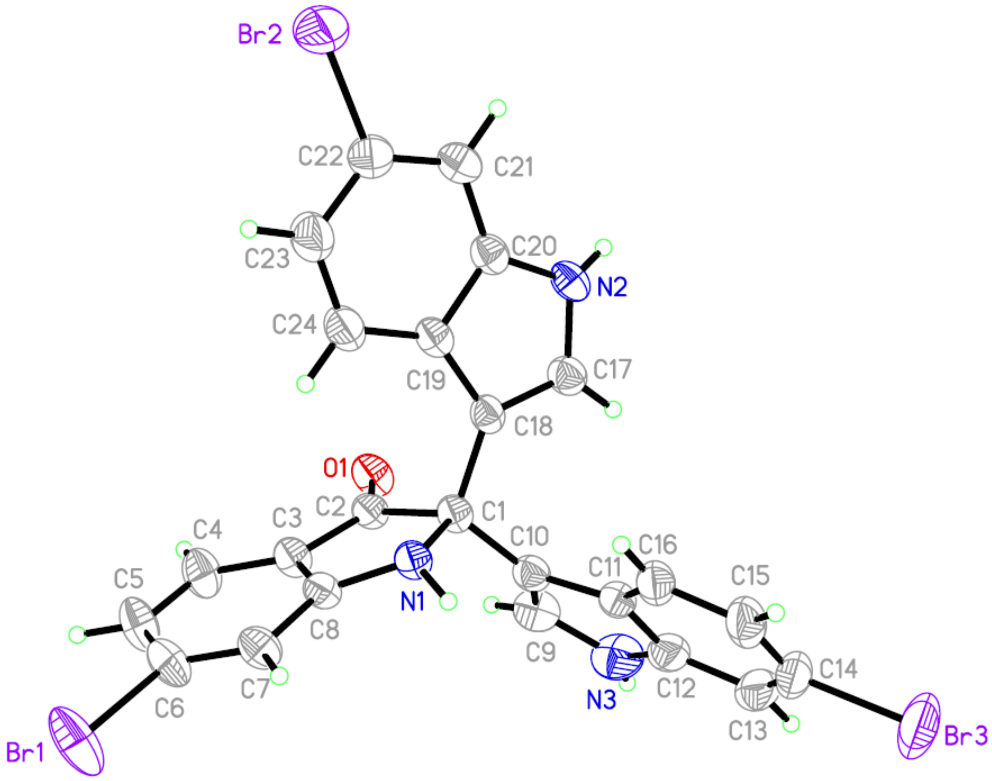
13), 465 (M^+, 32), 440 (33), 439 (28), 438 (98), 437 (30), 436 (100), 402 (12), 401 (12), 400 (14), 365 (9), 286 (12), 149 (39), 105 (18), 77 (7); exact mass calculated for $C_{24}H_{14}{}^{35}Cl_3N_3O$ (M^+): 465.0202; found: 465.0194.

Preparation of 6,6',6''-tribromo-[3,2':2',3''-terindolin]-3'-one (1f)



A magnetic stirring bar and 6-bromo-1*H*-indole (82.7 mg, 0.422 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of $Ru(bpy)_3Cl_2•6H_2O$ (6.8 mg, 0.01 mmol, 0.02 equiv), CH_3CN (2.0 mL) and H_2O (1.3 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 21 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **1f** ($R_f = 0.29$ in 40% EtOAc–hexane; 57.3 mg, 68% yield) as pale yellow solids. Selected data for **1f**: m.p 212–213 °C (decomp); IR (ATR) ν_{max}: 3445, 3319, 3278, 2924, 1663, 1596, 1451, 1291, 1101, 1054, 915, 850, 796 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 11.19 (brs, 2 H), 8.44 (s, 1 H), 7.56 (d, $J = 1.5$ Hz, 2 H), 7.42 (d, $J = 8.0$ Hz, 1 H), 7.18-7.14 (m, 4 H), 7.12 (d, $J = 1.5$ Hz, 1 H), 7.00 (dd, $J = 8.5$, 1.5 Hz, 2 H), 6.88 (dd, $J = 8.5$, 1.5 Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 199.2 (C), 160.7 (C), 137.8 (two C), 131.8 (C), 126.4 (CH), 125.0 (two CH), 124.4 (two C), 121.9 (two CH), 121.5 (two CH), 120.4 (CH), 116.5 (C), 114.3 (two CH) ,114.1 (CH), 114.0 (two C), 113.6 (two C), 67.6 (C); MS (*m/z*, relative intensity): 603 (M^++6, 13), 602 (M^++5, 11), 601 (M^++4, 36), 600 (M^++3, 14), 599 (M^++2, 36), 598 (M^++1, 8), 597 (M^+, 15), 575 (10), 574 (36), 573 (29), 572 (100), 571 (30), 570 (100), 569 (11), 568 (35), 493 (11), 492 (17), 491 (21), 490 (22), 489 (11), 488 (10), 411 (10), 404 (13), 377 (9), 376 (11), 330 (10), 296 (9), 216 (20), 197 (16), 195 (16), 116 (13); exact mass calculated for $C_{24}H_{14}{}^{79}Br_3N_3O$ (M^+): 596.8687; found: 596.8690.

2018, 2762–2767.



Thermal ellipsoids draw at the 50% probability level

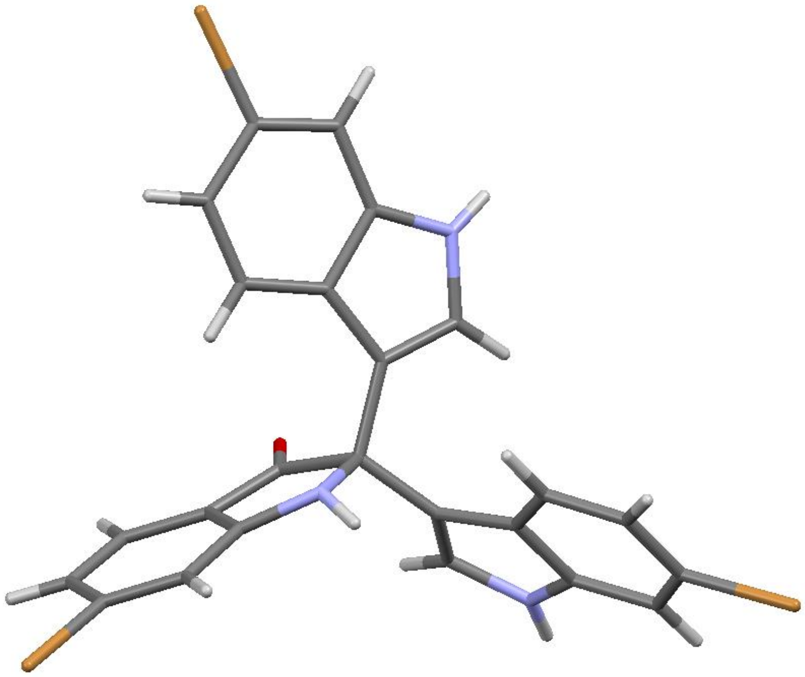


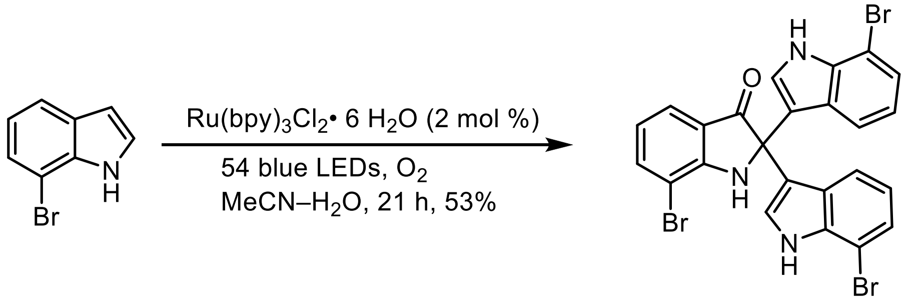
Figure S3. ORTEP and Stereo plots for X-ray crystal structures of **1f** (**ic19379**).

CCDC 2005724 contains the supplementary crystallographic data for **1f** (**ic19379**). 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 **1f** (**ic19379**).

Identification code	ic19379	
Empirical formula	$C_{24.25}H_{14.50}Br_3Cl_{0.50}N_3O$	
Formula weight	621.34	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.7209(6) Å	α= 90°.
	b = 15.6427(3) Å	β= 104.3612(4)°.
	c = 11.8698(3) Å	γ = 90°.
Volume	4806.38(19) $Å^3$	
Z	8	
Density (calculated)	1.717 Mg/m^3	
Absorption coefficient	6.913 mm^{-1}	
F(000)	2420	
Crystal size	0.170 x 0.109 x 0.075 mm^3	
Theta range for data collection	3.301 to 74.999°.	
Index ranges	-33<=h<=33, -18<=k<=19, -14<=l<=14	
Reflections collected	17387	
Independent reflections	4951 [R(int) = 0.0191]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7539 and 0.5857	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4951 / 5 / 304	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0628, wR2 = 0.1673	
R indices (all data)	R1 = 0.0655, wR2 = 0.1701	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.114 and -2.347 e.$Å^{-3}$	

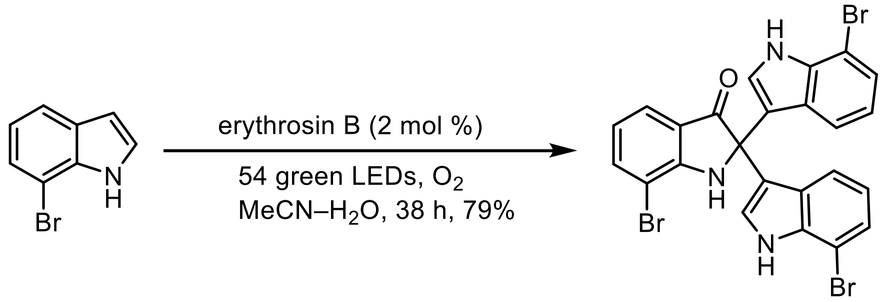
Preparation of 7,7',7''-tribromo-[3,2':2',3''-terindolin]-3'-one (1g), method 1.



1g

A magnetic stirring bar and 7-bromo-1*H*-indole (84.2 mg, 0.429 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of $Ru(bpy)_3Cl_2•6H_2O$ (6.8 mg, 0.01 mmol, 0.02 equiv), CH_3CN (2.0 mL) and H_2O (1.3 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 21 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane to afford **1g** ($R_f = 0.59$ in 40% EtOAc–hexane; 45.5 mg, 53% yield) as pale yellow solids. Selected data for **1g**: m.p 247–249 °C (decomp); IR (ATR) ν_{max}: 3409, 3378, 1699, 1606, 1482, 1431, 1116, 1090, 881, 816, 778, 742, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.29 (brs, 2 H), 7.70 (d, $J = 7.5$, 1 H), 7.66 (d, $J = 7.5$ Hz, 1 H), 7.32 (dd, $J = 7.5$, 7.5 Hz, 4 H), 7.25 – 7.23 (m, 2 H), 6.87 (dd, $J = 7.5$, 7.5 Hz, 2 H), 6.81 (dd, $J = 7.5$, 7.5 Hz, 1 H), 5.51 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7 (C), 157.5 (C), 139.6 (CH), 135.7 (two C), 126.6 (two C), 124.9 (two CH), 124.6 (CH), 124.4 (two CH), 121.4 (two CH), 121.1 (C), 120.6 (CH), 119.8 (two CH), 115.8 (two C), 106.4 (C), 105.0 (two C), 68.6 (C); MS (*m/z*, relative intensity): 603 (M^++6, 10), 602 (M^++5, 8), 601 (M^++4, 28), 600 (M^++3, 10), 599 (M^++2, 29), 598 (M^++1, 6), 597 (M^+, 10), 574 (32), 573 (25), 572 (98), 571 (26), 570 (100), 568 (32), 492 (12), 491 (15), 490 (16), 330 (8), 206 (9), 165 (10); exact mass calculated for $C_{24}H_{14}{}^{79}Br_3N_3O$ (M^+): 596.8687; found: 596.8683.

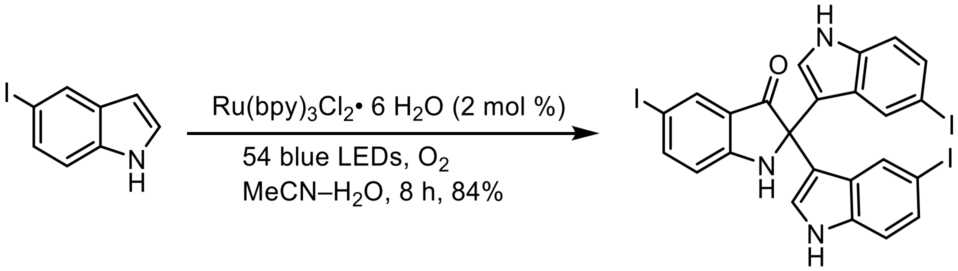
Preparation of 7,7',7''-tribromo-[3,2':2',3''-terindolin]-3'-one (1g), method 2.



1g

A magnetic stirring bar and 7-bromo-1*H*-indole (78.4 mg, 0.40 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of erythrosine B (7.8 mg, 0.01 mmol, 0.02 equiv), CH_3CN (2.4 mL) and H_2O (1.6 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 green LEDs, located 2-5 cm away from the reaction vial, for 21 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane to afford **1g** (R_f = 0.59 in 40% EtOAc–hexane; 63.2 mg, 79% yield) as pale yellow solids.

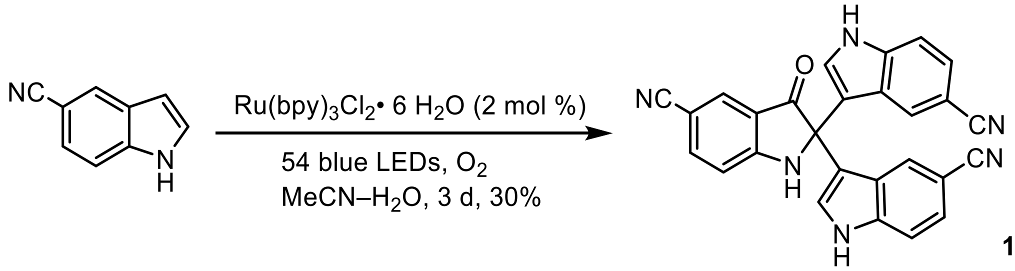
Preparation of 5,5',5''-triiodo-[3,2':2',3''-terindolin]-3'-one (1h)



1h

A magnetic stirring bar and 5-iodo-1*H*-indole (98.8 mg, 0.406 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of $Ru(bpy)_3Cl_2•6H_2O$ (6.1 mg, 0.01 mmol, 0.02 equiv), CH_3CN (2.0 mL) and H_2O (1.3 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 8 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **1h** (R_f = 0.30 in 40% EtOAc–hexane; 84.4 mg, 84% yield) as pale yellow solids. Selected data for **1h**: m.p. 249–250 °C (decomp); IR (ATR) ν_{max}: 3456, 3409, 3386, 1699, 1601, 1464, 1098, 799 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 11.25 (brs, 2 H), 8.50 (s, 1 H), 7.77 (d, J = 1.5 Hz, 1 H), 7.75 (s, 1 H), 7.59 (d, J = 1.5 Hz, 2 H), 7.30 (dd, J = 8.5, 1.5 Hz, 2 H), 7.24 (d, J = 8.5 Hz, 2 H), 7.13 (d, J = 2.5 Hz, 2 H), 6.84 (d, J = 8.5 Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 198.7 (C), 159.4 (C), 145.3 (CH), 136.0 (two C), 132.7 (CH), 129.2 (two CH), 128.6 (two CH), 128.0 (two C), 125.0 (two CH), 119.9 (C), 114.5 (CH), 114.3 (two CH), 112.6 (two C), 82.8 (two C), 78.3 (C), 67.5 (C); MS (*m/z*, relative intensity): 743 (M^++2, 2), 742 (M^++1, 18), 741 (M^+, 65), 725 (13), 713 (36), 712 (100), 586 (19), 585 (27), 498 (66), 470 (15), 343 (57), 330 (21), 243 (85), 216 (23), 141 (18), 128 (34), 116 (55), 89 (24), 75 (20); exact mass calculated for $C_{24}H_{14}I_3N_3O$ (M^+): 740.8271; found: 740.8279.

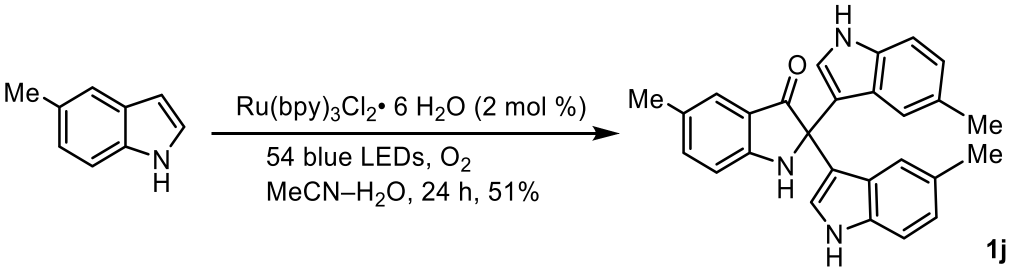
Preparation of 3'-oxo-[3,2':2',3''-terindoline]-5,5',5''-tricarbonitrile (1i)



1i

A magnetic stirring bar and 1*H*-indole-5-carbonitrile (60.7 mg, 0.43 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of Ru(bpy)$_3$Cl$_2$•6H$_2$O (7.0 mg, 0.01 mmol, 0.02 equiv), CH$_3$CN (2.0 mL) and H$_2$O (1.3 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 72 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over MgSO$_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 30% acetone–hexane to afford **1i** (R_f = 0.31 in 50% acetone–hexane; 18.7 mg, 30% yield) as pale yellow solids. Selected data for **1i**:[13] m.p. 175–177 °C (decomp); IR (ATR) $\nu_{\max}$: 3309, 2223, 1709, 1619, 1487 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d$_6$): δ 11.76 (brs, 2 H), 9.41 (s, 1 H), 8.03 (d, J = 1.5 Hz, 1 H), 7.87 (dd, J = 8.5, 1.5 Hz, 1 H), 7.63 (s, 2 H), 7.57 (d, J = 8.5 Hz, 2 H), 7.47 (d, J = 1.5 Hz, 2 H), 7.42 (dd, J = 8.5, 1.5 Hz, 2 H), 7.08 (d, J = 8.5 Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d$_6$): δ 198.0 (C), 161.2 (C), 140.6 (CH), 138.8 (two C), 130.8 (CH), 126.6 (two CH), 125.3 (two CH), 124.9 (two C), 124.1 (two CH), 120.5 (two C), 119.3 (C), 117.0 (C), 113.5 (two C), 113.4 (two CH), 112.6 (CH), 101.0 (two C), 99.0 (C), 67.5 (C); MS (*m/z*, relative intensity): 439 (M$^+$+1, 2), 438 (M$^+$, 10), 410 (20), 409 (63), 298 (29), 296 (16), 269 (31), 268 (46), 240 (15), 167 (21), 142 (100), 115 (58), 114 (31), 105 (18), 91 (22), 77 (27); exact mass calculated for C$_{27}$H$_{14}$N$_6$O (M$^+$): 438.1229; found: 438.1227.

Preparation of 5,5',5''-trimethyl-[3,2':2',3''-terindolin]-3'-one (1j), method 1.



1j

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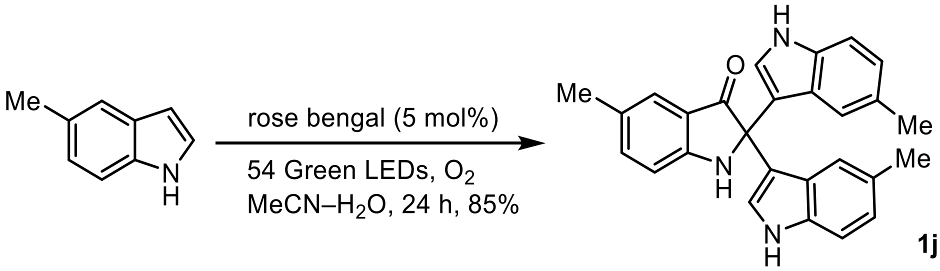
[13] (a) Kong, Y.-B.; Zhu, J.-Y.; Chen, Z.-W.; Liu, L.-X. *Can. J. Chem.* **2014**, *92*, 269 – 273. (b) Xue, J.; Bao, Y.; Qin, W.; Zhu, J.; Kong, Y.; Qu, H.; Chen, Z.; Liu, L. *Synth. Commun.* **2014**, *44*, 2215 – 2221.

A magnetic stirring bar and 1*H*-indole-5-carbonitrile (52.5 mg, 0.40 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of Ru(bpy)$_3$Cl$_2$•6H$_2$O (6.8 mg, 0.01 mmol, 0.02 equiv), CH$_3$CN (2.4 mL) and H$_2$O (1.6 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 24 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over MgSO$_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane to afford **1j** (R_f = 0.26 in 40% EtOAc–hexane; 27.4 mg, 51% yield) as pale yellow solids. Selected data for **1j**:[14] m.p. 254–256°C (decomp); IR (ATR) $\nu_{\max}$: 3363, 1722, 1653, 1622, 1498, 1420, 1253, 1041, 796, 765, 703 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 10.79 (brs, 2 H), 7.81 (s, 1 H), 7.34 (dd, J = 8.4, 2.0 Hz, 1 H), 7.26 (s, 1 H), 7.23 (d, J = 8.4 Hz, 2 H), 7.11 (s, 2 H), 7.01 (d, J = 2.0 Hz, 2 H), 6.91 – 6.82 (m, 3 H), 2.24 (s, 3 H), 2.21 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 200.8 (C), 159.1 (C), 138.6 (CH), 135.3 (two C), 126.4 (two C), 125.9 (two C), 125.8 (C), 124.0 (two CH), 123.6 (CH), 122.6 (two CH), 120.2 (two CH), 118.0 (C), 113.7 (two C), 111.9 (CH), 111.2 (two CH), 68.0 (C), 21.4 (two CH$_3$), 20.1 (CH$_3$);2^c MS (m/z, relative intensity): 406 (M$^+$+1, 4), 405 (M$^+$, 18), 377 (16), 376 (52), 359 (12), 330 (11), 274 (15), 246 (32), 165 (46), 149 (19), 130 (21), 105 (49), 84 (77), 66 (100); exact mass calculated for C$_{27}$H$_{23}$N$_3$O (M$^+$): 405.1841; found: 405.1846.

Preparation of 5,5',5''-trimethyl-[3,2':2',3''-terindolin]-3'-one (1j), method 2.



A magnetic stirring bar and 1*H*-indole-5-carbonitrile (53.2 mg, 0.41 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of rose bengal (23.0 mg, 0.02 mmol, 0.06 equiv), CH$_3$CN (2.0 mL) and H$_2$O (1.3 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 green LEDs, located 2-5 cm away from the reaction vial, for 24 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over MgSO$_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane to afford **1j** (R_f = 0.26 in 40% EtOAc–hexane; 46.4 mg, 85% yield) as pale yellow solids.

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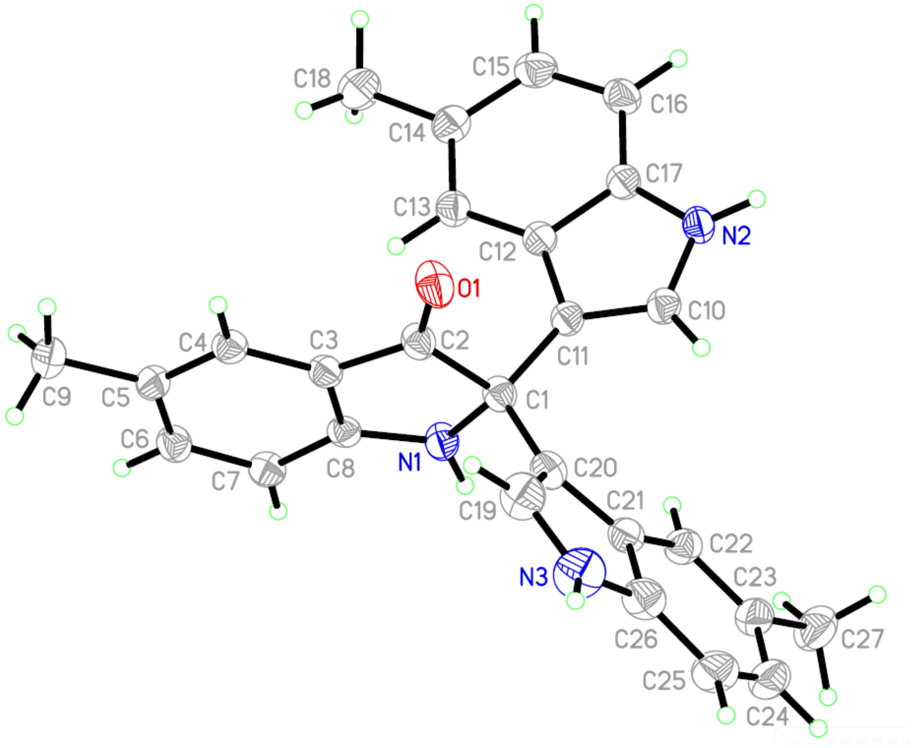
[14] Qin, W.-B.; Chang, Q.; Bao, Y.-H.; Wang, N.; Chen, Z.-W.; Liu, L.-X. *Org. Biomol. Chem.* **2012**, *10*, 8814 – 8821.



Thermal ellipsoids draw at the 50% probability level

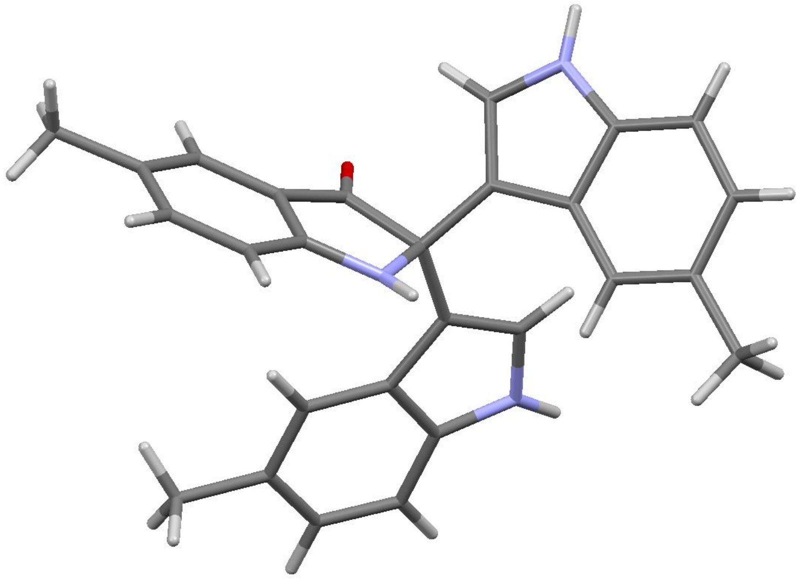


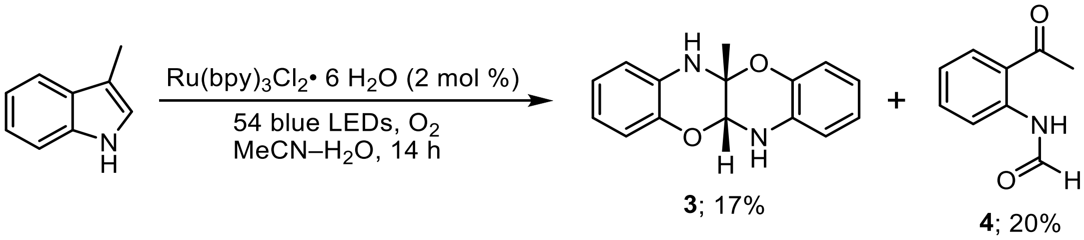
Figure S4. ORTEP and Stereo plots for X-ray crystal structures of **1j** (**ic19387**).

CCDC 2005725 contains the supplementary crystallographic data for **1j** (**ic19387**). 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 **1j** (**ic19387**).

Identification code	ic19387	
Empirical formula	C27 H23 N3 O	
Formula weight	405.48	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4157(2) Å	α= 112.5285(8)°.
	b = 10.5063(2) Å	β= 108.7529(8)°.
	c = 11.3815(2) Å	γ = 99.9684(8)°.
Volume	1024.96(3) Å ^{3}	
Z	2	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.637 mm^{-1}	
F(000)	428	
Crystal size	0.119 x 0.070 x 0.041 mm^3	
Theta range for data collection	4.650 to 74.991°.	
Index ranges	-13<=h<=12, -13<=k<=13, -14<=l<=14	
Reflections collected	8034	
Independent reflections	4193 [R(int) = 0.0127]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7539 and 0.7086	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4193 / 0 / 295	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0935	
R indices (all data)	R1 = 0.0437, wR2 = 0.1013	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.225 and -0.205 e.Å $^{-3}$	

Preparation of 3 and *N*-(2-acetylphenyl)formamide (4).



3; 17%

4; 20%

A magnetic stirring bar and 3-methyl-1*H*-indole (53.1 mg, 0.405 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of $Ru(bpy)_3Cl_2•6H_2O$ (6.0 mg, 0.008 mmol, 0.02 equiv), CH_3CN (2.0 mL) and H_2O (1.3 mL). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial, for 14 h until the completion of the reaction, as monitored by TLC. Upon completion, the reaction solution was diluted with EtOAc and extracted with water and brine. The organic solution was dried over $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 20% EtOAc–hexane to afford **3** ($R_f = 0.65$ in 40% EtOAc–hexane; 8.8 mg, 17% yield) as white solids, and **4** ($R_f = 0.52$ in 40% EtOAc–hexane; 13.2 mg, 20% yield) as white solids.

Selected data for **3**:[15] m.p. 205-206 °C; IR (neat): 3368, 2925, 1606, 1500, 1309, 1248, 1143, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.83 – 6.68 (m, 7 H), 6.63 (dd, $J = 7.8$, 1.4 Hz, 1 H), 5.06 (d, $J = 3.9$ Hz, 1 H), 4.88 (brs, 1 H), 4.64 (brs, 1 H), 1.52 (s, 3 H); ^{13}C NMR (125 MHz, CDCl3): δ 141.8 (C), 141.5 (C), 129.3 (C), 127. 6 (C), 121.8 (CH), 121.5 (CH), 120.8 (CH), 120.3 (CH), 117.3 (CH), 116.7 (CH), 115.1 (CH), 114.5 (CH), 79.3 (C), 79.0 (CH), 22.8 (CH_3); MS (*m/z*, relative intensity): 255 (M^++H, 18), 254 (M^+, 100), 225 (3), 147 (53), 146 (52), 134 (56), 120 (37); exact mass calculated for $C_{15}H_{14}N_2O_2$ (M^+): 254.1055; found: 254.1047.

Selected data for **4**:[16] m.p. 76-77 °C; lit. 75– 76 °C;[17] 77 °C.[18] IR (neat): 3252, 1700, 1654, 1578, 1508, 1452, 1358, 1309, 1251, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 11.59 (brs, 1 H), 8.73 (d, $J = 8.0$ Hz, 1 H), 8.48 (s, 1 H), 7.90 (dd, $J = 8.0$ Hz, 1 H), 7.55 (t, $J = 8.0$ Hz, 1 H), 7.15 (t, $J = 8.0$ Hz, 1 H), 2.66 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.7 (C), 159.9 (CH), 139.9 (C), 135.2 (CH), 131.6 (CH), 123.1 (CH), 122.0 (C), 121.6 (CH), 28.5 (CH_3).

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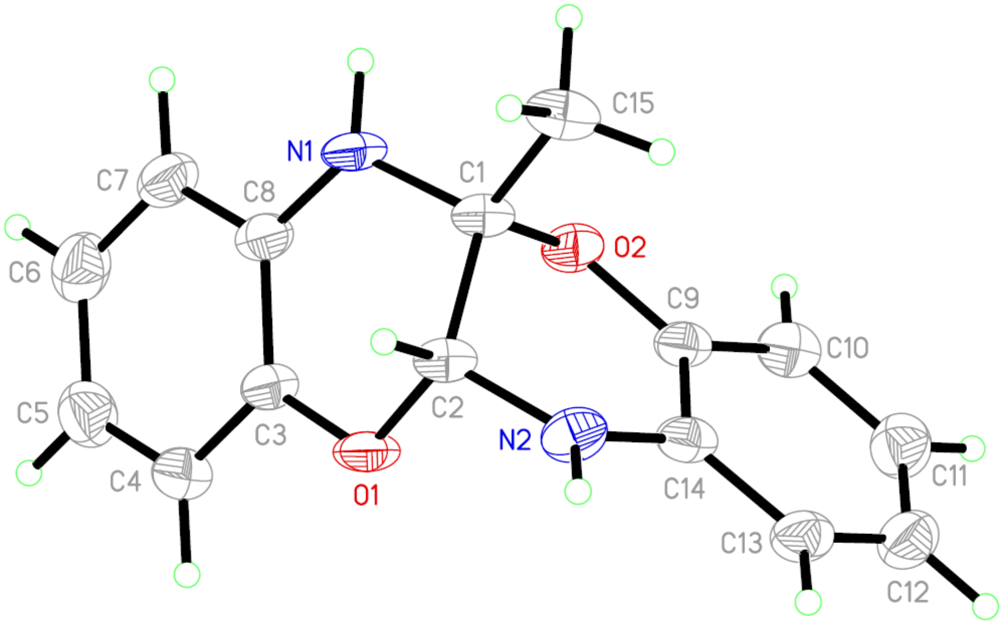
[15] (1) Tauer, E.; Grellmann, K.-H. *Chem. Ber.* **1990**, *123*, 1149 – 1154. (2) Barluenga, J.; Aznar, F.; Liz, R.; Cabal, M.-P.; Cano, F. H.; Foces-Foces, C. *Chem. Ber.* **1986**, *119*, 887 – 899.

[16] Yang, S.; Li, P.; Wang, Z.; Wang, L. *Org. Lett.* **2017**, *19*, 3386 – 3389. (2) Li, X.; Huang, H.; Yu, C.; Zhang, Y.; Li, H.; Wang, W. *Org. Lett.* **2016**, *18*, 5744 – 5747. (3) He, J.; Dong, J.; Su, L.; Wu, S.; Liu, L.; Yin, S.-F.; Zhou, Y. *Org. Lett.* **2020**, *22*, 2522–2526.

[17] Fuerstner, A.; Jumbam, D. N. *Tetrahedron* **1992**, *48*, 5991 – 6010.

[18] Chatterjee, A.; Biswas, K. M. *J. Org. Chem.*, **1973**, *38*, 23, 4002 – 4004.



Thermal ellipsoids draw at the 50% probability level

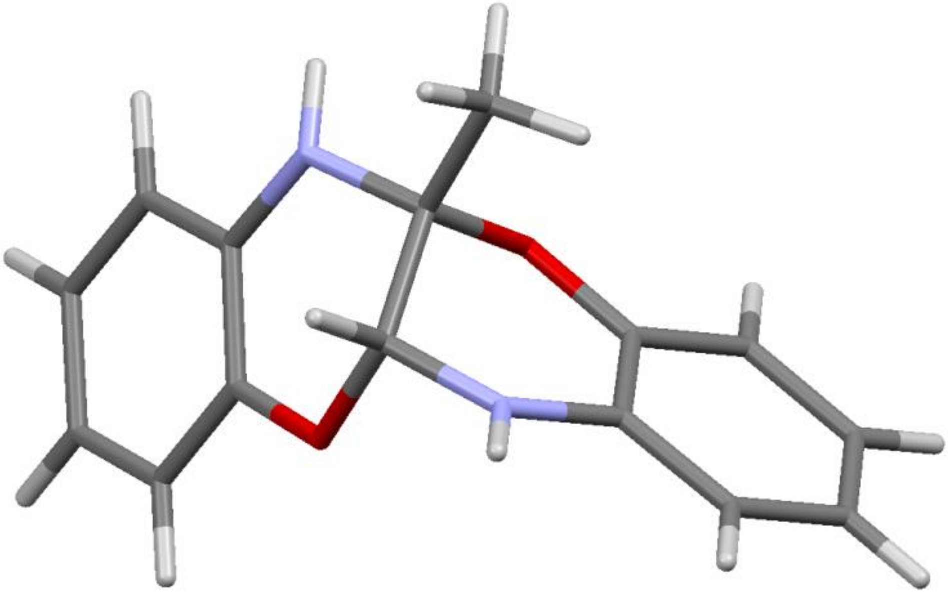
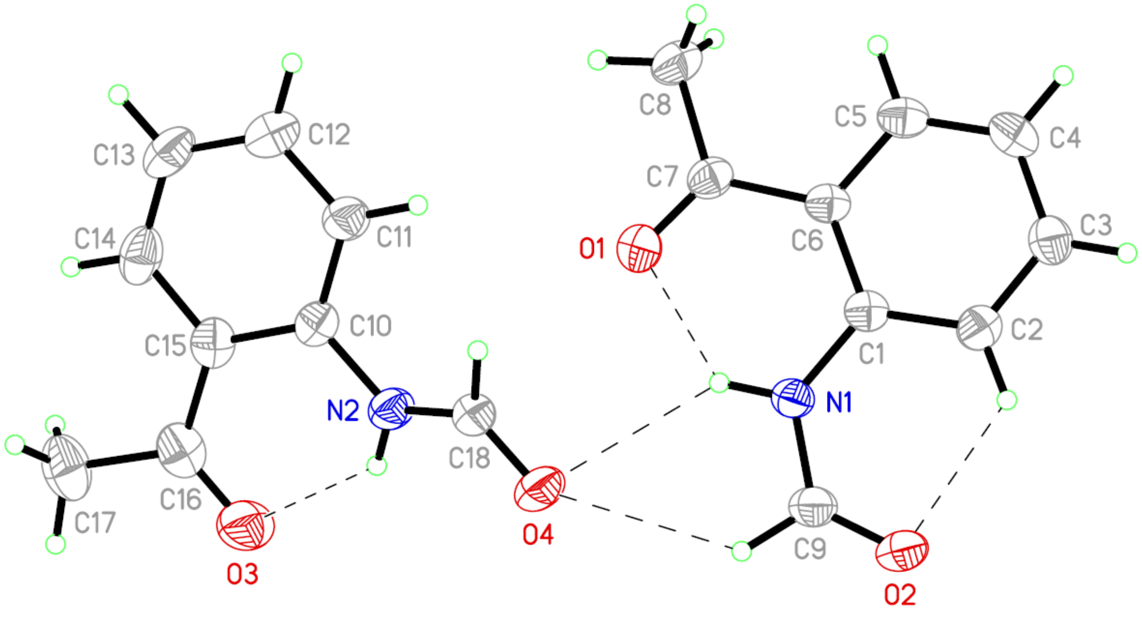


Figure S5. ORTEP and Stereo plots for X-ray crystal structures of **3** (**ic19495**).

