

**B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-Catalyzed Metal-Free Hydrogenation of Naphthylamines**

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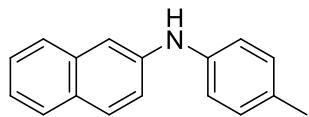
**Supporting Information**

**General consideration:** All air-sensitive compounds were handled under an atmosphere of argon or in a nitrogen-filled glovebox.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AV 400 at ambient temperature with  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  as solvent and TMS as internal standard. Chemical shifts ( $\delta$ ) were given in ppm, referenced to the residual proton resonance of TMS (0), to the carbon resonance of the  $\text{CDCl}_3$  (77.23). Coupling constants ( $J$ ) were given in Hertz (Hz). Flash column chromatography was performed on silica gel (200-300 mesh). All solvents were purified by conventional methods, distilled before use. Commercially available reagents were used without further purification.

**Representative procedure for metal-free hydrogenation of naphthylamines (Table 2, entry 1):** To a glass test tube (10 mL) was added  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.0126 g, 0.025 mmol), *N*-phenyl-2-naphthylamine (**1a**) (0.0548 g, 0.25 mmol) and dry toluene (1.0 mL) in a nitrogen atmosphere glovebox. The tube was then moved to a stainless-steel autoclave. After being sealed, the autoclave was purged three times with  $\text{H}_2$  and the final pressure of hydrogen was adjusted to 20 bar. The reaction mixture was stirred at 60 °C for 6 h. After cooling to ambient temperature, the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (100/1 to 50/1) as the eluent to give *N*-phenyl-1,2,3,4-tetrahydronaphthalen-2-amine (**2a**) as a colorless oil (0.0524 g, 94% yield).

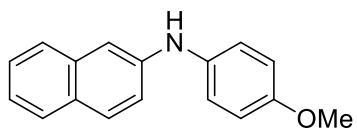
**Typical procedure for the synthesis of naphthylamines (1b):** A mixture of 2-bromonaphthalene (0.621 g, 3.0 mmol), *p*-toluidine (0.482 g, 4.5 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.057 g, 0.06 mmol), dppf (0.083 g, 0.15 mmol) and  $^t\text{BuONa}$  (0.432 g, 4.5 mmol) in toluene (10 mL) was stirred at 100 °C overnight. After cooling to ambient temperature, the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (100/1 to 50/1) as the eluent to give *N*-phenylnaphthalen-2-amine (**1b**) as a white solid (0.558 g, 85% yield).

M. Yu, M. Wang, X. Chen, B. Hong, X. Zhang and C. Cheng, *J. Chem. Res.*, 2005, **9**, 558.



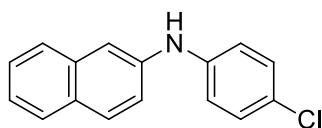
**1b**, white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.71 (d,  $J = 7.6$  Hz, 2H), 7.61 (d,  $J = 8.0$  Hz, 1H), 7.40-7.35 (m, 2H), 7.28-7.27 (m, 1H), 7.18-7.07 (m, 5H), 5.75 (brs, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  141.9, 140.3, 134.9, 131.6, 130.2, 129.3, 129.1, 127.8, 126.6, 126.5, 123.4, 119.8, 119.6, 110.5, 21.0.

J. Huang and L. Yang, *Org. Lett.*, 2011, **13**, 3750.



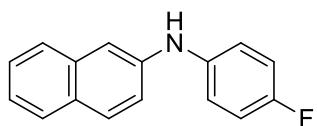
**1c**, white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.71-7.67 (m, 2H), 7.57 (d,  $J = 8.4$  Hz, 1H), 7.36 (dd,  $J = 7.6, 7.6$  Hz, 1H), 7.25-7.20 (m, 2H), 7.14 (d,  $J = 8.4$  Hz, 2H), 7.09 (dd,  $J = 8.8, 1.6$  Hz, 1H), 6.89 (d,  $J = 8.4$  Hz, 2H), 5.63 (brs, 1H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  155.7, 143.1, 135.7, 135.0, 129.3, 128.7, 127.8, 126.6, 126.4, 123.1, 122.8, 119.1, 114.9, 108.9, 55.8.

J. Huang and L. Yang, *Org. Lett.*, 2011, **13**, 3750.



**1d**, white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.73 (d,  $J = 8.8$  Hz, 2H), 7.63 (d,  $J = 8.0$  Hz, 1H), 7.43-7.38 (m, 2H), 7.33-7.29 (m, 1H), 7.25-7.22 (m, 2H), 7.17 (dd,  $J = 8.8, 2.4$  Hz, 1H), 7.07-7.03 (m, 2H), 5.79 (brs, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  141.9, 140.6, 134.7, 129.6, 129.5, 127.9, 126.8, 126.7, 126.1, 124.0, 120.2, 119.5, 112.3.

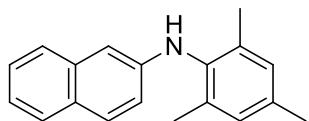
N. E. Shchepina, I. I. Boiko and G. A. Aleksandrova, *Pharm. Chem. J.*, 2011, **45**, 159.



**1e**, white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.72 (d,  $J = 8.4$  Hz, 2H), 7.61 (d,  $J = 8.0$  Hz, 1H), 7.41-7.37 (m, 1H), 7.30-7.26 (m, 2H), 7.15-7.10 (m, 3H), 7.05-6.99 (m, 2H), 5.71 (brs, 1H);  $^{13}\text{C}$  NMR

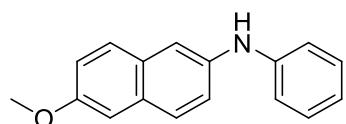
(100 MHz, CDCl<sub>3</sub>, ppm): δ 158.4 (d, *J* = 239.0 Hz), 141.8, 138.9 (d, *J* = 2.0 Hz), 134.8, 129.5, 129.1, 127.8, 126.7, 126.6, 123.6, 121.2 (d, *J* = 8.0 Hz), 119.5, 116.2 (d, *J* = 22.0 Hz), 110.5.

X. Li, J. Huang and L. Yang, *Org. Lett.*, 2011, **13**, 4950.



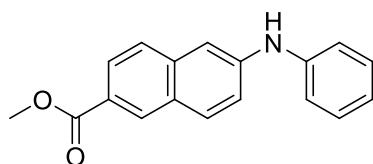
**1f**, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.74-7.70 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.38-7.34 (m, 1H), 7.25-7.21 (m, 1H), 7.04 (s, 2H), 6.99 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.60-6.59 (m, 1H), 5.30 (brs, 1H), 2.39 (s, 3H), 2.25 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 144.5, 136.3, 135.9, 135.5, 135.3, 129.5, 129.3, 128.0, 127.8, 126.5, 126.1, 122.3, 117.7, 106.0, 21.2, 18.4.

S. B. Cortright, J. C. Huffman, R. A. Yoder, J. N. Coalter and J. N. Johnston, *Organometallics*, 2004, **23**, 2238.



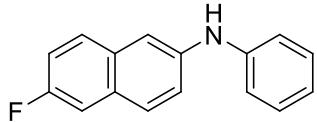
**1g**, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.65 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 7.30-7.22 (m, 3H), 7.11-7.09 (m, 4H), 6.93 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.78 (brs, 1H), 3.90 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 156.5, 143.9, 139.0, 130.5, 130.1, 129.6, 128.3, 128.1, 121.4, 121.0, 119.3, 117.6, 113.7, 106.3, 55.5.

V. I. Maslennikova, L. V. Shelenkova, O. S. Serkova, L. K. Vasyanina and E. E. Nifantiev, *Arkivoc*, 2012, **9**, 136.

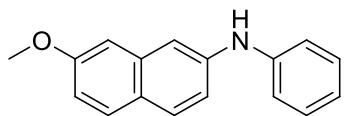


**1h**, white solid, m.p. 223-225 °C; IR (film): 3446, 3355, 1698, 1624, 1597, 1344, 1100 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 8.48 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.40-7.33 (m, 4H), 7.26-7.22 (m, 2H), 7.08-7.04 (m, 1H), 6.02 (brs, 1H), 3.96 (s, 3H); <sup>13</sup>C

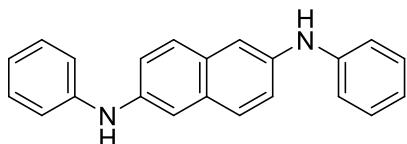
NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 167.7, 143.8, 141.9, 137.4, 131.1, 131.0, 129.8, 127.8, 126.6, 126.2, 124.8, 122.8, 120.1, 119.9, 109.5, 52.3; HRMS (ESI): calcd. for C<sub>18</sub>H<sub>16</sub>NO<sub>2</sub>(M+H)<sup>+</sup>: 278.1176; Found: 278.1176.



**1i**, white solid, m.p. 135-137 °C; IR (film): 3399, 1611, 1598, 1515 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.65 (d, *J* = 8.8 Hz, 1H), 7.60-7.56 (m, 1H), 7.40-7.30 (m, 5H), 7.23-7.11 (m, 3H), 7.01-6.99 (m, 1H), 5.76 (brs, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 159.5 (d, *J* = 241.5 Hz), 143.1, 140.5, 131.7, 129.6, 128.8, 128.7, 128.6, 128.5, 121.5 (d, *J* = 21.4 Hz), 118.3, 116.7 (d, *J* = 21.4 Hz), 112.1, 110.9 (d, *J* = 20.3 Hz); HRMS (ESI): calcd. for C<sub>16</sub>H<sub>13</sub>FN (M+H)<sup>+</sup>: 238.1027; Found: 238.1027.

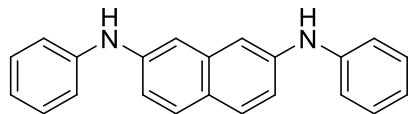


**1j**, white solid, m.p. 133-136 °C; IR (film): 3385, 1629, 1602, 1508 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.65-7.60 (m, 2H), 7.32-7.28 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.99-6.95 (m, 3H), 5.82 (brs, 1H), 3.87 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 158.4, 143.1, 141.7, 136.1, 129.6, 129.3, 129.1, 124.8, 121.6, 118.7, 117.7, 116.3, 110.8, 105.0, 55.5; HRMS (ESI): calcd. for C<sub>17</sub>H<sub>16</sub>NO (M+H)<sup>+</sup>: 250.1226; Found: 250.1227.



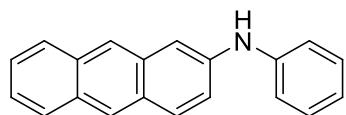
**1k**, white solid; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 8.15 (s, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.35 (s, 2H), 7.21-7.14 (m, 6H), 7.07 (d, *J* = 8.0 Hz, 4H), 6.78-6.75 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 149.2, 144.2, 134.8, 134.5, 132.7, 126.1, 124.8, 121.7, 116.3.

S. M. Shein, V. P. Rusov and V. I. Sokolenko, *J. Org. Chem.*, 1980, **16**, 2014.



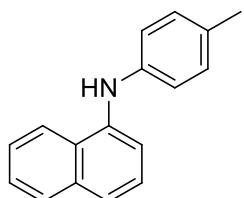
**1l**, white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.62 (d,  $J = 8.8$  Hz, 1H), 7.32-7.25 (m, 6H), 7.16 (d,  $J = 8.0$  Hz, 4H), 7.04 (d,  $J = 8.4$  Hz, 2H), 6.99-6.96 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  142.9, 141.6, 136.0, 129.6, 129.2, 125.2, 121.8, 118.8, 117.7, 110.6.

V. I. Maslennikova, L. V. Shelenkova, O. S. Serkova, L. K. Vasyanina and E. E. Nifantiev, *Arkivoc*, 2012, **9**, 136.



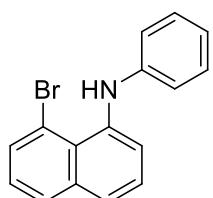
**1m**, yellow solid; m.p. 135-137 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.31 (s, 1H), 8.16 (s, 1H), 7.95-7.89 (m, 3H), 7.54 (s, 1H), 7.43-7.33 (m, 4H), 7.26-7.22 (m, 4H), 7.04 -7.00 (m, 1H), 5.92 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  142.8, 140.4, 133.1, 130.5, 129.8, 129.7, 128.6, 128.5, 127.8, 126.4, 125.7, 124.5, 123.9, 121.9, 121.5, 119.0, 109.1.

N. E. Shchepina, I. I. Boiko and G. A. Aleksandrova, *Pharm. Chem. J.* 2011, **45**, 159.

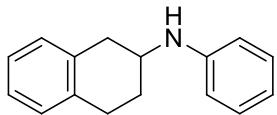


**1o**, white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.00-7.97 (m, 1H), 7.84-7.82 (m, 1H), 7.50-7.42 (m, 3H), 7.34 (dd,  $J = 7.6, 7.6$  Hz, 1H), 7.26 (d,  $J = 7.6$  Hz, 1H), 7.07 (d,  $J = 8.0$  Hz, 2H), 6.93 (d,  $J = 8.0$  Hz, 2H), 5.85 (brs, 1H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  142.0, 139.8, 134.9, 130.6, 130.1, 128.7, 127.2, 126.3, 126.2, 125.7, 122.2, 121.7, 118.7, 114.3, 20.9.

T. Ogata and J. F. Hartwig, *J. Am. Chem. Soc.*, 2008, **130**, 13848.

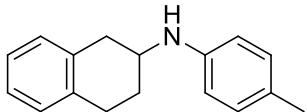


**1p**, white oil; IR (film): 3421, 3054, 1599, 1561, 1340, 1192, 918 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.50 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.38 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.29-7.19 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.94-6.90 (dd, *J* = 7.2, 7.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 144.2, 139.3, 137.7, 133.2, 129.6, 126.8, 126.2, 124.6, 123.3, 120.9, 118.7, 116.8. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>13</sub>BrN (M+H)<sup>+</sup>: 298.0226; Found: 298.0225.

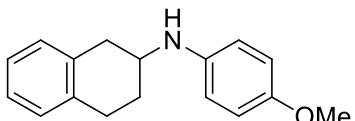


**2a**, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.20-7.08 (m, 6H), 6.70 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.64 (dd, *J* = 8.4, 0.4 Hz, 2H), 3.85-3.78 (m, 1H), 3.66 (brs, 1H), 3.22 (dd, *J* = 16.0, 4.4 Hz, 1H), 2.95-2.85 (m, 2H), 2.69 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.20-2.14 (m, 1H), 1.82-1.73 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 147.3, 136.1, 134.9, 129.7, 129.6, 129.0, 126.3, 126.1, 117.5, 113.5, 48.6, 36.7, 29.0, 27.7.

A. Abdel-Magid, K. Carson, B. Harris, C. Maryanoff and R. Shah, *J. Org. Chem.*, 1996, **61**, 3849.



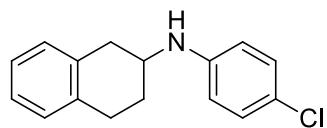
**2b**, white solid; m.p. 69-70 °C; IR (film): 3398, 1616, 1519 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.13-7.07 (m, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 3.81-3.75 (m, 1H), 3.52 (brs, 1H), 3.20 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.91-2.88 (m, 2H), 2.66 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.24 (s, 3H), 2.18-2.15 (m, 1H), 1.79-1.70 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 145.0, 136.1, 135.0, 130.0, 129.7, 129.0, 126.8, 126.2, 126.0, 113.8, 48.9, 36.7, 29.0, 27.7, 20.6; HRMS (ESI) calcd. for C<sub>12</sub>H<sub>20</sub>NO(M+H): 238.1590, Found: 238.1589.



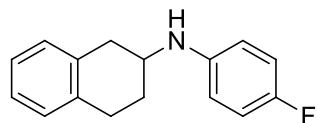
**2c**, pale yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.15-7.07 (m, 4H), 6.82-6.77 (m, 2H), 6.64-6.60 (m, 2H), 3.75 (s, 3H), 3.75-3.70 (m, 1H), 3.40 (brs, 1H), 3.20 (dd, *J* = 16.4, 4.4 Hz, 1H),

2.92-2.89 (m, 2H), 2.67 (dd,  $J = 16.4, 8.4$  Hz, 1H), 2.24-2.14 (m, 1H), 1.79-1.69 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  152.4, 141.5, 136.2, 135.1, 129.7, 129.0, 126.2, 126.1, 115.24, 115.19, 56.0, 49.7, 36.8, 29.1, 27.7.

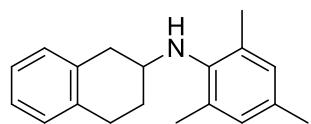
B. Yao, H. Ji, Y. Cao, Y. Zhou, J. Zhu, J. Lue, Y. Li, J. Chen, C. Zheng, Y. Jiang, R. Liang and H. Tang, *J. Med. Chem.*, 2007, **50**, 5293.



**2d**, pale yellow solid, m.p. 102-104 °C; IR (film): 3406, 1597, 1494  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.14-7.07 (m, 6H), 6.54 (d,  $J = 8.8$  Hz, 2H), 3.77-3.75 (m, 1H), 3.67 (brs, 1H), 3.19 (dd,  $J = 16.0, 4.0$  Hz, 1H), 2.92-2.88 (m, 2H), 2.67 (dd,  $J = 16.4, 8.0$  Hz, 1H), 2.16-2.13 (m, 1H), 1.81-1.71 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  145.9, 135.9, 134.6, 129.7, 129.4, 129.0, 126.4, 126.1, 121.9, 114.5, 48.7, 36.5, 28.7, 27.5; HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{17}\text{NCl}$  ( $\text{M}+\text{H}$ ): 258.1044; Found: 258.1043.

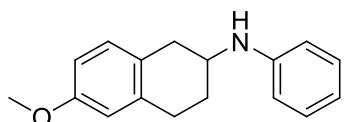


**2e**, white solid; m.p. 67-68 °C; IR (film): 3398, 1509, 1219  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.15-7.07 (m, 4H), 6.91-6.87 (m, 2H), 6.59-6.56 (m, 2H), 3.78-3.71 (m, 1H), 3.54 (brs, 1H), 3.20 (dd,  $J = 16.4, 4.4$  Hz, 1H), 2.92-2.89 (m, 2H), 2.68 (dd,  $J = 16.4, 8.0$  Hz, 1H), 2.19-2.14 (m, 1H), 1.80-1.71 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  155.9 (d,  $J = 234.0$  Hz), 143.6 (d,  $J = 2.0$  Hz), 136.0, 134.8, 129.7, 129.0, 126.3, 126.1, 115.9 (d,  $J = 23.0$  Hz), 114.5 (d,  $J = 7.0$  Hz), 49.3, 36.6, 28.9, 27.6; HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{17}\text{NF}$  ( $\text{M}+\text{H}$ ): 242.1340; Found: 242.1338.



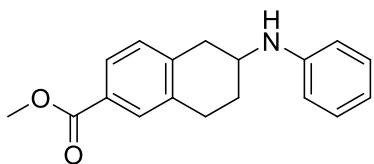
**2f**, colorless oil; IR (film): 1483, 1452, 1235  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.20-7.04 (m, 4H), 6.81 (s, 2H), 3.50-3.42 (m, 1H), 3.07 (dd,  $J = 16.0, 4.4$  Hz, 1H), 2.94-2.76 (m, 3H), 2.64 (dd,  $J = 16.0, 9.2$  Hz, 1H), 2.23 (s, 3H), 2.21 (s, 6H), 2.11-2.05 (m, 1H), 1.69-1.59 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,

$\text{CDCl}_3$ , ppm):  $\delta$  142.2, 136.2, 135.5, 131.0, 129.7, 129.6, 128.9, 126.1, 126.0, 53.2, 37.6, 30.7, 28.6, 20.8, 19.0; HRMS (ESI) calcd. for  $\text{C}_{19}\text{H}_{29}\text{N}$  ( $\text{M}+\text{H}$ ): 266.1903; Found: 266.1901.

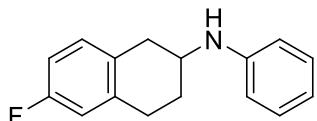


**2g**, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.24-7.15 (m, 2H), 6.99 (d,  $J = 8.4$ , 1H), 6.71-6.62 (m, 5H), 3.78 (brs, 1H), 3.77 (s, 3H), 3.14 (dd,  $J = 16.0, 4.8$  Hz, 1H), 2.88-2.86 (m, 2H), 2.61 (dd,  $J = 15.6, 8.0$  Hz, 1H), 2.17-2.14 (m, 1H), 1.80-1.71 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  158.1, 147.4, 137.2, 130.6, 129.5, 126.9, 117.5, 113.6, 113.5, 112.5, 55.5, 48.9, 35.9, 28.9, 27.9.

B. Yao, H. Ji, Y. Cao, Y. Zhou, J. Zhu, J. Lue, Y. Li, J. Chen, C. Zheng, Y. Jiang, R. Liang and H. Tang, *J. Med. Chem.*, 2007, **50**, 5293.

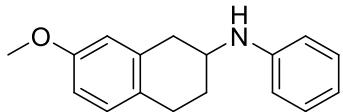


**2h** white solid; m.p. 103-105 °C; IR (film): 3392, 1716, 1602, 1285  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.81 (s, 1H), 7.77 (d,  $J = 8.0$ , 1H), 7.25-7.12 (m, 3H), 6.71 (dd,  $J = 7.2, 7.2$  Hz, 1H), 6.64 (d,  $J = 8.0$ , 2H), 3.90 (s, 3H), 3.84-3.80 (m, 1H), 3.66 (brs, 1H), 3.25 (dd,  $J = 16.8, 4.4$  Hz, 1H), 2.97-2.93 (m, 2H), 2.73 (dd,  $J = 16.8, 8.0$  Hz, 1H), 2.22-2.20 (m, 1H), 1.83-1.74 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  167.4, 147.1, 140.5, 136.3, 130.3, 129.8, 129.6, 128.2, 127.1, 117.7, 113.6, 52.2, 48.4, 36.9, 28.9, 27.6; HRMS (ESI): calcd. for  $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}$  ( $\text{M}+\text{H}$ )<sup>+</sup>: 282.1489; Found: 282.1489.



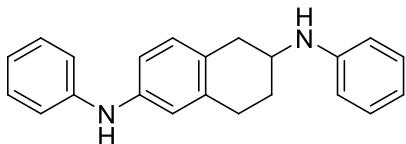
**2i** white solid; m.p. 98-100 °C; IR (film): 3399, 1602, 1499, 1180, 941  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.22-7.16 (m, 2H), 7.03-6.99 (m, 1H), 6.84-6.80 (m, 2H), 6.70 (dd,  $J = 7.2, 7.2$  Hz, 1H), 6.68-6.61 (m, 2H), 3.80-3.78 (m, 1H), 3.62 (brs, 1H), 3.15 (dd,  $J = 16.0, 4.0$  Hz, 1H), 2.90-2.86 (m, 2H), 2.62 (dd,  $J = 16.0, 8.0$  Hz, 1H), 2.17-2.14 (m, 1H), 1.79-1.70 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,

ppm):  $\delta$  161.4 (d,  $J = 242.5$  Hz), 147.2, 138.0 (d,  $J = 6.2$  Hz), 130.9 (d,  $J = 7.9$  Hz), 130.3, 129.6, 117.6, 115.1 (d,  $J = 20.4$  Hz), 113.5, 113.2 (d,  $J = 21.2$  Hz), 48.6, 36.0, 28.6, 27.8; HRMS (ESI): calcd. for  $C_{16}H_{17}FN$  ( $M+H$ )<sup>+</sup>: 242.1340; Found: 242.1339.

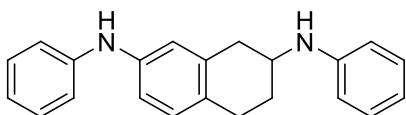


**2j** white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.22-7.15 (m, 2H), 7.02 (d,  $J = 8.0$  Hz, 1H), 6.73-6.69 (m, 2H), 6.64-6.61 (m, 3H), 3.80-3.78 (m, 1H), 3.78 (s, 3H), 3.65 (brs, 1H), 3.17 (dd,  $J = 16.0$ , 4.4 Hz, 1H), 2.87-2.78 (m, 2H), 2.65 (dd,  $J = 16.4$ , 8.4 Hz, 1H), 2.16-2.13 (m, 1H), 1.79-1.70 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  157.9, 147.4, 136.0, 129.9, 129.5, 128.1, 117.5, 114.2, 113.5, 112.7, 55.5, 48.6, 36.9, 29.2, 26.8.

B. Yao, H. Ji, Y. Cao, Y. Zhou, J. Zhu, J. Lue, Y. Li, J. Chen, C. Zheng, Y. Jiang, R. Liang and H. Tang, *J. Med. Chem.*, 2007, **50**, 5293.

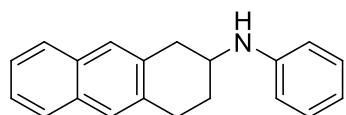


**2k**, white oil; IR (film): 3392, 1599, 1503, 1242 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.25-7.23 (m, 2H), 7.18-7.16 (m, 2H), 7.03 (d,  $J = 8.0$  Hz, 2H), 7.00-6.98 (m, 1H), 6.92-6.85 (m, 3H), 6.72-6.68 (m, 1H), 6.64 (m, d,  $J = 8.0$  Hz, 2H), 5.60 (brs, 1H), 3.80-3.79 (m, 1H), 3.69 (brs, 1H), 3.16 (dd,  $J = 16.0$ , 4.4 Hz, 1H), 2.87-2.84 (m, 2H), 2.62 (dd,  $J = 16.0$ , 8.4 Hz, 1H), 2.17-2.14 (m, 1H), 1.79-1.73 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  147.4, 143.8, 141.3, 137.1, 130.5, 129.5, 127.7, 120.8, 118.3, 117.5, 117.4, 116.7, 113.5, 48.8, 36.1, 28.9, 27.8; HRMS (ESI): calcd. for  $C_{22}H_{23}N_2$  ( $M+H$ )<sup>+</sup>: 315.1856; Found: 315.1857.

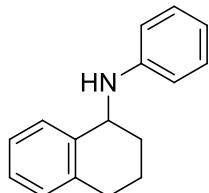


**2l**, white oil; IR (film): 3394, 1600, 1496, 1206, 1026 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.25-7.17 (m, 4H), 7.00 (d,  $J = 8.0$  Hz, 3H), 6.89-6.87 (m, 2H), 6.78-6.75 (m, 2H), 6.68-6.66 (m, 2H),

4.70 (brs, 2H), 3.78-3.76 (m, 1H), 3.09 (dd,  $J = 16.4, 4.0$  Hz, 1H), 2.84-2.83 (m, 2H), 2.63 (dd,  $J = 16.4, 8.4$  Hz, 1H), 2.15-2.12 (m, 1H), 1.79-1.70 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  145.8, 143.6, 141.2, 135.4, 129.9, 129.6, 129.5, 128.6, 120.9, 118.9, 118.8, 117.6, 117.0, 114.6, 49.8, 36.3, 28.8, 26.8; HRMS (ESI): calcd. for  $\text{C}_{22}\text{H}_{23}\text{N}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 315.1856; Found: 315.1855.

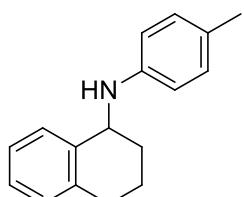


**2m**, yellow solid, m.p. 130-132 °C; IR (film): 3397, 1600, 1503, 1317, 1091  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.74-7.71 (m, 2H), 7.58 (d,  $J = 10.4$  Hz, 2H), 7.41-7.36 (m, 2H), 7.19 (dd,  $J = 7.6, 7.6$  Hz, 2H), 6.71 (dd,  $J = 7.6, 7.6$  Hz, 1H), 6.65 (d,  $J = 8.0$  Hz, 2H), 3.92-3.89 (m, 1H), 3.70 (brs, 1H), 3.4 (dd,  $J = 16.4, 4.0$  Hz, 1H), 3.12-3.06 (m, 2H), 2.88 (dd,  $J = 16.0, 8.0$  Hz, 1H), 2.29-2.25 (m, 1H), 1.86-1.82 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  147.3, 134.9, 133.8, 132.6, 132.4, 129.6, 127.7, 127.2, 126.8, 125.5, 125.4, 117.6, 113.6, 48.8, 37.0, 29.4, 27.8; HRMS (ESI): calcd. for  $\text{C}_{20}\text{H}_{19}\text{N}$  ( $\text{M}+\text{H}$ ) $^+$ : 274.1590; Found: 274.1589.



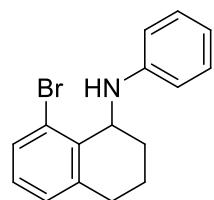
**2n**, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.40-7.38 (m, 1H), 7.23-7.10 (m, 5H), 6.70 (dd,  $J = 7.2, 7.2$  Hz, 1H), 6.66 (d,  $J = 8.0$  Hz, 2H), 4.64-4.61 (m, 1H), 3.86 (brs, 1H), 2.88-2.71 (m, 2H), 2.02-1.76 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  147.6, 138.4, 137.8, 129.6, 129.5, 129.2, 127.3, 126.3, 117.2, 113.0, 51.2, 29.5, 28.9, 19.6.

