

Experimental

All the nitriles and amines were purchased Sigma Aldrich, UK and used without further purification. Hexachloroplatinic acid and toluene were purchased from Fisher Scientific, UK and used as received. Synthesis of Pt/C catalyst (3% by wt.) was carried out by the reported procedure [H.E. van Dam and H. van Bekkum, *J. Catal.*, 1991, **131**, 335]. The mesoporous microspherical (110 - 150 μm) synthetic carbon supplied by Mast Carbon Ltd., Guildford, UK was used as a catalyst support in the present study. In a typical Pt/C catalyst synthesis procedure, 10 g activated carbon sample was suspended in 120 mL distilled water. The calculated amount of hexachloroplatinic acid solution was added to the activated carbon slurry and stirred at 550 rpm for 7 days at 25 °C in nitrogen atmosphere. The aqueous sodium borohydride solution (25 mL) was added drop wise to the slurry and stirred for 6 h at 25 °C. After that the slurry was filtered and dried in vacuum at 35 °C for 16 h. The characteristic peaks of Pt at (111), (200) and (220) planes were observed at 2θ values of about 40.1, 46.3 and 68.2 degree, respectively (Fig. 1). The BET surface area of Pt/C was found to be 1491 $\text{m}^2 \text{g}^{-1}$.

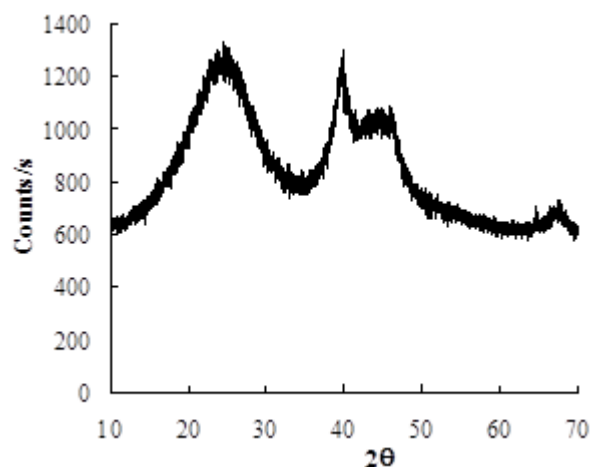


Fig. 1. P-XRD patterns of 3% Pt/C catalyst

Multichannel compact reactor and reaction procedure

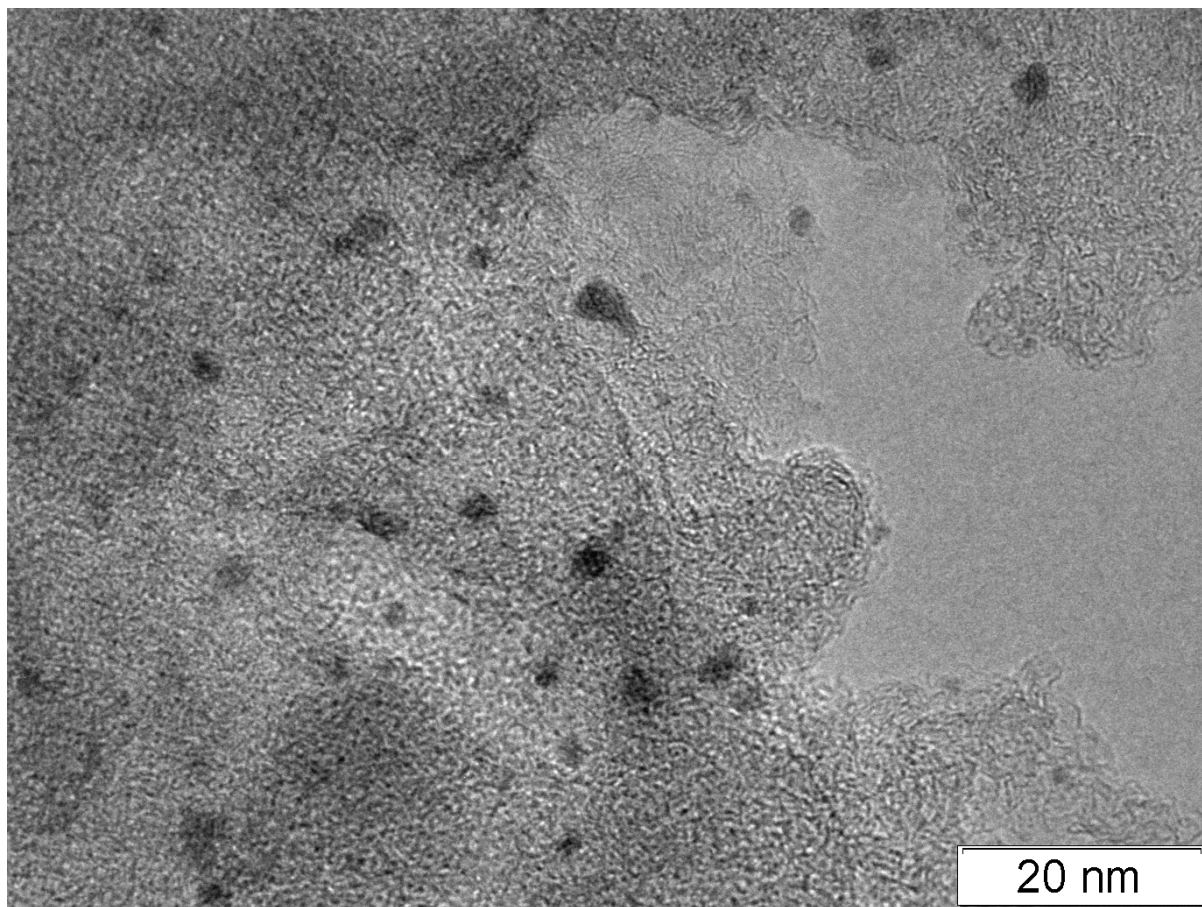
The catalytic reactions were performed in a structured multichannel reactor (316 stainless steel) which is suitable to work up to 75 bar pressure. The reaction channels in the reactor have a square cross-section of 2×2 mm, 3×3 mm, 5×5 mm and 12 cm length [P.K. Plucinski, D.V. Bavykin, S.T. Kolaczowski and A.A. Lapkin, *Ind. Eng. Chem. Res.* 2005, **44**, 9683]. The reactor also has a static mixer prior to the reaction channels for premixing and preheating the liquid and gas reactants before introducing into the reaction zone. The temperature of the reactor is controlled by circulating the heating fluid in micro-heat exchangers which were located underneath and above all the reaction channels (arranged in cross-flow with respect to reaction channels; Fig. 2). All reaction channels, therefore, have an even temperature field during operation.

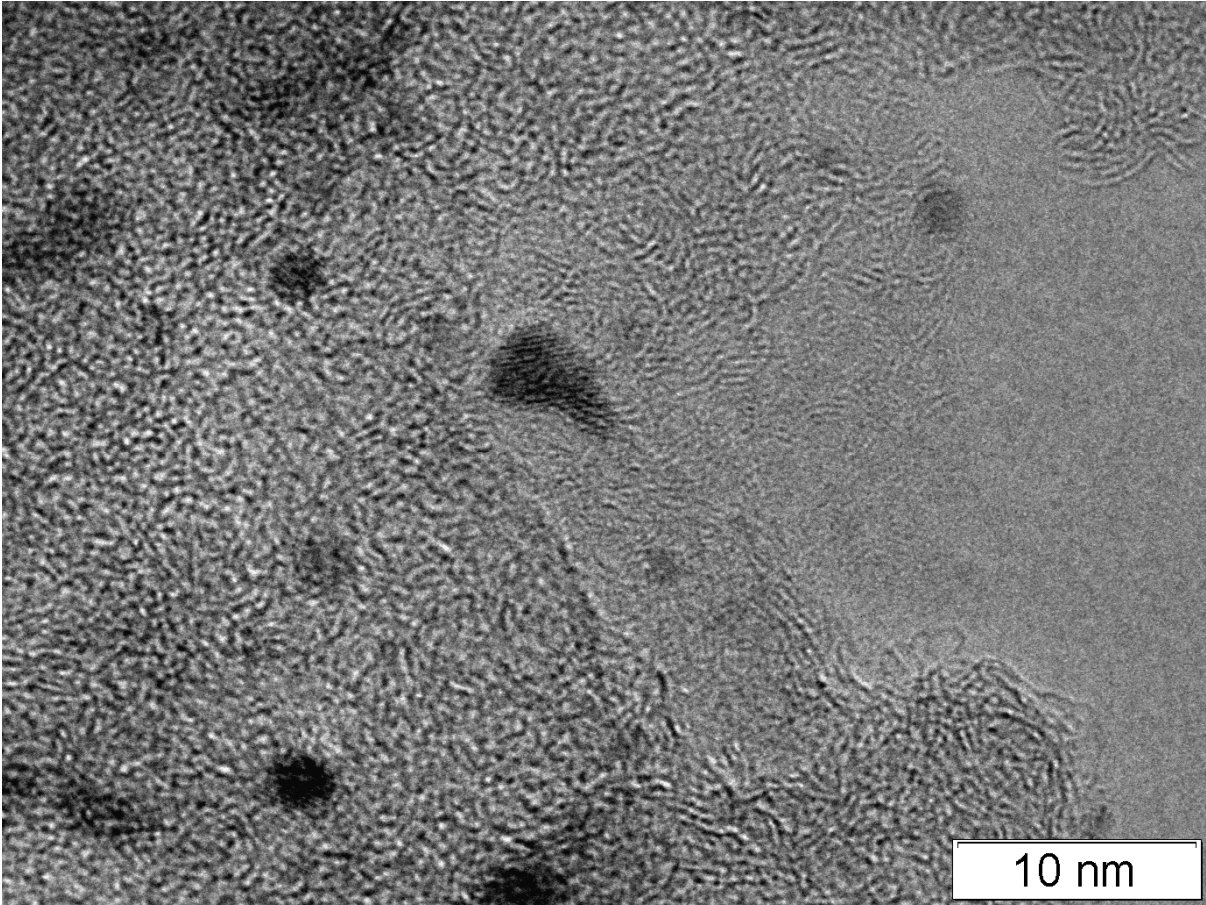
In a typical experimental run, liquid reactants (nitrile and primary amine) were premixed at desired concentration in the solvent and charged to the feed vessel. The liquid reactant mixture from feed vessel was fed into the reactor using HPLC pump (Kontron) at 0.1 mL/min flowrate. Hydrogen gas was supplied to the reactor using mass flow controller (Brooks) at 17 mL/min flowrate and 6 bar pressure. Reaction temperature (105 °C) of the reactor was controlled by circulating heat transfer fluid through the micro-heat exchangers using a recirculating bath (Haake). The pressure of the reactor was controlled by a back pressure regulator (Brooks) and pressure drop across the reactor was monitored using a differential pressure transducer (Bronkhorst). After completion of the reaction, the reaction mixture was collected from the bottom of second vessel via a high pressure valve.

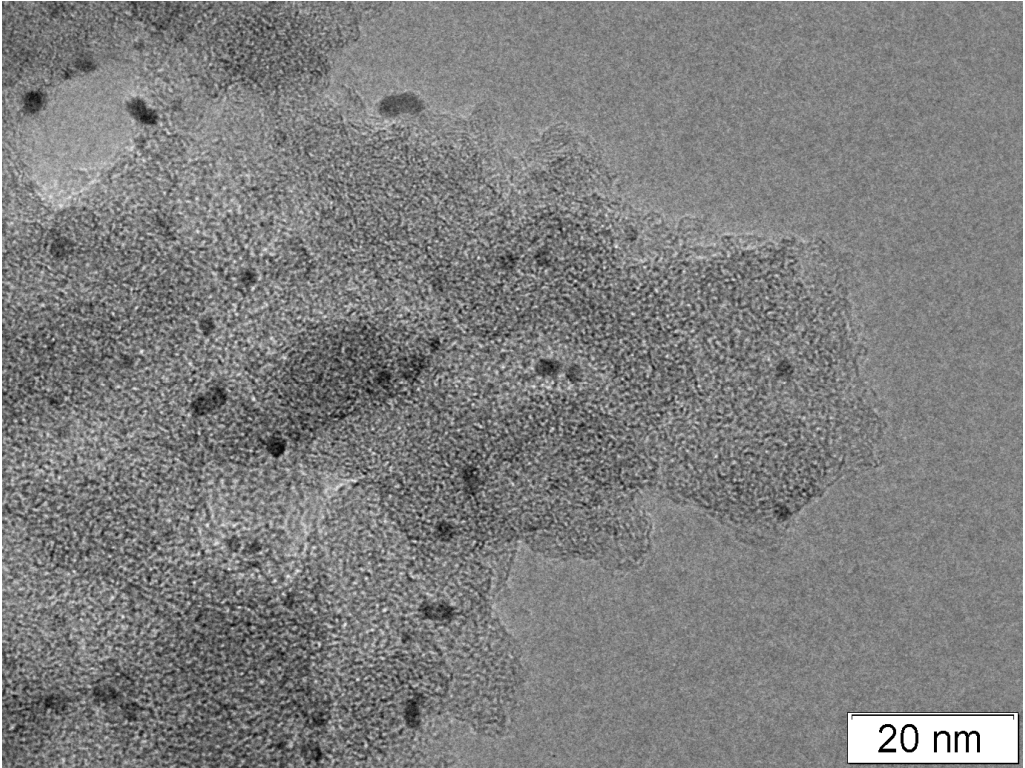
The analysis of reaction mixture was carried out by gas chromatography (Varian 3900) equipped with CP-Sil 5CB capillary column (15 m length and 0.25 mm diameter) and a flame ionization detector (FID). GC oven temperature was programmed from 100 to 120 °C at the rate of 8 °C/min and 120 to 280 °C at the rate of 25 °C/min. Helium was used as a carrier gas. Temperatures of injection port and FID were kept constant at 280 and 290 °C, respectively. Retention times of different compounds were determined by injecting pure compound under identical GC conditions. 1-dodecane was used as a GC internal standard. Furthermore, reaction mixture was also analyzed by GC-Mass to confirm the products. To ensure reproducibility of the reaction, repeated experiments were carried out under identical reaction conditions and results were found to be reproducible within ± 2.5% variation.

