

## Electronic Supplementary Information

### **Synthesis of Functionalized Resorcinols by Rhodium-Catalyzed [5+1] Cycloaddition Reaction of 1,4-Enyne Esters with CO**

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## General

<sup>1</sup>H NMR spectra were recorded using JEOL JMN-500 (500 MHz) or JMN-400 (400 MHz) spectrometer in CDCl<sub>3</sub>. <sup>13</sup>C NMR spectra were recorded using JEOL JMN-500 (125 MHz) or JMN-400 (100 MHz) spectrometer. NMR shifts are reported relative to the residual solvent signal (7.27 ppm) for <sup>1</sup>H NMR and solvent central peak for carbon spectra (77.0 ppm). Chemical shifts are given in parts per million (δ). Infrared spectra were obtained using a JASCO FT-IR 4100 spectrometer; absorptions are reported in reciprocal centimetres. Both conventional and high resolution mass spectra were recorded with JEOL JMS700 spectrometer. The products were purified by flash chromatography on silica gel (Nacalai Tesque Inc., Silica Gel 60, 230-400 mesh). All commercially available reagents were used without further purification. 1,4-enynes were prepared from aldehyde in two steps.

### Preparation of (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate (1a).

*Trans*-cinnamaldehyde (2.5 mL, 20 mmol) was slowly added to a solution of ethynylmagnesiumbromide (c = 0.44 M, 45 mL, 20 mmol) at -78°C. The reaction mixture was allowed to warm to rt. After completion the reaction, aqueous NH<sub>4</sub>Cl was added, and aqueous layer was extracted by Et<sub>2</sub>O. The combined organic layers were washed with NaCl, dried over MgSO<sub>4</sub>, filtered and evaporated *in vacuo* to give 3.1 g of the crude (*E*)-1-phenylpent-1-en-4-yn-3-ol. The yellow solid was used in the next step without further purification.

Pivaloyl chloride (0.7 mL, 5.5 mmol) was added to a solution of (*E*)-1-phenylpent-1-en-4-yn-3-ol (796 mg, 5 mmol) in triethylamine (0.8 mL, 5.5 mmol) and 17 mL of DCM. The reaction mixture was stirred at room temperature for 24 hours and was then quenched with aqueous NH<sub>4</sub>Cl, and aqueous layer was extracted by DCM. The combined organic layers were washed with NaCl and dried over MgSO<sub>4</sub>, filtered and evaporated *in vacuo* to give 1.23 g of the crude reaction mixture. Purification by flash chromatography on silica gel (5% AcOEt/hexane) gave (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate as a yellow oil (1.03 g, 84 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.44-7.40 (m, 2H), 7.33-7.36 (m, 2H), 7.30-7.29 (m, 1H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 15.6, 6.5 Hz, 1H), 6.06-6.04 (m, 1H), 2.62 (d, 1H, *J* = 2.3 Hz), 1.25 (s, 9H).

Shi, X.; Gorin, D. J.; Toste, F. D.; *J. Am. Chem. Soc.* **2005**, *127*, 5802.

### (*E*)-1-phenylpent-1-en-4-yn-3-yl acetate (1b)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.42-7.40 (m, 2H), 7.35-7.26 (m, 3H), 6.89 (d, *J* = 15.6 Hz, 1H), 6.23 (dd, *J* = 16.1, 6.5 Hz, 1H), 6.04 (d, *J* = 9.5 Hz, 1H), 2.64 (d, 1H, *J* = 2.3 Hz), 2.11

(s, 3H). Detz, R. J.; Delville, M. M. E.; Hiemstra, H.; van Marrseveen, J. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 3777.

**(E)-1-(4-(trifluoromethyl)phenyl)pent-1-en-4-yn-3-yl pivalate (1c)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.59 (d, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.31 (dd, *J* = *J* = 16.0, 6.4 Hz, 1H), 6.06 (d, *J* = 16.0, 1H), 2.63 (br, 1H), 1.25 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 177.3, 139.3, 133.0, 127.3, 126.4, 125.7, 79.3, 75.5, 63.6, 39.0, 27.2; IR (KBr) 2126, 1735, 1617 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 310 (M<sup>+</sup>, 19), 209 (74), 208 (68), 139 (36), 57 (100); HRMS (EI) *m/z* calcd for C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>F<sub>3</sub>: 310.1181, found: 310.1182.

**(E)-1-(4-methoxyphenyl)pent-1-en-4-yn-3-yl pivalate (1d)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.35 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 16.0 Hz, 1H), 6.09 (dd, *J* = 15.6, 6.5 Hz, 1H), 6.01 (d, *J* = 5.5 Hz, 1H), 3.81 (s, 3H), 2.60 (d, *J* = 1.8 Hz, 1H), 1.24 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 177.3, 160.0, 134.2, 128.5, 128.3, 121.4, 114.2, 79.9, 74.9, 64.2, 55.4, 38.9, 27.1; IR (neat) 2124, 1730, 1607 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 272 (M<sup>+</sup>, 19), 171 (100), 170 (77), 155 (35), 128 (61), 57 (65); HRMS (EI) *m/z* calcd for C<sub>17</sub>H<sub>20</sub>O<sub>3</sub>: 272.1412, found: 272.1411.

**(E)-2-methyl-1-phenylpent-1-en-4-yn-3-yl pivalate (1e)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.37-7.34 (m, 2H), 7.31-7.29 (m, 2H), 7.27-7.24 (m, 1H), 6.76 (s, 1H), 5.93 (bs, 1H), 2.56 (d, *J* = 2.3 Hz, 1H), 1.98 (s, 3H), 1.25 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 177.2, 136.8, 132.9, 129.6, 129.2, 128.3, 127.2, 79.9, 74.8, 68.9, 39.0, 27.2, 14.3. IR (neat) 2123, 1732, 1600 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 256 (M<sup>+</sup>, 25), 155 (59), 154 (82), 153 (100), 57 (60); HRMS (EI) *m/z* calcd for C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>: 272.1596, found: 272.1592.

**3-methyl-1-phenylpent-1-en-4-yn-3-yl acetate (1f)**

Obtained as an *E/Z* mixture (*E:Z* = 1:0.22), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) *E* isomer : δ 7.43-7.25 (m, 5H), 6.93 (d, *J* = 15.6 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 2.77 (s, 1H), 2.07 (s, 3H), 1.82 (s, 3H); *Z* isomer : 7.43-7.26 (m, 5H), 6.73 (d, *J* = 9.2 Hz, 1H), 5.94 (d, *J* = 9.2 Hz, 1H), 3.28 (s, 1H), 2.10 (s, 3H), 1.90 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) *E* isomer : δ 168.8, 139.0, 135.7, 131.1, 128.4, 126.7, 126.2, 82.2, 75.0, 28.6, 21.7; *Z* isomer : δ 169.6, 139.6, 129.3, 128.0, 127.9, 126.6, 120.6, 83.3, 73.9, 22.8, 21.0. IR (neat) 1743 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 214 (M<sup>+</sup>, 21), 171 (60), 154 (65), 153 (68), 85 (97), 83 (100); HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>: 214.0994, found: 214.0980.

**(E)-hex-4-en-1-yn-3-yl pivalate (1g)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 6.03-5.93 (m, 1H), 5.79-5.77 (m, 1H), 5.56-5.51 (m, 1H), 2.50 (bs, 1H), 1.73 (d, *J* = 6.6 Hz, 1H), 1.20 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 177.2, 131.4, 126.0, 80.2, 74.4, 63.9, 38.8, 27.1, 17.7; IR (neat) 2147, 1732 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>: 180.1150, found: 180.1148.

**(E)-non-4-en-1-yn-3-yl pivalate (1h)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 6.01-5.95 (m, 1H), 5.80 (d, *J* = 6.0 Hz, 1H), 5.52 (dd, *J* = 14.7, 6.4 Hz, 1H), 2.52 (d, 1H, *J* = 1.4 Hz), 2.09-2.05 (m, 2H), 1.41-1.35 (m, 2H), 1.35-1.28 (m, 2H), 1.21 (s, 9H), 0.89 (t, 3H, *J* = 7.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 177.3, 136.7, 124.7, 80.3, 74.4, 64.0, 38.8, 31.8, 31.0, 27.1, 22.3, 14.0; IR (neat) 2117, 1734 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>: 222.1620, found: 222.1624.

**(E)-6-methylhept-4-en-1-yn-3-yl pivalate (1i)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 5.96 (ddd, *J* = 15.6, 6.9, 1.4 Hz), 5.81 (d, *J* = 6.4 Hz, 1H), 5.47 (ddd, *J* = 15.5, 6.4, 1.4 Hz, 1H), 2.52 (d, *J* = 2.3 Hz, 1H), 2.31-2.37 (m, 1H), 1.20 (s, 9H), 1.01 (d, *J* = 6.9 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 177.3, 143.2, 122.0, 80.3, 74.4, 64.0, 38.8, 30.7, 27.1, 22.0; IR (neat) 2125, 1735 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>: 208.2967, found: 208.1457.

**1-cyclohexenylprop-2-ynyl pivalate (1j)**

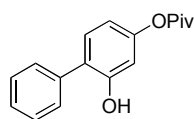
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 5.98 (bs, 1H), 5.73 (s, 1H), 2.48 (d, *J* = 1.9 Hz, 1H), 2.22-1.98 (m, 4H), 1.64-1.68 (m, 2H), 1.57-1.61 (m, 2H), 1.22 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 177.3, 133.2, 127.3, 80.1, 74.1, 67.4, 38.9, 27.1, 25.1, 24.4, 22.5, 22.1.; IR (neat) 2122, 1735 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 220 (M<sup>+</sup>, 4), 117 (34), 91 (23), 83 (22), 57 (100).; HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>: 220.1463, found: 220.1468.

**4-pentylpent-4-en-1-yn-3-yl pivalate (1k)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 5.81 (s, 1H), 5.32 (s, 1H), 5.02 (s, 1H), 2.50 (d, *J* = 2.3 Hz, 1H), 2.12-2.18 (m, 2H), 1.55-1.60 (m, 2H), 1.30-1.35 (m, 4H), 1.33 (s, 9H), 0.88 (t, *J* = 6.4 Hz, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 176.7, 144.1, 113.4, 79.7, 74.2, 65.9, 38.6, 31.8, 31.4, 27.1, 26.9, 22.4, 13.9; IR (neat) 2125, 1737 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 236 (M<sup>+</sup>, 0.2), 152 (46), 119 (72), 105 (88), 91 (100), 77 (55), 67 (16); HRMS (EI) *m/z* calcd for C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>: 236.1776, found: 236.1771.

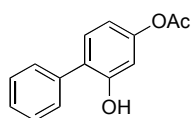
**Typical procedure for the rhodium-catalyzed carbonylation of enyne esters:** A magnetic stir bar, (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate (**1a**, 128.5 mg, 0.53 mmol), tetracarbonyldichlorodirhodium (4.9 mg, 0.013 mmol) and 10 mL of CH<sub>2</sub>Cl<sub>2</sub> were placed in a 50 mL stainless steel autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 80 atm of carbon monoxide and then heated at 80 °C for 5 h. Excess of CO was discharged at room temperature. The autoclave was washed with ether and solvents were removed under reduced pressure to give 135 mg of crude reaction mixture as a brown oil. The residue was then purified by short flash chromatography on SiO<sub>2</sub> (30 % Et<sub>2</sub>O/hexane) to give **3a** as an orange solid (108.7 mg, 76%).

### 2-hydroxybiphenyl-4-yl pivalate (**3a**)



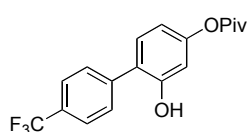
Reaction was carried out with 0.05 M in CH<sub>2</sub>Cl<sub>2</sub>. orange solid; (*R*<sub>f</sub> = 0.15, hexane:EtOAc = 9:1); mp = 97–99 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.48–7.44 (m, 4H), 7.40–7.38 (m, 1H), 7.25–7.23 (m, 1H), 6.72–6.71 (m, 2H), 5.57 (bs, 1H), 1.39 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 177.2, 153.2, 151.4, 136.5, 130.6, 129.1, 127.7, 125.8, 113.8, 109.3, 39.1, 27.1; IR (KBr) 3600–3100 (br), 3052, 2965, 2872, 2933, 1744, 1732, 1610, 1591, 1129, 1150 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 270 (M<sup>+</sup>, 32), 187 (20), 186 (100), 185 (21), 69 (24), 57 (49); HRMS (EI) *m/z* calcd for C<sub>17</sub>H<sub>18</sub>O<sub>3</sub> (M<sup>+</sup>): 270.1256, found: 270.1252.

### 2-hydroxybiphenyl-4-yl acetate (**3b**)



Reaction was carried out with 0.016 M in CH<sub>2</sub>Cl<sub>2</sub>. orange solid; (*R*<sub>f</sub> = 0.25, hexane:EtOAc = 4:1); mp = 109–111 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.49–7.46 (m, 2H), 7.45–7.43 (m, 2H), 7.41–7.38 (m, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.74–6.73 (m, 2H), 5.36 (bs, 1H), 2.31 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 169.5, 153.2, 151.0, 136.4, 130.7, 129.2, 127.9, 126.0, 113.9, 109.3, 21.1; IR (KBr) 3500–3100 (br), 3070, 2924, 1732, 1604, 1227, 1196 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 228 (M<sup>+</sup>, 37), 187 (34), 186 (100), 185 (62), 128 (21); HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>12</sub>O<sub>3</sub> (M<sup>+</sup>): 228.0786, found: 228.0782.

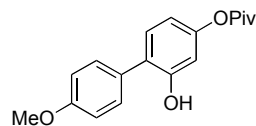
### 2-hydroxy-4'-(trifluoromethyl)biphenyl-4-yl pivalate (**3c**)



Reaction was carried out with 0.016 M in CH<sub>2</sub>Cl<sub>2</sub>. yellow solid; (*R*<sub>f</sub> = 0.23, hexane:EtOAc = 10:3); mp = 170–172 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 1H), 6.74 (dd, *J* = 8.3 Hz, 1.8 Hz, 1H), 6.70 (d, *J* = 2.3 Hz, 1H), 5.27 (bs, 1H), 1.40 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 177.6, 153.4, 151.7, 140.7, 130.9,

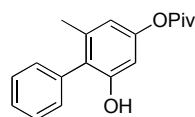
129.5, 125.6, 123.0, 114.0, 109.8, 39.2, 27.1; IR (KBr) 3600-3200, 2982, 2942, 2879, 1724, 1605, 1328, 1161, 1069  $\text{cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 338 ( $M^+$ , 31), 254 (100), 205 (17), 177 (22), 57 (37); HRMS (EI)  $m/z$  calcd for  $C_{18}H_{17}O_3F_3$  ( $M^+$ ): 338.1130, found: 338.1143.

### 2-hydroxy-4'-methoxybiphenyl-4-yl pivalate (3d)



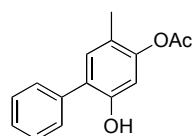
Reaction was carried out with 0.016 M in  $\text{CH}_2\text{Cl}_2$ . yellow solid; ( $R_f$  = 0.28, hexane:Et<sub>2</sub>O = 5:2); mp = 112–114 °C. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.37 (d,  $J$  = 8.7 Hz, 2H), 7.19 (d,  $J$  = 8.4 Hz, 1H), 7.02 (d,  $J$  = 8.3 Hz, 2H), 6.70-6.68 (m, 2H), 5.22 (bs, 1H), 3.86 (s, 3H), 1.37 (s, 9H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  177.1, 159.3, 153.2, 151.2, 130.5, 130.3, 128.6, 125.4, 114.7, 113.7, 109.1, 55.3, 39.1, 27.1; IR (KBr) 3500-3300, 2974, 2935, 1732, 1604, 1500, 1246, 11579  $\text{cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 300 ( $M^+$ , 25), 216 (63), 73 (100), 60 (67), 57 (89), 55 (67); HRMS (EI)  $m/z$  calcd for  $C_{18}H_{20}O_4$  ( $M^+$ ): 300.1362, found: 300.1363.

### 2-hydroxy-6-methylbiphenyl-4-yl pivalate (3e)



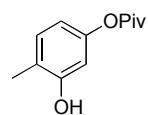
Reaction was carried out with 0.016 M in  $\text{CH}_2\text{Cl}_2$ . orange solid; ( $R_f$  = 0.28, hexane:AcOEt = 9:1); mp = 93–95 °C. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.52-7.49 (m, 2H), 7.44-7.41 (m, 1H), 7.29-7.26 (m, 2H), 6.57 (s, 2H), 4.85 (bs, 1H), 2.06 (s, 3H), 1.36 (s, 9H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  177.3, 153.7, 151.1, 138.3, 134.8, 130.5, 129.6, 128.4, 125.7, 115.1, 106.4, 39.2, 27.3, 20.6; IR (KBr) 3600-3100, 2973, 2933, 2872, 1752, 1616, 1137  $\text{cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 284 ( $M^+$ , 33), 200 (100), 83 (17), 57 (34). HRMS (EI)  $m/z$  calcd for  $C_{18}H_{20}O_3$  ( $M^+$ ): 284.1412, found: 284.1414.

### 2-hydroxy-5-methylbiphenyl-4-yl acetate (3f)



Reaction was carried out with 0.05 M in  $\text{CH}_2\text{Cl}_2$ . orange solid; ( $R_f$  = 0.26, hexane:AcOEt = 8:2); mp = 111–113 °C. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.49-7.37 (m, 5H), 7.09 (s, 1H), 6.68 (s, 1H), 5.18 (bs, 1H), 2.34 (s, 3H), 2.13 (s, 3H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  169.2, 151.1, 149.3, 136.5, 132.2, 129.2, 129.1, 127.9, 126.1, 122.0, 109.6, 20.8, 15.3; IR (KBr) 3500-3200 (br), 3028, 2931, 1720, 1612, 1038  $\text{cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 242 ( $M^+$ , 16), 200 (100), 199 (22), 69 (19). HRMS (EI)  $m/z$  calcd for  $C_{15}H_{14}O_3$  ( $M^+$ ): 242.0943, found: 242.0943.

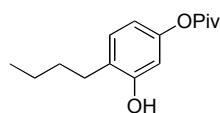
### 3-hydroxy-4-methylphenyl pivalate (3g)



Reaction was carried out with 0.05 M in  $\text{CH}_2\text{Cl}_2$ . yellow solid; ( $R_f$  = 0.25, hexane:AcOEt = 7:3); mp = 70–72 °C. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.05 (d,  $J$  = 7.9 Hz, 1H), 6.49 (dd,  $J$  = 7.9 Hz, 1.8 Hz, 1H), 6.39 (d,  $J$  = 1.8 Hz, 1H), 5.87

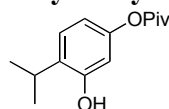
(bs, 1H), 2.13 (s, 3H), 1.36 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  178.4, 154.8, 149.6, 131.2, 122.0, 112.9, 108.7, 39.2, 27.2, 15.5. IR (KBr) 3600-3100 (br), 2975, 2933, 2873, 1727, 1608, 1153  $\text{cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 208 ( $\text{M}^+$ , 24), 124 (100), 57 (37); HRMS (EI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{16}\text{O}_3$  ( $\text{M}^+$ ): 208.1099, found: 208.1104.