CCDC 2005726 contains the supplementary crystallographic data for **3** (**ic19495**). 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 **3** (**ic19495**).

Identification code	ic19495	
Empirical formula	C15 H14 N2 O2	
Formula weight	254.28	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 19.1254(4) Å	α= 90°.
	b = 5.49360(10) Å	β= 98.8783(9)°.
	c = 11.5714(3) Å	γ = 90°.
Volume	1201.21(5) Å ^{3}	
Z	4	
Density (calculated)	1.406 Mg/m^3	
Absorption coefficient	0.770 mm^{-1}	
F(000)	536	
Crystal size	0.376 x 0.049 x 0.035 mm^3	
Theta range for data collection	2.338 to 74.885°.	
Index ranges	-23<=h<=23, -6<=k<=6, -14<=l<=14	
Reflections collected	8444	
Independent reflections	2456 [R(int) = 0.0218]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7539 and 0.6179	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2456 / 0 / 181	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1113	
R indices (all data)	R1 = 0.0473, wR2 = 0.1148	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.308 and -0.246 e.Å $^{-3}$	



Thermal ellipsoids draw at the 50% probability level

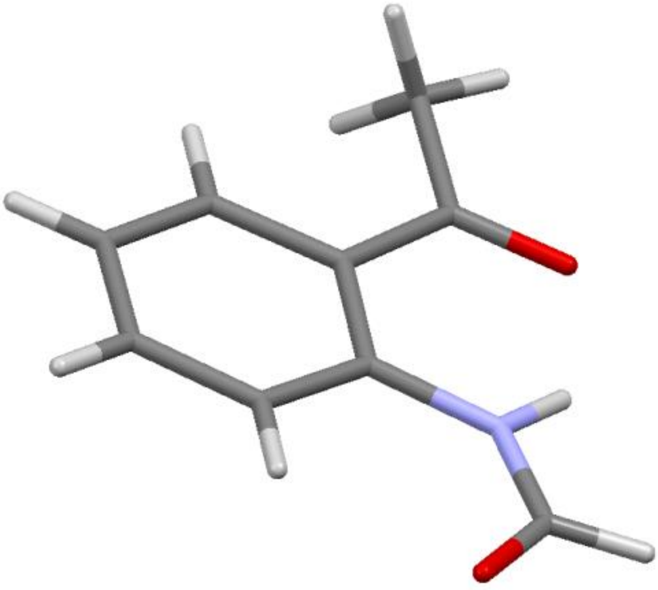


Figure S6. ORTEP and Stereo plots for X-ray crystal structures of **4** (**ic19457**).

CCDC 2005727 contains the supplementary crystallographic data for **4** (**ic19457**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk

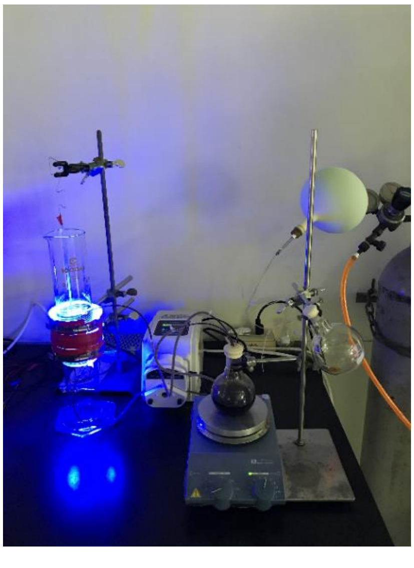
Table S5. Crystal data and structure refinement for **4** (**ic19457**).

Identification code	ic19457	
Empirical formula	C9 H9 N O2	
Formula weight	163.17	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	Pn	
Unit cell dimensions	a = 14.1319(5) Å	α= 90°.
	b = 3.86820(10) Å	β= 110.9456(10)°.
	c = 15.5153(5) Å	γ = 90°.
Volume	792.10(4) Å ^{3}	
Z	4	
Density (calculated)	1.368 Mg/m^{3}	
Absorption coefficient	0.806 mm^{-1}	
F(000)	344	
Crystal size	0.471 x 0.059 x 0.029 mm^{3}	
Theta range for data collection	3.635 to 74.974°.	
Index ranges	-17<=h<=17, -4<=k<=4, -19<=l<=18	
Reflections collected	5152	
Independent reflections	2954 [R(int) = 0.0182]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7539 and 0.6339	
Refinement method	Full-matrix least-squares on F^{2}	
Data / restraints / parameters	2954 / 2 / 235	
Goodness-of-fit on F^{2}	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0687	
R indices (all data)	R1 = 0.0270, wR2 = 0.0704	
Absolute structure parameter	0.22(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.132 and -0.112 e.Å $^{-3}$	

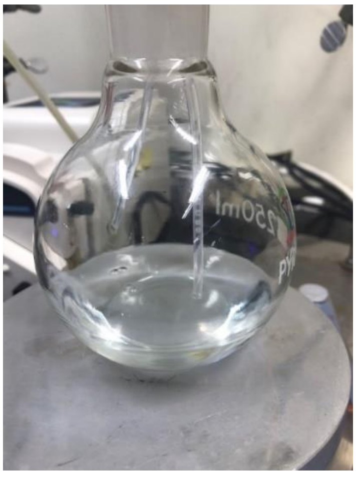
Homemade photoredox flow reactor device for circular flow experiments.

A 1000-mL glass graduated cylinder with approximately 39 cm in height and 7.3 cm in diameter was used for the construction of the circular photoreactor device, as shown in the following photos. The cylinder was coiled with a 7.5 meter PFA tube (ID: 2 mm and OD: 3 mm, total volume ca. 24 mL). The coiled PFA tube covered the 10.2-cm height of the cylinder and resulted in an area of 11 cm x 7.3 cm x 3.14 = 234 cm^2 exposure to the LED light. In the external surface of the PFA tube coiled cylinder, nine blue LED strips (each with 18 LED beads) are secured with insulating tape and placed in the center. A peristaltic pump (LongerPump, BT100-2J, YZ1515x) was used for delivering the solution of indole (**2a**, 2.0 g, 17.1 mmol) and 40% H_2O/CH_3CN (170 mL) at a certain flow rate stream to the photoredox flow reactor. At the speed of 100 rpm, a flow rate of 20 mL/min, the first drop of the reaction solution took only 72 seconds for traveling through the photoredox flow reactor device and back to the round bottle flask. The flask was equipped with a balloon of oxygen atmosphere and the inlet PFA tube was adjusted to just below the liquid level so that a small amount of gas will enter the tube when pumping liquid. In addition, the outlet tube was introduced into the reaction mixtures (Note: An oxygen environment is critical to the completion of the reaction; therefore, the solution must be repeatedly exposed to oxygen and then subjected to blue light irradiation. With careful sealing, a single balloon of oxygen can last for the duration of the circular flow reaction without the need to refill the oxygen gas).

A magnetic stirring bar and indole (2.00 g, 17.1 mmol) were placed in a 250-mL round bottle flask, followed by sequential addition of $Ru(bpy)_3Cl_2•6H_2O$ (384 mg, 0.05 mmol, 0.03 equiv), CH_3CN (102 mL) and H_2O (68 mL). The flask was equipped with a balloon of oxygen. The solution was stirred and connected with a set of PFA tube and flow reaction device as described above. The reaction mixture was stirred and irradiated for 24 h, and the reaction solution was extracted with EtOAc and brine. The organic solution was filtered through a pad of Celite, silica gel, and $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by recrystallization from EtOAc and hexane, and the mother liquor was purified by flash column chromatography with 30% EtOAc–hexane. The combined yellow solid product **1a** was obtained in 1.52 g (73% yield).



irradiation device



layout of the inlet and outlet PFA tube

bubbles in the PFA tube

(For clarity, solvent only, no catalysts and indole in the above two photos)

Circular flow Experiments for the reaction of 2h

A magnetic stirring bar and indole **2h** (2.00 g, 8.23 mmol) was placed in a 250-mL round bottle flask, followed by sequential addition of $Ru(bpy)_3Cl_2$•$6H_2O$ (182 mg, 0.02 mmol, 0.03 equiv), CH_3CN (49 mL) and H_2O (33 mL). The flask was equipped with a balloon of oxygen. With careful sealing, a single balloon of oxygen can last for the duration of the circular flow reaction without the need to refill the oxygen gas). The solution was stirred and connected with a set of PFA tubes and flow reaction device as described above. The reaction mixture was stirred and irradiated for 12 h, followed by slow addition of water to precipitate the product **2h** as a mustard-color solid. The precipitate was filter through a filter paper and collected, and the product was pure enough for spectroscopic analysis. The mother liquor filtrate was extracted with EtOAc and brine. The organic solution was filter through a pad of Celite, silica gel and $MgSO_4$, and concentrated *in vacuo* to give a crude residue. The crude product was purified by recrystallization from EtOAc and hexane, and the mother liquor was purified by flash column chromatography with 30% EtOAc–hexane. The combined mustard color solid product **1h** was obtained in 1.73 g (85% yield).

The light on/off experiment:

A magnetic stirring bar and indole (46.8 mg, 0.40 mmol) was placed in a 10-mL Schlenk tube vial, followed by sequential addition of $Ru(bpy)_3Cl_2$•$6H_2O$ (3.0 mg, 0.004 mmol, 0.01 equiv), a solution of CH_3CN (2.0 mL) and H_2O (1.3 mL), and 1,3,5-trimethylbenzene (18 µL, 0.13 mmol, 0.32 equiv). The Schlenk tube was equipped with a balloon of oxygen. The solution was stirred and irradiated with a strip of 54 blue LEDs, located 2-5 cm away from the reaction vial. After the indicated reaction time, ~50µL of the reaction mixture aliquot was collected, diluted with acetone-d_6 and analyzed by ^1H NMR.[19]

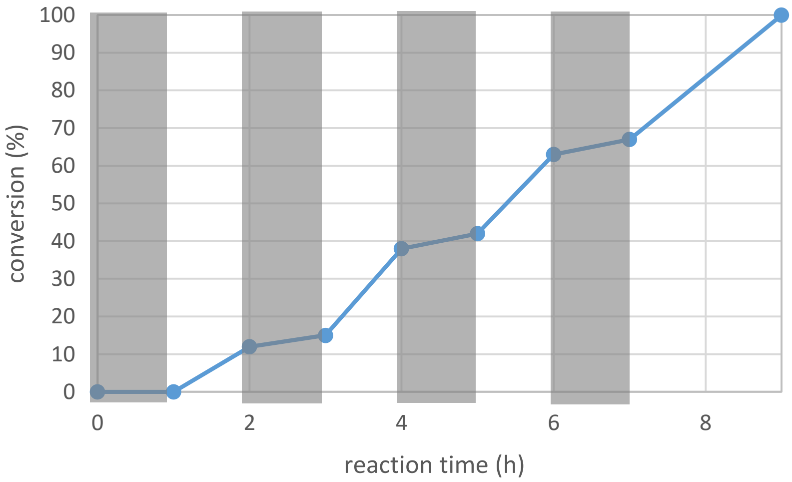


Fig S7. Conversion of **2a** to **1a** with ruthenium catalyst in the light/dark sequence.

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[19] The transformation of indole **2a** to indolone **1a** does not solely depend on the visible-light catalysis, as a small portion of the product can be generated in the absence of light with oxygen and oxidant, *e.g.* H_2O_2 and other radical species, but with much slower reaction rate and lower yields. As shown in Figure S6. Under light irradiation, the reaction was significantly promoted, but the reaction was slow under dark conditions. Since some H_2O_2 and other radical species have been produced in the reaction mixture after initial light irradiation, a small amount of **1a** could be produced, but the rate is much lower and the contribution in the dark environment is also lower.

Cyclic voltammetry was measured with the following conditions:

Electro chemical measurements were performed with CHI 440 electrochemical work station (CH Instruments, Inc, Austin, TX, USA). Indoles **1** [0.1 M] $TBABF_4$ in 40%H_2O/MeCN (*v/v*). Sweep rate: 0.1 V/s. Platinum working electrode (CHI102, CH Instruments, Inc), Non-Aqueous Ag/Ag^+ reference electrode ([0.01 M] $AgNO_3$/[0.1 M] TBAP, RE-7, BAS Inc, Japan), Platinum counter electrode (5 cm, Cat. No. 002233, BAS Inc, Japan) in a voltammetry cell (SVC3, BAS Inc, Japan)

Figure S8. Cyclic voltammetry (versus Ag/Ag^+ in CH_3CN) of indole **2a** in MeCN and 40% H_2O/MeCN+H_2O

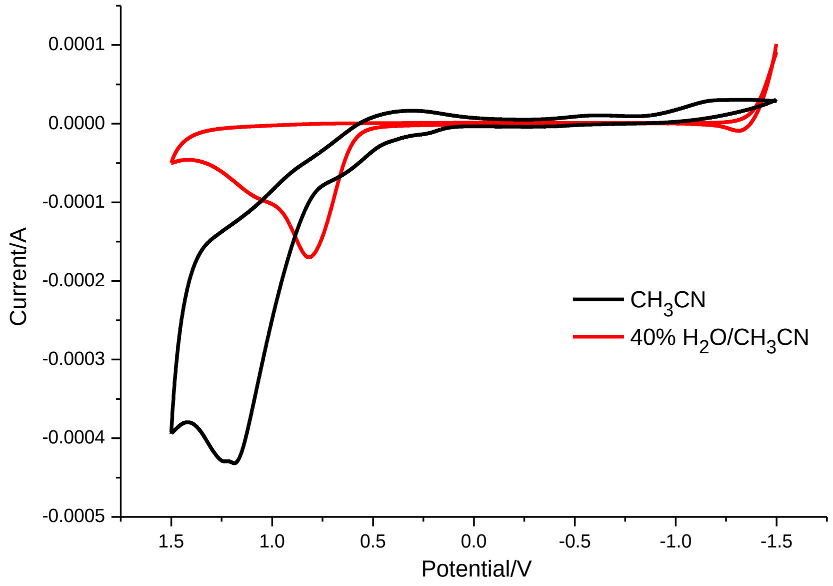


Figure S9. CV of indole **2a** in acetonitrile solutions with different proportions of water content (H_2O/MeCN+H_2O, *v/v*)

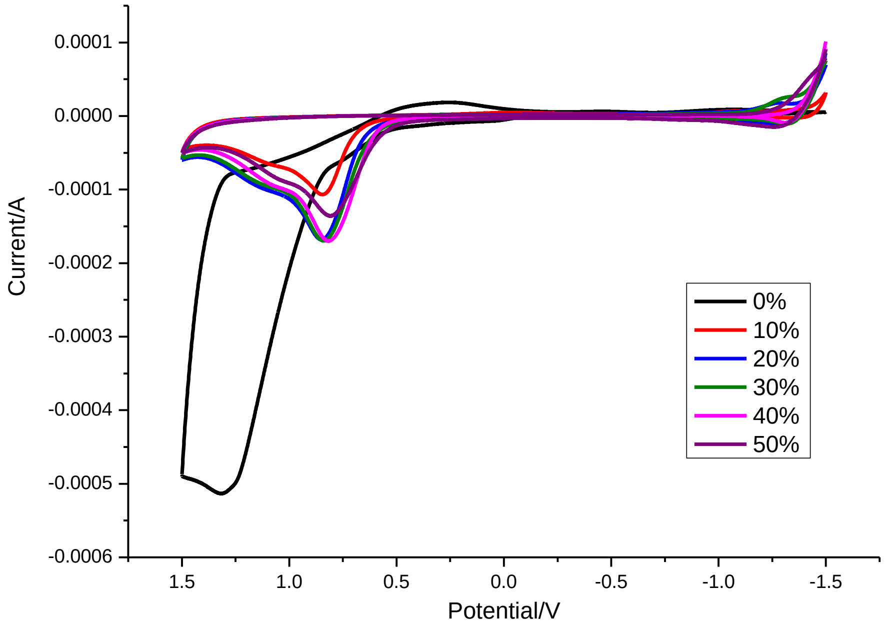


Figure S10. CV of triindole **1a** 40% H_2O–MeCN (0.01 M), Enlarged at 1.0-0.5 V

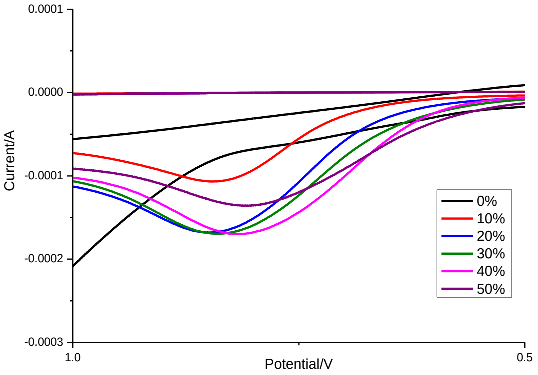


Figure S11. CV of indoles **2** in 40% H_2O–MeCN (*v/v*, 0.01 M)

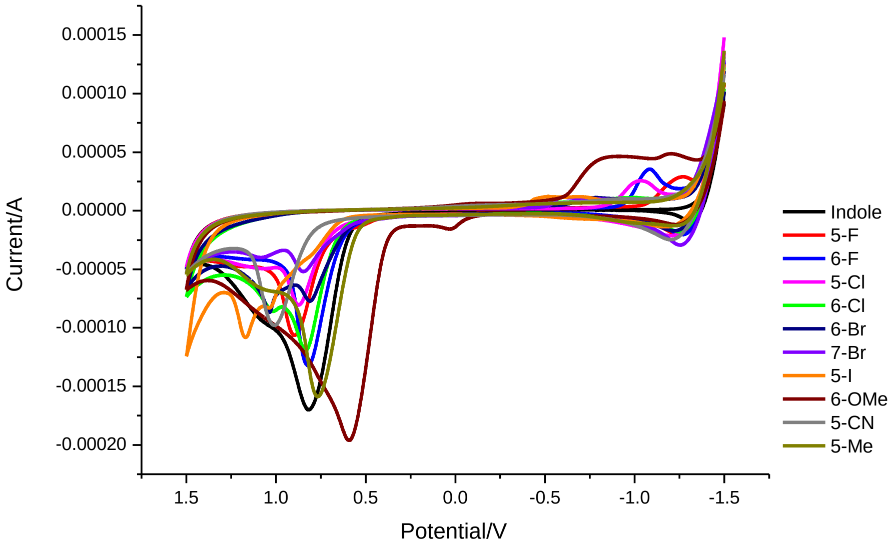
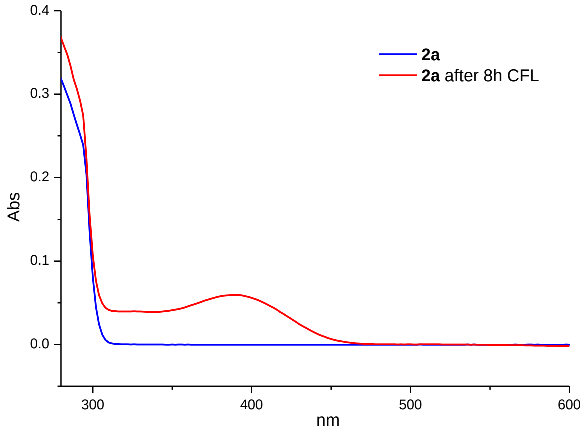


Figure S12. Visible light spectrum of **2a** in 40% H_2O/CH_3CN (0.01 M) and its spectrum after 8 hours of CFL irradiation.[20]



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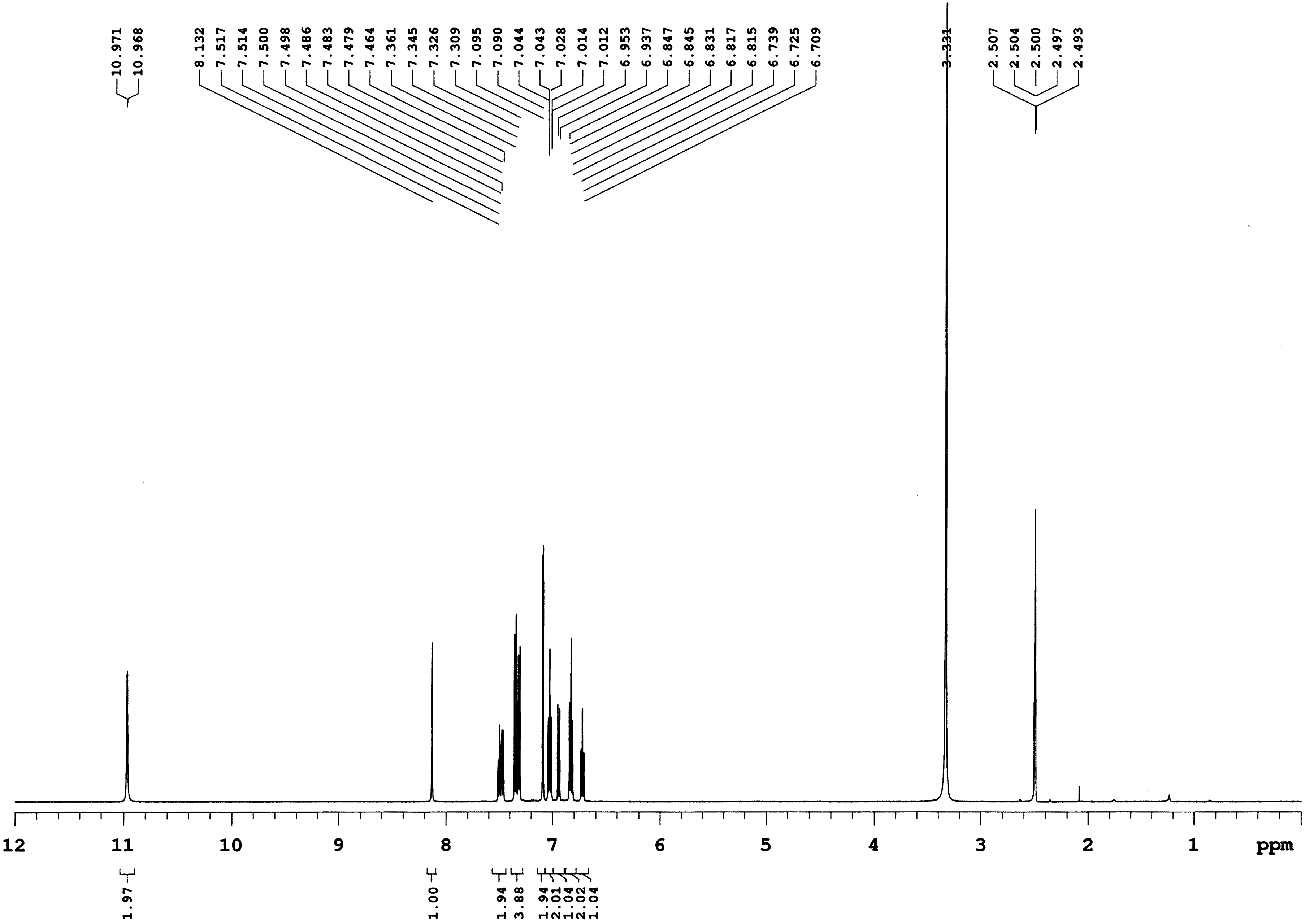
[20] A marked marron color appeared after a few hours of CFL-irradiation of the colorless solution of indole **2a** under a balloon of oxygen. The absorption spectrum of the solution after 8-h irradiation showed a new broad absorption band around 400 nm.

LTC-1-24-f5

Sample Name **LTC-1-24-f5**
Date collected **2018-11-18**
Pulse sequence **PROTON**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



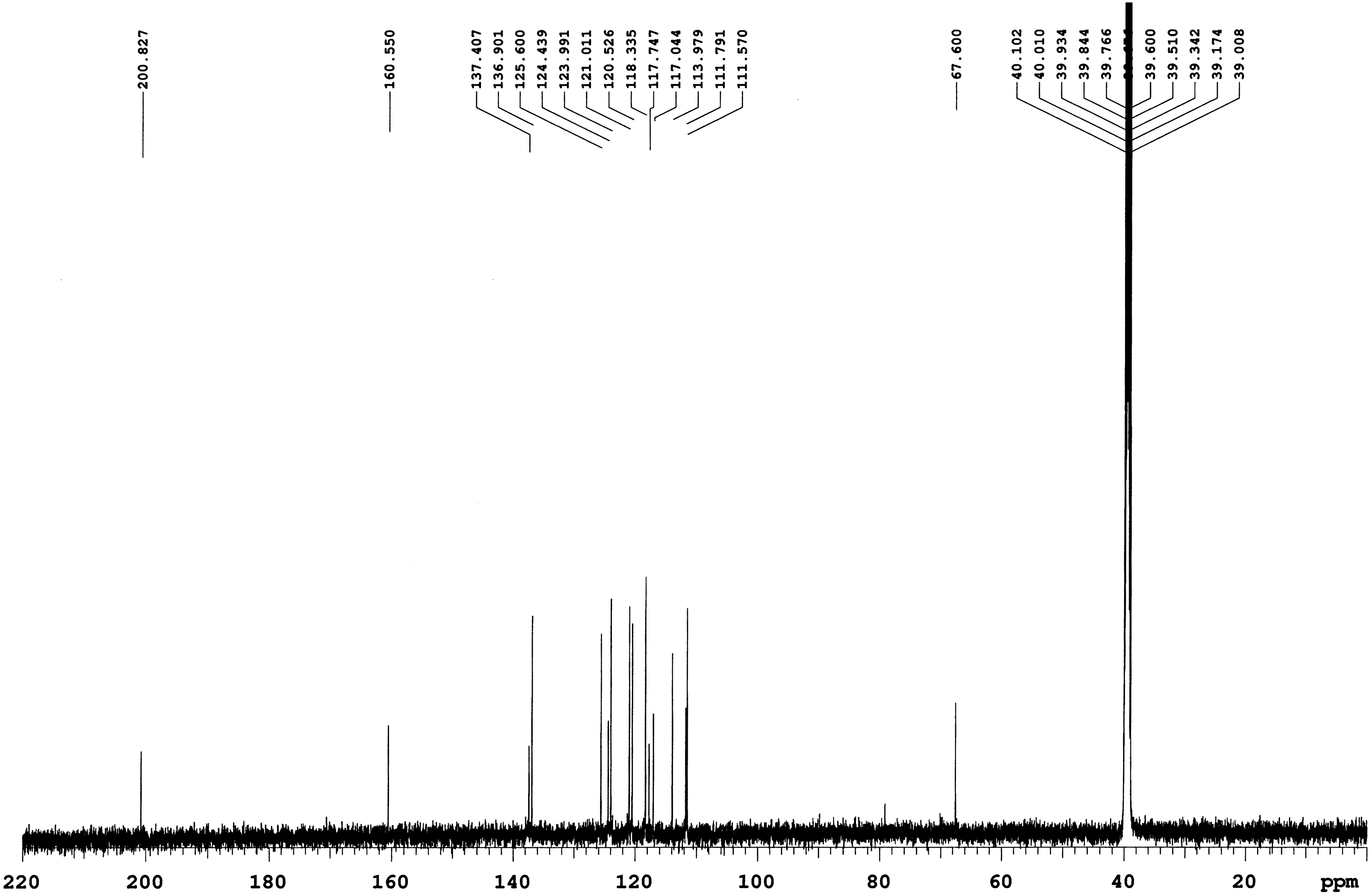
Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-24-f5/PROTON_12

1H NMR (DMSO-d6, 500 MHz) of **1a**

Plot date 2018-11-18

LTC-1-24-f5

Sample Name **LTC-1-24-f5**
Date collected **2018-01-30**
Pulse sequence **CARBON**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



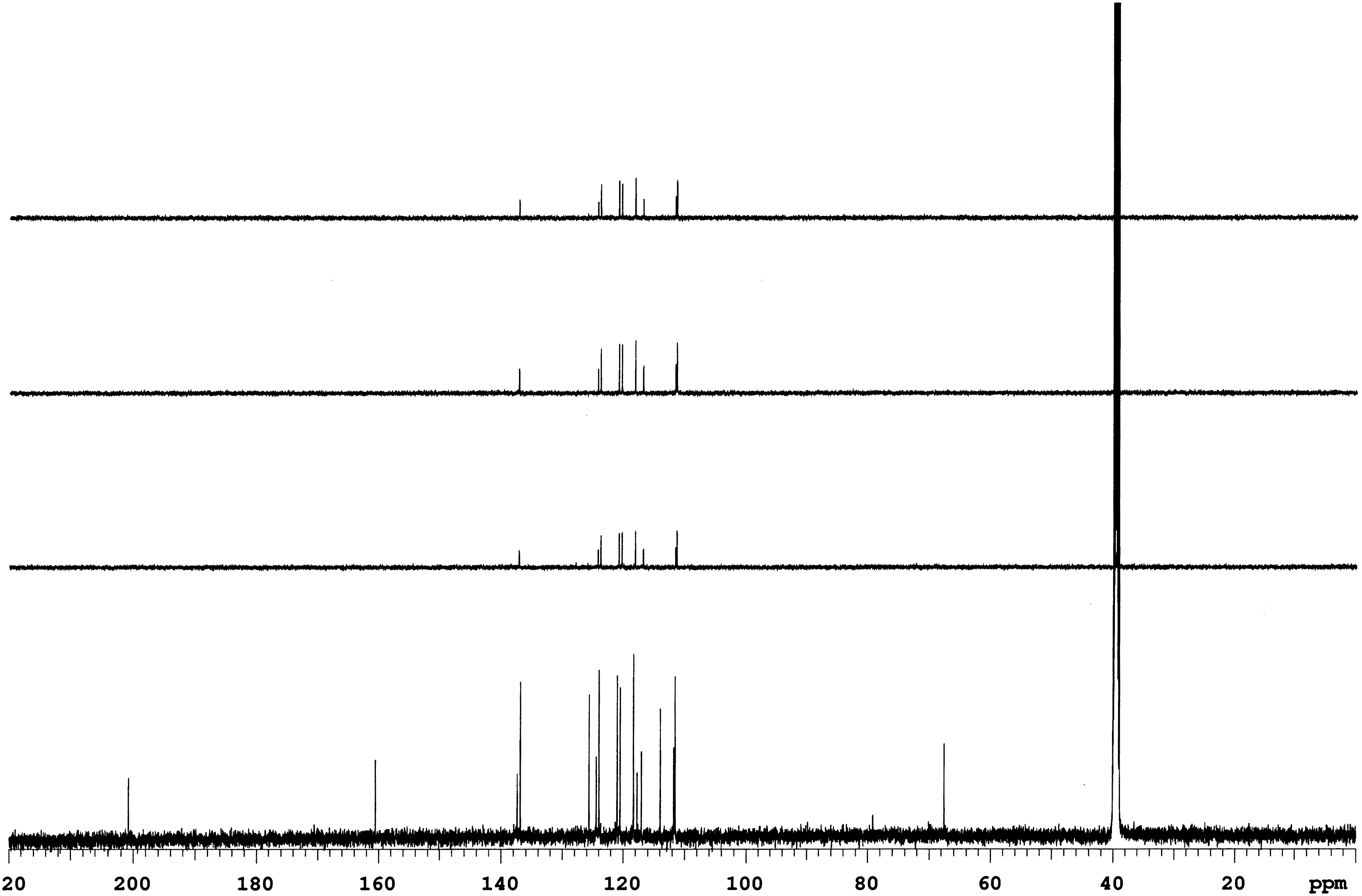
13C NMR (DMSO-d6, 125 MHz) of **1a**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-24-f5/CARBON_04

Plot date 2018-01-31

LTC-1-24-f5

Sample Name	**LTC-1-24-f5**	Pulse sequence	**DEPT**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2018-01-31**	Solvent	**dmso**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



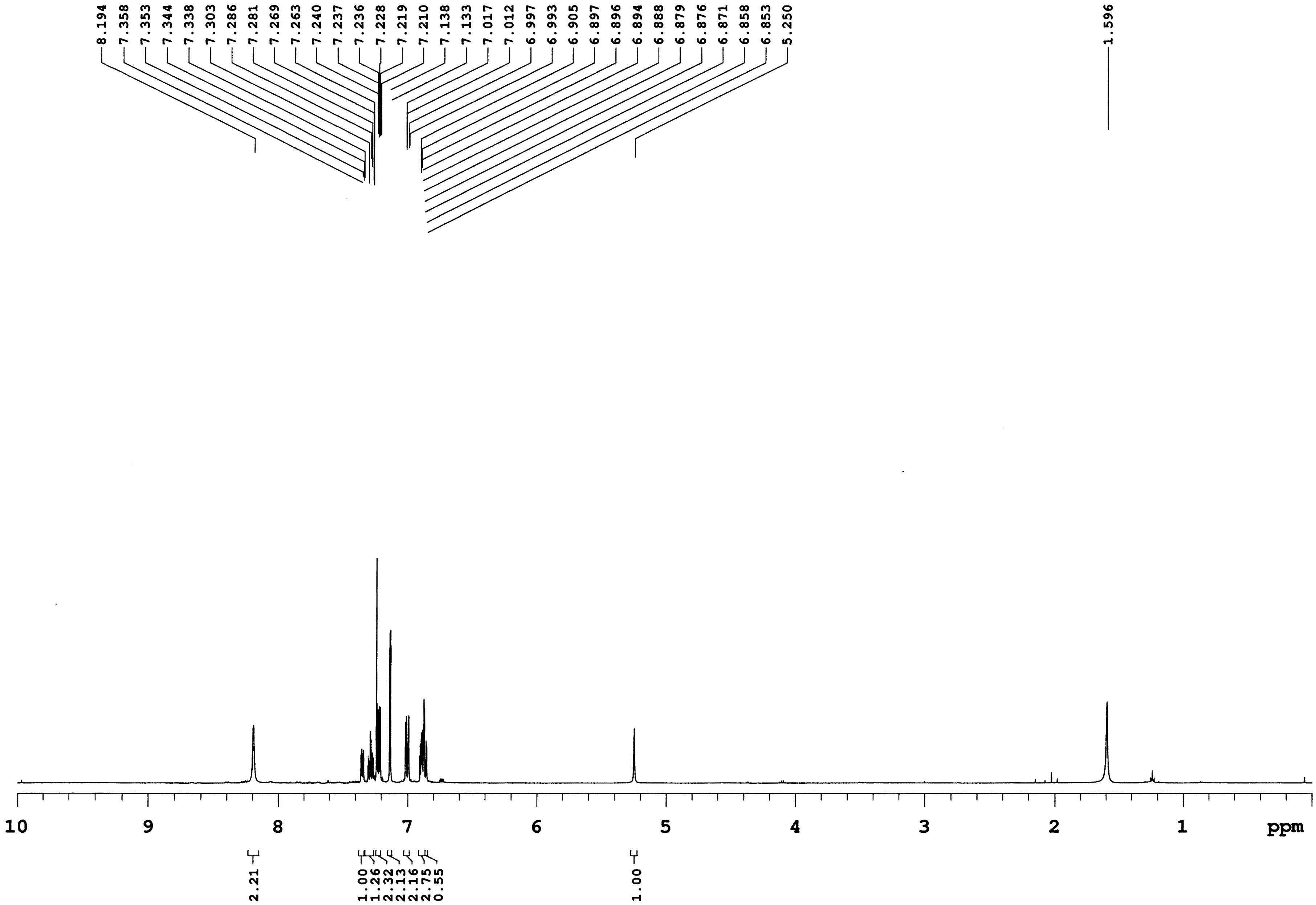
DEPT of **1a**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-24-f5/DEPT_01

Plot date 2018-01-31

LTC-1-167-f4

Sample Name **LTC-1-167-f4**
Date collected **2018-11-06**
Pulse sequence **PROTON**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



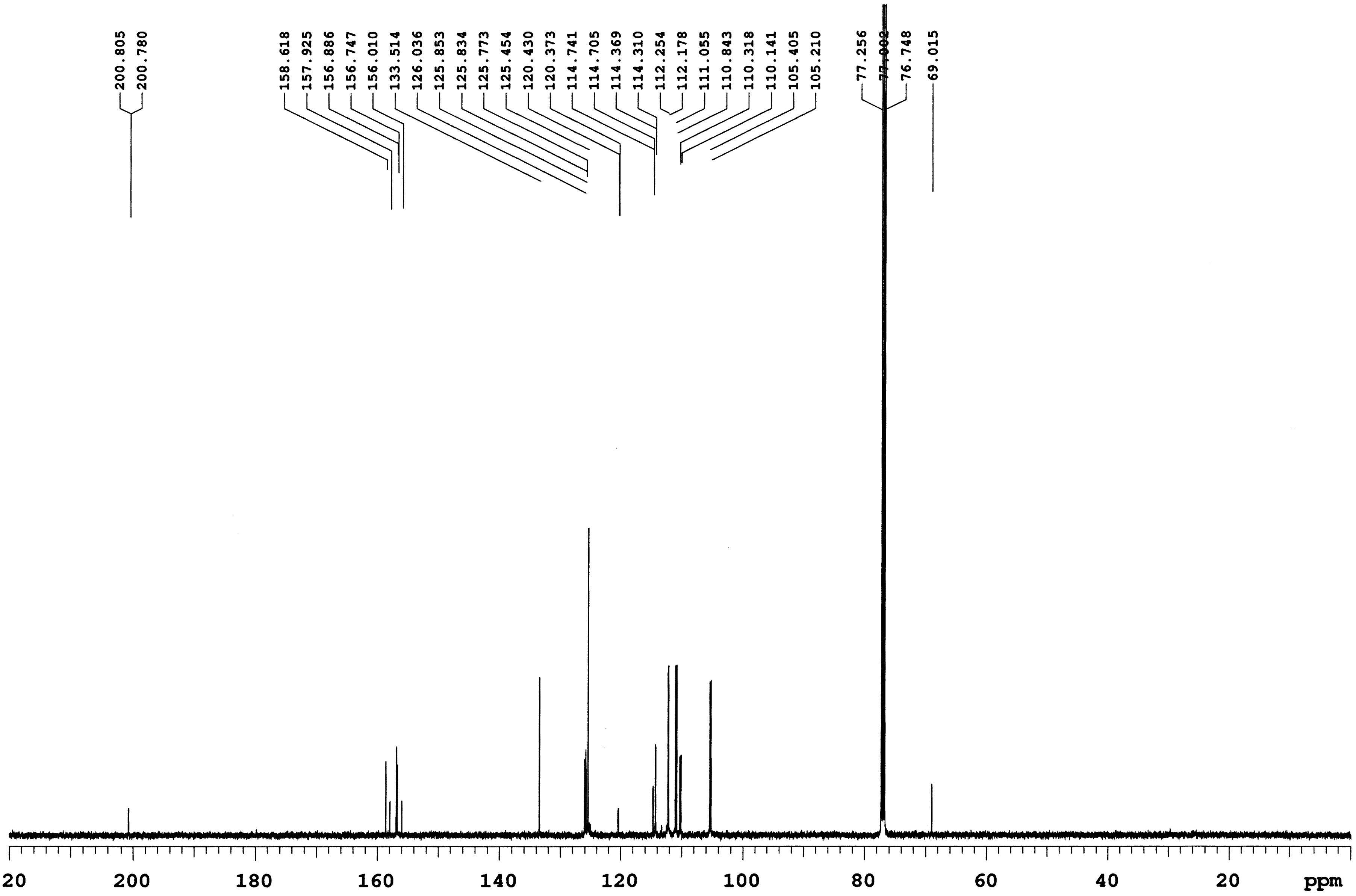
1H NMR (CDCl3, 500 Hz) of **1b**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-167-f4/PROTON_03

