

## Electronic Supplementary Information

### **Benzothiazines in organic synthesis. Synthesis of fluorescent 7-amino-2,1-benzothiazines**

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## 1. General Information

Glassware was oven dried (125 °C) and cooled by a continuous flow of dry nitrogen. The reaction involving organometallic reagents was carried out under anhydrous and oxygen-free condition. THF was dried over sodium metal and oxygen was removed by generation of a benzophenoneketyl. Toluene and DMF were used directly from commercial bottles without any distillation under anhydrous condition. Liquid reagents were distilled prior to use if liquid and solid reagents were crystallized or used directly from a newly purchased commercial container. Air and moisture sensitive reagents were handled under a dry argon atmosphere.

Melting points taken of new compounds were done so by a Fisher-Johns melting point apparatus. IR spectra were recorded via a liquid NaCl chamber on a Perkin Elmer 1600 series FT-IR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR were taken on Bruker ARX-300 Ultrashield spectrometers. Chemical shifts reported were in ppm with an internal TMS standard (TMS; δ = 0.0). Spectra were taken with CDCl<sub>3</sub> solution containing TMS. NMR data is reported as follows: chemical shift, ppm; splitting pattern (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, etc.); coupling constant, Hz; and integration. <sup>13</sup>C NMR spectra taken were <sup>1</sup>H decoupled and contained a CDCl<sub>3</sub> (TMS; δ = 0.00) internal standard. HRMS were analyzed by a Bruker 12 Tesla Apex-Qe FTICR-MS with an Apollo II ion source.

UV absorption spectra of the solutions were measured on Varian-CARY-100 BIO UV-VIS Spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer. Optical rotations were measured on a Jasco DIP-370 Digital Polarimeter.

## 2. General procedure for preparation of 4-amino-2-chlorobenzaldehydes

The rounded bottom flask equipped with a condenser was charged with 2-chloro-4-fluorobenzaldehyde (1 equiv), amine (1.5 equiv), potassium carbonate ( $K_2CO_3$ ) (1.6 equiv) and DMF (0.1 M of aldehyde in DMF). The reaction mixture was heated at 100°C for 20 hours. After 20 hours of stirring at 100°C, the mixture was cooled down to room temperature and diluted with ether, and then extracted with water. The combined organic layer was washed with brine, dried over  $MgSO_4$ , and concentrated in vacuo. The resulting crude product was purified by column chromatography on silica gel with 10% EtOAc:Hexane.

### 2-Chloro-4-morpholinobenzaldehyde (7a)

White solid; 87% yield; m.p: 79-81°C;  $R_f$  = 0.22 in 30% EtOAc/hexane; IR: 3015, 2859, 1593, 1221, 1033 726,  $cm^{-1}$ ;  $^1H$ -NMR (300 MHz,  $CDCl_3$ ):  $\delta$  10.24 (s, 1H), 7.82 (d,  $J$  = 9.3Hz, 1H), 6.79 (t,  $J$  = 2.6Hz, 2H), 3.85 (t,  $J$  = 5.0Hz, 4H), 3.35 (t,  $J$  = 5.0 Hz, 4H);  $^{13}C$ -NMR (75 MHz,  $CDCl_3$ ):  $\delta$  188.2, 155.2, 140.1, 130.8, 123.4, 113.9, 112.1, 66.3(2C), 47.0 (2C); HRMS calcd for  $C_{11}H_{12}ClNO_2Na$  [ $M+Na$ ] $^+$ 248.0449; Found 248.0450.

### 2-chloro-4-(pyrrolidin-1-yl)-benzaldehyde (7b)

Yellow crystal; 97% yield; m.p.: 78-80°C;  $R_f$  = 0.27 in 10% EtOAc/hexane; IR: 3018, 2856, 1663, 1594, 1217, 1023 721,  $cm^{-1}$ ;  $^1H$ -NMR (300 MHz,  $CDCl_3$ ):  $\delta$  10.19 (s, 1H), 7.80 (d,  $J$  = 9.3Hz, 1H), 6.47 (d,  $J$  = 2.1Hz, 2H), 3.38 (t,  $J$  = 6.6Hz, 4H), 2.06 (pentet,  $J$  = 3.4Hz, 4H);  $^{13}C$ -NMR (75 MHz,  $CDCl_3$ ):  $\delta$  188.1, 152.0, 140.2, 130.9, 120.8, 111.5, 110.4, 47.7(2C), 25.3(2C); HRMS calcd for  $C_{11}H_{12}ClNONa$  [ $M+Na$ ] $^+$ 232.0500; Found 232.0501.

### 2-chloro-4-(piperidin-1-yl)benzaldehyde (7c)

Yellow semi solid; 87% yield;  $R_f$  = 0.29 in 10% EtOAc/hexane; IR: 3019, 2942, 2859, 1658, 1589, 1229, 1025 730, 665  $cm^{-1}$ ;  $^1H$ -NMR (300 MHz,  $CDCl_3$ ):  $\delta$  10.18 (s, 1H), 7.77 (d,  $J$

= 9.6Hz, 1H), 6.75-6.73 (m, 2H), 3.40 (d,  $J = 5.1$ Hz, 4H), 1.17 (s, 6H);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.8, 155.0, 140.2, 130.8, 121.7, 113.3, 111.8, 48.1(2C), 25.2 (2C), 24.2; HRMS calcd for  $\text{C}_{12}\text{H}_{14}\text{ClNO}_2\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ 246.0656; Found 246.0656.

**4-(azepan-1-yl)-2-chlorobenzaldehyde (7d)**

Brown solid; 85% yield; mp.: 45-46°C;  $R_f = 0.47$  in 10% EtOAc/hexane; IR: 2933, 2855, 1658, 1589, 1221, 1029 784  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.16 (s, 1H), 7.77 (d,  $J = 9.6$ Hz, 1H), 6.60-6.58 (m, 2H), 3.50 (t,  $J = 6.0$ Hz, 4H), 1.80 (s, 4H), 1.56 (t,  $J = 2.9$ Hz, 4H);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.9, 153.7, 140.5, 131.1, 120.8, 111.0, 109.8, 49.7(2C), 27.2 (2C), 26.7 (2C); HRMS calcd for  $(\text{C}_{13}\text{H}_{16}\text{ClNO})_2\text{Na}$  [ $2\text{M}+\text{Na}$ ] $^+$  497.1733; Found 497.1738.

**2-Chloro-4-diallylaminobenzaldehyde (7e)**

Yellow oil; 98% yield;  $R_f = 0.51$  in 10% EtOAc/hexane; IR: 3088, 3015, 2864, 1667, 1593, 1392, 1233, 1148, 726, 661  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.17 (s, 1H), 7.75 (m, 1H), 6.58 (m, 2H), 5.87-5.76 (m, 2H) 5.24-5.12 (m, 4H) 3.98 (m, 4H);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.0, 153.6, 140.2, 131.8 (2C), 130.9, 121.6, 117.0 (2C), 111.9, 110.6, 52.8(2C); HRMS calcd for  $(\text{C}_{13}\text{H}_{14}\text{ClNO})_2\text{Na}$  [ $2\text{M}+\text{Na}$ ] $^+$ 493.1420; Found 493.1427.

**2-Chloro-4-diethylaminobenzaldehyde (7f)**

Yellow solid; 94% yield; mp: 25°C;  $R_f = 0.31$  in 10% EtOAc/hexane; IR: 3019, 2978, 2868, 1662, 1589, 1519, 1352, 1254, 1029, 788, 669  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.16 (s, 1H), 7.78 (d,  $J = 9.3$ Hz, 1H), 6.56-6.55 (m, 2H), 3.41 (q,  $J = 7.1$ Hz, 4H), 1.21 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.8, 152.5, 140.5, 131.0, 120.6, 110.9, 109.7, 44.8 (2C), 12.4 (2C); HRMS calcd for  $(\text{C}_{11}\text{H}_{14}\text{ClNO})_2\text{Na}$  [ $2\text{M}+\text{Na}$ ] $^+$ 445.1420; Found 445.1416.

### **2-Bromo-4-diallyaminobenzaldehyde (9e)**

Yellow oil; 98% yield;  $R_f = 0.37$  in 30% EtOAc/hexane; IR: 3011, 2859, 1662, 1580, 1507, 1384, 1021, 665  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.10 (s, 1H), 7.75 (m, 1H), 6.80 (d,  $J = 2.4\text{Hz}$ , 1H), 6.63 (dd,  $J = 9.0, 2.1\text{Hz}$ , 1H) 5.87-5.77 (m, 2H) 5.24-5.13 (m, 4H) 3.97 (m, 4H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.1, 153.6, 131.7 (2C), 131.2, 129.7, 122.5, 117.0 (2C), 115.2, 111.0, 52.7(2C); HRMS calcd for  $(\text{C}_{13}\text{H}_{14}\text{BrNO})_2\text{Na}$  [ $2\text{M}+\text{Na}$ ] $^+$  581.0410; Found 581.0414.

### **3. General procedure for Pd-Catalyzed *N*-Arylation of a sulfoximine with 4-amino - 2-chlorobenzaldehydes**

4-Amino-2-chlorobenzaldehyde (0.100 g), sulfoximine (1.2 equiv),  $\text{Pd}_2(\text{dba})_3$  (0.05 equiv),  $\text{Cs}_2\text{CO}_3$  (1.4 equiv), and RuPhos (0.1 equiv) were added together in a sealed tube in air with toluene (0.1 M concentration of aryl chloride in toluene). The sealed tube was capped in air and heated to 135 °C. The reaction was stopped after 36 hours. Once at room temperature, the reaction was diluted in dichloromethane (20 mL) and filtered through a plug of celite. After being concentrated in vacuo, the crude product was purified by flash chromatography (silica gel).

### **(*R*)-7-Morpholino-2,1-benzothiazine (8a)**

The product was purified by column chromatography on silica gel with 10% EtOAc:Hexane to give a pale yellow solid(98% yield);  $R_f = 0.36$  in 50% EtOAc/hexane; m.p.: 220-223°C; IR: 3019, 1605, 1511, 1204, 722  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90-7.86 (m, 2H), 7.60-7.53 (m, 4H), 7.30 (d,  $J = 2.7\text{Hz}$ , 1H), 6.70 (d,  $J = 2.4\text{Hz}$ , 1H), 6.65 (dd,  $J = 8.7, 2.7\text{Hz}$ , 1H) 6.15 (d,  $J = 9.6\text{Hz}$ , 1H), 3.85 (t,  $J = 5.0\text{Hz}$ , 4H), 3.28 (t,  $J = 5.0\text{Hz}$ , 4H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ): 154.1, 146.8, 142.3, 138.5, 133.0, 130.6, 128.9 (2C), 128.5(2C), 109.2, 109.1,

107.4, 105.6, 66.7(2C), 48.1(2C); HRMS calcd for (C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S) Na [M+Na]<sup>+</sup>349.0981; Found 349.0978.; [α]<sub>D</sub> = -660.8°.

**7-(Pyrrolidin-1-yl)-2,1-benzothiazine (8b)**

Yellow crystal, (93% yield); R<sub>f</sub> = 0.53 in 50% EtOAc/hexane; m.p.: 242-245°C; IR: 3015, 1609, 1507, 1254, 1121, 723 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.89-7.86 (m, 2H), 7.57-7.49 (m, 4H), 7.17 (d, *J* = 8.7 Hz, 1H), 6.38-6.33 (m, 2H), 6.00 (d, *J* = 9.6 Hz, 1H), 3.36 (t, *J* = 6.8 Hz, 4H), 2.01 (pentet, *J* = 3.3 Hz, 4H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 150.9, 146.9, 143.0, 139.1, 132.7, 130.9, 128.8 (2C), 128.3(2C), 106.9, 106.8, 103.7, 102.9, 47.6(2C), 25.5(2C); HRMS calcd for (C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>OS) Na [M+Na]<sup>+</sup>333.1032; Found 333.1032.

**(R)-7-Piperidinyl-2,1-benzothiazine (8c)**

Yellow crystal, (82% yield); R<sub>f</sub> = 0.56 in 50% EtOAc/hexane; m.p.: 200-203°C; IR: 3011, 2941, 1609, 1580, 1499, 1221, 1115, 723 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.90-7.87 (m, 2H), 7.56-7.50 (m, 4H), 7.19 (d, *J* = 8.7 Hz, 1H), 6.70-6.65 (m, 2H), 6.08 (d, *J* = 9.6 Hz, 1H), 3.35-3.32 (m, 4H), 1.67-1.65 (m, 6H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 154.5, 147.0, 142.7, 138.7, 133.0, 130.7, 129.0 (2C), 128.6(2C), 109.8, 108.3, 107.3, 104.6, 49.3(2C), 25.6(2C), 24.6; HRMS calcd for (C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>OS) Na [M+Na]<sup>+</sup>347.1189; Found 347.1185. [α]<sub>D</sub> = -896°.

**(R)-7-(azepan-1-yl)-2,1-benzothiazine (8d)**

Yellow crystal, (93% yield); R<sub>f</sub> = 0.63 in 50% EtOAc/hexane; m.p.: 148-149°C; IR: 2933, 1609, 1567, 1503, 1241, 1151, 726 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.91-7.88 (m, 2H), 7.57-7.48 (m, 4H), 7.16 (d, *J* = 8.7 Hz, 1H), 6.51-6.45 (m, 2H), 6.00 (d, *J* = 9.3 Hz, 1H), 3.52 (t, *J* = 5.9 Hz, 4H), 1.80 (s, 4H), 1.57-1.53 (m, 6H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 152.1, 147.1, 143.0, 138.8, 132.7, 131.0, 129.1, 128.8 (2C), 128.4(2C), 106.8, 106.2, 103.3, 103.0, 49.5(2C),

27.6(2C), 26.9 (2C); HRMS calcd for (C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>OS)Na [M+Na]<sup>+</sup>361.1345; Found 361.1350.[α]<sub>D</sub> = -1054°.

**(R)-7-Diethylamino-2,1-benzothiazine (8f)**

Yellow crystal, (88% yield); R<sub>f</sub> = 0.55 in 50% EtOAc/hexane; m.p.:148-150°C; IR: 3027, 2930, 1609, 1580, 1503, 1245, 1221, 722 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.90-7.87 (m, 2H), 7.56-7.50 (m, 4H), 7.16 (d, J = 8.7 Hz, 1H), 6.48-6.43 (m, 2H), 6.00 (d, J = 9.3 Hz, 1H), 3.41 (q, J = 7.2 Hz, 4H), 1.20 (t, J = 7.1Hz, 6H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 151.0, 147.1, 142.9, 138.8, 132.7, 131.0, 128.8 (2C), 128.4(2C), 106.6, 106.3, 103.3, 103.0, 44.5(2C), 12.7(2C); HRMS calcd for (C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>OS)Na [M+Na]<sup>+</sup>335.1189; Found 335.1181.[α]<sub>D</sub> = -160.0°.

**4-Diallylamino-2,1-benzothiazine (8e)**

2-Bromo-4-diallylaminobenzaldehyde(108 mg, 0.38mmol), (*rac*)-sulfozimine (71 mg, 0.46mmol), Pd(OAc)<sub>2</sub> (4.3 mg, 0.0193mmol), (*rac*)-BINAP (18 mg, 0.029mmol), Cs<sub>2</sub>CO<sub>3</sub>(176 mg, 0.54mmol) and toluene (3.8 mL) were added all together in sealed tube. The sealed tube was capped in air and heated at 135°C for 48 hours. The reaction was cooled down at room temperature, diluted with EtOAc and then filtered through Celite. The filtrate was concentrated in vacuo and then purified by column chromatography on silica gel with 10%EtOAc:Hexane to give a yellow oil, 107.9mg (83% yield); R<sub>f</sub> = 0.37 in 30% EtOAc/hexane;IR: 3002, 2978, 1605, 1508, 1221, 788 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.89-7.86 (m, 2H), 7.56-7.47 (m, 4H), 7.14 (d, J = 8.7 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 6.44 (dd, J = 9.0, 2.4Hz, 1H), 6.02 (d, J = 9.6Hz, 1H), 5.91-5.79 (m, 2H), 5.2-5.14(m, 4H), 3.97-3.96 (m, 4H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 152.0, 147.0, 142.8, 138.8, 133.1 (2C), 132.8, 130.9, 128.9 (2C), 128.5(2C), 116.4 (2C),

107.4, 107.0, 104.3, 103.8, 52.6(2C); HRMS calcd for (C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>OS)Na [M+Na]<sup>+</sup>359.1190;  
Found 359.1192.

#### **4. General procedure for synthesis of the synthesis of 7-amino-2,1-benzothiazines via SnAr**

##### **7-Benzylamino-2,1-benzothiazine (8g)**

The mixture of 7-fluoro-2,1-benzothiazine (80 mg, 0.31 mmol), benzylamine (0.17 mL, 1.54 mmol), potassium carbonate, K<sub>2</sub>CO<sub>3</sub> (86 mg, 0.62 mmol) in DMF (1 mL) was heated at 100°C for 48 hours. The cooled reaction mixture was diluted with EtOAc (10 mL), and then washed with water. The combined organic layer was washed with brine, dried over Mg<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The resulting crude product was purified by column chromatography on silica gel with 10% EtOAc:Hexane to give a yellow solid, 79mg (74 % yield); m.p.: 172-173°C; IR: 3688, 3027, 1614, 1536, 1238, 1213, 722 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.58-7.49 (m, 4H), 7.36-7.27 (m, 5H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.05 (d, *J* = 9.5 Hz), 4.39 (s, 3H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): 151.6, 147.4, 142.6, 138.9, 138.6, 132.8, 131.0, 128.9(2C), 128.7(2C), 128.4(2C), 127.5(2C), 127.4, 108.4, 108.1, 103.8, 103.7, 47.8; HRMS calcd for (C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>OS)Na [M+Na]<sup>+</sup>369.1032; Found 369.1033.

