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# Supporting Information

# Marine Bacteria from the *Roseobacter* Clade Produce Sulfur Volatiles via Amino Acid and Dimethylsulfoniopropionate Catabolism

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**Table 1.** Incorporation rates (%) for sulfur volatiles released by *O. indolifex* DSM 14862$^T$ (top) and by *P. inhibens* DSM 17395 wildtype and a *patB* mutant (bottom) from liquid cultures supplemented with 1 mM [$^{34}$S]DMSP or 1 mM [$^{34}$S]Cys.

| Compound | *I* | DSM 14862$^T$ + [$^{34}$S]DMSP | | | | | | **mean** | **SD** | DSM 14862$^T$ + [$^{34}$S]Cys | | | | | | **mean** | **SD** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *S*-methyl thioacetate (**33**) | 701 | x | 23,8 | x | 12,4 | x | 60,7 | **32,3** | **25,2** | x | 2,4 | x | 2,5 | x | 2,5 | **2,5** | **0,1** |
| dimethyl disulfide (**15**) | 739 | xxx | 54,8 | xxx | 67,7 | xxx | 61,1 | **61,2** | **6,5** | xxx | 5,1 | xxx | 9,8 | xxx | 9,5 | **8,1** | **2,6** |
| *S*-methyl propanethioate (**34**) | 799 | x | 59,4 | x | 65,4 | x | 64,4 | **63,1** | **3,2** | x | 0,9 | x | 3,4 | x | 3,5 | **2,6** | **1,5** |
| *S*-methyl 2-methylpropanethioate (**35**) | 850 | | | x | 29,3 | | | **29,3** | | | | | | | | | |
| *S*-methyl 3-methylbutanethioate (**36**) | 941 | x | 14,8 | x | 9,2 | | | **12,0** | **4,0** | | | | | | | | |
| dimethyl trisulfide (**20**) | 969 | x | 39,8 | x | 57,7 | xx | 40,6 | **46,0** | **10,1** | x | 30,8 | xx | 32,6 | xx | 29,5 | **31,0** | **1,6** |
| 4-methylthio-2-butanone (**41**) | 988 | x | 48,3 | x | 57,7 | x | 33,9 | **46,6** | **12,0** | | | | | | | | |
| *S*-methyl methanethiosulfonate (**25**) | 1063 | xx | 62,7 | x | 77,4 | xx | 65,5 | **68,5** | **7,8** | x | 2,3 | xxx | 2,9 | xx | 3,7 | **3,0** | **0,7** |
| methyl methylthiomethyl disulfide (**37**) | 1128 | x | 35,0 | x | 64,7 | | | **49,9** | **21,0** | | | x | 8,0 | x | 7,9 | **8,0** | **0,1** |
| *S*-methyl 3-(methylthio)propanethioate (**42**) | 1201 | x | 68,1 | x | 77,5 | x | 69,0 | **71,5** | **5,2** | | | | | | | | |
| dimethyl tetrasulfide (**24**) | 1221 | x | 54,5 | | | x | 25,2 | **39,9** | **20,7** | | | x | 49,5 | x | 48,4 | **49,0** | **0,8** |

| Compound | DSM 17395 + [$^{34}$S]DMSP | | | | | | **mean** | **SD** | DSM 17395 + [$^{34}$S]Cys | | | | | | **mean** | **SD** | DSM 17395 Δ*patB::kan* + [$^{34}$S]Cys | | | | | | **mean** | **SD** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **33** | | | | | | | | | | | | | | | | | | | | | | | | |
| **15** | xxx | 68,7 | xxx | 43,8 | xxx | 93,5 | **68,7** | **24,9** | xxx | 7,4 | xxx | 2,0 | xxx | 2,9 | **4,1** | **2,9** | xxx | 18,1 | xxx | 13,3 | xxx | 9,4 | **13,6** | **4,4** |
| **34** | | | | | | | | | | | | | | | | | | | | | | | | |
| **35** | | | | | | | | | | | | | | | | | | | | | | | | |
| **36** | | | | | | | | | | | | | | | | | | | | | | | | |
| **20** | x | 44,3 | x | 31,0 | x | 65,7 | **47,0** | **17,5** | x | 25,3 | x | 24,9 | x | 19,6 | **23,3** | **3,2** | x | 22,8 | x | 23,4 | x | 20,9 | **22,4** | **1,3** |
| **41** | | | | | | | | | | | | | | | | | | | | | | | | |
| **25** | x | 67,9 | x | 52,8 | x | 94,5 | **71,7** | **21,1** | x | 2,2 | x | 2,2 | xx | 1,7 | **2,0** | **0,3** | x | 22,1 | x | 11,5 | x | 11,8 | **15,1** | **6,0** |
| **37** | | | | | x | 87,8 | **87,8** | | | | | | | | | | | | x | 13,5 | x | 10,6 | **12,1** | **2,1** |
| **42** | | | x | 22,1 | | | **22,1** | | | | | | | | | | | | | | | | | |
| **24** | | | | | | | | | | | | | | | | | | | | | | | | |

The data from three repetitive experiments, mean ± standard deviation (SD) are given. The relative amounts of the emitted compounds are indicated by x: <2%, xx: 2 – 8%, xxx: >8% of total extract. Compound numbers refer to Scheme 4 of main text. Gas chromatographic retention indices *I* were determined on a HP5-MS column.

**Table 2.** Volatiles released by DSM 14862$^T$ and DSM 17395 from liquid cultures supplemented with 1 mM MPSP, 1 mM IMSP or 1 mM TMSP.

| Compound | *I* | Ident. | DSM 14862$^T$ + MPSP | | DSM 17395 + MPSP | DSM 14862$^T$ + IMSP | | DSM 17395 + IMSP | DSM 14862$^T$ + TMSP | | DSM 17395 + TMSP |
|---|---|---|---|---|---|---|---|---|---|---|---|
| isopropyl methyl sulfide (**13**) | 688 | std | | | | xxx | xxx | xxx | | | |
| *S*-methyl thioacetate (**33**) | 701 | std | x | x | | | | | | | x |
| methyl propyl sulfide (**12**) | 711 | std | xxx | xxx | xxx | | | | | | |
| dimethyl disulfide (**15**) | 739 | std | xx | xxx | xxx | xx | xx | xx | xx | xx | xxx |
| *S*-methyl propanethioate (**34**) | 799 | std | | x | | | x | | | | |
| tetrahydrothiophene (**14**) | 807 | std | | | | | | | xxx | xxx | xxx |
| isopropyl methyl disulfide (**17**) | 891 | ms[1] | | | | xx | xxx | | | | |
| propyl methyl disulfide (**16**) | 932 | ri (940)[2] | xx | xx | x | | | | | | |
| dimethyl trisulfide (**20**) | 969 | std | x | x | x | x | x | x | x | x | x |
| isopropyl methyl sulfoxide (**31**) | 985 | ms* | | | | xx | xx | x | | | |
| 4-methylthio-2-butanone (**41**) | 988 | std | | | | | | | x | x | |
| dihydro-2(3*H*)-thiophenone (**38**) | 999 | std | | | | | | | x | x | |
| methyl propyl sulfoxide (**30**) | 1013 | ms[1] | x | x | x | | | | | | |
| diisopropyl disulfide (**19**) | 1020 | std | | | | x | xx | | | | |
| 1,2-dithiane (**39**) | 1041 | std | | | | | | | xxx | xxx | x |
| *S*-methyl methanethiosulfonate (**25**) | 1063 | std | xx | xx | x | x | x | | x | x | xx |
| isopropyl methyl trisulfide (**22**) | 1107 | ms* | | | | x | x | | | | |
| dipropyl disulfide (**18**) | 1108 | std | x | x | | | | | | | |
| tetrahydrothiophene-1-oxide (**32**) | 1126 | ms[1] | | | | | | | xx | xx | xx |
| methyl methylthiomethyl disulfide (**37**) | 1128 | ri (1123)[3] | x | | x | | | | | | x |
| methyl propyl trisulfide (**21**) | 1154 | ri (1150)[4] | x | x | | | | | | | |
| 2-methylthiophenol (**40**) | 1164 | std | | | x | | | | | | x |
| *S*-isopropyl methanethiosulfonate (**26**) | 1166 | std | | | | | x | | | | |
| *S*-methyl isopropanethiosulfonate (**27**) | 1202 | ms* | | | | | x | | | | |
| *S*-propyl methanethiosulfonate (**28**) | 1223 | std | x | x | | | | | | | |
| diisopropyl trisulfide (**23**) | 1234 | ms[5] | | | | | x | | | | |
| *S*-methyl propanethiosulfonate (**29**) | 1234 | std | x | x | | | | | | | |
| methyl 3-(methyldisulfanyl)propionate (**43**) | 1242 | std | | | x | xx | x | x | | | x |

The relative amounts of the emitted compounds are indicated by x: <2%, xx: 2 – 8%, xxx: >8% of total extract. Compound numbers refer to Scheme 4 of main text. Gas chromatographic retention indices *I* were determined on a HP5-MS column. Compound identification was based on: std (comparison to a synthetic or commercially available standard), ms (comparison of mass spectrum to a data base spectrum), ri (comparison of retention index to literature data, in brackets, for the same or similar column type with a maximum difference of 10 points), and ms* (tentative identification based on mass spectrum).

**Table 3.** Enzymes for DMSP catabolism in *O. indolifex* and *P. inhibens*.

| Enzyme | *O. indolifex* DSM 14862$^T$ | *P. inhibens* DSM 17395 |
|---|---|---|
| *Demethylation pathway* | | |
| DmdA | WP_007119686 | YP_006575183 |
| DmdB | – | YP_006575184 |
| DmdC | – | YP_006575186 |
| DmdD | – | YP_006575185 |
| *DMSP hydrolysis* | | |
| DddD | – | – |
| *DMSP lysis* | | |
| DddL | – | – |
| DddP | – | AFO91571 |
| DddQ | – | – |
| DddW | – | – |
| DddY | – | – |

Accession numbers of the relevant enzymes were identified by a BLAST search using the amino acid sequences of the respective first characterised enzymes as a probe. Note that the genome of *O. indolifex* has not been closed, while the genome of *P. inhibens* is finished.

# Experimental Procedures and Spectral Data

**Bacterial strains, growth conditions and feeding experiments.** *Oceanibulbus infolifex* DSM 14862$^T$ and *Phaeobacter inhibens* DSM 17395 strains were grown in half strength Marine Broth (MB 2216, Roth) and shaking (160 rpm) or on corresponding solid agar medium (20 g/L agar) at 28 °C. For the feeding experiments, half strength MB liquid medium (50 mL) was spiked after autoclaving with 1 mM [$^{34}$S]DMSP hydrochloride, methyl propyl sulfoniopropionate hydrochloride, methyl isopropyl sulfoniopropionate hydrochloride or tetramethylenesulfoniopropionate hydrochloride, respectively. The flasks were inoculated with 1 mL of the preculture and shaken (160 rpm) for 16 h at 28 °C. The agar plates were inoculated with 1 mL of the preculture and incubated for 1–3 d at 28 °C. CLSA sampling was carried out for 20 h (elution with $CH_2Cl_2$, 30 µl) as described previously.[6]

**General Synthetic Methods.** Chemicals were purchased from Acros Organics (Geel, Belgium) or Sigma-Aldrich Chemie GmbH (Steinheim, Germany), and used without further purification. $^{34}S_8$ (99.93% enriched) was purchased from Campro Scientific GmbH (Berlin, Germany). Solvents were purified by distillation, and dried according to standard methods. Oxygen and/or moisture sensitive reactions were carried out under inert atmosphere ($N_2$) in vacuum-heated flasks with dried solvents. Thin-layer chromatography ($SiO_2$, TLC) was performed on 0.20 mm Macherey-Nagel silica gel plates (Polygram SIL G/UV$_{254}$). Column chromatography was performed on Merck silica gel 60 (0.040 - 0.063 mm) using standard flash chromatographic methods. The NMR spectra were recorded on Bruker AV II-300 (300 MHz), DRX-400 (400 MHz) or AV III-400 (400 MHz) spectrometers, and were referenced against TMS or DSS ($\delta$ = 0.00 ppm) for $^1$H-NMR and $CHCl_3$ ($\delta$ = 77.01 ppm) for $^{13}$C-NMR. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br. = broad. Infrared spectra were recorded on a Bruker Tensor 27 ATR spectrometer. UV spectra were recorded on a Varian Cary 100 Bio spectrometer. GC-MS analyses were carried out on an Agilent 7890 GC system connected to an Agilent 5977A Mass Selective Detector fitted with a HP-5MS UI fused silica capillary column (30 m x 0.25 mm i.d., 0.50 µm film, Agilent Technologies, Santa Clara, California, USA). Conditions were as follows: inlet pressure: 95.1 kPa, He 16.2 mL min$^{-1}$; injection volume: 1 µL; injector: 250 °C; transfer line: 250 °C; electron energy: 70 eV. The GC was programmed as follows: 50 °C (5 min isothermic), increasing at 5 °C min$^{-1}$ (for synthetic samples) or 10 °C min$^{-1}$ (for natural samples) to 320 °C, and operated in split mode; carrier gas (He): 1.2 mL min$^{-1}$. Retention indices were determined from a homologous series of *n*-alkanes ($C_7$–$C_{40}$).

**K$^{34}$SCN:** Elemental $^{34}S_8$ (0.189 g, 5.56 mmol, 1.0 equiv.) was added to a solution of KCN (0.362 g, 5.56 mmol, 1.0 equiv.) in water (22 mL) and was stirred under reflux until the sulfur was consumed (48 h). Filtration and concentration in vacuo gave K$^{34}$SCN (0.546 g, 5.52 mmol, 99%) as a colorless solid. $^{13}$C-NMR (75 MHz, $D_2O$): $\delta$ = 136.1 ($C_q$) ppm.

**[$^{34}$S]-*tert*-Butyl 3-thiocyanatopropanoate (9):** A suspension of **8** (4.31 g, 4.85 mmol, 1.14 equiv.) and K$^{34}$SCN (2.00 g, 20.2 mmol, 1.00 equiv.) in dry acetonitrile (25 mL) was stirred under reflux for 2 h. To the reaction was added water (200 mL) and the mixture was extracted with ethyl acetate (3 x 200 mL). After concentration in vacuo, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1) to give **9** (3.51 g, 18.6 mmol, 92%) as a pale yellow oil. TLC (hexane/ethyl acetate 10:1, $R_f$ = 0.28). $^1$H-NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 3.16 (t, $^3J$(H,H) = 6.8 Hz, 2H, $CH_2$), 2.78 (t, $^3J$(H,H) = 6.8 Hz, 2H, $CH_2$), 1.47 (s, 9H, 3 $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ = 169.3 ($C_q$), 111.9 ($C_q$), 82.0 ($C_q$), 35.5 ($CH_2$), 29.2 ($CH_2$), 28.0 (3 $CH_3$) ppm. IR (ATR) $\tilde{\nu}$ = 2980 (w), 2935 (w), 2155 (w), 1724

(s), 1458 (w), 1414 (w), 1393 (w), 1367 (m), 1252 (m), 1236 (m), 1146 (s), 966 (w), 930 (w), 841 (m), 753 (w) $cm^{-1}$. EI-MS (70 eV): *m/z* (%) = 134 (10), 116 (23), 88 (26), 57 (100), 41 (41).

**[$^{34}$S]-*tert*-Butyl 3-mercaptopropanoate (10):** To a solution of **9** (3.51 g, 18.6 mmol, 1.00 equiv.) and water (11.5 g, 639 mmol, 34.4 equiv.) in THF (425 mL) was added $SmI_2$ (17.0 g, 42.1 mmol, 2.26 equiv.) at room temperature. After stirring for 5 min, the reaction was quenched with a saturated aqueous $NH_4Cl$ solution (1 L), the mixture extracted with diethyl ether (3 x 500 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1) to give **10** (2.66 g, 16.2 mmol, 87%) as a pale yellow oil. $^1$H-NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 2.76–2.71 (m, 2H, $CH_2$), 2.56 (t, $^3J$(H,H) = 6.8 Hz, 2H, $CH_2$), 1.60 (t, $^3J$(H,H) = 8.3 Hz, 1H, SH), 1.47 (s, 9H, 3 $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ = 170.9 ($C_q$), 80.9 ($C_q$), 39.6 ($CH_2$), 28.1 (3 $CH_3$), 20.0 ($CH_2$) ppm. IR (ATR) $\tilde{\nu}$ = 2978 (w), 2933 (w), 1727 (s), 1479 (w), 1458 (w), 1392 (w), 1366 (m), 1249 (m), 1150 (s), 945 (w), 846 (w), 754 (w) $cm^{-1}$. EI-MS (70 eV): *m/z* (%) = 178 (30), 122 (87), 105 (52), 77 (67), 57 (100), 49 (36), 41 (83).

**[$^{34}$S]-*tert*-Butyl 3-(methylthio)propanoate (11):** To a solution of KOH (2.13 g, 38.0 mmol, 2.5 equiv.) in methanol (20 mL) was added a solution of **10** (2.49 g, 15.2 mmol, 1.0 equiv.) in methanol (15 mL) at 0 °C. MeI (2.59 g, 18.2 mmol, 1.2 equiv.) was added over 15 min and stirring was continued at room temperature overnight. The reaction was quenched with water (100 mL), and the mixture was extracted with diethyl ether (3 x 100 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1) to give **11** (1.71 g, 9.61 mmol, 63%) as a pale yellow oil. $^1$H-NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 2.73 (t, $^3J$(H,H) = 7.4 Hz, 2H, $CH_2$), 2.53 (t, $^3J$(H,H) = 7.3 Hz, 2H, $CH_2$), 2.12 (s, 3H, $CH_3$), 1.46 (s, 9H, 3 $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ = 171.3 ($C_q$), 80.8 ($C_q$), 35.7 ($CH_2$), 29.3 ($CH_2$), 28.1 (3 $CH_3$), 15.5 ($CH_3$) ppm. IR (ATR) $\tilde{\nu}$ = 2977 (w), 2921 (w), 1726 (s), 1512 (w), 1457 (w), 1429 (w), 1392 (w), 1366 (m), 1250 (m), 1139 (s), 988 (w), 935 (w), 844 (m), 755 (w), 677 (w), 580 (w) $cm^{-1}$.

**[$^{34}$S]Dimethylsulfoniopropionate hydrochloride (1):** To a solution of **11** (1.53 g, 8.60 mmol, 1.0 equiv.) in nitromethane (20 mL) was added trimethyloxonium tetrafluoroborate (1.41 g, 9.53 mmol, 1.1 equiv.) at 0 °C. After stirring at room temperature overnight, to the reaction was added trifluoroacetic acid (20 mL), stirring was continued for 2 h. The mixture was concentrated in vacuo and the residue was purified by ion-exchange column chromatography (Dowex® 50WX8, elution with 2 M HCl) to give **1** (0.753 g, 4.35 mmol, 51%) as a yellow solid. $^1$H-NMR (400 MHz, $D_2O$, DSS): $\delta$ = 3.55 (t, $^3J$(H,H) = 6.8 Hz, 2H, $CH_2$), 3.02 (t, $^3J$(H,H) = 6.9 Hz, 2H, $CH_2$), 2.95 (s, 6H, 2 $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $D_2O$): $\delta$ = 176.5 ($C_q$), 41.6 ($CH_2$), 31.4 ($CH_2$), 28.0 (2 $CH_3$) ppm.

***S*-Isopropyl methanethiosulfonate (26) and *S*-propyl methanethiosulfonate (28) with byproducts diisopropyl disulfide (19) and dipropyl disulfide (18):**[3] To a solution of 1-propanethiol (**53**) or 2-propanethiol (**51**) (0.76 g, 10.0 mmol, 1 equiv.) in dry pyridine (5 mL) was added dropwise methanesulfonyl chloride (**51**, 1.15 g, 10.0 mmol, 1 equiv.). The solution was stirred overnight, diluted with $Et_2O$ (100 mL), and acidified with 2 N HCl (50 mL). The mixture was extracted three times with diethyl ether (3 x 200 mL) and the combined extracts were concentrated in vacuo. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (5:1) to give the pure thiosulfonates and, as byproducts, the pure dialkyl disulfides as colourless oils.

**26:** Yield: 0.71 g (4.6 mmol, 46%). TLC (hexane/ethyl acetate = 5:1): $R_f$ = 0.24. GC (HP5-MS): *I* = 1166. $^1$H-NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 3.72 (sept, $^3J$(H,H) = 6.9 Hz, 1H, CH), 3.34 (s, 3H, $CH_3$), 1.49 (d, $^3J$(H,H) = 6.9 Hz, 6H, 2 $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$):

$\delta$ = 23.8 (2 $CH_3$), 43.2 (CH), 51.4 ($CH_3$) ppm. IR (ATR) $\tilde{\nu}$ = 2970 (w), 2930 (w), 2870 (w), 1464 (w), 1370 (w), 1310 (s), 1128 (s), 1055 (m), 953 (m), 743 (s), 623 (w), 551 (s) $cm^{-1}$. EI-MS (70 eV): *m/z* (%) = 154 (33), 139 (5), 112 (48), 96 (10), 74 (100), 59 (21), 43 (49).

**28:** Yield: 0.57 g (3.7 mmol, 37%). TLC (hexane/ethyl acetate = 5:1): $R_F$ = 0.14. GC (HP5-MS): *I* = 1223. $^1$H-NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 3.33 (s, 3H, $CH_3$), 3.16 (t, $^3J$(H,H) = 7.3Hz, 2H, $CH_2$), 1.81 (sext, $^3J$(H,H) = 7.3 Hz, 2H, $CH_2$), 1.05 (t, $^3J$(H,H) = 7.3 Hz, 3H, $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ = 13.1 ($CH_3$), 23.0 ($CH_2$), 38.3 ($CH_2$), 50.6 ($CH_3$) ppm. IR (ATR) $\tilde{\nu}$ = 2967 (w), 2931 (w), 2876 (w), 1459 (w), 1410 (w), 1310 (s), 1128 (s), 953 (m), 897 (w), 743 (s), 549 (s) $cm^{-1}$. EI-MS (70 eV): *m/z* (%) = 154 (48), 125 (18), 113 (19), 74 (100), 63 (17), 41 (40).

**19:** Yield: 0.29 g (1.9 mmol, 19%). TLC (hexane/ethyl acetate = 5:1): $R_f$ = 0.83. GC (HP5-MS): *I* = 1020. $^1$H-NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 2.97 (sept, $^3J$(H,H) = 6.7 Hz, 2H, 2 CH), 1.30 (d, $^3J$(H,H) = 6.7 Hz, 12H, 4 $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ = 22.3 (4 $CH_3$), 41.1 (2 CH) ppm. IR (ATR) $\tilde{\nu}$ = 2960 (s), 2923 (m), 2863 (m), 1447 (s), 1379 (m), 1363 (m), 1312 (w), 1231 (s), 1153 (s), 1108 (w), 1045 (s), 926 (w), 875 (w), 623 (w) $cm^{-1}$. EI-MS (70 eV): *m/z* (%) = 150 (100), 108 (95), 93 (3), 66 (16), 43 (88).

