Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for:

Ultrasound-assisted solventless synthesis of amines by *in situ* oxidation/reductive amination of benzyl halides

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Experimental Procedure

3.1. General methods

All reactions were conducted in a 5 mL sample vial and carried out with ultrasonic bath (Elma, S 30 H, Elmasonic, 280 Watt, 50-60 Hz, Germany). The reaction was monitored by thin-layer chromatography carried out on silica gel plates ($60F_{254}$, MERCK, Germany) and visualized under UV light (245 nm). Column chromatography was performed over silica gel 60 (70–230 mesh, MERCK, Germany). NMR measurements were conducted on a Bruker AVANCE^{TM} (400 MHz for ^{1}H) using chloroform-d ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts were reported in parts per million (ppm, δ) downfield from TMS. Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), and doublet of doublet (dd). Gas chromatography (GC) analysis was equipped with an HP model 6890A equipped with an HP-INNOWAX Polyethylene Glycol capillary column (30 m x 0.25 mm i.d., film thicknes 0.25 μm, temp 40-260/270 °C, Agilent Technologies, USA) with FID detector. Gas Chromatography–Mass Spectrometry (GC-MS) analysis was perform with an HP model 6850 gas chromatograph equipped with an HP-5MS (5% phenyl-polymethylsiloxane) capillary column (30 m x 0.25 mm i.d., film thickness 0.25 μm, Agilent Technologies, USA) interfaced to an HP model 5973 mass-selective detector. EI mass spectra were collected at 70 eV ionization voltages over the range of m/z 30-400 and electron multiplier voltage was 2000 V. The mass spectra were compared with mass spectra of individual components with the reference mass spectra in the Wiley 275 and NIST 98 databases.

3.2. General procedure for ultrasound assisted one-pot solventless in situ oxidation/reductive

Unless otherwise specified, benzyl halide (0.4 mmol), NMO (0.6 mmol), and KI (0.04 mmol) were mixed in a 5 mL glass vial. The mixture was then irradiated in a water bath of the 37 kHz ultrasonic cleaner (Elmasonic S 30H) at 80 °C for 30 min. After that, Montmorillonite K-10 (100 mg), amine (0.6 mmol), and $NaBH_4$ (0.030 g, 0.8 mmol) were added, followed by sonication at 80 °C for further 30 min. After cooling down to room temperature, the crude mixture was purified by applied directly to a short column chromatography (1:9 ethyl acetate/hexane) to afford pure product. All known products were characterized by ^{1}H-NMR, IR and GC-MS techniques and their spectroscopic data were consistent with those reported in the literature.

Spectroscopic data of the representative products

Dibenzylamine (Table 2, entry 1): pale yellow oil; yield 89%; R_f = 0.28 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53 – 7.20 (m, 10H), 3.86 (s, 4H), 1.98 (s, 1H); MS (IE) m/z (rel intensity) 196 (M-H, 20), 120 (9), 106 (60), 91 (100); FTIR (UATR) ν_{max} 3234, 3030, 2938, 2371, 1596, 1454, 1170 cm^{-1}.

***N*-Benzylcyclopropanamine** (Table 2, entry 2): colorless oil; yield 85%; R_f = 0.47 (2:8 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35 – 7.29 (m, 5H), 3.72 (s, 2H), 1.91 – 1.84 (m, 1H), 0.58 – 0.30 (m, 5H); MS (IE) m/z (rel intensity) 146 (M-H, 100), 91 (71), 65 (12); FTIR (UATR) ν_{max} 3023, 2924, 2809, 1598, 1493, 1450, 1352,1127 cm^{-1}.

***N*-Benzylaniline** (Table 2, entry 6): pale yellow oil; yield 87%; R_f = 0.51 (2:8 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51 – 6.73 (m, 10H), 4.41 (s, 2H), 4.11 (s, 1H); MS (IE) m/z (rel intensity) 183 (M^+, 97), 106 (19), 91 (100), 77 (19), 65 (17); FTIR (UATR) ν_{max} 3419, 3026, 2854, 1602, 1506, 1324, 1280,1180 cm^{-1}.

***N*-Benzyl-4-methoxyaniline** (Table 2, entry 7): pale yellow oil; yield 88%; R_f = 0.53 (2:8 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 – 7.28 (m, 5H), 6.83 – 6.64 (m, 4H), 4.41 (s, 2H), 3.87 (s, 3H); MS (IE) m/z (rel intensity) 213 (M^+, 100), 198 (9), 122 (77), 91 (66); FTIR (UATR) ν_{max} 3412, 3028, 2932, 2834, 1613, 1516, 1239, 1103 cm^{-1}.