TEM images of Pt supported on carbon

TEM images were recorded on JEOL JEM-1200EX II Transmission Electron Microscope (JEOL, Tokyo, Japan) equipped with a Gatan Dualvision Digital Camera & Digital Micrograph 3.4 Software (Gatan, Oxon, UK).

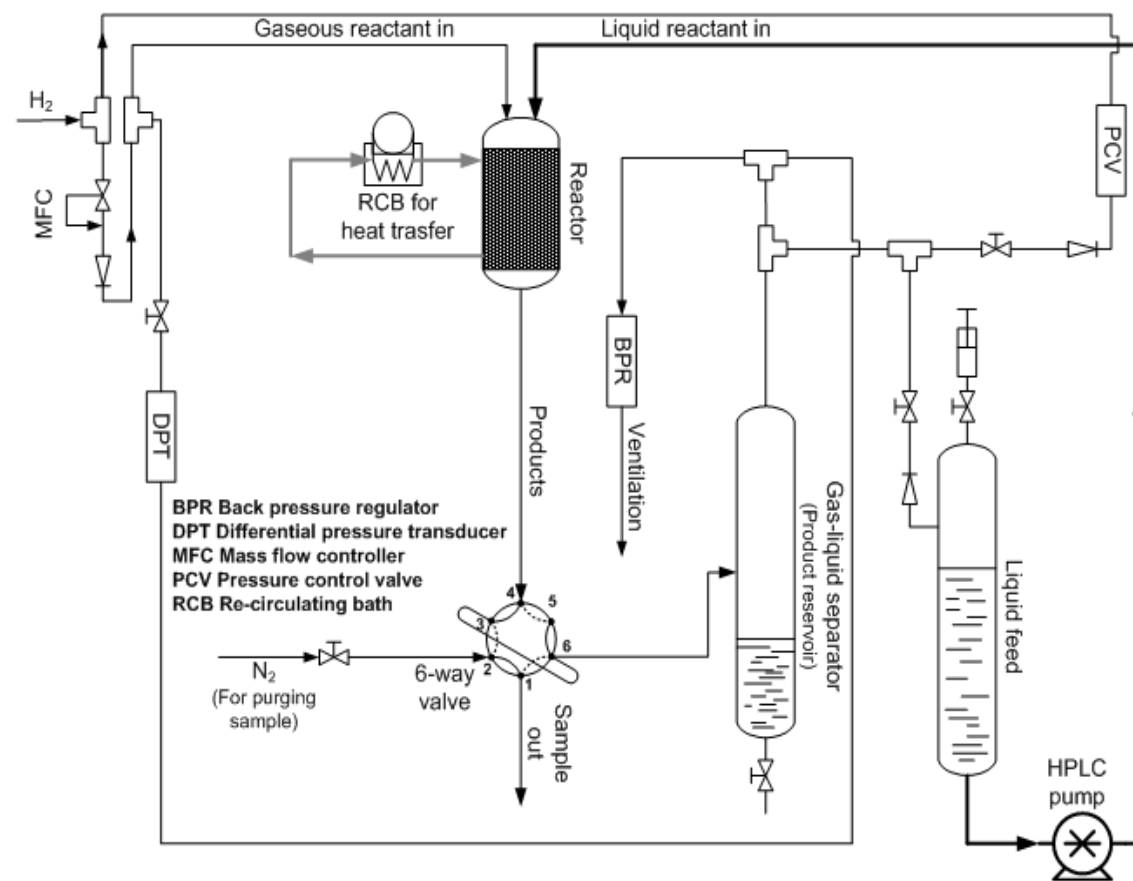
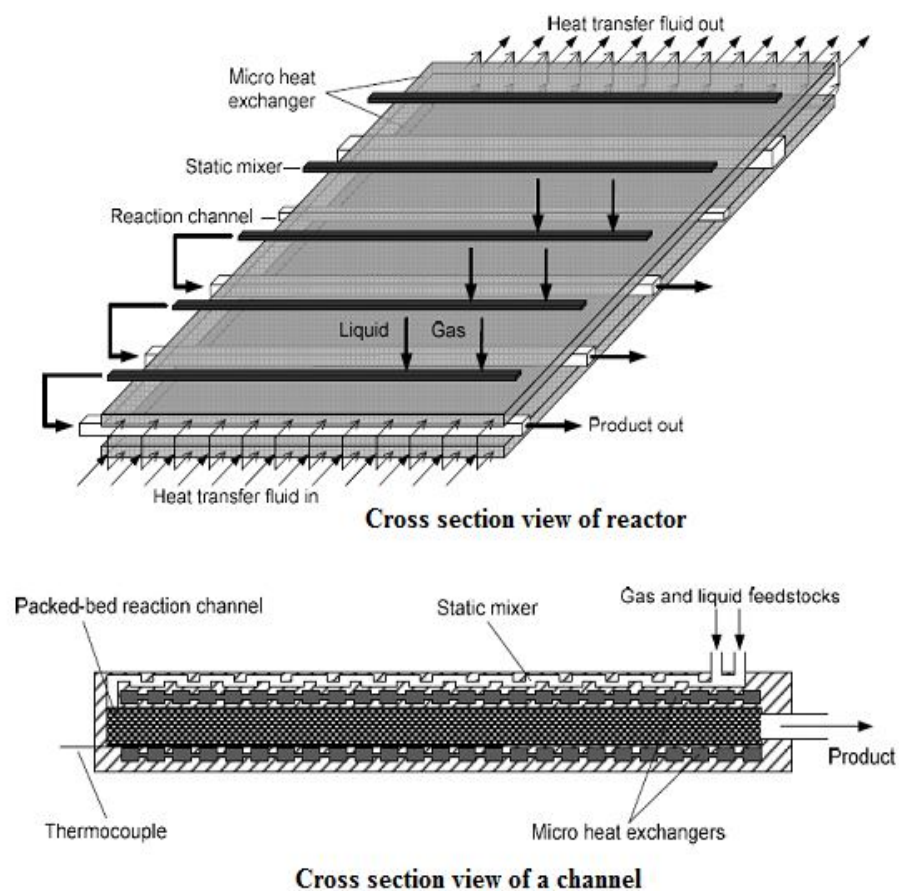






<i>Name*</i>	Surface area [m ² /g]	Size [μm]	Pore volume ml/g	Pt loading %	CO adsorption [ml/g Pt]	m ² /gPt
Q 297-41	624	340.2±28.4	0.41	3.5	42.3	184

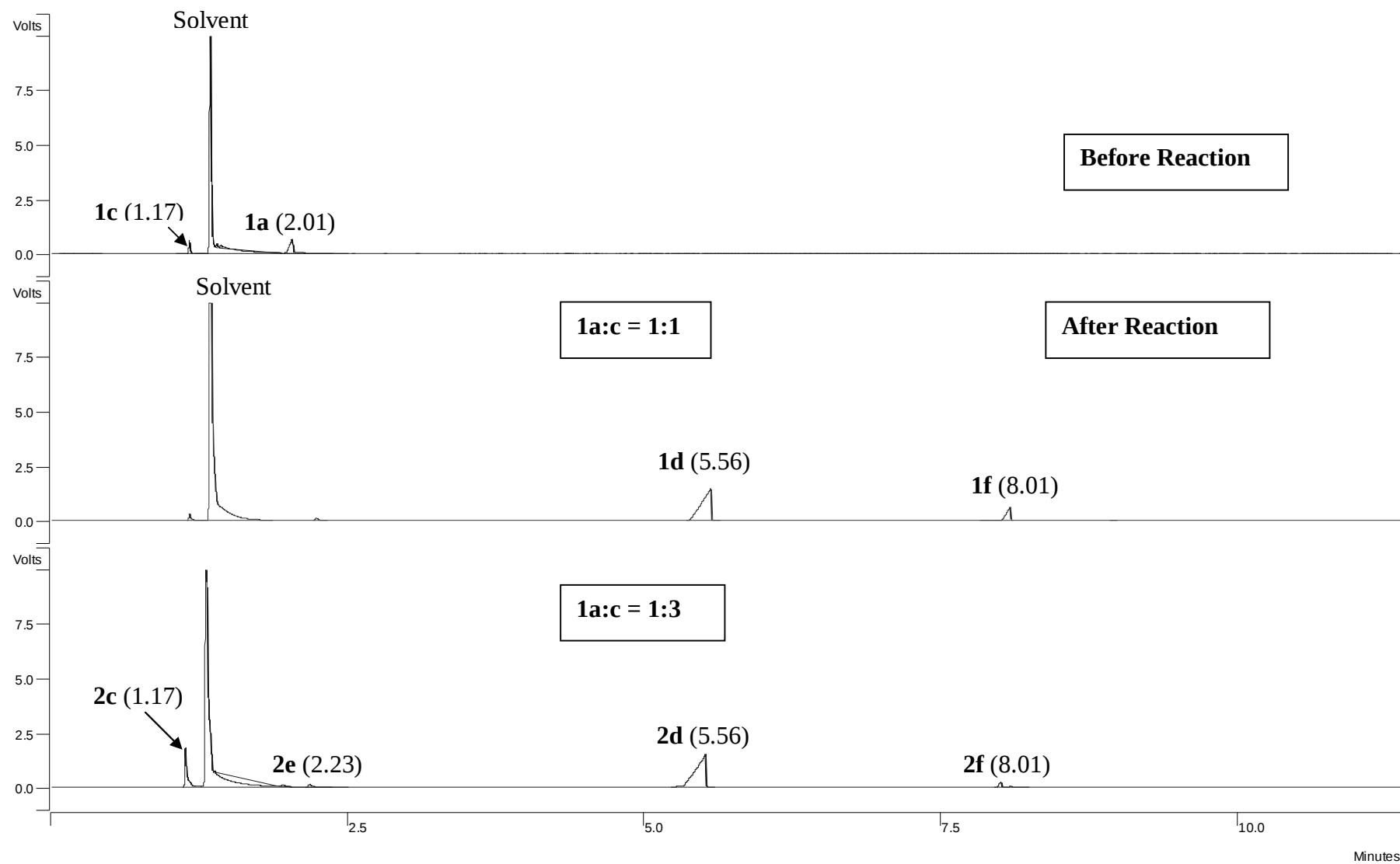
Size of Pt domains $d_{Pd} = 3.7 \pm 0.4$ nm.



