

Iridium-catalysed amine alkylation with alcohols in water

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Supporting Information

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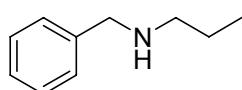
I. General considerations

All the reactions were carried out under a nitrogen atmosphere with dried solvents. Silica gel plates (GF_{254}) were used for TLC monitoring and silica gel (230–400 mesh) was used for flash column chromatography. The following chemicals were purchased from Aldrich and used as received: all the amines and the alcohol. $[Cp^*IrI_2]_2$ was prepared according to literature procedures.¹ All solvents were dry and degassed before use. The 1H , ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 300 instruments with TMS as the internal standard. The mass spectra were run on a microTOF electrospray time of flight (ESI-TOF) coupled to an Agilent 1200 LC system. IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrometer with only selected absorbances quoted as ν in cm^{-1} . Melting points were carried out on a Gallenkamp MF-370 hot stage melting point apparatus.

II. Representative experimental method for the alkylation of amine with alcohol

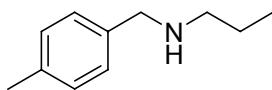
To a nitrogen-purged sealed carousel tube was added $[Cp^*IrI_2]_2$ (0.01 mmol, 11.6 mg), the amine (1 mmol), the alcohol (1.2 mmol), and deionised water (2 mL). The reaction was heated to reflux for 10 h, and then cooled down to room temperature. The crude mixture was extracted with ethyl acetate (x4) then purified by column chromatography with the appropriate eluent.

N-Benzylpropan-1-amine (Table 1, entry 1):²



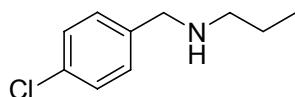
According to the representative method, using benzylamine (1 mmol, 109 µL), propanol (1.2 mmol, 120 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (107 mg, 72%). ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.17 (m, 5H), 3.74 (s, 2H), 2.55 (t, *J* = 7.2 Hz, 2H) 1.96 (br, s, 1H), 1.48 (sextet, *J* = 7.5 Hz, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 140.1, 128.3, 128.1, 126.9, 55.8, 51.2, 23.0, 11.7; HRMS calcd for C₁₀H₁₅NH⁺: 150.1283; Found: 150.1279.

N-(4-Methylbenzyl)propan-1-amine (Table 1, entry 2):²



According to the representative method, using 4-methylbenzylamine (1 mmol, 126 µL), propanol (1.2 mmol, 120 µL) and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (111 mg, 68%). ¹H NMR (300 MHz, CDCl₃) δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 3.76 (s, 2H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.67 (br, s, 1H), 1.54 (sextet, *J* = 7.5 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 137.3, 136.3, 128.9, 127.9, 53.6, 51.2, 23.0, 20.9, 11.7; HRMS calcd for C₁₁H₁₇NH⁺: 136.1126; Found: 136.1122.

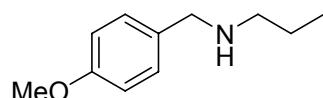
N-(4-Chlorobenzyl)propan-1-amine (Table 1, entry 3):²



According to the representative method, using 4-chlorobenzylamine (1 mmol, 122 µL), propanol (1.2 mmol, 120 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (173 mg, 94%). ¹H NMR (300 MHz, CDCl₃) δ 7.29-7.22 (m, 4H), 3.74 (s, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 1.69 (br, s, 1H), 1.51 (sextet, *J* = 7.5 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ

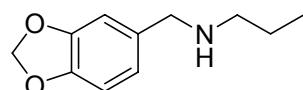
138.8, 132.5, 129.4, 128.4, 53.1, 51.2, 23.1, 11.7; HRMS calcd for C₁₀H₁₄ClNH⁺: 184.0930; Found: 184.0887.

N -(4-Methoxybenzyl)propan-1-amine (Table 1, entry 4):³



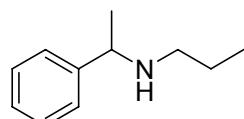
According to the representative method, using 4-methoxybenzylamine (1 mmol, 130 µL), propanol (1.2 mmol, 120 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (159 mg, 89%). ¹H NMR (300 MHz, CDCl₃) δ 7.24 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 3.73 (s, 2H), 2.59 (t, J = 6.9 Hz, 2H), 1.80 (br, s, 1H), 1.53 (sextet, J = 7.5 Hz, 2H), 0.92 (t, J = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 158.5, 132.4, 129.2, 128.2, 113.8, 113.6, 55.1, 53.2, 51.1, 23.0, 11.7; HRMS calcd for C₁₁H₁₇NOH⁺: 180.1388; Found: 180.1382.

N -(Benzo[1,3]dioxol-5-ylmethyl)propan-1-amine (Table 1, entry 5):²



According to the representative method, using piperonylamine (1 mmol, 124 µL), propanol (1.2 mmol, 120 µL), and the title compound was obtained by flash chromatography eluting with EtOAc then (DCM/MeOH; 98/2) to give a colourless solid (159 mg, 89%). ¹H NMR (300 MHz, CDCl₃) δ 6.98 (d, J = 1.5 Hz, 1H), 6.91 (m, 1H), 6.77 (d, J = 7.8 Hz, 1H), 5.92 (s, 2H), 4.92 (br, s, 1H), 3.83 (s, 2H), 2.65 (t, J = 7.5 Hz, 2H), 1.68 (sextet, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 147.9, 147.5, 128.9, 122.8, 109.6, 108.3, 101.1, 52.0, 49.2, 21.2, 11.5; HRMS calcd for C₁₁H₁₅NO₂H⁺: 194.1181; Found: 194.1175.

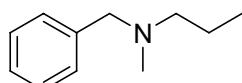
N -(1-Phenylethyl)propan-1-amine (Table 1, entry 6):⁴



According to the representative method, using 1-phenylethanamine (1 mmol, 127 µL), propanol (1.2 mmol, 120 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (137 mg, 84%). ¹H

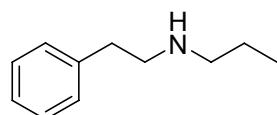
NMR (300 MHz, CDCl₃) δ 7.27-7.16 (m, 5H), 3.70 (q, *J* = 6.6 Hz, 1H), 2.44-2.28 (m, 2H), 1.45-1.39 (m, 3H), 1.30 (d, *J* = 6.6 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 145.9, 128.3, 126.7, 126.5, 58.3, 49.7, 24.3, 23.3, 11.7; HRMS calcd for C₁₁H₁₇NH⁺: 164.1439; Found: 164.1432.

***N*-Benzyl-N-methylpropan-1-amine (Table 1, entry 7):⁵**



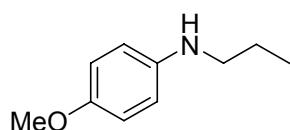
According to the representative method, using *N*-benzylmethylamine (1 mmol, 129 μL), propanol (1.2 mmol, 120 μL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (109 mg, 67%). ¹H NMR (300 MHz, CDCl₃) δ 7.34-7.20 (m, 5H), 3.49 (s, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.18 (s, 3H), 1.53 (sextet, *J* = 7.5 Hz, 2H), 0.88 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 138.7, 129.1, 128.2, 126.9, 62.2, 59.4, 42.1, 20.4, 11.8; HRMS calcd for C₁₁H₁₇NH⁺: 164.1439; Found: 164.1435.

***N*-phenethylpropan-1-amine (Table 1, entry 8):⁶**



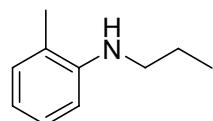
According to the representative method, using 2-phenylethanamine (1 mmol, 130 μL), propanol (1.2 mmol, 127 μL), and the title compound was obtained by flash chromatography eluting with hexane then (DCM/MeOH; 10/1) to give a colourless oil (111 mg, 68%). ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.18 (m, 5H), 2.96-2.82 (m, 4H), 2.64 (t, *J* = 7.2 Hz, 2H), 1.85 (br, s, 1H), 1.56 (sextet, *J* = 7.5 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 139.9, 128.6, 128.4, 126.1, 114.6, 51.6, 51.0, 36.2, 22.9, 11.7; HRMS calcd for C₁₁H₁₇NH⁺: 164.1435; Found: 164.1432.

4-Methoxy-N-propylaniline (Table 1, entry 9):⁷



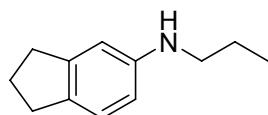
According to the representative method, using *p*-anisidine (1 mmol, 130 µL), propanol (1.2 mmol, 120 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (124 mg, 75%). ¹H NMR (300 MHz, CDCl₃) δ 6.78 (d, *J* = 9.0 Hz, 2H), 6.58 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 3.04 (t, *J* = 7.2 Hz, 2H), 1.63 (sextet, *J* = 7.5 Hz, 2H), 1.26 (br, s, 1H), 0.99 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 151.9, 142.7, 114.8, 114.1, 55.8, 46.9, 22.8, 11.6; HRMS calcd for C₁₀H₁₅NOH⁺: 166.1232; Found: 166.1226.

2-Methyl-N-propylaniline (Table 1, entry 10):⁷



According to the representative method, using *o*-toluidine (1 mmol, 123 µL), propanol (1.2 mmol, 120 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/3) to give a colourless oil (89 mg, 60%). ¹H NMR (300 MHz, CDCl₃) δ 7.26-7.11 (m, 2H), 6.75-6.67 (m, 2H) 6.57 (d, *J* = 8.7 Hz, 2H), 3.53 (br, s, 1H), 3.20 (t, *J* = 6.9 Hz, 2H), 2.21 (s, 3H), 1.76 (sextet, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 146.2, 129.9, 127.0, 121.6, 116.5, 109.5, 45.6, 22.7, 17.4, 11.6; HRMS calcd for C₉H₁₃NOH⁺: 150.1283; Found: 150.1278.

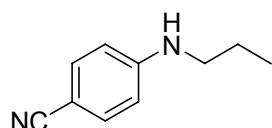
N-Propyl-2,3-dihydro-1H-inden-5-amine (Table 1, entry 11)



According to the representative method, using 5-aminoindan (1 mmol, 123 µL), propanol (1.2 mmol, 120 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/3) to give a colourless oil (124 mg, 71%). ν_{max} /cm⁻¹ (CH₂Cl₂): 2953, 2931, 2841, 1614. ¹H NMR (300 MHz, CDCl₃) δ 7.06 (d, *J* = 7.8 Hz, 1H), 6.57 (s, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 3.35 (br, s, 1H), 3.10 (t, *J* = 6.9 Hz, 4H), 2.86 (q, *J* =

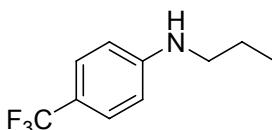
7.5 Hz, 2H), 2.08 (quintet, J = 7.2 Hz, 2H), 1.67 (sextet, J = 7.5 Hz, 2H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.3, 145.3, 132.7, 124.6, 111.2, 108.8, 46.3, 33.1, 31.8, 25.6, 22.7, 11.6; HRMS calcd for $\text{C}_{12}\text{H}_{17}\text{NH}^+$: 176.1439; Found: 176.1431. Anal. Calc. for $\text{C}_{12}\text{H}_{17}\text{N}_1$: C, 82.23; H, 9.78; N, 7.99; Found: C, 82.18; H, 9.74; N, 7.91.

4-(Propylamino)benzonitrile (Table 1, entry 12)



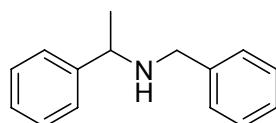
According to the representative method, using 4-aminobenzonitrile (1 mmol, 130 μL), propanol (1.2 mmol, 120 μL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless solid (29 mg, 18 %); mp 45-52 °C. ν_{max} /cm⁻¹ (neat): 3380, 2980, 2957, 2882, 2204. ^1H NMR (300 MHz, CDCl_3) δ 7.43-7.38 (m, 2H), 6.56-6.51 (m, 2H), 4.19 (br, s, 1H), 3.15-3.08 (m, 2H), 1.66 (sextet, J = 7.5 Hz, 2H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 151.4, 133.7, 120.5, 112.0, 98.4, 44.9, 22.4, 11.5; HRMS calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{H}^+$: 161.1078; Found: 161.1073. Anal. Calc. for $\text{C}_{10}\text{H}_{12}\text{N}_2$: C, 74.97; H, 7.55; N, 17.48; Found: C, 74.90, H, 7.52, N, 17.42.

N-propyl-4-(trifluoromethyl)aniline (Table 1, entry 13)



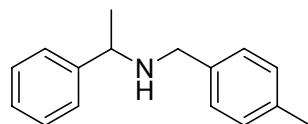
According to the representative method, using 4-(trifluoromethyl)aniline (1 mmol, 130 μL), propanol (1.2 mmol, 120 μL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (46 mg, 23%). ν_{max} /cm⁻¹ (neat): 3758, 2965, 2937, 2550, 2161, 1676, 1616. ^1H NMR (300 MHz, CDCl_3) δ 7.27-7.21 (m, 2H), 6.90 (d, J = 7.8 Hz, 1H), 6.78 (s, 1H), 6.74-6.70 (m, 1H), 3.82 (br, s, 1H), 3.11 (t, J = 6.9 Hz, 2H), 1.66 (sextet, J = 7.5 Hz, 2H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.6, 129.5, 115.6 (d, J = 12 Hz), 113.4 (quartet, J = 3.6 Hz), 108.2-108.5(m), 45.5, 22.5, 11.6; ^{19}F (376 MHz, CDCl_3): -62.96; HRMS calcd for $\text{C}_{10}\text{H}_{12}\text{F}_3\text{NH}^+$: 204.1000; Found: 204.0997. Anal. Calc. for $\text{C}_{10}\text{H}_{12}\text{NF}_3$: C, 59.11; H, 5.95; N, 6.89; Found: C, 59.80, H, 5.98, N, 6.85.

N -Benzyl-1-phenylethanamine (Table 2, entry 1):⁸



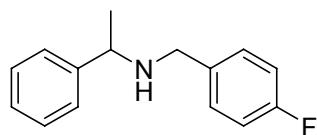
According to the representative method, using 1-phenylethanamine (1 mmol, 127 µL) benzyl alcohol (1 mmol, 104 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (207 mg, 98%). ¹H NMR (300 MHz, CDCl₃) δ 7.32-7.18 (m, 10H), 3.77 (q, *J* = 6.6 Hz, 1H), 3.62 and 3.54 (AB system, *J* = 13.2 Hz, 2H), 1.79 (br, s, 1H), 1.33 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 128.5, 128.4, 128.3, 128.2, 126.9, 126.8, 126.7, 57.5, 51.6, 24.4; HRMS calcd for C₁₅H₁₇NH⁺: 212.1439; Found: 212.1426.

N -(4-Methylbenzyl)-1-phenylethanamine (Table 2, entry 2):⁸



According to the representative method, using 1-phenylethanamine (1 mmol, 127 µL) 4-methylbenzyl alcohol (1 mmol, 122 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (175 mg, 78%). ¹H NMR (300 MHz, CDCl₃) δ 7.27-7.00 (m, 9H), 3.71 (q, *J* = 6.6 Hz, 1H), 3.53 and 3.46 (AB system, *J* = 13.2 Hz, 2H), 2.23 (s, 3H), 1.58 (br, s, 1H), 1.26 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 145.6, 137.5, 136.3, 128.9, 128.4, 128.0, 126.8, 126.7, 57.3, 51.3, 24.4, 21.0; HRMS calcd for C₁₆H₁₉NH⁺: 226.1595; Found: 226.1585.

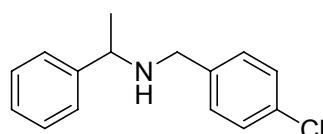
N -(4-Fluorobenzyl)-1-phenylethanamine (Table 2, entry 3):⁸



According to the representative method, using 1-phenylethanamine (1 mmol, 127 µL) 4-fluorobenzyl alcohol (1.2 mmol, 108 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (188 mg, 82%). ν_{max} /cm⁻¹ (CH₂Cl₂): 3801, 3031, 2966, 1601, 1507. ¹H NMR (300 MHz, CDCl₃) δ 7.25 (d, *J* = 4.2 Hz, 4H), 7.16-7.11 (m, 5H), 6.88 (t, *J* = 8.7, 2H), 3.69 (q, *J* = 6.6 Hz, 1H),

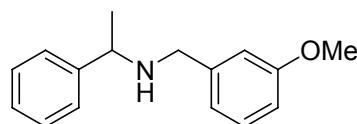
3.52 and 3.46 (AB system, $J = 13.2$ Hz, 2H), 1.49 (br, s, 1H), 1.27 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 162.0 (d, $J = 243.0$ Hz), 145.4, 136.3 (d, $J = 3.0$ Hz), 129.5 (d, $J = 7.8$ Hz), 128.4, 126.8, 128.6, 114.9 (d, $J = 21$ Hz), 57.4, 50.8, 24.4; ^{19}F (376 MHz, CDCl_3): -116.0(-116.2) (m); HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{FNH}^+$: 230.1345; Found: 230.1338.

***N*-(4-Chlorobenzyl)-1-phenylethanamine (Table 2, entry 4):⁸**



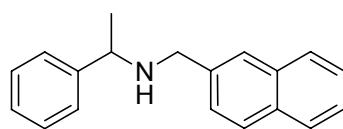
According to the representative method, using 1-phenylethanamine (1 mmol, 127 μL) 4-chlorobenzyl alcohol (1.2 mmol, 143 μL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (194 mg, 79%). ^1H NMR (300 MHz, CDCl_3) δ 7.28-7.11 (m, 9H), 3.70 (q, $J = 6.6$ Hz, 1H), 3.54 and 3.47 (AB system, $J = 13.2$ Hz, 2H), 1.63 (br, s, 1H), 1.28 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.2, 139.0, 132.4, 129.4, 128.5, 128.4, 126.9, 126.6, 56.4, 50.8, 24.4; HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{ClNH}^+$: 246.1049; Found: 246.1040.

***N*-(3-Methoxybenzyl)-1-phenylethanamine (Table 2, entry 5):⁹**



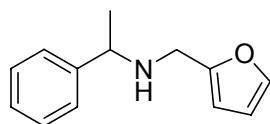
According to the representative method, using 1-phenylethanamine (1 mmol, 127 μL), 3-methoxybenzyl alcohol (1.2 mmol, 124 μL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (183 mg, 76%). ^1H NMR (300 MHz, CDCl_3) δ 7.29-7.05 (m, 6H), 6.82 (m, 3H), 3.72 (s, 3H), 3.70-3.64 (m, 1H), 3.61 and 3.48 (AB system, $J = 13.2$ Hz, 2H), 1.97 (br, s, 1H), 1.25 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.7, 145.5, 129.9, 128.3, 128.2, 126.8, 110.2, 57.2, 55.2, 47.1, 24.4; HRMS calcd for $\text{C}_{16}\text{H}_{19}\text{NOH}^+$: 242.1545; Found: 242.1533.

***N*-(Naphthalen-2-ylmethyl)-1-phenylethanamine (Table 2, entry 6)¹⁰**



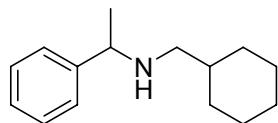
According to the representative method, using 1-phenylethanamine (1 mmol, 127 µL), naphthalen-2-ylmethanol (1.2 mmol, 190 mg), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (188 mg, 72%). ¹H NMR (300 MHz, CDCl₃) δ 7.70-7.67 (m, 2H), 7.58 (s, 1H), 7.33-7.12 (m, 9H), 3.75-3.60 (m, 3H), 1.63 (br, s, 1H), 1.27 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 145.5, 138.0, 133.3, 132.5, 128.4, 127.9, 127.6, 127.5, 126.9, 126.6, 126.5, 126.3, 125.8, 125.4, 57.4, 51.6, 24.5; HRMS calcd for C₁₉H₁₉NH⁺: 262.1595; Found: 262.1593.

***N*-(Furan-2-ylmethyl)-1-phenylethanamine (Table 2, entry 7):¹¹**



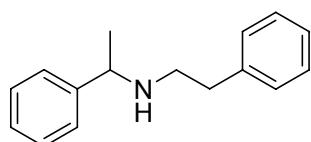
According to the representative method, using 1-phenylethanamine (1 mmol, 127 µL), furfuryl alcohol (1.2 mmol, 104 µL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (173 mg, 86%). ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.25 (m, 5H), 6.37-6.27 (m, 2H), 6.13 (d, *J* = 3.0 Hz, 1H), 3.81 (q, *J* = 6.9 Hz, 1H), 3.70 and 3.71 (AB system, *J* = 14.4 Hz, 2H), 2.11 (br, s, 1H), 1.39 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 153.7, 144.8, 141.6, 128.4, 126.9, 126.6, 109.9, 106.7, 56.9, 43.8, 24.1; HRMS calcd for C₁₃H₁₅NOH⁺: 224.1051; Found: 224.1044.

***N*-(Cyclohexylmethyl)-1-phenylethanamine (Table 2, entry 8):¹²**



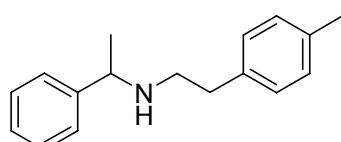
According to the representative method, using 1-phenylethanamine (1 mmol, 127 μ L), cyclohexanemethanol (1.2 mmol, 123 μ L), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (163 mg, 75%). 1 H NMR (300 MHz, CDCl₃) δ 7.27-7.16 (m, 5H), 3.68 (q, J = 6.6 Hz, 1H), 2.33-2.15 (m, 2H), 1.66-1.59 (m, 2H), 1.30 (d, J = 6.6 Hz, 3H), 1.21-1.03 (m, 6H), 0.85-0.72 (m, 4H); 13 C NMR (75 MHz, CDCl₃) δ 145.7, 128.3, 126.8, 126.6, 58.4, 54.5, 37.9, 31.5, 31.4, 26.6, 26.0, 25.9, 24.4; HRMS calcd for C₁₅H₂₃NH⁺: 218.1908; Found: 218.1893.

N -Phenethyl-1-phenylethanamine (Table 2, entry 9):¹³



According to the representative method, using 1-phenylethanamine (1 mmol, 127 μ L)), phenethyl alcohol (1.2 mmol, 151 μ L), and the title compound was obtained by flash chromatography eluting with (DCM/MeOH; 98/2) to give a colourless oil (185 mg, 82%). 1 H NMR (300 MHz, CDCl₃) δ 7.32-7.13 (m, 10H), 3.76 (q, J = 6.6 Hz, 1H), 2.81-2.67 (m, 4H), 1.62 (br, s, 1H), 1.31 (d, J = 6.6 Hz, 3H); 13 C NMR (75 MHz, CDCl₃) δ 145.4, 139.9, 128.6, 128.3, 126.8, 126.5, 126.0, 58.1, 48.8, 36.3, 24.2; HRMS calcd for C₁₆H₁₉NH⁺: 226.1595; Found: 226.1591.

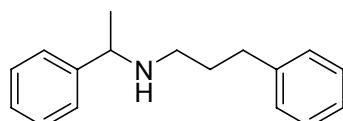
N -(4-Methylphenethyl)-1-phenylethanamine (Table 2, entry 10)



According to the representative method, using 1-phenylethanamine (1 mmol, 127 μ L), 4-methylphenethyl alcohol (1.2 mmol, 167 μ L), and the title compound was obtained by flash chromatography eluting with hexane then (DCM/MeOH; 98/2) to give a colourless oil (232 mg, 97%). ν_{max} /cm⁻¹ (CH₂Cl₂): 3324, 2961, 2922, 1735, 1591. 1 H NMR (300 MHz, CDCl₃) δ 7.32-7.23 (m, 5H), 7.11-7.04 (m, 4H), 3.78 (q, J = 6.6 Hz, 1H), 2.78-2.66 (m, 4H), 2.32 (s, 3H), 1.57 (br, s, 1H), 1.23 (t, J = 6.6 Hz, 3H); 13 C NMR (75 MHz, CDCl₃) δ 145.5, 136.8, 135.5, 129.0, 128.5, 128.4, 126.8, 126.5, 58.2, 48.9, 35.9, 24.2, 20.9; HRMS calcd for

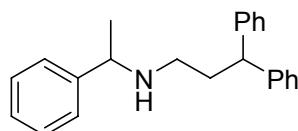
$C_{17}H_{21}NH^+$: 240.1752; Found: 240.1745. Anal. Calc. for $C_{17}H_{21}N$: C, 85.30; H, 8.84; N, 5.85; Found: C, 85.26; H, 8.80; 5.79.

3-Phenyl-N-(1-phenylethyl)propan-1-amine (Table 2, entry 11):¹⁴



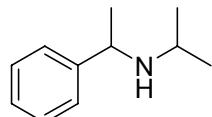
According to the representative method, using 1-phenylethanamine (1 mmol, 127 μ L), 3-phenyl-1-propanol (1.2 mmol, 162 μ L), and the title compound was obtained by flash chromatography eluting with hexane then (DCM/MeOH; 98/2) to give a colourless oil (218 mg, 91%). 1H NMR (300 MHz, $CDCl_3$) δ 7.31-7.09 (m, 10H), 3.70 (q, J = 6.6 Hz, 1H), 2.66-2.42 (m, 2H), 1.47 (br, s, 1H), 1.30 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 142.1, 128.5, 128.3, 128.2, 126.7, 126.5, 125.6, 58.3, 47.3, 33.6, 31.8, 24.2; HRMS calcd for $C_{17}H_{21}NH^+$: 240.1747; Found: 240.1752.

