Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Cobalt nanoparticles embedded in a nitrogen-doped carbon catalyst for reductive amination of biomass-derived furfural to furfurylamine

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Synthesis of 20wt.%Co/AC Catalyst

In a typical procedure, the required quantity of $Co(NO_3)_2.4H_2O$ was dissolved in distilled water, followed by the addition of activated carbon (AC) support. The resulting mixture was stirred at room temperature for a few hours, followed by the removal of excess water on a hot plate. The obtained solid mass was dried at 100 ^oC in an oven for 10 h. The 20wt.%Co/AC catalyst was obtained, first calcined at 500 ^oC for 4 h under N_2 followed by the reduction in an H_2 flow (20 mL/min) at 500 ^oC for 3h.

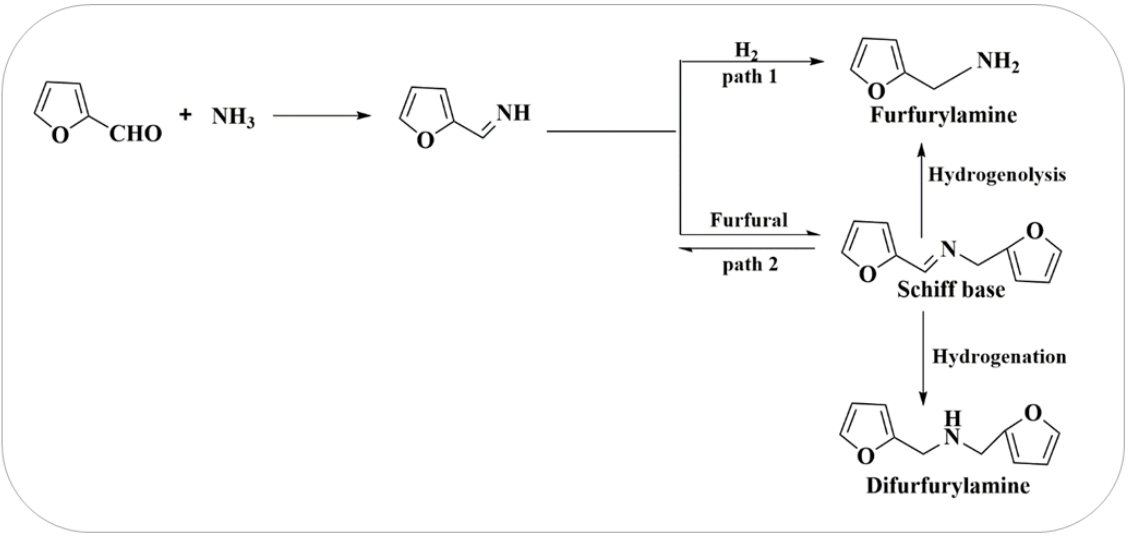
Synthesis of phosphated activated carbon (20P-AC) catalyst

The preparation of 20P-AC catalyst involves a two-step process. Initially, 10 g of AC was dispersed in 250 mL of water, followed by the addition of 40 mL H_2O_2. The resulting mixture was stirred at 40 ^oC for overnight. The oxidized AC was obtained by filtration, followed by drying at 100 ^oC overnight. In a second step, the required quantity of oxidized AC was dispersed in 50 mL of water, followed by the dropwise addition of a specific amount of H_3PO_4. The resulting mixture was stirred at room temperature for 3 h, followed by the evaporation of excess water by rotavapor under a vacuum. The obtained solid mass was calcined at 300 ^oC for 3 h under N_2 flow (30 mL/min).

Reaction procedure for dehydration of xylose to furfural

In a typical synthesis, 0.6 g of xylose, 2g of NaCl, 12 mL of water, THF (48 mL), 0.6 g of 20P-AC catalyst were charged into a 100 mL Parr autoclave reactor. The autoclave was flushed three times with N_2 and pressurized 1MPa N_2. The reaction mixture was vigorously stirred at160 ^oC for 3 h. After completion of the reaction, the reactor was quenched to room temperature, followed by the separation of the catalyst by centrifugation. Both aqueous and organic phases of liquid samples are analyzed separately by HPLC (SHIMADZU) analysis equipped with a refractive index (RI)

and UV detectors using a Shodex SC1011 sugar column. A binary mixture of HPLC grade water and acetonitrile (30:70 v/v) is used as a mobile phase (0.8 mL/min). The products were identified and quantified using known standards through an external calibration method.



Scheme S1. Reaction pathway for the reductive amination of furfural.

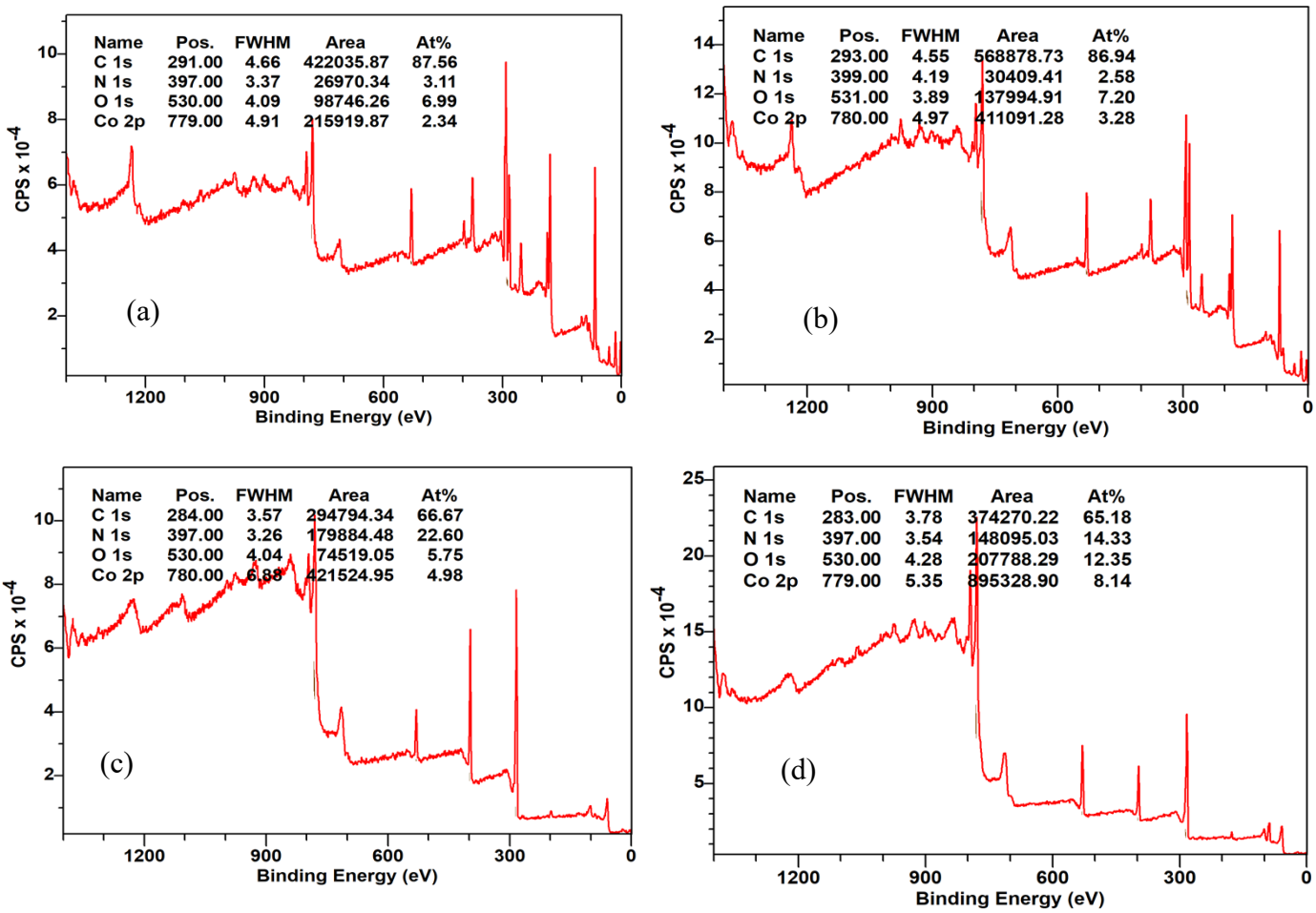


Figure S2. XPS survey scan spectra of (a) Co/NC-700, (b) Co/NC-600, (c) Co/NC-500, and (d) Co/NC-400 catalysts.

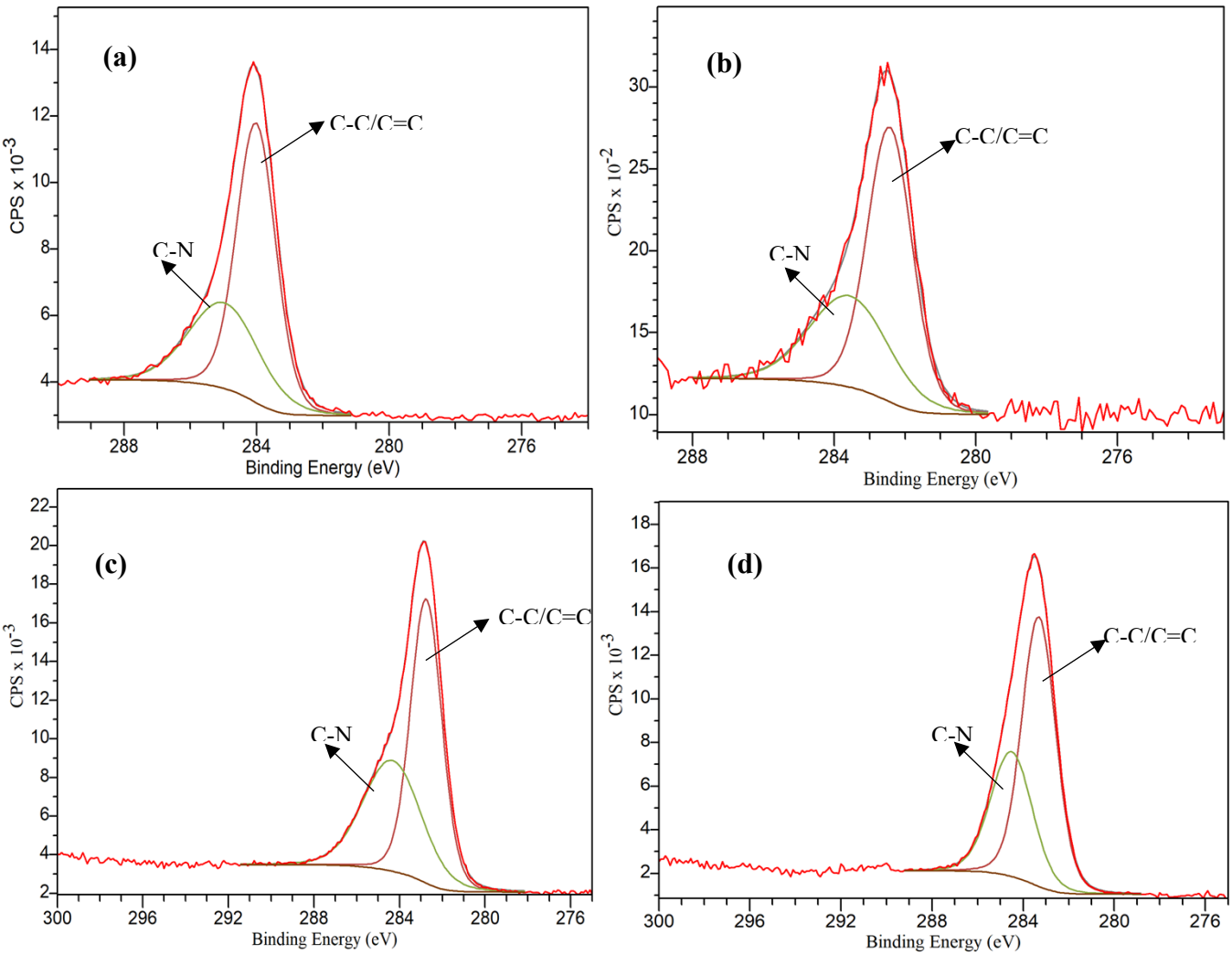


Figure S3: The C 1s XPS spectra of (a) Co/NC-700, (b) Co/NC-600, (c) Co/NC-500, and (d) Co/NC-400 catalysts.

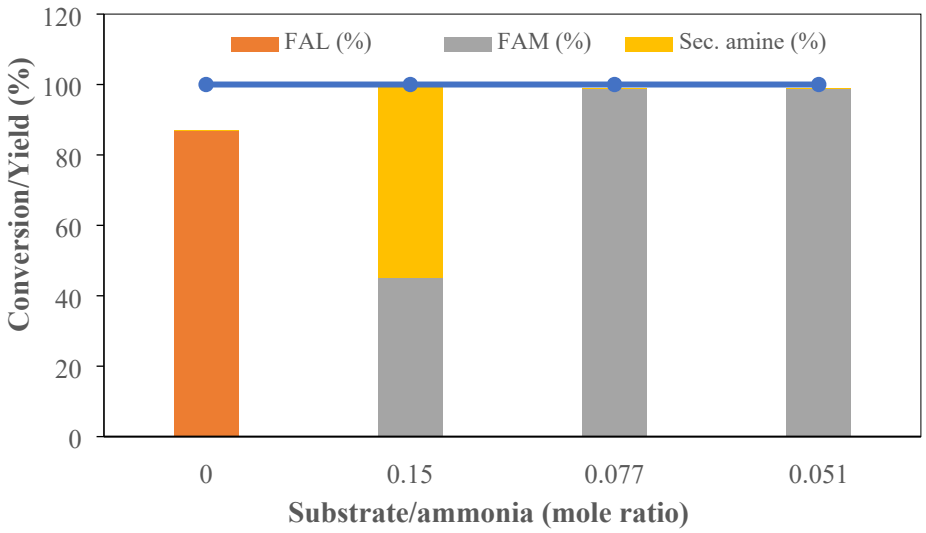


Fig. S4. Effect of substrate/ammonia (mole ratio) for reductive amination of furfural. Reaction conditions: FA (0.096 g), catalyst (50 mg), methanol (12 mL), H_2 pressure (2 MPa) reaction temperature (120 °C), reaction time (1 h).

