Supporting Information

Catalytic Fate of Structurally Characterized Manganese(III)-Salen Complexes towards Efficient Transformation of Primary Amides to Amines or Nitriles using Hydrosilane

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Table of Contents

1. Materials and methods ……..……..…….……...S1
2. Synthesis and characterization of ligands $\mathbf{L^1}$, $\mathbf{L^2}$ and its metal complexes **1-4**……..S1
3. X-ray crystal structural details of complexes **3** and **4**……...S12
4. Reaction optimization table……...S16
5. General procedure for reduction of primary amide to amine……S17
6. Kinetics of catalytic reduction of amide to amine …….……...S17
7. Procedure for gram-scale synthesis of amine…….……...S19
8. Stability of catalysts……..S19
9. Amide reduction in presence of other reactive functional groups…….S20
10. Mechanistic studies ……...…….……...S20
11. Characterization data of amines and nitriles…….…….……S26
12. ^{1}H NMR and ^{13}C NMR spectra of amines and nitriles …….....S36
13. Computational details……..S73
14. References……..…….S84

1. **Materials and methods**

The metal salt $Mn(OAc)_2.4H_2O$, $Mn(CO_3)$, triflic acid were purchased from Spectrochem, India. Salicylaldehyde, 5-fluoro salicylaldehyde, ethylene diamine, phenyl silane, potassium tert-butoxide, silver perchlorate hydrate were purchased from Sigma Aldrich. The primary amide substrates were purchased from commercial sources. All other chemicals and solvents were of analytical grade and used as supplied. The solvents used in catalysis were dried and distilled by using standard techniques. The ligand 2,2'-((1E,1'E)-(ethane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))diphenol (**L^1**) and 2,2'-((1E,1'E)-(ethane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))bis(4-fluorophenol) (**L^2**) were synthesized according to the literature method.[1,2] The metal precursor $Mn(OTf)_2$ was synthesized by the reaction of $Mn(CO_3)$ and triflic acid in water medium following the reported literature procedure.[3] All the catalytic reactions were accomplished under a nitrogen atmosphere using standard Schlenk techniques and dry solvents.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker advance 400 MHz spectrometer (Bruker, Massachusetts, USA). Electrospray ionization mass spectra (ESI) of synthesized complexes were recorded on a Q-tof-micro quadruple mass spectrometer. The elemental (C, H and N) analyses were performed on a Perkin Elmer 2400 CHN micro analyzer (Perkin Elmer, Waltham, USA). The infra-red spectra were performed on a FTIR-8400S SHIMADZU spectrophotometer (Shimadzu, Kyoto, Japan) with KBr pellet.

2. Synthesis and characterization of ligands (L^1, L^2) and Mn-salen complexes (1-4)

Synthesis of L^1:

The **L^1** was synthesized according to the literature procedure using salicylaldehyde and ethylene diamine.[1] ^1H NMR (400 MHz, $CDCl_3$, Figure S1) δ/ppm: 13.24 (s, 1H), 8.35 (s, 1H), 7.34 – 7.27 (m, 1H), 7.23 (dd, J = 7.7, 1.6 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.86 (td, J = 7.5, 0.9 Hz, 1H), 3.92 (s, 2H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, Figure S2) δ/ppm: 166.61, 161.10, 132.52, 131.61, 118.80, 118.73, 117.05, 59.82.

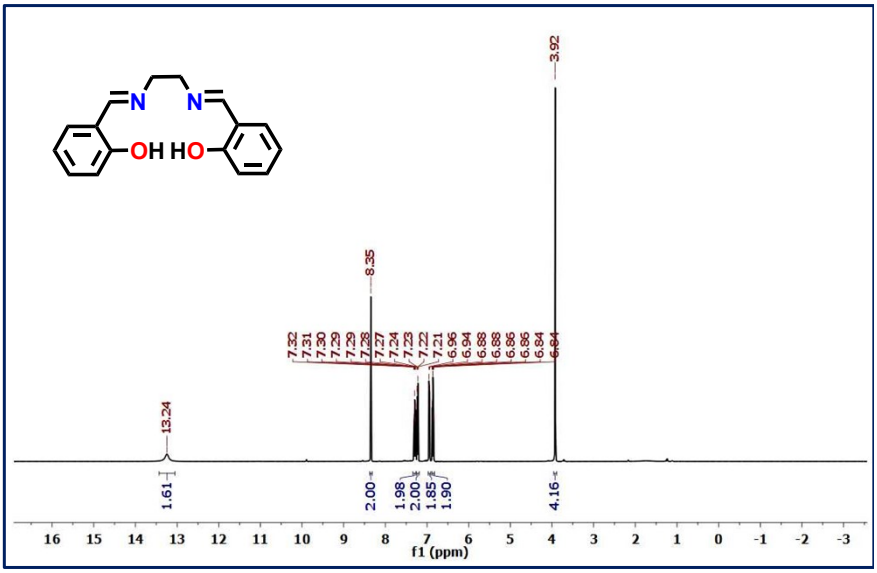


Figure S1: ^{1}H NMR spectra of **L^{1}**.

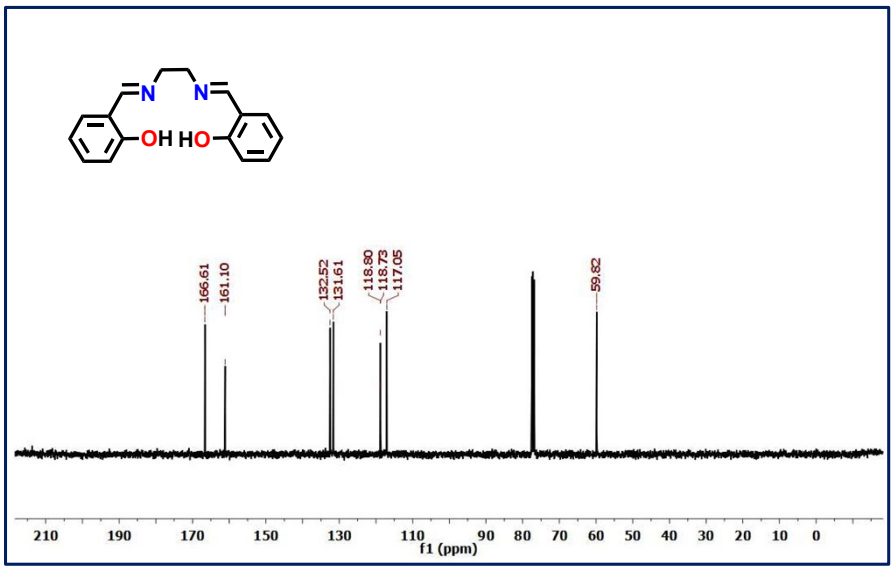


Figure S2: ^{13}C {^{1}H} NMR spectra of **L^{1}**.

Synthesis of L^{2}:

The ligand **L^{2}** were synthesized according to the literature procedure using 5-fluoro salicylaldehyde and ethylene diamine.[2] ^{1}H NMR (400 MHz, $CDCl_3$, Figure S3) δ/ppm: 12.88 (s, 1H), 8.30 (s, 1H), 7.02 (d, J = 3.1 Hz, 1H), 6.91 (ddd, J = 13.5, 8.6, 3.7 Hz, 2H), 3.96 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, Figure S4) δ/ppm: 165.62, 157.16, 156.65, 154.30,

119.75, 119.52, 118.39, 118.32, 118.17, 118.10, 116.74, 116.50, 59.74. $^{19}F\{^{1}H\}$ NMR (470.5 MHz, $CDCl_3$, FigureS5): -125.45.

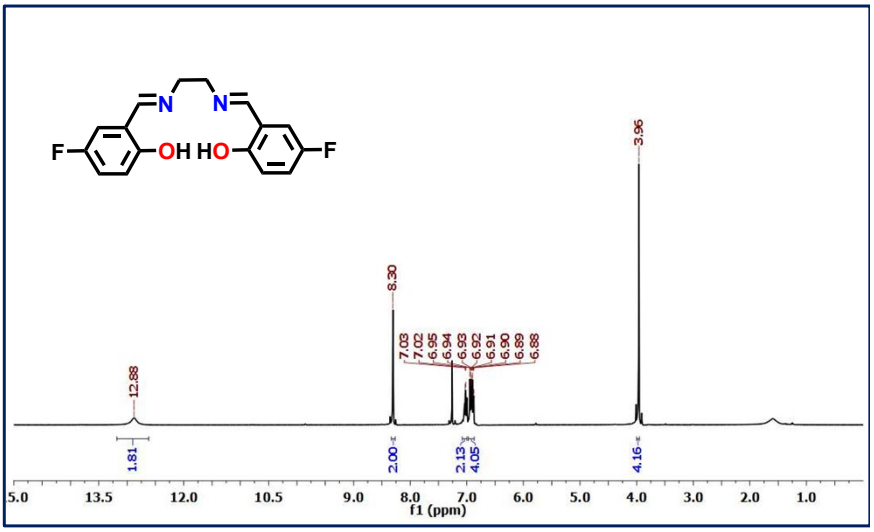


Figure S3: ^{1}H NMR spectra of **L^2**.

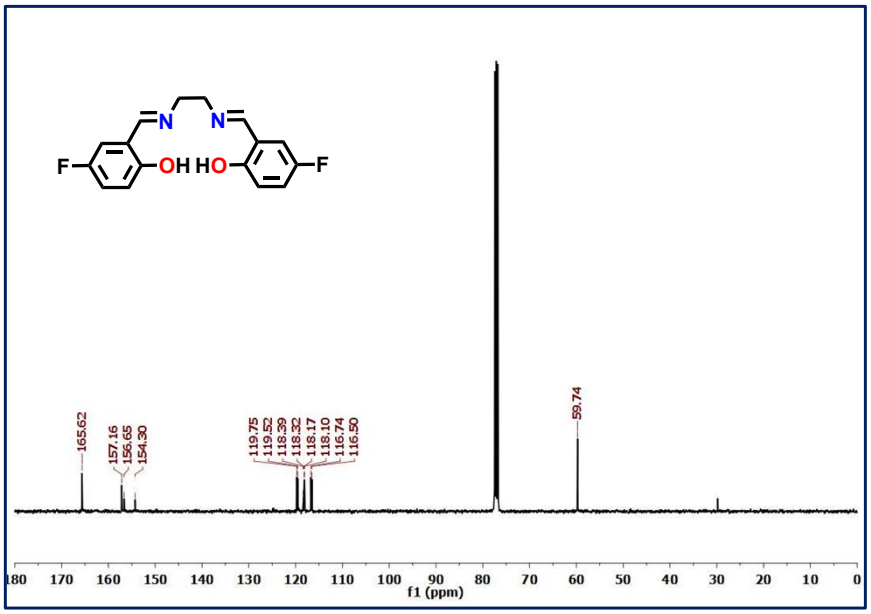


Figure S4: ^{13}C $\{^{1}H\}$ NMR spectra of **L^2**.

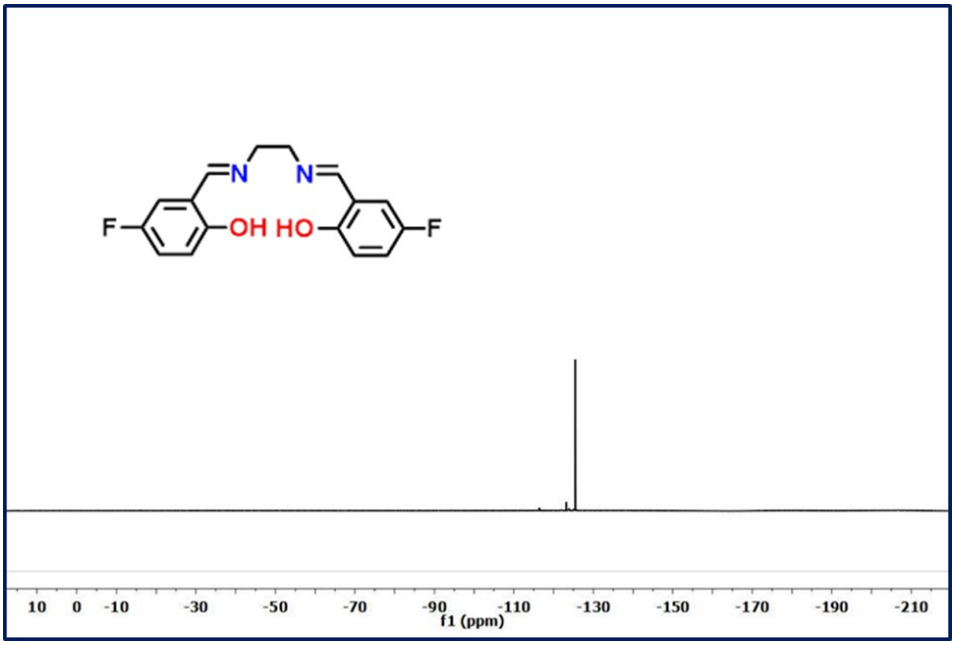


Figure S5: $^{19}F\{^{1}H\}$ NMR spectra of $\mathbf{L^2}$.

Synthesis of complex $[Mn^{III}(L^1)Cl]$, 1:

The complex **1** was synthesized according to the literature procedure by doing the reaction of manganese acetate with $\mathbf{L^1}$ followed by chloride exchange.[1] Yield: 91%. Elemental analysis calc. (%) for crystalline compound $C_{16}H_{14}ClMnN_2O_2$: C 53.88, H 3.96, N 7.85; found: C 53.52, H 3.66, N 7.98; ESI-MS: (m/z): calc. for $C_{16}H_{14}MnN_2O_2$: 321.0473 $[M\text{-}Cl]^+$; found: 321.0436 (Figure S6). IR (KBr, cm^{-1}; Figure S7): 3470, 1626; UV-Vis (λ_{max}, nm; Figure S8): 308, 410, 480.

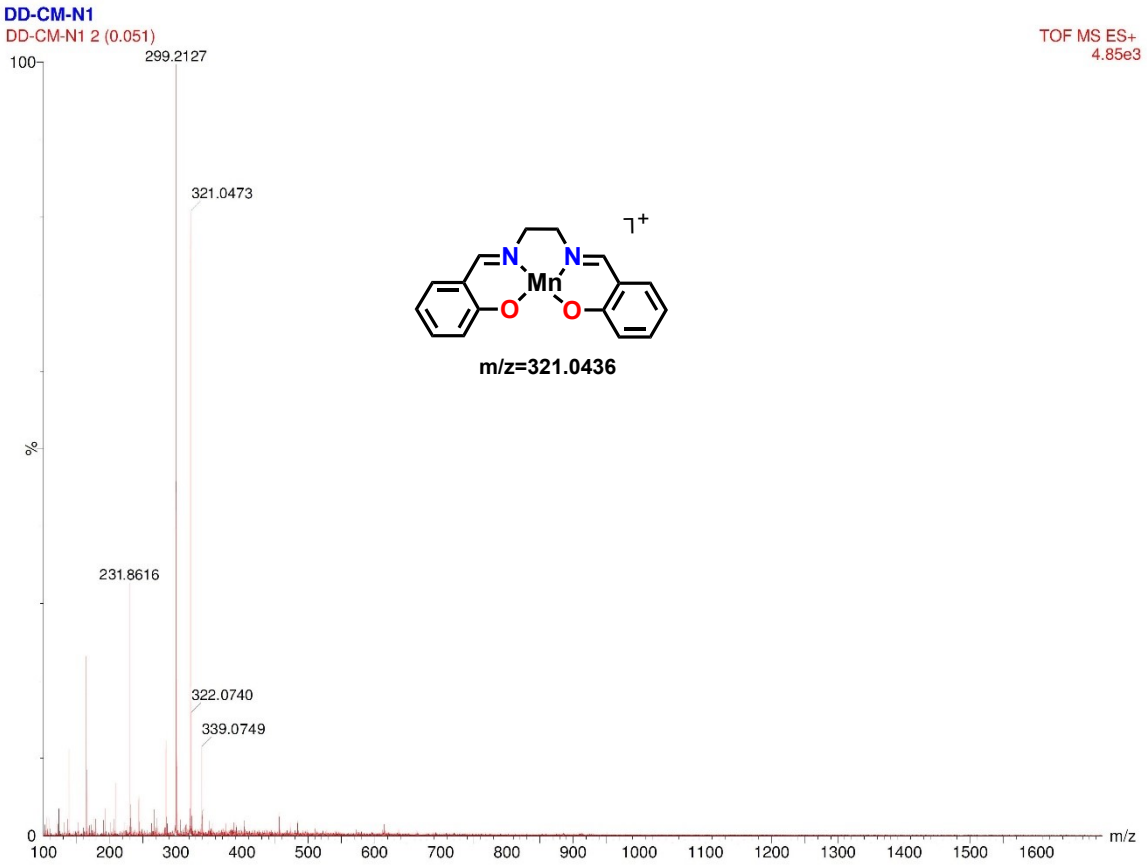


Figure S6: ESI-MS spectrum of complex **1** in acetonitrile.

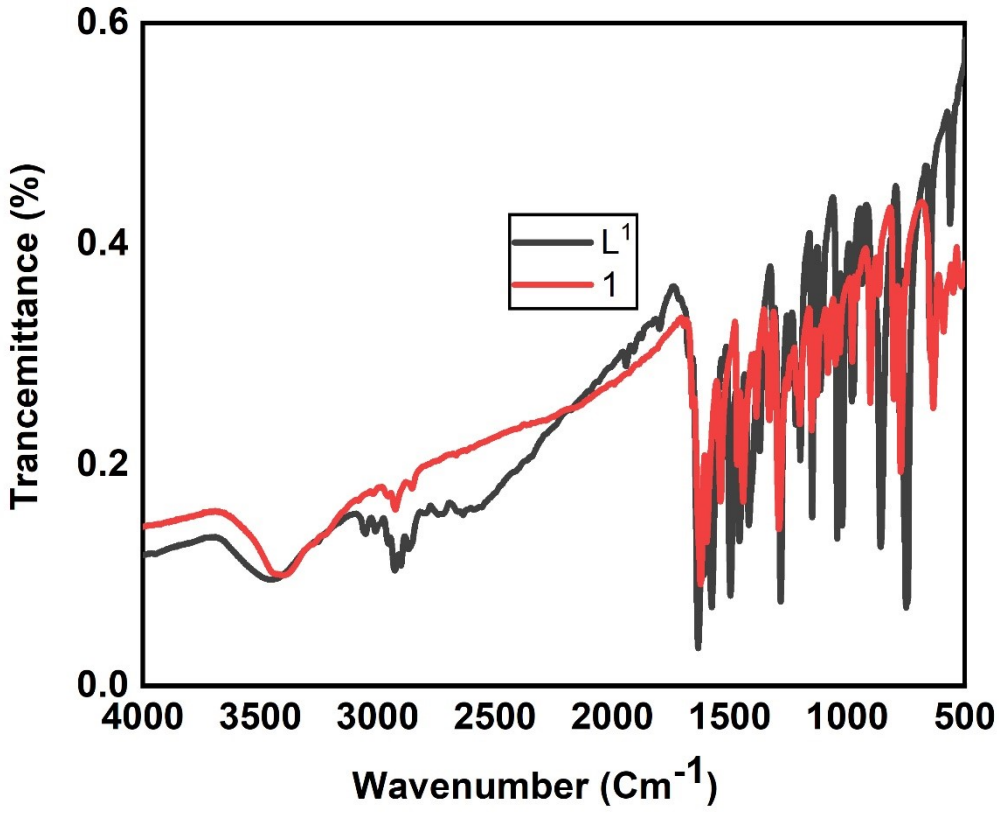


Figure S7: FT-IR spectra of $\mathbf{L^1}$ and complex **1**.

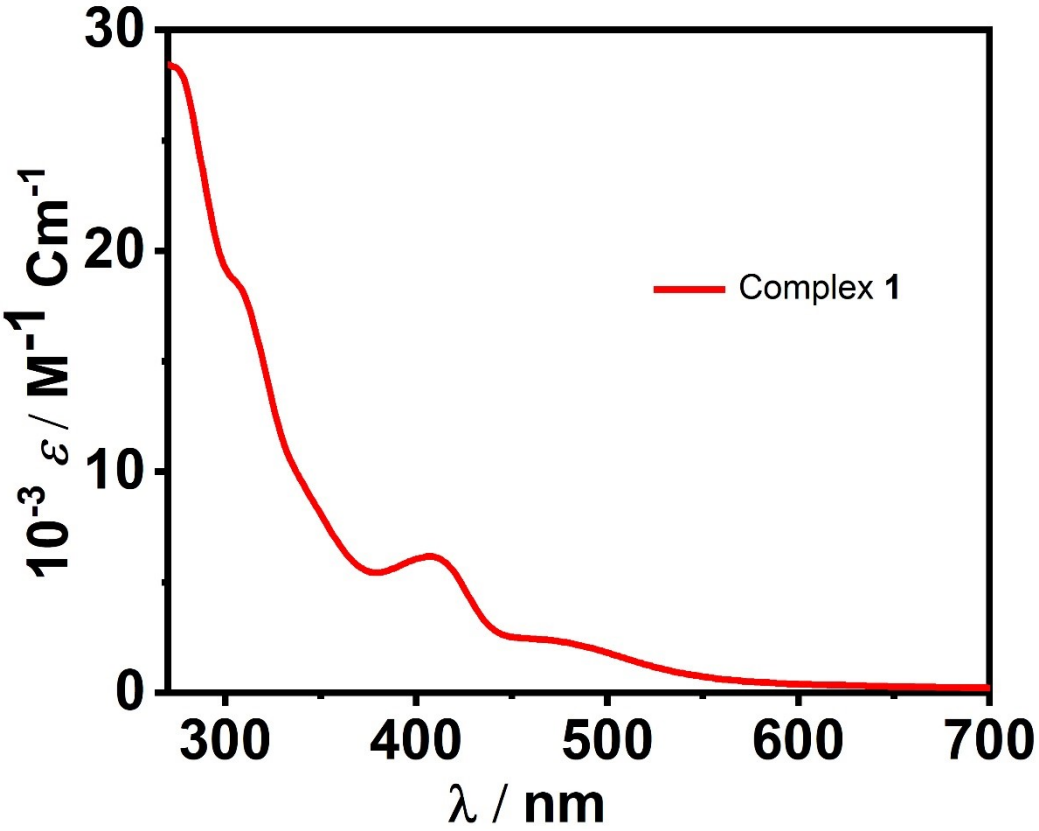


Figure S8: UV-Vis-NIR spectra of complex **1** in acetonitrile.

Synthesis of complex [$Mn^{III}(L^2)Cl$], 2:

The complex **2** was synthesized according to the literature procedure by doing the reaction of manganese acetate with $\mathbf{L^2}$ followed by chloride exchange.[2] Yield: 64%. Elemental analysis calc. (%) for crystalline compound $C_{16}H_{12}ClF_2MnN_2O_2$: C 48.94, H 3.08, N 7.13; found: C 48.61, H 2.93, N 7.34; ESI-MS: (m/z): calc. for $C_{16}H_{12}F_2MnN_2O_2$: 357.0237 $[M\text{-}Cl]^+$; found: 357.0247 (Figure S9). IR (KBr, cm^{-1}; Figure S10): 3478, 1627; UV-Vis (λ_{max}, nm; Figure S11): 424, 490.

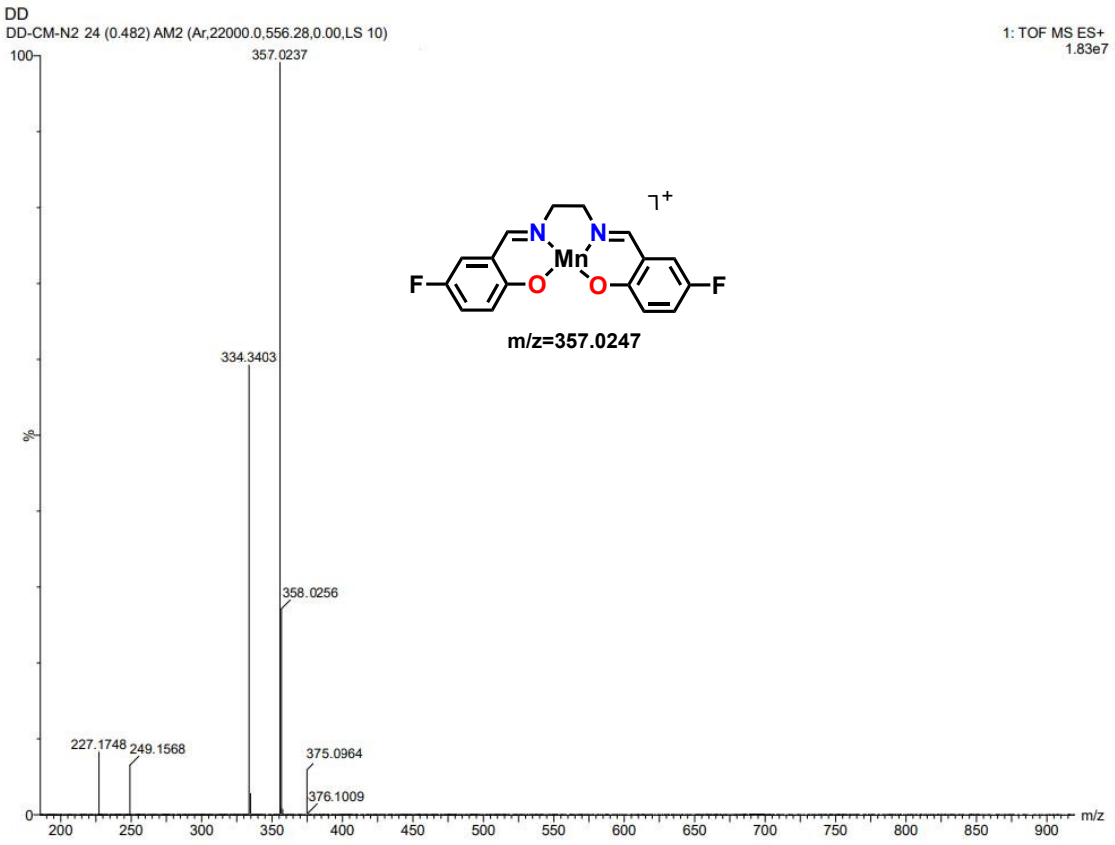


Figure S9: ESI-MS spectrum of complex **2** in acetonitrile.

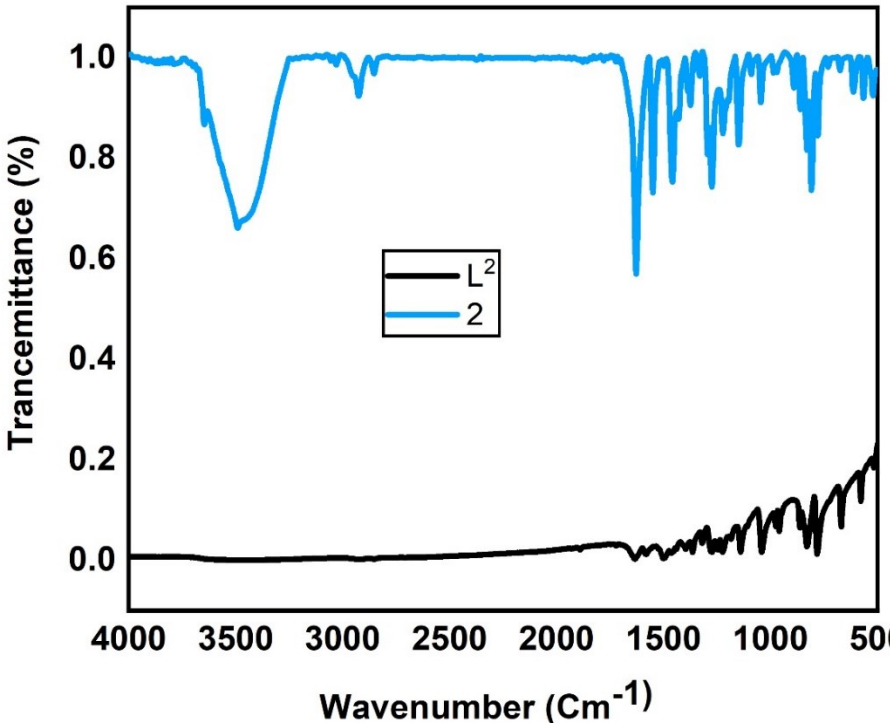


Figure S10: FT-IR spectra of L^2 and complex **2**.

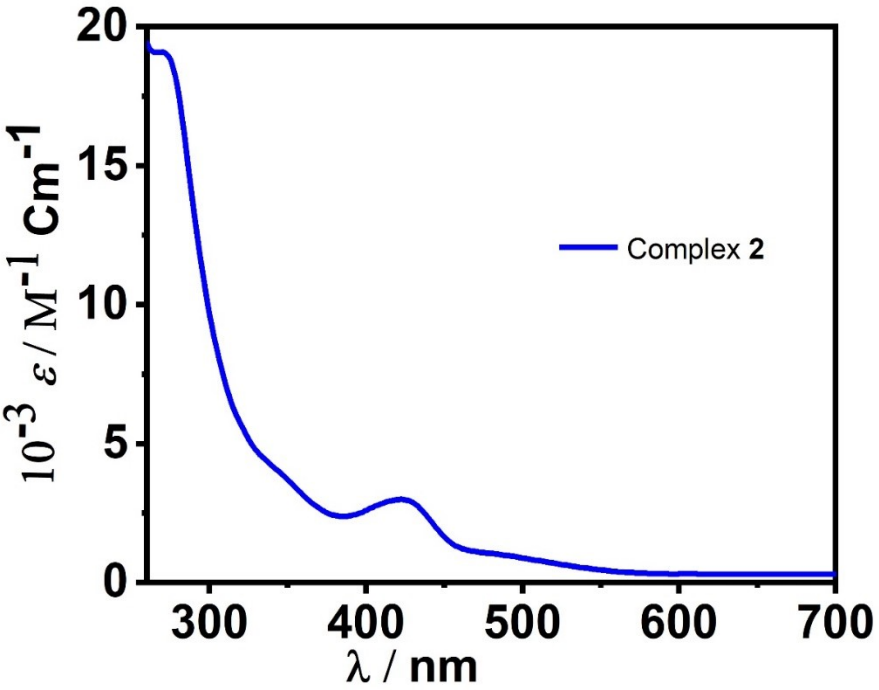
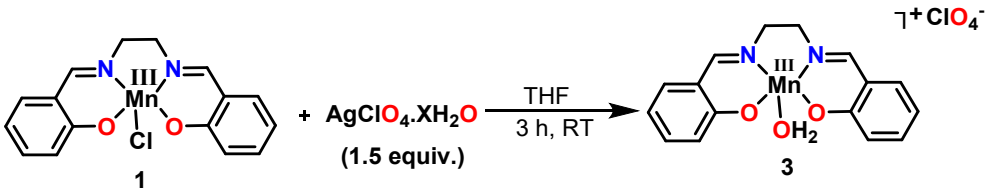


Figure S11: UV-Vis-NIR spectra of complex **2** in acetonitrile.

Synthesis of complex $[Mn^{III}(L^1)]ClO_4^-$, 3:

To a stirred solution of complex **1** (50 mg, 0.14 mmol) in THF (10 mL), silver perchlorate hydrate (44 mg 0.21 mmol) was added. Then the solution mixtures were allowed to stir for 3 h in dark condition resulting in deep reddish-brown colored solution with white precipitate. The precipitate was filtered using G4-crucible through celite bed. Evaporation of the filtrate under reduced pressure to get the brown colored complex $[Mn^{III}(\mathbf{L^1})]ClO_4^-$ **, 3**. Yield: 56 mg, 92%. The complex **3** was used as a catalyst after drying the powder form at 100°C temperature under vacuum for 2 h. Single crystals of **3** suitable for X-ray diffraction studies were obtained by slow evaporation of ethanolic solution at room temperature. Elemental analysis calc. (%) for crystalline compound $C_{16}H_{16}ClMnN_2O_7$: C 43.80, H 3.68, N 6.39; found: C 43.51, H 3.47, N 6.78; IR (KBr, cm^{-1}; Figure S12): 3452, 1622, 1080, 628; UV-Vis (λ_{max}, nm; Figure S13): 305, 404, 494.



Scheme S1: Synthetic route for complex **3**.

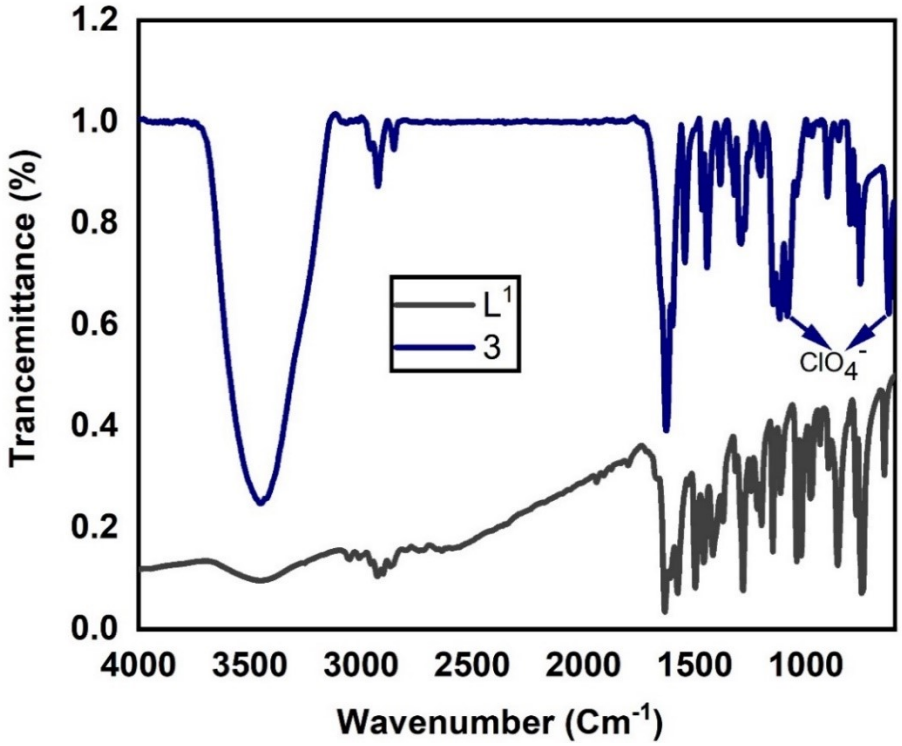


Figure S12: FT-IR spectra of ligand $\mathbf{L^1}$ and complex **3**.

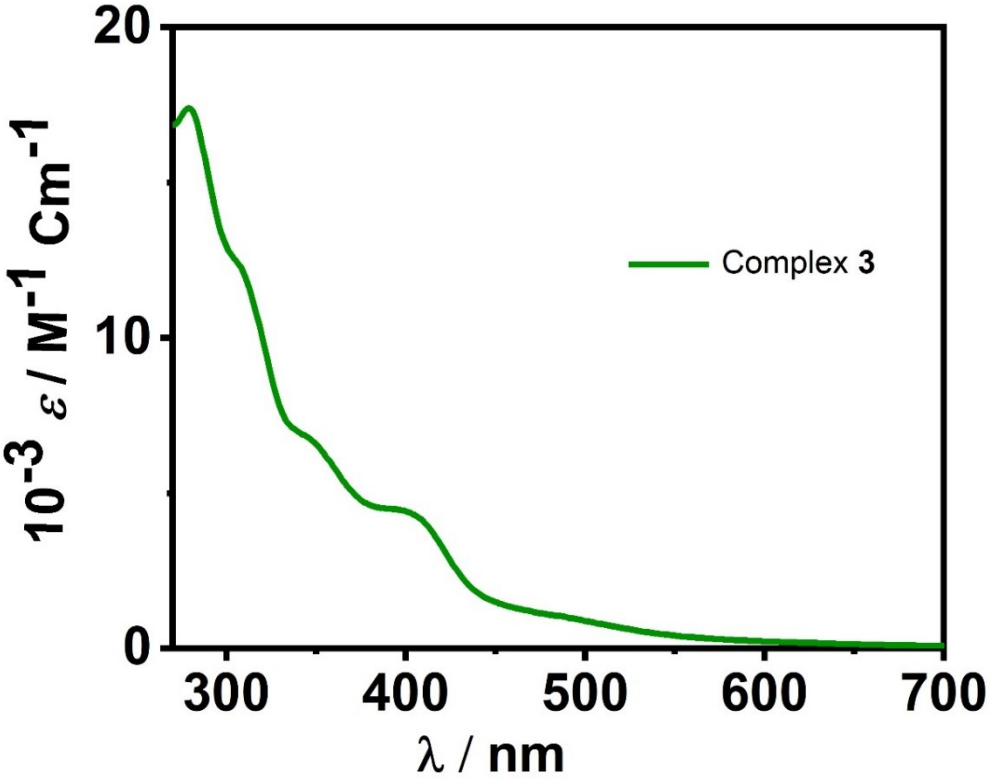
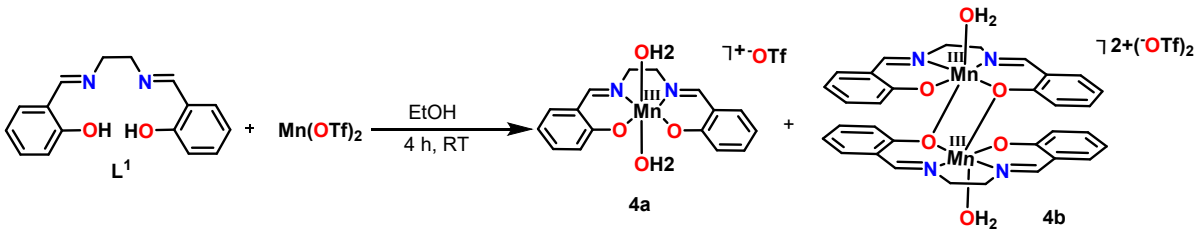


Figure S13: UV-Vis-NIR spectra of complex **3** in acetonitrile.

Synthesis of complex $[Mn^{III}(L^2)]^{-}OTf$, 4:

To a stirred 10 mL ethanolic solution of ligand $\mathbf{L^1}$ (0.18 mmol, 50 mg), a 5 mL ethanolic solution of $Mn(OTf)_2$ (0.18 mmol, 66 mg) was added dropwise. The yellow colored solution changed to deep brown immediately. The reaction mixture was stirred for 5 h at room temperature. After that the solvent was removed under reduced pressure and recrystallized from ethanol. Yield of complex **4**: 98 mg, 85%. The complex **4** was used as a catalyst after drying the powder form at 100°C temperature under vacuum for 2h. Single crystals of **4** suitable for X-ray diffraction studies were obtained by slow evaporation of ethanolic solution at room temperature. Elemental analysis calc. (%) for crystalline compound $C_{68}H_{72}Mn_4N_8O_{28}F_{12}S_4$: C 40.32, H 3.58, N 5.53; found: C 40.09, H 3.74, N 5.27; ESI-MS: (m/z): calc. for: $C_{16}H_{14}MnN_2O_2$ 321.0501 $[4a\text{-}2H_2O\text{-}OTf]^+$ (**4b** also dissociate to mononuclear cationic species); found: 321.0436 (Figure S14). IR (KBr, cm^{-1}; Figure S15): 3454, 1625; UV-Vis (λ_{max}, nm; Figure S16): 310, 350, 410, 496.



Scheme S2: Synthetic route for complex **4**(**4a** and **4b**).

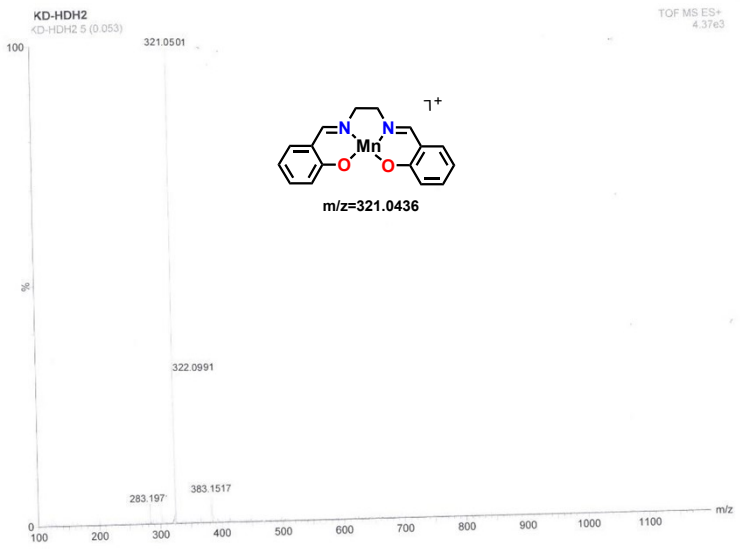


Figure S14: ESI-MS spectrum of complex **4** in acetonitrile.

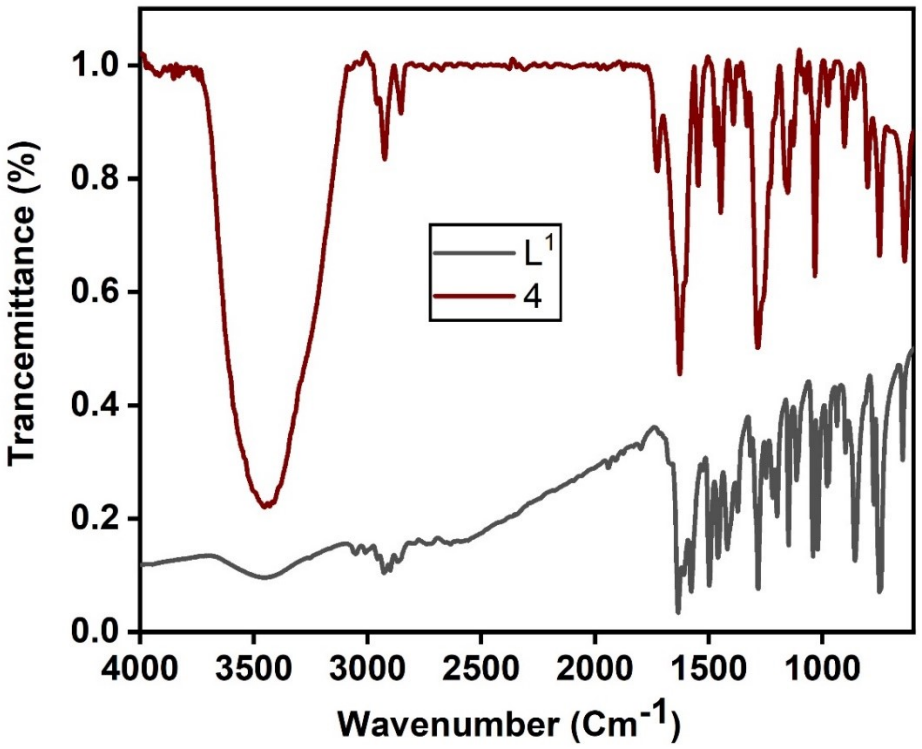


Figure S15: FT-IR spectra of ligand L^1 and complex **4**.

