

***Diversity Oriented One-Pot Synthesis of Novel Iminosugar C-Glycosides***

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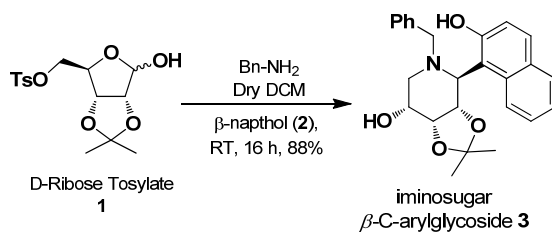
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**General Methods:** All the solvents were distilled prior to use. Dry solvents were prepared according to the standard procedures. All other reagents were used as received from either Aldrich or Lancaster chemical companies. Reactions requiring inert atmosphere were carried out under argon atmosphere. Infrared (IR) spectra were recorded on a JASCO 4100 FT-IR spectrometer.  $^1\text{H}$  NMR spectra were measured on Bruker AVANCE 400 MHz and 500 MHz spectrometers. Chemical shifts were reported in ppm from tetramethylsilane in the case of  $\text{CDCl}_3$  as an internal standard.  $^{13}\text{C}$  NMR spectra were recorded on Bruker 100 MHz and 125 MHz spectrometers with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. The high-resolution mass spectra (HRMS) were performed on Micromass Q-TOF micro mass spectrometer equipped with a Harvard apparatus syringe pump. Optical rotations were measured on a JASCO P-2000 polarimeter. X-ray crystallographic data were recorded using Bruker-AXS Kappa CCD-Diffractometer with graphite-monochromator  $\text{Cu}_{\text{K}\alpha}$  radiation ( $\lambda=1.5418$  Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares techniques against  $F^2$  (SHELXL-97). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program. For thin layer chromatography (TLC) analysis throughout this work, E-merck precoated TLC plates (silica gel 60 F254 grade, 0.25 mm) were used. Acme (India) silica gel (100-200 mesh) was used for column chromatography.

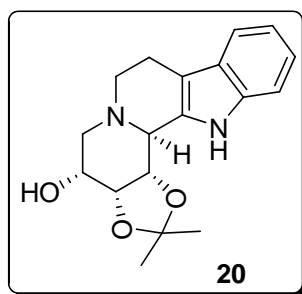
**General procedure for the synthesis of hydrophobically modified iminosugar C-aryl glycosides:**



To a stirred solution of azeotropically dried D-ribose tosylate **1** (100 mg, 0.29 mmol) in dry DCM (2 mL) was slowly added benzylamine (66  $\mu\text{L}$ , 0.61 mmol) and the resultant mixture was stirred at room temperature for about 2 h. To this stirred solution,  $\beta$ -naphthol (**2**) (50 mg, 0.35 mmol) was added and the resultant mixture was stirred further at room temperature for 14 h. After completion of the reaction, as indicated by TLC, reaction

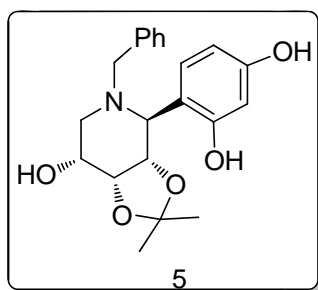
mixture was diluted with water (5 mL) and extracted with DCM (3 × 10 mL). Combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give crude product. Purification of the crude product by column chromatography over silica gel (gradient elution with 20-25% EtOAc in hexane) afforded the pure iminosugar C-aryl glycoside **3** (103 mg, 88 %) as a colorless solid, m.p. 147 – 149 °C,  $[\alpha]_D^{24} -17.3$  (*c* 1.0, CHCl<sub>3</sub>); **IR (Neat) cm<sup>-1</sup>**: 3448, 2989, 2931, 2846, 1620, 1597, 1520, 1462, 1408, 1377, 1238, 1165, 1103, 1057, 860, 814, 702, 752, 509, 447; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ ppm 7.91 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.08 (m, 7H), 4.38 (d, *J* = 7.2 Hz, 2H), 4.16 (d, *J* = 6.8 Hz, 1H), 3.98 (t, *J* = 5.2 Hz, 1H), 3.83 (d, *J* = 13.2 Hz, 1H), 3.01 - 2.94 (m, 2H), 2.37 (t, *J* = 10.8 Hz, 1H), 1.65 (s, 3H), 1.22 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ ppm 154.6, 135.7, 133.1, 130.2, 129.8, 129.1, 129.0, 128.7, 127.9, 126.4, 123.0, 122.3, 119.3, 116.3, 110.5, 79.0, 75.4, 65.9, 63.6, 58.8, 51.6, 28.2, 26.2; **HRMS (ESI) m/z** calcd for C<sub>25</sub>H<sub>28</sub>NO<sub>4</sub> (M<sup>+</sup>+H) 406.2018 found 406.2026.

**General experimental procedure for the Synthesis of Hybrid molecules from Carbohydrate derivatives:**

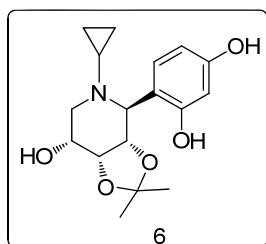


To a stirred solution of azeotropically dried D-ribose tosylate **1** (250 mg, 0.73 mmol) in dry DCM (2 mL), tryptamine (**20**) (245 mg, 1.53 mmol) was added and the resultant mixture was stirred at the room temperature for 57 h. After completion of the reaction as indicated by TLC, saturated NaHCO<sub>3</sub> (10 mL) was added to the reaction mixture and extracted with DCM (3 × 20 mL). Combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give crude product, which on column chromatographic purification over silica gel using 40-45% EtOAc in hexane as eluent afforded the pure hybride molecule **20** (155 mg, 68 %) as a colorless solid, m.p. 188 –

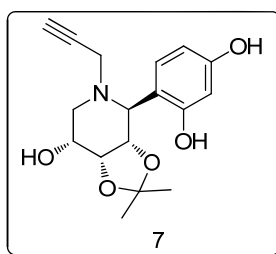
190 °C,  $[\alpha]_D^{27} +1.8$  ( *c* 1.0, CHCl<sub>3</sub>); **IR (Neat) cm<sup>-1</sup>** : 3451, 2985, 2926, 2813, 1457, 1376, 1325, 1215, 1166, 1117, 1073, 1033, 985, 913, 868, 735, 474, 417; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ ppm 8.46 (bs, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 4.52 (t, *J* = 4.4 Hz, 1H), 4.22 – 4.13 (m, 2H), 3.41 (d, *J* = 8.8 Hz, 1H), 3.11 – 3.03 (m, 2H), 2.98 – 2.89 (m, 1H), 2.75 – 2.65 (m, 2H), 2.53 (t, *J* = 10.8 Hz, 2H), 1.68 (s, 3H), 1.50 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ ppm 136.2, 133.3, 126.7, 121.7, 119.4, 118.2, 111.0, 110.4, 108.1, 78.2, 75.6, 66.5, 60.1, 57.6, 52.6, 28.5, 26.6, 21.5; **HRMS (ESI) *m/z*** calcd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> (M<sup>+</sup> + H) 315.1709 found 315.1722.



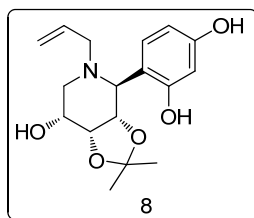
**Compound 5:** Colorless solid, m.p. 115 – 117 °C,  $[\alpha]_D^{21} -40.8$  ( *c* 1.0, MeOH); **IR (Neat) cm<sup>-1</sup>** : 3394, 2839, 1616, 1458, 1385, 1308, 1234, 1103, 1041, 976, 856, 725, 471; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ ppm 7.26 – 7.17 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.34 (d, *J* = 2.0 Hz, 1H), 6.26 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.30 (t, *J* = 4.0 Hz, 1H), 4.15 (dd, *J* = 8.5, 5.0 Hz, 1H), 3.93 – 3.88 (m, 2H), 3.16 (d, *J* = 8.0 Hz, 1H), 2.98 (d, *J* = 13.5 Hz, 1H), 2.89 (dd, *J* = 11.0, 4.5 Hz, 1H), 2.22 (t, *J* = 11.0 Hz, 1H), 1.53 (s, 3H), 1.27 (s, 3H); **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ ppm 157.5, 156.6, 135.7, 130.8, 129.8, 128.7, 127.9, 115.8, 110.6, 107.5, 104.2, 77.9, 75.3, 69.0, 65.6, 58.9, 51.7, 28.3, 26.4; **HRMS (ESI) *m/z*** calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>5</sub> (M<sup>+</sup> + H) 372.1811 found 372.1808.



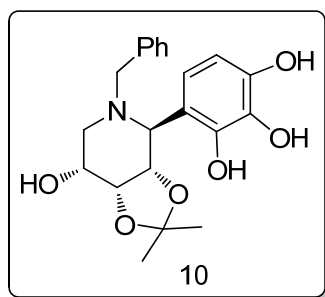
**Compound 6:** Colorless solid, m.p. 155 – 157 °C,  $[\alpha]_D^{24} -10.7$  (*c* 1.0, MeOH); **IR (Neat)**  $\text{cm}^{-1}$ : 3423, 2846, 1617, 1460, 1380, 1220, 1097, 754;  **$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )**  $\delta$  ppm 6.91 (d, *J* = 8.0 Hz, 1H), 6.27 (d, *J* = 8.8 Hz, 1H), 6.25 (s, 1H), 4.39 (t, *J* = 4.0 Hz, 1H), 4.23 (dd, *J* = 8.8, 4.8 Hz, 1H), 4.04 – 3.99 (m, 1H), 3.47 (d, *J* = 8.4 Hz, 1H), 3.04 (dd, *J* = 11.2, 4.8 Hz, 1H), 2.63 (t, *J* = 11.2 Hz, 1H), 1.65 – 1.62 (m, 1H), 1.61 (s, 3H), 1.33 (s, 3H), 0.40 – 0.30 (m, 2H), 0.26 – 0.19 (m, 1H), 0.10 – 0.04 (m, 1H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )**  $\delta$  ppm 159.0, 158.2, 131.6, 118.0, 110.9, 107.5, 103.9, 79.6, 76.8, 68.9, 66.7, 56.2, 39.0, 28.5, 26.5, 8.5, 4.4; **HRMS (ESI)** *m/z* calcd for  $\text{C}_{17}\text{H}_{24}\text{NO}_5$  ( $\text{M}^+ + \text{H}$ ) 322.1654 found 322.1655.



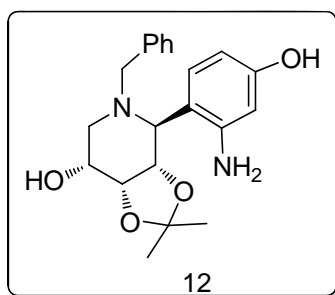
**Compound 7:** Colorless solid, m.p. 60 – 62 °C,  $[\alpha]_D^{24} +44.5$  (*c* 1.0,  $\text{CHCl}_3$ ); **IR (Neat)**  $\text{cm}^{-1}$ : 3401, 2989, 2944, 2361, 2334, 1626, 1226, 1160, 1107, 757, 664;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  ppm 6.88 (d, *J* = 7.6 Hz, 1H), 6.31 – 6.27 (m, 2H), 4.40 (t, *J* = 4.0 Hz, 1H), 4.17 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.13 – 4.08 (m, 1H), 3.41 – 3.31 (m, 3H), 2.96 (dd, *J* = 11.2, 5.2 Hz, 1H), 2.81 (t, *J* = 11.2 Hz, 1H), 2.31 (s, 1H), 1.66 (s, 3H), 1.37 (s, 3H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  ppm 157.4, 156.7, 130.9, 115.0, 110.6, 107.6, 104.0, 78.0, 76.1, 75.3, 75.2, 66.0, 65.9, 52.4, 43.5, 28.3, 26.4; **HRMS (ESI)** *m/z* calcd for  $\text{C}_{17}\text{H}_{22}\text{NO}_5$  ( $\text{M}^+ + \text{H}$ ) 320.1498 found 320.1499.



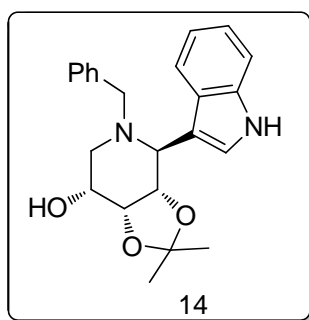
**Compound 8:** Colorless solid, m.p. 78 – 80 °C,  $[\alpha]_D^{23} -48.5$  ( $c$  1.0,  $\text{CHCl}_3$ ); **IR (Neat)  $\text{cm}^{-1}$**  : 3379, 2951, 2873, 1608, 1481, 1350, 1203, 1126, 1084, 1011, 825, 629, 478;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm** 6.83 (d,  $J = 8.0$  Hz, 1H), 6.31 (s, 1H), 6.29 (d,  $J = 8.0$  Hz, 1H), 5.80 – 5.70 (m, 1H), 5.19 (d,  $J = 10.0$  Hz, 1H), 5.11 (d,  $J = 16.8$  Hz, 1H), 4.37 (s, 1H), 4.14 (dd,  $J = 8.0, 4.4$  Hz, 1H), 4.06 – 4.02 (m, 1H), 3.34 (dd,  $J = 14.0, 4.4$  Hz, 1H), 3.18 (d,  $J = 8.4$  Hz, 1H), 3.10 (dd,  $J = 11.2, 4.8$  Hz, 1H), 2.69 (dd,  $J = 14.0, 8.4$  Hz, 1H), 2.36 (t,  $J = 11.2$  Hz, 1H), 1.63 (s, 3H), 1.35 (s, 3H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm** 157.3, 156.9, 132.8, 130.5, 119.9, 115.8, 110.4, 107.3, 104.0, 78.2, 75.3, 68.4, 65.9, 57.0, 52.0, 28.3, 26.3; **HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{24}\text{NO}_5$  ( $\text{M}^+ + \text{H}$ )** 322.1654 found 322.1646.



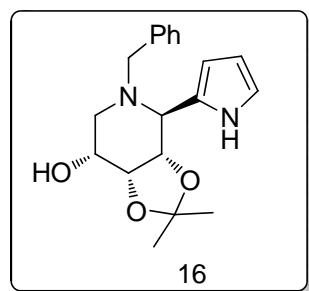
**Compound 10:** Light brown solid, m.p. 168 – 170 °C; **IR (Neat)  $\text{cm}^{-1}$**  : 3398, 2924, 2353, 1612, 1470, 1362, 1227, 1049, 760, 436;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm** 7.19 – 7.15 (m, 5H), 7.12 – 7.05 (m, 2H), 6.45 (d,  $J = 8.0$  Hz, 1H), 6.38 (d,  $J = 8.0$  Hz, 1H), 4.27 (s, 1H), 4.15 – 4.08 (m, 1H), 3.90 – 3.83 (m, 2H), 3.15 (d,  $J = 8.0$  Hz, 1H), 3.0 (d,  $J = 13.2$  Hz, 1H), 2.88 – 2.80 (m, 1H), 2.21 (t,  $J = 10.8$  Hz, 1H), 1.50 (s, 3H), 1.23 (s, 3H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm** 144.9, 143.1, 135.9, 132.4, 129.7, 128.7, 127.8, 120.6, 116.4, 110.4, 107.4, 78.1, 75.2, 69.1, 65.8, 58.9, 51.4, 28.2, 26.3; **HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{26}\text{NO}_6$  ( $\text{M}^+ + \text{H}$ )** 388.1760 found 388.1744.



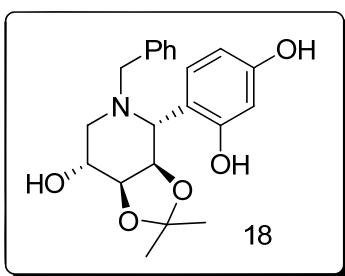
**Compound 12:** Light brown solid, m.p. 132 – 134 °C,  $[\alpha]_D^{27} -197.1$  (*c* 1.0, CHCl<sub>3</sub>); **IR (Neat) cm<sup>-1</sup>** : 3379, 2943, 2835, 2522, 2226, 2040, 1655, 1454, 1115, 1022, 752, 667; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm** 7.26 – 7.15 (m, 5H), 6.78 (d, *J* = 8 Hz, 1H), 6.19 (d, *J* = 2 Hz, 1H), 6.13 (dd, *J* = 8.2 Hz, 1H), 4.34 (t, *J* = 4.4 Hz, 1H), 4.13 (dd, *J* = 8, 4.8 Hz, 1H), 3.94 – 3.89 (m, 2H), 3.57 (bs, 1H), 3.10 (d, *J* = 8 Hz, 1H), 2.95 (d, *J* = 13.2 Hz, 1H), 2.88 (dd, *J* = 11.2, 4.8 Hz, 1H), 2.17 (t, *J* = 11.2 Hz, 1H), 1.55 (s, 3H), 1.29 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm** 156.6, 147.9, 136.5, 130.6, 129.7, 128.6, 127.7, 114.3, 110.2, 107.1, 103.5, 78.2, 75.3, 69.4, 65.9, 58.9, 51.9, 28.3, 26.4; **HRMS (ESI) *m/z*** calcd for C<sub>21</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub> (M<sup>+</sup> + H) 371.1971 found 371.1981.



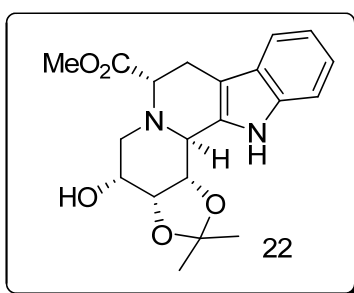
**Compound 14:** White solid, m.p. 94 – 96 °C,  $[\alpha]_D^{27} -12.0$  (*c* 1.0, CHCl<sub>3</sub>); **IR (Neat) cm<sup>-1</sup>** : 3456, 3059, 2978, 1635, 1435, 1261, 1049, 895, 729, 405; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm** 8.04 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8 Hz, 1H), 7.17 – 7.03 (m, 8H), 4.41 – 4.38 (m, 2H), 4.07 – 4.02 (m, 1H), 3.75 (d, *J* = 13.2 Hz, 1H), 3.42 (d, *J* = 7.6 Hz, 1H), 2.90 (dd, *J* = 11.2, 5.6 Hz, 1H), 2.82 (d, *J* = 13.6 Hz, 1H), 2.14 (t, *J* = 11.2 Hz, 1H), 2.06 (bs, 1H), 1.57 (s, 3H), 1.27 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm** 139.4, 137.3, 128.9, 128.3, 126.9, 126.1, 123.9, 122.5, 120.4, 119.7, 115.1, 111.6, 109.5, 79.0, 75.8, 67.0, 64.2, 58.3, 53.9, 28.5, 26.5; **HRMS (ESI) *m/z*** calcd for C<sub>23</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub> (M<sup>+</sup> + H) 379.2022 found 379.2039.



**Compound 16:** Colorless solid, m.p. 184 – 186 °C,  $[\alpha]_D^{24} -14.8$  ( $c$  1.0, CH<sub>3</sub>OH); **IR (Neat) cm<sup>-1</sup>:** 3383, 3005, 2943, 2835, 1643, 1450, 1416, 1219, 1026, 760; **<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)**  $\delta$  ppm 10.65 (s, 1H), 7.20 – 7.10 (m, 5H), 6.61 (s, 1H), 5.92 (d,  $J$  = 18.4 Hz, 2H), 4.81 (d,  $J$  = 6 Hz, 1H), 4.22 (t,  $J$  = 3.6 Hz, 1H), 4.13 (dd,  $J$  = 8.4, 4.4 Hz, 1H), 3.75 – 3.71 (m, 1H), 3.16 (d,  $J$  = 8.8 Hz, 1H), 2.74 (d,  $J$  = 13.2 Hz, 1H), 2.47 (dd,  $J$  = 10.4, 4.8 Hz, 1H), 2.40 (s, 1H), 2.04 (t,  $J$  = 10.8 Hz, 1H), 1.42 (s, 3H), 1.18 (s, 3H); **<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)**  $\delta$  ppm 139.4, 130.4, 128.5, 128.1, 126.7, 117.4, 108.3, 107.4, 107.3, 78.5, 75.9, 65.3, 63.1, 57.0, 53.0, 28.3, 26.4; **HRMS (ESI)  $m/z$**  calcd for C<sub>19</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub> ( $M^+$  + H) 329.1865 found 329.1850.

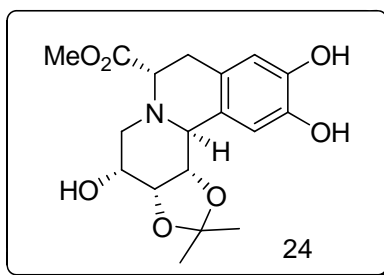


**Compound 18:** Colorless solid, m.p. 170 – 172 °C,  $[\alpha]_D^{27} +45.9$  ( $c$  1.0, CHCl<sub>3</sub>); **IR (Neat) cm<sup>-1</sup>:** 3386, 2986, 2924, 2851, 1658, 1626, 1461, 1379, 1225, 1059, 979, 852, 754; **<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD)**  $\delta$  ppm 7.26 – 7.22 (m, 5H), 6.92 (d,  $J$  = 7 Hz, 1H), 6.33 – 6.30 (m, 2H), 4.22 (t,  $J$  = 5 Hz, 1H), 4.14 (s, 1H), 3.97 (s, 1H), 3.85 (d,  $J$  = 13 Hz, 1H), 3.24 (d,  $J$  = 7 Hz, 1H), 3.01 (d,  $J$  = 13.5 Hz, 1H), 2.87 (d,  $J$  = 12.5 Hz, 1H), 2.36 (d,  $J$  = 12.5 Hz, 1H), 1.53 (s, 3H), 1.28 (s, 3H); **<sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD)**  $\delta$  ppm 159.4, 158.1, 138.1, 131.8, 130.6, 129.4, 128.3, 117.7, 110.5, 107.6, 104.4, 77.9, 77.2, 69.7, 65.8, 59.4, 53.0, 28.5, 26.5; **HRMS (ESI)  $m/z$**  calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>5</sub> ( $M^+$  + H) 372.1811 found 372.1812.

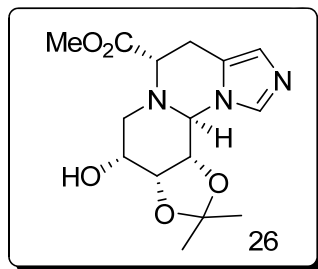




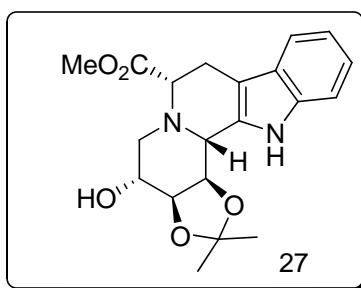
**Compound 22:** Colorless fluffy solid, m.p. 71 – 73 °C,  $[\alpha]_D^{27} -16.1$  ( $c$  1.0,  $\text{CHCl}_3$ ); **IR (Neat)  $\text{cm}^{-1}$ :** 3433, 2951, 1728, 1601, 1462, 1365, 1234, 1034, 872, 752, 482;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm** 8.36 (s, 1H), 7.46 (d,  $J = 8.0$  Hz, 1H), 7.34 (d,  $J = 8.0$  Hz, 1H), 7.17 – 7.12 (m, 1H), 7.10 – 7.05 (m, 1H), 4.50 (t,  $J = 4.4$  Hz, 1H), 4.33 (d,  $J = 9.2$  Hz, 1H), 4.10 – 4.02 (m, 1H), 3.97 (dd,  $J = 8.8, 4.4$  Hz, 1H), 3.86 (dd,  $J = 5.2, 2.8$  Hz, 1H), 3.60 (s, 3H), 3.24 (t,  $J = 10.8$  Hz, 1H), 3.17 – 3.14 (m, 2H), 2.97 (dd,  $J = 10.8, 6.0$  Hz, 1H), 2.24 (d,  $J = 10.4$  Hz, 1H), 1.72 (s, 3H), 1.47 (s, 3H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm** 173.0, 136.4, 133.5, 126.6, 121.7, 119.3, 118.0, 111.0, 110.3, 104.9, 78.6, 75.9, 66.7, 61.0, 54.7, 54.7, 51.5, 28.5, 26.6, 25.0; **HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_5\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 395.1583 found 395.1602.**



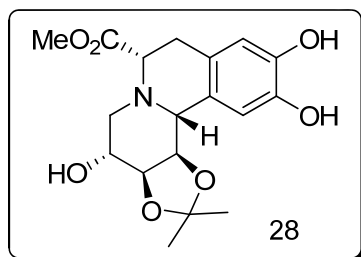
**Compound 24:** Colorless solid, m.p. 89 – 91 °C,  $[\alpha]_D^{25} -23.7$  ( $c$  1.0,  $\text{CHCl}_3$ ); **IR (Neat)  $\text{cm}^{-1}$ :** 3402, 2931, 1724, 1608, 1524, 1450, 1365, 1215, 1034, 879, 760, 648, 513;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm** 7.19 (s, 1H), 6.48 (s, 1H), 4.39 (t,  $J = 4.4$  Hz, 1H), 4.04 (d,  $J = 8.8$  Hz, 1H), 3.99 (dd,  $J = 9.2, 4.4$  Hz, 1H), 3.87 (dd,  $J = 8.0, 4.4$  Hz, 1H), 3.70 (d,  $J = 4.8$  Hz, 1H), 3.58 (s, 3H), 3.17 (t,  $J = 10.8$  Hz, 1H), 3.08 (dd,  $J = 15.6, 6.0$  Hz, 1H), 2.90 (dd,  $J = 11.2, 6.0$  Hz, 1H), 2.84 (d,  $J = 15.6$  Hz, 1H), 1.62 (s, 3H), 1.38 (s, 3H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm** 173.5, 143.0, 142.4, 128.1, 123.7, 114.9, 113.9, 109.5, 80.2, 76.3, 66.8, 60.8, 57.9, 55.4, 51.7, 32.5, 28.3, 26.5; **HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{23}\text{NO}_7\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 388.1372 found 388.1361.**



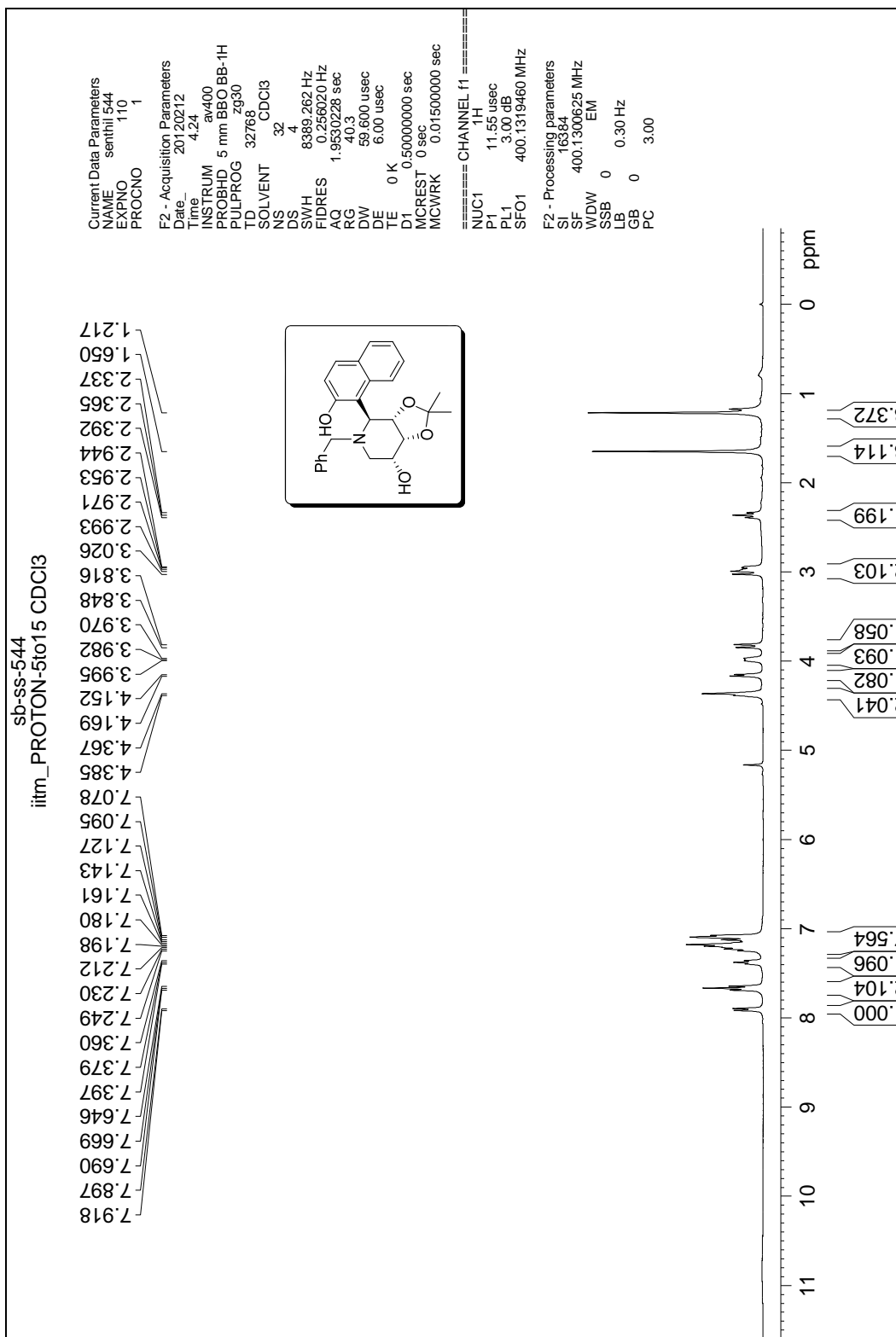
**Compound 26:** Colorless solid, m.p. 154 – 156 °C,  $[\alpha]_D^{24} -20.5$  (*c* 1.0, CHCl<sub>3</sub>); **IR (Neat) cm<sup>-1</sup>:** 3167, 2943, 1732, 1601, 1470, 1373, 1215, 1034, 941, 729, 509; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ ppm 7.86 (s, 1H), 6.74 (s, 1H), 5.15 (d, *J* = 7.6 Hz, 1H), 4.50 (t, *J* = 4.8 Hz, 1H), 4.10 – 4.04 (m, 1H), 4.01 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.75 (dd, *J* = 6.0, 1.6 Hz, 1H), 3.63 (s, 3H), 3.22 (d, *J* = 11.2 Hz, 1H), 3.18 (s, 1H), 3.14 (d, *J* = 1.6 Hz, 1H), 3.08 (dd, *J* = 16, 6.0 Hz, 1H), 2.97 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.64 (s, 3H), 1.44 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ ppm 171.6, 134.3, 124.0, 122.9, 110.7, 79.7, 76.2, 70.6, 65.9, 59.1, 53.5, 51.9, 28.2, 26.4, 25.0; **HRMS (ESI) *m/z*** calcd for C<sub>15</sub>H<sub>22</sub>N<sub>3</sub>O<sub>5</sub> (M<sup>+</sup> + H) 324.1559 found 324.1560.



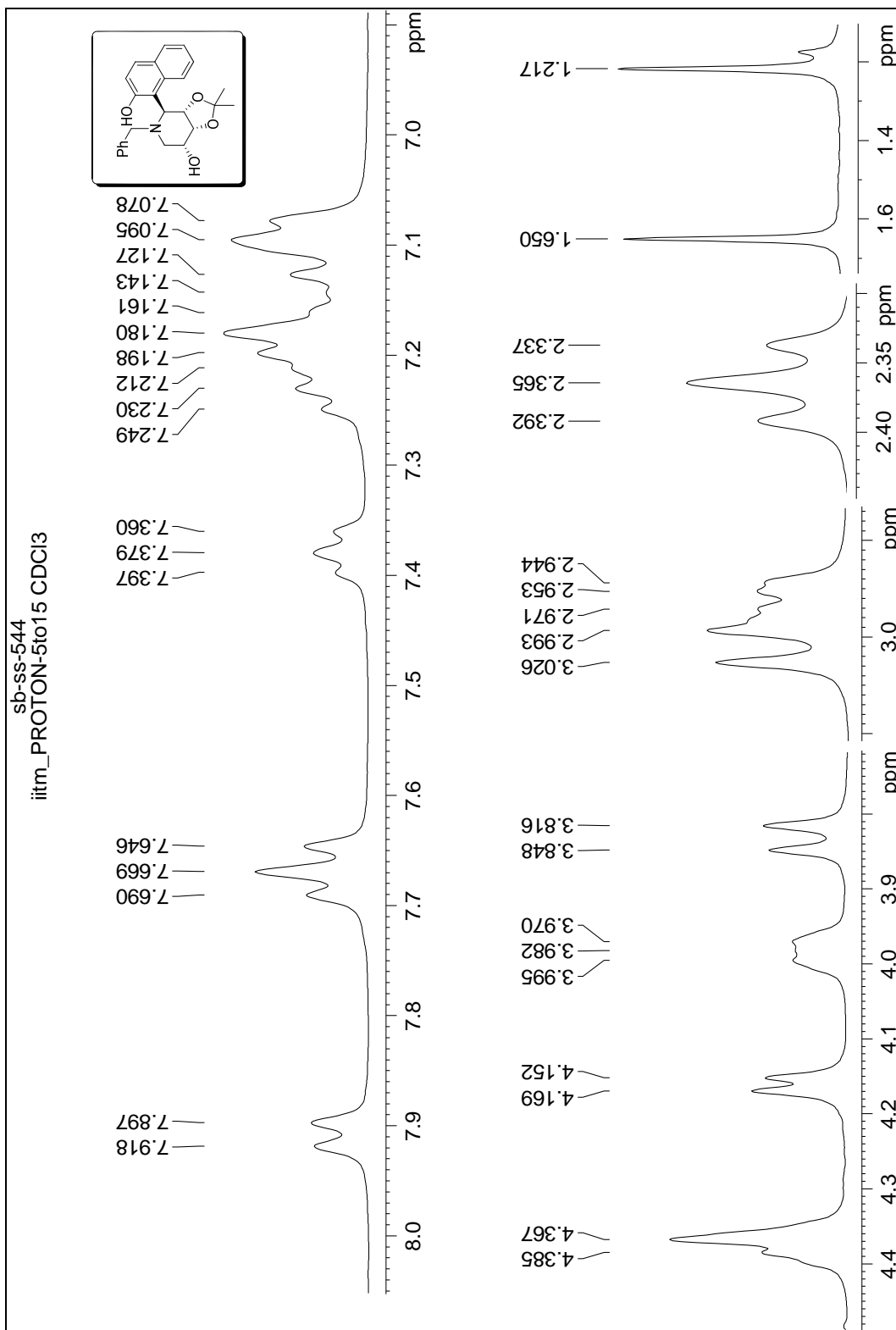
**Compound 27:** Yellow solid, m.p. 163 – 165 °C,  $[\alpha]_D^{21} +50.4$  (*c* 1.0, CHCl<sub>3</sub>); **IR (Neat) cm<sup>-1</sup>:** 3388, 2988, 2940, 2858, 1725, 1457, 1376, 1211, 1171, 1054, 1027, 910, 735; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ ppm 8.02 (bs, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8 Hz, 1H), 7.20 – 7.05 (m, 2H), 4.73 (s, 1H), 4.57 (s, 1H), 4.05 (t, *J* = 5.6 Hz, 1H), 4.0 – 3.95 (m, 1H), 3.93 (d, *J* = 5.6 Hz, 1H), 3.61 (s, 3H), 3.28 (dd, *J* = 15.2, 5.6 Hz, 1H), 3.17 (d, *J* = 15.2 Hz, 1H), 3.08 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.99 (t, *J* = 11.2 Hz, 1H), 1.45 (s, 3H), 1.36 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ ppm 173.6, 136.7, 130.9, 127.3, 121.8, 119.5, 118.3, 111.2, 110.2, 107.4, 80.5, 74.8, 71.0, 61.3, 55.6, 53.5, 51.7, 28.2, 26.5, 24.8; **HRMS (ESI) *m/z*** calcd for C<sub>20</sub>H<sub>25</sub>N<sub>2</sub>O<sub>5</sub> (M<sup>+</sup> + H) 373.1763 found 373.1745.