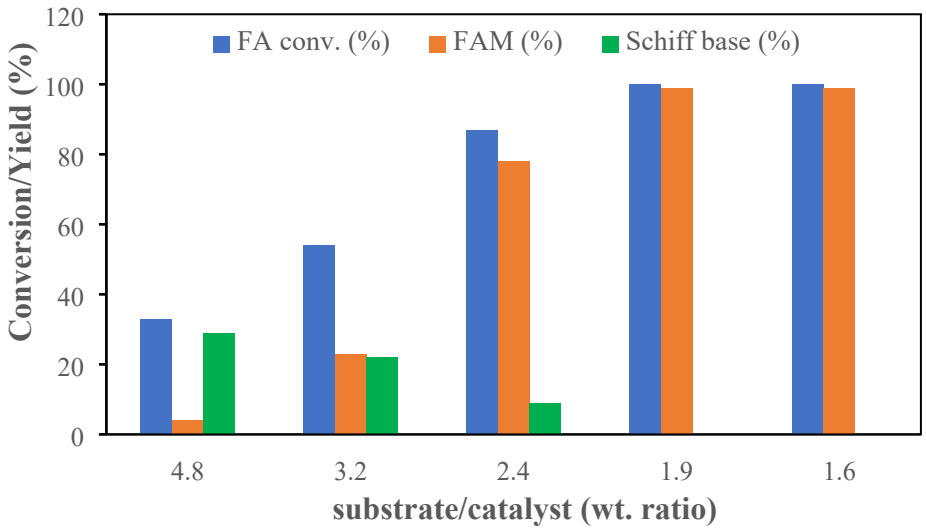


Fig. S5. Effect of substrate/catalyst (wt. ratio) for the reductive amination of furfural. Reaction conditions: FA (0.096 g), Aq. NH_3 (1 mL), methanol (12 mL), H_2 pressure (2 MPa) reaction temperature (120 °C), reaction time (1 h).

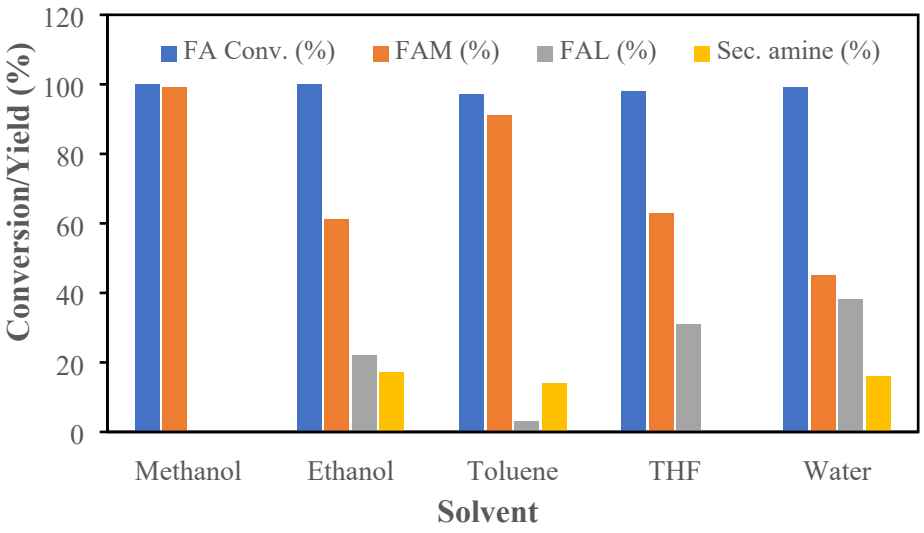


Fig. S6. Effect of solvent for reductive amination of furfural.

Reaction conditions: FA (0.096 g), catalyst (50 mg), Aq. NH_3 (1 mL), methanol (12 mL), H_2 pressure (2 MPa), reaction temperature (120 °C), reaction time (1 h).

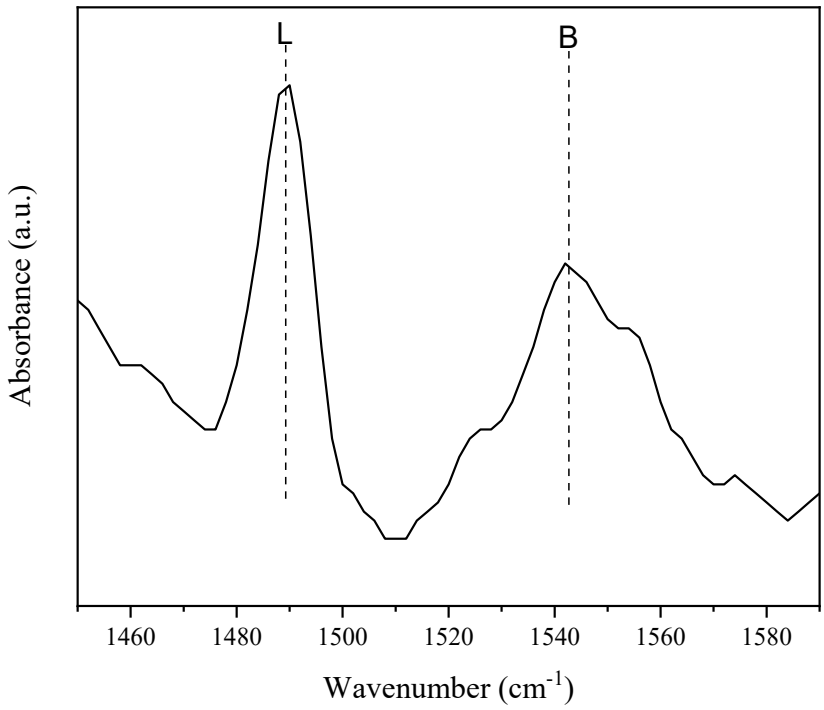


Fig. S7. Pyridine FT-IR spectra of a 20P-AC catalyst.

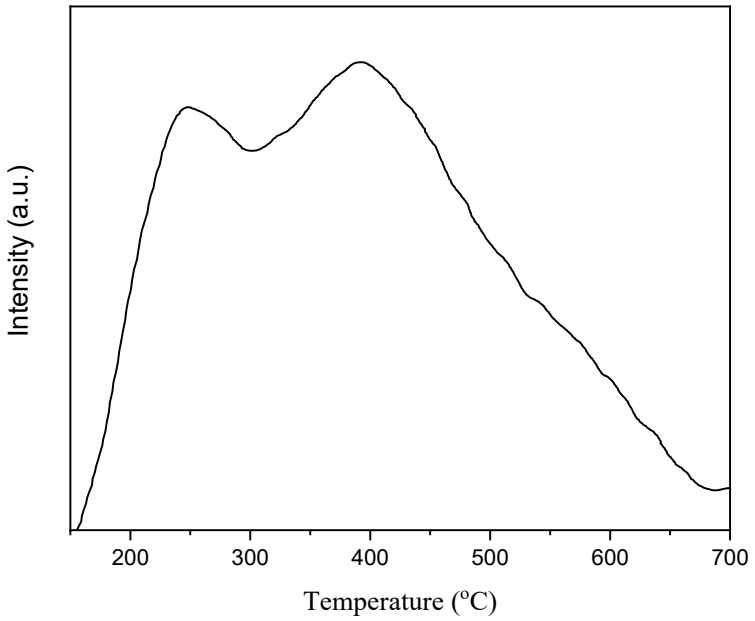


Fig. S8. NH_3 -TPD spectra of a 20P-AC catalyst.

NMR And GC-MS spectra of synthesized molecules

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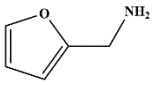
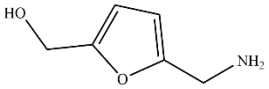


^{1}H NMR (400 MHz $CDCl_3$) δ (ppm): 7.33 (s, 1H), 6.29 (s, 1H), 6.12 (s, 1H), 3.80 (s, 2H), 1.61 (s, 2H)

^{13}C NMR (100 MHz $CDCl_3$) δ (ppm): 156.54, 141.51, 104.97, 101.14, 39.27

GCMS *m/z (%)*: 97 (93.6), 96 (45.7), 69 (100), 53 (37), 41 (35.8).



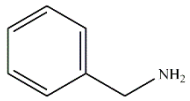
Entry 2: **(5-(aminomethyl)furan-2-yl)methanol**

^{1}H NMR (400 MHz $CDCl_3$) δ (ppm): 6.17 (d, 1H), 6.06 (d, 1H), 4.53 (s, 2H), 3.77 (s. 2H).

^{13}C NMR (100 MHz $CDCl_3$) δ (ppm): 155.05, 152.75, 107.44, 105.19, 56.40, 30.25.

GCMS *m/z (%)*: 127 (24.8), 96 (100), 68 (13.3), 41 (13.7), 30 (11.4).

Entry 3: **phenylmethanamine**

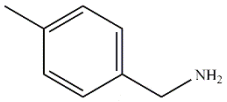


^{1}H NMR (400 MHz $CDCl_3$) δ (ppm): 7.30- 7.18 (m, 5H), 3.76 (s, 2H), 1.53 (s, 2H).

^{13}C NMR (100 MHz $CDCl_3$) δ (ppm): 143.41, 127.10, 126.79, 46.55.

GCMS *m/z (%)*: 107 (100), 106 (100), 79 (86.8), 78 (33.7), 77 (57.4)

Entry 4: **(4-methylphenyl)methanamine**

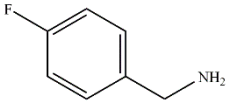


^{1}H NMR (400 MHz $CDCl_3$) δ (ppm): 7.18 (d, 1H), 7.14 (d, 1H), 3.78 (s, 2H), 2.34 (s, 3H), 1.96 (s, 2H).

^{13}C NMR (100 MHz $CDCl_3$) δ (ppm): 140.51, 136.32, 129.35, 127.11, 46.28, 21.09.

GCMS *m/z (%)*: 120 (95), 106 (80), 104 (100), 93 (61), 91 (66).

Entry 5: **(4-fluorophenyl)methanamine**

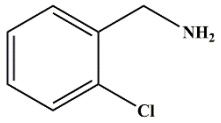


^{1}H NMR (400 MHz $CDCl_3$) δ (ppm): 7.32-7.28 (q, 2H), 7.05-7.00 (t, 2H), 3.88 (s, 2H).

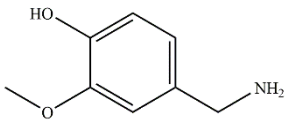
^{13}C NMR (100 MHz $CDCl_3$) δ (ppm): 163.20, 160.53, 136.71, 135.98, 128.99, 128.91, 115.48, 115.23, 45.03.

GCMS *m/z (%)*: 125 (37), 124 (100), 109 (26.4), 105 (49.3), 97 (38).

Entry 6: **(2-chlorophenyl)methanamine**



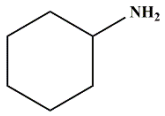
GCMS *m/z* : 142, 106, 79, 77, 51, 31



Entry 7: **4-(aminomethyl)-2-methoxyphenol**

GCMS *m/z (%)*: 153 (41.4), 152 (46.1), 137 (100), 122 (50), 32 (81).

Entry 8: **Cyclohexylamine**

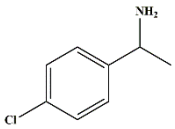


^{1}H NMR (400 MHz $CDCl_3$) δ (ppm): 2.65-2.58 (m, 1H), 1.83-1.58 (m, 5H), 1.31-1.00 (m, 7H).

^{13}C NMR (100 MHz $CDCl_3$) δ (ppm): 50.28, 36.66, 25.77, 25.04.

GCMS *m/z (%)*: 99 (16), 70 (19.5), 56 (100), 43 (22.6), 42 (6.6).

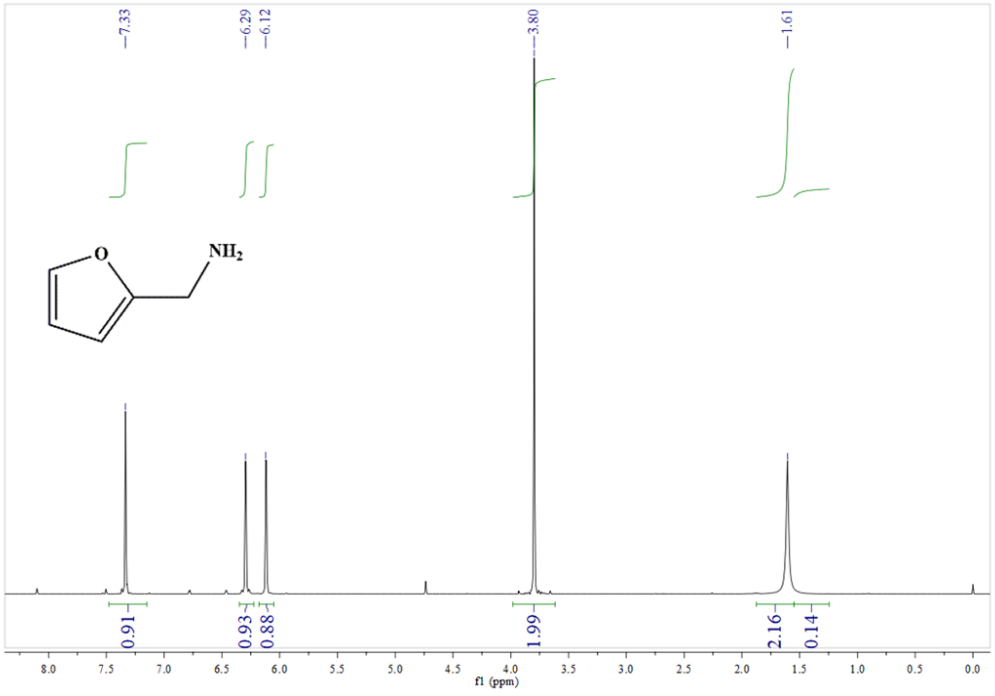
Entry 9: **(4-chlorophenyl)ethan-1-amine**



