Supporting Information

A Facile Manganese Dioxide Mediated Oxidation of Primary Benzylamines to Benzamides

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Contents

S1 General

Infrared spectra were obtained on a Perkin Elmer 100 FTIR Spectrometer operating in ATR mode. Only significant absorptions (ν_{max}) are reported and all absorptions are recorded in wavenumbers (cm^{-1}). Melting points were measured with an Electrothermal apparatus and are uncorrected.

Proton magnetic resonance spectra (^{1}H-NMR) were recorded at 400 MHz using a Bruker spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to the residual protonated solvent peak. The order of citation in parentheses is (i) number of equivalent nuclei (by integration), (ii) multiplicity (s, singlet; d, doublet; t, triplet; q, quartet and m, multiplet), (iii) coupling constant (J) quoted in Hertz (Hz) to one decimal place, (iv) assignment. Carbon magnetic resonance spectra (^{13}C-NMR) were recorded at 100.6 MHz using a Bruker spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to the appropriate solvent peak. The assignment is quoted in parentheses.

Flash Chromatography was carried out using silica gel (Aldrich, 230-400 mesh) as the stationary phase. Thin Layer Chromatography was carried out on aluminium plates pre-coated with silica (Merck silica gel 60 F_{254} on aluminium) which was visualized by the quenching of ultraviolet fluorescence (λ_{max}=254 nm) and/or by staining with potassium permanganate solution followed by heat.

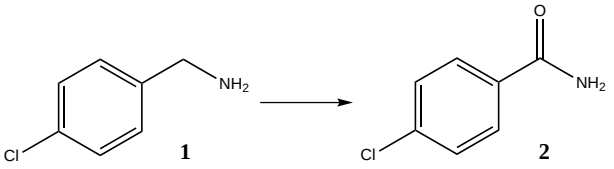
All reactions were carried out at atmospheric pressure with stirring unless otherwise stated. Molecular Sieves were purchased from *Alfa Aesar* (Cat.No. L05512.30, Molecular sieves, 4 Å, 0.4-0.8 mm (0.02-0.03 in) beads, 250 g). All reagents were used as received unless otherwise stated. The fractions of light petroleum ether boiling between 40 and 60°C are referred to as 'hexanes'.

S2 Experimental procedures

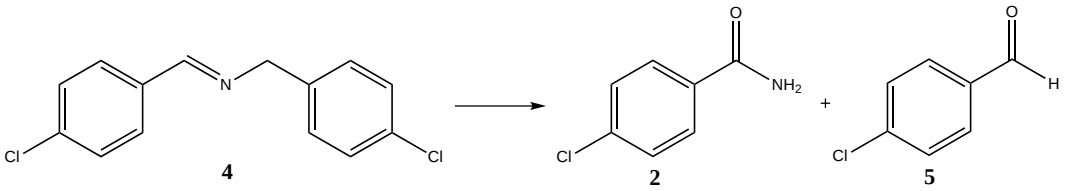
Preparation of activated manganese dioxide

MnO_2 was purchased from *Alfa Aesar* (Cat. No. 014340.22, Manganese(IV) oxide, activated, tech., Mn 58% min, 100 g) and further activated by treatment with dilute nitric acid:
MnO_2 (50 g) was placed on a large Büchner funnel and 10% nitric acid (80 mL) was added slowly. After the addition was completed, the MnO_2 cake was washed with a large amount of water (2-3 L) or until the filtrate was neutral. The MnO_2 was subsequently dried at 105°C for two days and could then be stored under normal laboratory conditions for several weeks without loss of activity.

4-Chlorobenzamide 2



To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 4-chloro-benzylamine (142 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). Concentration under reduced pressure gave 4-chlorobenzamide **2** (152 mg, 98%) as a white solid;

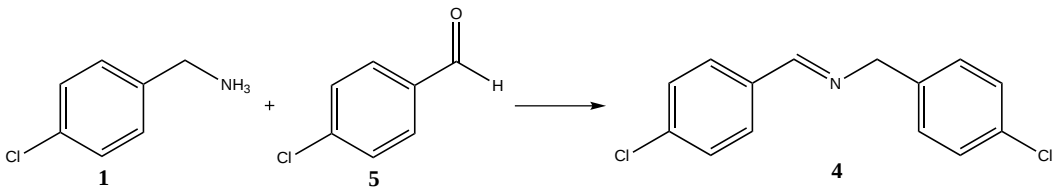


To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added *N*-(4-Chlorobenzylidene)-1-(4-chlorophenyl)methanamine **4** (263 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). Concentration under reduced pressure and recrystallisation (hexane) gave 4-chlorobenzamide **2** (148 mg, 95%) as a white solid. Concentration of the hexane filtrate under reduced pressure gave 4-chlorobenzaldehyde **5** (0.136 mg, 97%) as a white solid;

4-Chlorobenzamide **2**: mp 176-177°C; ν_{max} (solid) 3368 (N-H), 3177 (N-H), 1658 (C=O), 1620, 1568, 1493, 1407, 1388, 1089, 1013; δ_H (400 MHz, DMSO-d_6) 8.06 (1H, s, -CONH), 7.89 (2H, d, *J* 8.3 Hz, *ortho* Ar-H), 7.53 (2H, d, *J* 9.6 Hz, *meta* Ar-H), 7.47 (1H, s, -CONH); δ_C (100.6 MHz, DMSO-d_6) 166.78 (C=O), 136.04 (*para* Ar), 133.00 (*ipso* Ar), 129.38 (*meta* Ar), 128.28 (*ortho* Ar). *In agreement with published data.*[1,2]

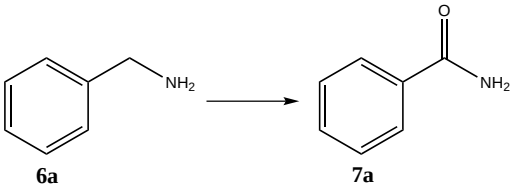
4-Chlorobenzaldhyde **5**: mp 43-46°C; ν_{max} (solid) 1690 (C=O), 1575, 1386, 1292, 1206, 1153, 1092, 1011, 838, 813; δ_H (400 MHz, DMSO-d_6) 10.00 (1H, s, CHO), 7.91-7.94 (2H, m, *ortho* Ar-H), 7.65-7.68 (2H, m, *meta* Ar-H); δ_C (100.6 MHz, DMSO-d_6) 192.15 (CHO), 139.40 (*para* Ar), 134.85 (*ipso* Ar), 131.20 (*ortho* Ar), 129.38 (*meta* Ar). *In agreement with published data.*[3]

N-(4-Chlorobenzylidene)-1-(4-chlorophenyl)methanamine 4



To a suspension of 4 Å molecular sieves (3 g) in dichloromethane (30 mL) was added 4-chlorobenzaldehyde (1.66 g, 11.8 mmol, 1.0 equiv) and 4-chloro-benzylamine (1.67 g, 11.8 mmol, 1.0 equiv). The reaction was left to stir at 40°C for 1.5 h. The molecular sieves were filtered off and washed with some acetone. Concentration under reduced pressure gave *N*-(4-chlorobenzylidene)-1-(4-chlorophenyl)methanamine **4** (3.051 mg, 99%) as a white solid; mp 62-64 °C; ν_{max} (solid) 2817, 1642, 1593, 1568, 1489, 1428, 1404, 1372, 1090, 1047, 1013, 862; δ_H (400 MHz, DMSO-d_6) 8.50 (1H, s, Ar-CH=N-), 7.79 (2 H, d, *J* 8.6 Hz, 1 x Ar-H), 7.52 (2 H, d, *J* 8.4 Hz, 2 x Ar-H), 7.34-7.41 (4 H, m, 2 x Ar-H), 4.76 (2H, s, N-CH_2-Ar); δ_C (100.6 MHz, DMSO-d_6) 161.11, 138.55, 135.48, 134.80, 131.45, 129.72, 129.68, 128.86, 128.36, 62.90. *In agreement with published data.*[4]

Benzamide 7a

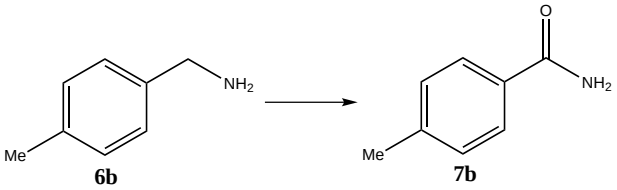


6a **7a**

To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added benzylamine (107 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). Concentration under reduced pressure and recrystallisation (hexane) gave benzamide **7a** (119 mg, 98%) as a white solid;

To a suspension of 4 Å molecular sieves (10.0 g) in dichloromethane (130 mL) was added benzylamine (2.00 g, 18. 7 mmol, 1.0 equiv). Manganese dioxide (40.57 g, 466.6 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (600 mL). Concentration under reduced pressure and recrystalisation (hexane) gave benzamide **7a** (2.18 g, 96%) as a white solid; mp 125-127°C; ν_{max} (solid) 3360 (N-H), 3162 (N-H), 3062, 1651 (C=O), 1618, 1575, 1448, 1296, 1178, 1141, 1120, 1024, 917; δ_H (400 MHz, DMSO-d_6) 7.99 (1H, s, -CON<u>H</u>), 7.88 (2H, d, *J* 8.4 Hz, *ortho* Ph-H), 7.52 (1H, t, *J* 7.3 Hz, *para* Ph-H), 7.45 (2 H, t, *J* 7.4 Hz, *meta* Ph-H), 7.37 (1 H, s, -CON<u>H</u>); δ_C (100.6 MHz, DMSO-d_6) 167.91 (C=O), 134.26 (*ipso* Ph), 131.24 (*para* Ph), 128.23 (*meta* Ph), 127.47 (*ortho* Ph). *In agreement with published data.*[5,6]

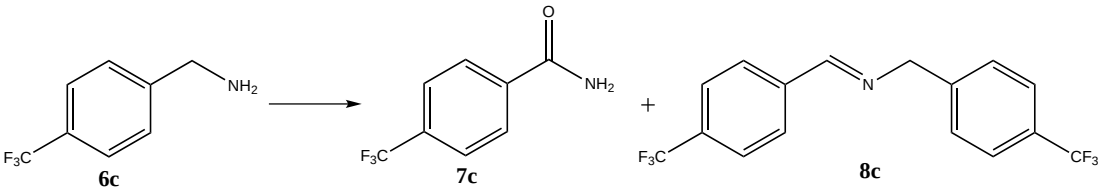
4-Methylbenzamide 7b



6b **7b**

To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 4-methyl-benzylamine (121 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). Concentration under reduced pressure afforded 4-methylbenzamide **7b** (132 mg, 98%) as a white solid; mp 159-160°C; ν_{max} (solid) 3337 (N-H), 3157 (N-H), 2929, 1666 (C=O), 1613, 1568, 1411, 1395, 1189, 1144, 1123, 1021; δ_H (400 MHz, DMSO-d_6) 7.89 (1H, s, -CON<u>H</u>), 7.77 (2 H, d, *J* 8.1 Hz, *ortho* Ar-H), 7.24 (3H, d, *J* 8.0 Hz, *meta* Ar-H and -CON<u>H</u>), 2.34 (3H, s, C<u>H</u>$_3$); δ_C (100.6 MHz, DMSO-d_6) 167.78 (C=O), 141.07 (*para* Ar), 131.47 (*ipso* Ar), 128.74 (*meta* Ar), 127.51 (*ortho* Ar), 20.96 (-<u>C</u>H$_3$). *In agreement with published data.*[6,7]

4-Trifluoromethylbenzamide 7c and *p*-trifluoromethyl-*N*-[*p*-(trifluoromethyl)-benzylidene]-benzylamine 8c

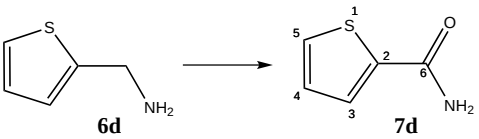


To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 4-trifluoromethyl-benzylamine (175 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). The filtrate was concentrated under reduced pressure and the crude product was washed with a small amount of hexane (5 mL). 4-Trifluoromethylbenzamide **7c** was obtained as a white solid (165 mg, 0.87 mmol) in a yield of 87%. Concentration of the hexane filtrate under reduced pressure gave *p*-trifluoromethyl-*N*-[*p*-(trifluoromethyl)-benzylidene]-benzylamine **8c** (21 mg, 12%) as a pale yellow solid;

4-Trifluoromethylbenzamide **7c**:
mp 182-184°C; $\nu_{\max}$ (solid) 3375 (N-H), 3177 (N-H), 1655 (C=O), 1627, 1579, 1516, 1418, 1322, 1067, 1016 δ_{H} (400 MHz, DMSO-d_6) 8.21 (1H, s, -CONH), 8.06 (2H, d, J 8.1 Hz, *ortho* Ar-H), 7.83 (2H, d, J 8.2 Hz, *meta* Ar-H), 7.63 (1H, s, -CONH); δ_{C} (100.6 MHz, DMSO-d_6) 166.73 (C=O), 138.11 (*ipso* Ar), 131.18 (q, *para* Ar, $^{2}J_{CF}$ 32 Hz), 128.37 (*ortho* Ar), 125.31 (q, *meta* Ar, $^{3}J_{CF}$ 3.2 Hz), 122.65 (one peak from q, -$\underline{\mathrm{C}}\mathrm{F}_3$); ^{19}F-NMR δ (376 MHz, DMSO) -61.30. *In agreement with published data.*[6,8]

p-Trifluoromethyl-*N*-[*p*-(trifluoromethyl)-benzylidene]-benzylamine **8c**:
mp 35-36°C; $\nu_{\max}$ (film) 2929, 2855, 1650 (imine), 1620, 1583, 1418, 1377, 1326, 1222, 1166, 1126, 1067, 1019, 953, 839; δ_{H} (400 MHz, $CDCl_3$) 8.47 (1H, s, Ar-CH=N-), 7.91 (2H, d, J 8.1 Hz, Ar-H), 7.69 (2 H, d, J 8.2 Hz, Ar-H), 7.62 (2H, d, J 8.1 Hz, Ar-H), 7.47 (2 H, d, J 8.0 Hz, Ar-H), 4.90 (2H, s, N-C$\underline{\mathrm{H}}_2$-Ar); δ_{C} (100.6 MHz, $CDCl_3$) 161.26 (Ar-CH=N-), 143.11 (*ipso* Ar-CH=N-), 139.10 (*ipso* Ar-CH_2N), 132.71 (q, *para* Ar-CH=N-, $^{2}J_{CF}$ 32.4 Hz), 129.57 (q, *para* Ar-CH_2N, $^{2}J_{CF}$ 32.4 Hz), 128.66 (*ortho* Ar-CH=N-), 128.26 (*ortho* Ar-CH_2N), 125.80 (q, *meta* Ar-CH=N-, $^{3}J_{CF}$ 3.8 Hz), 125.63 (q, *meta* Ar-CH_2N, $^{3}J_{CF}$ 3.8 Hz), 124.02 (q, -$\underline{\mathrm{C}}\mathrm{F}_3$, $^{1}J_{CF}$ 272.3 Hz), 64.55 (N-$\underline{\mathrm{C}}\mathrm{H}_2$-Ar). *In agreement with published data.*[9,10]