M. Rueping, E. Suigungo, C. Azap, T. Theissmann and M. Bolte, *Org. Lett.*, 2005, **7**, 3781.

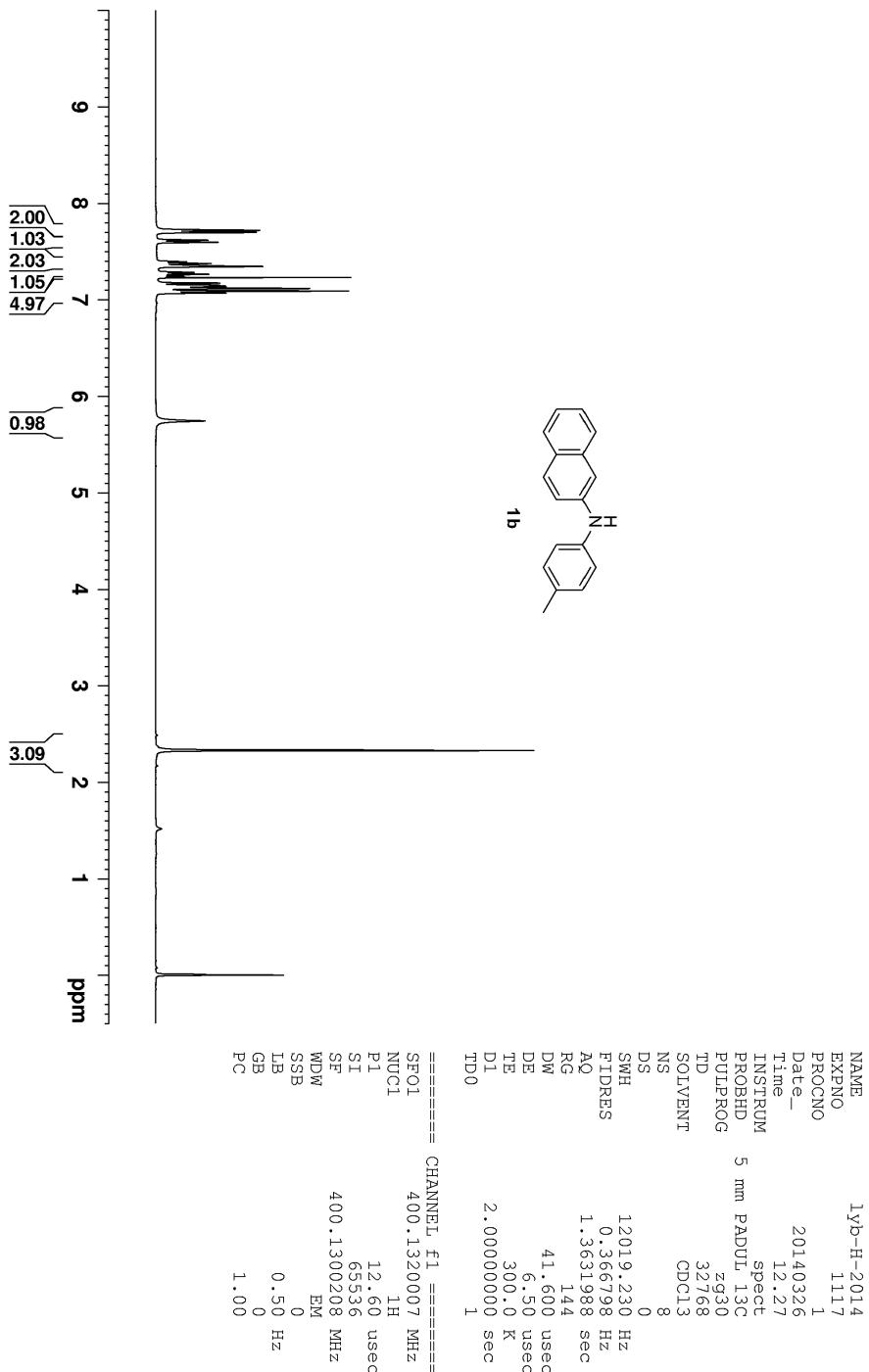


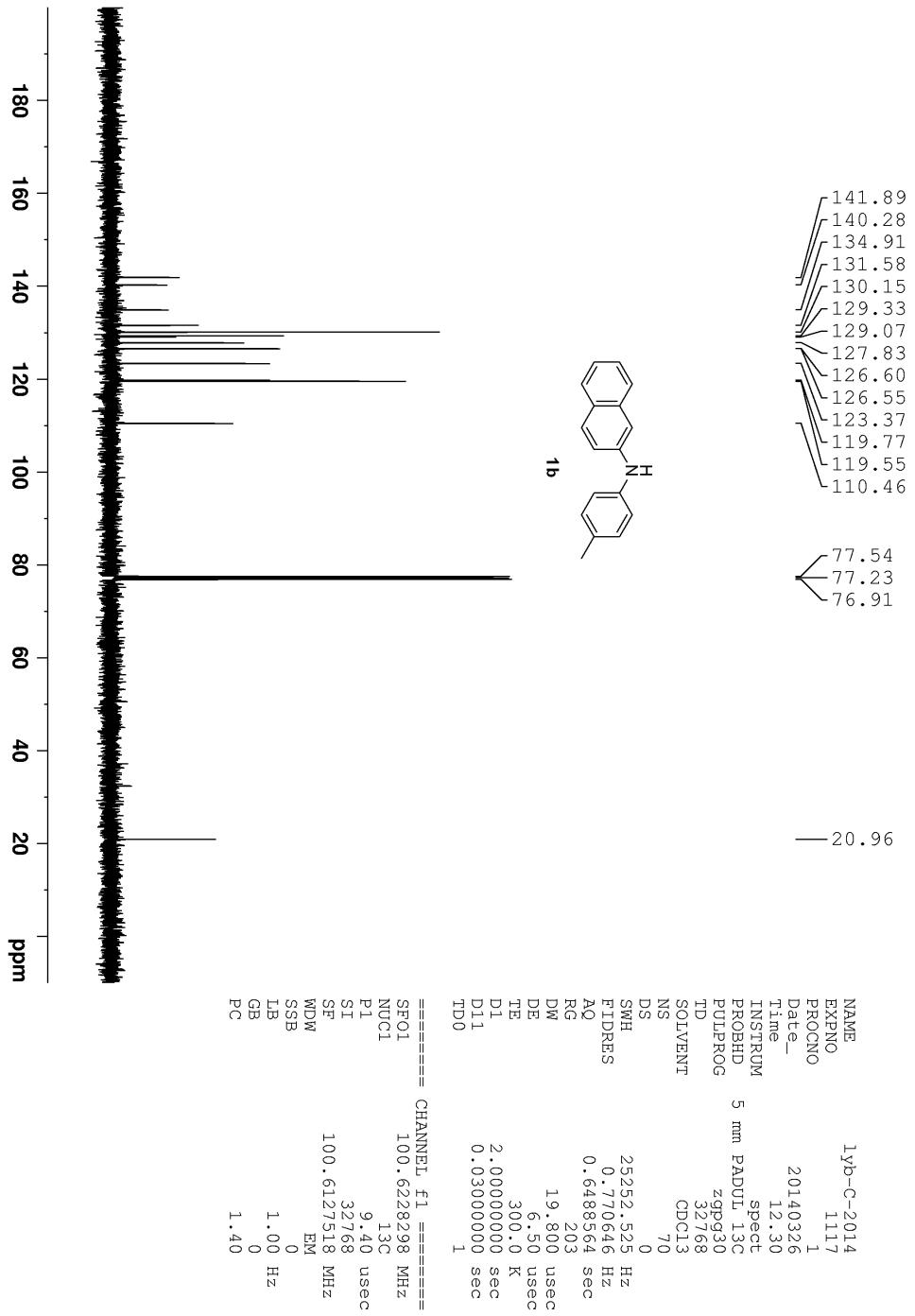
**2o**, white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.39 (d,  $J = 6.8$  Hz, 1H), 7.18-7.14 (m, 2H), 7.13-7.10 (m, 1H), 7.00 (d,  $J = 8.0$  Hz, 2H), 6.59 (d,  $J = 8.0$  Hz, 2H), 4.58 (dd,  $J = 4.8, 4.0$  Hz, 1H), 3.73 (brs, 1H), 2.87-2.70 (m, 2H), 2.25 (s, 3H), 1.97-1.91 (m, 2H), 1.90-1.75 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  145.4, 138.6, 137.8, 130.1, 129.5, 129.2, 127.3, 126.5, 126.3, 113.2, 51.5, 29.6, 28.9, 20.6, 19.6.

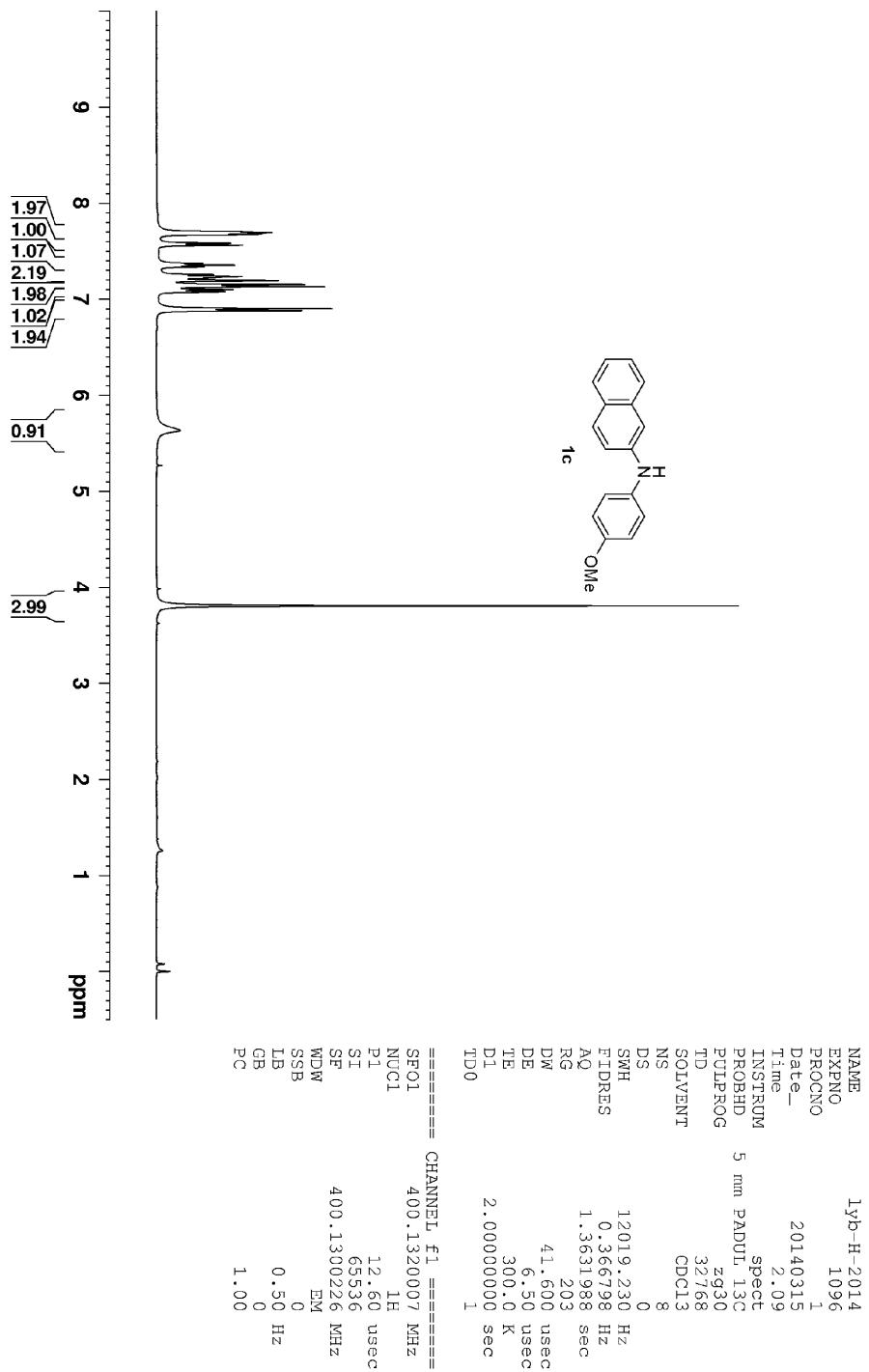
X. Zhou, M. Bao and Y. Zhou, *Adv. Synth. Catal.*, 2011, **353**, 84.

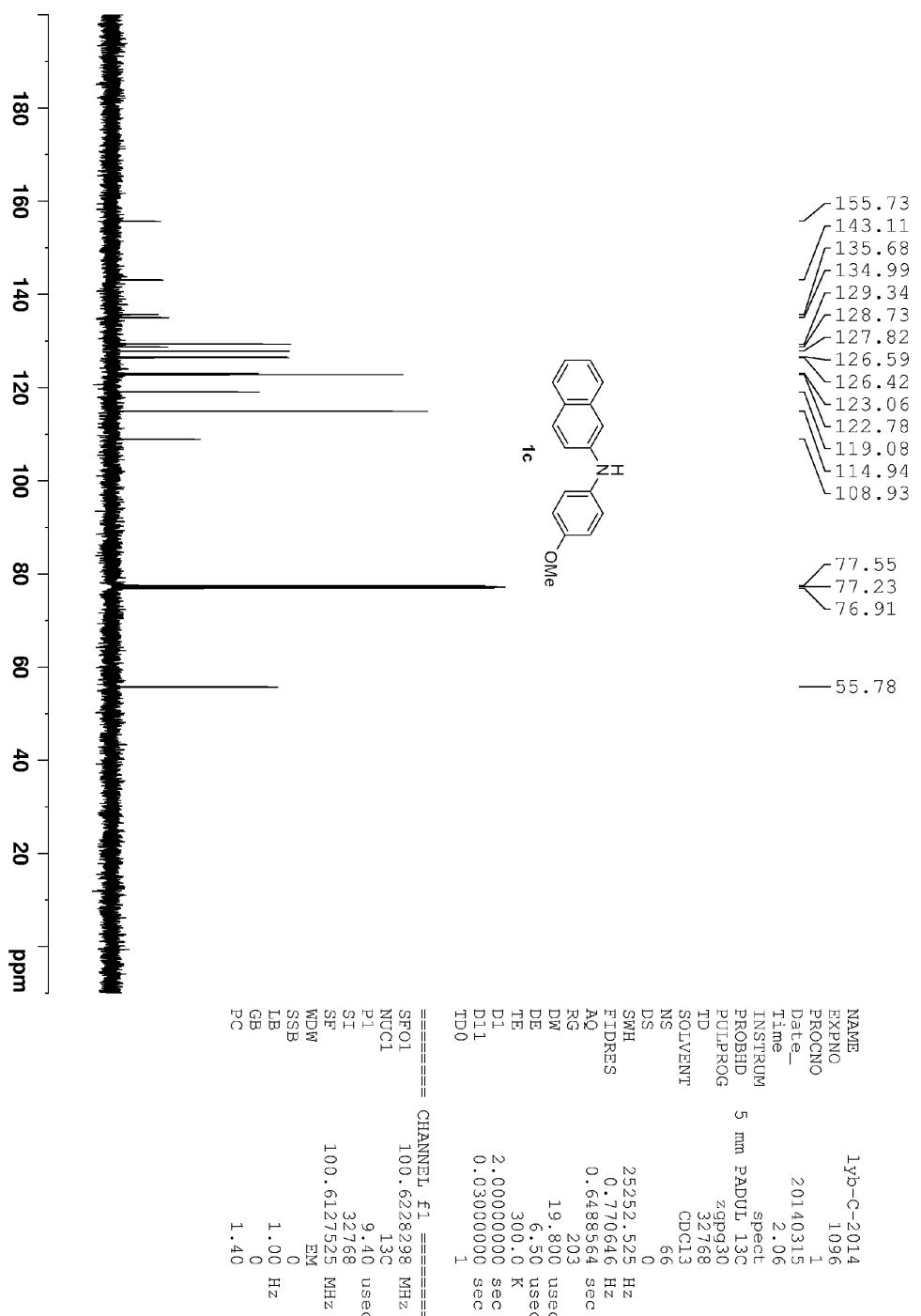


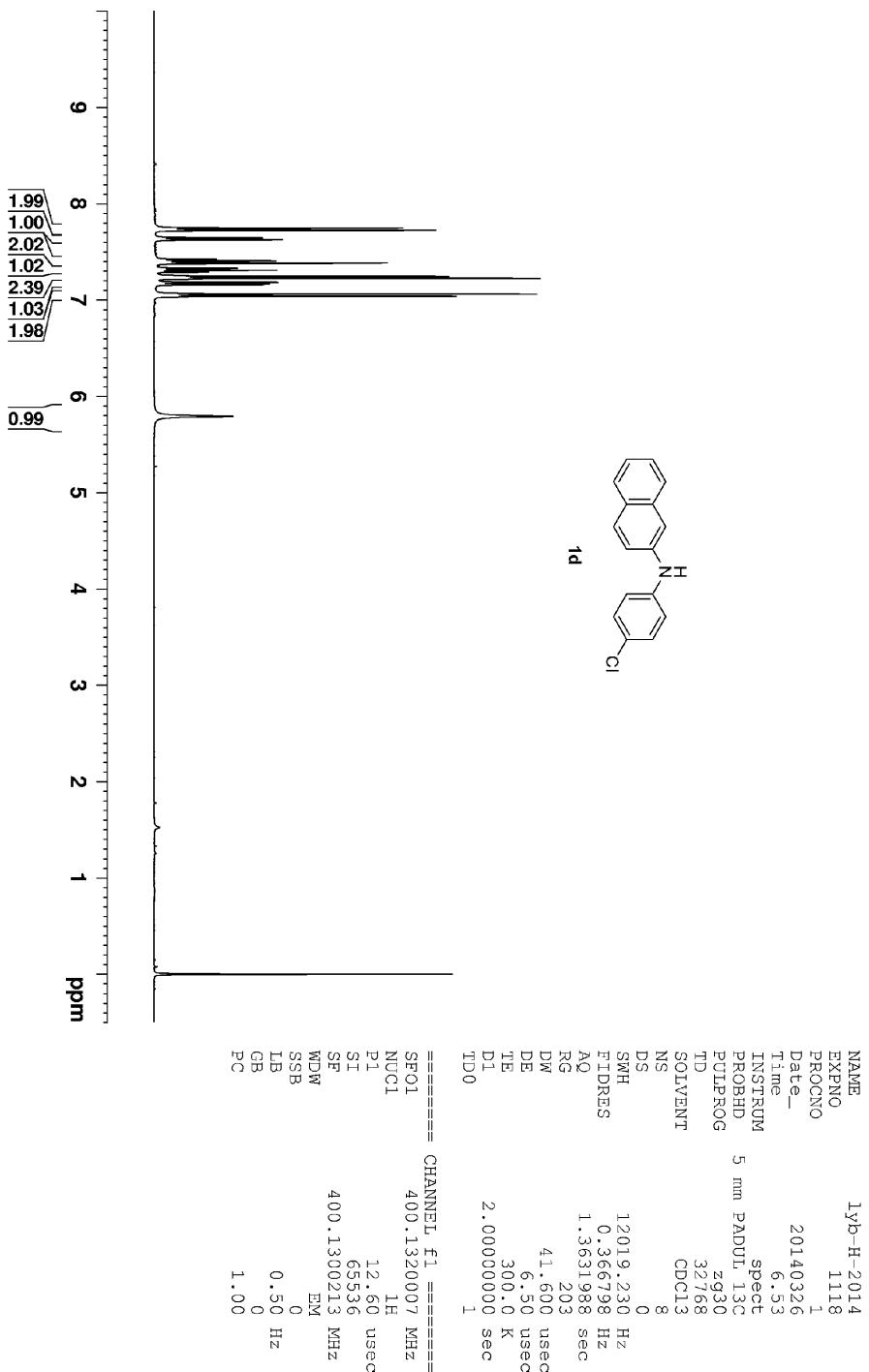
**2p**, white oil; IR (film): 3411, 1600, 1502, 1410, 1262, 935  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.43 (d,  $J = 6.8$  Hz, 1H), 7.20 (dd,  $J = 8.4, 7.6$  Hz, 1H), 7.08-7.06 (m, 2H), 6.70-6.68 (m, 3H), 4.74 (brs, 1H), 3.70 (brs, 1H), 2.89-2.83 (m, 1H), 2.78-2.73 (m, 1H), 2.31-2.26 (m, 1H), 1.91-1.77 (m, 2H), 1.66-1.52 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  147.5, 140.6, 136.5, 131.0, 129.5, 128.8, 128.7, 127.3, 117.4, 112.9, 50.5, 29.7, 27.7, 17.7; HRMS (ESI): calcd. for  $\text{C}_{16}\text{H}_{16}\text{BrN}$  ( $\text{M}+\text{H}$ ) $^+$ : 302.0539; Found: 302.0538.