The complete results are summarized in communication (**Table 3**).

#### **5. Synthesis of aldehyde 11**

To the solution of 8b (100 mg, 0.32 mmol) in THF (10 mL), was added *n*-butyllithium (2.36M, 0.15 mL, 0.35 mmol) at -78°C under argon. After stirring for 30 minutes, anhydrous DMF (30 μL, 0.38 mmol) was added to the reaction mixture. The reaction was carried



out for 2 hours then worked up with saturated NH<sub>4</sub>Cl solution, extracted with ether, washed with brine. The combined organic layer was dried over MgSO<sub>4</sub>. The organic solvents were removed under vacuo afforded crude as bright yellow oil. The crude was purified by column chromatography on silica gel with 10% EtOAc:Hexane to give a bright yellow solid, 64.8mg (60% yield); R<sub>f</sub> = 0.46 in 50% EtOAc/hexane; m.p.: 242-245°C; IR: 3019, 1609, 1576, 1478, 1397, 1204, 910, 784 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 9.39 (s, 1H), 7.97-7.92 (m, 3H), 7.61-7.51 (m, 3H), 7.28 (d, *J* = 10.2Hz, 2H), 6.44 (dd, *J* = 8.7, 2.1Hz, 1H), 6.30 (d, *J* = 2.1Hz, 1H), 3.44 (t, *J* = 6.6Hz, 4H), 2.05 (pentet, *J* = 3.4Hz, 4H), <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 183.6, 153.5, 150.8, 145.4, 141.1, 133.7, 133.0, 129.1 (2C), 128.6(2C), 112.7, 109.5, 108.6, 102.6, 47.9(2C), 25.3(2C); HRMS calcd for (C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S) Na [M+Na]<sup>+</sup> 361.0981; Found 361.0979

#### 6. Determination of Fluorescence Quantum Yield ( $\Phi_F$ ):

Determination of  $\Phi_F$  for compounds **8a-g** and **11** in chloroform was accomplished by comparison of the wavelength integrated intensity for each of the compound to that of a carefully chosen standard, in this case a dilute solution of quinine sulfate (QS) in 0.1 M H<sub>2</sub>SO<sub>4</sub>, whose  $\Phi_F$  was taken as 0.577 at 22 °C for 350 nm excitation. All samples were excited at 350 nm and  $\Phi_F$  for each sample was estimated under ambient conditions using the following expression

$$\Phi_{F,Sample} = \Phi_{F,QS} \times \frac{\left[ \int I(\lambda) d\lambda \right]_{Sample}}{\left[ \int I(\lambda) d\lambda \right]_{QS}} \times \frac{A_{QS@350nm}}{A_{Sample@350nm}} \times \frac{n_{Chloroform}^2}{n_{water}^2}$$

where  $\int I(\lambda) d\lambda$  is the area under the fluorescence emission band, *A* is the absorbance, and *n* is the solvent's refractive index.

**7. Lippert-Mataga Treatment of General Solvent Effects:** In the absence of any chemical interactions, physical interactions between the solvent milieu and the fluorophore can affect the energy difference between the ground and the excited states of a fluorophore in a general way. The refractive index ( $n$ ) and the static dielectric constant ( $\epsilon$ ) of the solvent are found to be related to this energy difference empirically according to the Lippert-Mataga expression

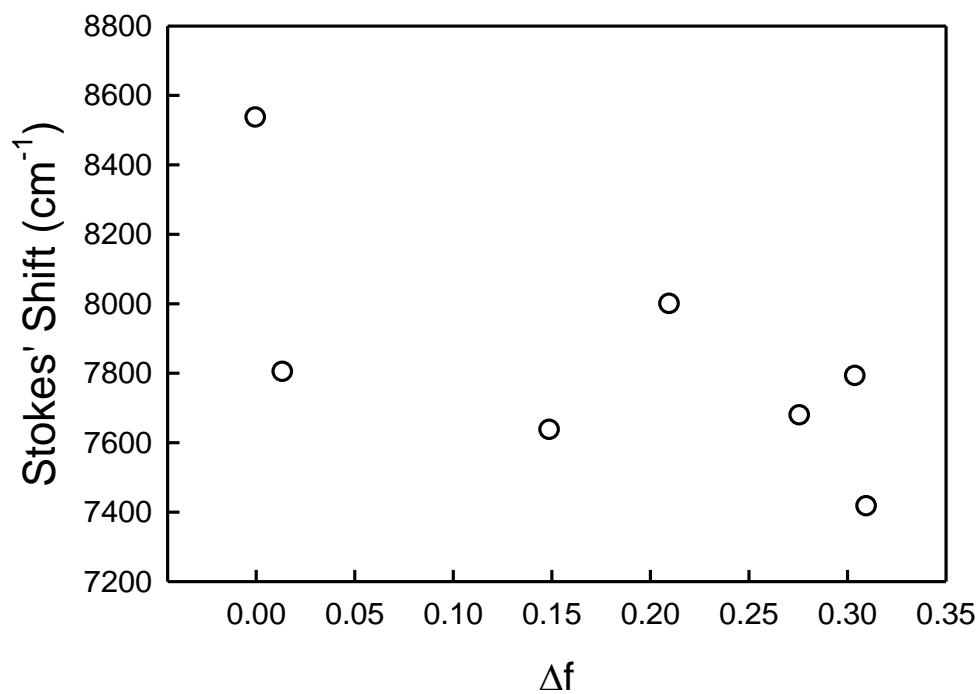
$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc} \left( \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \frac{(\mu_E - \mu_g)^2}{a^3} + \text{constant}$$

where  $\bar{\nu}_A$  and  $\bar{\nu}_F$  are the absorbance and the fluorescence emission maxima in  $\text{cm}^{-1}$ ,  $h$  is Planck's constant,  $c$  is the speed of light, and  $\mu_E$  and  $\mu_g$  are the dipole moments of the fluorophore in the excited ( $E$ ) and ground ( $g$ ) states, respectively.

**Table S1.** Absorption maxima and fluorescence emission maxima under 350 nm excitation for **8a** in selected solvents.

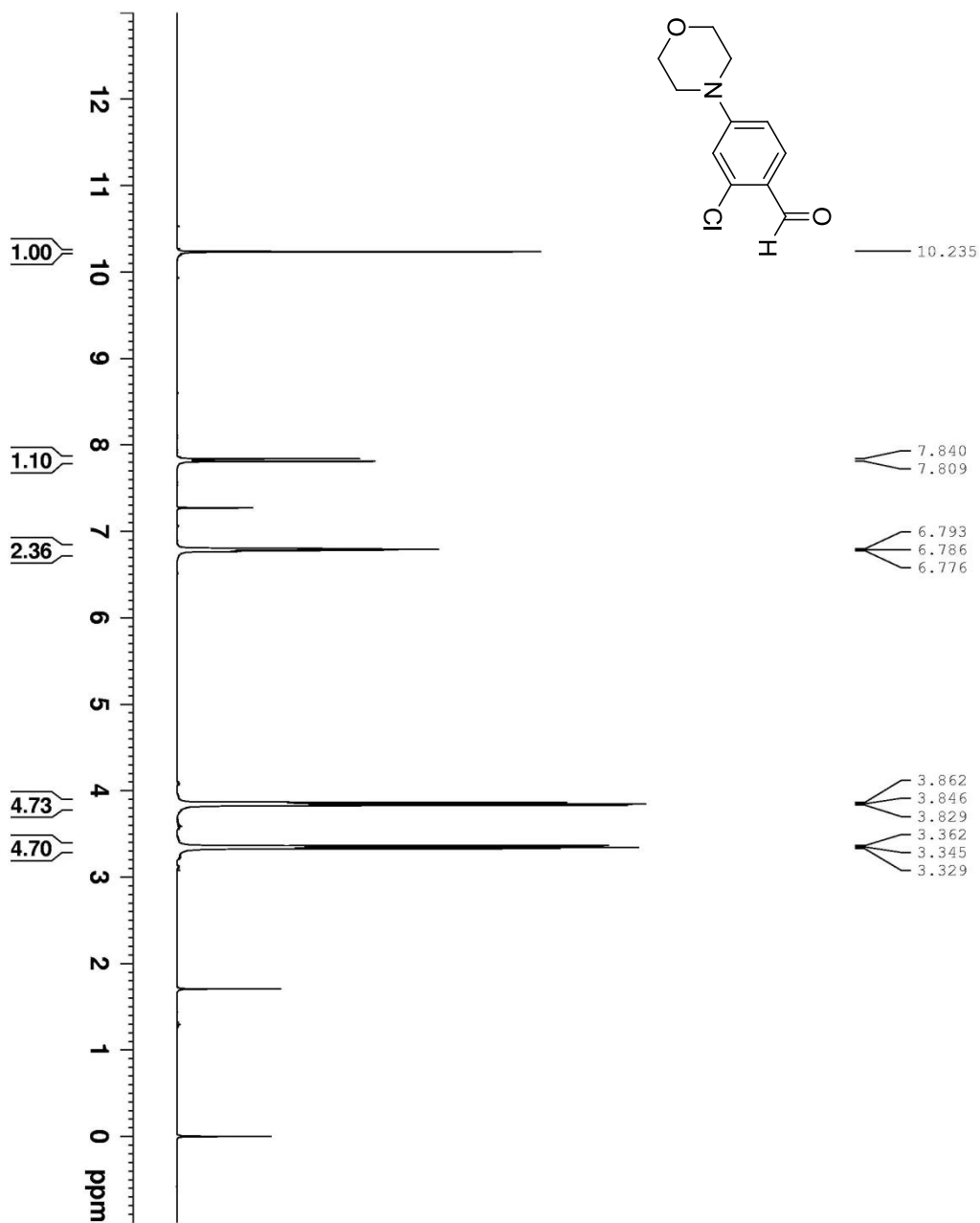
Solvent	Absorbance maxima (nm)	Fluorescence emission maxima (nm)
Hexane	347	493
Toluene	355	491
Chloroform	355	487
THF	351	488
DMF	355	488
ACN	352	485
Methanol	354	480

S11



**Figure S1.** Stokes shift [ $\bar{\nu}_A - \bar{\nu}_F$ ] versus orientational polarizability [ $\Delta f = \left( \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right)$ ] of benzothiazine **8a** at ambient conditions. The solvents represented are those listed in Table S1.

S12



```

Current Data Parameters
NAME      Ny-V-083
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20100802
Time      22:17
INSTRUM   DRX300
PROBHD    5 mm Multinuc1
PULPROG   zg30p0ad
TD         32768
SOLVENT   CDCl3
NS         16
DS         1
SWH        6172.832 Hz
FIDRES     0.186580 Hz
AQ         2.6542380 sec
RG         267.4
DM         81.000 usec
DE         6.000 usec
TE         300.0 K
D1         1.00000000 sec
D31        0.00000000 sec

===== CHANNEL f1 =====
NUC1       1H
P1         7.65 usec
PL1        0.00 dB
SFO1       300.1318934 MHz

F2 - Processing parameters
SI         32768
SF         300.1300028 MHz
RG         267.4
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.30
    
```