3,3-Diphenyl-N-(1-phenylethyl)propan-1-amine (Table 2, entry 12):¹⁵



According to the representative method, using 1-phenylethanamine (1 mmol, 127 μ L) 3,3-diphenyl-1-propanol (1.2 mmol, 239 μ L), and the title compound was obtained by flash chromatography eluting with hexane then (DCM/MeOH; 98/2) to give a colourless oil (268 mg, 85%). 1H NMR (300 MHz, $CDCl_3$) δ 7.32-7.17 (m, 5H), 4.01 (t, J = 7.8 Hz, 1H), 3.73 (q, J = 6.6 Hz, 1H), 2.58-2.48 (m, 2H), 2.40-2.21 (m, 2H), 2.05 (br, s, 1H), 1.34 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 144.8, 144.5, 128.3 (d, J = 1.8 Hz), 127.7 (d, J = 7.8 Hz), 126.8, 126.4, 126.0, 58.1, 48.9, 45.8, 35.8, 24.1; HRMS calcd for $C_{23}H_{25}NH^+$: 316.2065; Found: 316.2064

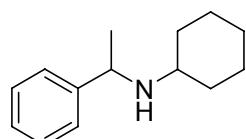
N-(1-phenylethyl)propan-2-amine (Table 2, entry 13)¹⁶



According to the representative method, using 1-phenylethanamine (1 mmol, 127 μ L), isopropanol (1.2 mmol, 92 μ L), and the title compound was obtained by flash

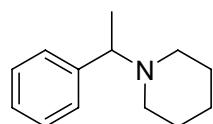
chromatography eluting with hexane then (EtOAc/Hexane; 1/3) to give a yellow oil (148 mg, 91%). ^1H NMR (300 MHz, CDCl_3) δ 7.32-7.18 (m, 5H), 3.85 (q, $J = 6.6$ Hz, 1H), 2.58 (heptet, $J = 6.0$ Hz, 1H), 1.31 (d, $J = 6.6$ Hz, 3H), 1.00-0.94 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.9, 128.3, 126.6, 126.3, 54.9, 45.4, 24.8, 24.0, 22.1; HRMS calcd for $\text{C}_{11}\text{H}_{17}\text{NH}^+$: 164.1434; Found: 164.1429.

***N*-(1-Phenylethyl)cyclohexanamine (Table 2, entry 14):¹⁷**



According to the representative method, using 1-phenylethanamine (1 mmol, 127 μL) cyclohexanol (1 mmol, 104 μL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (138 mg, 68%). ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.13 (m, 5H), 3.92 (q, $J = 6.6$ Hz, 1H), 2.28-2.19 (m, 1H), 2.00-1.89 (m, 2H), 1.70-1.58 (m, H), 1.51 (br, s, 1H), 1.29 (d, $J = 6.6$ Hz, 3H), 1.14-0.96 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.1, 128.3, 126.4, 54.4, 53.6, 34.4, 33.1, 26.1, 25.2, 24.9; HRMS calcd for $\text{C}_{14}\text{H}_{21}\text{NH}^+$: 204.1747; Found: 204.1752.

1-(1-Phenylethyl)piperidine (Table 2, entry 15)¹⁸



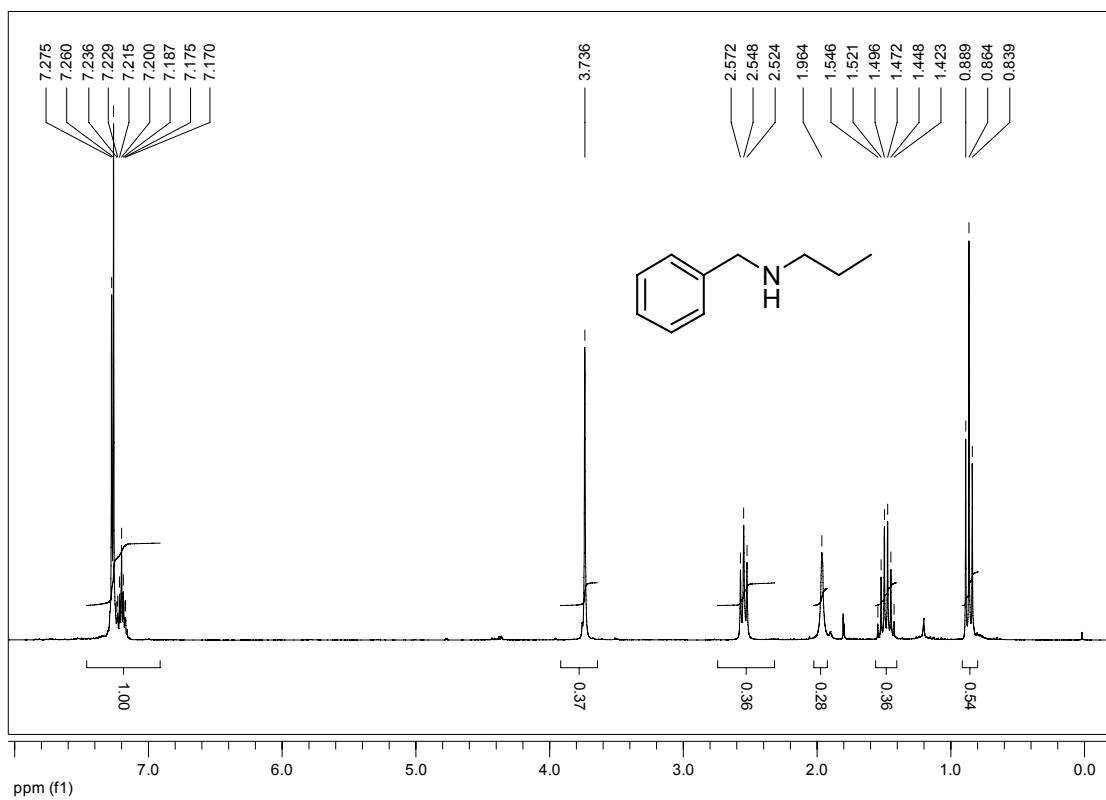
According to the representative method, using 1-phenylethanamine (1 mmol, 127 μL), pentane-1,5-diol (1 mmol, 105 μL), and the title compound was obtained by flash chromatography eluting with hexane then (EtOAc/Hexane; 1/10) to give a colourless oil (180 mg, 95%). ^1H NMR (300 MHz, CDCl_3) δ 7.27-7.16 (m, 5H), 3.35 (q, $J = 6.6$ Hz, 1H), 2.39-2.28 (m, 6H), 1.54-1.48 (m, 4H), 1.33 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.9, 127.9, 127.7, 126.6, 65.1, 51.5, 26.2, 24.6, 19.3; HRMS calcd for $\text{C}_{13}\text{H}_{19}\text{NH}^+$: 190.1595; Found: 190.1589.

III. References

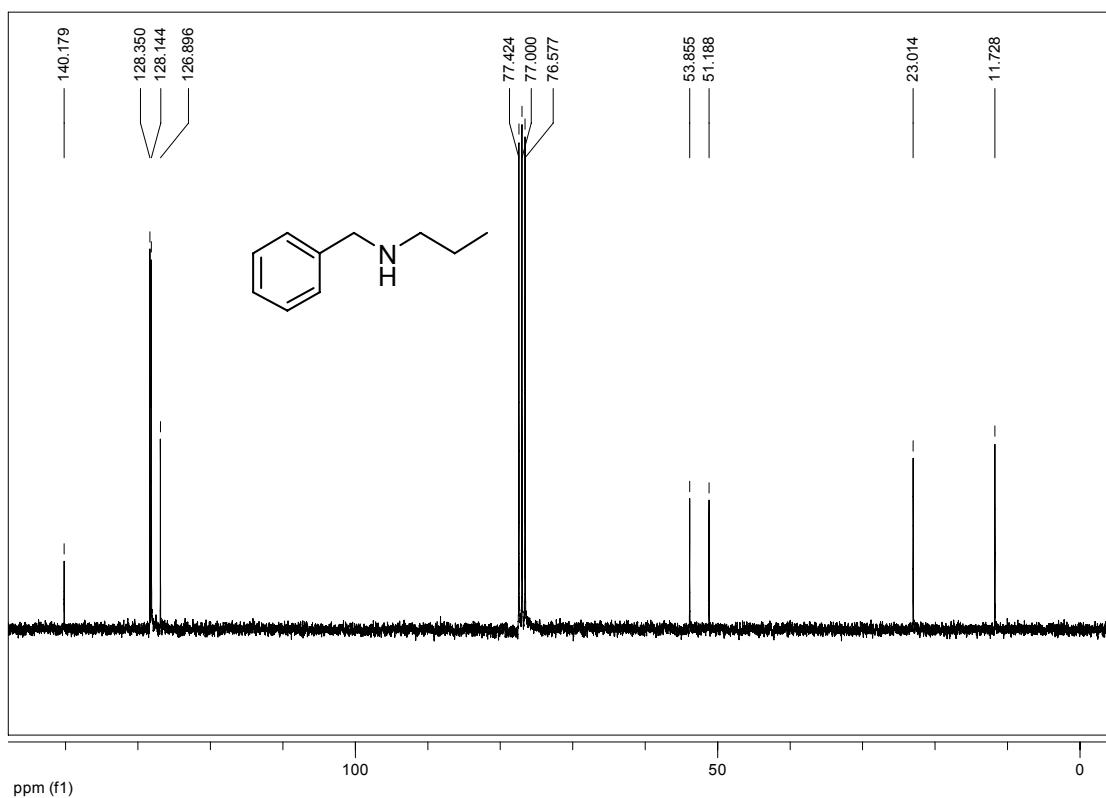
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IV. ^1H NMR and ^{13}C NMR spectra

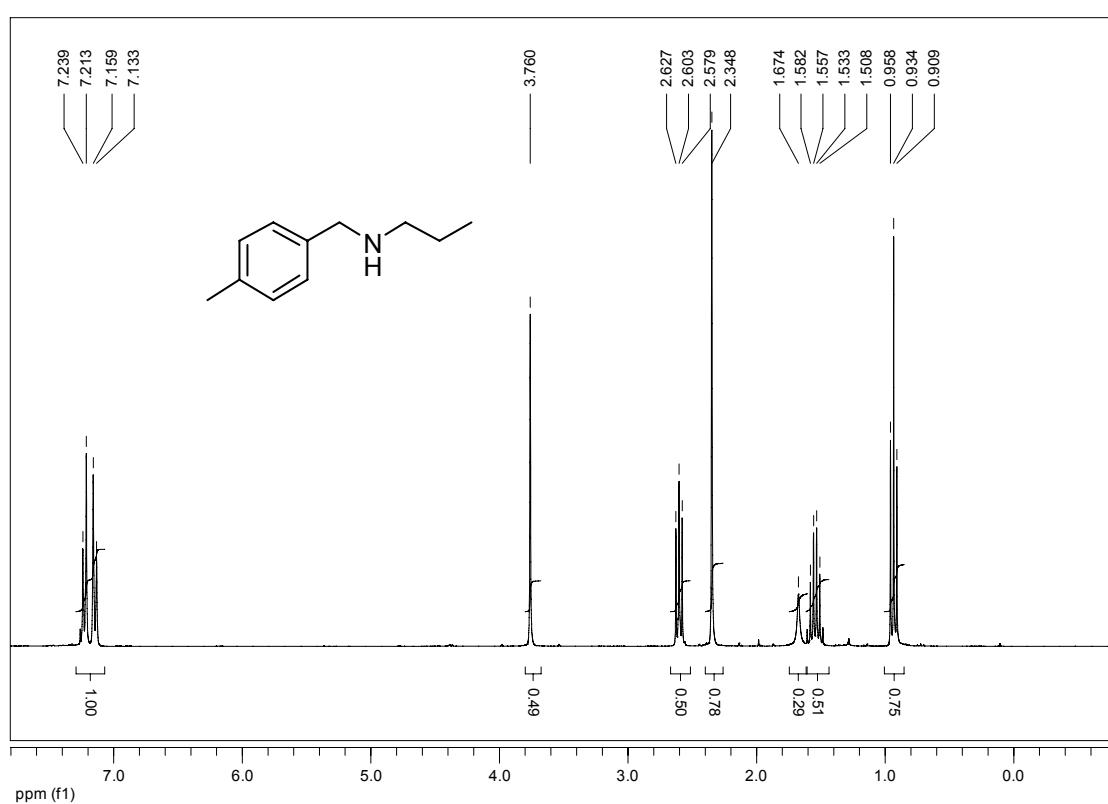
^1H NMR (300 MHz, CDCl_3): *N*-benzylpropan-1-amine (Table 1, entry 1)



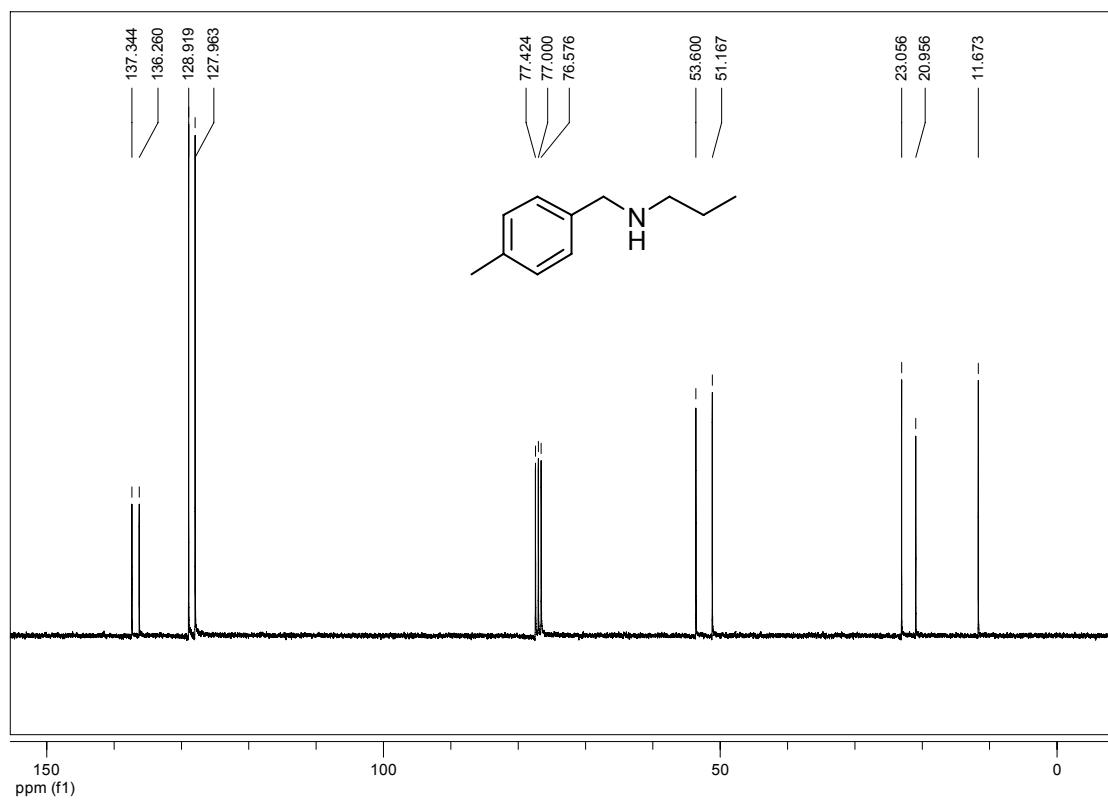
^{13}C NMR (75 MHz, CDCl_3): *N*-benzylpropan-1-amine (Table 1, entry 1)



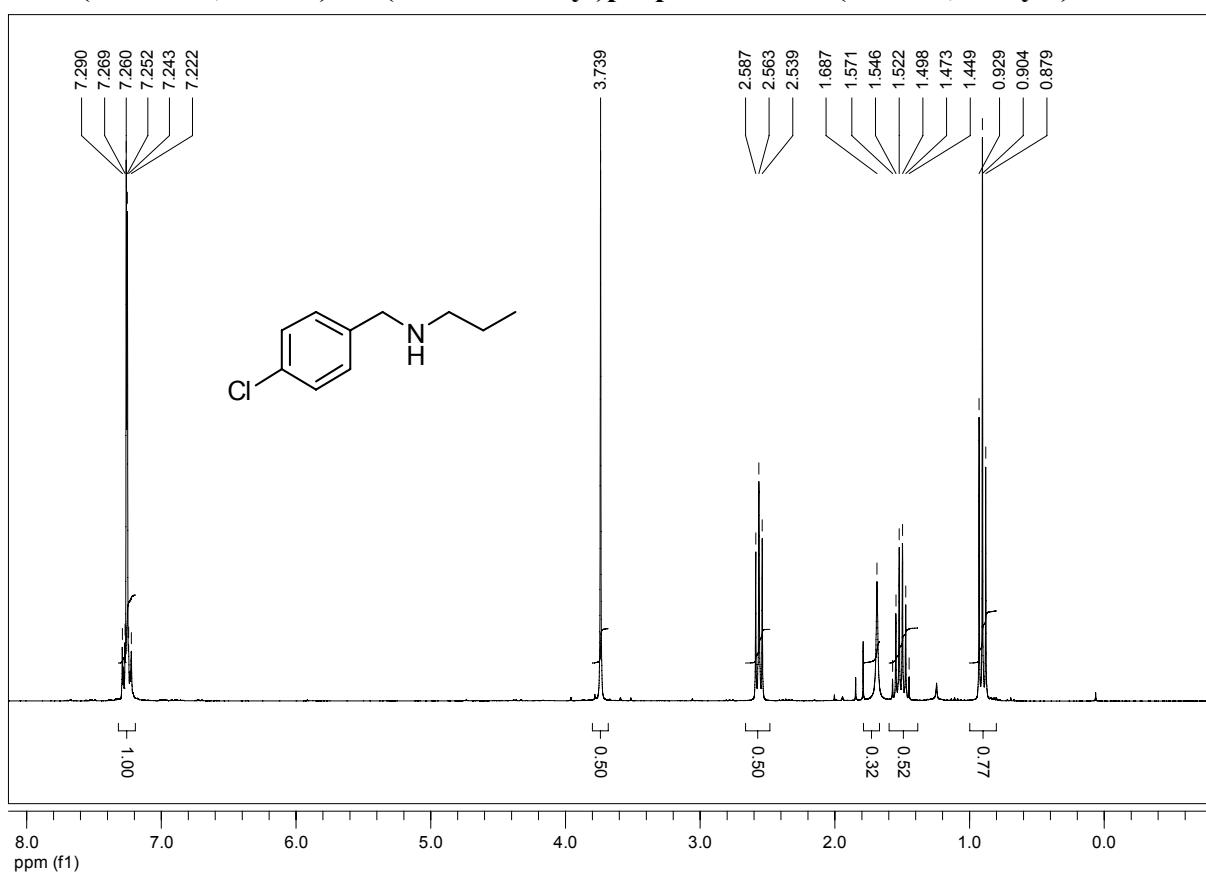
¹H NMR (300 MHz, CDCl₃): N-(4-methylbenzyl)propan-1-amine (Table 1, entry 2)



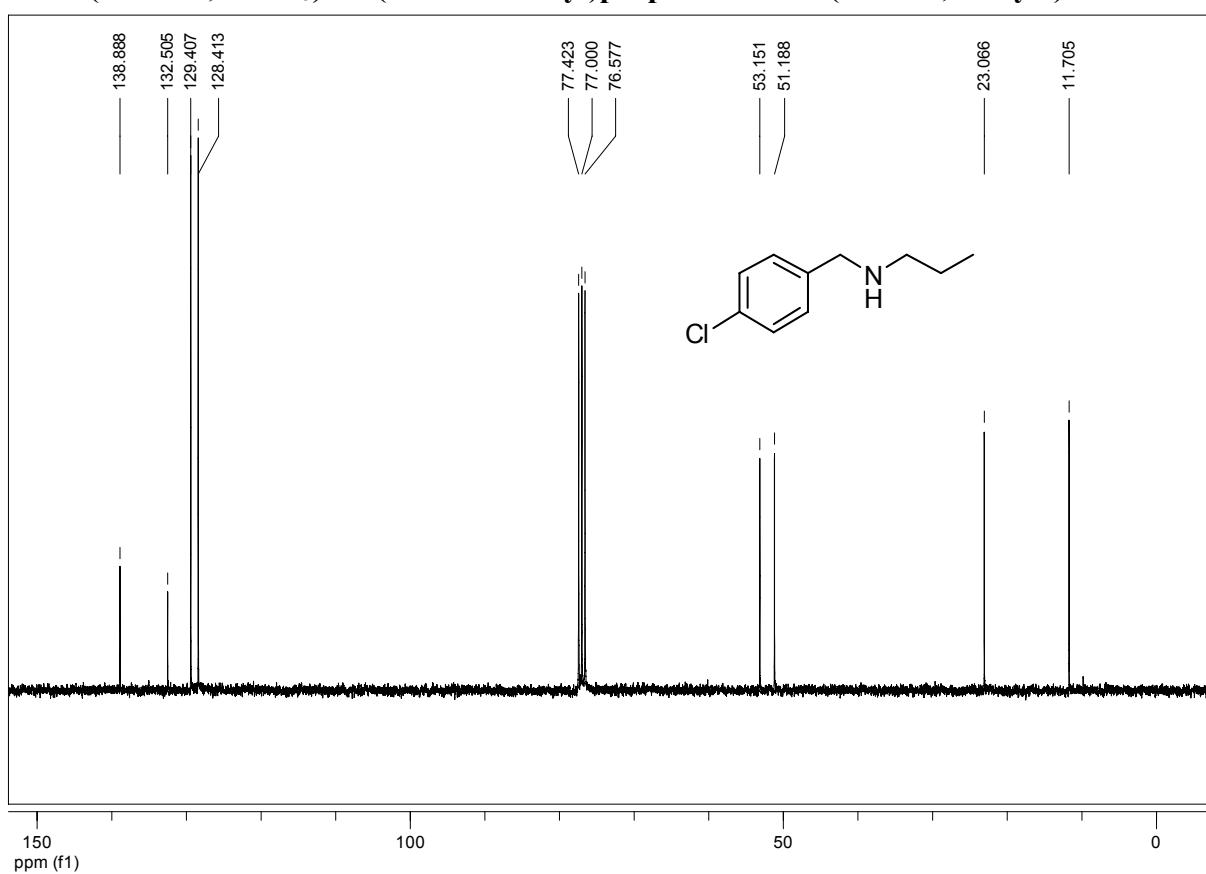
¹³C NMR (75 MHz, CDCl₃): N-(4-methylbenzyl)propan-1-amine (Table 1, entry 2)



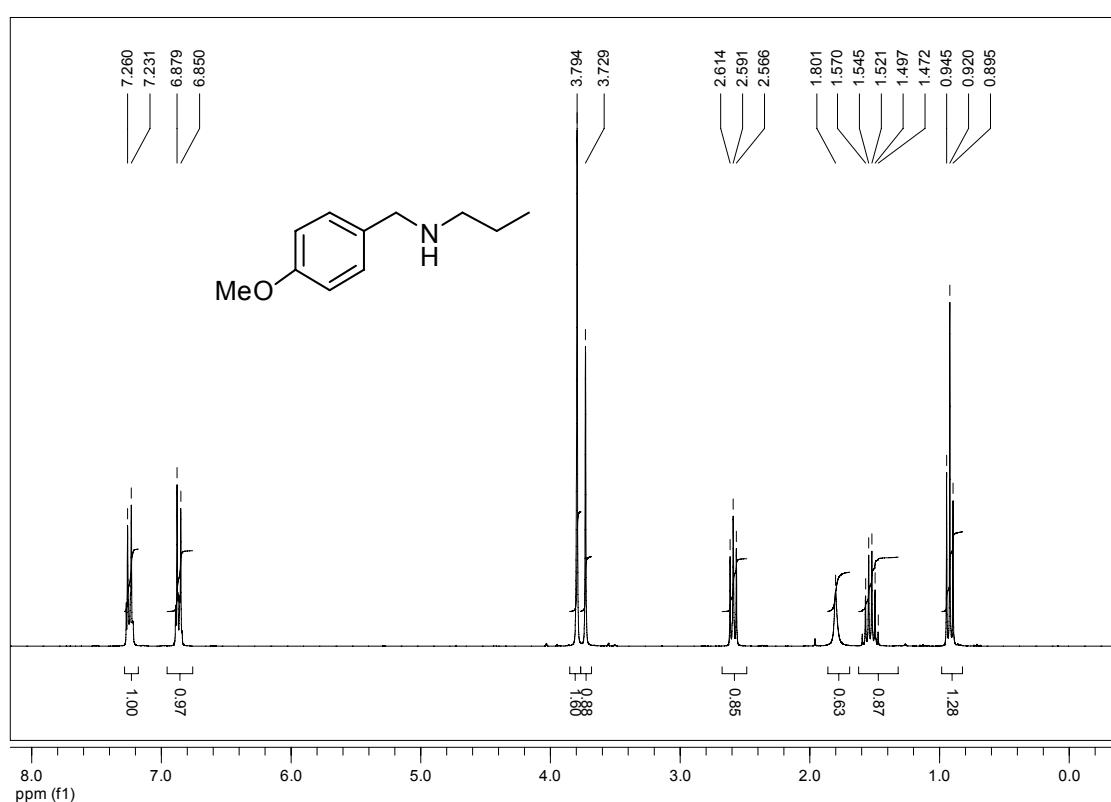
¹H NMR (300 MHz, CDCl₃): *N*-(4-chlorobenzyl)propan-1-amine (Table 1, entry 3)