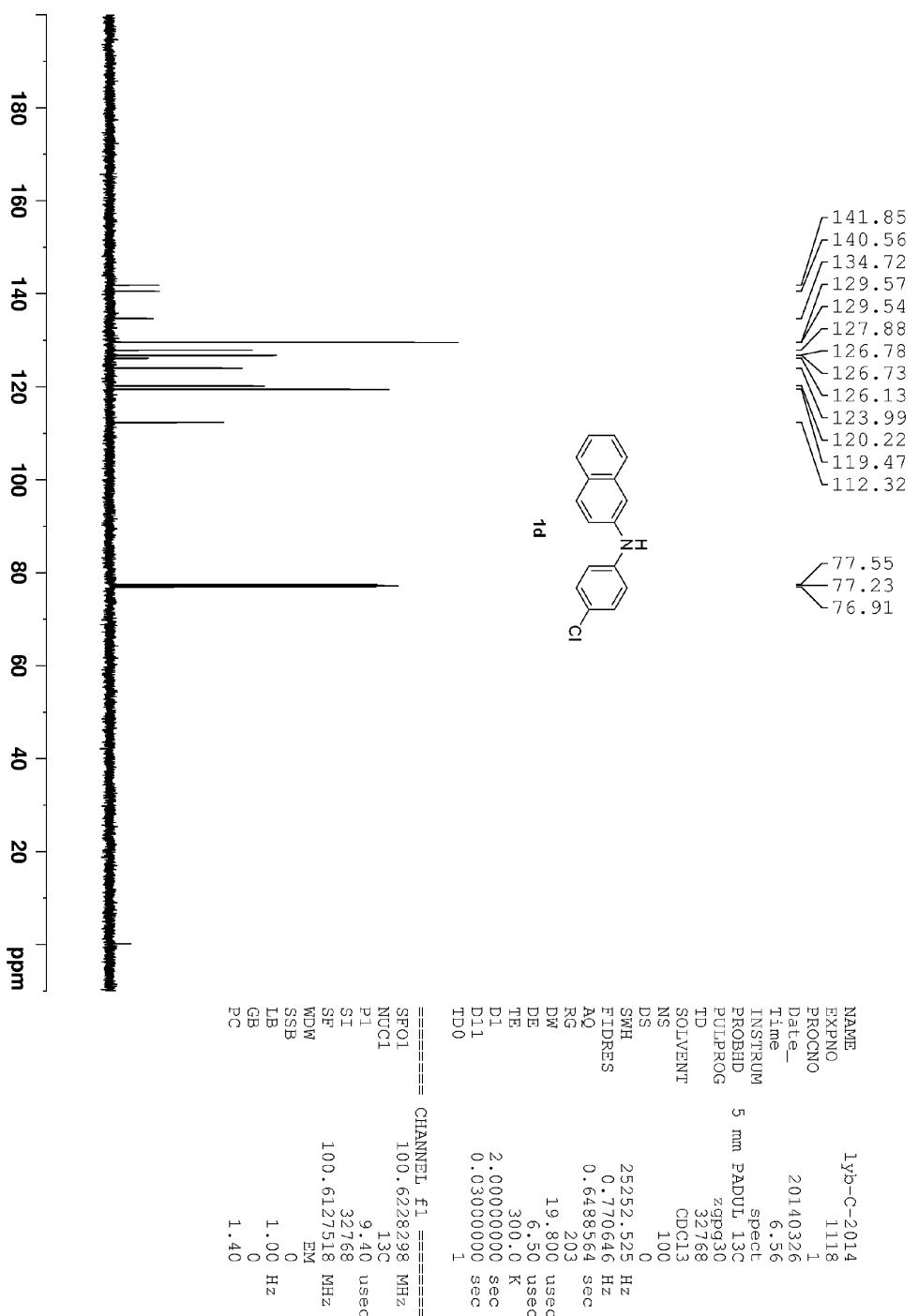


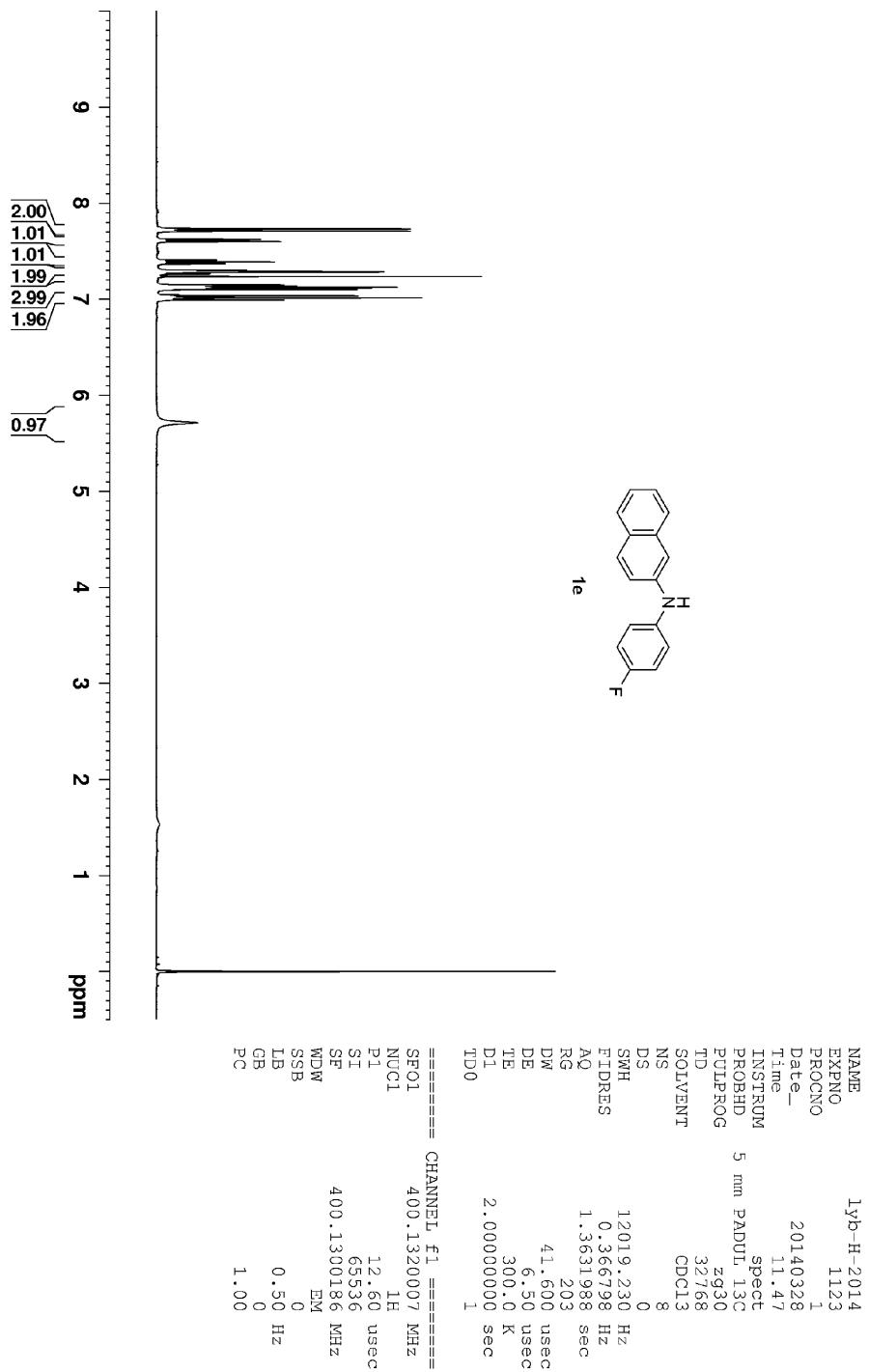


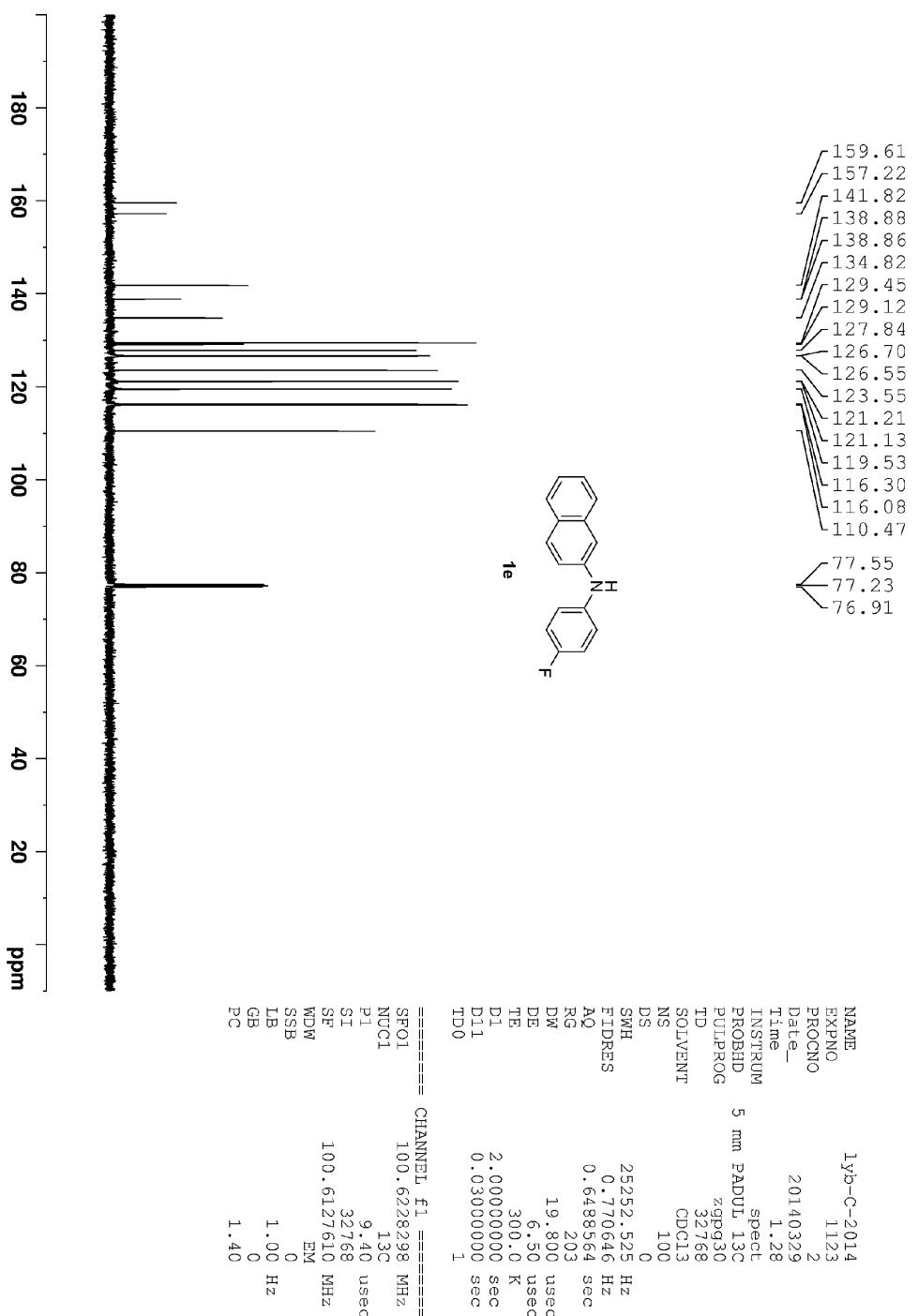


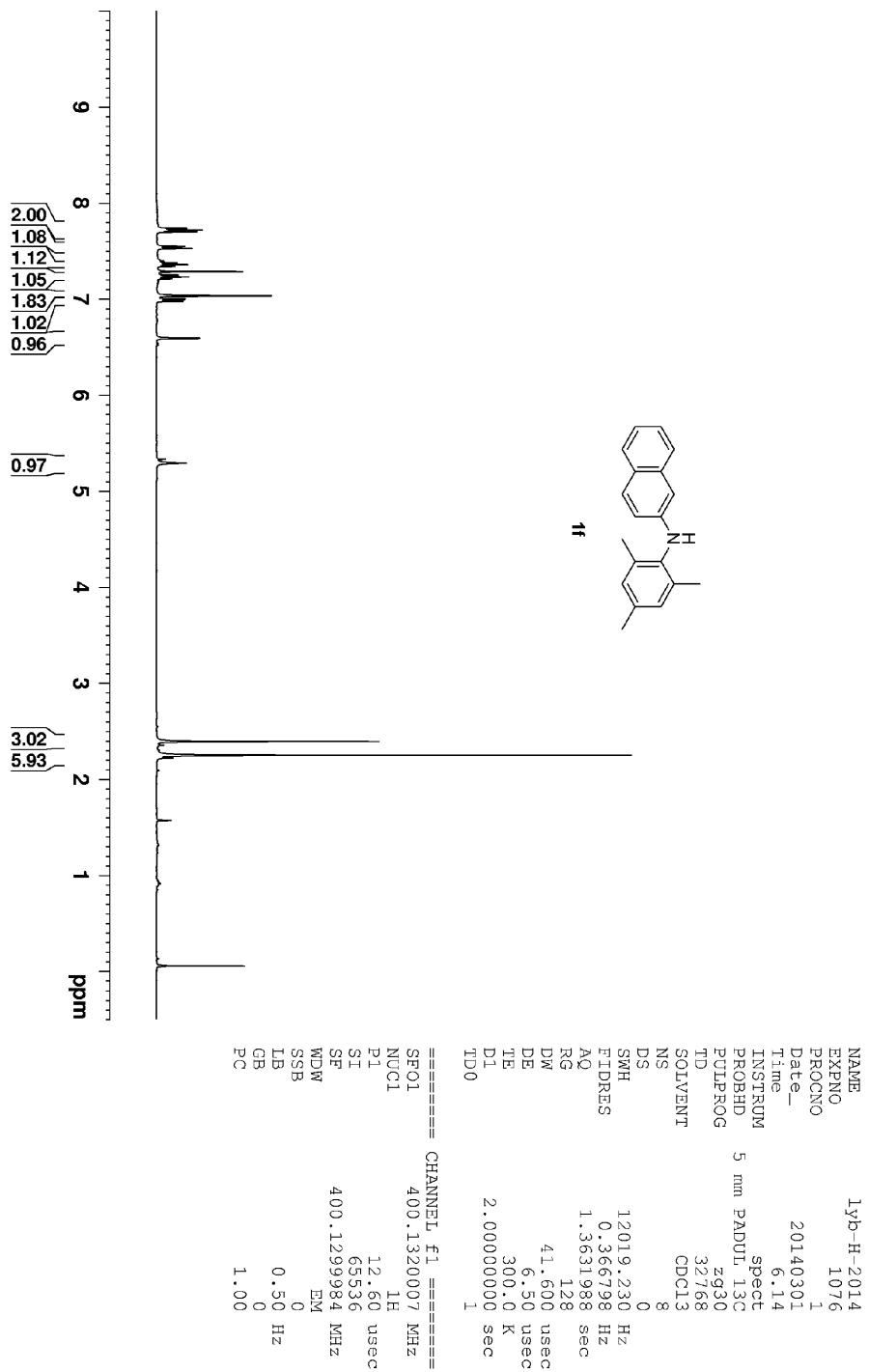


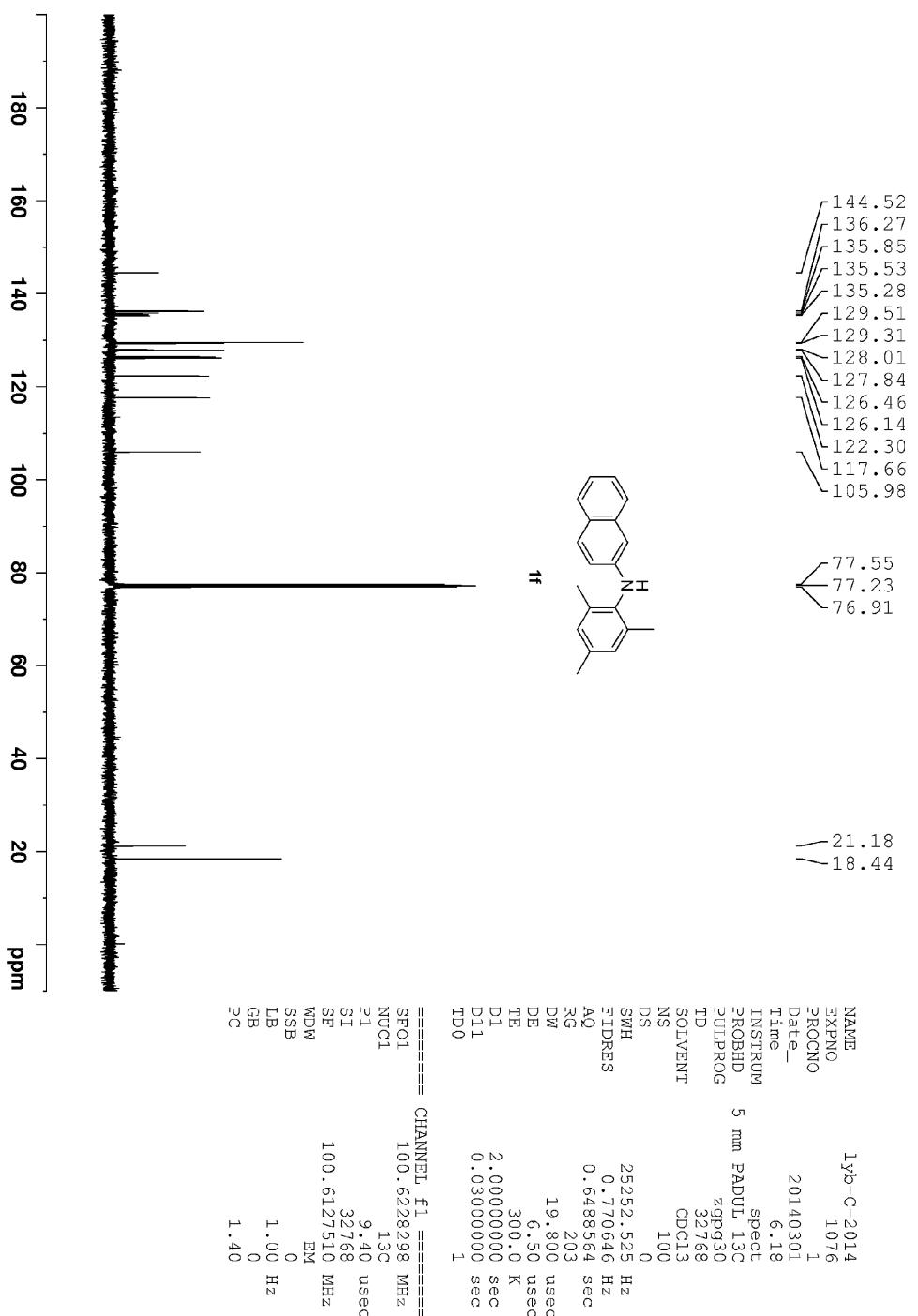


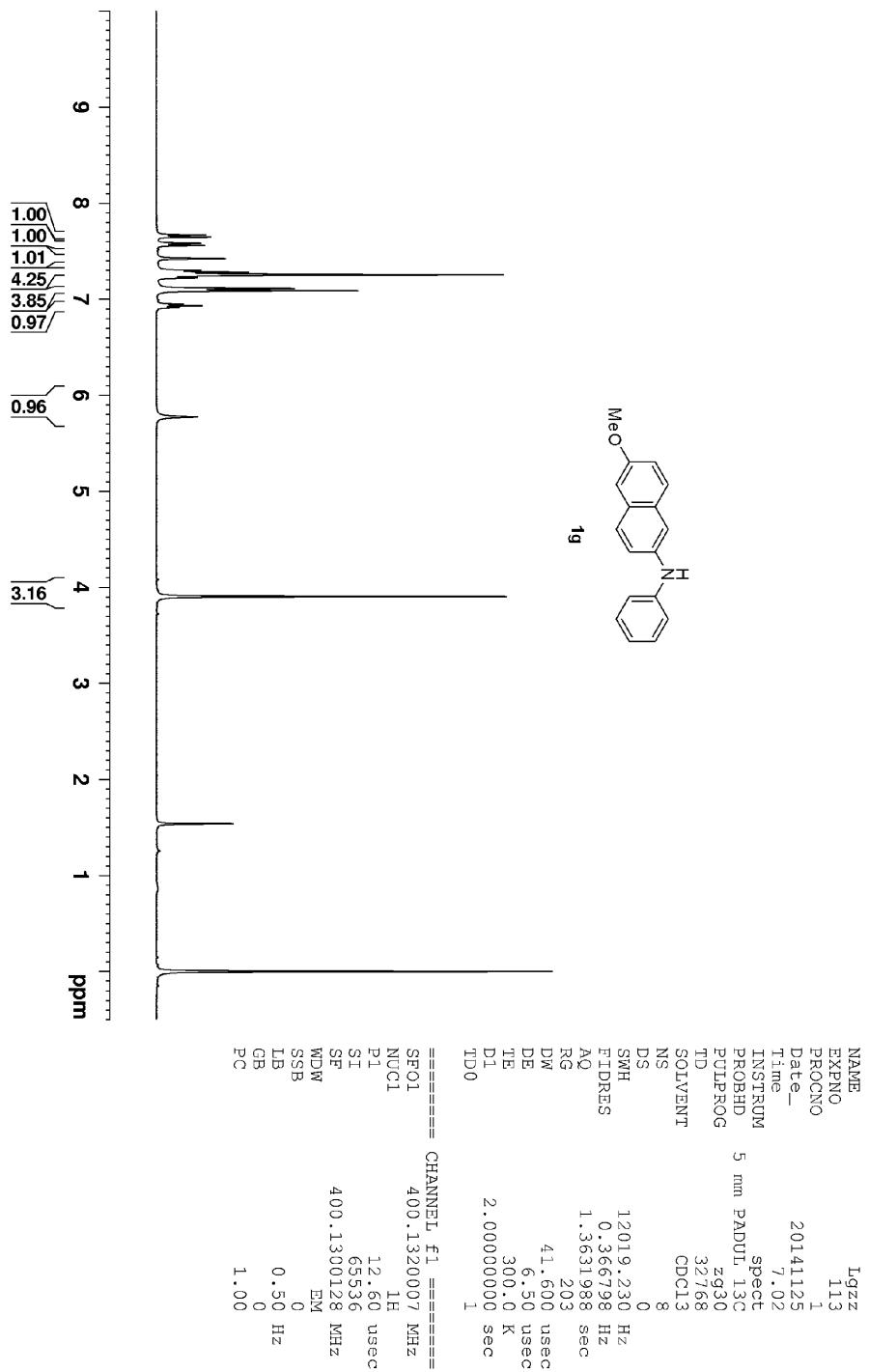


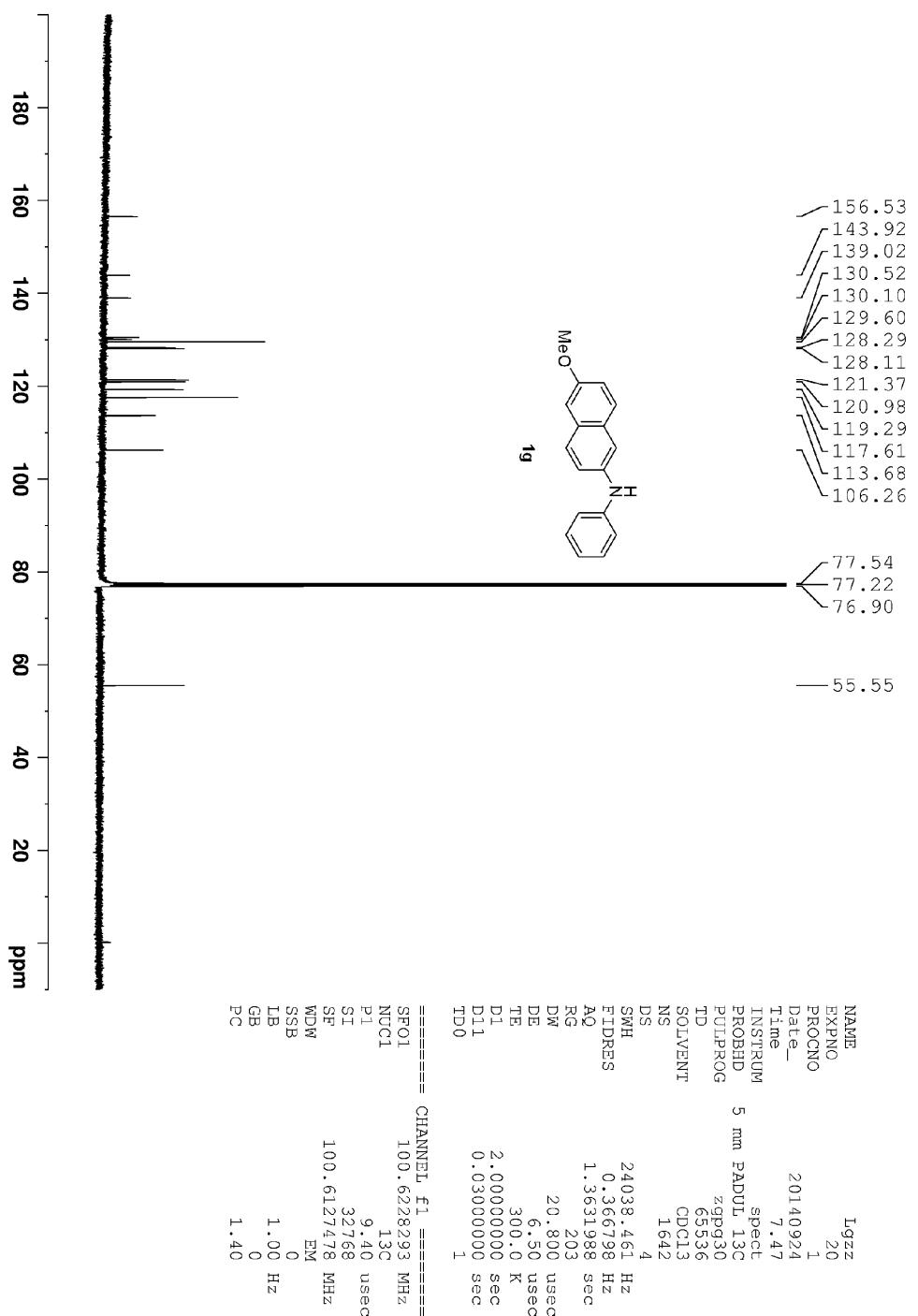


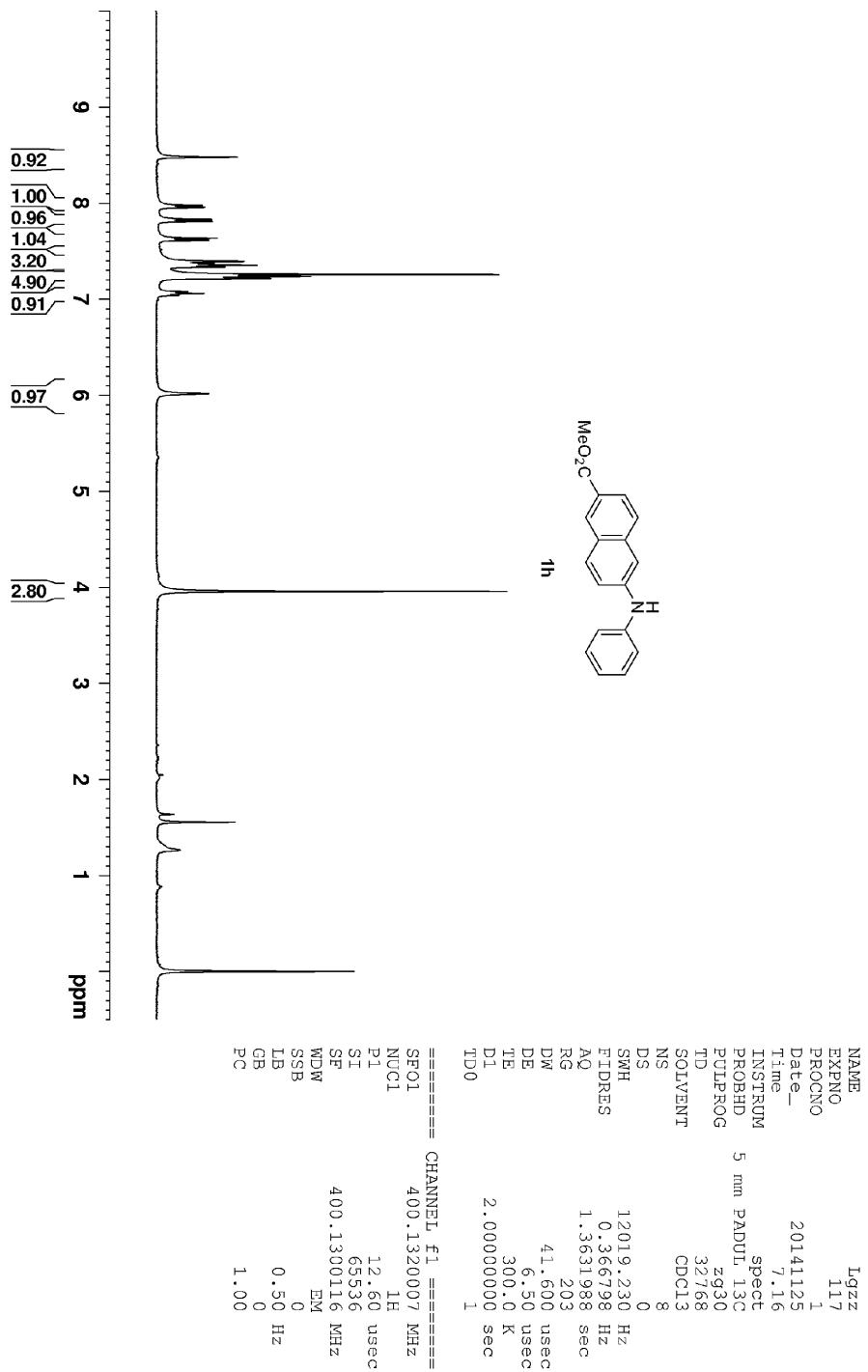


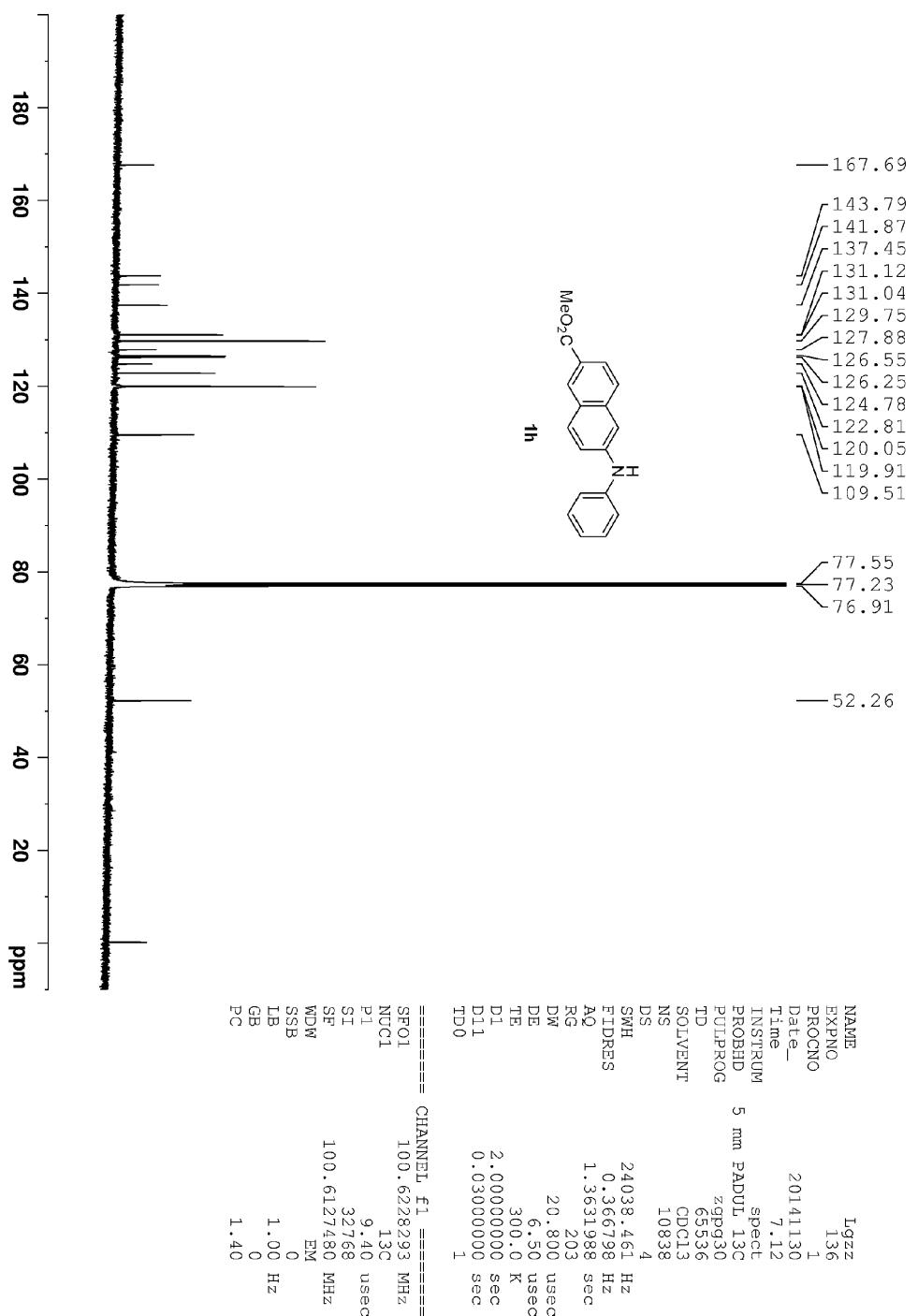


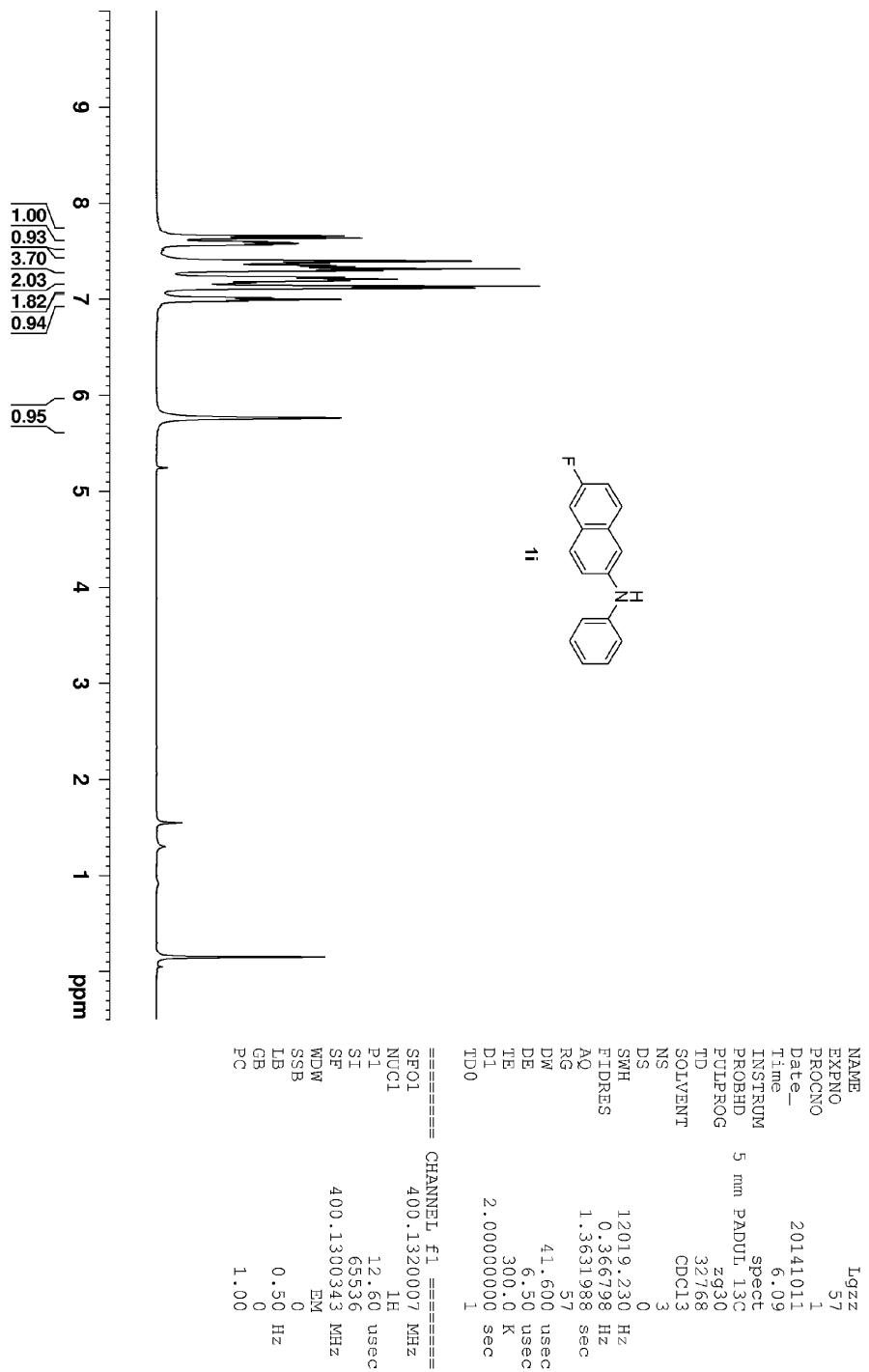


