Electronic Supplementary Material (ESI) for RSC Advances.

Economical and Efficient Aqueous Reductions of High Melting-Point Imines and Nitroarenes to Amines: Promotion Effects of Granular PTFE

Tao Li,‡[a] Xiaoxue Cui,‡[a] Lili Sun‡[a] and Chunbao Li*[a]

Department of Chemistry, College of Science, Tianjin University, Tianjin, 300072, P. R. of China. Fax: +862227403475, E-mail: lichunbao@tju.edu.cn

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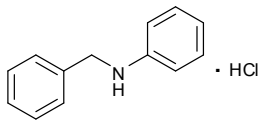
General experimental information

All of the chemicals were obtained from commercial sources or prepared according to standard methods. The ^{1}H NMR (400 or 600 MHz) and ^{13}C NMR (100 or 150 MHz) were recorded on a Bruker AM-400 spectrometer or a Bruker Avance III spectrometer respectively. Chemical shifts (δ) are reported relative to TMS (^{1}H) or $CDCl_3$ (^{13}C). IR spectra were recorded on BIO-RAD FTS 3000 spectrometer. Melting points were recorded on an X-4 Micro-melting Point Apparatus. High resolution mass spectra (ESI) were obtained on a Bruker micrOTOF-QII. All the aqueous reductions were performed in 100-mL flasks and agitated by a modified stirring rod. The stirring rod was modified by inserting a 25-cm PTFE wire into the blades and has been described previously. The granular PTFE is 70 pieces/g.

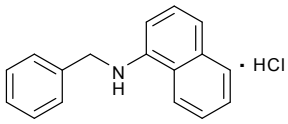
General procedure for the reduction of imines

Zn powder (5 equiv) was added to a mixture of imine (**1a-1m**, 2 g), Aliquat 336 (0.06 equiv), granular PTFE (5 g) and 5% aq NaOH solution (10 mL). The reaction mixture was mechanically stirred for 0.6-2.8 h at room temperature. TLC (thin layer chromatography) was used to determine when the reaction was complete. The aqueous solution was decanted and the solid residue was extracted with a small amount of ethyl acetate and then followed by acidified with conc. HCl to give amine hydrochlorides: **2a** (85%), **2b** (88%), **2c** (89%), **2d** (90%), **2e** (86%), **2f** (90%), **2g** (89%), **2i** (93%)**,** and **2m** (92%). This procedure was applied to the synthesis of **2d** (91%, 8 h) from 11 gram of **1d**. Alternatively the product was crystallized with

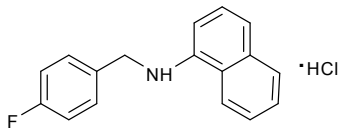
ethanol after the ethyl acetate was evaporated to give **2h** (88%), **2j** (95%), **2k** (89%), and **2l** (90%). Products **2a**,[1] **2b**,[2] **2d**,[3] **2j**,[4] **2k**,[5] and **2l**[6] are known compounds.



N-Phenylbenzylamine hydrochloride (**2a**): Mp 156-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.43-7.37 (m, 4H), 7.34-7.30 (m, 1H), 7.22 (dd, *J* = 8.2, 7.6 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 2H), 4.37 (s, 2H); IR (KBr, cm^{-1}) ν: 2710, 2671, 2555, 2424, 1595, 1494, 1438, 1386, 1202, 1075, 1024, 973, 910, 755, 689, 528, 422.

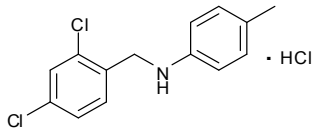


N-Benzyl-1-naphthalenamine hydrochloride (**2b**): Mp 150-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.44 (d, *J* = 8.4 Hz, 1H), 7.84 (dd, *J* = 29.0, 8.2 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.58-7.50 (m, 2H), 7.29 (dd, *J* = 11.4, 7.8 Hz, 3H), 7.11 (t, *J* = 6.5 Hz, 3H), 4.65 (s, 2H); IR (KBr, cm^{-1}) ν: 2911, 2716, 2662, 2629, 2505, 2361, 1576, 1516, 1448, 1402, 1372, 1291, 1225, 1078, 772, 748, 697, 480.

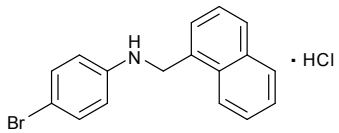


N-(4-Fluorobenzyl)-1-naphthalenamine hydrochloride (**2c**): Mp 159-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.42 (d, J = 8.5 Hz, 1H), 7.87 (dd, J = 20.7, 8.2 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.60-7.52 (m, 2H), 7.32 (t, J = 7.8 Hz, 1H), 7.24 (dd, J = 8.4, 5.3 Hz, 2H), 6.75 (t, J = 8.6 Hz, 2H), 4.65 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 163.22 (d, *J* = 249.7 Hz), 134.27, 133.26 (d, *J* = 8.6 Hz), 130.06, 129.72,

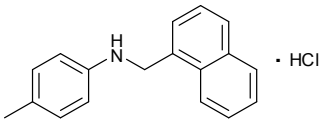
128.85, 128.04, 127.07, 126.34, 125.38 (d, *J* = 3.3 Hz), 124.80, 123.29, 121.59, 115.44 (d, *J* = 21.7 Hz), 54.68; IR (KBr, cm^{-1}) ν: 2894, 2768, 2668, 2591, 2542, 1601, 1574, 1511, 1449, 1404, 1222, 1162, 839, 799, 771, 542, 465, 427; ESI HRMS: Calcd: 252.1183 ($C_{17}H_{14}FN + H^+$); Found: *m/z* = 252.1186.



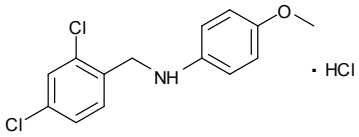
N-(2,4-Dichlorobenzyl)-4-methylaniline hydrochloride (**2d**): Mp 152-155 °C; ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.86 (d, J = 8.4 Hz, 1H), 7.28 (t, J = 5.7 Hz, 3H), 7.13 (d, J = 8.1 Hz, 2H), 7.09 (dd, J = 8.3, 1.9 Hz, 1H), 4.55 (s, 2H), 2.34 (s, 3H); IR (KBr, cm^{-1}) ν: 2895, 2691, 2622, 2541, 2410, 1585, 1511, 1472, 1438, 1387, 1199, 1100, 1056, 860, 819, 567, 534, 495, 420.



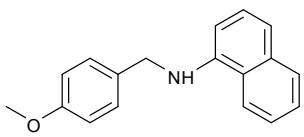
4-Bromo-*N*-(1-naphthalenylmethyl)aniline hydrochloride (**2e**): Mp 120-123 °C; ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.90-7.87 (m, 1H), 7.81 (d, J = 7.7 Hz, 2H), 7.58 (d, J = 7.0 Hz, 1H), 7.50-7.48 (m, 2H), 7.38-7.27 (m, 3H), 7.11 (d, *J* = 8.6 Hz, 2H), 4.84 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 135.88, 133.55, 132.54, 131.56, 130.21, 130.02, 128.83, 127.10, 126.24, 125.19, 124.88, 123.57, 123.45, 122.95, 51.14; IR (KBr, cm^{-1}) ν: 2870, 2814, 2685, 2624, 2536, 2425, 1593, 1510, 1485, 1427, 1370, 1070, 1015, 960, 808, 775, 514, 486, 422; ESI HRMS: Calcd: 312.0382 ($C_{17}H_{14}{}^{79}BrN + H^+$); Found: *m/z* = 312.0380; Calcd: 314.0362 ($C_{17}H_{14}{}^{81}BrN + H^+$); Found: *m/z* = 314.0367.



