Electronic Supplementary Information

Ligand-Metal Cooperativity in Quinonoid Based Nickel(II) and Cobalt(II) Complexes for Catalytic Hydrosilylative Reduction of Nitrile to Amine: Electron Transfer and Mechanistic Insight

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I. Characterization data for complexes 1 and 2:

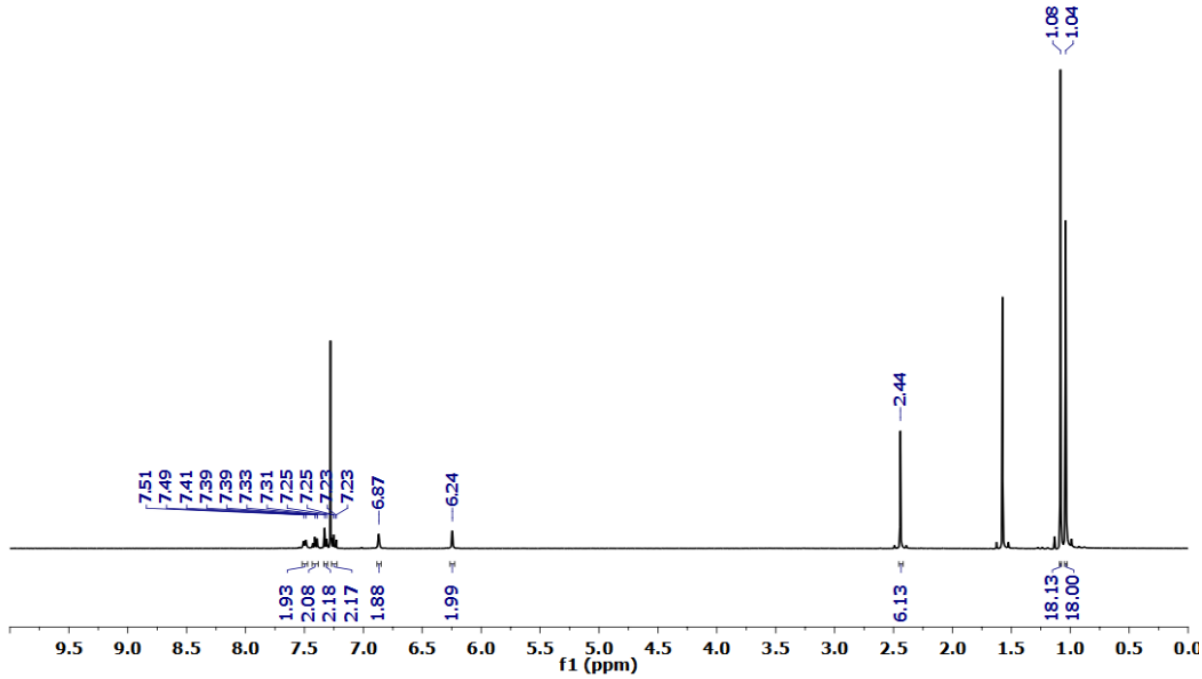


Figure S1. ^{1}H NMR spectra of complex **1**.

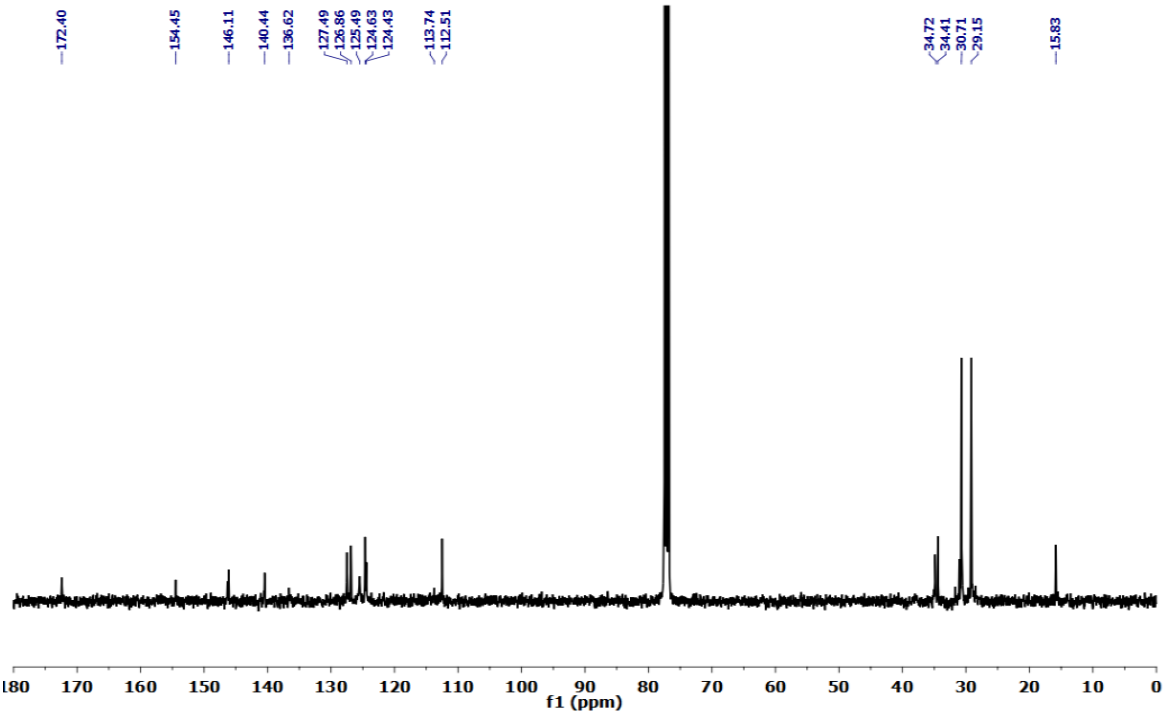


Figure S2. ^{13}C {^{1}H} NMR spectra of complex **1**.

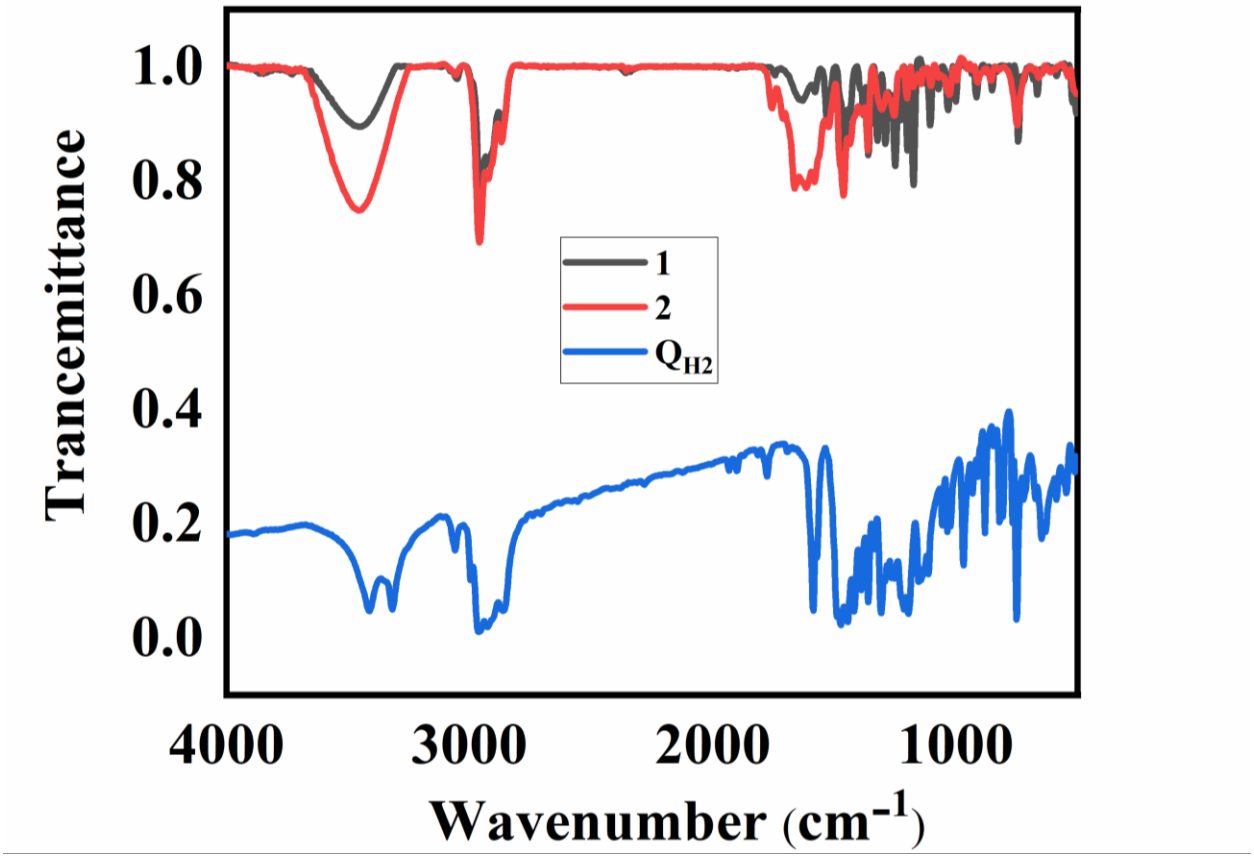


Figure S3: FT-IR spectra of ligand $\mathbf{Q}_{H2}$, complex **1** and **2**.

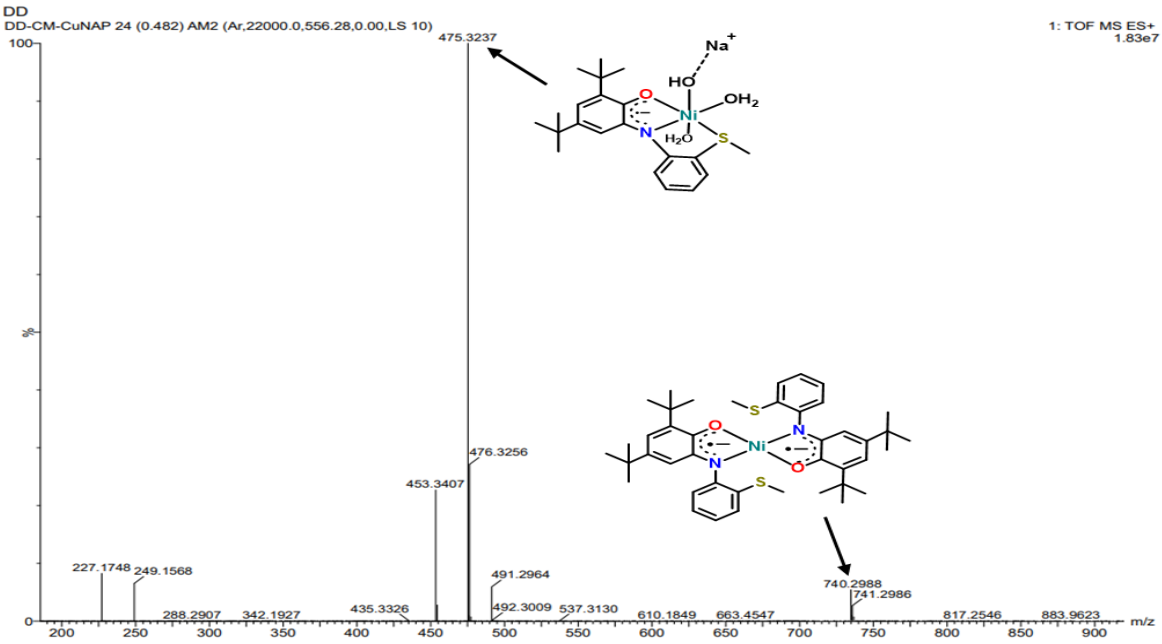


Figure S4: ESI-MS spectrum of complex **1** in methanol.

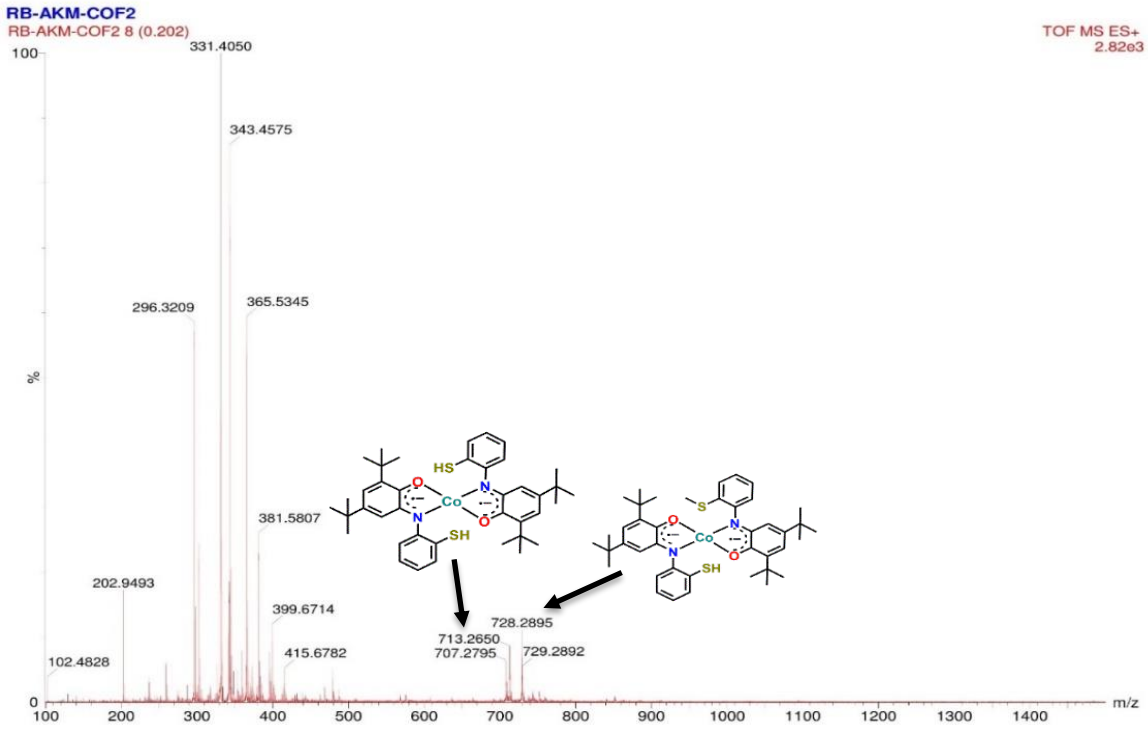


Figure S5: ESI-MS spectrum of complex **2** in methanol.

II. X-ray crystal structural details of complexes 1 and 2:

Table S1: X-ray structural data of complex **1** and **2**.

Parameters	Complex **1**	Complex **2**
Empirical formula	$C_{42}H_{54}N_2O_2S_2Ni$	$C_{42}H_{54}N_2O_2S_2Co$
Formula weight	741.70	741.94
T (K)	100.0	293
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C*2	*C*2/c
Unit cell dimensions		
a (Å))	23.7335 (11)	24.0419 (8)
b (Å)	13.5133(7)	13.7697 (5)
c (Å)	12.4009(7)	12.5722 (6)
α (°)	90	90
β (°)	97.156(5)	98.519 (4)
γ (°)	90	90
V (Å3)	3946.2(4)	4116.1 (3)
Z	4	8
ρ (gm cm^{-3})	1.248	1.197
Absorption coefficient (mm^{-1})	0.634	0.669
F(000)	1584	1580
Theta range for data collection	3.3 to 28.0°.	2.5 to 27.5
Index ranges (h, k, l)	-34: 34 ; -15: 18 ; -17: 16	-31: 31; -16: 17; -16; 16
Reflections collected	22011	18261
Independent reflections	8756	4711
R(int)	0.0485	0.030
Final R indices [I>0.0sigma(I)]	R1 = 0.0447, wR2 = 0.1040,	R1 = 0.1663 wR2 = 0.5638
Largest diff. peak and hole	0.678 and -2.81, e. $Å^{-3}$	1.10 and -1.21, e. $Å^{-3}$

Table S2: Selected X-ray crystallographic bond angles (°) of complex **1**.

Bond angles (°)			
O1–Ni1–N1	86.7 (3)	O1–Ni1–O2	179.3 (3)
O1–Ni1–N2	93.5 (2)	N1–C2–C3	127.3 (5)
N1–Ni1–N2	179.0 (4)	Ni1–O1–C1	111.0 (4)
C21–S1–C20	103.3 (3)	Ni1–N1–C2	111.7 (4)
Ni1–N1–C15	126.9 (3)	S1–C20–C19	124.0 (4)
C15–N1–C2	120.7 (5)	C19–C20–C15	119.4 (5)
S1–C20–C15	116.6 (4)	N1–C15–C16	120.4 (5)
N1–C15–C20	118.9 (5)		

Table S3: Selected X-ray crystallographic bond lengths (Å) of complex **1**.

Bond lengths (Å)			
Ni1–O1	1.825 (5)	Ni1–N1	1.835 (9)
O1–C1	1.313 (8)	N1–C15	1.414 (7)
N1–C2	1.353 (6)	S1–C21	1.890 (6)
S1–C20	1.737 (5)	C2–C1	1.431 (8)
Ni1–O2	1.829 (7)	Ni1–N2	1.845 (6)
O2–C22	1.312 (7)	N2–C23	1.344 (8)

Table S4: List of non-covalent interactions present in the crystal structure of **1**.

Interections	Atomic distance (Å)	Sum of van der Waals radius
S...S	3.306	3.6
C10–H…C39	2.822	2.9
C38–H…C26	2.759	2.9

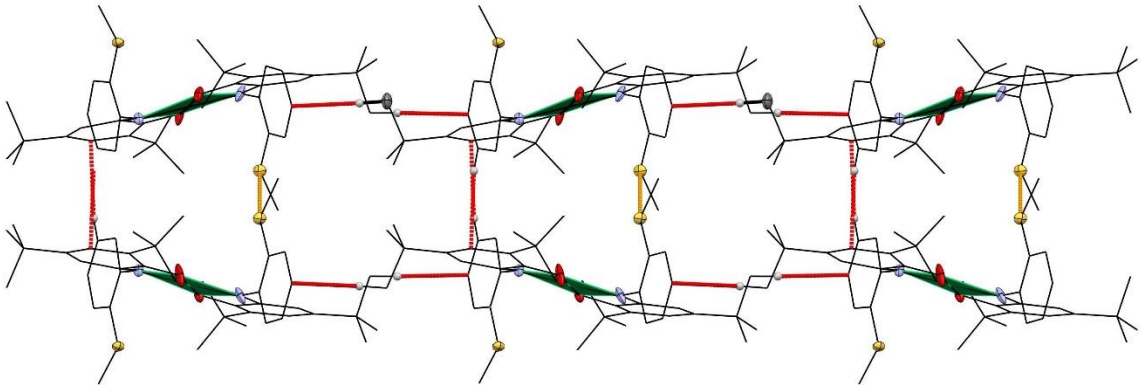


Figure S6: Formation of 3D supramolecular framework of **1** through non-covalent interactions.

