Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.
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Supplementary Information

Heterogeneous palladium-based catalyst promoted reduction of oximes to amines: using H_2 of 1 atm in H_2O under mild conditions

1. General

All chemicals were commercially available and purchased from Aladdin (Shanghai, China Mainland) and were used as received without any further purification. All chemicals used are of analytical grade. ^{1}H NMR and ^{13}C NMR spectrum were recorded on a Bruker Avance-400 instrument, 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, with $CDCl_3$ or DMSO-d6 or CD_3OD-d4 as solvent in all cases. All chemical shifts (δ) were quoted in parts per million (ppm) and reported relative to an internal tetramethylsilane (TMS, δ 0.00) standard. The following abbreviations were used to explain the multiplicities: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet. Yields of some products were measured on a SHIMADZU instrument equipped with a C18 reverse column (Wonda Sil C18-WR 5μm) using ultrapure water and methyl alcohol (60:40, v/v) as the mobile phase at the flow rate of 0.8 ml/min, pH of mobile phase was set at 1.8, column temperature was 25°C, the wavelength of detector is 210nm. Yields of some others were measured by GC analysis using a FULI 9790II instrument equipped with a DB-624 capillary column (30 m × 1.4 um × 0.25 mm i.d). High-resolution mass spectrometry (HRMS) spectra was recorded on a SHIMADZU liquid chromatography/mass spectrometry ion-trap time-of-flight (LCMS-IT-TOF) instrument.

The High-Resolution Transmission Electron Microscope (HRTEM) measurements were performed on a JEM 2100F microscope. The samples were dispersed in ethanol solution with ultrasonic treatment for 5 min and then dropped onto a carbon film on copper grid. And the instrument was operated at 200 kV. Inductively coupled plasma-optical emission spectrometer (ICP-OES) from Perkin Elmer Nexion 300 was used to identify the Pd content of the nanoparticles. Samples were prepared by digesting 10 mg of nanoparticles in 2.0 mL of H_2O_2 and 8ml aqua regia using constant temperature drying oven for 3 hours. The solutions was made up to 50 mL in standard flask and start to detect Pd.

X-ray diffraction (XRD) patterns was collected from 5° to 90° with a step of 0.02 on a Bruker D 8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a Lynxeye one-dimensional detector. Elemental analysis (EA) measurement was performed using the Flash 2000. X-Ray photoelectron spectroscopy (XPS) measurements were obtained in ultra-high vacuum (base pressure of 1×10^{-10} mbar) equipped with an Al source (Kα radiation of 1486.6 eV) and an Escalab 250Xi analyser at 53° detection angle.

2. General procedure for the preparation of Pd-L8

To a mixed solution of the 4-nitrobenzene-1,2-diamine (15.3 mg, 0.1 mmol) and HBF_4 (40%,1ml), sodium nitrite (13.8mg, 0.2mmol) dissolved in ultrapure water (1ml) was added dropwise, with light-yellow solid 2'-(4-nitro-1,2-phenylene)bis(1-(trifluoro-λ^5-boranylidene)diazen-1-ium) fluoride generated. After being stirred at 0°C for 1 h, the light-yellow solid was obtained, reacting subsequently with toluene (1ml), ultrapure water(2ml) and potassium tetrachloropalladate (K_2PdCl_4, 26.0mg, 0.08mmol) in another new reaction system, which was stirred with a magnetic bar for another 1 h. $NaBH_4$ (22.6mg, 0.6mmol) dissolved in ultrapure water(1ml) was dropped at room temperature to the previous solution and incubated at room temperature for 2 h. After that, the mixed solution was transferred to a 10 ml centrifuge tube and centrifuged, the aqueous phase was separated and the rest of solid phase was washed with diluted H_2SO_4 (0.5M) three times, following three times washing with a solution of

$NaHCO_3$(0.5M). The resulted suspension was centrifuged again, its solid phase was washed with ethanol and sonicated for 5 minutes, and centrifuged to remove ethanol. The resulted solid was dried to provide Pd-L8.

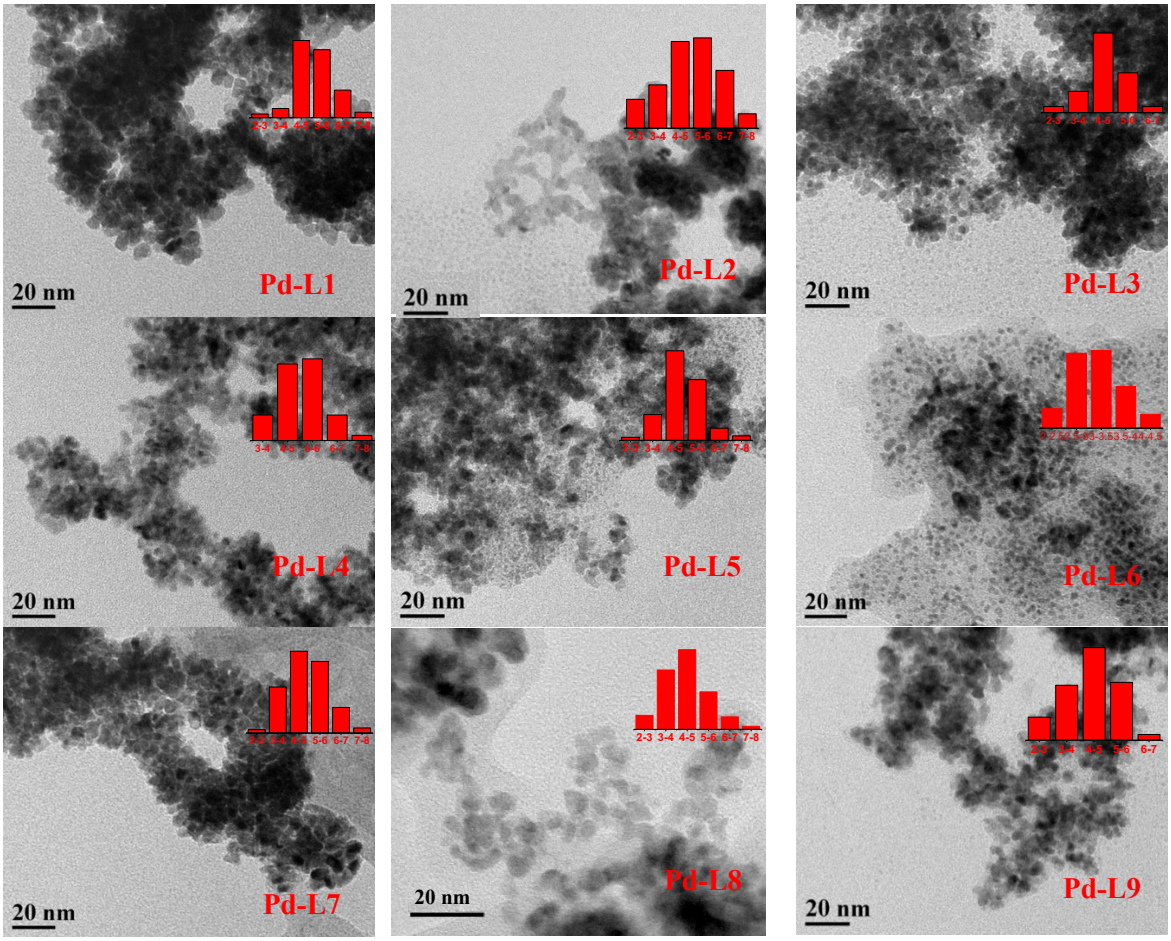


Figure S1 High resolution TEM patterns of Pd-ligand

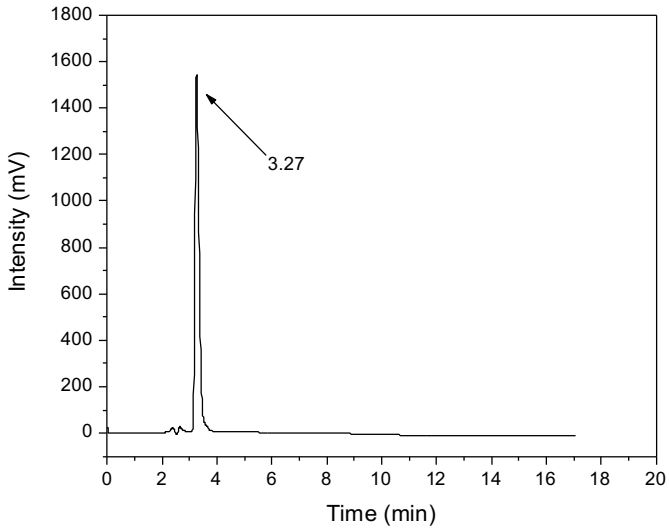
High resolution transmission electron microscopy(HRTEM) image of the catalyst Pd-(L1-L9) was presented in **Figure S1** to observe their morphology clearly. The HRTEM analysis showed the catalyst Pd-(L1-L7), and Pd-L9 were not well dispersed nanoparticles as an average diameter of these nanoparticles Pd-(L1-L9) were measured as 5.2nm, 5.1nm,4.5nm, 5.1nm, 4.8nm, 4.1nm, 4.9nm, 4.4nm, and 4.2nm, respectively, falling within the range of nanoparticle and therefore was called Palladium nanoparticles. All the nanoparticles had some levels of aggregation, however, the catalyst Pd-L8 was found to be relatively well dispersed.

3. General procedure for synthesis of primary amines

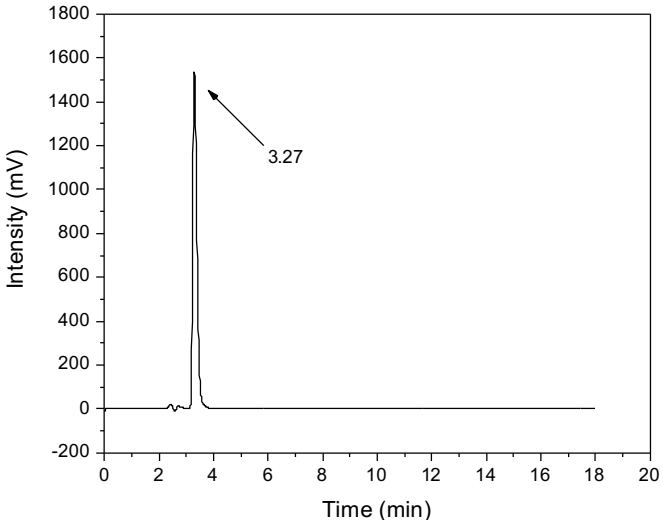
Oxime (0.05 mmol), and Pd-L8 (0.5 mg, 4 mol %) were taken in an oven dried reaction bottle (25 ml) equipped with magnetic pellet. H_2O (10 ml, pH = 9.0) were added to the reaction tube and the reaction mixture was stirred at room temperature with H_2 balloon. The reaction was monitored by TLC. The reaction conversions and yields were determined by HPLC analysis equipped

with a C18 column. When the substrate completely consumed, the reaction was stopped and then the solution was extracted with saturated salt water and ethyl acetate (3×10ml). The organic phase was dried by using Na_2SO_4 and concentrated in vacuum. The crude product was purified by column chromatography using silica gel. The products were characterized with NMR (Due to the small scales of the reactions, higher concentration samples were afforded by combining several runs.).

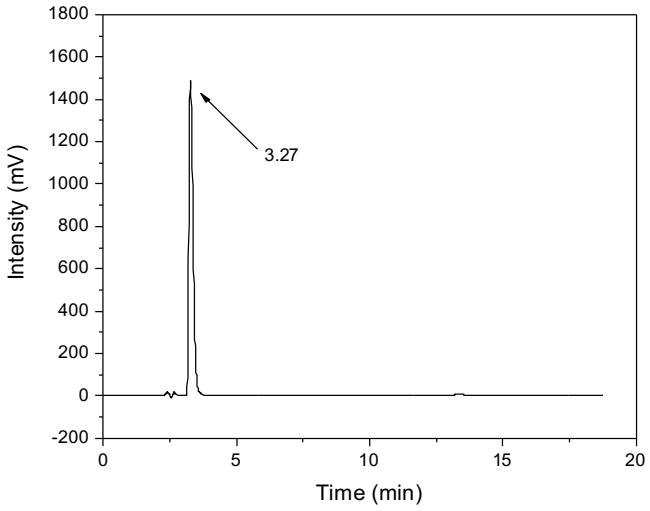
4. High performance liquid chromatogram under different reaction conditions



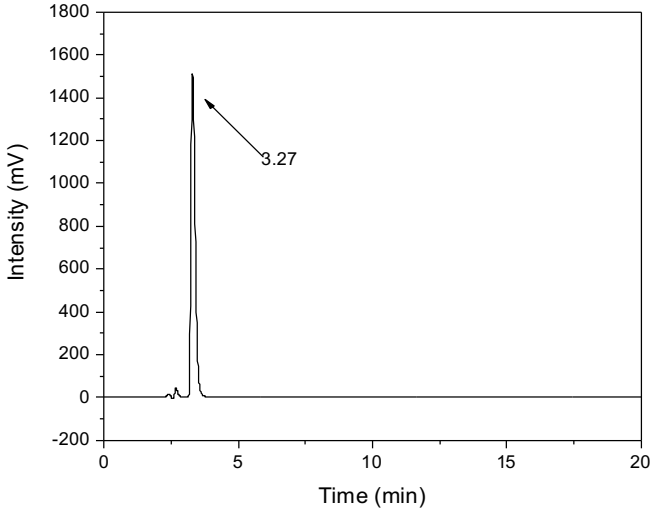
Chromatogram of the reaction performed at pH=1.0 (Table1 Entry 18).



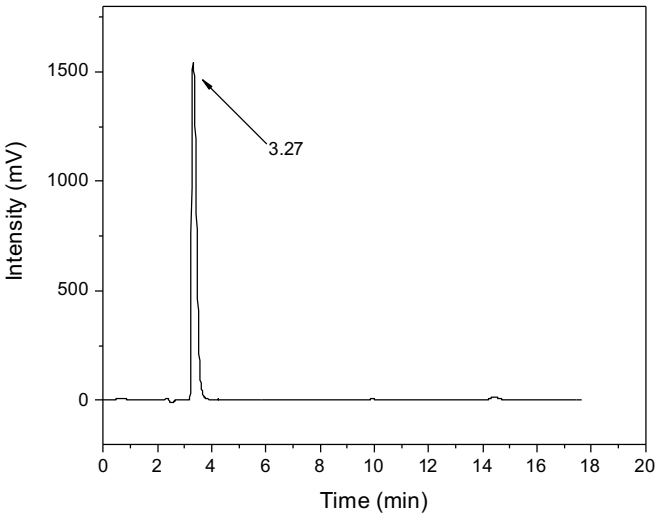
Chromatogram of the reaction performed at pH=3.0 (Table1 Entry 19).



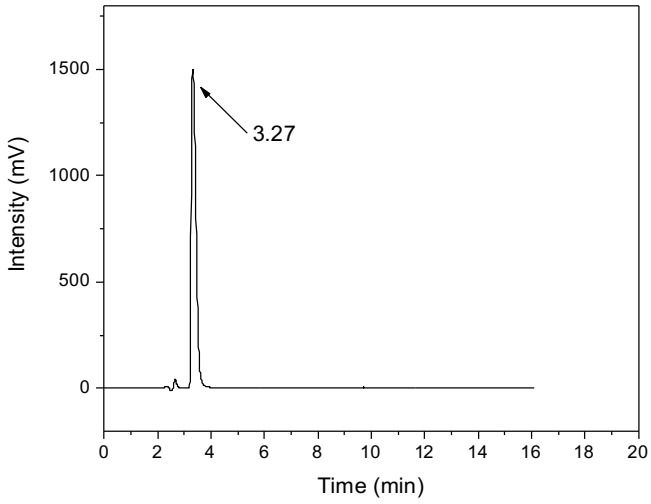
Chromatogram of the reaction performed at pH=5.0 (Table1 Entry 20).



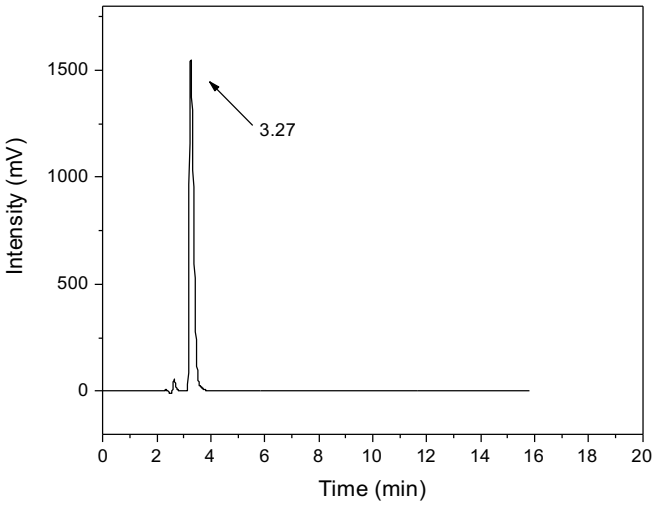
Chromatogram of the reaction performed at pH=7.0 (Table1 Entry 21).



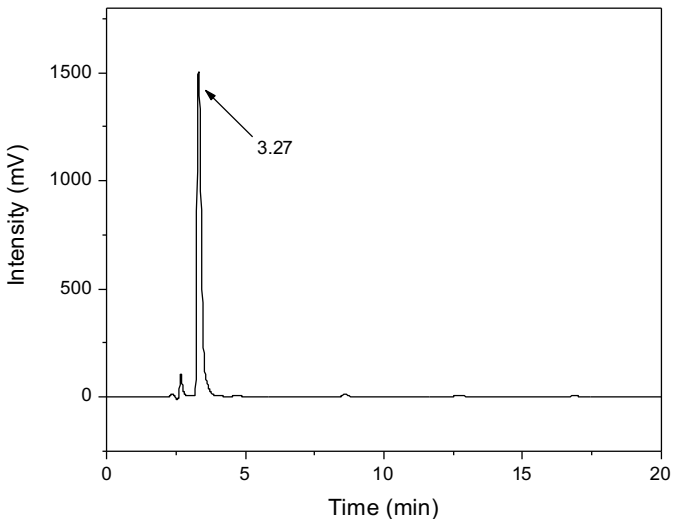
Chromatogram of the reaction performed at pH = 8.0 (Table1 Entry 22).



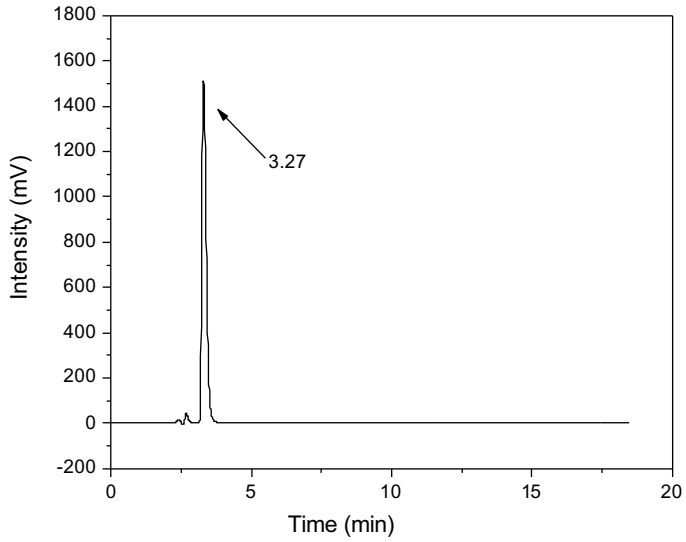
Chromatogram of the reaction performed at pH = 9.0 (Table1 Entry 23).



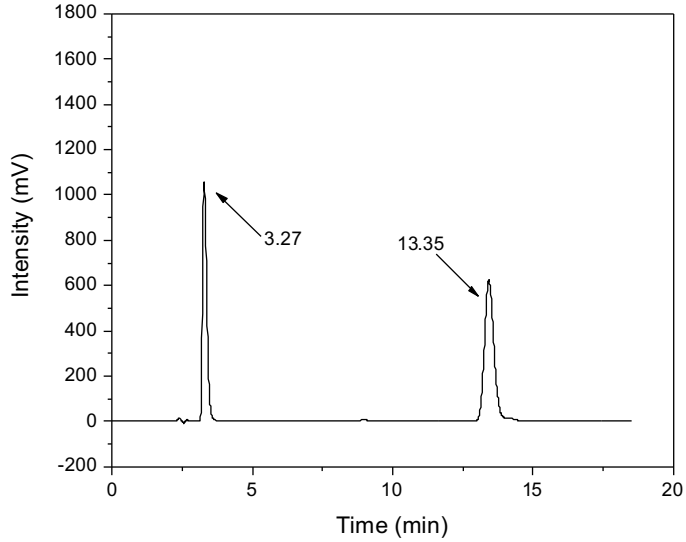
Chromatogram of the reaction performed at pH = 10.0 (Table1 Entry 24).



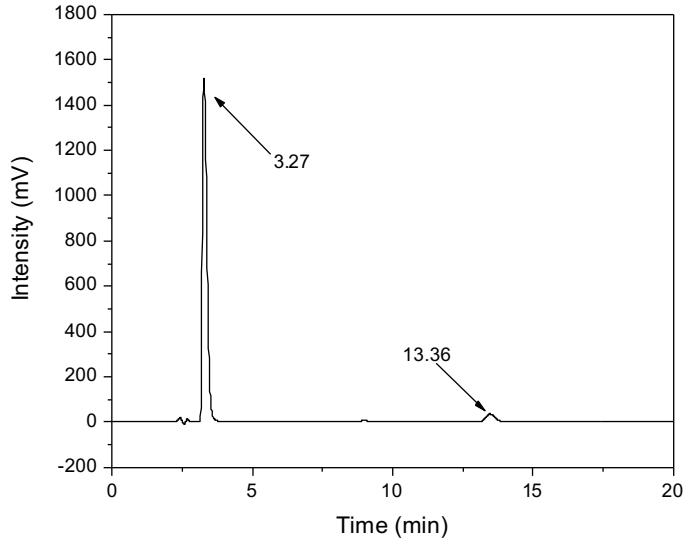
Chromatogram of the reaction performed at pH=11.0 (Table1 Entry 25).



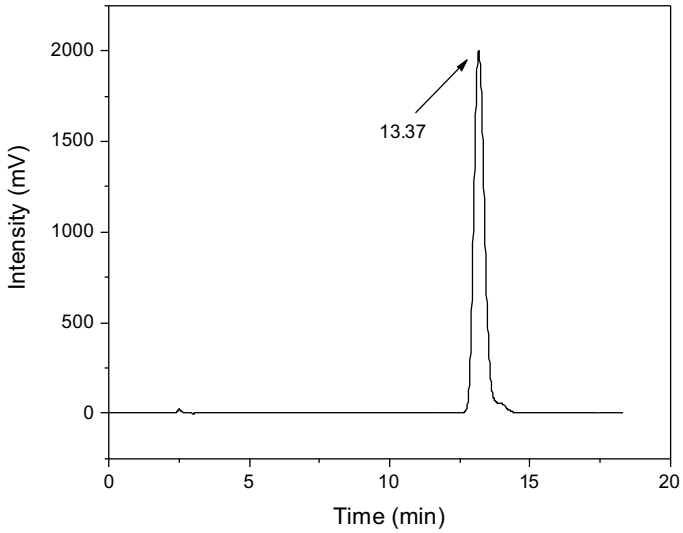
Chromatogram of the reaction performed at pH= 12.0 (Table1 Entry 26).



Chromatogram of the reaction result from hydrogenation of benzaldoxime (Entry 28, Table1).



Chromatogram of the reaction result from hydrogenation of benzaldoxime (Entry 29, Table1).



Chromatogram of benzaldoxime (**1a**)

5. ^{1}H NMR spectrum analysis of diazonium salt and Pd-L8.

