

# Enantioselective Total Synthesis of (+)-galbulin via organocatalytic domino Michael–Michael–aldol condensation.

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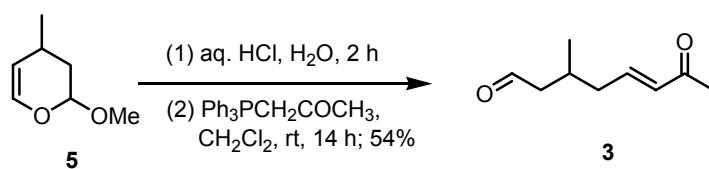
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## SUPPORTING INFORMATION:

Contents: (1) Experimental procedures and characterization data for compounds **1-10**.  
(2) Spectra data for compounds **1-10**.

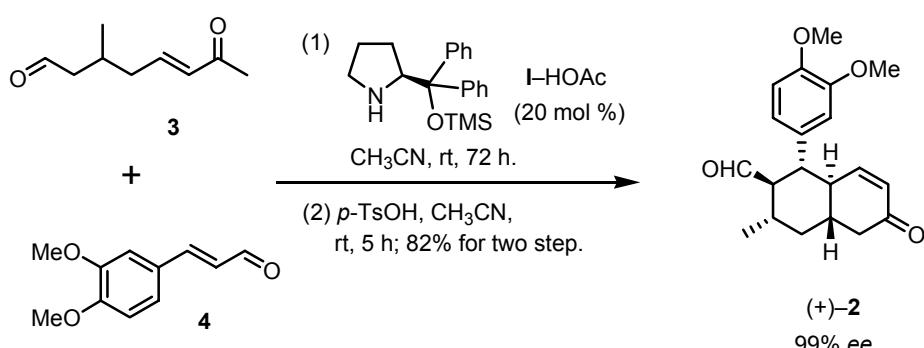
**General Procedure.** All solvents were reagent grade. L-proline (99+%) was purchased from Bachem. Other chemicals were purchased from Aldrich or Acros Chemical Co. Reactions were normally carried out under argon atmosphere in glassware. Merck silica gel 60 (particle size 0.04-0.063 mm) was employed for flash chromatography. Melting points are uncorrected. <sup>1</sup>H NMR spectra were obtained in CDCl<sub>3</sub> unless otherwise noted at 400 MHz (Bruker DPX-400) or 500 MHz (Varian-Unity INOVA-500). <sup>13</sup>C NMR spectra were obtained at 100 MHz or 125 MHz. *E.e.* values were measured by HPLC on a chiral column (chiraldak IA, chiraldak IB, chiraldak IC or chiralcel OD-H, 0.46 cm ID x 25 cm, particle size 5 μ) by elution with IPA-hexane. The flow rate of the indicated elution solvent is maintained at 1 mL/min, and the retention time of a compound is recorded accordingly. HPLC was equipped with the ultraviolet and refractive index detectors. The melting point was recorded on a melting point apparatus (MPA100 – Automated melting point system, Stanford Research Systems, Inc.) and is uncorrected. The optical rotation values were recorded with a Jasco-P-2000 digital polarimeter.

### Preparation of ketoaldehyde **3**.

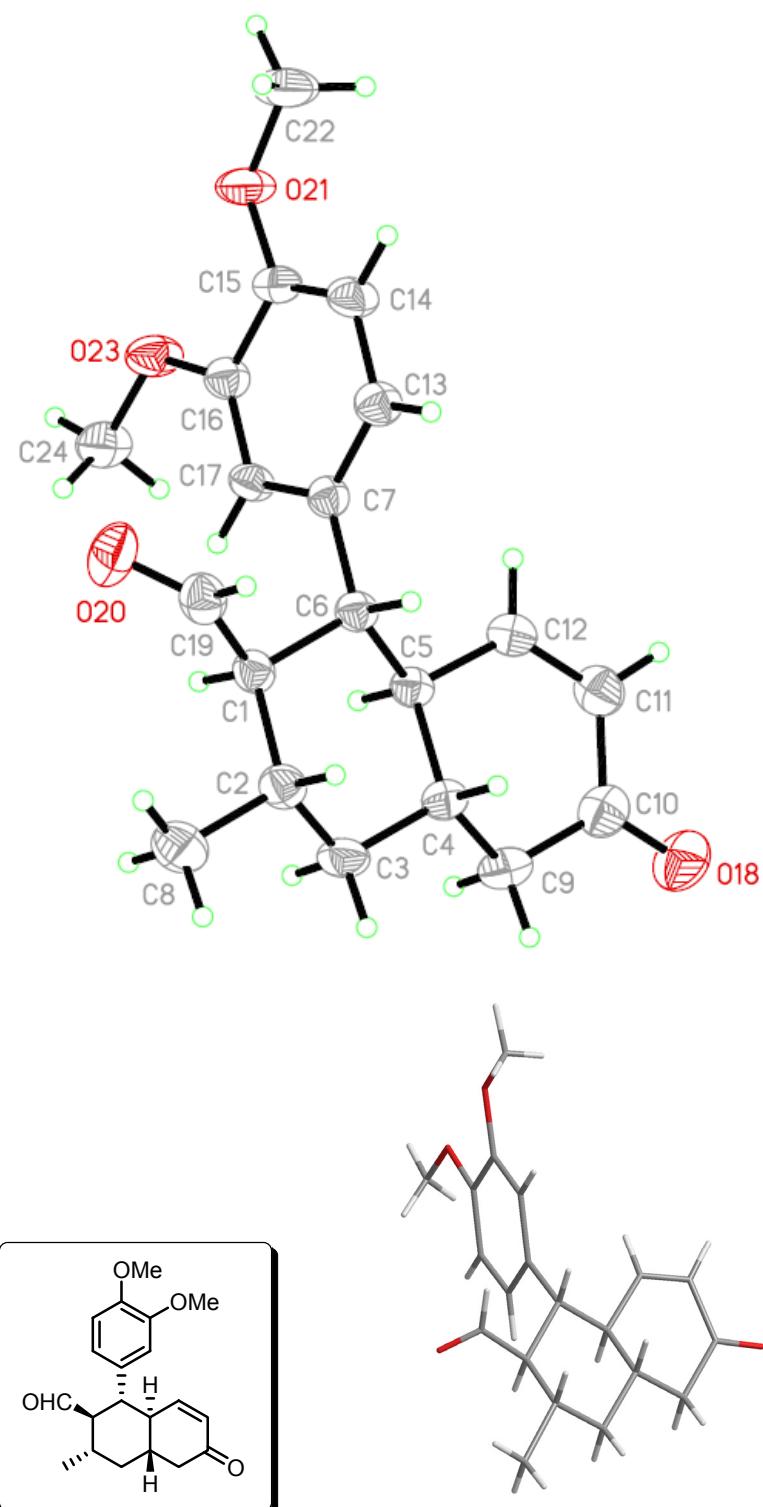


To a solution of 3,4-dihydro-2-methoxy-4-methyl-2*H*-pyran **5** (300 mg, 2.34 mmol) in H<sub>2</sub>O (5.0 mL) was added a concentrate aqueous HCl solution (0.5 mL). The resulting mixture was stirred at 25 °C for 2 h until the solution turned to clear. The solution was neutralized to pH 7 by slow addition of NaHCO<sub>3</sub>, monitored by pH indicator paper. To this mixture was slowly added a solution of 1-(triphenylphosphoranylidene)acetone (460.0 mg, 1.445 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) over 1.5 h. After the addition, the resulting mixture was stirred at ambient temperature for 14 h until the completion of reaction, as monitored by TLC. The reaction mixture was extracted with EtOAc (25 mL x 2), and the organic solution was washed with brine (10 mL x 2), dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 25% EtOAc-hexane (*R*<sub>f</sub> = 0.56 for **3** in 50 % EtOAc-hexane) to give **3** as a colorless oil (120 mg, 54% yield). Selected spectroscopic data: IR (neat): 3428, 2960, 2727, 1722, 1671, 1626, 1363, 1255, 1175, 984 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 9.74 (t, *J* = 1.5 Hz, 1 H), 6.75–6.67 (m, 1 H), 6.06 (d, *J* = 15.5 Hz, 1 H), 2.50 – 2.10 (m, 5 H), 2.22 (s, 3 H), 0.99 (d, *J* = 6.3 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 201.6 (CH), 198.2 (C), 145.3 (CH), 133.0 (CH), 50.3 (CH<sub>2</sub>), 39.4 (CH<sub>2</sub>), 27.5 (CH), 27.1 (CH<sub>3</sub>), 19.9 (CH<sub>3</sub>); MS (*m/z*, relative intensity): 55 (M<sup>+</sup>+1, 32.57), 154 (M<sup>+</sup>, 2.), 129 (58), 111 (63), 99 (64), 95 (47), 85 (49), 71 (67), 69 (100), 58 (62), 55 (70); exact mass calculate for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub> (M<sup>+</sup>): 154.0994; found (M<sup>+</sup>): 154.0984.

Preparation of (+)-2.



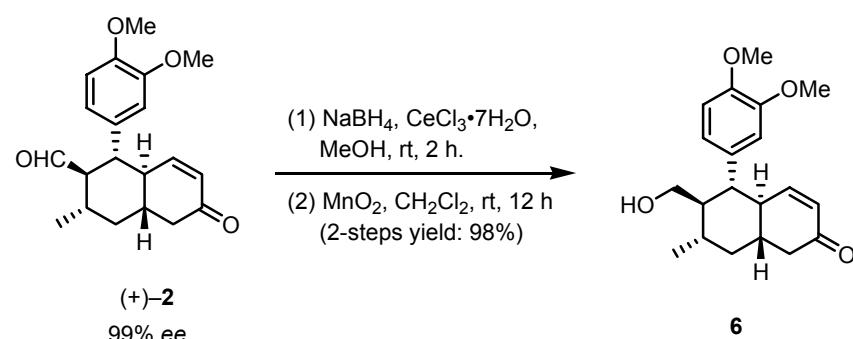
To a solution of (*E*)-3-(3,4-dimethoxyphenyl)acrylaldehyde **4** (290 mg, 1.51 mmol) and (*E*)-3-methyl-7-oxooct-5-enal **3** (565 mg, 3.66 mmol) in CH<sub>3</sub>CN (5.0 mL) was added dropwise a solution of catalyst **I** (98 mg, 0.30 mmol) and acetic acid (18 mg, 0.30 mmol) in CH<sub>3</sub>CN (1 mL). The resulting solution was stirred at ambient temperature for 72 h until the completion of reaction, as monitored by TLC, and followed by the addition of *p*-TsOH (430 mg, 2.50 mmol), and stirring for an additional 5 h. The solution was extracted with EtOAc (10 mL x 3), washed with brine (5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 25% EtOAc–hexane (*R*<sub>f</sub> = 0.43 for **2** in 20% EtOAc–hexane) to give **2** as a white solid (407 mg, 82% yield); mp. 109–111 °C. Selected spectroscopic data for (+)-**2**: [α]<sub>D</sub><sup>26</sup> +58.9 (*c* 6.3, CHCl<sub>3</sub>); IR (neat): 2957, 1723, 1678, 1516, 1463, 1262, 1226, 1142, 1026, 759, 668 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 9.37 (d, *J* = 4.5 Hz, 1 H), 6.82 – 6.78 (m, 1 H), 6.74 – 6.65 (m, 1 H), 6.62 – 6.60 (m, 1 H), 6.48 (d, *J* = 10.0 Hz, 1 H), 5.88 (dd, *J* = 10.0, 2.5 Hz, 1 H), 3.86 (s, 3 H), 3.84 (s, 3 H), 2.64 (t, *J* = 11.5 Hz, 1 H), 2.50 (dd, *J* = 16.5, 3.0, 1 H), 2.44 – 2.38 (m, 1 H), 2.35 – 2.25 (m, 1 H), 2.23 – 2.15 (m, 1 H), 2.05 – 1.80 (m, 3 H), 1.30 – 1.08 (m, 1 H), 0.96 (d, *J* = 6.5 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 203.7 (CH), 199.2 (C), 150.6 (CH), 148.3 (C), 131.8 (C), 130.0 (CH), 111.5 (CH), 63.7 (CH), 55.9 (CH<sub>3</sub>), 55.8 (CH<sub>3</sub>), 47.8 (CH), 46.2 (CH), 44.8 (CH<sub>2</sub>), 40.6 (CH), 40.3 (CH<sub>2</sub>), 32.1 (CH), 19.9 (CH<sub>3</sub>), some aryl carbons are broadened and disappeared due to the slow rotation and coalescence phenomenon; MS (*m/z*, relative intensity): 328 (M<sup>+</sup>, 66), 243 (5), 221(5), 194 (11), 151 (100), 138 (30), 128 (6), 115 (11), 91 (9), 77 (11), 73 (7), 66 (6); exact mass calculated for C<sub>20</sub>H<sub>24</sub>O<sub>4</sub>(M<sup>+</sup>): 328.1675; found 328.1673.



**Figure S1** Stereo plots of the X-ray crystal structures of (+)-2: C, gray; O, red, and the ORTEP diagram.

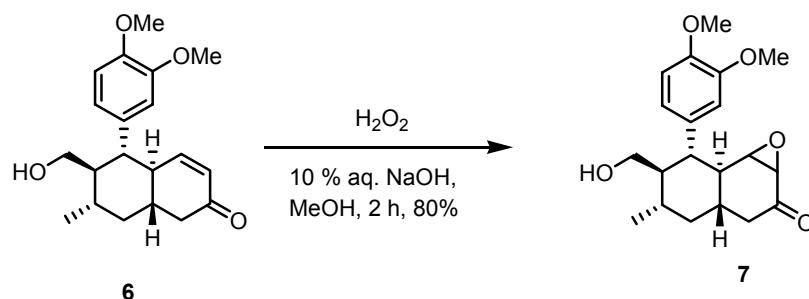
CCDC 844400 contains the supplementary crystallographic data for (+)-2. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Preparation of alcohol **6**.



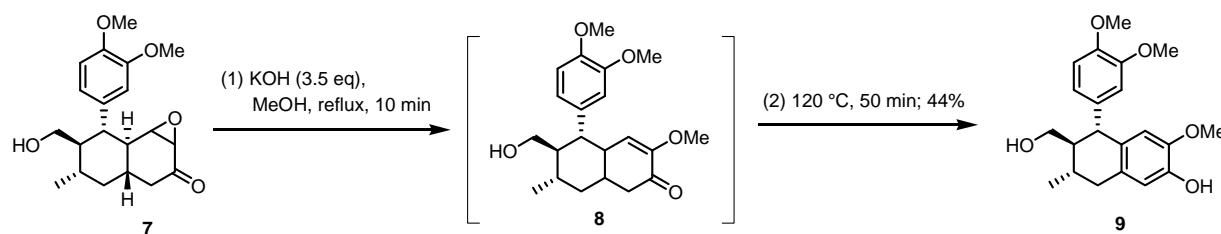
To a solution of **2** (20.0 mg, 0.06 mmol) and CeCl<sub>3</sub>•7H<sub>2</sub>O (34.0 mg, 0.09 mmol) in MeOH (3 mL) was added NaBH<sub>4</sub> (3.0 mg, 0.08 mmol) at 0 °C. The resulting solution was stirred at ambient temperature for 2 h until the completion of reaction, monitored by TLC, followed by addition of a 1N aqueous NaOH solution (1.0 mL). The resulting mixture was filtered through Celite and extracted with EtOAc (15 mL x 2). The organic solution was washed with brine (5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to give the crude product. To a solution of this residue in CH<sub>2</sub>Cl<sub>2</sub> (3.0 mL) was added MnO<sub>2</sub> (80.0 mg, 0.92 mmol) and the resulting mixture was stirred at room temperature for 12 h until the completion of reaction, monitored by TLC. The resulting mixture was filtered through Celite and extracted with EtOAc (10 mL x 2). The organic solution was washed with brine (5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 40% EtOAc–hexane ( $R_f$  = 0.33 for **6** in 60% EtOAc–hexane) to give **6** as a colorless oil (19.7 mg, 98% yield). Selected spectroscopic data:  $[\alpha]_D^{26} +30.2$  (*c* 2.4, CHCl<sub>3</sub>); IR (neat): 3478, 3006, 2903, 2839, 1668, 1516, 1464, 1261, 1225, 1153, 1027, 806, 755, 665 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  6.90 – 6.61 (m, 3 H), 6.45 (dd, *J* = 10.2, 1.3 Hz, 1 H), 5.83 (dd, *J* = 10.2, 2.6 Hz, 1 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 3.64 (dd, *J* = 11.2, 2.6 Hz, 1 H), 3.21 (dd, *J* = 11.2, 1.7 Hz, 1 H), 2.65 – 2.42 (m, 2 H), 2.32 – 2.18 (m, 2 H), 2.02 – 1.85 (m, 1 H), 1.80 – 1.70 (m, 1 H), 1.40 – 1.00 (m, 4 H), 1.04 (d, *J* = 6.3 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  199.9 (C), 152.9 (CH), 129.4 (CH), 60.5 (CH<sub>2</sub>), 55.9 (CH<sub>3</sub>), 55.8 (CH<sub>3</sub>), 48.3 (CH), 45.1 (CH<sub>2</sub>), 41.6 (CH<sub>2</sub>), 40.9 (CH), 31.5 (CH), 19.9 (CH<sub>3</sub>); Some aryl carbons are broadened and disappeared due to the slow rotation and coalescence phenomenon; MS (*m/z*, relative intensity): 330 (M<sup>+</sup>, 47), 316 (1), 314 (0.86), 284 (0.86), 267 (0.61), 256 (0.66), 243 (1), 239 (1), 205 (5), 191 (3), 177 (5), 153 (6), 151 (100), 138 (7), 115 (5), 107 (5), 91 (6), 77 (5), 57 (4), 55 (4); exact mass calculated for C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>(M<sup>+</sup>): 330.1831; found 330.1832.

### Preparation of epoxide 7.



To a solution of **6** (20.0 mg, 0.06 mmol) in MeOH (1 mL) was added a 10% aqueous solution of NaOH (0.005 mL) and  $\text{H}_2\text{O}_2$  (30%, 0.016 mL) at 0 °C. After the addition, the resulting solution was stirred at ambient temperature for 2 h until the completion of reaction, monitored by TLC. In order to remove methanol, the solution was concentrated *in vacuo* to *ca.* 3/4 of the original volume. To the resulting mixture was added ice water (2.0 mL), and the solution was extracted with EtOAc (5.0 mL x 2), washed with brine (5.0 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 40% EtOAc–hexane ( $R_f = 0.42$  for **7** in 60% EtOAc–hexane) to give **7** as a colorless oil (17 mg, 80% yield). Selected spectroscopic data:  $[\alpha]_{\text{D}}^{26} +65$  (*c* 2.45,  $\text{CHCl}_3$ ); IR (neat): 3515, 3009, 2960, 2913, 2839, 1706, 1516, 1261, 1027, 808, 756  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  6.93 – 6.63 (m, 3 H), 3.87 (s, 3 H), 3.86 (s, 3 H), 3.66 (d, *J* = 12.0 Hz, 1 H), 3.25 (d, *J* = 12.0 Hz, 1 H), 3.09 (d, *J* = 3.5 Hz, 1 H), 2.97 (brs, 1 H), 2.85 – 2.70 (m, 1 H), 2.48 (dd, *J* = 19.0, 4.5 Hz, 1 H), 2.10 – 1.95 (m, 1 H), 1.88 – 1.70 (m, 4 H), 1.31 (t, *J* = 11.0 Hz, 1 H), 1.03 (d, *J* = 6.0 Hz, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  205.0 (C), 60.6 ( $\text{CH}_2$ ), 56.3 (CH), 56.0 (2  $\text{CH}_3$ ), 55.7 (2 CH), 47.6 (CH), 43.6 ( $\text{CH}_2$ ), 41.7 ( $\text{CH}_2$ ), 31.5 (CH), 30.0 (CH), 19.9 ( $\text{CH}_3$ ); Some aryl protons and carbons are broadened and disappeared due to the slow rotation and coalescence phenomenon; MS (*m/z*, relative intensity): 346 ( $\text{M}^+$ , 72), 330 (2), 310 (2), 295 (3), 284 (6), 267 (3), 256 (19), 239 (5), 213 (14), 211 (5), 185 (10), 169 (9), 151 (53), 149 (26), 129 (25), 111 (28), 97 (41), 85 (70), 71 (90), 57 (100); exact mass calculated for  $\text{C}_{20}\text{H}_{26}\text{O}_5(\text{M}^+)$ : 346.1780; found 346.1779.

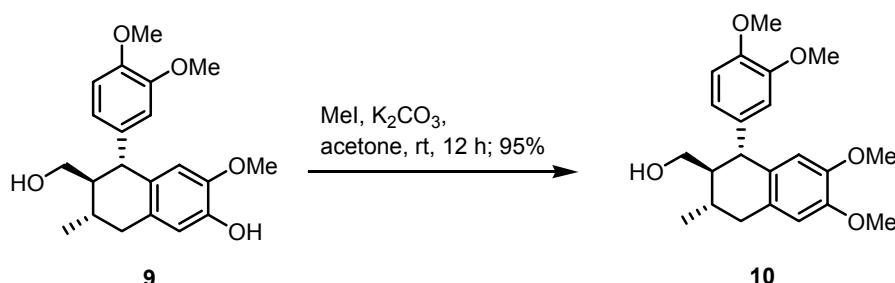
### Preparation of alcohol **9**.



A solution of **7** (10.0 mg, 0.03 mmol) and NaOH (5.7 mg, 0.14 mmol) in MeOH (0.11 mL) was heated to reflux for 10 min. The solution was concentrated *in vacuo* to remove most methanol but not dried and gave a sticky residue. The residue **8** was heated to 120 °C under N<sub>2</sub>, with a reflux condenser, for 50 min until the completion of reaction, as monitored by TLC. The solution was washed with aqueous saturated NaHCO<sub>3</sub> solution, extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL x 2). The combined organic solution was washed with brine (5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 40% EtOAc–hexane ( $R_f$  = 0.33 for **9** in 50% EtOAc–hexane) to give **9** as a yellow oil (4.4 mg, 44% yield). Selected spectroscopic data:  $[\alpha]_D^{26} +8.4$  (*c* 2.15, CHCl<sub>3</sub>); IR (neat): 3401, 3003, 2959, 2926, 1726, 1666, 1593, 1513, 1464, 1260, 1026, 759 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  6.78 (d, *J* = 8.0 Hz, 1 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 6.61 (d, *J* = 12.0 Hz, 2 H), 6.17 (s, 1 H), 5.40 (s, 1 H), 3.97 (d, *J* = 11.0 Hz, 1 H), 3.87 (s, 3 H), 3.80 – 3.75 (m, 1 H), 3.79 (s, 3 H), 3.58 (s, 3 H), 3.43 (d, *J* = 11.0 Hz, 1 H), 2.75 (dd, *J* = 16.0, 4.5 Hz, 1 H), 2.62 – 2.56 (m, 1 H), 2.07 – 1.98 (m, 1 H), 1.59 – 1.52 (m, 2 H), 1.12 (d, *J* = 6.5 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  149.0 (C), 147.5 (C), 144.8 (C), 143.6 (C), 138.5 (C), 131.8 (C), 129.6 (C), 121.7 (CH), 113.4 (CH), 112.1 (CH), 111.9 (CH), 110.9 (CH), 61.1 (CH<sub>2</sub>), 55.9 (2 CH<sub>3</sub>), 55.8 (CH<sub>3</sub>), 50.7 (CH), 47.4 (CH), 38.6 (CH<sub>2</sub>), 30.1 (CH), 19.7 (CH<sub>3</sub>); MS (*m/z*, relative intensity): 358 (M<sup>+</sup>, 11), 339 (15), 323 (12), 309 (7), 299 (5), 285 (6), 269 (24), 255 (10), 254 (7), 211 (4), 203 (16), 189 (7), 178 (8), 167 (7), 151 (15), 149 (14), 111 (14), 97 (20), 85 (20), 71 (28), 58 (100), 57 (35); exact mass calculated for C<sub>21</sub>H<sub>26</sub>O<sub>5</sub> (M<sup>+</sup>): 358.1780; found: 358.1777.

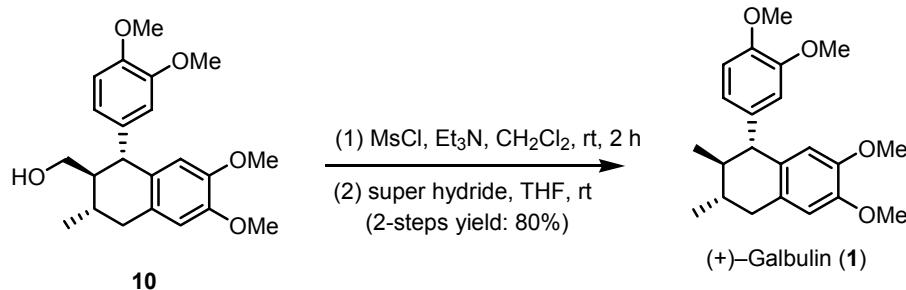
$R_f$  = 0.12 for **8** in 50% EtOAc–hexane. Selected spectroscopic data for **8**:  $[\alpha]_D^{26} +31.6$  (*c* 2.26, CHCl<sub>3</sub>); IR (neat): 3515, 3010, 2925, 2839, 1687, 1619, 1515, 1464, 1261, 1155, 1027, 753 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  6.82 – 6.69 (m, 3 H), 5.28 (s, 1 H), 3.87 (s, 6 H), 3.64 (d, *J* = 11.0 Hz, 1 H), 3.32 (s, 3 H), 3.20 (d, *J* = 11.0 Hz, 1 H), 2.58–2.47 (m, 2 H), 2.37 (t, *J* = 10.5 Hz, 1 H), 2.24 (dd, *J* = 16.5, 14 Hz, 1 H), 1.92–1.89 (m, 1 H), 1.79 – 1.75 (m, 2 H), 1.31 (t, *J* = 10.5 Hz, 1 H), 1.20 (brs, 1 H), 1.03 (d, *J* = 6.5 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  194.0 (C), 151.4 (C), 147.8 (C), 134.4 (C), 122.9 (CH), 118.6 (CH), 117.6 (CH), 114.5 (C), 112.2 (C), 110.8 (CH), 108.1 (CH), 60.6 (CH<sub>2</sub>), 55.9 (CH<sub>3</sub>), 55.8 (CH<sub>3</sub>), 54.7 (CH<sub>3</sub>), 49.4 (CH), 41.0 (CH), 40.9 (CH<sub>2</sub>), 31.5 (CH), 47.4 (CH), 19.9 (CH<sub>3</sub>); MS (*m/z*, relative intensity): 360 (M<sup>+</sup>, 15), 347 (2), 333 (2), 320 (2), 305 (3), 285 (5), 277 (3), 263 (3), 249 (4), 239 (7), 221 (15), 205 (20), 193 (12), 191 (11), 165 (15), 151 (43), 137 (24), 125 (36), 97 (81), 83 (73), 71 (84), 57 (100); exact mass calculated for C<sub>22</sub>H<sub>28</sub>O<sub>4</sub> (M<sup>+</sup>): 360.1937; found: 360.1937.

### Preparation of **10**.



To a solution of **9** (10.0 mg, 0.03 mmol) and  $K_2CO_3$  (8.0 mg, 0.06 mmol) in acetone (1 mL) was added MeI (6.0 mg, 0.04 mmol). The solution was stirred at room temperature for 12 h until the completion of reaction, as monitored by TLC, followed by addition of  $H_2O$  (4 mL). The solution was extracted with EtOAc (15 mL x 2), washed with brine (10 mL), dried over  $Na_2SO_4$ , and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 30% EtOAc–hexane ( $R_f = 0.38$  for **10** in 50% EtOAc–hexane) to give **10** as a yellow oil (9.9 mg, 95% yield). Selected spectroscopic data:  $[\alpha]_D^{26} -4.5$  (*c* 2.2,  $CHCl_3$ ); IR (neat): 3469, 2926, 2850, 2834, 1738, 1607, 1514, 1464, 1256, 1028, 808, 756  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta$  6.79 (d, *J* = 8.0 Hz, 1 H), 6.74 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.59 (d, *J* = 2.0 Hz, 1 H), 6.56 (s, 1 H), 6.20 (s, 1 H), 3.99 (dd, *J* = 10.0, 1.0 Hz, 1 H), 3.86 (s, 3 H), 3.83 (s, 3 H), 3.80 – 3.76 (m, 1 H), 3.78 (s, 3 H), 3.56 (s, 3 H), 3.47 – 3.42 (m, 1 H), 2.79 (dd, *J* = 16.0, 4.5 Hz, 1 H), 2.67 – 2.59 (m, 1 H), 2.06 – 1.97 (m, 1 H), 1.54 – 1.50 (m, 2 H), 1.14 (d, *J* = 6.5 Hz, 3 H);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz):  $\delta$  149.0 (C), 147.5 (C), 147.1 (C), 147.0 (C), 138.4 (C), 132.2 (C), 128.8 (C), 121.8 (CH), 112.9 (CH), 112.0 (CH), 110.9 (CH), 110.6 (CH), 61.1 (CH<sub>2</sub>), 55.9 (CH<sub>3</sub>), 55.83 (2 CH<sub>3</sub>), 55.78 (CH<sub>3</sub>), 50.7 (CH), 47.3 (CH), 38.9 (CH<sub>2</sub>), 30.2 (CH), 19.7 (CH<sub>3</sub>); MS (*m/z*, relative intensity): 372 ( $M^+$ , 100), 356 (9), 339 (16), 323 (18), 313 (7), 299 (9), 284 (16), 269 (65), 256 (10), 239 (21), 238 (10), 203 (22), 189 (6), 178 (10), 165 (8), 151 (22), 133 (7), 118 (7), 98 (9), 91 (43), 71 (14), 58 (61), 57 (19); exact mass calculated for  $C_{22}H_{28}O_5(M^+)$ : 372.1937; found: 372.1936.

## Synthesis of (+)-Galbulin.



To a solution of **10** (12.0 mg, 0.03 mmol) and Et<sub>3</sub>N (6.5 mg, 0.06 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added methanesulfonyl chloride (7.4 mg, 0.06 mmol). The resulting solution was stirred at ambient temperature for 2 h until the completion of reaction, as monitored by TLC, and followed by addition of H<sub>2</sub>O (3 mL). The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL x 2), washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to give the crude product. To a solution of the residue in THF (2.0 mL) was added a Super-Hydride® solution (lithium triethylborohydride, 1M in THF, 0.071 mL, 0.07 mmol), and the resulting solution was stirred at ambient temperature for 2 h until the completion of reaction, as monitored by TLC. To the reaction mixture was added H<sub>2</sub>O (3 mL). The solution was extracted with EtOAc (15 mL x 2), washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography with 10% EtOAc–hexane (*R*<sub>f</sub> = 0.71 for **1** in 50% EtOAc–hexane) to give **1** as a white solid (9.1 mg, 80% yield); mp. 130–131 °C. Selected spectroscopic data: [α]<sub>D</sub><sup>30</sup> +8.0 (c 0.3, CHCl<sub>3</sub>); IR (neat): 2960, 2872, 2833, 1607, 1516, 1464, 1417, 1249, 1217, 1029, 801, 754 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 6.78 (d, *J* = 8.5 Hz, 1 H), 6.69 (dd, *J* = 8.0, 1.5 Hz, 1 H), 6.56 – 6.54 (m, 2 H), 6.14 (s, 1 H), 3.86 (s, 3 H), 3.82 (s, 3 H), 3.79 (s, 3 H), 3.54 (s, 3 H), 3.41 (d, *J* = 10.5 Hz, 1 H), 2.74 (dd, *J* = 16.0, 4.5 Hz, 1 H), 2.63 – 2.56 (m, 1 H), 1.68 – 1.58 (m, 1 H), 1.56 – 1.45 (m, 1 H), 1.06 (d, *J* = 6.5 Hz, 3 H), 0.85 (d, *J* = 6.5 Hz, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 148.8 (C), 147.3 (C), 147.0 (C), 146.9 (C), 139.0 (C), 132.4 (C), 129.1 (C), 121.9 (CH), 112.8 (CH), 112.0 (CH), 110.7 (CH), 110.6 (CH), 55.9 (2 CH<sub>3</sub>), 55.8 (2 CH<sub>3</sub>), 54.3 (CH), 43.8 (CH), 39.0 (CH<sub>2</sub>), 35.5 (CH), 20.0 (CH<sub>3</sub>), 17.2 (CH<sub>3</sub>); MS (*m/z*, relative intensity): 356 (M<sup>+</sup>, 4), 355 (M<sup>+</sup>–1, 11), 341 (4), 339 (2), 316 (4), 295 (21), 281 (13), 269 (4), 256 (5), 239 (6), 221 (38), 207 (10), 185 (4), 167 (4), 147 (20), 141 (5), 129 (11), 111 (11), 97 (17), 85 (24), 71 (35), 58 (100), 57 (44); exact mass calculated for C<sub>22</sub>H<sub>28</sub>O<sub>4</sub>(M<sup>+</sup>): 356.1988; found: 356.1988.