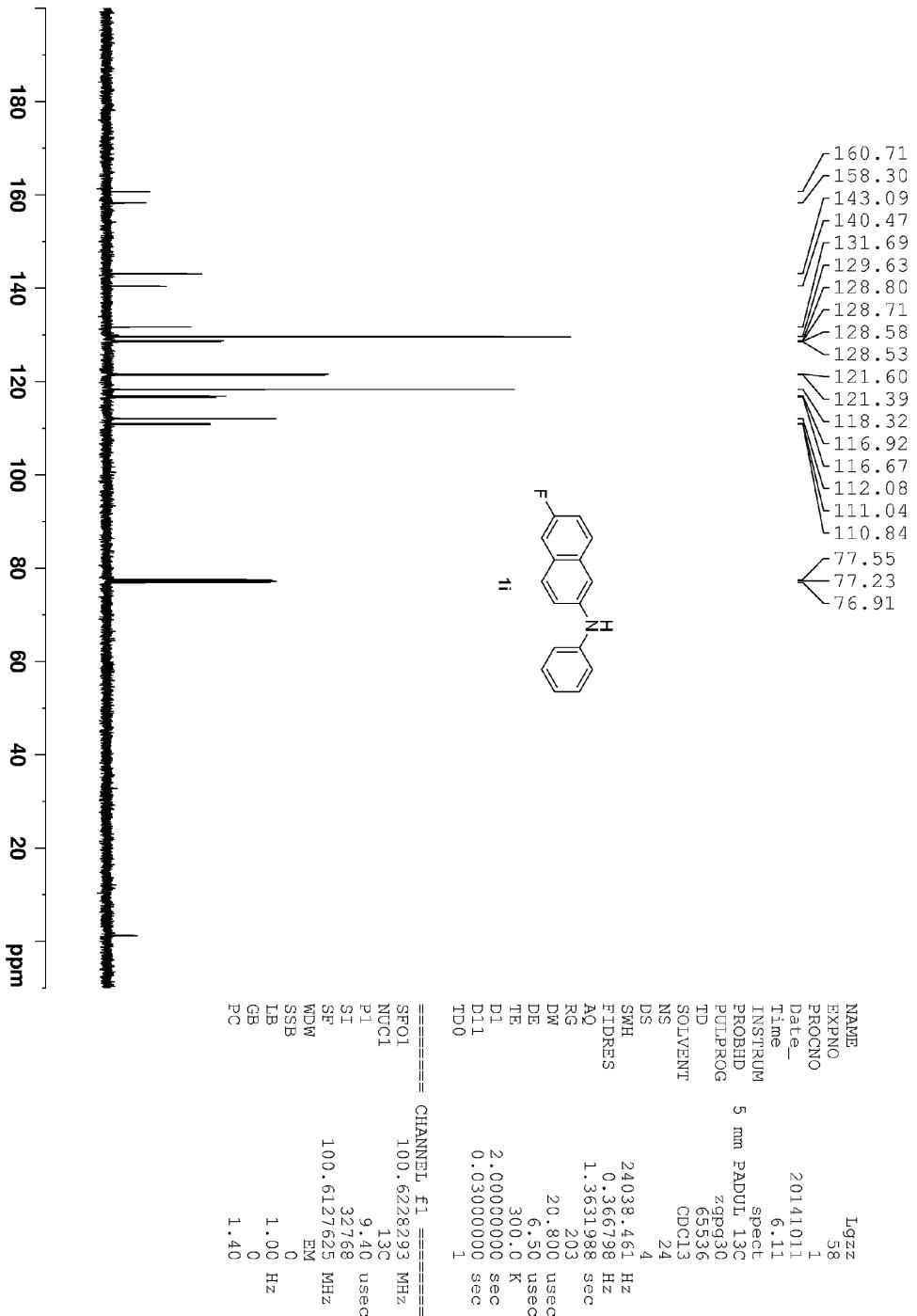


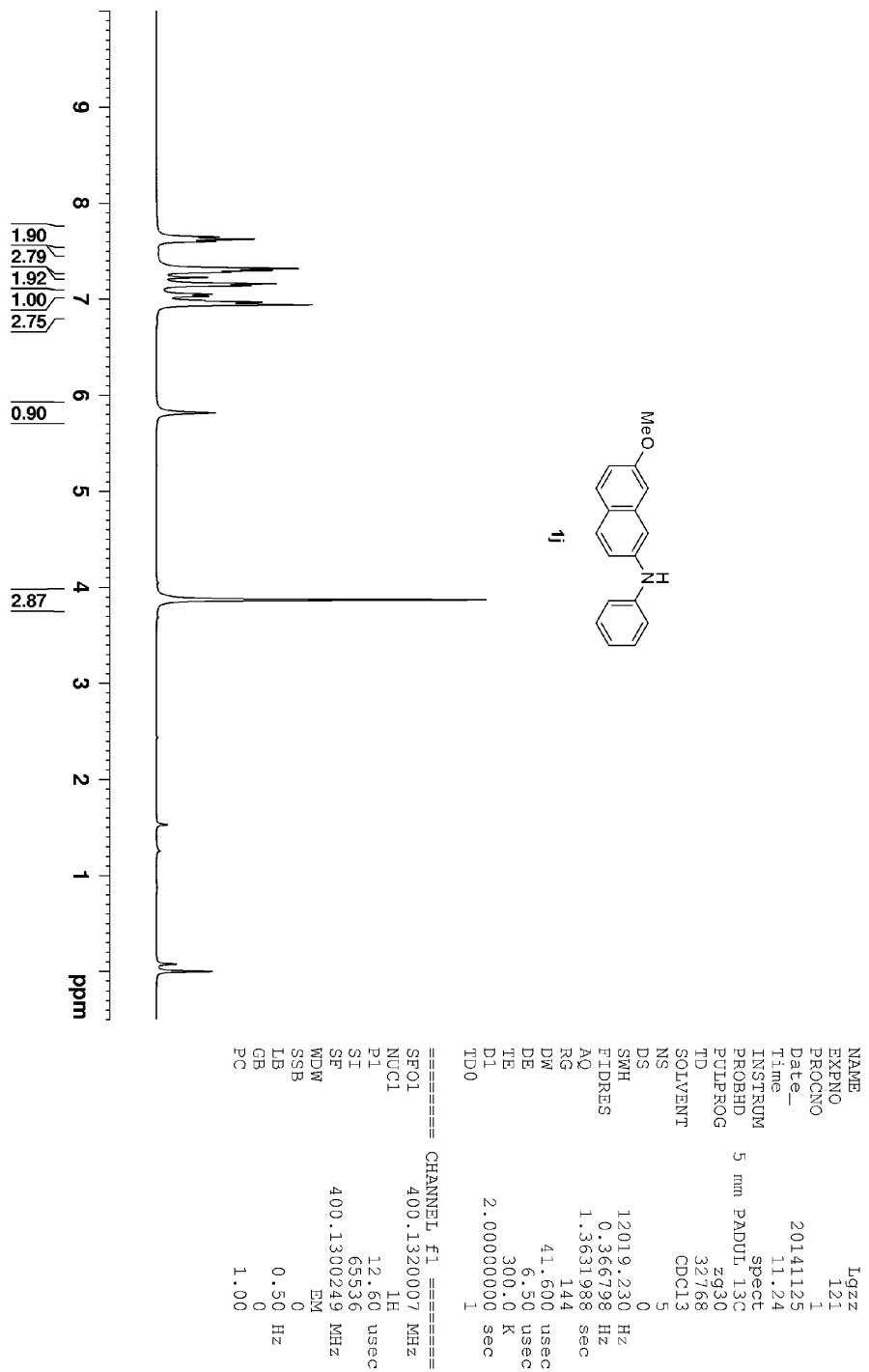


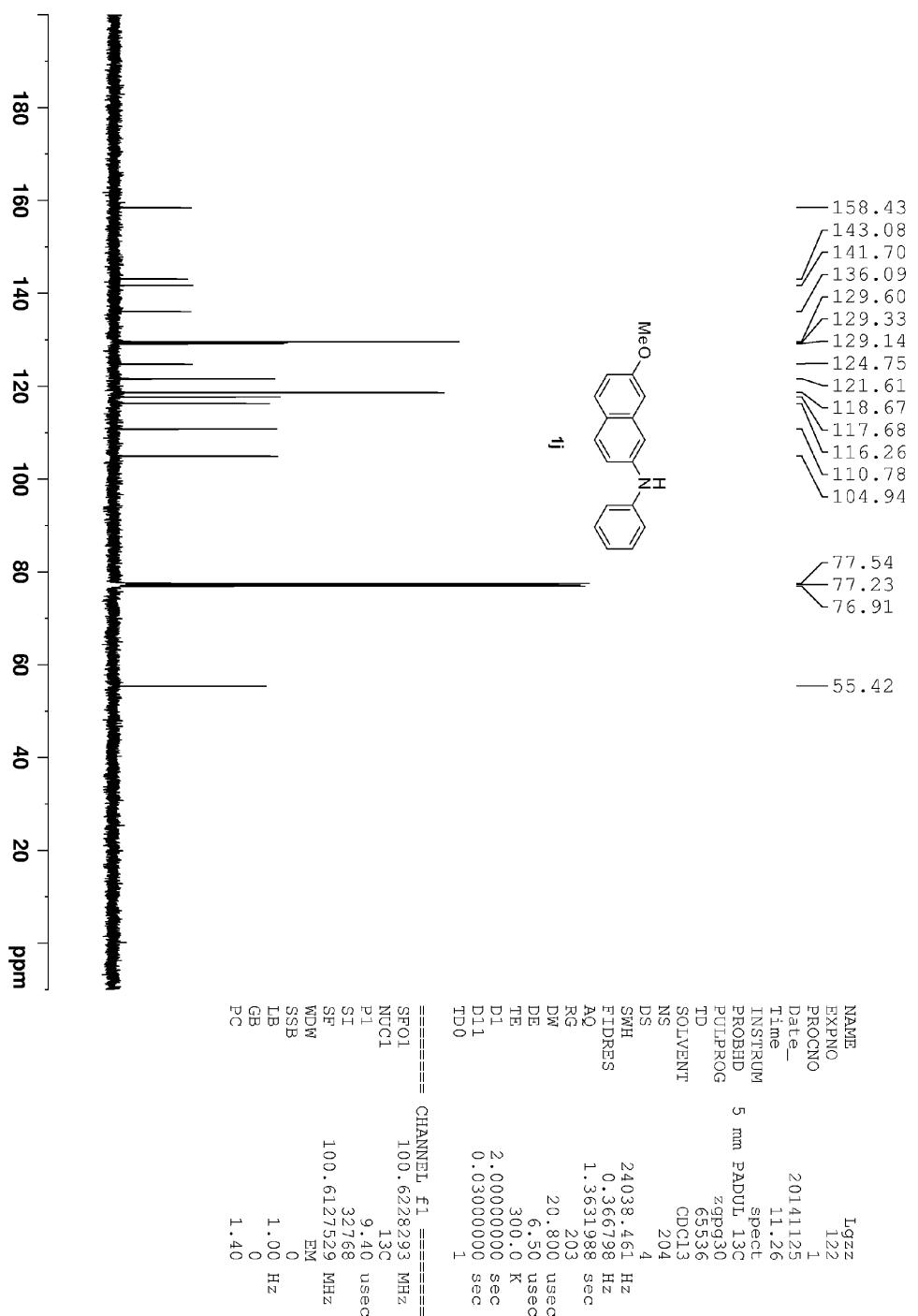


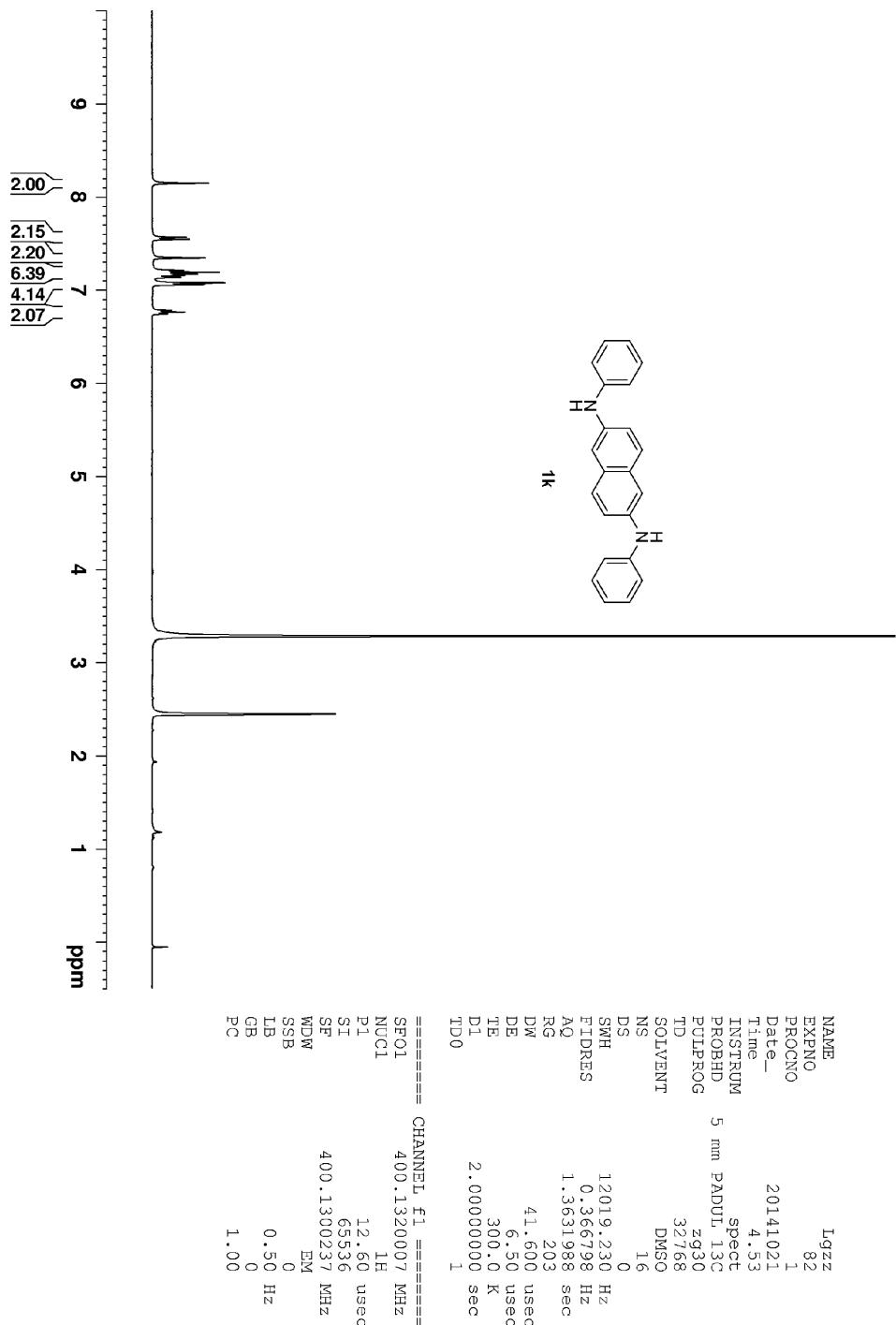


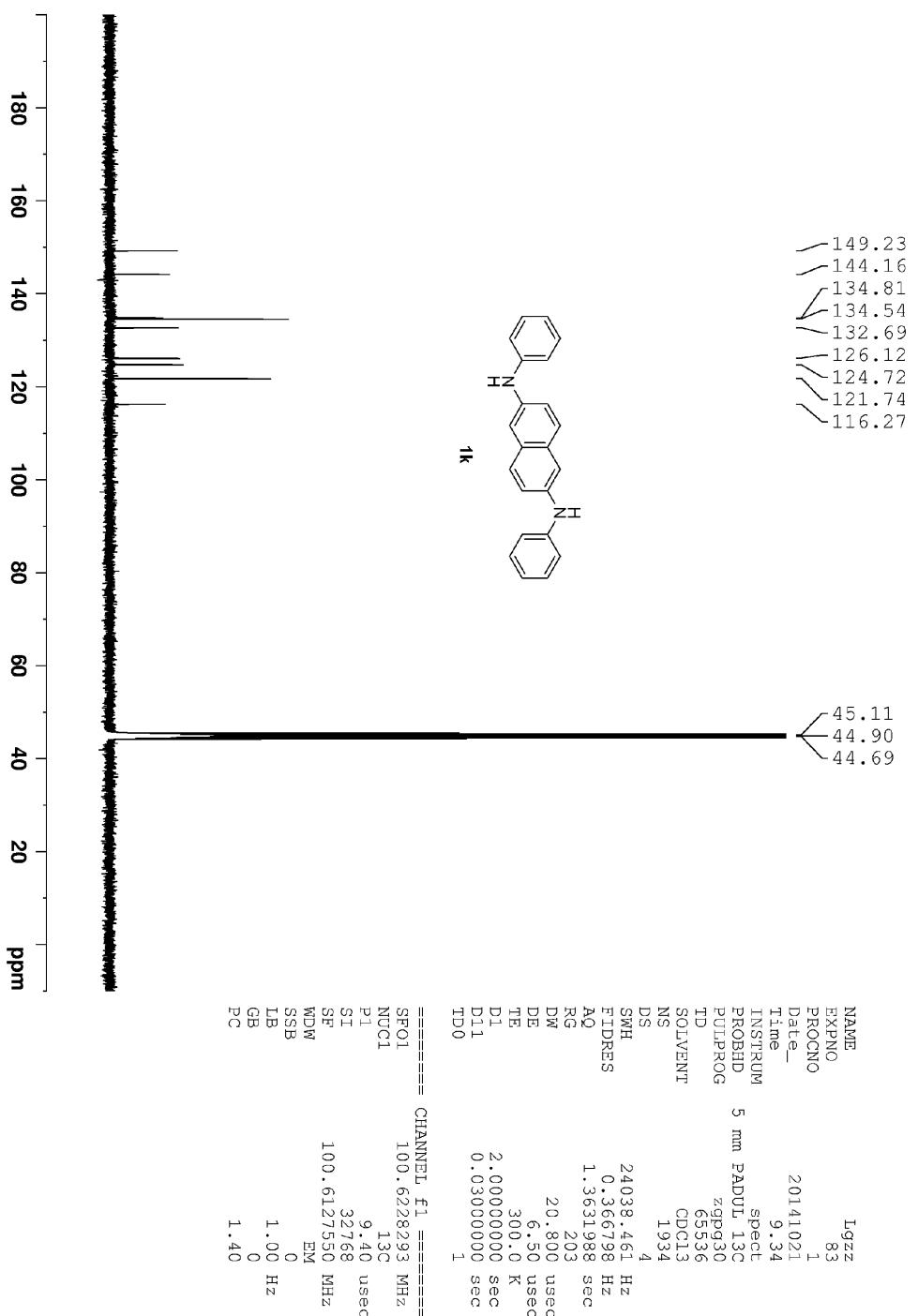


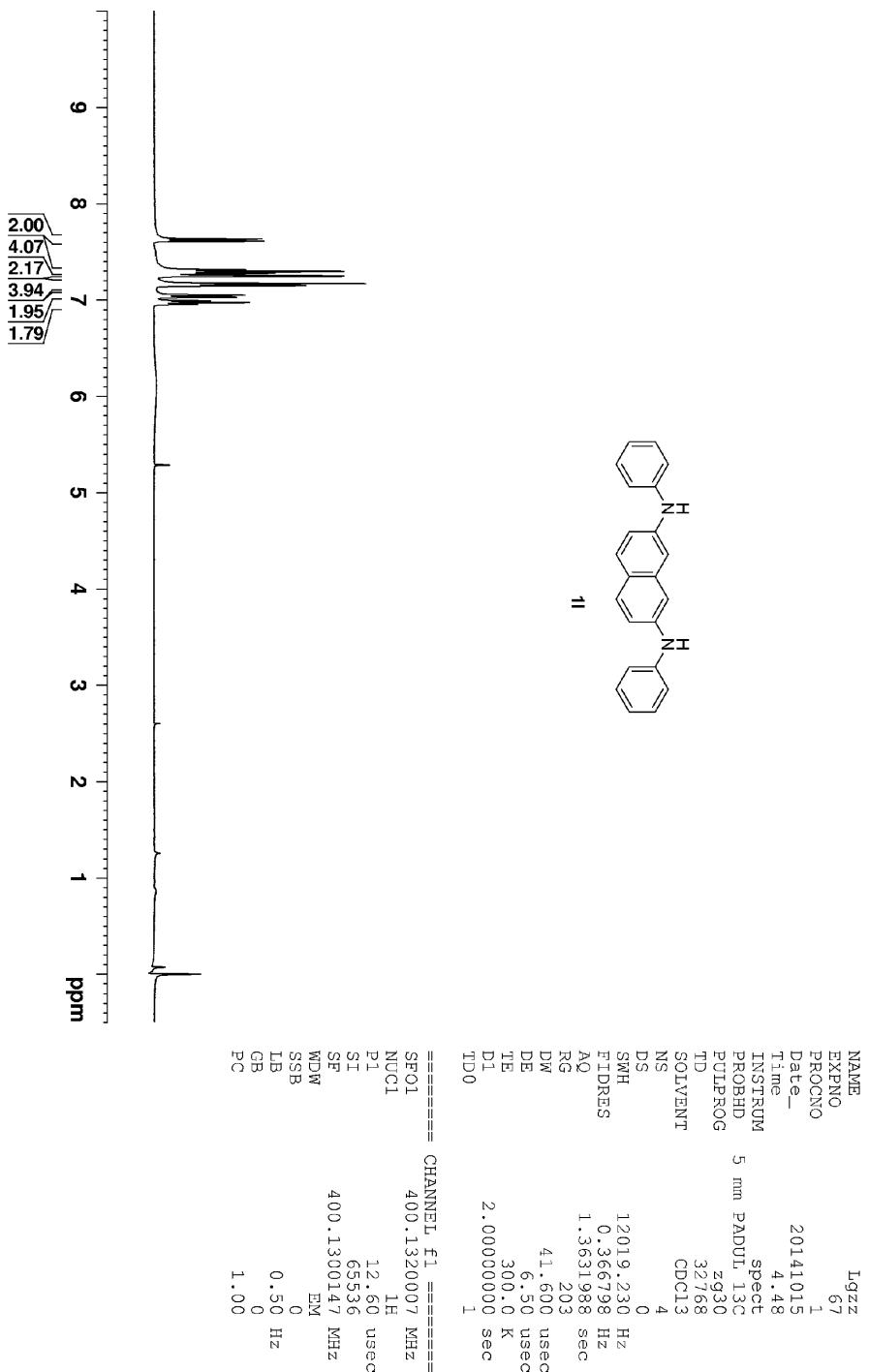


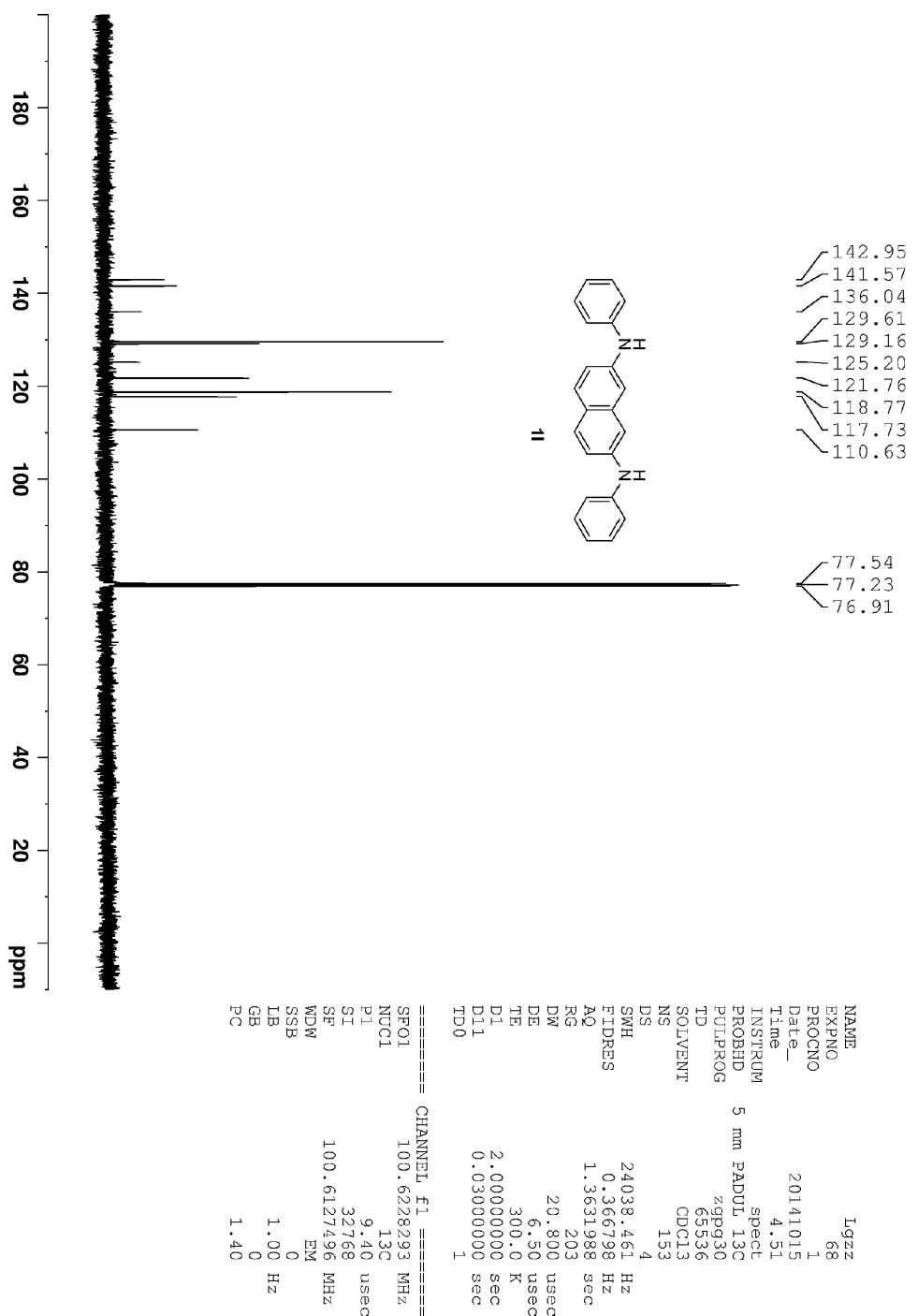


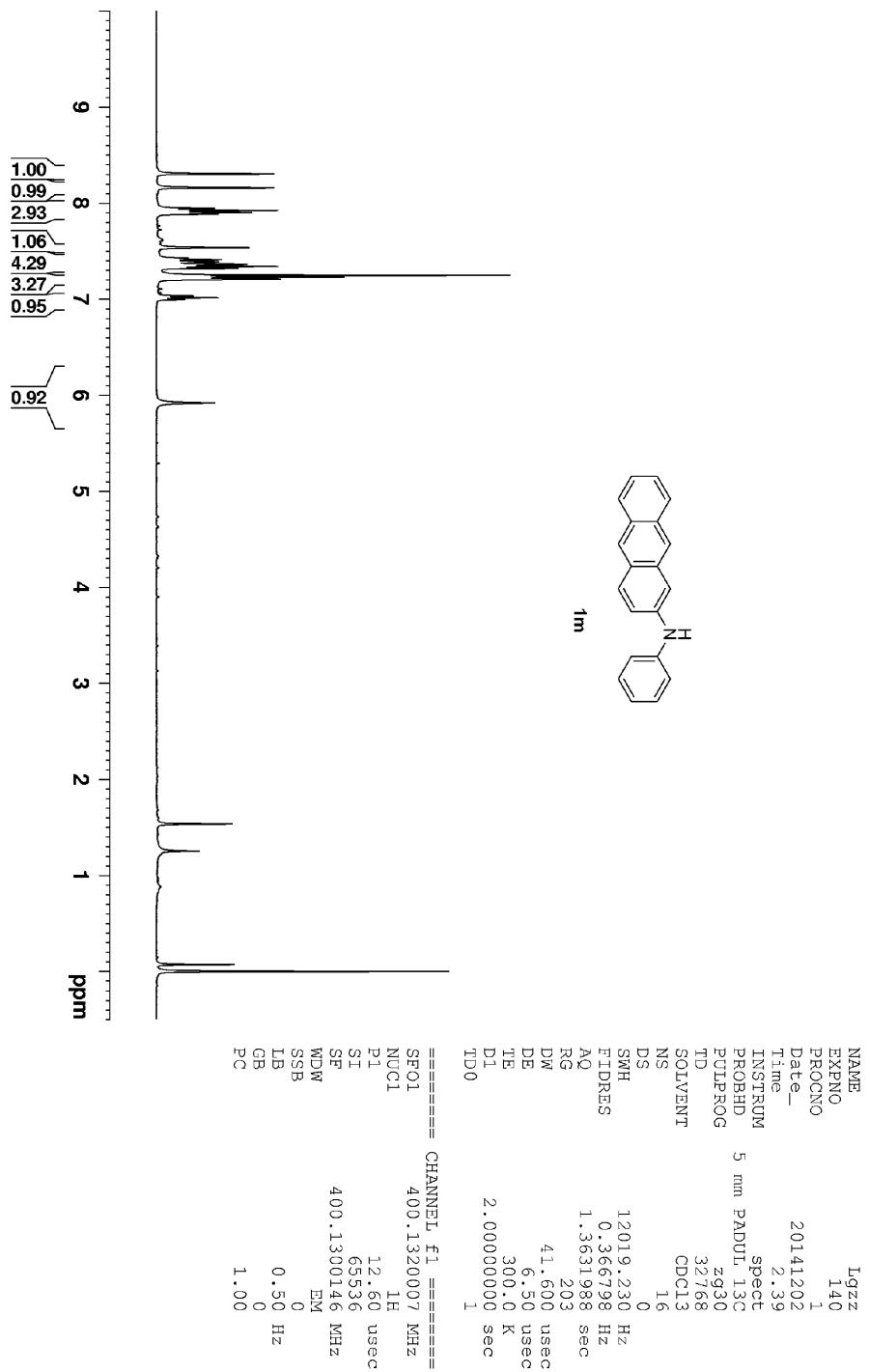


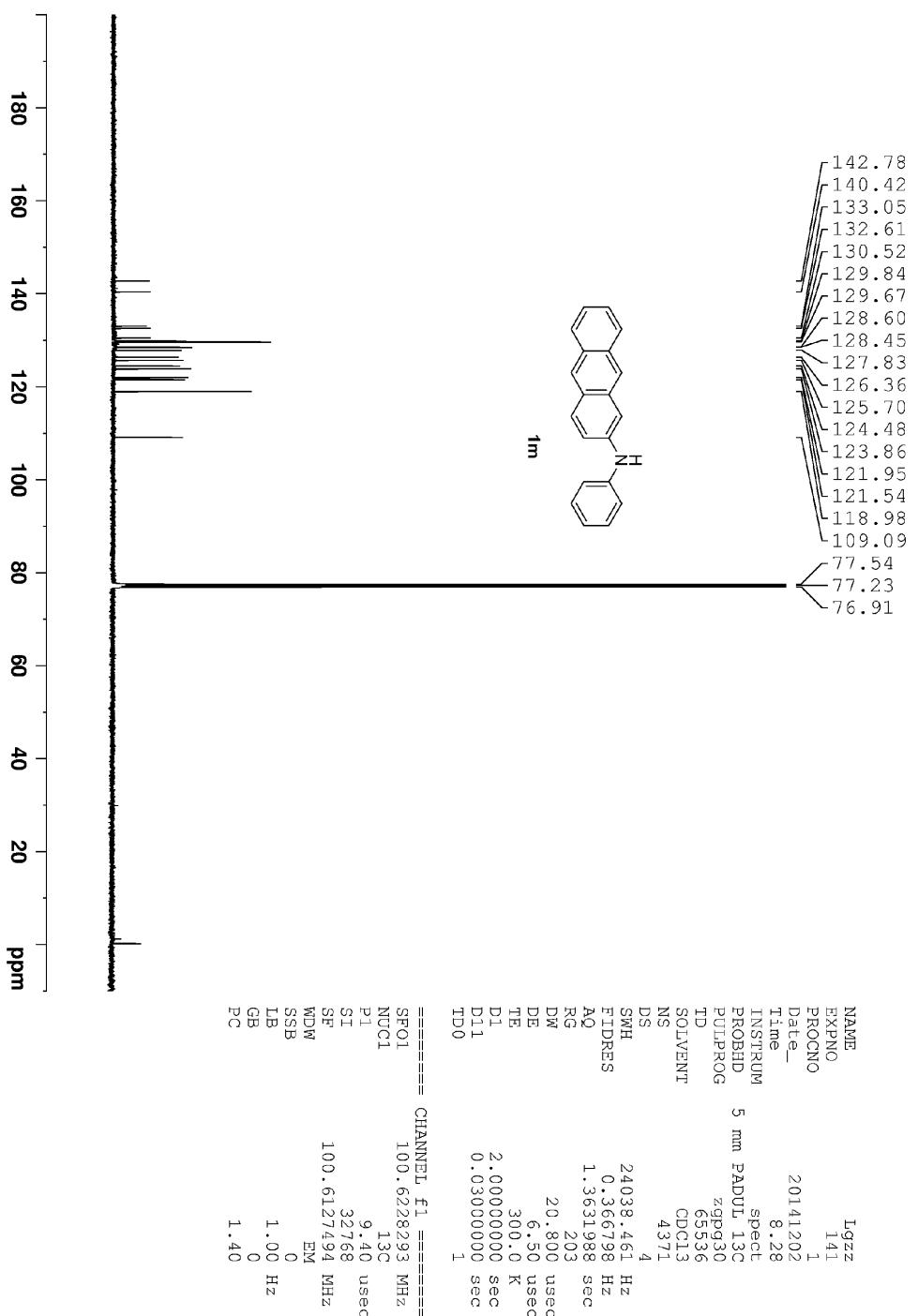