Plot date 2018-11-12

LTC-1-167-f4

Sample Name **LTC-1-167-f4**
Date collected **2018-11-06**
Pulse sequence **CARBON**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



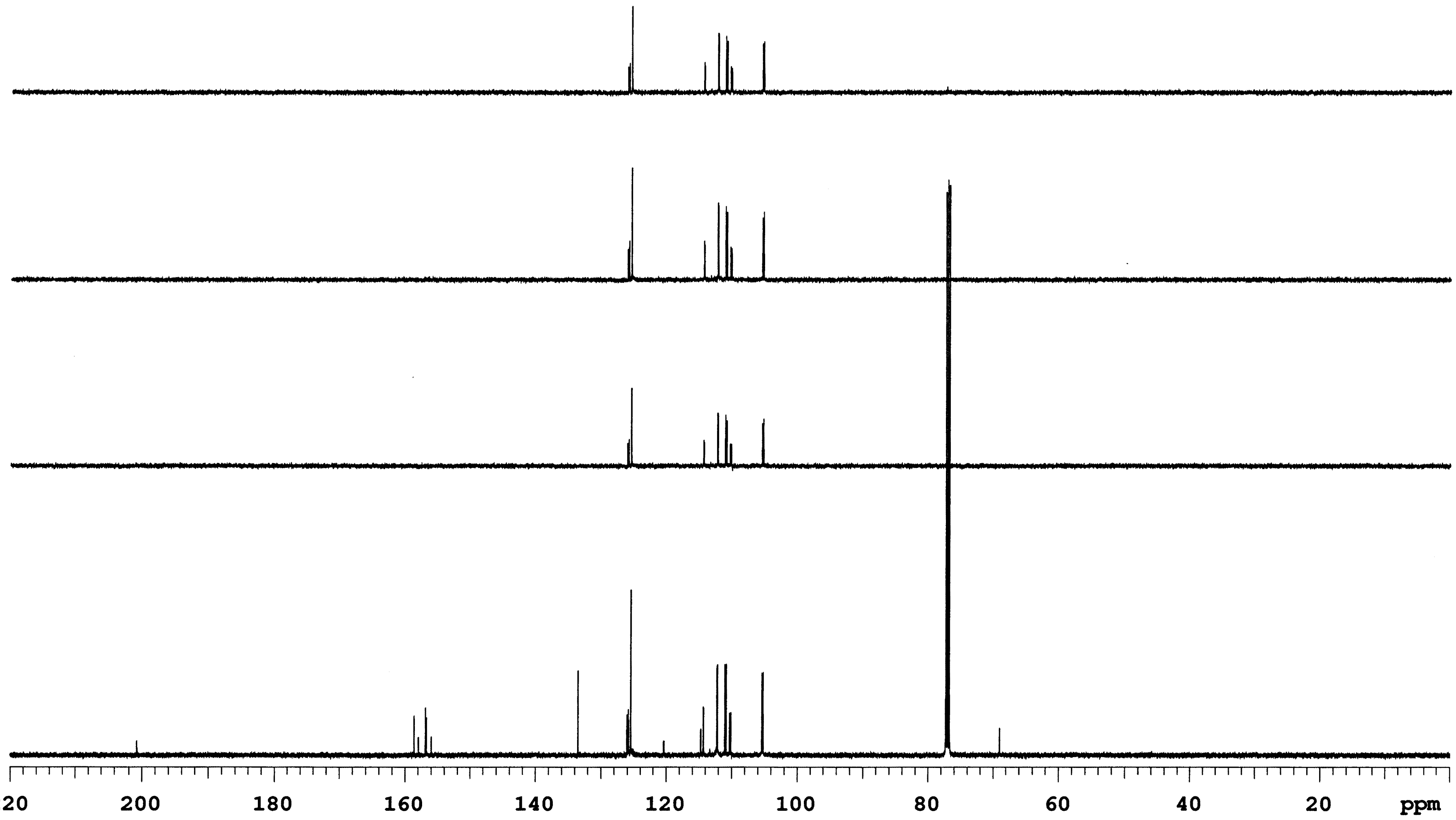
13C NMR (CDCl3, 125 Hz) of **1b**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-167-f4/CARBON_02

Plot date 2018-11-12

LTC-1-167-f4

Sample Name **LTC-1-167-f4** Pulse sequence **DEPT** Temperature **25** Study owner **vnmr2**
Date collected **2018-11-06** Solvent **cdcl3** Spectrometer **Agilent-NMR-inova500** Operator **vnmr2**



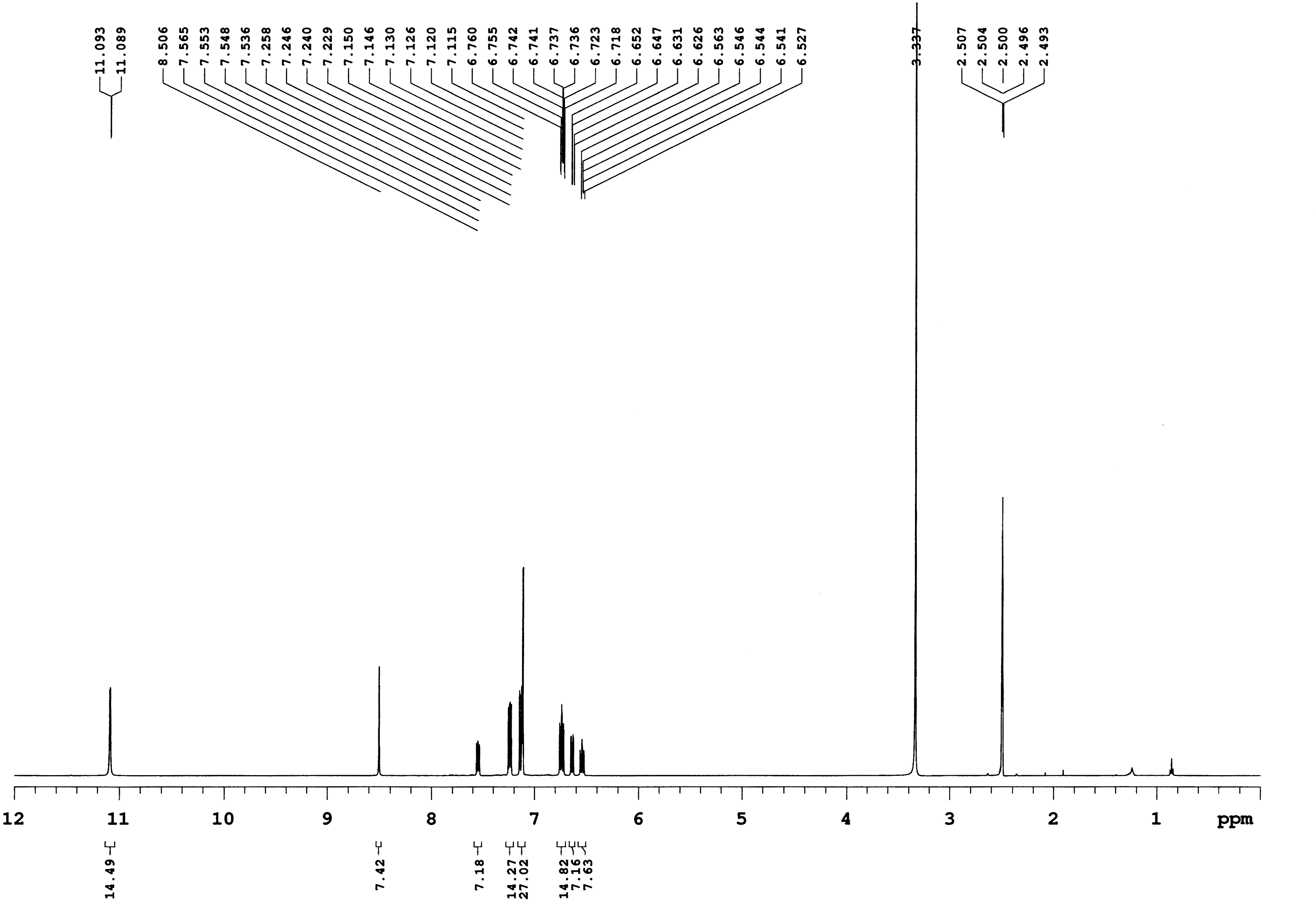
DEPT of **1b**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-167-f4/DEPT_01

Plot date 2018-11-12

LTC-1-156-f6

Sample Name **LTC-1-156-f6** Pulse sequence **PROTON** Temperature **25** Study owner **vnmr2**
Date collected **2018-10-12** Solvent **dmso** Spectrometer **Agilent-NMR-inova500** Operator **vnmr2**



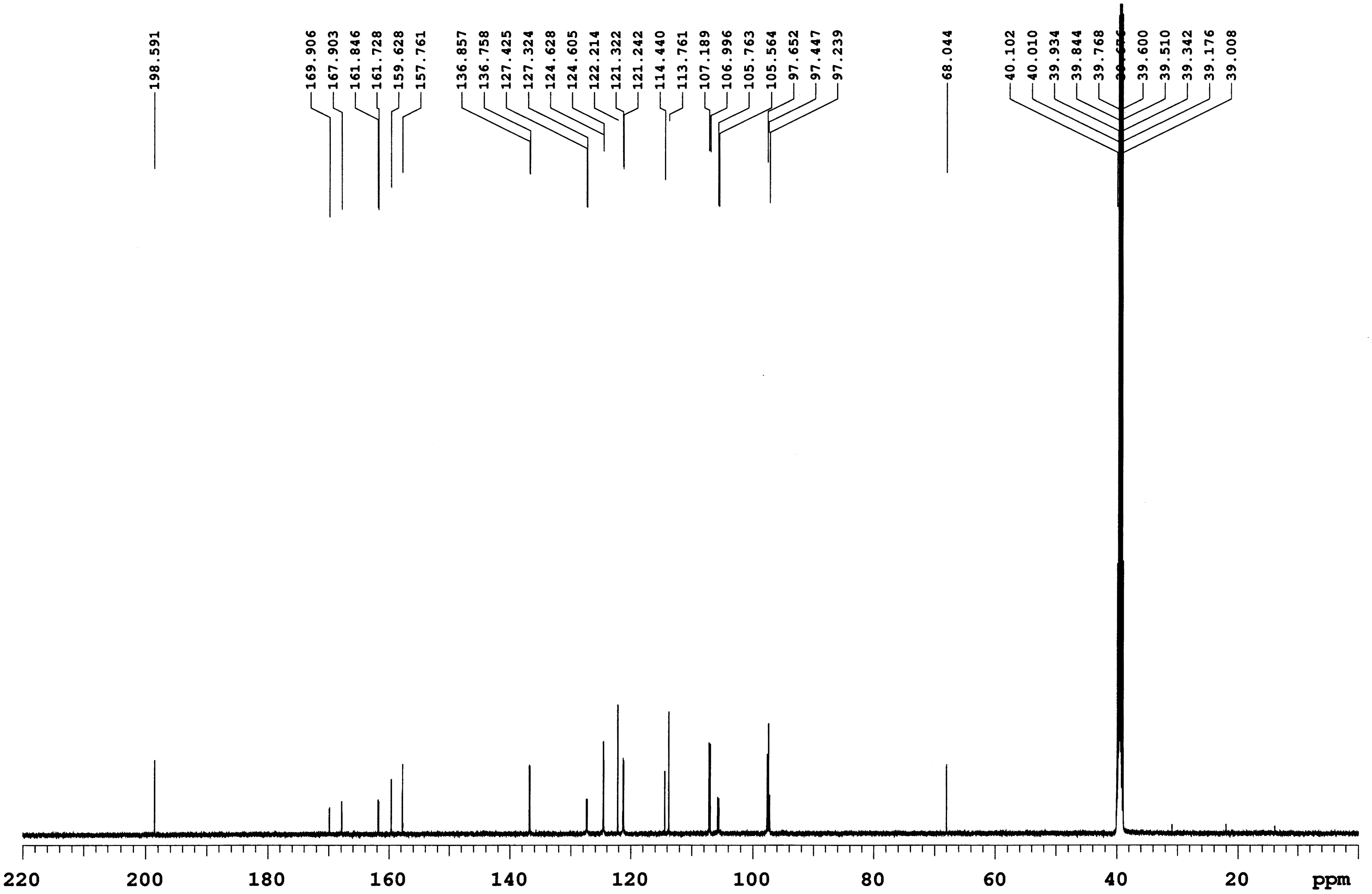
Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-156-f6/PROTON_04

1H NMR (DMSO-d6, 500 Hz) of **1c**

Plot date 2018-11-06

LTC-1-156-f6

Sample Name **LTC-1-156-f6** Pulse sequence **CARBON** Temperature **25** Study owner **vnmr2**
Date collected **2018-10-12** Solvent **dmso** Spectrometer **Agilent-NMR-inova500** Operator **vnmr2**



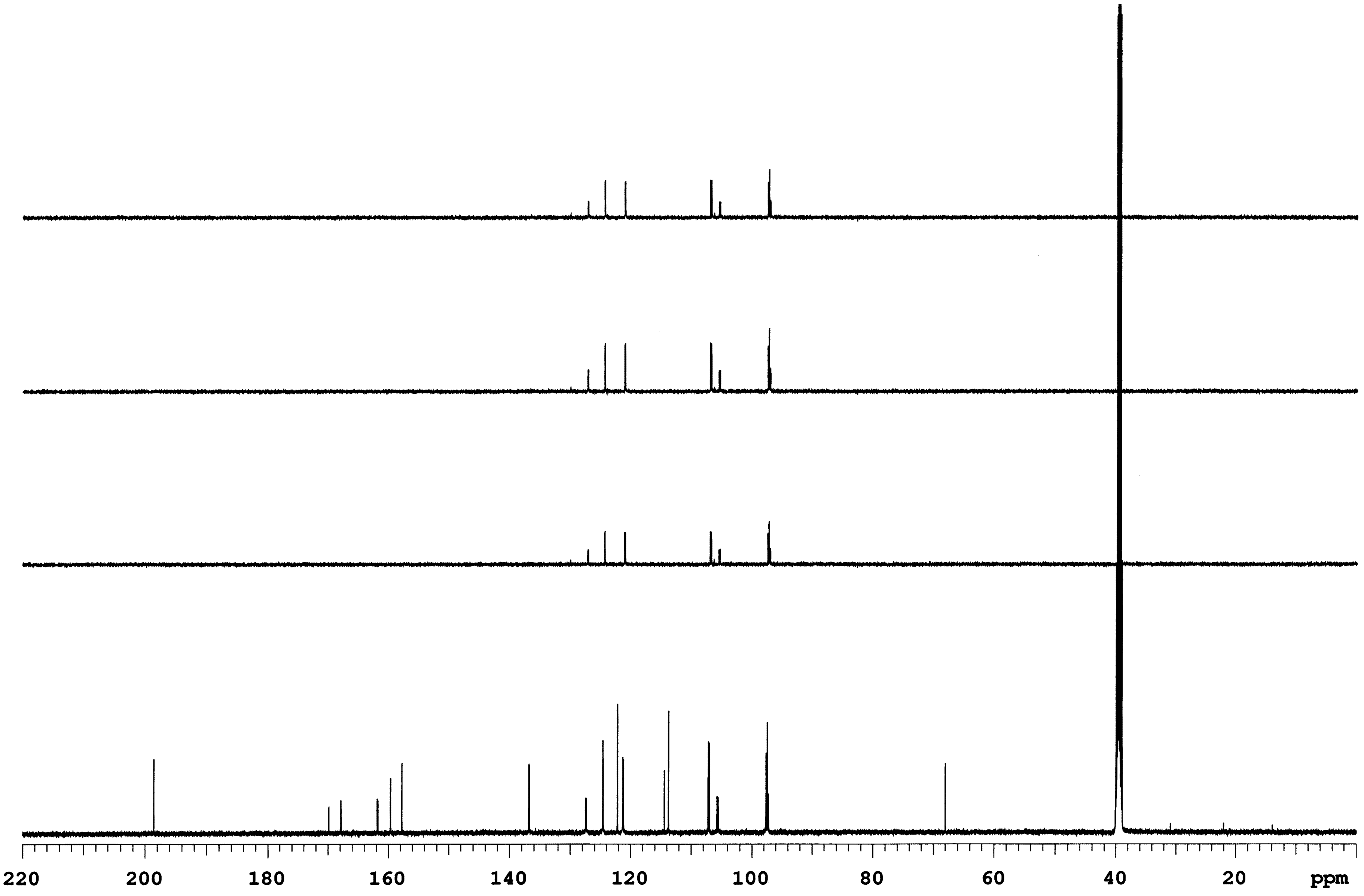
13C NMR (DMSO-d6, 125 Hz) of **1c**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-156-f6/CARBON_02

Plot date 2018-11-06

LTC-1-156-f6

Sample Name **LTC-1-156-f6** Pulse sequence **DEPT** Temperature **25** Study owner **vnmr2**
Date collected **2018-10-12** Solvent **dmso** Spectrometer **Agilent-NMR-inova500** Operator **vnmr2**



DEPT of **1c**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-156-f6/DEPT_01

Plot date 2018-11-06

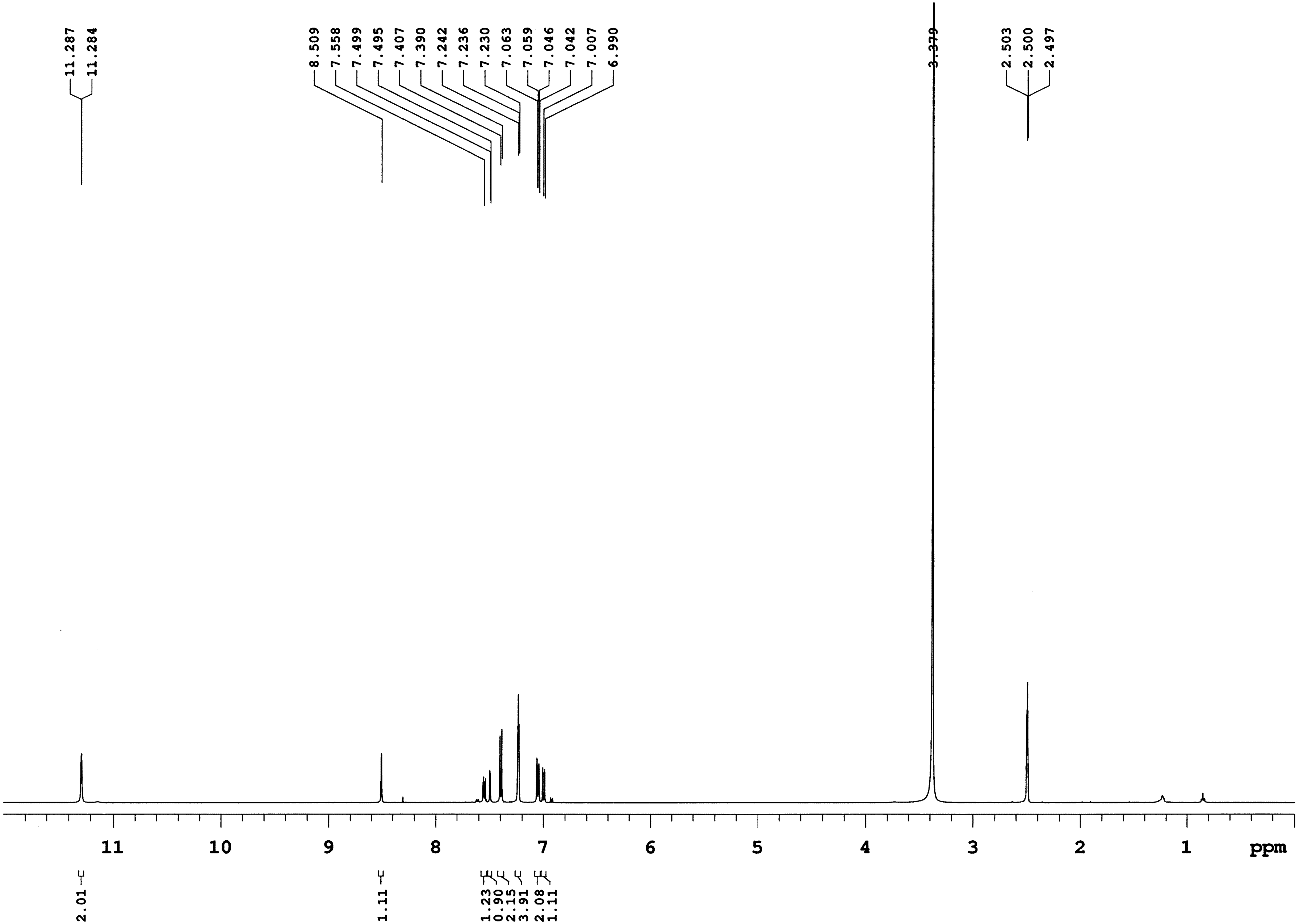
LTC-1-140-2

Sample Name **LTC-1-140-2**
Date collected **2018-09-24**

Pulse sequence **PROTON**
Solvent **dmso**

Temperature **25**
Spectrometer **Agilent-NMR-inova500**

Study owner **vnmr2**
Operator **vnmr2**



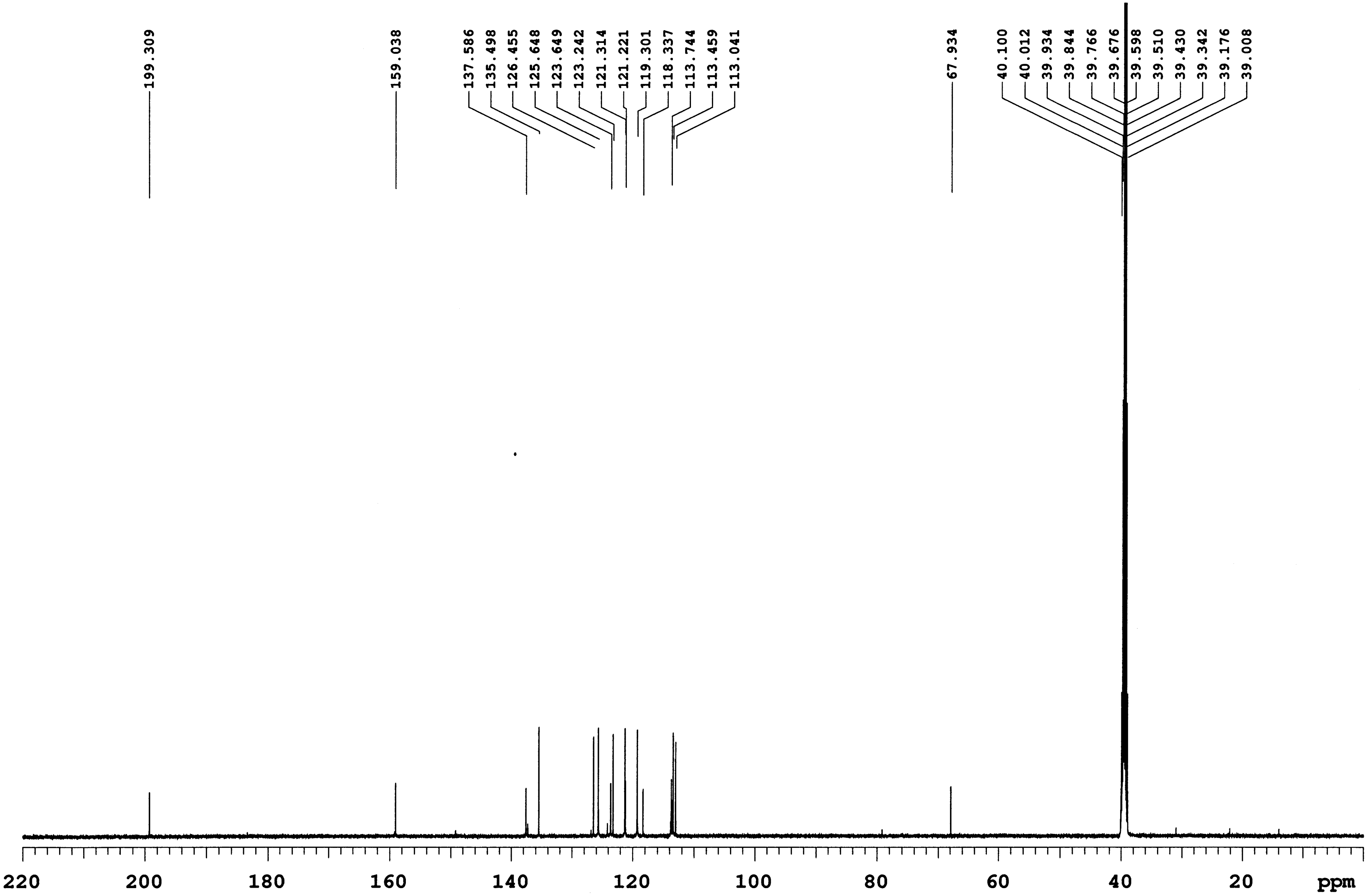
1H NMR (DMSO-d6, 500 MHz) of **1d**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-2/PROTON_13

Plot date 2018-11-06

LTC-1-140-2

Sample Name **LTC-1-140-2**
Date collected **2018-09-25**
Pulse sequence **CARBON**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



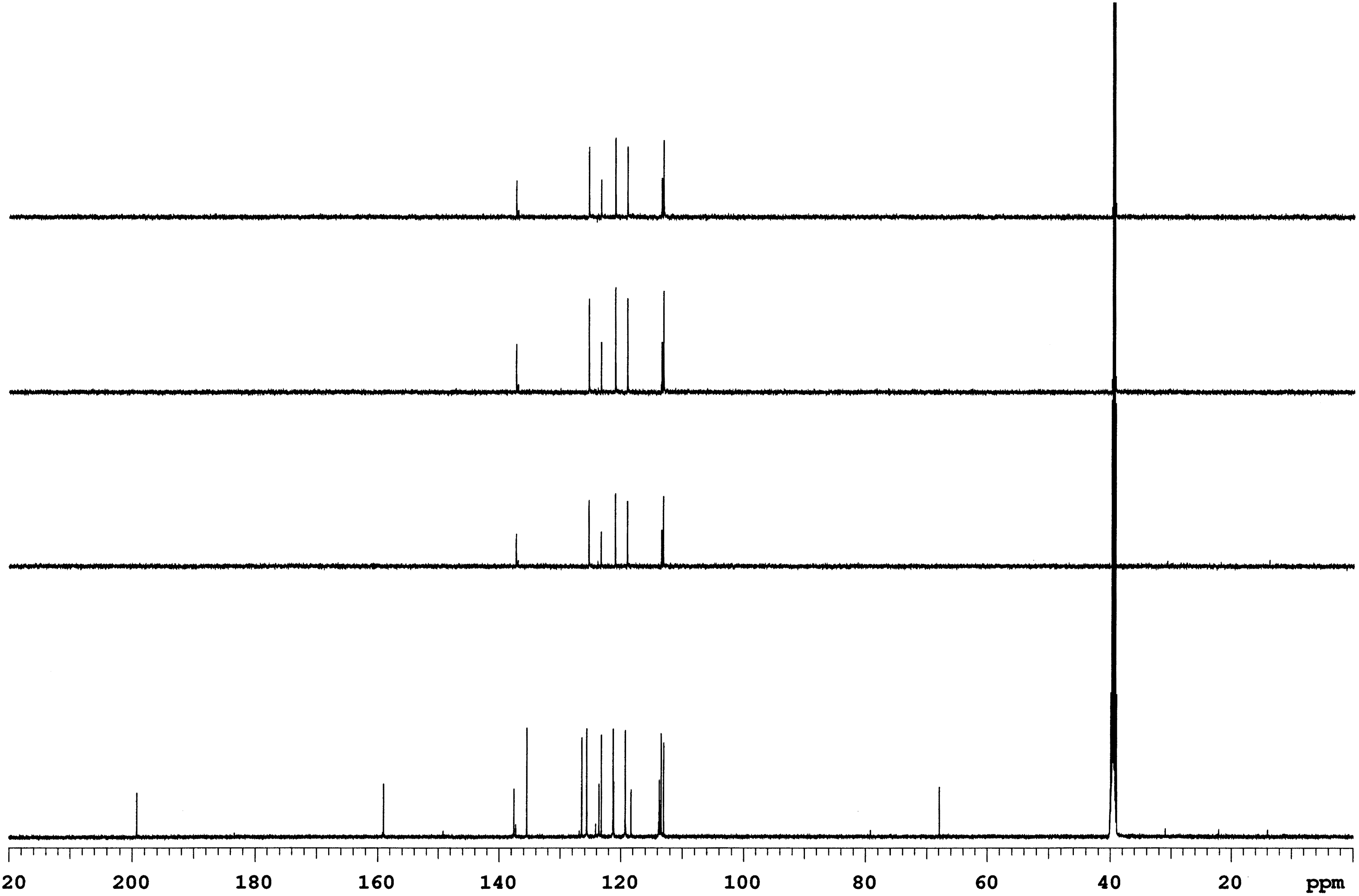
13C NMR (DMSO-d6, 125 MHz) of **1d**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-2/CARBON_02

Plot date 2018-09-25

LTC-1-140-2

Sample Name **LTC-1-140-2**
Date collected **2018-09-22**
Pulse sequence **DEPT**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



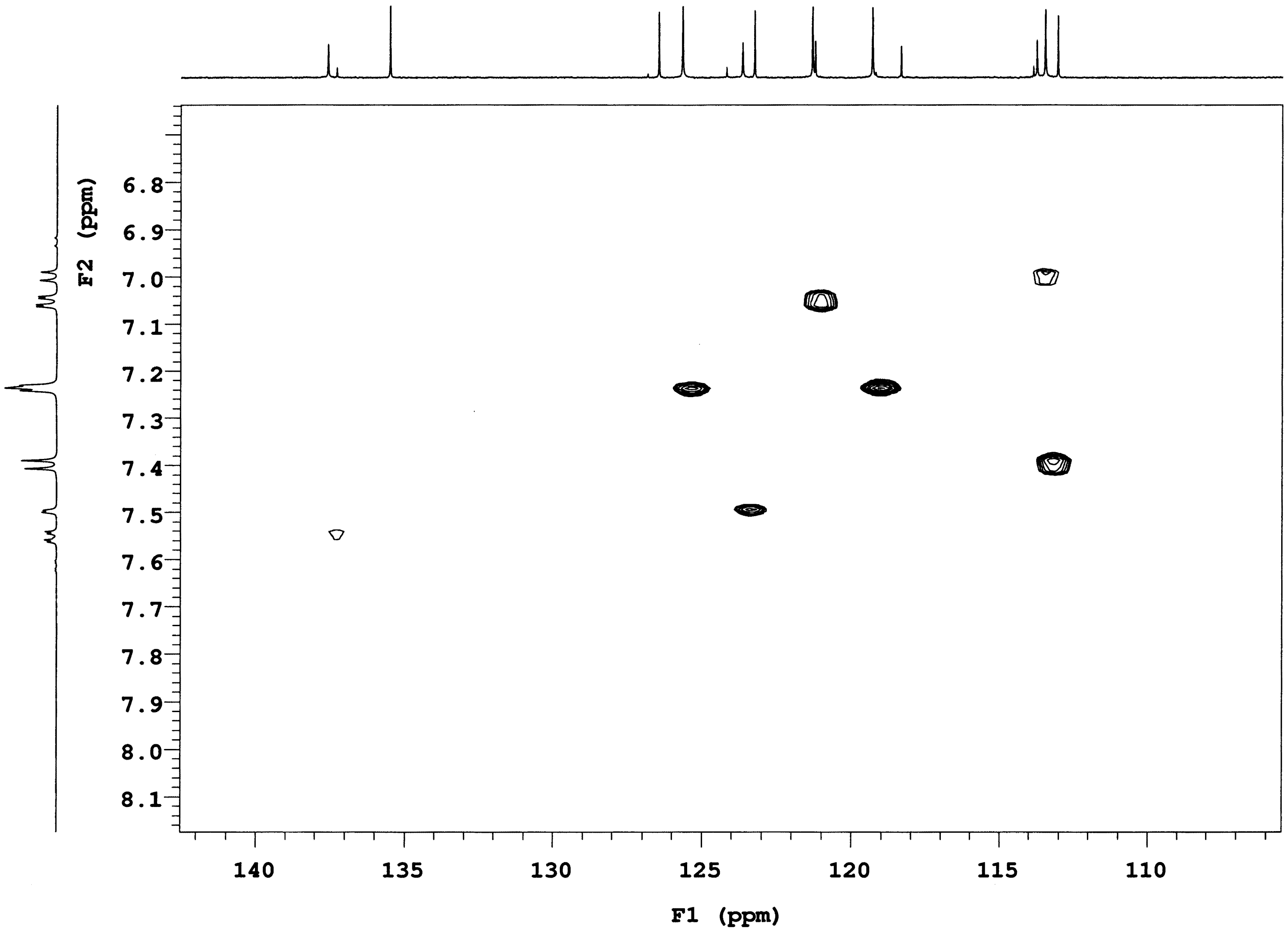
DEPT of **1d**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-2/DEPT_01

Plot date 2018-09-25

LTC-1-140-2

Sample Name **LTC-1-140-2**
Date collected **2018-11-19**
Pulse sequence **gHSQC**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



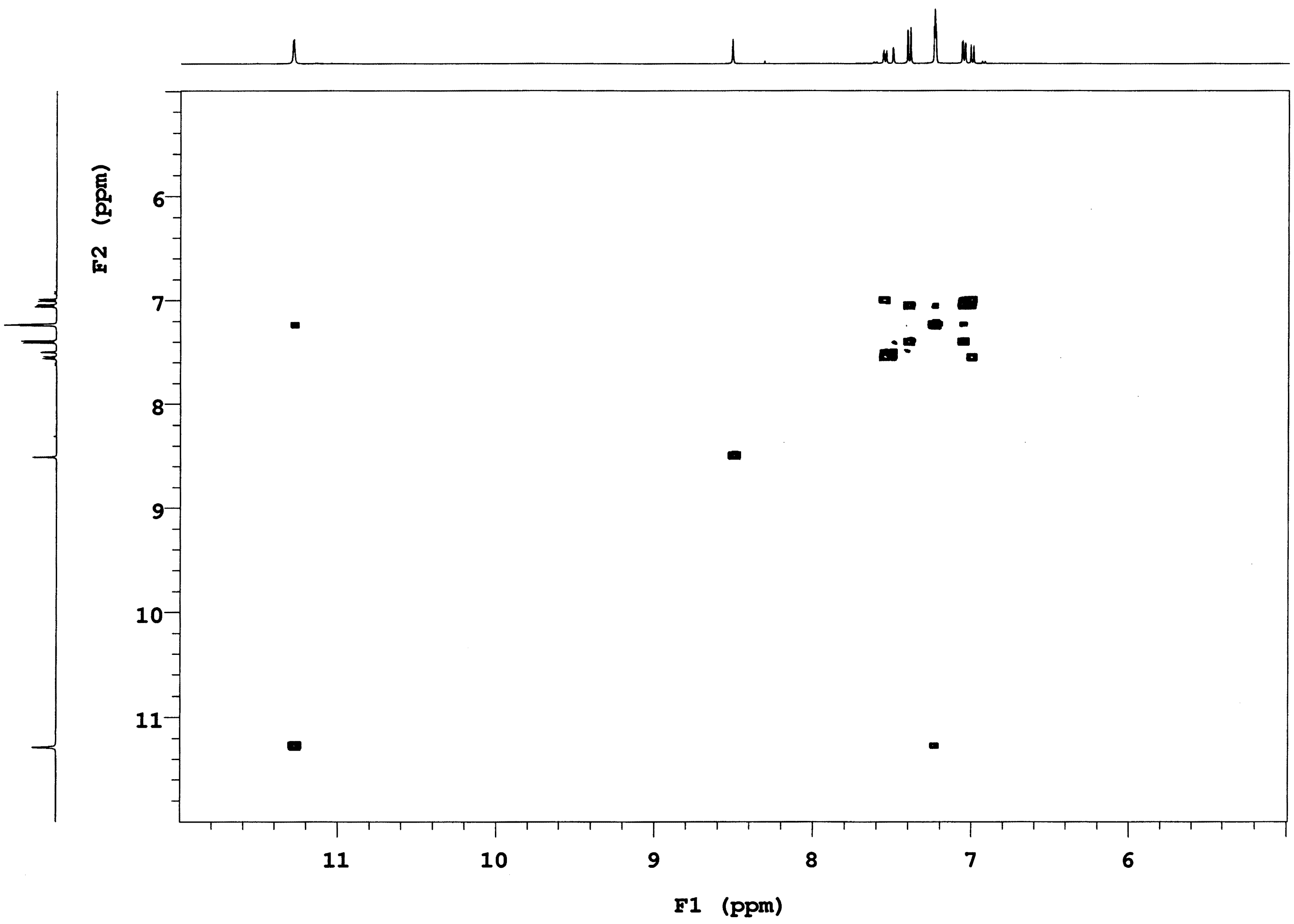
HSQC of **1d**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-2/gHSQC_01

Plot date 2018-11-21

LTC-1-140-2

Sample Name	**LTC-1-140-2**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2018-11-18**	Solvent	**dmso**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