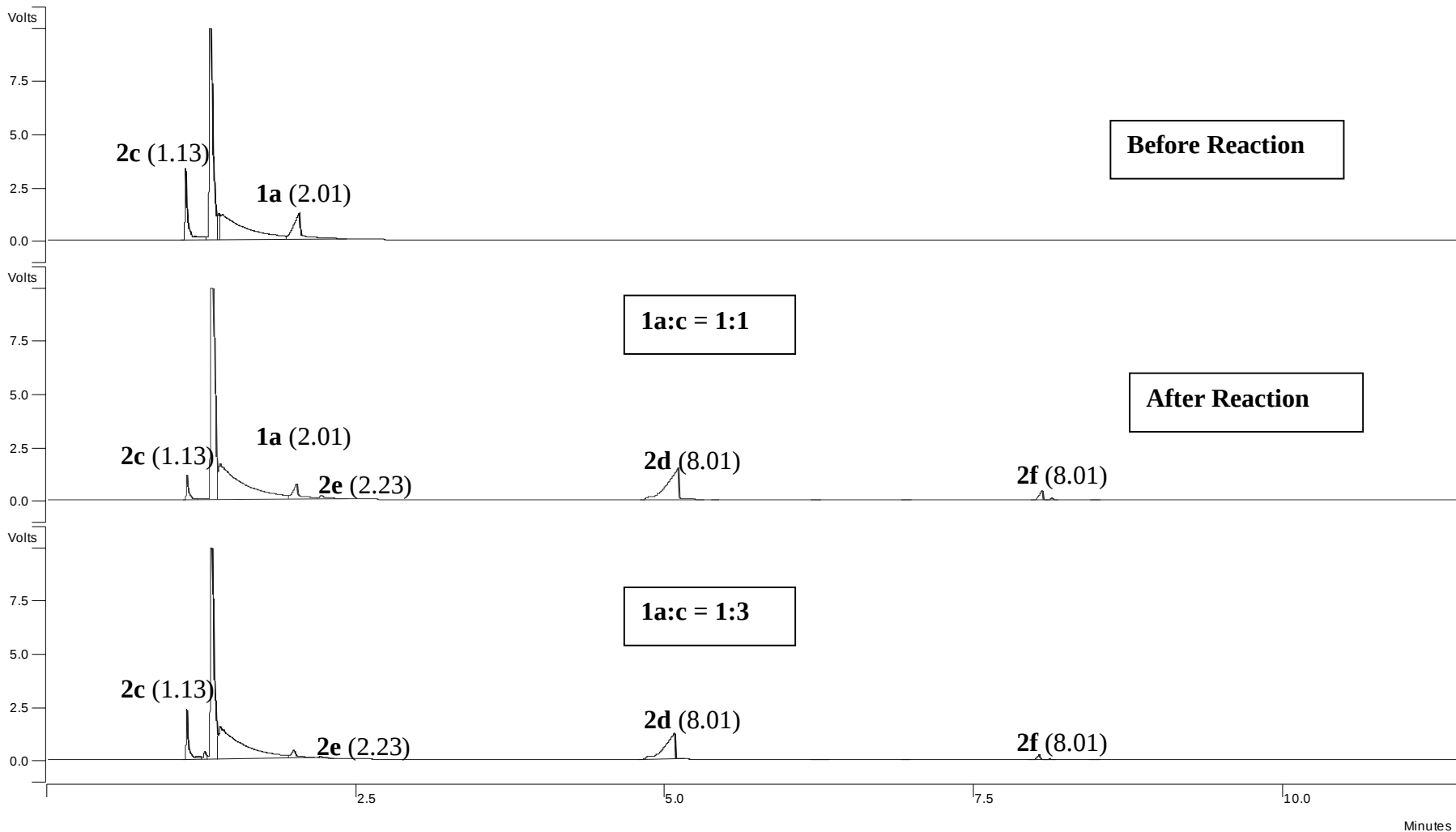
Experimental rig

Fig. 2. Experimental set-up

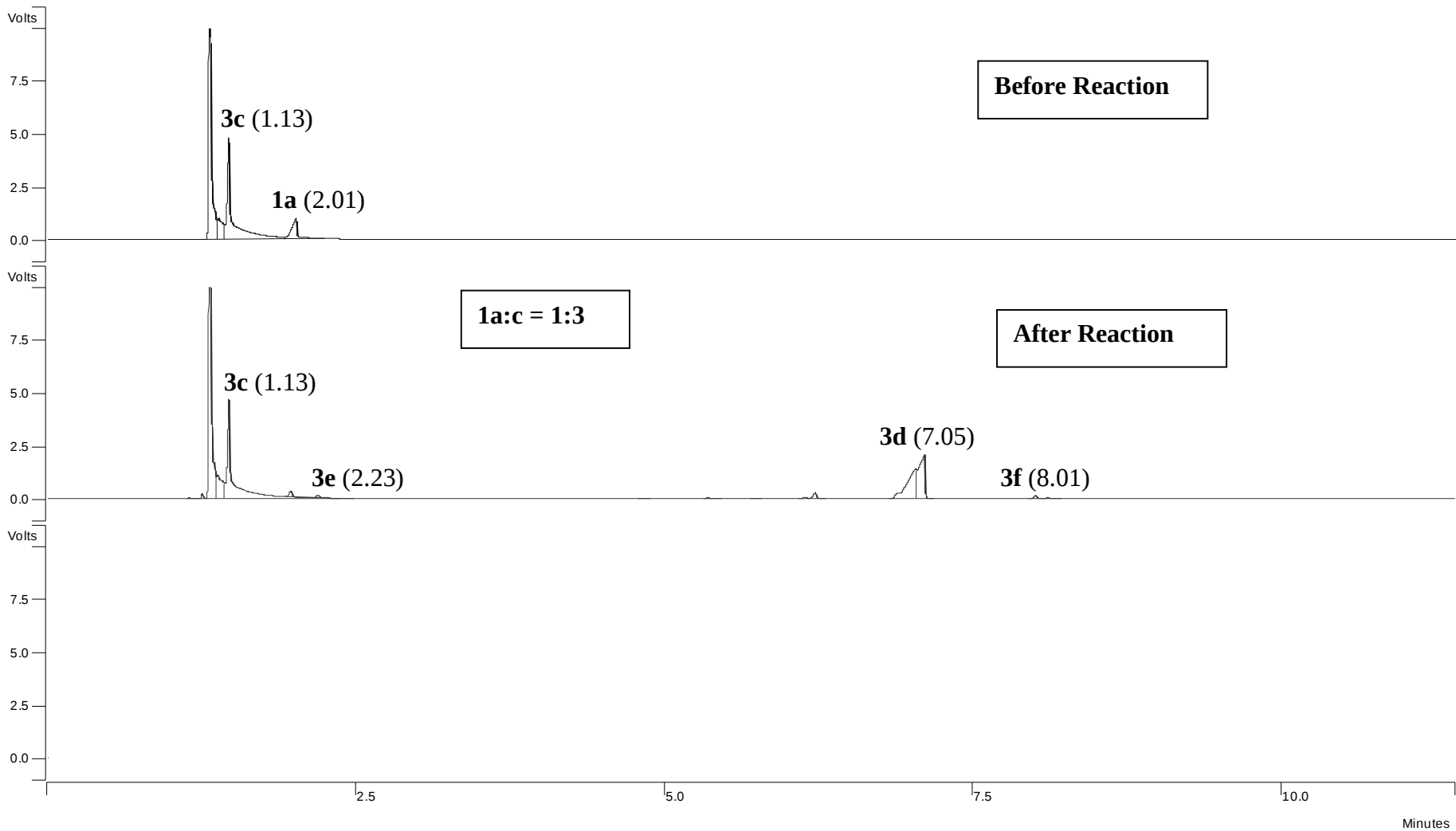
GC chromatograms for Entries 1 and 2



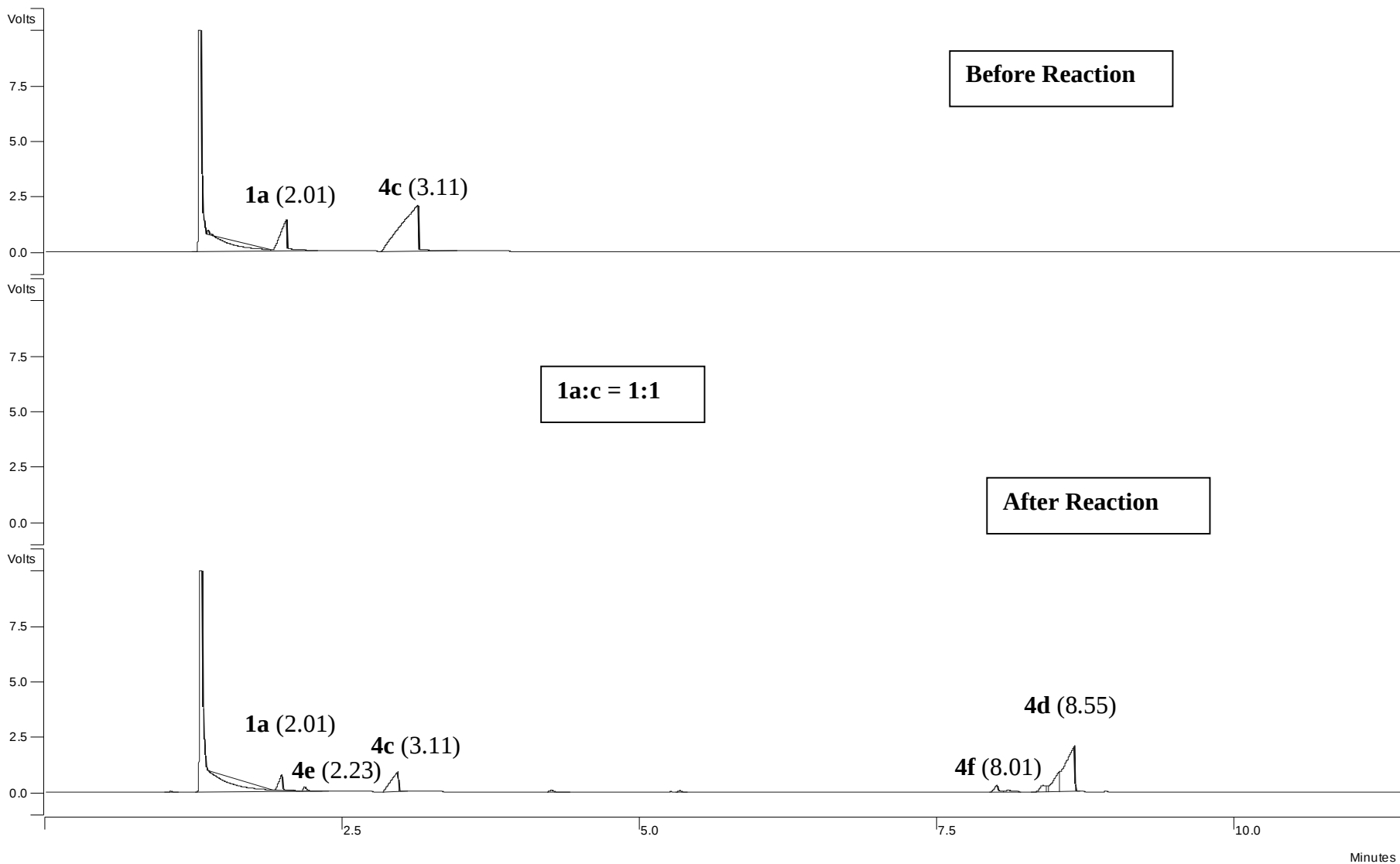
GC chromatograms for Entries 3 and 4



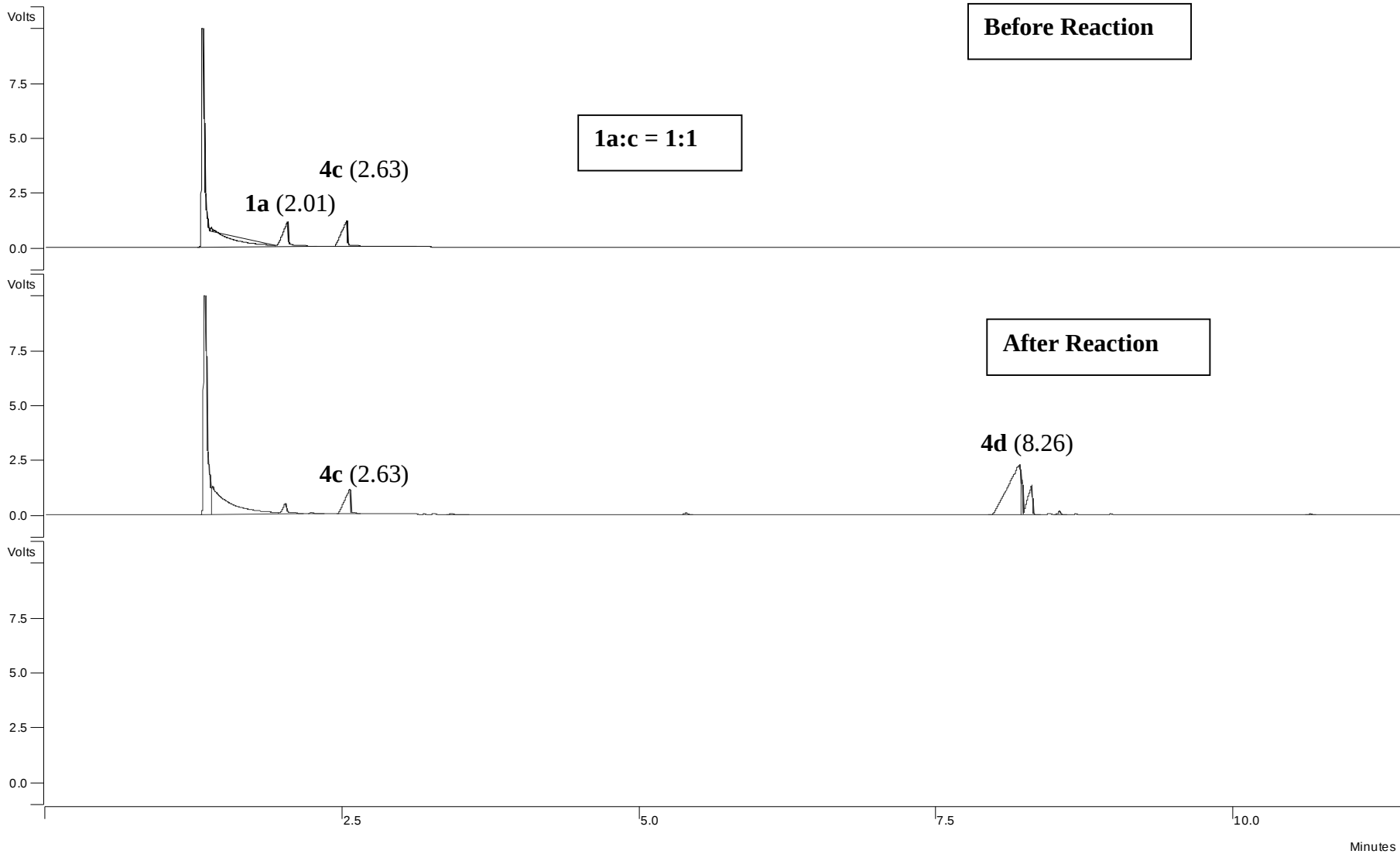
GC chromatograms for Entry 6



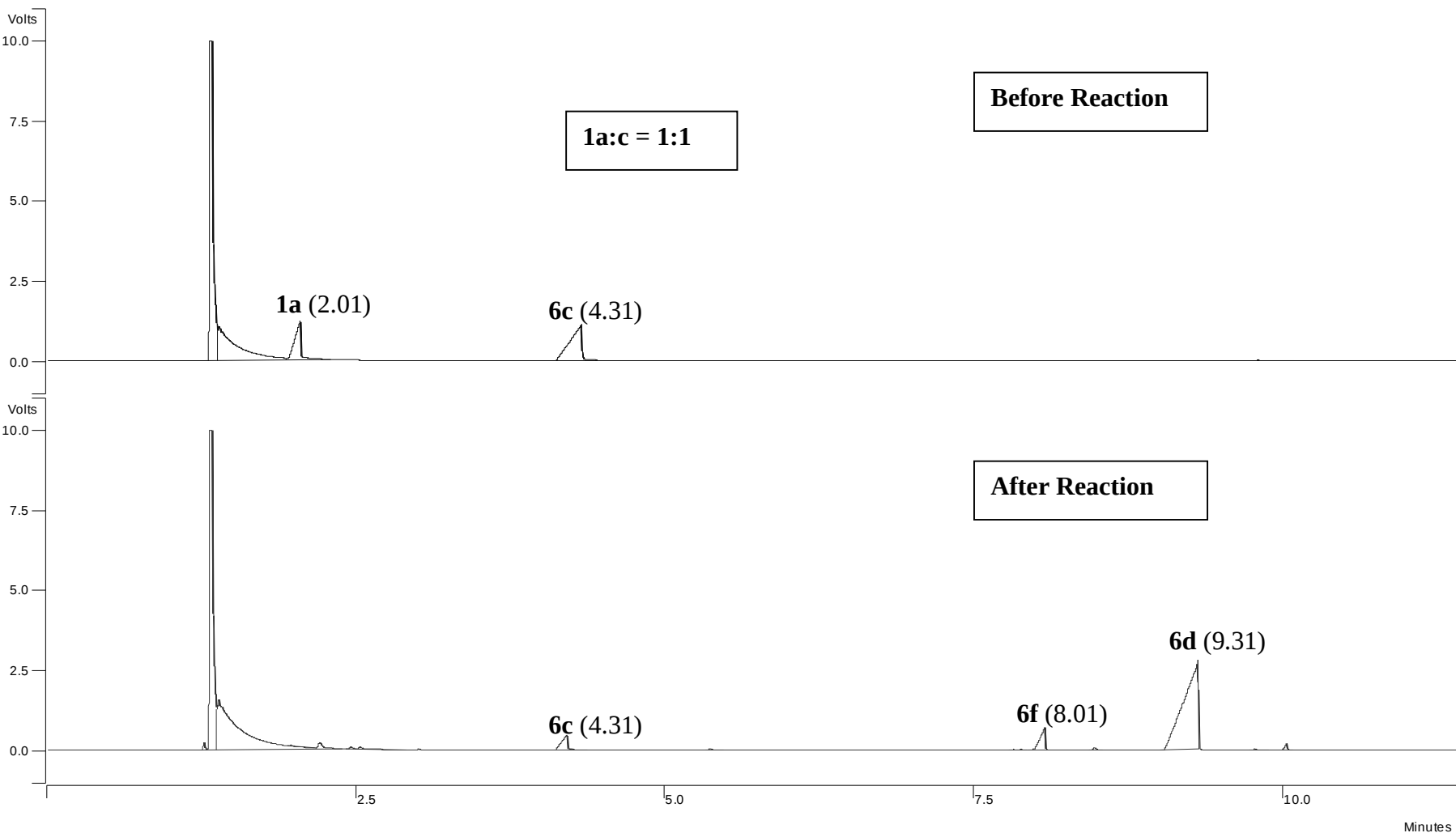
GC chromatograms for Entry 7



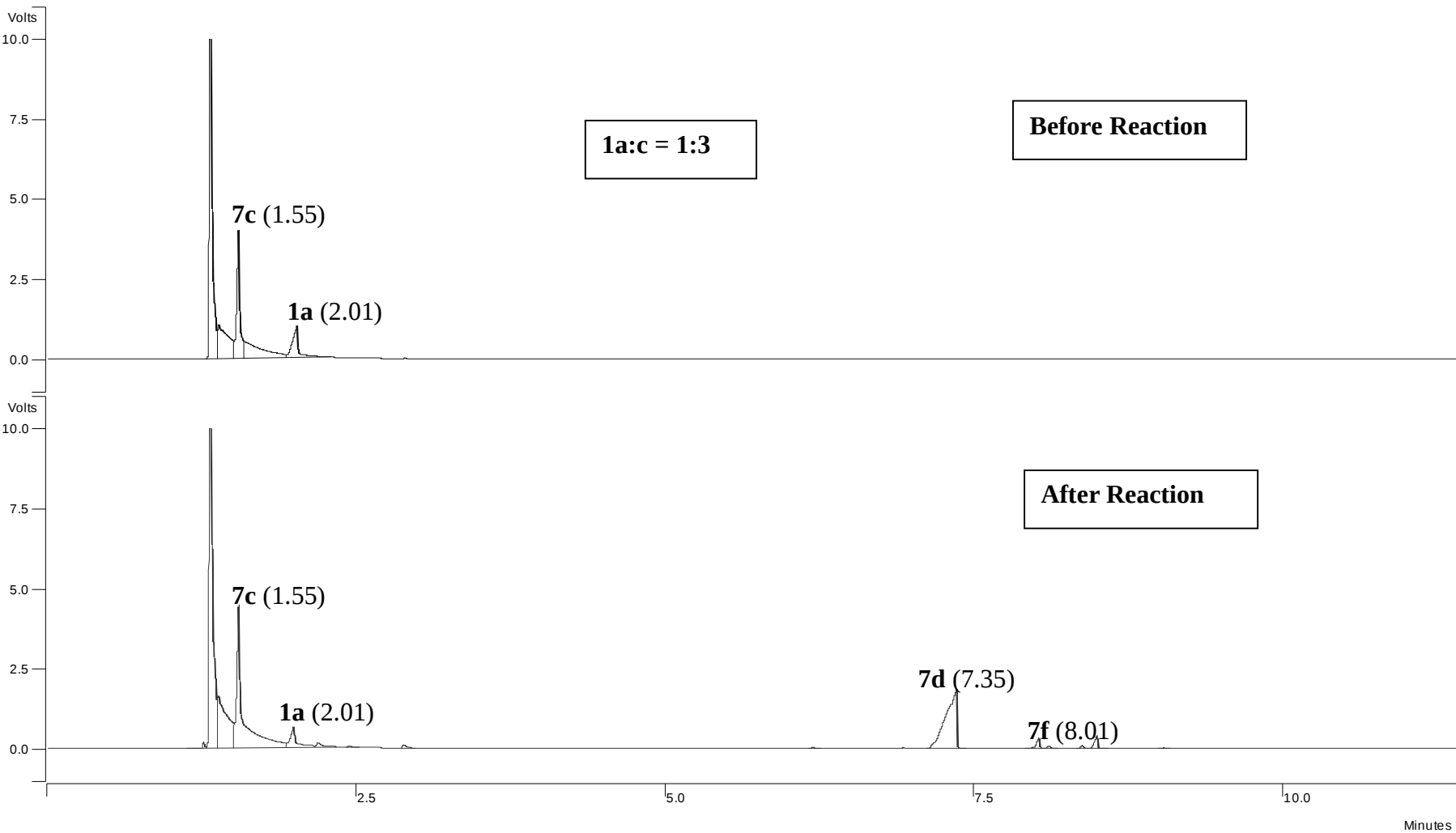
GC chromatograms for Entry 8

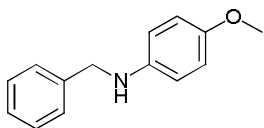


GC chromatograms for Entry 9