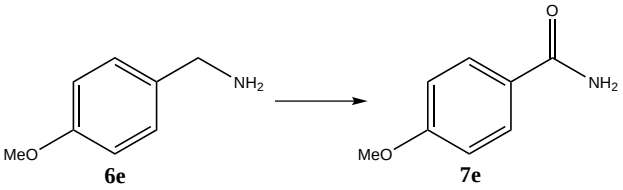
Thiophene-2-carboxamide 7d



To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 2-(aminomethyl)-thiophene (113 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). Concentration under reduced pressure afforded thiophene-2-carboxamide **7d** (125 mg, 98%) as a white solid; mp 176-178°C; $\nu_{\max}$ (solid) 3356 (N-H), 3164 (N-H), 1650 (C=O), 1601, 1524, 1429, 1392, 1242, 1123, 1096, 1041, 858; δ_{H} (400 MHz, DMSO-d_6) 7.98 (1H, s, -CONH), 7.75-7.73 (2H, m, H-3 and H-5), 7.38 (1H, s, -CONH), 7.12 (1H, t, J 4.1 Hz, H-4);

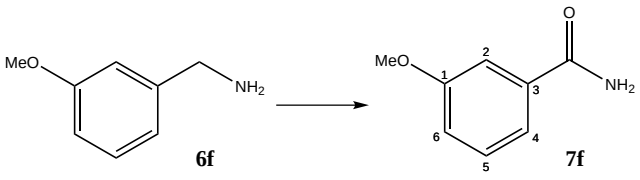
δ_C (100.6 MHz, DMSO-d_6) 162.90 (C=O), 140.35 (C2), 131.01 (C3), 128.70 (C5), 127.93 (C4). *In agreement with published data.*[11,12]

4-Methoxybenzamide 7e



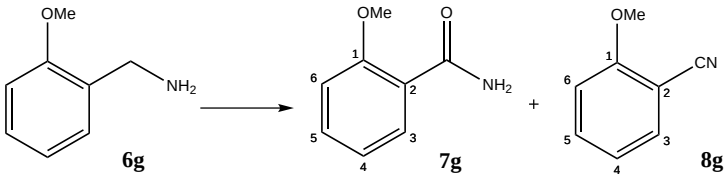
To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 4-methoxy-benzylamine (137 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). The solvent was removed under reduced pressure and the crude was purified by column-chromatography (ethyl acetate:hexane, 1:1 → 4:1). 4-Methoxybenzamide **7e** (140 mg, 93%) was obtained as a white solid; mp 165-167°C; ν_{max} (solid) 3387 (N-H), 3159 (N-H), 2843, 1641 (C=O), 1615, 1572, 1515, 1457, 1421, 1391, 1308, 1249, 1190, 1179, 1145, 1114, 1023, 848; δ_H (400 MHz, DMSO-d_6) 7.84 (3H, d, *J* 8.7 Hz, *ortho* Ar-H and -CONH), 7.18 (1H, s, -CONH), 6.97 (2H, d, *J* 8.7 Hz, *meta* Ar-H), 3.79 (3H, s, -OCH_3); δ_C (100.6 MHz, DMSO-d_6) 167.47 (C=O), 161.61 (*para* Ar), 129.39 (*ortho* Ar), 126.51 (*ipso* Ar), 113.41 (*meta* Ar), 55.35 (-OCH_3). *In agreement with published data.*[6]

3-Methoxybenzamide 7f



To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 3-methoxy-benzylamine (137 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). The solvent was removed under reduced pressure and the crude was purified by column-chromatography (ethyl acetate:hexane, 1:1 → 4:1). 3-Methoxybenzamide **7f** (125 mg, 83%) was obtained as a white solid; mp 131-133°C; ν_{max} (solid) 3128, 1664 (C=O), 1627, 1581, 1463, 1429, 1330, 1247, 1131, 1030, 902, 877; δ_H (400 MHz, DMSO-d_6) 7.96 (1H, s, -CONH), 7.46-7.33 (4H, m, 3 x Ar-H and -CONH), 7.08 (1H, ddd, *J* 8.1 Hz, 2.6 Hz, 0.8 Hz, H-6), 3.79 (3H, s, -OCH_3); δ_C (100.6 MHz, DMSO-d_6) 167.64 (C=O), 159.14 (C1), 135.73 (C3), 129.33 (C5), 119.69 (C4), 117.07 (C6), 112.63 (C2), 55.23 (-OCH_3). *In agreement with published data.*[8]

2-Methoxybenzamide 7g and 2-methoxybenzonitrile 8g

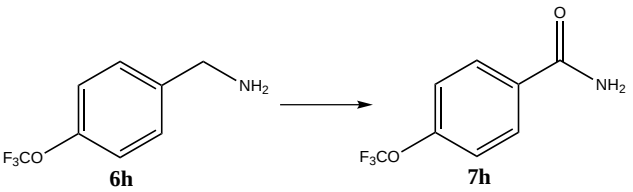


To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 2-methoxy-benzylamine (137 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). The solvent was removed under reduced pressure and the crude was purified by column-chromatography (ethyl acetate:hexane, 1:1 → 3:1). 2-Methoxybenzamide **7g** (104 mg, 69%) was obtained as a white solid and 2-methoxybenzonitrile **8g** (37 mg, 28%) was obtained as colorless oil;

2-Methoxybenzamide **7g**: mp 126-128°C; ν_{max} (solid) 3410 (N-H), 3190 (N-H), 3013, 2980, 2948, 2840, 1623 (C=O), 1597, 1573, 1488, 1462, 1434, 1394, 1274, 1240, 1179, 1106, 1020; δ_H (400 MHz, DMSO-d_6) 7.79 (1H, dd, *J* 7.7 Hz, 1.8 Hz, H-3), 7.63 (1H, s, -CON$\underline{H}$), 7.52 (1H, s, -CON$\underline{H}$), 7.49-7.45 (1H, m, H-5), 7.12 (1H, d, *J* 10.0 Hz, H-6), 7.02 (1H, td, *J* 7.6 Hz, 0.9 Hz, H-4), 3.88 (3H, s, -OC$\underline{H}_3$); δ_C (100.6 MHz, DMSO-d_6) 166.34 (C=O), 157.24 (C1), 132.48 (C5), 130.74 (C3), 122.73 (C4), 120.41 (C2), 111.99 (C6), 55.82 (-O$\underline{C}H_3$). *In agreement with published data.*[6,13]

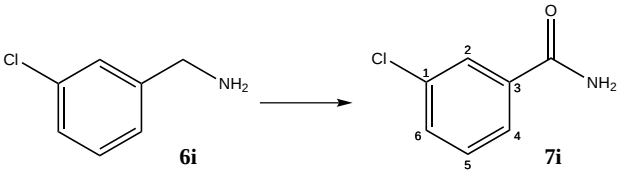
2-Methoxybenzonitrile **8g**: ν_{max} (film) 2975, 2948, 2843, 2228 (CN), 1688, 1599, 1494, 1465, 1290, 1262, 1021, 758; δ_H (400 MHz, $CDCl_3$) 7.72-7.25 (2H, m, H-3 and H-5), 7.16-6.64 (2H, m, H-4 and H-6), 3.87 (3H, m, -OC$\underline{H}_3$); δ_C (100.6 MHz, $CDCl_3$) 161.25 (C1), 134.39 (C5), 133.79 (C3), 120.77 (C4), 116.52 (C6), 111.27 (CN), 101.83 (C2), 56.00 (-O$\underline{C}H_3$). *In agreement with published data.*[14,15]

4-Trifluoromethoxybenzamide 7h



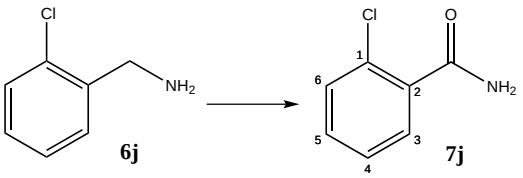
To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 4-trifluoromethoxy-benzylamine (191 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). The solvent was removed under reduced pressure and the crude was purified by column-chromatography (ethyl acetate:hexane, 1:1 → 3:1). 4-Trifluoromethoxybenzamide **7h** (181 mg, 88%) was obtained as a white solid; mp 152-154°C; ν_{max} (solid) 3372 (N-H), 3172 (N-H), 1652 (C=O), 1622, 1585, 1510, 1419, 1397, 1207, 1153, 1015, 926, 858; δ_H (400 MHz, DMSO-d_6) 8.11 (1H, s, -CON$\underline{H}$), 8.00 (2H, d, *J* 8.7 Hz, *ortho* Ar-H), 7.51 (1H, s, -CON$\underline{H}$), 7.45 (2H, d, *J* 8.3 Hz, *meta* Ar-H); δ_C (100.6 MHz, DMSO-d_6) 166.59 (C=O), 150.26 (*para* Ar), 133.37 (*ipso* Ar), 129.75 (*ortho* Ar), 120.50 (*meta* Ar), 119.93 (q, -O$\underline{C}F_3$, $^1J_{CF}$ 255 Hz); ^{19}F-NMR δ (376 MHz, DMSO) -56.68. *In agreement with published data.*[16]

3-Chlorobenzamide 7i



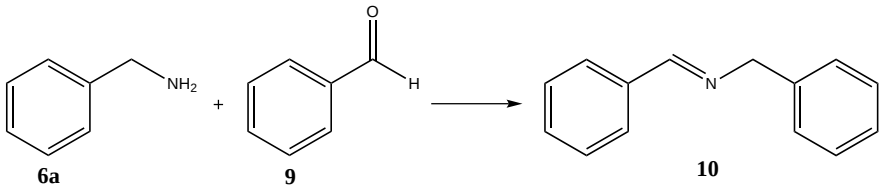
To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 3-chloro-benzylamine (142 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). Concentration under reduced pressure and recrystallisation (hexane) gave 3-chlorobenzamide **7i** (142 mg, 92%) as a white solid; mp 132-134°C; ν_{max} (solid) 3347 (N-H), 3167 (N-H), 1656 (C=O), 1620, 1561, 1426, 1387, 1122, 901; δ_H (400 MHz, DMSO-d_6) 8.11 (1H, s, -CONH), 7.91 (1H, s, H-2), 7.83 (1H, d, *J* 7.7 Hz, H-4), 7.59 (1H, d, *J* 8.0 Hz, H-6), 7.54 (1H, s, -CONH), 7.49 (1H, t, *J* 7.9 Hz, H-5); δ_C (100.6 MHz, DMSO-d_6) 166.44 (C=O), 136.32 (C3), 133.16 (C1), 131.12 (C6), 130.30 (C5), 127.33 (C2), 126.22 (C4). *In agreement with published data.*[2]

2-Chlorobenzamide 7j



To a suspension of 4 Å molecular sieves (800 mg) in dichloromethane (7 mL) was added 2-chloro-benzylamine (142 mg, 1.00 mmol, 1.0 equiv). Manganese dioxide (2.17 g, 25.0 mmol, 25.0 equiv) was added portionwise and the mixture stirred at 40°C for 24 h. The reaction mixture was filtered through a pad of Celite and washed with hot (60°C) methanol (250 mL). The solvent was removed under reduced pressure and the crude was purified by column-chromatography (ethyl acetate:hexane, 1:1 → 4:1). 2-Chlorobenzamide **7j** (128 mg, 83%) was obtained as a white solid; mp 139-141°C; ν_{max} (solid) 3357 (N-H), 3172 (N-H), 1638 (C=O), 1563, 1480, 1432, 1401, 1119, 1047, 953; δ_H (400 MHz, DMSO-d_6) 7.87 (1H, s, -CONH), 7.59 (1H, s, -CONH), 7.47-7.35 (4H, m, 4 x Ar-H); δ_C (100.6 MHz, DMSO-d_6) 168.17 (C=O), 137.17 (C), 130.56 (CH), 129.62 (C), 129.60 (CH), 128.66 (CH), 127.03 (CH). *In agreement with published data.*[7]

N-Benzylidene benzylamine 10



To a suspension of 4 Å molecular sieves (1 g) in dichloromethane (15 mL) was added benzaldehyde (212 mg, 2.00 mmol, 1.0 equiv) and benzylamine (214 mg, 2.00 mmol, 1.0 equiv). The reaction was left to stir at 40°C for 1.5 h. The molecular sieves were filtered off and washed with some ethyl acetate. The solvent was removed under reduced pressure and *N*-benzylidene benzylamine **10** (386 mg, 99%) was obtained as colourless oil; ν_{max} (film) 3085, 3062, 3028, 2872, 2840, 1702, 1644 (imine), 1601, 1580, 1496, 1452, 1379, 1343, 1311, 1292, 1027, 753, 694; δ_H (400 MHz, $CDCl_3$) 8.41 (1H, s, Ph-C$\underline{H}$=N-), 7.81-7.78 (2H, m, 2 x Ar-H), 7.43-7.26 (8H, m, 8 x Ar-H), 4.84 (2H, s, N-C$\underline{H}_2$-Ph); δ_C (100.6 MHz, $CDCl_3$) 162.15 (Ph-$\underline{C}$H=N-), 139.42 (*ipso* Ph-CH=N-), 136.28 (*ipso* Ph-CH_2N), 130.91, 128.74, 128.63, 128.41, 128.12, 127.13, 65.20 (N-$\underline{C}H_2$-Ph). *In agreement with published data.*[17,18]