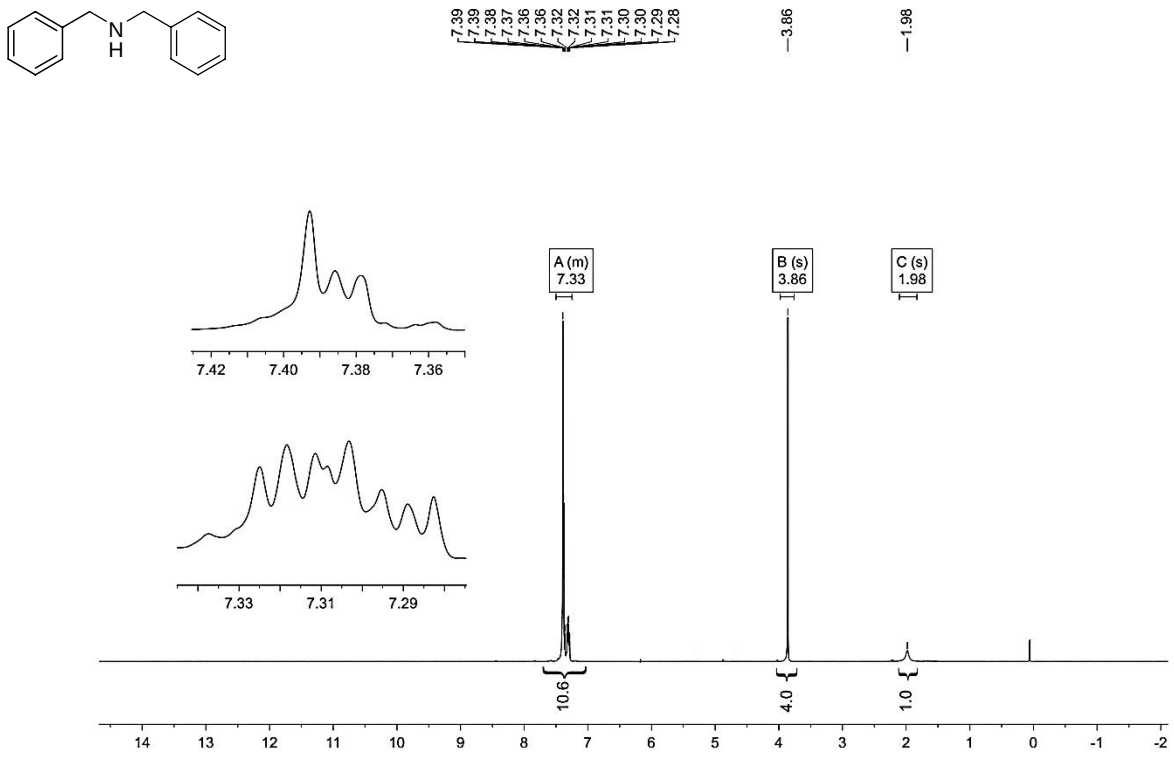
1-(4-Methylbenzyl)piperidine (Table 2, entry 20): pale yellow oil; yield 88%; R_f = 0.41 (2:8 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34 – 6.97 (dd, 4H), 3.47 (s, 2H), 2.36 (s, 3H), 1.65–1.52 (dt, 6H), 1.49–1.39 (dd, 4H); MS (IE) m/z (rel intensity) 189 (M^+, 7), 174 (100), 112 (21), 105 (19), 91 (10); FTIR (UATR) ν_{max} 3387, 2928, 2854, 1745, 1643, 1514, 1460, 1021 cm^{-1}.

***N*-Benzyl-1-(4-chlorophenyl)methanamine** (Table 2, entry 22): colorless oil; yield 82%; R_f = 0.47 (2:8 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42 – 7.16 (m, 9H), 3.80 (t, J = 8.1 Hz, 4H), 1.66 (s, 1H); MS (IE) m/z (rel intensity) 230 (M-H, 30), 196 (10), 140 (63), 125 (76), 106 (29), 91 (100); FTIR (UATR) ν_{max} 3304, 3028, 2920, 2824, 2368, 1598, 1453, 1170 cm^{-1}.