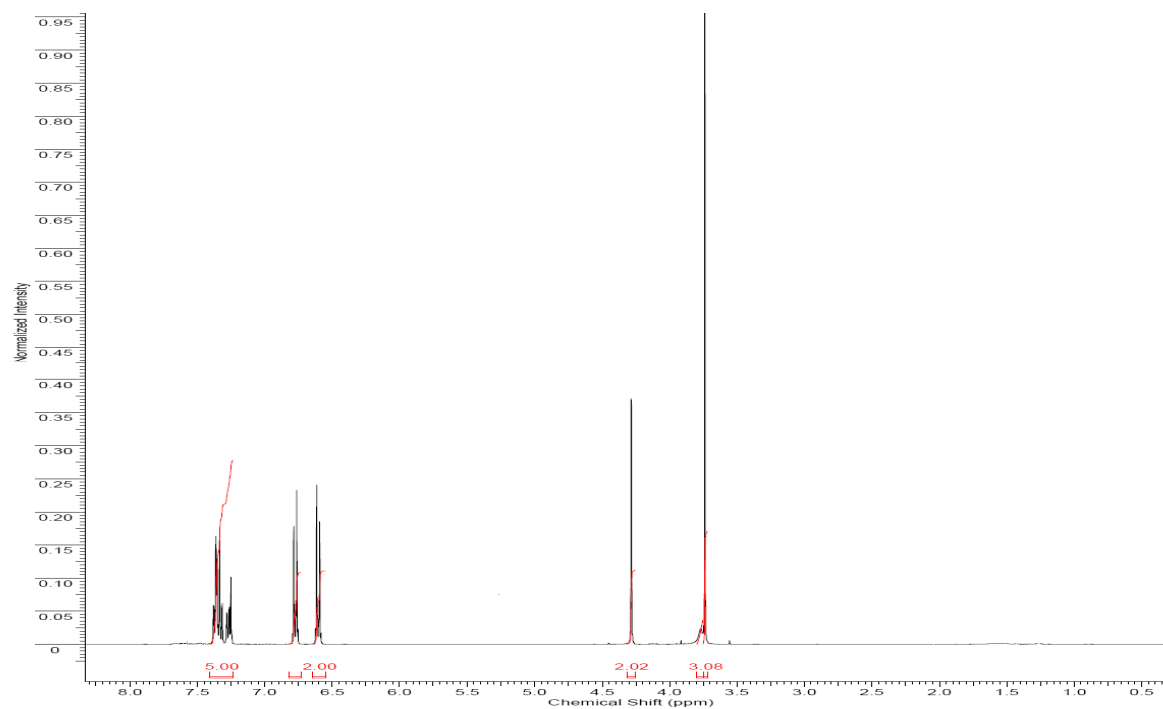


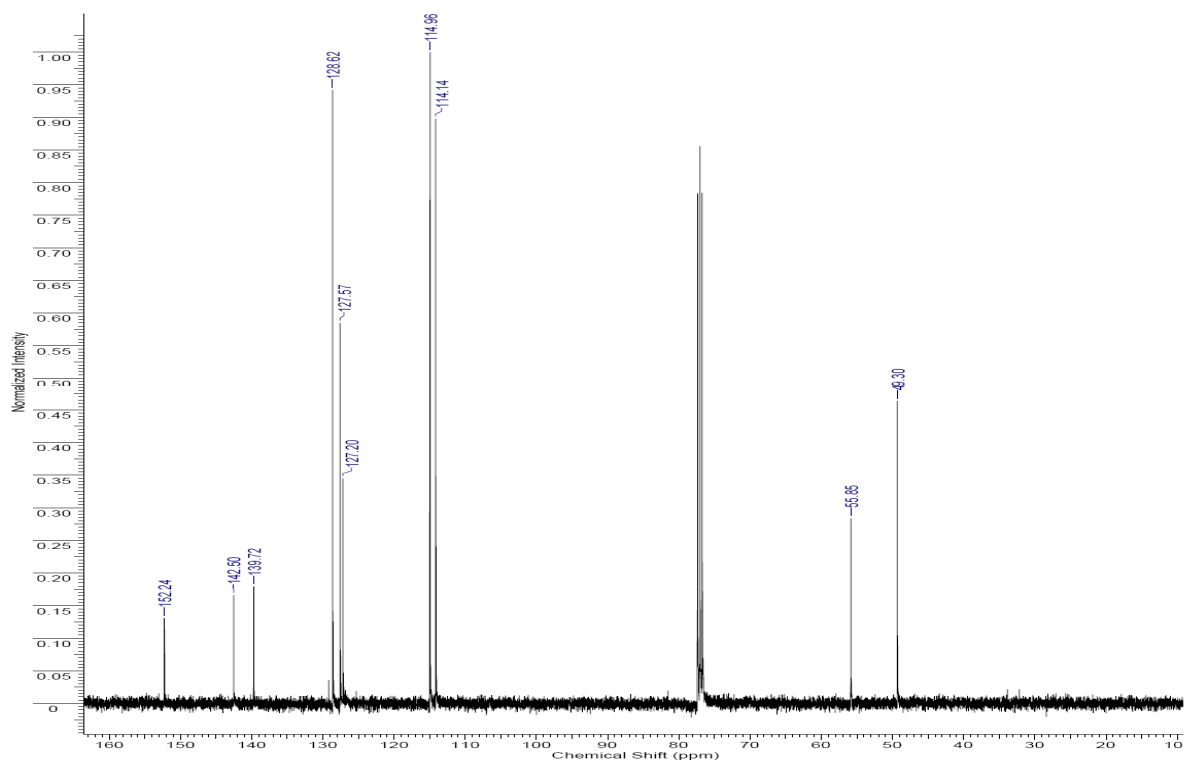
GC chromatograms for Entry 11

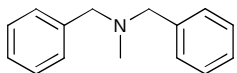




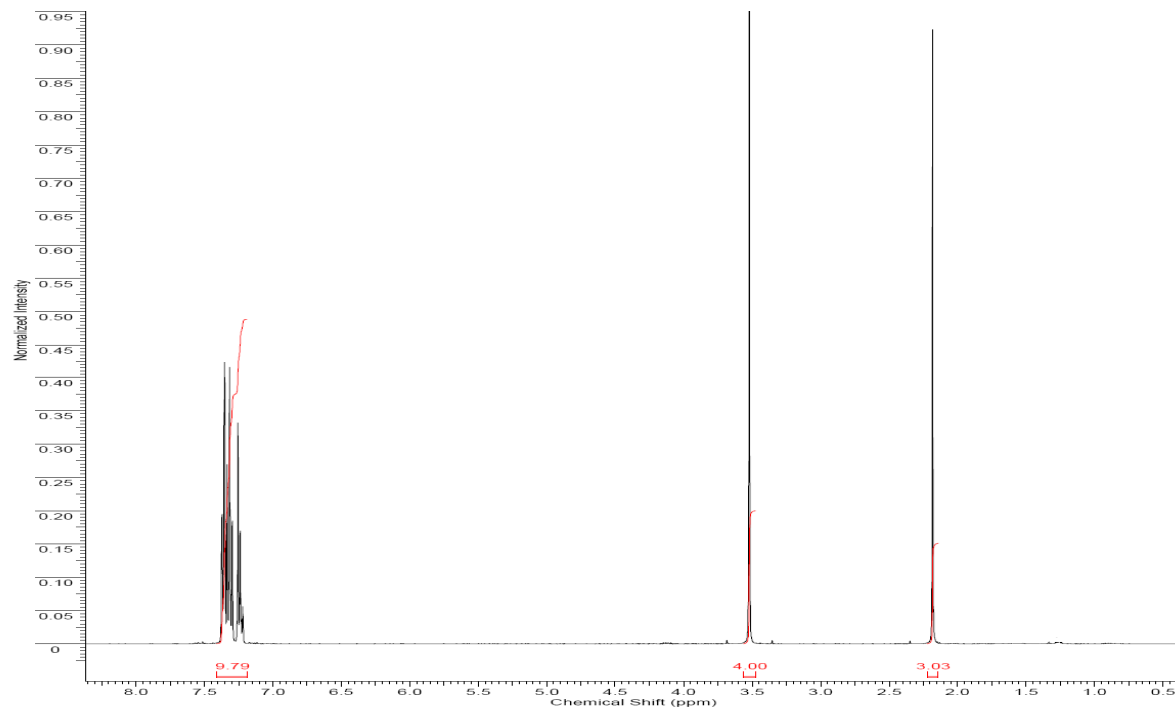
¹H NMR (400 MHz, CDCl₃): δ = 3.74 (3H, s, CH₃), 3.77 (1H, br s, NH), 6.60 (2H, d, J = 8.80 Hz, Aromatic), 6.78 (2H, d, J = 9.05 Hz, Aromatic), 7.24-7.4 (5H, m, Aromatic). ¹³C NMR (100 MHz, CDCl₃): δ = 43.90, 55.85, 114.14, 114.96, 127.20, 127.57, 128.62, 139.72, 142.50, 152.24. ESI-MS of [C₁₄H₁₅NO]⁺; theoretical m/z of [M+H]⁺ = 214.12, measured m/z of [M+H]⁺ = 214.19.¹

