

Supporting Information

Rearrangement Strategy for the Synthesis of 2-Aminoanilines

Achim Porzelle, Michael D. Woodrow and Nicholas C. O. Tomkinson.

School of Chemistry, Main Building, Cardiff University, Park Place, Cardiff, CF10 3AT, U.K.

tomkinsonnc@cardiff.ac.uk

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General Procedures: Commercially available solvents and reagents were used without further purification. Flash chromatography was carried out using Merck Kieselgel 60 H silica or Matrex silica 60. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF₂₅₄ that were visualised under UV light (at 254 and/or 360 nm). Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ at 18 °C unless stated otherwise and were reported in ppm; *J* values were recorded in Hz and multiplicities were expressed by the usual conventions. Low-resolution mass spectra (MS) were determined using atmospheric pressure chemical ionization (APCI) unless otherwise stated. ES refers to electrospray ionization, CI refers to chemical ionization (ammonia) and EI refers to electron ionization. High-resolution mass spectra were obtained courtesy of the EPSRC Mass Spectrometry Service at University of Wales, Swansea, U.K. using the ionization methods specified. *In vacuo*

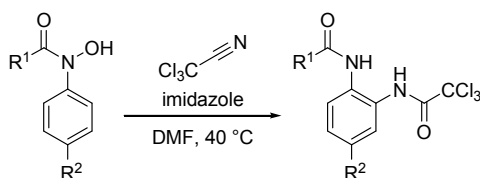
refers to evaporation at reduced pressure using a rotary evaporator and diaphragm pump, followed by the removal of trace volatiles using a vacuum (oil) pump. Melting points were determined with a Gallenkamp SG92 melting point apparatus and are uncorrected.

Experimental Procedures

tert-Butyl *N*-aryl-*N*-hydroxy carbamates were obtained following literature procedures.¹

Methyl and benzyl *N*-aryl-*N*-hydroxy carbamates were obtained following literature procedures.²

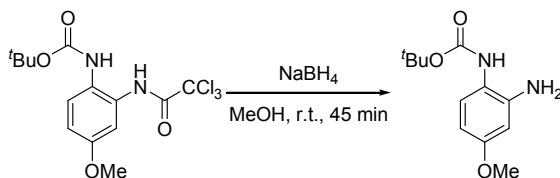
General procedure for rearrangement:



To a solution of *N*-hydroxy carbamate (1 mmol) in DMF (3 mL) was added trichloroacetonitrile (0.4 mL, 4 equiv) and a solution of imidazole (72 mg, 1.05 equiv) in DMF (1 mL) at room temperature. The reaction mixture was stirred at either room temperature for 17 h or 6 h at 40 °C. After completion of the reaction the mixture was diluted with ethyl acetate (30 mL) and washed with saturated ammonium chloride, water and brine (25 mL each). The organic layer was evaporated and the crude product was purified by column chromatography on silica (10 % ethyl acetate/cyclohexane).

Typical procedure for deprotection of trichloroacetate:

tert-Butyl *N*-(2-amino-4-methoxyphenyl) carbamate **21**:



To a solution of *tert*-butyl *N*-(2-(2',2'-trichloroacetylamino)-4-methoxy-1-phenyl)-carbamate (130 mg, 0.34 mmol) in methanol (5 mL) were added 4 portions of

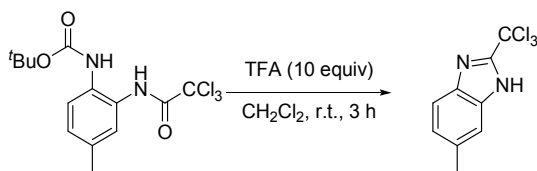
¹ A. Porzelle, M. D. Woodrow, N. C. O. Tomkinson, *Org. Lett.* **2009**, *11*, 233.

² A. Porzelle, M. D. Woodrow, N. C. O. Tomkinson, *Synlett* **2009**, 798.

sodiumborohydride (12 mg, 0.34 mmol each) over a periode of 45 minutes. After which LCMS analysis showed complete consumption of starting material. The reaction mixture was evaporated, dissolved in ether (10 mL) and washed with water (2x 10 mL). The organic layer was evaporated and the crude furher purified by column chromatography on silica (10% ethyl acetate/cyclohexane) to obtain *tert*-butyl *N*-(2-amino-4-methoxyphenyl) carbamate **21** (56 mg, 69%) as a white solid.

Typical procedure for the formation of 2-trichloromethyl 1H-benzimidazoles:

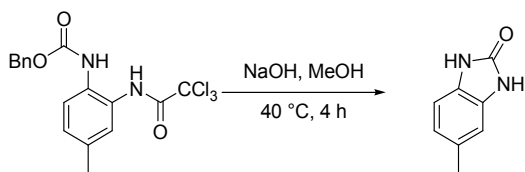
2-Trichloromethyl-6-methyl 1H-benzimidazole **17**:



To a solution of *tert*-butyl 2-(2',2',2'-trichloroacetamino)-4-methylphenyl carbamate **17** (160 mg, 0.44 mmol) in dichloromethane (5 mL) was added trifluoroacetic acid (0.29 mL, 4.40 mmol) at room temperature. The mixture was stirred until LCMS showed complete consumption of starting material (3 h). The mixture was evaporated and the crude purified by column chromatography on silica (10% ethyl acetate on silica) to give 2-trichloromethyl-6-methyl 1H-benzimidazole³ **19** (98 mg, 84%).

Typical procedure for formation of benzimidazolinone:

5-Methyl benzimidazolinone **15**:



To a solution of benzyl *N*-(2-(2',2',2'-trichloroacetyl-amino)-4-methyl-1-phenyl)-carbamate (278 mg, 0.69 mmol) in methanol (5 mL) was added 2 M sodium hydroxide solution (0.2 mL) and the mixture was stirred at 40 °C for 4 h. The mixture was concentrated, diluted with ether (10 mL) and washed with saturated ammonium chloride,

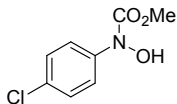
³ J. D. Venable *et al.*, *J. Med. Chem.* **2005**, *48*, 8289.

water and brine (10 mL each). The organic layer was evaporated and the product purified by column chromatography on silica (20% ethyl acetate:cyclohexane) to obtain the title compound 5-methyl benzimidazolinone⁴ **15** (71 mg, 70%).

⁴ I. W. Harvey, M. D. McFarlane, D. J. Moody, D. M. Smith, *J. Chem. Soc., Perkin Trans. I* **1988**, 681.

Spectroscopic data of new alkyl-*N*-aryl-*N*-hydroxy carbamates:

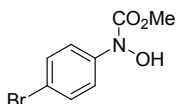
***N*-Methoxycarbonyl-*N*-(4-chlorophenyl) hydroxylamine**



Ivory solid; m.p. 64–65 °C; R_f = 0.58 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 8.28 (br s, 1H), 7.40 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.9 (s), 139.4 (s), 131.2 (s), 128.7 (d), 123.0 (d), 54.0 (q); HRMS (EI) found 202.0280 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_8\text{H}_9^{35}\text{ClNO}_3$ 202.0271.

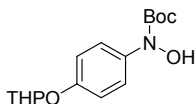
***N*-Methoxycarbonyl-*N*-(4-bromophenyl) hydroxylamine**



Ivory solid; m.p. 90–92 °C; R_f = 0.58 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, J = 6.8 Hz, 2H), 7.37 (d, J = 6.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (60 MHz, CDCl_3) δ 155.7 (s), 139.2 (s), 131.2 (s), 128.7 (d), 122.9 (d), 54.0 (q); HRMS (EI) found 245.9768 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_8\text{H}_9^{79}\text{BrNO}_3$ 245.9766.

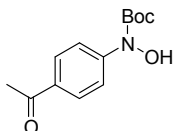
***N*-Boc-*N*-(4-Tetrahydropyranyloxyphenyl) hydroxylamine**



Colourless solid; m.p. 81–83 °C; R_f = 0.76 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 8.27 (br s, 1H), 7.31 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 5.39 (t, J = 3.1 Hz, 1H), 3.93–3.88 (m, 1H), 3.62–3.59 (m, 1H), 2.05–1.95 (m, 1H), 1.86–1.84 (m, 2H), 1.73–1.57 (m, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0 (s), 154.9 (s), 135.2 (s), 124.2 (d), 116.3 (d), 96.6 (d), 82.8 (s), 62.1 (t), 30.4 (t), 28.3 (q), 25.2 (t), 18.8 (t); HRMS (EI) found 327.1922 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{16}\text{H}_{27}\text{N}_2\text{O}_5$ 327.1920.

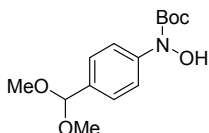
***N*-Boc-*N*-(4-Acetophenyl) hydroxylamine**



Colourless solid; m.p. 104–105 °C; R_f = 0.50 (petroleum ether:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 8.28 (br s, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 2.56 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (60 MHz, CDCl_3) δ 197.2 (s), 153.4 (s), 145.0 (s), 132.5 (s), 129.0 (d), 119.0 (d), 84.2 (s), 28.2 (q), 26.4 (q); HRMS (ES) found 252.1231 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_{13}\text{H}_{18}\text{NO}_4$ 252.1230.

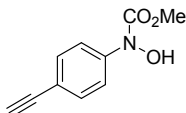
***N*-Boc-*N*-(4-Dimethoxymethylphenyl) hydroxylamine**



Colourless waxy solid; R_f = 0.74 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 8.36 (br s, 1H), 7.46 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 5.38 (s, 1H), 3.32 (s, 6H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.3 (s), 141.3 (s), 134.4 (s), 126.7 (d), 120.9 (d), 102.8 (d), 83.3 (s), 52.7 (q), 28.3 (q); HRMS (EI) found 301.1767 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{14}\text{H}_{25}\text{N}_2\text{O}_5$ 301.1763.

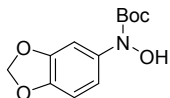
***N*-Methoxycarbonyl-*N*-(4-ethynylphenyl) hydroxylamine**



Colourless solid; m.p. 80–81 °C; R_f = 0.60 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 7.48–7.45 (m, 4H), 3.86 (s, 3H), 3.07 (s, 1H); ^{13}C NMR (60 MHz, CDCl_3) δ 155.3 (s), 140.7 (s), 132.5 (d), 120.5 (d), 119.0 (s), 83.1 (s), 77.3 (d), 54.0 (q); HRMS (EI) found 191.0668 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_{10}\text{H}_{10}\text{NO}_3$ 192.0661.

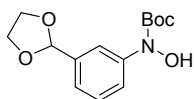
***N*-Boc-*N*-(3,4-Methylenedioxyphenyl) hydroxylamine**



Colourless solid; m.p. 77–78 °C; R_f = 0.74 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 8.41 (br s, 1H), 6.93 (d, J = 2.1 Hz, 1H), 6.88 (dd, J = 8.5, 2.1 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 5.96 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.1 (s), 147.4 (s), 145.7 (s), 135.5 (s), 117.0 (d), 107.6 (d), 105.2 (d), 101.4 (t), 83.0 (s), 28.3 (q); HRMS (EI) found 271.1293 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{12}\text{H}_{19}\text{N}_2\text{O}_5$ 271.1294.

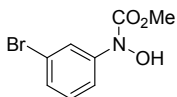
***N*-Boc-*N*-(3-(1,3-Dioxolan-2-yl)phenyl) hydroxylamine**



Colourless solid; m.p. 59–60 °C; R_f = 0.66 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 8.17 (br s, 1H), 7.59 (s, 1H), 7.46–7.43 (m, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 5.80 (s, 1H), 4.11–4.02 (m, 4H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.3 (s), 141.3 (s), 138.3 (s), 128.4 (d), 123.0 (d), 121.9 (d), 119.3 (d), 103.5 (d), 83.3 (s), 65.3 (t), 28.3 (q); HRMS (EI) found 299.1602 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{14}\text{H}_{23}\text{N}_2\text{O}_5$ 299.1601.

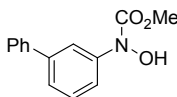
***N*-Methoxycarbonyl-*N*-(3-bromophenyl) hydroxylamine**



Colourless solid; m.p. 78–79 °C; R_f = 0.70 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 7.72 (br s, 1H), 7.72–7.70 (m, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.6 (s), 141.9 (s), 129.8 (s), 128.5 (d), 124.3 (d), 122.1 (d), 119.9 (d), 54.0 (q); HRMS (EI) found 245.9770 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_8\text{H}_9^{79}\text{BrNO}_3$ 245.9766.

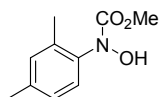
***N*-Methoxycarbonyl-*N*-(3-biphenyl) hydroxylamine**



Yellow oil; R_f = 0.66 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 7.73 (br s, 1H), 7.59 (d, J = 7.0 Hz, 2H), 7.46–7.43 (m, 5H), 7.36–7.30 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7 (s), 141.9 (s), 140.9 (s), 140.5 (s), 129.0 (d), 128.8 (d), 127.6 (d), 127.2 (d), 124.7 (d), 120.5 (d), 53.9 (q); HRMS (EI) found 244.0975 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_{14}\text{H}_{14}\text{NO}_3$ 244.0974.

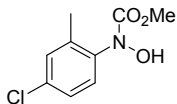
***N*-Methoxycarbonyl-*N*-(2,4-dimethylphenyl) hydroxylamine**



Yellow oil; R_f = 0.58 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, J = 7.8 Hz, 1H), 7.07–7.02 (m, 2H), 3.75 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.4 (s), 139.0 (s), 136.7 (s), 135.9 (s), 131.5 (d), 127.4 (d), 127.3 (d), 53.7 (q), 21.1 (q), 17.4 (q); HRMS (EI) found 196.0974 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_{10}\text{H}_{14}\text{NO}_3$ 196.0974.

***N*-Methoxycarbonyl-*N*-(4-chloro-2-methylphenyl) hydroxylamine**

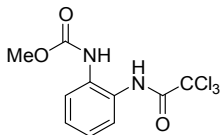


Brown solid; m.p. 75–76 °C; R_f = 0.60 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 8.88 (br s, 1H), 7.29–7.27 (m, 2H), 7.23–7.21 (m, 1H), 3.77 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.3 (s), 138.0 (s), 134.3 (s), 130.7 (d), 128.7 (d), 126.7 (d), 53.8 (q), 17.5 (t); HRMS (EI) found 216.0431 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_9\text{H}_9^{35}\text{ClNO}_3$ 216.0427.

Table 1:

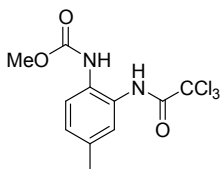
***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-aniline Table 1 Entry 1**



Colourless solid; m.p. 64–66 °C; R_f = 0.75 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.46 (br s, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.30–7.21 (m, 3H), 6.79 (br s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.8 (s), 155.8 (s), 130.2 (s), 129.4 (s), 127.4 (d), 126.6 (d), 125.9 (d), 124.7 (d), 92.9 (s), 53.3 (q); HRMS (ES) found 328.0020 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{10}\text{H}_{13}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 328.0017.

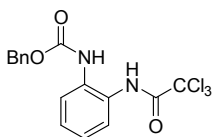
***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-methylaniline Table 1 Entry 2**



Colourless solid; m.p. 86–88 °C; R_f = 0.77 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.46 (br s, 1H), 7.49 (s, 1H), 7.07–7.00 (m, 2H), 6.75 (br s, 1H), 3.77 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.6 (s), 155.9 (s), 137.0 (s), 129.6 (s), 128.1 (d), 127.3 (s), 126.2 (d), 124.8 (d), 93.0 (s), 53.2 (q), 21.0 (q); HRMS (ES) found 342.0290 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{11}\text{H}_{15}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 342.0285.

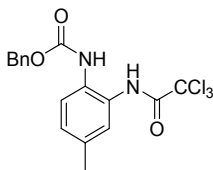
***N*-Cbz-2-(2',2',2'-Trichloroacetyl-amino)-aniline Table 1 Entry 3**



Colourless solid; m.p. 77–78 °C; R_f = 0.84 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.51 (br s, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.35 (br s, 5H), 7.27–7.26 (m, 1H), 7.20–7.19 (m, 1H), 7.16–7.15 (m, 1H), 6.88 (br s, 1H), 5.20 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.7 (s), 155.1 (s), 135.5 (s), 129.8 (s), 128.7 (d), 128.7 (d), 128.4 (d), 127.3 (d), 126.9 (d), 126.0 (d), 125.0 (s), 124.8 (d), 92.9 (s), 68.0 (t); HRMS (ES) found 404.0334 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{16}\text{H}_{17}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 404.0330.

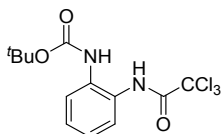
***N*-Cbz-2-(2',2'-Trichloroacetyl-amino)-4-methylaniline Table 1 Entry 4**



Colourless solid; m.p. 82–83 °C; R_f = 0.86 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.48 (br s, 1H), 7.51 (s, 1H), 7.38 (br s, 5H), 7.04–7.02 (m, 2H), 6.81 (br s, 1H), 5.20 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.6 (s), 155.2 (s), 137.1 (s), 135.6 (d), 129.7 (s), 128.7 (d), 128.6 (d), 128.3 (d), 128.0 (s), 127.1 (d), 126.1 (s), 124.7 (d), 92.9 (s), 67.9 (t), 20.9 (q); HRMS (ES) found 418.0490 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{17}\text{H}_{19}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 418.0487.

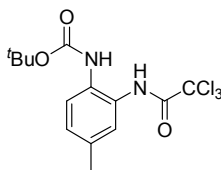
***N*-Boc-2-(2',2'-Trichloroacetyl-amino)-aniline Table 1 Entry 5**



Colourless solid; m.p. 111–112 °C; R_f = 0.75 (cyclohexane:ethyl acetate 1:1);

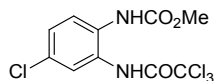
^1H NMR (400 MHz, CDCl_3) δ 9.88 (br s, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.27–7.25 (m, 1H), 7.18–7.17 (m, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.70 (br s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.6 (s), 154.7 (s), 130.0 (s), 127.1 (d), 126.5 (d), 125.9 (d), 124.6 (d), 93.1 (s), 82.1 (s), 28.3 (q); HRMS (ES) found 370.0486 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{13}\text{H}_{19}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 370.0487.

***N*-Boc-2-(2',2'-Trichloroacetyl-amino)-4-methylaniline Table 1 Entry 6**



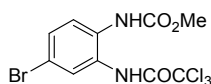
Colourless solid; m.p. 125–126 °C; R_f = 0.82 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.84 (br s, 1H), 7.54 (s, 1H), 6.97–6.93 (m, 2H), 6.57 (s, 1H), 2.34 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.5 (s), 154.8 (s), 136.7 (s), 129.9 (s), 127.7 (d), 127.2 (s), 126.1 (d), 124.4 (d), 93.1 (s), 81.9 (s), 28.3 (q), 21.0 (q); HRMS (ES) found 384.0647 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{14}\text{H}_{21}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 384.0643.

Table 2:***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-chloroaniline Table 2 Entry 1**

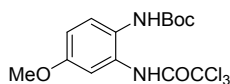
Colourless solid; m.p. 92–93 °C; R_f = 0.69 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.49 (br s, 1H), 7.77 (s, 1H), 7.23 (dd, J = 8.6, 2.3 Hz, 1H), 7.14 (d, J = 8.6 Hz, 1H), 6.66 (br s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.5 (s), 155.6 (s), 132.3 (s), 130.9 (s), 128.3 (s), 127.4 (d), 125.7 (d), 92.7 (s), 53.5 (q); HRMS (ES) found 366.9193 $[\text{M} + \text{Na}]^+$; calculated for $\text{C}_{10}\text{H}_8^{35}\text{Cl}_4\text{N}_2\text{O}_3\text{Na}$ 366.9187.

***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-bromoaniline Table 2 Entry 2**

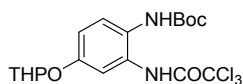
Colourless solid; m.p. 94–95 °C; R_f = 0.73 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.42 (br s, 1H), 7.58–7.56 (m, 1H), 7.44–7.31 (m, 2H), 6.75 (br s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.8 (s), 155.5 (s), 132.0 (s), 131.5 (s), 129.6 (d), 128.4 (s), 127.5 (d), 120.2 (s), 92.7 (s), 53.5 (q); HRMS (ES) found 405.9127 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{10}\text{H}_{12}^{79}\text{Br}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 405.9122.

***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4-methoxyaniline Table 2 Entry 3**

Colourless solid; m.p. 106–107 °C; R_f = 0.78 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.83 (br s, 1H), 7.40 (s, 1H), 6.76 (d, J = 8.8 Hz, 1H), 6.73 (dd, J = 8.8, 2.8 Hz, 1H), 6.39 (br s, 1H), 3.80 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.3 (s), 158.0 (s), 155.0 (s), 131.5 (s), 125.6 (d), 122.4 (s), 113.3 (d), 109.6 (d), 93.1 (s), 81.7 (s), 55.7 (q), 28.3 (q); HRMS (ES) found 400.0594 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{14}\text{H}_{21}^{35}\text{Cl}_3\text{N}_3\text{O}_4$ 400.0592.

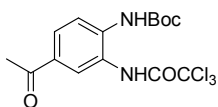
***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4-(OTHP)aniline Table 2 Entry 4**

Colourless solid; m.p. 83–85 °C; R_f = 0.75 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.81 (br s, 1H), 7.51 (br s, 1H), 6.97 (d, J = 8.8 Hz, 1H), 6.89 (dd, J = 8.8, 2.8 Hz, 1H), 6.51 (br s, 1H), 5.43 (t, J = 2.9 Hz, 1H), 3.90–3.85 (m, 1H), 3.63–3.59 (m, 1H), 1.99–1.97 (m,

1H), 1.87–1.84 (m, 2H), 1.68–1.67 (m, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.2 (s), 155.5 (s), 154.9 (s), 131.4 (s), 125.6 (d), 123.2 (s), 114.9 (d), 113.5 (d), 96.4 (d), 93.0 (s), 81.9 (s), 61.9 (t), 30.1 (t), 28.3 (q), 25.1 (t), 18.5 (t); HRMS (ES) found 475.0580 $[\text{M} + \text{Na}]^+$; calculated for $\text{C}_{18}\text{H}_{23}^{35}\text{Cl}_3\text{N}_2\text{O}_5\text{Na}$ 475.0570.

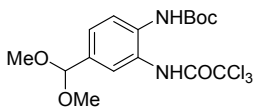
***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4-(1,1-dimethoxymethyl)aniline Table 2 Entry 5**



Colourless waxy solid; R_f = 0.69 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.89 (br s, 1H), 7.79 (s, 1H), 7.26 (dd, J = 8.1, 1.8 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.82 (br s, 1H), 5.39 (s, 1H), 3.32 (s, 6H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.8 (s), 153.7 (s), 133.9 (s), 132.6 (s), 127.9 (d), 126.7 (d), 126.1 (s), 123.4 (d), 102.0 (d), 92.3 (s), 80.7 (s), 65.1 (q), 28.3 (q); HRMS (ES) found 403.0002 $[\text{M} + \text{Na}]^+$; calculated for $\text{C}_{14}\text{H}_{15}^{35}\text{Cl}_3\text{N}_2\text{O}_4\text{Na}$ 402.9995 (accurate mass was performed on corresponding aldehyde).

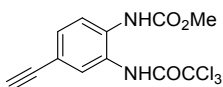
***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-ethynylaniline Table 2 Entry 6**



Colourless solid; m.p. 97–98 °C; R_f = 0.64 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.57 (br s, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.41 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 7.32 (d, J = 1.8 Hz, 1H), 6.84 (br s, 1H), 3.80 (s, 3H), 3.11 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.5 (s), 155.7 (s), 133.1 (d), 130.5 (d), 129.7 (s), 128.3 (d), 125.6 (s), 121.2 (s), 92.8 (s), 82.1 (s), 78.5 (d), 53.5 (q); HRMS (ES) found 352.0022 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{12}\text{H}_{13}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 352.0017.

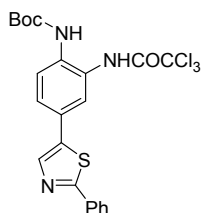
***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4-(2-phenylthiazol-5-yl)-aniline Table 2 Entry 7**



Colourless solid; m.p. 118–120 °C; R_f = 0.53 (cyclohexane /ethyl acetate 3:1);

^1H NMR (400 MHz, CDCl_3): δ 9.91 (br s, 1H), 8.30 (d, J = 1.7 Hz, 1H), 8.04–8.00 (m, 2H), 7.87 (dd, J = 8.3, 2.0 Hz, 1H), 7.50 (s, 1H), 7.46–7.42 (m, 3H), 7.16 (d, J = 8.3 Hz, 1H), 6.68 (br s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.0 (s), 160.6 (s), 154.7 (s), 154.5 (s), 133.6 (s), 133.0 (s), 130.1 (d), 130.0 (s), 129.6 (s), 128.9 (d), 126.7 (d), 125.2 (d), 124.7 (d), 123.5 (d), 113.4 (d), 93.1 (s), 82.1 (s), 28.3 (q); HRMS (ES) found 512.0369 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_{22}\text{H}_{21}^{35}\text{Cl}_3\text{N}_3\text{O}_3\text{S}$ 512.0369.

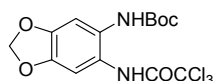
***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4-(2-phenylthiazol-5-yl)-aniline Table 3 Entry 8**



Colourless solid; m.p. 118–120 °C; R_f = 0.53 (cyclohexane /ethyl acetate 3:1);

^1H NMR (400 MHz, CDCl_3): δ 9.91 (br s, 1H), 8.30 (d, J = 1.7 Hz, 1H), 8.04–8.00 (m, 2H), 7.87 (dd, J = 8.3, 2.0 Hz, 1H), 7.50 (s, 1H), 7.46–7.42 (m, 3H), 7.16 (d, J = 8.3 Hz, 1H), 6.68 (br s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.0 (s), 160.6 (s), 154.7 (s), 154.5 (s), 133.6 (s), 133.0 (s), 130.1 (d), 130.0 (s), 129.6 (s), 128.9 (d), 126.7 (d), 125.2 (d), 124.7 (d), 123.5 (d), 113.4 (d), 93.1 (s), 82.1 (s), 28.3 (q); HRMS (ES) found 512.0369 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_{22}\text{H}_{21}^{35}\text{Cl}_3\text{N}_3\text{O}_3\text{S}$ 512.0369.

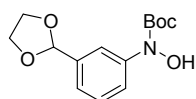
***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4,5-methylenedioxyaniline Table 2 Entry 9**



Colourless waxy solid; R_f = 0.73 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.52 (br s, 1H), 7.14 (s, 1H), 6.57 (br s, 2H), 5.98 (s, 2H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.6 (s), 154.6 (s), 146.2 (s), 146.0 (s), 124.0 (d), 123.9 (d), 106.1 (s), 105.3 (s), 102.0 (t), 92.8 (s), 81.9 (s), 28.3 (q); HRMS (ES) found 418.9953 $[\text{M} + \text{Na}]^+$; calculated for $\text{C}_{14}\text{H}_{15}^{35}\text{Cl}_3\text{N}_2\text{O}_5\text{Na}$ 418.9944.

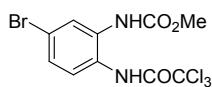
***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-5-(1,3-dioxylane-2-yl)aniline Table 2 Entry 10**



Colourless waxy solid; R_f = 0.70 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.54 (br s, 1H), 7.75 (bs, 1H), 7.36–7.35 (m, 2H), 6.81 (br s, 1H), 5.89 (s, 1H), 4.11–4.05 (m, 4H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.9 (s), 153.7 (s), 133.9 (s), 132.6 (d), 127.9 (d), 126.7 (s), 126.1 (s), 123.4 (d), 102.0 (s), 92.3 (s), 80.7 (s), 65.1 (t), 28.3 (q); HRMS (ES) found 447.0265 $[\text{M} + \text{Na}]^+$; calculated for $\text{C}_{16}\text{H}_{19}^{35}\text{Cl}_3\text{N}_2\text{O}_5\text{Na}$ 447.0257.

***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetylamino)-5-bromoaniline Table 2 Entry 11**

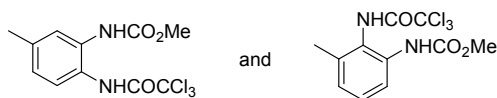


Colourless solid; m.p. 106–107 °C; R_f = 0.75 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.47 (br s, 1H), 7.90 (s, 1H), 7.38 (dd, J = 8.5, 2.3 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 6.72 (br s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.6 (s), 155.5 (s), 130.9 (s), 130.4 (d), 129.0 (s), 128.8 (s), 126.0 (d), 119.6 (d), 92.6 (s), 53.5 (q); HRMS (ES) found 388.8876 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_{10}\text{H}_9^{79}\text{Br}^{35}\text{Cl}_3\text{N}_2\text{O}_3$ 388.8862.

***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetylamino)-5-methylaniline and**

***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetylamino)-3-methylaniline Table 2 Entry 12**

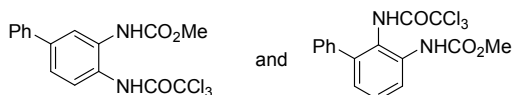


Colourless oil; R_f = 0.73 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.42 (br s, 0.58H), 9.00 (br s, 0.42H), 7.46–7.44 (m, 0.58H), 7.15–6.98 (m, 3.5H), 3.73 (s, 1.7H), 3.72 (s, 1.3H), 2.28 (s, 1.7H), 2.25 (s, 1.3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.8 (s), 160.5 (s), 155.8 (s), 155.5 (s), 137.7 (s), 137.0 (s), 132.8 (s), 130.1 (s), 128.4 (d), 128.2 (d), 127.4 (s), 127.3 (d), 126.7 (s), 125.8 (d), 125.1 (d), 121.8 (d), 92.9 (s), 92.8 (s), 53.2 (q), 53.0 (q), 21.0 (q), 18.0 (q); HRMS (ES) found 342.0290 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{11}\text{H}_{15}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 342.0285.

***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetylamino)-5-phenylaniline and**

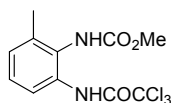
***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetylamino)-3-phenylaniline Table 2 Entry 13**



Colourless solid; m.p. 134–135 °C; R_f = 0.75 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.58 (br s, 0.63H), 8.46 (br s, 0.37H), 7.92 (br s, 0.63 H), 7.59–7.52 (m, 1.89H), 7.45–7.32 (m, 4.85H), 7.26–7.20 (m, 0.63H), 6.97 (br s, 0.37H), 6.88 (br s, 0.63 H), 3.79 (s, 1.89H), 3.76 (s, 1.11H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.7 (s), 160.4 (s), 155.7 (s), 155.1 (s), 140.3 (s), 140.0 (s), 139.4 (s), 137.7 (s), 133.5 (s), 129.9 (d), 129.0 (d), 128.9 (d), 128.7 (d), 128.7 (d), 128.0 (d), 127.8 (d), 127.4 (d), 127.1 (d), 125.9 (d), 125.5 (d), 125.0 (d), 124.4 (d), 124.0 (d), 120.0 (s), 93.0 (s), 92.2 (s), 53.3 (q), 52.8 (q); HRMS (ES) found 387.0073 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_{16}\text{H}_{14}^{35}\text{Cl}_3\text{N}_2\text{O}_3$ 387.0070.