**18:** Yield: 0.12 g (0.8 mmol, 8%). TLC (hexane/ethyl acetate = 5:1): $R_F$ = 0.84. GC (HP5-MS): *I* = 1108. $^1$H-NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 2.67 (t, $^3J$(H,H) = 7.3 Hz, 4H, 2 $CH_2$), 1.71 (sext, $^3J$(H,H) = 7.3 Hz, 4H, 2 $CH_2$), 1.00 (t, $^3J$(H,H) = 7.3 Hz, 6H, 2 $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ = 13.1 (2 $CH_3$), 22.5 (2 $CH_2$), 41.2 (2 $CH_2$) ppm. IR (ATR) $\tilde{\nu}$ = 2961 (s), 2930 (m), 2872 (m), 1456 (s), 1412 (w), 1377 (m), 1335 (w), 1289 (m), 1228 (s), 1088 (w), 1050 (w), 895 (w), 829 (w), 782 (m), 732 (m), 704 (w), 629 (w) $cm^{-1}$. EI-MS (70 eV): *m/z* (%) = 150 (90), 108 (58), 76 (14), 66 (13), 43 (100).

***S*-Methyl propanethiosulfonate (29):** A mixture of propanesulfonyl chloride (2.14 g, 15 mmol) and sodium methanethiolate (1.05 g, 15 mmol) in dry diethyl ether (10 mL) was stirred for 4 h. The reaction was quenched by the addition of water (100 mL) and the aqueous layer was extracted three times with diethyl ether (3 x 100 mL). The combined extracts were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1), yielding mainly propanesulfonic acid, but a small sample of the target compound **29** (20 mg, 0,13 mmol, 1%) could also be isolated. TLC (hexane/ethyl acetate = 3:1): $R_f$ = 0.32. GC (HP5-MS): *I* = 1234. $^1$H-NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 3.28–3.32 (m, 2H, $CH_2$), 2.66 (s, $^1J$(C,H) = 143.5 Hz, 3H, $CH_3$), 1.91–2.06 (m, 2H, $CH_2$), 1.10 (t, $^3J$(H,H) = 7.4 Hz, 3H, $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ = 12.7 ($CH_3$), 17.3 ($CH_2$), 18.2 ($CH_3$), 62.9 ($CH_2$) ppm. EI-MS (70 eV): *m/z* (%) = 154 (25), 112 (12), 90 (35), 75 (30), 64 (20), 61 (14), 48 (93), 43 (100).

**Methylpropylsulfoniopropionate hydrochloride (46):** A mixture of methyl propyl sulfide (**12**, 2.25 g, 24.9 mmol, 1 equiv.) and acrylic acid (1.80 g, 25.0 mmol, 1 equiv.) in aqueous hydrochloric acid (2 N, 18.8 mL) was heated to 80 °C for 14 h. The mixture was washed with diethyl ether (100 mL) and concentrated in vacuo to give **46** (4.01 g, 20.2 mmol, 81%) as a white solid. Mp. 106°C. $^1$H-NMR (400 MHz, $D_2O$, DSS): $\delta$ = 3.60 (dt, $^2J$(H,H) = 13.6 Hz, $^3J$(H,H) = 7.0 Hz, 1H, $CH_2$), 3.49 (dt, $^2J$(H,H) = 13.6 Hz, $^3J$(H,H) = 6.6 Hz, 1H, $CH_2$), 3.38 (ddd, $^2J$(H,H) = 12.9 Hz, $^3J$(H,H) = 8.6 Hz, $^3J$(H,H) = 6.9 Hz, 1H, $CH_2$), 3.29 (ddd, $^2J$(H,H) = 12.9 Hz, $^3J$(H,H) = 8.6 Hz, $^3J$(H,H) = 6.5 Hz, 1H, $CH_2$), 3.02 (t, $^3J$(H,H) = 6.8 Hz, 2H, $CH_2$), 2.92 (s, 3H, $CH_3$), 1.95–1.78 (m, 2H, $CH_2$), 1.08 (t, $^3J$(H,H) = 7.4 Hz, 3H, $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $D_2O$): 176.6 ($C_q$), 46.6 ($CH_2$), 39.7 ($CH_2$), 31.4 ($CH_2$), 25.4 ($CH_3$), 20.1 ($CH_2$), 14.8 ($CH_3$) ppm. IR (ATR) $\tilde{\nu}$ = 3372 (br), 2973 (m), 2924 (m), 2819 (m), 2700 (m), 2490 (w), 1718 (s), 1461 (w), 1404 (s), 1232 (m), 1187 (s), 1095 (w), 1054 (w), 1012 (w), 925 (w), 891 (m),

810 (m), 746 (w), 635 (w), 565 (w) $cm^{-1}$. HR-MS (ESI): calculated for $C_7H_{15}O_2S^+$: $m/z$ = 163.07872, found: $m/z$ = 163.07886.

**Isopropylmethylsulfoniopropionate hydrochloride (47):** A mixture of isopropyl methyl sulfide (**13**, 2.25 g, 24.9 mmol, 1 equiv.) and acrylic acid (1.80 g, 25.0 mmol, 1 equiv.) in aqueous hydrochloric acid (2 N, 18.8 mL) was heated to 80 °C for 10 h. The mixture was washed with diethyl ether (100 mL) and concentrated in vacuo to give **47** (4.39 g, 22.1 mmol, 88%) as a colorless oil. $^1$H-NMR (400 MHz, $D_2O$, DSS): $\delta$ = 3.79 (quint, $^3J$(H,H) = 6.8 Hz, 1H, CH), 3.59 (dt, $^2J$(H,H) = 13.7 Hz, $^3J$(H,H) = 7.1 Hz, 1H, $CH_2$), 3.41 (dt, $^2J$(H,H) = 13.7 Hz, $^3J$(H,H) = 6.5 Hz, 1H, $CH_2$), 3.03 (dt, $^2J$(H,H) = 18.2 Hz, $^3J$(H,H) = 6.6 Hz, 1H, $CH_2$), 3.01 (ddd, $^2J$(H,H) = 18.2 Hz, $^3J$(H,H) = 7.4 Hz, $^3J$(H,H) = 6.7 Hz, 1H, $CH_2$), 2.87 (s, 3H, $CH_3$), 1.53 (d, $^3J$(H,H) = 6.9 Hz, 3H, $CH_3$), 1.51 (d, $^3J$(H,H) = 6.8 Hz, 3H, $CH_3$) ppm. $^{13}$C-NMR (100 MHz, $D_2O$): 176.5 ($C_q$), 49.2 (CH), 37.1 ($CH_2$), 31.6 ($CH_2$), 21.9 ($CH_3$), 19.7 ($CH_3$), 19.0 ($CH_3$) ppm. IR (ATR) $\tilde{\nu}$ = 3413 (br), 2998 (w), 2938 (w), 2484 (br), 1710 (s), 1465 (w), 1395 (m), 1258 (m), 1209 (m), 1071 (w), 978 (w), 942 (w) $cm^{-1}$. HR-MS (ESI): calculated for $C_7H_{15}O_2S^+$: $m/z$ = 163.07872, found: $m/z$ = 163.07897.

**Tetramethylenesulfoniopropionate hydrochloride (48):** A mixture of tetrahydrothiophene (**14**, 2.65 g, 30.0 mmol, 1 equiv.) and acrylic acid (2.16 g, 30.0 mmol, 1 equiv.) in aqueous hydrochloric acid (2 N, 22.5 mL) was heated to 80 °C for 2 h. The mixture was washed with diethyl ether (100 mL) and concentrated in vacuo. The residue was recrystallized from a diethyl ether/methanol mixture (1:1) to give **48** (3.20 g, 16.2 mmol, 54%) as a white solid. Mp. 150°C. $^1$H-NMR (400 MHz, $D_2O$, DSS): $\delta$ = 3.66–3.60 (m, 2H, 2 $CH_2$), 3.53–3.47 (m, 2H, 2 $CH_2$), 3.44 (t, $^3J$(H,H) = 6.8 Hz, 2H, $CH_2$), 3.00 (t, $^3J$(H,H) = 6.8 Hz, 2H, $CH_2$), 2.42–2.24 (m, 4H, 2 $CH_2$) ppm. $^{13}$C-NMR (100 MHz, $D_2O$): 176.8 ($C_q$), 47.2 (2 $CH_2$), 40.8 ($CH_2$), 32.6 ($CH_2$), 31.1 (2 $CH_2$) ppm. IR (ATR) $\tilde{\nu}$ = 3400 (br), 2951 (w), 2482 (br), 1709 (s), 1392 (m), 1258 (m), 1203 (m), 1037 (w), 951 (w), 878 (w), 776 (w) $cm^{-1}$. HR-MS (ESI): calculated for $C_7H_{13}O_2S^+$: $m/z$ = 161.06307, found: $m/z$ = 161.06308.

# References


1 NIST database, http://webbook.nist.gov/chemistry/

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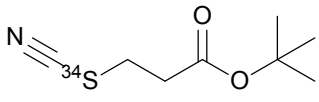
5 O. Higuchi, K. Tateshita, H. Nishimura, *J. Agric. Food Chem.*, 2003, **51**, 7208.

6 J. S. Dickschat, S. C. Wenzel, H. B. Bode, R. Müller and S. Schulz, *ChemBioChem*, 2004, **5**, 778.

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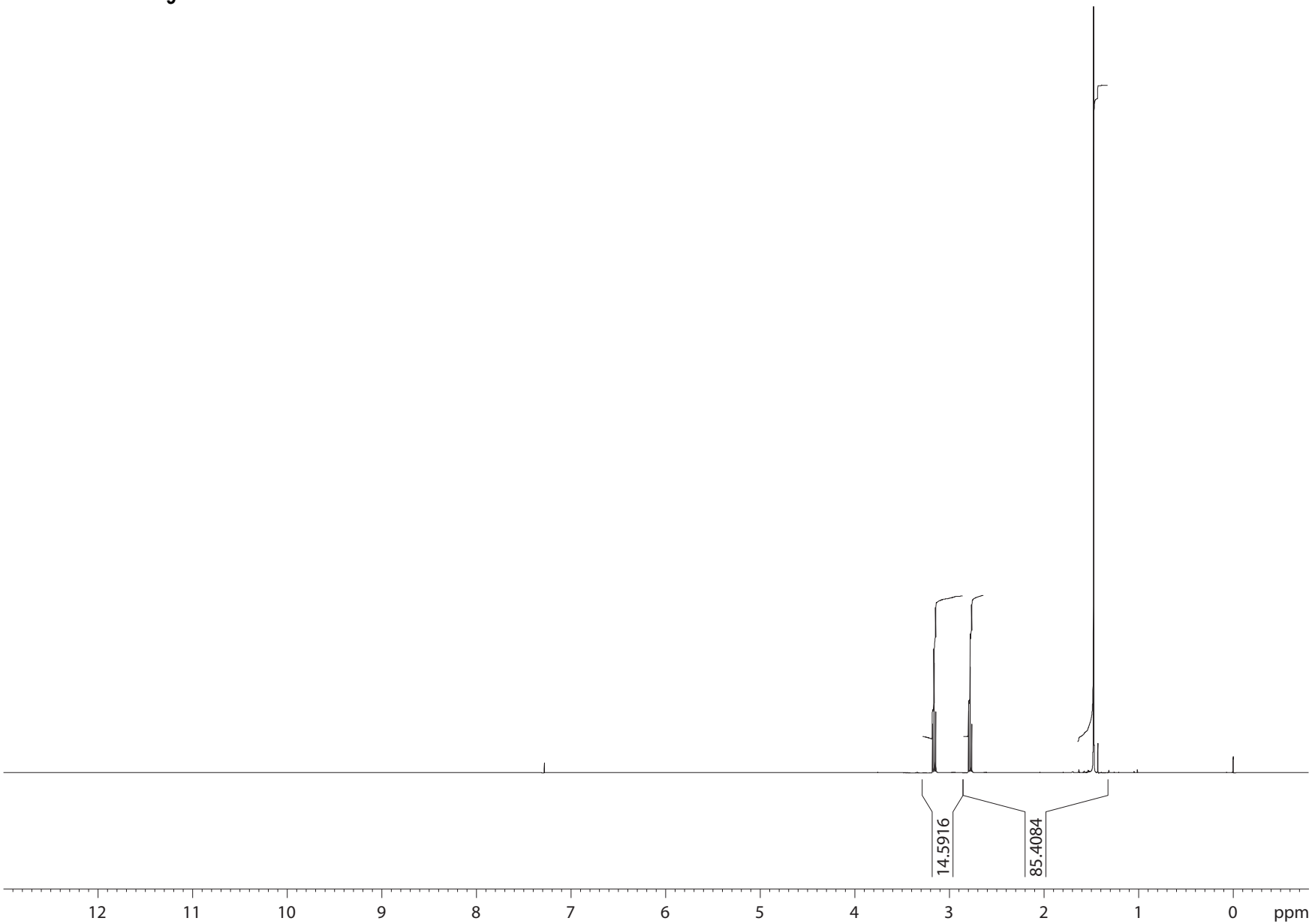


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DS                    2
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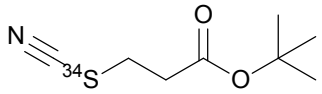


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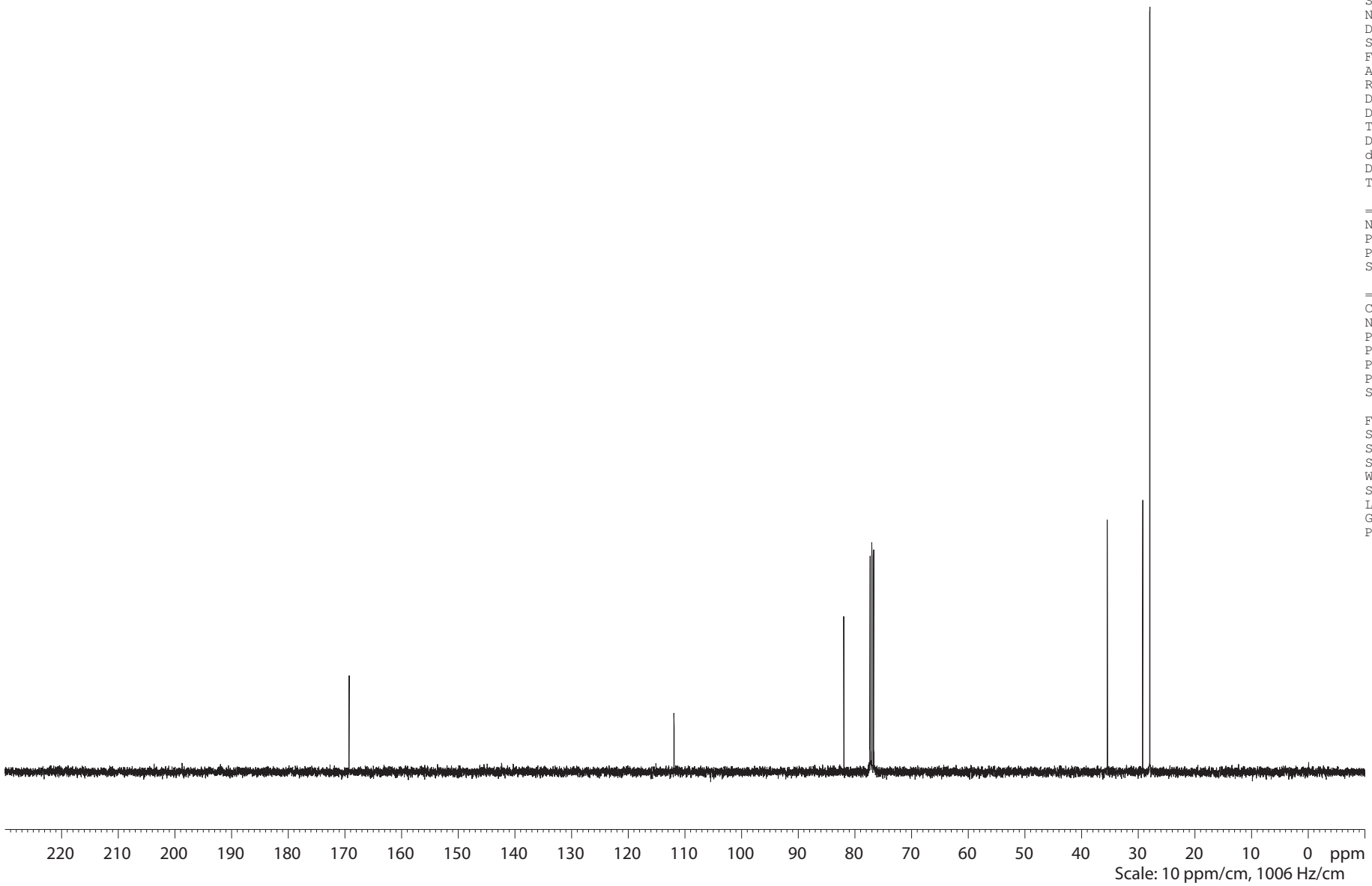


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PL1                -3.00 dB
SFO1         100.5635842 MHz

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NUC2                   1H
PCPD2              80.00 use
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PL12               16.06 dB
PL13               16.06 dB
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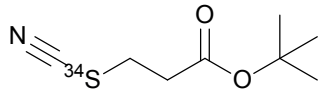


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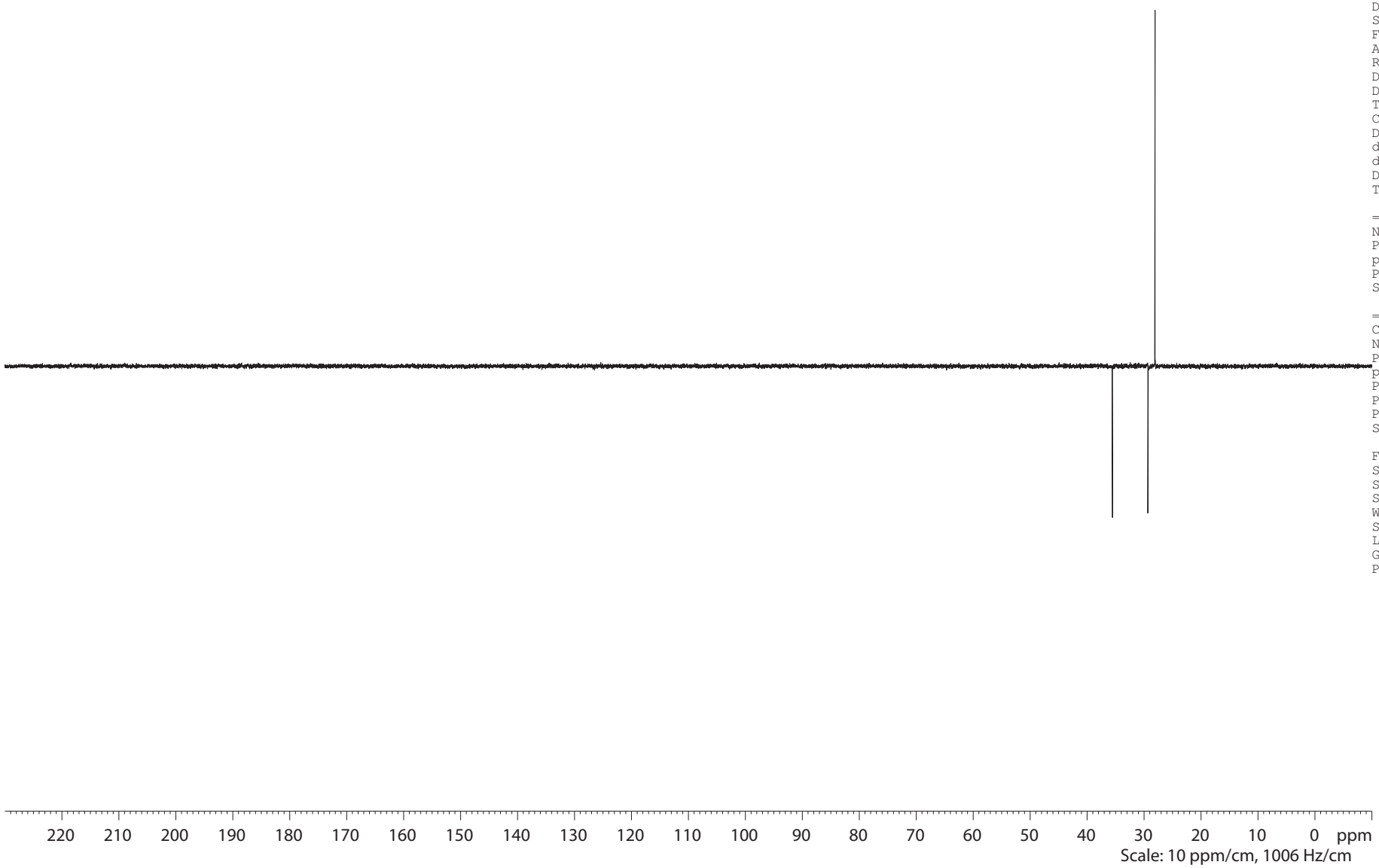


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PL1                -3.00 dB
SFO1         100.5635842 MHz

======== CHANNEL f2 =======
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NUC2                  1H
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PCPD2              80.00 use
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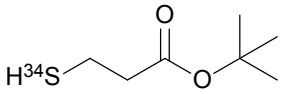


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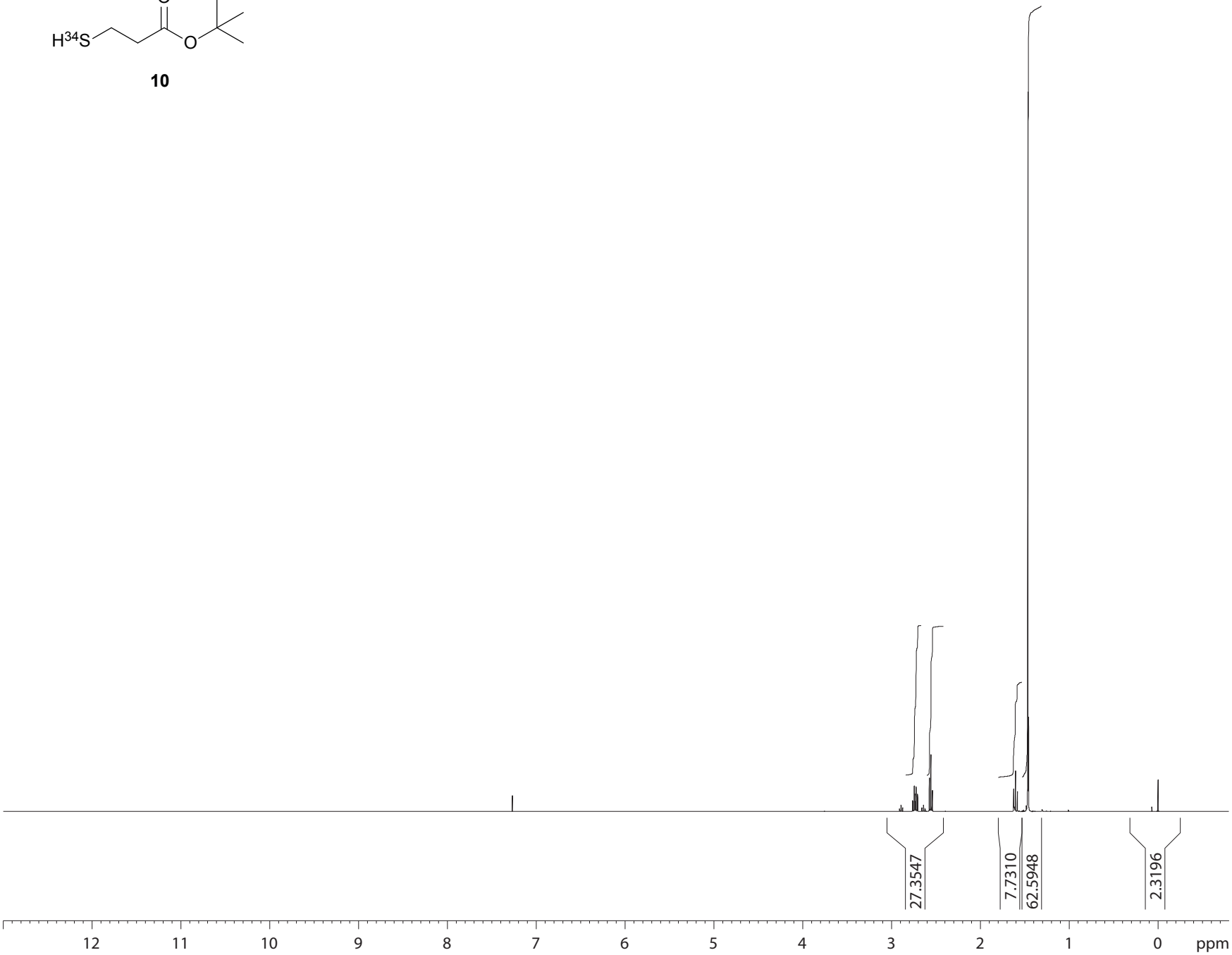