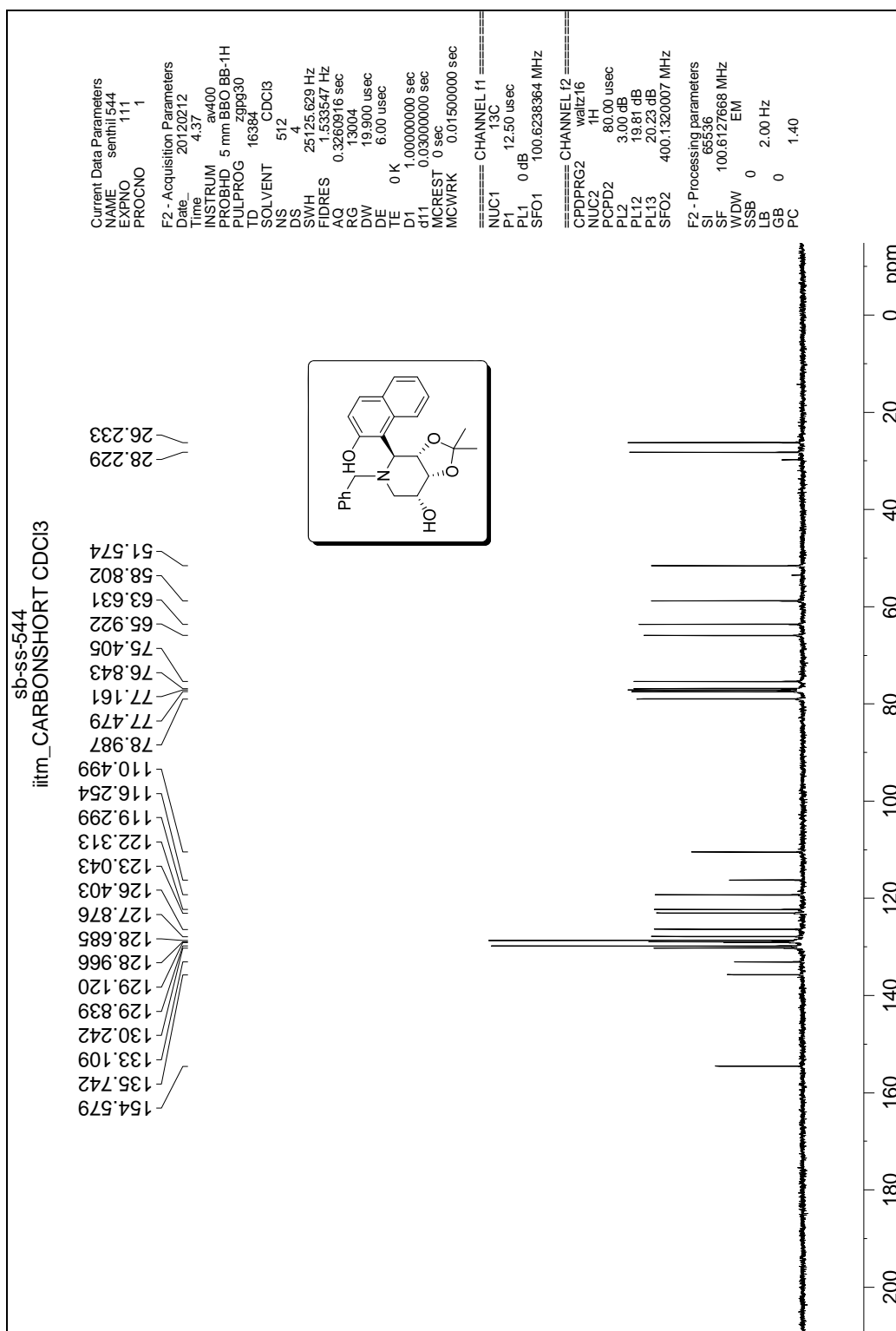


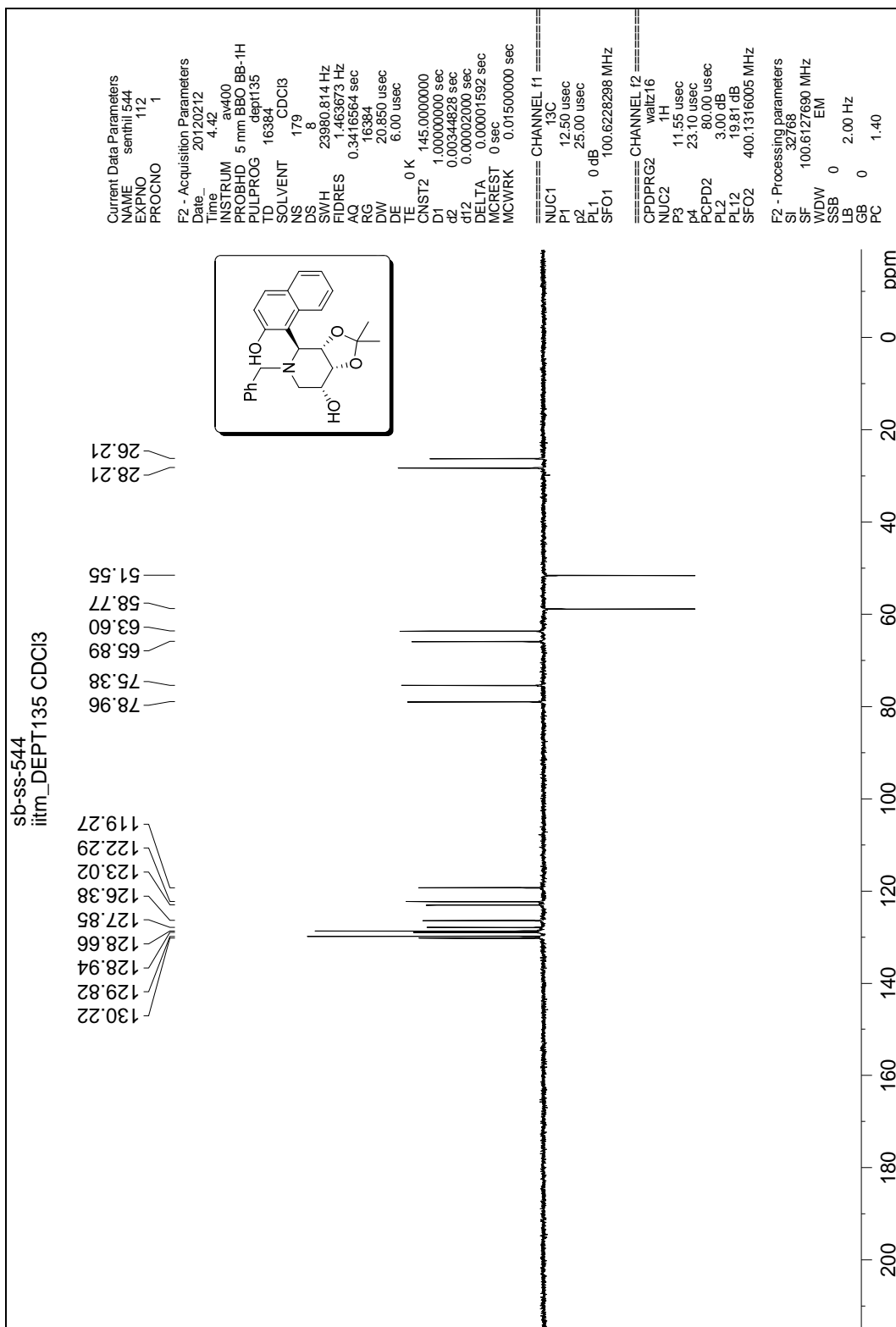
**Compound 28:** gummy solid,  $[\alpha]_D^{25} -84.1$  (*c* 1.0, CHCl<sub>3</sub>); **IR (Neat) cm<sup>-1</sup>:** 3442, 2985, 2936, 2843, 1731, 1614, 1525, 1451, 1374, 1221, 1162, 1058; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  ppm 7.32 (s, 1H), 6.53 (s, 1H), 4.30 – 4.25 (m, 1H), 4.15 (dd, *J* = 8.5, 5.0 Hz, 1H), 4.01 (bs, 1H), 3.76 (s, 3H), 3.51 (d, *J* = 5.0 Hz, 1H), 3.46 (dd, *J* = 10.5, 4.0 Hz, 1H), 2.97 (dd, *J* = 15.5, 4.5 Hz, 1H), 2.91 – 2.82 (m, 2H), 2.74 (dd, *J* = 15.5, 3.5 Hz, 1H), 1.57 (s, 3H), 1.39 (s, 3H); **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  ppm 174.2, 143.2, 142.5, 127.6, 124.6, 114.3, 113.7, 109.3, 78.2, 77.4, 66.0, 63.3, 62.0, 55.5, 52.6, 32.9, 28.5, 26.5; **HRMS (ESI) *m/z*** calcd for C<sub>18</sub>H<sub>23</sub>NO<sub>7</sub>Na (M<sup>+</sup> + Na) 388.1372 found 388.1382.

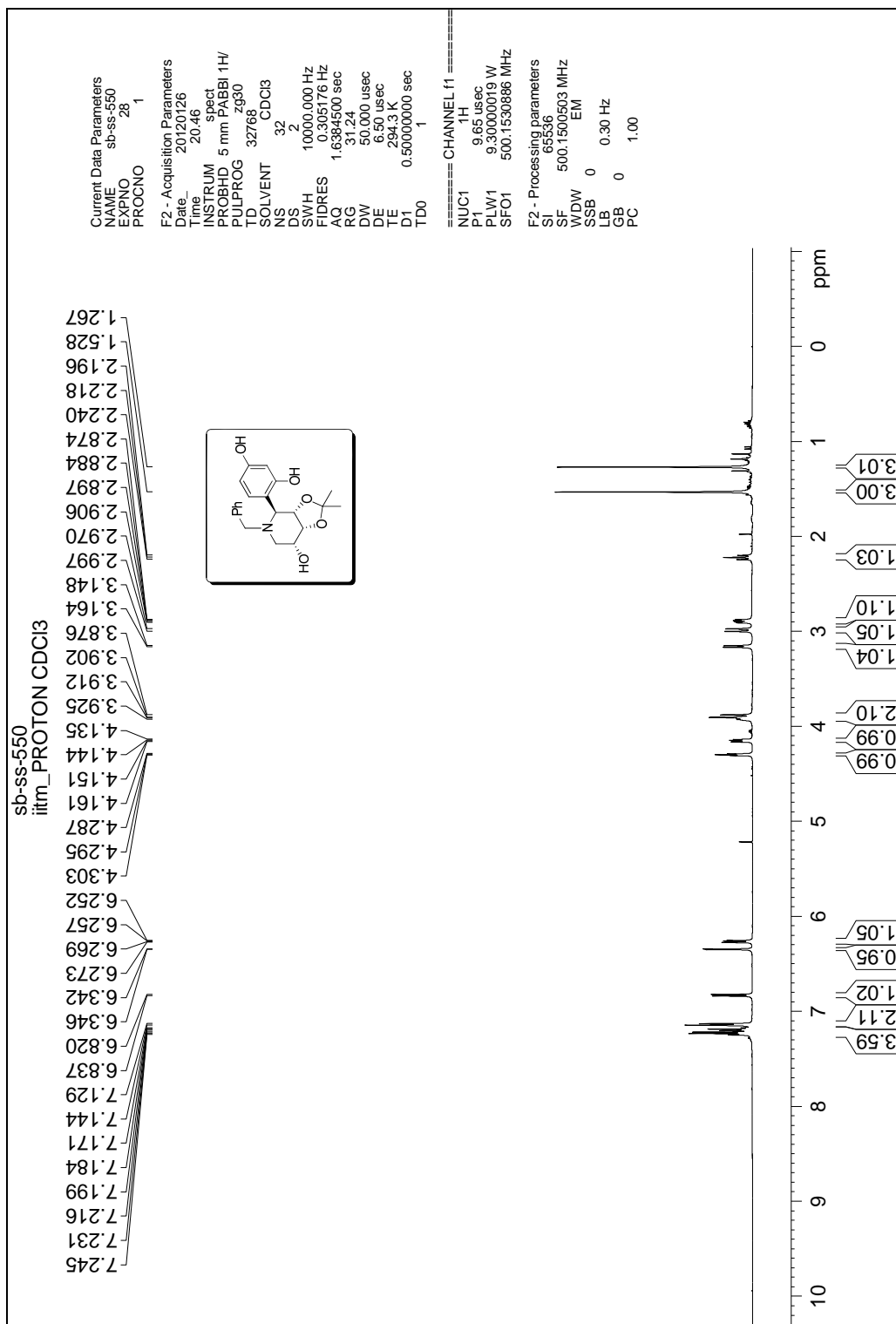


<sup>1</sup>H NMR spectrum of compound 3



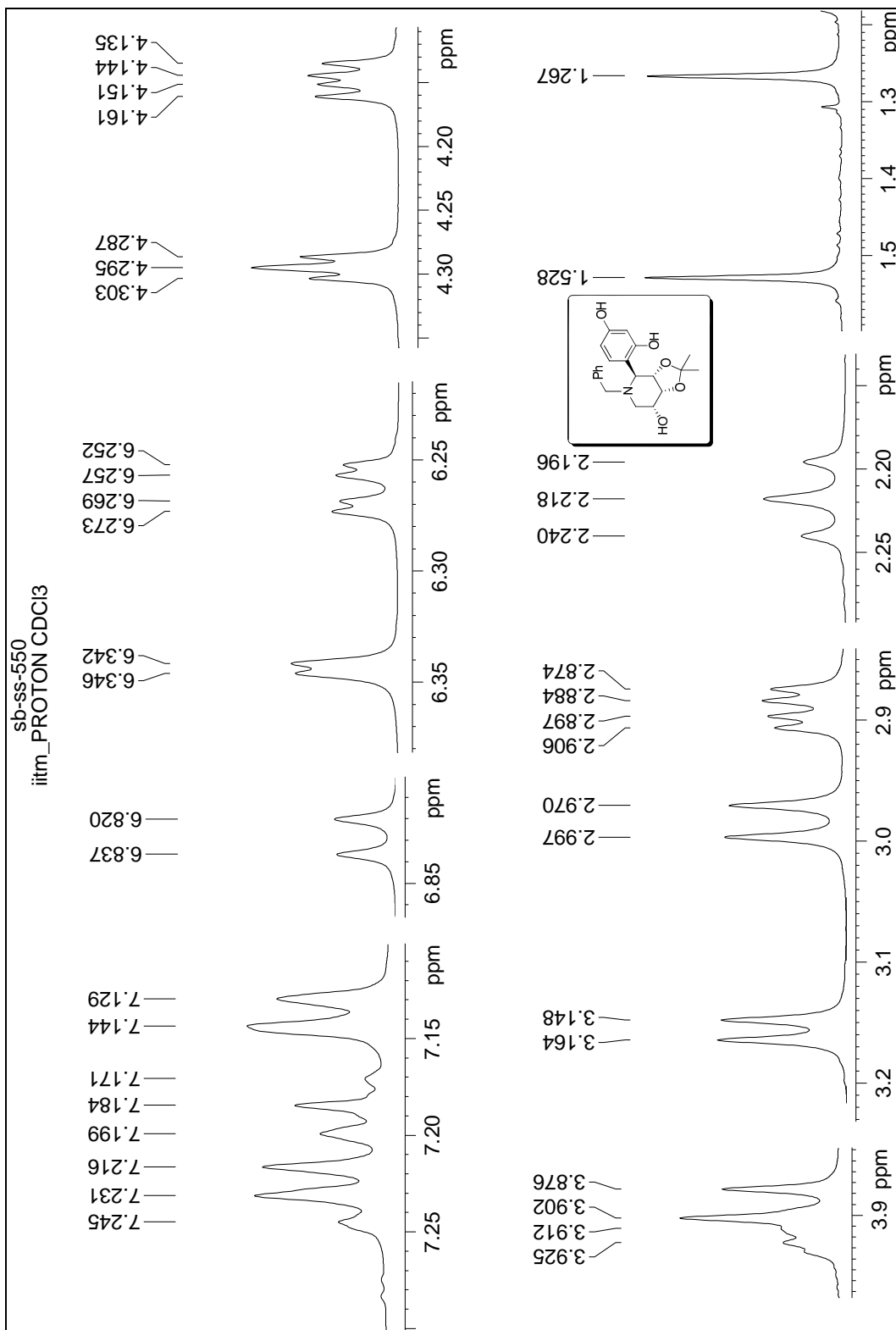


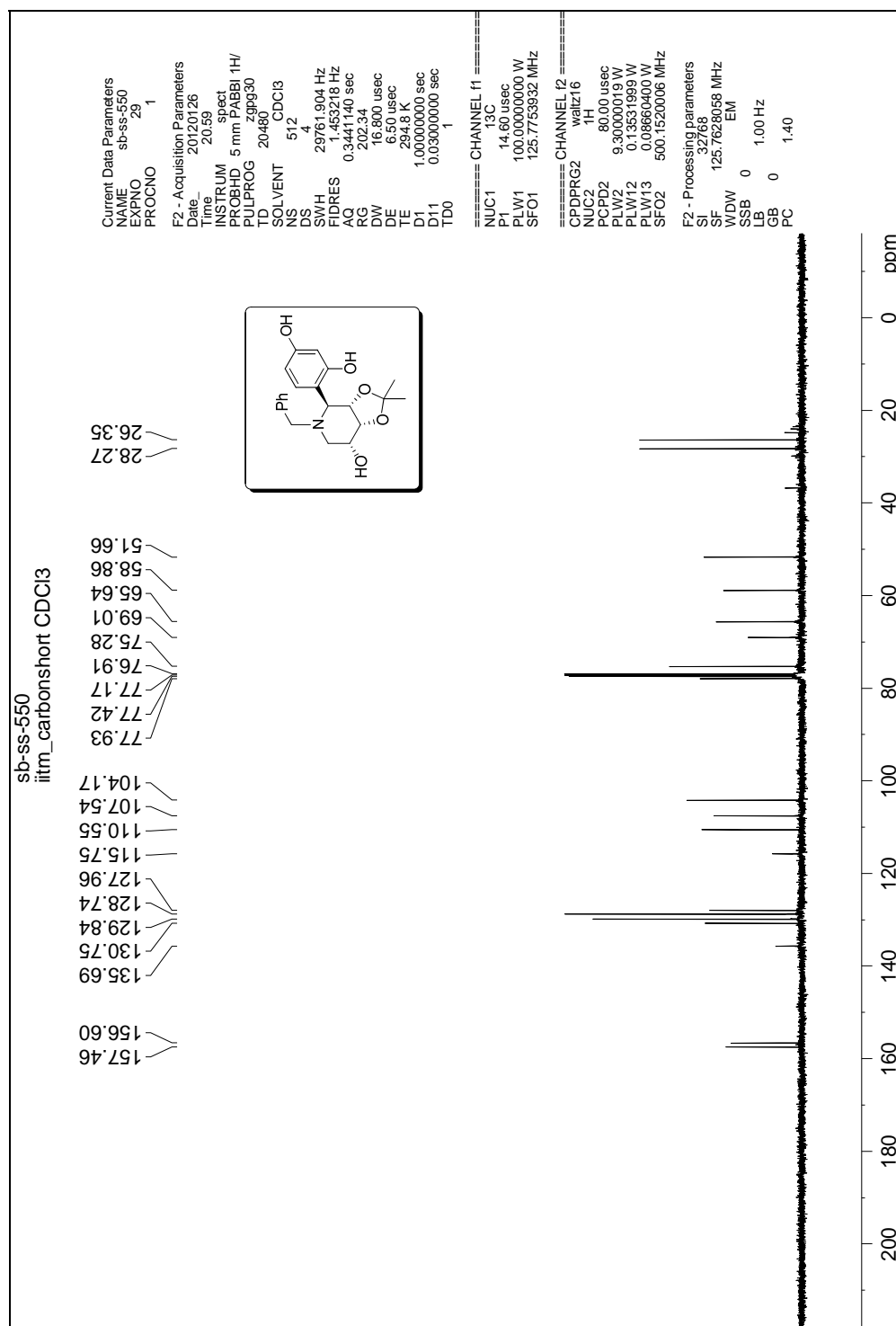




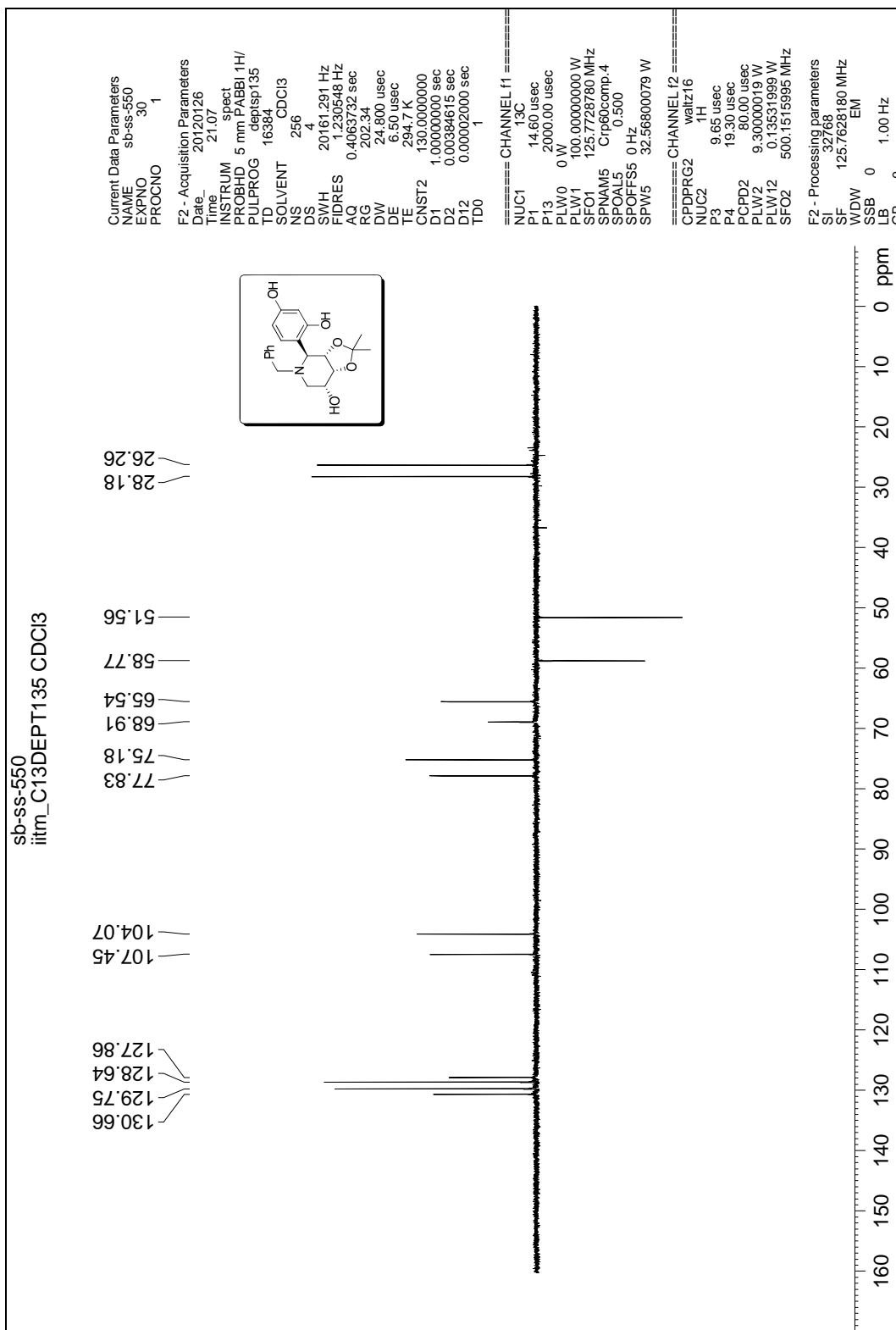
<sup>1</sup>H NMR spectrum of compound 5

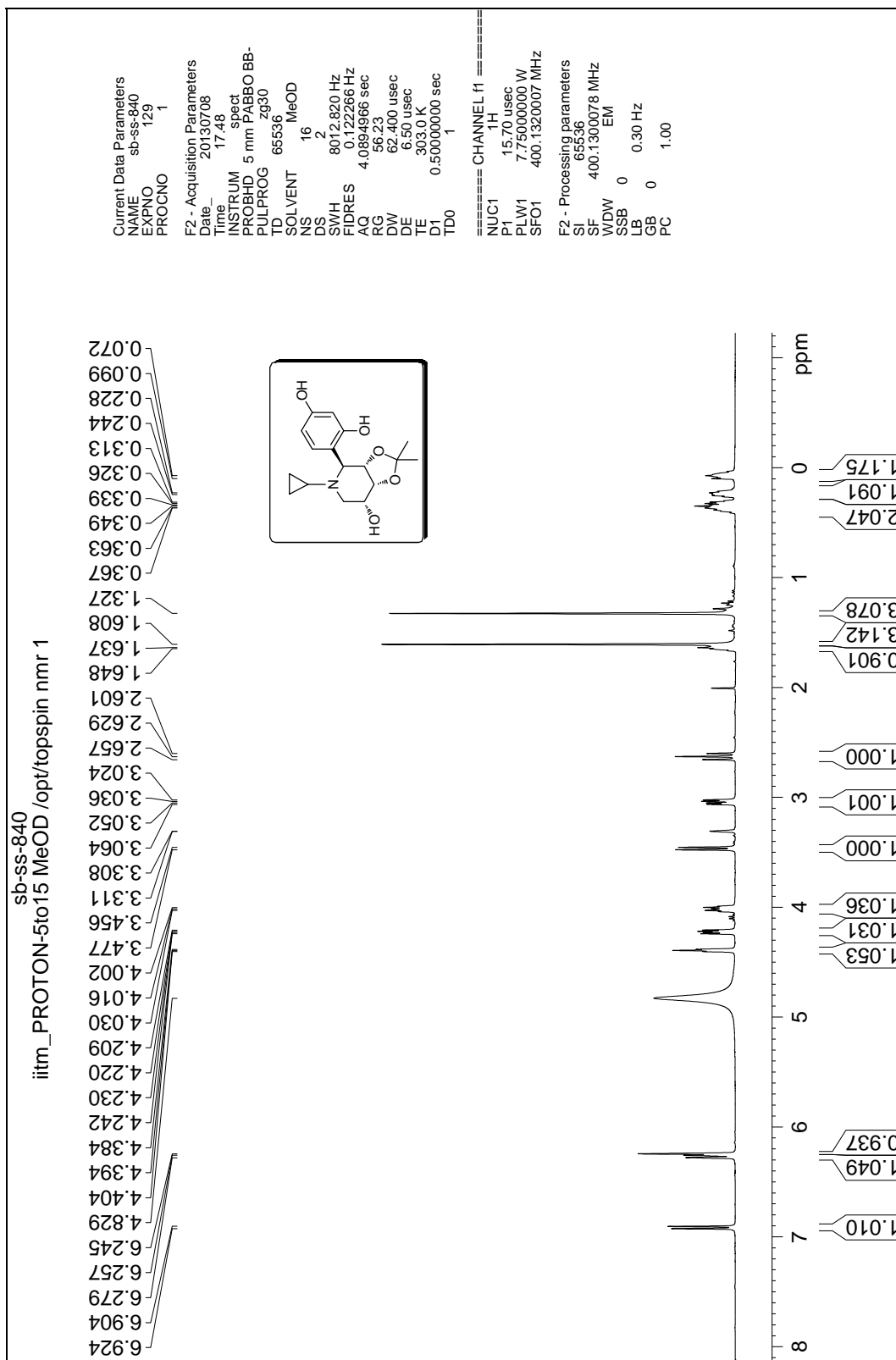




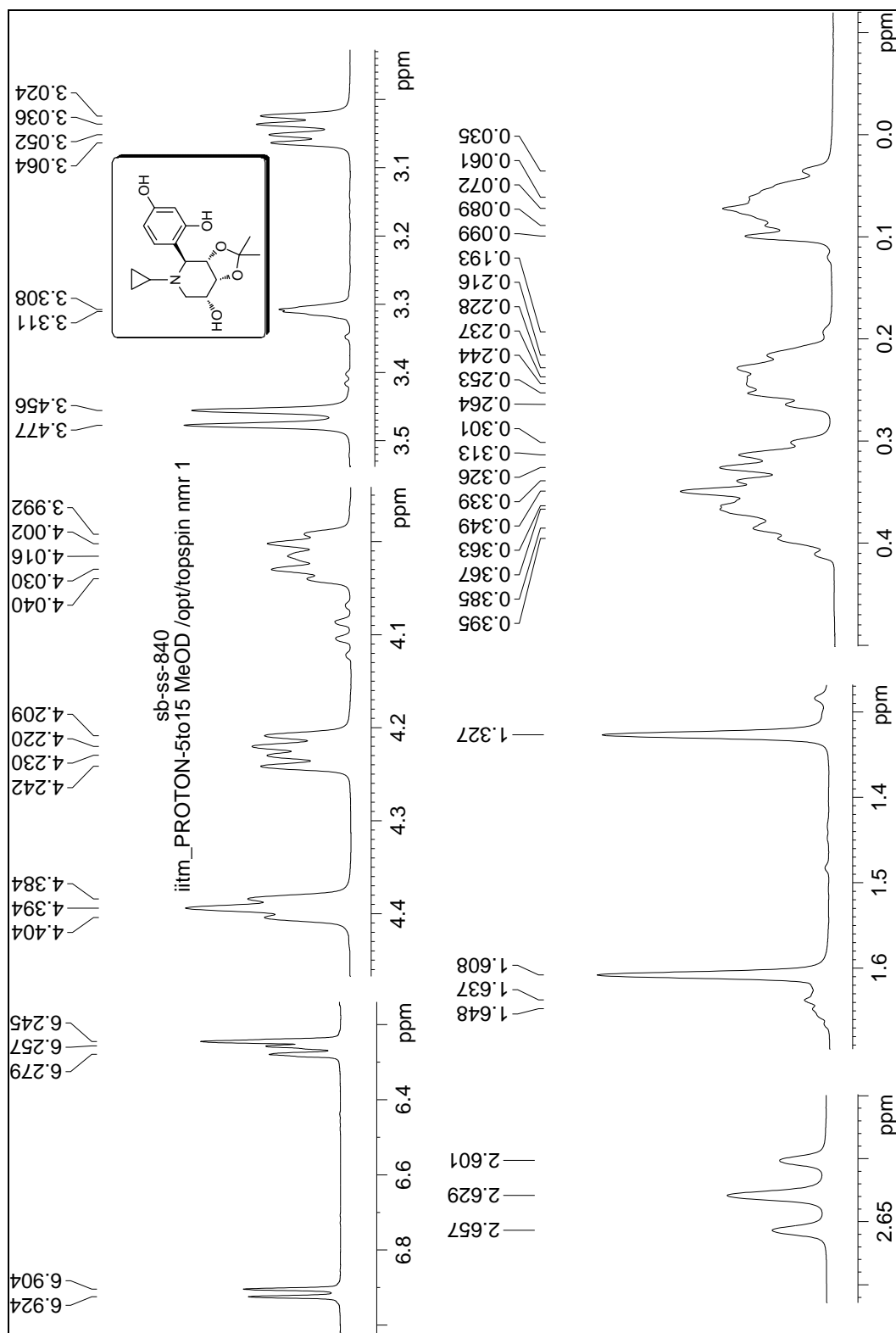


<sup>13</sup>C NMR spectrum of compound 5

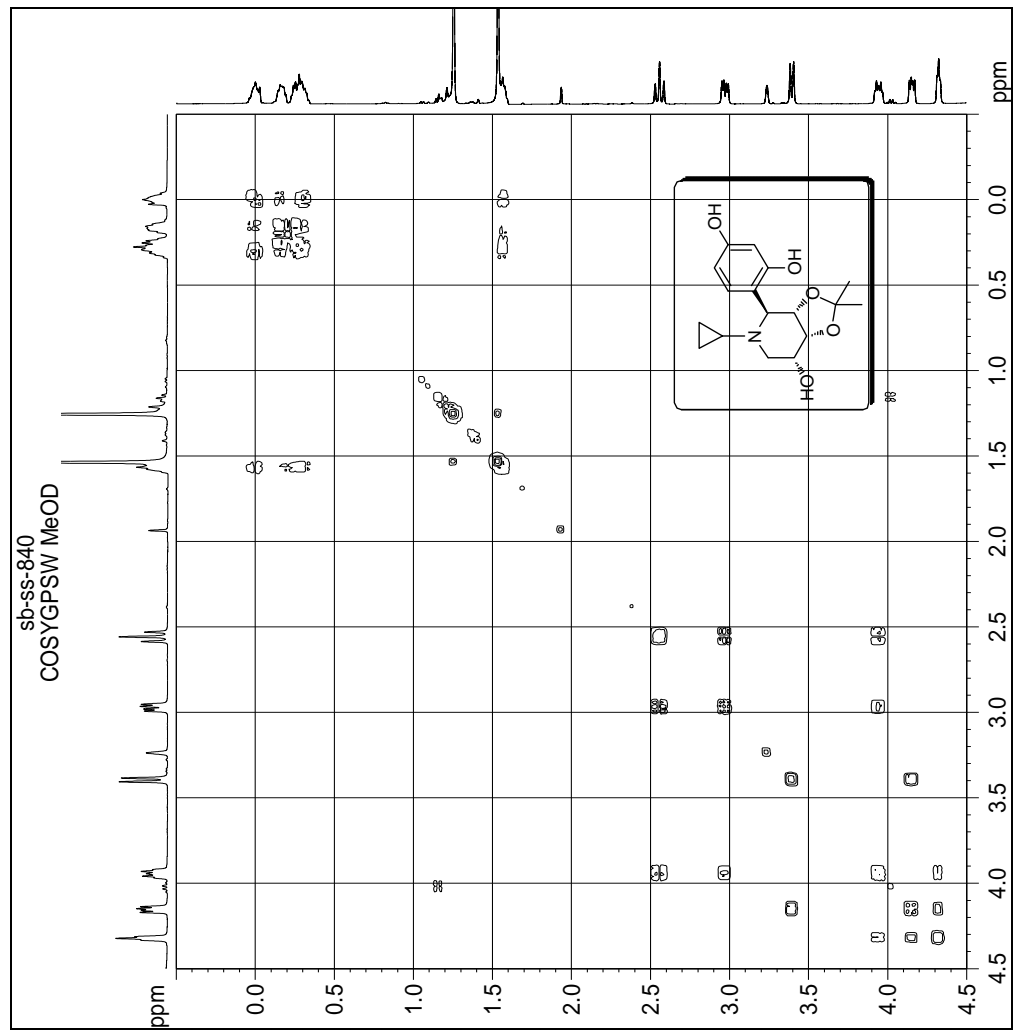




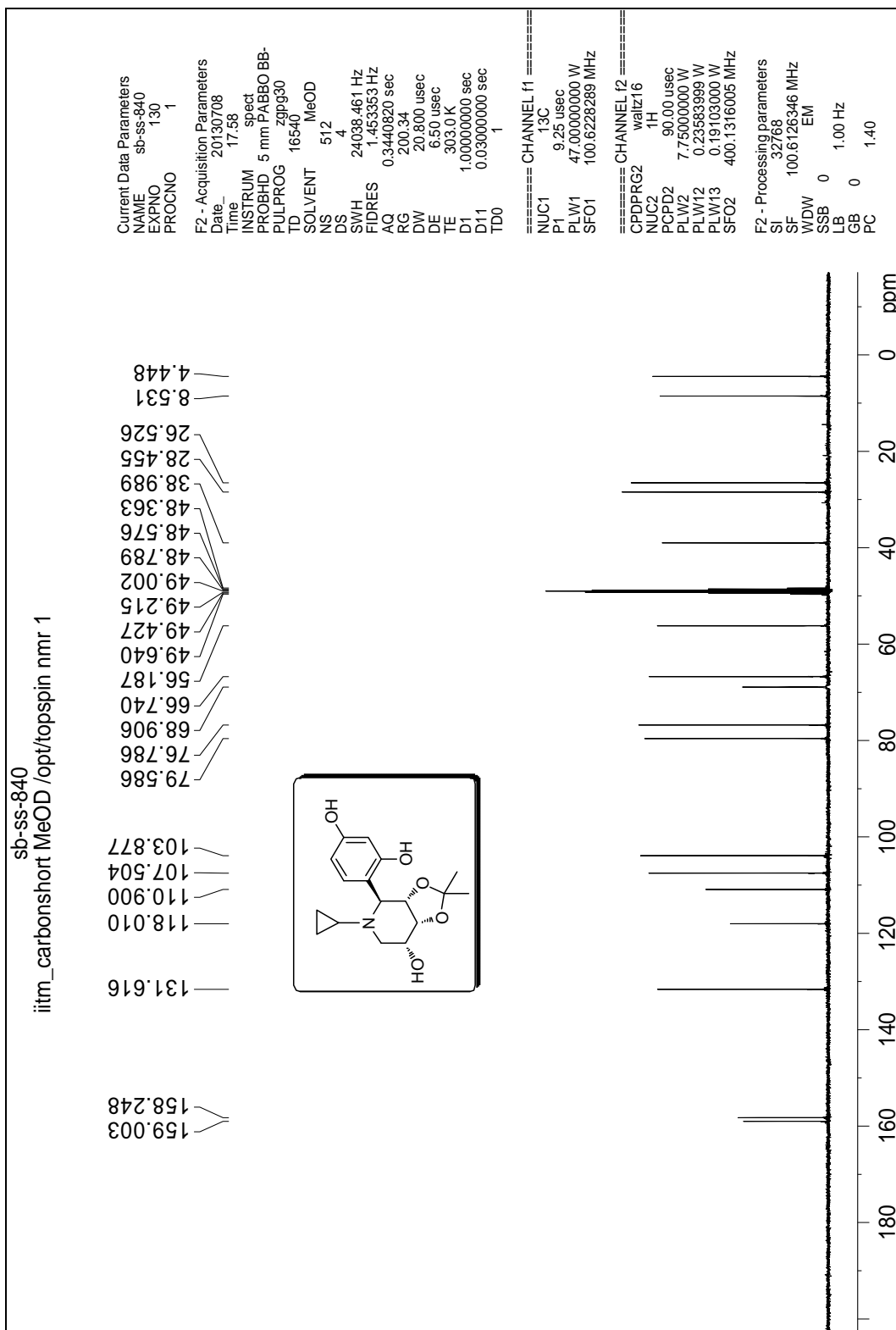
<sup>1</sup>H NMR spectrum of compound 6