Figure 1 <sup>1</sup>H-NMR spectrum of 7a

S13

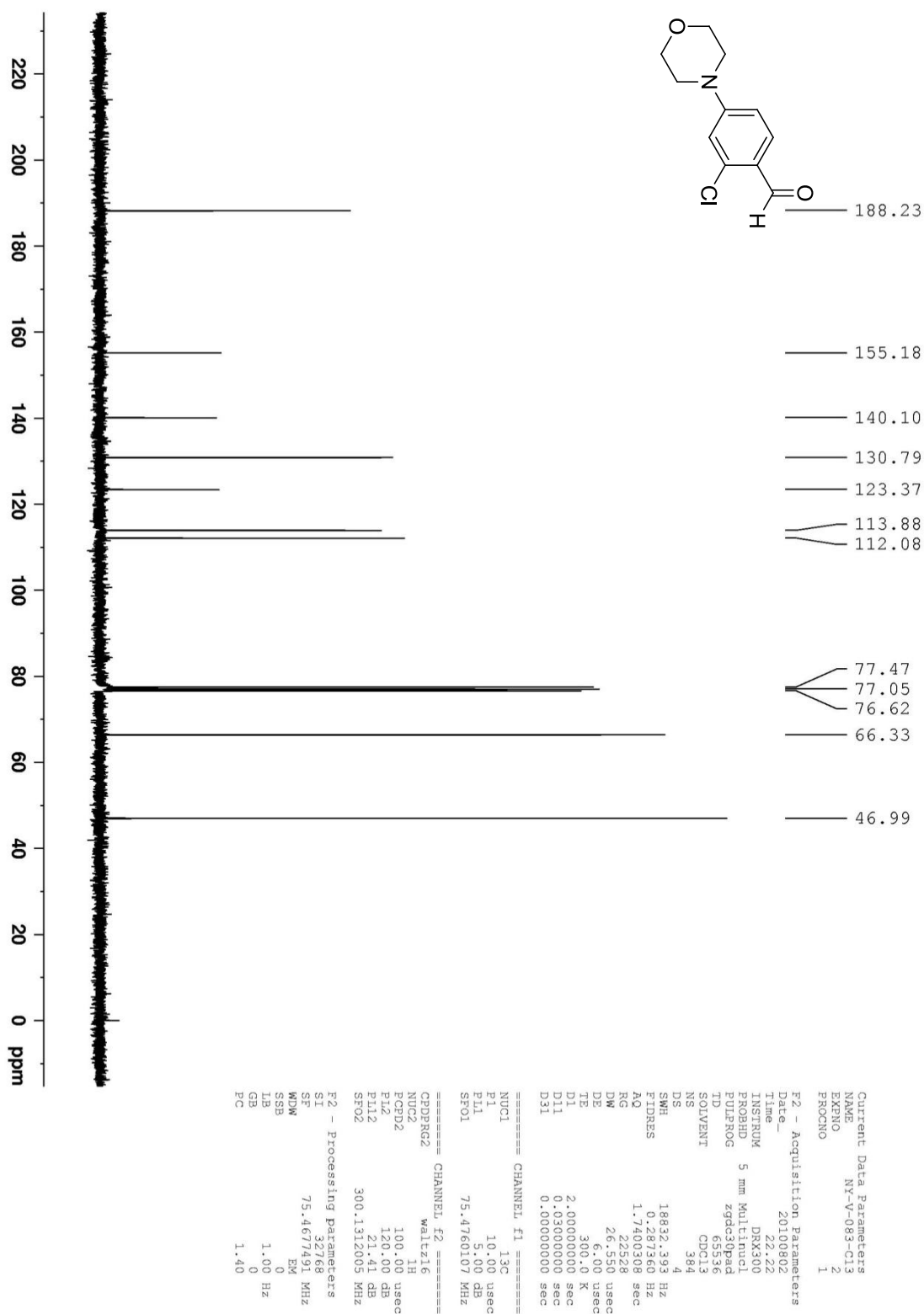


Figure2 <sup>13</sup>C-NMR spectrum of 7a

S14

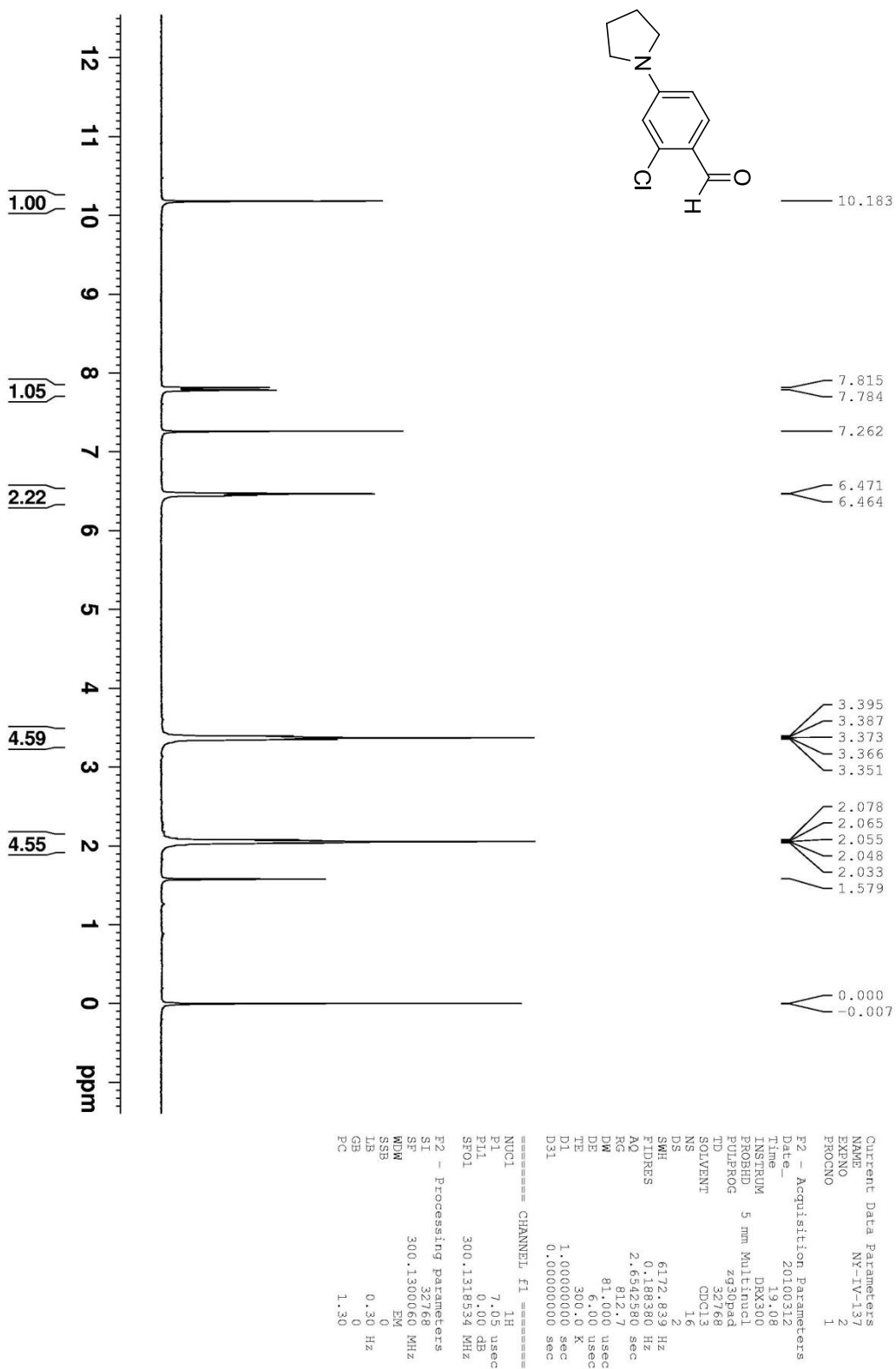
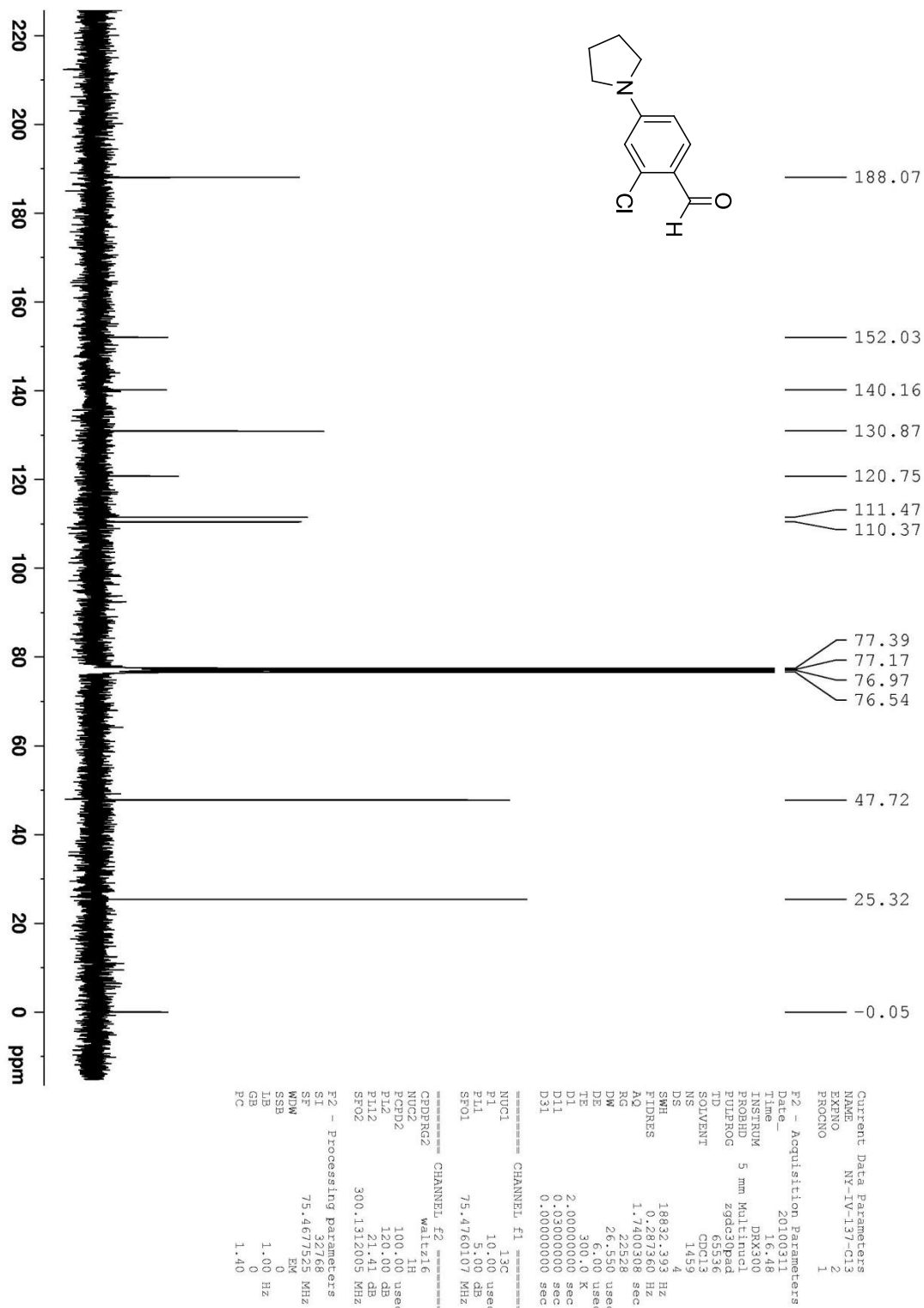


Figure 3 <sup>1</sup>H-NMR spectrum of 7b

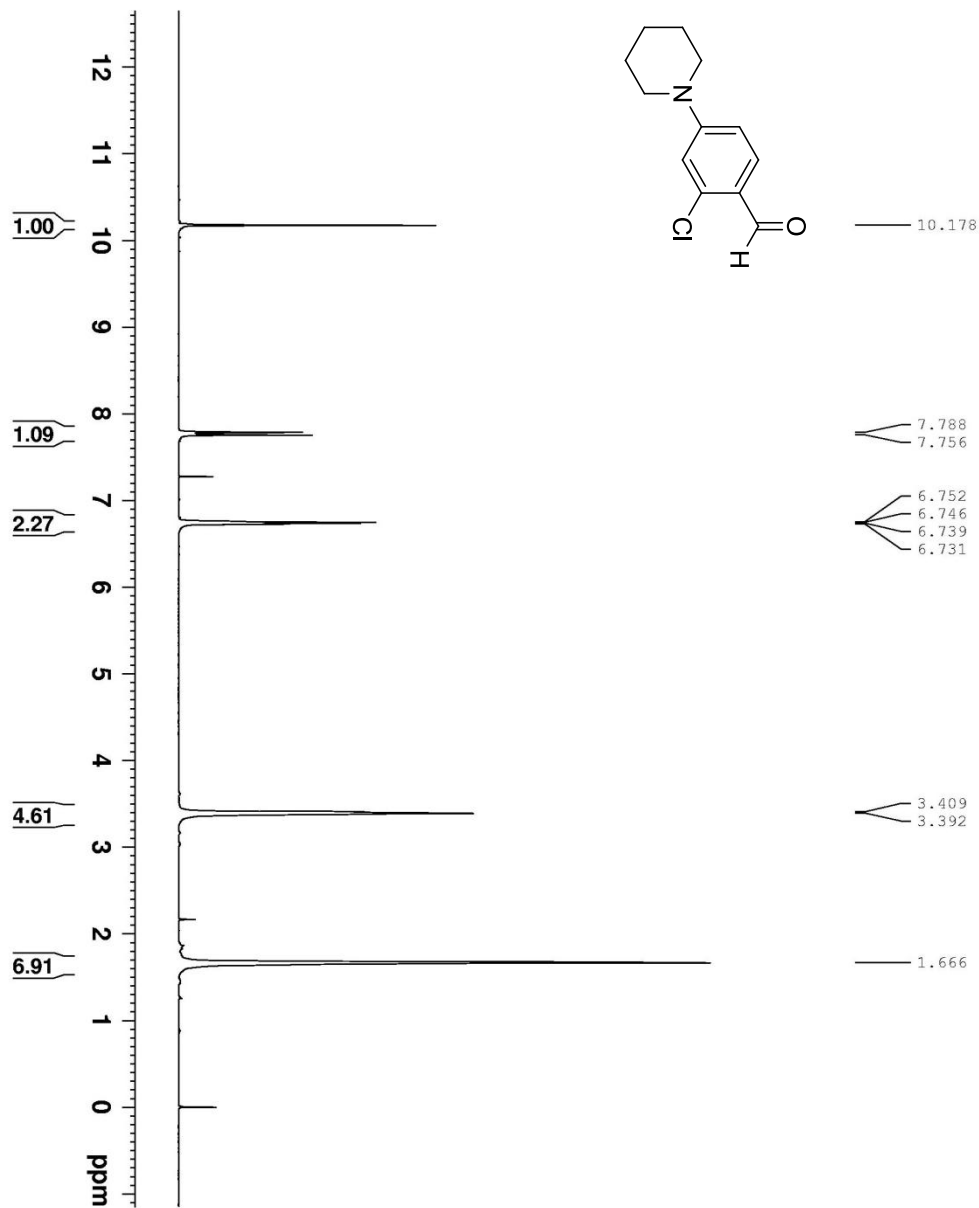
S15



NY-IV-137-13C NMR

Figure 4 <sup>13</sup>C-NMR spectrum of 7b

S16



```

Current Data Parameters
NAME          NZ-V-081-1
EXPNO         2
PROCNO       1
-----
P2 - Acquisition Parameters
Date_         20101129
Time         14.45
INSTRUM      DRX300
PROBHD       5 mm Mpl1mmcl
PULPROG      zg30pgrad
TD            32768
SOLVENT      CDCl3
NS            16
DS            2
SWH           6172.839 Hz
FIDRES       0.188380 Hz
AQ           2.6542580 sec
RG           114
DM           81.000 usec
DE           6.00 usec
TE           300.0 K
D1           1.00000000 sec
D31          0.00000000 sec
-----
CHANNEL F1
NUC1          1H
P1            7.05 usec
PL1           0.00 dB
SFO1          300.1318534 MHz
-----
P2 - Processing parameters
SI            32768
SF           300.1300005 MHz
WDW           EM
SSB           0
LB           0.30 Hz
GB            0
PC           1.30
    
```