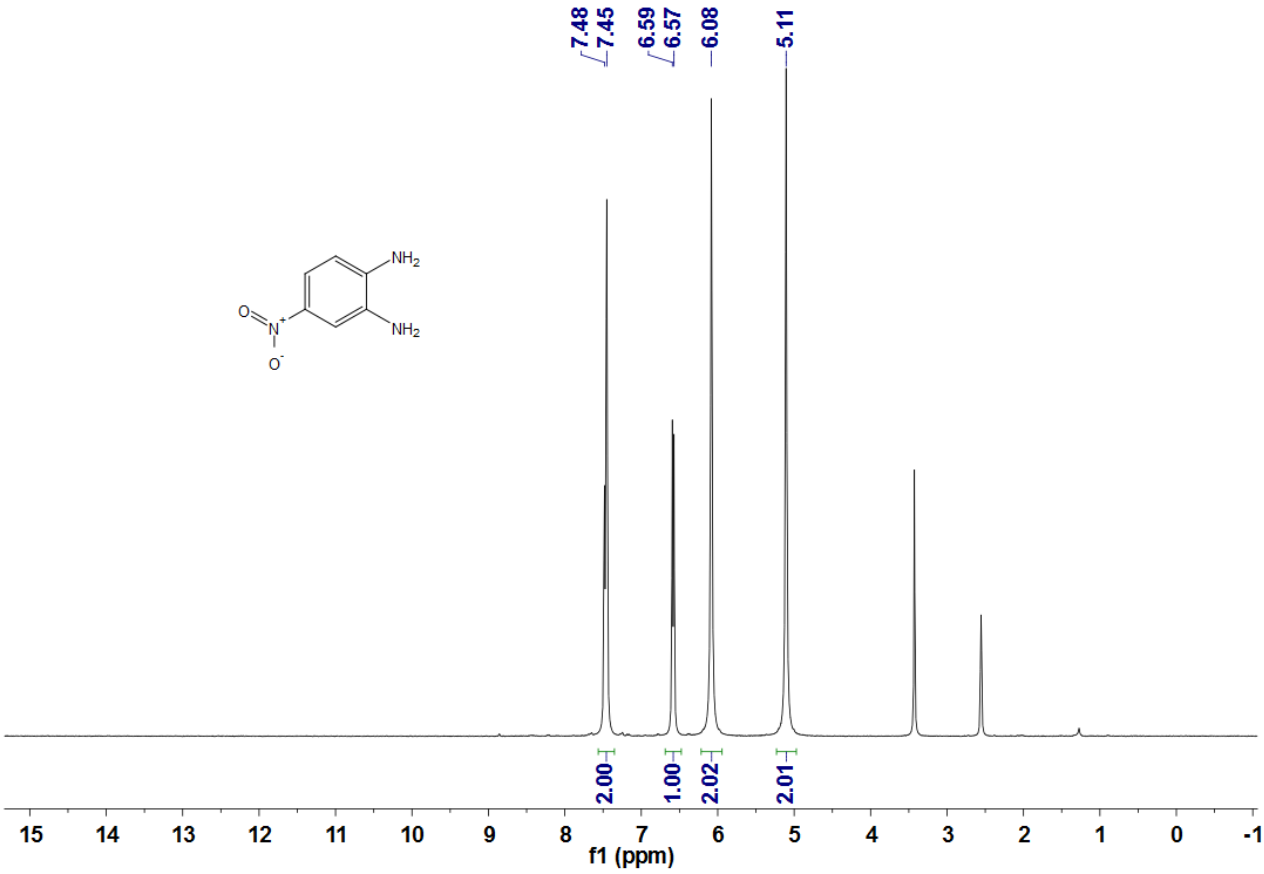


Figure S2. 1H NMR spectrum of 4-nitrobenzene-1,2-diamine

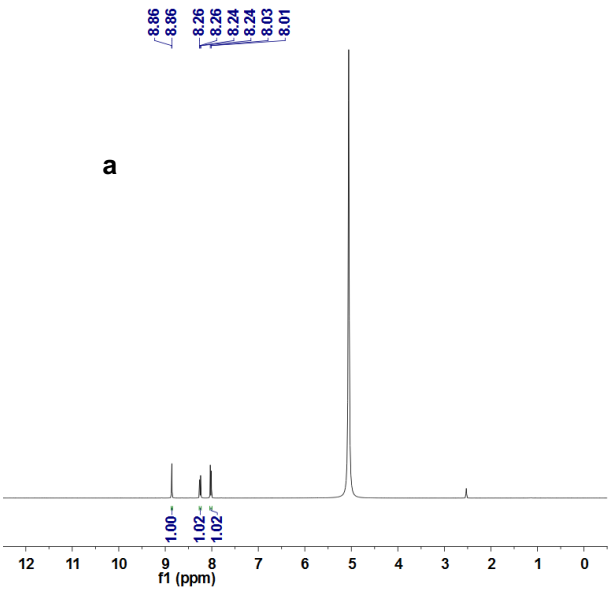


Figure S3. ^{1}H NMR spectrum of diazonium salt(a)

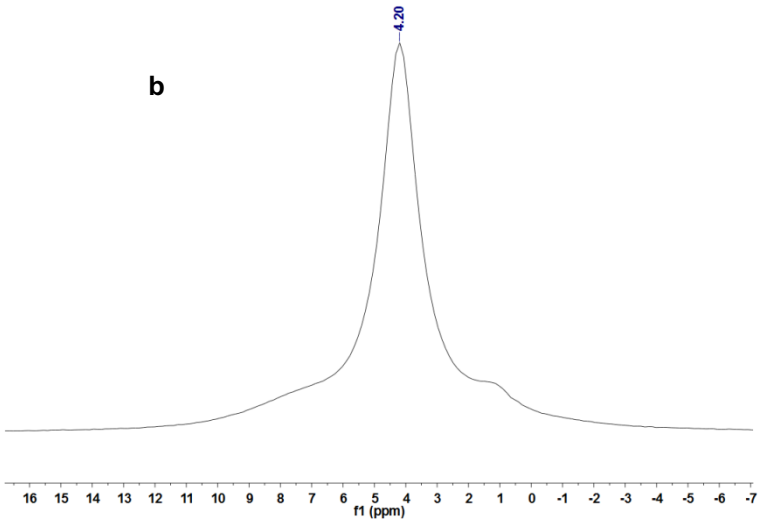


Figure S4. Solid state ^{1}H NMR spectrum of Pd-L8

6. The selectivity and catalytic activity of Pd-L8 toward benzaldoxime

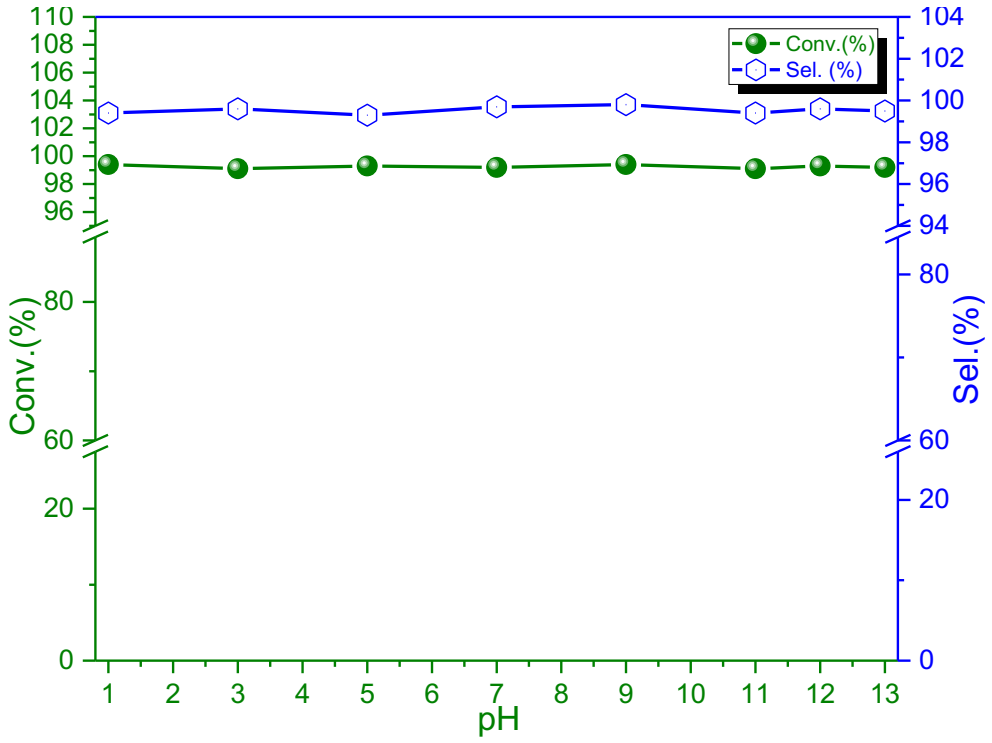


Figure S5. Schematic profile of conversions and selectivity with pH of reaction medium

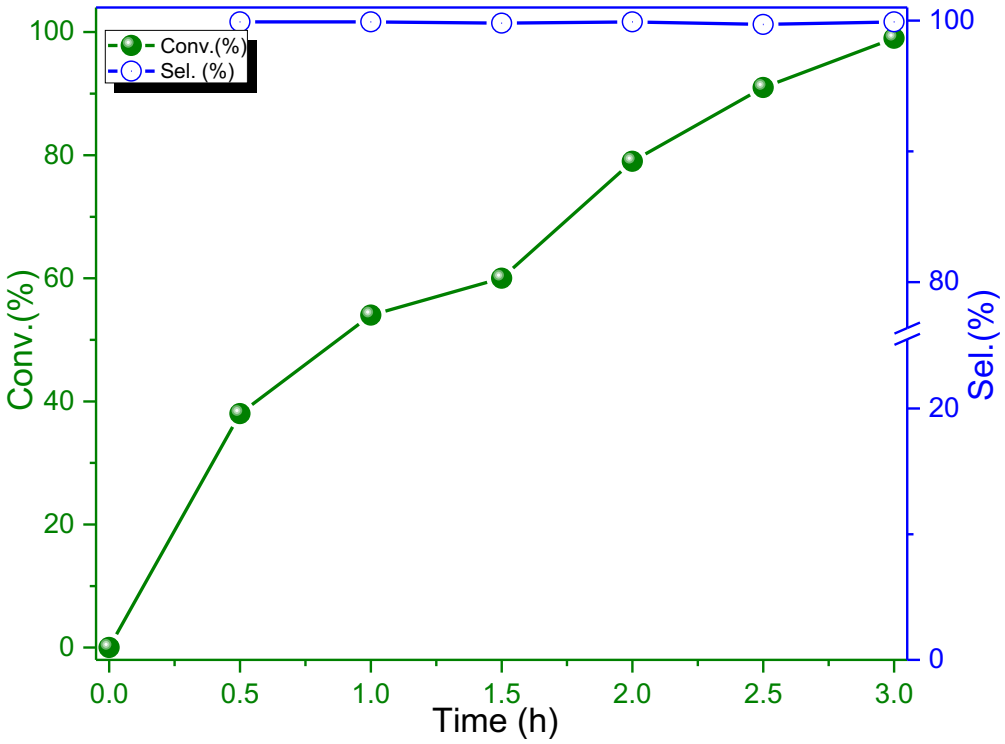


Figure S6. Schematic profile of conversions and selectivities with time

7. The recycling of Pd-L8

For recyclability, the reaction was repeated with benzaldehyde oxime as substrate (0.05 mmol) and the same conditions as described above, except using the recovered catalyst. When the reaction was accomplished, the reaction mixture was allowed to settle down in 1 hour, and the liquid was moved out. The resulting solid was washed using ethanol (6 ml) and dried under vacuum. The recovered Pd-L8 were applied to further cycles experiment.

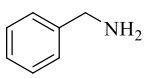
8. Elemental analysis and ICP-OES of Pd-L8

Table S1 Elemental analysis and ICP-OES of Pd-L8

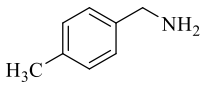
Content (wt %)				
C[a]	H[a]	O[a]	N[a]	Pd[b]
13.33	1.66	9.96	8.29	43.51

[a] Measured by elemental analysis (EA). [b] Measured by inductively coupled plasma-optical emission spectrometer (ICP-OES).

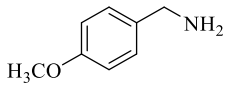
9. Characterization data for products



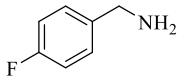
2a, **2f, 2g, 2j, 2h, 2i, 2m** phenylmethanamine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.31-7.18 (m 5H); 3.79 (s 2H); 1.43 (brs 2H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 143.42, 128.53, 127.09, 126.76, 46.51



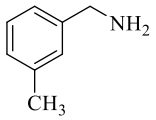
2b p-tolylmethanamine **^{1}H NMR (400MHz DMSO-d6):** δ (ppm) 7.21 (d *J* = 8.0 Hz 2H); 7.10 (d *J* = 8.0 Hz 2H); 3.68 (s 2H); 2.27 (s 3H); 1.72 (brs 2H); **^{13}C NMR (100MHz DMSO-d6)**: δ (ppm) 141.76, 135.46, 129.08, 127.39 , 45.93, 21.12



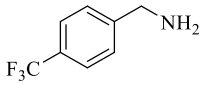
2c (4-methoxyphenyl)methanamine **^{1}H NMR (400MHz DMSO-d6)**: δ (ppm) 7.24 (d *J* = 8.0 Hz 2H); 6.86 (d *J* = 8.0 Hz 2H); 3.72 (s 3H); 3.65 (s 2H); 1.68 (brs 2H); **^{13}C NMR (100MHz DMSO-d6)**: δ (ppm) 158.25, 136.82, 128.56, 113.91, 55.41, 45.60



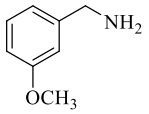
2d (4-fluorophenyl)methanamine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.25-7.22 (q *J* = 4.0 Hz 2H); 6.97 (t *J* = 8.0Hz 2H); 3.78 (s 2H); 1.55 (brs 2H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 161.68 (d *J* = 242.0 Hz), 138.97 (d *J* = 3.0 Hz), 128.5 7 (d *J* = 8.0 Hz), 115.10 (d *J* = 21.0 Hz), 45.61



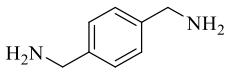
2e m-tolylmethanamine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.24-7.20 (m 1H); 7.12-7.04 (m 3H); 3.81 (s 2H); 2.34 (s 3H); 1.51 (brs 2H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 143.34, 138.18, 128.48, 127.89, 127.53, 124.11, 46.51, 21.42



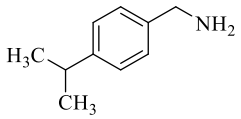
2k (4-(trifluoromethyl)phenyl)methanamine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.58 (d *J* = 8.0Hz 2H); 7.43 (d *J* = 8.0Hz 2H); 3.93 (s 2H); 1.64 (brs 2H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 147.07, 128.66 (q *J* = 40.0Hz), 127.30, 125.41 (q *J* = 4.0Hz), 122.91, 45.93



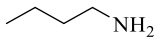
2l (3-methoxyphenyl)methanamine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.24 (t *J* = 8.0Hz 1H); 6.89-6.76 (m 3H); 3.82 (s 2H); 3.79 (s 3H); 1.50 (brs 2H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 159.85, 145.08, 129.55, 119.32, 112.59, 112.21, 55.18, 46.50



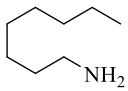
2n, 2o 1,4-phenylenedimethanamine **^{1}H NMR (400MHz DMSO-d6)**: δ (ppm) 7.25 (s 4H); 3.68 (s 4H); 2.21 (brs 4H); **^{13}C NMR (100MHz, DMSO-d6)**: δ (ppm) 142.59, 127.24, 45.95



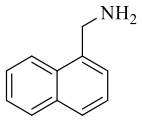
2p (4-isopropylphenyl)methanamine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.23-7.18 (m 4H); 3.81 (s 2H); 2.92-2.85 (m 1H); 1.51 (brs 2H); 1.24 (d *J* = 8.0Hz 6H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 147.45, 140.85, 127.11, 126.60, 46.29, 33.82, 24.10



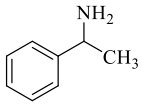
2q butan-1-amine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 2.69 (t *J* = 8.0Hz 2H); 1.43-1.32 (m 4H); 1.15 (brs 2H); 0.92 (t *J* = 8.0Hz 3H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 41.82, 35.93, 19.85, 13.77



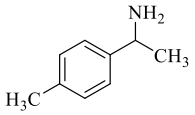
2r octan-1-amine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 2.68 (t *J* = 8.0Hz 2H) ; 1.45-1.40 (m 2H); 1.34-1.28 (m 10H); 1.14 (brs 2H); 0.88 (t *J* = 8.0Hz 3H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 42.23, 33.86, 31.78, 29.41, 29.24, 26.84, 22.58, 13.98



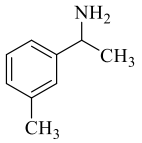
2s naphthalen-1-ylmethanamine **^{1}H NMR (400MHz DMSO-d6)**: δ (ppm) 8.12 (t *J* = 12.0Hz 1H); 7.93-7.91 (m 1H); 7.78 (d *J* = 8.0Hz 1H); 7.59-7.45 (m 4H); 4.21 (s 2H); 1.94 (brs 2H); **^{13}C NMR (100MHz DMSO-d6)**: δ (ppm) 140.07, 133.74, 131.42, 128.90, 127.17, 126.31, 126.02, 125.99, 124.62, 124.02, 43.56



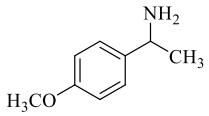
2a', **2f'**, **2g'**, **2h'**, **2j'**, **2k'**, **2l'**, 1-phenylethan-1-amine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm)7.29-7.16 (m 5H); 4.04 (q *J* = 8.0Hz 1H); 1.66 (brs 2H); 1.34 (d *J* = 4.0Hz 2H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 147.79, 128.49, 126.81, 125.71, 51.31, 25.70



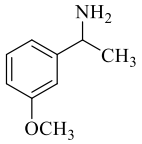
2b' 1-(p-tolyl)ethan-1-amine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.22 (d *J* = 8.0Hz 2H); 7.13 (d *J* = 8.0Hz 2H); 4.06 (q *J* = 8.0Hz 1H); 2.32 (s 3H); 1.77 (brs 2H); 1.36 (d *J* = 8.0Hz 3H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 144.76, 136.37, 129.17, 125.61, 51.04, 25.63, 21.03



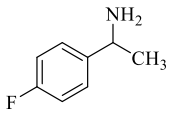
2c' 1-(m-tolyl)ethan-1-amine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.26-7.04 (m 4H); 4.07 (q *J* = 8.0Hz 1H), 2.35 (s 3H); 1.82 (brs 2H); 1.38 (d *J* = 8.0Hz 3H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 147.61, 138.12, 128.43, 127.60, 126.45, 122.74, 51.31, 25.57, 21.49



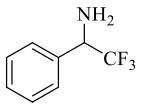
2d' 1-(4-methoxyphenyl)ethan-1-amine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.19 (d *J* = 8.0Hz 2H); 6.80 (d *J* = 12.0Hz 2H); 4.01 (q *J* = 8.0Hz 1H); 3.72 (s 3H); 1.93 (brs 2H); 1.30 (d *J* = 8.0Hz 3H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 158.49, 139.63, 126.78, 113.85, 55.31, 50.69, 25.57



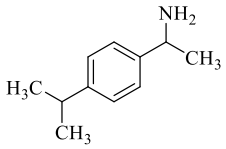
2e' 1-(3-methoxyphenyl)ethan-1-amine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.17 (q *J* = 8.0Hz 1H); 6.83 (d *J* = 8.0Hz 2H); 6.70-6.67 (m 1H); 4.00 (q *J* = 8.0Hz 1H); 3.72(s 3H); 1.93 (brs 2H); 1.29 (d *J* = 8.0Hz 3H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 159.78, 149.34, 129.53, 118.07, 112.11, 111.43, 55.20, 51.32, 25.49



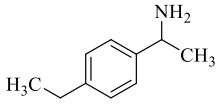
2i' 1-(4-fluorophenyl)ethan-1-amine **^{1}H NMR (400MHz $CDCl_3$)**: δ (ppm) 7.32-7.28 (m 2H); 6.99 (t *J* = 8.0Hz 2H); 4.10 (q *J* = 8.0Hz 1H); 1.63 (brs 2H); 1.35 (d *J* = 4.0Hz 3H); **^{13}C NMR (100MHz $CDCl_3$)**: δ (ppm) 161.69 (d *J* = 243.0Hz), 143.36 (d *J* = 3.0Hz), 127.21 (d *J* = 7.0Hz), 115.12 (d *J* = 21.0Hz), 50.65, 25.81



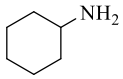
2m' 2,2,2-trifluoro-1-phenylethan-1-amine **^{1}H NMR (400MHz CDCl$_3$)**: δ (ppm) 7.43-7.36(m 5H); 4.37 (q *J* = 8.0Hz 1H); 1.93 (brs 2H); **^{13}C NMR (100MHz CDCl$_3$)**: δ (ppm) 135.35, 130.11,129.00,128.70, 124.94 (q *J* = 279.0Hz), 57.92 (q *J* = 29.0Hz)



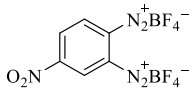
2n' 1-(4-isopropylphenyl)ethan-1-amine **^{1}H NMR (400MHz CDCl$_3$)**: δ (ppm) 7.25 (d *J* = 8.0Hz 2H); 7.18 (d *J* = 8.0Hz 2H); 4.07 (q *J* = 8.0Hz 1H); 2.92-2.85 (m 1H); 1.93 (brs 2H); 1.37 (d *J* = 8.0Hz 3H); 1.24 (d *J* = 8.0Hz 6H); **^{13}C NMR (100MHz CDCl$_3$)**: δ (ppm) 147.44, 145.03, 126.53, 125.65, 51.03, 33.76, 25.50, 24.06. **HRMS** (ESI) Calcd for $[C_{11}H_{17}N+H]^+$: 164.1439; found: 164.1426



2o' 1-(4-ethylphenyl)ethan-1-amine **^{1}H NMR (400MHz CDCl$_3$)**: δ (ppm) 7.25 (d *J* = 8.0Hz 2H); 7.16 (d *J* = 8.0Hz 2H); 4.08 (q *J* = 8.0Hz 1H); 2.63 (q *J* = 8.0Hz 2H); 1.72 (brs 2H); 1.38 (d *J* = 4.0Hz 3H); 1.23 (t *J* = 8.0Hz 3H); **^{13}C NMR (100MHz CDCl$_3$)**: δ (ppm) 145.04, 142.80, 127.98, 125.67, 51.07, 28.49, 25.63, 15.66

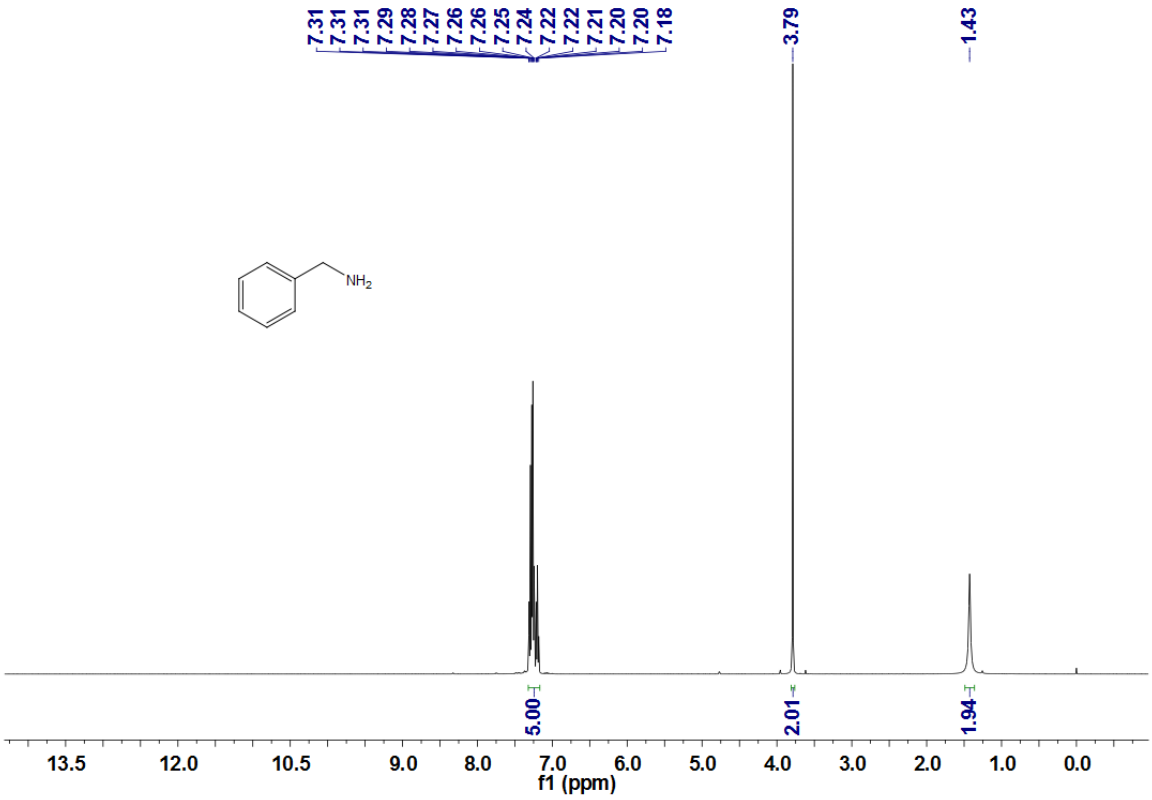


2p' cyclohexanamine **^{1}H NMR (400MHz CDCl$_3$)**: δ (ppm) 2.65-2.58 (m 1H); 1.79-1.57 (m 5H); 1.29-0.99 (m 7H); **^{13}C NMR (100MHz CDCl$_3$)**: δ (ppm) 50.36, 36.81, 25.59, 25.05

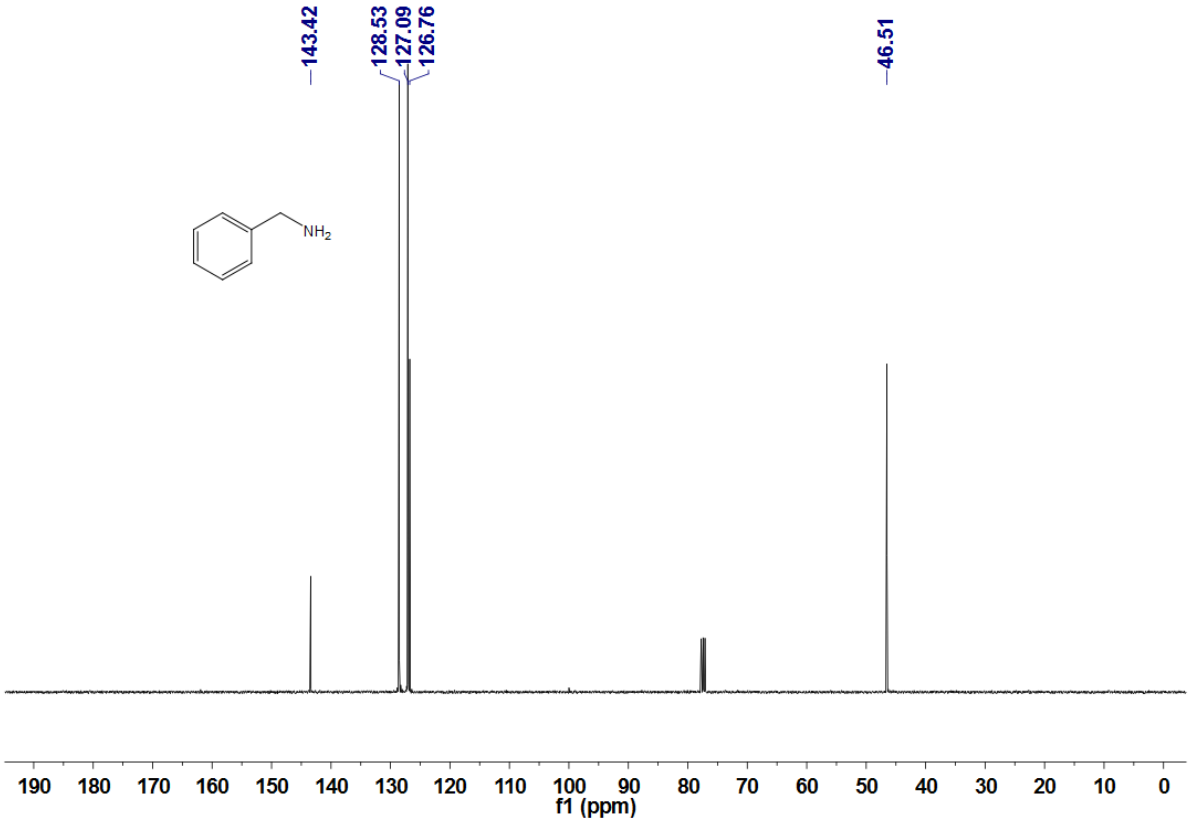


2,2'-(4-nitro-1,2-phenylene)bis(1-(trifluoro-λ^5-boranylidene)diazen-1-ium) fluoride **^{1}H NMR (400MHz DMSO-d6**): δ (ppm) 8.86 (d *J* = 2Hz 1H); 8.26-8.24 (m 1H); 8.02 (d *J* = 4Hz 1H); **^{13}C NMR (100MHz DMSO-d6)**: δ (ppm) 145.04, 140.76, 139,18, 121.47, 114.75, 114.42.