4-Methyl-*N*-(1-naphthalenylmethyl)aniline hydrochloride (**2f**): Mp 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.90-7.88 (m, 1H), 7.78 (d, J = 7.9 Hz, 2H), 7.65 (d, J = 7.0 Hz, 1H), 7.48-7.43 (m, 2H), 7.37-7.33 (m, 1H), 7.18 (d, J = 8.3 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 4.83 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 139.14, 133.39, 131.76, 131.66, 130.85, 130.24, 129.98, 128.63, 126.96, 126.07, 125.68, 125.12, 123.76, 123.13, 52.03, 20.97; IR (KBr, cm^{-1}) ν: 3046, 2875, 2824, 2693, 2635, 2543, 2425, 1596, 1511, 1464, 1427, 1374, 1022, 966, 804, 775, 532, 489, 441, 422; ESI HRMS: Calcd: 248.1434 ($C_{18}H_{17}N + H^+$); Found: *m/z* = 248.1435.

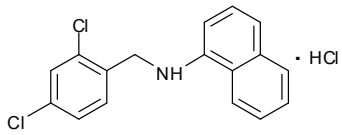


N-(2,4-Dichlorobenzyl)-4-methoxyaniline hydrochloride (**2g**): Mp 152-155 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ /ppm: 7.86 (d, J = 8.4 Hz, 1H), 7.30 (dd, J = 14.5, 5.5 Hz, 3H), 7.14 (dd, J = 8.3, 2.0 Hz, 1H), 6.82 (d, J = 8.9 Hz, 2H), 4.53 (s, 2H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ/ppm: 160.08, 136.33, 136.21, 133.86, 129.45, 127.68, 126.54, 125.02, 114.86, 55.48, 51.52; IR (KBr, cm^{-1}) ν: 2884, 2833, 2784, 2693, 2630, 2558, 2420, 1589, 1510, 1474, 1431, 1386, 1255, 1190, 1029, 866, 827, 721, 551, 524, 451; ESI HRMS: Calcd: 282.0447 ($C_{14}H_{13}Cl_2NO + H^+$); Found: *m/z* = 282.0447.

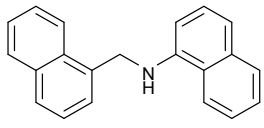


N-(4-Methoxybenzyl)-1-naphthalenamine (**2h**): Mp 67-69 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm: 7.84 (d, *J* = 8.7 Hz, 2H), 7.51-7.35 (m, 5H), 7.29 (d, *J* = 7.4 Hz, 1H),

6.95 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 1H), 4.45 (s, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ/ppm: 159.09, 143.37, 134.38, 131.16, 129.12, 128.75, 126.72, 125.81, 124.78, 123.47, 120.02, 117.63, 114.20, 104.77, 55.37, 48.15; IR (KBr, cm^{-1}) ν: 3439, 3047, 2998, 2891, 2837, 1585, 1533, 1508, 1441, 1408, 1340, 1294, 1241, 1169, 1026, 816, 769, 425; ESI HRMS: Calcd: 264.1383 ($C_{18}H_{17}NO + H^+$); Found: *m/z* = 264.1366.

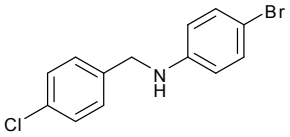


N-(2,4-Dichlorobenzyl)-1-naphthalenamine hydrochloride (**2i**): Mp 125-127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm: 8.48 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 14.9, 8.2 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.57 (dd, *J* = 15.2, 7.5 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 1.9 Hz, 1H), 7.04 (dd, *J* = 8.3, 1.9 Hz, 1H), 4.82 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ/ppm: 136.64, 136.27, 134.42, 134.32, 130.19, 129.95, 129.30, 128.80, 127.92, 127.49, 127.07, 126.83, 126.47, 124.87, 122.58, 121.48, 51.11; IR (KBr, cm^{-1}) ν: 2928, 2736, 2631, 2582, 2535, 2456, 2367, 1569, 1518, 1473, 1443, 1394, 1262, 1102, 1052, 993, 937, 903, 802, 766, 733, 499, 456; ESI HRMS: Calcd: 302.0498 ($C_{17}H_{13}Cl_2N + H^+$); Found: *m/z* = 302.0501.

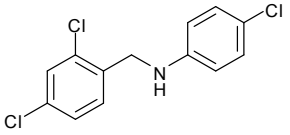


N-(1-Naphthalenylmethyl)-1-naphthalenamine (**2j**): Mp 125-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.19-8.16 (m, 1H), 7.98-7.96 (m, 1H), 7.88 (dd, *J* = 15.7, 8.2 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.56 (dd, *J* = 6.6, 2.7 Hz, 2H), 7.51-7.47 (m, 2H), 7.45-7.38 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 7.5

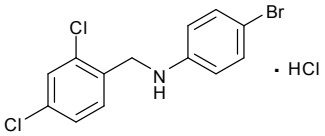
Hz, 1H), 4.94 (s, 2H); IR (KBr, cm^{-1}) ν: 3433, 3048, 2831, 1578, 1526, 1477, 1407, 1314, 1282, 1121, 1079, 1016, 791, 765, 418.



4-Bromo-*N*-(4-chlorobenzyl)aniline (**2k**): Mp 78-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.34-7.25 (m, 6H), 6.50 (d, *J* = 8.4 Hz, 2H), 4.30 (s, 2H); IR (KBr, cm^{-1}) ν: 3400, 3023, 2925, 2850, 1590, 1492, 1464, 1398, 1310, 1242, 1179, 1088, 1009, 876, 813, 617, 503.



4-Chloro-*N*-(2,4-dichlorobenzyl)aniline (**2l**): Mp 69-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.43 (d, *J* = 1.9 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.23-7.19 (m, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.39 (d, *J* = 5.8 Hz, 2H); IR (KBr, cm^{-1}) ν: 3401, 2863, 1591, 1498, 1470, 1391, 1314, 1244, 1090, 1051, 872, 812.



4-Bromo-*N*-(2,4-dichlorobenzyl)aniline hydrochloride (**2m**): Mp 128-130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm: 7.81 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.32-7.27 (m, 3H), 7.16 (dd, *J* = 8.3, 1.9 Hz, 1H), 4.55 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ/ppm: 136.59, 136.25, 133.66, 133.48, 133.02, 129.65, 127.81, 126.33, 125.16, 123.44, 51.28; IR (KBr, cm^{-1}) ν: 2889, 2818, 2690, 2617, 2538, 2409, 1586, 1482, 1437, 1389, 1196, 1102, 1062, 1011, 861, 825, 563, 512, 417; ESI HRMS:

Calcd: 329.9446 ($C_{13}H_{10}{}^{79}BrCl_2N + H^+$); Found: *m/z* = 329.9446; Calcd: 331.9426 ($C_{13}H_{10}{}^{81}BrCl_2N + H^+$); Found: *m/z* = 331.9425.

Control experiments for the function of Aliquat 336 and granular PTFE in the reduction of imines

1. Reduction of **1a** without Aliquat 336 and granular PTFE

Zn powder (5 equiv, 0.06 mol) was added to a mixture of **1a** (2 g) and 5% aq. NaOH solution (10 mL). The reaction mixture was stirred for 40 min at room temperature. TLC indicated that the reaction did not take place. After 13 h, ^{1}H NMR indicated that the reaction was complete.

2. Reduction of **1b** without Aliquat 336 and granular PTFE

Zn powder (5 equiv, 0.04 mol) was added to a mixture of **1b** (2 g) and 5% aq. NaOH solution (10 mL). The reaction mixture was stirred for 50 min at room temperature. TLC indicated that the reaction did not take place. After 24 h, ^{1}H NMR indicated that the reaction was complete.