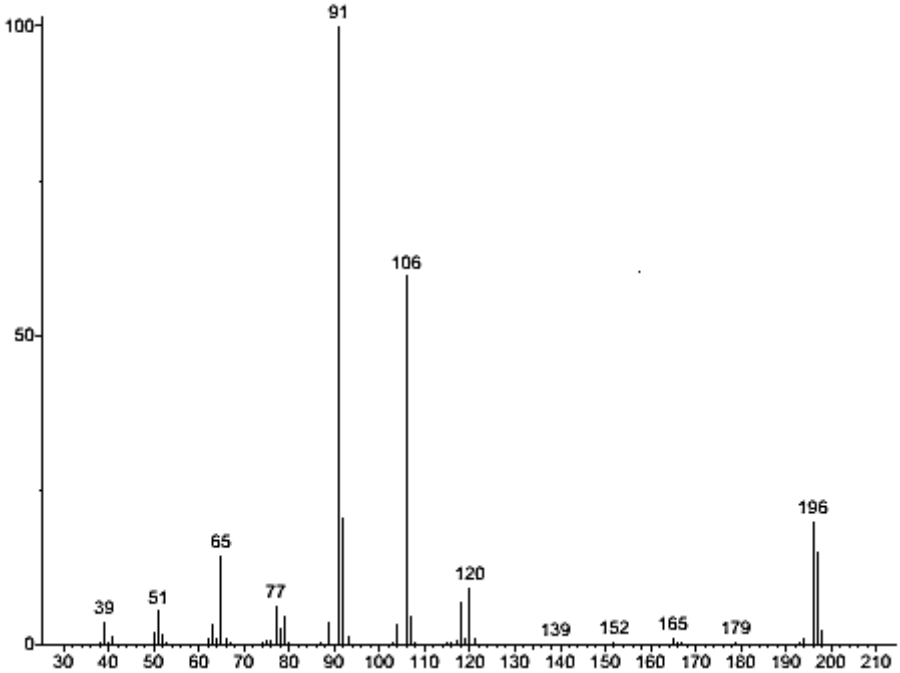
^{1}H NMR and mass spectra of the representative products

Dibenzylamine

^{1}H NMR (400 MHz, $CDCl_3$)

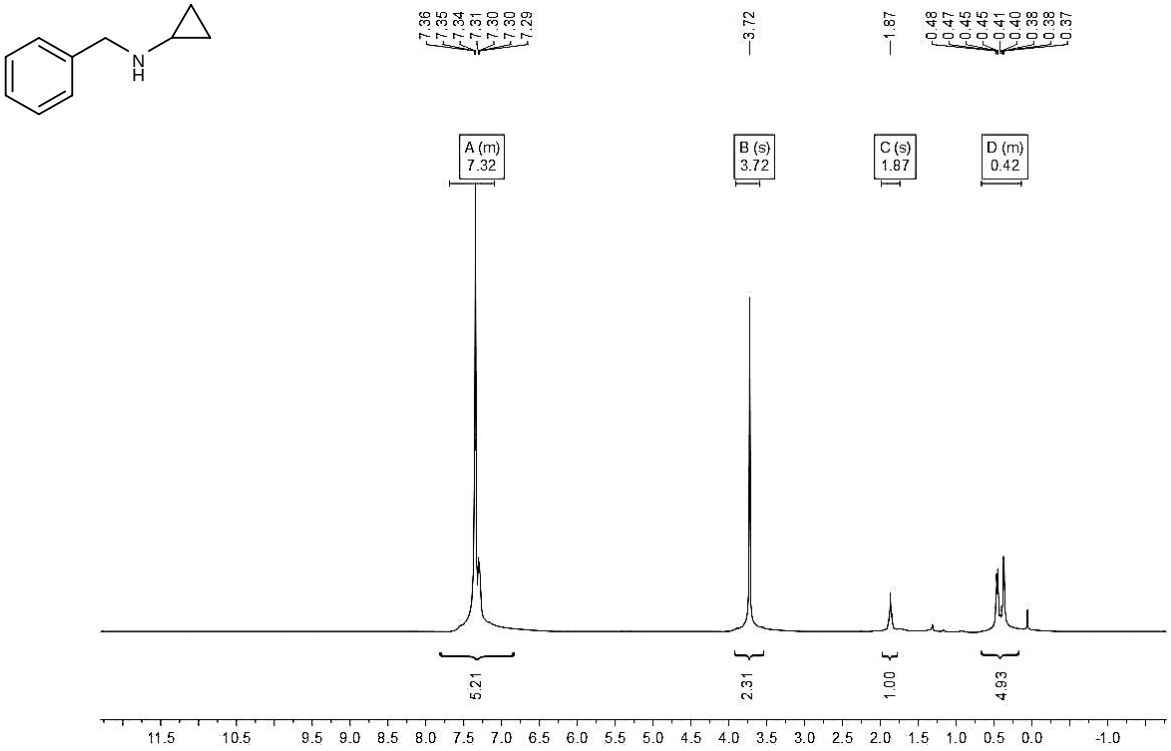


MS (IE) m/z (rel intensity) 196 (M-H, 20)