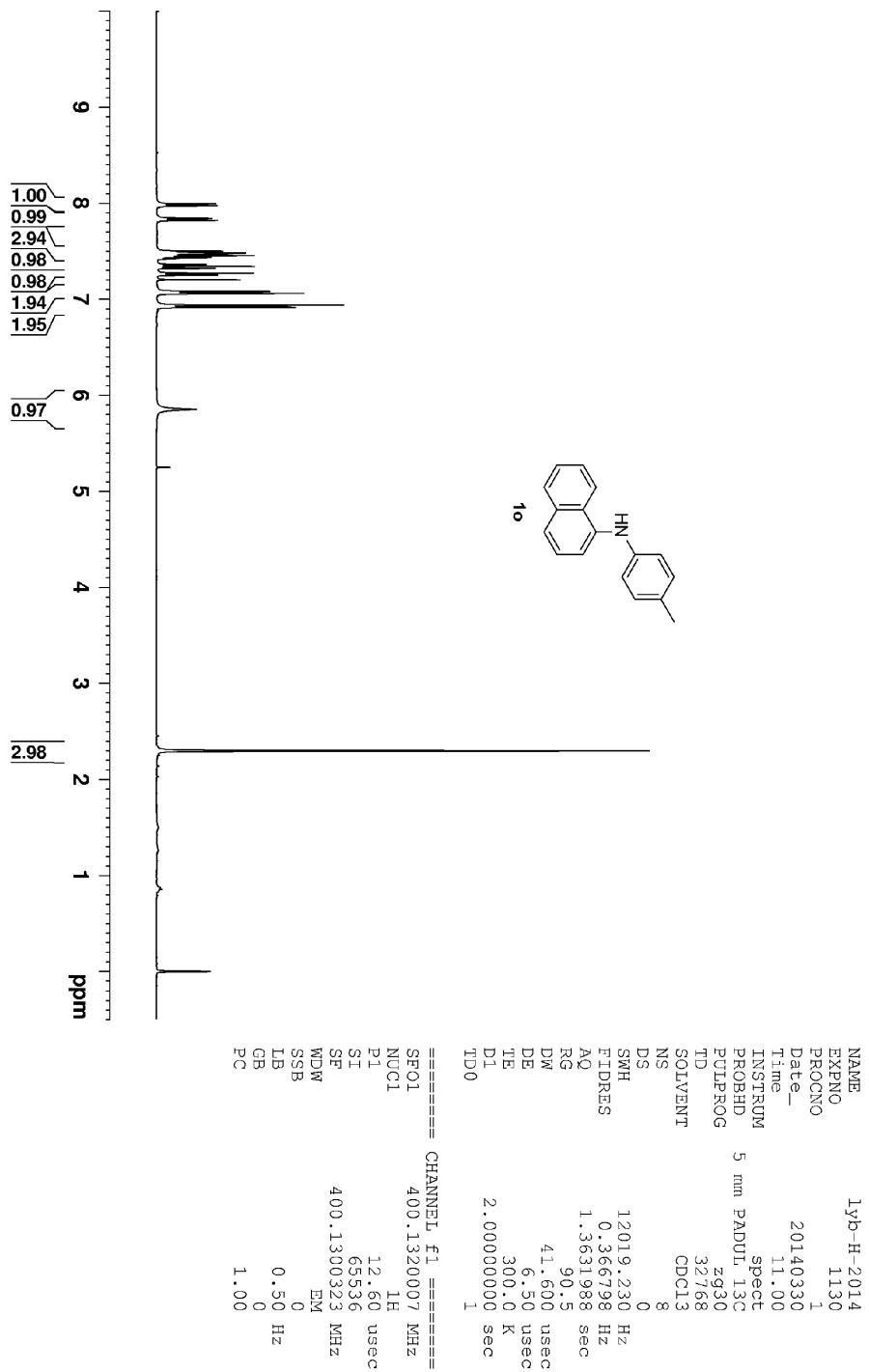


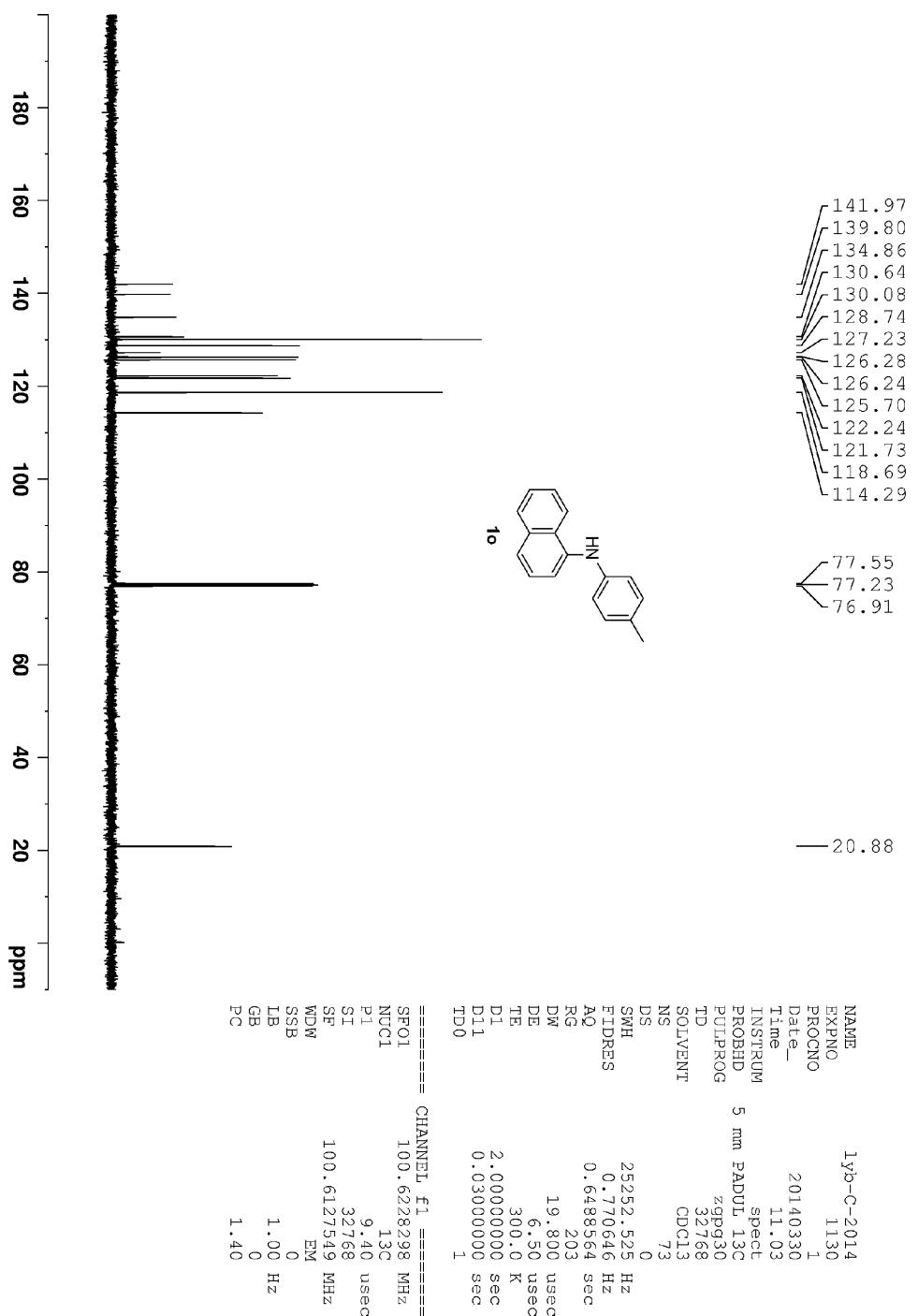


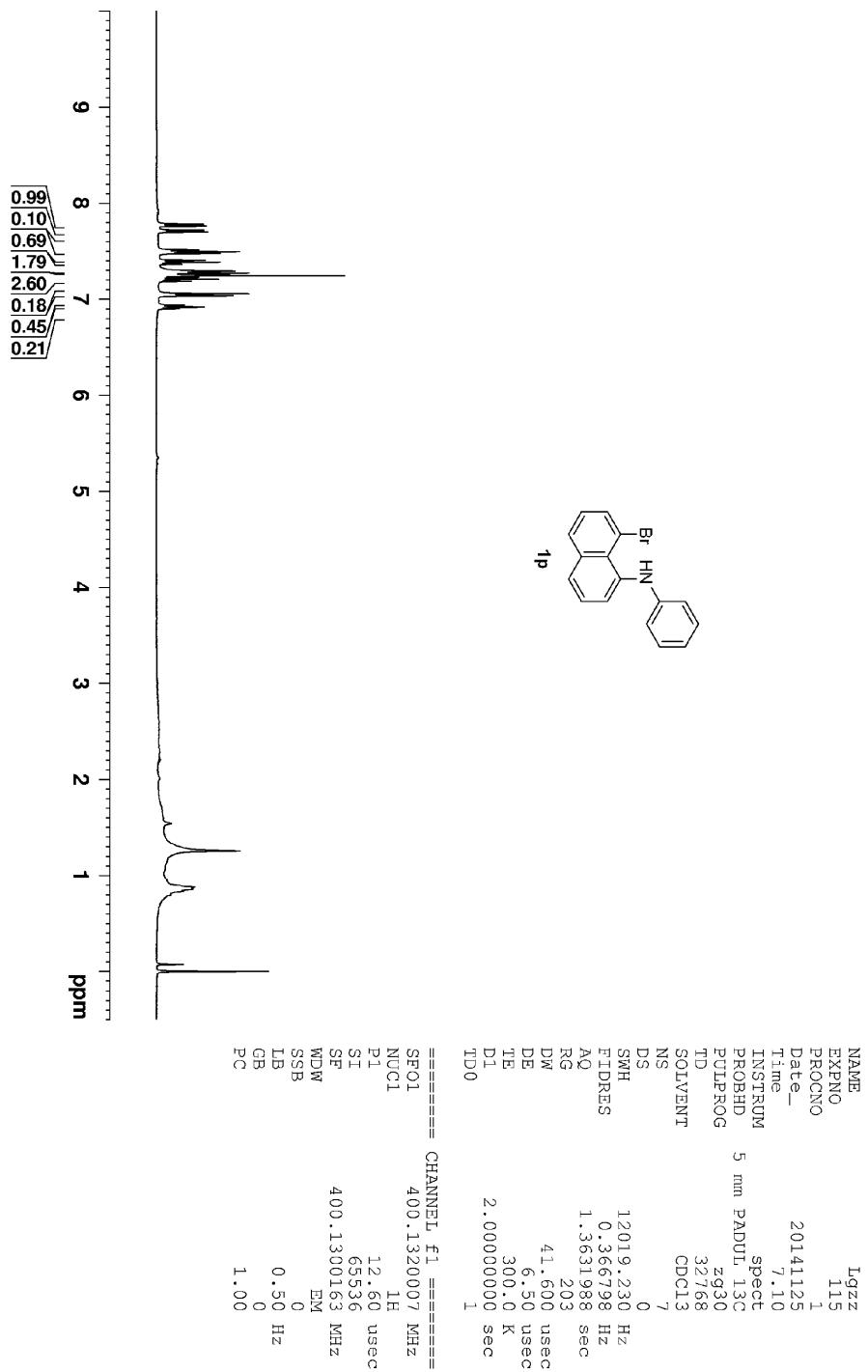


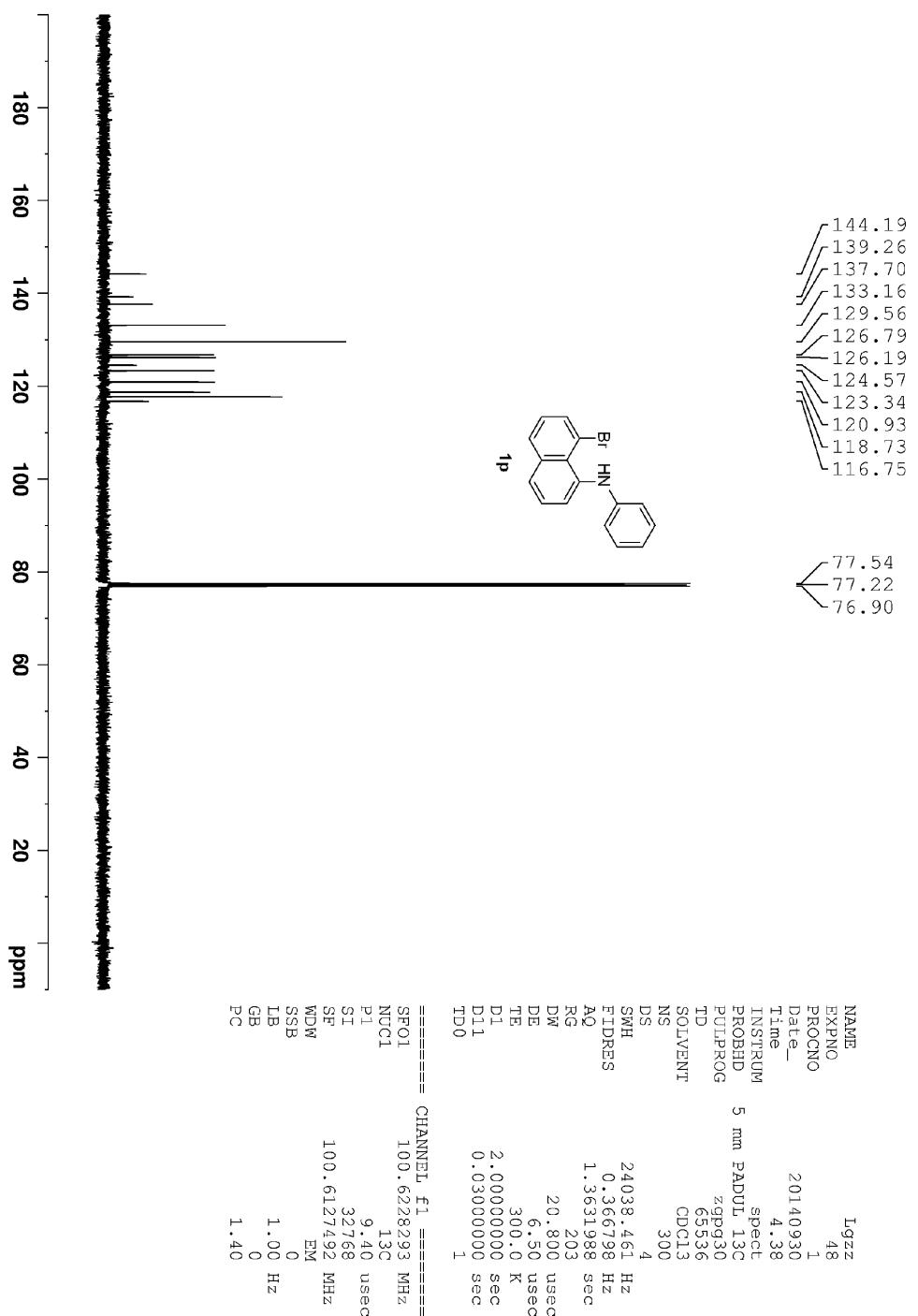


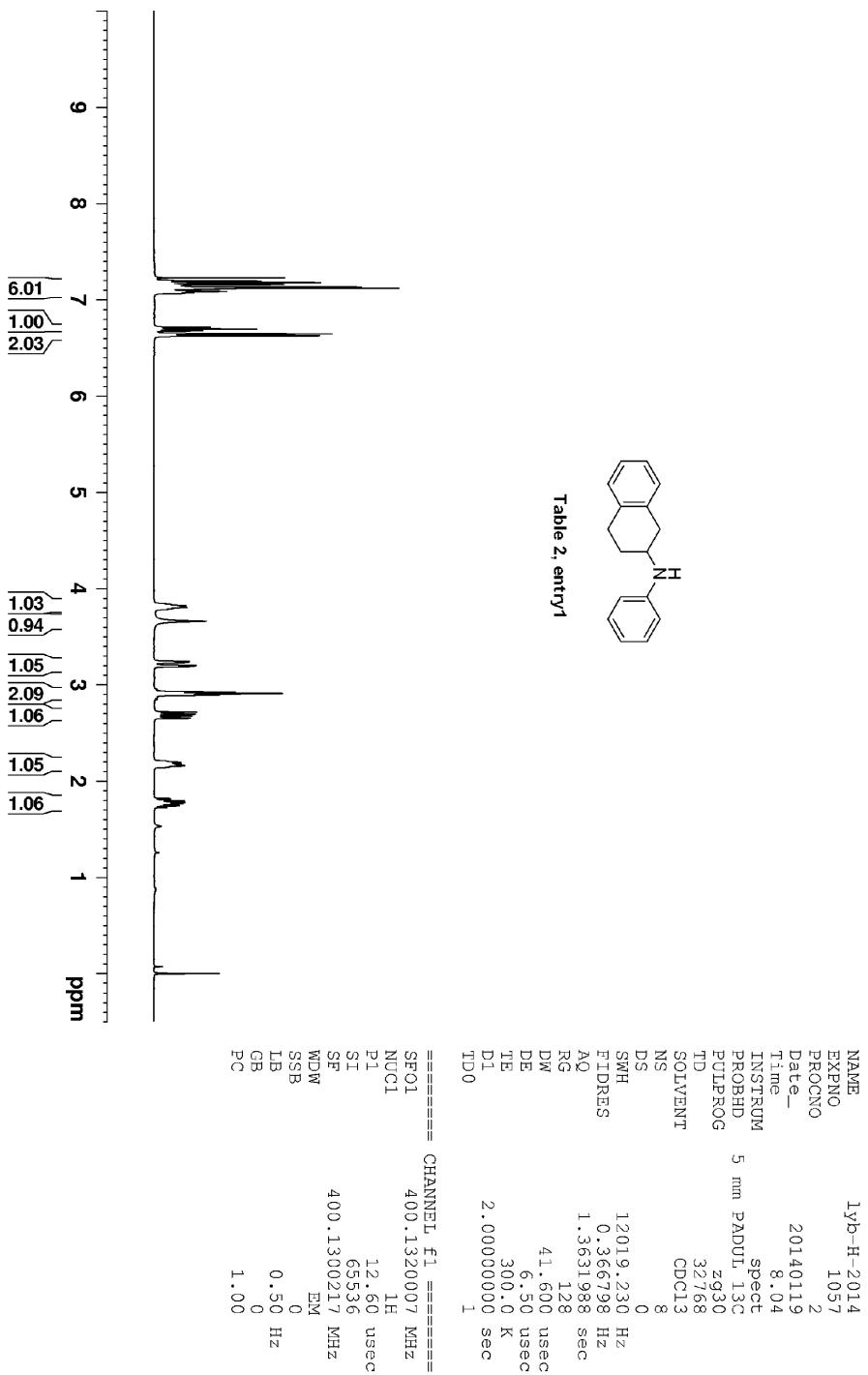












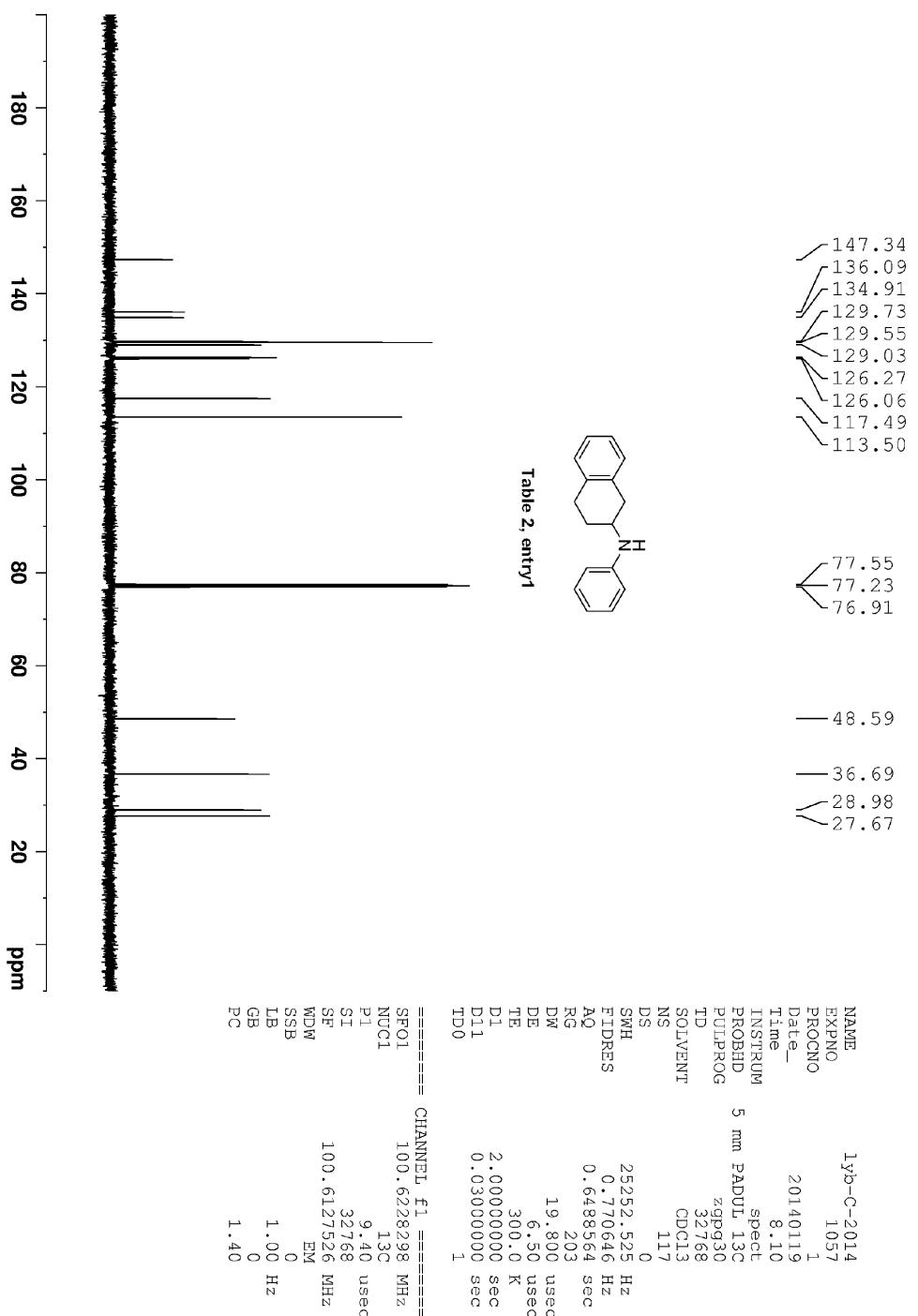
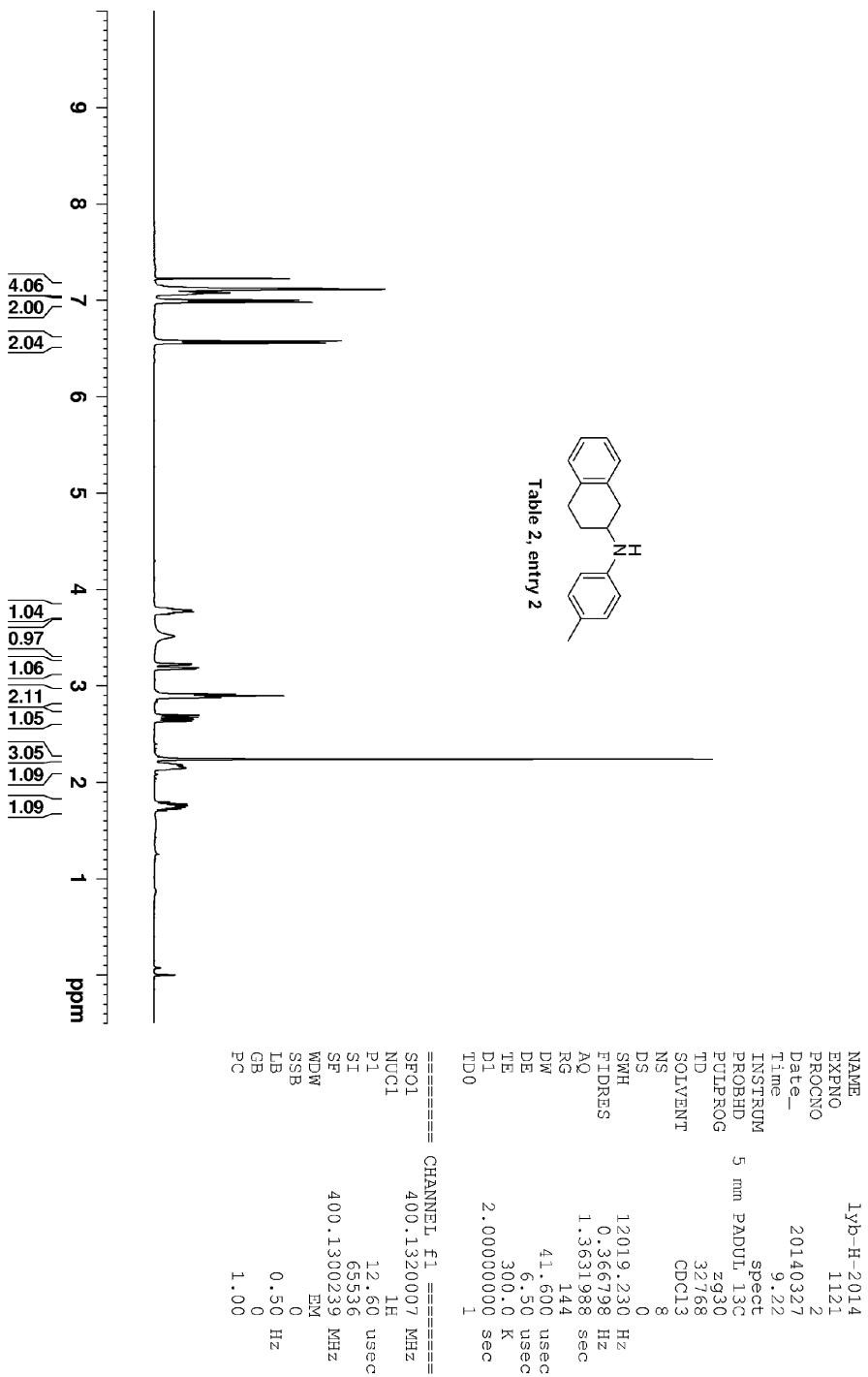
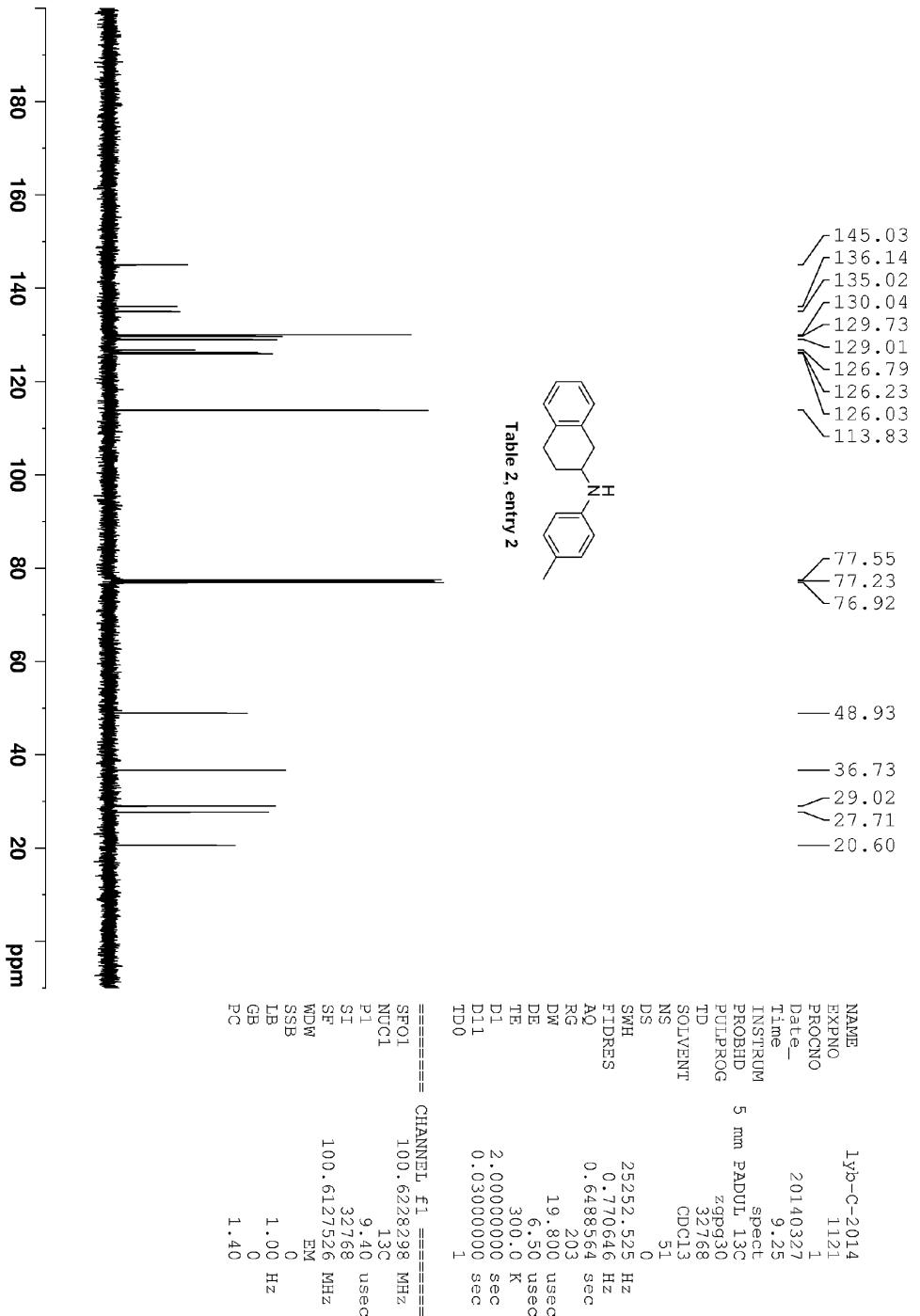
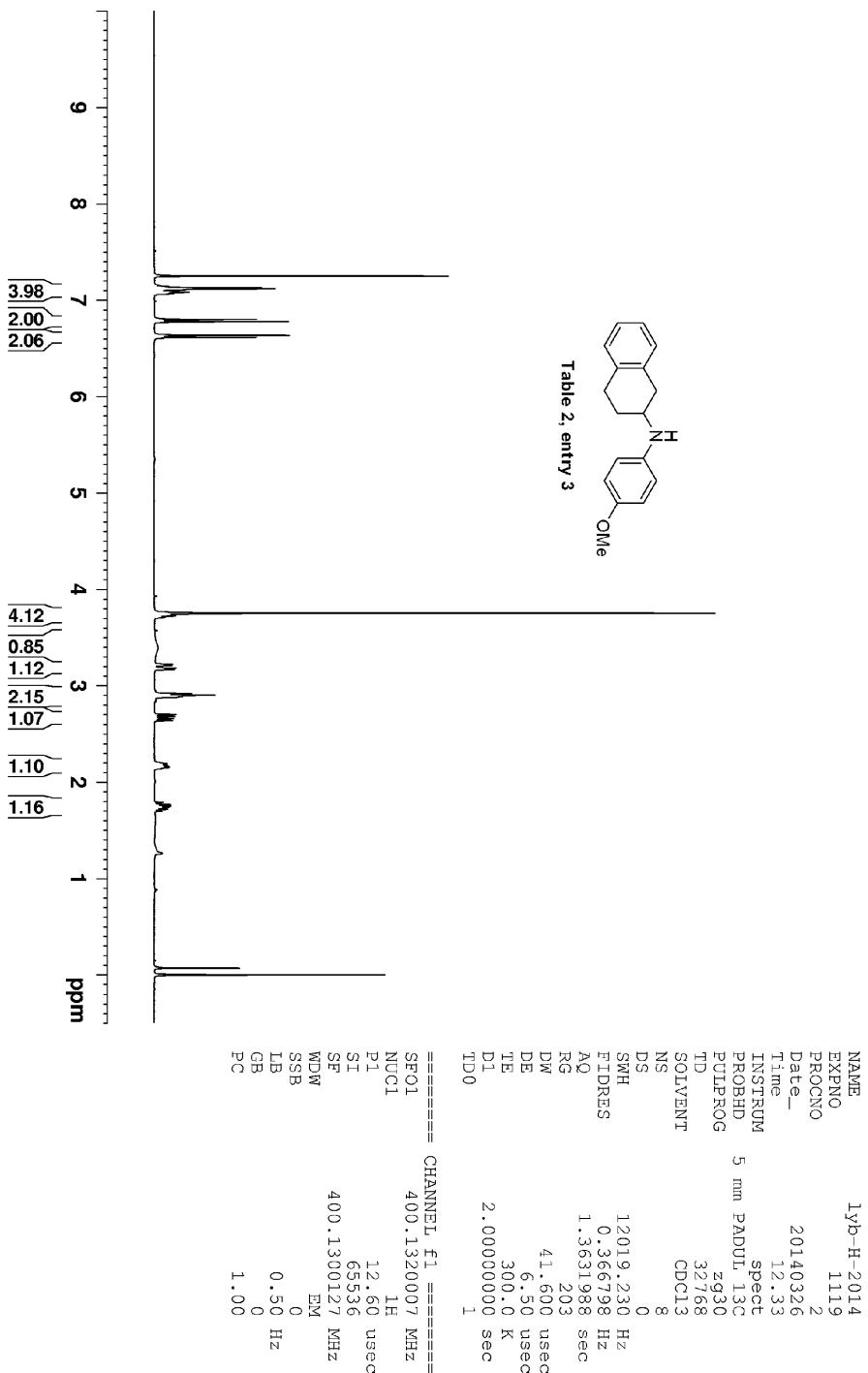
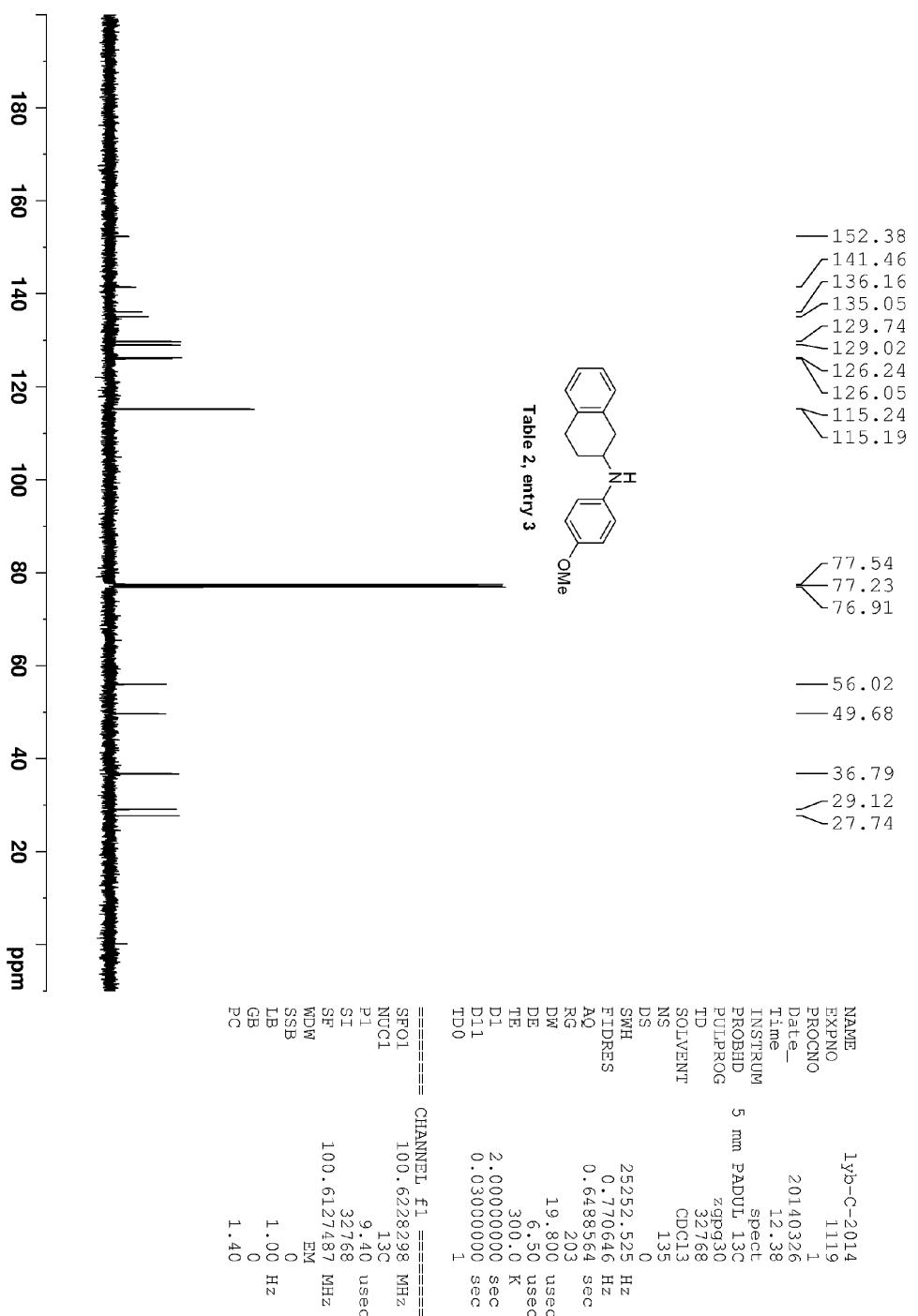