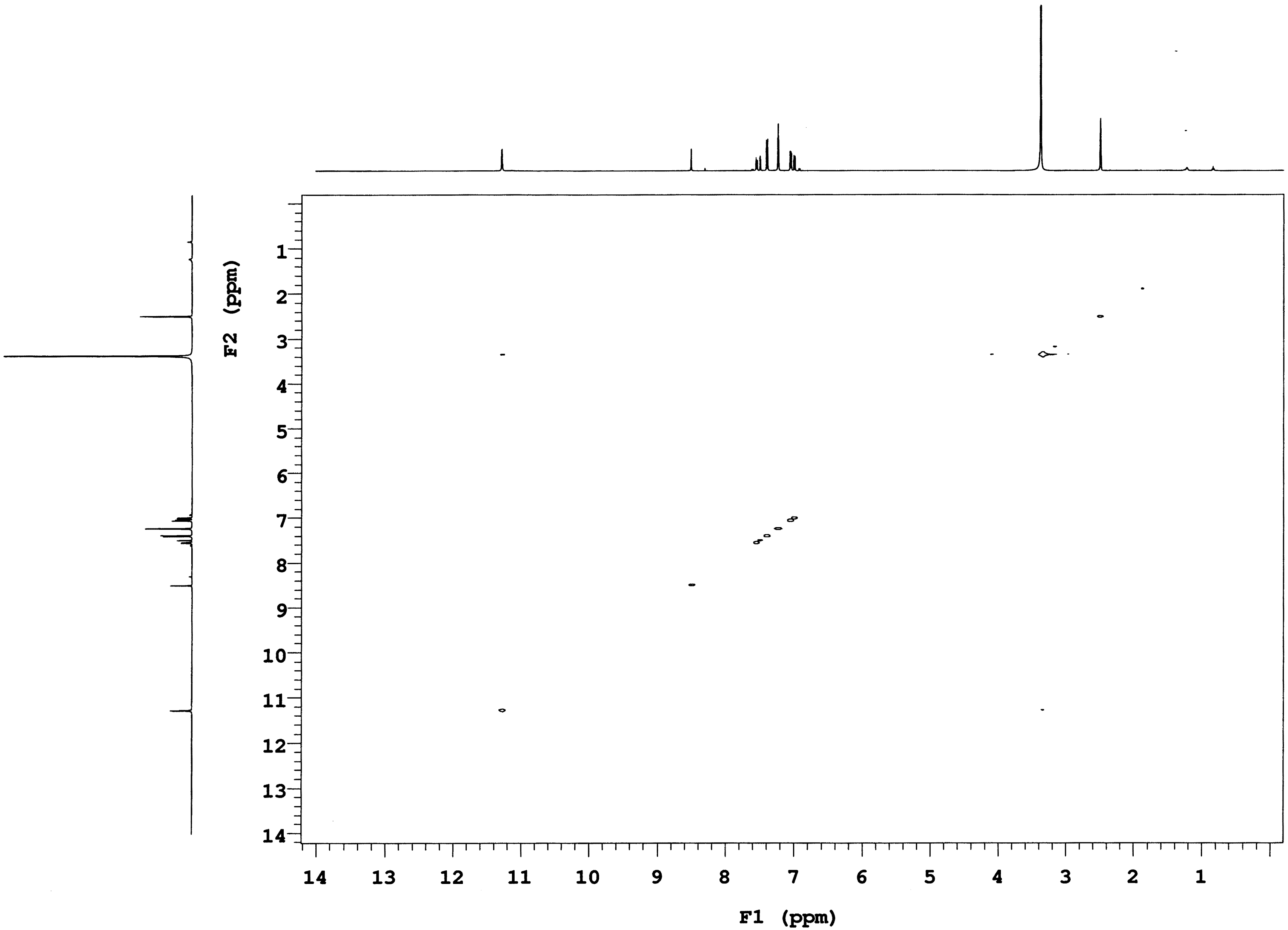
COSY of **1d**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-2/gCOSY_01

Plot date 2018-11-21

LTC-1-140-2

Sample Name **LTC-1-140-2**
Date collected **2018-11-18**
Pulse sequence **NOESY**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



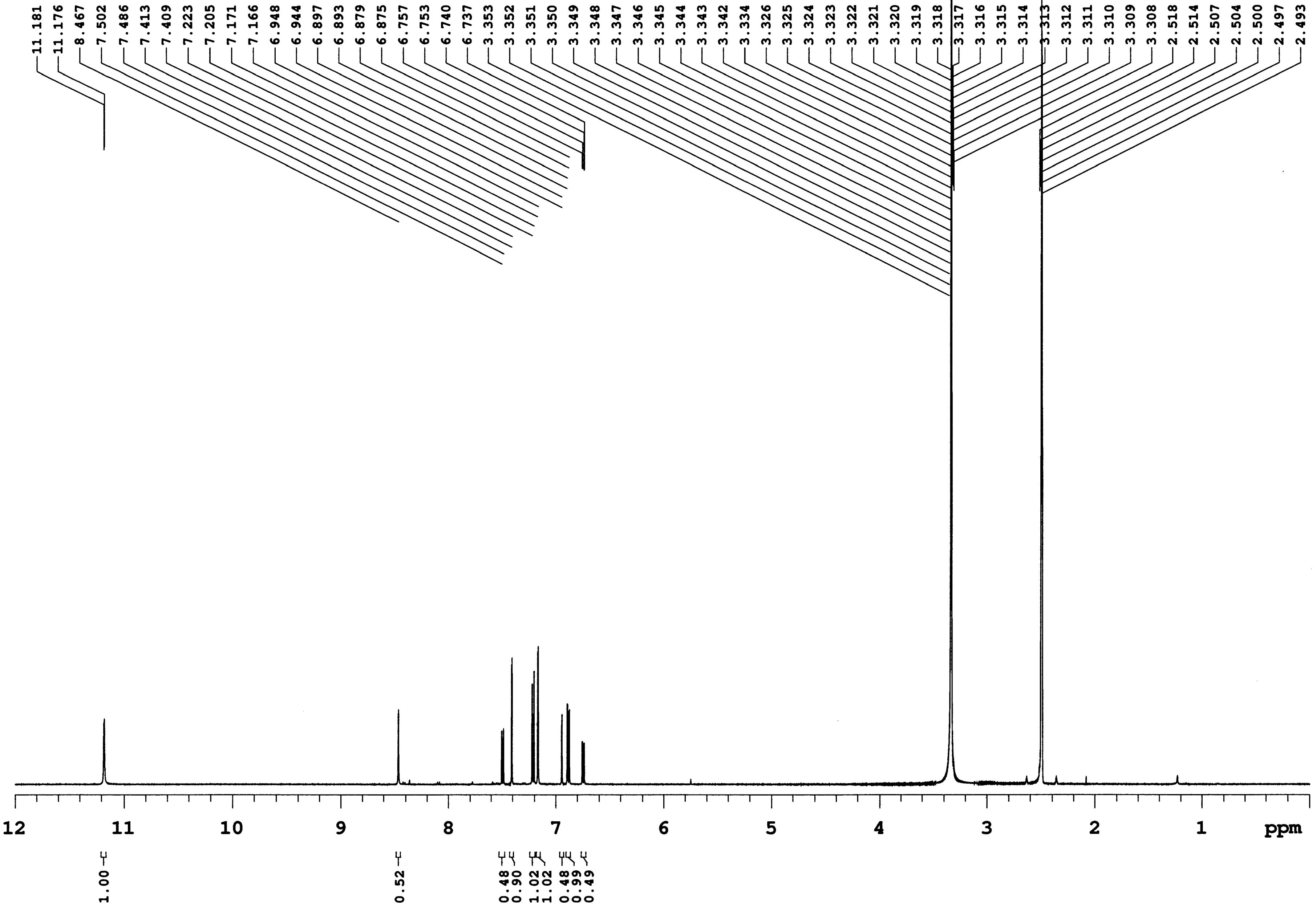
NOESY of **1d**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-2/NOESY_01

Plot date 2018-11-21

LTC-1-138-3

Sample Name **LTC-1-138-3**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2018-09-20**	Solvent **dmso**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



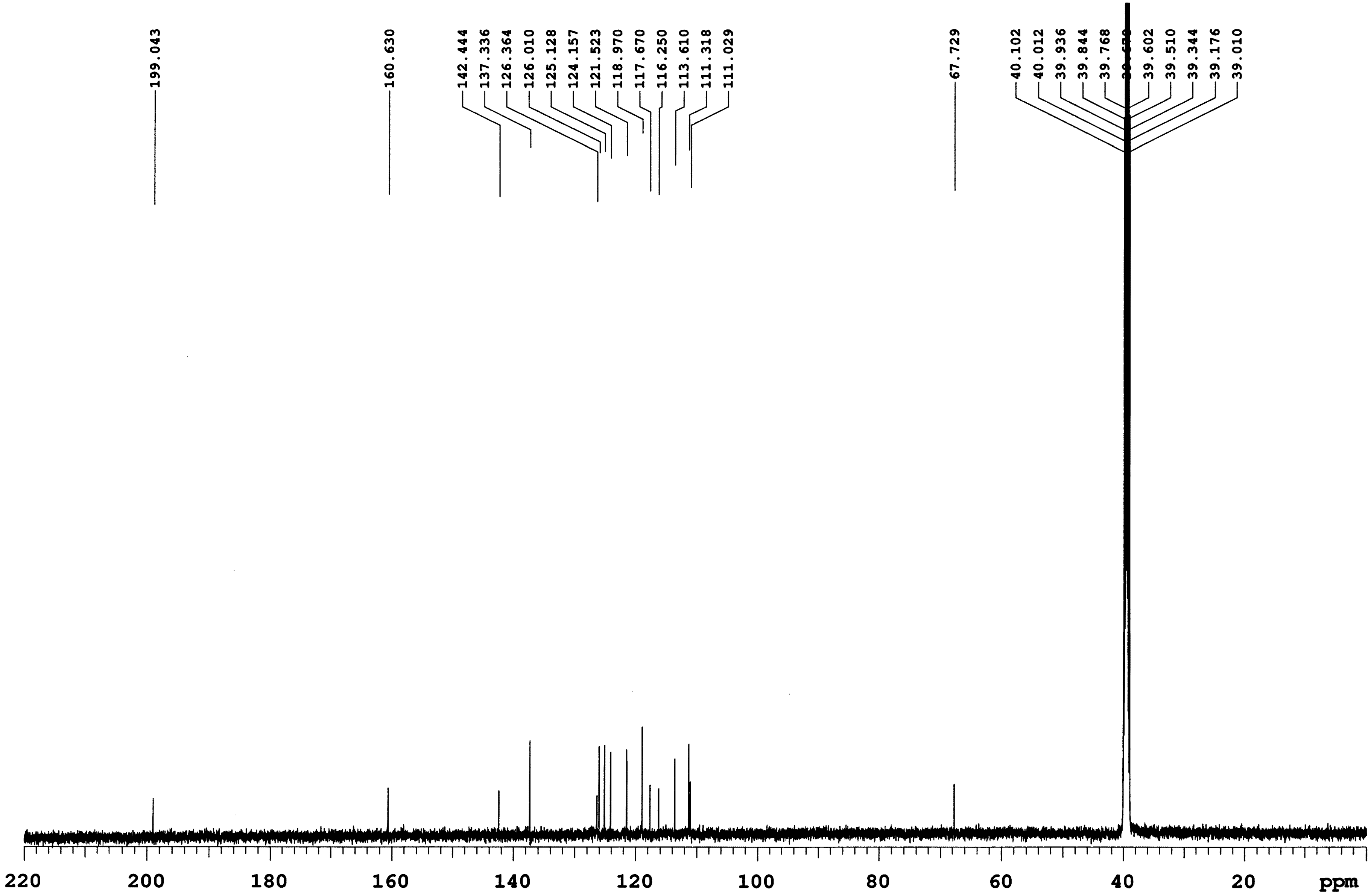
1H NMR (DMSO-d6, 500 MHz) of **1e**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-138-3/PROTON_04

Plot date 2018-09-20

LTC-1-138-3

Sample Name **LTC-1-138-3**
Date collected **2018-09-20**
Pulse sequence **CARBON**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



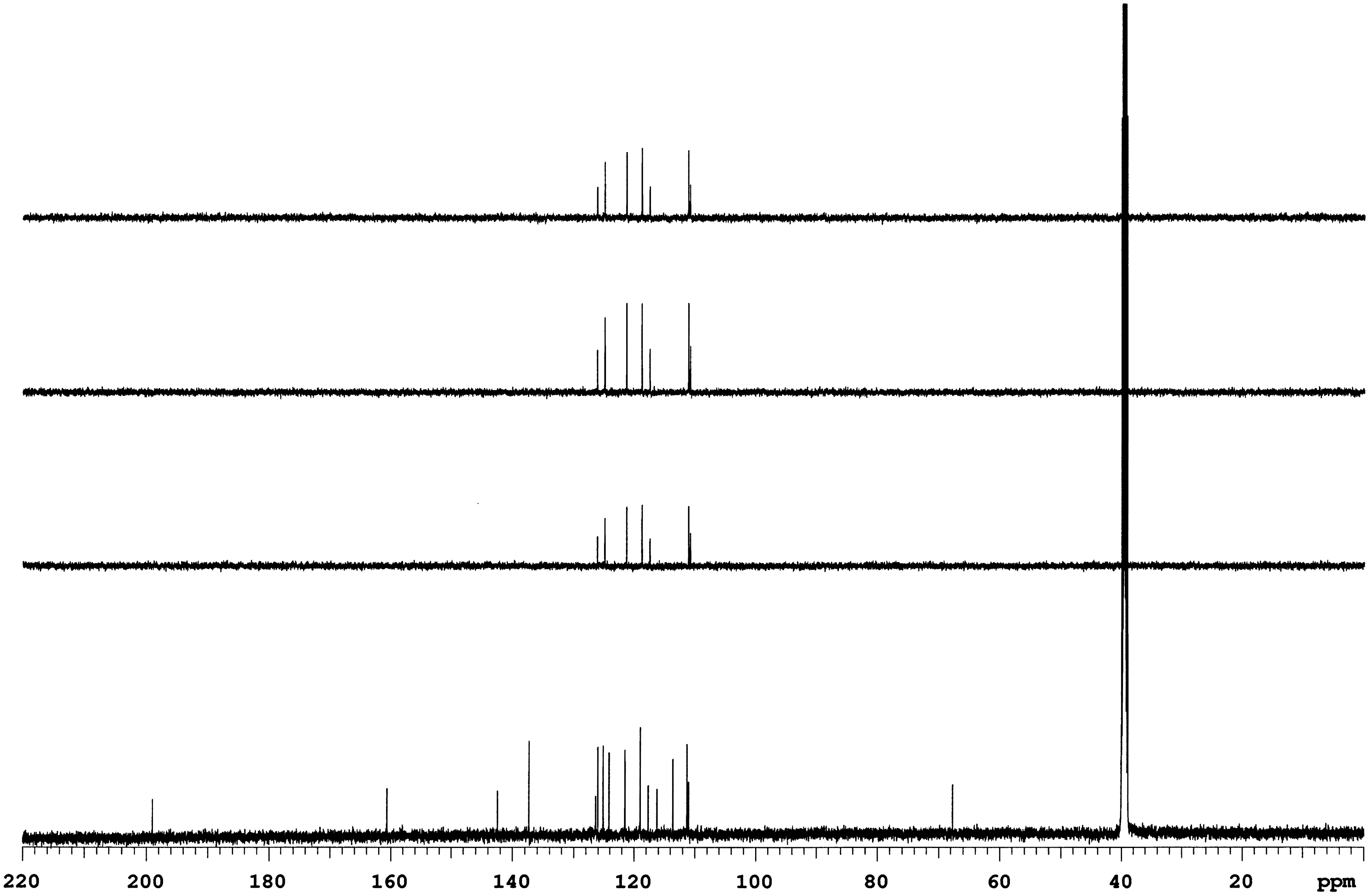
13C NMR (DMSO-d6, 125 MHz) of **1e**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-138-3/CARBON_02

Plot date 2018-09-20

LTC-1-138-3

Sample Name **LTC-1-138-3**
Date collected **2018-09-20**
Pulse sequence **DEPT**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



DEPT of **1e**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-138-3/DEPT_01

Plot date 2018-09-20

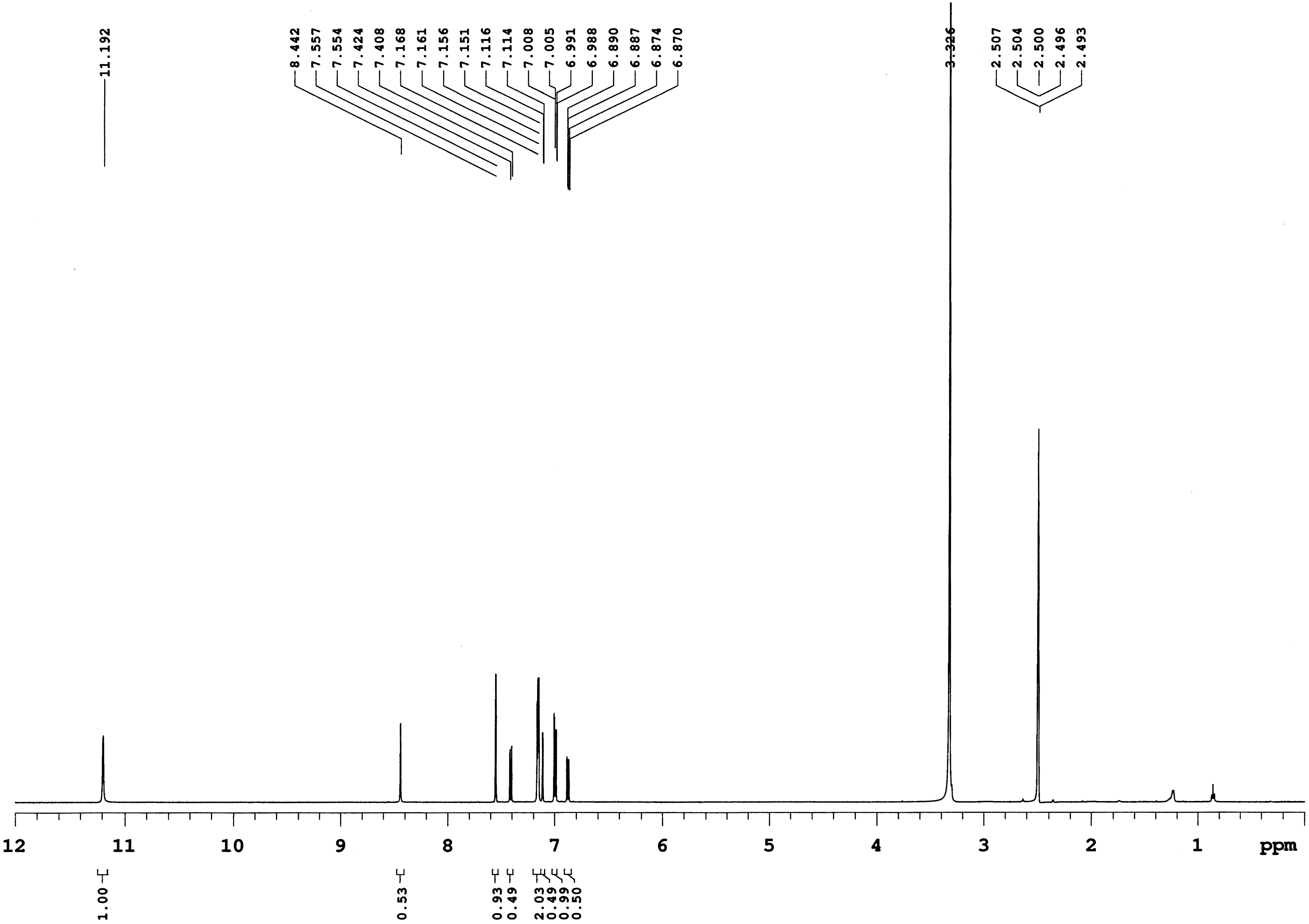
LTC-1-140-f4

Sample Name **LTC-1-140-f4**
Date collected **2018-11-09**

Pulse sequence **PROTON**
Solvent **dmso**

Temperature **25**
Spectrometer **Agilent-NMR-inova500**

Study owner **vnmr2**
Operator **vnmr2**



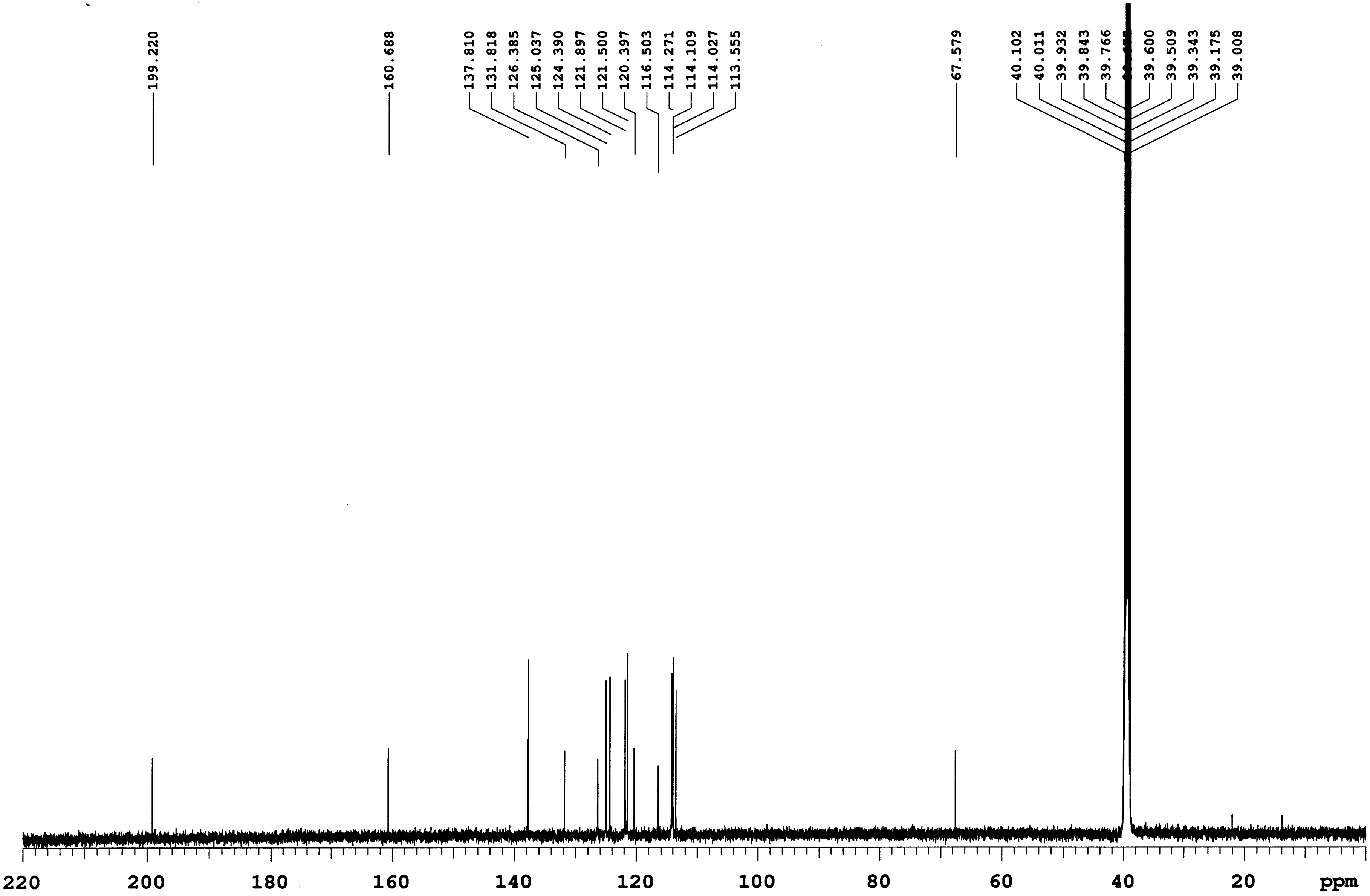
1H NMR (DMSO-d6, 500 MHz) of **1f**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-f4/PROTON_04

Plot date 2018-11-13

LTC-1-140-f4

Sample Name **LTC-1-140-f4**
Date collected **2018-11-09**
Pulse sequence **CARBON**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



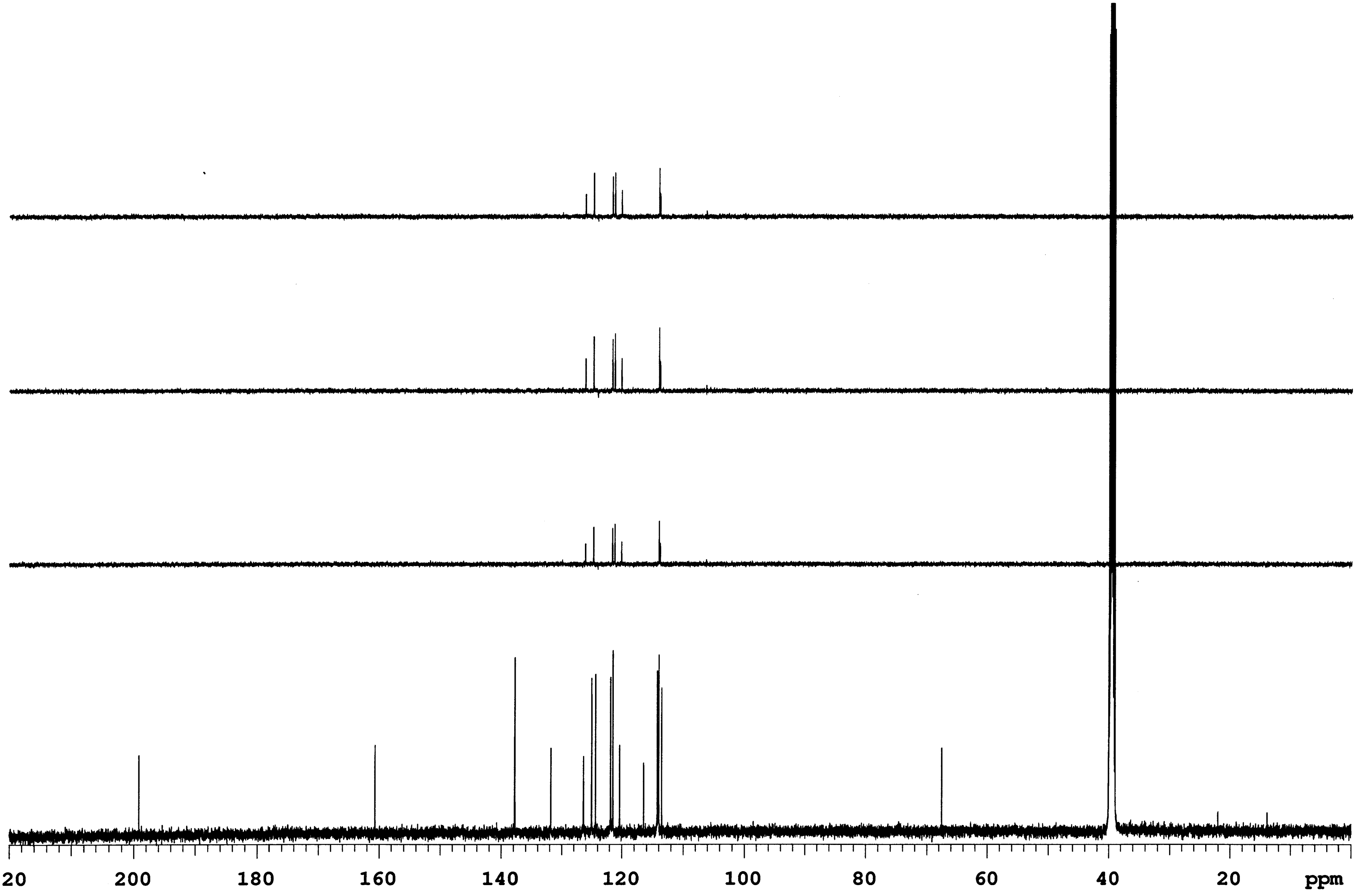
13C NMR (DMSO-d6, 125 MHz) of **1f**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-f4/CARBON_02

Plot date 2018-11-13

LTC-1-140-f4

Sample Name **LTC-1-140-f4**
Date collected **2018-11-09**
Pulse sequence **DEPT**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



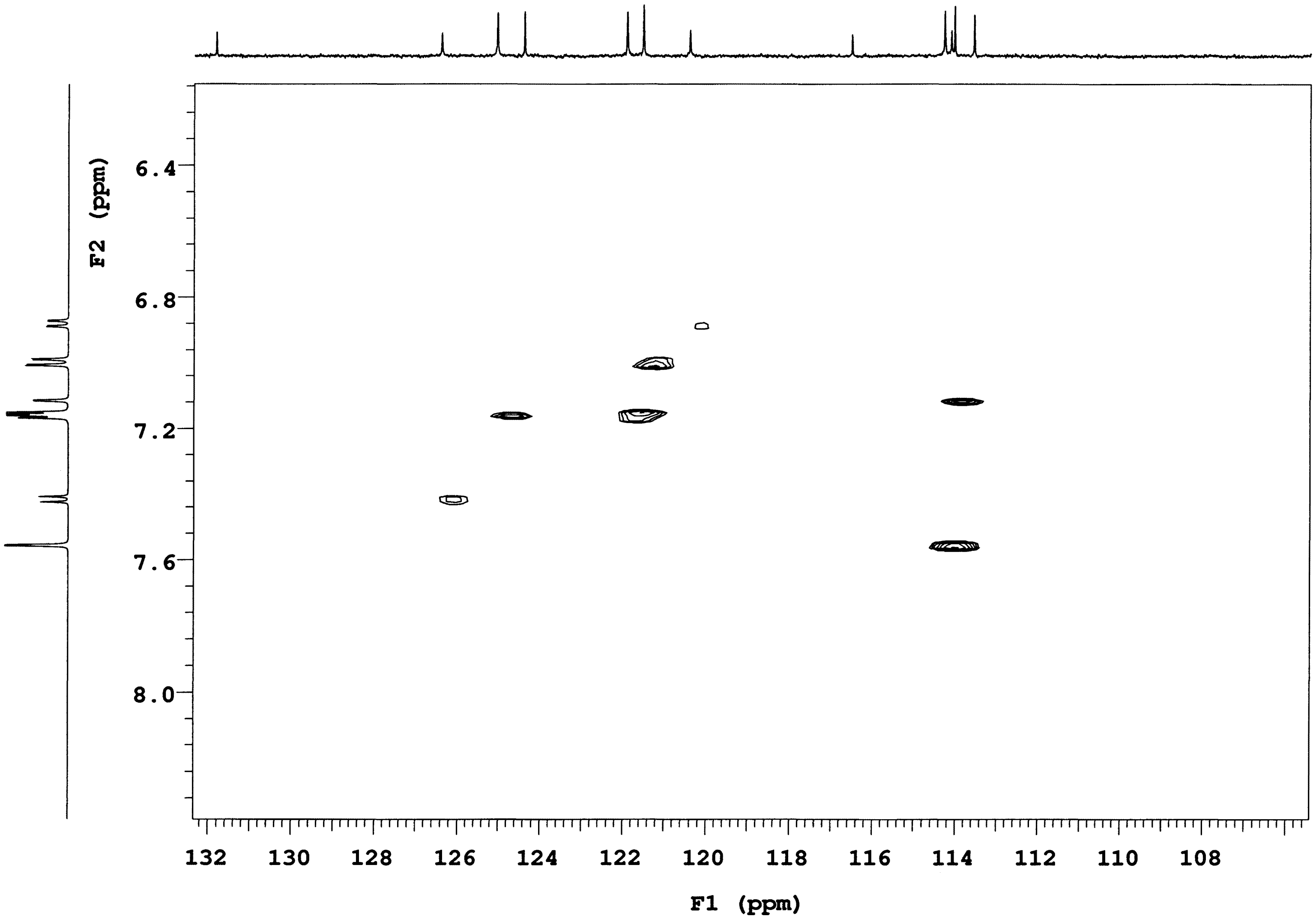
DEPT of **1f**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-f4/DEPT_01

Plot date 2018-11-13

LTC-1-140-f4

Sample Name **LTC-1-140-f4**
Date collected **2018-11-09**
Pulse sequence **gHSQC**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



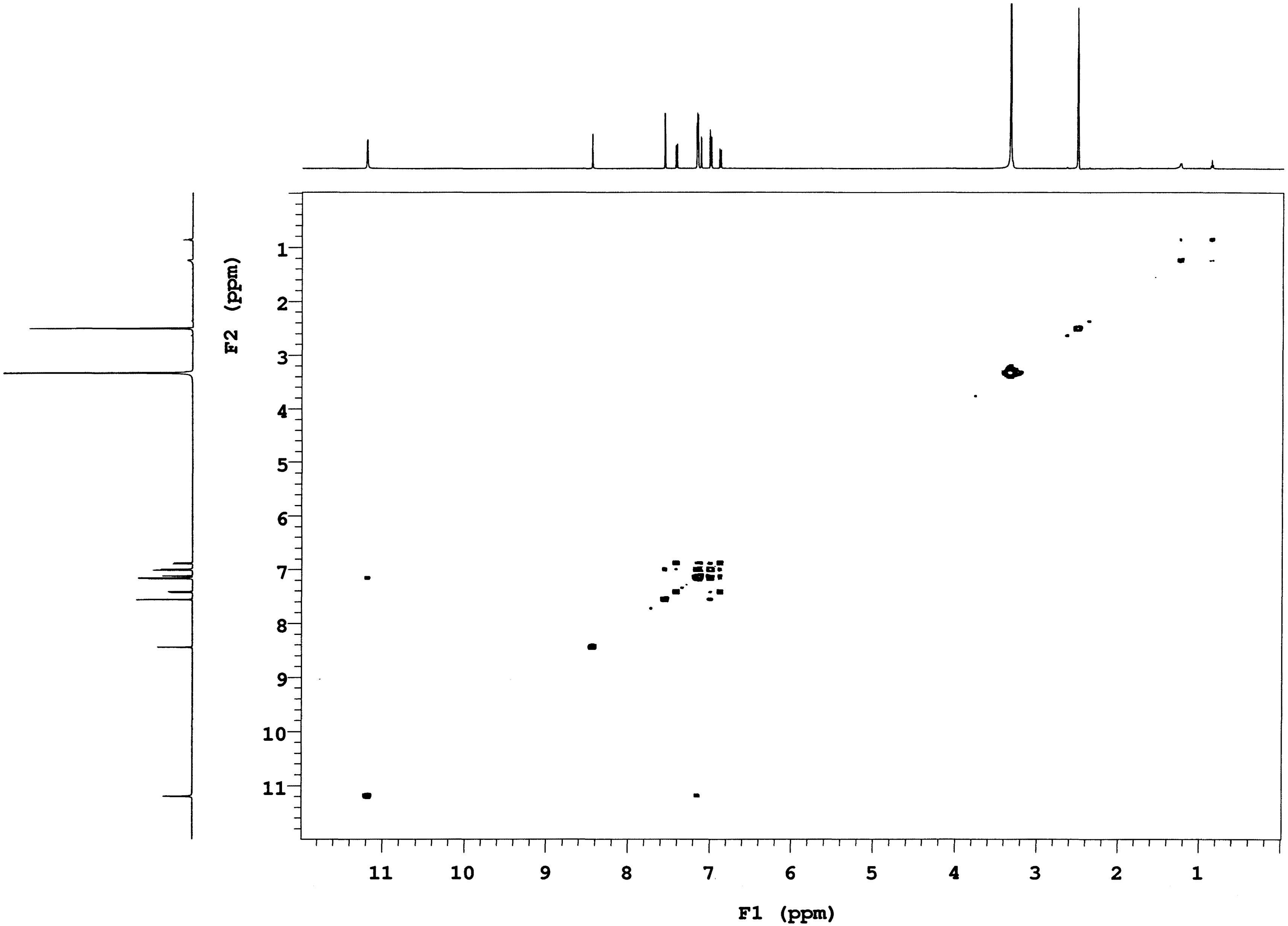
HSQC of **1f**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-f4/gHSQC_01

Plot date 2018-11-13

LTC-1-140-f4

Sample Name **LTC-1-140-f4**
Date collected **2018-11-09**
Pulse sequence **gCOSY**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



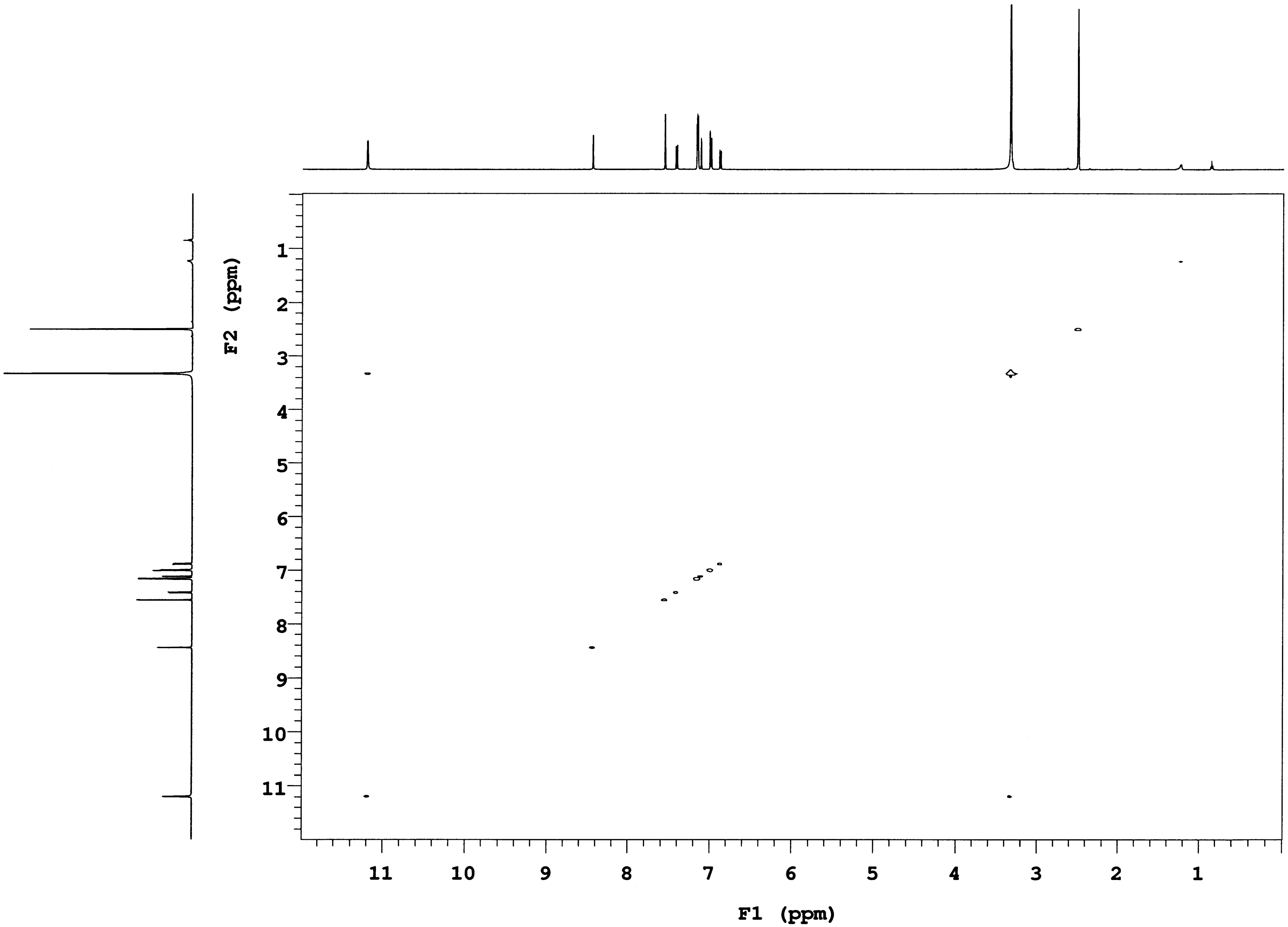
COSY of **1f**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-f4/gCOSY_01