**Table S1.** Comparison of compound **1** and Galbulin ( $^{13}\text{C}$  NMR spectra with literature data).

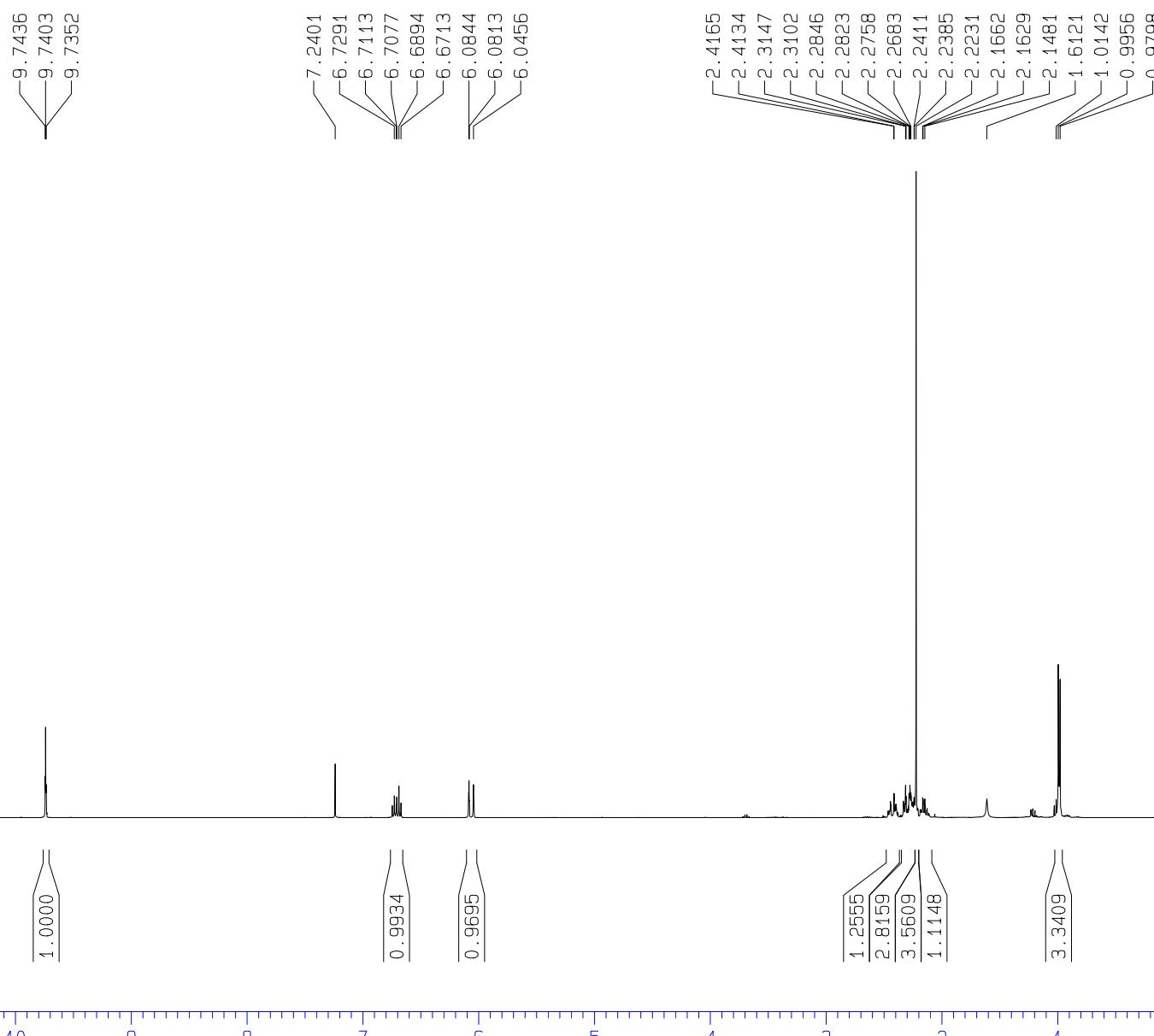
Lit. <sup>1</sup>	Lit. <sup>2</sup>	Compound <b>1</b>
148.9	148.9	148.8
147.4	147.3	147.3
147.0	147.0	147.0
146.9	146.9	146.9
139.1	139.0	139.0
132.5	132.5	132.4
129.1	129.1	129.1
121.9	121.9	121.9
112.9	112.9	112.8
112.2	112.1	112.0
110.8	110.7	110.7
110.7	110.6	110.6
55.9 (2C)	55.9 (2C)	55.9 (2C)
55.8 (2C)	55.8, 55.7	55.8 (2C)
54.3	54.3	54.3
43.8	43.8	43.8
39.1	39.0	39.0
35.6	35.6	35.5
20.0	20.0	20.0
17.2	17.2	17.2

<sup>1</sup> Buckleton, J. S.; Cambie, R. C.; Clark, G. R.; Craw, P. A.; Rickard, C. E. F.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* **1988**, *41*, 305-324.

<sup>2</sup> Datta, P. K.; Yau, C.; Hooper, T. S.; Yvon, B. L.; Charlton, J. L. *J. Org. Chem.* **2001**, *66*, 8606-8611.

Fig S11.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) of compound 3.

ppm



Current Data Parameters

NAME HCS-005  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters

Date\_ 20110106  
Time 21.06  
INSTRUM spect  
PROBHD 5 mm QNP 1H  
PULPROG zg30  
TD 16384  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 0  
SWH 5995.204 Hz  
FIDRES 0.365918 Hz  
AQ 1.3664756 sec  
RG 1290.2  
DW 83.400 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.5000000 sec

===== CHANNEL f1 =====

NUC1 1H  
P1 10.90 usec  
PL1 -3.00 dB  
SF01 400.1326008 MHz

F2 - Processing parameters

SI 8192  
SF 400.1300171 MHz  
WDW EM  
SSB 0  
LB 0.10 Hz  
GB 0  
PC 1.00

1D NMR plot parameters

CX 21.50 cm  
CY 10.00 cm  
F1P 12.000 ppm  
F1 4801.56 Hz  
F2P -0.000 ppm  
F2 -0.00 Hz  
PPMCM 0.55814 ppm/cm  
HZCM 223.32838 Hz/cm

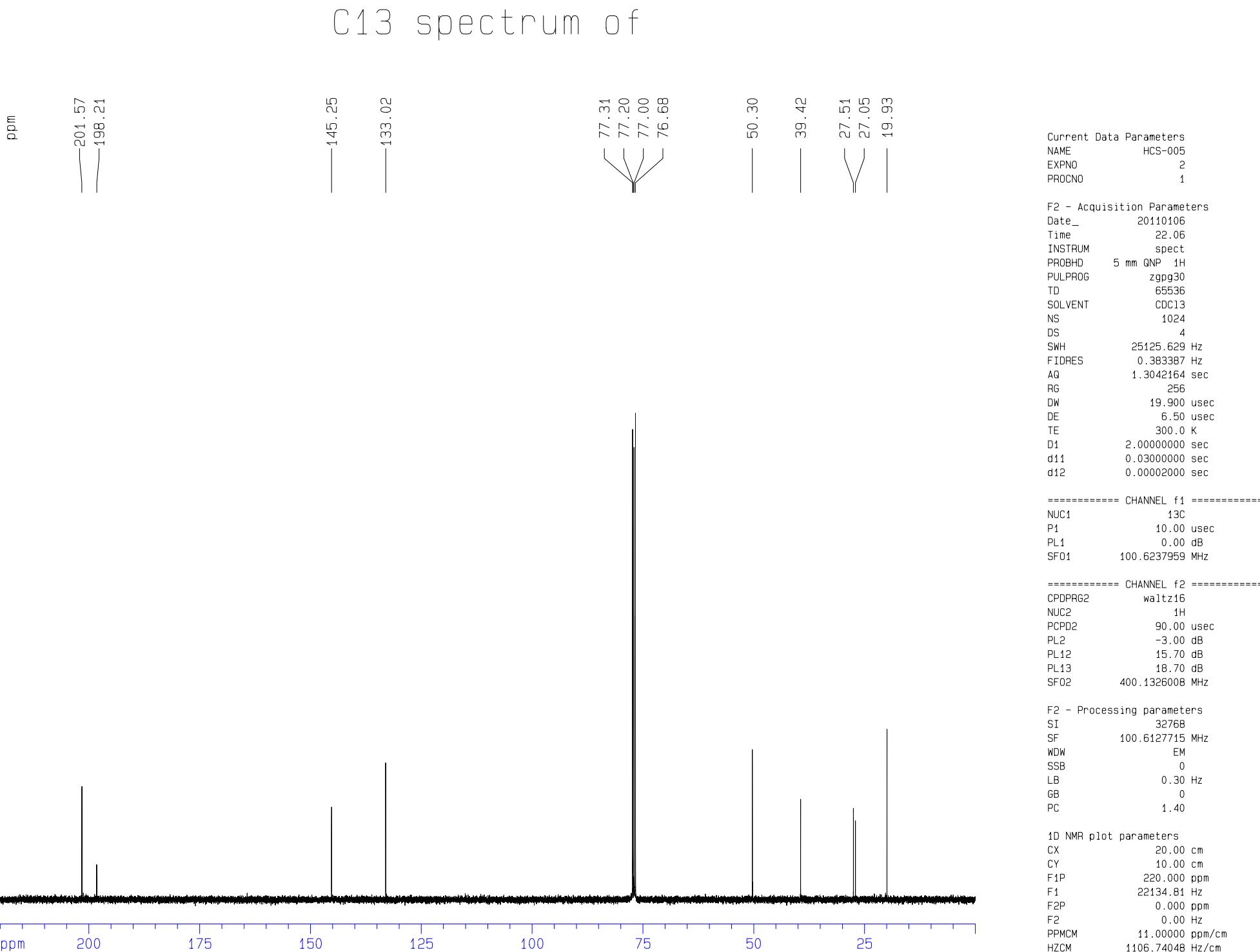


Fig S13. DEPT of compound 3.

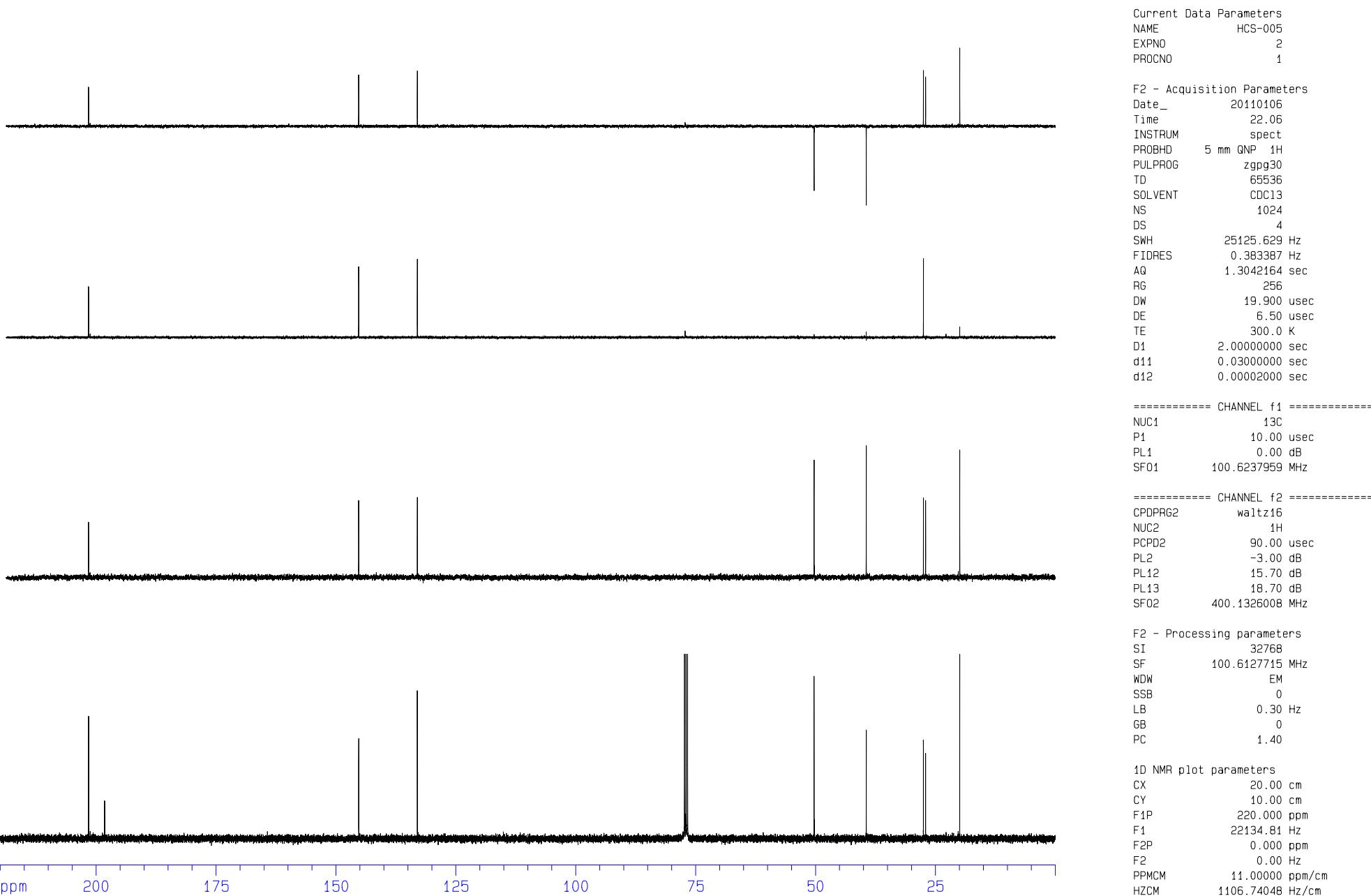


Fig S14.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) of compound 2.

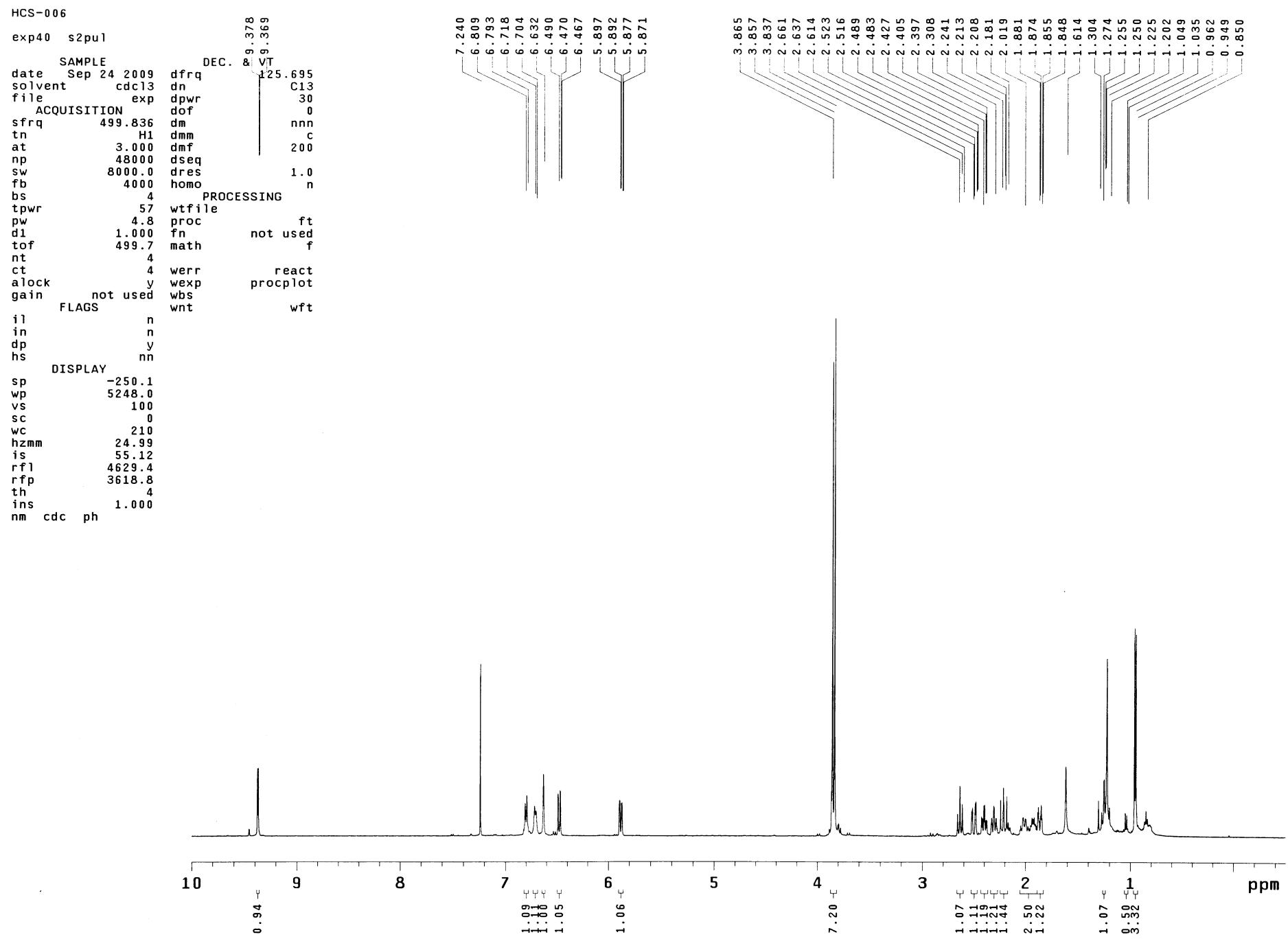


Fig S15.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) of compound 2.

HCS-006  
exp41 s2pul

SAMPLE	DEC.	VT
date Sep 24 2009	dfrq	499.836
solvent cdc13	dn	H1
file exp	dpwr	39
ACQUISITION	dof	0
sfrq 125.698	dm	yyy
tn C13	dmm	w
at 1.000	dmf	11905
np 62894	dseq	
sw 31446.5	dres	1.0
fb 17000	homo	n
bs 16	PROCESSING	
ss 2	lb	1.00
tpwr 54	wtfile	
pw 4.0	proc	ft
d1 1.000	fn	not used
tof 2512.2	math	f
nt 1000		
ct 1000	werr	react
alock y	wexp	procplot
gain not used	wbs	testsn
FLAGS	wnt	
il n		
in n		
dp y		
hs nn		

DISPLAY

sp -1256.9
wp 27650.1
vs 188
sc 0
wc 210
hzmm 131.67
is 500.00
rfl 10979.6
rfp 9677.6
th 3
ins 100.000
nm ph

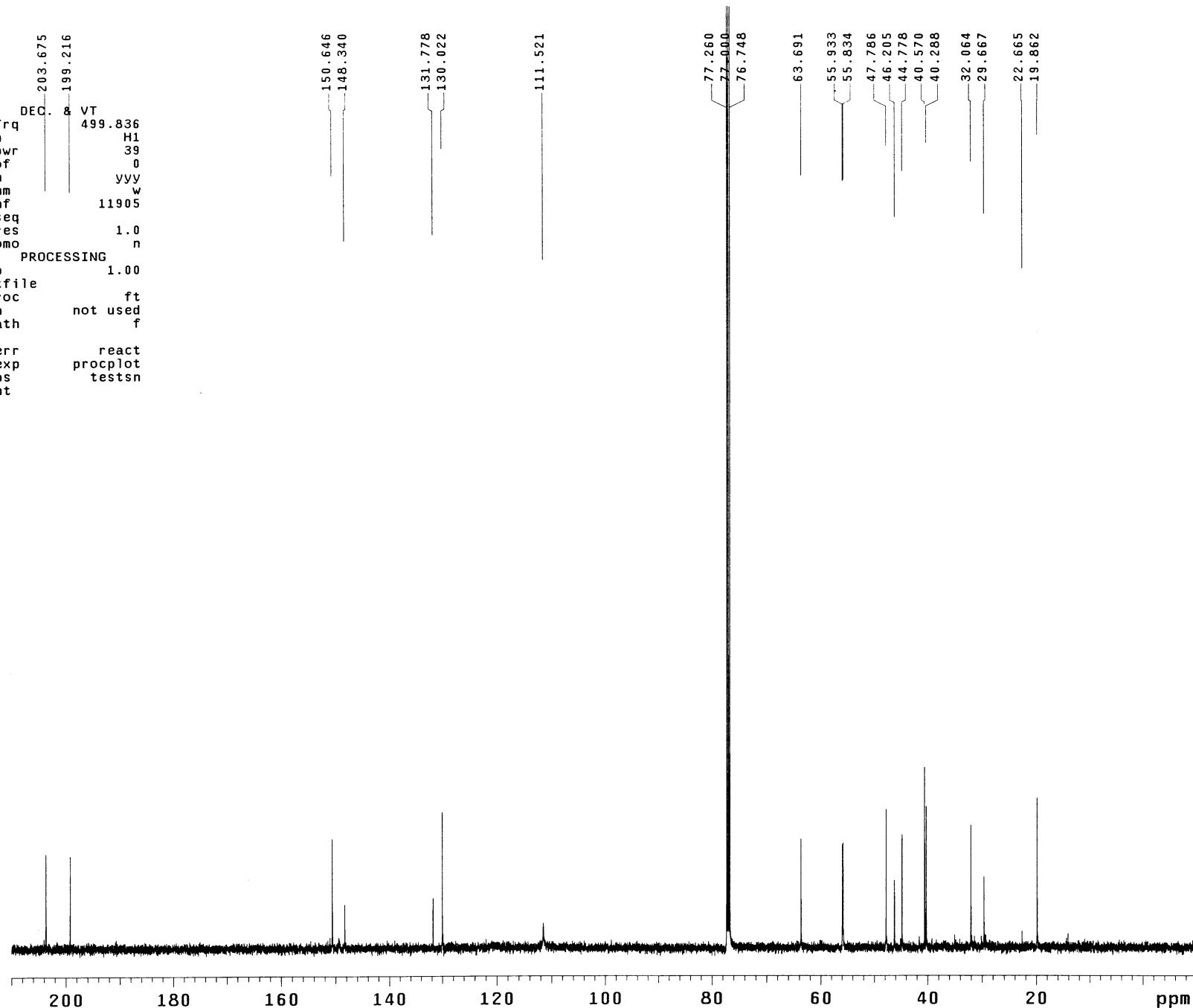


Fig S16. DEPT of compound 2.

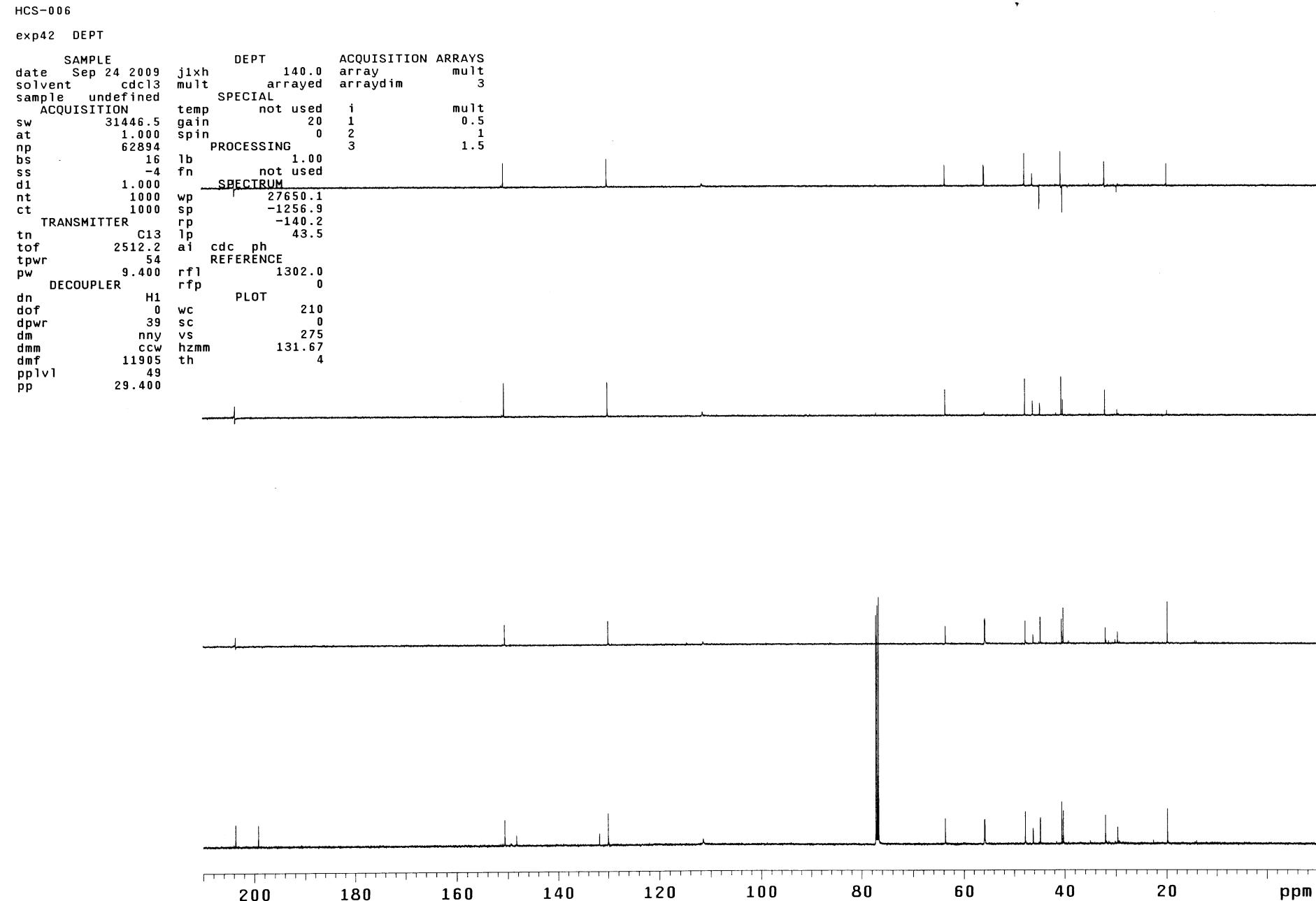




Fig S18. COSY of compound 2, expanded.

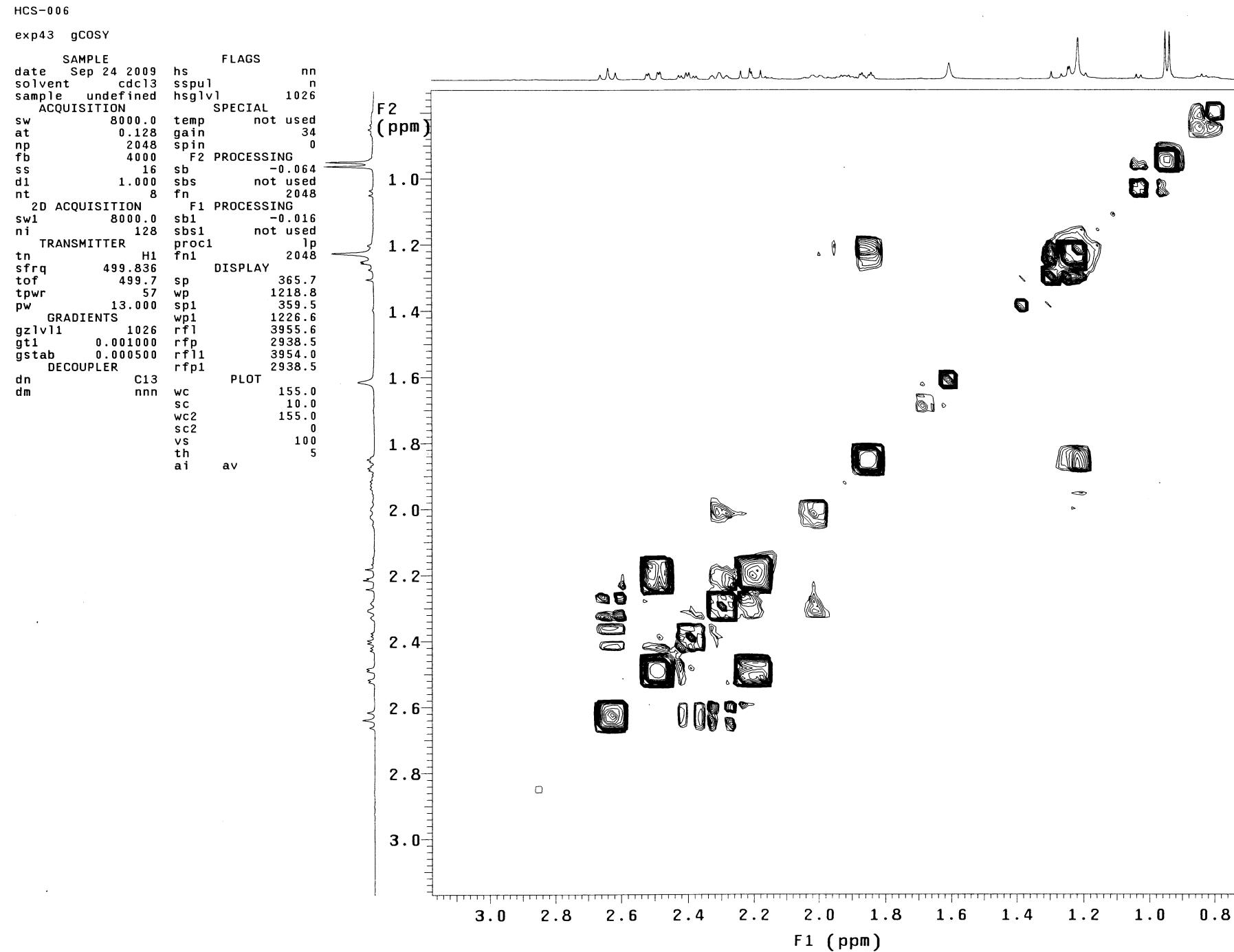


Fig S19. HMQC of compound 2.

HCS-006

exp45 gHMQC

```
SAMPLE          FLAGS          ACQUISITION ARRAYS
date   Sep 24 2009 hs      n      array    phase
solvent cdc13  sspul   y      arraydim  256
sample  undefined PFGflg   y
ACQUISITION   hsglv1  1026   i      phase
sw     8000.0   SPECIAL   1
at     0.128    temp     not used  2
np     2048     gain     54
fb     4000     spin     0
ss     32       GRADIENTS
d1     1.000    gzlv11  1026
nt     8        gt1      0.001000
2D ACQUISITION   gzlv13  516
sw1    21367.5  gt3      0.001000
ni     128      gstab    0.000500
phase  arrayed  F2 PROCESSING
TRANSMITTER   gf      0.059
tn     H1       gfs     not used
sfreq  499.836 fn      2048
tof    499.7   F1 PROCESSING
tpwr   57       gfi     0.006
pw     13.000  gfsi    not used
DECOUPLER    proc1   1p
dn     C13     fni     2048
dof    -2515.1 DISPLAY
dm     nny      sp      123.5
dmm    ccp      wp      4523.4
dmf    32258   spi     1871.5
dpwr   35       wpi     17423.7
pxl1v1 51       rfp     3950.9
pxw   14.700   rfp1    2941.5
      HMQC    rfp1    15316.5
j1xh  140.0    rfp1    14016.3
nullflg y       PLOT
wc     150.0
sc     6.2
wc2   116.2
sc2   0
vs    100
th
ai   cdc   ph
```

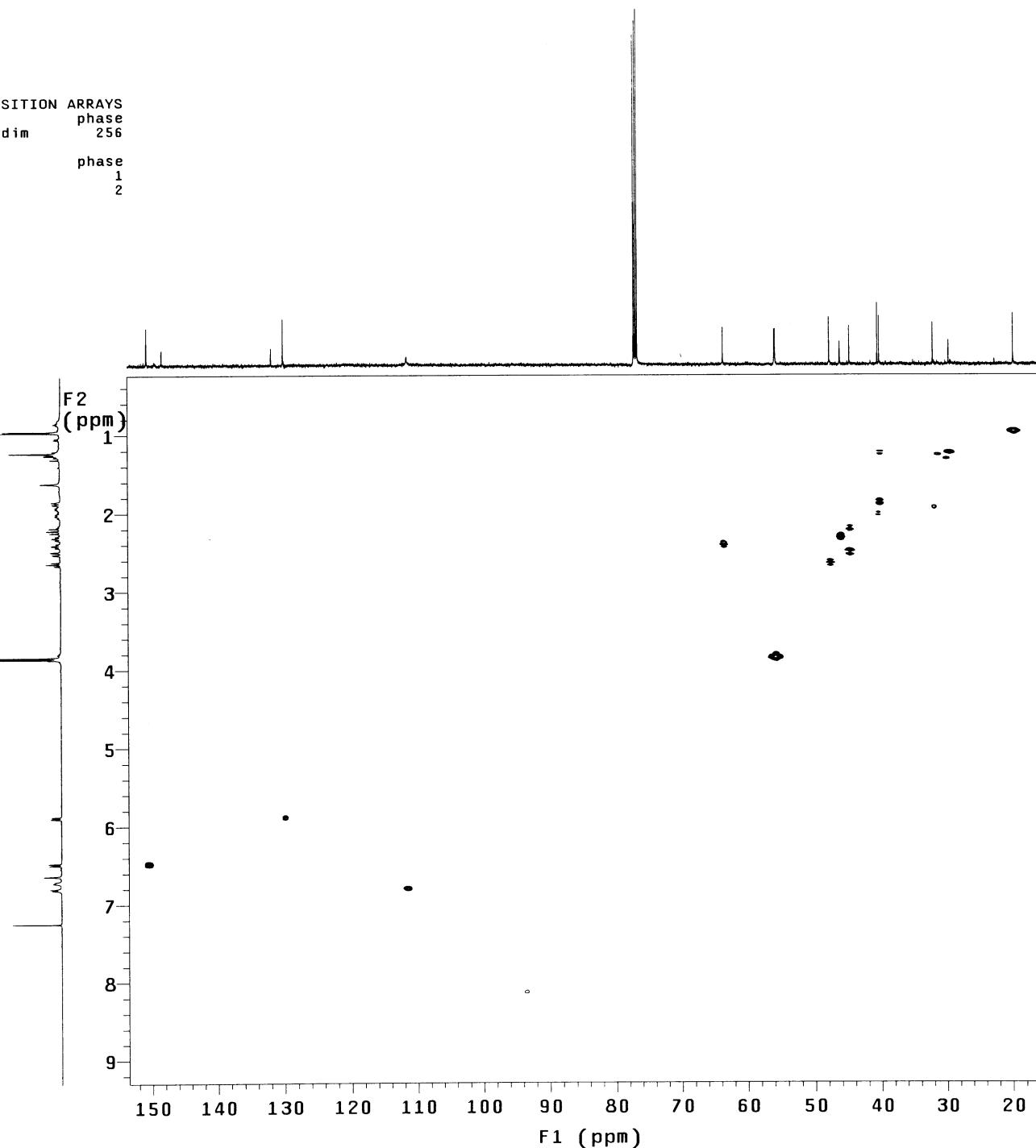


Fig S20. NOESY of compound 2.