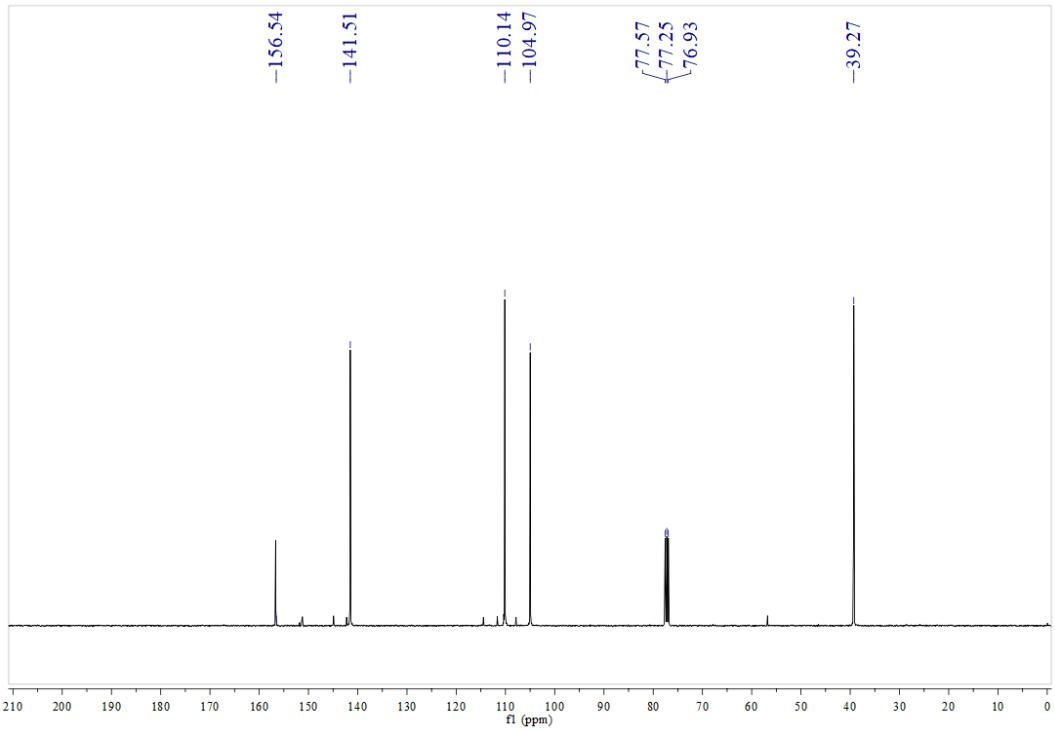
^{1}H NMR (400 MHz $CDCl_3$) δ (ppm): 7.31 (s, 4H), 4.91-4.86 (q, 1H), 2.0 (s, 2H), 1.48-1.47 (d, 3H)

GCMS *m/z (%)*: 142 (32), 141 (8), 140 (100), 113 (9), 77 (19.7).

^{1}H NMR, ^{13}C NMR and GC-MS of synthesized products



^{1}H NMR spectra of furfurylamine



^{13}C spectra NMR of furfurylamine

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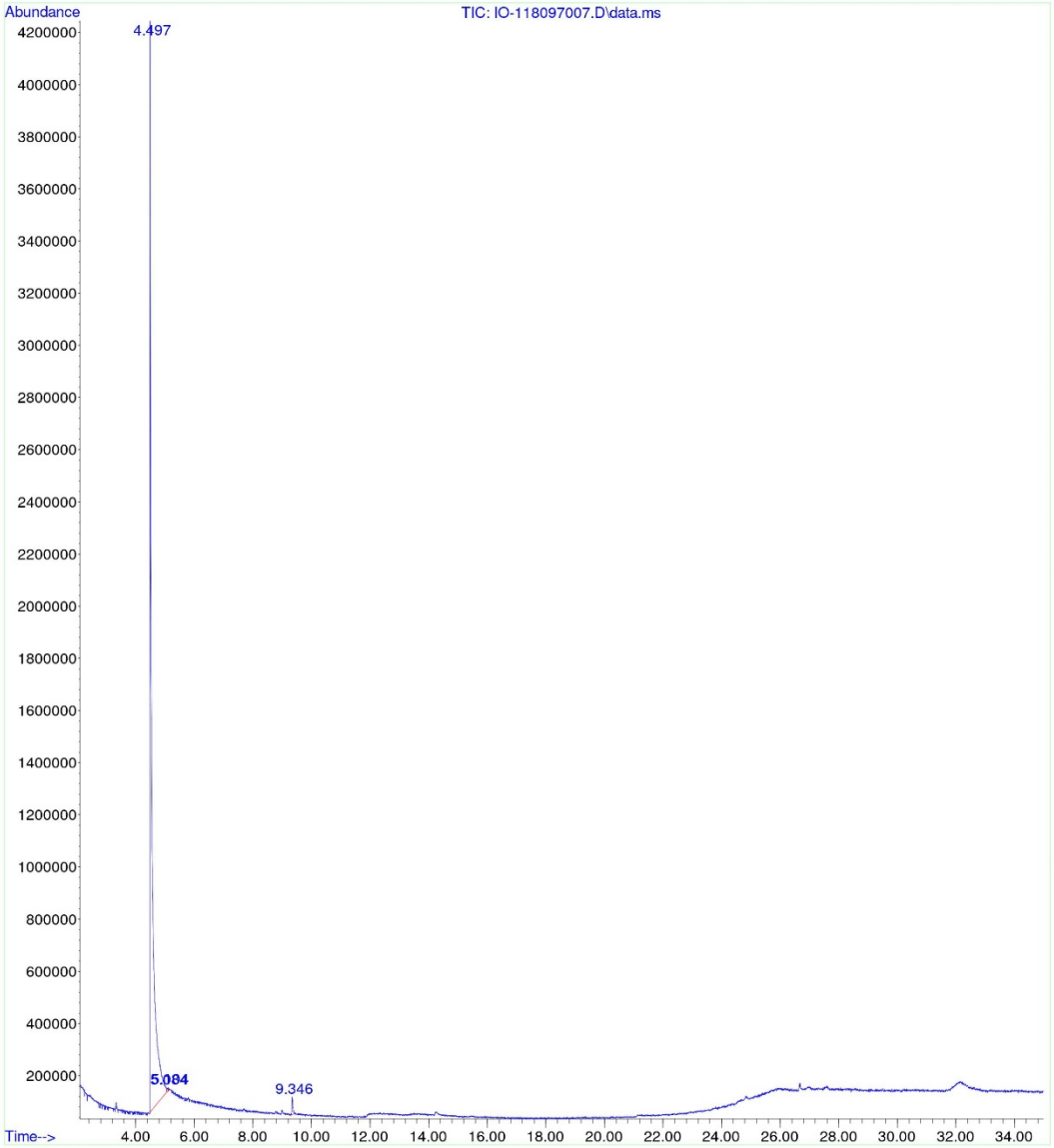
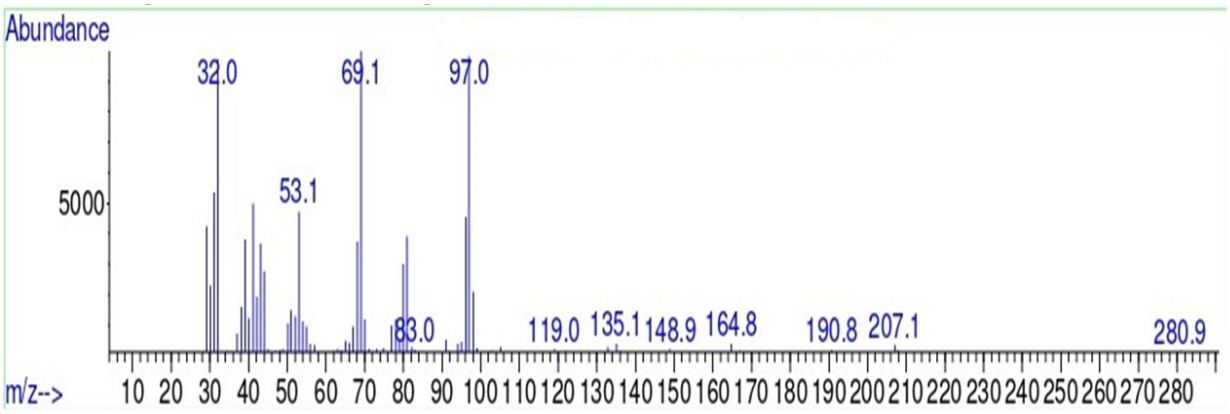
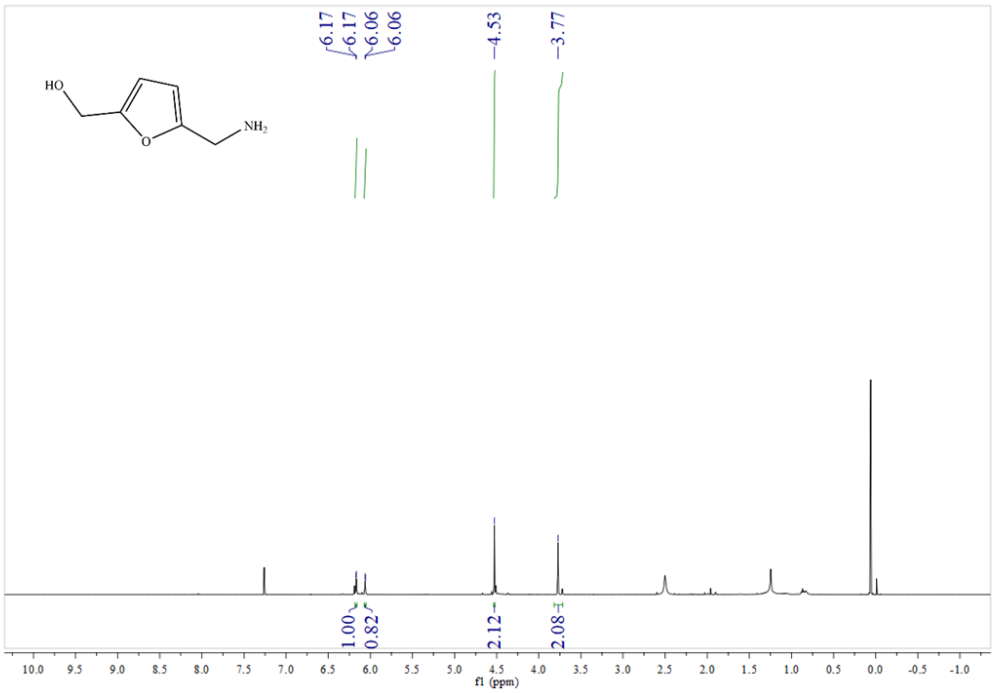


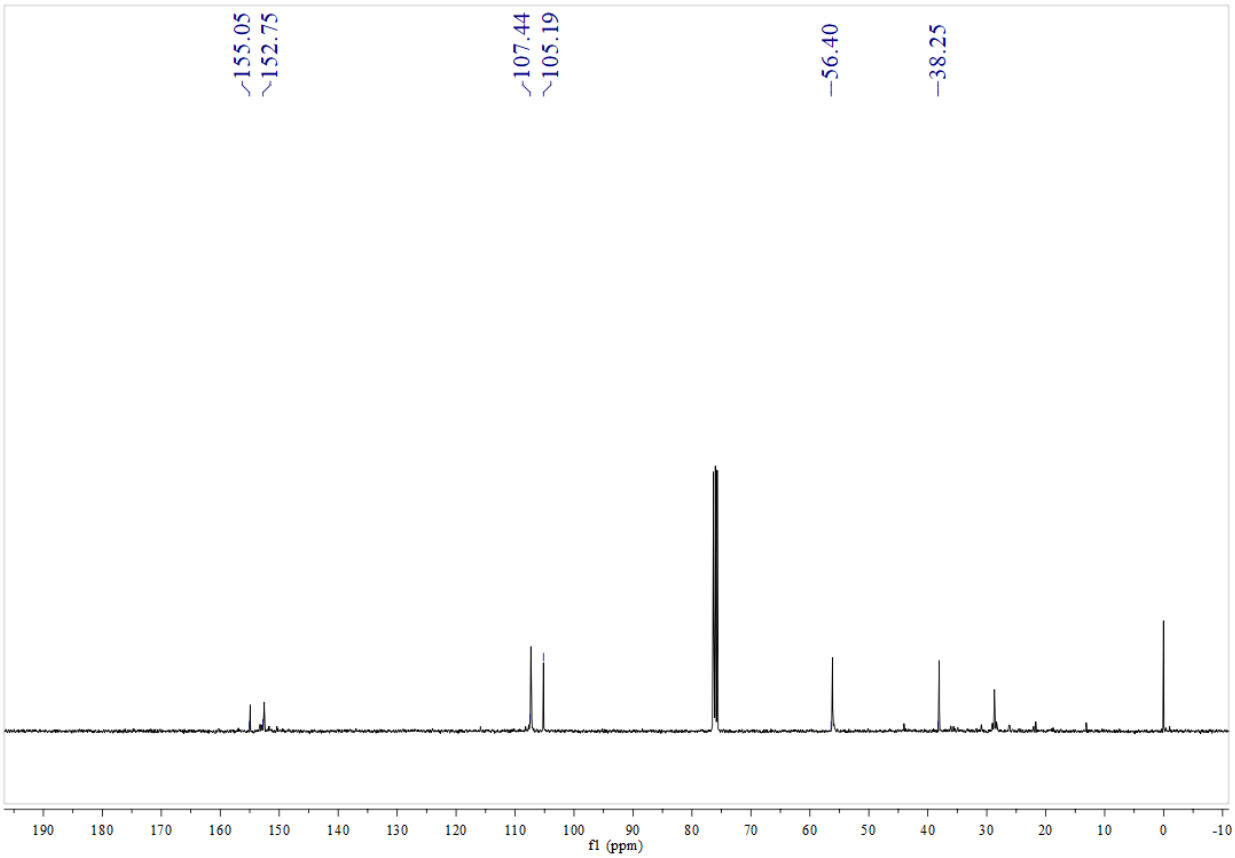
GC spectra of reductive amination of furfural.