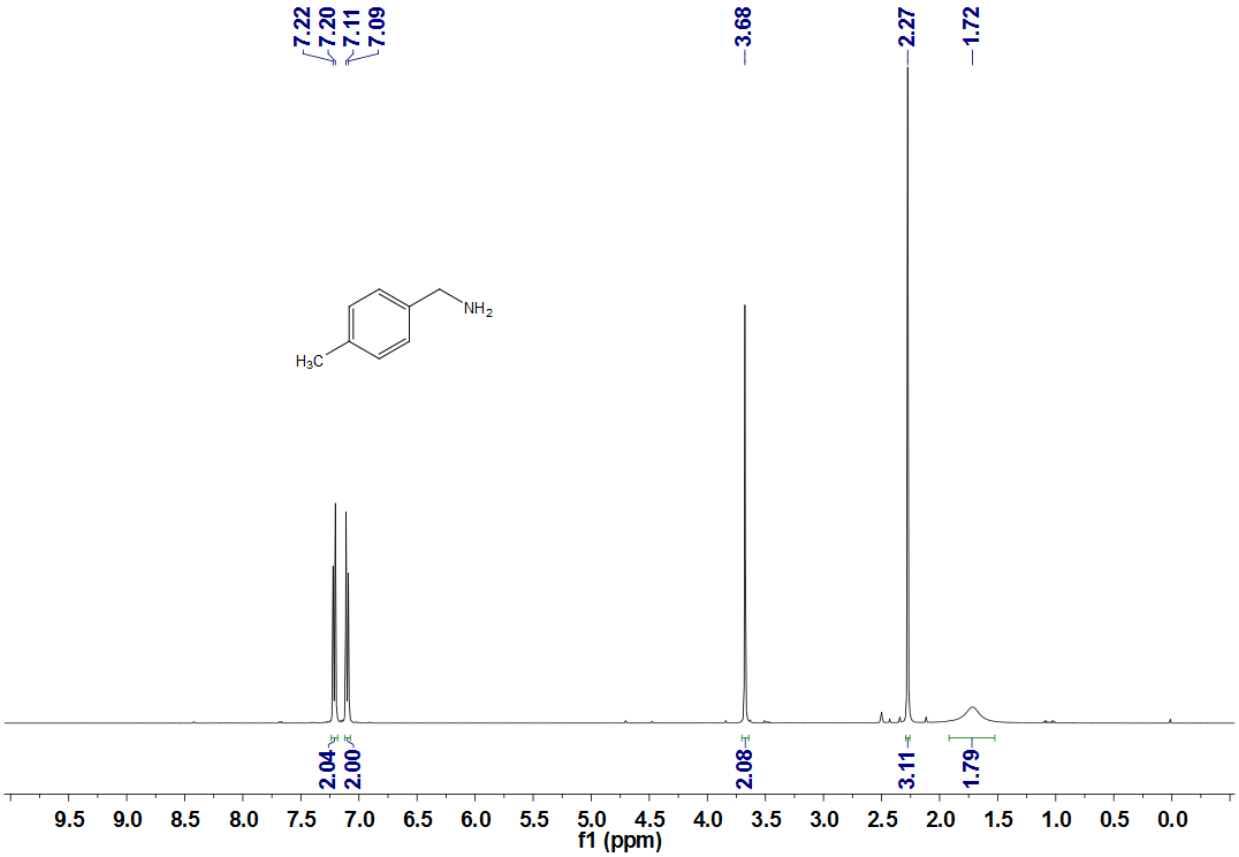
10. ^{1}H NMR and ^{13}C NMR spectra of products



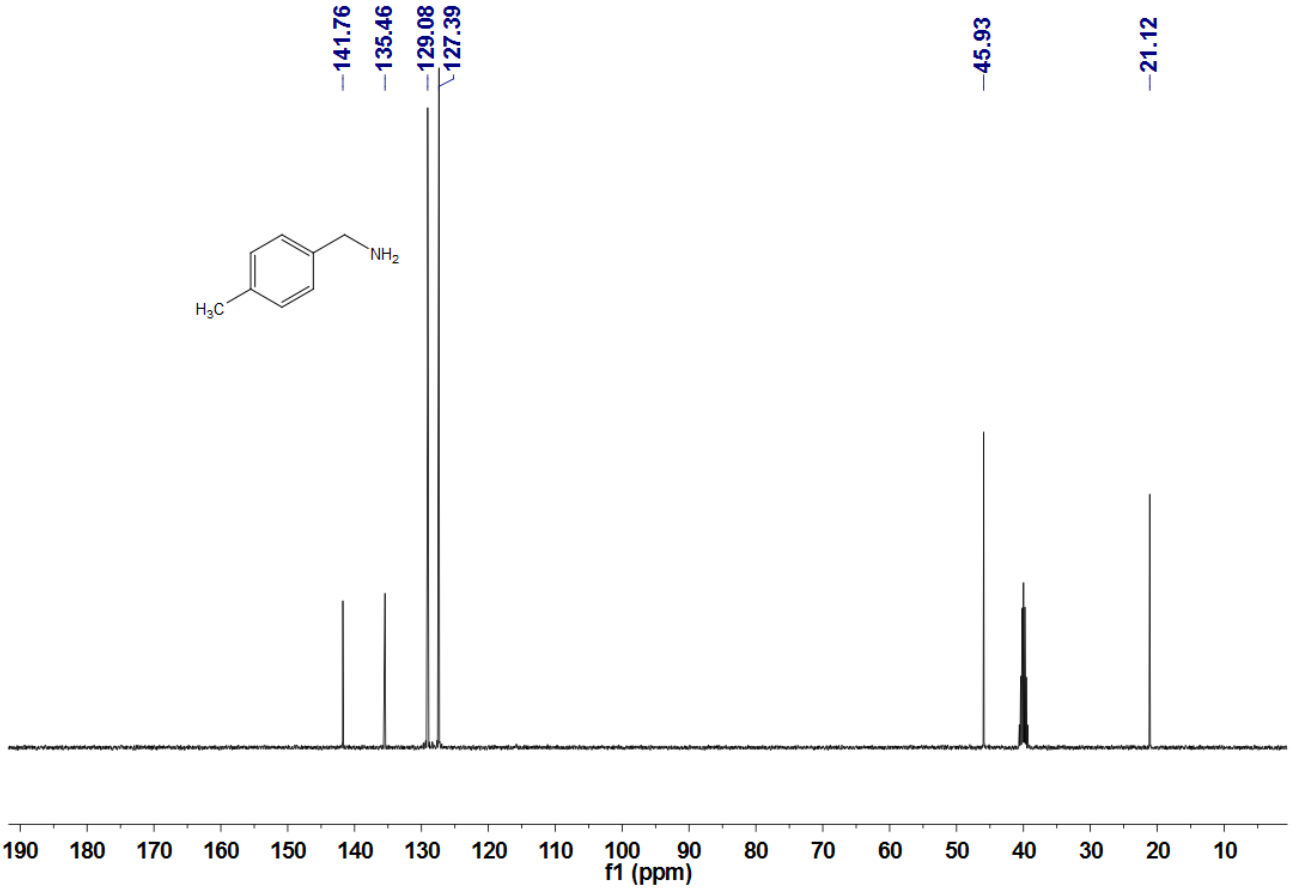
^{1}H NMR of phenylmethanamine (**2a**, **2f, 2g, 2j, 2h, 2i, 2m**)



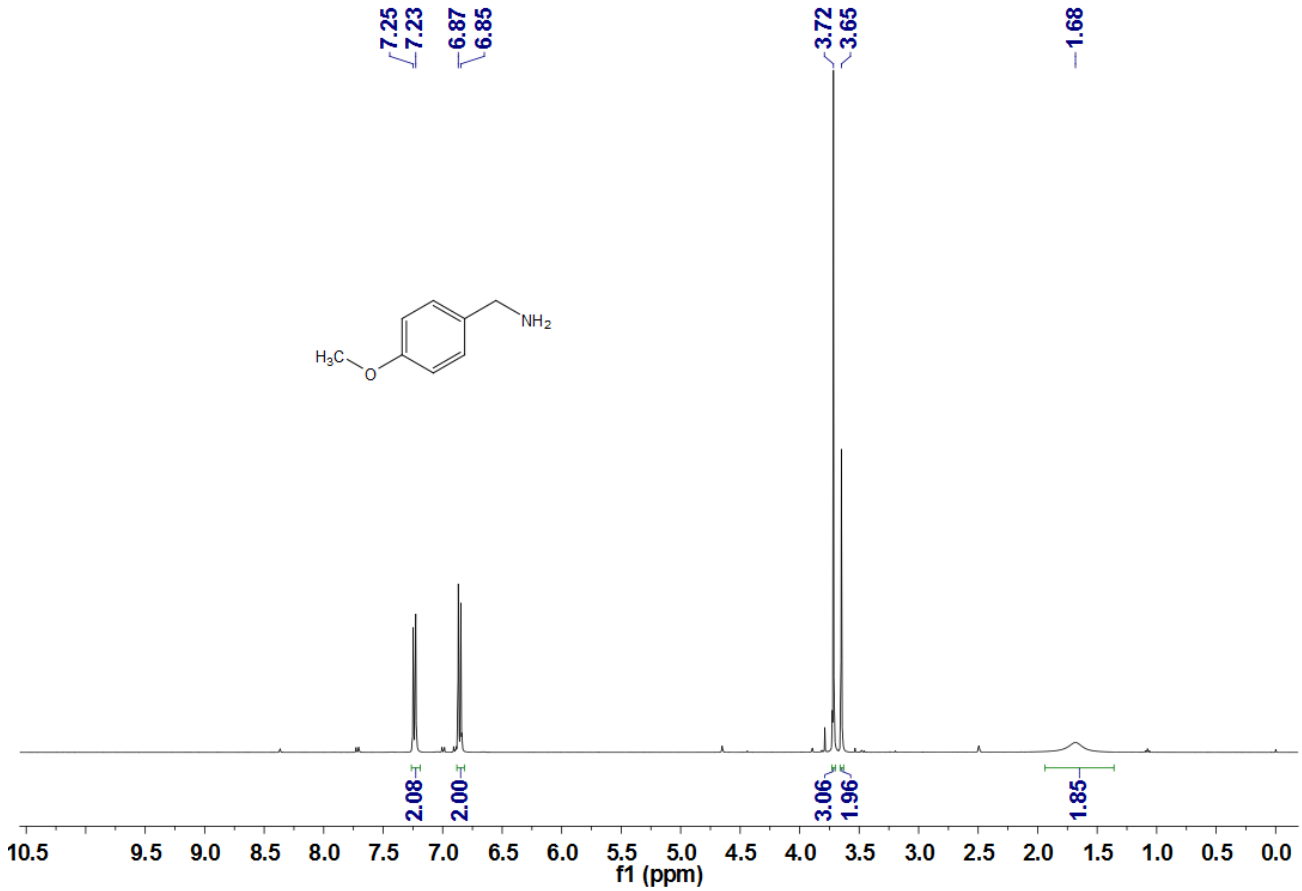
^{13}C NMR of phenylmethanamine (**2a**, **2f, 2g, 2j, 2h, 2i, 2m**)



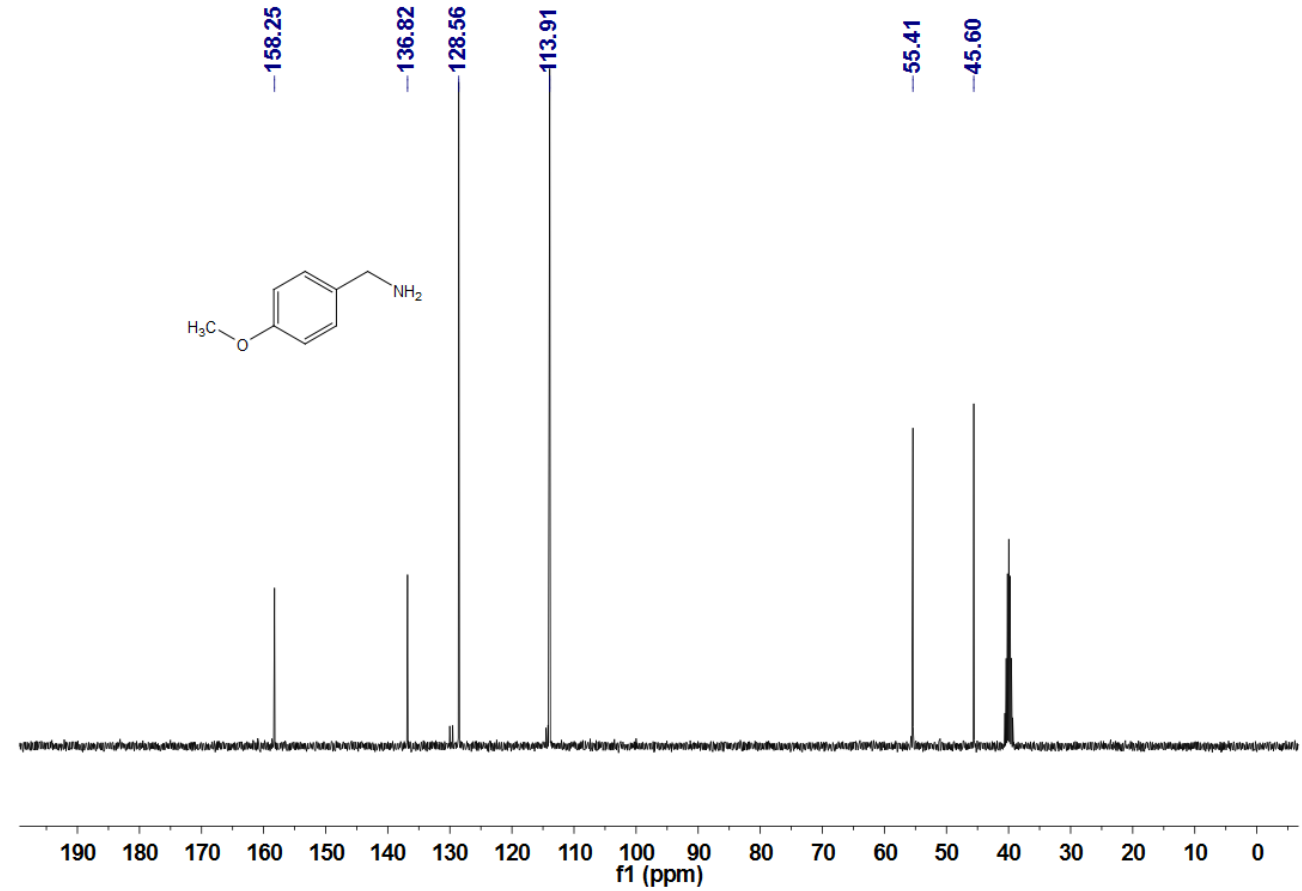
^{1}H NMR of p-tolylmethanamine (**2b**)



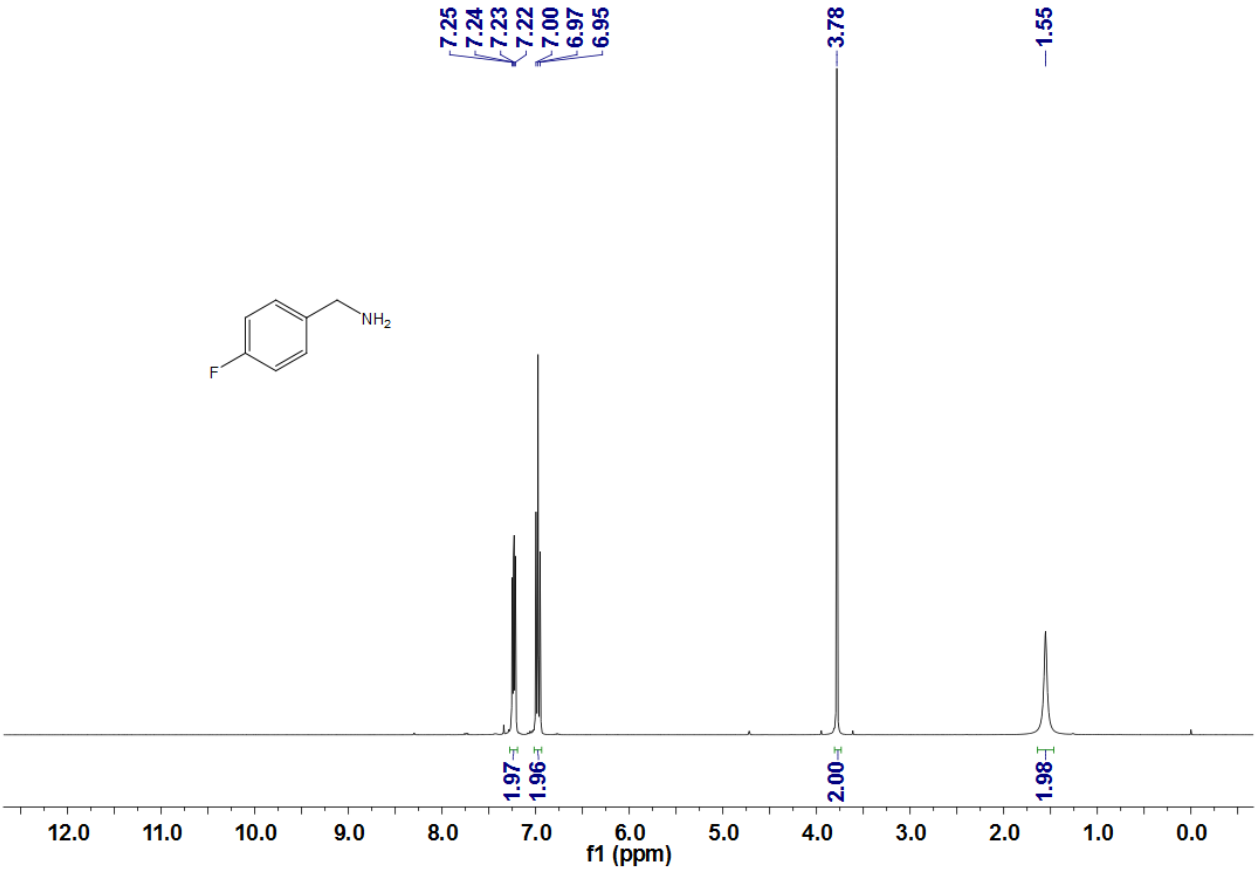
^{13}C NMR of p-tolylmethanamine (**2b**)



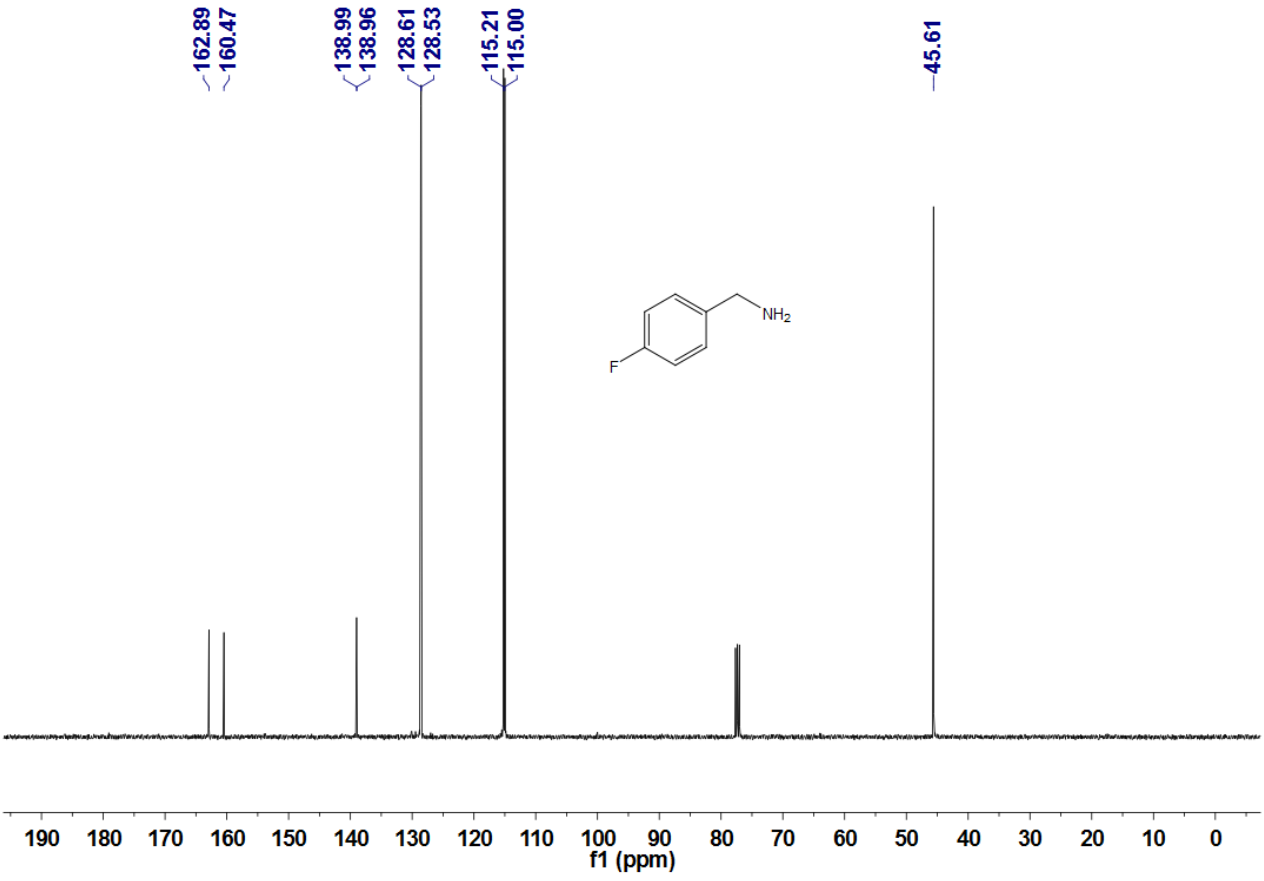
^{1}H NMR of (4-methoxyphenyl)methanamine (**2c**)



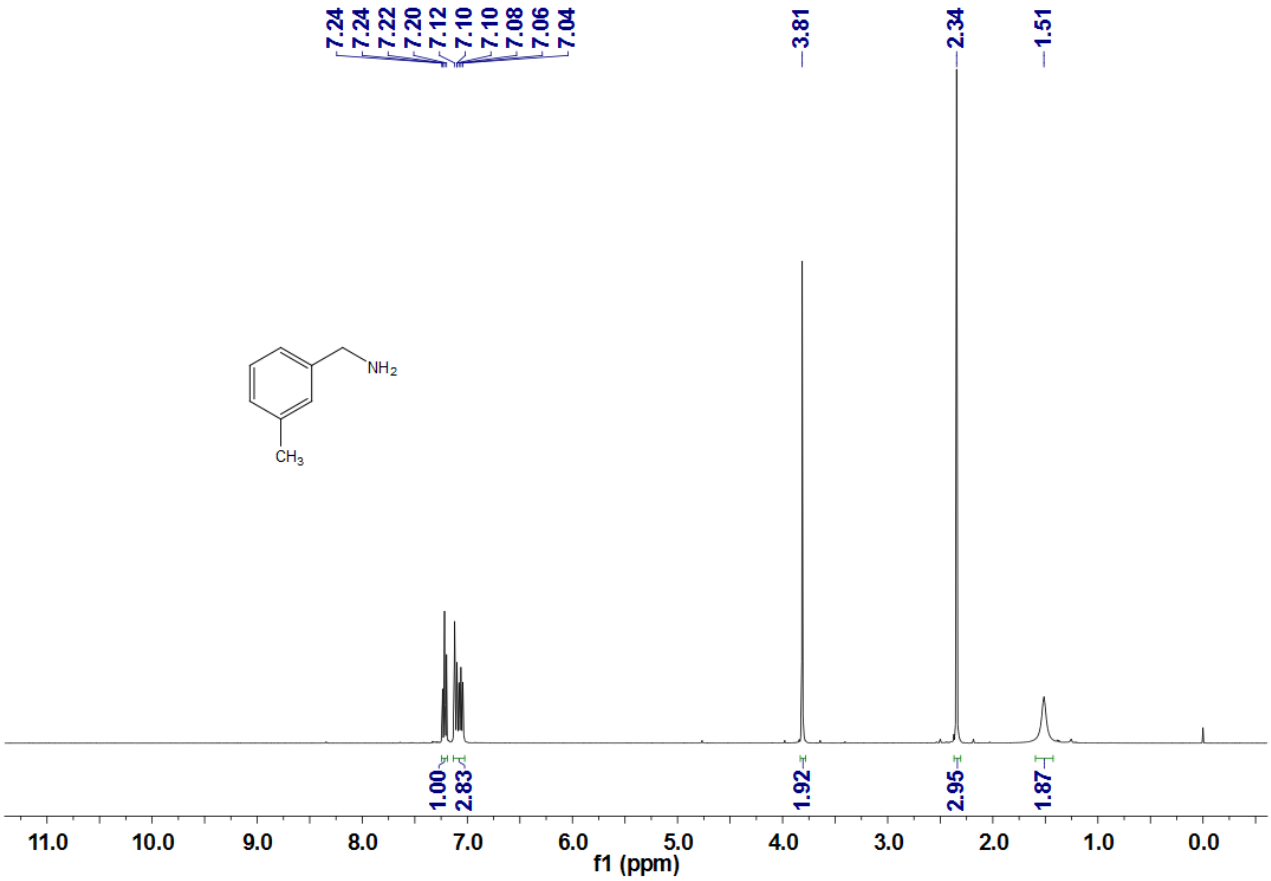
^{13}C NMR of (4-methoxyphenyl)methanamine (**2c**)



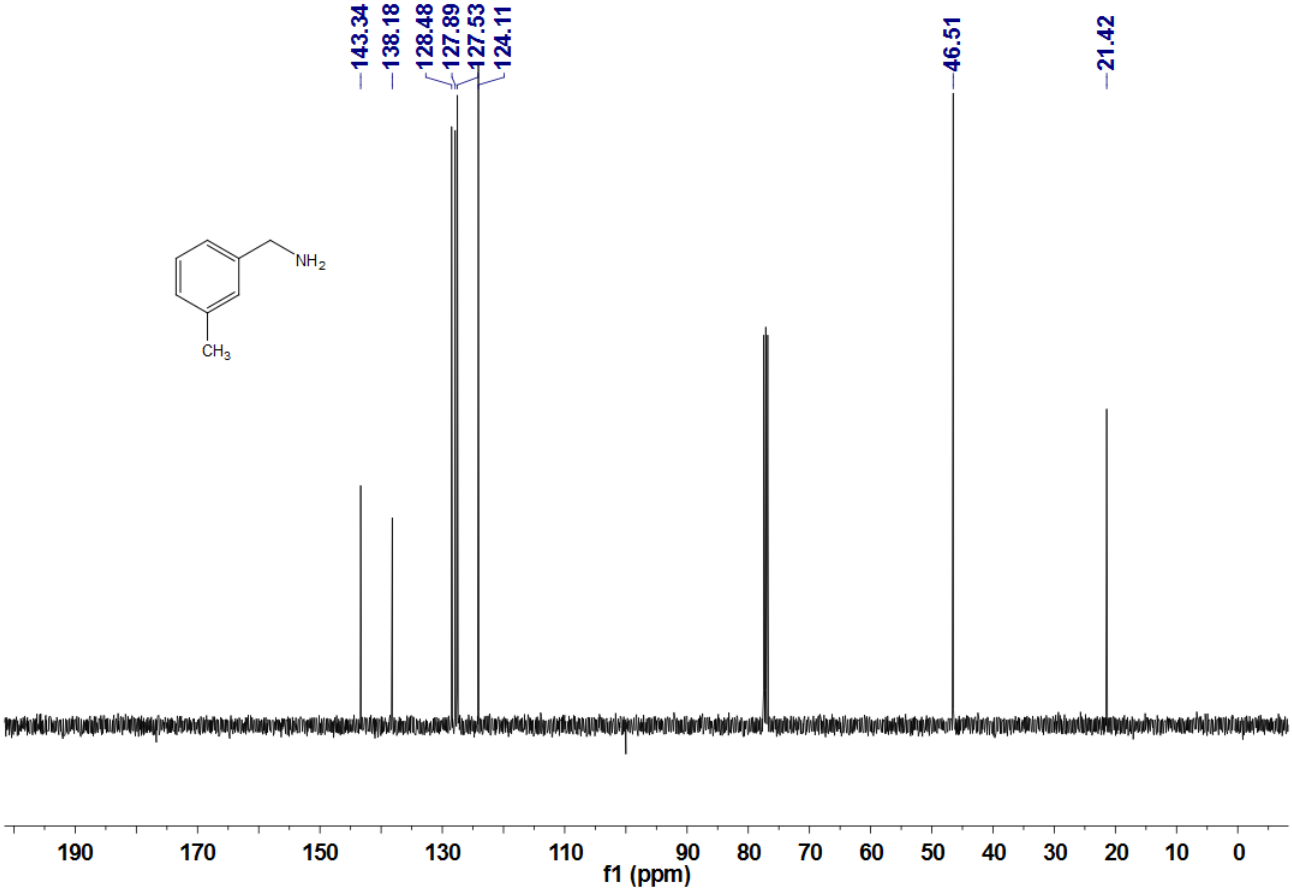
^{1}H NMR of (4-fluorophenyl)methanamine (**2d**)