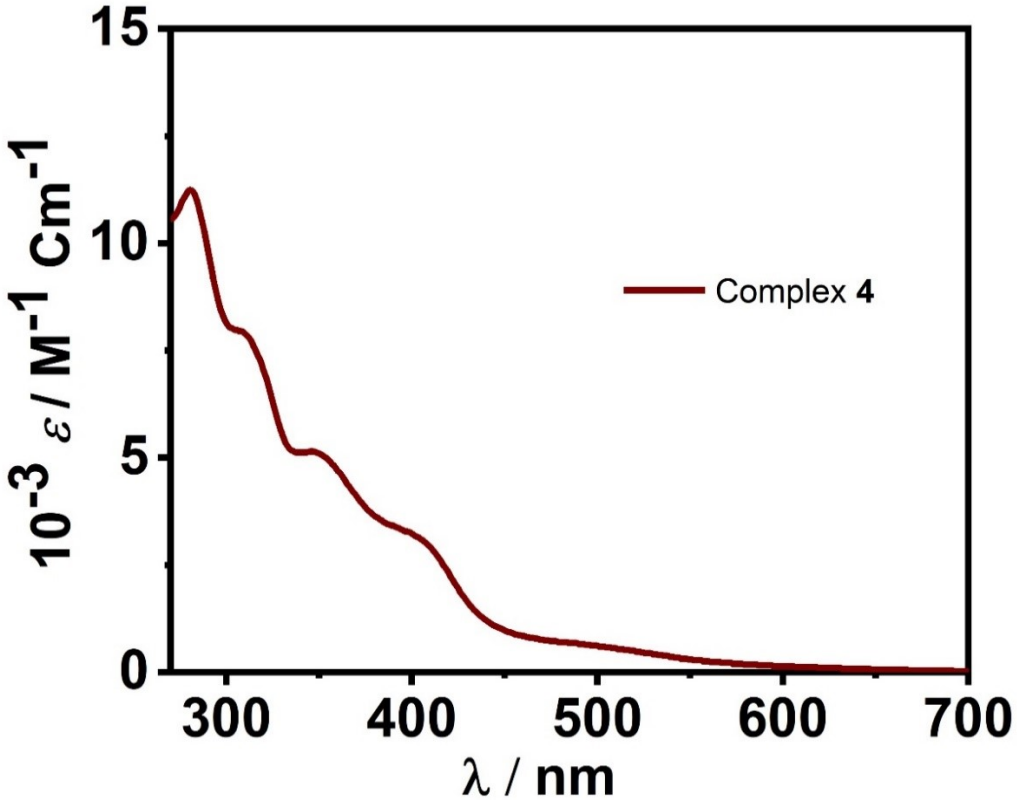


Figure S16: UV-Vis-NIR spectra of complex **4** in acetonitrile.

3. X-ray crystal structural details of complexes 3 and 4:

Table S1: X-ray structural data of complex **3** and **4**.

Parameters	**Complex** 3	**Complex** 4
Crystal Data	CCDC (2242834)	CCDC (2242835)
Empirical formula	$C_{16}H_{16}MnN_2O_3,ClO_4,H_2O$	$2(C_{16}H_{18}MnN_2O_4)$, $C_{32}H_{32}Mn_2N_4O_6$, $4(CF_3O_3S)$, $2(H_2O)$
Formula weight	456.71	2025.33
T (K)	298	100
Wavelength (Å)	0.71073	1.54184
Crystal system	Monoclinic	Monoclinic
Space group	P21/n	P21/n
Unit cell dimensions		
a (Å)	7.2081(14)	13.6561(1)
b (Å)	13.4249(19)	21.2356(2)
c (Å)	19.416(5)	14.0327(1)
α (°)	90	90
β (°)	94.88(2)	96.341(1)
γ (°)	90	90
V (Å3)	1872.0(7)	4044.52(6)
Z	4	2
ρ (gm cm^{-3})	1.620	1.663
Absorption coefficient (mm^{-1})	0.896	6.938
F(000)	936	2064
Theta range for data collection (Deg.)	2.6, 25.0	3.8, 79.6
Index ranges (h, k, l)	-8: 8 ; -15: 15 ; -23: 23	-17: 16 ; -26: 26 ; -12: 17
Reflections collected	20292	36119
Independent reflections	3284	8636
R(int)	0.134	0.043
Final R indices [I>0.0sigma(I)]	R1 = 0.0883, wR2 = 0.2708,	R1 = 0.0387 wR2 = 0.0987
Largest diff. peak and hole	-0.44, 1.93, e. $Å^{-3}$	-0.65, 0.60, e. $Å^{-3}$

Table S2: Selected X-ray crystallographic bond lengths (Å) and angles (°) of **3**.

Bond lengths			
Mn1-O1	1.8910	Cl00-O00R	1.381(12)
Mn1-O2	1.8749	Cl00-O1	1.327(14)
Mn1-O3	2.2048	O1-C1	1.3427
Mn1-N1	1.9677	O2-C16	1.3377
Mn1-N2	1.9698	O3-H3B	0.8800
		O3-H3A	0.8800
Mn1-O1_a	2.4953		
Cl1-O6	1.3807	O4-H4B	0.8500
		O4-H4A	0.8500
Cl1-O7	1.3271		
Cl1-O8	1.3890		
Cl1-O5	1.3796		
N1-C8	1.4808	N2-C10	1.2878
N1-C7	1.2907	N2-C9	1.5016
Bond angles			
O1-Mn1-O2	94.52	O3-Mn1-N2	94.26
O1-Mn1-O3	94.44	O1_a-Mn1-O3	172.88
O1-Mn-N1	90.35	N1-Mn1-N2	82.76
O1-Mn1-N2	168.78	O1_a-Mn1-N1	85.83
O1-Mn1-O1_a	80.90	O1_a-Mn1-N2	89.75
O2-Mn1-O3	93.05	Mn1-O2-C16	128.93
O2-Mn1-N1	174.63	Mn1-O1-Mn1_a	99.10
O2-Mn1-N2	92.08	Mn1_a-O1-C1	112.99
O1_a-Mn1-O2	92.68	Mn1-O1-C1	122.52
O3-Mn1-N1	88.84	Mn1-O3-H3B	111.00
Mn1-O3-H3A	111.00	Mn1-N2-C10	125.16
Mn1-N1-C7	125.09	Mn1-N2-C9	113.69
Mn1-N1-C8	112.53		

Table S3: Selected X-ray crystallographic bond lengths (Å) and angles (°) of **4a** and **4b**.

Bond lengths			
Mn2-O5	1.9066(14)	Mn1-N2	1.9865(17)
Mn2-O6	1.8838(15)	Mn1-O1	1.8921(14)
Mn2-O7	2.1652(14)	N3-C23	1.290(3)
Mn2-N3	1.9774(18)	N3-C24	1.478(3)
Mn2-N4	1.9849(17)	N4-C26	1.286(3)
Mn2-O5_a	2.3453(14)	N4-C25	1.472(3)
Mn1-O2	1.8857(14)	N1-C8	1.478(3)
Mn1-O3	2.2561(14)	N1-C7	1.286(3)
Mn1-O4	2.2017(14)	N2-C9	1.473(3)
Mn1-N1	1.9865(17)	N2-C10	1.285(3)
Bond angles			
O5-Mn2-O6	95.01(6)	O7-Mn2-N4	88.50(6)
O5-Mn2-O7	90.71(6)	O5_a-Mn2-O7	169.60(5)
O5-Mn2-N3	170.82(7)	N3-Mn2-N4	82.35(7)
O5-Mn2-N4	90.35(6)	O5_a-Mn2-N3	94.38(6)
O5-Mn2-O5_a	79.69(5)	O5_a-Mn2-N4	87.58(6)
O6-Mn2-O7	94.19(6)	O3-Mn1-N2	86.99(6)
O6-Mn2-N3	92.04(7)	O4-Mn1-N1	92.57(6)
O6-Mn2-N4	173.97(7)	O4-Mn1-N2	87.96(6)
O5_a-Mn2-O6	90.65(6)	N1-Mn1-N2	82.10(7)
O7-Mn2-N3	94.64(6)	O1-Mn1-O2	93.48(6)
O1-Mn1-O3	91.63(6)	O2-Mn1-N2	92.12(6)
O1-Mn1-O4	93.53(6)	O3-Mn1-O4	174.76(6)
O1-Mn1-N1	92.27(6)	O3-Mn1-N1	88.11(6)
O1-Mn1-N2	174.25(7)	Mn2-O5-Mn2_a	100.31(6)
O2-Mn1-O3	90.57(6)	Mn2-O5-C32	121.45(12)
O2-Mn1-O4	88.23(6)	Mn2_a-O5-C32	115.39(11)
O2-Mn1-N1	174.13(7)	Mn2-O6-C17	129.22(13)
Mn2-O7-H7A	125.00	Mn1-O2-C12	125.43(12)
Mn2-O7-H7B	123.00	Mn1-O3-H3B	120(3)
Mn1-O1-C1	127.03(12)	Mn1-O3-H3A	110.00
Mn1-O4-H4B	128.00	Mn1-O4-H4A	126.00
Mn2-N3-C23	126.02(15)	Mn2-N4-C26	124.47(14)
Mn2-N3-C24	113.60(13)	Mn2-N4-C25	112.74(13)
Mn1-N1-C8	113.50(12)	Mn1-N2-C9	113.15(12)
Mn1-N1-C7	124.89(14)	Mn1-N2-C10	124.83(14)

Table S4: Hydrogen bonding interactions (Å) and π····π interactions (Å) in the crystal networks of **3** and **4**.

Hydrogen bond parameters donor/acceptor scheme (Å and °) interactions in **3**

D–H….A	D–H	H…..A	D…..A	∠D–H…A
O3–H3a....O2	0.881	2.000	2.809	152.07
O3–H3b....O4	0.880	1.997	2.761	144.45

Hydrogen bond parameters donor/acceptor scheme (Å and °) interactions in **4**

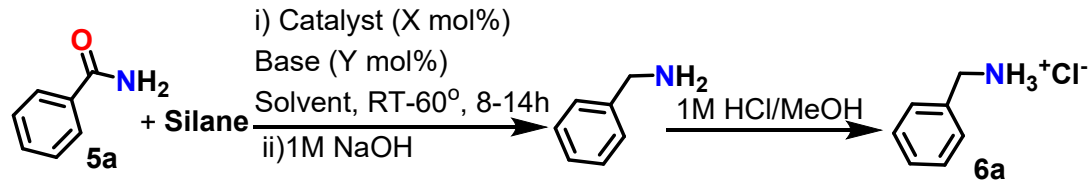
D–H….A	D–H	H…..A	D…..A	∠D–H…A
O3–H3B....O6	0.800	1.967	2.765	175.27
O3–H3A....O9	0.871	1.850	2.712	169.92
O4–H4A....O1	0.870	1.888	2.752	172.11
O4–H4B....O8	0.870	1.897	2.765	175.52
O7–H7A....O2	0.870	1.851	2.715	172.06
O7–H7B....O8	0.870	1.861	2.725	171.39
O8–H8B....O10	0.870	1.904	2.774	178.13
O8–H8C....O13	0.871	1.838	2.708	177.57

π····π interactions (Å) in **3** and **4**

Interactions	Distances (Å)
Cg(**3**-Ar.)....Cg(**3**-Ar.)	3.569
Cg(**4a**-Ar.)....Cg(**4b**-Ar.)	3.804
Cg(**4b**-Ar.)....Cg(**4b**-Ar.)	3.708

4. Reaction optimization table:

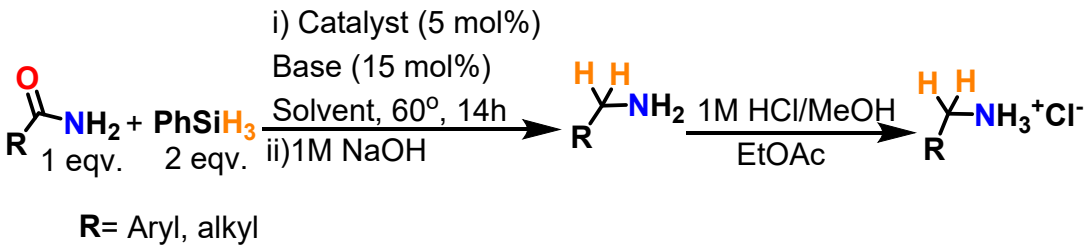
Table S5: Optimization of the reduction of benzamide (**5a**) into benzylamine salt (**6a**)[a]



Entry	Catalyst (mol%)	Solvent	Base	Silane (equiv.)	Yield of 6a[b] (%)
1	1 (5)	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	68%
2	2 (5)	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	73%
3	3 (5)	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	84%
4	4 (5)	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	87%
5	-	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
6	$MnCl_2$ (5)	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	<10
7	$Mn(OTf)_2$ (5)	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	<15
8	L^1	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
9	L^2	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
10	4 (2.5)	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	64%
11	4 (5)	THF	KO^{t}Bu (7.5)	$PhSiH_3$ (2)	68%
12	4 (5)	THF	NaOMe (15)	$PhSiH_3$ (2)	77%
13	4 (5)	THF	KOH (15)	$PhSiH_3$ (2)	-
14	4 (5)	THF	NaO^{t}Bu (15)	$PhSiH_3$ (2)	86%
15	4 (5)	THF	$CaCO_3$ (15)	$PhSiH_3$ (2)	-
16	4 (5)	THF	NaOAC (15)	$PhSiH_3$ (2)	-
17[c]	4 (5)	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	62%
18[d]	4 (5)	THF	KO^{t}Bu (15)	$PhSiH_3$ (2)	67%
19	4 (5)	THF	KO^{t}Bu (15)	Ph_2SiH_2 (3)	30%
20	4 (5)	THF	KO^{t}Bu (15)	Ph_3SiH (6)	-
21	4 (5)	THF	KO^{t}Bu (15)	Et_3SiH (6)	<20%
22	4 (5)	THF	KOtBu (15)	TMDS (3)	-
23	4 (5)	THF	KOtBu (15)	PMHS (6)	-
24	4 (5)	THF	KO^{t}Bu (15)	$(EtO)_3SiH$ (6)	-
25	4 (5)	DMSO	KO^{t}Bu (15)	$PhSiH_3$ (2)	72%
26	4 (5)	Dioxane	KO^{t}Bu (15)	$PhSiH_3$ (2)	68%
27	4 (5)	MeCN	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
28	4 (5)	DCM	KO^{t}Bu (15)	$PhSiH_3$ (2)	24%
29	4 (5)	Tolune	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
30	4 (5)	C_6H_6	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
31	4 (5)	Et_2O	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
32	4 (5)	MeOH	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
33	1(5)	Hexane	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
34	4 (5)	$CHCl_3$	KO^{t}Bu (15)	$PhSiH_3$ (2)	-
35	4 (5)	DMF	KO^{t}Bu (15)	$PhSiH_3$ (2)	-

[a] $PhCONH_2$ (0.5 mmol), silane (2–6 equivalent), catalyst (2.5–5 mol%), base (5–15 mol%), solvent (3 mL) for 14 h at 60 °C followed by alkaline hydrolysis using 1M NaOH. [b] Isolated yield of amine-hydrochloride salts. [c] Reaction carried out at RT. [d] Reaction time 7 h.

5. General procedure for reduction of primary amides to amines



Scheme S3: General procedure for amide to amine transformation.

In a 15 ml schlenk tube catalyst **1-4** (5 mol%) and KO^{t}Bu (15 mol%, 9 mg) were taken and 3 mL of dry THF was added to this under nitrogen atmosphere and stirred for 5 minutes. After that $PhSiH_3$ (1 mmol, 125μl) and primary amide (0.5 mmol, 65 mg) were added to the reaction mixture subsequently. The closed reaction vessel was allowed to stir for 14 h at 60 °C. After completion of the reaction, the solution was cooled to room tempatature and 2 mL of 1 M NaOH solution was added slowly to the reaction mixture and stirred for another 3 h. The amine was extracted in 30 mL (3 x 10 mL) of diethyl-ether (Et_2O) and dried over anhydrous sodium sulphate. The evaporetion of the solvent under reduced pressure resulting the crude amine. Afterwards, the crude amine was further treated with 1 mL of 1 M methanolic HCl and the corresponding amine salt was precipitated out on adding 20 mL of ethyl-acetate. The precipitate was isolated by filtration and then washed with 5 mL (2 x 2.5 mL) of ethyl-acetate leads to the pure amine salt. The isolated amine salts were dried in vacuum and characterized by NMR spectroscopy.

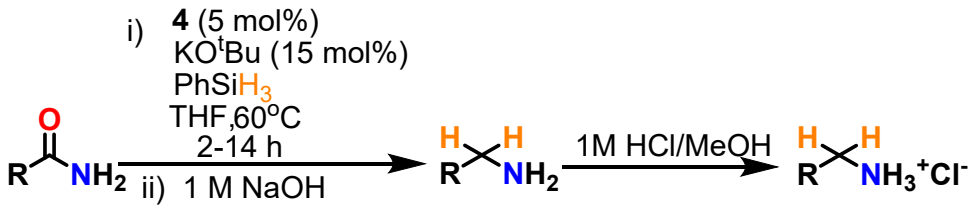
The amines were isolated as amine salt because the amine salts are stable, less volatile and easy to separate from the reaction mixture without performing column chromatography.

6. Kinetics of catalytic reduction of amide to amine

A series of reactions was performed in a 15 mL oven dried schlenk tube containing a magnetic spin bar, catalyst **4** (5 mol%, 12 mg) and KO^{t}Bu (15 mol%, 9 mg) were dissolved in 3 mL dry THF after purging the schlenk tube with nitrogen. The reaction mixture was stirred for 5 minutes. Then primary amide (0.5 mmol, 65 mg) and $PhSiH_3$ (1.2 mmol, 150μl) were added respectively to the reaction mixture and were allowed to stir at 60 °C. The reaction mixture was quenched by adding 2 mL of 1 (M) NaOH solution in different time intervals (2, 4, 6, 8, 10, 12 and 14 h) and then stirred for additional 3 h. The amine was extracted in 30 mL (3x10 mL) of diethyl-ether (Et_2O) and dried over anhydrous sodium sulphate (Na_2SO_4). After

filtration, the crude amine was obtained by removal of the solvent under reduced pressure. Further treating the crude amine with 1 mL of 1 (M) methanolic HCl followed by the addition of 20 mL of ethyl-acetate, the amine salt gets precipitated. The precipitate was washed with 5 mL (2 x 2.5 mL) of ethyl-acetate to get pure amine salt, which was dried in vacuum. In different time intervals the yields of pure amine salt are listed in Table S6. In the kinetics plot (time *vs* yield) shows that the completion of the reaction within 14 h (Figure S20).

Table S6. Yield of benzyl-amine hydrochloride salt (**6a**) at different time intervals.[a]



Entry	Reaction time	Yield (%)[b]
1	2 h	22
2	4 h	38
3	6 h	57
4	8 h	72
5	10 h	81
6	12 h	86
7	14 h	87
8	16 h	87

[a] $PhCONH_2$ (0.5 mmol), $PhSiH_3$ (1.2 mmol). [b] Isolated yield of amine as amine salt

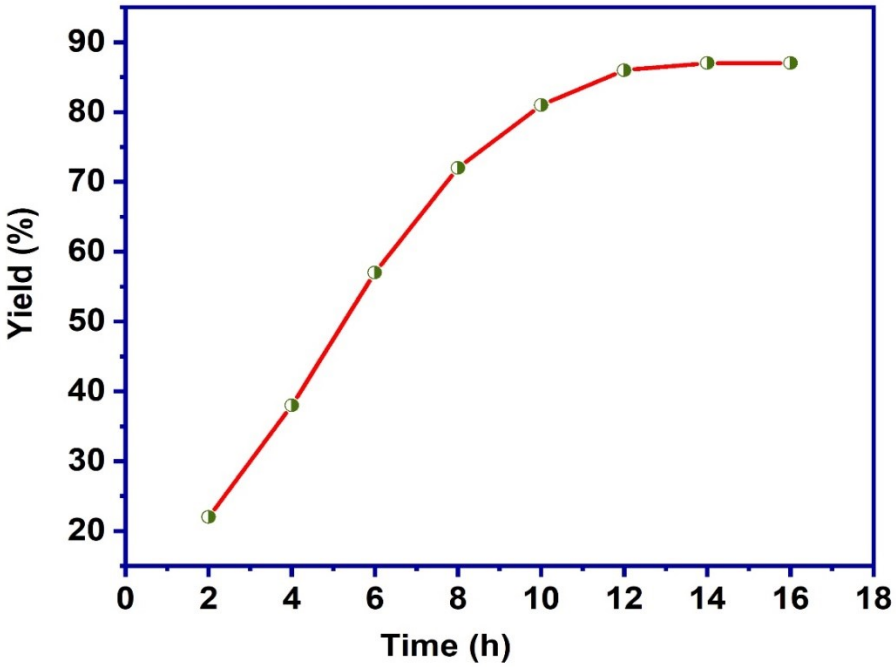
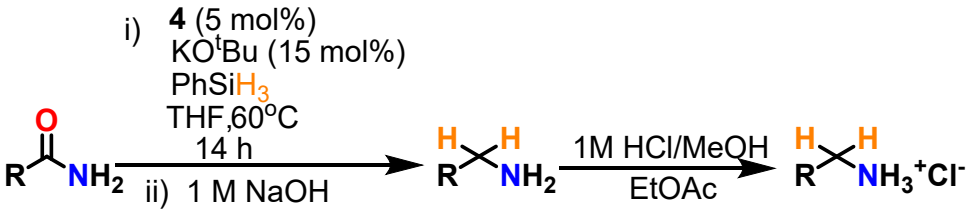


Figure S17: Graphical representation of yield of benzylamine *vs* reaction time.

7. Procedure for gram-scale synthesis of benzylamine salt

In a 250 ml schlenk flask, catalyst **4** (5 mol%, 195 mg) and KO^{t}Bu (15 mol%, 138 mg) were taken and 60 mL of dry THF was added to this under nitrogen atmosphere, then the mixture was stirred for 5 minutes. After stirring, $PhSiH_3$ (9.91 mmol, 2.065 mL) and benzamide (1 g, 8.26 mmol) were added to the reaction mixture and allowed to stir for 16 h at 60 °C. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and to this 34 mL of NaOH (1 M) solution was added slowly and stirred for additional 3 h. The crude amine was extracted in 600 mL (3 x 200 mL) diethyl-ether (Et_2O) by using a separating funnel and dried over anhydrous sodium sulphate. After evaporation of solvent under reduced pressure, the crude amine was obtained which was further treated with 20 mL of 1 M methanolic HCl followed by addition of ethyl-acetate to get the precipitation of amine salt. After filtration, the amine salt was washed with 15 mL (3 x 5 mL) of ethyl-acetate and dried under vacuum leads to pure amine salt (857 mg, 85% yields).



Scheme S4: Gram-scale synthesis for amide to amine.

8. Stability of catalyst 4 under reducing conditions

The Uv-Vis spectroscopic studies were carried out to understand the stability of the paramagnetic complex **4** under reducing conditions. For this, in a 15 ml schlenk tube catalyst **4** (5 mol%) and KO^{t}Bu (15 mol%, 9 mg) were taken and then 3 mL of dry THF was added to this under nitrogen atmosphere and stirred for 5 minutes. After that $PhSiH_3$ (1 mmol, 125µl) and primary amide (0.5 mmol, 65 mg) were added to the reaction mixture subsequently. The closed reaction vessel was allowed to stir for 14 h at 60 °C. After completion of the reaction, the UV-Vis spectrum of the reaction mixture was recorded and compared with Uv-Vis spectrum of native complex (Figure S18). The analysis of Uv-Vis spectra shows that the characteristic absorption peaks are remain unchanged which confirms the stability of catalyst under reducing condition.

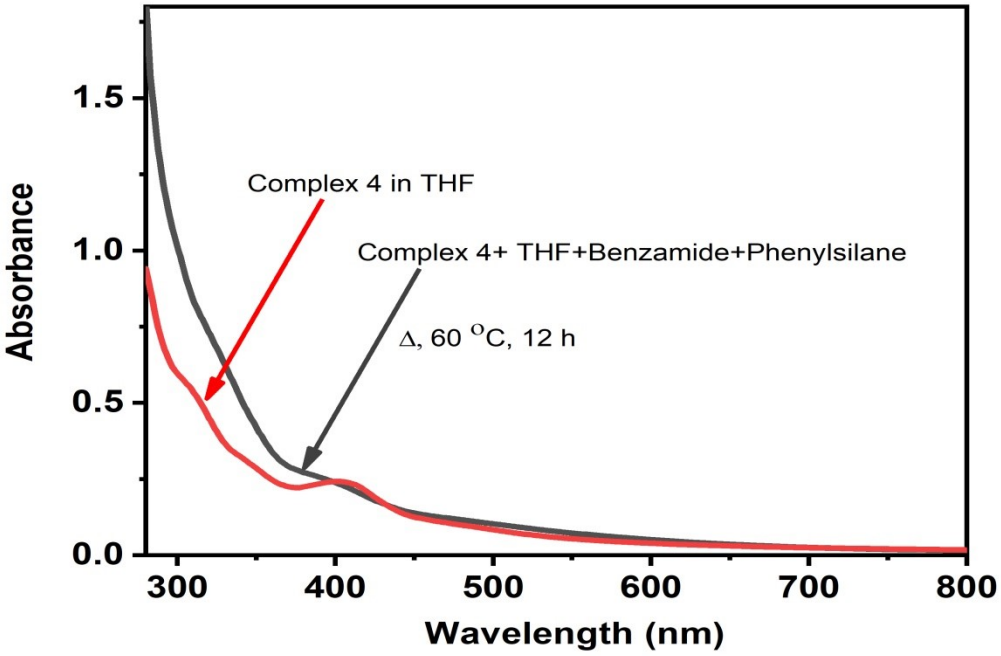
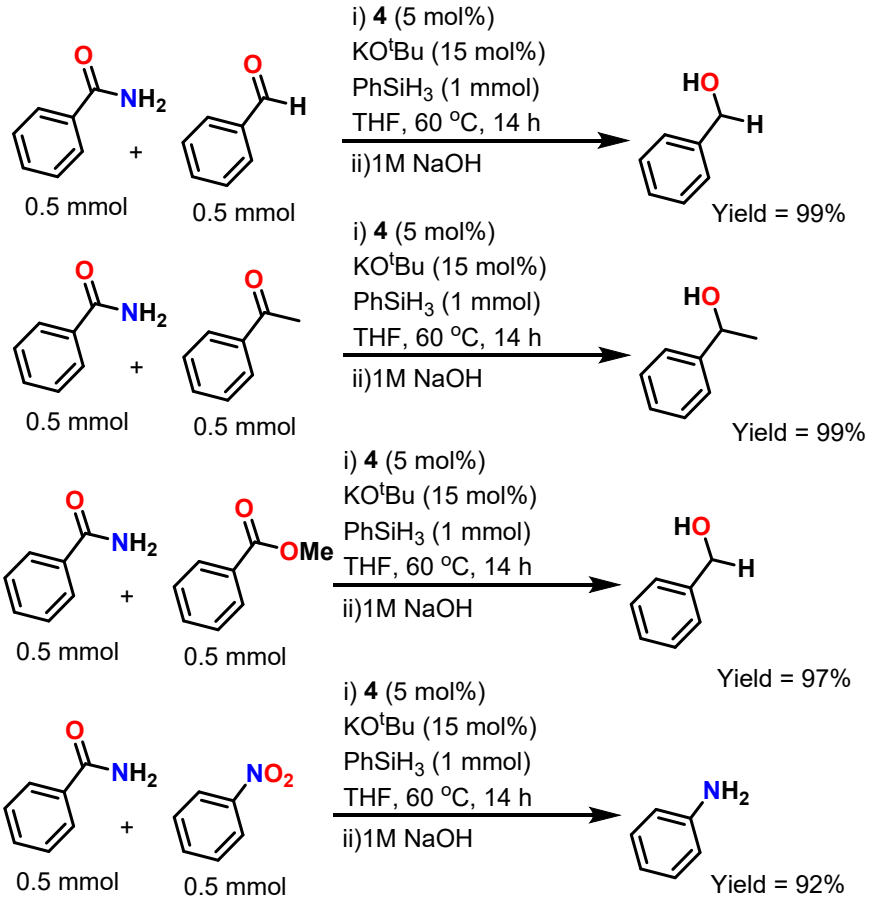


Figure S18: Uv-Vis spectra of complex **4** before and after the amide reduction.

9. Amide reduction in presence of other reactive functional groups

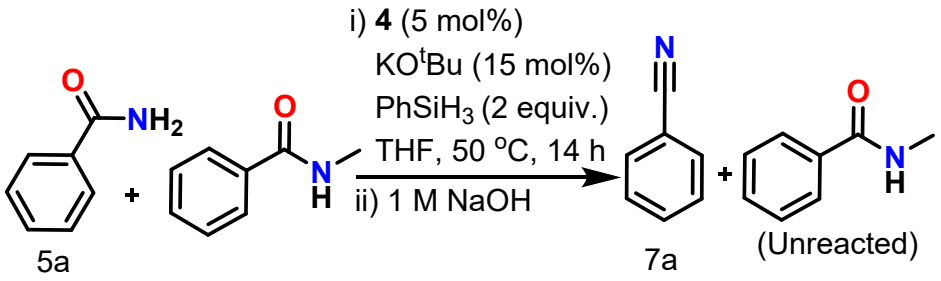


Scheme S5: Intolerance of reactive functional groups in amide reduction. Yields are based on internal standard p-nitrotoluene**.**

10. Mechanistic studies

10a. General procedure for transformation of amide to nitrile

In a 15 mL schlenk tube, catalyst **4** (5 mol%, 12 mg) and KO^{t}Bu (15 mol%, 9 mg) were taken with 3 mL dry THF under nitrogen atmosphere. The reaction mixture was stirred for 5 minutes. Then $PhSiH_3$ (1.2 mmol, 150µl), primary amide (0.5 mmol, 65 mg) and N-methyl benzamide (20 mol%, 14 mg) were added to the reaction mixture and allowed to stir for overnight at 60^{0}C under nitrogen atmosphere. After completion of the reaction, the solution was cooled to room temperature and 2 mL of 1 molar NaOH solution was slowly added to the reaction mixture and again stirred for another 3 h. The crude product was extracted in 30 mL (3 x 10 mL) of diethyl-ether (Et_2O) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (60-120 mesh) by eluting with 0-2.5% ethyl acetate in hexane to isolate the nitrile products.



Scheme S6. Transformation of amide to nitrile by using catalyst **4** and secondary amide blocking agent.

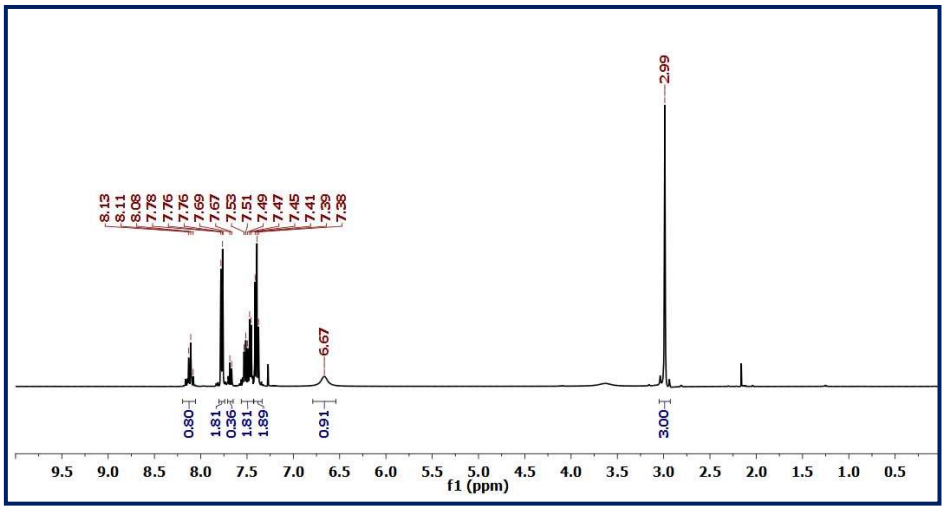


Figure S19: ^{1}H NMR spectrum ($CDCl_3$) of crude reaction mixture described in scheme S6.

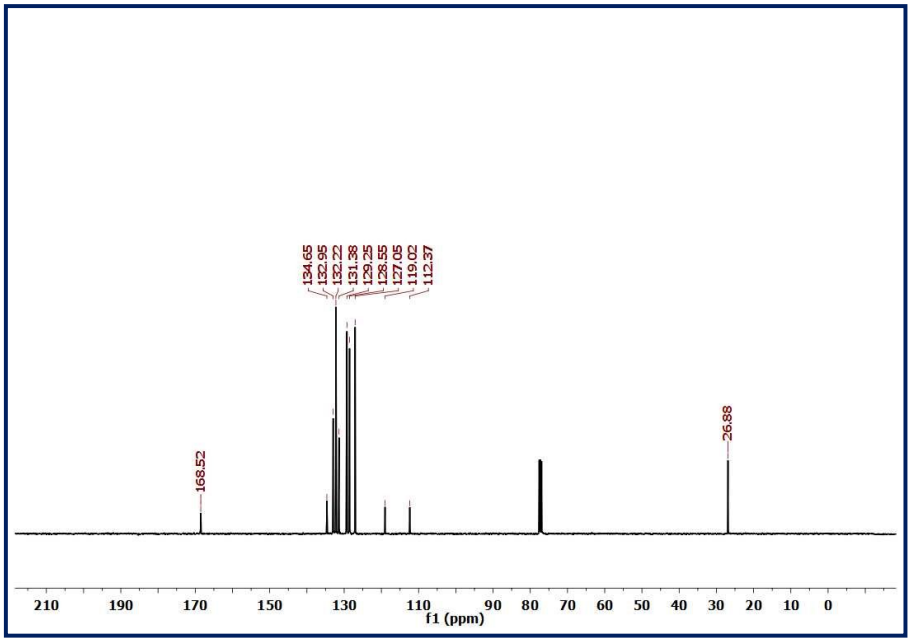
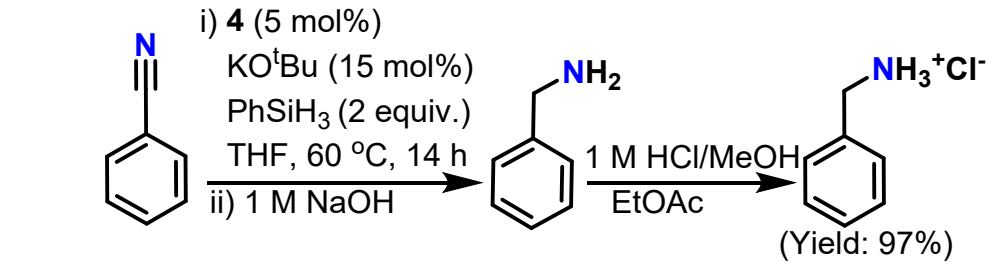


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of crude reaction mixture described in scheme S6.

10b. Procedure for benzonitrile to benzylamine using $PhSiH_3$

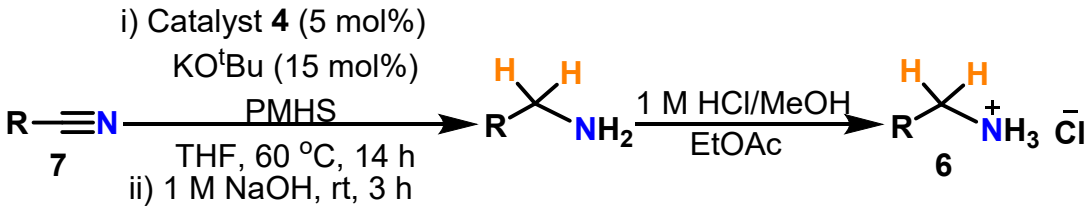
In a 15 mL schlenk tube containing a magnetic stirring bar, catalyst **4** (5 mol%, 12 mg) and KO^{t}Bu (15 mol%, 9 mg) were dissolved in 3 mL dry THF under inert atmosphere. After stirring for 5 minutes, $PhSiH_3$ (1.2 mmol, 150µl) and benzonitrile (0.5 mmol 55 mg) were added to the reaction mixture. The glass tube was sealed and the reaction mixture was allowed to stir for 14 h at 60^{0}C under inert condition. After completion of the reaction, 2 mL of 1 molar NaOH solution was added slowly to the reaction mixture and the reaction mixture was stirred for another 3 hours. The amine was extracted in 30 mL (3 x 10 mL) of diethyl-ether (Et_2O) and it was dried over anhydrous sodium sulphate. After the removal of the solvent under reduced pressure leads to the crude amine which was further treated with 1 ml methanolic HCl (1M) followed by addition of ethyl-acetate to get the precipitation of amine salt. After filtration, the amine salt was washed with 5 mL (2 x 2.5 mL) of ethyl-acetate and dried in vacuum leads to pure amine salt (69 mg, 96% yields).



Scheme S7: Benzonitrile to benzyl amine using $PhSiH_3$.

10c. General procedure for nitriles to amines using PMHS

In a 15 mL schlenk tube containing a magnetic stirring bar, catalyst **4** (5 mol%, 12 mg) and KO^{t}Bu (15 mol%, 9 mg) were dissolved in 3 mL dry THF under inert atmosphere. After stirring for 5 minutes, PMHS (2 mmol, 250 µl) and nitrile compound (0.5 mmol) were added to the reaction mixture. Then the reaction mixture was allowed to stir for 14 h at 60 ^{0}C under nitrogen atmosphere. After completion of the reaction, 2 mL of 1 molar NaOH solution was added dropwise to the reaction mixture and stirred for another 3 hours. The crude amine was extracted in 30 mL (3 x 10 mL) of diethyl-ether (Et_2O) and the combined organic layers were dried over anhydrous sodium sulphate. After the removal of the solvent under reduced pressure leads to the crude amine which was further treated with 1 ml methanolic HCl (1M) followed by addition of ethyl-acetate leads to the precipitation of amine salt. After filtration, the amine salt was washed with 5 mL (2 x 2.5 mL) of ethyl-acetate and dried in vacuum leads to pure amine salt.

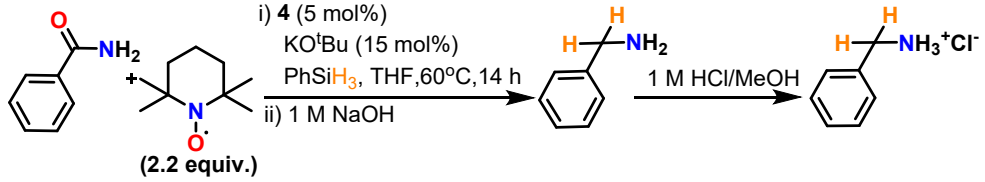


Scheme S8: Nitriles to amine using PMHS.

10d. Reduction of amide in presence of excess TEMPO

In a 15 mL schlenk tube, catalyst **4** (5 mol%, 12mg) and KO^{t}Bu (15 mol%, 9 mg), $PhSiH_3$ (1.2 mmol, 150 μL), benzamide (0.5 mmol, 65 mg) and TEMPO (1.25 mmol, 195 mg) were dissolved in 3 mL dry THF under nitrogen atmosphere and stirred for 14 h at 60 ^{0}C temperature. After completion of the reaction, 2 mL of 1 M NaOH solution was added slowly to the reaction mixture and then allowed to stir for additional 3 h. Next, the crude product was extracted from

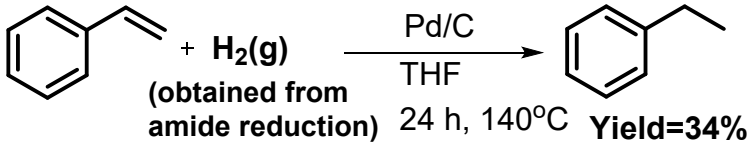
reaction mixture with 30 mL (3 x 10 mL) of Et_2O and removal of solvent under reduced pressure leads to the crude amine. The amine product was isolated as amine salt by adding 1 M methanolic HCl followed by ethyl-acetate. After filtration, the amine salt was washed with 5 mL (2x2.5 mL) ethyl-acetate and dried in vacuum leads to pure amine salt (61 mg, 85% yields).



Scheme S9: Reaction of benzamide to benzyl amine in presence of 2.5 equivalent TEMPO.

10e. Hydrogenation of styrene by evolved hydrogen during amide to amine transformation reaction

In a 15 mL schlenk tube, styrene (1 mmol), Pd/C (0.5 g) and dry THF (3 ml) were added under nitrogen atmosphere. Then this schlenk tube was connected with another schlenk tube containing catalyst **4** (10 mol%, 24 mg) and KO^{t}Bu (15 mol%, 18 mg), $PhSiH_3$ (2.4 mmol, 300 μL) and benzamide (1 mmol, 130 mg) in 5 mL dry THF under nitrogen atmosphere. Next, the system was closed properly with metal clip and heated both the tubes at 60 °C for 24 h. The evolved hydrogen from amide reduction schlenk moves to the styrene reduction. The reduction of styrene to ethyl-benzene was detected by tacking ^{1}H NMR of the reaction mixture passing after a small silica column.