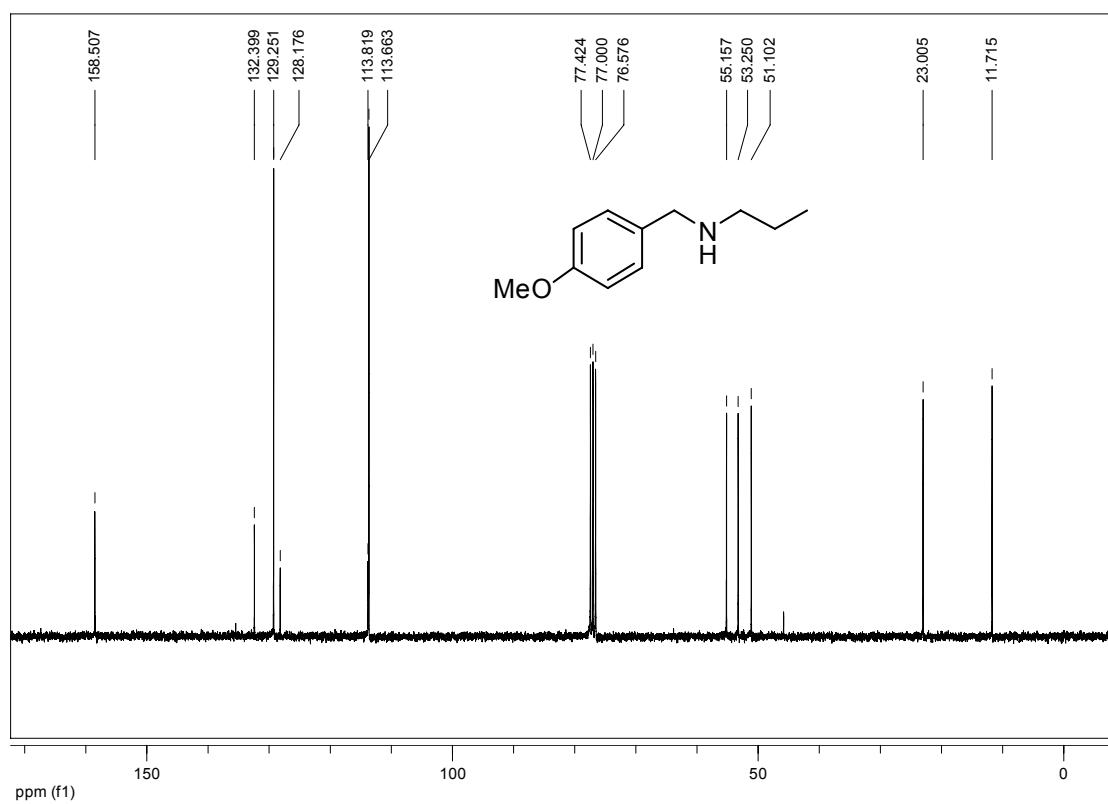
¹³C NMR (75 MHz, CDCl₃): *N*-(4-chlorobenzyl)propan-1-amine (Table 1, entry 3)



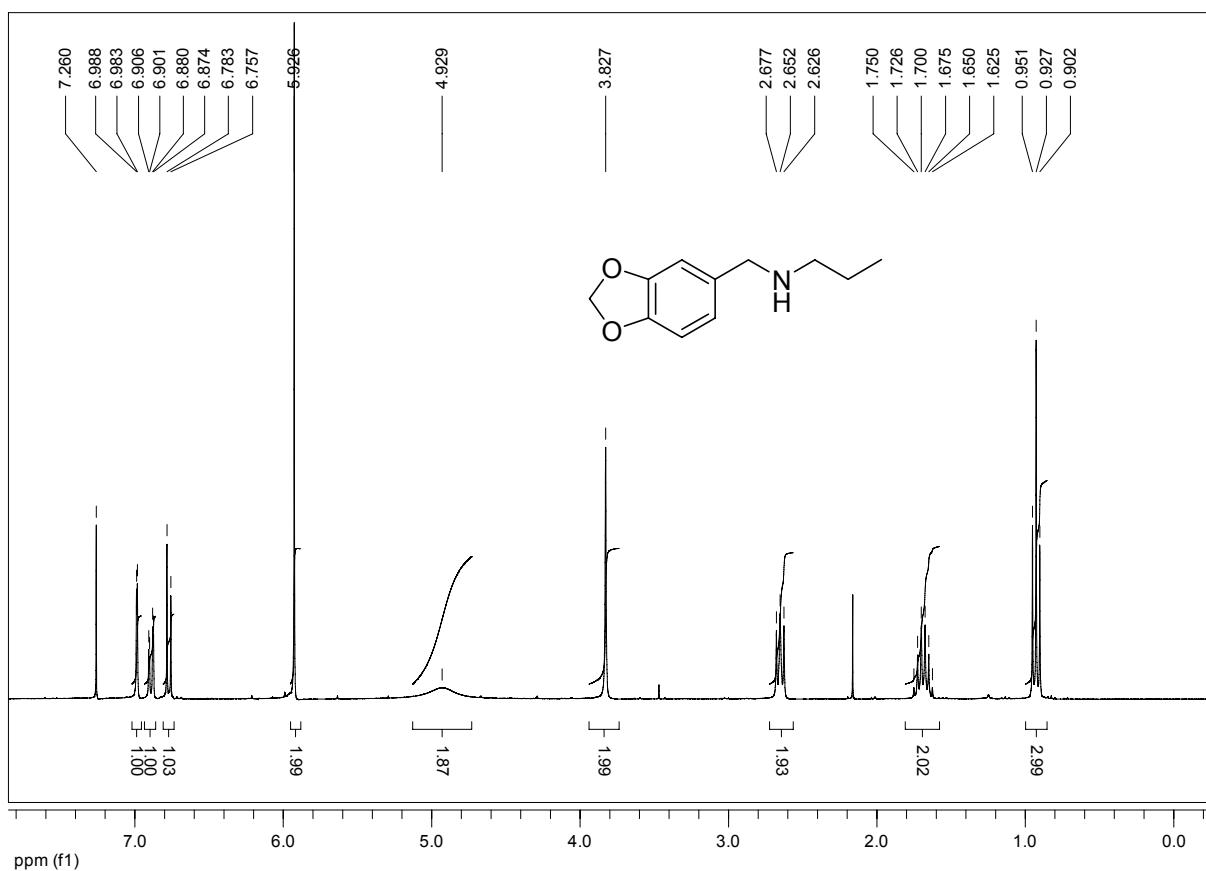
¹H NMR (300 MHz, CDCl₃): N-(4-methoxybenzyl)propan-1-amine (Table 1, entry 4)



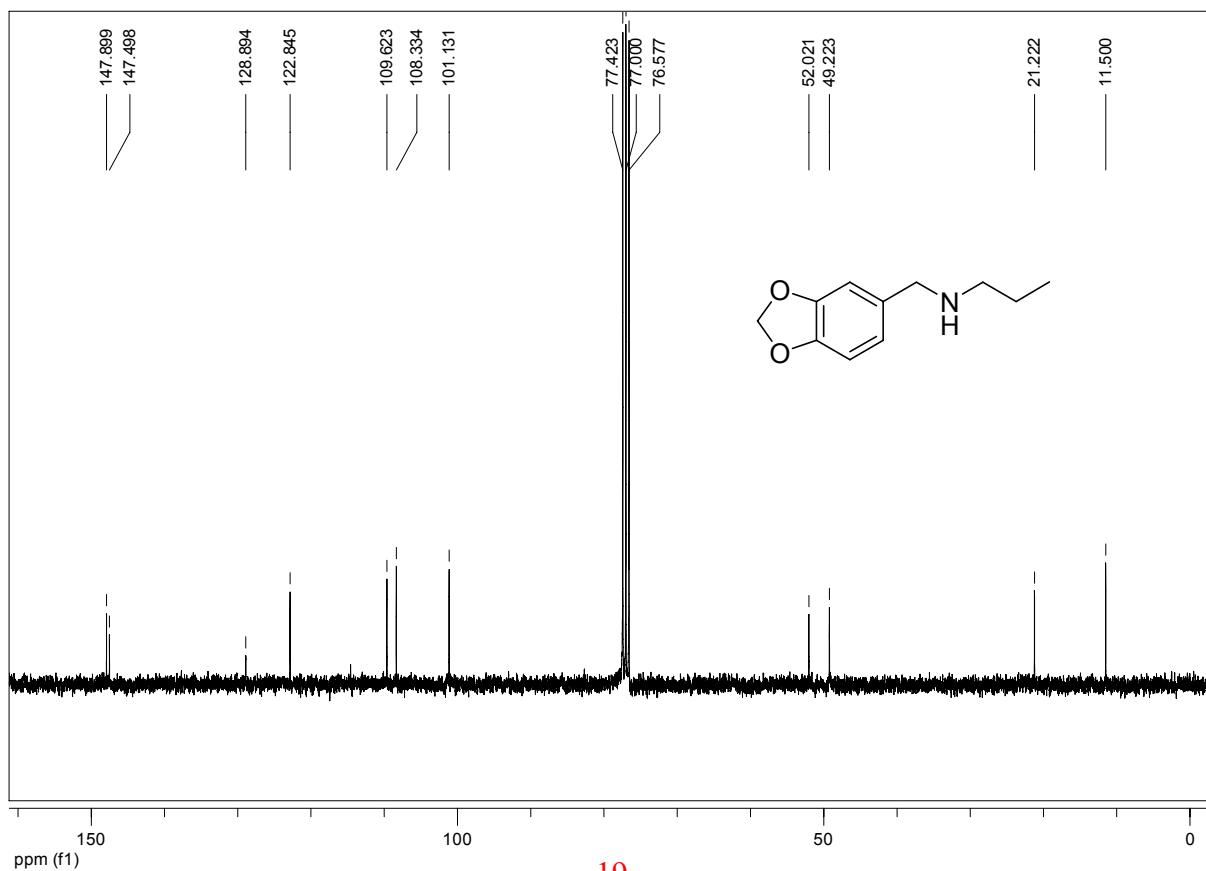
¹³C NMR (75 MHz, CDCl₃): N-(4-methoxybenzyl)propan-1-amine (Table 1, entry 4)



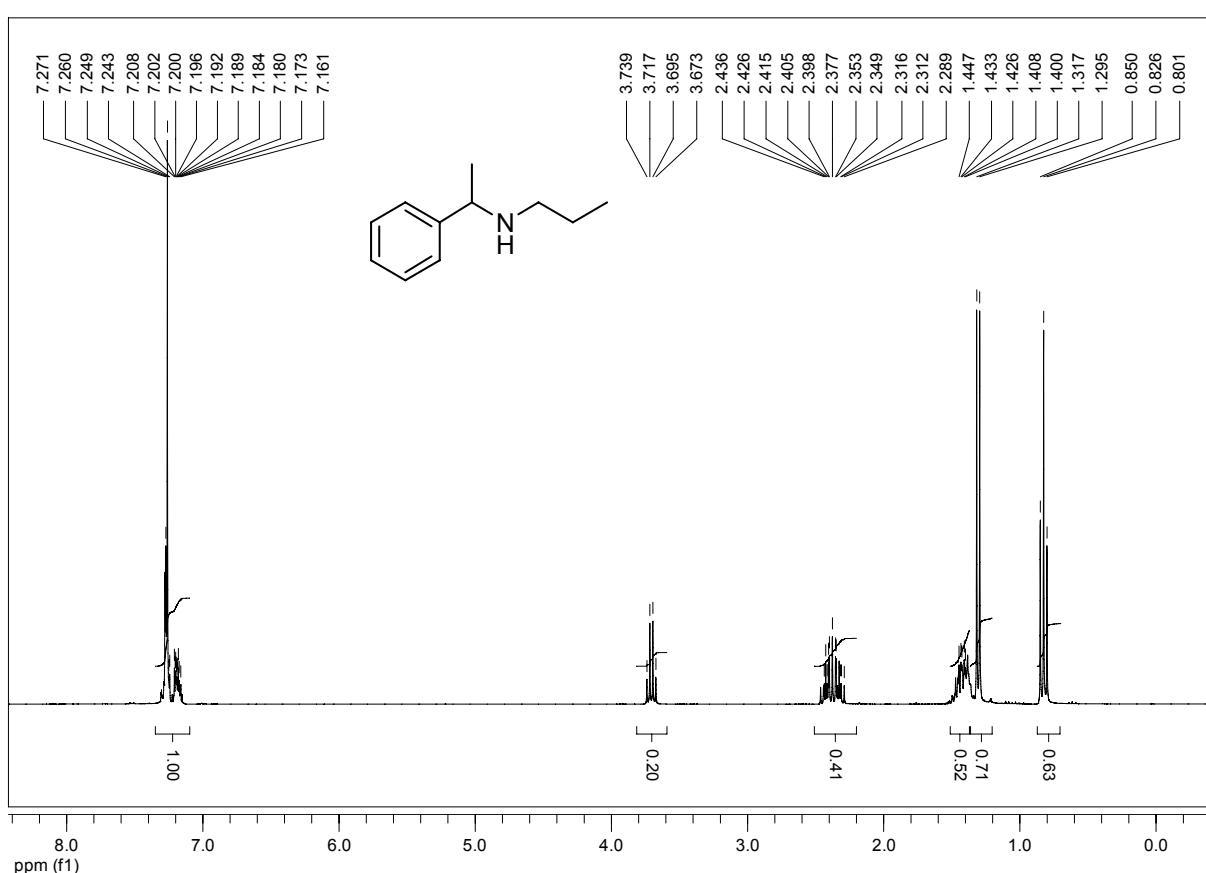
¹H NMR (300 MHz, CDCl₃): *N*-(benzo[1,3]dioxol-5-ylmethyl)propan-1-amine (Table 1, entry 5)



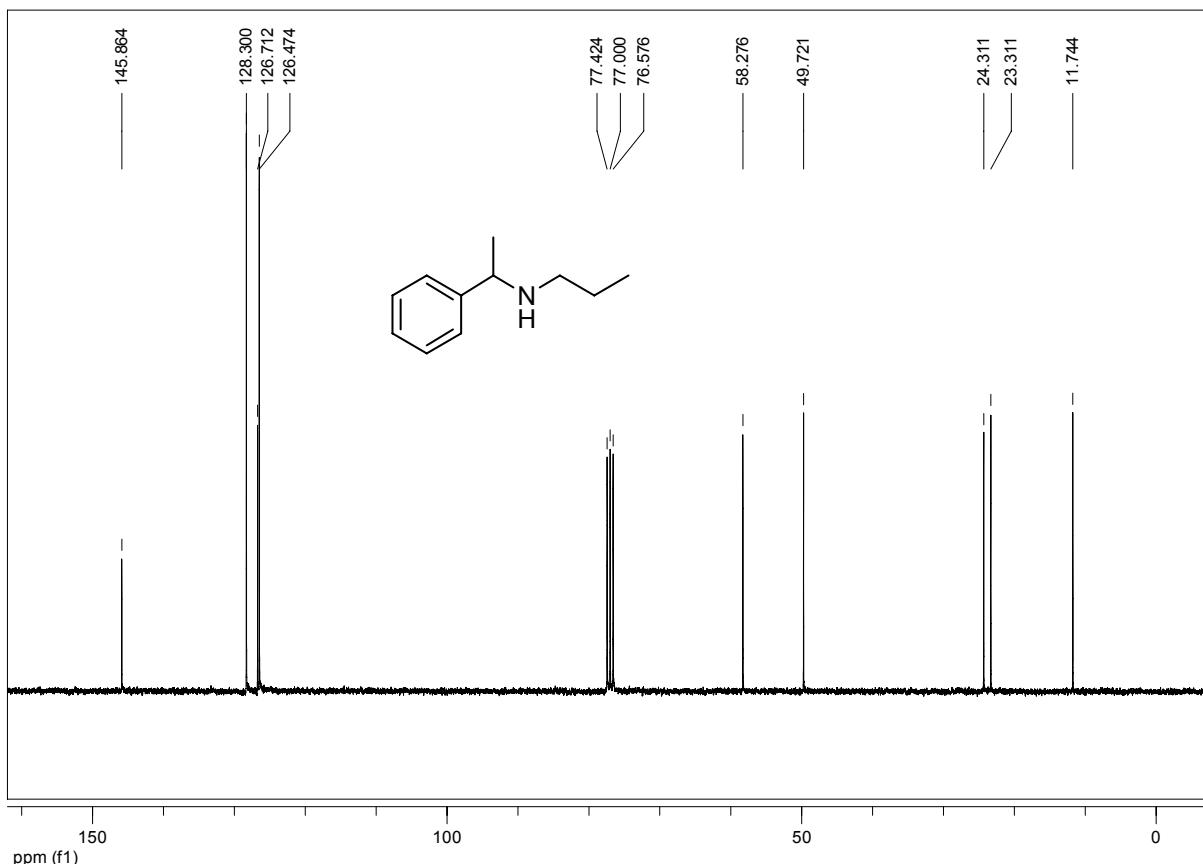
¹³C NMR (75 MHz, CDCl₃): *N*-(benzo[1,3]dioxol-5-ylmethyl)propan-1-amine (Table 1, entry 5)



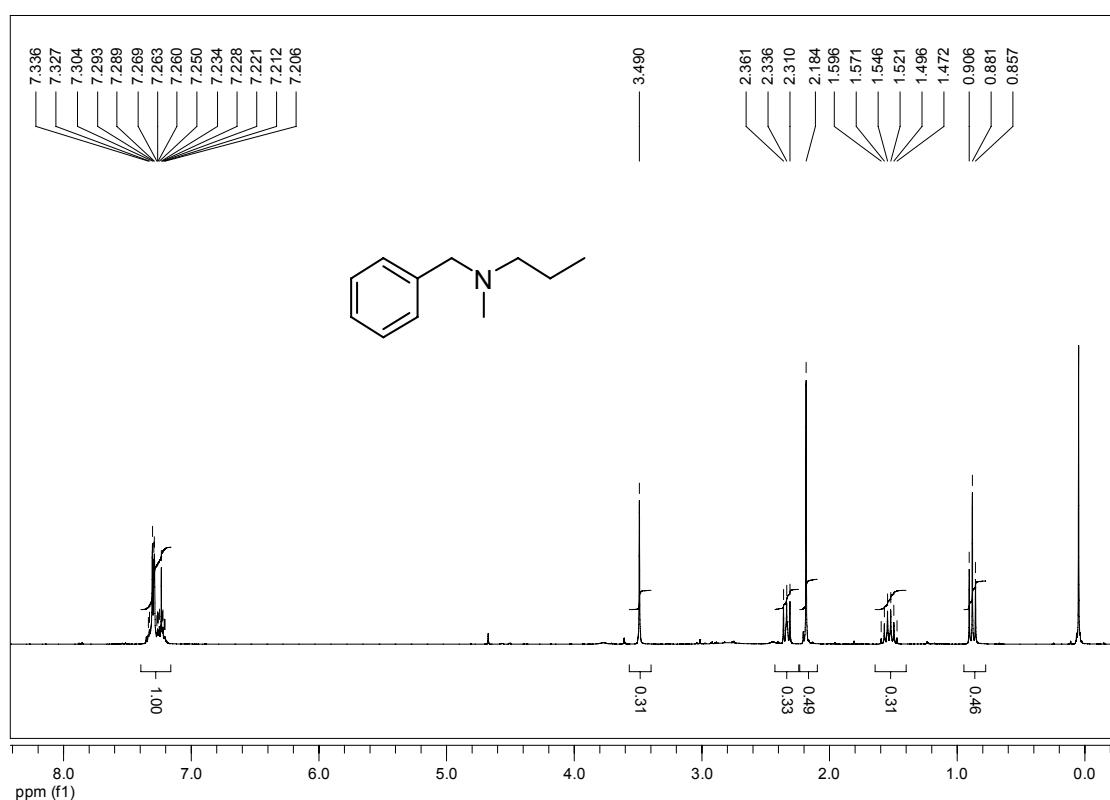
¹H NMR (300 MHz, CDCl₃): N-(1-phenylethyl)propan-1-amine (Table 1, entry 6)



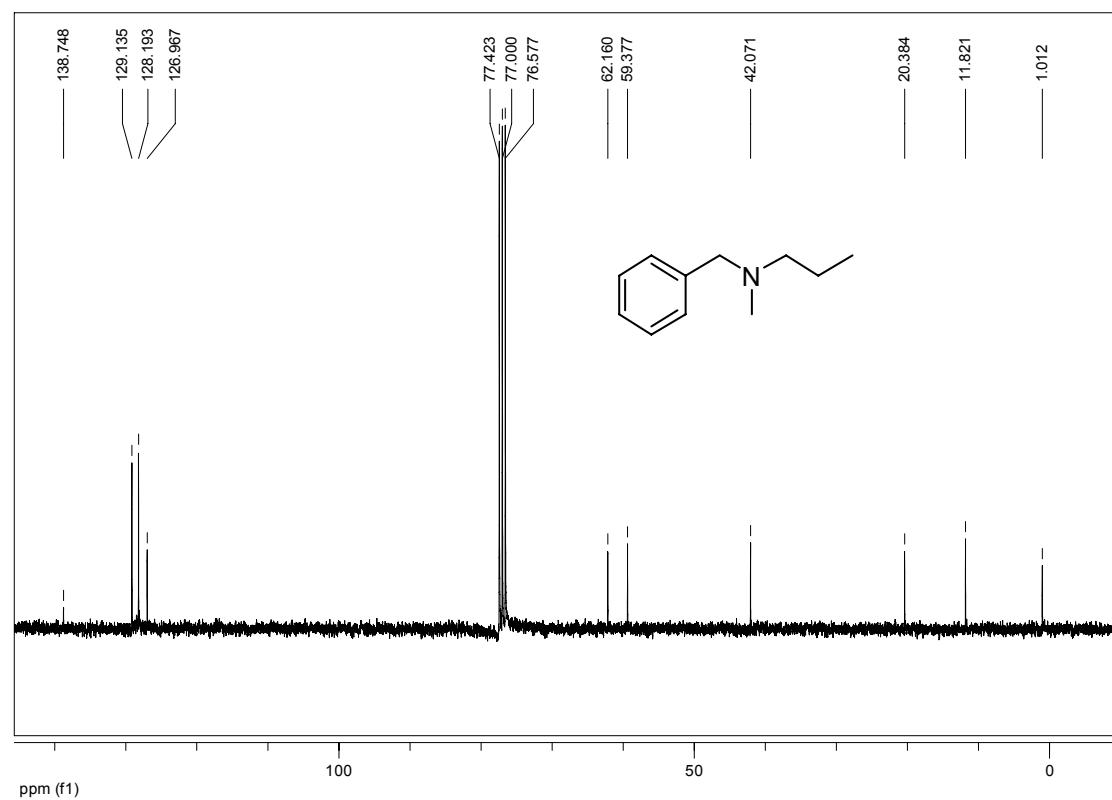
¹³C NMR (75 MHz, CDCl₃): N-(1-phenylethyl)propan-1-amine (Table 1, entry 6)



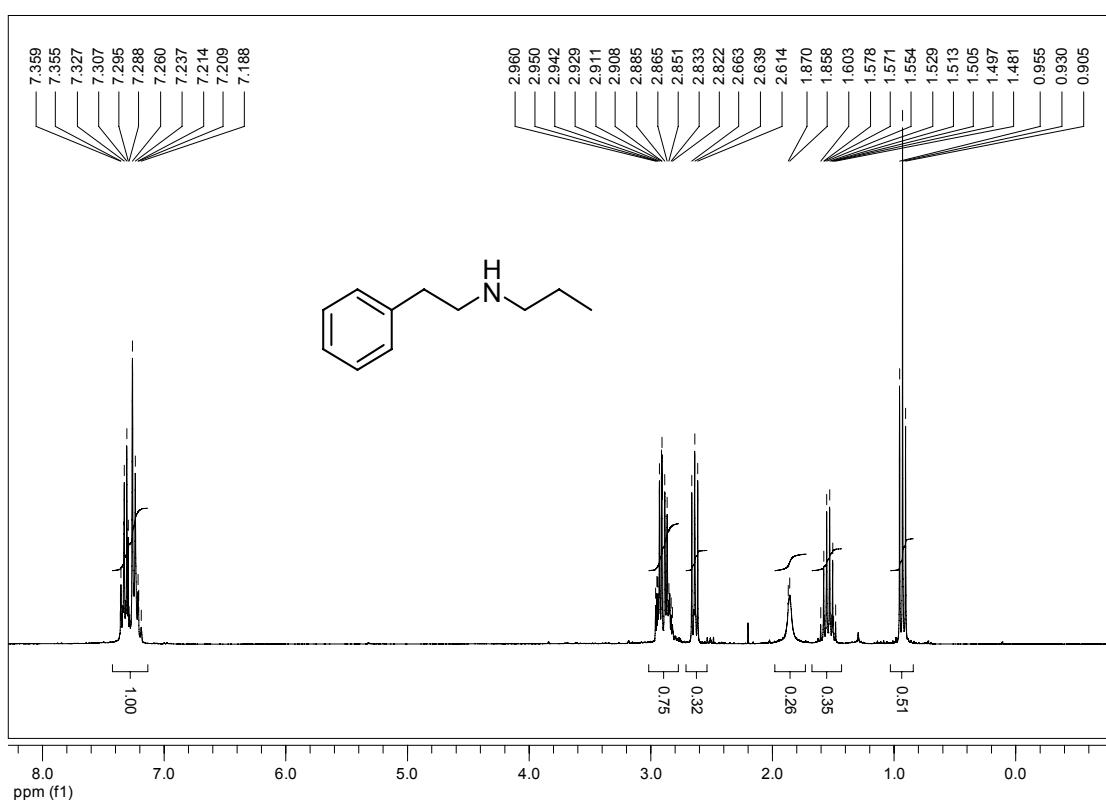
¹H NMR (300 MHz, CDCl₃): N-benzyl-N-methylpropan-1-amine (Table 1, entry 7)