#### 4-butyl-3-hydroxyphenyl pivalate (3h)



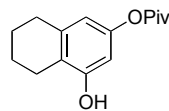
Reaction was carried out with 0.016 M in  $\text{CH}_2\text{Cl}_2$ . orange oil, ( $R_f$  = 0.52, hexane:AcOEt = 8:2).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.10-7.06 (m, 1H), 6.56 (dd,  $J$  = 8.3 Hz, 2.3 Hz, 1H), 6.49 (d,  $J$  = 2.3 Hz, 1H), 4.78 (bs, 1H), 2.56 (t,  $J$  = 7.8 Hz, 2H), 1.59-1.53 (m, 2H), 1.41-1.33 (m, 2H), 1.34 (s, 9H), 0.93 (t,  $J$  = 7.3 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  178.2, 154.3, 145.3, 130.2, 126.7, 112.6, 108.6, 39.1, 31.7, 29.2, 27.1, 22.5, 13.9; IR (neat) 3600-3100 (br), 2958, 2932, 2872, 2861, 1728, 1606, 1156, 1124  $\text{cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 250 ( $\text{M}^+$ , 29), 166 (62), 123 (100), 57 (59). HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_3$  ( $\text{M}^+$ ): 250.1569, found: 250.1560.

#### 3-hydroxy-4-isopropylphenyl pivalate (3i)



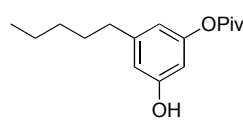
Reaction was carried out with 0.05 M in  $\text{CH}_2\text{Cl}_2$ . orange solid; ( $R_f$  = 0.23, hexane:AcOEt = 9:1); mp = 52–54 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.16 (d,  $J$  = 8.7 Hz, 1H), 6.61 (dd,  $J$  = 8.3 Hz, 2.3 Hz, 1H), 6.50 (d,  $J$  = 2.4 Hz, 1H), 4.73 (bs, 1H), 3.13-3.18 (m, 1H), 1.34 (s, 9H), 1.24 (d,  $J$  = 6.9 Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  178.3, 153.8, 149.2, 132.5, 126.8, 112.9, 108.8, 39.2, 27.2, 26.8, 22.6; IR (KBr) 3600-3300 (br), 2960, 2931, 2871, 1720, 1606, 1164  $\text{cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 236 ( $\text{M}^+$ , 55), 152 (80), 137 (100), 57 (70). HRMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_3$  ( $\text{M}^+$ ): 236.1412, found: 236.1422.

#### 4-hydroxy-5,6,7,8-tetrahydronaphthalen-2-yl pivalate (3j)



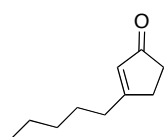
Reaction was carried out with 0.01 M in  $\text{CH}_2\text{Cl}_2$ . orange solid; ( $R_f$  = 0.26, hexane:AcOEt = 9:1); mp = 99–101 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  6.35 (s, 1H), 6.28 (d,  $J$  = 2.5 Hz, 1H), 5.2-5.5 (br, 1H), 2.71-2.52 (m, 4H), 1.81-1.72 (m, 4H), 1.34 (m, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  178.0, 154.3, 149.0, 139.7, 121.1, 113.7, 105.8, 39.2, 29.8, 27.3, 22.8, 22.7, 22.6; IR (KBr) 3600-3300, 3424, 2940, 2842, 1720, 1598, 1154  $\text{cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 248 ( $\text{M}^+$ , 25), 164 (100), 136 (30), 85 (25), 83 (39), 57 (44); HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_3$  ( $\text{M}^+$ ): 248.1412, found: 248.1402.

### 5-pentyl-3-hydroxyphenyl pivalate (3k)



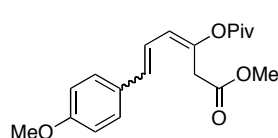
Reaction was carried out with 0.016 M in CH<sub>2</sub>Cl<sub>2</sub>. yellow oil; (R<sub>f</sub> = 0.25, hexane:Et<sub>2</sub>O = 5:1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 6.51 (s, 1H), 6.46 (s, 1H), 6.38 (s, 1H), 4.85 (s, 1H), 2.53 (t, *J* = 8.0 Hz, 2H), 1.60-1.55 (m, 2H), 1.34 (s, 9H), 1.32-1.25 (m, 4H), 0.89 (t, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 177.6, 156.4, 151.6, 145.6, 113.4, 113.0, 106.3, 39.1, 35.7, 31.4, 30.6, 27.1, 22.5, 13.9; IR (neat) 3434 (br), 1753, 1730 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 264 (M<sup>+</sup>, 51), 206 (61), 124 (87), 57 (100); HRMS (EI) *m/z* calcd for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub> (M<sup>+</sup>): 264.1725, found: 264.1726.

### 3-pentylcyclopenten-2-one (4k)



yellow oil; (R<sub>f</sub> = 0.13, hexane:Et<sub>2</sub>O = 5:1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 5.94 (s, 1H), 2.59-2.57 (m, 2H), 2.41-2.38 (m, 4H), 1.61-1.55 (m, 2H), 1.36-1.29 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 13.9, 22.4, 26.7, 29.7, 31.3, 33.5, 35.3, 129.4, 183.4, 210.3; IR (neat) 1709, 1673, 1614 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) 152 (M<sup>+</sup>, 22), 96 (100), 95 (31), 81 (53), 68 (30), 67 (29); HRMS (EI) *m/z* calcd for C<sub>10</sub>H<sub>16</sub>O: 152.1201, found: 152.1200.

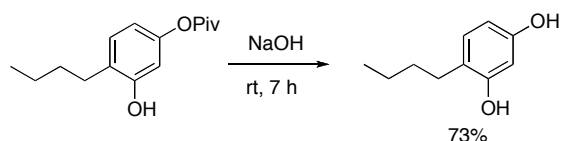
### 3-(2,2-dimethyl-1-oxopropoxy)-6-(4-methoxyphenyl)-3,5-hexadienoic acid methyl ester



(5) Obtained as an *E/Z* mixture. yellow oil; (R<sub>f</sub> = 0.20, hexane:Et<sub>2</sub>O = 5:2); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) major isomer: δ 7.28 (d, *J* = 9.2 Hz, 2H), 6.85 (d, *J* = 9.2 Hz, 2H), 6.63 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.51 (d, *J* = 15.6 Hz, 1H), 5.96 (d, *J* = 10.5 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.36 (s, 2H), 1.35 (s, 9H); minor isomer: δ 7.25 (d, *J* = 9.2 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 2H), 6.44 (d, *J* = 11.5 Hz), 6.30 (d, *J* = 11.0 Hz, 1H), 6.16 (dd, *J* = 11.5, 11.0 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 3.34 (s, 2H), 1.31 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 176.2, 169.7, 169.6, 159.4, 158.9, 143.3, 141.3, 132.8, 131.0, 130.3, 129.8, 129.6, 127.6, 120.5, 120.2, 118.9, 116.6, 114.1, 113.7, 55.2, 52.1, 39.7, 39.5, 39.2, 27.1; IR (neat) 2972, 1746, 1662, 1605 cm<sup>-1</sup>; EIMS *m/z* (relative intensity) major isomer: 332 (M<sup>+</sup>, 13), 248 (36), 174 (40), 147 (32), 57 (100); minor isomer: 332 (M<sup>+</sup>, 12), 248 (34), 174 (41), 147 (33), 57 (100); HRMS (EI) *m/z* calcd for C<sub>19</sub>H<sub>24</sub>O<sub>5</sub> (M<sup>+</sup>): 332.1624, found: major isomer : 332.1626, minor isomer : 332.1629.



### hydrolysis of 4-butyl-3-hydroxyphenyl pivalate (**3h**) to 4-butylbenzene-1,3-diol



A mixture of a 2N NaOH aq. (8 mL) and 67 mg (0.26 mmol) of 4-butyl-3-hydroxyphenyl pivalate (**3h**) was vigorously stirred at rt. After 7 h, the reaction mixture was acidified by conc. HCl. The resulting mixture was extracted with EtOAc. The organic layer were washed with brine, dried over MgSO<sub>4</sub>, filtered and evaporated *in vacuo* to give 49.5 mg of a crude brown oil. Purification was achieved by flash chromatography on silica gel (20 % AcOEt/hexane) to give 4-buthylbenzene-1,3-diol as a pale yellow oil (31.7 mg, 73 %).

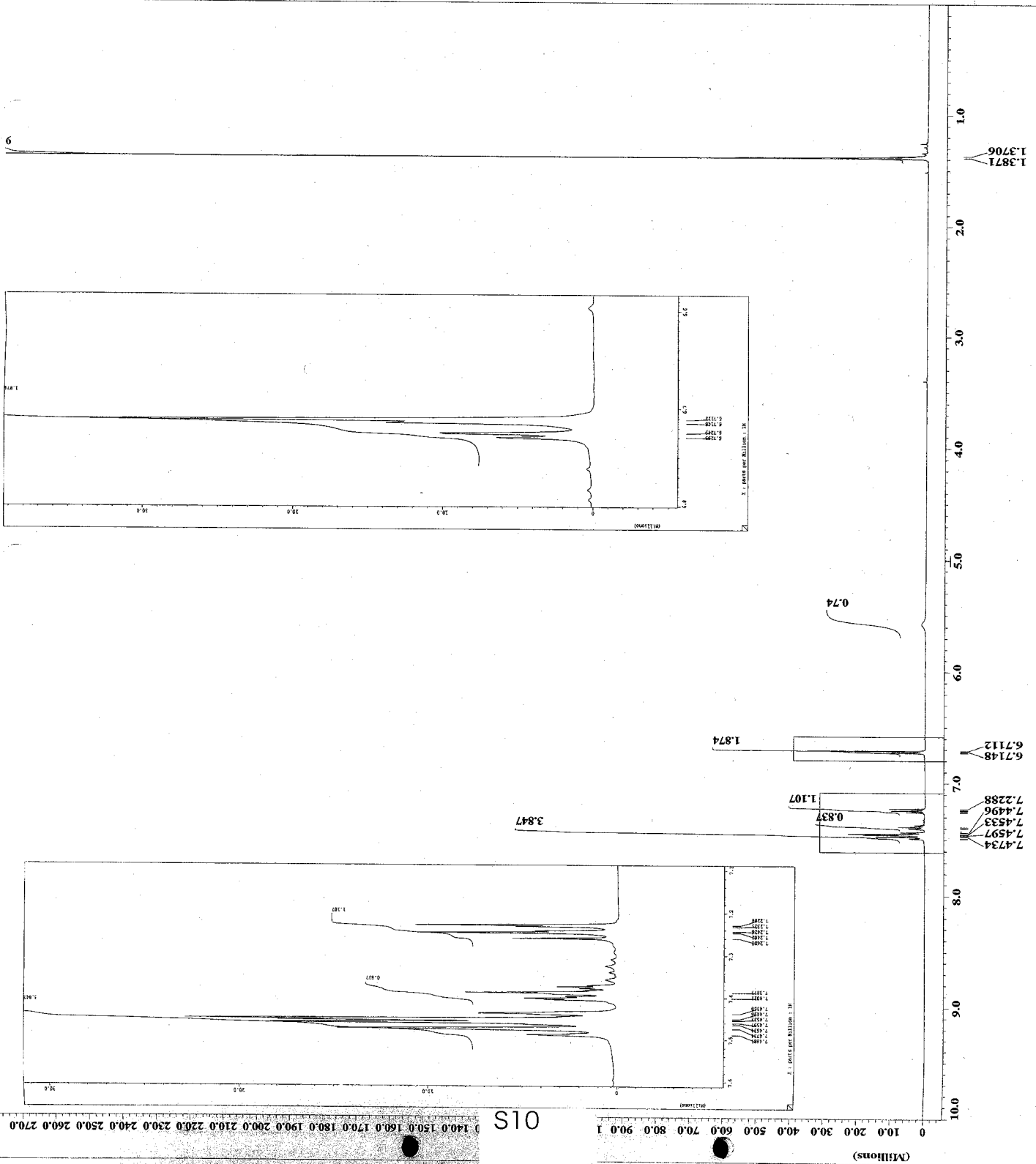
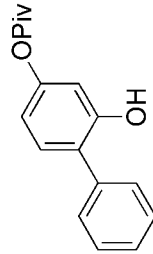
pale yellow oil; ( $R_f = 0.13$ , hexane:AcOEt = 4:1) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  6.95 (d,  $J = 8.9$  Hz, 1H), 6.35 (dd,  $J = 8.3$  Hz, 2.3 Hz, 1H), 6.32 (d,  $J = 2.3$  Hz, 1H), 4.80 (bs, 2H), 2.52 (t,  $J = 7.8$  Hz, 2H), 1.57-1.54 (m, 2H), 1.39-1.35 (m, 2H), 0.93 (t,  $J = 7.5$  Hz, 3H); IR (neat) 3600-3000 (br), 2931, 1612, 1515, 1458; EIMS  $m/z$  (relative intensity) 166 ( $M^+$ , 23), 123 (100); HRMS (EI)  $m/z$  calcd for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub> ( $M^+$ ) 166.0994, found: 166.0999.



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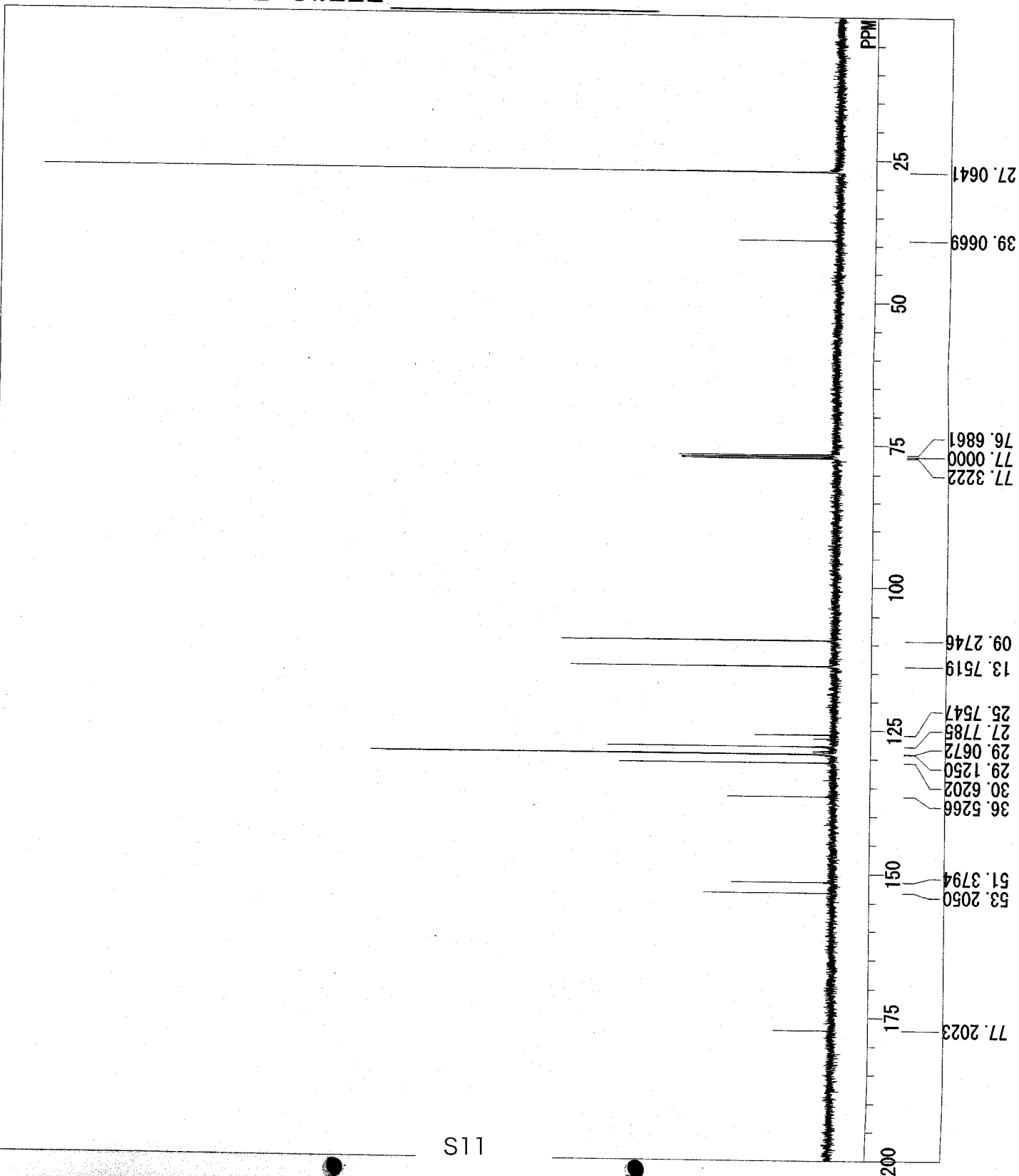
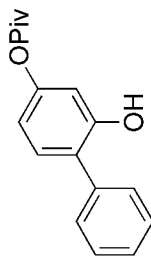
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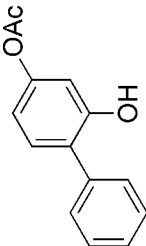
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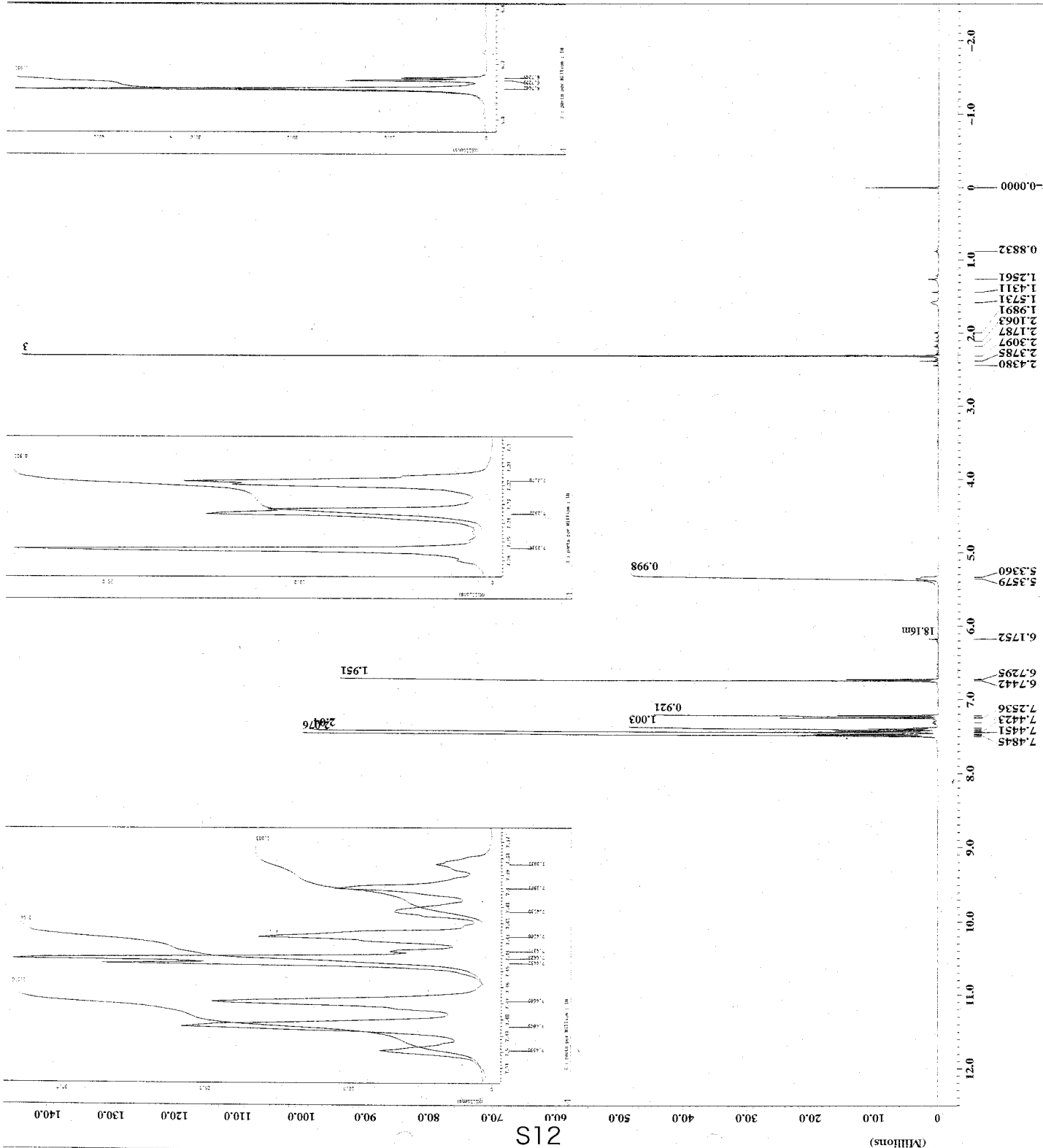