Plot date 2018-11-13

LTC-1-140-f4

Sample Name	**LTC-1-140-f4**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2018-11-09**	Solvent	**dmso**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



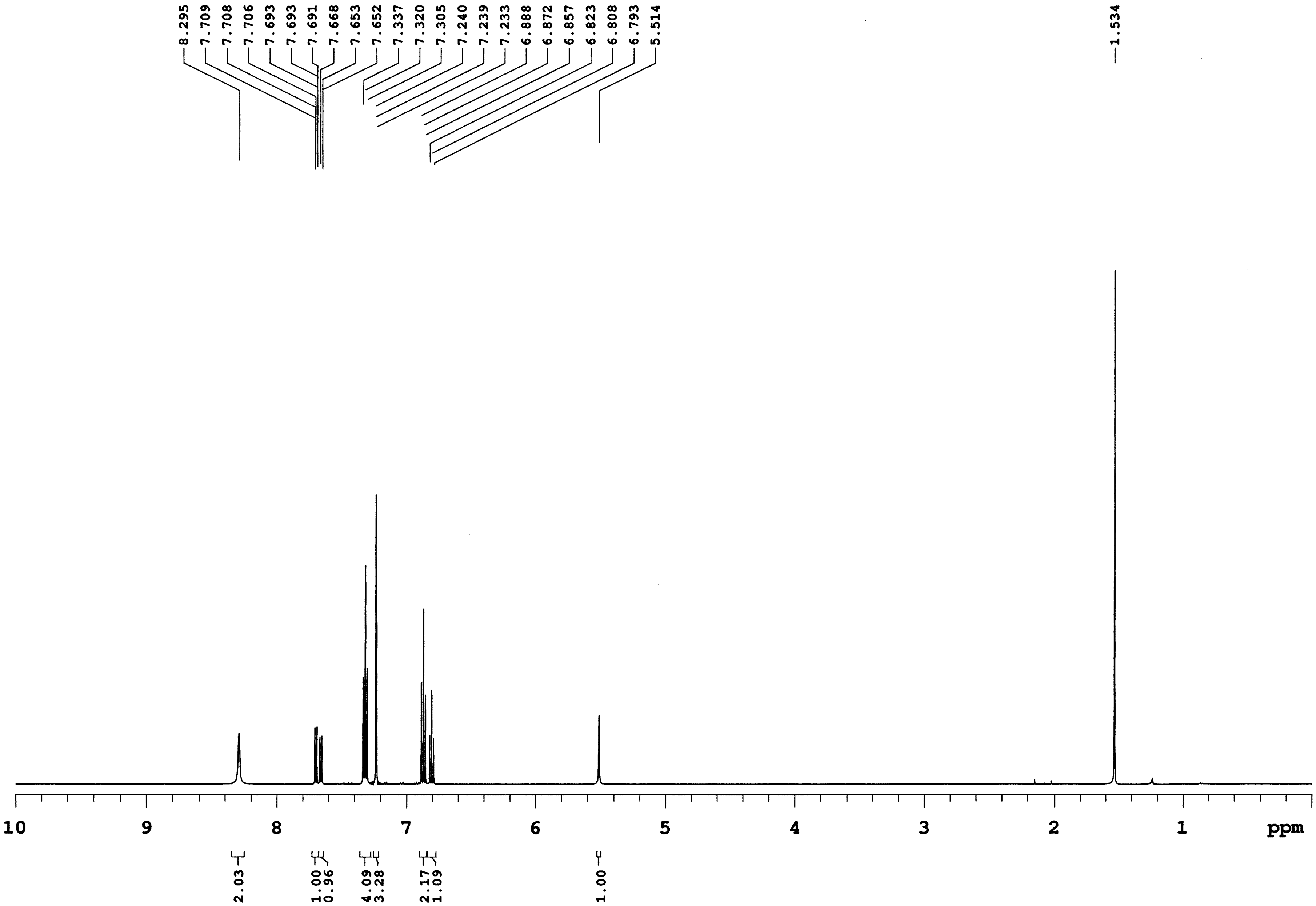
NOESY of **1f**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-140-f4/NOESY_01

Plot date 2018-11-13

LTC-1-144-7Br

Sample Name **LTC-1-144-7Br**
Date collected **2018-11-14**
Pulse sequence **PROTON**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



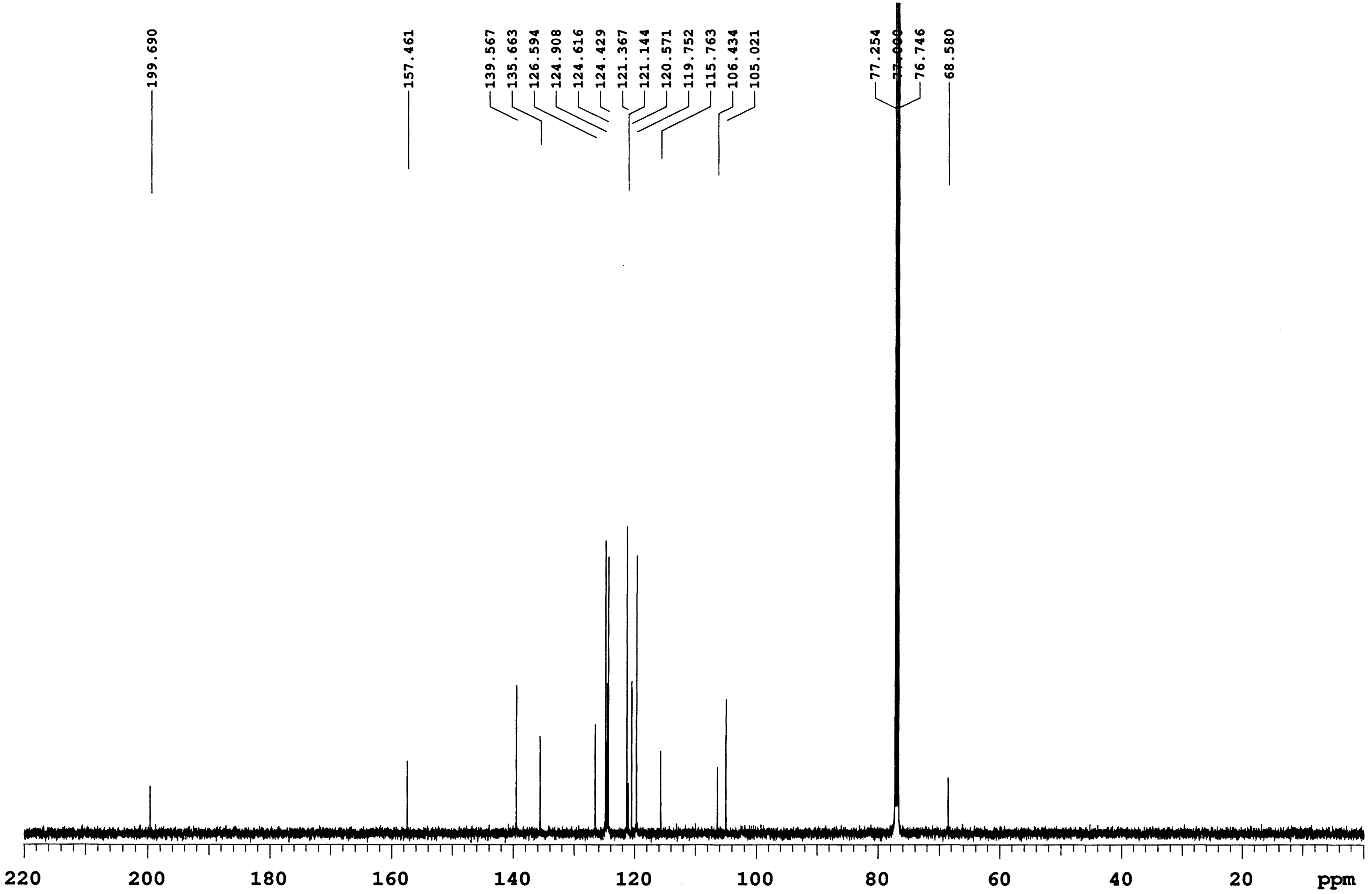
1H NMR (CDCl3, 500 Hz) of **1g**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-144-7Br/PROTON_03

Plot date 2018-11-16

LTC-1-144-7Br

Sample Name **LTC-1-144-7Br**
Date collected **2018-11-14**
Pulse sequence **CARBON**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



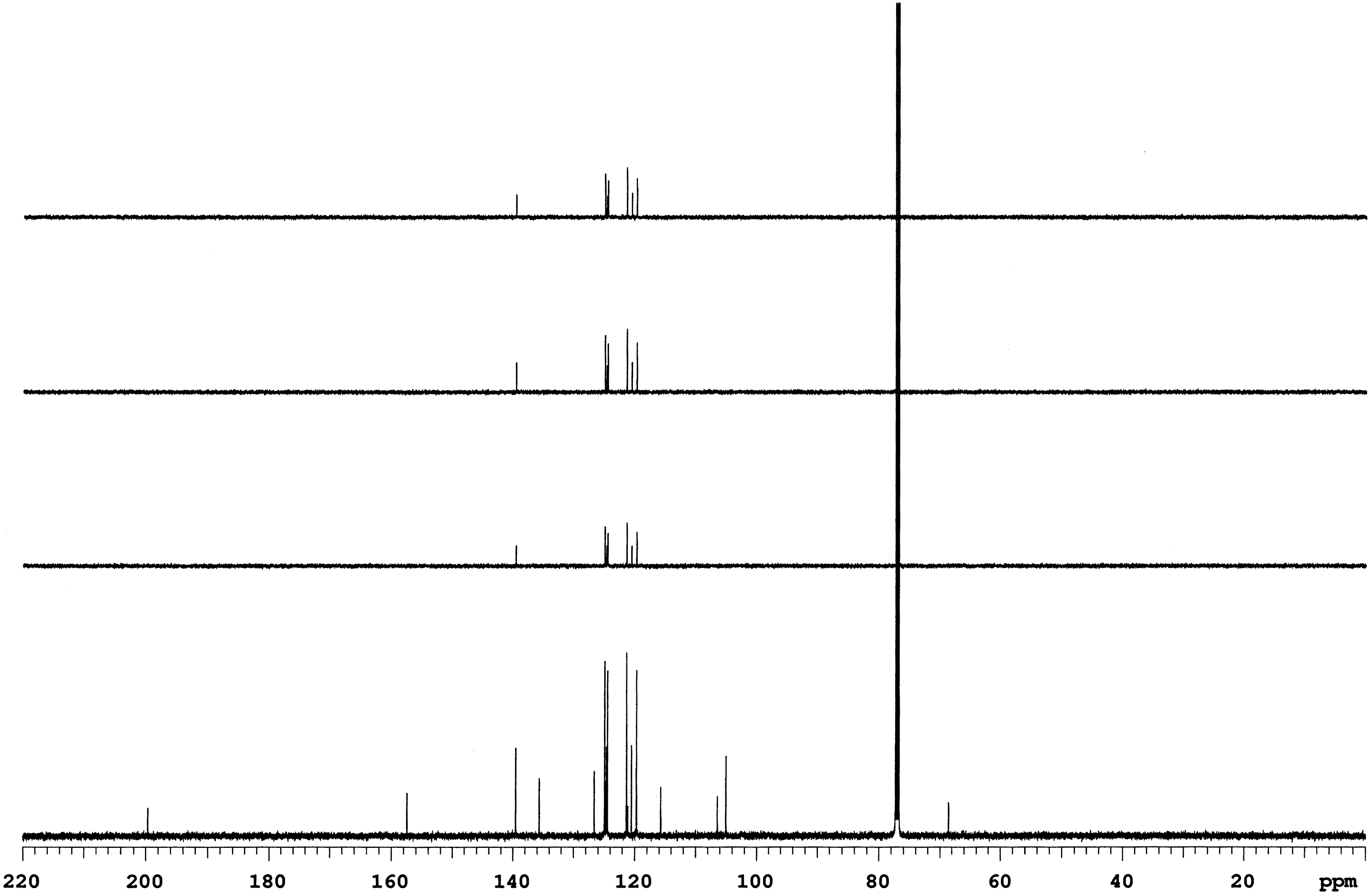
13C NMR (CDCl3, 125 MHz) of **1g**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-144-7Br/CARBON_02

Plot date 2018-11-16

LTC-1-144-7Br

Sample Name **LTC-1-144-7Br** Pulse sequence **DEPT** Temperature **25** Study owner **vnmr2**
Date collected **2018-11-15** Solvent **cdcl3** Spectrometer **Agilent-NMR-inova500** Operator **vnmr2**



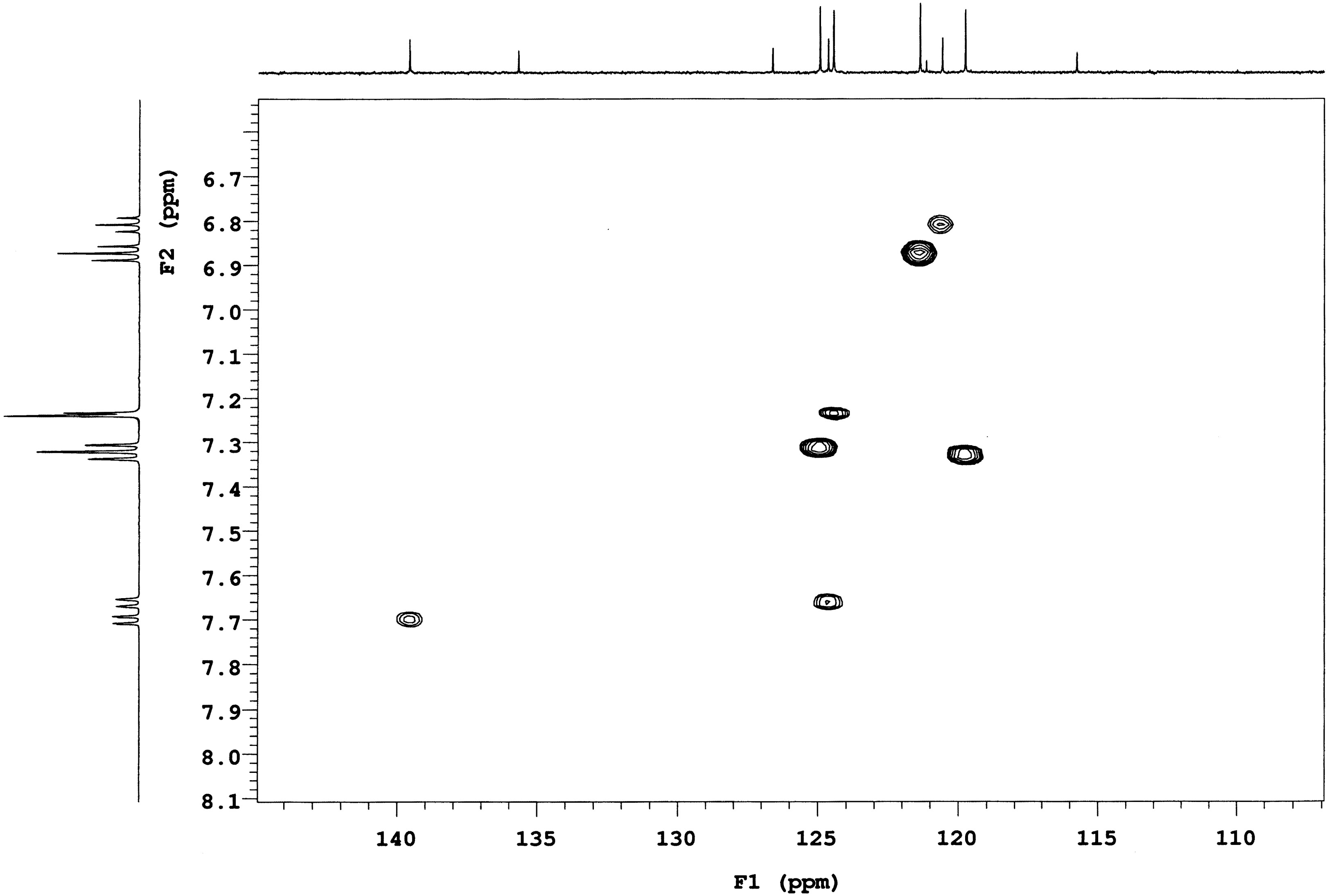
DEPT of **1g**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-144-7Br/DEPT_01

Plot date 2018-11-16

LTC-1-144-7Br

Sample Name **LTC-1-144-7Br**
Date collected **2018-11-15**
Pulse sequence **gHSQC**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



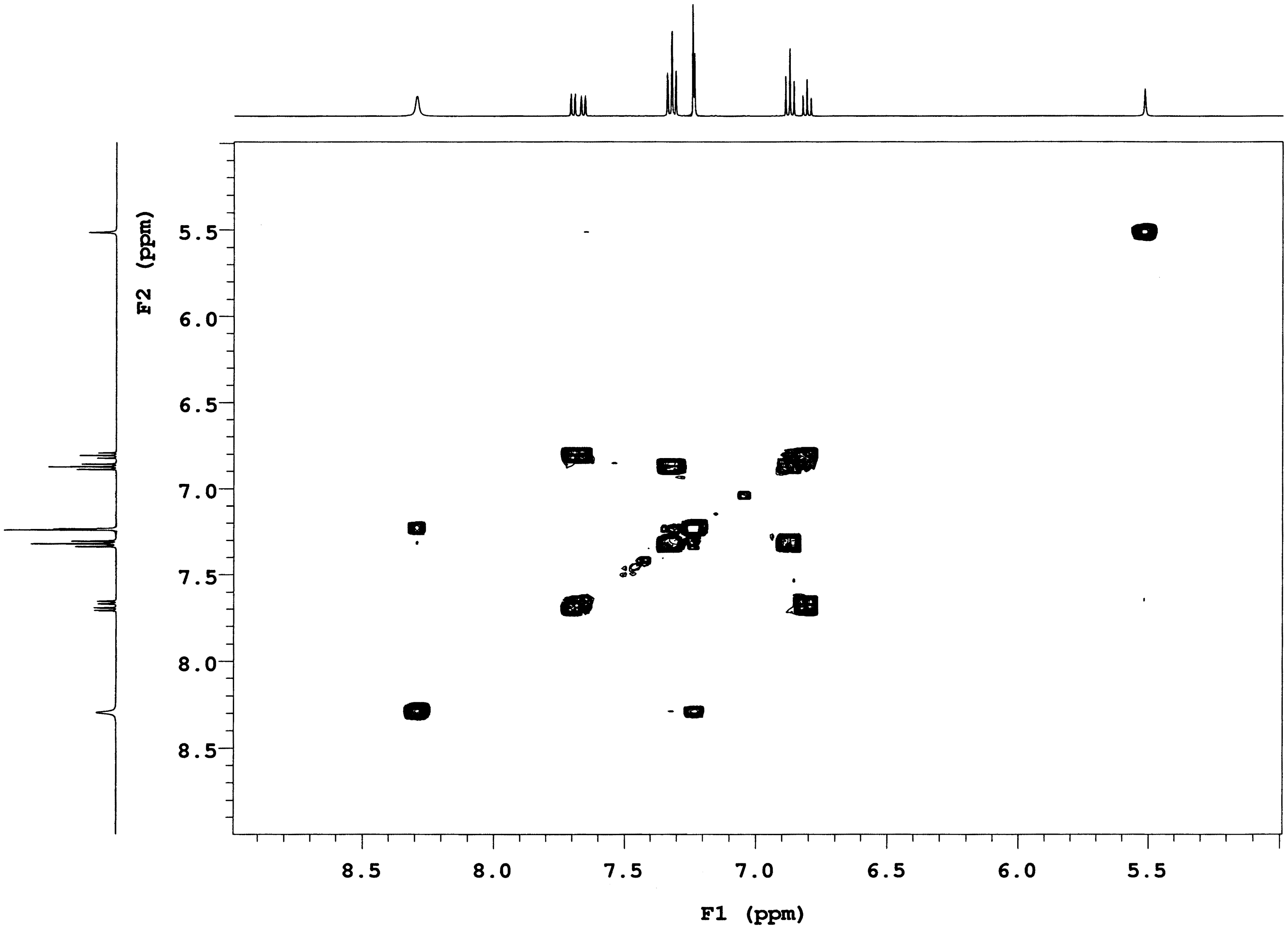
HSQC of **1g**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-144-7Br/gHSQC_01

Plot date 2018-11-20

LTC-1-144-7Br

Sample Name **LTC-1-144-7Br**
Date collected **2018-11-15**
Pulse sequence **gCOSY**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



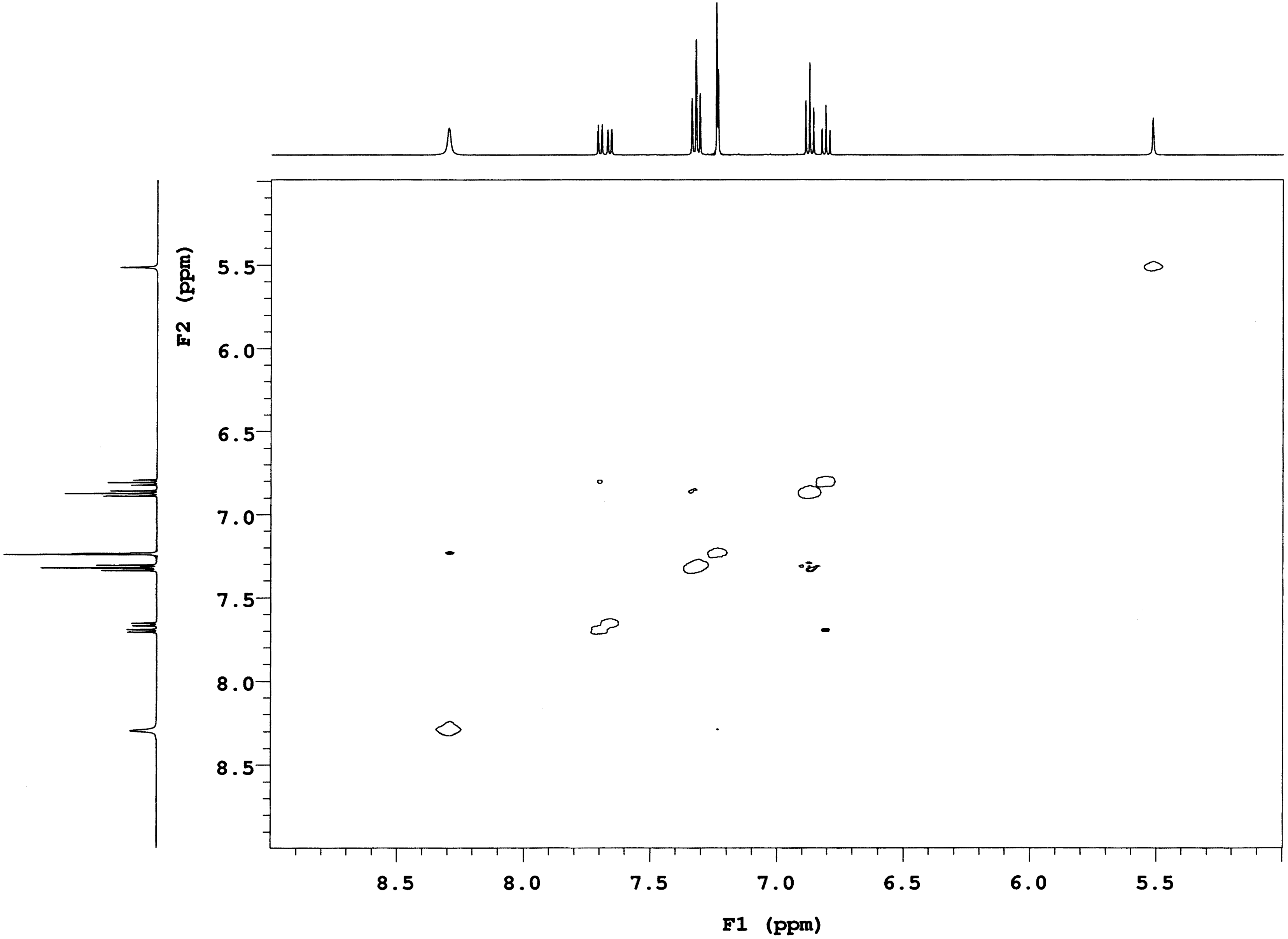
COSY of **1g**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-144-7Br/gCOSY_01

Plot date 2018-11-16

LTC-1-144-7Br

Sample Name	**LTC-1-144-7Br**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2018-11-15**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



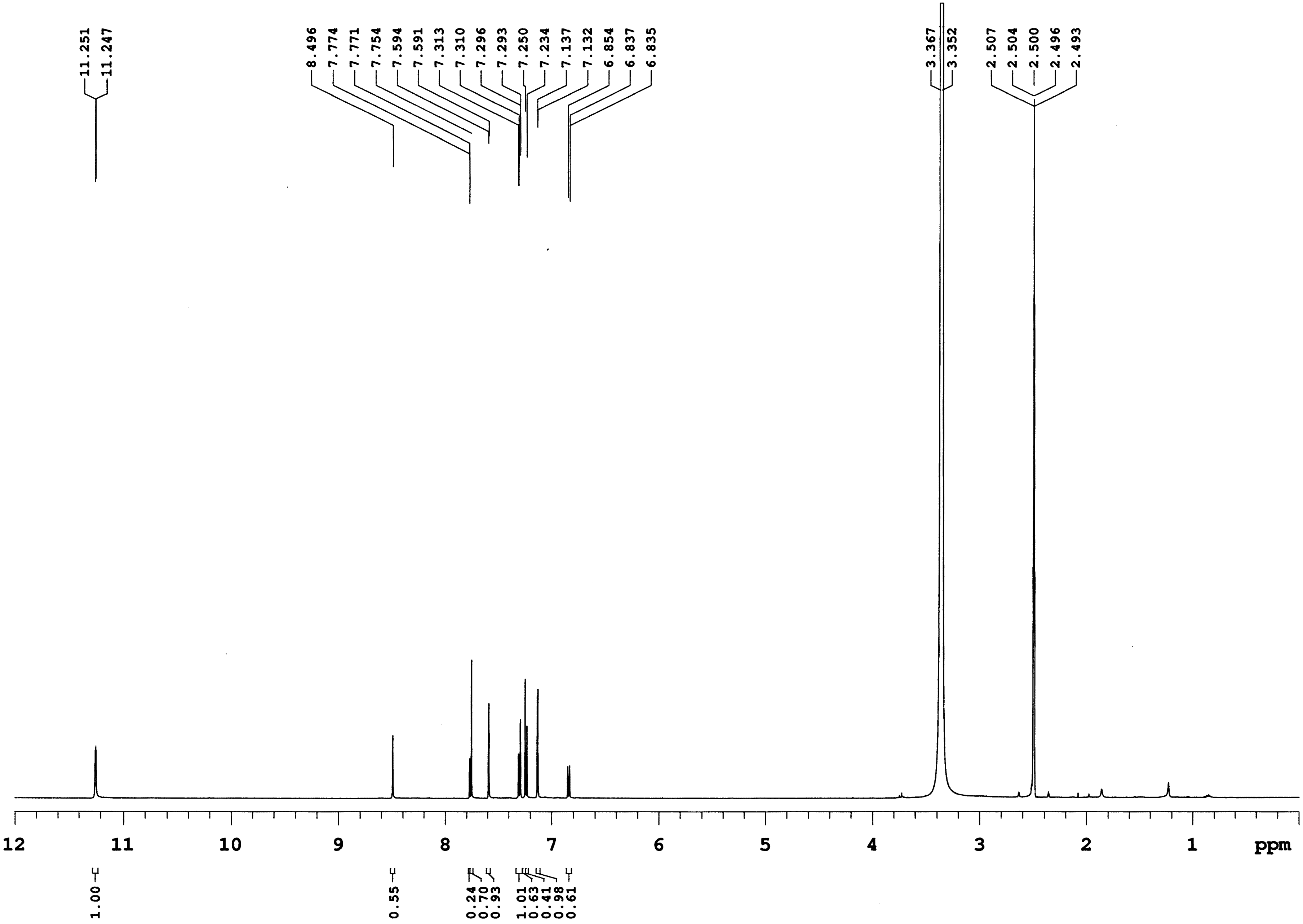
NOESY of **1g**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-144-7Br/NOESY_01

Plot date 2018-11-20

LTC-138-5

Sample Name **LTC-138-5**
Date collected **2018-09-13**
Pulse sequence **PROTON**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



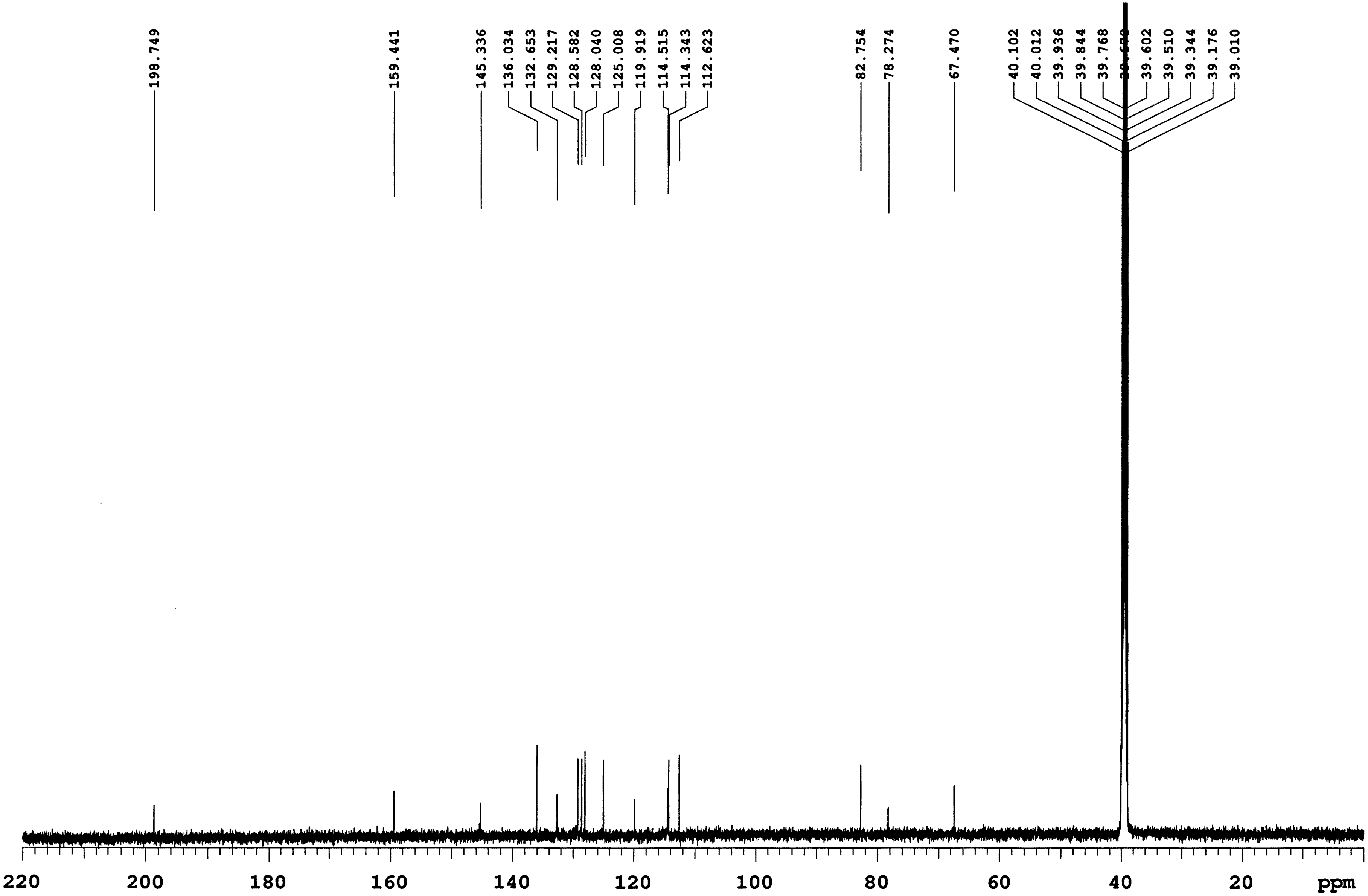
Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-138-5/PROTON_03

1H NMR (DMSO-d6, 500 Hz) of **1h**

Plot date 2018-09-20

LTC-138-5

Sample Name **LTC-138-5**
Date collected **2018-09-13**
Pulse sequence **CARBON**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



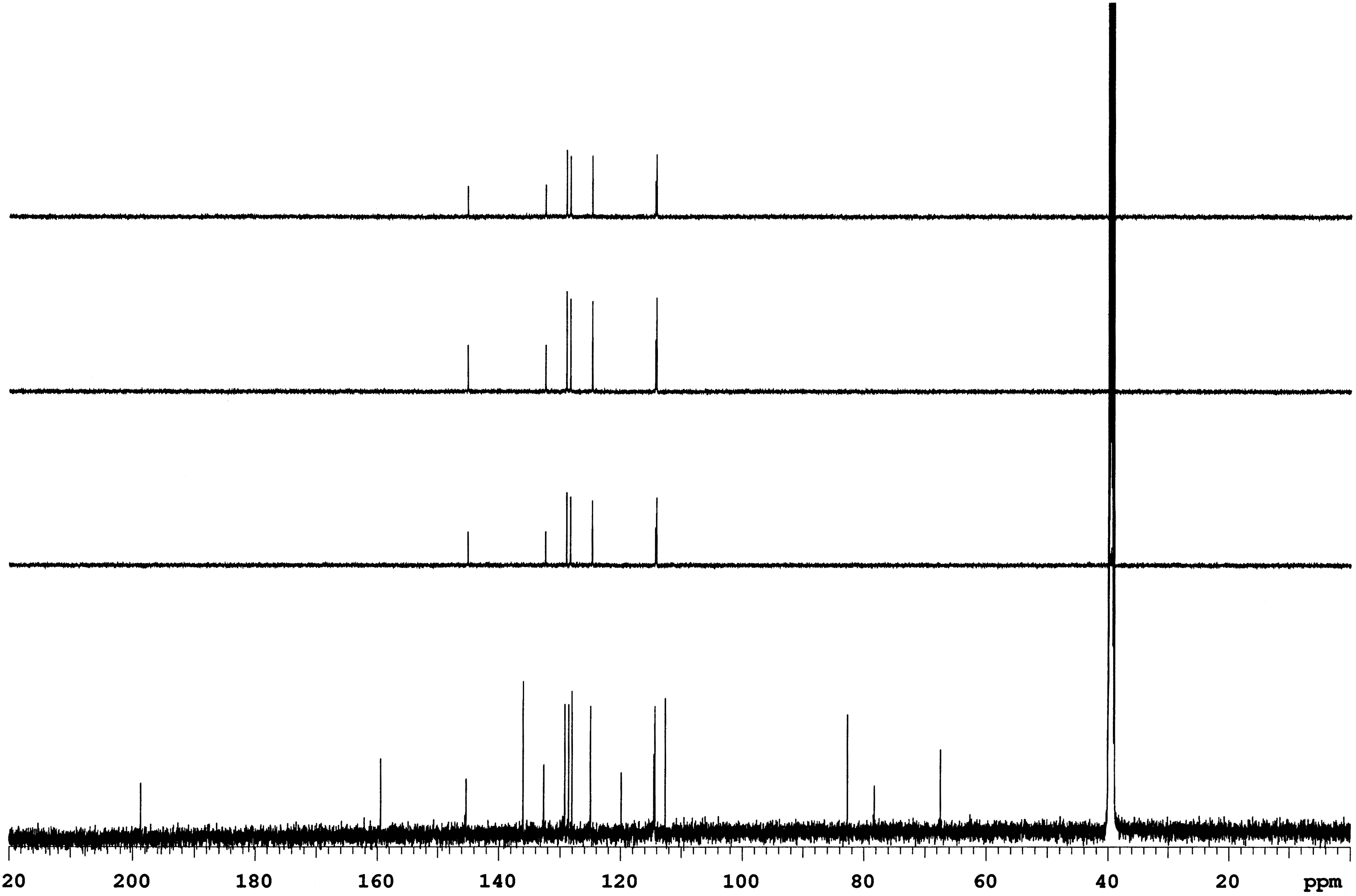
13C NMR (DMSO-d6, 125 Hz) of **1h**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-138-5/CARBON_02

Plot date 2018-09-20

LTC-138-5

Sample Name **LTC-138-5**
Date collected **2018-10-03**
Pulse sequence **DEPT**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



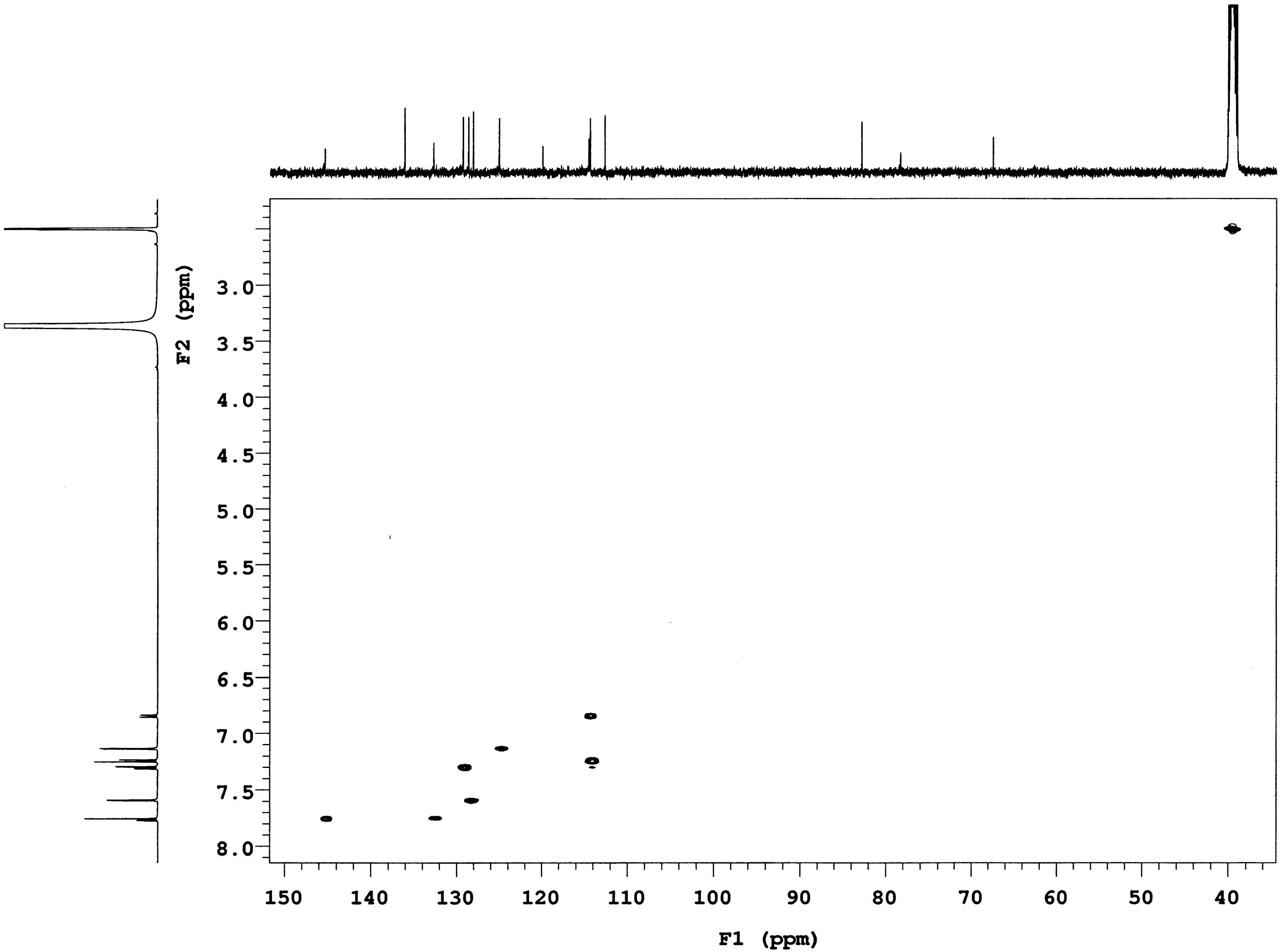
DEPT of **1h**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-138-5/DEPT_03