3. Reduction of **1h** without Aliquat 336 and granular PTFE

Zn powder (5 equiv, 0.04 mol) was added to a mixture of **1h** (2 g) and 5% aq. NaOH solution (10 mL). The reaction mixture was stirred for 2.8 h at room temperature. TLC indicated that the reaction did not take place. After 72 h, ^{1}H NMR indicated that half of reaction was complete.

4. Reduction of **1d** without Aliquat 336

Zn powder (5 equiv, 0.04 mol) was added to a mixture of **1d** (2 g), granular PTFE (5

g), and 5% aq. NaOH solution (10 mL). The reaction mixture was stirred for 0.75 h at room temperature. TLC indicated that the reaction did not take place. After 20 h, ^{1}H NMR indicated that the reaction was complete.

Control experiments for the function of PTC in the reduction of imines

1. Reduction of **1j** with benzyltriethylammonium chloride

Zn powder (5 equiv, 0.04 mol) was added to a mixture of **1j** (2 g), benzyltriethylammonium chloride (0.06 equiv, 0.43 mmol) and 5% aq. NaOH solution (10 mL). The reaction mixture was stirred for 1.2 h at room temperature. ^{1}H NMR indicated that the reaction did not take place.

2. Reduction of **1k** with tetrabutylammonium bromide

Zn powder (5 equiv, 0.04 mol) was added to a mixture of **1k** (2 g), tetrabutylammonium bromide (0.06 equiv, 0.41 mmol) and 5% aq. NaOH solution (10 mL). The reaction mixture was stirred for 1.8 h at room temperature. ^{1}H NMR indicated that the reaction did not take place.

3. Reduction of **1f** with sodium dodecanesulfonate

Zn powder (5 equiv, 0.04 mol) was added to a mixture of **1f** (2 g), sodium dodecanesulfonate (0.06 equiv, 0.49 mmol) and 5% aq. NaOH solution (10 mL). The reaction mixture was stirred for 40 min at room temperature. ^{1}H NMR indicated that the reaction did not take place.

4. Reduction of **1m** in Aliquat 336

Zn powder (5 equiv, 0.04 mol) was added to a mixture of **1m** (2 g), 5% aq. NaOH

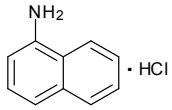
solution (5 mL) and Aliquat 336 (15 mL). The reaction mixture was stirred for 0.75 h at room temperature. ^{1}H NMR indicated that the reaction did not take place.

5. Reduction of **1l** with liquid *N*-butyl-*N*-methyl imidazolium chloride

Zn powder (5 equiv, 0.04 mol) was added to a mixture of **1l** (2 g), *N*-butyl-*N*-methyl imidazolium chloride (0.06 equiv, 0.42 mmol) and 5% aq. NaOH solution (10 mL). The reaction mixture was stirred for 1.5 h at room temperature. ^{1}H NMR indicated that the reaction did not take place.

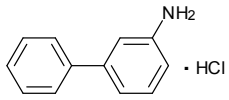
General procedure for the reduction of nitroarenes

Zn powder (7 equiv) was added to a mixture of nitroarene (**3a**-**3k**, 2 g), Aliquat 336 (0.06 equiv), NH_4Cl (2 equiv), granular PTFE (5 g) and H_2O (20 mL). The reaction mixture was mechanically stirred for 0.25-13 h at room temperature. TLC (thin layer chromatography) was used to determine when the reaction was complete. The aqueous solution was decanted and the solid residue was extracted with a small amount of ethyl acetate and then followed by acidified with conc. HCl to give amine hydrochlorides: **4a** (87%), **4b** (92%), and **4e** (90%). Alternatively after the ethyl acetate was evaporated the product was crystallized with ethanol to give **4c** (86%), and **4d** (88%) or distillation under vacuum to give **4f** (82%), **4g** (88%), **4h** (86%), **4i** (92%), **4j** (91%), and **4k** (88%). Products **4a**-**4k** are known compounds.[7-17]

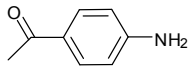


1-naphthalenamine hydrochloride (**4a**): Mp >200 °C (decomp.); ^{1}H NMR (400 MHz, D_2O) δ/ppm: 7.82 (dd, *J* = 16.7, 8.4 Hz, 3H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.5

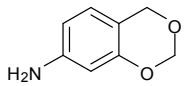
Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.38 (m, 1H); IR (KBr, cm^{-1}) ν: 2833, 2624, 2600, 1606, 1566, 1531, 1455, 1396, 1269, 793, 767, 568, 480, 455, 409.



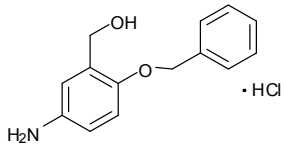
3-Phenylaniline hydrochloride (**4b**): Mp 152-155 °C; ^{1}H NMR (400 MHz, D_2O) δ/ppm: 7.56-7.43 (m, 5H), 7.41-7.22 (m, 4H); IR (KBr, cm^{-1}) ν: 2890, 2622, 1598, 1575, 1535, 1480, 1426, 1123, 870, 789, 752, 695, 580, 533, 505, 453, 426.



1-(4-Aminophenyl)ethanone (**4c**): Mp 100-102 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.81-7.80 (m, 2H), 6.65-6.64 (m, 2H), 4.14 (s, 2H), 2.50 (s, 3H); IR (KBr, cm^{-1}) ν: 3395, 3330, 3221, 1648, 1593, 1562, 1437, 1360, 1306, 1278, 1174, 1133, 958, 840, 594, 562.

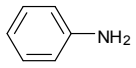


4*H*-1,3-Benzodioxin-7-amine (**4d**): Mp 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.74 (d, *J* = 8.1 Hz, 1H), 6.31 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.23 (d, *J* = 1.9 Hz, 1H), 5.22 (s, 2H), 4.83 (s, 2H), 3.66 (s, 2H); IR (KBr, cm^{-1}) ν: 3457, 3369, 3027, 2870, 2791, 1631, 1579, 1512, 1467, 1451, 1405, 1361, 1313, 1185, 1107, 1065, 996, 938, 841, 810, 556.

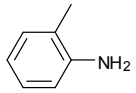


[5-Amino-2-(benzyloxy)phenyl]methanol hydrochloride (**4e**): Mp >190 °C (decomp.); ^{1}H NMR (400 MHz, D_2O) δ/ppm: 7.38-7.27 (m, 6H), 7.18 (dd, *J* = 8.7, 2.5 Hz, 1H),

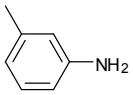
7.04 (d, J = 8.8 Hz, 1H), 5.09 (s, 2H), 4.58 (s, 2H); IR (KBr, cm^{-1}) ν: 3284, 3033, 2870, 2559, 1552, 1498, 1456, 1378, 1288, 1254, 1211, 1108, 1042, 1001, 913, 850, 812, 746, 694, 620, 549, 461.



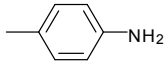
Aniline (**4f**): ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.15 (dd, J=8.3, 7.5, 2H), 6.75 (t, J=7.4, 1H), 6.69-6.67 (m, 2H), 3.62 (s, 2H); IR (KBr, cm^{-1}) ν: 3429, 3355, 3214, 3071, 3034, 1622, 1605, 1498, 1472, 1276, 1174, 881, 754, 691, 503.



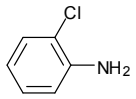
o-Toluidine (**4g**): ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.05-7.02 (m, 2H), 6.72-6.69 (m, 1H), 6.67 (d, J=7.8, 1H), 3.57 (s, 2H), 2.16 (s, 3H); IR (KBr, cm^{-1}) ν: 3449, 3370, 3224, 3023, 2929, 1623, 1586, 1498, 1467, 1303, 1269, 1148, 1035, 752, 712, 671, 536, 440.