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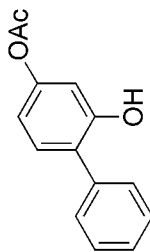
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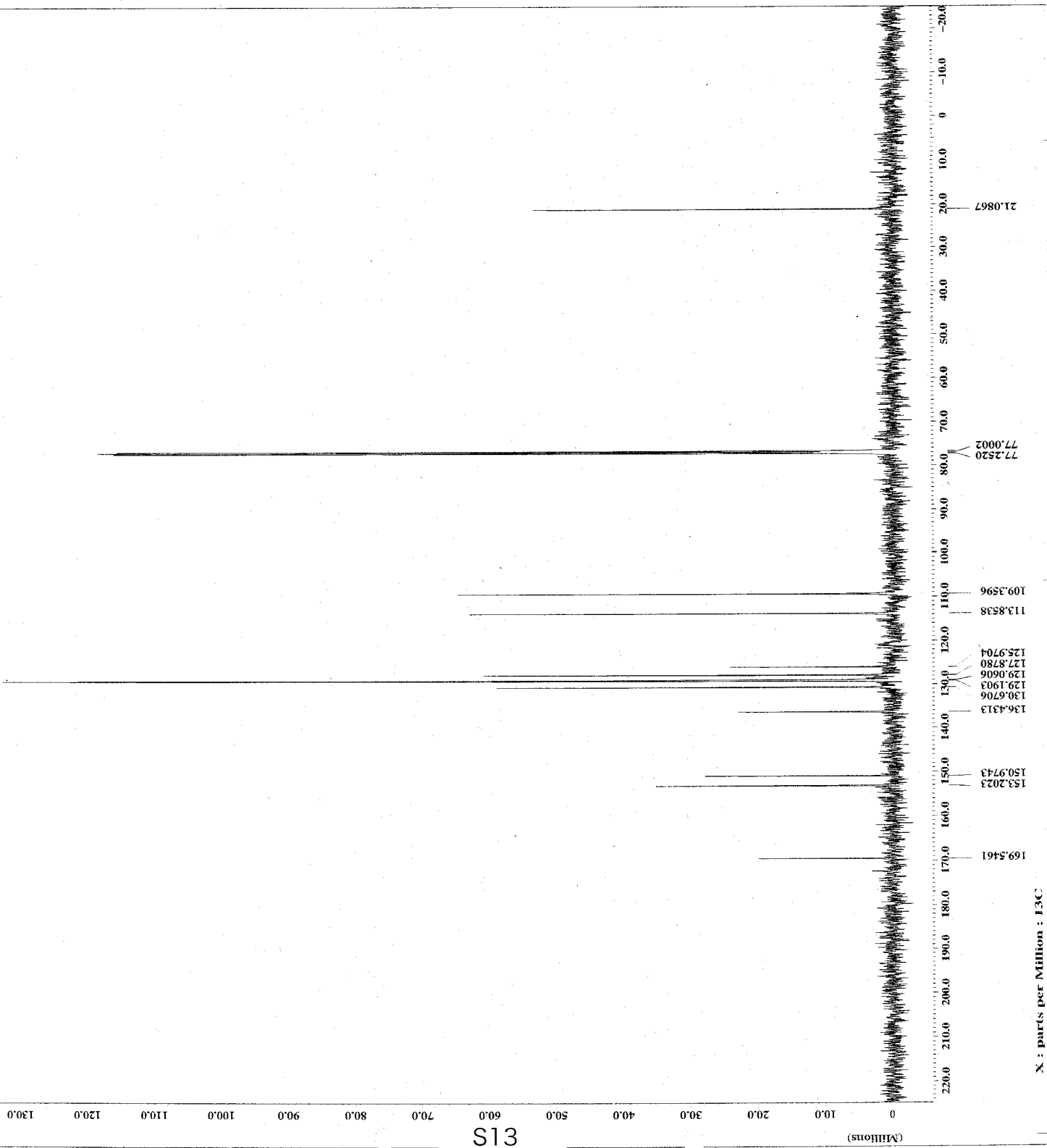
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3b

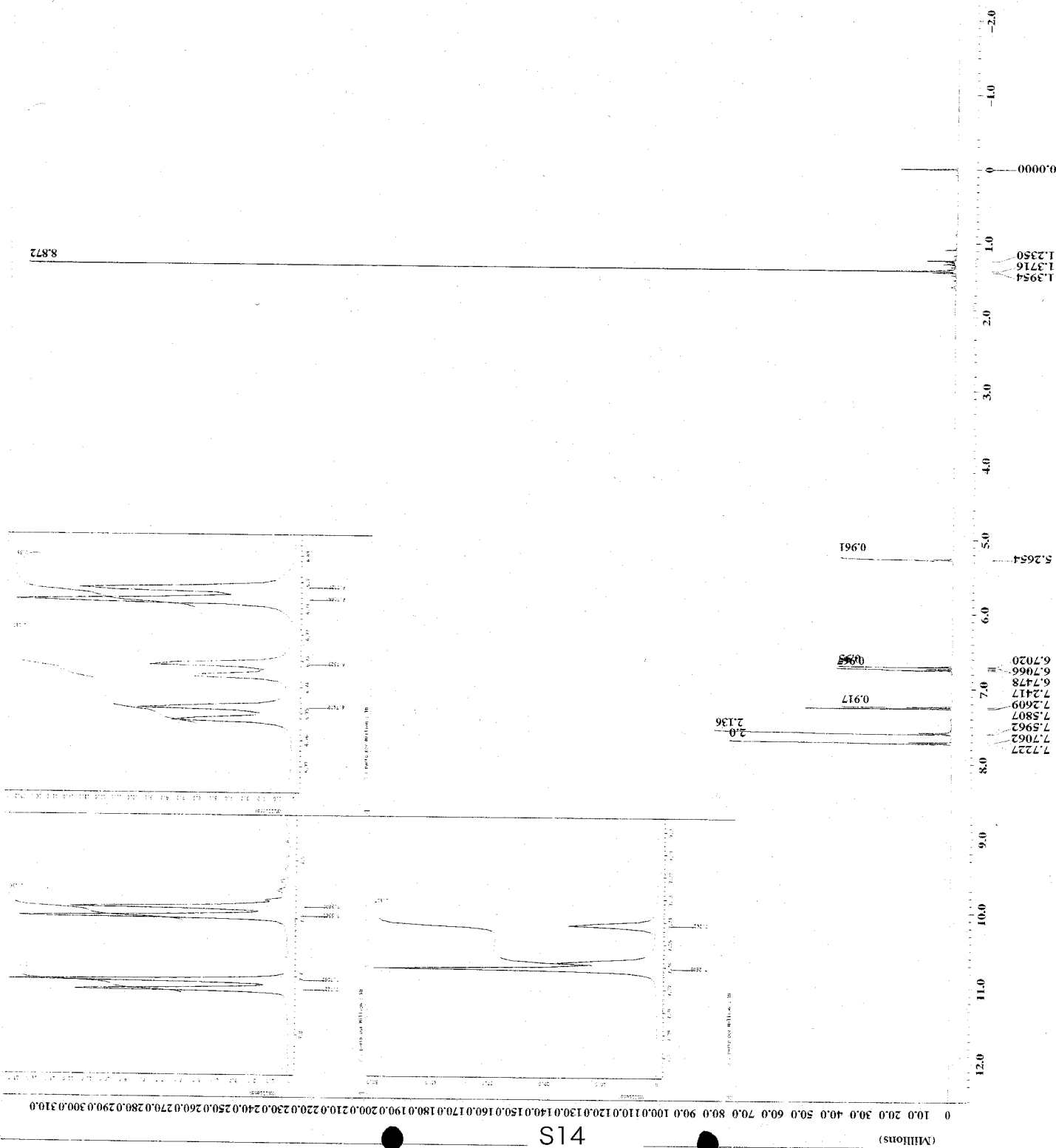
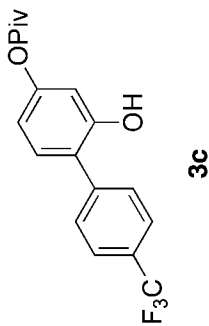


X : parts per Million : 13C



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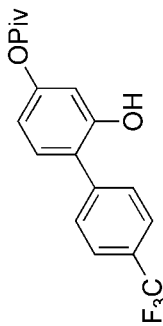
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X : Parts per Million : 1H



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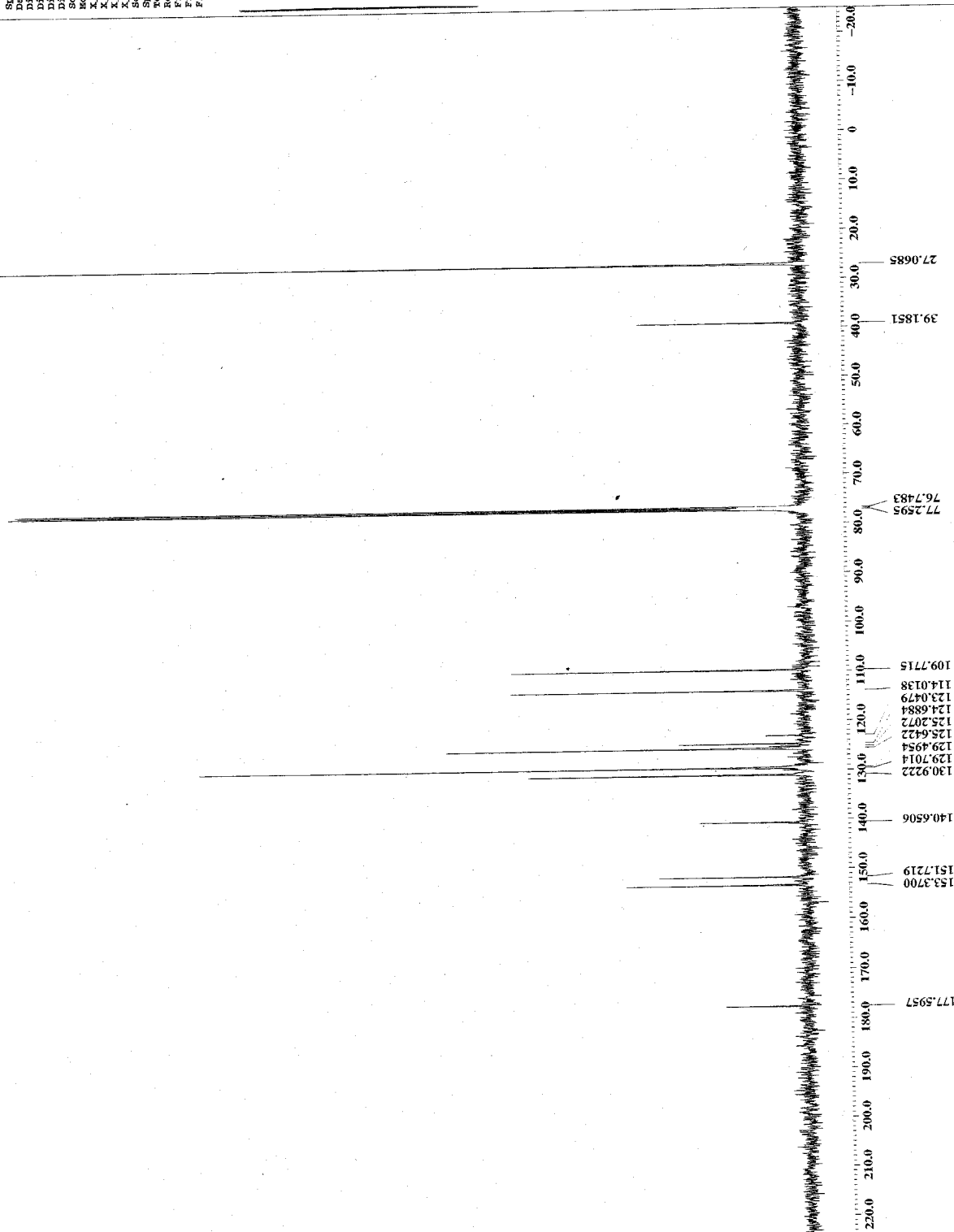


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S15

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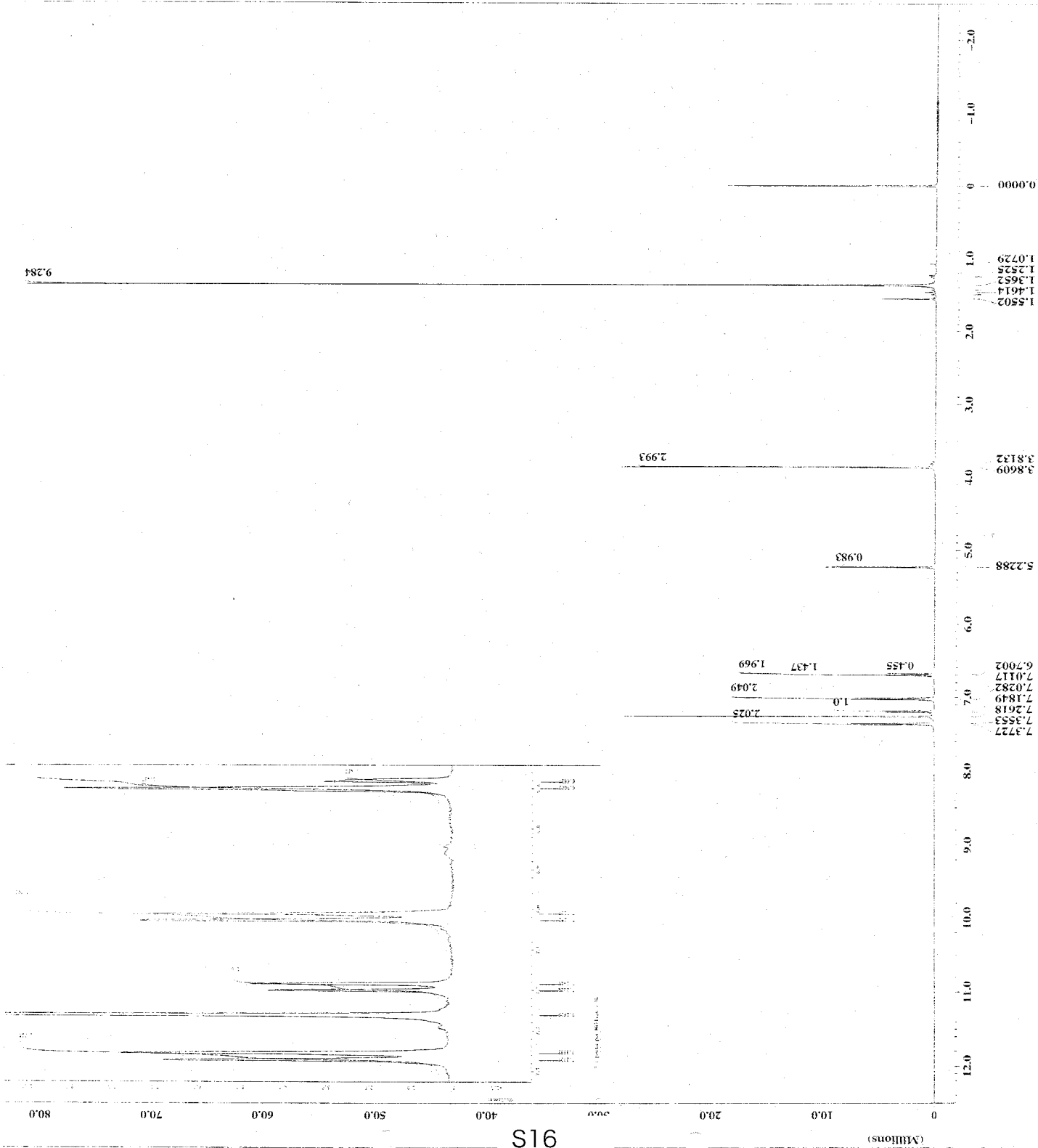
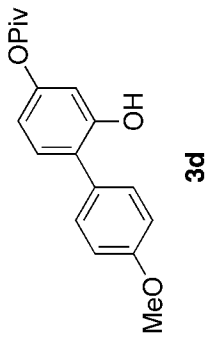
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X : parts per Million : 13C