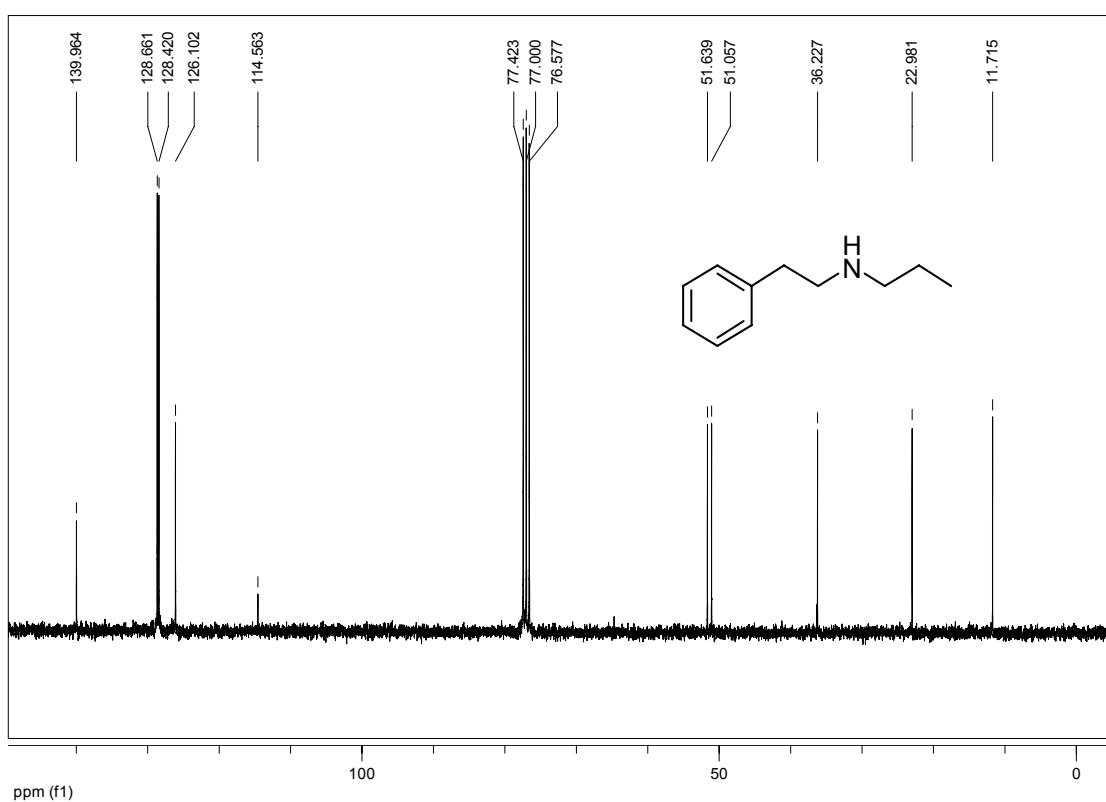
¹³C NMR (75 MHz, CDCl₃): N-benzyl-N-methylpropan-1-amine (Table 1, entry 7)



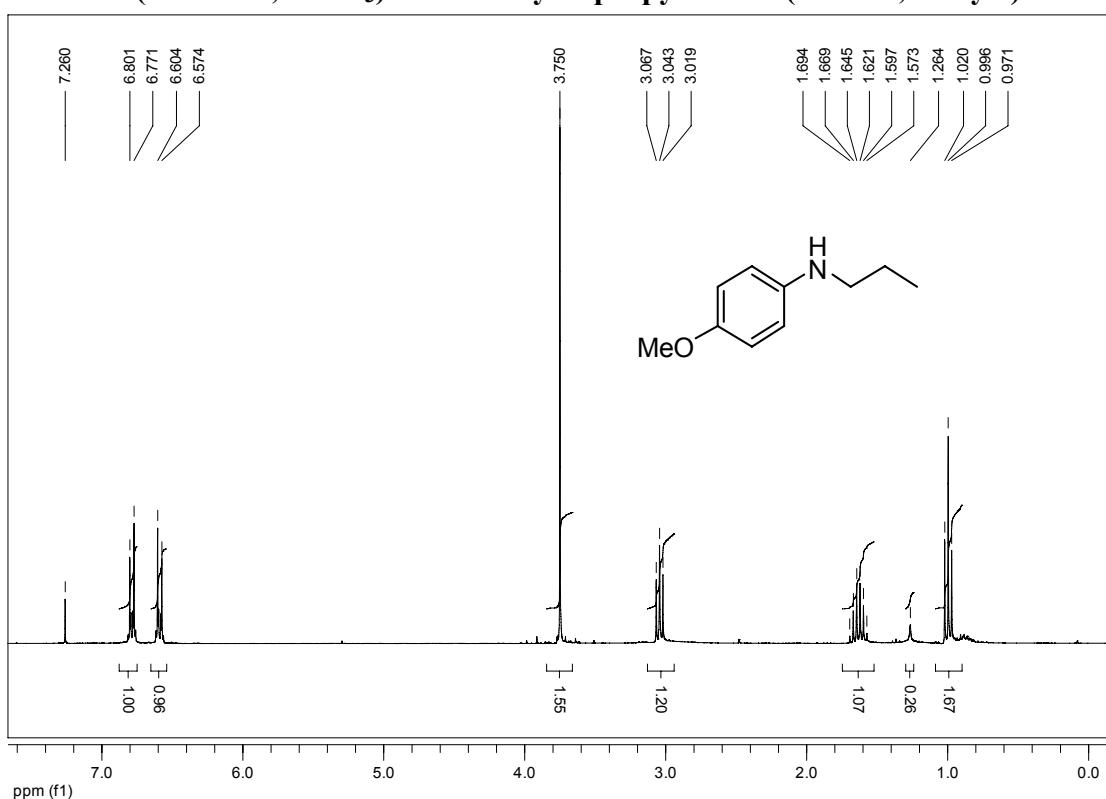
¹H NMR (300 MHz, CDCl₃): N-phenethylpropan-1-amine (Table 1, entry 8)



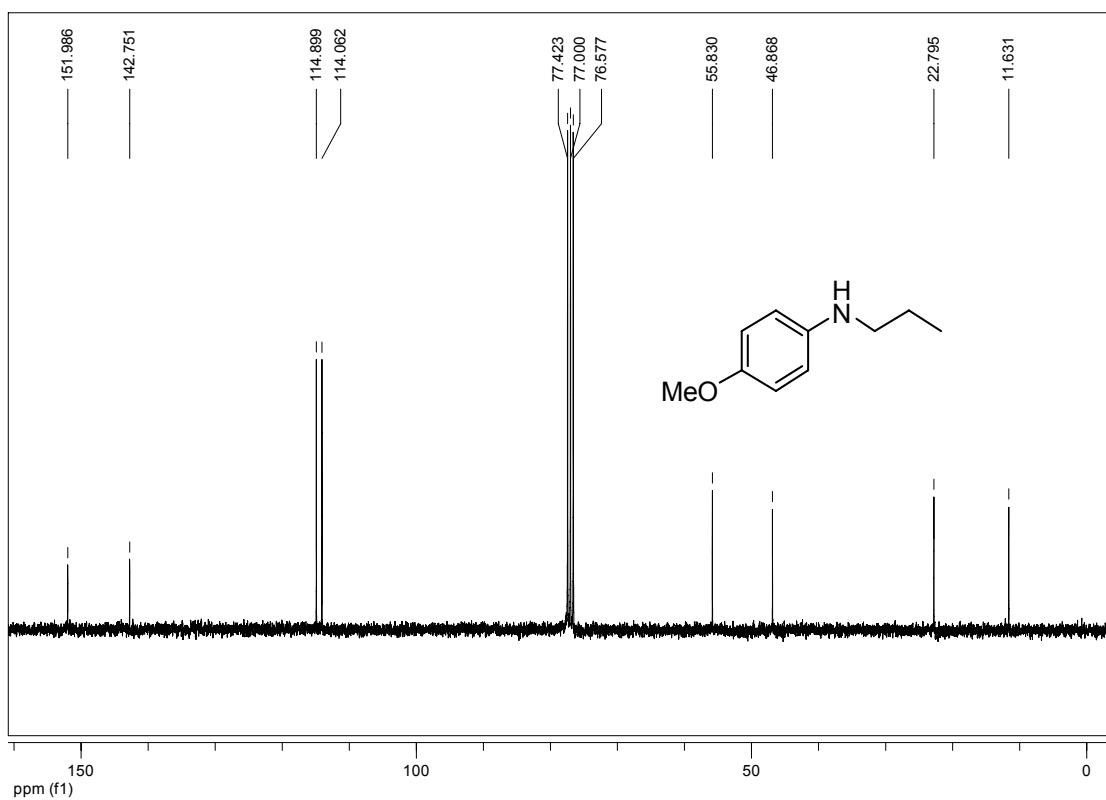
¹³C NMR (75 MHz, CDCl₃): N-phenethylpropan-1-amine (Table 1, entry 8)



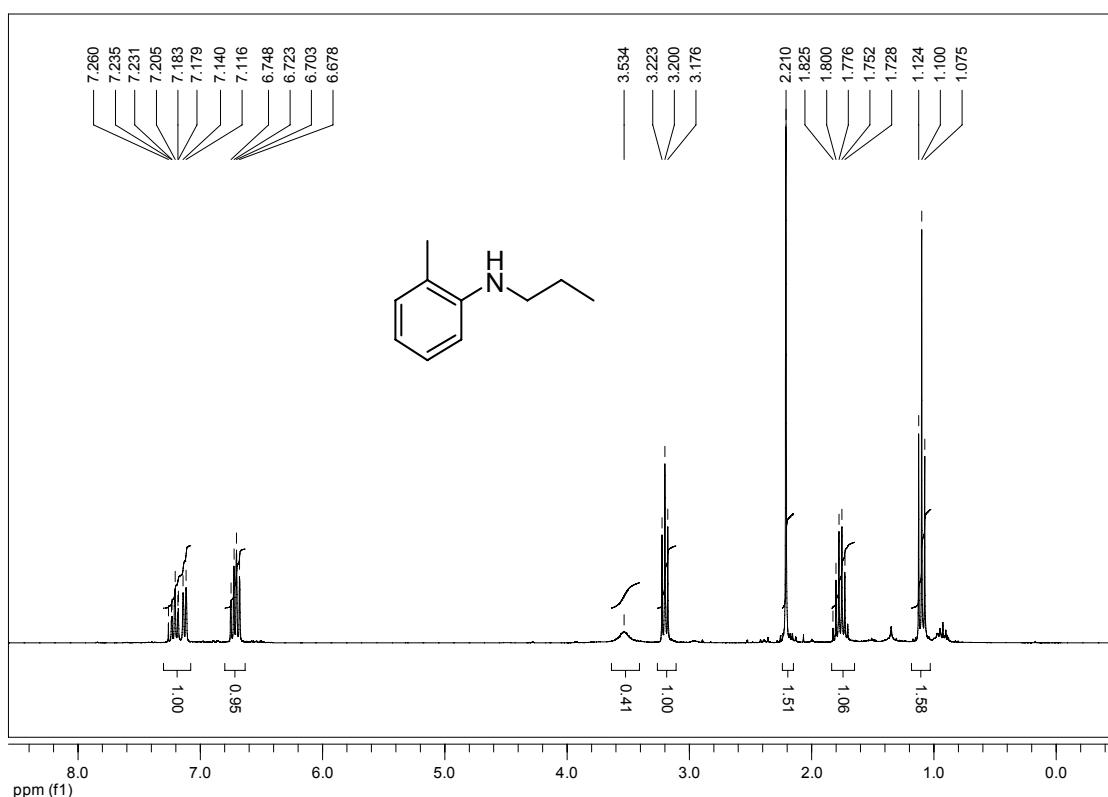
¹H NMR (300 MHz, CDCl₃): 4-methoxy-N-propylaniline (Table 1, entry 9)



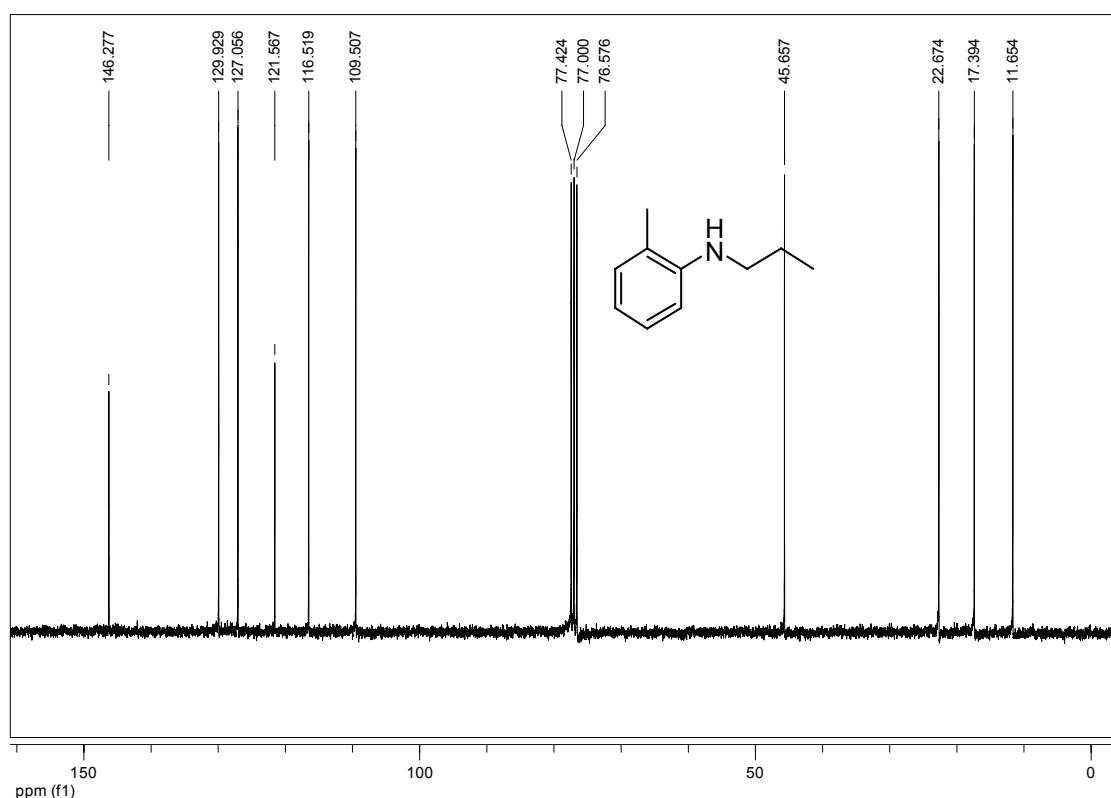
¹³C NMR (75 MHz, CDCl₃): 4-methoxy-N-propylaniline (Table 1, entry 9)



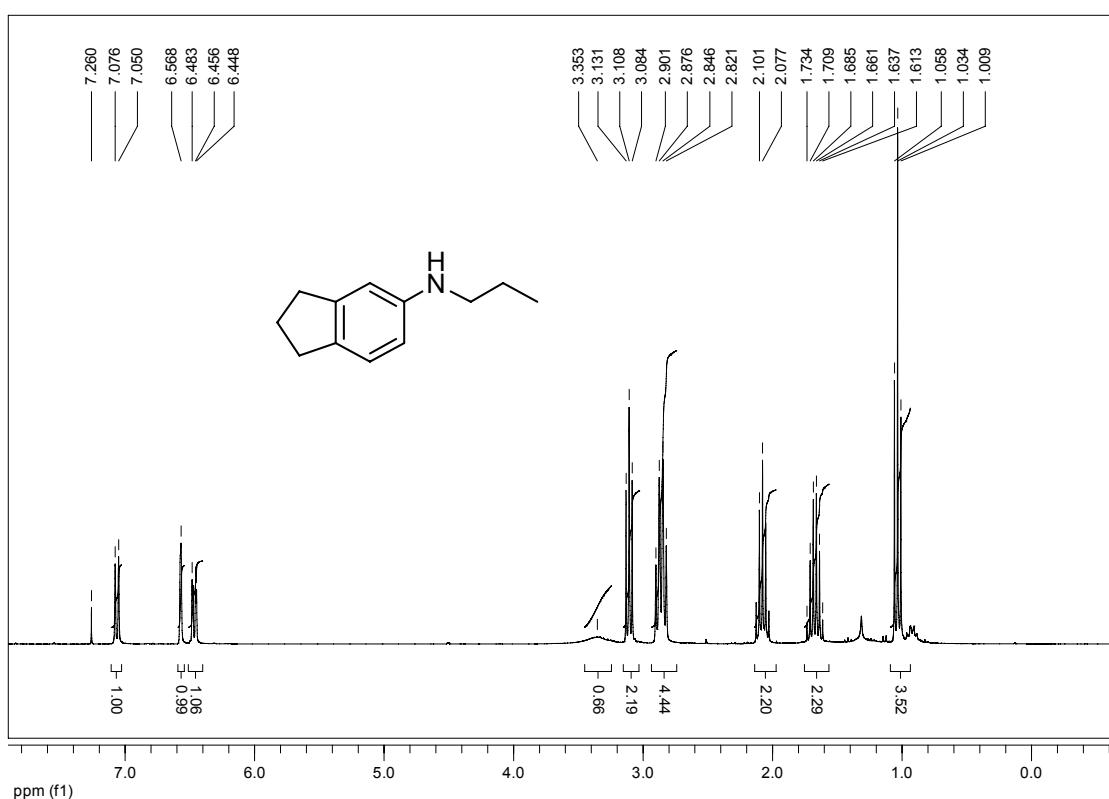
¹H NMR (300 MHz, CDCl₃): 2-methyl-N-propylaniline (Table 1, entry 10)



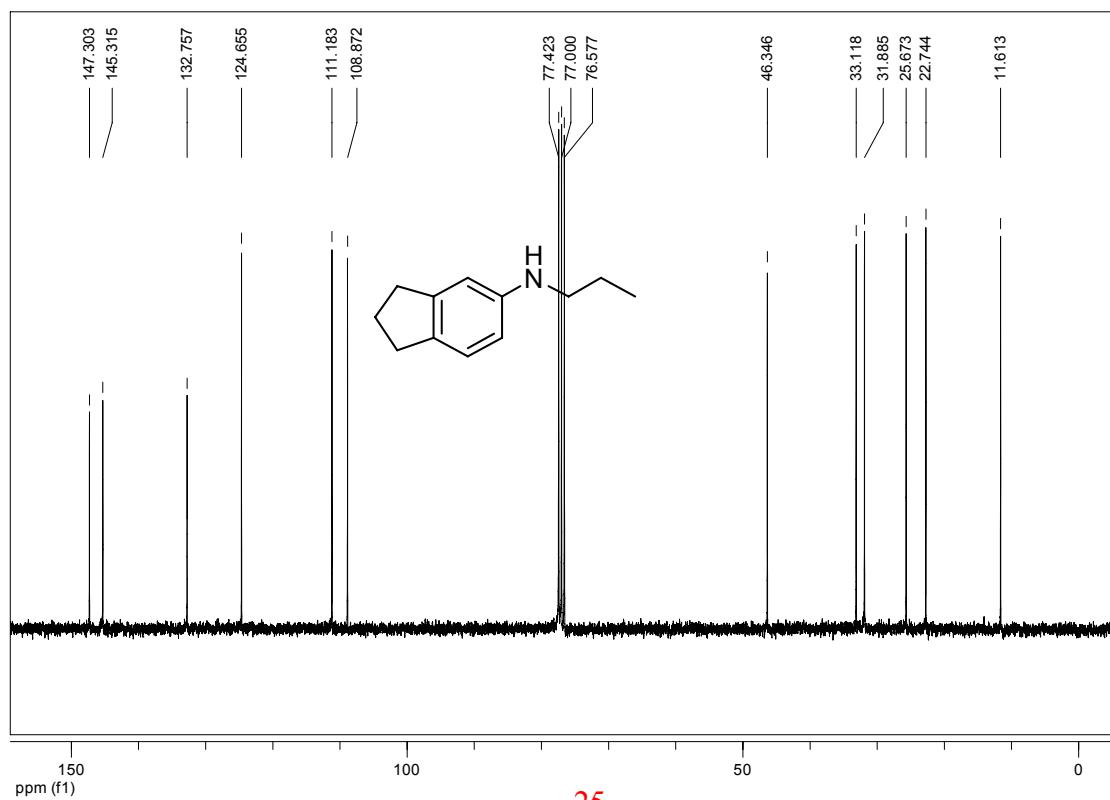
¹³C NMR (75 MHz, CDCl₃): 2-methyl-N-propylaniline (Table 1, entry 10)



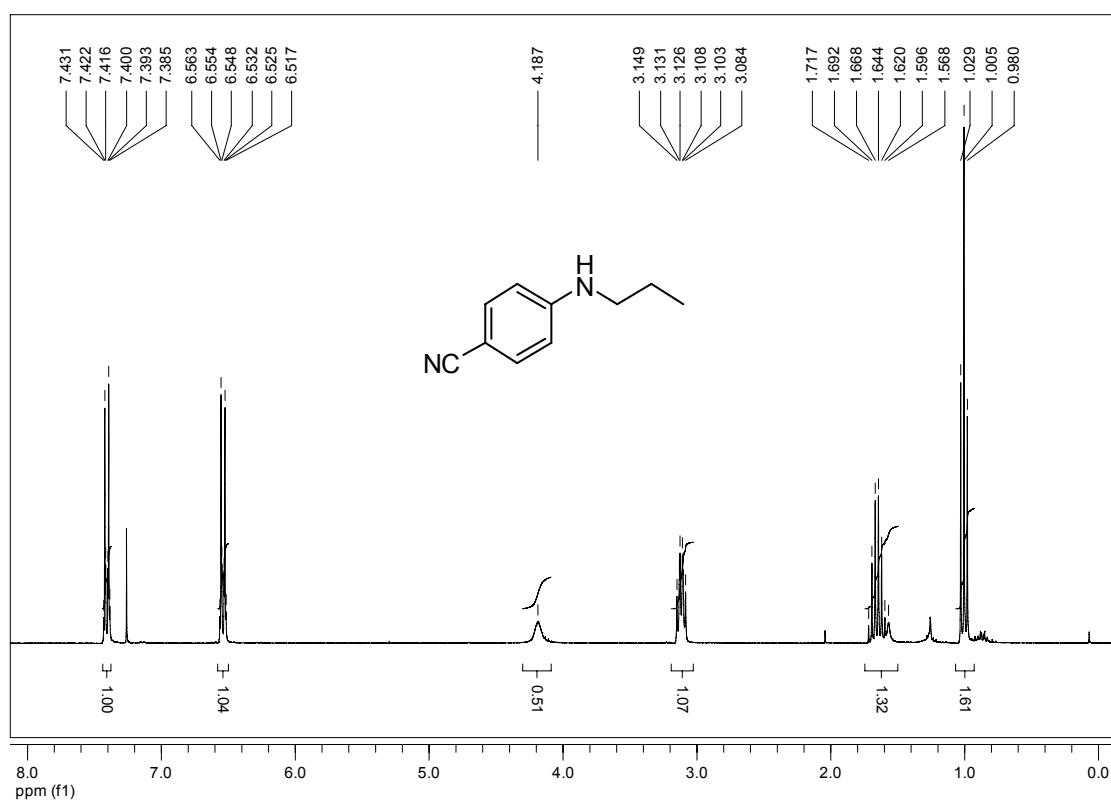
¹H NMR (300 MHz, CDCl₃): N-propyl-2,3-dihydro-1H-inden-5-amine (Table 1, entry 11)