Table S5: Selected X-ray crystallographic bond angles (°) of complex **2**.

Bond angles (°)			
O1–Co1–O1a	180.0	O1–Co1–N1	87.0 (3)
N1–C2–C3	120.7 (8)	O1–Co1–N1a	93.0 (3)
Co1–O1–C1	112.0 (5)	N1–Co1–N1a	180.0
Co1–N1–C2	110.7 (8)	C16–S1–C21	100.6 (5)
S1–C16–C17	124.7 (8)	Co1–N1–C2	110.7 (6)
C15–C20–C19	103.4 (10)	C2–N1–C15	122.5 (7)
N1–C15–C20	110.0 (9)	S1–C16–C15	115.6 (6)
N1–C15–C16	119.1 (7)		

Table S6: Selected X-ray crystallographic bond lengths (Å) of complex **2**.

Bond lengths (Å)			
Co1–N1	1.909 (7)	Co1–O1	1.833 (5)
N1–C15	1.459 (10)	O1–C1	1.340 (10)
S1–C21	1.810 (13)	N1–C2	1.343 (11)
C1–C2	1.438 (11)	S1–C16	1.759(8)

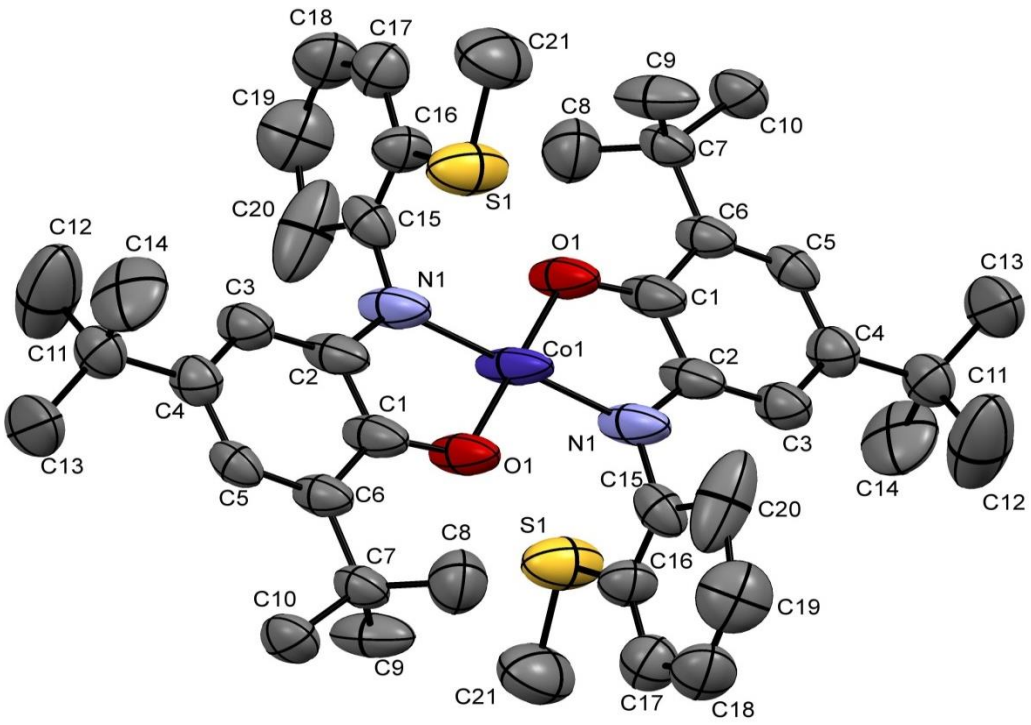


Figure S7: Perspective view of **2** with 50% thermal ellipsoidal probability.

III. Theoretical calculation:

Geometry optimizations of both the complexes (**1** and **2**) and their hydride complexes (**1**$_{-H}$ and **2**$_{-H}$) were carried out with the help of Gaussian16[1] at ub3lyp level of theory with basis set lanl2dz for transition metals (Ni and Co) and 6-31g(d) for other elements.

Table S7. Bond lengths of DFT optimized complex **1** and its hydride complex (**1**$_{-H}$)

Bond lengths (Å)		
Bonds	Complex **1**	Complex **1**$_{-H}$
Ni1-O1	1.858	1.862
O1-C9	1.341	1.377
N1-C8	1.372	1.401
S002-C2	1.840	1.843
Ni1-N1	1.862	1.885
N1-C7	1.434	1.418
S002-C1	1.881	1.881
C8-C9	1.444	1.421

Table S8. Bond lengths of DFT optimized complex **2** and its hydride complex (**2-H**)

Bond lengths (Å)		
Bonds	Complex **2**	Complex **2-H**
Co1-O1	1.849	1.891
O1-C1	1.355	1.363
N1-C2	1.385	1.391
S1-C16	1.841	1.844
Co1-N1	1.859	1.879
N1-C15	1.436	1.426
S1-C21	1.881	1.882
C1-C2	1.435	1.434

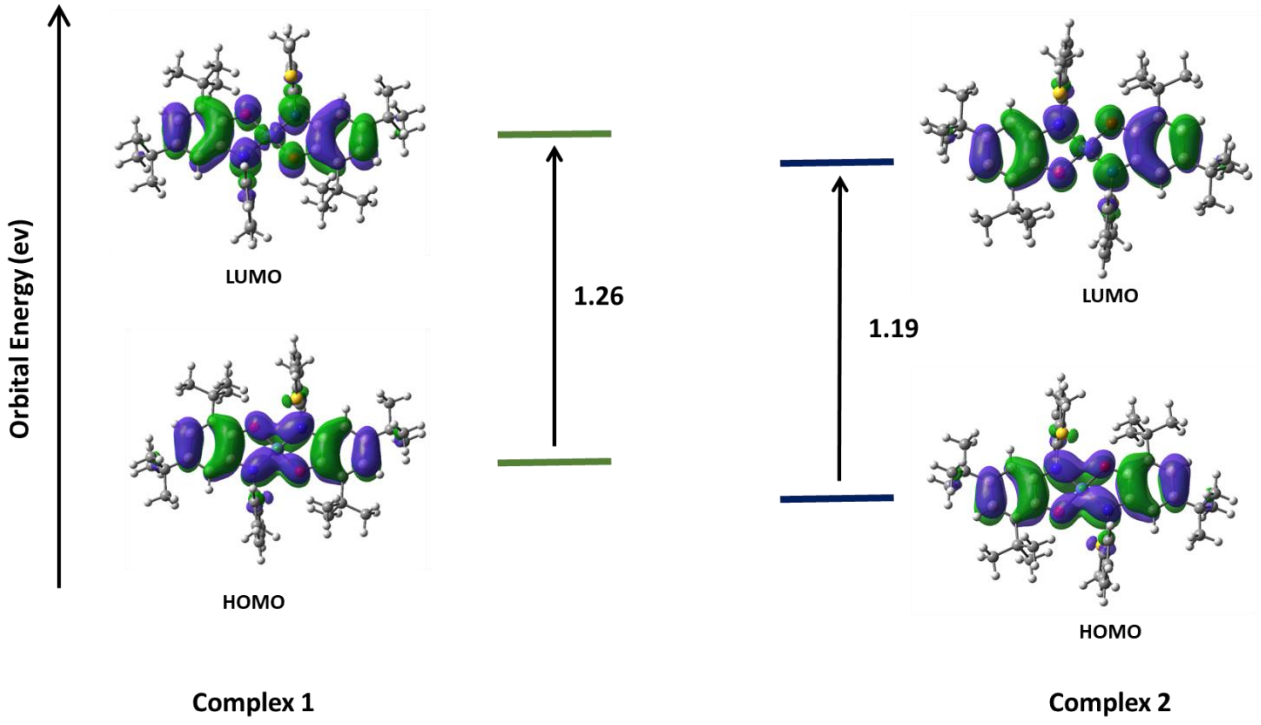
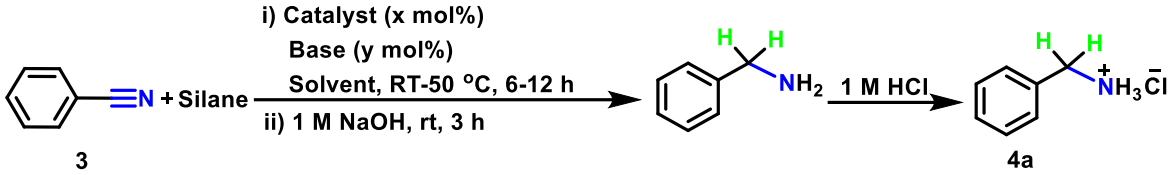


Figure S8: Qualitative DFT calculated MO scheme of the complex **1**(left) and **2** (right).

IV. Reaction optimization table:

Table S9: Optimization of the reduction of benzonitrile (**3a**) into benzylamine (**4a**)[a]



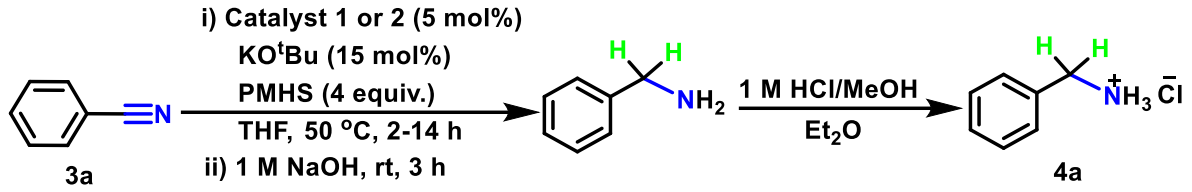
Entry	Catalyst (x mol %)	Base (y mol %)	Silane (z equiv.)	Solvent	Yield of 3a[b] (%)
1	**1** (5)	—	PMHS (4)	THF	—
2	**2** (5)	—	PMHS (4)	THF	—
3	**1 (5)**	**KO^{t}Bu (15)**	**PMHS (4)**	**THF**	**83**
4	**2 (5)**	**KO^{t}Bu (15)**	**PMHS (4)**	**THF**	**91**
5	$NiCl_2$. $6H_2O$ (5)	KO^{t}Bu (15)	PMHS (4)	THF	< 10
6	$CoCl_2$. $6H_2O$ (5)	KO^{t}Bu (15)	PMHS (4)	THF	< 10
7	$\mathbf{Q}_{H2}$(5)	KO^{t}Bu (15)	PMHS (4)	THF	—
8	**1** (2.5)	KO^{t}Bu (15)	PMHS (4)	THF	63
9	**2** (2.5)	KO^{t}Bu (15)	PMHS (4)	THF	68
10	**2** (5)	KOtBu (7.5)	PMHS (4)	THF	71
11[c]	**2** (5)	KO^{t}Bu (15)	PMHS (4)	THF	63
12[d]	**2** (5)	KOtBu (15)	PMHS (4)	THF	65
13	**2** (5)	NaO^{t}Bu (15)	PMHS (4)	THF	90
14	**2** (5)	NaOMe (15)	PMHS (4)	THF	78
15	**2** (5)	KOH (15)	PMHS (4)	THF	—
16	**2** (5)	NaOAc (15)	PMHS (4)	THF	—
17	**2** (5)	$CaCO_3$ (15)	PMHS (4)	THF	—
18	**2** (5)	KO^{t}Bu (15)	PMHS (4)	MeCN	—
19	**2** (5)	KO^{t}Bu (15)	PMHS (4)	MeOH	—
20	**2** (5)	KO^{t}Bu (15)	PMHS (4)	DMSO	—
21	**2** (5)	KO^{t}Bu (15)	PMHS (4)	DCM	83
22	**2** (5)	KO^{t}Bu (15)	PMHS (4)	Toluene	72
23	**2** (5)	KO^{t}Bu (15)	PMHS (4)	Et_2O	65
24	**2** (5)	KO^{t}Bu (15)	PMHS (4)	Hexane	40
25	**2** (5)	KO^{t}Bu (15)	PMHS (4)	Acetone	—
26	**2** (5)	KO^{t}Bu (15)	PMHS (4)	Chloroform	46
27	**2** (5)	KO^{t}Bu (15)	TMDS (2)	THF	93
28	**2** (5)	KO^{t}Bu (15)	Ph_2SiH_2 (2)	THF	67
29	**2** (5)	KO^{t}Bu (15)	Ph_3SiH (4)	THF	45
30	**2** (5)	KO^{t}Bu (15)	$PhSiH_3$ (1.2)	THF	97
31	**2** (5)	KO^{t}Bu (15)	Et_3SiH (4)	THF	95
32	**2** (5)	KO^{t}Bu (15)	$PhMe_2SiH$ (4)	THF	78

[a] PhCN (0.5 mmol), silane (1.2-4 equiv.), catalyst (2.5-5 mol%), base (7.5-15 mol%), solvent (3mL) for 12 h at 50 °C followed by base hydrolysis using 1M NaOH. [b] Isolated yield of aminehydrochloride salts. [c] Reaction performed at RT. [d] Reaction time 6 h.

V. Kinetics of 1 and 2 catalyzed nitrile reduction:

In a 15 mL schlenk tube, catalyst **1** or **2** (5 mol%) and KO^{t}Bu (15 mol%, 9 mg) were dissolved in 3 mL THF under nitrogen atmosphere. The mixture was stirred for 5 minutes, then PMHS (2 mmol, 4 equiv.) and benzonitrile (0.5 mmol, 52 mg) were added to the reaction mixture and were allowed to stir at 50 °C. After different time intervals (2, 4, 6, 8, 10, 12, 14 h), the reaction mixture was quenched by adding 1.5 mL 1(M) NaOH solution and allowed to stir for additional 3 h. The amine product was extracted in 30 mL (3 x 10 mL) diethyl ether and dried over anhydrous Na_2SO_4. After filtration, crude amine product was obtained by removing solvent under reduce pressure. Then the amine was isolated as amine salt by treating with 1mL methanolic HCl (1M) solution followed by precipitation by adding 15 mL diethyl ether. The precipitate was filtered off, washed with ethyl acetate and dried under vacuum to get amine salt. The yield of amine salt (**4a**) in different time intervals is listed in Table S10. The plot of time *vs* yield shows completion of reaction within 12 h (Figure S9).

Table S10. Yield of benzylamine hydrochloride salt (**4a**) at different time intervals.



Entry	Reaction time	Yield (%)[a]	Yield (%)[b]
1	2 h	18	26
2	4 h	44	57
3	6 h	63	79
4	8 h	73	86
5	10 h	79	89
6	12 h	83	91
7	14 h	83	91

[a] Complex **1** used as catalyst. [b] Complex **2** used as catalyst.

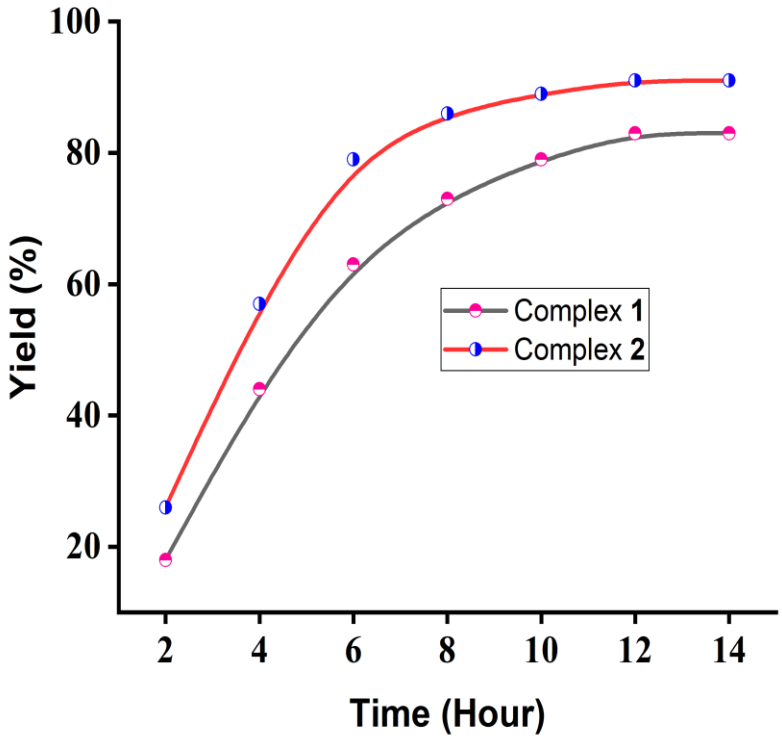
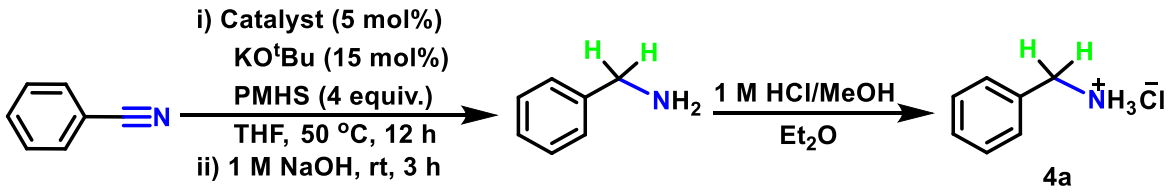


Figure S9. Graphical representation of yield of benzyl amine as hydrochloric salt (**4a**) *vs* time.