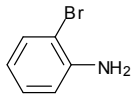
m-Toluidine (**4h**): ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.04 (t, J=7.7, 1H), 6.58 (d, J=7.5, 1H), 6.51-6.49 (m, 2H), 3.58 (s, 2H), 2.26 (s, 3H); IR (KBr, cm^{-1}) ν: 3432, 3354, 3217, 3033, 2919, 2859, 1622, 1493, 1468, 1292, 1168, 996, 925, 867, 776, 689, 556, 535, 440.



p-Toluidine (**4i**): Mp 41-42 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 6.96 (d, J=8.1, 2H), 6.60 (d, J=8.2, 2H), 3.51 (s, 2H), 2.24 (s, 3H); IR (KBr, cm^{-1}) ν: 3417, 3336, 3220, 3016, 2913, 2859, 1623, 1514, 1272, 1175, 1120, 813, 761, 722, 688, 505.



2-Chloroaniline (**4j**): ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.25-7.23 (m, 1H), 7.07-7.04 (m, 1H), 6.76 (dd, *J*=8.0, 1.2, 1H), 6.70-6.67 (m, 1H), 4.02 (s, 2H); IR (KBr, cm^{-1}) ν: 3470, 3380, 3199, 3068, 3026, 1617, 1487, 1450, 1308, 1260, 1153, 1080, 1050, 1023, 929, 839, 746, 677, 533, 436.



2-Bromoaniline (**4k**): ^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 7.40 (d, *J*=8.0, 1H), 7.10 (t, *J*=7.6, 1H), 6.76 (dd, *J*=8.0, 1.2, 1H), 6.61 (t, *J*=7.6, 1H), 4.06 (s, 2H); IR (KBr, cm^{-1}) ν: 3463, 3413, 3377, 3301, 3191, 3065, 1617, 1482, 1445, 1307, 1257, 1152, 1066, 1043, 1016, 931, 848, 747, 657, 531, 433.

References

1 B. Carboni, M. Vaultier, T. Courgeon and R. Carrie, *Bull. Soc. Chim. Fr.*, 1989, **6**, 844-849.

2 A. Bisai, S. De, D. Dey, B. N. Kakde and S. Mishra, *J. Org. Chem.*, 2013, **78**, 7823-7844.

3 J. Gao, G. -W. Wang, J. -J. Xia and Z. Zhang, *Org. Biomol. Chem.*, 2005, **3**, 1617-1619.

4 M. Paventi and A. S. Hay, *J. Org. Chem.*, 1991, **56**, 5875-5882.

5 *Eur. Pat.*, EP 2272817 A1, 2011.

6 G. N. Walker and M. A. Klett, *J. Med. Chem.*, 1966, **9**, 624-630.

7 S. Chiba, M. Kitamura, K. Narasaka and T. Suga, *Org. Lett.*, 2004, **6**, 4619-4621.

8 G. C. Levy , T. Holak and A. Steigel, *J. Am. Chem. Soc.*, 1976, **98**, 495-499.

9 N. Desmira, Y. Motoyama, M. Taguchi, I. Mochida, H. Nagashima and S. -H. Yoon, *Chem. Asian J.*, 2014, **9**, 71-74.

10 M. Antoine, *Chim. Ther.*, 1972, **7**, 443-449.

11 *US Pat.*, US 20080004241 A1, 2008.

12 O. Kreye, M. A. Meier and S. Wald, *Adv. Synth. Catal.*, 2013, **355**, 81-86.

13 B. Devi Bala, S. Michael Rajesh and S. Perumal, *Green Chem.*, 2012, **14**, 2484-2490.

14 J. F. Hartwig and D. -Y. Lee, *Org. Lett.*, 2005, **7**, 1169-1172.

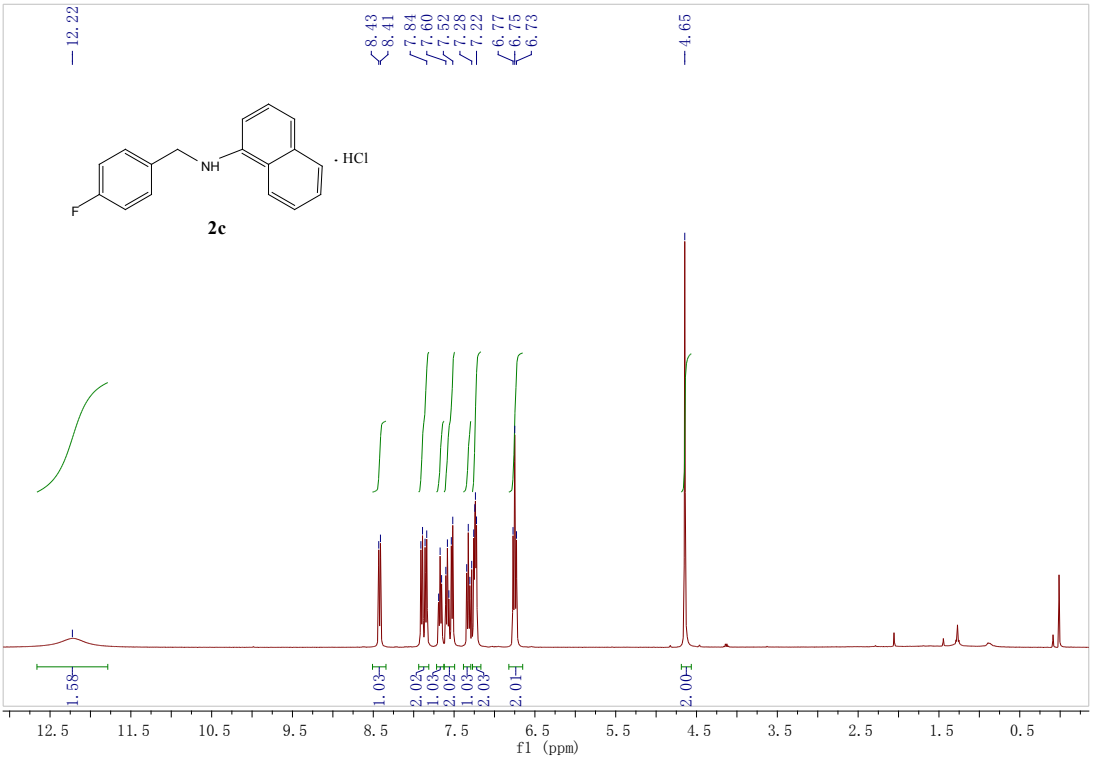
15 M. W. Luedtke, A. Yoshimura and V. V. Zhdankin, *J. Org. Chem.*, 2012, **77**, 2087-2091.