Figure 5 <sup>1</sup>H-NMR spectrum of 7c



S17

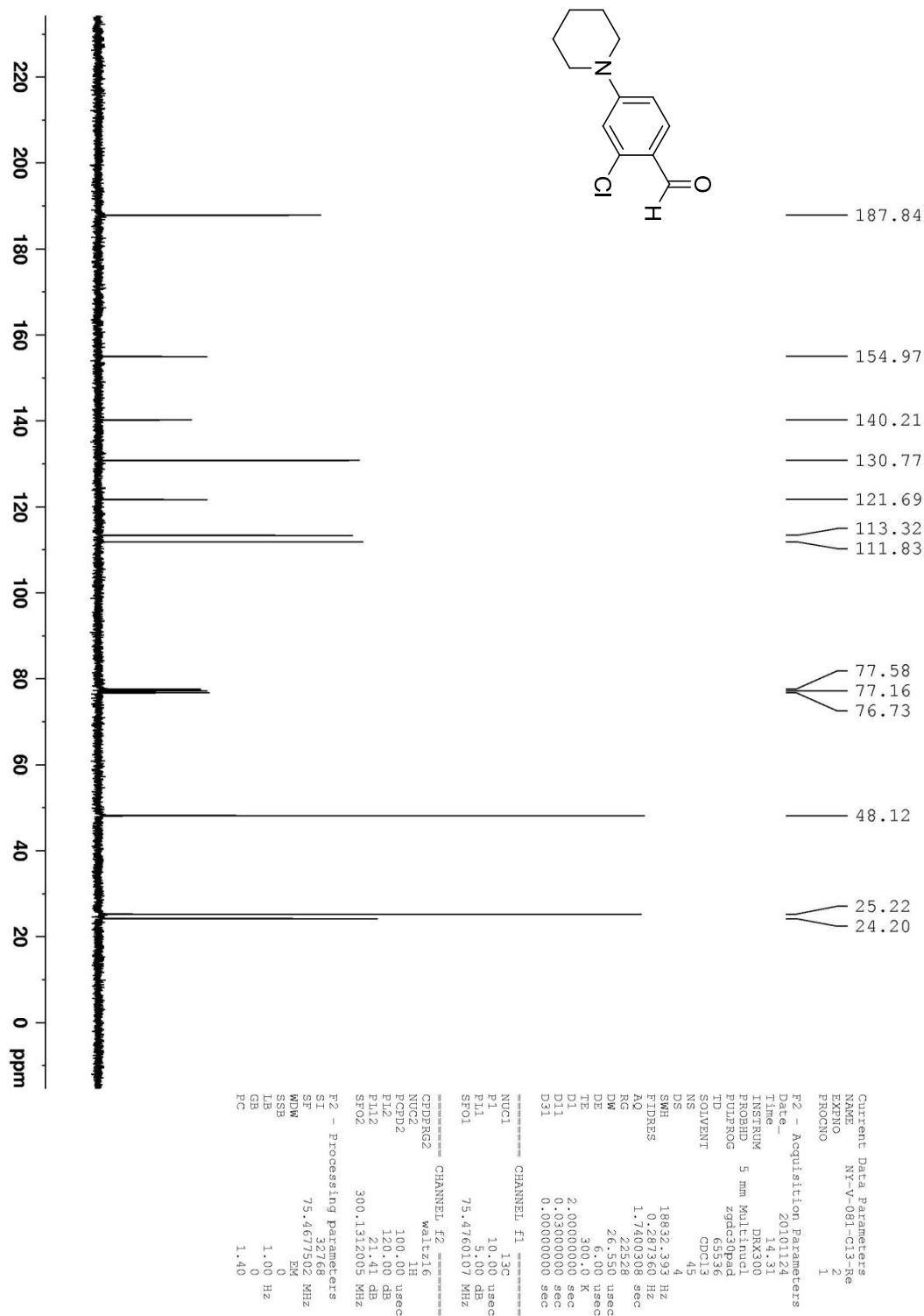


Figure 6 <sup>13</sup>C-NMR spectrum of 7c

S18

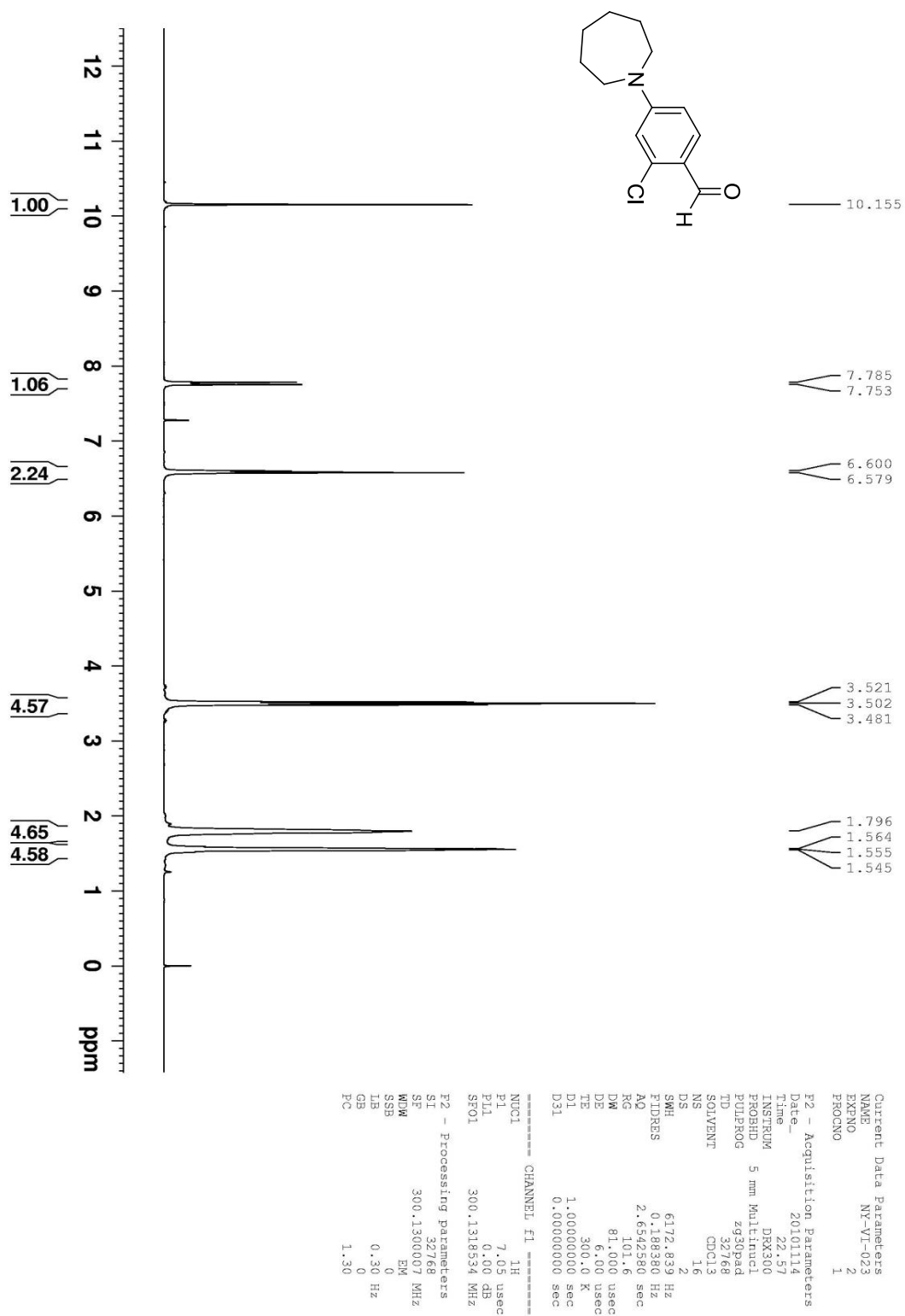


Figure7 <sup>1</sup>H-NMR spectrum of 7d

S19

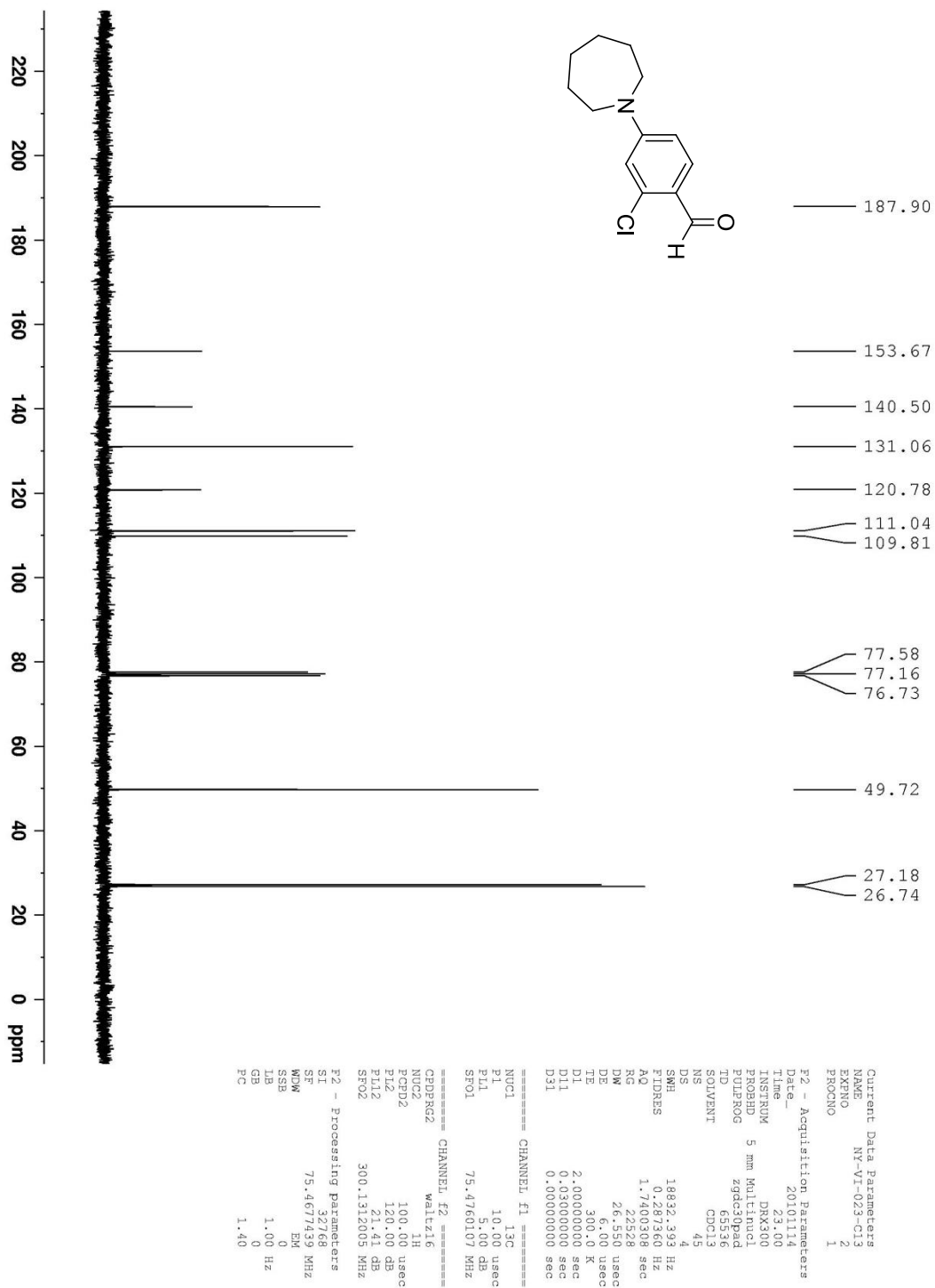


Figure 8 <sup>13</sup>C-NMR spectrum of 7d

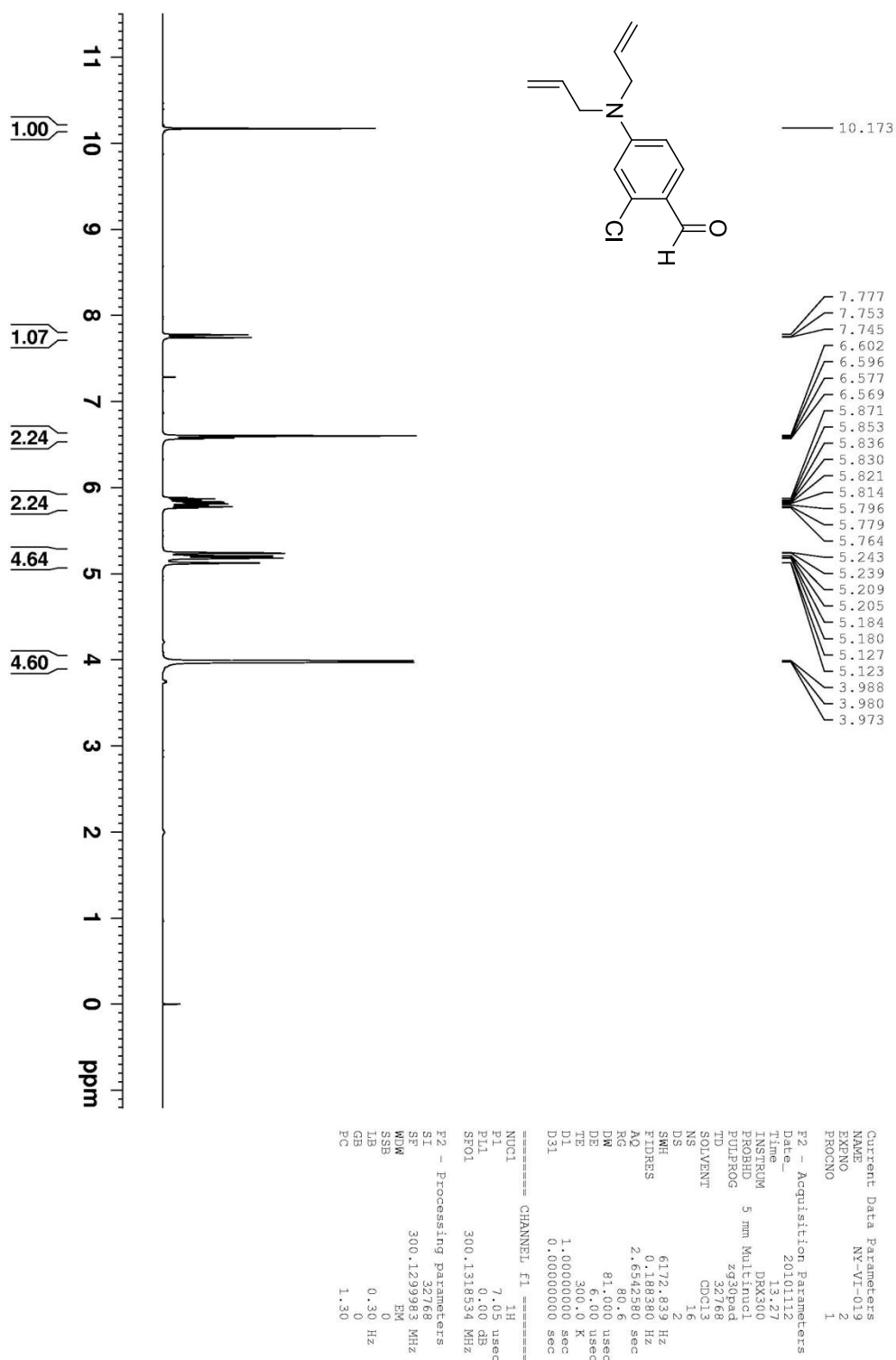


Figure9 <sup>1</sup>H-NMR spectrum of 7e

S21

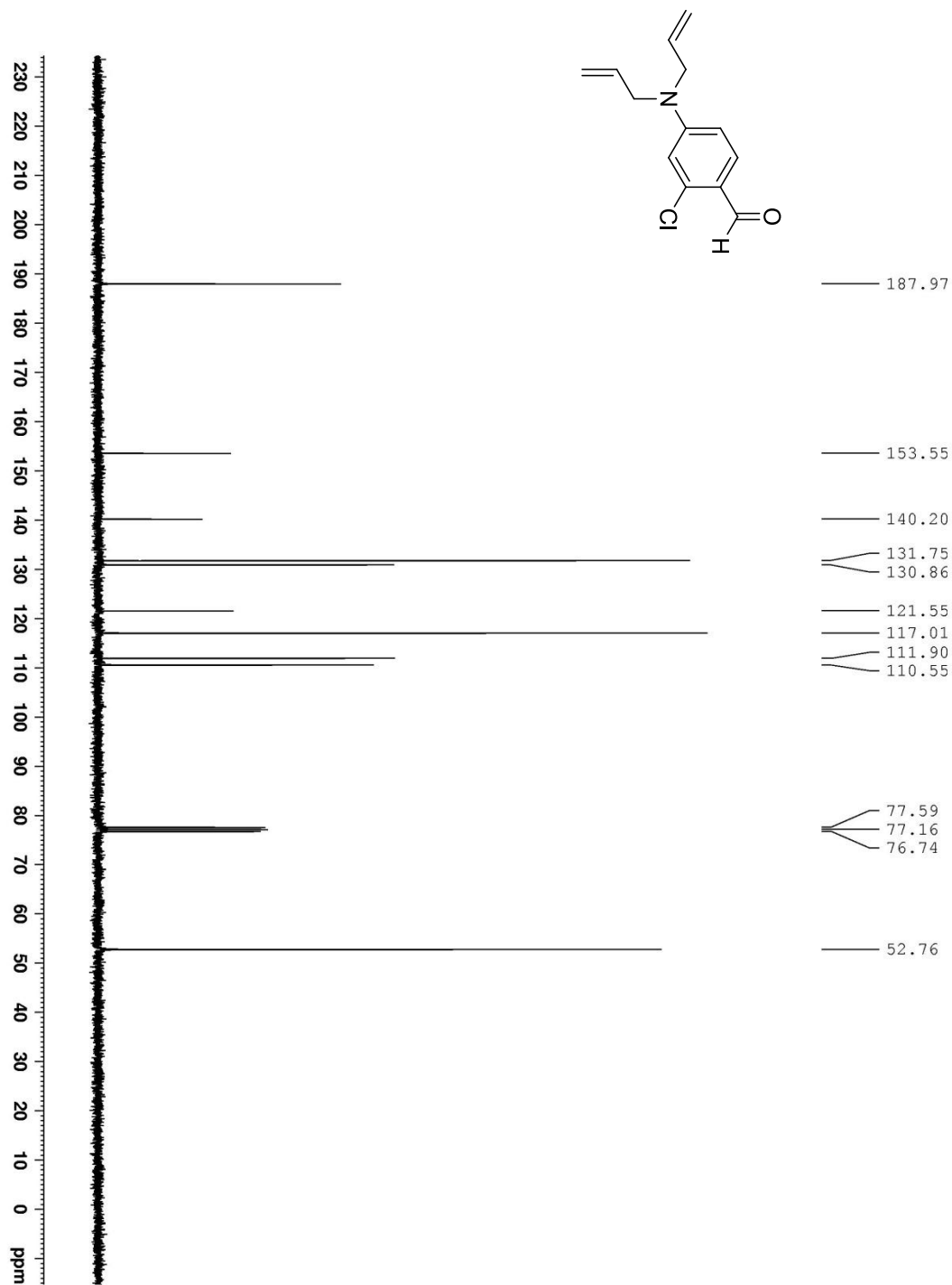