m/z value of furfurylamine



^{1}H NMR spectra of (5-(aminomethyl)furan-2-yl)methanol



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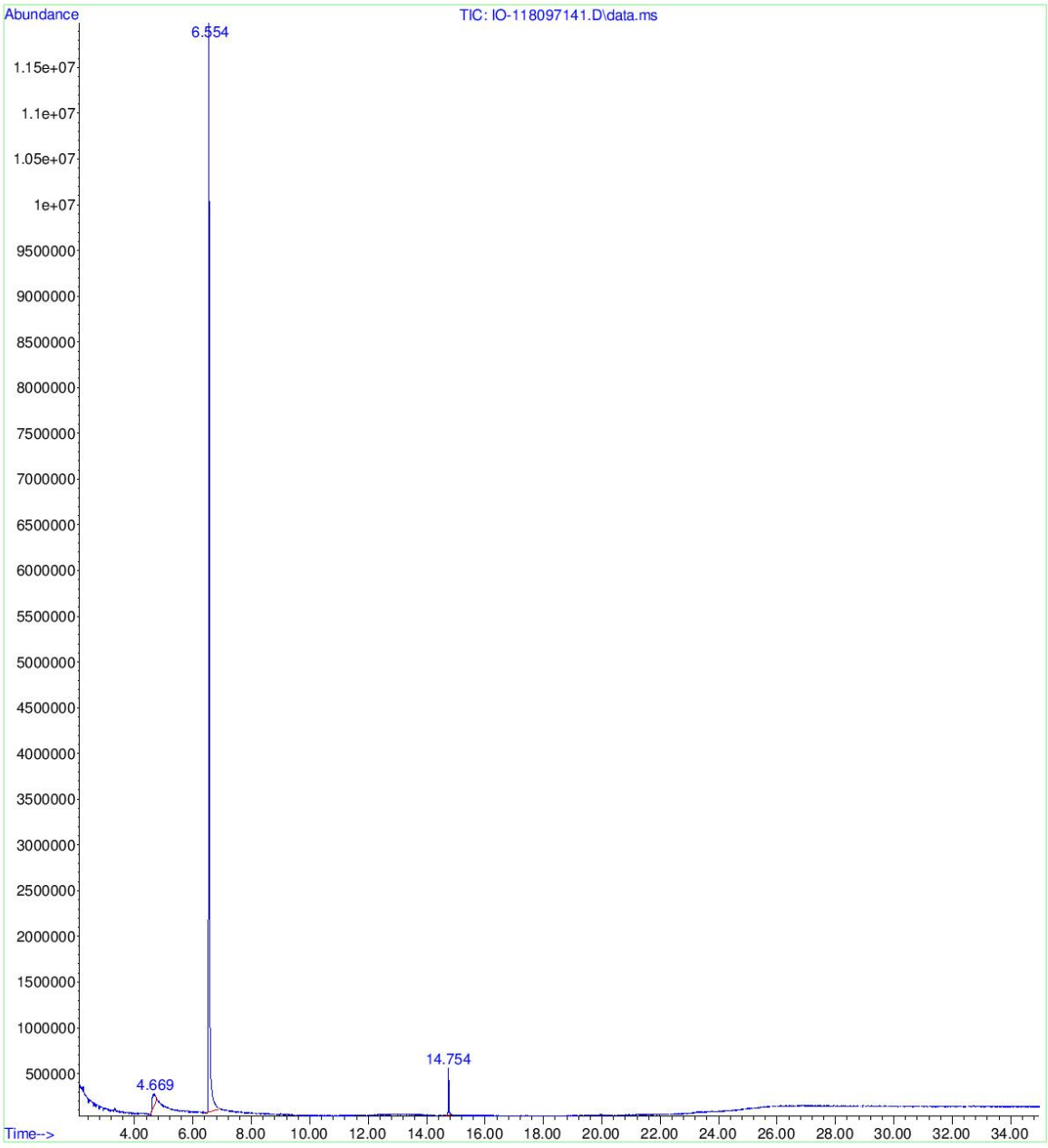

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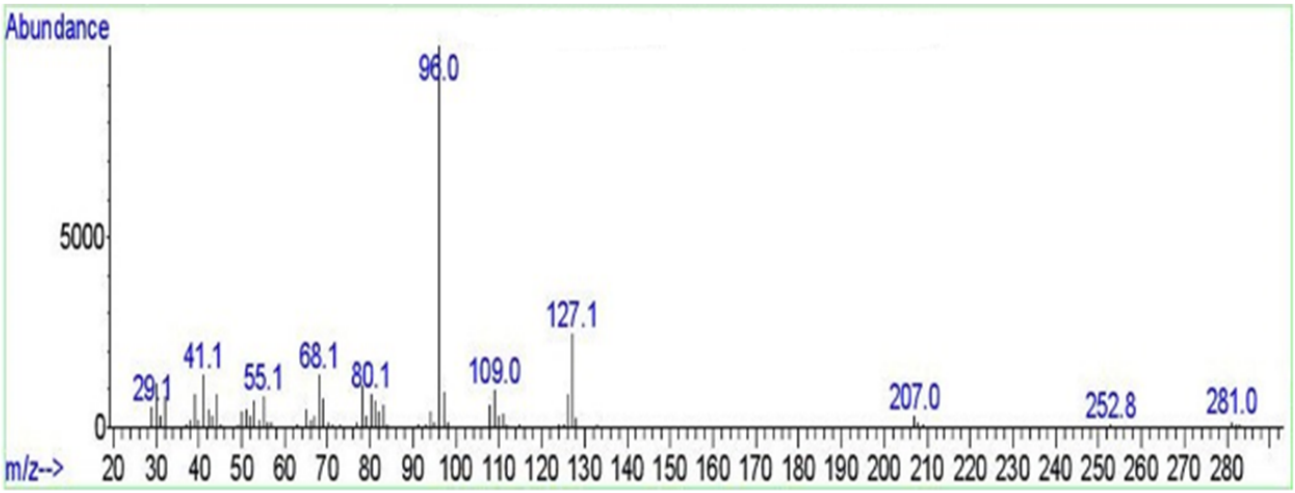
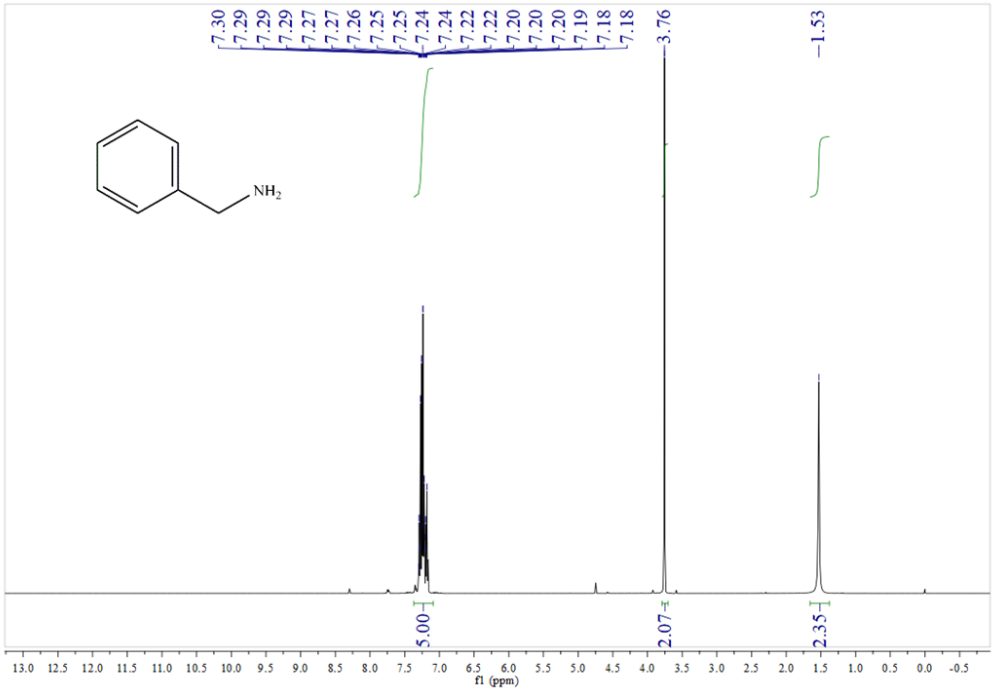
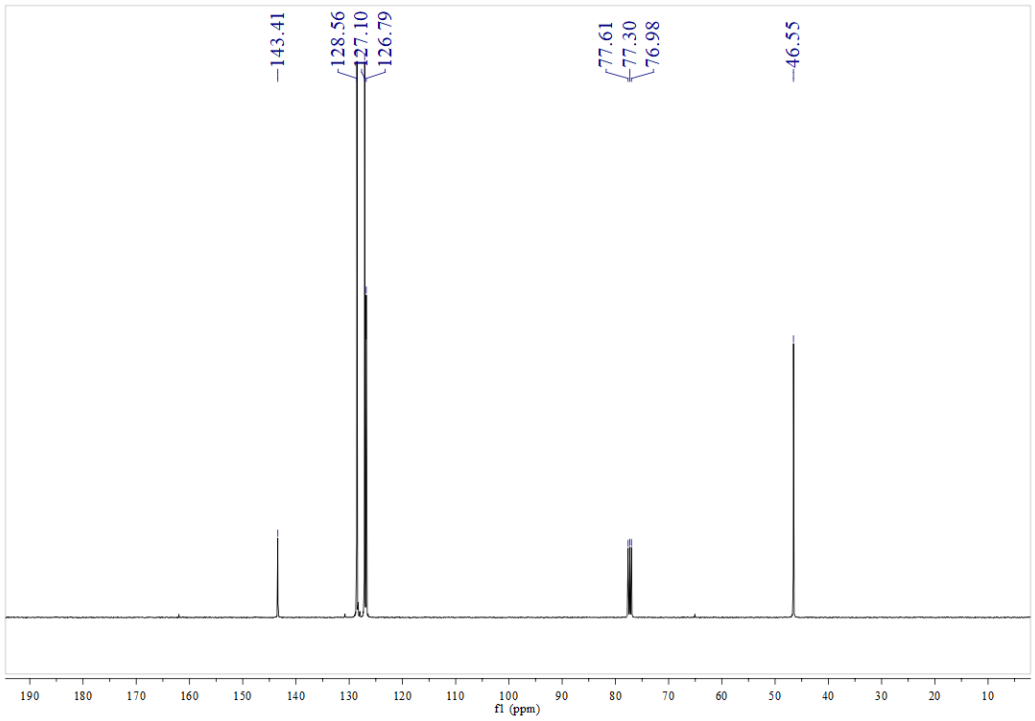


m/z values of (5-(aminomethyl)furan-2-yl)methanol



^{1}H spectra NMR of phenylmethanamine



^{13}C NMR spectra of phenylmethanamine

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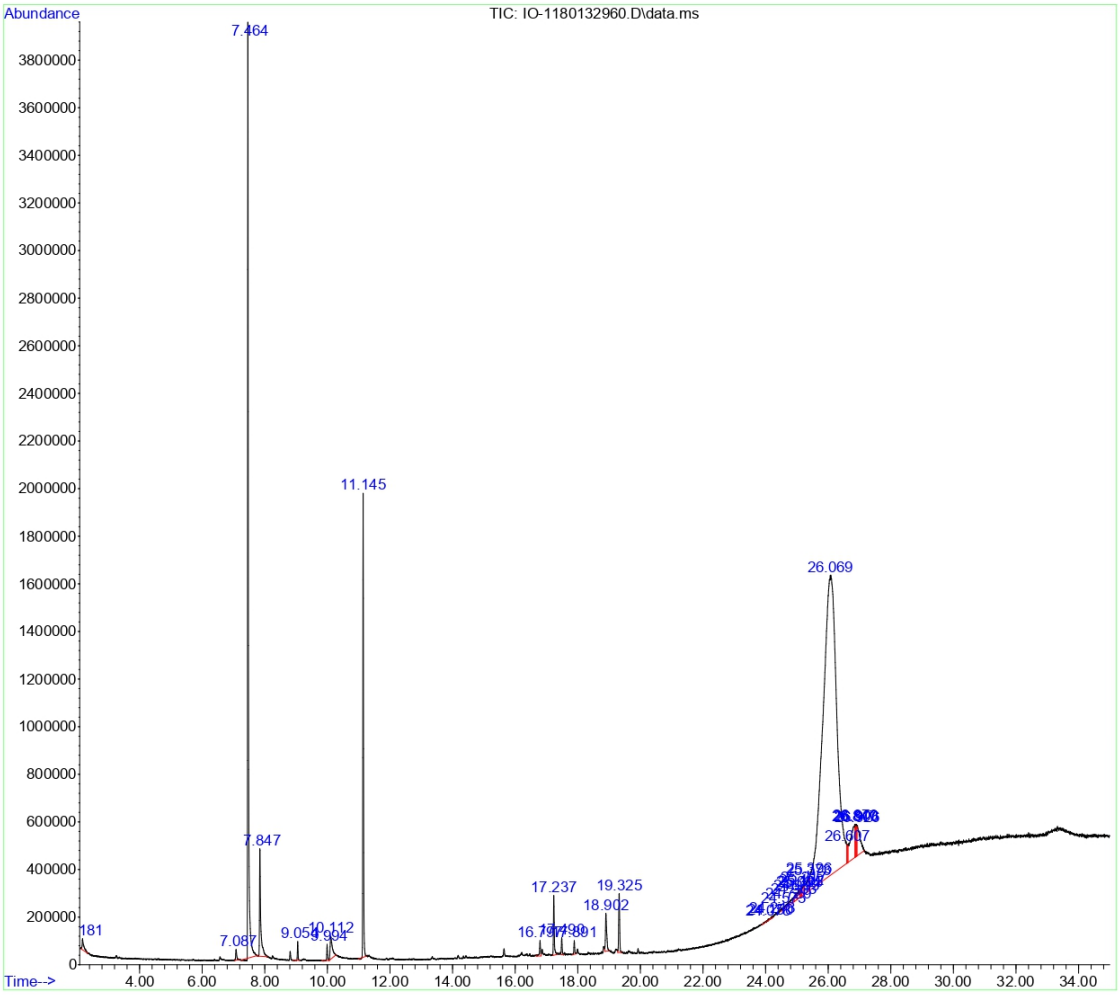
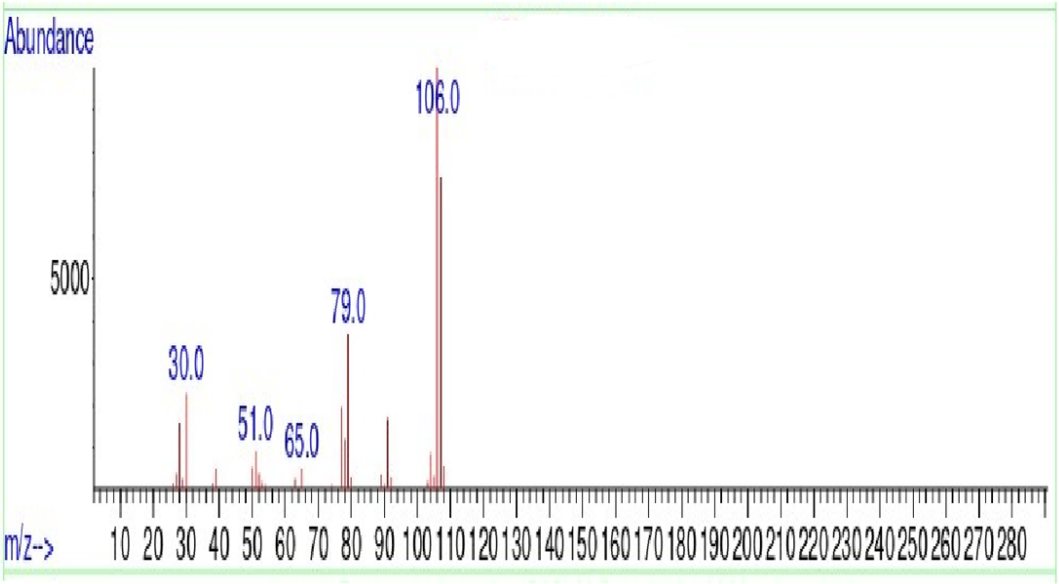
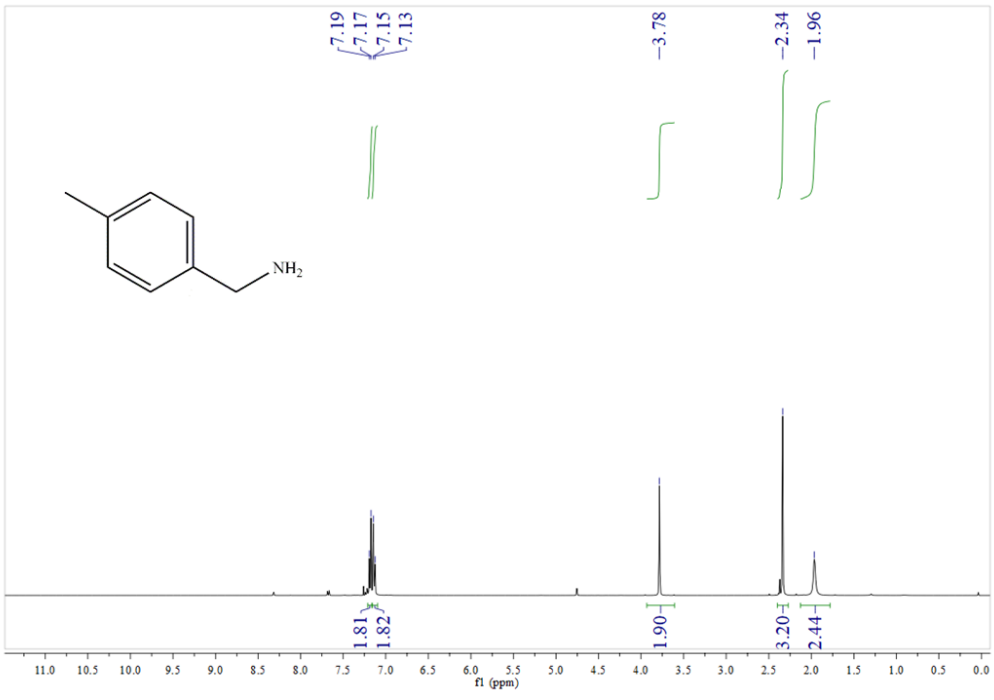