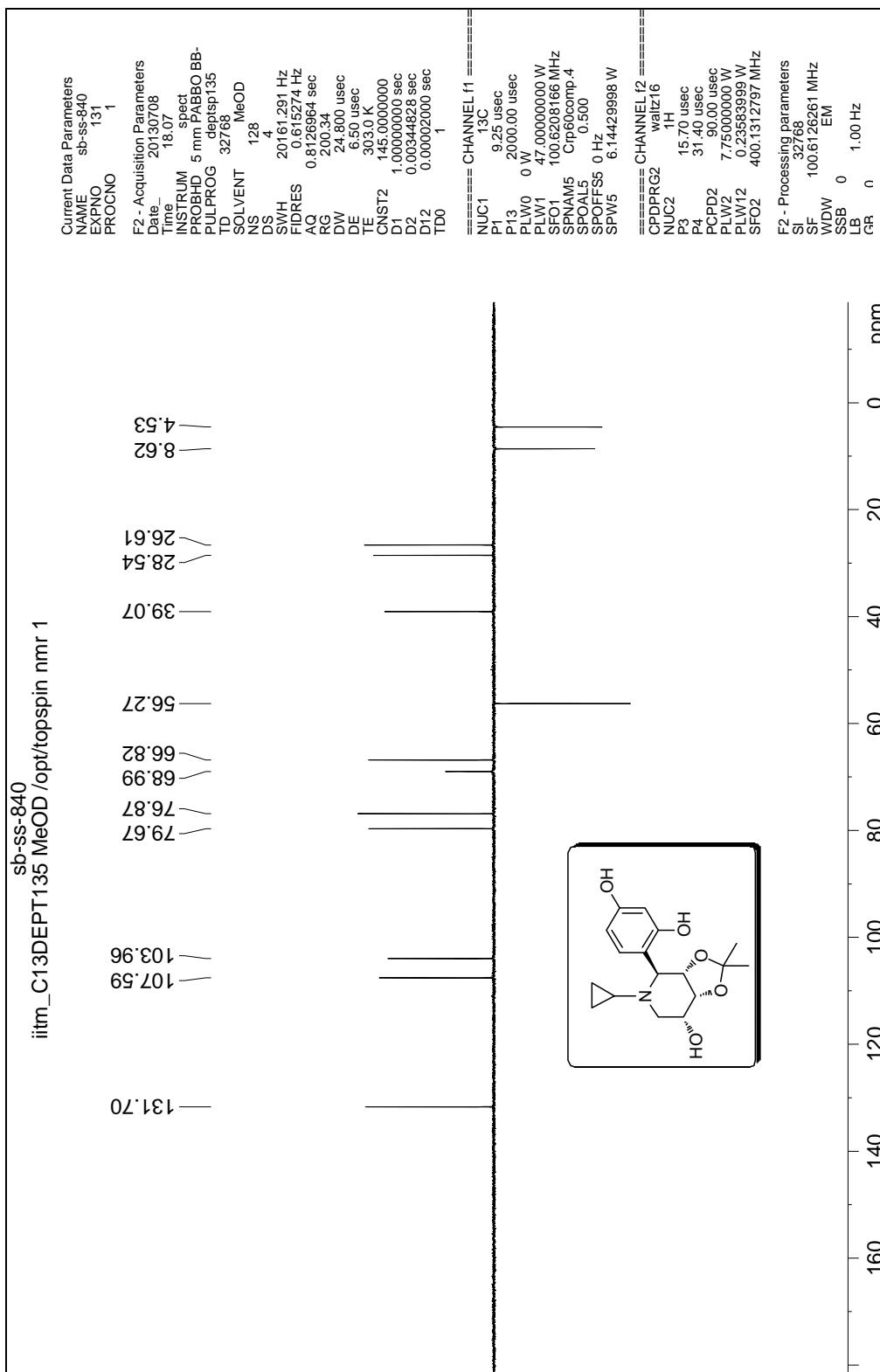


Expanded  $^1\text{H}$  NMR spectrum of compound **6**

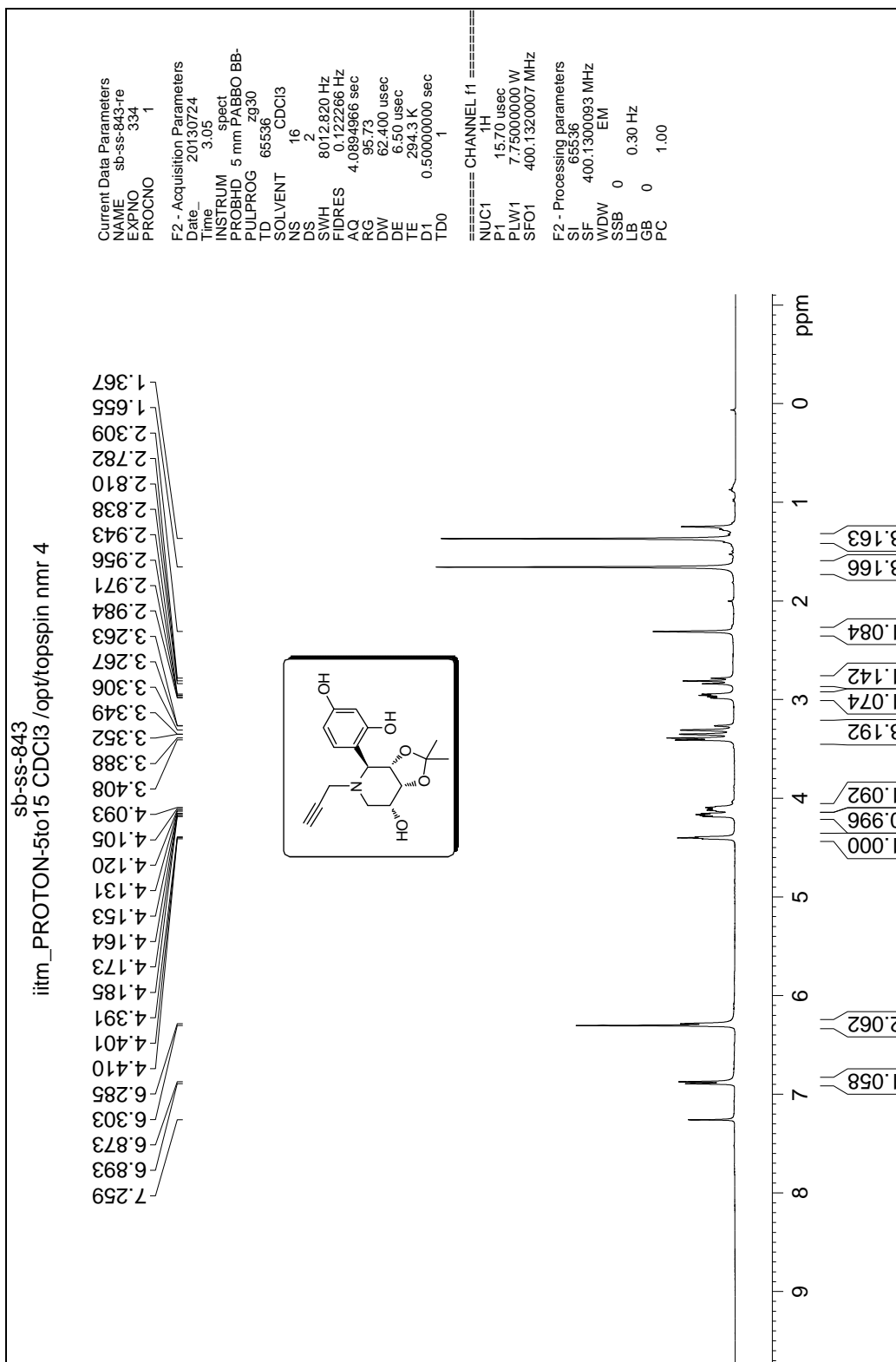


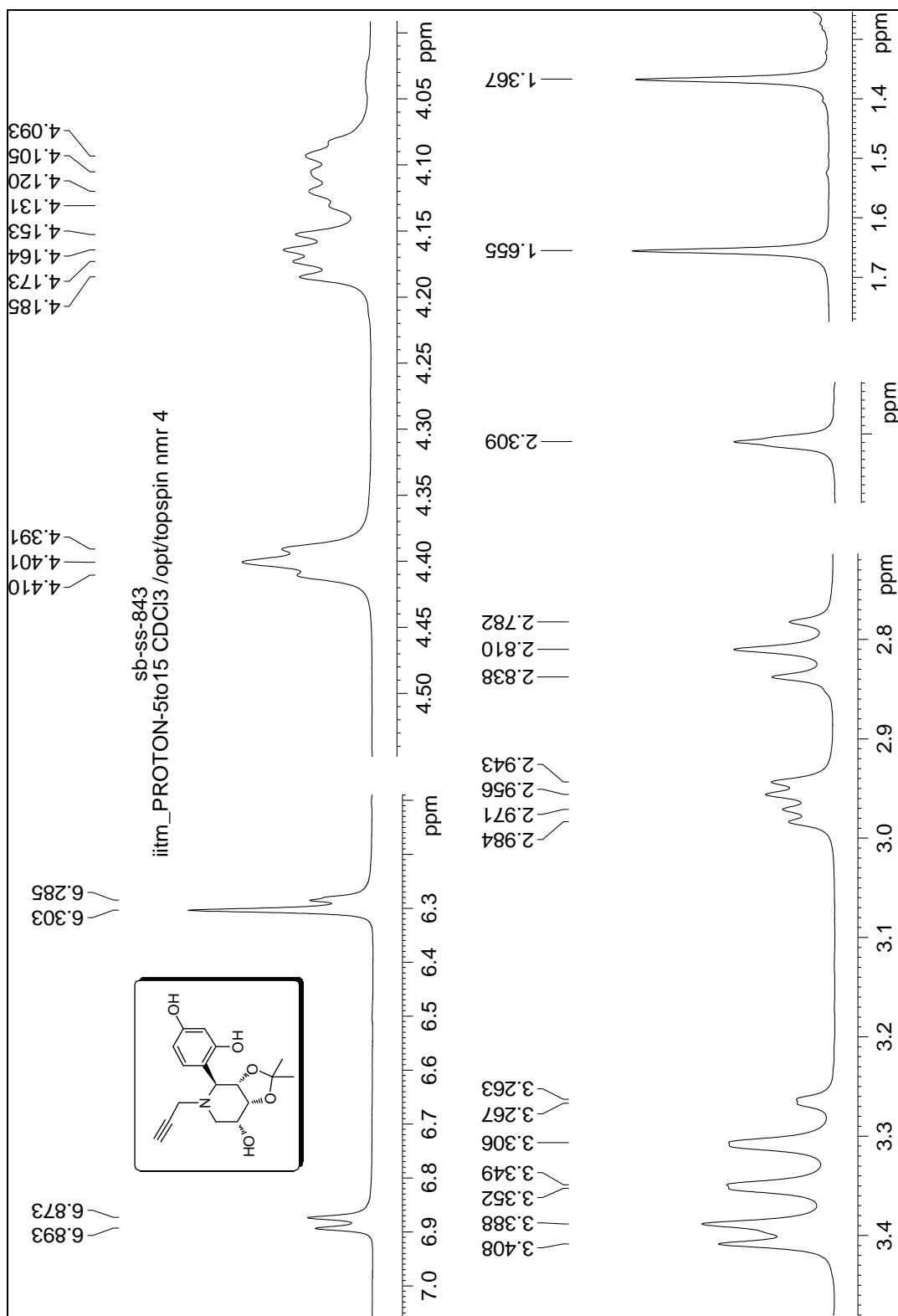
<sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of Compound **6**



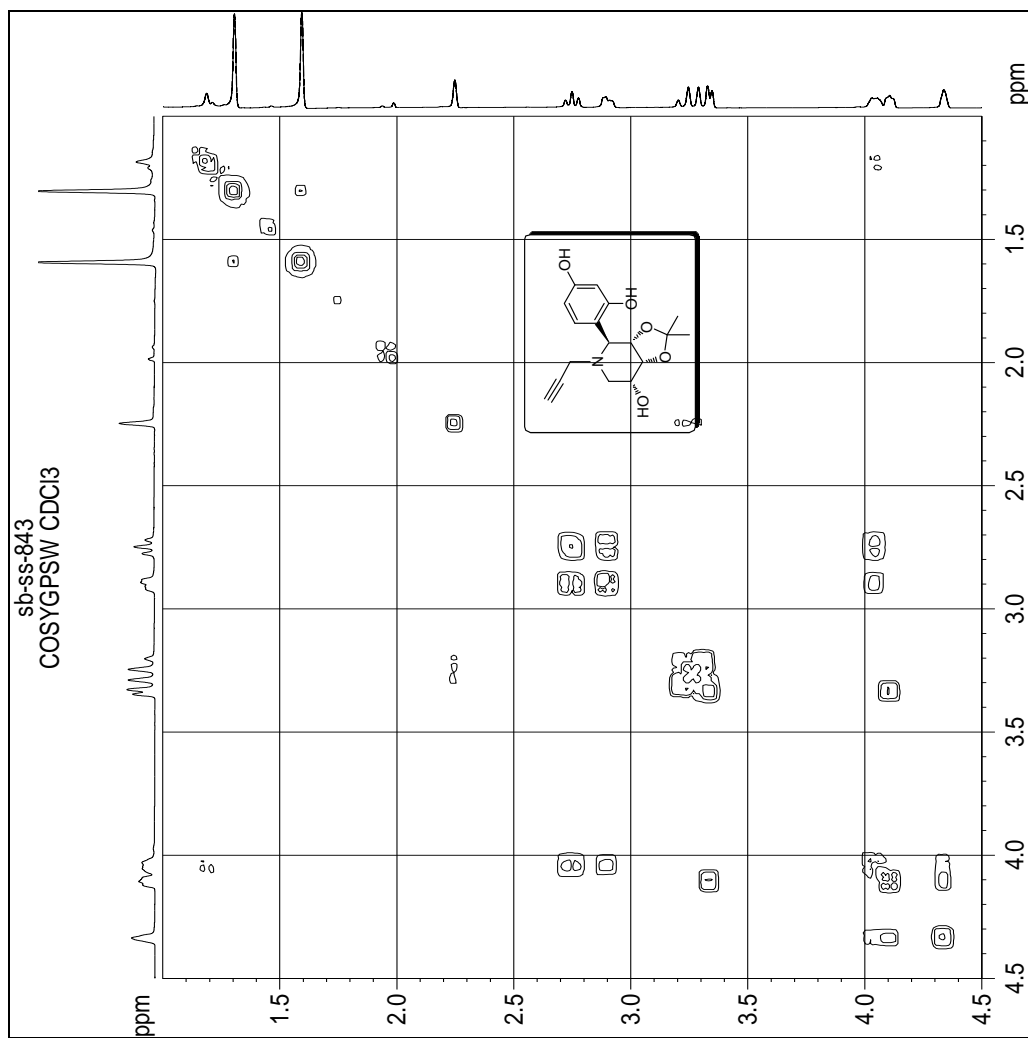




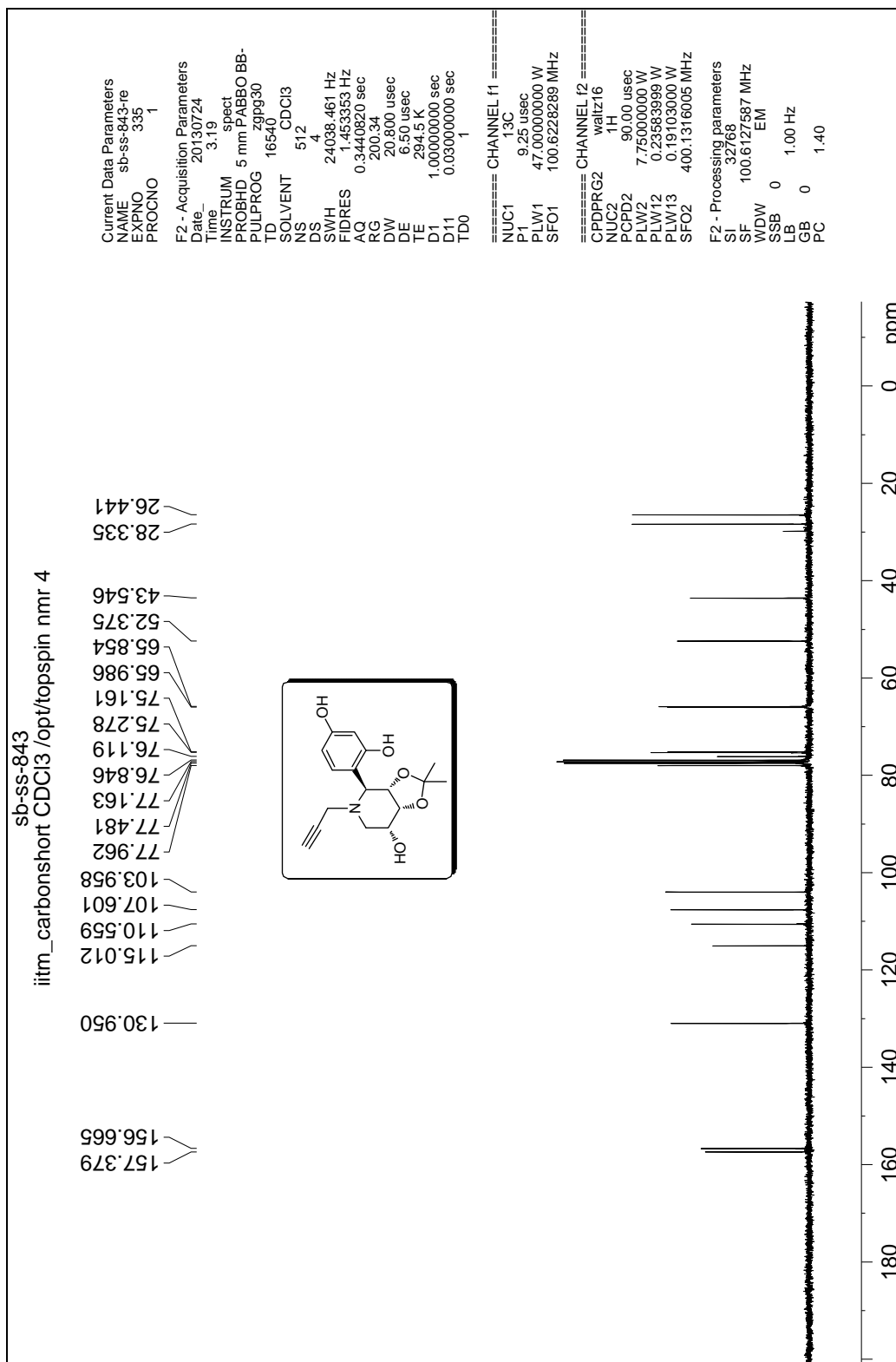


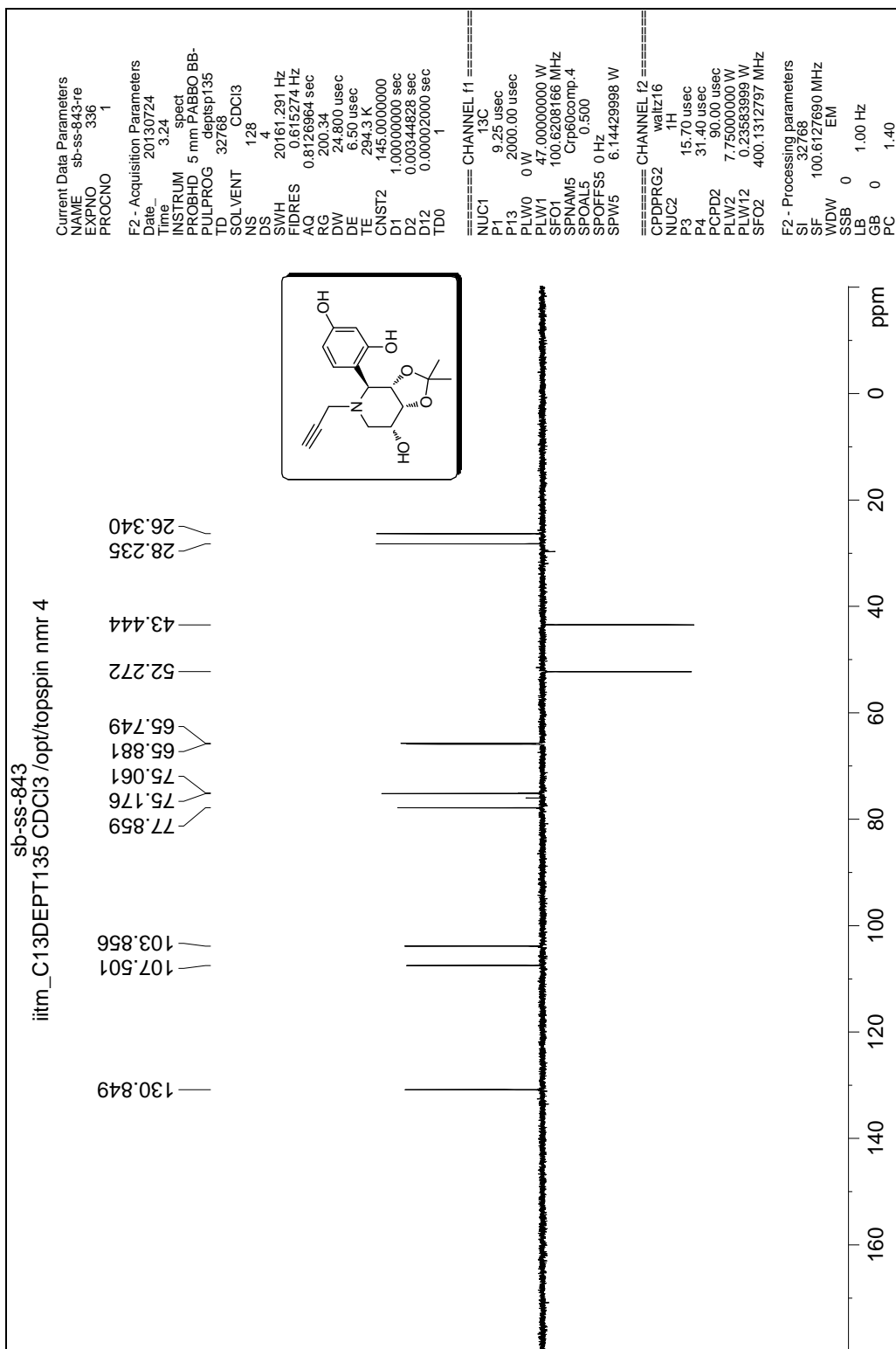


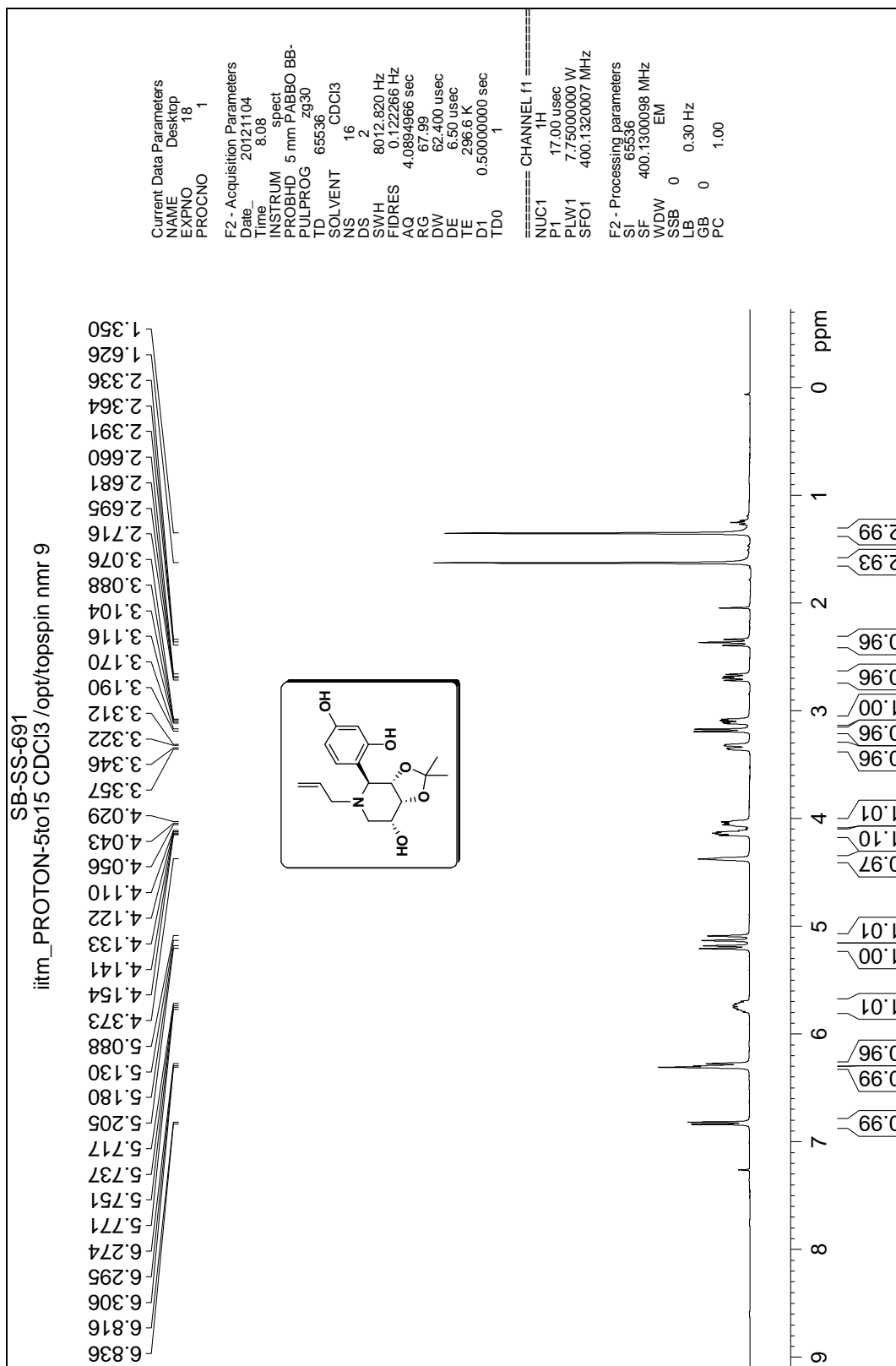
Expanded  $^1\text{H}$  NMR spectrum of compound 7

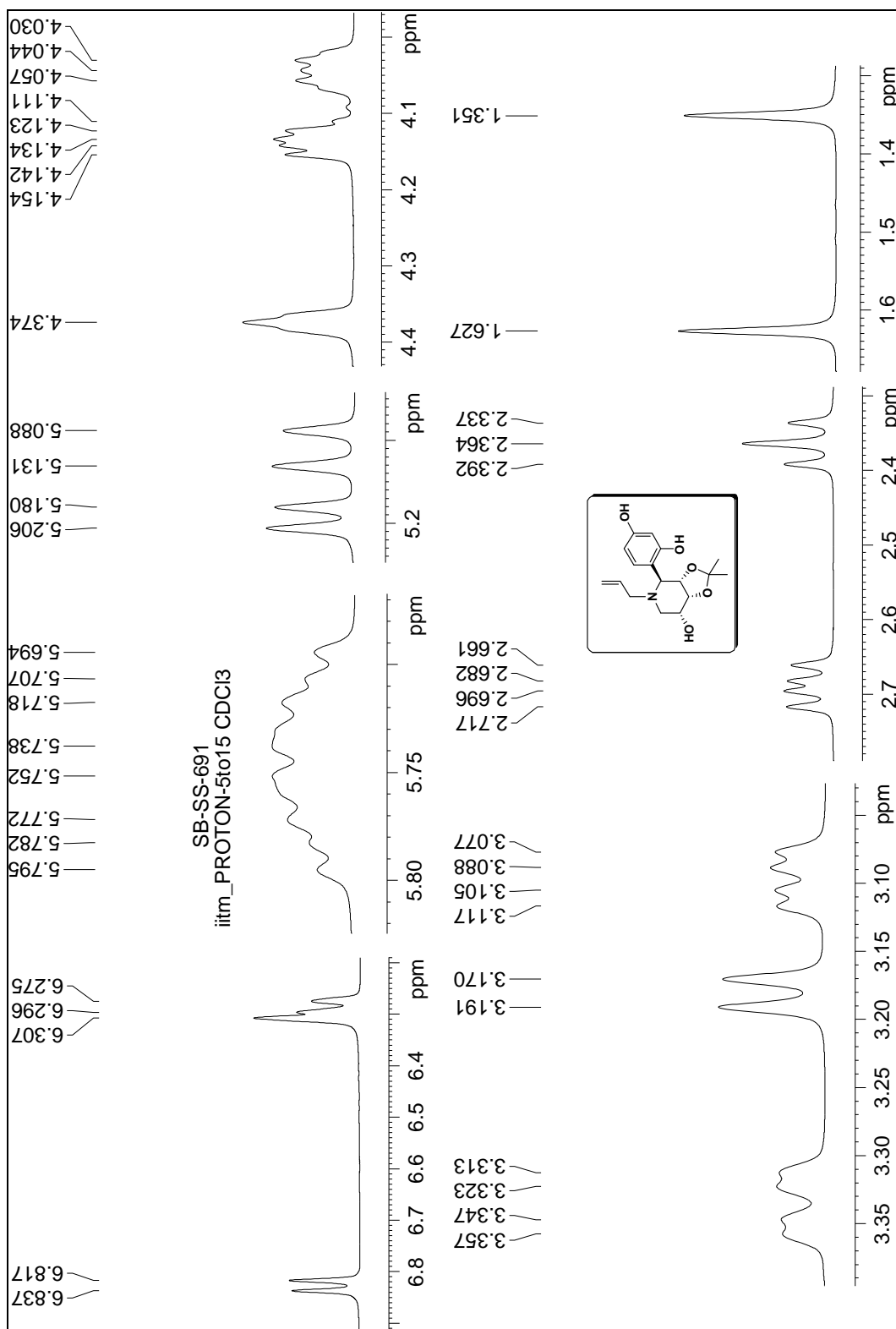


<sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of Compound **7**

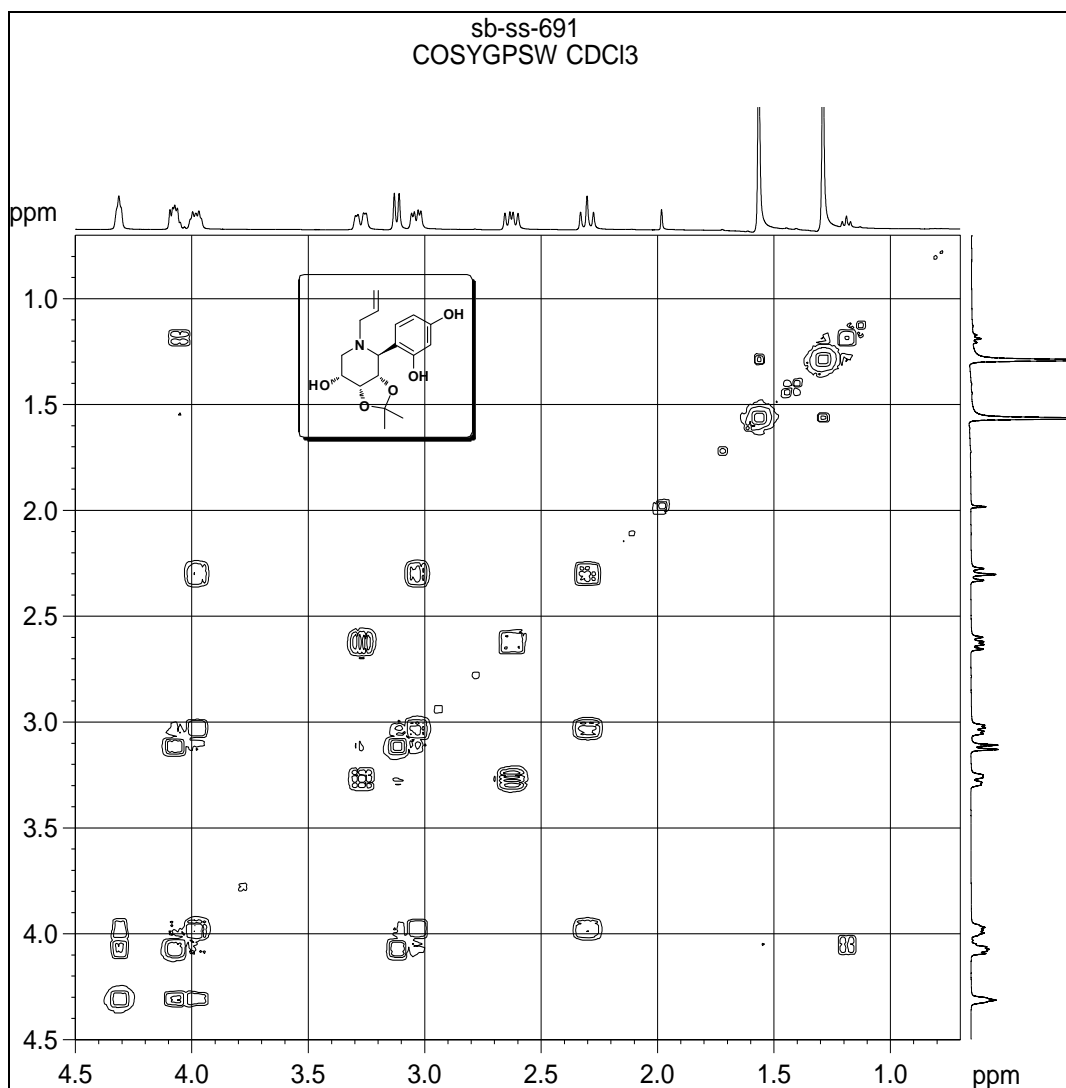






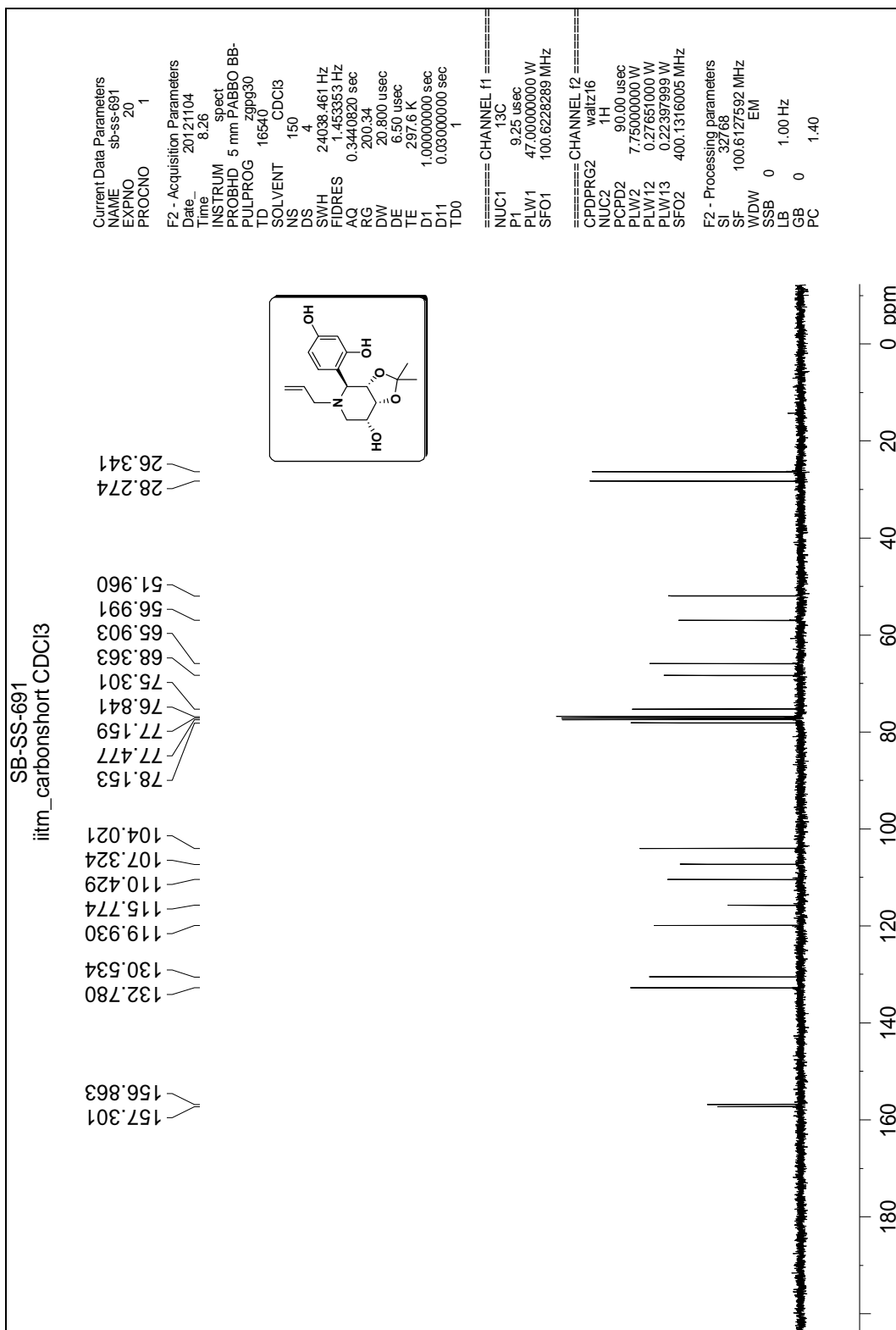


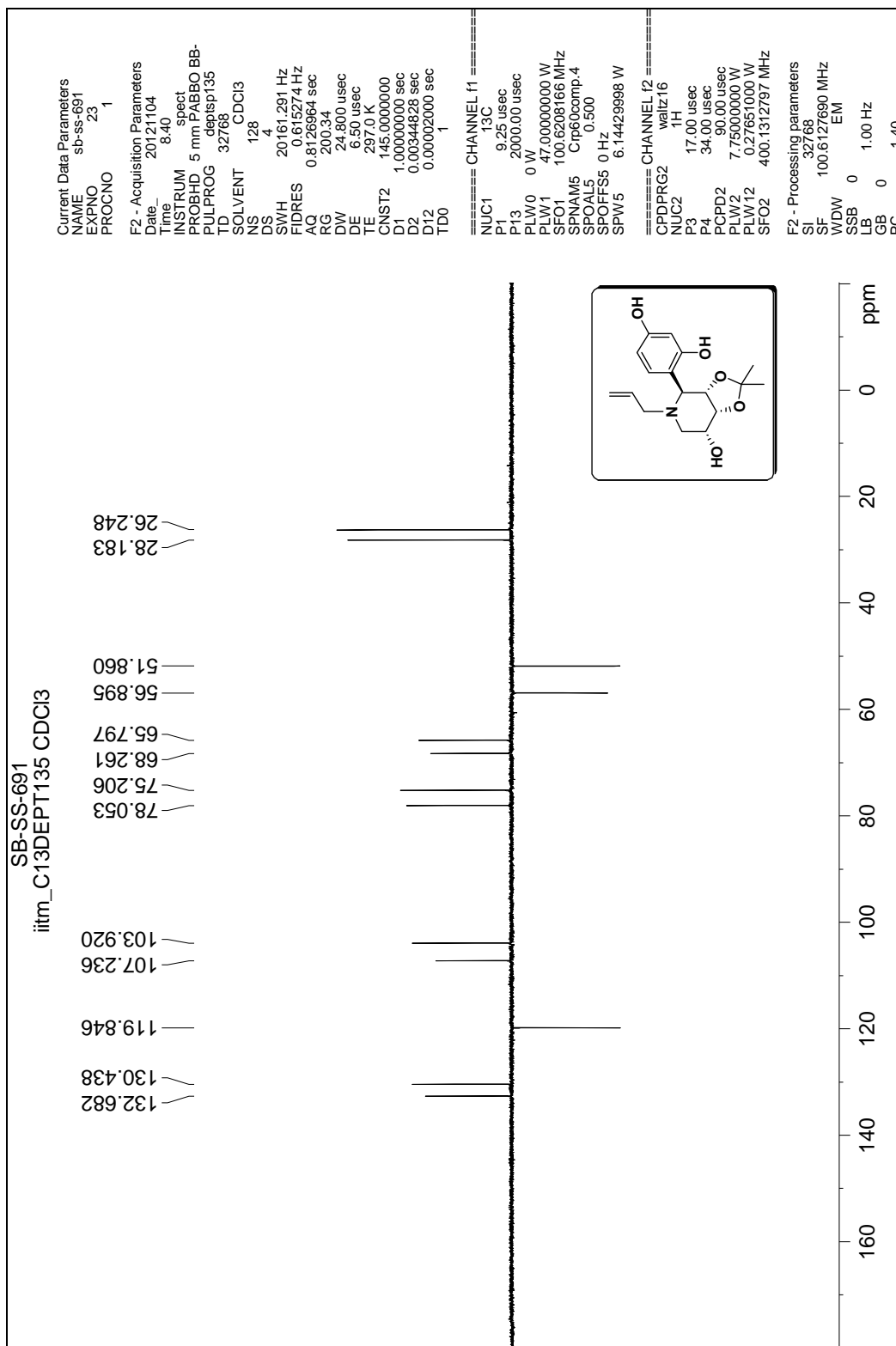
Expanded  $^1\text{H}$  NMR spectrum of compound 8