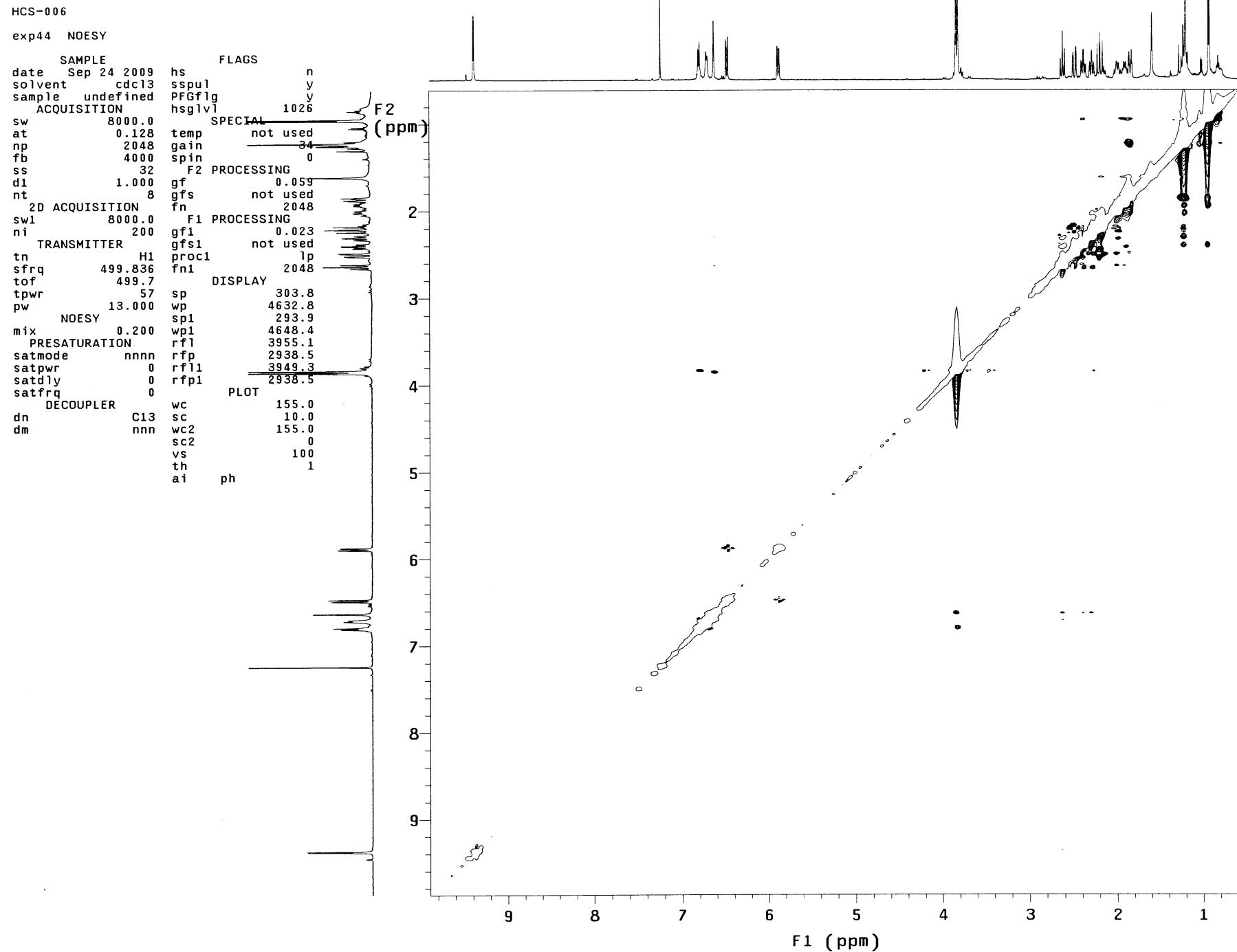
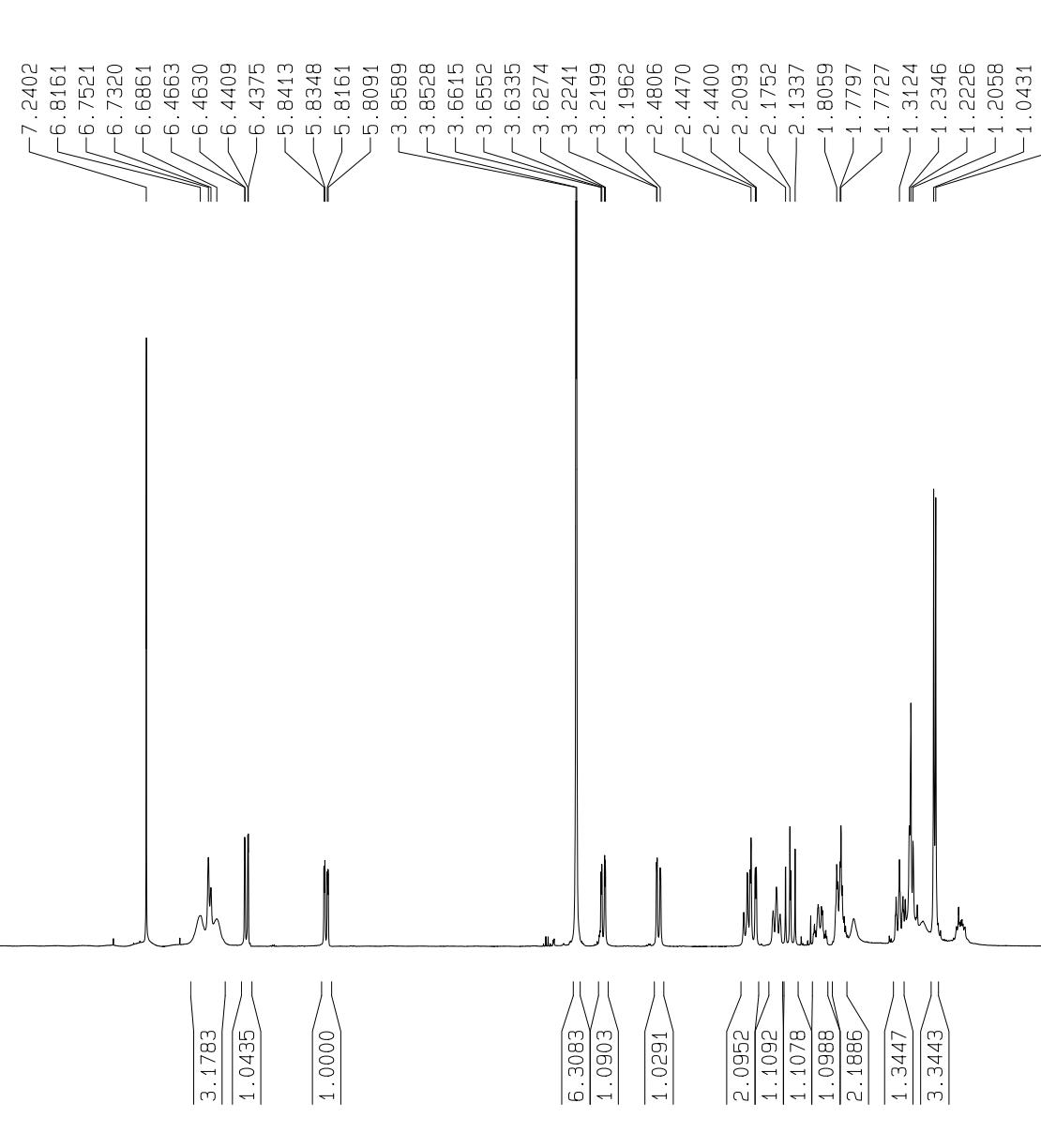


Fig S21.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) of compound 6.

ppm

Integral

ppm



Current Data Parameters

NAME HCS-3-80-P  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters

Date\_ 20110405  
Time 15.44  
INSTRUM spect  
PROBHD 5 mm QNP 1H  
PULPROG zg30  
TD 16384  
SOLVENT CDCl<sub>3</sub>  
NS 16  
DS 0  
SWH 5995.204 Hz  
FIDRES 0.365918 Hz  
AQ 1.3664756 sec  
RG 645.1  
DW 83.400 usec  
DE 6.50 usec  
TE 300.0 K  
D1 1.5000000 sec

===== CHANNEL f1 =====

NUC1 1H  
P1 10.90 usec  
PL1 -3.00 dB  
SF01 400.1326008 MHz

F2 - Processing parameters

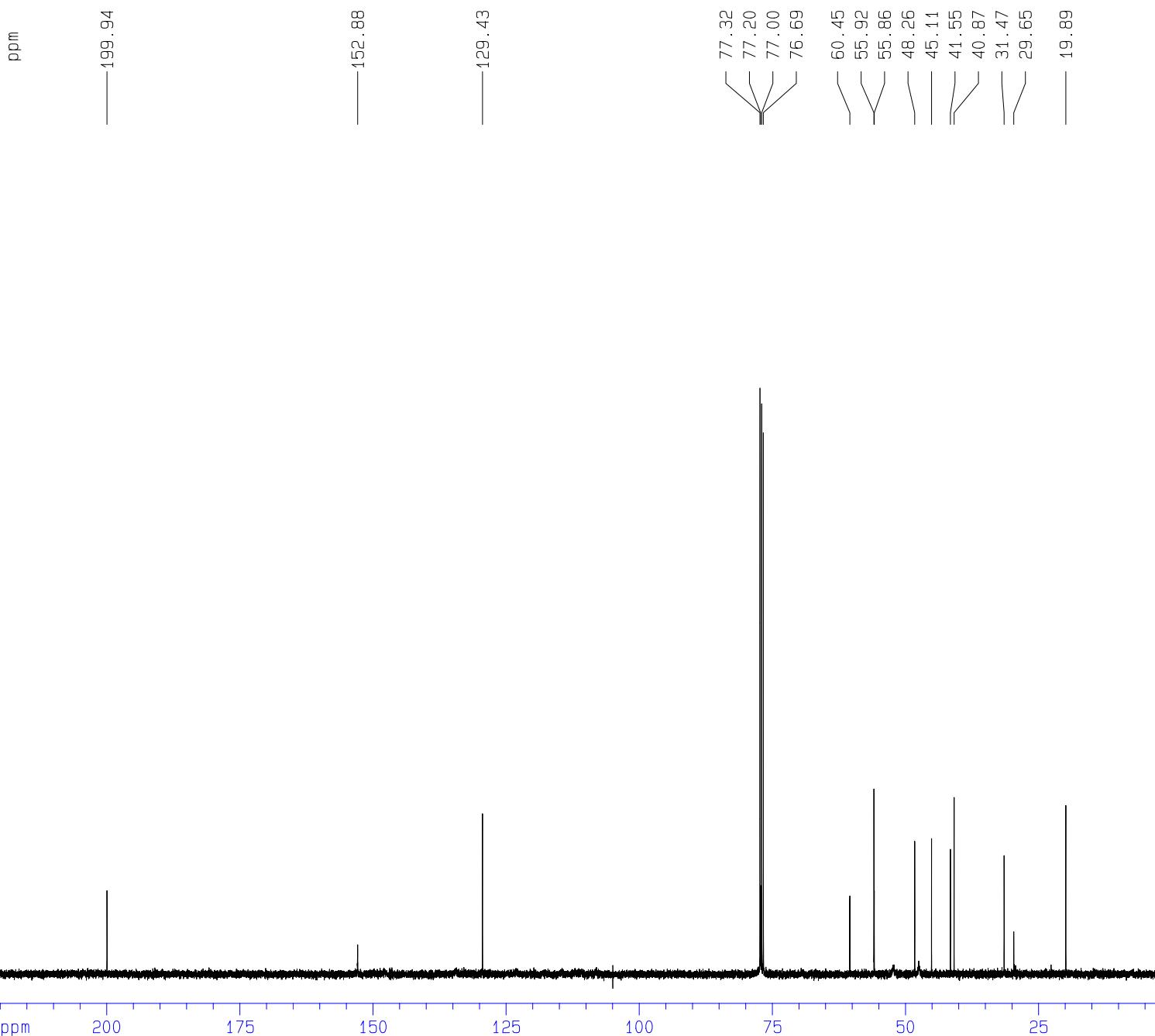
SI 8192  
SF 400.1300171 MHz  
WDW EM  
SSB 0  
LB 0.10 Hz  
GB 0  
PC 1.00

1D NMR plot parameters

CX 21.50 cm  
CY 25.00 cm  
F1P 12.000 ppm  
F1 4801.56 Hz  
F2P -0.000 ppm  
F2 -0.00 Hz  
PPMCM 0.55814 ppm/cm  
HZCM 223.32838 Hz/cm

Fig S22.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz) of compound 6.

$\text{C}^{13}$  spectrum of



Current Data Parameters  
NAME HCS-3-80-P  
EXPNO 2  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20110405  
Time 16.24  
INSTRUM spect  
PROBHD 5 mm QNP 1H  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 1024  
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 2.0000000 sec  
d11 0.03000000 sec  
d12 0.00002000 sec

===== CHANNEL f1 =====  
NUC1 13C  
P1 10.00 usec  
PL1 0.00 dB  
SF01 100.6237959 MHz

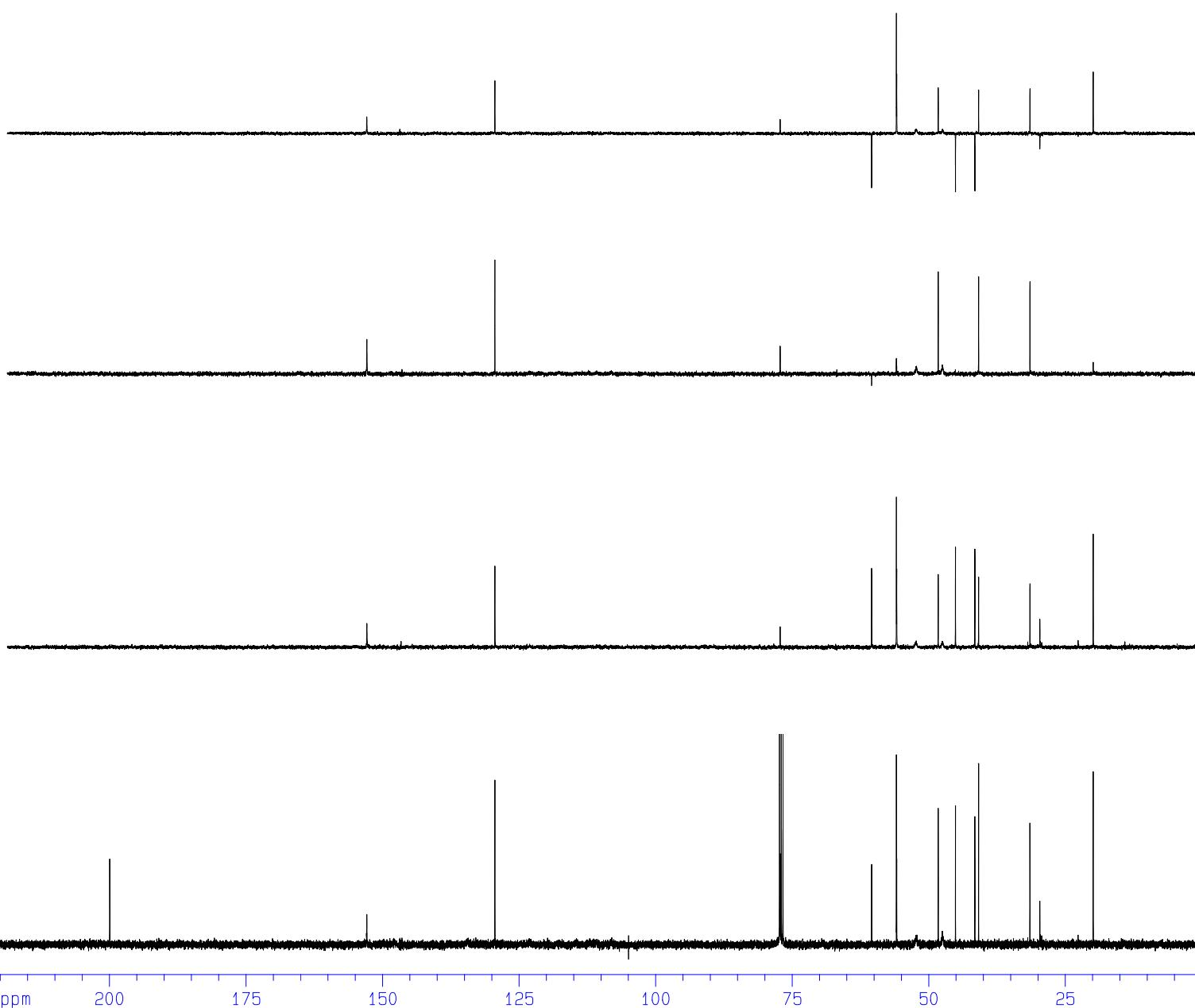
===== CHANNEL f2 =====  
CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PL2 -3.00 dB  
PL12 15.70 dB  
PL13 18.70 dB  
SF02 400.1326008 MHz

F2 - Processing parameters  
SI 32768  
SF 100.6127738 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.40

1D NMR plot parameters  
CX 20.00 cm  
CY 10.00 cm  
F1P 220.000 ppm  
F1 22134.81 Hz  
F2P 0.000 ppm  
F2 0.00 Hz  
PPCM 11.00000 ppm/cm  
HZCM 1106.74048 Hz/cm

Fig S23. DEPT of compound 6.

S23



Current Data Parameters

NAME HCS-3-80-P  
EXPNO 2  
PROCNO 1

F2 - Acquisition Parameters

Date\_ 20110405  
Time 16.24  
INSTRUM spect  
PROBHD 5 mm QNP 1H  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 1024  
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 2.0000000 sec  
d11 0.03000000 sec  
d12 0.00002000 sec

===== CHANNEL f1 =====

NUC1 13C  
P1 10.00 usec  
PL1 0.00 dB  
SF01 100.6237959 MHz

===== CHANNEL f2 =====

CPDPG2 waltz16  
NUC2 1H  
PCPD2 90.00 usec  
PL2 -3.00 dB  
PL12 15.70 dB  
PL13 18.70 dB  
SF02 400.1326008 MHz

F2 - Processing parameters

SI 32768  
SF 100.6127738 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.40

1D NMR plot parameters

CX 20.00 cm  
CY 10.00 ppm  
F1P 220.000 ppm  
F1 22134.81 Hz  
F2P 0.000 ppm  
F2 0.00 Hz  
PPCM 11.00000 ppm/cm  
HZCM 1106.74048 Hz/cm

Fig S24.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) of compound 7.

HCS-3-82-c  
exp51 s2pul  
  
SAMPLE DEC. & VT  
date Jul 17 2011 dfrq 125.693  
solvent cdc13 dn C13  
file exp dpwr 30  
ACQUISITION dof 0  
sfrq 499.830 dm nnn  
tn H1 dmm c  
at 3.000 dmf 200  
np 48000 dseq  
sw 8000.0 dres 1.0  
fb not used homo n  
bs 4  
tpwr 58 wfile  
pw 4.8 proc ft  
d1 1.000 fn not used  
tof 499.7 math f  
nt 4  
ct 4 werr react  
alock y wexp procplot  
gain not used wbs  
FLAGS wnt wft  
il n  
in  
dp y  
hs nn  
  
DISPLAY  
sp -250.1  
wp 5747.8  
vs 85  
sc 0  
wc 210  
hzmm 27.37  
is 284.06  
rfl 4637.9  
rfp 3618.7  
th 2  
ins 100.000  
nm cdc ph

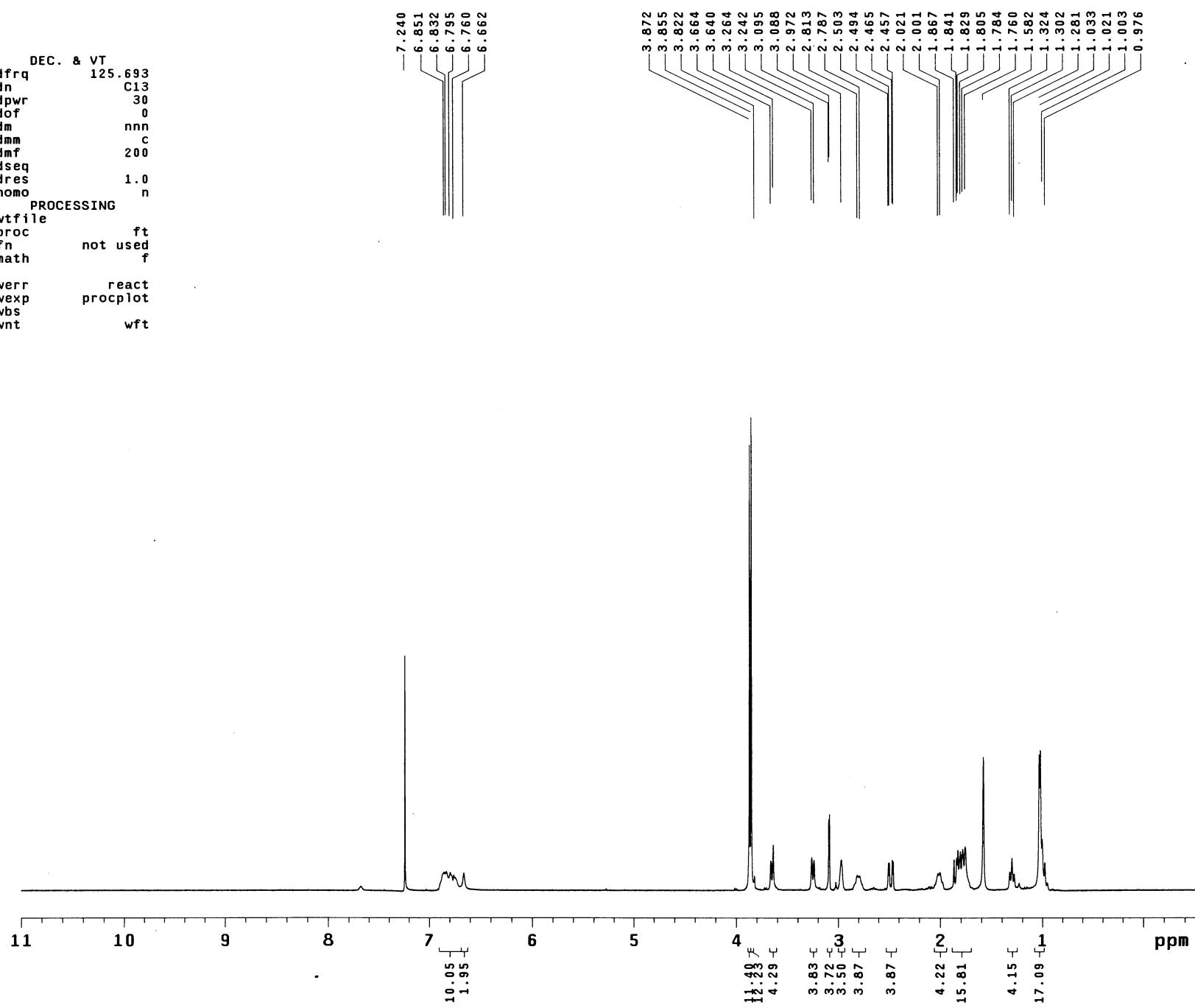


Fig S25.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) of compound 7.

HCS-3-82-c  
exp52 s2pul  
  
SAMPLE DEC. & VT  
date Jul 17 2011 dfrq 499.829  
solvent cdc13 dn H1  
file exp dpwr 42  
ACQUISITION dof 0  
sfrq 125.696 dm yyy  
tn C13 dmm w  
at 1.000 dmf 11696  
np 62894 dseq  
sw 31446.5 dres 1.0  
fb not used homo n  
bs 16 PROCESSING  
ss 2 lb 1.00  
tpwr 56 wfile  
pw 3.0 proc ft  
d1 2.000 fn not used  
tof 2512.2 math f  
nt 5000  
ct 5000 werr react  
alock y wexp procplot  
gain not used wbs testsn  
FLAGS wnt  
il n  
in n  
dp y  
hs nn  
  
DISPLAY  
sp -0.8  
wp 27649.1  
vs 546  
sc 0  
wc 210  
hzmm 131.67  
is 500.00  
rfl 10980.6  
rfp 9677.5  
th 7  
ins 100.000  
nm cdc ph

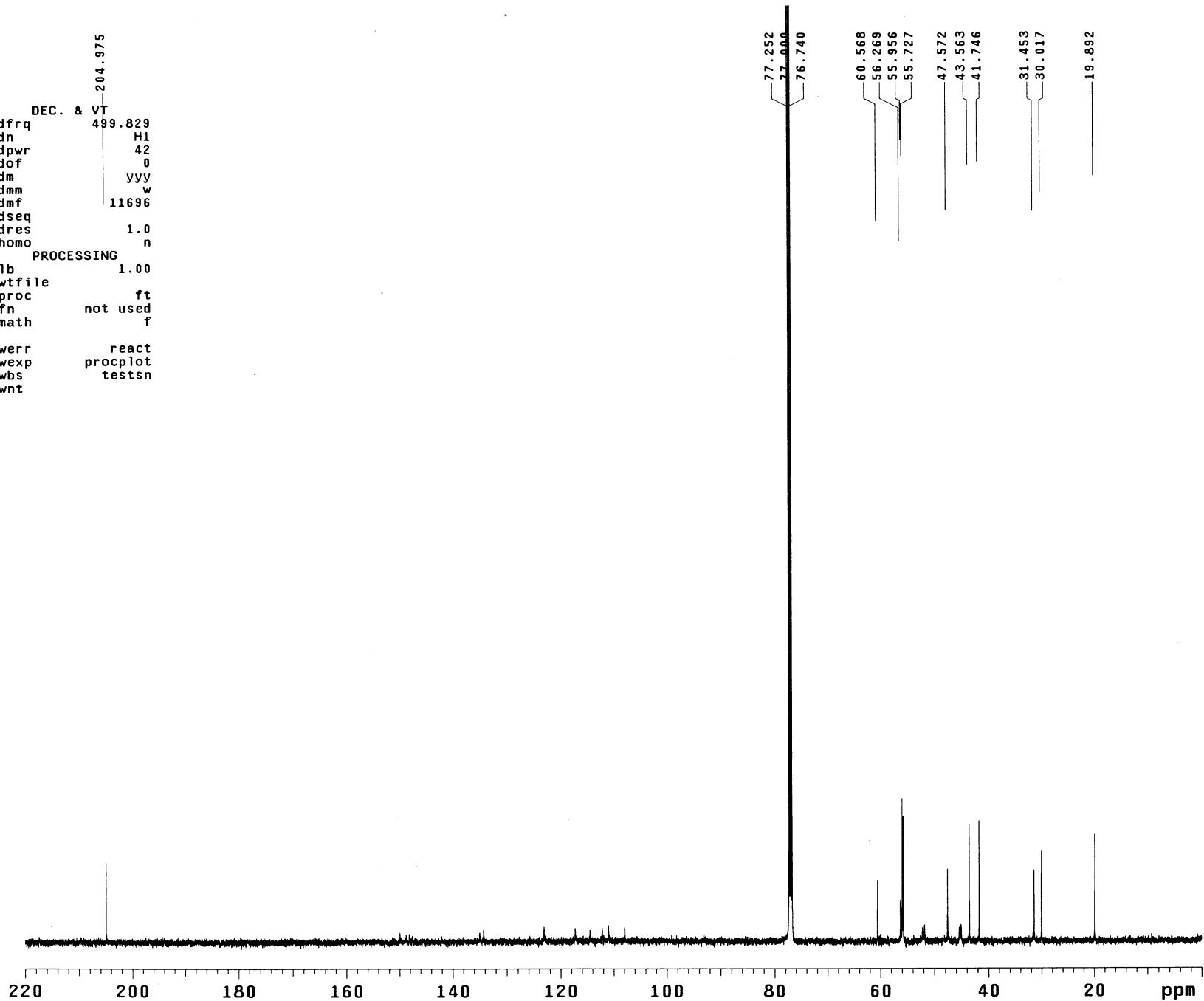


Fig S26.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) of compound 7.

HCS-3-82-c  
exp52 s2pul  
  
SAMPLE  
date Jul 17 2011 dfrq 219.384  
solvent cdc13 dn 203.112  
file exp dpwr 829  
ACQUISITION  
sfrq 125.696 dof 49.924.975  
tn C13 dm 42  
at 1.000 dmm 0  
np 62894 dseq 11696  
sw 31446.5 dres 1.0  
fb not used homb vvv  
bs 16 PROCESSING w  
ss 2 lb 1.00  
tpwr 56 wtfile ft  
pw 3.0 proc not used f  
d1 2.000 fn math f  
tof 2512.2 react  
nt 5000 werr  
ct 5000 wexp procplot  
alock y testsn  
gain not used wbs  
FLAGS wnt  
il n  
in n  
dp y  
hs nn  
  
DISPLAY  
sp -0.8  
wp 27649.1  
vs 3355  
sc 0  
wc 210  
hzmm 131.67  
is 500.00  
rf1 10980.6  
rfp 9677.5  
th 7  
ins 100.000  
nm cdc ph

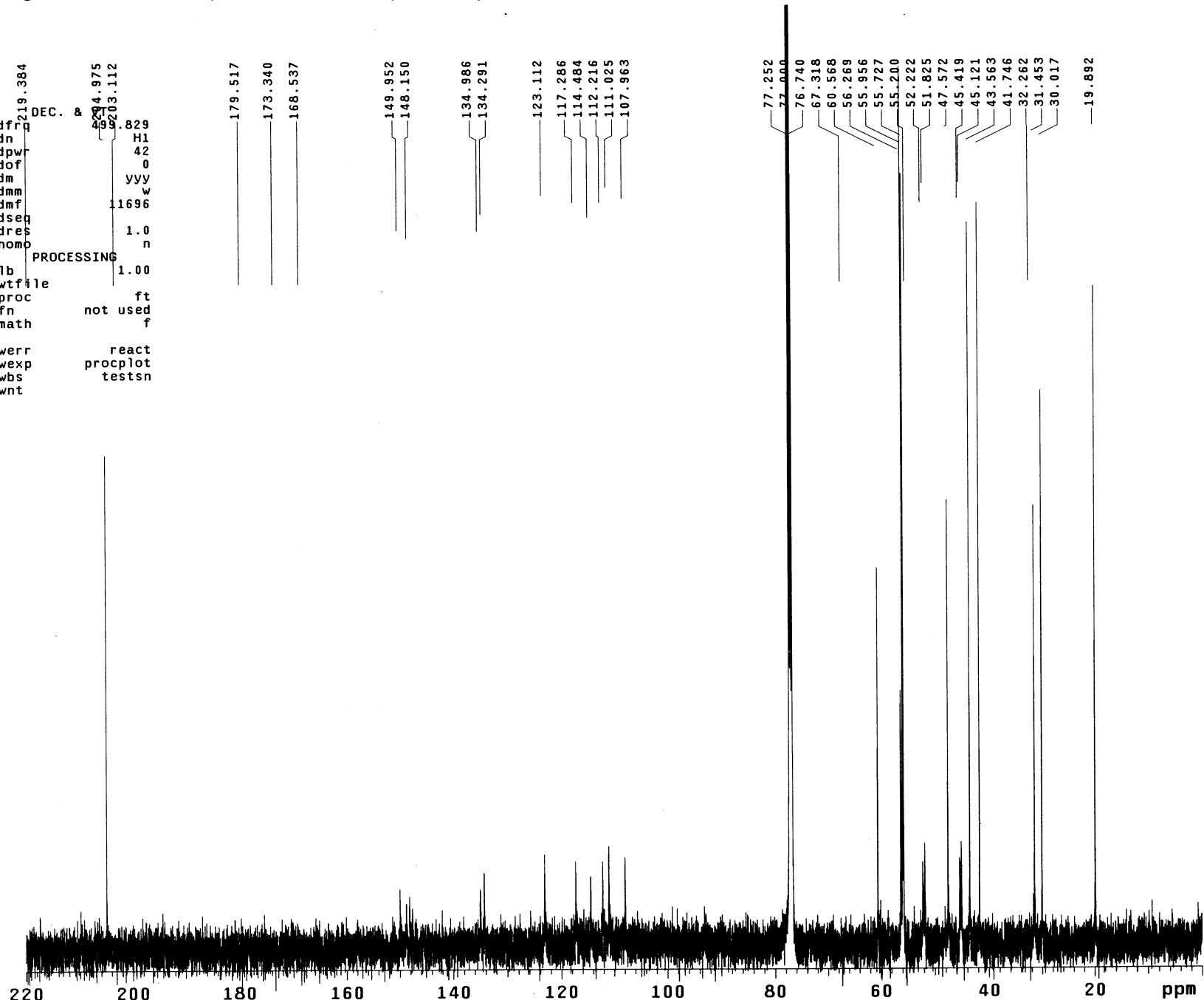


Fig S27.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) of compound 7, expanded.

