Electronic Supplementary Material (ESI) for RSC Advances.

Copper-Catalyzed selective C-N Bond Formation with Unprotected 2-Amino, 2-Hydroxy and 2-Bromo-5-halopyridine

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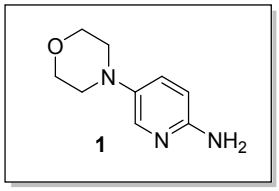
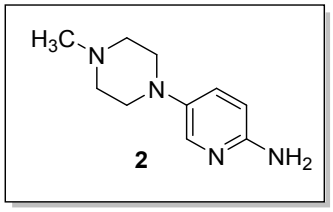
General Methods (Compound 1-22). 2-Amino-5-iodo pyridine/2-Hydroxy-5-iodo pyridine (0.5 mmol), CuI (10 mol%), K_3PO_4 (3.0 equiv) was taken in a sealed tube. After purging it with nitrogen, dry isopropanol was added to it followed by addition of amine and ethylene glycol (10 mol%). The reaction mixture was again flashed with nitrogen and then the tube was finally sealed under nitrogen atmosphere. The reaction mixture was heated to 110 ºC for 10-12 hours. Formation of product was confirmed after checking the TLC. Then the reaction mixture was passed through celite bed using methanol. Product was purified by Flash chromatography using Methanol/$CHCl_3$ system.



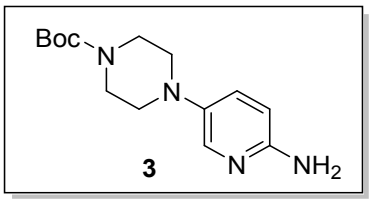
1

*5-Morpholinopyridin-2-amine, **1***. Brown gummy solid, yield 87%. 1H NMR (600 MHz, CD_3OD) δ 7.59 (br s, 1H), 7.32 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 6.59 (d, *J* = 9.0 Hz, 1H), 3.81 (t, *J* = 4.8 Hz, 4H), 2.98 (t, *J* = 4.8 Hz, 4H); ^{13}C NMR (150 MHz, CD_3OD) δ 155.9, 136.0, 131.4, 111.3, 68.1, 52.4. HRMS (ESI): m/z calcd for $C_9H_{14}N_3O$ $[M+H]^+$ 180.1138; found 180.1148.



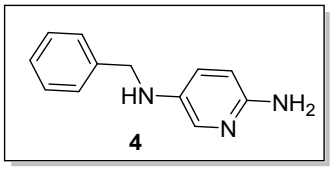
2

*5-(4-Methylpiperazin-1-yl)pyridine-2-amine,**2***. Brown gummy solid, yield 92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 3.0 Hz, 1H), 7.17(dd, *J* = 8.7 Hz, 2.7 Hz, 1H), 6.48 (d, *J* = 8.7 Hz, 1H), 3.05 (t, *J* = 5.1 Hz, 4H), 2.58 (t, *J* = 4.8 Hz, 4H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.1, 140.7, 137.0, 129.0, 109.3, 55.2, 50.8, 46.2. HRMS (ESI): m/z calcd for $C_{10}H_{17}O_4$ $[M+H]^+$ 193.1454; found 193. 1458.

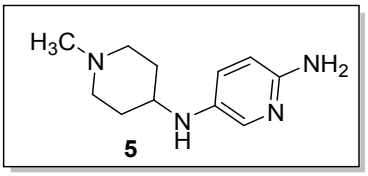


3

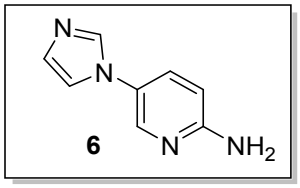
*t-Butyl 4-(6-Aminopyridin-3-yl)piperazine-1-carboxylate, **3***. Brown gummy solid, yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (br s, 1H), 7.16 (dd, *J* = 8.7 Hz, 2.7 Hz, 1H), 6.48 (d, *J* = 8.7 Hz, 1H), 3.56 (t, *J* = 5.1 Hz, 4H), 2.94 (t, *J* = 5.1 Hz, 4H), 1.47 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.8, 153.3, 140.6, 136.3, 130.4, 109.8, 80.1, 51.0, 28.5. HRMS (ESI): m/z calcd for $C_{14}H_{23}N_4O_2$ $[M+H]^+$ 279.1822; found 279.1821.



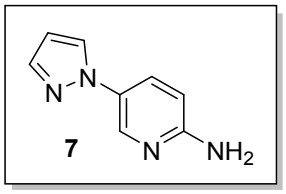
*N5-Benzylpyridine-2,5-diamine, **4***. Brown gummy solid, yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 3.0 Hz, 1H), 7.35-7.26 (m, 5H), 6.91 (dd, *J* = 8.7 Hz, 2.7 Hz, 1H), 6.44 (d, *J* = 8.7 Hz, 1H), 4,26 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.3, 139.3, 137.6, 132.2, 128.8, 127.7, 127.5 125.5, 110.0, 49.5; HRMS (EI): m/z calcd for $C_{12}H_{13}N_3$ $[M]^+$ 199.1109; found 199.1095.



*N5-(1-methylpiperidin-4-yl)pyridine-2,5-diamine **5***. Yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.7 Hz, 1H), 6.88 (dd, *J* = 8.4 Hz, 2.7 Hz, 1H), 6.43 (d, *J* = 8.7 Hz, 1H), 4.04 (br s, -NH), 3.15-3.08 (m, 1H), 2.79 (m, 2H), 2.28 (s, 3H), 2.11-1.98 (m, 4H), 1.49-1.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 136.3, 134.5, 126.2, 109.7, 54.6, 51.2, 46.3, 32.8; HRMS (EI): m/z calcd for $C_{11}H_{18}N_4$ $[M]^+$ 206.1531; found 206.1524.

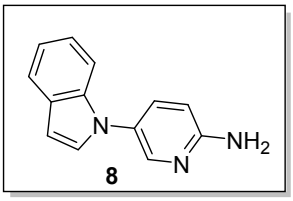


*5-(1H-Imidazol-1-yl)pyridin-2-amine **6***. Brown gummy solid, yield 85%. ^{1}H NMR (600 MHz, CD_3OD) δ 8.07 (d, *J* = 2.4 Hz, 1H), 7.94 (s, 1H), 7.61 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.39 (s, 1H), 7.11 (s, 1H), 6.67 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 160.7, 141.9, 137.3, 133.9, 129.8, 126.0, 120.6, 110.4. HRMS (ESI): m/z calcd for $C_8H_9N_4$ $[M+H]^+$ 161.0828; found 161.0832.



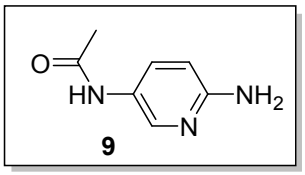
*5-(1H-pyrazol-1-yl)pyridin-2-amine **7***. Off white solid, yield 82%. ^{1}H NMR (300 MHz, CD_3OD) δ 8.19 (d, *J* = 2.1 Hz, 1H), 8.00 (d, *J* = 2.4 Hz, 1H), 7.74 (dd, *J* = 9.0 Hz, 2.7 Hz, 1H), 7.66 (d, *J* = 1.5 Hz, 1H),

6.65 (d, *J* = 9.0 Hz, 1H), 6.47 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 159.9, 141.7, 140.2, 132.3, 129.3, 110.2, 108.2. HRMS (ESI): m/z calcd for $C_8H_8N_4$ $[M+Na]^+$ 183.0647; found 183.0643.



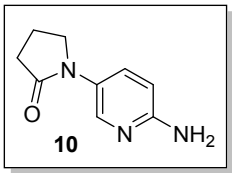
8

5-(1H-Indol-1-yl)pyridin-2-amine ***8***. Yellow gummy solid, yield 88%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.28 (s, 1H), 7.24-7.16 (m, 4H), 6.69 (d, *J* = 3.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 136.8, 135.4, 129.0, 128.3, 122.5, 121.2, 120.4, 110.2, 103.4; HRMS (EI): m/z calcd for $C_{13}H_{11}N_3$ $[M]^+$ 209.0953; found 209.0950.



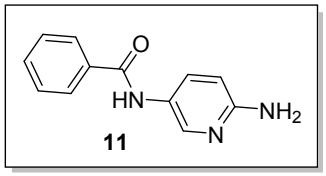
9

N-(6-Aminopyridin-3-yl)acetamide ***9***. Brown gummy solid, yield 76%. ^{1}H NMR (300 MHz, $CDCl_3$ + 1 drop CD_3OD) δ 7.85 (d, *J* = 2.1 Hz, 1H), 7.69 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.43 (d, *J* = 8.7 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 171.7, 157.9, 140.4, 133.5, 127.1, 110.0, 23.3. HRMS (ESI): m/z calcd for $C_7H_9N_3O$ $[M+Na]^+$ 174.0644; found 174.0645.



10

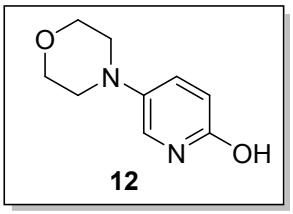
1-(6-Aminopyridin-3-yl)pyrrolidin-2-one ***10***. Brown gummy solid, yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (br s, 1H), 7.88 (dd, *J* = 11.1 Hz, 2.4 Hz, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 3.78 (t, *J* = 6.9 Hz, 2H), 2.55 (t, *J* = 7.8 Hz, 2H), 2.19-2.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 174.9, 156.2, 139.9, 132.3, 109.3, 64.2, 49.4, 32.5, 18.6. HRMS (EI): m/z calcd for $C_9H_{11}N_3O$ $[M]^+$ 177.0902; found 177.0891.



11

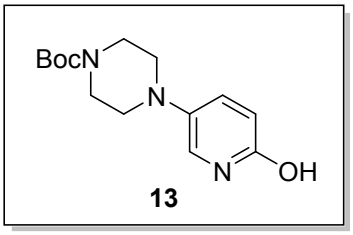
N-(6-Aminopyridin-3-yl)benzamide ***11***. Yield 70%. ^{1}H NMR (300 MHz, $CDCl_3$ + 1 drop CD_3OD) δ 8.01 (br s, 1H), 7.86-7.80 (m, 3H), 7.48-7.36 (m, 3H), 7.62-7.49 (m , 3H), 6.52 (d, *J* = 9.0 Hz, 1H); ^{13}C

NMR (75 MHz, CD_3OD) 168.9, 158.2, 141.7, 135.8, 134.5, 132.9, 129.6, 128.5, 127.0, 109.9. HRMS (EI): m/z calcd for $C_{12}H_{11}N_3O$ $[M]^+$ 213.0902; found 213.0888.



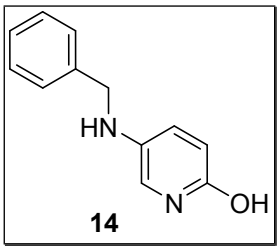
12

5-Morpholinopyridin-2-ol ***12***. Brown solid. M.p- 218 ^oC. Yield 82%. ^1H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 9.6 Hz, 3.0 Hz, 1H), 6.85 (d, *J* = 3.0 Hz, 1H), 6.57 (d, *J* = 9.9 Hz, 1H), 3.81 (t, *J* = 4.5 Hz, 4H), 2.87 (t, *J* = 4.8 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 137.6, 135.2, 120.7, 120.3, 66.8, 51.1; HRMS (EI): m/z calcd for $C_9H_{12}N_2O_2$ $[M]^+$ 180.0899; found 180.0897.



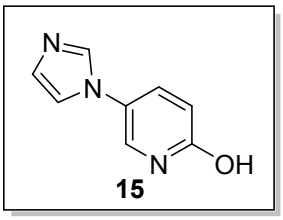
13

tert-Butyl 4-(6-hydroxypyridin-3-yl)piperazine-1-carboxylate ***13***. Green gummy solid. Yield 80%. δ ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 9.6 Hz, 3.0 Hz, 1H), 7.36 (dd, *J* = 6.6 Hz, 1.8 Hz, 1H), 6.84 (d, *J* = 3.0 Hz, 1H), 3.55 (t, *J* = 4.8 Hz, 4H), 2.82 (t, *J* = 4.8 Hz, 4H), 1.48 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.5, 141.7, 138.2, 134.4, 120.6, 106.9, 80.0, 50.8, 28.3; HRMS (EI): m/z calcd for $C_{14}H_{21}N_3O_3$ $[M]^+$ 279.1583; found 279.1583.



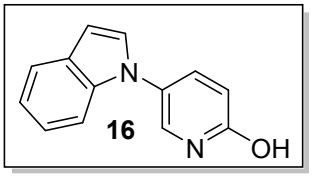
14

5-(Benzylamino)pyridin-2-ol ***14***. Brown gummy solid. Yield 72%. ^1H NMR (600 MHz, $CDCl_3$ + 1 drop CD_3OD) δ 7.25-7.23 (m, 3H), 7.19-7.17 (m, 2H), 7.13 (dd, *J* = 6.6 Hz, 3.0 Hz, 1H), 6.43-6.41 (m, 2H), 4.04 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$ + 1 drop CD_3OD) δ 160.8, 138.0, 135.9, 132.1, 128.4, 127.24, 127.21, 120.1, 113.3, 29.4. HRMS (EI): m/z calcd for $C_{12}H_{12}N_2O$ $[M]^+$ 200.0950; found 200.0946.



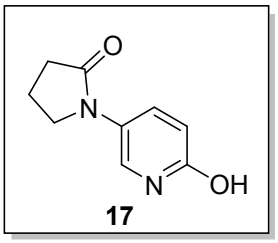
15

5-(1H-Imidazol-1-yl)pyridin-2-ol ***15***. White solid. M.p- 195 °C Yield 91%. ^{1}H NMR (600 MHz, $CDCl_3$ + 1 drop CD_3OD) δ 7.64 (s, 1H), 7.51-7.48 (m, 2H), 7.07 (d, *J* = 5.4 Hz, 2H), 6.61 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$ + 1 drop CD_3OD) δ 163.1, 137.7, 135.9, 129.6, 128.9, 121.1, 119.7, 119.0. HRMS (EI): m/z calcd for $C_8H_7N_3O$ $[M]^+$ 161.0589; found 161.0554.



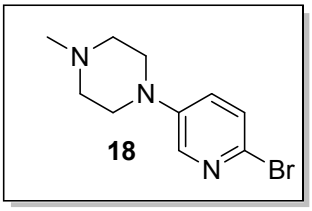
16

5-(1H-indol-1-yl)pyridine-2-ol ***16***. Grey solid. M.p- 180 °C (decomposed). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.22-7.17 (m, 3H), 6.68 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.7, 128.9, 128.0, 122.9, 121.4, 120.8, 109.9, 104.0. HRMS (EI) Calcd for $C_{13}H_{10}N_2O$ $[M]^+$ 210.0793, found 210.0789.



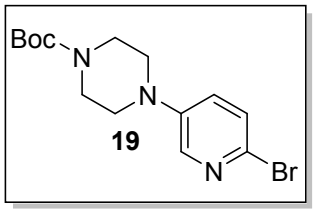
17

1-(6-Hydroxypyridin-3-yl)pyrrolidin-2-one ***17***. Green solid. M.p- 180 °C. Yield 84%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.66 (d, *J* = 3.0 Hz, 1H), 6.57 (d, *J* = 9.6 Hz, 1H), 3.70-3.67 (m, 2H), 2.53 (t, *J* = 7.8 Hz, 2H), 2.14 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 136.8, 126.7, 122.3, 120.0, 63.8, 48.6, 31.8, 17.9. HRMS (EI): m/z calcd for $C_9H_{10}N_2O_2$ $[M]^+$ 178.0742; found 178.0734.

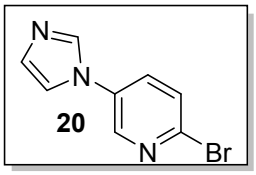


18

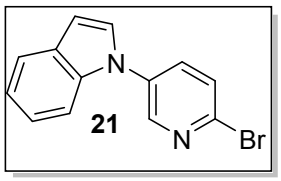
1-(6-bromopyridin-3-yl)-4-methylpiperazine ***18***. Yellow gummy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 3.3 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.06 (dd, *J* = 8.7 Hz, 5.7 Hz, 1H), 3.20 (t, *J* = 4.8 Hz, 2H), 2.56 (t, *J* = 5.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 137.1, 129.8, 126.7, 124.6, 53.7, 47.2, 45.2. HRMS (ESI) Calcd for $C_{10}H_{15}BrN_3$ $[M+H]^+$ 258.0430; found 258.0427.



Tert-butyl 4-(6-bromopyridin-3-yl)piperazine-1-carboxylate ***19***. Light yellow solid. Mp- 140ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.7 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.09 (dd, *J* = 8.7 Hz, 3.3 Hz, 1H), 3.59 (t, *J* = 5.1 Hz, 4H), 3.14 (t, *J* = 5.4 Hz, 4H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 146.6, 138.5, 131.4, 127.8, 126.2, 80.3, 48.6, 28.5. HRMS (EI): m/z calcd for $C_{14}H_{20}BrN_3O_2$ $[M]^+$ 341.0739; found 341.0746.

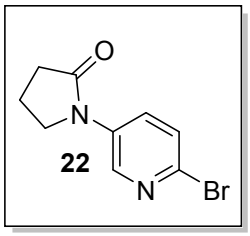


2-bromo-5-(1H-imidazol-1-yl)pyridine ***20.*** Yellow fluffy solid. Mp- 130ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.92 (s, 1H), 7.66-7.59 (m, 2H), 7.29 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 140.4, 135.6, 133.5, 131.6, 131.5, 129.1, 118.1. HRMS (ESI) Calcd for $C_8H_7BrN_3$ $[M+H]^+$ 223.9824, found 223.9824.

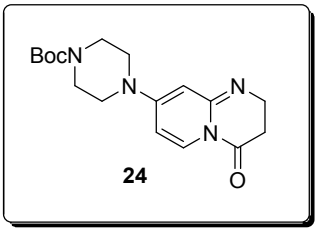


1-(6-bromopyridin-3-yl)-1H-indole ***21.*** Yellow gummy solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.98-6.95 (m, 4H), 6.64-6.55

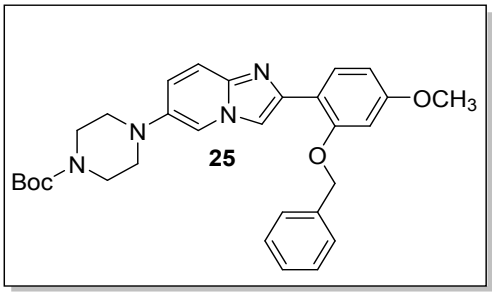
(m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7, 136.7, 130.5, 126.9, 126.1, 121.9, 119.8, 119.7, 119.3,118.9, 115.9, 111.2. HRMS (EI) Calcd for $C_{13}H_9BrN_2$ $[M]^+$ 271.9955, found 271.9951.



1-(6-bromopyridin-3-yl)pyrrolidin-2-one ***22***. Yellow solid. Mp- 85ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.7 Hz, 1H), 8.14 (dd, *J* = 8.7 Hz, 2.7 Hz, 1H), 7.41(d, *J* = 8.7 Hz, 1H), 3.82 (t, *J* = 6.9 Hz, 2H), 2.58 (t, *J* = 8.1 Hz, 2H), 2.23-2.13 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.9, 140.2, 136.1, 135.8, 129.6, 127.9, 47.9, 32.3, 18.0. HRMS (ESI) Calcd for $C_9H_{10}BrN_2O$ $[M+H]^+$ 242.9957, found 242.9967.

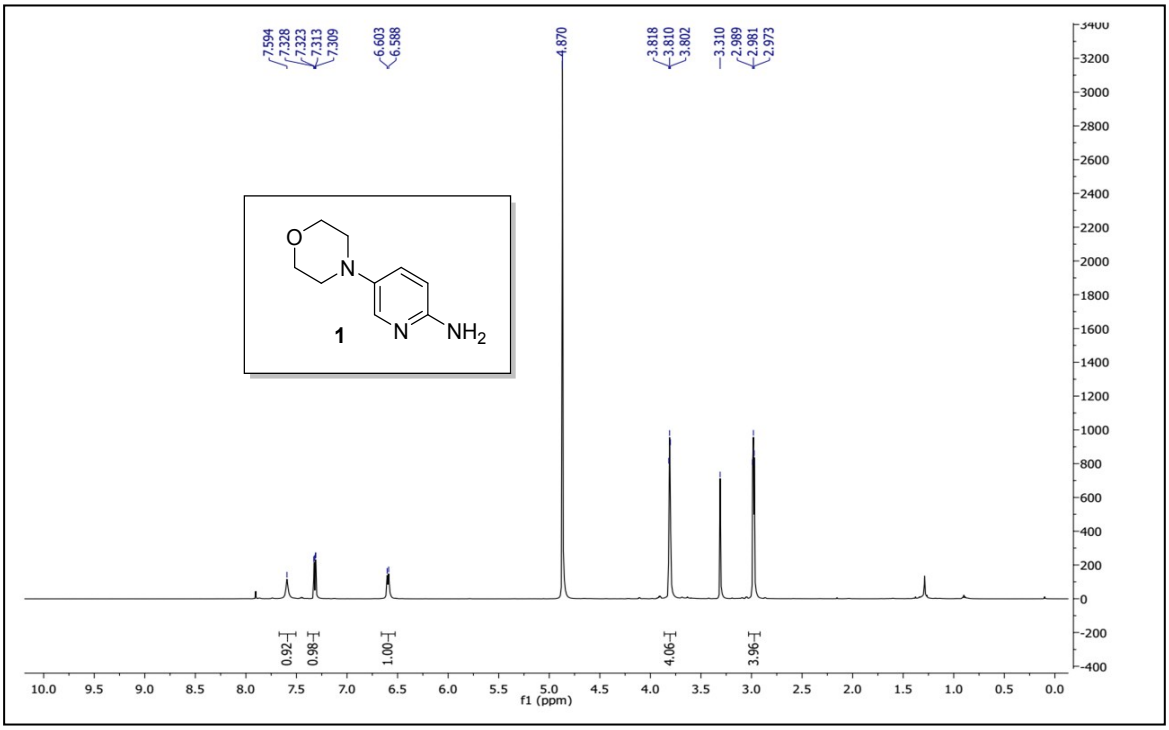


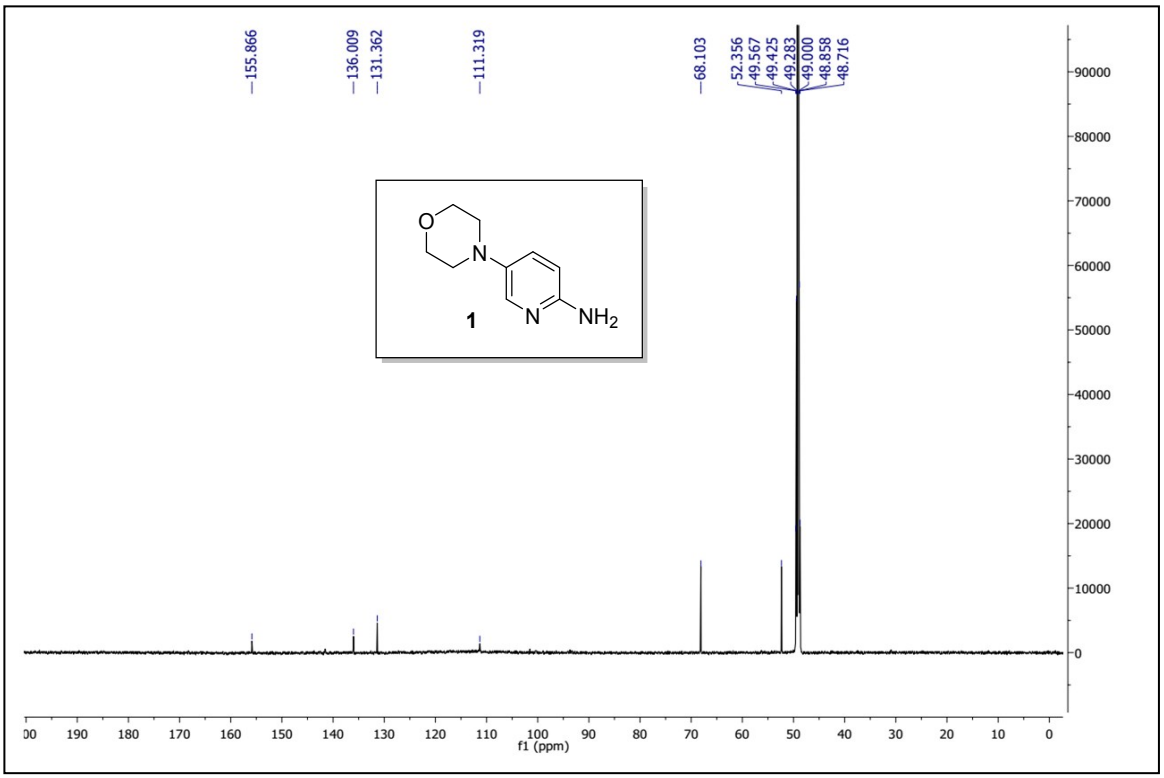
t-Butyl 4-(4-oxo-3,4-dihydro-2H-pyrido[1,2-a]pyrimidin-7-yl)piperazine-1-carboxylate ***24***. *t*-Butyl 4-(6-aminopyridin-3-yl)piperazine-1-carboxylate (1 mmol) was mixed with methyl acrylate (1.5 mmol) in hexafluoroisopropanol (1 mL) in a sealed tube and the mixture was heated to 70 ºC for 12 h. Formation of product was confirmed after checking the TLC. After completion of the reaction, solvents were evaporated and residue was purified by flash chromatography using $CHCl_3$/MeOH/NH_3 system to provided purified compound **24** as brown gummy solid. Yield 87%. ^{1}H NMR (300 MHz,$CDCl_3$) δ 7.45 (dd, *J* = 6.9, 2.7 Hz, 1H), 7.07 (d, *J* = 4.8 Hz, 1H), 6.98 (d, *J* = 2.7 Hz, 1H), 4.37-4.29 (m, 2H), 3.57 (t, *J* = 5.1 Hz, 4H), 2.98 (t, *J* = 5.1 Hz, 4H), 2.76-2.71 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 162.5, 154.4, 140.5, 134.8, 134.6, 123.9, 122.1, 80.3, 72.8, 51.1, 49.1, 29.6, 28.3, 21.7. HRMS (EI): m/z calcd for $C_{17}H_{24}N_4O_3$ $[M]^+$ 332.1848; found 332.1854.

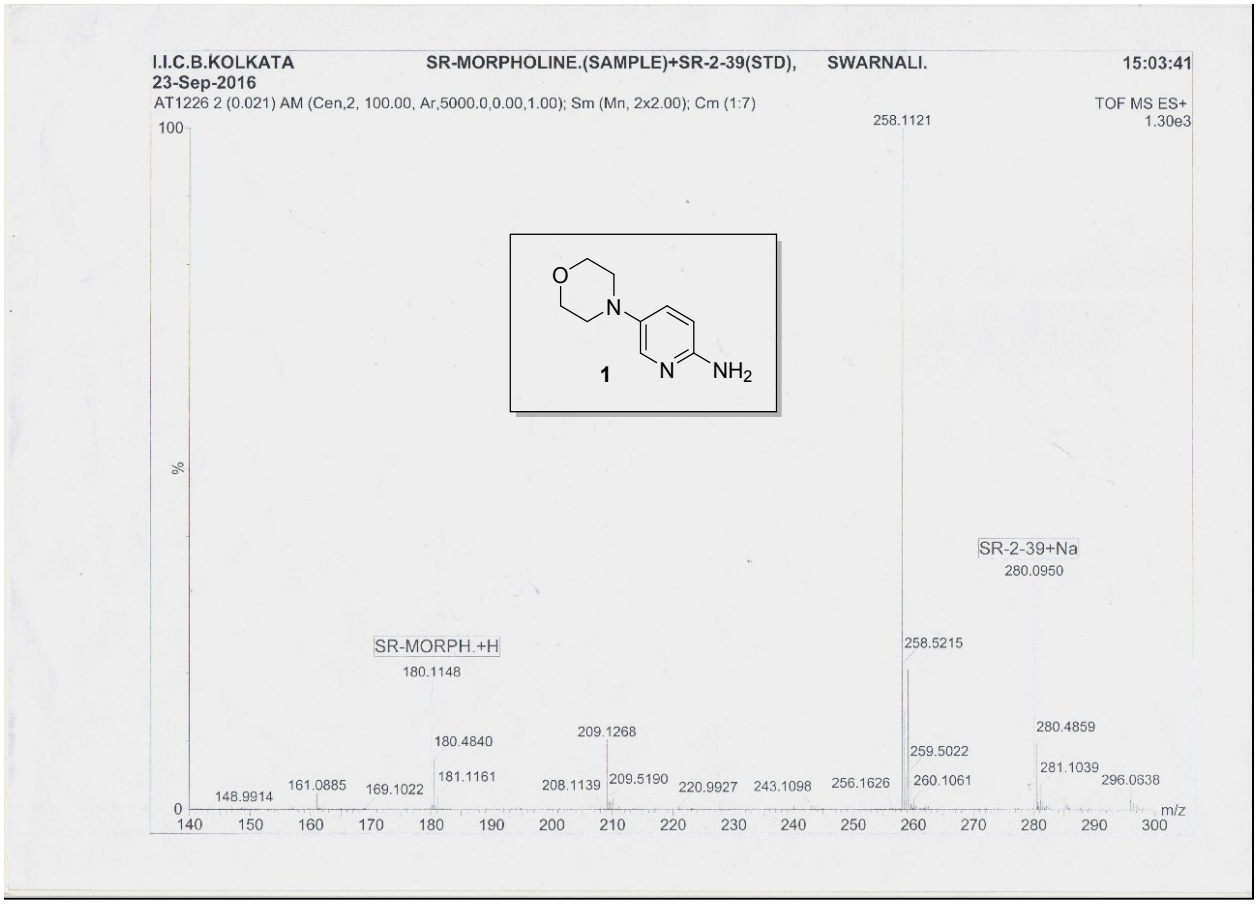


t-Butyl 4-(2-(2-(benzyloxy)-4-methoxyphenyl)imidazo[1,2-a]pyridin-6-yl)piperazine-1-carboxylate ***25.*** 1-(2-(Benzyloxy)-4-methoxyphenyl)-2-bromoethanone (0.54 mmol, **23**), **4** (0.36 mmol) and $NaHCO_3$ (1.08 mmol) were taken in a round bottom flask and refluxed in dry acetone for 4 hours. Formation of product was confirmed after checking the TLC. After completion of the reaction, acetone was evaporated and the organic part was extracted using ethyl acetate. Flash chromatography using Methanol/$CHCl_3$ system provided purified compound **25** as brown gummy solid. Yield 83%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1H), 7.93 (s, 1H), 7.52-7.38 (m, 7H), 7.00 (dd, J = 9.6 Hz, 2.1 Hz, 1H), 6.67-6.60 (m, 2H), 5.19 (s, 2H), 3.82 (s, 3H), 3.59 (t, J = 4.8 Hz, 4H), 2.97 (t, J = 4.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) 160.3, 156.9, 154.7, 141.6, 141.1, 139.6, 136.9, 129.6, 128.8, 128.3, 127.9, 121.8, 117.0, 115.9, 112.4, 112.3, 105.4, 100.0, 80.2, 70.7, 55.6, 50.9, 28.6. HRMS (ESI): m/z calcd for $C_{30}H_{35}N_4O_4$ $[M+H]^+$ 515.2659; found 515.2664.