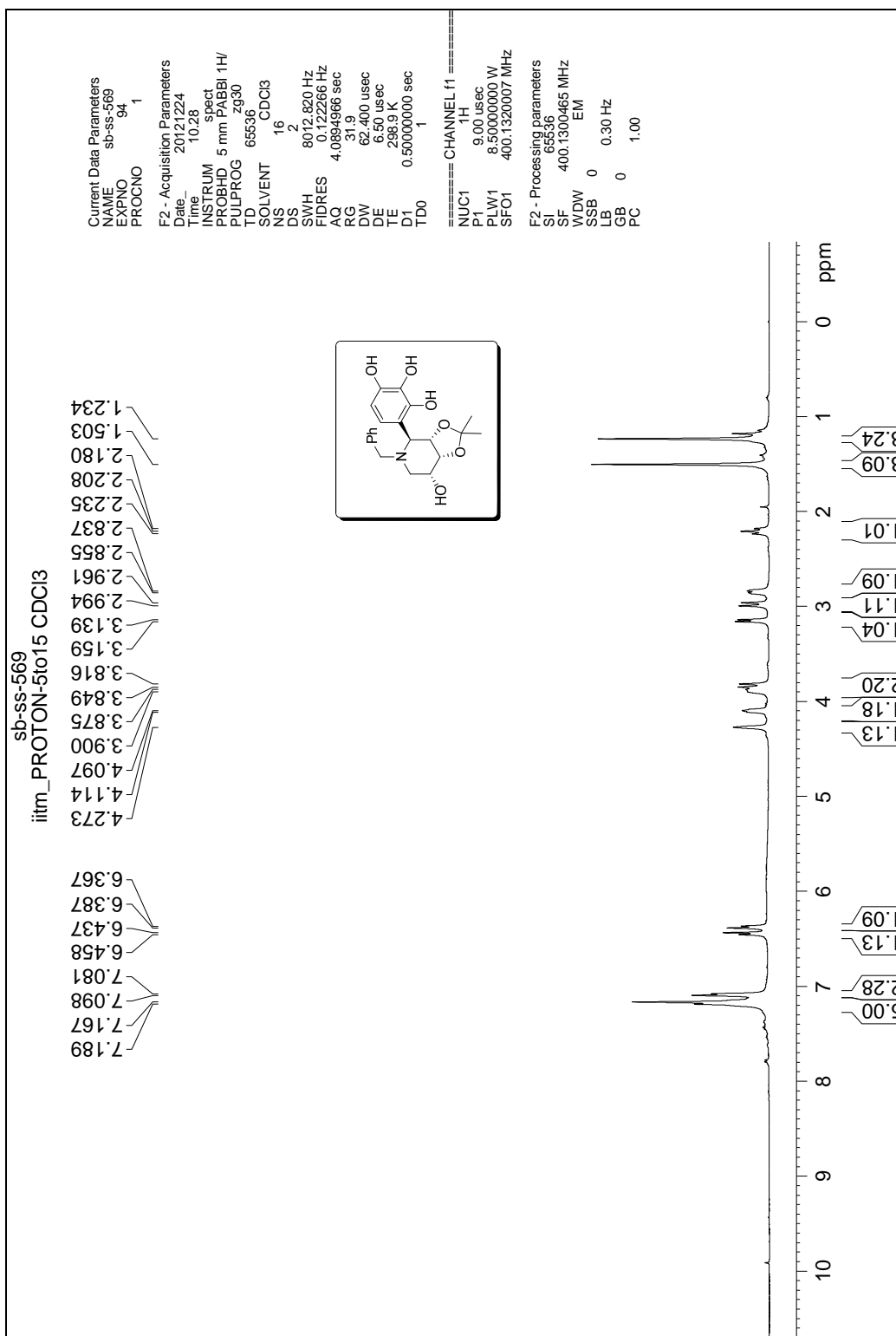


<sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of Compound **8**

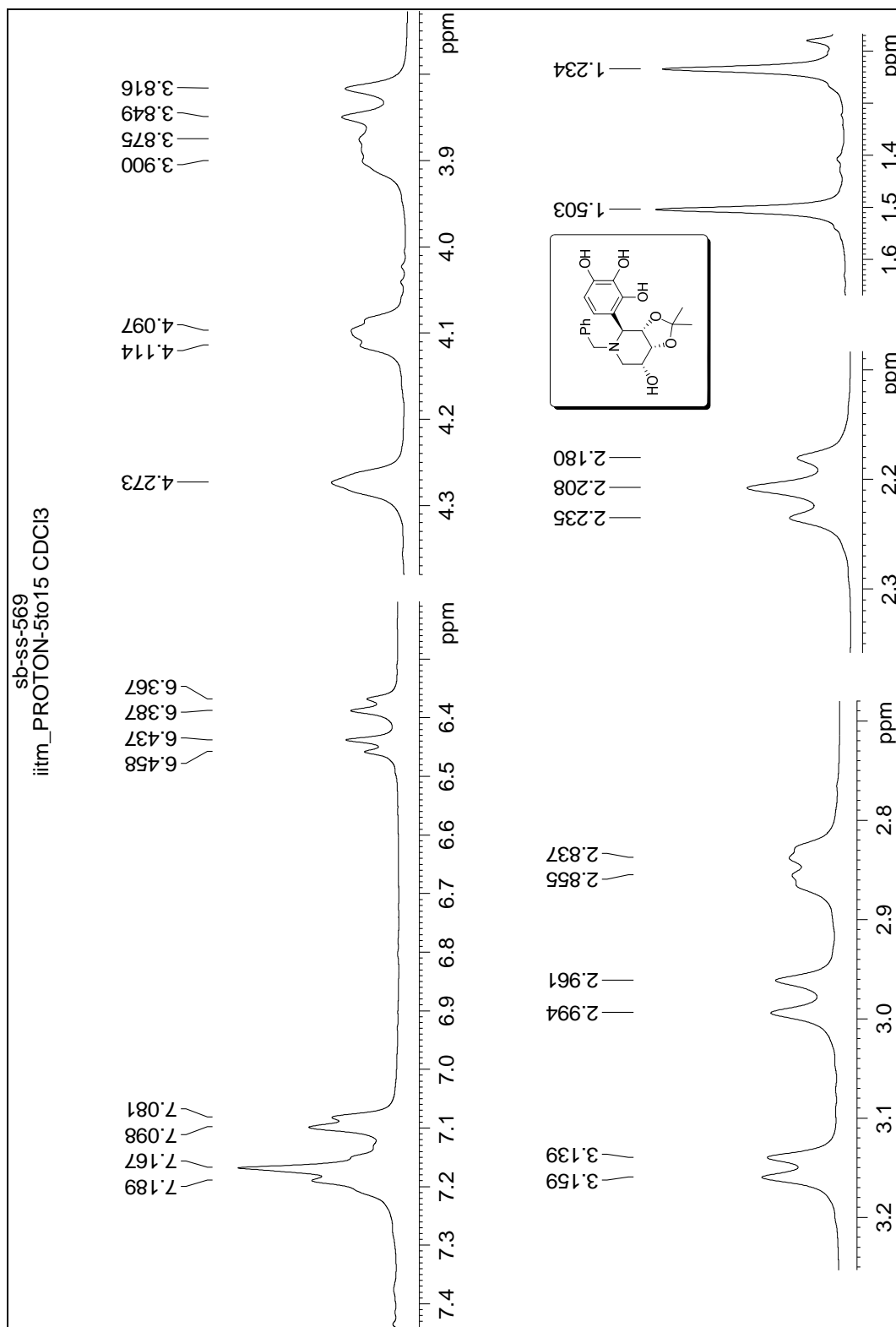


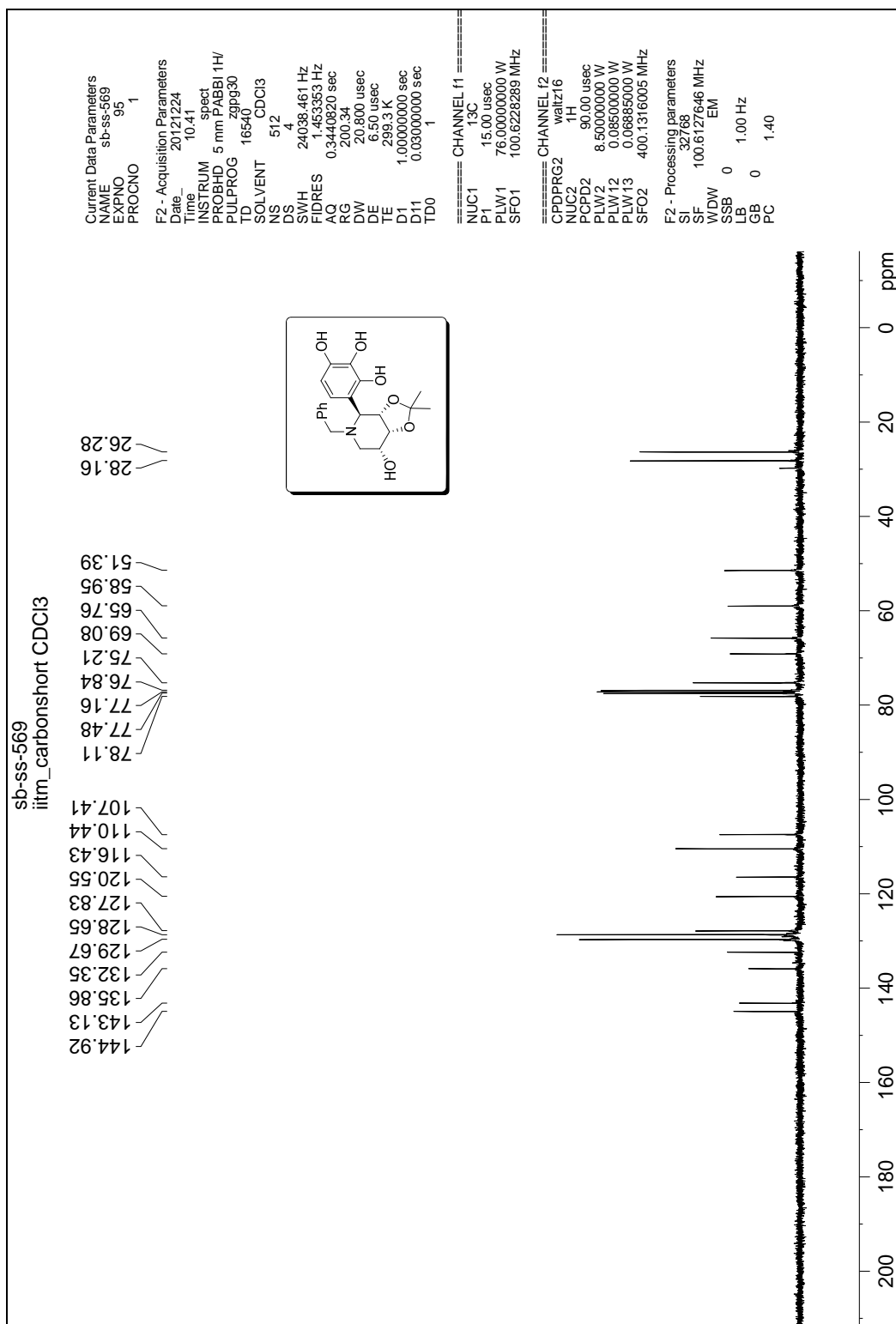




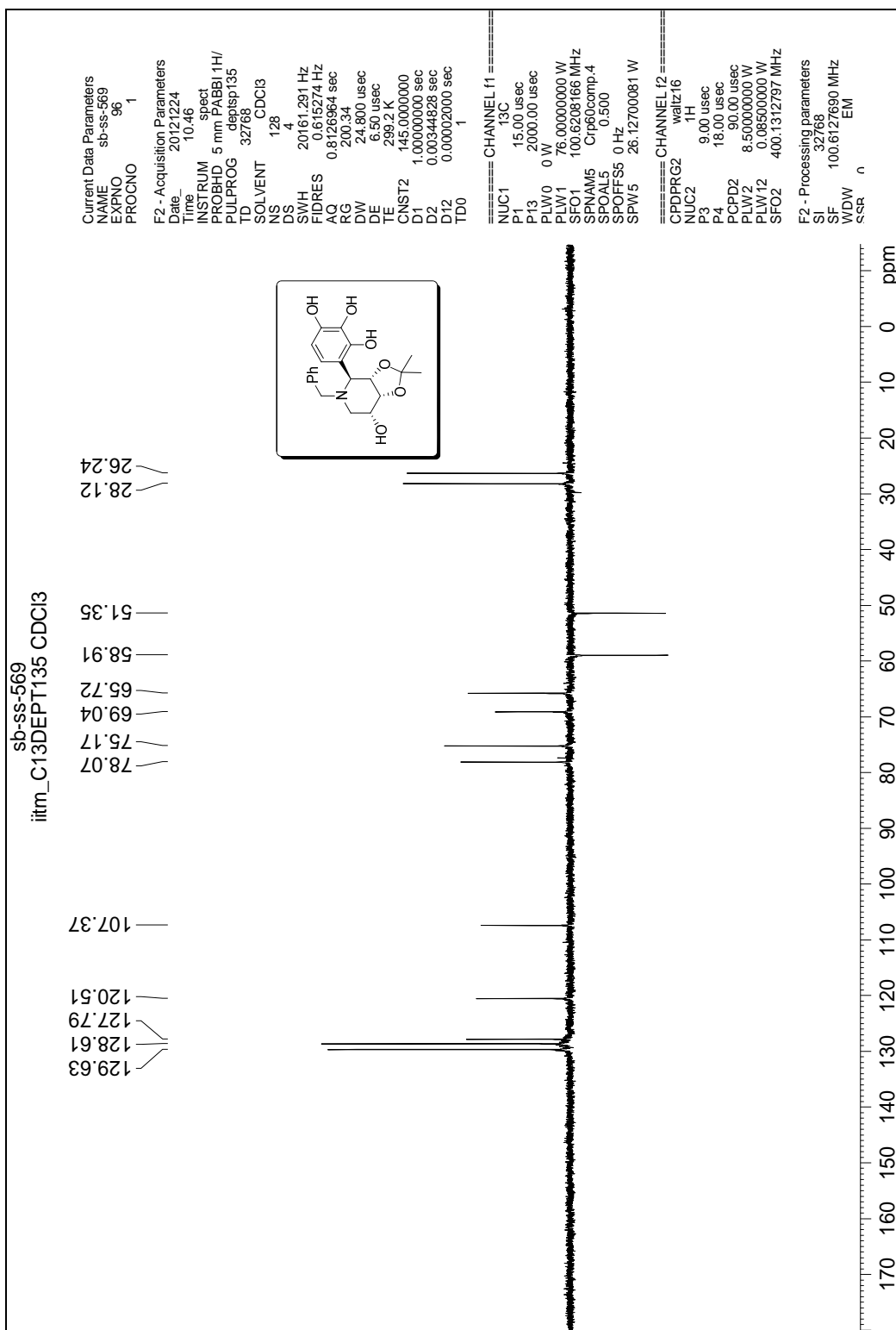


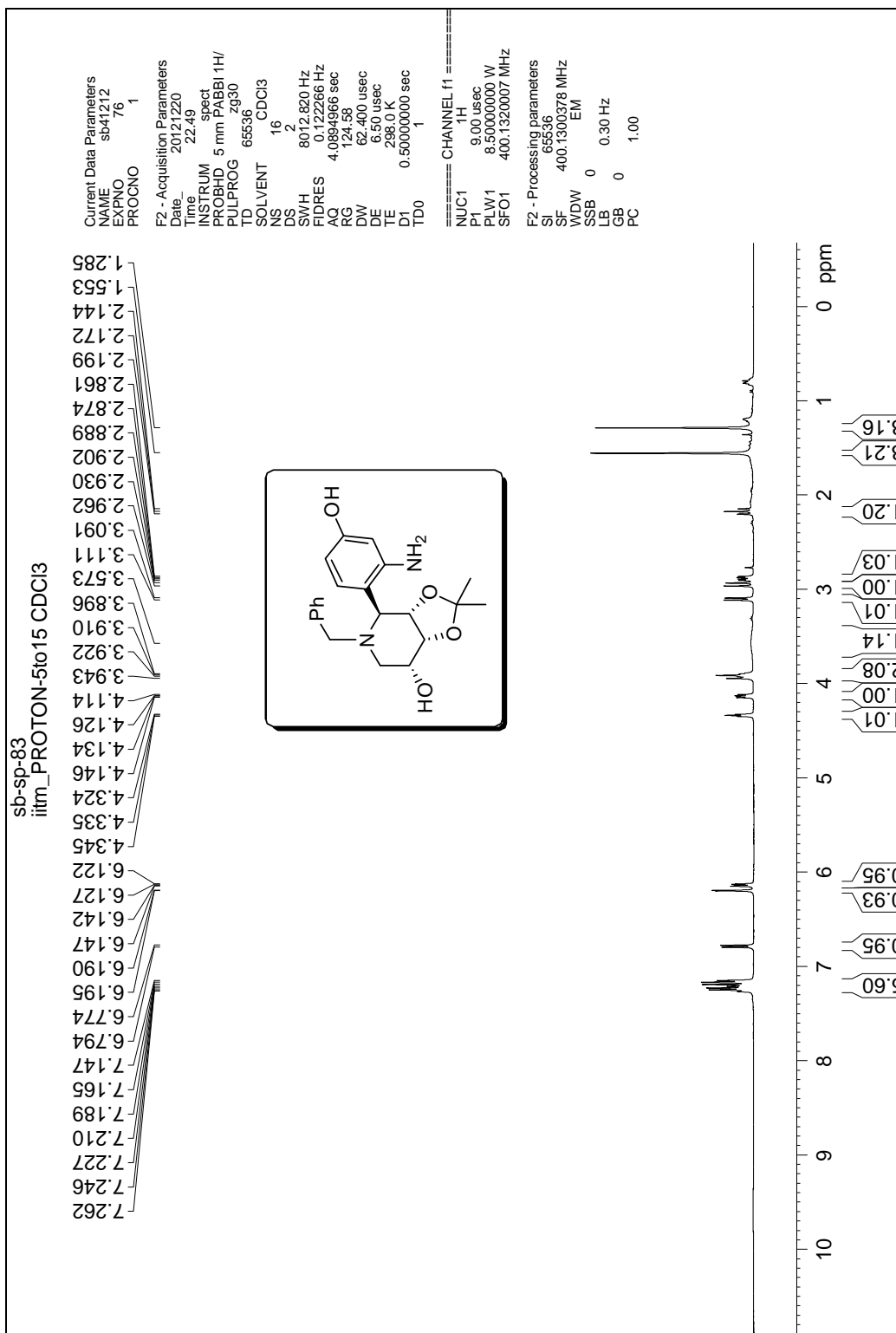
<sup>1</sup>H NMR spectrum of compound 10