Plot date 2018-10-05

LTC-138-5

Sample Name **LTC-138-5**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2018-09-29**	Solvent **dmso**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



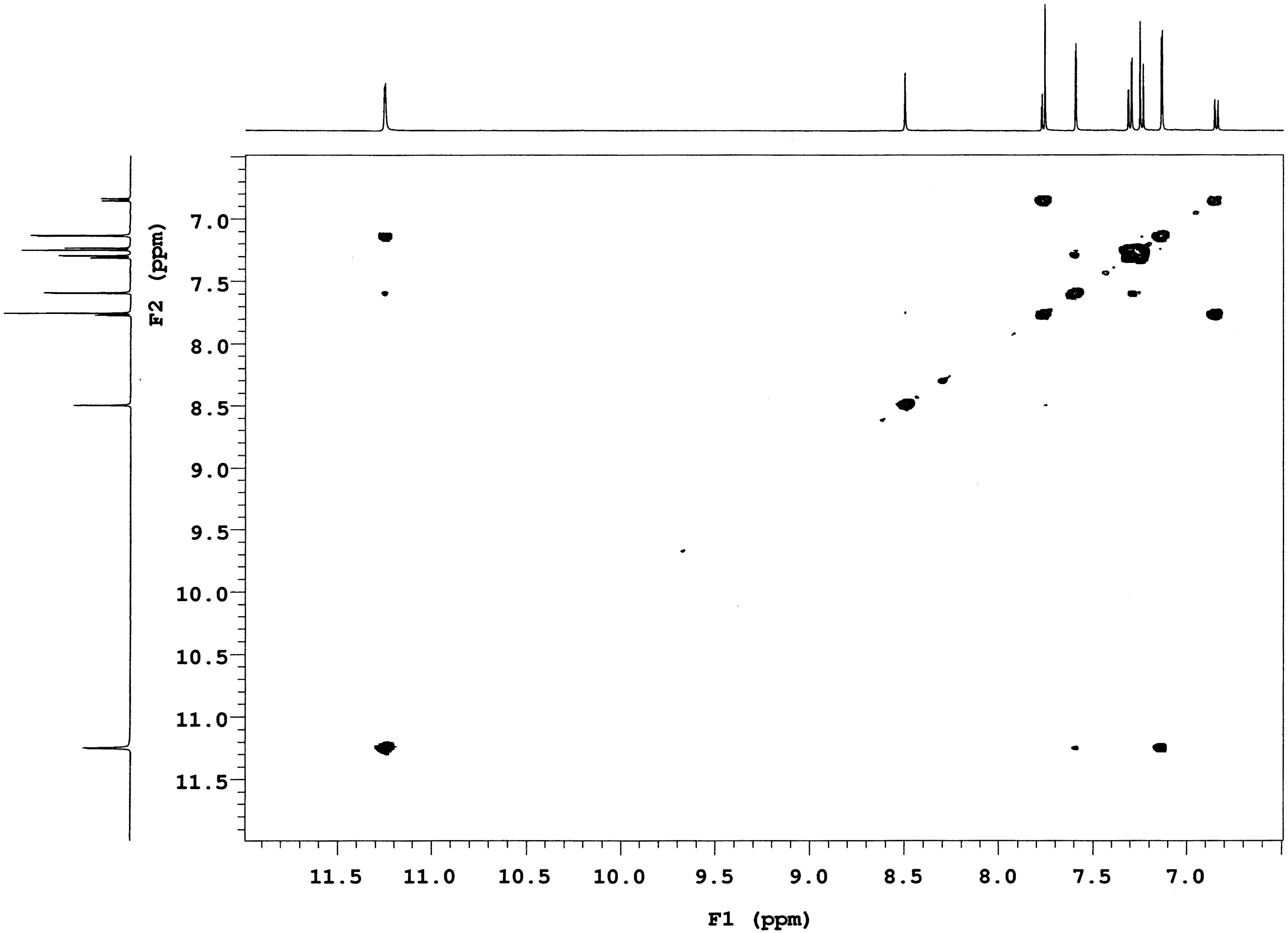
HSQC of **1h**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-138-5/gHSQC_02

Plot date 2018-10-05

LTC-138-5

Sample Name **LTC-138-5**	Pulse sequence **gCOSY**	Temperature **25**	Study owner **vnmr2**
Date collected **2018-10-03**	Solvent **dmso**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



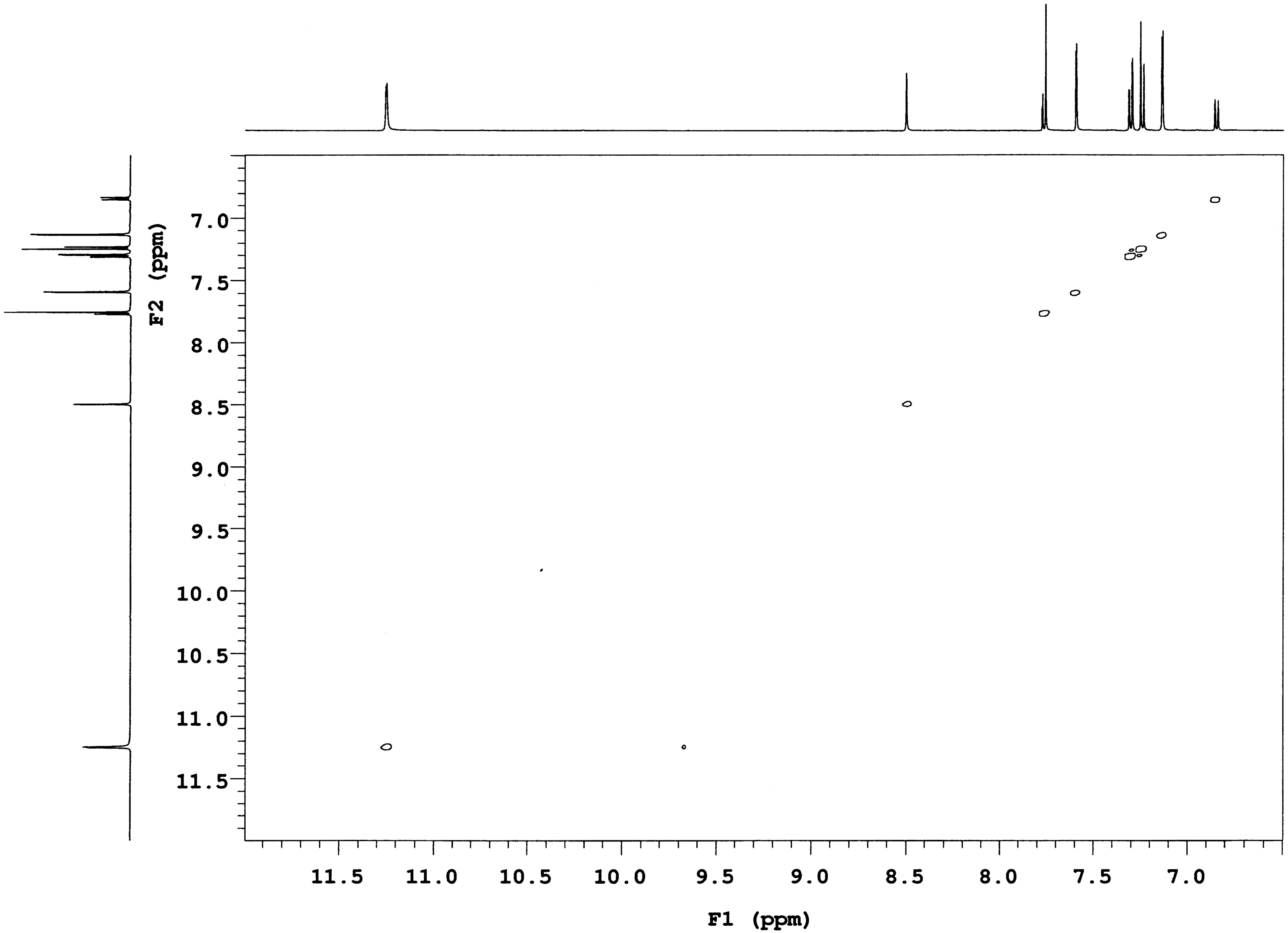
COSY of **1h**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-138-5/gCOSY_03

Plot date 2018-10-05

LTC-138-5

Sample Name **LTC-138-5**
Date collected **2018-10-03**
Pulse sequence **NOESY**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



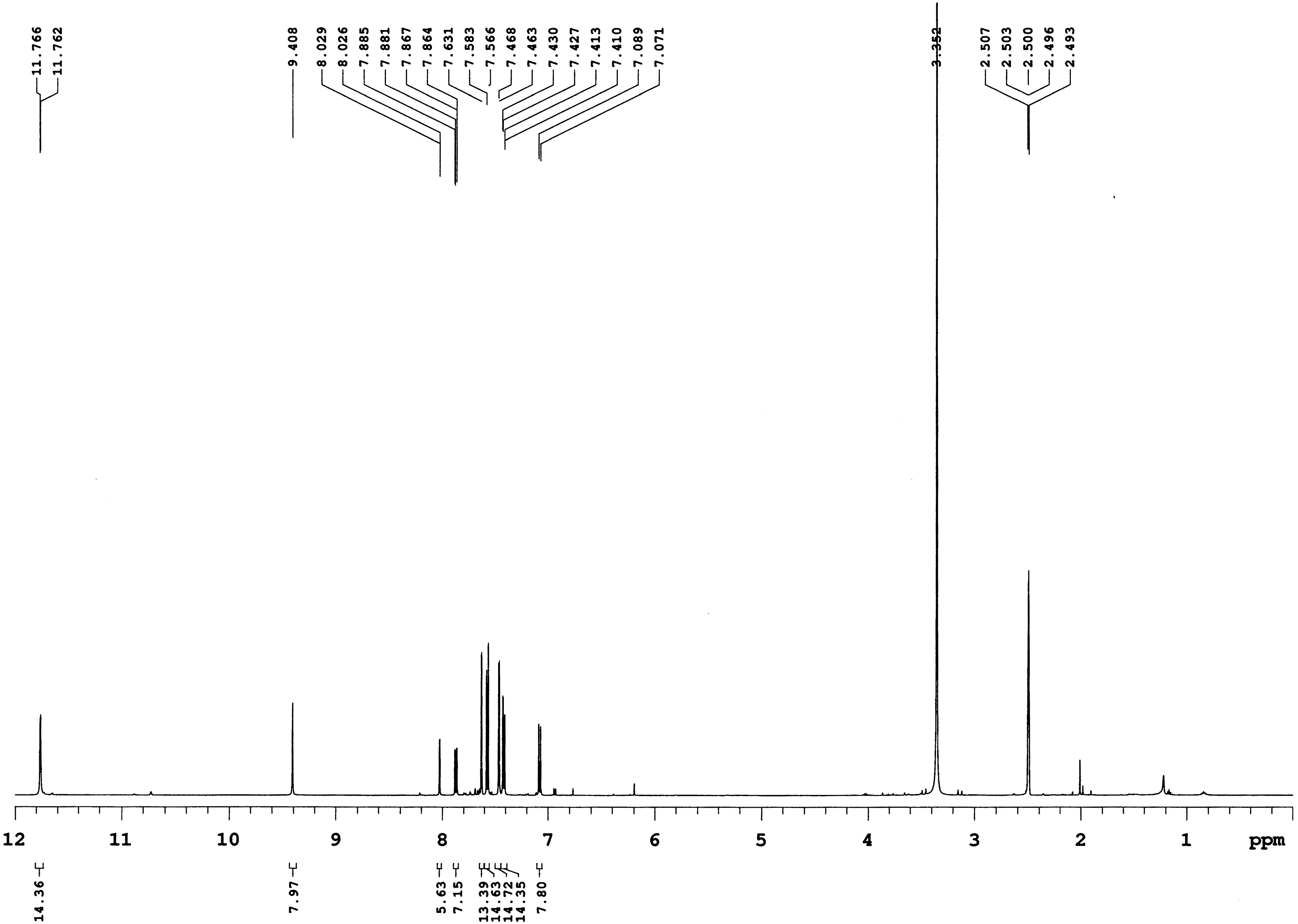
NOESY of **1h**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-138-5/NOESY_03

Plot date 2018-10-05

LTC-1-138-6

Sample Name **LTC-1-138-6**
Date collected **2018-09-27**
Pulse sequence **PROTON**
Solvent **dmso**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



1H NMR (DMSO-d6, 500 Hz) of **1i**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-138-6/PROTON_06

Plot date 2018-09-29

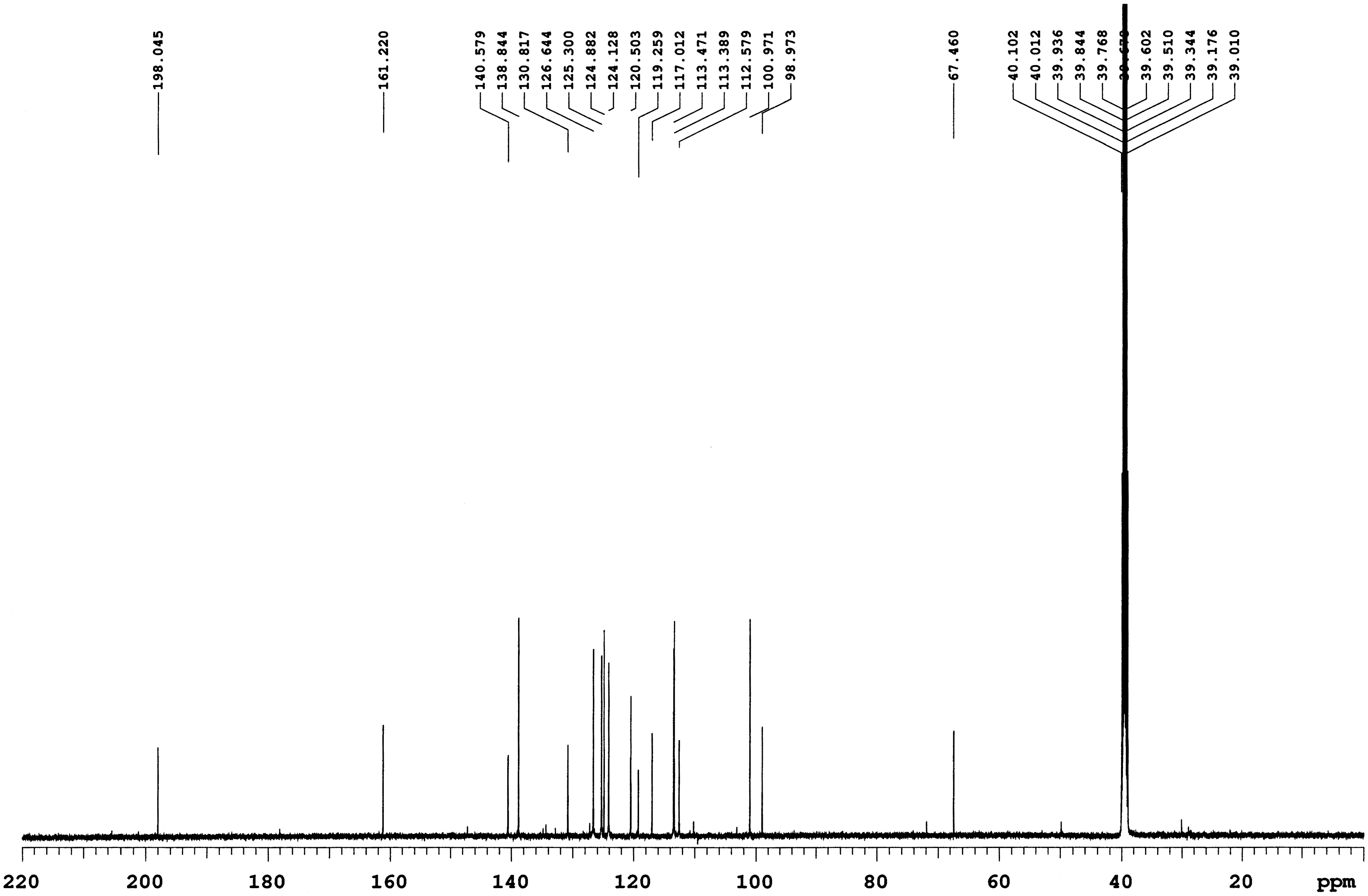
LTC-1-138-6

Sample Name **LTC-1-138-6**
Date collected **2018-09-27**

Pulse sequence **CARBON**
Solvent **dmso**

Temperature **25**
Spectrometer **Agilent-NMR-inova500**

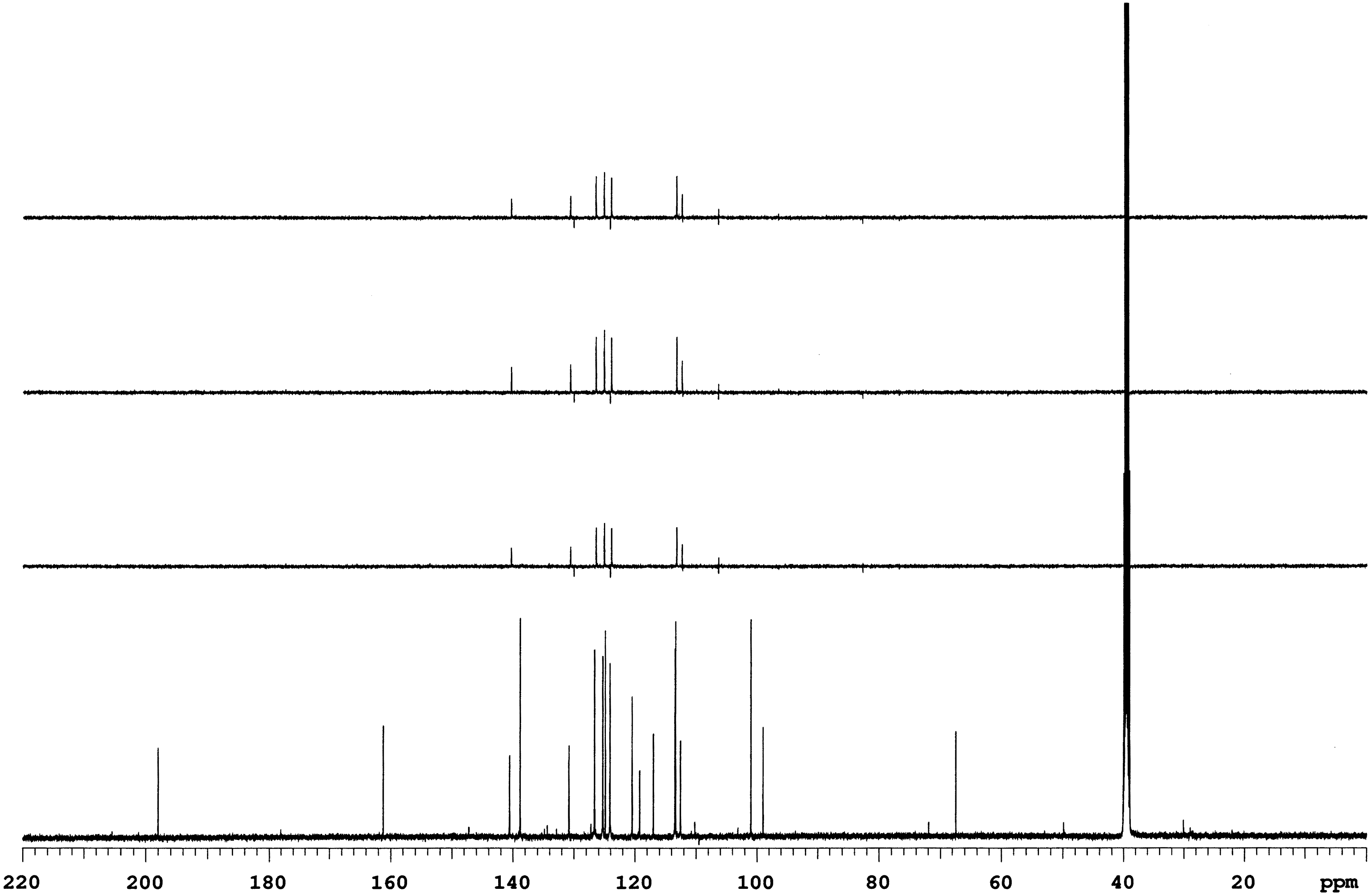
Study owner **vnmr2**
Operator **vnmr2**



1H NMR (DMSO-d6, 500 Hz) of 1i

LTC-1-138-6

Sample Name **LTC-1-138-6**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2018-09-28**	Solvent **dmso**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**

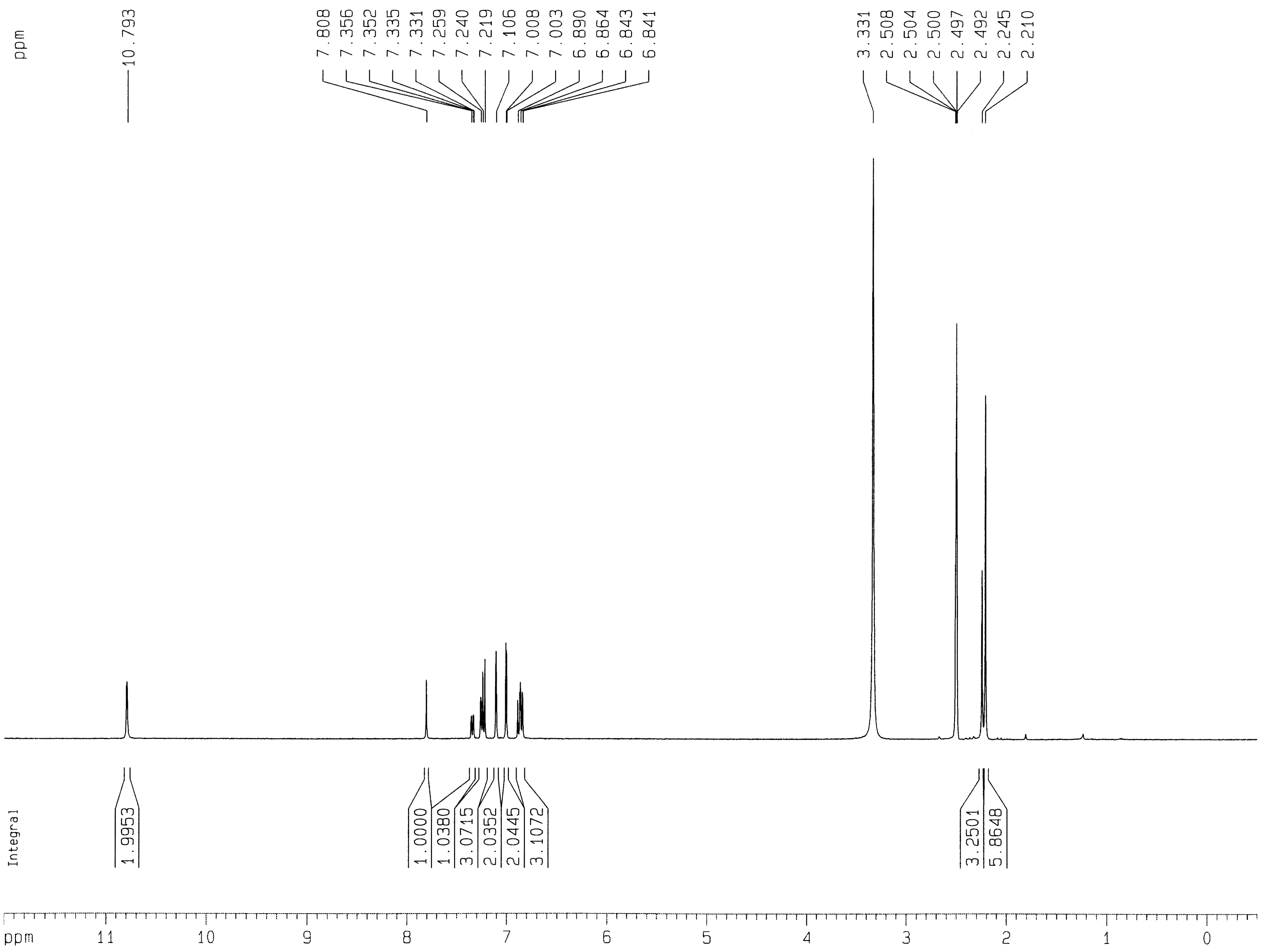


DEPT of **1i**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-1-138-6/DEPT_01

Plot date 2018-09-29

1H NMR (DMSO-d6, 400 Hz) of **1j**



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PROCNO                 1

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TD                 16384
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AQ             1.3664756 sec
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DE                  6.50 usec
TE                 300.0 K
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PL1                 1.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
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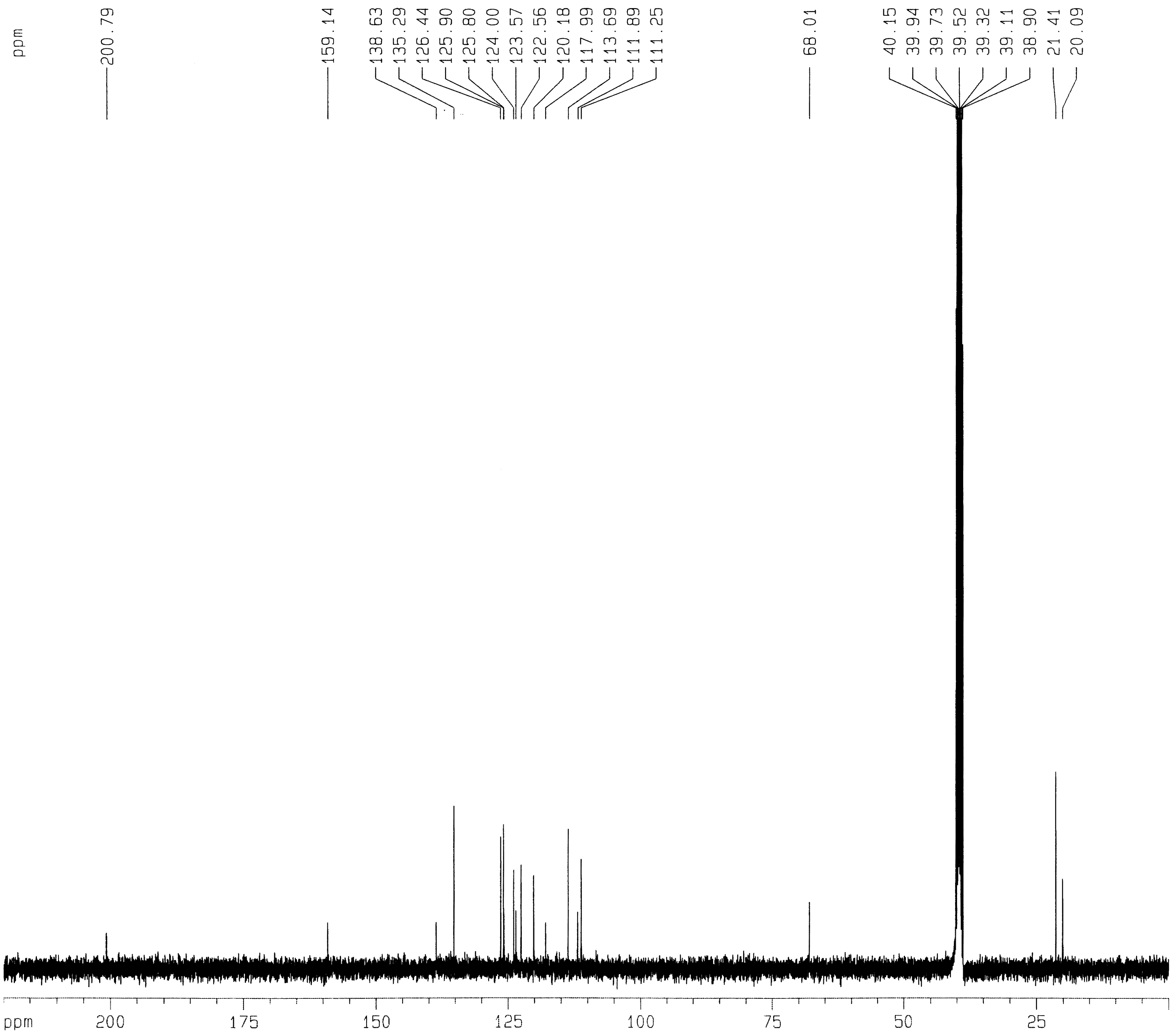
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 21.50 cm
F1P               12.000 ppm
F1               4801.56 Hz
F2P               -0.500 ppm
F2               -200.07 Hz
PPMCM            0.58140 ppm/cm
HZCM           232.63374 Hz/cm
```

1H NMR (DMSO-d6, 100 Hz) of **1j**



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Current Data Parameters
NAME      LTC-1-144-5ch3
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20181001
Time                3.45
INSTRUM            spect
PROBHD     5 mm QNP  1H
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

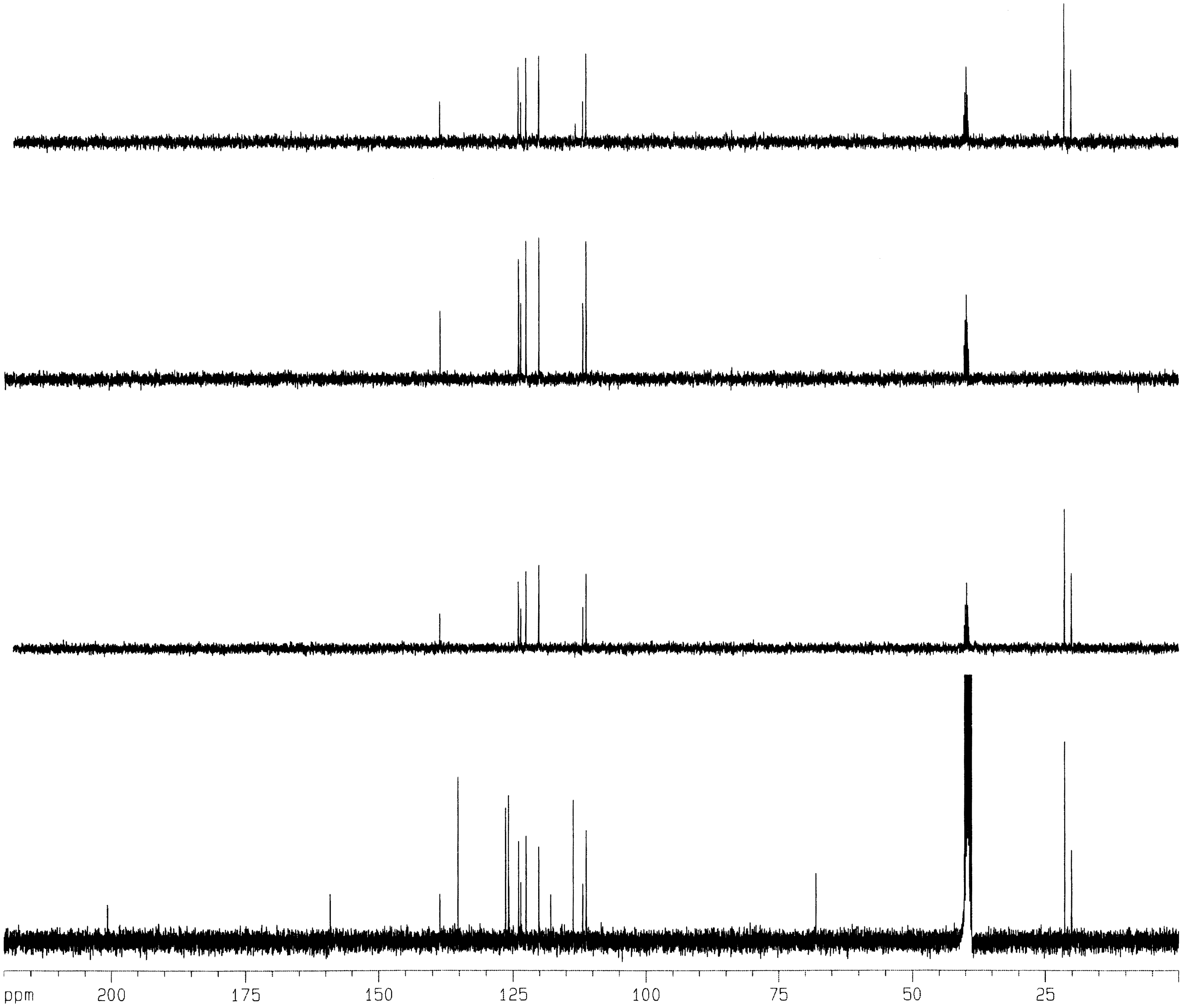
============ CHANNEL f1 =============
NUC1                 13C
P1                 10.00 usec
PL1                -0.30 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.20 dB
PL12               14.90 dB
PL13               17.90 dB
SFO2         400.1326008 MHz

F2 - Processing parameters
SI                 32768
SF           100.6128183 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              22134.82 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM           11.00000 ppm/cm
HZCM          1106.74109 Hz/cm
```

DEPT of **1j**



```
Current Data Parameters
NAME     LTC-1-144-5ch3
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20181001
Time               3.45
INSTRUM            spect
PROBHD     5 mm QNP  1H
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

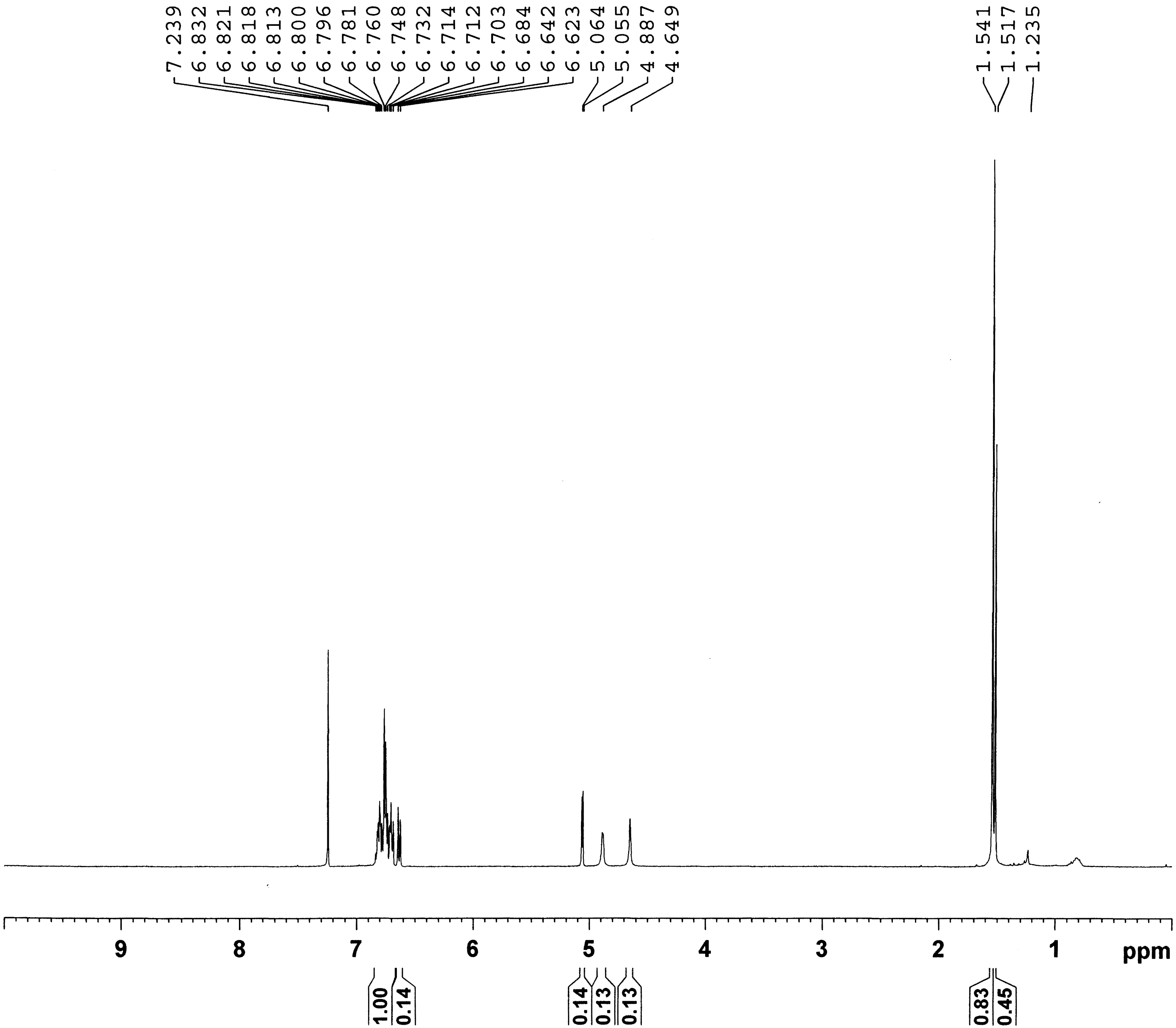
============ CHANNEL f1 ============
NUC1                13C
P1                10.00 usec
PL1               -0.30 dB
SFO1        100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -1.20 dB
PL12              14.90 dB
PL13              17.90 dB
SFO2        400.1326008 MHz

F2 - Processing parameters
SI                32768
SF          100.6128183 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             22134.82 Hz
F2P               0.000 ppm
F2                 0.00 Hz
PPMCM          11.00000 ppm/cm
HZCM         1106.74109 Hz/cm
```