VI. Procedure for gram-scale synthesis of amine:

In a 250 mL Schlenk flask, catalyst (5 mol%, 359 mg) and KO^{t}Bu (15 mol%, 163 mg) were dissolved in 50 mL THF under nitrogen atmosphere. After stirring for few minutes, PMHS (40 mmol, 4 equiv.) and benzonitrile (1 g, 9.69 mmol) were added to the reaction mixture and were allowed to stir for 12 h at 50° C. The reaction mixture was allowed to cool to room temperature, 30 mL 1(M) NaOH solution was added to the reaction mixture and stir for another 3 h. The amine product was extracted in 450 mL (3 x 150 mL) diethyl ether and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduce pressure. The crude amine product was treated with 20 mL 1(M) HCl solution followed by precipitation as amine salt by adding 250 mL diethyl ether. The precipitate was filtered off, washed with ethyl acetate and dried under vacuum to obtain pure amine salt (1182 mg, 85% yields in case of **2** and 1084 mg, 78% yields in case of **1**).

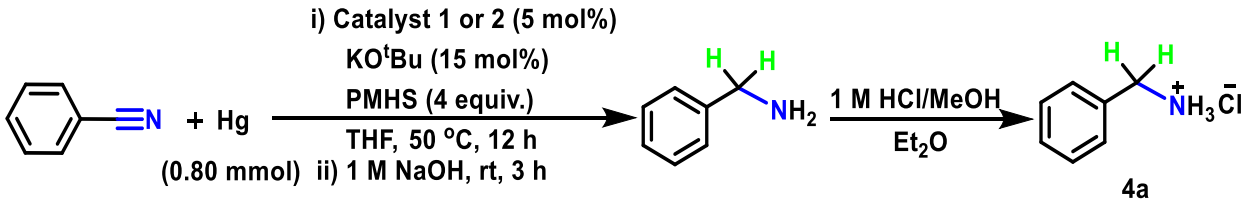


Scheme S1. Reduction of benzonitrile to benzyl amine (**4a**) in gram-scale.

VII. Mechanistic studies and computational details:

Hg Drop Test:

In a 15 mL schlenk tube, catalyst **1** or **2** (18 mg, 5 mol%), KO^{t}Bu (9 mg, 15 mol%), PMHS (2 mmol, 4 equiv.), benzonitrile (52 mg, 0.5 mmol) and Hg (160 mg, 0.8 mmol) were dissolved in 3 mL THF. Then the reaction mixture was stirred for 12 h at 50 °C. After that 1.5 mL of 1 M NaOH solution was added to the reaction mixture and stirred for another 3 h at room temperature. The amine was extracted with diethyl ether (3 x 10 mL) and dried over Na_2SO_4. The crude amine was obtained by evaporation of solvent under reduced pressure. On treatment with 1 mL of 1 (M) methanolic HCl followed by addition of Et_2O leads to precipitation of amine salt. The precipitate was filtered off, washed with ethyl-acetate and dried in vacuum to obtain pure amine salt (4a). 80% yield for complex **1** and 86% yield for complex **2**.



Scheme S2: The reduction of nitrile in presence of excess mercury.

UV-Visible spectroscopic Studies:

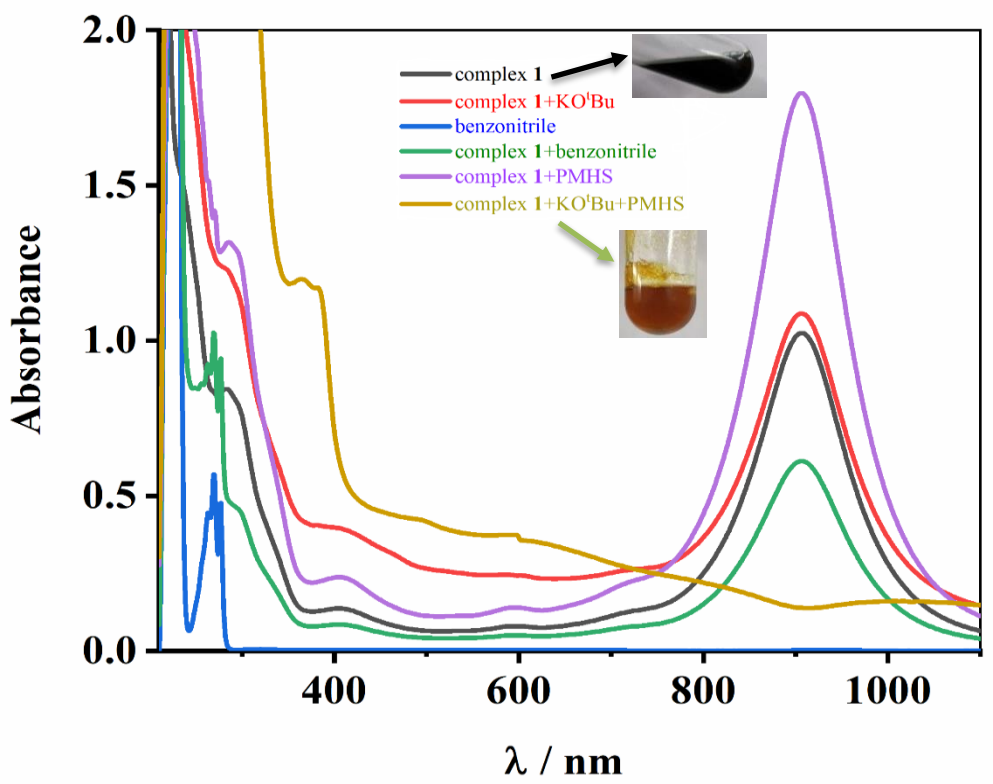


Figure S10. UV-Vis-NIR spectra of complex **1** with different reagents used in nitrile reduction.

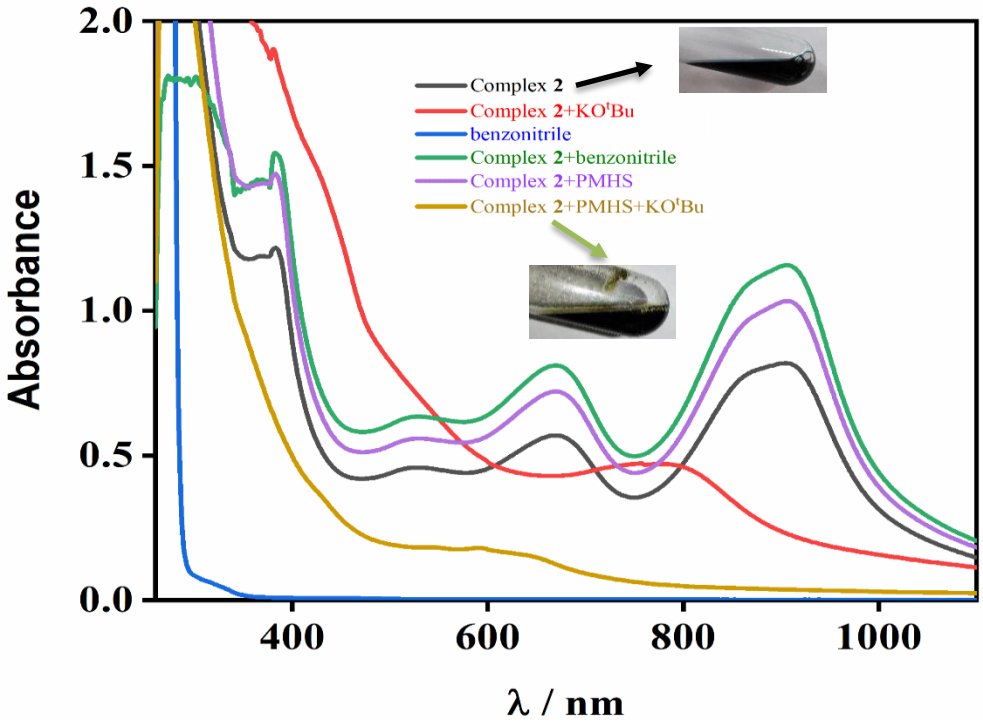


Figure S11. UV-Vis-NIR spectra of complex **2** with different reagents used in nitrile reduction.

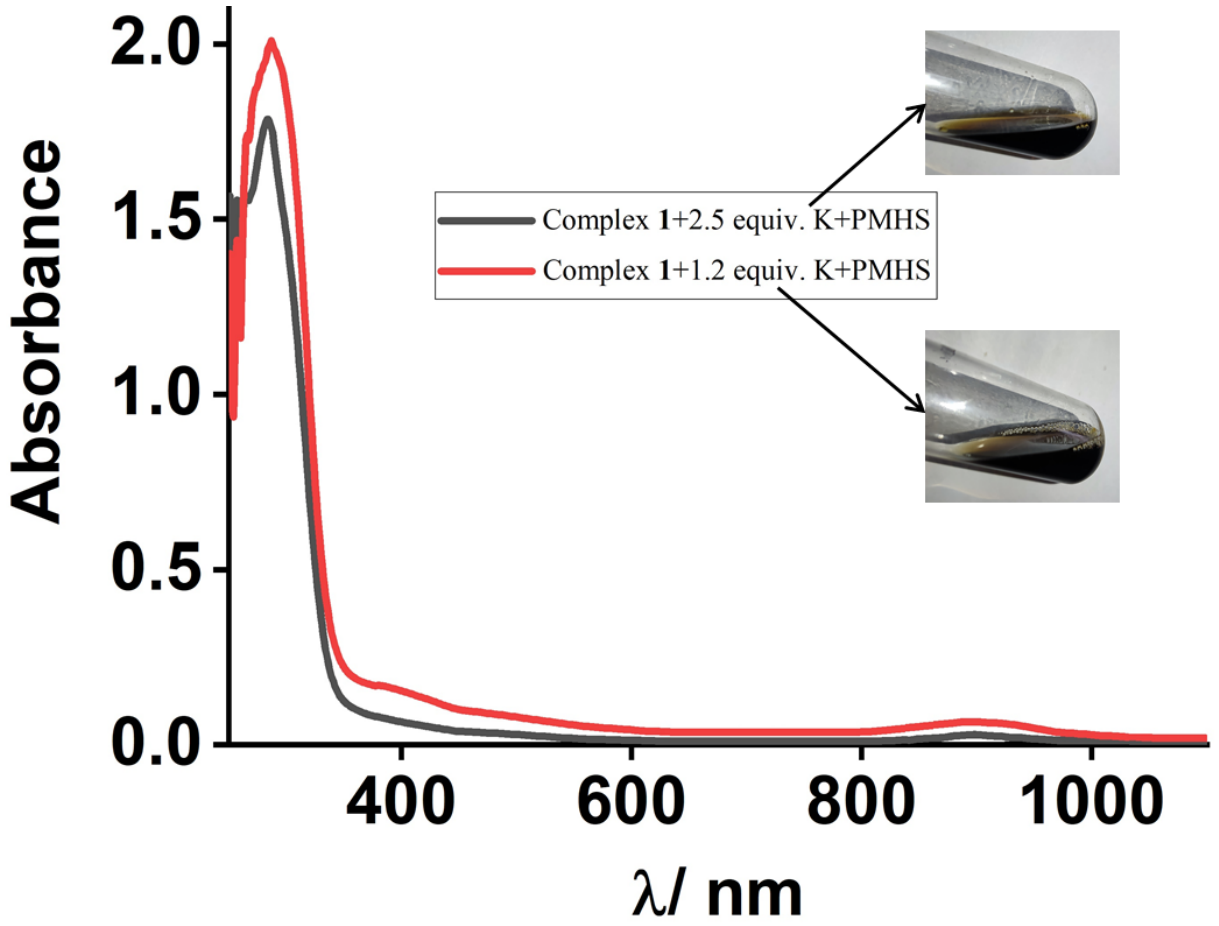
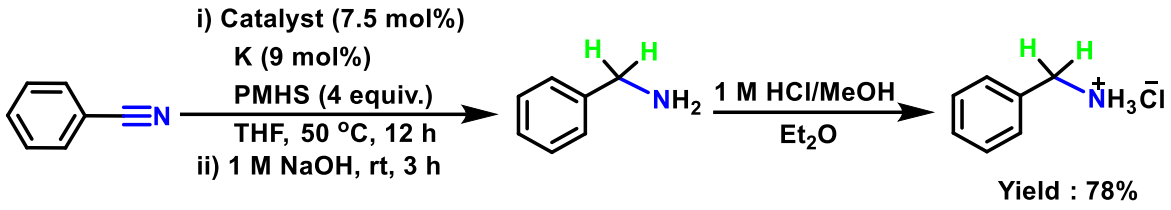


Figure S12. UV-Vis spectra of catalytically active species generated by the reaction of complex **1** with potassium and PMHS mixture.

Reduction of nitrile to amine using potassium:

In a 15 mL schlenk tube, catalyst **1** (27 mg, 7.5 mol%), K (1.75 mg, 9 mol%), PMHS (2 mmol, 4 equiv.) and benzonitrile (52 mg, 0.5 mmol) were dissolved in 3 mL THF. Then the reaction mixture was stirred for 12 h at 50 °C. After that 2 mL of 1 M NaOH solution was added to the reaction mixture and stirred for 3 h at room temperature. The amine was extracted with diethyl ether (3 x 10 mL) and dried over Na_2SO_4. The crude amine was obtained by evaporation of solvent under reduced pressure. On treatment with 1 mL of 1 (M) methanolic HCl followed by

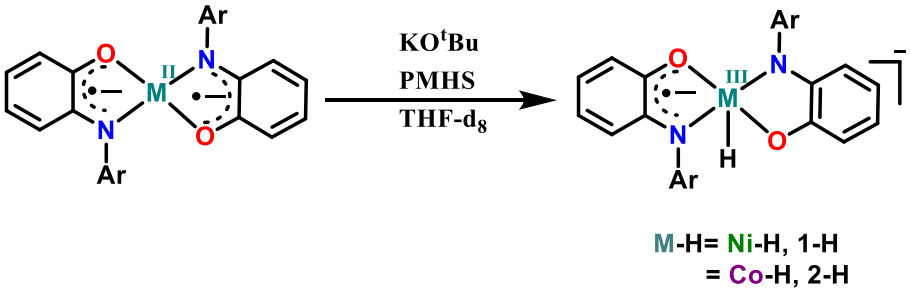
addition of Et_2O leads to precipitation of amine salt. The precipitate was filtered off, washed with ethyl-acetate and dried in vacuum to obtain pure amine salt (**4a**) with 78% yield.



Scheme S3: Reduction of nitrile to amine using catalytically active species generated by the reaction of complex **1** with potassium-PMHS mixture.

Detection of key intermediate metal hydride in hydrosilylative nitrile reduction:

The metal catalyst **1** (0.013 mmol,) and KO^{t}Bu (0.026 mmol, 2.9 mg) were taken in a 15 mL schlenk tube with 700 μL THF-d_8 under nitrogen atmosphere and then PMHS (0.026 mmol, 3.12 μL) was added to the mixture and stirred for 10 minutes. Then 600 μL of the reaction mixtures were taken in a screw cap NMR tube and analyzed with ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, THF-d_8): δ = -9.20.



Scheme S4. Formation of metal-hydride (**1**$_{\text{-H}}$) during catalytic reaction.

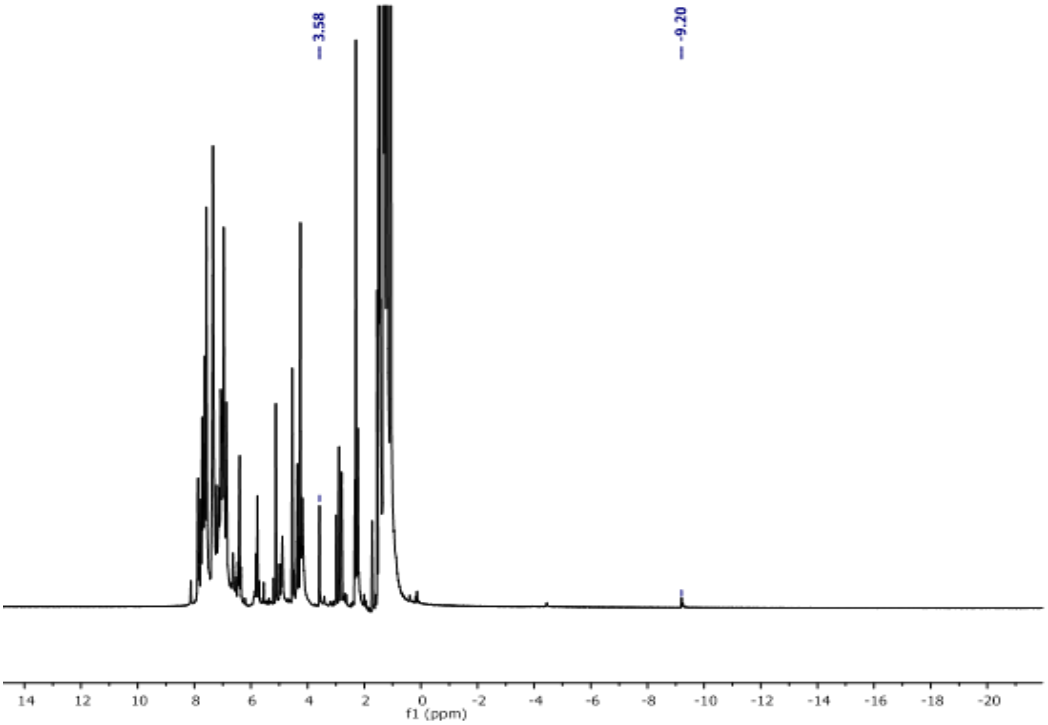
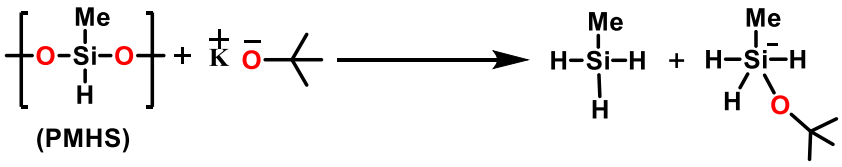


Figure S13. ^{1}H NMR spectrum (THF-d_8) of the reaction mixture containing **1** and active silane in a screw cap NMR tube.