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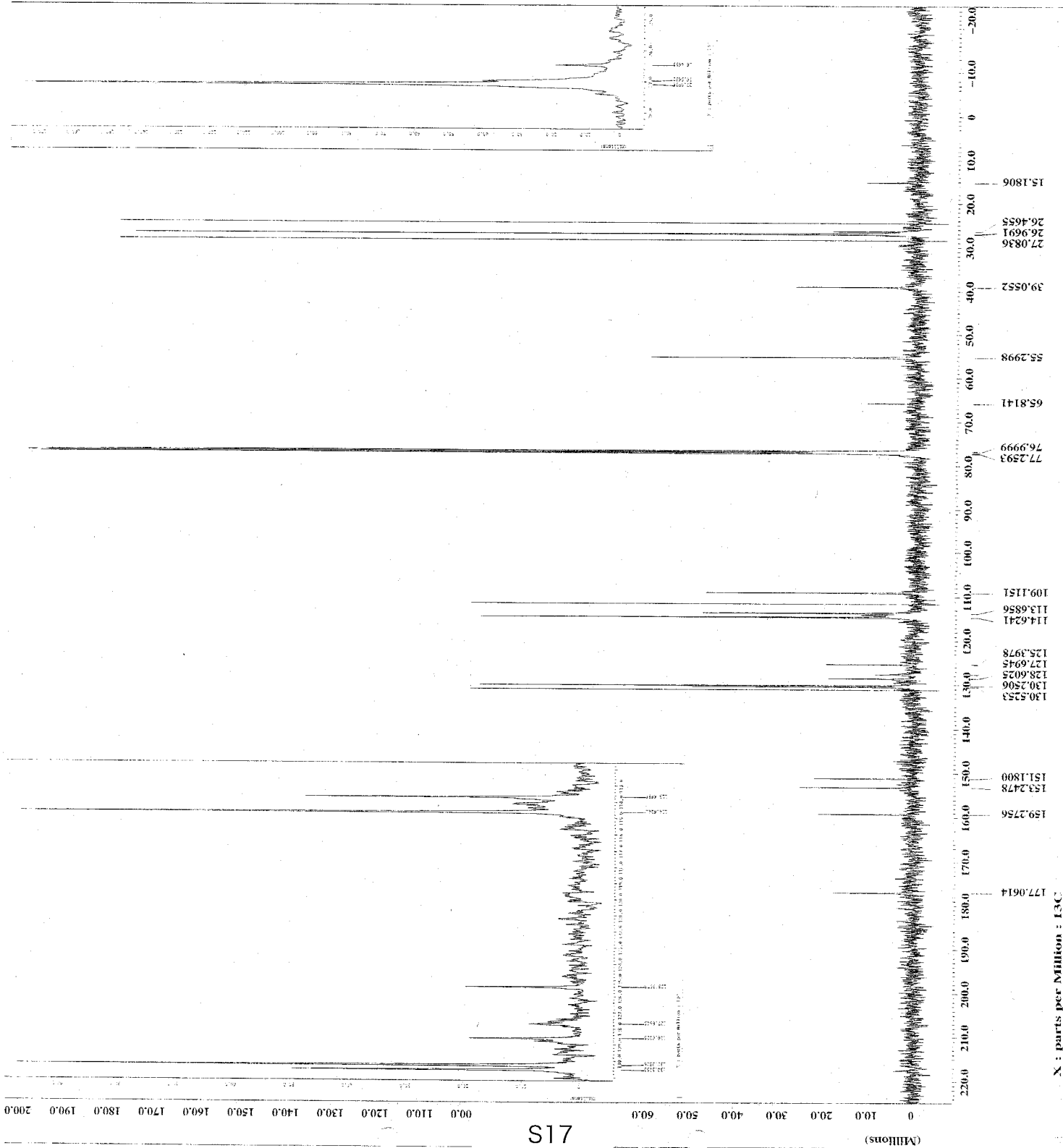
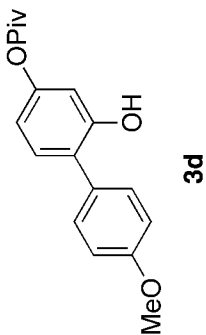


X : parts per Million : 1H





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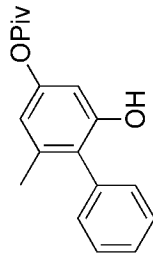
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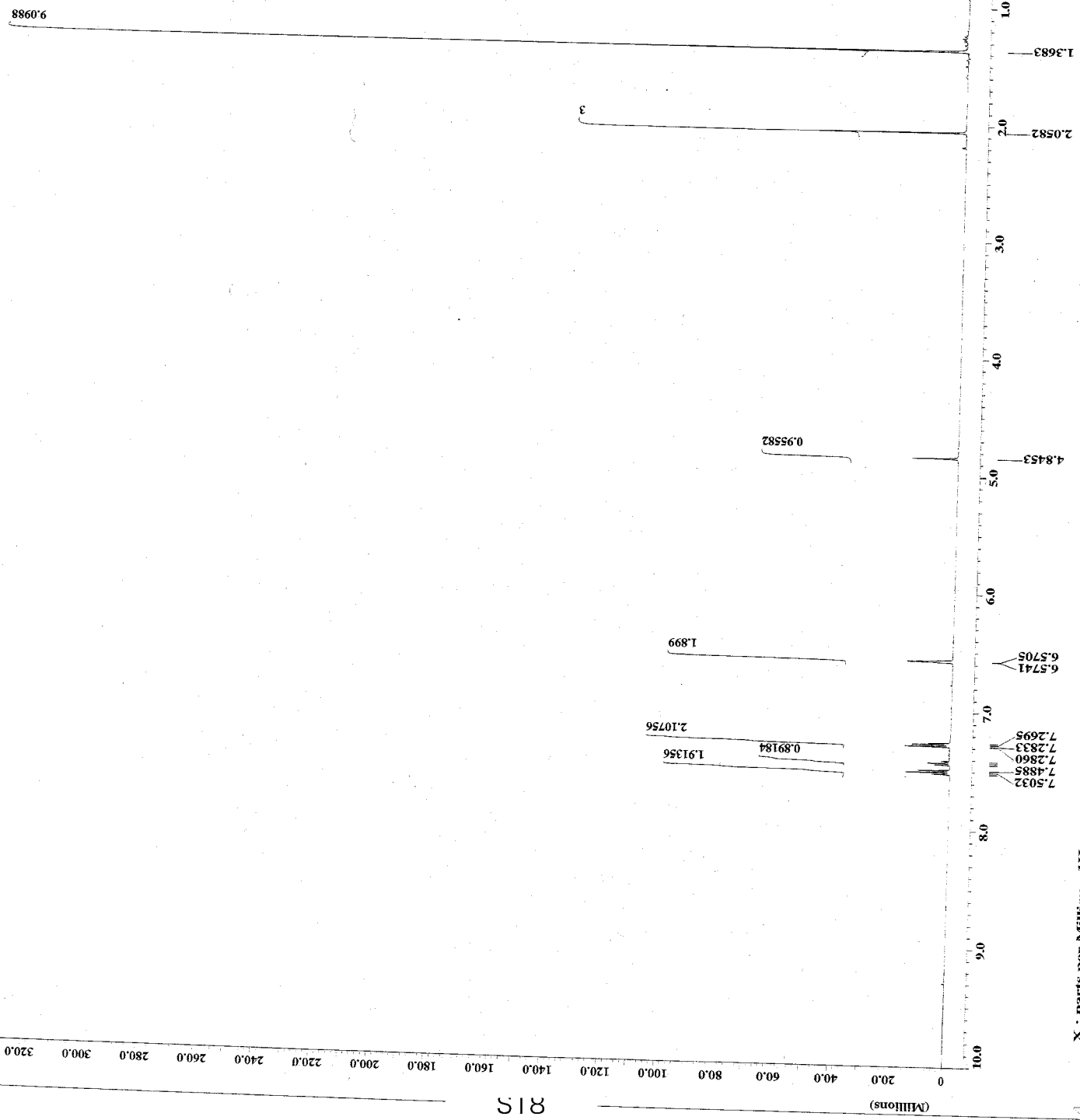
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 Filter\_mode = BUTTERWORTH  
 Filter\_width = 3.75119936 [MHz]



3e



Int : parts per Million : 1H

815

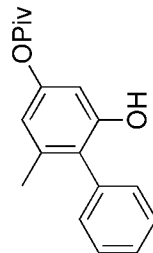


PROCESSING PARAMETERS

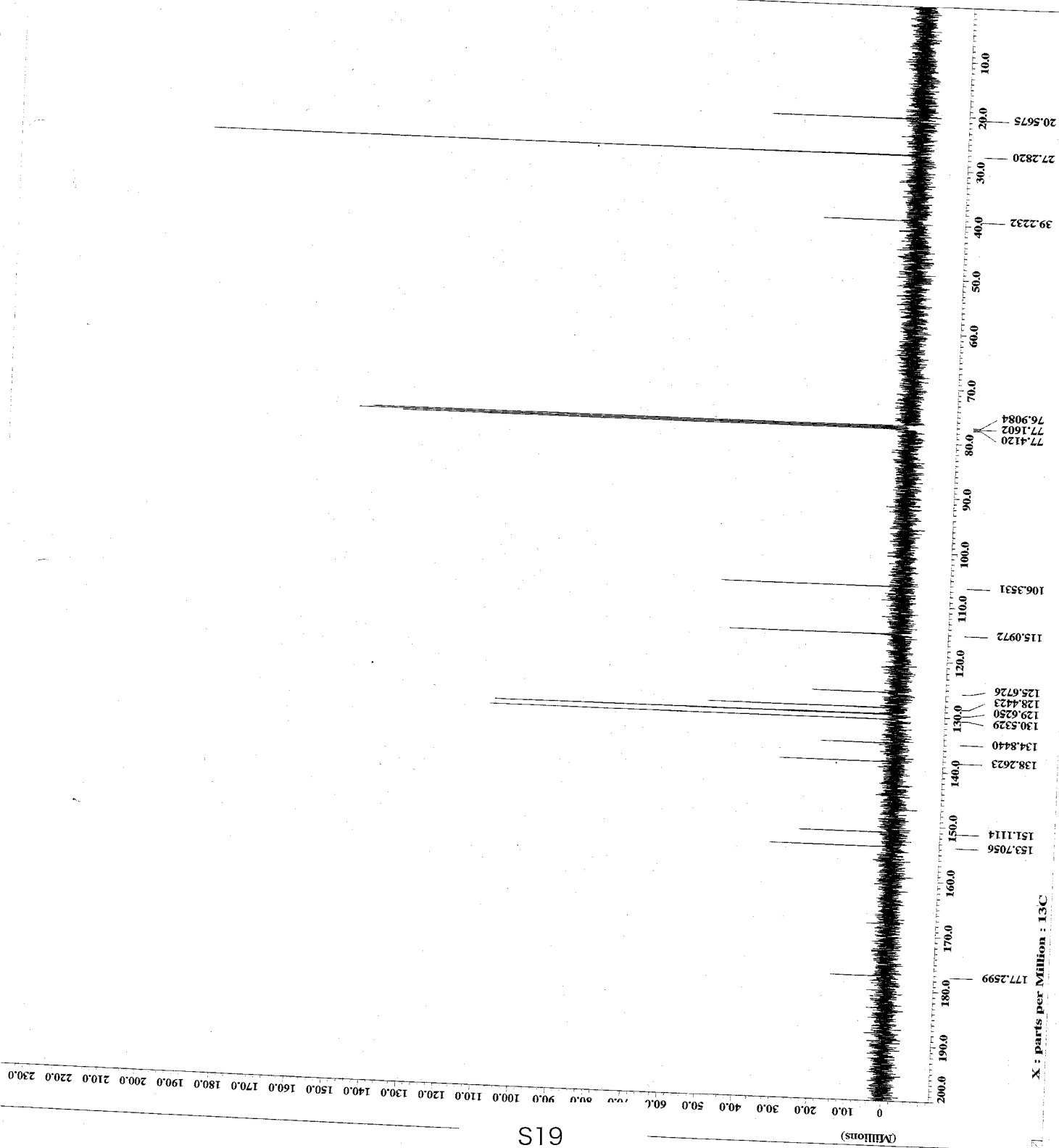
dc\_balance = 1 [Hz]  
 freq = 125.76 [MHz]  
 machinebase = JEOL  
 dc\_correct = 0 [ppm]  
 ppm = 1000000 [ppm]  
 Peak\_pick : 0 [Hz] : 50 [Hz] : Both

ACQUISITION PARAMETERS

File Name = c0b863p.c.3  
 Sample ID = c0b863p.c  
 Content = Same as file with Broad  
 Creation Date = 13-JAN-2009 21:06:37  
 Revision Date = 14-MAY-2009 20:44:20  
 Spec Site = ECP500  
 Spec Type = DELTA\_NMR  
 Data Format = ID COMPLEX  
 Dimensions = X  
 Dia Title = 13C  
 Dia Size = 5mm  
 Dia Units = [mm]  
 Scans = 80  
 Acq\_return = 1  
 X\_offset = 13C  
 X\_freq = 125.76 [MHz]  
 X\_sweep = 31.4654088 [MHz]  
 Solvent = CHLOROFORM-D  
 Temp\_set = 16 [Hz]  
 Temp = 24.2 [C]  
 Recv\_gain = 11.7473579 [f]  
 Field\_strength = 11.7473579 [f]  
 Filter\_mode = HYPERWORKN  
 Filter\_width = 15.72066221 [kHz]



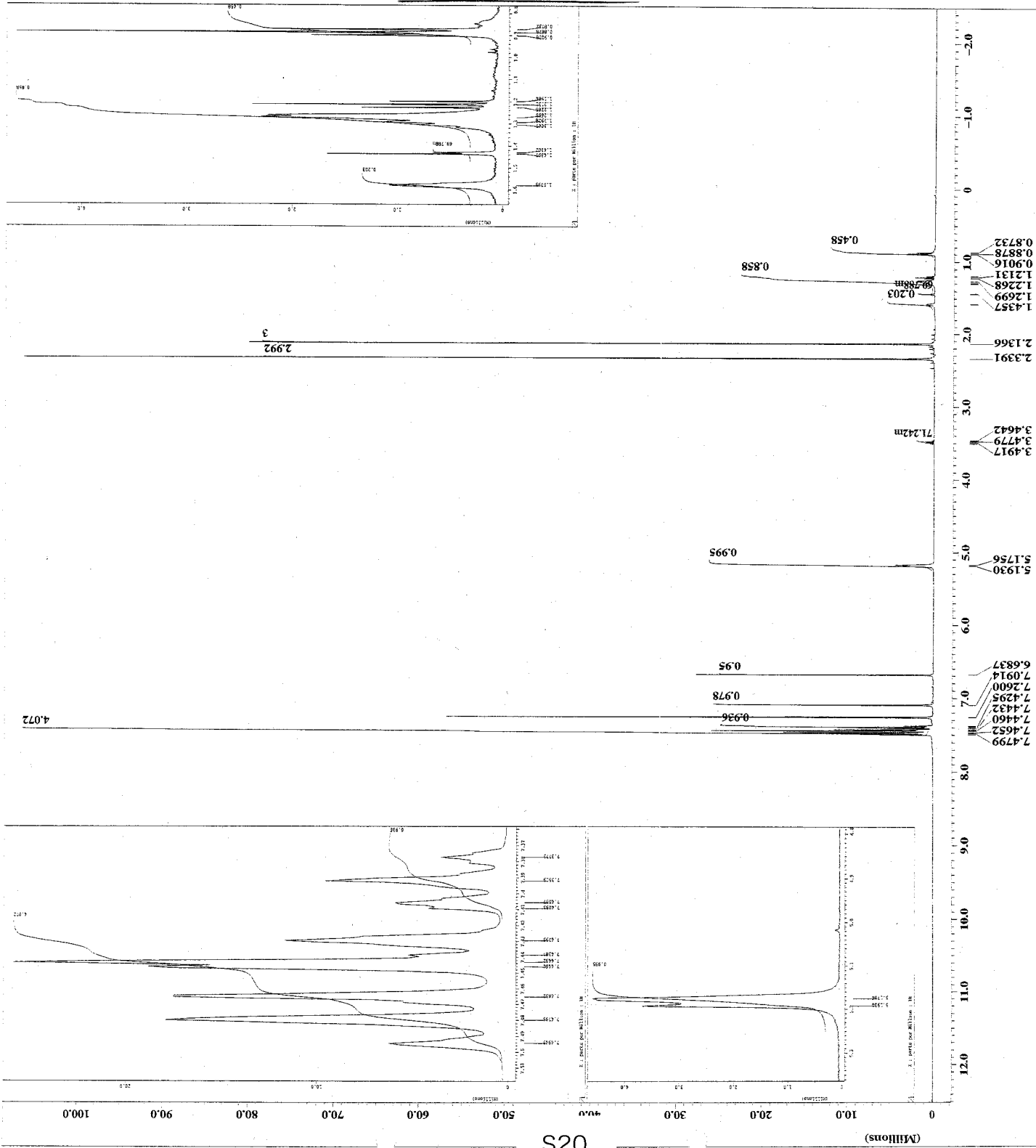
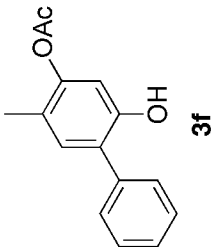
3e



X : parts per Million : 13C

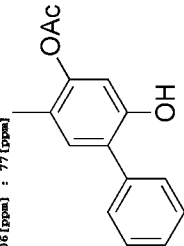


ACQUISITION PARAMETERS  
 File Name = 1d\_spectrum.612  
 Author = yca-967-fr.16-22  
 Sample ID = Single Pulse Experiment  
 Content = 4-MAR-2009 15:40:50  
 Creation Date = 6-MAR-2009 18:27:34  
 Revision Date = ECP500  
 Spec Site =  
 Spec Type = HETCOR  
 Data Format = ID COMPLEX  
 Dimensions = 1H  
 Dia Title = 16384  
 Dia Size = (ppm)  
 Dia Units = 1  
 Mod Return = 1H  
 X\_Gamma = 5 [ppm]  
 X\_Offset = 500.16241602 [MHz]  
 X\_Freq = 507.50751 [MHz]  
 Solvent = (CDCl3) (Polar-3)  
 Spin = 16 [Hz]  
 Temp\_Get = 21.9 [dC]  
 Recv Gain = 25  
 P1 = 11.7473579 [r]  
 P2 = 11.7473579 [r]  
 Filter\_Width = 3.75119956 [kHz]