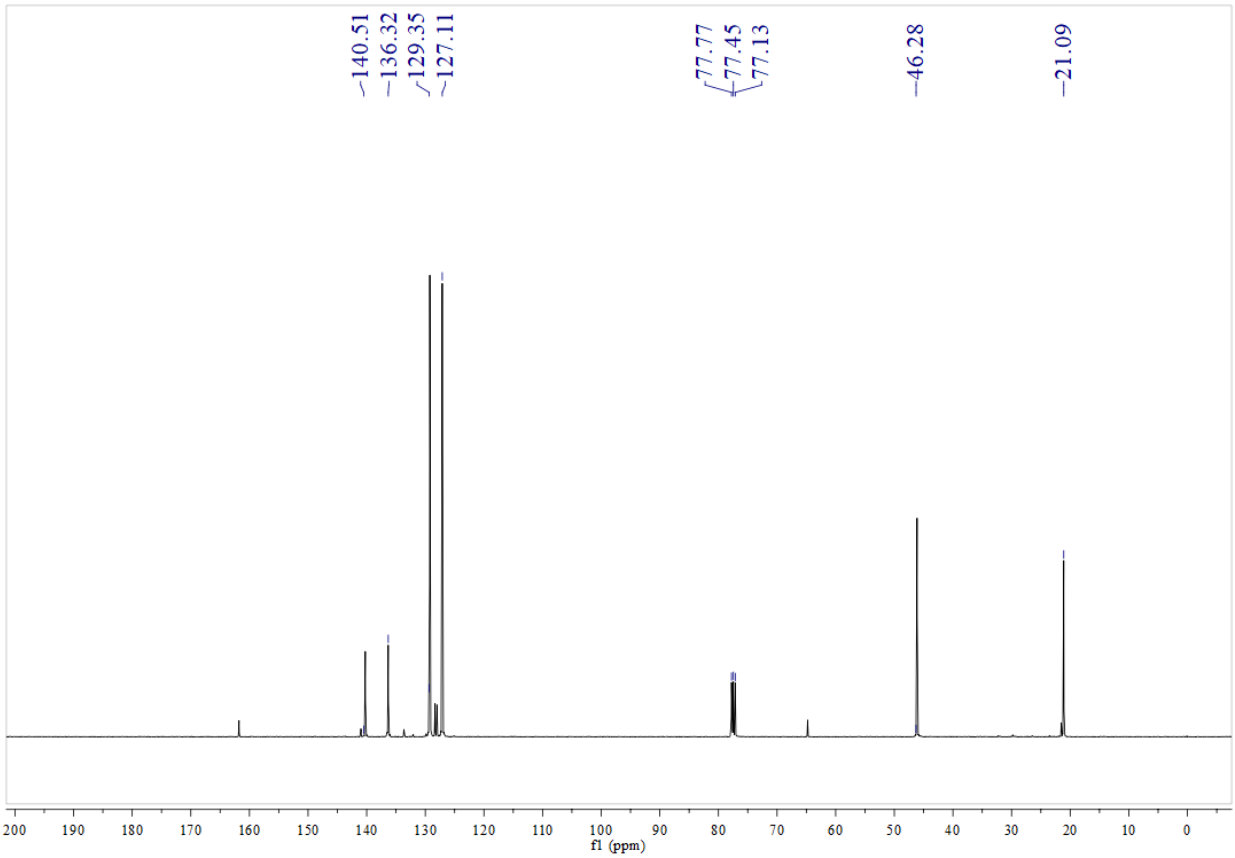
GCMS spectra of reaction mixture of benzaldehyde reductive amination



m/z values of phenylmethanamine



^{1}H NMR spectra of (4-methylphenyl)methanamine



^{13} C NMR spectra of (4-methylphenyl)methanamine

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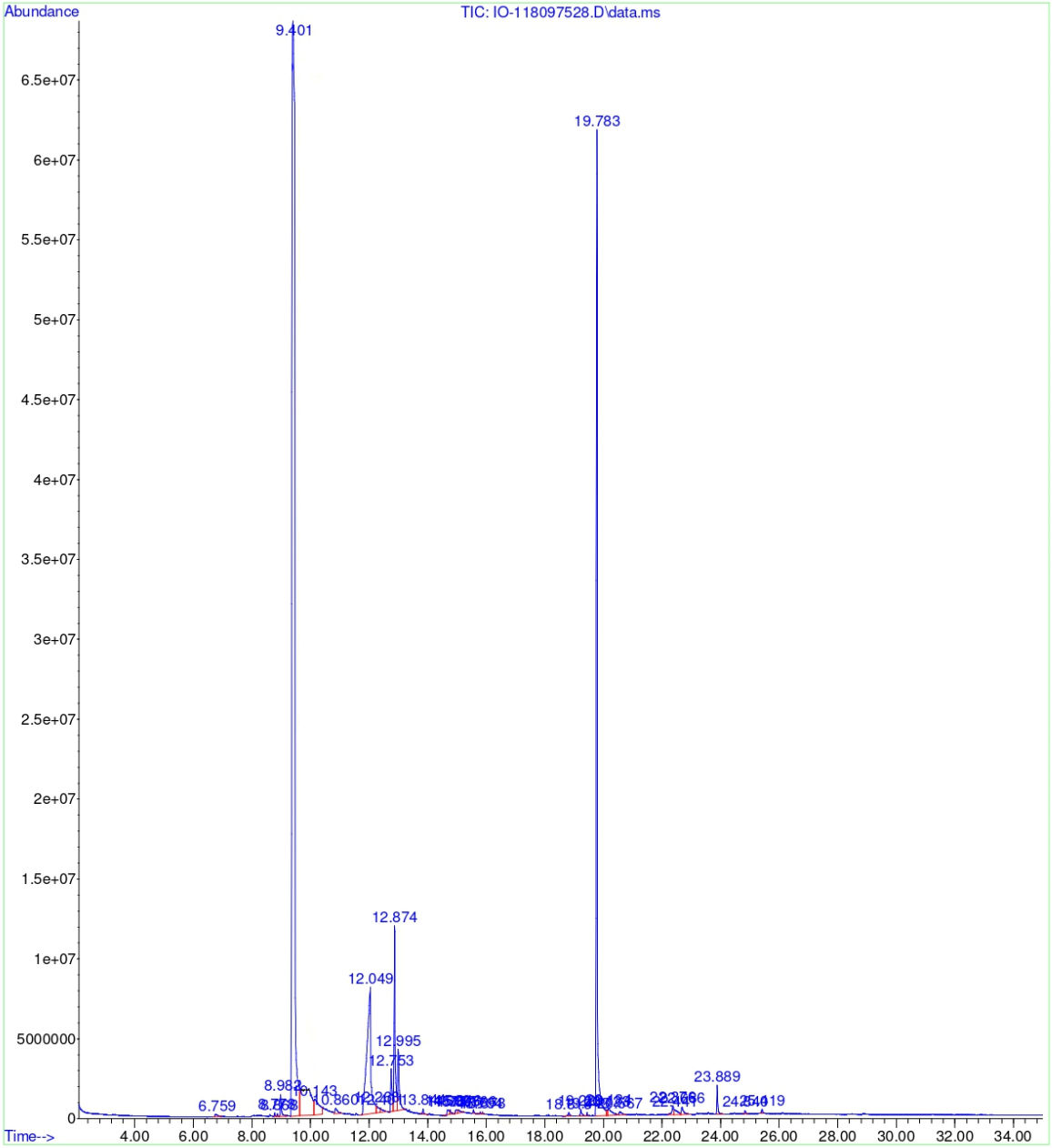