Base-catalyzed rearrangement of PMHS to $MeSiH_3$ and formation of active silane 'ate' species [$H_3SiMe–O^tBu$]$^-$:

In a screw cap NMR tube, PMHS (0.21 mmol, 25 μl) and base KO^tBu (0.21 mmol, 24 mg) were dissolved in 600 μl dry $CDCl_3$ under nitrogen atmosphere. Then the tube was warmed at 50 °C for 5 minutes and then ^{1}H NMR spectra was recorded. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 0.18 (q, $J_{H\text{-}H}$ = 9.2 Hz, 3C–*H* of $MeSiH_3$) 3.52 (q, $J_{H\text{-}H}$ = 9.0 Hz, 3Si–*H* of $MeSiH_3$), 5.29 (s, 3Si–*H* of [$H_3SiMe–O^tBu$]$^-$.



Scheme S5. Formation of active silane by reaction of PMHS and KO^tBu in dry $CDCl_3$ at RT.

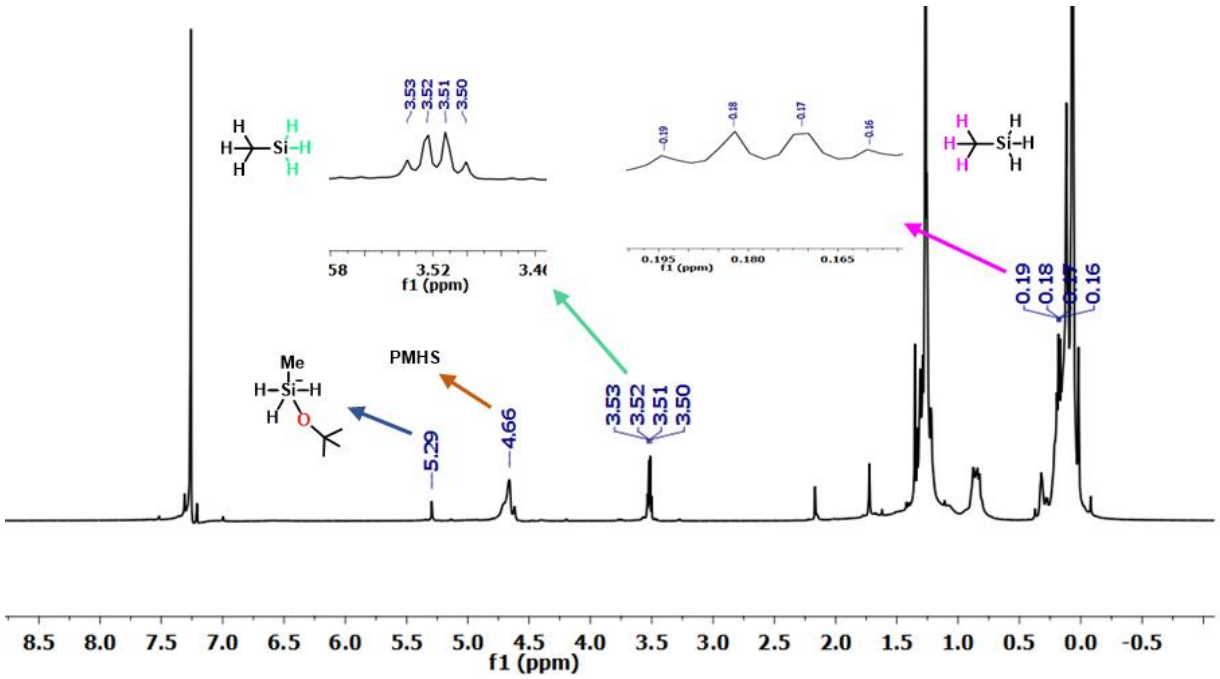
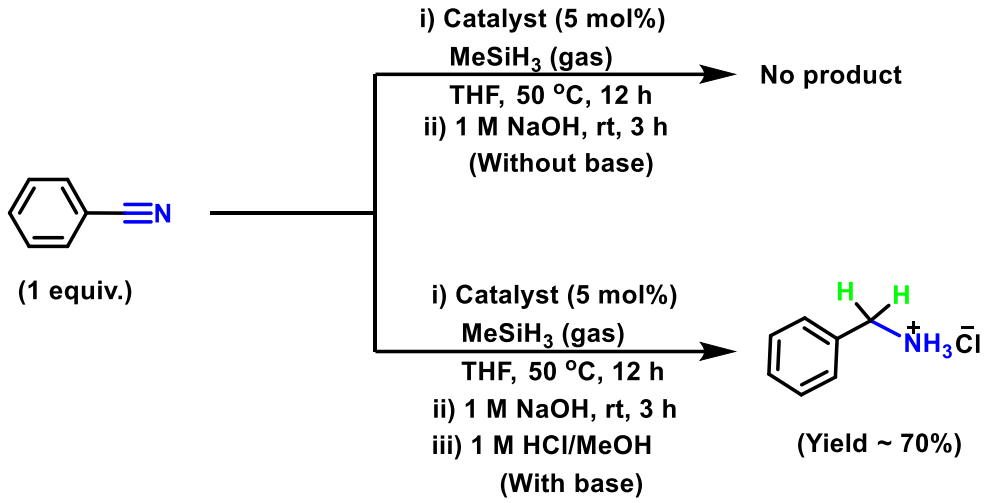


Figure S14. ^{1}H NMR spectrum ($CDCl_3$) of active silane described in Scheme S4.

Procedure for nitrile reduction using $MeSiH_3$ gas:

In a 15 mL schlenk tube, catalyst (**1,** 5 mol%, 18 mg), KO^{t}Bu (15 mol%, 9 mg) and benzonitrile (0.5 mmol, 52 mg) were dissolved in 3 ml THF and connected with an another15 mL schlenk tube through silicone gas pipe containing PMHS (3 mmol, 6 Equiv.) and KO^{t}Bu (15 mol%, 9 mg) in 3 ml THF under nitrogen atmosphere. The freezing of the substrate containing tube followed by warming the PMHS containing tube at 50 °C leads to the transfer of $MeSiH_3$ gas from PMHS tube to the substrate tube. After 30 minutes of $MeSiH_3$ gas passing, the substrate containing tube was closed by a glass stopper and stirred at 50 °C for 12 h. Then 1.5 mL of NaOH (1 M) solution was added at room temperature and stir for another 3 h. The product was extracted with diethyl ether (3 x 10 mL) and dried over Na_2SO_4. The amine product was obtained by evaporation of solvent under reduced pressure. On treatment with 1 mL of 1 (M) methanolic

HCl followed by Et_2O addition leads to precipitation of hydrochloric acid salt of desired product. Yield ~70%. Without KO^{t}Bu in the substrate containing tube the yield of amine salt was negligible.



Scheme S6. Catalytic reduction of nitrile using $MeSiH_3$ gas generated by siloxane-silane rearrangement

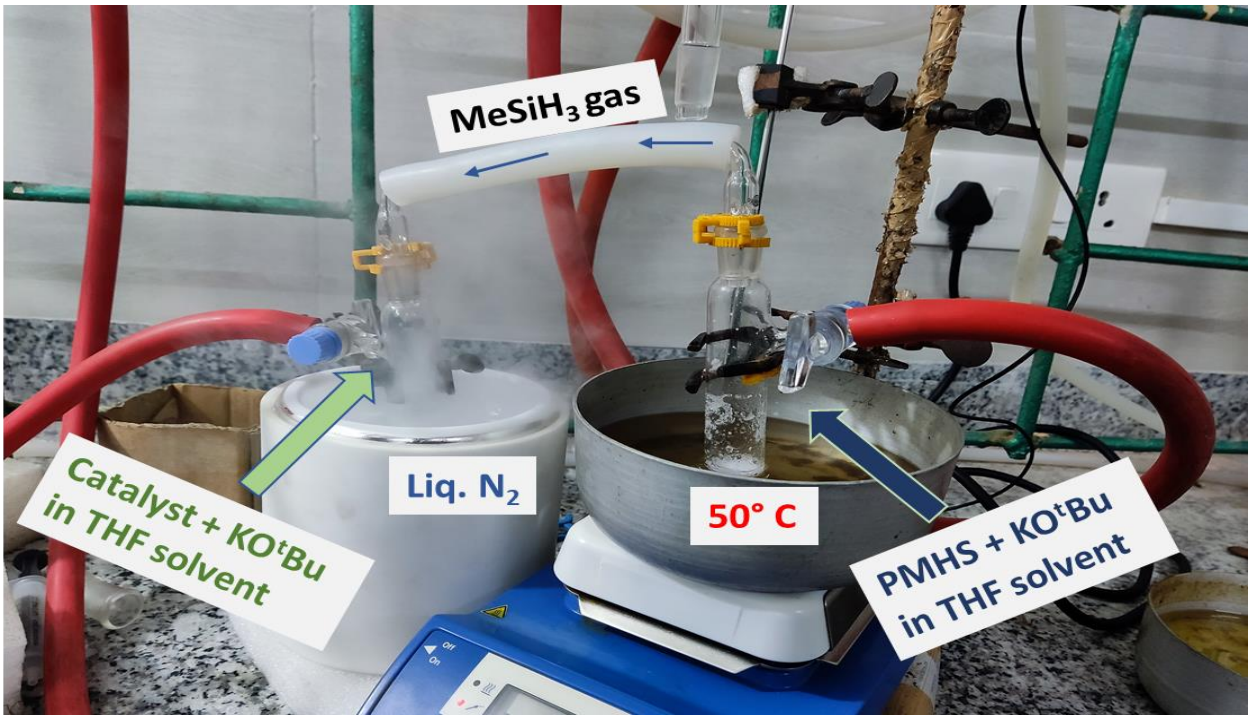
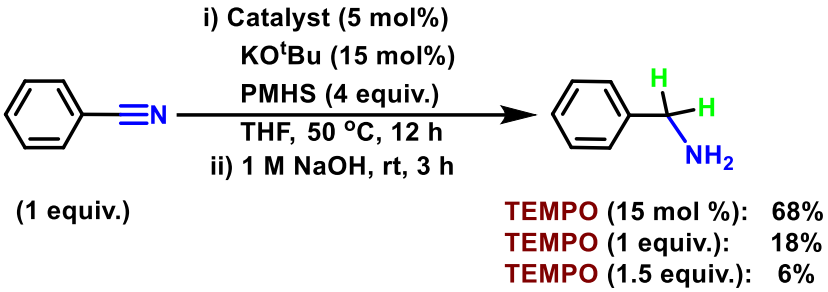


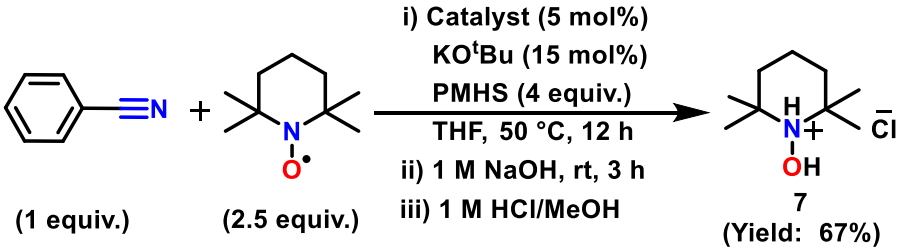
Figure S15. Reaction setup for the nitrile reduction using $MeSiH_3$ gas.

Procedure for reactions in presence of radical scavenger TEMPO:



In a 15 mL schlenk tube, catalyst (**1,** 5 mol%, 18 mg), KO^{t}Bu (15 mol%, 9 mg), PMHS (2 mmol, 4 Equiv.), benzonitrile (0.5 mmol, 52 mg) and required amount of TEMPO were dissolved in 3mL THF. The reaction mixture was stirred at 50 °C for 12 h. Then 1.5 mL NaOH (1 M) solution was added at room temperature and stir for another 3 h. The product was extracted with diethyl ether (3 x 10 mL) and dried over Na_2SO_4. The product was obtained by evaporation of solvent under reduced pressure. On treatment with 1 mL of 1 (M) methanolic HCl followed by Et_2O addition leads to precipitation of hydrochloric acid salt of desired product. The same procedures were also carried out using catalyst **2** and showed similar result.

Procedure for TEMPO-trapped intermediate preparation:



In a 15 mL schlenk tube, catalyst (**1,** 5 mol%, 18 mg), KO^{t}Bu (15 mol%, 9 mg), PMHS (2 mmol, 4 Equiv.), benzonitrile (0.5 mmol, 52 mg) and TEMPO (1.25 mmol, 195 mg) were dissolved in 3mL THF. The reaction mixture was stirred at 50 °C for 12 h. After completion of the reaction, 1.5 mL NaOH (1 M) solution was added at room temperature and stir for another 3 h. Then the TEMPO adduct was extracted with diethyl ether (3 x 10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the product **7** was precipitated out as a pure hydrochloride salt by doing the treatment with 1 (M) methanolic HCl followed by addition of Et_2O. Yield 67%. ^{1}H NMR (400 MHz, DMSO-d6) δ/ppm: 8.52 (s, 1H), 1.64 (d, J = 3.9 Hz, 2H), 1.53 (m, 4H), 1.36 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ/ppm: 56.26, 34.88, 27.25,

16.35. Nearly same amount of product (compound **7**) was also formed in identical condition when **2** was used as a catalyst.

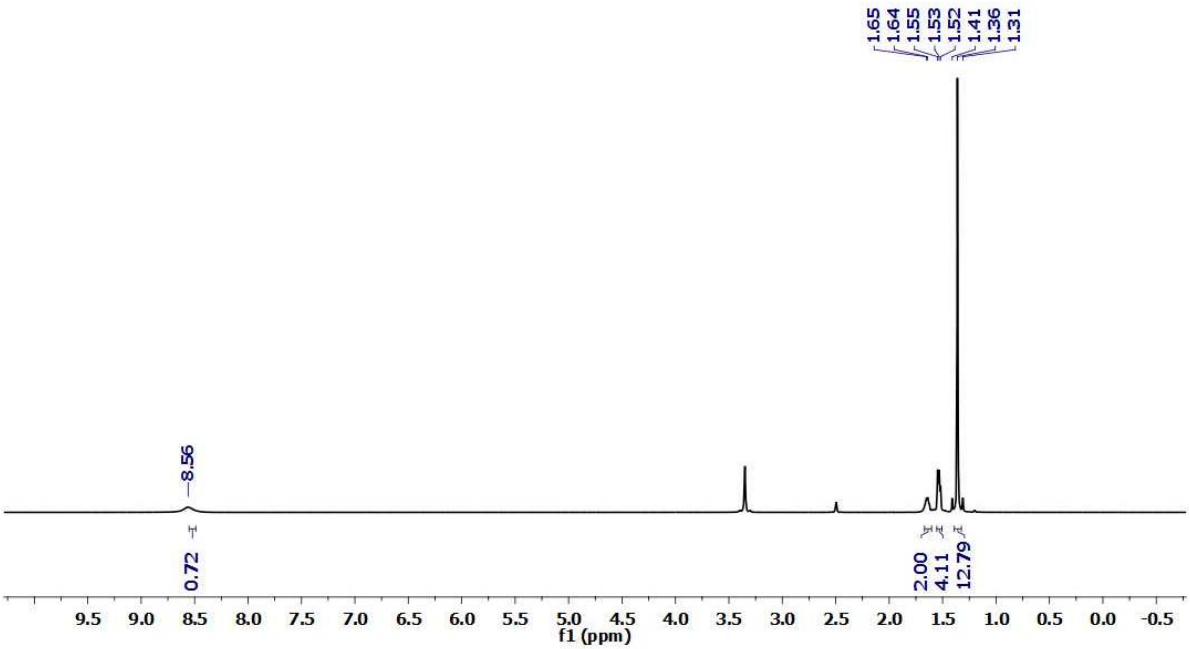


Figure S16. ^{1}H NMR spectrum (DMSO-d_6) of hydrochloric salt of reduced TEMPO (**7**).

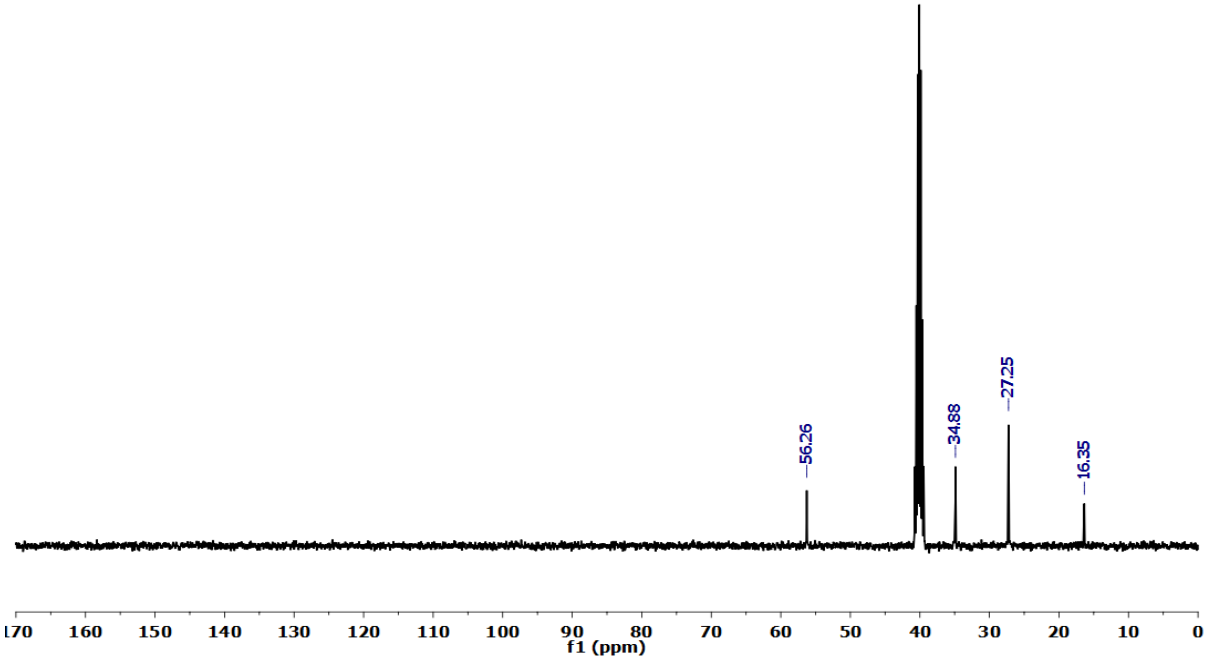
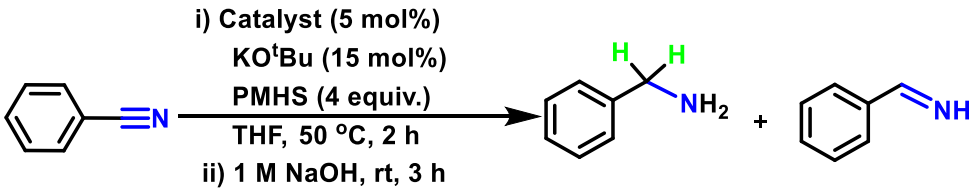


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) of hydrochloric salt of reduced TEMPO (**7**).