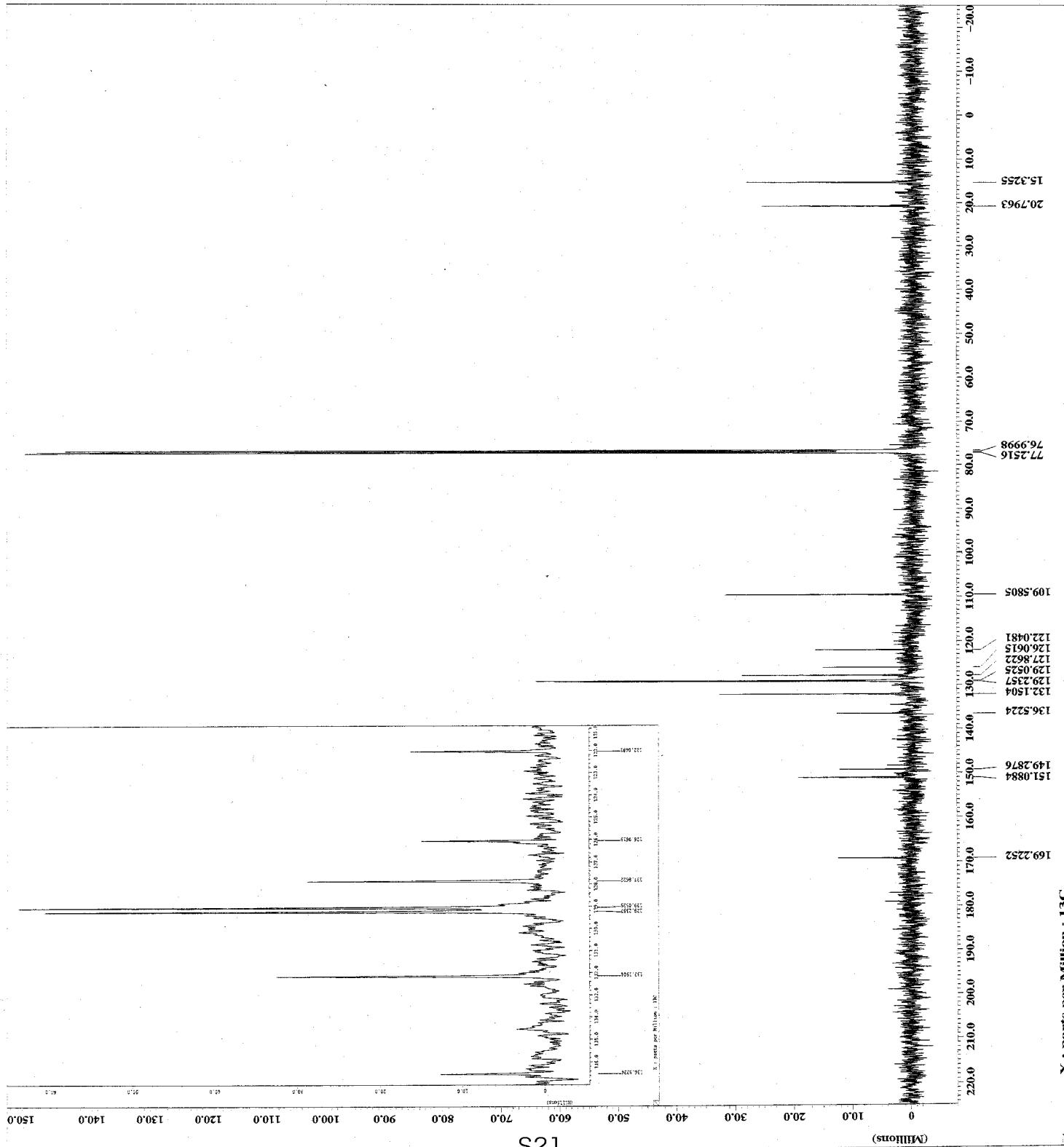


PROCESSING PARAMETERS  
dc\_balance = 5 [Hz]  
freq = 1  
ppm = 1  
machinephase = 77.106 [ppm]  
reference : 77.106 [ppm] : 77 [ppm]



3f

ACQUISITION PARAMETERS  
F1 Name = 1d\_13c\_spectrum.103  
Author = y04-67-fr.16-24  
Sample ID = y04-67-fr.16-24  
Content = Single Pulse with Broad  
Creation Date = 8-MAY-2009 19:59:33  
Revision Date = 10-MAY-2009 23:44:36  
Spec Site = ECP500  
Spec Type = DEXTRA\_NMR  
Data Format = ID\_COMPLEX  
PulsProgram = 13c  
Dim Title = 13c  
Dim Size = 32768  
Dim Units = [ppm]  
Scans = 213  
AcqTime = 13c  
X\_offset = 100 [ppm]  
X\_freq = 125.77787547 [MHz]  
X\_sweep = 31.44654088 [kHz]  
Solvent = CDCl3  
SolvProc = 3  
Temp Set = 25.2 [degC]  
RecvGain = 30  
Field\_strength = 11.7473579 [T]  
Filter\_mode = BURKAWORTH  
Filter\_width = 15.72066221 [kHz]



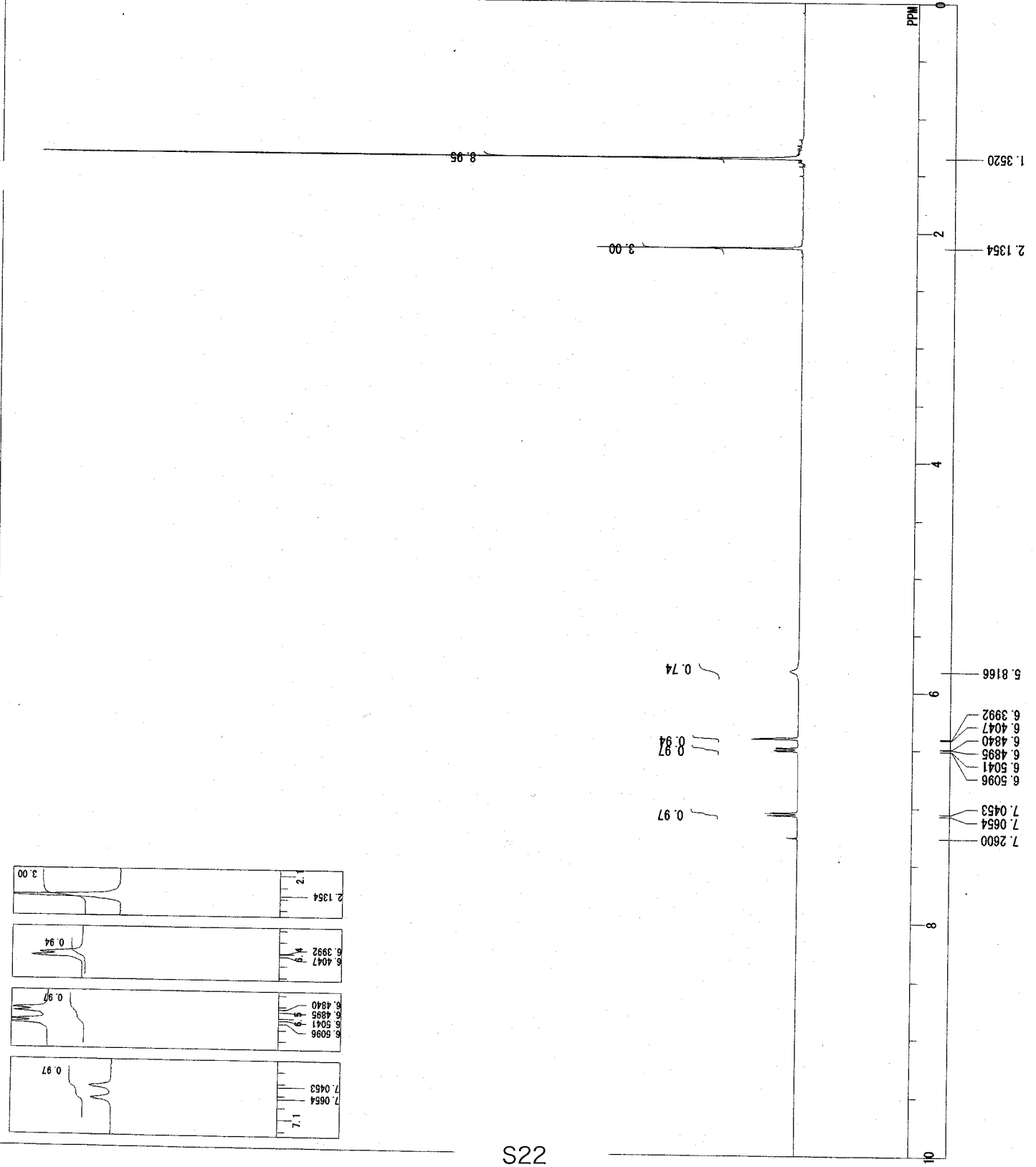
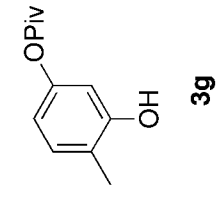
12S1

C:\Documents and Settings\JEOL\Desktop\トップ\RRYufce\ia\ceb829ph. a1s  
 ceb829ph

1H\_NMR  
 1H  
 MENUF 399.65 MHz  
 CERNUC 124.00 KHz  
 OFR 10500.00 Hz  
 OBF IN 5.80 usec  
 PW1 72.10 usec  
 DEADT 0.20000 msec  
 PREDL 1.0000 msec  
 INT 32768  
 POINT 8  
 SPO 7992.01 Hz  
 TIMES 1  
 DUMMY 8  
 FREQU 50.00 usec  
 FLT 4.1001 sec  
 DELAY 2.9010 sec  
 ACQTM PD  
 ADBIT 16  
 RGAIN 9  
 BF 0.12 Hz  
 T1 0.00  
 T2 0.00  
 T3 90.00  
 T4 100.00

NON  
 EXMOD NON: Single coupled: PW1, ACQTM, PD: 1H, 13C, 17O, 29F  
 IRMUC 1H

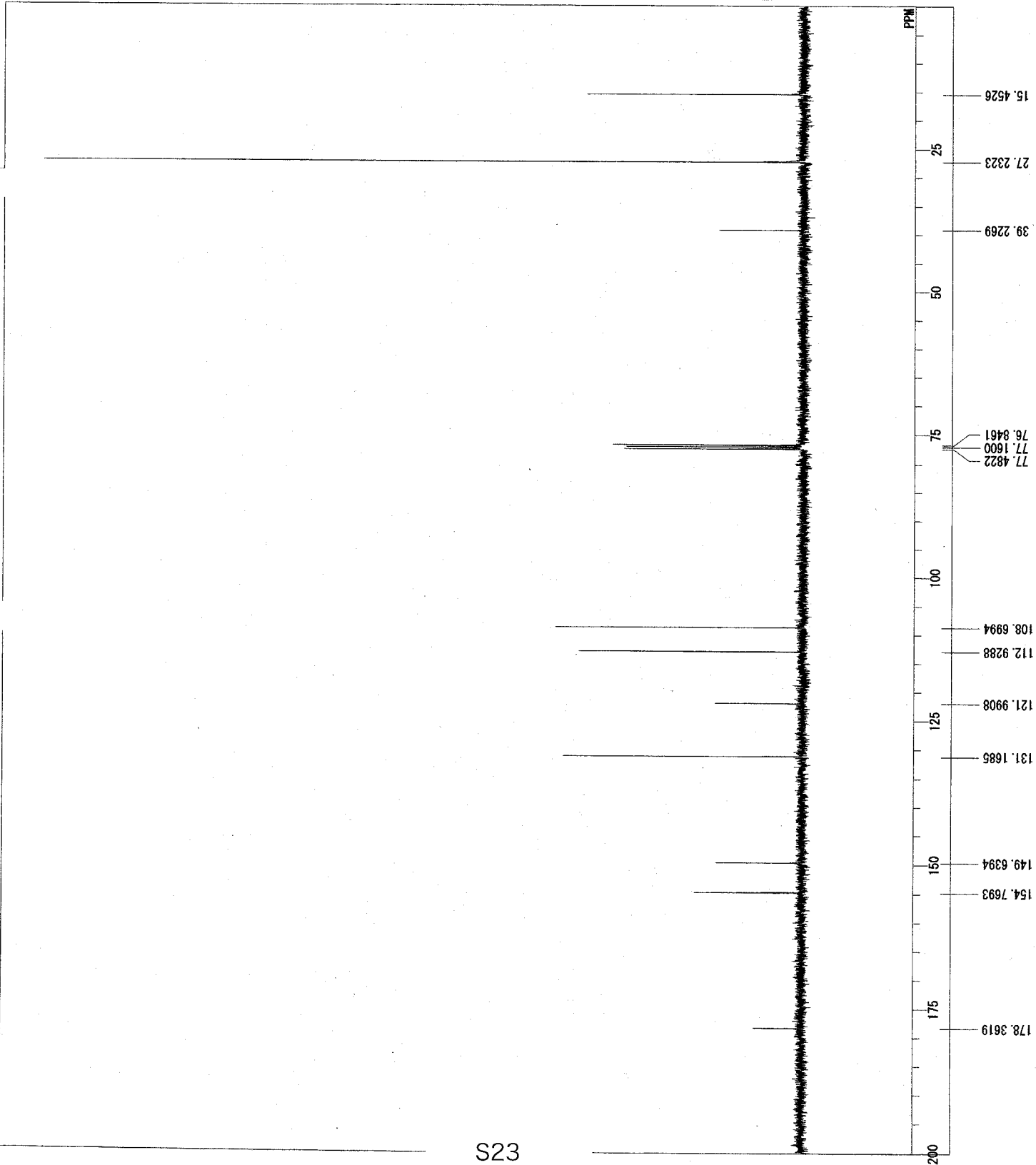
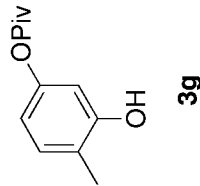
C:\Documents and Settings\JEOL\Desktop\トップ\RRYufce\ia\ceb829ph. a1s  
 TH5ATF02  
 SF 511  
 LKSET 61.60 KHz  
 LKFN 79.0 Hz  
 LKLEV 180  
 LGAIN 24  
 LKPHS 278  
 LKSIG 1012  
 CSPED 13 Hz  
 FILDG  
 FILDF



C:\Documents and Settings\JEOL\Desktop\トップRyuKoe\lie\ceb829pc.als  
 ceb829pc

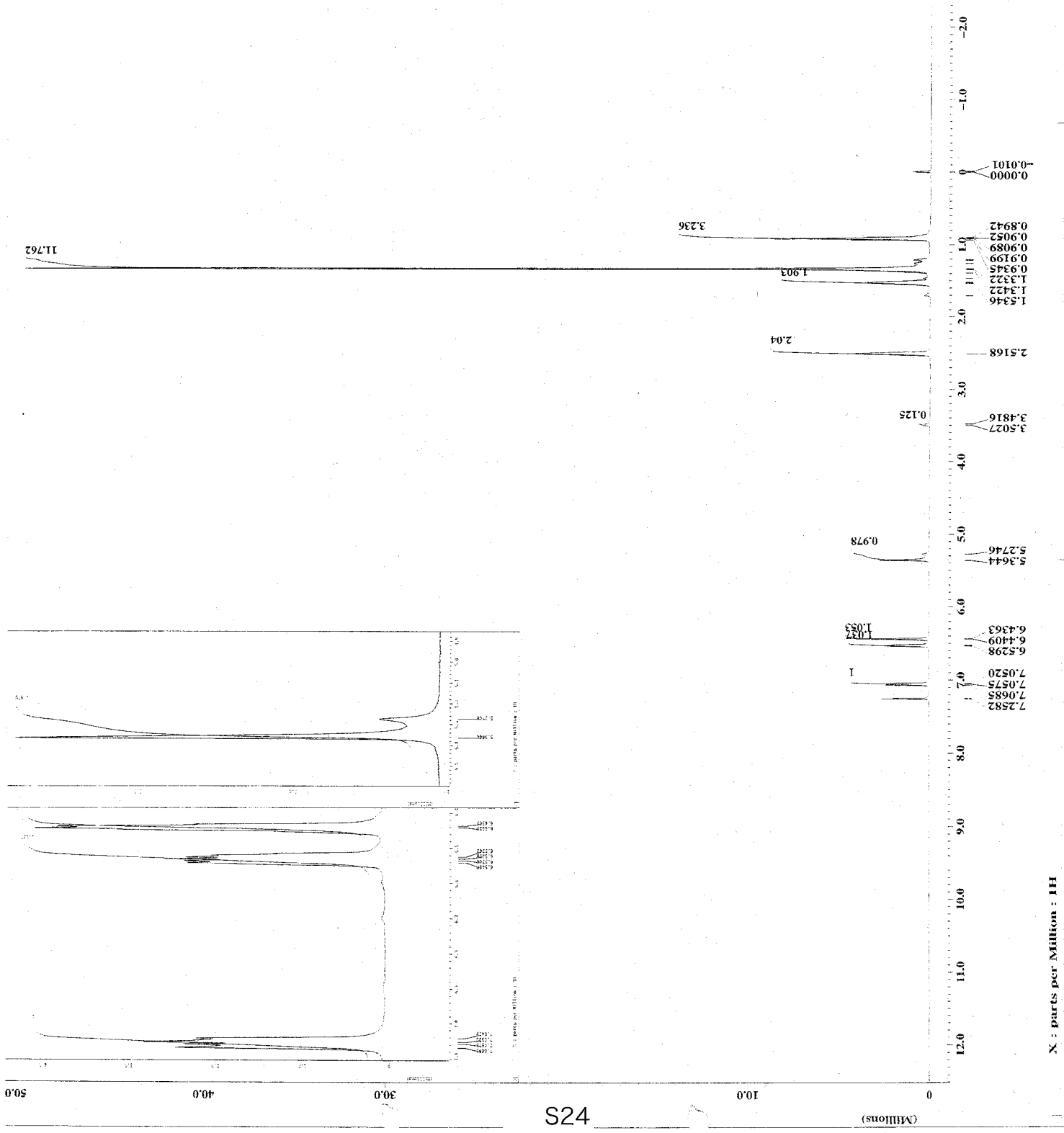
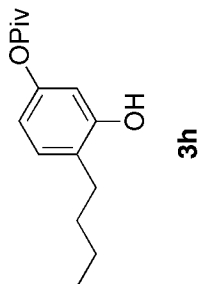
```

MENUF 13C_BCM
OENUC 13C
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
PWI 5.50 usec
DEADT 19.30 usec
PREDL 0.20000 msec
INT 1.0000 msec
POINT 32768
SFO 64
TIMES 1
DUMMY 1
FREQU 27210.88 Hz
FLT
DELAY 14.70 usec
ACQTM 1.2042 sec
PD 1.7940 sec
ADBIT 16
RGAIN 24
BF 1.20 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD BCM
EXPCN Bilevel, complete decoupling; Set_IRRFW
IRNUC 1H
IRSET 399.65 MHz
IRFIN 124.00 KHz
IRRPW 10500.00 Hz
IRATN 511
SF TH5ATFG2
LKSET 61.60 KHz
LKFIN 79.0 Hz
LKLEV 180
LGAIN 24
LKPHS 278
LKSIG 983
GSPED 14 Hz
FILDC
FILDF
    
```





ACQUISITION PARAMETERS  
 File name = IG\_spectrum.194  
 Sample ID = y04-046-ff-6-9  
 Content = Single Pulse Experiment  
 Creation Date = 9-NOV-2008 18:27:54  
 Revision Date = 7-NOV-2008 19:05:24  
 Spec Site = ECP300  
 Spec Type = DELTA\_NMR  
 Data Format = ID COMPLEX  
 Measurements = 16  
 Dim Size = 16384  
 Dim Units = [ppm]  
 Scans = 8  
 Rod\_return = 1  
 X\_offset = 11  
 X\_freq = 500.16241602[MHz]  
 X\_sweep = 7.50750751[MHz]  
 Solvent = CHLOROFORM-D  
 Spin\_get = 15[Hz]  
 Recvr\_gain = 22.1[dc]  
 Field\_strength = 11.7473579[G]  
 Filter\_mode = BUTTERWORTH  
 Filter\_width = 3.75119936[MHz]