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SOLVENT           CDCl3
NS                   64
DS                    2
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FIDRES         0.126314 Hz
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TE               299.2 K
D1            1.00000000 sec
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PL1               -2.00 dB
SFO1        399.8924689 MHz

F2 - Processing parameters
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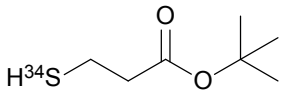


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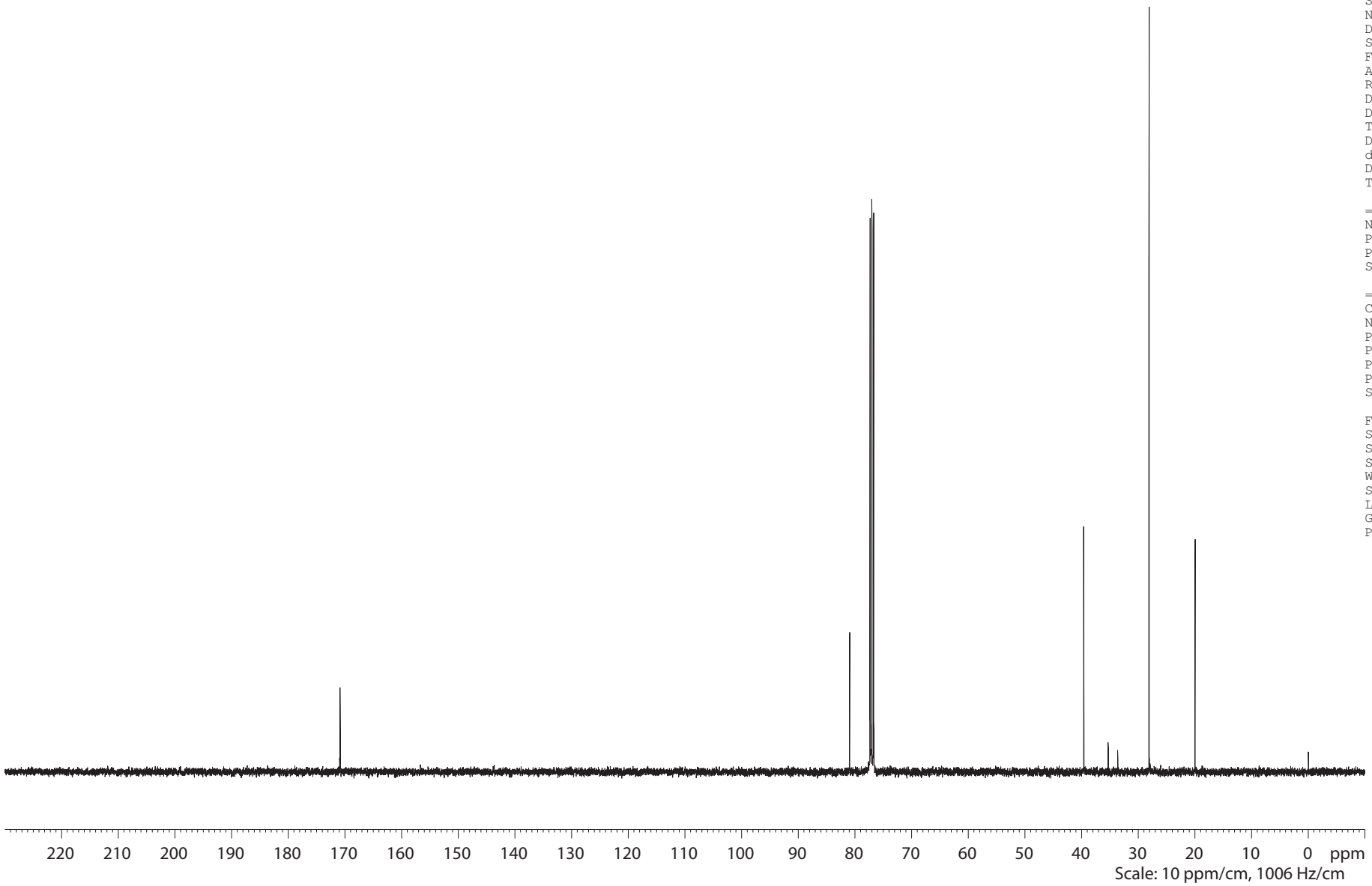


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RG              10321.3
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DE                 6.00 use
TE                299.2 K
D1           2.00000000 sec
d11          0.03000000 sec
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TD0                   1

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PL1                -3.00 dB
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======== CHANNEL f2 =======
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NUC2                 1H
PCPD2              80.00 use
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PL12               16.06 dB
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SFO2        399.8915996 MHz

F2 - Processing parameters
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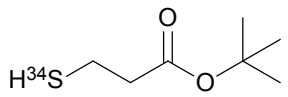


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TD0                    1

======== CHANNEL f1 =======
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PL1                -3.00 dB
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======== CHANNEL f2 =======
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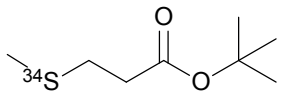


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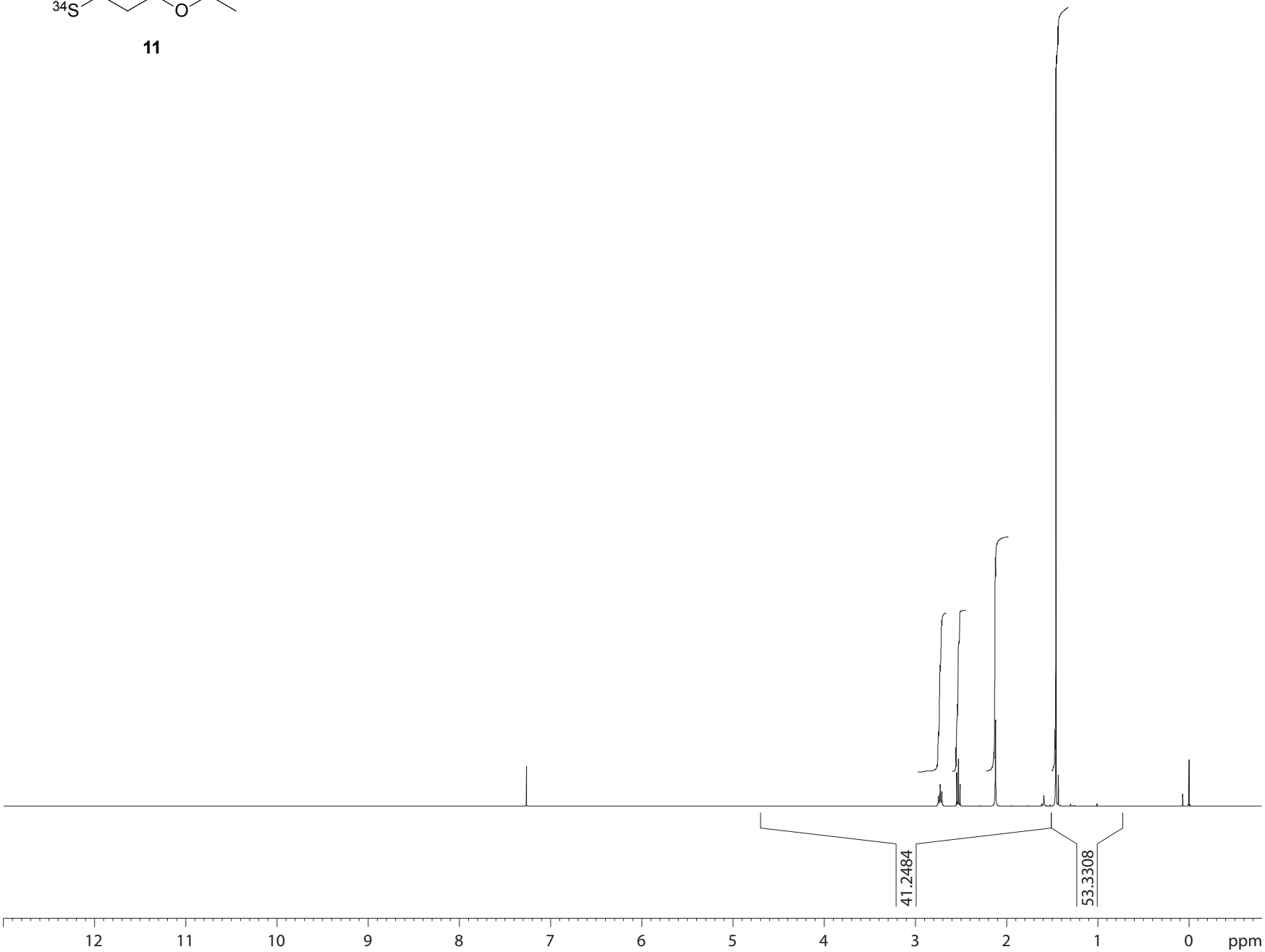


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| FIDRES | 0.125483 Hz |
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| F2P | -0.800 ppm |

**11**

| | |
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| SOLVENT | CDC13 |
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| FIDRES | 0.200774 Hz |
| AQ | 2.4904180 sec |
| RG | 80.6 |
| DW | 19.000 use |
| DE | 6.50 use |
| TE | 298.3 K |
| D1 | 2.00000000 sec |
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| TD0 | 1 |
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| PL1 | -3.00 dB |
| SFO1 | 100.6918371 MHz |
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| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| PCPD2 | 80.00 use |
| PL2 | -4.00 dB |
| PL12 | 13.78 dB |
| PL13 | 14.00 dB |
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| SF | 100.6806635 MHz |
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| WDW | EM |
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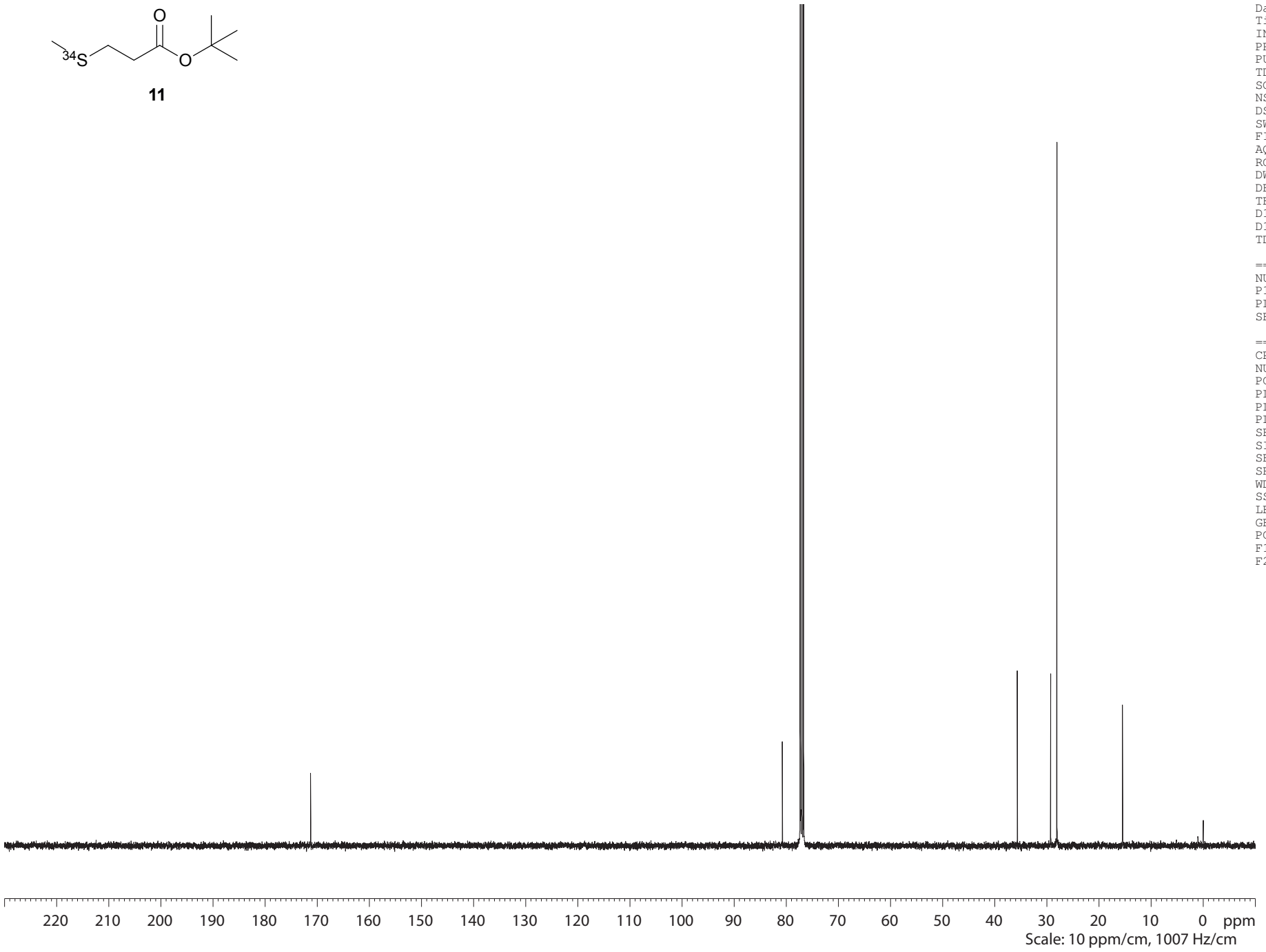

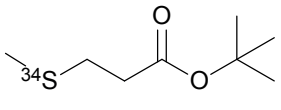


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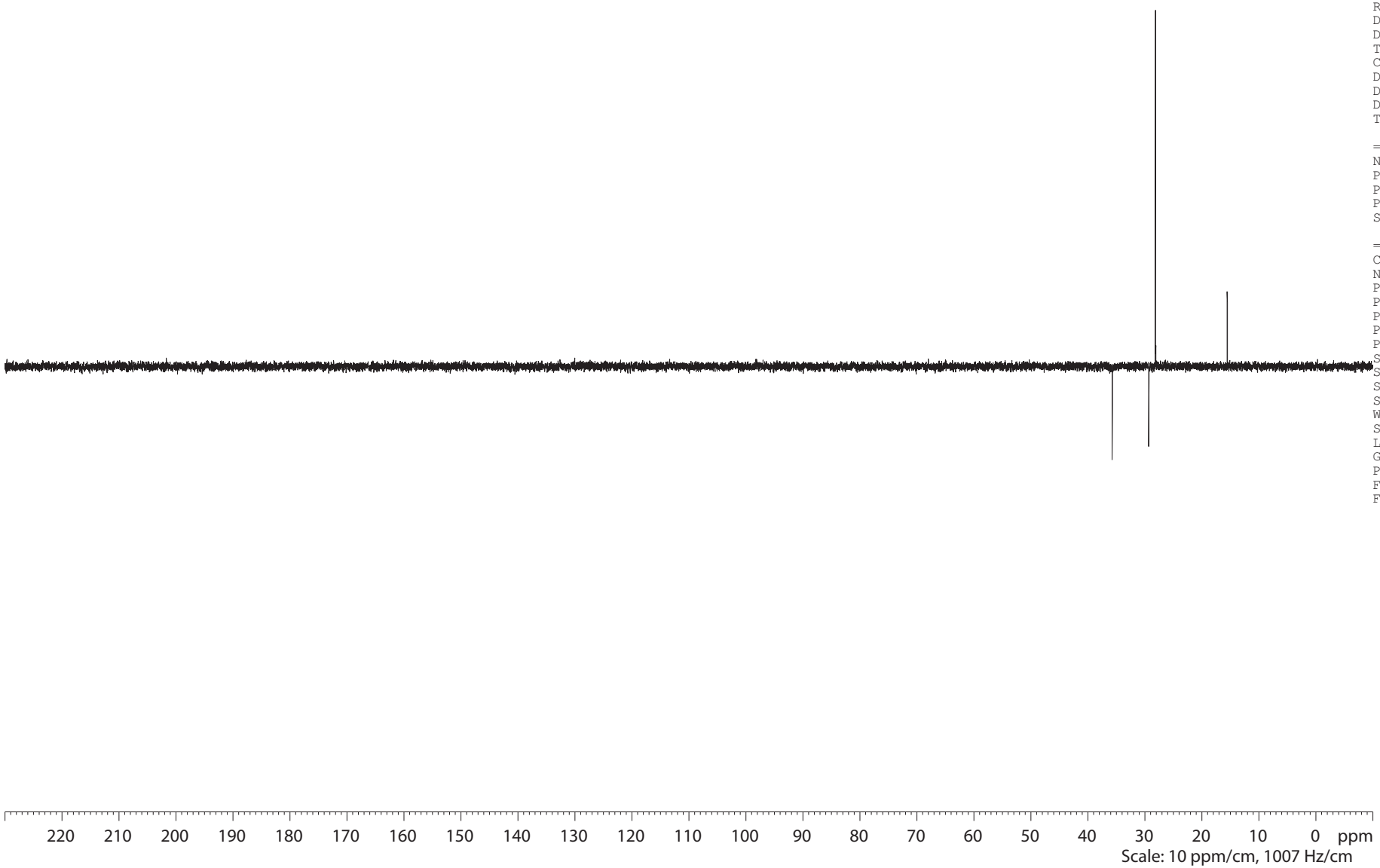


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| SOLVENT | CDCl3 |
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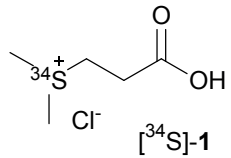
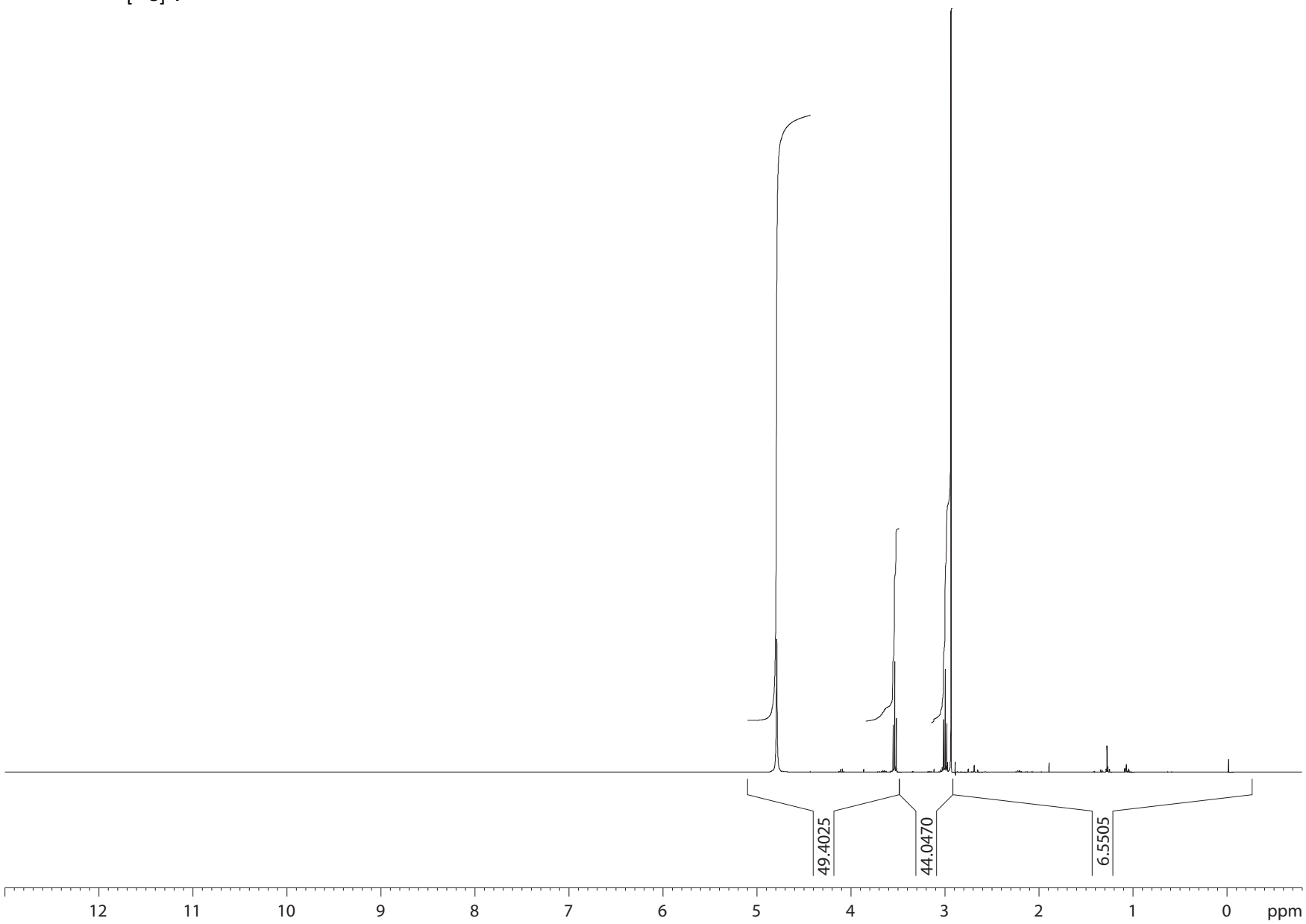
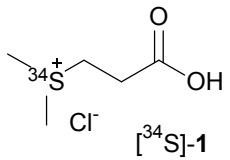
| DS | 4 |
| SWH | 26315.789 Hz |
| FIDRES | 0.200774 Hz |
| AQ | 2.4904180 sec |
| RG | 2050 |
| DW | 19.000 use |
| DE | 6.50 use |
| TE | 297.8 K |
| CNST2 | 145.0000000 |
| D1 | 2.00000000 sec |
| D2 | 0.00344828 sec |
| D12 | 0.00002000 sec |
| TD0 | 5 |
| ======== CHANNEL f1 ======= | |
| NUC1 | 13C |
| P1 | 8.50 use |
| P2 | 17.00 use |
| PL1 | -3.00 dB |
| SFO1 | 100.6918371 MHz |
| ======== CHANNEL f2 ======= | |
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| P3 | 10.33 use |
| P4 | 20.66 use |
| PCPD2 | 80.00 use |
| PL2 | -4.00 dB |
| PL12 | 13.78 dB |
| SFO2 | 400.4016016 MHz |
| SI | 65536 |
| SF | 100.6806578 MHz |
| SR | -3.20 Hz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |
| F1P | 230.000 ppm |
| F2P | -10.000 ppm |