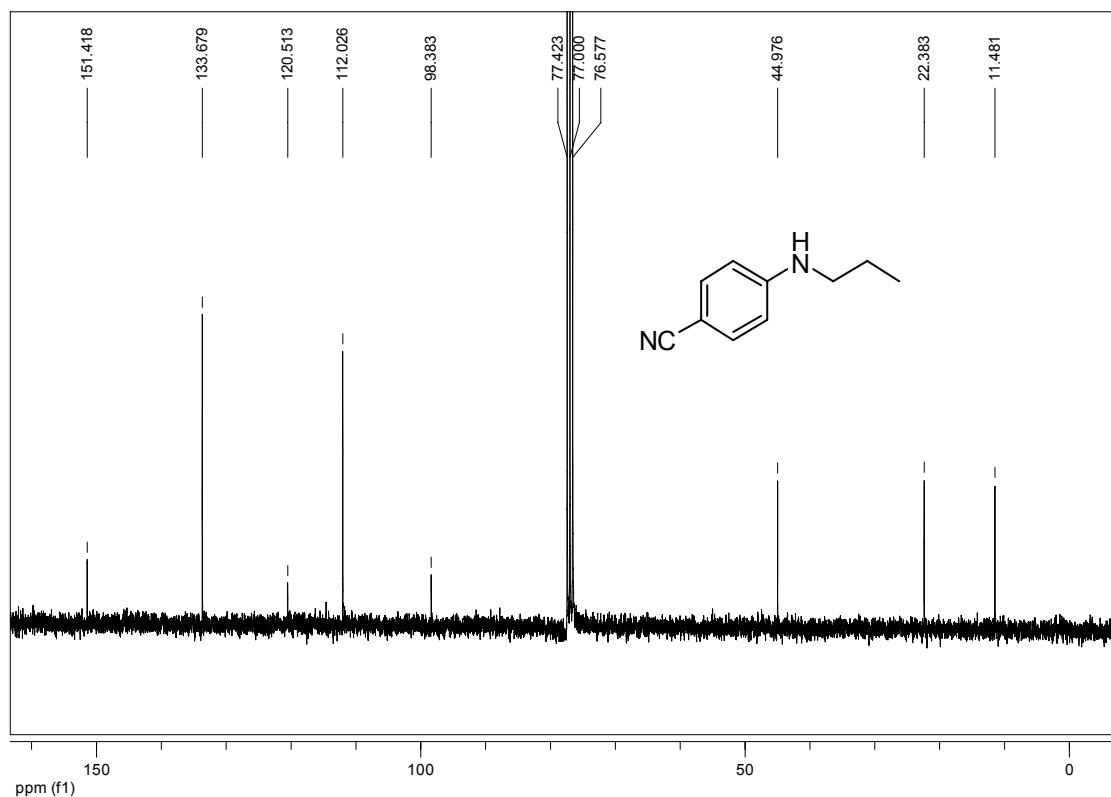
¹³C NMR (75 MHz, CDCl₃): N-propyl-2,3-dihydro-1H-inden-5-amine (Table 1, entry 11)



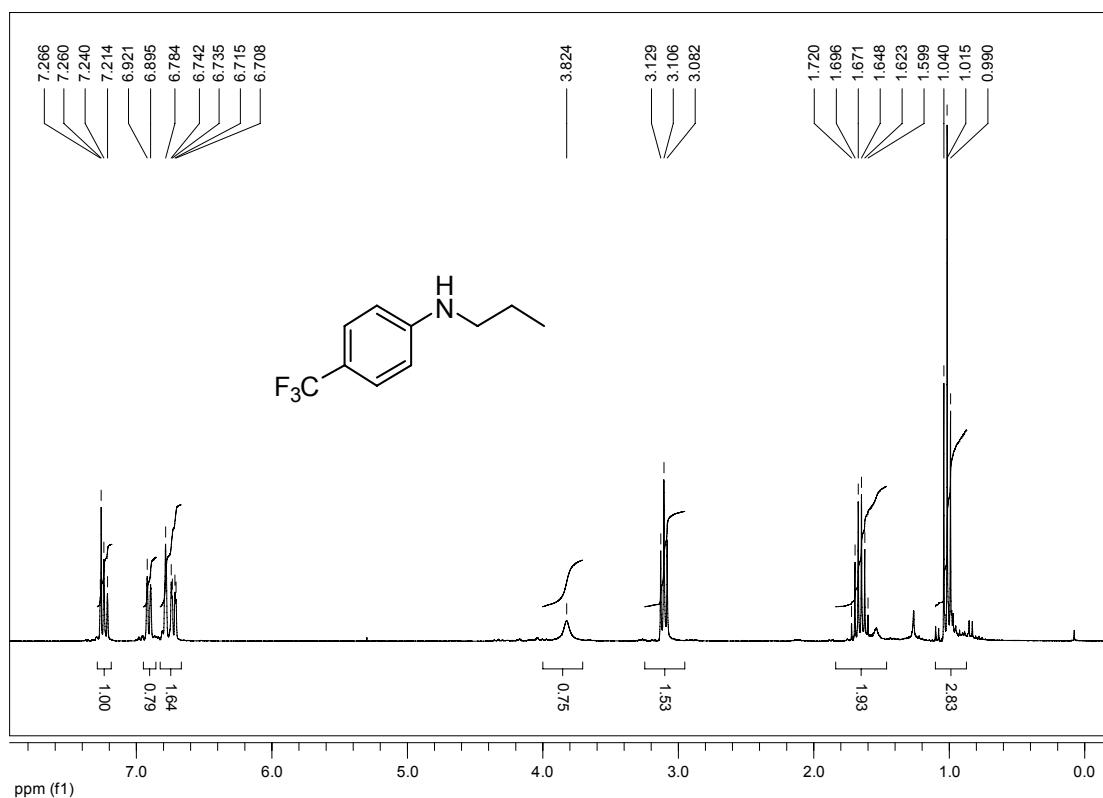
¹H NMR (300 MHz, CDCl₃): 4-(propylamino)benzonitrile (Table 1, entry 12)



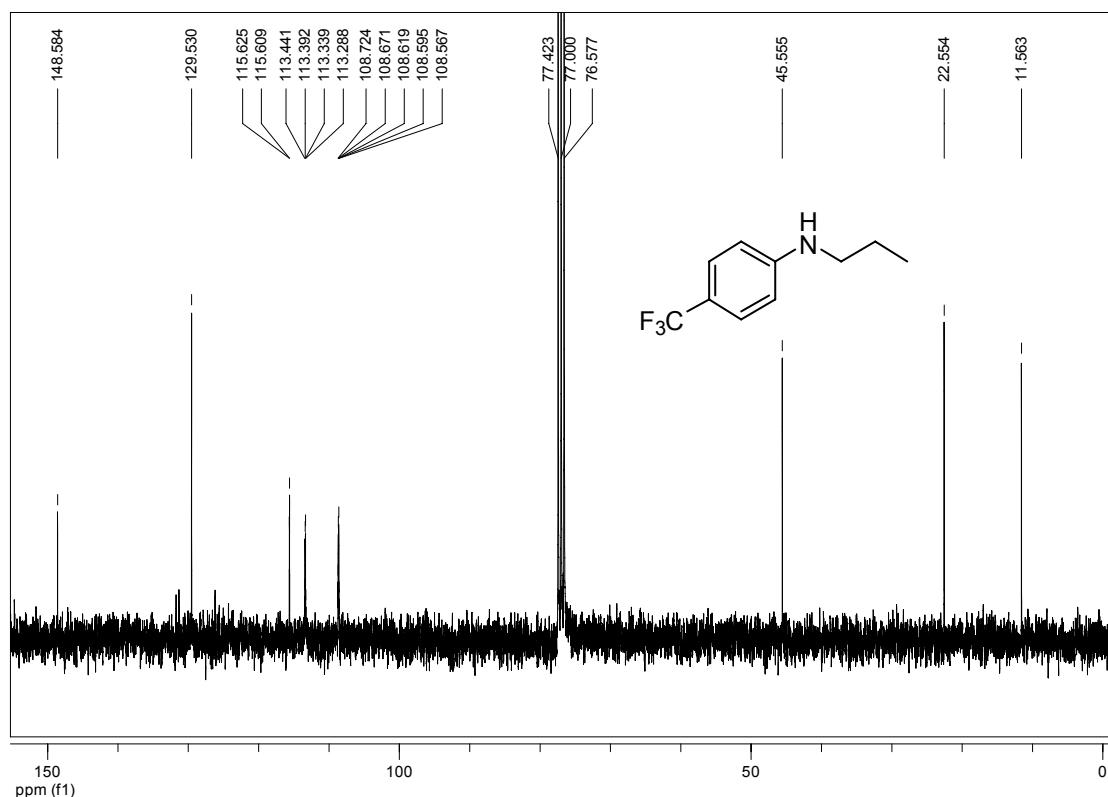
¹³C NMR (75 MHz, CDCl₃): 4-(propylamino)benzonitrile (Table 1, entry 12)



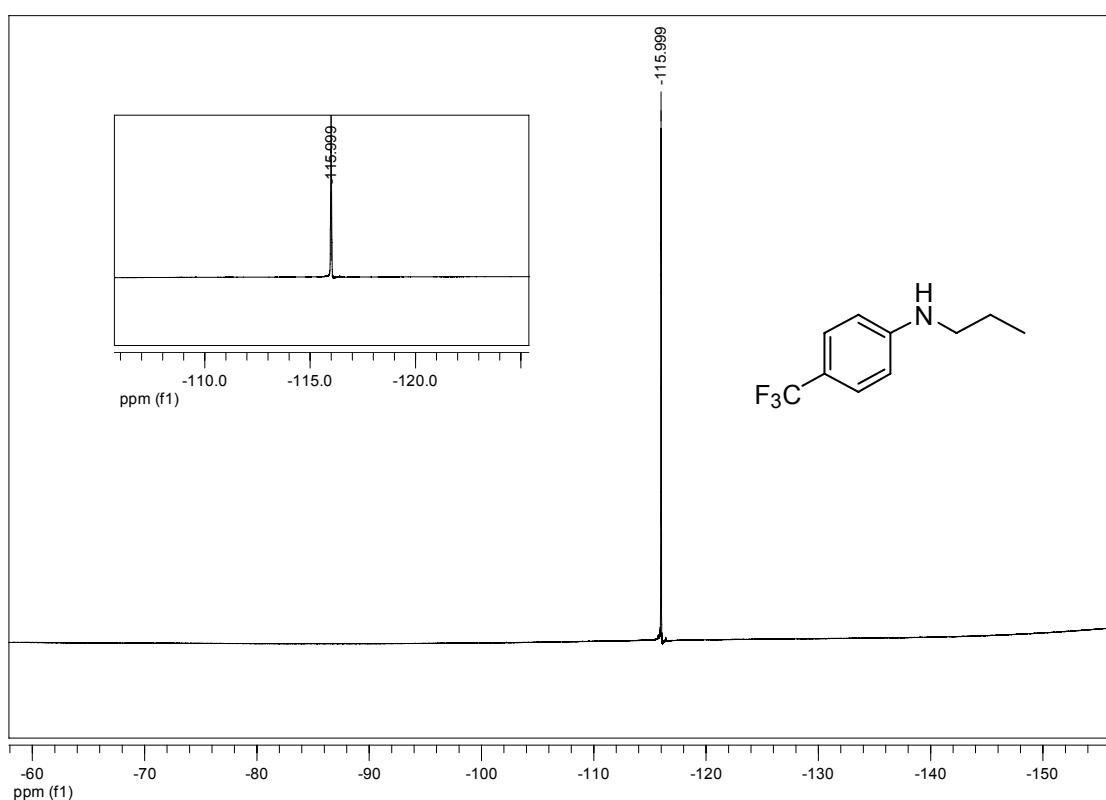
¹H NMR (300 MHz, CDCl₃): N-propyl-4-(trifluoromethyl)aniline (Table 1, entry 13)



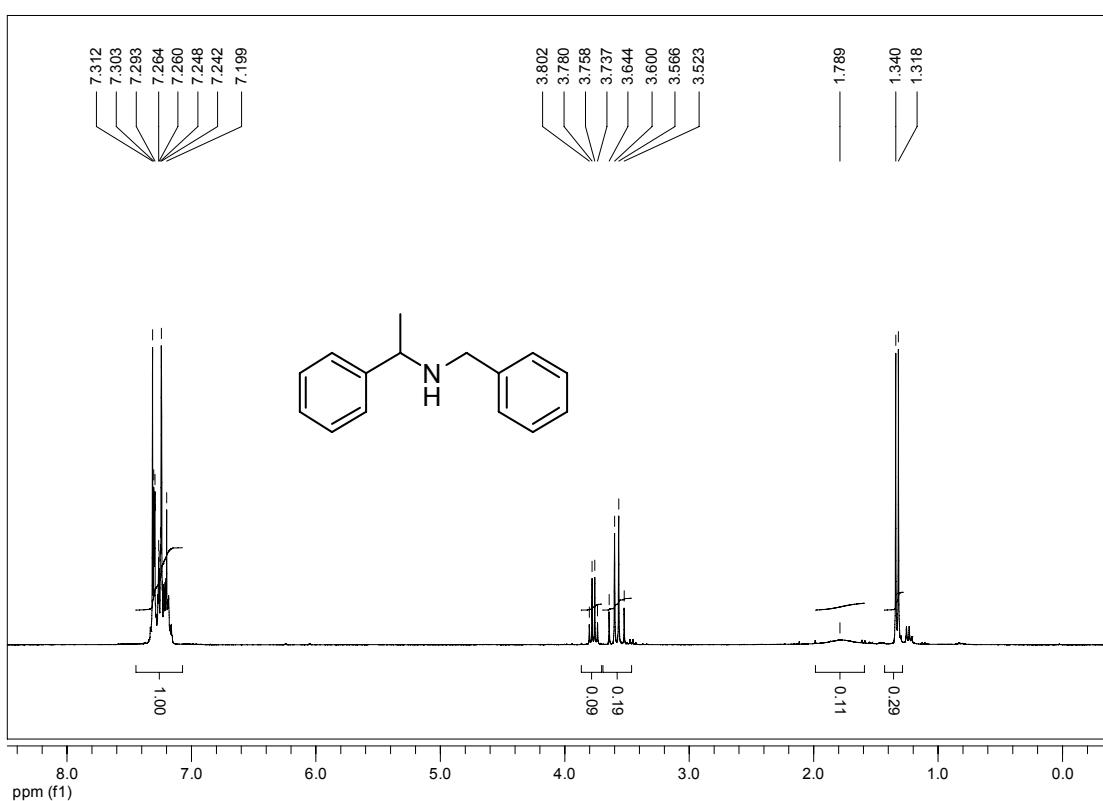
¹³C NMR (75 MHz, CDCl₃): N-propyl-4-(trifluoromethyl)aniline (Table 1, entry 13)



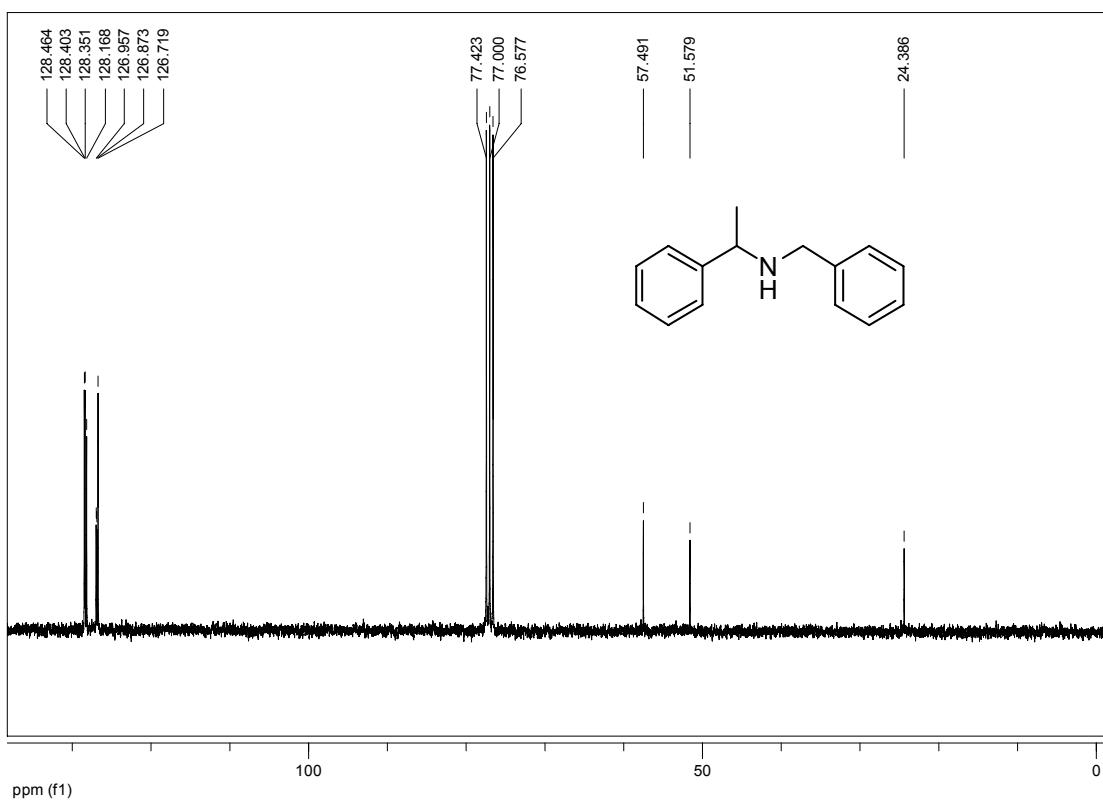
¹⁹F NMR (376 MHz, CDCl₃): N-propyl-4-(trifluoromethyl)aniline (Table 1, entry 13)



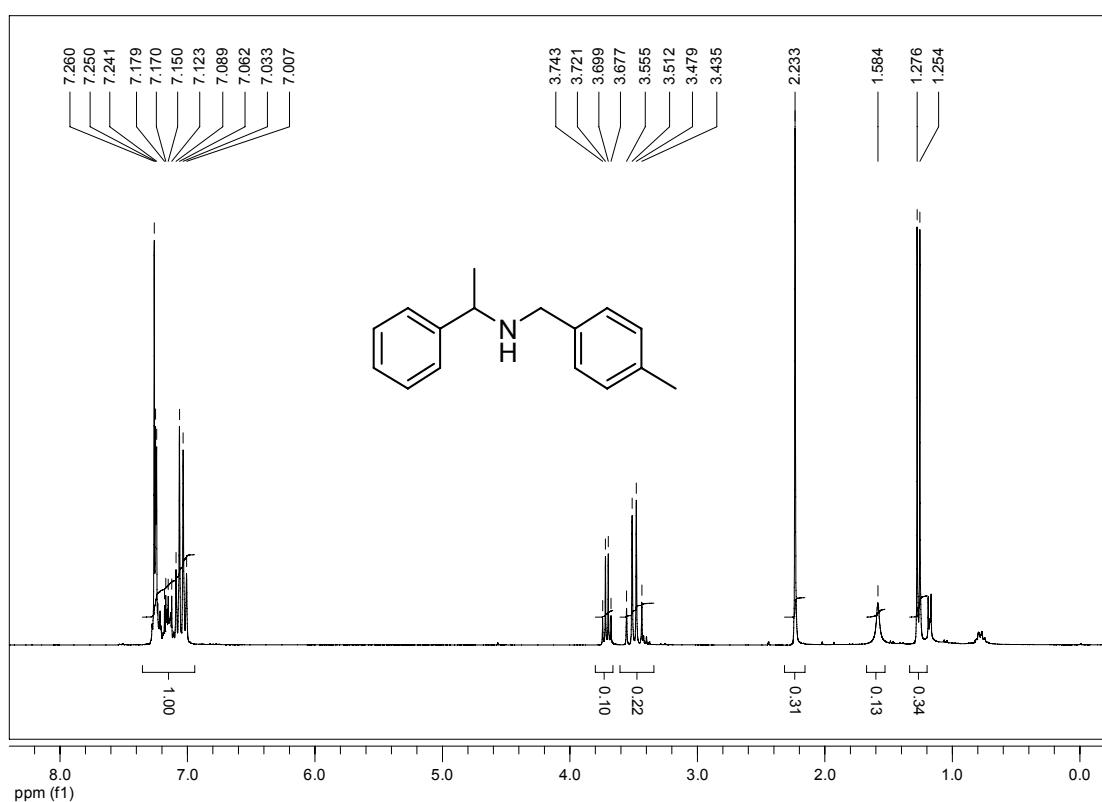
¹H NMR (300 MHz, CDCl₃): N-benzyl-1-phenylethanamine (Table 2, entry 1)



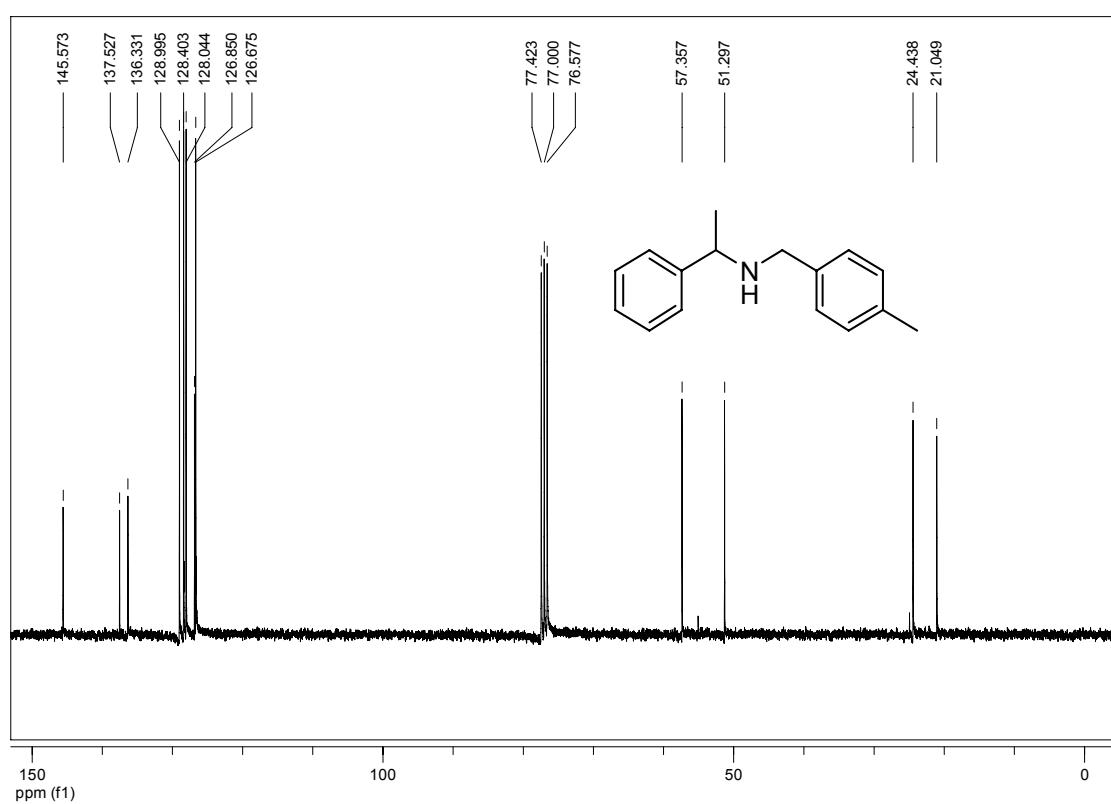
¹³C NMR (75 MHz, CDCl₃): N-benzyl-1-phenylethanamine (Table 2, entry 1)



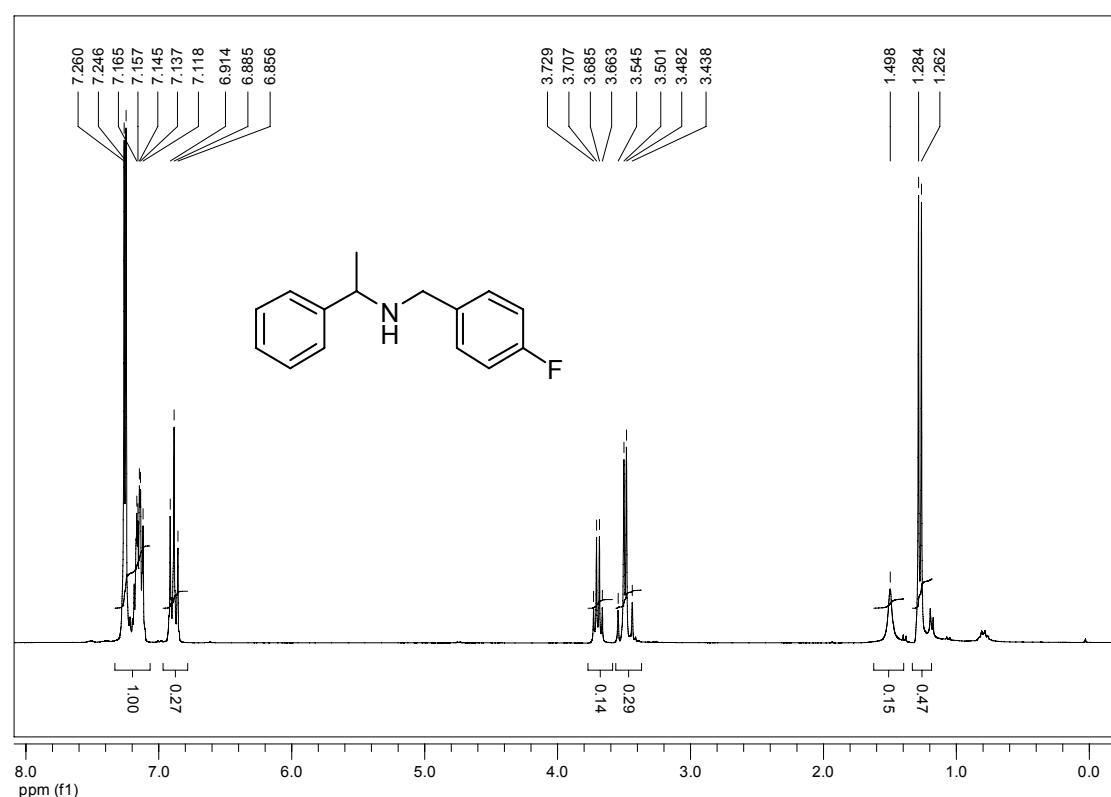
¹H NMR (300 MHz, CDCl₃): N-(4-methylbenzyl)-1-phenylethanamine (Table 2, entry 2)