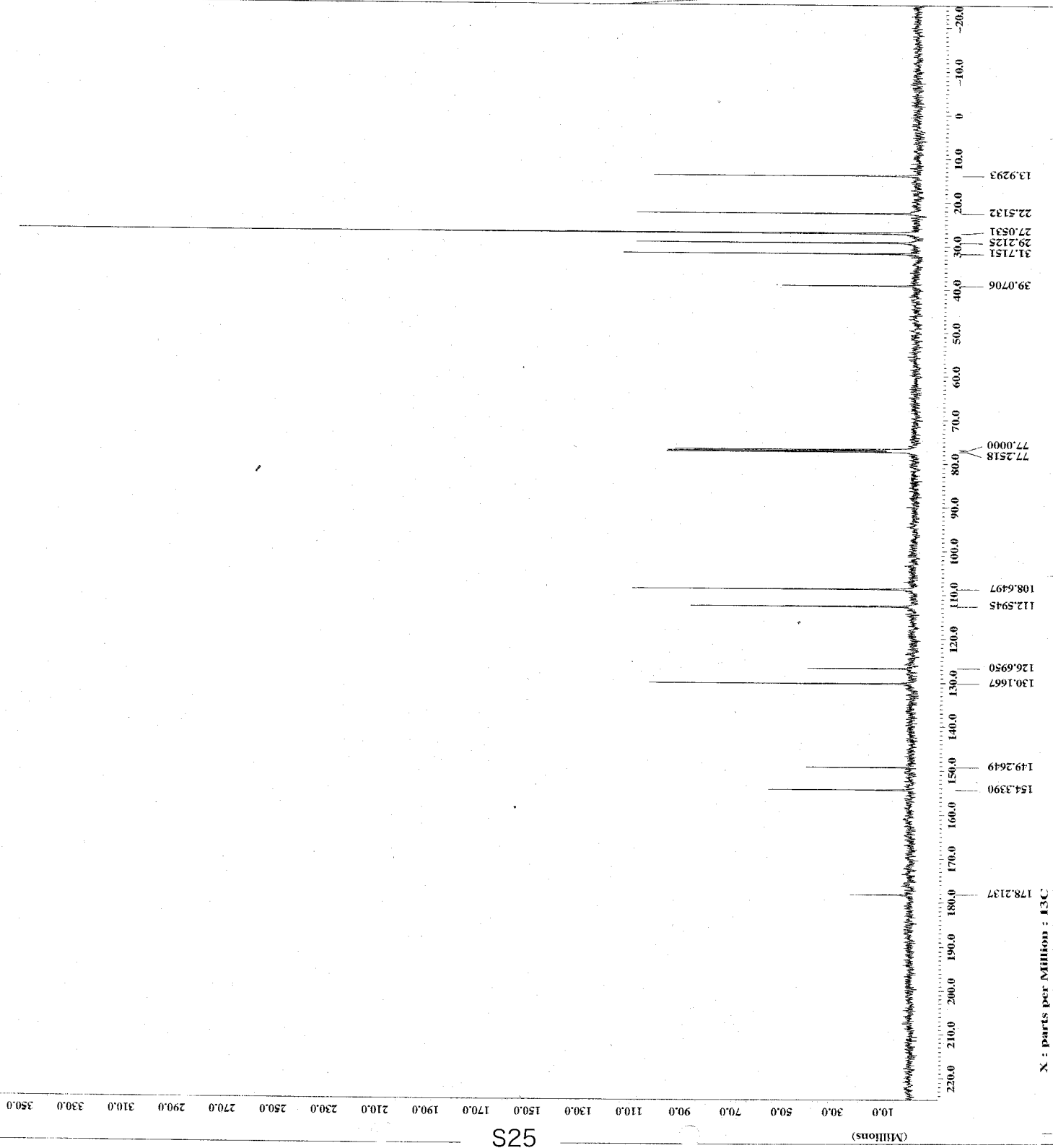
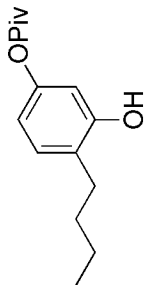


X : parts per Million : 1H





----- ACQUISITION PARAMETERS -----  
File Name = id\_13c\_spectrum\_61  
Author = yed.04c.ir.6-0  
Sample ID = 51843  
Context = 5-NOV-2008 19:48:47  
Creation Date = 5-NOV-2008 19:48:47  
Revision Date = 7-NOV-2008 19:44:07  
Spec Site = ECP500  
Spec Type = DELTA\_NMR  
Data Format = 1D COMPLEX  
Dimensions = X  
Dim Title = 13C  
Dim Units = Hz  
Dim Units = 192  
Scans = 192  
Mod\_return = 1  
X\_Gemain = 13C  
X\_C13set = 100 [ppm]  
X\_F13 = 125.7617 [MHz]  
X\_sweep = 31.44654088 [kHz]  
Solvent = CHLOROFORM-D  
Temp\_set = 17 [Hz]  
Temp\_set = 23.7 [dC]  
X13 = 192  
Field\_strength = 11.7473579 [T]  
Filter\_mode = BUTTERWORTH  
Filter\_width = 15.72066221 [kHz]



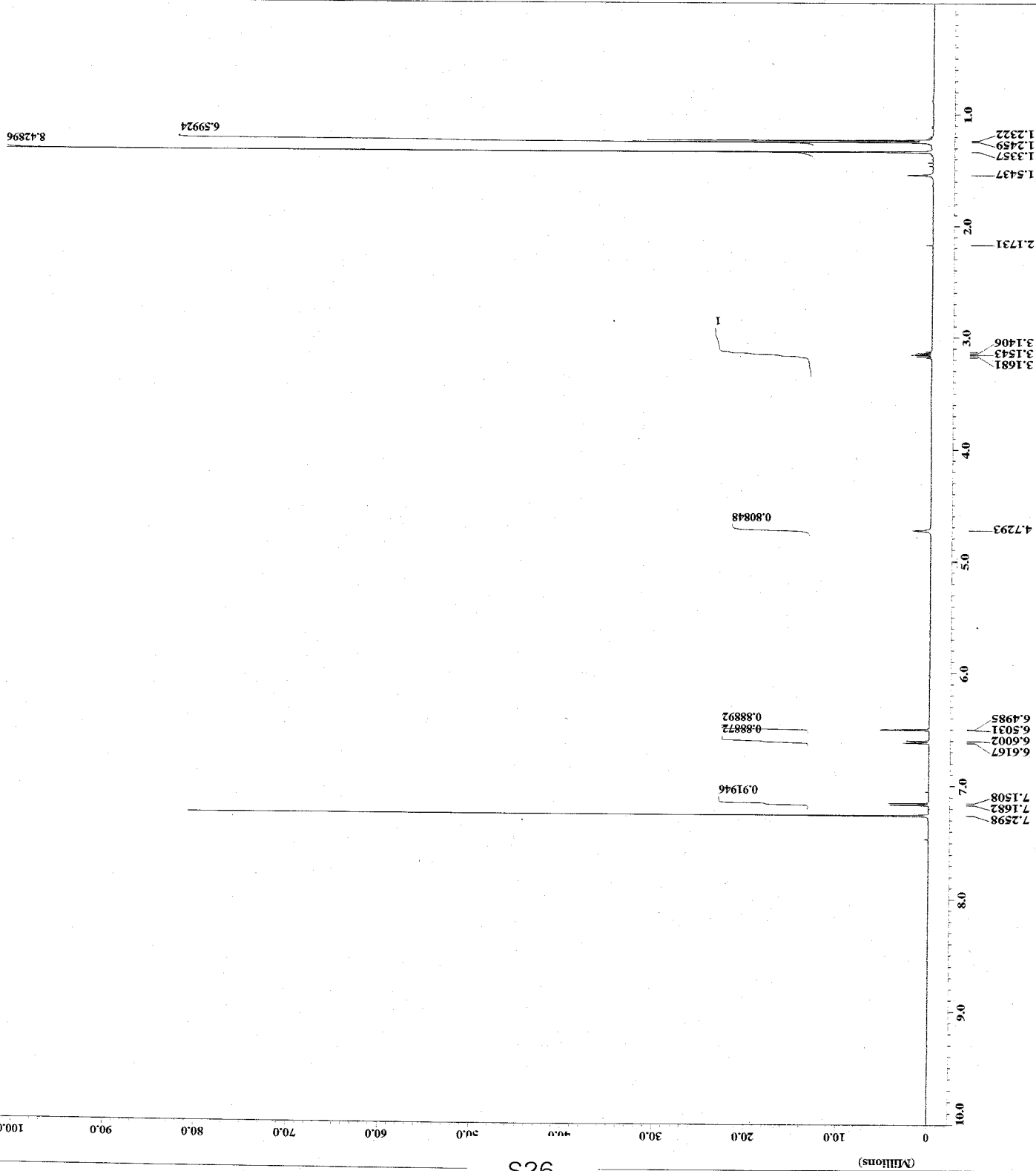
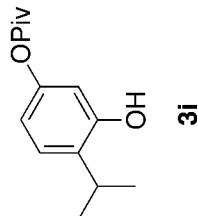


PROCESSING PARAMETERS

dc\_balance = 0.2 [Hz]  
 f1c = 1  
 machinephase = ppm

ACQUISITION PARAMETERS

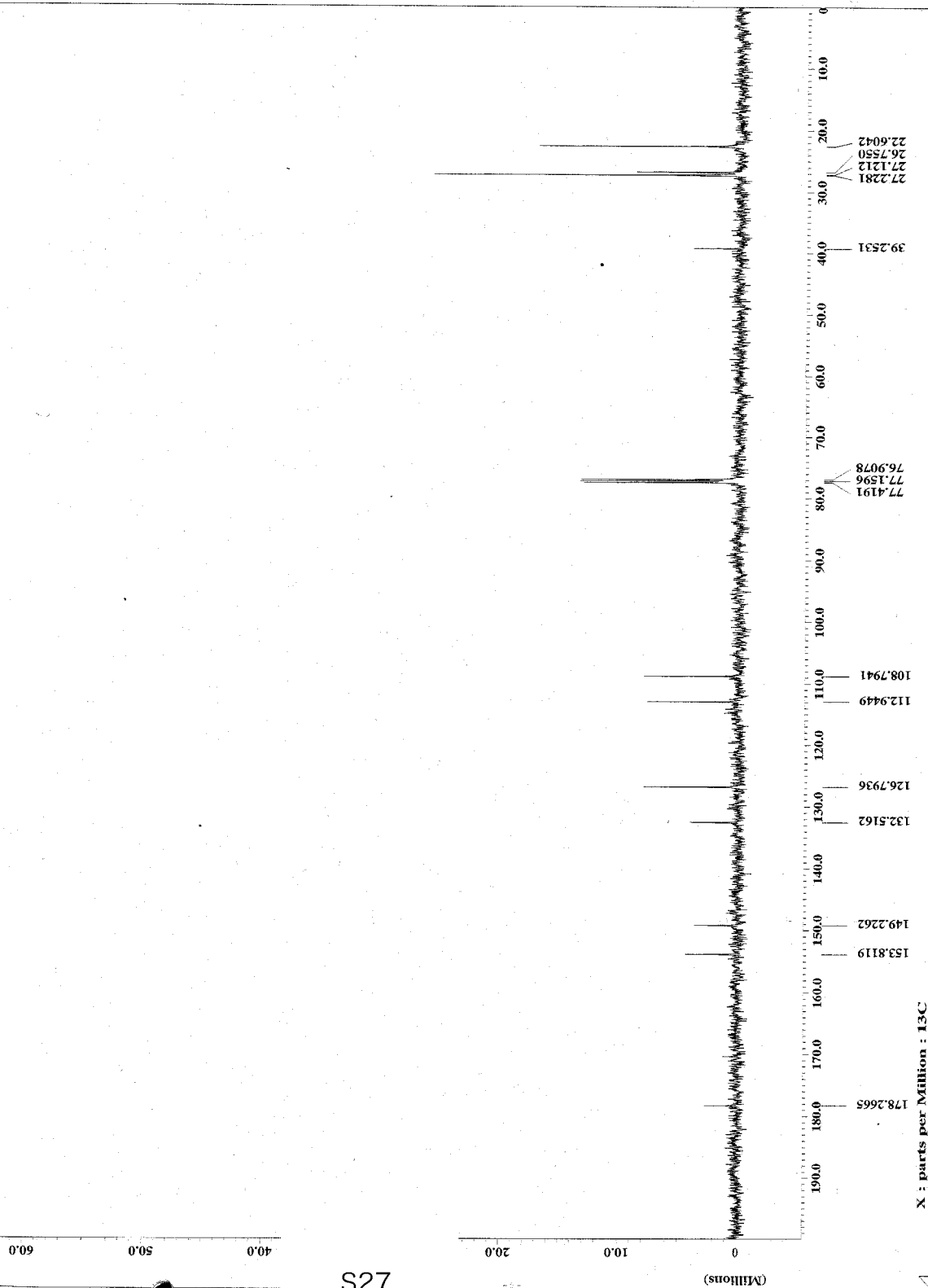
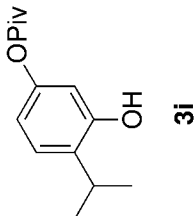
File Name = ccb388r.3  
 Author = ccb388r  
 Sample ID = ccb388H  
 Content = Single Pulse Experiment  
 Creation Date = 18-NOV-2008 18:14:15  
 Revision Date = 14-MAY-2009 20:48:32  
 Spec Site = ECF500  
 Spec Type = DELTA\_NMR  
 Xdim = X  
 Ydim = Y  
 Zdim = Z  
 Dim Title = 1H  
 Dim Size = 16384  
 Dim Units = Dgms  
 Xdim = 9  
 Ydim = 9  
 Zdim = 9  
 X\_domain = 1H  
 X\_offset = 5 [ppm]  
 X\_freq = 500.16241602 [MHz]  
 X\_sweep = 7.50750751 [Hz]  
 Channel = COMB-D  
 Spin Set = 15 [Hz]  
 Temp Set = 22.6 [dC]  
 Recv\_gain = 30  
 Field\_strength = 11.7473579 [T]  
 File Name = ccb388r.3  
 File Size = 3.7511936 [MB]



X : parts per Million : 1H



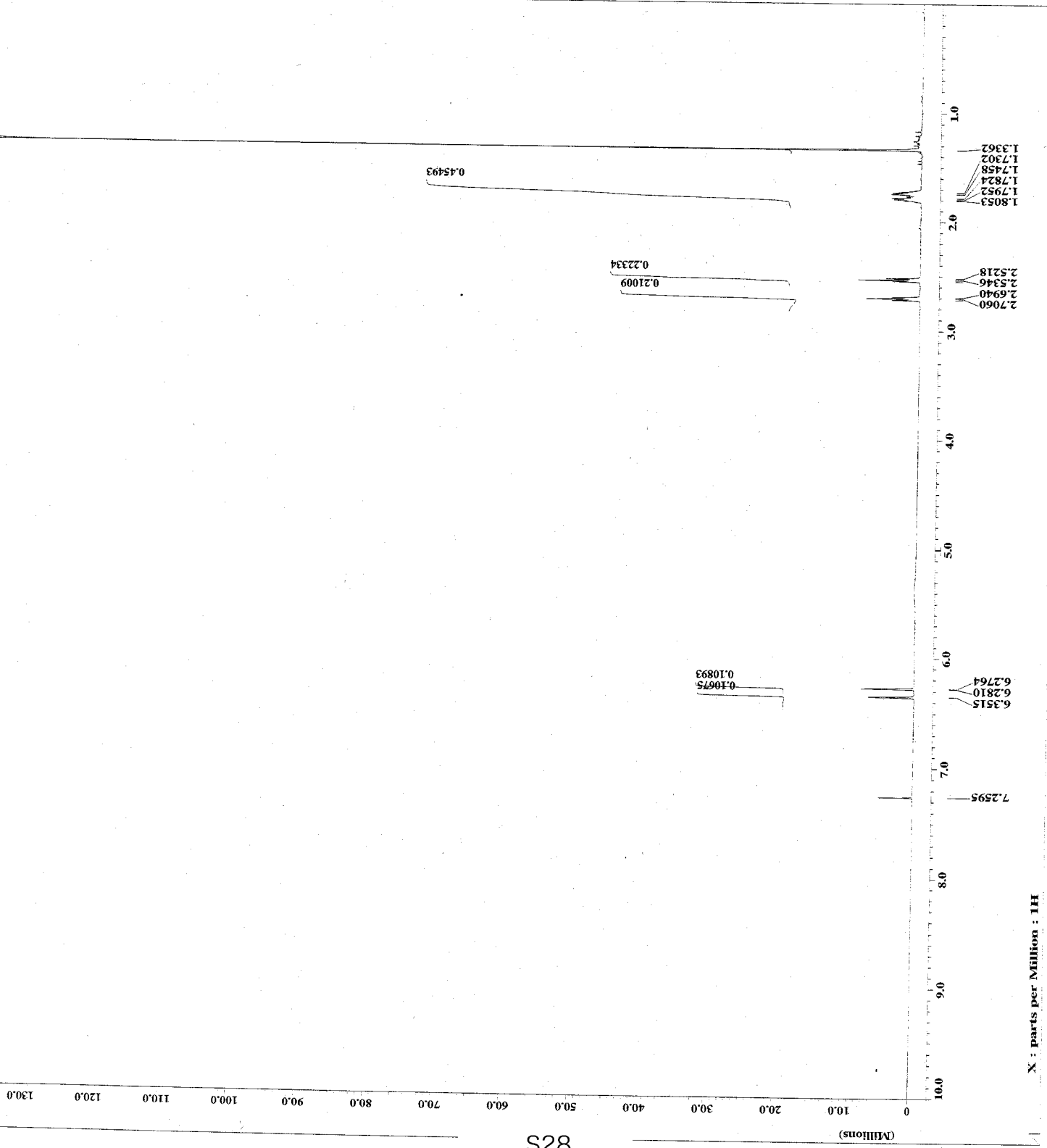
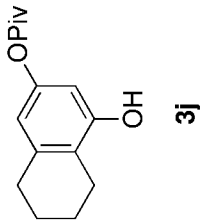
ACQUISITION PARAMETERS  
File Name = 1d\_13c\_spectrum.225  
Author = ceh31c  
Sample ID = Single Pulse with Broad  
Content = 18-NOV-2008 18:40:57  
Creation Date = 20-NOV-2008 19:32:52  
Revision Date = ECF500  
Spec Slice = DELTA\_NMR  
Data Format = 1D COMPLEX  
Dimensions = X  
Dim 1 Units = 13C  
Dim 2 Units = 3268  
Dim 3 Units = [ppm]  
Scans = 15  
Mod\_Return = 1  
X\_Gamma = 13C [ppm]  
X\_Offset = 126.77787547 [MHz]  
X\_Sweep = 31.44654088 [kHz]  
Solvent = CHLOROFORM-D  
Spia\_Set = 16 [Hz]  
Temp\_Set = 22.8 [°C]  
Field\_Strength = 11.7473579 [T]  
Filter\_Mode = BUTTERWORTH  
Filter\_Width = 15.7266221 [kHz]





----- PROCESSING PARAMETERS -----  
dc\_balance = 0.000000  
sweep : 0.2 [Hz]  
fft : 1  
gain : 1  
ppm : 400.139  
-----

----- ACQUISITION PARAMETERS -----  
File Name = ccb844ph.3  
Author = ccb844  
Content = Single Pulse Experiment  
Creation Date = 25-NOV-2008 22:41:21  
Revision Date = 14-MAR-2009 20:52:20  
Spec Site = ECP500  
Spec Type = DELTA NMR  
Data Format = ID COMPLEX  
Dimensions = X  
Dim 1 Size = 1H  
Dim 2 Size = 1H  
Dim 3 Size = 1H  
Dim Units = [ppm]  
Scans = 8  
Mod\_return = 1  
X\_domain = 1H  
X\_offset = 0.000000  
X\_freq = 500.136241603 [MHz]  
X\_sweep = 7.50750751 [Hz]  
Solvent = CHLOROFORM-D  
spin\_get = 16 [Hz]  
temp\_get = 20.8 [dC]  
Recip = 1  
Field\_strength = 11.7473579 [T]  
Filter\_mode = BUTTERWORTH  
Filter\_width = 3.75119936 [Hz]