[34S]-**1**

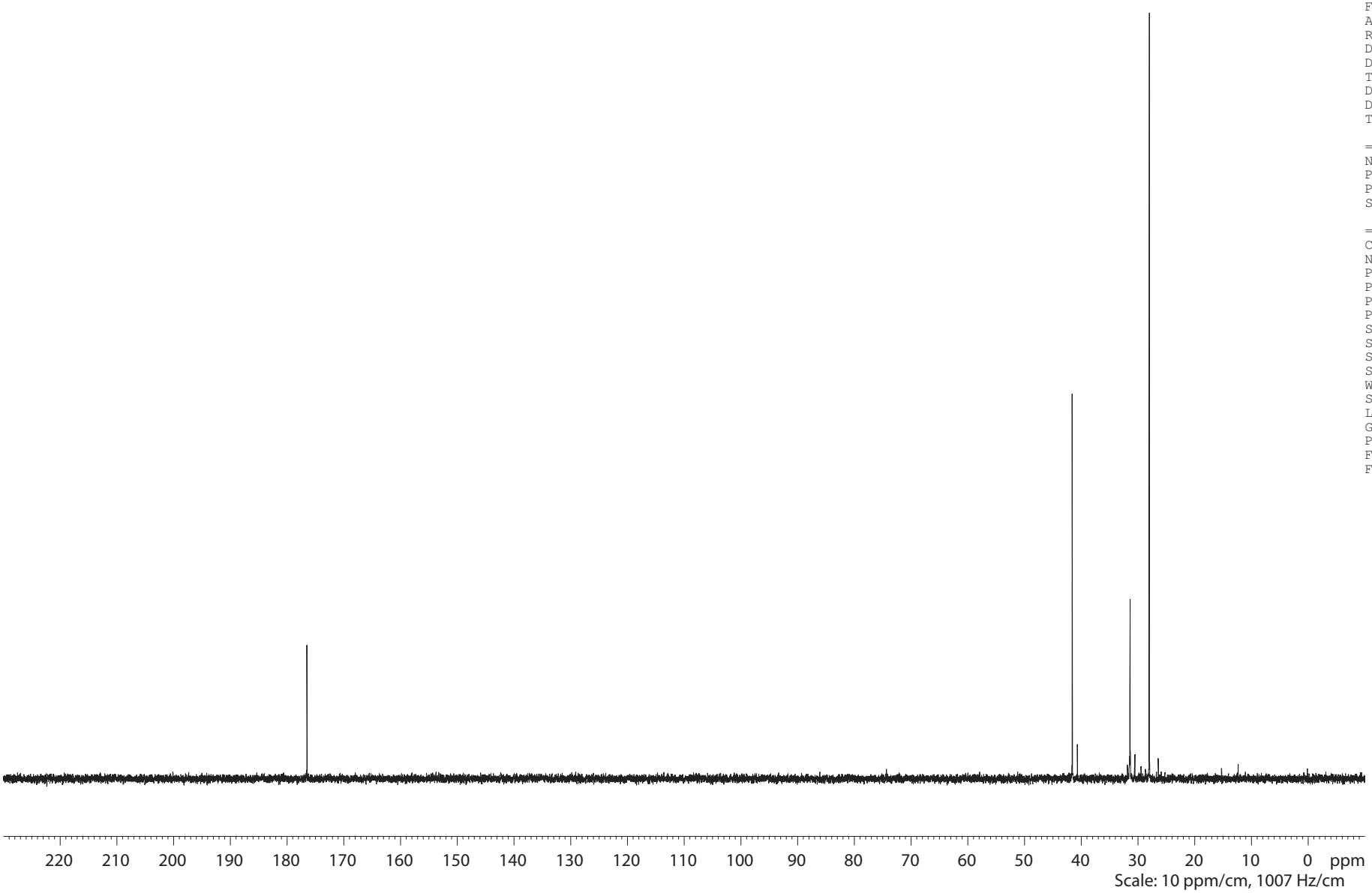


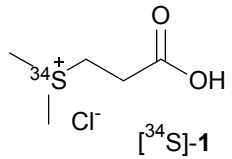

| | |
|---|---|
| NAME | brn122050_od |
| EXPNO | 1 |
| PROCNO | 1 |
| Date_ | 20130923 |
| Time | 22.04 |
| INSTRUM | AVIII400 |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | D2O |
| NS | 64 |
| DS | 2 |
| SWH | 8223.685 Hz |
| FIDRES | 0.125483 Hz |
| AQ | 3.9846387 sec |
| RG | 144 |
| DW | 60.800 use |
| DE | 6.50 use |
| TE | 296.6 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======= | |
| NUC1 | 1H |
| P1 | 10.33 use |
| PL1 | -4.00 dB |
| SFO1 | 400.4024726 MHz |
| SI | 32768 |
| SF | 400.4000025 MHz |
| SR | 2.46 Hz |
| WDW | EM |
| SSB | 0 |
| LB | 0.00 Hz |
| GB | 0 |
| PC | 1.40 |
| F1P | 13.000 ppm |
| F2P | -0.800 ppm |



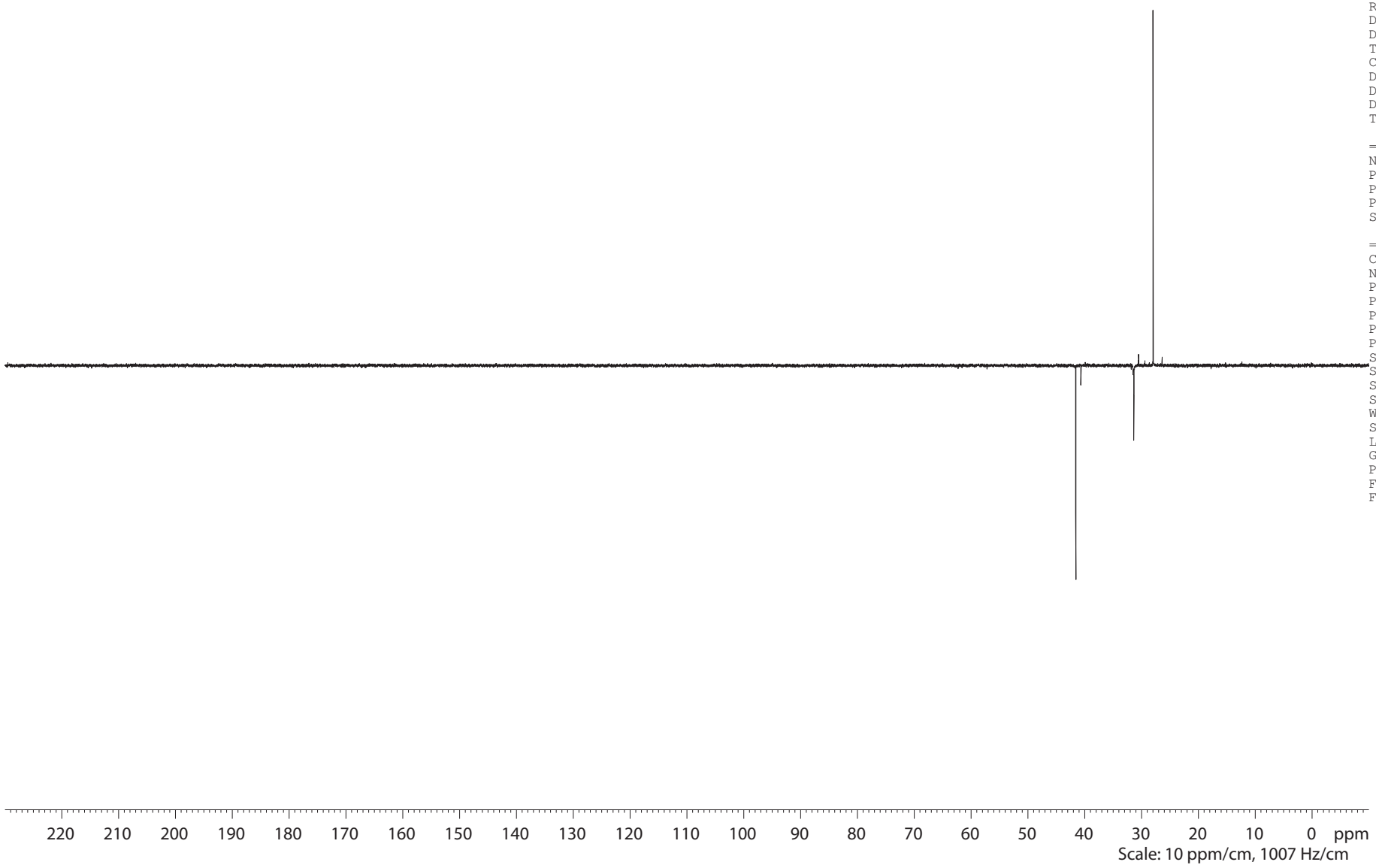

[34S]-**1**

```
NAME        brn122050_od
EXPNO                  2
PROCNO                 1
Date_           20130924
Time                0.42
INSTRUM         AVIII400
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                131072
SOLVENT              D2O
NS                  2048
DS                     4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ            2.4904180 sec
RG                   256
DW                19.000 use
DE                 6.50 use
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                 13C
P1                  8.50 use
PL1                -3.00 dB
SFO1        100.6918371 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 use
PL2                -4.00 dB
PL12               13.78 dB
PL13               14.00 dB
SFO2        400.4016016 MHz
SI                 65536
SF          100.6803827 MHz
SR              -278.29 Hz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
F1P              230.000 ppm
F2P              -10.000 ppm
```

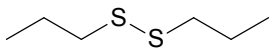




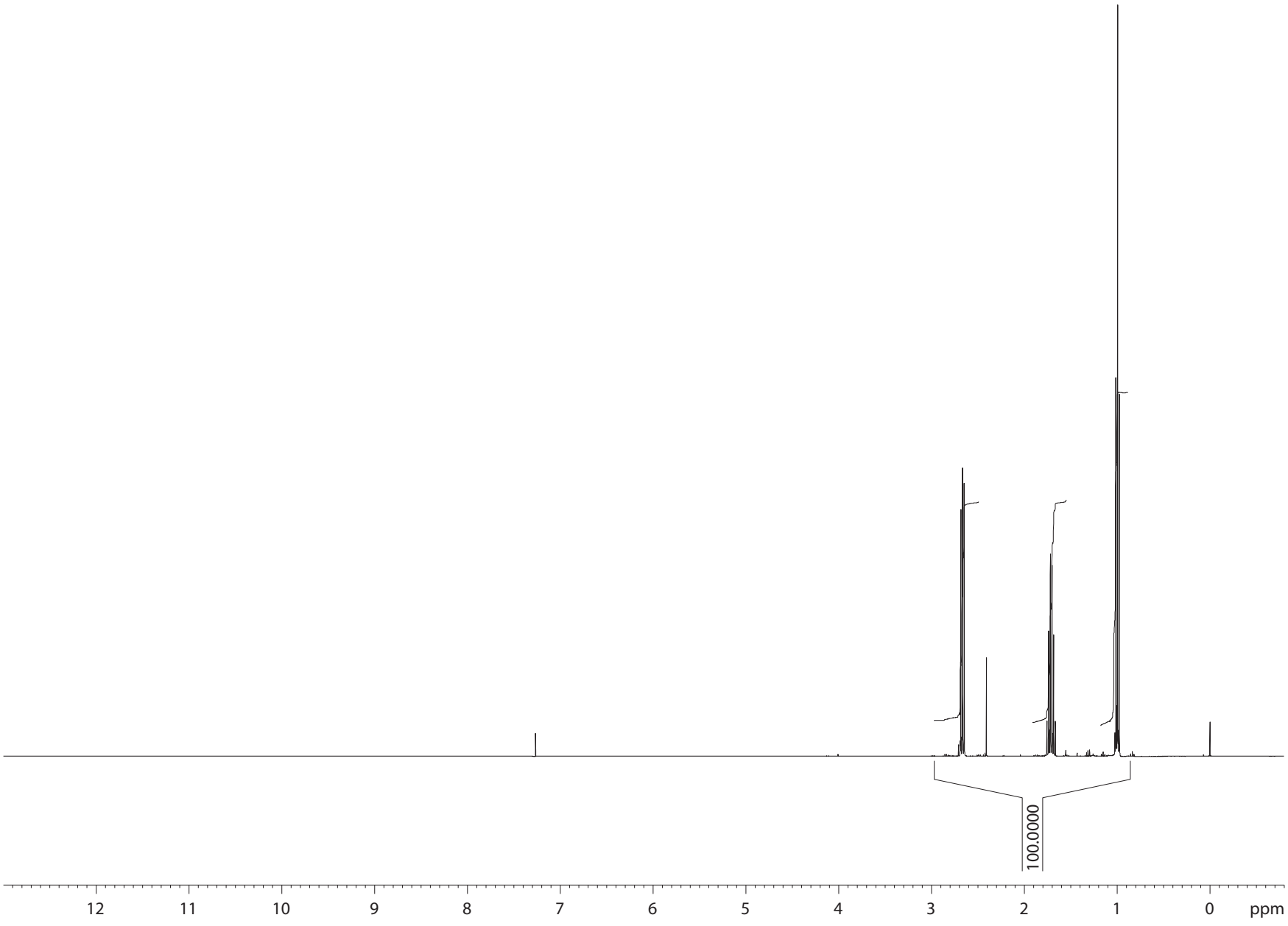

[$^{34}$S]-**1**



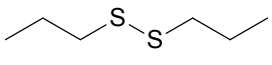

```
NAME        brn122050_od
EXPNO                  3
PROCNO                 1
Date_           20130924
Time                2.02
INSTRUM         AVIII400
PROBHD   5 mm PABBO BB-
PULPROG          dept135
TD                131072
SOLVENT              D2O
NS                  1024
DS                     4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ             2.4904180 sec
RG                  2050
DW                19.000 use
DE                 6.50 use
TE                297.3 K
CNST2        145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  13C
P1                   8.50 use
P2                  17.00 use
PL1                 -3.00 dB
SFO1         100.6919063 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
P3                  10.33 use
P4                  20.66 use
PCPD2               80.00 use
PL2                 -4.00 dB
PL12                13.78 dB
SFO2         400.4016016 MHz
SI                 65536
SF           100.6803827 MHz
SR               -278.29 Hz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
F1P              230.000 ppm
F2P              -10.000 ppm
```



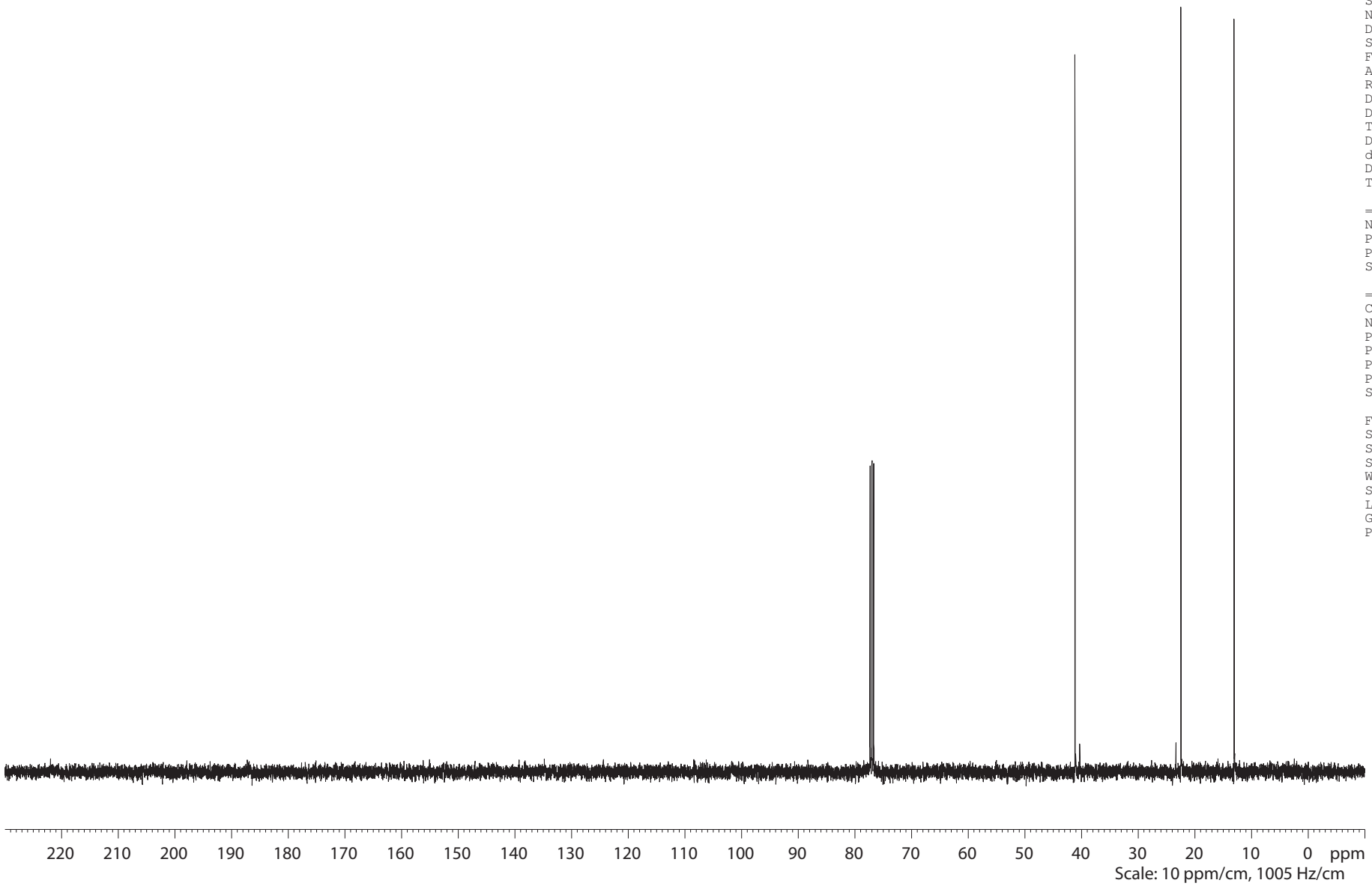
**18**



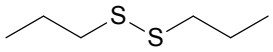

```
Current Data Parameters
NAME       rap123587_od
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              18.26
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                    32
DW               60.400 usec
DE                6.00 usec
TE                298.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.20 usec
PL1               -2.00 dB
SFO1        399.8324685 MHz

F2 - Processing parameters
SI                 32768
SF          399.8300133 MHz
SR                13.34 Hz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
```



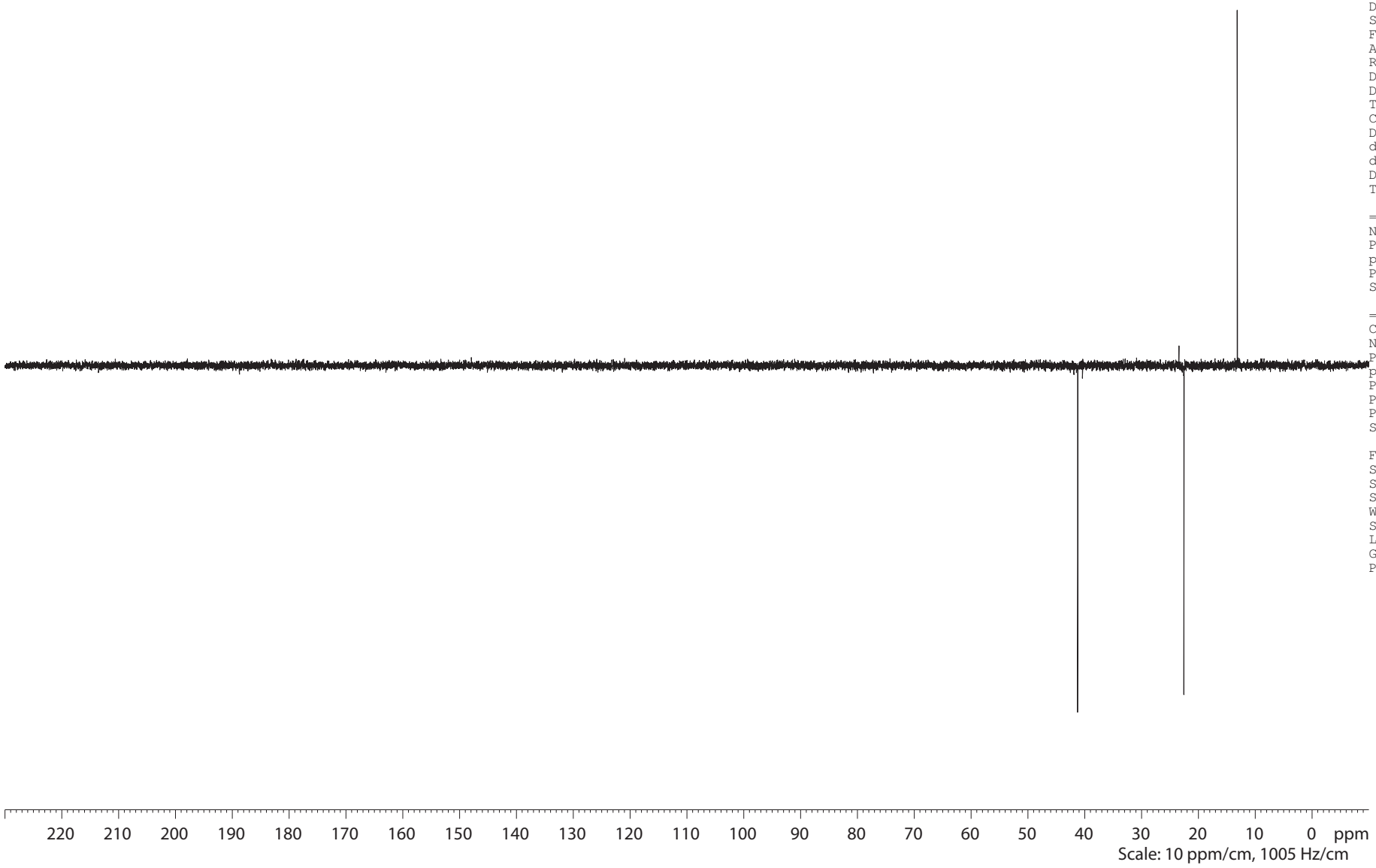
**18**



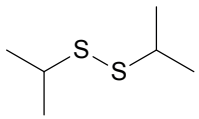

```
Current Data Parameters
NAME       rap123587_od
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              18.34
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD               131072
SOLVENT            CDCl3
NS                    96
DS                     4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ             2.4904180 sec
RG                9195.2
DW               19.000 use
DE                6.00 use
TE                298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 13C
P1                  9.70 use
PL1                 4.00 dB
SFO1        100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 use
PL2               -2.00 dB
PL12              16.06 dB
PL13              16.06 dB
SFO2        399.8315993 MHz

F2 - Processing parameters
SI                65536
SF          100.5373382 MHz
SR                 4.21 Hz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



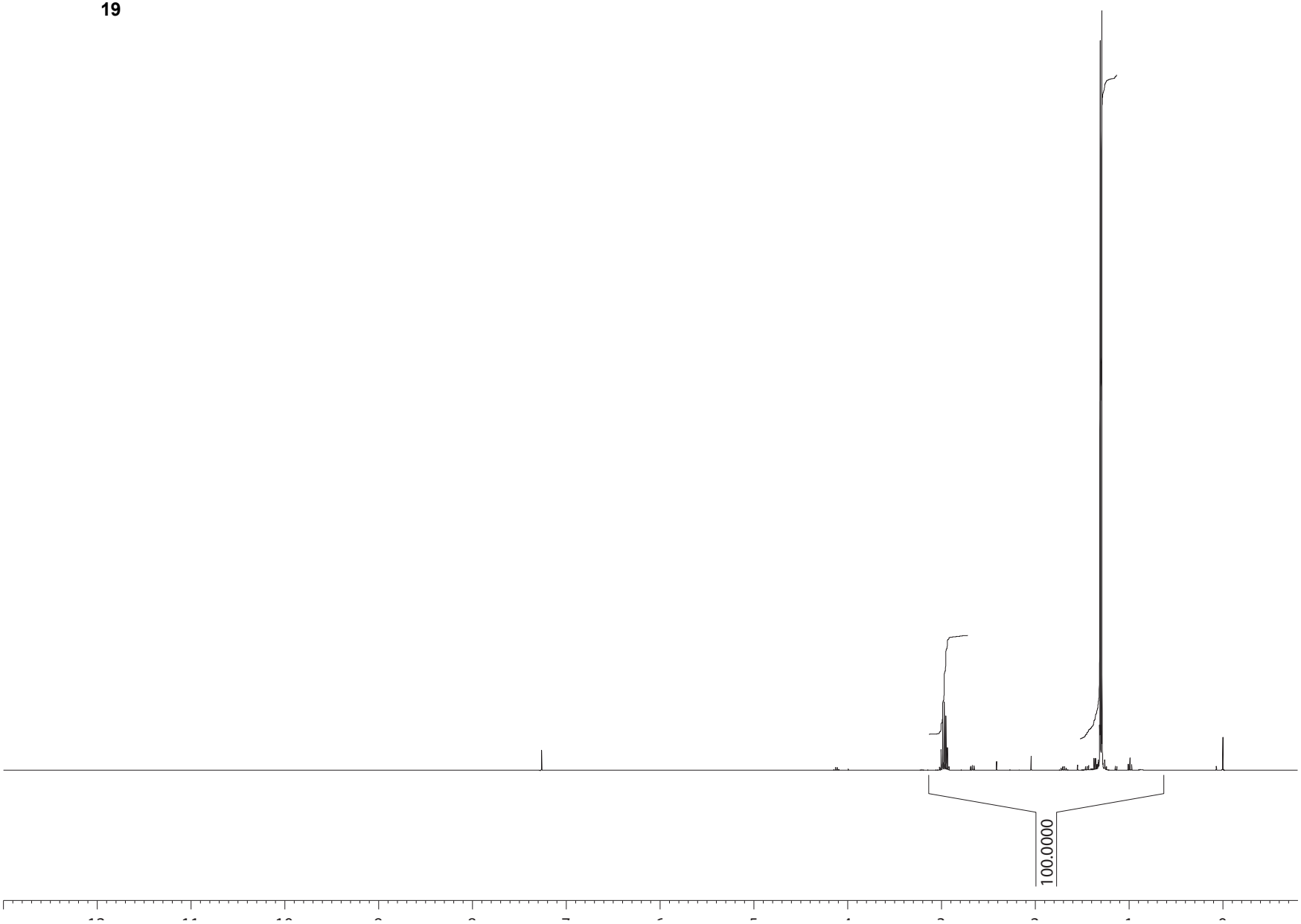
**18**



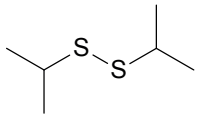