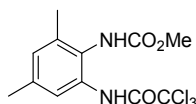
***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-6-methylaniline Table 2 Entry 14**



Colourless solid; m.p. 82–83 °C; R_f = 0.72 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, DMSO) δ 9.91 (br s, 1H), 8.91 (br s, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.22 (dd, J = 7.6, 7.6 Hz, 1H), 6.52 (br s, 1H), 3.83 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 159.7 (s), 155.0 (s), 135.8 (s), 132.3 (s), 131.0 (s), 128.7 (d), 126.6 (d), 123.4 (d), 92.9 (s), 52.2 (q), 17.9 (q); HRMS (ES) found 342.0290 $[\text{M} + \text{NH}_4]^+$; calculated for $\text{C}_{11}\text{H}_{15}^{35}\text{Cl}_3\text{N}_3\text{O}_3$ 342.0285.

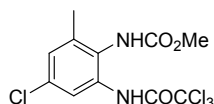
***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4,6-dimethylaniline Table 2 Entry 15**



Colourless solid; m.p. 85–87 °C; R_f = 0.76 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.31 (br s, 1H), 7.39 (br s, 1H), 6.92 (s, 1H), 6.47 (br s, 1H), 3.76 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.3 (s), 155.8 (s), 137.4 (s), 134.0 (s), 131.4 (s), 129.5 (d), 125.5 (d), 123.7 (s), 93.0 (s), 53.2 (q), 21.0 (q), 18.0 (q); HRMS (ES) found 360.9889 $[\text{M} + \text{Na}]^+$; calculated for $\text{C}_{12}\text{H}_{13}^{35}\text{Cl}_3\text{N}_2\text{O}_3\text{Na}$ 360.9893.

***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-chloro-6-methylaniline Table 2 Entry 16**

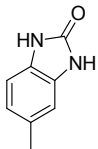


Colourless solid; m.p. 89–90 °C; R_f = 0.69 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, CDCl_3) δ 9.36 (br s, 1H), 7.68 (s, 1H), 7.13 (s, 1H), 6.36 (br s, 1H), 3.80 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.3 (s), 155.6 (s), 132.7 (s), 129.4 (d), 128.5 (d), 126.5 (s), 123.2 (s), 122.9 (s), 92.8 (s), 53.5 (q), 18.2 (q); HRMS (ES) found 380.9341 $[\text{M} + \text{Na}]^+$; calculated for $\text{C}_{11}\text{H}_{10}^{35}\text{Cl}_4\text{N}_2\text{O}_3\text{Na}$ 380.9343.

Scheme 2:

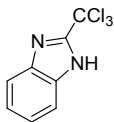
5-Methyl-1H-benzo[d]imidazol-2(3H)-one 15



Colourless solid; m.p. >250 °C; (lit.:297–302 °C)⁴; R_f = 0.20 (cyclohexane:ethyl acetate 1:1);

^1H NMR (400 MHz, DMSO) δ 10.50 (s, 1H), 10.46 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.73–6.71 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 155.5 (s), 129.9 (s), 129.4 (s), 127.5 (s), 121.0 (d), 109.1 (d), 108.2 (d), 21.1 (q). For comparison see ref 4.

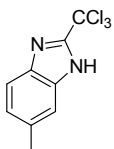
2-(2',2',2'-Trichloromethyl)-benzimidazole 18



Colourless solid; m.p. >250 °C; R_f = 0.42 (cyclohexane:ethyl acetate 3:1);

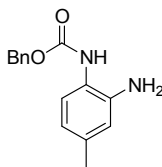
^1H NMR (400 MHz, DMSO) δ 7.68–7.65 (m, 2H), 7.35–7.31 (m, 2H); ^{13}C NMR (100 MHz, DMSO) δ 150.6 (s), 138.5 (s), 130.4 (s), 126.1 (d), 123.8 (d), 116.5 (d), 114.4 (d), 88.9 (s); HRMS (ES) found 234.9592 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_8\text{H}_6^{35}\text{Cl}_3\text{N}_2$ 234.9597.

2-(2',2',2'-Trichloromethyl)-5-methyl benzimidazole 19



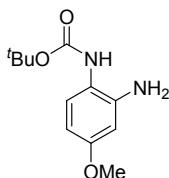
Colourless solid; m.p. 186–188 °C; R_f = 0.51 (cyclohexane:ethyl acetate 3:1);

^1H NMR (400 MHz, CDCl_3) δ 13.45 (br s, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.67 (s, 1H), 7.31 (d, J = 8.5 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.6 (s), 138.0 (s), 133.5 (s), 131.6 (s), 128.9 (d), 115.4 (d), 114.8 (d), 84.5 (s), 21.8 (q); HRMS (ES) found 248.9761 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_9\text{H}_8^{35}\text{Cl}_3\text{N}_2$ 248.9761.

Benzyl-(2-Aminophenyl) carbamate 20

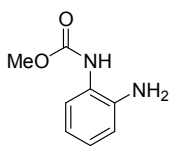
Pale yellow solid; m.p. 65–66 °C; R_f = 0.30 (cyclohexane:ethyl acetate 3:1);

^1H NMR (400 MHz, CDCl_3) δ 7.40–7.35 (m, 5H), 7.12 (d, J = 6.8 Hz, 1H), 6.62–6.59 (m, 2H), 6.45 (br s, 1H), 5.20 (s, 2H), 3.49 (br s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.8 (s), 139.9 (s), 136.8 (s), 136.4 (s), 128.6 (d), 128.2 (d), 128.2 (d), 125.5 (d), 121.8 (s), 120.6 (d), 118.3 (d), 67.2 (t), 20.9 (q); HRMS (ES) found 257.1279 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_2$ 257.1290.

***tert*-Butyl-(2-Amino-4-methoxyphenyl) carbamate 21**

Colourless solid; m.p. 84–86 °C; R_f = 0.25 (cyclohexane:ethyl acetate 3:1);

^1H NMR (400 MHz, CDCl_3) δ 7.04 (d, J = 8.3 Hz, 1H), 6.33–6.30 (m, 2H), 6.06 (br s, 1H), 3.84 (br s, 2H), 3.74 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6 (s), 154.4 (s), 142.7 (s), 127.3 (d), 117.1 (s), 104.4 (d), 102.4 (d), 80.3 (s), 55.3 (q), 28.3 (q); HRMS (ES) found 261.1205 $[\text{M} + \text{Na}]^+$; calculated for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_3\text{Na}$ 261.1215.

Methyl-(2-aminophenyl) carbamate 22

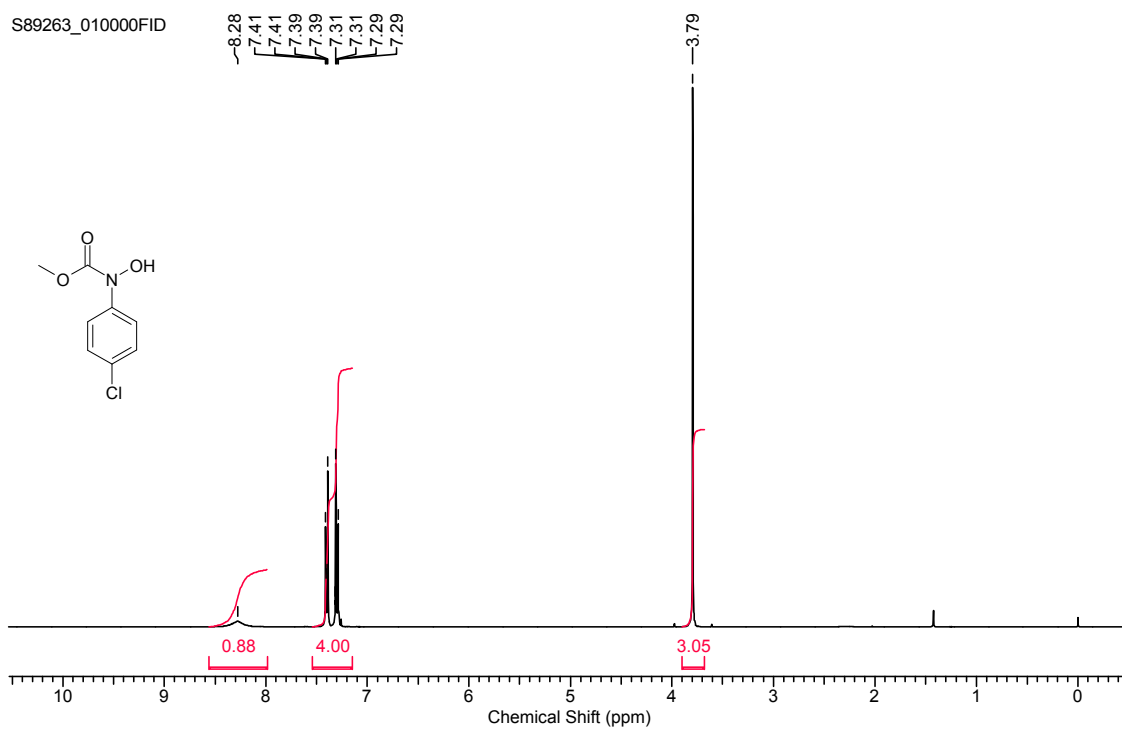
Colourless solid; m.p. 64–66 °C; R_f = 0.21 (cyclohexane:ethyl acetate 3:1);

^1H NMR (400 MHz, CDCl_3) δ 7.25 (br s, 1H), 7.05–7.01 (m, 1H), 6.81–6.75 (m, 2H), 6.59 (br s, 1H), 3.77 (s, 3H), 3.77–3.55 (br s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.3 (s), 140.2 (s), 126.6 (d), 125.1 (d), 124.2 (s), 119.5 (d), 117.4 (d), 52.5 (q); HRMS (ES) found 167.0818 $[\text{M} + \text{H}]^+$; calculated for $\text{C}_8\text{H}_{11}\text{N}_2\text{O}_2$ 167.0821.