Scheme S10: pd/c catalysed styrene to ethyl benzene.

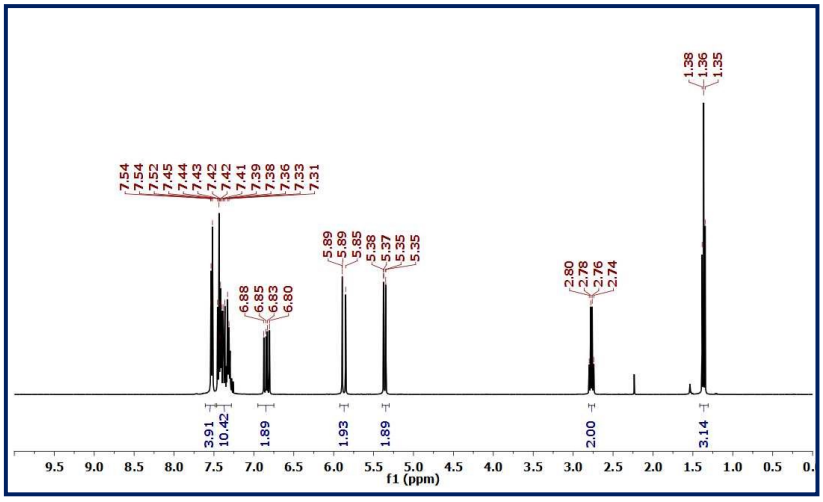
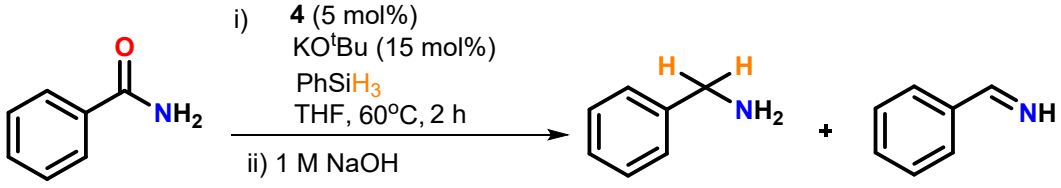


Figure S21. ^{1}H NMR spectrum ($CDCl_3$) of crude reaction mixture described in Scheme S10.

10f. Detection of imine intermediate during amide to amine transformation reaction

To trap the reaction key intermediates, we stopped our catalytic reaction prematurely. **4** (5 mol%, 12 mg) and KO^{t}Bu (15 mol%, 9 mg) were taken in a 15 mL schlenk tube dissolved in 3 mL dry THF under nitrogen atmosphere. The reaction mixture was stirred for 5 minutes, $PhSiH_3$ (1.2 mmol, 150 μL) and benzamide (0.5 mmol, 65 mg) were added to the reaction mixture successively and the reaction mixture was allowed to stir at 60 ^{o}C under inert atmosphere. We stopped the reaction after 2 h by adding 2 mL NaOH solution (1 M) followed by stirring for 2 hours. The reaction mixture was extracted in 30 mL (3 x 10 mL) diethyl-ether and dried over anhydrous sodium sulphate. Then the crude product was obtained by evaporation of solvent under reduced pressure. ^{1}H NMR of crude product was measured. The analysis of ^{1}H NMR spectra of crude product suggests the formation of an imine intermediate in our catalytic reaction. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, PhC*H*=NH) (see Figure S20).[4]



Scheme S11: Stopping the reduction prematurely after 2 h during conversion of benzamide to benzylamine.

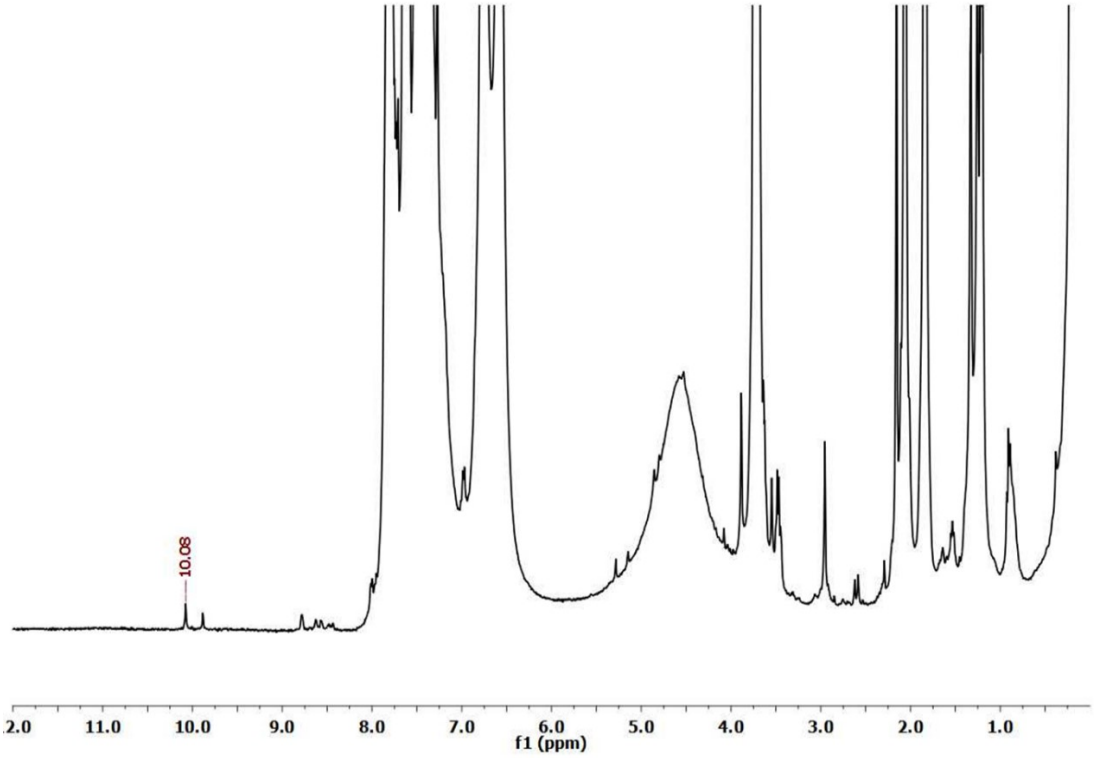
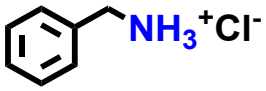


Figure S22. ^{1}H NMR spectrum ($CDCl_3$) of crude reaction mixture obtained after 2 h reaction.

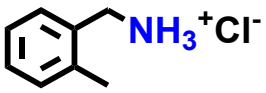
11. Characterization data of amines and nitriles

11a. Characterization data of amine salts



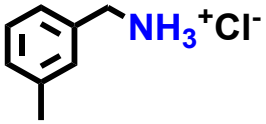
Phenylmethanamine hydrochloride, 6a[5,6,7]

Colourless solid, Yield: 87%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.30 (s, 3H), 7.41 (d, J = 7.2 Hz, 2H), 7.33 (dd, J = 16.6, 8.7 Hz, 3H), 3.94 (d, J = 4.9 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 133.98, 128.82, 128.52, 128.37, 42.13.



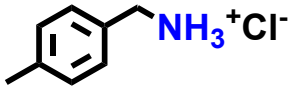
o-tolylmethanamine Hydrochloride, 6b[7]

Colourless solid, Yield: 91%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.35 (s, 3H), 7.32 (d, J = 7.0 Hz, 1H), 7.21-7.11 (m, *3*H), 3.94- 3.87 (m, 2H), 2.26 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 136.64, 132.31, 130.29, 129.15, 128.46, 126.03, 39.45, 18.79.



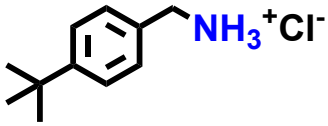
m-tolylmethanamine Hydrochloride, 6c[5]

Colourless solid, Yield: 89%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.44 (s, 3H), 7.29-7.25 (m, 3H), 7.18- 7.14 (m, 1H), 3.93 (d, J = 5.6 Hz, 2H), 2.29 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 137.97, 134.22, 129.79, 129.22, 128.75, 126.26, 42.38, 21.22.



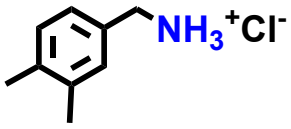
p-tolylmethanamine Hydrochloride, 6d[7]

Colourless solid, Yield: 92%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.54 (s, 3H), 7.50 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 4.08 (q, J = 5.5 Hz, 2H), 2.44 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 137.66, 130.94, 128.97, 128.80, 41.81, 20.63.



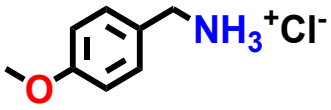
4-(1,1-dimethylethyl)Benzenemethanamine Hydrochloride, 6e[8]

Colourless solid, Yield: 96%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.59 (s, 3H), 7.53 (s, 4H), 4.06 (q, J = 5.7 Hz, 2H), 1.38 (s, 9H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 151.70, 131.98, 129.60, 126.09, 42.57, 35.13, 31.87.



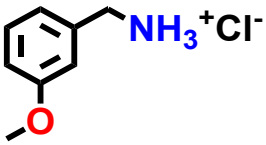
(3,4-dimethylphenyl)methanamine Hydrochloride, 6f[9]

Colourless solid, Yield: 95%. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ 8.50 (s, 3H), 7.27 (s, 1H), 7.22(dd, J = 7.7, 1.3 Hz, 1H), 7.16 (d, J = 7.7 Hz, 1H) 3.91 (d, J = 5.8 Hz, 2H), 2.33 (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d$_6$): δ 136.70, 136.59, 131.75, 42.20, 19.72, 19.44.



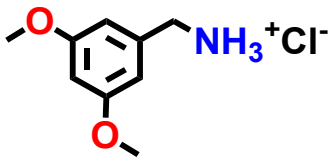
(4-methoxyphenyl)methanamine Hydrochloride, 6g[5]

Colourless solid, Yield: 92%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.73 (s, 3H), 7.67 (dd, *J* = 8.9, 2.2 Hz 2H), 7.22-7.14 (m, 2H), 4.15 (d, *J* = 5.8 Hz, 2H), 3.99 (d, *J* = 3.7 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 159.22, 130.54, 125.90, 113.79, 55.13, 41.55.



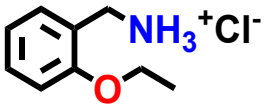
(3-methoxyphenyl)methanamine Hydrochloride, 6h[5]

Colourless solid, Yield: 88%. **^{1}H NMR** (400 MHz, DMSO-d_6): *δ* 8.40 (s, 3H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 1.2 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.4, 1H), 6.82 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.86 (d, *J* = 5.5, 2H), 3.65 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): *δ* 159.35, 135.59, 129.72, 120.96, 114.50, 113.95, 55.22, 42.10.



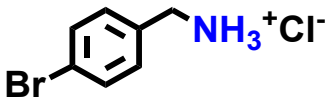
(3,5-dimethoxyphenyl)methanamine Hydrochloride, 6i[10]

Colourless solid, Yield: 95%. **^{1}H NMR** (400 MHz, DMSO-d_6): *δ* 8.58 (s, 3H), 6.90 (d, *J* = 1.8 Hz, 2H), 6.69 (d, *J* = 1.9 Hz, 1H), 4.14 (q, *J* = 5.6 Hz, 2H), 3.93 (d, *J* = 20.0 Hz, 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): *δ* 160.54, 136.19, 106.81, 99.96, 55.32, 42.19, 8.42.



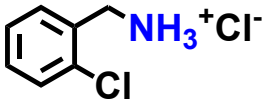
(2-ethoxyphenyl)methanamine Hydrochloride, 6j[10]

Colourless solid, Yield: 93%. **^{1}H NMR** (400 MHz, DMSO-d_6): *δ* 8.17 (s, 3H), 7.28 – 7.20 (m, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.84 (t, *J* = 7.3 Hz, 1H), 3.96 (q, *J* = 7.0 Hz, 2H), 3.82 (s, 2H), 1.25 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): *δ* 156.31, 130.05, 121.68, 120.06, 111.59, 63.42, 37.29, 14.44.



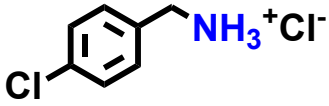
(4-bromophenyl)methanamine Hydrochloride, 6k[5]

Colourless solid, Yield: 82%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.56 (s, 3H), 7.72 (d, (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 4.09 (s, 2H), 4.08 (q, J = 7.0 Hz, 2H), 3.95 (s, 2H), 1.37 (t, J = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 133.58, 131.47, 131.28, 121.74, 41.48.



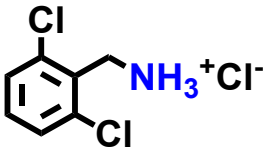
(2-chlorophenyl)methanamine Hydrochloride, 6l[5,7]

Colourless solid, Yield: 77%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.15 (s, 3H), 7.43-7.38 (m, 1H), 7.31 (dd, J = 6.0, 3.0 Hz, 1H), 7.23-7.17 (m, 2H), 3.87 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 132.83, 132.28, 130.55, 129.44, 127.50,39.52.



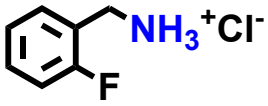
(4-chlorophenyl)methanamine Hydrochloride, 6m[7]

Colourless solid, Yield: 79%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.41 (s, 3H), 7.49 – 7.42 (m, 2H), 7.40 (d, J = 8.5 Hz, 2H), 3.92 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 133.12, 130.97, 128.93, 128.50, 41.39.



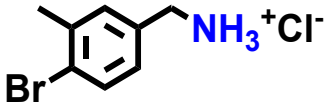
(2,6-dichlorophenyl)methanamine Hydrochloride, 6n[9]

Colourless solid, Yield: 71%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.53 (s, 3H), 7.46 (d, J = 7.8 Hz, 2H), 7.40-7.34 (m, 1H), 4.12 (d, J = 4.2 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 136.44, 132.50, 130. 41, 129.40, 38.09.



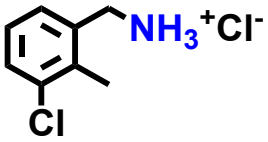
(2-Fluorophenyl)methanamine Hydrochloride, 6o[11]

Colourless solid, Yield: 63%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.48 (s, 3H), 7.51 (t, J = 7.7 Hz, 1H), 7.32 (dd, J = 10.3, 4.2 Hz, 1H), 7.23-7.06 (m, 2H), 3.93 (d, J = 5.6 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 161.49, 159.04, 131.35, 130.95, 130.87, 124.65, 121.15, 115.59, 115.38, 35.54.



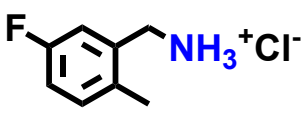
(4-bromo-3-methylphenyl)methanamine Hydrochloride, 6p[9]

Colourless solid, Yield: 86%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.72 (s, 3H), 7.79 (d, J = 8.3 Hz, 1H), 7.67 (s, 1H), 7.45 (d, J = 7.6 Hz, 1H), 4.12 (d, J = 5.5 Hz, 2H), 2.51 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 137.38, 137.00, 133. 73, 133.48, 131.89, 128.19, 125.71, 123.75, 41.78, 41.12, 22.13, 20.60.



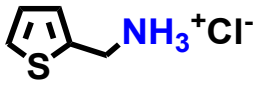
(3-chloro-2-methylphenyl)methanamine Hydrochloride, 6q[9]

Colourless solid, Yield: 85%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.50 (s, 3H), 7.33 (dd, J = 11.4, 7.9 Hz 2H), 7.16 (t, J = 7.8 Hz, 1H), 3.96 (d, J = 5.7 Hz, 2H), 2.28 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 135.58, 135.49, 134.86, 130.16, 129.34, 128.14, 40.98, 16.65.



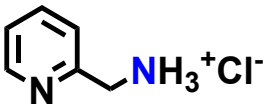
(5-fluoro-2-methylphenyl)methanamine Hydrochloride, 6r[9]

Colourless solid, Yield: 68%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.91 (s, 3H), 7.59 (dd, J = 10.1, 2.7 Hz, 1H),7.51 (dd, J = 8.3, 6.2 Hz, 1H), 7.34 (td, J = 8.6, 2.7 Hz, 1H), 4.24 (d, J = 5.3 Hz, 2H), 2.55 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 162.46, 160.06, 135.31, 135.23, 133.57, 133.54,132.90, 132.83, 116.71, 116.48, 115.94, 115.73, 40.01, 18.97.



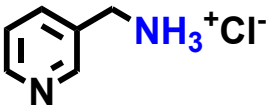
Thiophen-2-ylmethanamine Hydrochloride, 6s[5,9]

Colourless solid, Yield: 62%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.32 (s, 3H), 7.46 (d, J = 4.9 Hz, 1H), 7.14 (d, J = 2.6 Hz, 1H), 7.02-6.85 (m, 1H), 4.10 (d, J = 4.5 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 135.33, 129.11, 127.29. 127.24, 36.65.



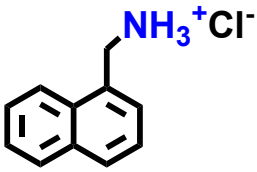
Pyridin-2-ylmethanamine Hydrochloride, 6t[12]

Colourless solid, Yield: 68%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.67 (d, J = 4.7 Hz, 1H), 8.03-7.89 (m, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.51-7.37 (m, 1H), 7.00 (s, 3H), 4.20 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 154.68, 148.89, 137.06. 123.11, 122.48, 43.38.



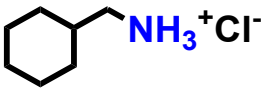
Pyridin-3-ylmethanamine Hydrochloride, 6u[9]

Colourless solid, Yield: 64%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.88 (s, 1H), 8.77 (s, 3H), 8.69 (s, 1H), 8.54 (s, 1H), 7.87 (s, 1H), 4.05 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 145.81, 142.67, 141.79, 133.32, 126.34, 38.71.



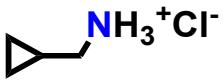
Naphthalen-1-ylmethanamine Hydrochloride, 6v[6,9]

Colourless solid, Yield: 76%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.75 (s, 3H), 8.25 (d, J = 8.1 Hz, 1H), 8.09 (dd, J = 10.6, 8.7 Hz, 2H), 7.77-7.63 (m, 4H), 4.61 (d, J = 5.7 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 133.22, 130.66, 129.95, 129.04, 128.64, 127.30, 126.75, 126.23, 125.36, 123.48, 39.10.



Cyclohexylmethanamine Hydrochloride, 6w[5,9]

Colourless solid, Yield: 83%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.09 (s, 3H), 2.73 (s, 2H), 1.88-1.61 (m, 6H), 1.36-1.18 (m, 3H), 1.10-0.96 (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 44.41, 35.45, 29.75, 25.66, 25.06.

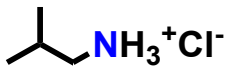


Cyclopropylmethanamine Hydrochloride, 6x[9,13]

Colourless solid, Yield: 67%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.09 (s, 3H), 2.59-2.43 (m, 2H), 0.99-0.80 (m, 1H), 0.37 (dd, J = 8.0, 1.9 Hz, 2H), 0.18 (dd, J = 4.7, 1.3 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 43.23, 8.34, 3.66.

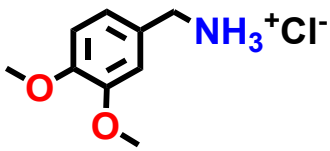
Butan-1-amine Hydrochloride, 6y[9]

Colourless solid, Yield: 68%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.97 (s, 3H), 2.53 (s, 2H), 1.34 (d, J = 6.7 Hz, 2H), 1.12 (d, J = 1.4 Hz, 2H), 0.67 (t, J = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 38.77, 29.31, 19.55, 13.87.



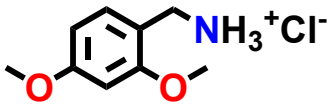
2-Methylpropan-1-amine Hydrochloride, 6z[9]

Colourless solid, Yield: 71%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.20 (s, 3H), 2.72-2.66 (m, 2H), 2.02-1.93 (m, 1H), 1.01 (d, J= 6.8 Hz, 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 46.28, 31.36, 26.98, 20.44.



(3,4-di-methoxyphenyl)methanamine Hydrochloride, 6za[14]

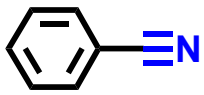
Colourless solid, Yield: 67%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.13 (s, 3H), 6.97-6.85 (m, 2H), 3.81 (s, 2H), 3.72 (s, 3H), 3,70 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 148.66, 148.54, 128.72, 120.88, 112.54, 111.62, 55.61, 55.56, 42.80.



(2,4-di-methoxyphenyl)methanamine Hydrochloride, 6zb[15]

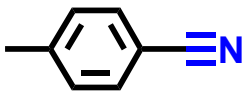
Colourless solid, Yield: 68%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.21 (s, 2H), 7.30 (d, J = 8.5 Hz, 1H), 6.65-6.50 (m, 2H), 3.86 (d, J = 2.5 Hz, 2H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 161.19, 158.38, 131.33, 114.01, 104.70, 98.31, 55.61, 55.37, 37.18.

10b. Characterization data of nitriles



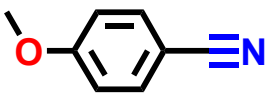
Benzonitrile, 7a[9]

Colourless liquid, Yield: 72%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.96-8.76 (m, 2H), 8.04-7.93 (m, 1H), 7.49-7.39 (m, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 153.09, 152.55, 139.41, 123.77, 116.61, 110.24. The compound was purified by column chromatography using silica gel (60-120 mesh) with 2.5% of EtOAc in hexane.



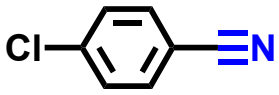
4-methylbenzonitrile, 7b[9]

Colourless liquid, Yield: 77%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 2.41 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 143.82, 132.14, 129.95, 119.29, 109.38, 21.94. The compound was purified by column chromatography using silica gel (60-120 mesh) with 2.5% of EtOAc in hexane.



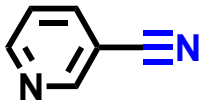
4-methoxybenzonitrile, 7c[9]

Colourless liquid, Yield: 80%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62-7.57 (m, 2H), 6.97-6.92 (m, 2H), 3.86 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 162.94, 134.09, 114.84, 55.64. The compound was purified by column chromatography using silica gel (60-120 mesh) with 2.5% of EtOAc in hexane.



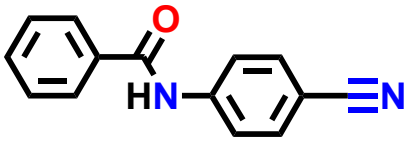
4-chlorobenzonitrile, 7d[9]

Colourless liquid, Yield: 71%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.96-8.76 (m, 2H), 8.04-7.93 (m, 1H), 7.49-7.39 (m, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 153.09, 152.55, 139.41, 123.77, 116.61, 110.24. The compound was purified by column chromatography using silica gel (60-120 mesh) with 2.5% of EtOAc in hexane.



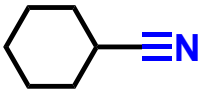
3-pyridinecarbonitrile, 7e[9]

Colourless liquid, Yield: 65%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.96-8.76 (m, 2H), 8.04-7.93 (m, 1H), 7.49-7.39 (m, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 153.09, 152.55, 139.41, 123.77, 116.61, 110.24. The compound was purified by column chromatography using silica gel (60-120 mesh) with 2.5% of EtOAc in hexane.



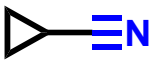
N-(4-cyanophenyl)benzamide, 7f[9]

Colourless liquid, Yield: 83%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.71 (s, 1H), 8.06 – 7.99 (m, 4H), 7.87 (d, J = 8.6 Hz, 2H), 7.72 (m, 1H), 7.65 (m, 2H), 3.95 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 166.38, 143.59, 134.39, 133.26, 132.16, 128.59, 127.97, 120.29, 119.17, 105.48 The compound was purified by column chromatography using silica gel (60-120 mesh) with 10% of EtOAc in hexane.



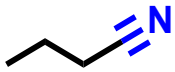
Cyclohexanecarbonitrile, 7g[9]

Colourless liquid, Yield: 76%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.60 (m, 1H), 1.83 (m, 2H), 1.68 (m, 4H), 1.43 (m, 4H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 122.59, 29.45, 27.91, 25.19, 24.01. The compound was purified by column chromatography using silica gel (60-120 mesh) with 2.5% of EtOAc in hexane.



Cyclopropanecarbonitrile, 7h[16]

Colourless liquid, Yield: 64%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.37-1.29 (m, 1H), 1.06 (dd, J = 7.2, 3.2 Hz, 2H), 1.00 (dt, J = 9.2,3.2 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 122.32, 7.22, -3.43. The compound was purified by column chromatography using silica gel (60-120 mesh) with 2.5% of EtOAc in hexane.



Butyronitrile, 7i[17]

Colourless liquid, Yield: 61%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.31 (t, J= 7.2 Hz, 2H), 1.68 (d, J = 7.1 Hz, 2H), 1.06 (t, J = 7.4 Hz, 3H); **^{13}C{1H} NMR** (101 MHz, $CDCl_3$): δ 119.78, 19.12, 18.93, 13.22. The compound was purified by column chromatography using silica gel (60-120 mesh) with 2.5% of EtOAc in hexane.

12. ^{1}H and ^{13}C NMR spectra of amines and nitriles

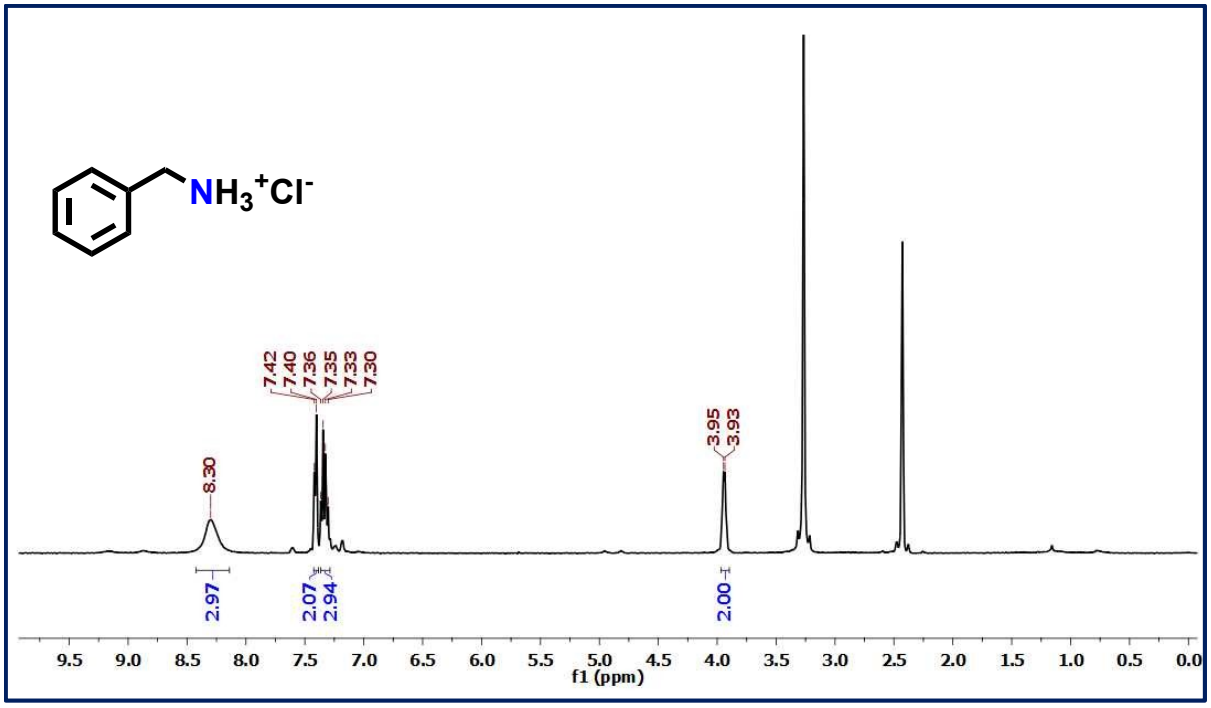


Figure S23. ^{1}H NMR spectrum (DMSO-d_6) of Phenylmethanamine hydrochloride.

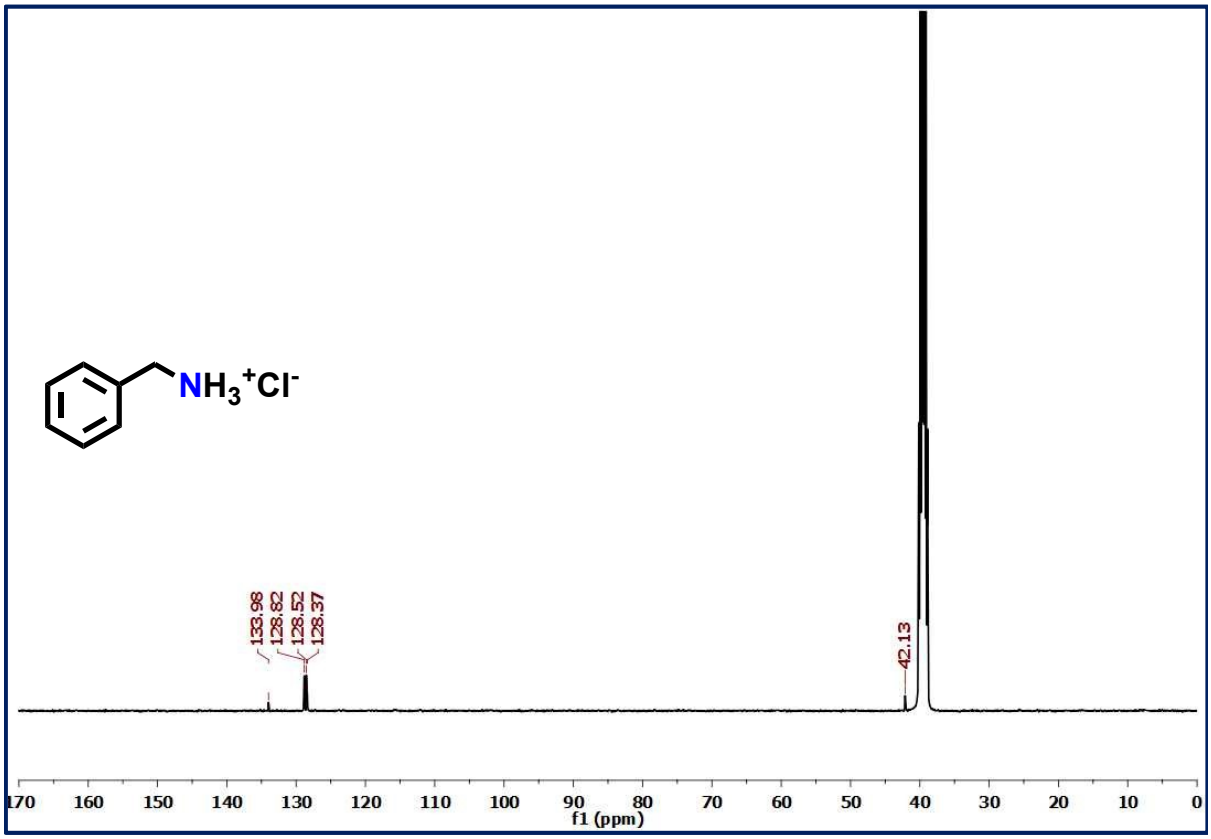


Figure S24. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of Phenylmethanamine hydrochloride.

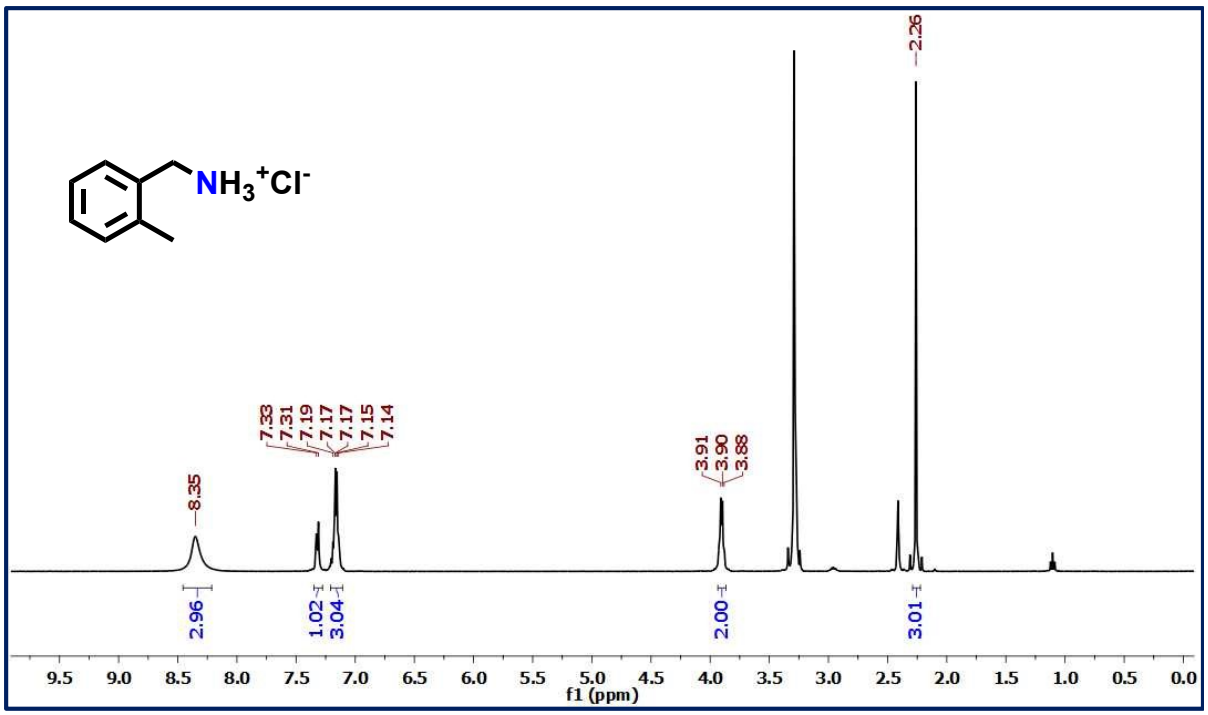


Figure S25. ^{1}H NMR spectrum (DMSO-d_6) of o-tolylmethanamine Hydrochloride.

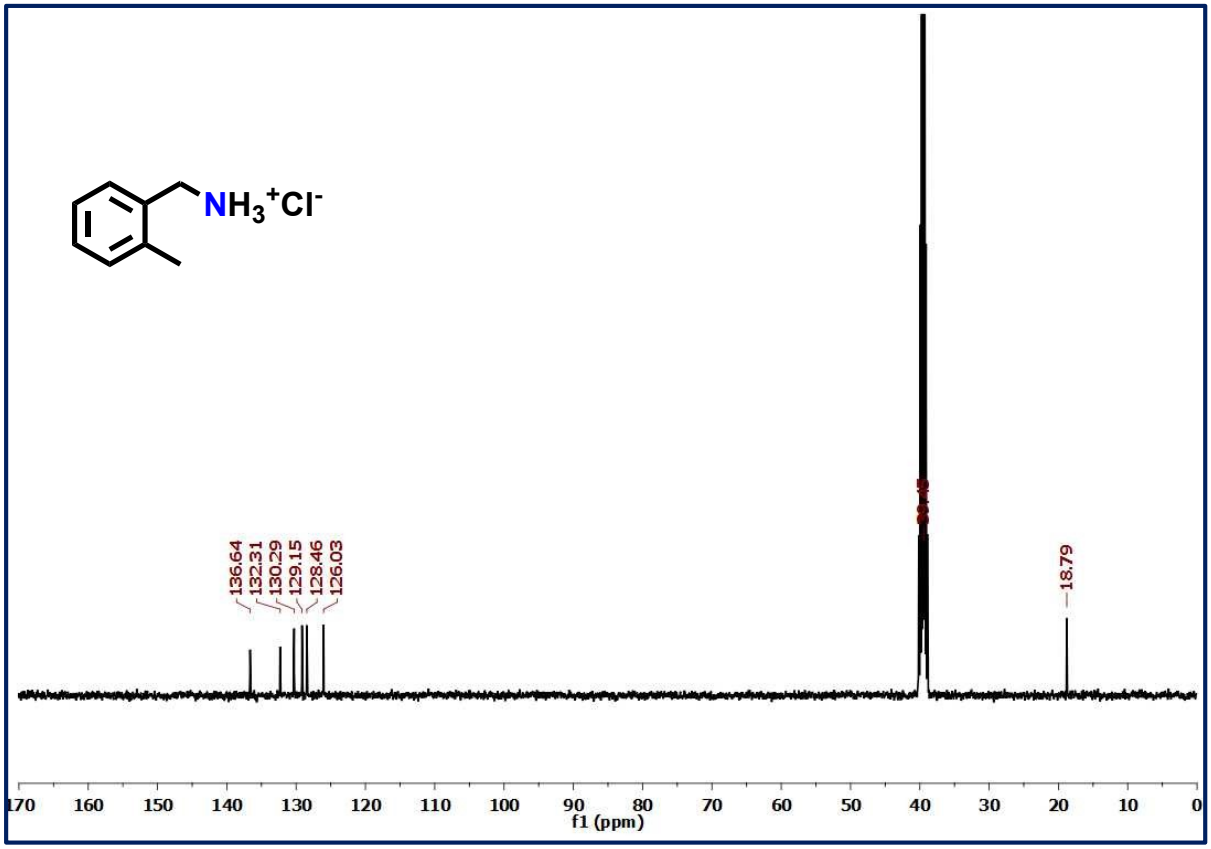


Figure S26. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of o-tolylmethanamine Hydrochloride.

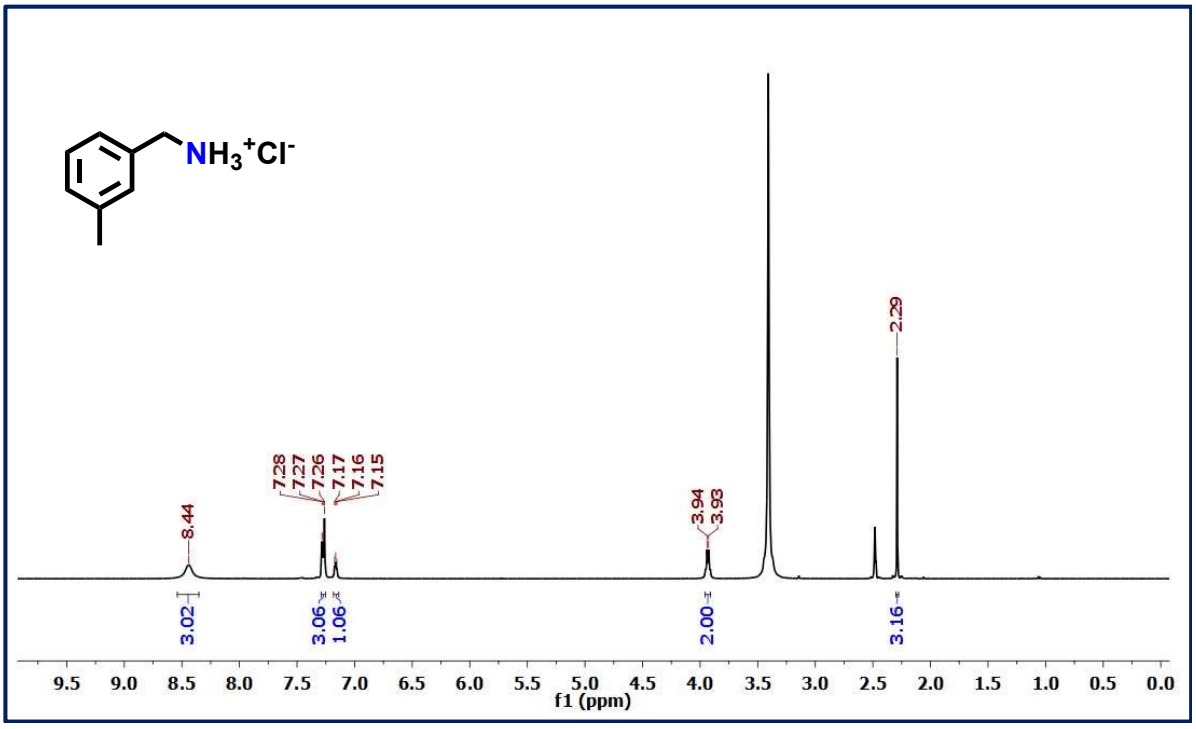


Figure S27.[1]H NMR spectrum (DMSO-d_6) of m-tolylmethanamine Hydrochloride.