```
Current Data Parameters
NAME       rap123587_od
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              18.43
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG          dept135
TD                131072
SOLVENT             CDC13
NS                    96
DS                     4
SWH            26315.789 Hz
FIDRES          0.200774 Hz
AQ             2.4904180 sec
RG               10321.3
DW                19.000 use
DE                 7.00 use
TE                298.2 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
d12            0.00002000 sec
DELTA          0.00001235 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  13C
P1                   9.70 use
p2                  19.40 use
PL1                  4.00 dB
SFO1         100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
P3                  10.00 use
p4                  20.00 use
PCPD2               80.00 use
PL2                 -2.00 dB
PL12                16.06 dB
SFO2         399.8315993 MHz

F2 - Processing parameters
SI                 65536
SF           100.5373308 MHz
SR                 -3.20 Hz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



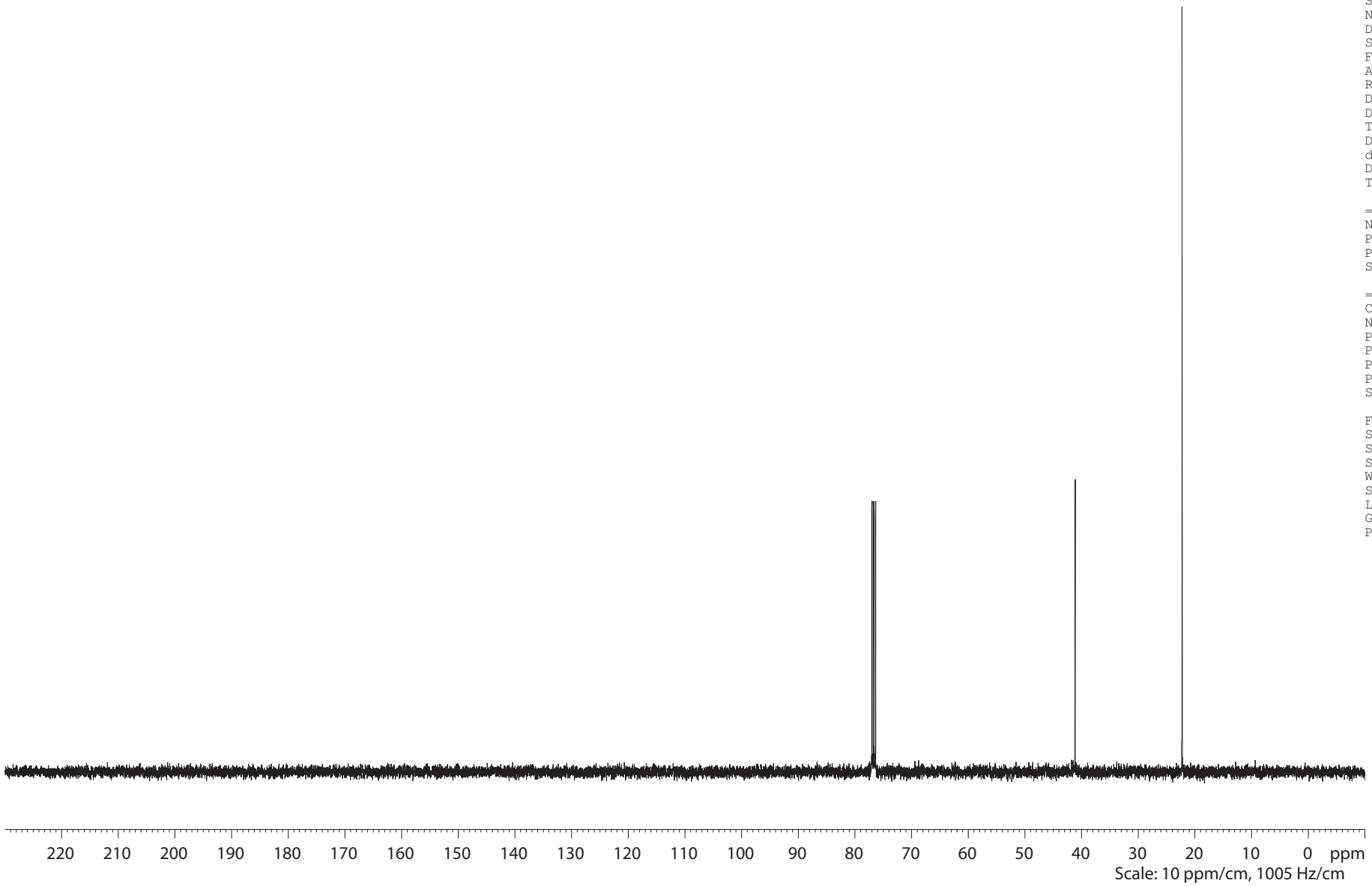
**19**



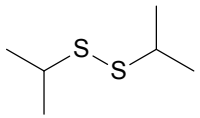

```
Current Data Parameters
NAME       rap123586_od
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              17.58
INSTRUM         drx400
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ             3.9584243 sec
RG                71.8
DW               60.400 use
DE                6.00 use
TE               298.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                  1H
P1                10.20 use
PL1               -2.00 dB
SFO1        399.8324685 MHz

F2 - Processing parameters
SI                32768
SF          399.8300145 MHz
SR                14.51 Hz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
```



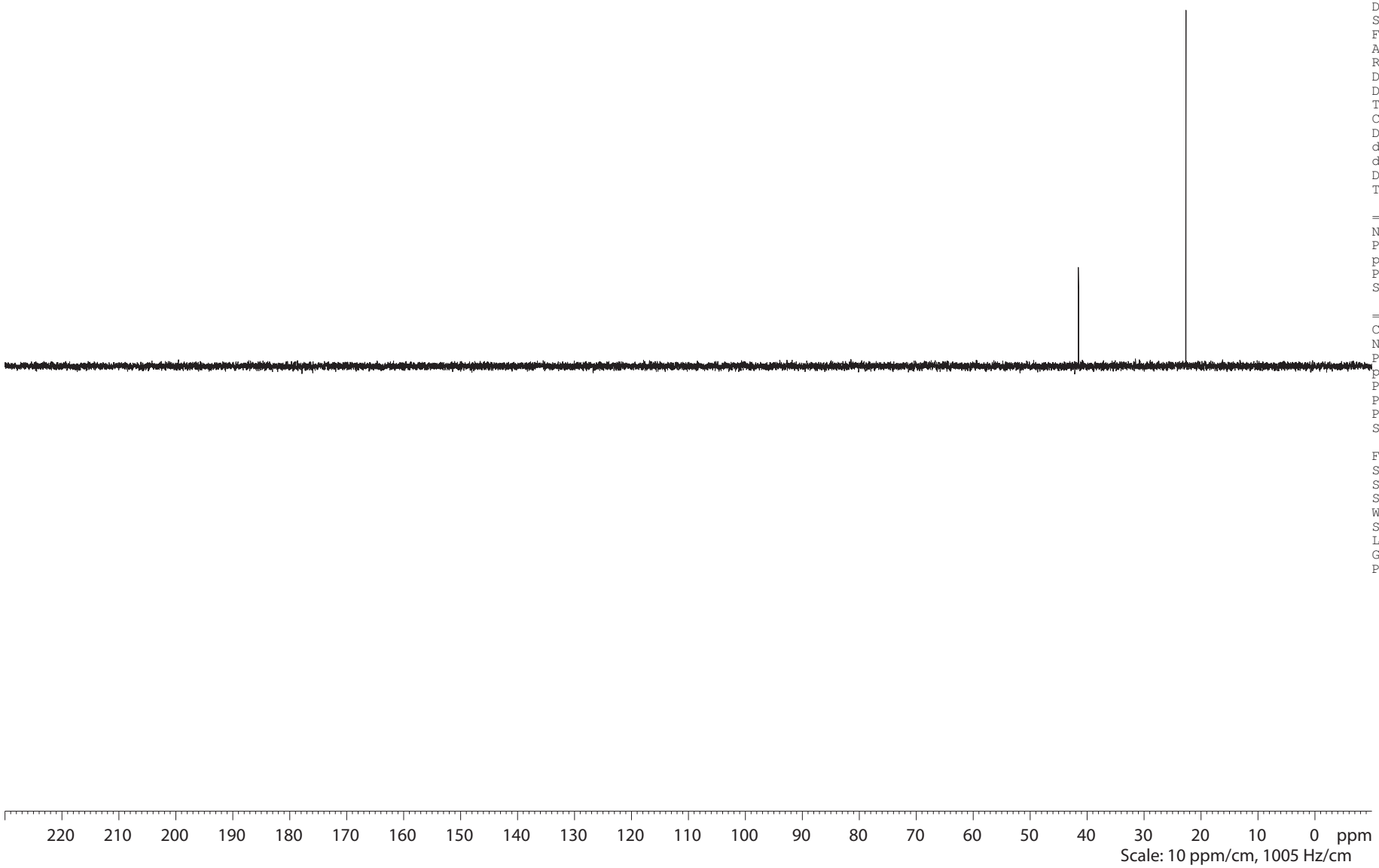
**19**



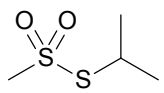

```
Current Data Parameters
NAME       rap123586_od
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              18.06
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD               131072
SOLVENT            CDCl3
NS                    96
DS                     4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ            2.4904180 sec
RG               7298.2
DW              19.000 use
DE                6.00 use
TE               298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 13C
P1                  9.70 use
PL1                 4.00 dB
SFO1        100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 use
PL2                -2.00 dB
PL12               16.06 dB
PL13               16.06 dB
SFO2        399.8315993 MHz

F2 - Processing parameters
SI                65536
SF          100.5373687 MHz
SR                34.69 Hz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



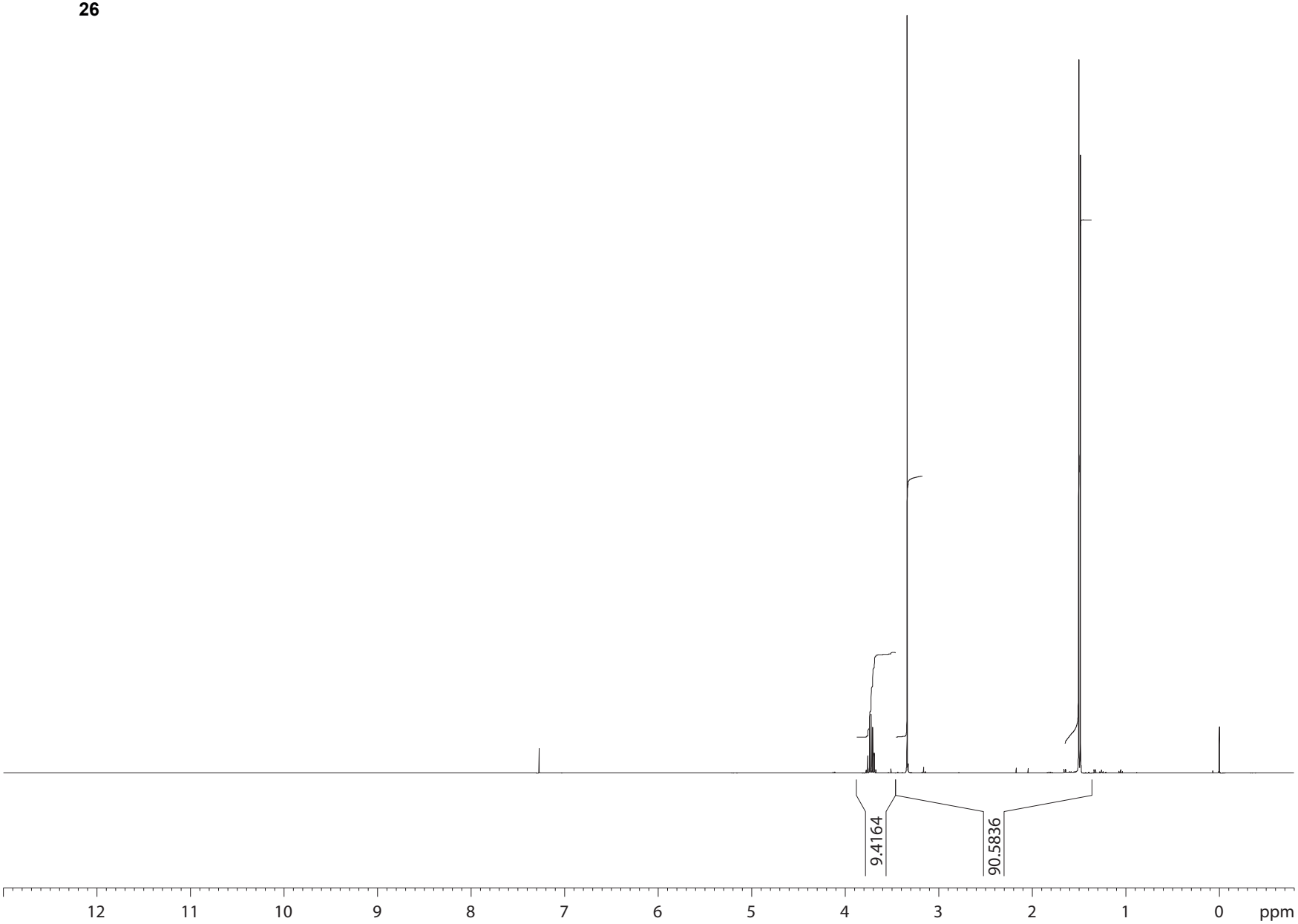
**19**



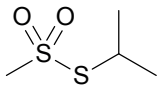

```
Current Data Parameters
NAME       rap123586_od
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              18.15
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG         dept135
TD               131072
SOLVENT             CDCl3
NS                   96
DS                    4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ            2.4904180 sec
RG               9195.2
DW               19.000 use
DE                7.00 use
TE               298.2 K
CNST2       145.0000000
D1           2.00000000 sec
d2           0.00344828 sec
d12          0.00002000 sec
DELTA        0.00001235 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 13C
P1                  9.70 use
p2                 19.40 use
PL1                4.00 dB
SFO1        100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
P3                 10.00 use
p4                 20.00 use
PCPD2              80.00 use
PL2                -2.00 dB
PL12               16.06 dB
SFO2        399.8315993 MHz

F2 - Processing parameters
SI                65536
SF          100.5373308 MHz
SR               -3.20 Hz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```



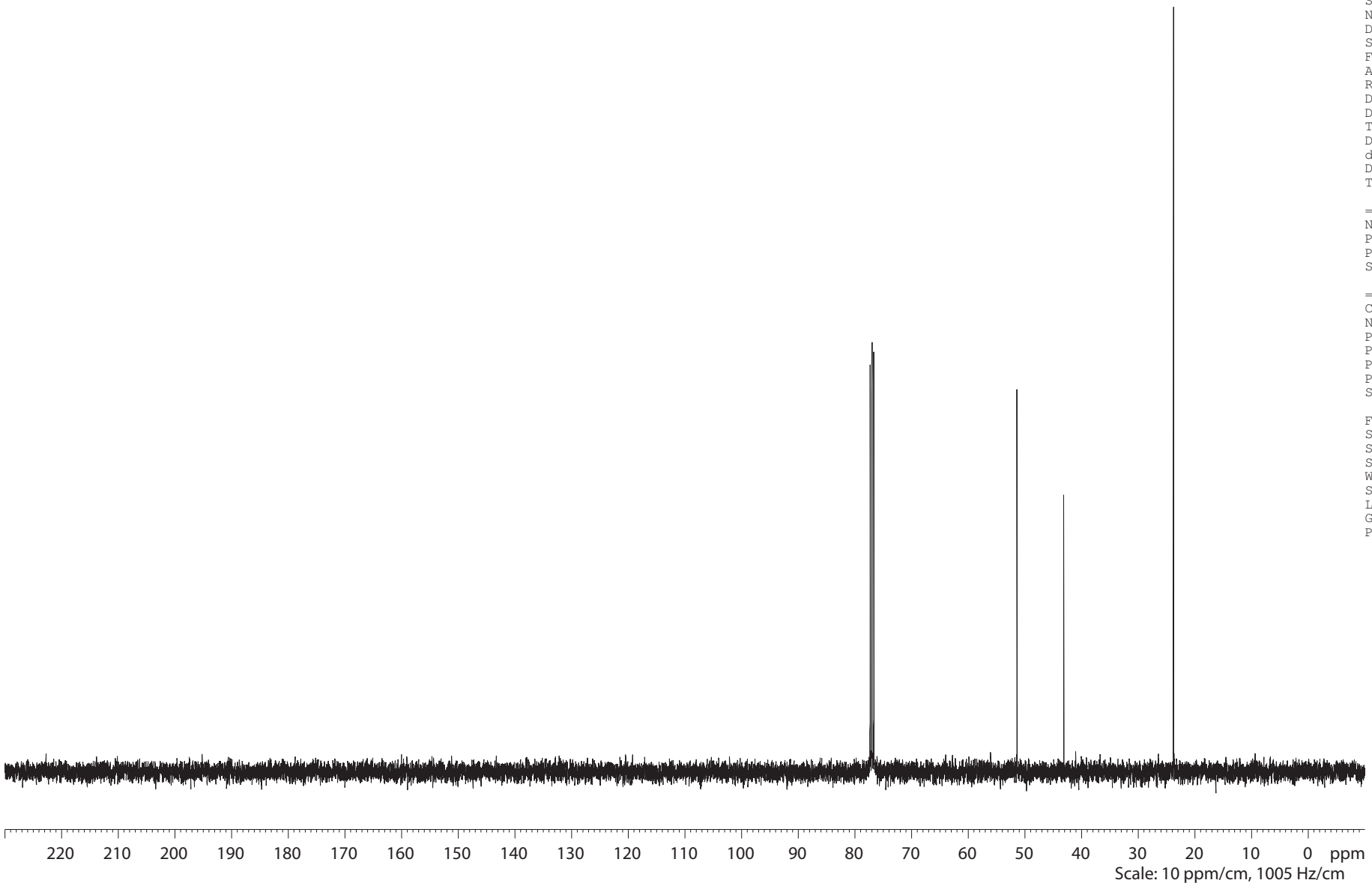
**26**



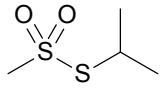

```
Current Data Parameters
NAME       rap123584_od
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              17.02
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  80.6
DW                60.400 use
DE                 6.00 use
TE                298.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  1H
P1                10.20 use
PL1               -2.00 dB
SFO1        399.8324685 MHz

F2 - Processing parameters
SI                 32768
SF          399.8300105 MHz
SR                10.51 Hz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
```