S3 NMR-time experiment

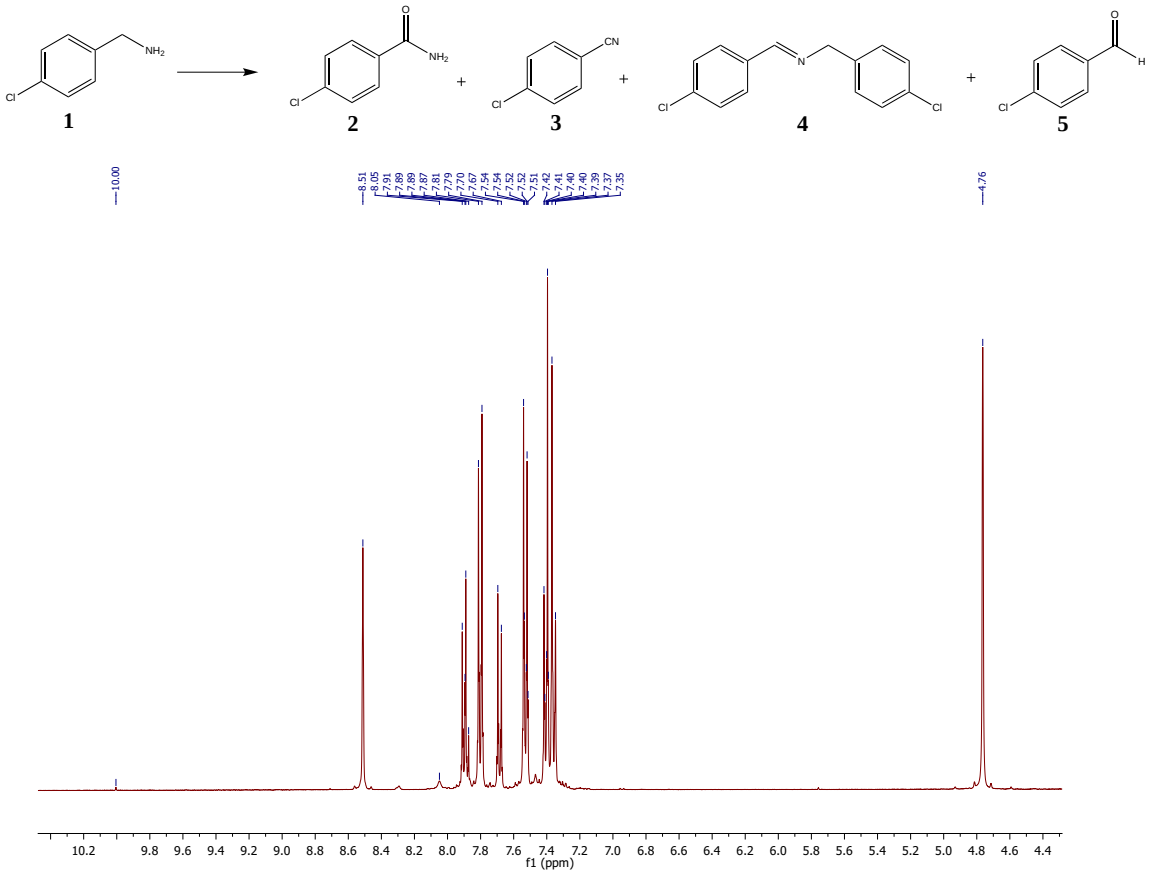


Figure S1: Intermediate products in the oxidation of 4-chlorobenzylamine **1** to 4-chlorobenzamide **2**. Expanded ^{1}H-NMR spectrum (4.4-10.2 ppm) after a reaction time of one hour recorded in DMSO-d_6 at 400 MHz.

Chemical shifts of all the intermediates in DMSO-d_6:

4-Chlorobenzamide 2

δ_H (400 MHz, DMSO-d_6) 8.06 (1H, s), 7.89 (2H, d, J 8.3 Hz), 7.53 (2H, d, J 9.6 Hz), 7.47 (1H, s)

4-Chlorobenzonitrile 3

δ_H (400 MHz, DMSO-d_6) 7.87-7.90 (2H, m), 7.65-7.68 (2H, m)

N-(4-Chlorobenzylidene)-1-(4-chlorophenyl)methanamine 4

δ_H (400 MHz, DMSO-d_6) 8.50 (1H, s), 7.79 (2H, d, J 8.6 Hz), 7.52 (2H, d, J 8.4 Hz), 7.34-7.41 (4H, m), 4.76 (2H, s)

4-Chlorobenzaldehyde 5

δ_H (400 MHz, DMSO-d_6) 10.00 (1H, s), 7.91-7.94 (2H, m), 7.65-7.68 (2H, m)

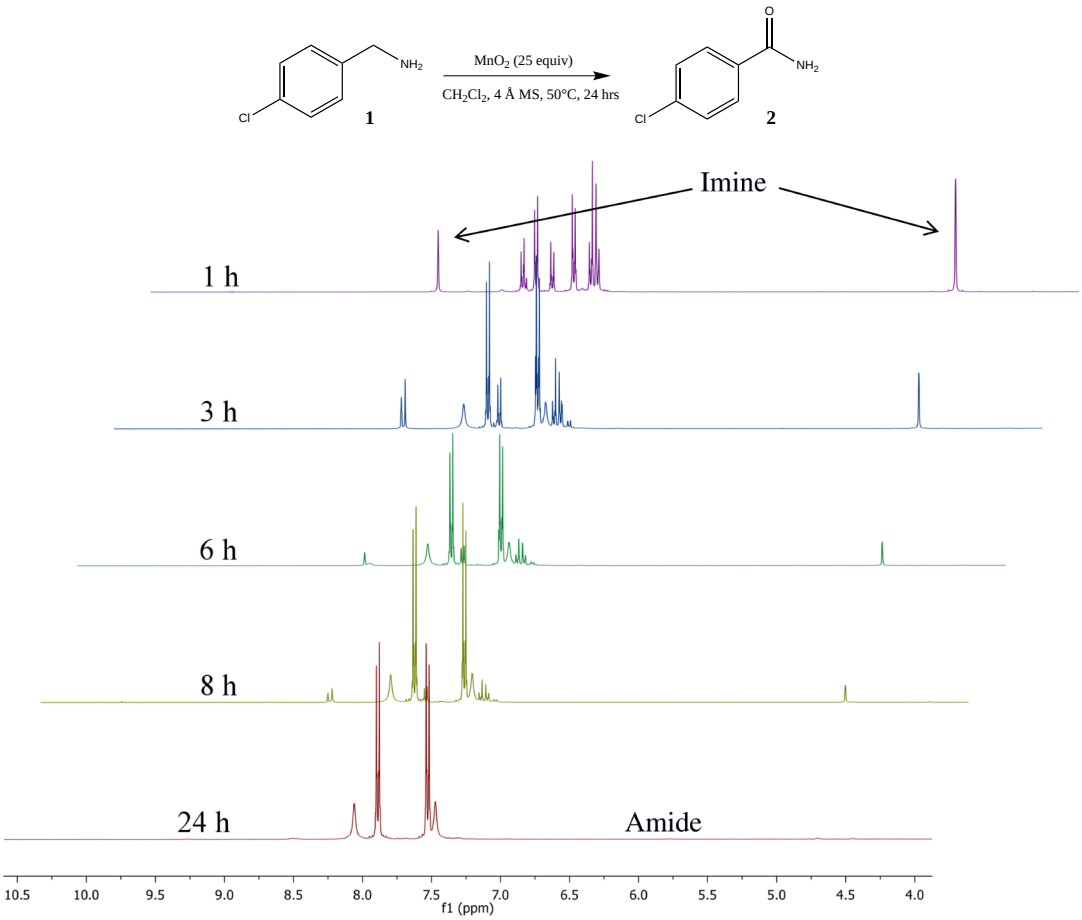
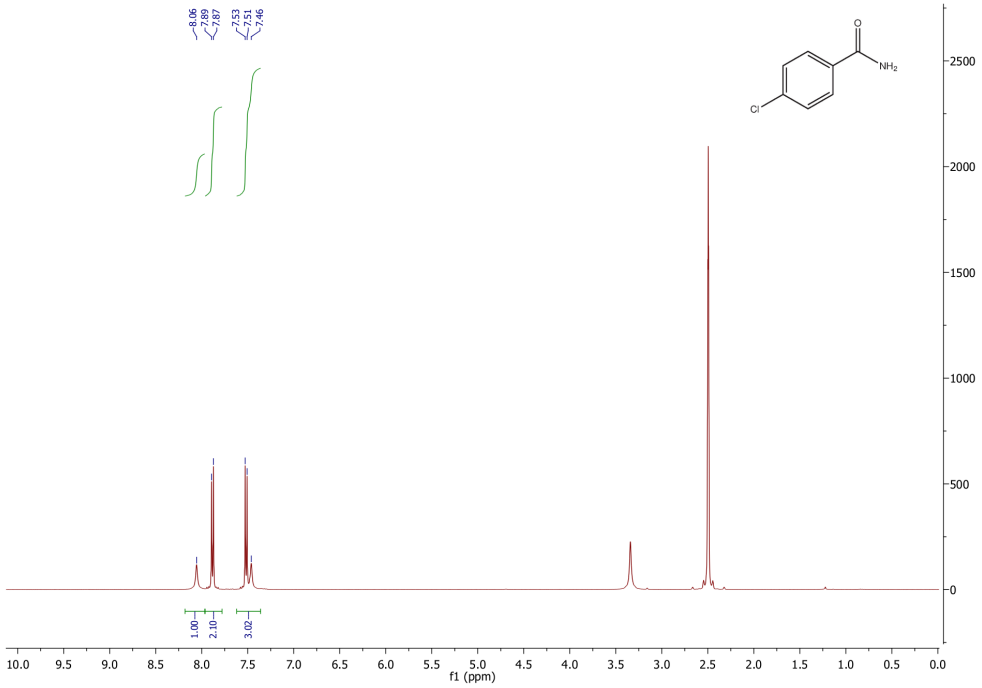
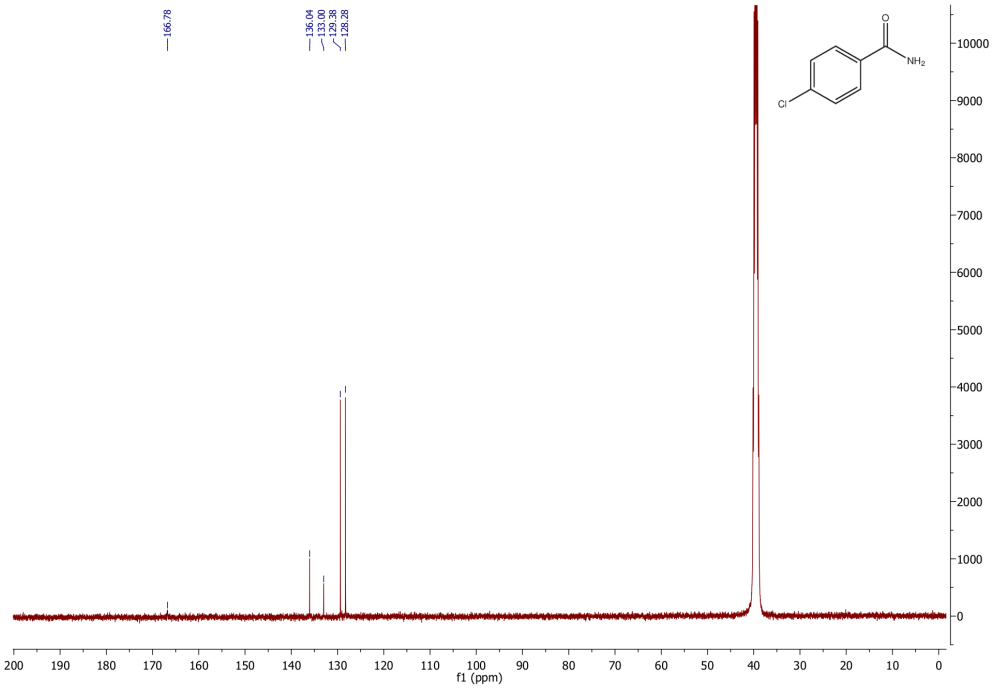


Figure S2: Expanded ^{1}H-NMR spectra (4.0 -10.5 ppm) of the NMR-investigation experiment for the full conversion of 4-chlorobenzylamine **1** to amide **2**. The spectrum was recorded at 400 MHz in DMSO-d_6.