[1]H, [13]C NMR and Mass spectra of Compound 1:

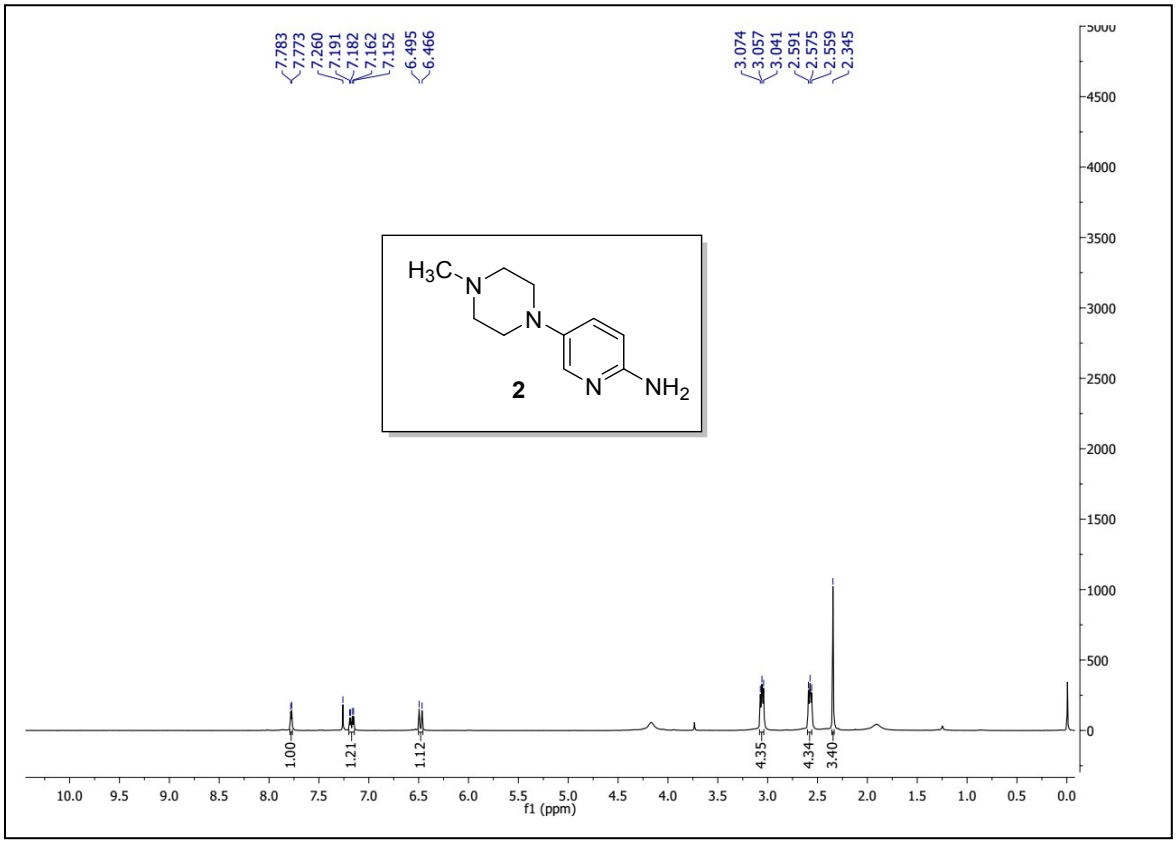


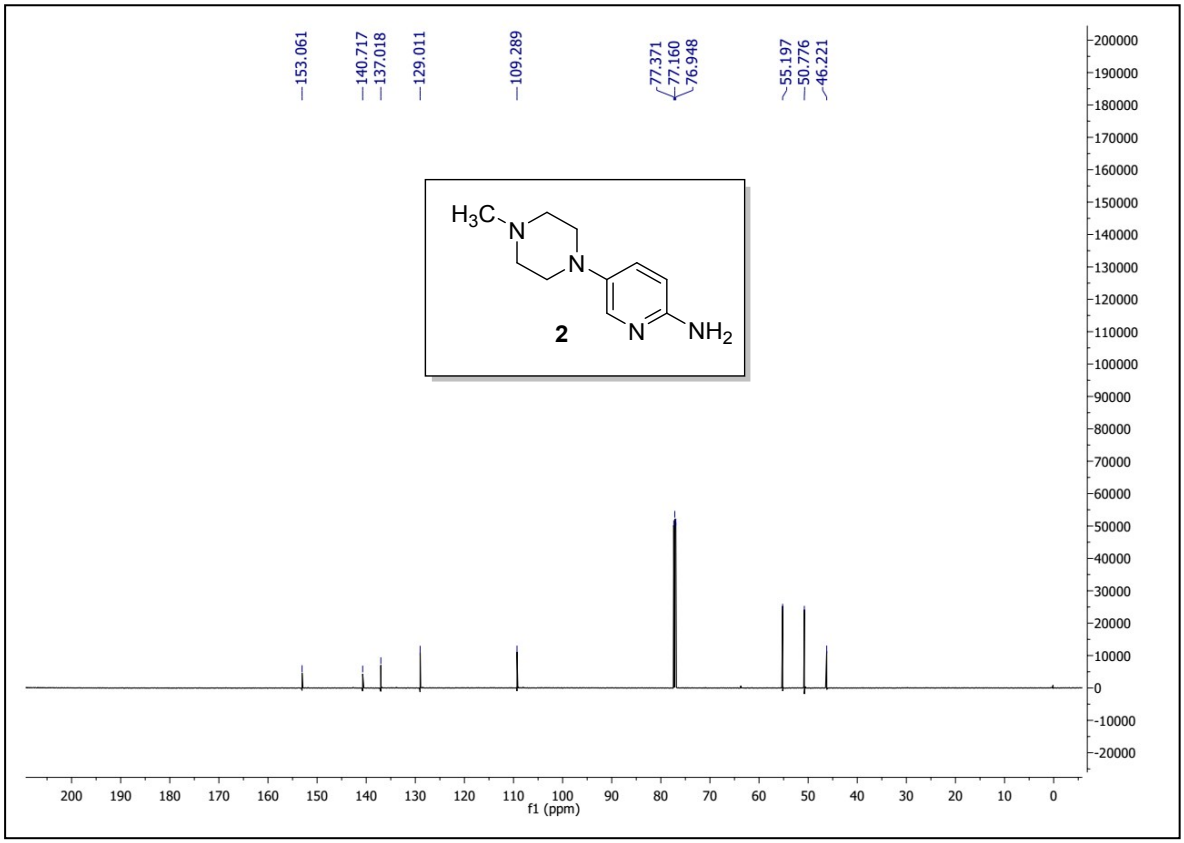


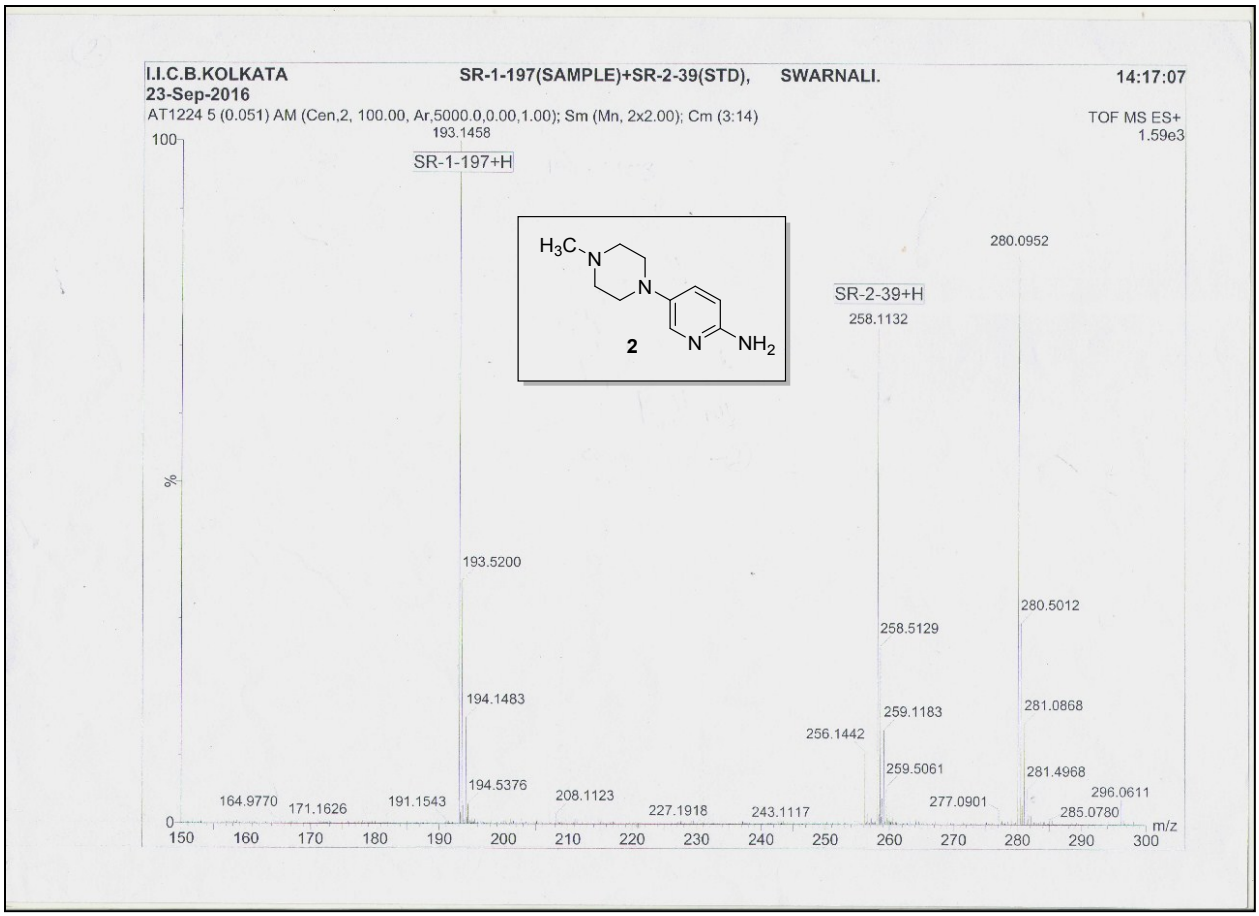


180.1148 is the $[M+H]^+$ peak of **1**. 258.1121 and 280.0950 are the $[M+H]^+$ and $[M+Na]^+$ peak of standard compound.

[1]H, [13]C NMR and Mass spectra of Compound 2:

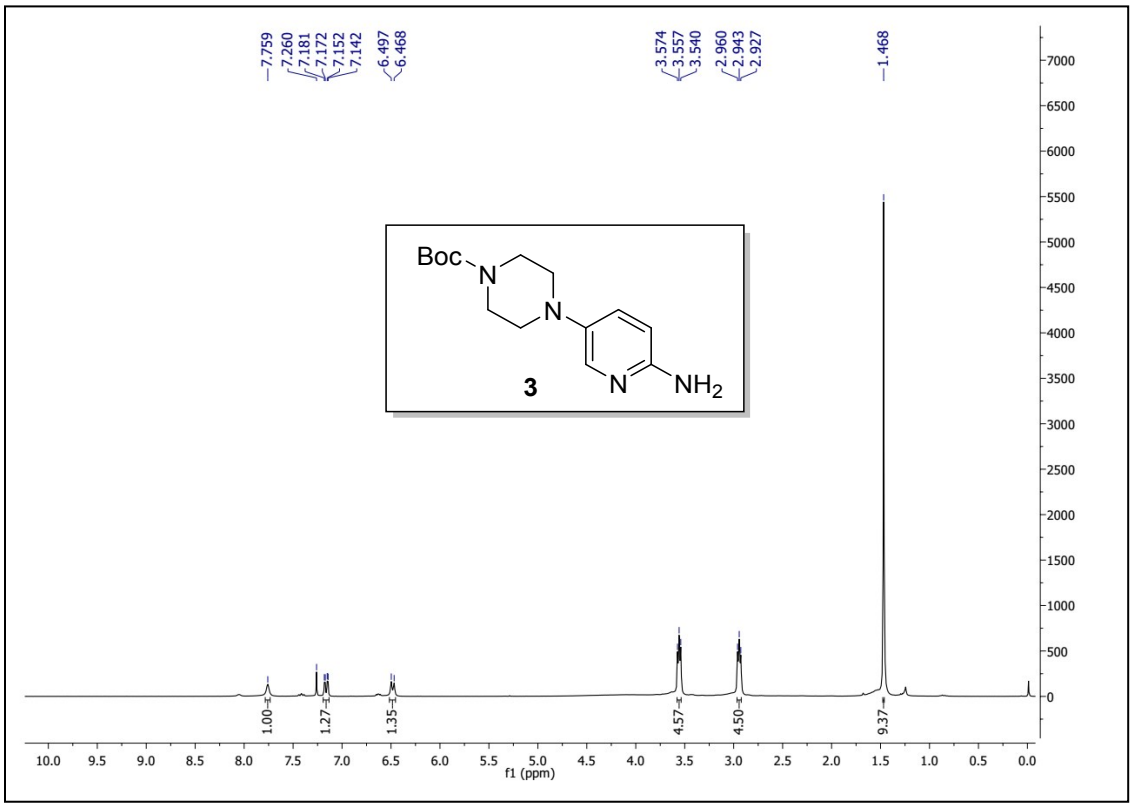


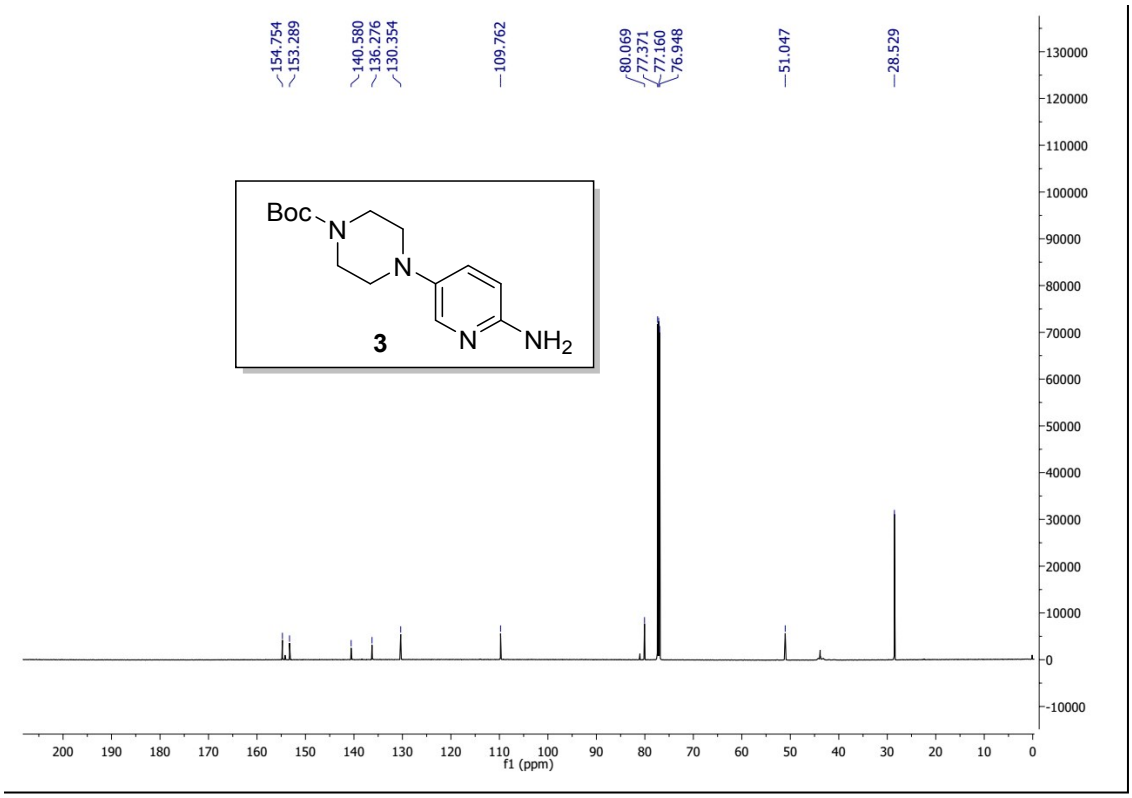


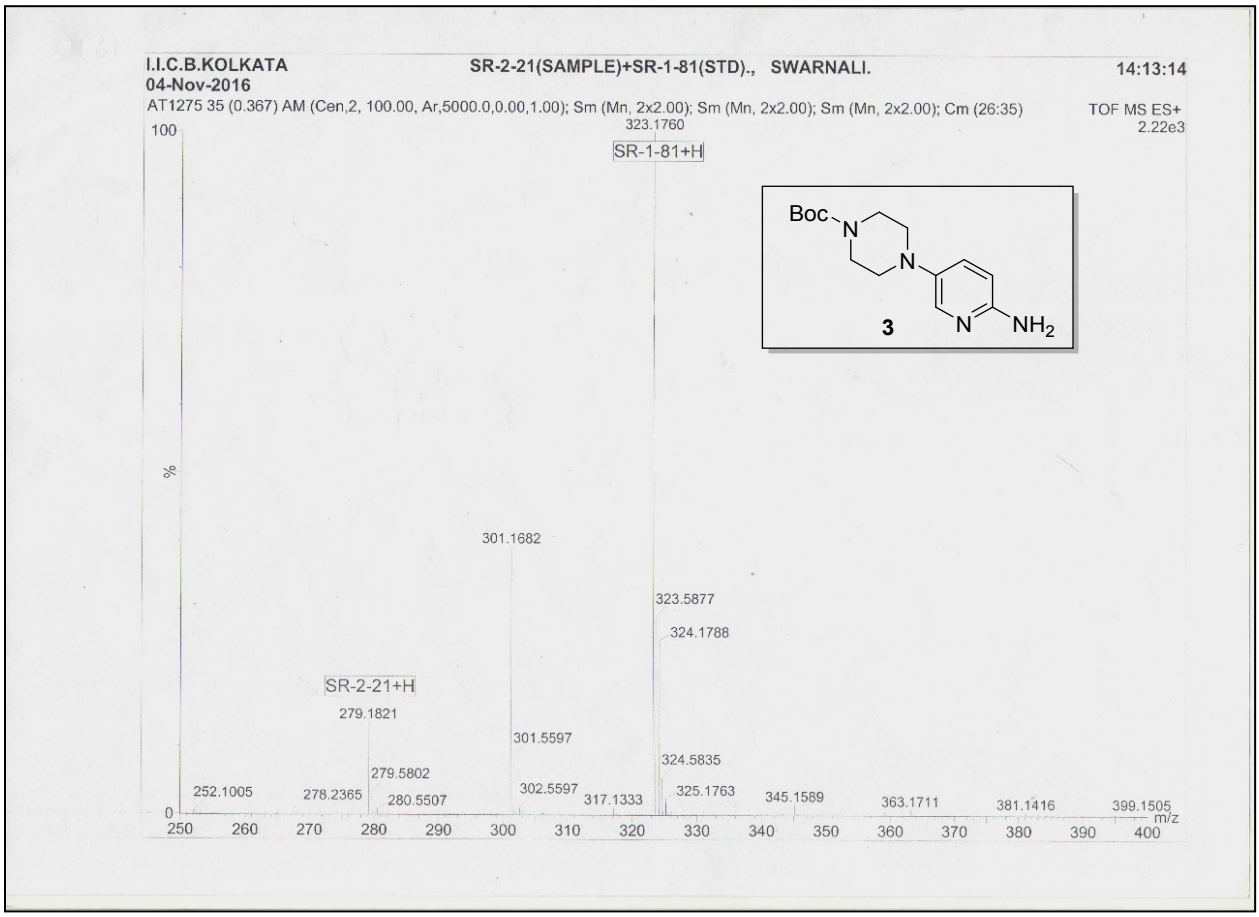


193.1458 is the $[M+H]^+$ peak of **2** and 258.1132 and 289.0952 are the $[M+H]^+$ and $[M+Na]^+$ peak of standard compound.

[1]H, [13]C NMR and Mass spectra of Compound 3:

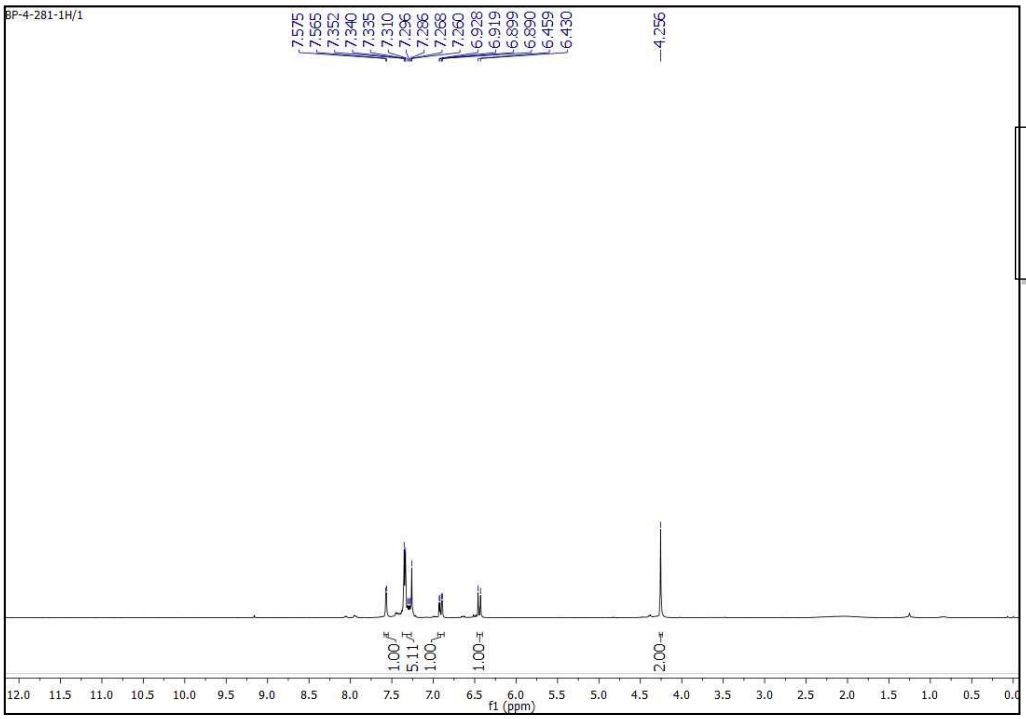


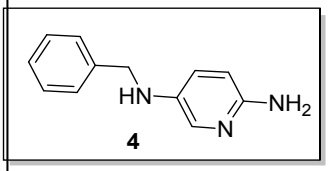


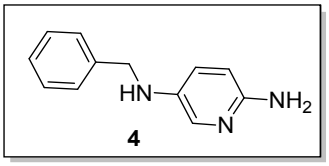


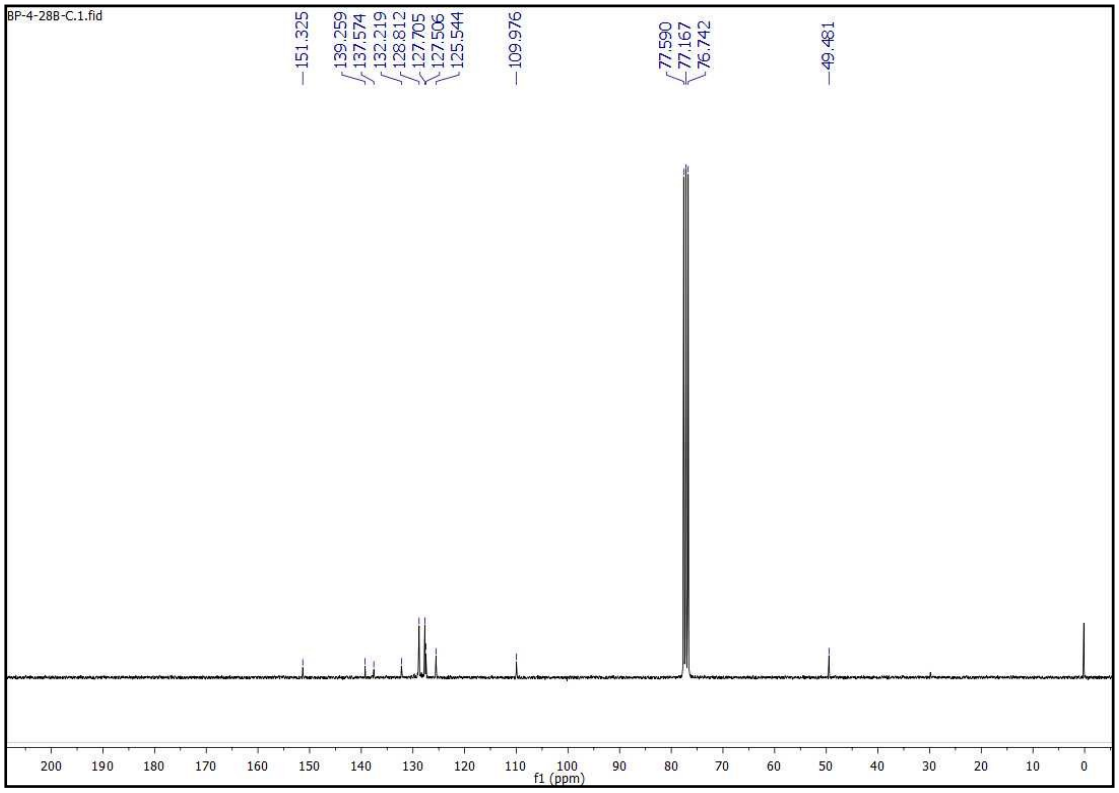
279.1821 is the $[M+H]^+$ peak of **3** and 323.1760 is the $[M+H]^+$ peak of standard.

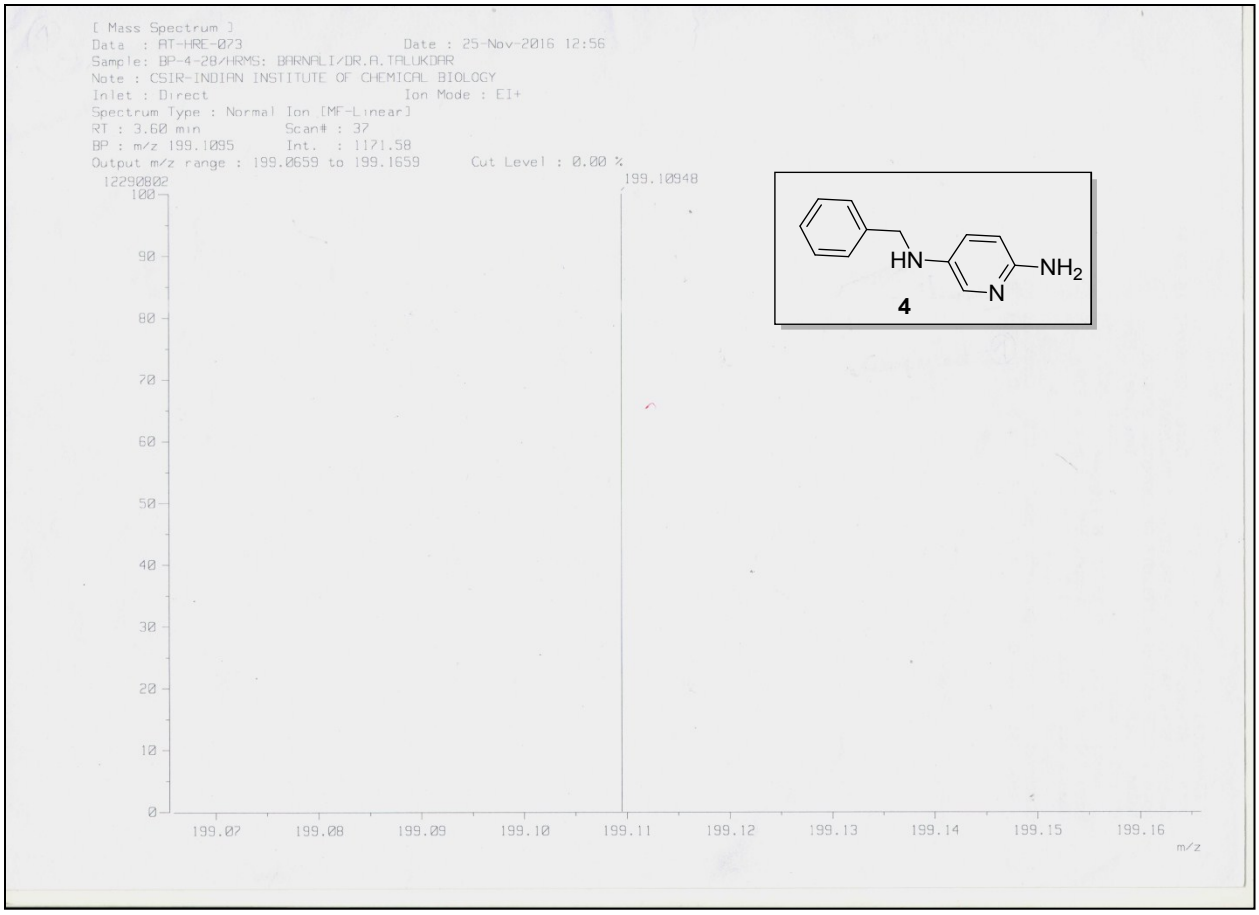
^{1}H and ^{13}C NMR and Mass spectra of Compound 4:





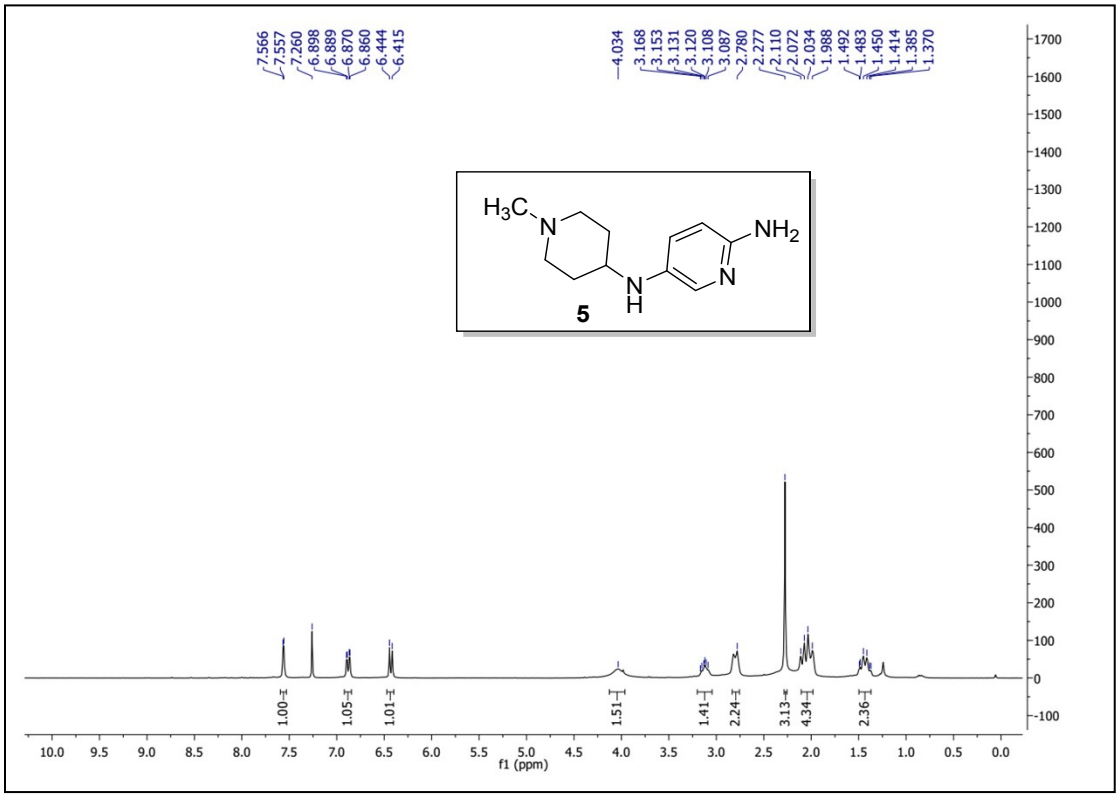


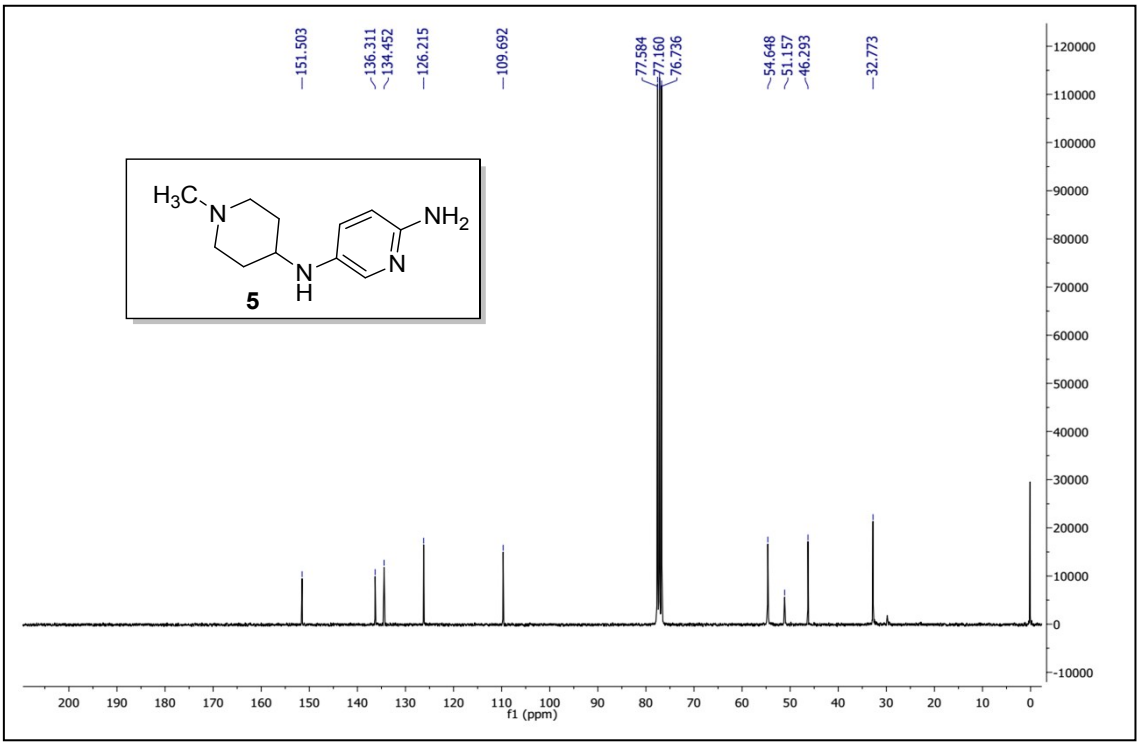

BP-4-288-C.1.fid
151.325
139.259
137.574
132.219
128.812
127.705
127.506
125.544
109.976
77.590
77.167
76.742
49.481
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

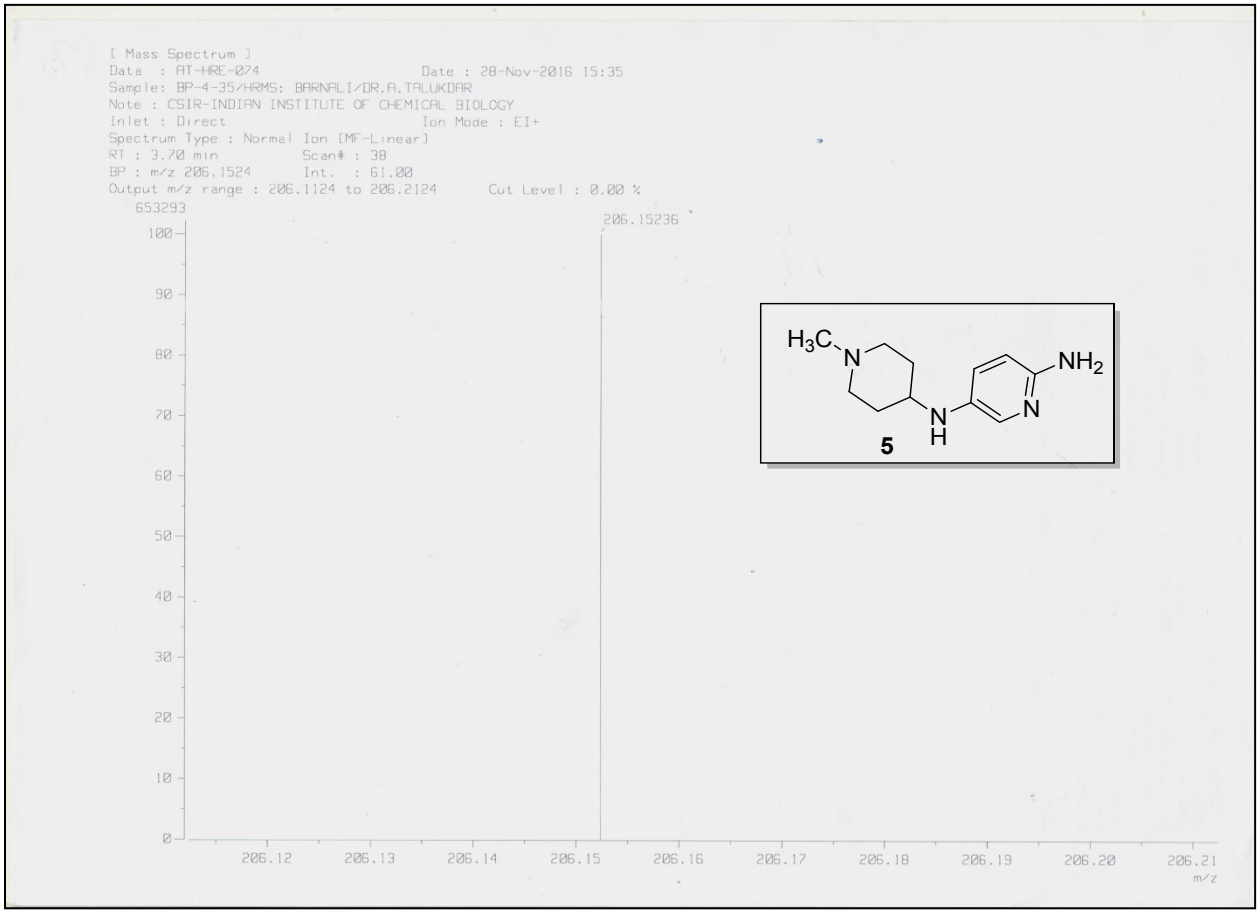


Mass Spectra of compound **4.**

<u>^{1}H,^{13}C NMR and Mass spectra of Compound 5:</u>

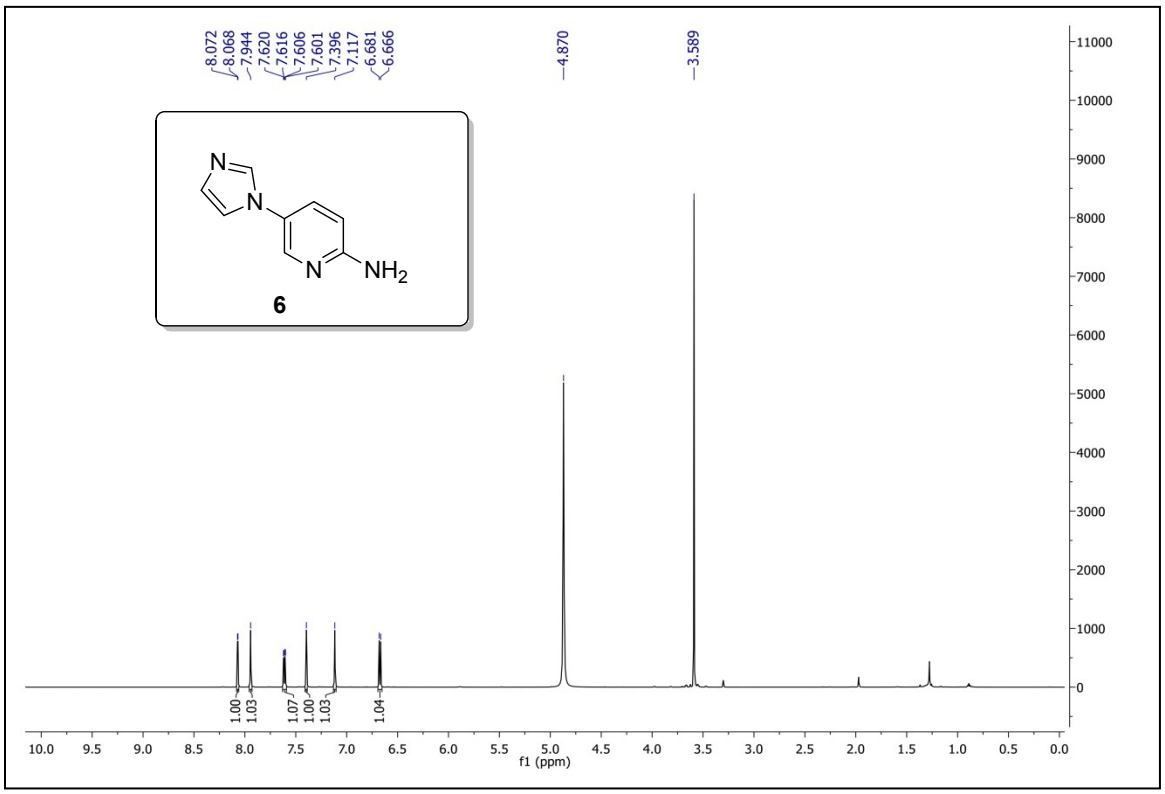

7.566
7.557
7.260
6.898
6.889
6.870
6.860
6.444
6.415
4.034
3.168
3.153
3.131
3.120
3.108
3.087
2.780
2.277
2.110
2.072
2.034
1.988
1.492
1.483
1.450
1.414
1.385
1.370
H3C
N
NH2
N
N
H
5
1.00
1.05
1.01
1.51
1.41
2.24
3.13
4.34
2.36
f1 (ppm)

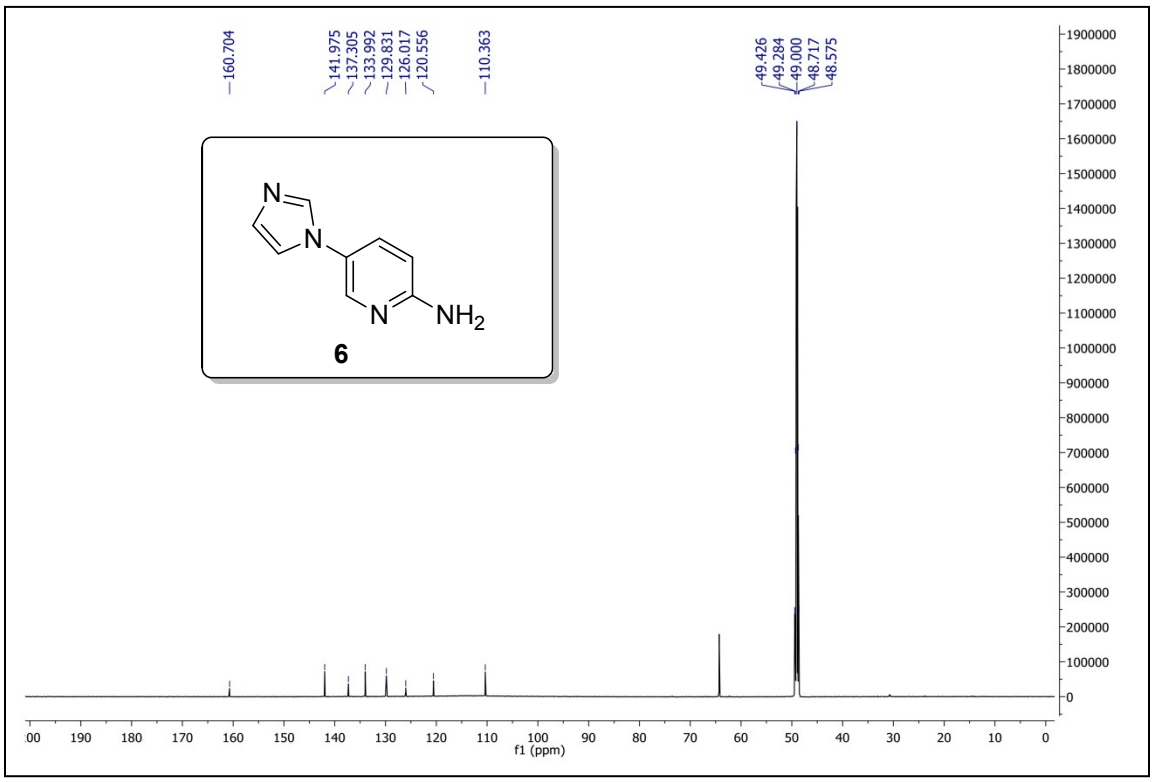

151.503
136.311
134.452
126.215
109.692
77.584
77.160
76.736
54.648
51.157
46.293
32.773
H3C
N
NH2
N
N
H
5
f1 (ppm)

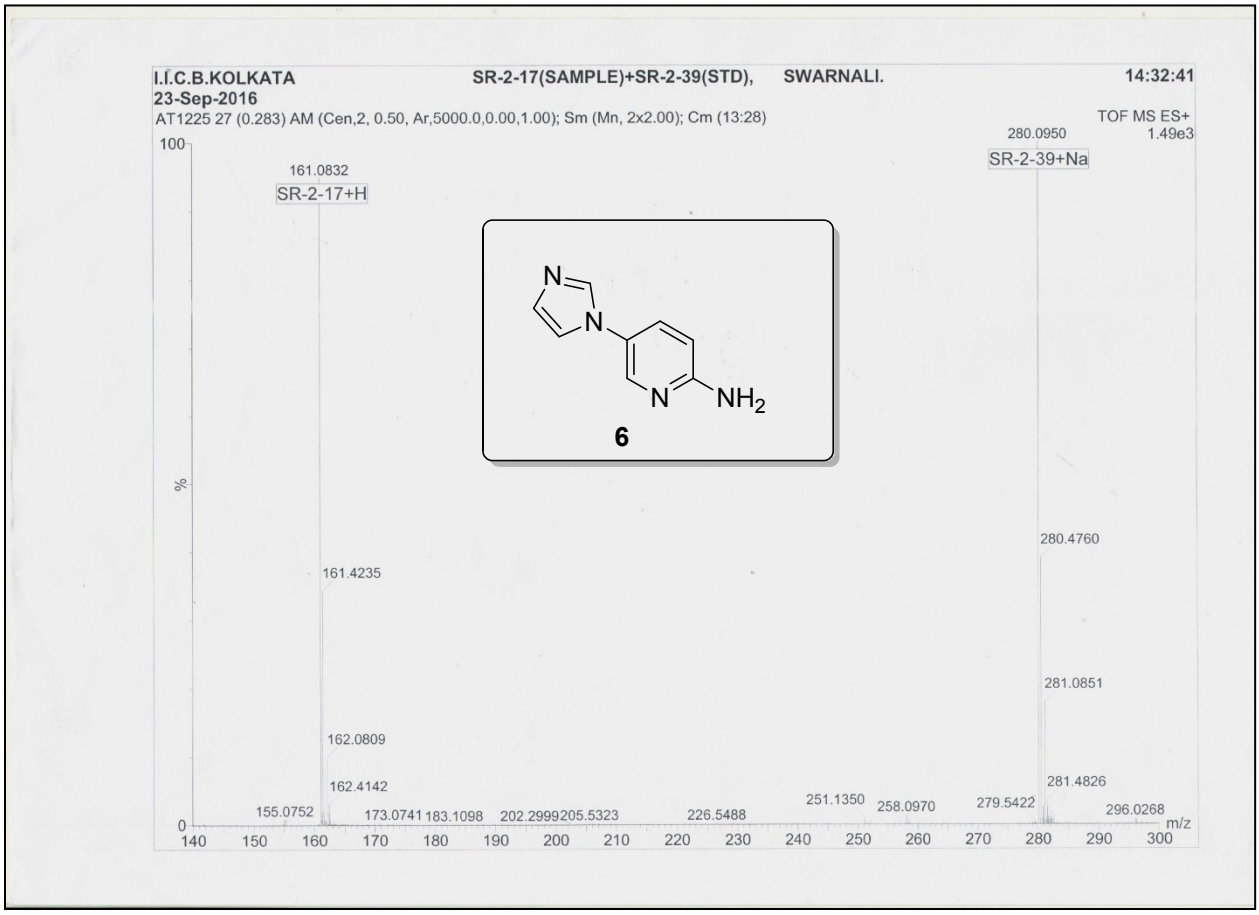


Mass Spectra of compound **5**.

$^{1}H,^{13}C$ NMR and Mass spectra of Compound 6:

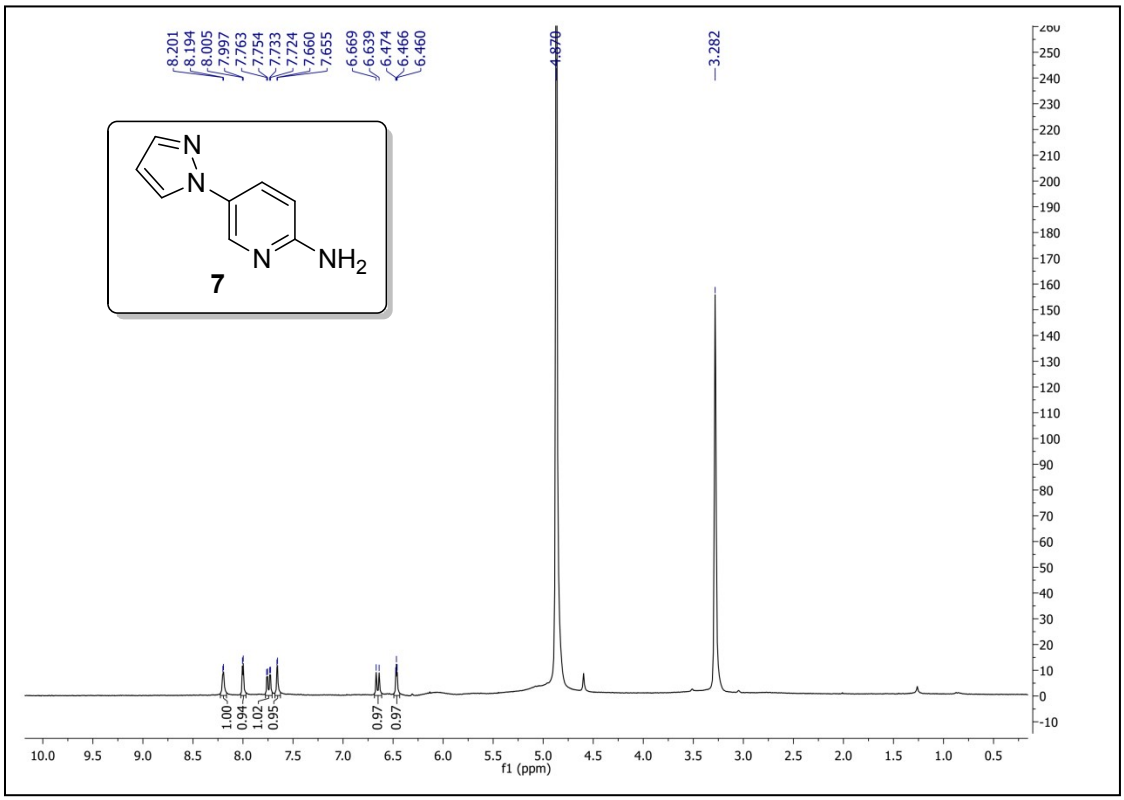


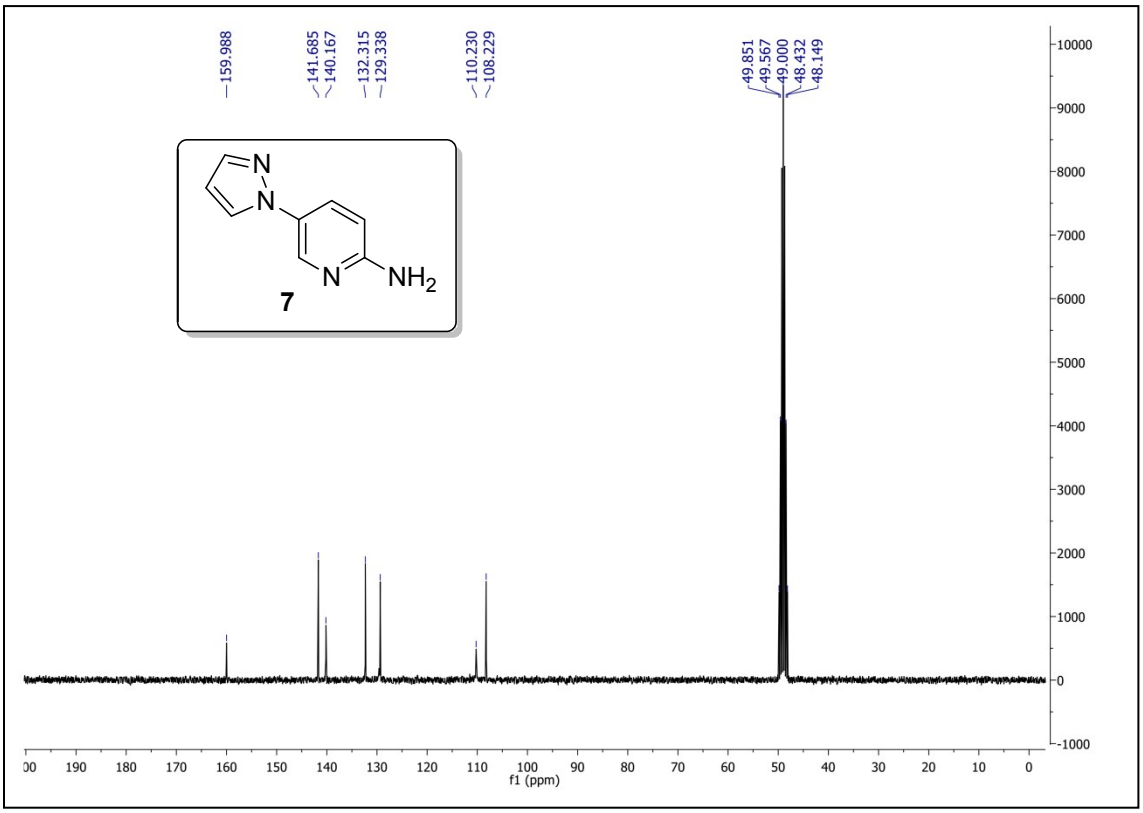


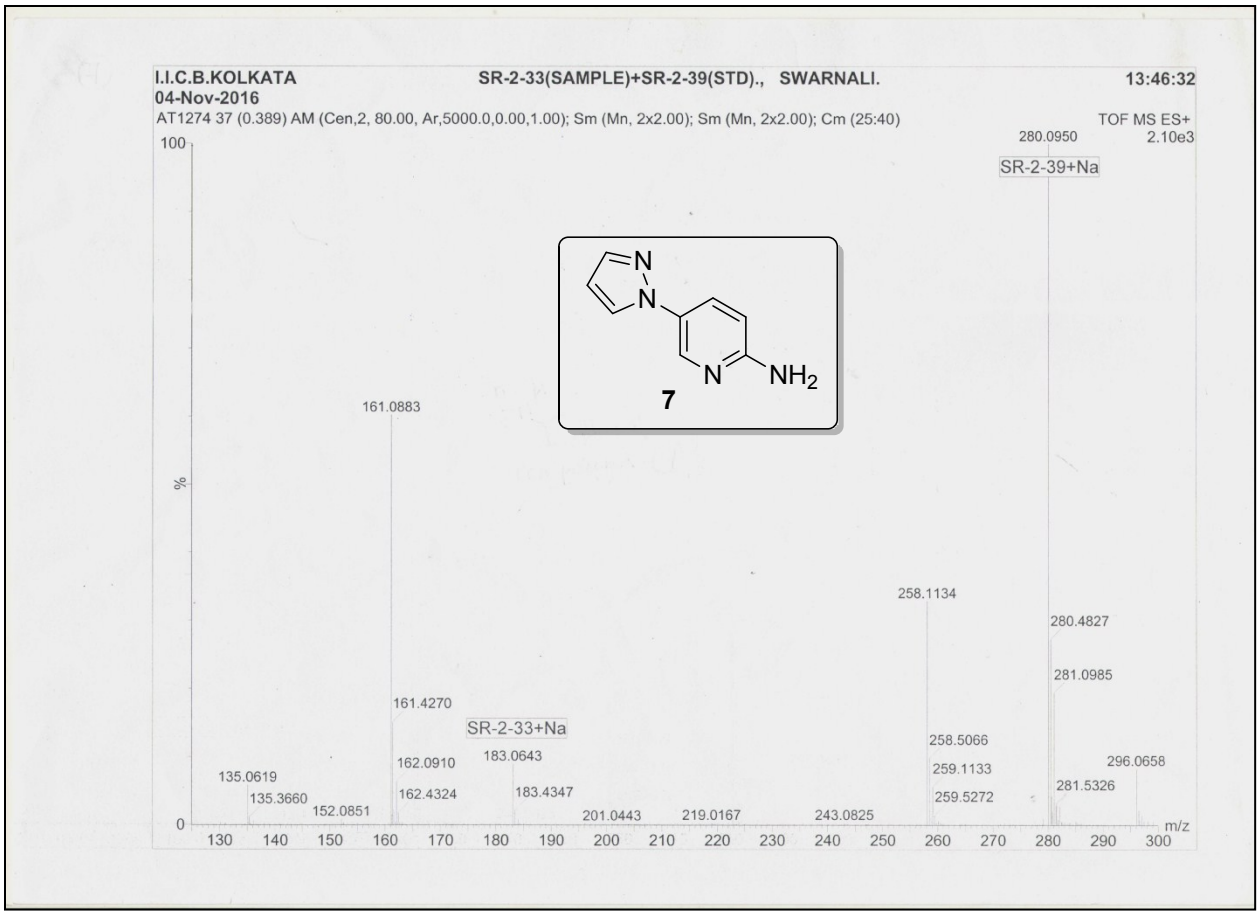


161.0832 is the $[M+H]^+$ peak of **6** and 280.0950 is the $[M+Na]^+$ peak of standard.

$^{1}H,^{13}C$ NMR and Mass spectra of Compound 7:

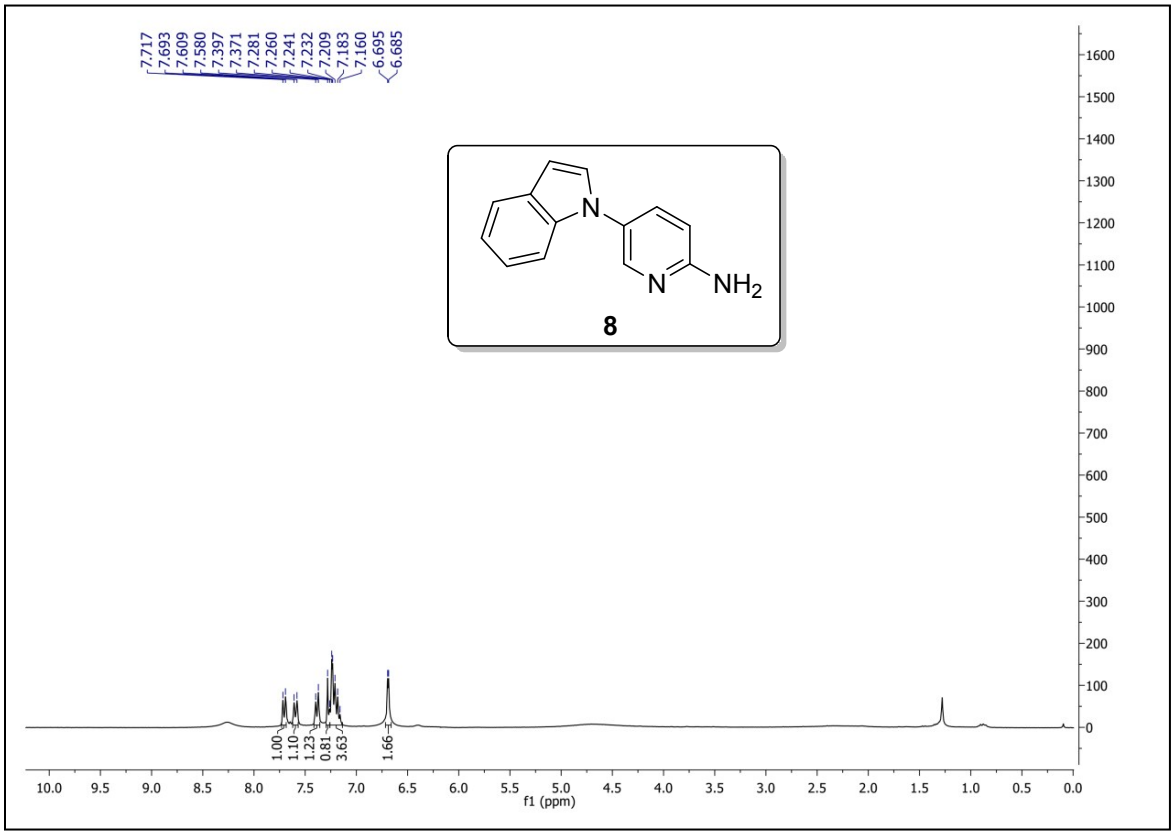


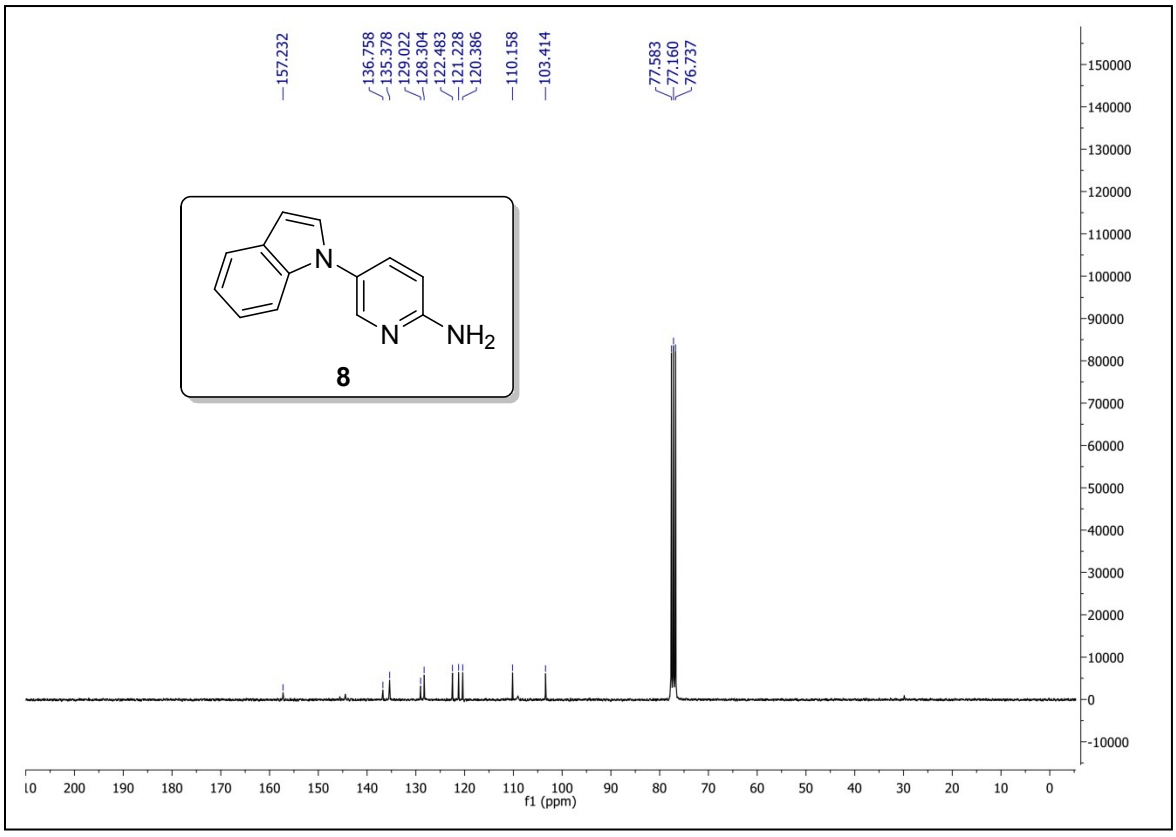


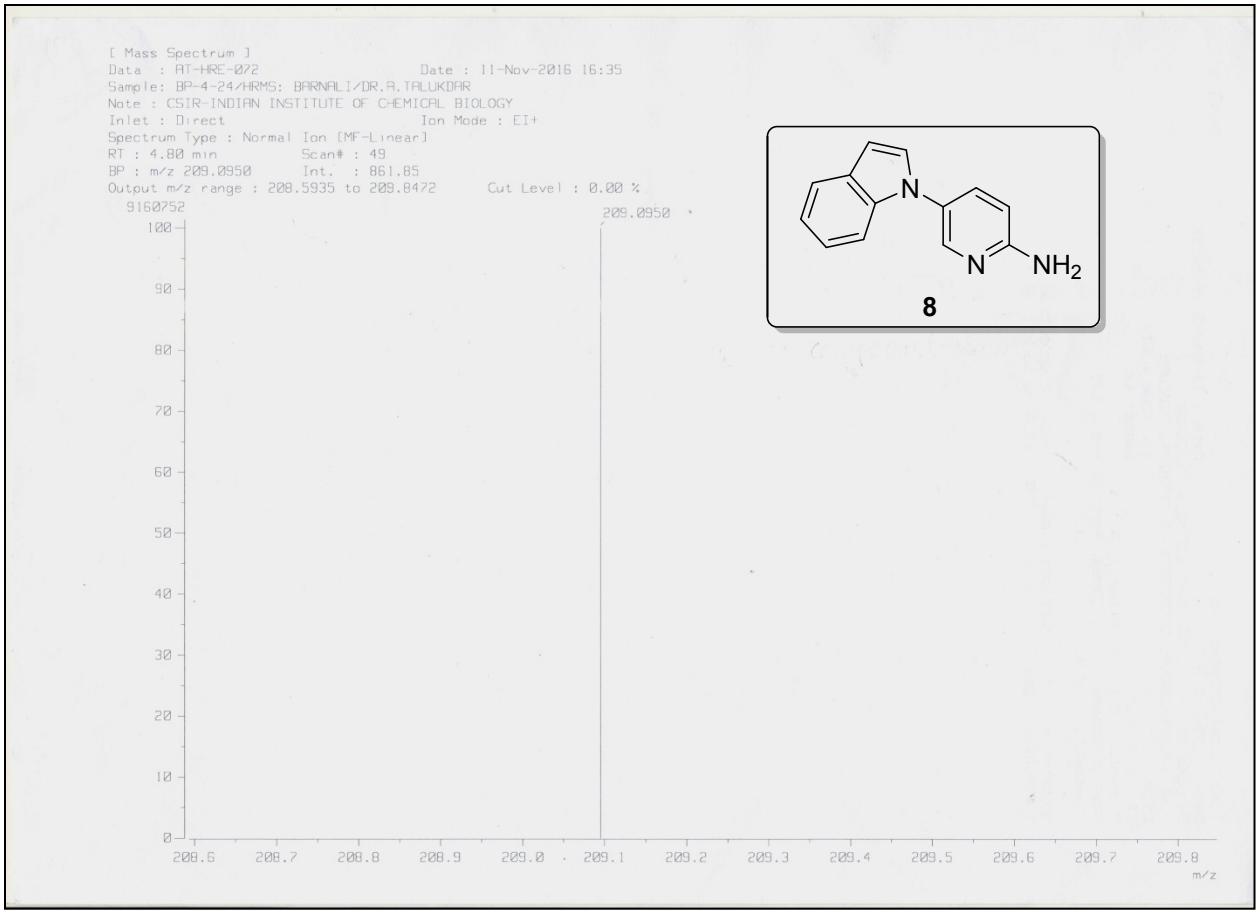


161.0883 and 183.0643 are the $[M+H]^+$ and $[M+Na]^+$ peak of **7**. 258.1134 and 280.0950 are the $[M+H]^+$ and $[M+Na]^+$ peak of standard.