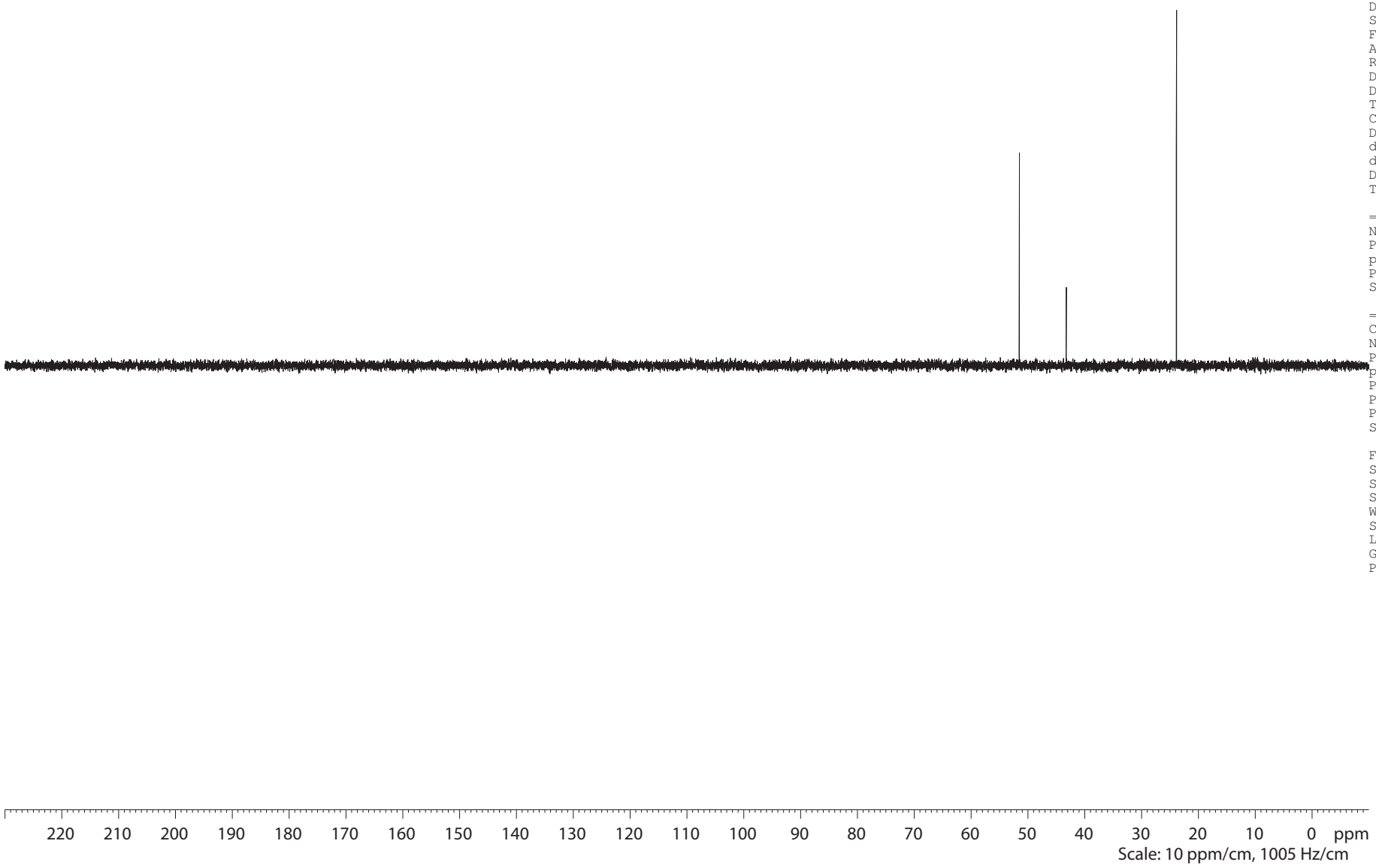
**26**



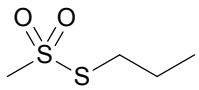

```
Current Data Parameters
NAME       rap123584_od
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              17.10
INSTRUM         drx400
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD              131072
SOLVENT            CDC13
NS                    96
DS                     4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ            2.4904180 sec
RG                  8192
DW                19.000 use
DE                 6.00 use
TE                298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 13C
P1                  9.70 use
PL1                 4.00 dB
SFO1        100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 use
PL2                -2.00 dB
PL12               16.06 dB
PL13               16.06 dB
SFO2        399.8315993 MHz

F2 - Processing parameters
SI                65536
SF          100.5373400 MHz
SR                 5.97 Hz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



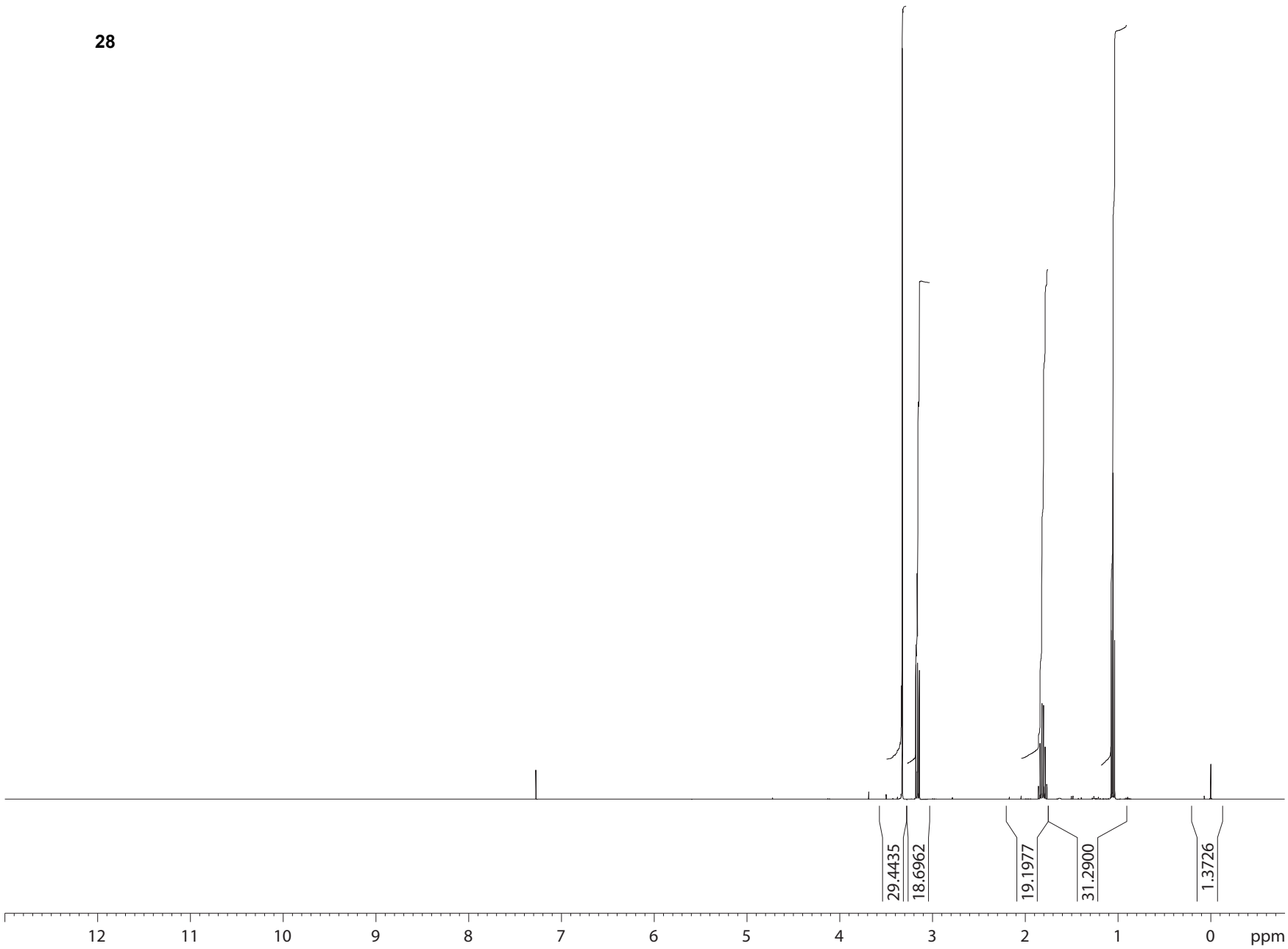
**26**



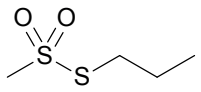

```
Current Data Parameters
NAME       rap123584_od
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              17.18
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG          dept135
TD               131072
SOLVENT             CDC13
NS                     96
DS                      4
SWH            26315.789 Hz
FIDRES          0.200774 Hz
AQ             2.4904180 sec
RG                9195.2
DW                19.000 use
DE                 7.00 use
TE                298.2 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
DELTA         0.00001235 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  13C
P1                   9.70 use
p2                  19.40 use
PL1                  4.00 dB
SFO1         100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
P3                  10.00 use
p4                  20.00 use
PCPD2               80.00 use
PL2                 -2.00 dB
PL12                16.06 dB
SFO2         399.8315993 MHz

F2 - Processing parameters
SI                 65536
SF           100.5373308 MHz
SR                 -3.20 Hz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



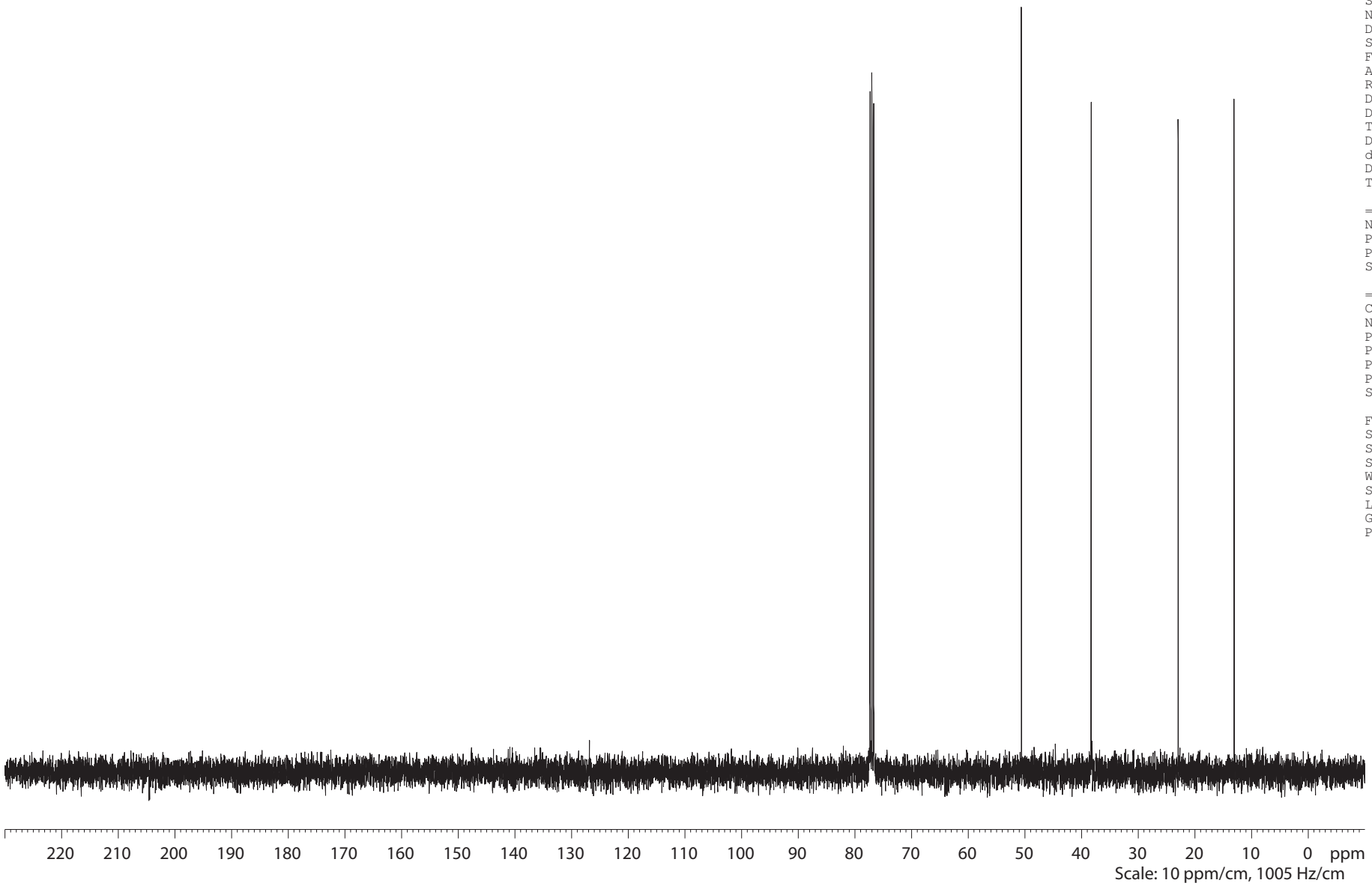
**28**



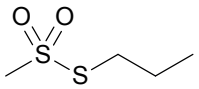

```
Current Data Parameters
NAME       rap123585_od
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time               17.30
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                 71.8
DW               60.400 use
DE                6.00 use
TE               298.2 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                  1H
P1                10.20 use
PL1               -2.00 dB
SFO1        399.8324685 MHz

F2 - Processing parameters
SI                32768
SF          399.8300099 MHz
SR                9.90 Hz
WDW                 EM
SSB                   0
LB                0.00 Hz
GB                    0
PC                 1.40
```



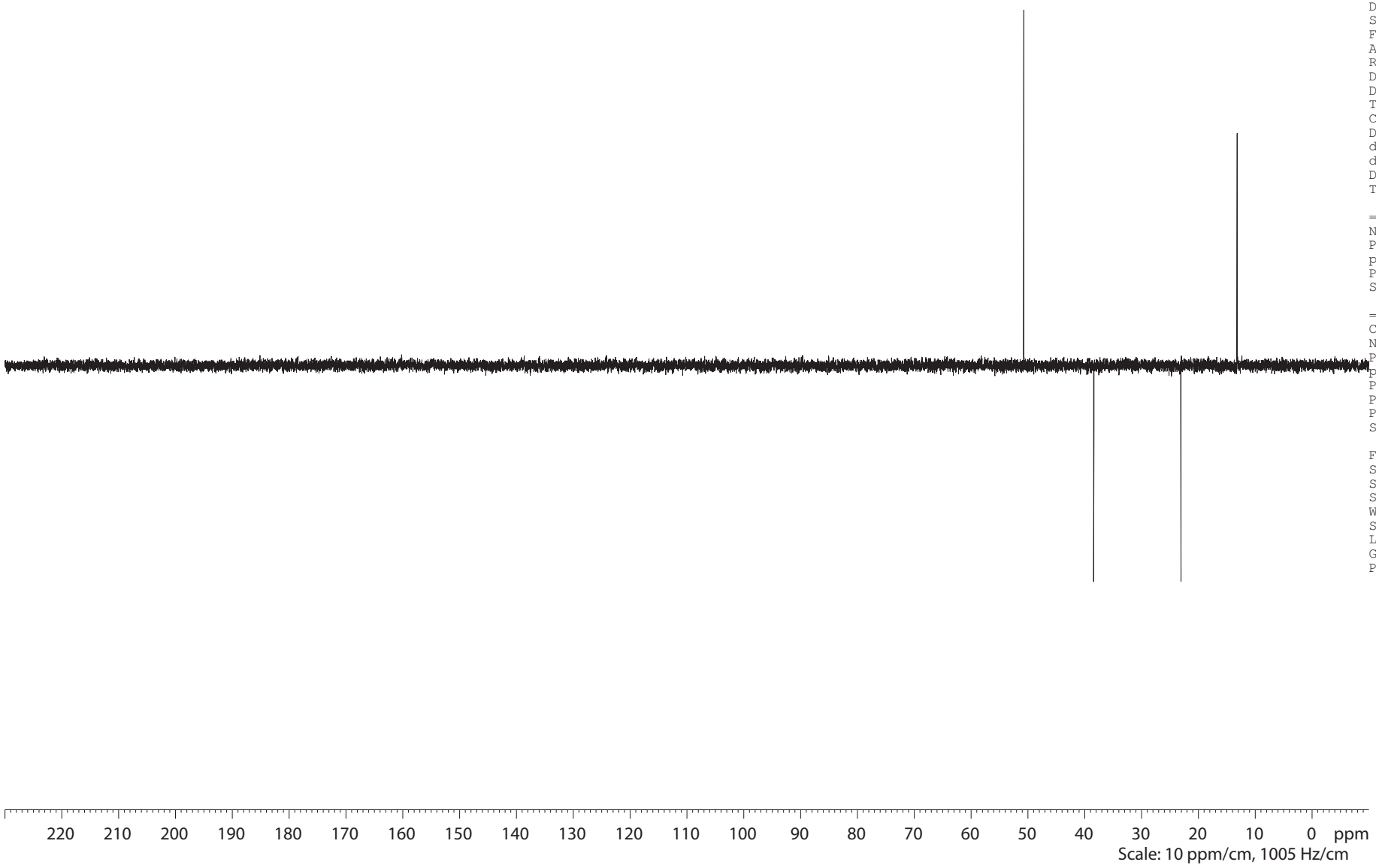
**28**



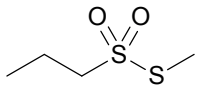

```
Current Data Parameters
NAME       rap123585_od
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              17.38
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD               131072
SOLVENT            CDCl3
NS                    96
DS                     4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ            2.4904180 sec
RG               9195.2
DW              19.000 use
DE               6.00 use
TE              298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 13C
P1                  9.70 use
PL1                 4.00 dB
SFO1        100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 use
PL2                -2.00 dB
PL12               16.06 dB
PL13               16.06 dB
SFO2        399.8315993 MHz

F2 - Processing parameters
SI                  65536
SF          100.5373408 MHz
SR                  6.83 Hz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



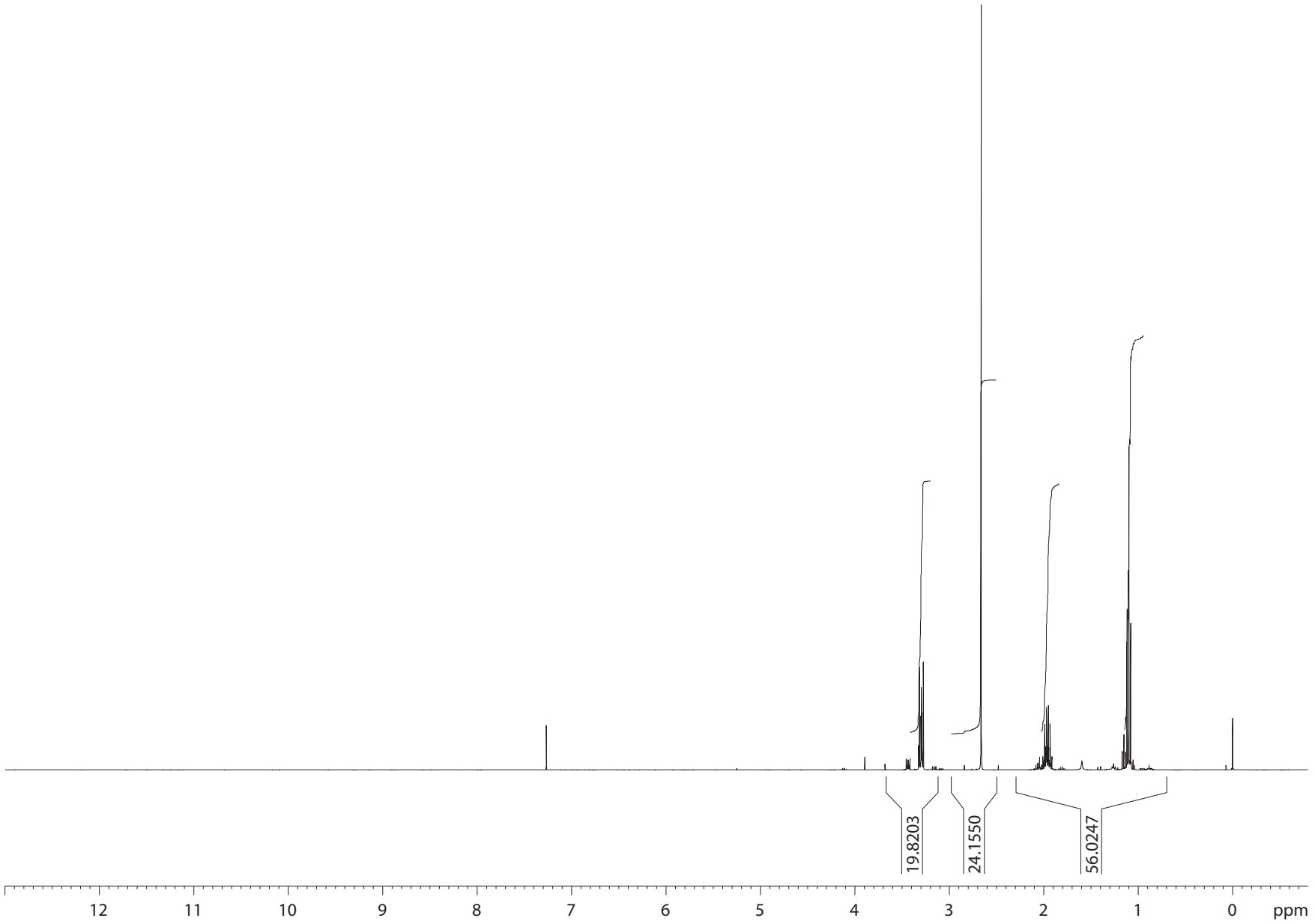
**28**



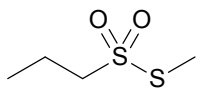

```
Current Data Parameters
NAME       rap123585_od
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20140317
Time              17.46
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG         dept135
TD               131072
SOLVENT             CDC13
NS                     96
DS                      4
SWH            26315.789 Hz
FIDRES          0.200774 Hz
AQ             2.4904180 sec
RG                   8192
DW                19.000 use
DE                 7.00 use
TE                298.2 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
DELTA         0.00001235 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  13C
P1                   9.70 use
p2                  19.40 use
PL1                  4.00 dB
SFO1         100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                   1H
P3                  10.00 use
p4                  20.00 use
PCPD2               80.00 use
PL2                 -2.00 dB
PL12                16.06 dB
SFO2         399.8315993 MHz

F2 - Processing parameters
SI                 65536
SF           100.5373308 MHz
SR                 -3.20 Hz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



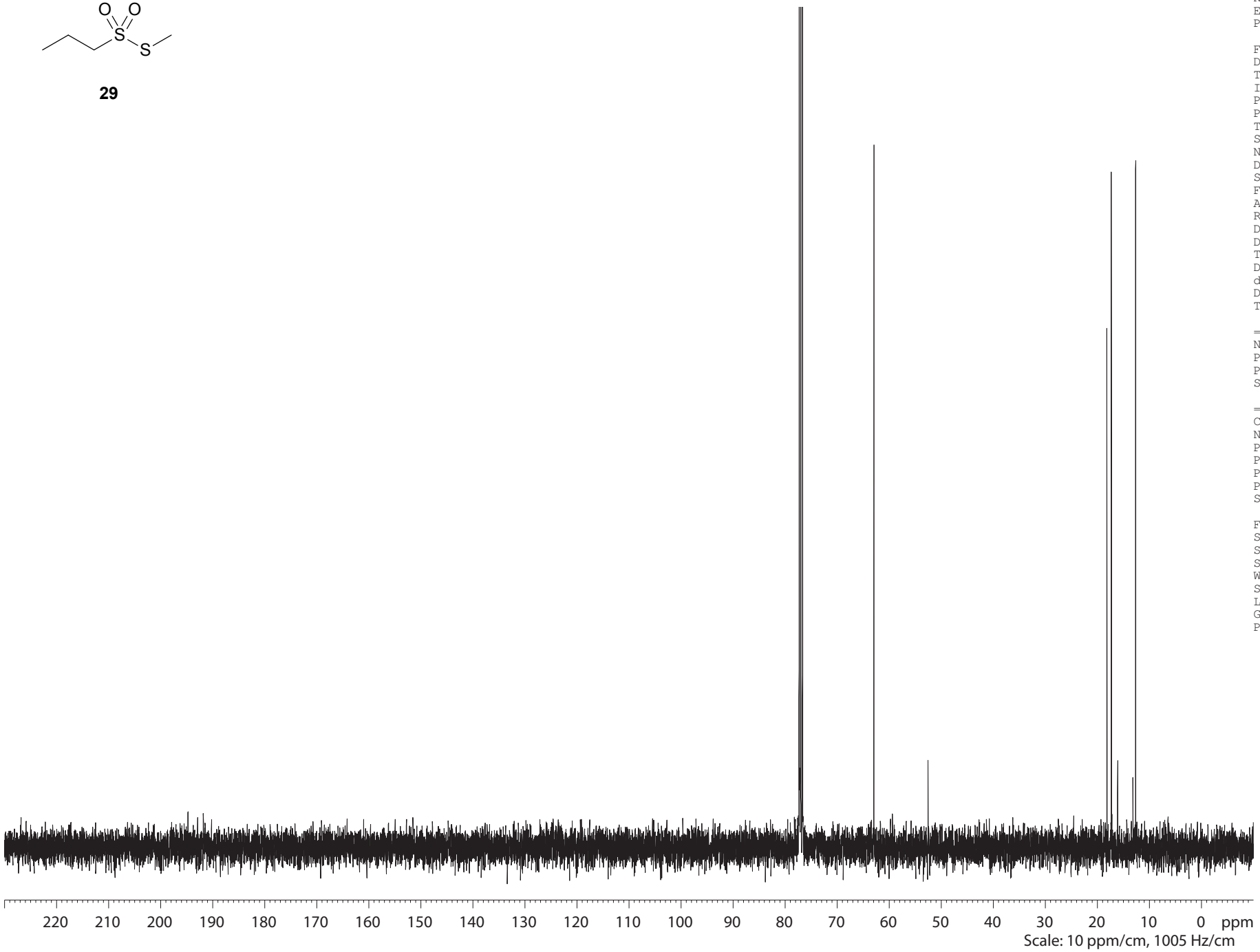
**29**



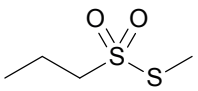

```
Current Data Parameters
NAME       rap123738_od
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140331
Time              12.41
INSTRUM         drx400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                  128
DW               60.400 use
DE                6.00 use
TE               298.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 1H
P1                10.20 use
PL1               -2.00 dB
SFO1       399.8324685 MHz

F2 - Processing parameters
SI                32768
SF         399.8300128 MHz
SR               12.78 Hz
WDW                  EM
SSB                   0
LB                0.00 Hz
GB                    0
PC                 1.40
```