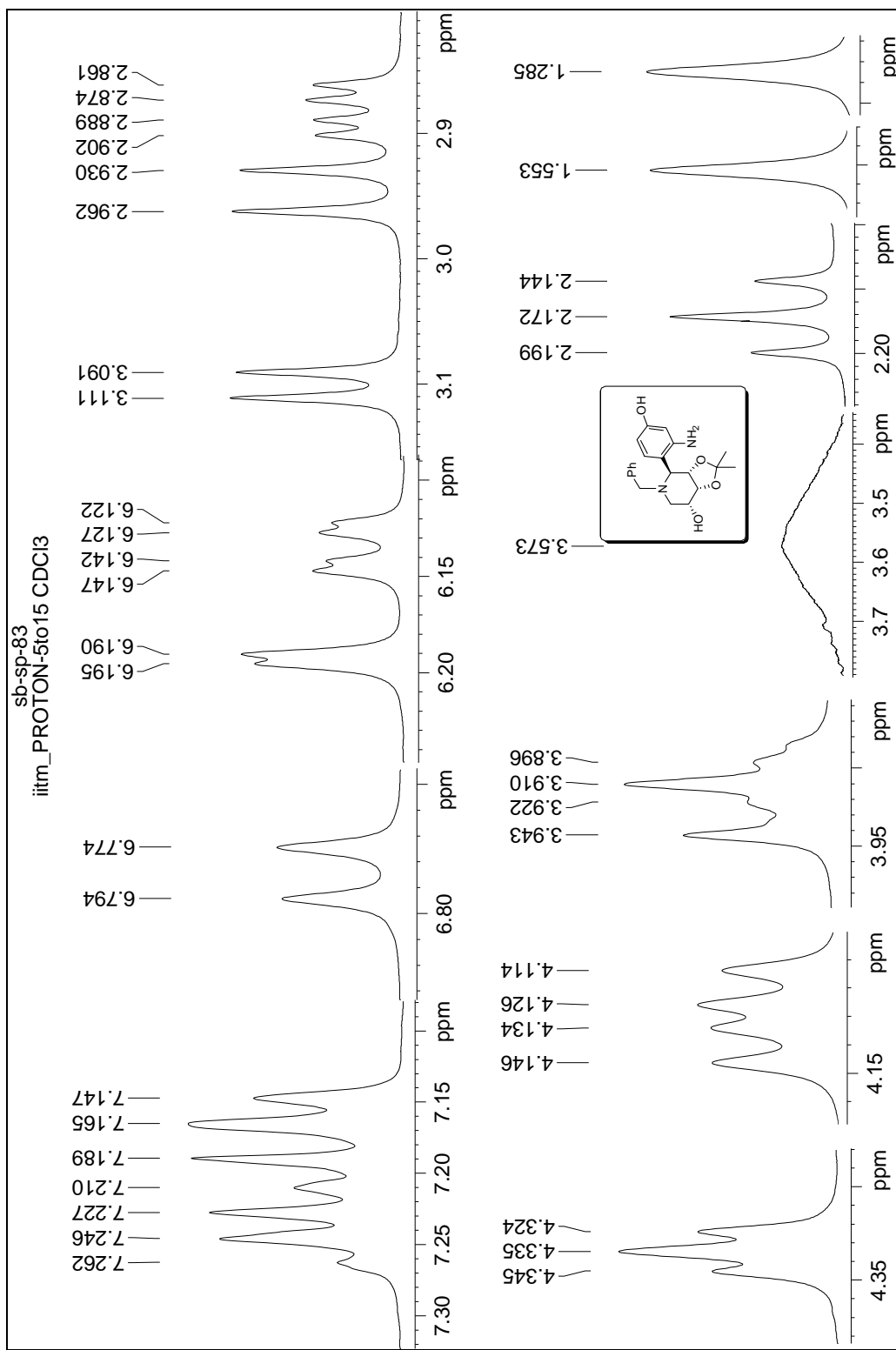




<sup>13</sup>C NMR spectrum of compound 10

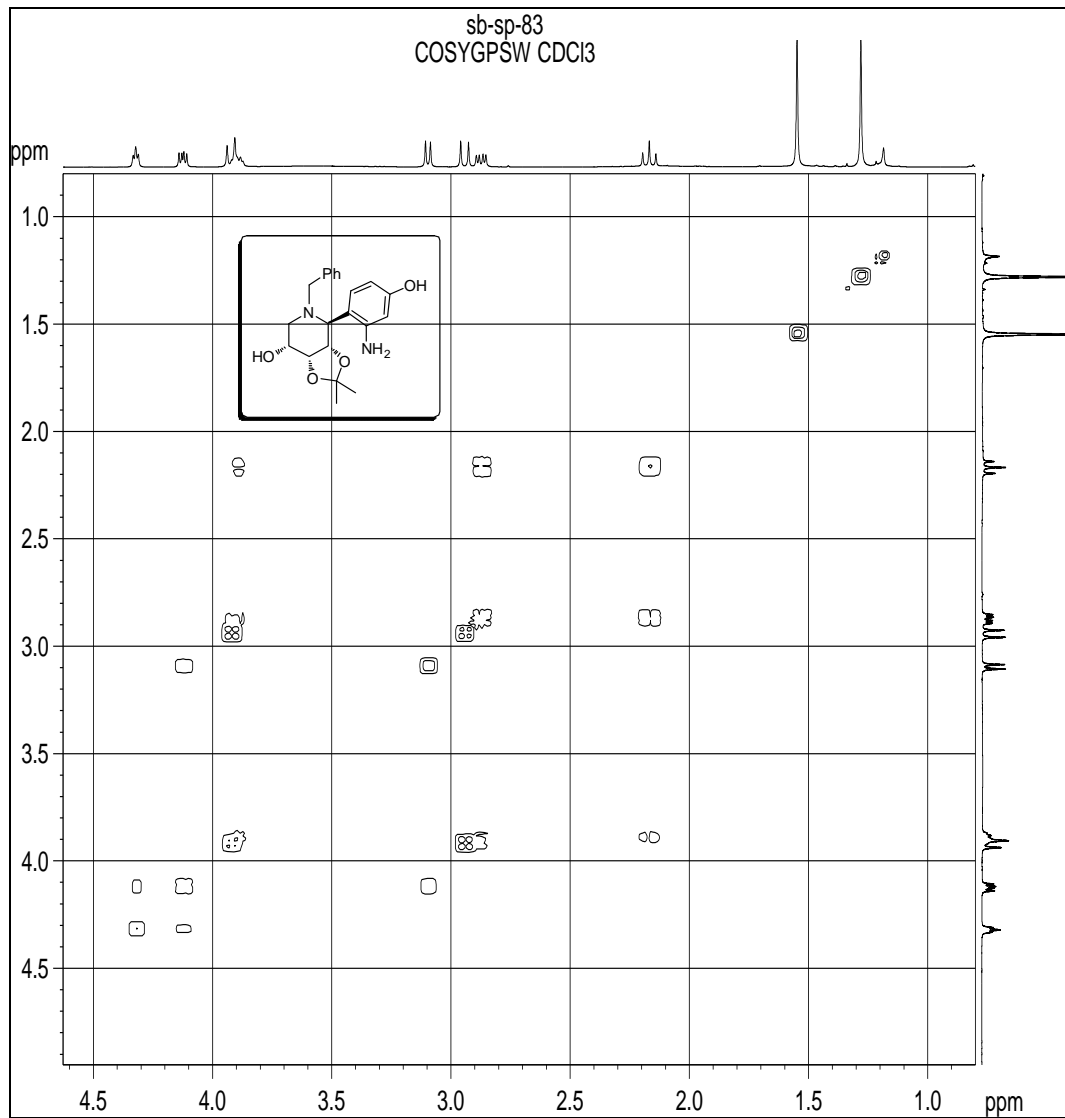




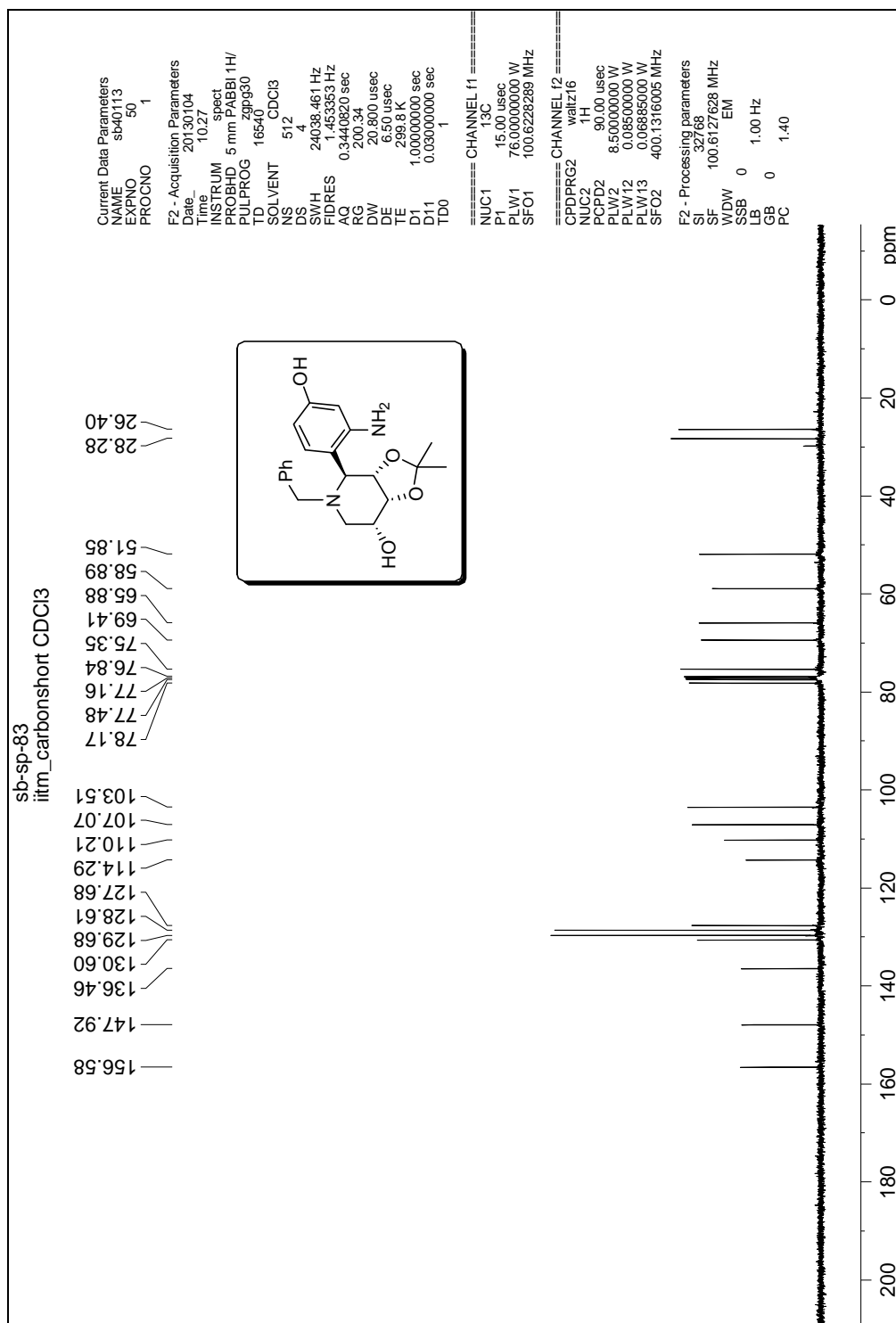


Expanded  $^1\text{H}$  NMR spectrum of compound 12

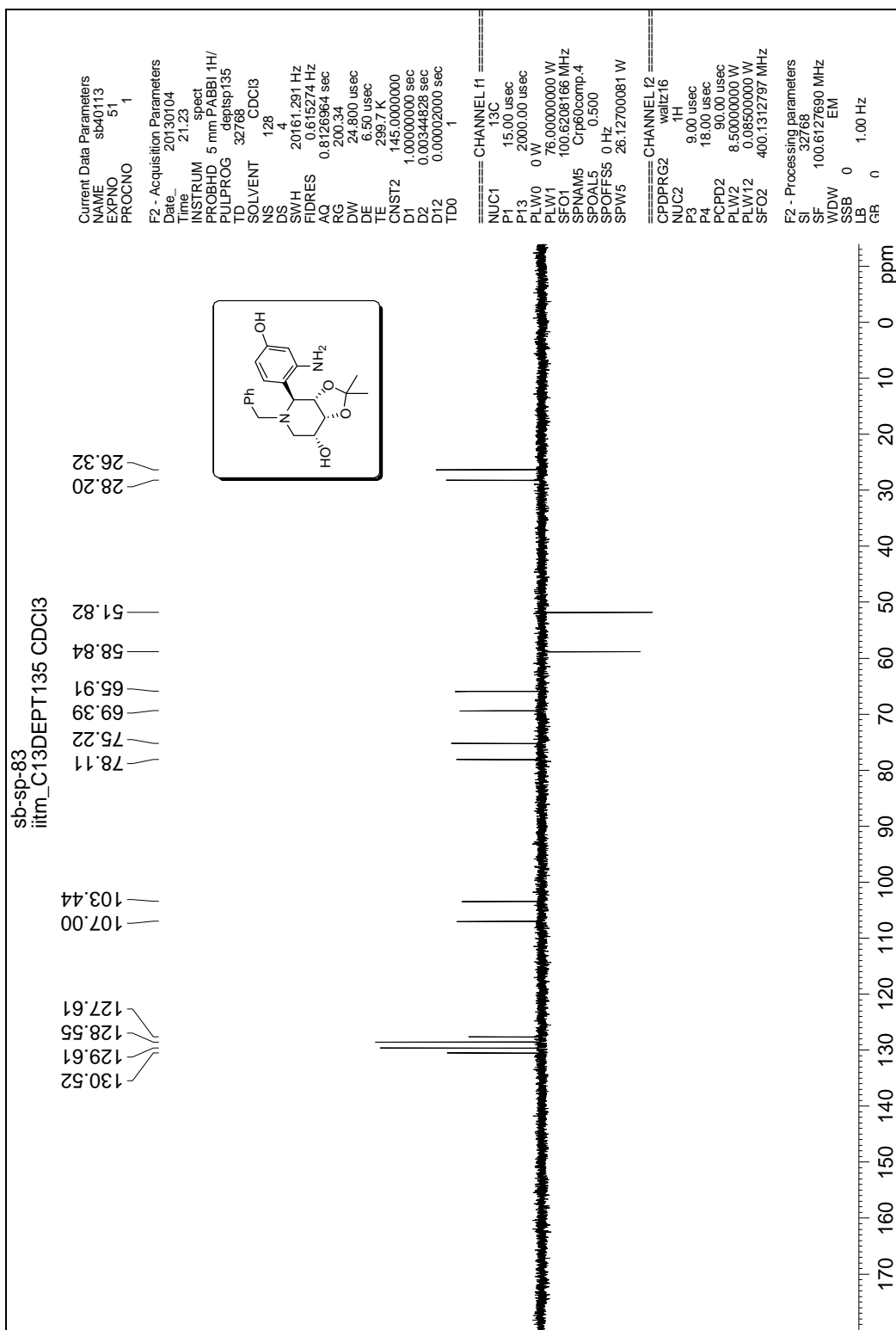




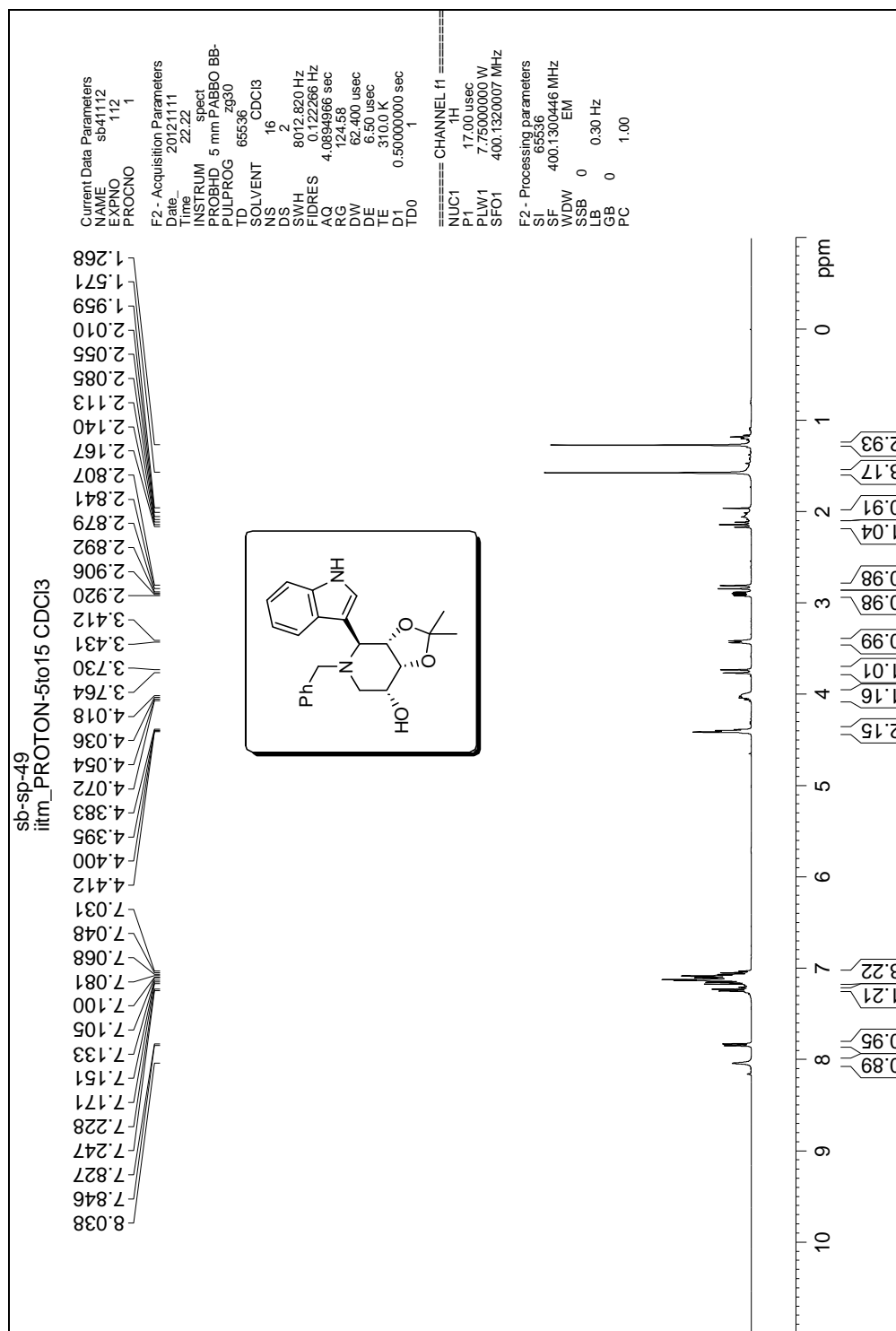
<sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of Compound **12**



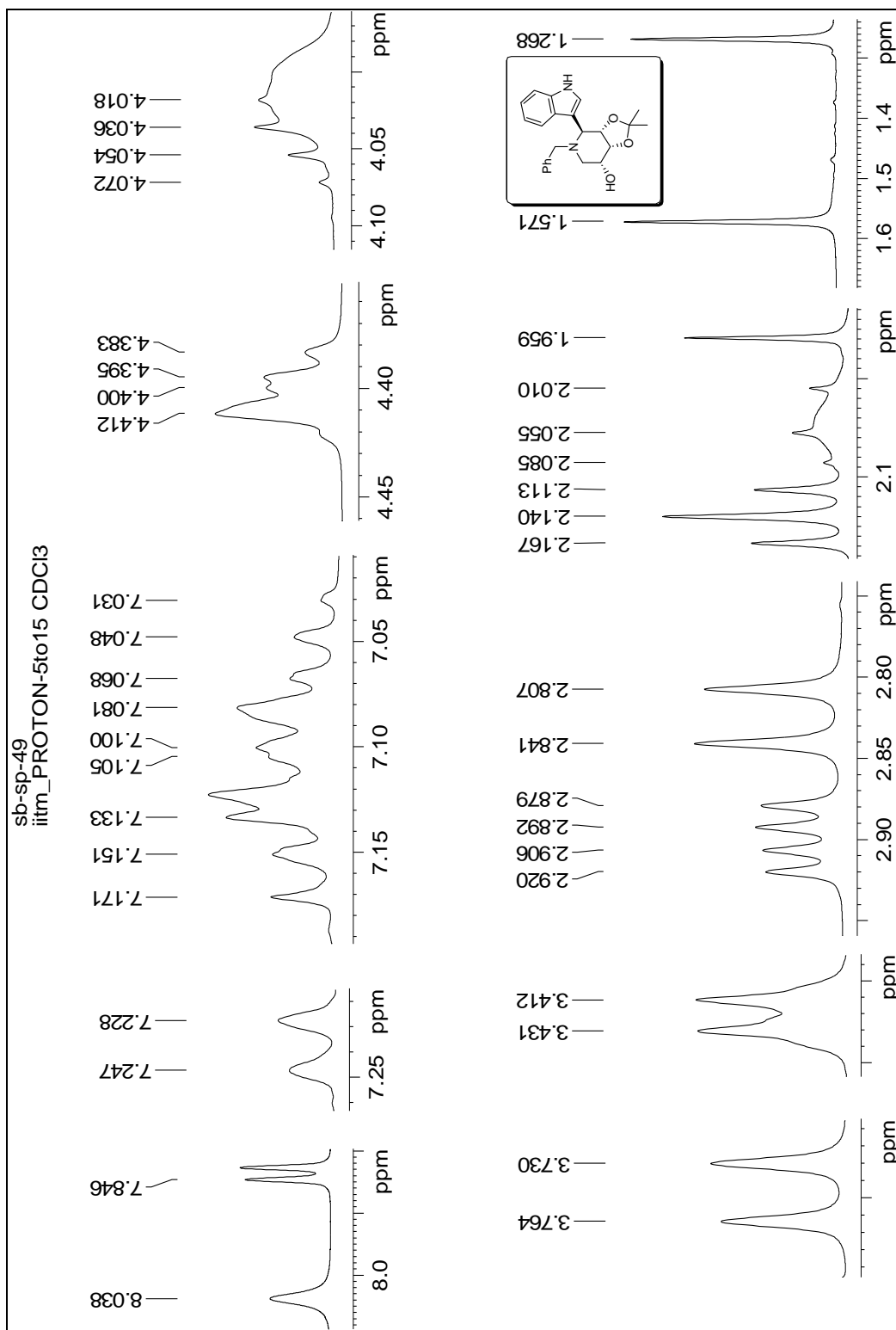
<sup>13</sup>C NMR spectrum of compound **12**



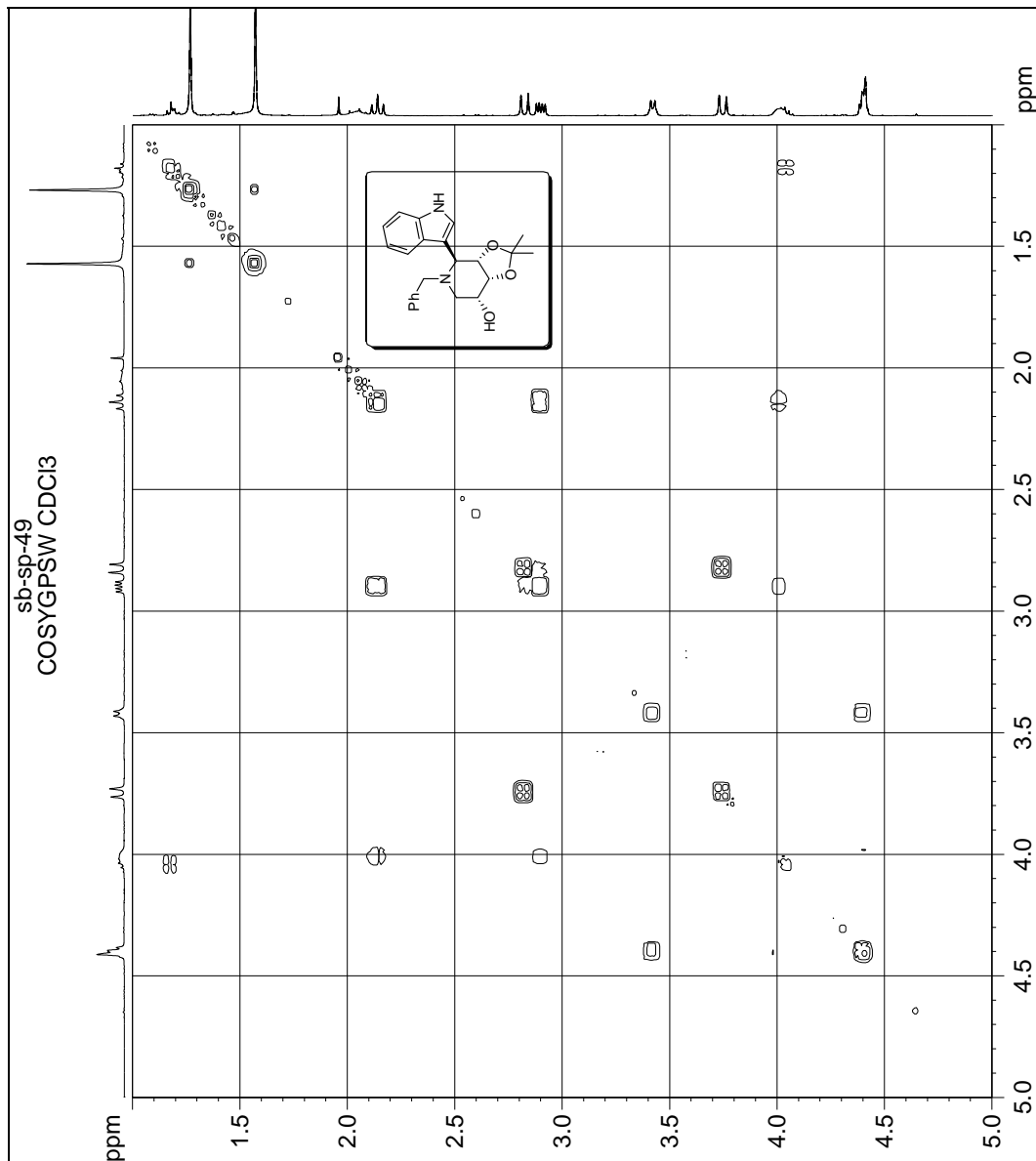
DEPT NMR spectrum of compound 12



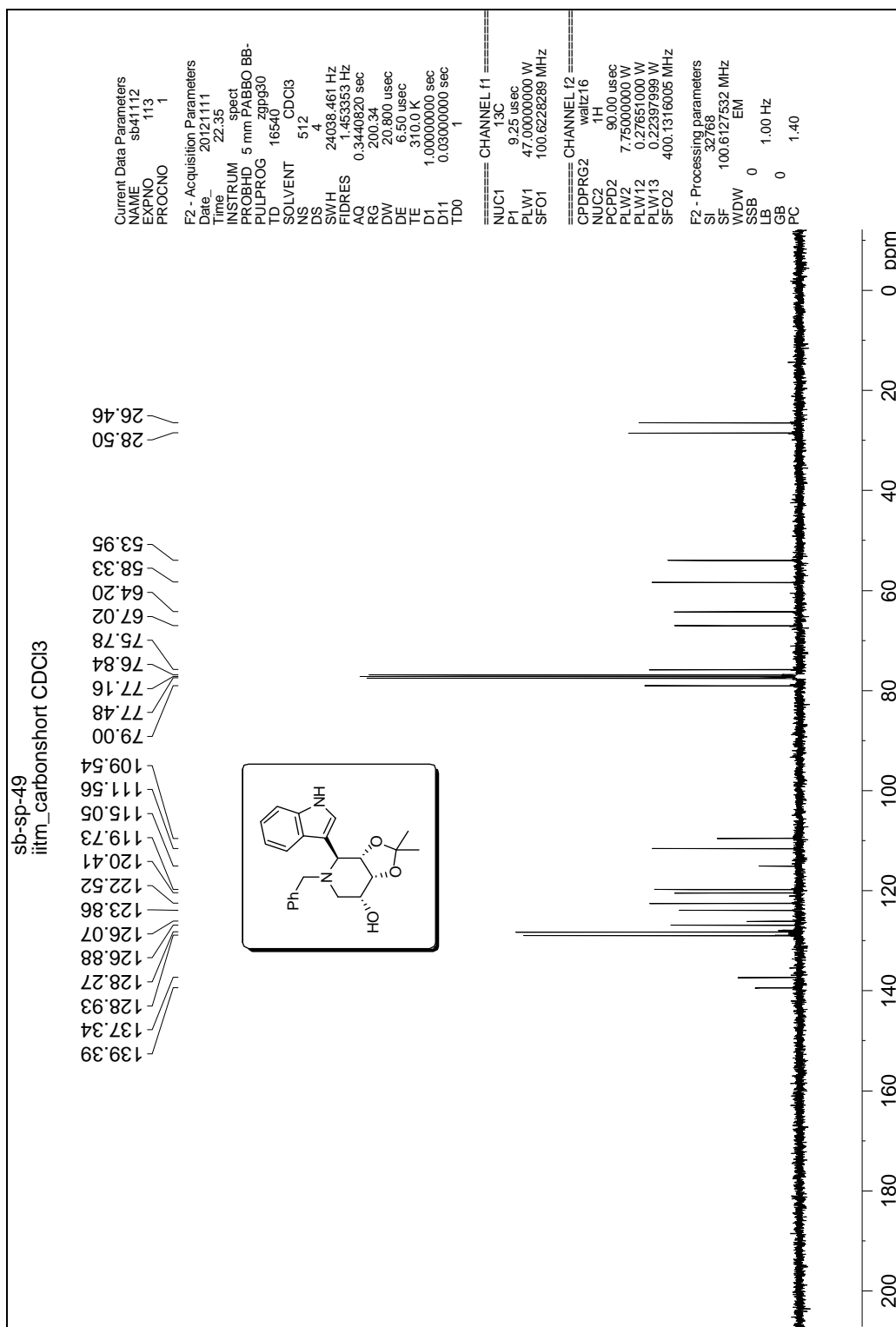
<sup>1</sup>H NMR spectrum of compound 14

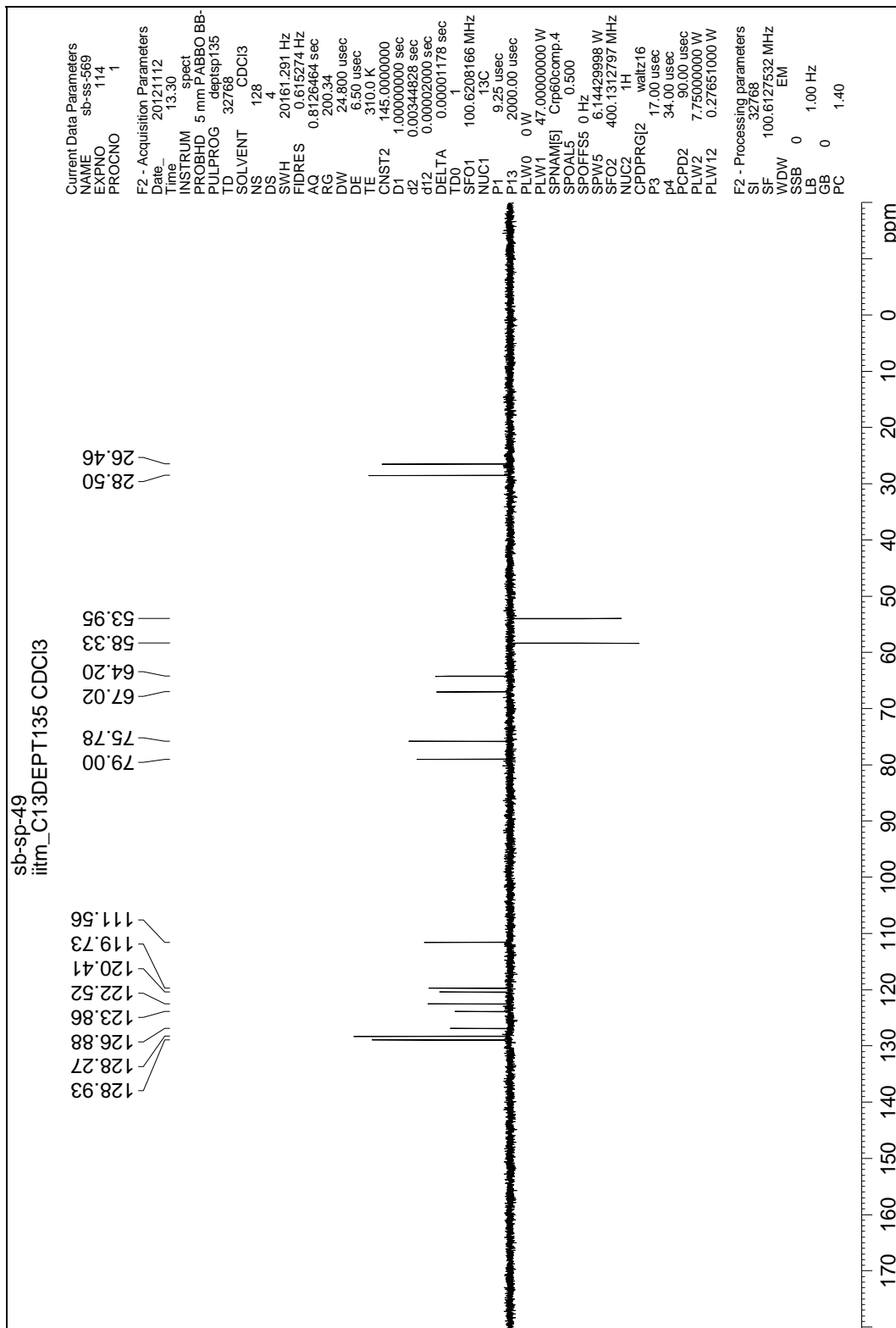


Expanded <sup>1</sup>H NMR spectrum of compound 14



$^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of Compound **14**

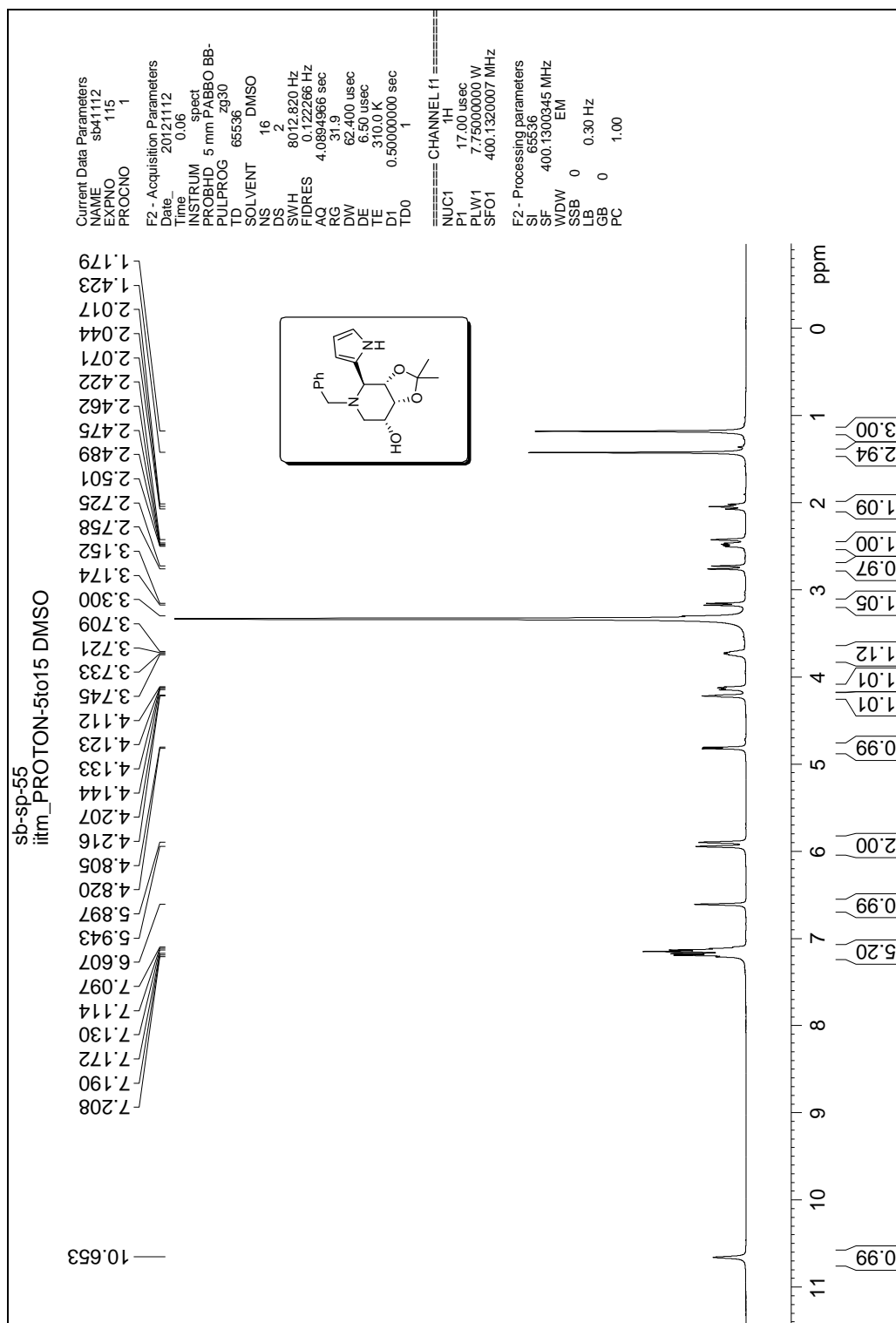




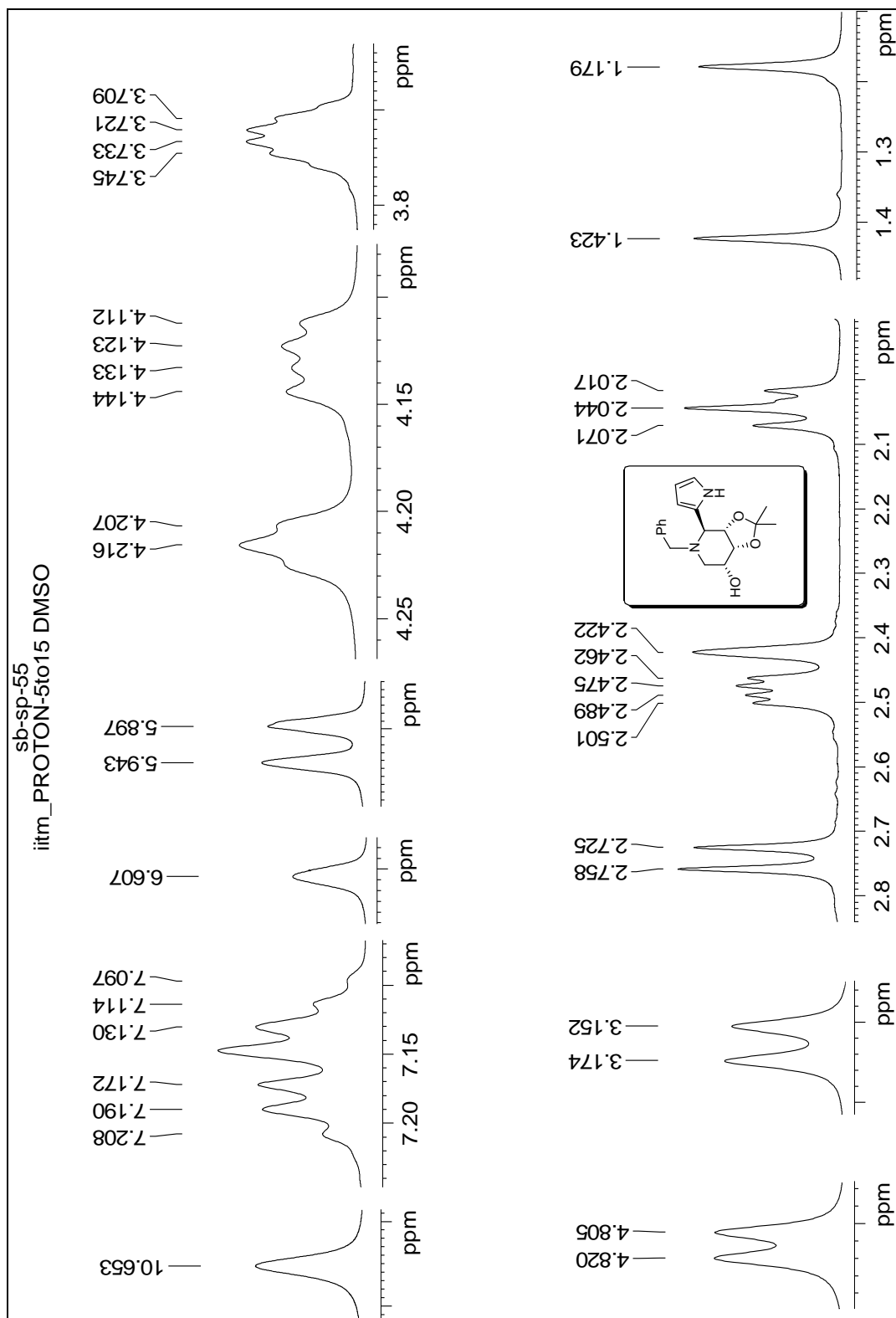
DEPT NMR spectrum of compound 14



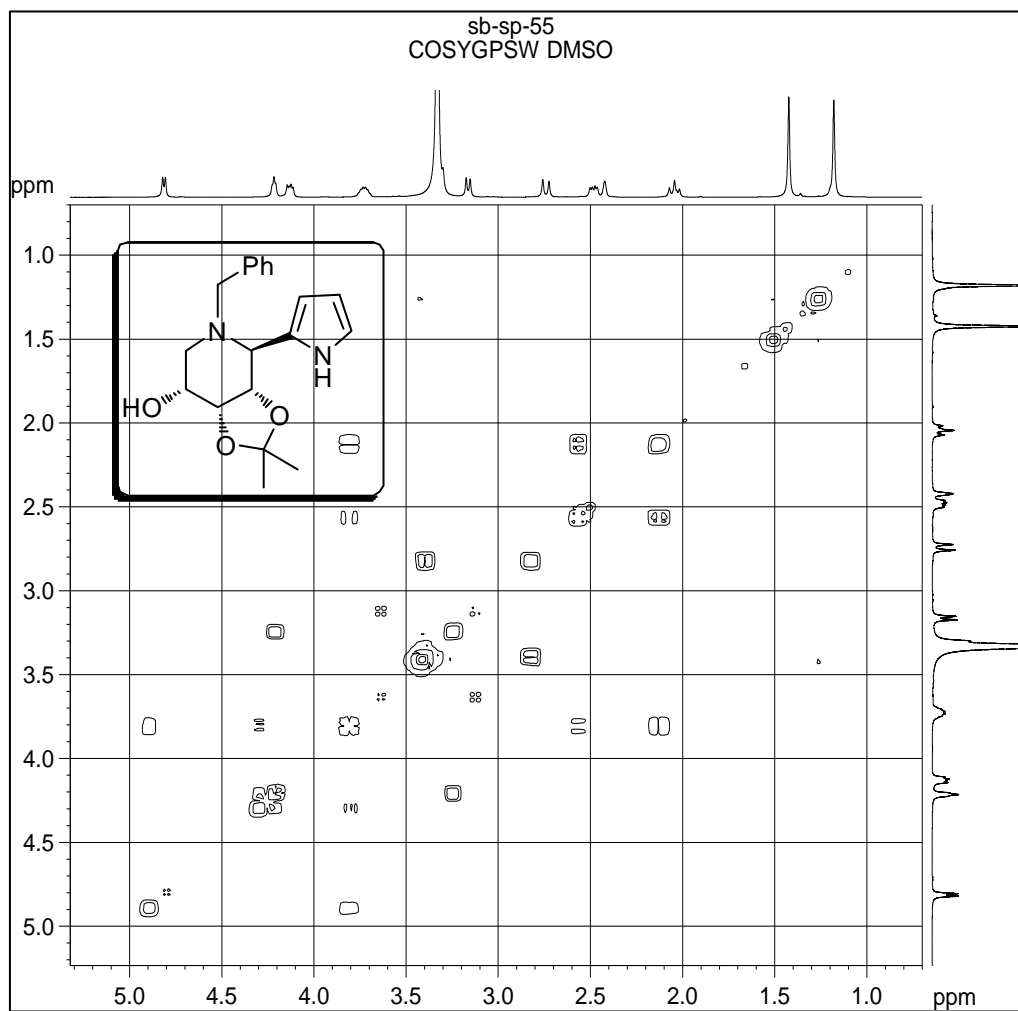
DEPT NMR spectrum of compound **14**



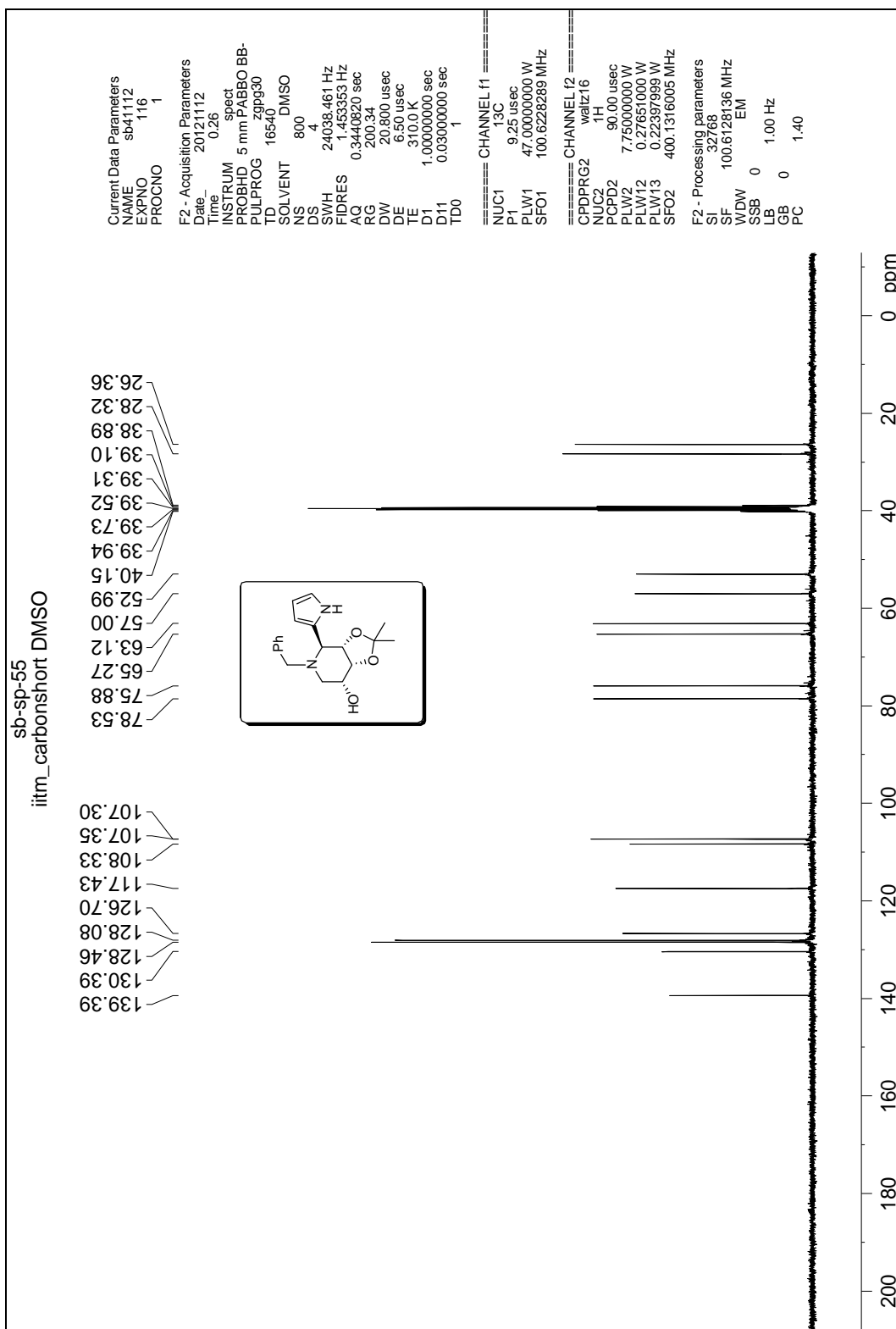
<sup>1</sup>H NMR spectrum of compound **16**