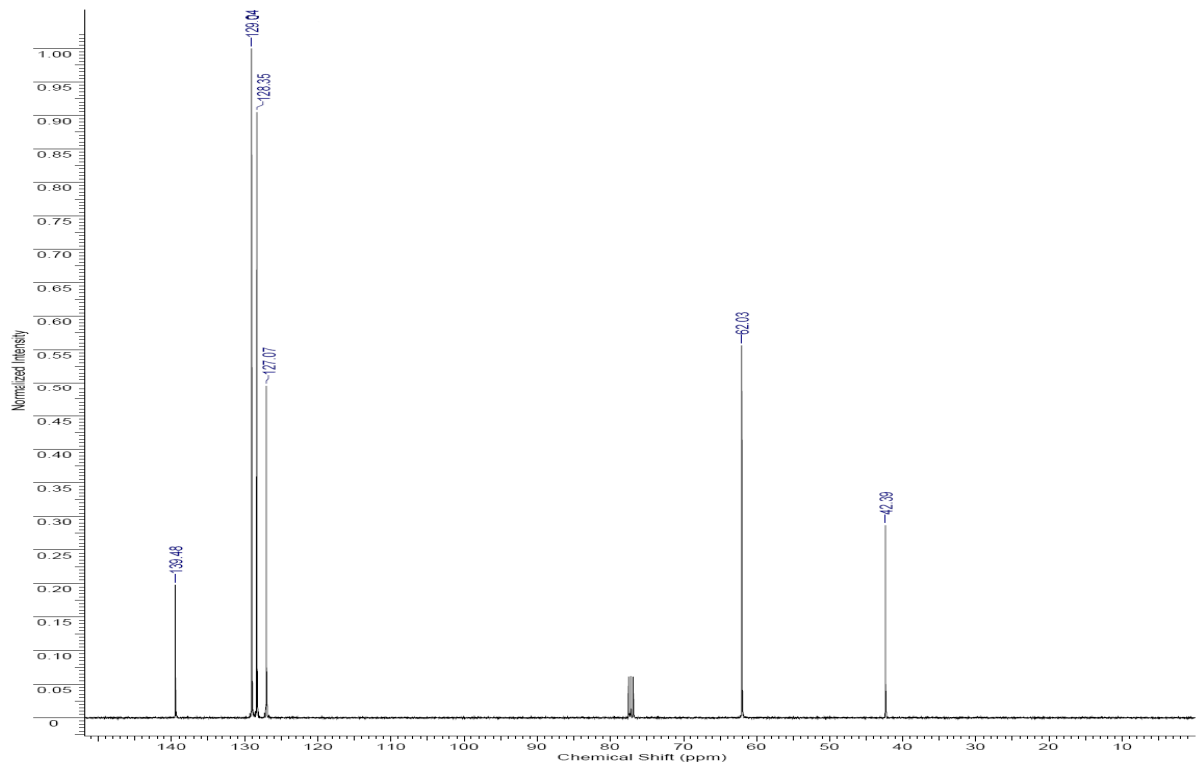


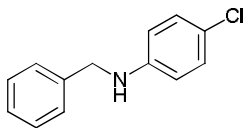




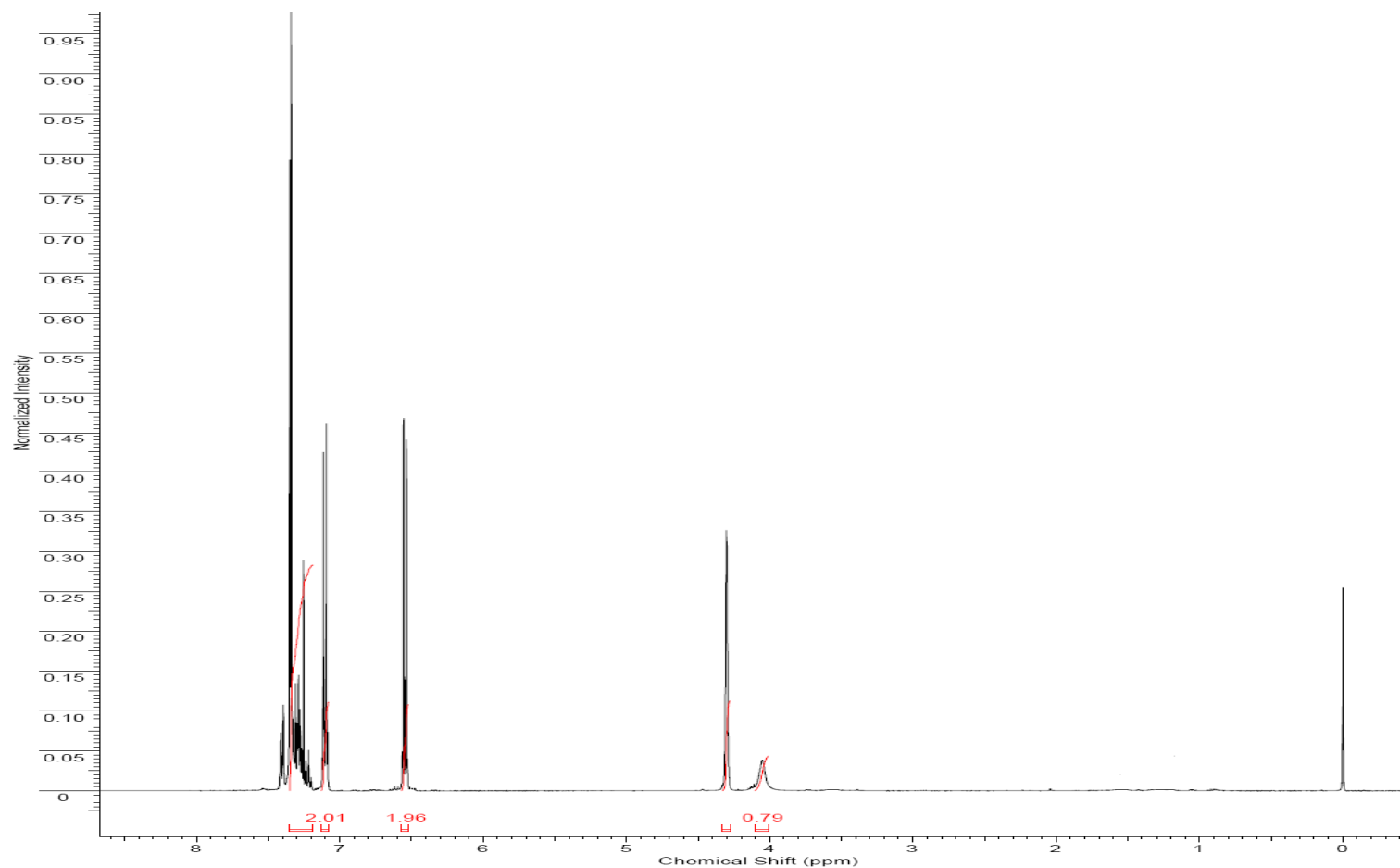
^1H NMR (400 MHz, CDCl_3) δ : 2.19 (3H, s, CH_3), 3.52 (4H, s, CH_2), 7.20-7.40 (10H, m, Aromatic). ^{13}C NMR (100 MHz, CDCl_3): δ = 42.39, 62.03, 127.07, 128.35, 129.04, 139.48. ESI-MS of $[\text{C}_{15}\text{H}_{17}\text{N}]^+$; theoretical m/z of $[\text{M}+\text{H}]^+ = 212.14$, measured m/z of $[\text{M}+\text{H}]^+ = 212.21$.²