^{1}H,^{13}C NMR and Mass spectra of Compound 8:

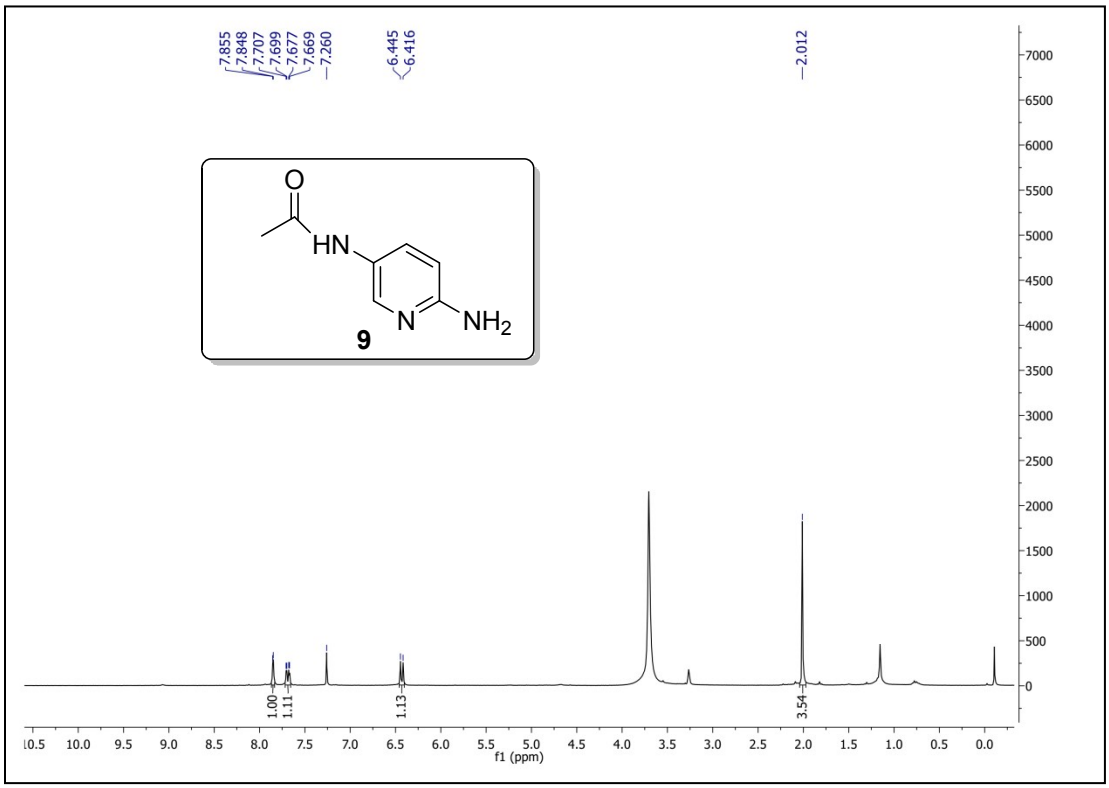

7.717
7.693
7.609
7.580
7.397
7.371
7.281
7.260
7.241
7.232
7.209
7.183
7.160
6.695
6.685
N
N
NH2
8
1.00
1.10
1.23
0.81
3.63
1.66
f1 (ppm)

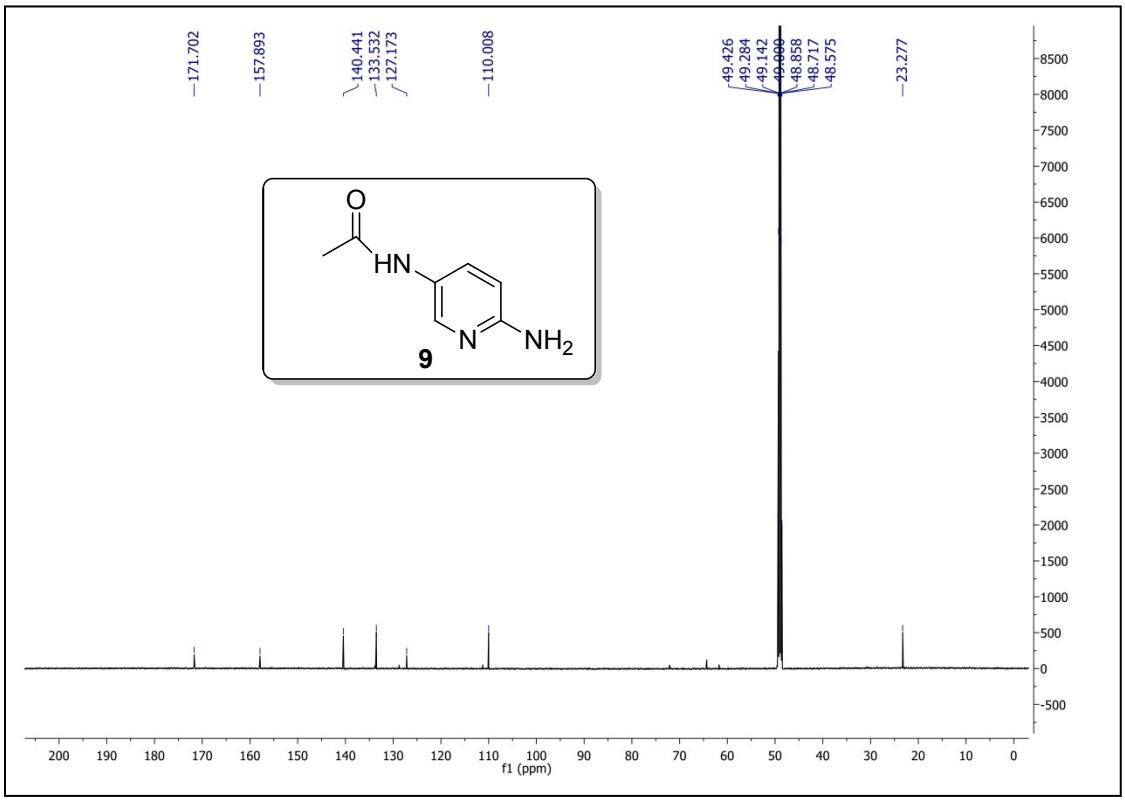

157.232
136.758
135.378
129.022
128.304
122.483
121.228
120.386
110.158
103.414
77.583
77.160
76.737
N
N
NH2
8
f1 (ppm)

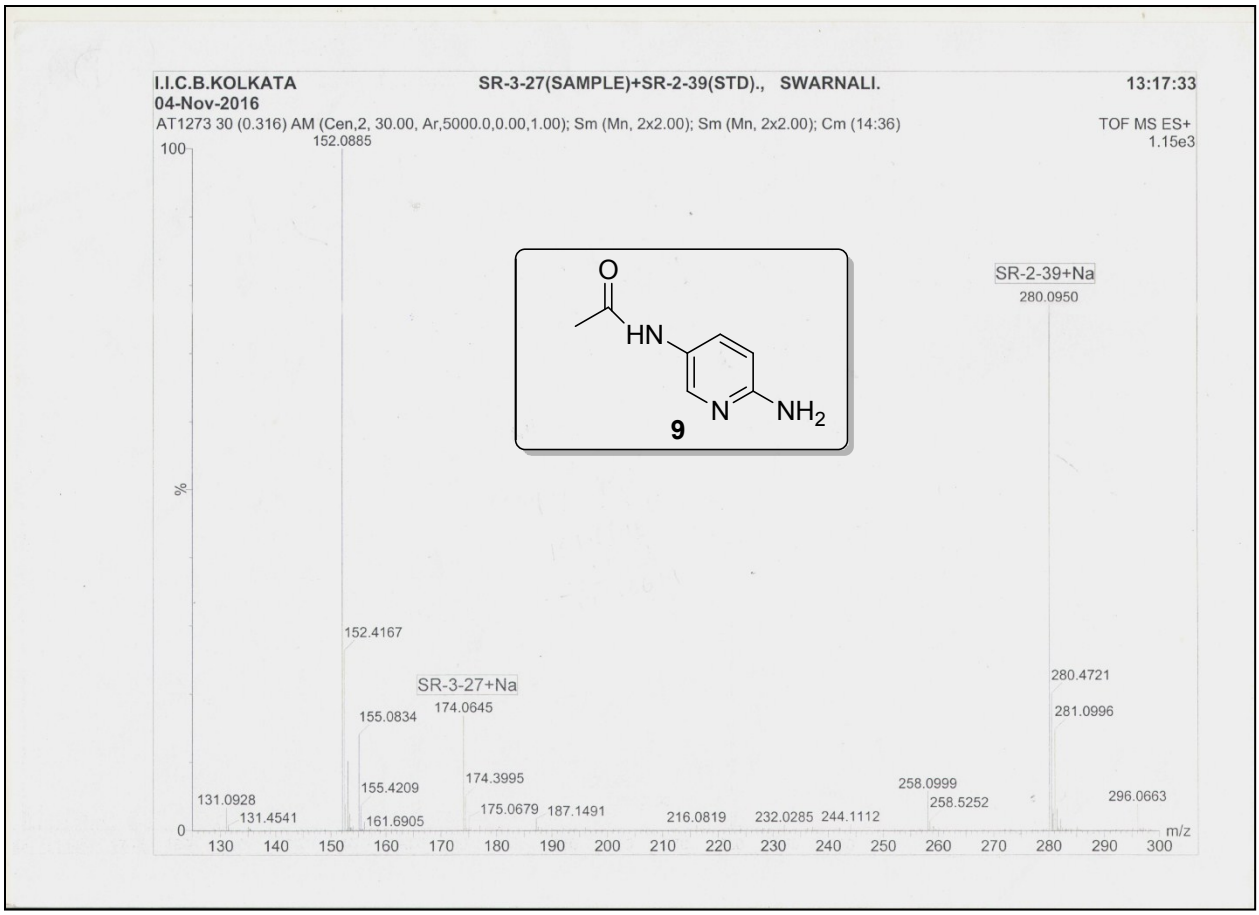


Mass Spectrum of **8**.

[1]H, [13]C NMR and Mass spectra of Compound 9:

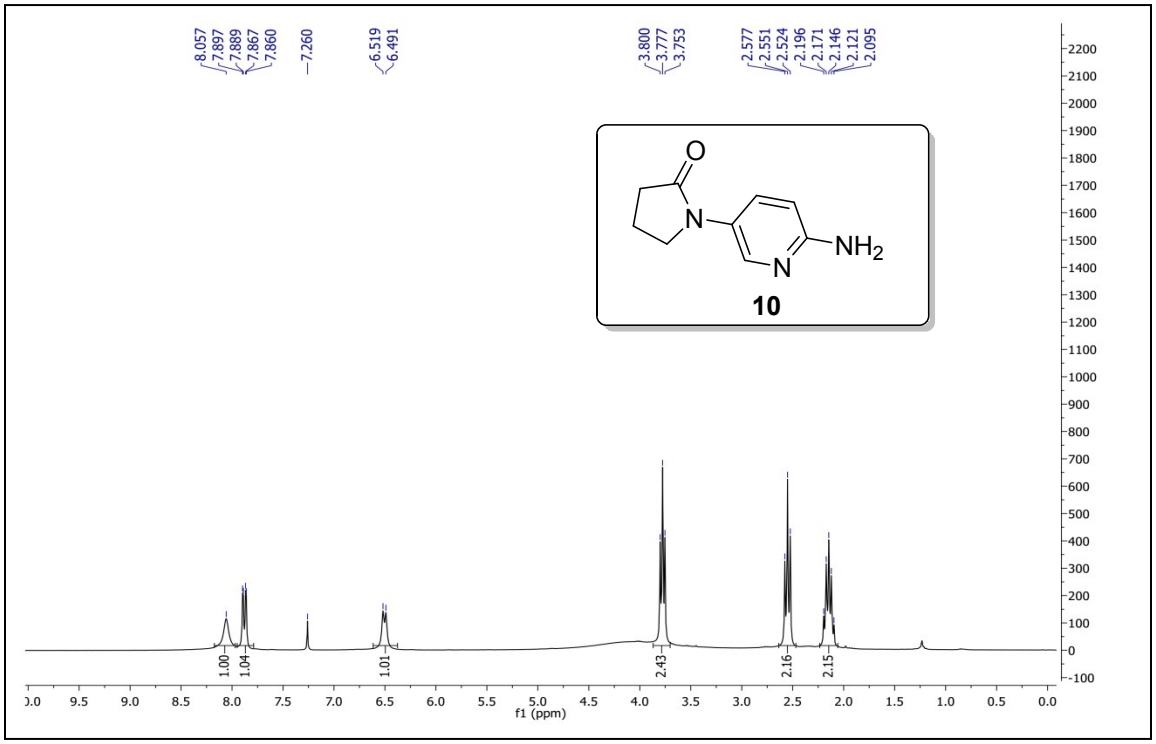


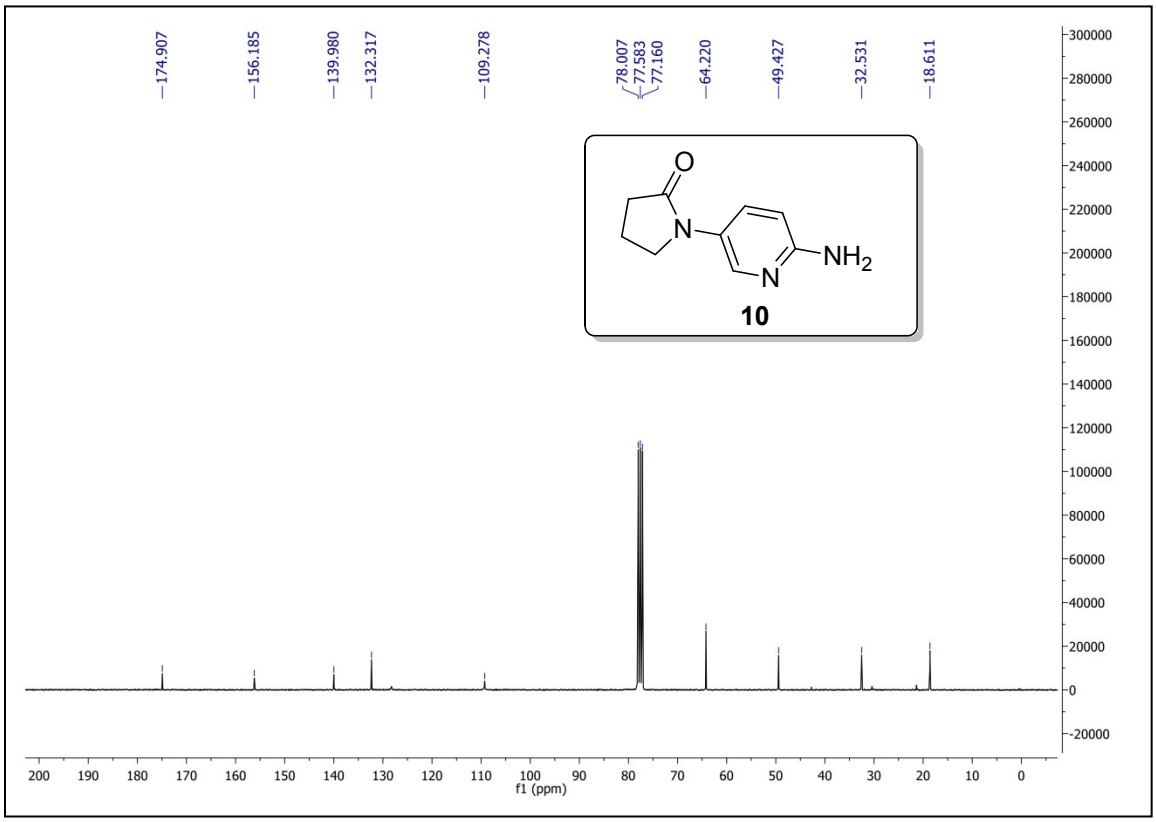


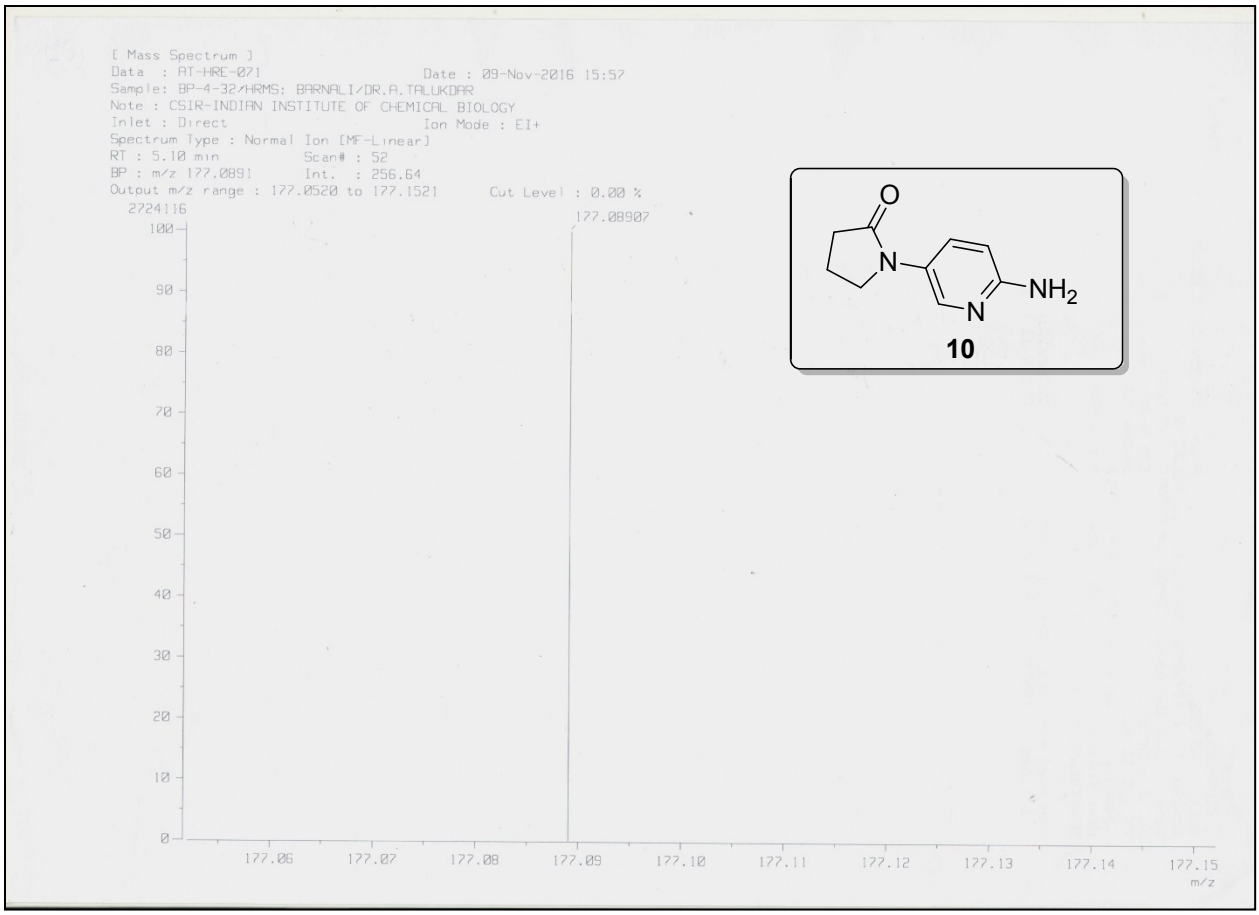


152.0885 and 174.0645 are the $[M+H]^+$ and $[M+Na]^+$ peak of **9**. 258.0999 and 280.0950 are the $[M+H]^+$ and $[M+Na]^+$ peak of standard compound.

[1]H, [13]C NMR and Mass spectra of compound 10:

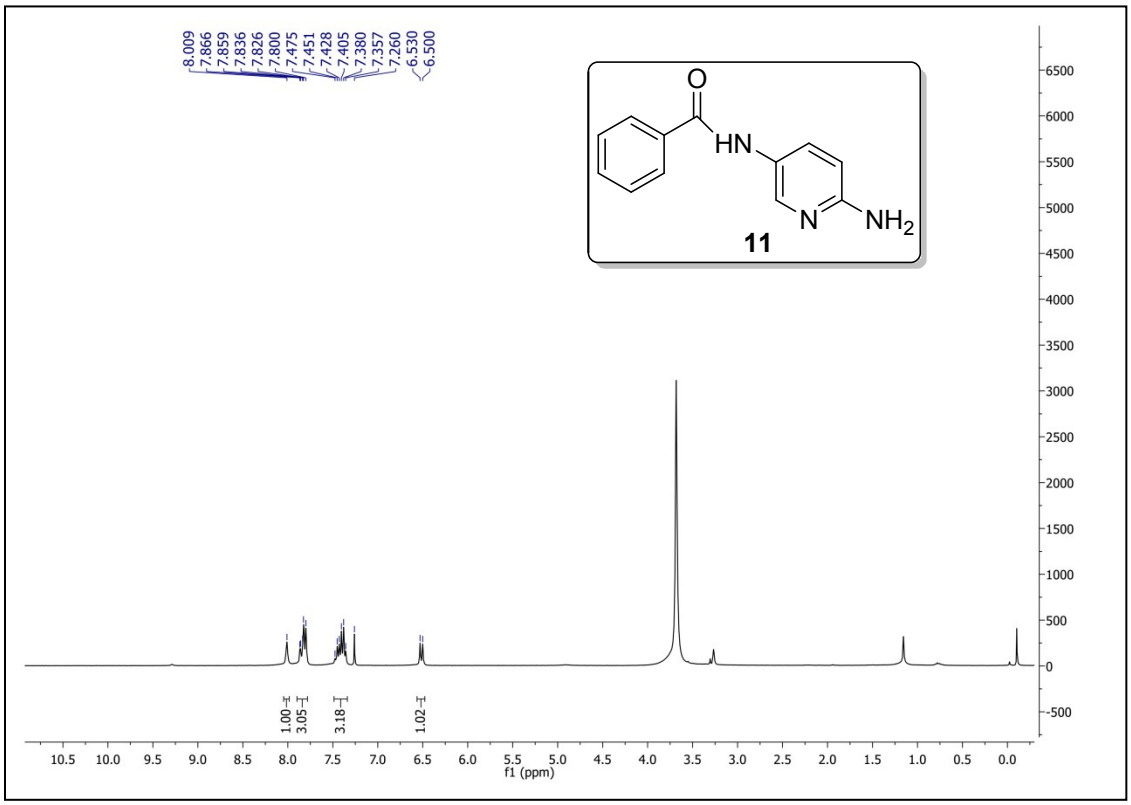


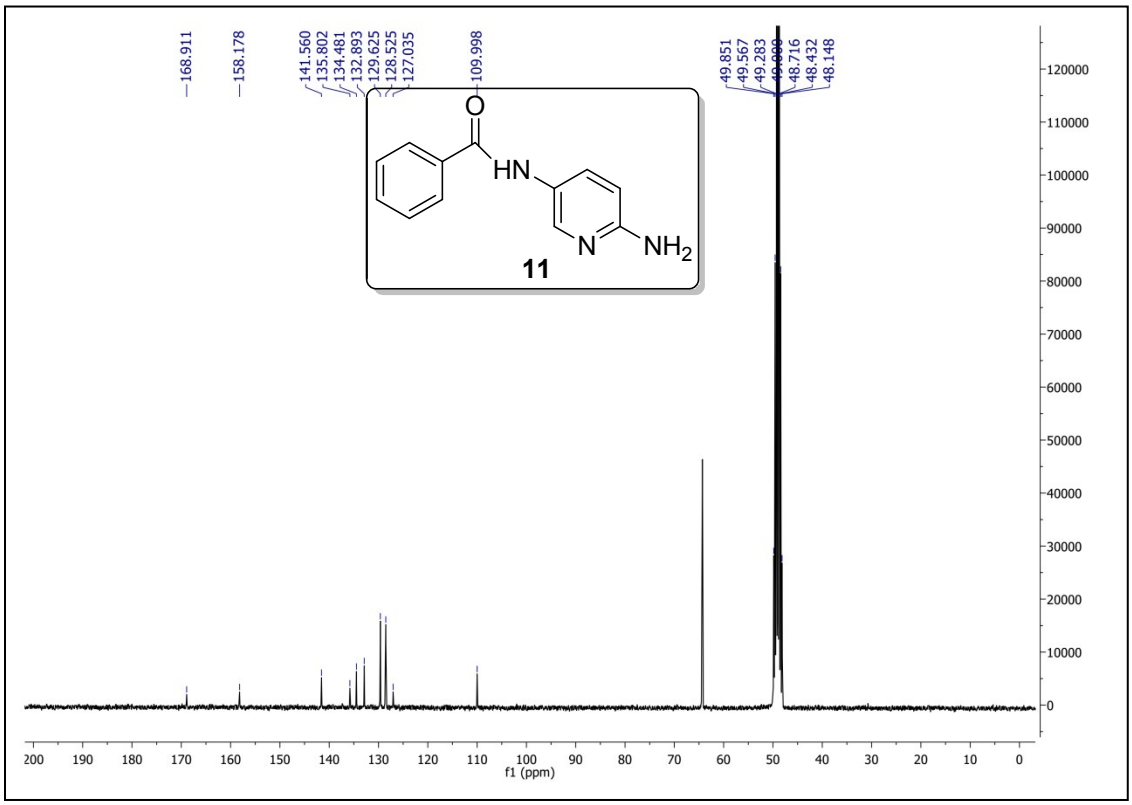


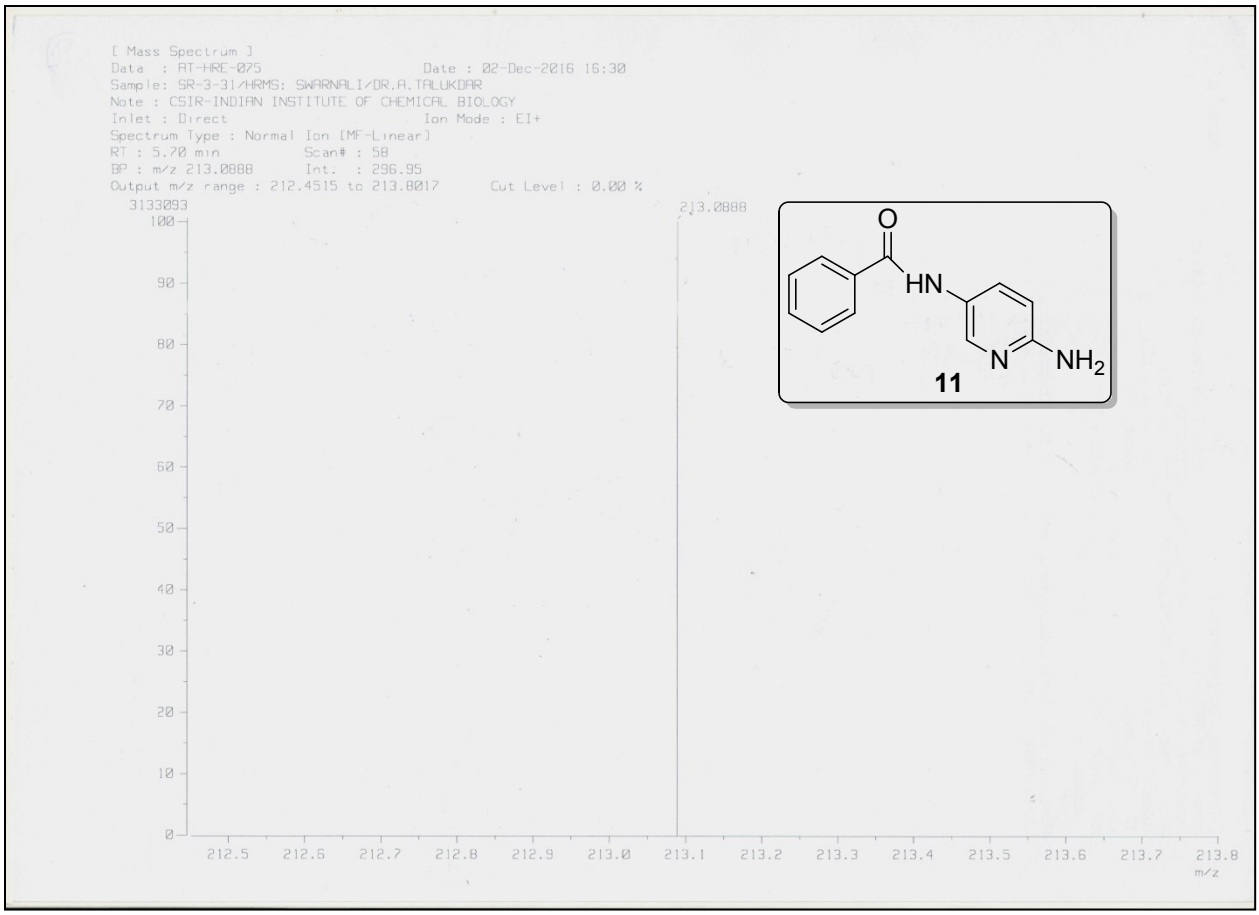


Mass Spectrum of **10**.