***N*-Methoxycarbonyl-*N*-(4-chlorophenyl) hydroxylamine**

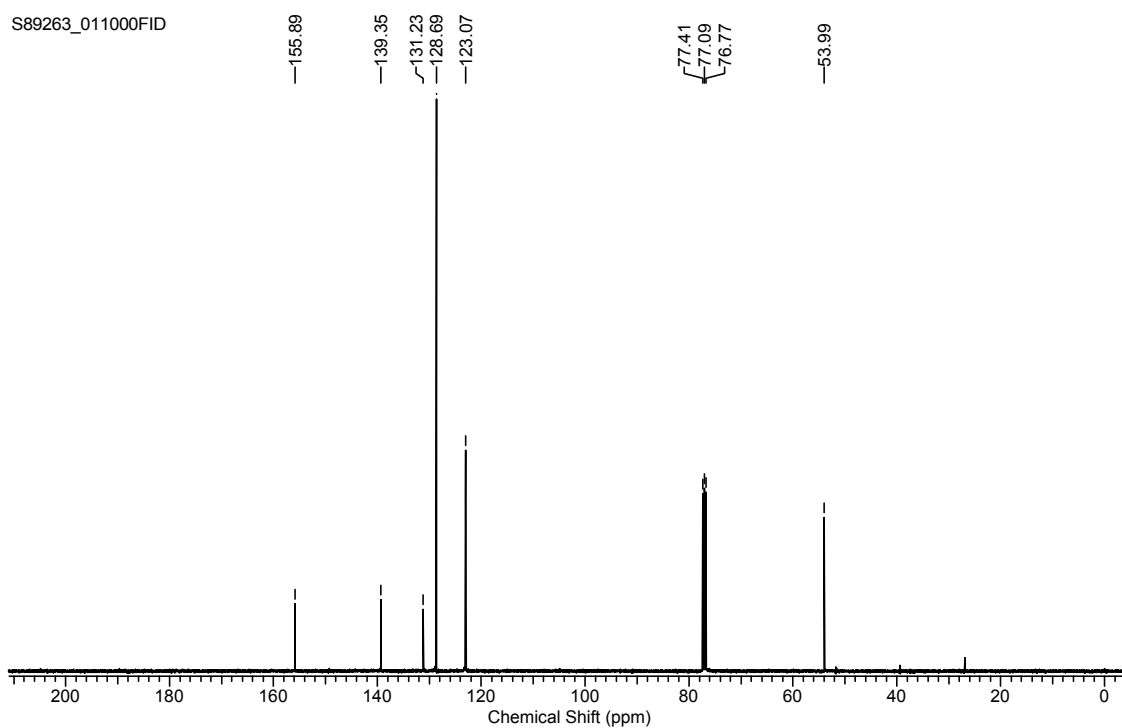
¹H NMR, CDCl₃, 400 MHz

S89263_010000FID



¹³C NMR, CDCl₃, 100 MHz

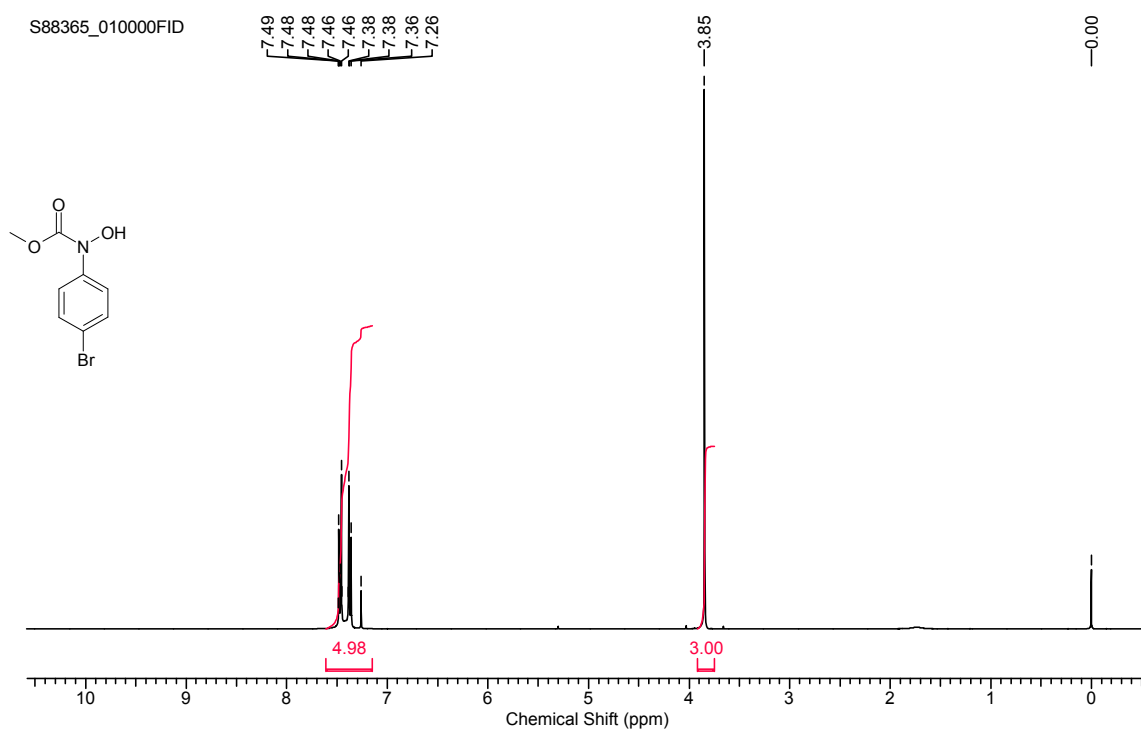
S89263_011000FID



***N*-Methoxycarbonyl-*N*-(4-bromophenyl) hydroxylamine**

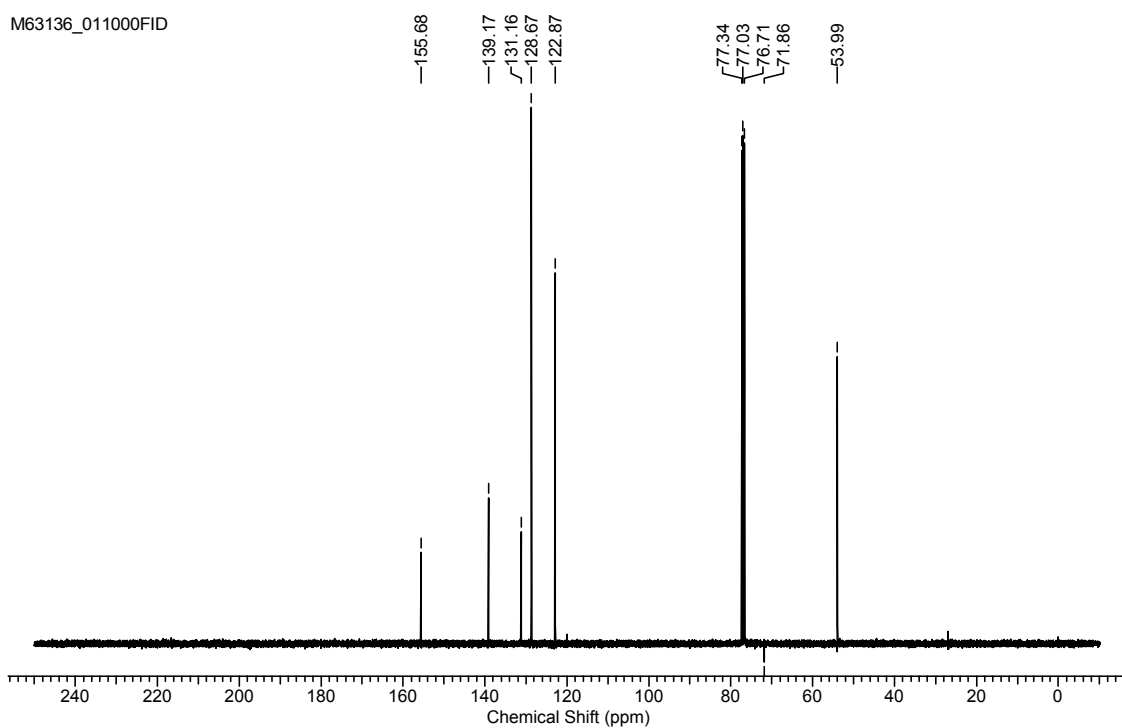
¹H NMR, CDCl₃, 400 MHz

S88365_010000FID



¹³C NMR, CDCl₃, 100 MHz

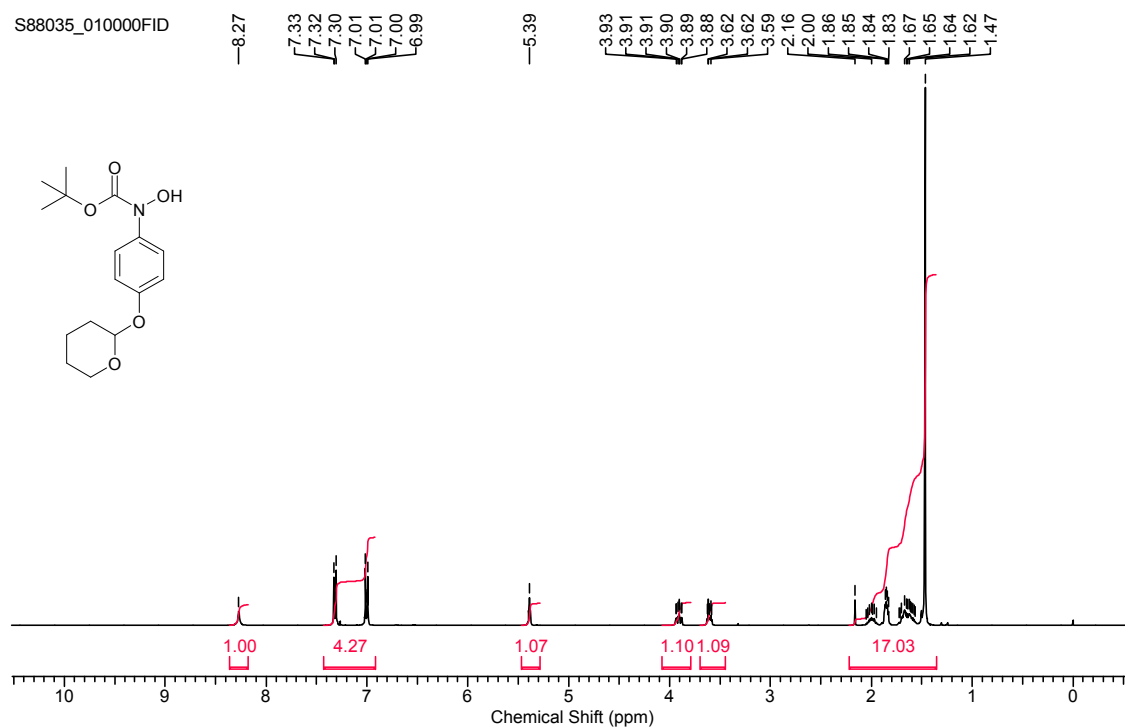
M63136_011000FID



***N*-Boc-*N*-(4-(tetrahydropyranyloxy)phenyl) hydroxylamine**

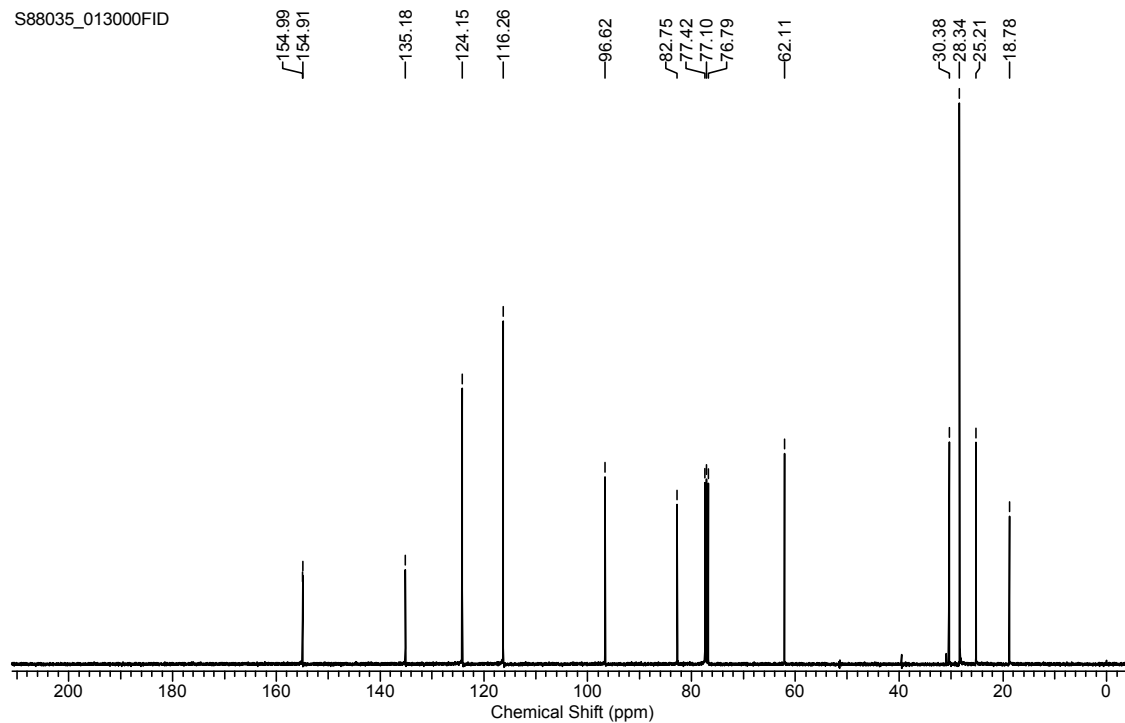
¹H NMR, CDCl₃, 400 MHz

S88035_010000FID



¹³C NMR, CDCl₃, 100 MHz

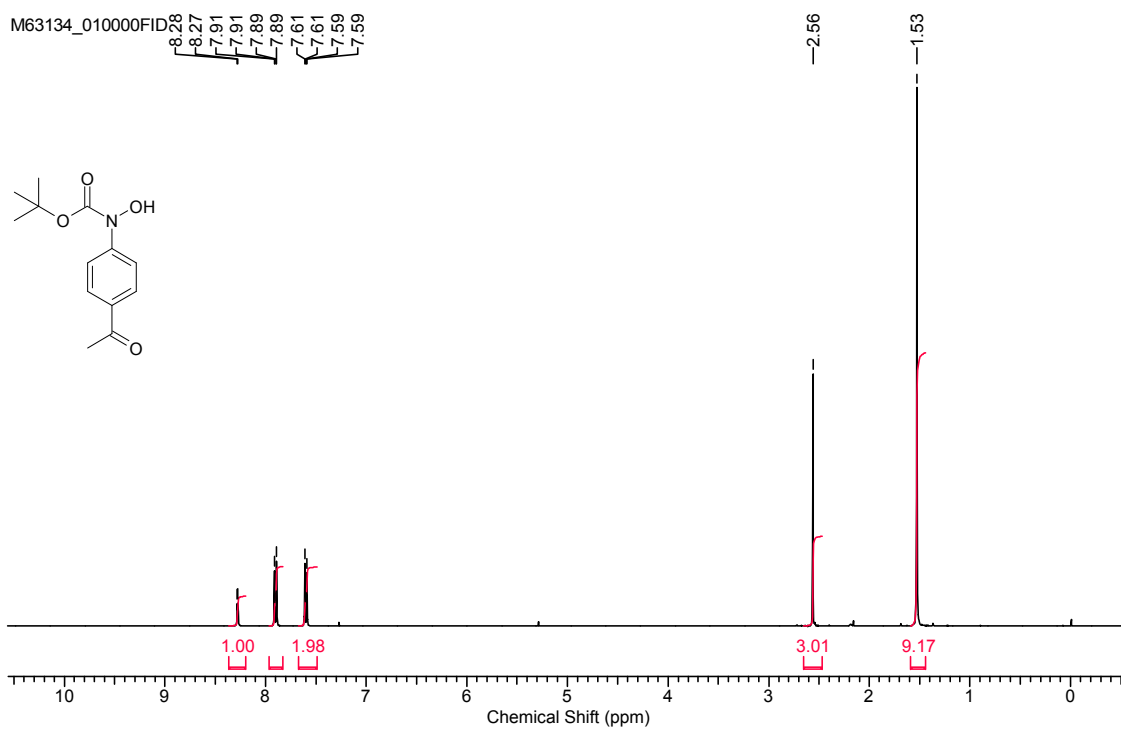
S88035_013000FID



***N*-Boc-*N*-(4-Acetophenyl) hydroxylamine**

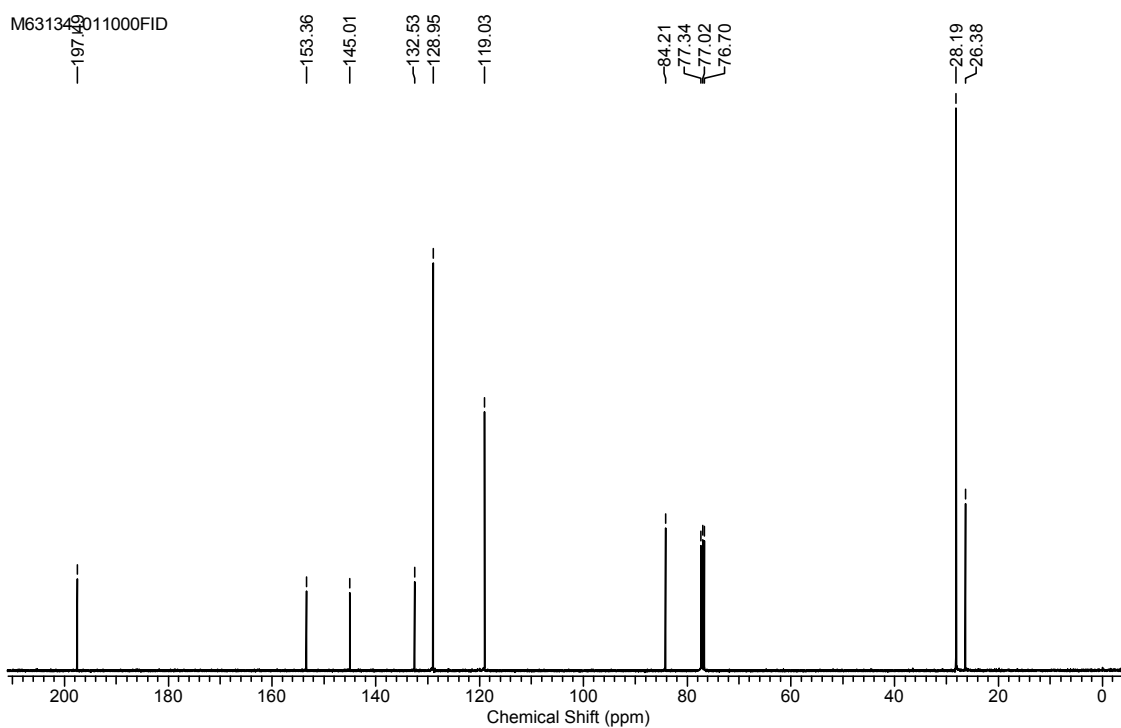
¹H NMR, CDCl₃, 400 MHz

M63134_010000FID



¹³C NMR, CDCl₃, 60 MHz

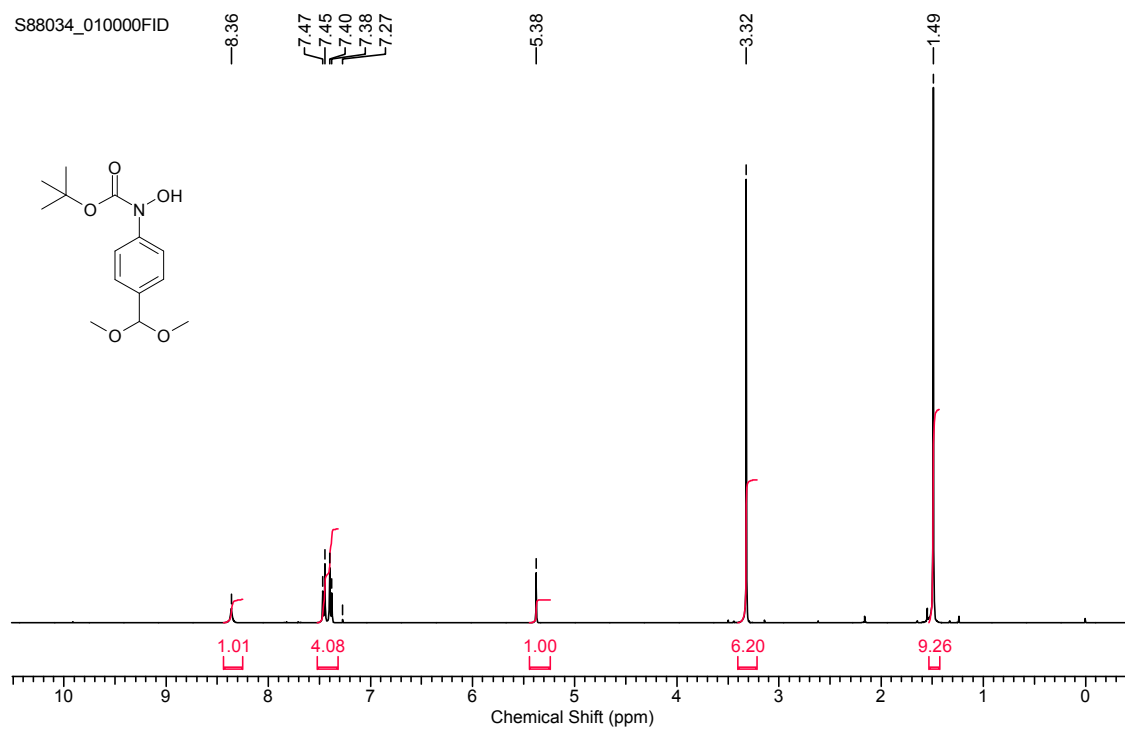
M63134_011000FID



***N*-Boc-*N*-(4-Dimethoxymethylphenyl) hydroxylamine**

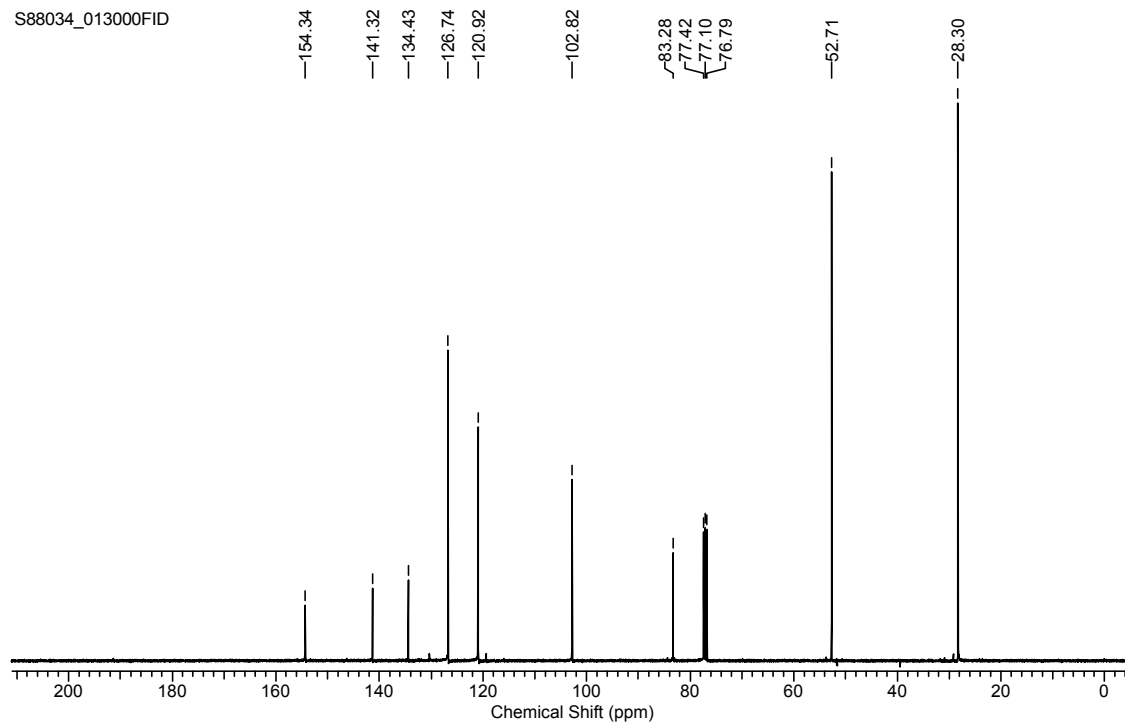
¹H NMR, CDCl₃, 400 MHz

S88034_010000FID



¹³C NMR, CDCl₃, 100 MHz

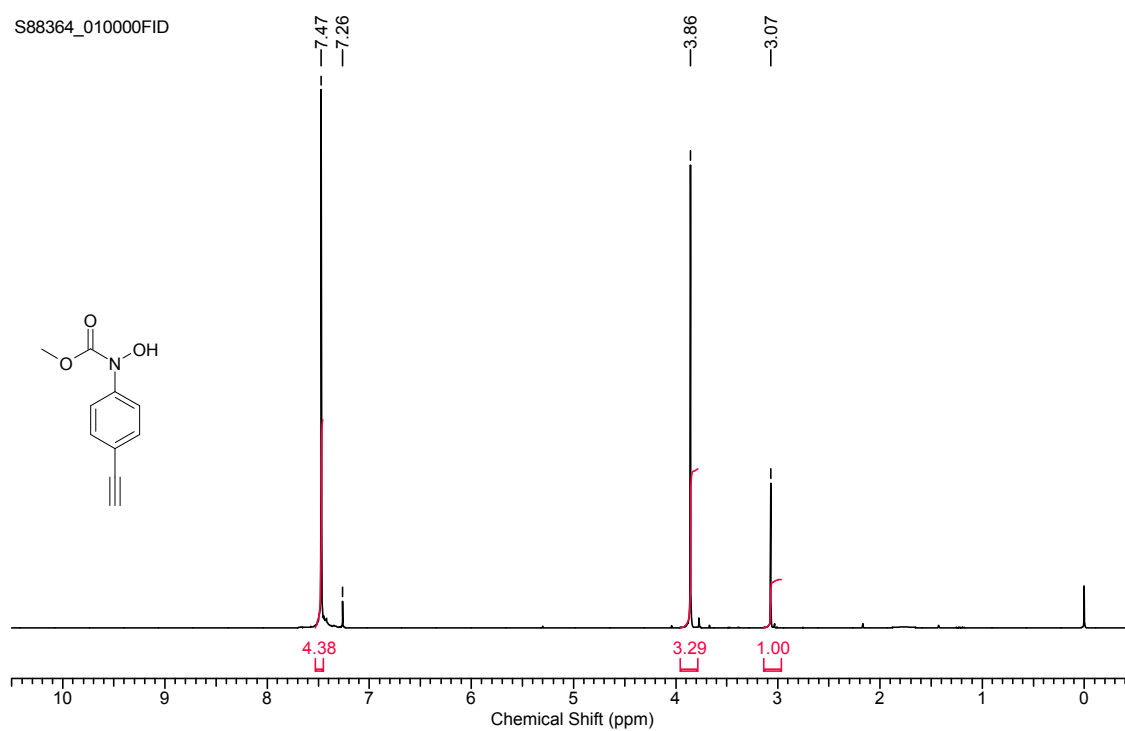
S88034_013000FID



***N*-Methoxycarbonyl-*N*-(4-ethynylphenyl) hydroxylamine**

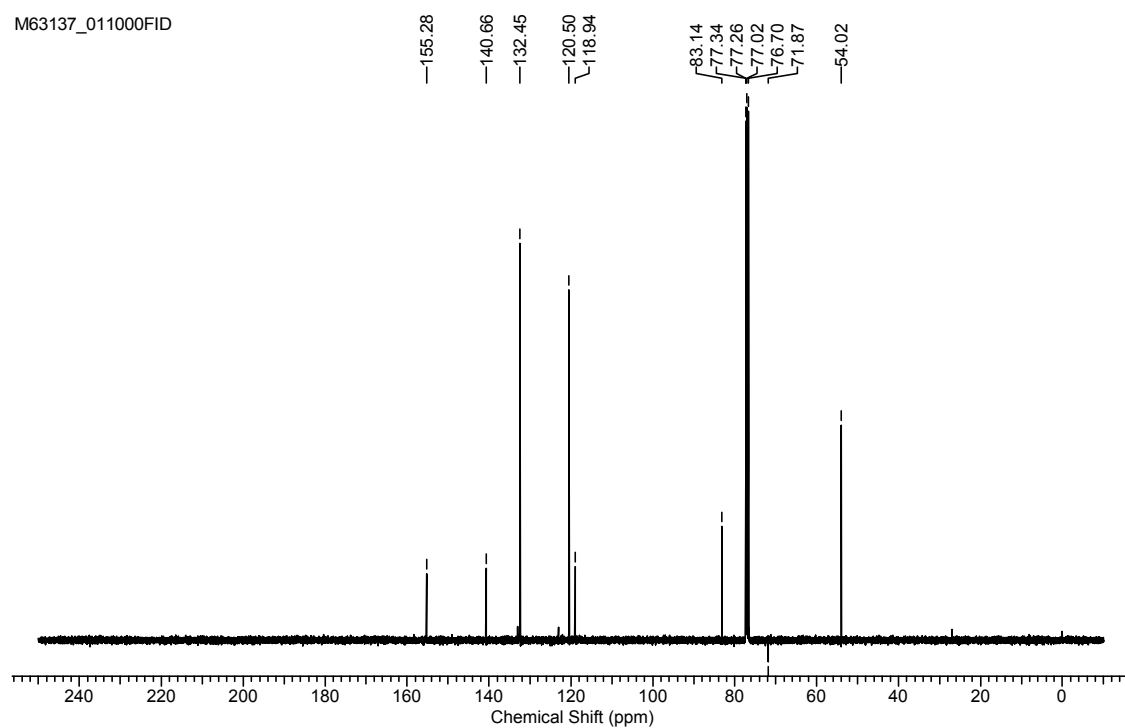
¹H NMR, CDCl₃, 400 MHz

S88364_010000FID



¹³C NMR, CDCl₃, 60 MHz

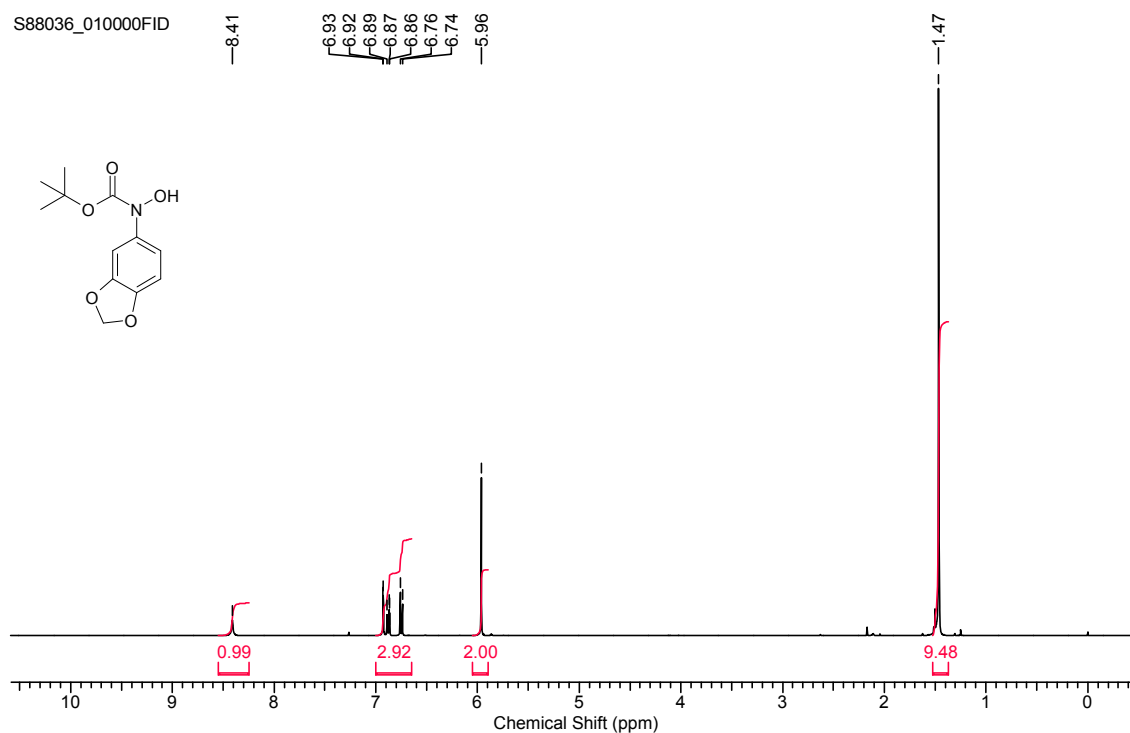
M63137_011000FID



***N*-Boc-*N*-(3,4-Methylenedioxyphenyl) hydroxylamine**

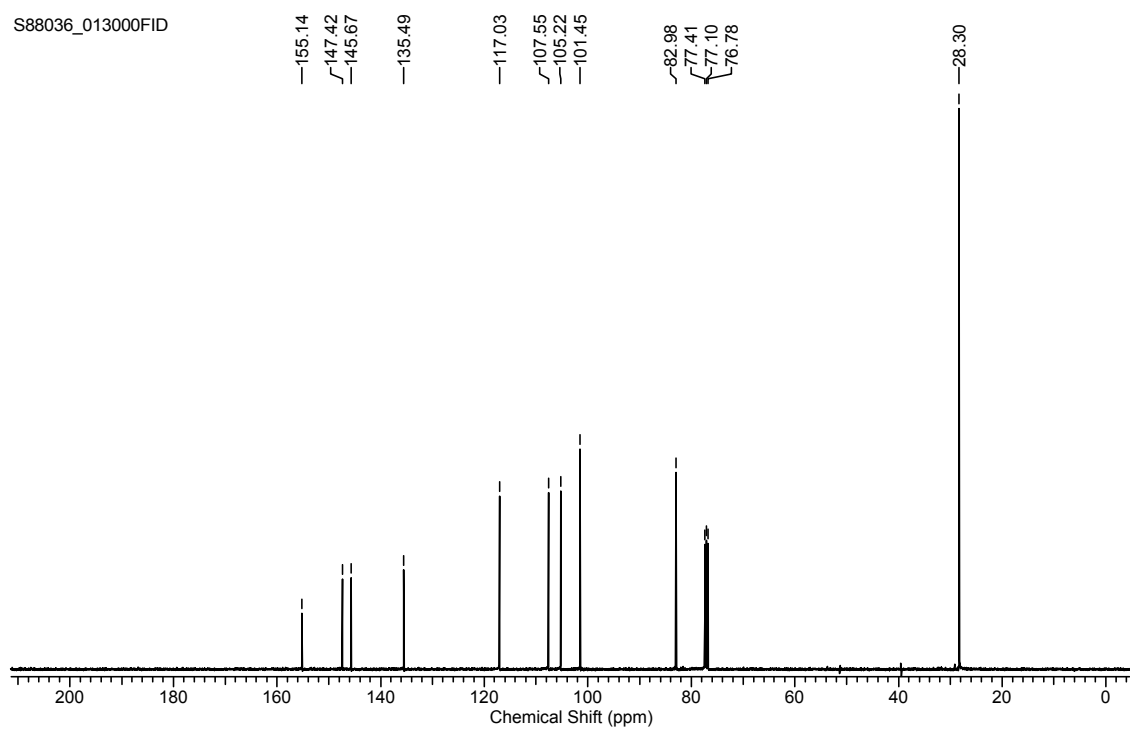
¹H NMR CDCl₃, 400 MHz

S88036_010000FID



¹³C NMR, CDCl₃, 100 MHz

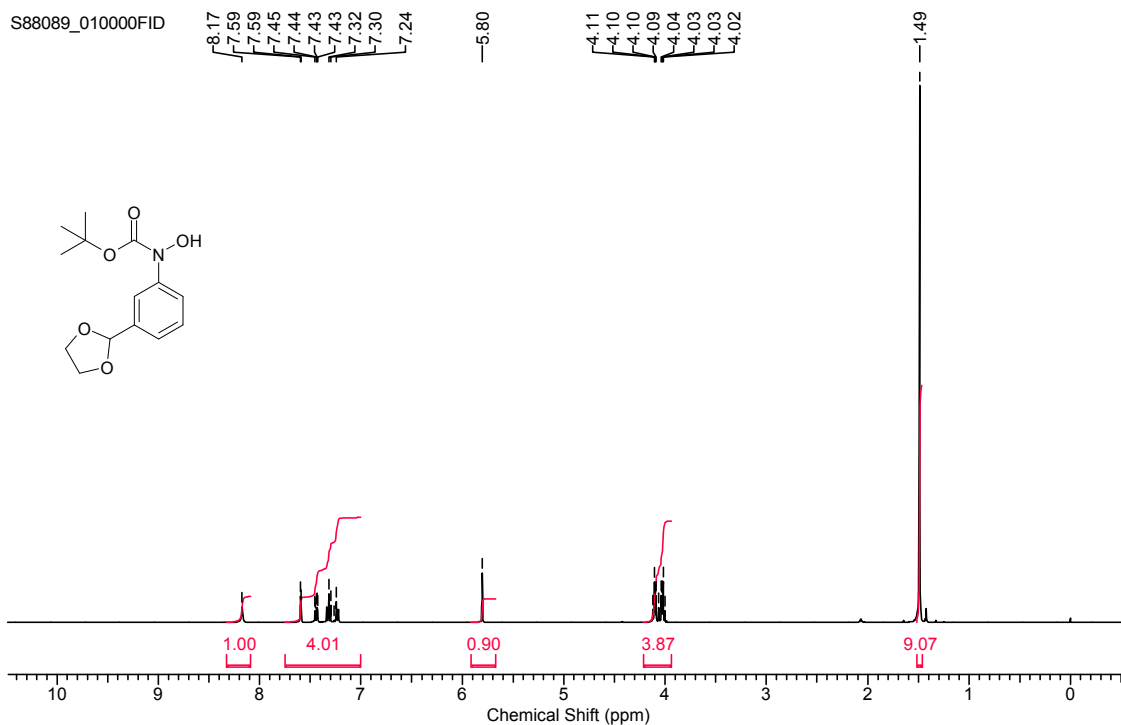