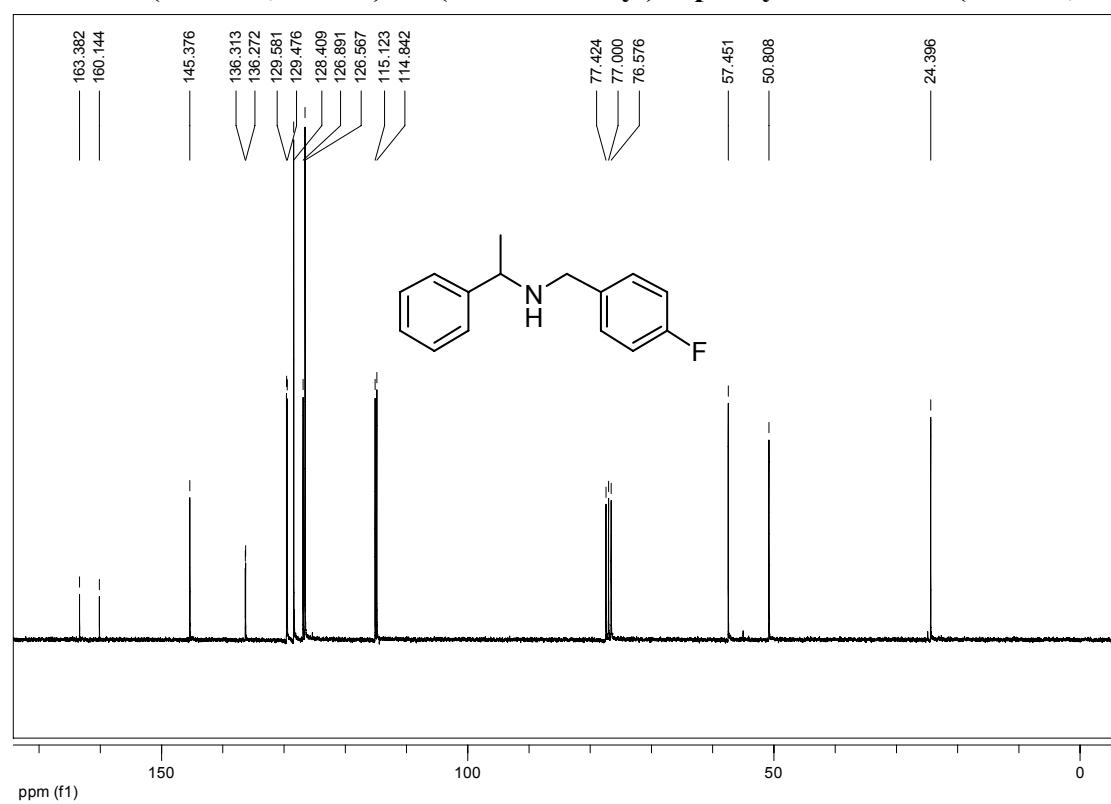
¹³C NMR (75 MHz, CDCl₃): N-(4-methylbenzyl)-1-phenylethanamine (Table 2, entry 2)



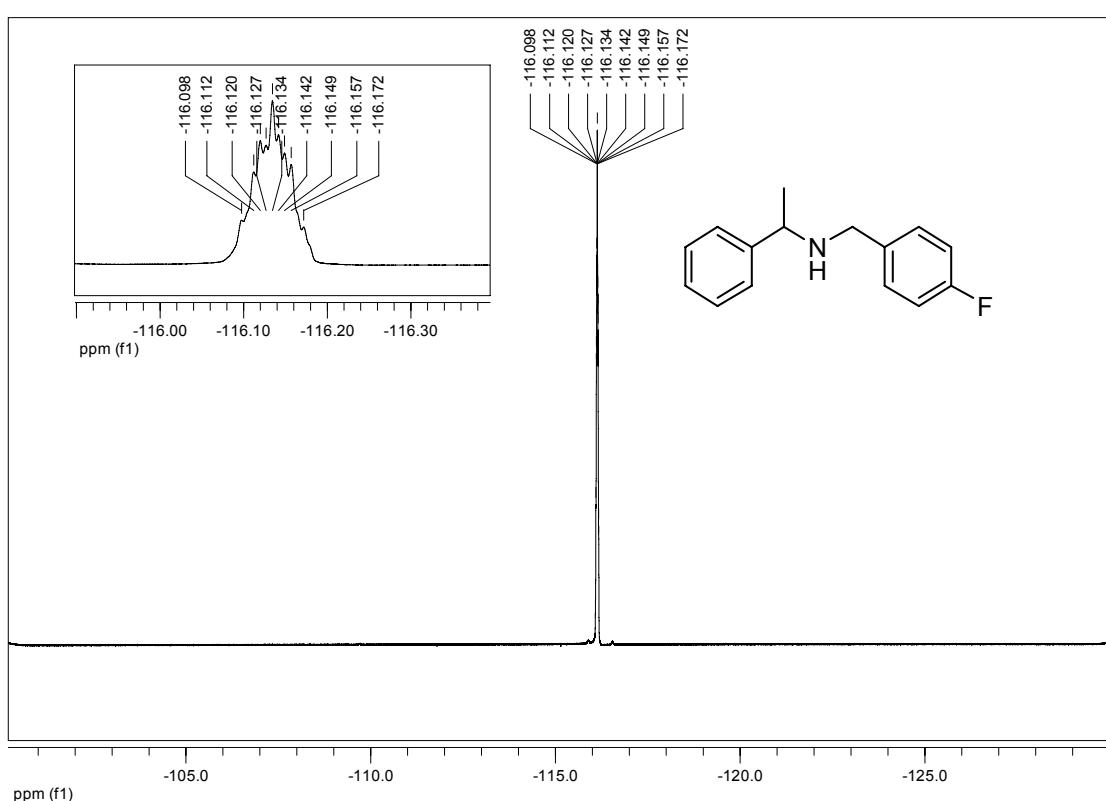
¹H NMR (300 MHz, CDCl₃): N-(4-fluorobenzyl)-1-phenylethanamine (Table 2, entry 3)



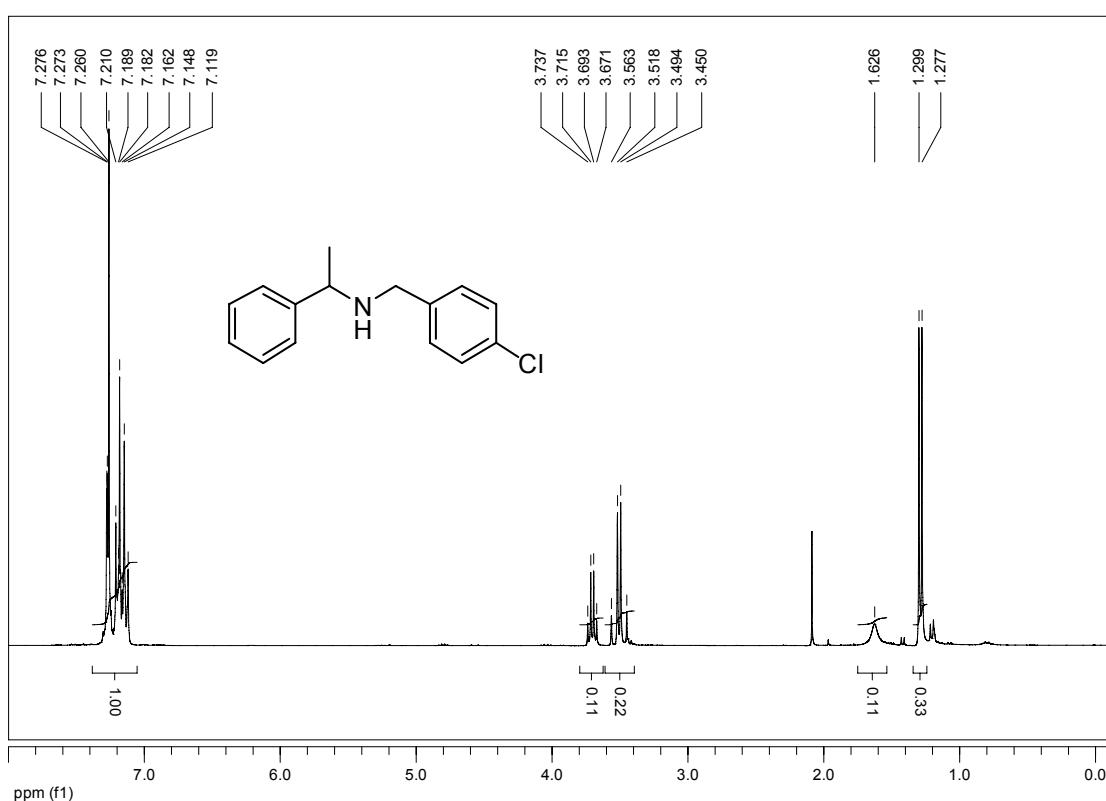
¹³C NMR (75 MHz, CDCl₃): N-(4-fluorobenzyl)-1-phenylethanamine (Table 2, entry 3)



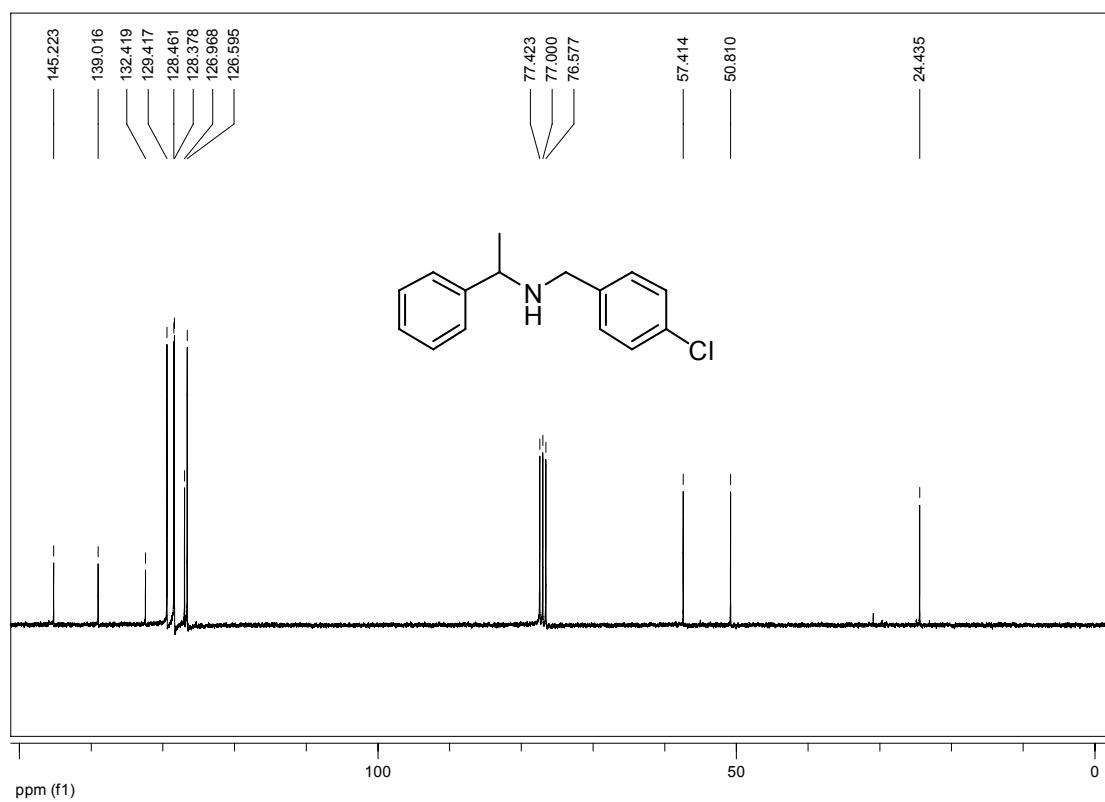
¹⁹F NMR (376 MHz, CDCl₃): N-(4-fluorobenzyl)-1-phenylethanamine (Table 2, entry 3)



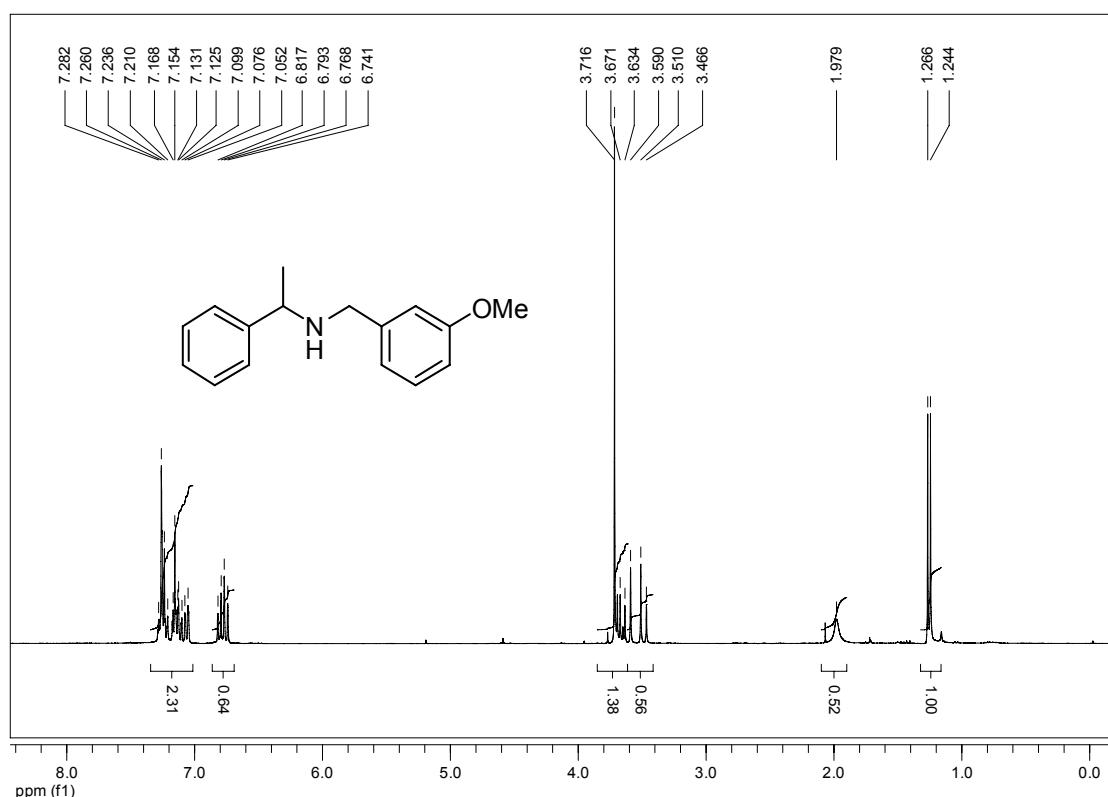
¹H NMR (300 MHz, CDCl₃): N-(4-chlorobenzyl)-1-phenylethanamine (Table 2, entry 4)



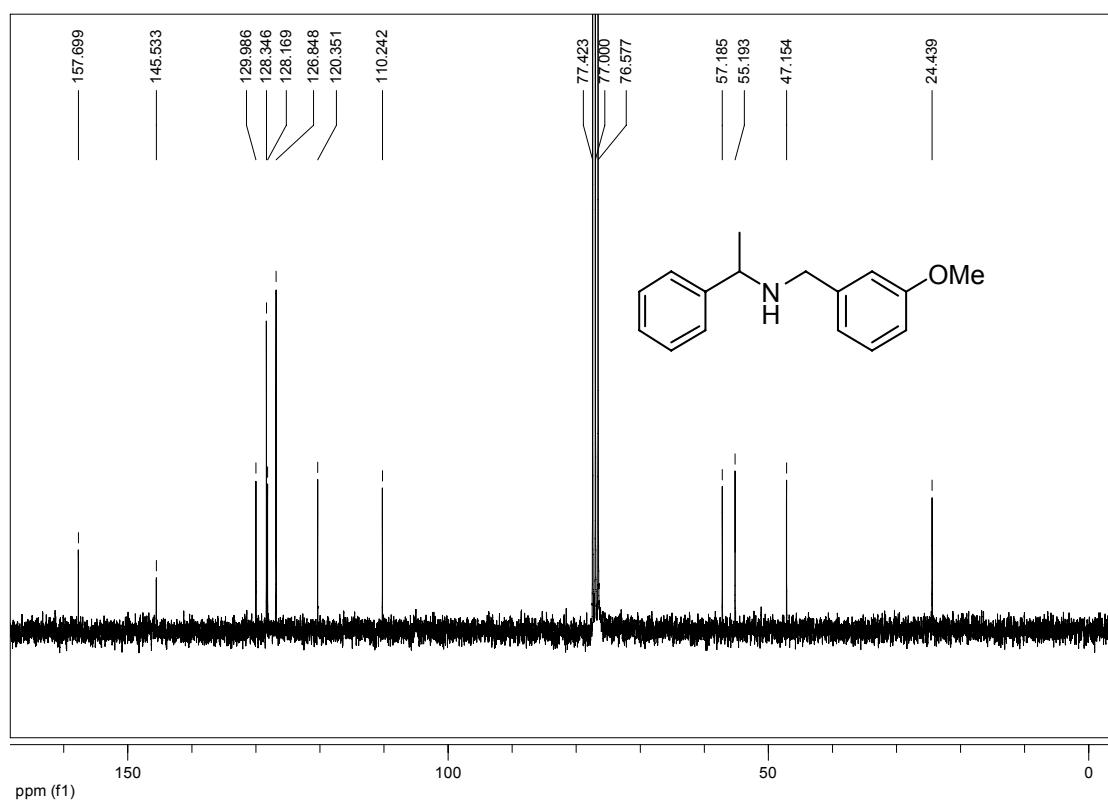
¹³C NMR (75 MHz, CDCl₃): N-(4-chlorobenzyl)-1-phenylethanamine (Table 2, entry 4)



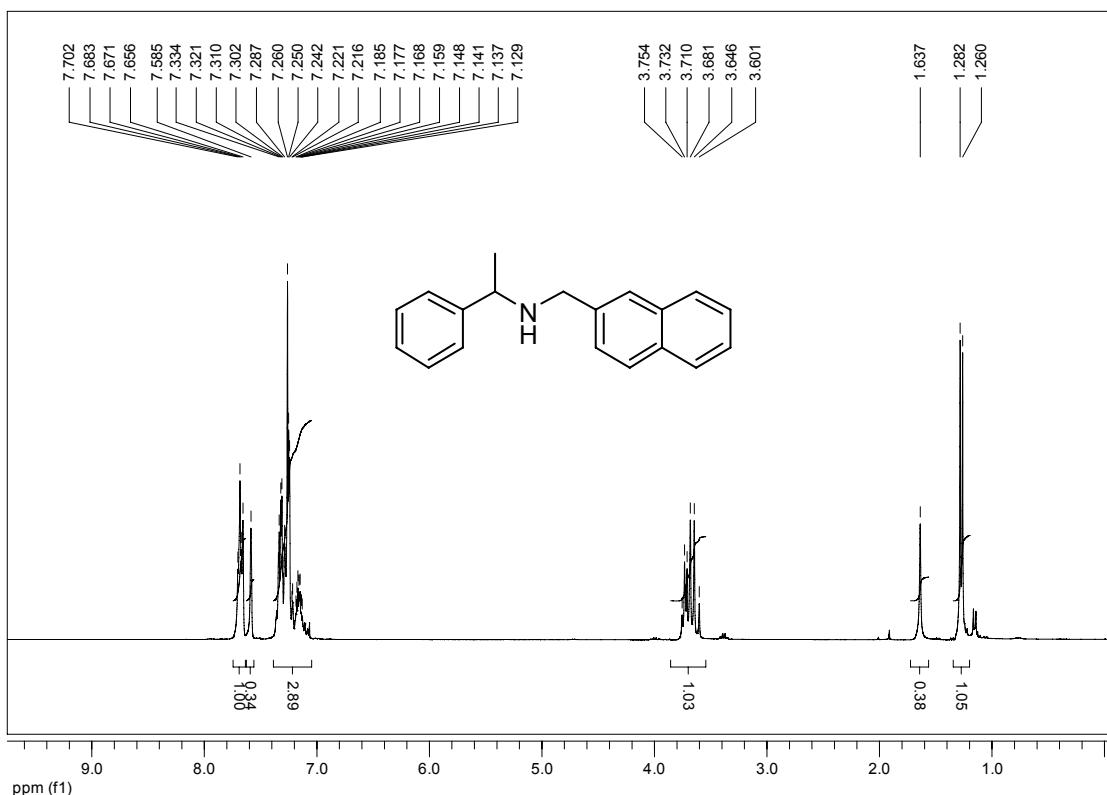
¹H NMR (300 MHz, CDCl₃): N-(3-methoxybenzyl)-1-phenylethanamine (Table 2, entry 5)



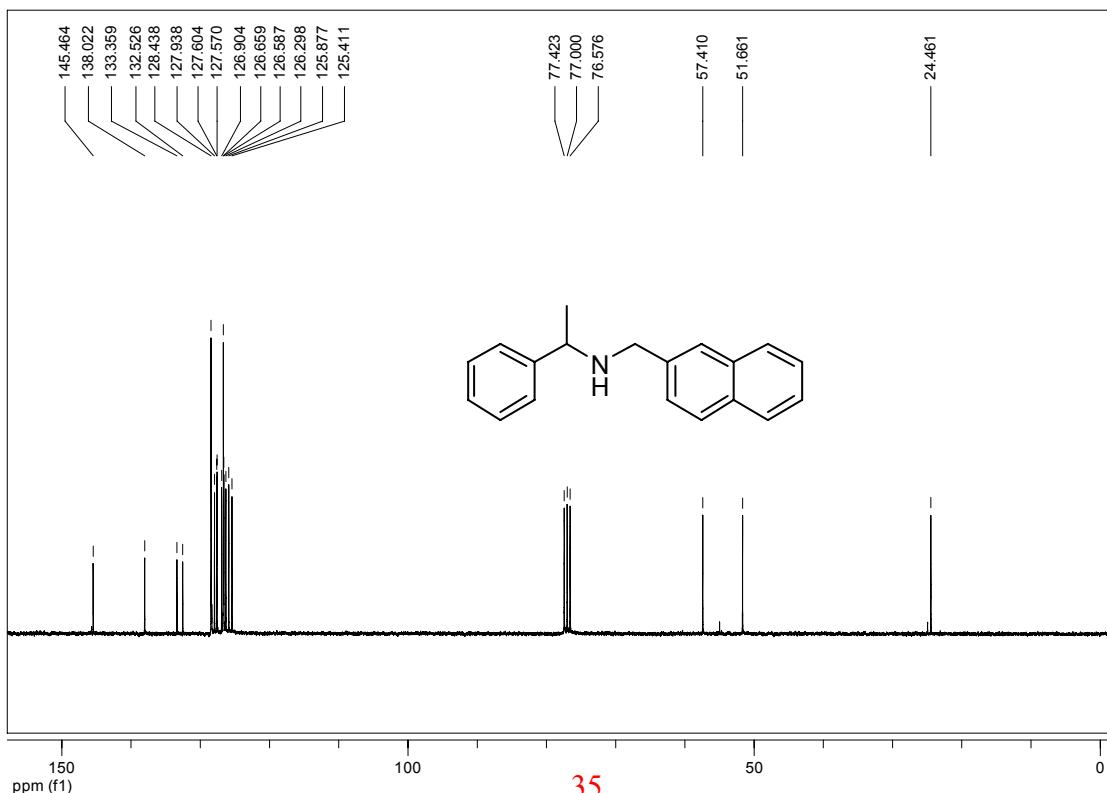
¹³C NMR (75 MHz, CDCl₃): N-(3-methoxybenzyl)-1-phenylethanamine (Table 2, entry 5)