[1]H, [13]C NMR and Mass spectra of Compound 11:

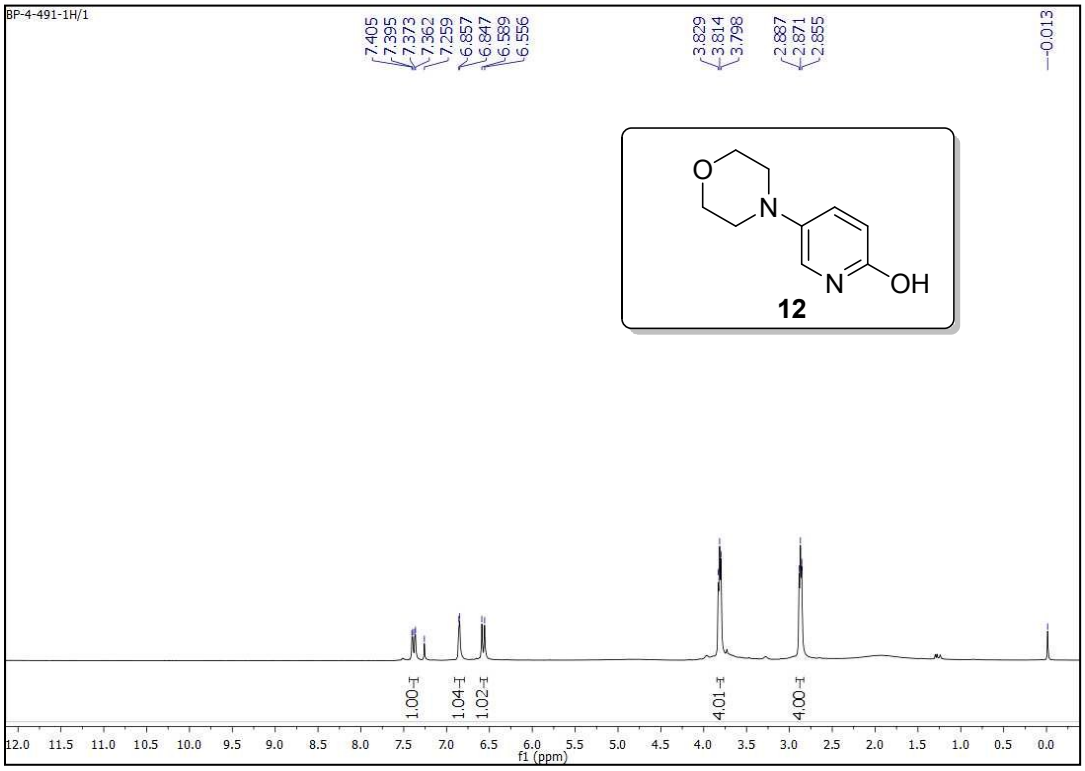


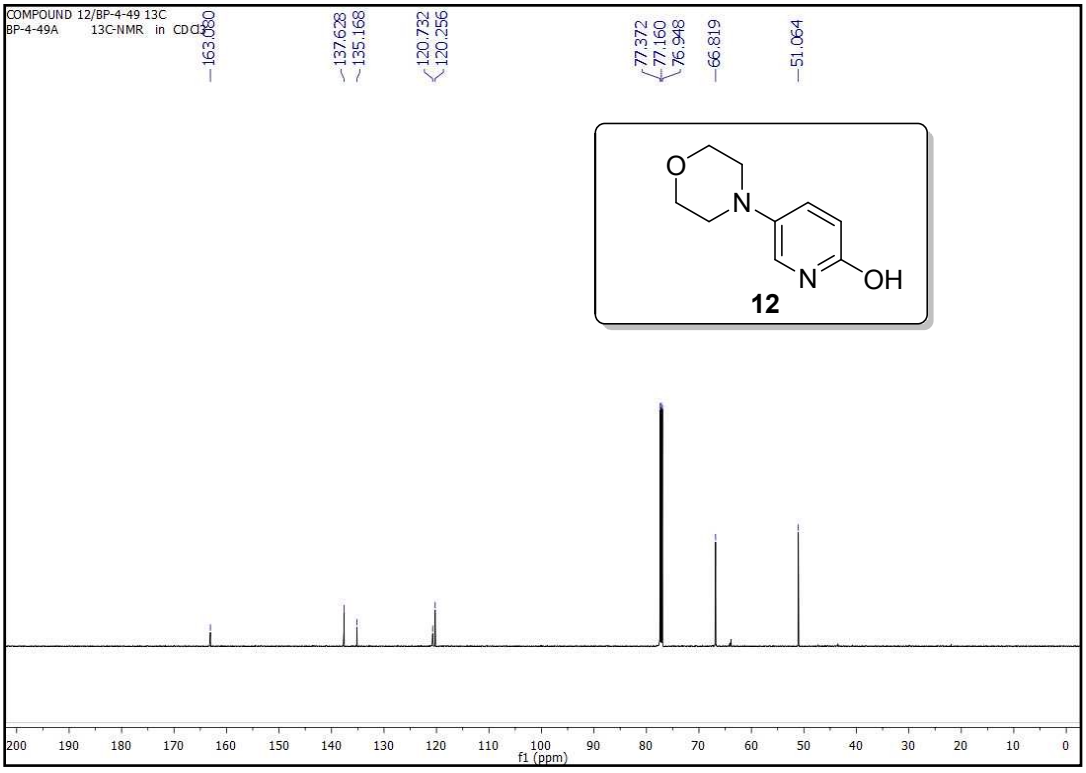


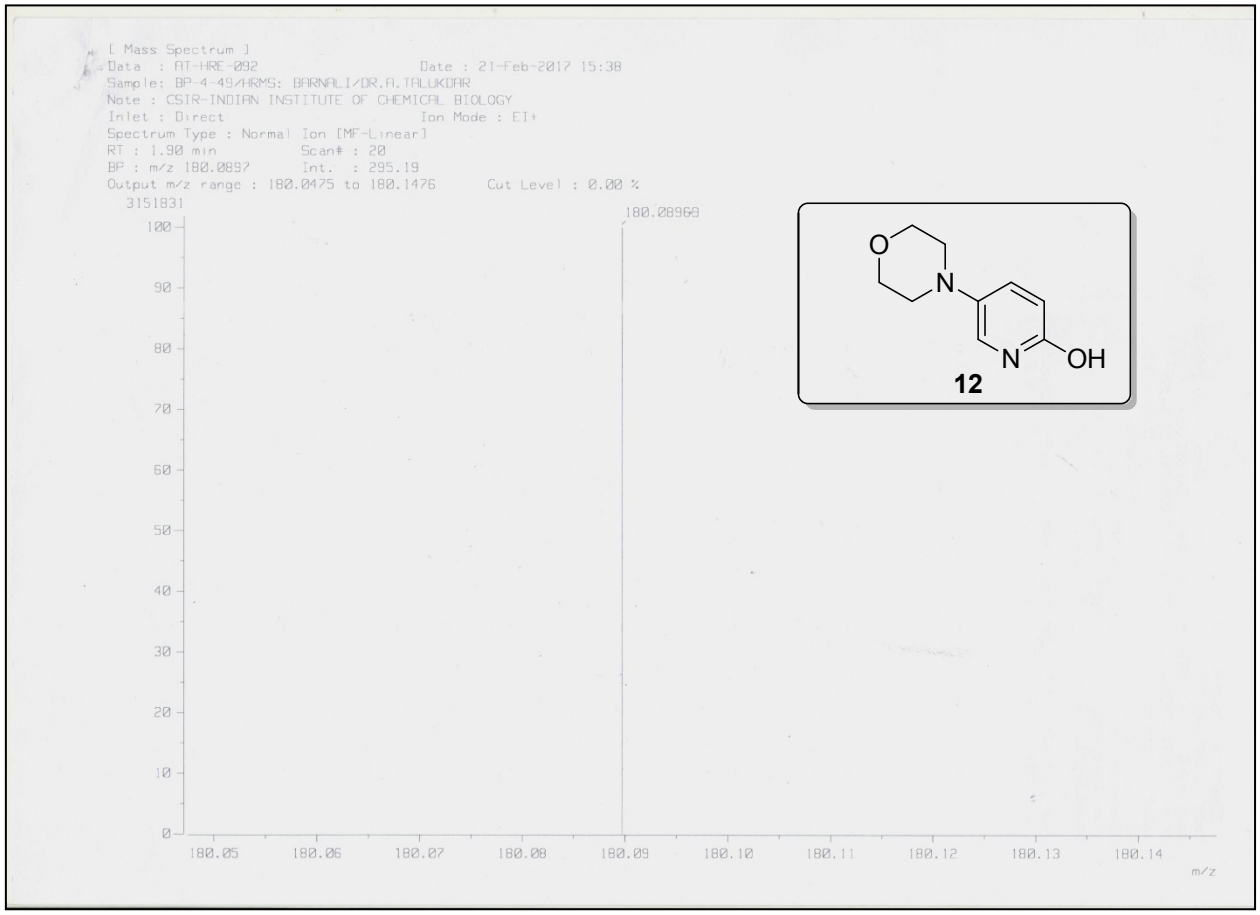


Mass Spectrum of **11**.

[1]H, [13]C NMR and Mass spectra of Compound 12:

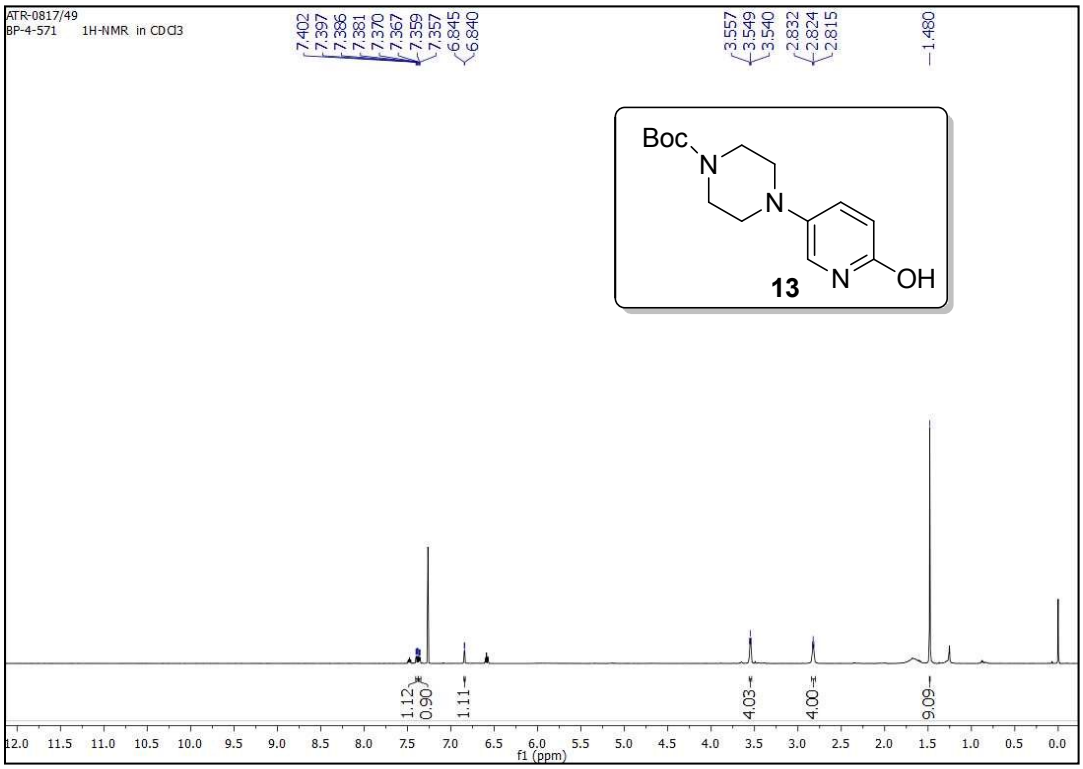

BP-4-491-1H/1
7.405
7.395
7.373
7.362
7.259
6.857
6.847
6.589
6.556
3.829
3.814
3.798
2.887
2.871
2.855
-0.013
O
N
N
OH
12
1.00
1.04
1.02
4.01
4.00
f1 (ppm)

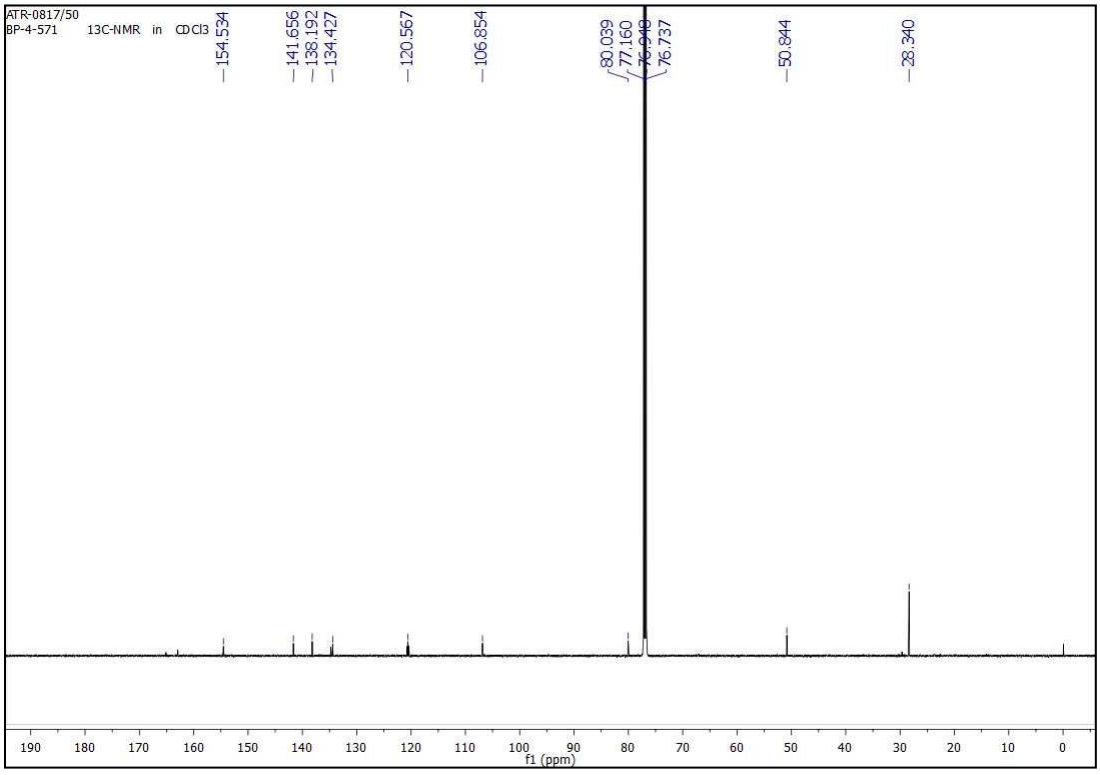

COMPOUND 12/BP-4-49 13C
BP-4-49A 13C-NMR in CDCl3
163.080
137.628
135.168
120.732
120.256
77.372
77.160
76.948
66.819
51.064
O
N
N
OH
12
f1 (ppm)

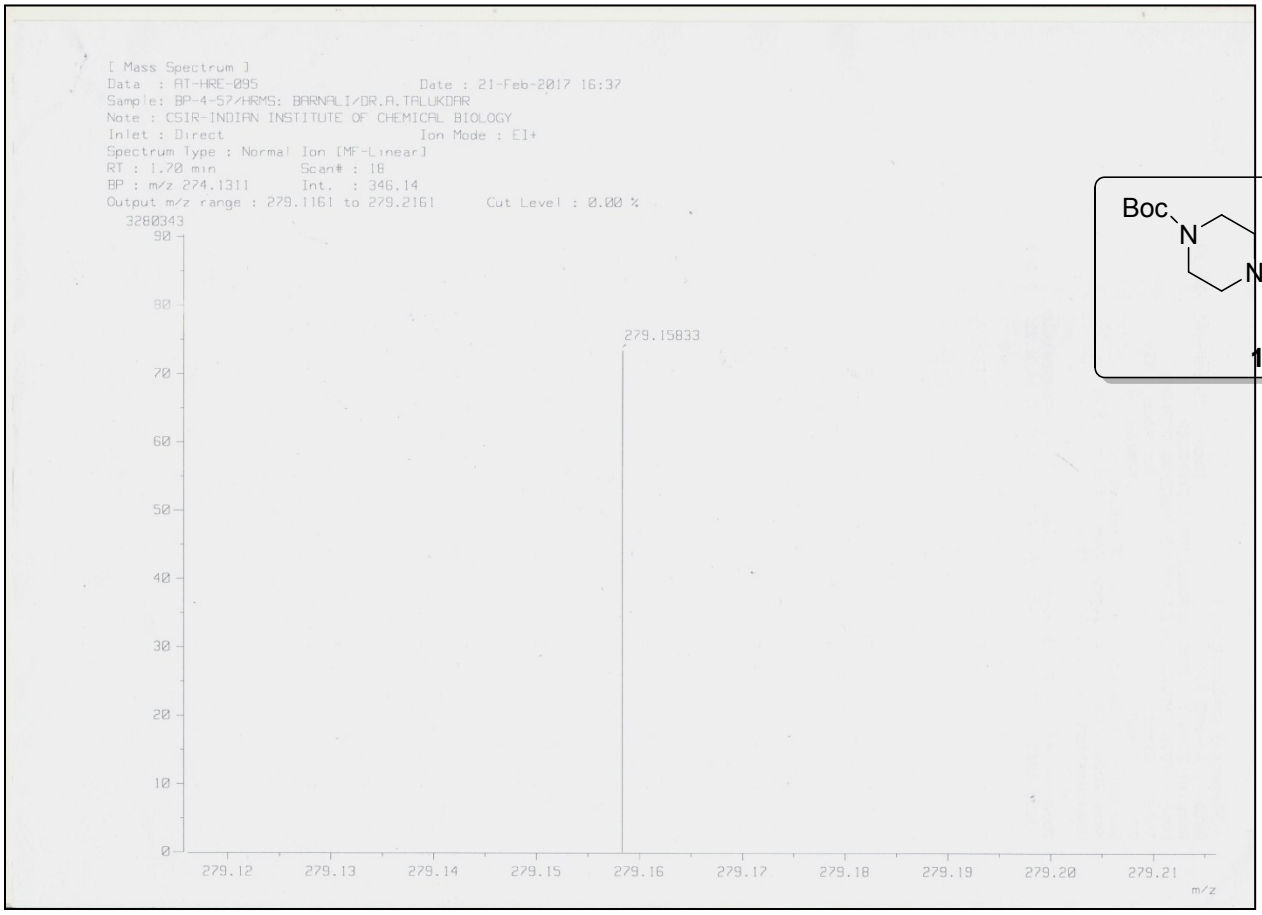


Mass Spectrum of **12**.

^{1}H, ^{13}C NMR and Mass spectra of Compound 13:

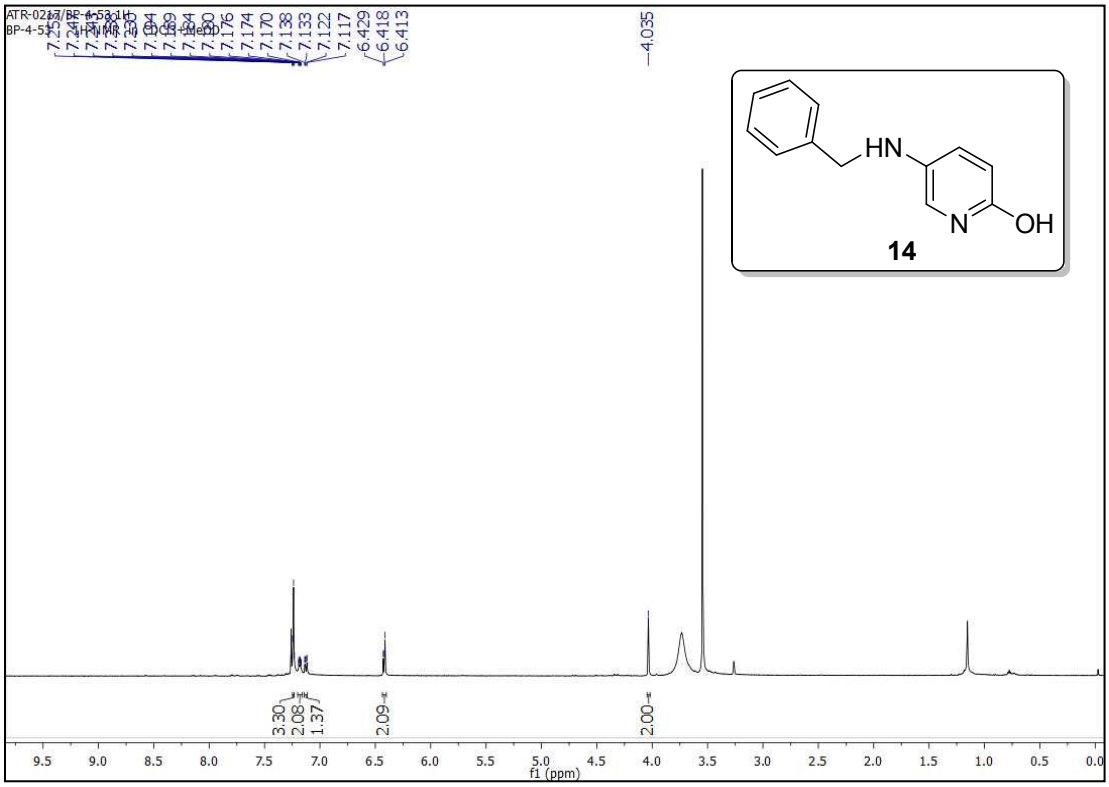


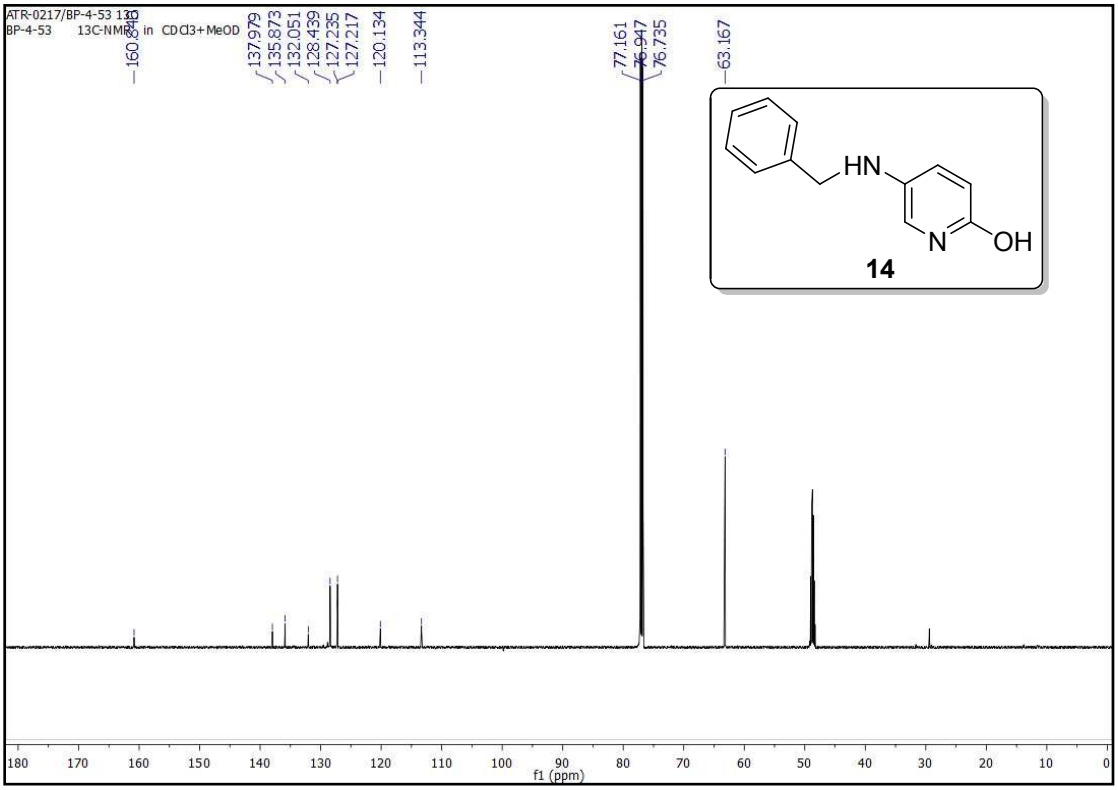


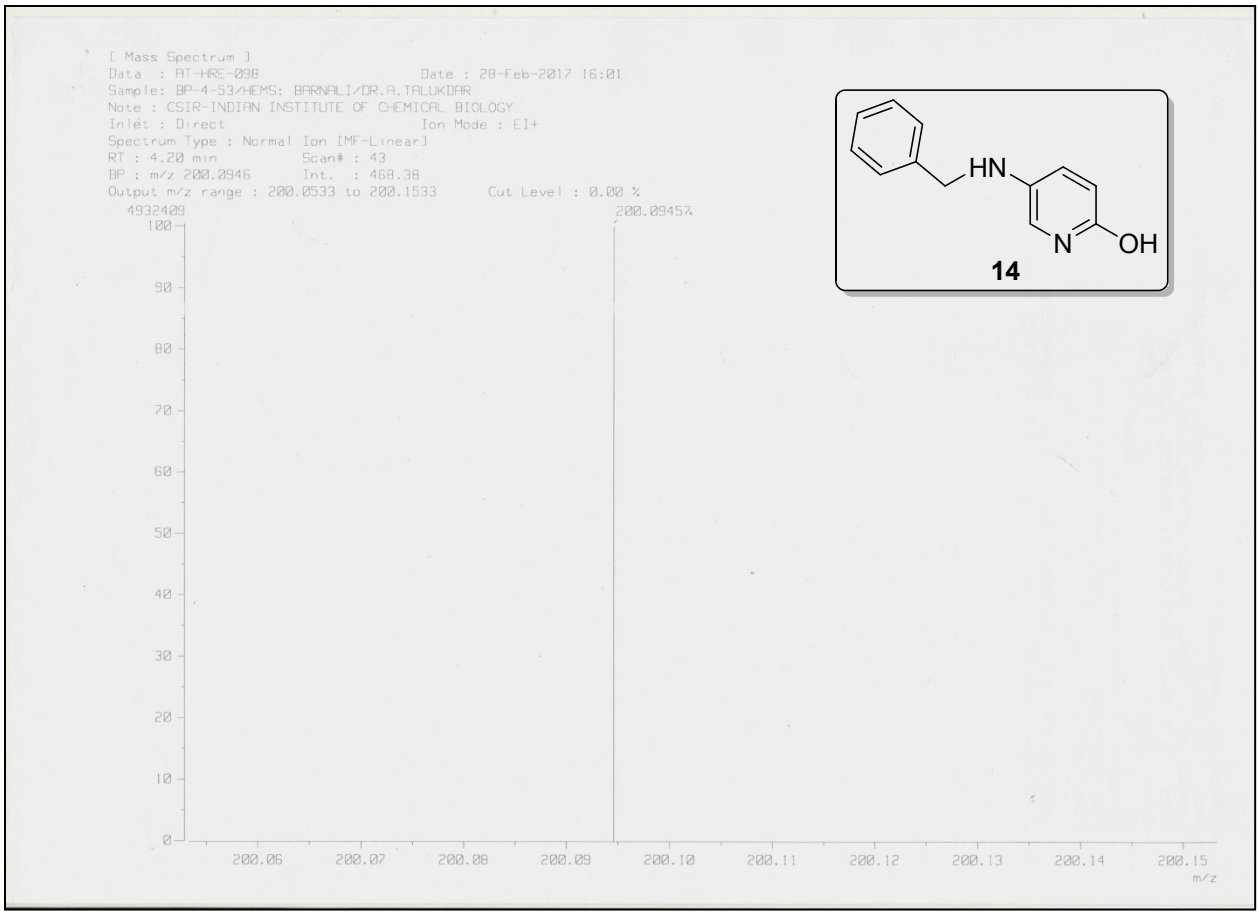


Mass Spectrum of **13**.