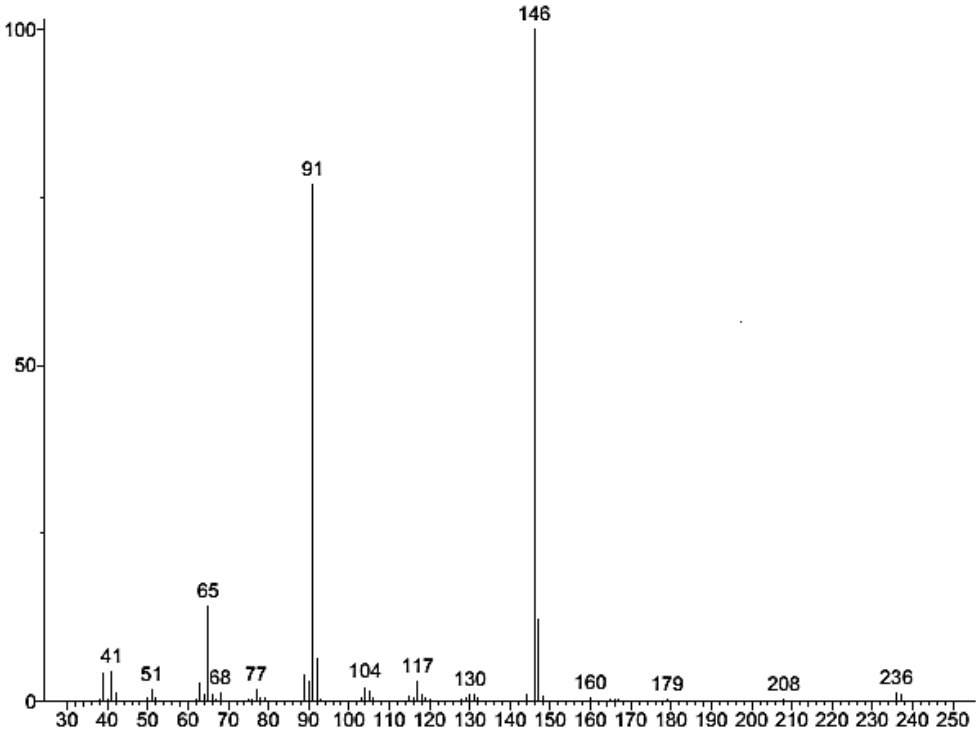


***N*-Benzylcyclopropanamine**

^{1}H NMR (400 MHz, $CDCl_3$)