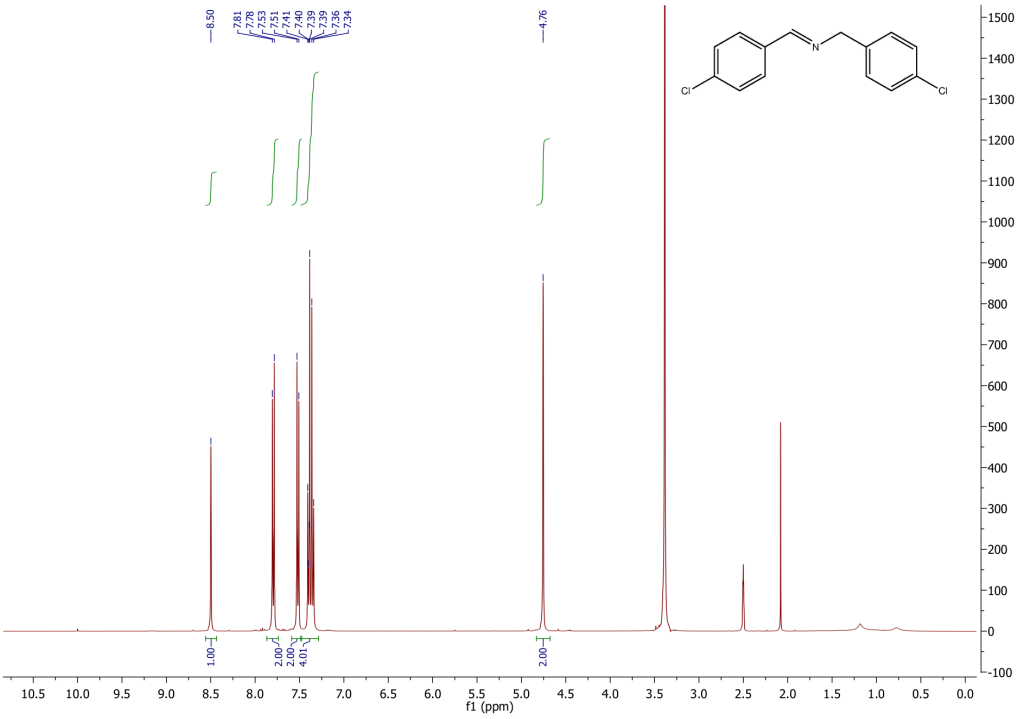
S4 ^{1}H-NMR and ^{13}C-NMR spectra

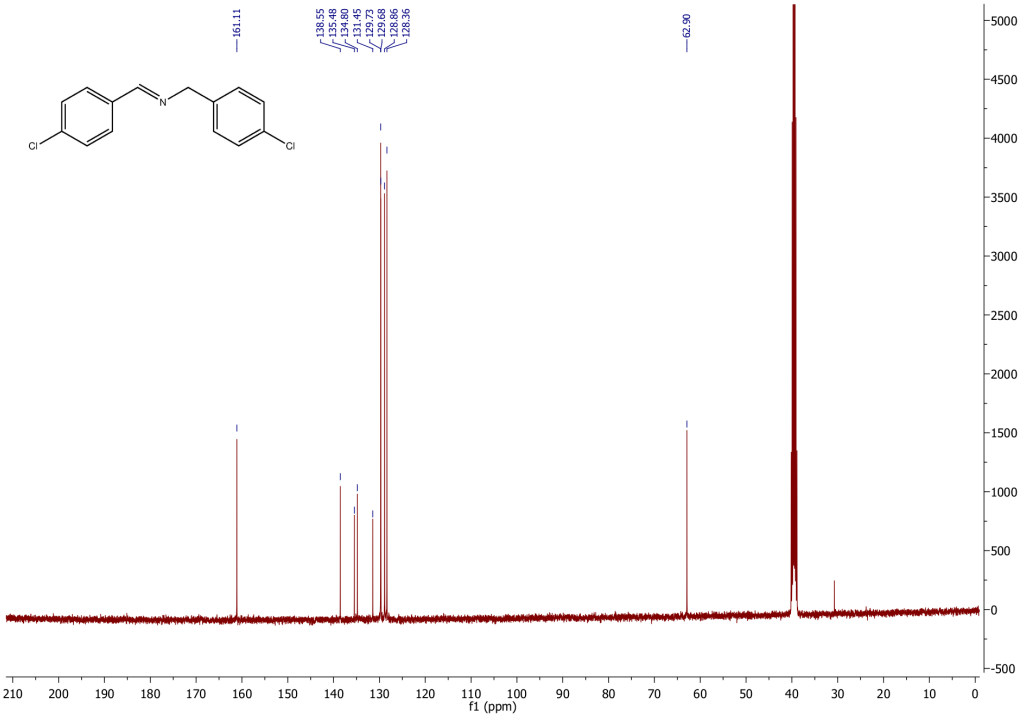
4-Chlorobenzamide 2



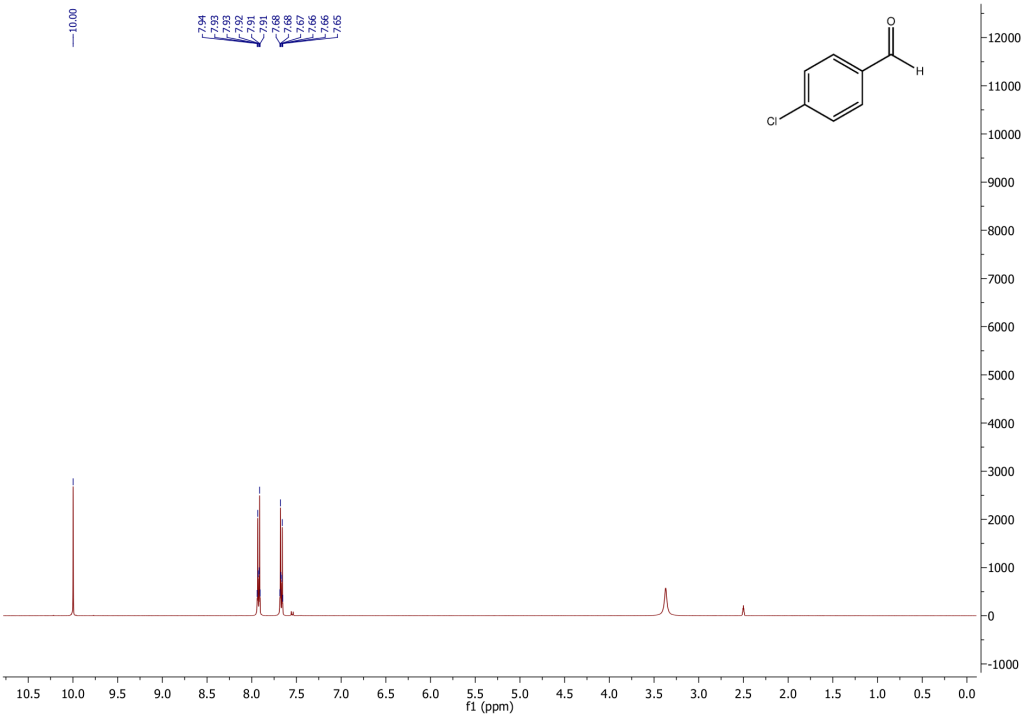


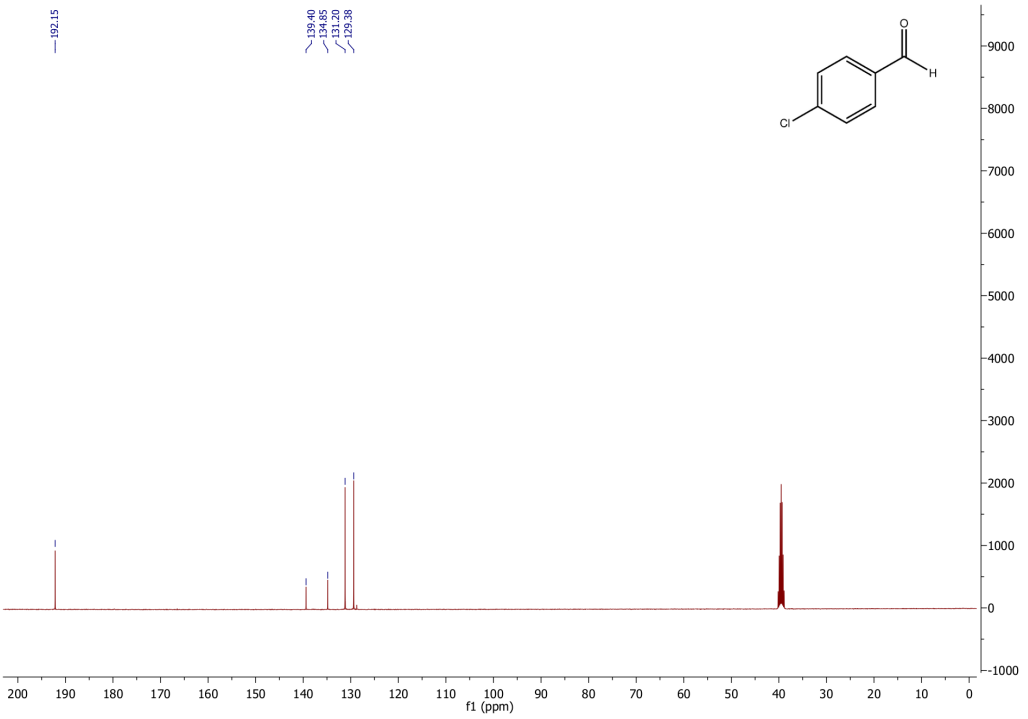
N-(4-Chlorobenzylidene)-1-(4-chlorophenyl)methanamine 4