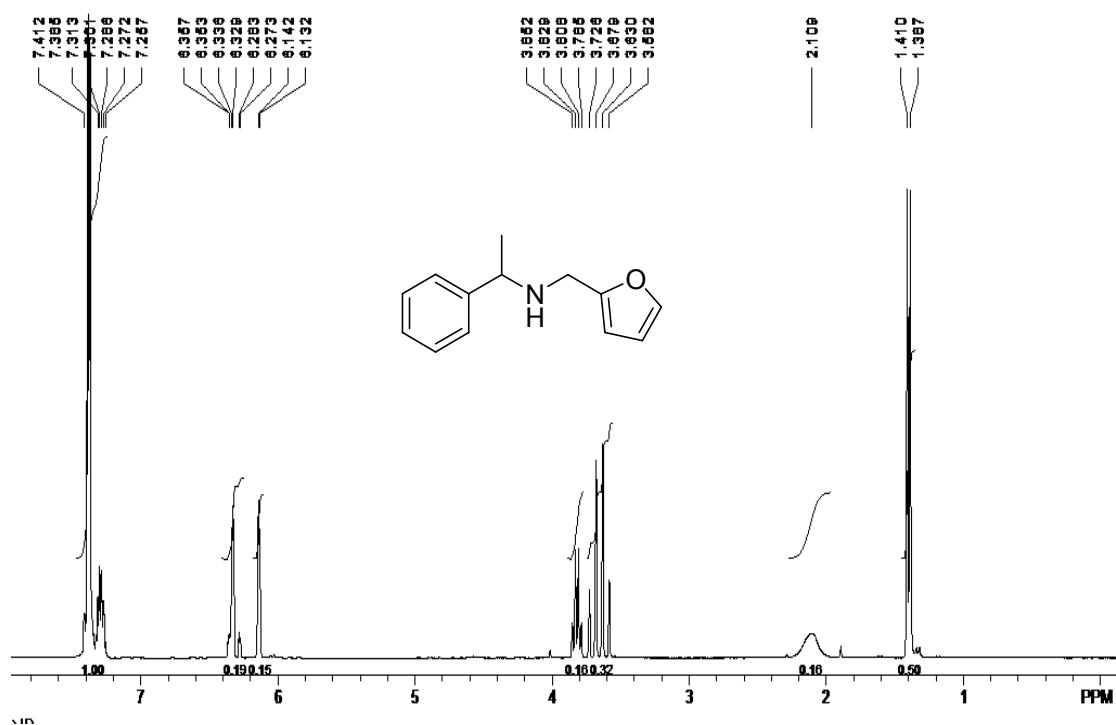
¹H NMR (300 MHz, CDCl₃): N-(naphthalen-2-ylmethyl)-1-phenylethanamine (Table 2, entry 6)



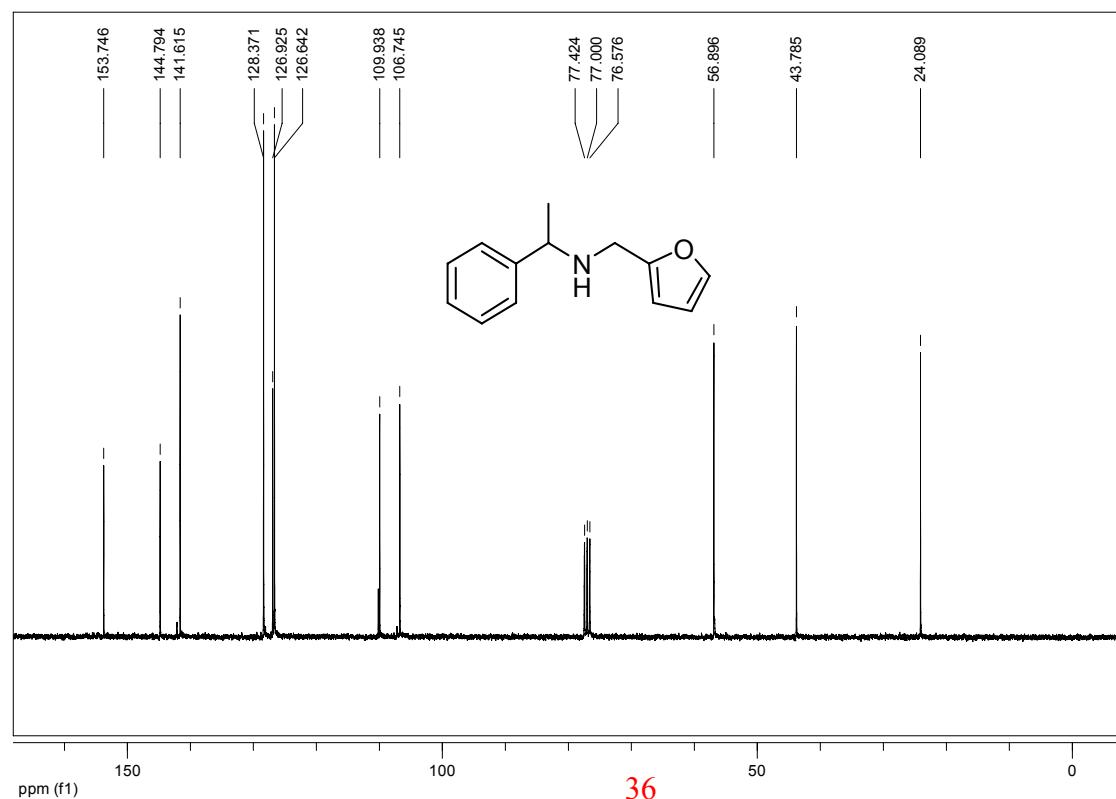
¹H NMR (300 MHz, CDCl₃): N-(naphthalen-2-ylmethyl)-1-phenylethanamine (Table 2, entry 6)



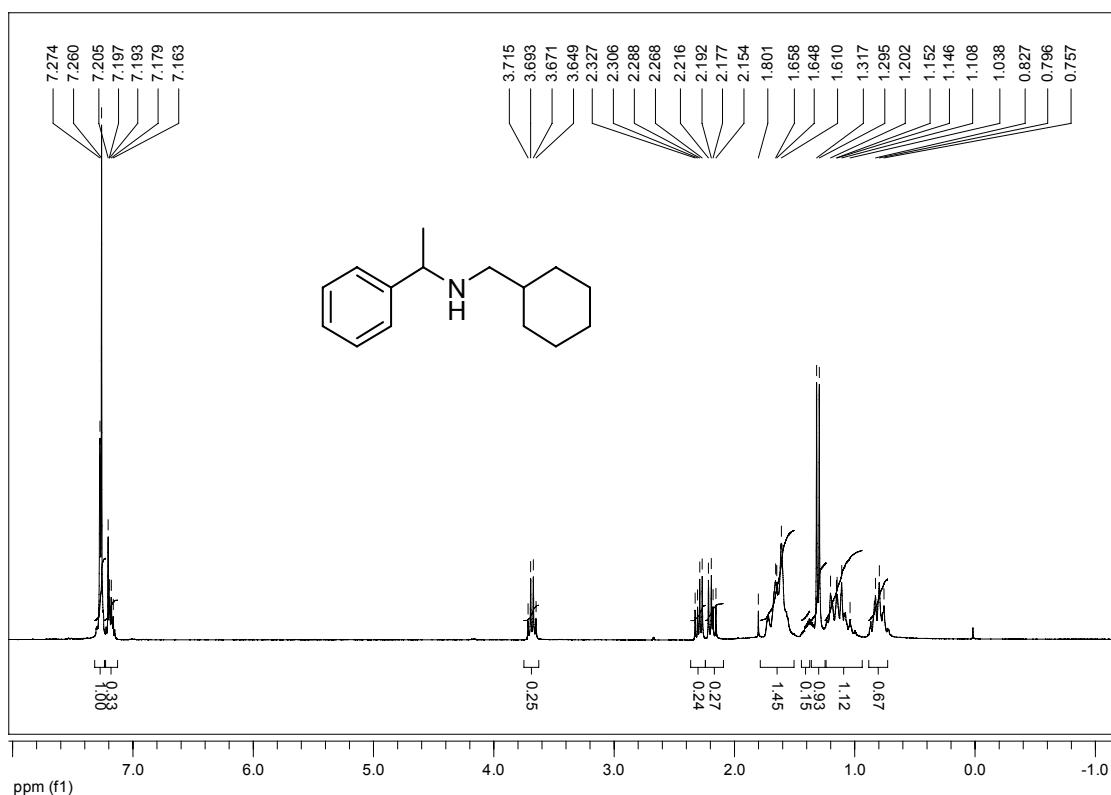
¹H NMR (300 MHz, CDCl₃): *N*-(furan-2-ylmethyl)-1-phenylethanamine (Table 2, entry 7)



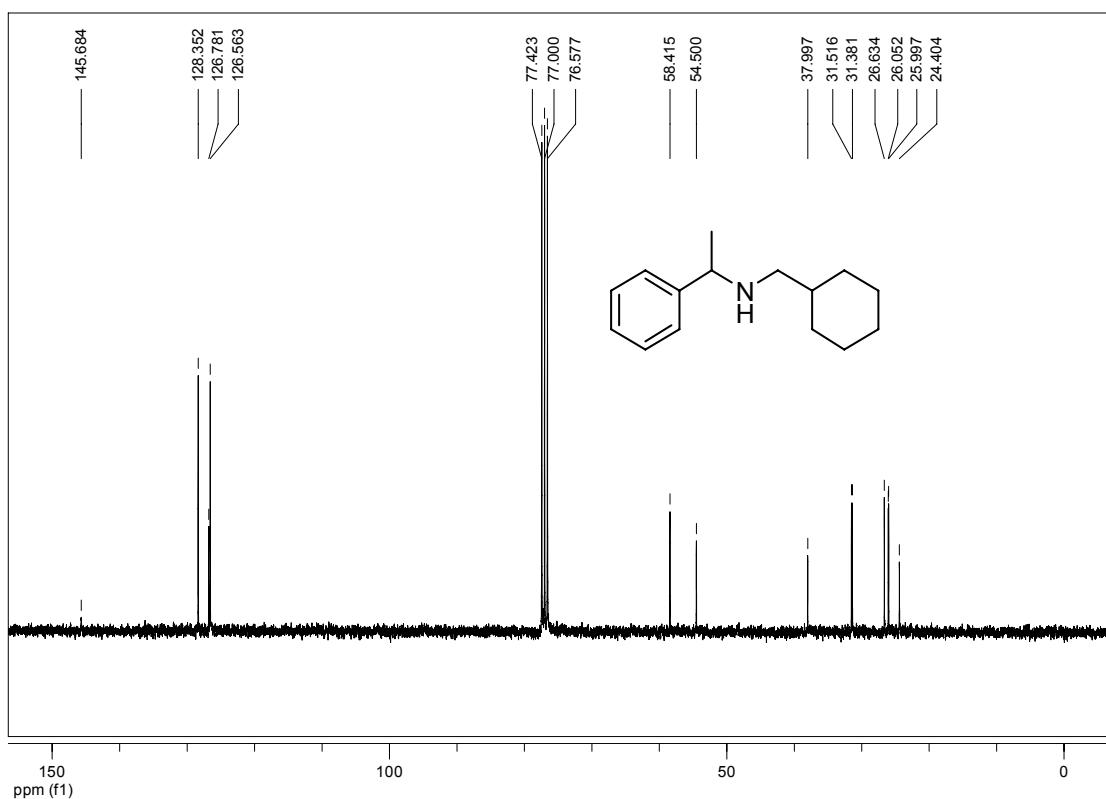
¹³C NMR (75 MHz, CDCl₃): *N*-(furan-2-ylmethyl)-1-phenylethanamine (Table 2, entry 7)



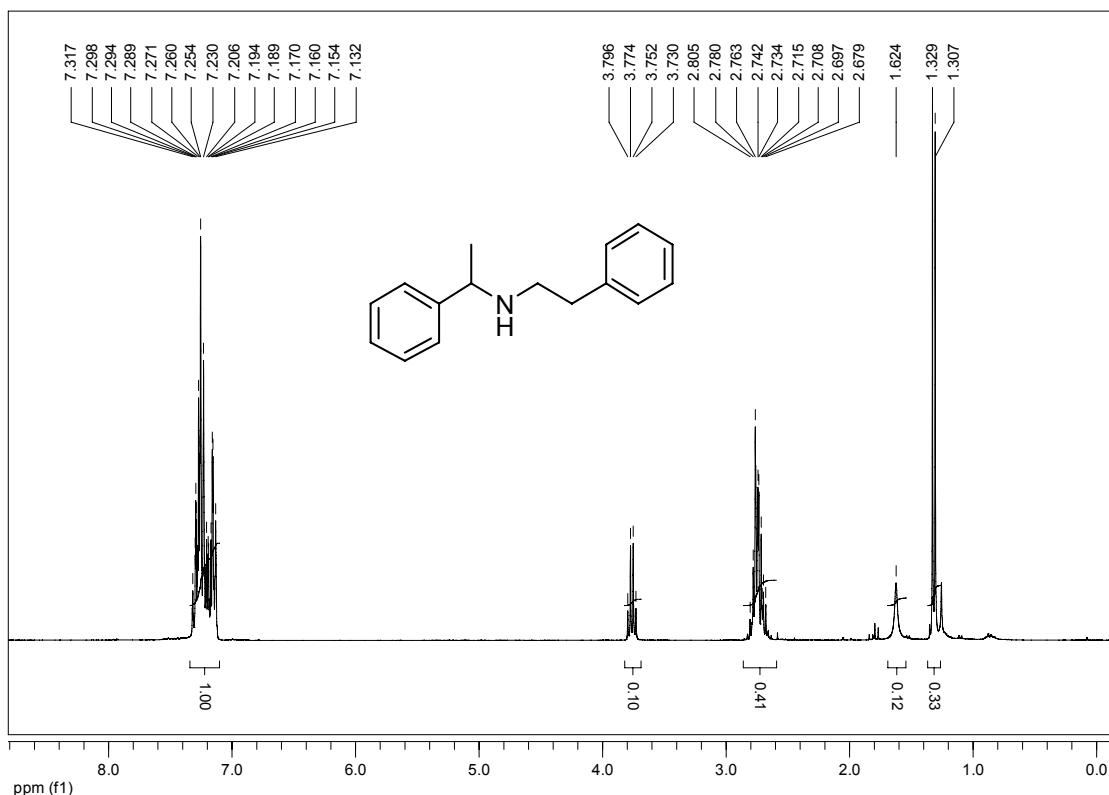
¹H NMR (300 MHz, CDCl₃): N-(cyclohexylmethyl)-1-phenylethanamine (Table 2, entry 8)



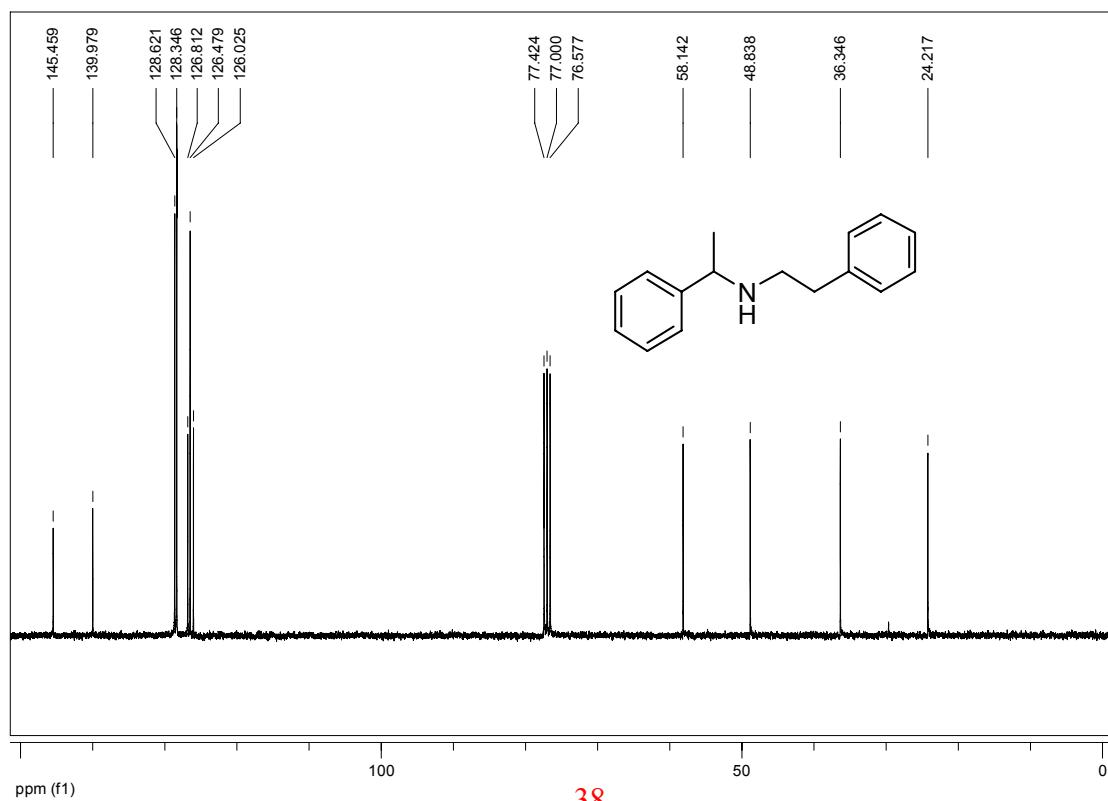
¹³C NMR (75 MHz, CDCl₃): N-(cyclohexylmethyl)-1-phenylethanamine (Table 2, entry 8)



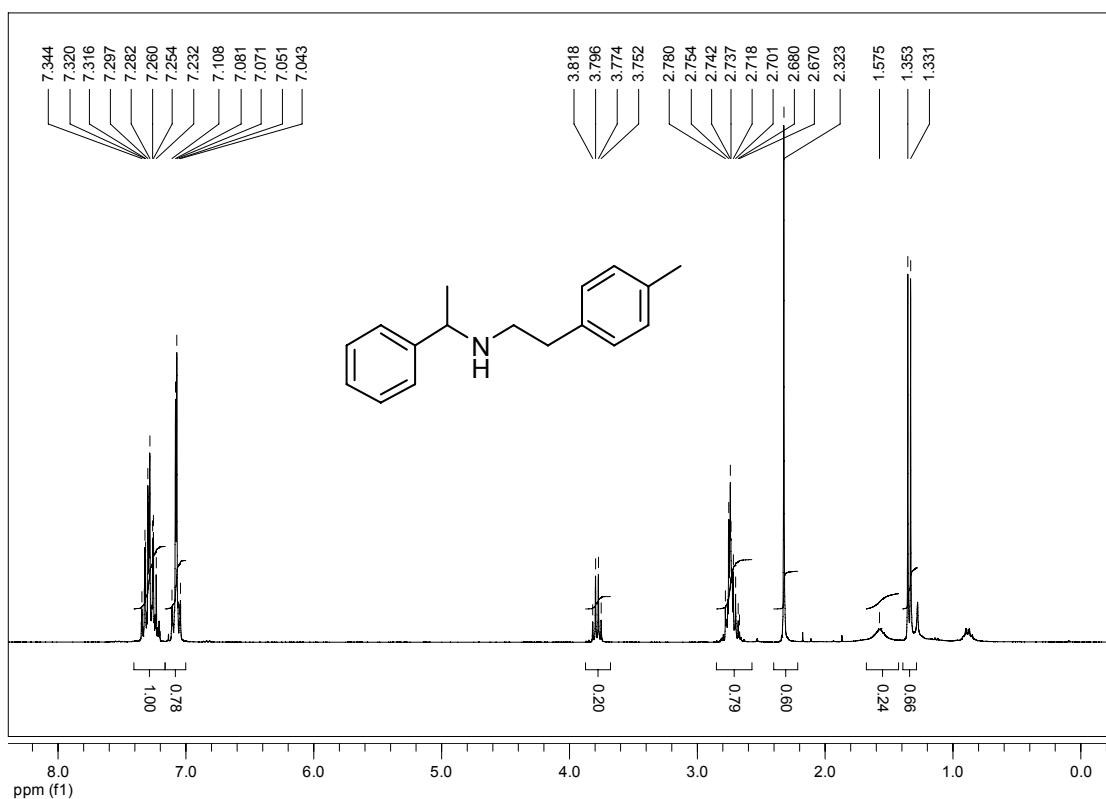
¹H NMR (300 MHz, CDCl₃): N-phenethyl-1-phenylethanamine (Table 2, entry 9)



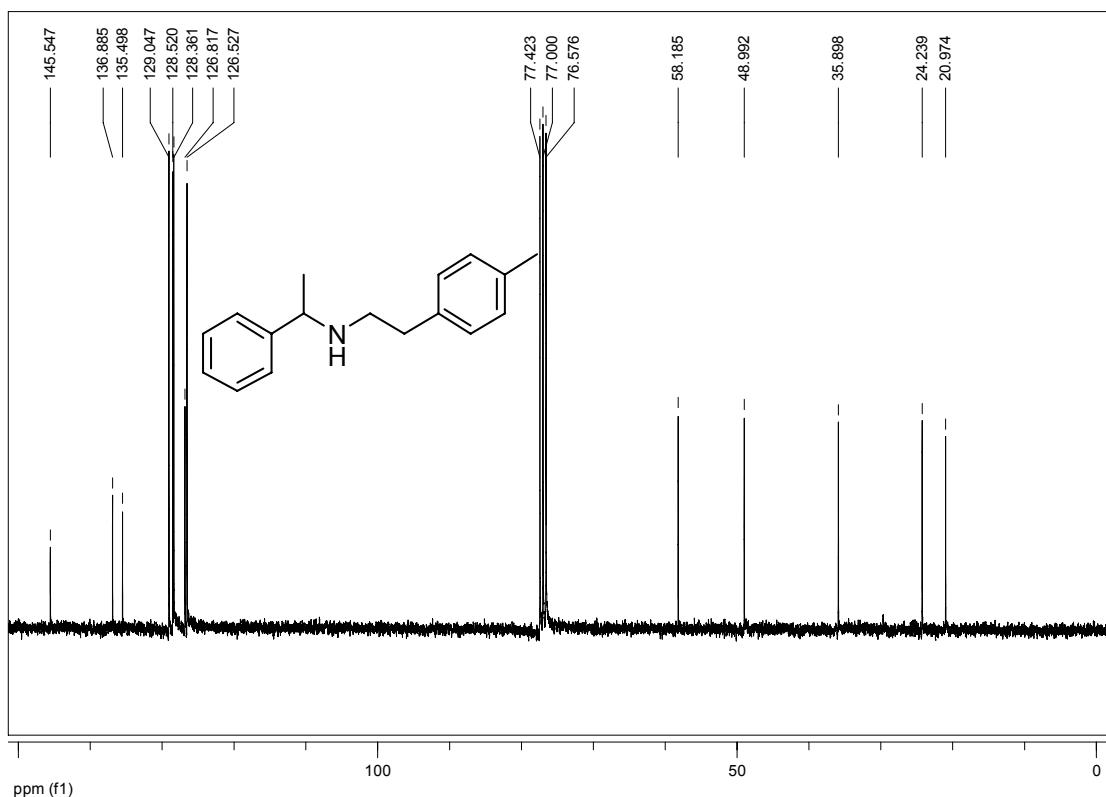
¹³C NMR (75 MHz, CDCl₃): N-phenethyl-1-phenylethanamine (Table 2, entry 9)



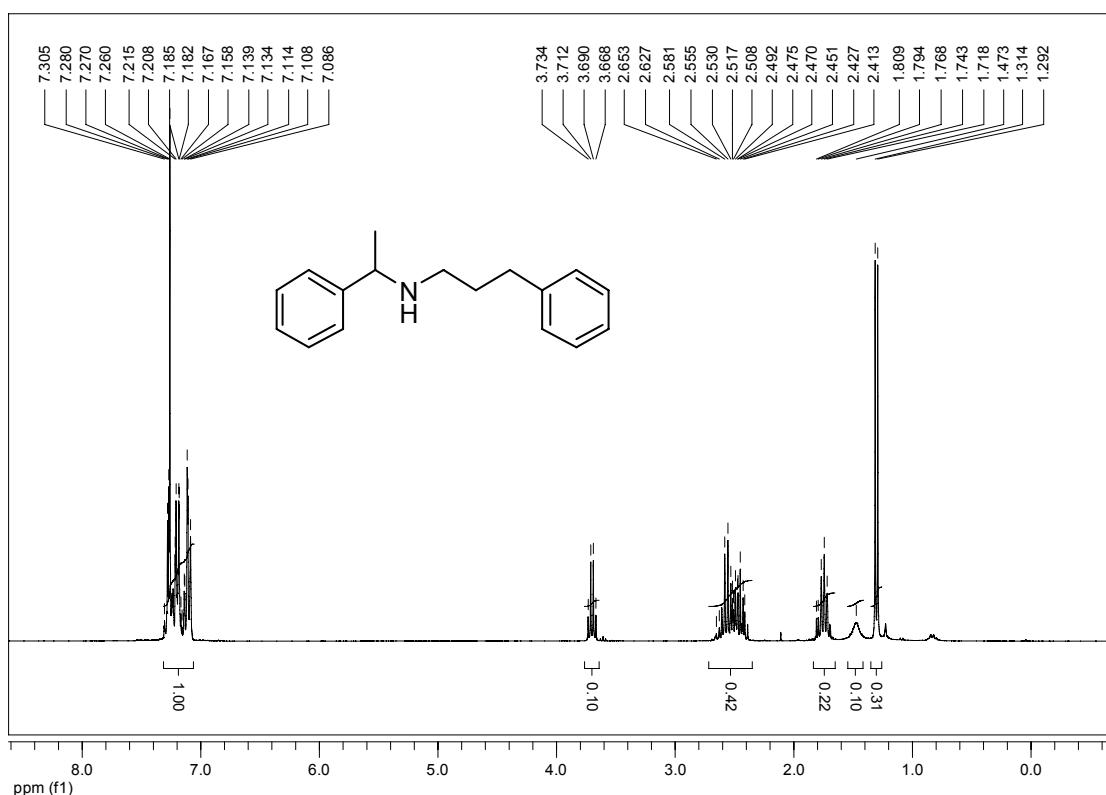
¹H NMR (300 MHz, CDCl₃): N-(4-methylphenethyl)-1-phenylethanamine (Table 2, entry 10)