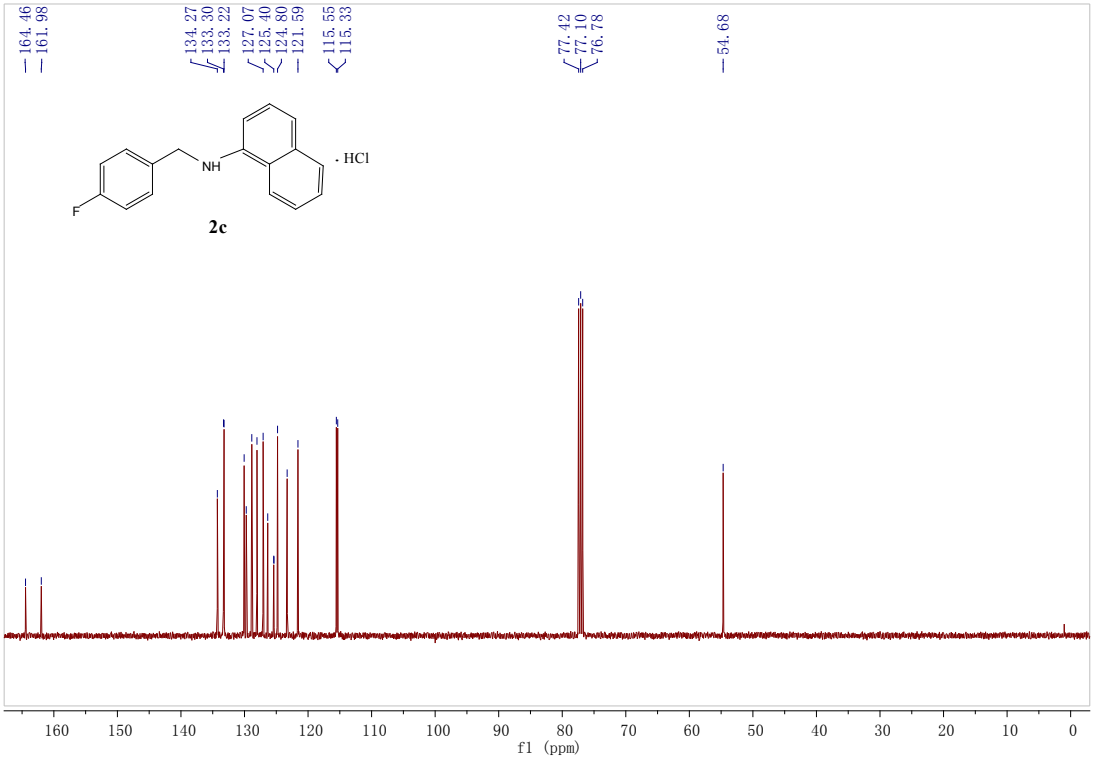
16 D. Cantillo, C. O. Kappe and M. M. Moghaddam, *J. Org. Chem.*, 2013, **78**, 4530-4542.

17 S. M. Islam, M. Mobarak, P. Mondal, A. S. Roy, K. Tuhina and J. Mondal, *Tetrahedron Lett.*, 2012, **53**, 127-131.

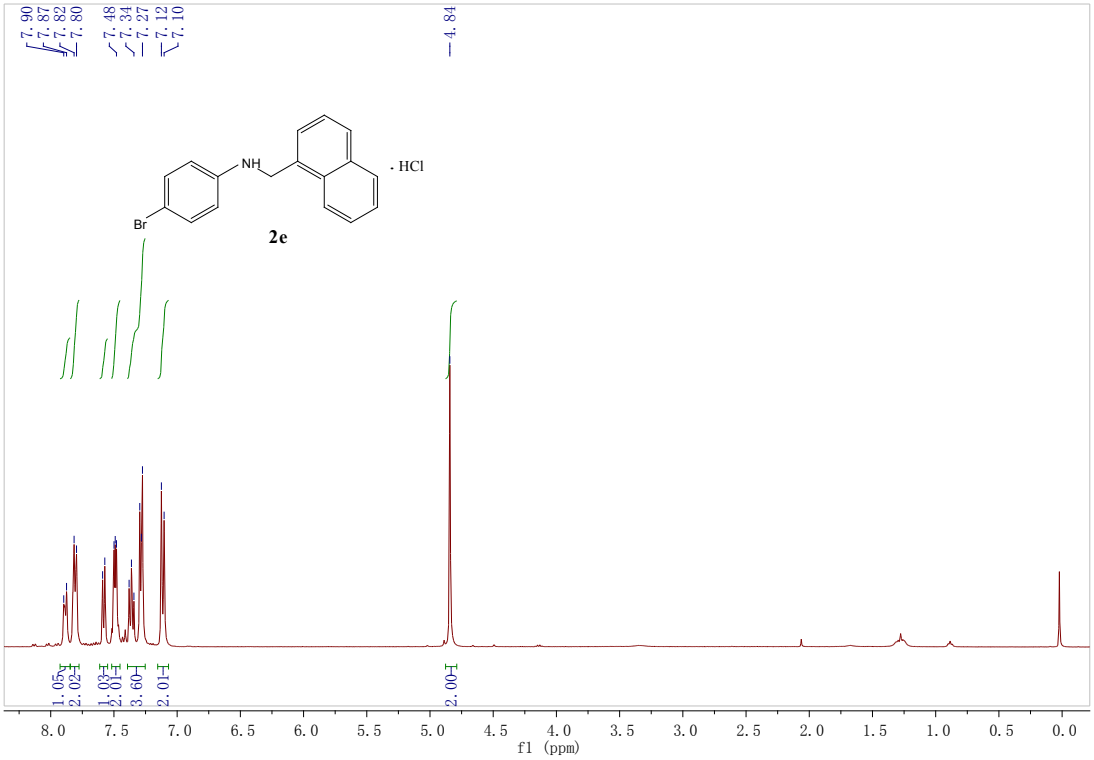
^{1}H NMR and ^{13}C NMR for new compounds

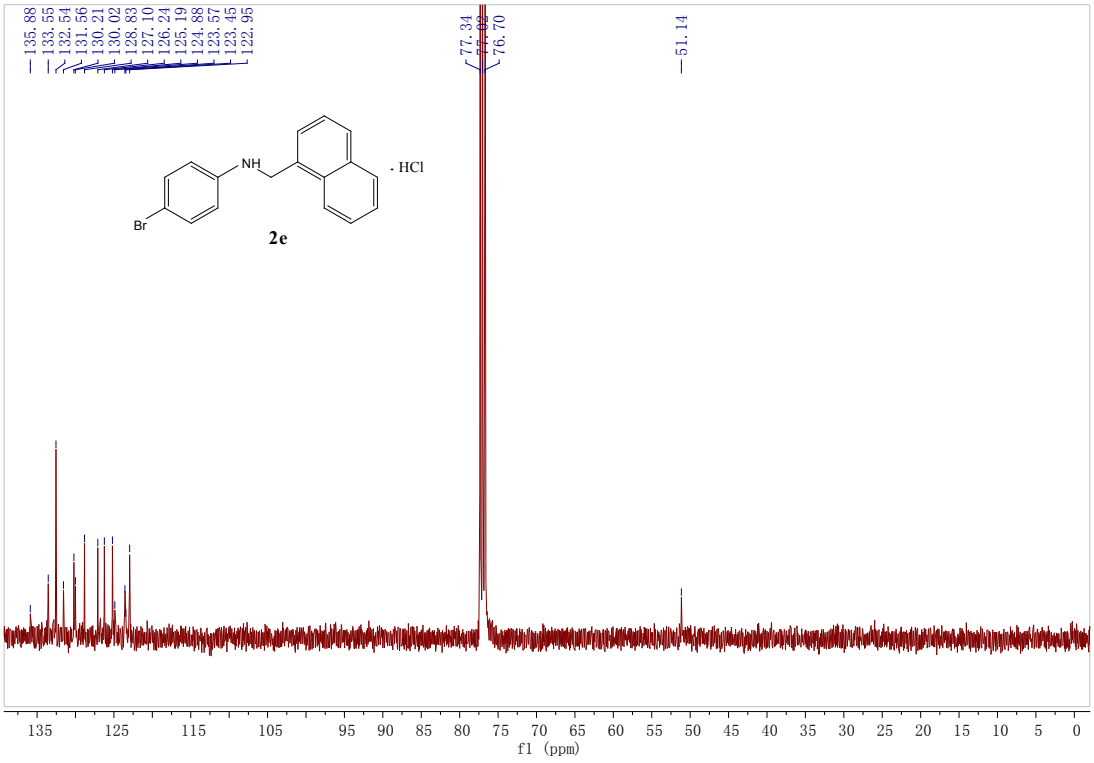
N-(4-Fluorobenzyl)-1-naphthalenamine hydrochloride (**2c**):