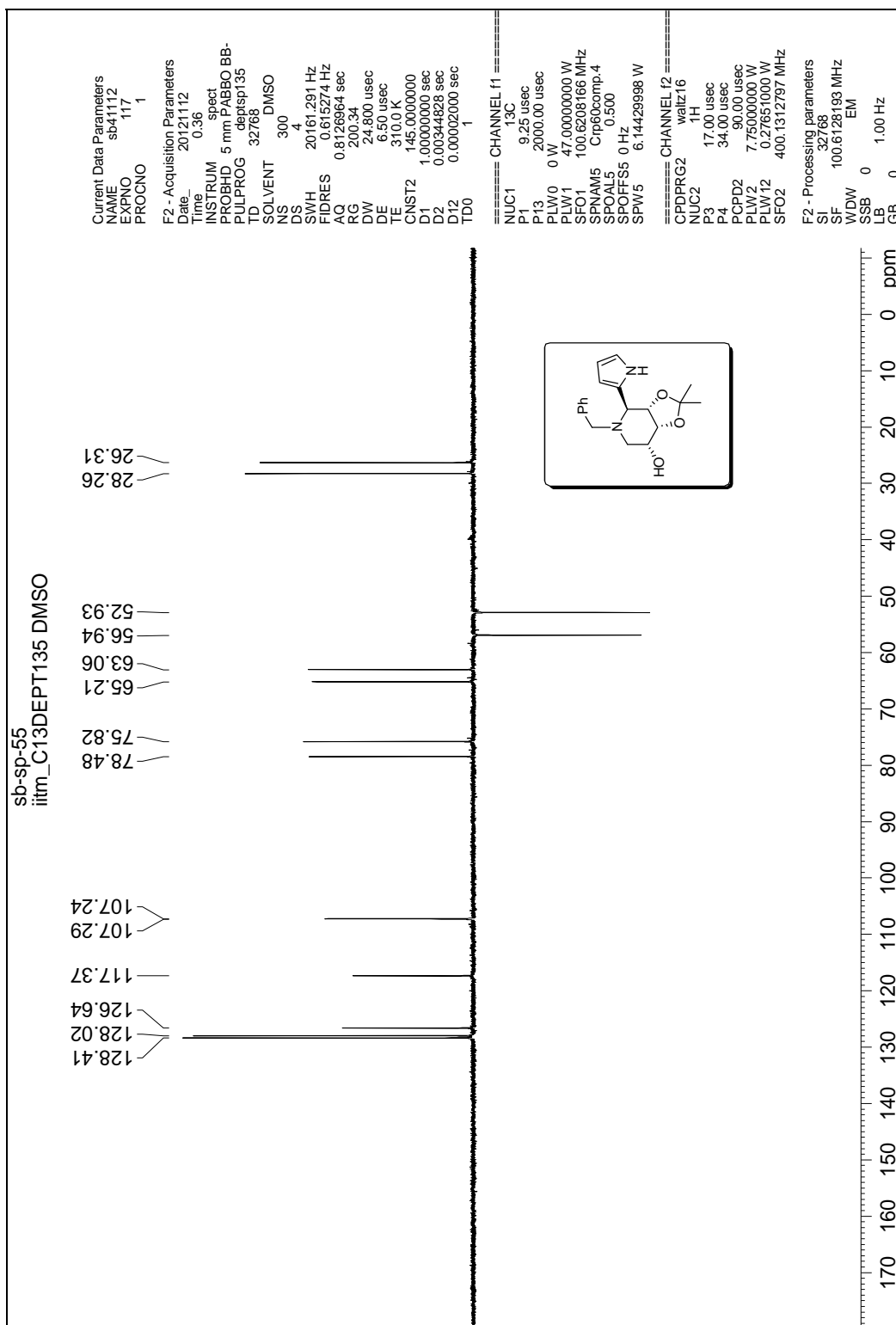


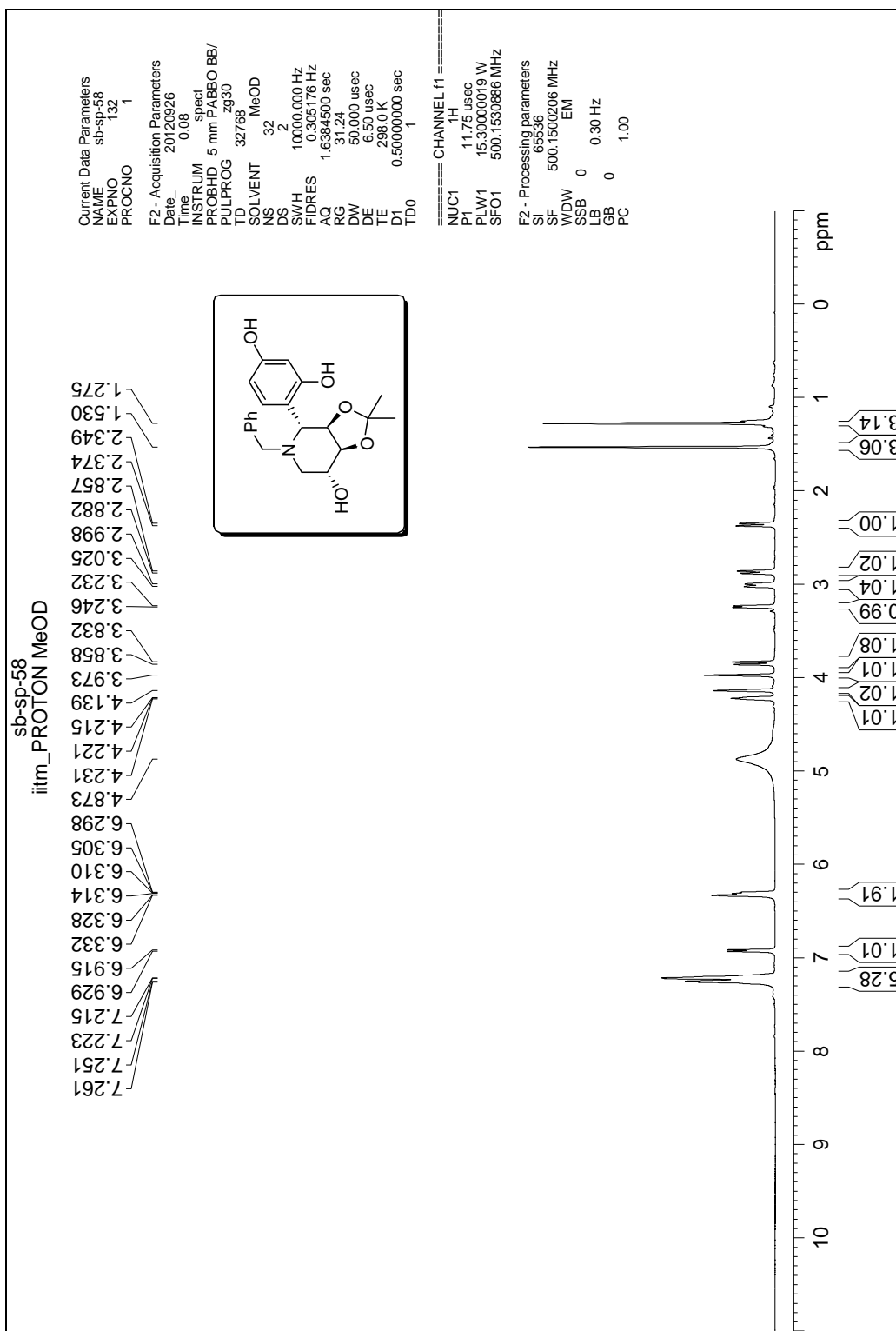
Expanded  $^1\text{H}$  NMR spectrum of compound **16**

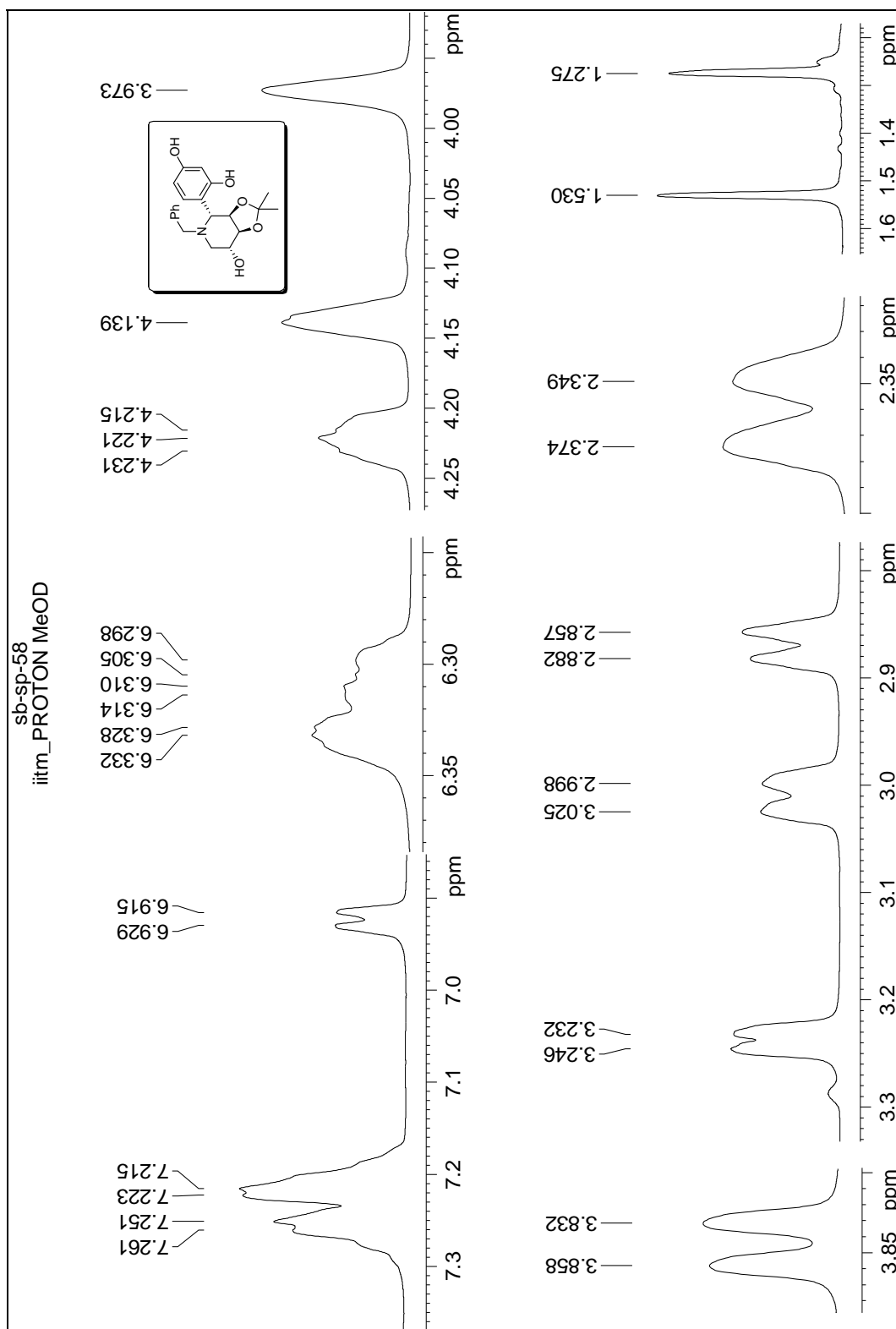


$^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of Compound **16**

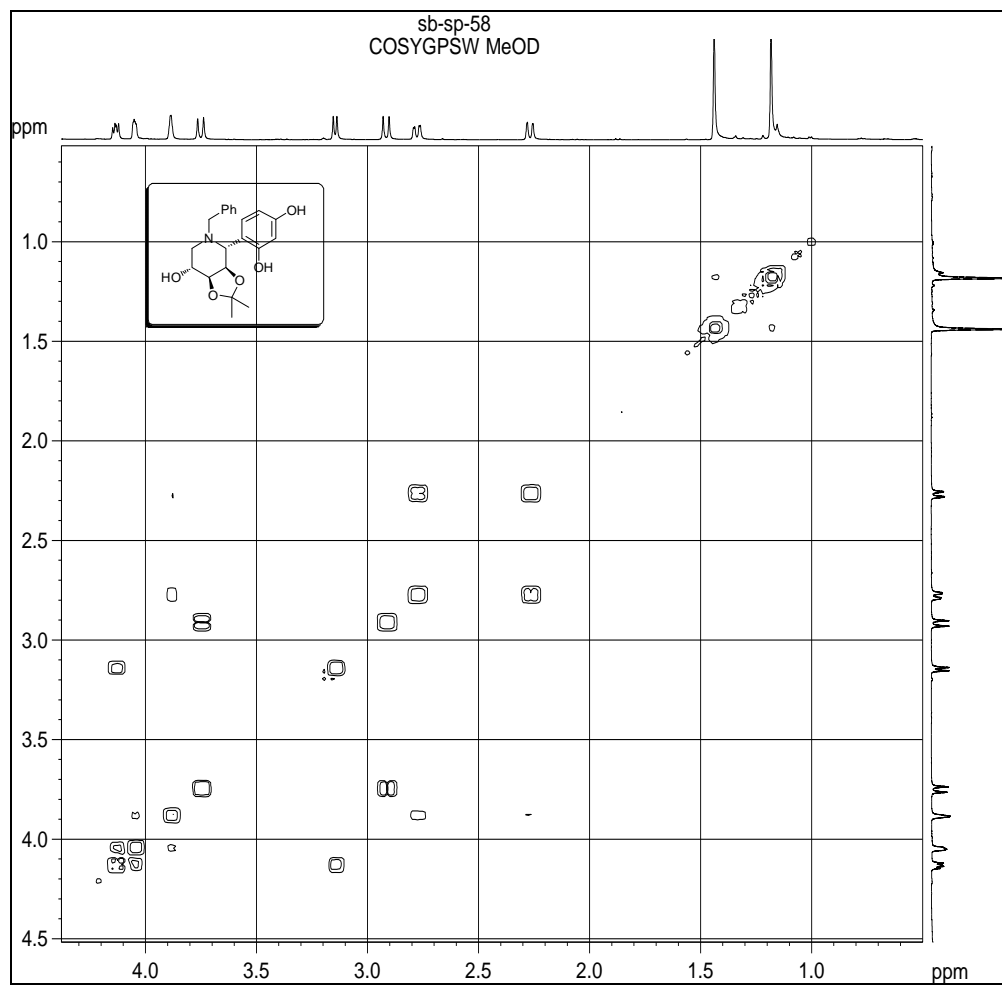






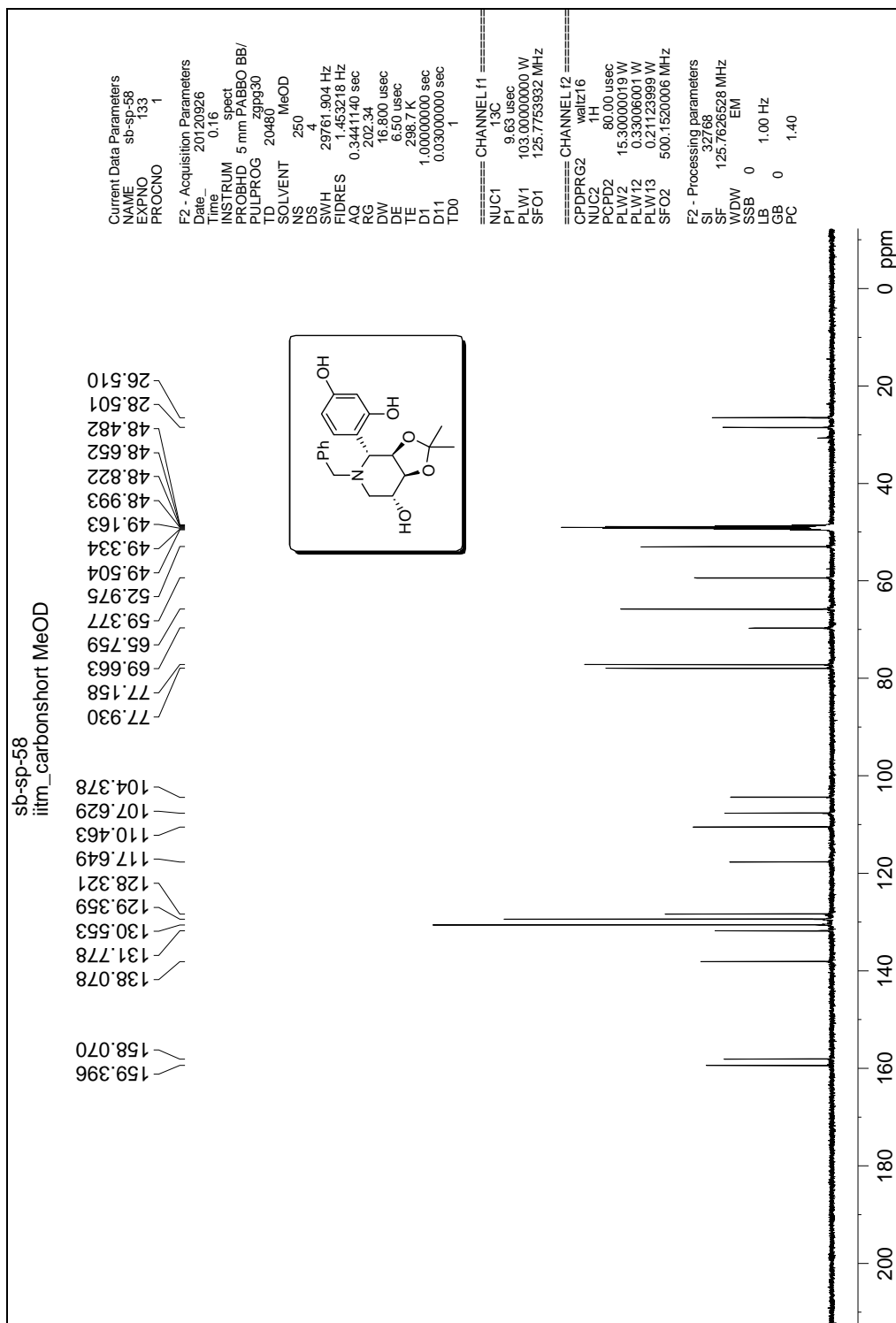


Expanded  $^1\text{H}$  NMR spectrum of compound **18**

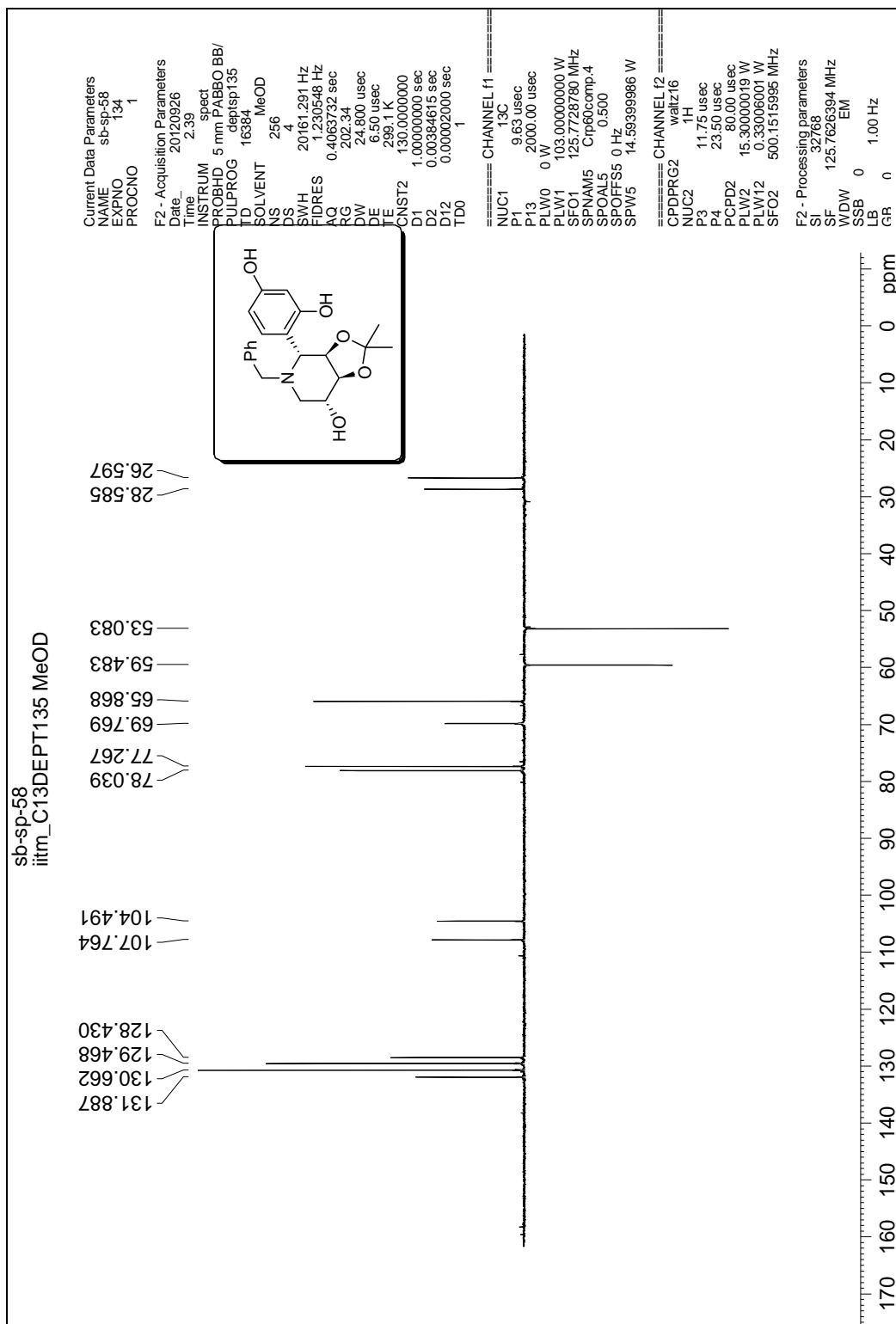


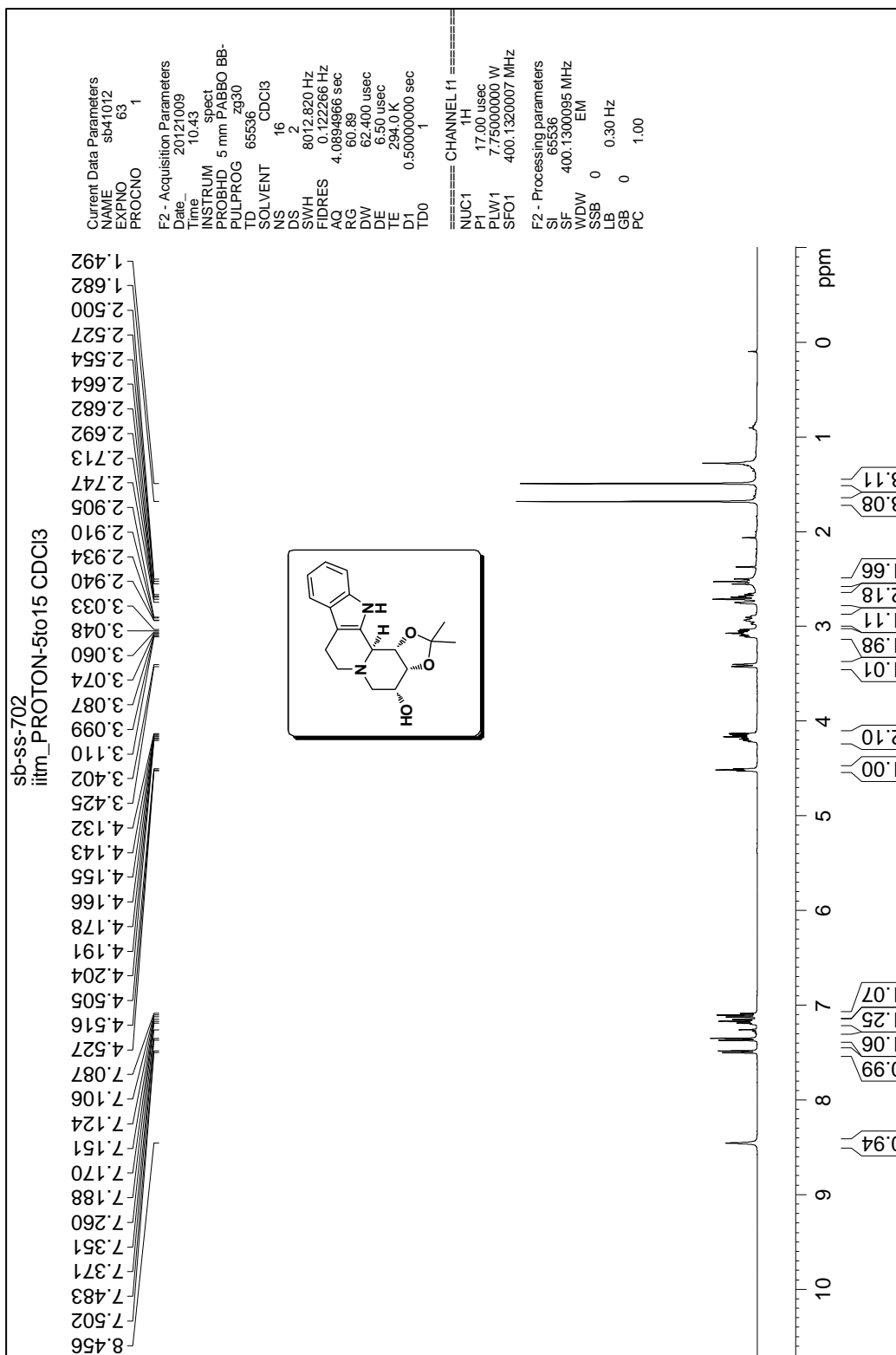
$^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of Compound **18**

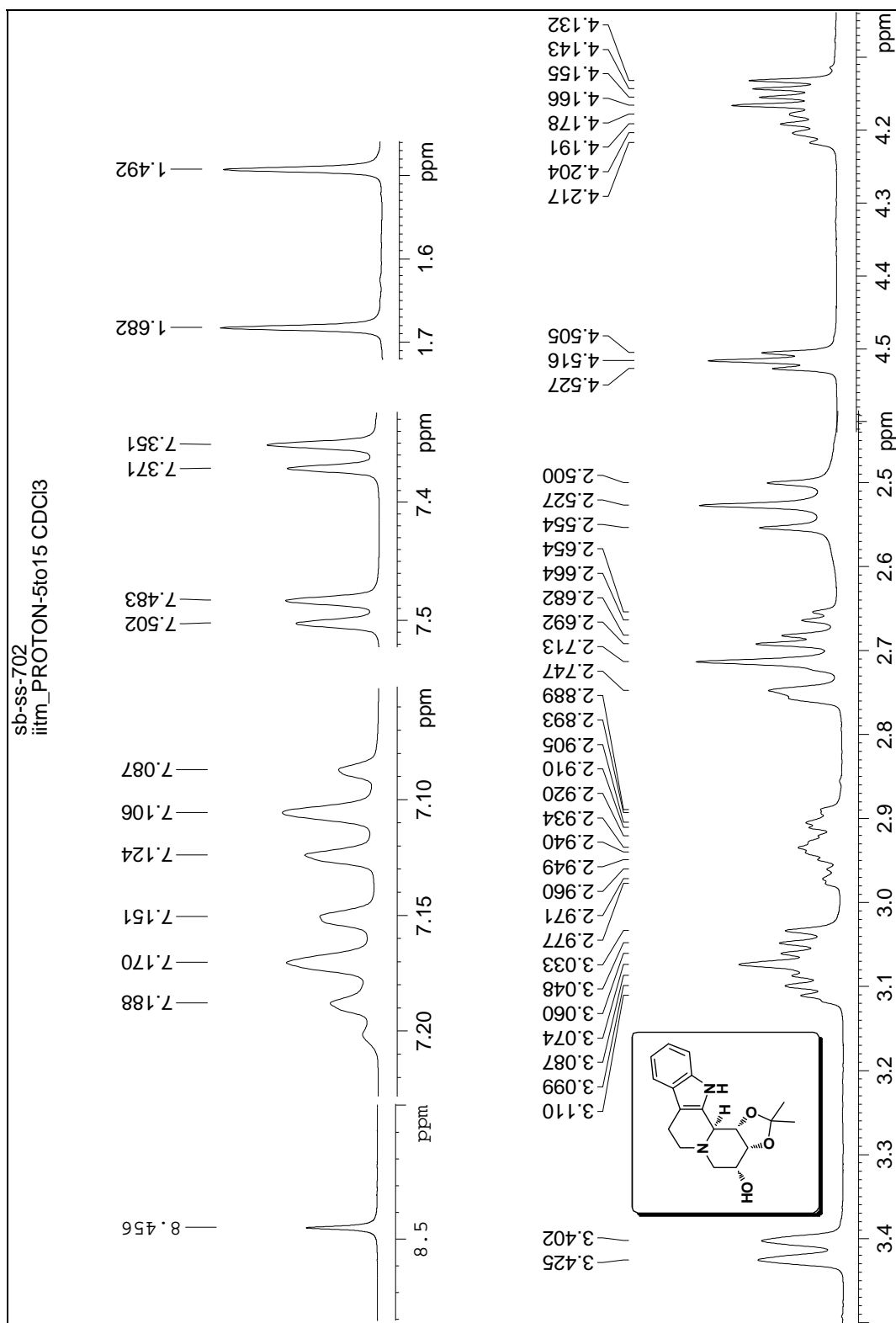




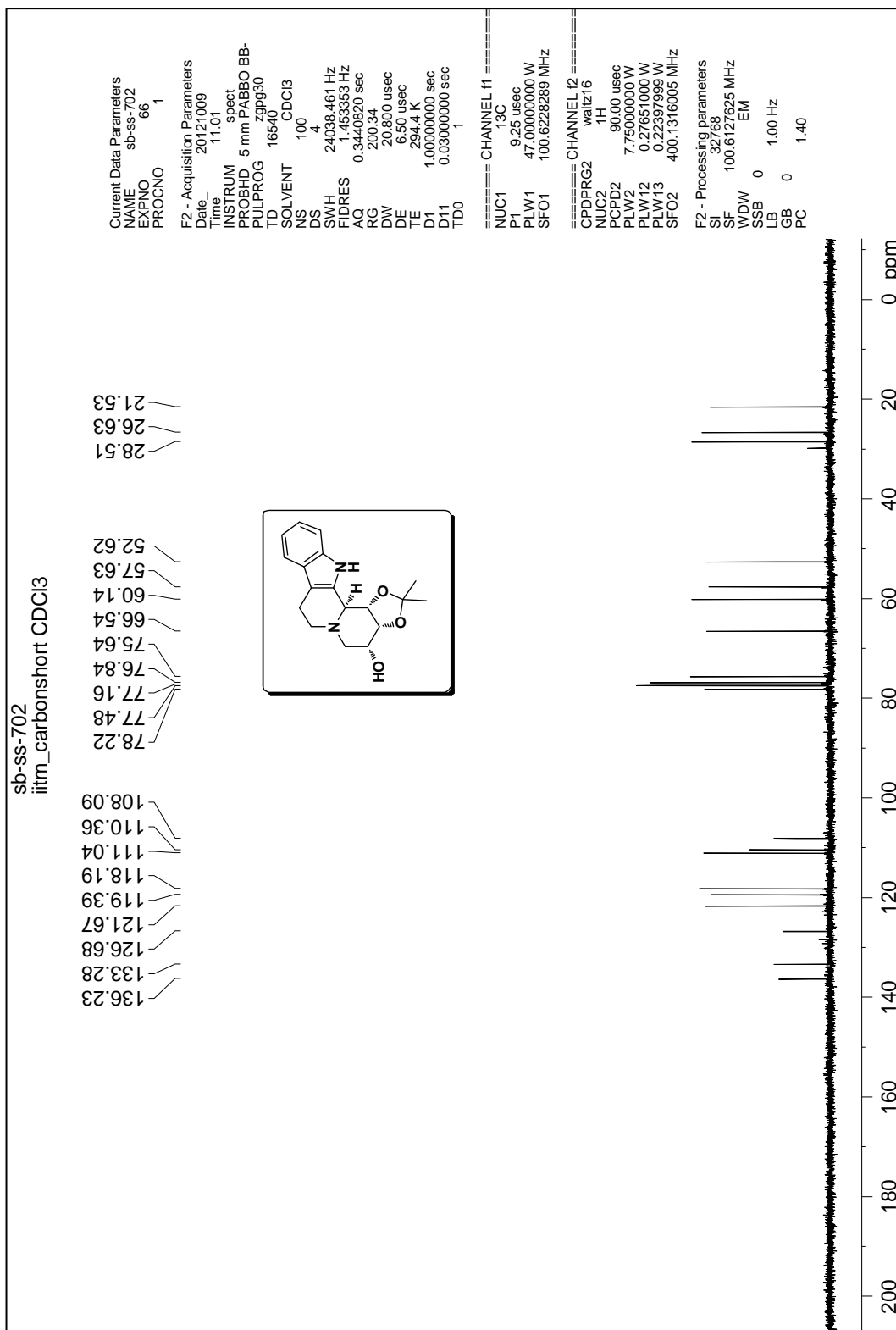
<sup>13</sup>C NMR spectrum of compound 18