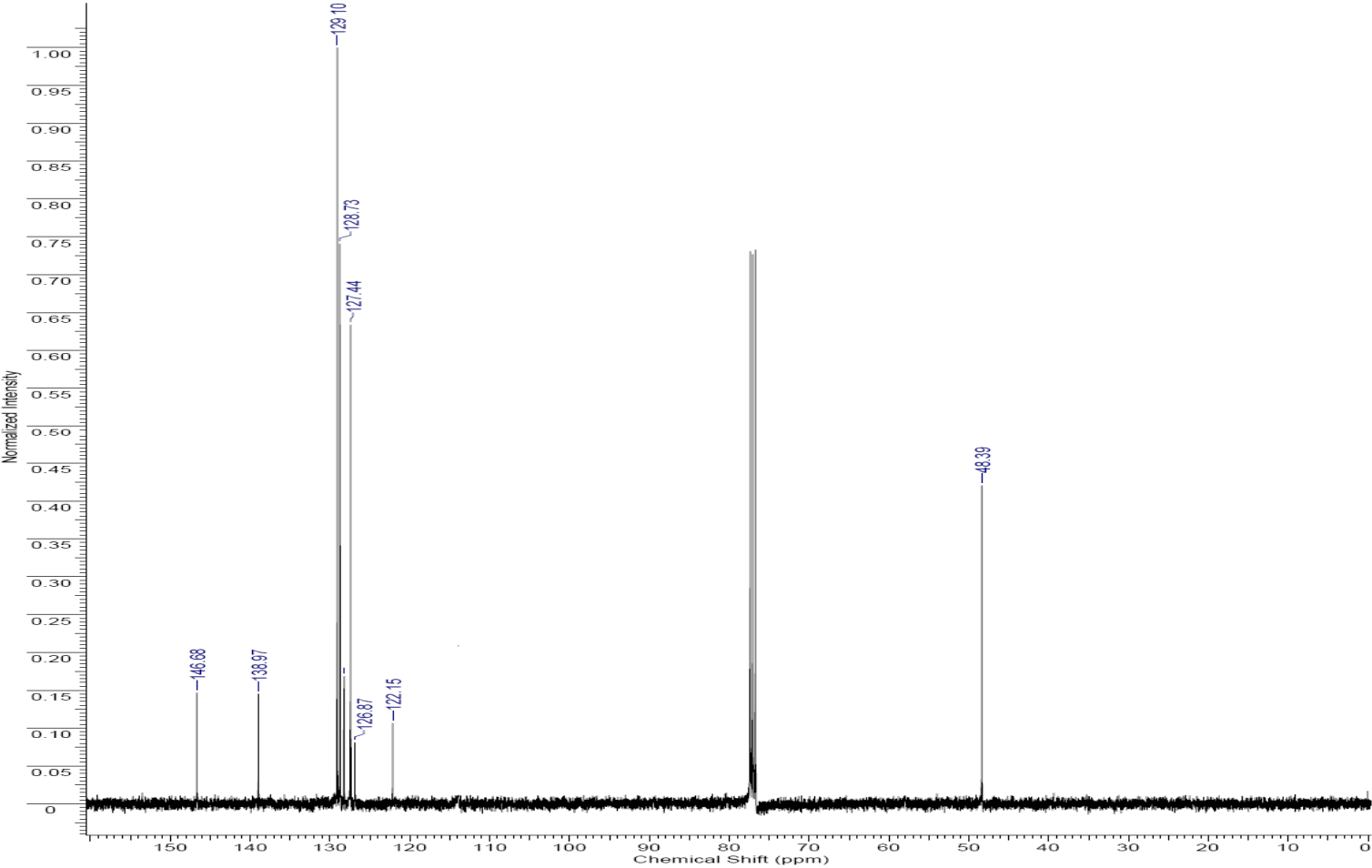


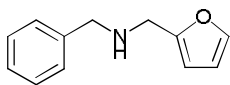




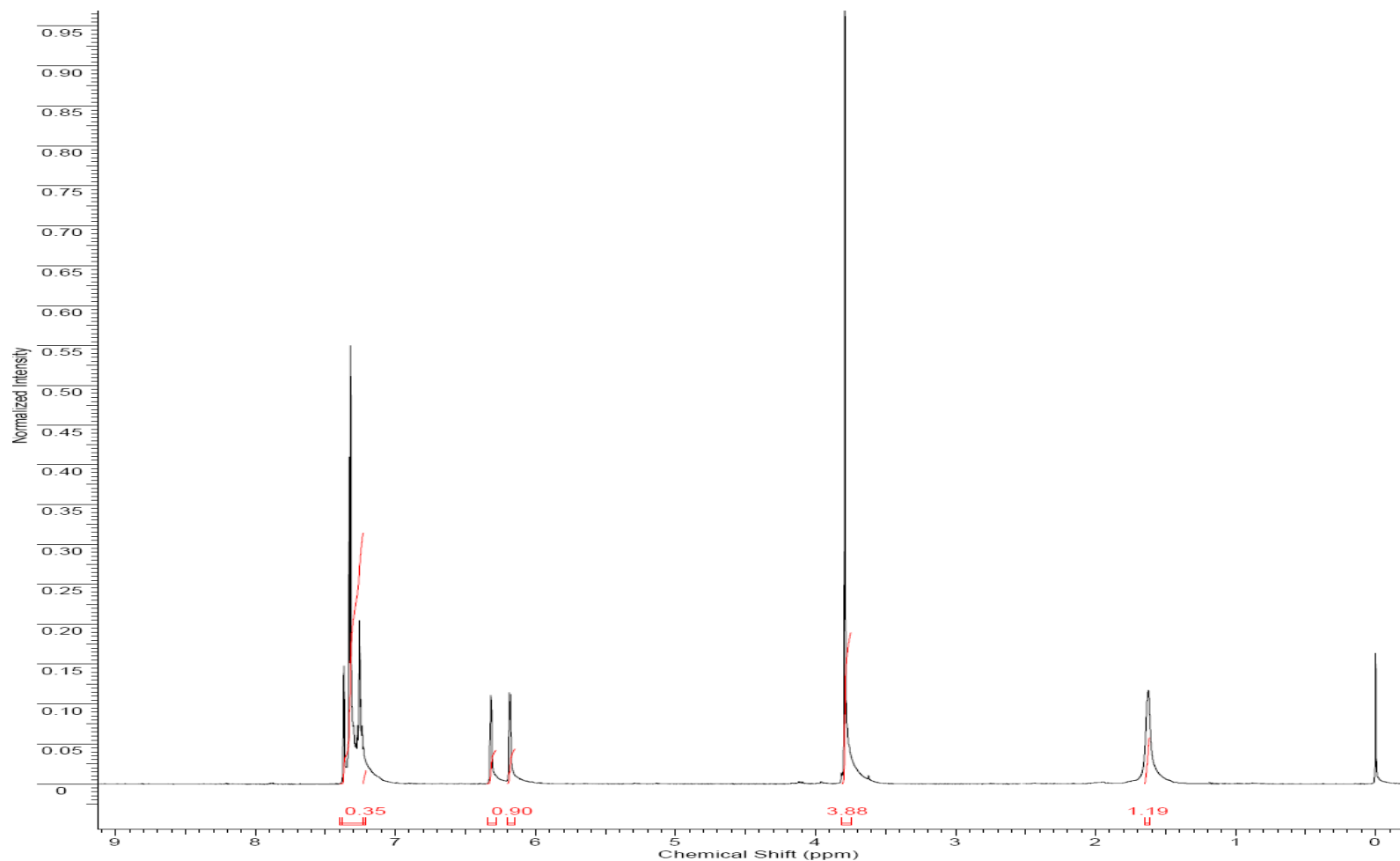
^1H NMR (400 MHz, CDCl_3): δ = 4.05 (1H, br s, NH), (2H, s, CH_2), 6.55 (2H, d, J = 8.80 Hz, Aromatic), 7.10 (2H, d, J = 8.80 Hz), 7.19-7.43 (5H, m, Aromatic). ^{13}C NMR (100 MHz, CDCl_3): δ = 48.39, 122.15, 126.87, 127.44, 128.73, 129.10, 138.97, 146.68. ESI-MS of $[\text{C}_{13}\text{H}_{12}\text{ClO}]^+$; theoretical m/z of $[\text{M}+\text{H}]^+ = 219.06$, measured m/z of $[\text{M}+\text{H}]^+ = 219.08$.³

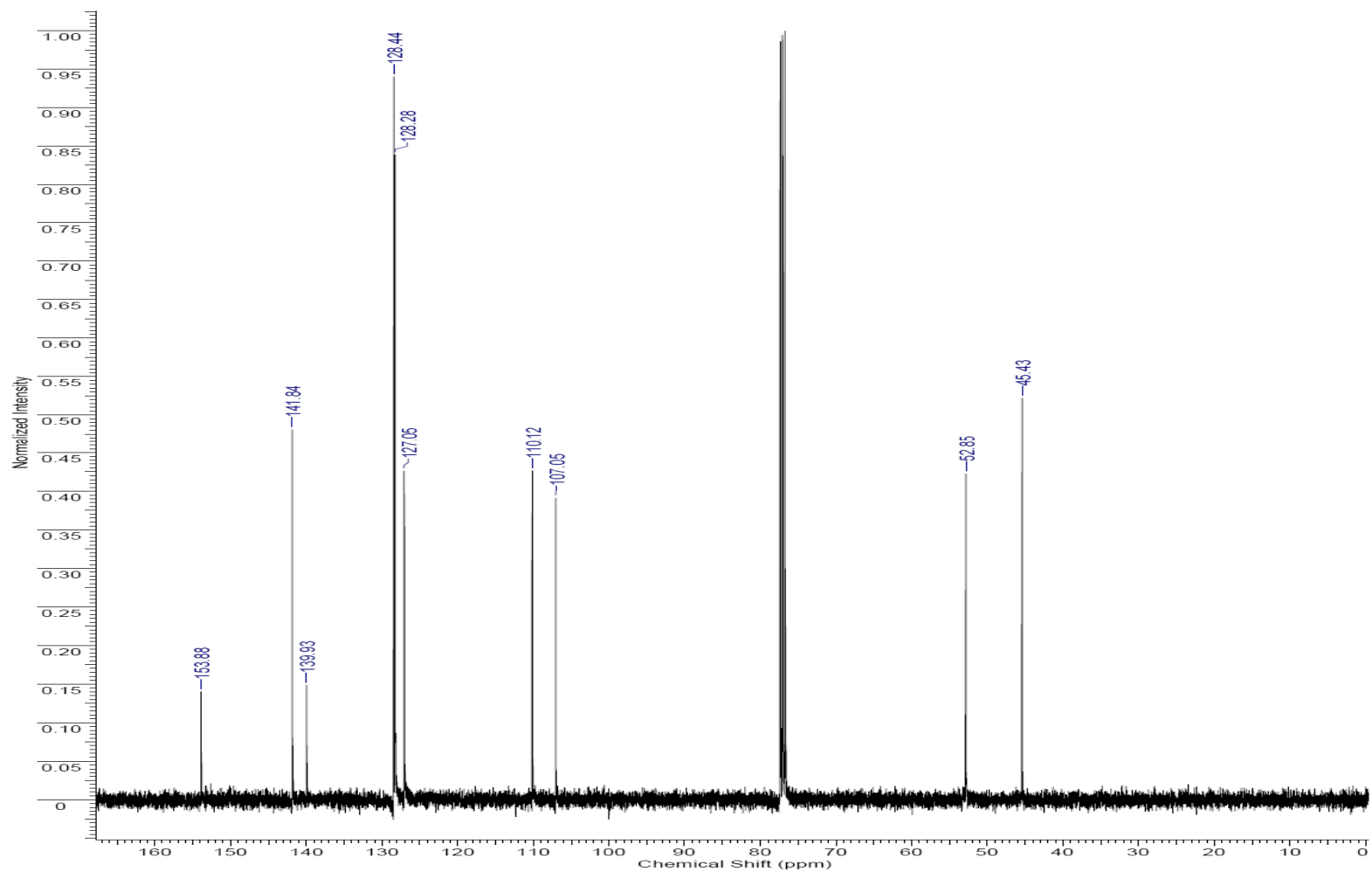


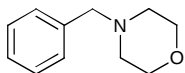




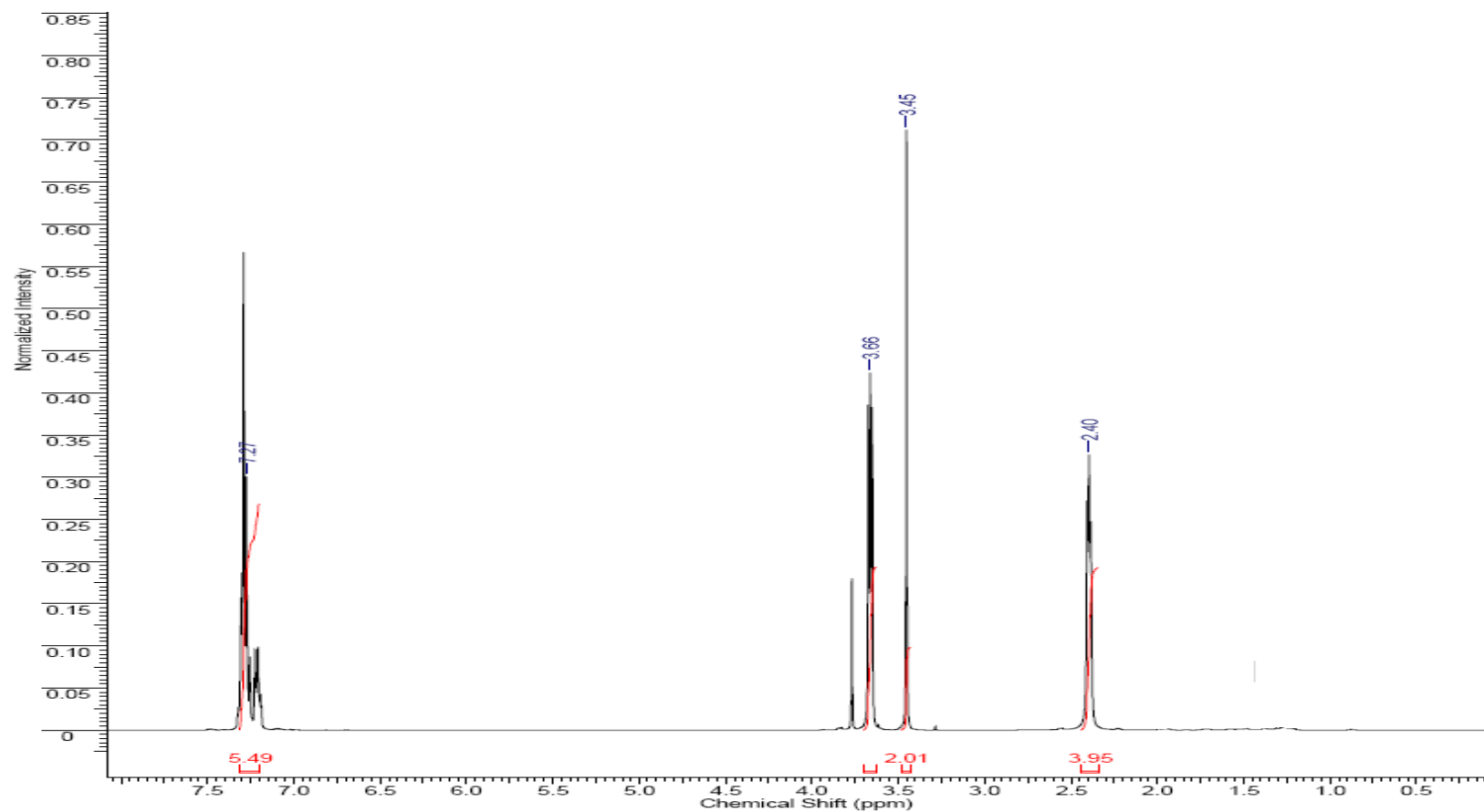
^1H NMR (400 MHz, CDCl_3): δ = 1.63 (1H, br s, NH), 3.79 (4H, s, CH_2), 6.18 (1H, d, J = 3.18 Hz, CH), 6.32 (1H, dd, J = 3.16, 1.92 Hz, CH), 7.22-7.38 (6H, m, Aromatic). ^{13}C NMR (100 MHz, CDCl_3): δ = 45.43, 52.85, 107.05, 110.12, 127.05, 128.28, 128.44, 139.93, 141.84, 153.88. ESI-MS of $[\text{C}_{12}\text{H}_{13}\text{NO}]^+$; theoretical m/z of $[\text{M}+\text{H}]^+ = 188.10$, measured m/z of $[\text{M}+\text{H}]^+ = 188.12$.⁴