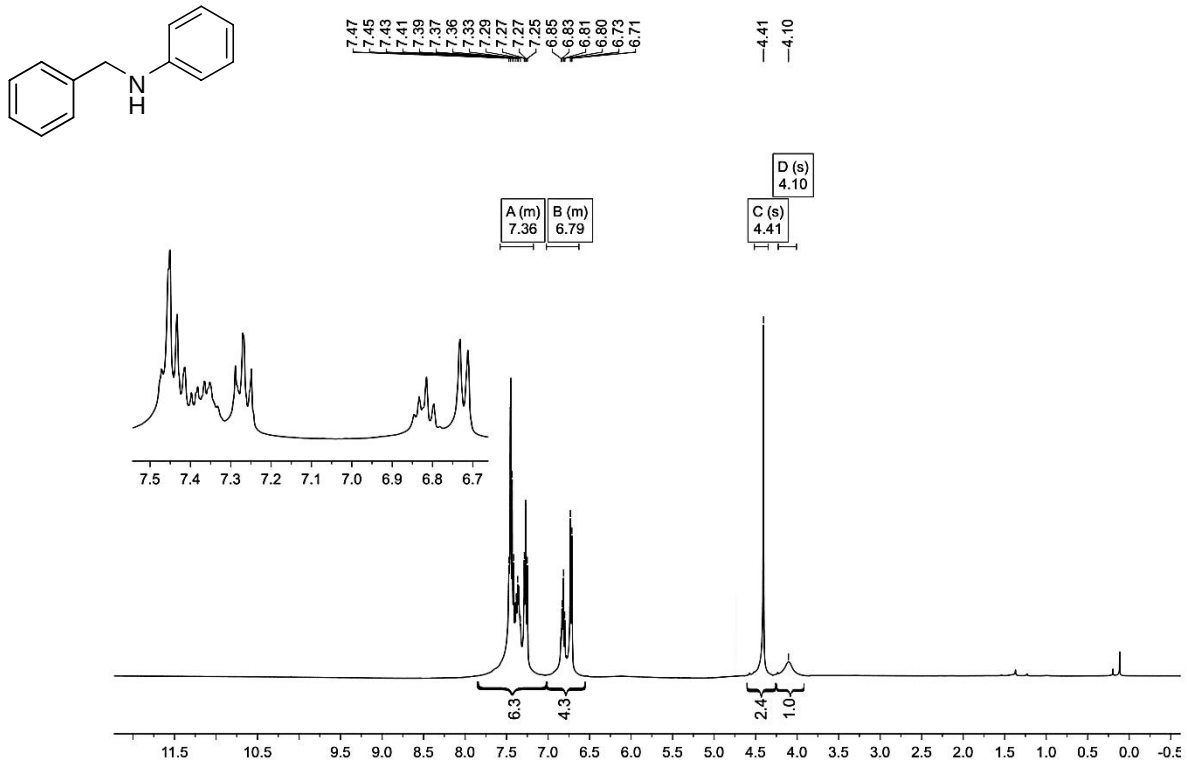


MS (IE) m/z (rel intensity) 146 (M-H, 100)

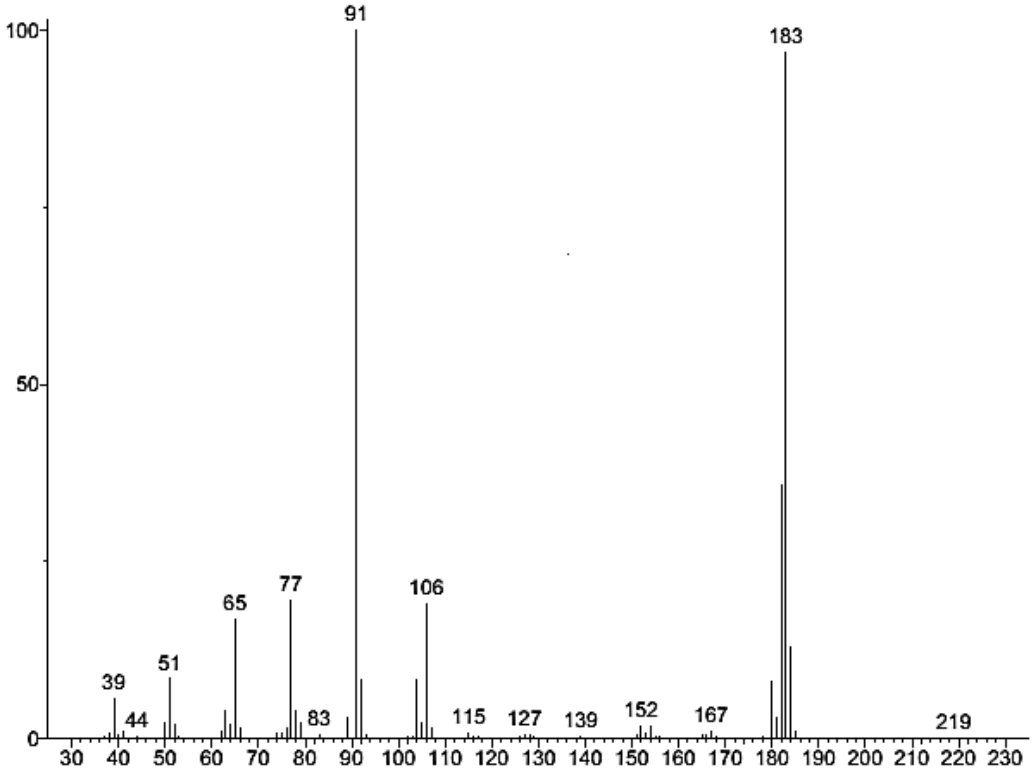


***N*-Benzylaniline**

^{1}H NMR (400 MHz, $CDCl_3$)