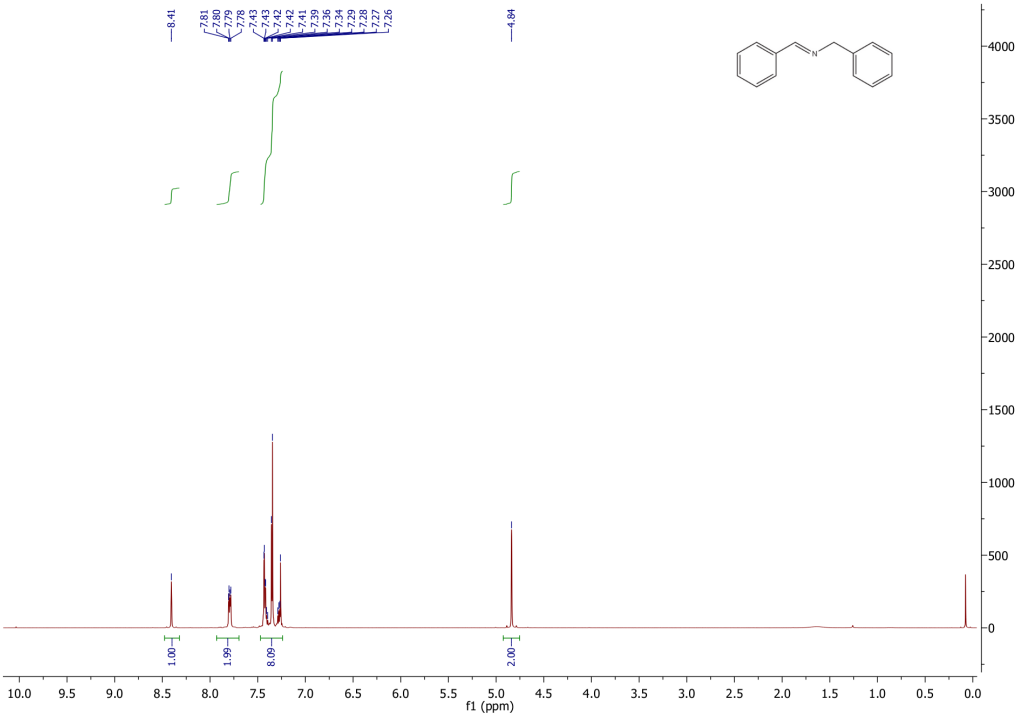


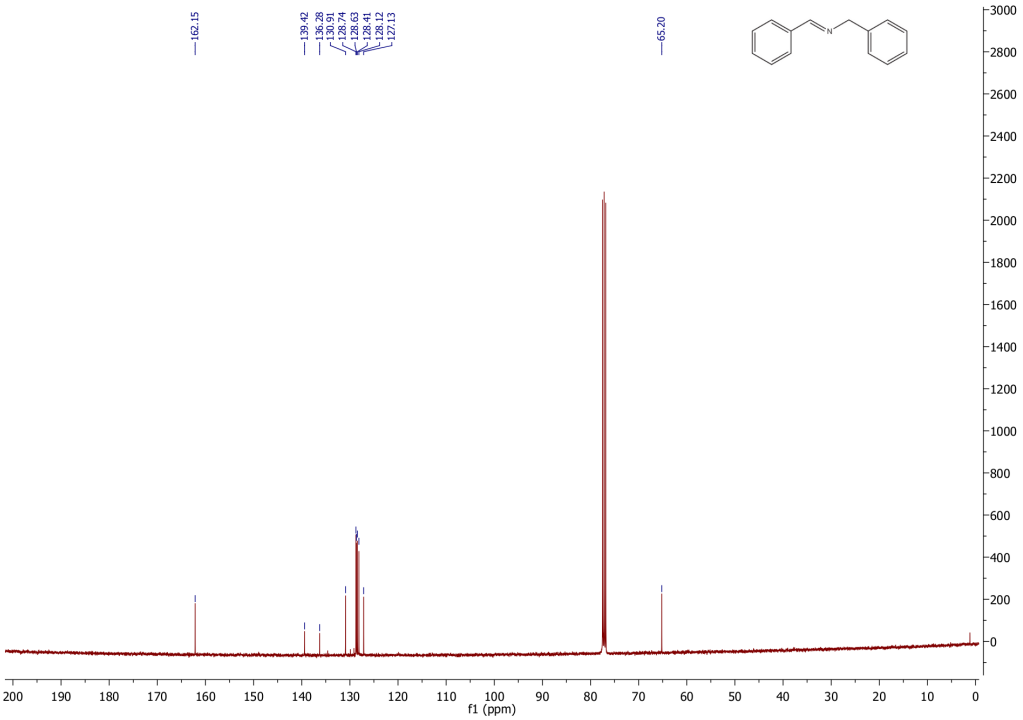
4-Chlorobenzaldhyde 5



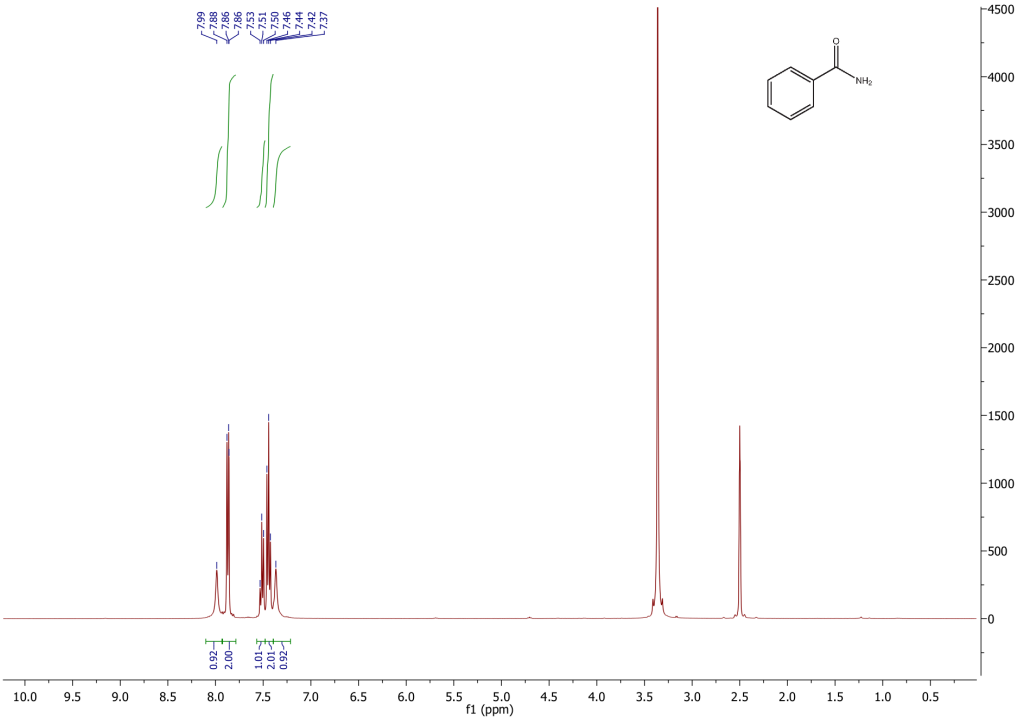


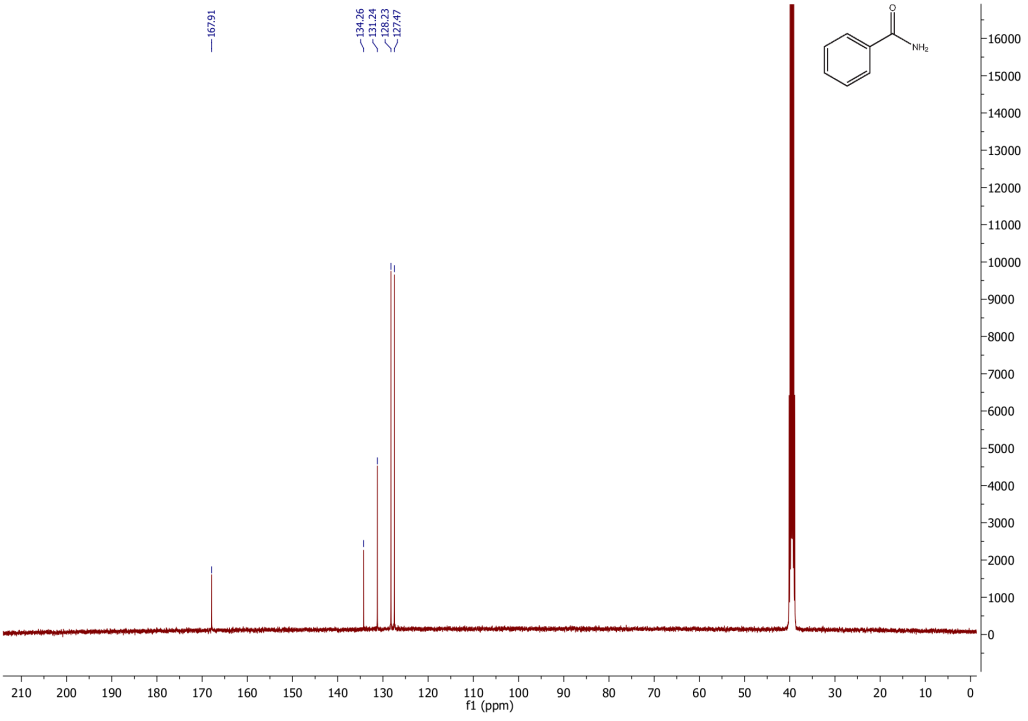
N-Benzylidene benzylamine 10



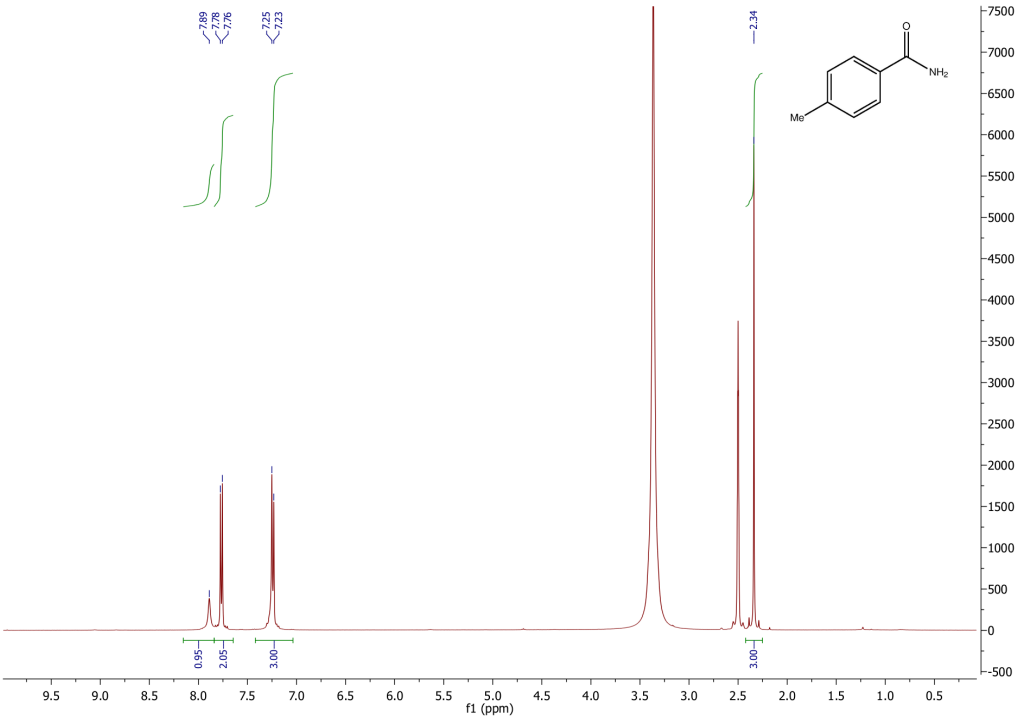


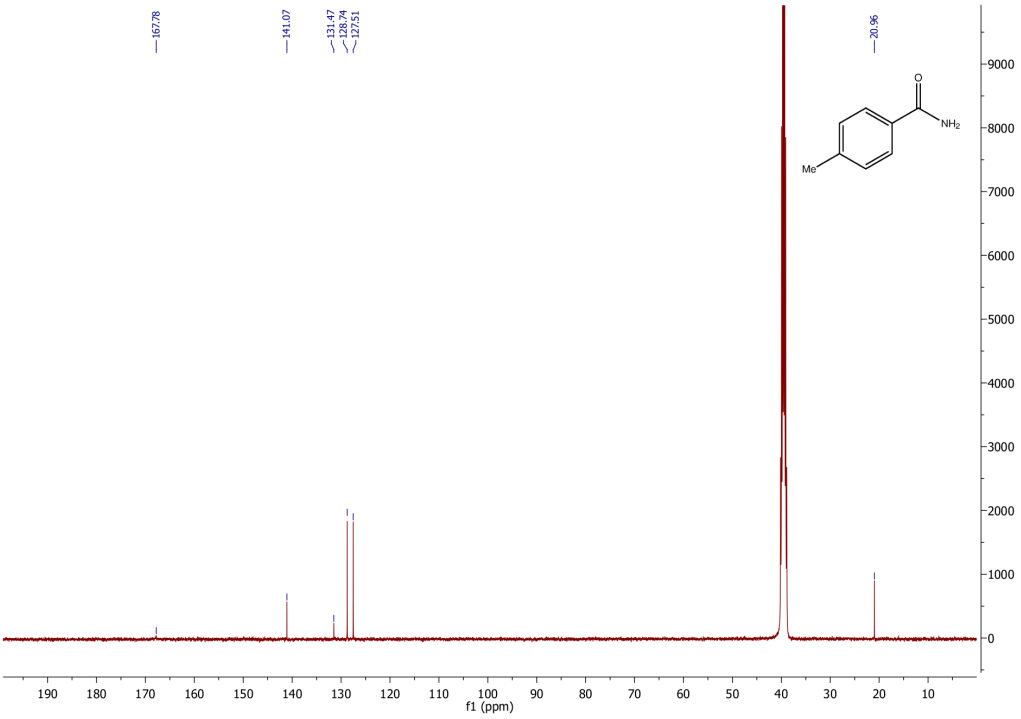
Benzamide 7a



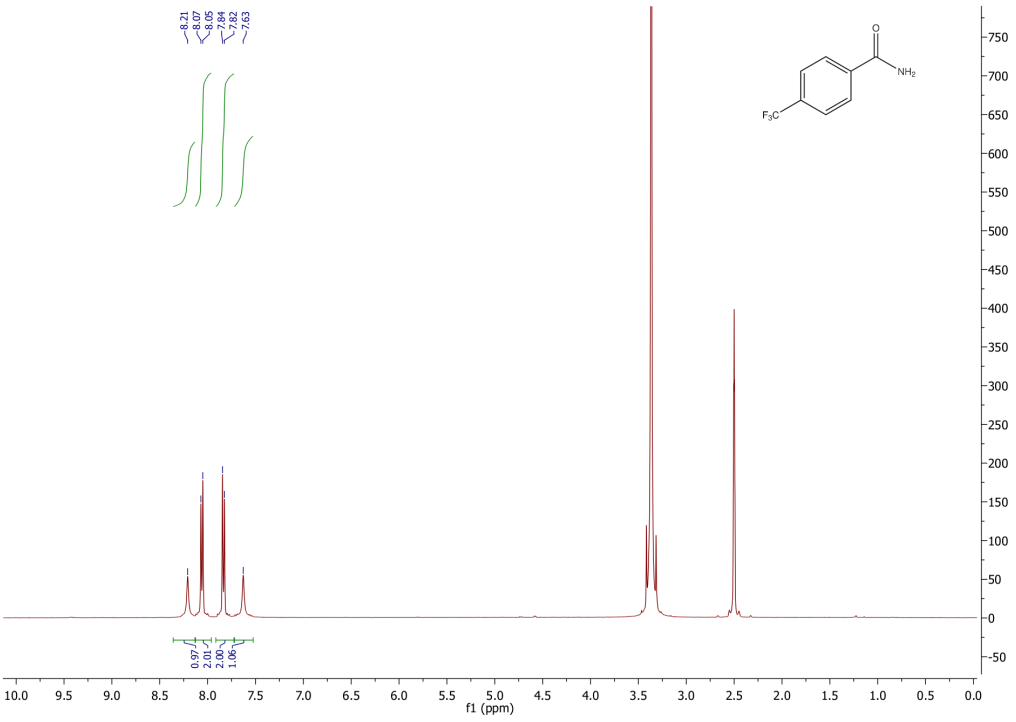


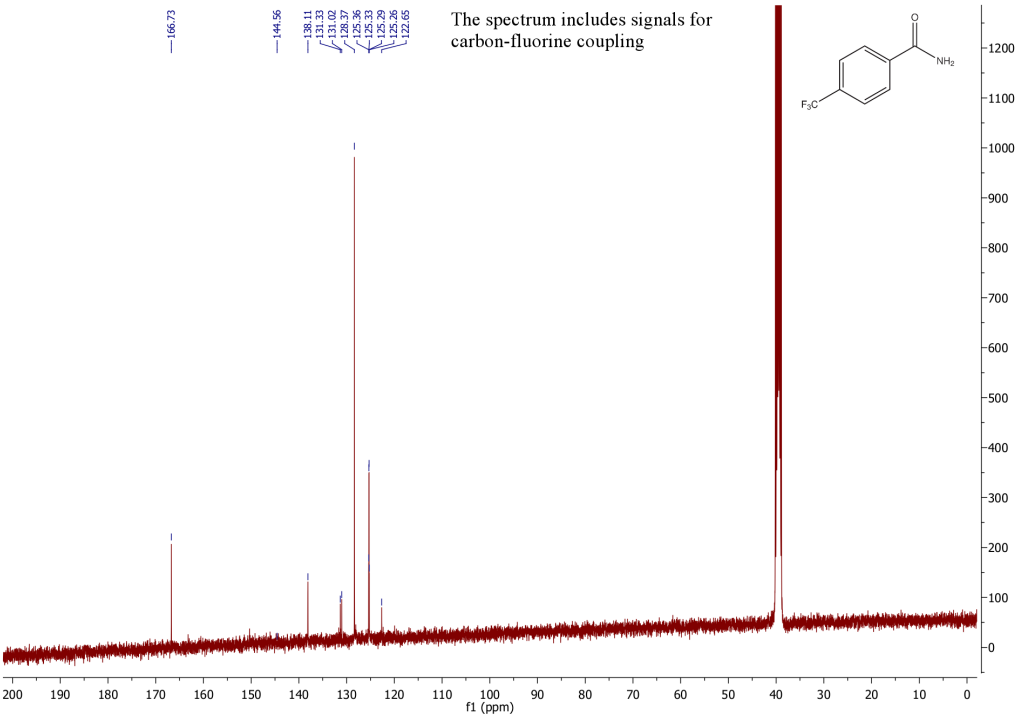