Detection of imine intermediate during amide to amine catalytic reaction:

To trap the reaction key intermediates, we stopped our catalytic reaction prematurely. Catalyst **1** (5 mol%) and KO^{t}Bu (15 mol%, 9 mg) were taken in a 15 mL schlenk tube with 3 mL THF under nitrogen atmosphere. The mixture was stirred for 5 minutes and then PMHS (2 mmol, 4 equiv.) and benzonitrile (0.5 mmol, 52 mg) were added to the reaction mixture successively. The final reaction mixture was then allowed to stir at 50 ^{0}C in inert atmosphere. We stopped the reaction after 2 h by adding 1.5 mL 1 M NaOH solution followed by stirring for 3 h. The reaction mixture was extracted in 40 mL diethyl-ether (Et_2O) and dried over anhydrous Na_2SO_4. 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 9.89 (s, PhC*H*=NH) (see Figure S17).[10]



Scheme S7: Stopping the reduction prematurely after 2 h during conversion of benzonitrile to benzyl amine.

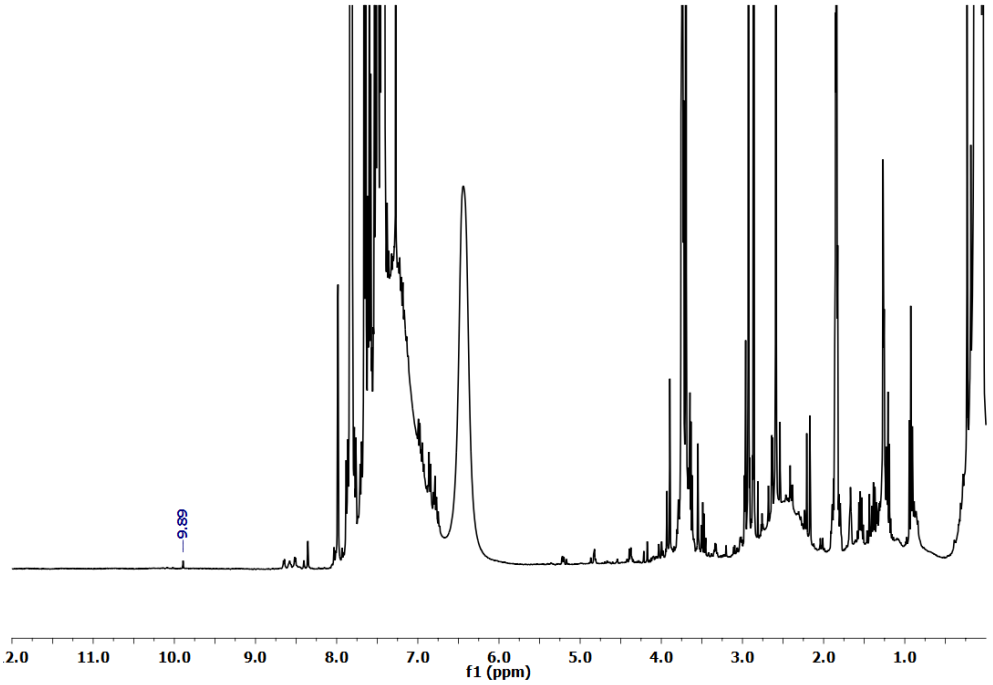
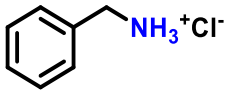


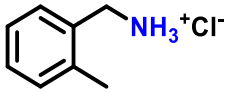
Figure S18. ^{1}H NMR spectrum ($CDCl_3$) of crude reaction mixture obtained after 2 h reaction.

VIII. Characterization data of amine products:



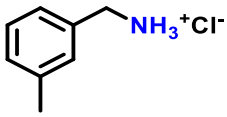
Phenylmethanamine Hydrochloride, 4a[2,3,4]

Colourless solid, Yield: 91%. **^{1}H NMR** (400 MHz, DMSO-*d*6): δ 8.37 (s, 3H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 (dd, *J* = 16.6 Hz, 8.7 Hz, 3H), 4.01 (d, *J* = 4.9 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-*d*6): δ 134.6, 129.5, 129.2, 129.0, 42.7.



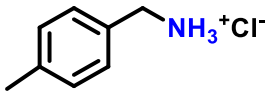
o-tolylmethanamine Hydrochloride, 4b[4]

Colourless solid, Yield: 90%. **^{1}H NMR** (400 MHz, DMSO-*d*6): δ 8.44 (s, 3H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.30-7.20 (m, *3*H), 4.03- 3.96 (m, 2H), 2.35 (s, 3H); **^{13}C{1H} NMR** (101 MHz, DMSO-*d*6): δ 134.5, 130.2, 128.2, 127.1, 126.4, 123.9, 37.3, 16.7.



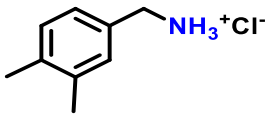
m-Tolylmethanamine Hydrochloride, 4c[2]

Colourless solid, Yield: 92%. **^{1}H NMR** (400 MHz, DMSO-d6): δ 8.51 (s, 3H), 7.36-7.33 (m, 3H), 7.24-7.21 (m, 1H), 4.01 (d, J = 5.6 Hz, 2H) 2.36 (s, 3H); **^{13}C{1H} NMR** (101 MHz, DMSO-d6): δ 138.4, 134.6, 130.2, 129.6, 129.1, 126.6, 42.8, 21.6.



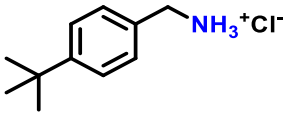
p-tolylmethanamine Hydrochloride, 4d[4]

Colourless solid, Yield: 93%. **^{1}H NMR** (400 MHz, DMSO-*d*6): δ 8.41 (s, 3H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 3H), 3.94 (q, *J* = 5.5 Hz, 2H), 2.30 (s, 3H); **^{13}C{1H} NMR** (101 MHz, DMSO-*d*6): δ 138.3, 131.6, 129.6, 129.5, 42.5, 21.3.



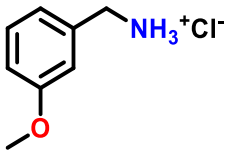
(3,4-dimethylphenyl)methanamine Hydrpochloride, 4e[5]

Colourless solid, Yield: 93%. **^{1}H NMR** (400 MHz, DMSO-d6): δ 8.60 (s, 3H), 7.38 (s, 1H), 7.33(dd, *J* = 7.7, 1H), 7.27 (d, *J* = 7.7 Hz, 1H) 4.02 (d, *J* = 5.8 Hz, 2H), 2.33 (s, 6H); **^{13}C{1H} NMR** (101 MHz, DMSO-d6): δ 1363, 136.2, 131.3, 130.0, 129.5, 126.3, 41.8, 19.3, 19.0.



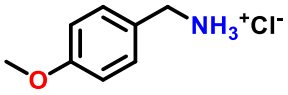
4-(1,1-dimethylethyl)Benzenemethanamine Hydrochloride, 4f[6]

Colourless solid, Yield: 95%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.48 (s, 3H), 7.43 (s, 4H), 3.95 (q, *J* = 5.7 Hz, 2H), 1.28 (s, 9H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 151.0, 131.3, 128.9, 125.4, 41.9, 34.5, 31.2.



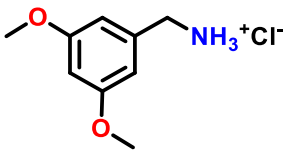
(3-methoxyphenyl)methanamine Hydrpochloride, 4g[2]

Colourless solid, Yield: 92%. **^{1}H NMR** (400 MHz, DMSO-*d*6): δ 8.51 (s, 3H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.15 (d, J = 1.2Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.93 (dd, J = 8.3, 2.4 Hz, 1H), 3.97 (d, J = 5.5Hz, 2H), 3.76 (s, 3H); **^{13}C{1H} NMR** (101 MHz, DMSO-*d*6): δ 159.9, 136.1, 130.3, 121.5, 115.0, 114.5, 55.7, 42.6.



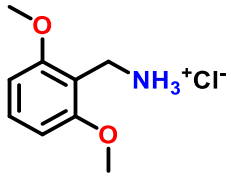
(4-methoxyphenyl)methanamine Hydrpochloride, 4h[2]

Colourless solid, Yield: 94%. **^{1}H NMR** (400 MHz, DMSO-d6): δ 8.90 (s, 3H), 7.84 (dd, J = 8.9, 2.2 Hz, 2H), 7.39 – 7.31 (m, 2H), 4.32 (d, J = 5.8 Hz, 2H), 4.16 (d, J = 3.7 Hz, 3H); **^{13}C{1H} NMR** (101 MHz, DMSO-d6): δ 158.9, 130.3, 125.6, 113.5, 54.8, 41.3.



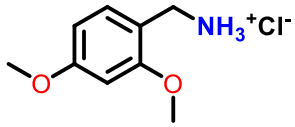
(3,5-dimethoxyphenyl)methanamine Hydrochloride, 4i[7]

Colourless solid, Yield: 94%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.38 (s, 3H), 6.70 (d, *J* = 1.8 Hz, 2H), 6.49 (d, *J* = 1.9 Hz, 1H), 3.94 (q, *J* = 5.6 Hz, 2H), 3.73 (d, J = 20.0 Hz, 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 158.4, 134.1, 104.7, 97.9, 53.2, 40.1.



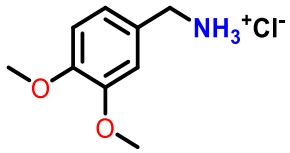
(2,6-Dimethoxyphenyl)methanamine Hydrochloride, 4j[8]

Colourless solid, Yield: 97%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.04 (s, 3H), 6.21 (d, J = 2.2 Hz, 2H), 5.96 (t, J = 2.2 Hz, 1H), 3.41 (d, J = 5.8 Hz, 2H), 3.23 (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 160.9, 136.7, 107.3, 100.4, 55.8, 42.6.



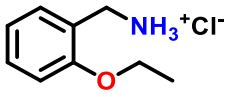
(2,4-Dimethoxyphenyl)methanamine Hydrochloride, 4k[9]

Colourless solid, Yield: 97%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.25 (s, 2H), 7.35 (d, J = 8.5 Hz, 1H), 6.69-6.53 (m, 2H), 3.91 (d, J = 2.5 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 161.7, 158.9, 131.8, 114.6, 105.25, 98.8, 56.2, 55.9, 37.7.



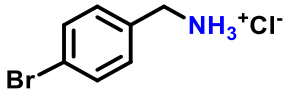
(3,4-Dimethoxyphenyl)methanamine Hydrochloride, 4l[10]

Colourless solid, Yield: 97%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.21 (s, 1H), 7.05 – 6.93 (m, 2H), 3.89 (s, 2H), 3.79 (d, J = 8.4 Hz, 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 149.2, 149.0, 129.2, 121.4, 113.0, 112.1, 56.1, 56.0, 43.3.



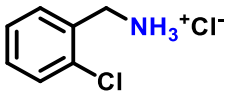
(2-ethoxyphenyl)methanamine Hydrpochloride, 4m[7]

Colourless solid, Yield: 92%. **^{1}H NMR** (400 MHz, DMSO-*d*6): δ 8.29 (s, 3H), 7.41 – 7.33 (m, 2H), 7.05 (d, J = 8.2 Hz, 1H), 6.96 (t, *J* = 7.3 Hz, 1H), 4.08 (q, J = 7.0 Hz, 2H), 3.95 (s, 2H), 1.37 (t, J = 6.9 Hz, 3H); **^{13}C{1H} NMR** (101 MHz, DMSO-*d*6): δ 154.3, 128.1, 119.7, 118.1, 109.6, 61.4, 35.3, 12.4.



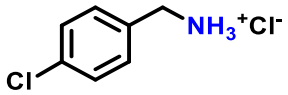
(4-Bromophenyl)methanamine Hydrochloride, 4n[2]

Colourless solid, Yield: 72%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.46 (s, 3H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 3.99 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 134.1, 132.0, 131.8, 122.3, 42.0.



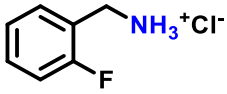
(2-Chlorophenyl)methanamine Hydrochloride, 4o[2,4]

Colourless solid, Yield: 68%. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.37 (s, 3H), 7.65 – 7.60 (m, 1H), 7.53 (dd, *J* = 6.0, 3.0 Hz, 1H), 7.45 – 7.39 (m, 2H), 4.09 (s, 2H).**^{13}C{^{1}H} NMR** (101 MHz, DMSO- d_6) δ 133.4, 132.8, 131.1, 130.7, 129.9, 128.0, 40.0.



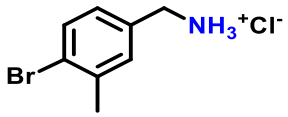
(4-Chlorophenyl)methanamine Hydrochloride, 4p[4]

Colourless solid, Yield: 66%. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.50 (s, 3H), 7.58 – 7.51 (m, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 4.01 (s, 2H).**^{13}C{^{1}H} NMR** (101 MHz, DMSO- d_6) δ 133.7, 131.5, 129.5, 129.1, 41.9.



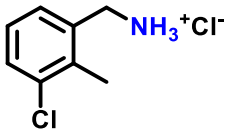
(2-Fluorophenyl)methanamine Hydrochloride, 4q[11]

Colourless solid, Yield: 64%.**^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.59 (s, 3H), 7.62 (t, J = 7.7 Hz, 1H), 7.43 (dd, J = 10.3, 4.2 Hz, 1H), 7.34 – 7.17 (m, 2H), 4.04 (d, *J* = 5.6 Hz, 1H).**^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ 162.0, 159.6, 131.9, 131.5, 131.4, 125.2, 121.7, 116.1, 115.9, 36.1.



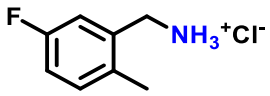
(4-bromo-3-methylphenyl)methanamine Hydrochloride, 4r[5]

Colourless solid, Yield: 76%.**^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.84 (s, 3H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.79 (s,1H), 7.57 (d, J = 7.6 Hz, 1H), 4.24 (d, J = 5.5 Hz, 2H), 2.63 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 138.5, 138.1, 134.8, 134.6, 132.9, 132.6, 132.5, 130.3, 129.7, 129.3, 126.8, 124.8,42.8, 42.2, 23.2, 21.7.



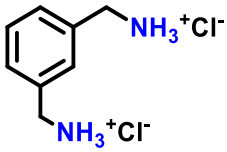
(3-chloro-2-methylphenyl)methanamine Hydrochloride, 4s[5]

Colourless solid, Yield: 73%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.67 (s, 3H), 7.50 (dd, J = 11.4 Hz, 2H), 7.33 (t, J = 7.8 Hz, 1H), 4.12 (d, J = 5.7 Hz, 2H), 2.44 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 134.8, 134.7, 134.1, 129.4, 128.5, 127.3, 40.1, 15.8.



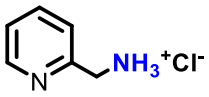
(5-fluoro-2-methylphenyl)methanamine Hydrochloride, 4t[5]

Colourless solid, Yield: 78%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 9.03 (s, 3H), 7.70 (dd, J = 10.1 Hz, J = 2.7 Hz, 1H), 7.62 (dd, J = 8.3 Hz, J = 6.2 Hz, 1H), 7.45 (td, J = 8.6 Hz, J = 2.6 Hz, 1H), 4.35 (d, J = 5.3 Hz, 2H) 2.66 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 161.4, 158.9, 134.2, 134.1, 132.5, 132.4, 131.8, 131.7, 115.6, 115.4, 114.8, 114.6, 38.9, 17.9.



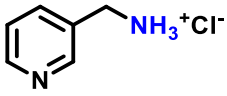
1, 3-phenylenedimethanamine Hydrochloride, 4u[2]

White solid, Yield: 76%. **^{1}H NMR** (400 MHz, CD_3OD): δ 7.53 (dd, J = 12.2, 7.1, 4H), 4.12 (s, 4H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 136.4, 129.4, 128.6, 128.5, 43.4.



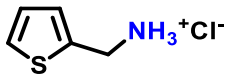
Pyridine-2-ylmethanamine Hydrochloride, 5a[12]

White solid, Yield: 76%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.68-8.50 (m, 1H), 7.97-7.83 (m, 1H), 7.55 (dd, J = 19.9, 7.8 Hz, 1H), 7.45-7.31 (m, 1H), 6.94 (s, 3H) 4.16 (d, J = 19.9, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 155.2, 149.4, 137.6, 123.6, 122.9, 43.9.



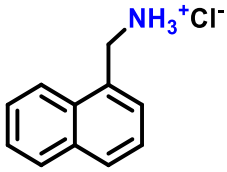
Pyridine-3-ylmethanamine Hydrochloride, 5b[5]

White solid, Yield: 76%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 9.11 (s, 1H), 9.00 (s, 3H), 8.92 (s, 1H), 8.77 (s, 1H), 8.10 (s, 1H) 4.28 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 146.2, 143.1, 142.2, 133.7, 126.7, 39.1.



Thiophen-2-ylmethanamine Hydrochloride, 5c[2]

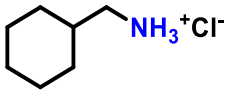
White solid, Yield: 71%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.43 (s, 3H), 7.58 (d, J = 4.9 Hz, 1H), 7.26 (d, J = 2.6 Hz, 1H), 7.14 – 6.97 (m, 1H), 4.22 (d, J = 4.5 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 135.9, 129.6, 127.8, 127.7, 37.2.