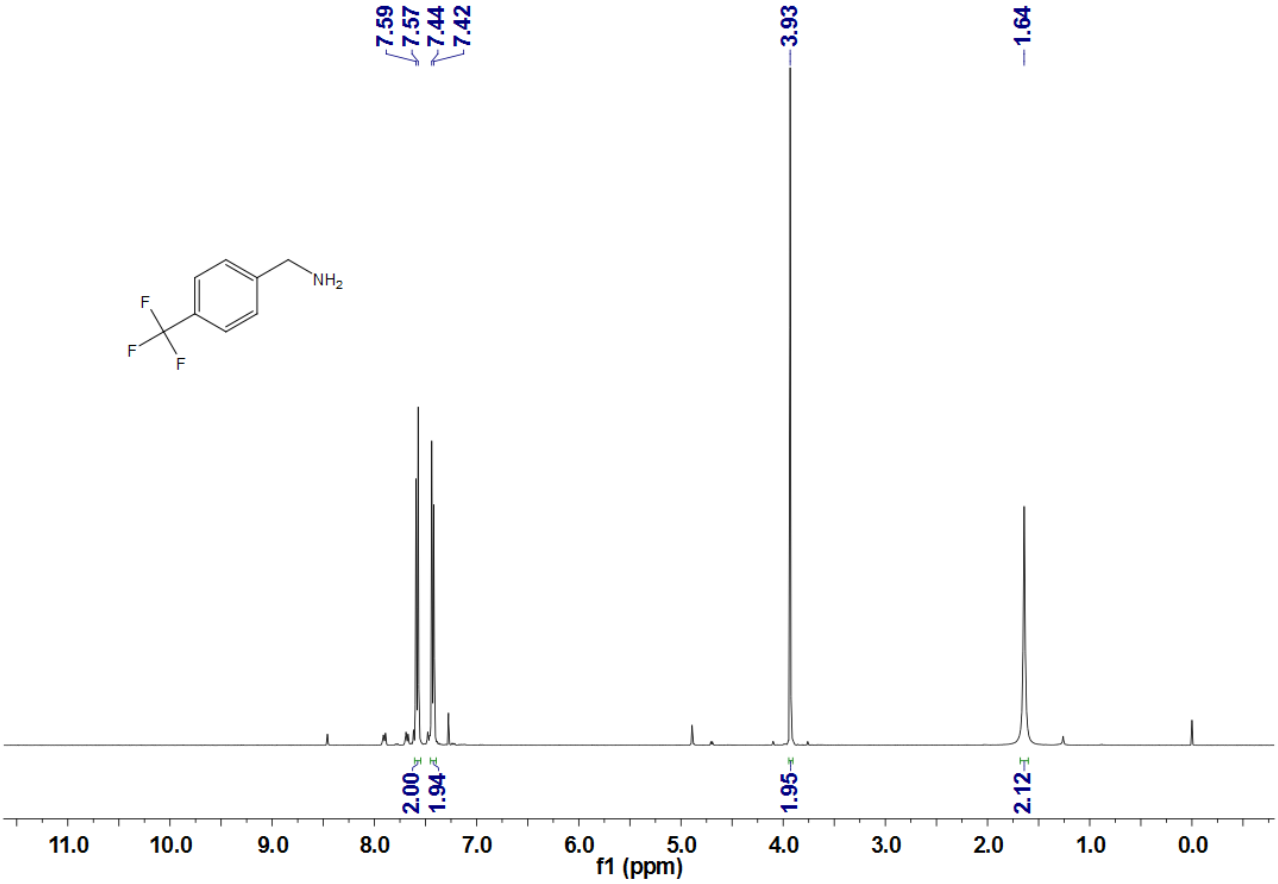
^{13}C NMR of (4-fluorophenyl)methanamine (**2d**)



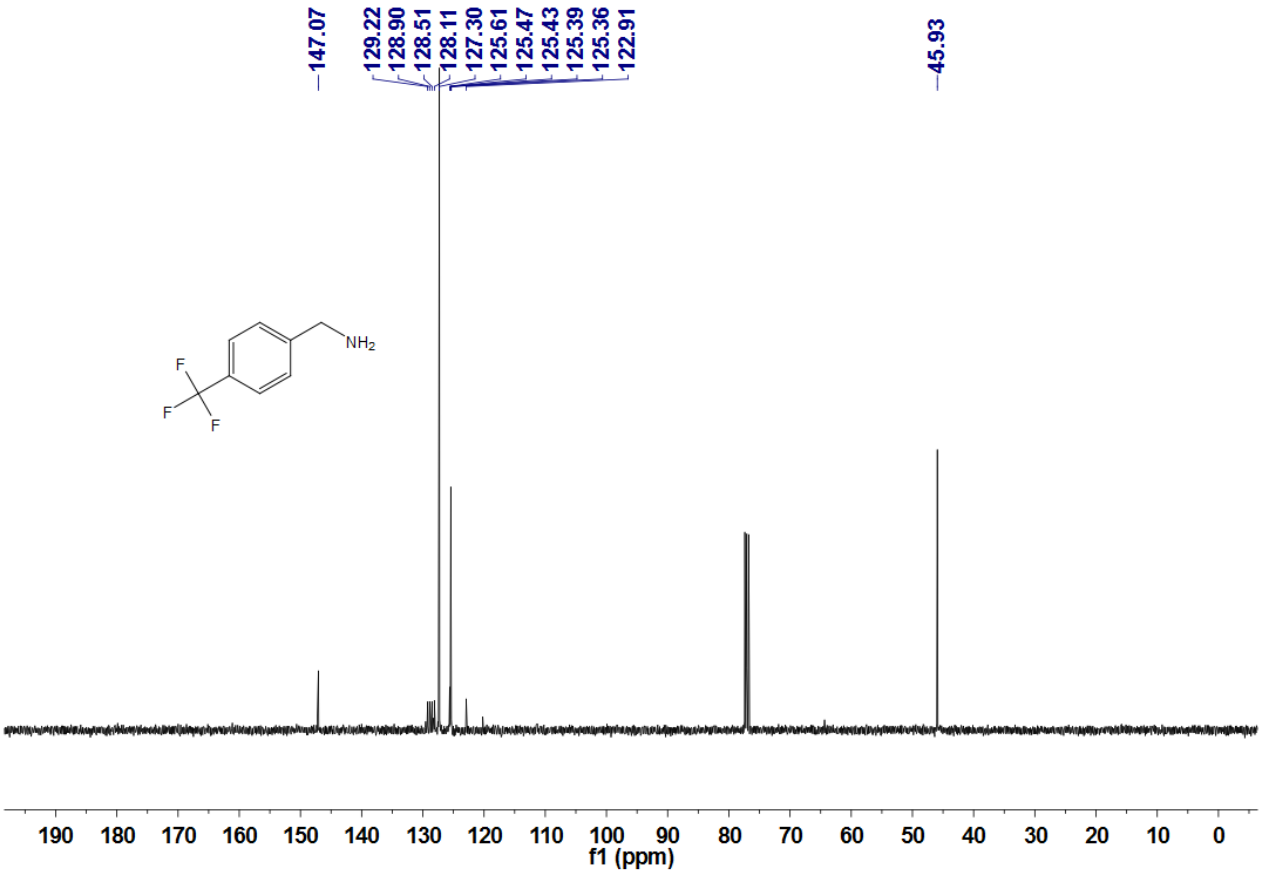
^{1}H NMR of m-tolylmethanamine (**2e**)



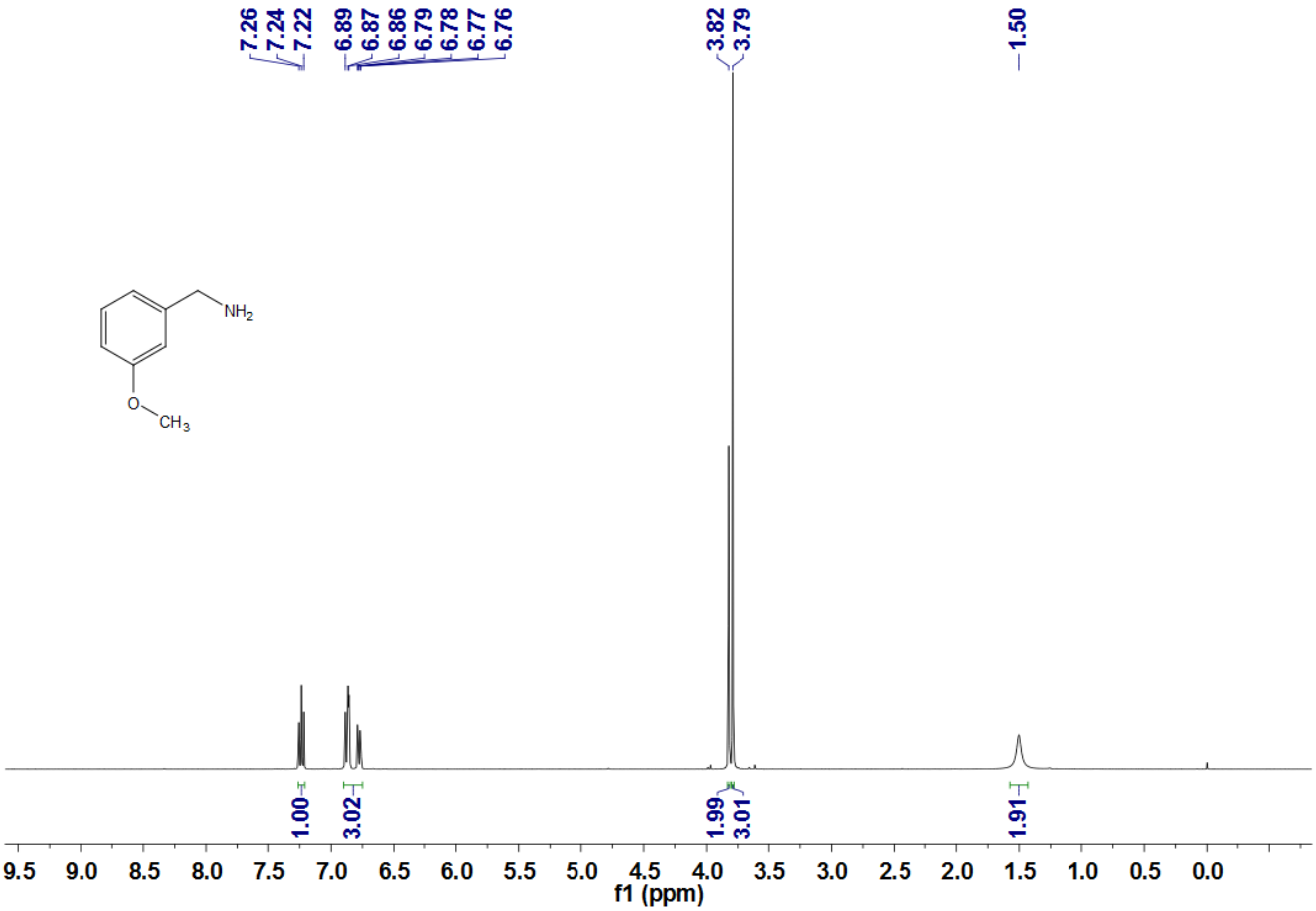
^{13}C NMR of m-tolylmethanamine (**2e**)



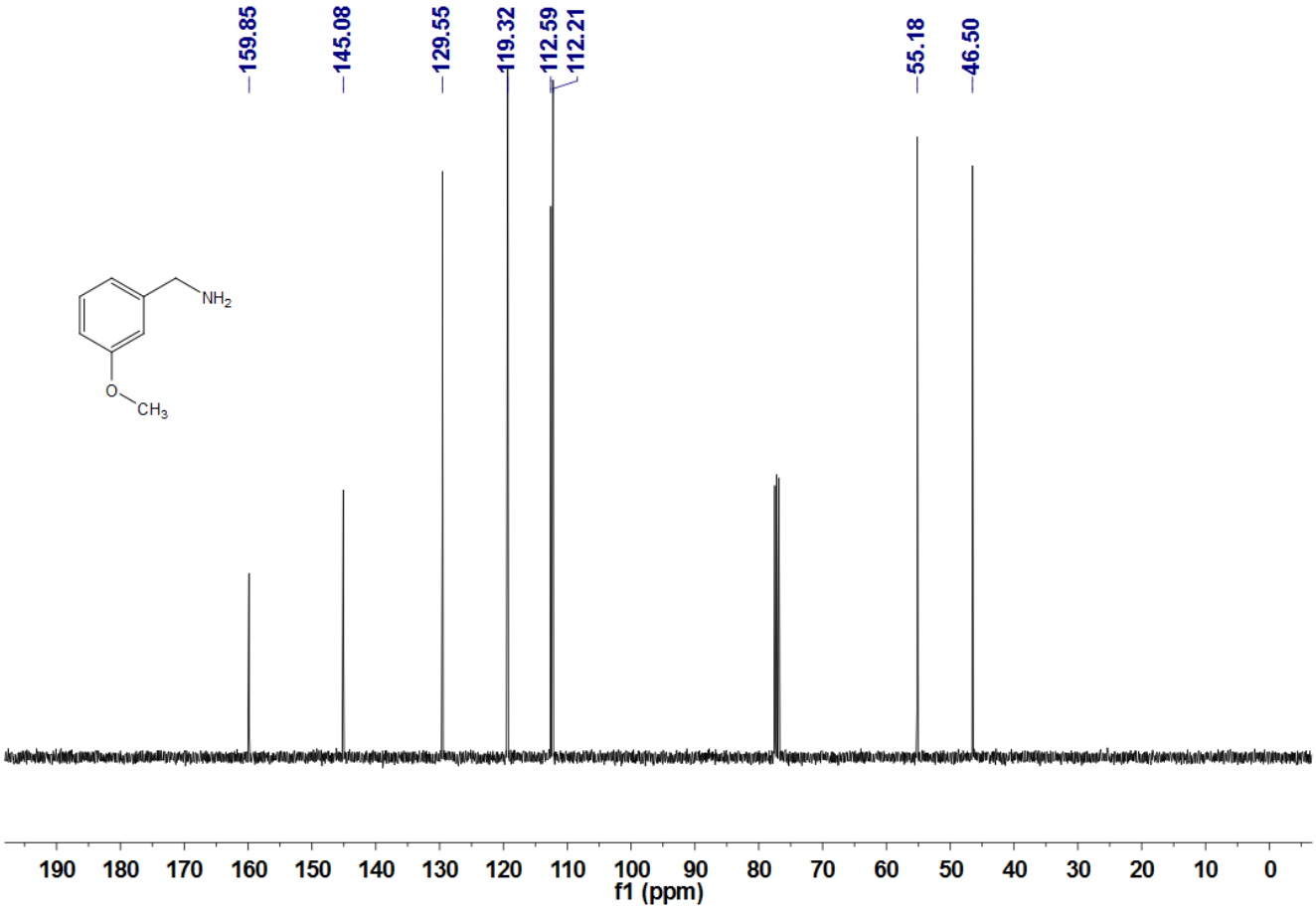
^{1}H NMR of (4-(trifluoromethyl)phenyl)methanamine (**2k**)



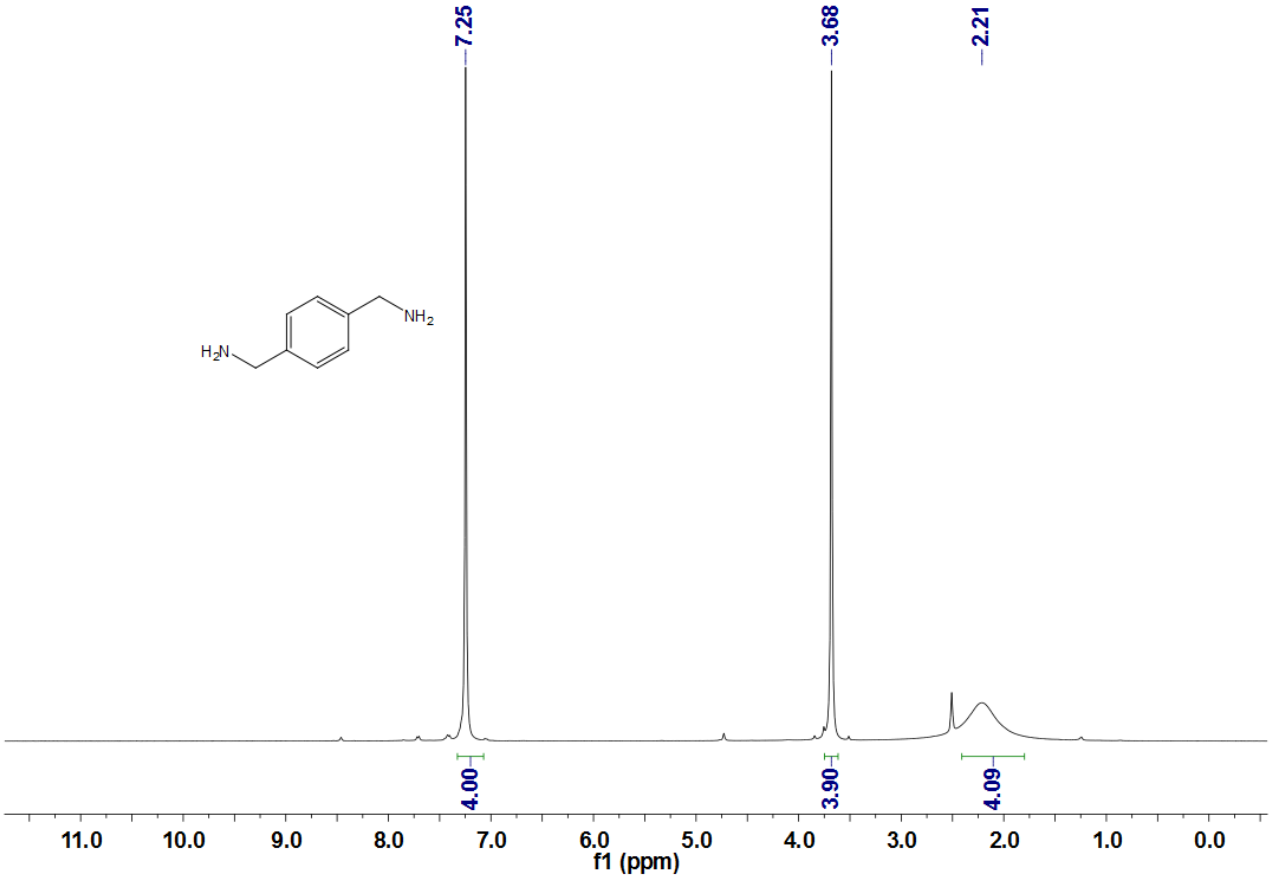
^{13}C NMR of (4-(trifluoromethyl)phenyl)methanamine (**2k**)



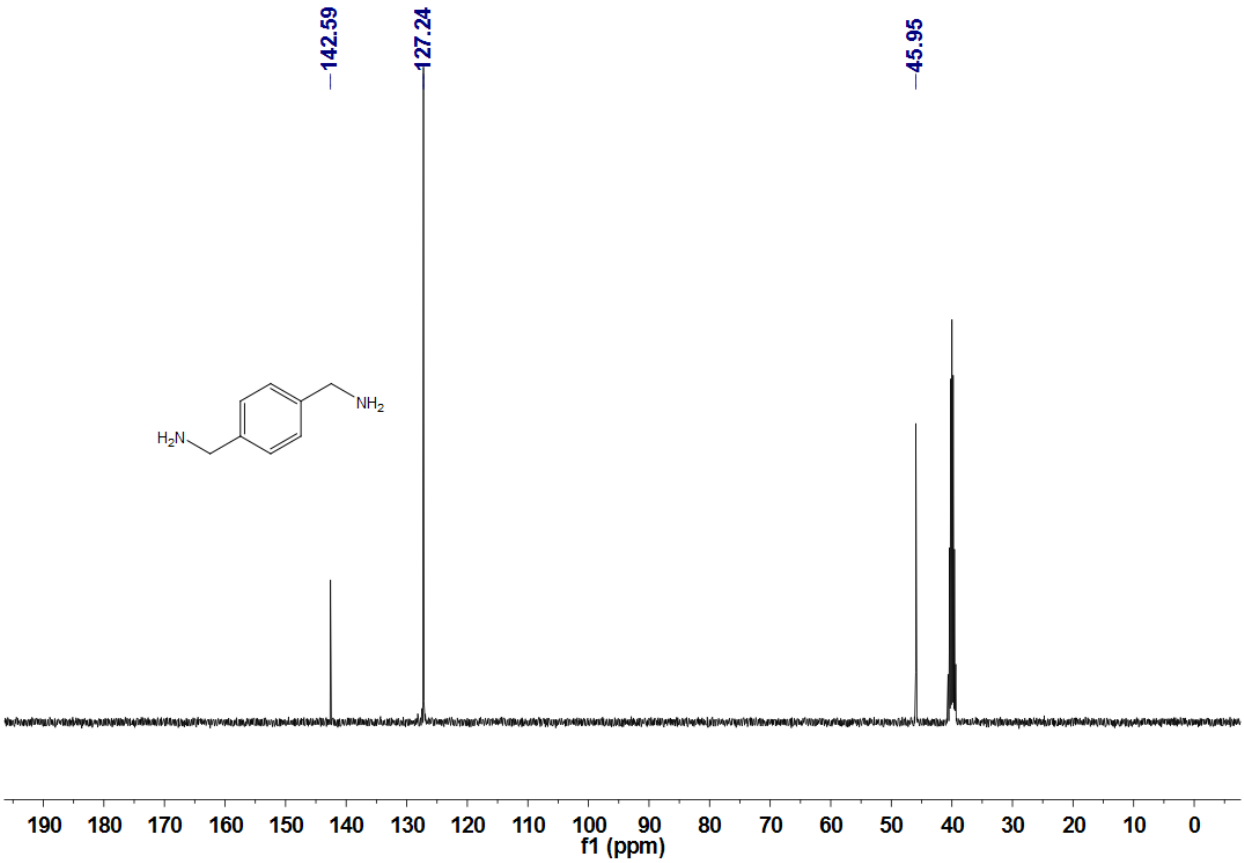
^{1}H NMR of (3-methoxyphenyl)methanamine (**2l**)



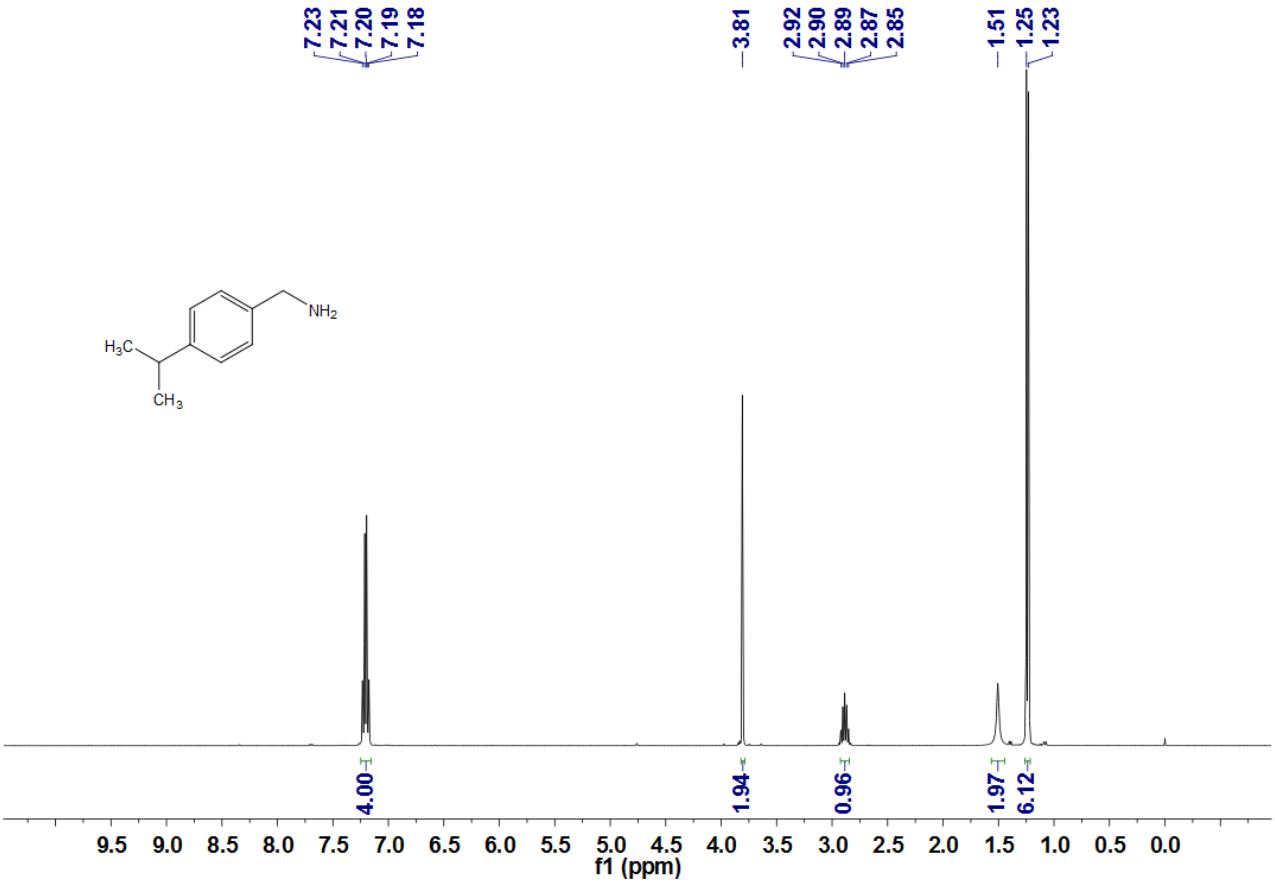
^{13}C NMR of (3-methoxyphenyl)methanamine (**2l**)