Figure10  $^{13}\text{C}$ -NMR spectrum of 7e

S22

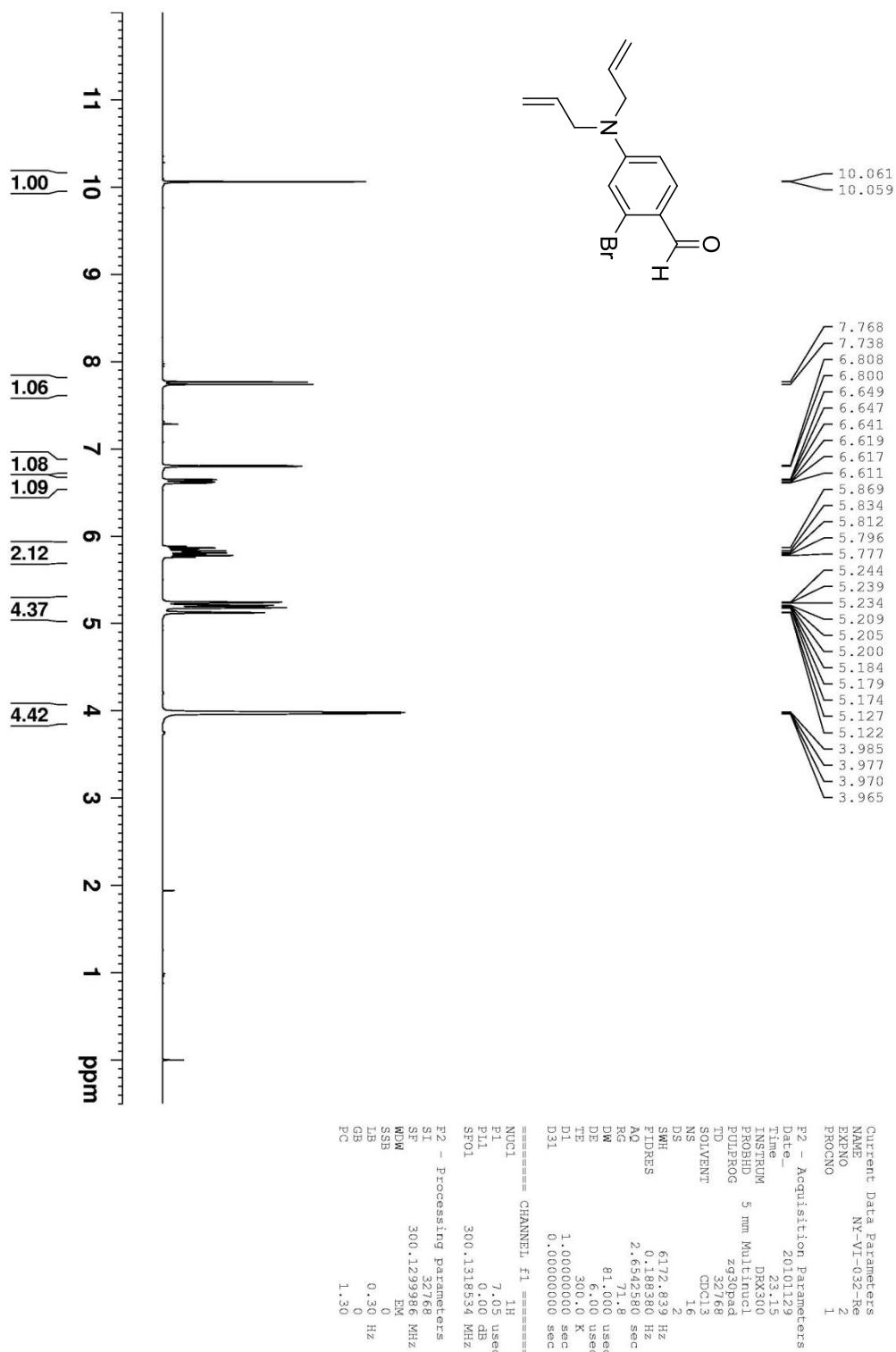


Figure 11 <sup>1</sup>H-NMR spectrum of 9e

S23

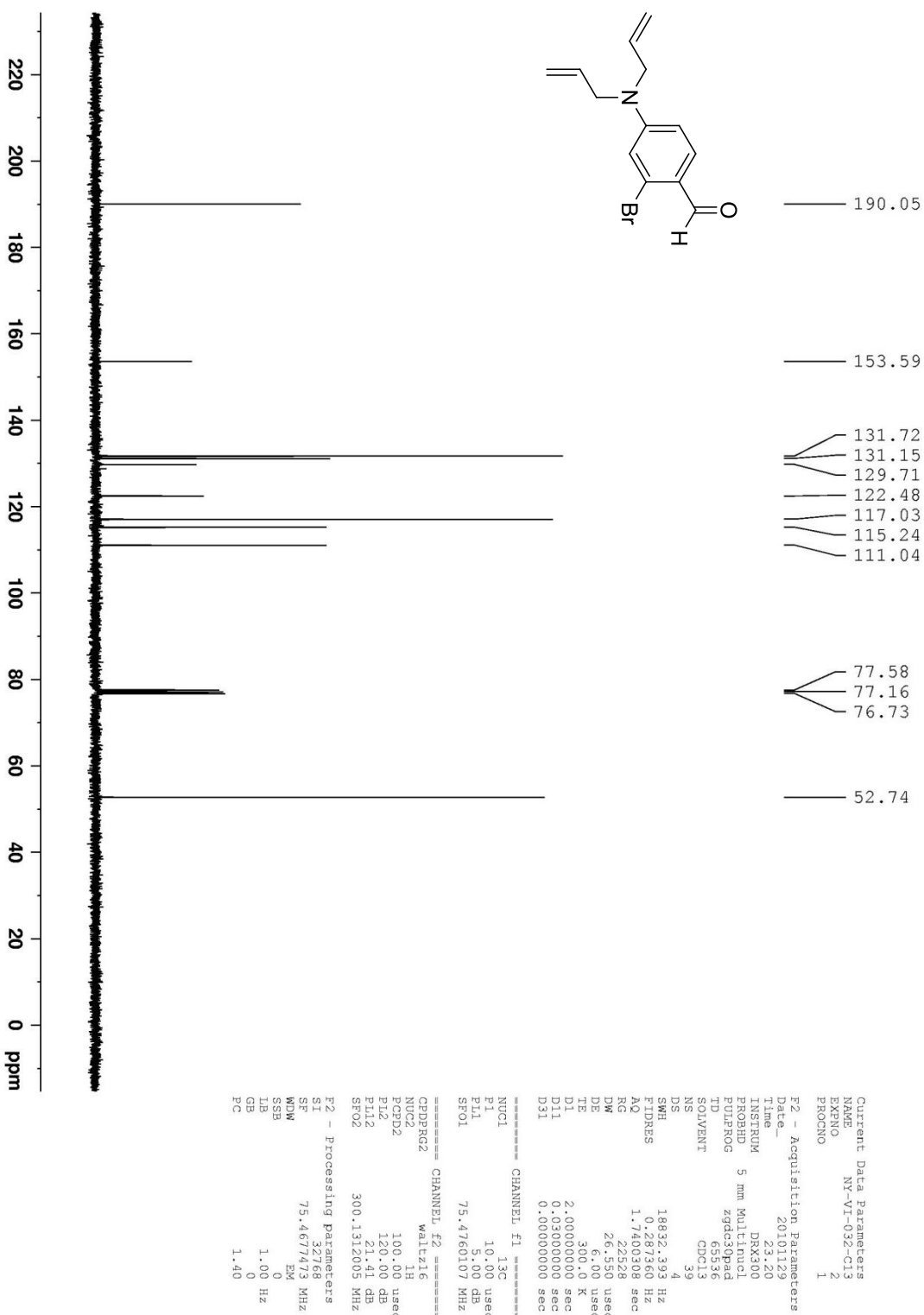


Figure12 <sup>13</sup>C-NMR spectrum of 9e

S24

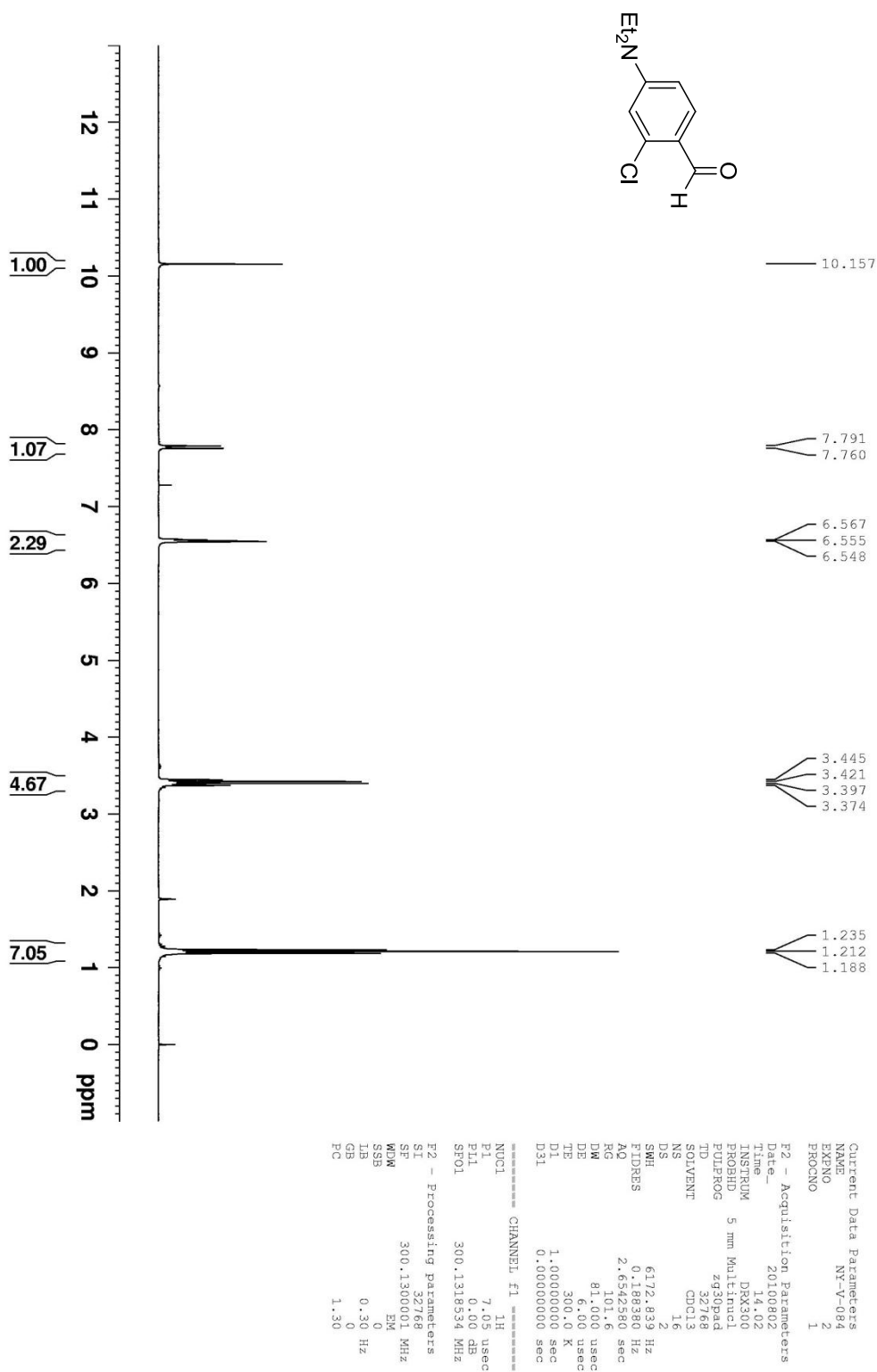


Figure13 <sup>1</sup>H-NMR spectrum of 7f



S25

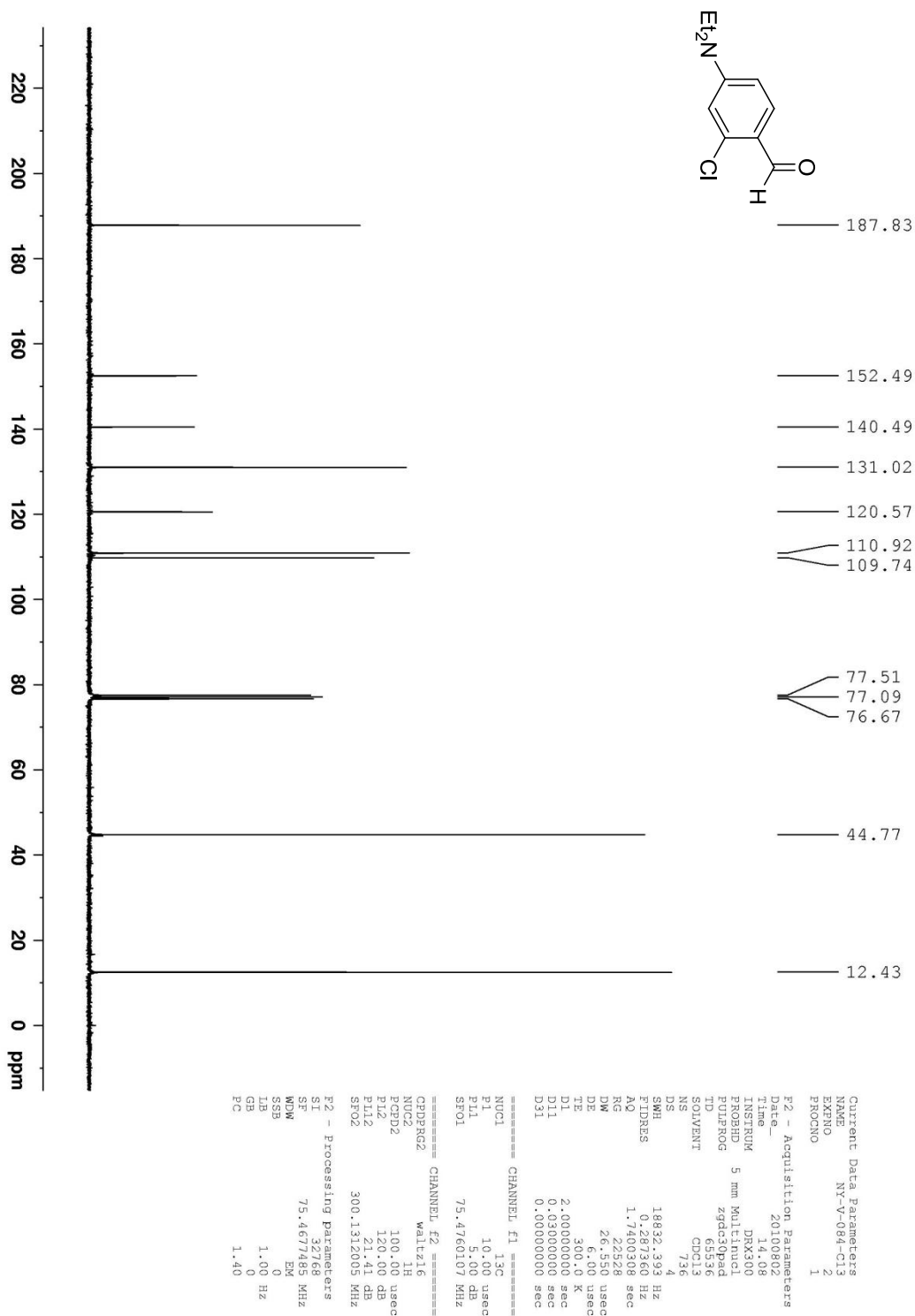


Figure 14 <sup>13</sup>C-NMR spectrum of 7f

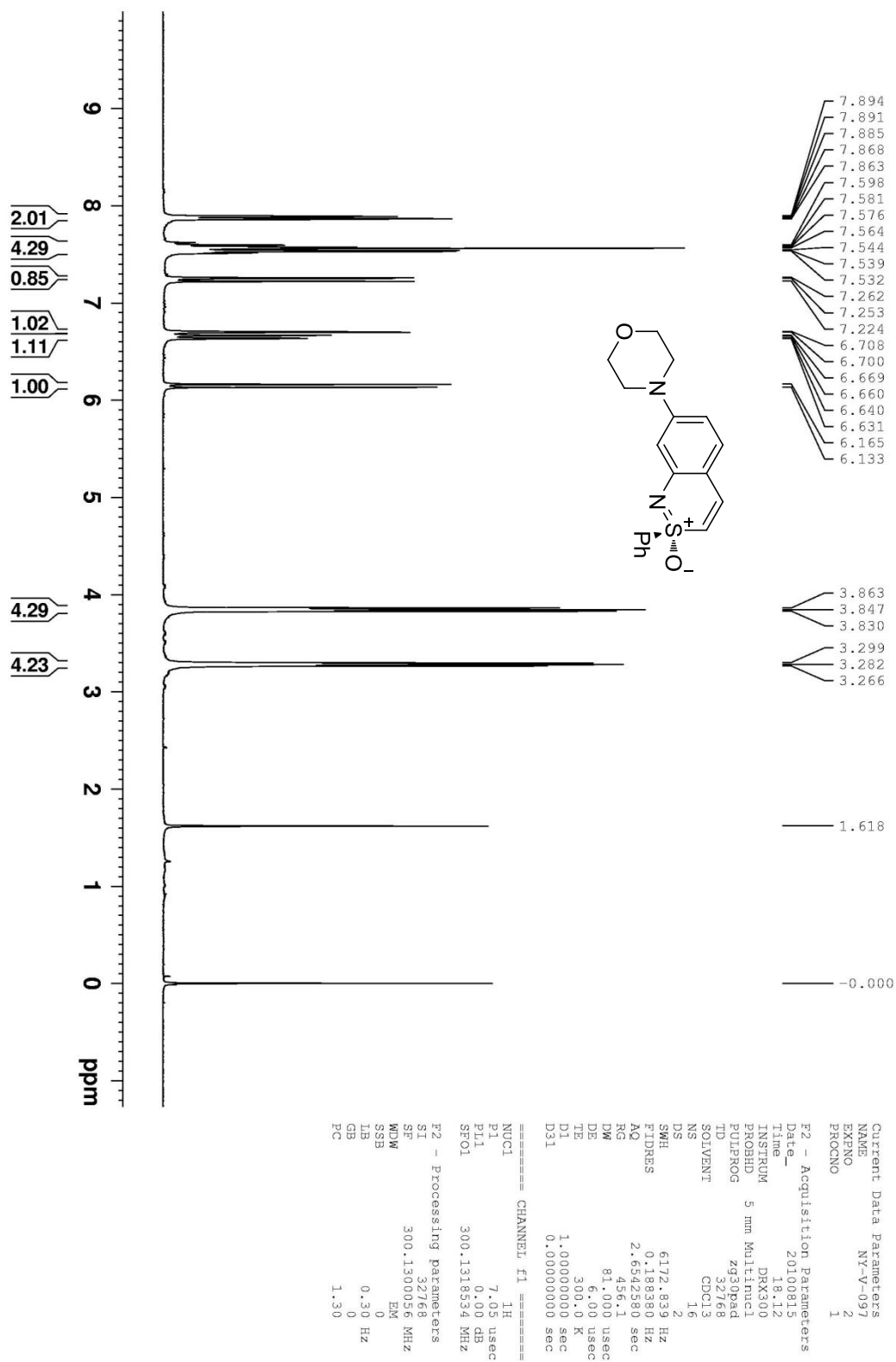