Naphthalene-1-ylmethanamine Hydrochloride, 5d[3]

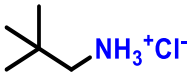
Off-white solid, Yield: 85%.**^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.65 (s, 3H), 8.15 (d, J = 8.1 Hz, 1H), 7.99 (dd, J = 10.6, 8.7 Hz, 2H), 7.67 - 7.53 (m,4H), 4.51 (d, J = 5.7 Hz, 2H); **^{13}C{^{1}H} NMR**

(101 MHz, DMSO-d_6): δ 133.7, 131.2, 130.5, 129.6, 129.2, 127.8, 127.3, 126.8, 125.9, 124.0, 39.6.



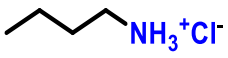
Cyclohexylmethanamine Hydrochloride, 6a[2]

Colourless solid, Yield: 75%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.97 (s, 3H), 2.61 (s, 2H), 1.76 - 1.49 (m, 6H), 1.24 - 1.06 (m, 3H), 0.98-0.84 (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 44.9, 35.9, 30.3, 26.2, 25.6.



2, 2-Dimethylpropan-1-amine Hydrochloride, 6b[2]

Colourless solid, Yield: 82%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.10 (d, J = 11.8 Hz, 3H), 2.59 (d, J = 6.0 Hz, 2H), 0.95 (s, 9H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 49.5, 29.9, 26.7.



***n*-butylamine Hydrochloride, 6c**[13]

Colourless solid, Yield: 65%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.15 (s, 3H), 2.71 (s, 2H), 1.52 (d, J = 6.7Hz 2H), 1.30 (d, J = 7.4 Hz, 2H), 0.85 (t, J = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 38.4, 28.9, 19.2**,** 13.5.

IX. ^{1}H NMR and ^{13}C NMR spectra of the products:

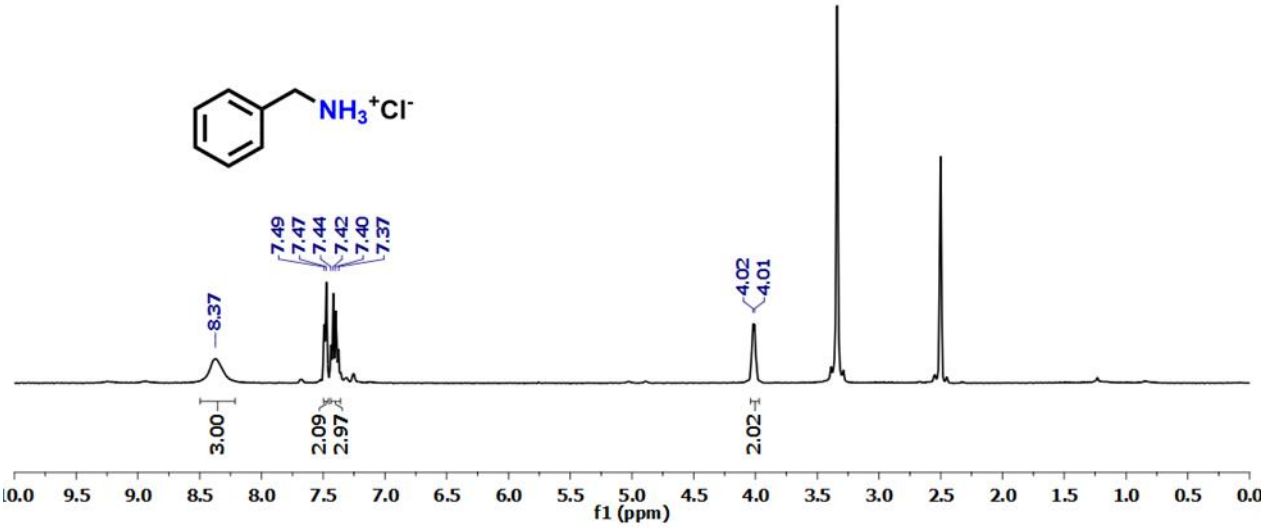


Figure S19. ^{1}H NMR spectrum (DMSO-d_6) of phenylmethanaminium chloride.

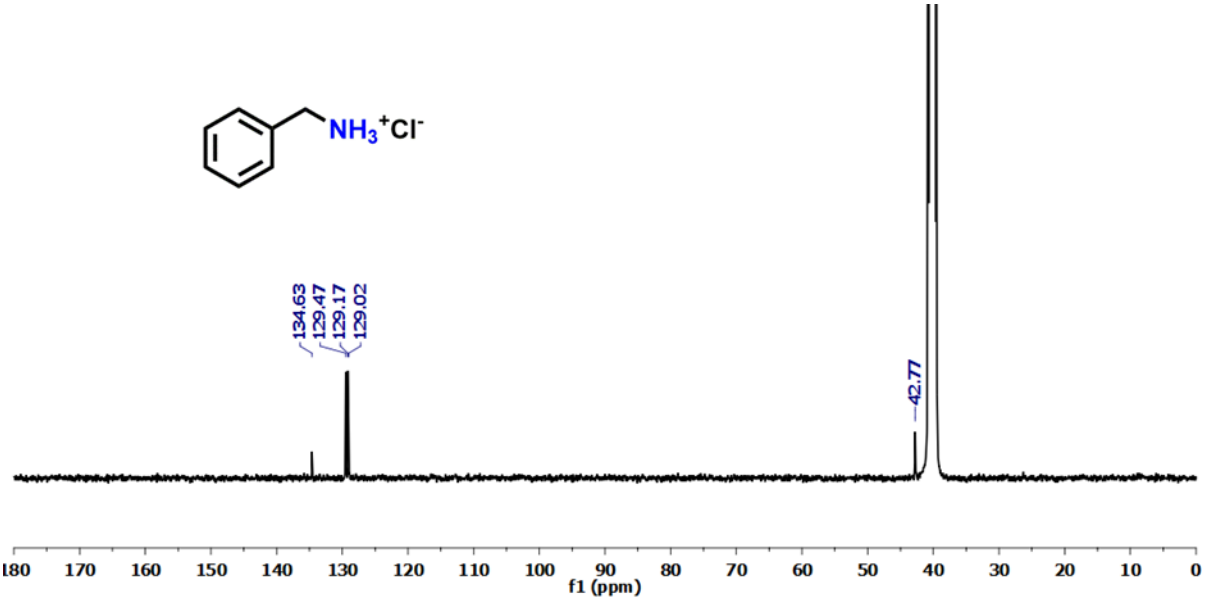


Figure S20. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of phenylmethanaminium chloride.

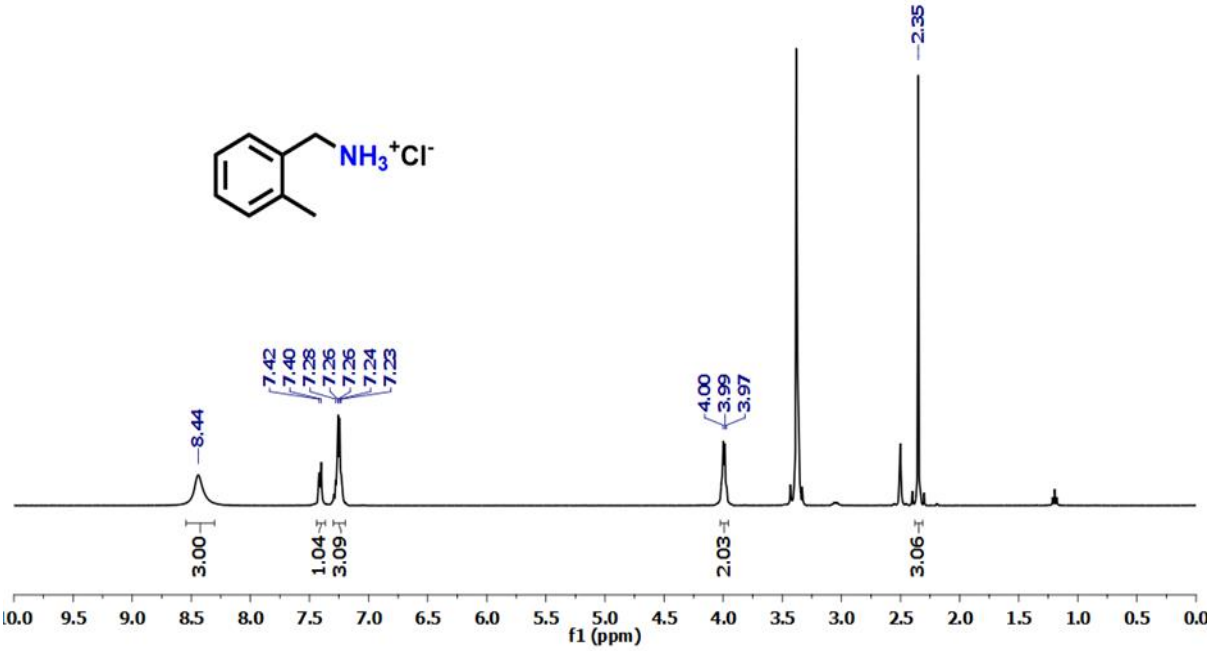


Figure S21. ^{1}H NMR spectrum (DMSO-*d*6) of o-tolylmethanamine hydrochloride.

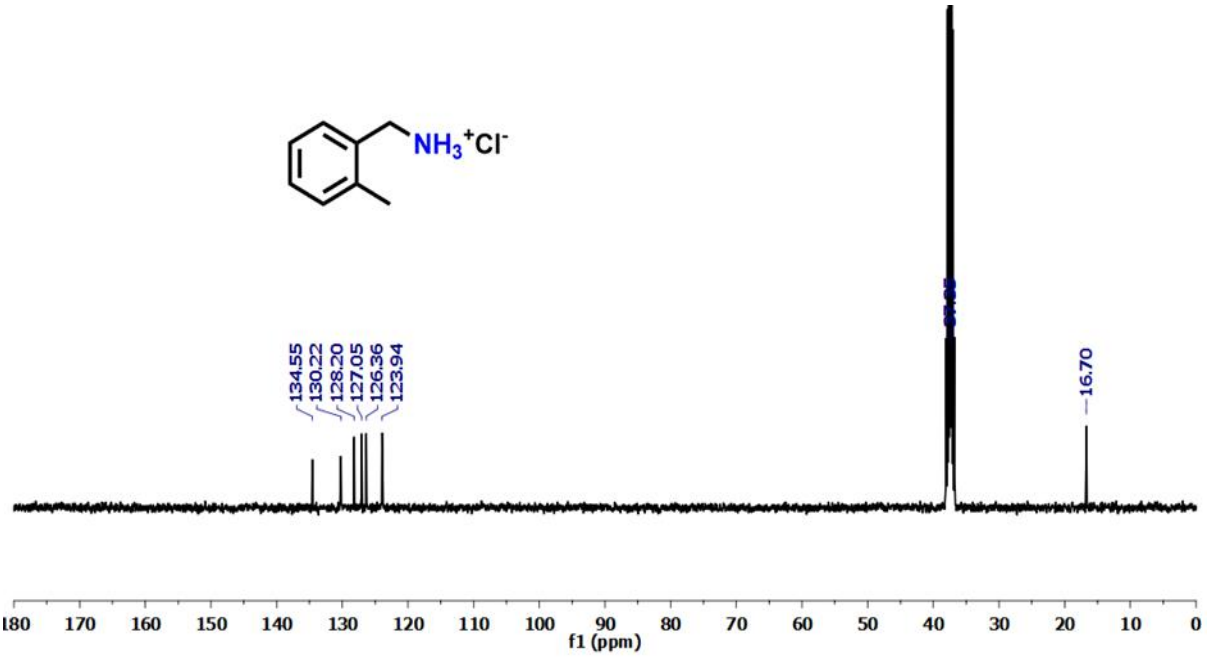


Figure S22. ^{13}C{^{1}H} NMR spectrum (DMSO-d6) of o-tolylmethanamine hydrochloride.

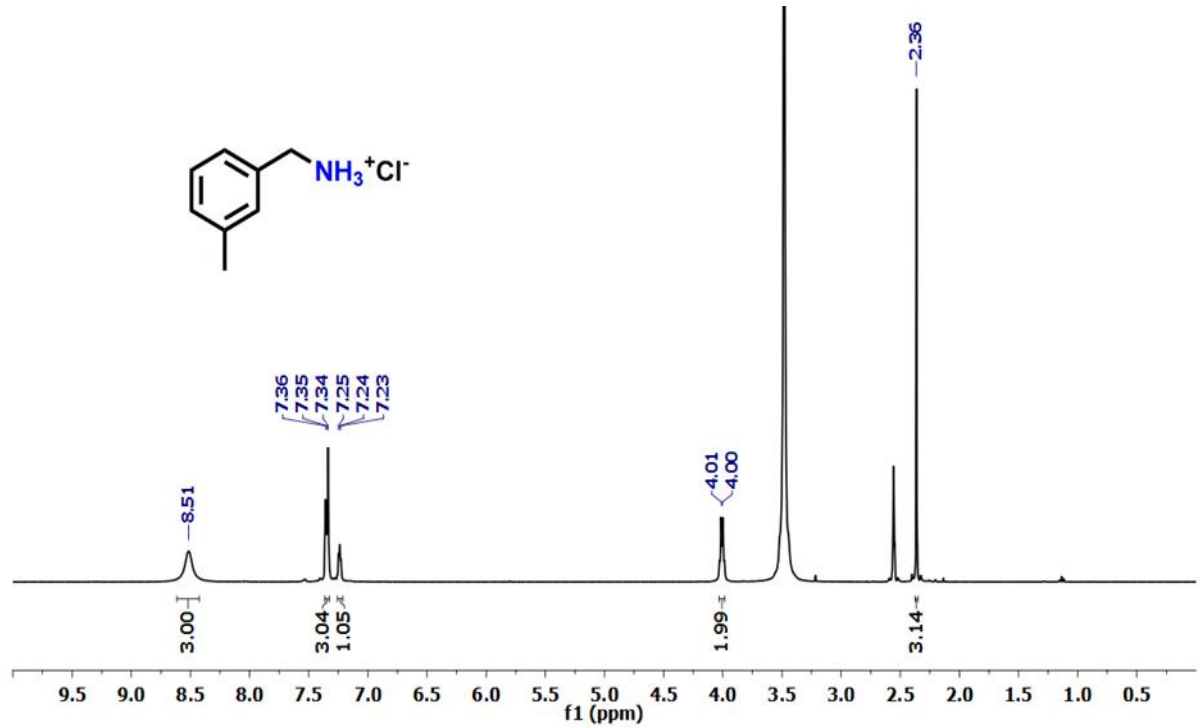


Figure S23. ^{1}H NMR spectrum (DMSO-d6) of m-tolylmethanamine hydrochloride.

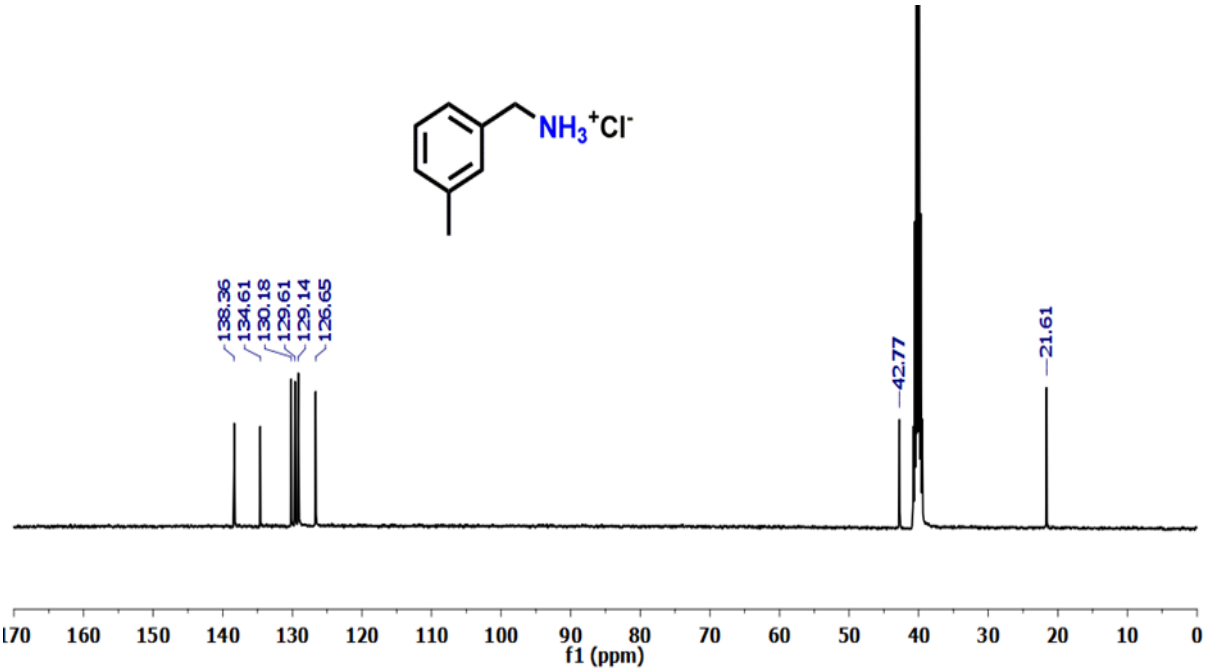


Figure S24. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of m-tolylmethanaminium chloride.