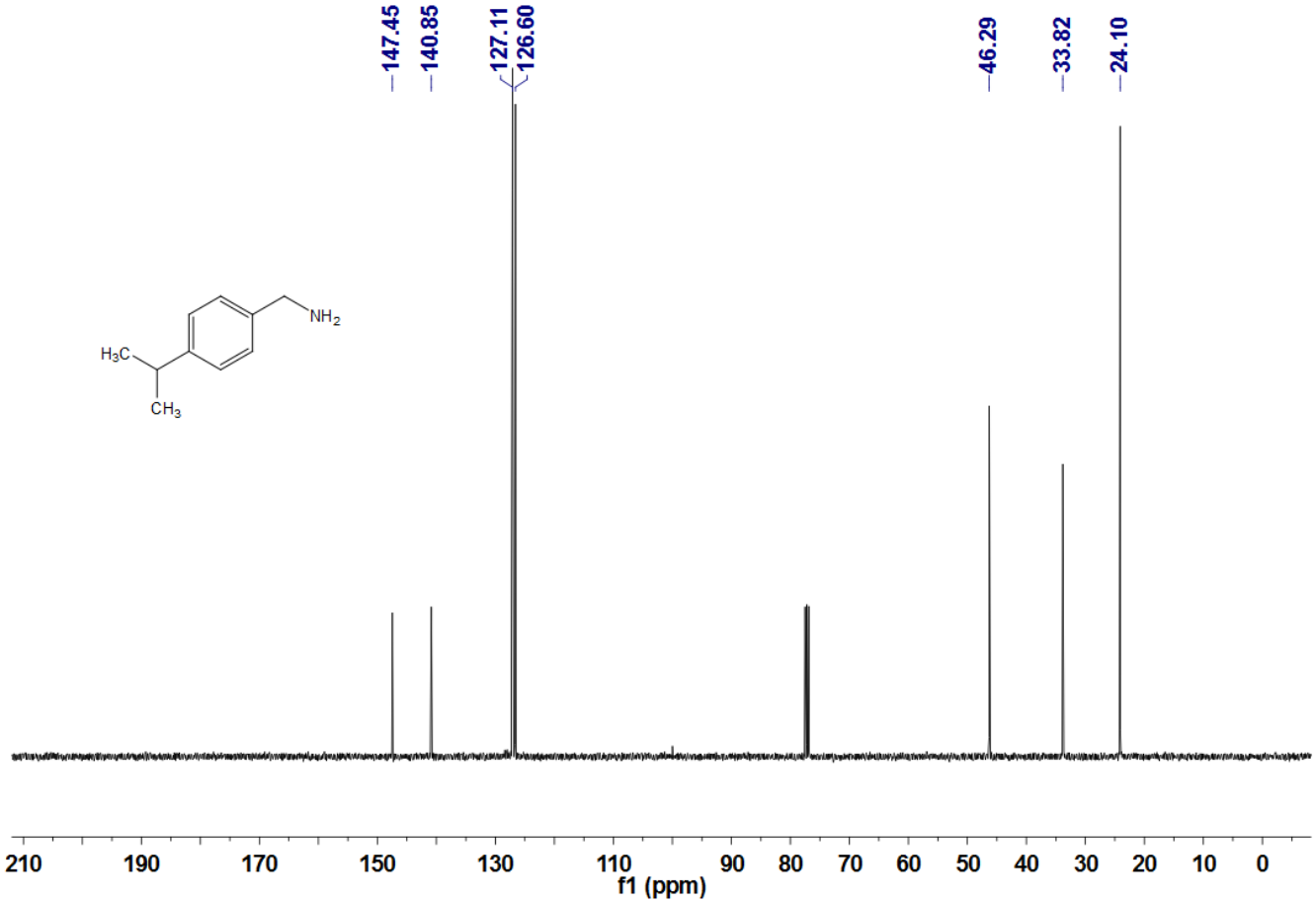
^{1}H NMR of 1,4-phenylenedimethanamine (**2n**, **2o**)



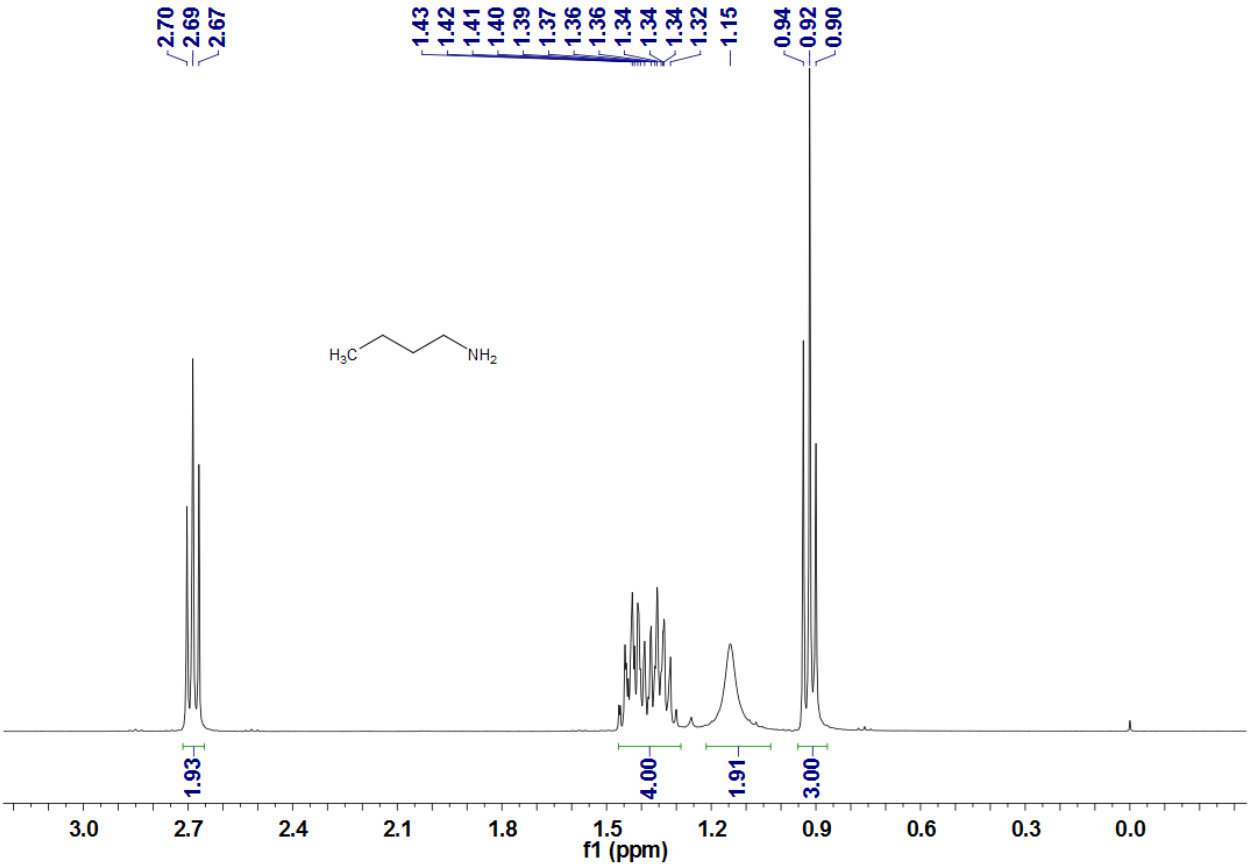
^{13}C NMR of 1,4-phenylenedimethanamine (**2n**, **2o**)



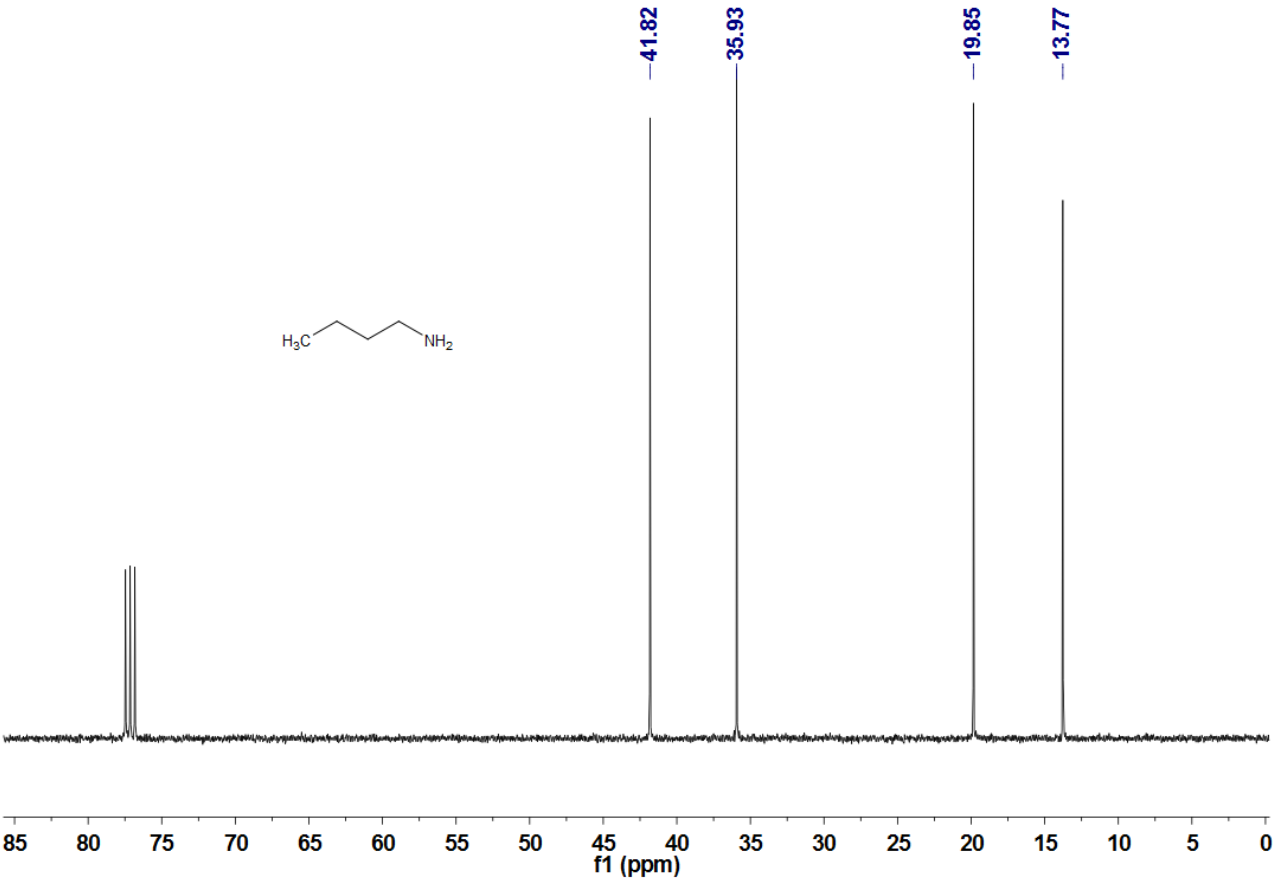
^{1}H NMR of (4-isopropylphenyl)methanamine (**2p**)



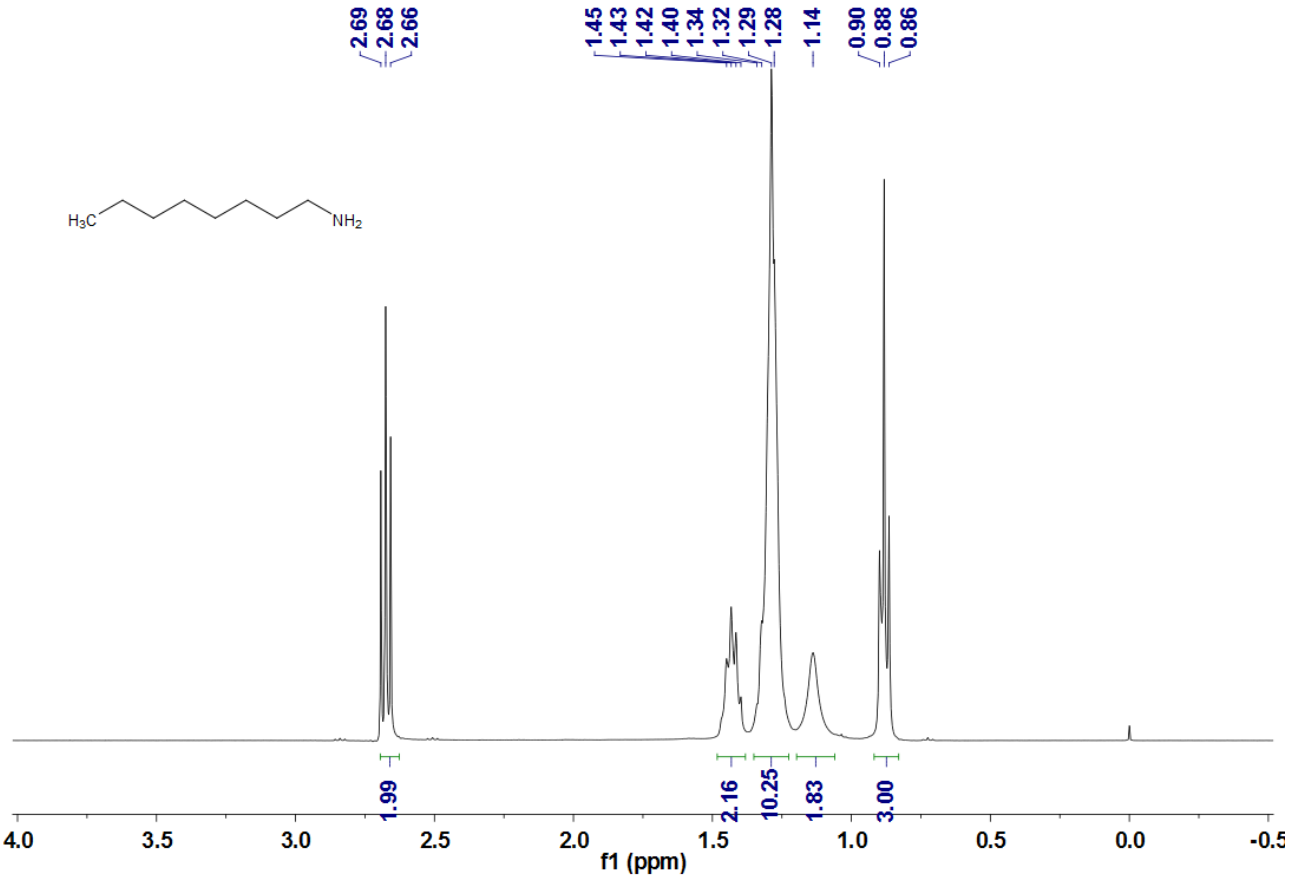
^{13}C NMR of (4-isopropylphenyl)methanamine (**2p**)



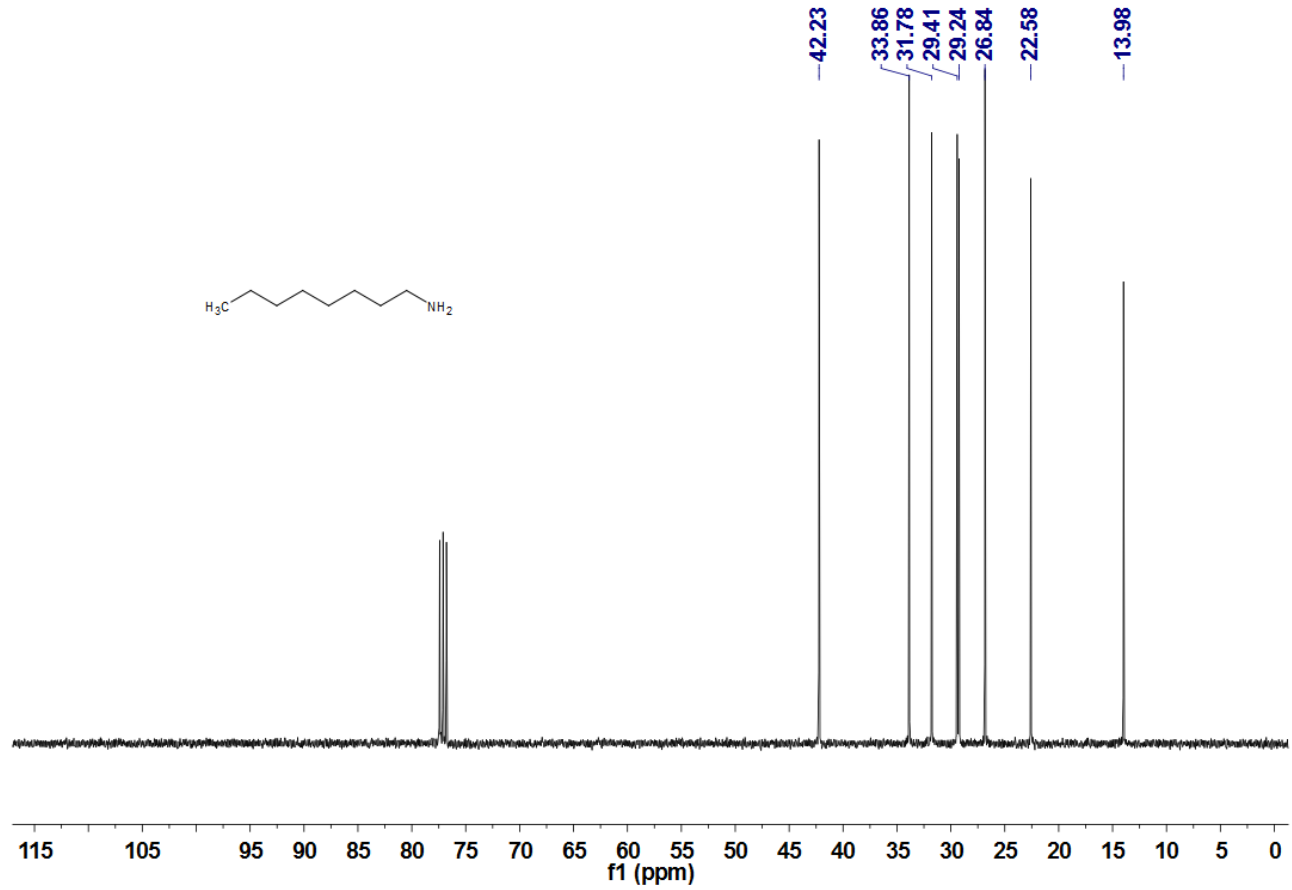
^{1}H NMR of butan-1-amine (**2q**)



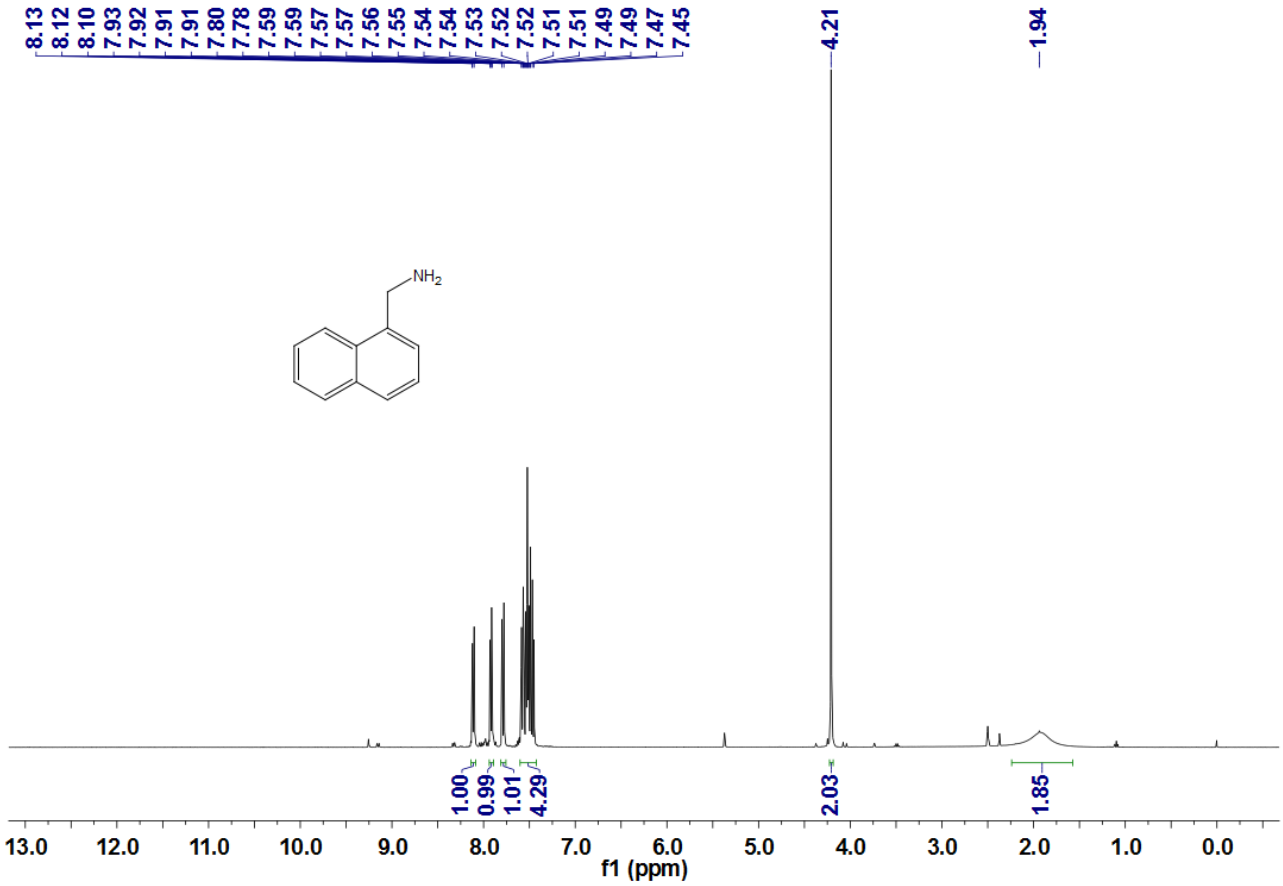
^{13}C NMR of butan-1-amine (**2q**)



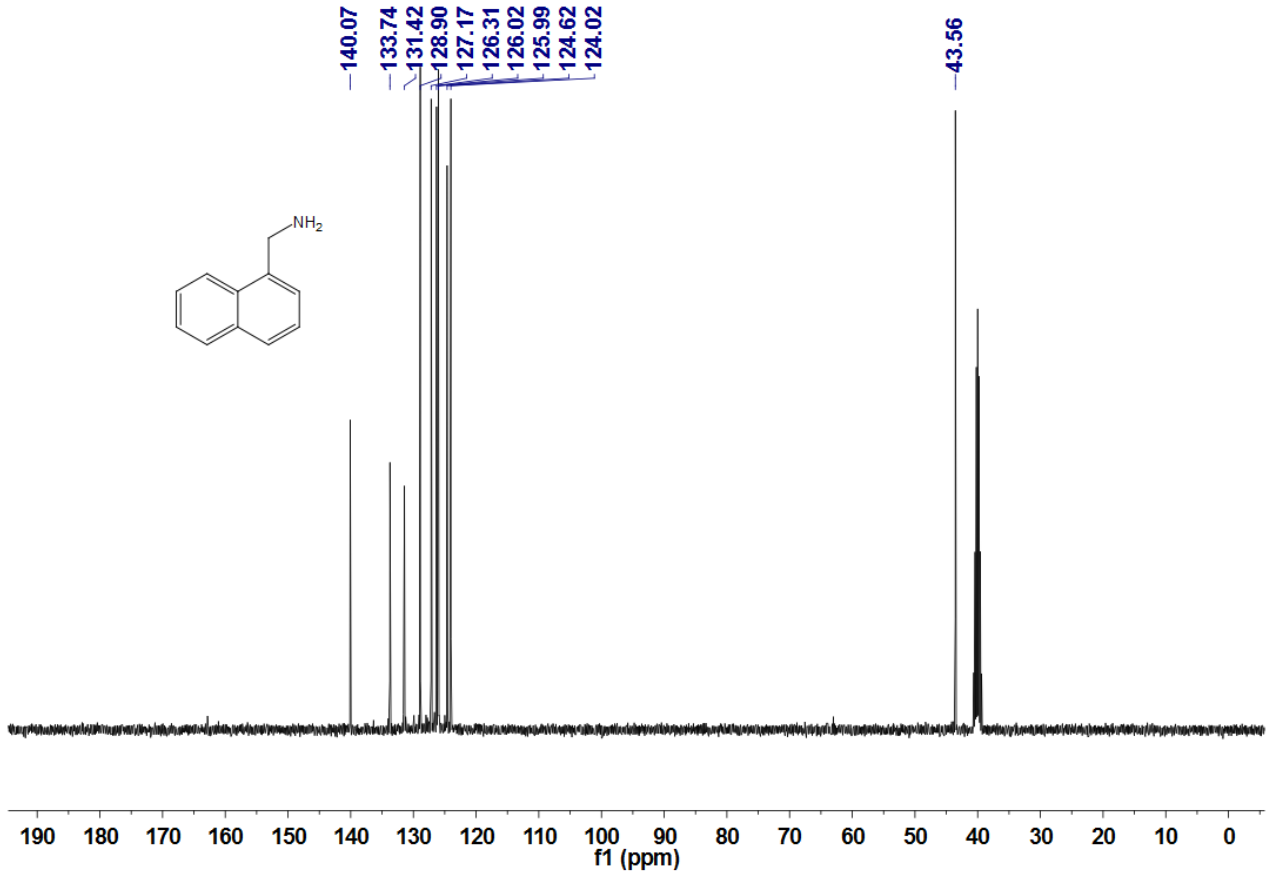
^{1}H NMR of octan-1-amine (**2r**)



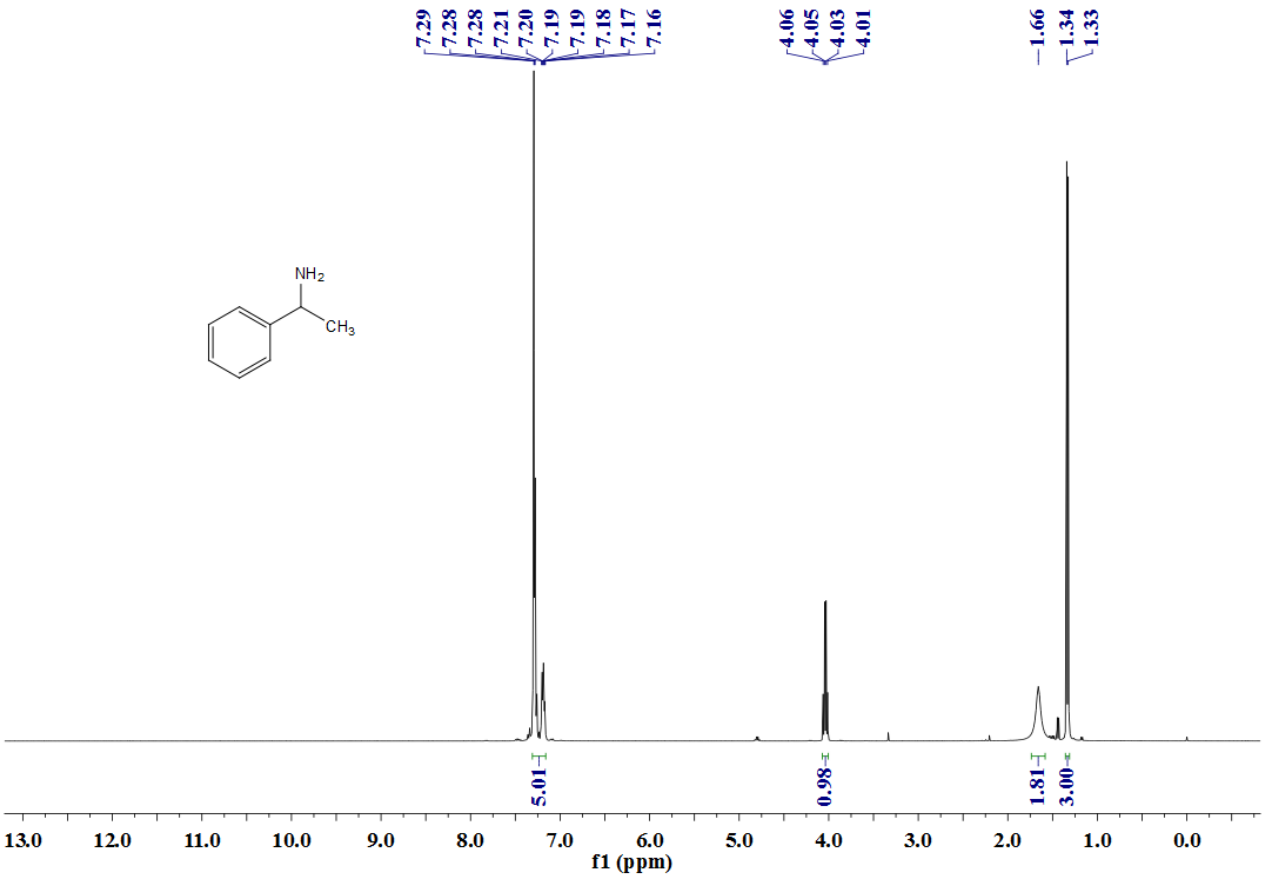
^{13}C NMR of octan-1-amine (**2r**)