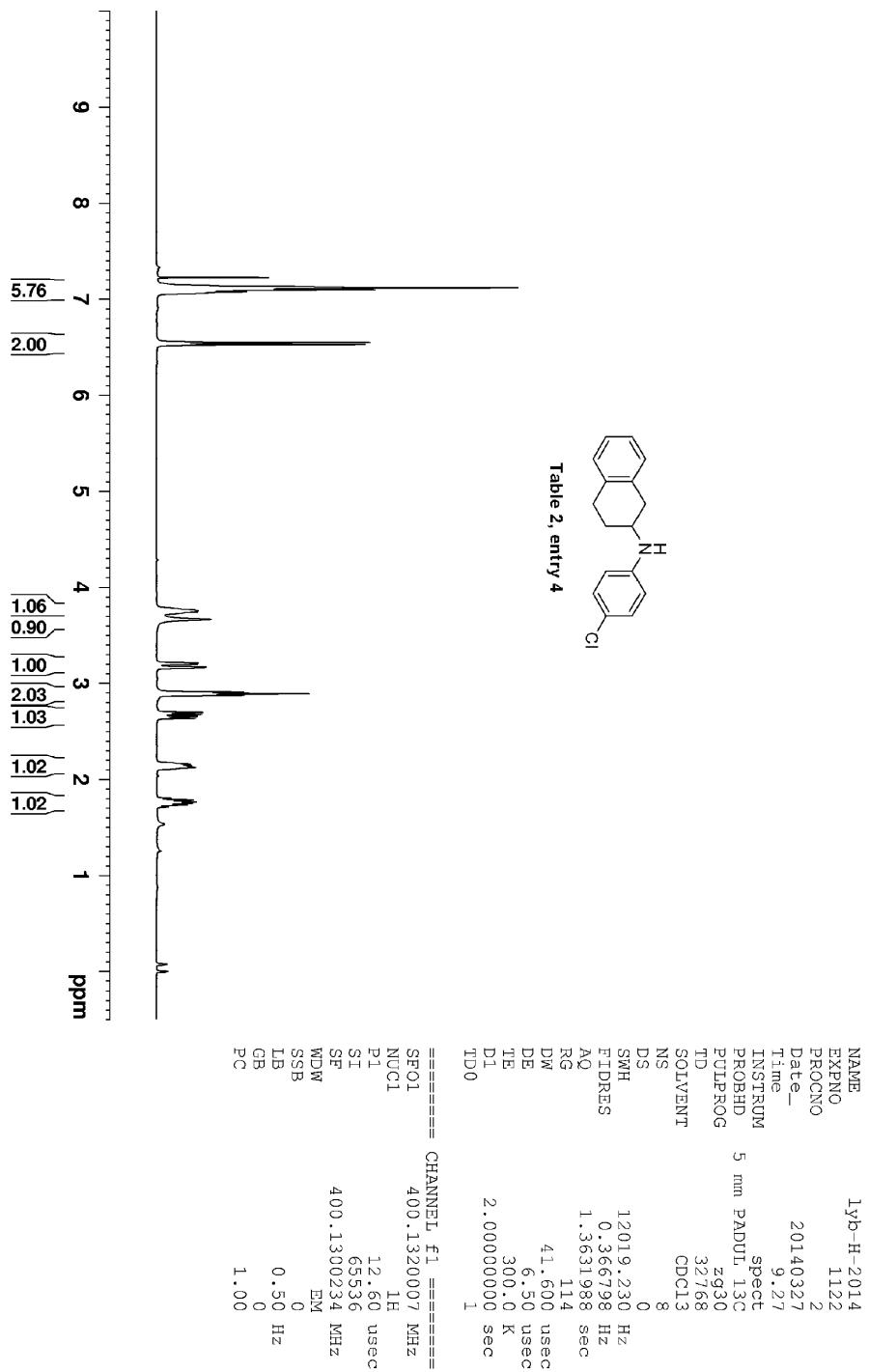
Table 2, entry 1











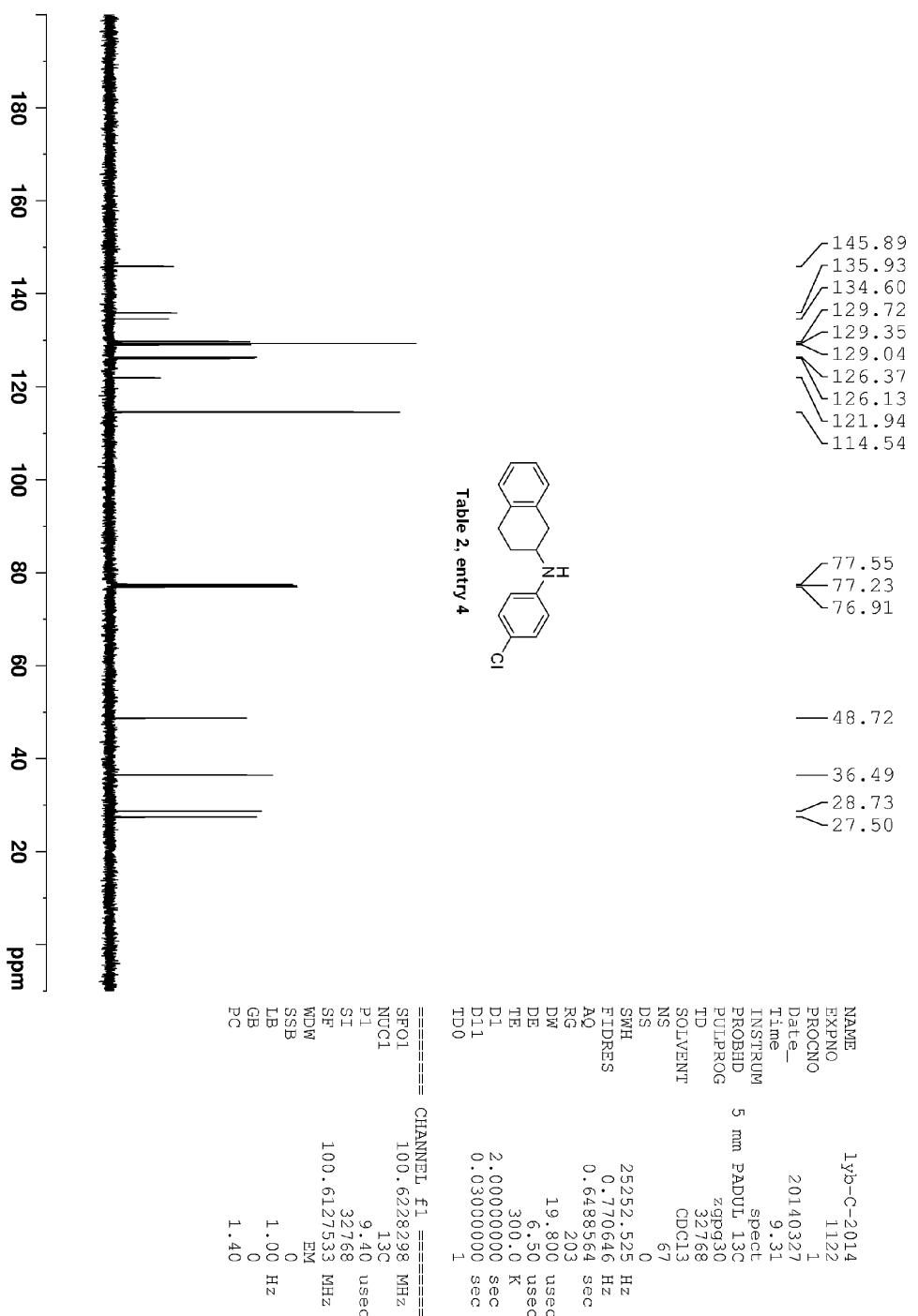
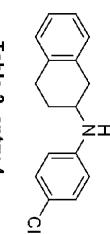


Table 2, entry 4



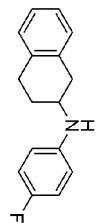
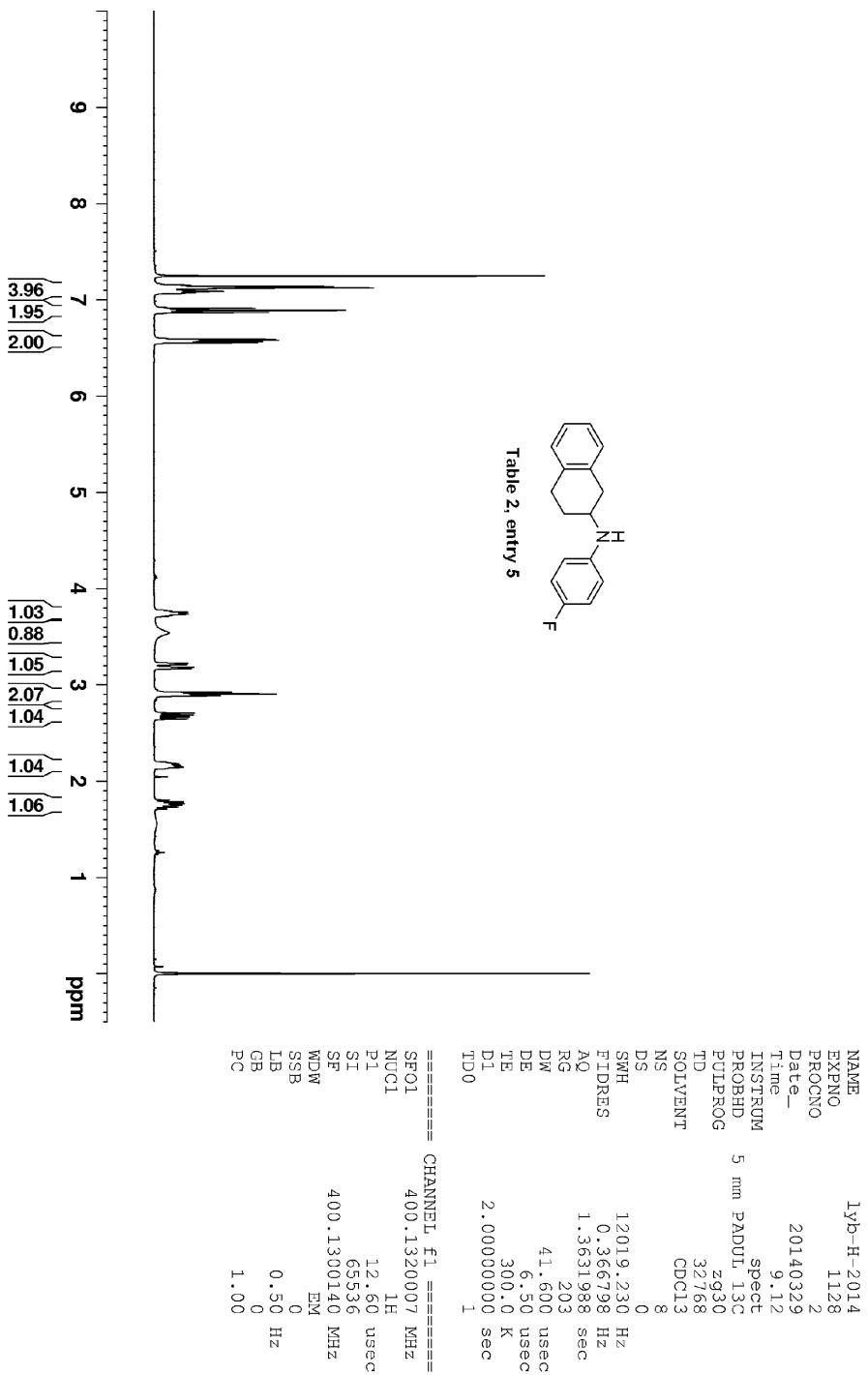
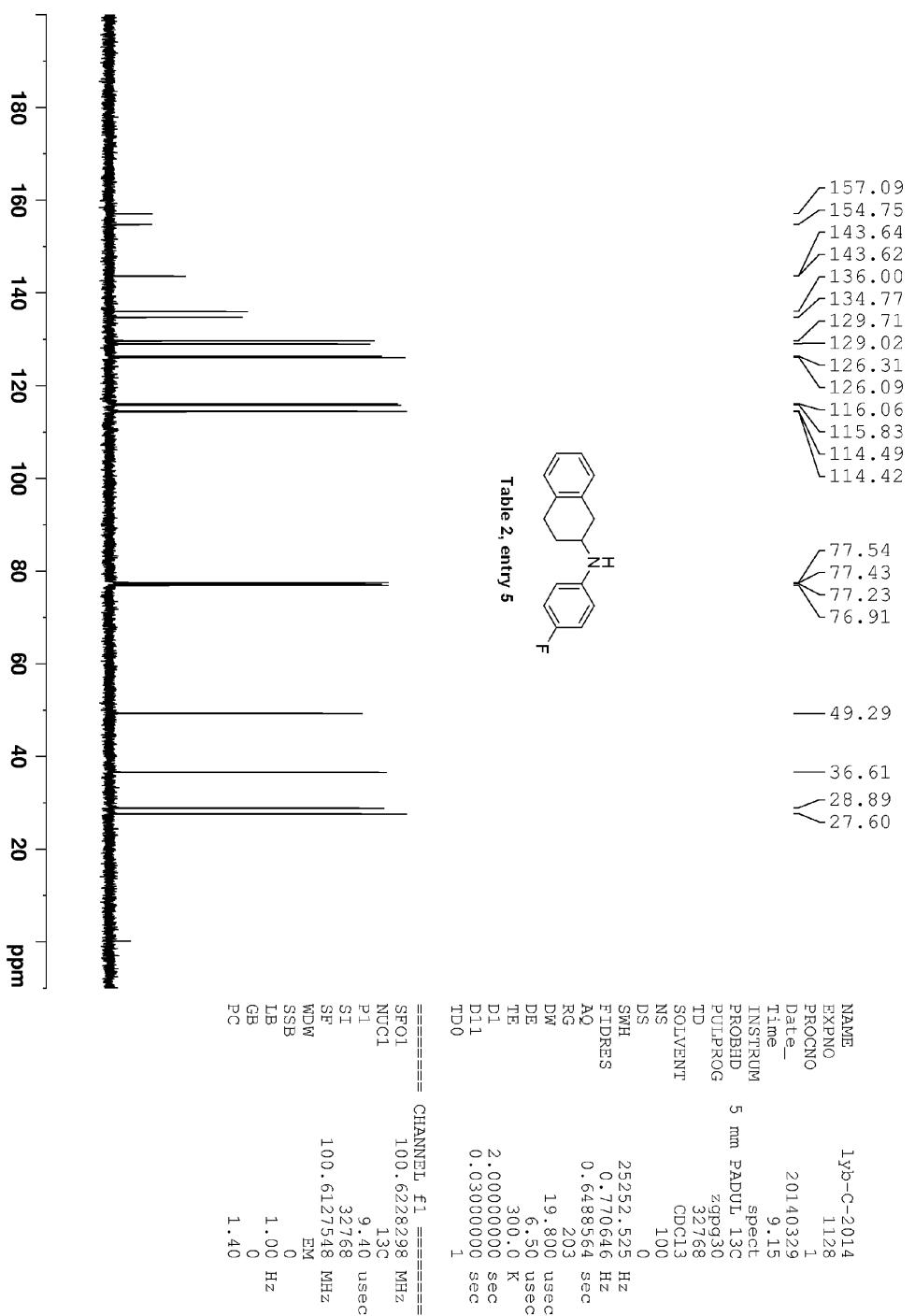
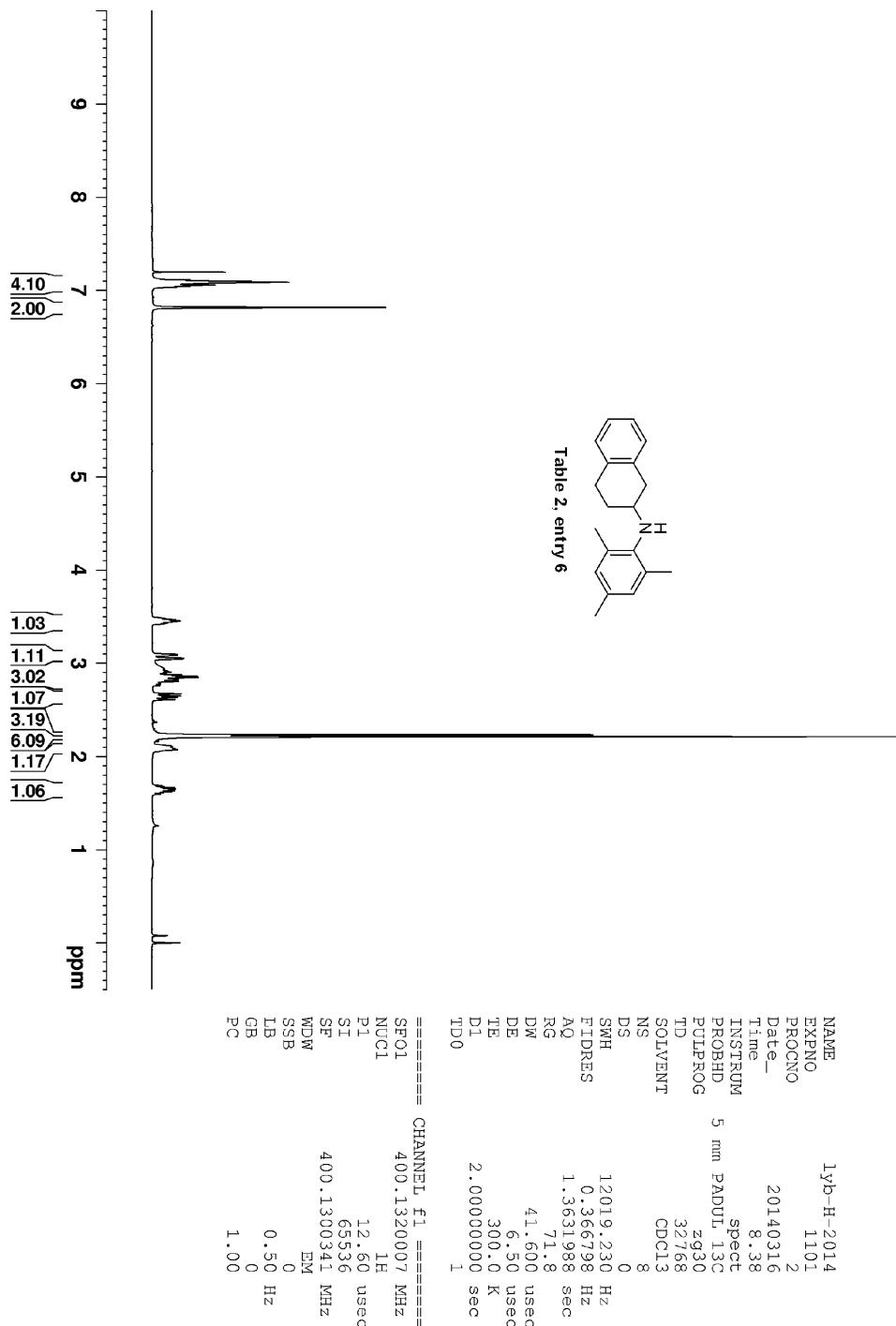


Table 2, entry 5





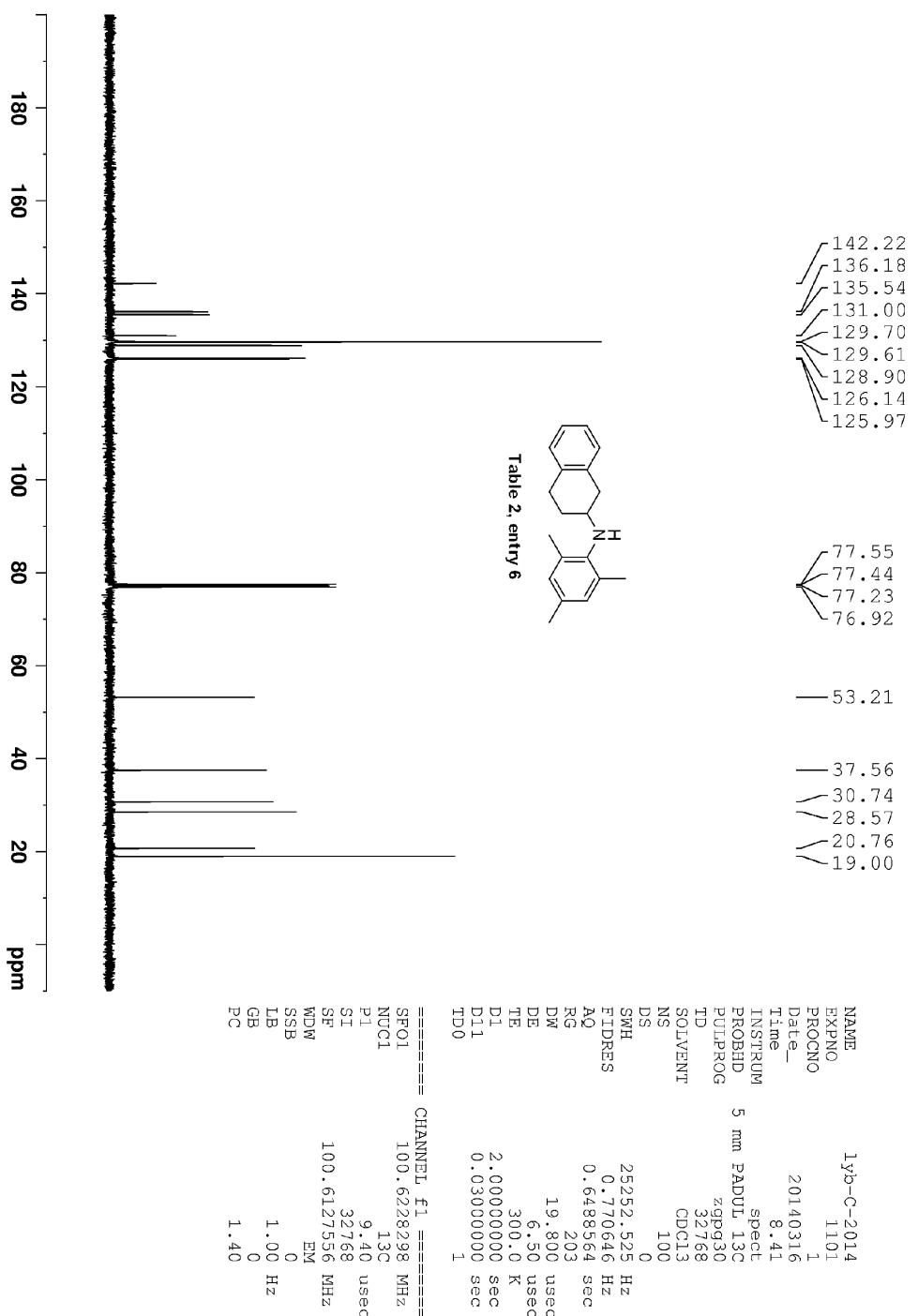
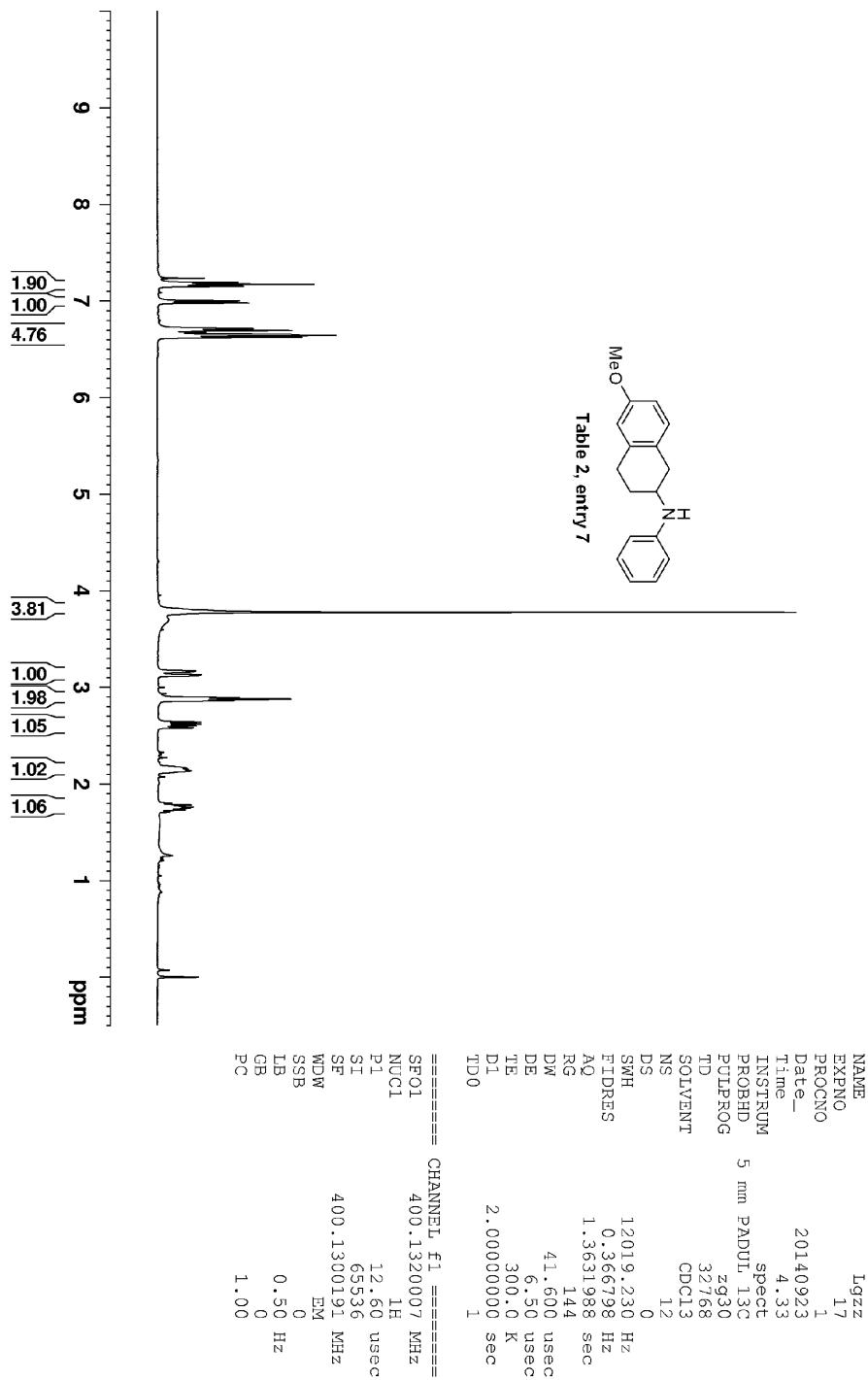
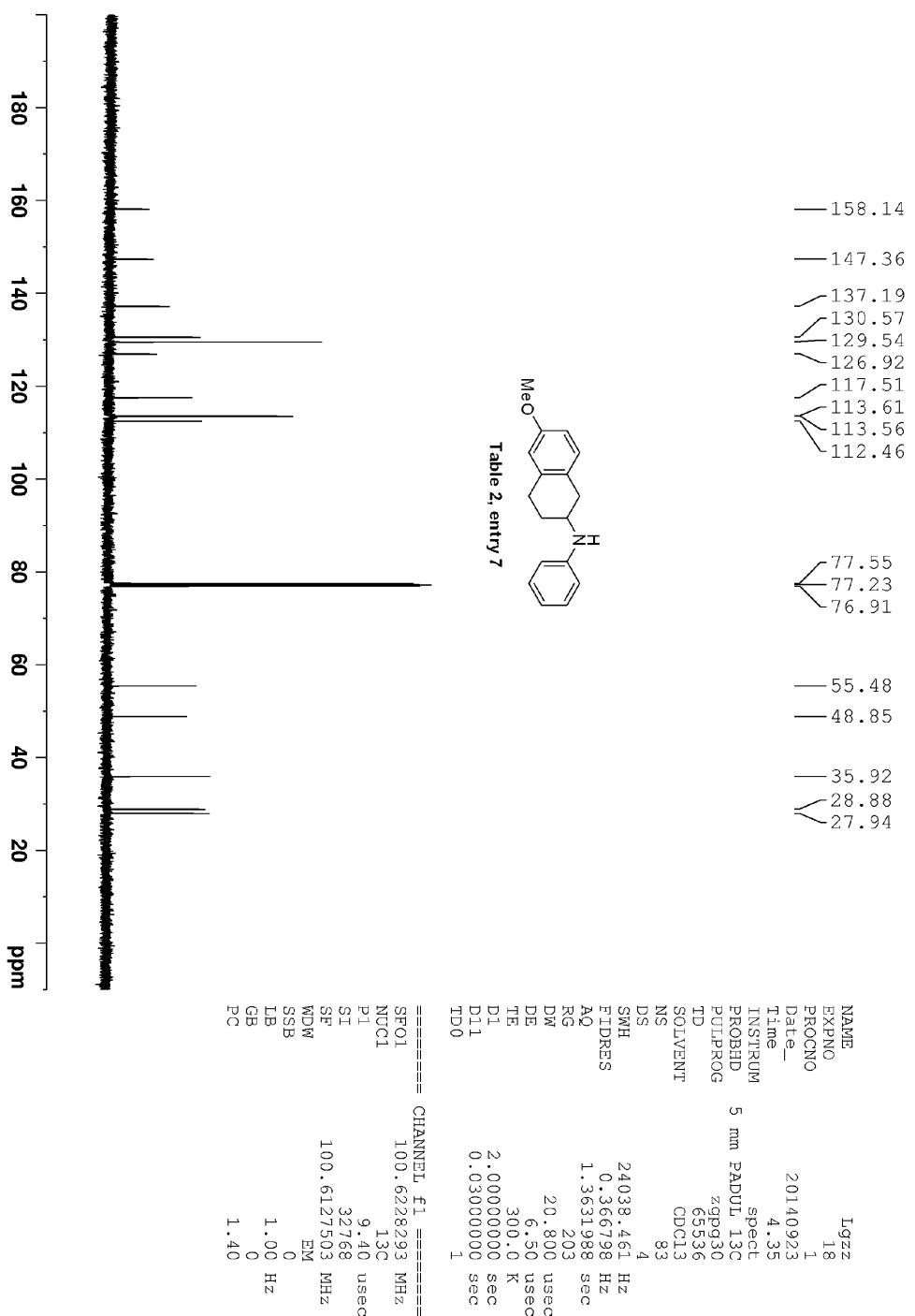
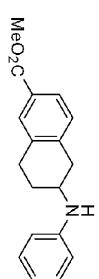