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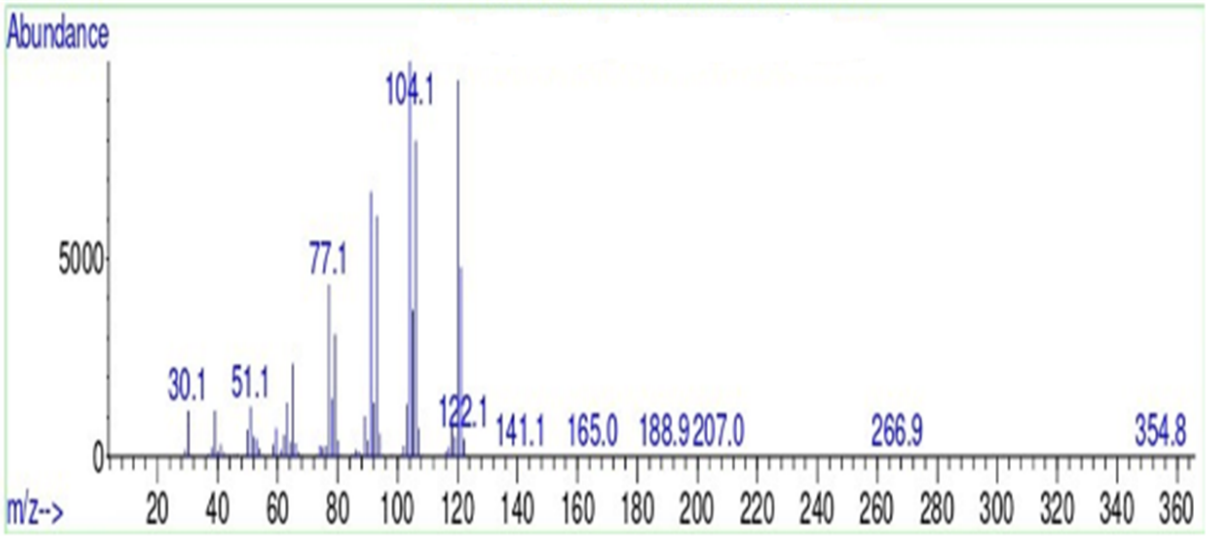
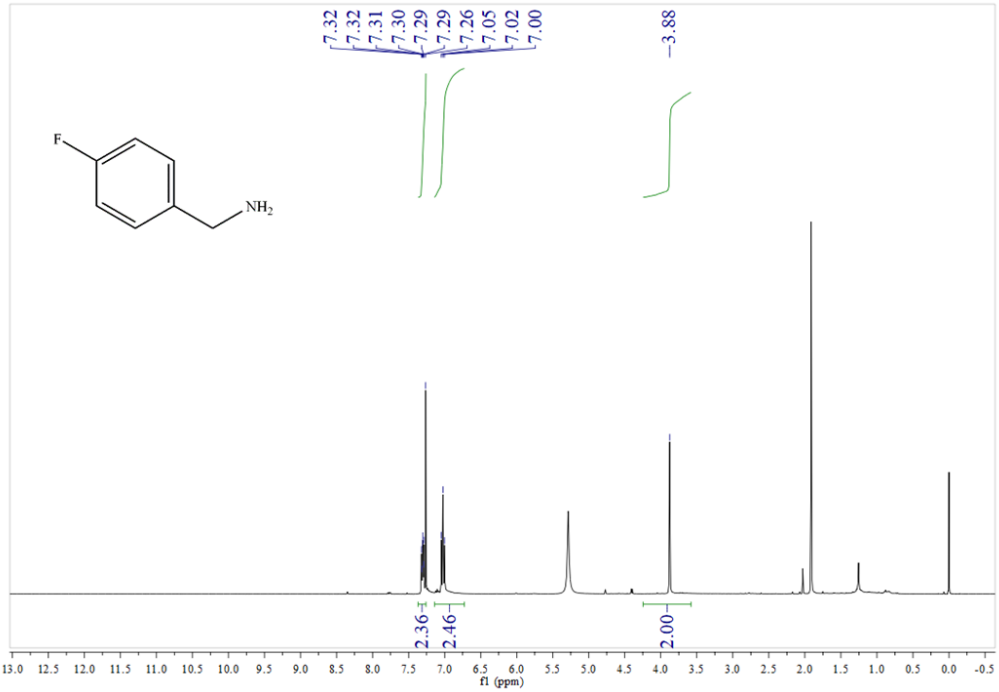
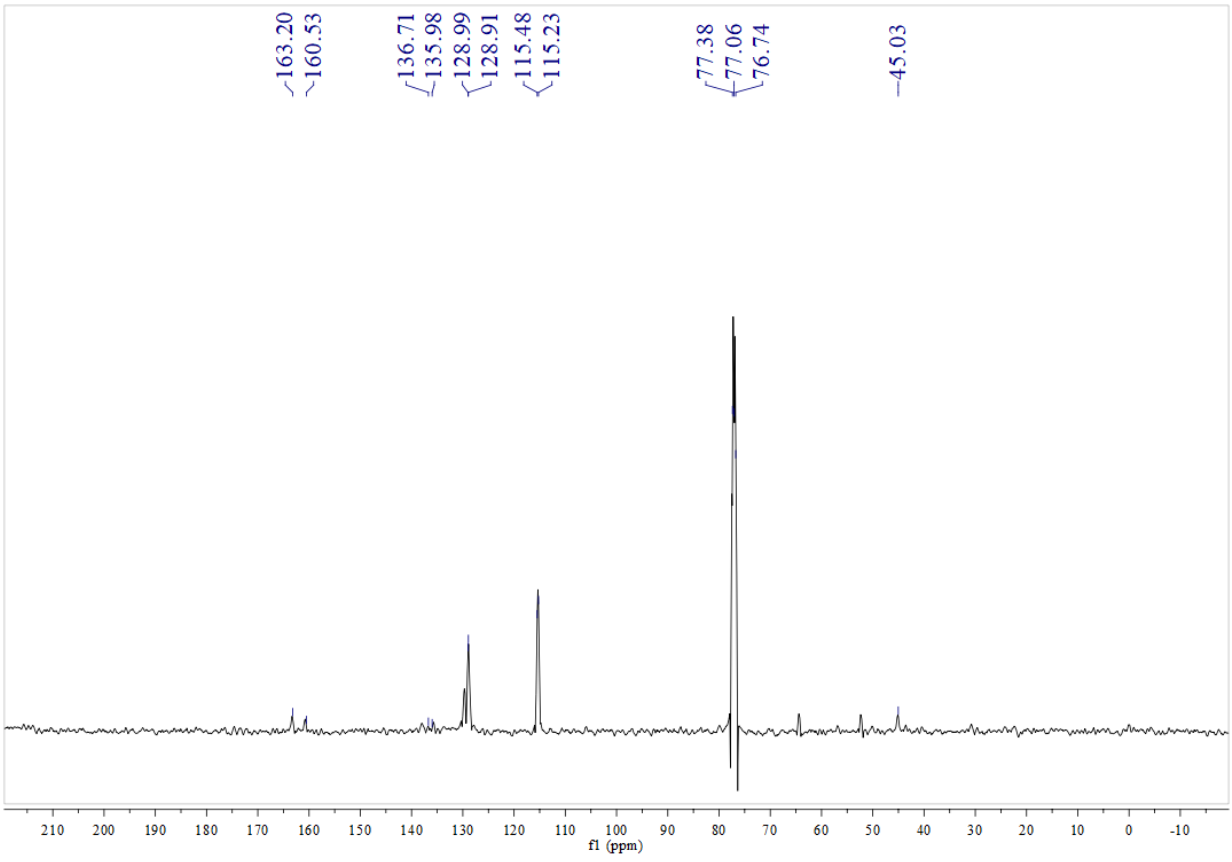


m/z values of (4-methylphenyl)methanamine



^{1}H NMR spectra of (4-fluorophenyl)methanamine



^{13}C NMR spectra of (4-fluorophenyl)methanamine

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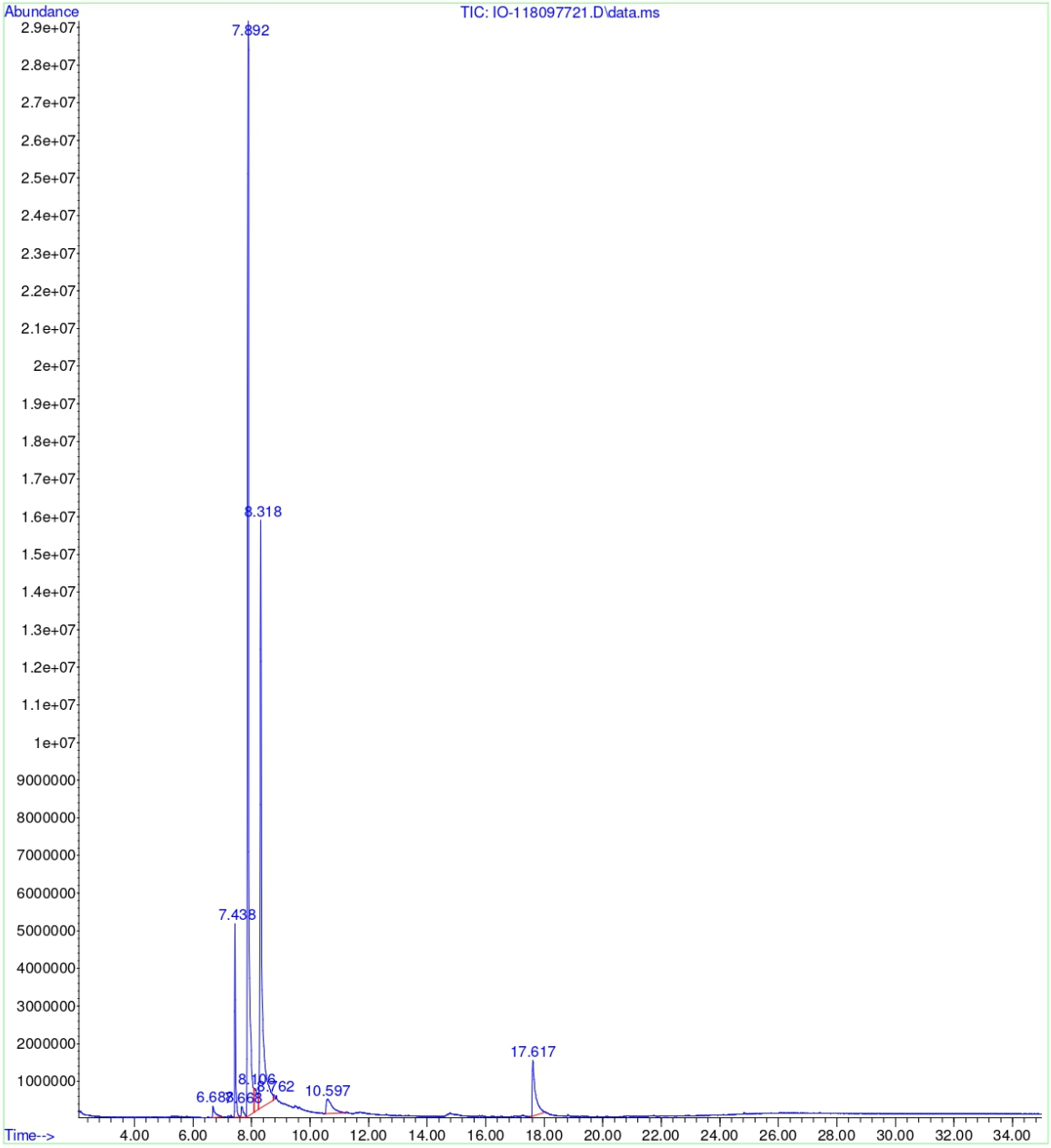
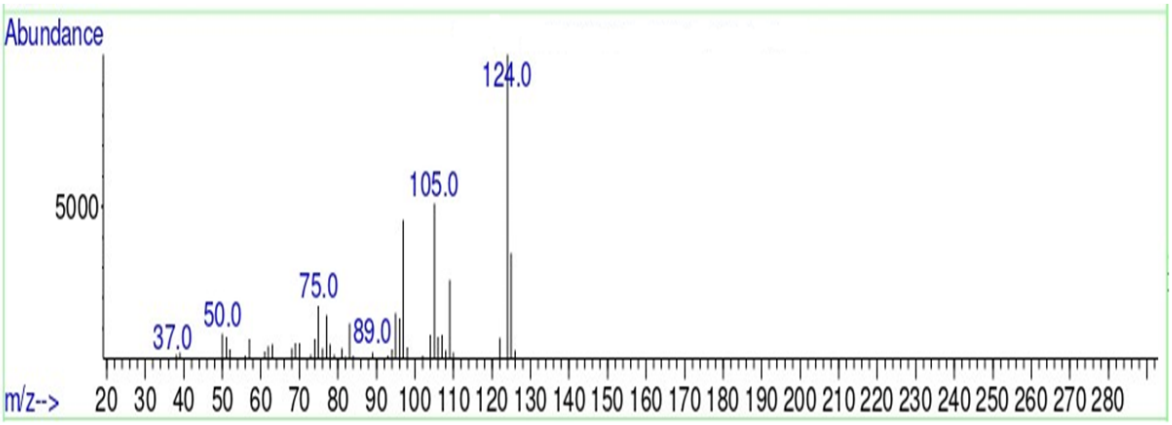
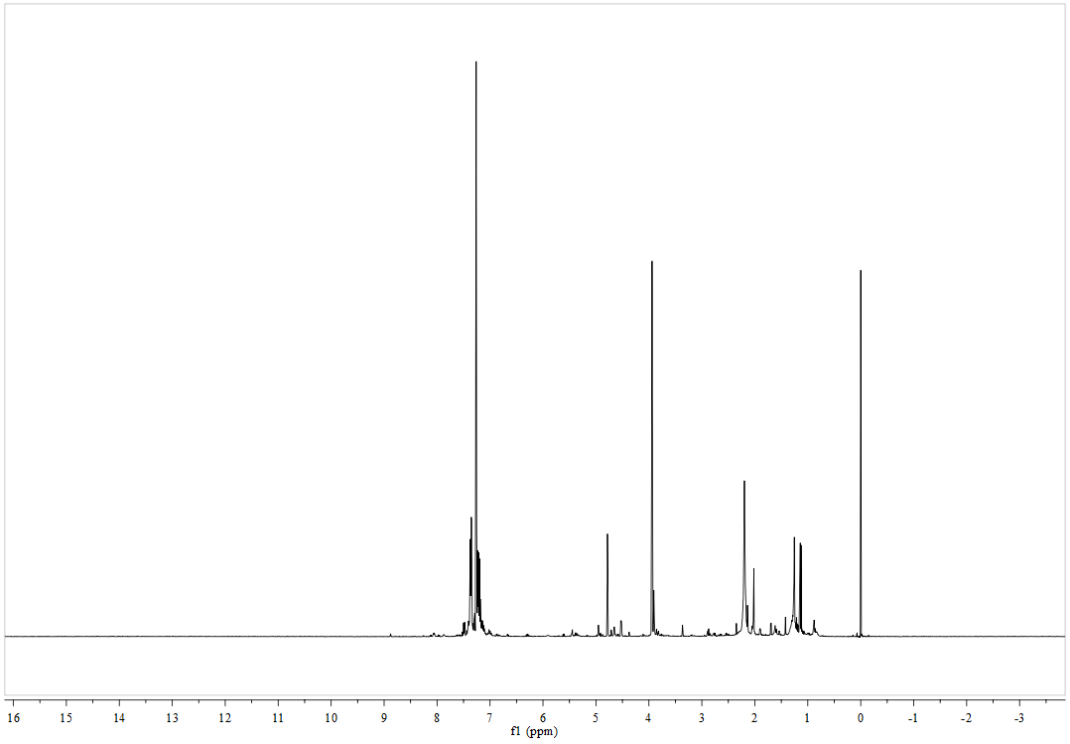