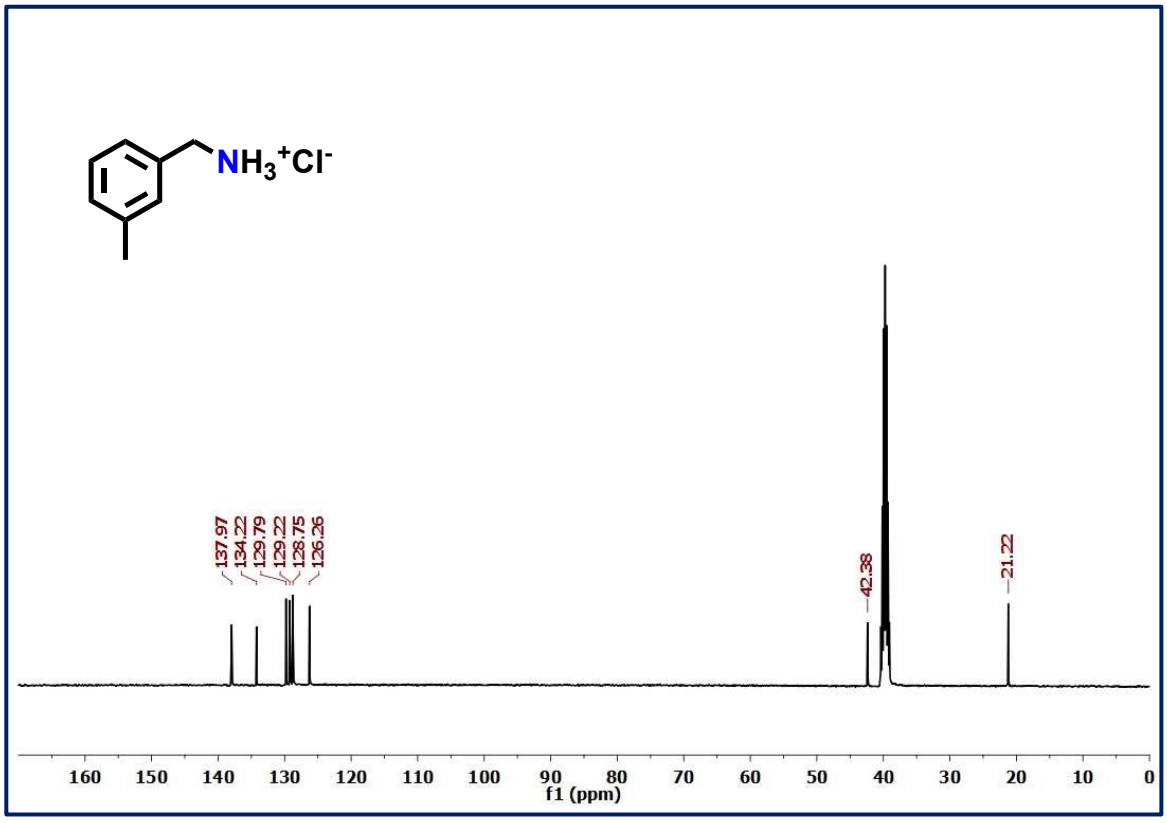


Figure S28. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of m-tolylmethanamine Hydrochloride.

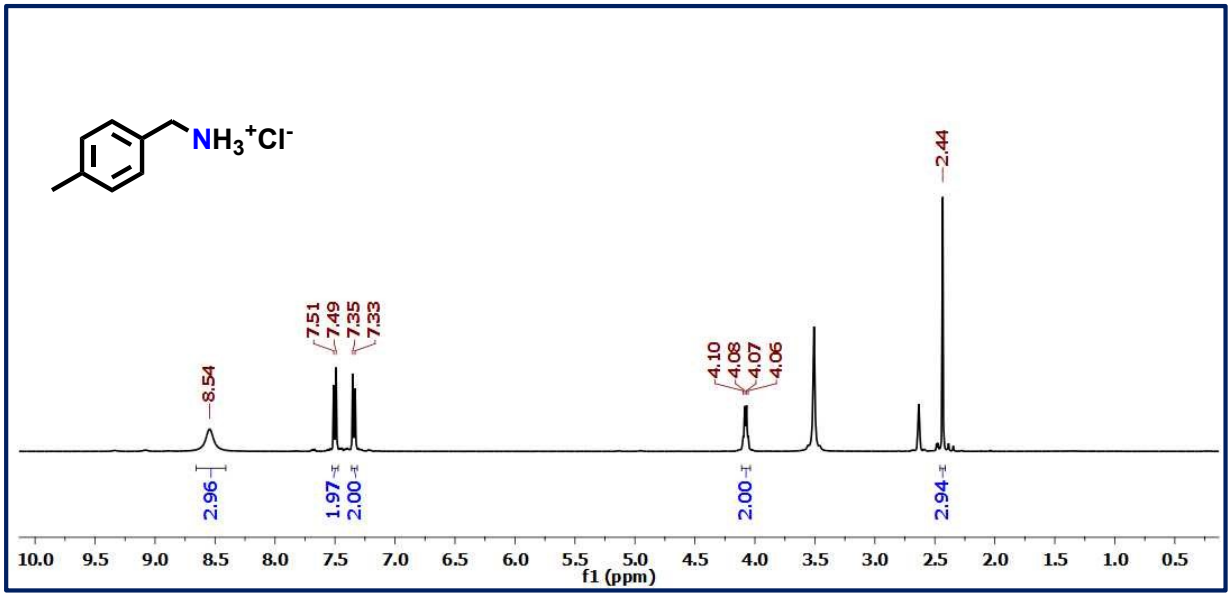


Figure S29.[1]H NMR spectrum (DMSO-d_6) of p-tolylmethanamine Hydrochloride.

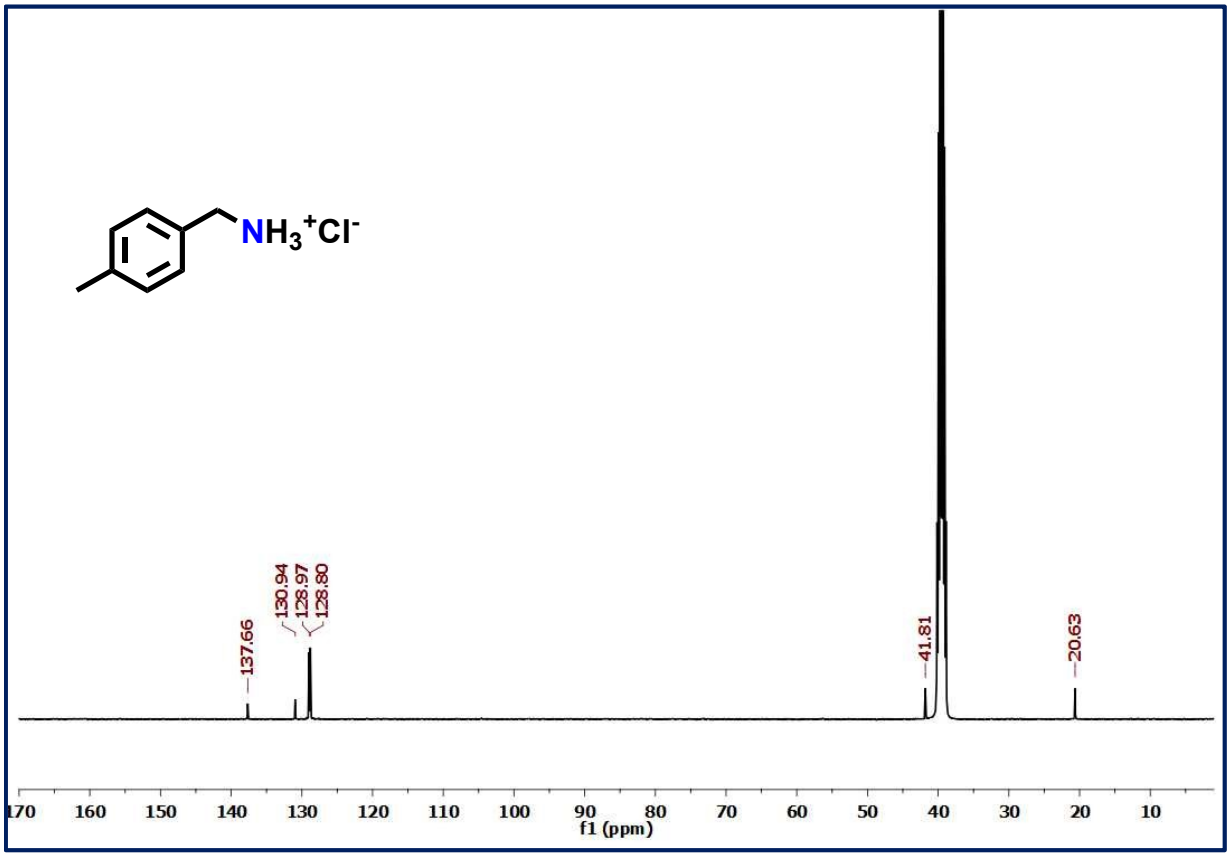


Figure S30. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of p-tolylmethanamine Hydrochloride.

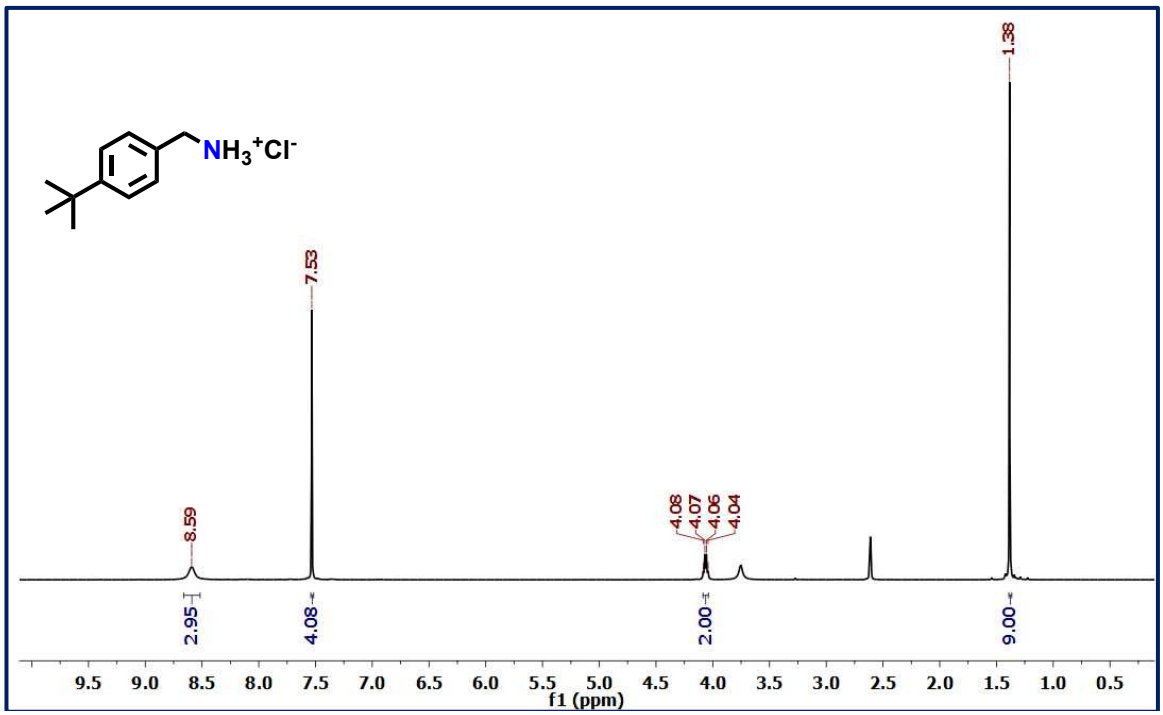


Figure S31.[1]H NMR spectrum (DMSO-d_6) of (4-(tert-butyl)phenyl)methanamine Hydrochloride.

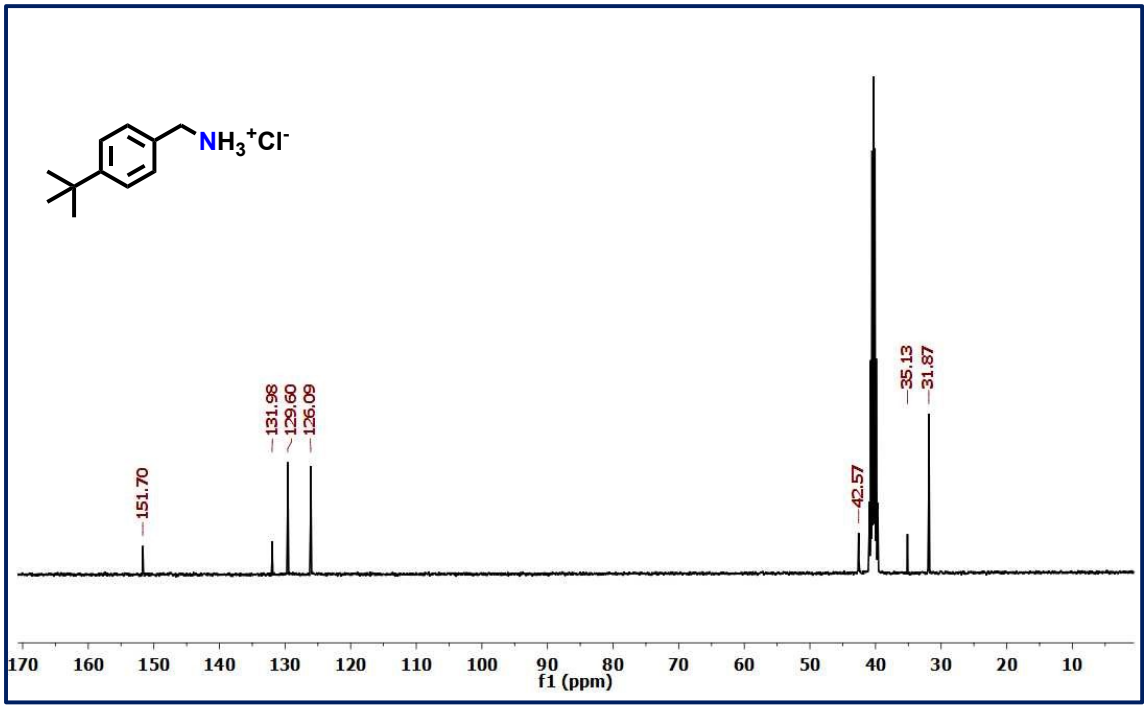


Figure S32. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (4-(tert-butyl)phenyl)methanamine Hydrochloride.

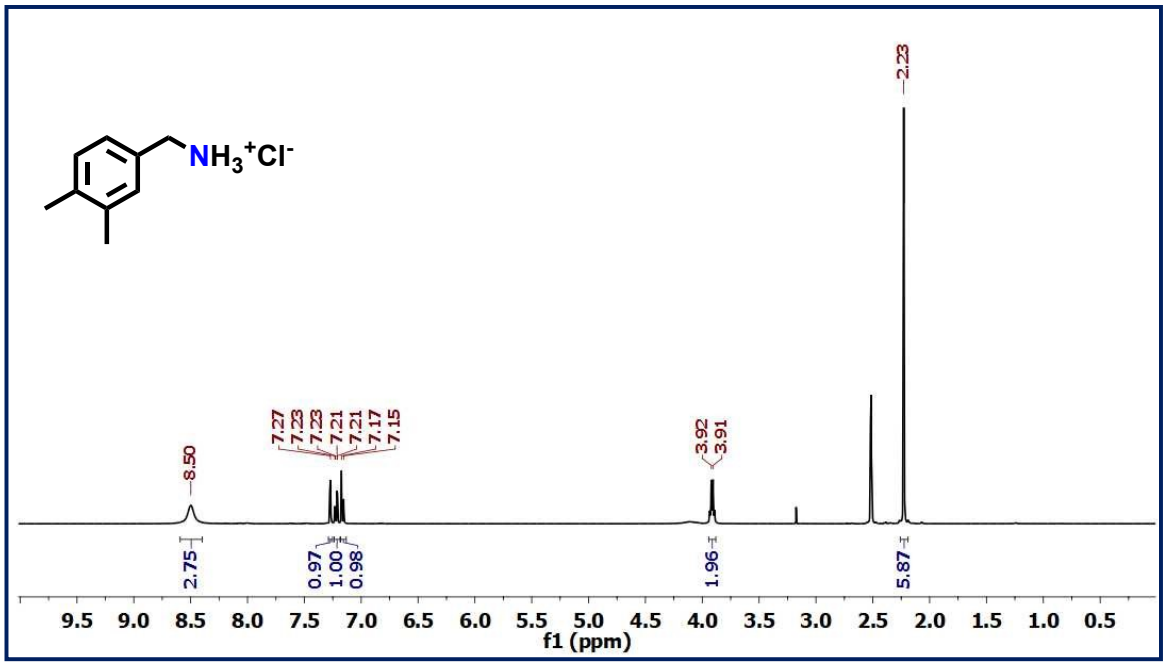


Figure S33.[1]H NMR spectrum (DMSO-d_6) of (3,4-dimethylphenyl)methanamine hydrochloride.

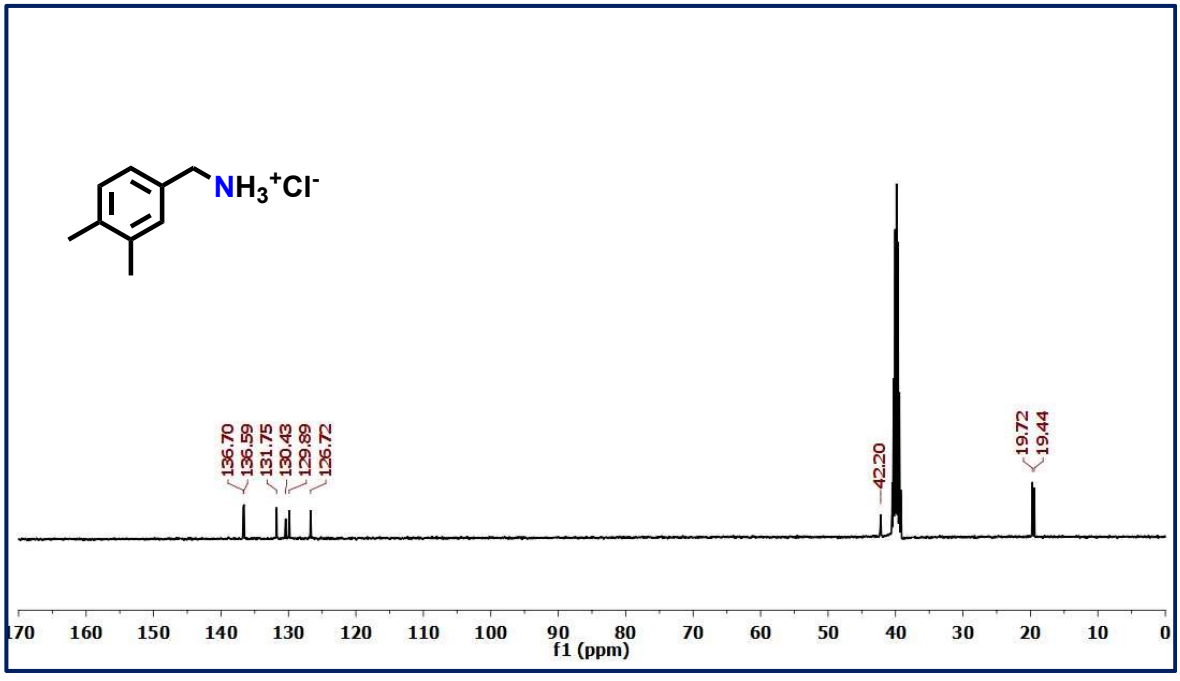


Figure S34. [13]C{[1]H} NMR spectrum (DMSO-d_6) of (3,4-dimethylphenyl)methanamine hydrochloride.

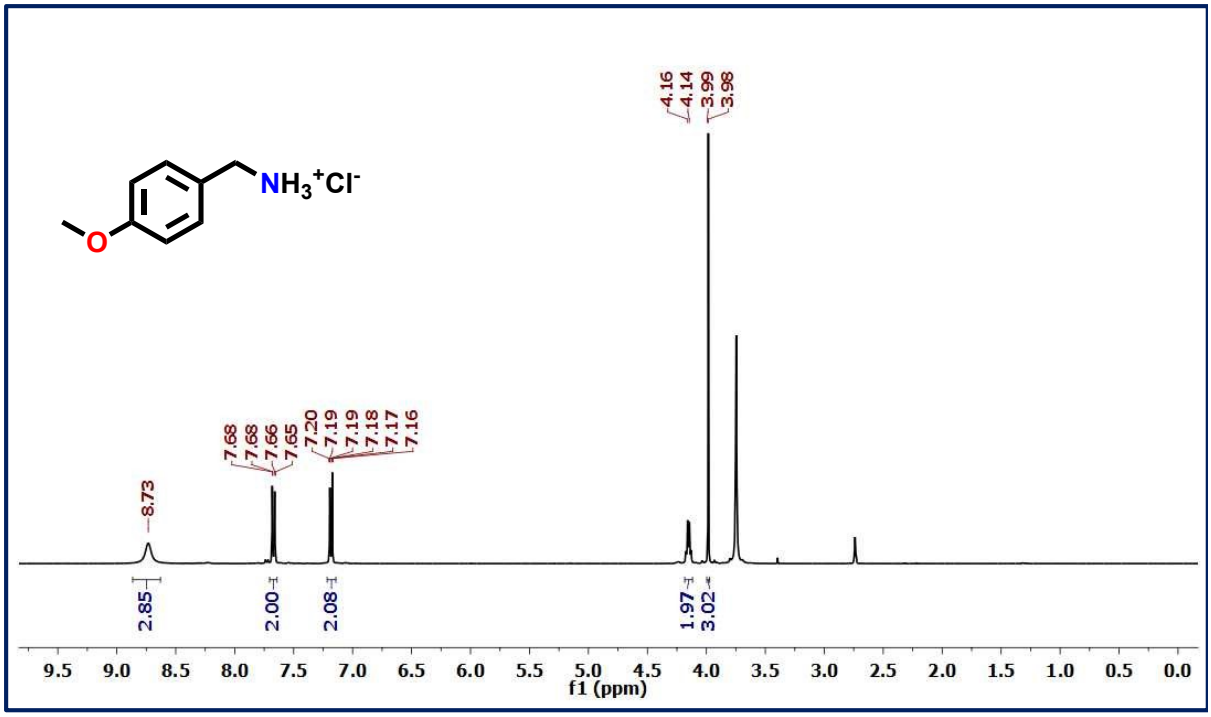


Figure S35.[1]H NMR spectrum (DMSO-d_6) of (4-methoxyphenyl)methanamine hydrochloride.

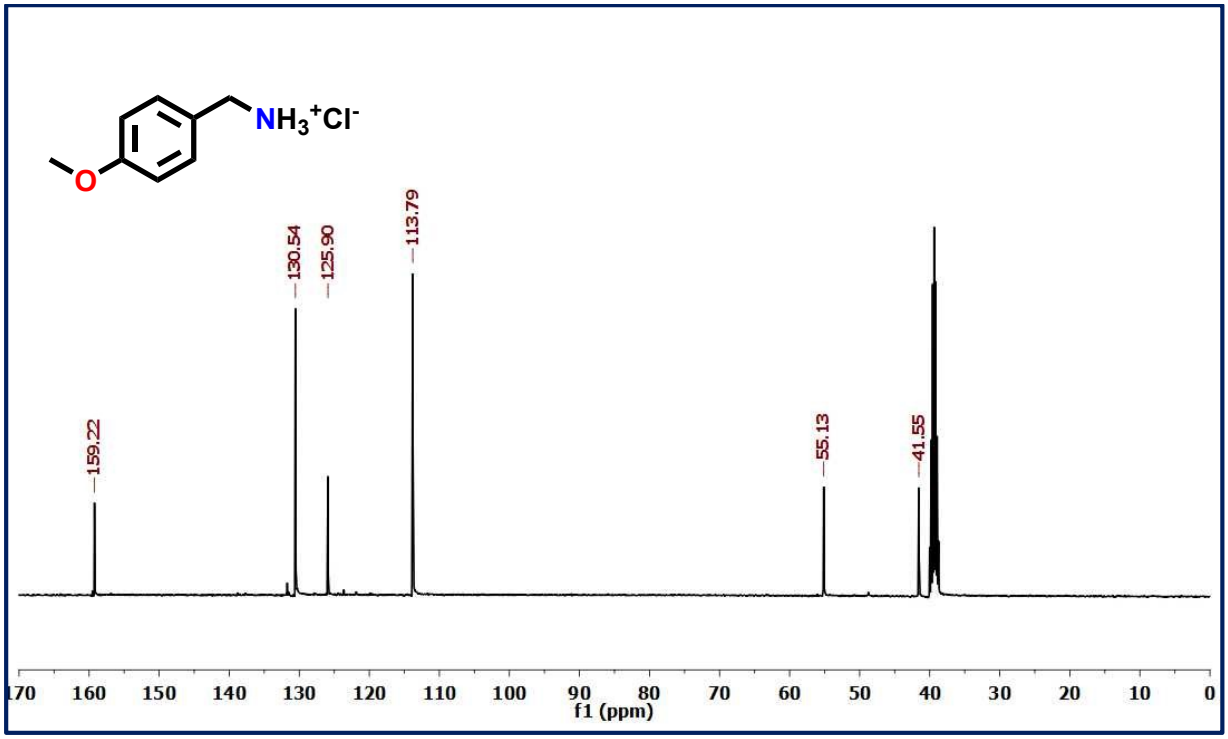


Figure S36. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (4-methoxyphenyl)methanamine hydrochloride.

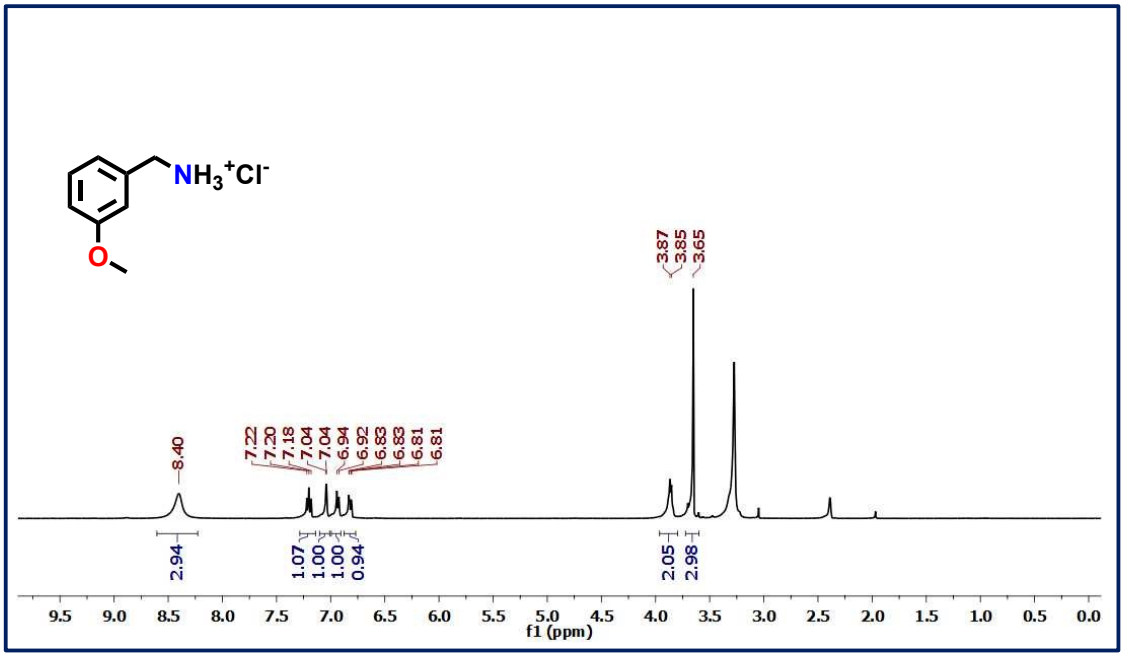


Figure S37.[1]H NMR spectrum (DMSO-d_6) of (3-methoxyphenyl)methanamine hydrochloride.

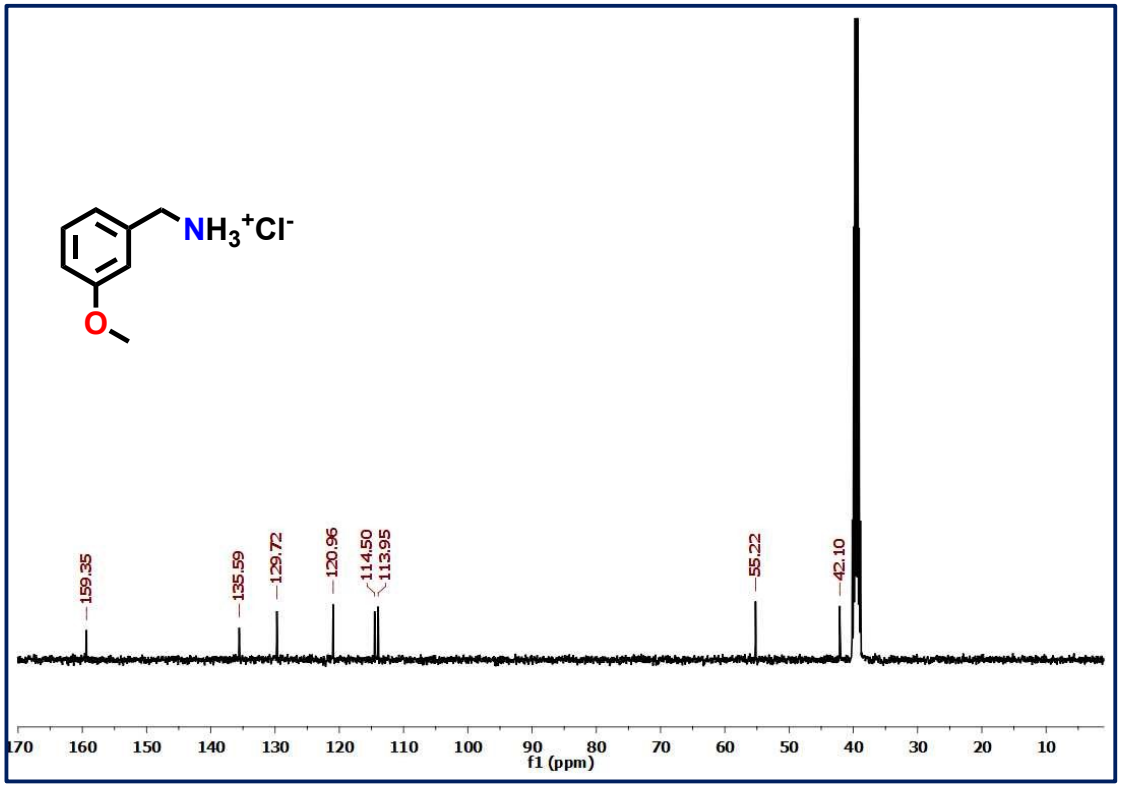


Figure S38.[13]C{[1]H} NMR spectrum (DMSO-d_6) of (3-methoxyphenyl)methanamine hydrochloride.

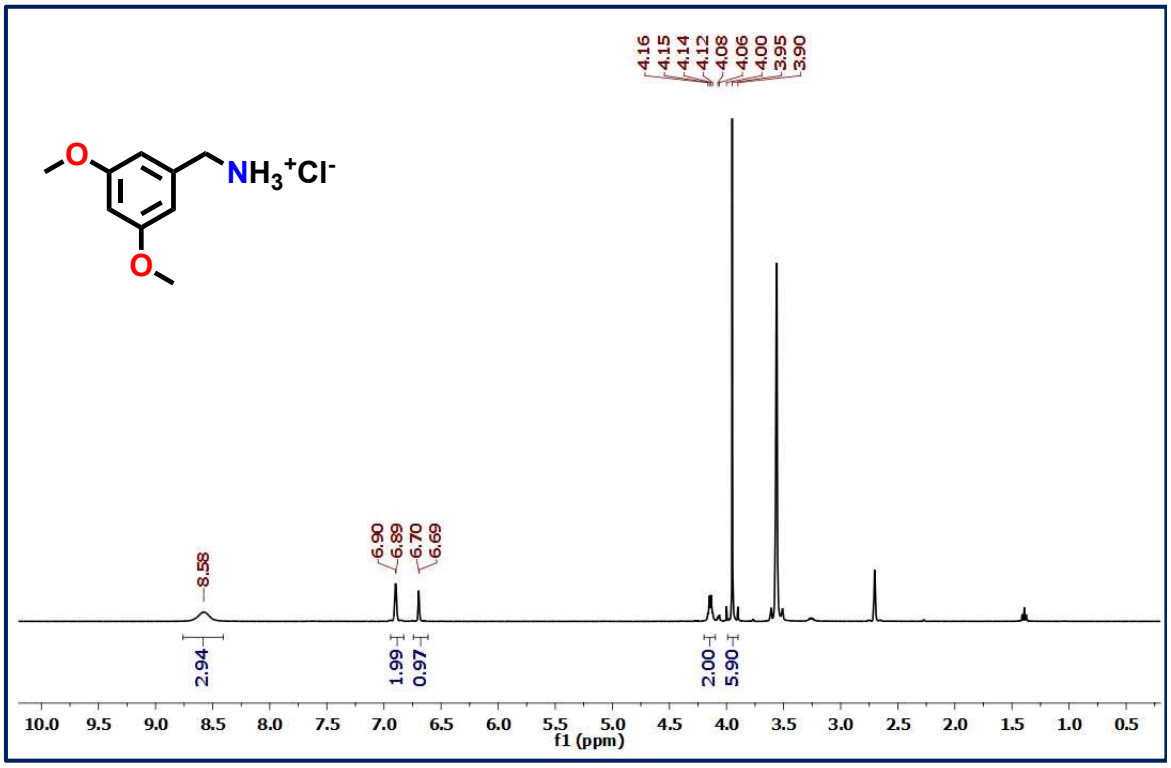


Figure S39.[1]H NMR spectrum (DMSO-d_6) of (3,5-dimethoxyphenyl)methanamine hydrochloride.

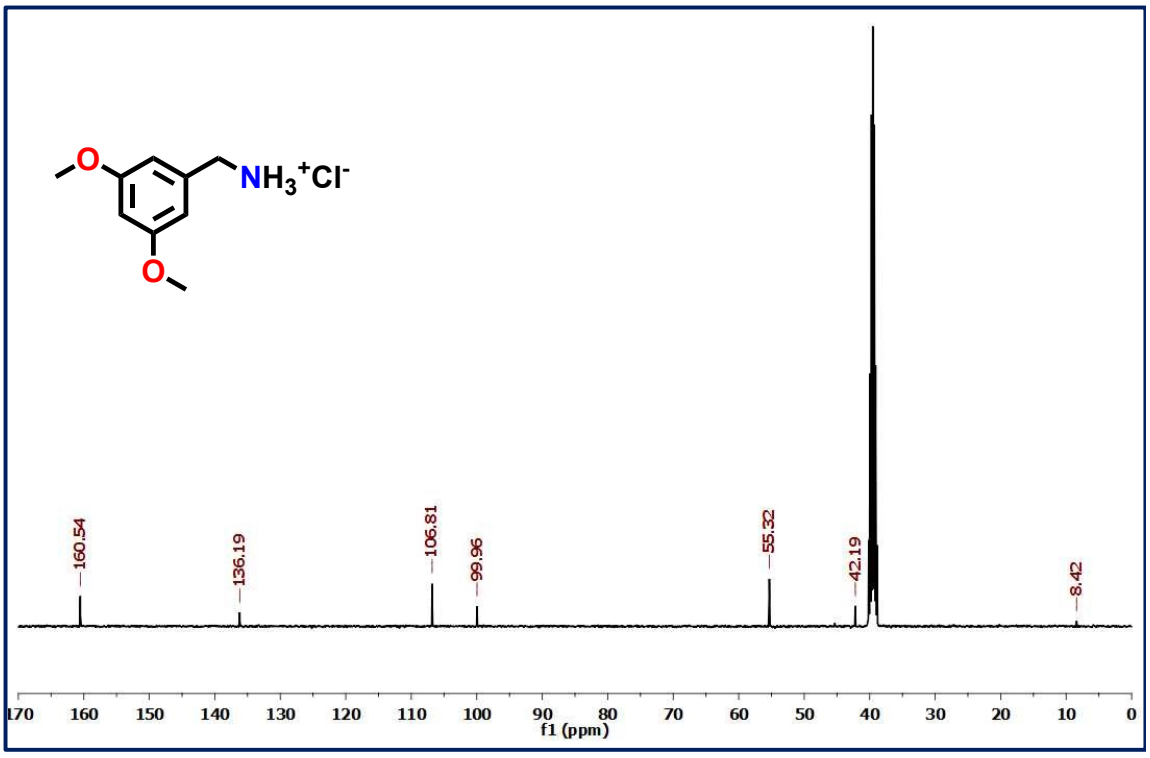


Figure S40. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (3,5-dimethoxyphenyl)methanamine hydrochloride.

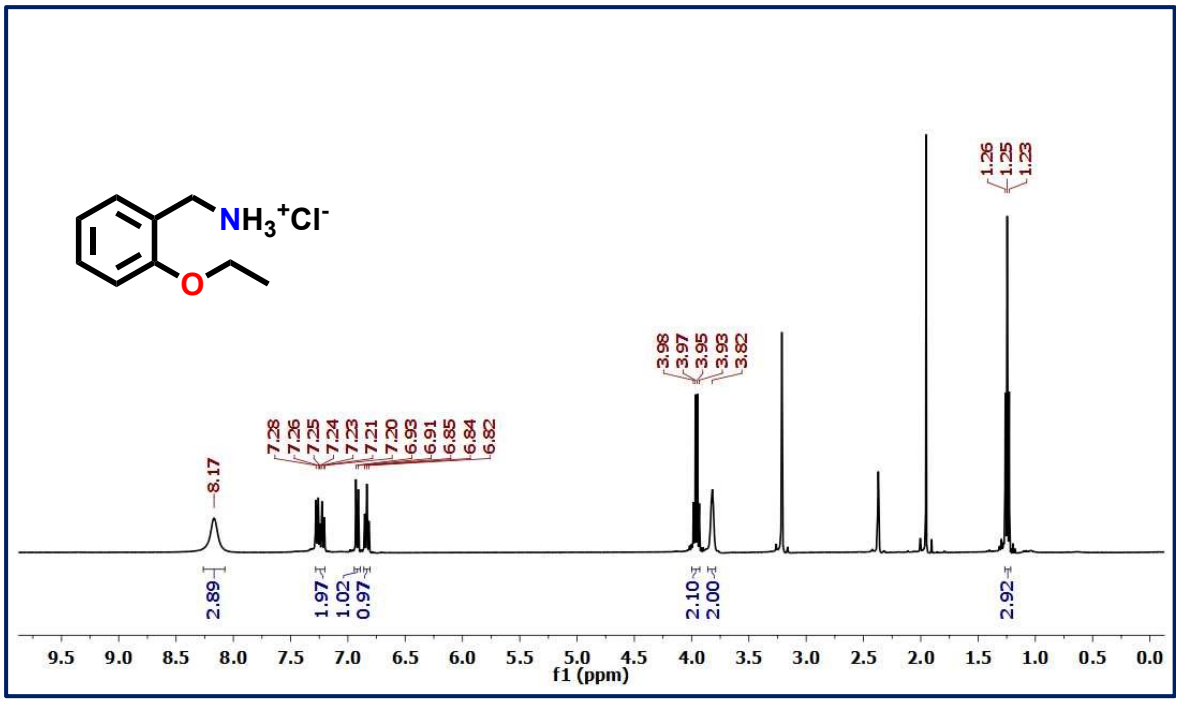


Figure S41.[1]H NMR spectrum (DMSO-d_6) of (2-ethoxyphenyl)methanamine hydrochloride.

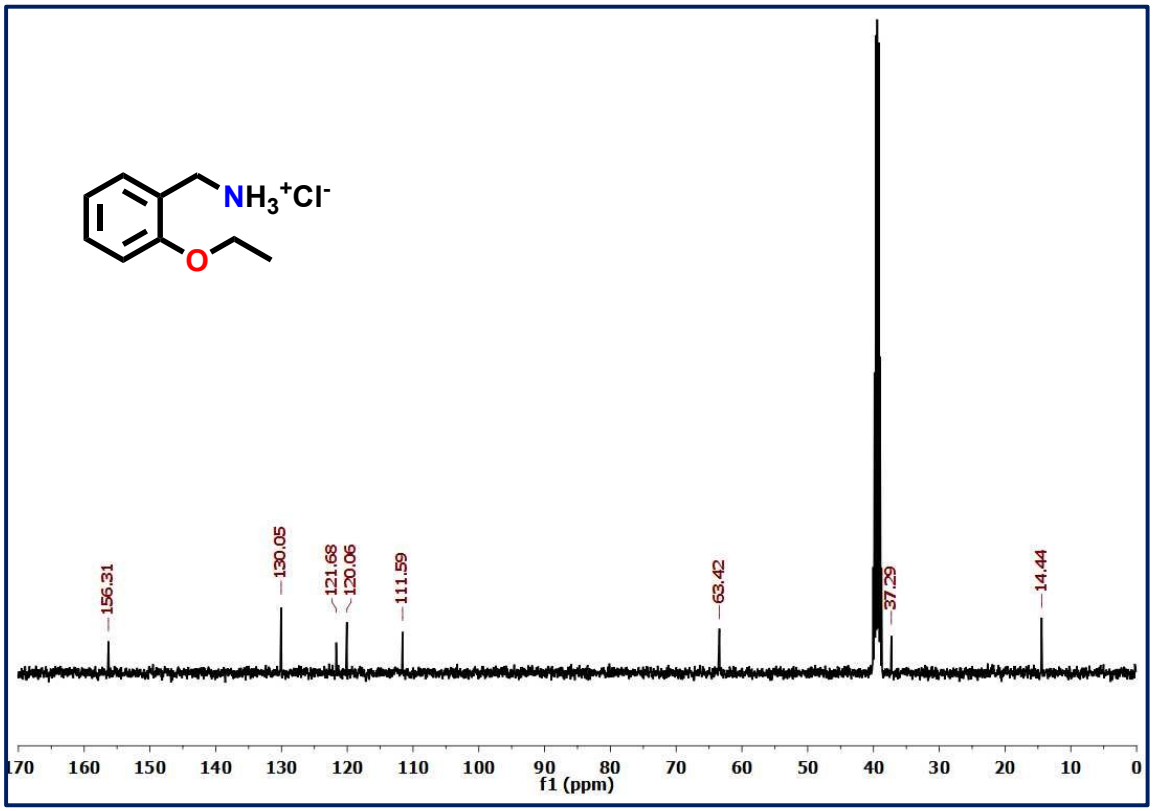


Figure S42. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (2-ethoxyphenyl)methanamine hydrochloride.