Figure15 <sup>1</sup>H-NMR spectrum of 8a

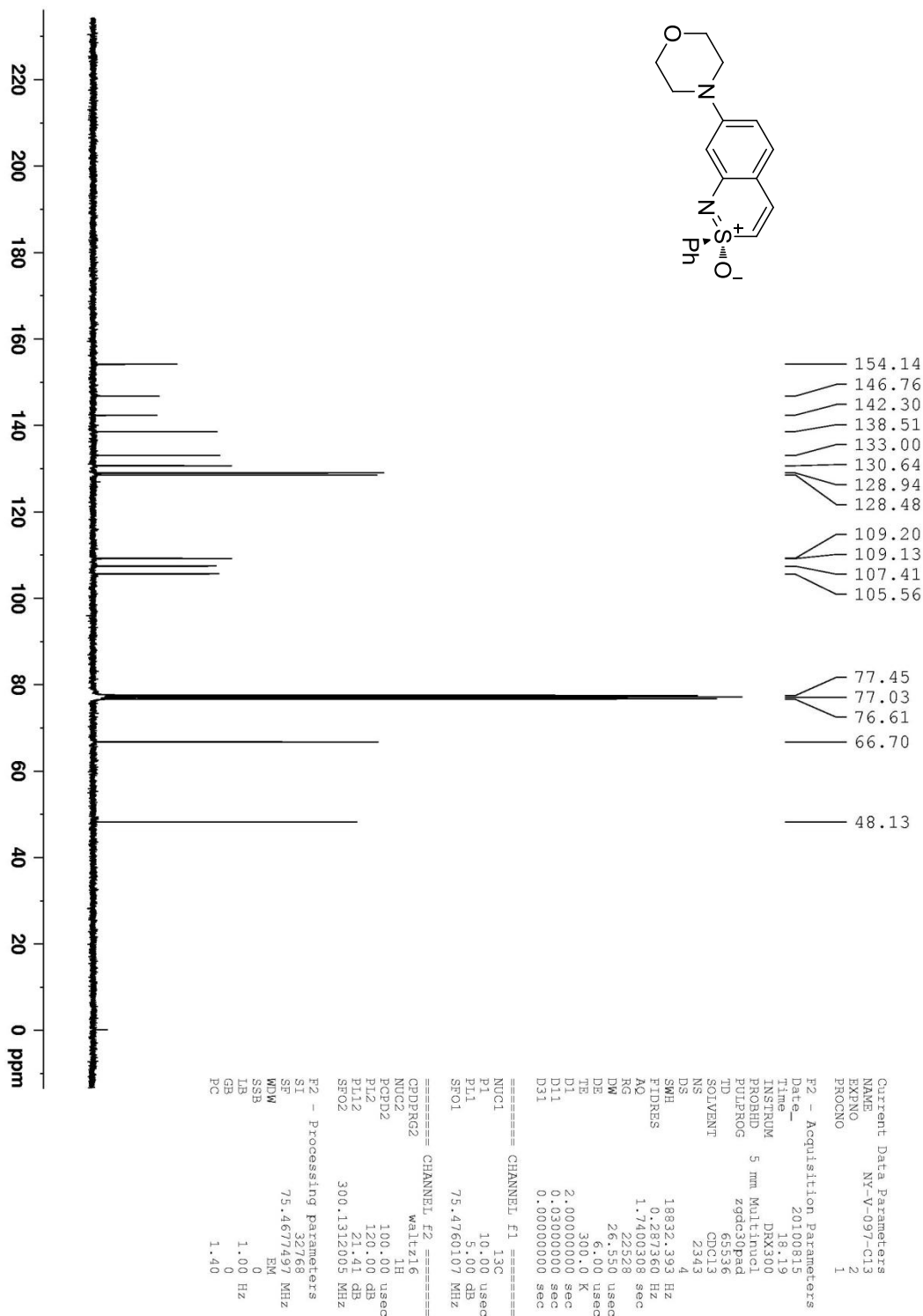


Figure 16 <sup>13</sup>C-NMR spectrum of 8a

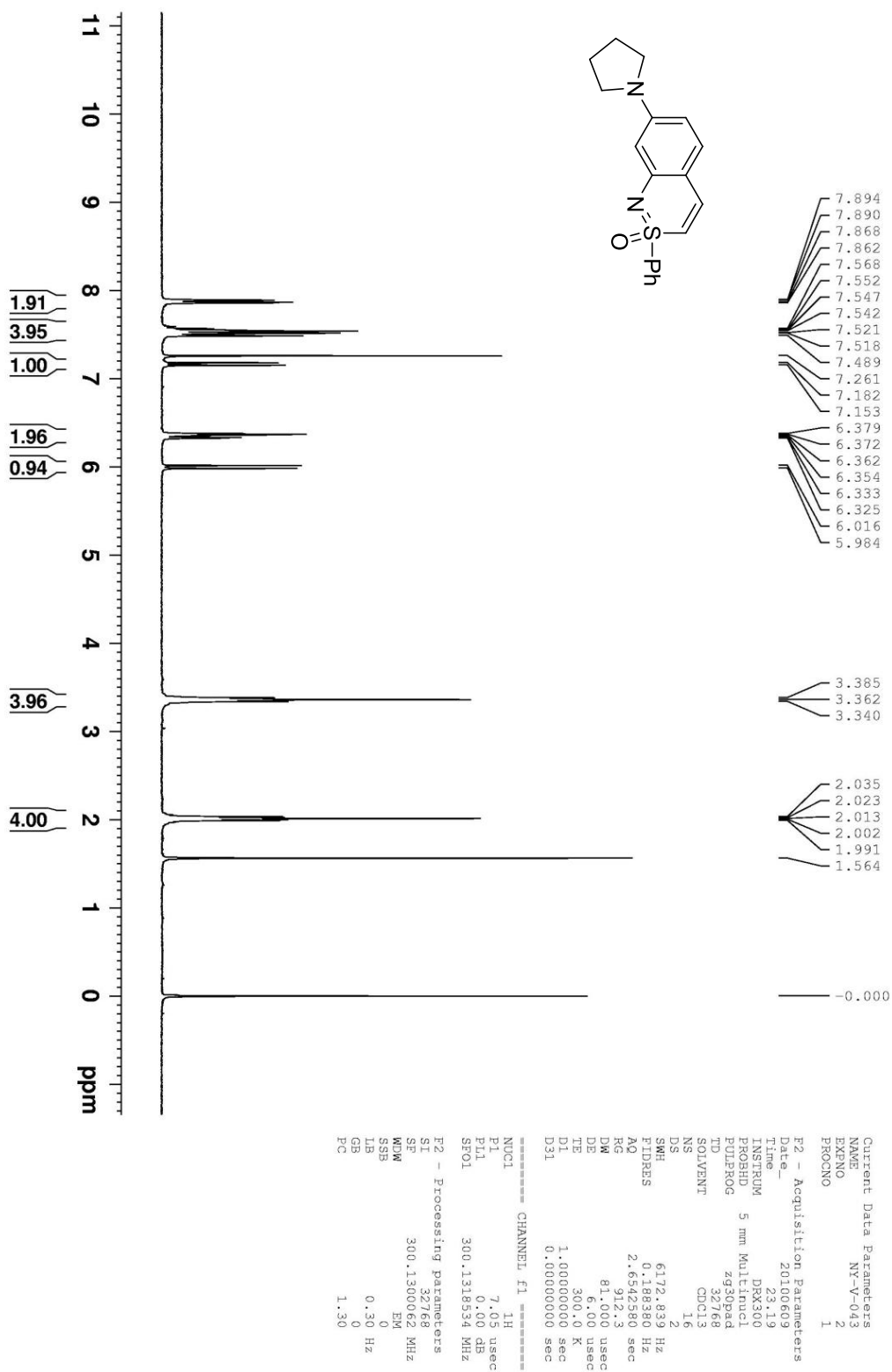


Figure 17 <sup>1</sup>H-NMR spectrum of 8b

S29

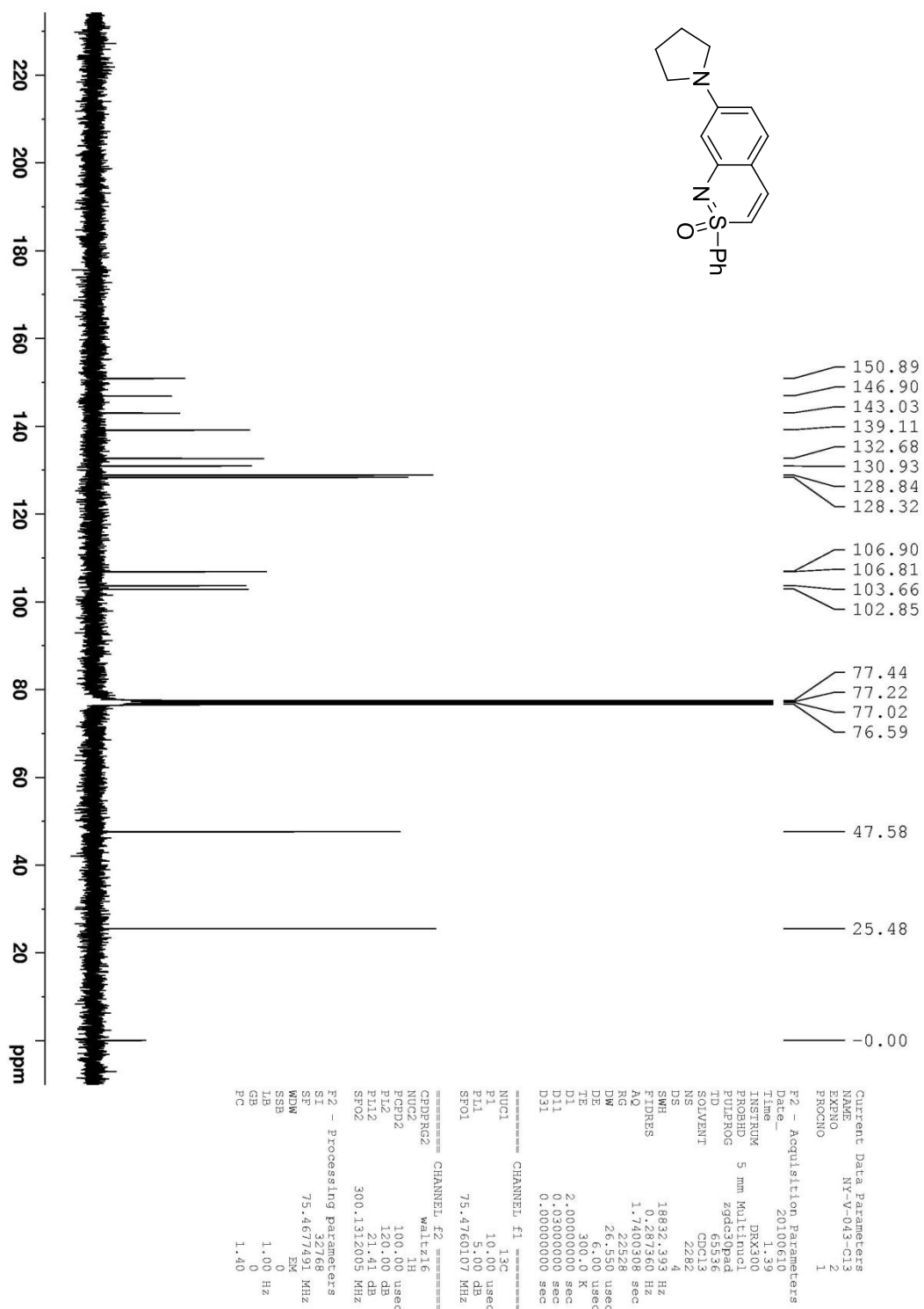


Figure 18 <sup>13</sup>C-NMR spectrum of 8b

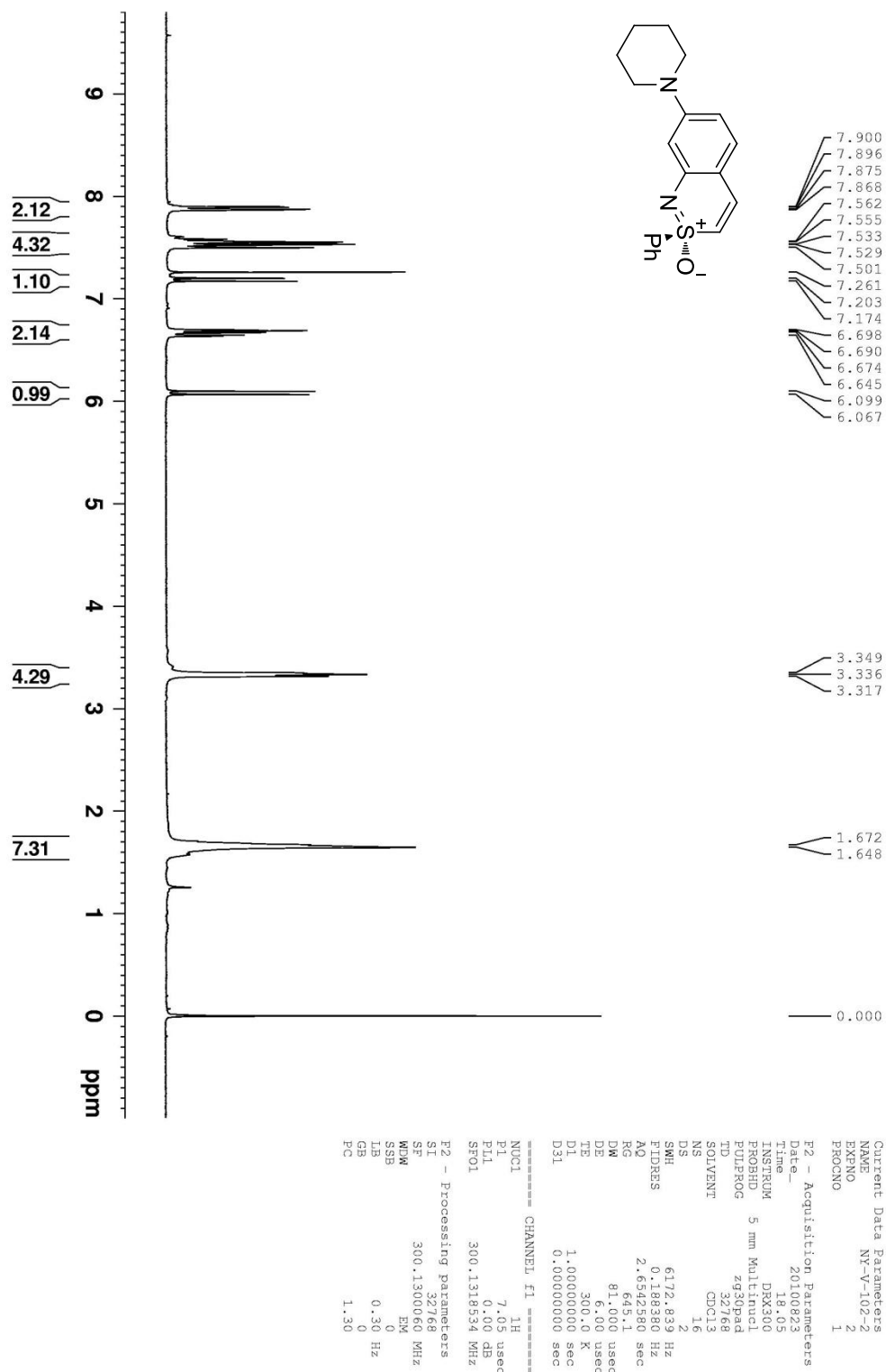


Figure 19 <sup>1</sup>H-NMR spectrum of 8c

S31

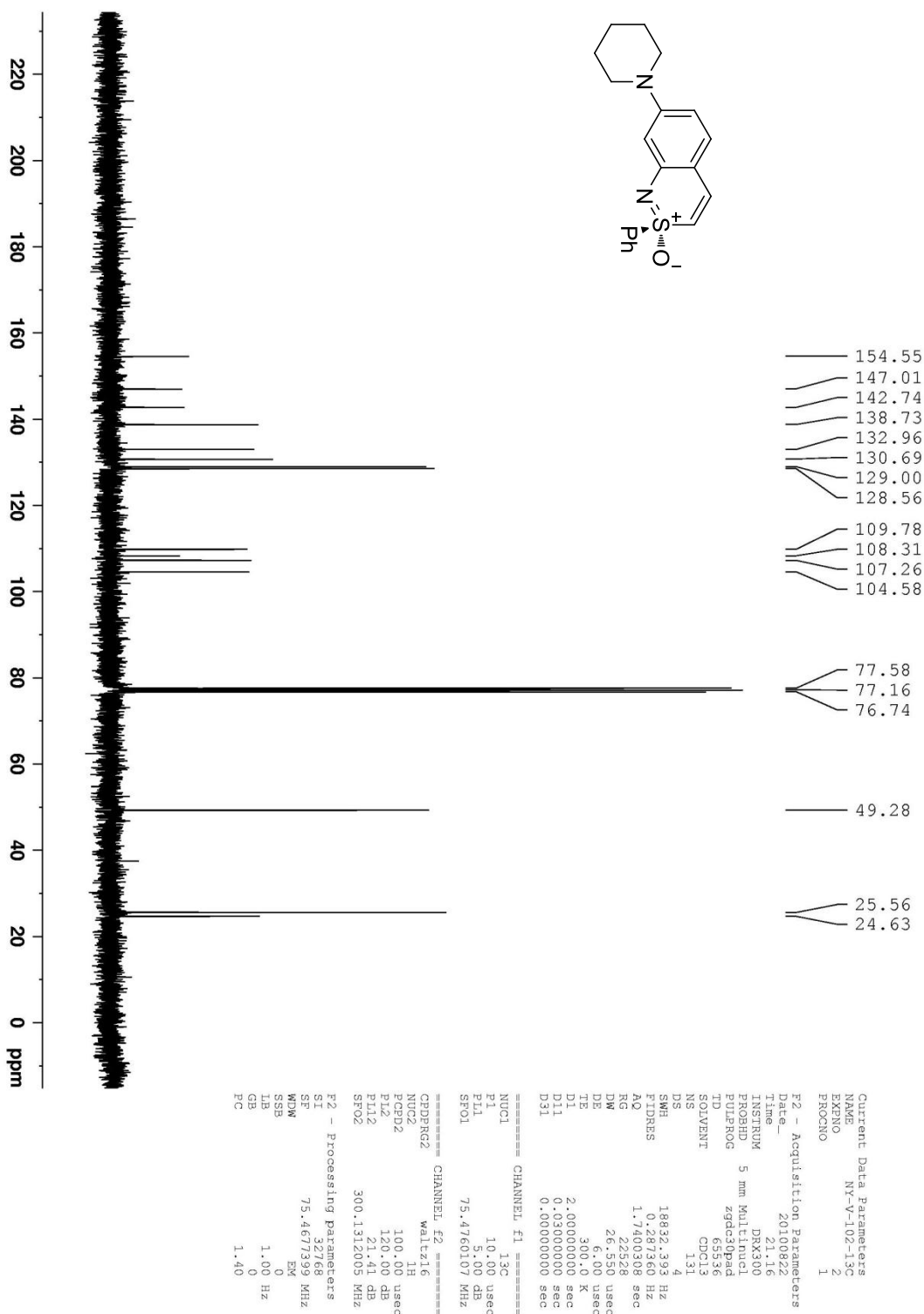