4-Methylbenzamide 7b



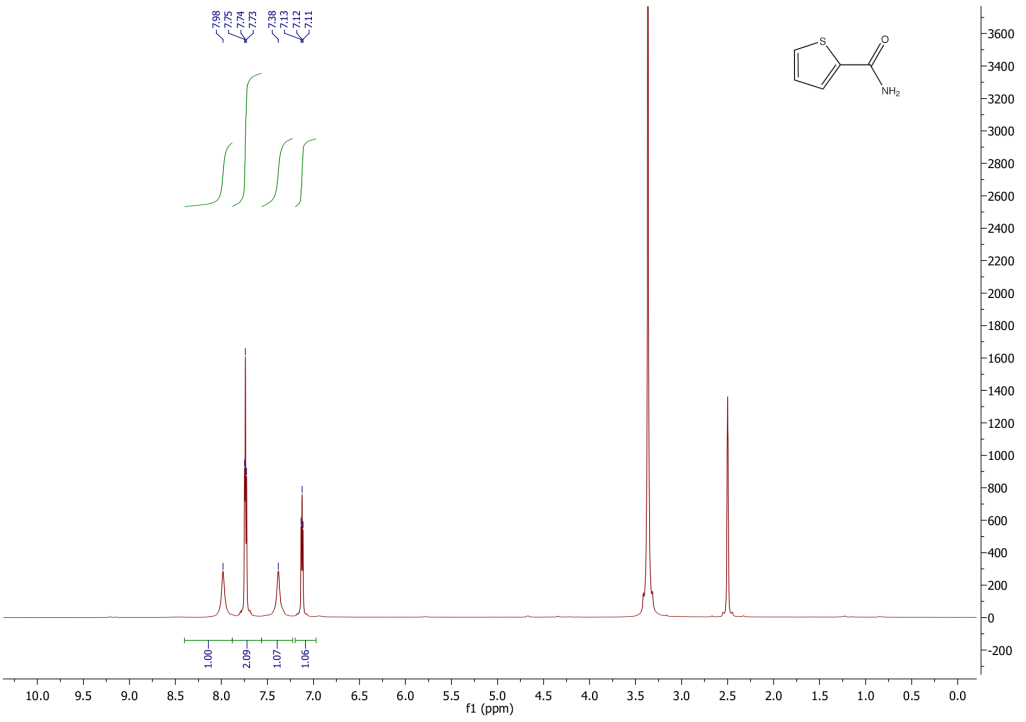


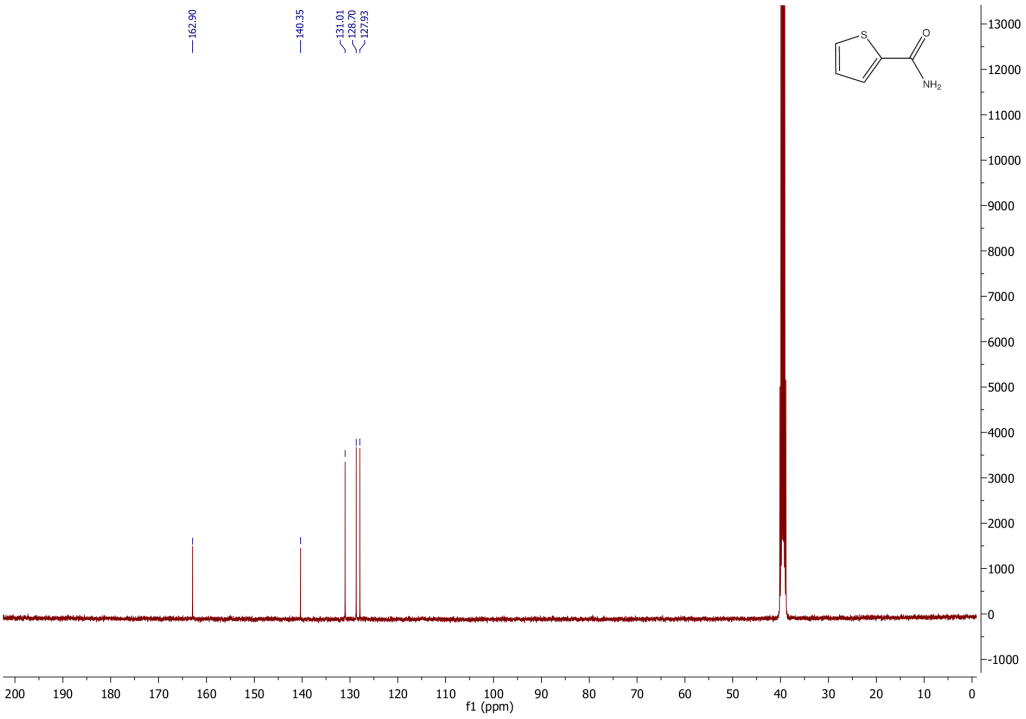
4-Trifluoromethylbenzamide 7c



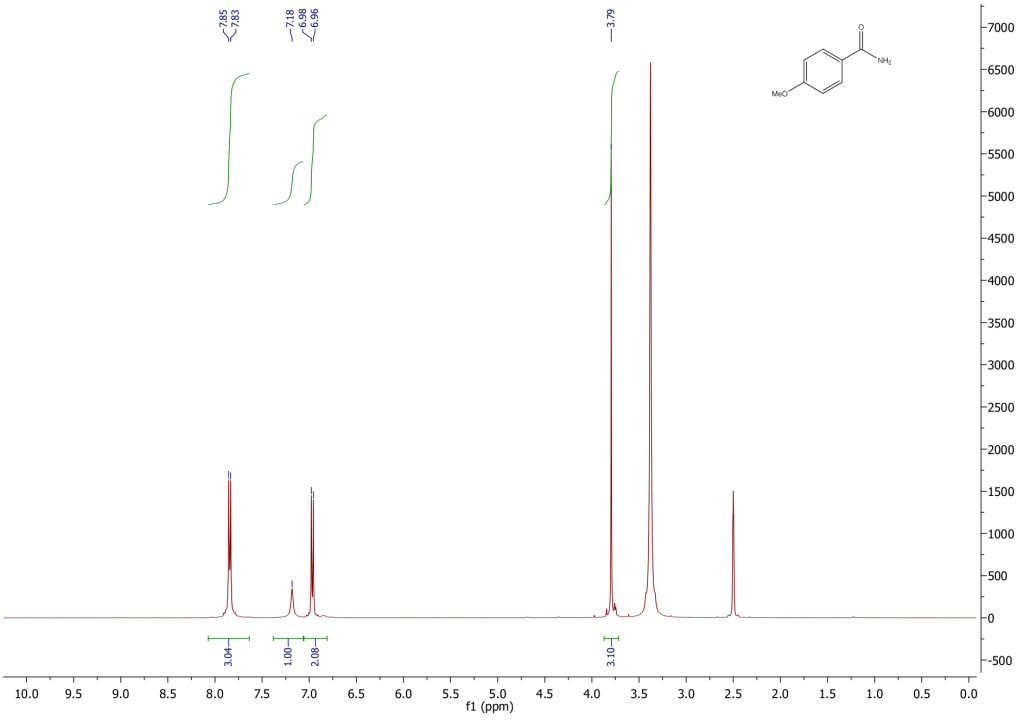


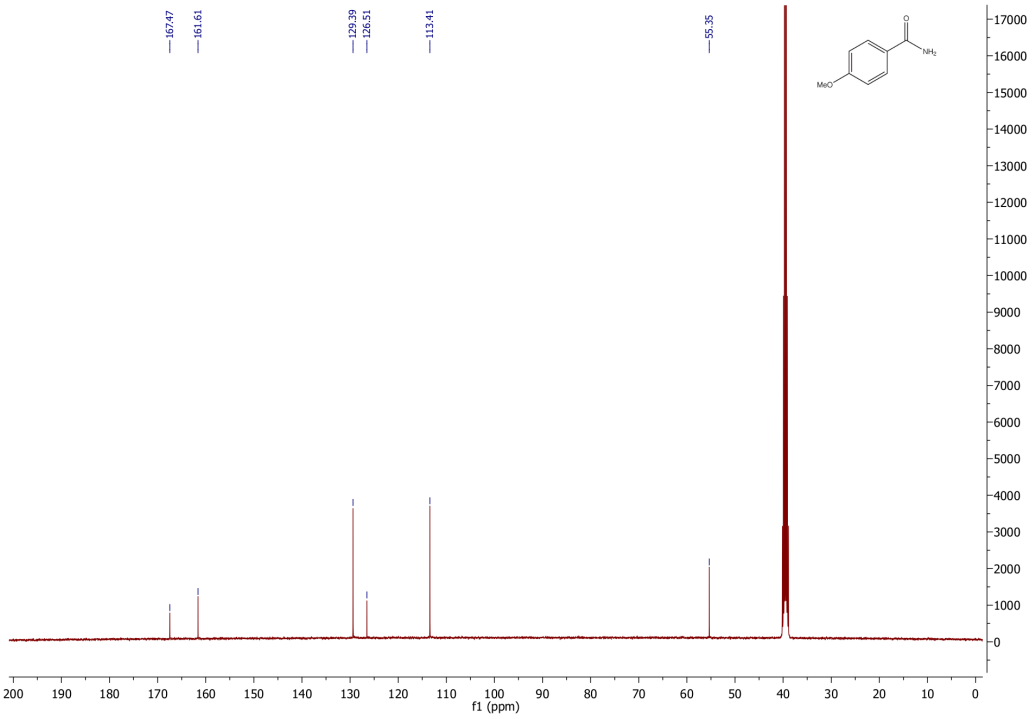
Thiophene-2-carboxamide 7d



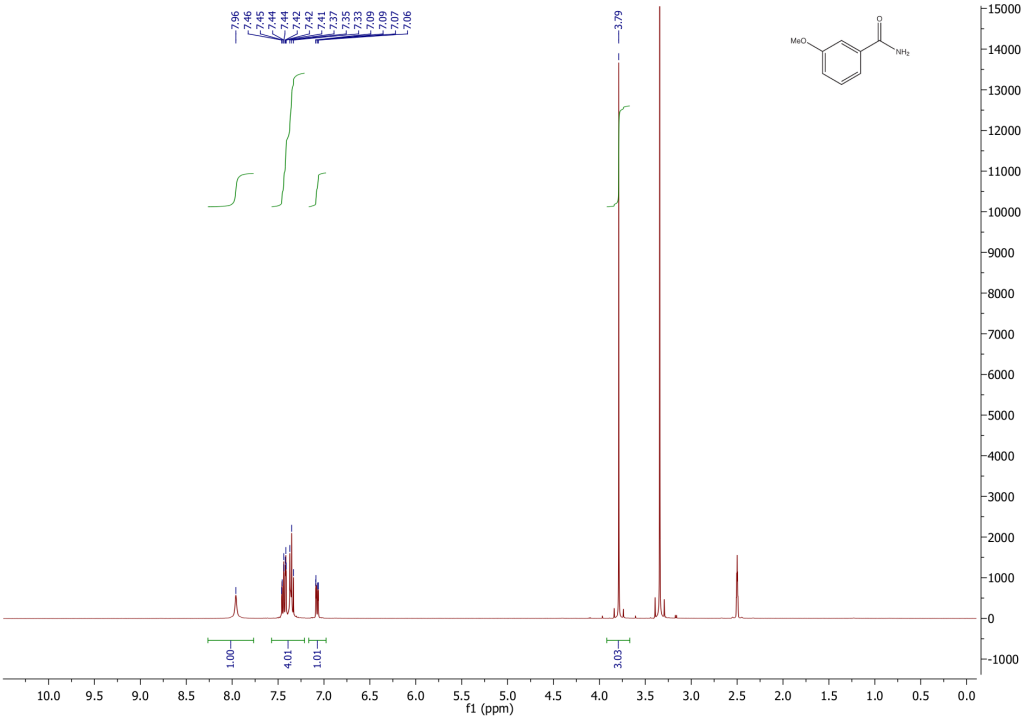


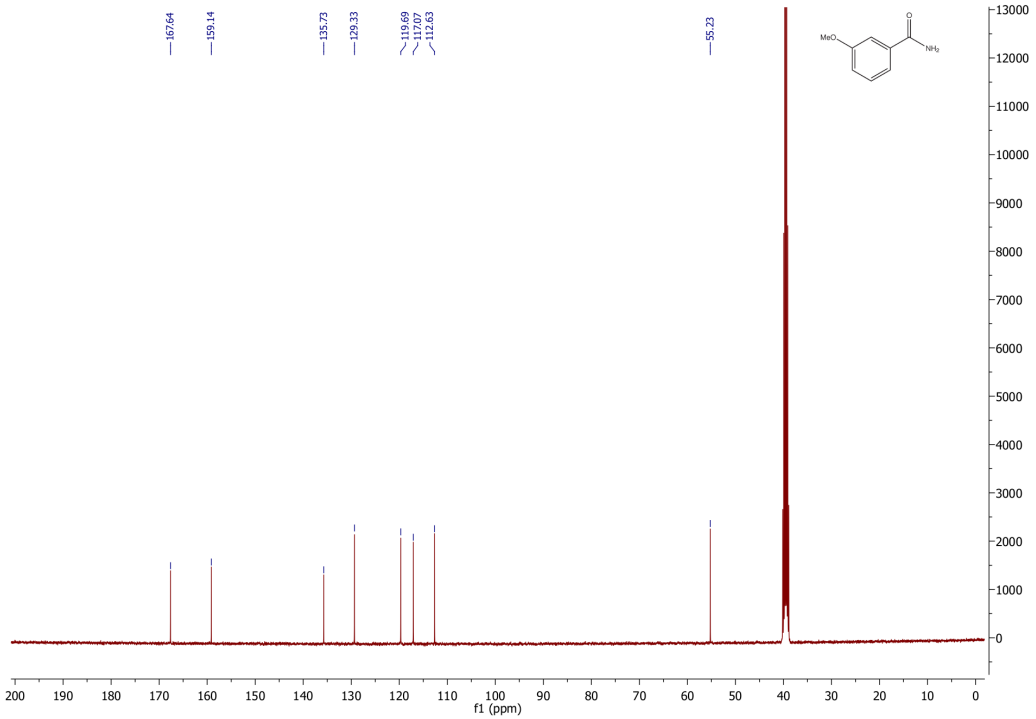
4-Methoxybenzamide 7e



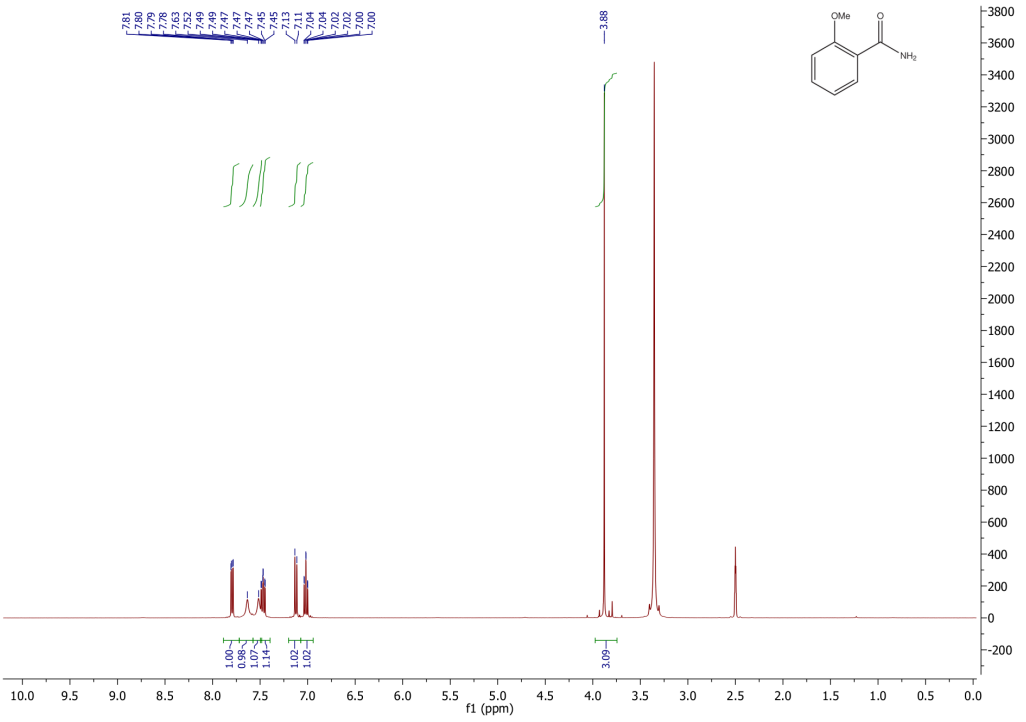