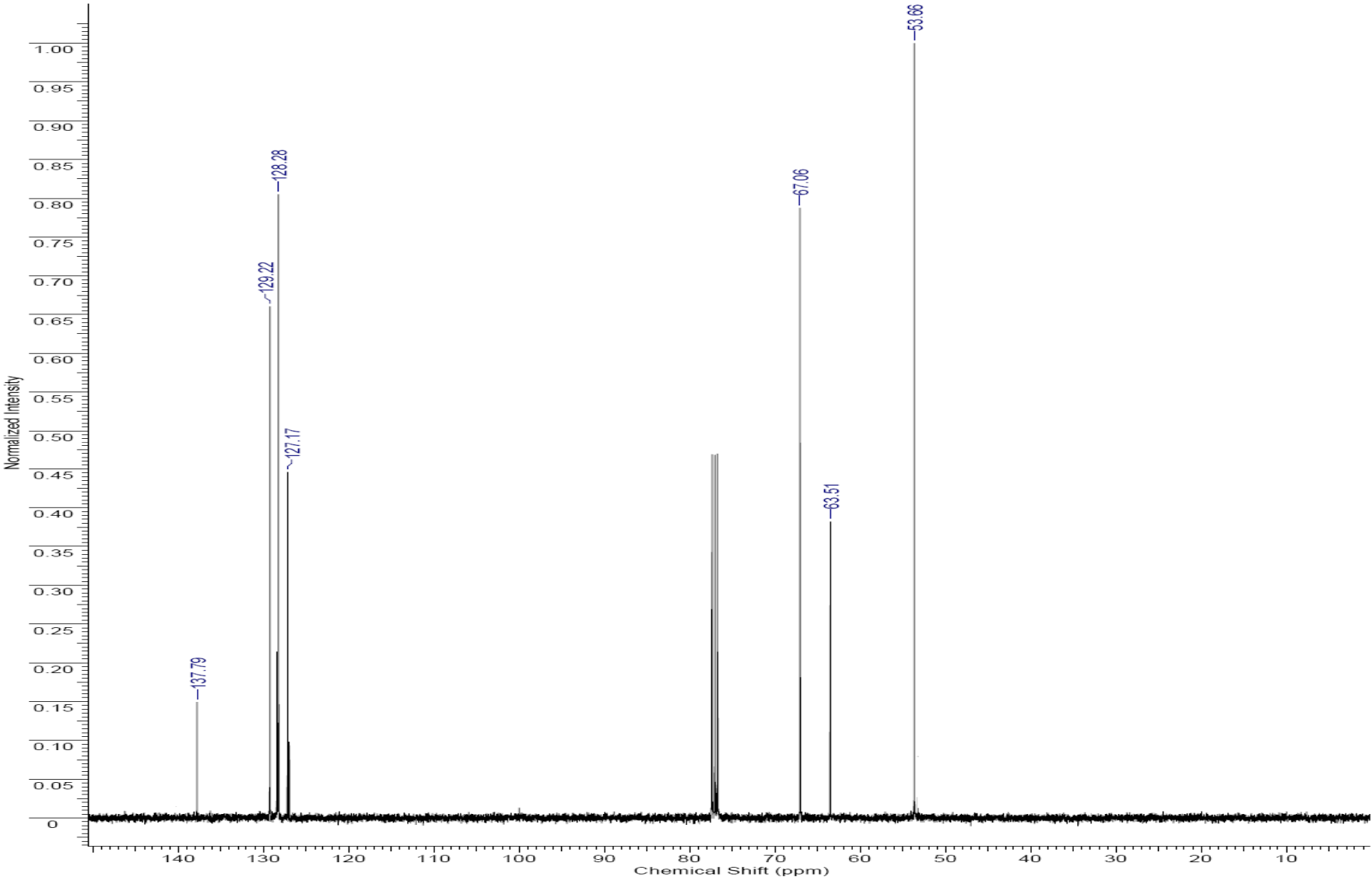


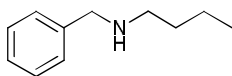




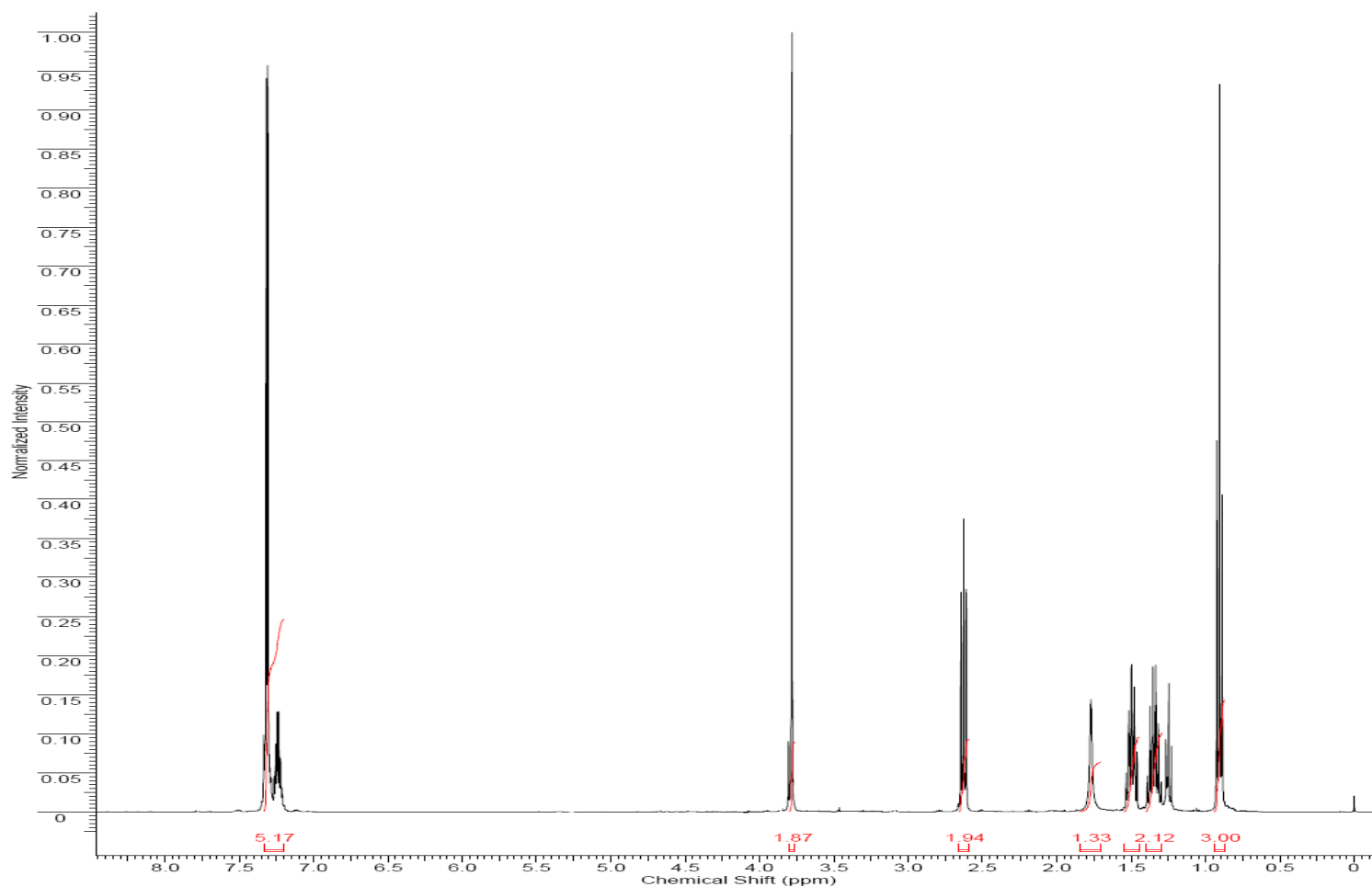
^1H NMR (400 MHz, CDCl_3): δ = 2.36-2.45 (4H, m, CH_2), 3.45 (2H, s, CH_2), 3.63-3.70 (4H, m, CH_2), 3.77 (1H, br s, NH), 7.18-7.33 (5H, m, Aromatic). ^{13}C NMR (100 MHz, CDCl_3): δ = 53.66, 63.51, 67.06, 127.17, 128.28, 129.22, 137.79. ESI-MS of $[\text{C}_{11}\text{H}_{15}\text{NO}]^+$; theoretical m/z of $[\text{M}+\text{H}]^+ = 178.12$, measured m/z of $[\text{M}+\text{H}]^+ = 178.20$.⁵

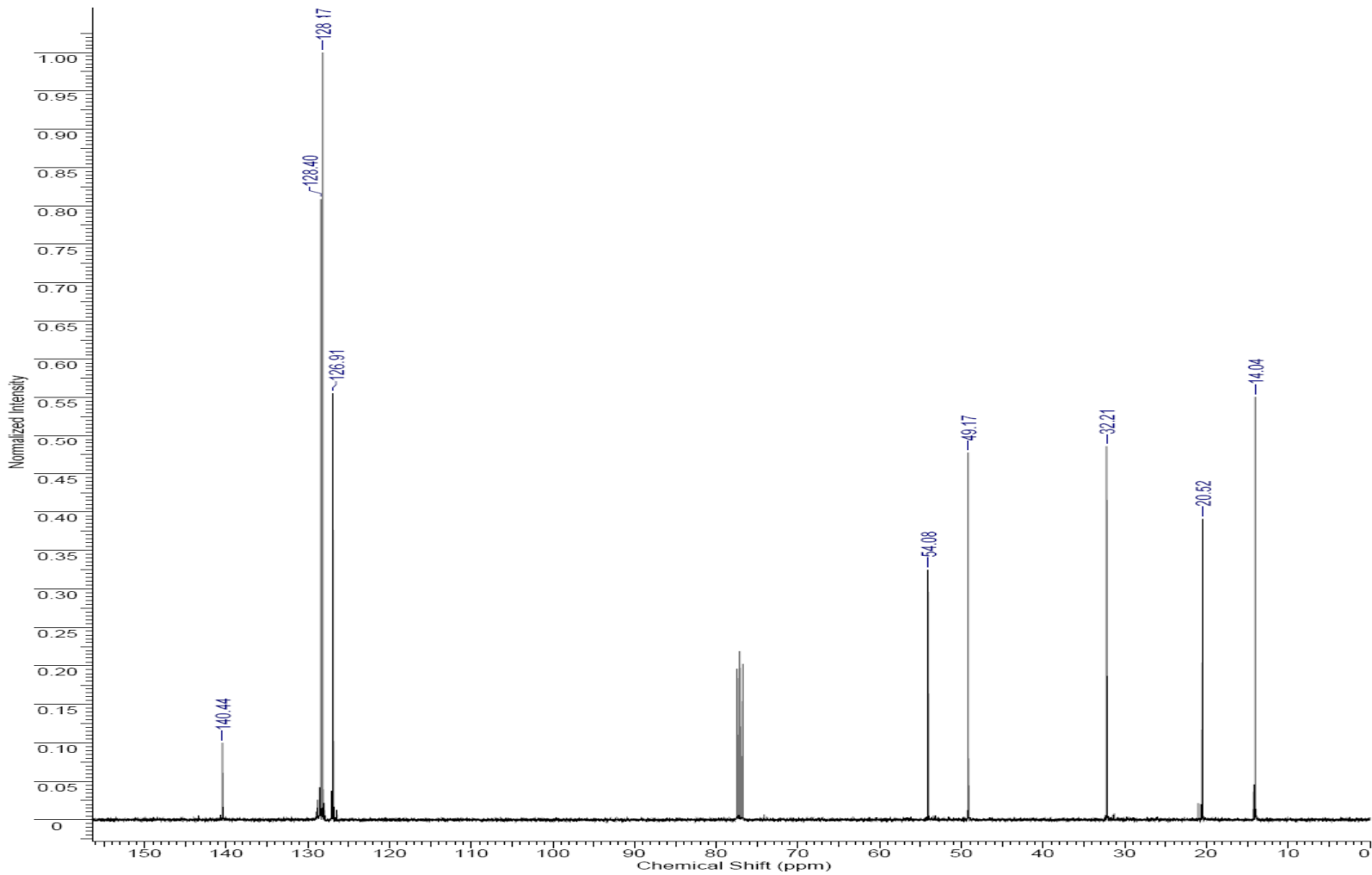


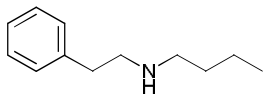




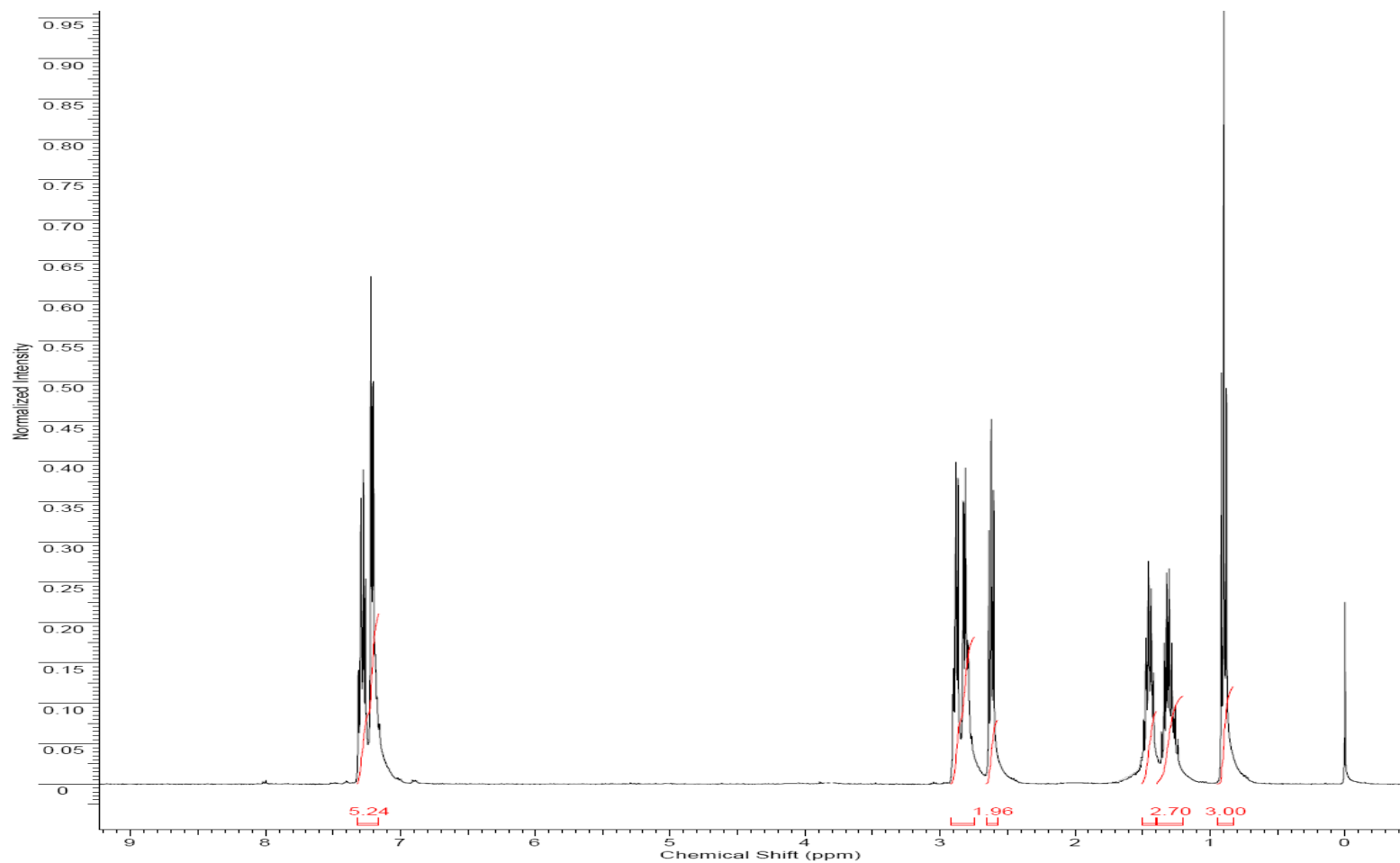
^1H NMR (400 MHz, CDCl_3): δ = 7.12-7.51 (m, 5 H), 3.82 (s, 2 H), 2.67 (t, J = 7.2 Hz, 2 H), 1.54 (q, J = 7.4 Hz, 2 H), 1.38 (dq, J = 14.9, 7.3 Hz, 2 H), 0.94 (t, J = 7.3 Hz, 3 H). ^{13}C NMR (400 MHz, CDCl_3): δ = 14.04, 20.52, 32.21, 49.17, 54.08, 126.91, 128.17, 128.40, 140.44. ESI-MS of $[\text{C}_{11}\text{H}_{17}\text{N}]^+$; theoretical m/z of $[\text{M}+\text{H}]^+ = 164.14$, measured m/z of $[\text{M}+\text{H}]^+ = 164.17$.⁵