Figure 20 <sup>13</sup>C-NMR spectrum of 8c

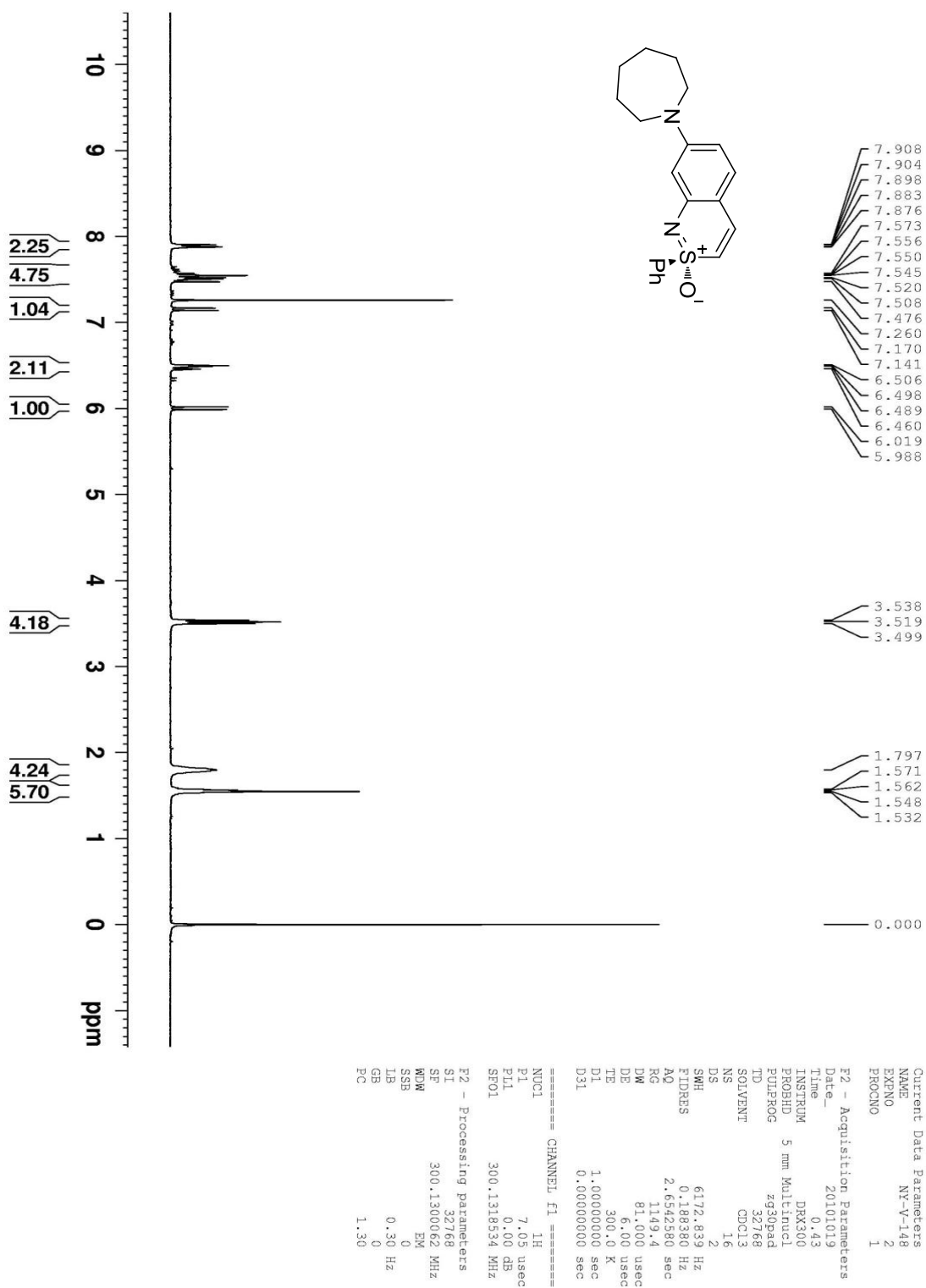


Figure 21 <sup>1</sup>H-NMR spectrum of 8d



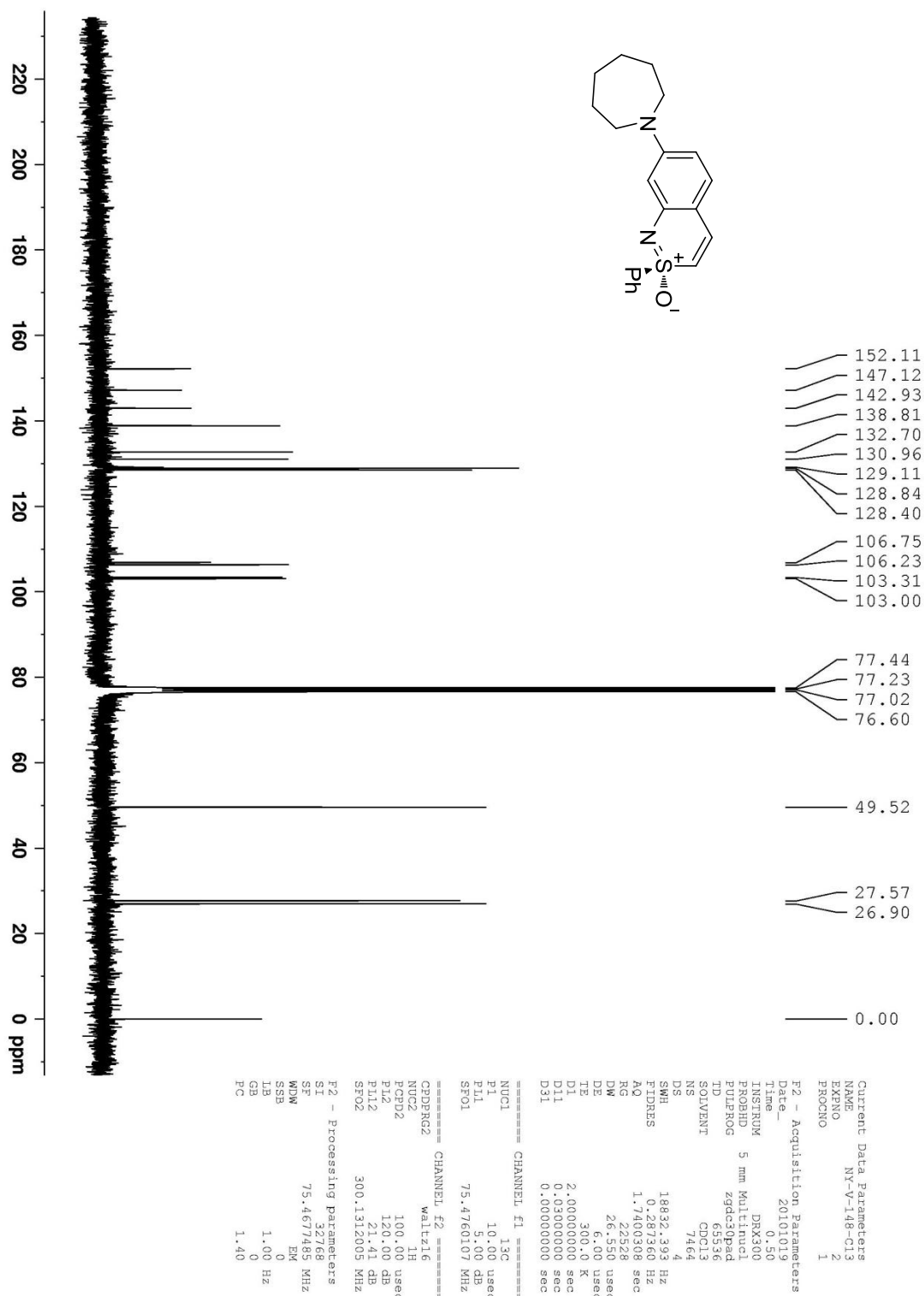


Figure 22 <sup>13</sup>C-NMR spectrum of 8d

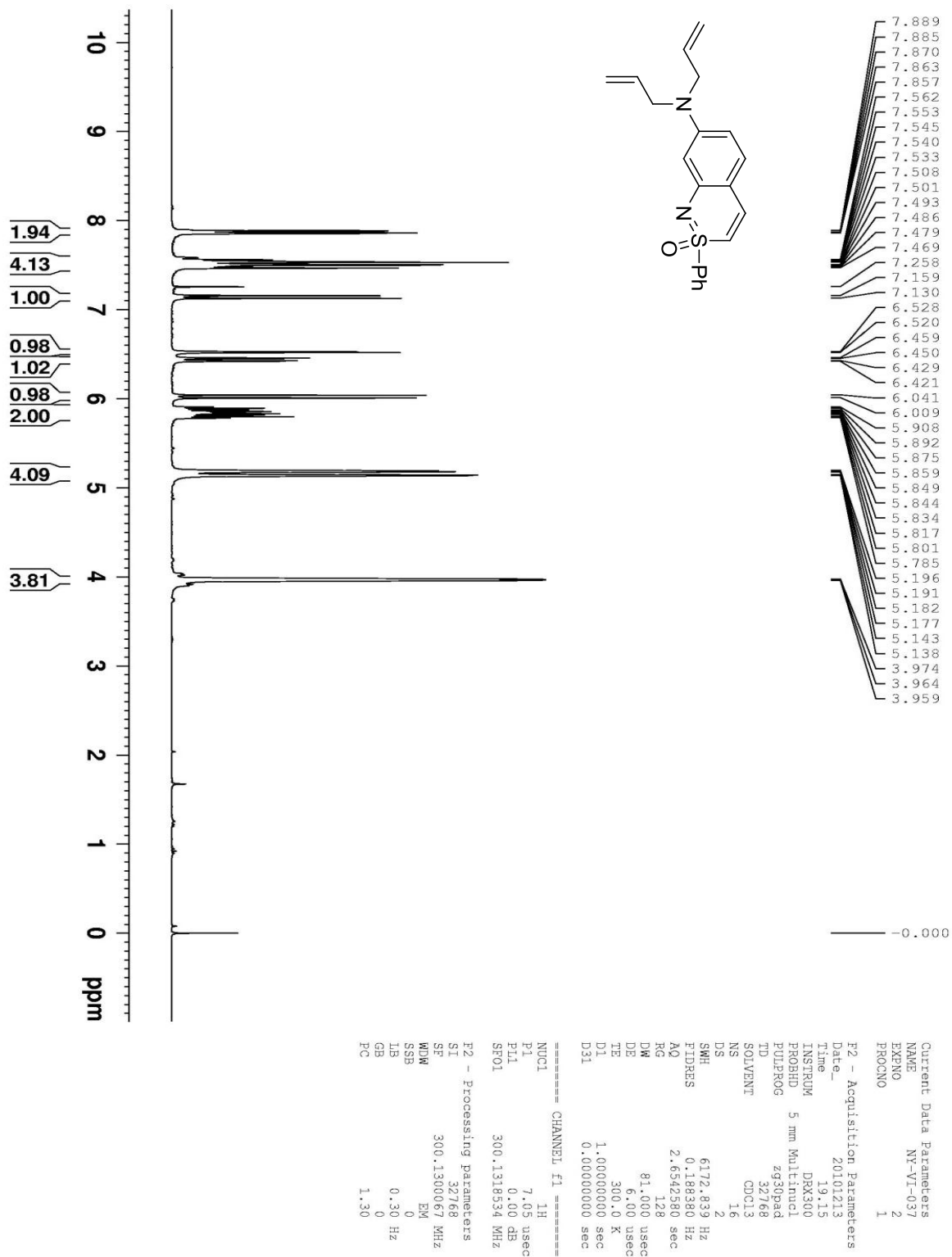


Figure23 <sup>1</sup>H-NMR spectrum of 8e

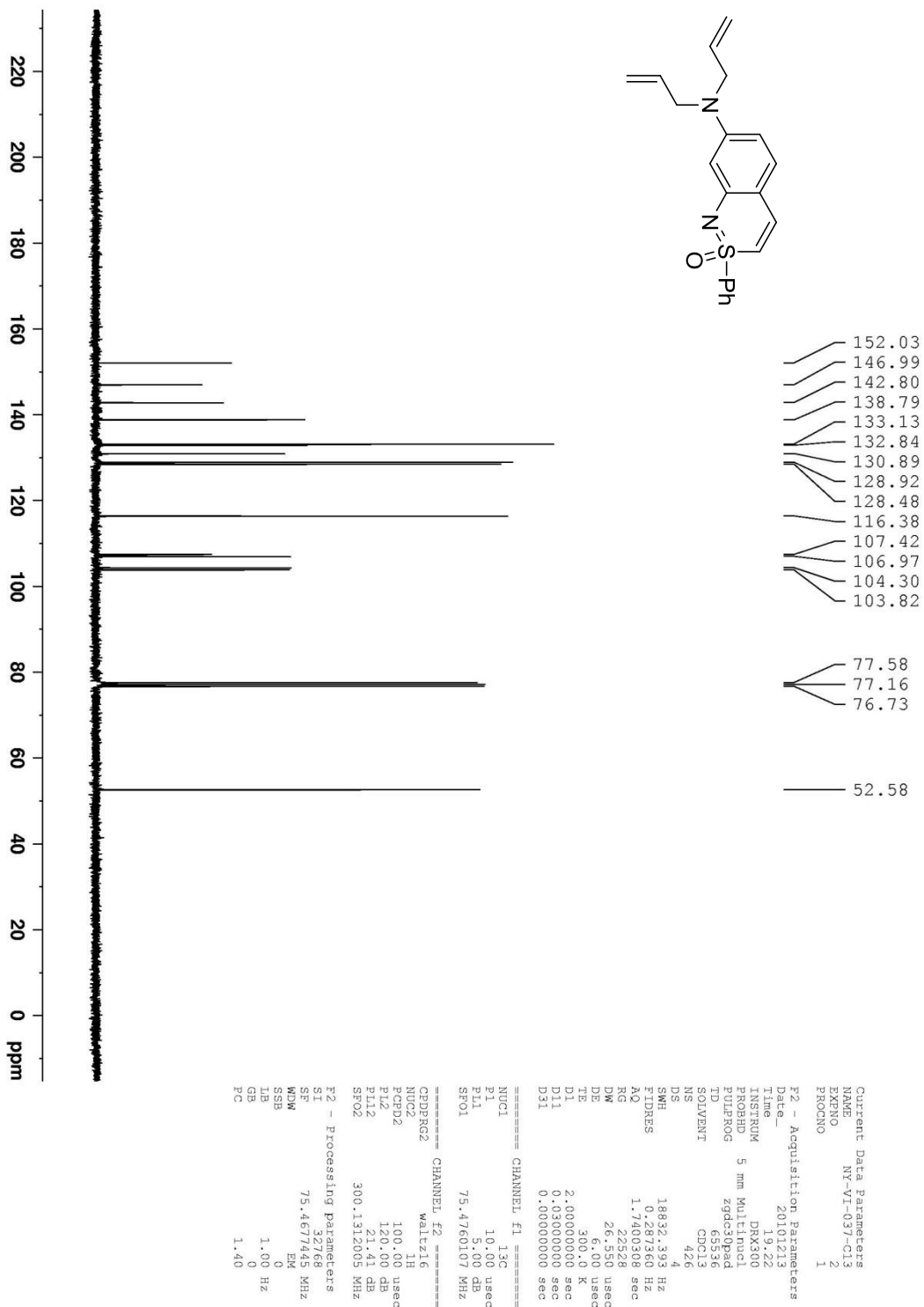


Figure 24 <sup>13</sup>C-NMR spectrum of **8e**

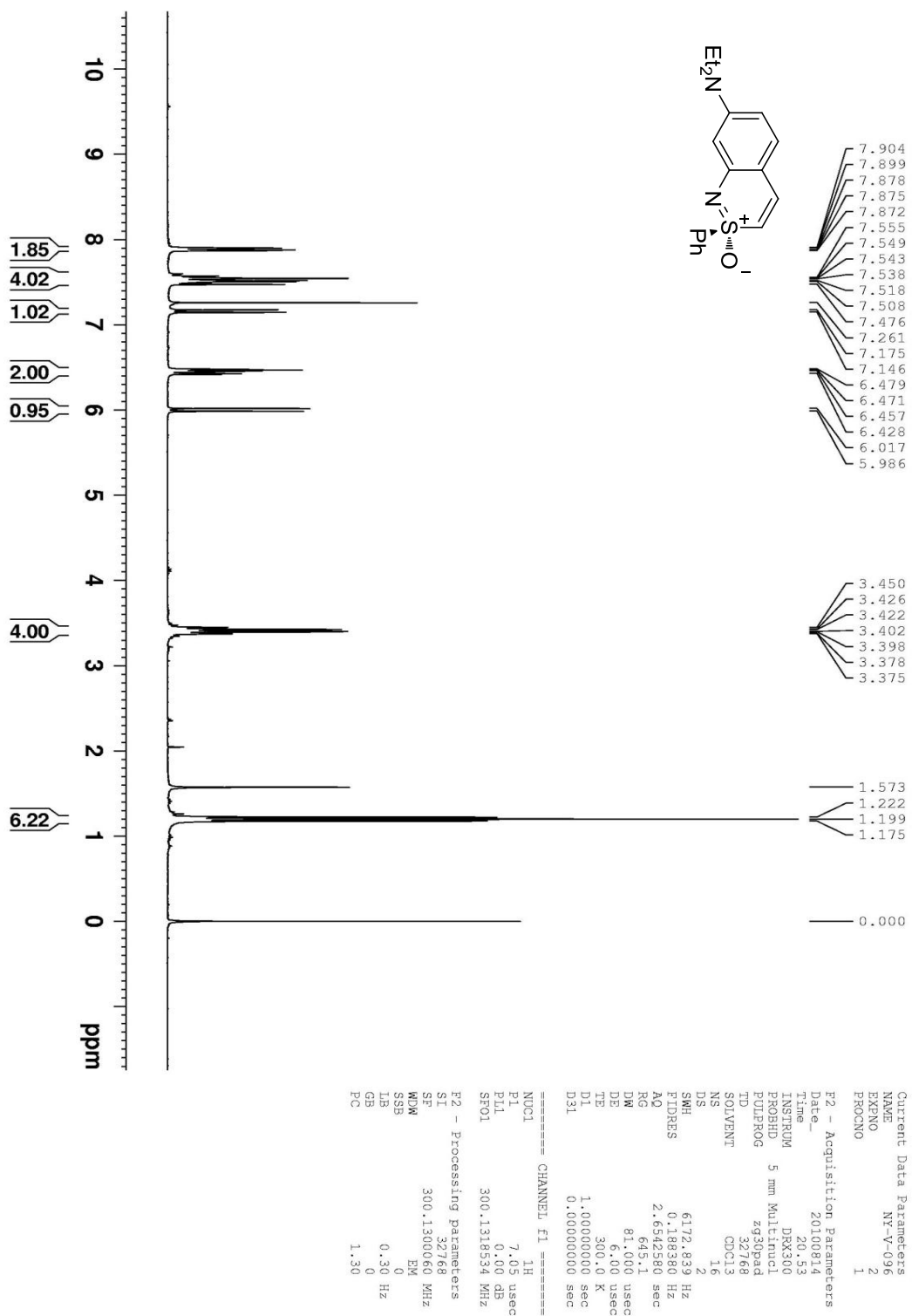


Figure 25 <sup>1</sup>H-NMR spectrum of 8f