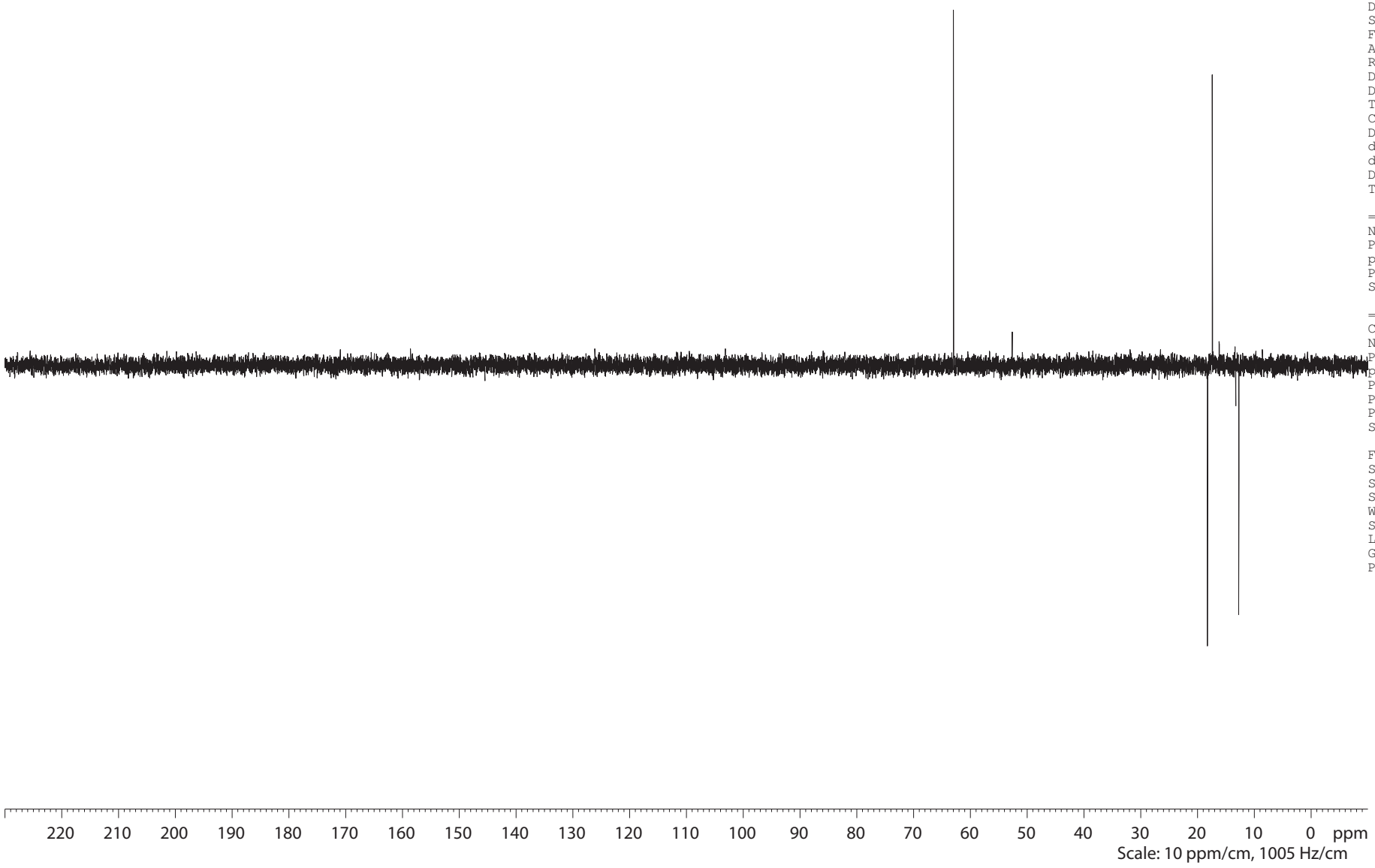
**29**



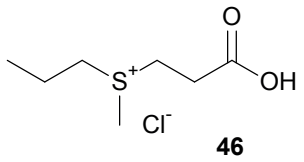

```
Current Data Parameters
NAME       rap123738_od
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140331
Time              12.49
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD               131072
SOLVENT             CDC13
NS                    384
DS                      4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ            2.4904180 sec
RG              10321.3
DW               19.000 use
DE                6.00 use
TE               299.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 13C
P1                  9.70 use
PL1                 4.00 dB
SFO1        100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 use
PL2                -2.00 dB
PL12               16.06 dB
PL13               16.06 dB
SFO2        399.8315993 MHz

F2 - Processing parameters
SI                 65536
SF          100.5373380 MHz
SR                 3.99 Hz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



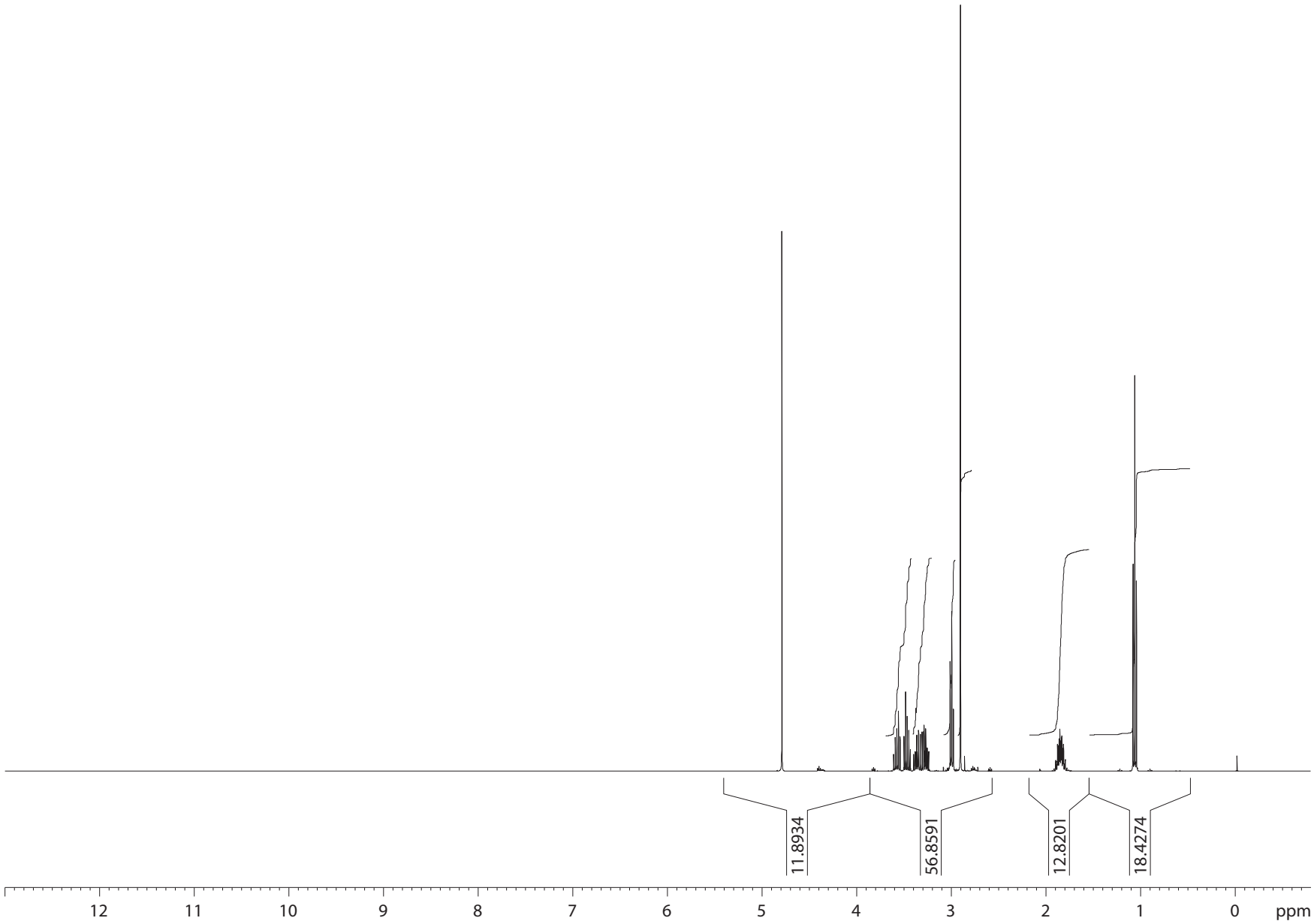
**29**



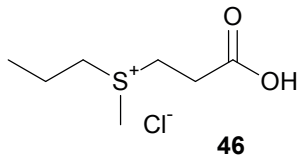

```
Current Data Parameters
NAME       rap123738_od
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20140331
Time              13.19
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG          dept135
TD                131072
SOLVENT             CDC13
NS                    384
DS                      4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ            2.4904180 sec
RG               7298.2
DW               19.000 use
DE                7.00 use
TE                298.2 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
DELTA         0.00001235 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 13C
P1                  9.70 use
p2                 19.40 use
PL1                4.00 dB
SFO1        100.5484940 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
P3                 10.00 use
p4                 20.00 use
PCPD2              80.00 use
PL2                -2.00 dB
PL12               16.06 dB
SFO2        399.8315993 MHz

F2 - Processing parameters
SI                 65536
SF          100.5373308 MHz
SR                -3.20 Hz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



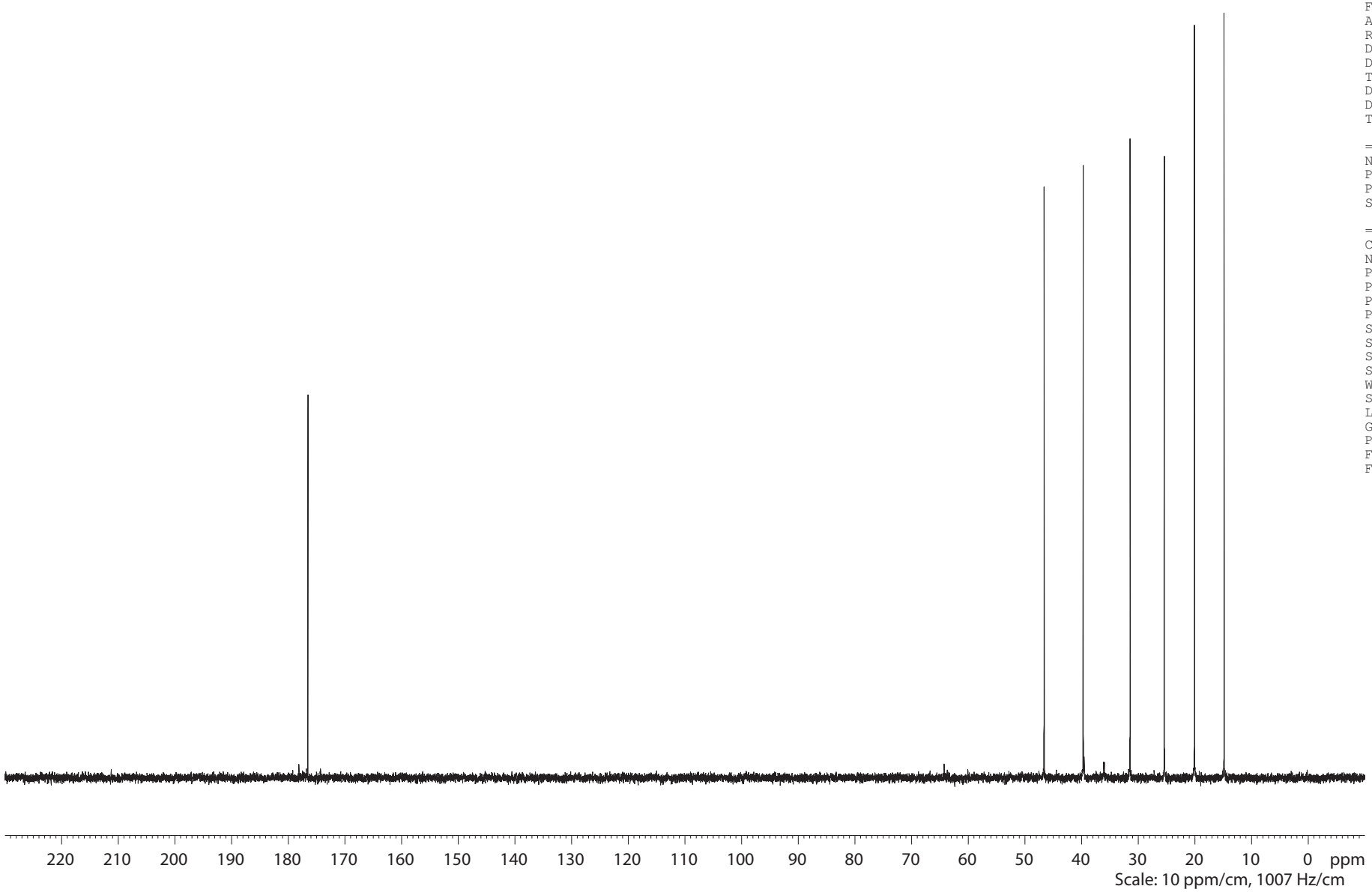

**46**



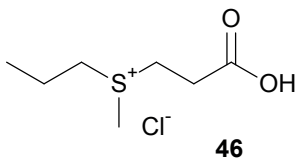

| | |
|---|---|
| NAME | brn122898_od |
| EXPNO | 1 |
| PROCNO | 1 |
| Date_ | 20140114 |
| Time | 1.30 |
| INSTRUM | AVIII400 |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | D2O |
| NS | 64 |
| DS | 2 |
| SWH | 8223.685 Hz |
| FIDRES | 0.125483 Hz |
| AQ | 3.9846387 sec |
| RG | 57 |
| DW | 60.800 use |
| DE | 6.50 use |
| TE | 296.2 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======= | |
| NUC1 | 1H |
| P1 | 10.33 use |
| PL1 | -4.00 dB |
| SFO1 | 400.4024726 MHz |
| SI | 32768 |
| SF | 400.4000032 MHz |
| SR | 3.17 Hz |
| WDW | EM |
| SSB | 0 |
| LB | 0.00 Hz |
| GB | 0 |
| PC | 1.40 |
| F1P | 13.000 ppm |
| F2P | -0.800 ppm |



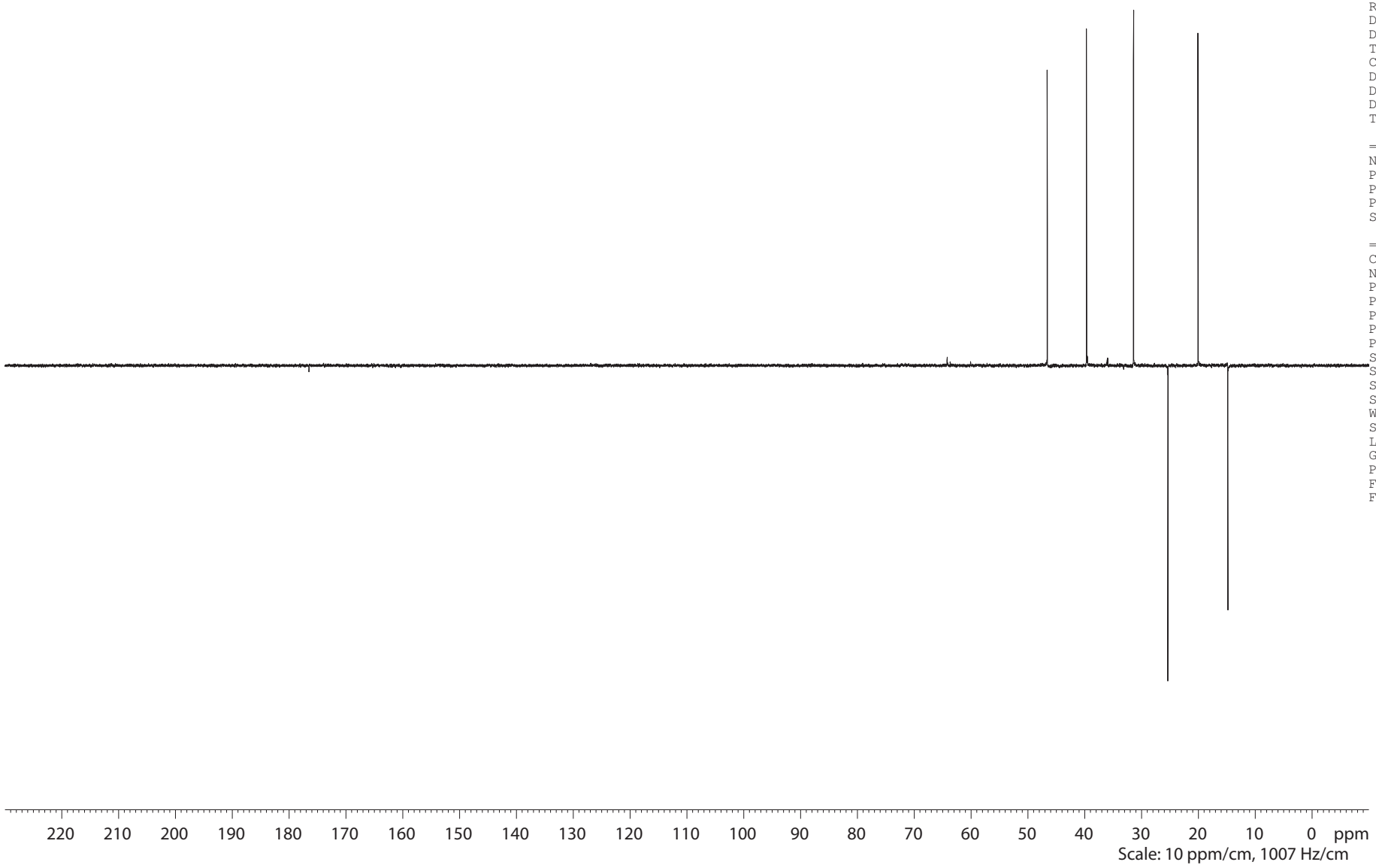

**46**



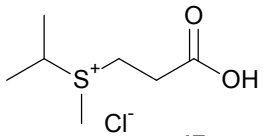

```
NAME          brn122898_od
EXPNO                    2
PROCNO                   1
Date_             20140114
Time                 2.50
INSTRUM           AVIII400
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                  131072
SOLVENT                D2O
NS                     1024
DS                        4
SWH              26315.789 Hz
FIDRES            0.200774 Hz
AQ                2.4904180 sec
RG                      256
DW                   19.000 use
DE                    6.50 use
TE                   297.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 =======
NUC1                    13C
P1                    8.50 use
PL1                  -3.00 dB
SFO1          100.6918371 MHz

======== CHANNEL f2 =======
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 use
PL2                  -4.00 dB
PL12                 13.78 dB
PL13                 14.00 dB
SFO2          400.4016016 MHz
SI                    65536
SF            100.6803827 MHz
SR                -278.29 Hz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
F1P                 230.000 ppm
F2P                 -10.000 ppm
```



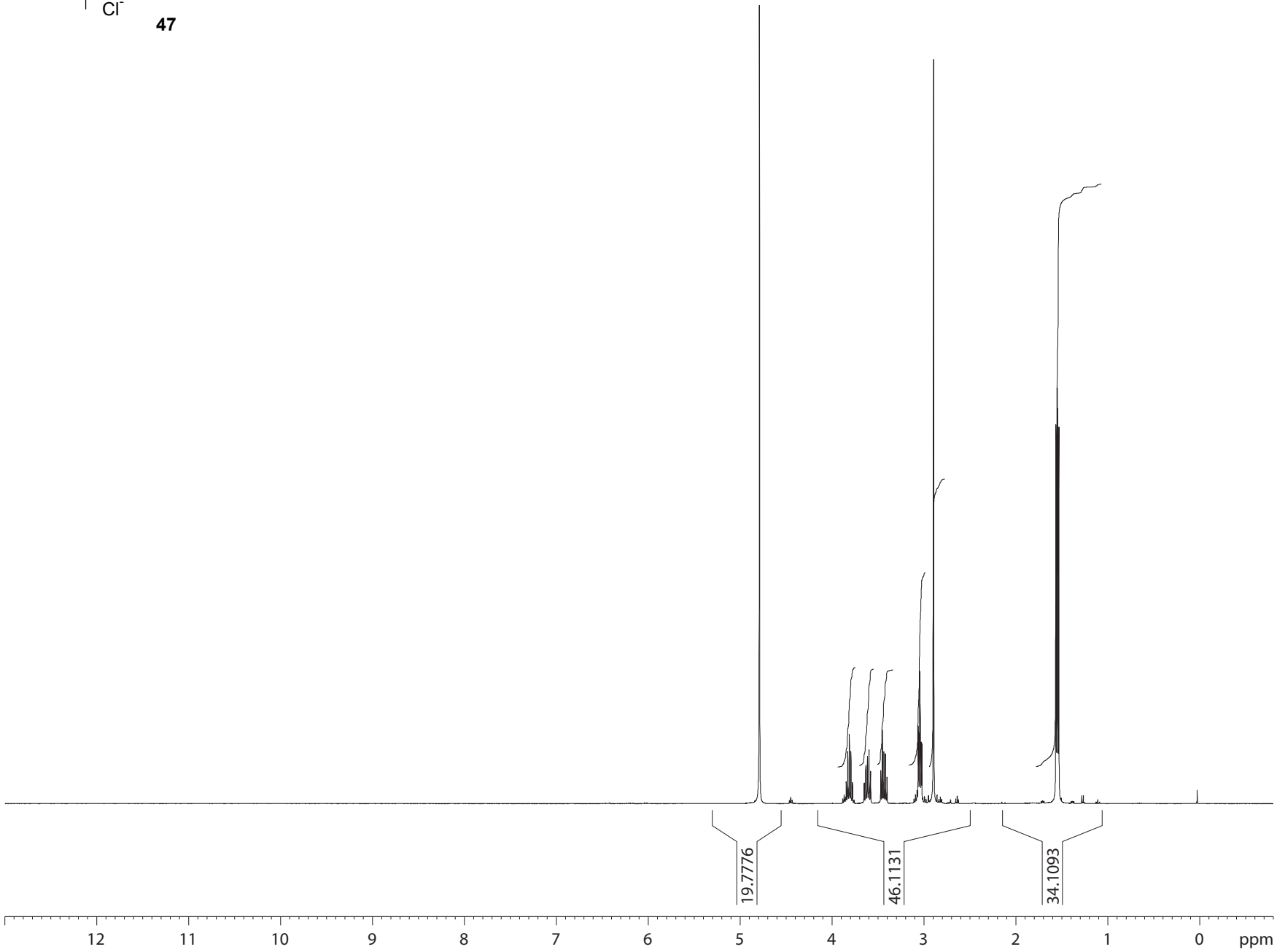

**46**



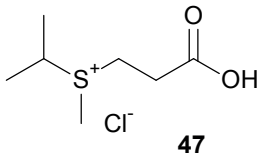

| | |
|---|---|
| NAME | brn122898_od |
| EXPNO | 3 |
| PROCNO | 1 |
| Date_ | 20140114 |
| Time | 3.31 |
| INSTRUM | AVIII400 |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | dept135 |
| TD | 131072 |
| SOLVENT | D2O |
| NS | 512 |
| DS | 4 |
| SWH | 26315.789 Hz |
| FIDRES | 0.200774 Hz |
| AQ | 2.4904180 sec |
| RG | 2050 |
| DW | 19.000 use |
| DE | 6.50 use |
| TE | 296.9 K |
| CNST2 | 145.0000000 |
| D1 | 2.00000000 sec |
| D2 | 0.00344828 sec |
| D12 | 0.00002000 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======= | |
| NUC1 | 13C |
| P1 | 8.50 use |
| P2 | 17.00 use |
| PL1 | -3.00 dB |
| SFO1 | 100.6919063 MHz |
| ======== CHANNEL f2 ======= | |
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| P3 | 10.33 use |
| P4 | 20.66 use |
| PCPD2 | 80.00 use |
| PL2 | -4.00 dB |
| PL12 | 13.78 dB |
| SFO2 | 400.4016016 MHz |
| SI | 65536 |
| SF | 100.6803827 MHz |
| SR | -278.29 Hz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |
| F1P | 230.000 ppm |
| F2P | -10.000 ppm |