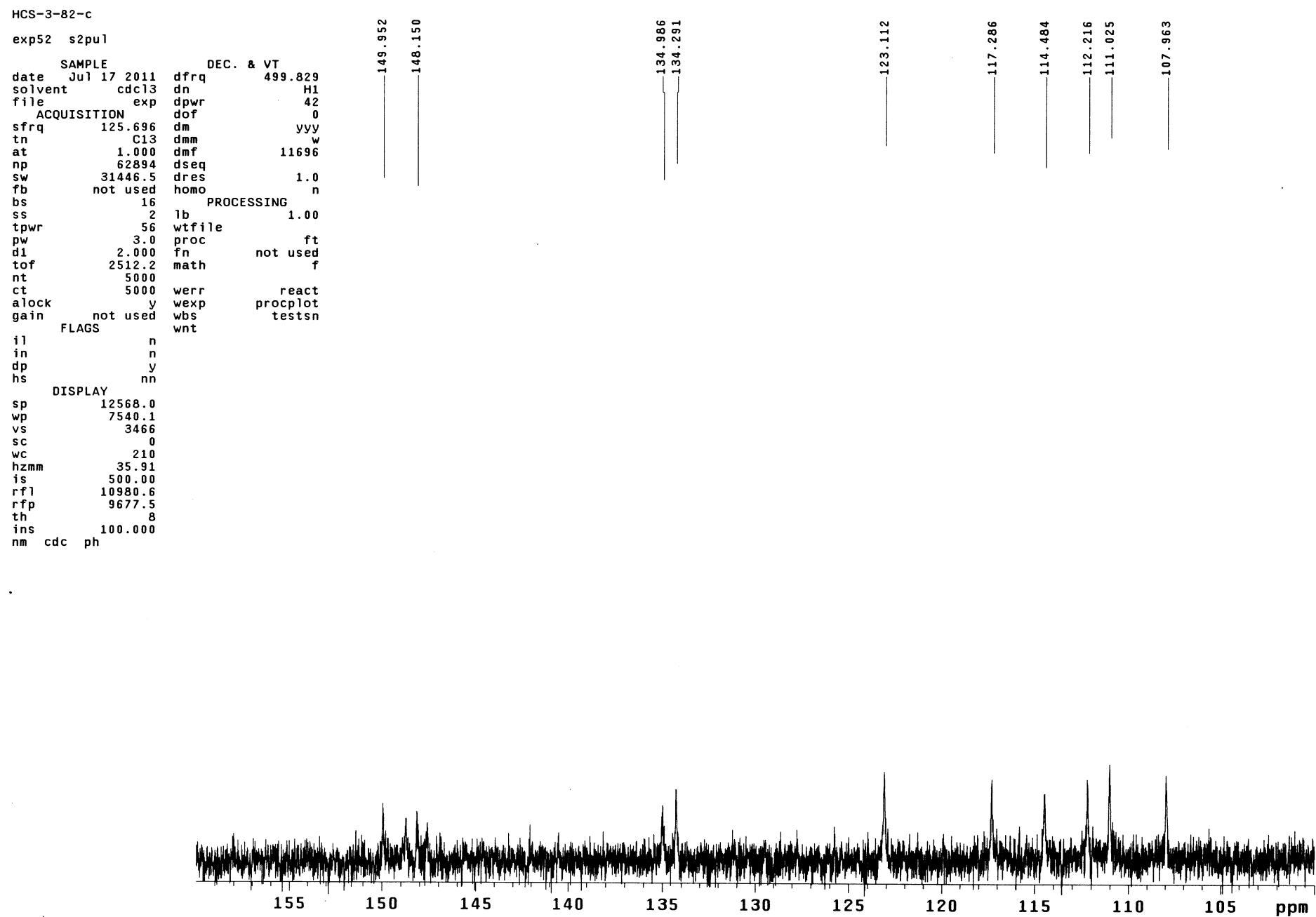


Fig S28. DEPT of compound 7

HCS-3-82-c

exp53 DEPT

```

SAMPLE          DEPT      ACQUISITION ARRAYS
date   Jul 17 2011 j1xh     140.0 array    multi
solvent    cdcl3    mult     arrayed   arraydim
sample    undefined
ACQUISITION
sw       31446.5  temp     not used  i      multi
at        1.000   gain      54      1      0.1
np       62894    spin      0       2
bs        16      lb        1.00
ss        -4      fn        not used
di       1.000   PROCESSING
nt       2048    wp        27649.1
ct       2048    sp        -0.8
          TRANSMITTER
tn       C13     rp        126.3
tof      2512.2  ai        cdc ph
tpwr     56      REFERENCE
pw       10.800  rfl       1303.1
          DECOUPLER
dn        H1      rfp       0
dof       0       wc        210
dpwr     42      sc        0
dm       nny     vs        977
dmm      ccw     hzmm     131.67
dmf      11696   th        68
pp1vl    53
pp       27.400

```

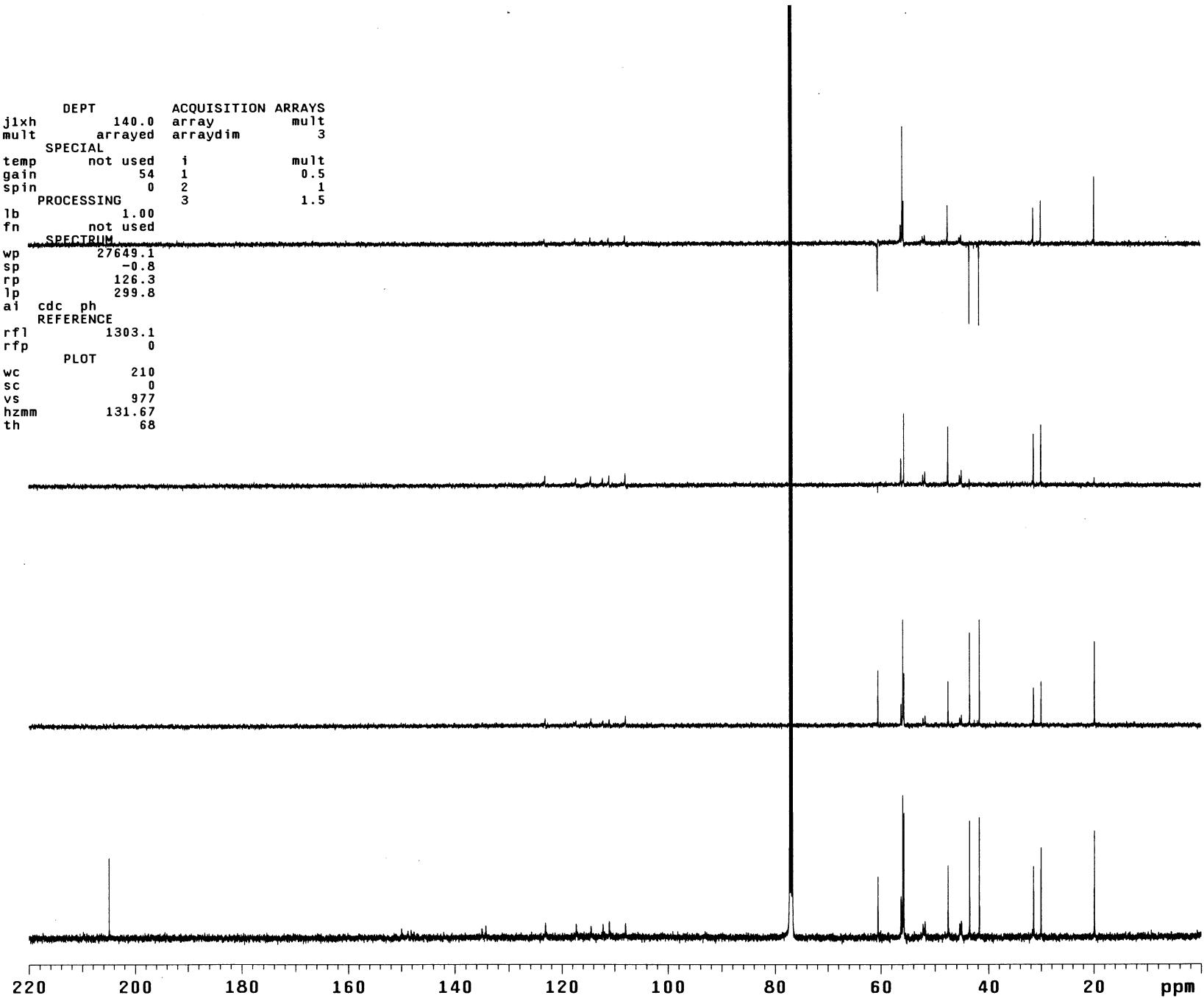


Fig S29. DEPT of compound 7, expanded.

HCS-3-82-c

exp53 DEPT

SAMPLE	DEPT	ACQUISITION ARRAYS
date Jul 17 2011	j1xh 140.0	array mult
solvent cdc13	mult arrayed	arraydim 3
sample undefined	SPECIAL	
ACQUISITION	temp not used	i mult
sw 31446.5	gain 54	1 0.5
at 1.000	spin 0	2 1
np 62894	PROCESSING 3 1.5	
bs 16	lb 1.00	
ss -4	fn not used	
d1 1.000		
nt 2048	wp 12568.1	
ct 2048	sp 12568.0	
TRANSMITTER		
tn C13	rp 126.3	
tof 2512.2	lp 299.8	
tpwr 56	ai cdc ph	
pw 10.800	REFERENCE	
DECOUPLER		
dn H1	PLOT	
dof 0	wc 210	
dpwr 42	sc 0	
dm nny	vs 7192	
dmm ccw	hzmm 35.91	
dmf 11696	th 68	
pplv1 53		
pp 27.400		

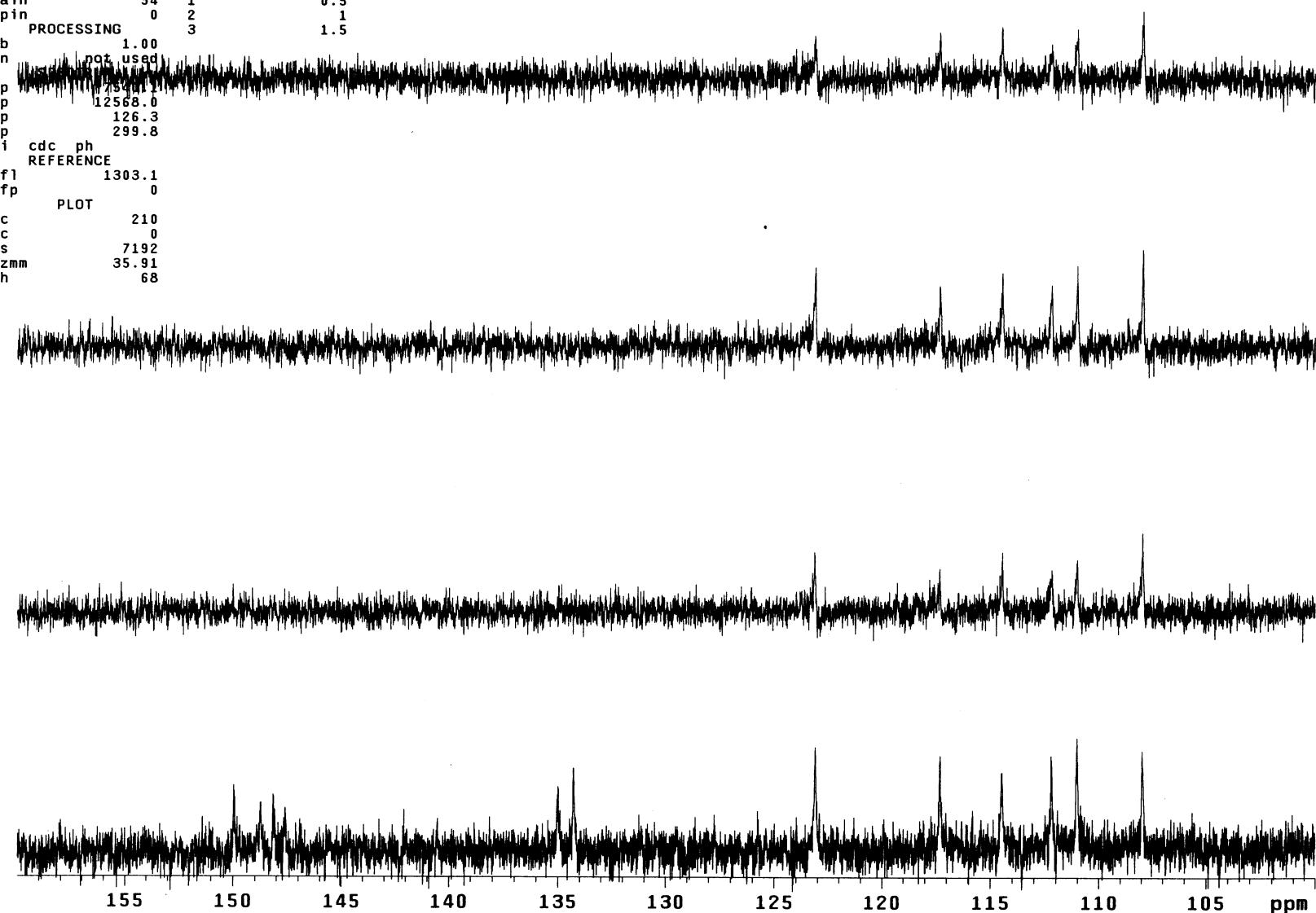


Fig S30. HSQC of compound 7.

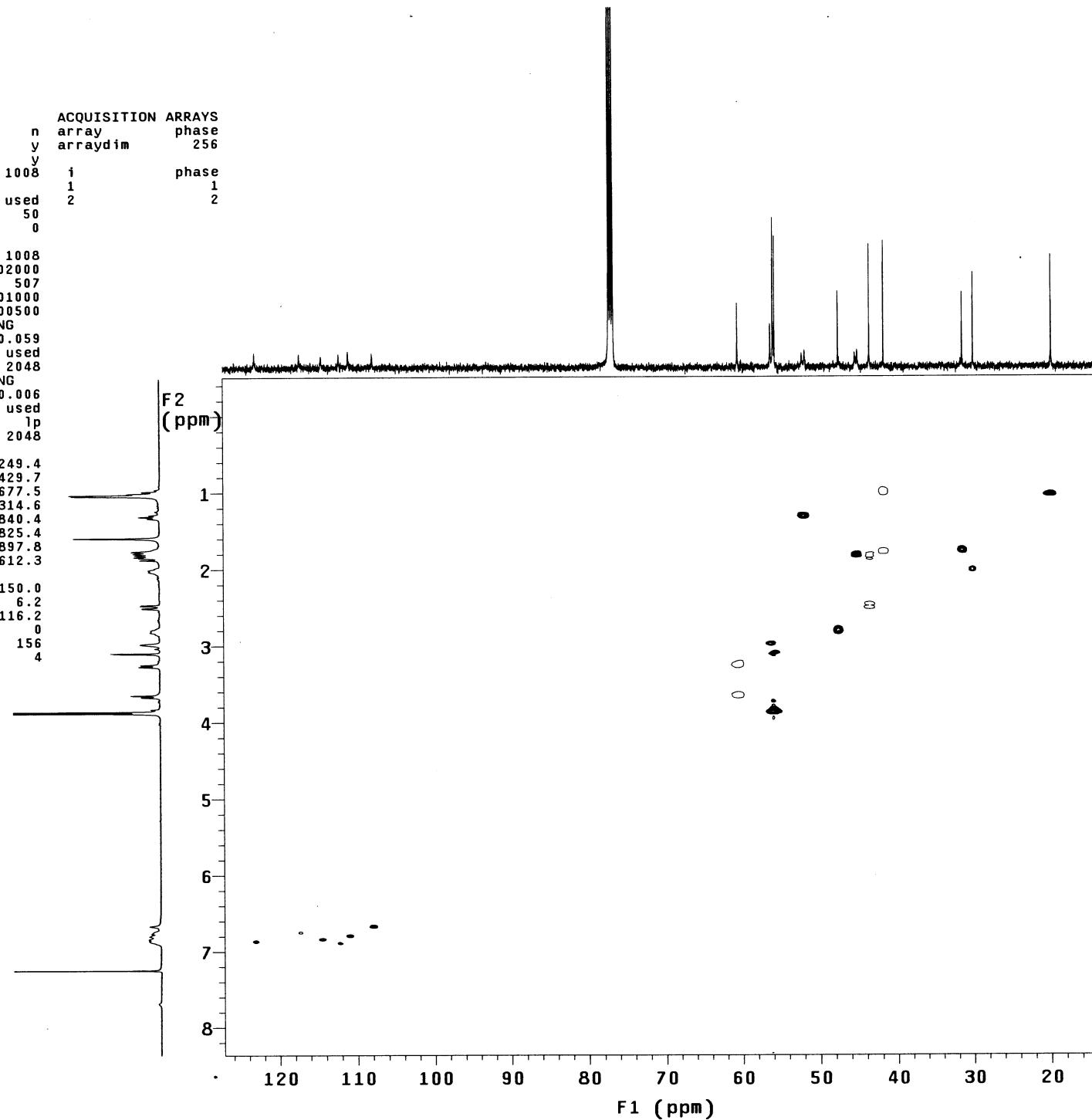
HCS-3-82-c

exp58 gHSQC

```

SAMPLE          FLAGS          ACQUISITION ARRAYS
date Jul 20 2011 hs      n    array      phase
solvent   cdc13 sspul   y    arraydim   256
sample   undefined PFGflg
ACQUISITION   hsglvl  1008 i    phase
sw      8000.0  SPECIAL  1    1
at      0.128   temp     not used  2
np      2048    gain     50
fb      not used spin     0
ss      32      GRADIENTS
d1      1.000   gzlvl1  1008
nt      8        gt1     0.002000
2D ACQUISITION  gzlvl13 507
sw1     21367.5 gt3     0.001000
ni      128     gstab   0.000500
phase   arrayed
TRANSMITTER   F2 PROCESSING
tn      H1      gfs     not used
sfreq  499.830 fn      2048
tof     499.7   F1 PROCESSING
tpwr   58      gfi     0.006
pw     14.000  gfs1    not used
DECOUPLER    proc1   1p
dn      C13    fn1    2048
dof    -2515.2 DISPLAY
dm      nny    sp     -249.4
dmm    ccp    wp     4429.7
dmf    32258  spi    1677.5
dpwr   38     wp1    14314.6
pxl1v1 54     rfp    2840.4
pxw    14.000 rfp1   1825.4
HSQC
j1xh  140.0   rfp1   8897.8
nullflg y      PLOT
mult   2      wc     150.0
      sc     6.2
      wc2   116.2
      sc2   0
      vs    156
      th    4
ai    cdc  ph

```



HCS-3-82-c

exp58 gHSQC

```

SAMPLE          FLAGS          ACQUISITION ARRAYS
date   Jul 20 2011 hs      n    array      phase
solvent   cdc13 sspul     y    arraydim   256
sample   undefined PFGflg
ACQUISITION   hsglvl    1008 i      phase
sw      8000.0  SPECIAL    1
at      0.128   temp       not used  2
np      2048    gain       50
fb      not used spin       0
ss      32       GRADIENTS
d1      1.000   gzlvl1    1008
nt      8        gt1        0.002000
2D ACQUISITION   gzlvl13   507
sw1     21367.5 gt3        0.001000
ni      128     gstab      0.000500
phase   arrayed   F2 PROCESSING
TRANSMITTER   gf        0.059
tn      H1       gfs       not used
sfrq   499.830 fn        2048
tof     499.7   F1 PROCESSING
tpwr   58       gfi        0.006
pw     14.000   gfs1      not used
DECOUPLER    C13       proc1    1p
dn      -2515.2  DISPLAY
dm      nny      sp        39.7
dmm    ccp      wp        2648.4
dmf    32258   spi       1823.6
dpwr   38       wp1       8513.6
pxl1v1 54       rfl       2840.4
px     14.000   rfp       1825.4
HSQC
j1xh   140.0   rfp1      8897.8
nullflg y       PLOT
mult   2        wc        150.0
      sc        6.2
      wc2      116.2
      sc2      0
      vs        156
      th        4
ai      cdc      ph

```

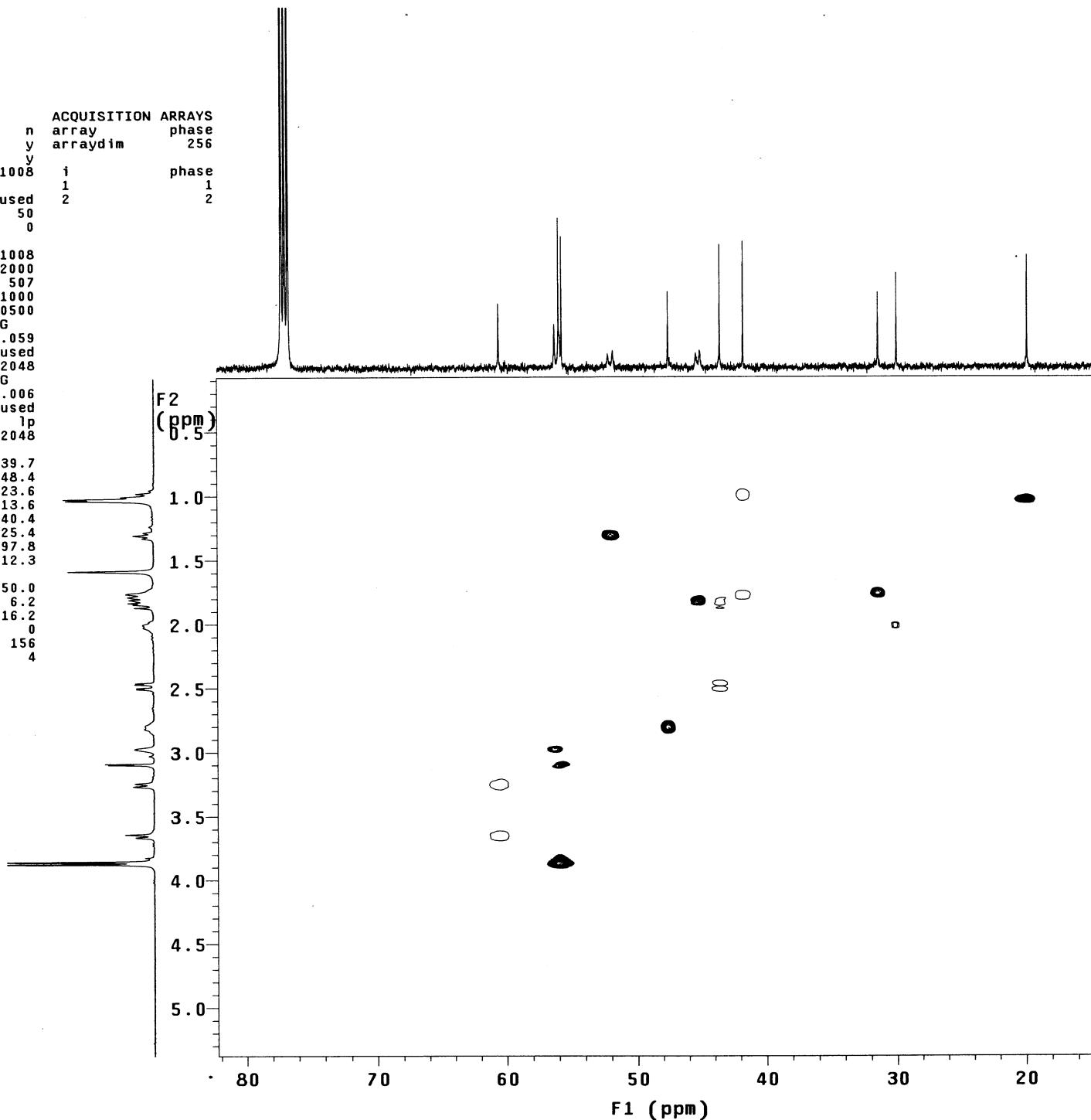


Fig S32. COSY of compound 7.

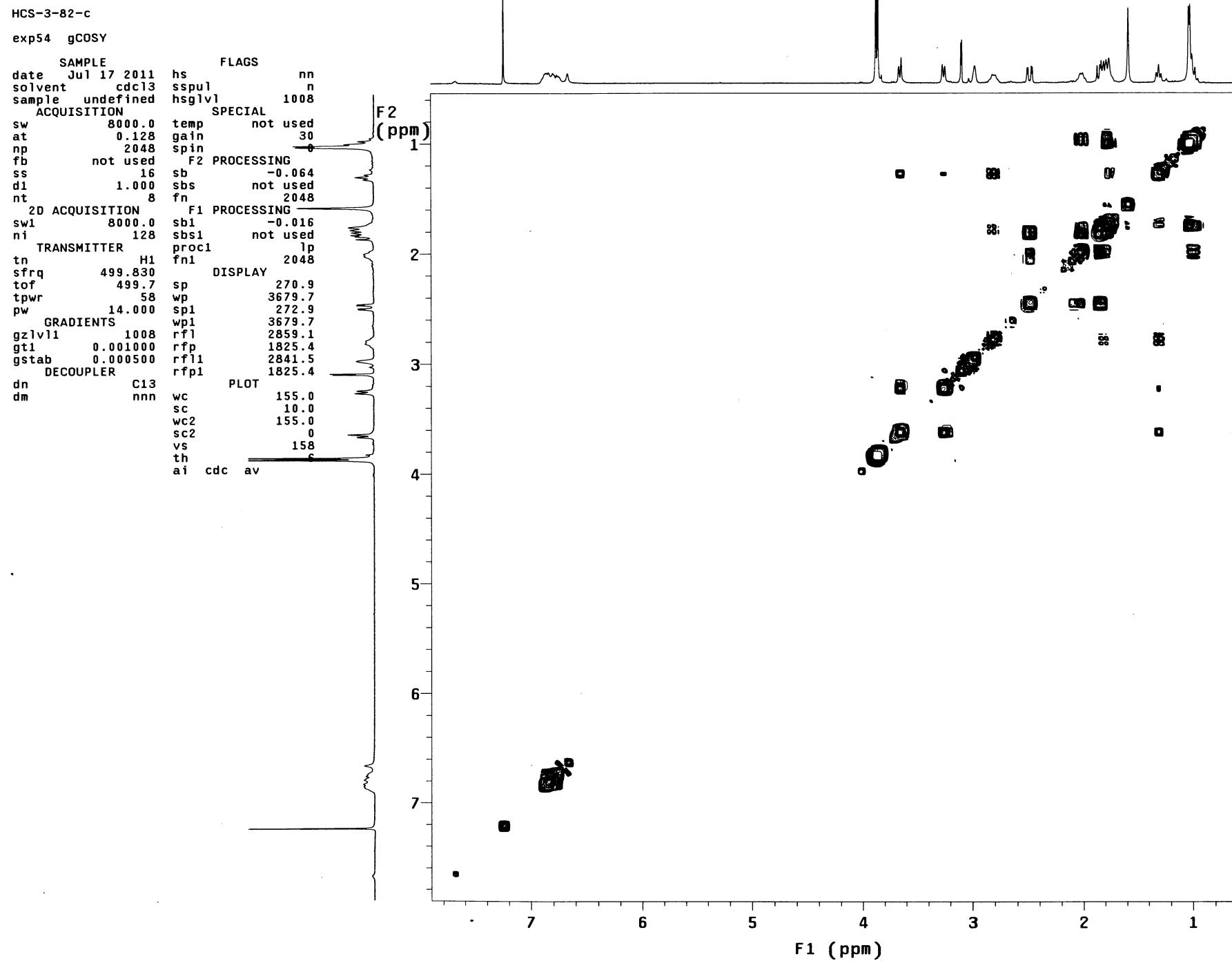


Fig S33. NOESY of compound 7.

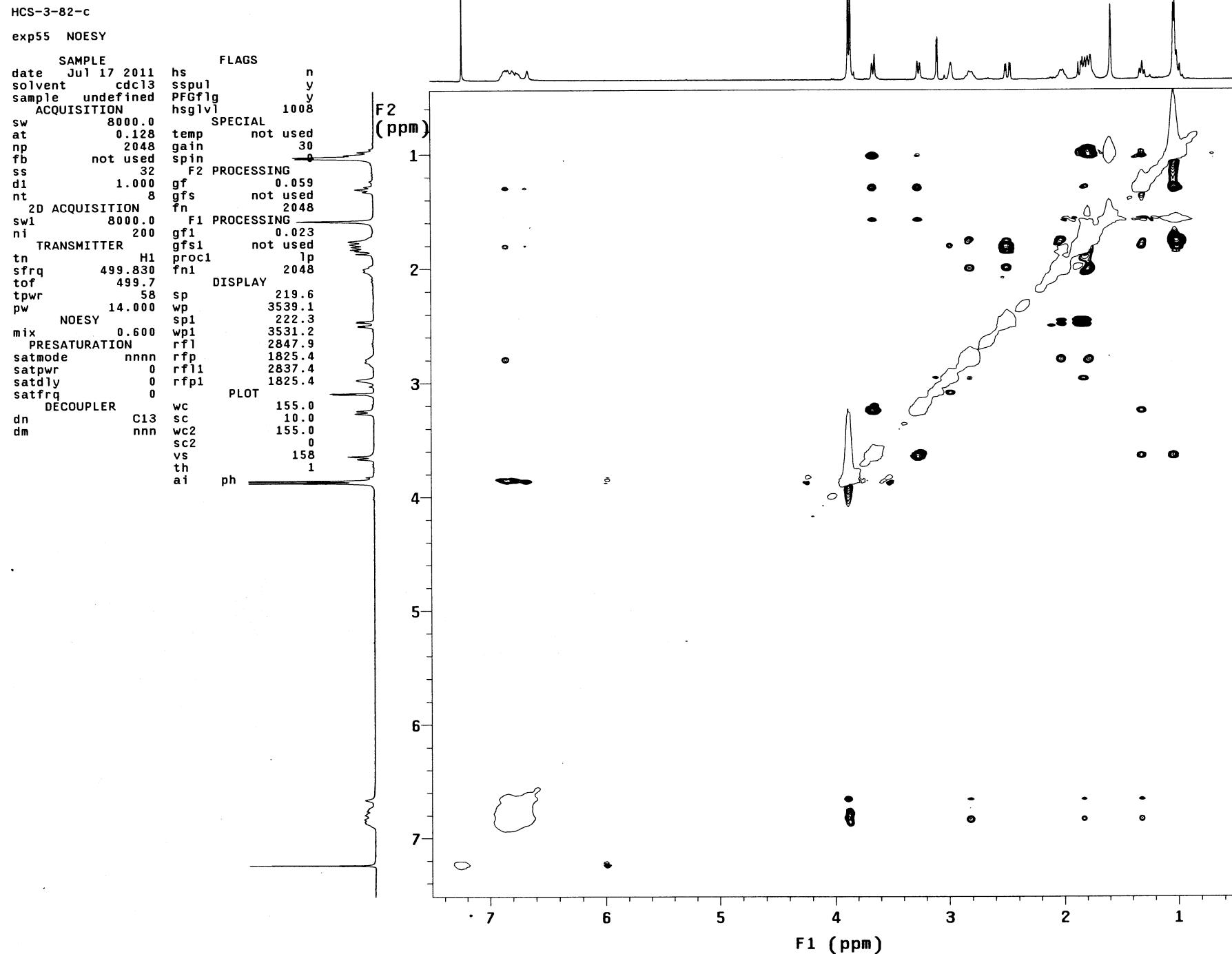


Fig S34.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) of compound 8.

S34

HCS-3-130

exp22 s2pul

```

SAMPLE          DEC. & VT
date Aug 9 2011 dfrq    125.693
solvent   cdc13 dn      C13
file /export/home/~/dpwr    30
vnmr1/vnmrsys/data~ dof    0
/HCS/HCS-3-130/H.f~ dm      nnn
id dmm      c
ACQUISITION dmf     200
sfrq    499.830 dseq
tn      H1      dres    1.0
at      3.000 homo      n
np      48000  PROCESSING
sw      8000.0 wtfile
fb      not used proc      ft
bs      4 fn      not used
tpwr    58 math      f
pw      4.8
d1      1.000 werr      react
tof     499.7 wexp      procplot
nt      4 wbs
ct      4 wnt      wft
alock    y
gain      not used
FLAGS
il      n
in      n
dp      y
hs      nn
DISPLAY
sp      -250.1
wp      5498.0
vs      150
sc      0
wc      210
hzmm    26.18
is      366.43
rf1     4638.7
rfp     3618.7
th      4
ins     100.000
nm cdc ph

```

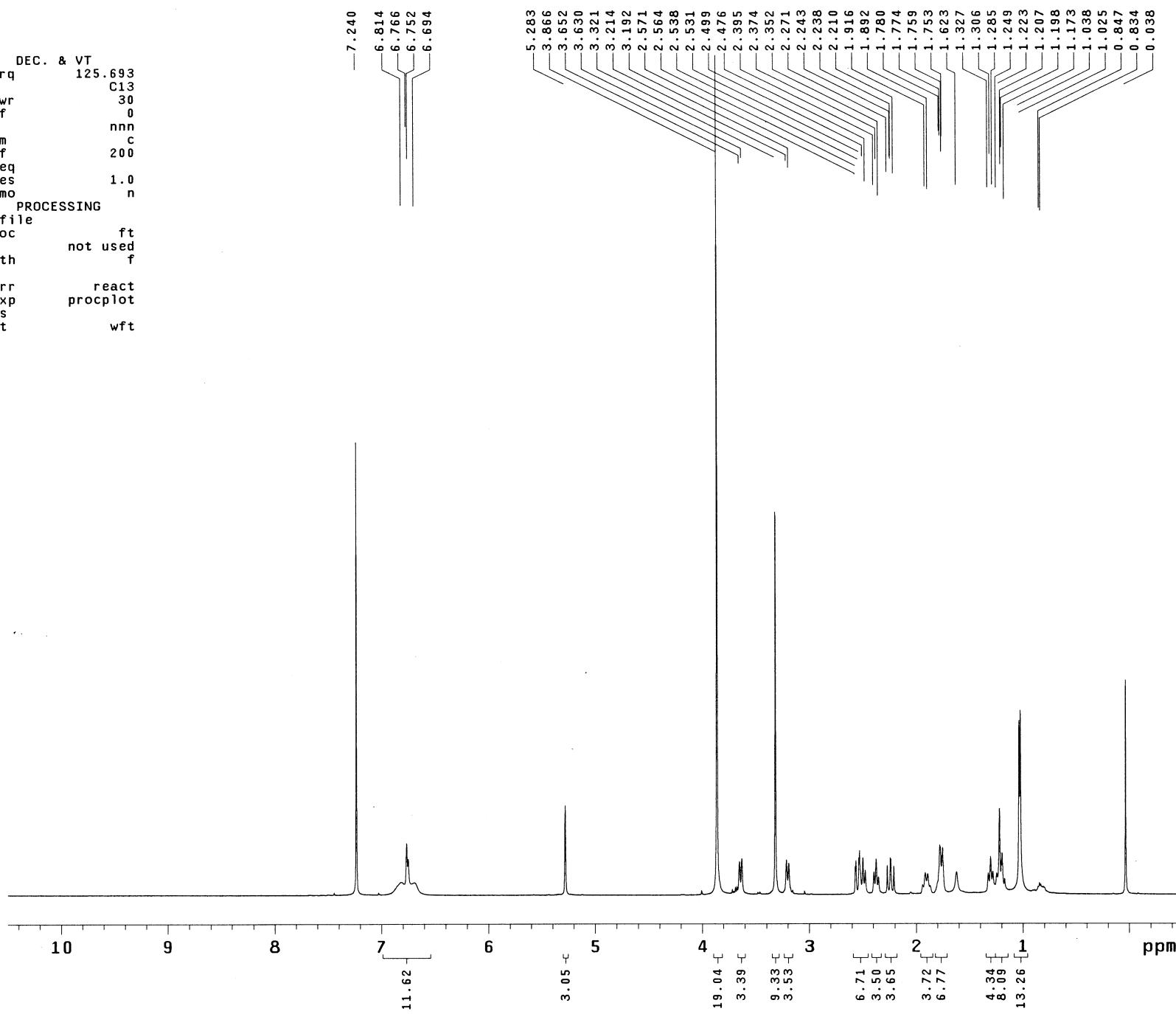


Fig S35.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 126 MHz) of compound 8.