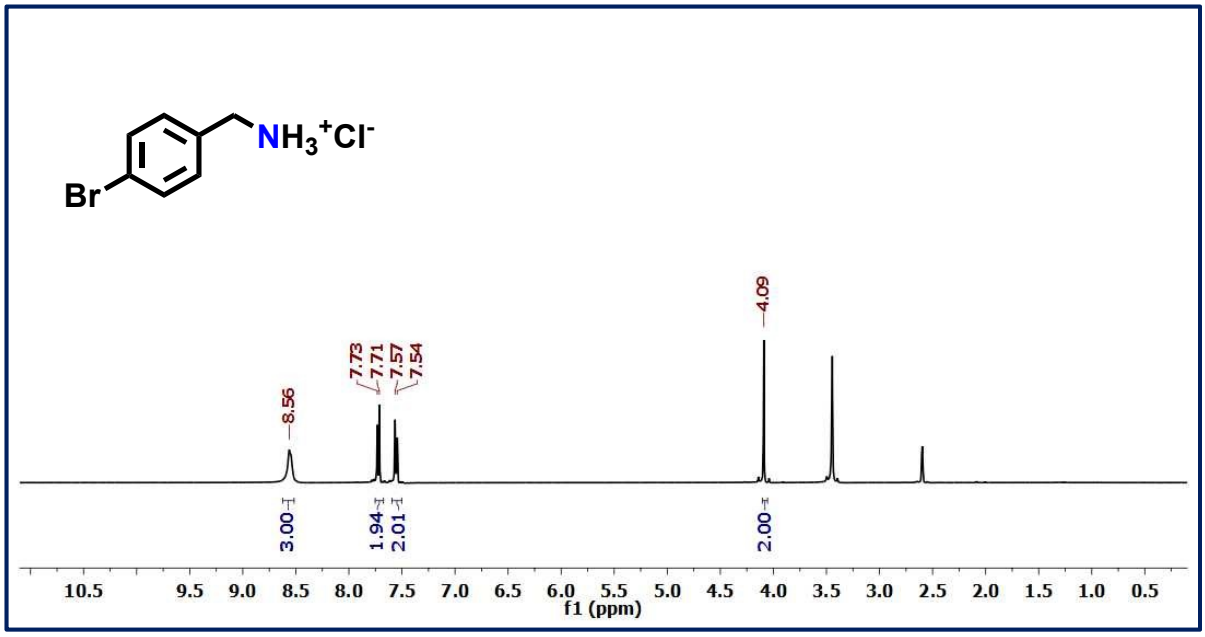


Figure S43.[1]H NMR spectrum (DMSO-d_6) of (4-bromophenyl)methanamine hydrochloride.

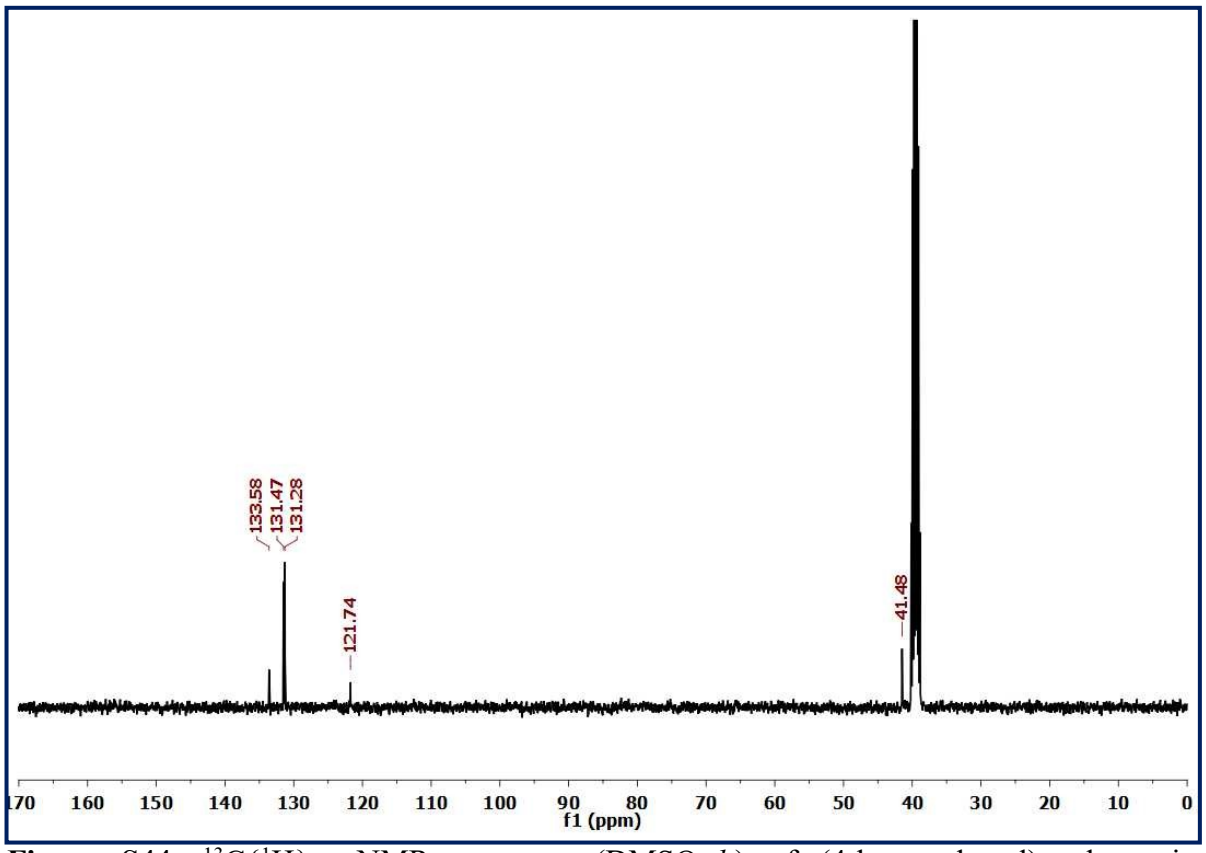


Figure S44. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (4-bromophenyl)methanamine hydrochloride.

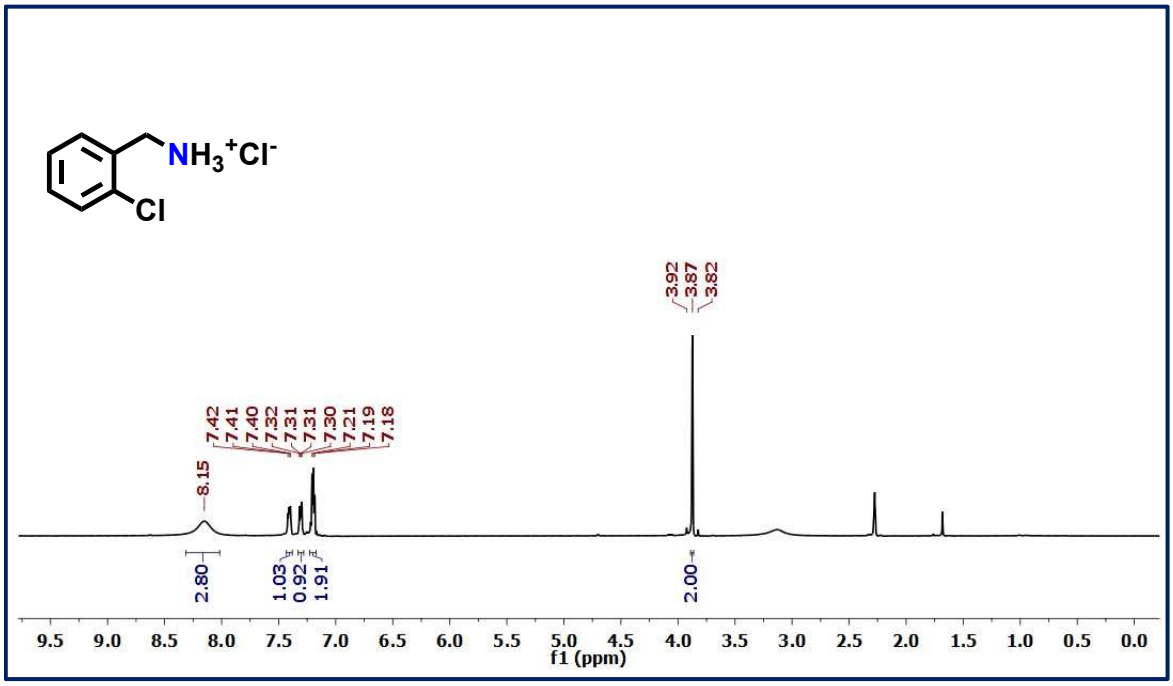


Figure S45.[1]H NMR spectrum (DMSO-d_6) of (2-chlorophenyl)methanamine hydrochloride.

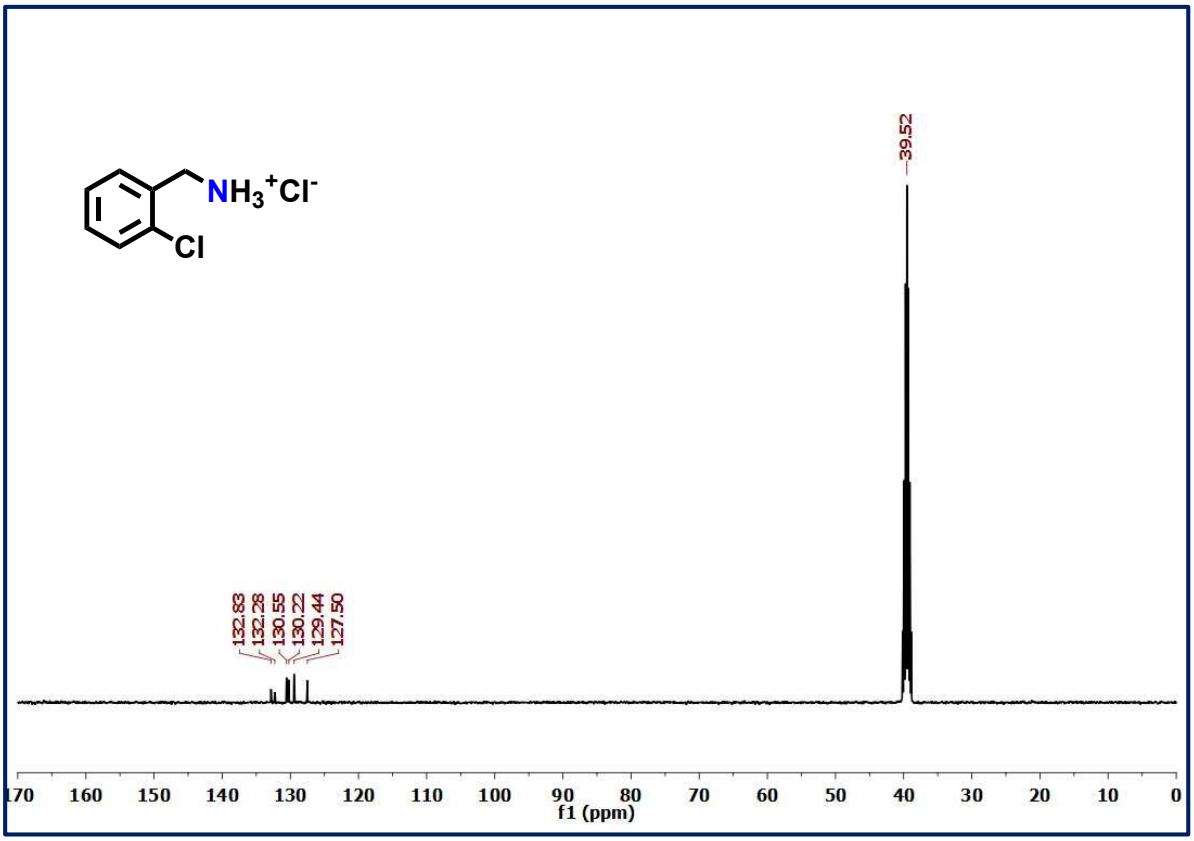


Figure S46. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (2-chlorophenyl)methanamine hydrochloride.

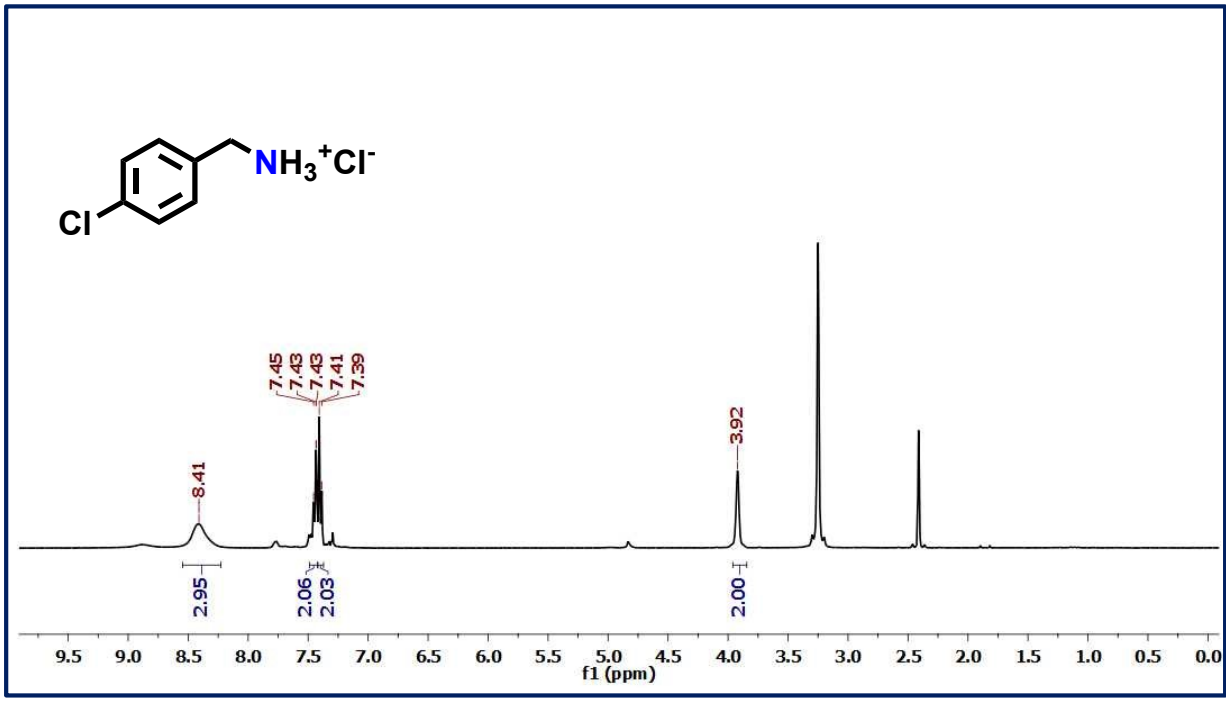


Figure S47.[1]H NMR spectrum (DMSO-d_6) of (4-chlorophenyl)methanamine hydrochloride.

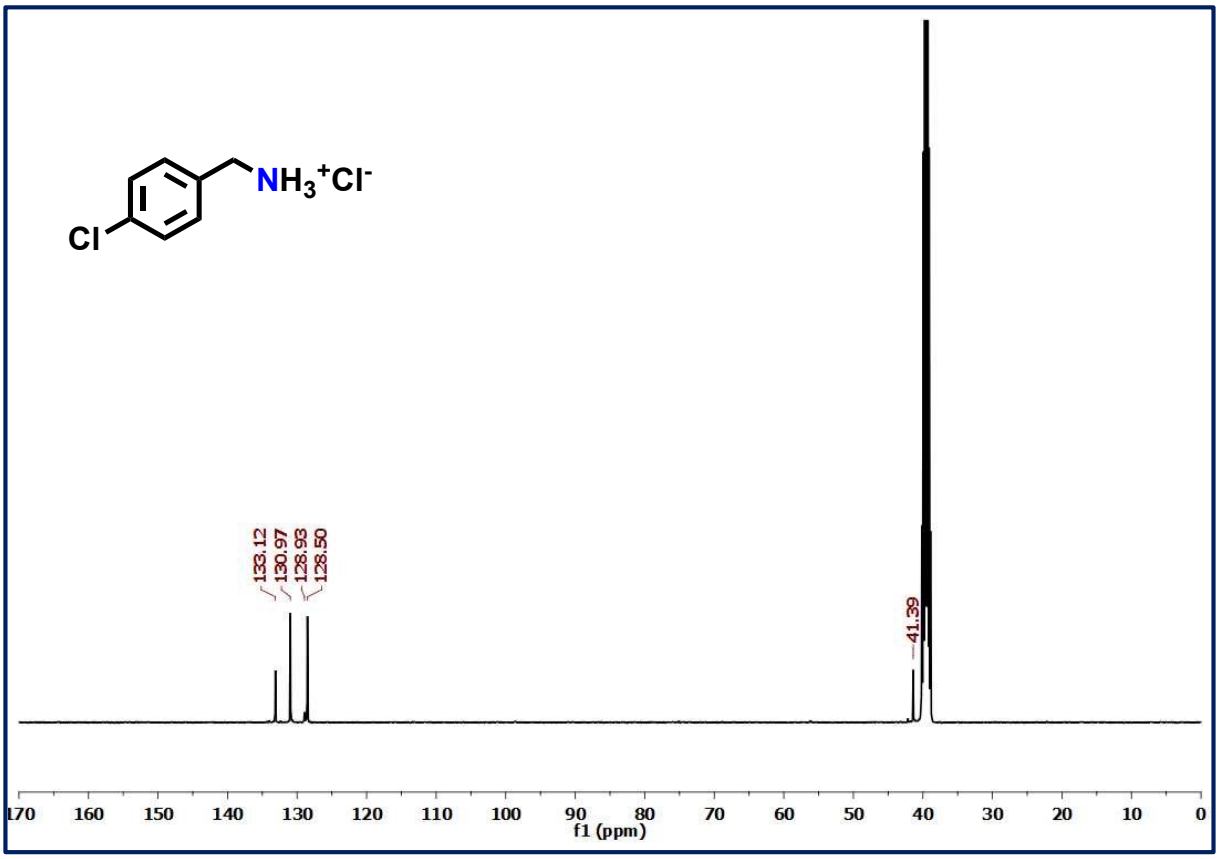


Figure S48. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (4-chlorophenyl)methanamine hydrochloride.

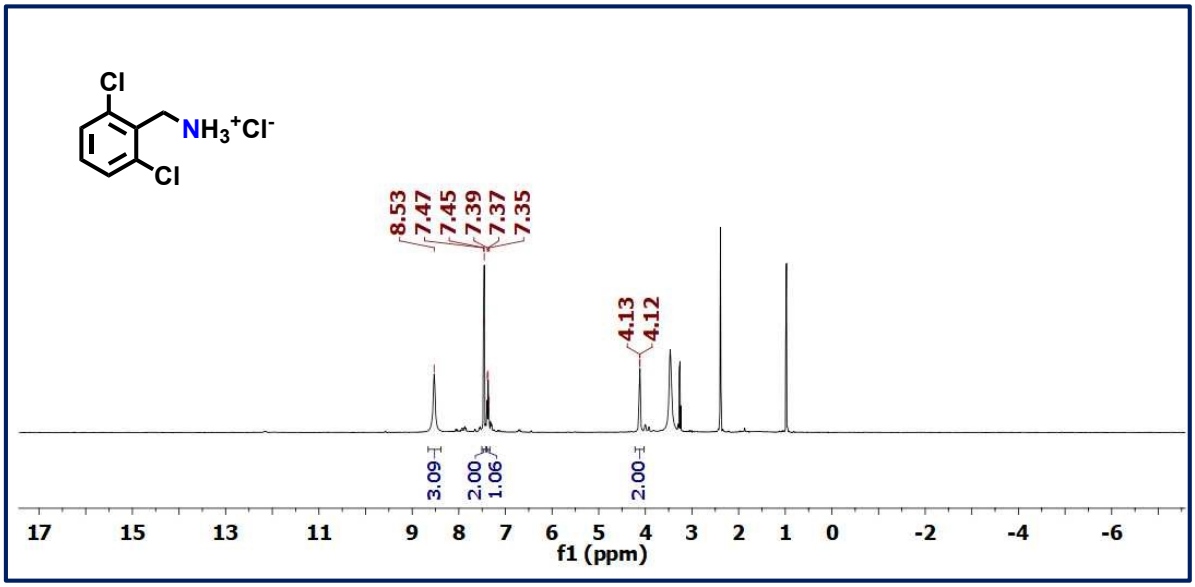


Figure S49.[1]H NMR spectrum (DMSO-d_6) of (2,6-dichlorophenyl)methanamine hydrochloride.

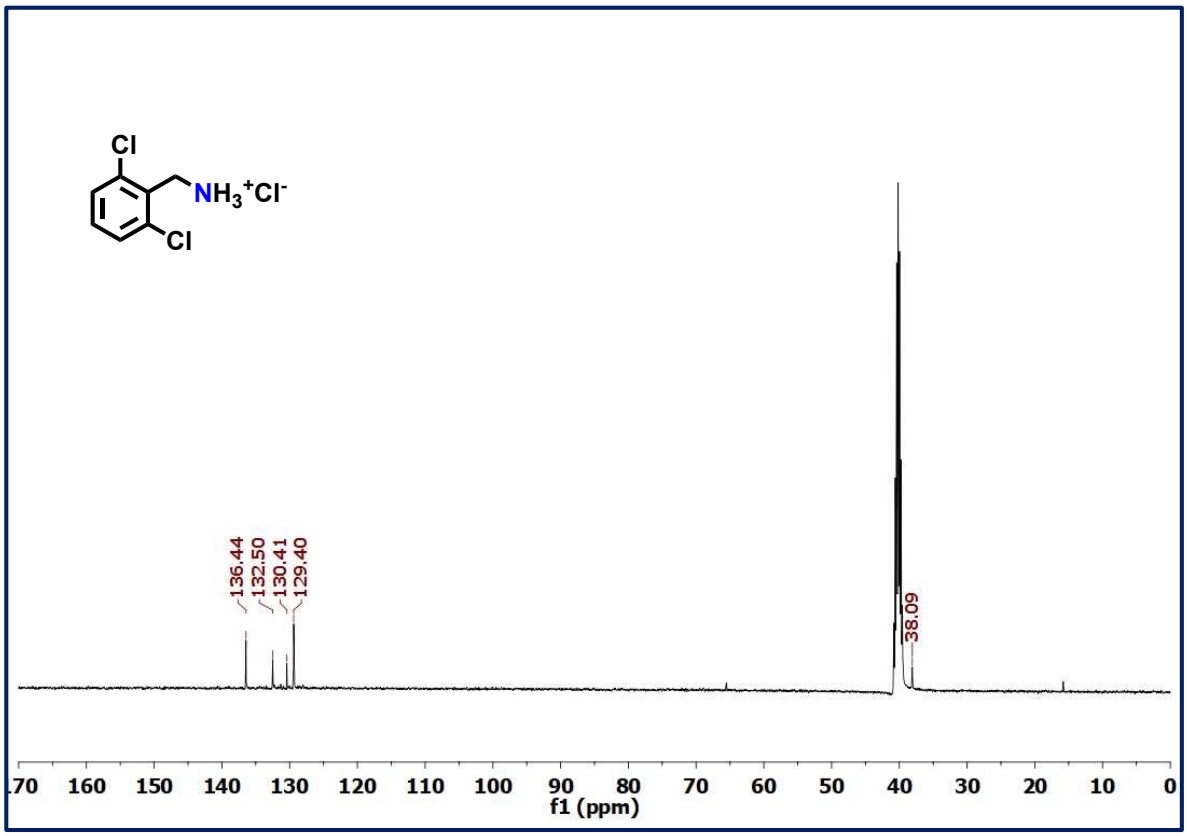


Figure S50. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (2,6-dichlorophenyl)methanamine hydrochloride.

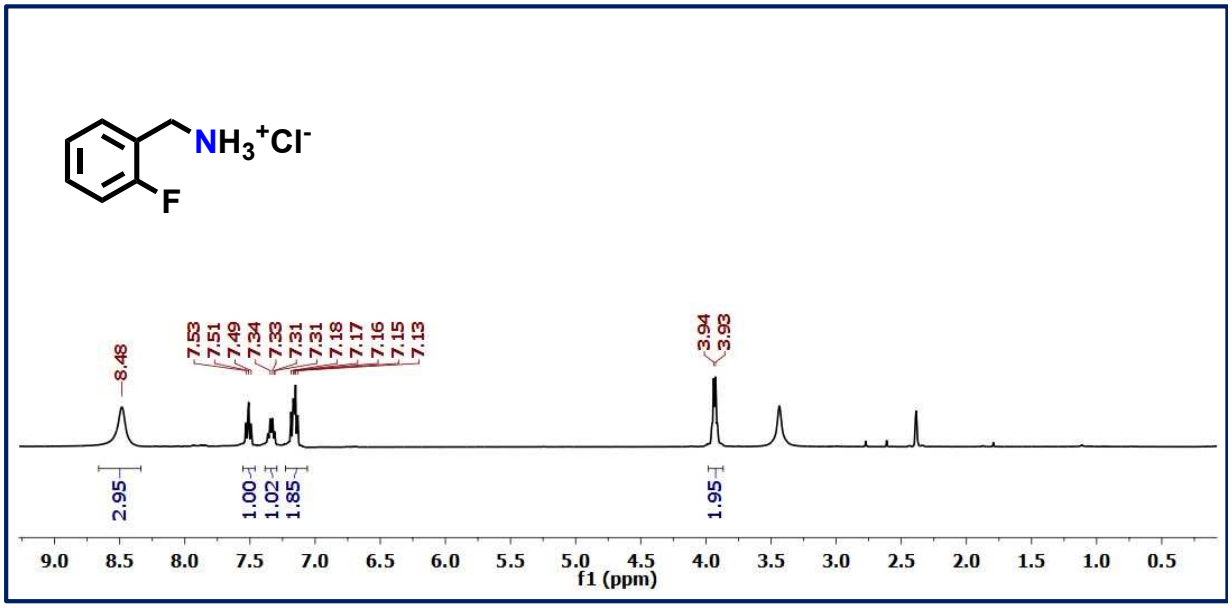


Figure S51.[1]H NMR spectrum (DMSO-d_6) of (2-flurophenyl)methanamine hydrochloride.

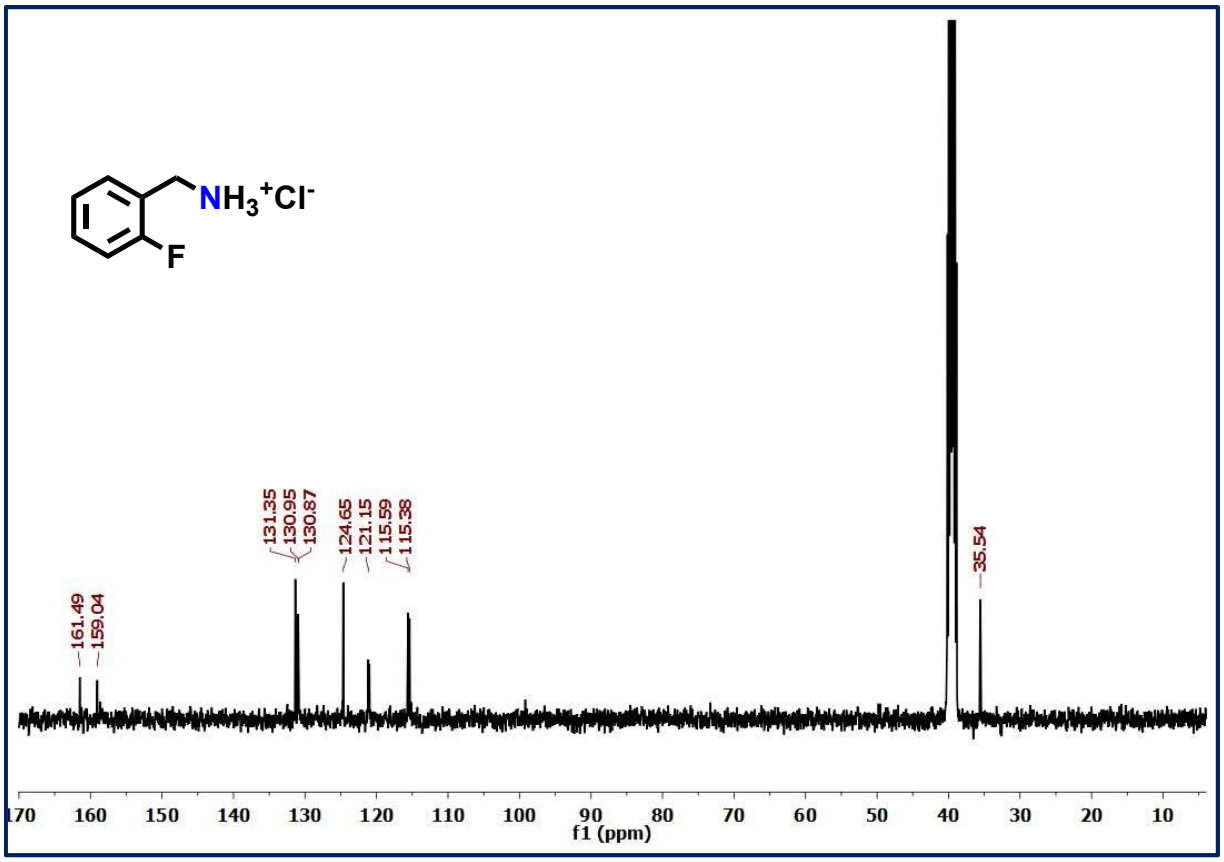


Figure S52. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (2-flurophenyl)methanamine hydrochloride.

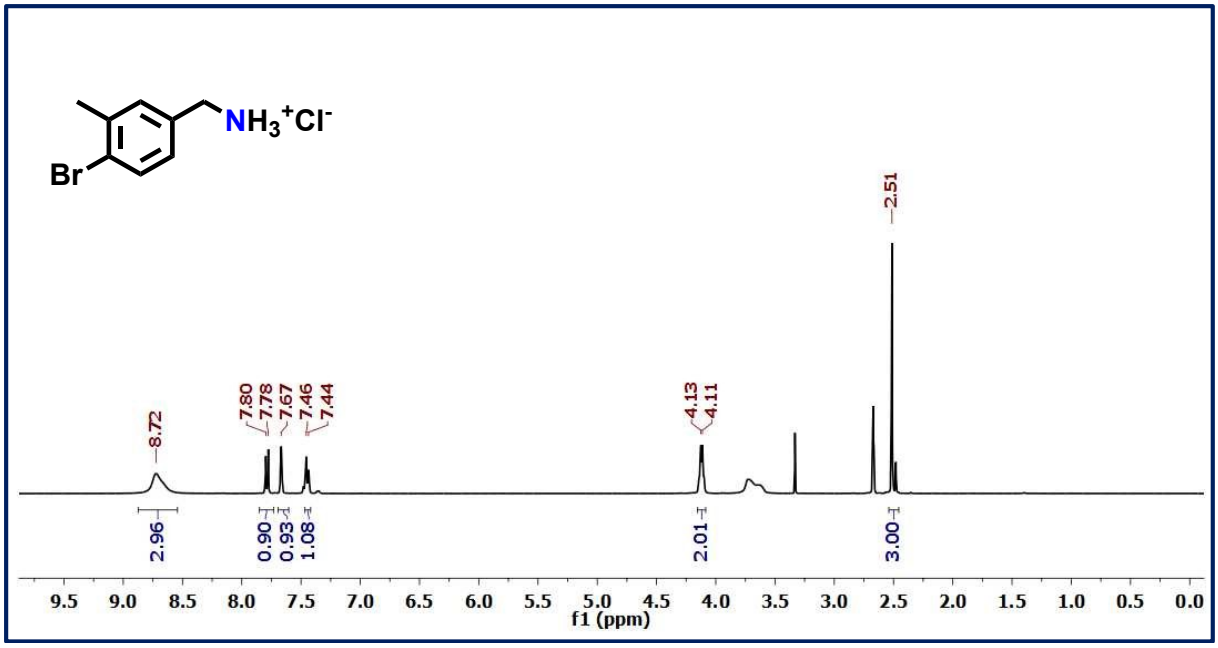


Figure S53.[1]H NMR spectrum (DMSO-d_6) of (4-bromo-3-methylphenyl)methanamine Hydrochloride

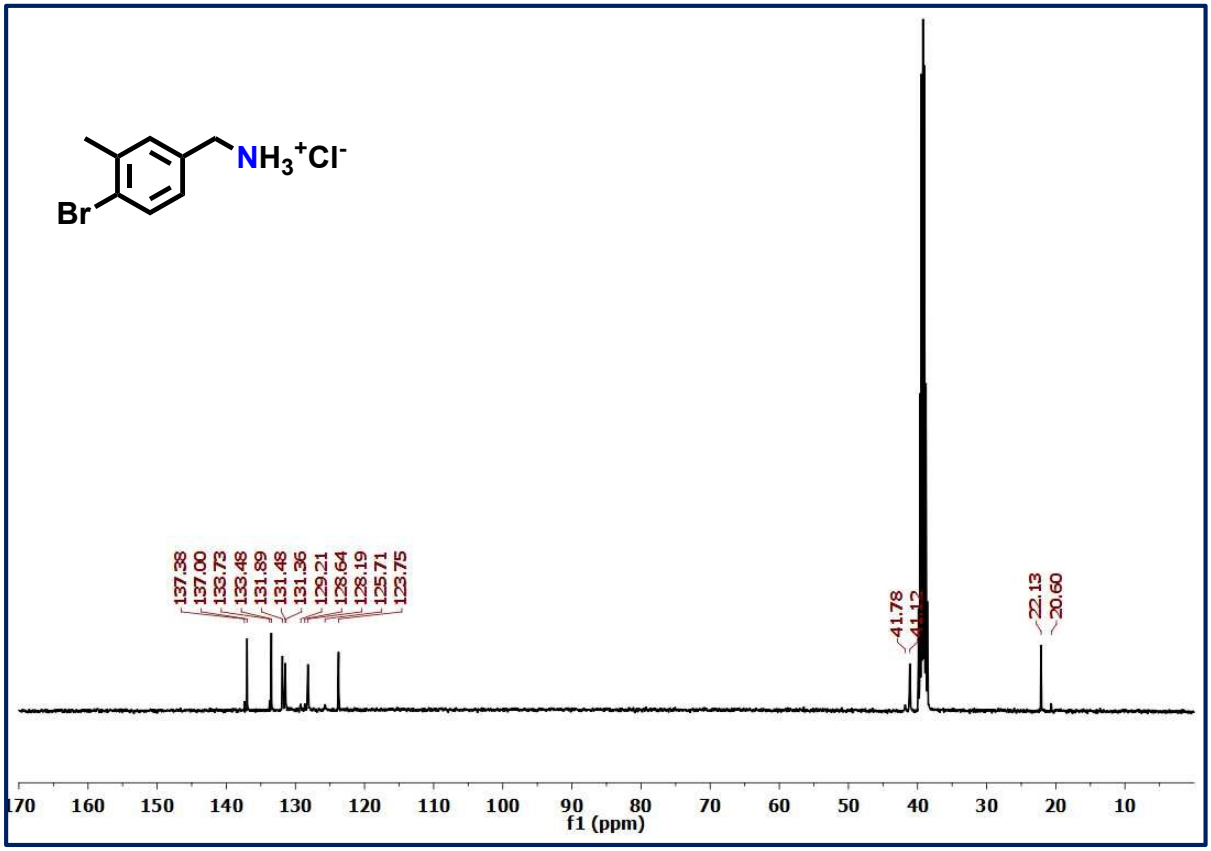


Figure S54. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (4-bromo-3-methylphenyl)methanamine Hydrochloride.

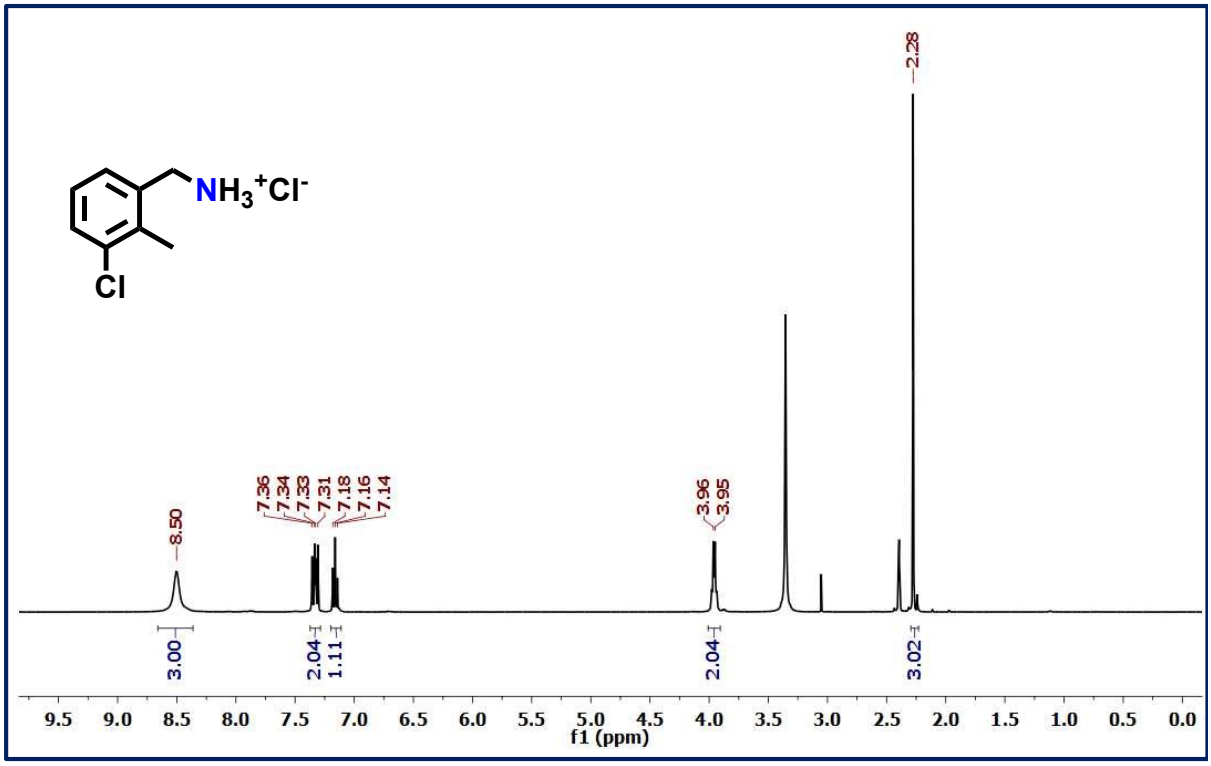


Figure S55.[1]H NMR spectrum (DMSO-d_6) of (3-chloro-2-methylphenyl)methanamine Hydrochloride.

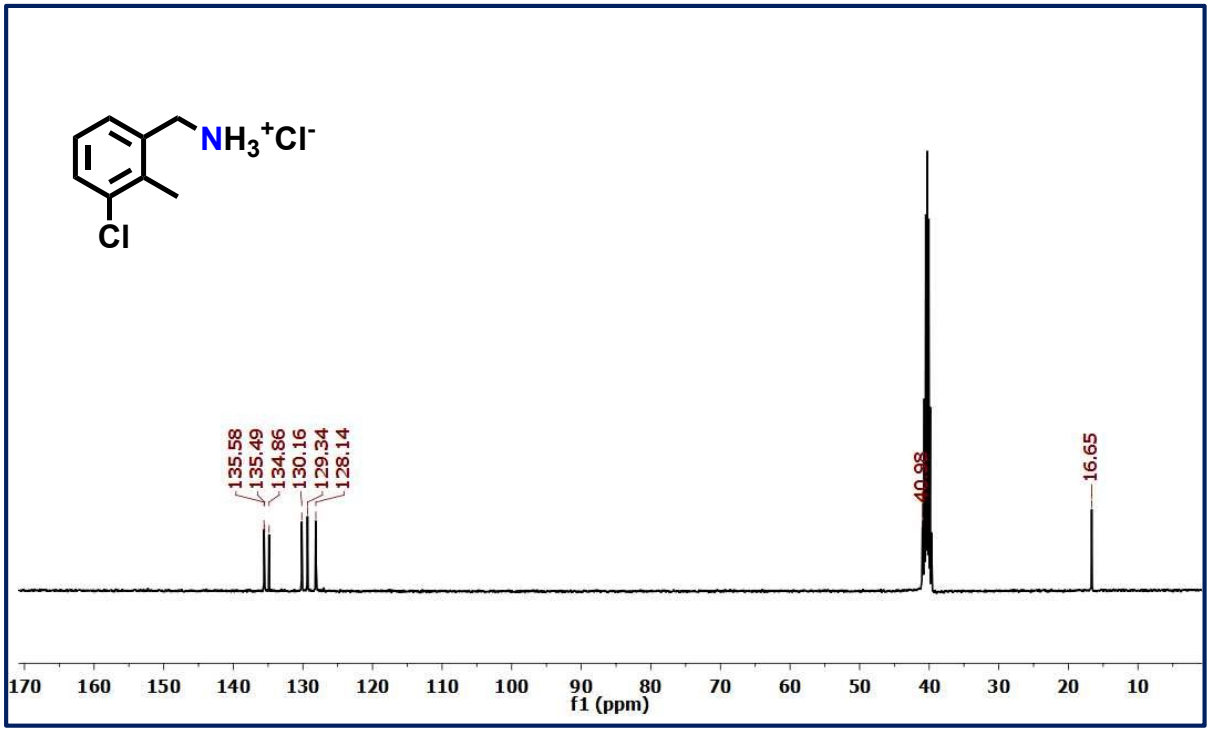


Figure S56. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (3-chloro-2-methylphenyl)methanamine Hydrochloride.