<u>^{1}H, ^{13}C NMR and Mass spectra of Compound 14:</u>

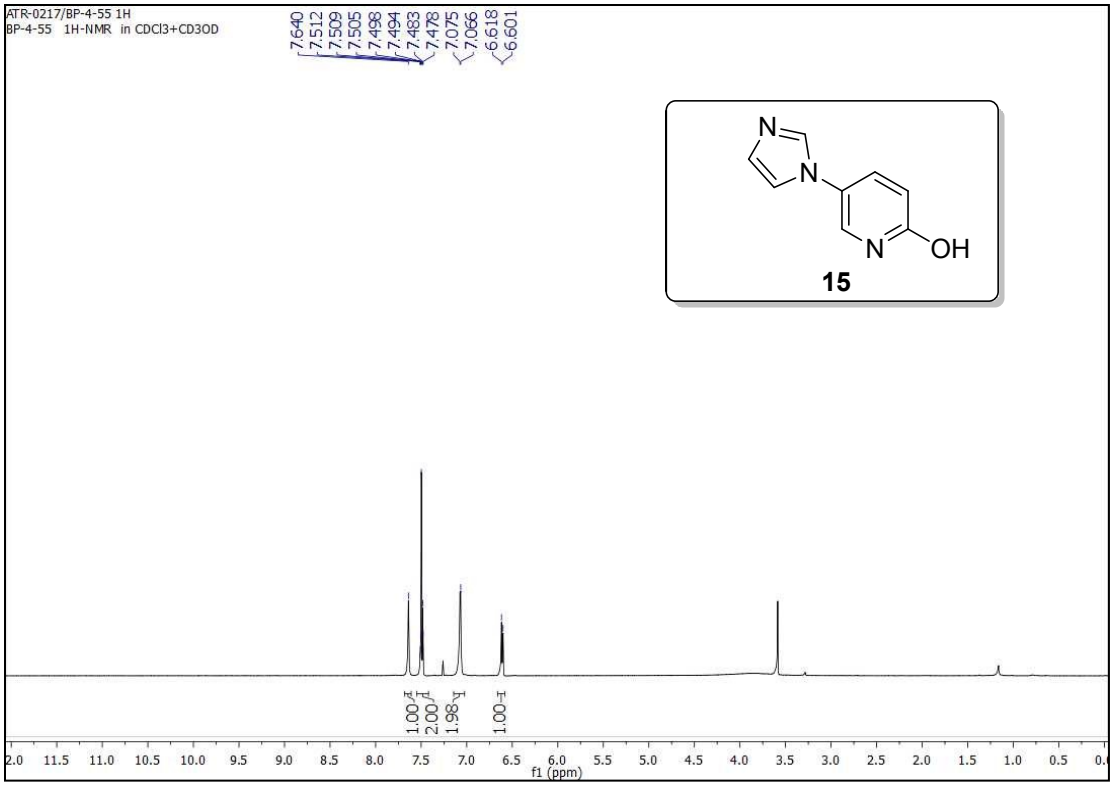

4.035
HN
N
OH
14
3.30
2.08
1.37
2.09
2.00
f1 (ppm)

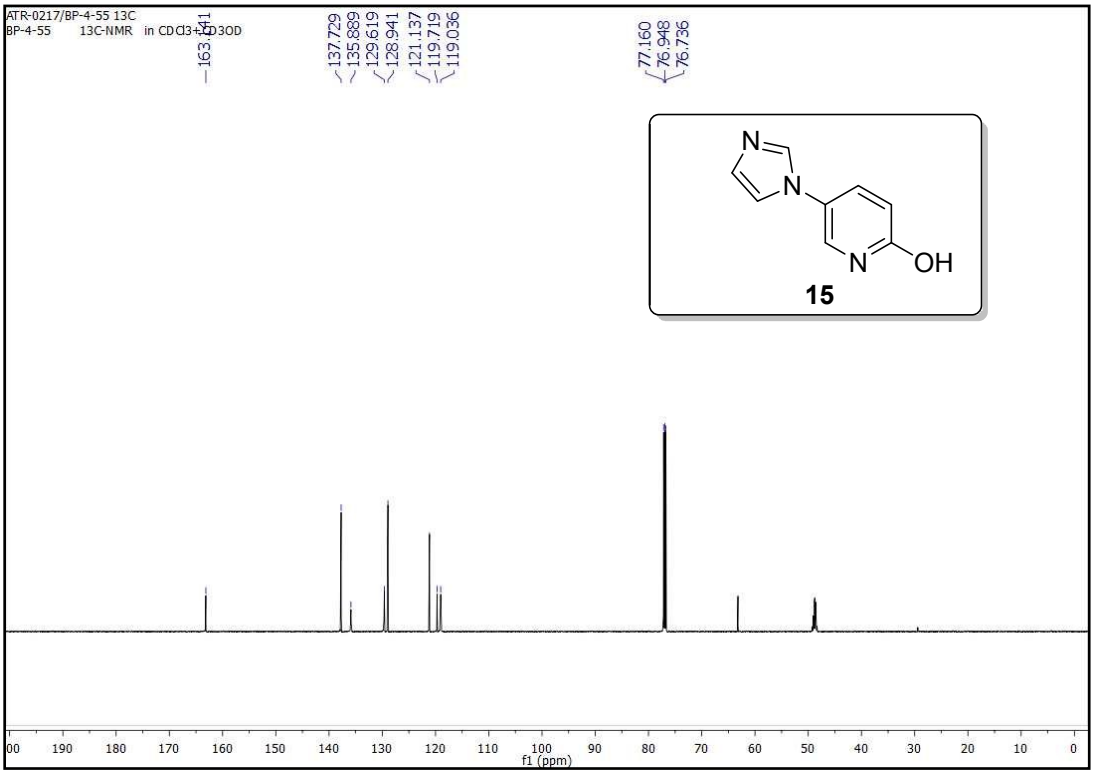

160.843
137.979
135.873
132.051
128.439
127.235
127.217
120.134
113.344
77.161
76.947
76.735
63.167
HN
N
OH
14
f1 (ppm)

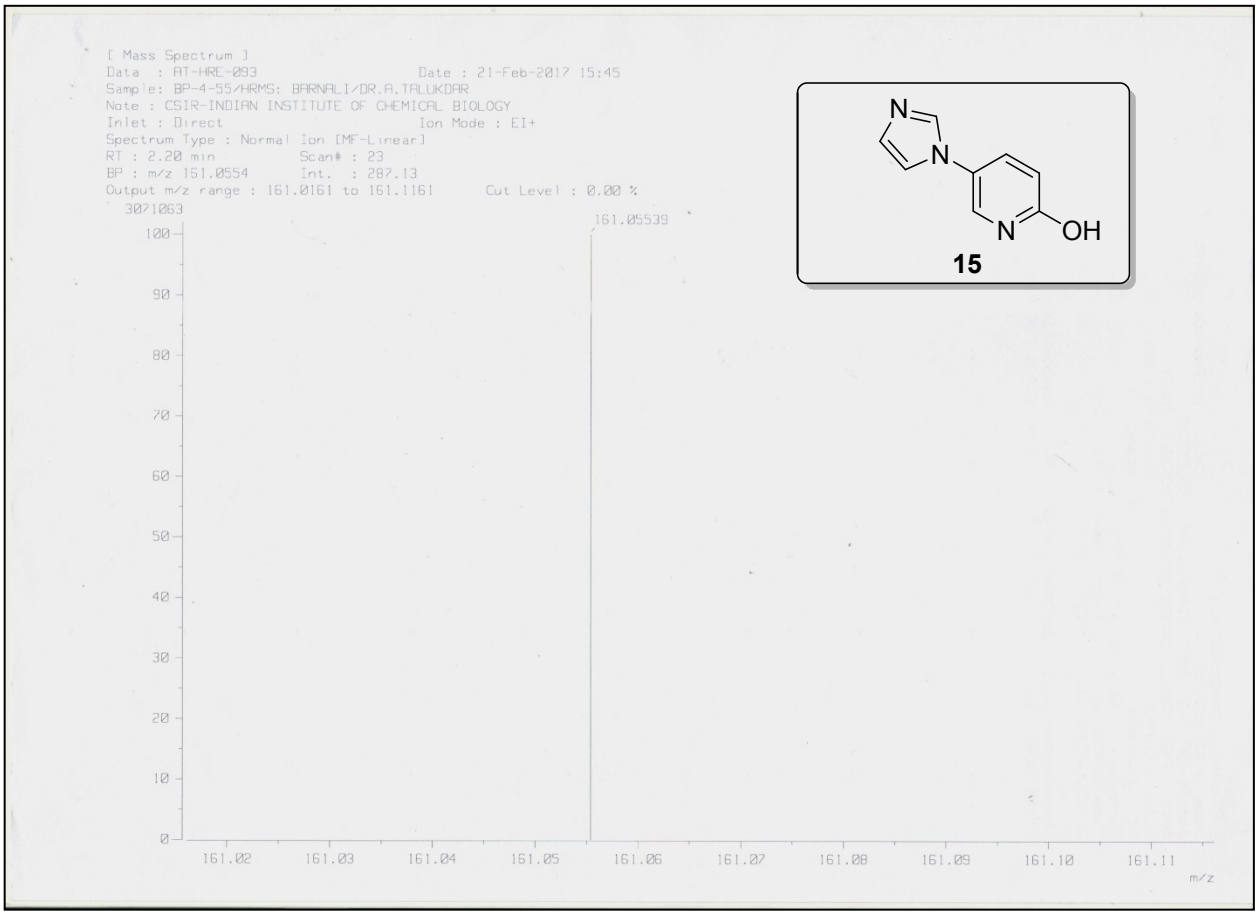


Mass Spectrum of **14**.

<u>^{1}H, ^{13}C NMR and Mass spectra of Compound 15:</u>

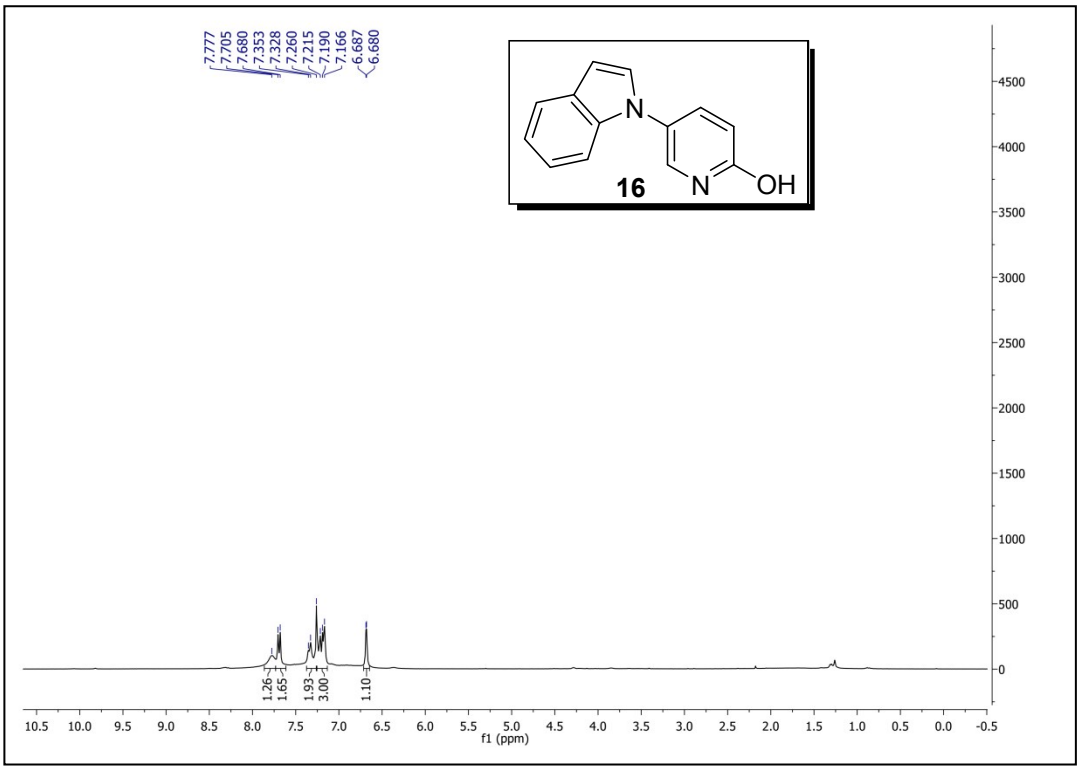

ATR-0217/BP-4-55 1H
BP-4-55 1H-NMR in CDCl3+CD3OD
7.640
7.512
7.509
7.505
7.498
7.494
7.483
7.478
7.075
7.066
6.618
6.601
N
N
N
OH
15
1.00
2.00
1.98
1.00
f1 (ppm)

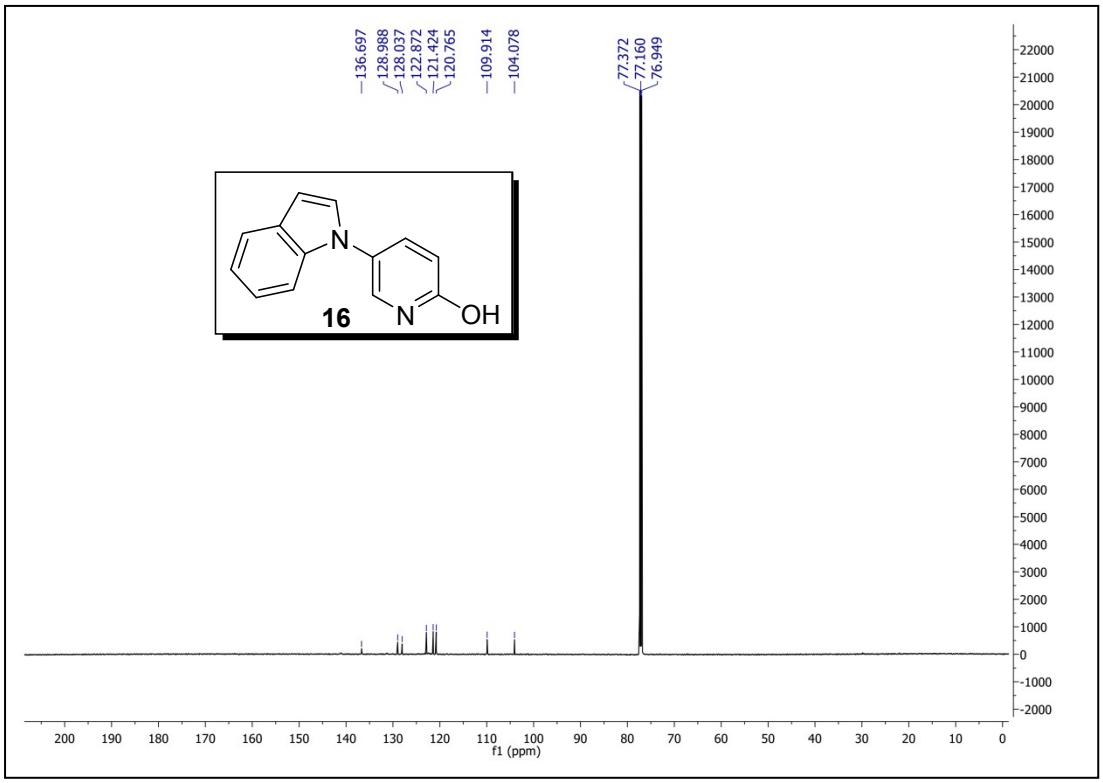

ATR-0217/BP-4-55 13C
BP-4-55 13C-NMR in CDCl3+CD3OD
163.541
137.729
135.889
129.619
128.941
121.137
119.719
119.036
77.160
76.948
76.736
N
N
N
OH
15
f1 (ppm)

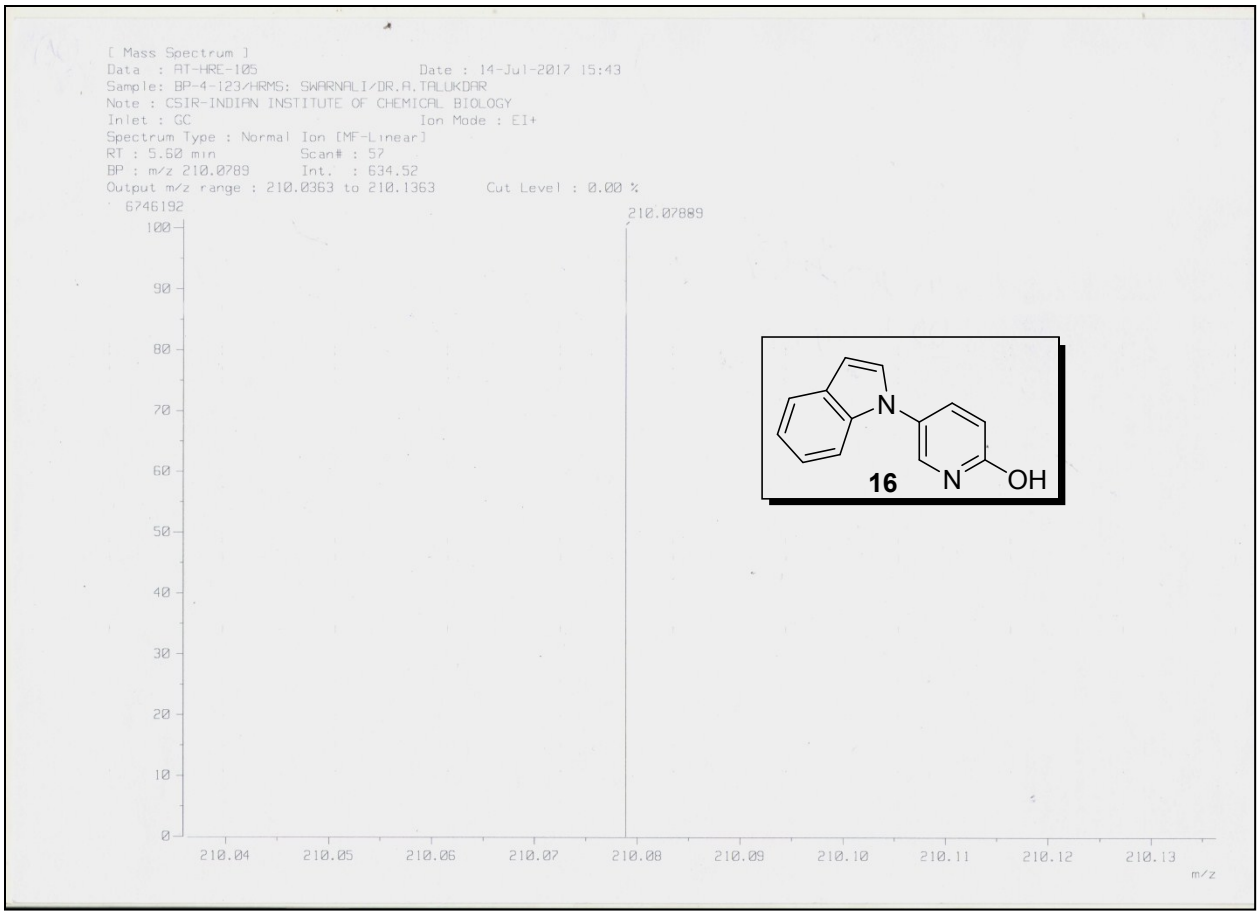


Mass Spectrum of **15**.

^{1}H, ^{13}C NMR and Mass spectra of Compound 16:

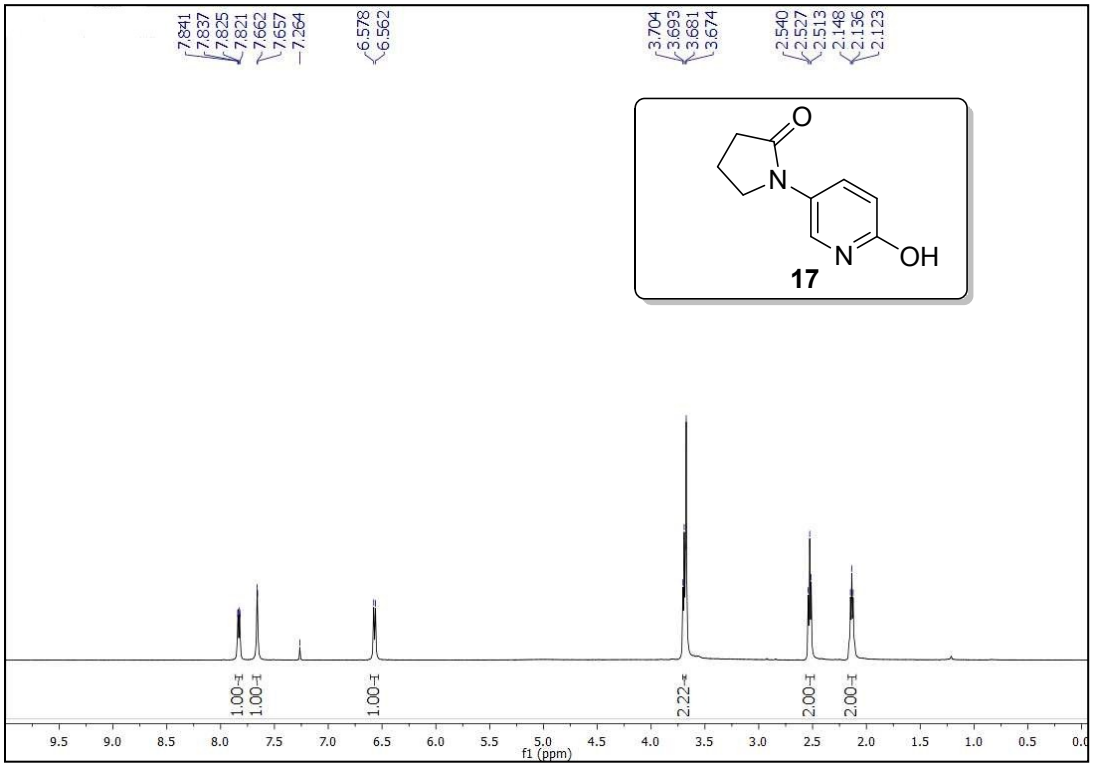


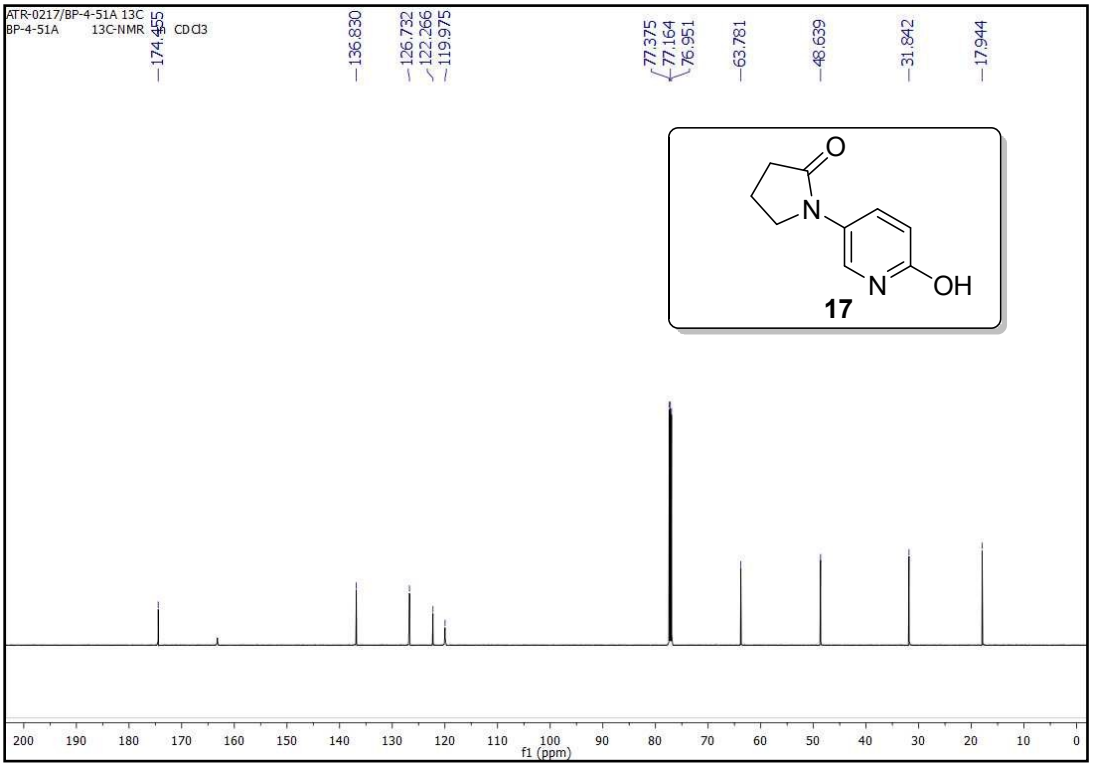


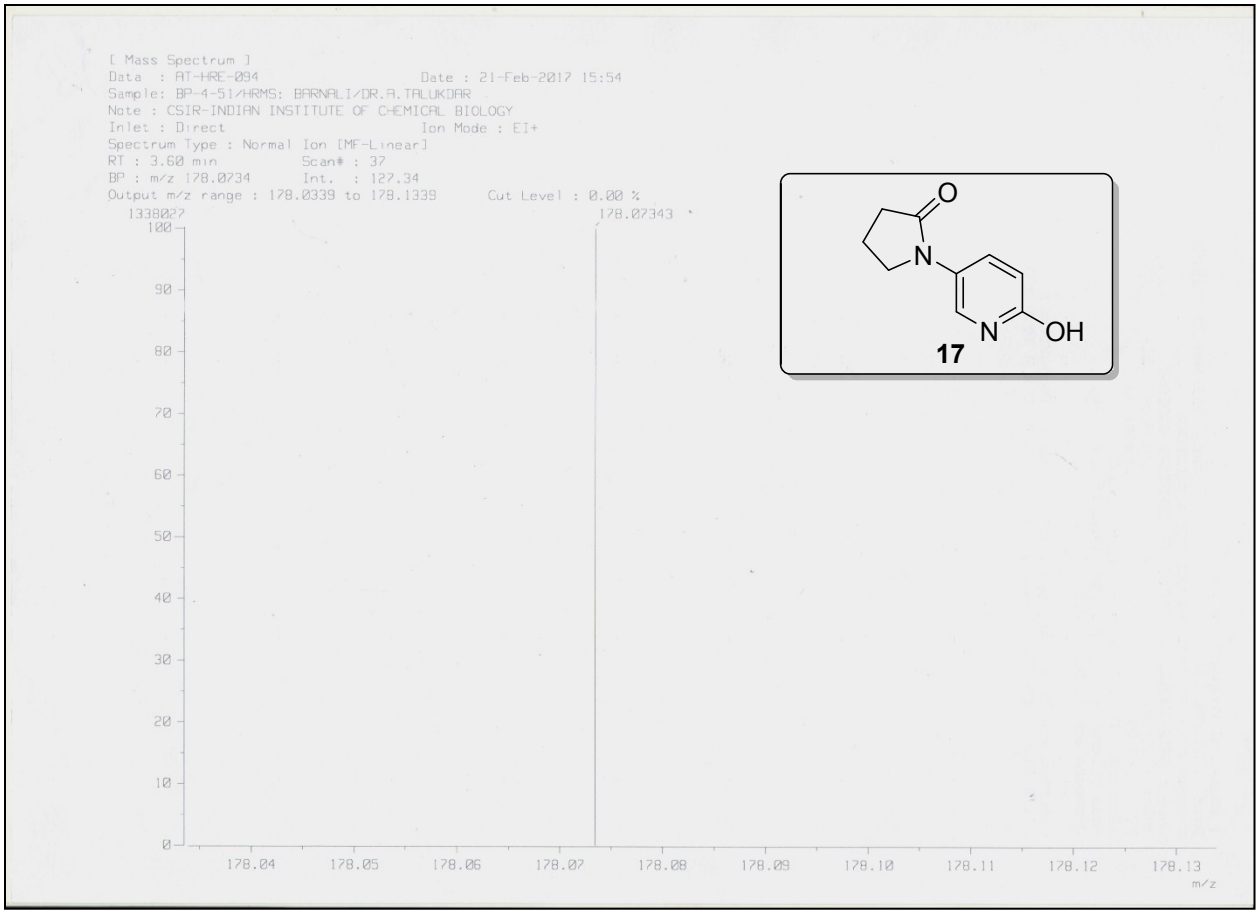


Mass Spectrum of **16**.

[1]H, [13]C NMR and Mass spectra of Compound 17:

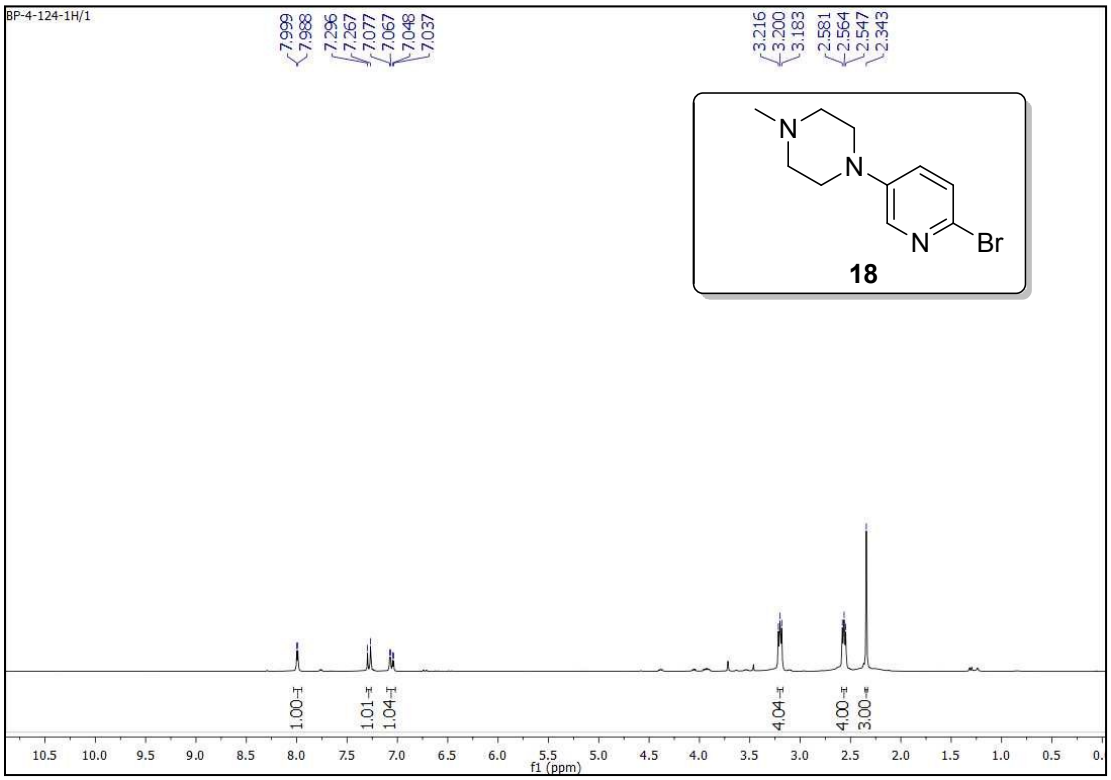


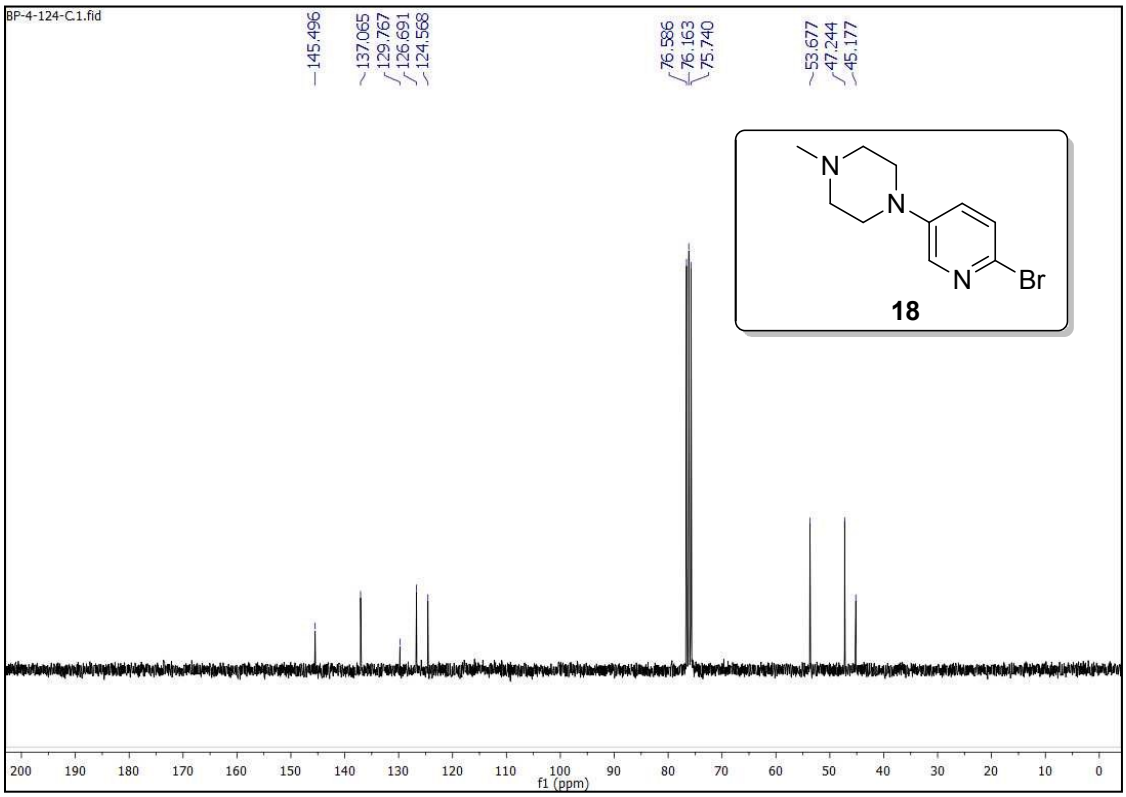


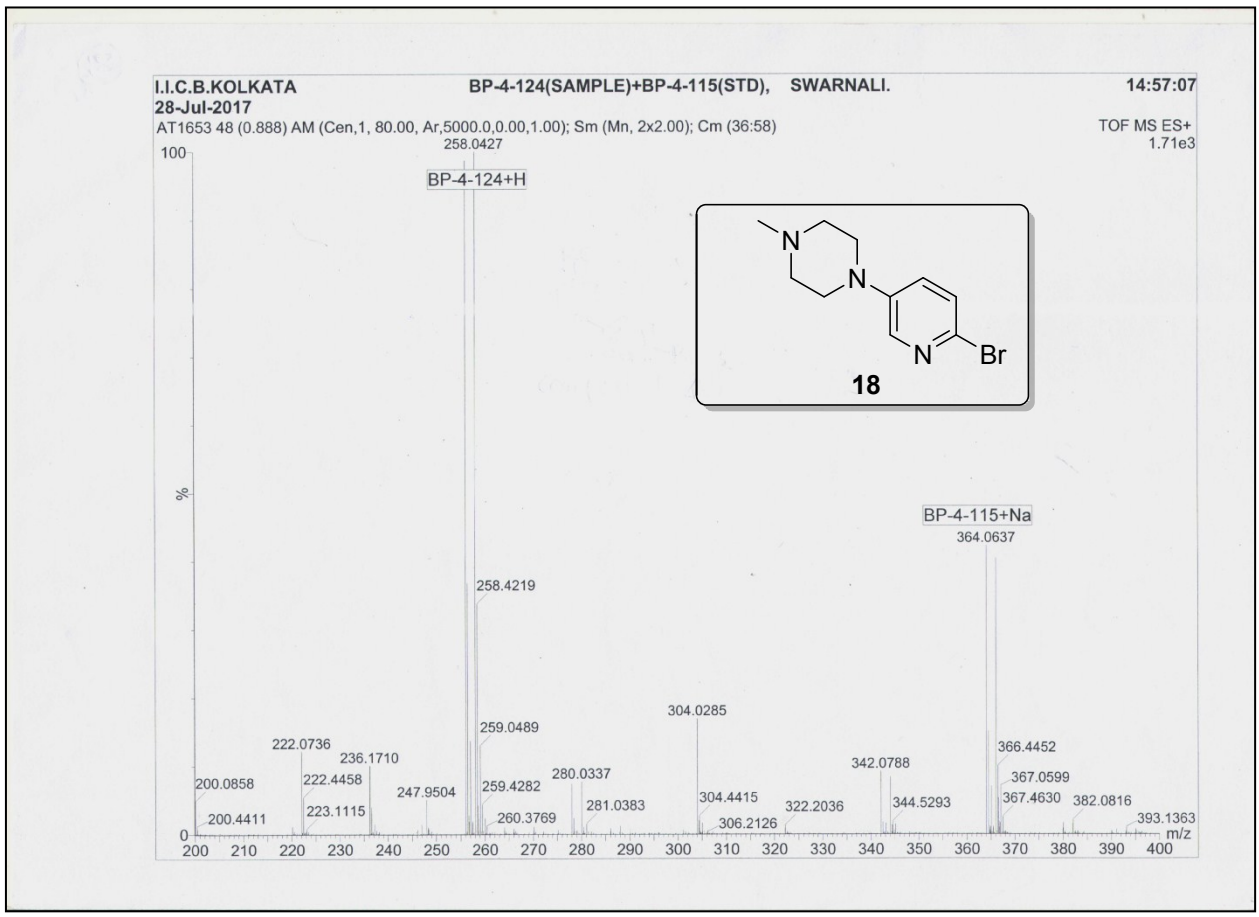


Mass Spectrum of **17**.