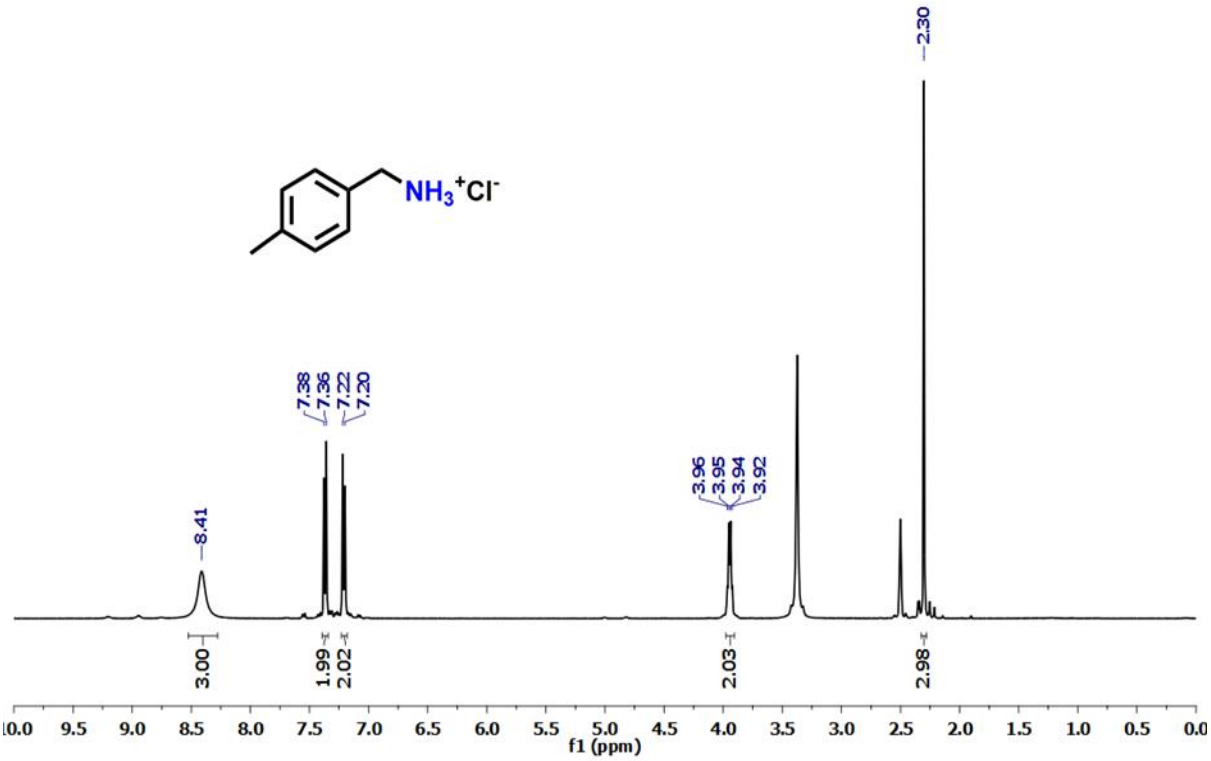


Figure S25. ^{1}H NMR spectrum (DMSO-*d*6) of p-tolylmethanamine Hydrochloride

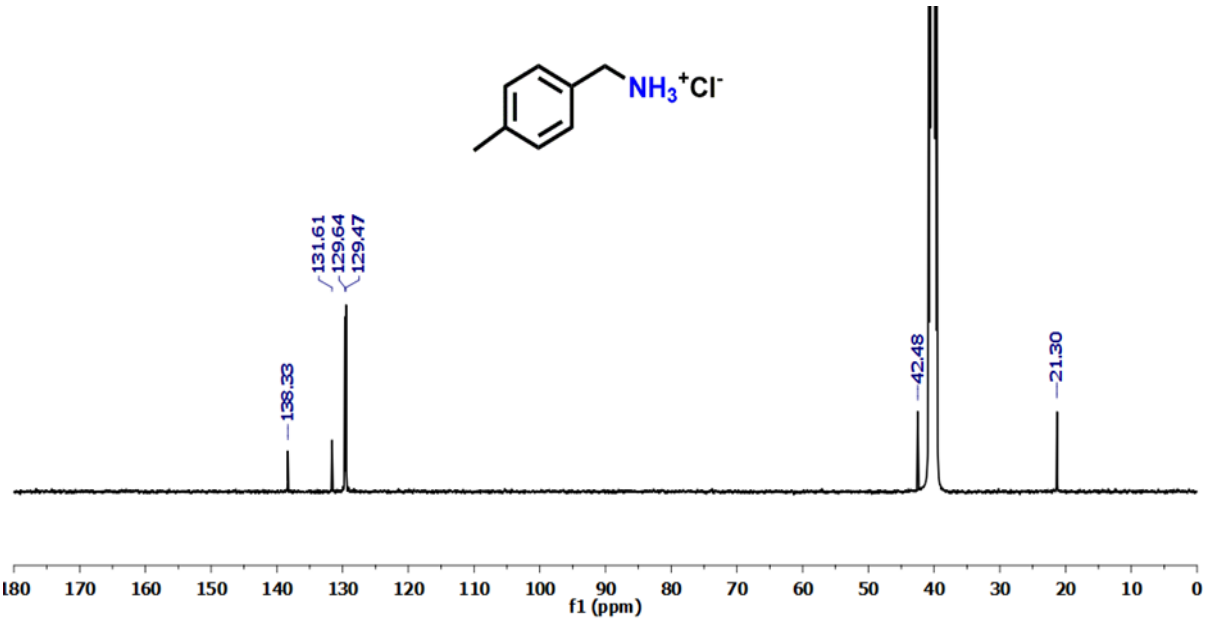


Figure S26. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of p-tolylmethanamine Hydrochloride.

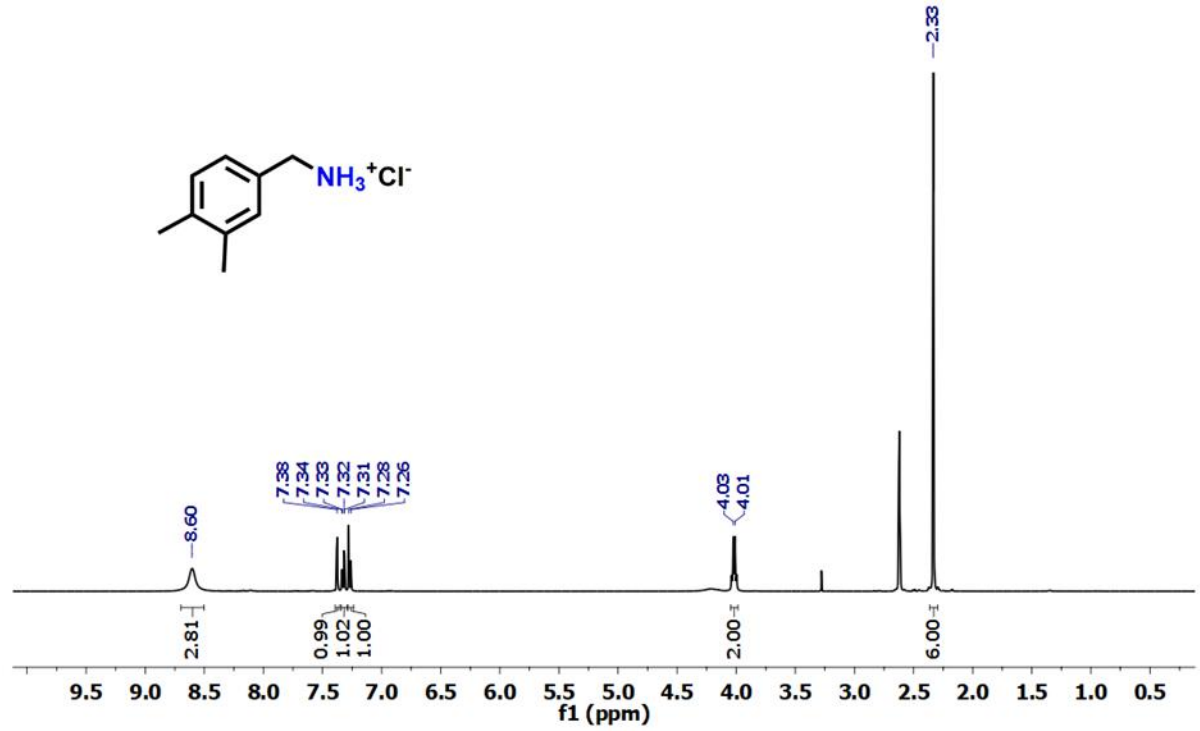


Figure S27. ^{1}H NMR spectrum (DMSO-*d*6) of (3,4-dimethylphenyl)methanamine hydrochloride.

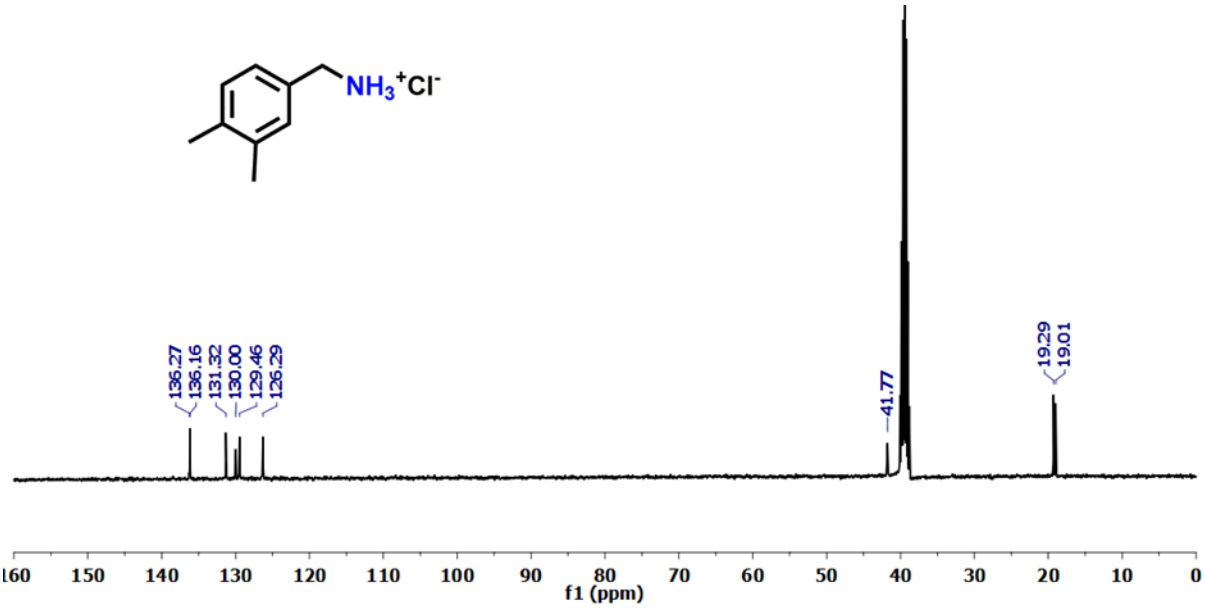


Figure S28. ^{13}C{^{1}H} NMR spectrum (DMSO-d6) of (3,4-dimethylphenyl)methanamine hydrochloride.

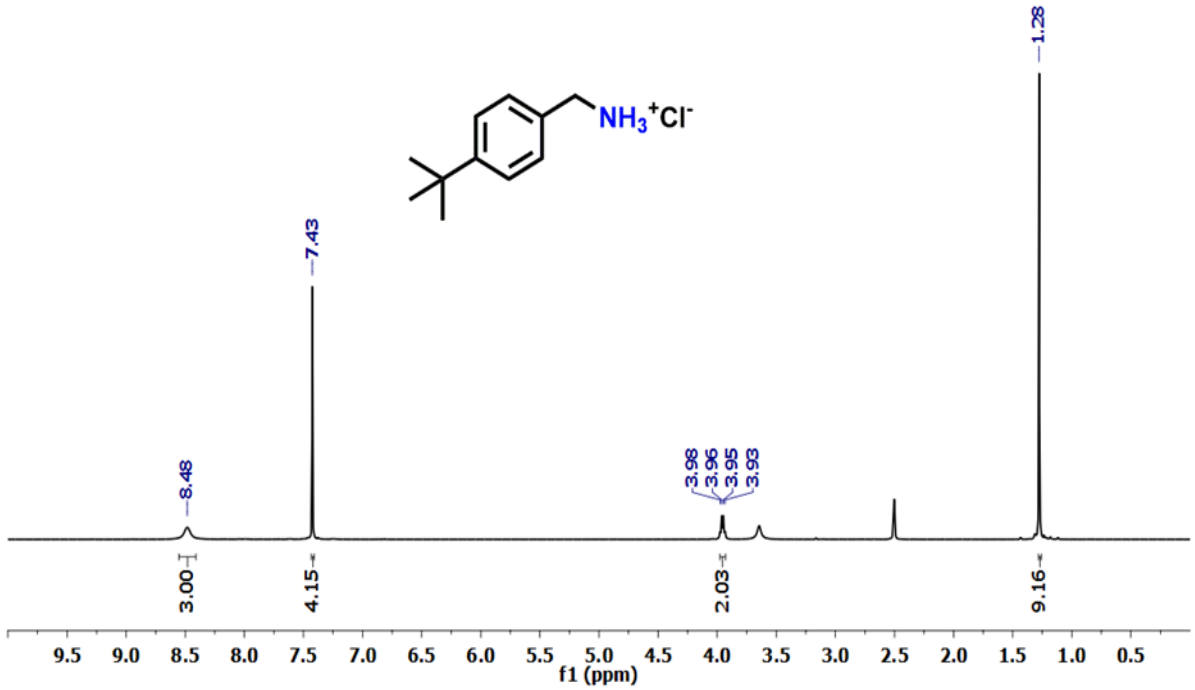


Figure S29. ^{1}H NMR spectrum (DMSO-d_6) of (4-(tert-butyl)phenyl)methanamine Hydrochloride.

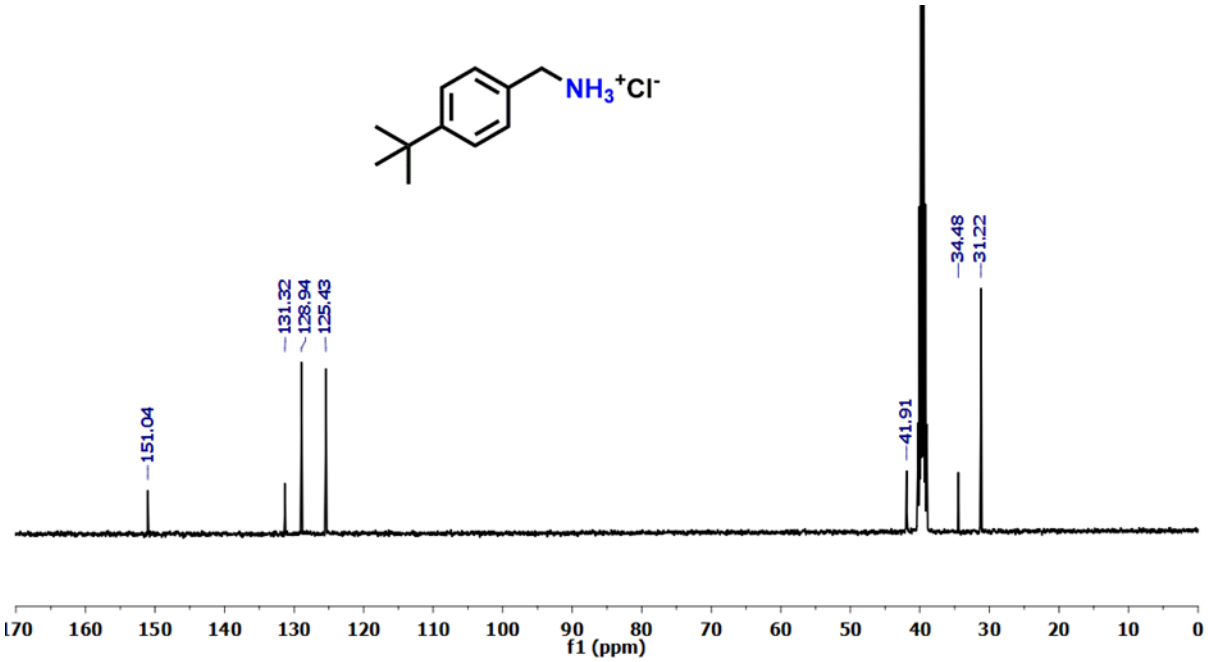


Figure S30. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (4-(tert-butyl)phenyl)methanamine Hydrochloride.

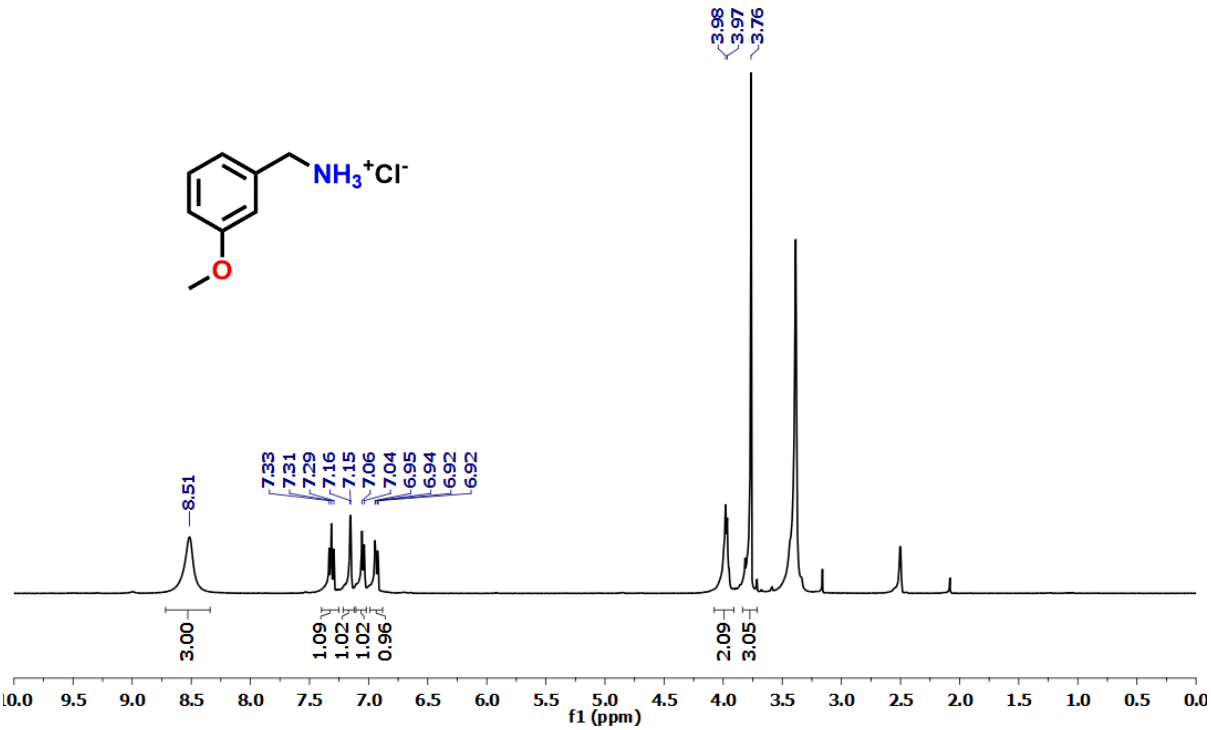


Figure S31. ^{1}H NMR spectrum (DMSO-*d*6) of (3-methoxyphenyl)methanamine hydrochloride.