S88036_013000FID



***N*-Boc-*N*-(3-(1,3-Dioxolan-2-yl)phenyl) hydroxylamine**

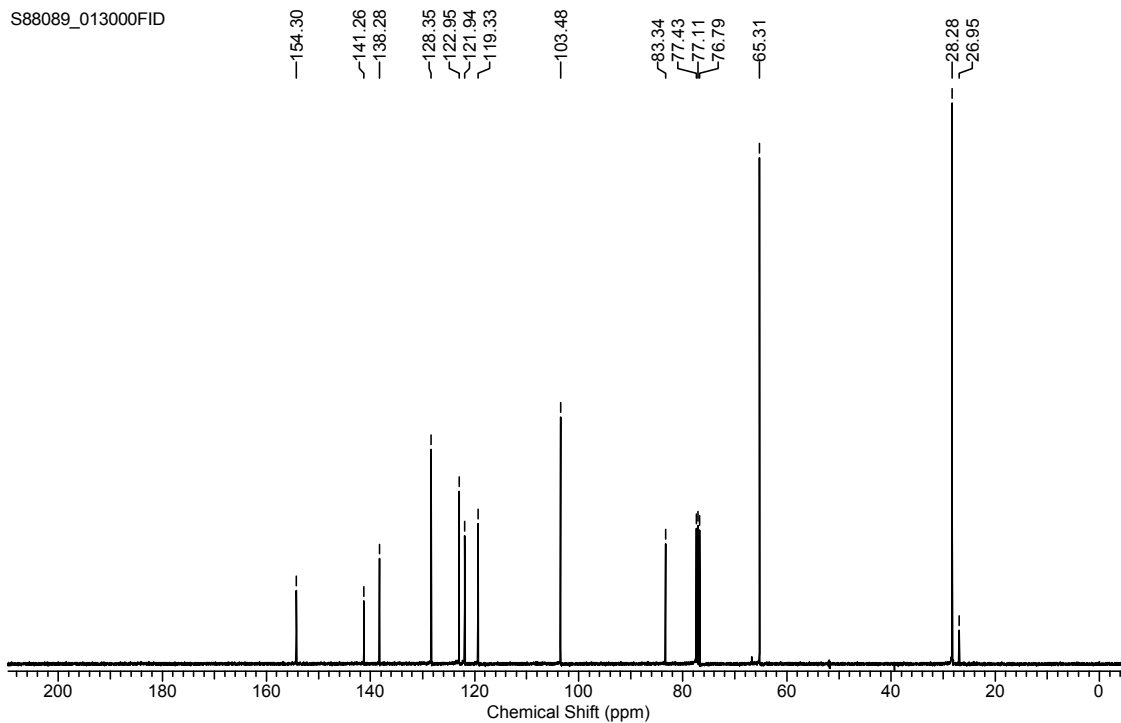
¹H NMR, CDCl₃, 400 MHz

S88089_010000FID



¹³C NMR, CDCl₃, 100 MHz

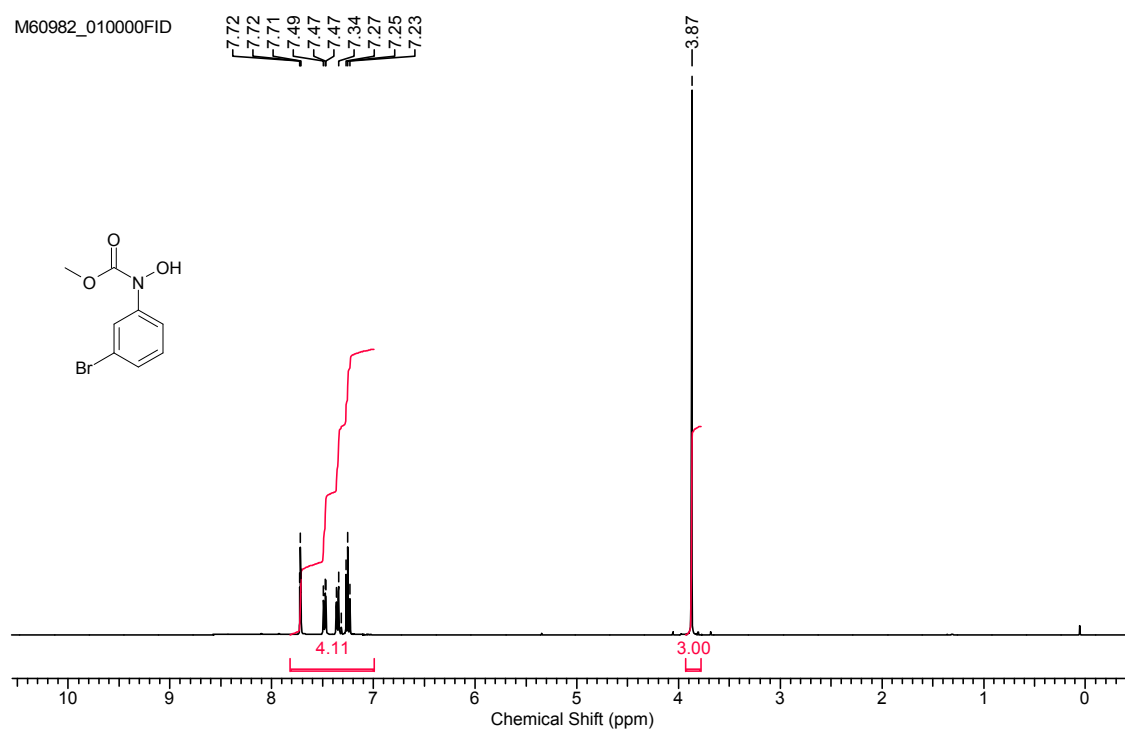
S88089_013000FID



***N*-Methoxycarbonyl-*N*-(3-bromophenyl) hydroxylamine**

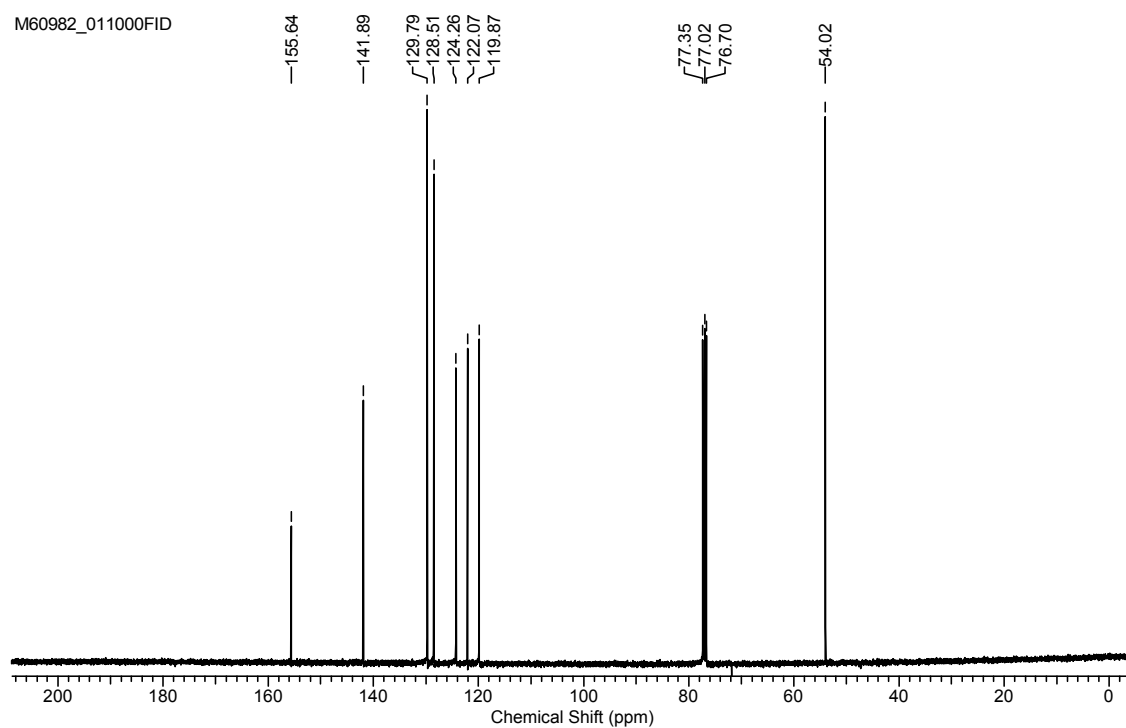
¹H NMR, CDCl₃, 400 MHz

M60982_010000FID



¹³C NMR, CDCl₃, 100 MHz

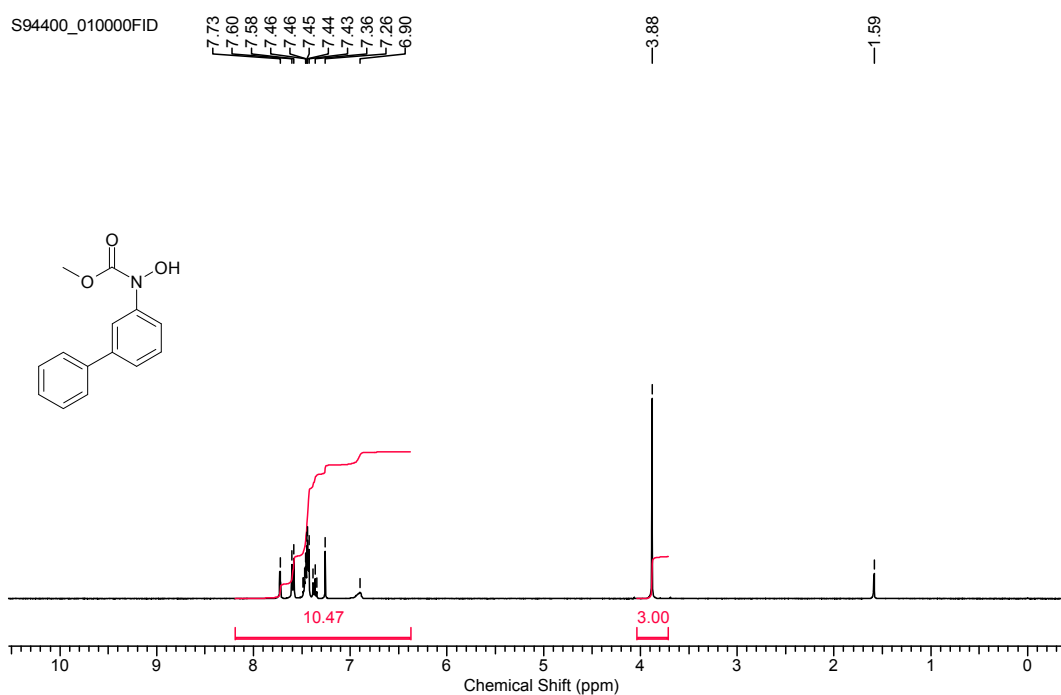
M60982_011000FID



***N*-Methoxycarbonyl-*N*-(3-biphenyl) hydroxylamine**

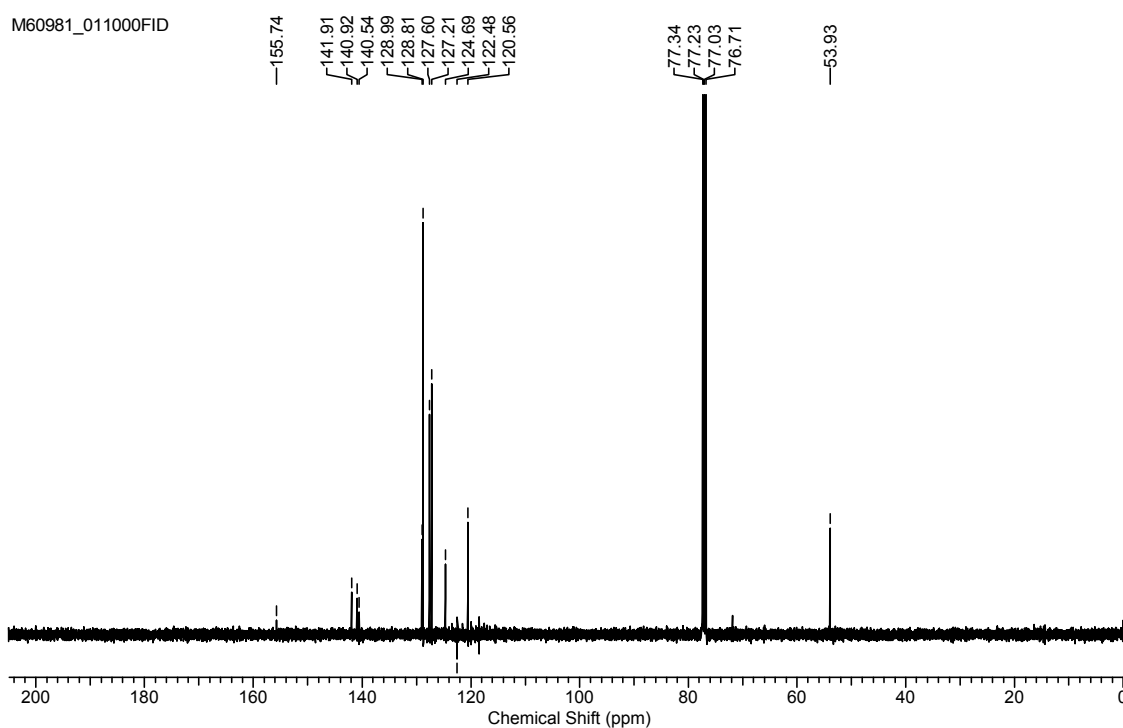
¹H NMR, CDCl₃, 400 MHz

S94400_010000FID



¹³C NMR, CDCl₃, 100 MHz

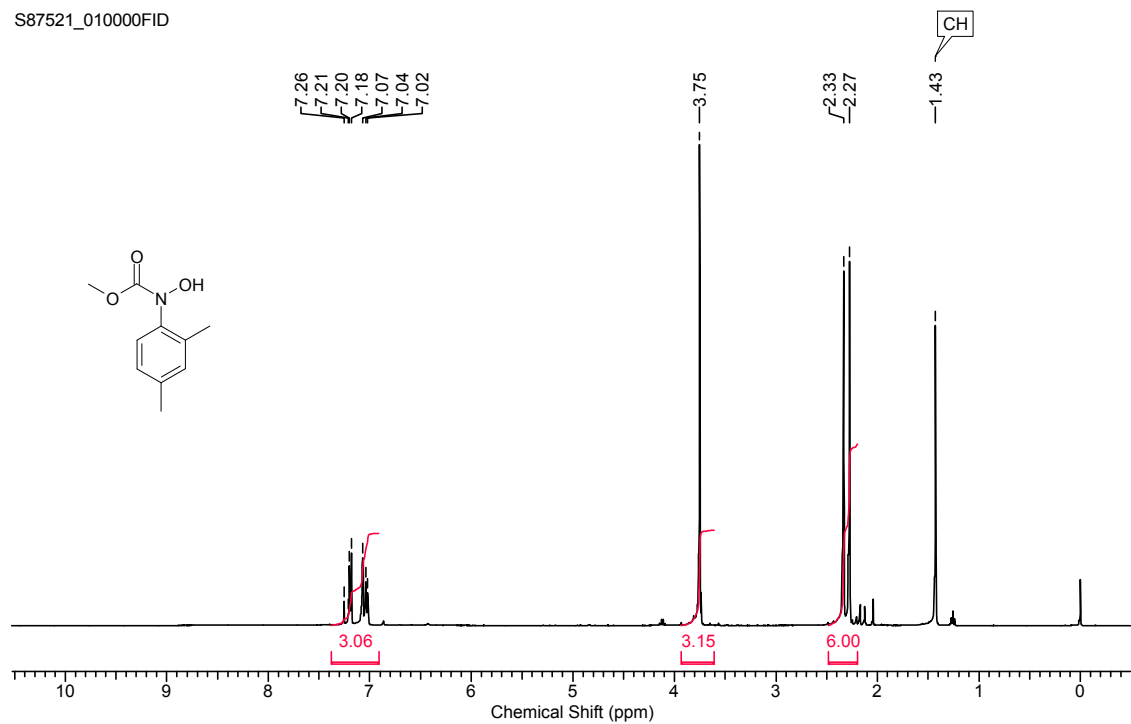
M60981_011000FID



***N*-Methoxycarbonyl-*N*-(2,4-dimethylphenyl) hydroxylamine**

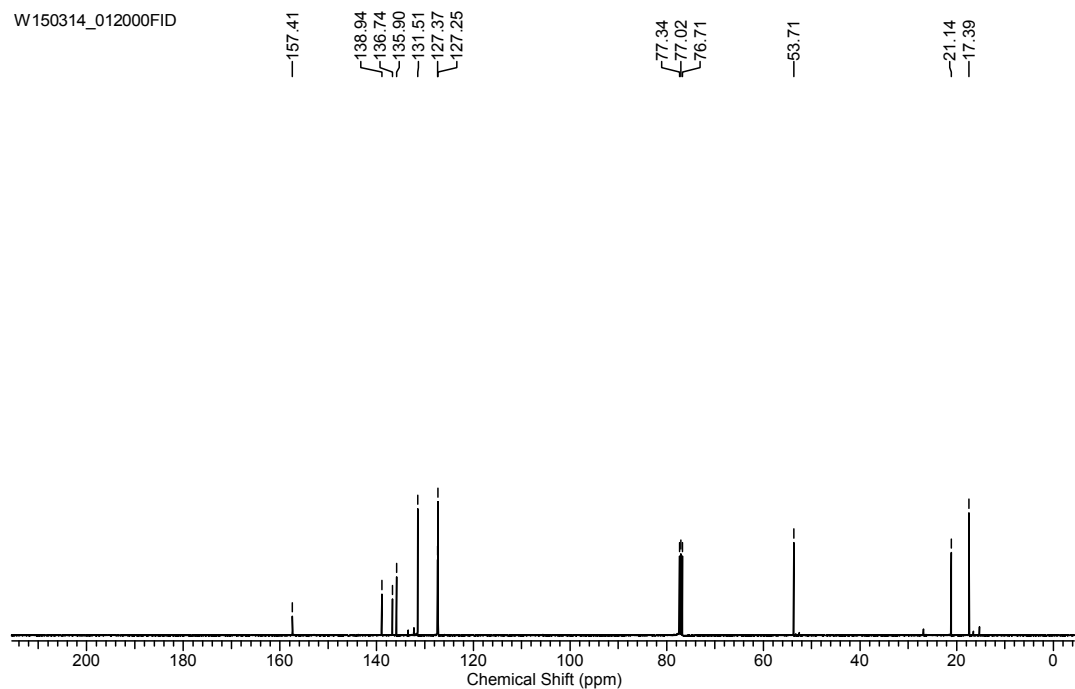
¹H NMR, CDCl₃, 400 MHz

S87521_010000FID



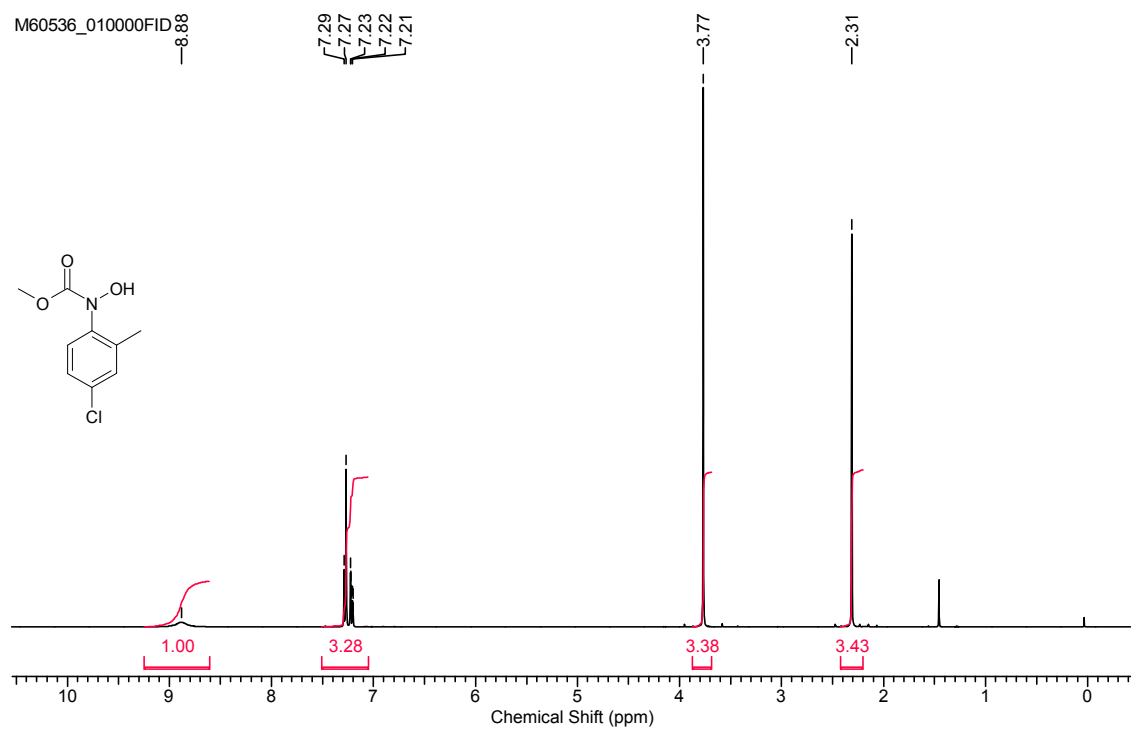
¹³C NMR, CDCl₃, 100 MHz

W150314_012000FID

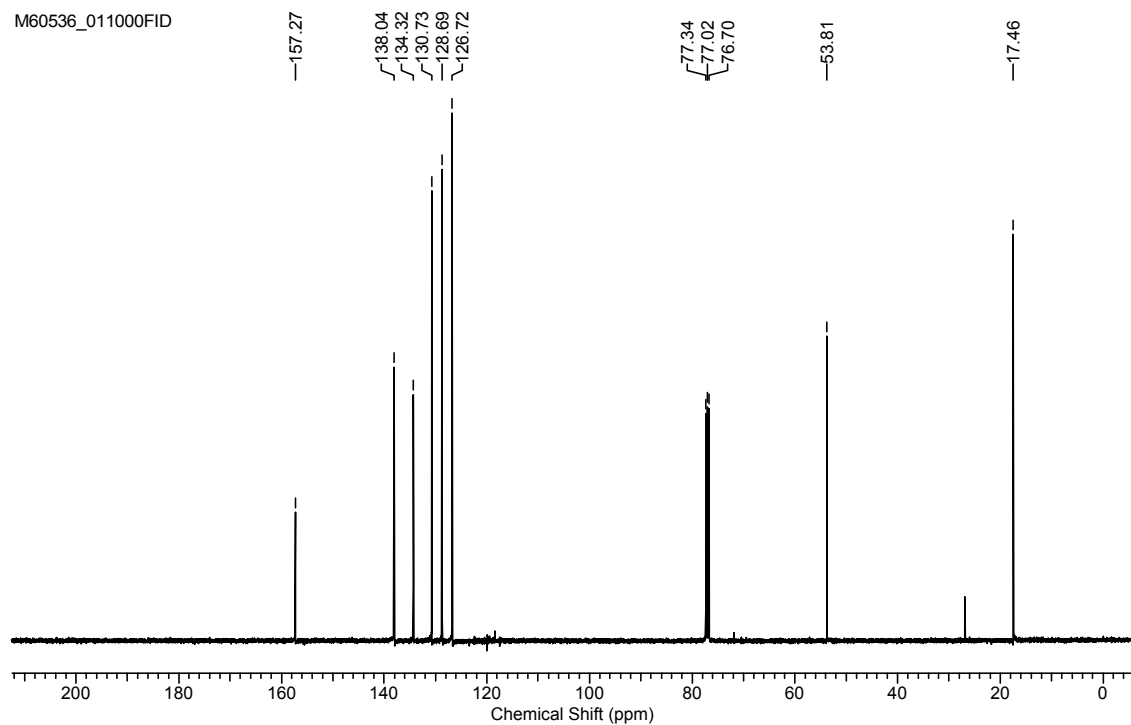


***N*-Methoxycarbonyl-*N*-(4-chloro-2-methylphenyl) hydroxylamine**

¹H NMR, CDCl₃, 400 MHz



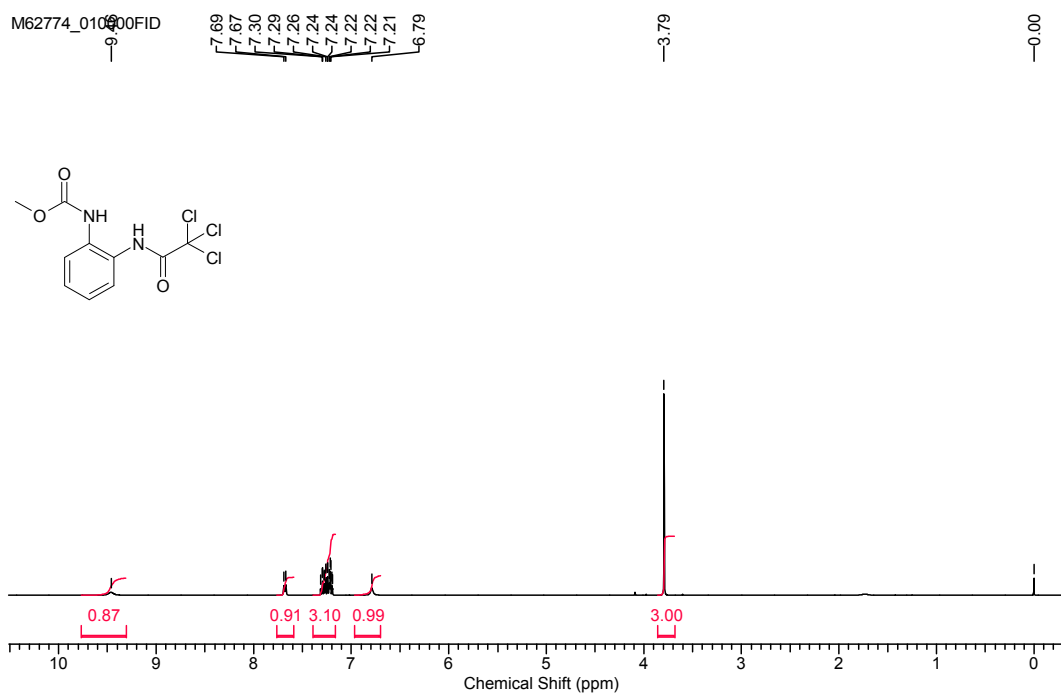
¹³C NMR, CDCl₃, 100 MHz



***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-aniline Table 1, Entry 1**

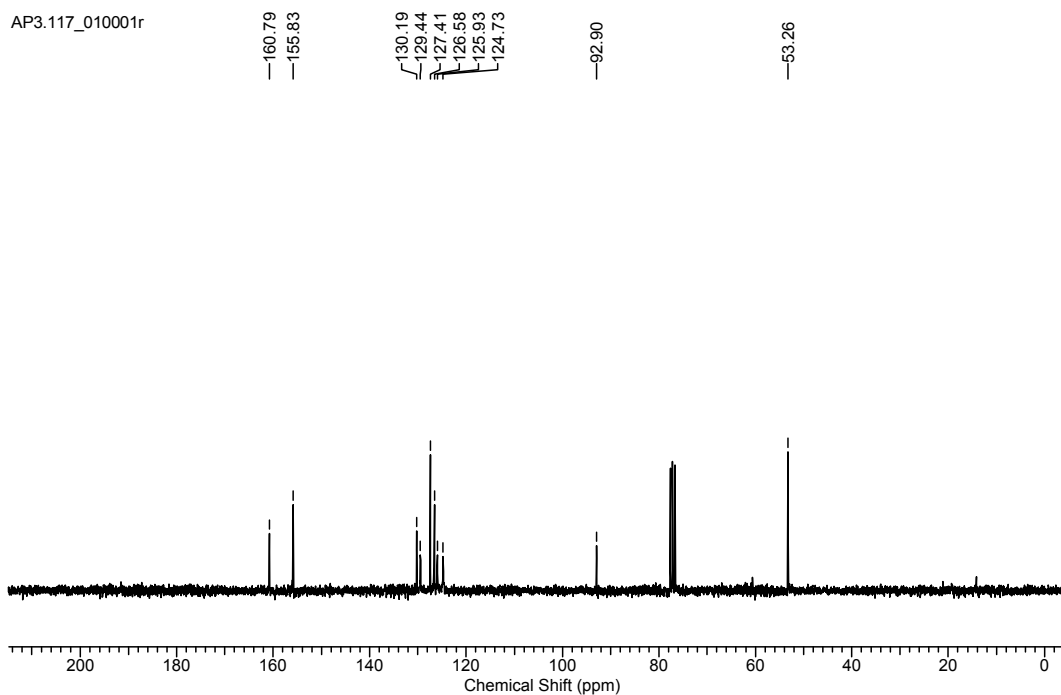
¹H NMR, CDCl₃, 400 MHz

M62774_010000FID



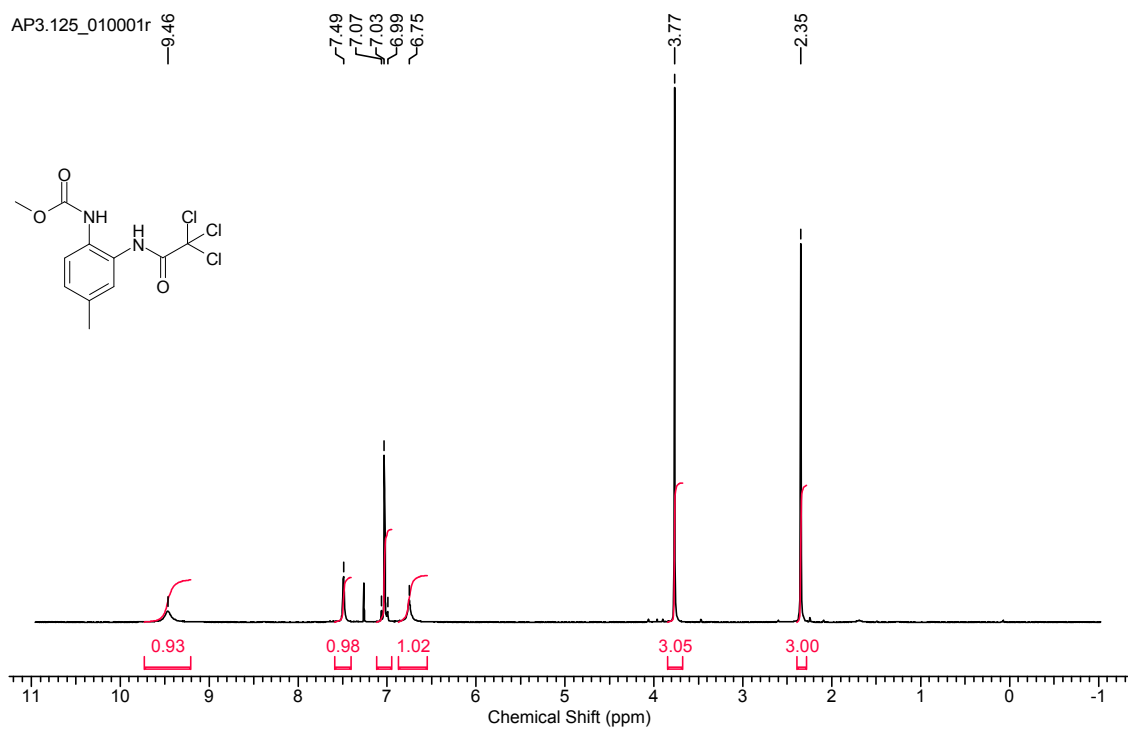
¹³C NMR, CDCl₃, 100 MHz

AP3.117_010001r

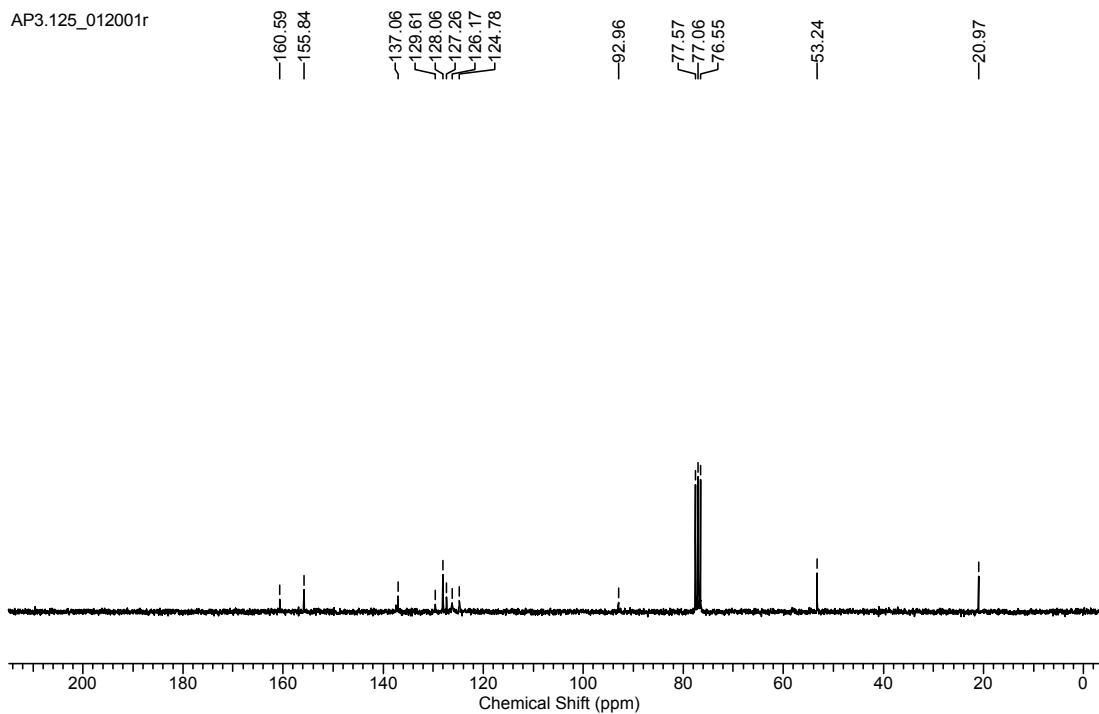


***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-methylaniline Table 1 Entry 2**

¹H NMR, CDCl₃, 400 MHz