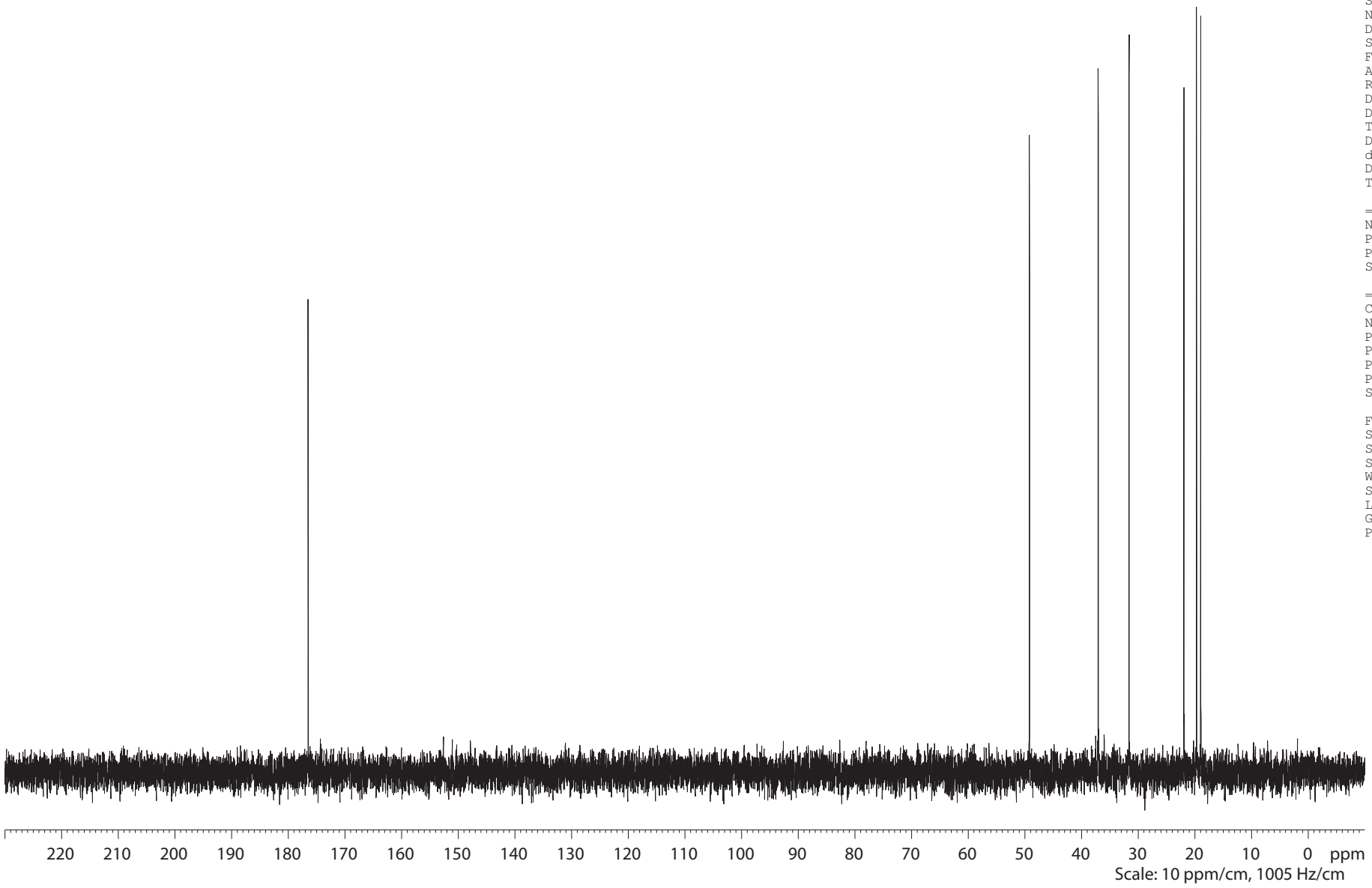

**47**



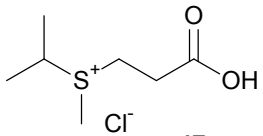

```
Current Data Parameters
NAME       brn121053_od
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130614
Time              15.30
INSTRUM         drx400
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT             D2O
NS                   64
DS                    2
SWH            8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                 71.8
DW               60.400 use
DE                6.00 use
TE               302.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                  1H
P1                10.20 use
PL1               -2.00 dB
SFO1        399.8724688 MHz

F2 - Processing parameters
SI                32768
SF          399.8700003 MHz
SR               0.27 Hz
WDW                 EM
SSB                  0
LB               0.00 Hz
GB                   0
PC                1.40
```



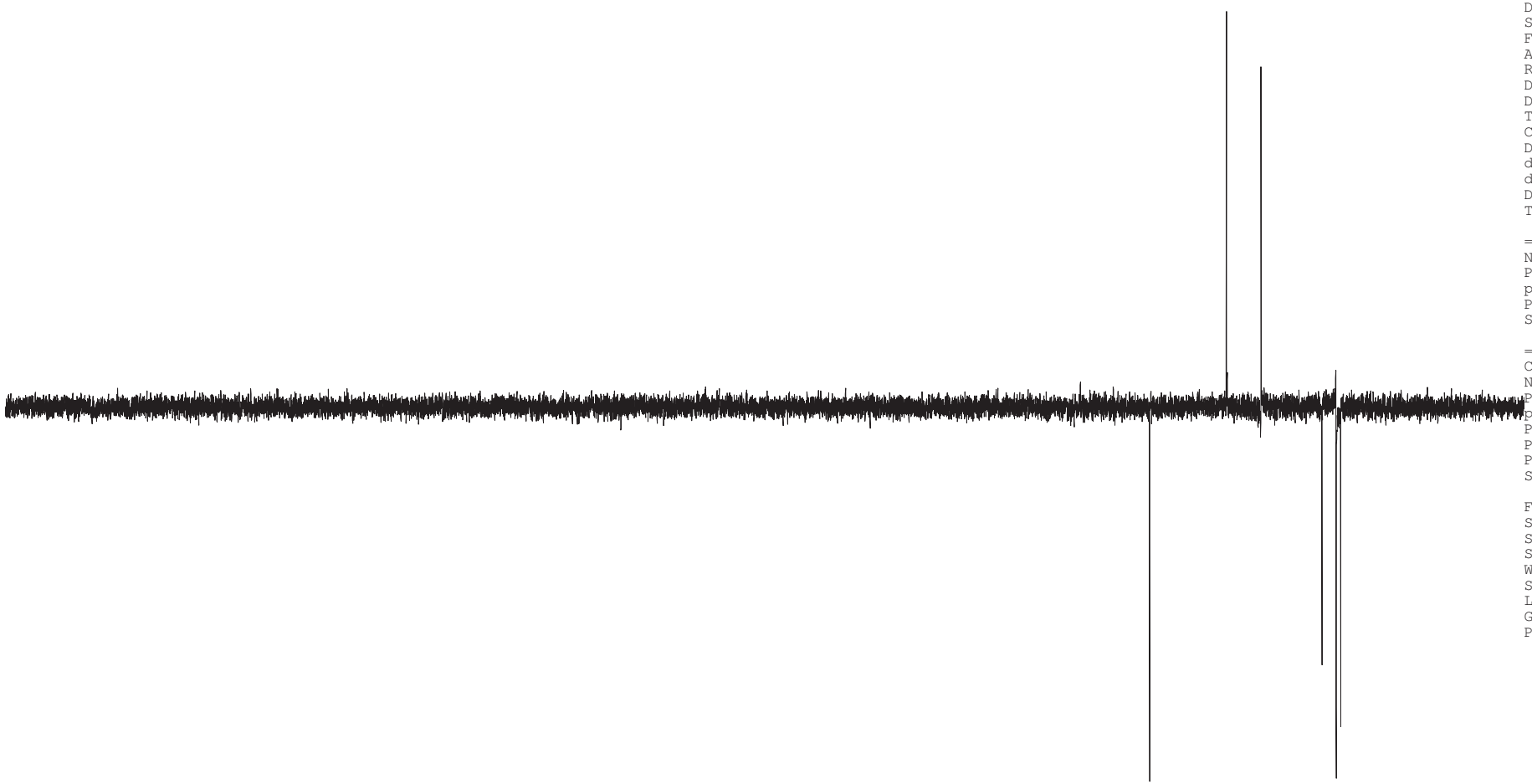

**47**

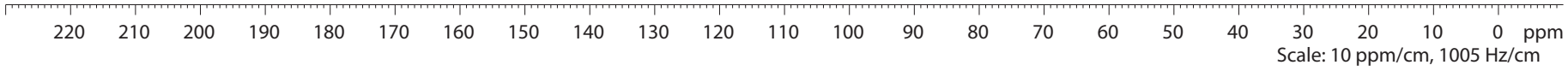



```
Current Data Parameters
NAME       brn121053_od
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20130614
Time              15.39
INSTRUM          drx400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD               131072
SOLVENT             D2O
NS                  576
DS                    4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ            2.4904180 sec
RG               9195.2
DW              19.000 use
DE               6.00 use
TE              302.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 13C
P1                11.00 use
PL1               -3.00 dB
SFO1        100.5585542 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 use
PL2              -2.00 dB
PL12             16.06 dB
PL13             16.06 dB
SFO2        399.8715995 MHz

F2 - Processing parameters
SI                 65536
SF          100.5471141 MHz
SR              -277.92 Hz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

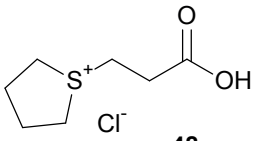



**47**

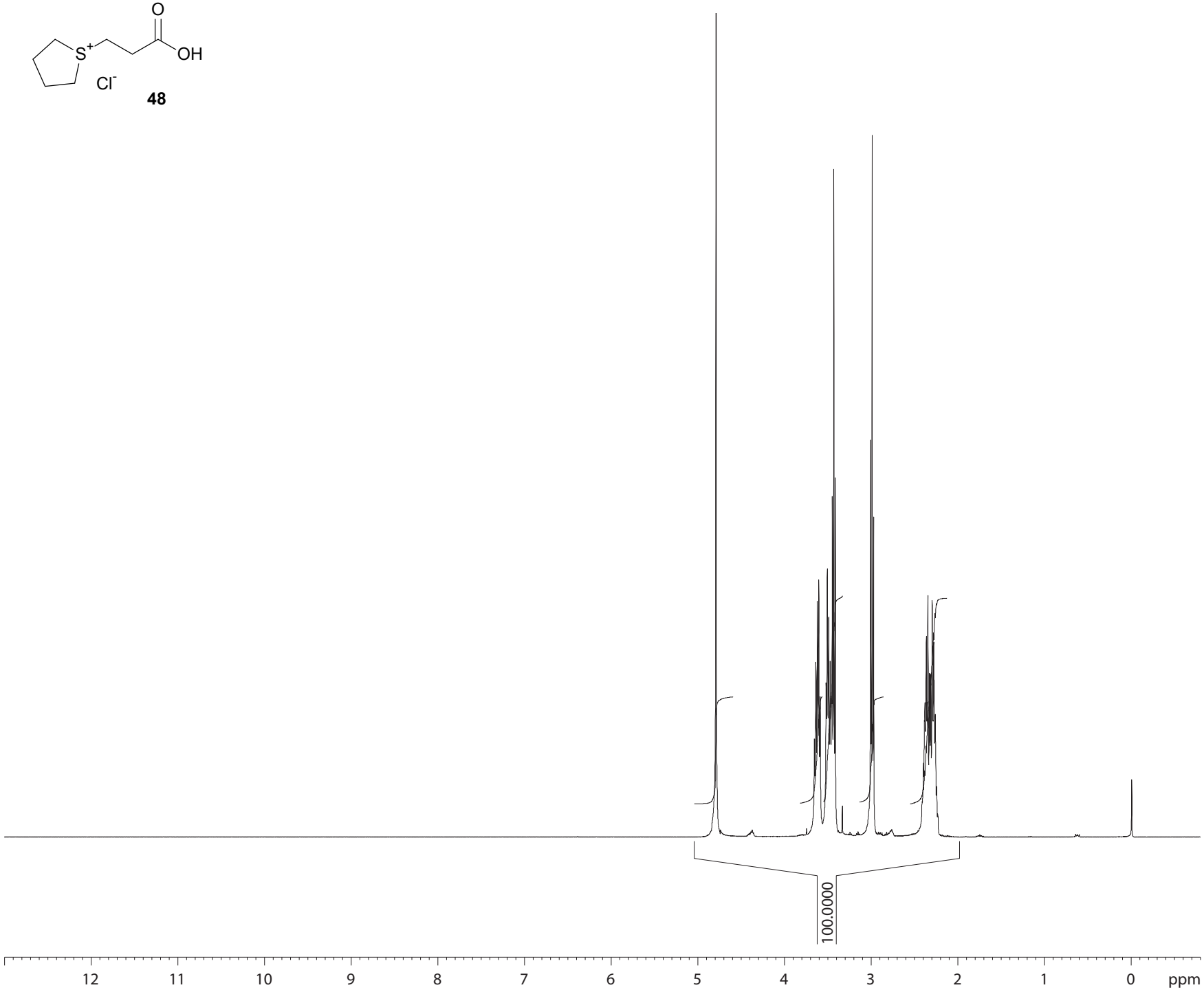




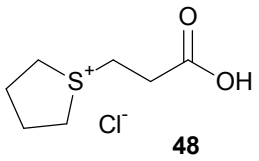

```
Current Data Parameters
NAME       brn121053_od
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20130614
Time              16.26
INSTRUM         drx400
PROBHD   5 mm QNP 1H/13
PULPROG         dept135
TD               131072
SOLVENT             D2O
NS                  480
DS                    4
SWH           26315.789 Hz
FIDRES         0.200774 Hz
AQ            2.4904180 sec
RG              10321.3
DW                19.000 use
DE                 7.00 use
TE                302.2 K
CNST2       145.0000000
D1           2.00000000 sec
d2           0.00344828 sec
d12          0.00002000 sec
DELTA        0.00001401 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 13C
P1                 11.00 use
p2                 22.00 use
PL1                -3.00 dB
SFO1        100.5585542 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                 1H
P3                 10.00 use
p4                 20.00 use
PCPD2              80.00 use
PL2                -2.00 dB
PL12               16.06 dB
SFO2        399.8715995 MHz

F2 - Processing parameters
SI                 65536
SF          100.5471141 MHz
SR              -277.92 Hz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



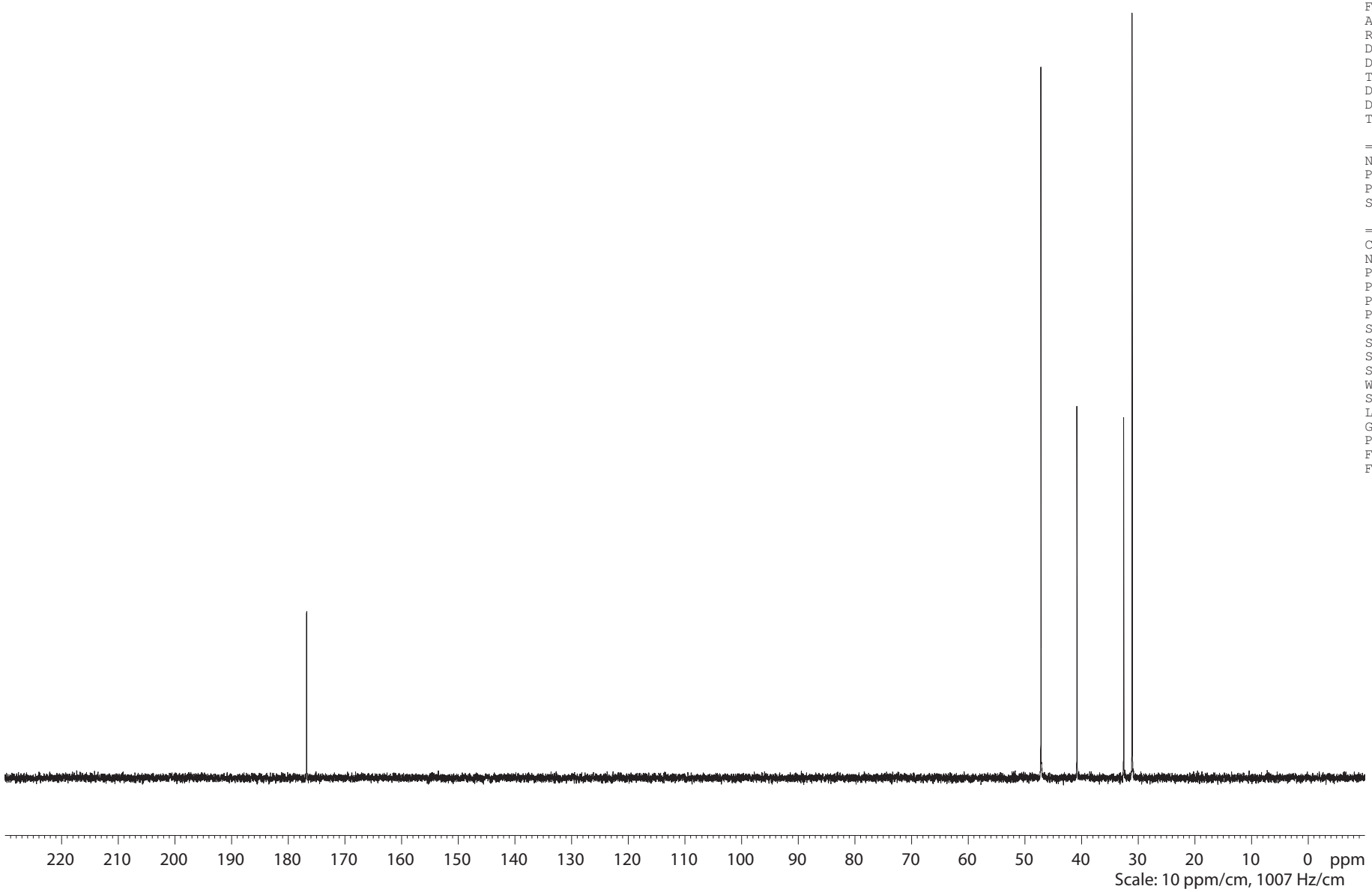

**48**



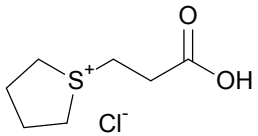

| | |
|---|---|
| NAME | brn120730_od |
| EXPNO | 1 |
| PROCNO | 1 |
| Date_ | 20130511 |
| Time | 0.51 |
| INSTRUM | AVIII400 |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | D2O |
| NS | 64 |
| DS | 2 |
| SWH | 8223.685 Hz |
| FIDRES | 0.125483 Hz |
| AQ | 3.9846387 sec |
| RG | 128 |
| DW | 60.800 use |
| DE | 6.50 use |
| TE | 296.7 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======= | |
| NUC1 | 1H |
| P1 | 10.33 use |
| PL1 | -4.00 dB |
| SFO1 | 400.4024726 MHz |
| SI | 32768 |
| SF | 400.4000027 MHz |
| SR | 2.71 Hz |
| WDW | EM |
| SSB | 0 |
| LB | 0.00 Hz |
| GB | 0 |
| PC | 1.40 |
| F1P | 13.000 ppm |
| F2P | -0.800 ppm |




**48**




| | |
|---|---|
| NAME | brn120730_od |
| EXPNO | 2 |
| PROCNO | 1 |
| Date_ | 20130511 |
| Time | 2.11 |
| INSTRUM | AVIII400 |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zgpg30 |
| TD | 131072 |
| SOLVENT | D2O |
| NS | 1024 |
| DS | 4 |
| SWH | 26315.789 Hz |
| FIDRES | 0.200774 Hz |
| AQ | 2.4904180 sec |
| RG | 256 |
| DW | 19.000 use |
| DE | 6.50 use |
| TE | 298.0 K |
| D1 | 2.00000000 sec |
| D11 | 0.03000000 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======= | |
| NUC1 | 13C |
| P1 | 8.50 use |
| PL1 | -3.00 dB |
| SFO1 | 100.6918371 MHz |
| ======== CHANNEL f2 ======= | |
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| PCPD2 | 80.00 use |
| PL2 | -4.00 dB |
| PL12 | 13.78 dB |
| PL13 | 14.00 dB |
| SFO2 | 400.4016016 MHz |
| SI | 65536 |
| SF | 100.6803827 MHz |
| SR | -278.29 Hz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |
| F1P | 230.000 ppm |
| F2P | -10.000 ppm |




**48**

| | |
|---|---|
| NAME | brn120730_od |
| EXPNO | 3 |
| PROCNO | 1 |
| Date_ | 20130511 |
| Time | 2.20 |
| INSTRUM | AVIII400 |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | dept135 |
| TD | 131072 |
| SOLVENT | D2O |
| NS | 96 |
| DS | 4 |
| SWH | 26315.789 Hz |
| FIDRES | 0.200774 Hz |
| AQ | 2.4904180 sec |
| RG | 2050 |
| DW | 19.000 use |
| DE | 6.50 use |
| TE | 297.5 K |
| CNST2 | 145.0000000 |
| D1 | 2.00000000 sec |
| D2 | 0.00344828 sec |
| D12 | 0.00002000 sec |
| TD0 | 5 |
| ======== CHANNEL f1 ======= | |
| NUC1 | 13C |
| P1 | 8.50 use |
| P2 | 17.00 use |
| PL1 | -3.00 dB |
| SFO1 | 100.6918371 MHz |
| ======== CHANNEL f2 ======= | |
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| P3 | 10.33 use |
| P4 | 20.66 use |
| PCPD2 | 80.00 use |
| PL2 | -4.00 dB |
| PL12 | 13.78 dB |
| SFO2 | 400.4016016 MHz |
| SI | 65536 |
| SF | 100.6803827 MHz |
| SR | -278.29 Hz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |
| F1P | 230.000 ppm |
| F2P | -10.000 ppm |

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Scale: 10 ppm/cm, 1007 Hz/cm