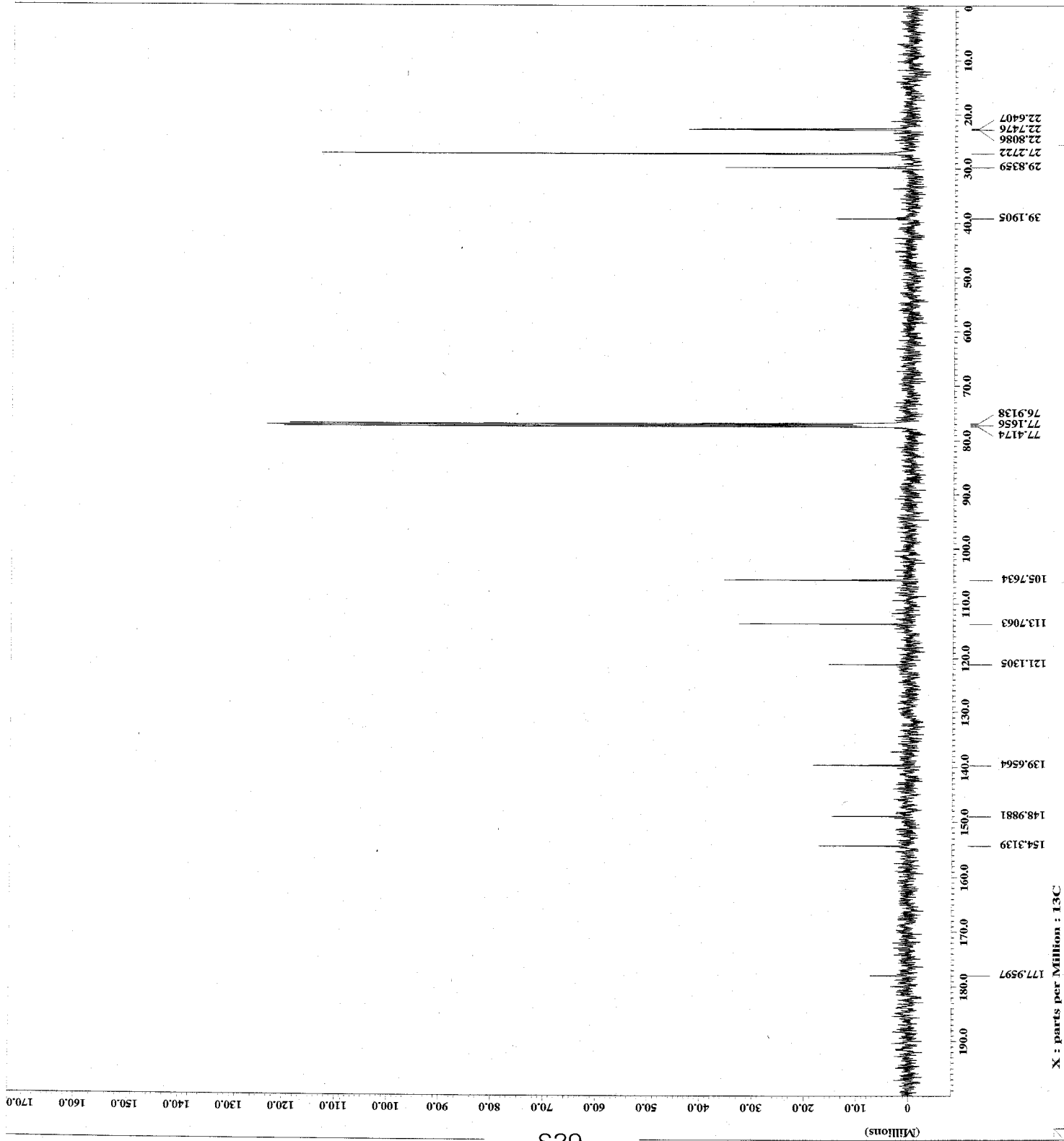
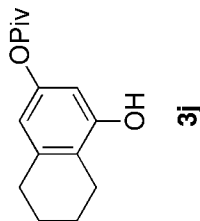


X : parts per Million : 1H



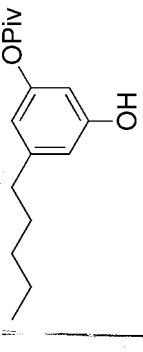
----- PROCESSING PARAMETERS -----  
dc\_balance =  
exp = 5 [Hz]  
fft = 1  
machinephase =

----- ACQUISITION PARAMETERS -----  
File Name = ccb844pc.2  
Sample ID = ccb844p  
Contest = Single Pulse with Broad  
Creation Date = 25-NOV-2008 22:47:43  
Revision Date = 14-MAY-2009 20:54:53  
Spec Site = ECP500  
Spec Type = DELTA\_NMR  
Data Format = 1D COMPLEX  
Dimensions = X  
Dim Size = 32768  
Dim Units = [ppm]  
Scans = 157  
Mod\_return = 1  
X\_center = 100 [ppm]  
X\_offset = 125.77787547 [MHz]  
X\_freq = 31.44654088 [MHz]  
Solvent = CHLOROFORM-D  
Spin\_set = 0 [Hz]  
Sweep = 2 [ppm]  
Revx\_gain = 30  
Field\_strength = 11.7473579 [T]  
Filter\_mode = BUTTERWORTH  
Filter\_width = 15.72066231 [kHz]



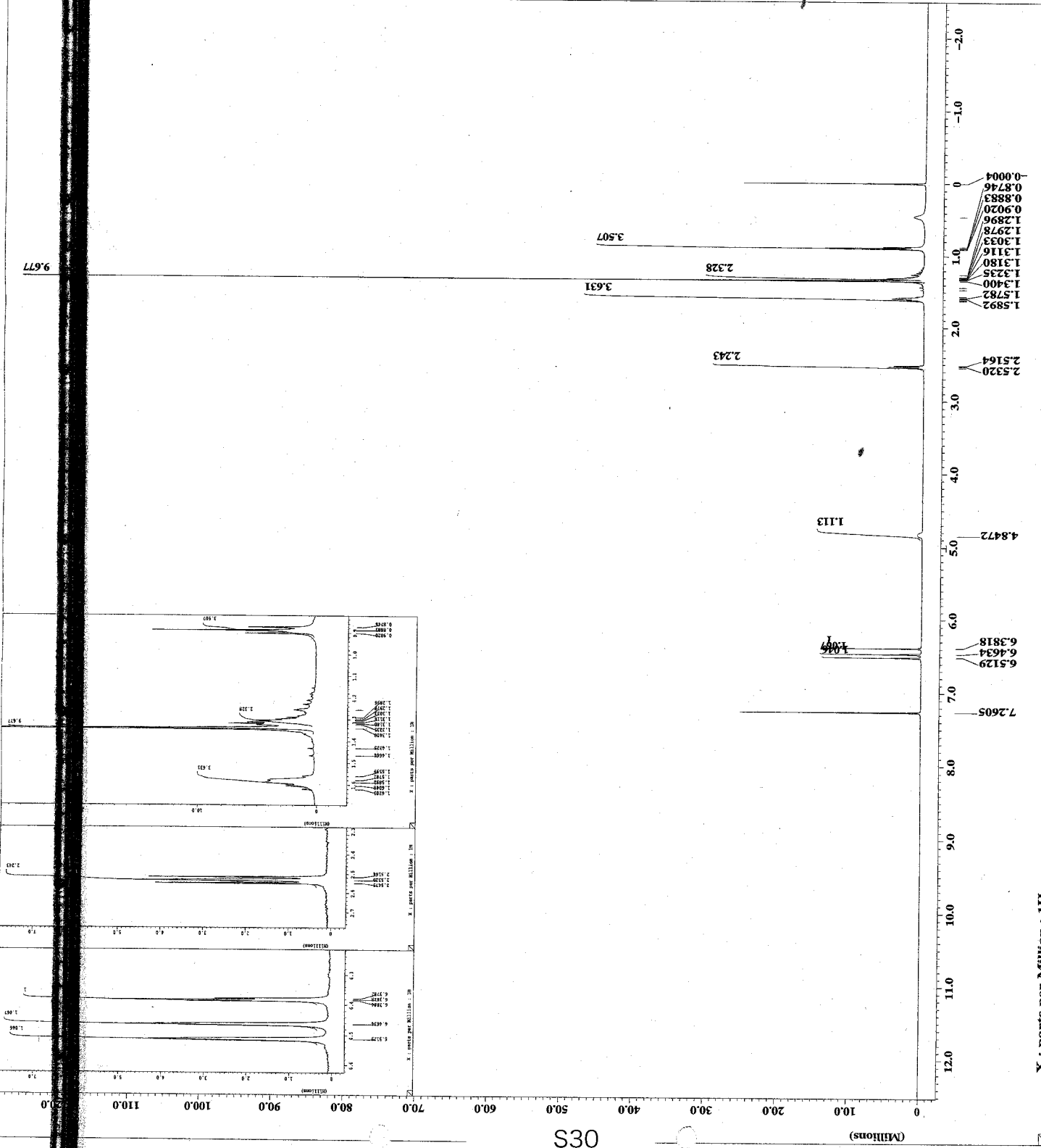
**JEOL**

-----  
 PROCESSING PARAMETERS -----  
 acq - 1  
 aqc - 1  
 ascp : 0.2 [Hz]  
 fft : 1  
 machinephase  
 phase : 0  
 reference : 7.252 [ppm] : 7.26 [ppm]  
 -----



3K

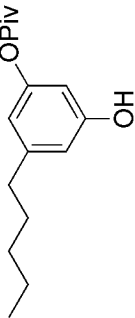
-----  
 ACQUISITION PARAMETERS -----  
 File Name = 1d\_spectrum.224  
 Author =  
 Sample ID = 20-MI-057-fr-5-10  
 Sample Name = 20-MI-057-fr-5-10  
 Creation Date = 23-NOV-2009 09:01:26  
 Revision Date = 27-NOV-2009 16:27:04  
 Spec Site = ECP500  
 Spec Type = DELTA NMR  
 Data Format = 1D COMPLEX  
 Dimensions = X  
 Dim Title = 1H  
 Dim 1 Size = 16384  
 Dim 1 Units = [ppm]  
 Scans = 8  
 Mod\_return = 1  
 X\_domain = 1H  
 X\_offset = 5 [ppm]  
 X\_freq = 241.602 [MHz]  
 X\_sweep = 7.50750751 [kHz]  
 Solvent = CHLOROFORM-D  
 Spin\_get = 14 [Hz]  
 Temp\_get = 23.1 [dC]  
 Recycle\_delay = 1.00 [s]  
 Field\_strength = 11.7473579 [T]  
 Filter\_mode = BUTTERWORTH  
 Filter\_width = 3.75119936 [MHz]  
 -----



X : parts per Million : 1H

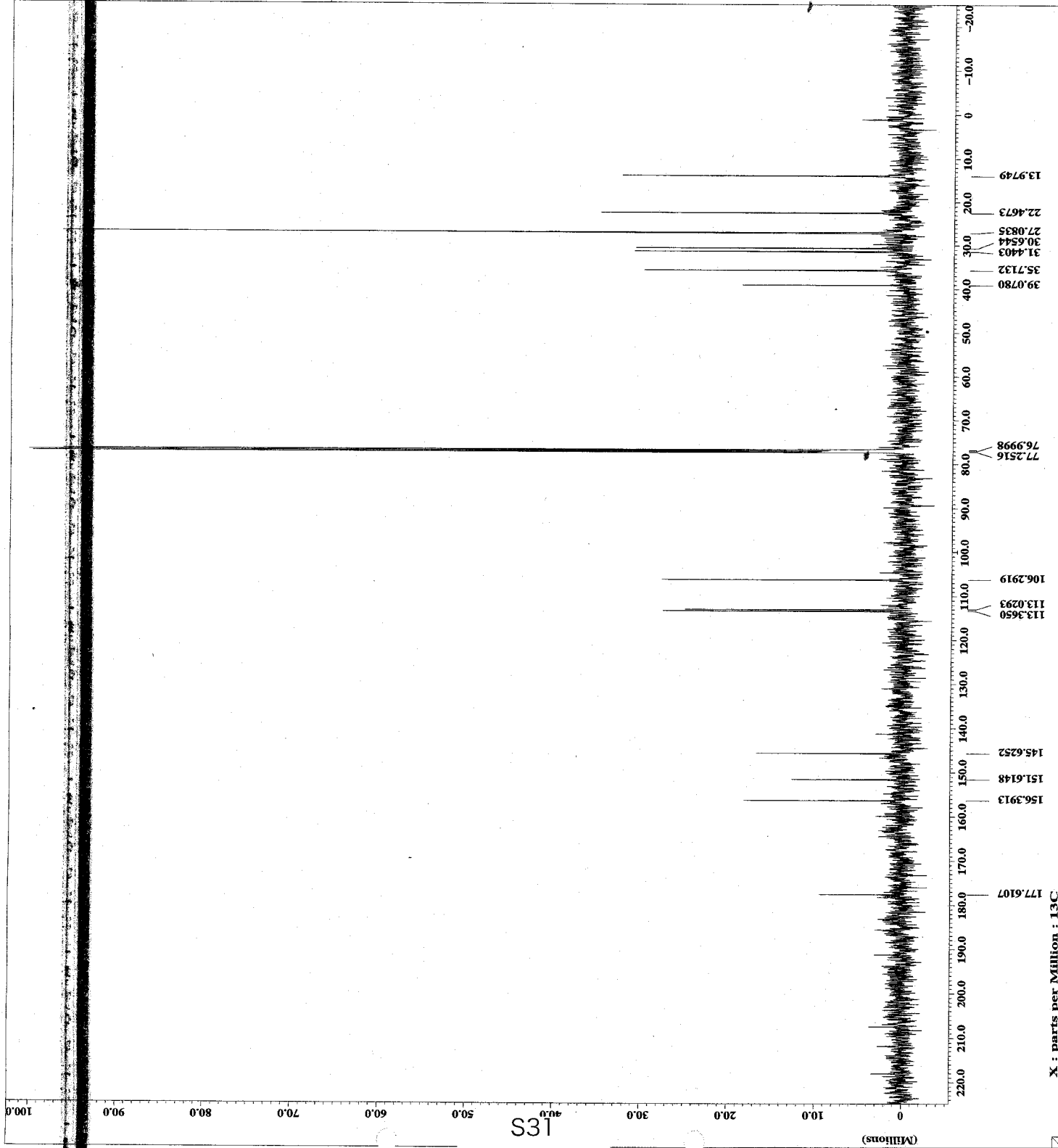
S30

----- PROCESSING PARAMETERS -----  
 GC\_Balance = 1.0000  
 GC\_Offset = 0.0000 [Hz]  
 GC\_Scale = 1.0000  
 ppm = 1000000.0000  
 machinePhase = 0.0000  
 Reference = 77.106 [ppm] : 77 [ppm]



3k

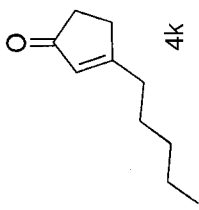
----- ACQUISITION PARAMETERS -----  
 File Name = 14\_13c\_spectrum.69  
 Author = Y. M. 057-fr.5-10  
 Sample ID = 25-NOV-2009 11:22:30  
 Content = Single Pulse with Broad  
 Creation Date = 27-NOV-2009 18:43:47  
 Revision Date = 27-NOV-2009 18:43:47  
 Spec Site = ECP500  
 Spec Type = 13C  
 Data Format = 13C  
 Dimensions = 13C  
 Dim Title = 13C  
 Dim Size = 22768  
 Dim Units = [ppm]  
 Mod Return = 1  
 X\_Domain = 13C  
 X\_Offset = 100 [ppm]  
 X\_Freq = 125.77787547 [MHz]  
 X\_Solvent = CDCl3  
 Solvent = CDCl3  
 Spin\_Set = 17 [Hz]  
 Temp\_Set = 24.8 [degC]  
 Recv\_Gain = 30  
 File\_Length = 11.7473579 [s]  
 Filter\_Width = 15.72066221 [MHz]



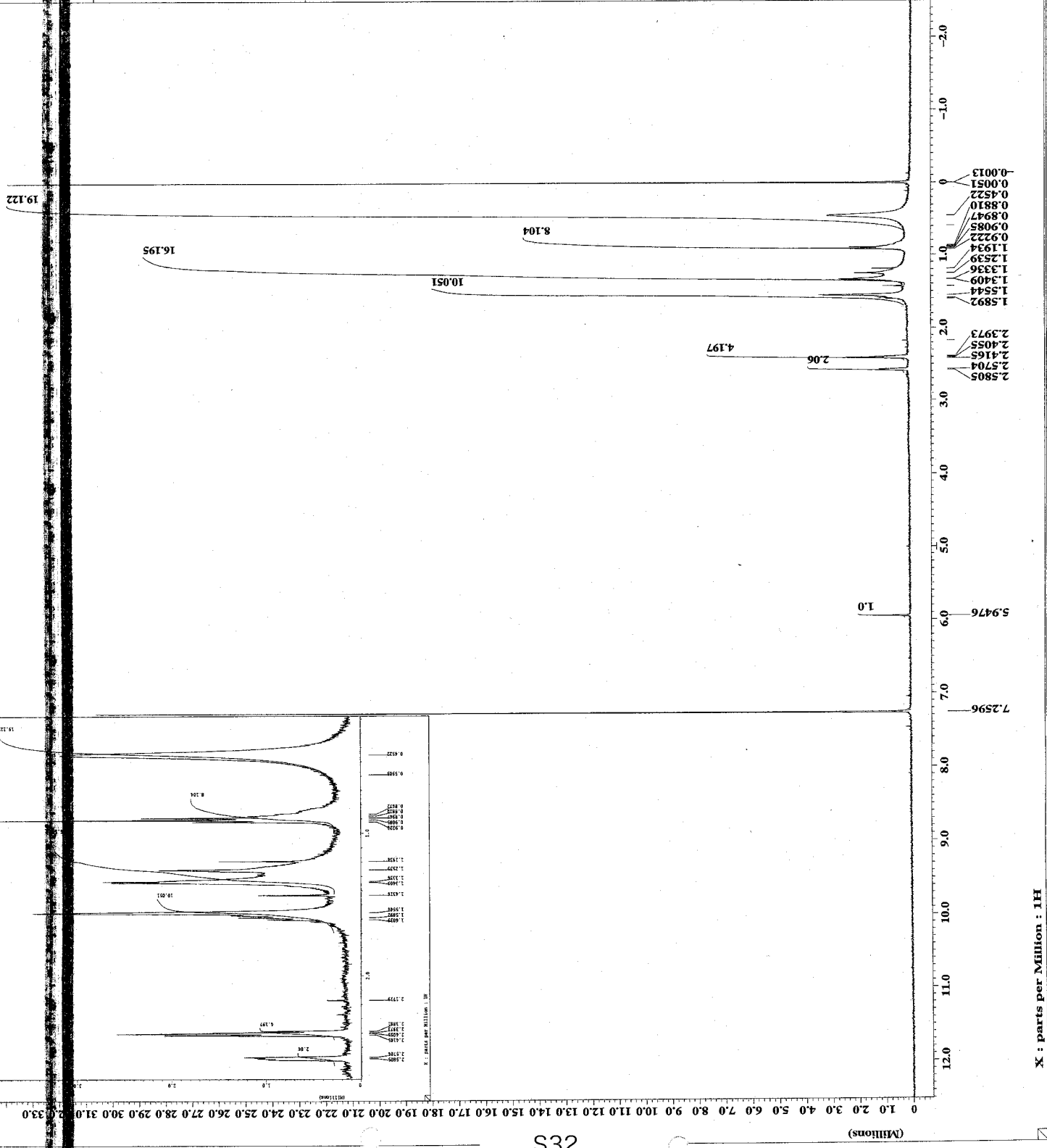
X : parts per Million : 13C

**JEOL**

-----  
 PROCESSING PARAMETERS  
 -----  
 dc\_balance = 0.0000  
 f2 = 0.2 [Hz]  
 machinephase = 1  
 ppm = 0.0000  
 reference = 7.262 [ppm] : 7.26 [ppm]