^{1}H, ^{13}C NMR and Mass spectra of compound 18:

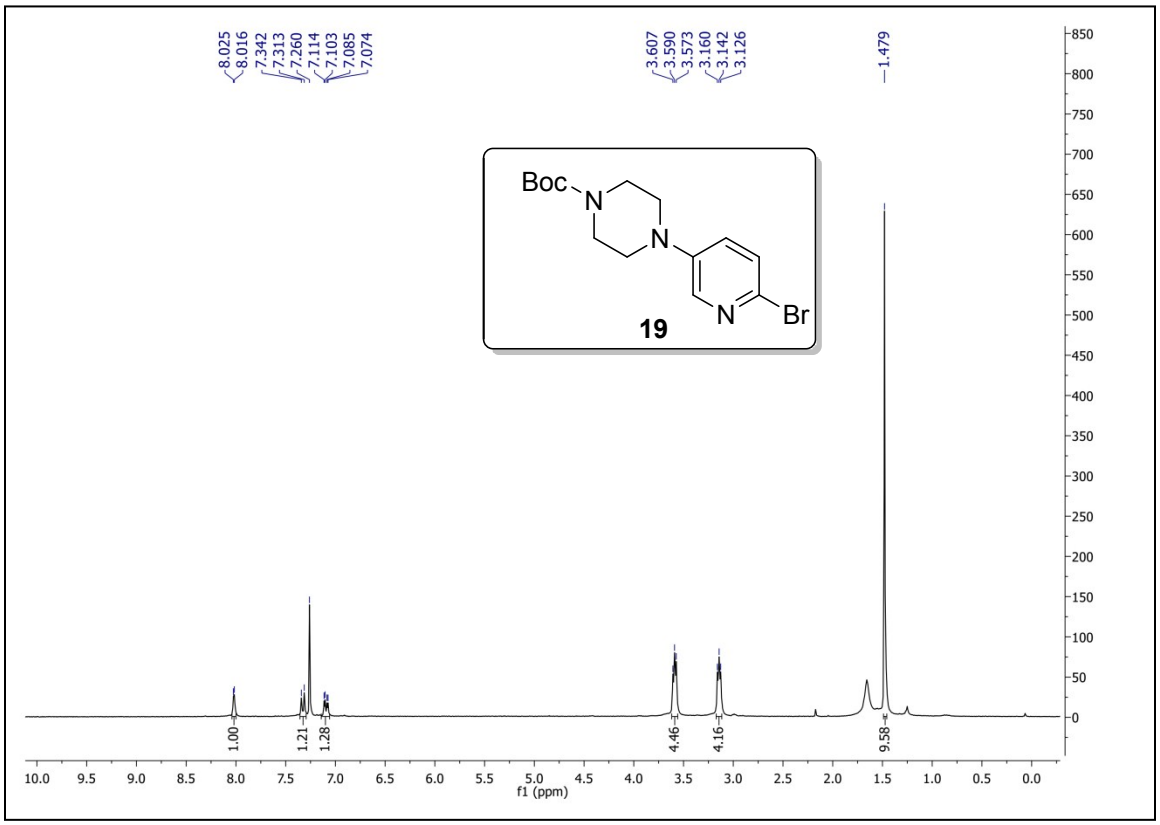


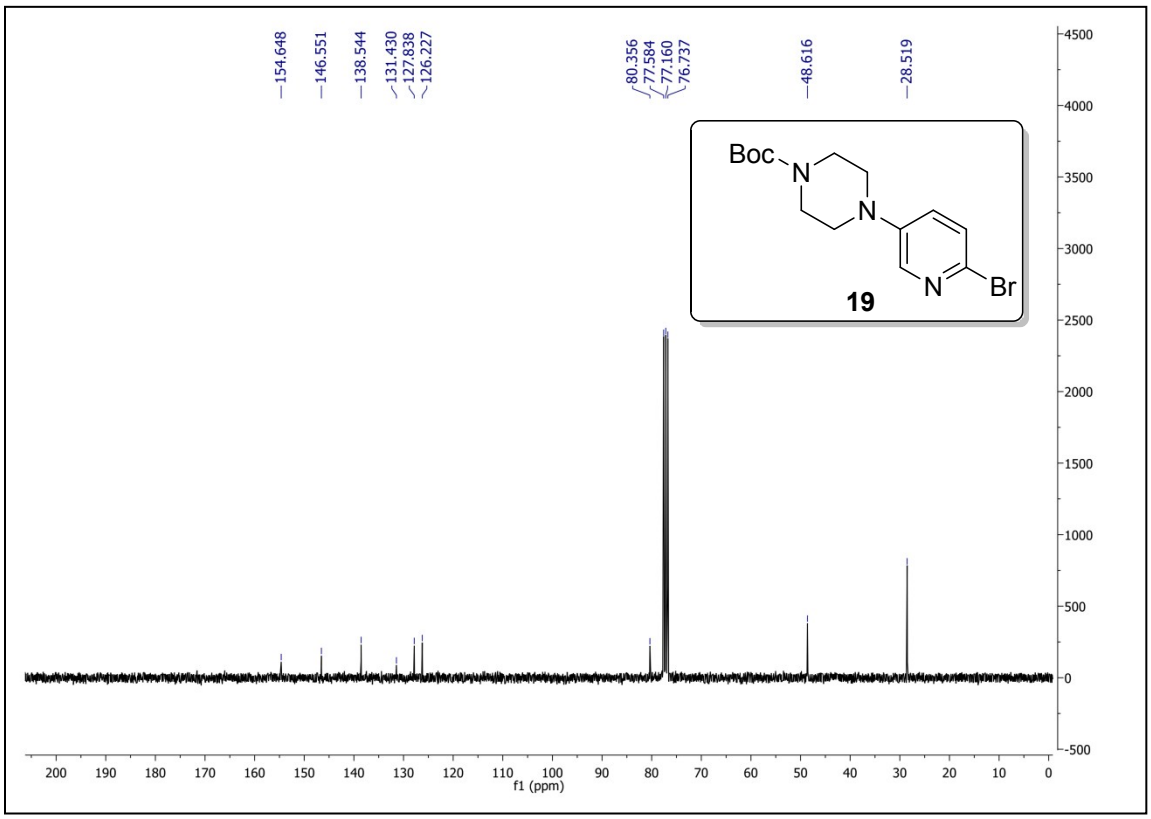


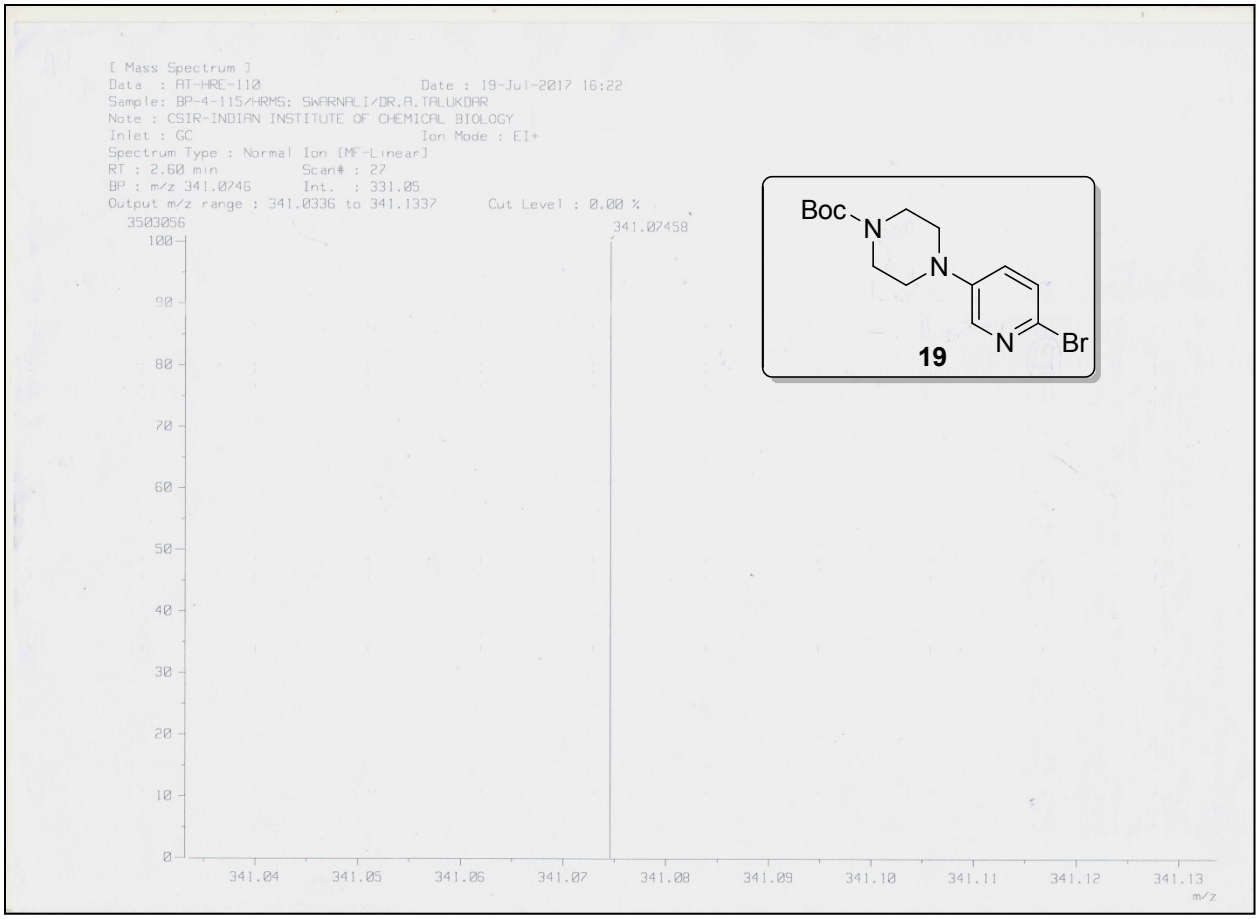


258.0427 is the $[M+H]^+$ peak of **18**. 364.0637 is the $[M+Na]^+$ peak of standard.

[1]H, [13]C NMR and Mass spectra of Compound 19:

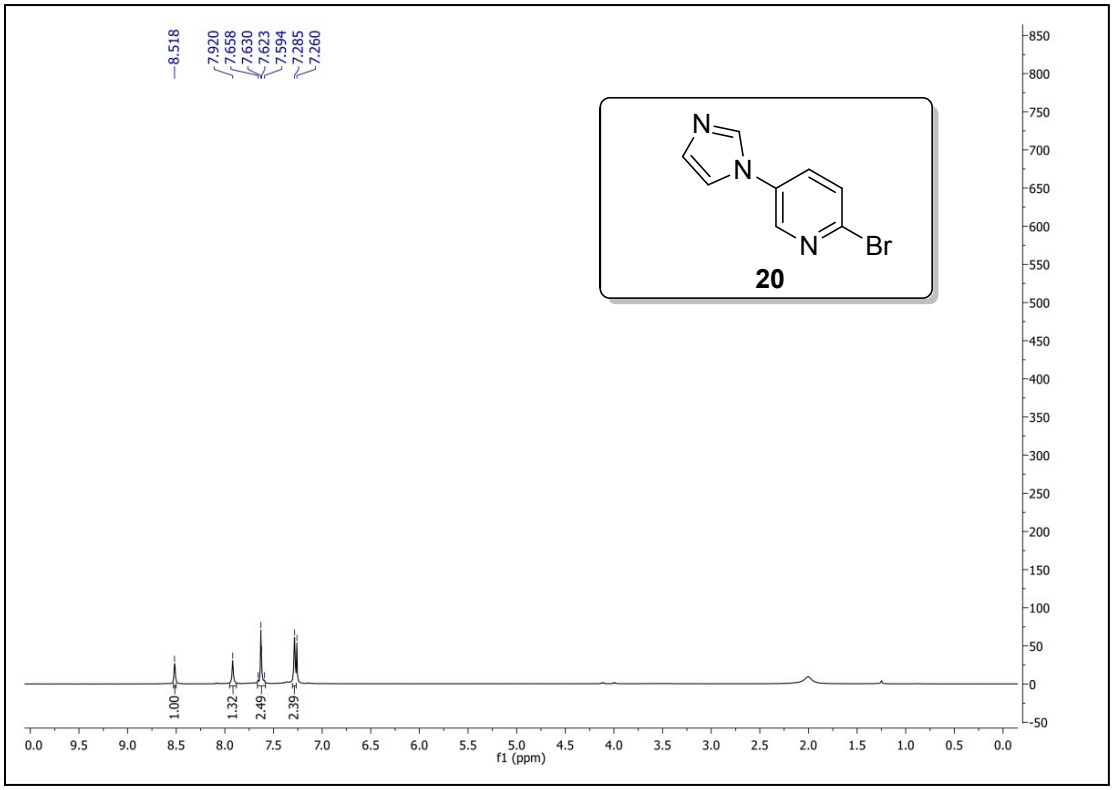


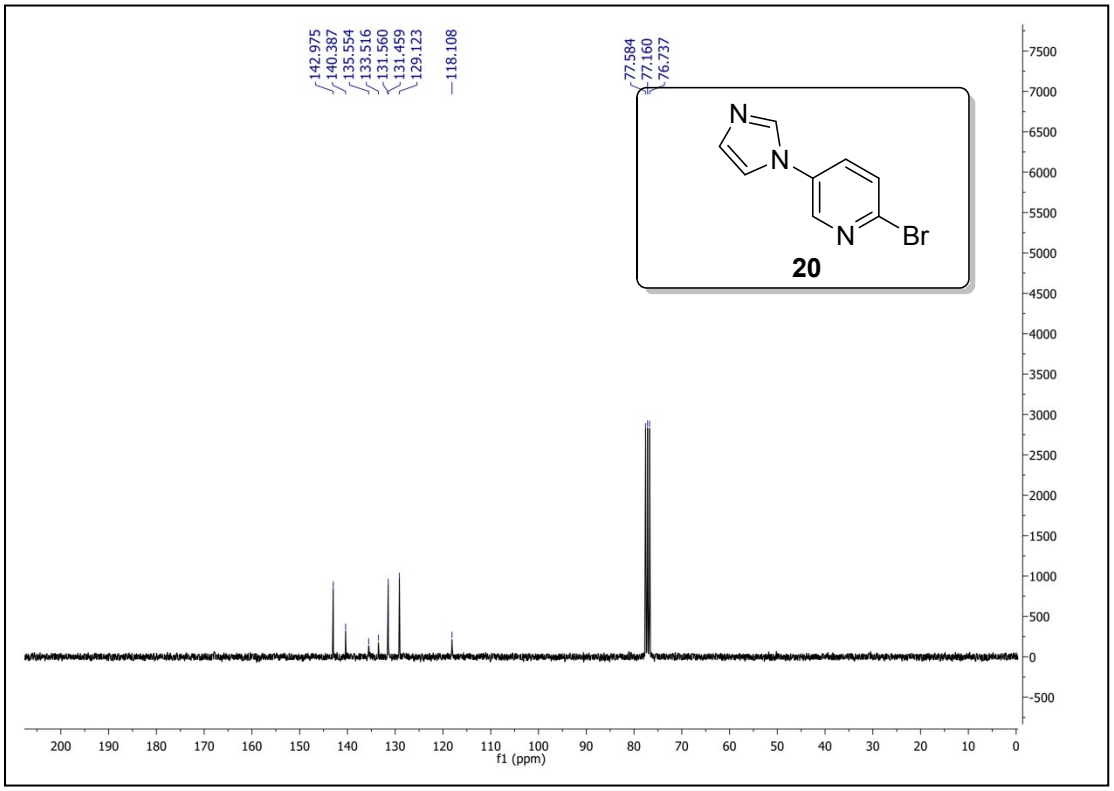


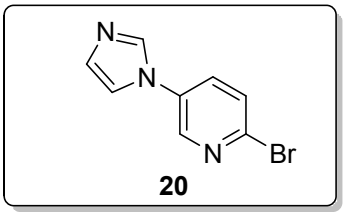


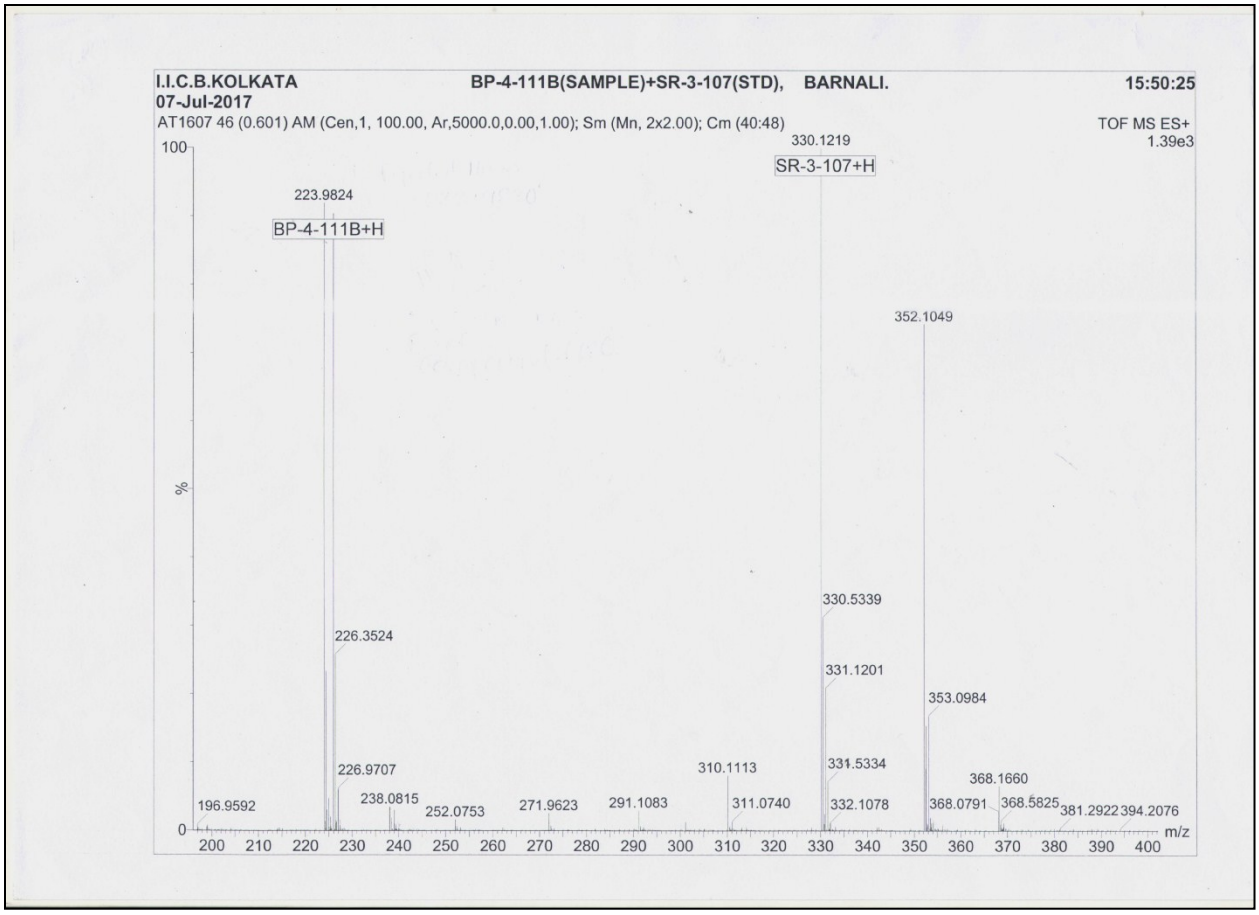
Mass Spectrum of **19**.

[1]H, [13]C NMR and Mass spectra of Compound 20:



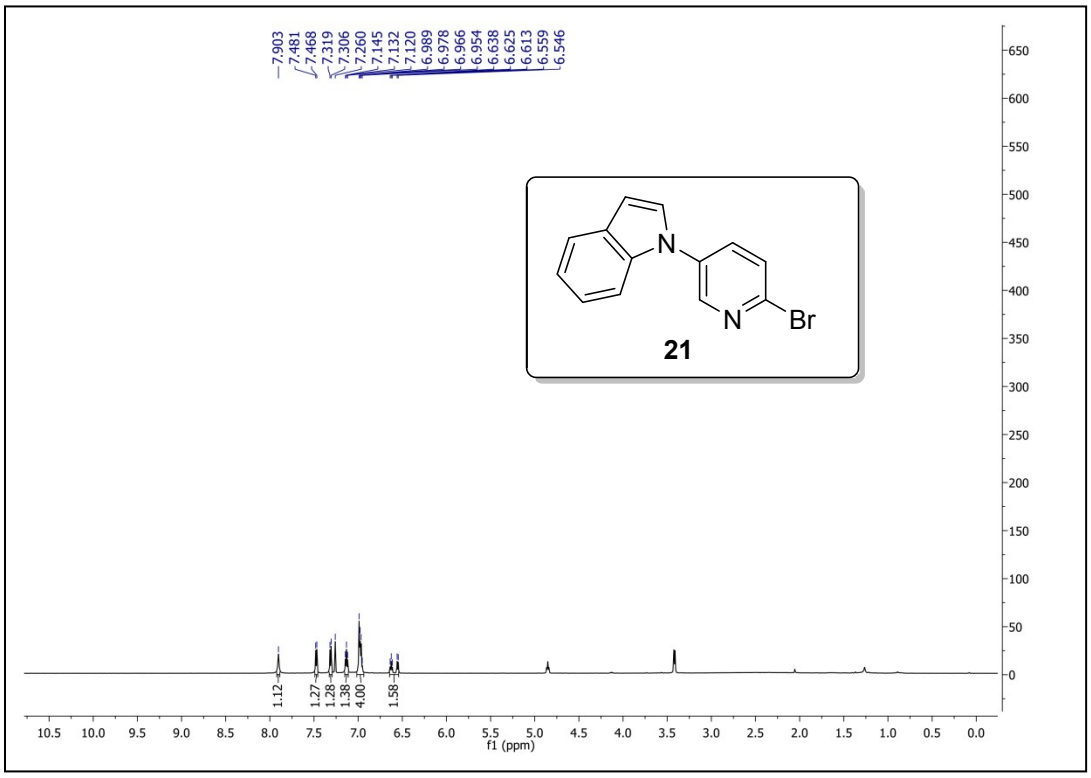


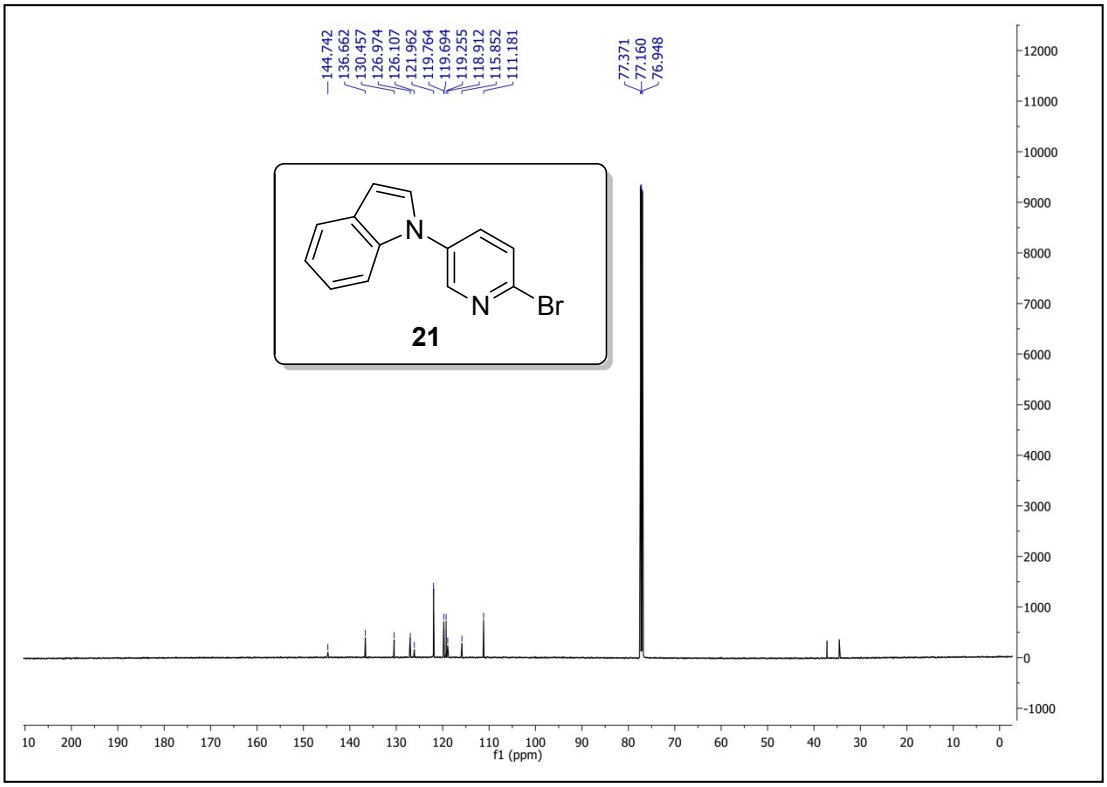


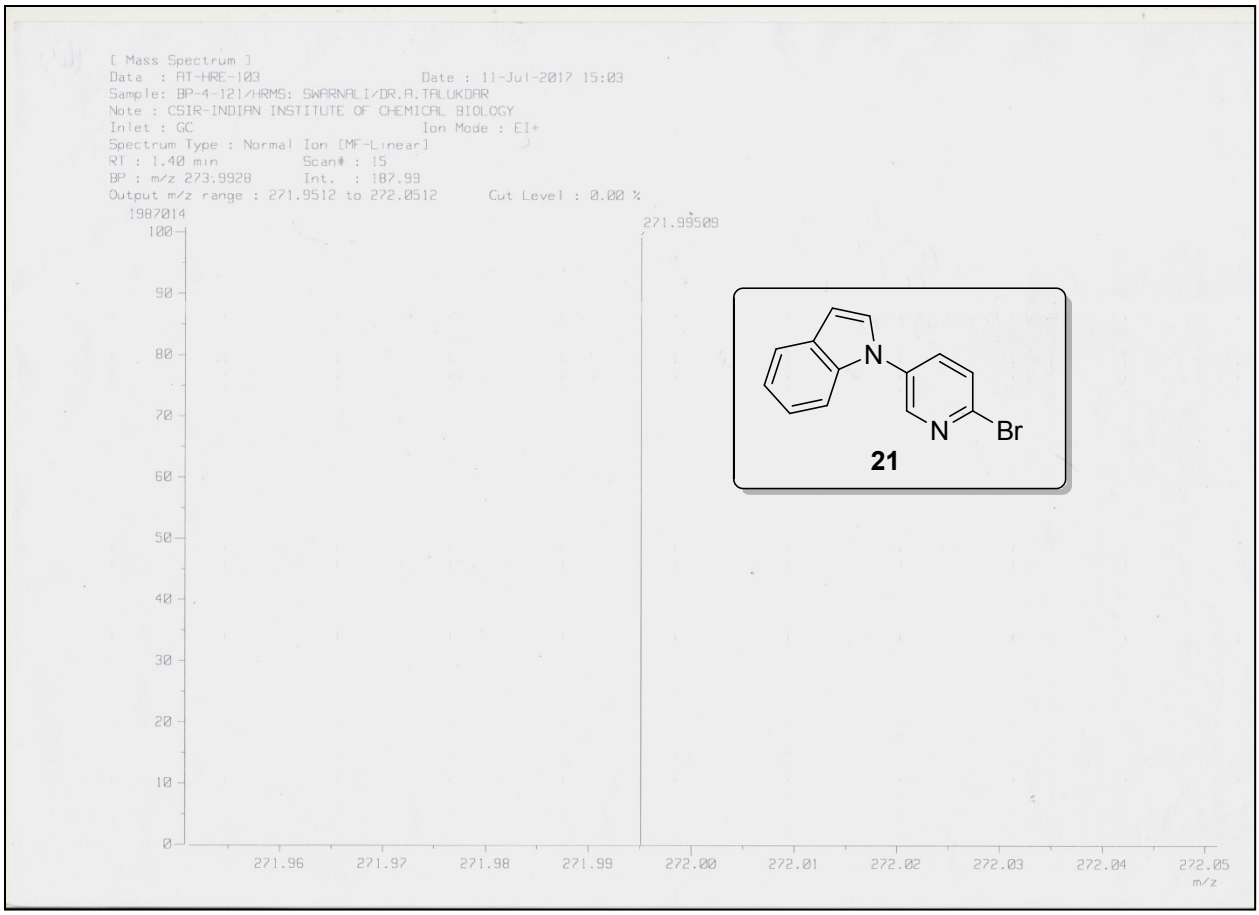


223.9824 is the $[M+H]^+$ peak of **20**. 330.1219 is the $[M+H]^+$ and 352.1049 is $[M+Na]^+$ peak of standard.