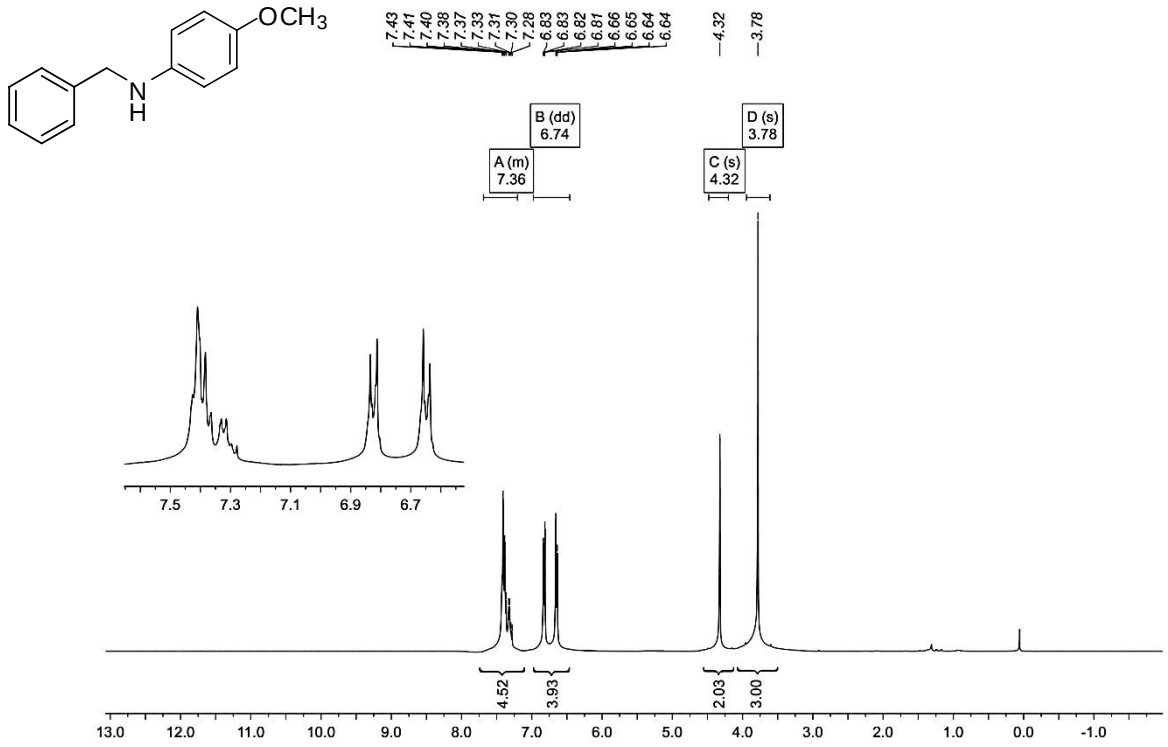


MS (IE) m/z (rel intensity) 183 (M^+, 97)

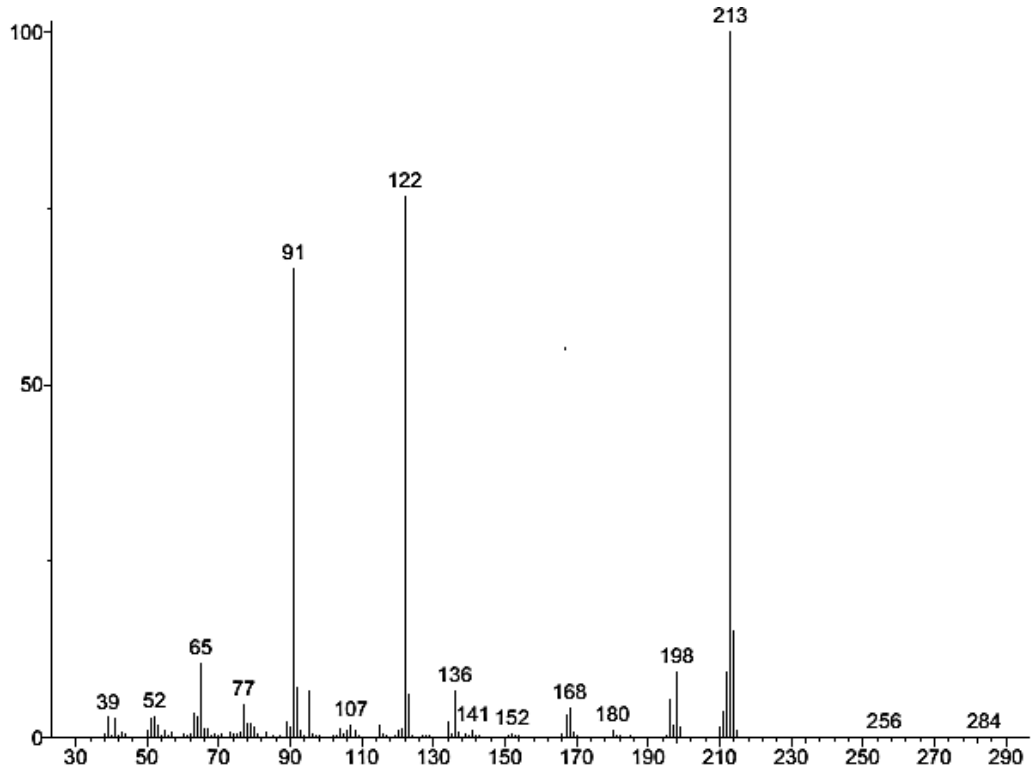


***N*-Benzyl-4-methoxyaniline**

^{1}H NMR (400 MHz, $CDCl_3$)