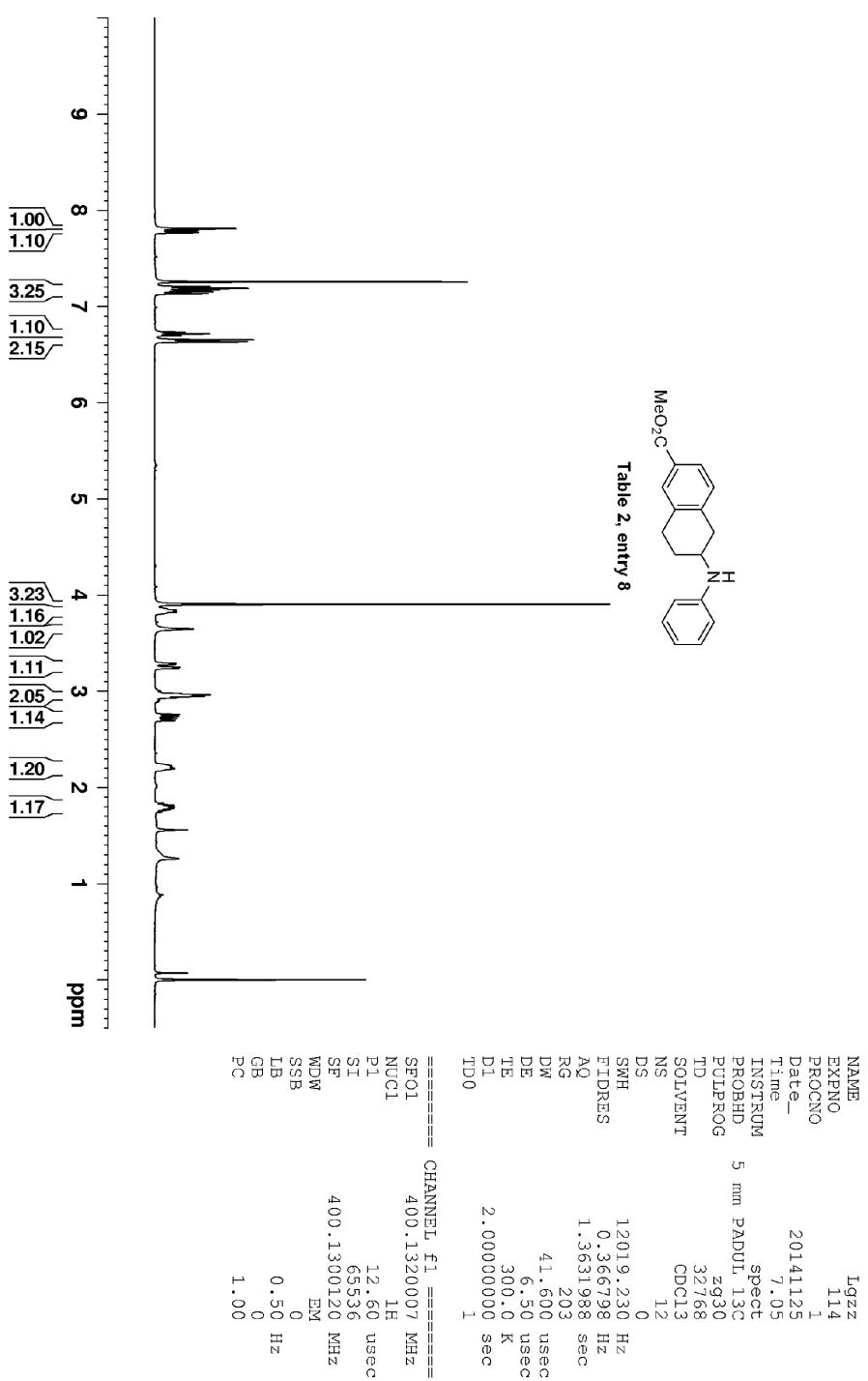
Table 2, entry 6

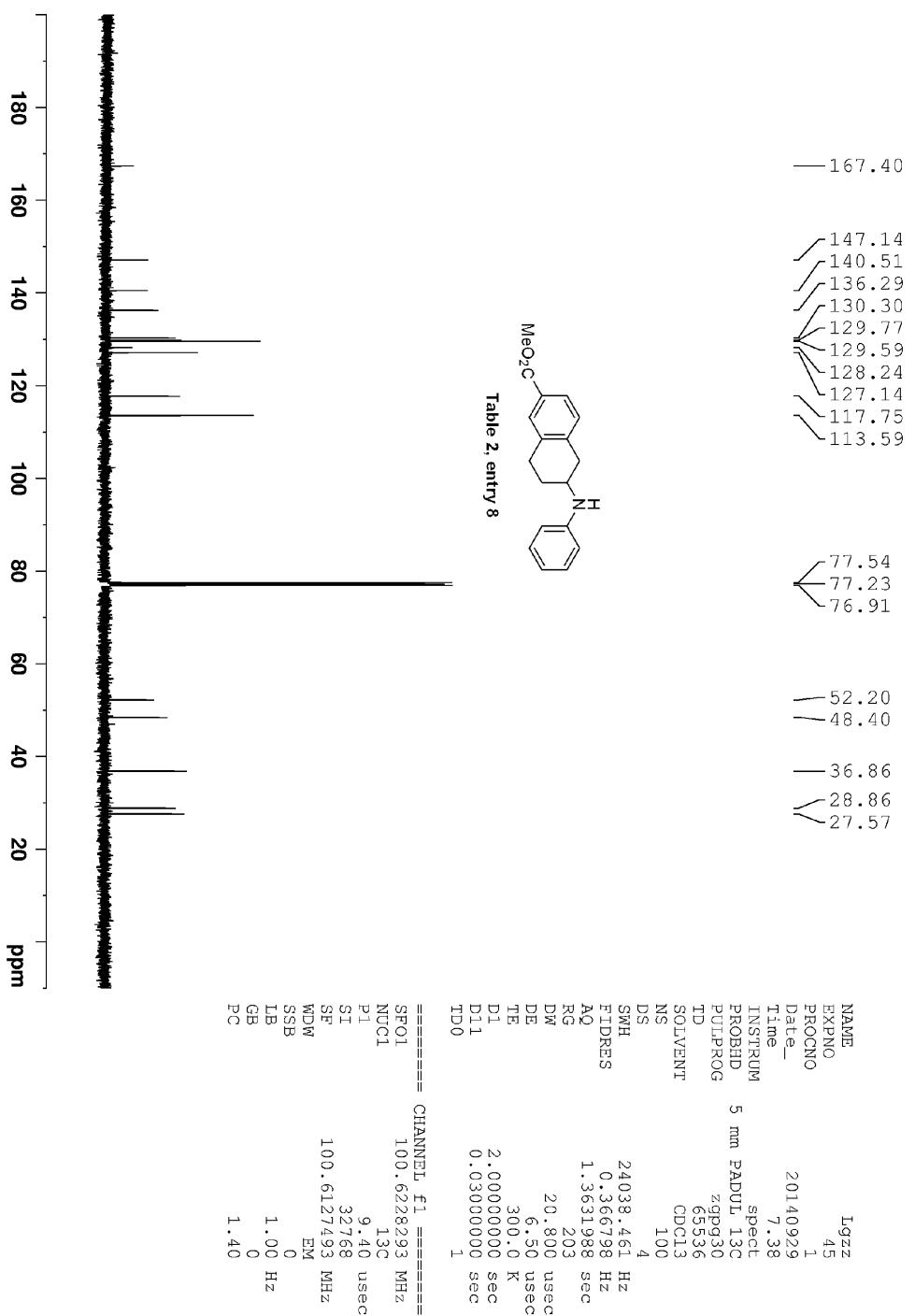


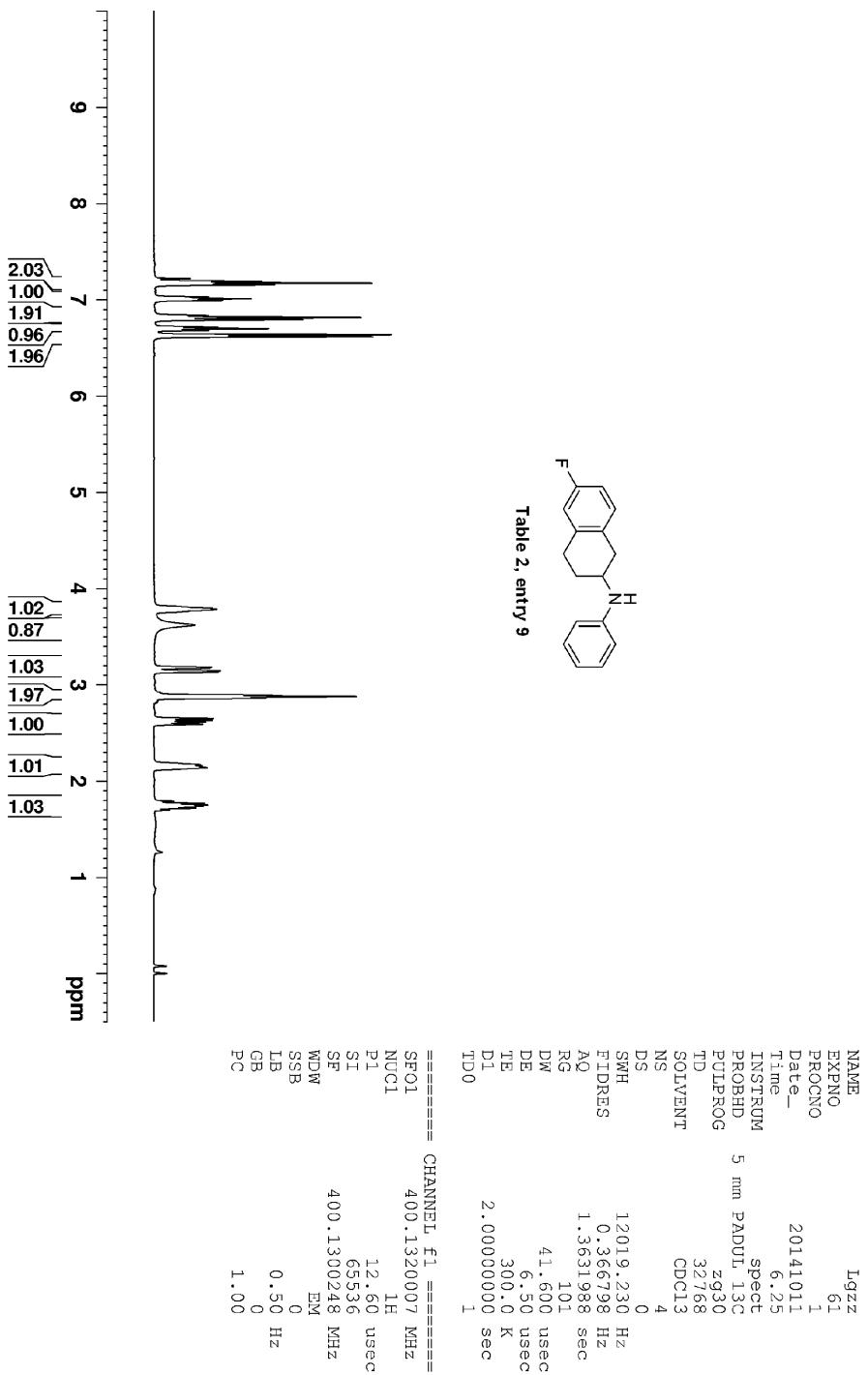


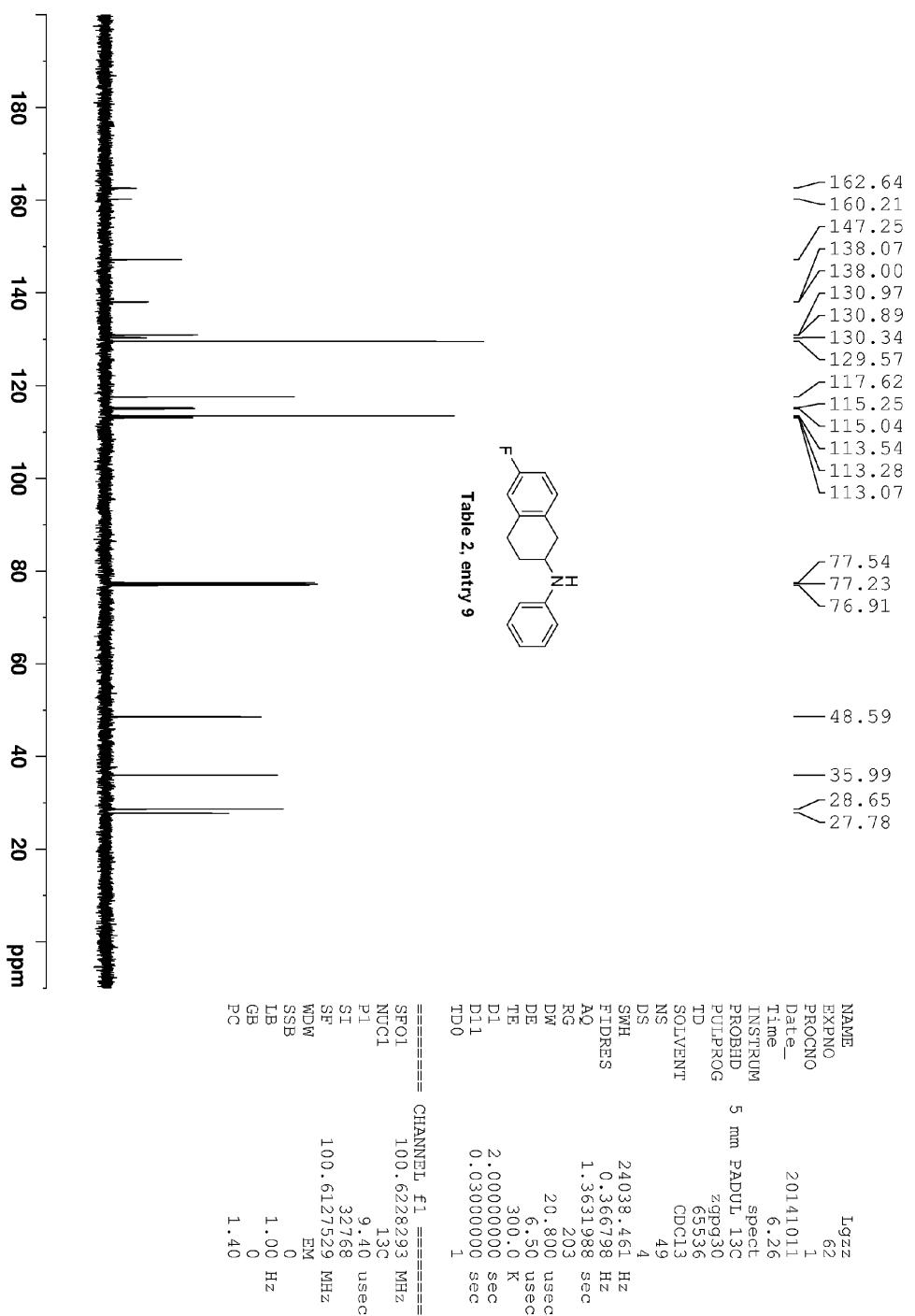


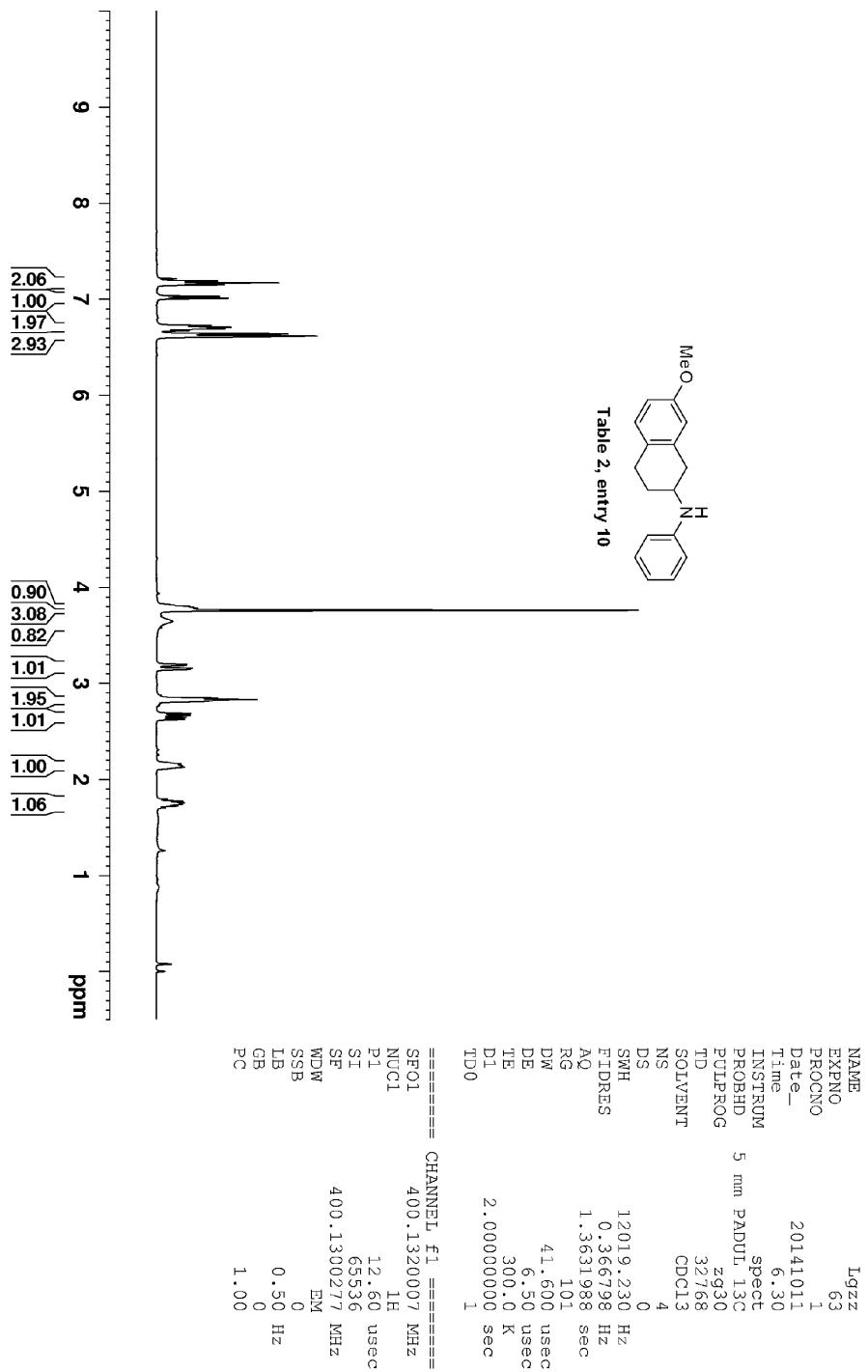
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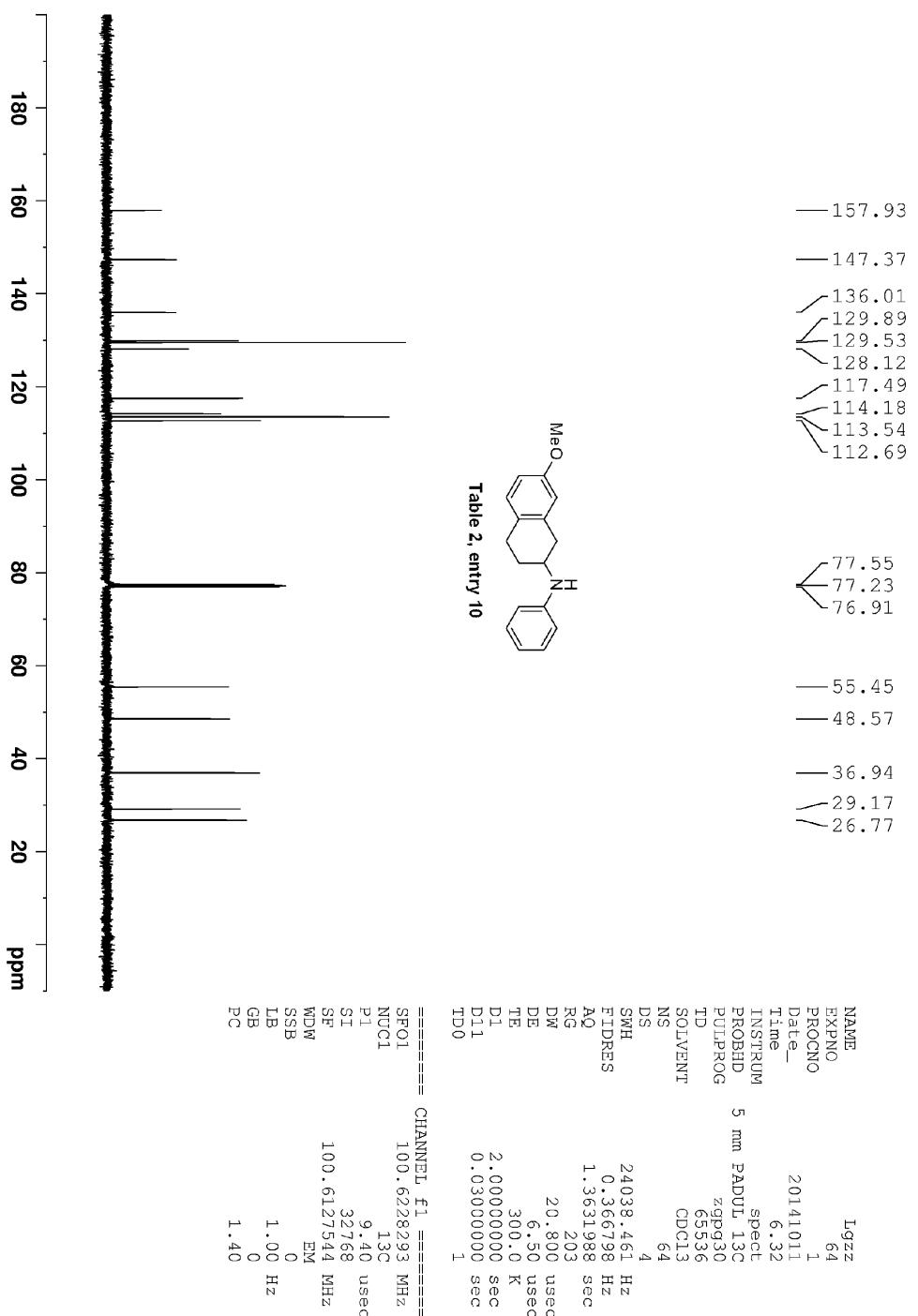












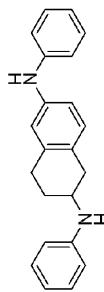
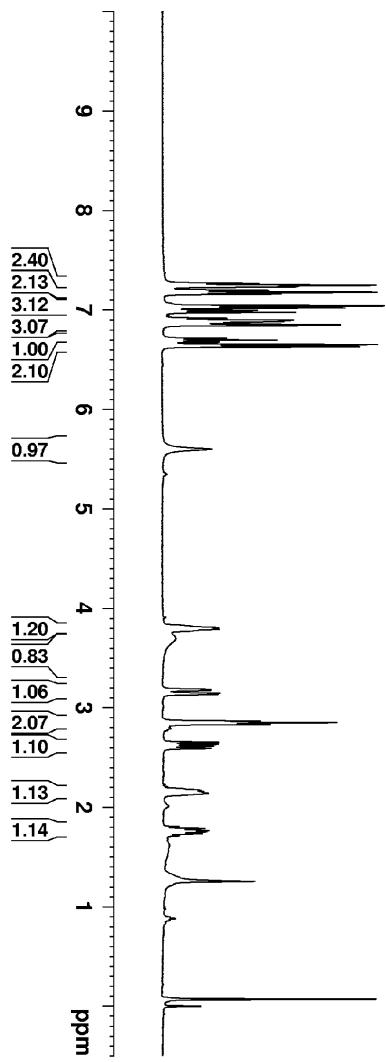
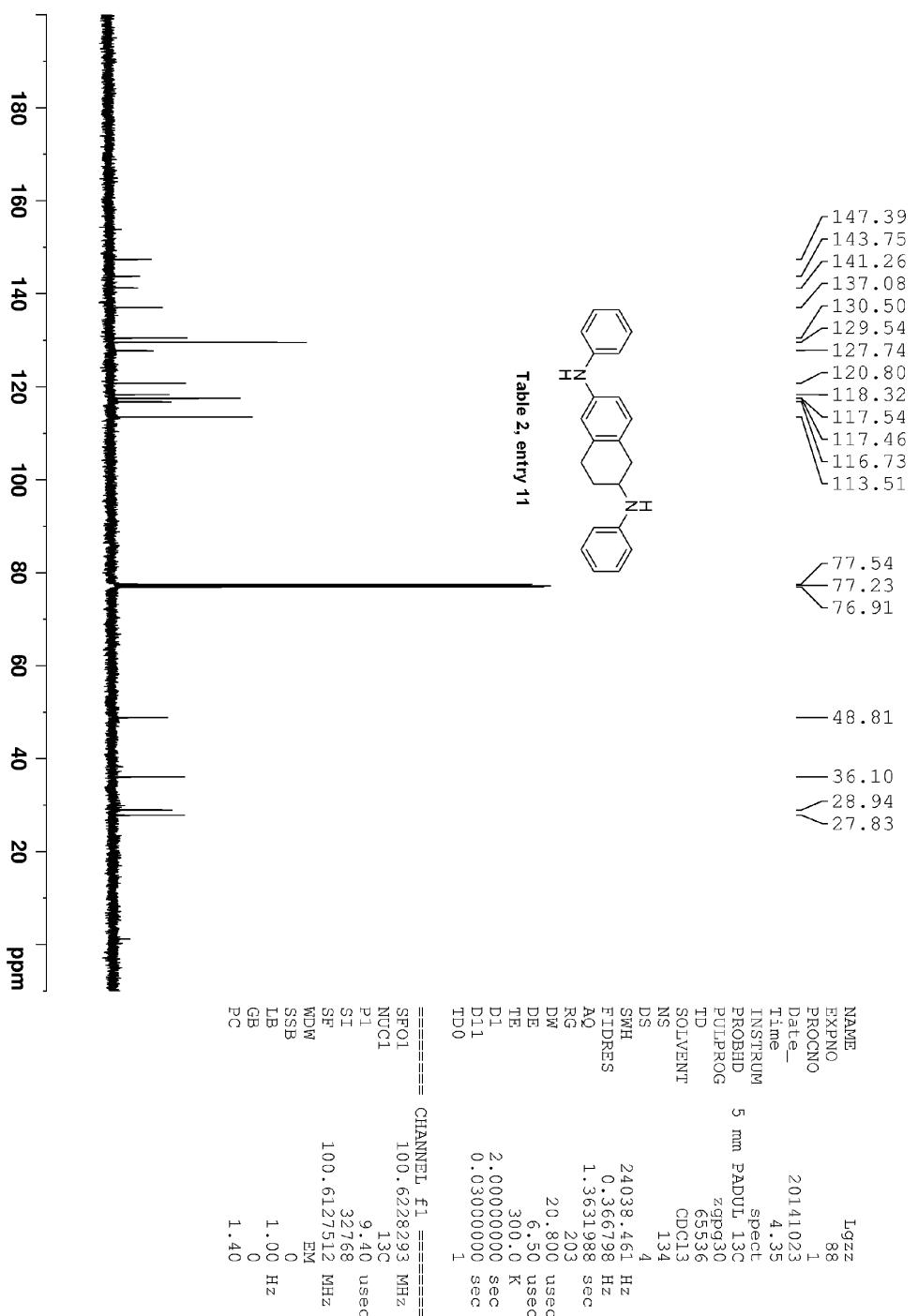