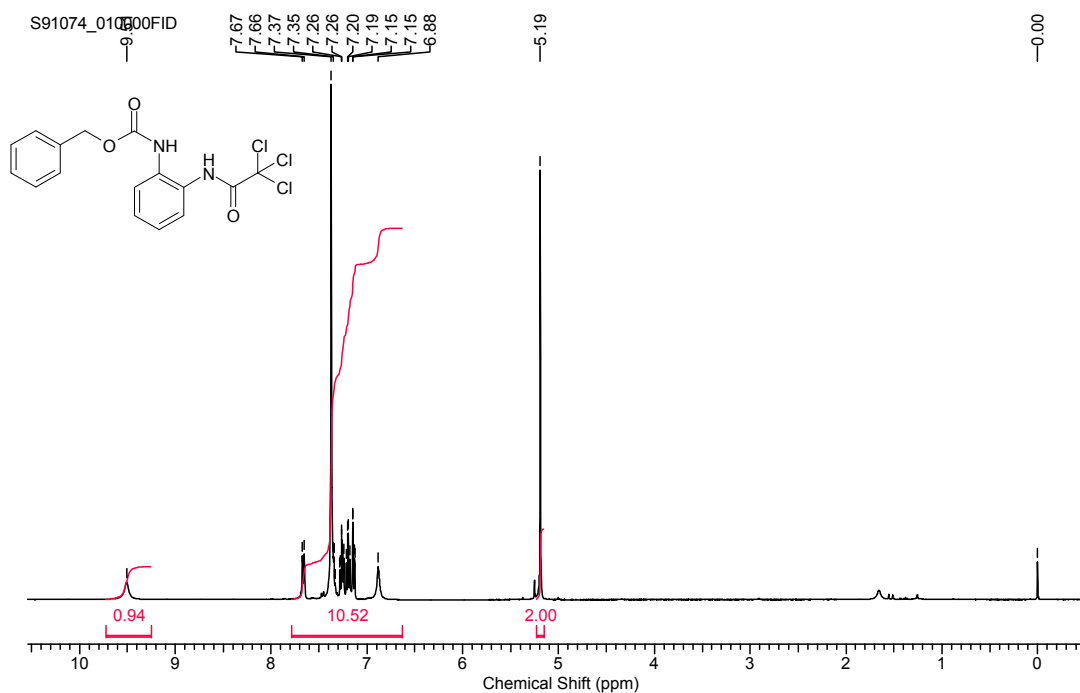


¹³C NMR, CDCl₃, 100 MHz

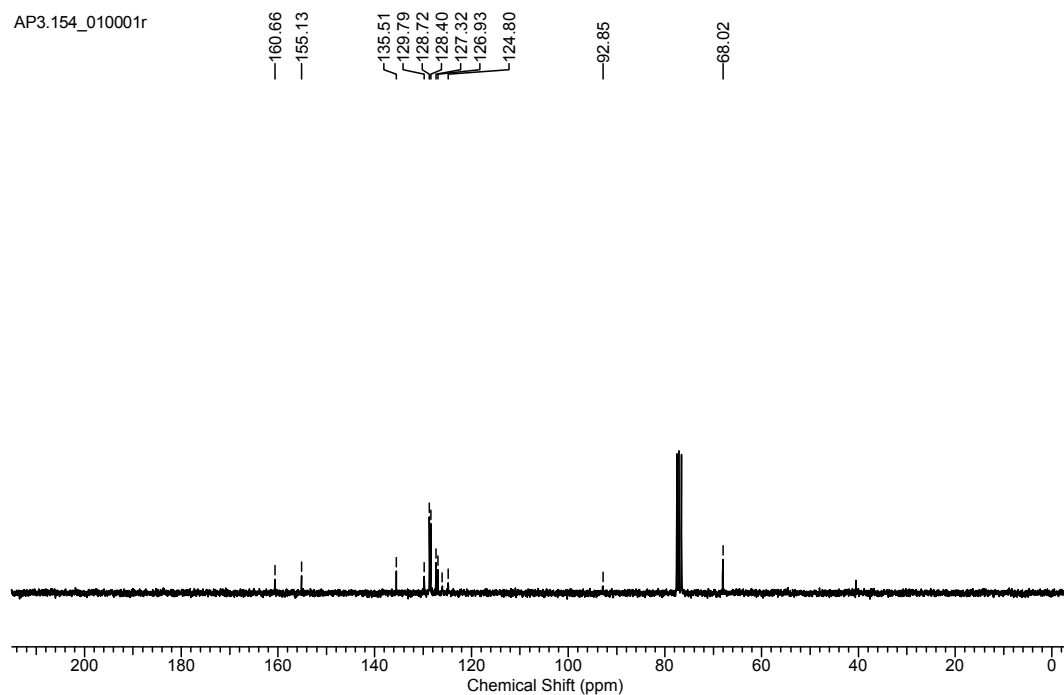


***N*-Cbz-2-(2',2',2'-Trichloroacetyl-amino)-aniline Table 1 Entry 3**

¹H NMR, CDCl₃, 400 MHz

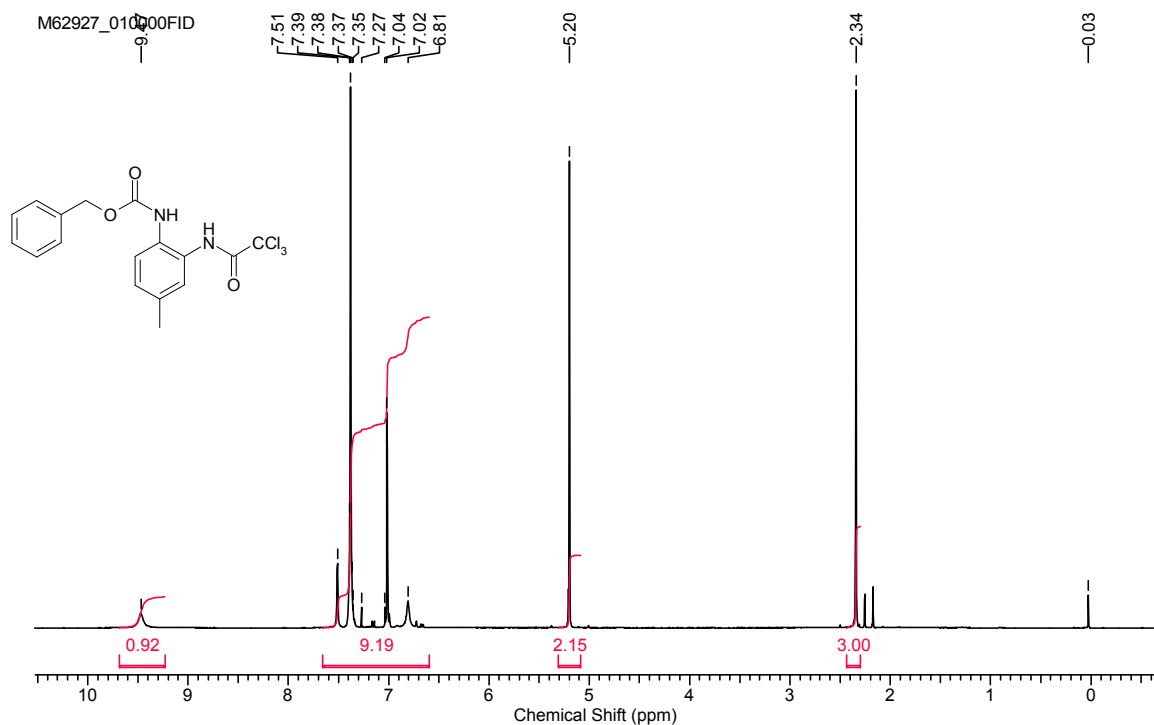


¹³C NMR, CDCl₃, 100 MHz

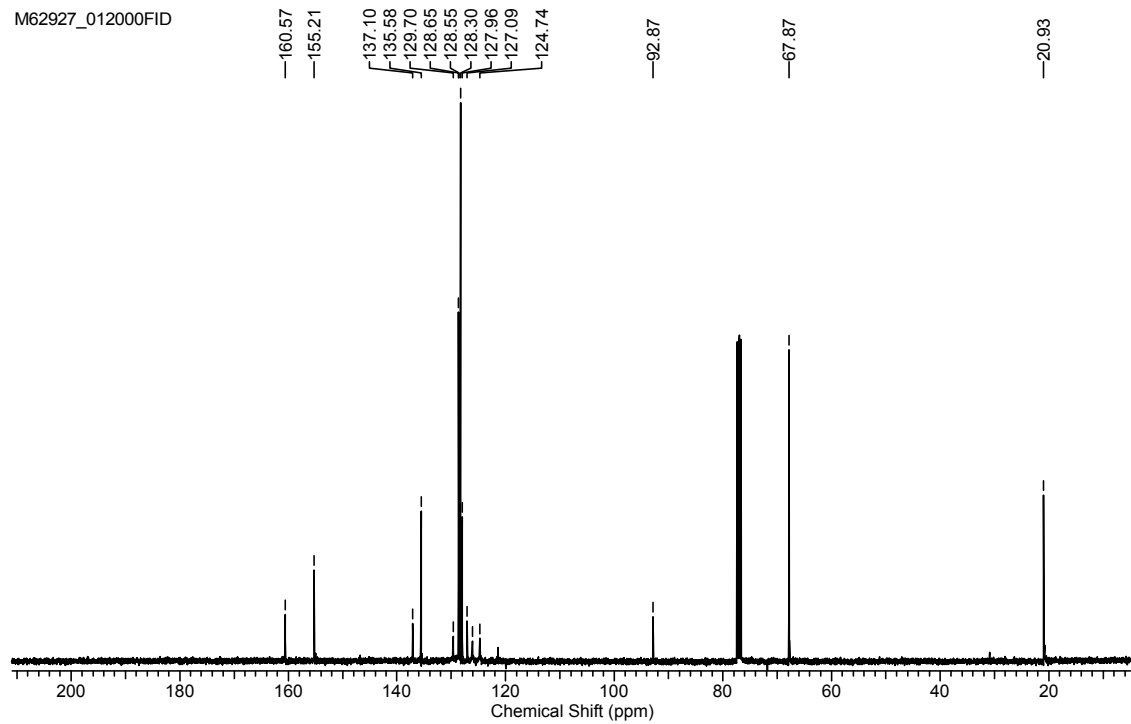


***N*-Cbz-2-(2',2',2'-Trichloroacetyl-amino)-4-methylaniline Table 1 Entry 4**

¹H NMR, CDCl₃, 400 MHz



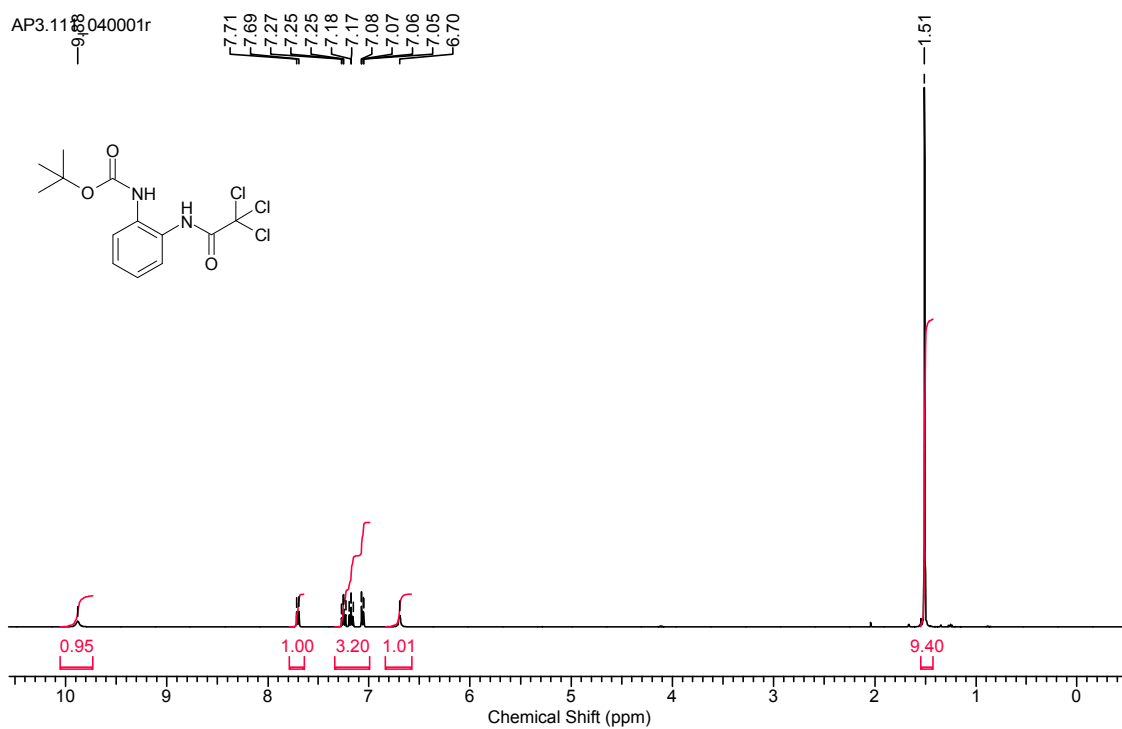
¹³C NMR, CDCl₃, 100 MHz



***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-aniline Table 1 Entry 5**

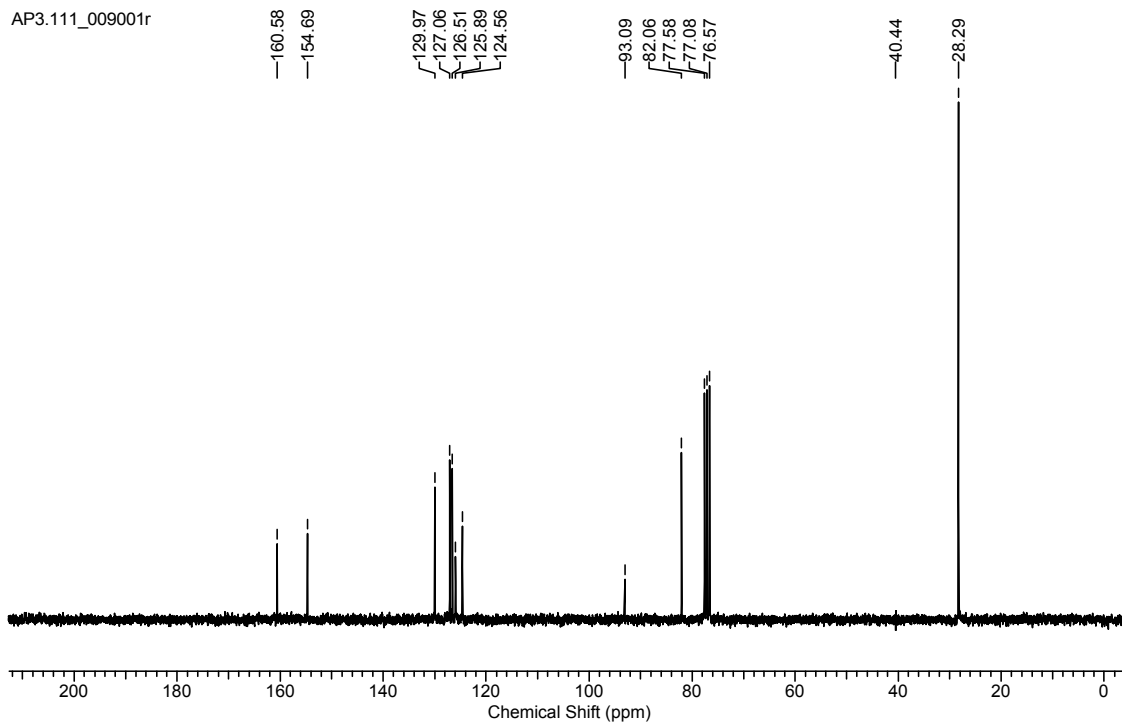
¹H NMR, CDCl₃, 400 MHz

AP3.111_040001r



¹³C NMR, CDCl₃, 100 MHz

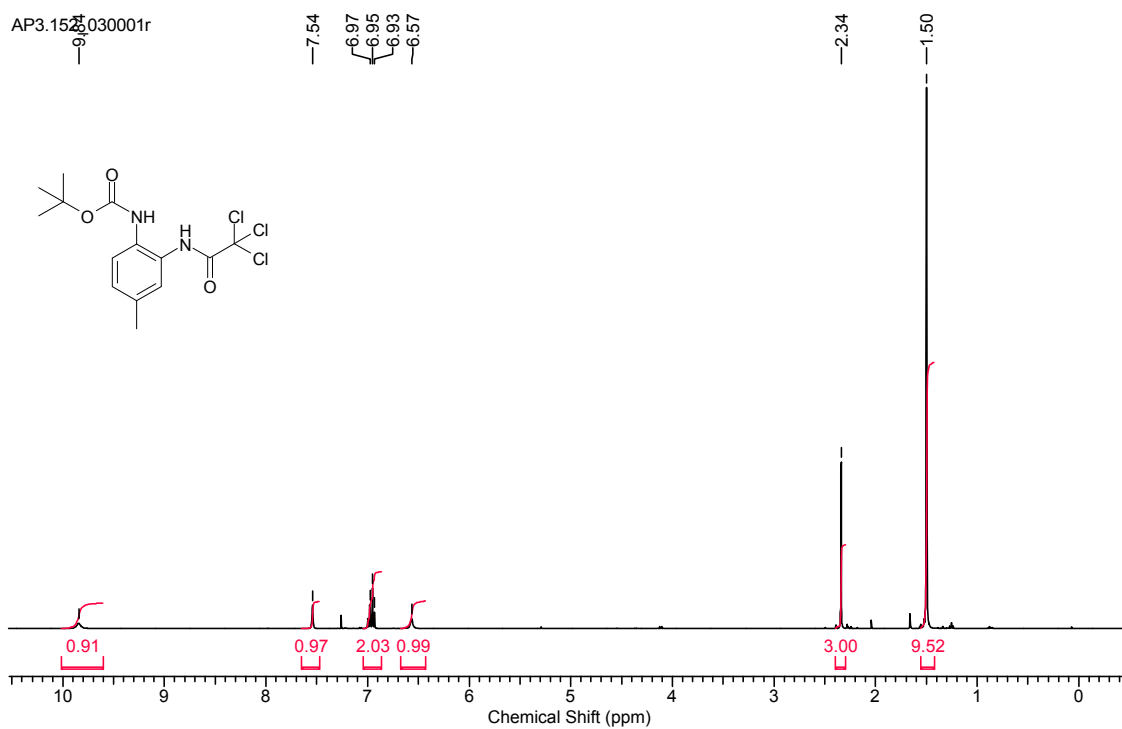
AP3.111_009001r



***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4-methylaniline Table 1 Entry 6**

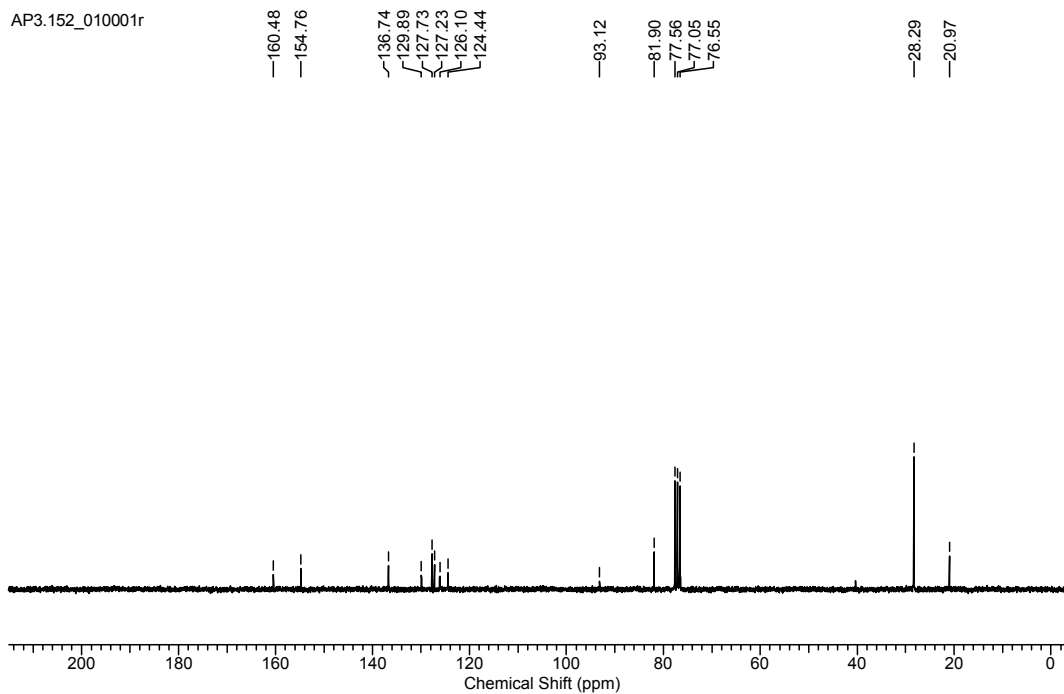
¹H NMR, CDCl₃, 400 MHz

AP3.152_030001r



¹³C NMR, CDCl₃, 100 MHz

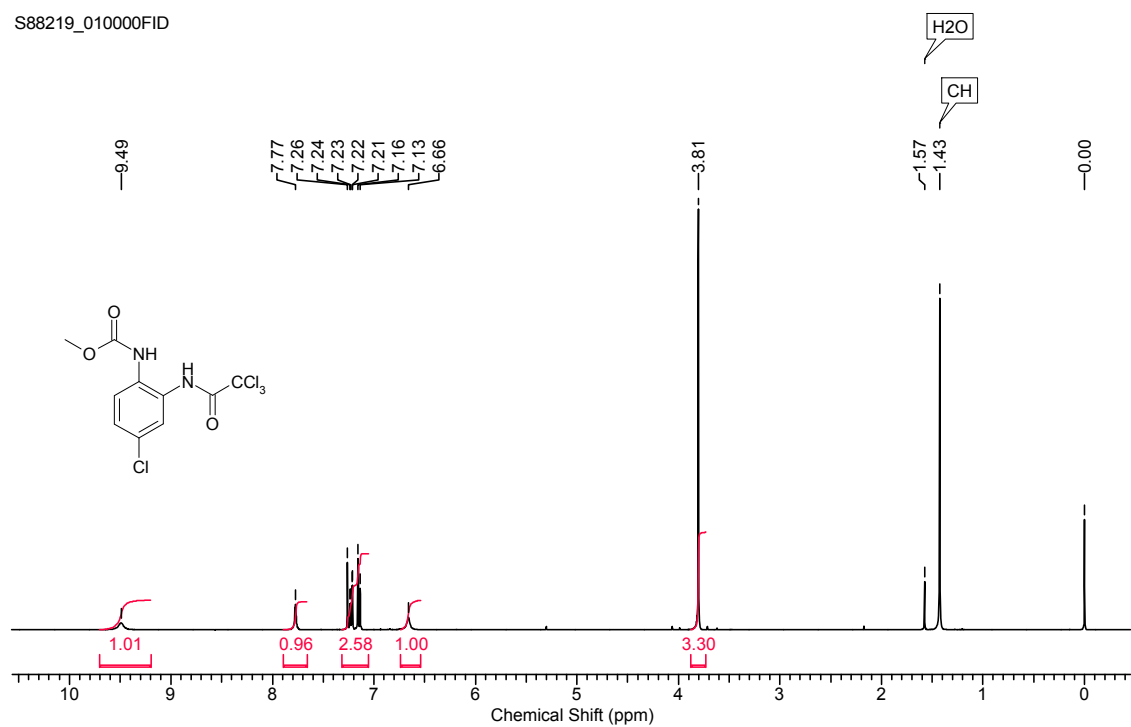
AP3.152_010001r



***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-chloroaniline Table 2 Entry 1**

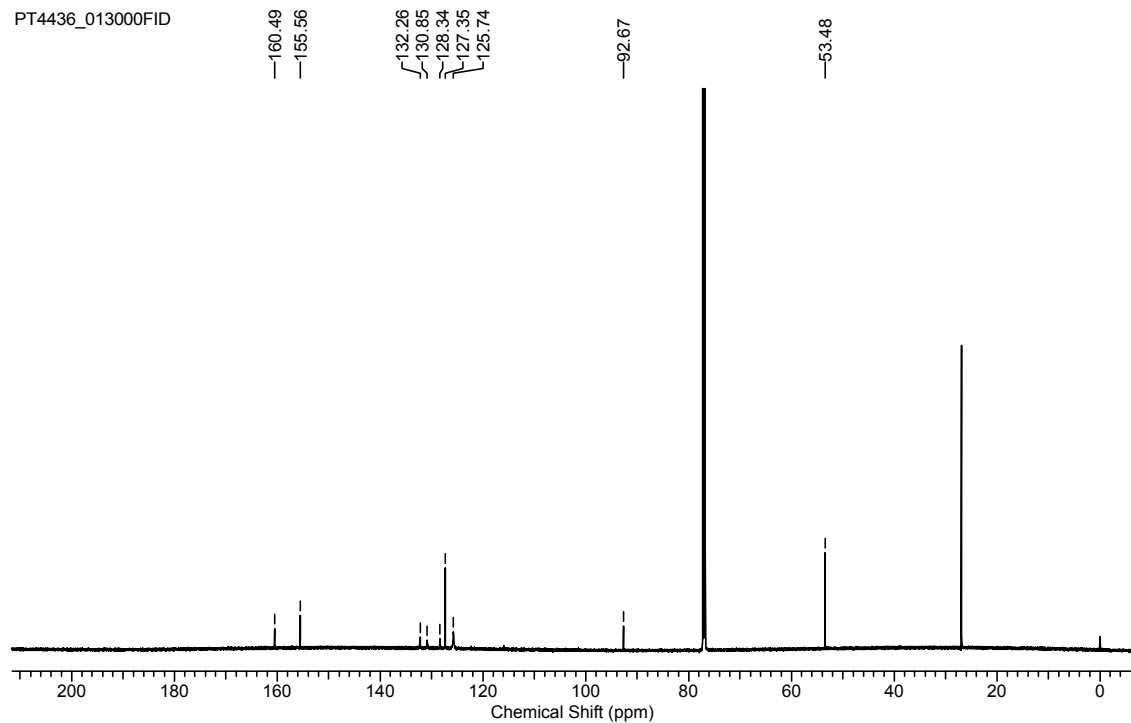
¹H NMR, CDCl₃, 400 MHz

S88219_010000FID



¹³C NMR, CDCl₃, 100 MHz

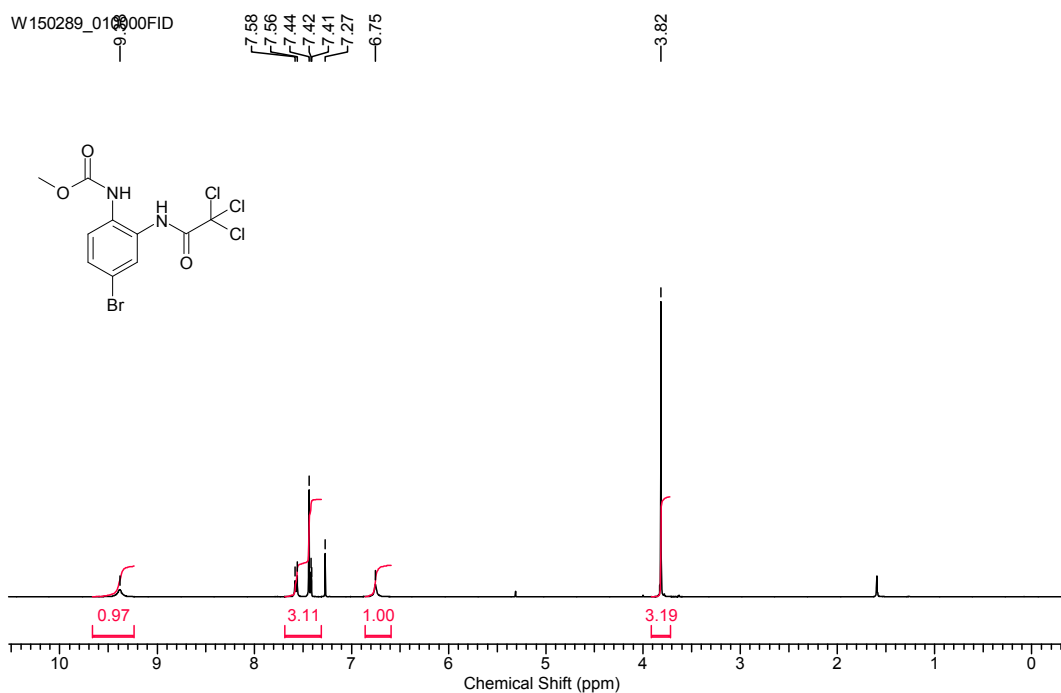
PT4436_013000FID



***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-bromoaniline Table 2 Entry 2**

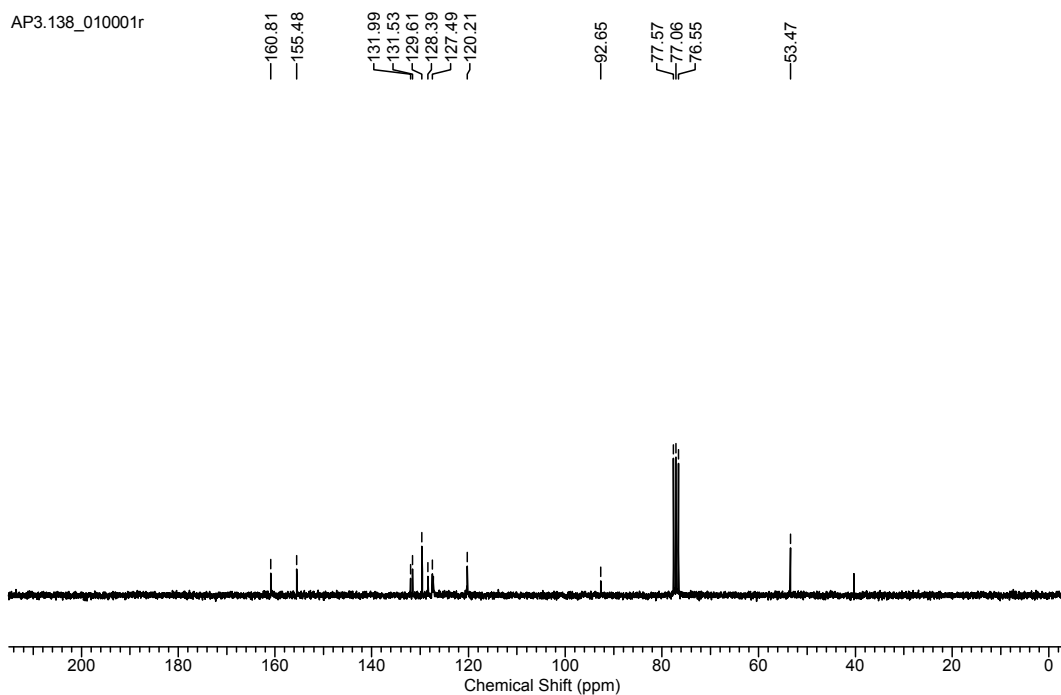
¹H NMR, CDCl₃, 400 MHz

W150289_010000FID



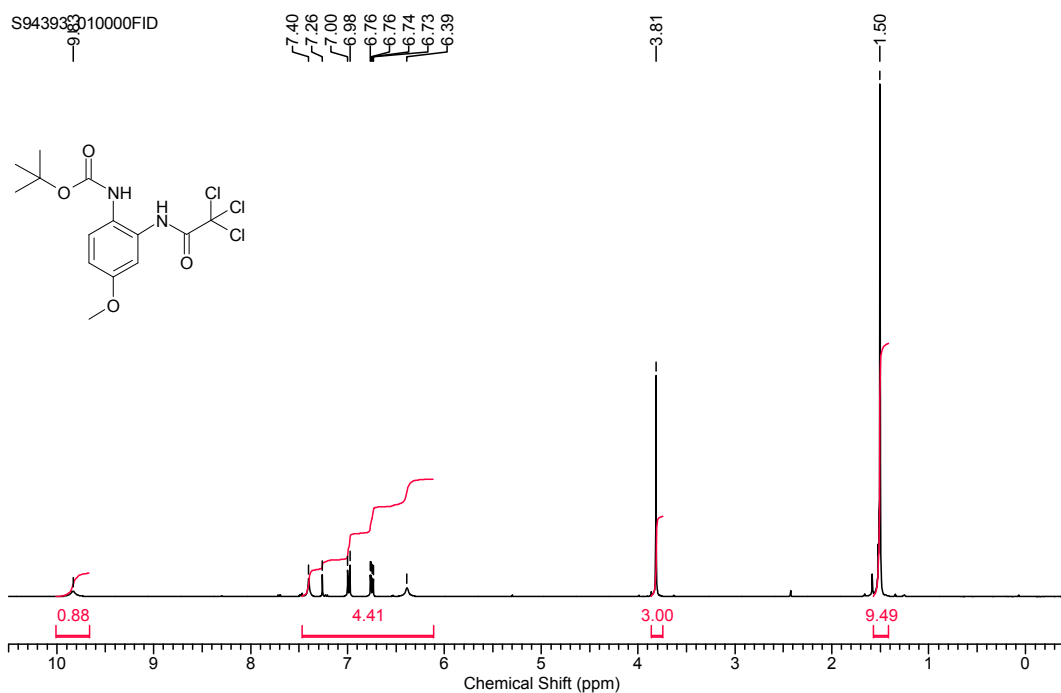
¹³C NMR, CDCl₃, 100 MHz

AP3.138_010001r

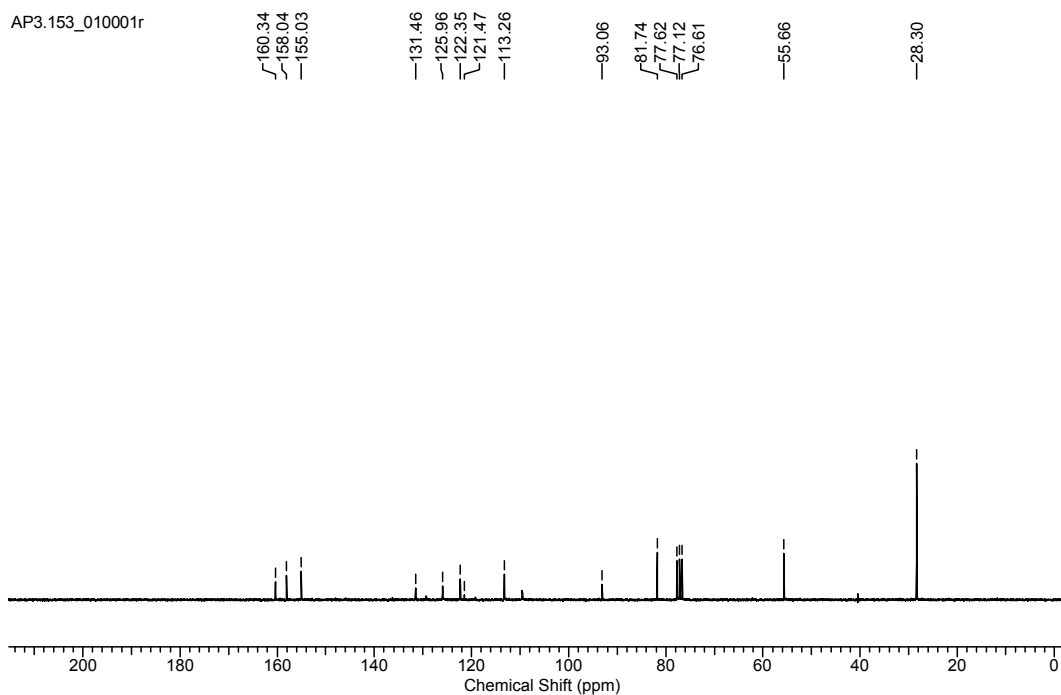