1H NMR (CDCl3, 500 Hz) of compound **3**



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Current Data Parameters
NAME        LTC-1-129-f1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180830
Time               17.29 h
INSTRUM            spect
PROBHD    Z108618_0922 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             8012.820 Hz
FIDRES          0.489064 Hz
AQ             2.0447233 sec
RG                210.28
DW                62.400 usec
DE                 16.43 usec
TE                 297.8 K
D1            2.00000000 sec
TD0                    1
SFO1       400.1324008 MHz
NUC1                  1H
P1                 14.50 usec
PLW1         12.50000000 W

F2 - Processing parameters
SI                 16384
SF         400.1300173 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```

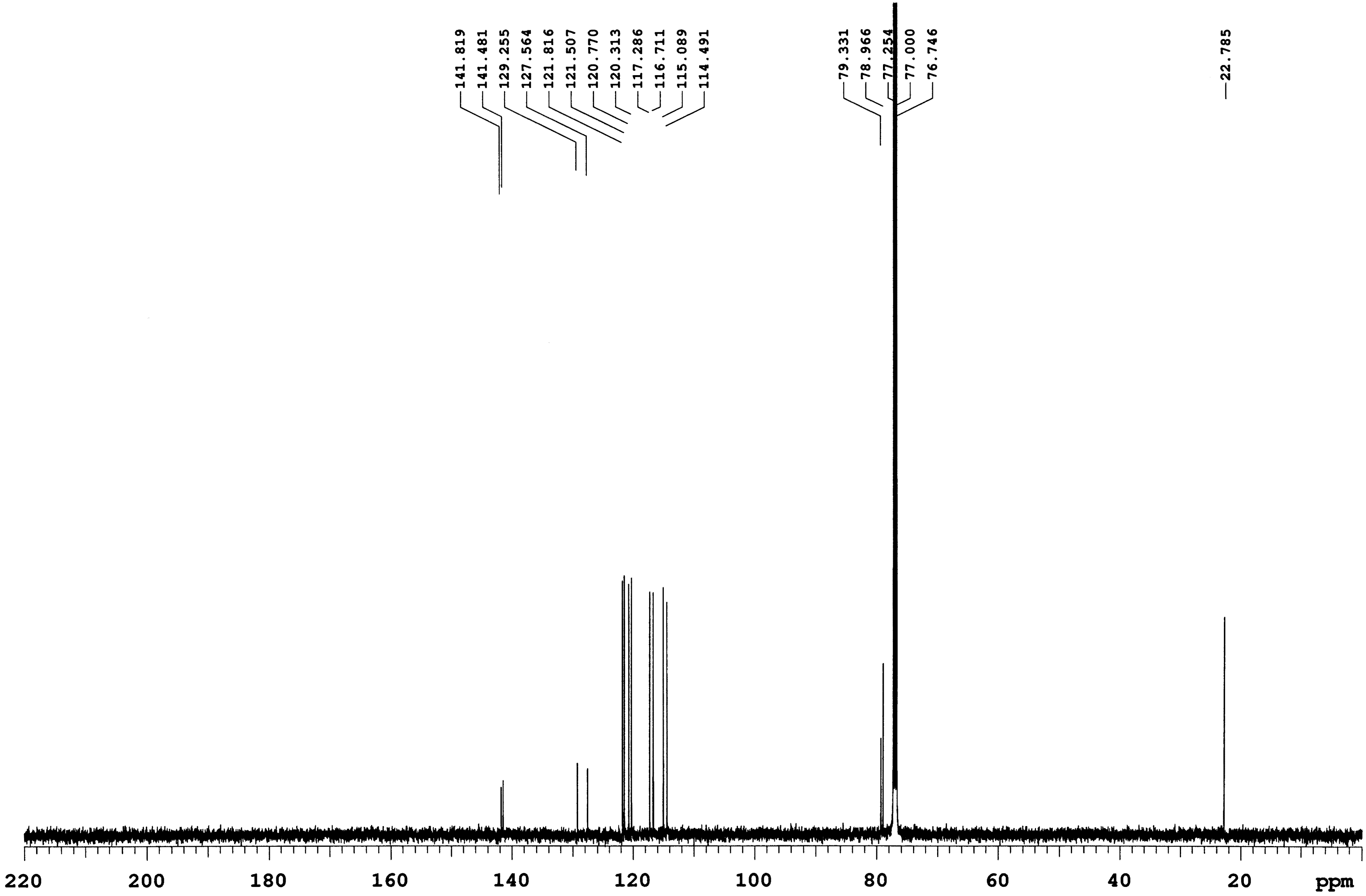
LTC-0-129-f1

Sample Name **LTC-0-129-f1**
Date collected **2018-09-05**

Pulse sequence **CARBON**
Solvent **cdcl3**

Temperature **25**
Spectrometer **Agilent-NMR-inova500**

Study owner **vnmr2**
Operator **vnmr2**



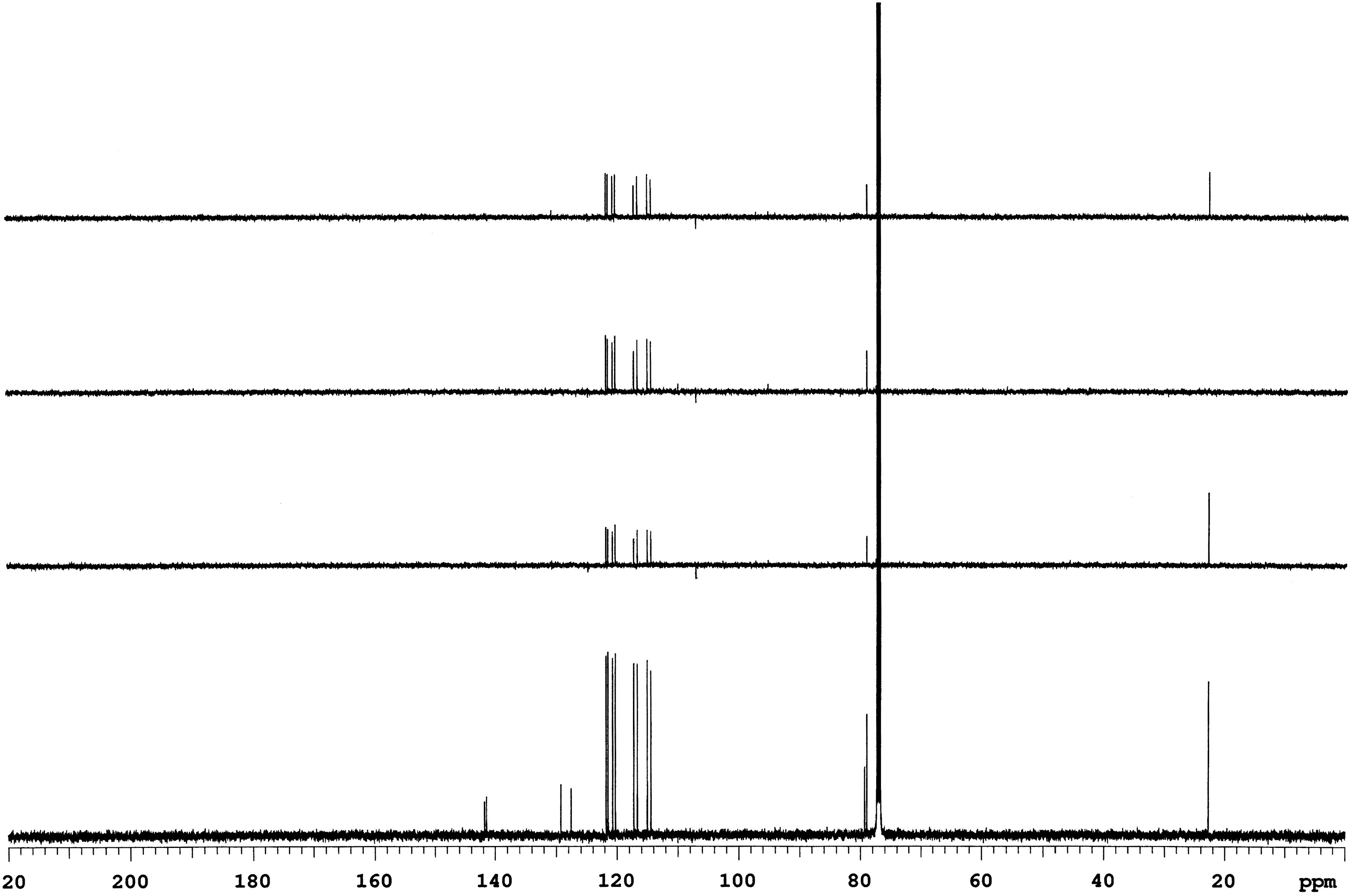
13C NMR (CDCl3, 125 Hz) of compound **3**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-0-129-f1/CARBON_01

Plot date 2018-09-07

LTC-0-129-f1

Sample Name	**LTC-0-129-f1**	Pulse sequence	**DEPT**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2018-09-05**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



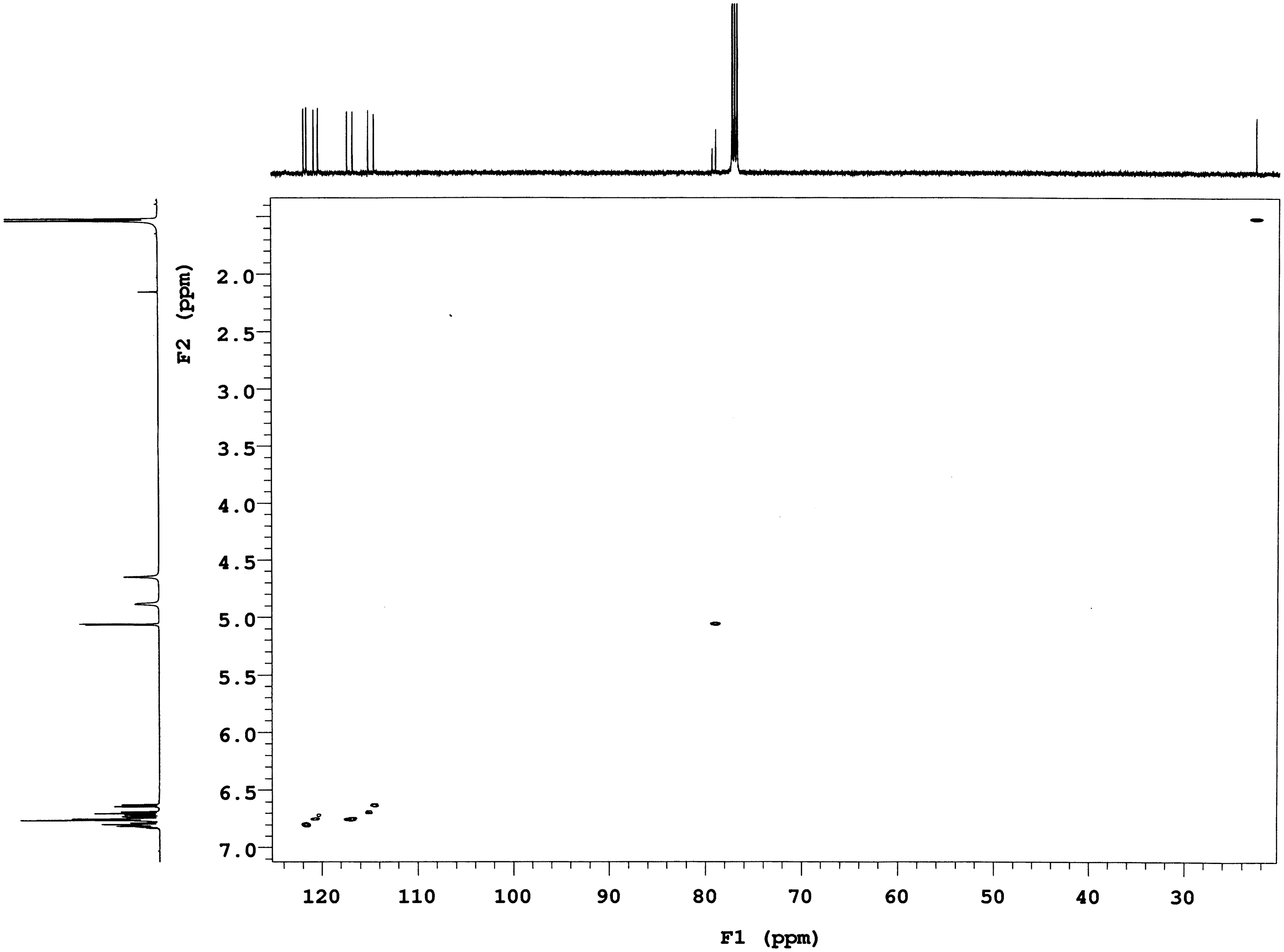
DEPT of compound **3**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-0-129-f1/DEPT_01

Plot date 2018-09-07

LTC-0-129-f1

Sample Name	**LTC-0-129-f1**	Pulse sequence	**gHSQC**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2018-09-05**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



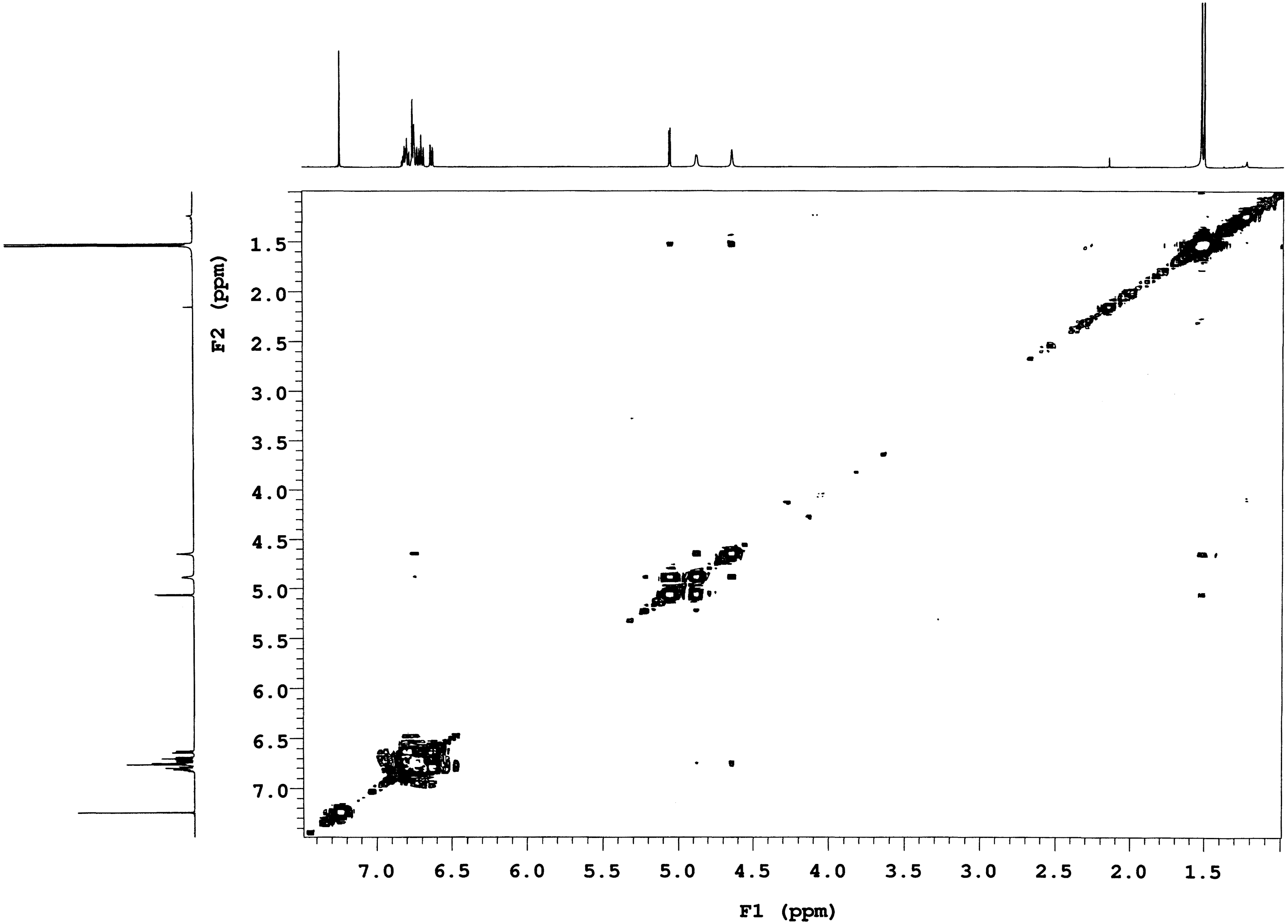
HSQC of compound **3**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-0-129-f1/gHSQC_01

Plot date 2018-09-07

LTC-0-129-f1

Sample Name **LTC-0-129-f1**
Date collected **2018-09-05**
Pulse sequence **gCOSY**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



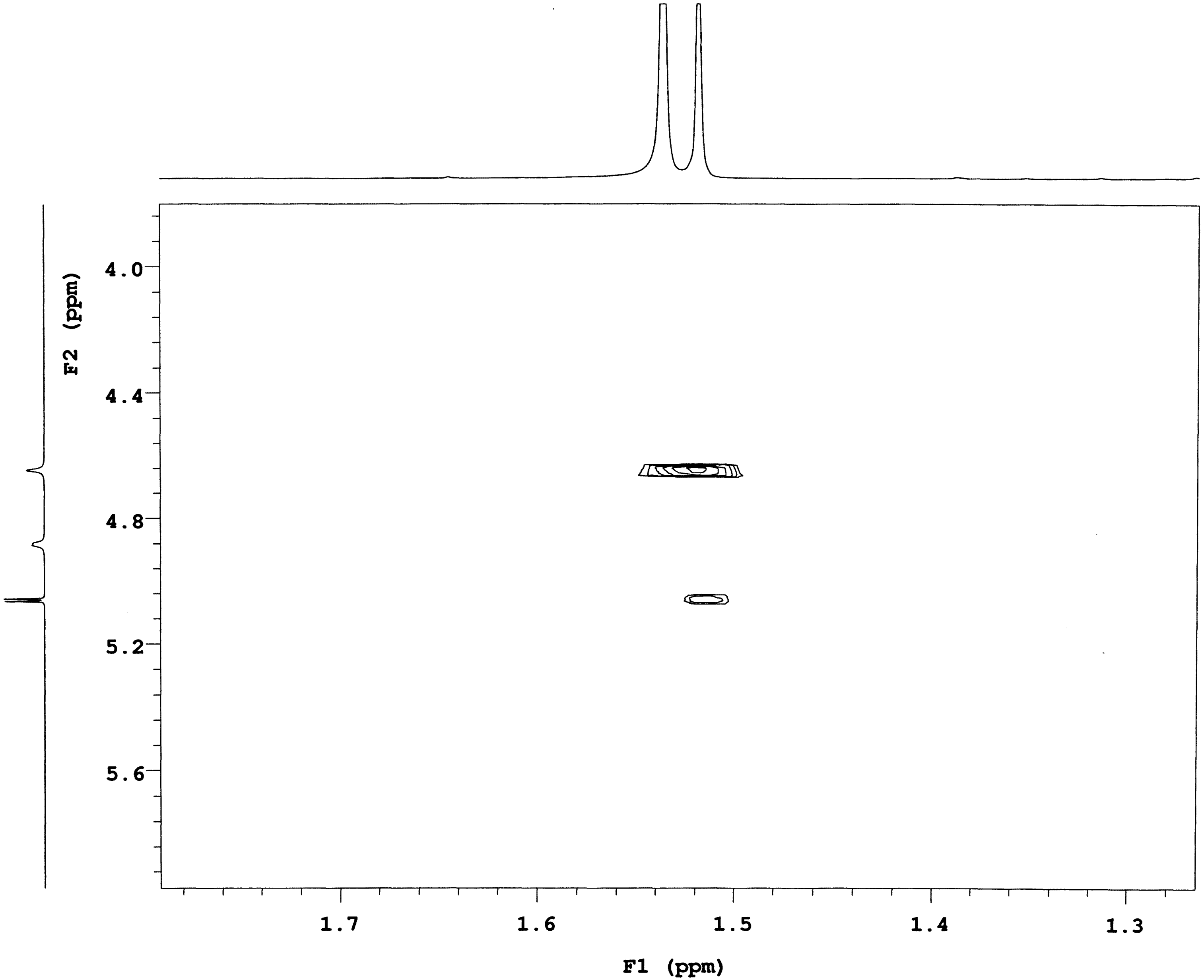
COSY of compound **3**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-0-129-f1/gCOSY_01

Plot date 2018-09-07

LTC-0-129-f1

Sample Name	**LTC-0-129-f1**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2018-09-05**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



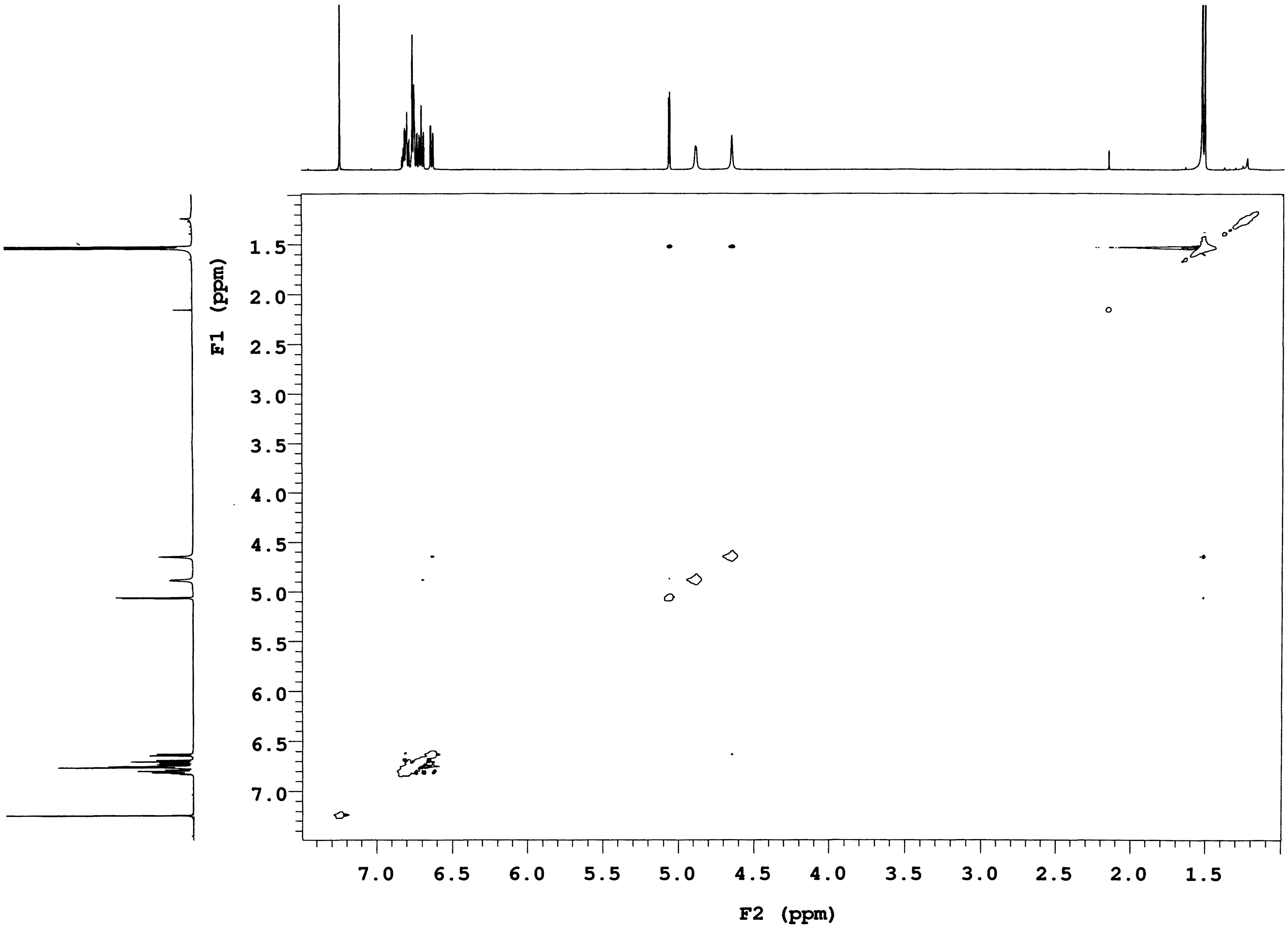
COSY of compound **3**, expanded

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-0-129-f1/gCOSY_01

Plot date 2018-09-07

LTC-0-129-f1

Sample Name **LTC-0-129-f1**
Date collected **2018-09-05**
Pulse sequence **NOESY**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



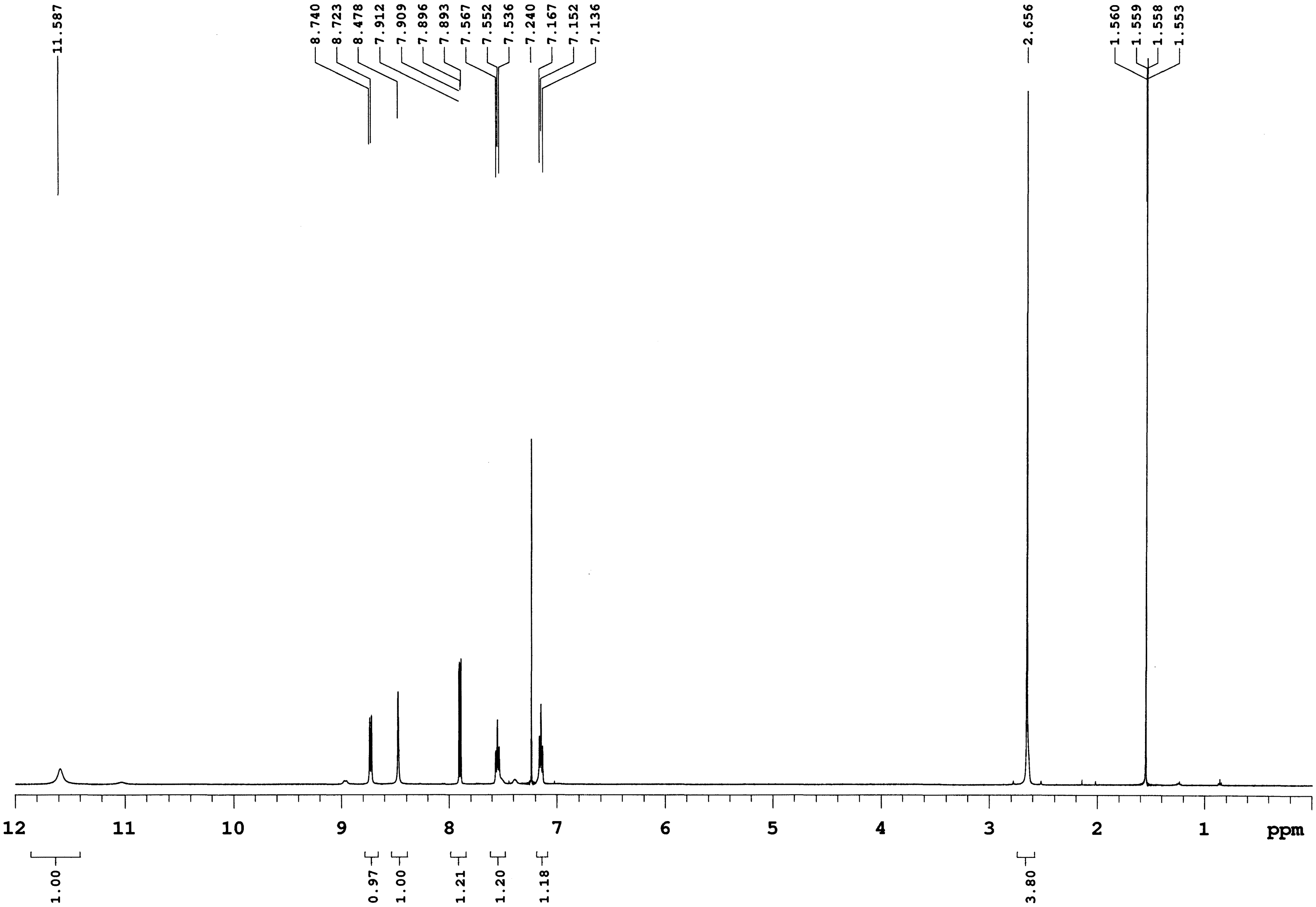
NOESY of compound **3**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-0-129-f1/NOESY_01

Plot date 2018-09-07

LTC-2-202-f2

Sample Name **LTC-2-202-f2**	Pulse sequence **PROTON**	Temperature **25**	Study owner **vnmr2**
Date collected **2018-12-08**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



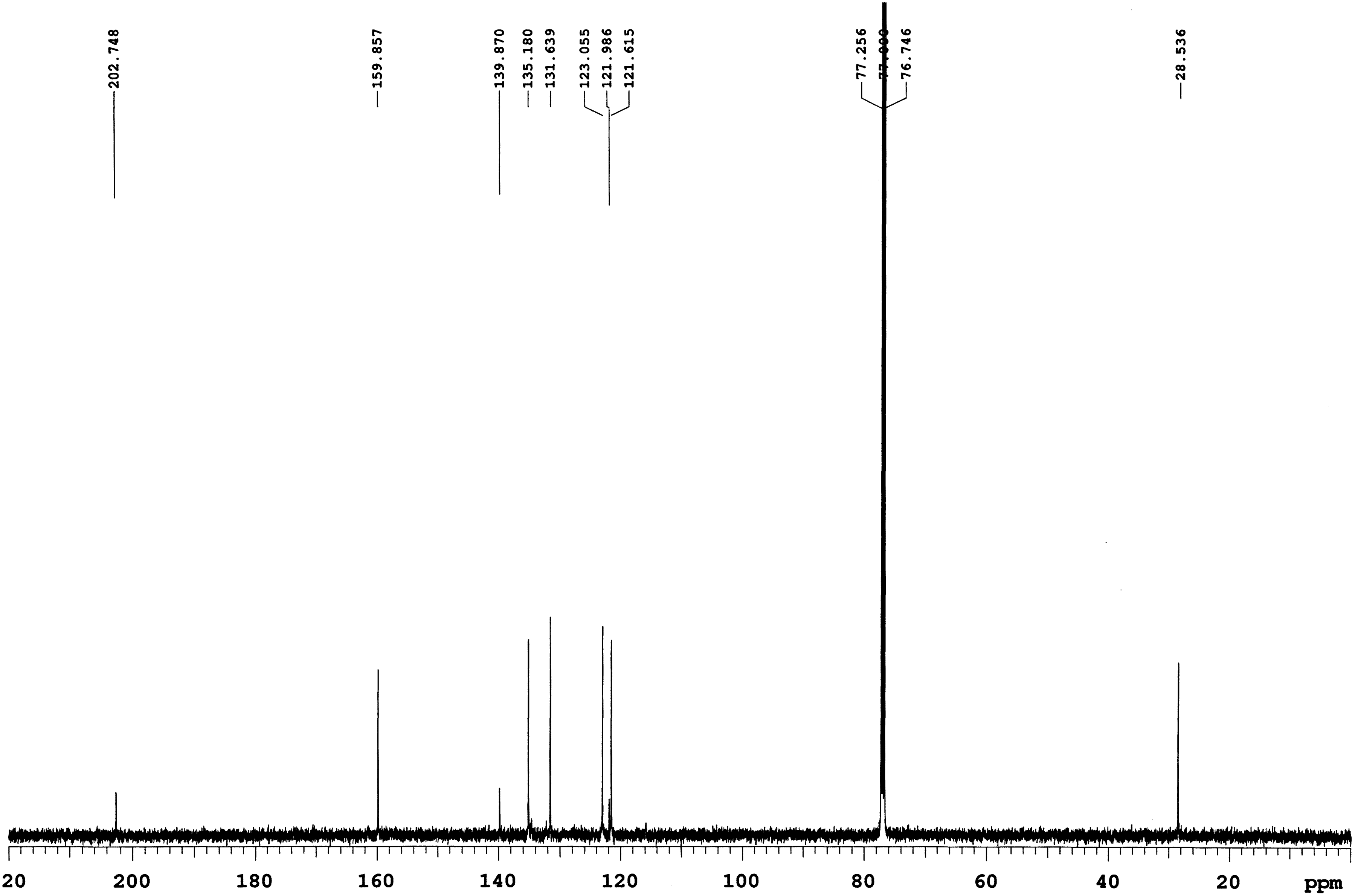
1H NMR (CDCl3, 500 Hz) of compound **4**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-2-202-f2/PROTON_04

Plot date 2018-12-10

LTC-2-202-f2

Sample Name **LTC-2-202-f2**
Date collected **2018-12-08**
Pulse sequence **CARBON**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



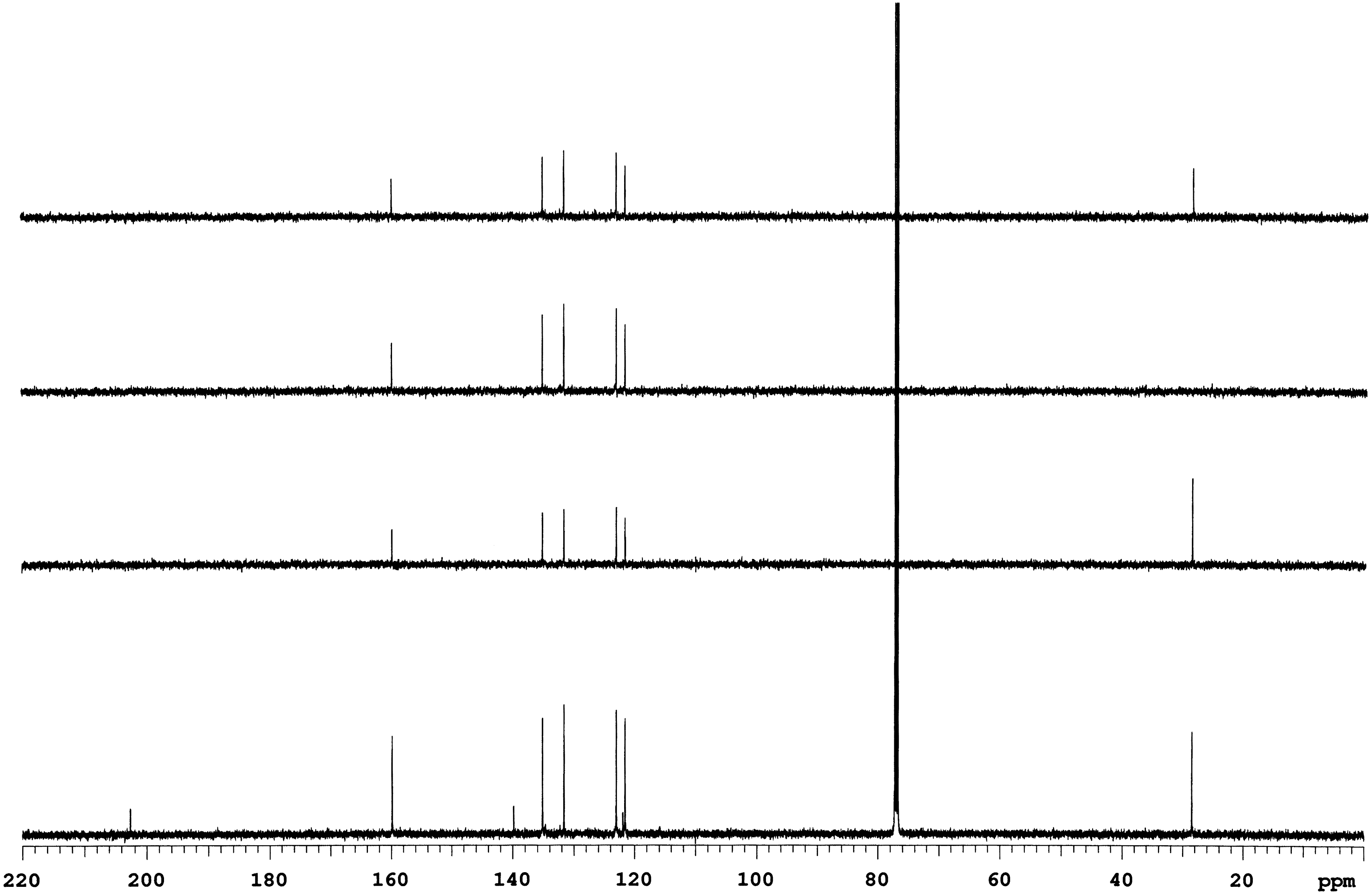
13C NMR (CDCl3, 500 Hz) of compound **4**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-2-202-f2/CARBON_03

Plot date 2018-12-10

LTC-2-202-f2

Sample Name **LTC-2-202-f2**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2018-12-08**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



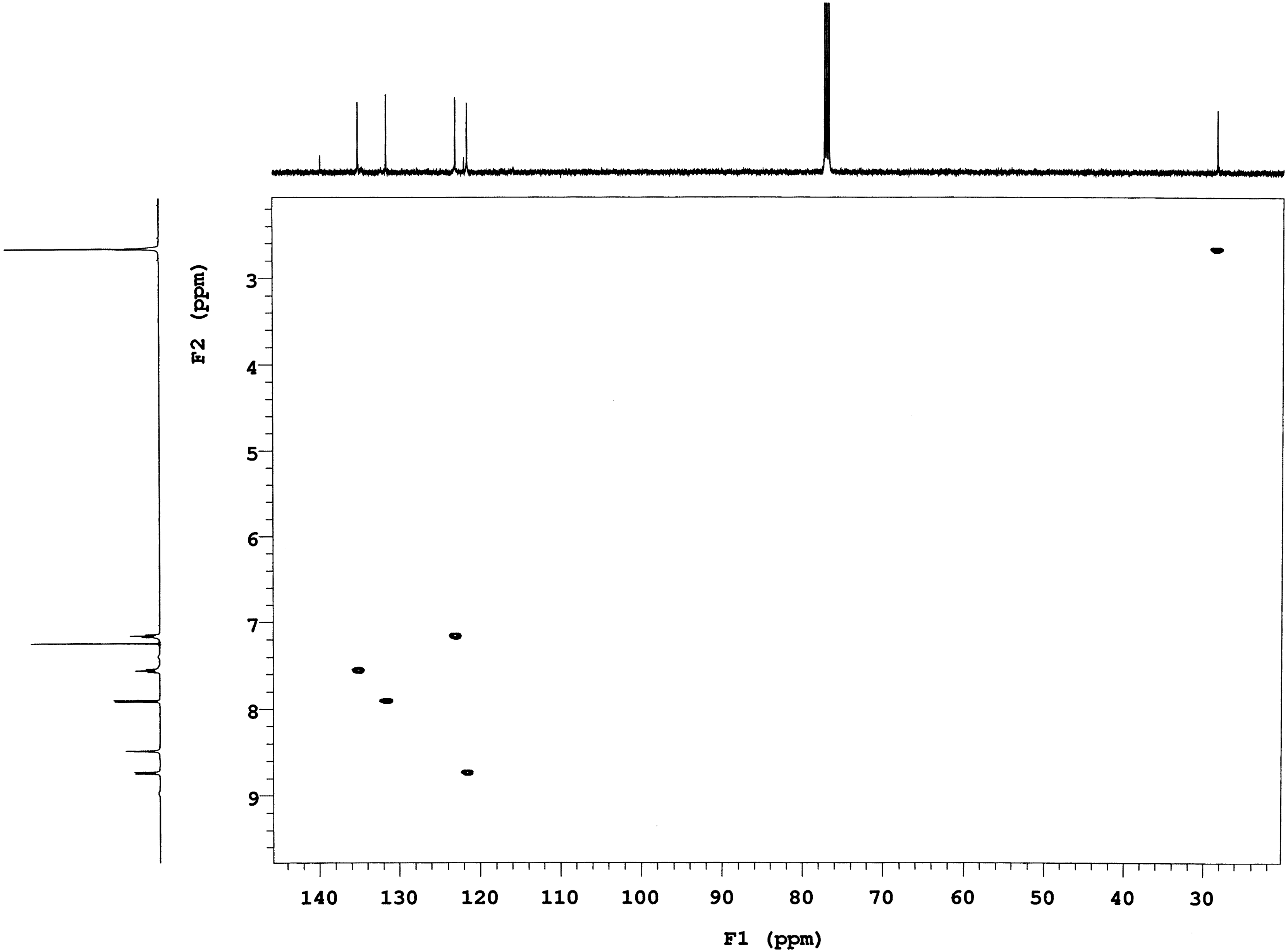
DEPT of compound **4**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-2-202-f2/DEPT_01