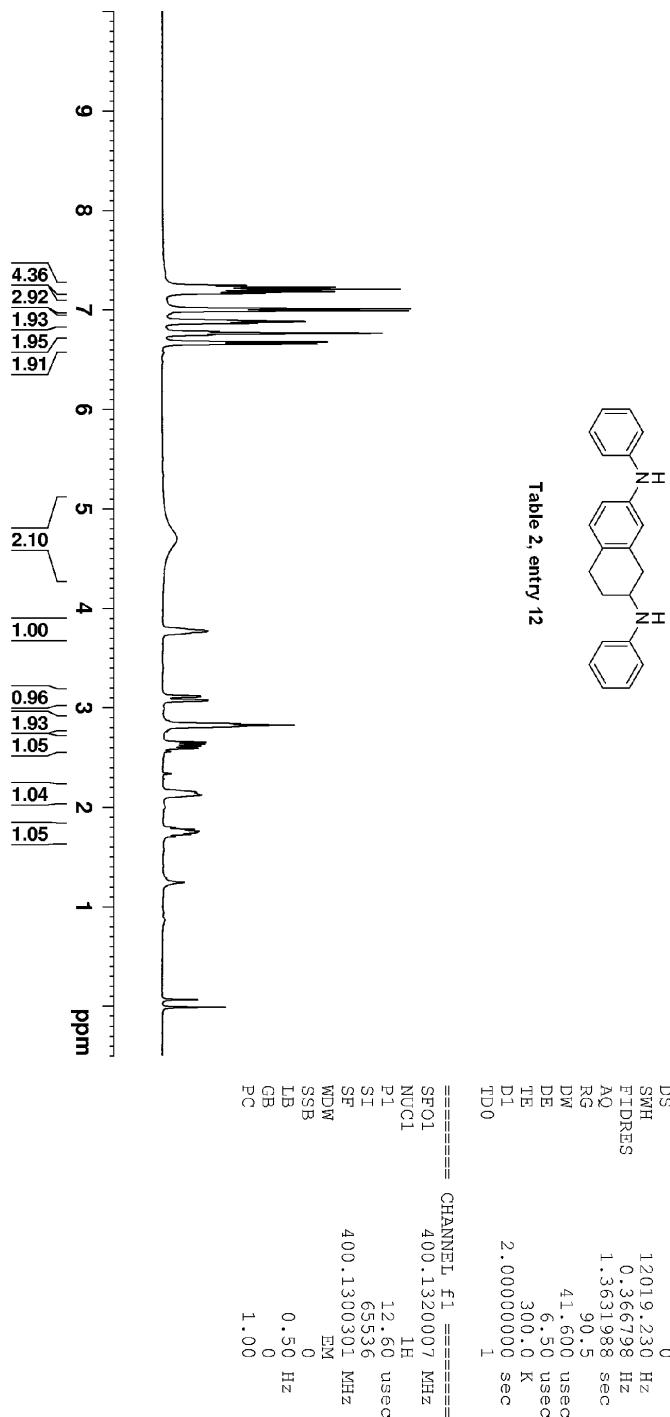
Table 2, entry 11

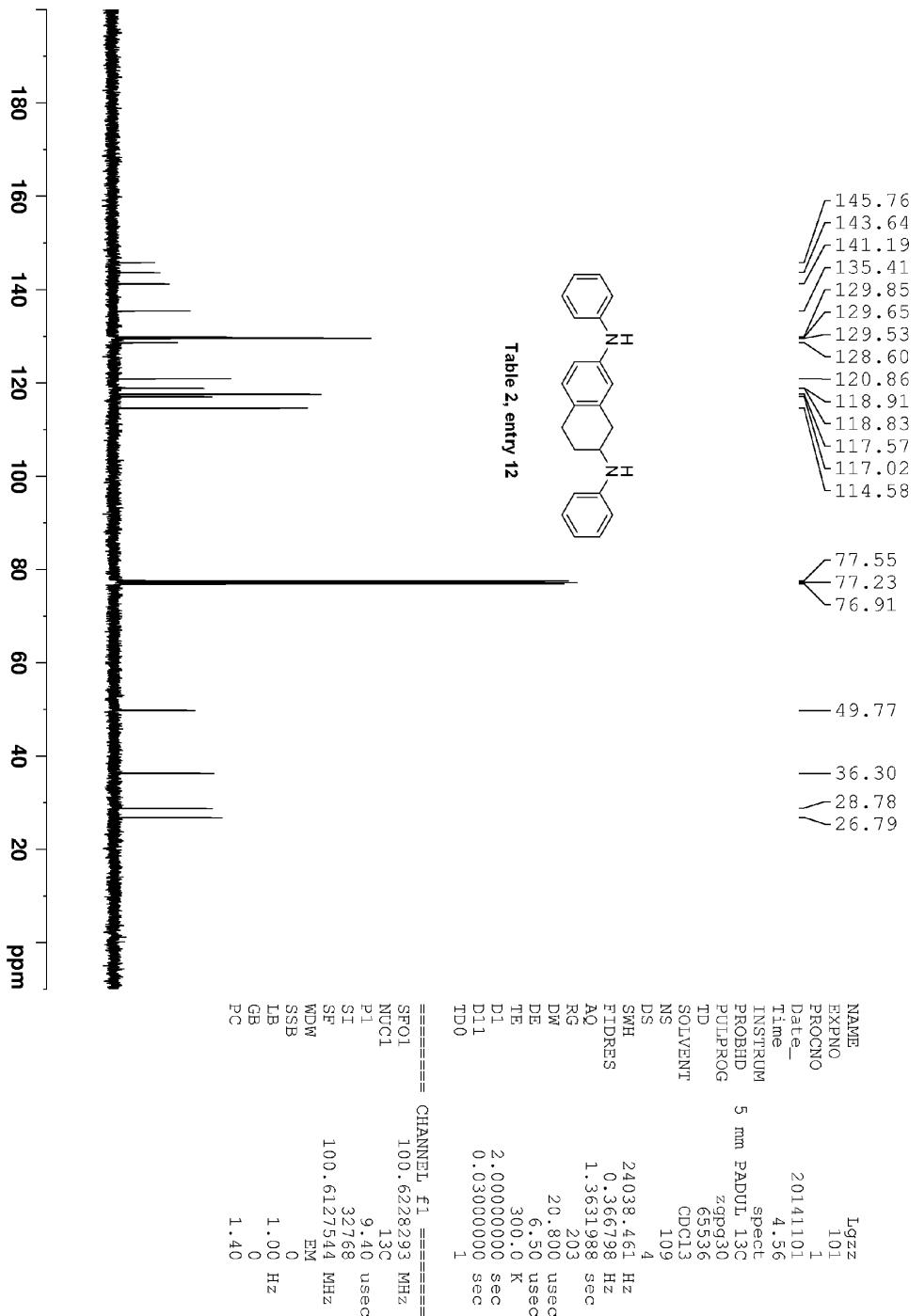
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	EXPNO	87
	PROCNO	1
Date_	20141023	
Time	4.33	
INSTRUM	5 mm PABU1 13C spect	
PROBHD	PULPROG	
PULFRQ	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	4	
DS	0	
SWH	12019.230 Hz	
FLDRES	0.366798 Hz	
AQ	1.3031988 sec	
RG	144	
DW	41.600 usec	
DE	6.50 usec	
TE	300.0 K	
D1	2.0000000 sec	
TDO	1	

	===== CHANNEL f1 =====
SFO1	400.1320007 MHz
NUCL1	1H
P1	12.60 usec
SI	655.36
SF	400.1300180 MHz
WDW	EM
SSB	0
LB	0.50 Hz
GB	0
PC	1.00







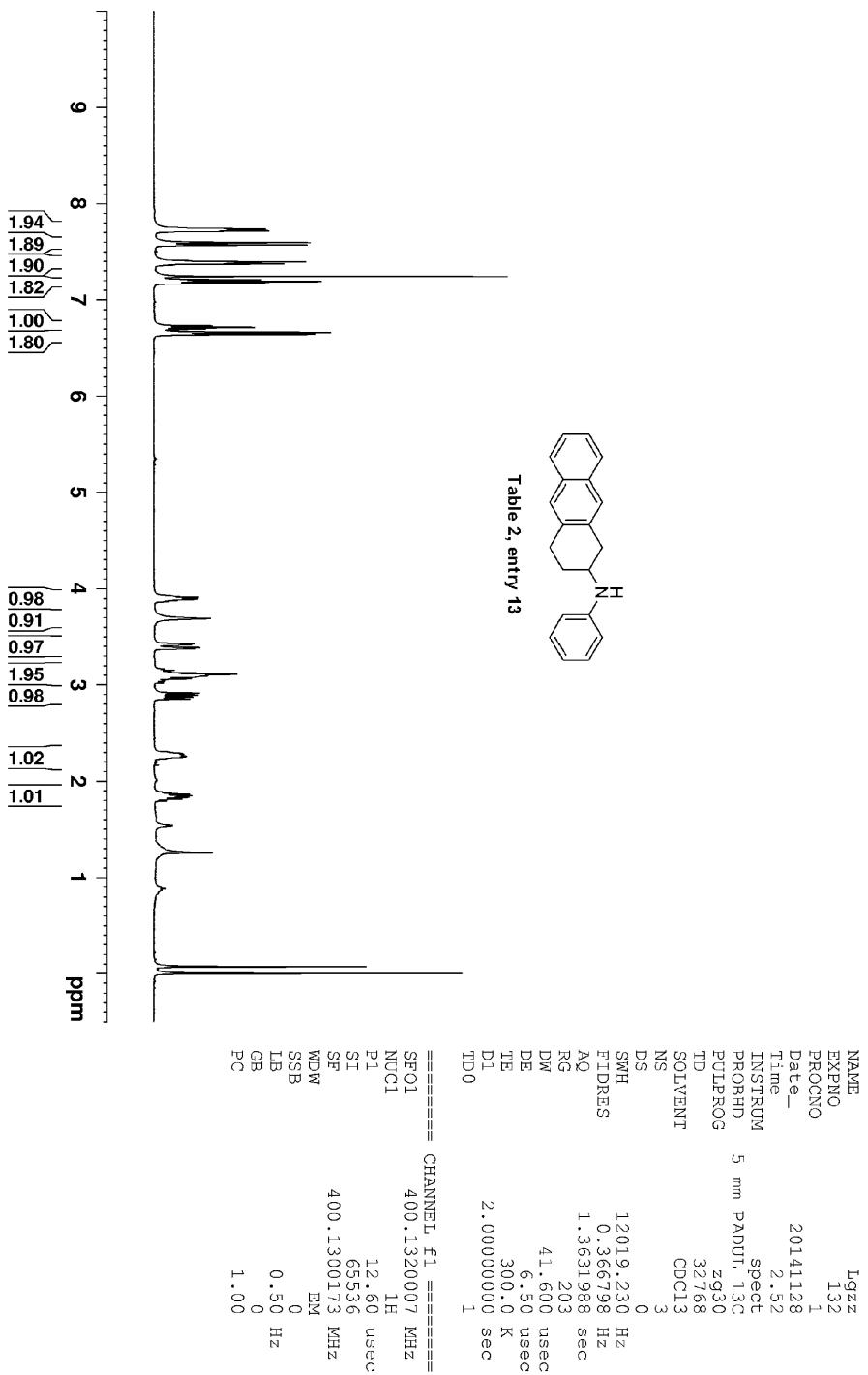
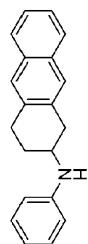
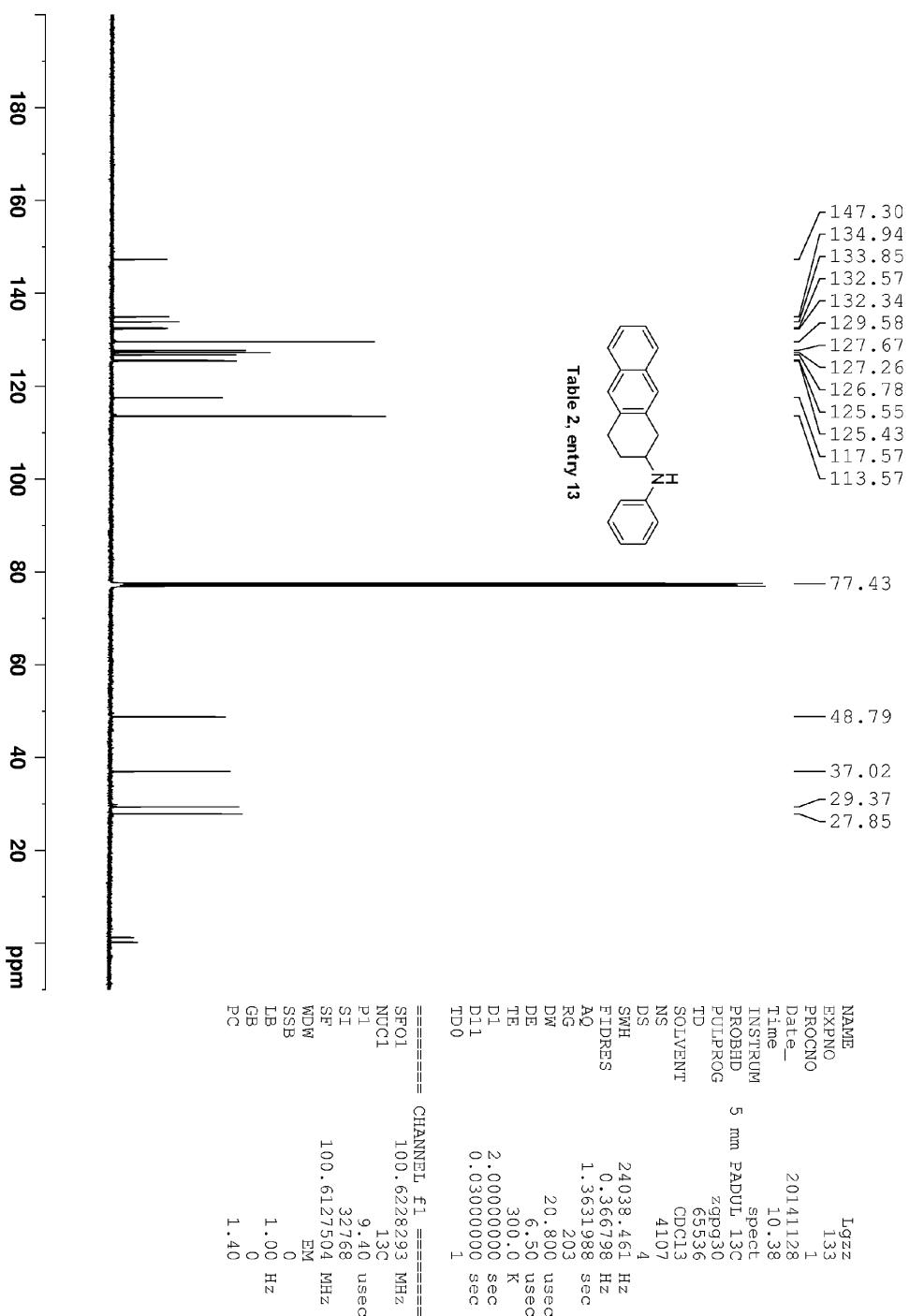
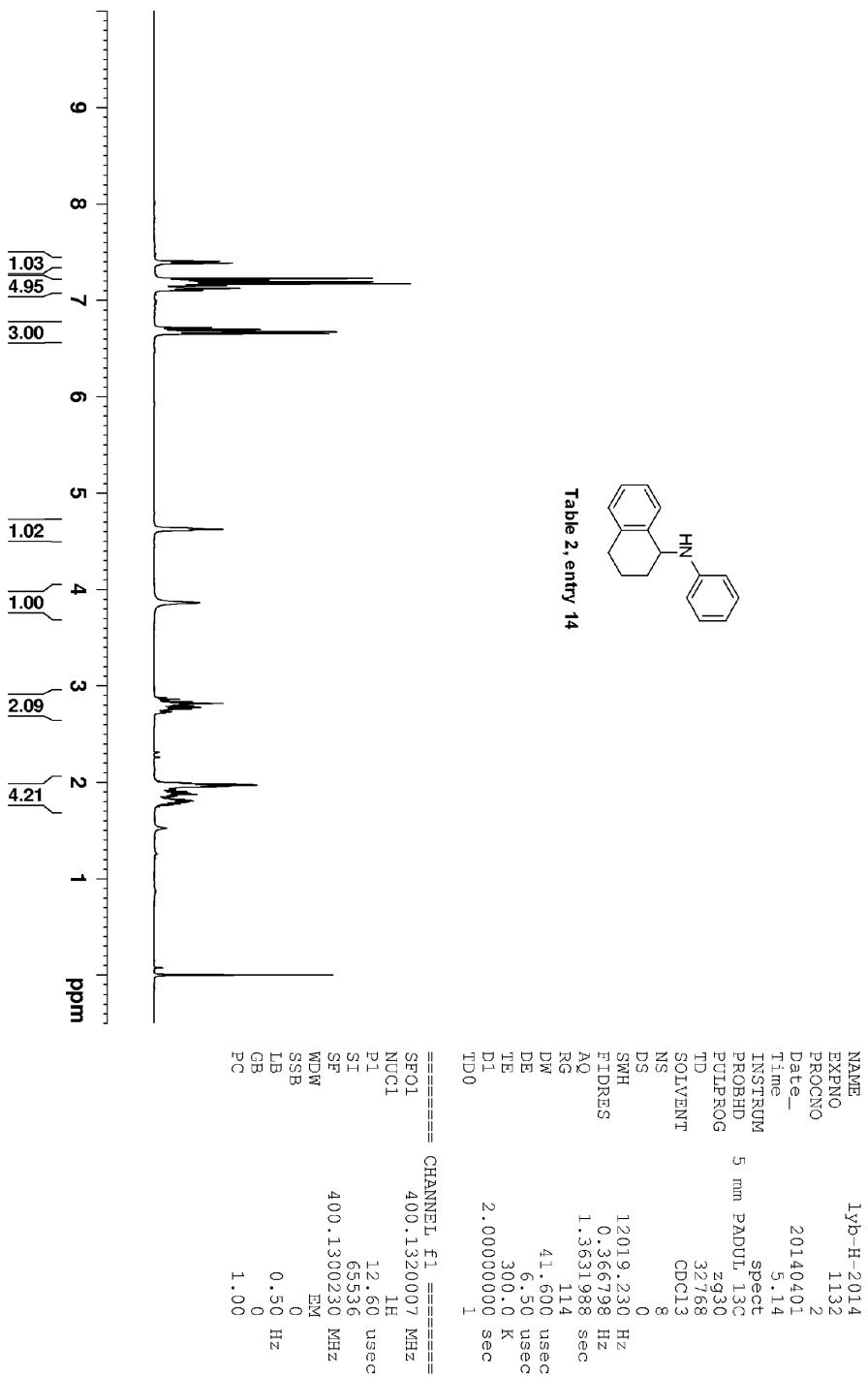
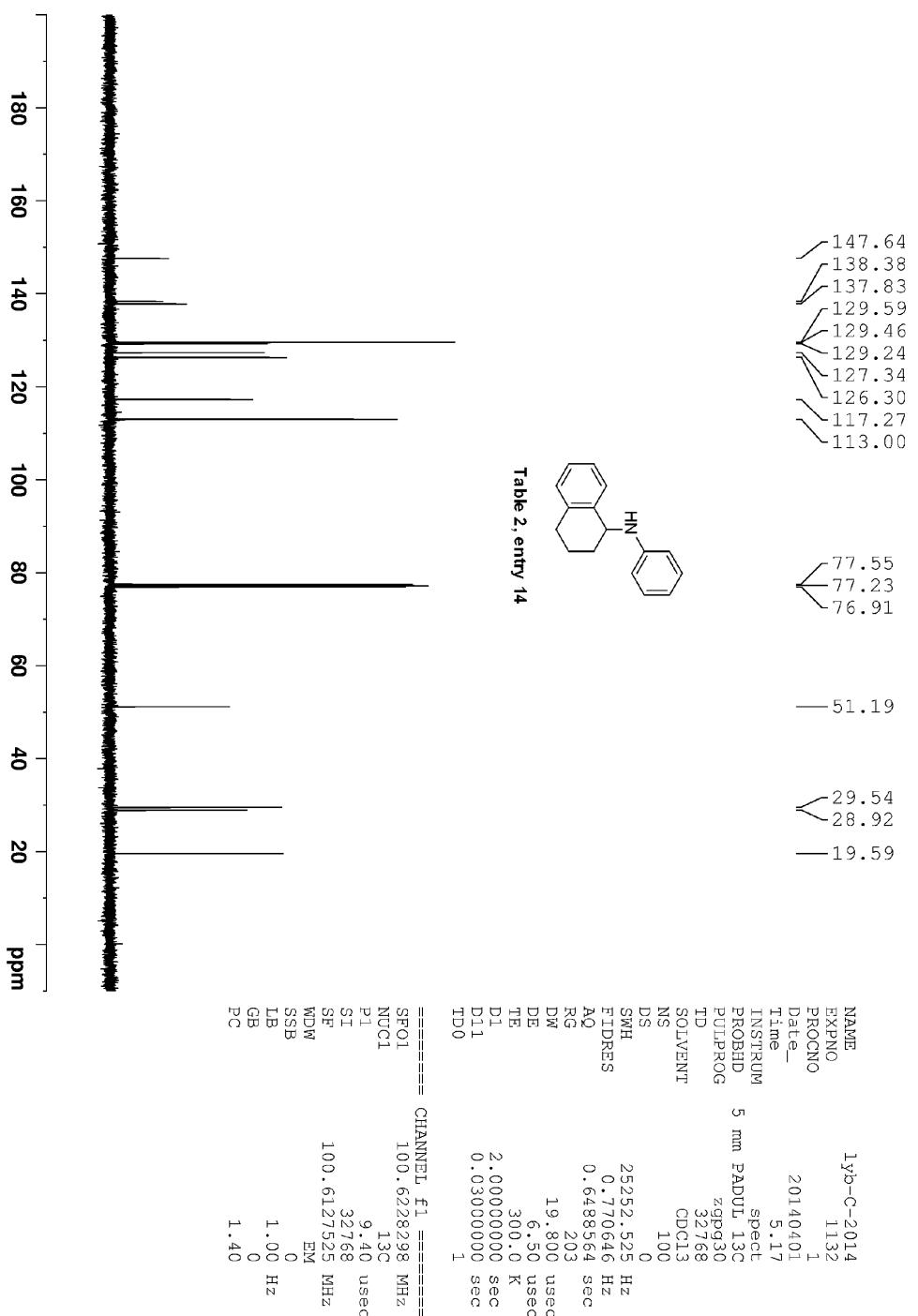


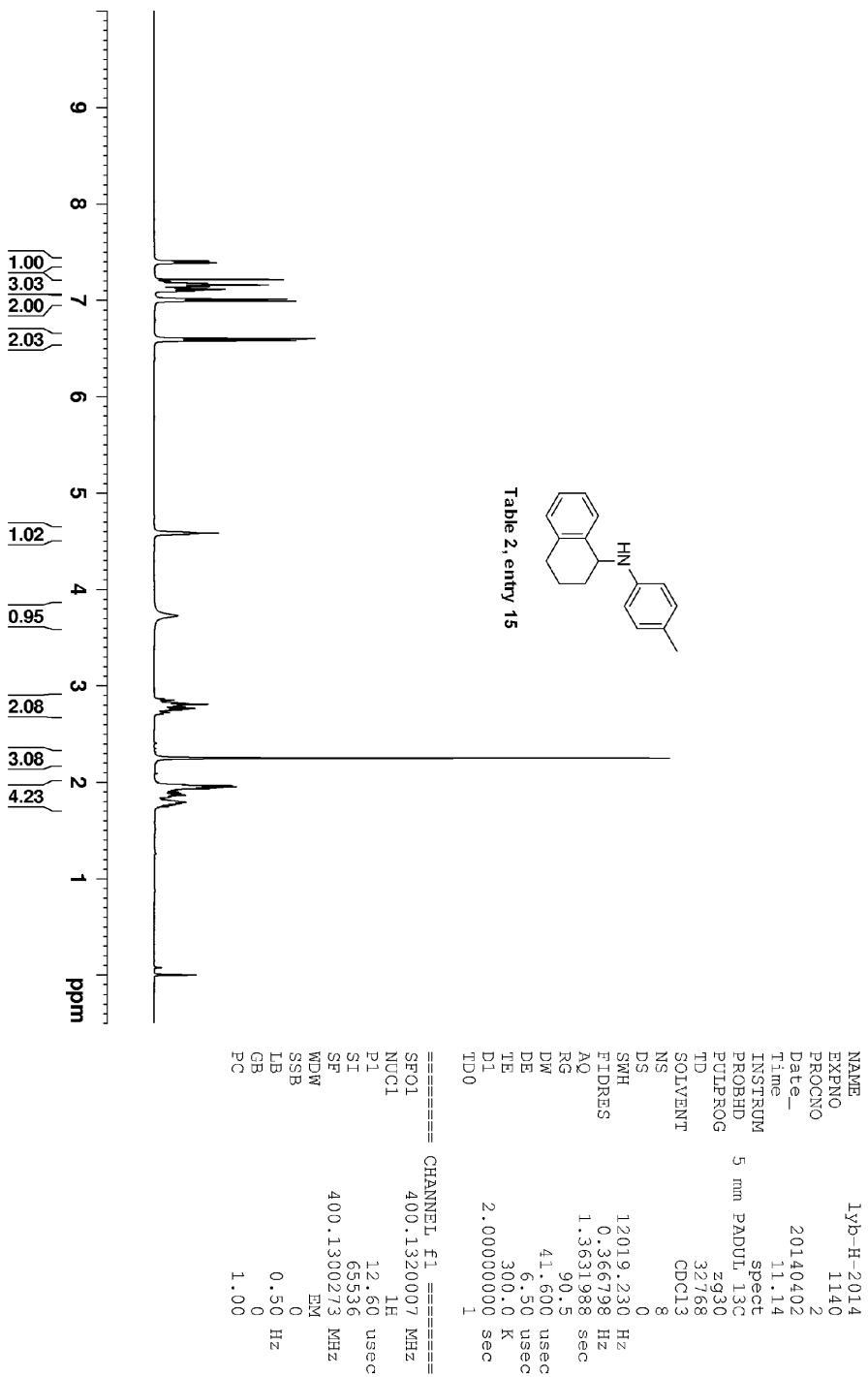
Table 2, entry 13











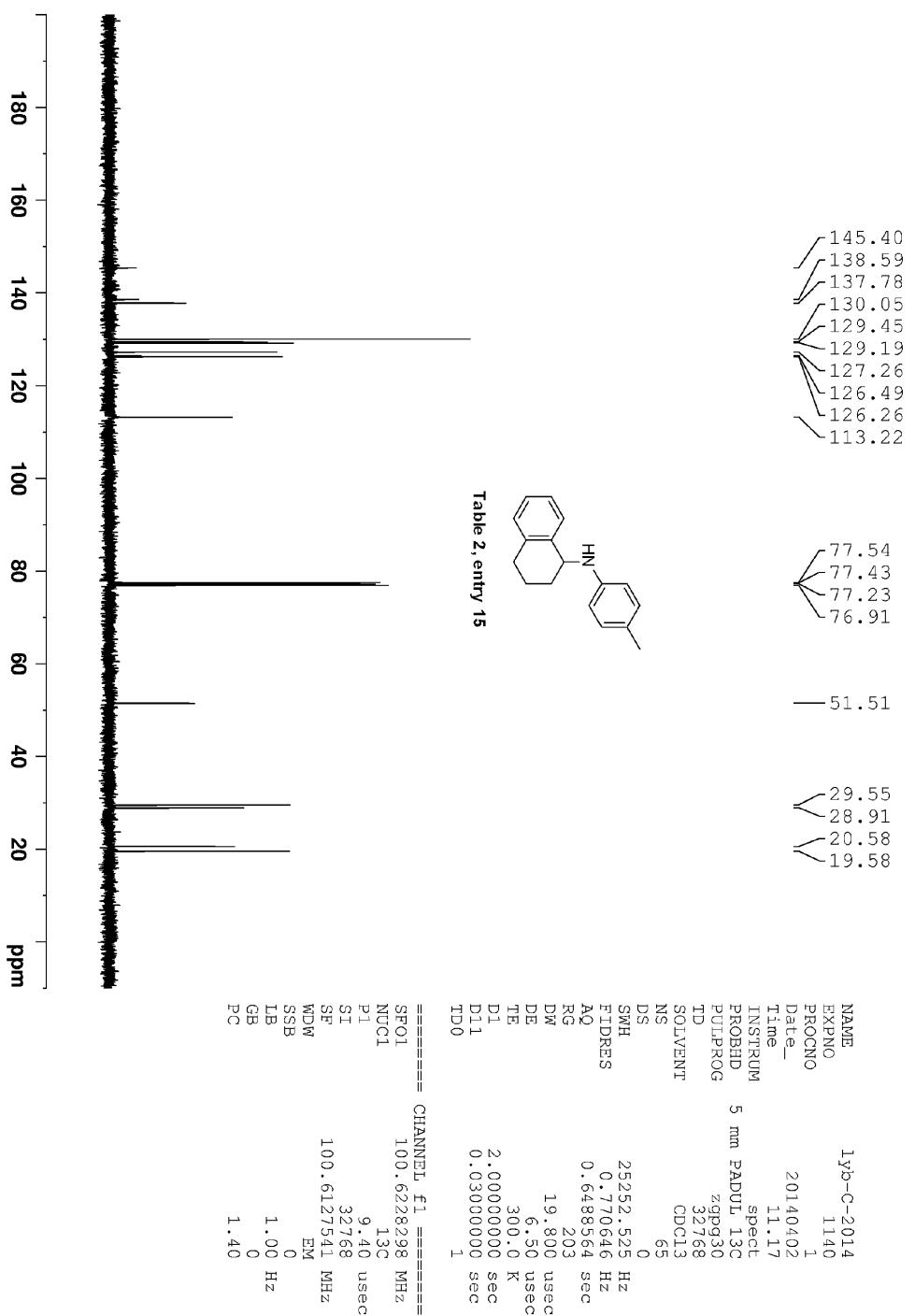


Table 2, entry 15

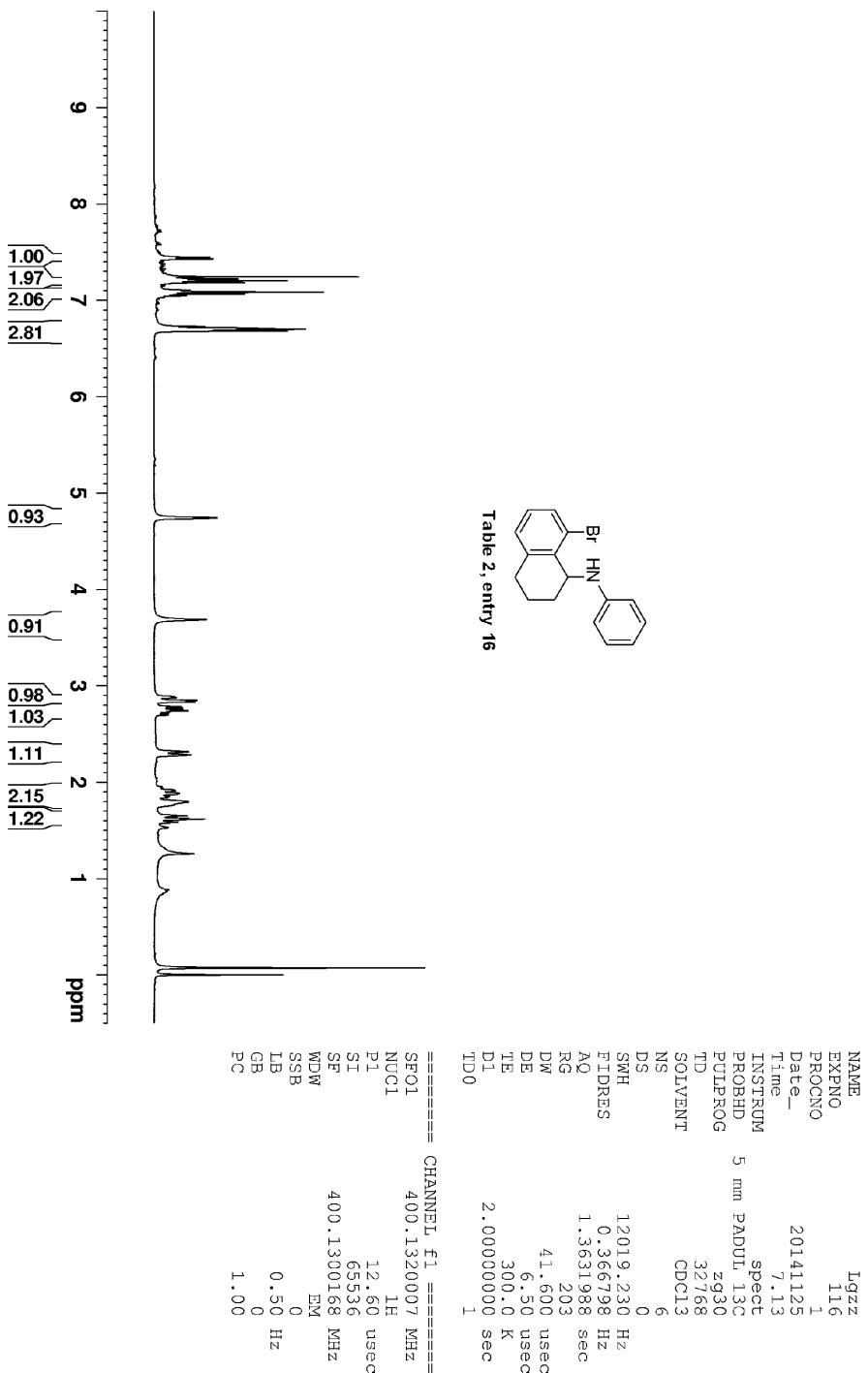


Table 2, entry 16