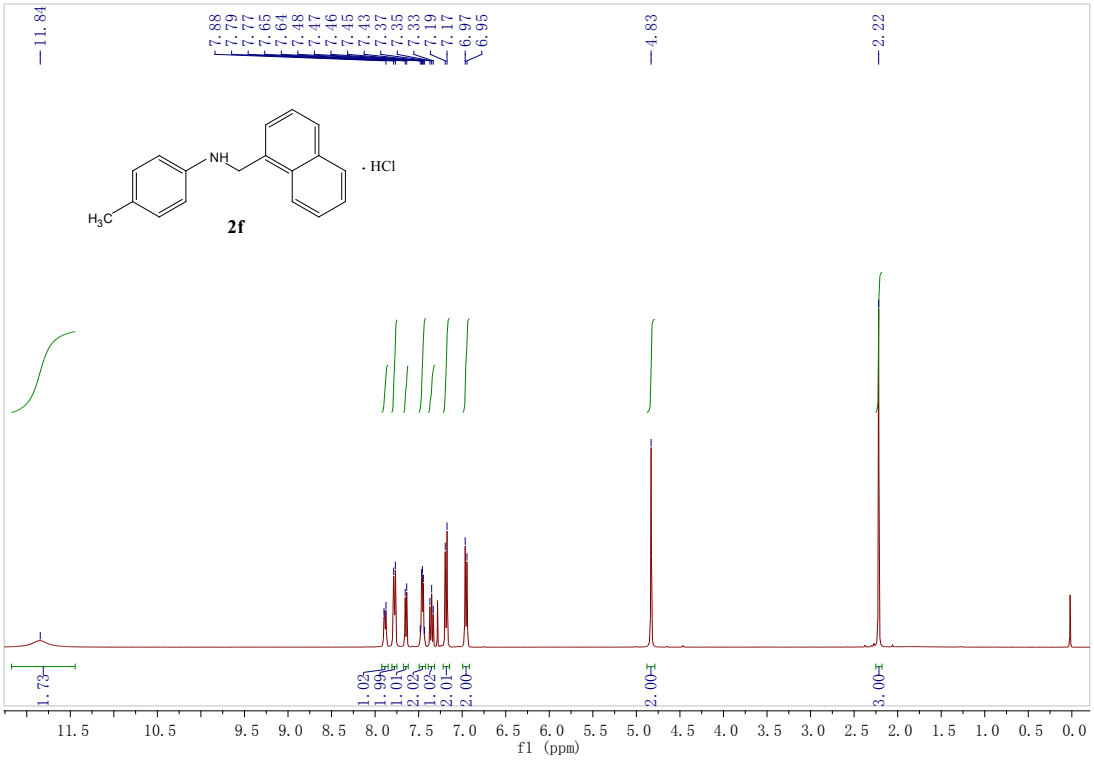


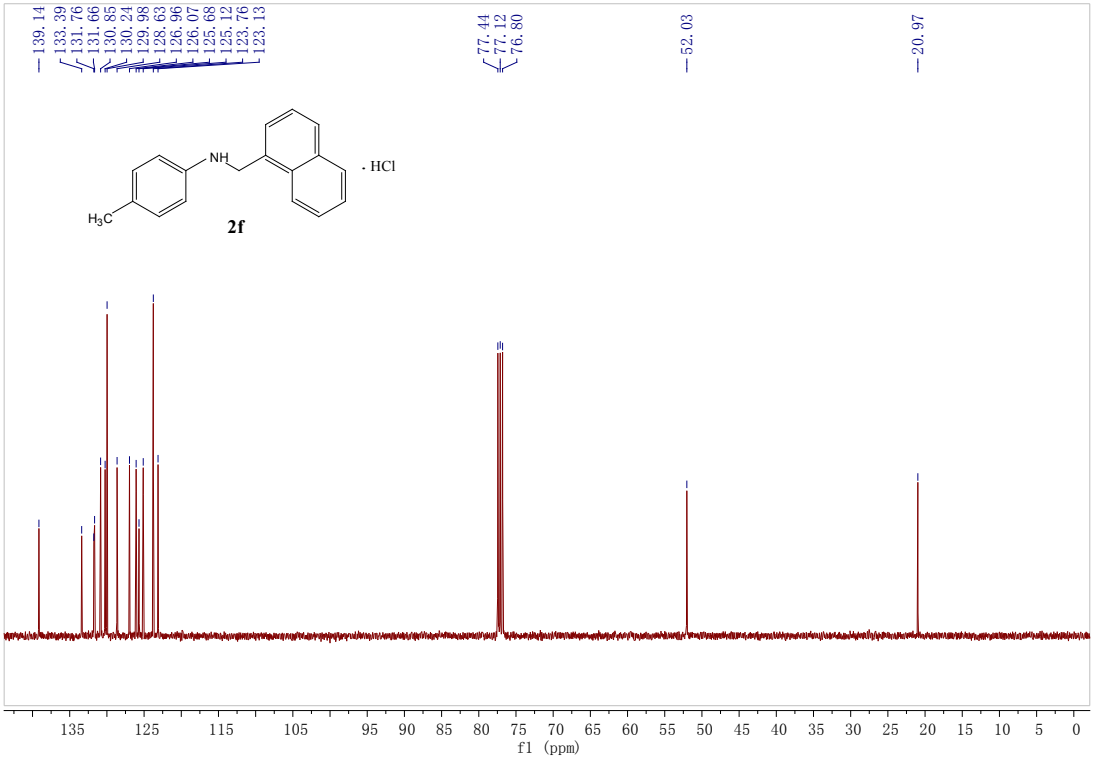
4-Bromo-*N*-(1-naphthalenylmethyl)aniline hydrochloride (**2e**):