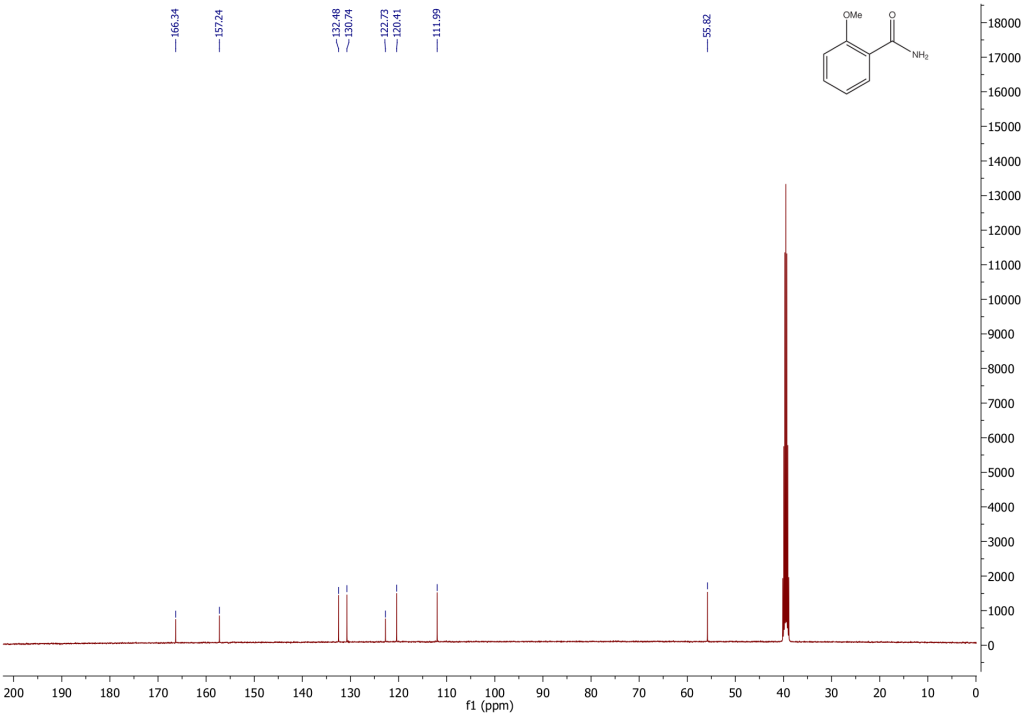
3-Methoxybenzamide 7f



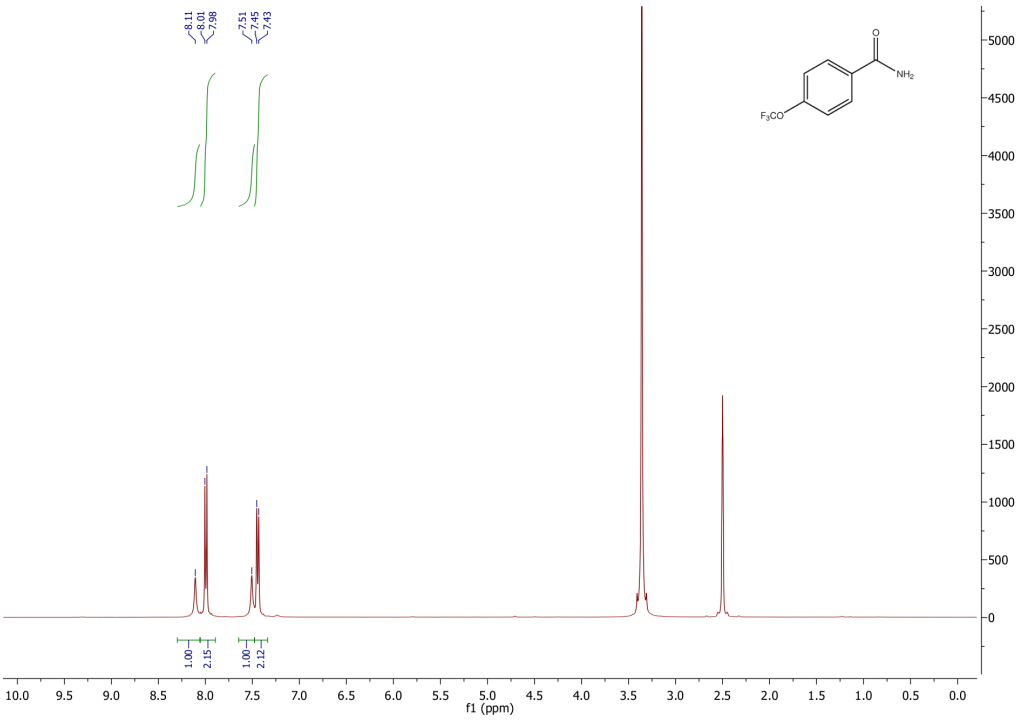


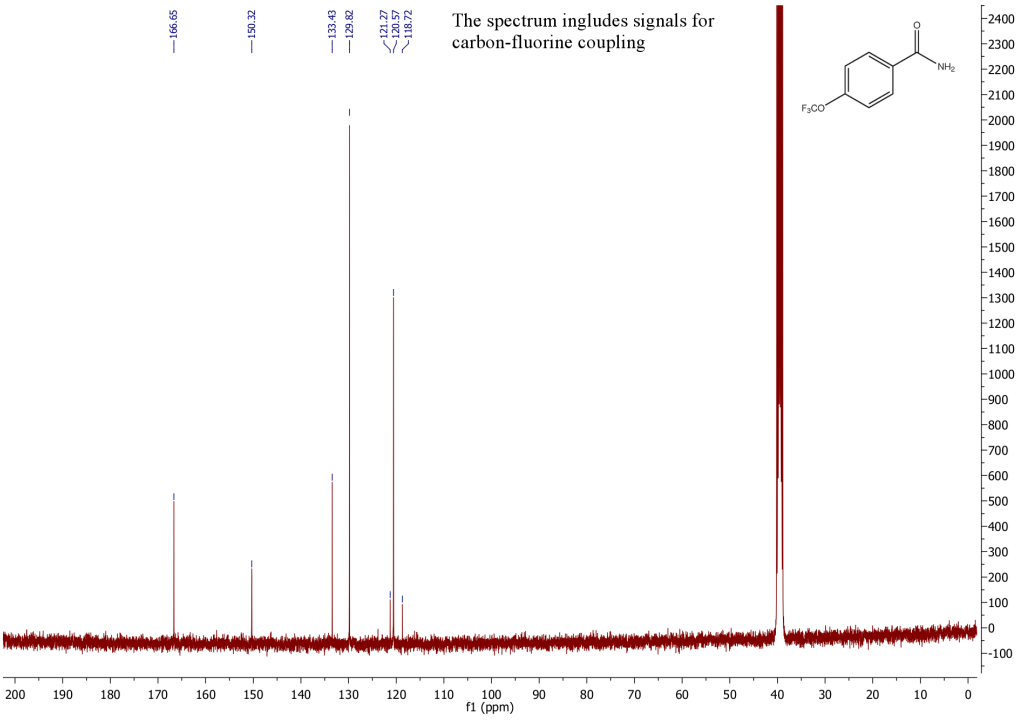
2-Methoxybenzamide 7g



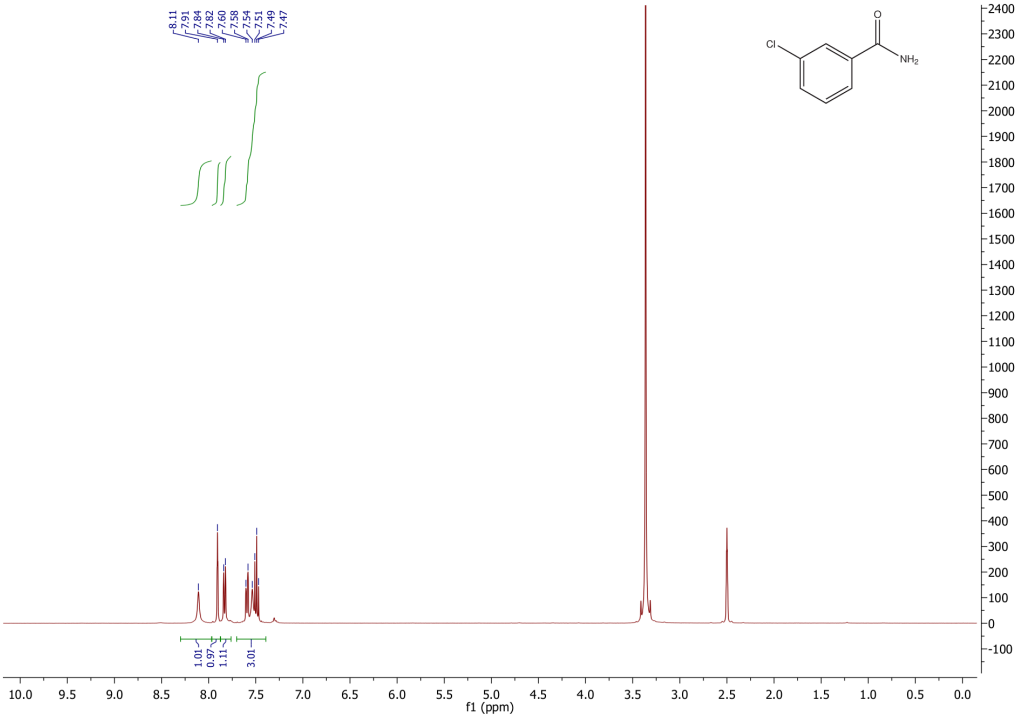


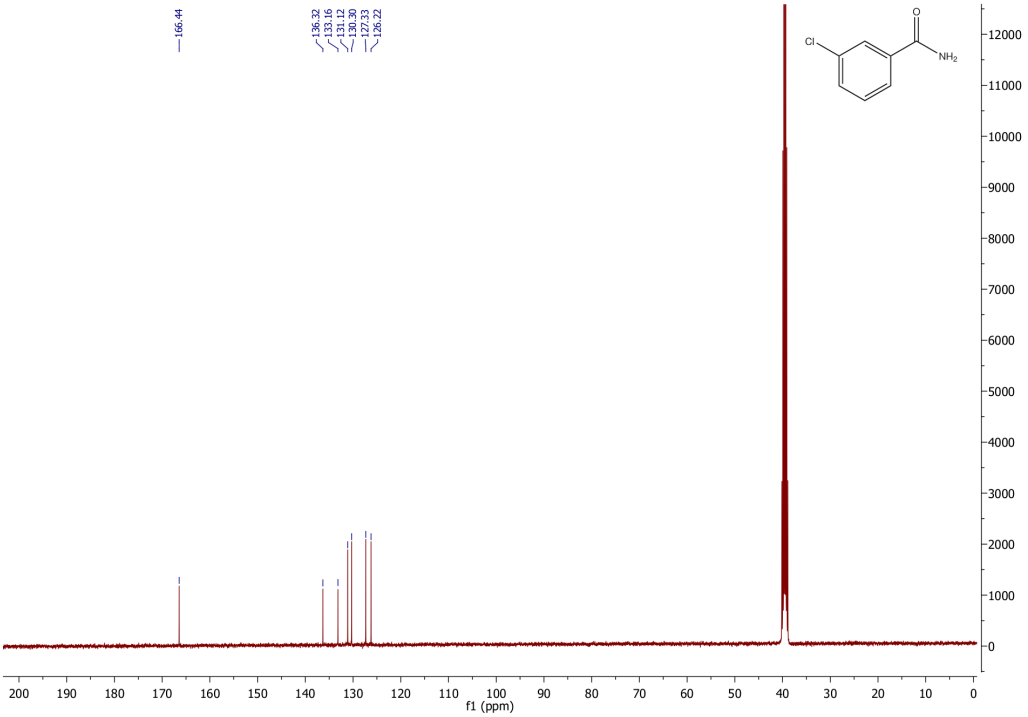
4-Trifluoromethoxybenzamide 7h



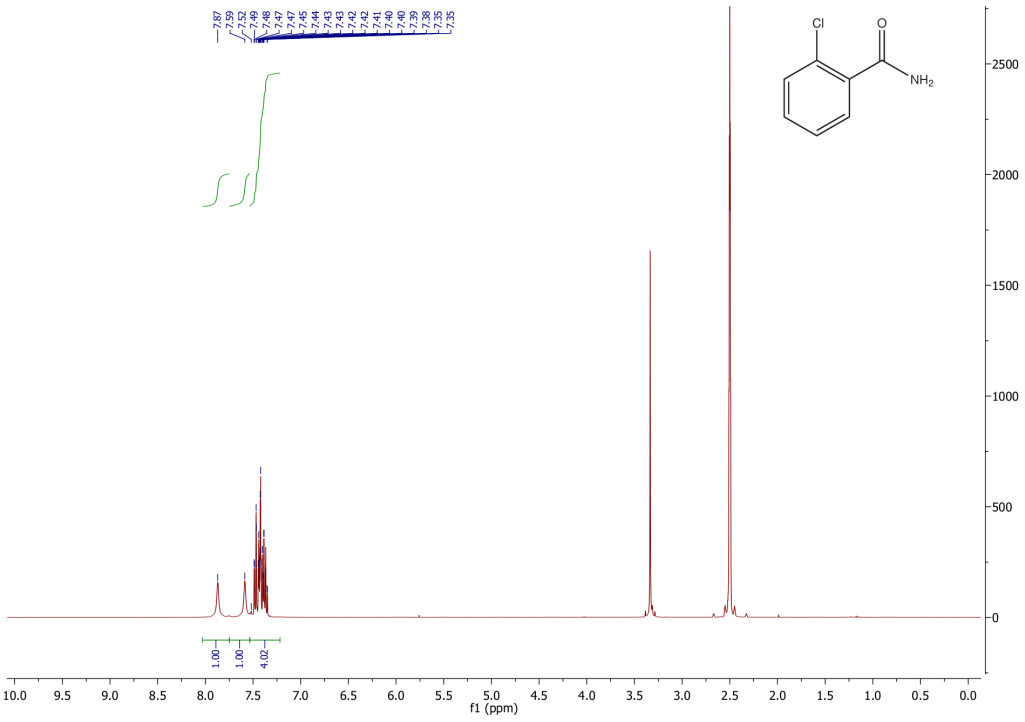


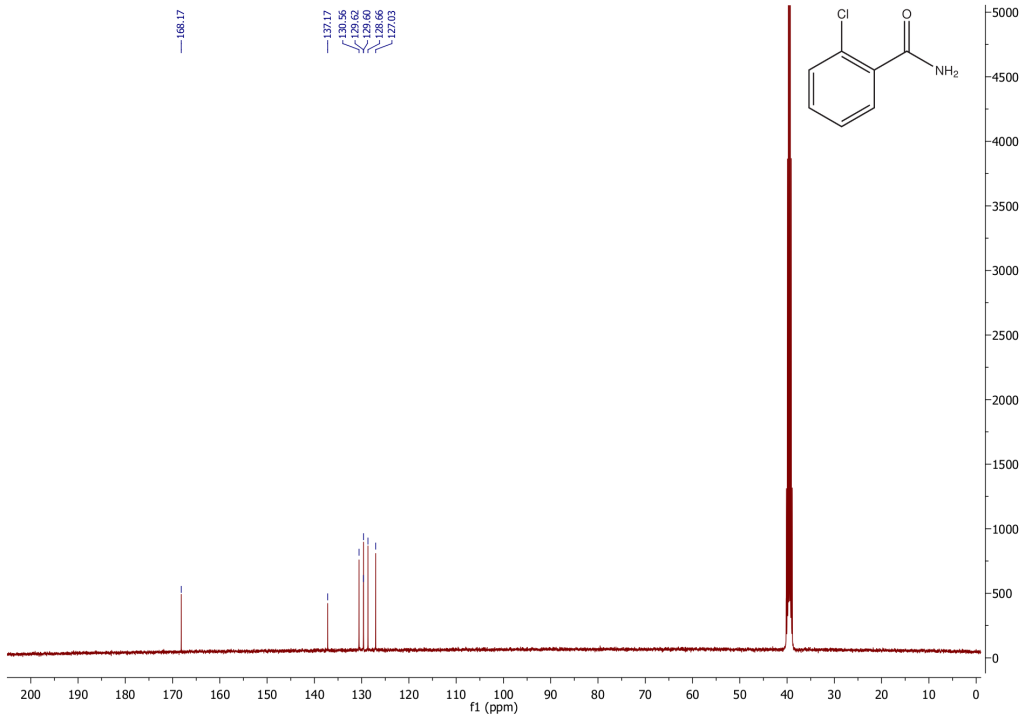
3-Chlorobenzamide 7i