***N*-Boc-2-(2',2',2'-Trichloroacetylamino)-4-methoxyaniline Table 2 Entry 3**

¹H NMR, CDCl₃, 400 MHz

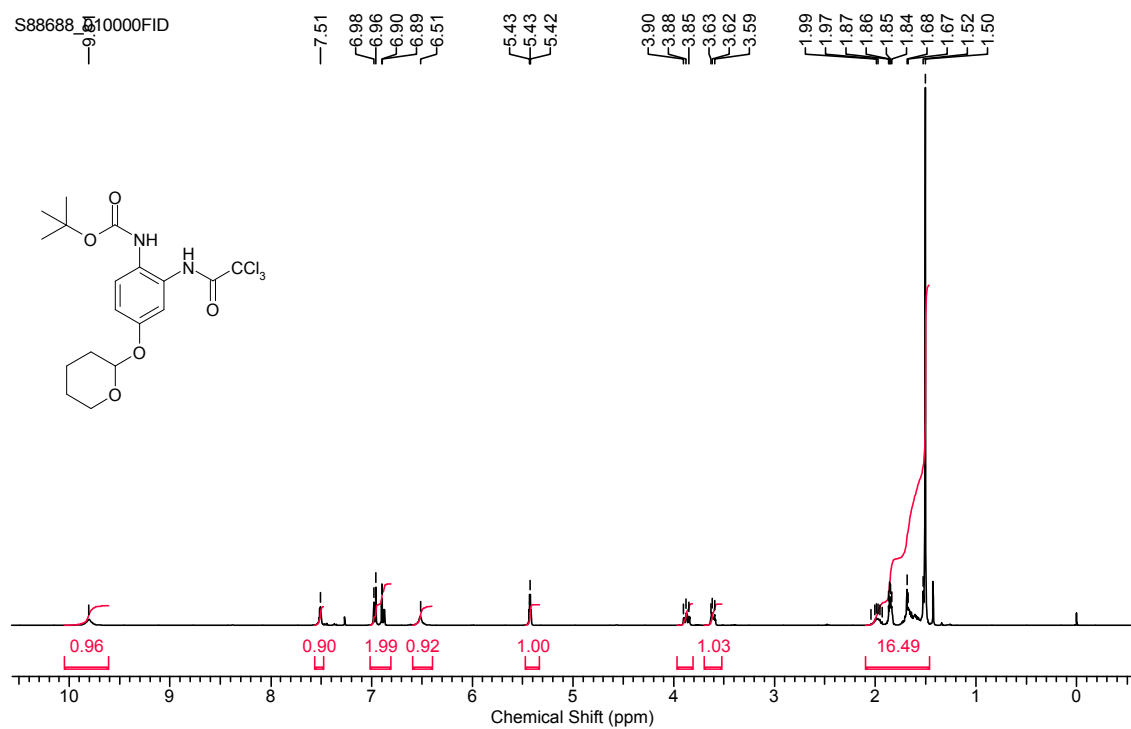


¹³C NMR, CDCl₃, 100 MHz

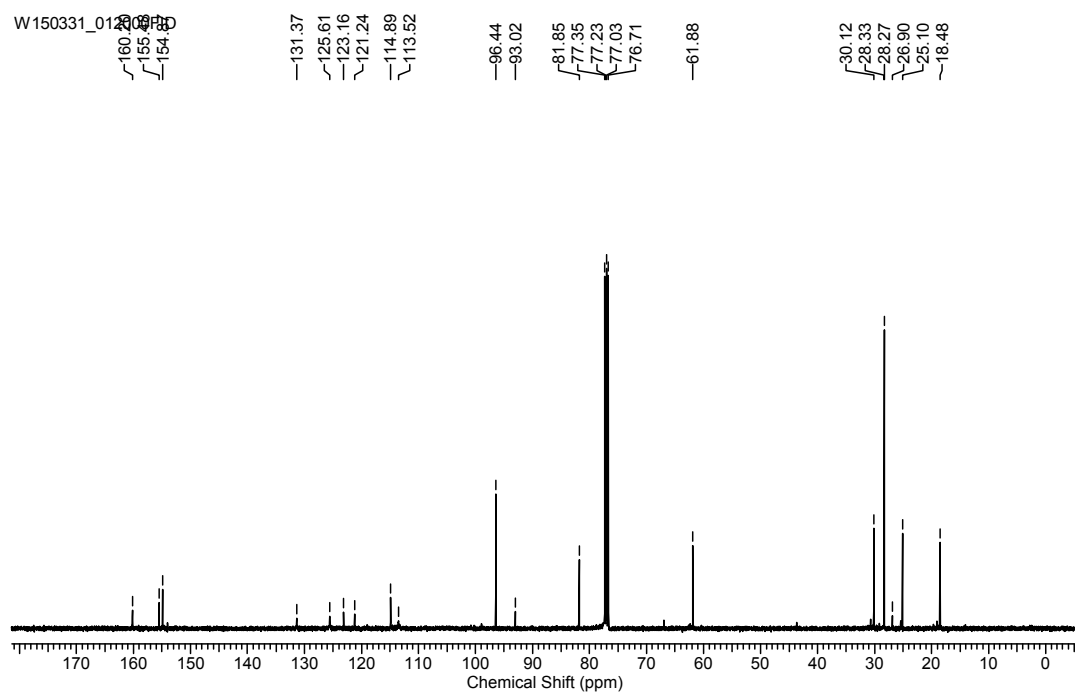


***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4-(OTHP)aniline Table 2 Entry 4**

¹H NMR, CDCl₃, 400 MHz



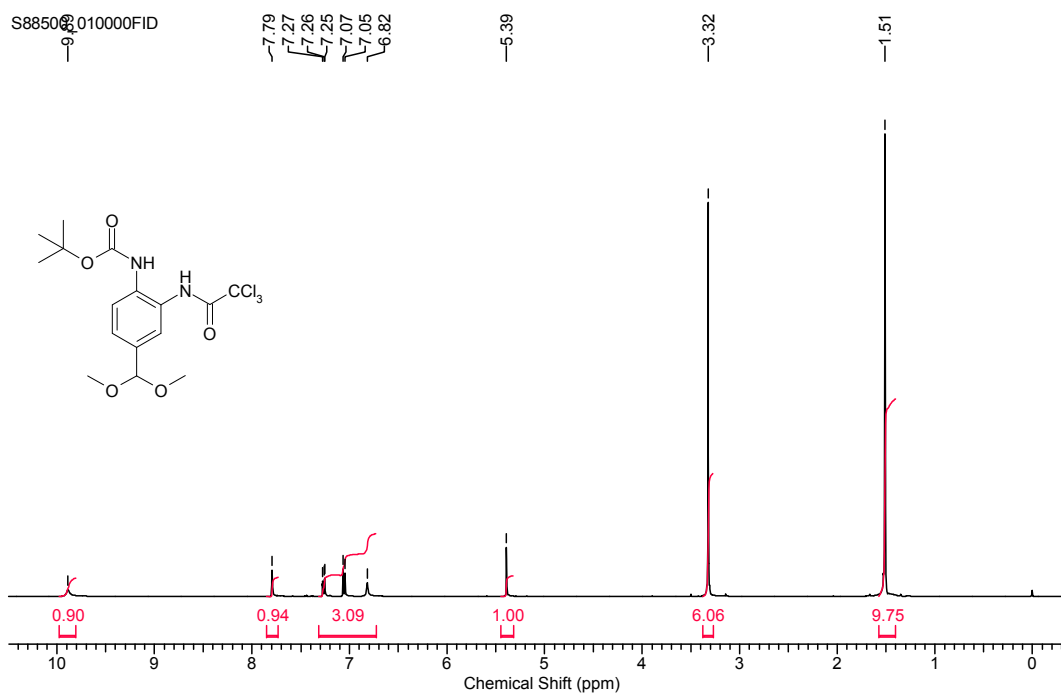
¹³C NMR, CDCl₃, 100 MHz



***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4-(1,1-dimethoxymethyl)aniline Table 2 Entry 6**

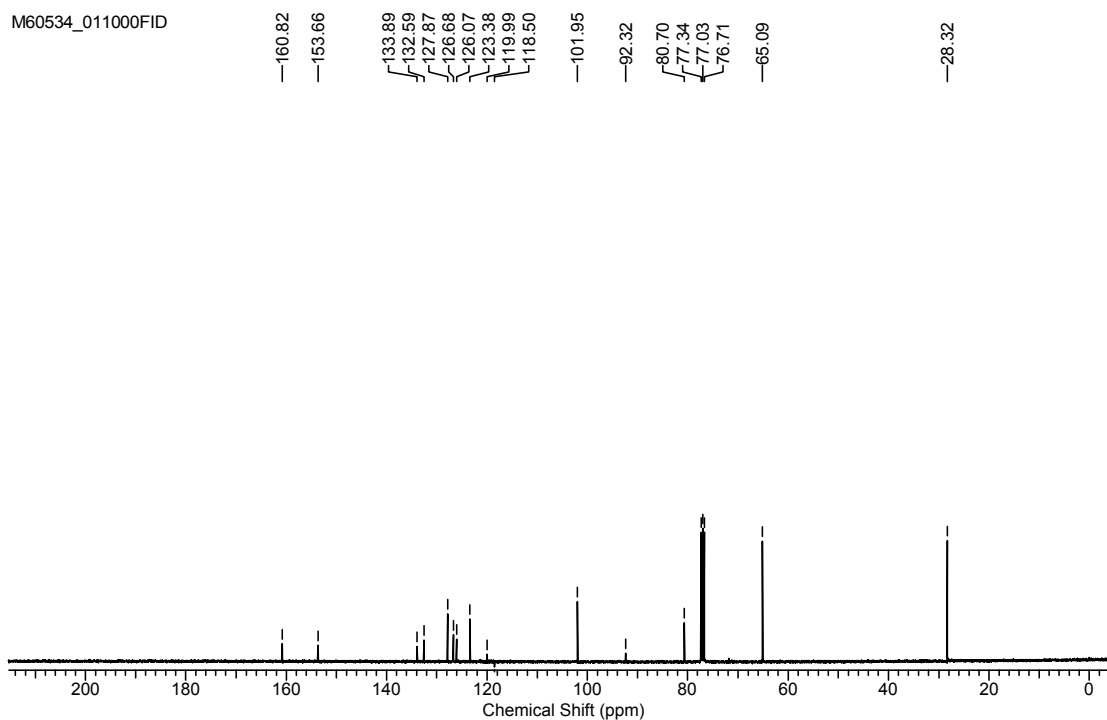
¹H NMR, CDCl₃, 400 MHz

S88506_010000FID



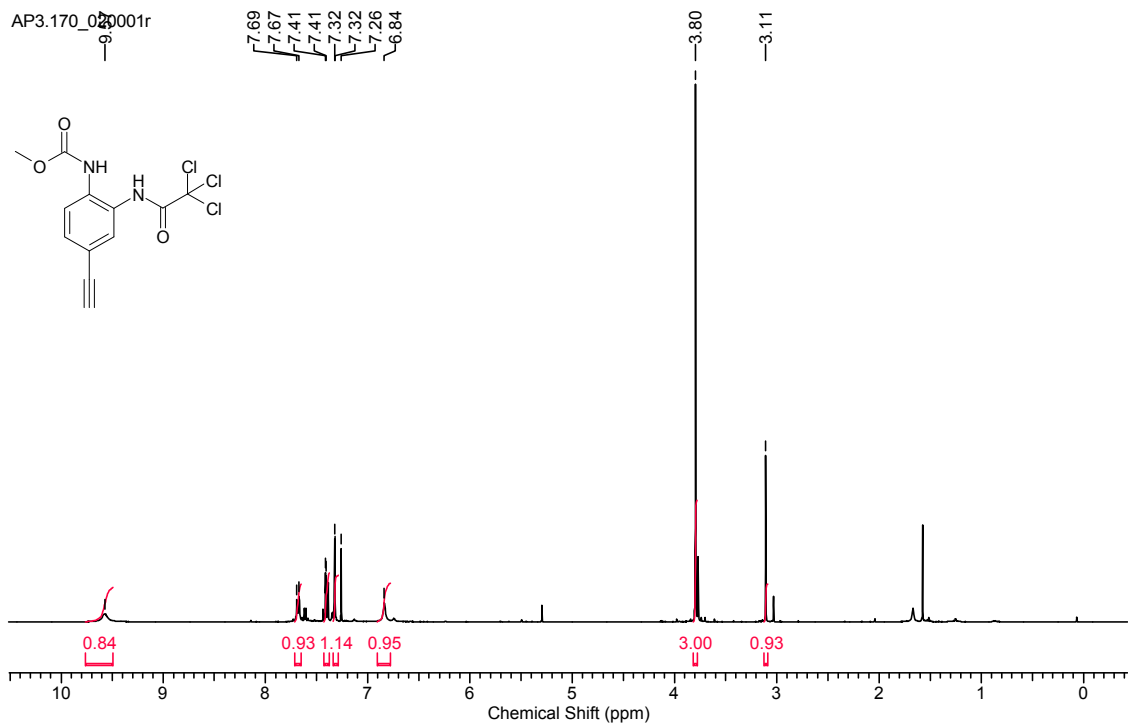
¹³C NMR, CDCl₃, 100 MHz

M60534_011000FID

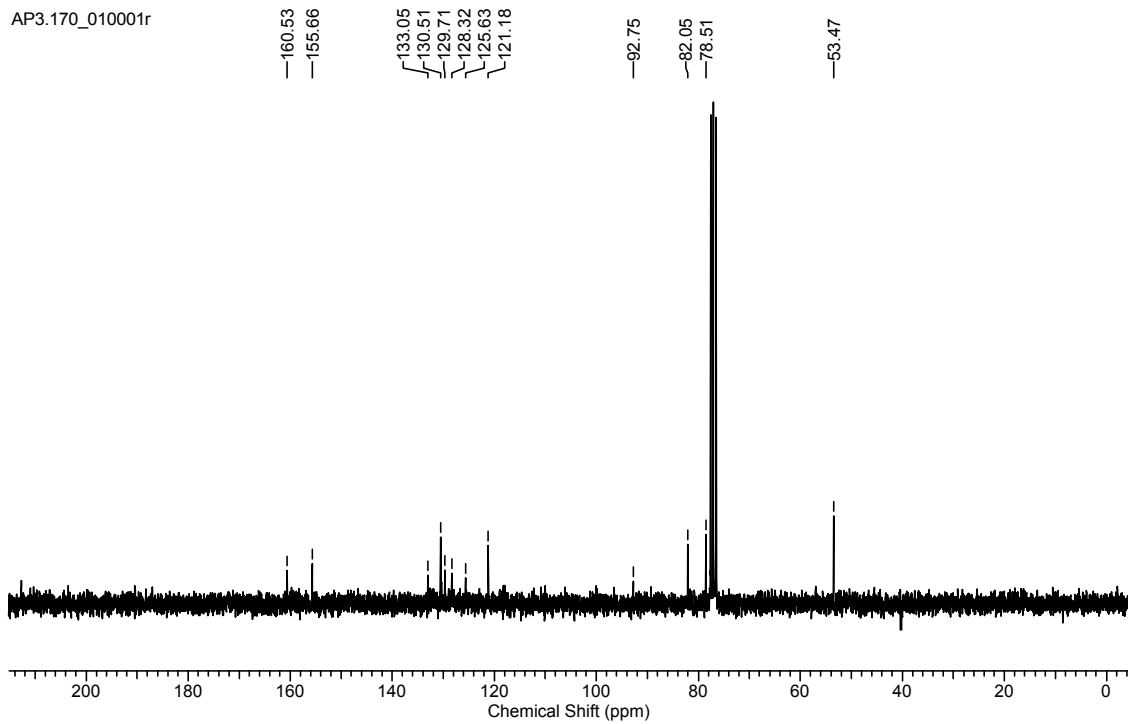


***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-ethynylaniline Table 2 Entry 7**

¹H NMR, CDCl₃, 400 MHz

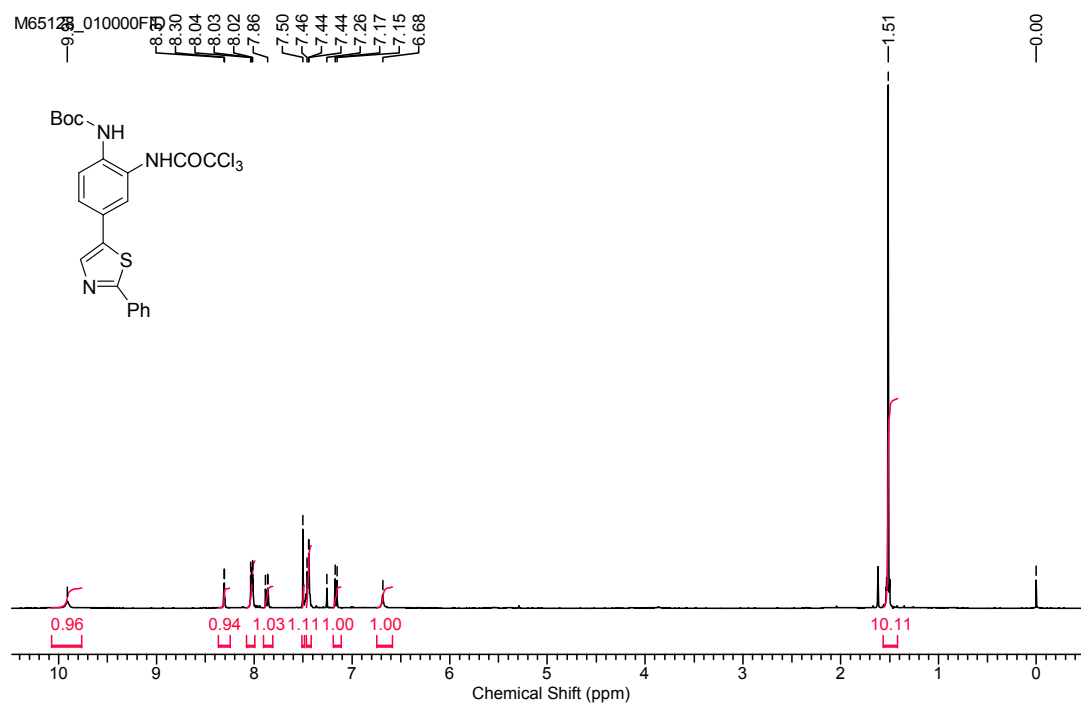


¹³C NMR, CDCl₃, 100 MHz

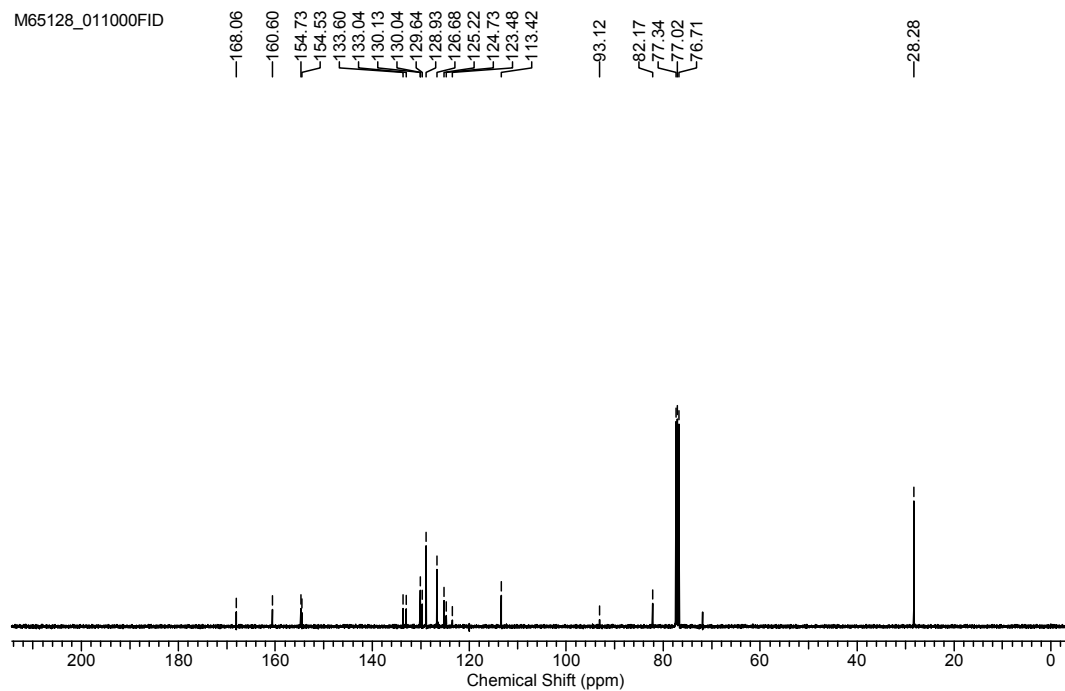


***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-4-(2-phenylthiazol-5-yl)-aniline Table 2, Entry 8**

¹H NMR, CDCl₃, 400 MHz

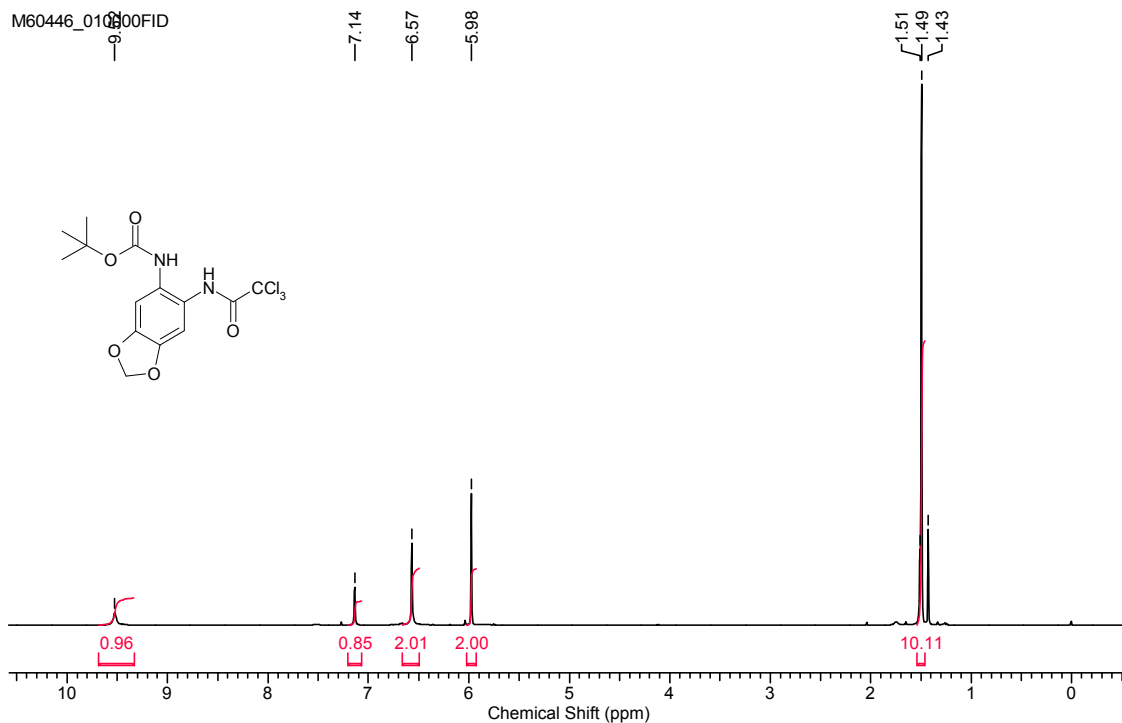


¹³C NMR, CDCl₃, 100 MHz

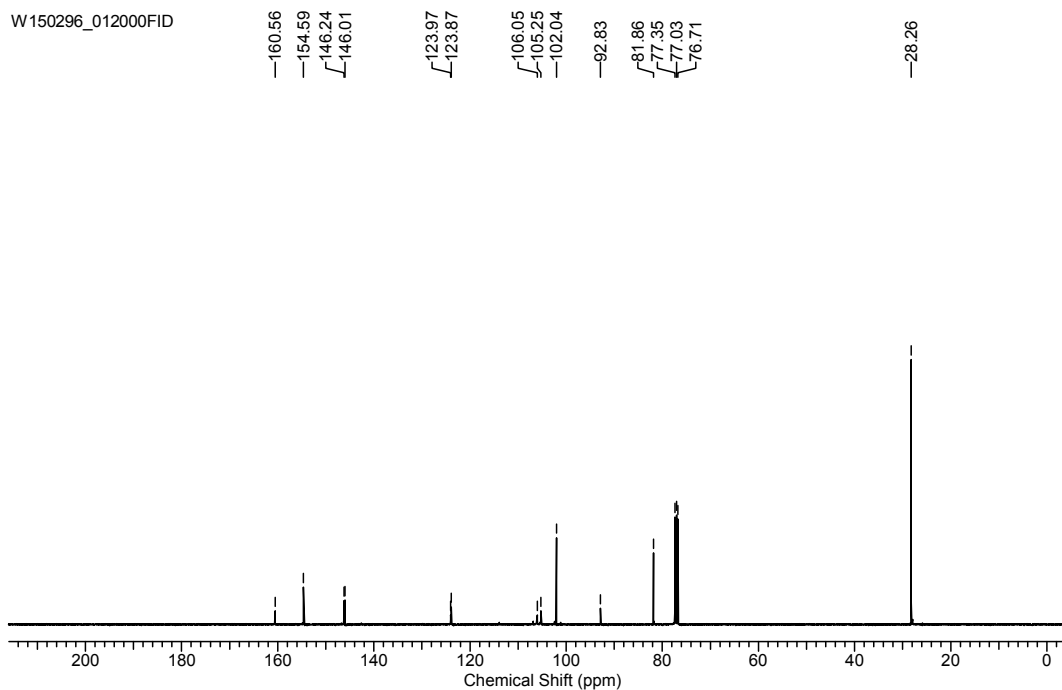


***N*-Boc-2-(2',2',2'-Trichloroacetylamino)-4,5-methylenedioxyaniline Table 2 Entry 9**

¹H NMR, CDCl₃, 400 MHz

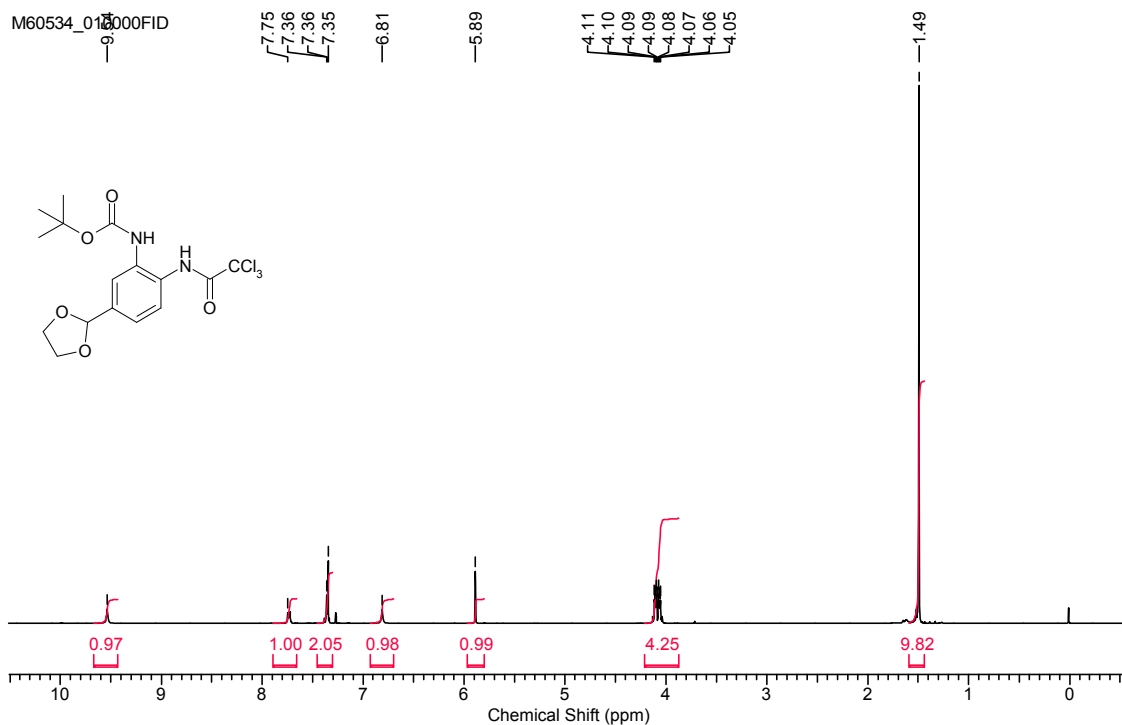


¹³C NMR, CDCl₃, 100 MHz

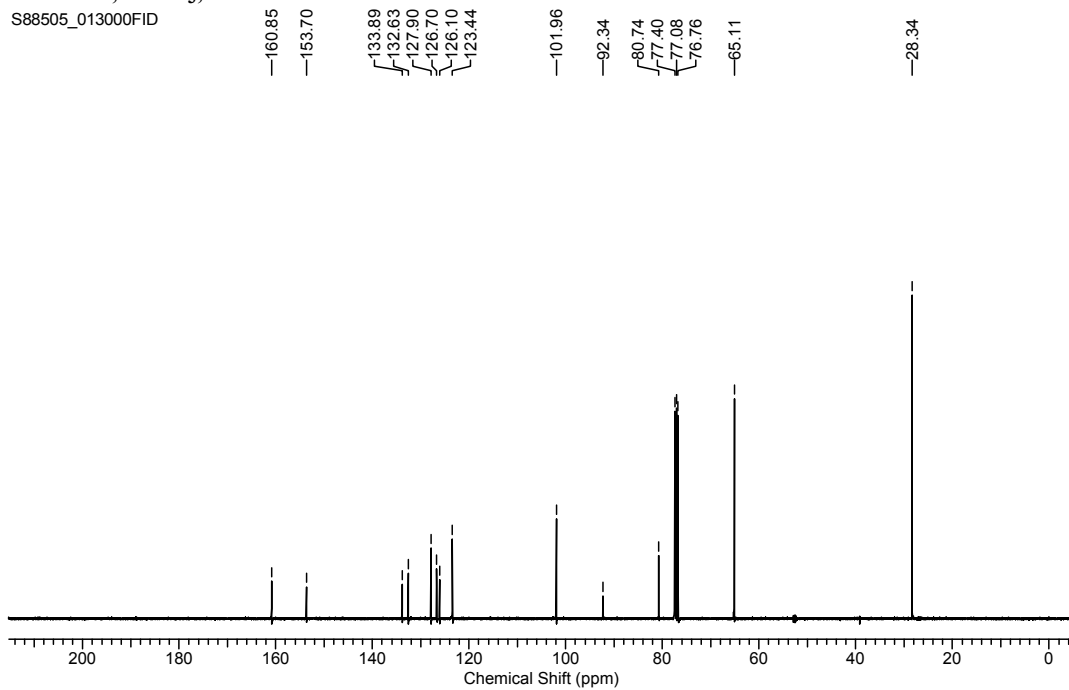


***N*-Boc-2-(2',2',2'-Trichloroacetyl-amino)-5-(1,3-dioxolane-2-yl)aniline Table 2 Entry 10**

¹H NMR, CDCl₃, 400 MHz