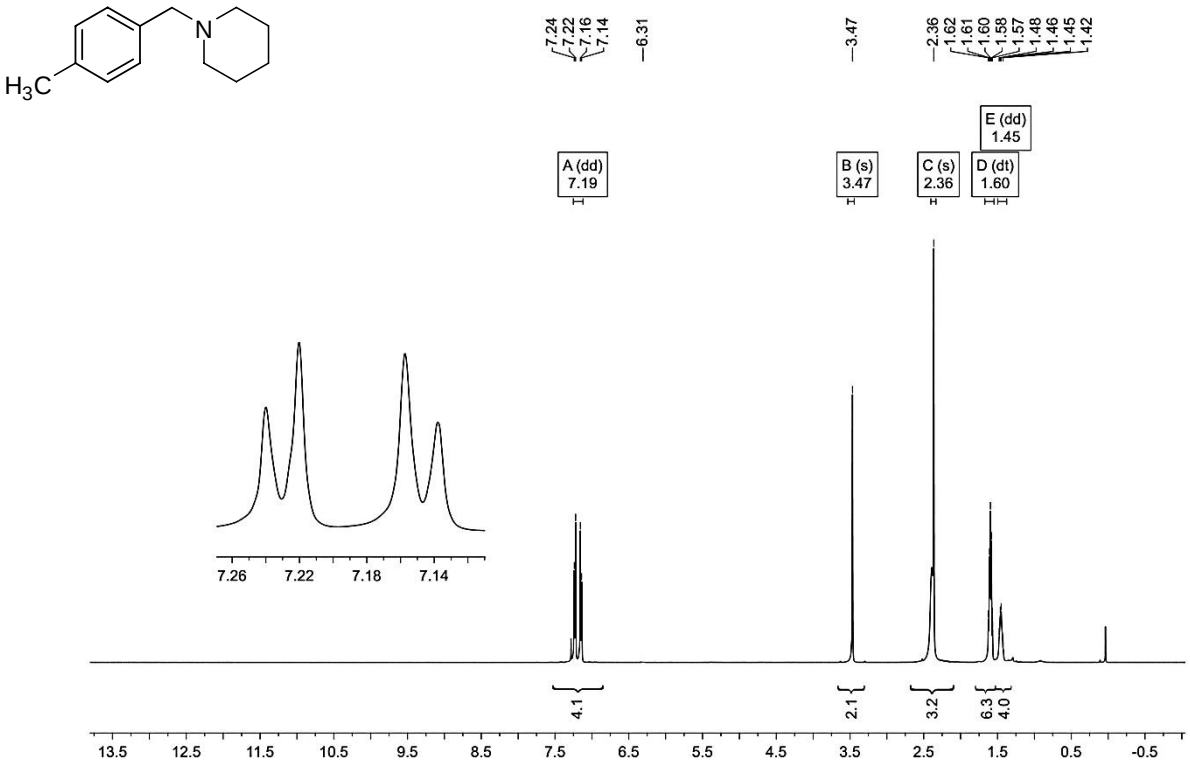


MS (IE) m/z (rel intensity) 213 (M^+, 100)