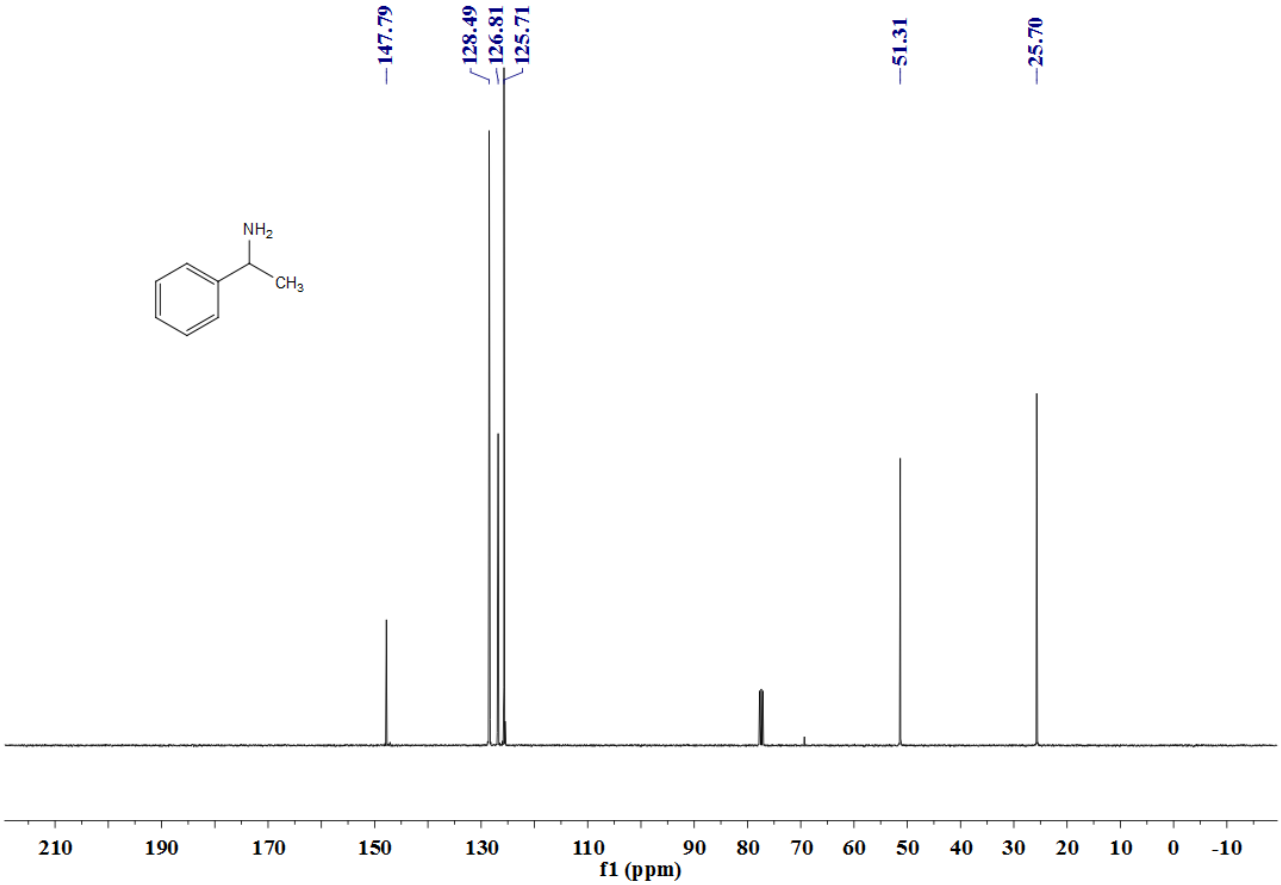
^{1}H NMR of naphthalen-1-ylmethanamine (**2s**)



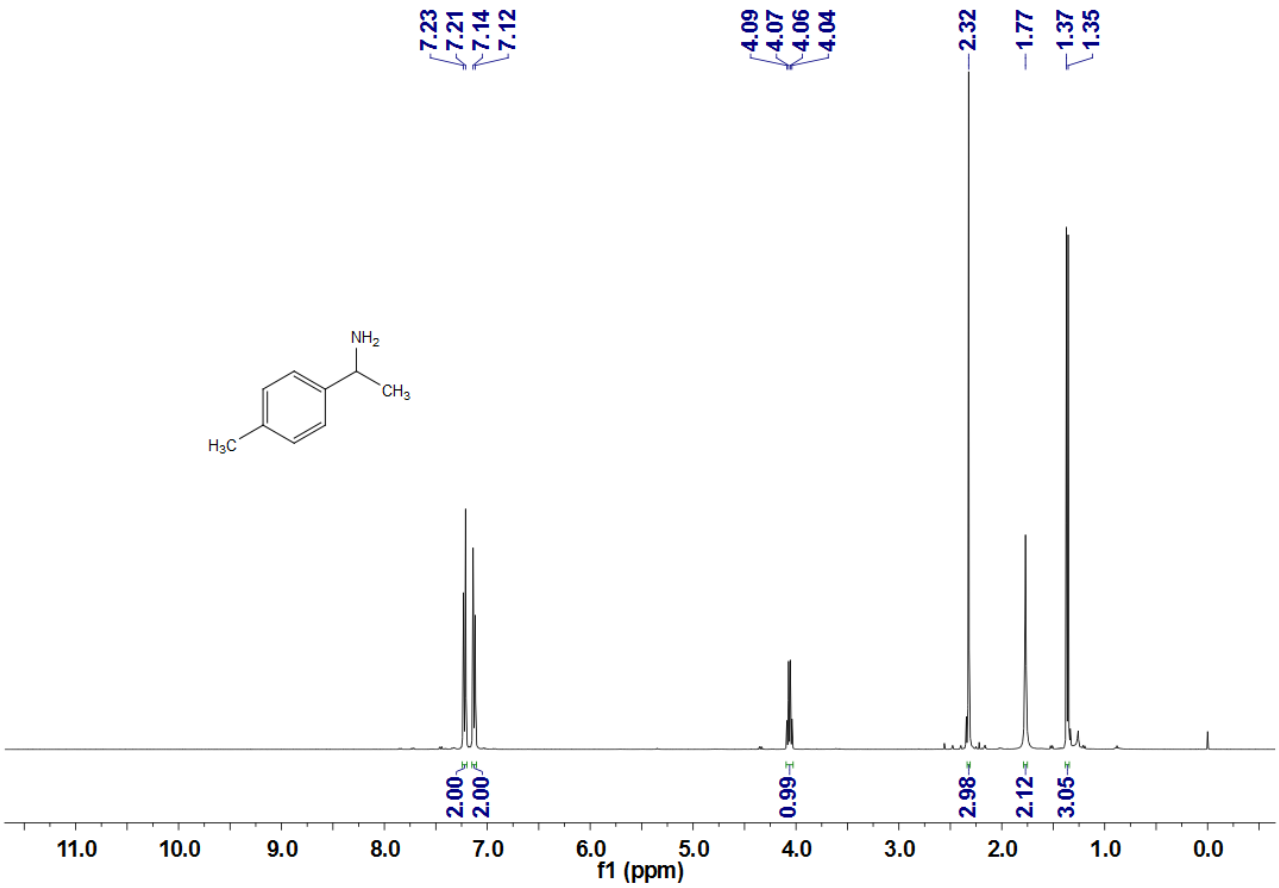
^{13}C NMR of naphthalen-1-ylmethanamine (**2s**)



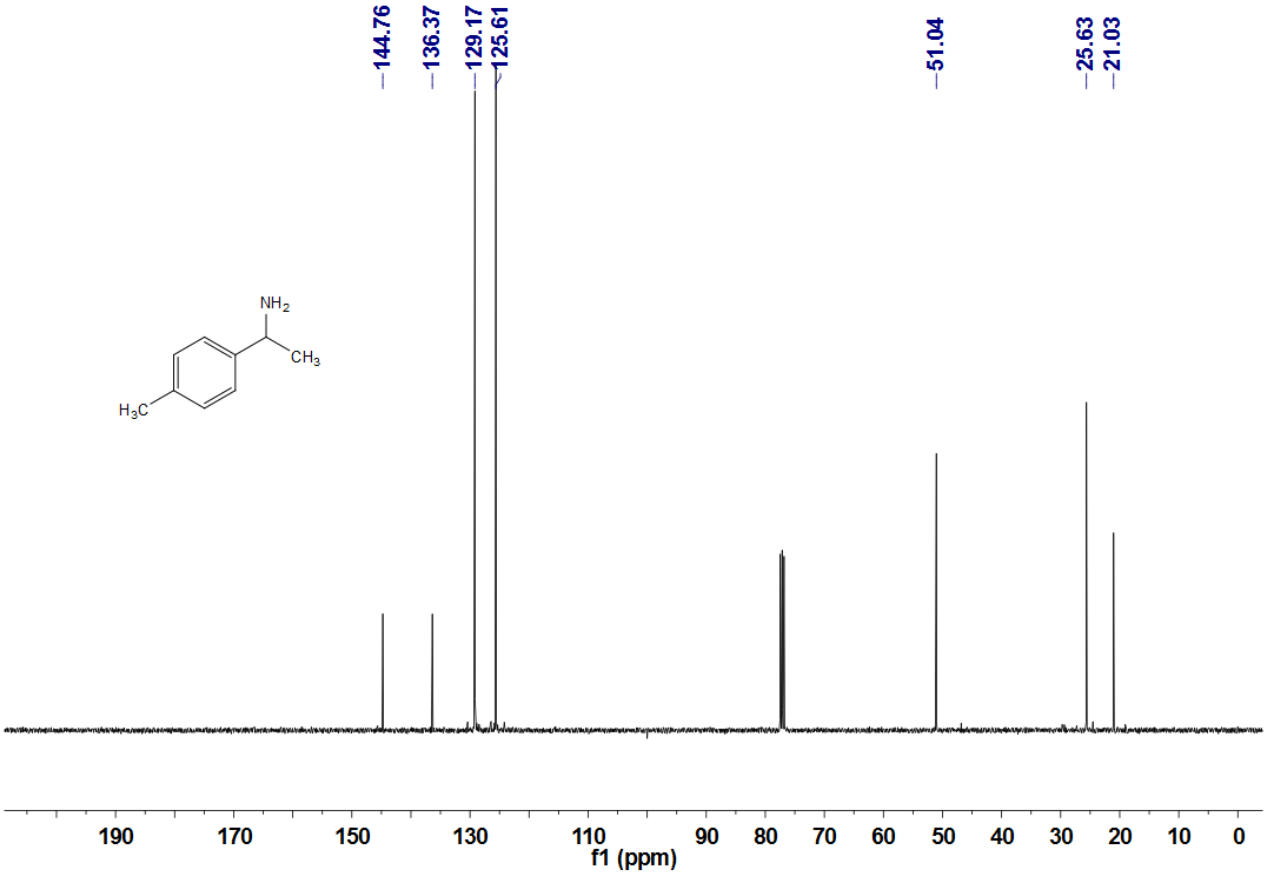
^{1}H NMR of 1-phenylethan-1-amine (**2a'**, **2f'**, **2g'**, **2h'**, **2j'**, **2k'**, **2l'**)



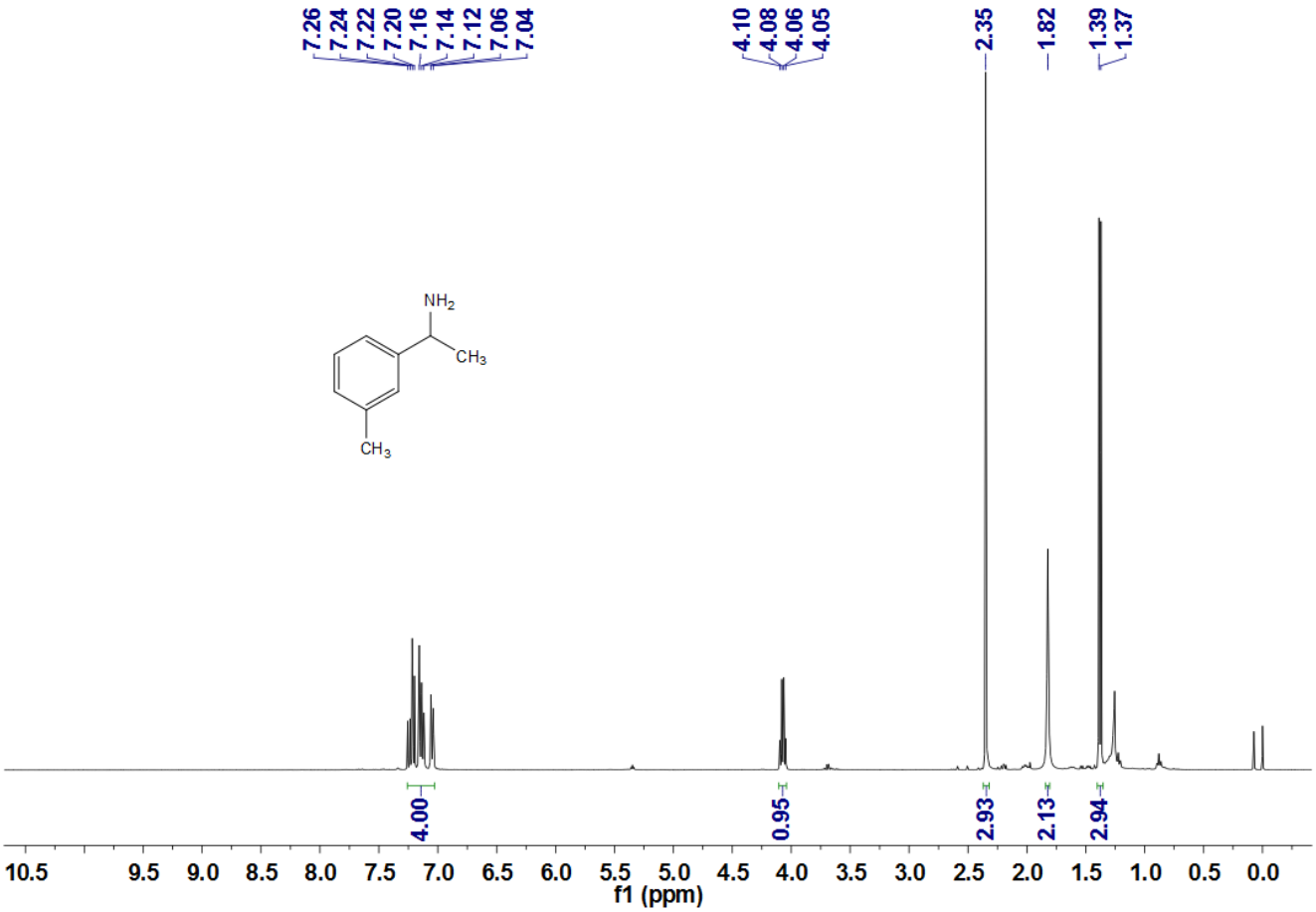
^{13}C NMR of 1-phenylethan-1-amine (**2a'**, **2f'**, **2g'**, **2h'**, **2j'**, **2k'**, **2l'**)



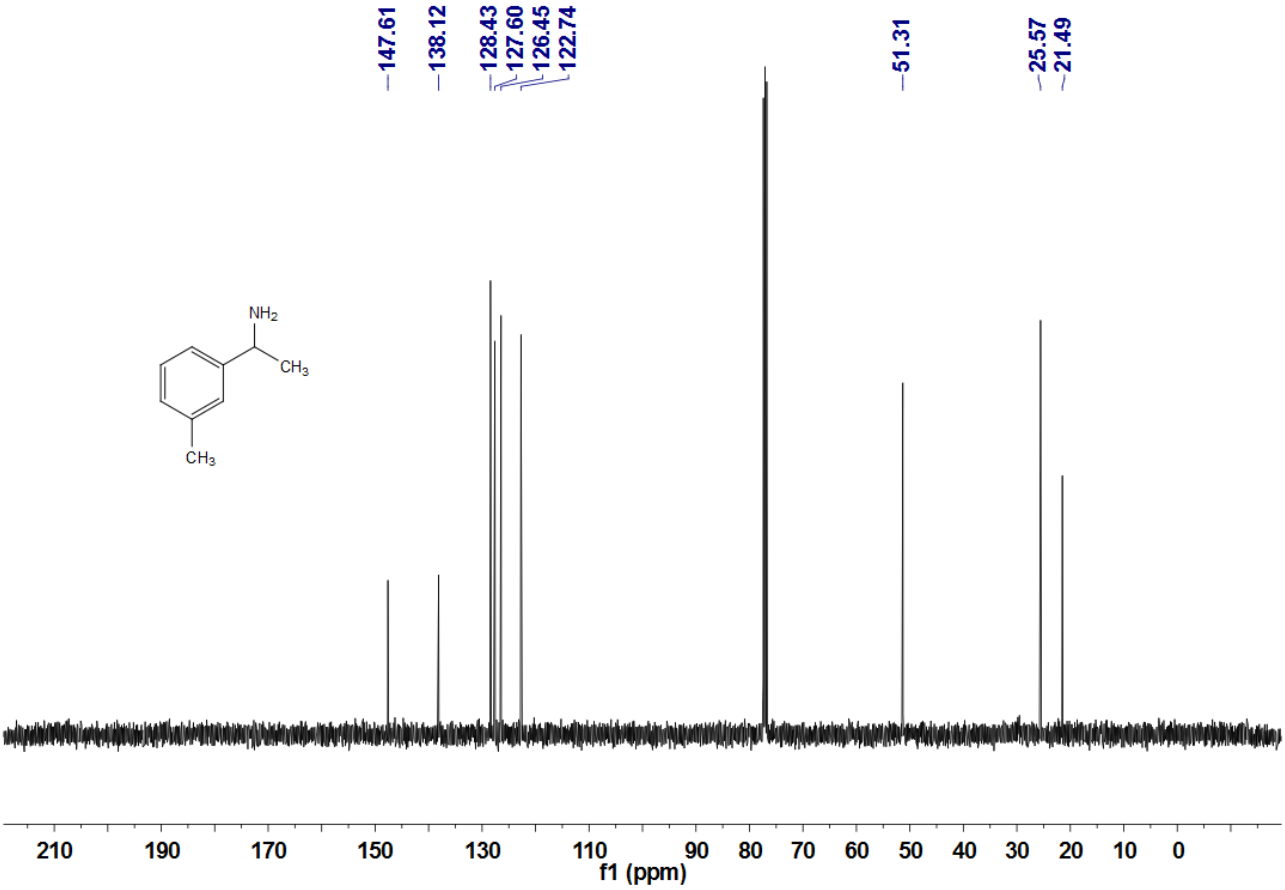
^{1}H NMR of 1-(p-tolyl)ethan-1-amine (**2b'**)



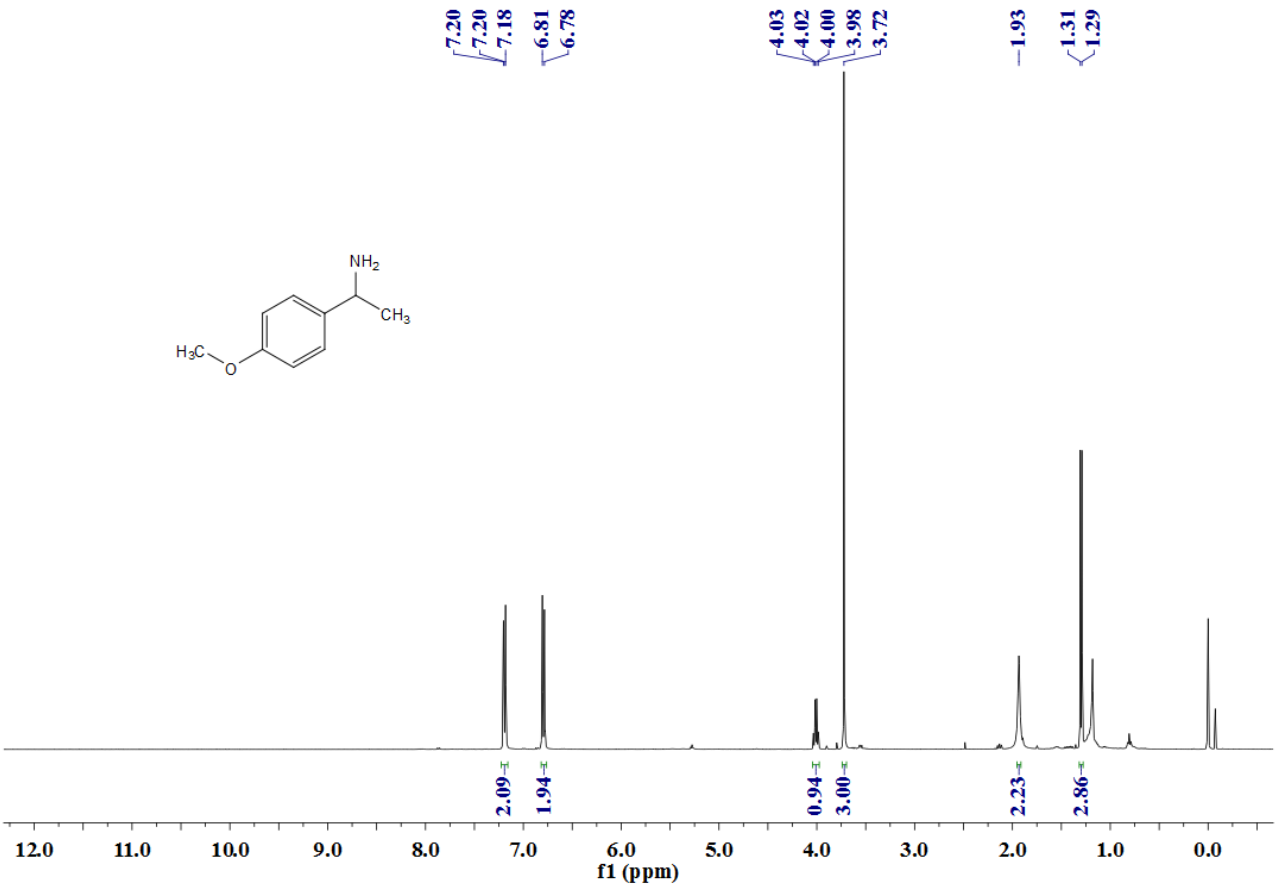
^{13}C NMR of 1-(p-tolyl)ethan-1-amine (**2b'**)



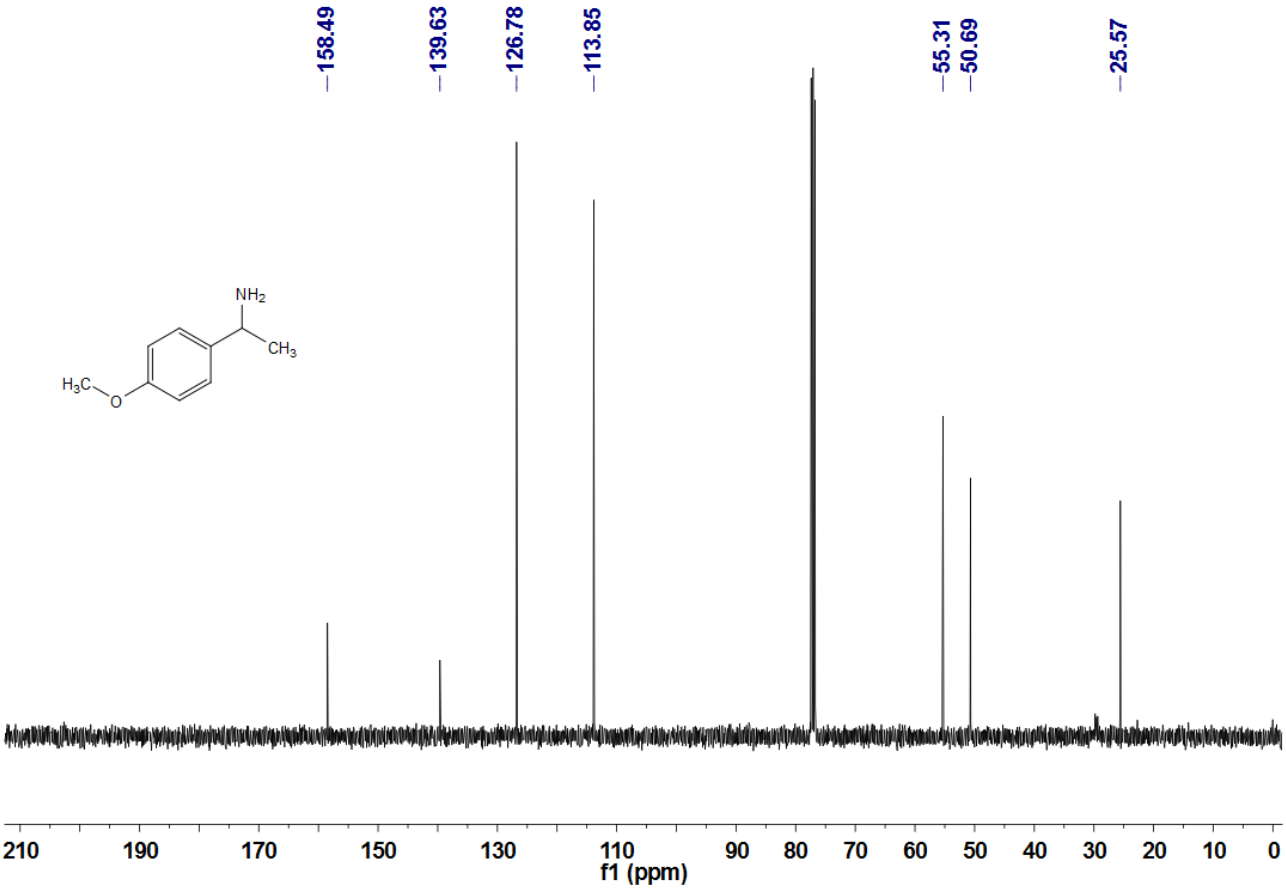
^{1}H NMR of 1-(m-tolyl)ethan-1-amine (**2c'**)