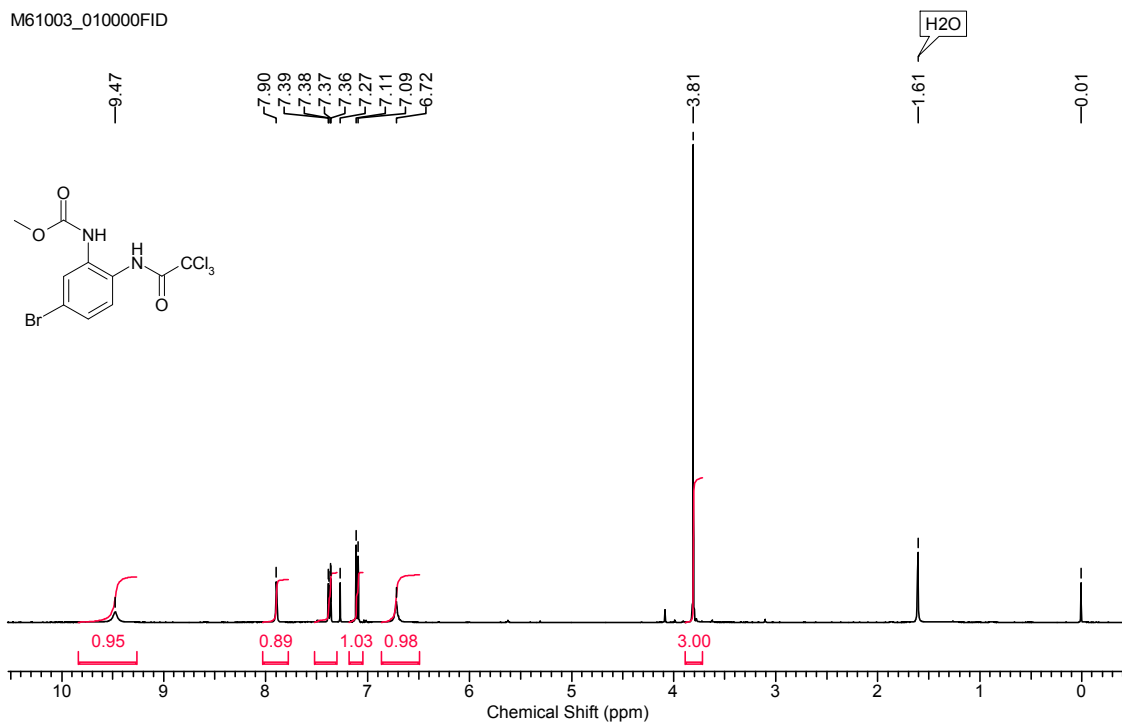
¹³C NMR, CDCl₃, 100 MHz



***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-5-bromoaniline Table 2 Entry 11**

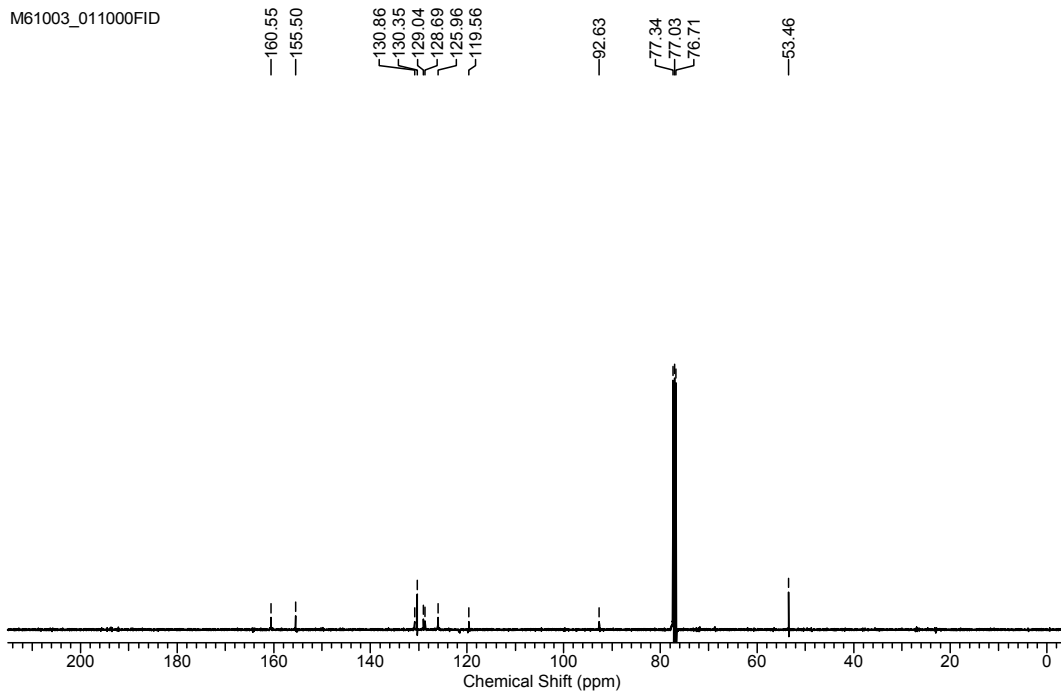
¹H NMR, CDCl₃, 400 MHz

M61003_010000FID



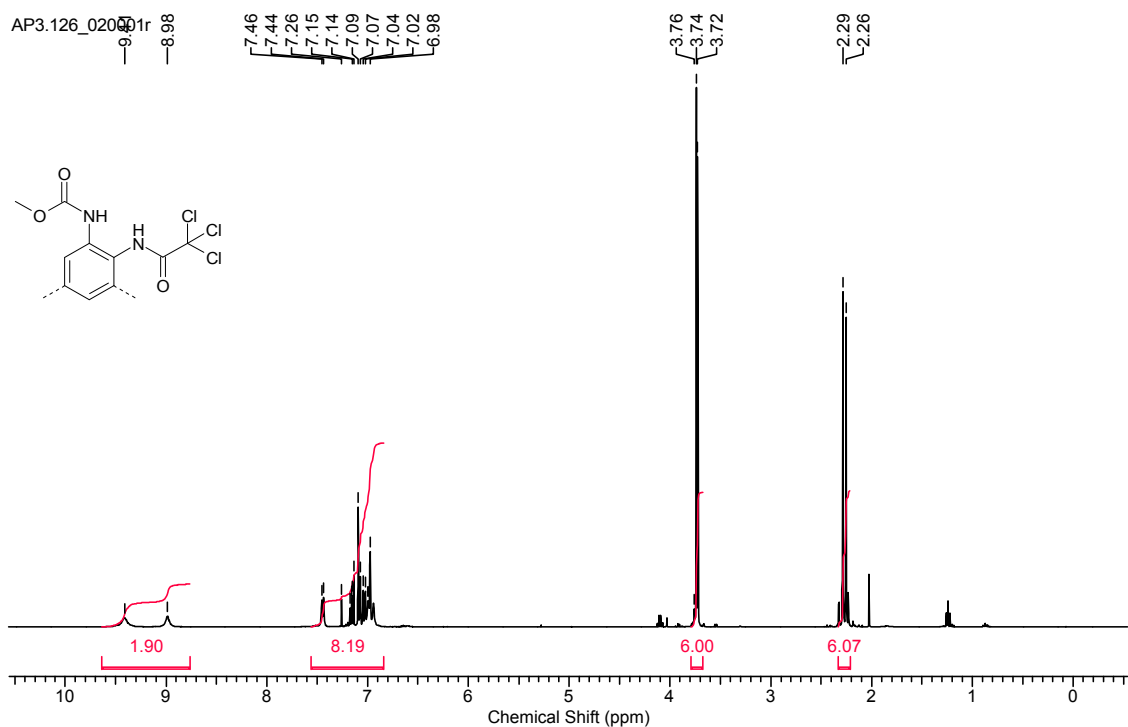
¹³C NMR, CDCl₃, 100 MHz

M61003_011000FID

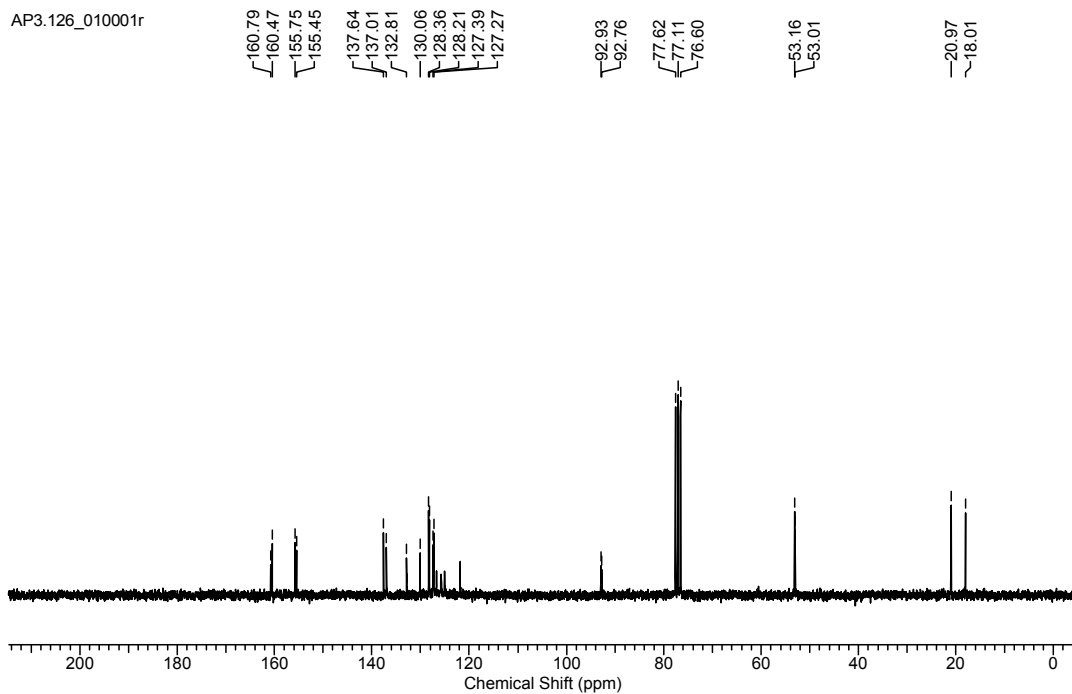


***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-5-methylaniline Table 2 Entry 12**

¹H NMR, CDCl₃, 400 MHz



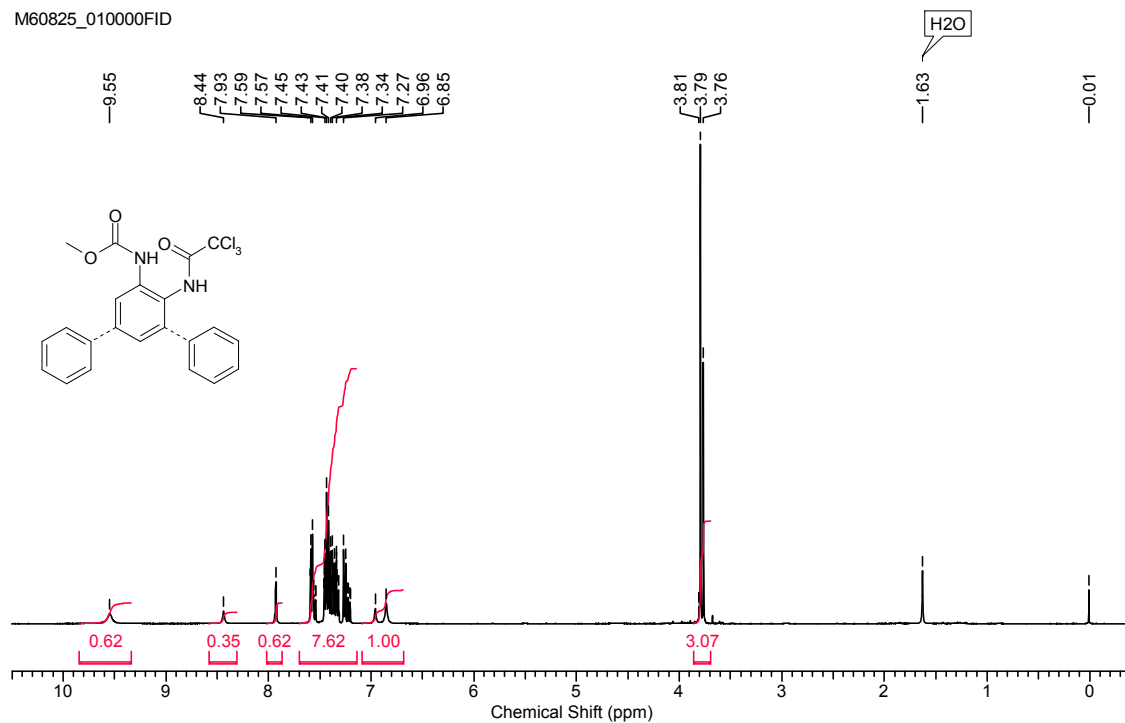
¹³C NMR, CDCl₃, 100 MHz



***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-5-phenylaniline (major isomer) Table 2 Entry 13**

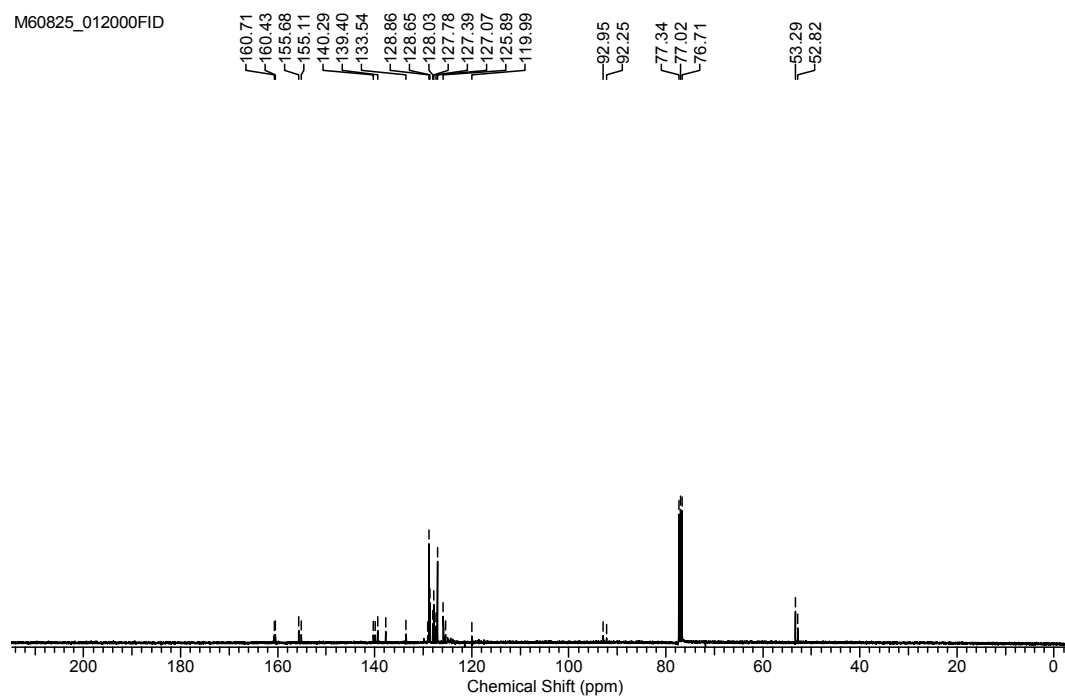
¹H NMR, CDCl₃, 400 MHz

M60825_010000FID



¹³C NMR, CDCl₃, 100 MHz

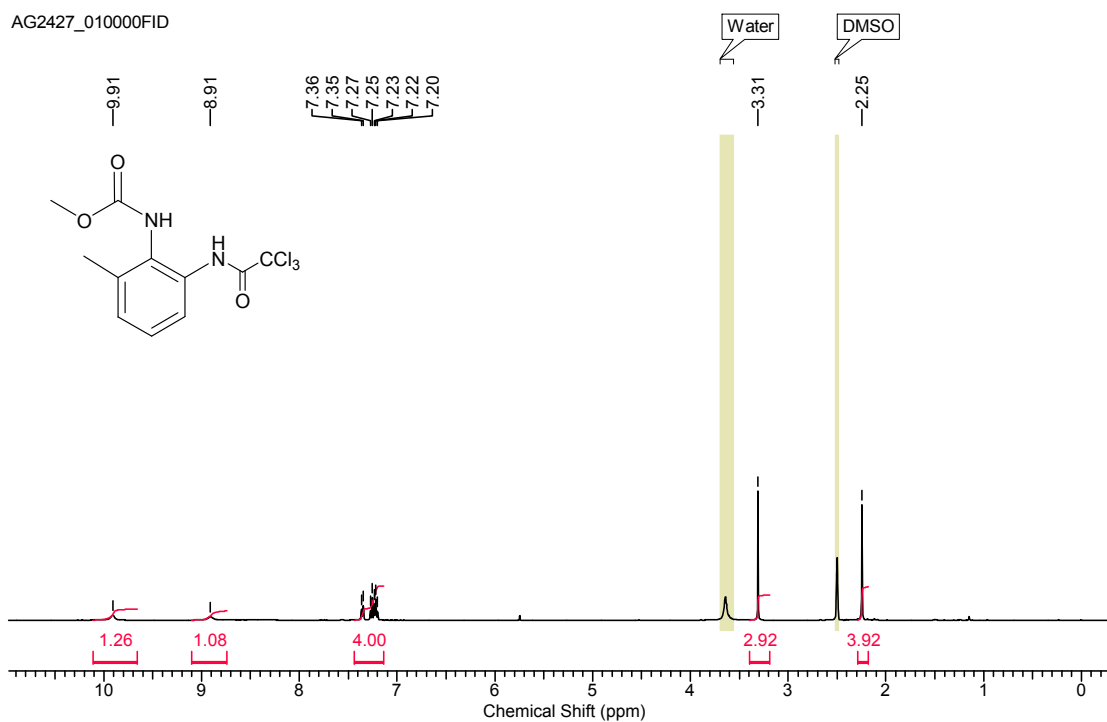
M60825_012000FID



***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-6-methylaniline Table 2 Entry 14**

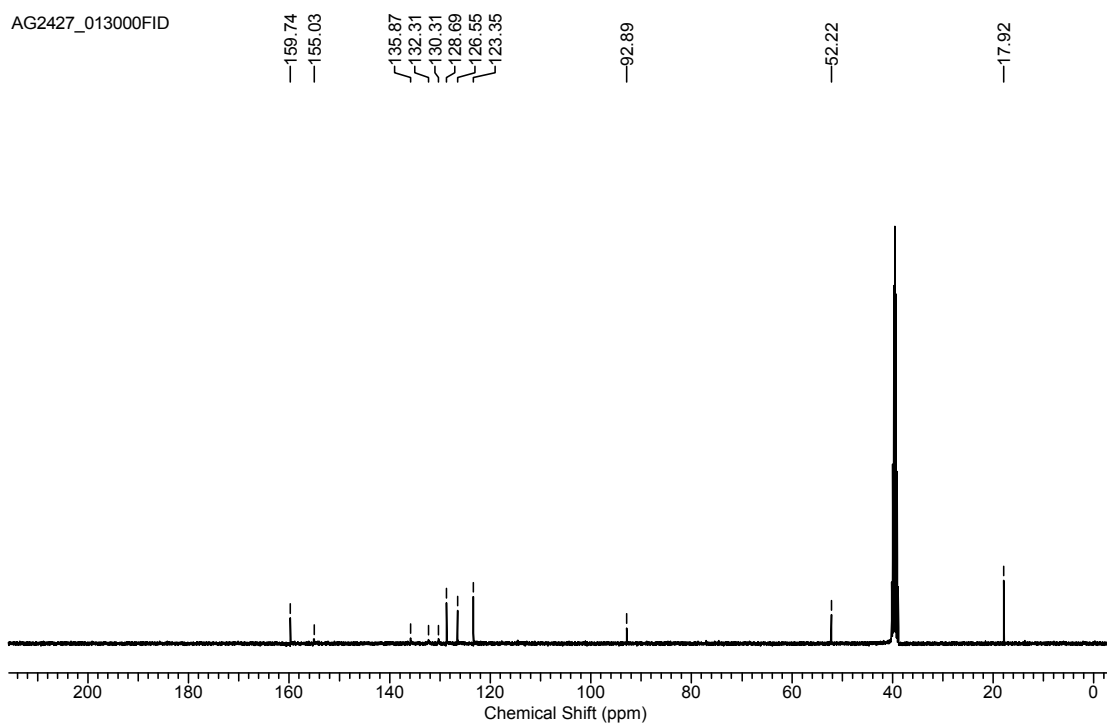
¹H NMR, DMSO, 400 MHz

AG2427_010000FID



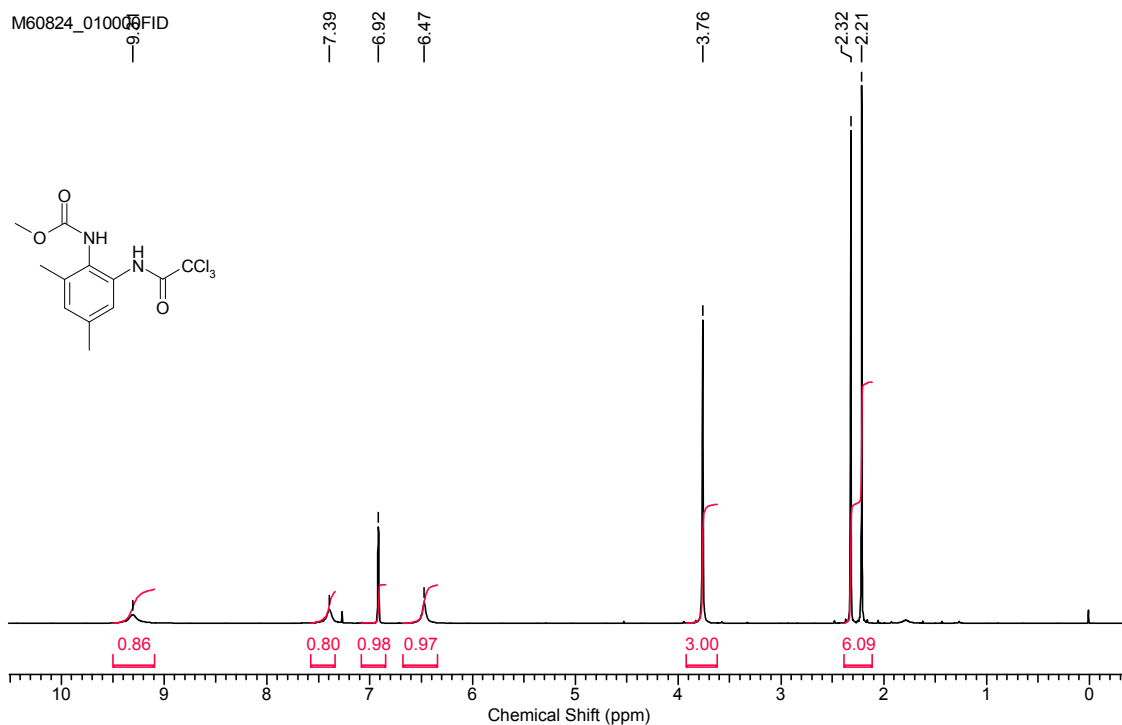
¹³C NMR, DMSO, 100 MHz

AG2427_013000FID

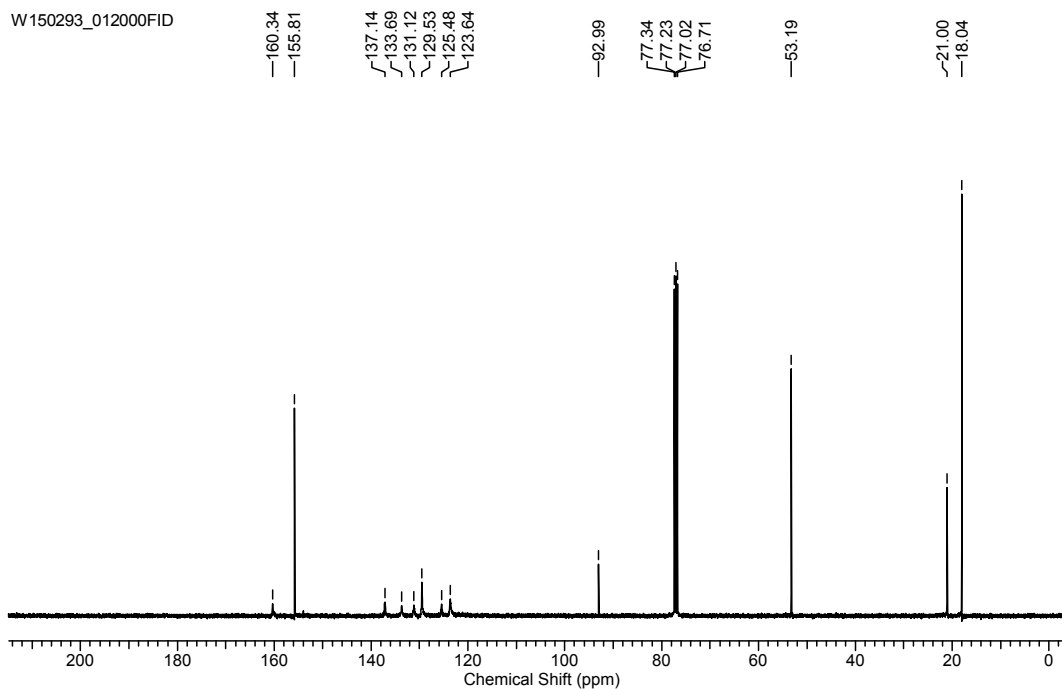


***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4,6-dimethylaniline Table 2 Entry 15**

¹H NMR, CDCl₃, 400 MHz

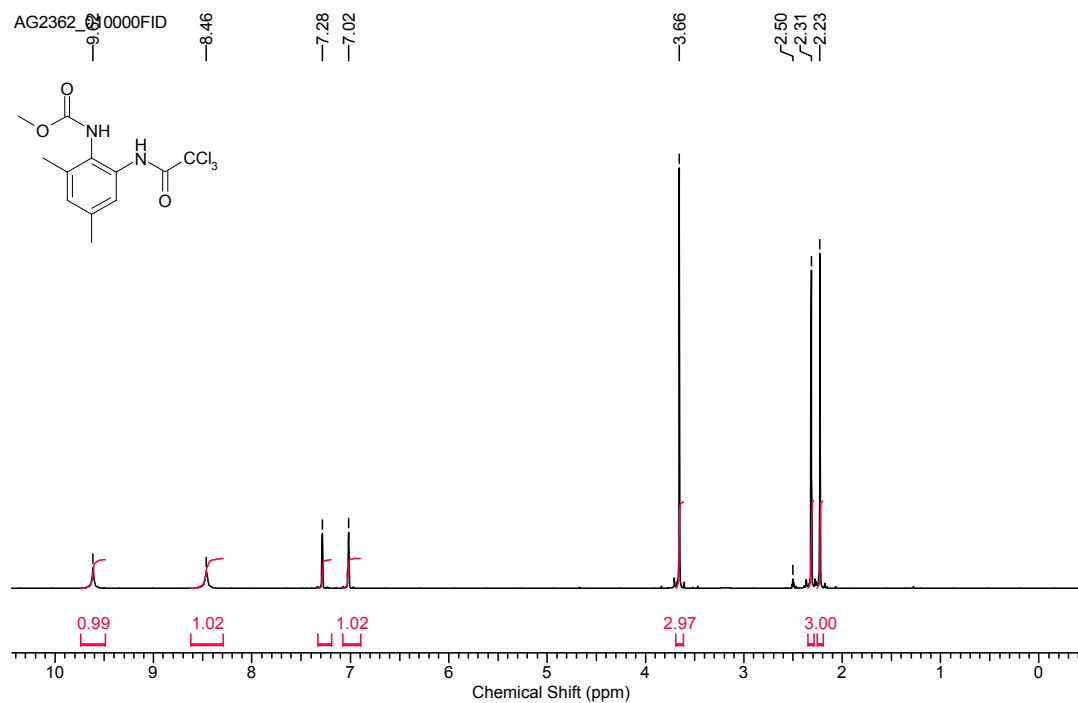


¹³C NMR, CDCl₃, 100 MHz

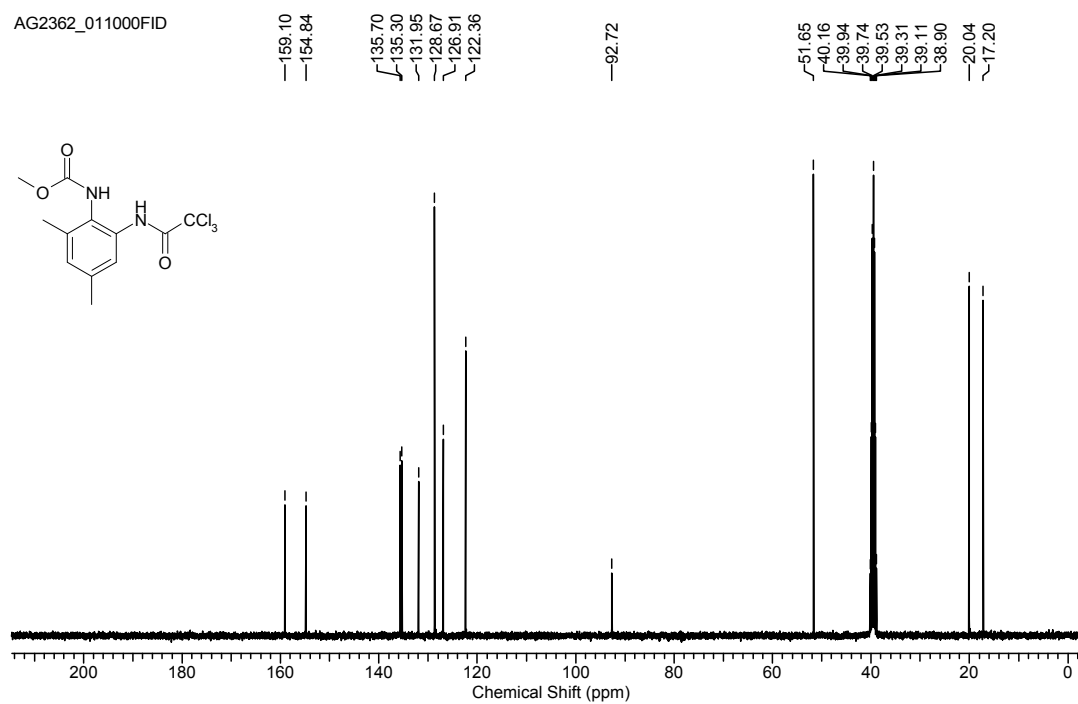


***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4,6-dimethylaniline Table 2 Entry 15**

¹H NMR (400 MHz, DMSO, 353 K)



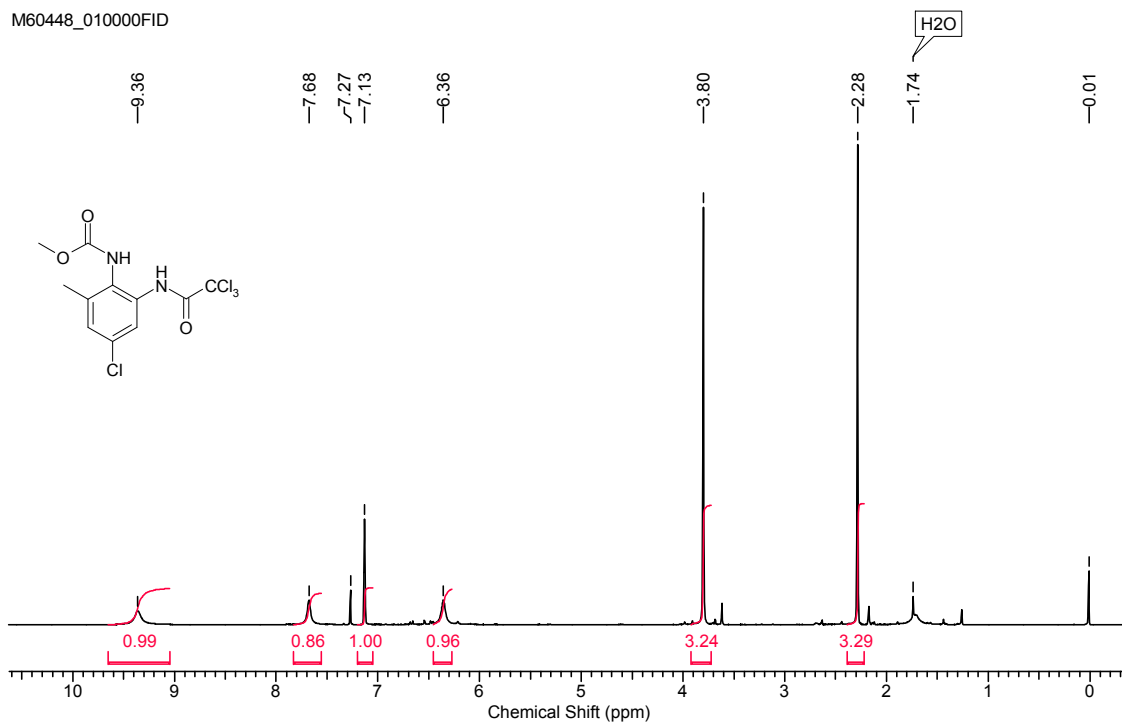
¹³C NMR (100 MHz, DMSO, 353 K)