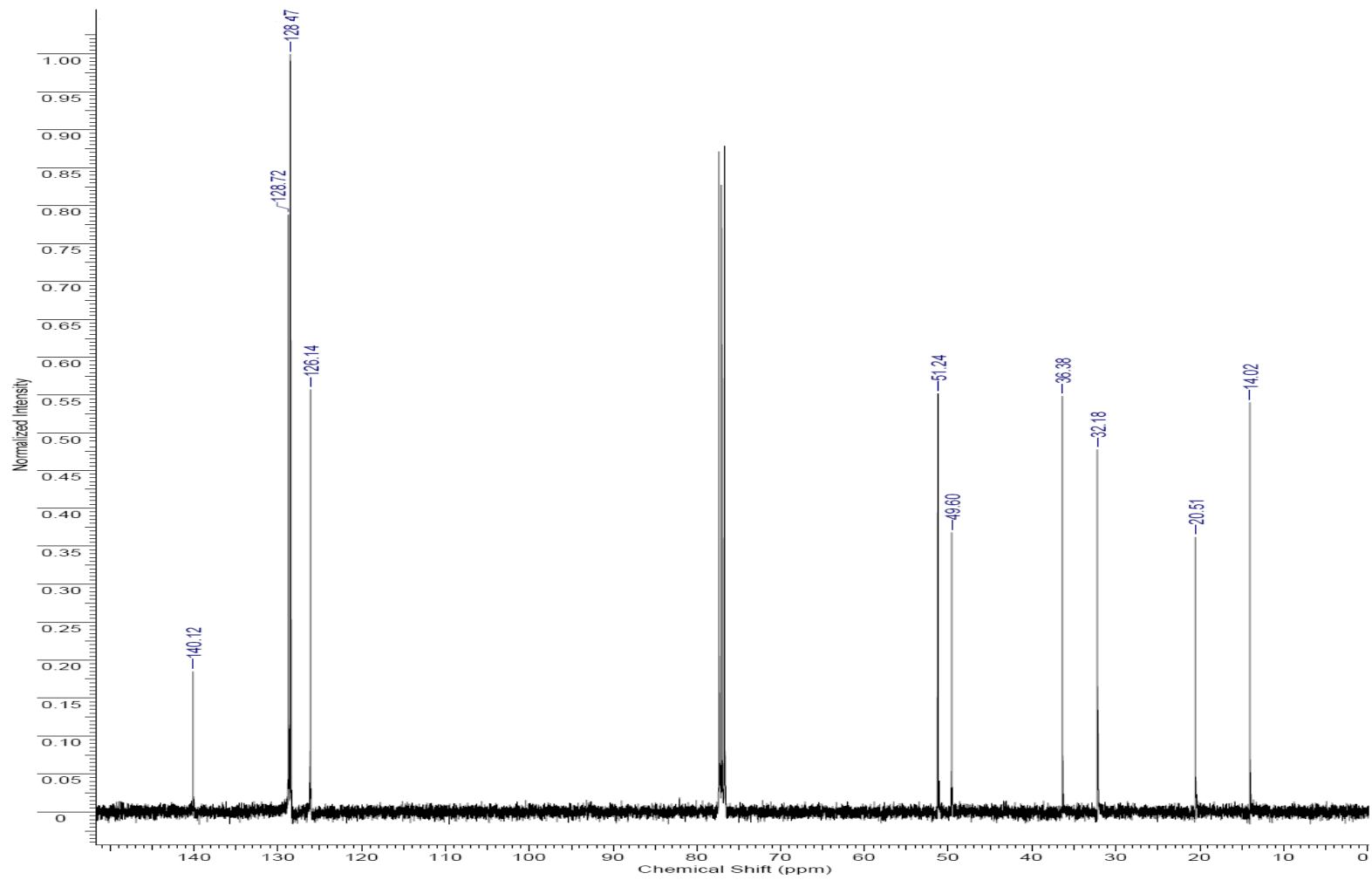


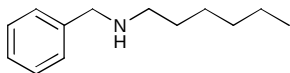




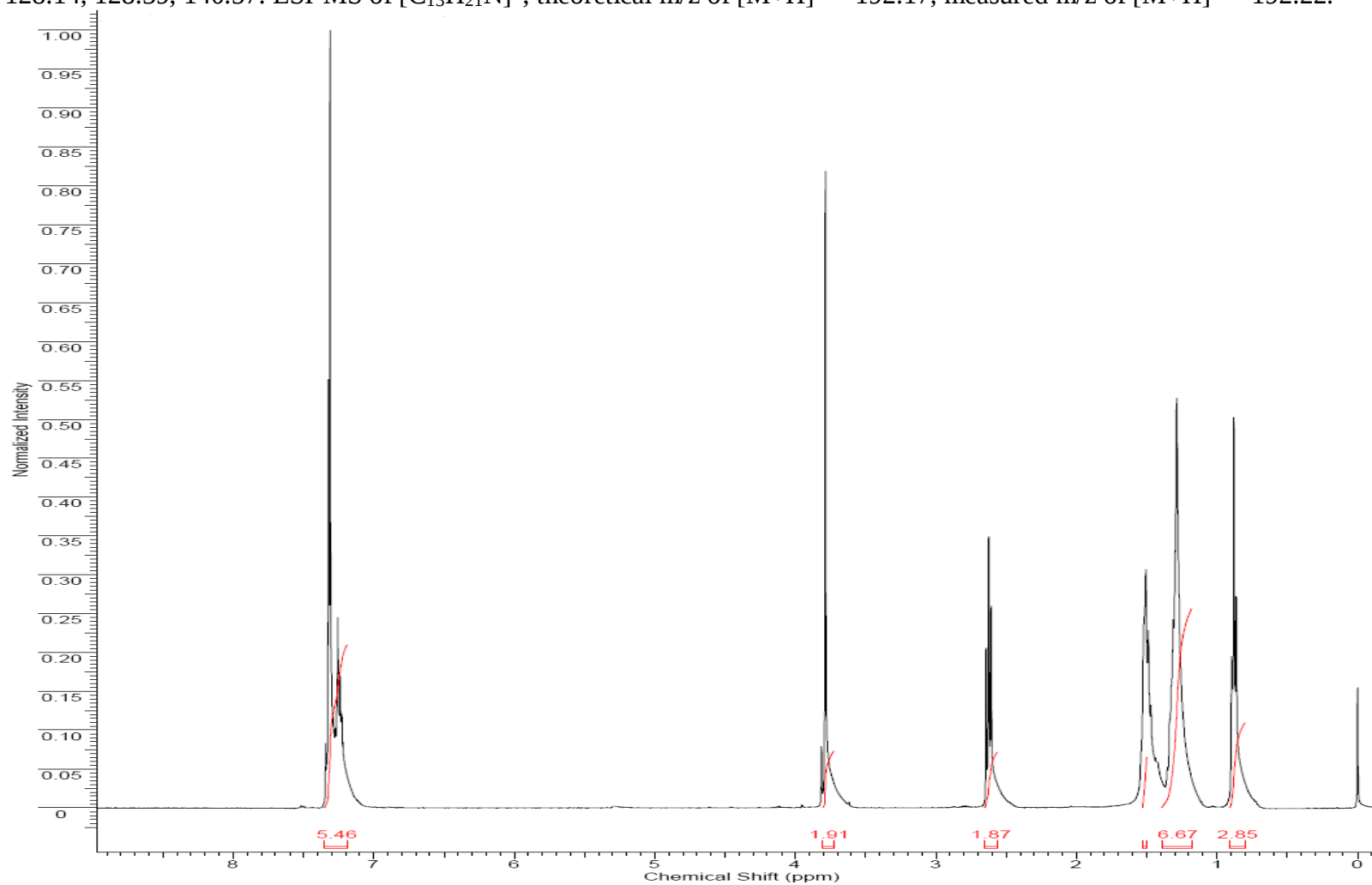
^1H NMR (400 MHz, CDCl_3): δ = δ 0.90 (3H, t, J = 7.34 Hz, CH_3), 1.22-1.37 (3H, m, CH_2), 1.39-1.51 (2H, m, CH_2), 2.63 (2H, t, J = 7.34 Hz, CH_2), 2.75-2.84 (2H, m, CH_2), 2.85-2.93 (2H, m, CH_2), 7.12-7.34 (5H, m, Aromatic). ^{13}C NMR (100 MHz, CDCl_3): δ = 14.02, 20.51, 32.18, 36.38, 49.60, 51.24, 126.14, 128.47, 128.72, 140.12. ESI-MS of $[\text{C}_{12}\text{H}_{19}\text{N}]^+$; theoretical m/z of $[\text{M}+\text{H}]^+ = 178.16$, measured m/z of $[\text{M}+\text{H}]^+ = 178.22$.⁶

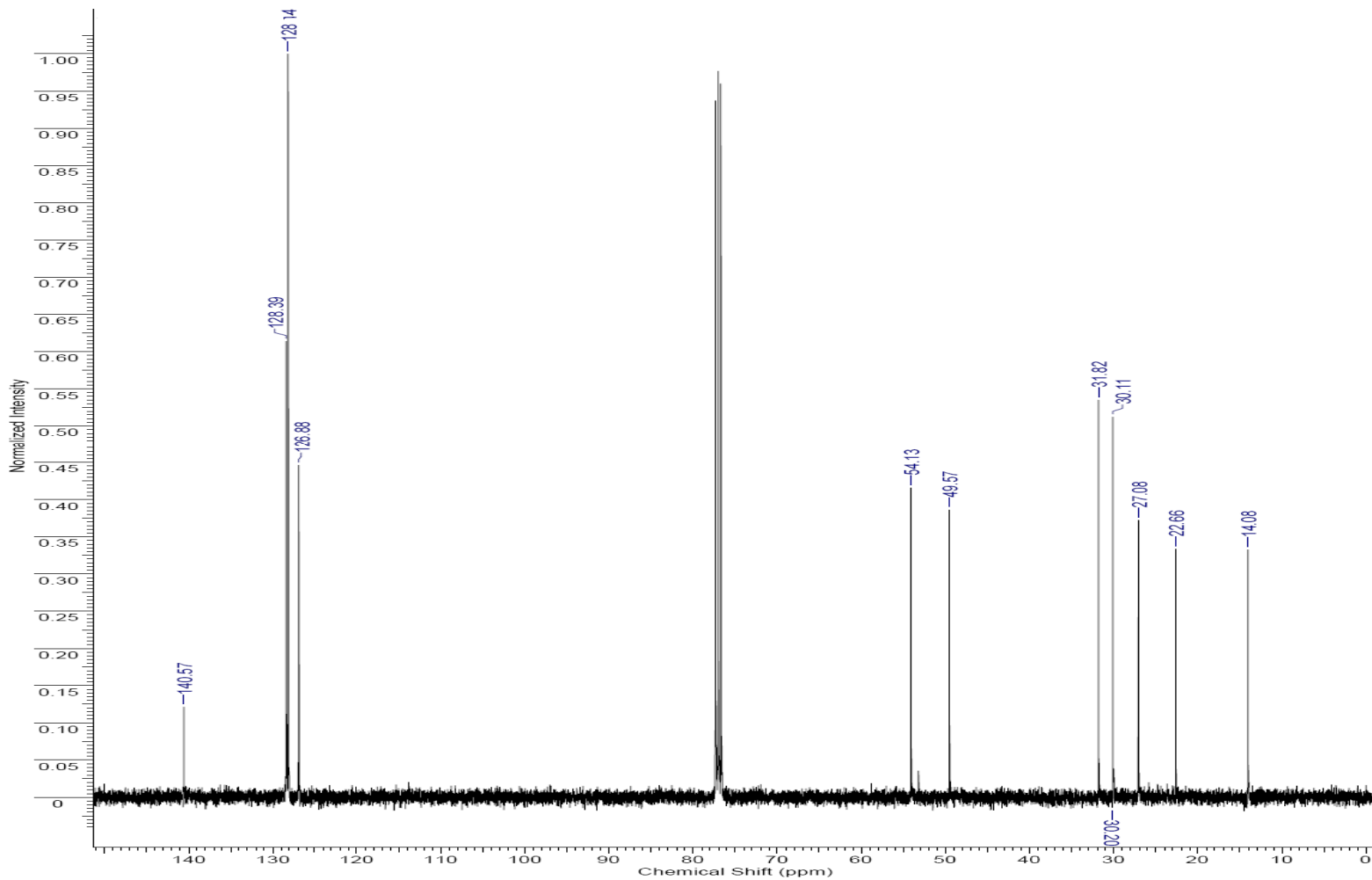






^1H NMR (400 MHz, CDCl_3): δ = 0.88 (3H, t, J = 7.09 Hz), 1.15 - 1.37 (7H, m, CH_2), 1.43 - 1.58 (2H, m, CH_2), 2.63 (2H, t, J = 7.09 Hz, CH_2), 3.79 (2H, s, CH_2), 7.15 - 7.37 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ = 14.08, 22.66, 27.08, 30.11, 31.82, 49.57, 54.13, 126.88, 128.14, 128.39, 140.57. ESI-MS of $[\text{C}_{13}\text{H}_{21}\text{N}]^+$; theoretical m/z of $[\text{M}+\text{H}]^+ = 192.17$, measured m/z of $[\text{M}+\text{H}]^+ = 192.22$.⁷





References

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