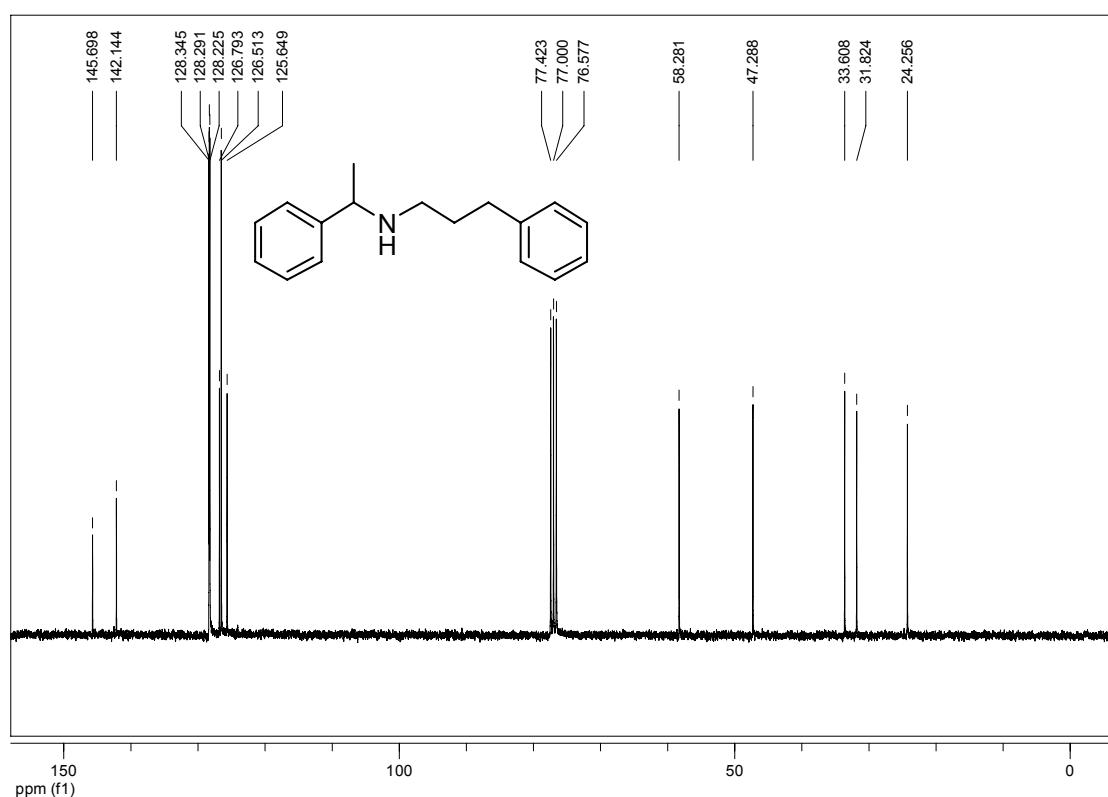
¹³C NMR (75 MHz, CDCl₃): N-(4-methylphenethyl)-1-phenylethanamine (Table 2, entry 10)



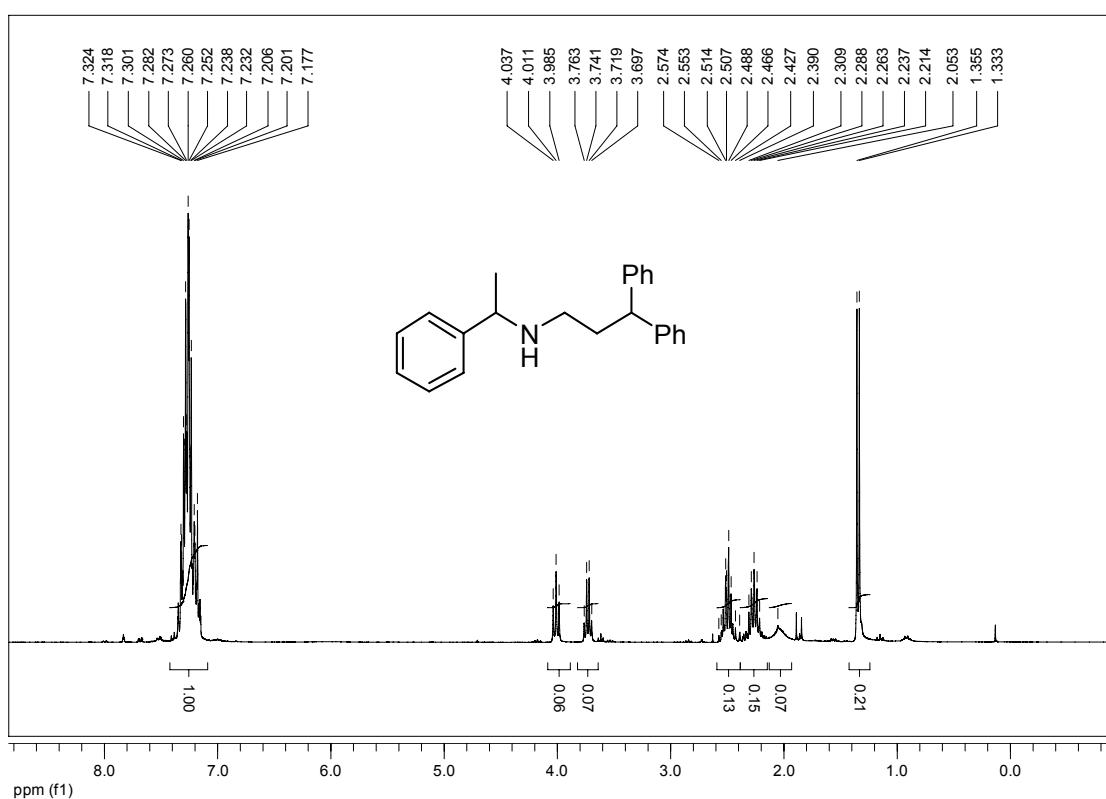
¹H NMR (300 MHz, CDCl₃): 3-phenyl-N-(1-phenylethyl)propan-1-amine (Table 2, entry 11)



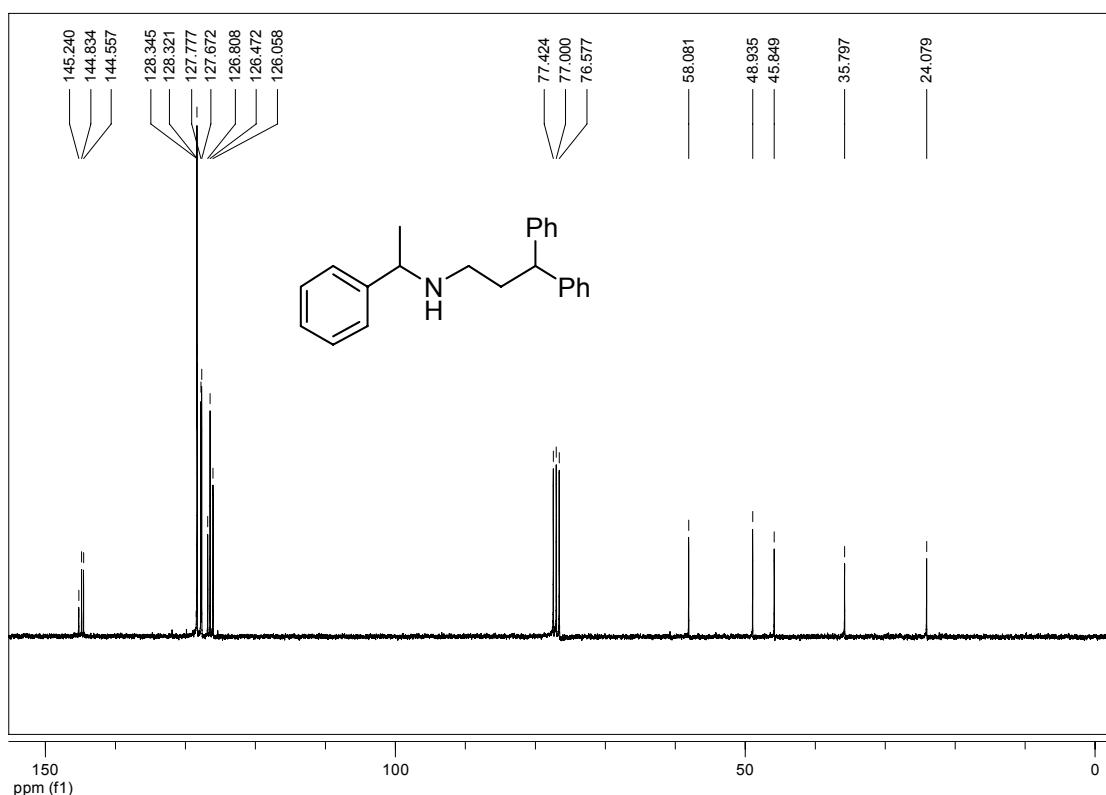
¹³C NMR (75 MHz, CDCl₃): 3-phenyl-N-(1-phenylethyl)propan-1-amine (Table 2, entry 11)



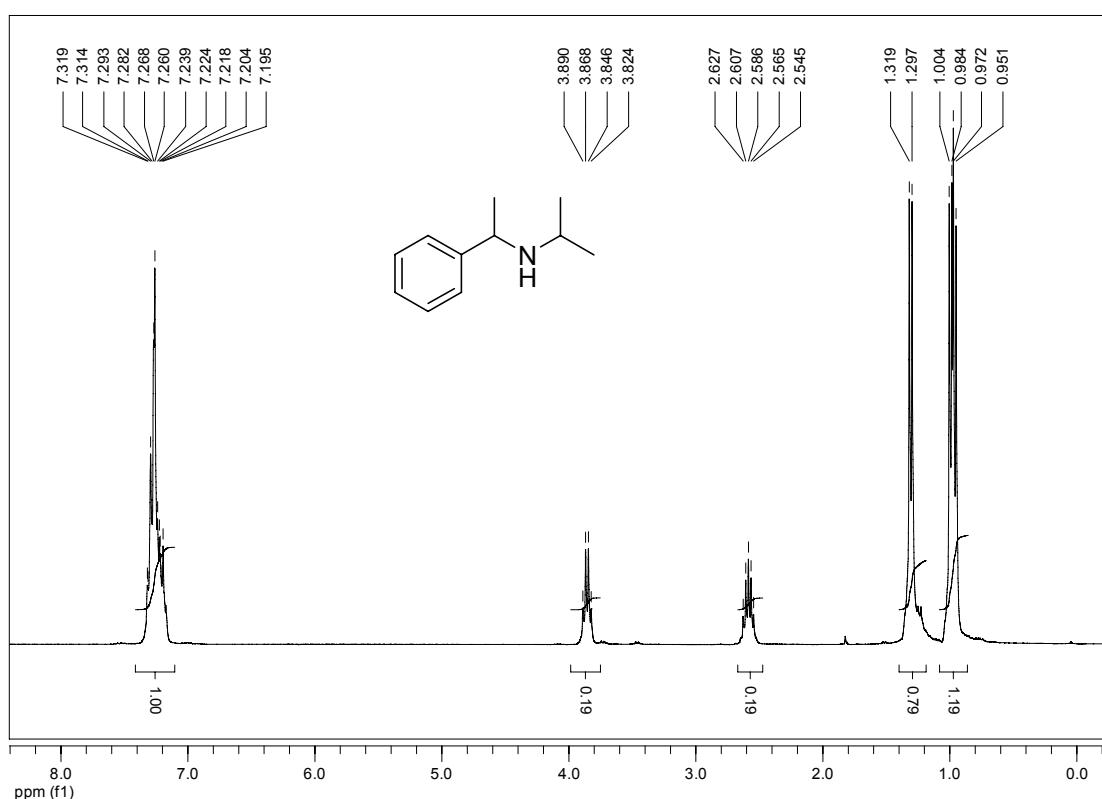
¹H NMR (300 MHz, CDCl₃): 3,3-diphenyl-N-(1-phenylethyl)propan-1-amine (Table 2, entry 12)



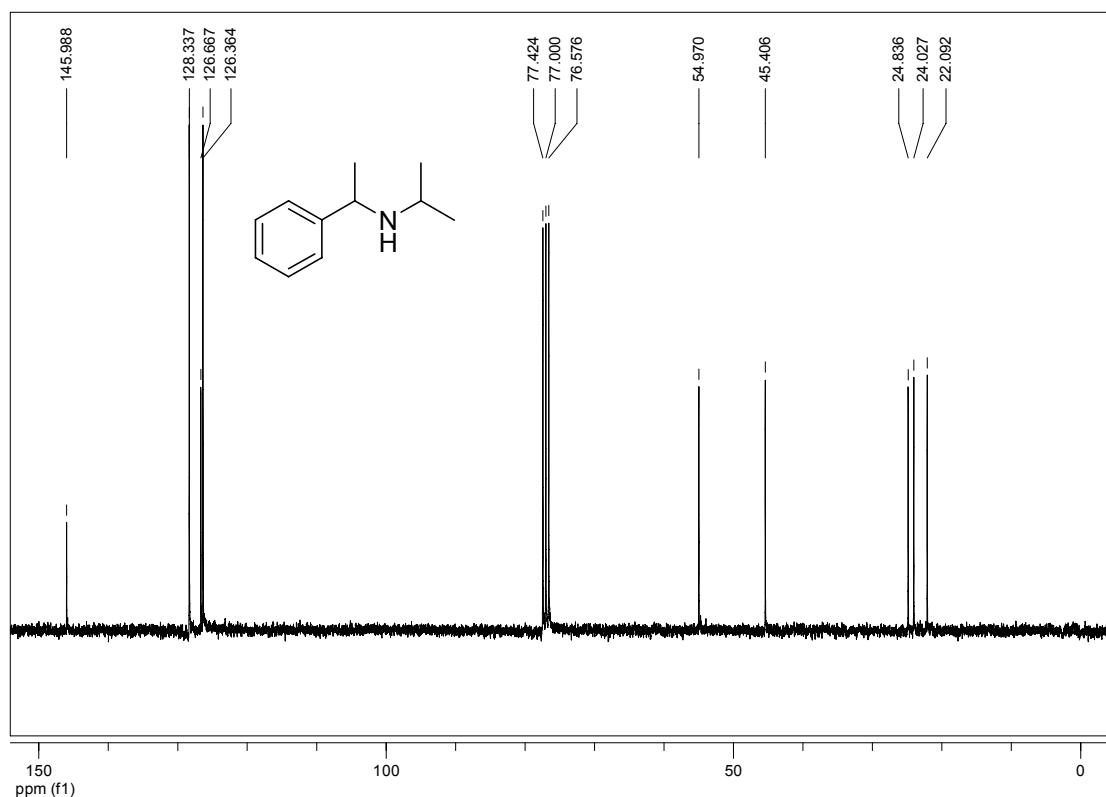
¹³C NMR (75 MHz, CDCl₃): 3,3-diphenyl-N-(1-phenylethyl)propan-1-amine (Table 2, entry 12)



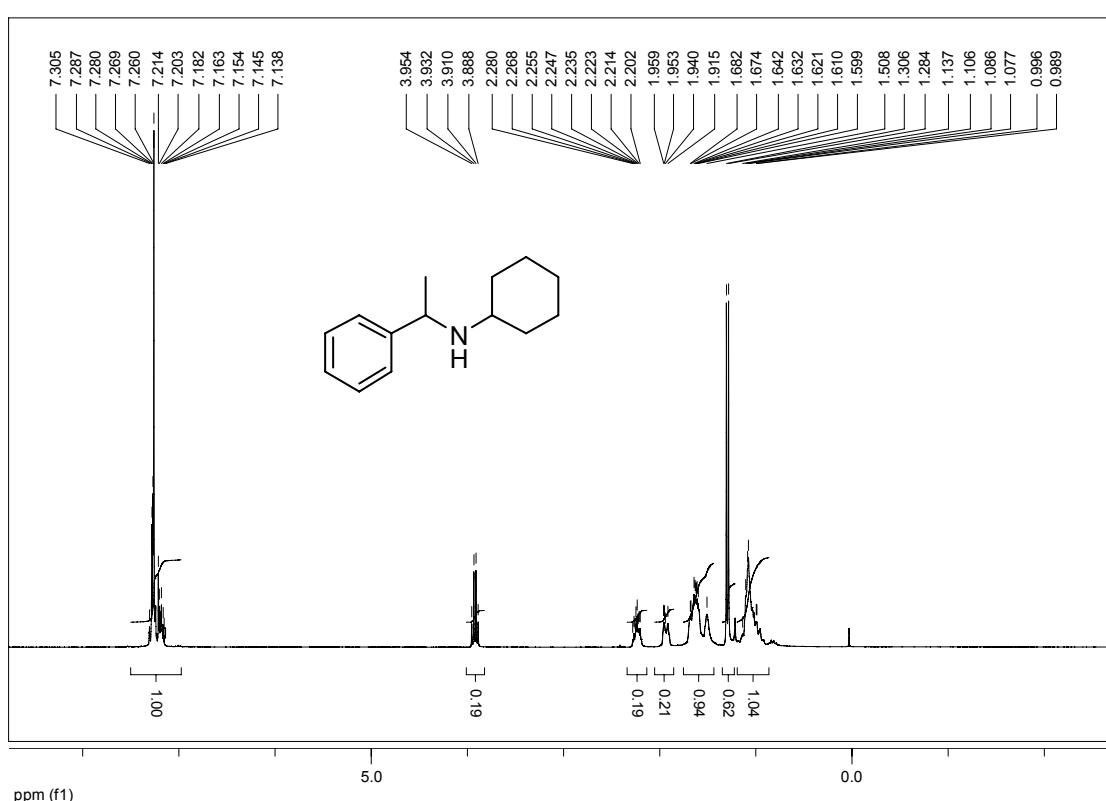
¹H NMR (300 MHz, CDCl₃): N-(1-phenylethyl)propan-2-amine (Table 2, entry 13)



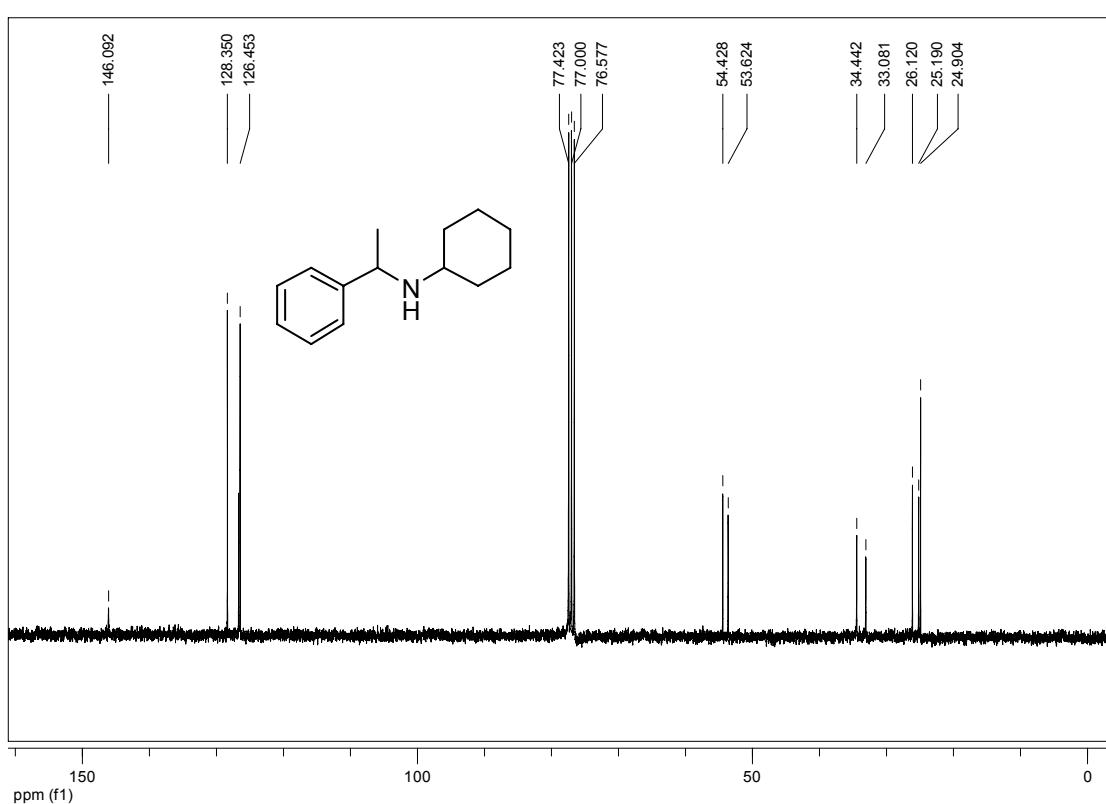
¹³C NMR (75 MHz, CDCl₃): N-(1-phenylethyl)propan-2-amine (Table 2, entry 13)



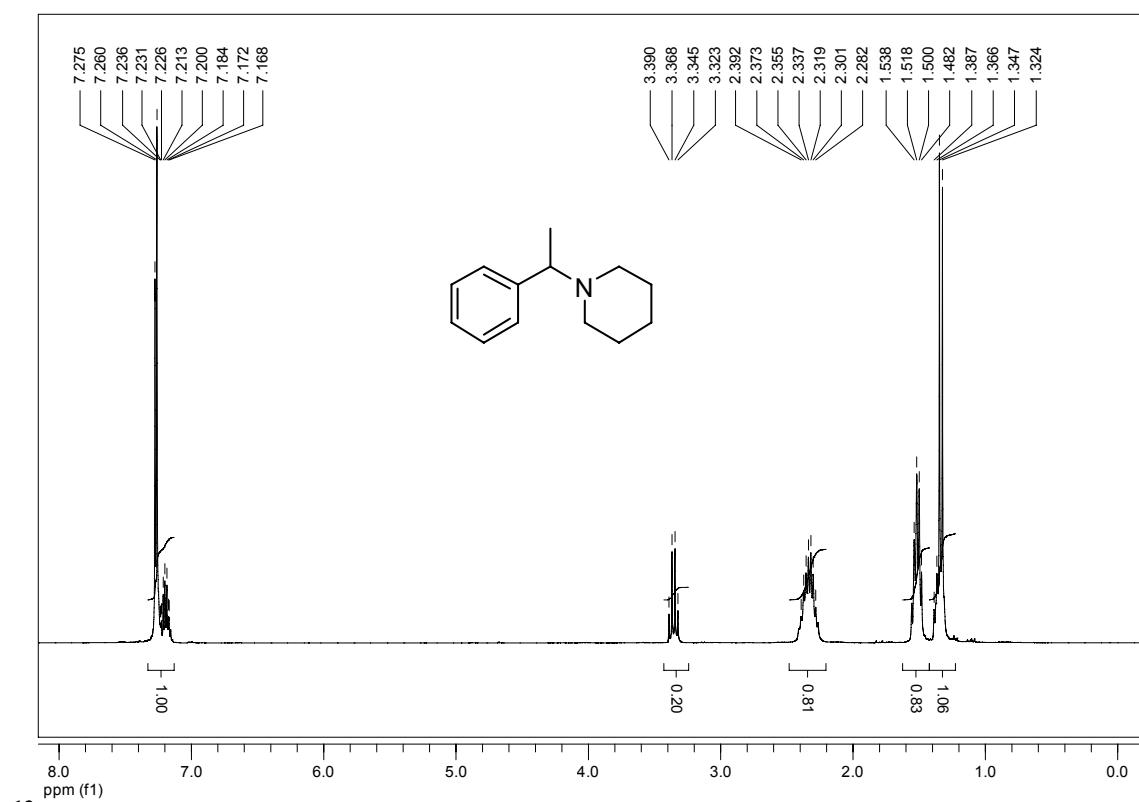
¹H NMR (300 MHz, CDCl₃): N-(1-phenylethyl)cyclohexanamine (Table 2, entry 14)



¹³C NMR (75 MHz, CDCl₃): N-(1-phenylethyl)cyclohexanamine (Table 2, entry 14)



¹H NMR (300 MHz, CDCl₃): 1-(1-phenylethyl)piperidine (Table 2, entry 15)



¹³C NMR (75 MHz, CDCl₃): 1-(1-phenylethyl)piperidine (Table 2, entry 15)