HCS-3-130

exp24 s2pul

```

SAMPLE          DEC. & VT      194.216
date   Aug 9 2011 dfrq    499.829
solvent cdc13    dn      H1
file    exp     dpwr    40
ACQUISITION dof      0
sfrq   125.696 dm      yyy
tn     C13      dmm    w
at     1.000  dmf    9259
np     62894  dseq
sw     31446.5 dres    1.0
fb     not used homo   n
bs     16      PROCESSING
ss     2       lb      1.00
tpwr   56      wtfile
pw     4.0     proc    ft
d1     4.000  fn      not used
tof    2512.2 math   f
nt     10000  werr    react
ct     4992   wexp   procplot
alock  y       wexp
gain   not used wbs   testsn
FLAGS   wnt
il     n
in     n
dp     y
hs     nn
DISPLAY
sp     -1257.0
wp     28906.3
vs     200
sc     0
wc     210
hzmm  137.65
is     500.00
rfl    10981.5
rfp    9677.5
th     8
ins    100.000
nm    cdc ph

```

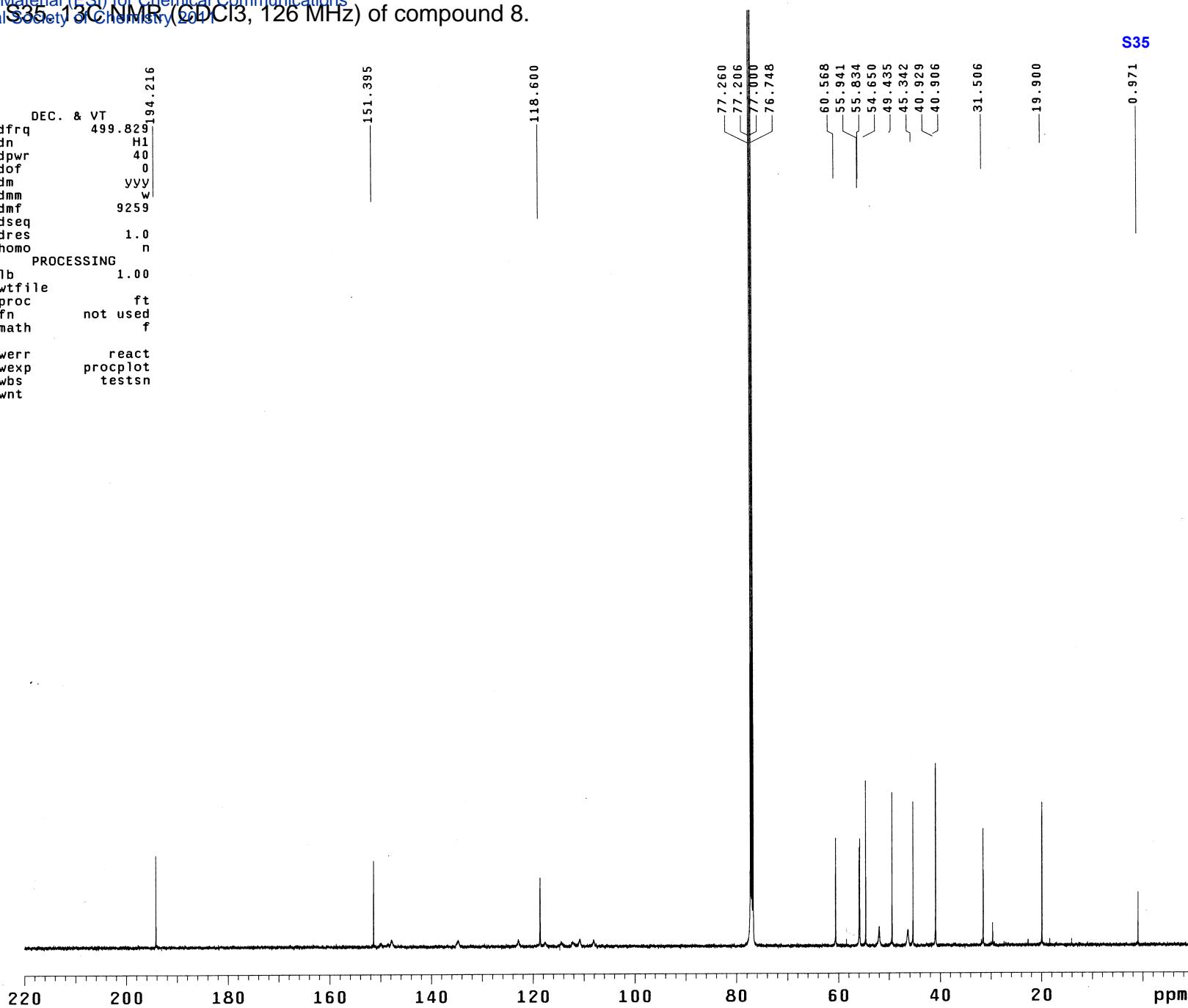


Fig S36.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 126 MHz) of compound 8, expanded.

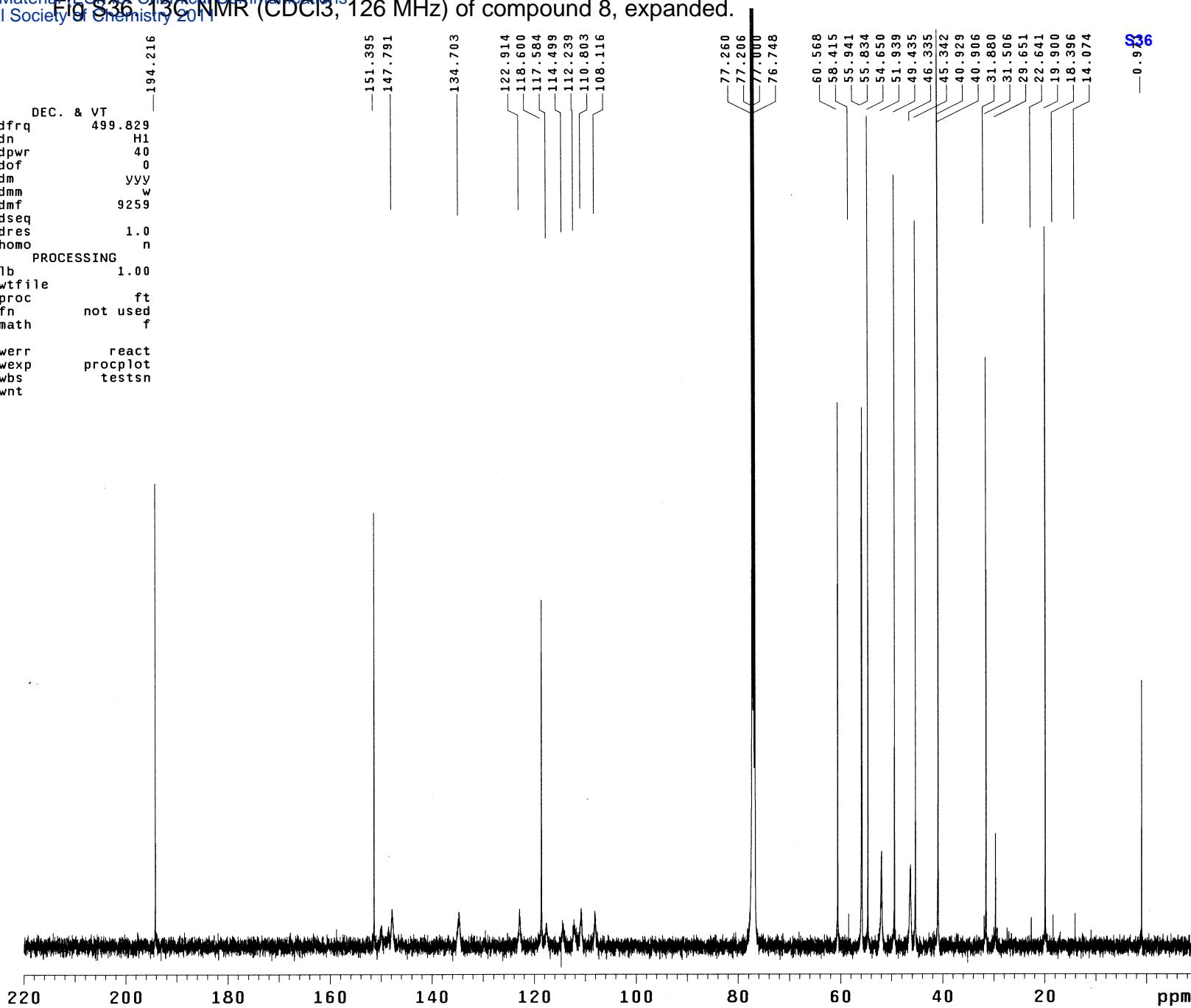
HCS-3-130

exp24 s2pu1

```

SAMPLE           DEC. & VT
date Aug 9 2011 dfreq 499.829
solvent cdc13 dn H1
file exp dpwr 40
ACQUISITION dof 0
sfrq 125.696 dm yyy
tn C13 dmm w
at 1.000 dmf 9259
np 62894 dseq
sw 31446.5 dres 1.0
fb not used homo n
bs 16 PROCESSING
ss 2 lb 1.00
tpwr 56 wtfile
pw 4.0 proc ft
di 4.000 fn not used
tof 2512.2 math f
nt 10000
ct 4992 werr react
alock y wexp procplot
gain not used wbs testsn
FLAGS wnt
il n
in n
dp y
hs nn
DISPLAY
sp -1257.0
wp 28906.3
vs 1000
sc 0
wc 210
hzmm 137.65
is 500.00
rfl 10981.5
rfp 9677.5
th 8
ins 100.000
nm cdc ph

```



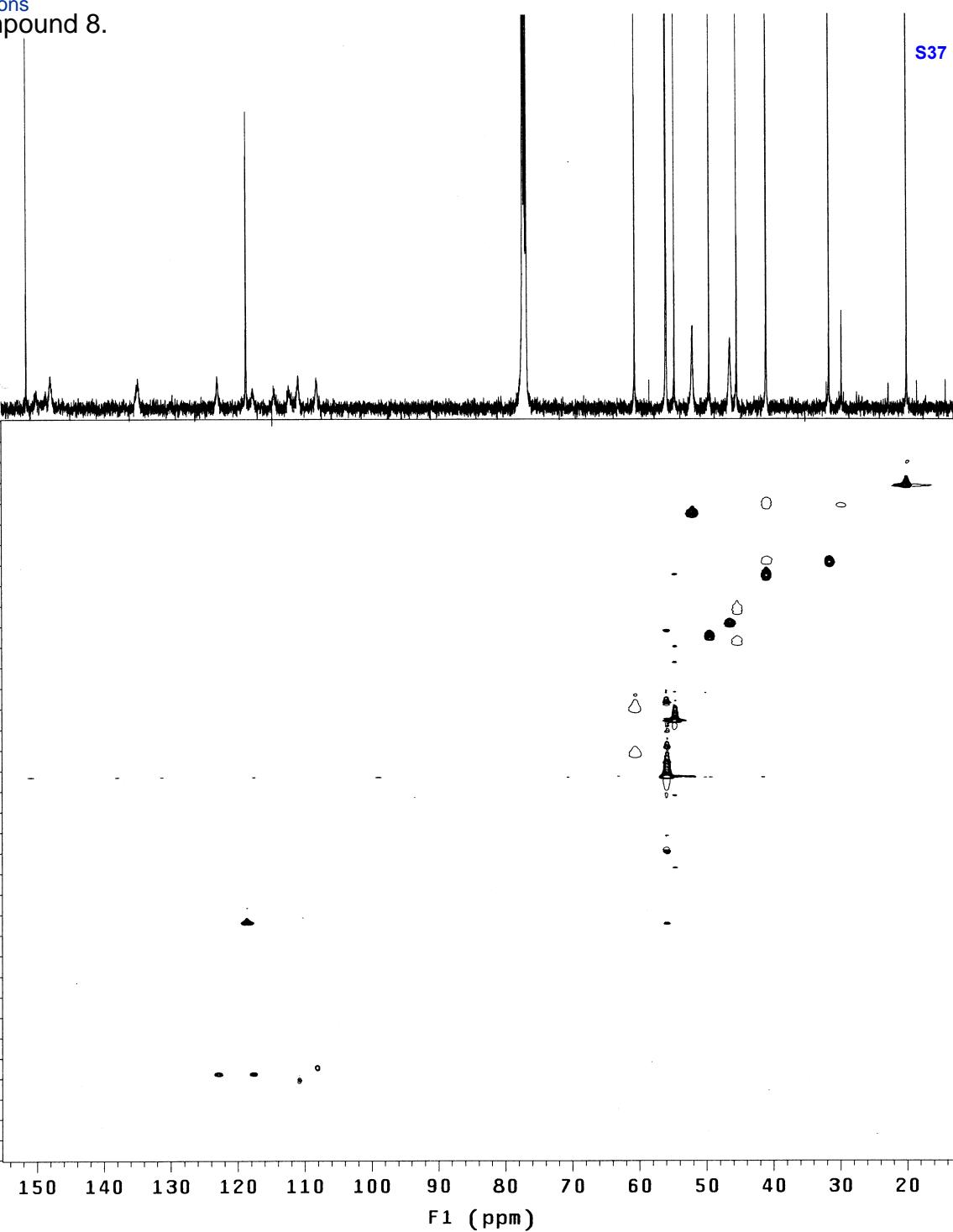
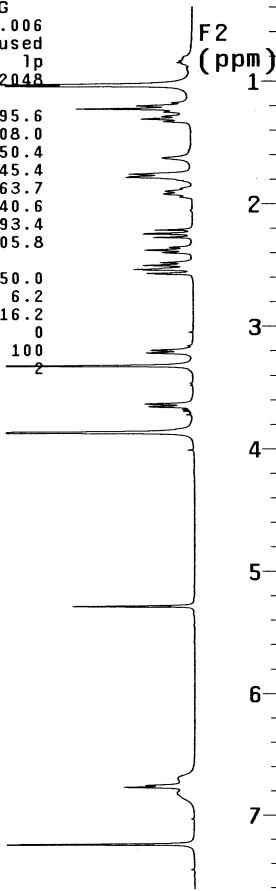
HCS-3-130

exp26 gHSQC

```

SAMPLE           FLAGS          ACQUISITION ARRAYS
date   Aug 9 2011 hs      n array    phase
solvent cdc13  ssppul   y arraydim 256
sample undefined PFGflg   y
ACQUISITION      hsglvl   1008 i      phase
sw     5006.3  SPECIAL    1
at     0.205   temp       not used  2
np     2048    gain       48
fb     not used spin      0
ss     32      GRADIENTS
d1     1.000   gzlv11   1008
nt     16      gt1       0.002000
2D ACQUISITION  gzlv13   507
sw1    21367.5 gt3       0.001000
ni     128     gstab     0.000500
phase  arrayed F2 PROCESSING
TRANSMITTER      gf       0.094
tn      H1      gfs      not used
sfrq   499.829 fn       2048
tof    -499.9   F1 PROCESSING
tpwr   58      gfi      0.006
pw     14.000   gfs1     not used
DECOUPLER        proc1    1p
dn      C13    fn1      2048
dof    -2515.2 DISPLAY
dm      nny    sp       195.6
dmm    ccp    wp       3608.0
dmf    32258  spi      1550.4
dpwr   38     wpi     17945.4
pxl    54     rfl      3163.7
pxw    14.000 rfp      2640.6
      HSQC   rfp1     16193.4
j1xh   140.0   rfp1     14905.8
nullflg  y      PLOT
mult   2      wc      150.0
      ai      sc      6.2
      cdc    wc2     116.2
      ph      sc2     0
      vs      th      100
      ai      wc      2
      cdc
      ph

```



HCS-3-130

exp28 gCOSY

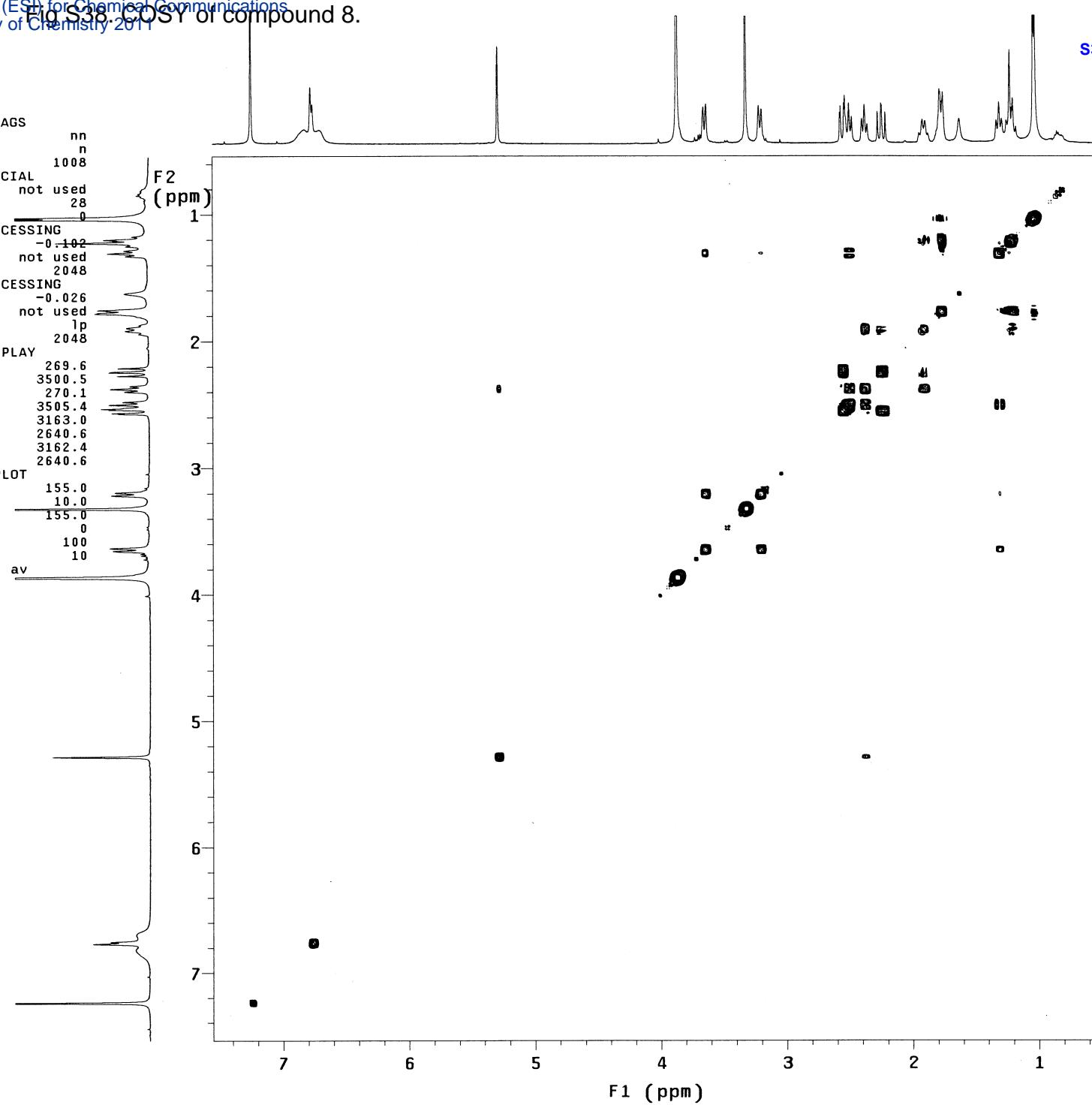
SAMPLE   FLAGS  
date Aug 10 2011 hs nn  
solvent cdc13 sspul n  
sample undefined hsglvl 1008

ACQUISITION   SPECIAL  
sw 5006.3 temp not used  
at 0.205 gain 28  
np 2048 spin 0  
fb not used F2 PROCESSING  
ss 16 sb -0.102  
d1 1.000 sbs not used  
nt 8 fn 2048

2D ACQUISITION   F1 PROCESSING  
sw1 5006.3 sb1 -0.026  
ni 128 sbs1 not used  
proc1 1p  
fn1 2048

TRANSMITTER   DISPLAY  
tn H1  
sfrq 499.829 sp 269.6  
tof -499.9 wp 3500.5  
tpwr 58 sp1 270.1  
pw 14.000 wpi 3505.4  
GRADIENTS rfp 3163.0  
gzlv11 1008 rfp1 2640.6  
gt1 0.001000 rfp11 3162.4  
gstab 0.000500 rfp11 2640.6

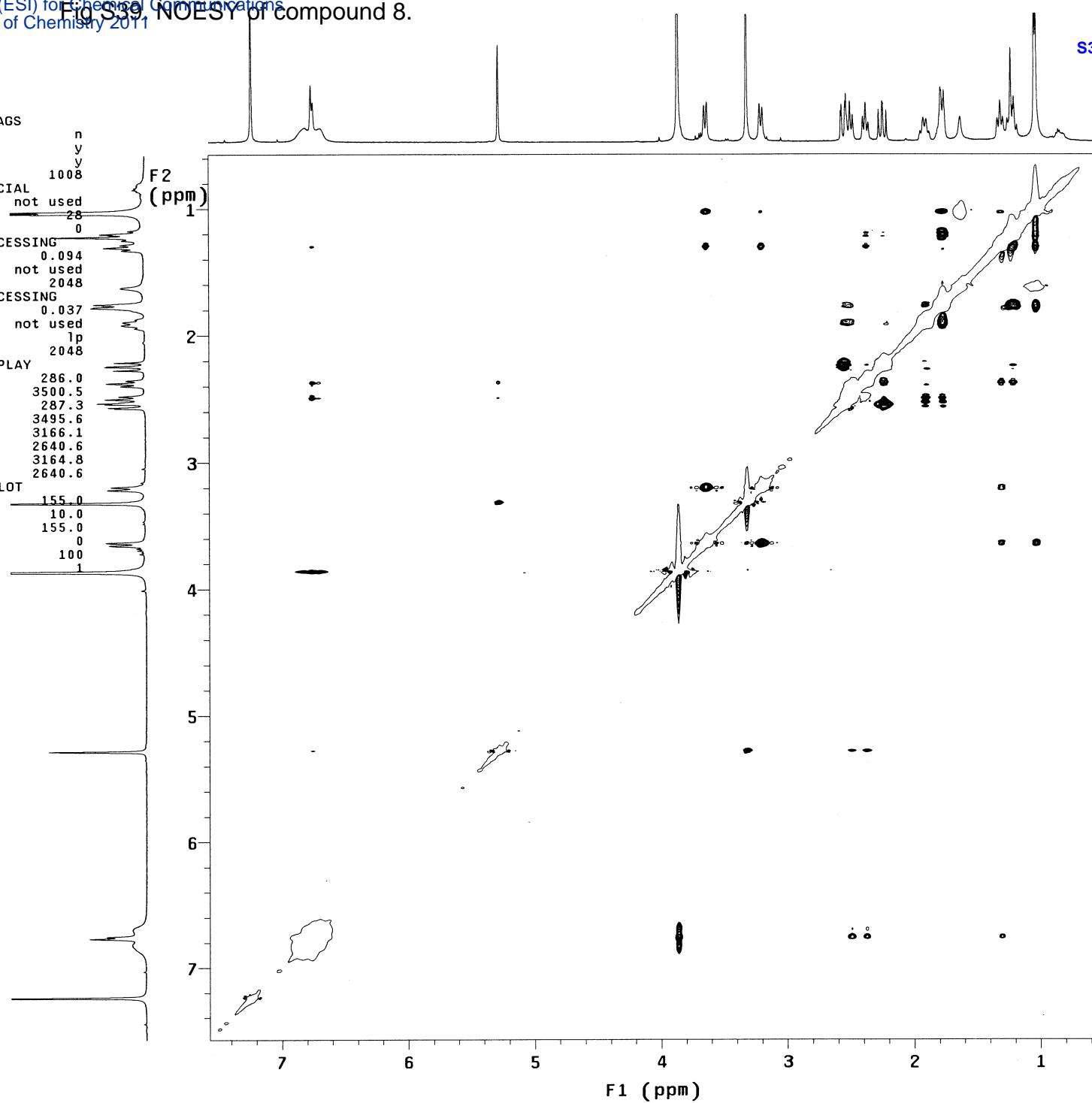
DECOUPLER   PLOT  
dn C13  
dm nnn wc 155.0  
wc 10.0  
wc2 155.0  
sc2 0  
vs 100  
th 10  
ai cdc av



HCS-3-130

exp29 NOESY

SAMPLE		FLAGS	
date	Aug 10 2011	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsgv1	1008
sw	5006.3	SPECIAL	
at	0.205	temp	not used
np	2048	gain	<del>28</del>
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.094
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	5006.3	F1 PROCESSING	
ni	200	gf1	0.037
TRANSMITTER		gfs1	not used
tn	H1	proc1	1p
sfrq	499.829	fn1	2048
tof	-499.9	DISPLAY	
tpwr	58	sp	286.0
pw	14.000	wp	3500.5
NOESY		sp1	287.3
mix	0.600	wp1	3495.6
PRESATURATION		rfl	3166.1
satmode	nnnn	rfp	2640.6
satpwr	0	rf1	3164.8
satdly	0	rfp1	2640.6
satfrq	0	PLOT	
DECOUPLER		wc	<u>155.0</u>
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	100
		th	<u>1</u>
		ai	ph



## Fig S40. 1H-MBC of compound 8.

S40

HCS-3-130

exp27 gHMBC

```

SAMPLE          FLAGS
date Aug 9 2011 hs      n
solvent cdc13 sspul   n
sample undefined PF6flg  y
ACQUISITION hsglv1 1008
sw      5006.3 SPECIAL
at      0.205 temp    not used
np      2048  gain    20
fb      not used spin    0
ss      32   GRADIENTS
d1      1.000 gzlvl1 1008
nt      16   gt1     0.001000
2D ACQUISITION gzlvl3 507
sw1     30165.9 gt3     0.001000
ni      400   gstab   0.000500
phase   0    F2 PROCESSING
TRANSMITTER sb      0.102
tn      H1   sbs     not used
sfrq   499.829 fn      2048
tof    -499.9 F1 PROCESSING
tpwr   58   sb1     0.007
pw     14.000 sbs1    not used
fnl    2048
DECOUPLER   C13  DISPLAY
dn      1255.3 sp      262.0
dm      nnn   wp      3788.9
dmm     ccc   spi     1083.6
dmf    32258  wpi    25275.7
dpwr   38    rfi     3165.7
pxxlv1 54    rfp     2640.6
pxx   14.000 rfi1   26330.5
           HMBC  rfp1   24409.4
j1xh   140.0 PLOT
jnxh   8.0   wc      150.0
           sc      6.2
           wc2    116.2
           sc2    0
           vs     100
           th     13
           ai    cdc av

```

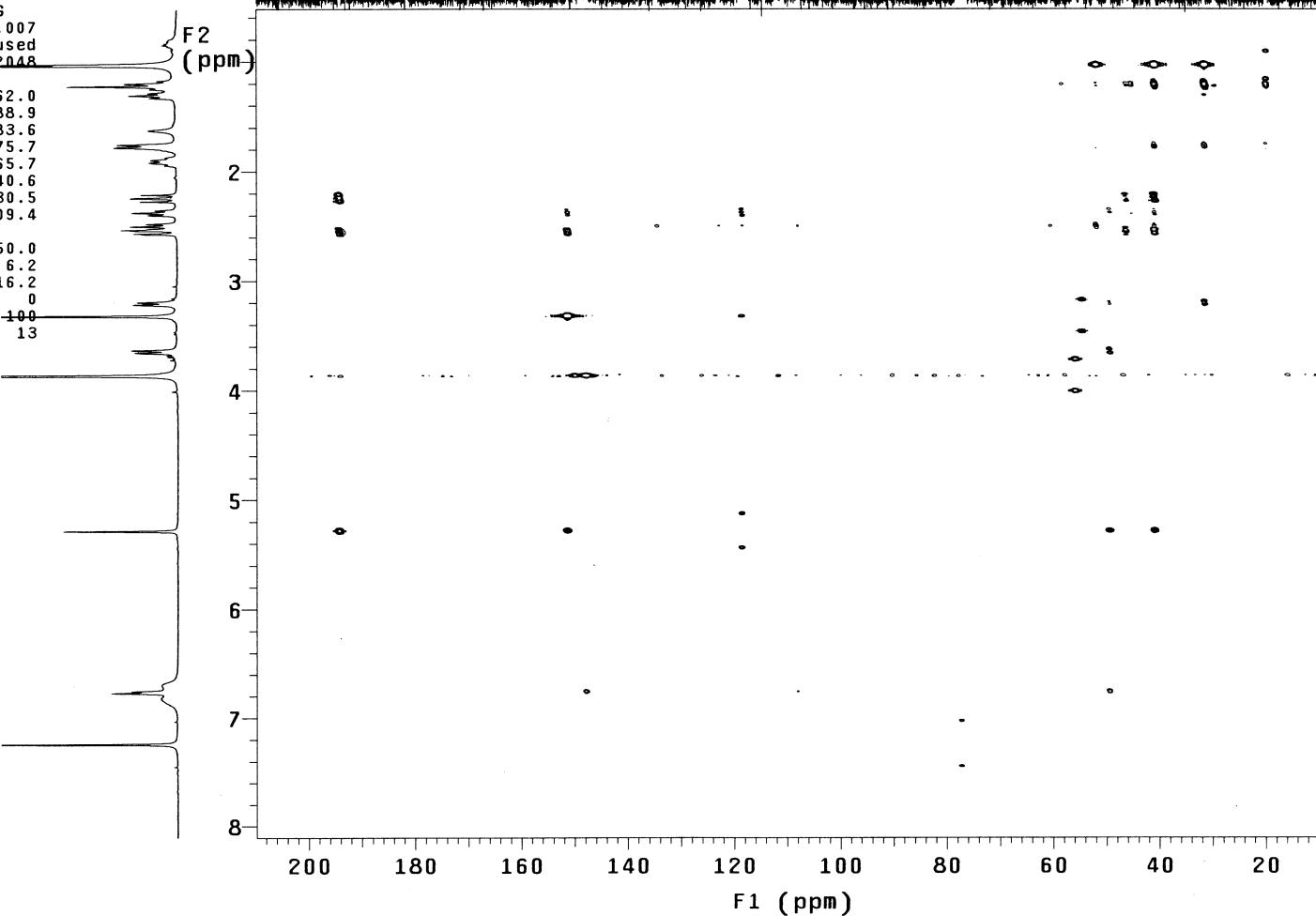


Fig S41.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) of compound 9.

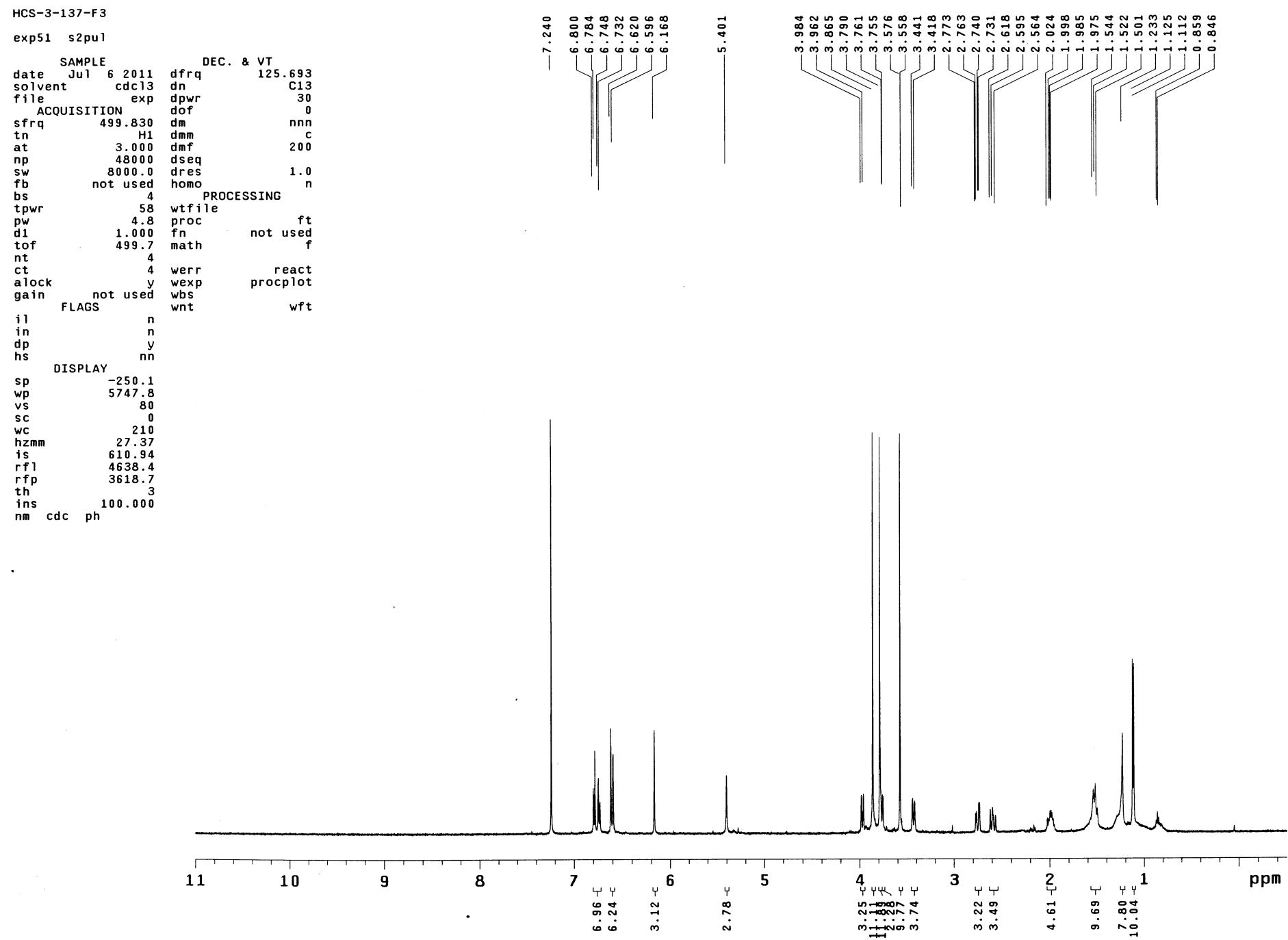


Fig S42.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) of compound 9.