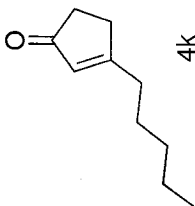
-----  
 ACQUISITION PARAMETERS  
 -----  
 File Name = 1d\_spectrum.100  
 Author =  
 Sample ID = YO-MI-059-fr.15-20  
 Content = Single Pulse Experiment  
 Creation Date = 30-NOV-2009 16:12:30  
 Revision Date = 2-DEC-2009 23:40:15  
 Spec Site = ECF500  
 Spec Type = 1H NMR  
 Dimensions = 1D COMPLEX  
 Dim Title =  
 Dim Size = 16384  
 Dim Units = [ppm]  
 Mod\_return = 1  
 X\_domain = 1H  
 X\_offset = 5 [ppm]  
 X\_freq = 500.16241602 [MHz]  
 X2\_freq = 500.16241602 [MHz]  
 X2\_offset = 0 [ppm]  
 Spin\_set = 16 [Hz]  
 Temp\_set = 23.5 [dC]  
 Recvr\_gain = 10  
 Field\_strength = 11.783578 [T]  
 Filter\_width = 3.751199316 [Hz]



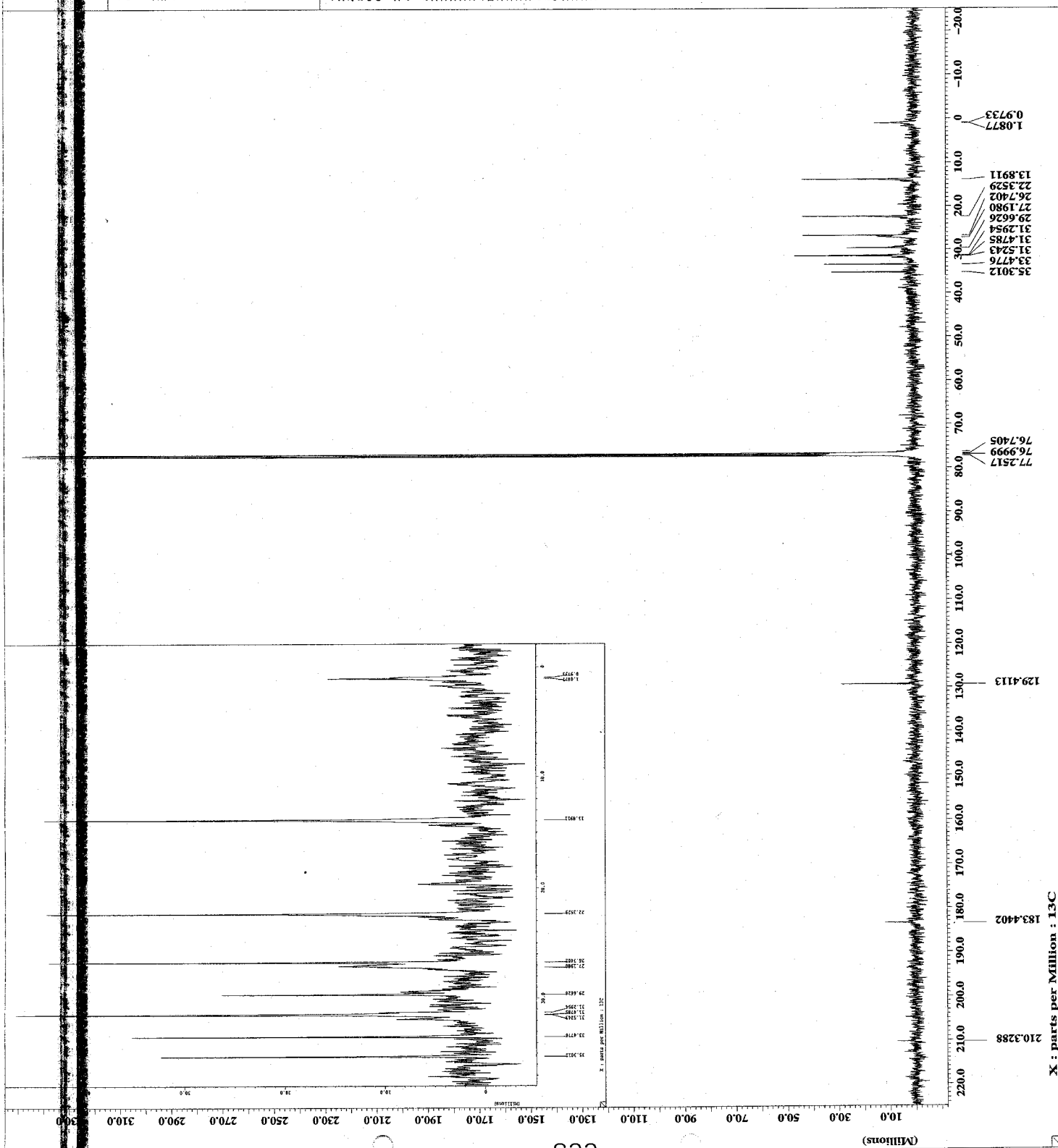
X : parts per Million : 1H



----- PROCESSING PARAMETERS -----  
 dc\_balance  
 smp : 5 [Hz]  
 pc : 1  
 machinephase  
 reference : 77.083 [ppm] : 77 [ppm]



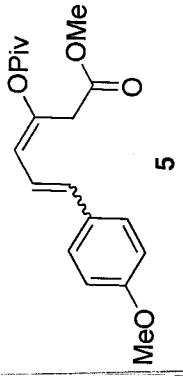
----- ACQUISITION PARAMETERS -----  
 File Name = id\_13c\_spectrum.11  
 Sample ID = yo-MI-059-fr-15-20  
 Content = Single Pulse with Broad  
 Creation Date = 2-DEC-2009 12:43:43  
 Revision Date = 4-DEC-2009 20:12:27  
 Spec Site = ECP500  
 Spec Type = DELTA\_NMR  
 Data Format = ID COMPLEX  
 Processing = 13C  
 Dim Title = 13C  
 Dim Size = 32768  
 Dim Units = [ppm]  
 Scans = 500  
 Xod\_return = 13c  
 X\_offset = 100 [ppm]  
 X\_freq = 125.77787547 [MHz]  
 X\_sweep = 31.44654088 [MHz]  
 Solvent = CHLOROFORM-D  
 Temp\_set = 28.3 [deg]  
 Recv\_gain = 30  
 Field\_strength = 11.7473579 [T]  
 Filter\_mode = BURKHAUWORTH  
 Filter\_width = 15.72066221 [MHz]



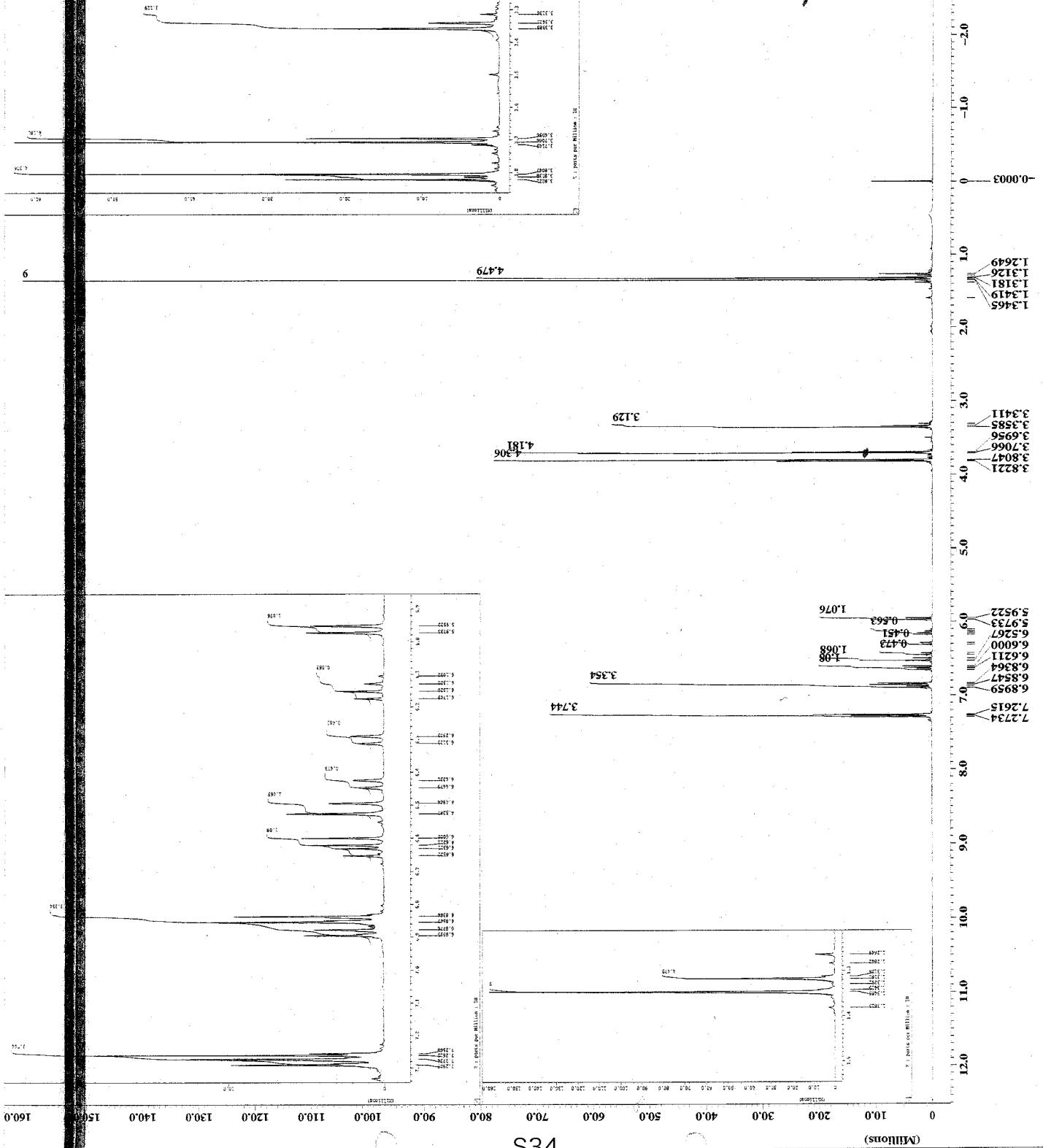
X : parts per Million : 13C



----- PROCESSING PARAMETERS -----  
 GC\_Etaloc03  
 F2: 0.2 [Hz]  
 fft: 1  
 machinephase  
 ppm  
 reference: -9 [ppm] : 0 [ppm]



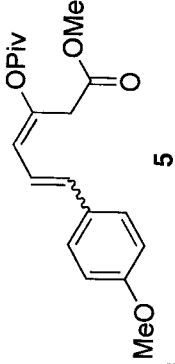
----- ACQUISITION PARAMETERS -----  
 File Name = id\_spectrum.16  
 Author =  
 Sample ID = 70-MI-035-HPIC-3  
 Content = Single Pulse Experiment  
 Creation Date = 22-OCT-2009 10:20:31  
 Revision Date = 24-OCT-2009 18:12:46  
 Spec site = ECP500  
 Spec Type = NMR  
 Data Format = ID COMPLEX  
 Dimensions = X  
 Dim Title = 1H  
 Dim Size = 16384  
 Scans = 1  
 Mod\_return = 1  
 X\_domain = 1H  
 X\_offset = 5 [ppm]  
 X\_freq = 500.1364602 [MHz]  
 X\_solvent = CHLOROFORM-D  
 Spin\_get = 16 [Hz]  
 Temp\_get = 23.9 [dC]  
 Recr\_gain = 23.747879 [fs]  
 Filter\_mode = HERTZKORNH  
 Filter\_width = 3.75119936 [kHz]



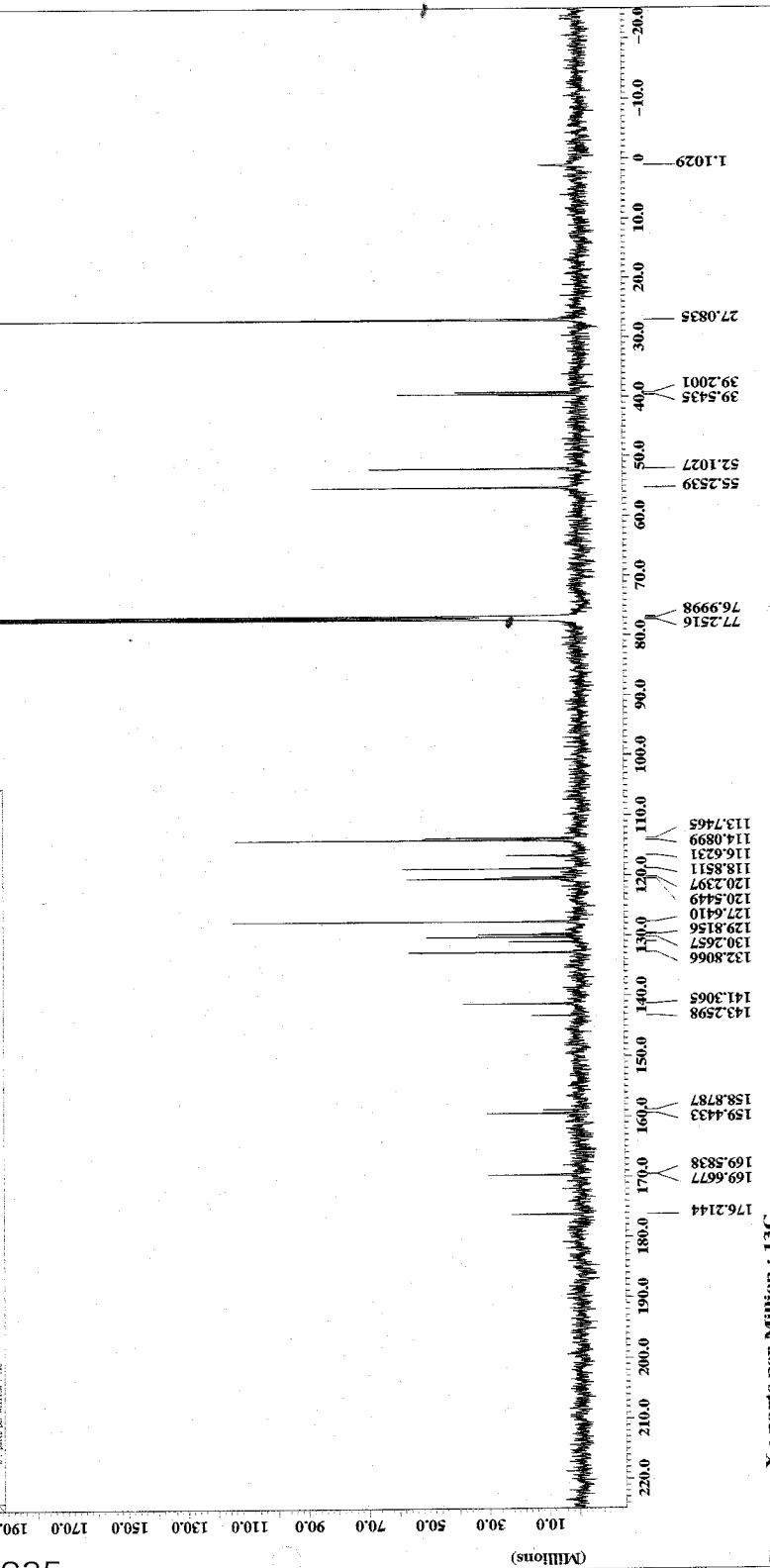
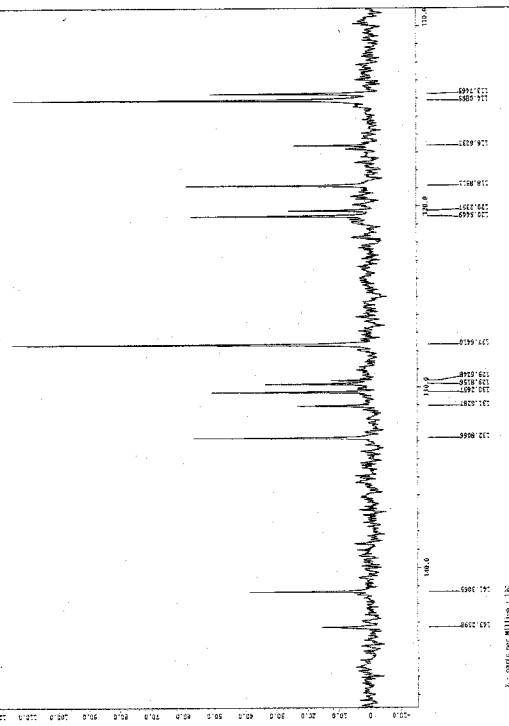
X : parts per Million : 1H

1501

PROCESSING PARAMETERS  
 dc Bal : 5 [Hz]  
 SFO : 5 [Hz]  
 f1 : 1  
 ppm : 1  
 reference : 77.106 [ppm] : 77 [ppm]



ACQUISITION PARAMETERS  
 File Name = 1d\_13c\_spectrum.6  
 Author =  
 Sample ID = 07-MI-05-HPZ-3  
 Name = 51-MI-05-HPZ-3 with Broad  
 Creation Date = 22-OCT-2009 11:32:12  
 Revision Date = 24-OCT-2009 19:18:29  
 Spec Site = ECP500  
 Spec Type = DELTA NMR  
 Data Format = 1D COMPLEX  
 Dimensions = X  
 Dia Title = 13C  
 Dia Date = 2008  
 Dia Units = ppm  
 Scans = 603  
 Mod\_return = 1  
 X\_domain = 13C  
 X\_offset = 126 [ppm]  
 X\_freq = 125.77787547 [MHz]  
 X\_sweep = 31.44654088 [MHz]  
 Solvent = CHLOROFORM-D  
 Spia\_get = 17 [Hz]  
 Temp\_get = 25.8 [dC]  
 Field\_strength = 11.7473579 [T]  
 Filter\_mode = BUTTERWORTH  
 Filter\_width = 15.72066221 [MHz]



X : parts per Million : 13C