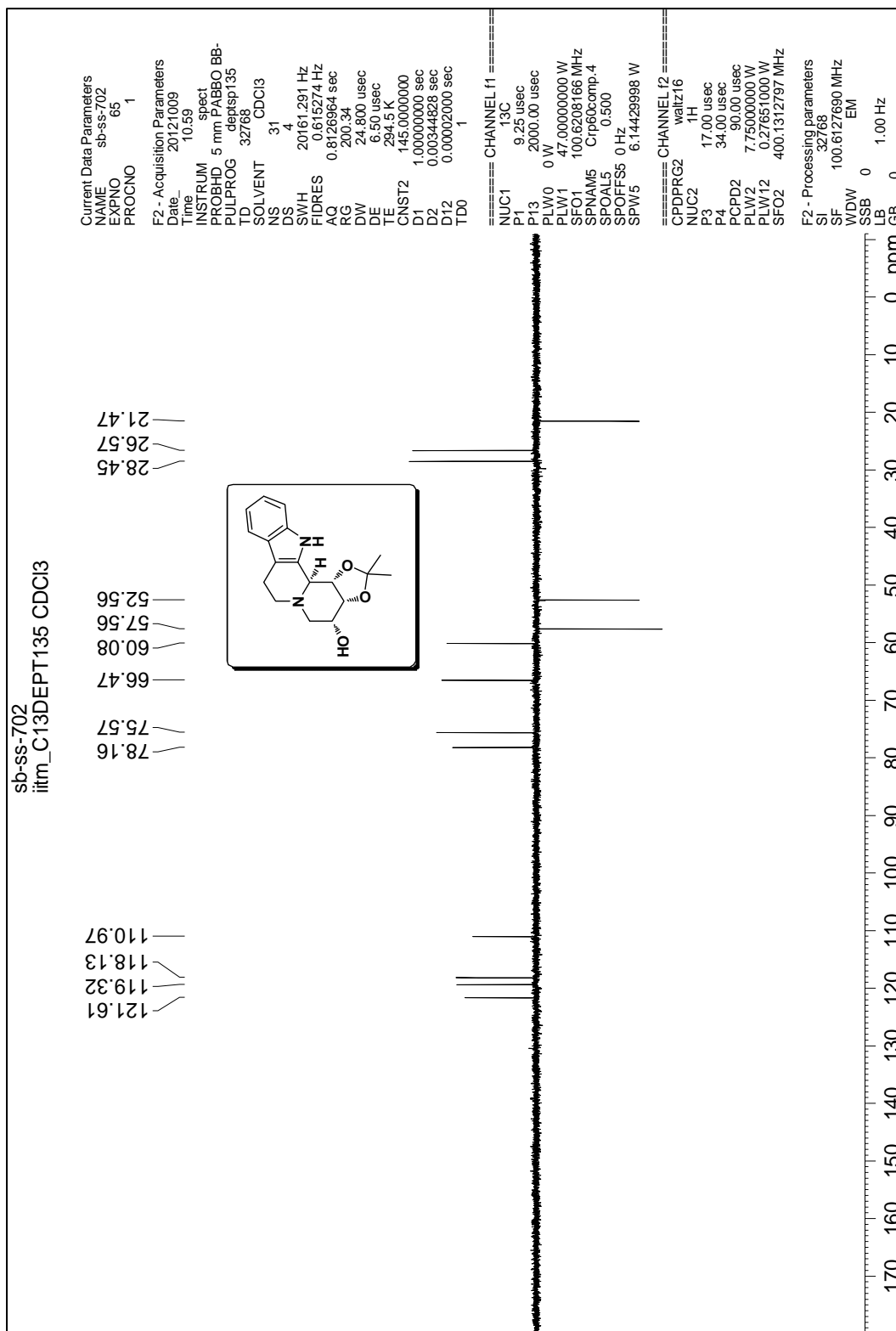


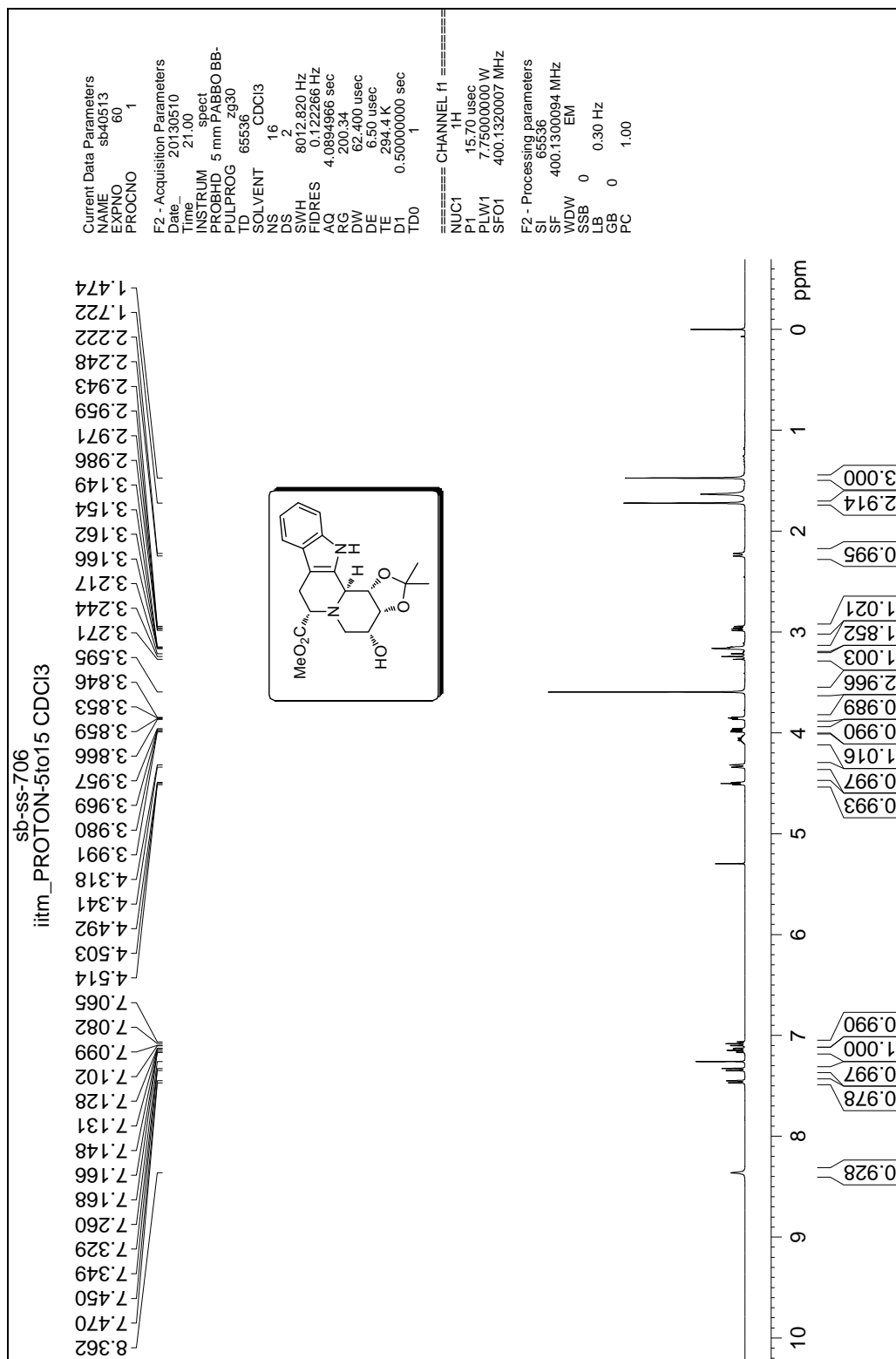




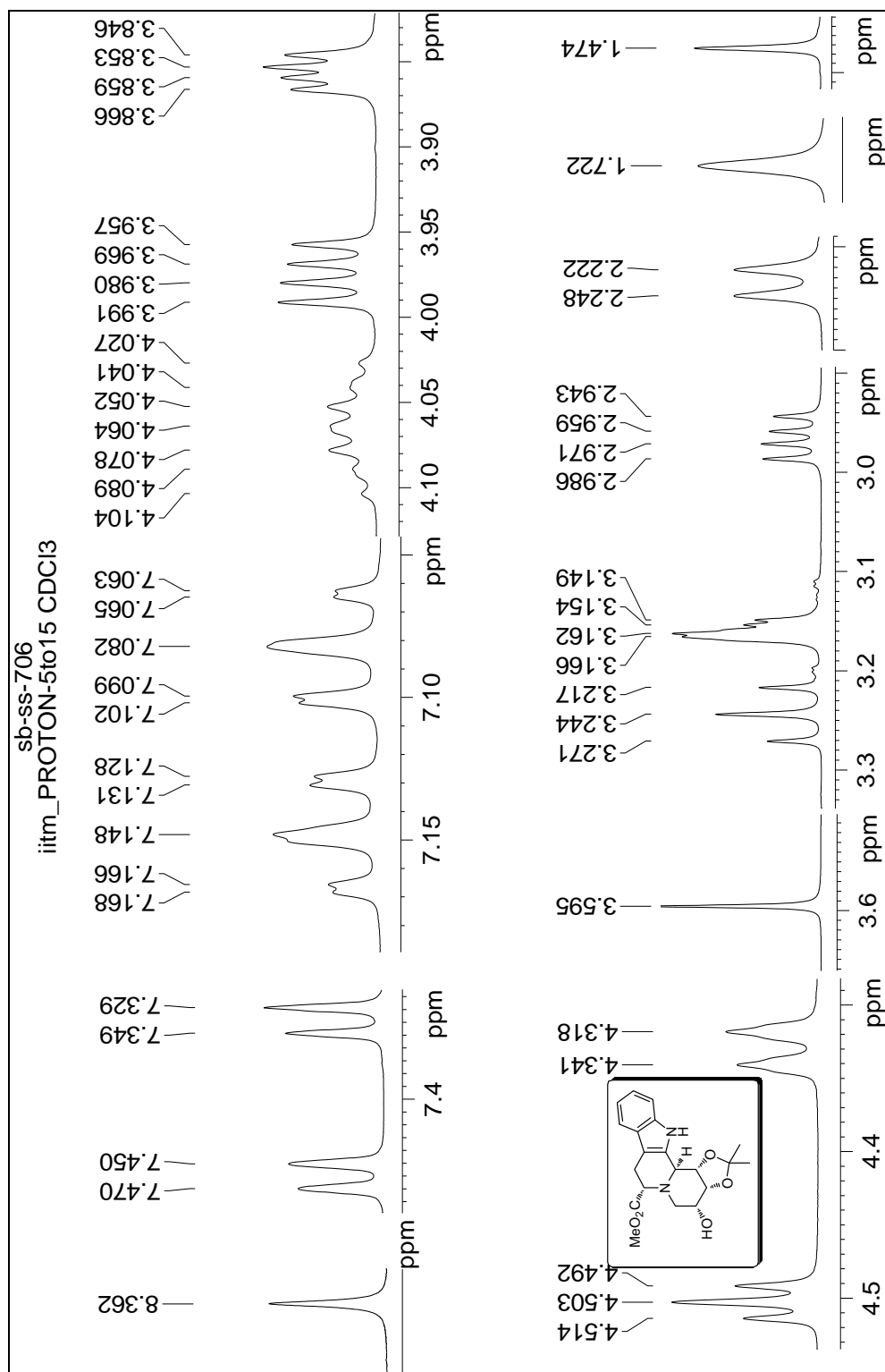
Expanded  $^1\text{H}$  NMR spectrum of compound **20**





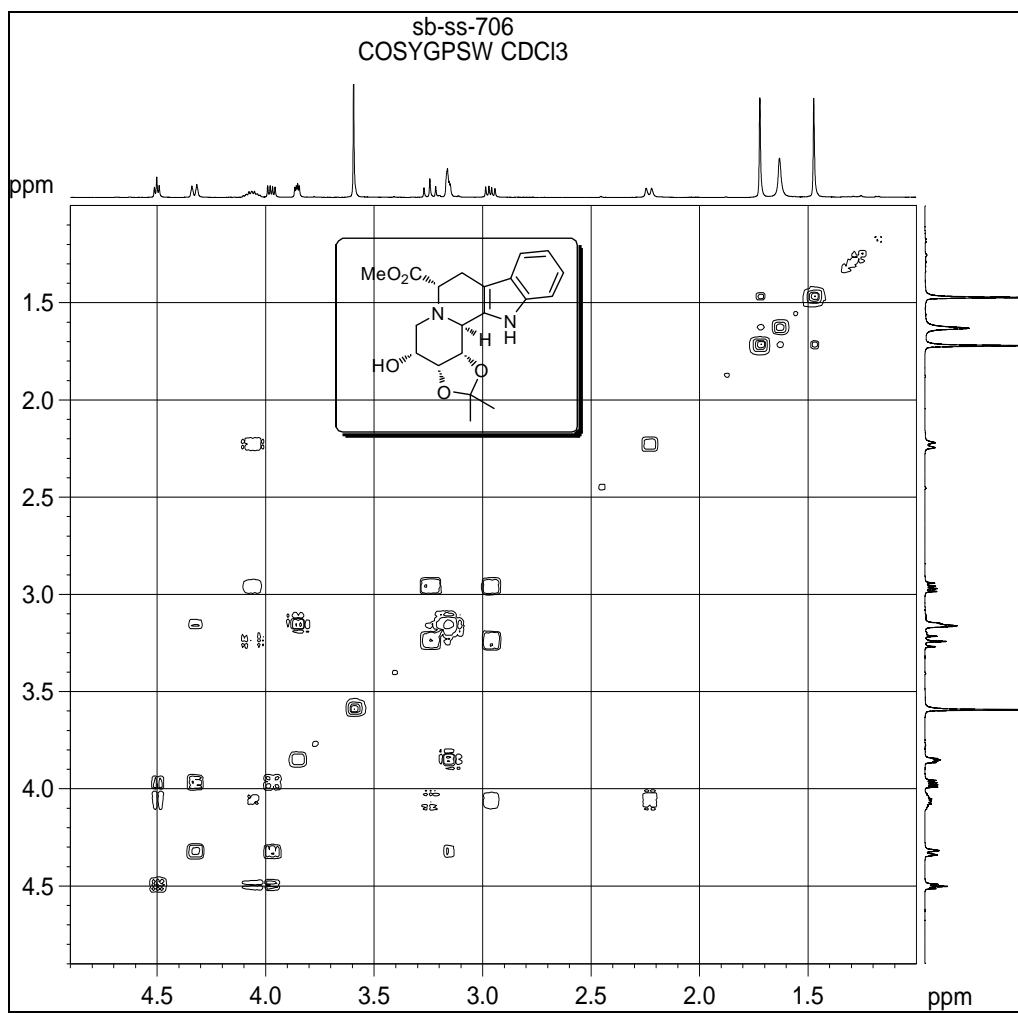


<sup>1</sup>H NMR spectrum of compound 22

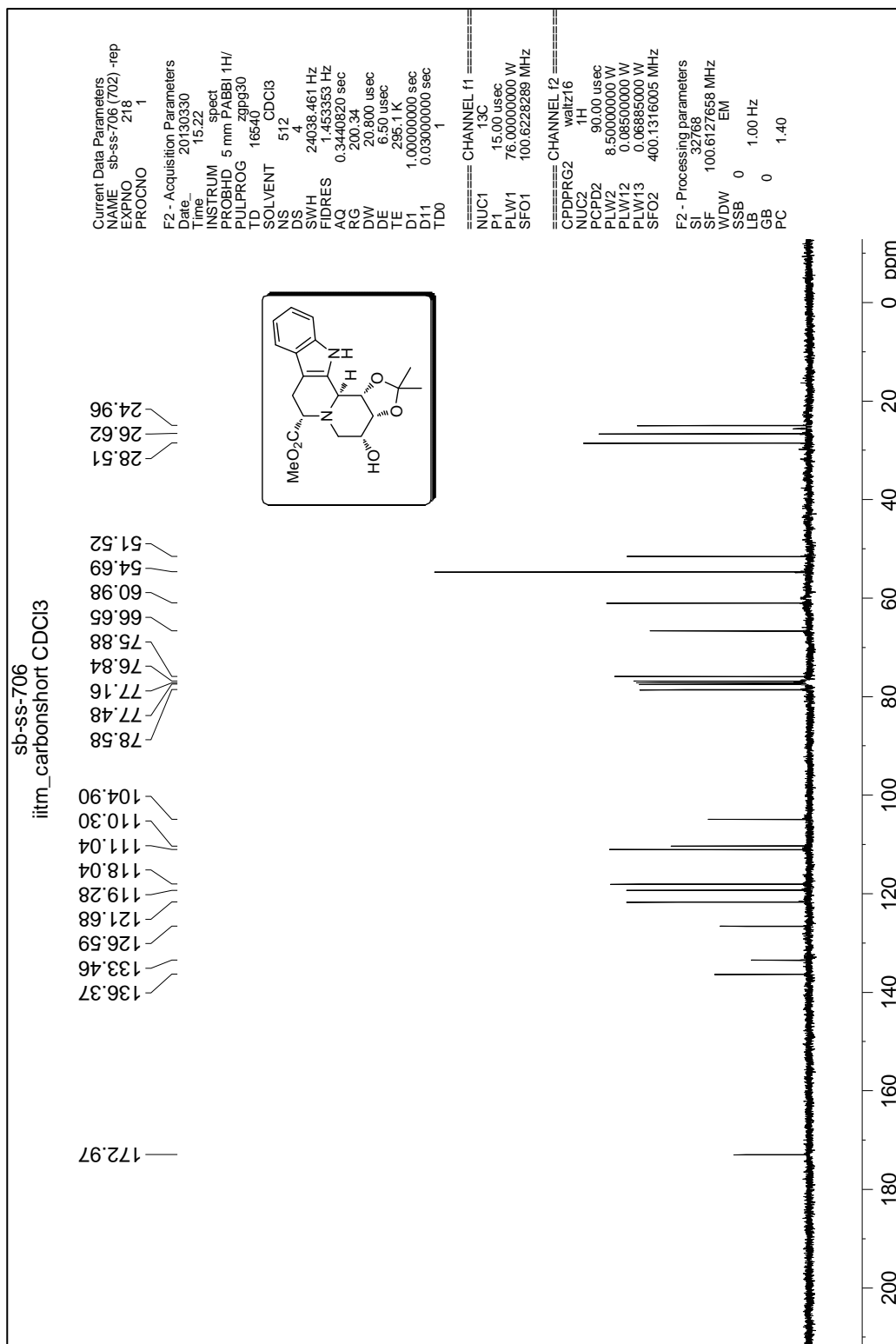


Expanded  $^1\text{H}$  NMR spectrum of compound **22**

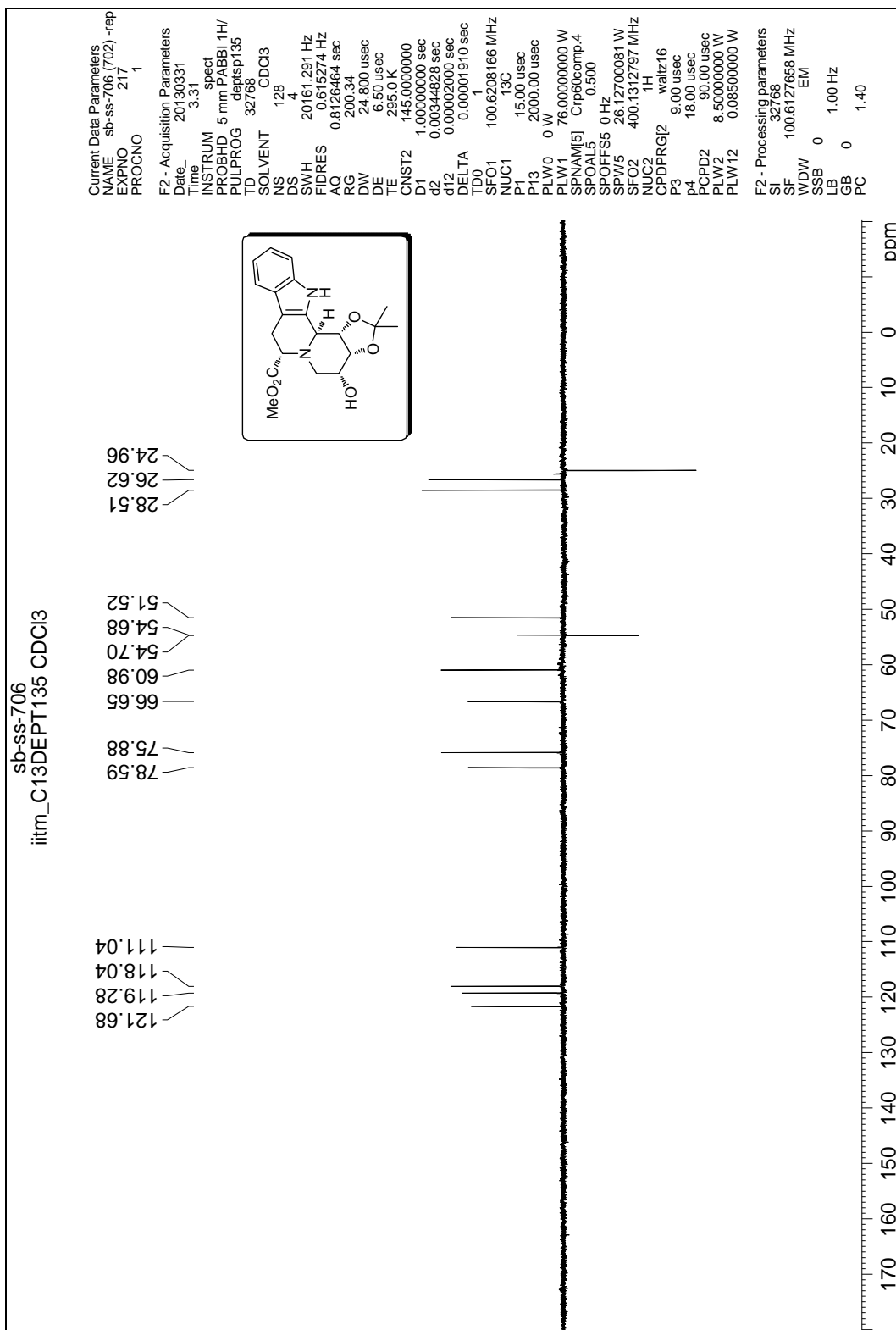


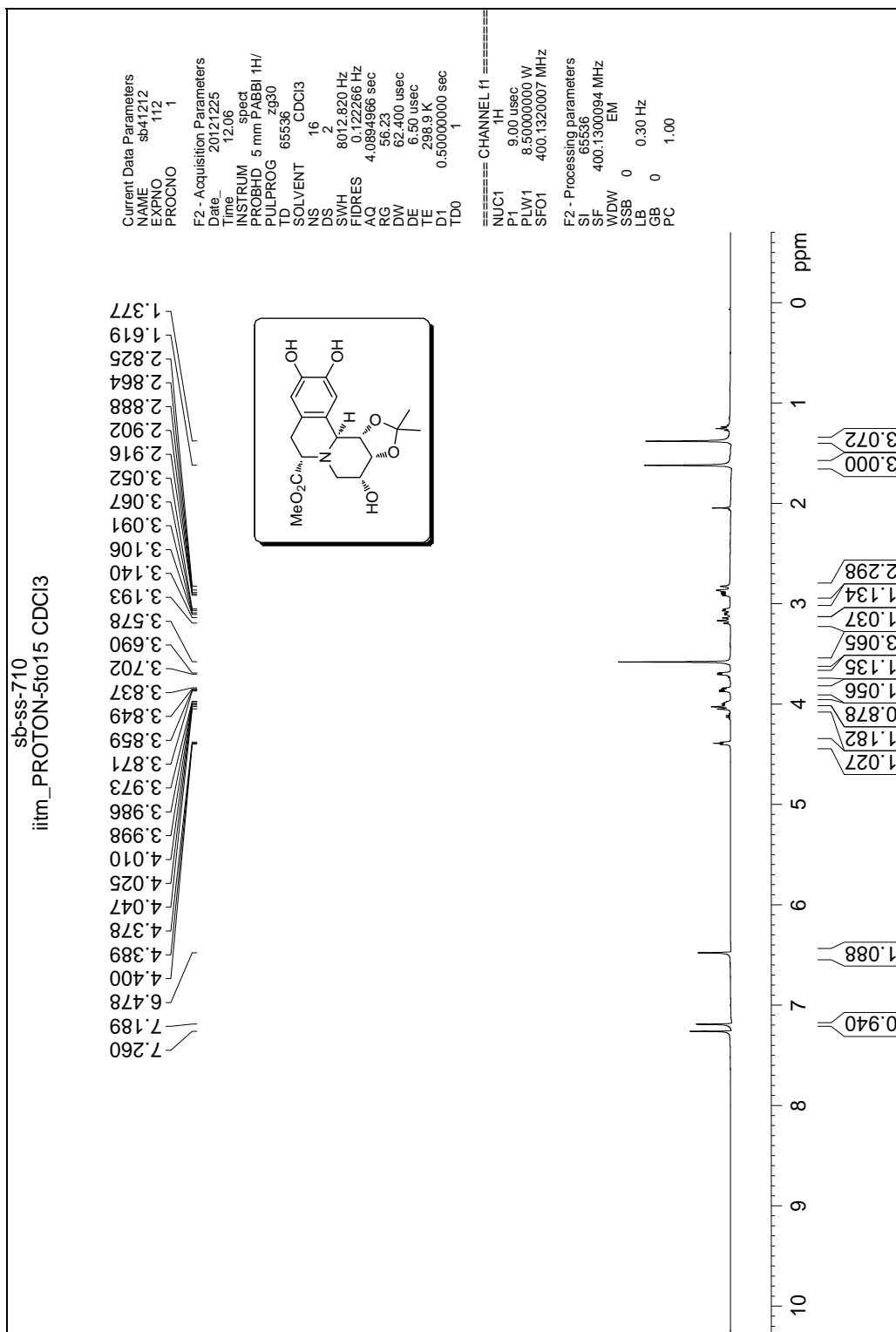


<sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of Compound **22**

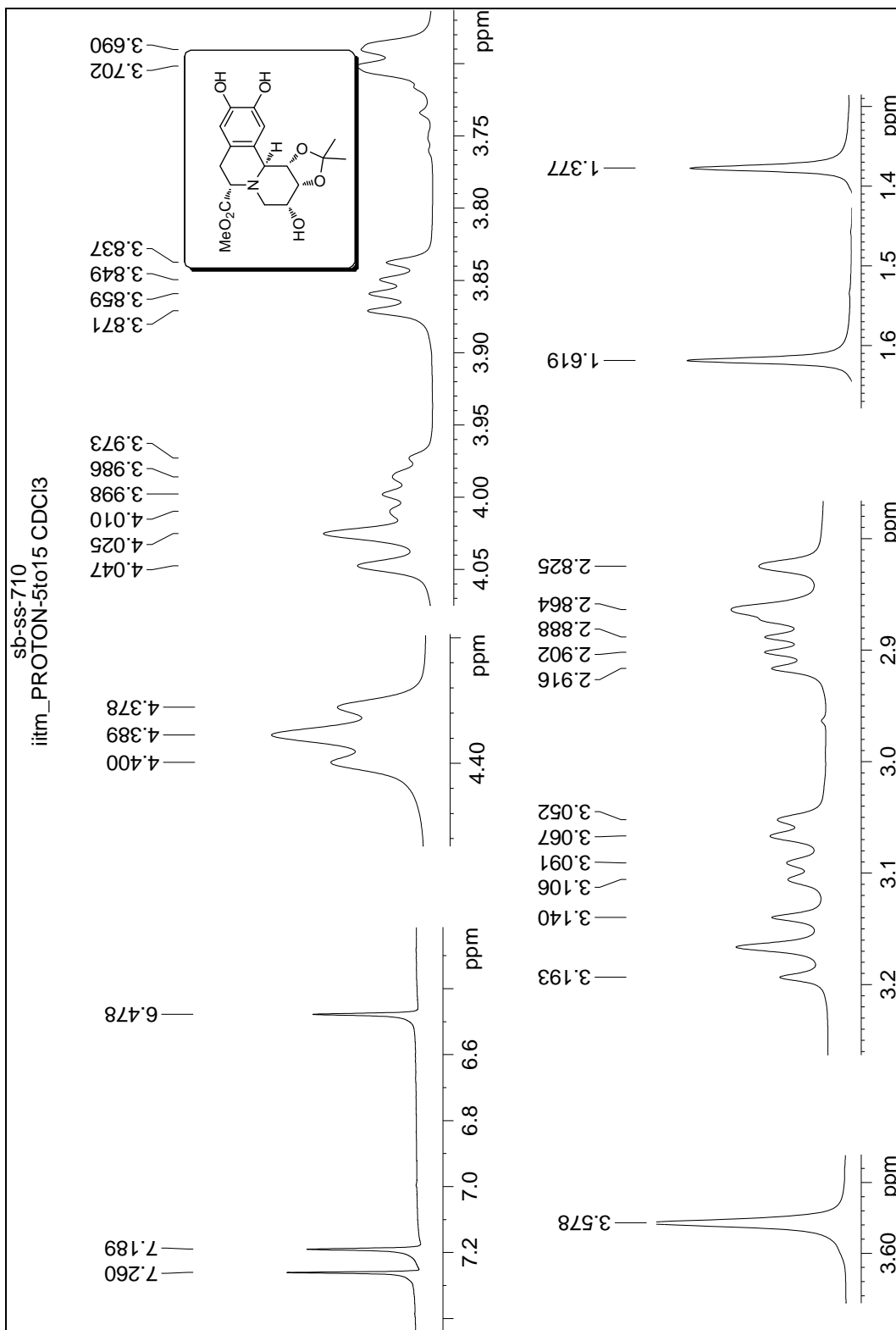


<sup>13</sup>C NMR spectrum of compound 22

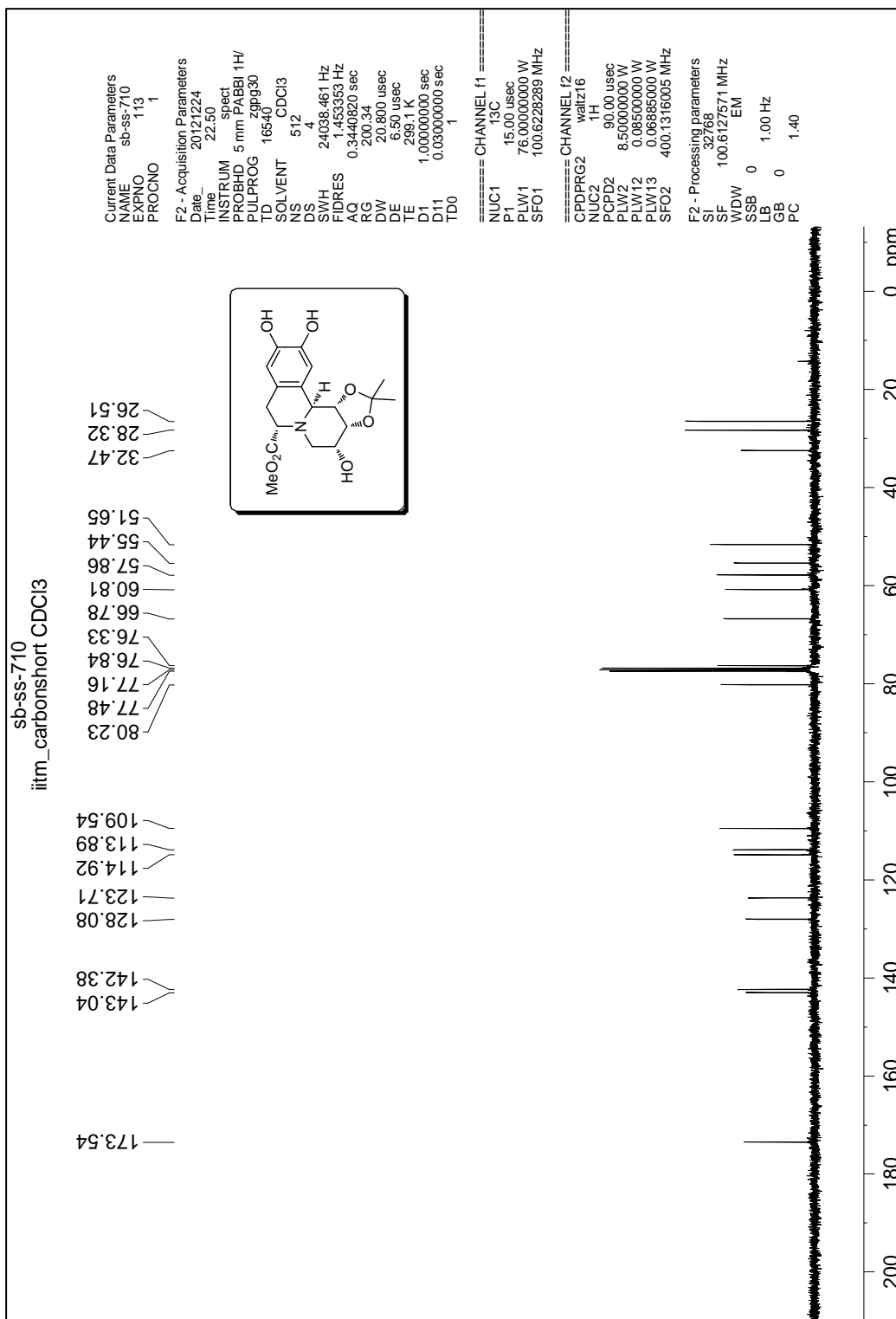




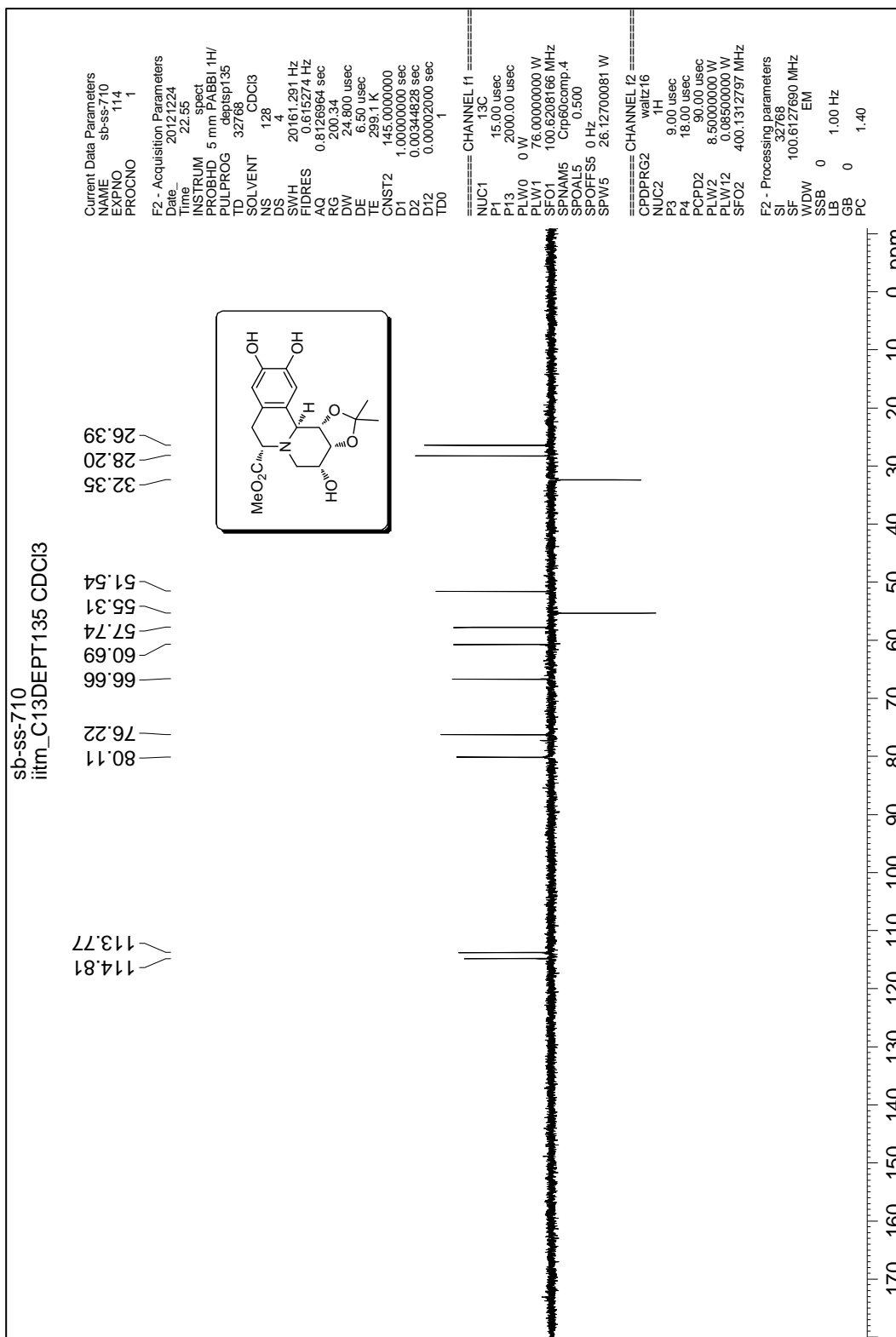
<sup>1</sup>H NMR spectrum of compound 24



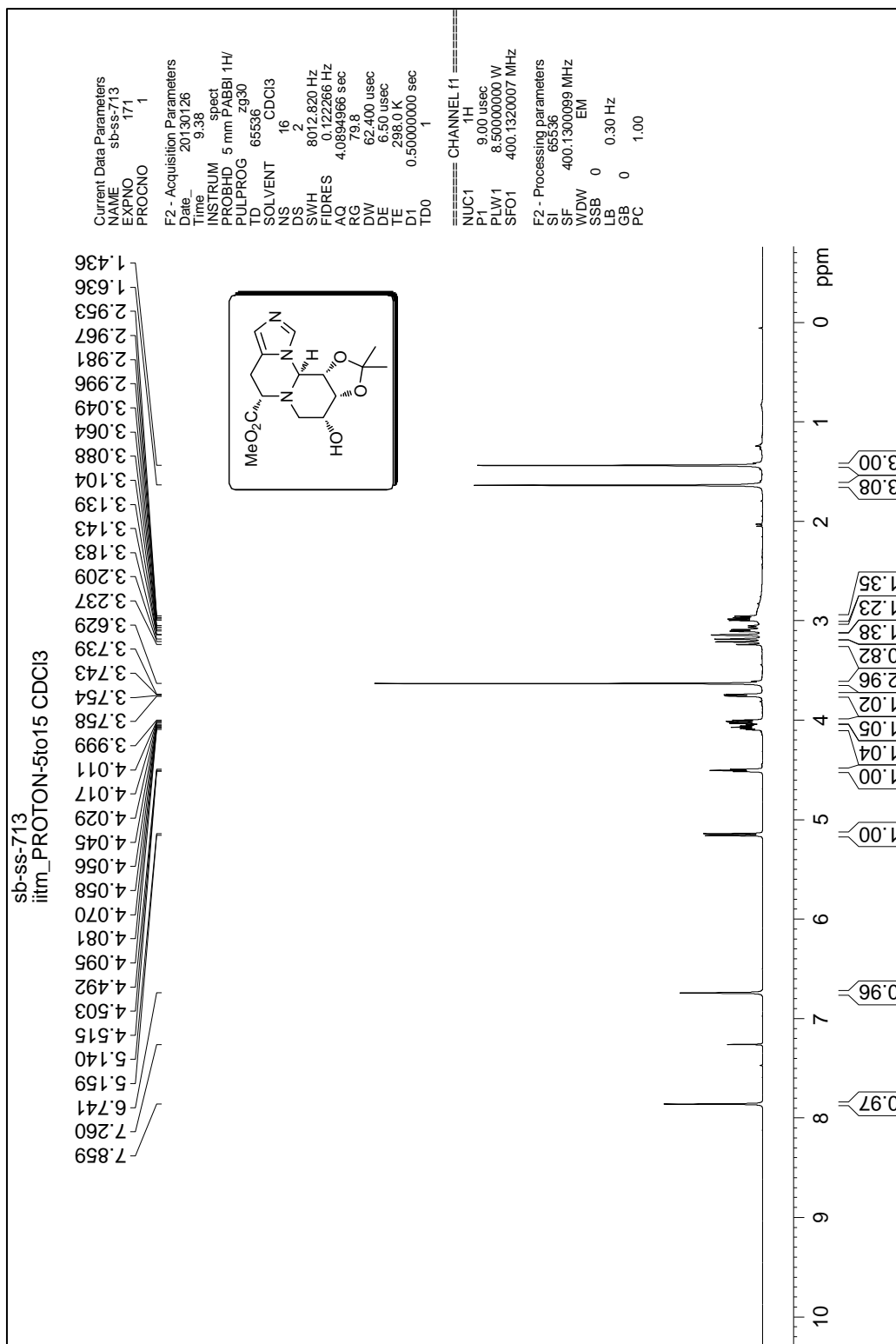
Expanded <sup>1</sup>H NMR spectrum of compound **24**