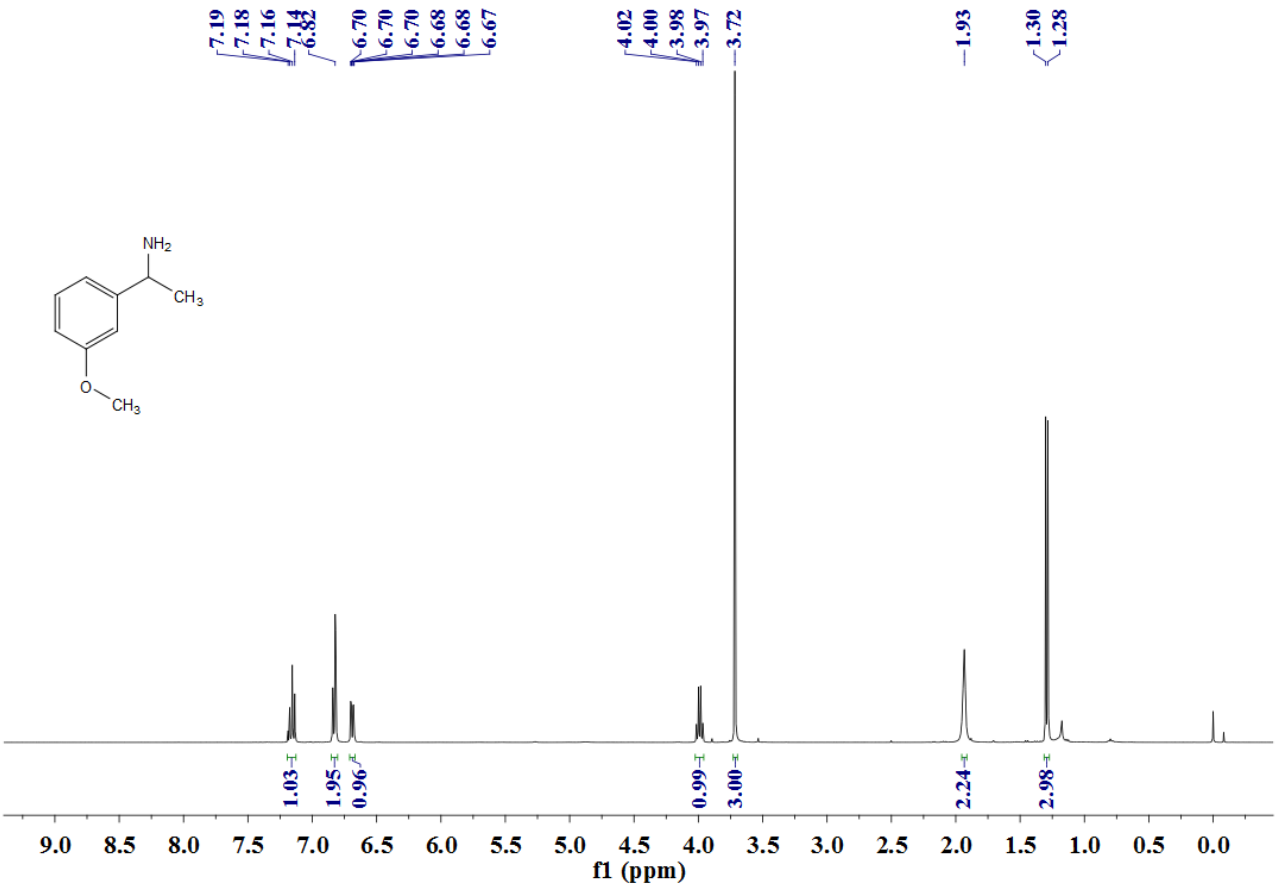
^{13}C NMR of 1-(m-tolyl)ethan-1-amine (**2c'**)



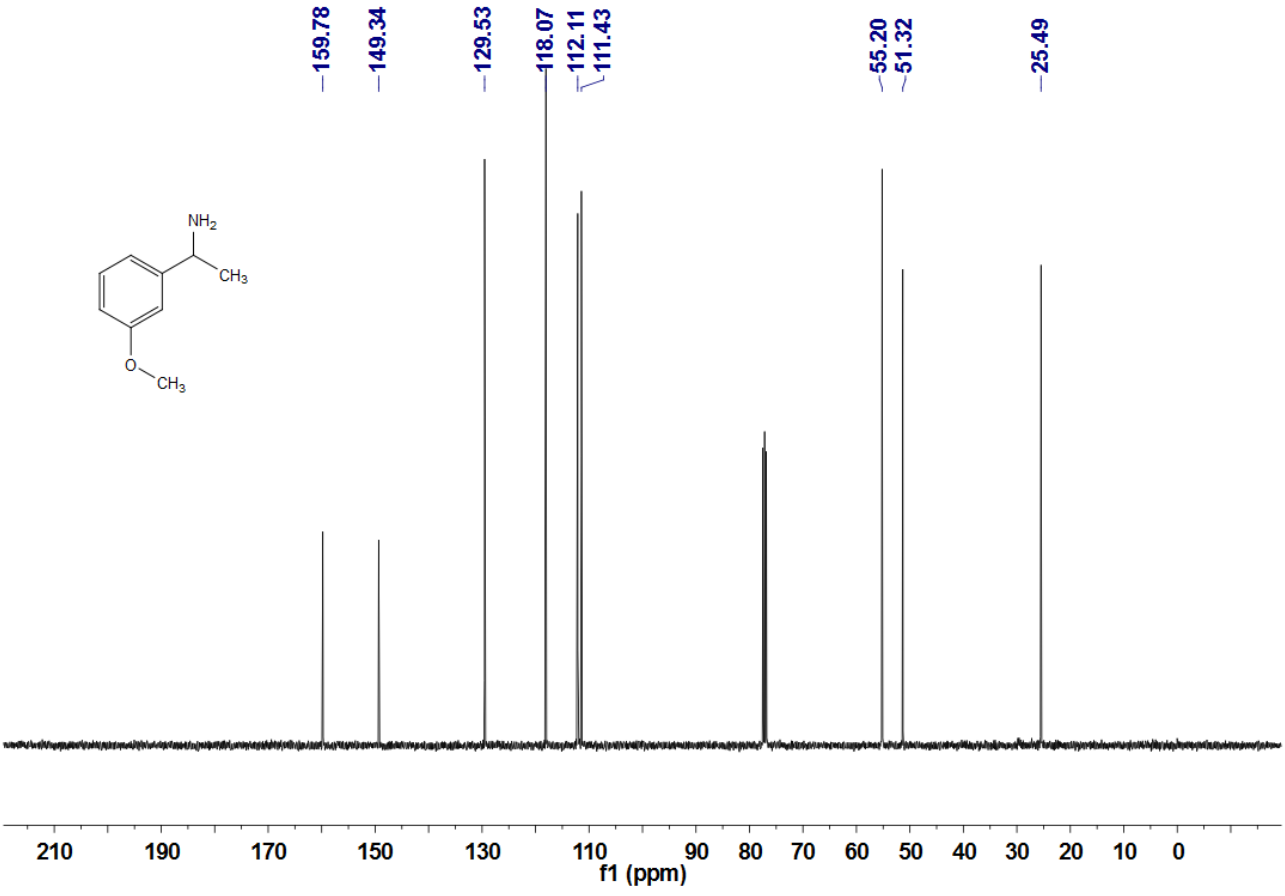
^{1}H NMR of 1-(4-methoxyphenyl)ethan-1-amine (**2d'**)



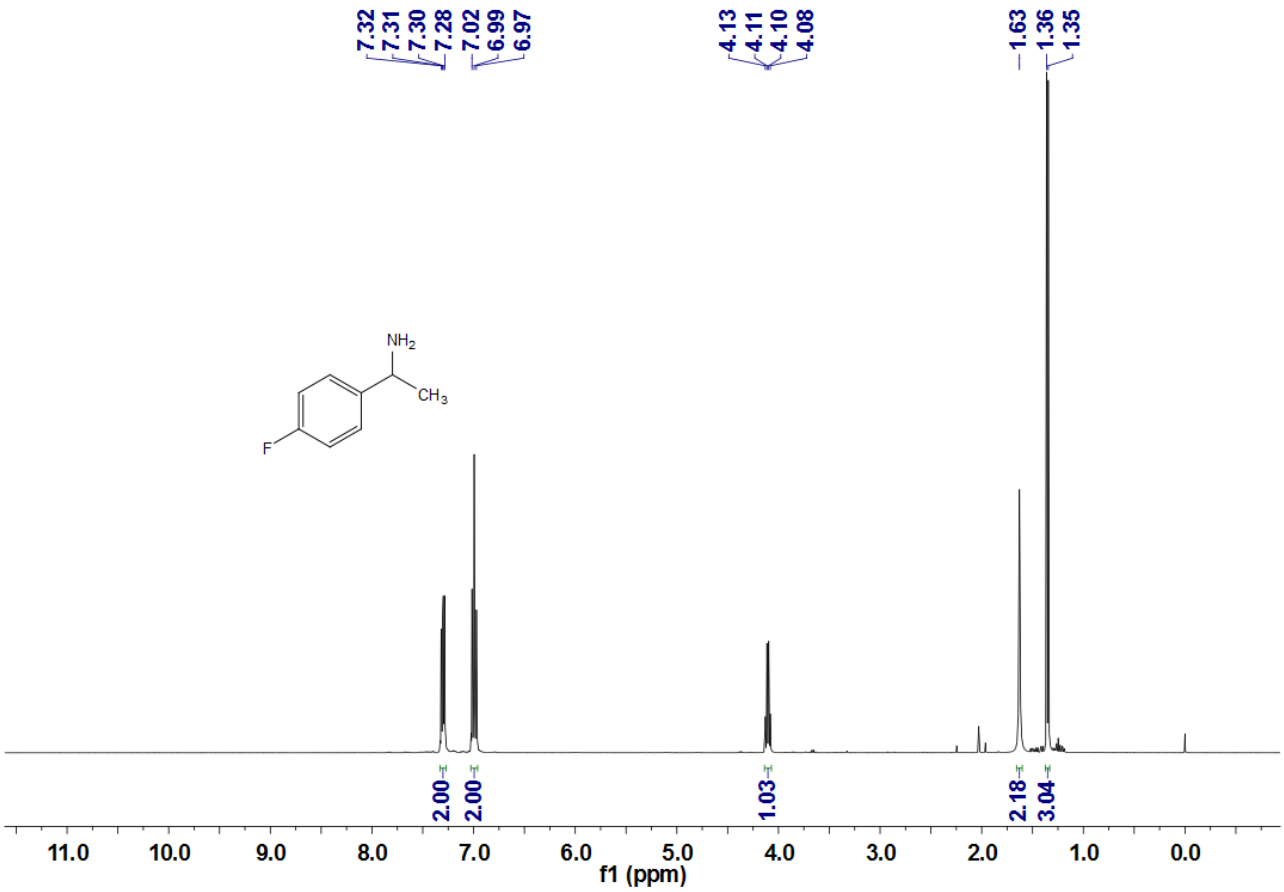
^{13}C NMR of 1-(4-methoxyphenyl)ethan-1-amine (**2d'**)



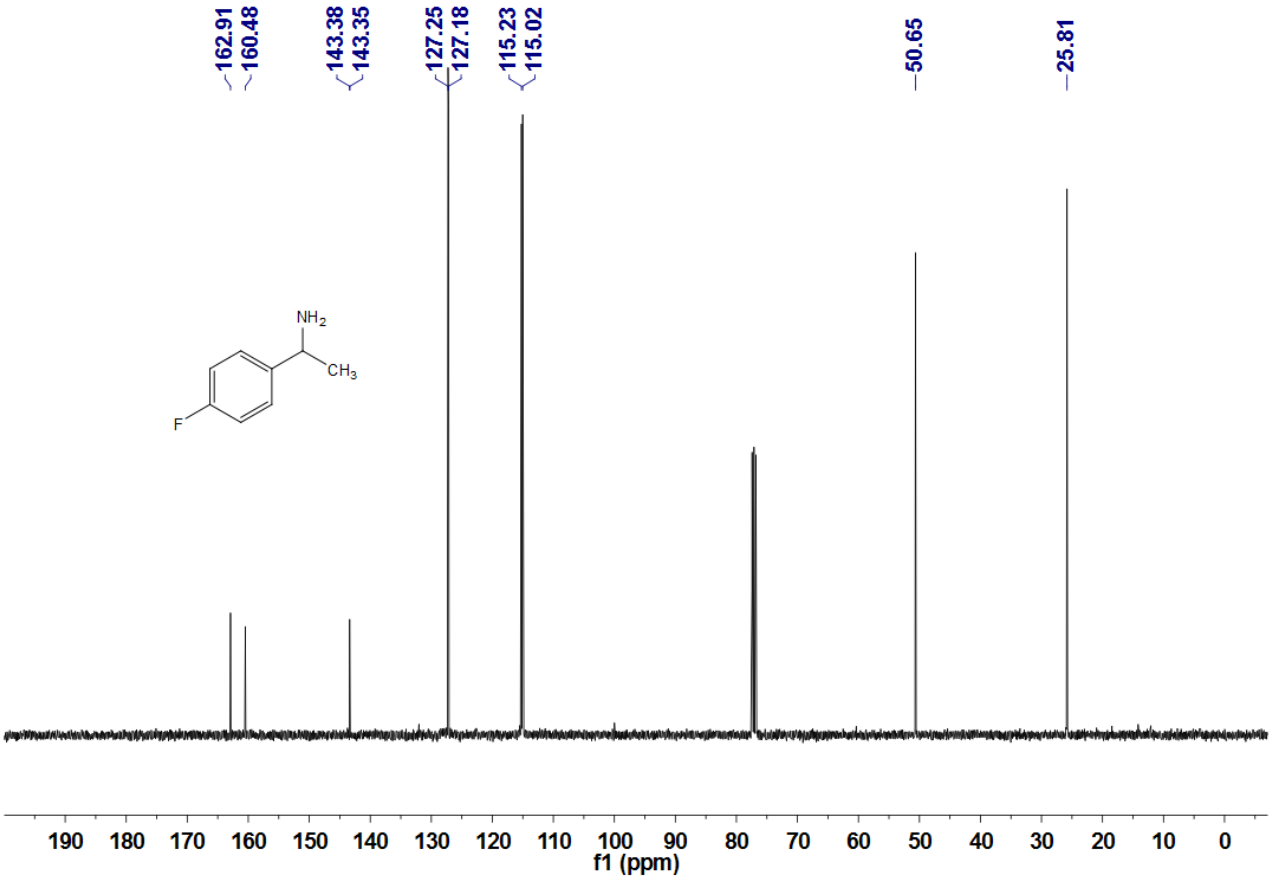
^{1}H NMR of 1-(3-methoxyphenyl)ethan-1-amine (**2e'**)



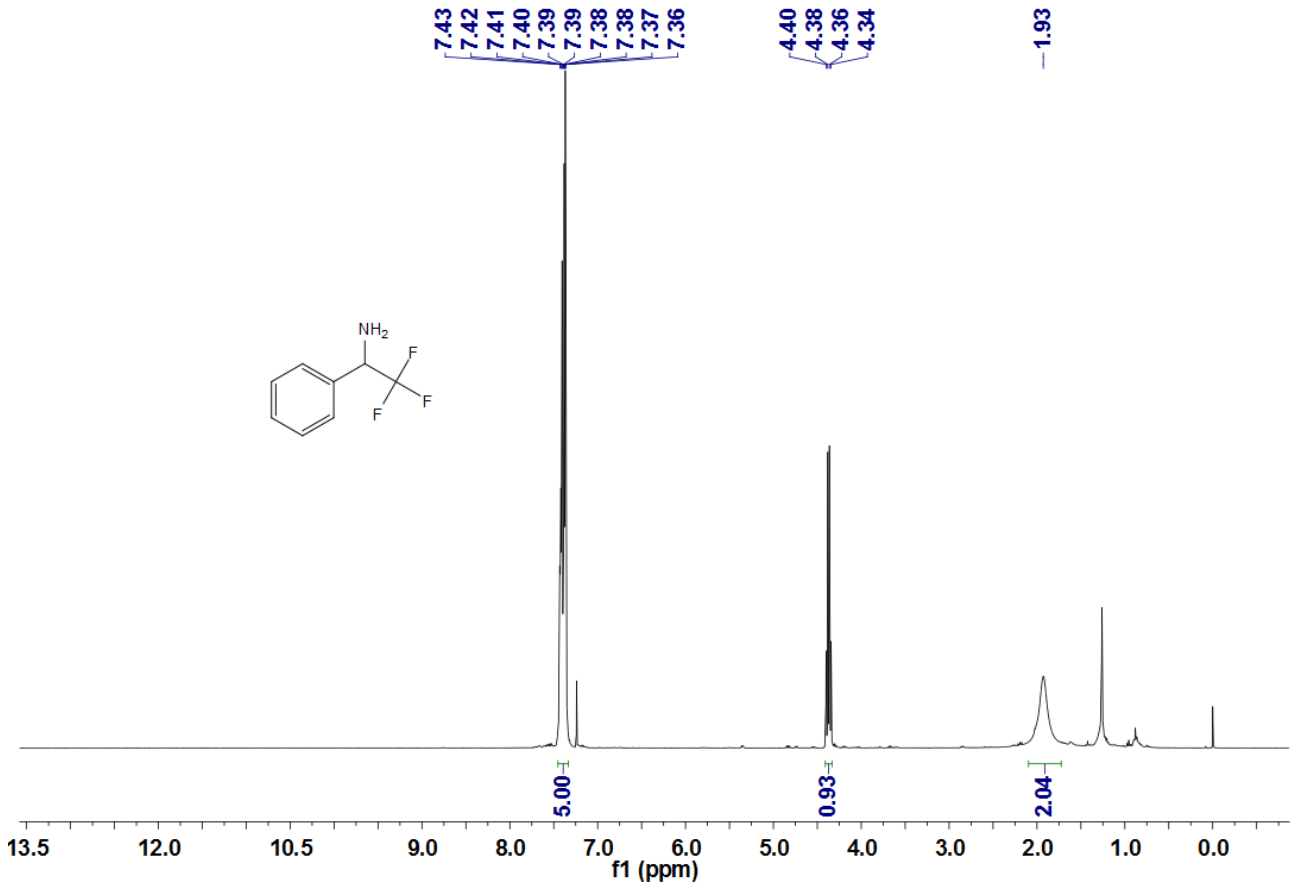
^{13}C NMR of 1-(3-methoxyphenyl)ethan-1-amine (**2e'**)



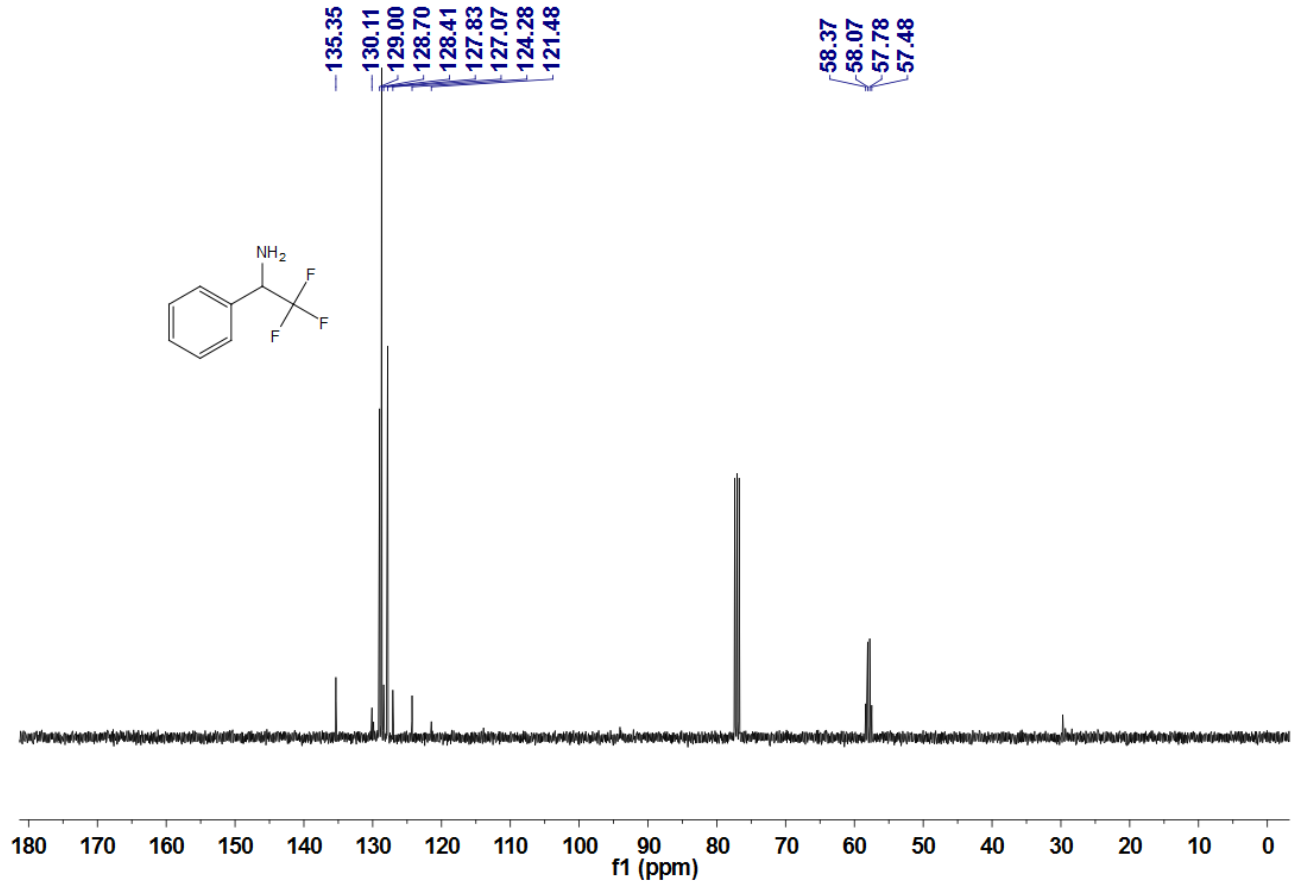
^{1}H NMR of 1-(4-fluorophenyl)ethan-1-amine (**2i'**)



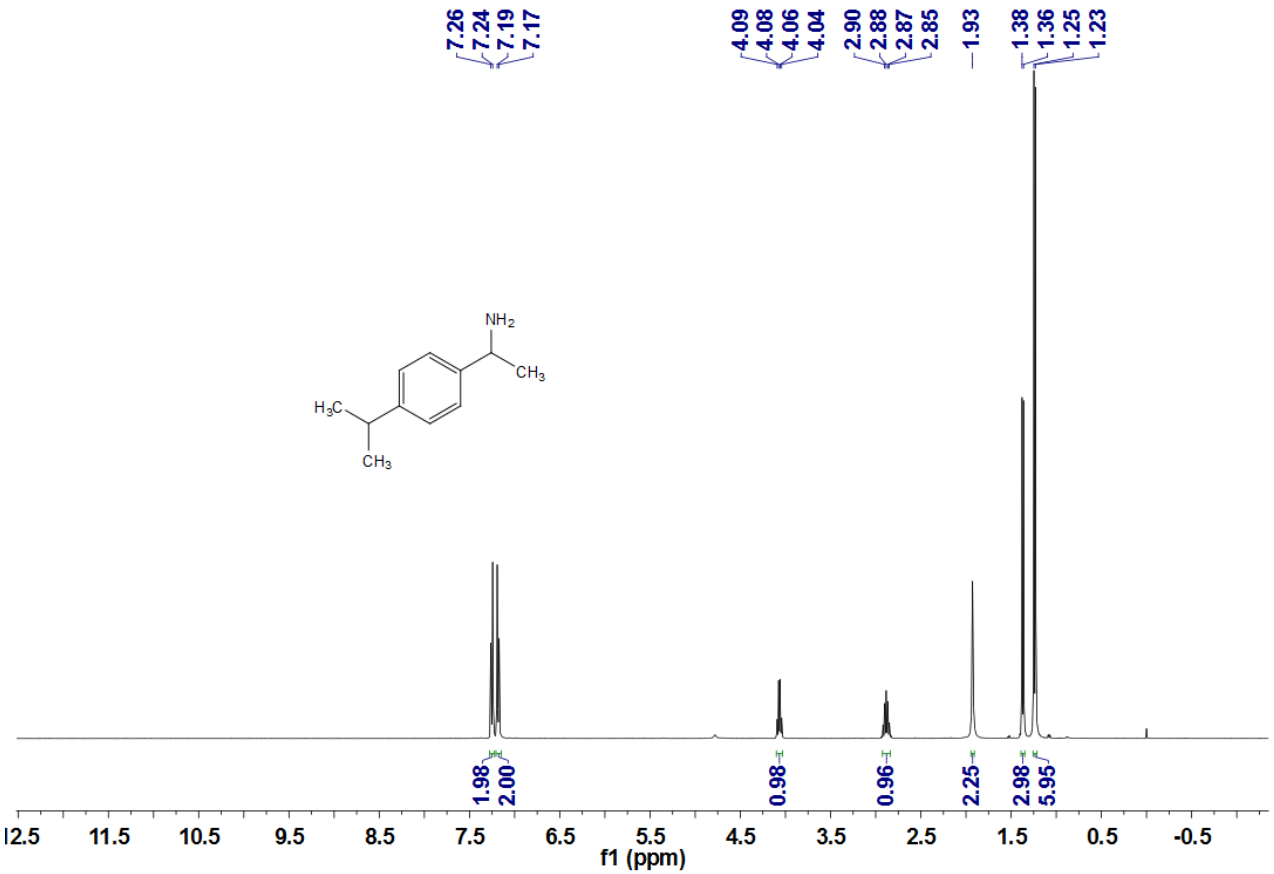
^{13}C NMR of 1-(4-fluorophenyl)ethan-1-amine (**2i'**)



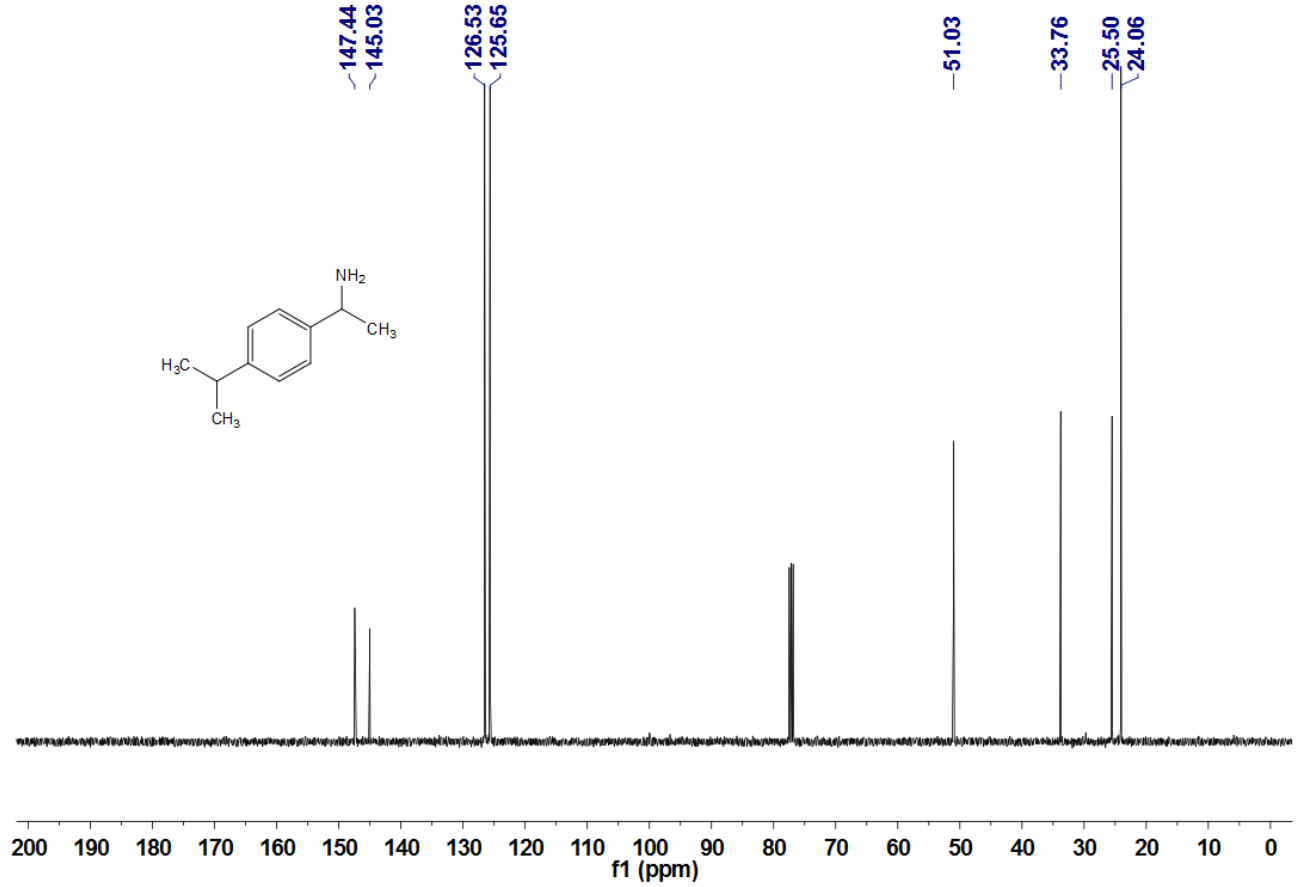
^{1}H NMR of 2,2,2-trifluoro-1-phenylethan-1-amine (**2m'**)