[1]H, [13]C NMR and Mass spectra of Compound 21:

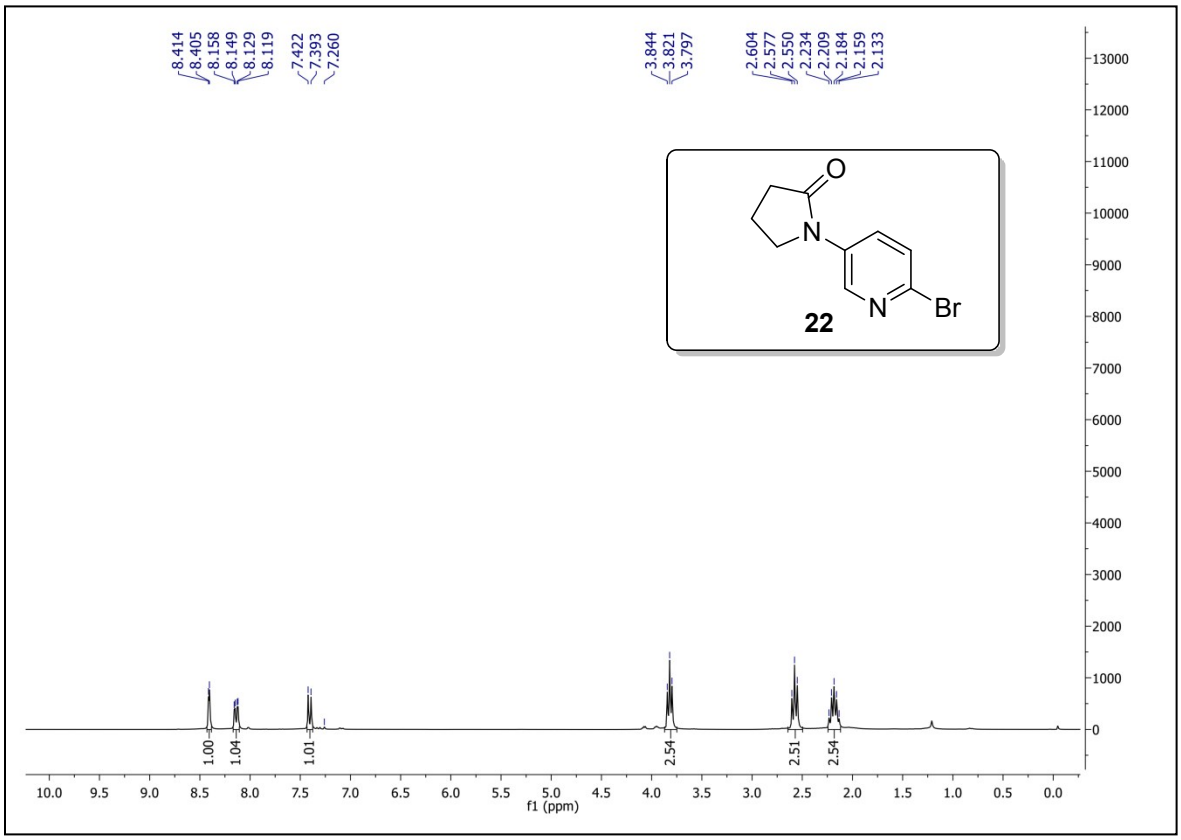


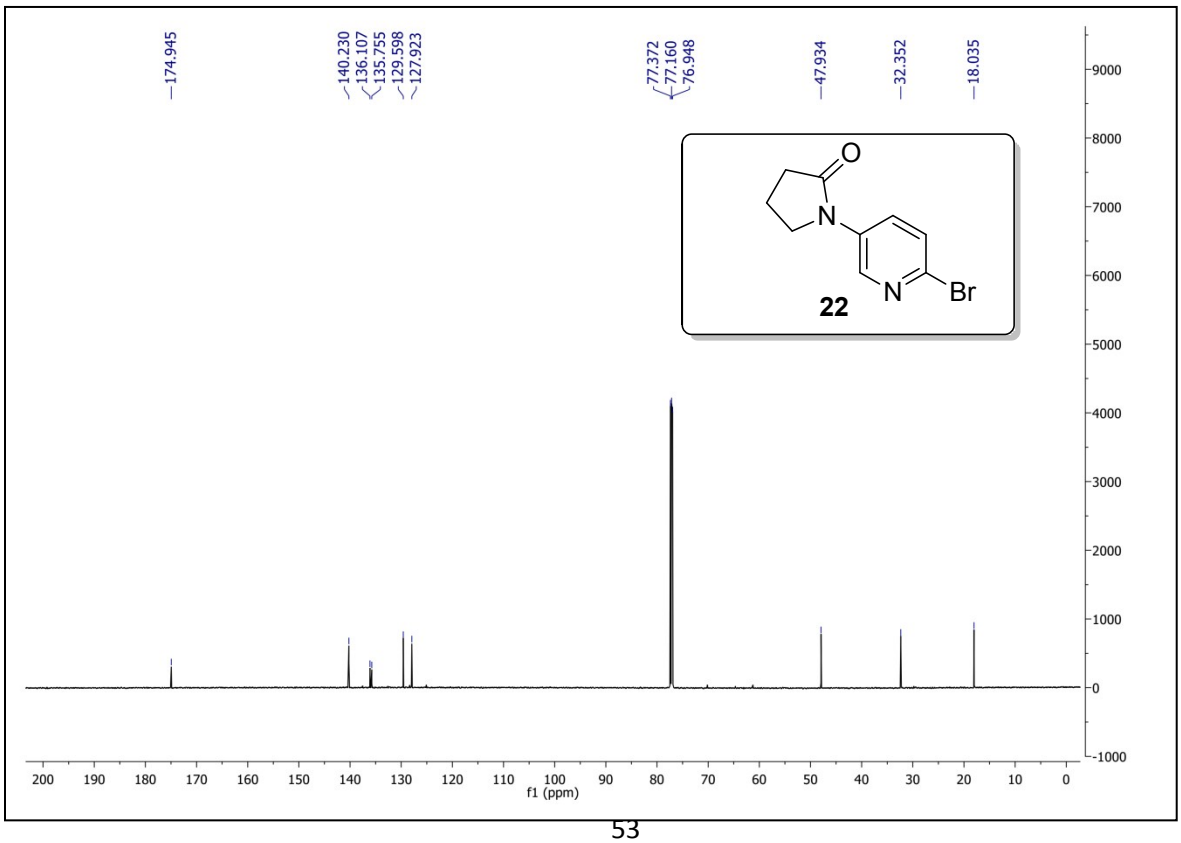


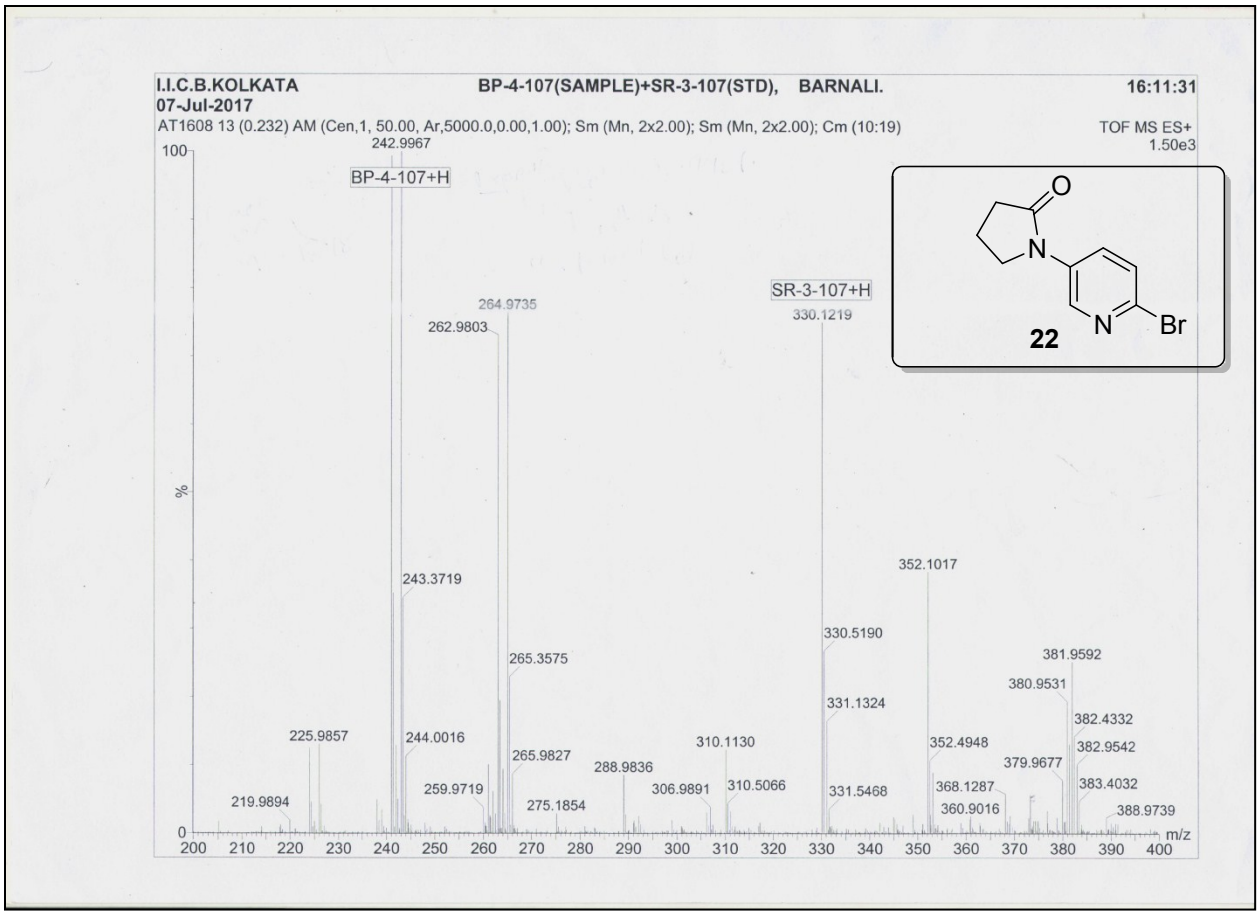


Mass Spectrum of **21**.

[1]H, [13]C NMR and Mass spectra of Compound 22:

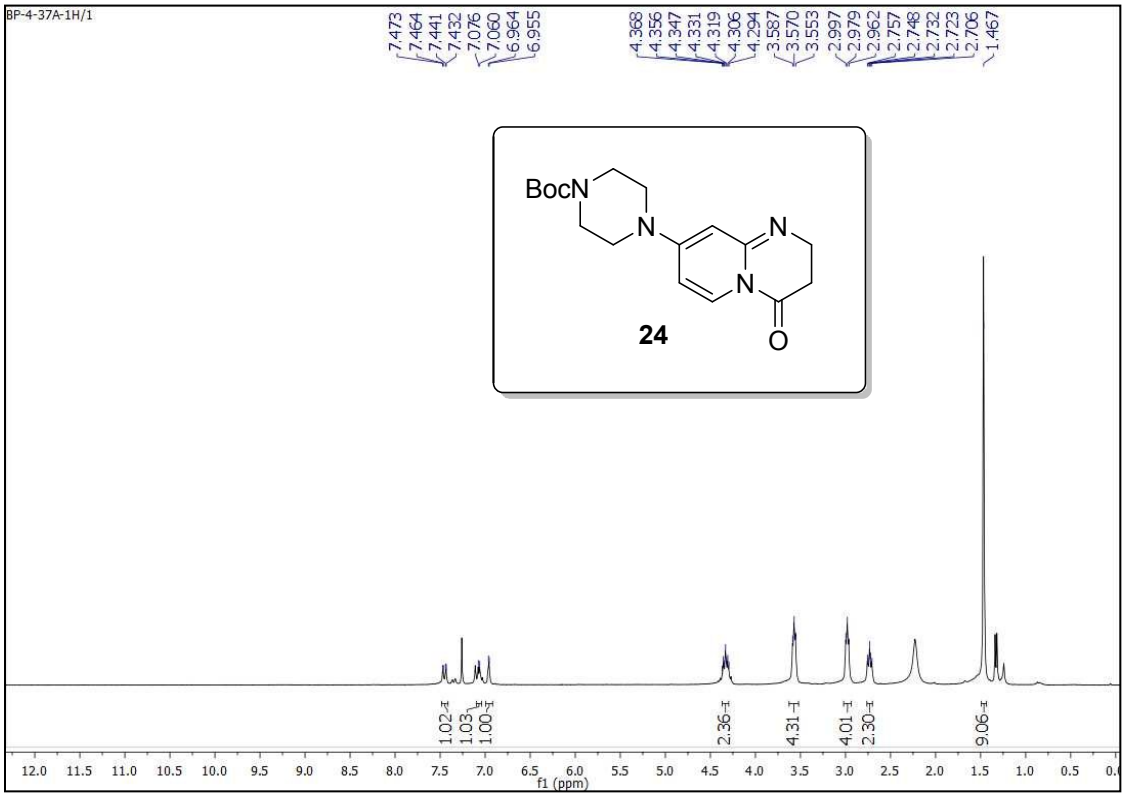


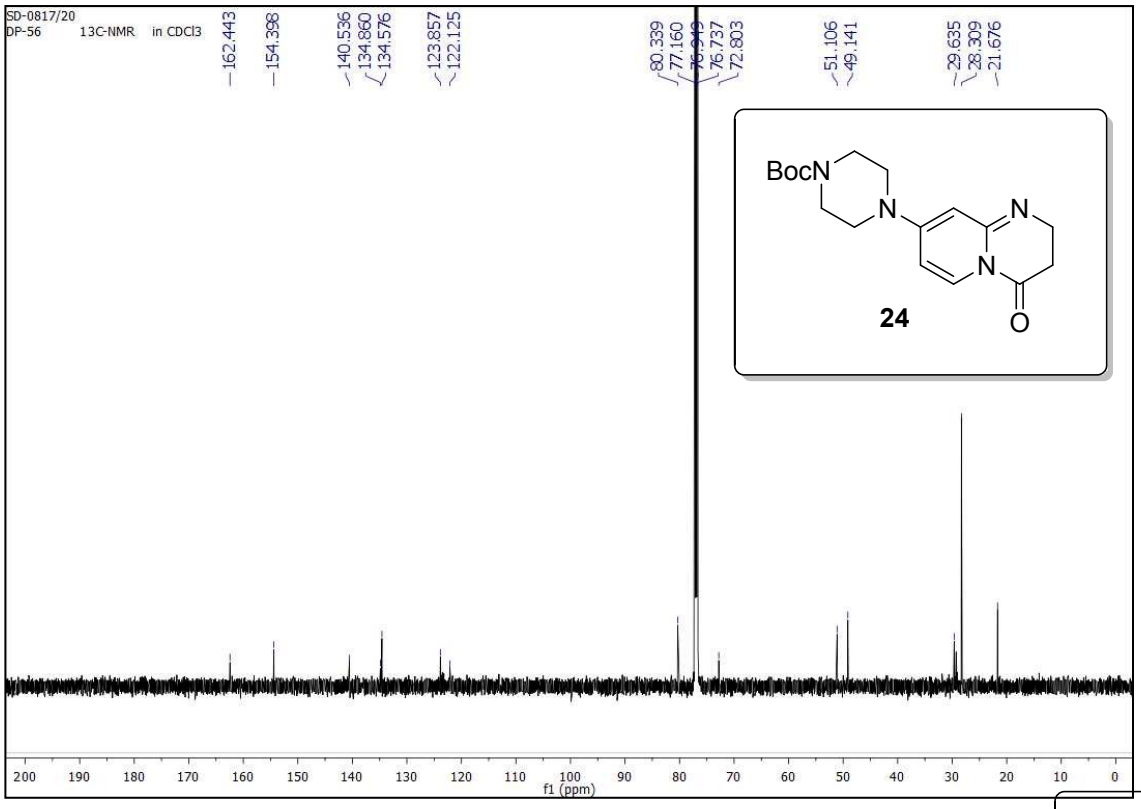


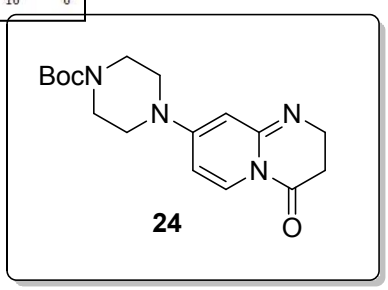


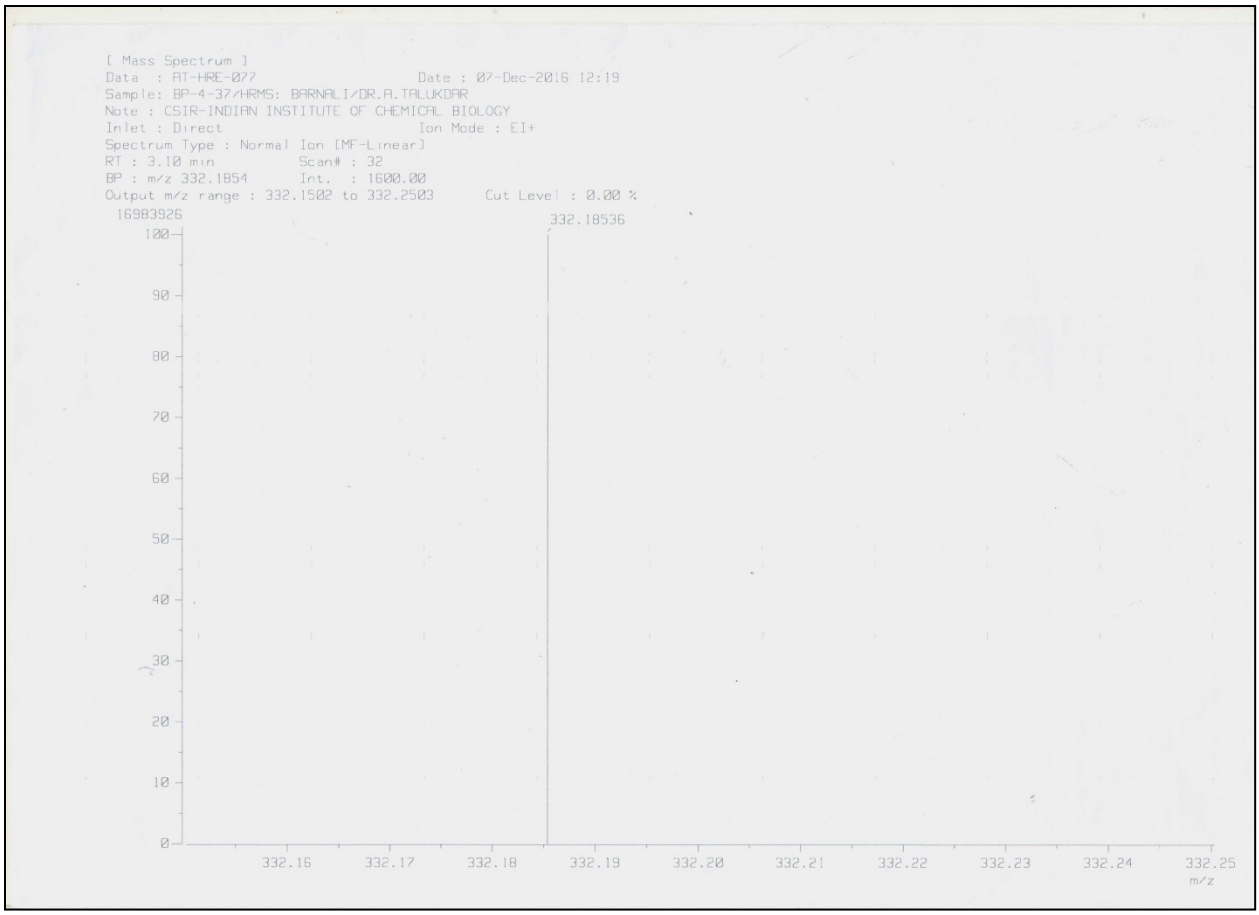
242.9967 is the $[M+H]^+$ and 264.9735 is $[M+Na]^+$ peak of **22**. 330.1219 is the $[M+H]^+$ and 352.1017 is $[M+Na]^+$ peak of standard.

^{1}H, ^{13}C NMR and Mass spectra of Compound 24:


BP-4-37A-1H/1
7.473
7.464
7.441
7.432
7.076
7.060
6.964
6.955
4.368
4.356
4.347
4.331
4.319
4.306
4.294
3.587
3.570
3.553
2.997
2.979
2.962
2.757
2.748
2.732
2.723
2.706
1.467
BocN
N
N
N
O
24
1.02
1.03
1.00
2.36
4.31
4.01
2.30
9.06
f1 (ppm)

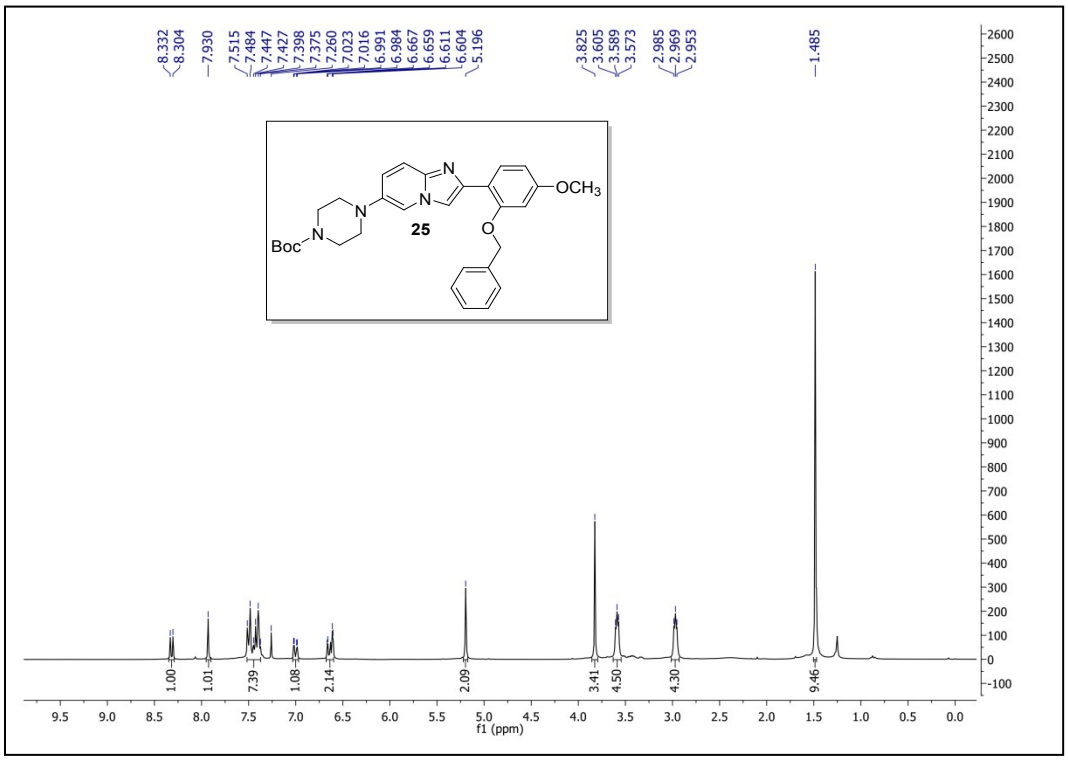

SD-0817/20
DP-56
13C-NMR
in CDCl3
162.443
154.398
140.536
134.860
134.576
123.857
122.125
80.339
77.160
76.737
72.803
51.106
49.141
29.635
28.309
21.676
BocN
N
N
N
O
24
f1 (ppm)

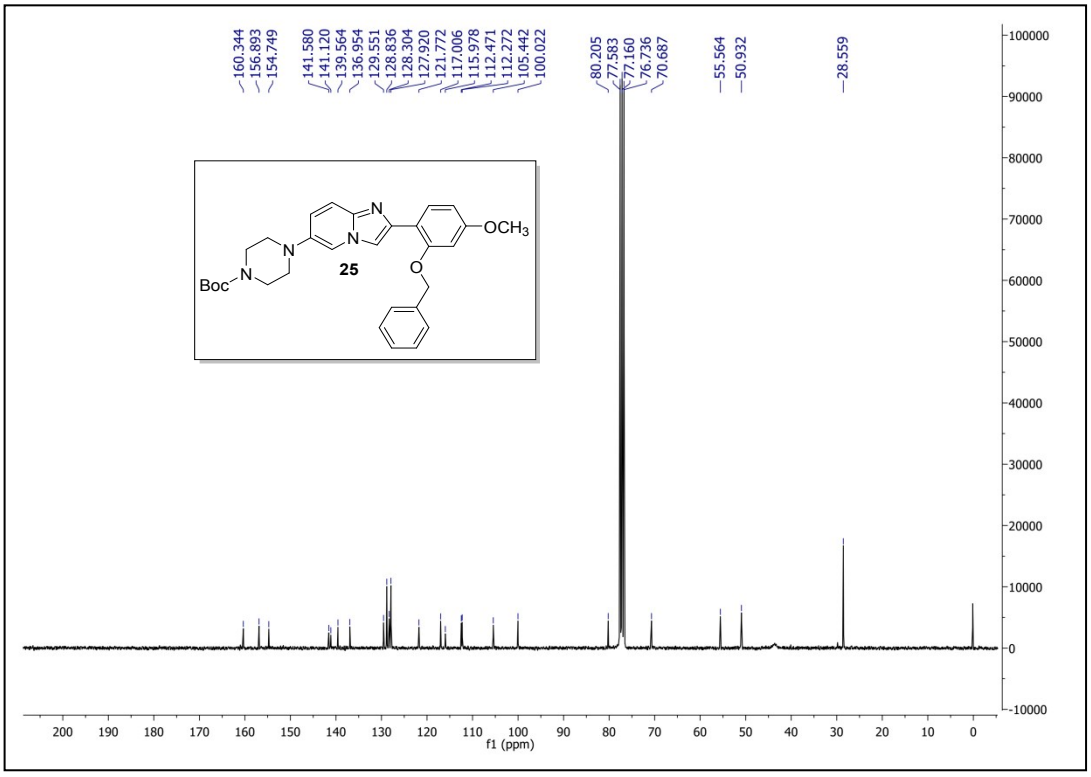

BocN
N
N
N
O
24

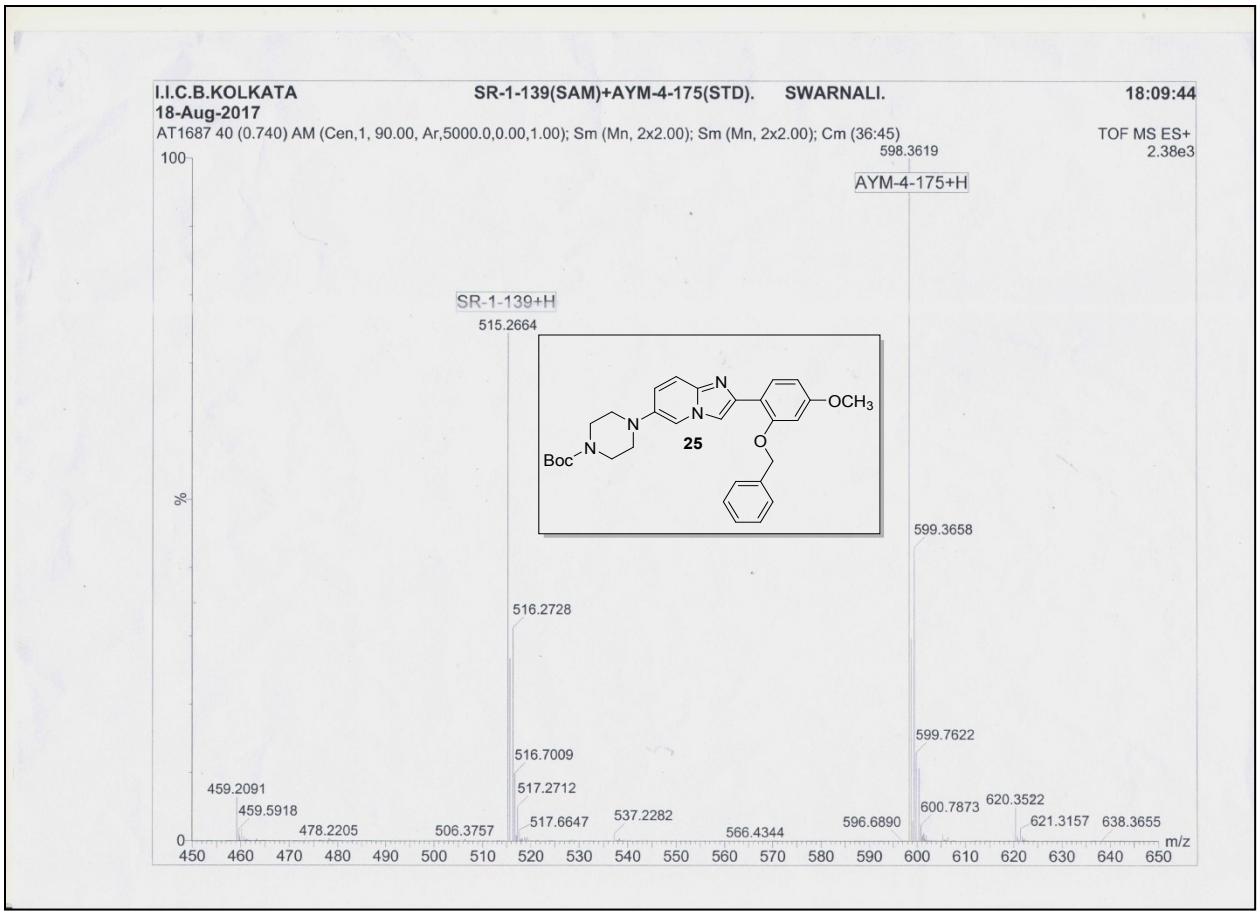


Mass Spectrum of **24**.

^{1}H, ^{13}C NMR and Mass spectra of Compound 25:


8.332
8.304
7.930
7.515
7.484
7.447
7.427
7.398
7.375
7.260
7.023
7.016
6.991
6.984
6.667
6.659
6.611
6.604
5.196
3.825
3.605
3.589
3.573
2.985
2.969
2.953
1.485
OCH3
Boc
25
1.00
1.01
7.39
1.08
2.14
2.09
3.41
4.50
4.30
9.46
f1 (ppm)


160.344
156.893
154.749
141.580
141.120
139.564
136.954
129.551
128.836
128.304
127.920
121.772
117.006
115.978
112.471
112.272
105.442
100.022
80.205
77.583
77.160
76.736
70.687
55.564
50.932
28.559
OCH3
Boc
25
f1 (ppm)



515.2664 is the $[M+H]^+$ peak of **25**. 598.3619 is the $[M+H]^+$ peak of standard.