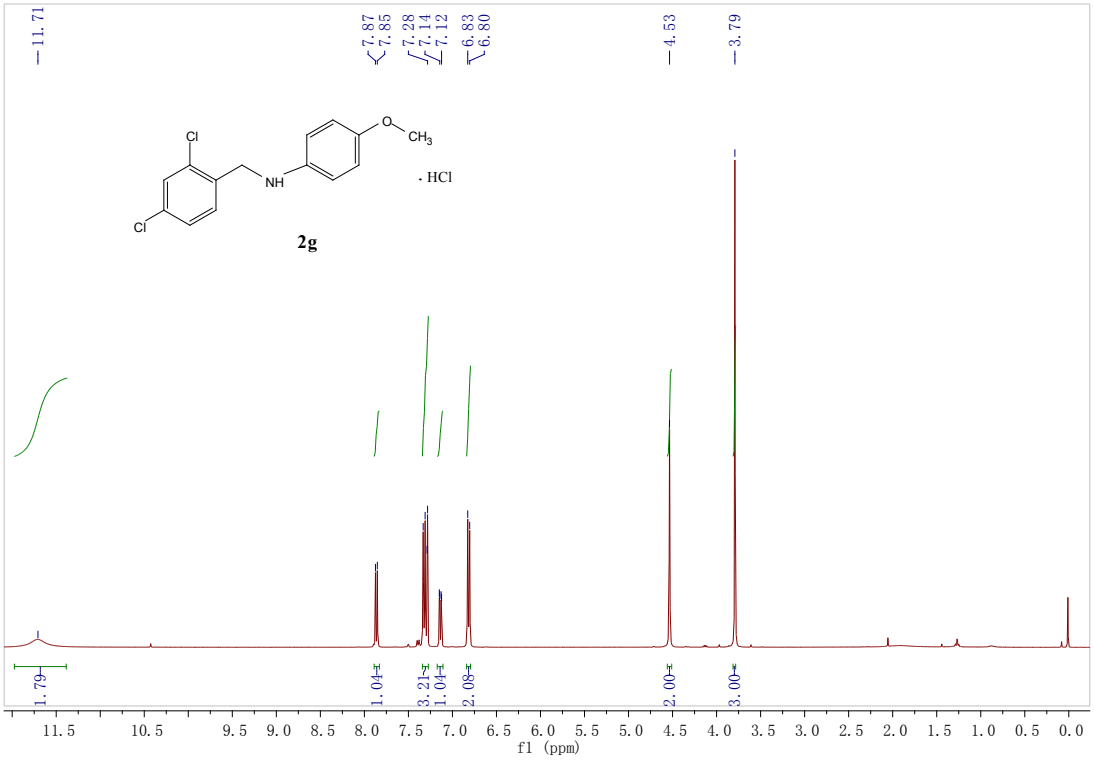


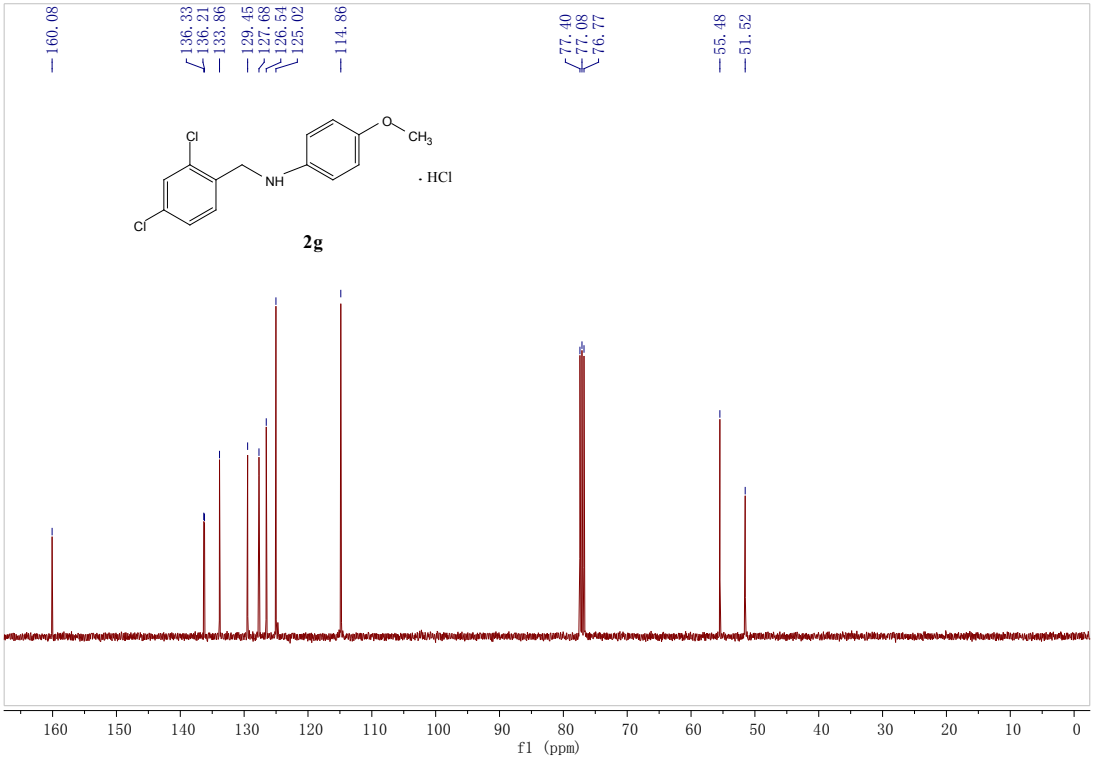
4-Methyl-*N*-(1-naphthalenylmethyl)aniline hydrochloride (**2f**):