***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-chloro-6-methylaniline Table 2 Entry 16**

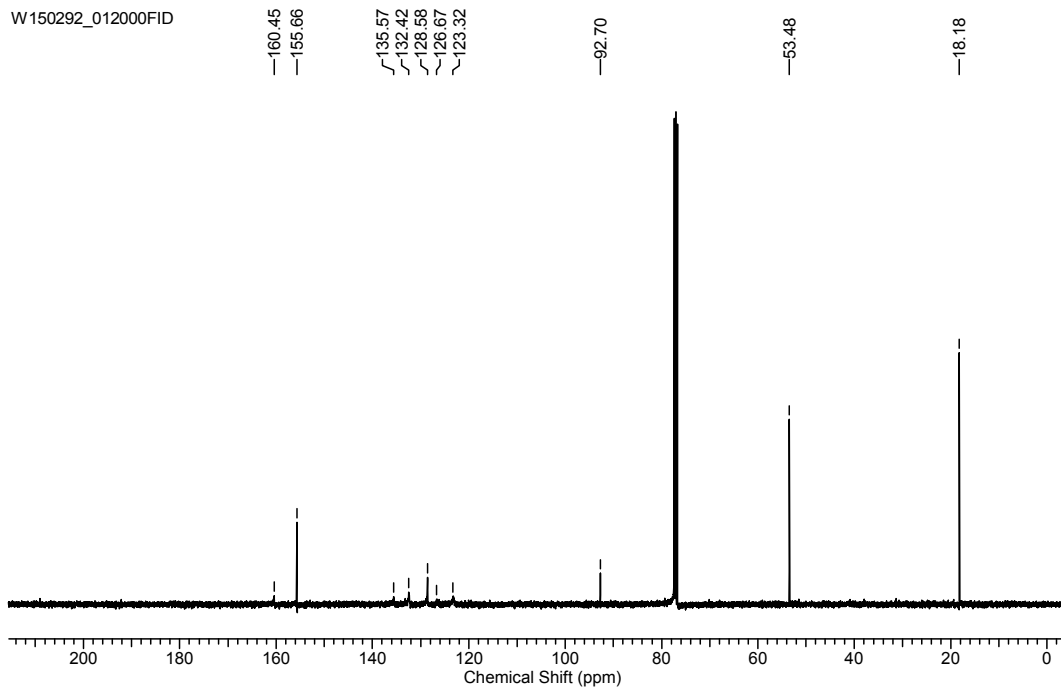
¹H NMR, CDCl₃, 400 MHz

M60448_010000FID



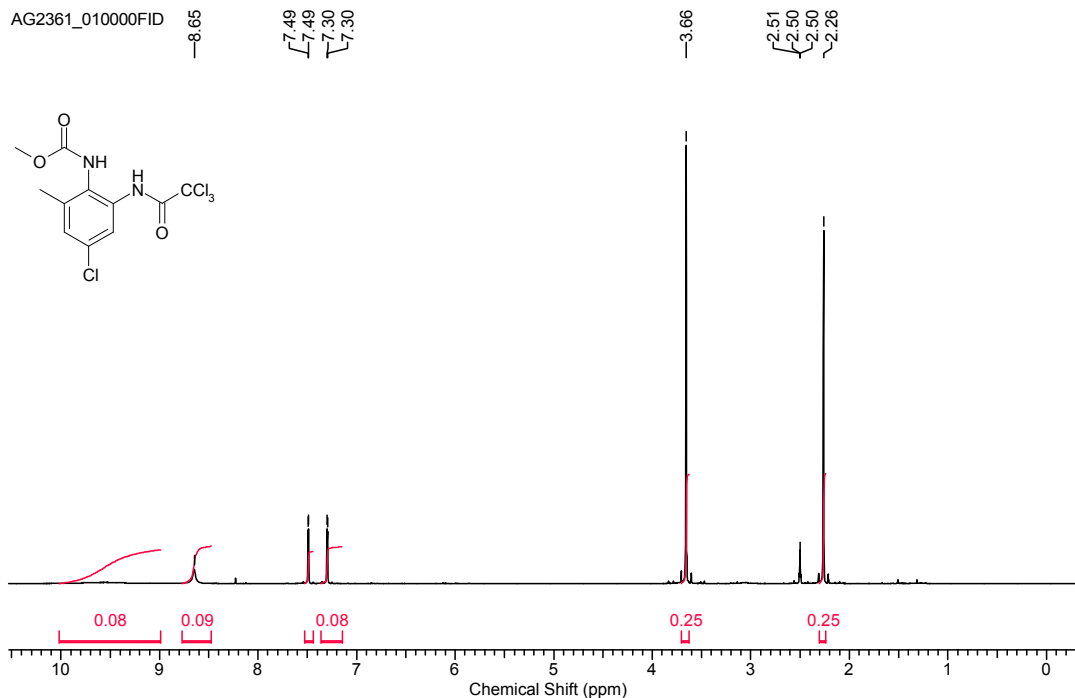
¹³C NMR, CDCl₃, 100 MHz

W150292_012000FID

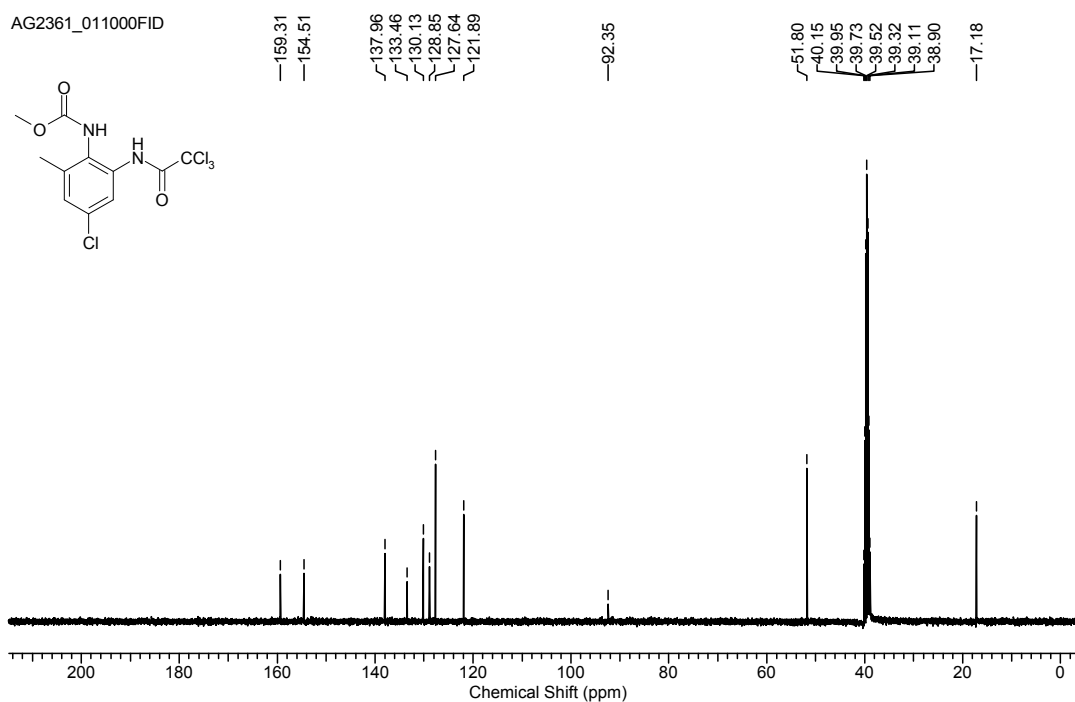


***N*-Methoxycarbonyl-2-(2',2',2'-trichloroacetyl-amino)-4-chloro-6-methylaniline Table 2 Entry 16**

¹H NMR (400 MHz, DMSO, 353 K) Entry 16

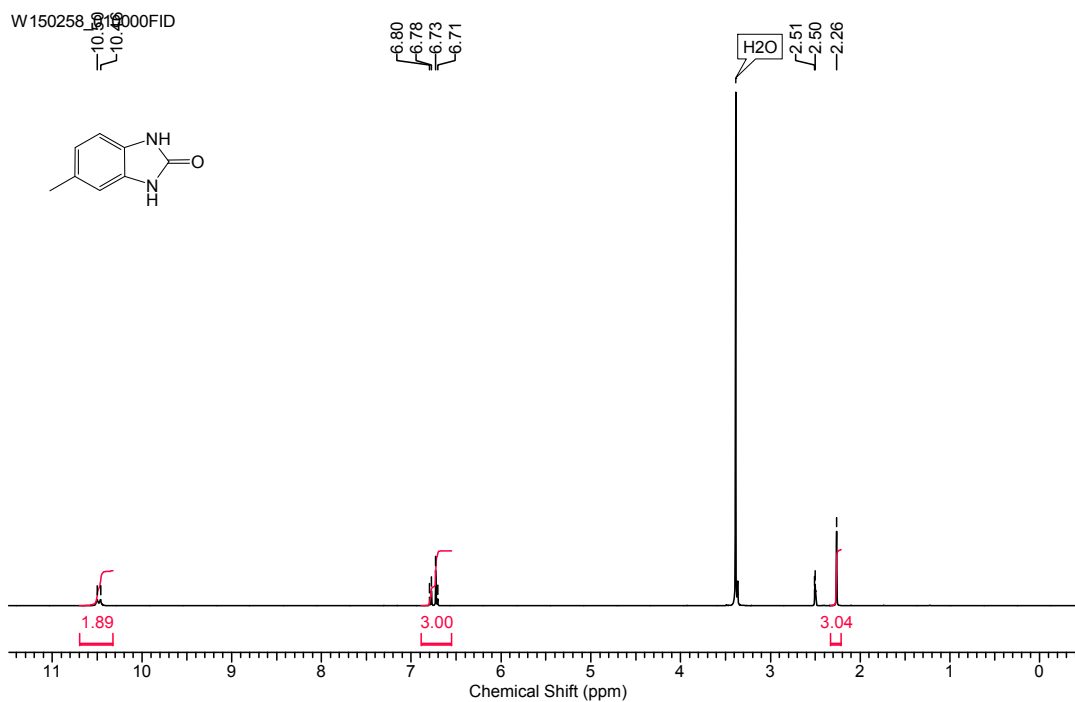


¹³C NMR (100 MHz, DMSO, 353 K)

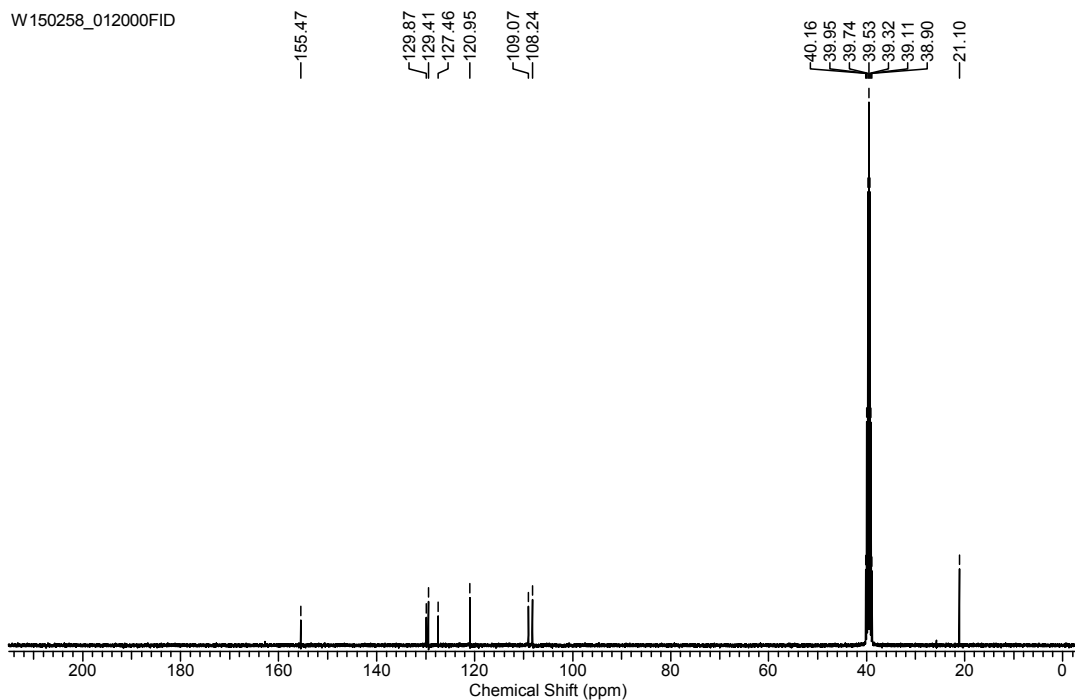


5-Methyl-1H-benzo[d]imidazol-2(3H)-one 15

¹H NMR, DMSO, 400 MHz



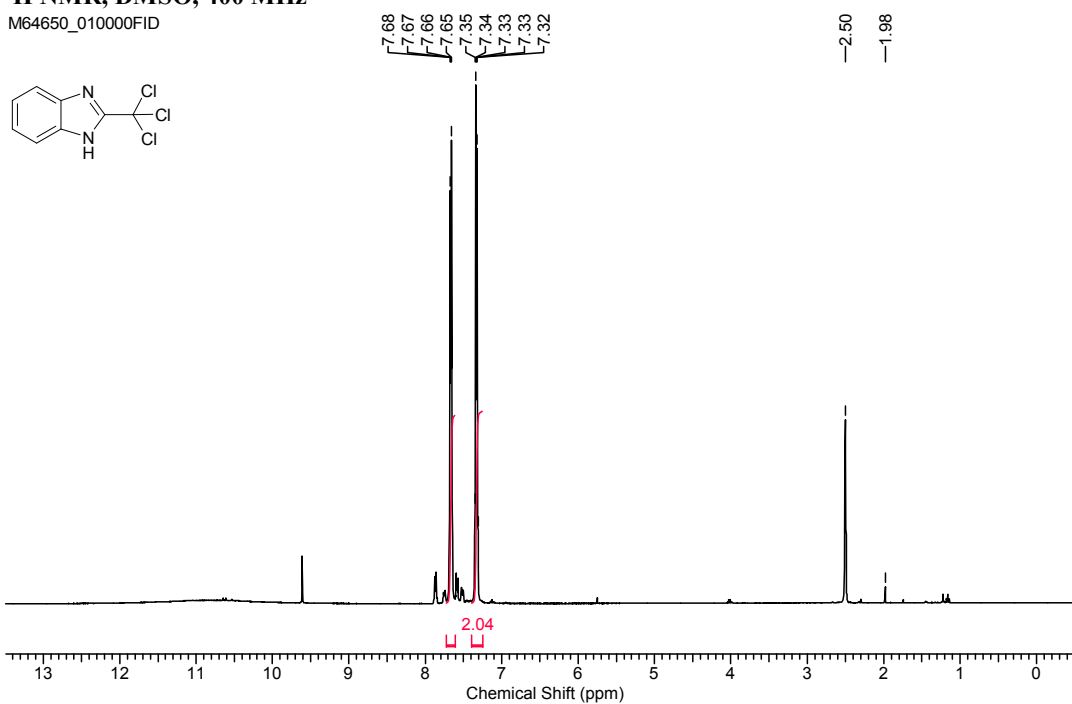
¹³C NMR, DMSO, 100 MHz



2-(2',2',2'-Trichloromethyl)-benzimidazole 18

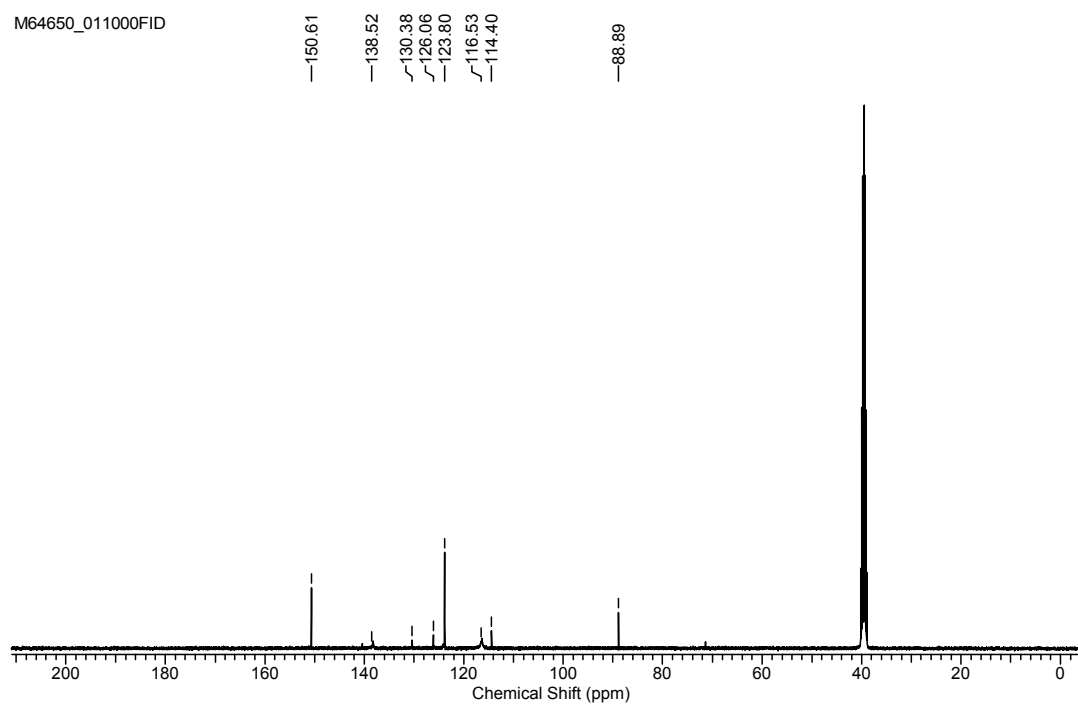
¹H NMR, DMSO, 400 MHz

M64650_010000FID



¹³C NMR, DMSO, 100 MHz

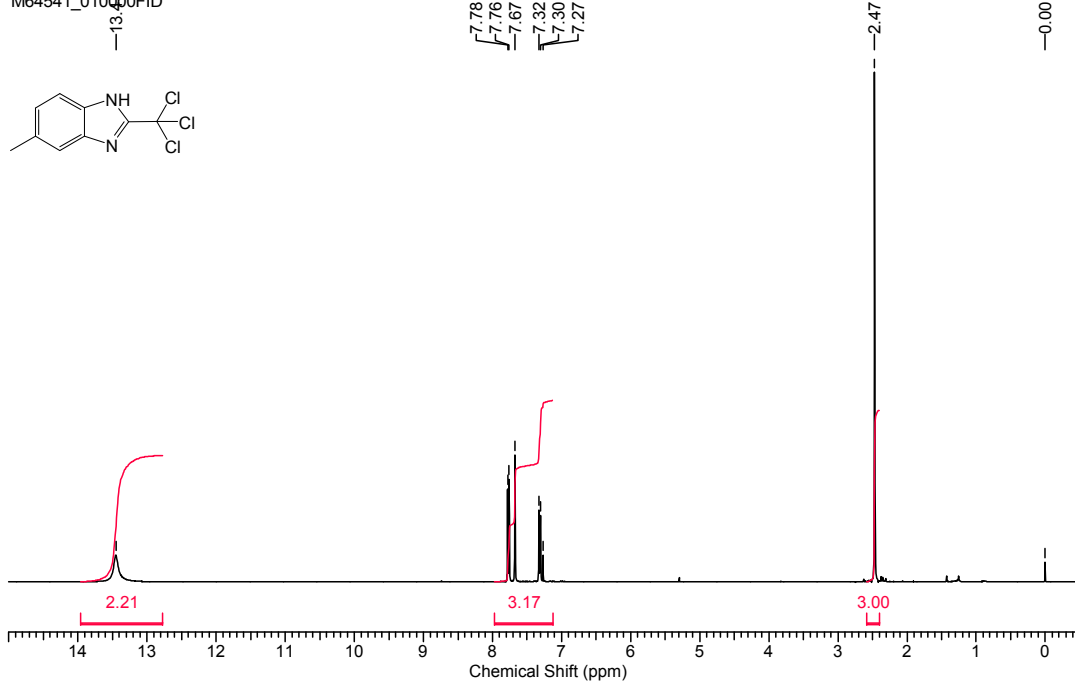
M64650_011000FID



2-(2',2',2'-Trichloromethyl)-5-methyl benzimidazole 19

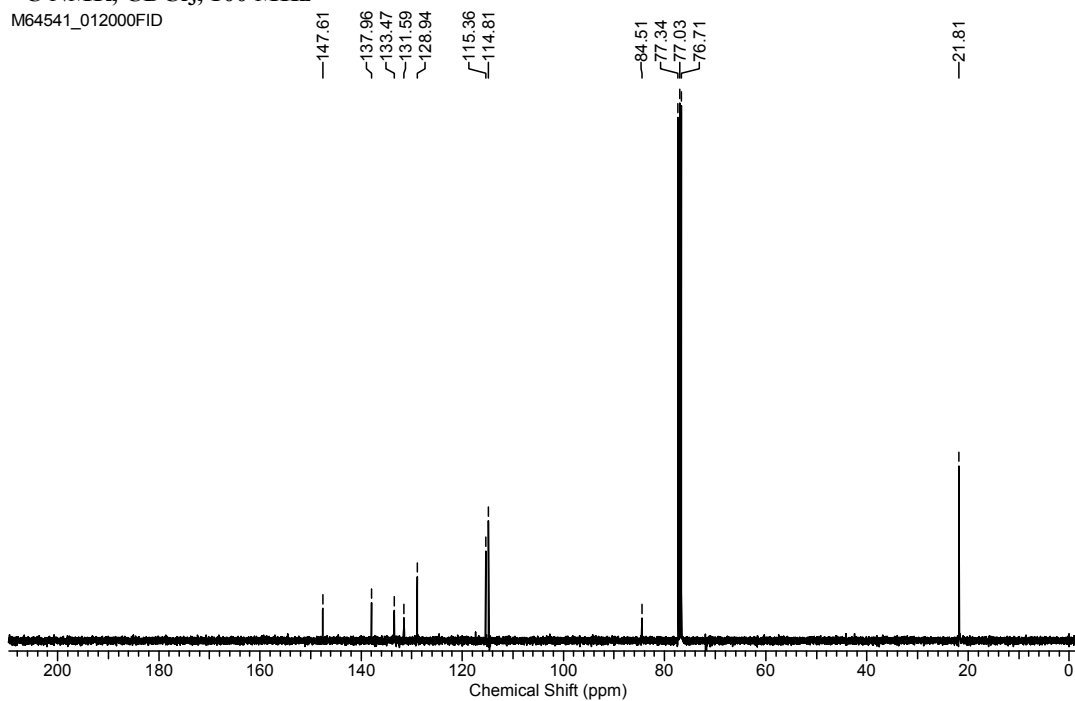
¹H NMR, CDCl₃, 400 MHz

M64541_010000FID



¹³C NMR, CDCl₃, 100 MHz

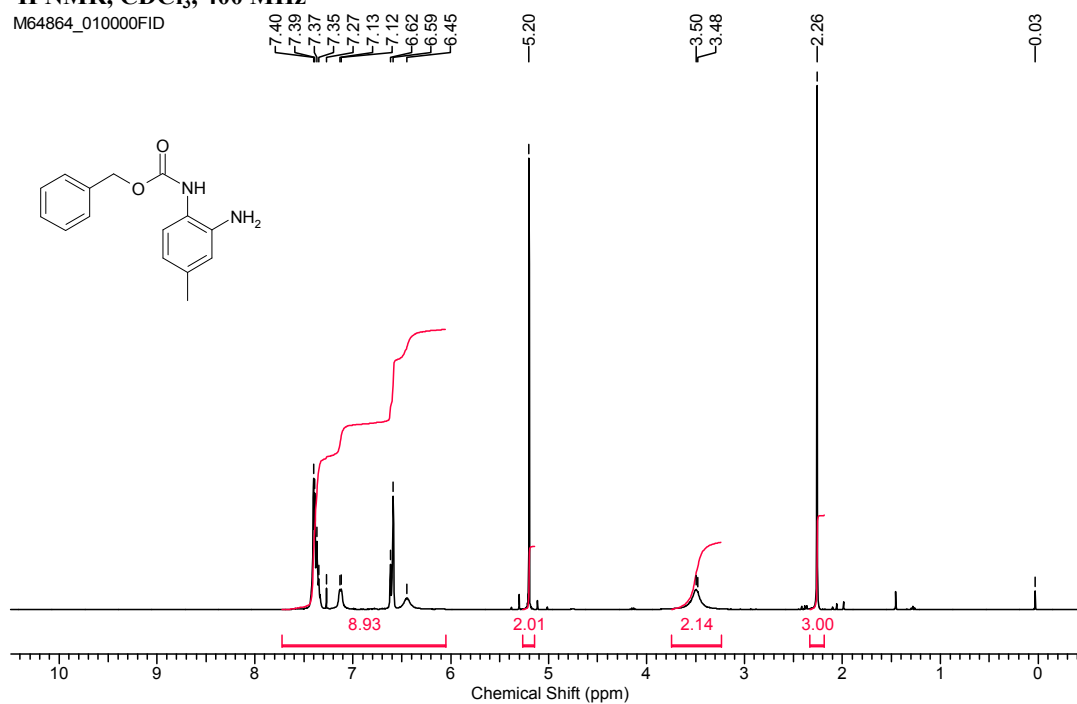
M64541_012000FID



Benzyl (2-aminophenyl) carbamate 20

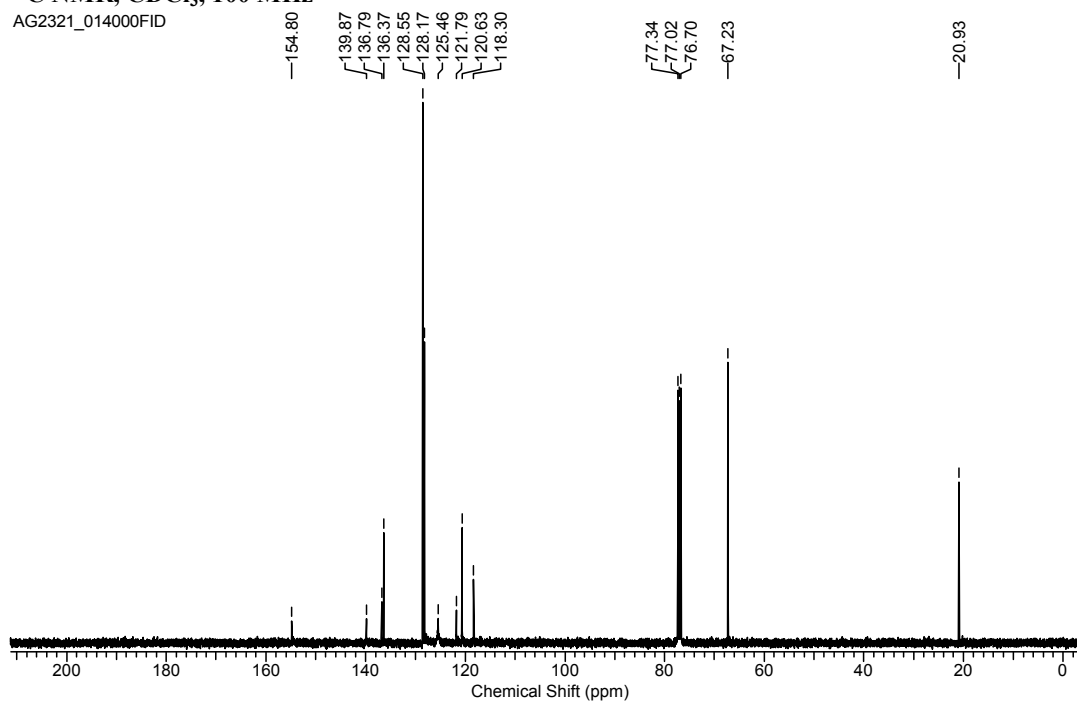
¹H NMR, CDCl₃, 400 MHz

M64864_010000FID



¹³C NMR, CDCl₃, 100 MHz

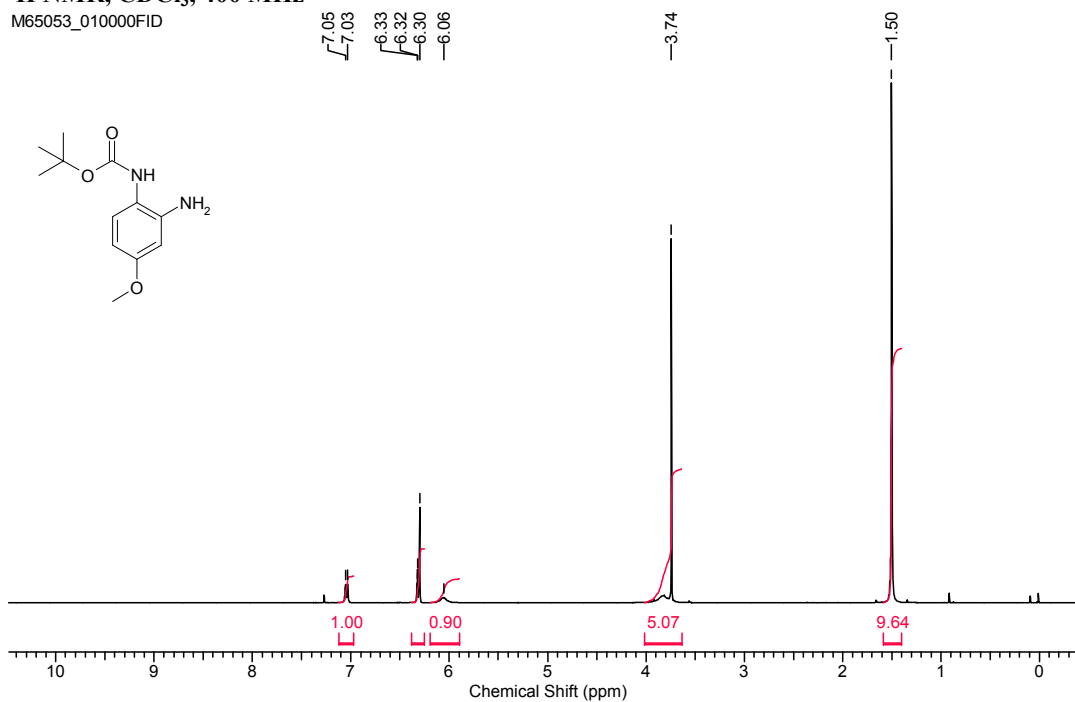
AG2321_014000FID



***tert*-Butyl (2-amino-4-methoxyphenyl) carbamate 21**

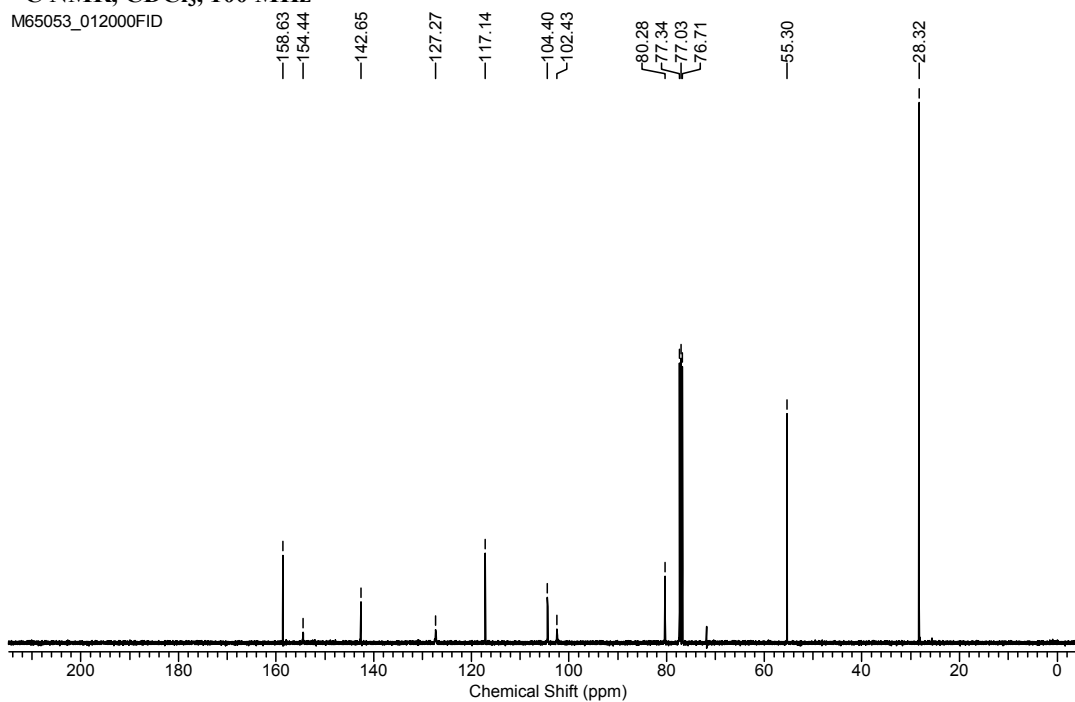
¹H NMR, CDCl₃, 400 MHz

M65053_010000FID



¹³C NMR, CDCl₃, 100 MHz

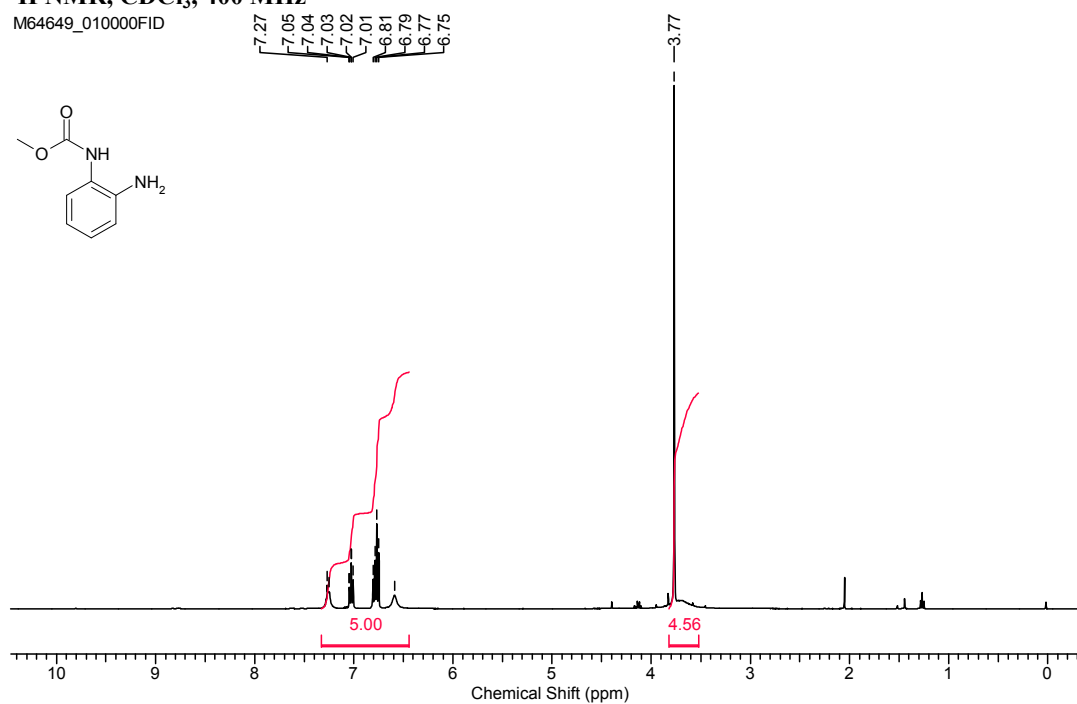
M65053_012000FID



Methyl (2-aminophenyl) carbamate 22

¹H NMR, CDCl₃, 400 MHz

M64649_010000FID



¹³C NMR, CDCl₃, 100 MHz

M64649_012000FID