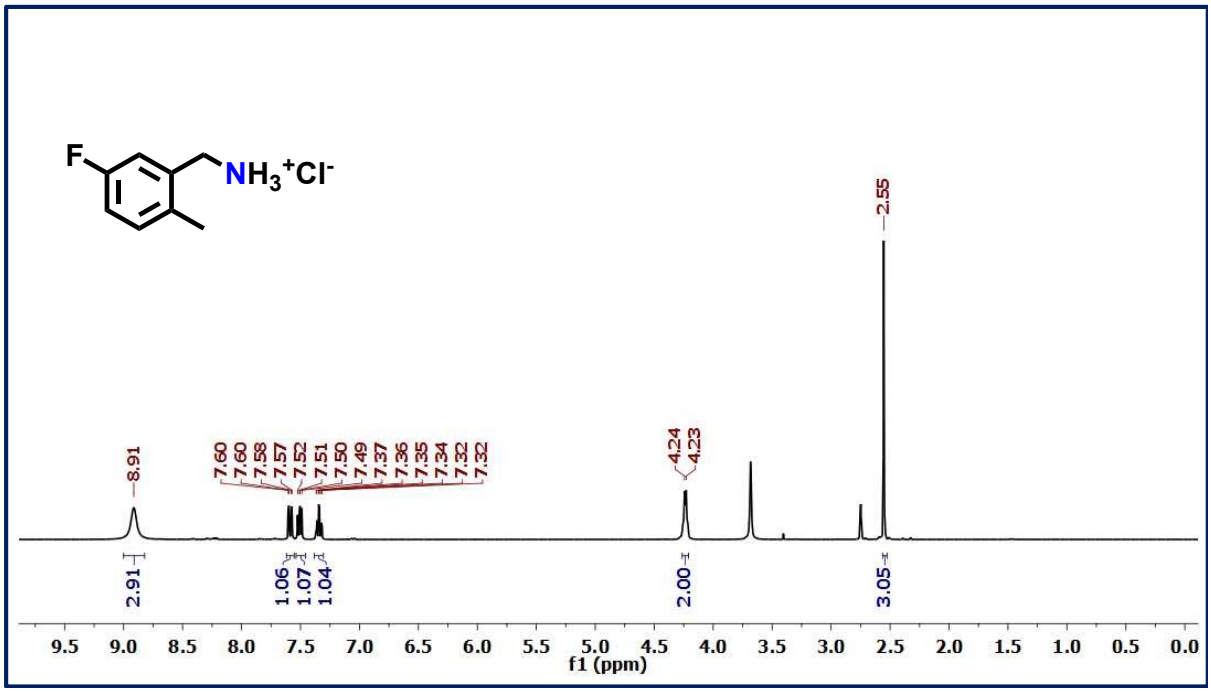


Figure S57.[1]H NMR spectrum (DMSO-d_6) of (5-fluro-2-methylphenyl)methanamine Hydrochloride.

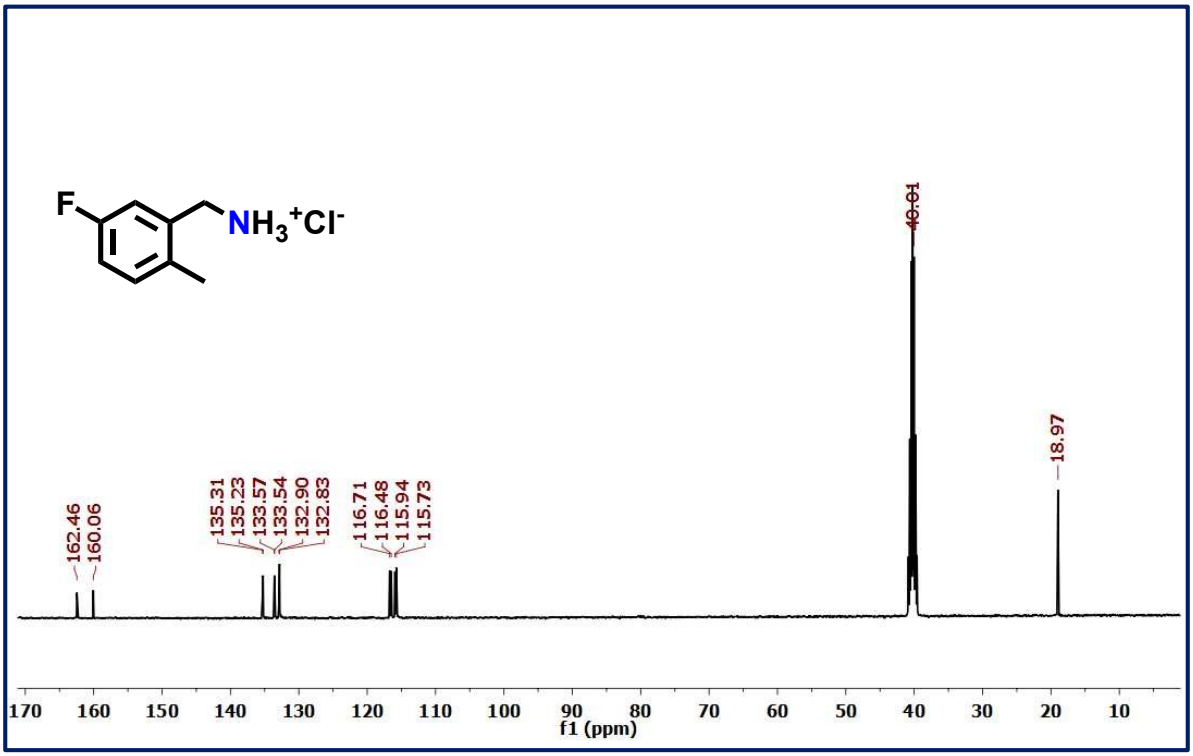


Figure S58. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (5-fluro-2-methylphenyl)methanamine Hydrochloride.

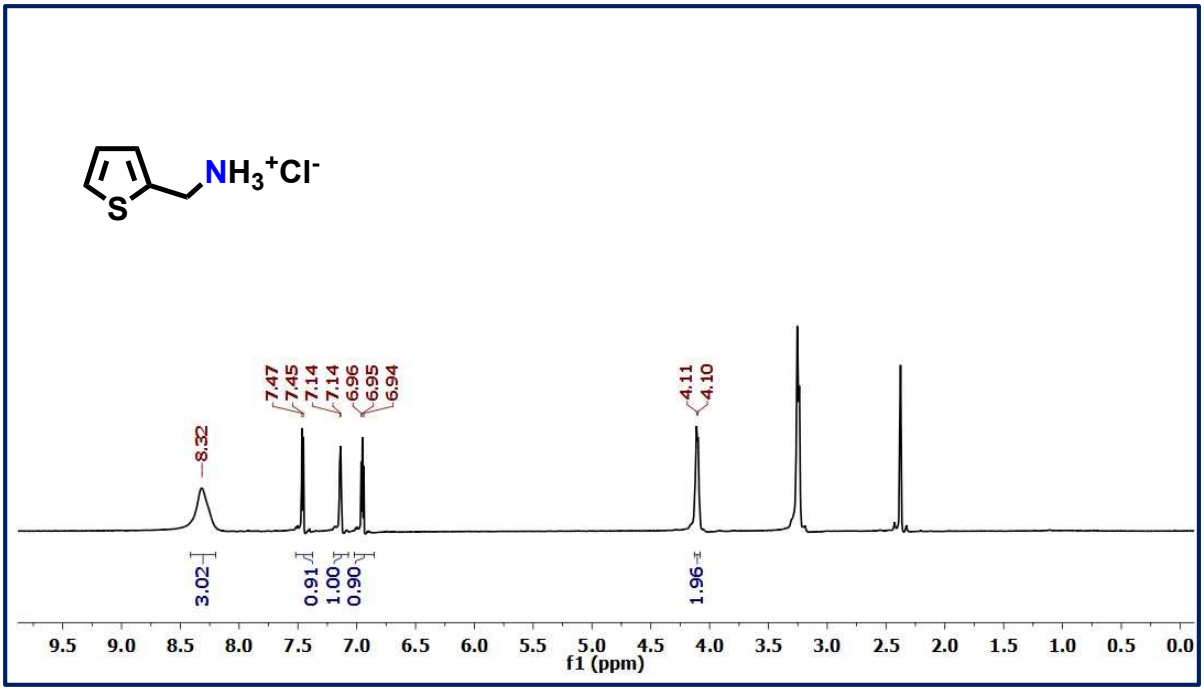


Figure S59.[1]H NMR spectrum (DMSO-d_6) of thiophen-2-ylmethanamine Hydrochloride.

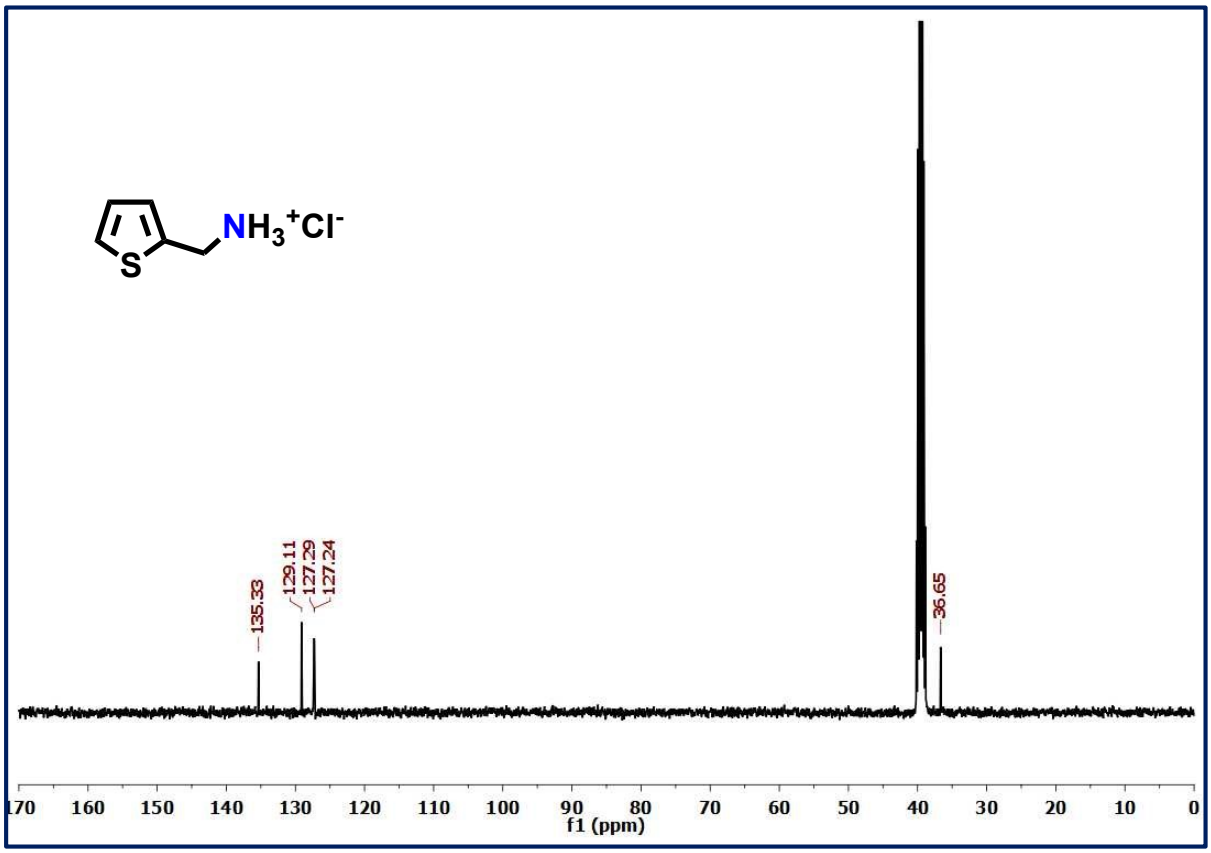


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) of thiophen-2-ylmethanamine Hydrochloride.

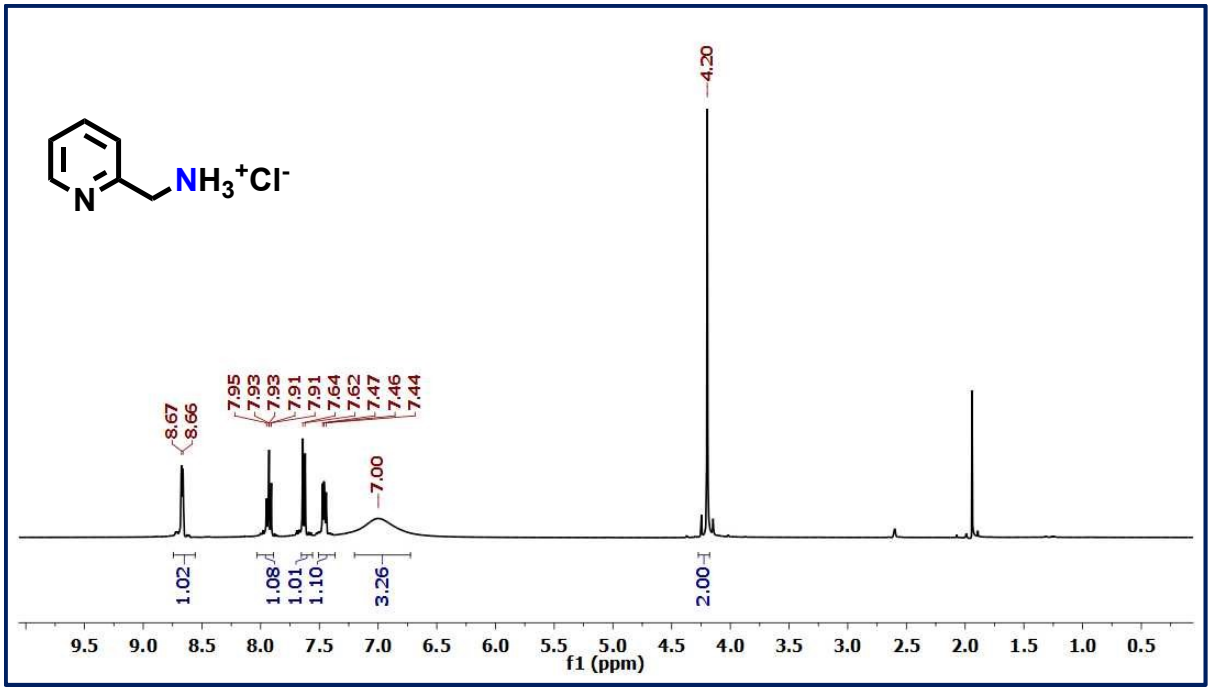


Figure S61.[1]H NMR spectrum (DMSO-d_6) of pyridine-2-ylmethanamine Hydrochloride.

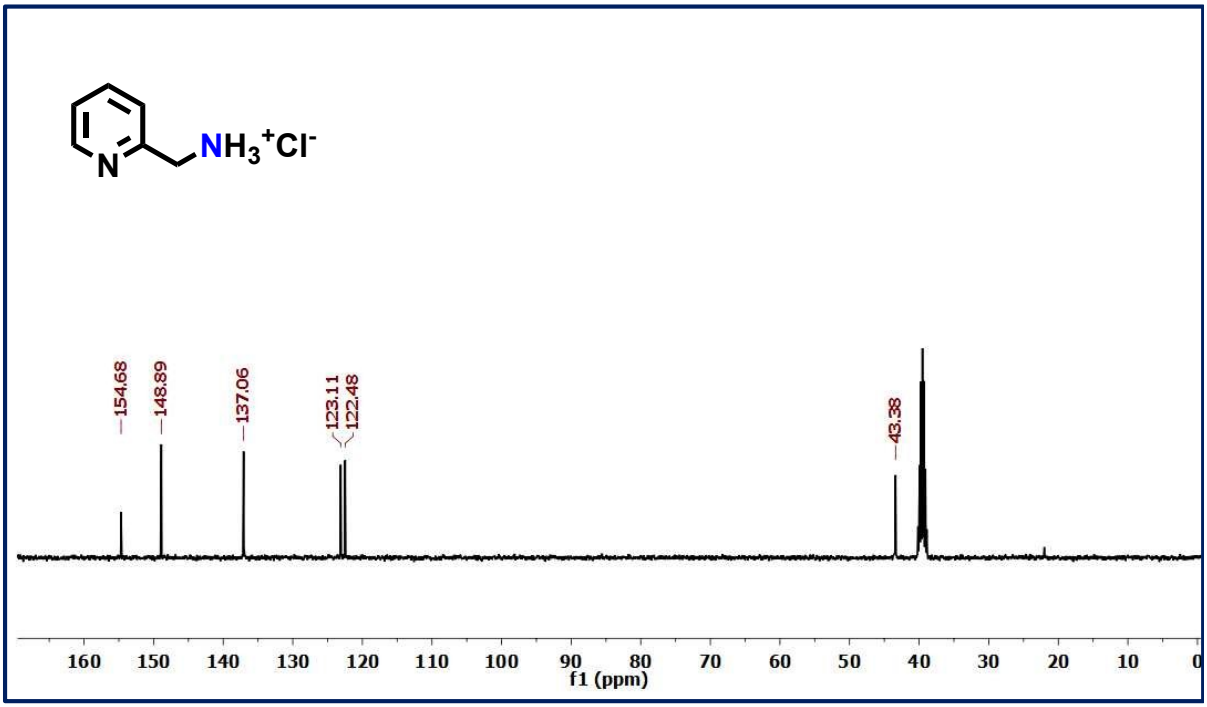


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) of pyridine-2-ylmethanamine Hydrochloride.

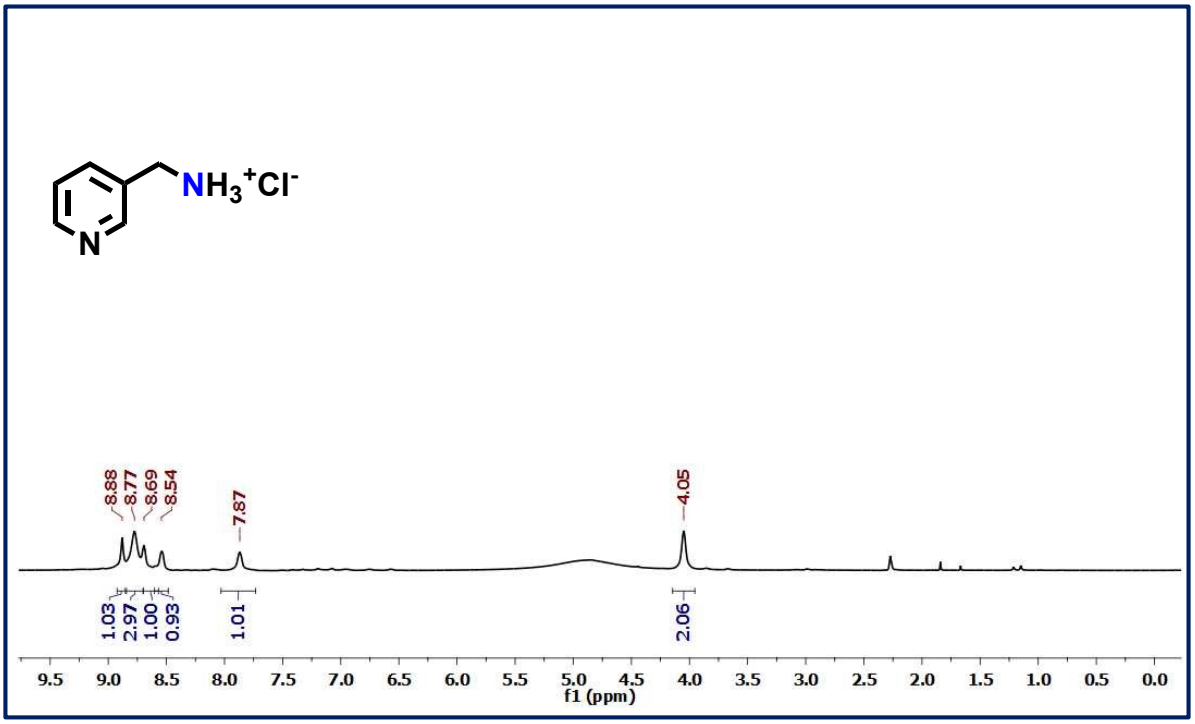


Figure S63.[1]H NMR spectrum (DMSO-d_6) of pyridine-3-ylmethanamine Hydrochloride.

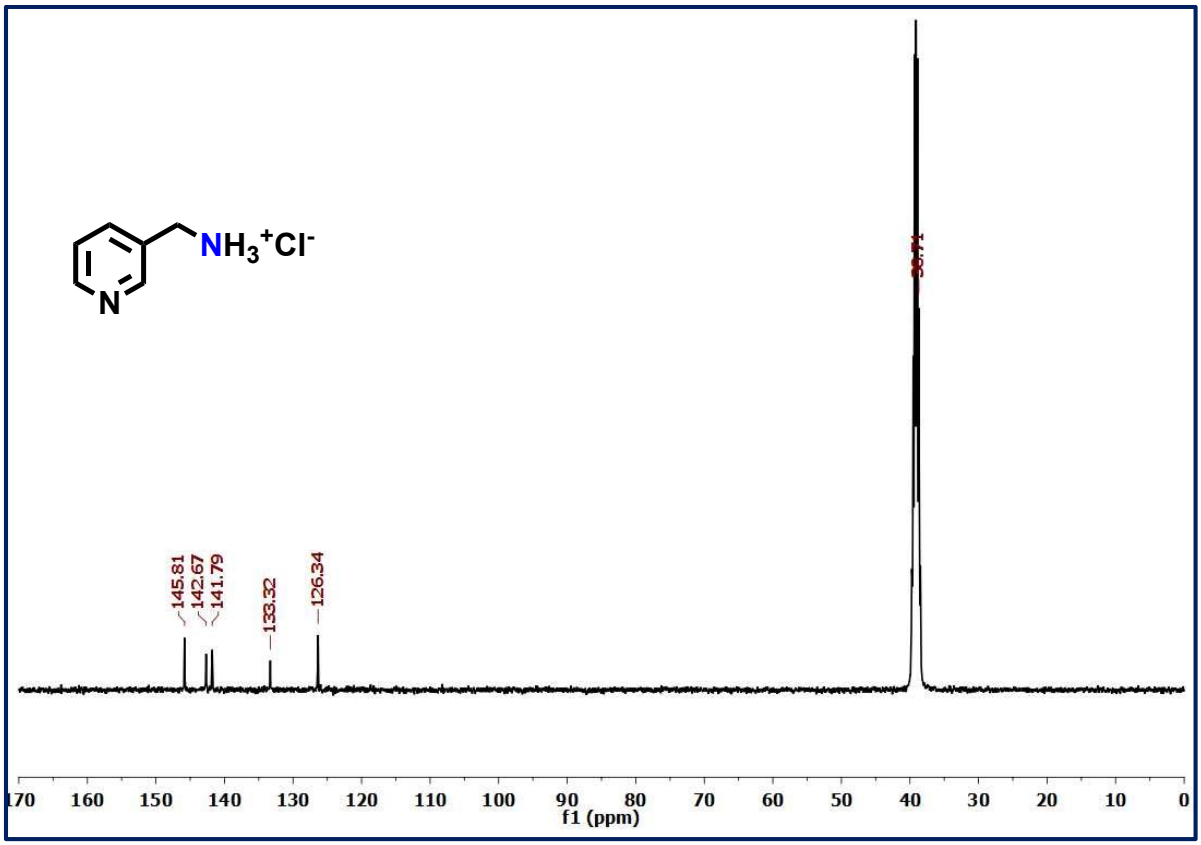


Figure S64. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of pyridine-3-ylmethanamine Hydrochloride.

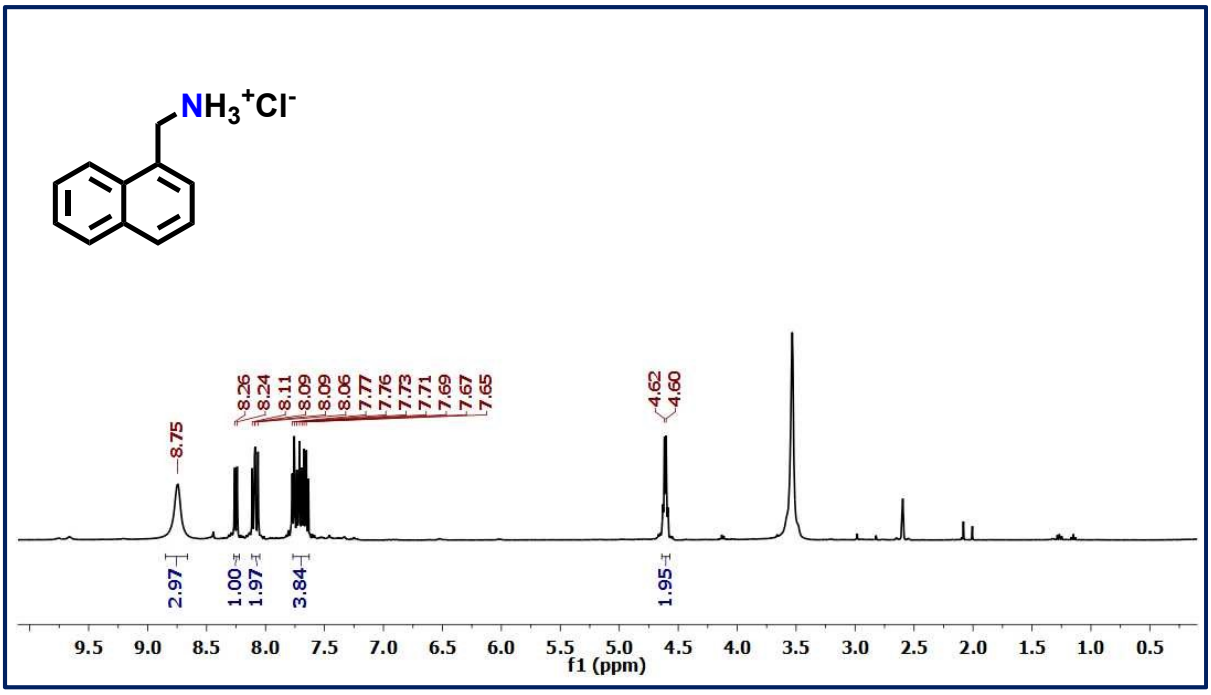


Figure S65.[1]H NMR spectrum (DMSO-d_6) of naphthalen-1-ylmethanamine Hydrochloride.

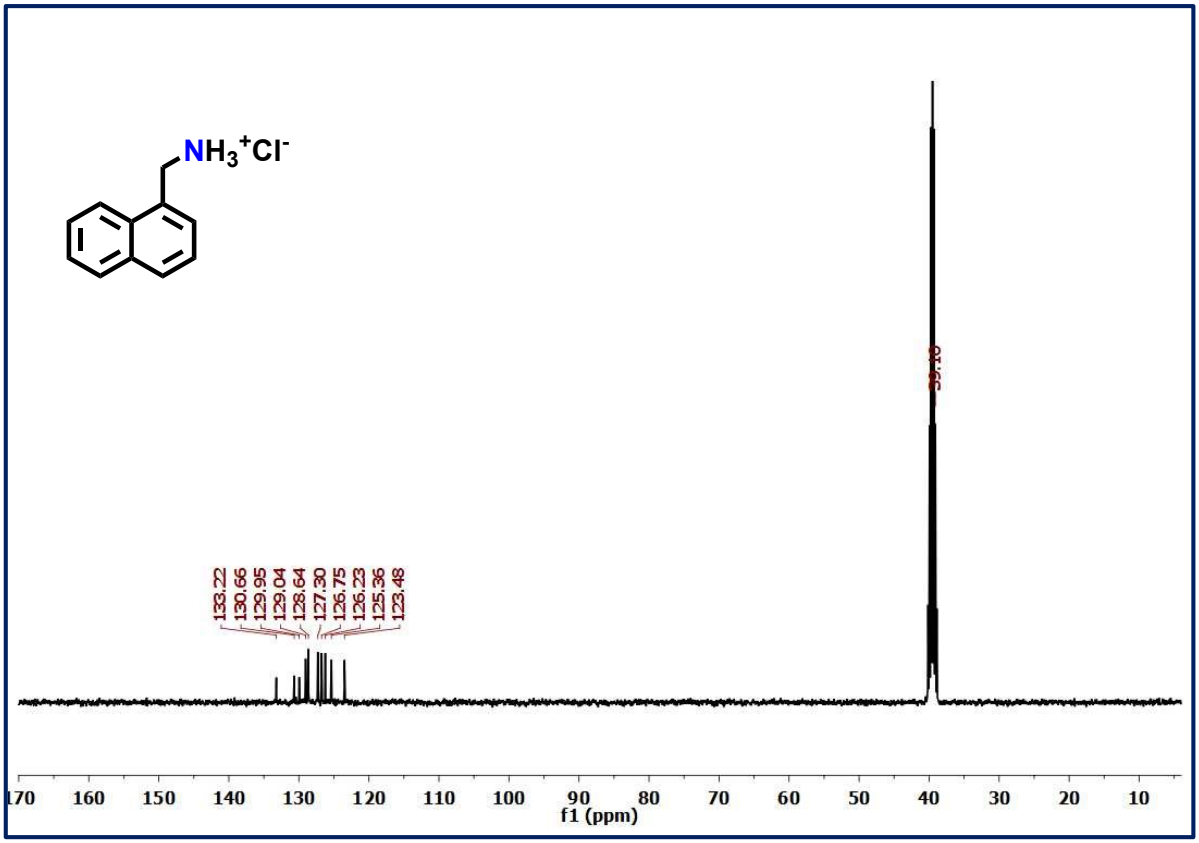


Figure S66. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of naphthalen-1-ylmethanamine Hydrochloride.

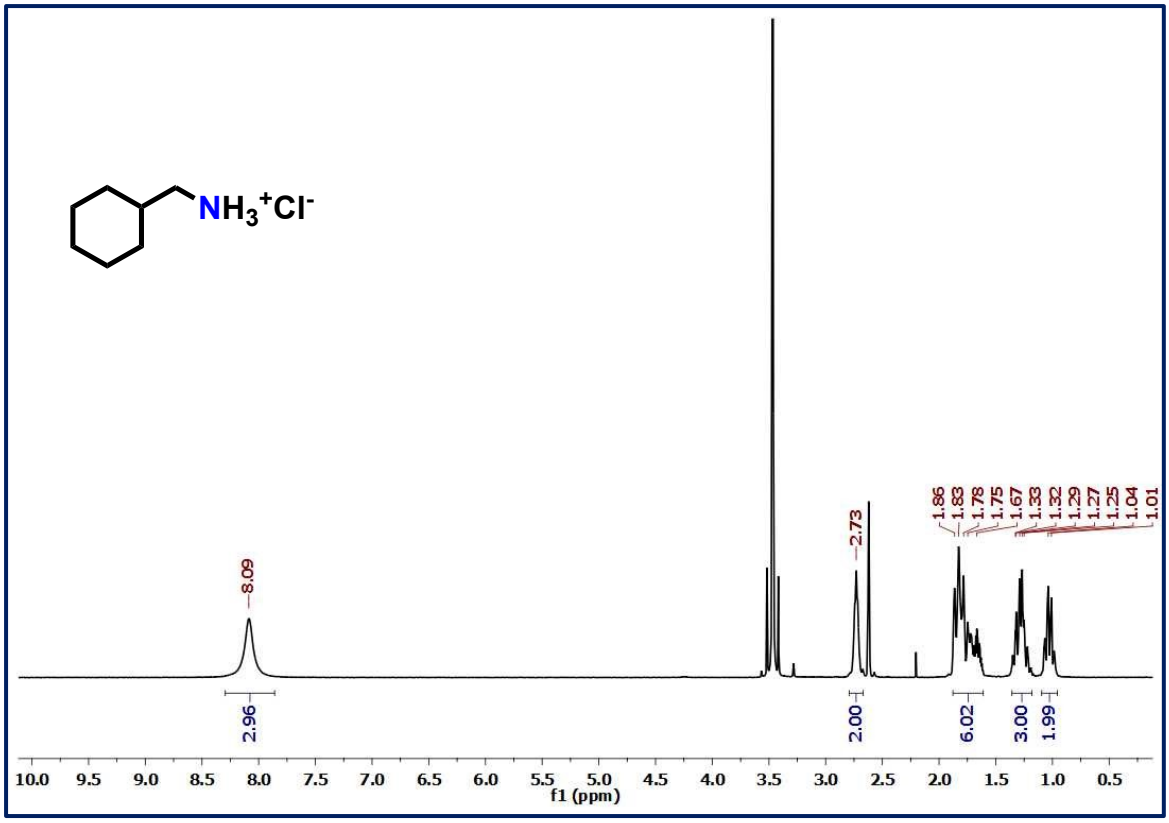


Figure S67.[1]H NMR spectrum (DMSO-d_6) of cyclohexylmethanamine hydrochloride.

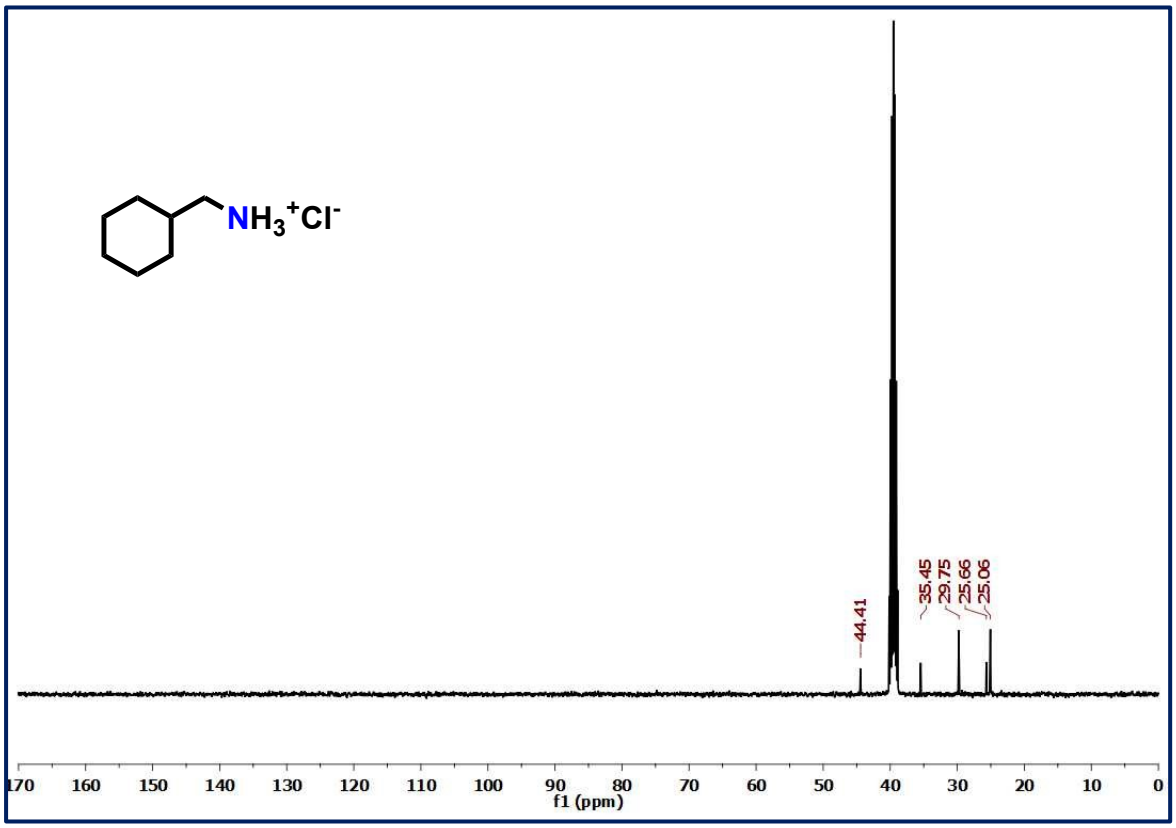


Figure S68. [13]C{[1]H} NMR spectrum (DMSO-d_6) of cyclohexylmethanamine hydrochloride.

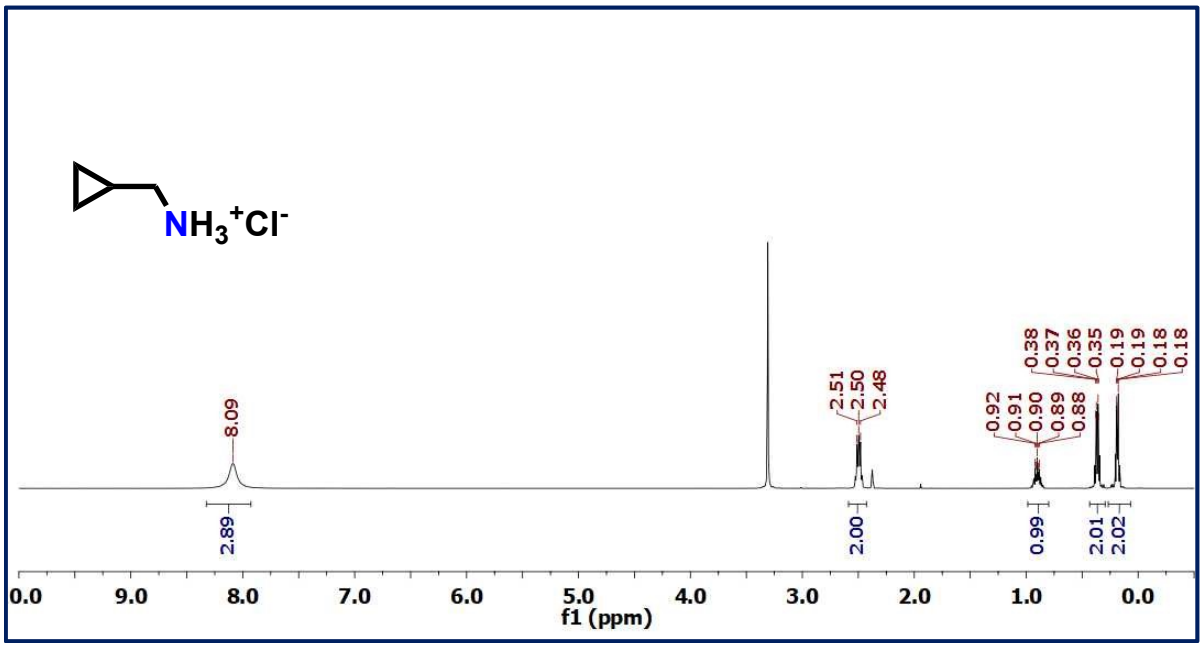


Figure S69.[1]H NMR spectrum (DMSO-d_6) of cyclopropylmethanamine hydrochloride.

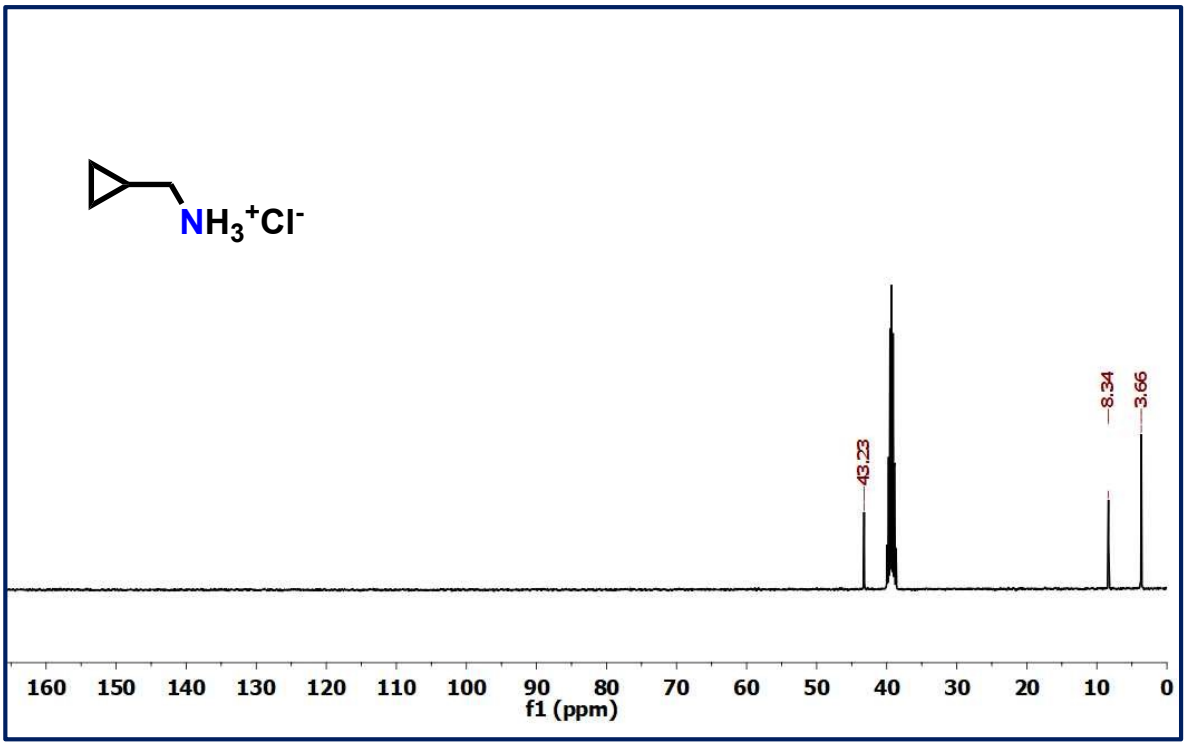


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) of cyclopropylmethanamine hydrochloride.