HCS-3-137-F3

exp52 s2pul

SAMPLE DEC. & VT  
date Jul 5 2011 dfreq 499.829  
solvent cdc13 dn H1  
file exp dpwr 42  
ACQUISITION dof 0  
sfreq 125.696 dm yyy  
tn C13 dmm w  
at 1.000 dmf 11696  
np 62894 dseq  
sw 31446.5 dres 1.0  
fb not used homo n  
bs 16 PROCESSING  
ss 2 lb 1.00  
tpwr 56 wtfile  
pw 3.0 proc ft  
d1 2.000 fn not used  
tof 2512.2 math f  
nt 5000  
ct 5000 werr react  
alock y wexp procplot  
gain not used wbs testsn  
FLAGS wnt  
il n  
in n  
dp y  
hs nn

DISPLAY  
sp -0.8  
wp 25135.7  
vs 2000  
sc 0  
wc 210  
hzmm 119.70  
is 500.00  
rf1 10979.6  
rfp 9677.5  
th 13  
ins 100.000  
nm cdc ph

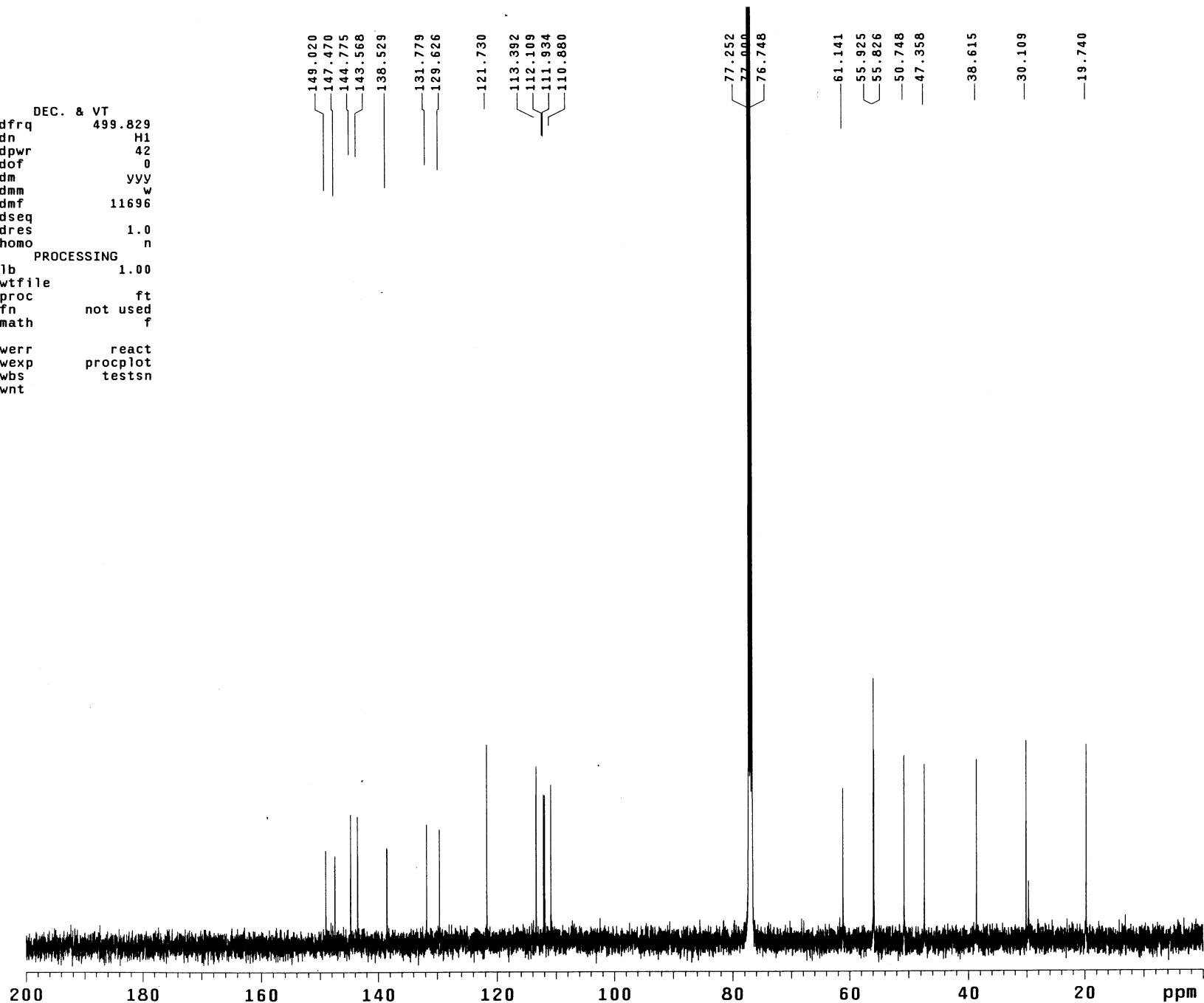


Fig S43. DEPT of compound 9.

HCS-3-137-F3

exp53 DEPT

SAMPLE	DEPT	ACQUISITION ARRAYS
date Jul 5 2011	j1xh 140.0	array mult
solvent cdc13	mult arrayed	arraydim 3
sample undefined	SPECIAL	
ACQUISITION	temp not used	i mult
sw 31446.5	gain 20	1 0.5
at 1.000	spin 0	2 1
np 62894	PROCESSING	3 1.5
bs 16	lb 1.00	
ss -4	fn not used	
d1 1.000	SPECTRUM	
nt 2046	wp 25135.7	
ct 2046	sp -0.8	
TRANSMITTER	rp 153.3	
tn C13	lp	
tof 2512.2	ai cdc ph	
tpwr 56	REFERENCE	
pw 10.800	rfl 1302.1	
DECOUPLER	rfp 0	
dn H1	PLOT	
dof 0	wc 210	
dpwr 42	sc 0	
dm nny	vs 1692	
dmm ccw	hzmm 119.70	
dmf 11696	th 68	
pplvl 53		
pp 27.400		

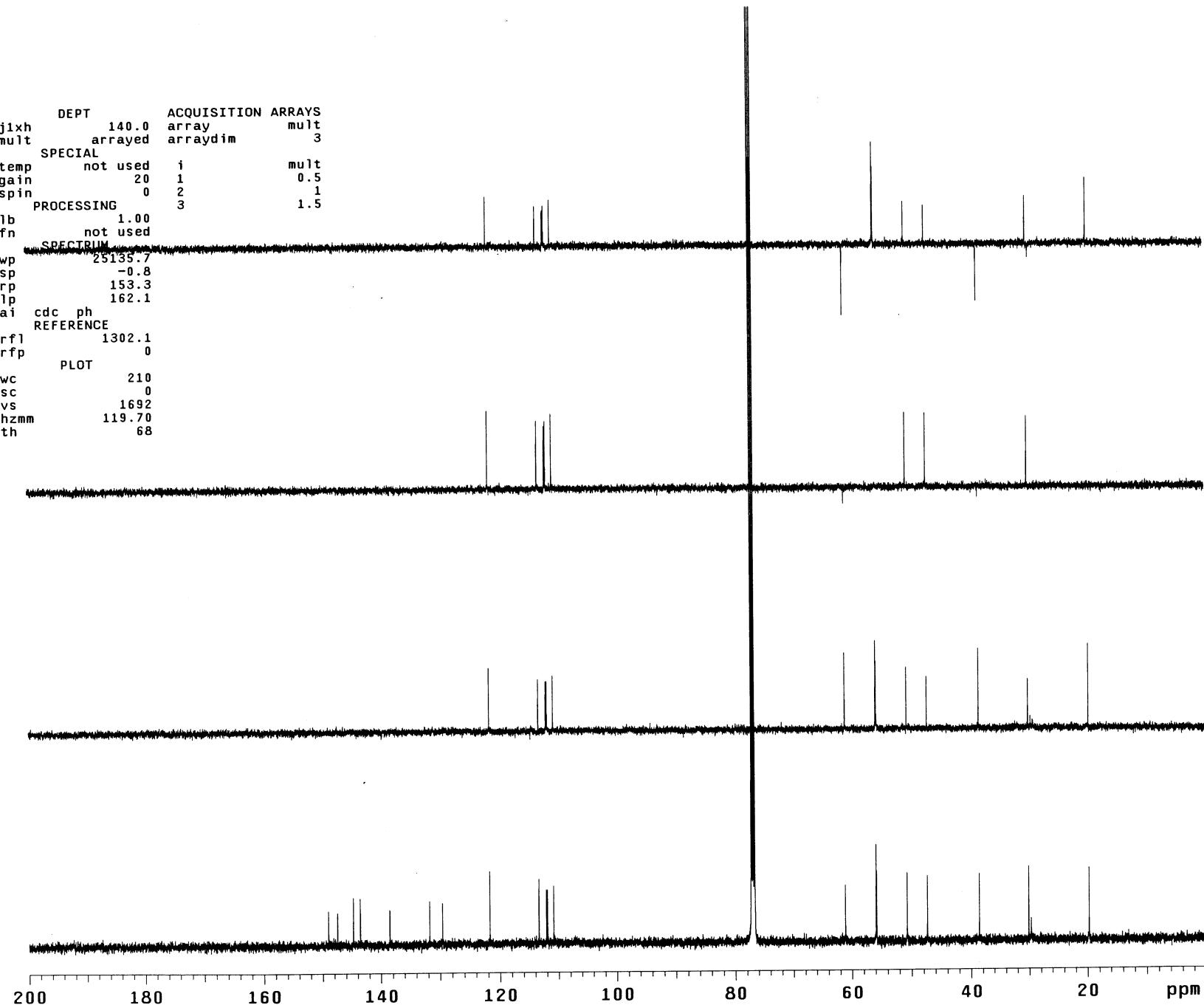
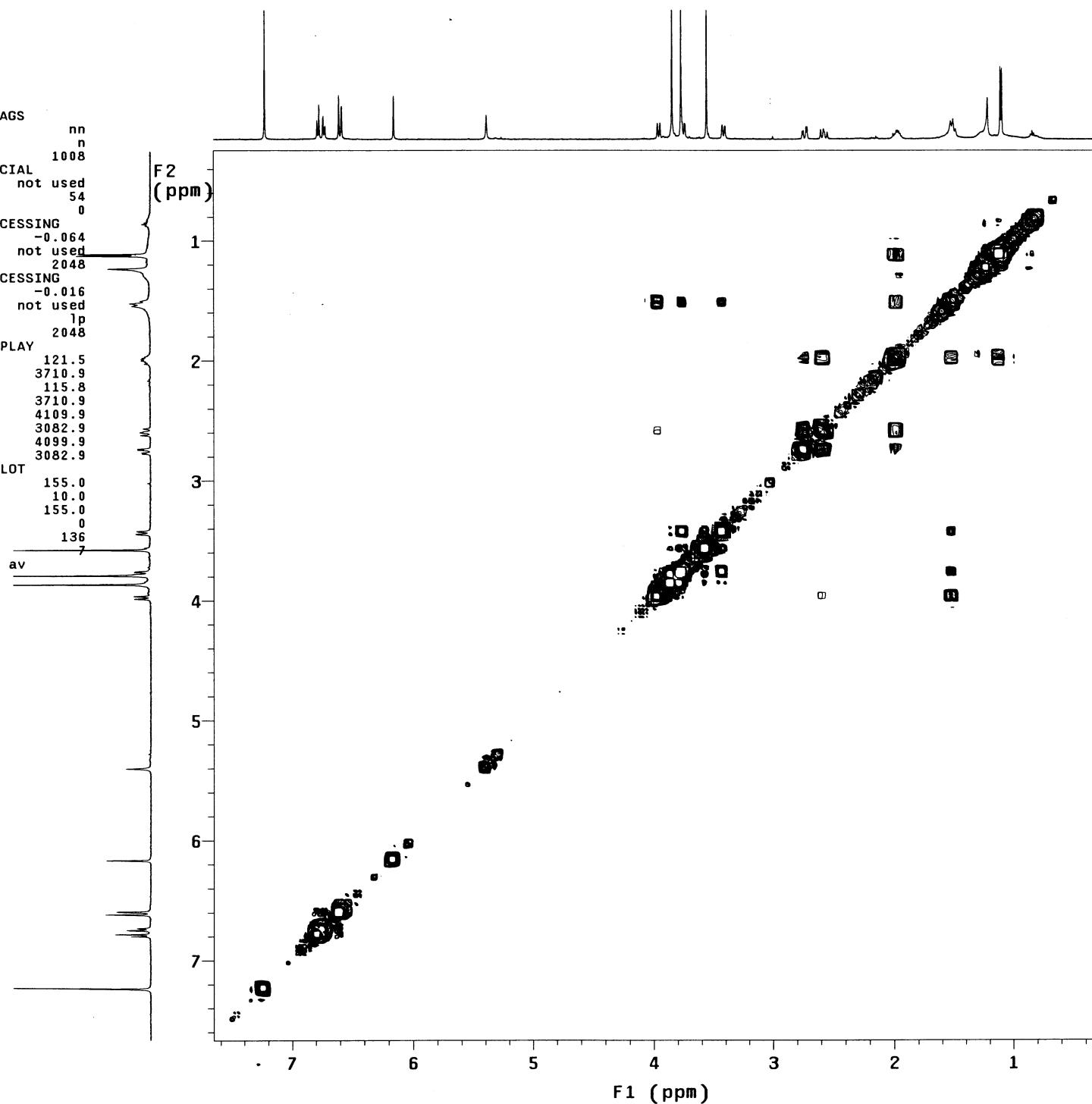


Fig S44. COSY of compound 9.

HCS-3-137-F3

exp54 gCOSY

SAMPLE	hs	nn	
date	Jul 5 2011	sspu1	n
solvent	cdcl3	hsglv1	1008
sample	undefined		
ACQUISITION		SPECIAL	
sw	8000.0	temp	not used
at	0.128	gain	54
np	2048	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.064
di	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	8000.0	sb1	-0.016
ni	128	sbs1	not used
TRANSMITTER	H1	proc1	lp
tn	499.830	fn1	2048
sfrq		DISPLAY	
tof	499.7	sp	121.5
tpwr	58	wp	3710.9
pw	14.000	spi	115.8
GRADIENTS		wpi	3710.9
gzlvl1	1008	rfl	4109.9
gt1	0.001000	rfp	3082.9
gstab	0.000500	rfl1	4099.9
DECOPPLER		rfp1	3082.9
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	136
		th	7
		ai	cdc
		av	



## Fig S45. HSQC of compound 9.

HCS-3-137-F3

exp56 gHSQC

```

SAMPLE          FLAGS          ACQUISITION ARRAYS
date    Jul 5 2011  hs      n      array      phase
solvent   cdc13   sspul   y      arraydim   256
sample   undefined PFGflg   y
ACQUISITION   hsglvl  1008   i      phase
sw       8000.0   SPECIAL   1
at        0.128   temp     not used  2
np        2048    gain     34
fb        not used spin     0
ss        32      GRADIENTS
di       1.000   gzlvl1  1008
nt        8       gt1      0.002000
2D ACQUISITION   gzlvl3  507
sw1      21367.5  gt3      0.001000
ni        128    gstab    0.000500
phase    arrayed   F2 PROCESSING
TRANSMITTER   gf      0.059
tn       H1      gfs     not used
sfrq    499.830  fn      2048
tof      499.7   F1 PROCESSING
tpwr    58      gf1     0.006
pw       14.000   gfs1    not used
DECOUPLER    C13    proc1   1p
dn       -2515.2   fni    2048
dof      -2515.2   DISPLAY
dm       nny     sp      285.0
dmm      ccp     wp      3656.2
dmf      32258   sp1     1581.7
dpwr    38      wpi     14502.4
pxlvl1  54      rfl     4102.7
pxw     14.000   rfp     3082.9
HSQC    140.0   rfp1    15387.9
j1xh    140.0   rfp1    14090.0
nullflg  y      PLOT
mult    2       wc      150.0
        sc      6.2
        wc2    116.2
        sc2    0
        vs      136
        th      6
ai      cdc ph

```

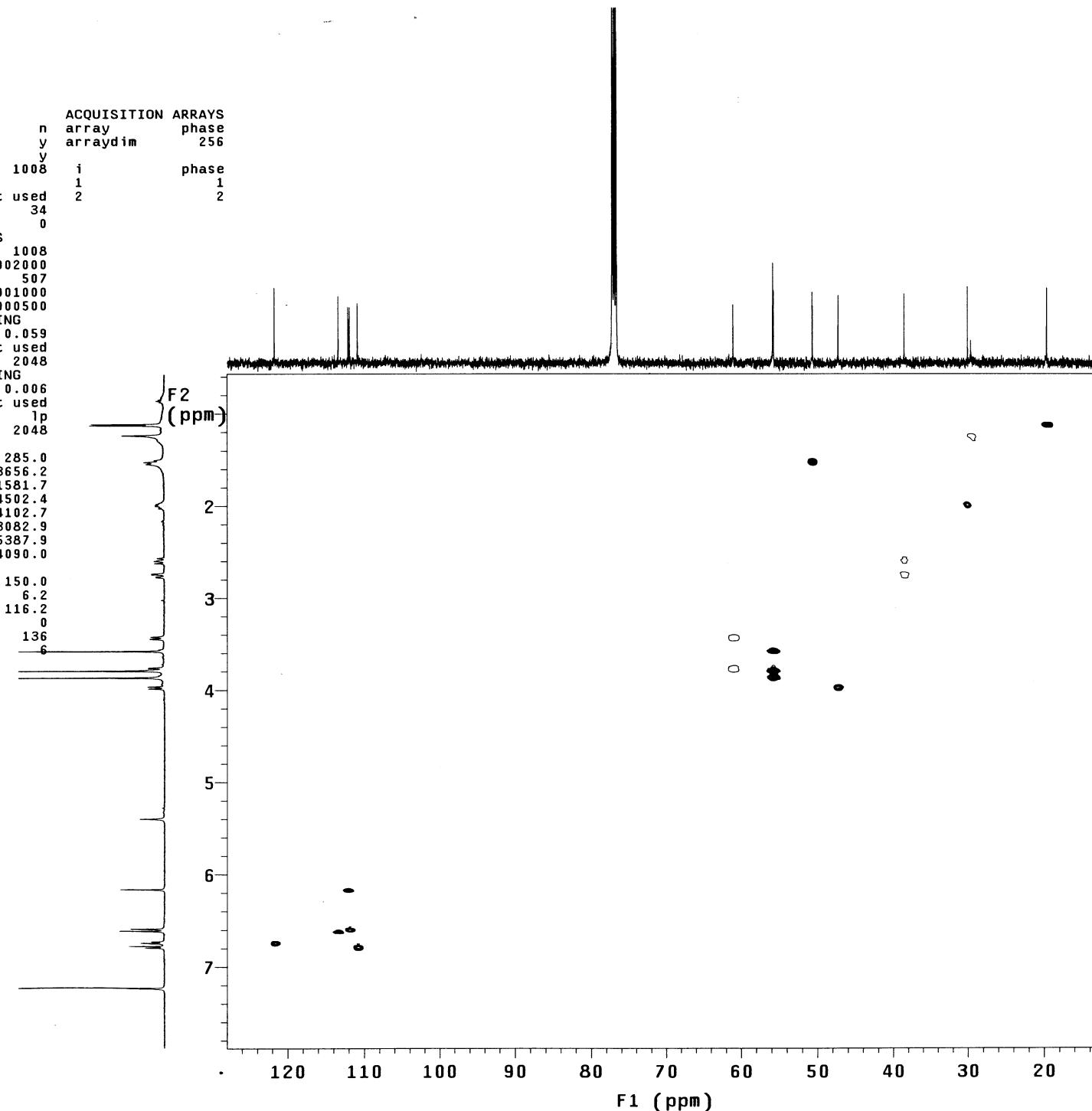
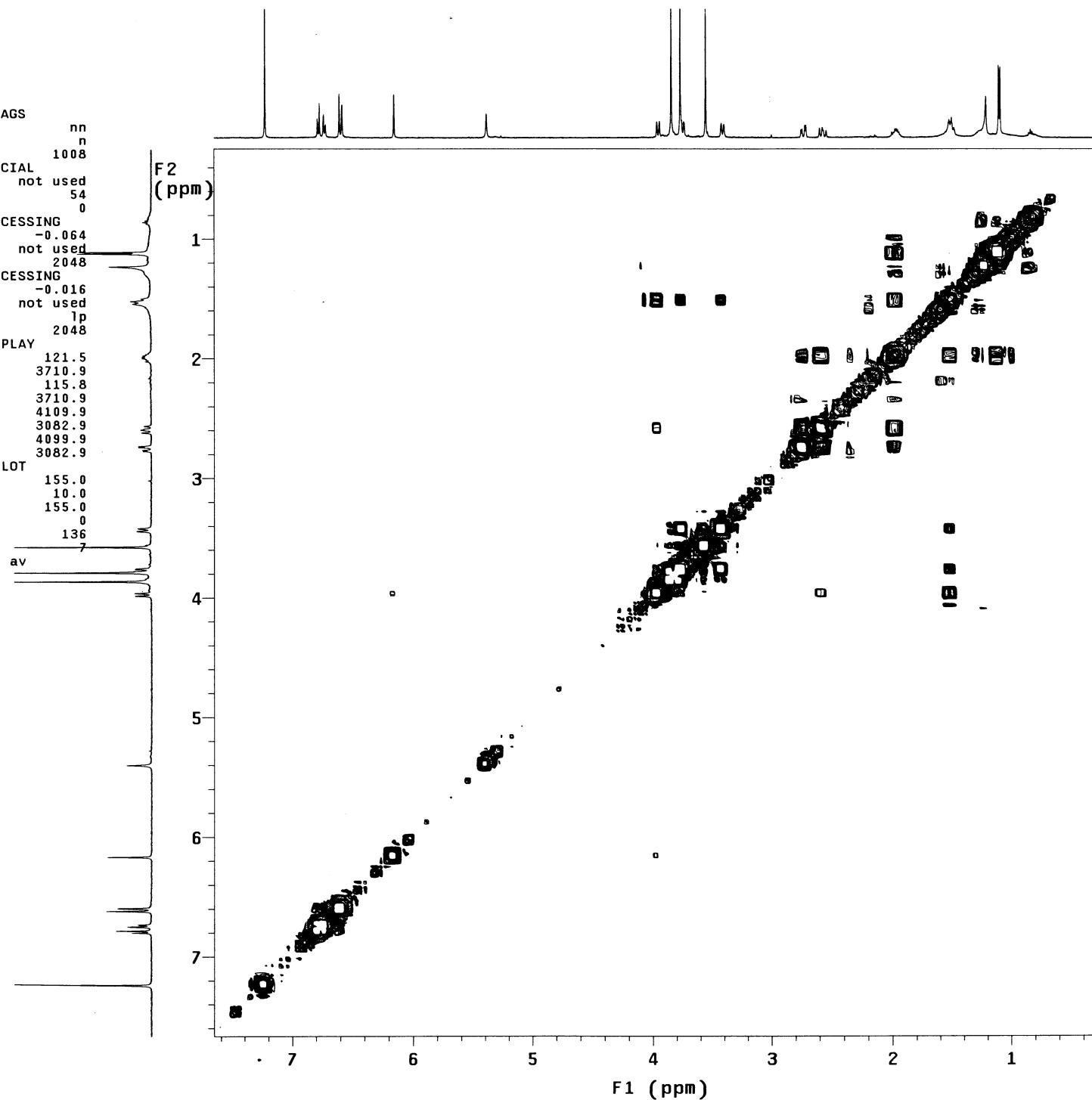


Fig S46. COSY of compound 9.

HCS-3-137-F3

exp54 gCOSY

SAMPLE	hs	nn	
date	Jul 5 2011	sspu	n
solvent	cdcl3	hsplv1	1008
sample	undefined		
ACQUISITION		SPECIAL	
sw	8000.0	temp	not used
at	0.128	gain	54
np	2048	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.064
di	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	8000.0	sb1	-0.016
ni	128	sbs1	not used
TRANSMITTER	H1	proc1	lp
tn	499.830	fn1	2048
sfrq		DISPLAY	
tof	499.7	sp	121.5
tpwr	58	wp	3710.9
pw	14.000	sp1	115.8
GRADIENTS		wpi	3710.9
gzlv11	1008	rfl	4109.9
gt1	0.001000	rfp	3082.9
gstab	0.000500	rfl1	4099.9
DECOUPLER		rfpi	3082.9
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	136
		th	7
		ai	cdc
		av	



HCS-3-137-F3

exp55 NOESY

```

SAMPLE          FLAGS
date Jul 5 2011 hs      n
solvent   cdcl3 sspul  y
sample  undefined PFGflg  y
ACQUISITION    hsgrl1  1008
sw       8000.0 SPECIAL
at        0.128 temp    not used
np        2048  gain   34
fb        not used spin   0
ss        32   F2 PROCESSING
di        1.000 gf     0.059
nt         8   gfs    not used
fn        2048
2D ACQUISITION F1 PROCESSING
sw1      8000.0
ni        200  gfi    0.023
TRANSMITTER    gfs1   not used
tn        H1   proc1  1p
sfrq     499.830 fn1    2048
tof       499.7
tpwr      58   sp     176.8
pw       14.000 wp     3914.1
NOESY      mix    0.600
           0.600 wpi    3921.9
PRESATURATION rfi    4101.5
satmode    nnnn rfp    3082.9
satpwr     0   rfl1   4101.1
satdly     0   rfp1   3082.9
satfrq    0
DECOUPLER    wc    155.0
dn        C13  sc    10.0
dm        nnn  wc2   155.0
           nnn  sc2    0
           nnn  vs    136
           nnn  th    1
           nnn  ai    ph

```

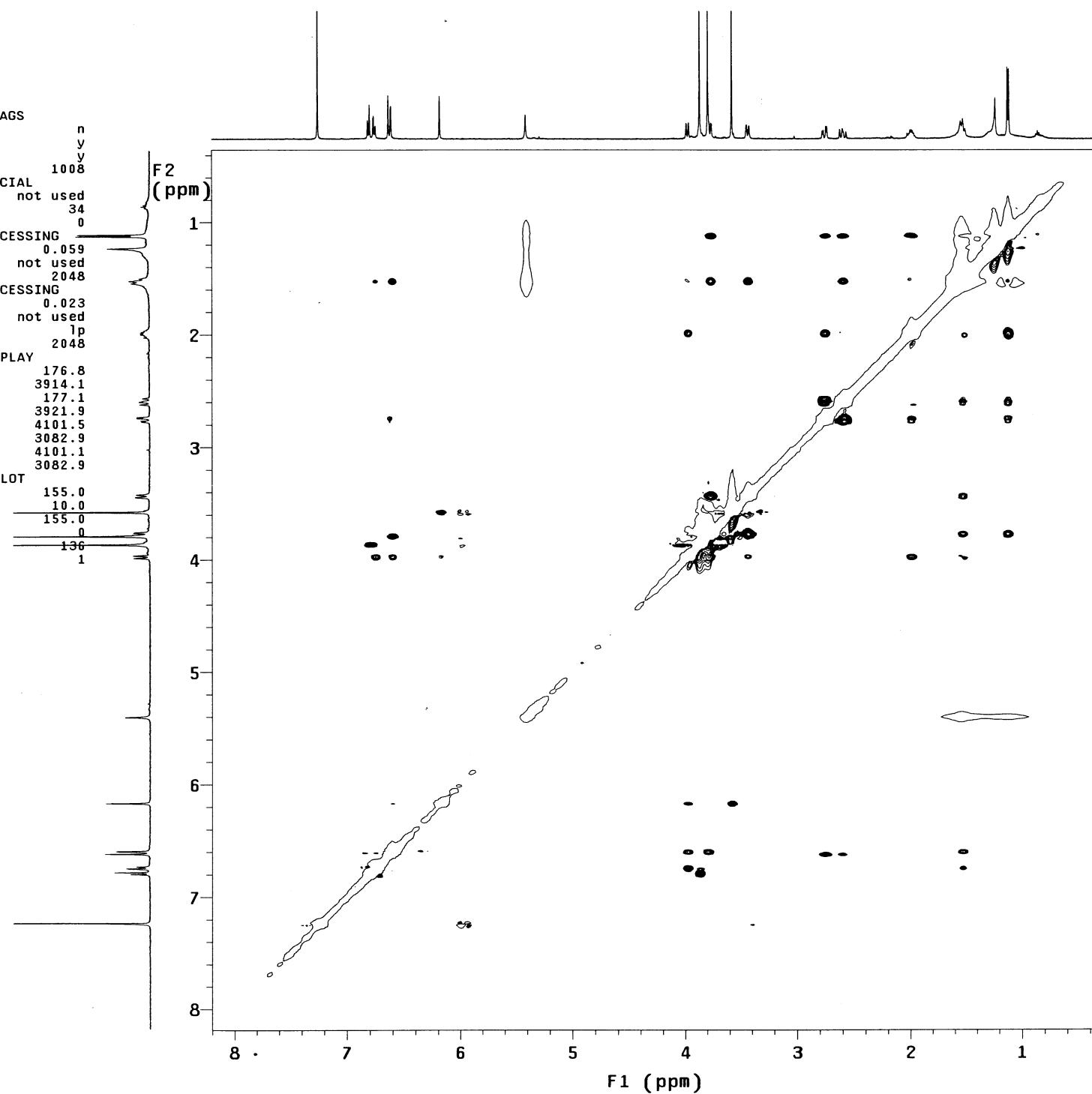


Fig S48.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) of compound 10.

HCS-3-139-P  
exp51 s2pul  
  
SAMPLE DEC. & VT  
date Jul 8 2011 dfreq 125.693  
solvent cdc13 dn C13  
file exp dpwr 30  
ACQUISITION dof 0  
sfrq 499.830 dm nnn  
tn H1 dmm c  
at 3.000 dmf 200  
np 48000 dseq  
sw 8000.0 dres 1.0  
fb not used homo n  
bs 4 PROCESSING  
tpwr 58 wtfile  
pw 4.8 proc ft  
d1 1.000 fn not used  
tof 499.7 math f  
nt 4  
ct 4 werr react  
alock y wexp procplot  
gain not used wbs  
FLAGS wnt wft  
il n  
in n  
dp y  
hs nn  
  
DISPLAY  
sp -250.1  
wp 5747.8  
vs 113  
sc 0  
wc 210  
hzmm 27.37  
is 33.57  
rfl 4638.7  
rfp 3618.7  
th 5  
ins 1.000  
nm cdc ph

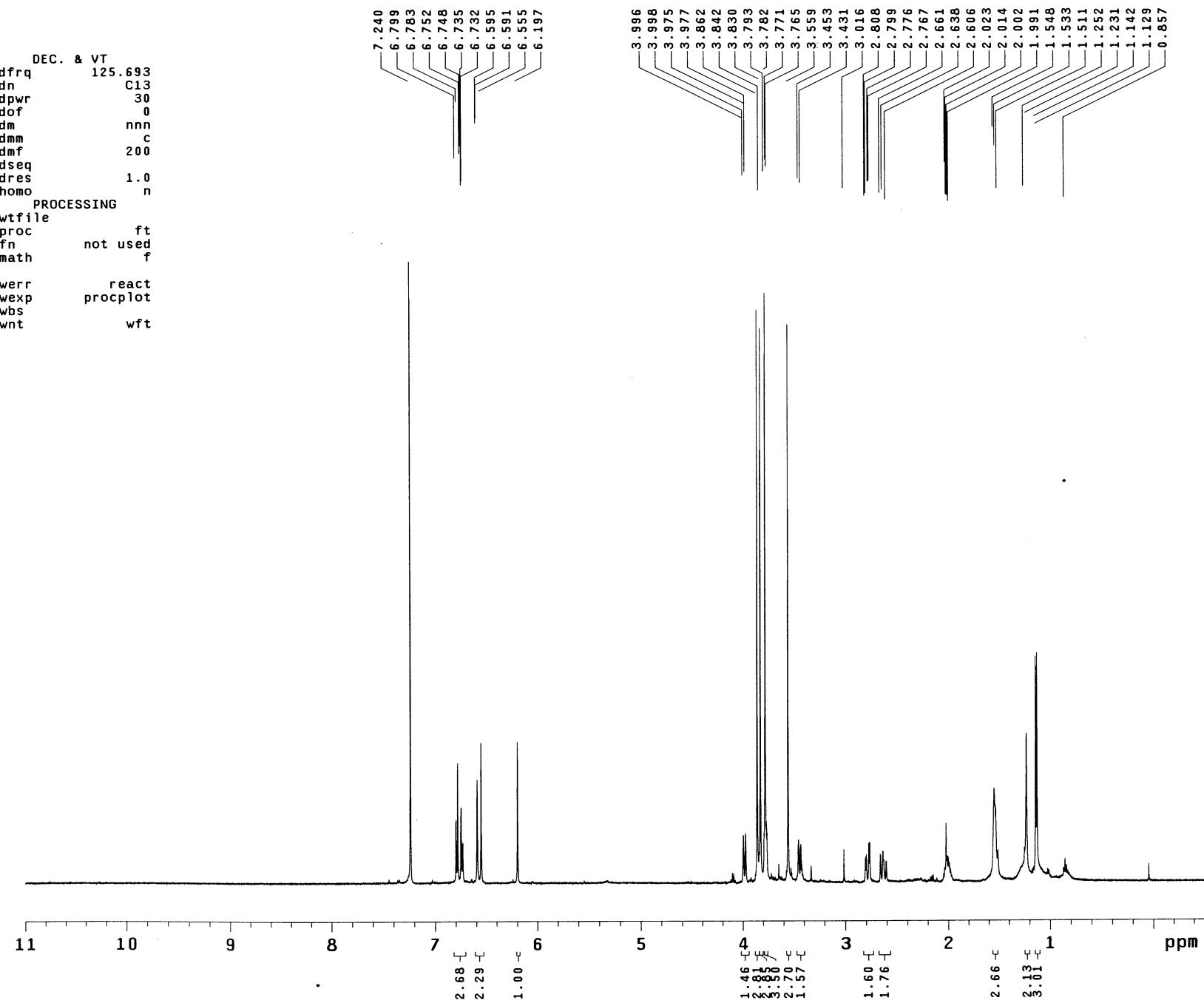


Fig S49. <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 126 MHz) of compound 10.