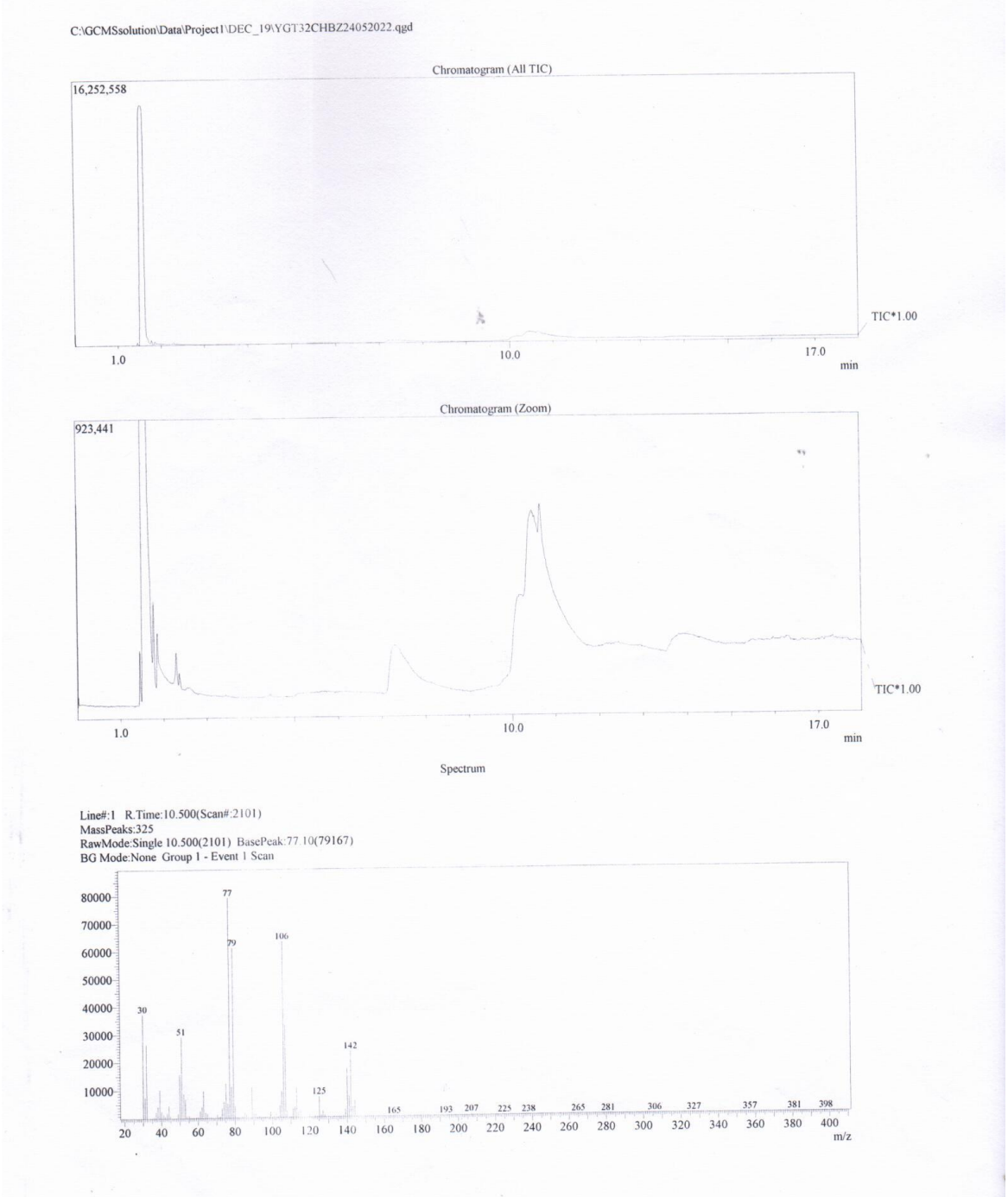
GCMS spectra of reaction mixture of 4-fluorobenzaldehyde reductive amination



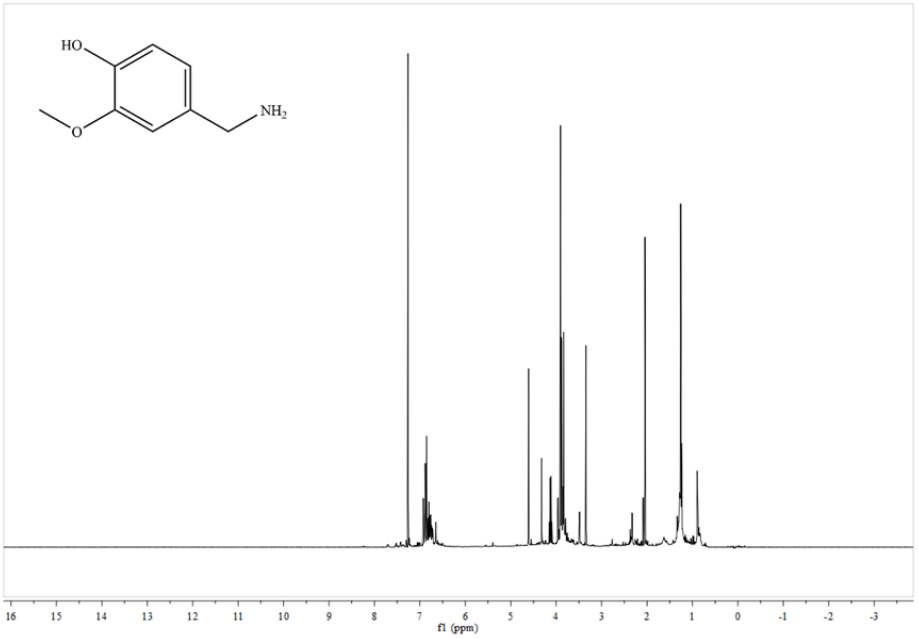
m/z values of (4-fluorophenyl)methanamine



^{1}H NMR spectra of crude (2-chlorophenyl)methanamine.



GCMS spectra of reaction mixture of 2-chlorobenzaldehyde reductive amination



^{1}H NMR spectra of crude 4-(aminomethyl)-2-methoxyphenol

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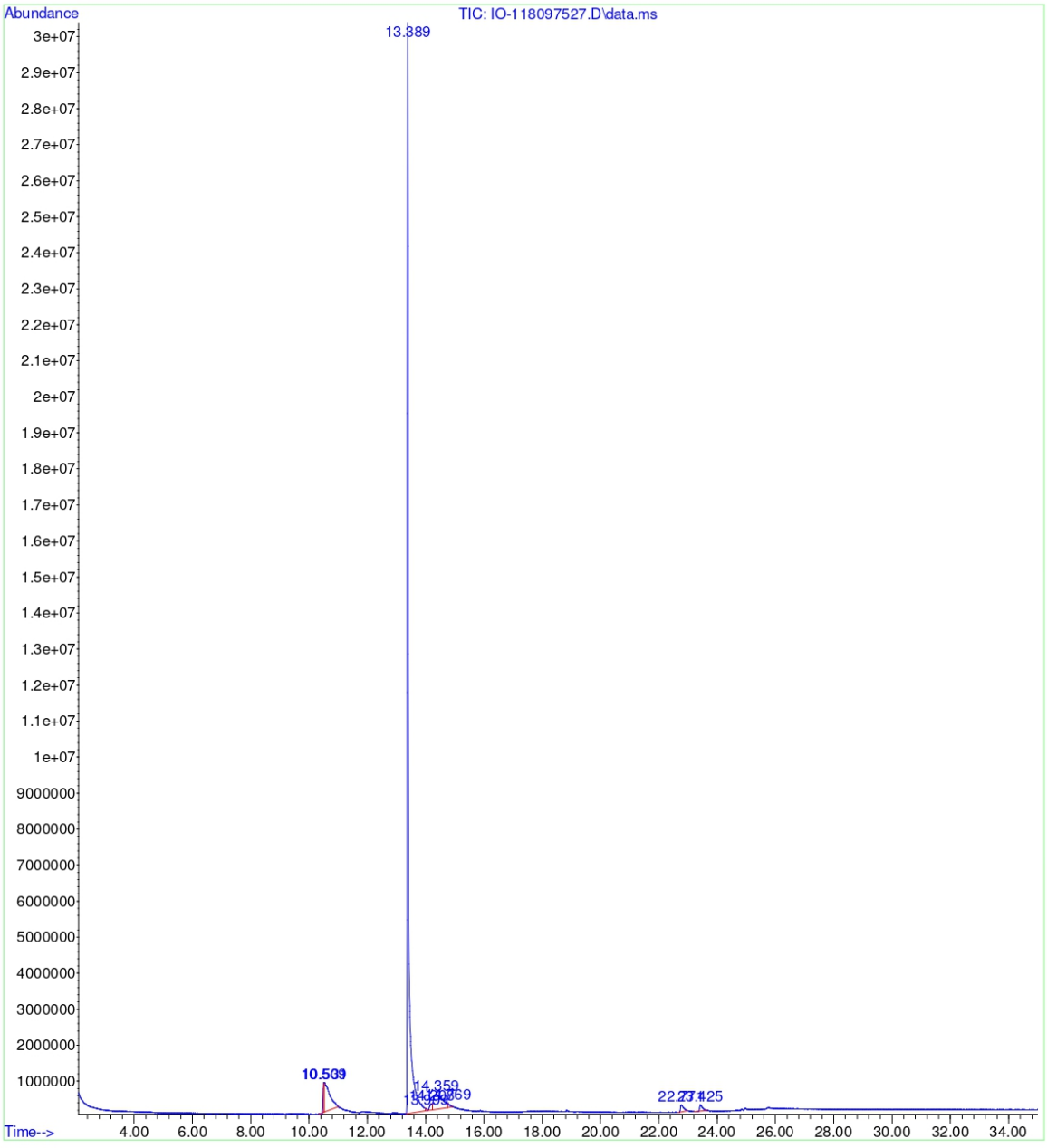
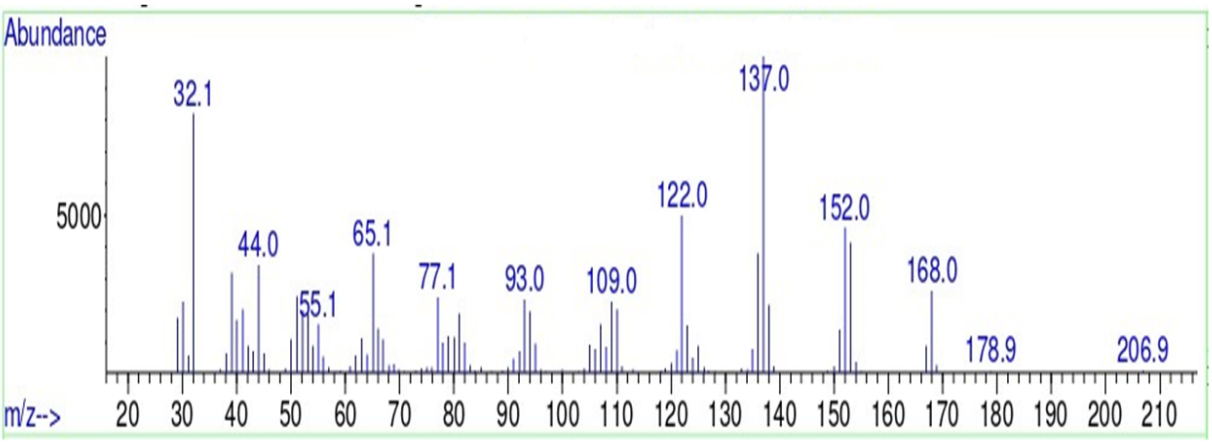
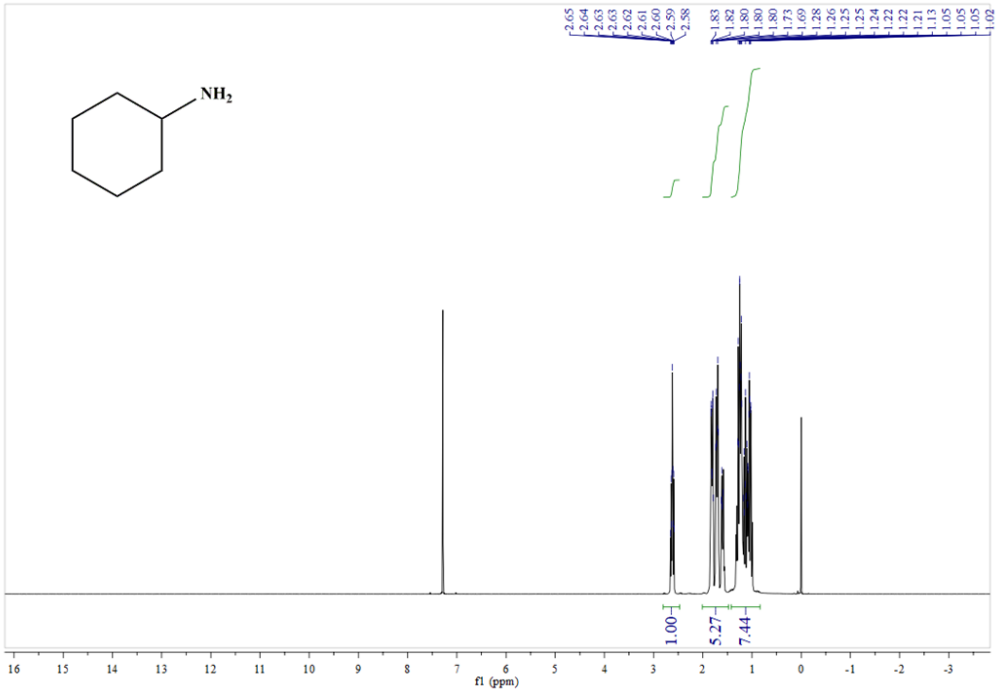