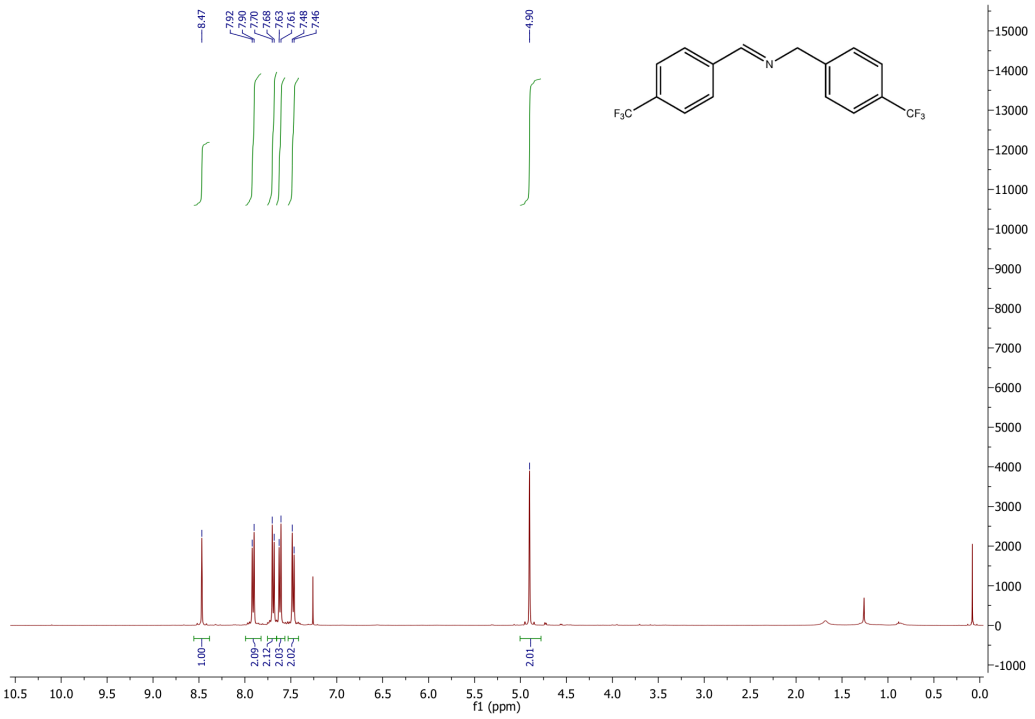


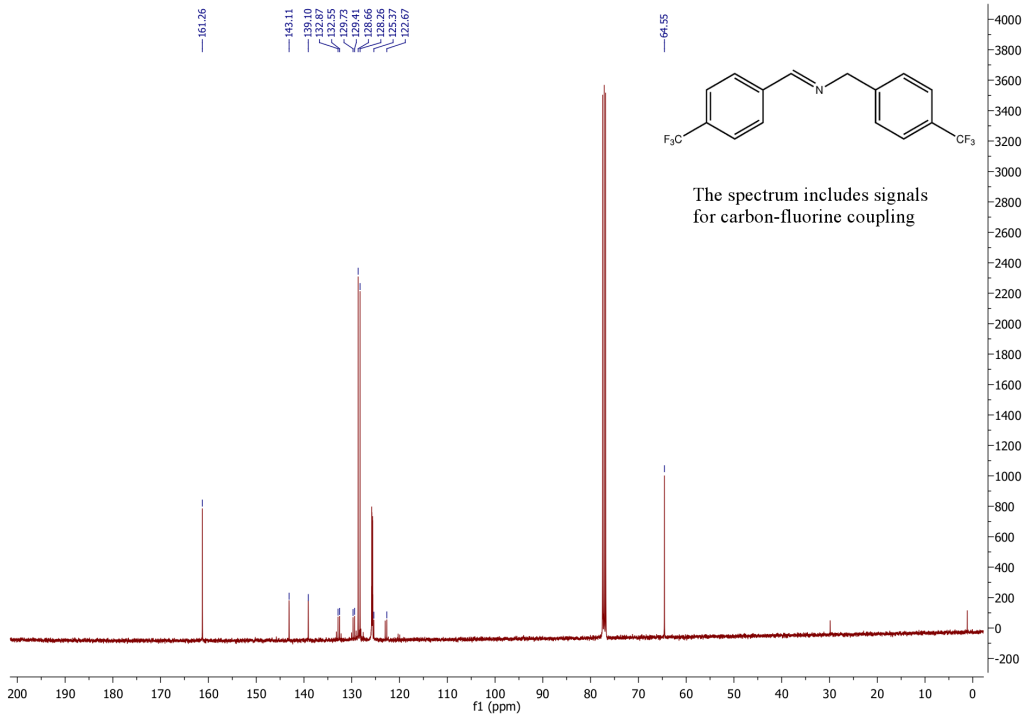
2-Chlorobenzamide 7j





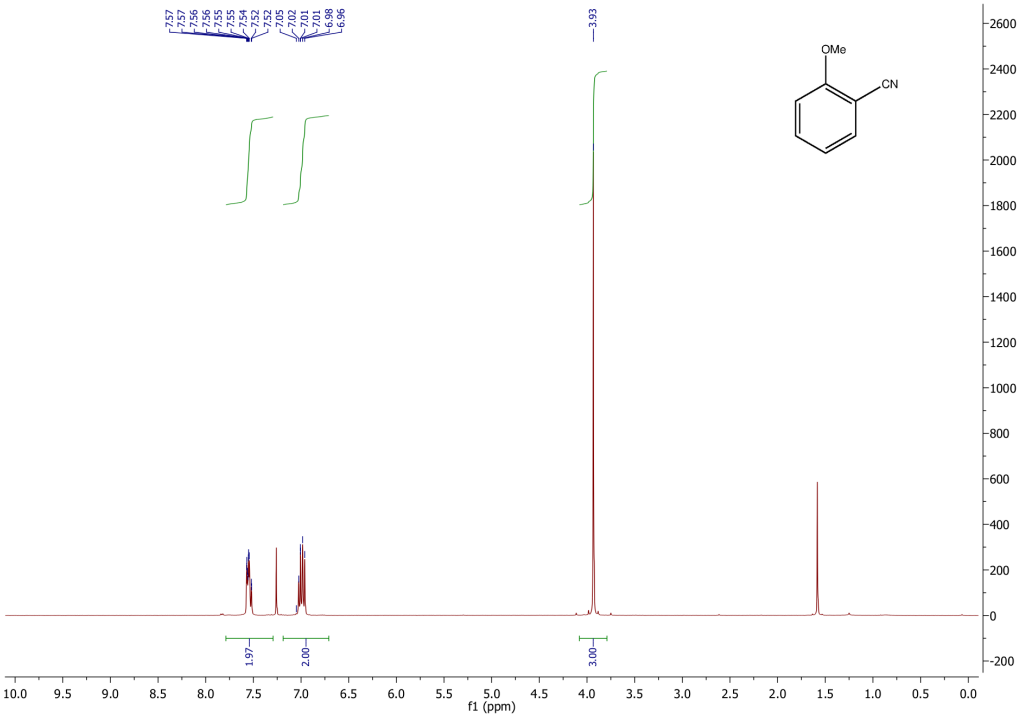
p-Trifluoromethyl-*N*-[*p*-(trifluoromethyl)-benzylidene]-benzylamine 8c

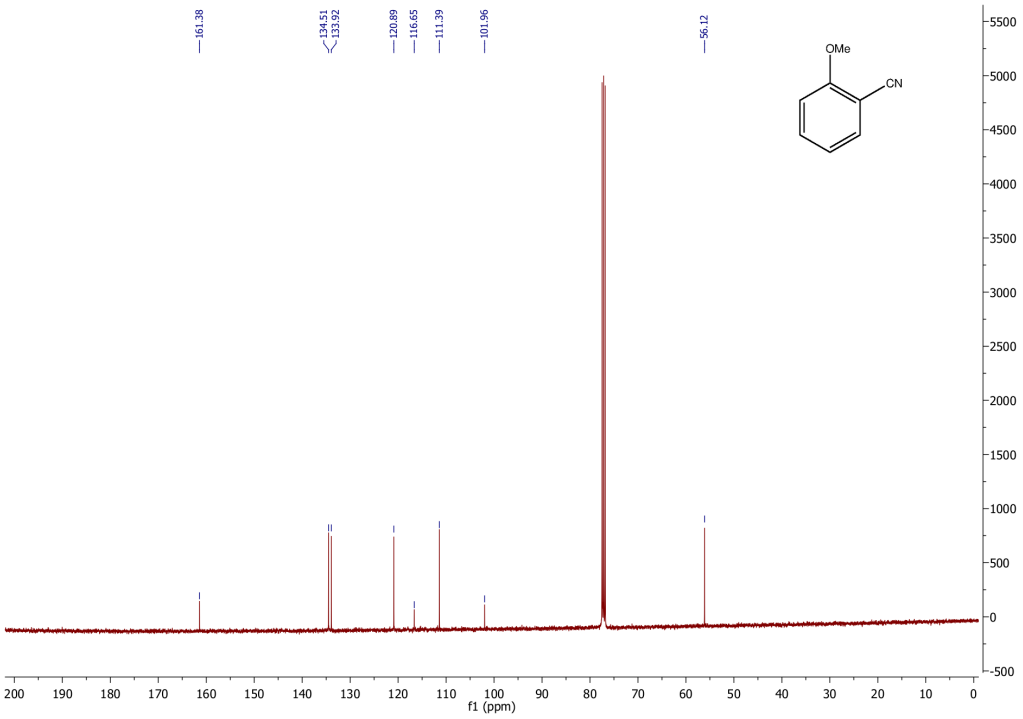




The spectrum includes signals for carbon-fluorine coupling

2-Methoxybenzonitrile 8g





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