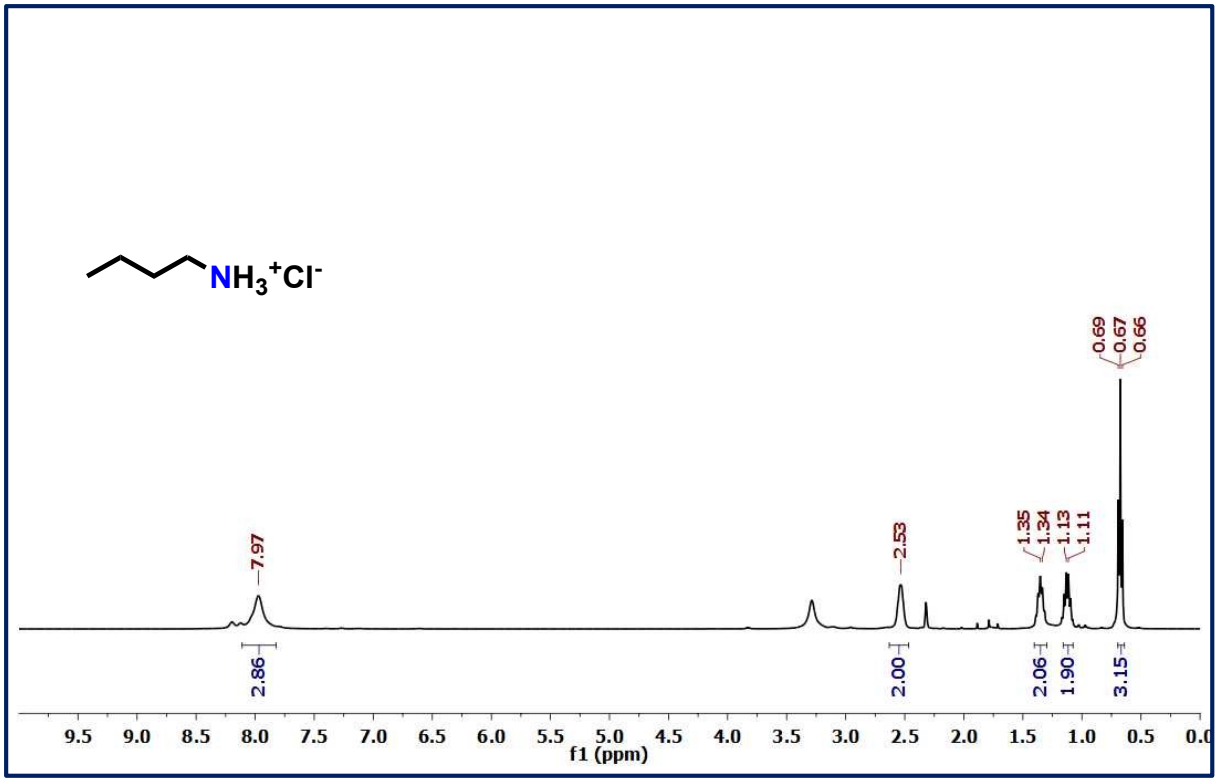


Figure S71.^{1}H NMR spectrum (DMSO-d_6) of butan-1-amine hydrochloride.

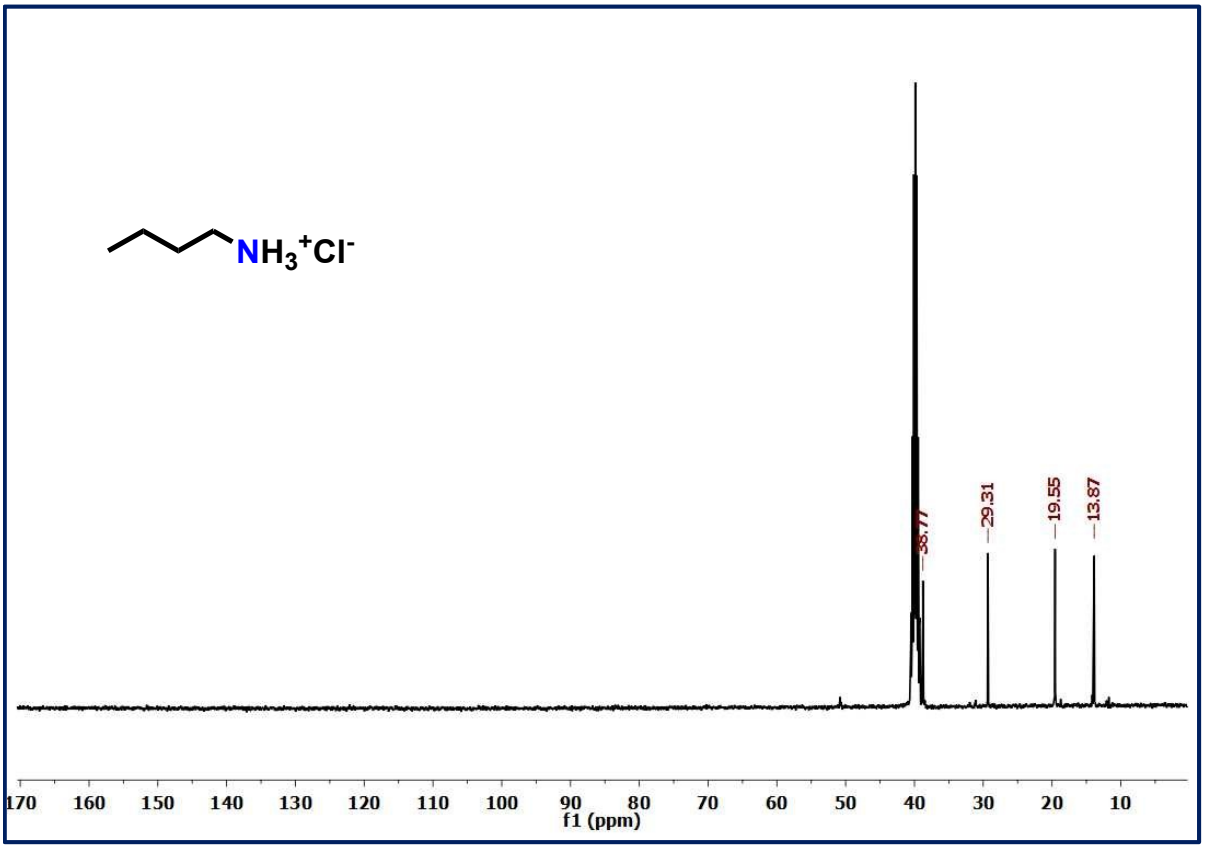


Figure S72. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of butan-1-amine hydrochloride.

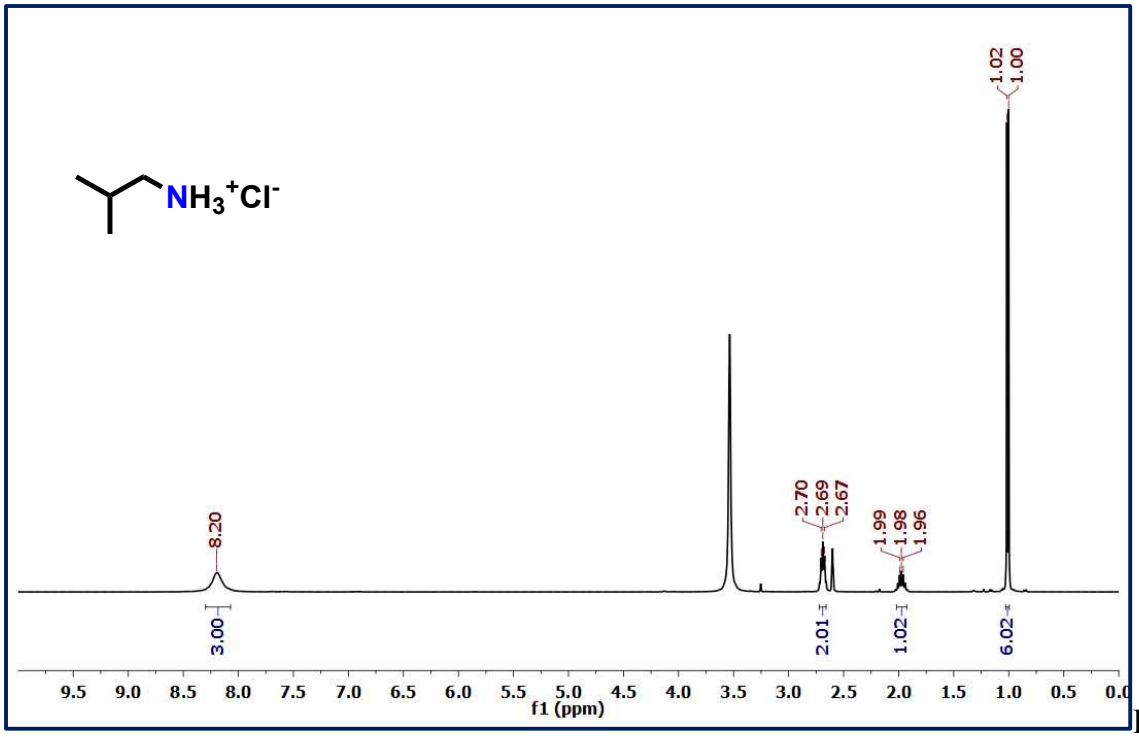


Figure S73. ^{1}H NMR spectrum (DMSO-d_6) of 2-methylpropan-1-amine hydrochloride.

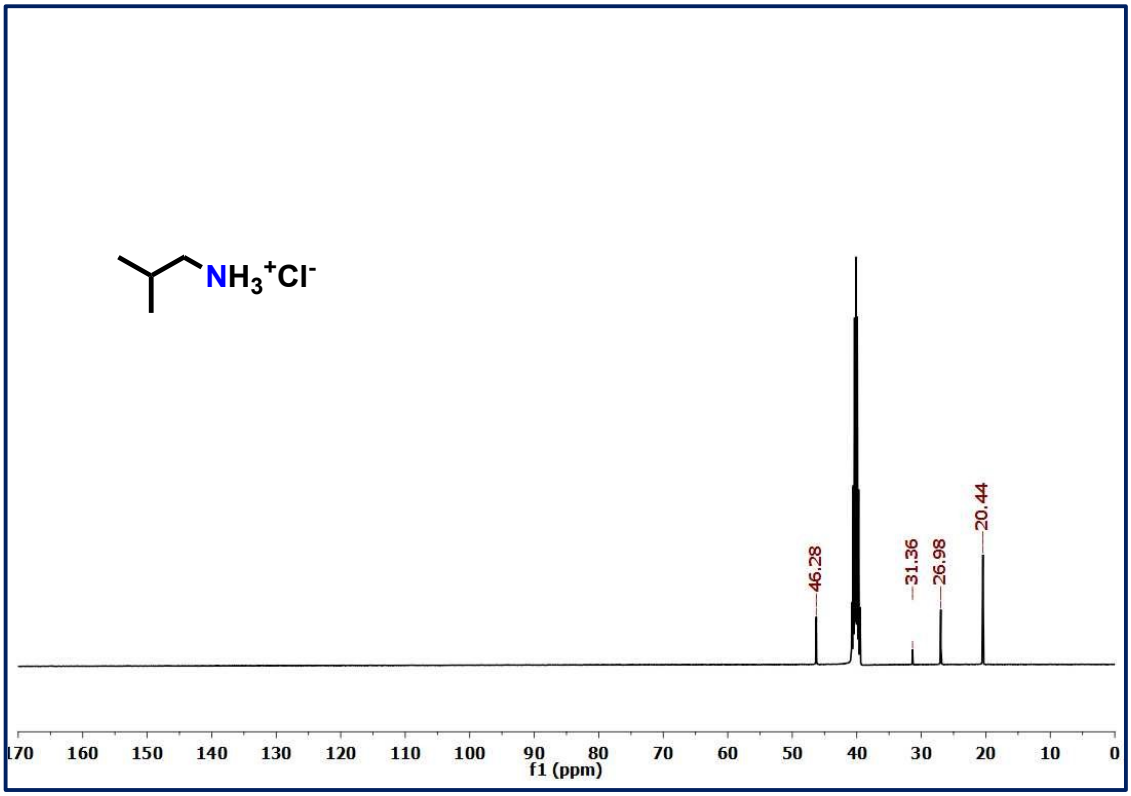


Figure S74. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of 2-methylpropan-1-amine hydrochloride.

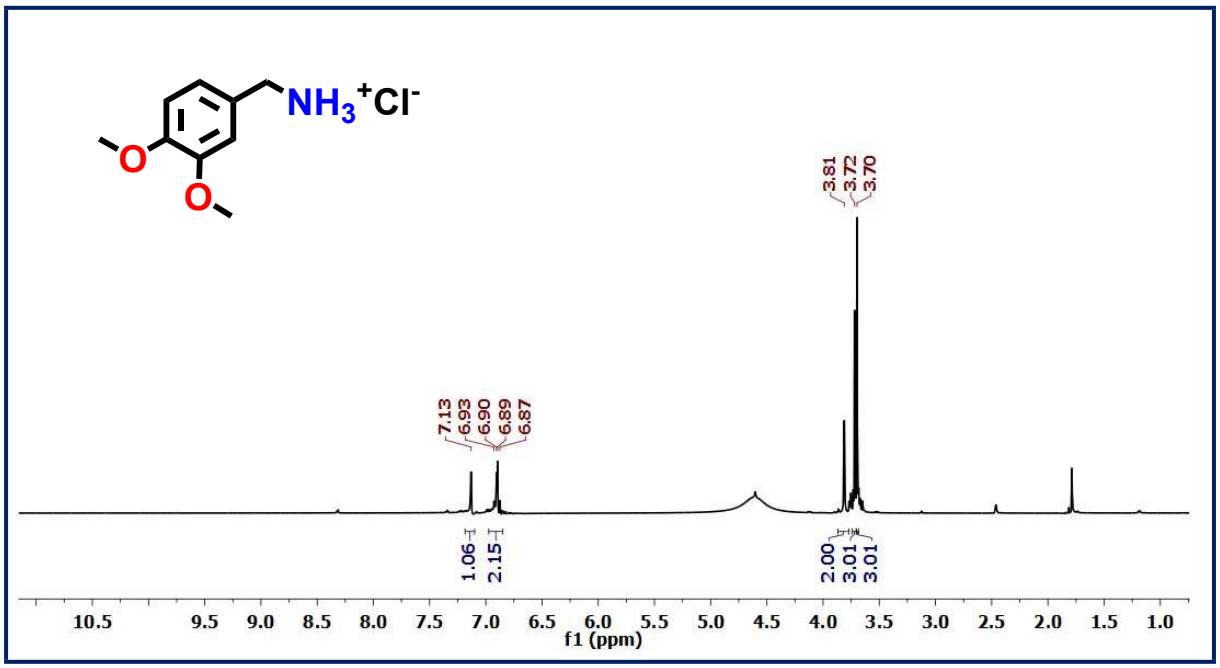


Figure S75.[1]H NMR spectrum (DMSO-d_6) of (3,4-dimethoxyphenyl)methanamine hydrochloride.

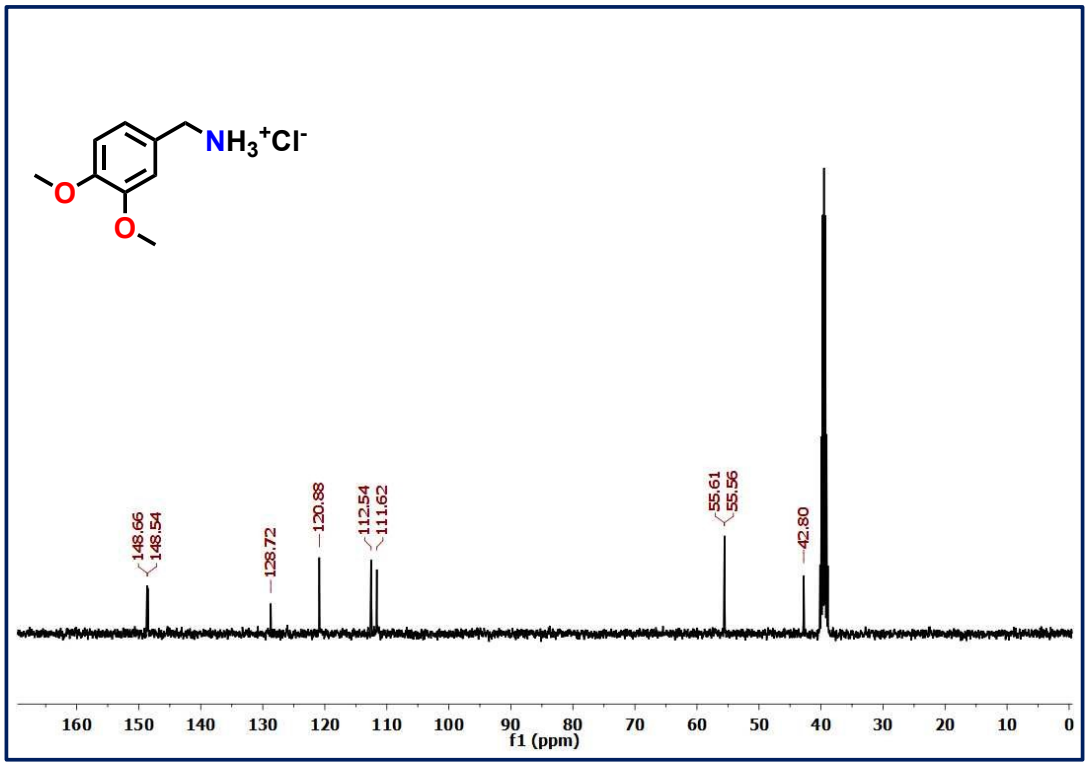


Figure S76. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (3,4-dimethoxyphenyl)methanamine hydrochloride.

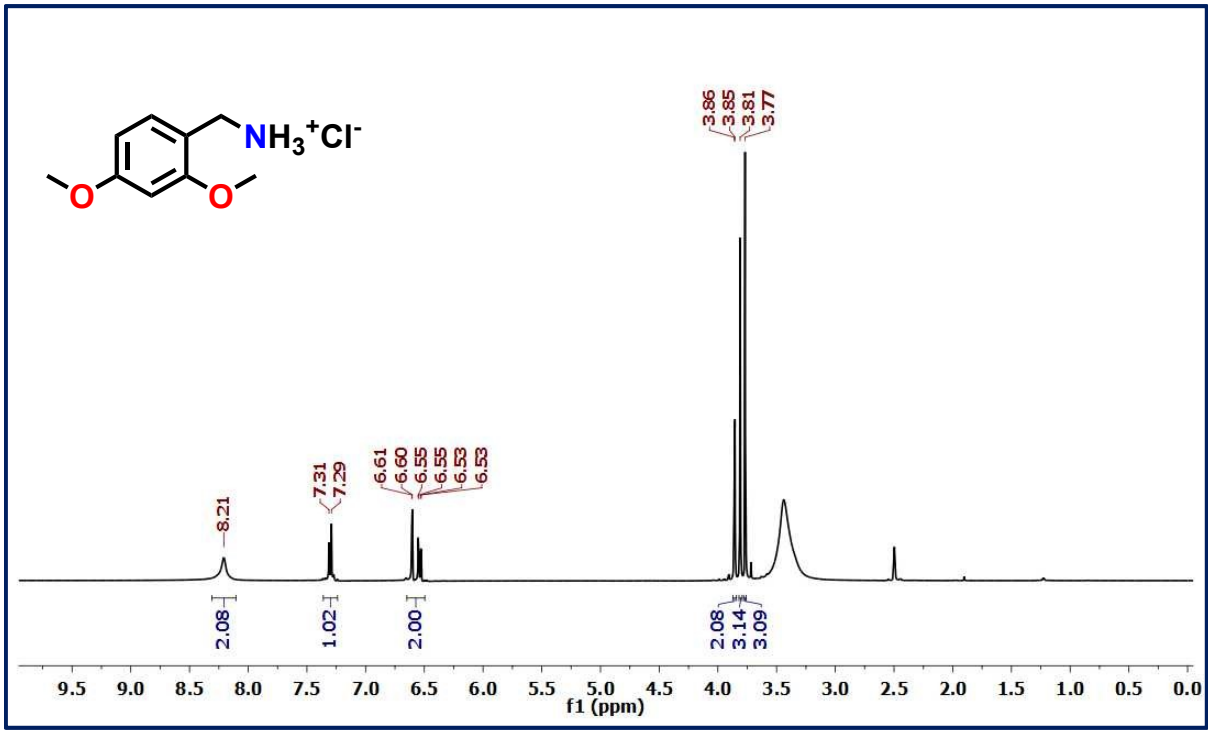


Figure S77.[1]H NMR spectrum (DMSO-d_6) of (2,4-dimethoxyphenyl)methanamine hydrochloride.

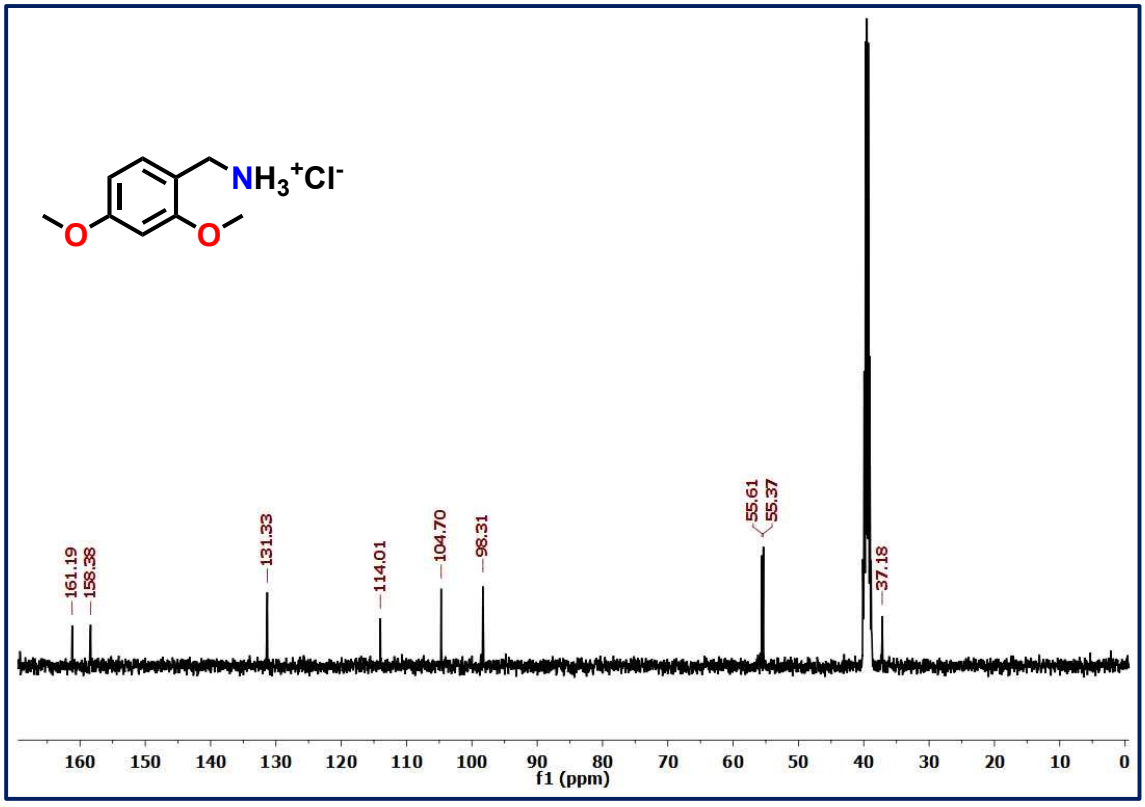


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) of (2,4-dimethoxyphenyl)methanamine hydrochloride.

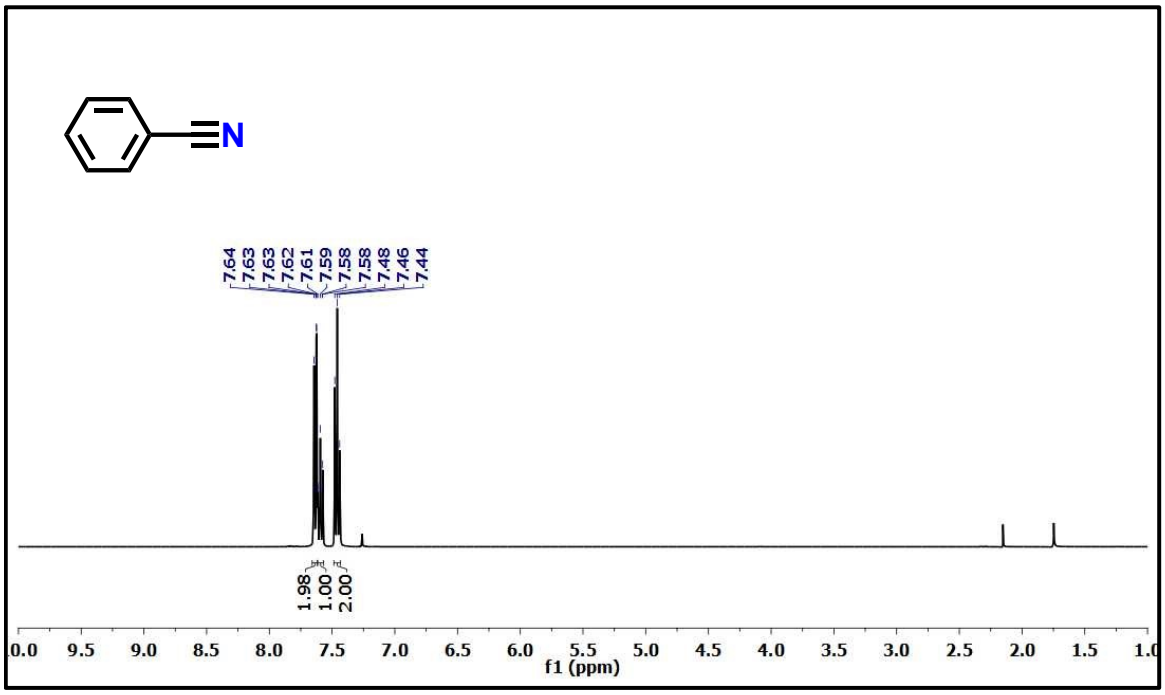


Figure S79.[1]H NMR spectrum ($CDCl_3$) of benzonitrile.

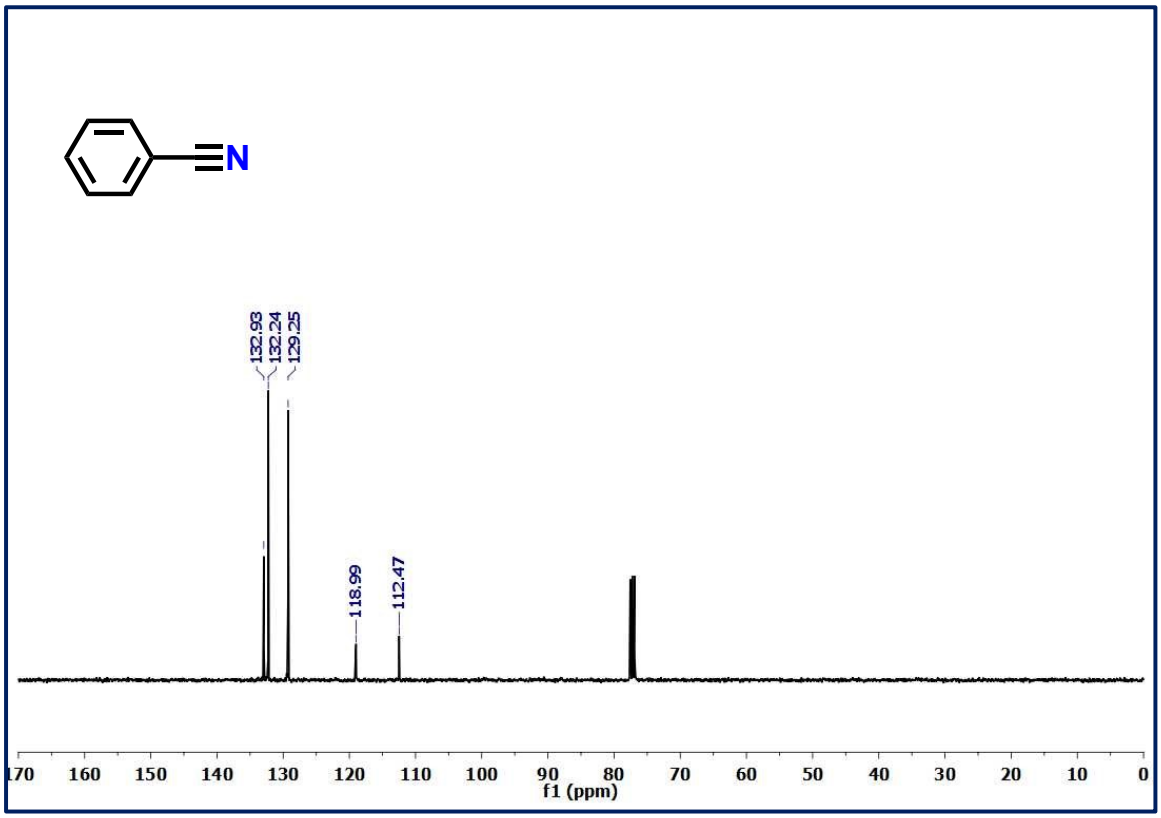


Figure S80. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of benzonitrile.

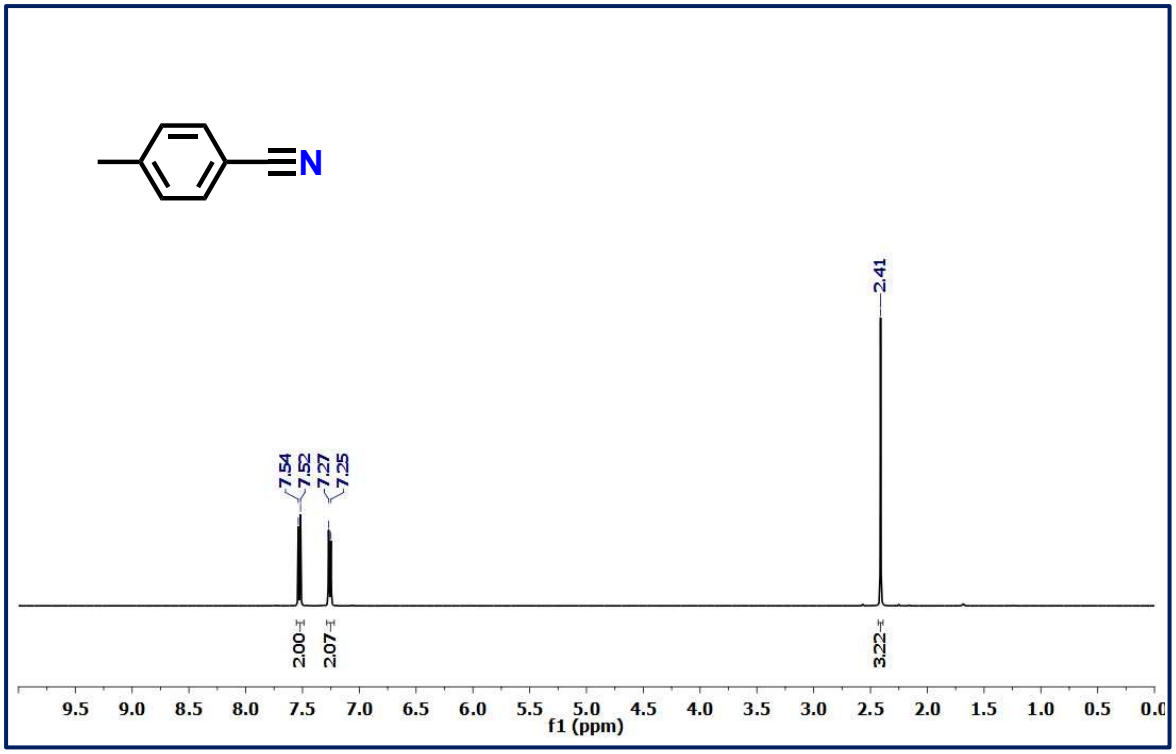


Figure S81.[1]H NMR spectrum ($CDCl_3$) of 4-methyl benzonitrile.

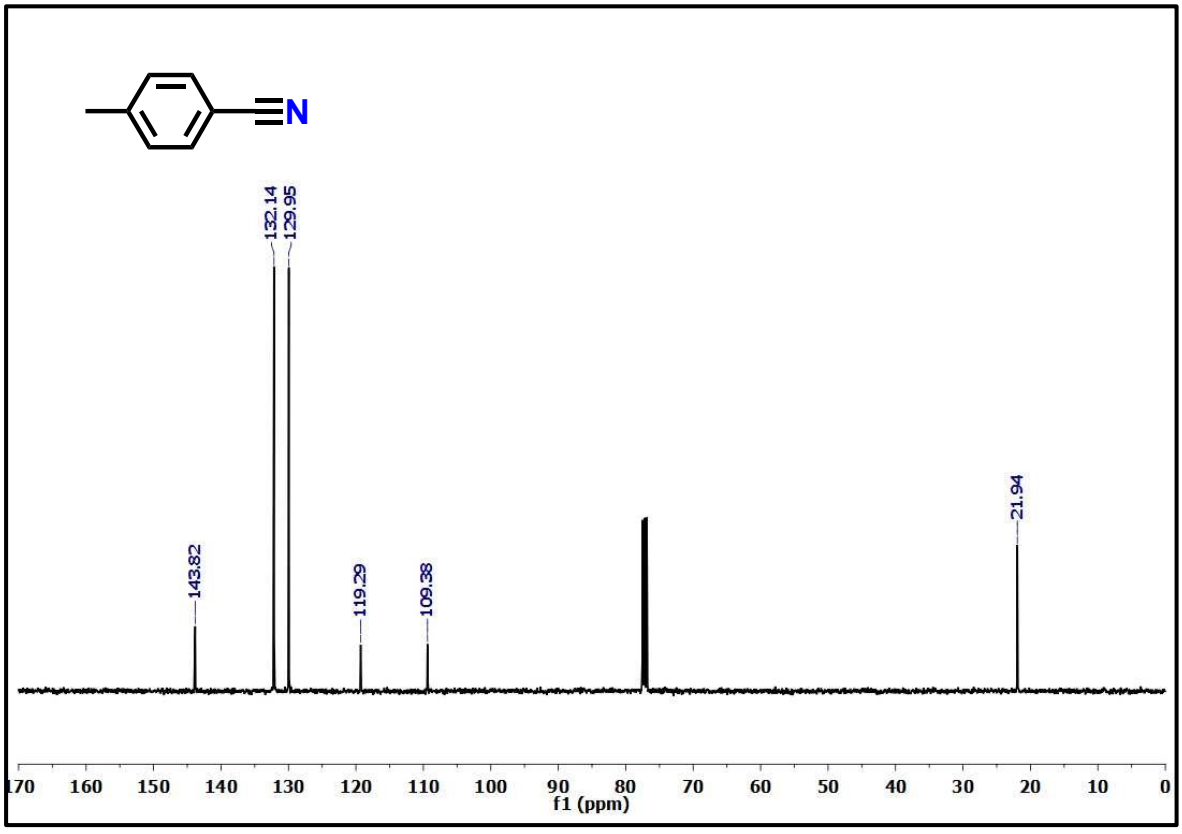


Figure S82. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of 4-methyl benzonitrile.

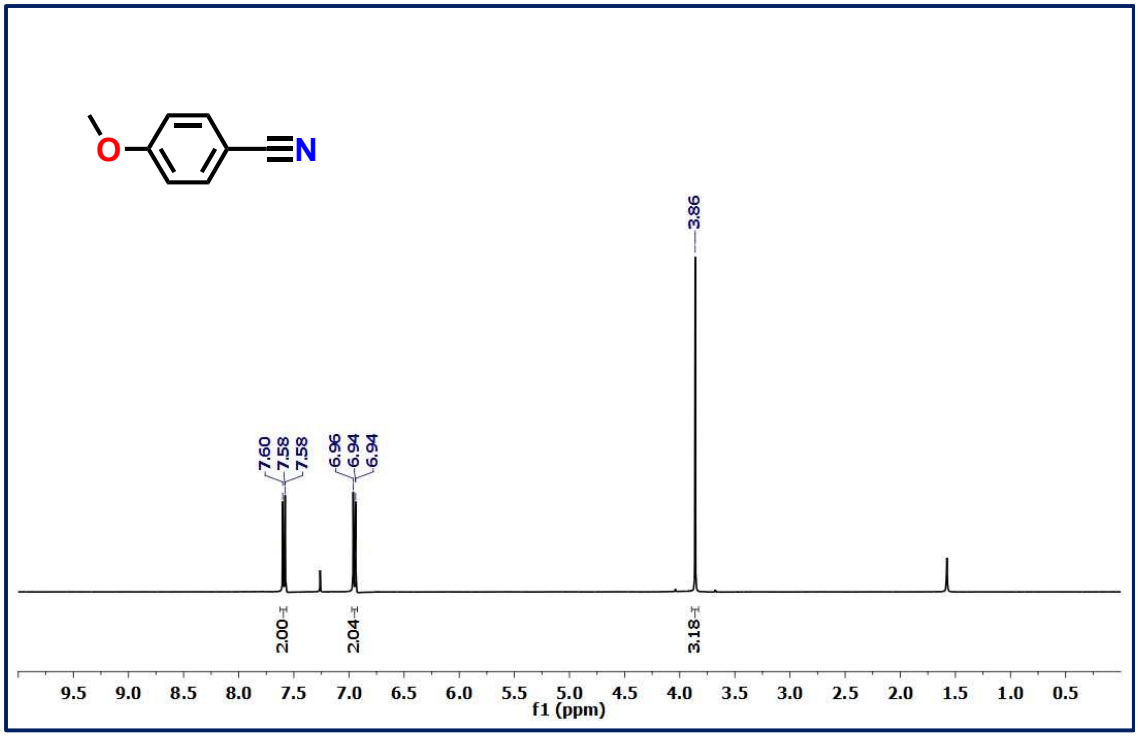


Figure S83.[1]H NMR spectrum ($CDCl_3$) of 4-methoxy benzonitrile.

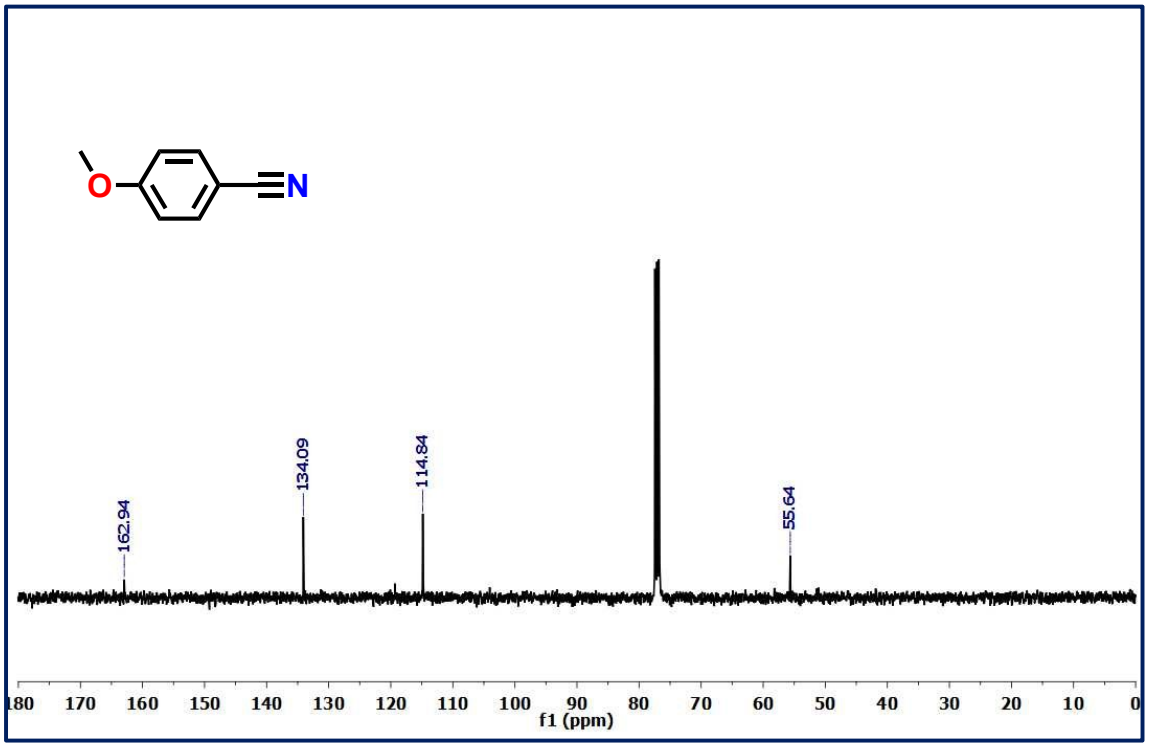


Figure S84. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of 4-methoxy benzonitrile.