HCS-3-139-P

exp52 s2pul

```

SAMPLE          DEC. & VT
date Jul 8 2011 dfreq 499.829
solvent cdc13 dn H1
file exp dpwr 42
ACQUISITION dof 0
sfrq 125.696 dm yvv
tn C13 dmm w
at 1.000 dmf 11696
np 62894 dseq
sw 31446.5 dres 1.0
fb not used homo n
bs 16 PROCESSING
ss 2 lb 1.00
tpwr 56 wtfile
pw 3.0 proc ft
d1 2.000 fn not used
tof 2512.2 math f
nt 6000
ct 6000 werr react
alock y wexp procplot
gain not used wbs testsn
FLAGS wnt

i1 n
in n
dp y
hs nn

DISPLAY
sp -0.8
wp 25135.7
vs 1106
sc 0
wc 210
hzmm 119.70
is 500.00
rfl 10979.6
rfp 9677.5
th 10
ins 100.000
nm cdc ph

```

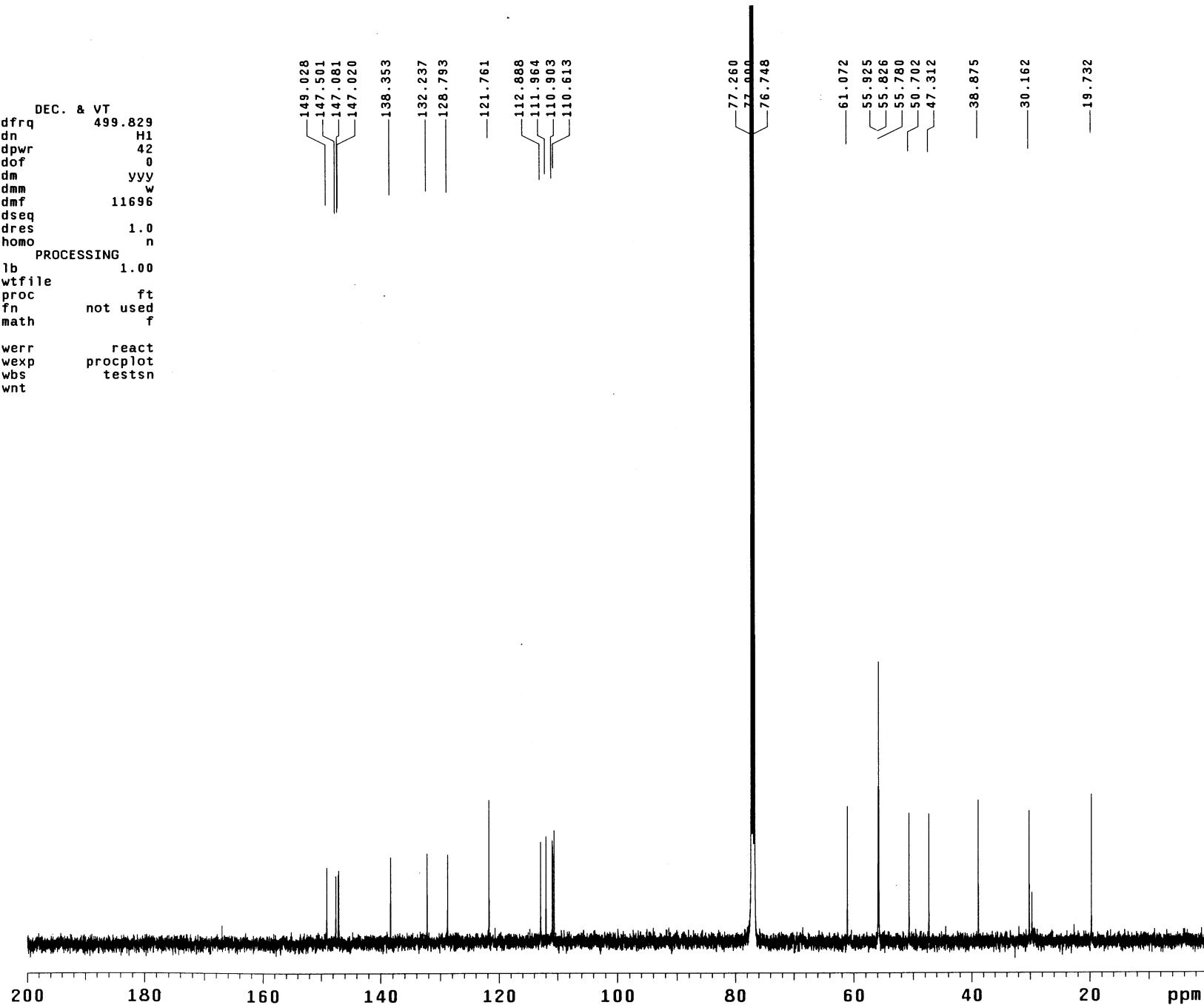


Fig S50. DEPT of compound 10.

HCS-3-139-P

exp53 DEPT

SAMPLE DEPT ACQUISITION ARRAYS  
date Jul 8 2011 j1xh 140.0 array mult  
solvent cdc13 mult arrayed arraydim 3  
sample undefined SPECIAL  
ACQUISITION temp not used i mult  
sw 31446.5 gain 20 1 0.5  
at 1.000 spin 0 2 1  
np 62894 PROCESSING 3 1.5  
bs 16 lb 1.00  
ss -4 fn not used  
d1 1.000 SPECTRUM  
nt 3072 wp 25135.7  
ct 3072 sp -0.8  
TRANSMITTER rp -210.1  
tn C13 lp 169.5  
tof 2512.2 ai cdc ph  
tpwr 56 REFERENCE  
pw 10.800 rfl 1302.1  
DECOUPLER rfp 0  
dn H1 PLOT  
dof 0 wc 210  
dpwr 42 sc 0  
dm nny vs 1800  
dmm ccw hzmm 119.70  
dmf 11696 th 68  
ppvl 53  
pp 27.400

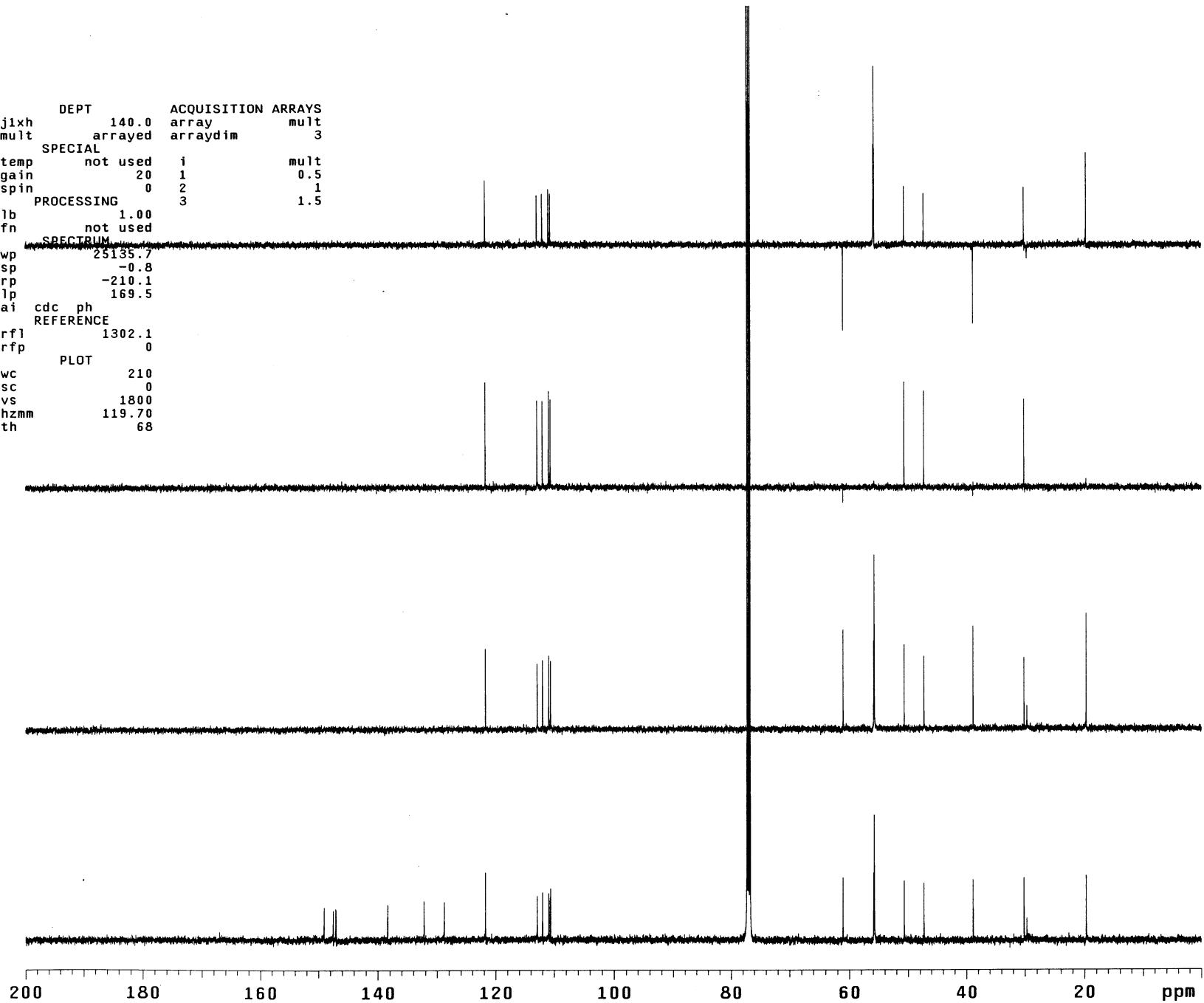
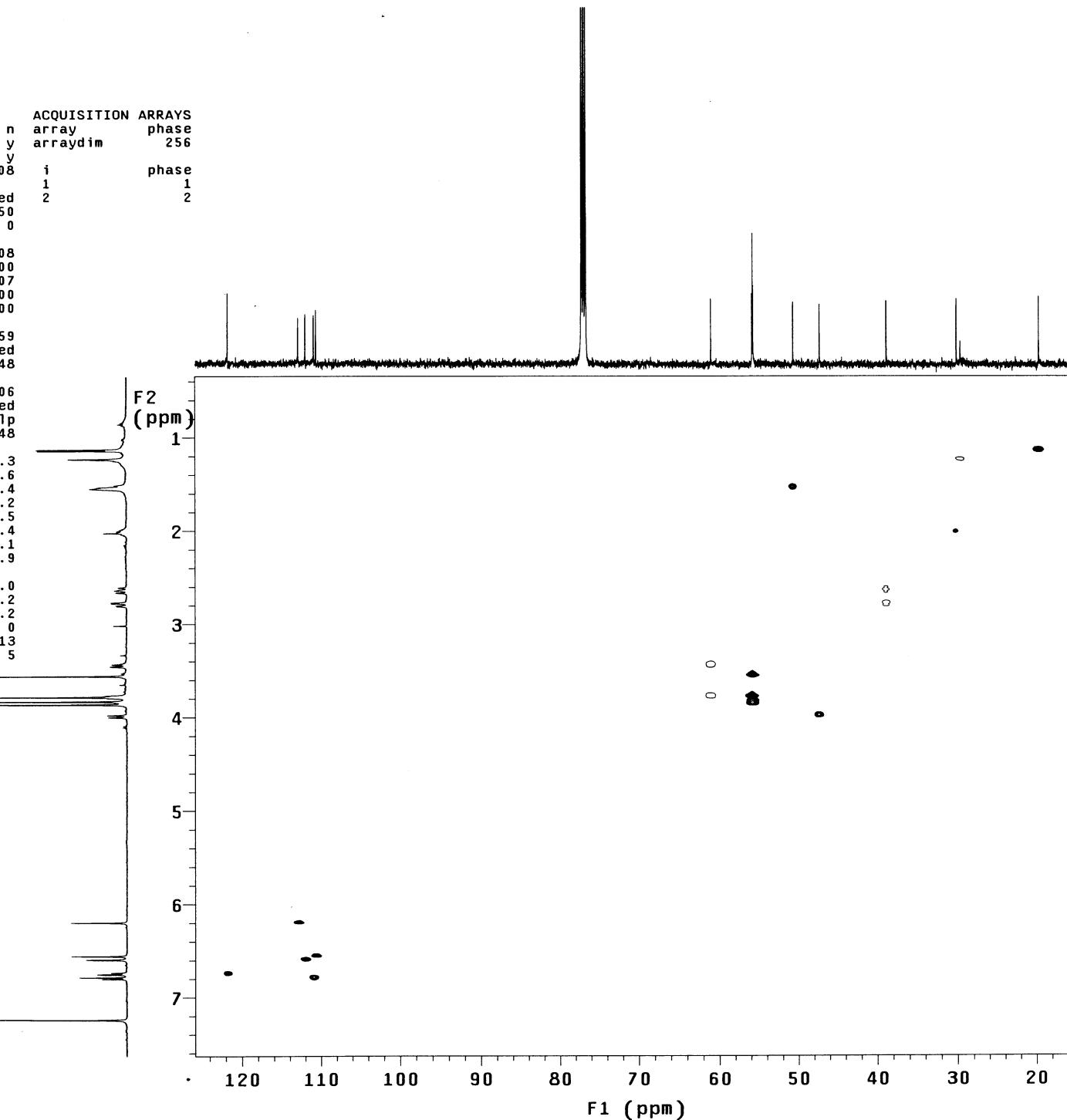


Fig S51. HSQC of compound 10.

HCS-3-139-P

exp56 gHSQC

SAMPLE	FLAGS	ACQUISITION	ARRAYS
date Jul 8 2011	hs	n	array phase
solvent cdc13	sspu1	y	arraydim 256
sample undefined	PFGflg	y	
ACQUISITION	hsglv1	1008	i phase
sw 8000.0	SPECIAL	1	1
at 0.128	temp not used	2	2
np 2048	gain	50	
fb not used	spin	0	
ss 32	GRADIENTS		
di 1.000	gzlv11	1008	
nt 12	gt1	0.002000	
2D ACQUISITION	gzlv13	507	
sw1 21367.5	gt3	0.001000	
ni 128	gstab	0.000500	
phase arrayed	F2 PROCESSING		
TRANSMITTER	gf	0.059	
tn H1	gfs	not used	
sfrq 499.830	fn	2048	
tof 499.7	F1 PROCESSING		
tpwr 58	gf1	0.006	
pw 14.000	gfs1	not used	
DECOUPLER	proc1	1p	
dn C13	fn1	2048	
dof -2515.2	DISPLAY		
dm nny	sp	173.3	
dmm ccp	wp	3640.6	
dmf 32258	sp1	1909.4	
dpwr 38	wp1	13897.2	
pwx1v1 54	rfl1	4119.5	
pwx 14.000	rfp	3097.4	
HSQC	rfl1	15472.1	
j1xh 140.0	rfp1	14188.9	
nullflg y	PLOT		
mult 2	wc	150.0	
	sc	6.2	
	wc2	116.2	
	sc2	0	
	vs	113	
	th	5	
ai cdc ph			



HCS-3-139-P

exp54 gCOSY

SAMPLE		FLAGS	
date	Jul 8 2011	hs	nn
solvent	cdcl3	sspu1	n
sample	undefined	hsglvl	1008
ACQUISITION		SPECIAL	
sw	8000.0	temp	not used
at	0.128	gain	54
np	2048	spin	0
fb	not used	F2	PROCESSING
ss	16	sb	-0.064
d1	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	8000.0	sbi	-0.016
ni	128	sbs1	not used
TRANSMITTER		proc1	1p
tn	H1	fn1	2048
sfrq	499.830	DISPLAY	
tof	499.7	sp	281.5
tpwr	58	wp	3554.7
pw	14.000	spi	279.0
GRADIENTS		wpi	3554.7
gzlvll	1008	rfl	4120.6
gt1	0.001000	rfp	3097.4
gstab	0.000500	rfl1	4115.3
DECOUPLER		rfp1	3097.4
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0

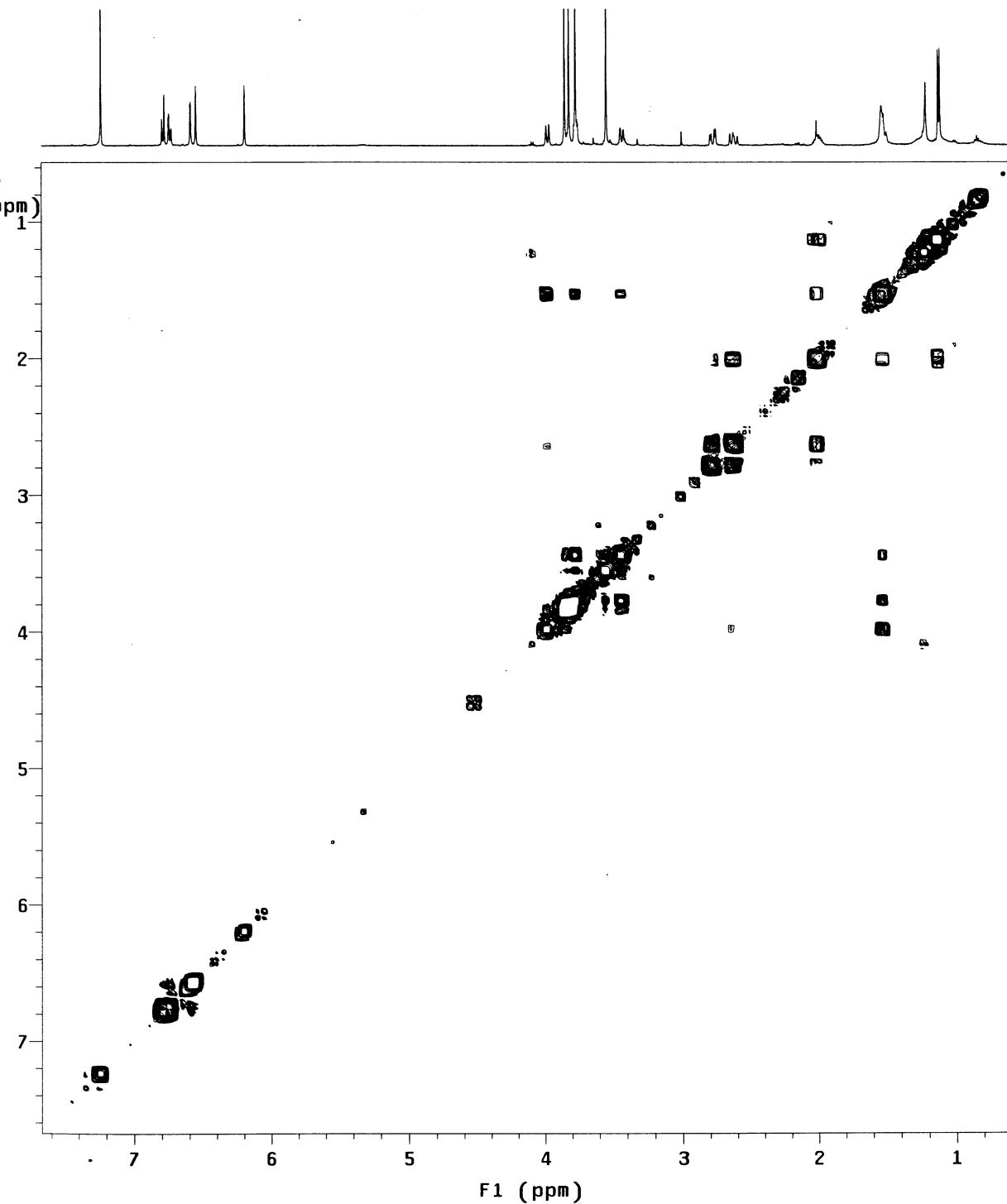


Fig S53. NOESY of compound 10.

HCS-3-139-P

exp55 NOESY

SAMPLE	hs	FLAGS
date	Jul 8 2011	n
solvent	cdcl3	sspul
sample	undefined	PFgflg
ACQUISITION	hsgrlvi	1008
sw	8000.0	SPECIAL
at	0.128	temp not used
np	2048	gain 30
fb	not used	spin 0
ss	32	F2 PROCESSING
di	1.000	gf 0.059
nt	8	gfs not used
2D ACQUISITION	fn 2048	
sw1	8000.0	F1 PROCESSING
ni	200	gf1 0.023
TRANSMITTER	H1	gfs1 not used
tn	499.830	proc1 lp
sfrq	499.7	fn1 2048
tpwr	58	DISPLAY
pw	14.000	sp 234.5
mix	0.600	wp 3625.0
NOESY	wpi 3625.0	sp1 242.8
PRESATURATION	rfl 4120.7	
satmode	nnnn	rfp 3097.4
satpwr	0	rfl1 4112.5
satdly	0	rfp1 3097.4
satfrq	0	
DECOUPLER	wc 155.0	PLOT
dn	C13 sc 10.0	
dm	nnn wc2 155.0	
	sc2 0	
	vs 113	
	th	
	ai	
	ph	

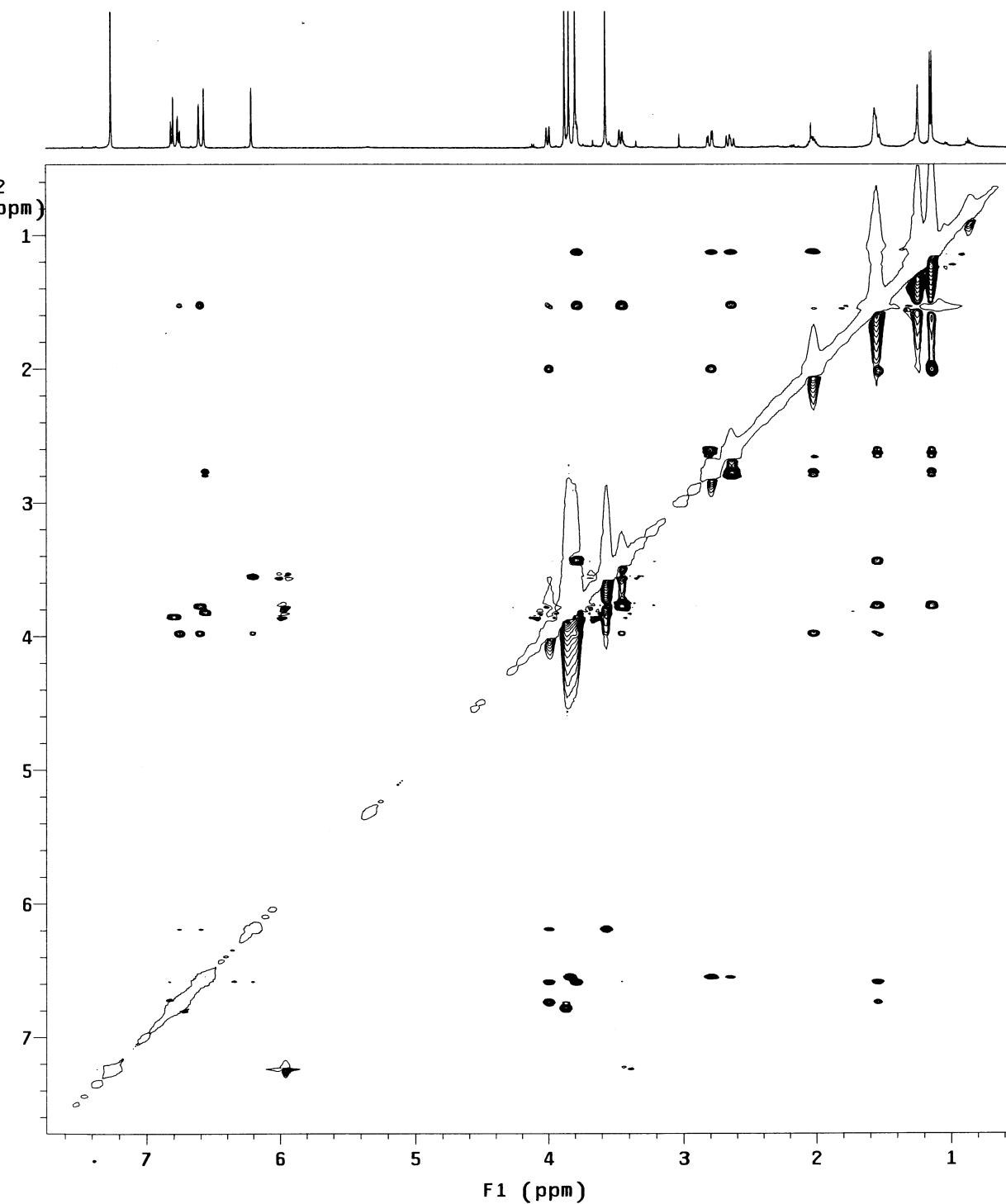


Fig S54.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) of compound 1

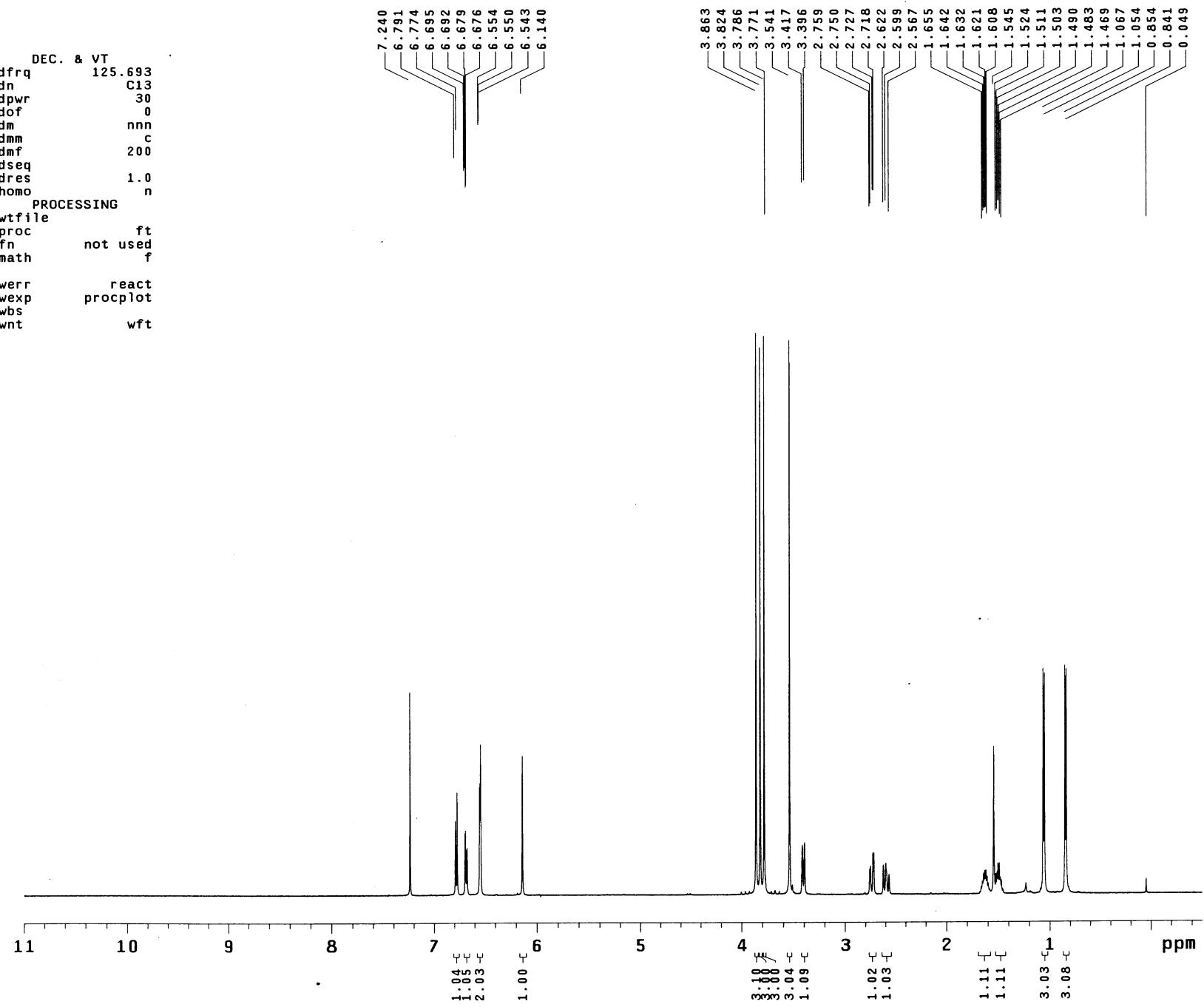
S54

```

HCS-3-143-p
exp23 s2pul

SAMPLE           DEC. & VT
date   Jul 11 2011 dfrq   125.69
solvent    cdc13   dn      C1
file       exp     dof
ACQUISITION
sfrq      499.830 dm
tn        1       dmm
at        3.000  dmf
np        48000  dseq
sw        8000.0  dres
fb        not used homo
bs        4       PROCESSING
tpwr      58      wtfile
pw        4.8     proc
d1        1.000   fn      not used
tof       499.7   math
nt        4       werr
ct        4       wexp
alock     y       wbs
gain      not used wnt
FLAGS
il        n
in        n
dp        y
hs        nn
DISPLAY
sp        -250.1
wp        5747.8
vs        100
sc        0
wc        210
hzmm     27.37
is        281.66
rfl      4638.4
rfp      3618.7
th        2
ins      1.000
nm  cdc  ph

```



S53

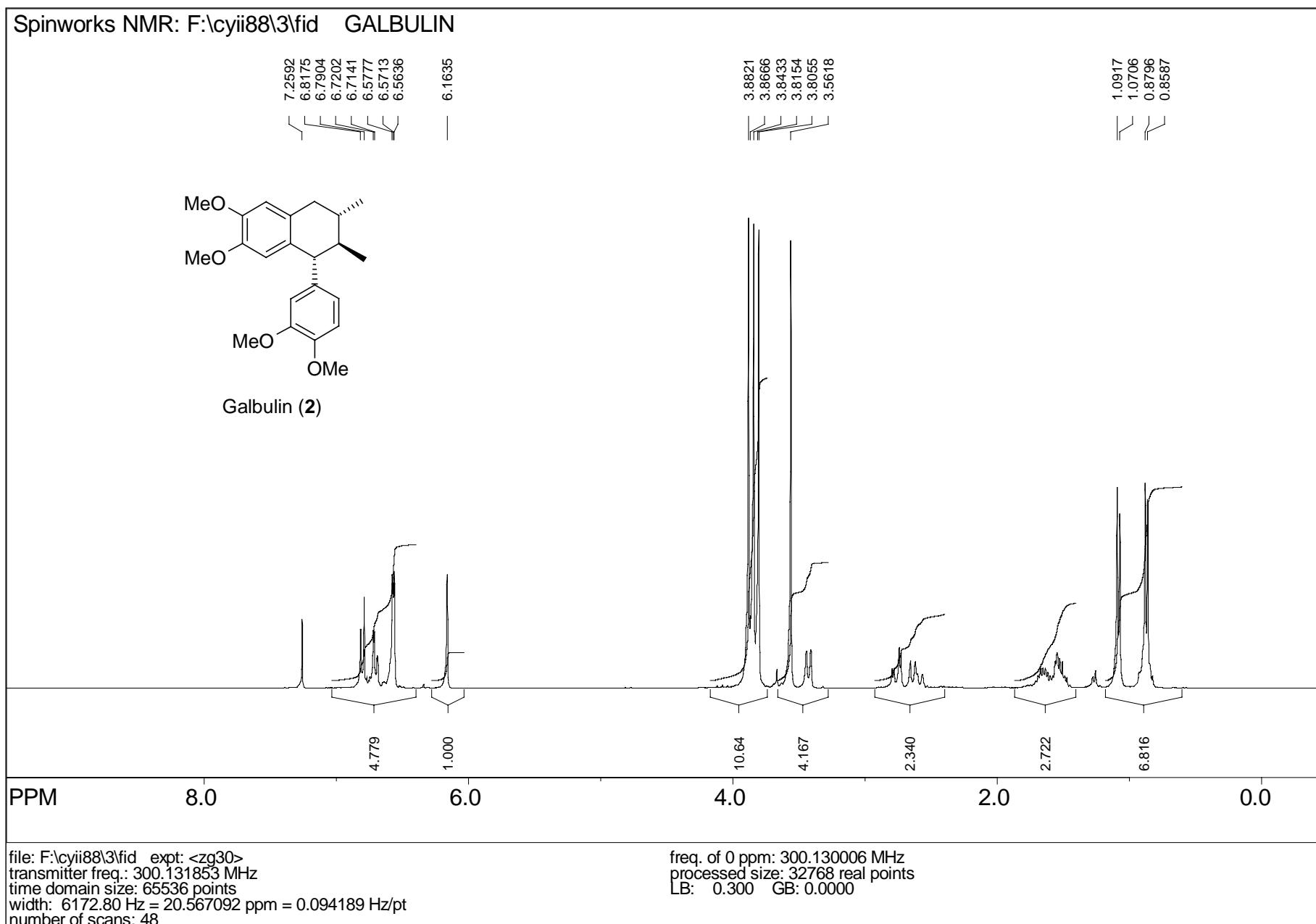
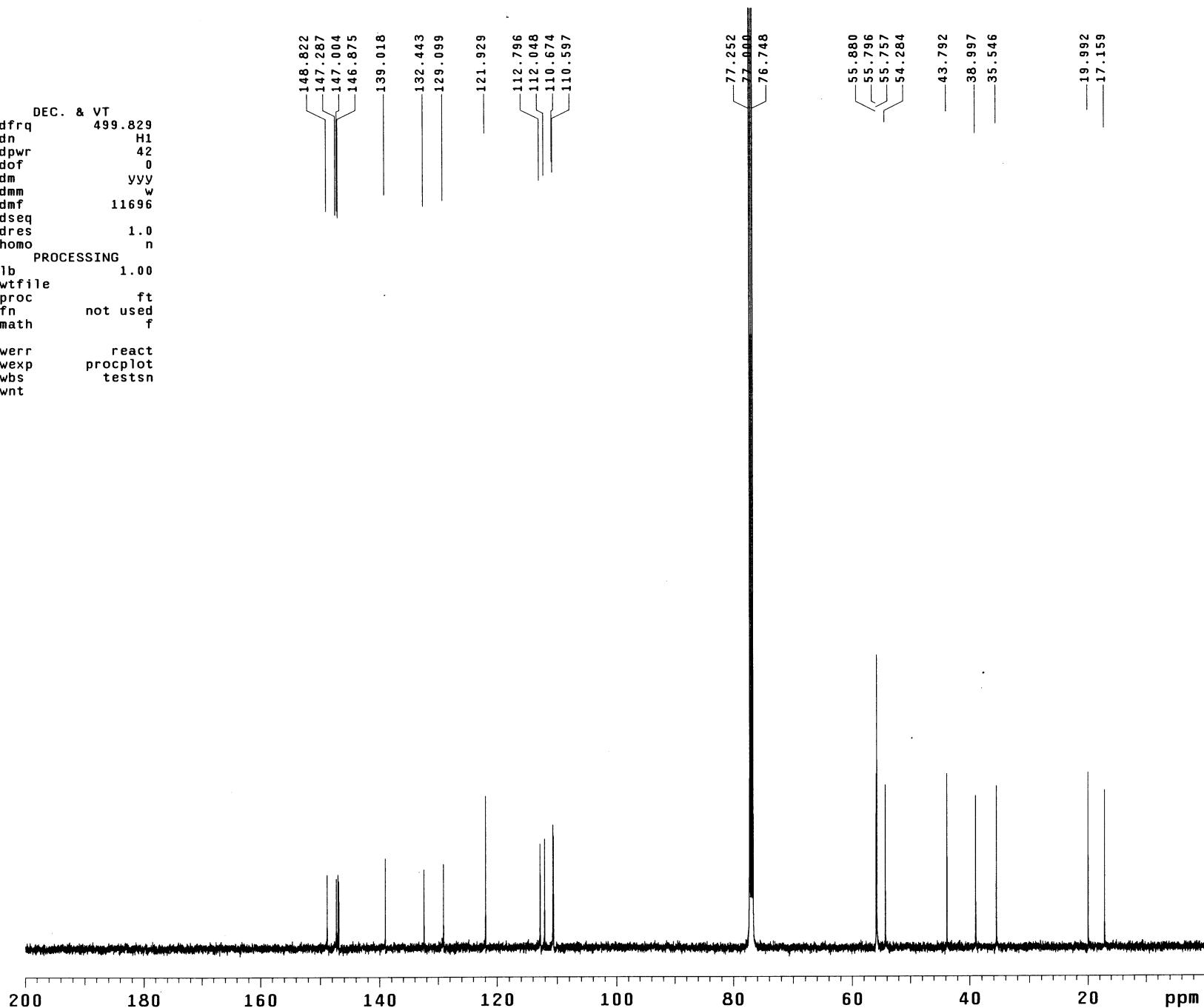


Fig S56.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) of compound 1.