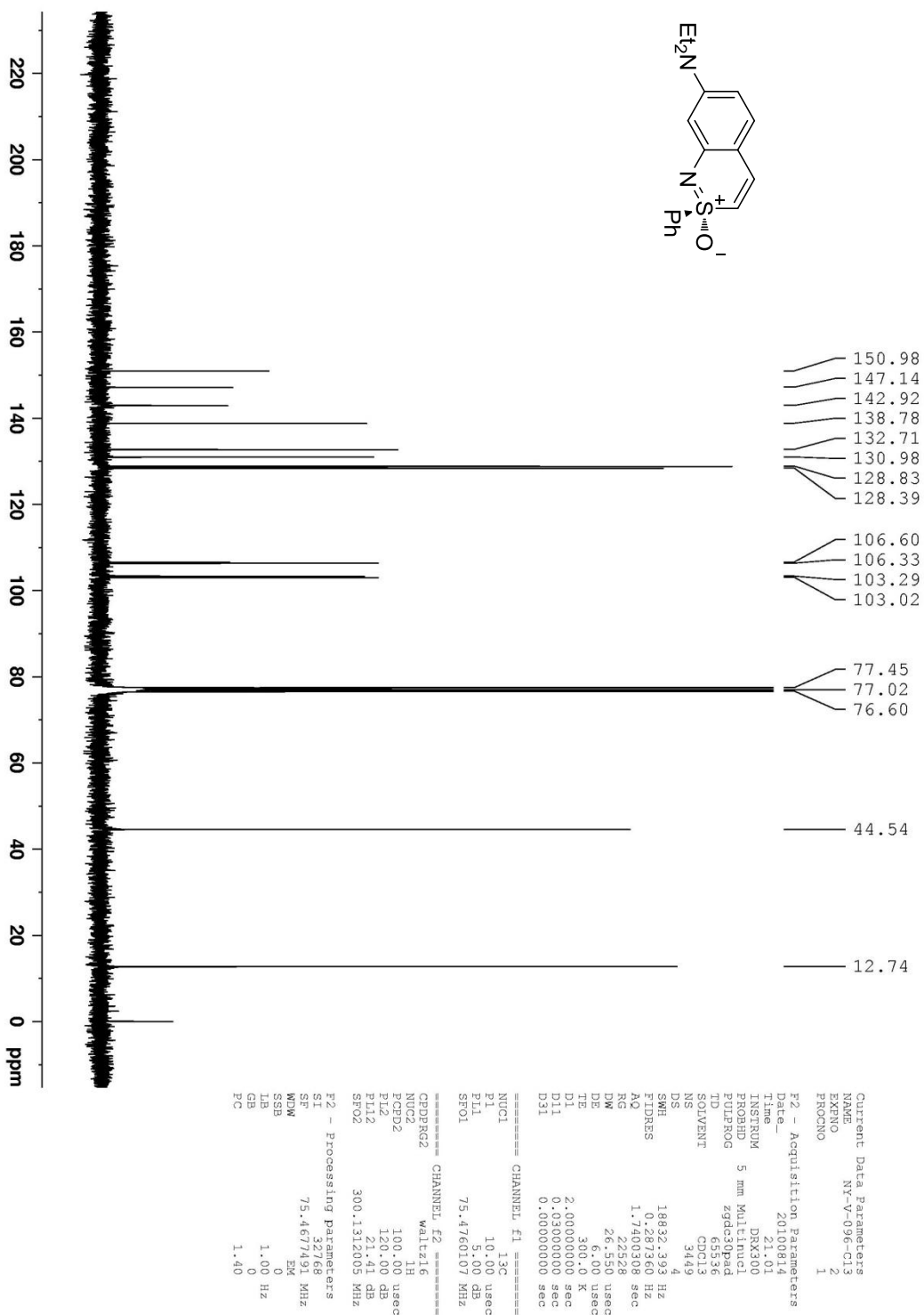


Figure 26 <sup>13</sup>C-NMR spectrum of 8f

S38

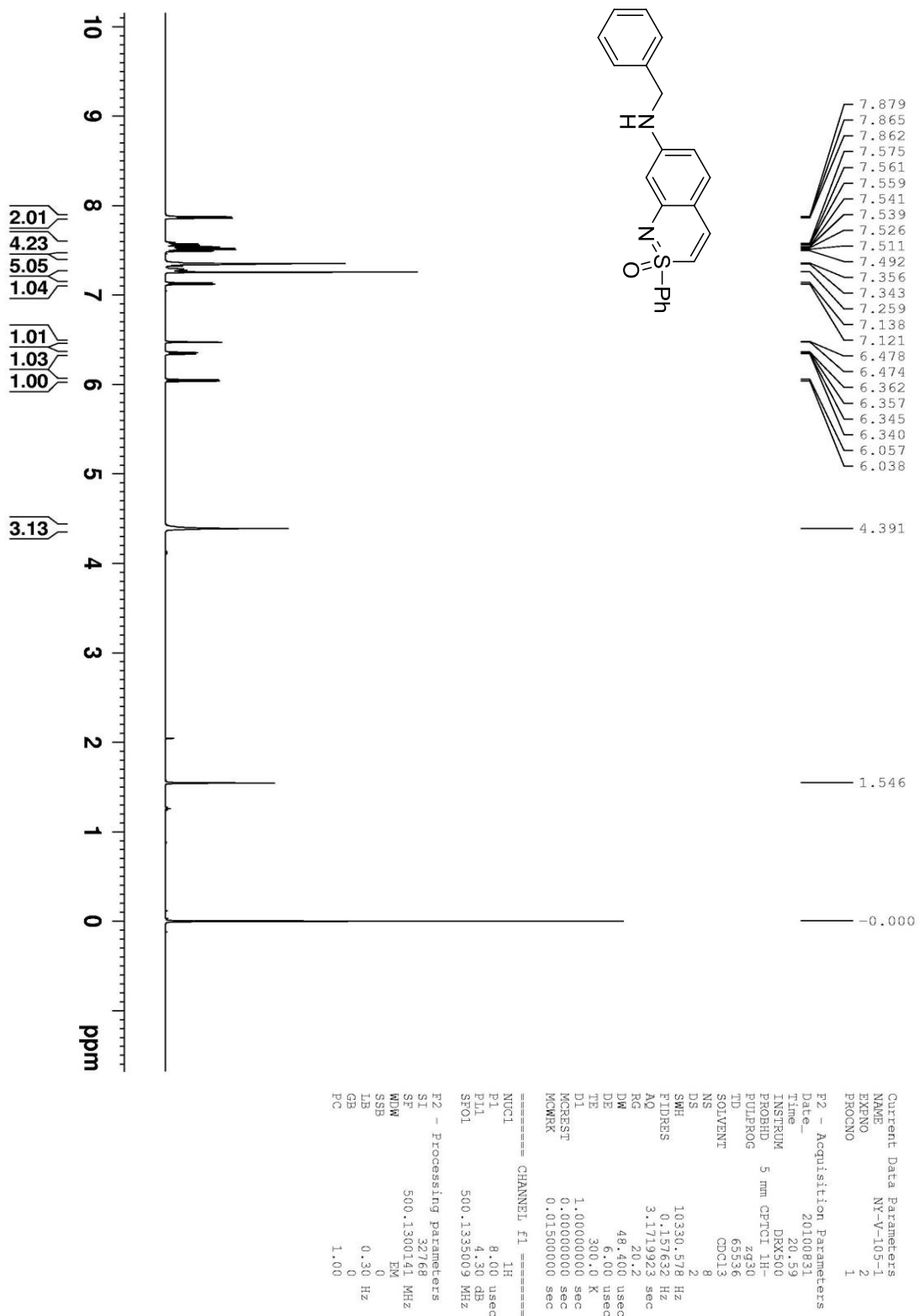


Figure 27 <sup>1</sup>H-NMR spectrum of 8g

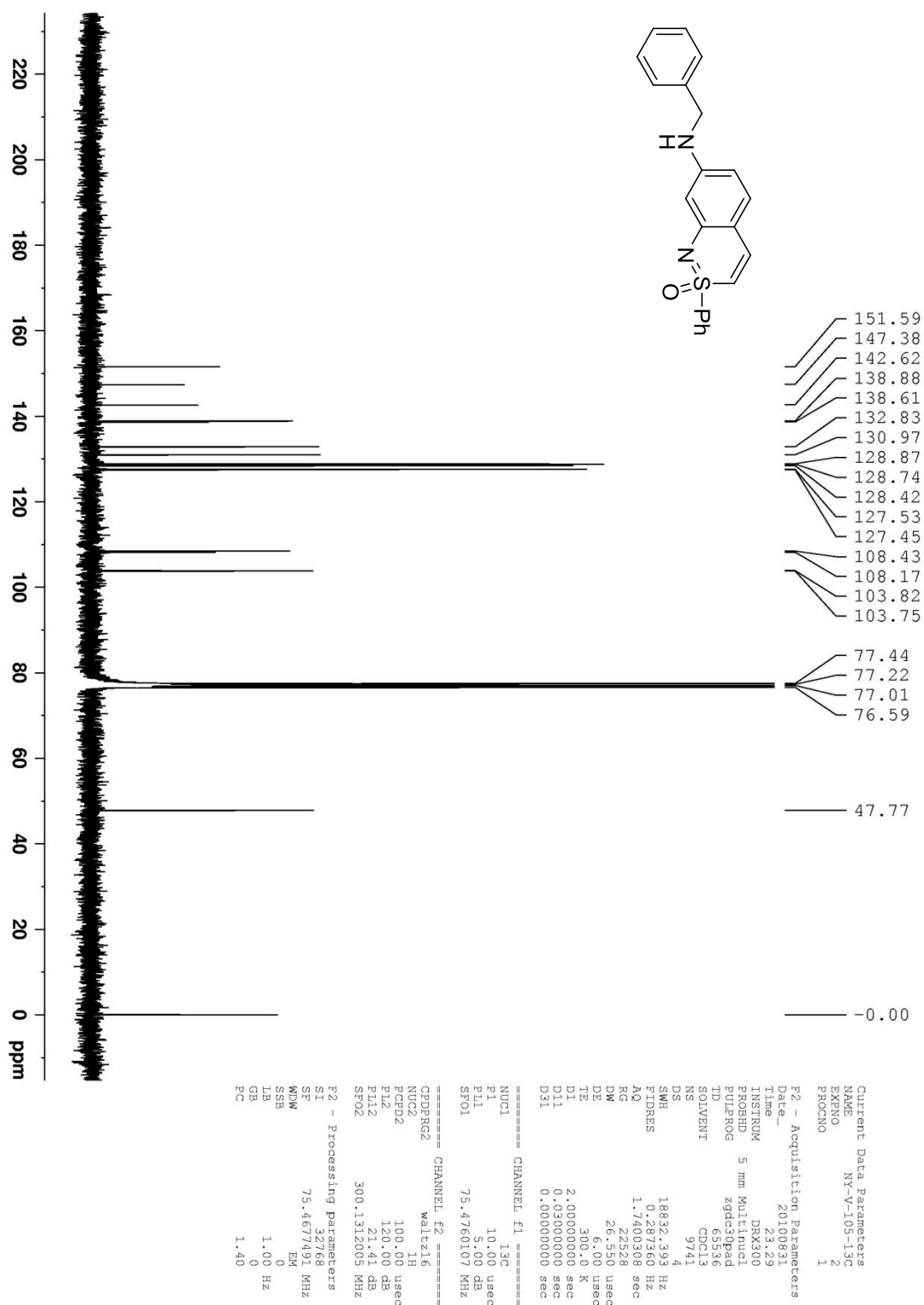


Figure 28 <sup>13</sup>C-NMR spectrum of 8g

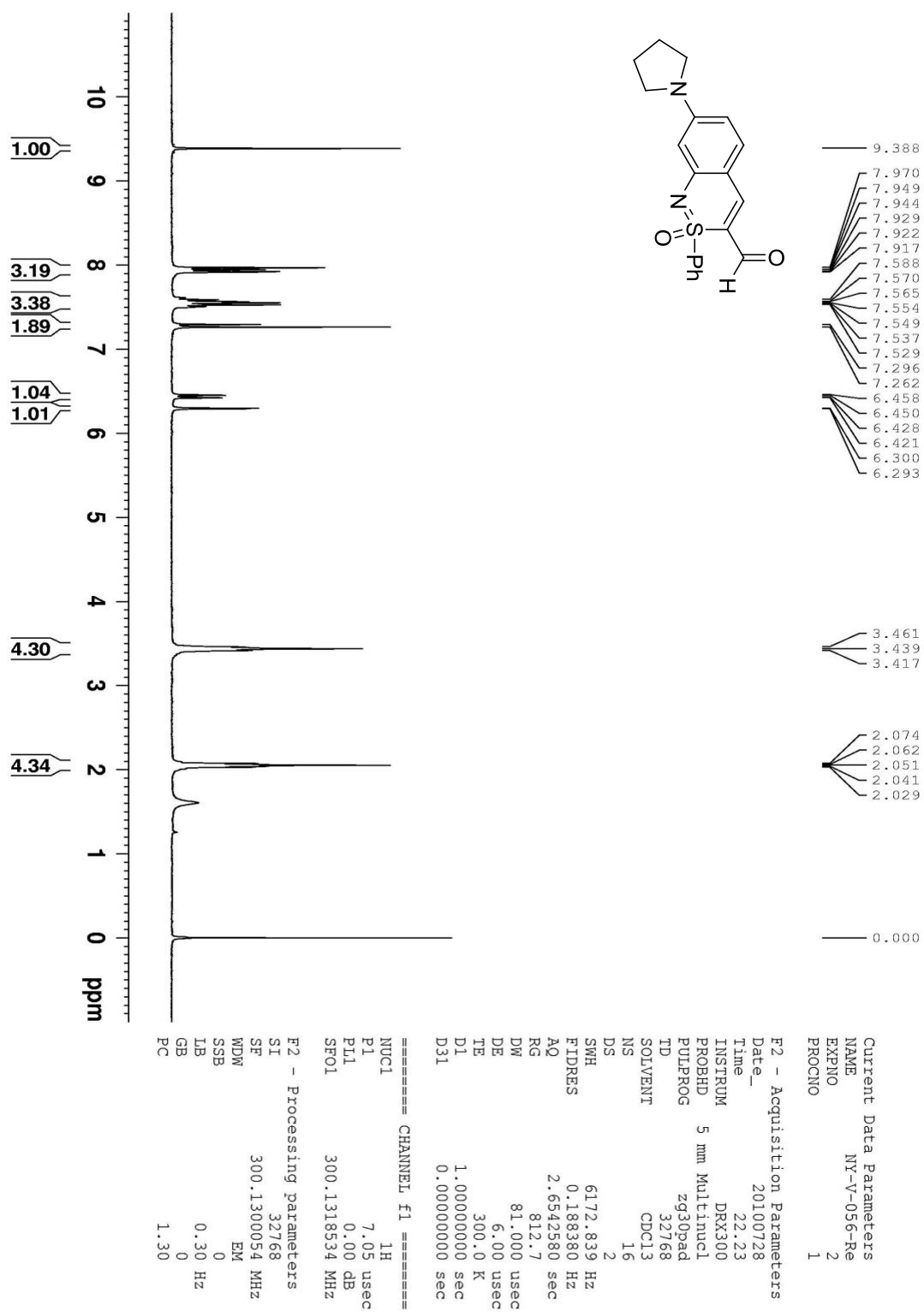


Figure 29 <sup>1</sup>H-NMR spectrum of 11



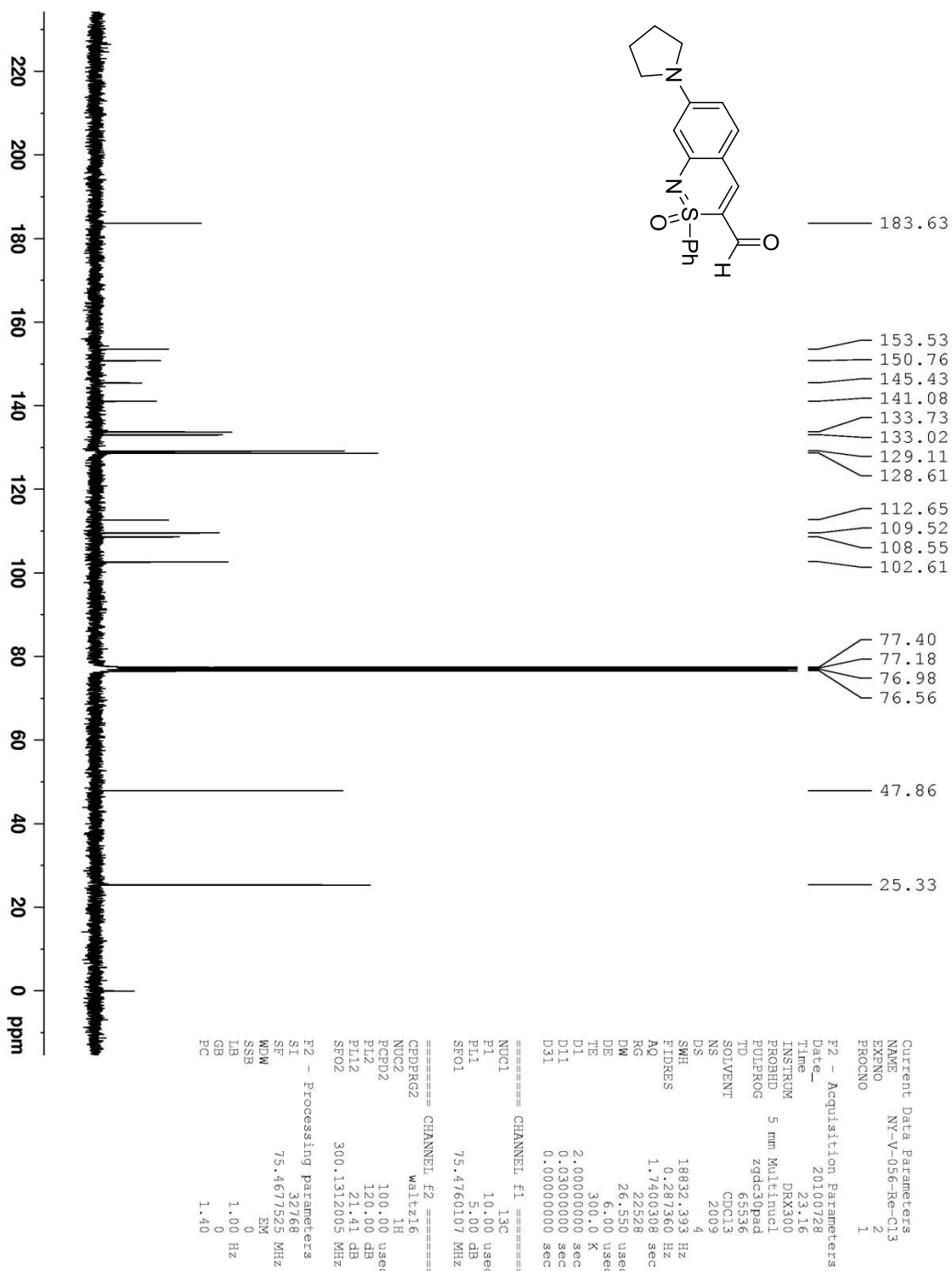


Figure30 <sup>13</sup>C-NMR spectrum of 11