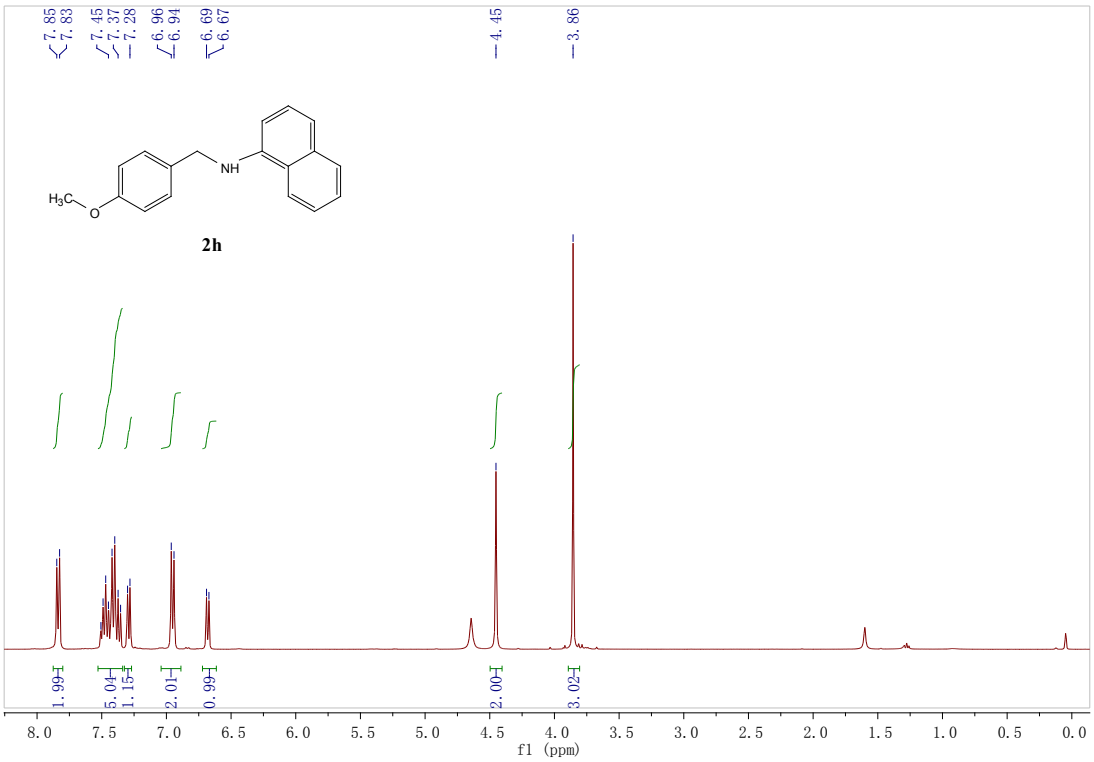


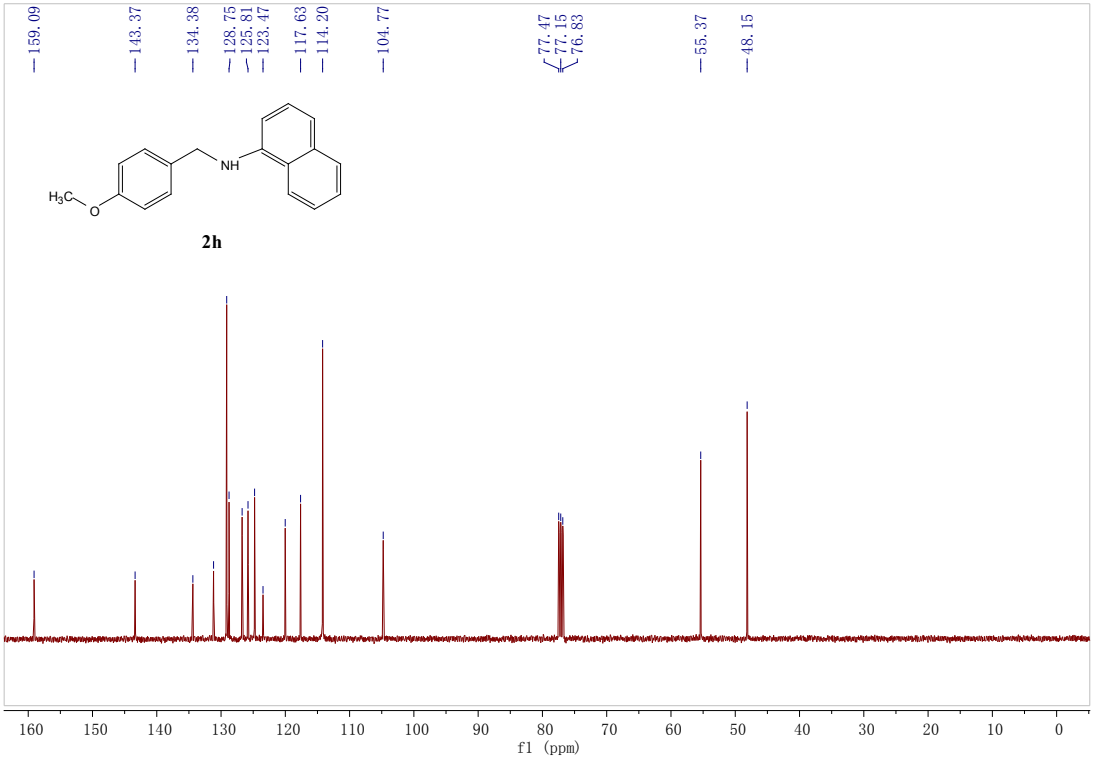
N-(2,4-Dichlorobenzyl)-4-methoxyaniline hydrochloride (**2g**):



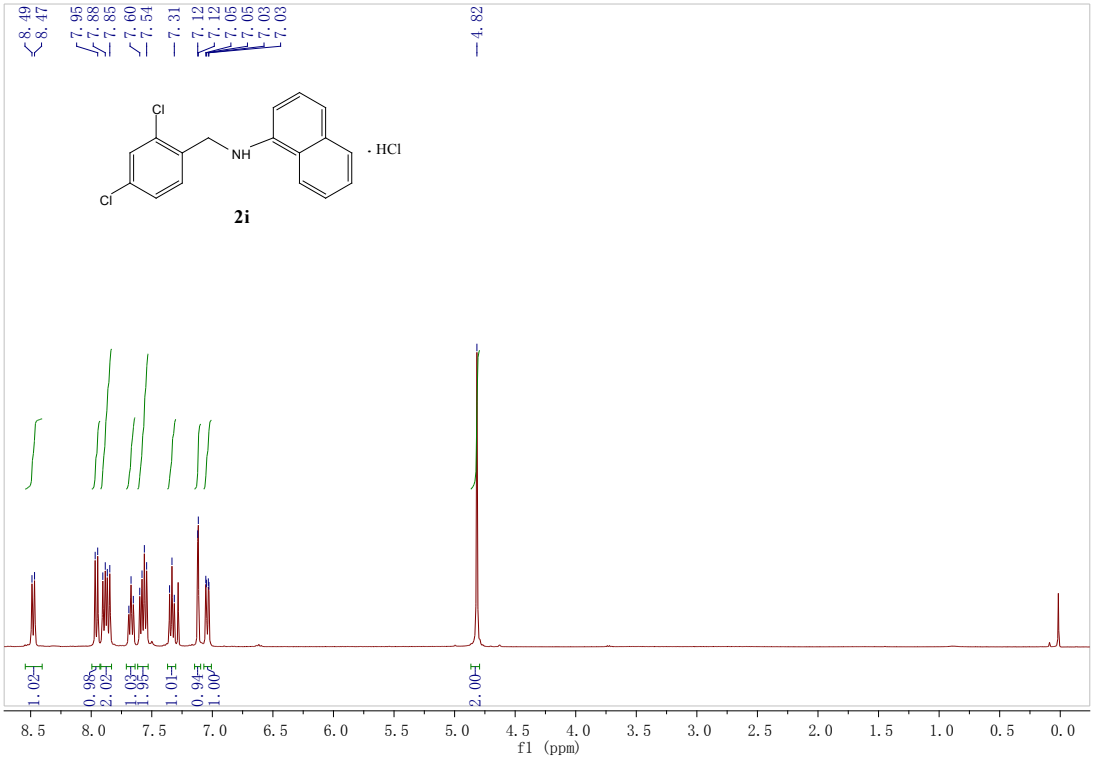


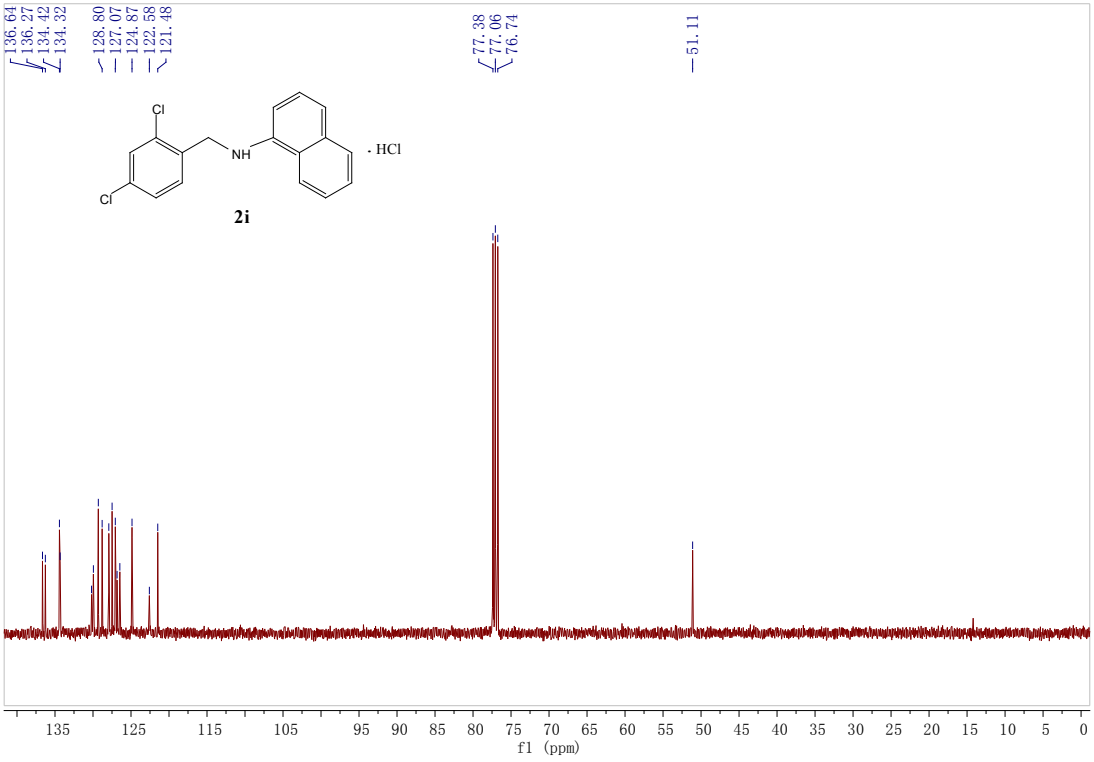
N-(4-Methoxybenzyl)-1-naphthalenamine (**2h**):





N-(2,4-Dichlorobenzyl)-1-naphthalenamine hydrochloride (**2i**):





4-Bromo-*N*-(2,4-dichlorobenzyl)aniline hydrochloride (**2m**):