HCS-3-143-p

exp24 s2pul

SAMPLE	DEC. & VT		
date	Jul 11 2011	dfreq	499.829
solvent	cdcl3	dn	H1
file	exp	dpwr	42
ACQUISITION	dof	0	
sfreq	125.696	dm	yyy
tn	C13	dmm	w
at	1.000	dmf	
np	62894	dseq	
sw	31446.5	dres	1.0
fb	not used	homo	n
bs	16	PROCESSING	
ss	2	lb	1.00
tpwr	56	wtfile	
pw	3.0	proc	ft
d1	2.000	fn	not used
tof	2512.2	math	f
nt	3072		
ct	3072	werr	react
alock	y	wexp	procplot
gain	not used	wbs	testsn
FLAGS	wnt		
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-0.8		
wp	25135.7		
vs	426		
sc	0		
wc	210		
hzmm	119.70		
is	500.00		
rfl	10980.6		
rfp	9677.5		
th	7		
ins	100.000		
nm	cdc ph		



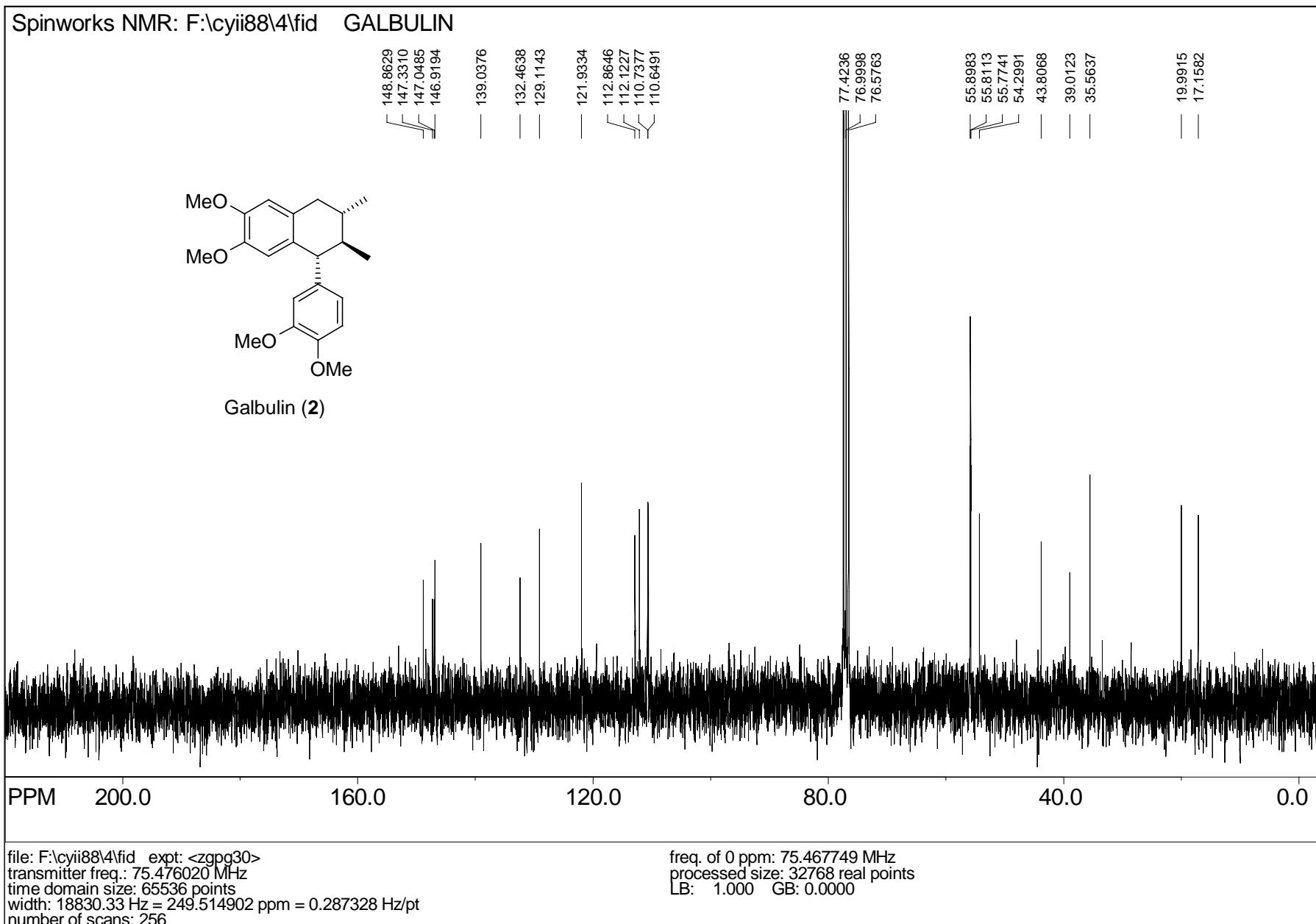


Fig S58. DEPT of compound 1.

HCS-3-143-p

exp25 DEPT

SAMPLE DEPT ACQUISITION ARRAYS  
date Jul 11 2011 j1xh 140.0 array mult  
solvent cdc13 mult arrayed arraydim 3  
sample undefined SPECIAL  
ACQUISITION temp not used i mult  
sw 31446.5 gain 20 1 0.5  
at 1.000 spin 0 2 1  
np 62894 PROCESSING 3 1.5  
bs 16 lb 1.00  
ss -4 fn not used  
d1 1.000 SPECTRUM  
nt 2048 wp 25135.7  
ct 2048 sp -0.8  
TRANSMITTER rp -219.6  
tn C13 lp 192.8  
tof 2512.2 ai cdc ph  
tpwr 56 REFERENCE  
pw 10.800 rfl 1303.1  
DECOUPLER rfp 0  
dn H1 PLOT  
dof 0 wc 210  
dpwr 42 sc 0  
dm nny vs 600  
dmm ccw hzmm 119.70  
dmf 11696 th 68  
pp1v1 53  
pp 27.400

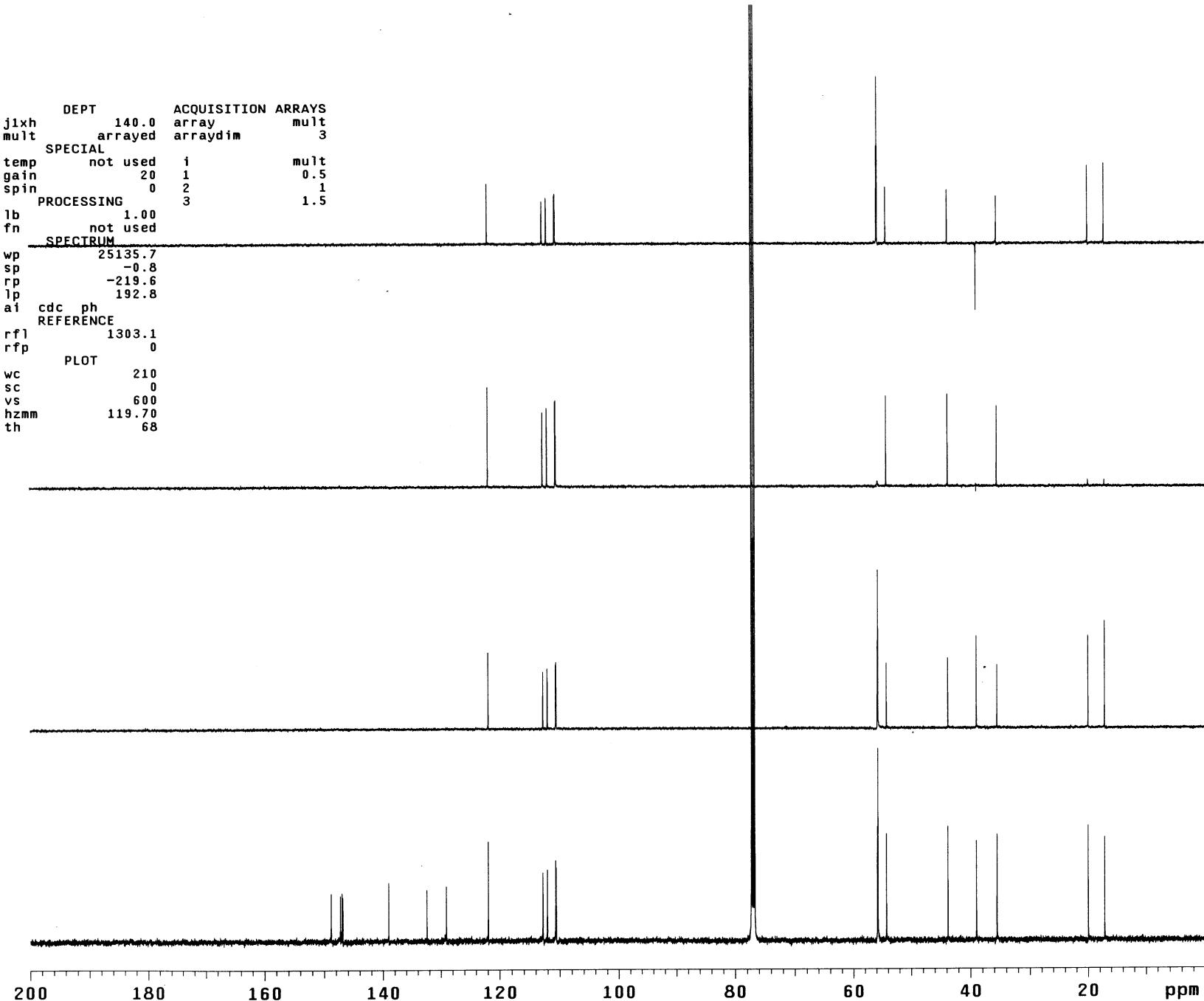


Fig S59. HSQC of compound 1

S59

HCS-3-143-p

exp28 gHSQC

SAMPLE		FLAGS		ACQUISITION		ARRAYS
date	Jul 11 2011	hs	n	array		phase
solvent	cdcl3	sspul	y	arraydim	25	
sample	undefined	PFGflg	y			
ACQUISITION		hsgv1	1008	i		phase
sw	5006.3	SPECIAL		1		
at	0.205	temp	not used	2		
np	2048	gain	50			
fb	not used	spin	0			
ss	32	GRADIENTS				
d1	1.000	gzlv1	1008			
nt	16	gt1	0.002000			
2D ACQUISITION		gzlv13	507			
sw1	21367.5	gt3	0.001000			
ni	128	gstab	0.000500			
phase	arrayed	F2 PROCESSING				
TRANSMITTER		gf	0.094			
tn	H1	gfs	not used			
sfrq	499.829	fn	2048			
tof	-499.9	F1 PROCESSING				
tpwr	58	gfi	0.006			
pw	14.000	gfs1	not used			
DECOUPLER		proc1	1p			
dn	C13	fn1	2048			
dof	-2515.2	DISPLAY				
dm	nny	sp	249.3			
dmm	ccp	wp	3510.2			
dmf	32258	sp1	1487.9			
dpwr	38	wpi	14690.2			
pxw1v1	54	rfl	3592.0			
pxw	14.000	rfp	3068.9			
HSQC		rfl1	15463.7			
j1xh	140.0	rfp1	14176.4			
nullflg	y	PLOT				
mult	2	wc	150.0			
		sc	6.2			
		wc2	116.2			
		sc2	0			
		vs	200			
		th	4			
		ai	cdc ph			

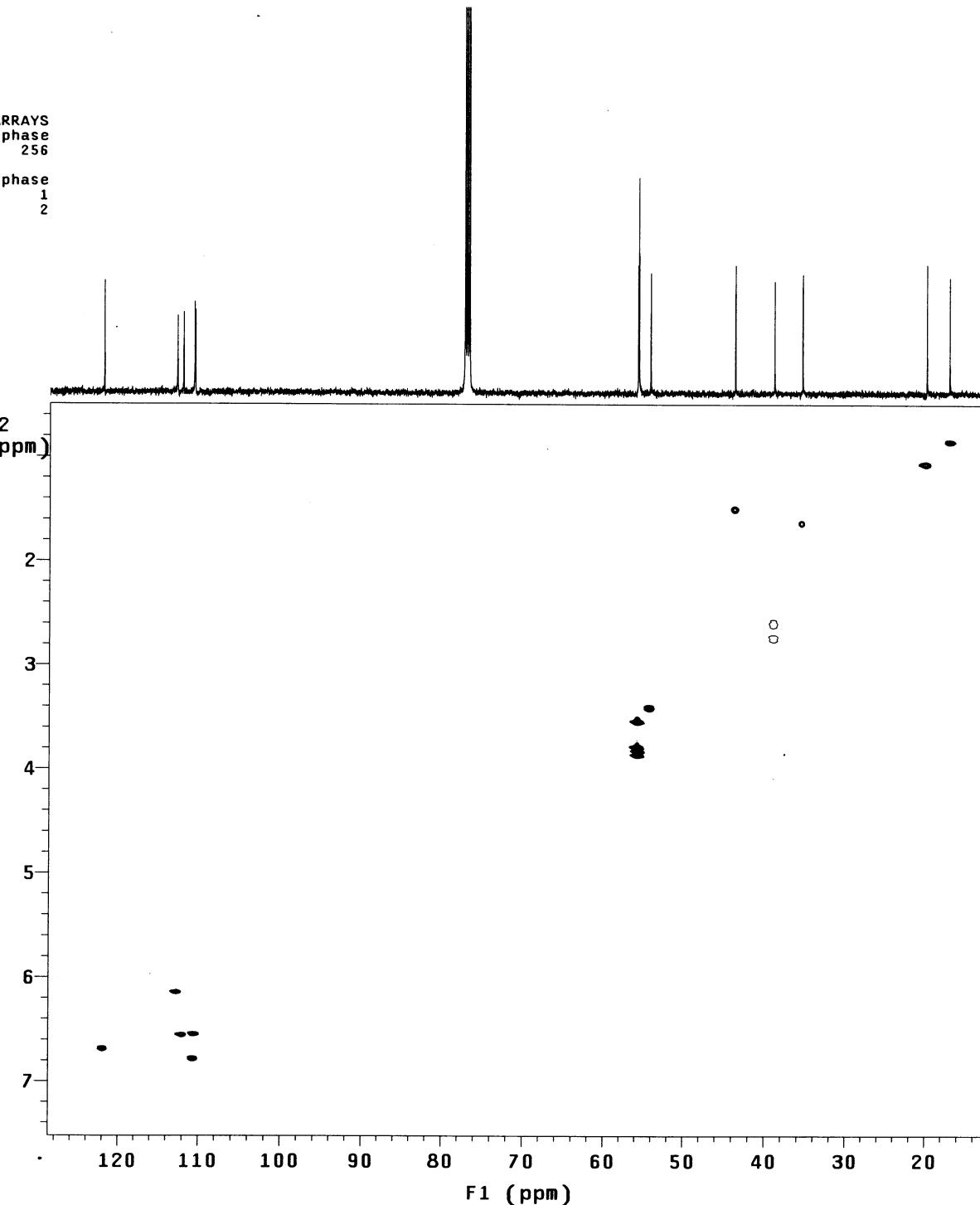


Fig S60. COSY of compound 1.

S60

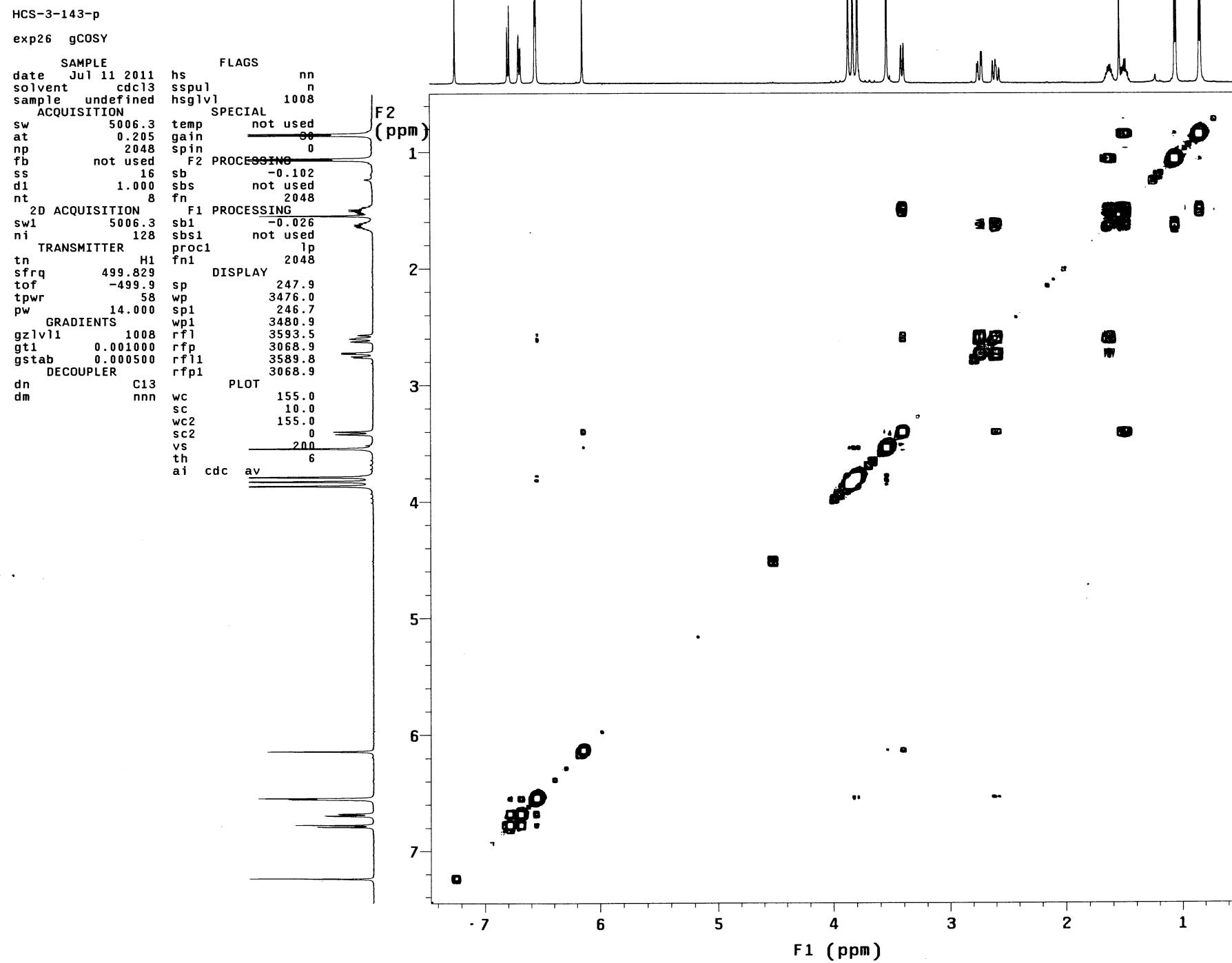
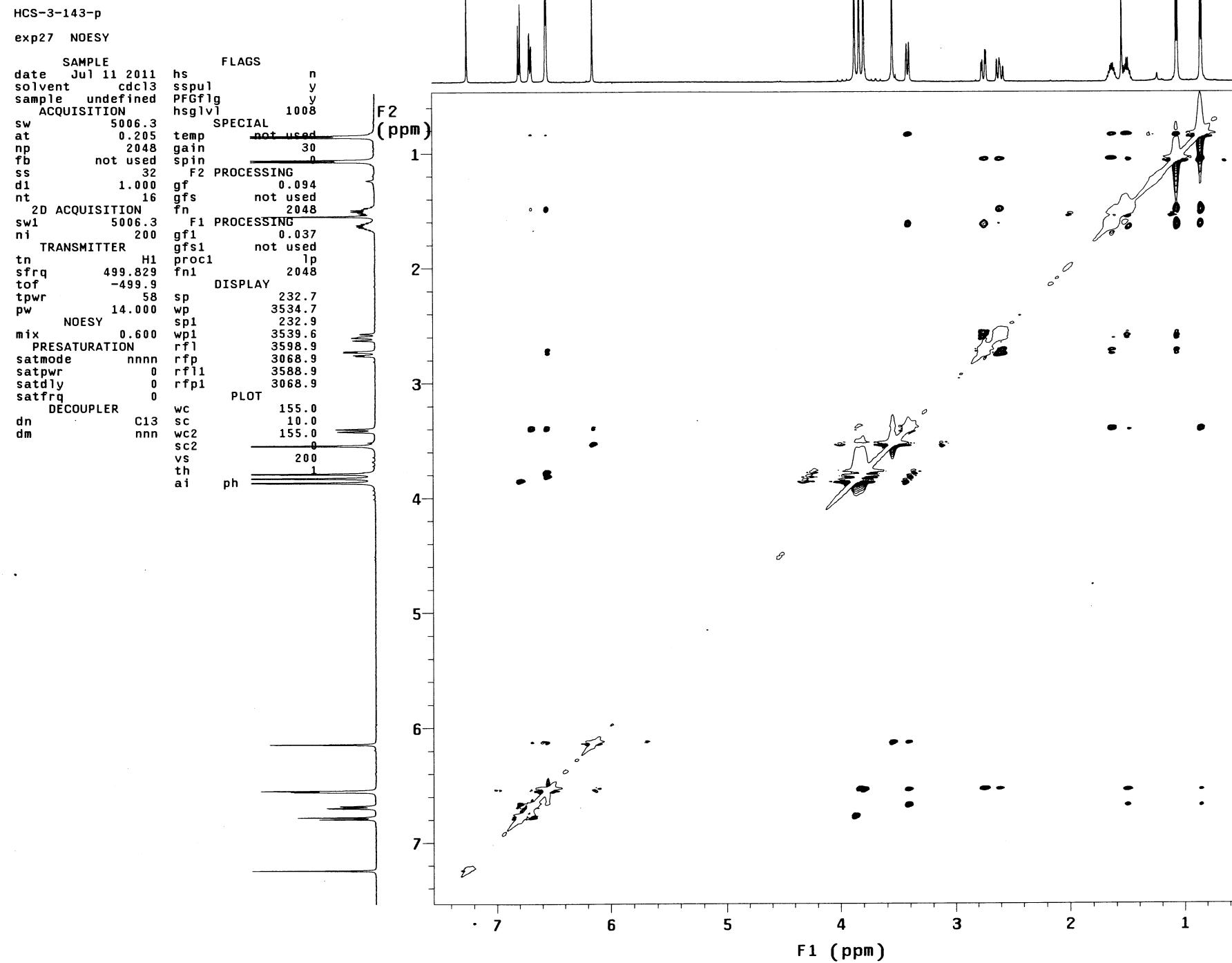


Fig S61. NOESY of compound 1.

S61



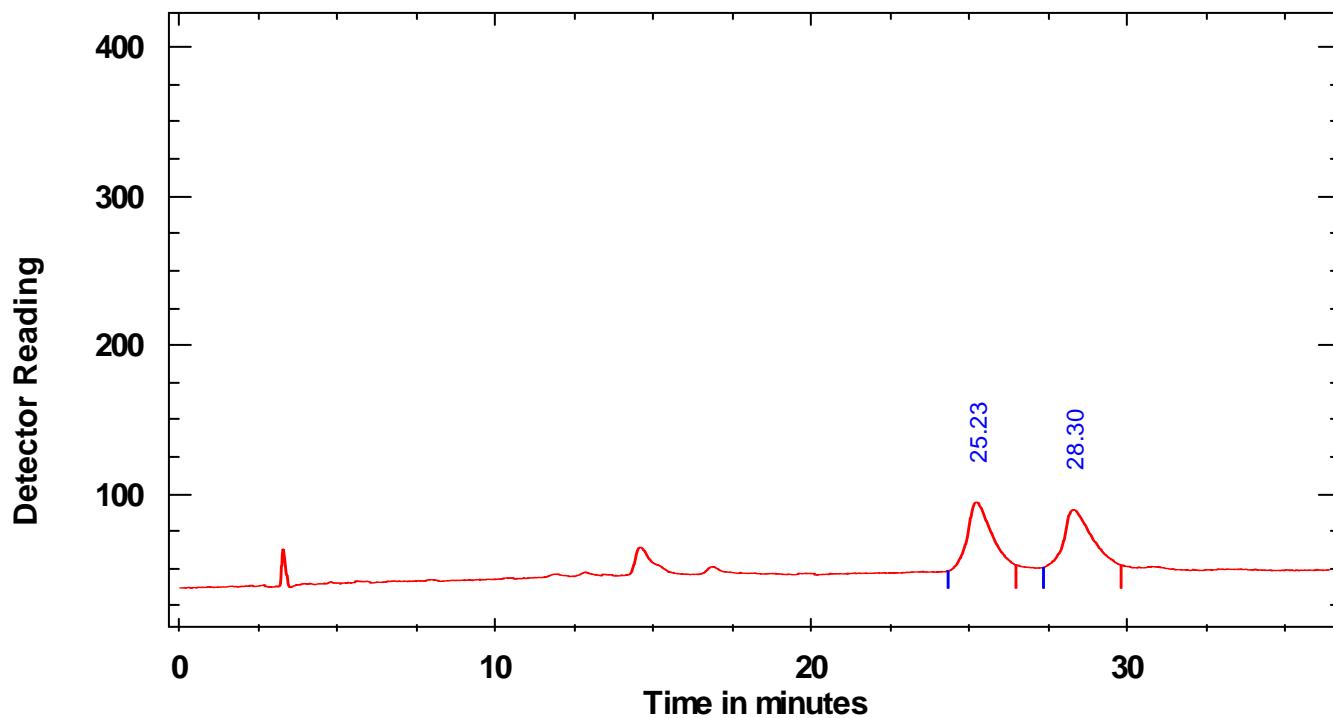


# Chromatogram Report

HCS-3-81-RACEMATE-COL-IA-20%-EA/HEX

First line of organization's address  
Second line of organization's address

Report produced on 2011/7/26 at 下午 01:31:04 by Put your name here



2011/7/26 11:52:04 Flow set to 1.00 at 0.00 minutes

2011/7/26 12:28:32 Run stopped by operator

## PEAK REPORT

#	begin	end	area	percent	maximum	time	begins as	name
1	24.33	26.48	2292	50.4	94.39	25.23	Baseline	
2	27.35	29.81	2257	49.6	89.36	28.30	Baseline	

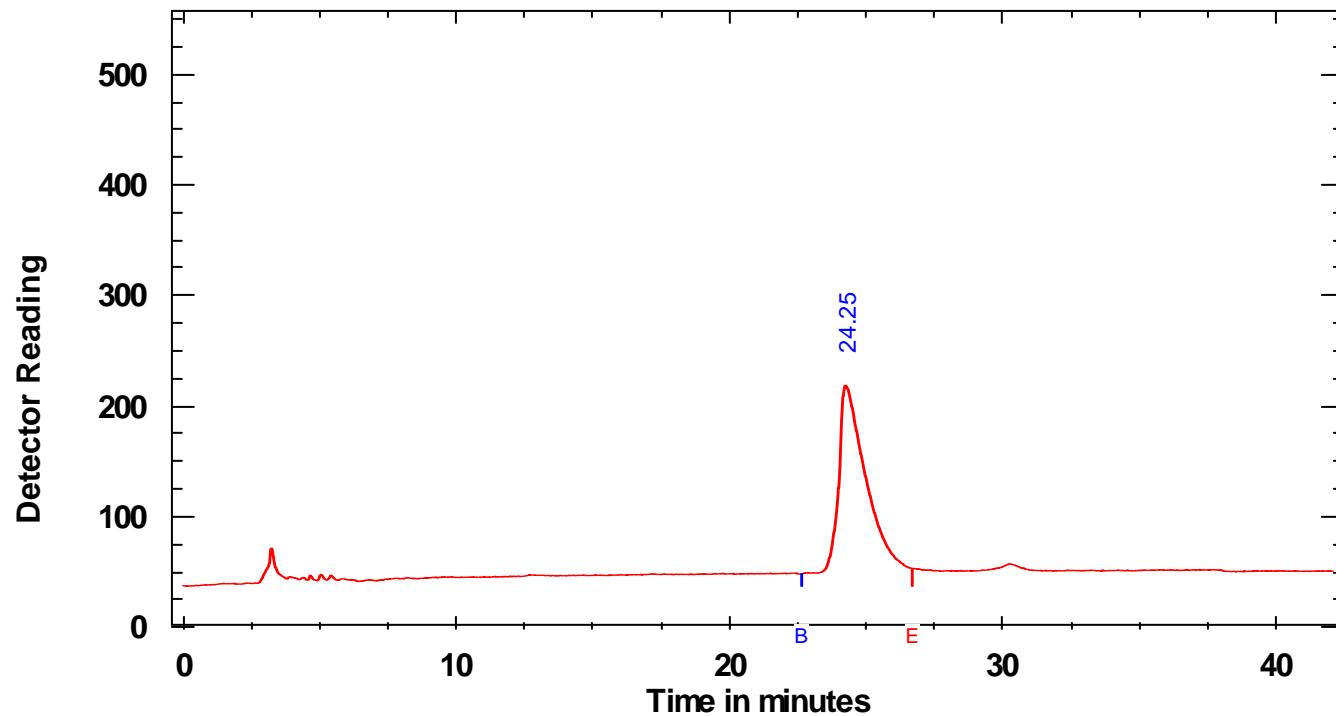


# Chromatogram Report

HCS-006(CHIRAL)COL-IA 20% EA+HX

First line of organization's address  
Second line of organization's address

Report produced on 2011/7/26 at 下午 02:33:10 by Put your name here



2011/7/26 01:49:21 Flow set to 1.00 at 0.00 minutes

2011/7/26 02:31:29 Run stopped by operator

## PEAK REPORT

#	begin	end	area	percent	maximum	time	begins as	name
1	22.64	26.69	11390	100.0	218.31	24.25	Baseline	

Fig S64. HPLC analysis of the mixture of racemic and chiral compound (+)-3 obtained.

(For comparison)

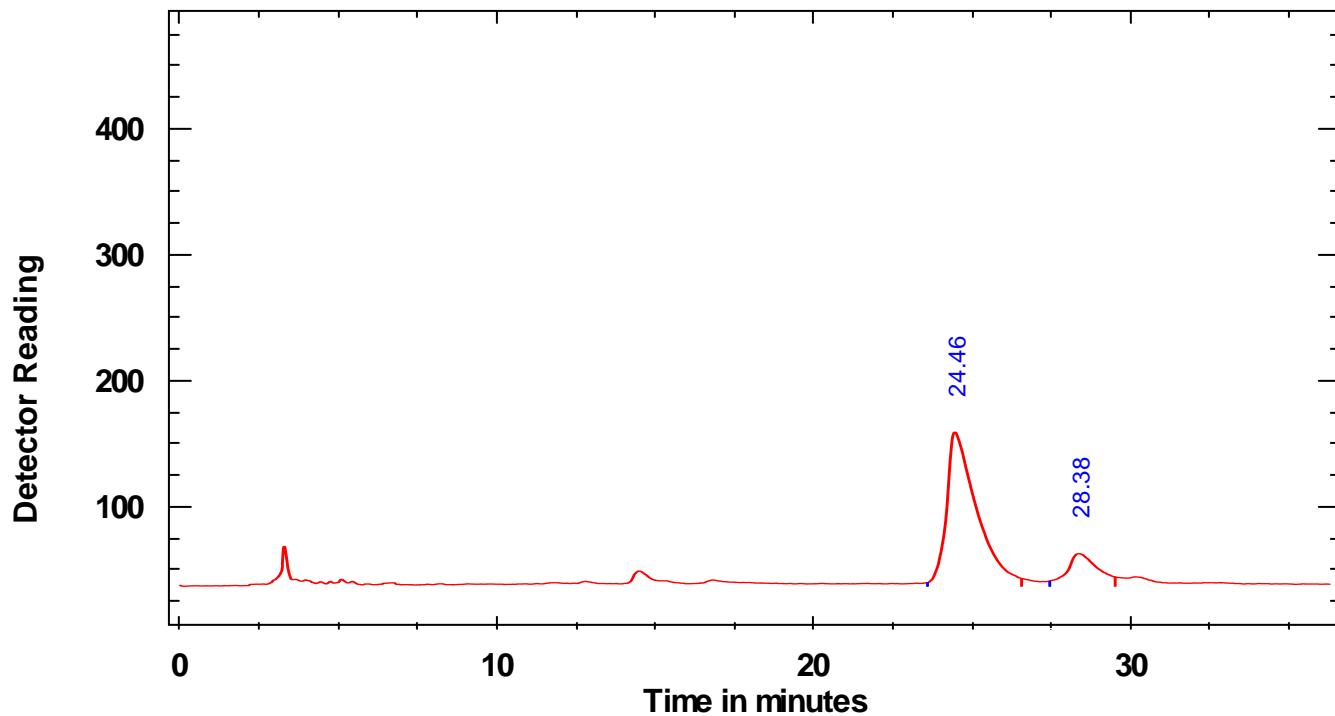


# Chromatogram Report

HCS-006(CO)COL-IA 20% EA+HX

First line of organization's address  
Second line of organization's address

Report produced on 2011/7/26 at 下午 03:13:54 by Put your name here



2011/7/26 02:34:54 Flow set to 1.00 at 0.00 minutes

2011/7/26 03:11:15 Run stopped by operator

## PEAK REPORT

#	begin	end	area	percent	maximum	time	begins as	name
1	23.59	26.56	7389	87.5	159.20	24.46	Baseline	
2	27.45	29.51	1052	12.5	62.81	28.38	Baseline	