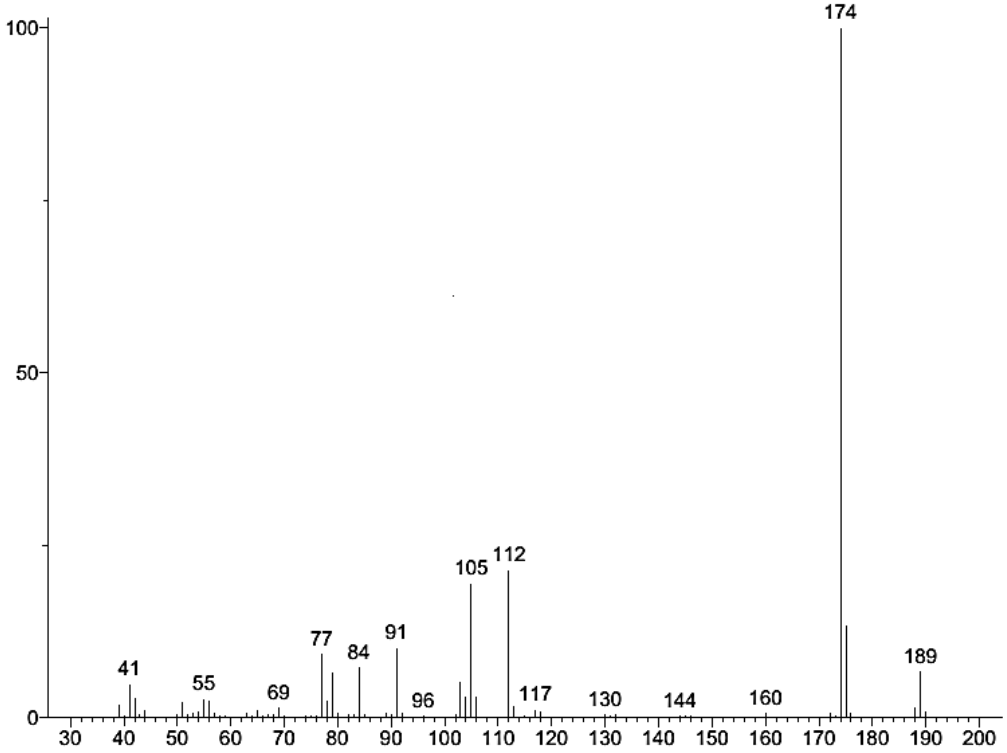


1-(4-Methyl benzyl)piperidine

^{1}H NMR (400 MHz, $CDCl_3$)

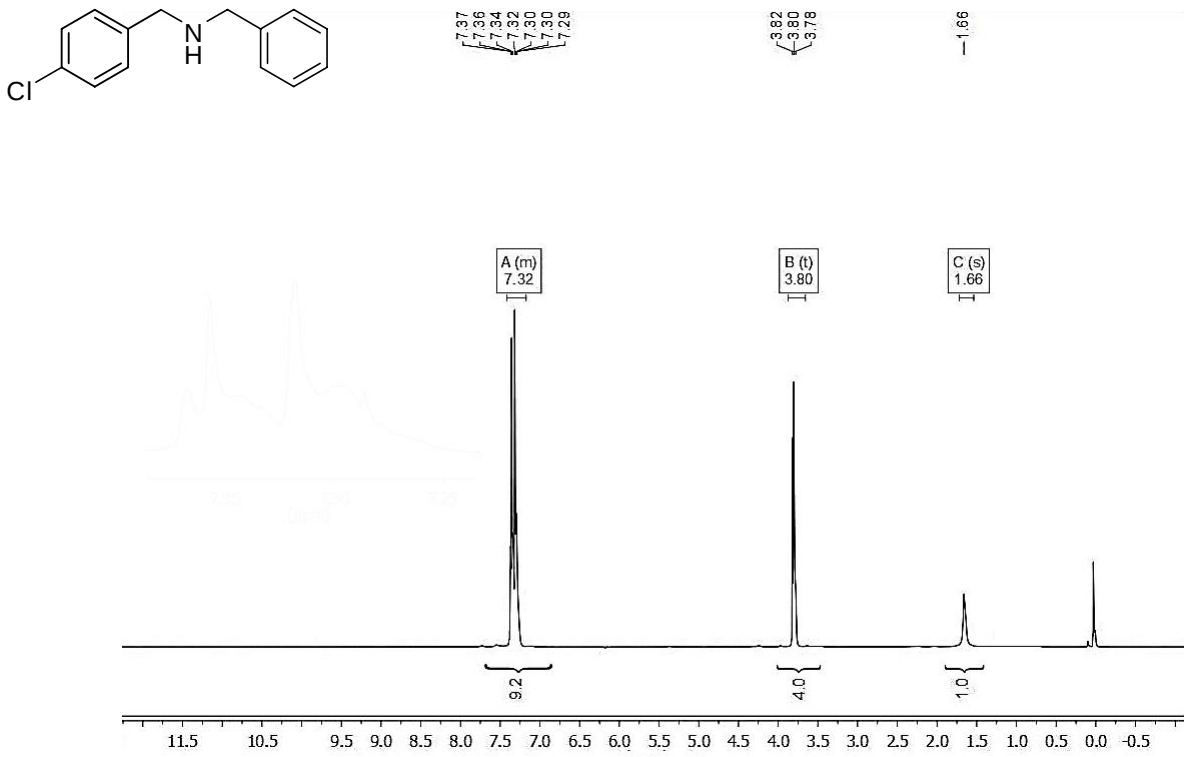


MS (IE) m/z (rel intensity) 189 (M^+, 7)



***N*-Benzyl-1-(4-chlorophenyl)methanamine**

^{1}H NMR (400 MHz, $CDCl_3$)



MS (IE) m/z (rel intensity) 230 (M-H, 30)