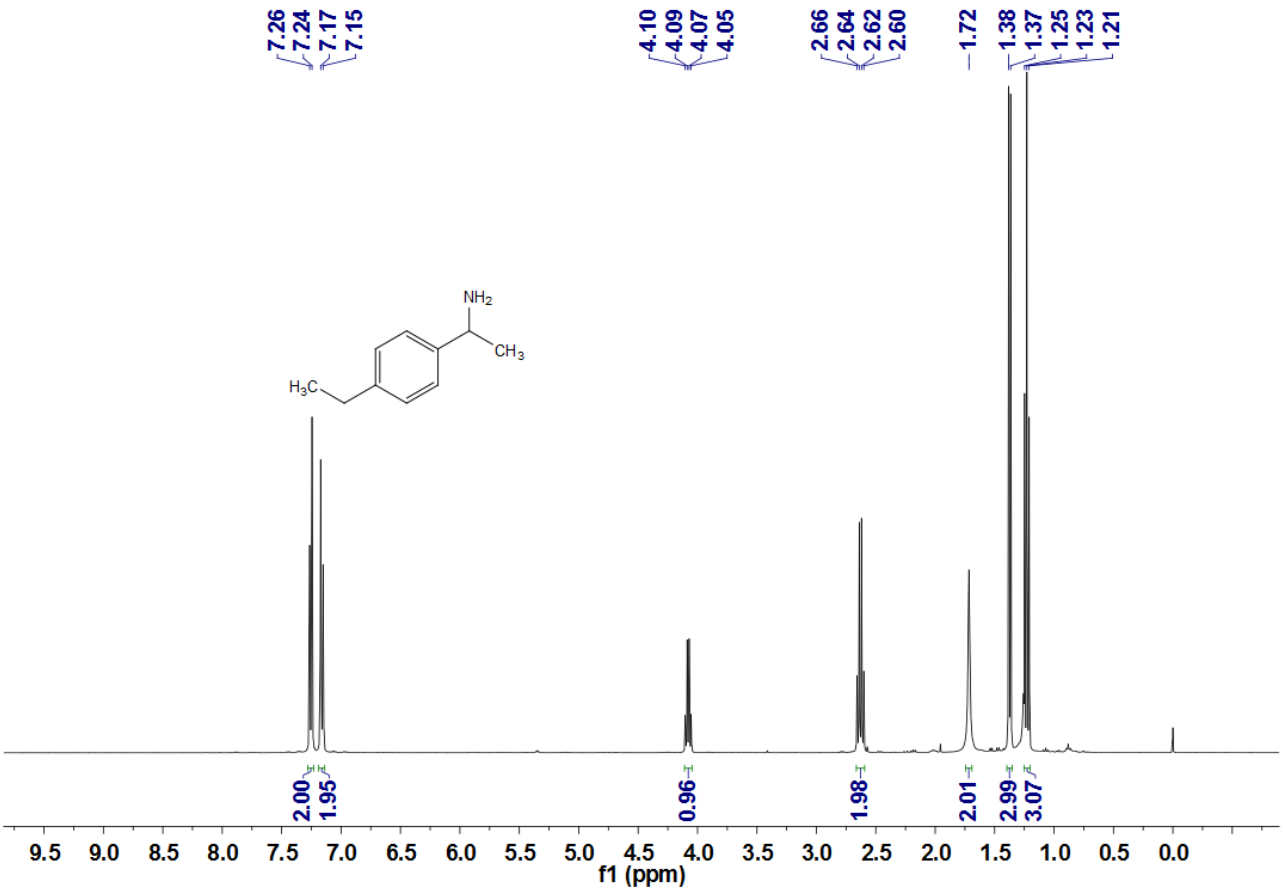
^{13}C NMR of 2,2,2-trifluoro-1-phenylethan-1-amine (**2m'**)



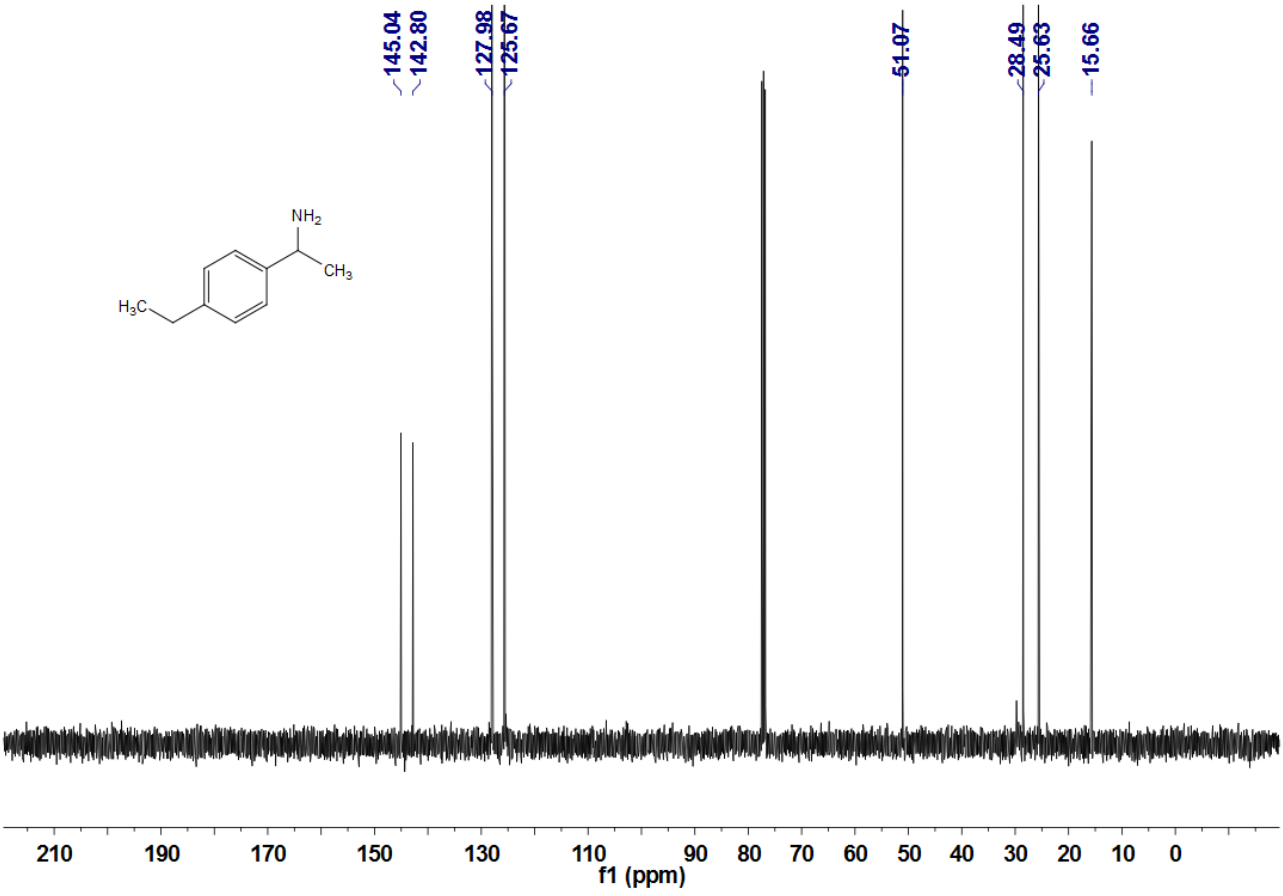
^{1}H NMR of 1-(4-isopropylphenyl)ethan-1-amine (**2n'**)



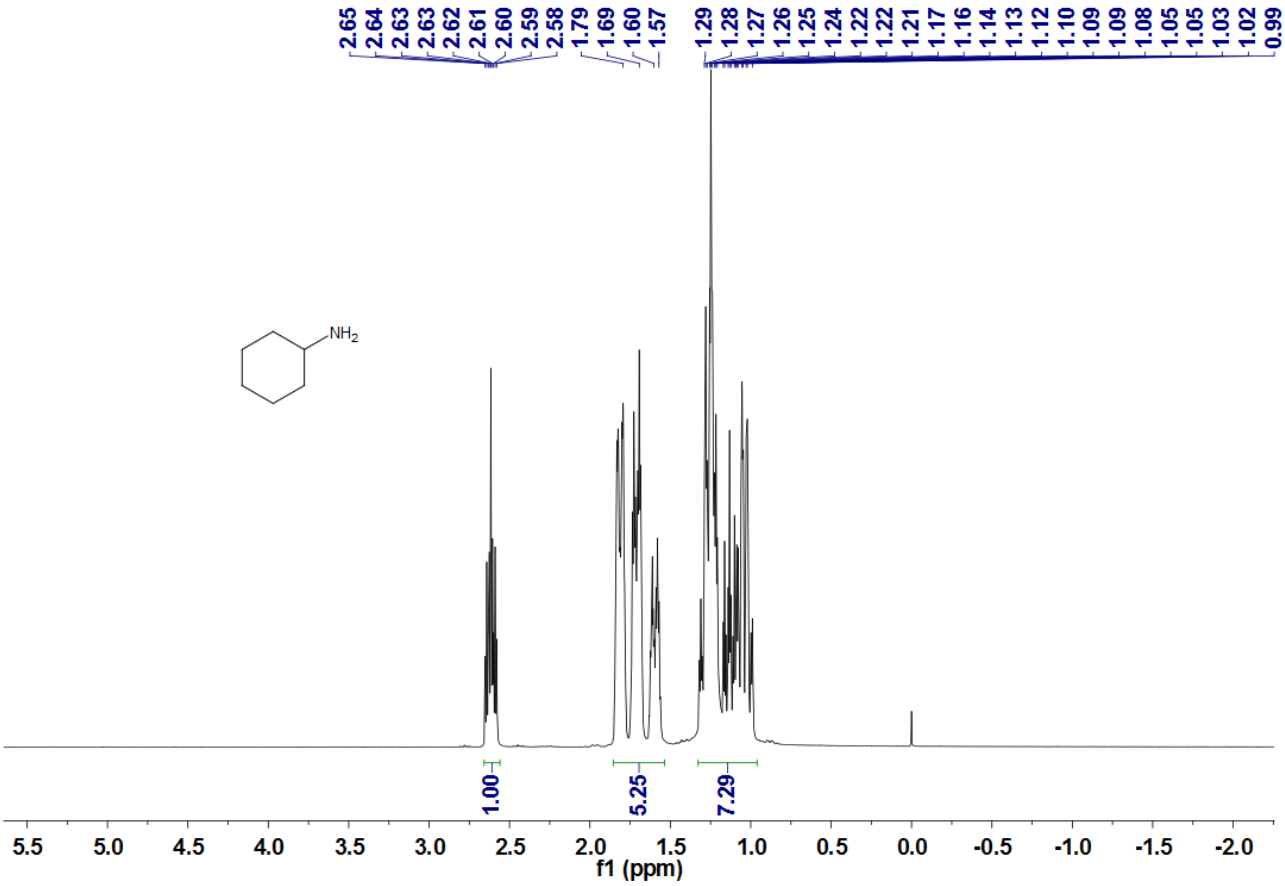
^{13}C NMR of 1-(4-isopropylphenyl)ethan-1-amine (**2n'**)



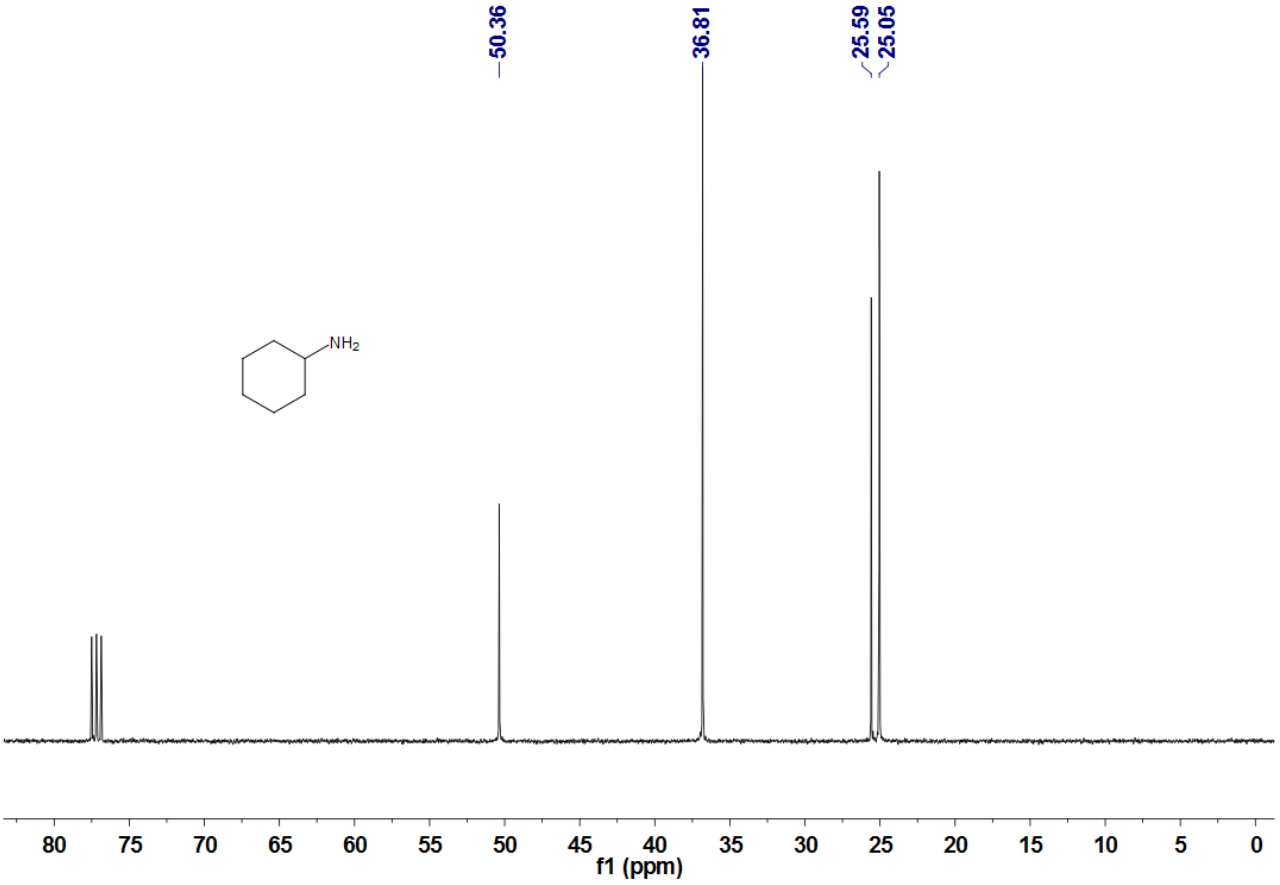
^{1}H NMR of 1-(4-ethylphenyl)ethan-1-amine (**2o'**)



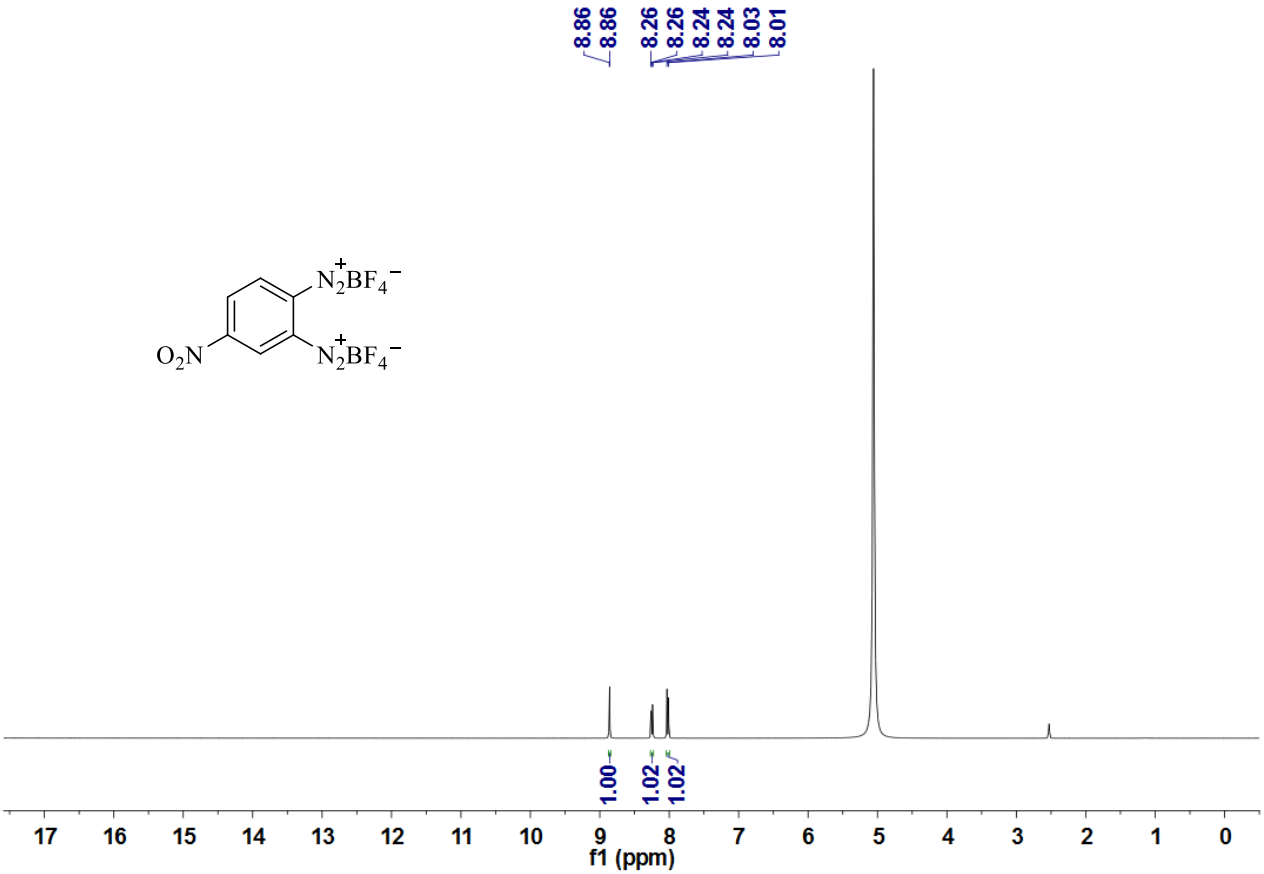
^{13}C NMR of 1-(4-ethylphenyl)ethan-1-amine (**2o'**)



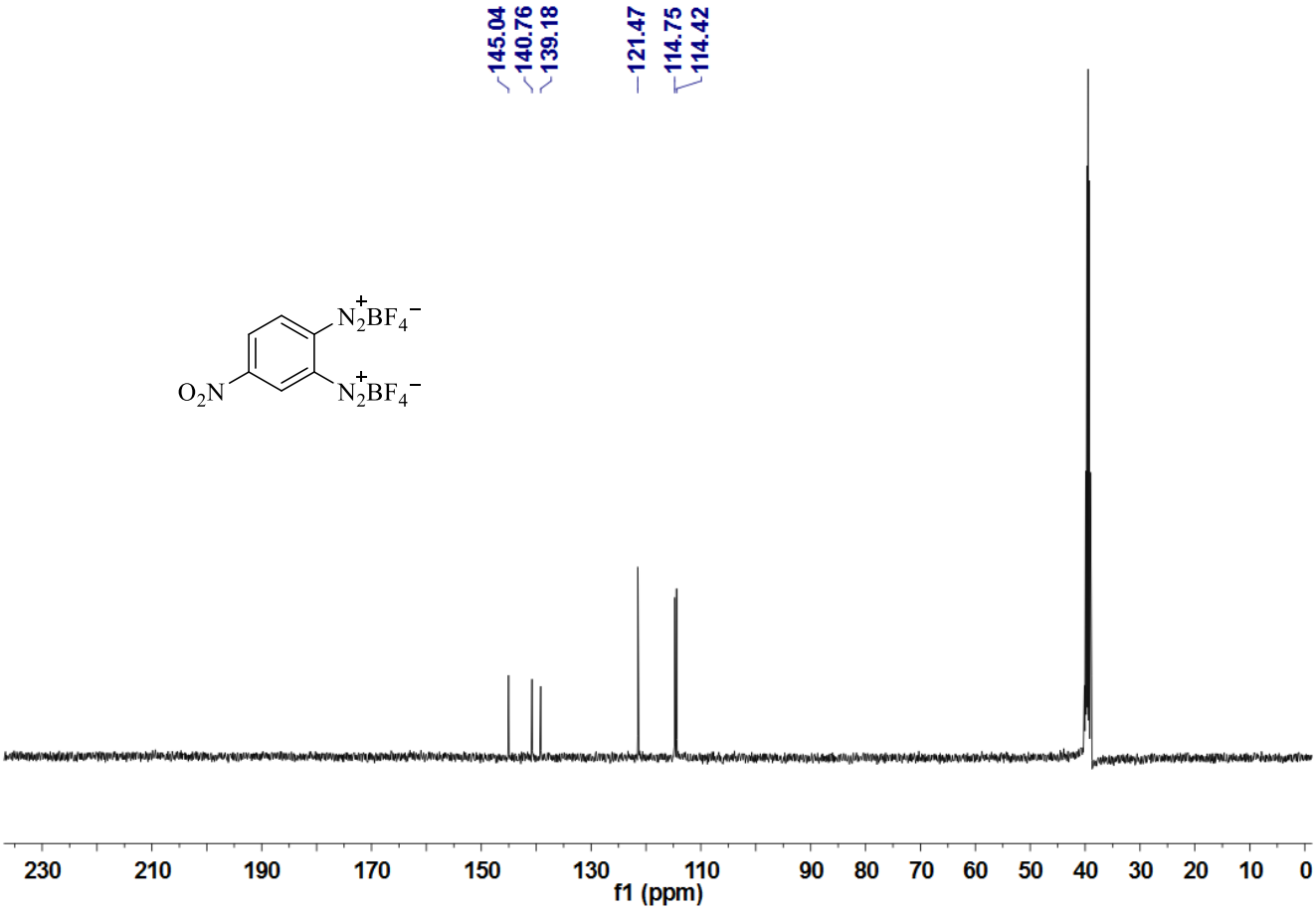
^{1}H NMR of cyclohexanamine (**2p'**)



^{13}C NMR of cyclohexanamine (**2p'**)

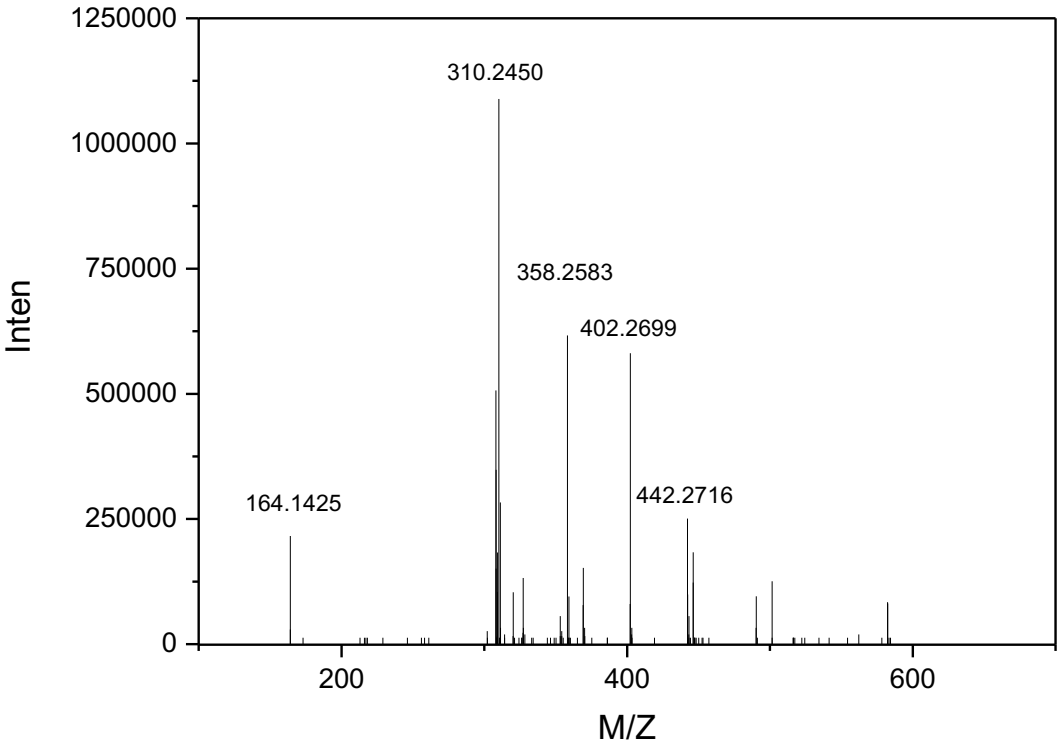


^{1}H NMR of 2,2'-(4-nitro-1,2-phenylene)bis(1-(trifluoro-λ^{5}-boranylidene)diazen-1-ium) fluoride



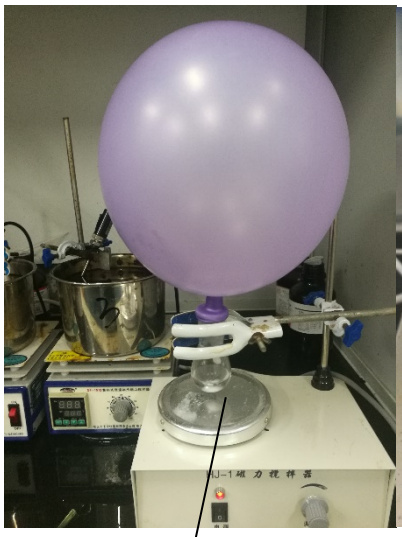
^{13}C NMR of 2,2'-(4-nitro-1,2-phenylene)bis(1-(trifluoro-λ^{5}-boranylidene)diazen-1-ium) fluoride

11. High-resolution mass spectrometry (HRMS) spectra of 2n'



HRMS of 1-(4-isopropylphenyl)ethan-1-amine (**2n'**)

12. Some images of experimental apparatus

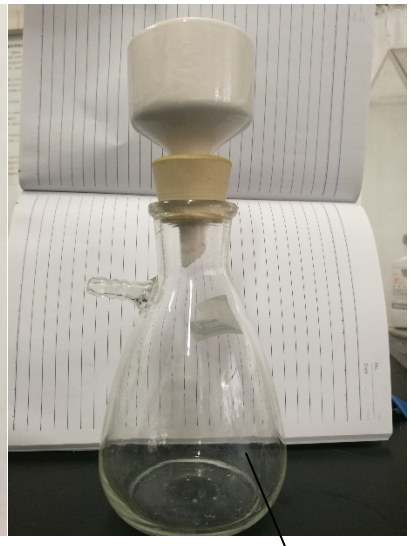


Hydrogennation of oxime under 1 atm H_2

Diazotization of 4-nitrobenzene-1,2-diamine in ice bath

2'-(4-nitro-1,2-phenylene)bis(1-(trifluoro-λ^5-boranylidene)diazen-1-ium) fluoride

Pd-L8



Buchner funnel