Plot date 2018-12-10

LTC-2-202-f2

Sample Name **LTC-2-202-f2**
Date collected **2018-12-09**
Pulse sequence **gHSQC**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



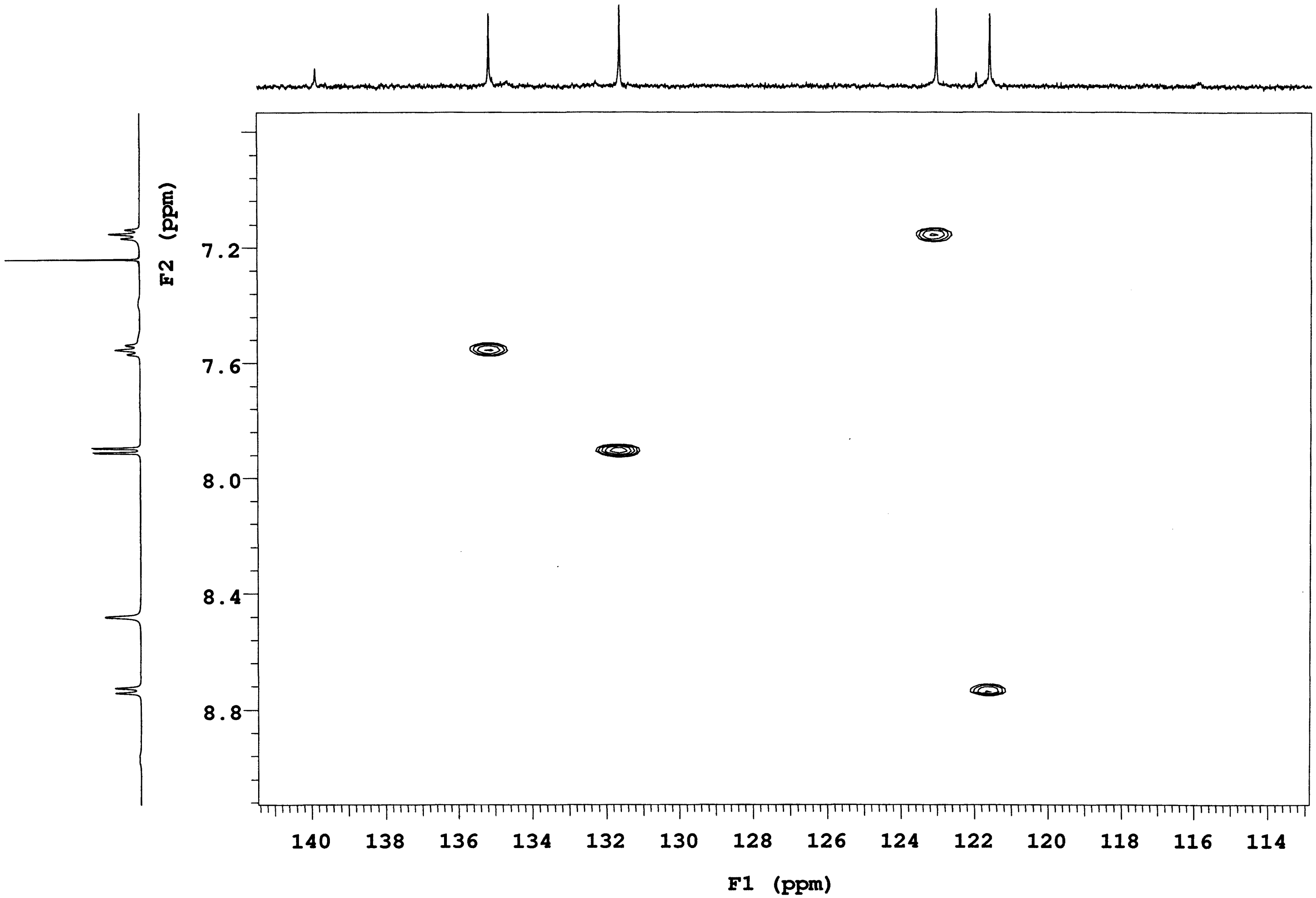
HSQC of compound **4**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-2-202-f2/gHSQC_01

Plot date 2018-12-10

LTC-2-202-f2

Sample Name **LTC-2-202-f2**	Pulse sequence **gHSQC**	Temperature **25**	Study owner **vnmr2**
Date collected **2018-12-09**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



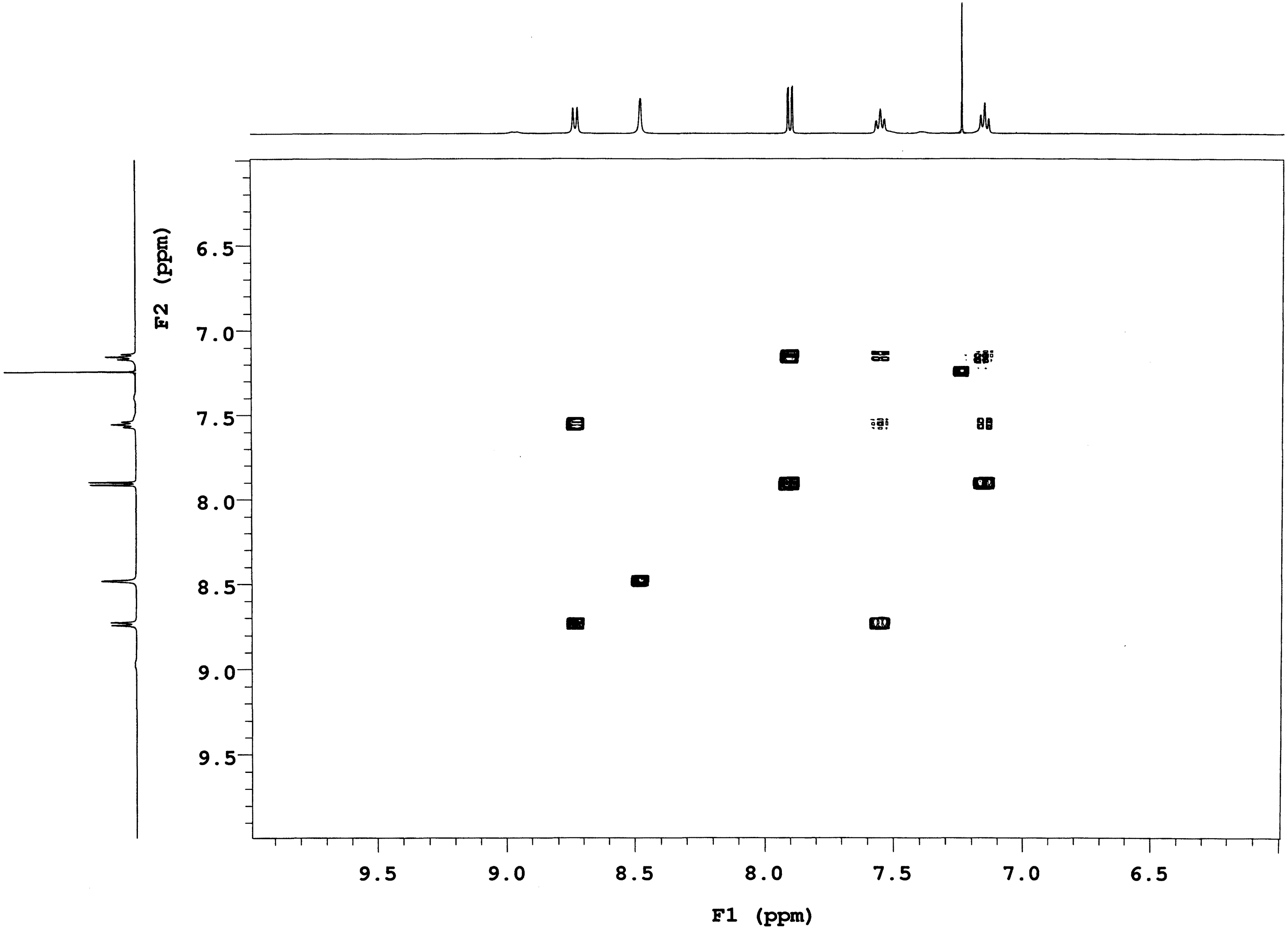
HSQC of compound **4**, expanded

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-2-202-f2/gHSQC_01

Plot date 2018-12-10

LTC-2-202-f2

Sample Name	**LTC-2-202-f2**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2018-12-08**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



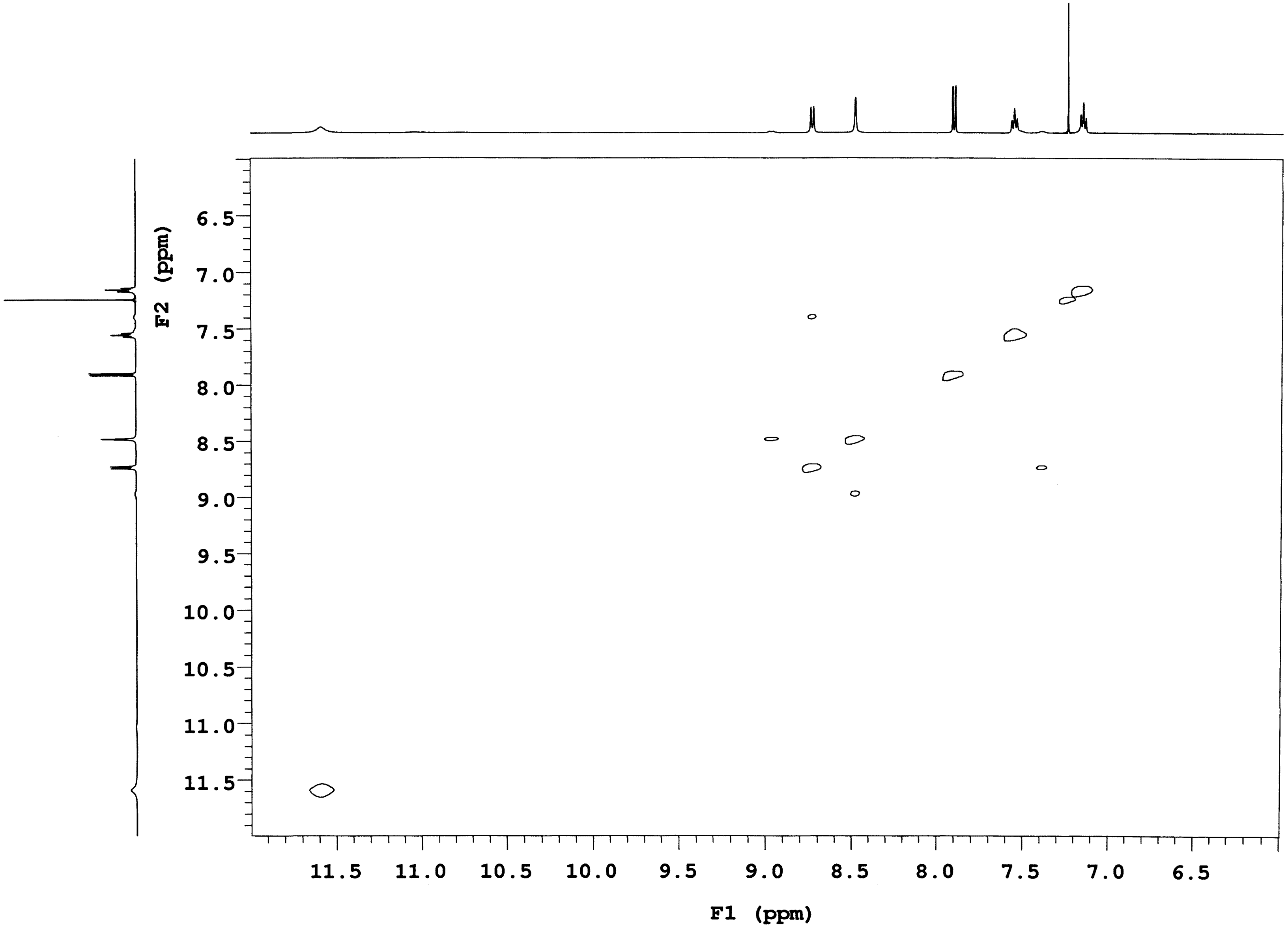
COSY of compound **4**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-2-202-f2/gCOSY_01

Plot date 2018-12-10

LTC-2-202-f2

Sample Name **LTC-2-202-f2**
Date collected **2018-12-08**
Pulse sequence **NOESY**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



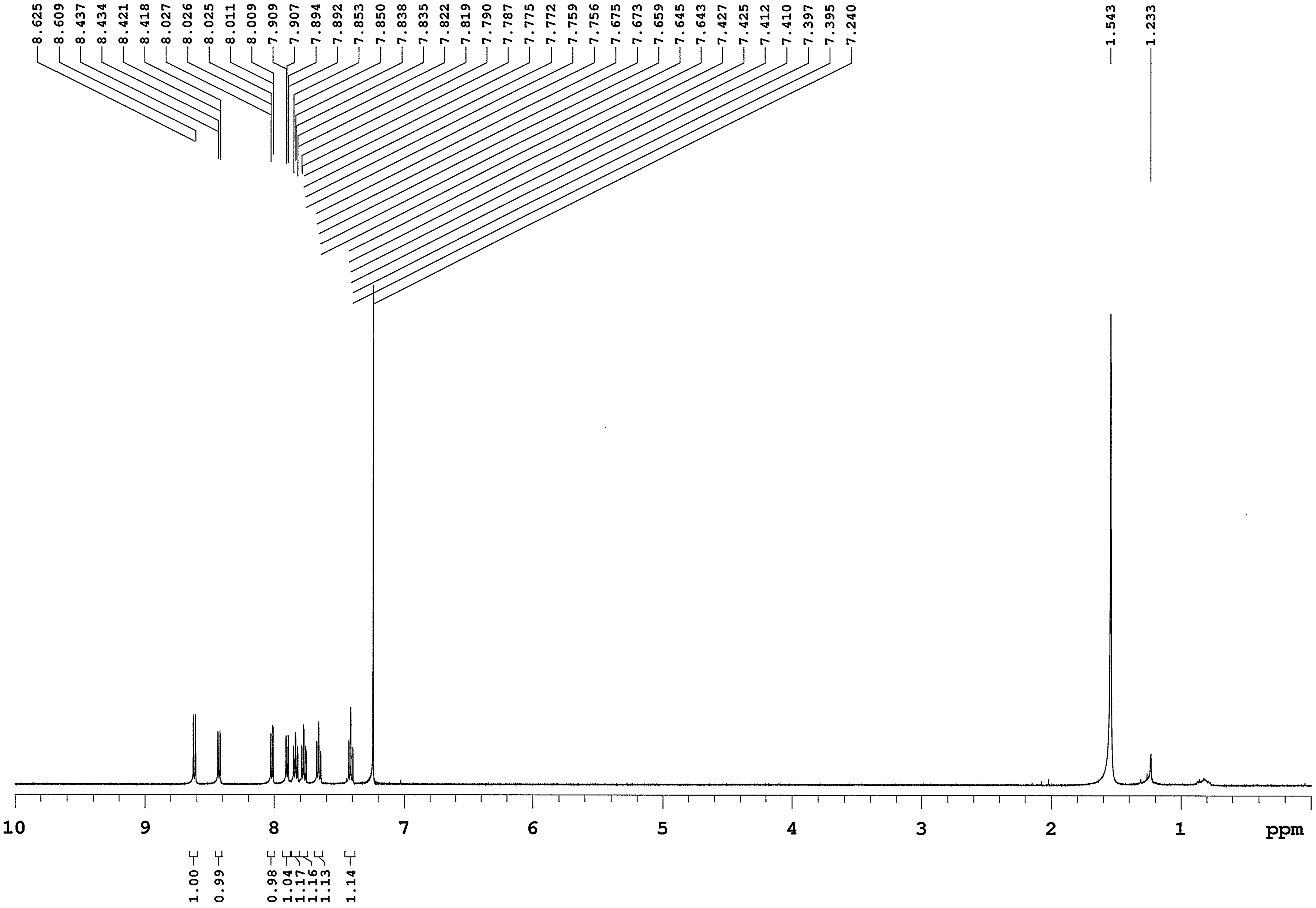
NOESY of compound **4**

Data file /home/vnmr2/vnmrsys/data/511/LTC/LTC-2-202-f2/NOESY_01

Plot date 2018-12-10

SQL-050

Sample Name **SQL-050**
Date collected **2020-04-19**
Pulse sequence **PROTON**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**



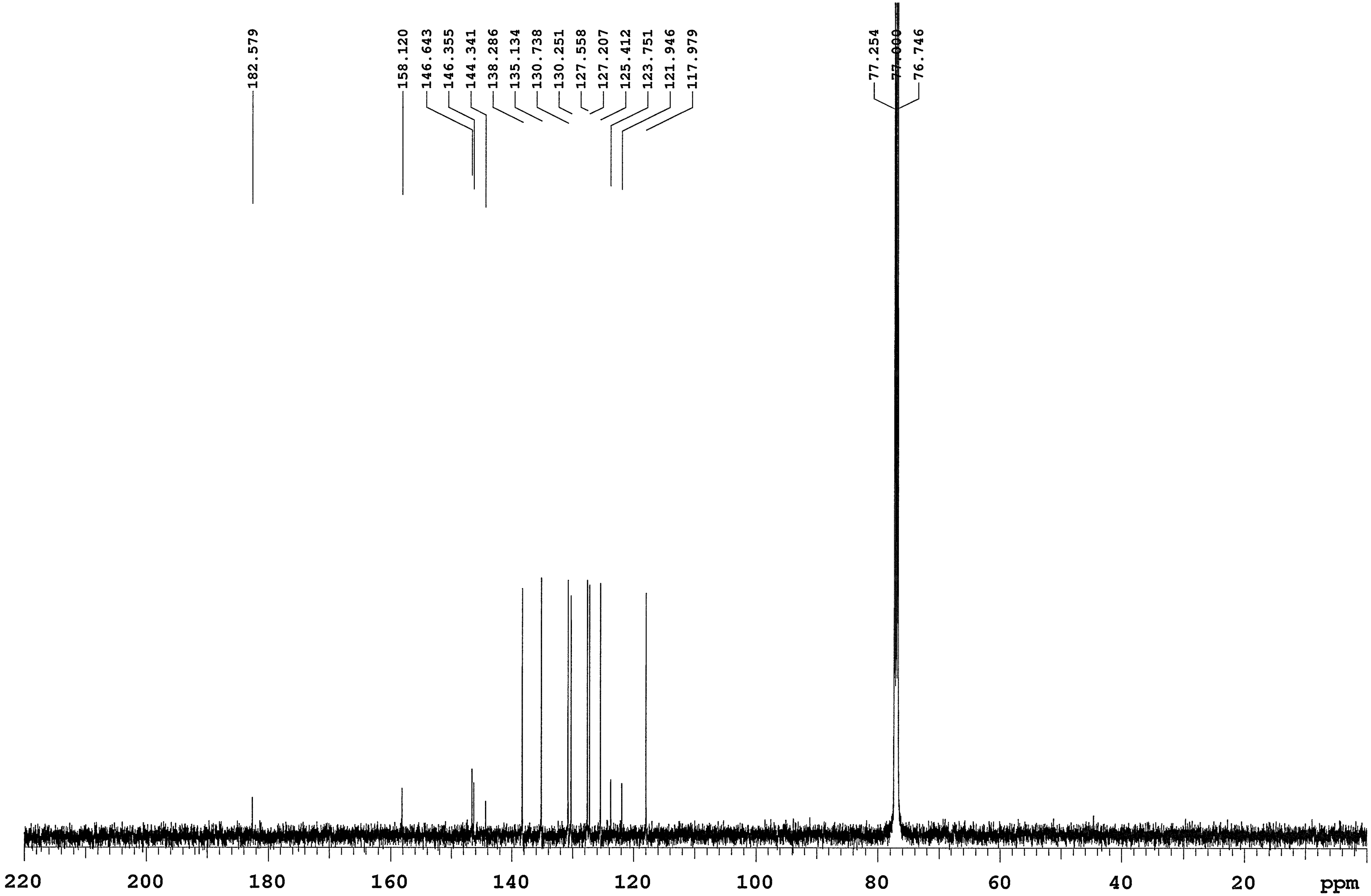
1H NMR (CDCl3, 500 Hz) of tryptanthrin

Data file /home/vnmr2/vnmrsys/data/511/SQL/SQL-050/PROTON_04

Plot date 2020-04-21

SQL-050

Sample Name **SQL-050**	Pulse sequence **CARBON**	Temperature **25**	Study owner **vnmr2**
Date collected **2020-04-19**	Solvent **cdcl3**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



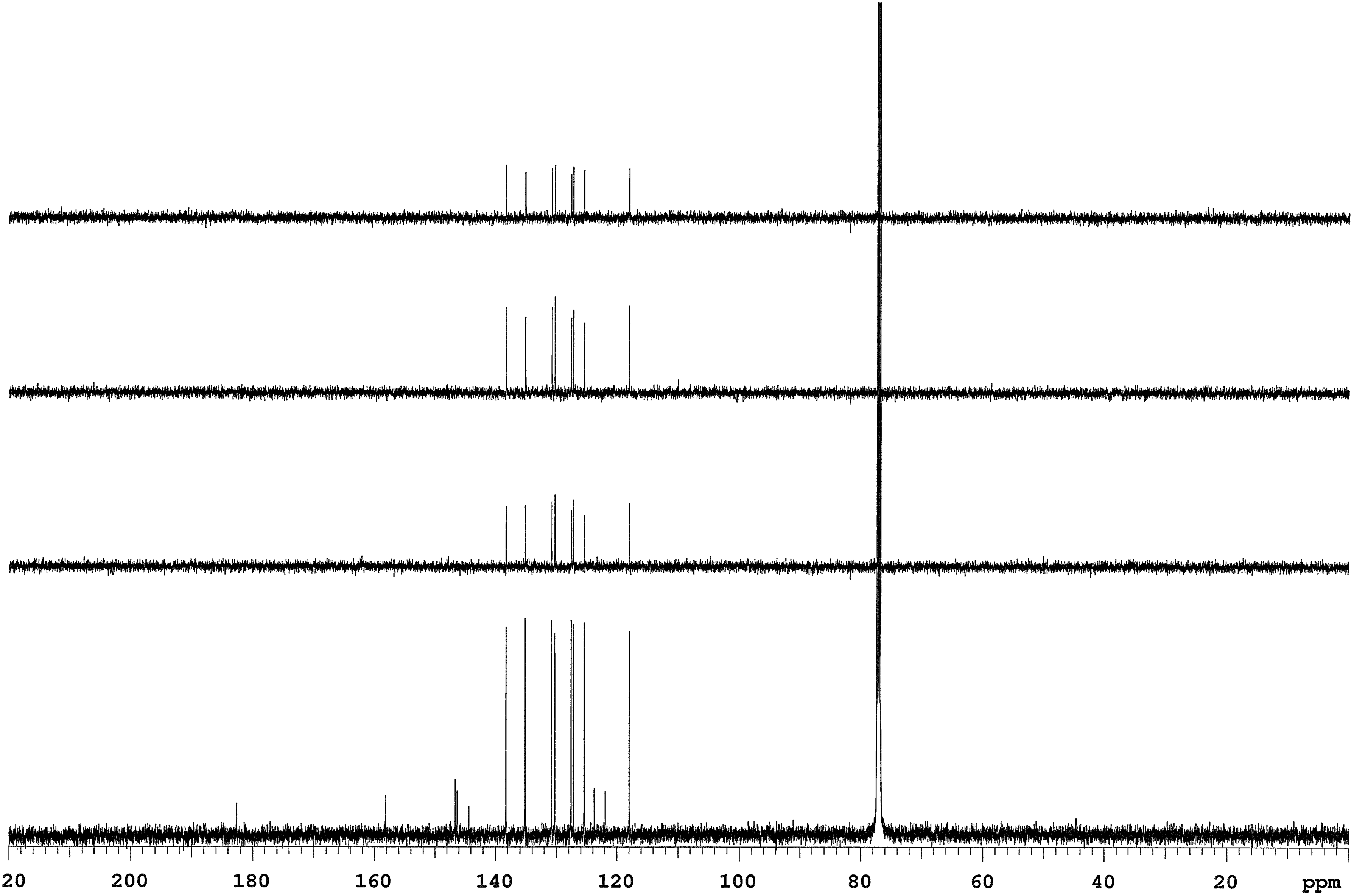
13C NMR (CDCl3, 125 Hz) of tryptanthrin

Data file /home/vnmr2/vnmrsys/data/511/SQL/SQL-050/CARBON_02

Plot date 2020-04-21

SQL-050

Sample Name **SQL-050**
Date collected **2020-04-20**
Pulse sequence **DEPT**
Solvent **cdcl3**
Temperature **25**
Spectrometer **Agilent-NMR-inova500**
Study owner **vnmr2**
Operator **vnmr2**

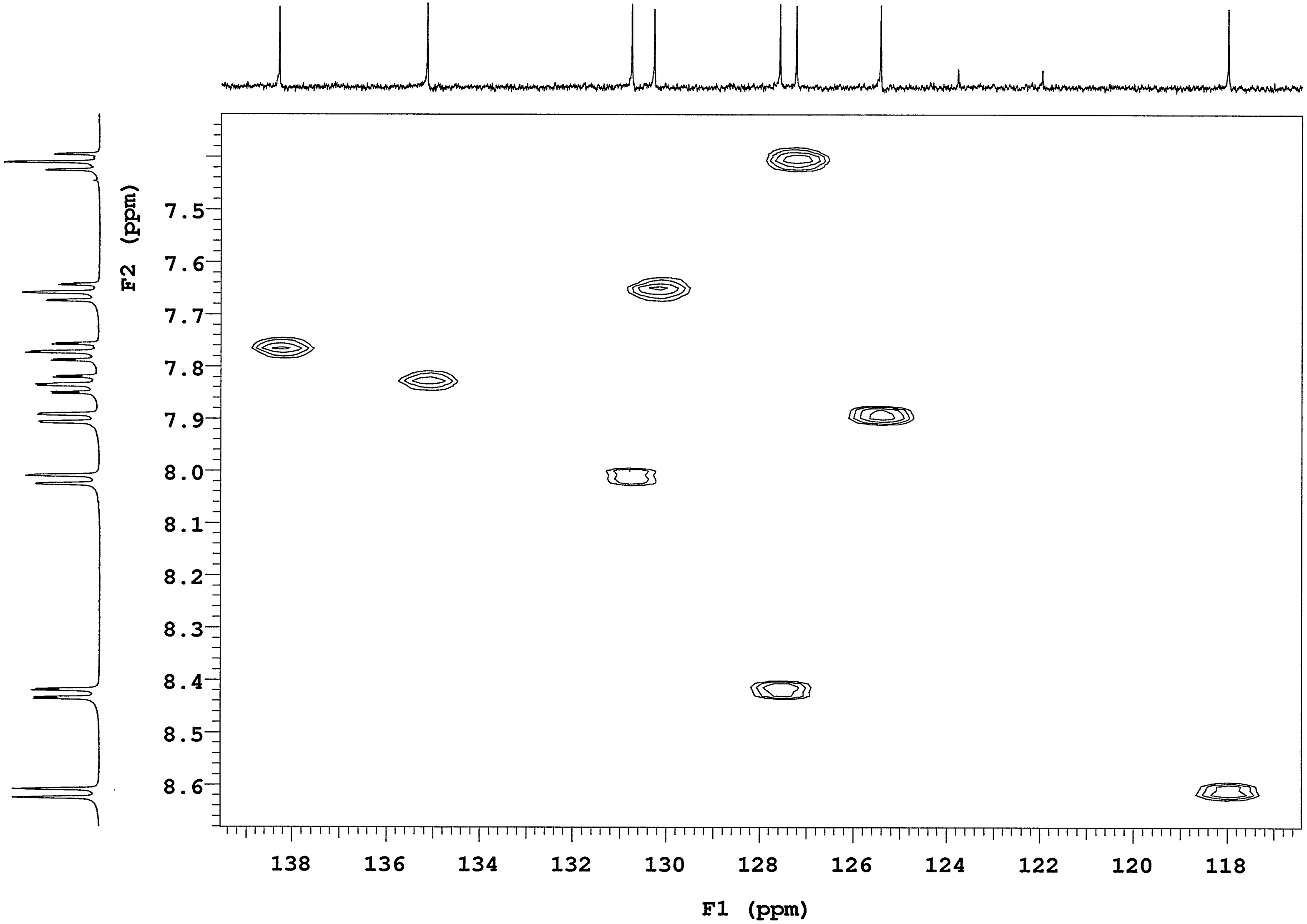


DEPT of tryptanthrin

Data file /home/vnmr2/vnmrsys/data/511/SQL/SQL-050/DEPT_01

Plot date 2020-04-21

Sample Name	**SQL-050**	Pulse sequence	**gHSQC**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2020-04-20**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



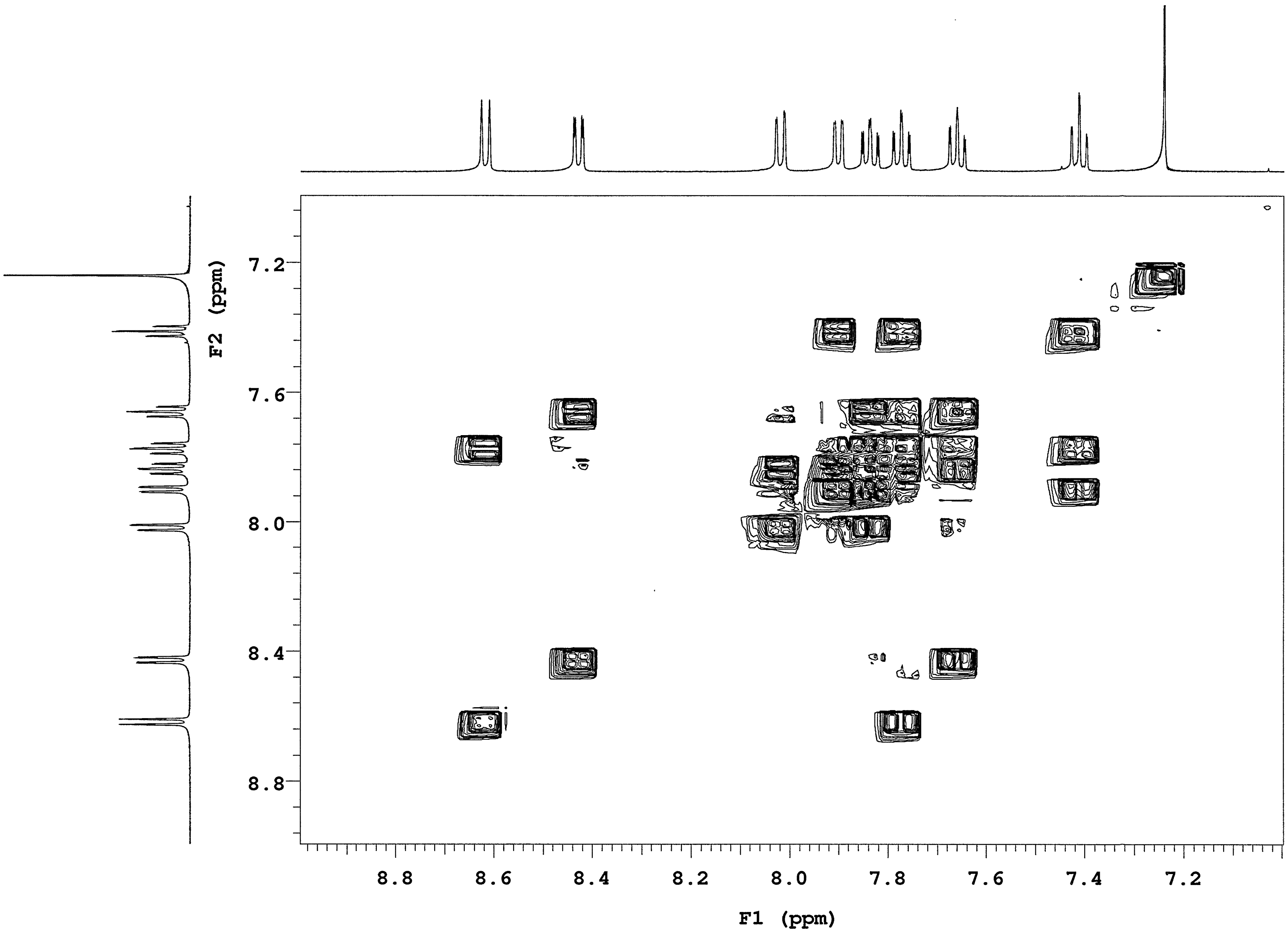
HSQC of tryptanthrin

Data file /home/vnmr2/vnmrsys/data/511/SQL/SQL-050/gHSQC_01

Plot date 2020-06-04

SQL-050

Sample Name	**SQL-050**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2020-04-20**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



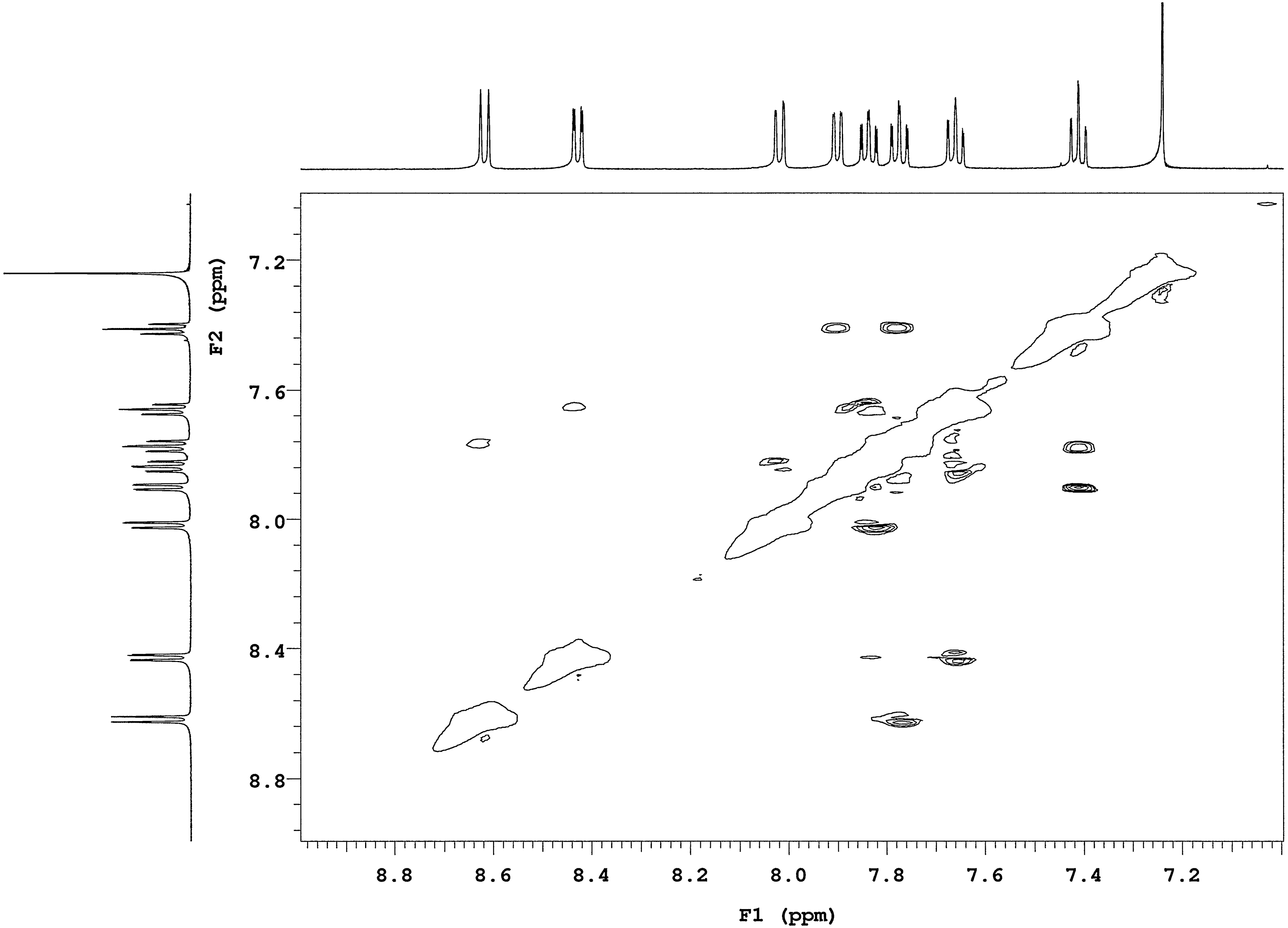
COSY of tryptanthrin

Data file /home/vnmr2/vnmrsys/data/511/SQL/SQL-050/gCOSY_01

Plot date 2020-06-04

SQL-050

Sample Name **SQL-050** Pulse sequence **NOESY** Temperature **25** Study owner **vnmr2**
Date collected **2020-04-20** Solvent **cdcl3** Spectrometer **Agilent-NMR-inova500** Operator **vnmr2**



NOESY of tryptanthrin

Data file /home/vnmr2/vnmrsys/data/511/SQL/SQL-050/NOESY_01

Plot date 2020-06-04