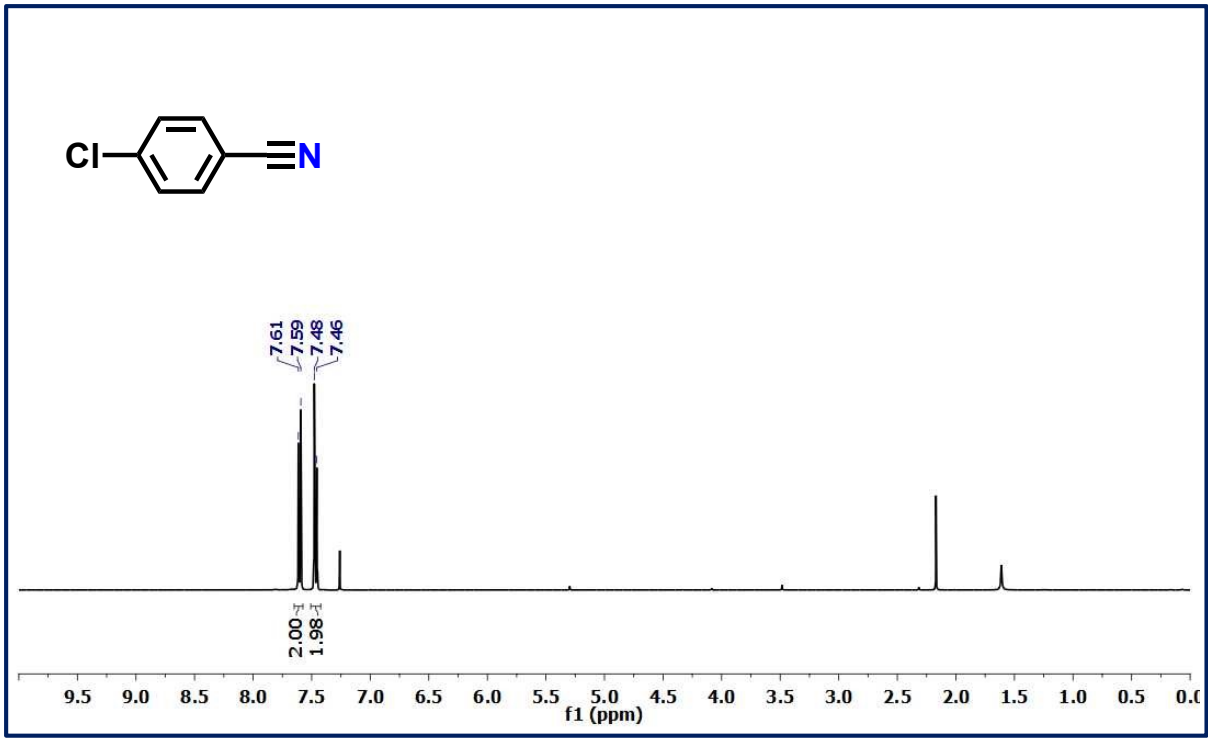


Figure S85.[1]H NMR spectrum ($CDCl_3$) of 4-chloro benzonitrile.

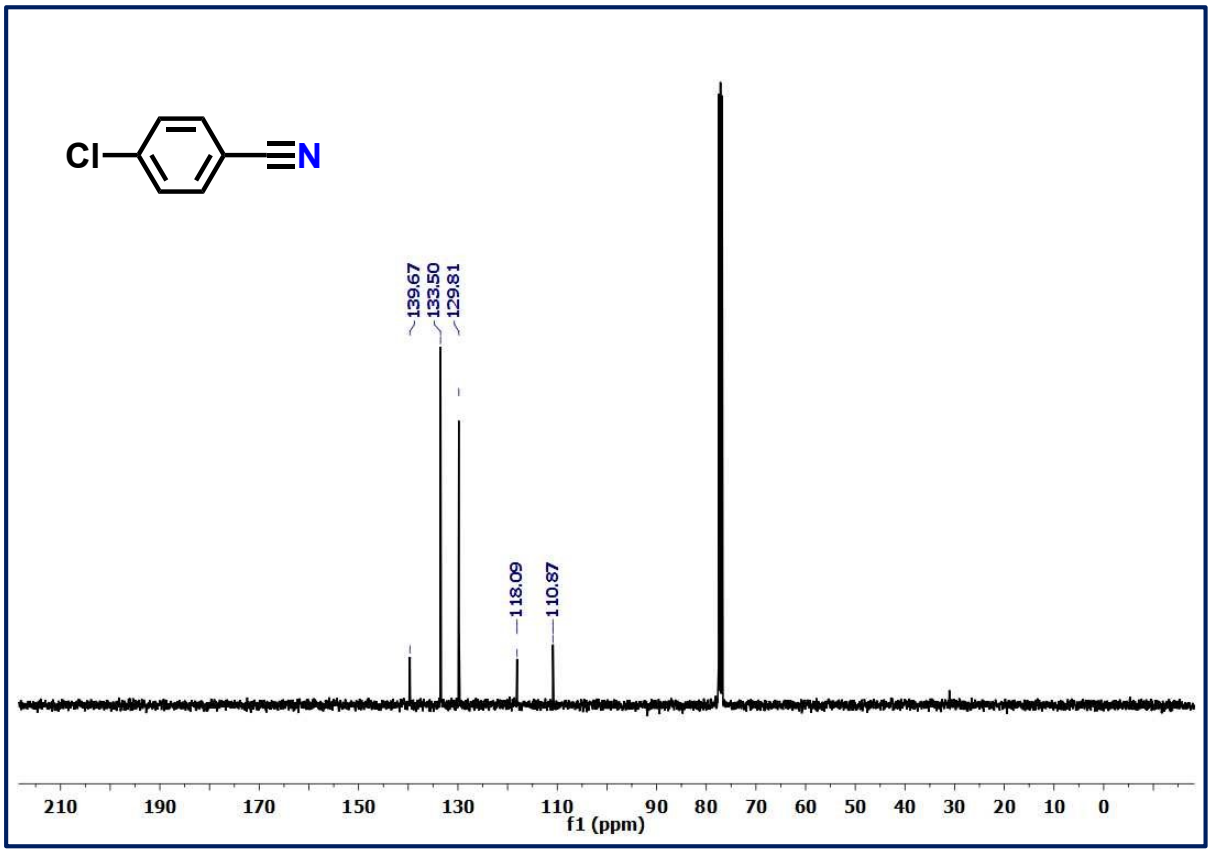


Figure S86. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of 4-chloro benzonitrile.

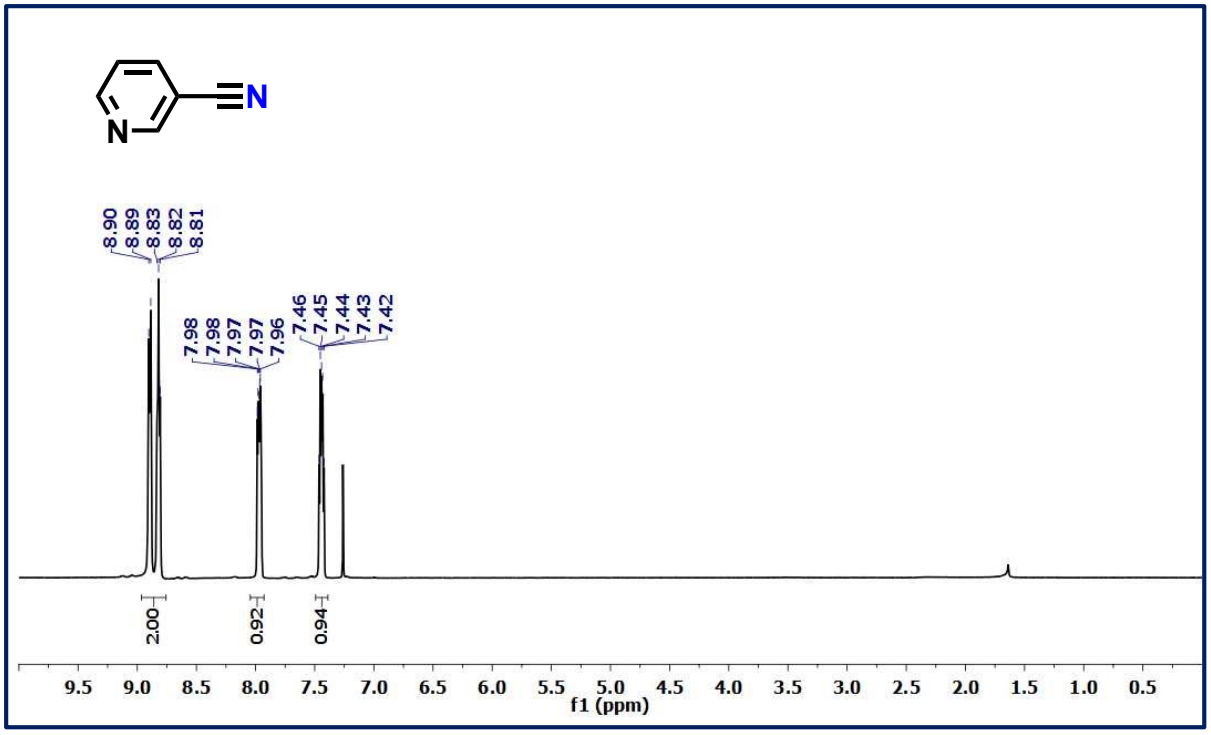


Figure S87.[1]H NMR spectrum ($CDCl_3$) of 3-pyridine carbonitrile.

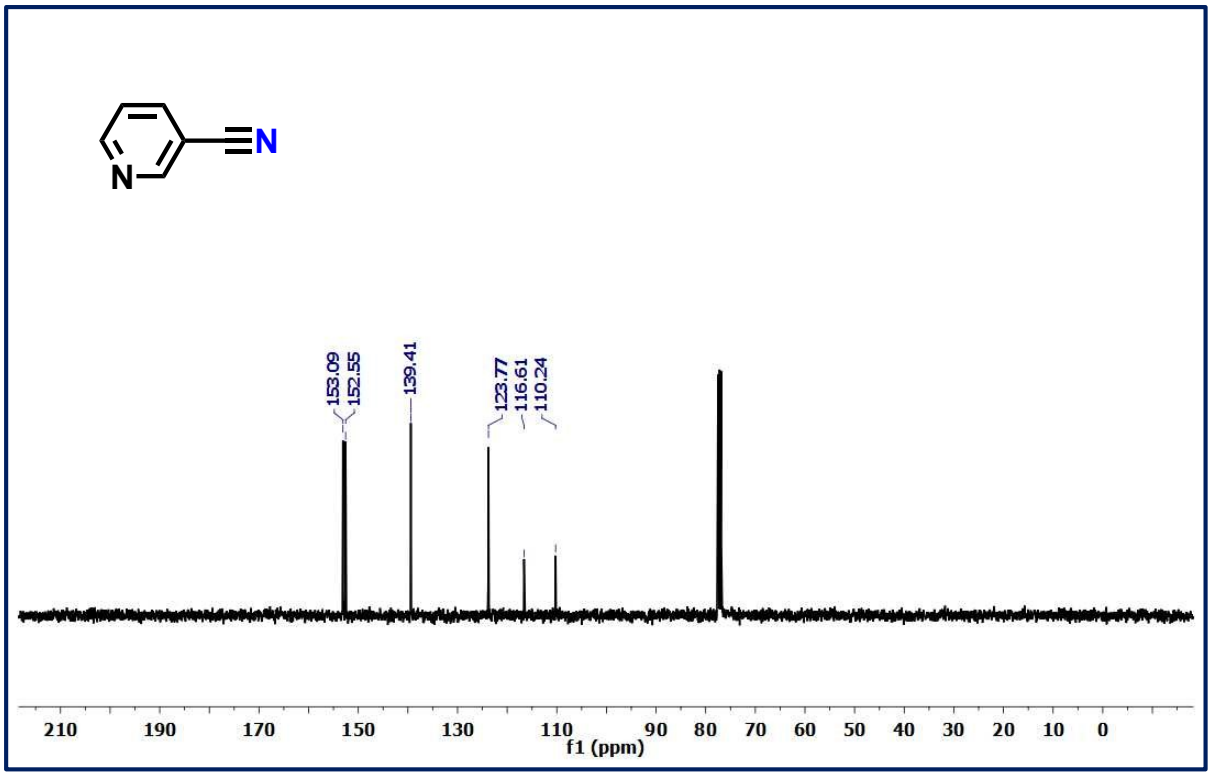


Figure S88. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of 3-pyridinecarbonitrile.

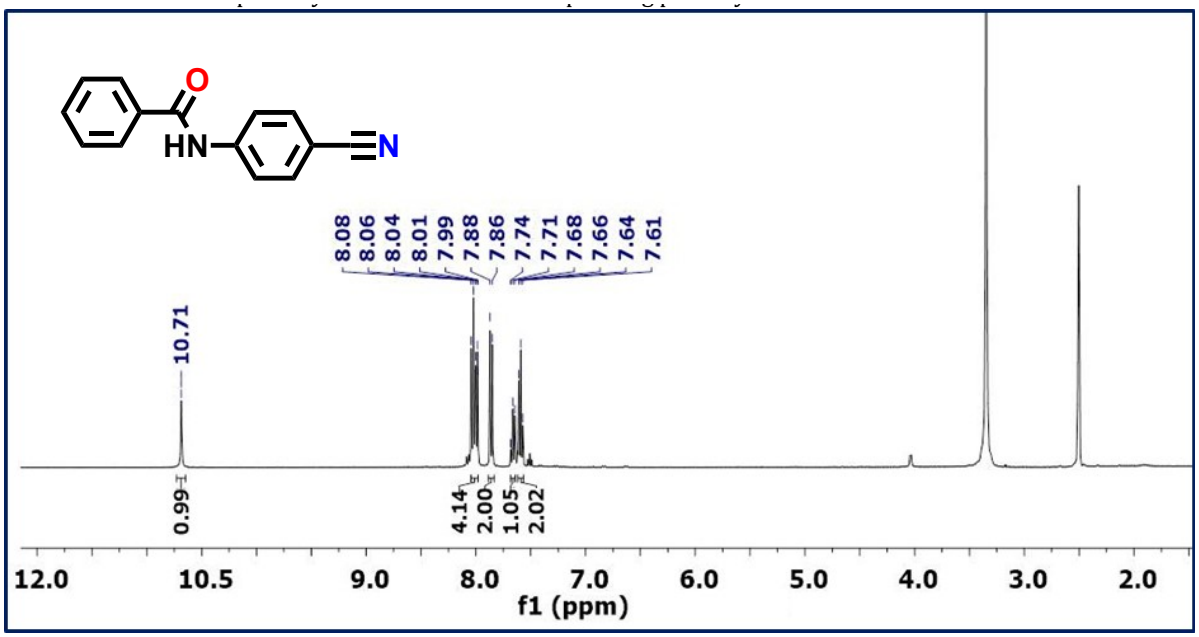


Figure S89.[1]H NMR spectrum ($CDCl_3$) of N-(4-cyanophenyl)benzamide.

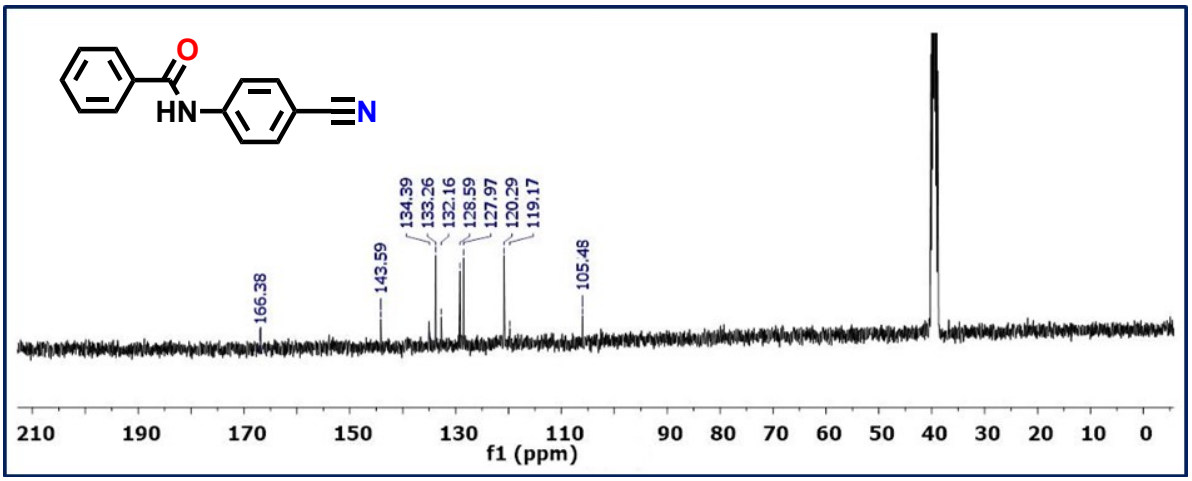


Figure S90. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of N-(4-cyanophenyl)benzamide.

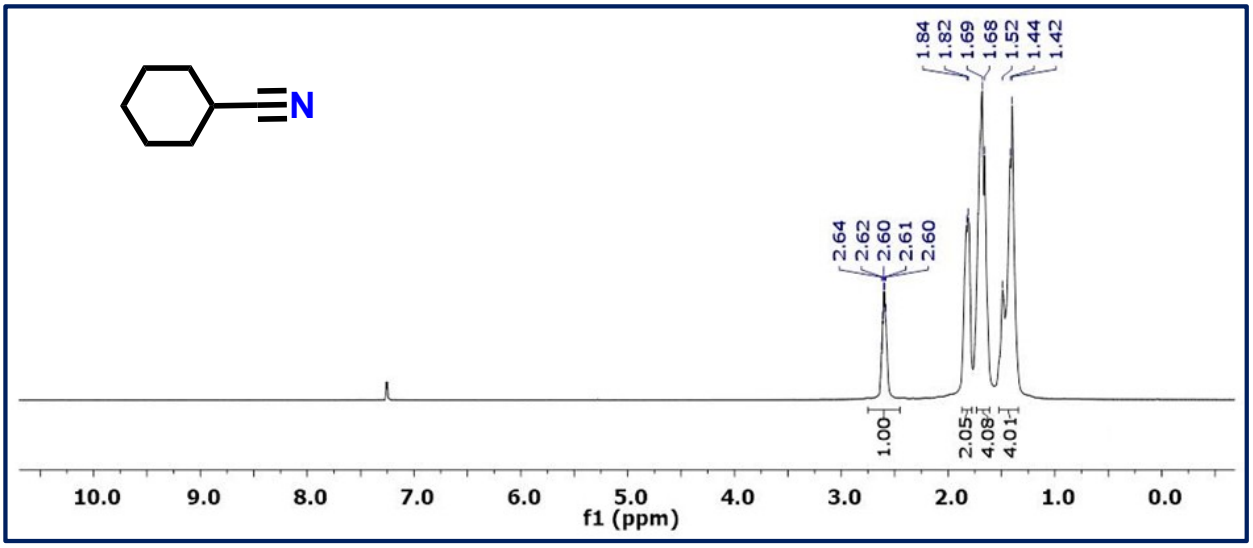


Figure S91.[1]H NMR spectrum ($CDCl_3$) of Cyclohexanecarbonitrile.

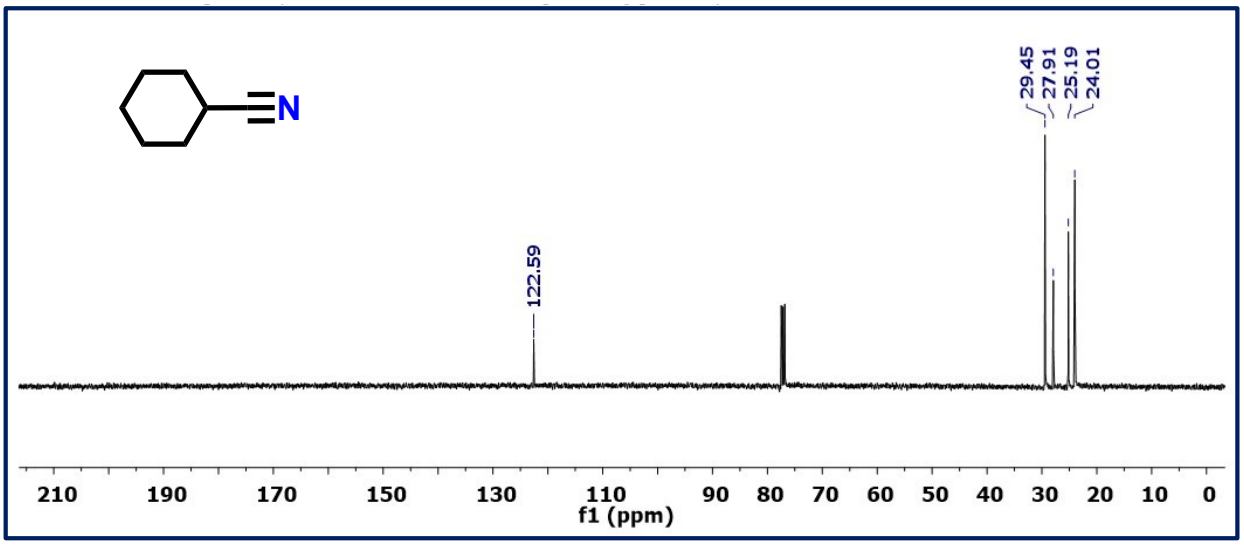


Figure S92. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of Cyclohexanecarbonitrile.

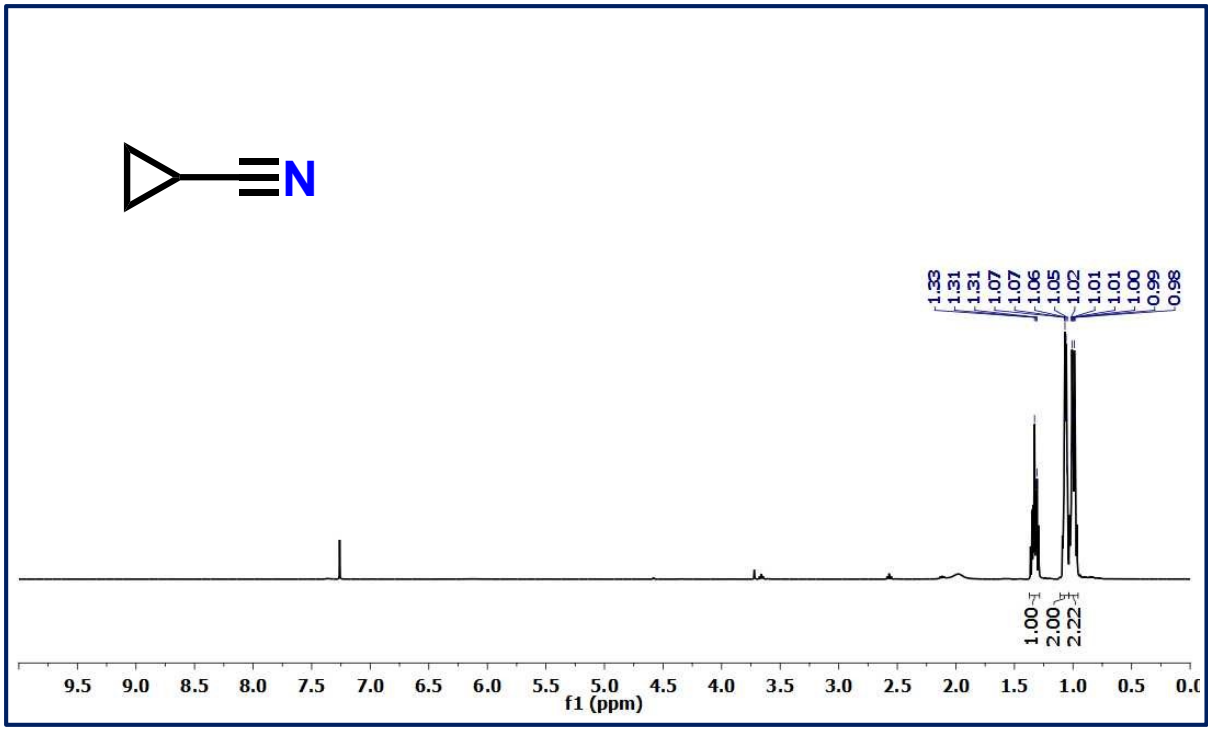


Figure S93.[1]H NMR spectrum ($CDCl_3$) of cyclopropanecarbonitrile.

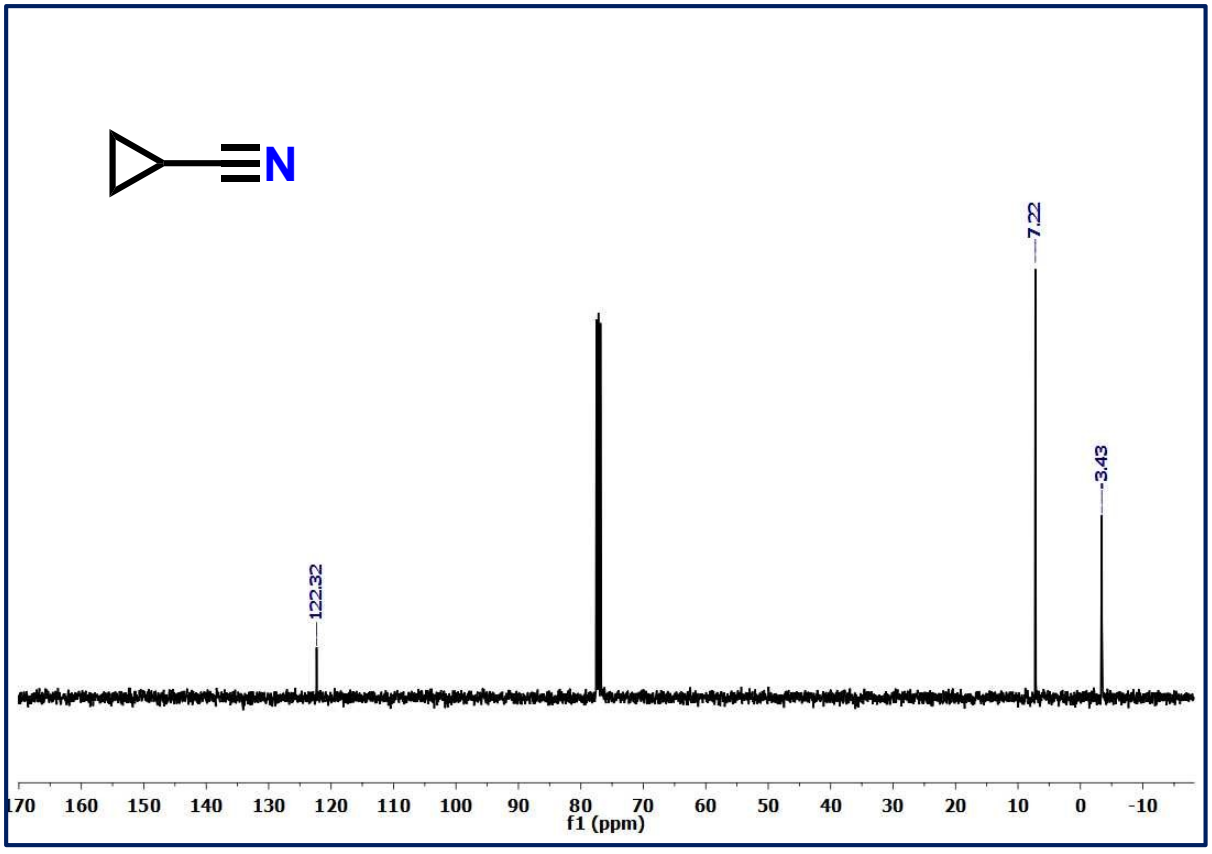


Figure S94. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of cyclopropanecarbonitrile.

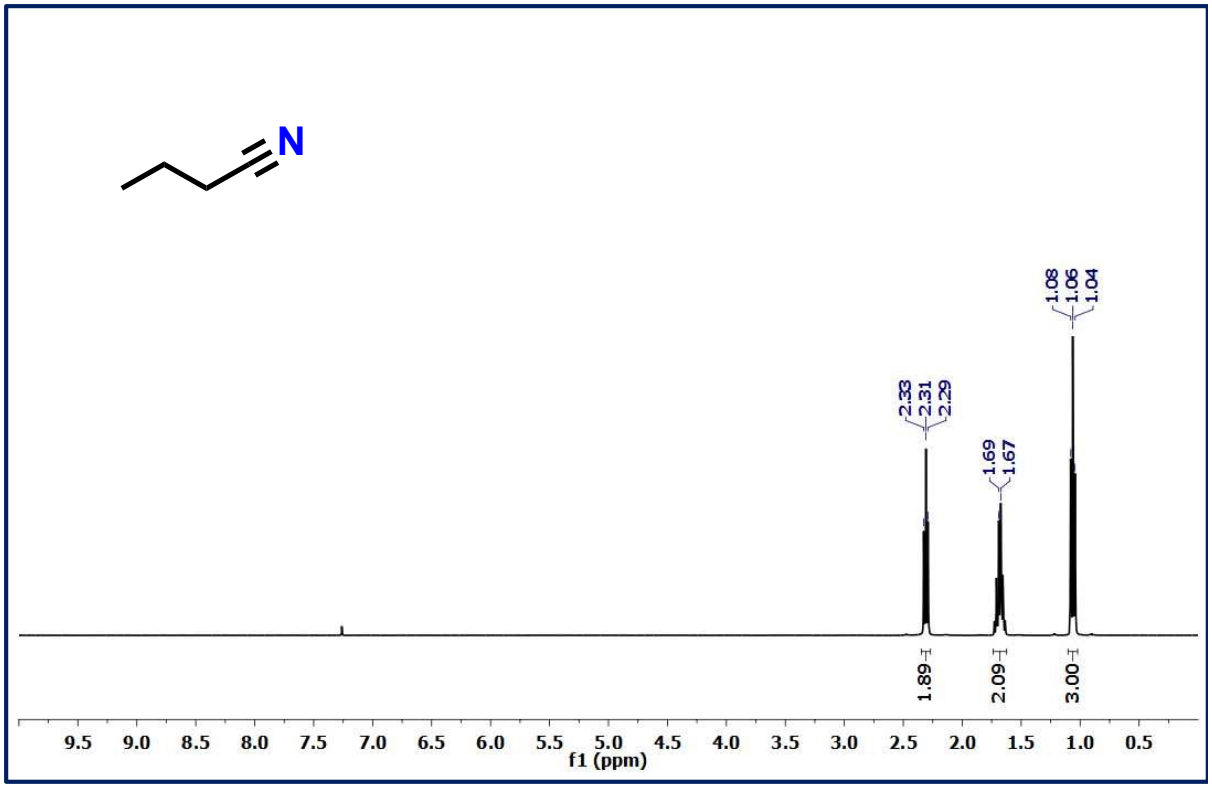


Figure S95. ^{1}H NMR spectrum ($CDCl_3$) of butyronitrile.

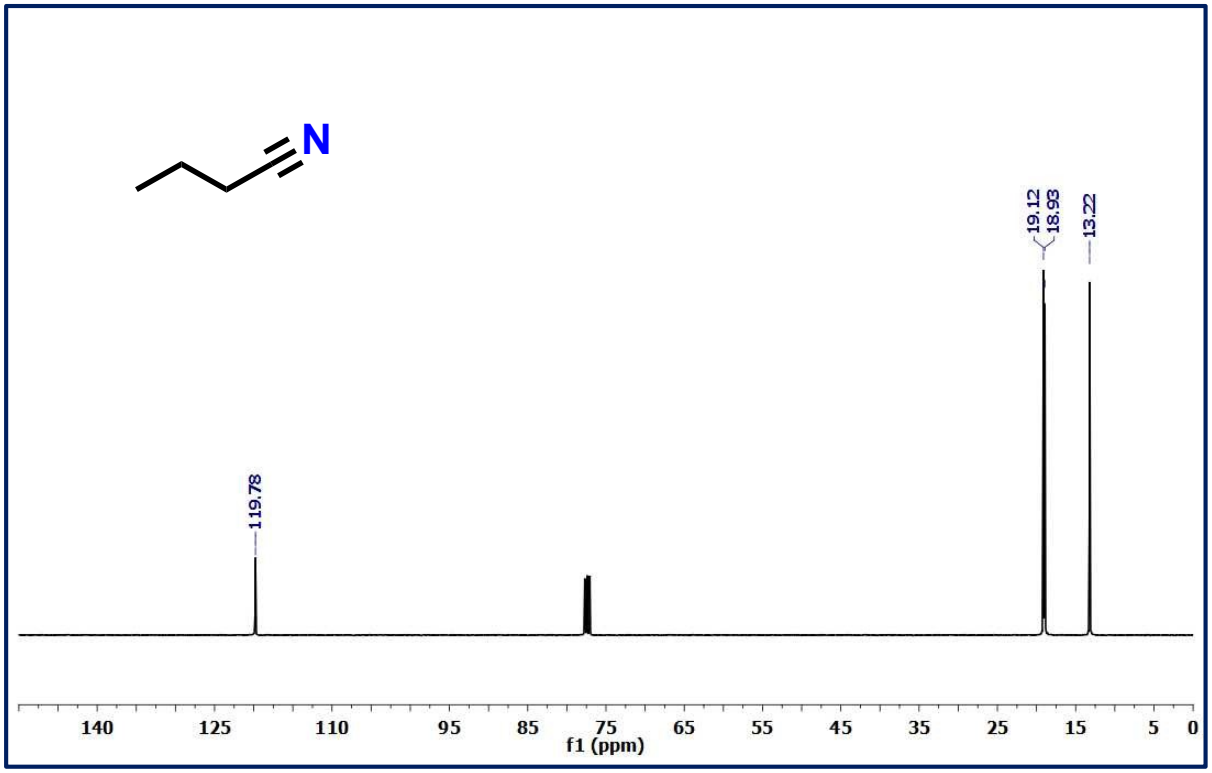
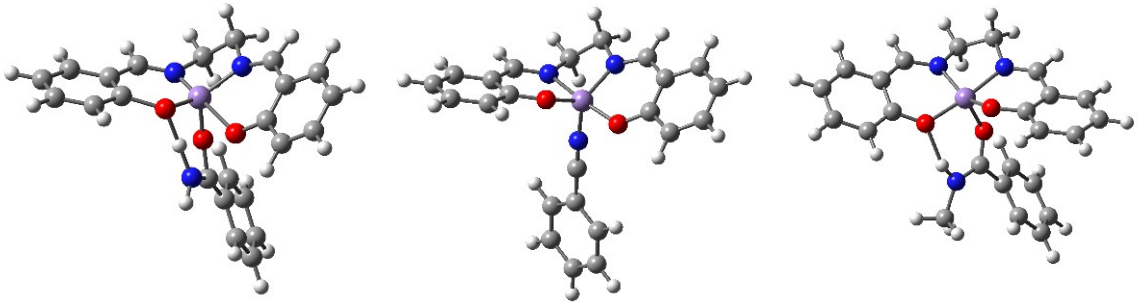


Figure S96. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of butyronitrile.

13. Computational details

Theoretical calculation:

The binding energies of benzamide, N-methyl benzamide and benzonitrile to Mn(III) centre of Mn-salen complex were theoretically calculated with the help of Gaussian16 at B3LYP level of theory with basis set lanl2dz for Mn and 6-31g(d) for other elements



9
Binding nergy:
-8.03 (Kcal/mol)

11
Binding Energy:
-1.67 (Kcal/mol)

13
Binding Energy:
-2.95 (Kcal/mol)

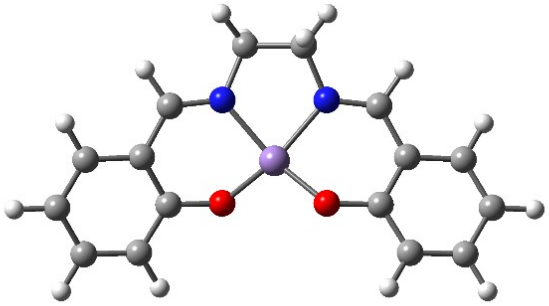
Figure S97. Binding energies in DFT-optimized structures of primary amide, nitrile and secondary amide bound intermediates.

Table S7: Energies, enthalpies, and free energies (in Hartree) of the optimized geometries calculated at B3LYP level with basis set lanl2dz for Mn and 6-31g(d) for other elements.

Compound	ZPE	ΔE	ΔH	ΔG	E	H	G
N1 Complex **1**	0.274431	0.290810	0.291754	0.229985	-981.407277	-981.406333	-981.468102
N2 ($PhCONH_2$)	0.128428	0.135760	0.136704	0.096231	-400.809814	-400.808870	-400.849343
N3 ($PhCONHCH_3$)	0.156477	0.165479	0.166423	0.121682	-440.085274	-440.084330	-440.129071
N4 (PhCN)	0.099582	0.105594	0.106538	0.069364	-324.376750	-324.375806	-324.412980
9 (Mn-PhCONH2)	0.406199	0.430919	0.431863	0.350344	-1382.249670	-1382.248726	-1382.330246
11 (Mn-PhCONHCH3)	0.437295	0.464067	0.465011	0.005865	-1421.514673	-1421.513728	-1421.601887
10 (Mn-PhCN)	0.376534	0.400353	0.401297	0.320263	-1305.803656	-1305.802712	-1305.883747

Coordinates of all the optimized structures:

Mn-salen moiety:



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N	-1.290016	1.635387	0.012174
C	2.623666	-0.958159	0.338595
C	-2.623745	-0.957978	-0.338888
C	3.281699	0.220213	-0.145040
C	-3.281713	0.220299	0.145126
C	2.587787	1.486301	-0.182069
H	3.204673	2.382686	-0.292098
C	-3.353966	-2.146216	-0.543880
H	-2.837909	-3.016707	-0.935611
C	-2.587819	1.486398	0.182135
H	-3.204661	2.382799	0.292140
C	3.353978	-2.146321	0.543841
H	2.837839	-3.016903	0.935269
C	4.671896	0.159021	-0.440345

H	5.181567	1.052833	-0.794004
C	4.717323	-2.183137	0.220369
H	5.273343	-3.106511	0.357383
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H	-1.313945	3.771354	0.240792
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H	1.314042	3.771327	-0.240497
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C	-4.671774	0.158920	0.440963
H	-5.181435	1.052645	0.794849
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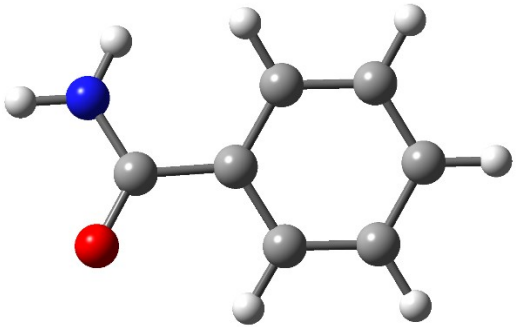
H	-6.438024	-1.078851	0.517340
Mn	-0.000059	0.128246	-0.000366



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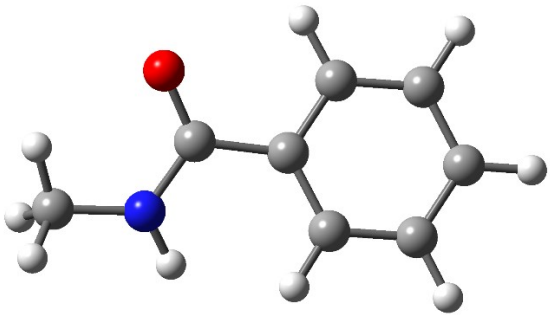
C	0.957562	1.331235	0.401823
C	-0.370614	1.255852	0.846379
C	-1.342274	0.633084	0.064702
H	-1.748597	-0.419742	-1.771626
H	0.605963	-0.334284	-2.549743
H	2.329500	0.747751	-1.168298
H	-0.612236	1.686227	1.807340
H	-2.364930	0.585863	0.413794
C	1.949100	2.010133	1.292690
O	1.730760	2.176523	2.514395
N	3.107690	2.458927	0.716106
H	3.785278	2.901268	1.312984
H	3.258789	2.467913	-0.275476



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C	-1.357739	1.635529	0.711334
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H	-3.243082	0.630781	0.933111
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H	2.386062	1.676925	-0.388301
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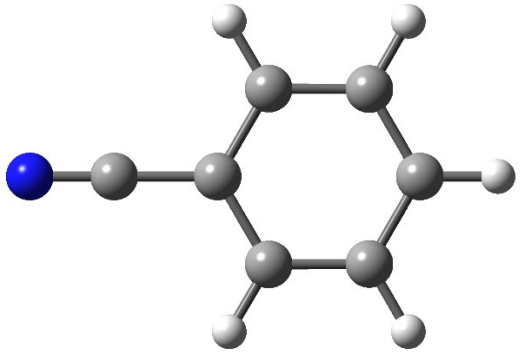

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C	-1.348635	1.692875	0.838724
C	-2.314619	0.912498	0.205763
H	-2.765972	-0.351832	-1.477197
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H	1.218851	1.248452	-1.362237
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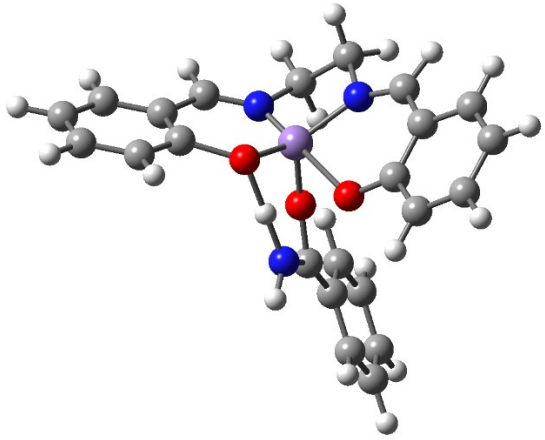

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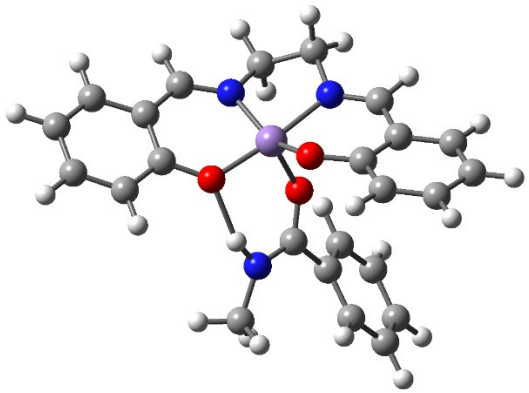

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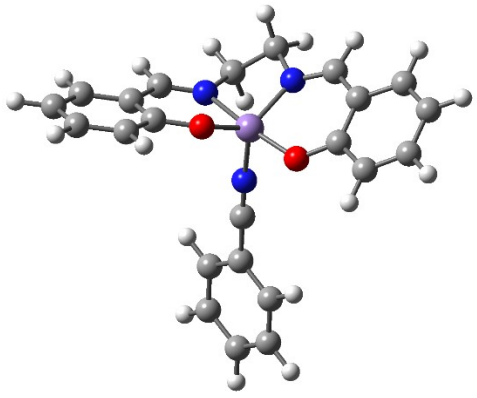

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N	-0.998318	0.623435	0.478523
Mn	0.582178	-0.455771	0.397159

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