<sup>13</sup>C NMR spectrum of compound 24

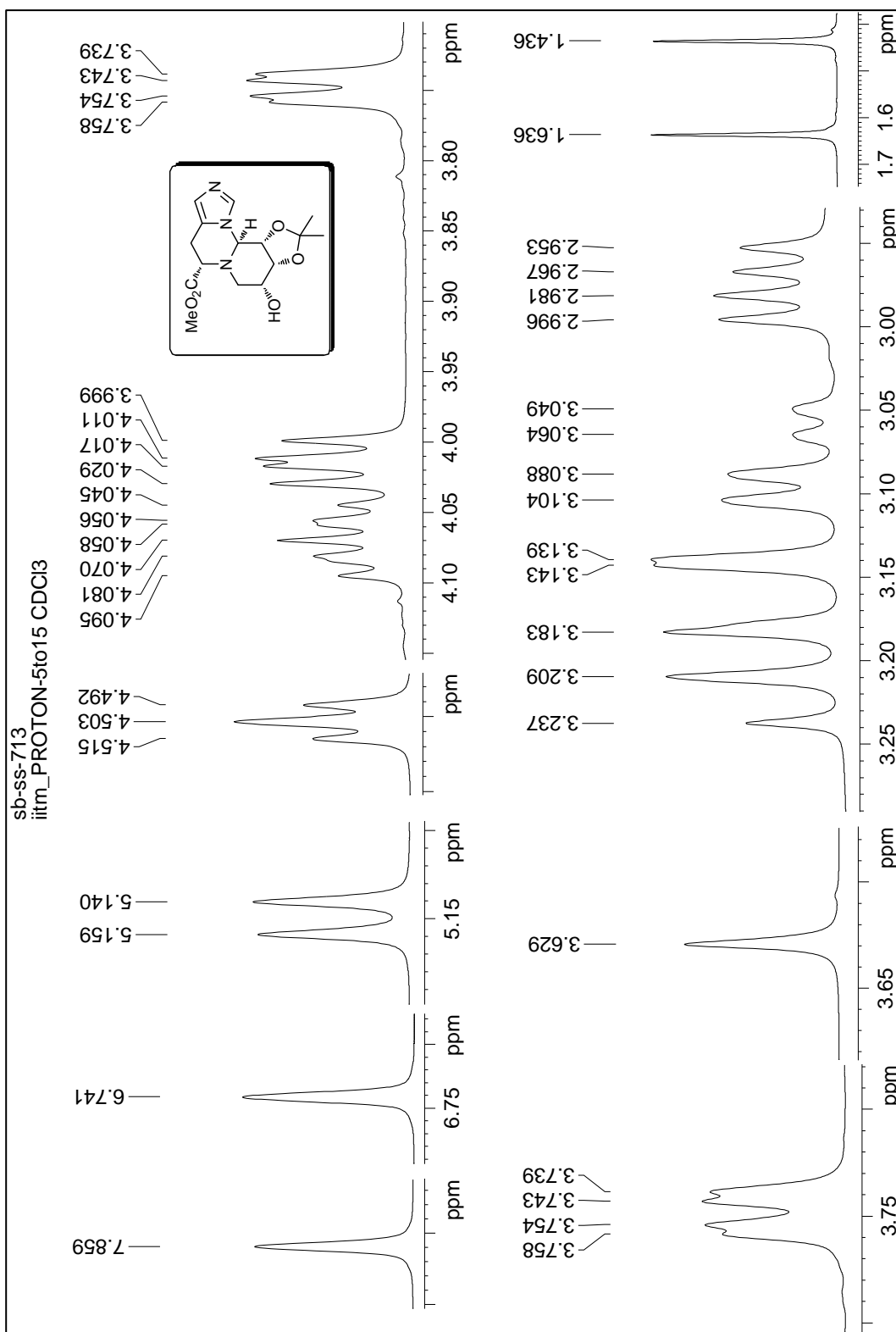


DEPT NMR spectrum of compound **24**

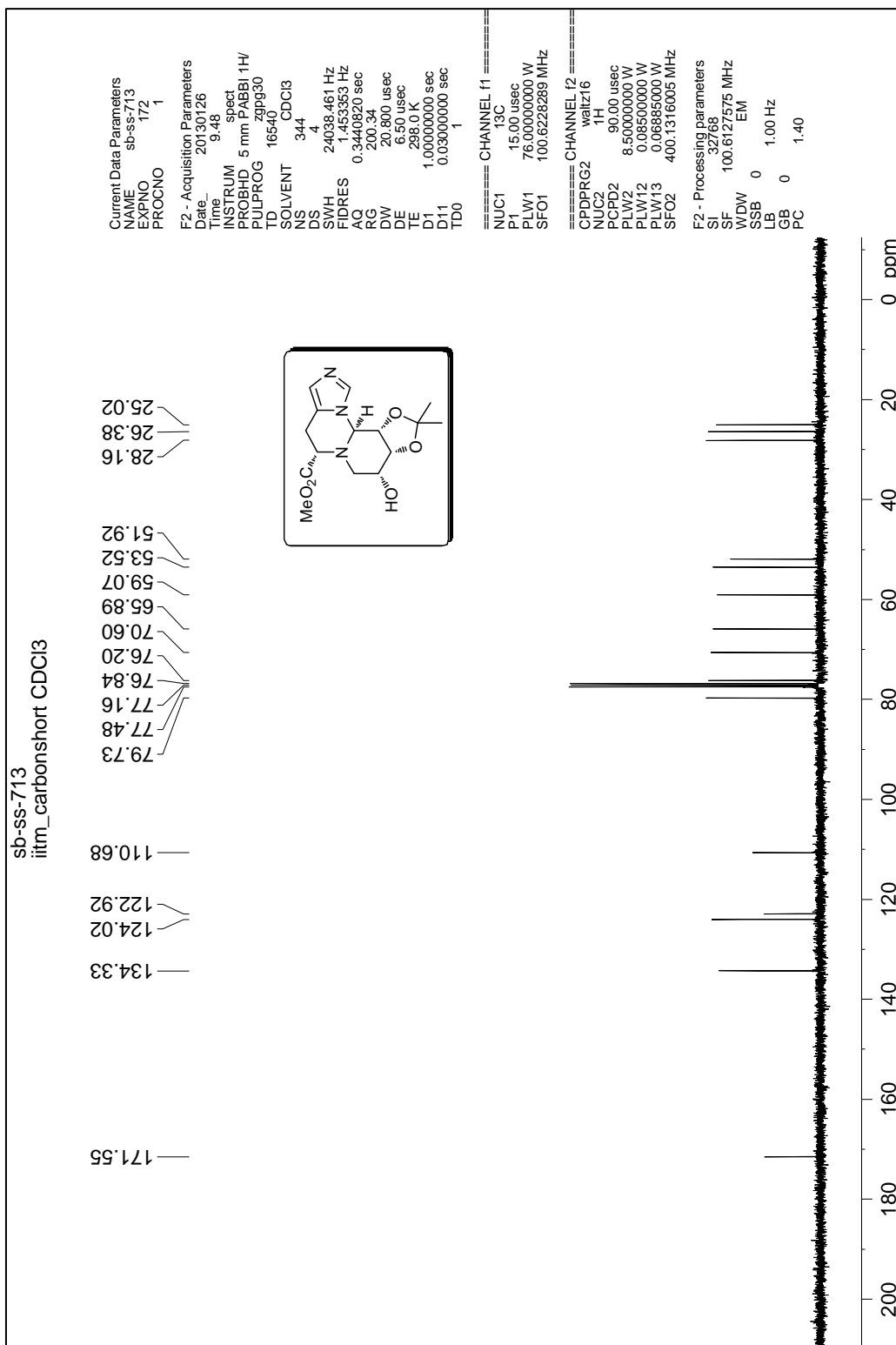


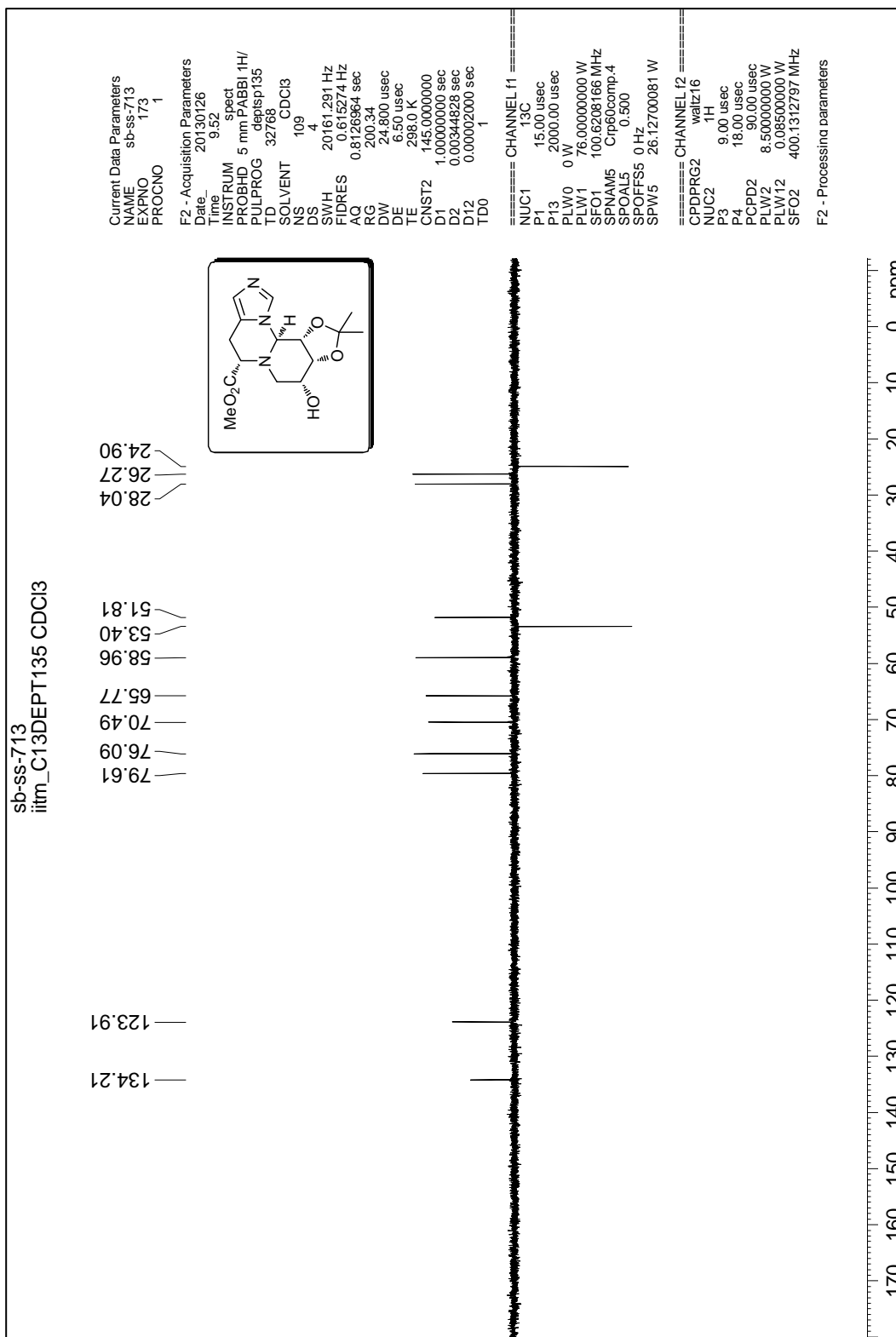
<sup>1</sup>H NMR spectrum of compound 26

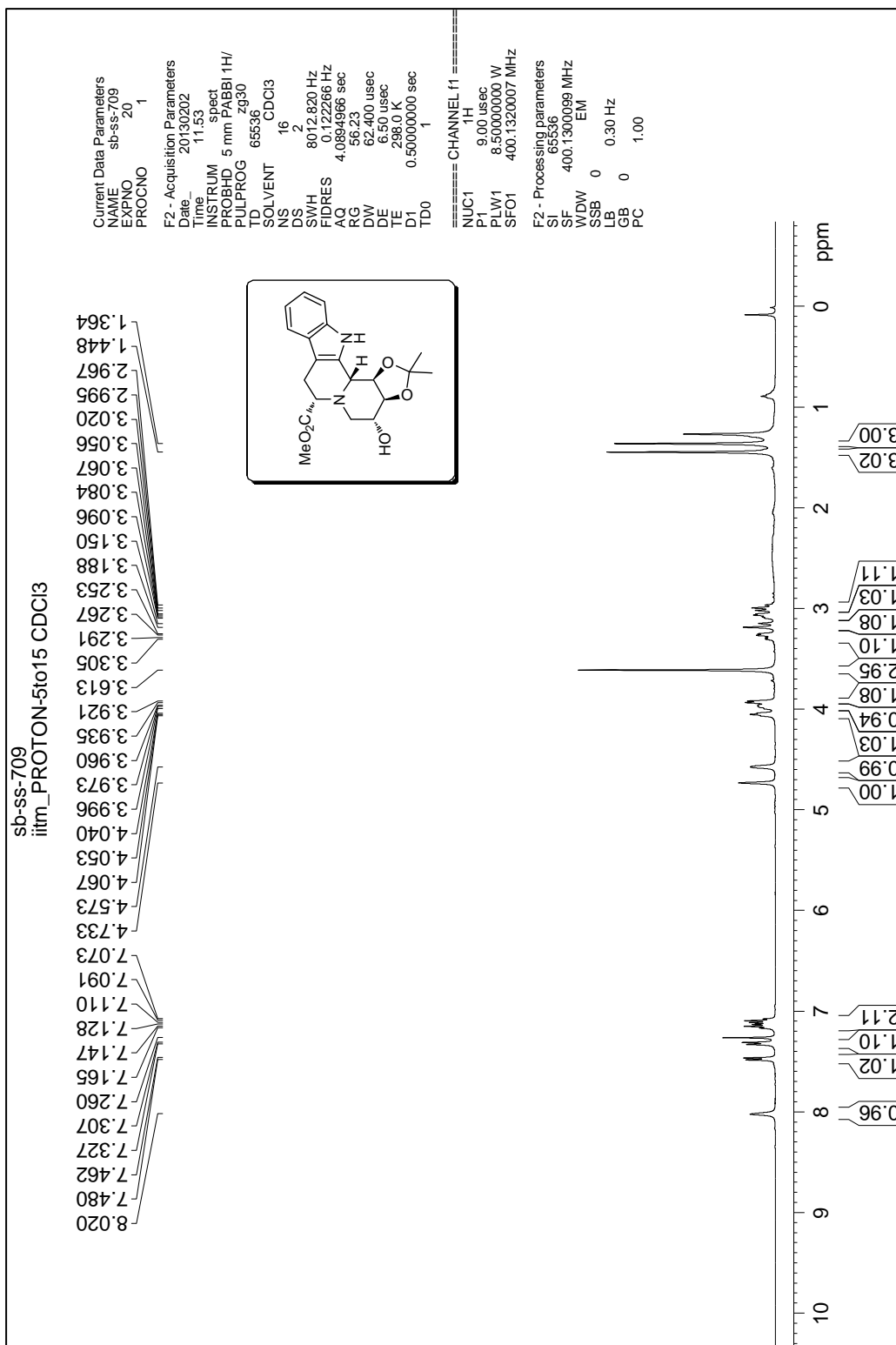




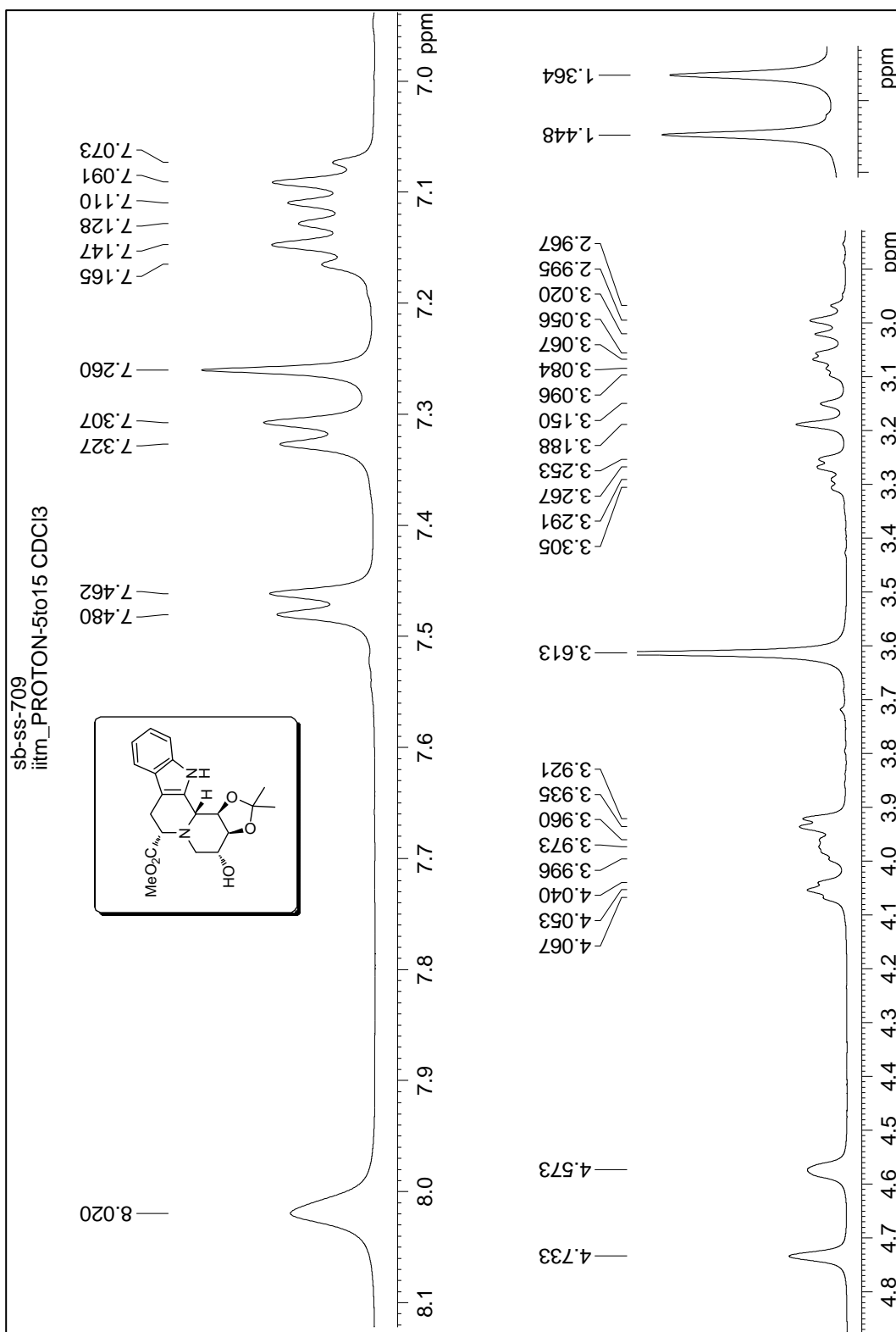
Expanded  $^1\text{H}$  NMR spectrum of compound 26



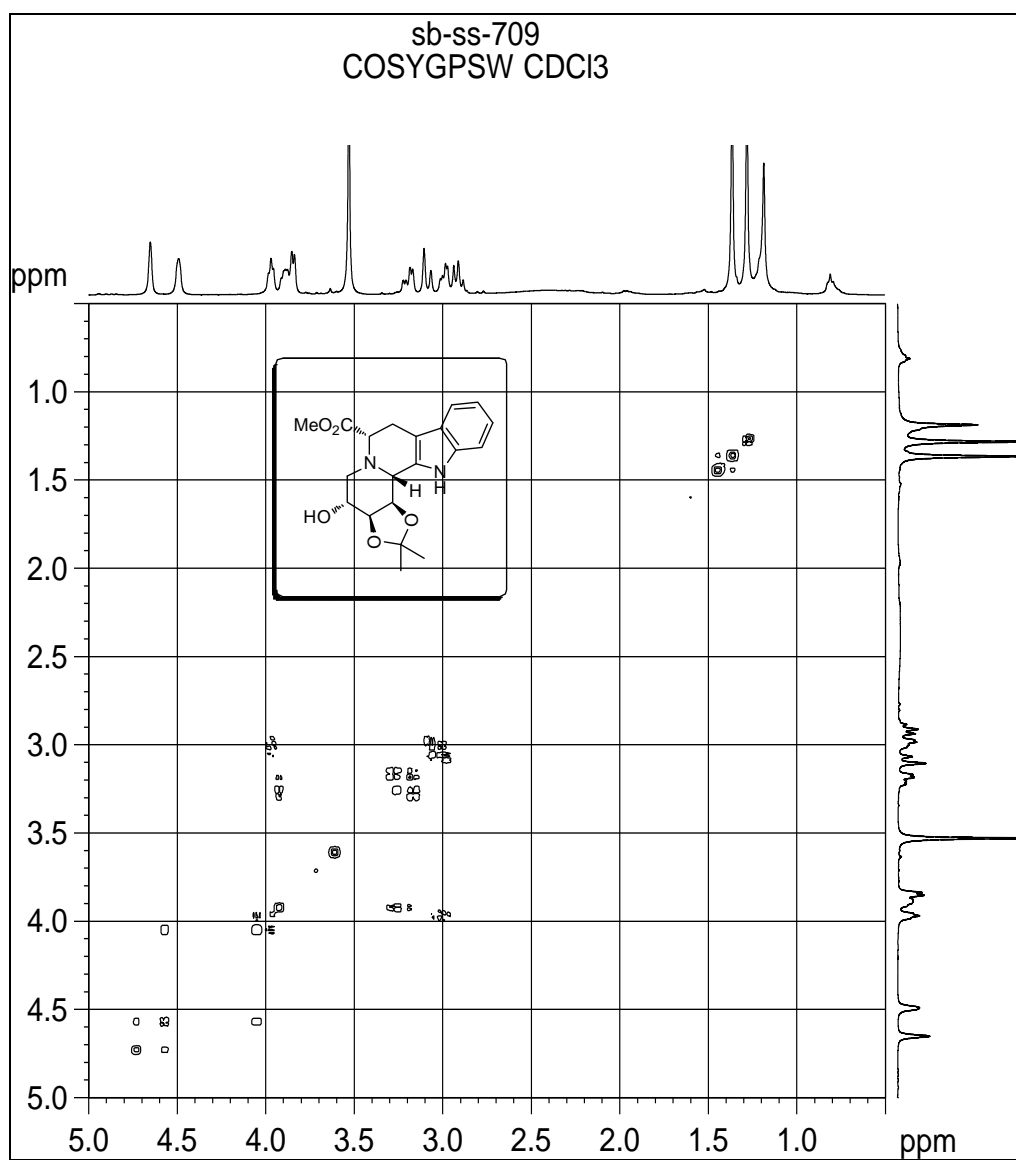




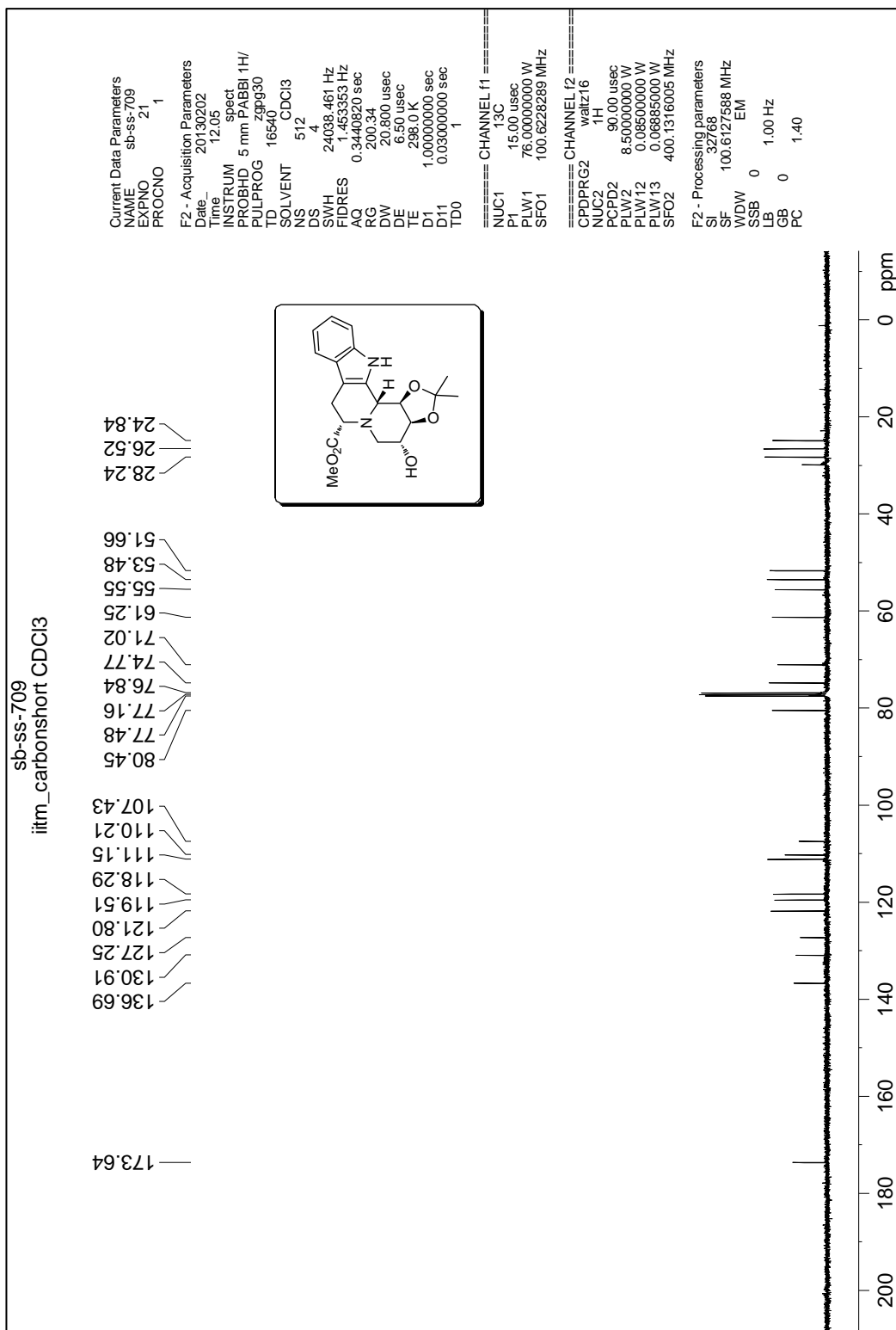
<sup>1</sup>H NMR spectrum of compound **27**



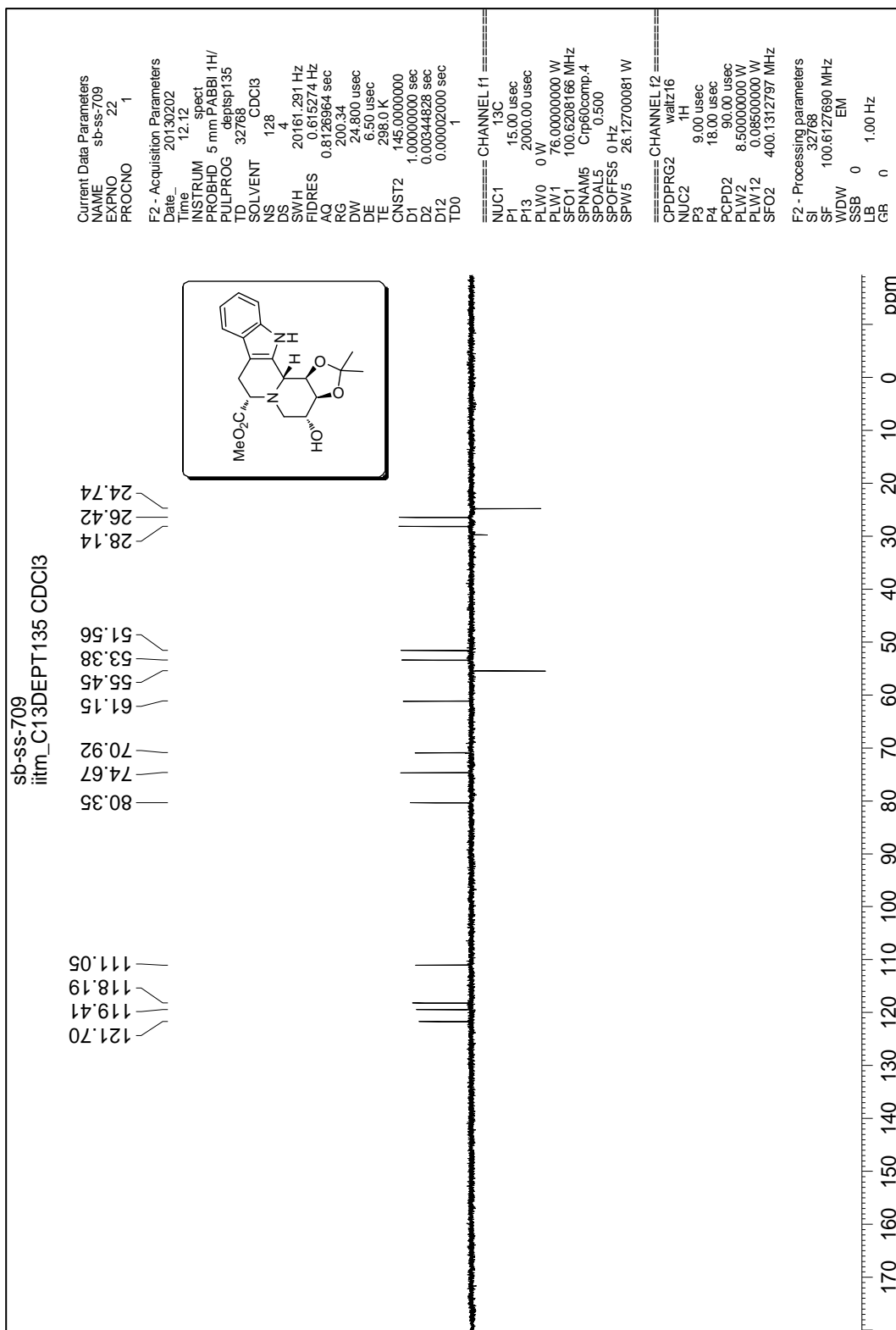
Expanded  $^1\text{H}$  NMR spectrum of compound **27**



<sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of Compound **27**

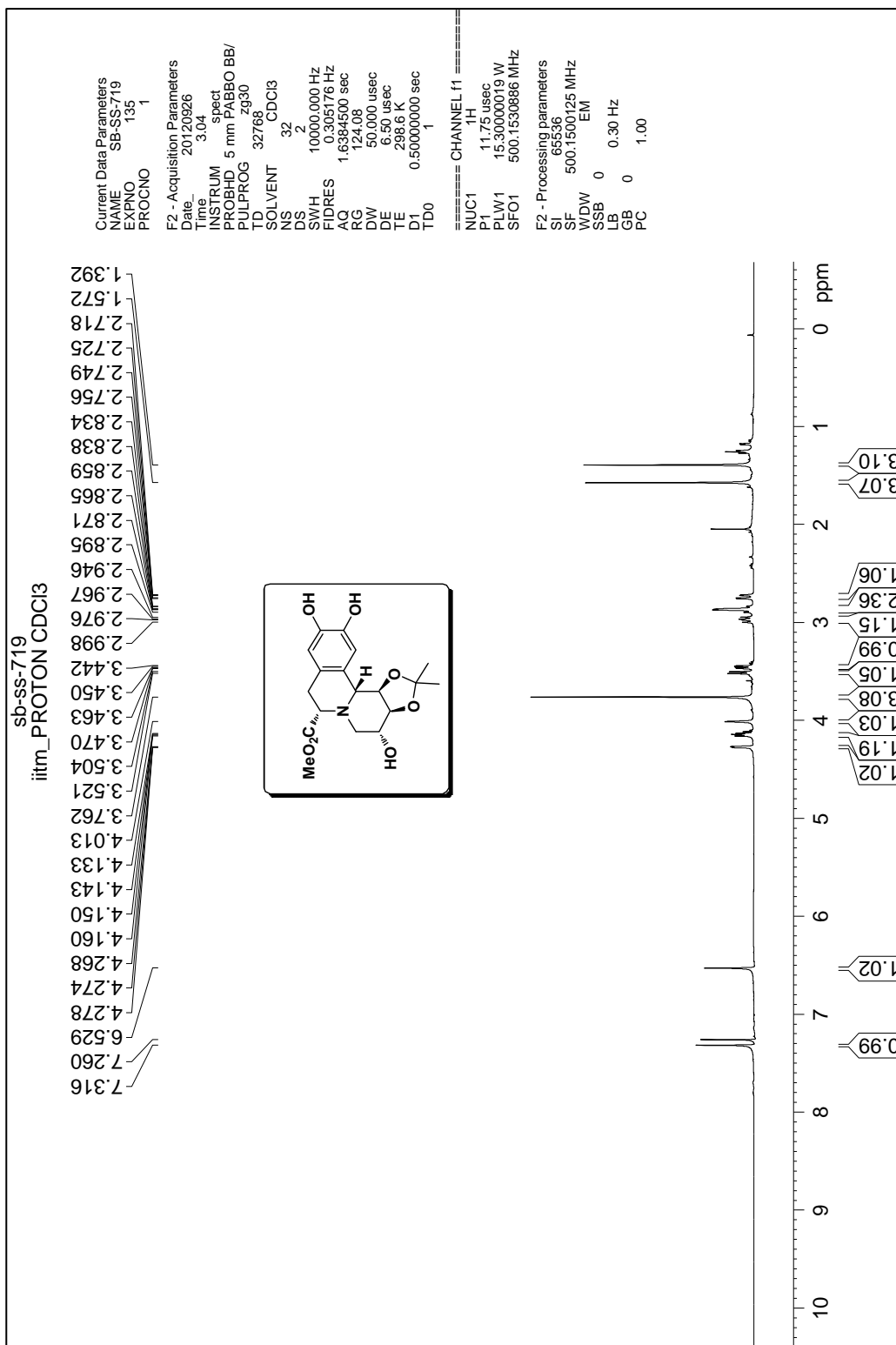


<sup>13</sup>C NMR spectrum of compound **27**

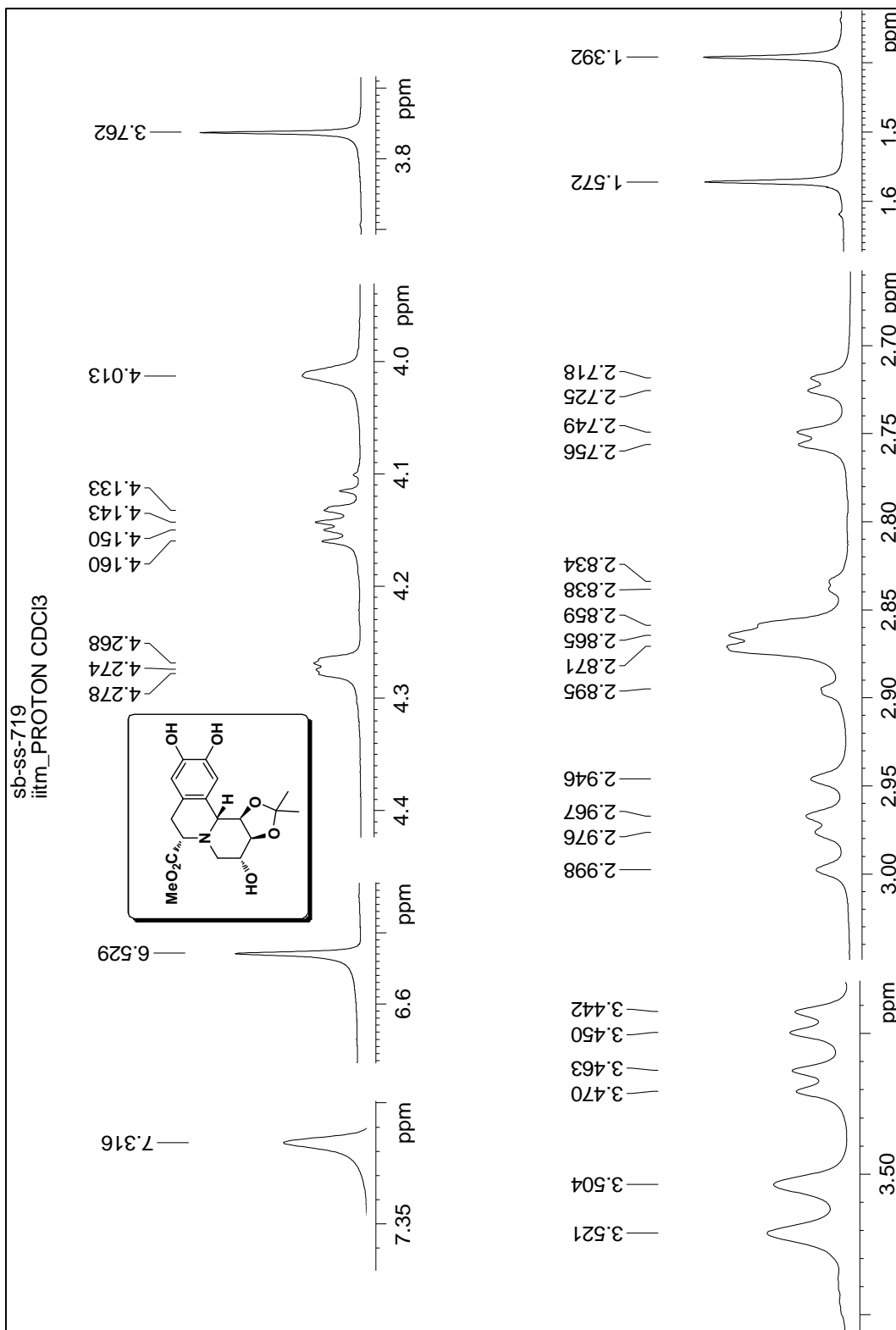


DEPT NMR spectrum of compound 27





<sup>1</sup>H NMR spectrum of compound 28



Expanded <sup>1</sup>H NMR spectrum of compound 28