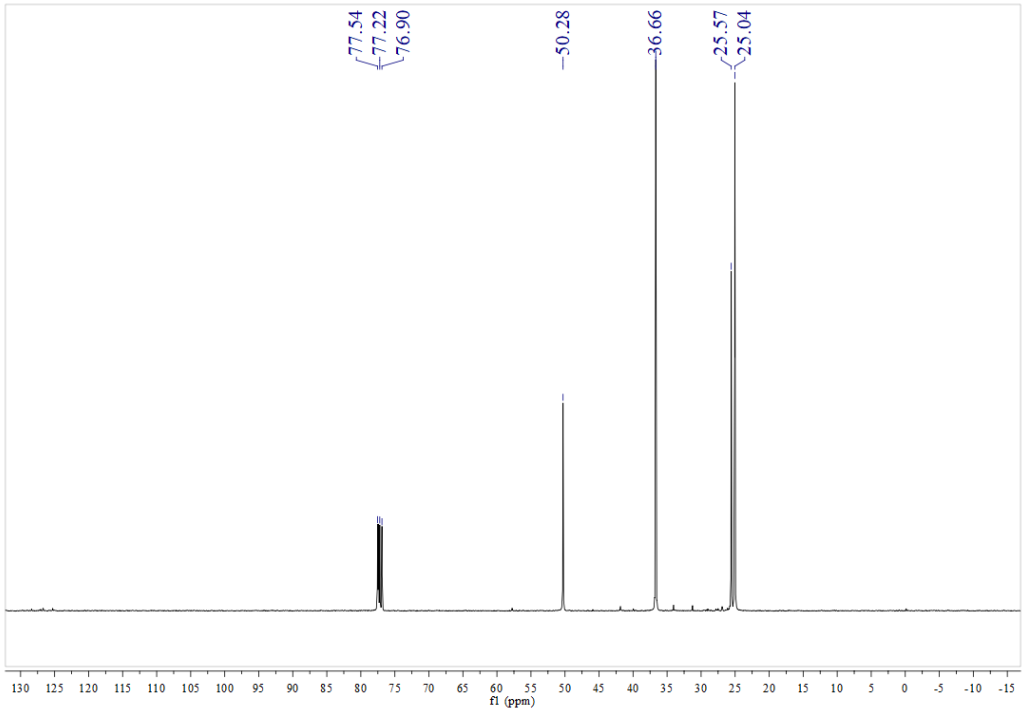
GCMS spectra of reaction mixture of 4-Hydroxy-3-methoxybenzaldehyde reductive amination



m/z values of 4-(aminomethyl)-2-methoxyphenol



^{1}H NMR spectra of cyclohexylamine



^{13}C NMR spectra of cyclohexylamine

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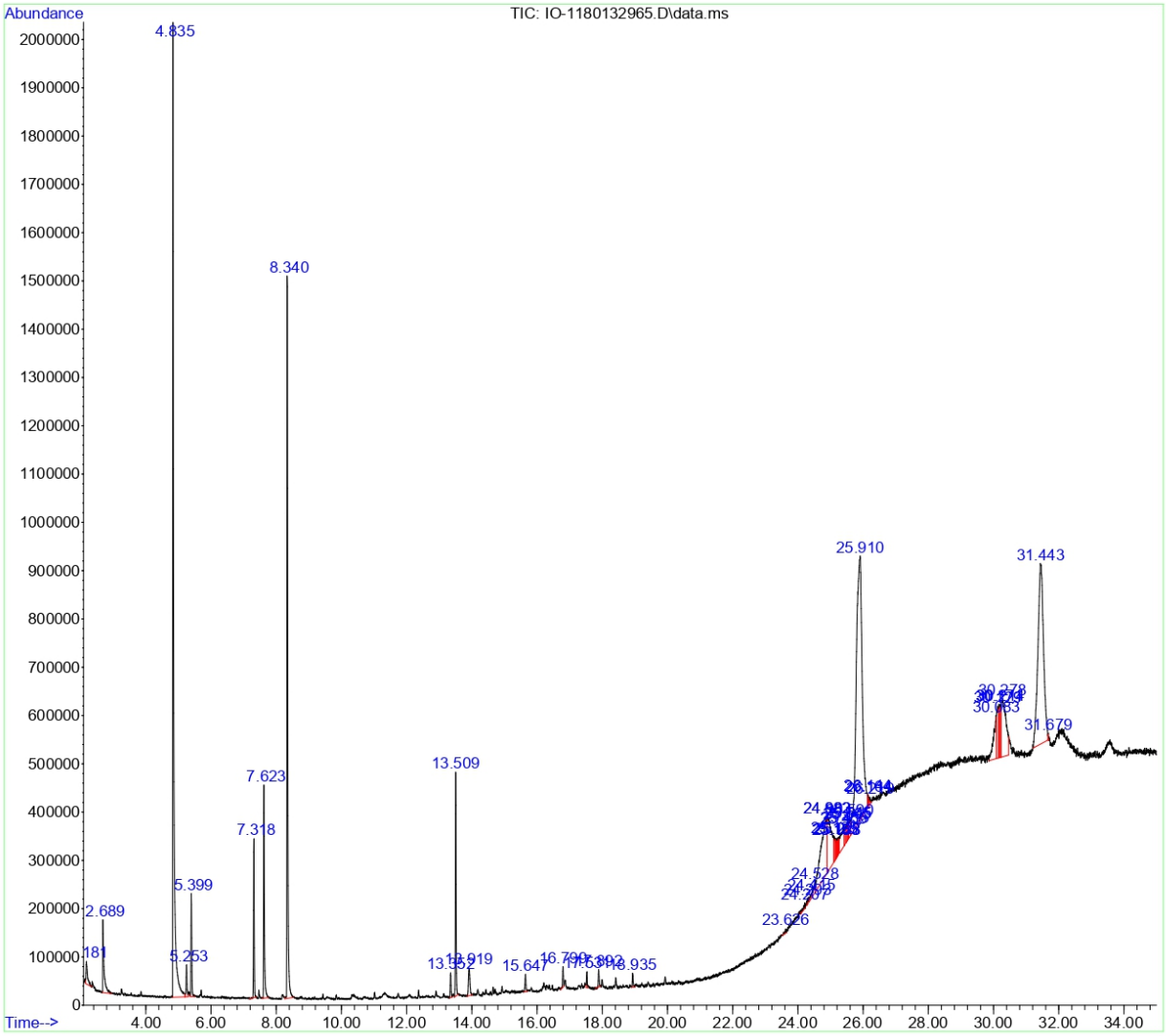
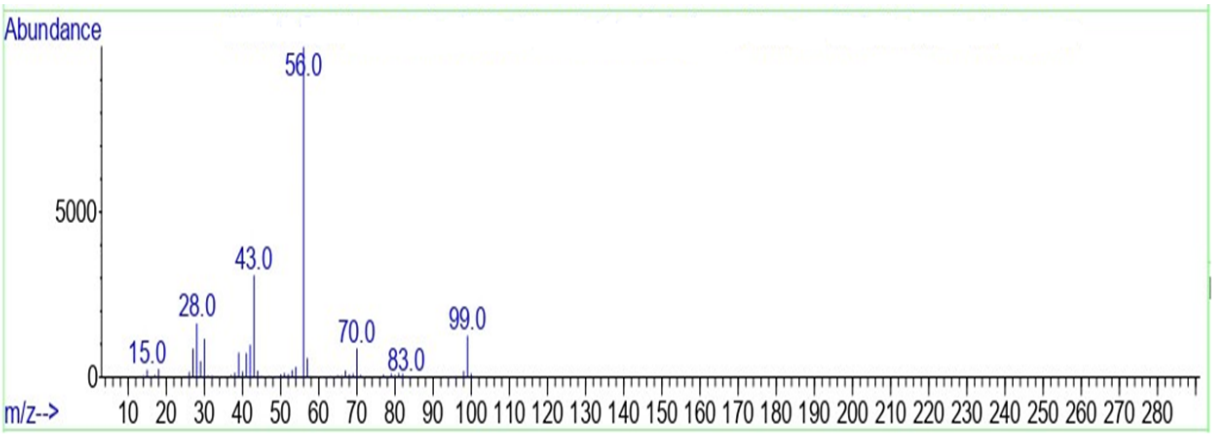
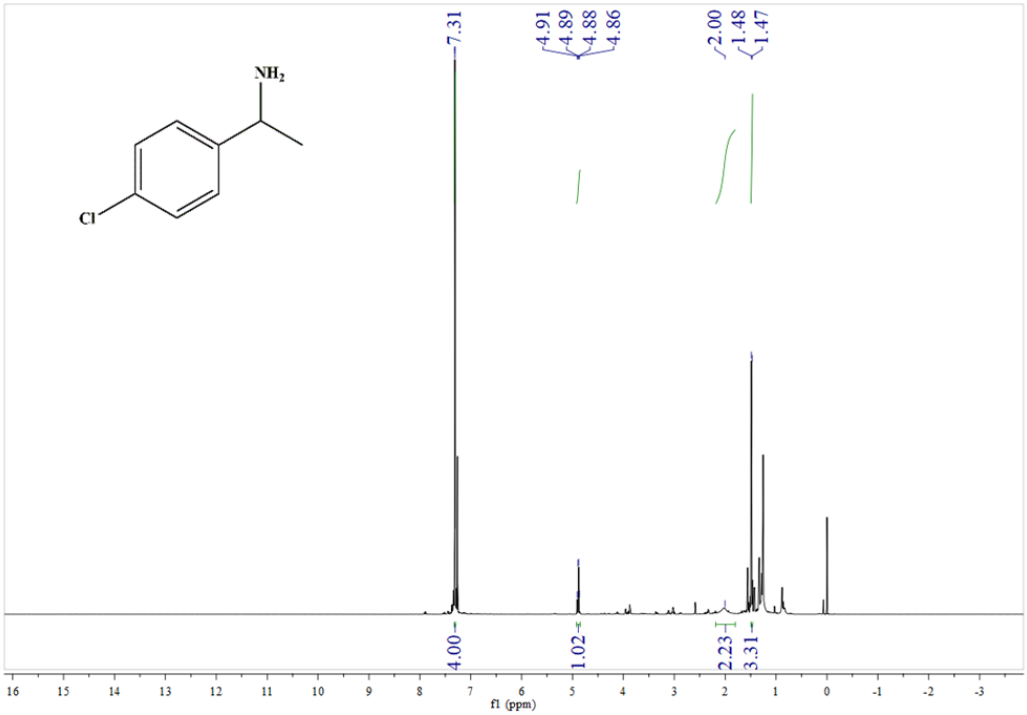


GCMS spectra of reaction mixture of cyclohexanone reductive amination



m/z values of cyclohexylamine



^{1}H NMR spectra of (4-chlorophenyl)ethan-1-amine

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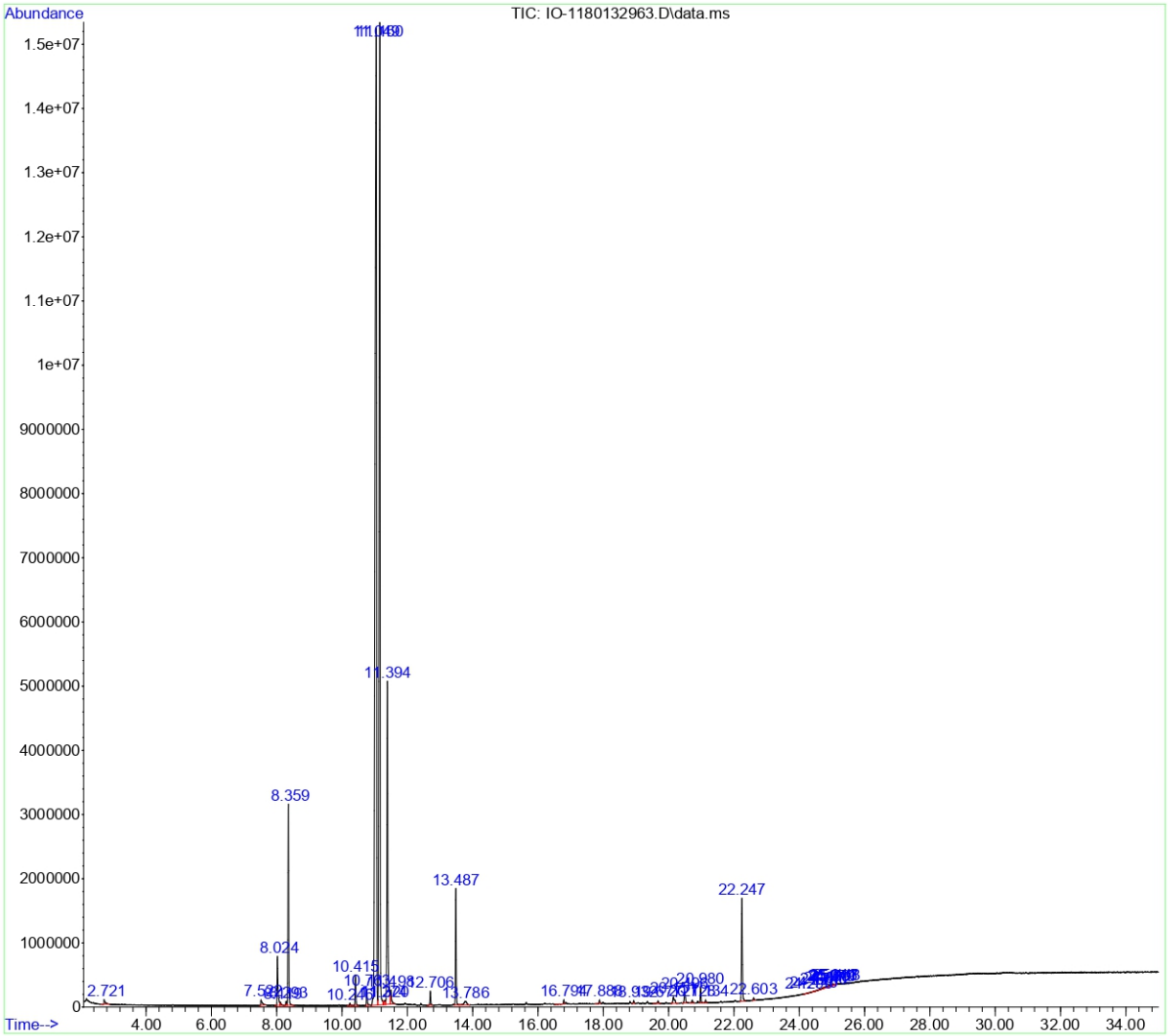
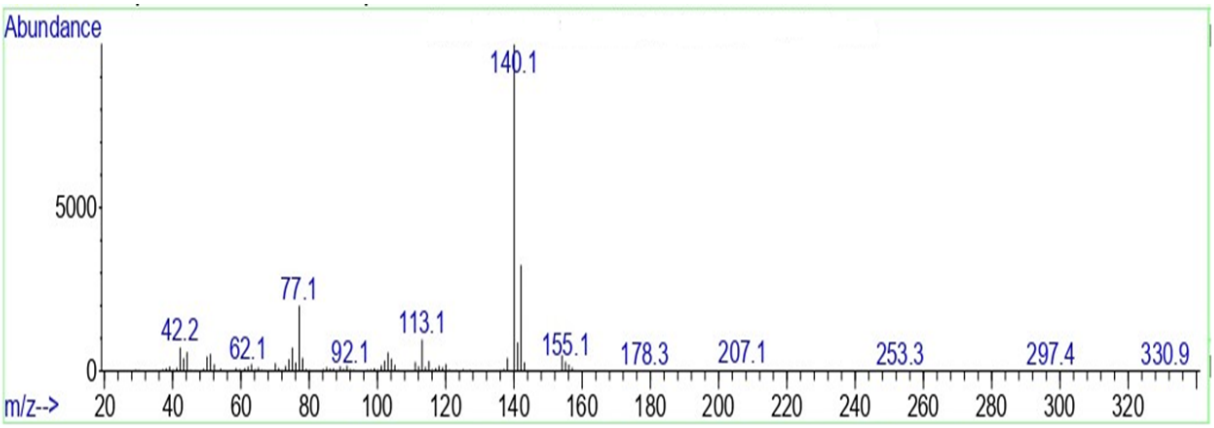


GCMS spectra of reaction mixture of 4-chloroacetophenone reductive amination



m/z values of (4-chlorophenyl)ethan-1-amine