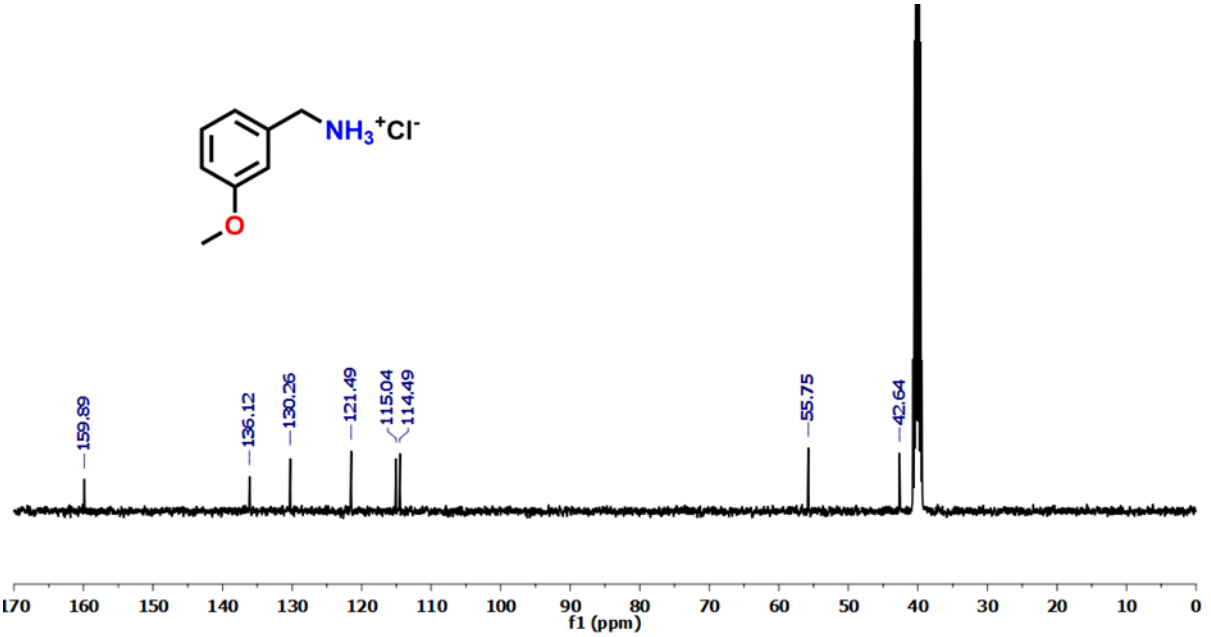


Figure S32. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (3-methoxyphenyl)methanamine hydrochloride.

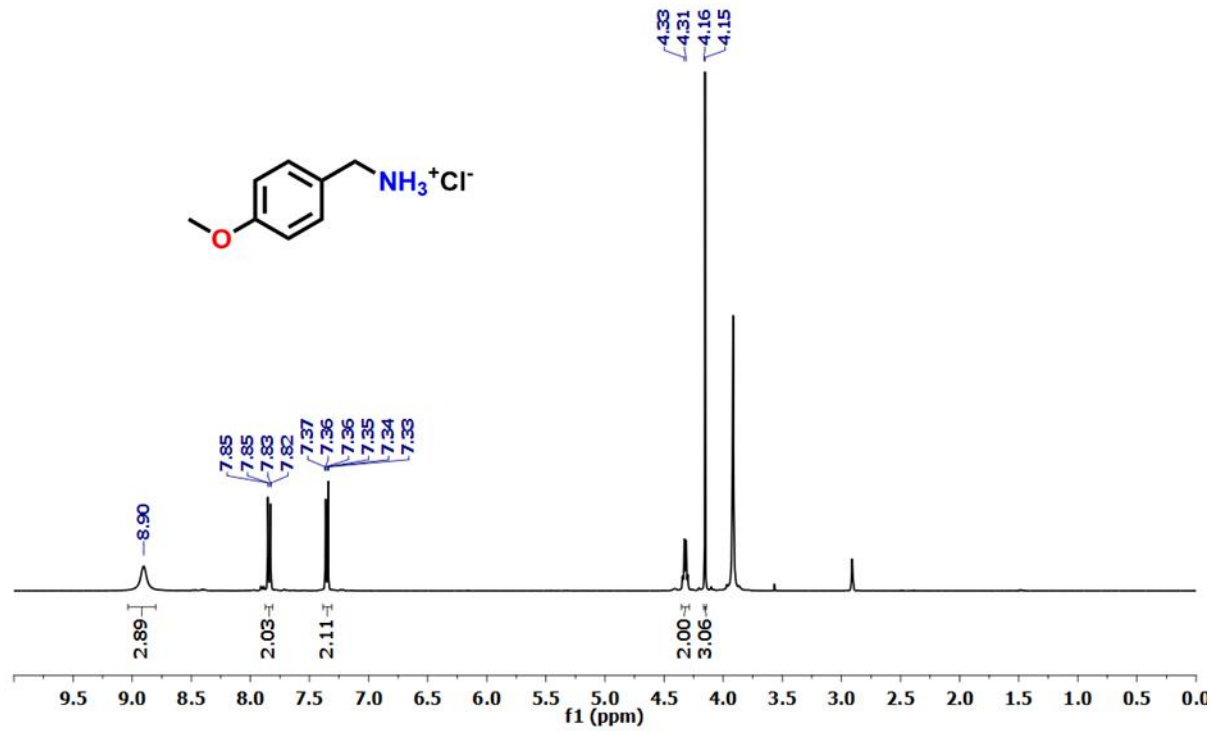


Figure S33. ^{1}H NMR spectrum (DMSO-*d*6) of (4-methoxyphenyl)methanamine hydrochloride.

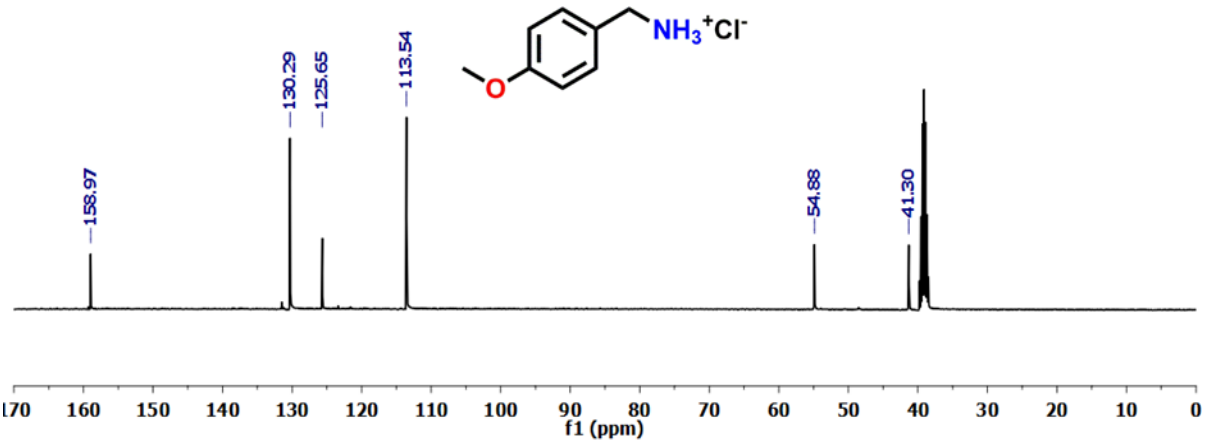


Figure S34. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (4-methoxyphenyl)methanamine hydrochloride.

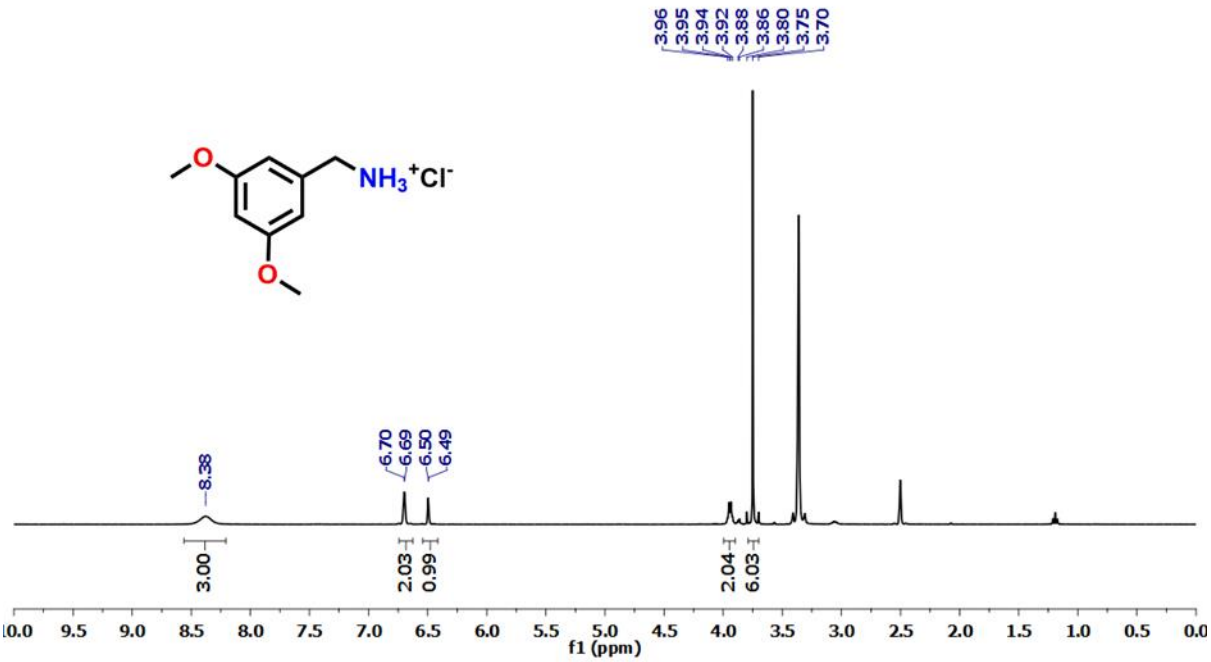


Figure S35. ^{1}H NMR spectrum (DMSO-*d*6) of (3,5-dimethoxyphenyl)methanamine hydrochloride.

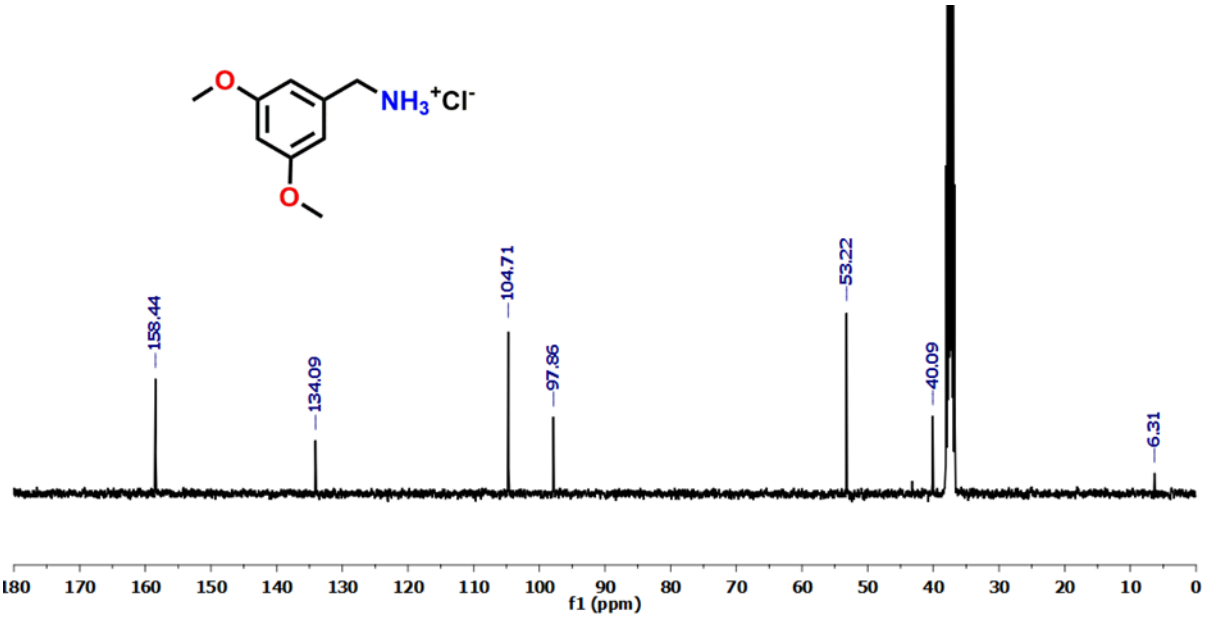


Figure S36. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (3,5-dimethoxyphenyl)methanamine hydrochloride.

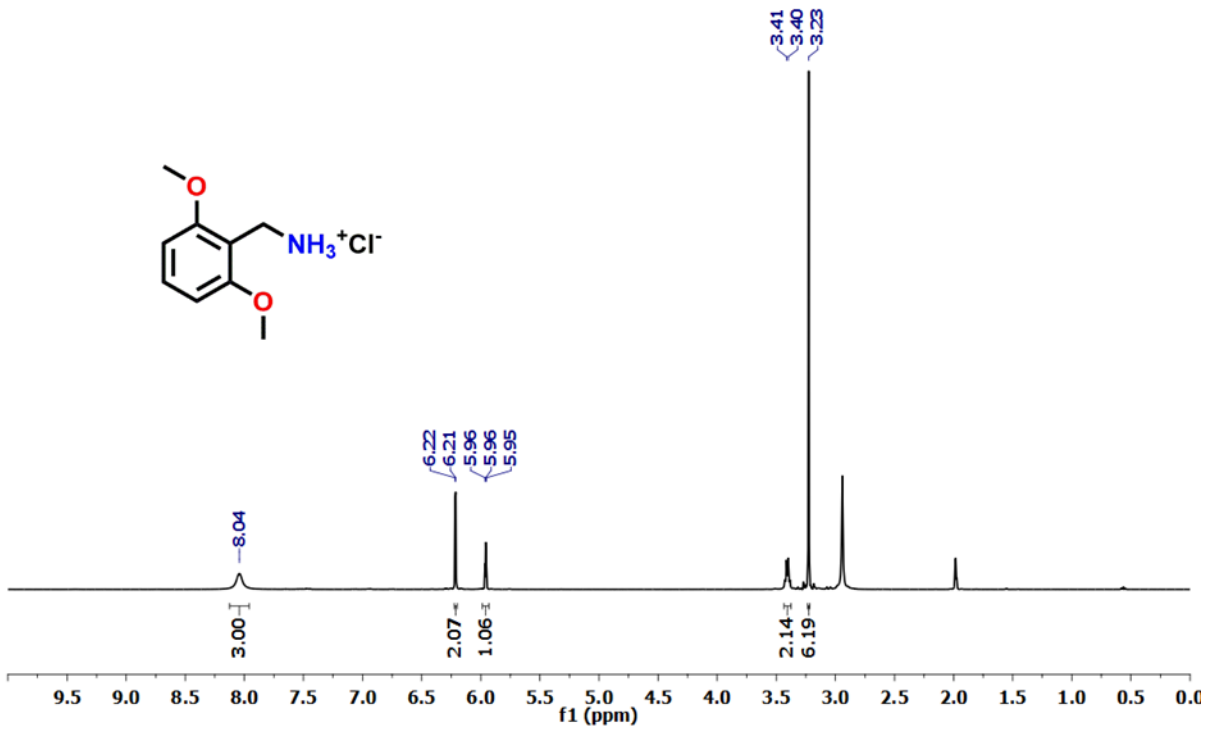


Figure S37. ^{1}H NMR spectrum (DMSO-*d*6) of (2,6-dimethoxyphenyl)methanamine hydrochloride.

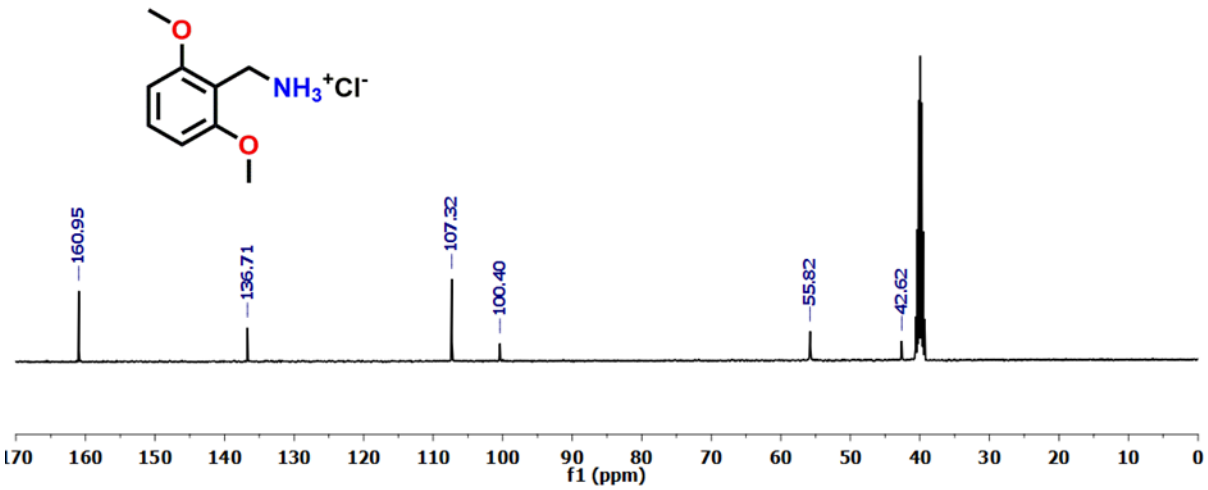


Figure S38. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (2,6-dimethoxyphenyl)methanamine hydrochloride.

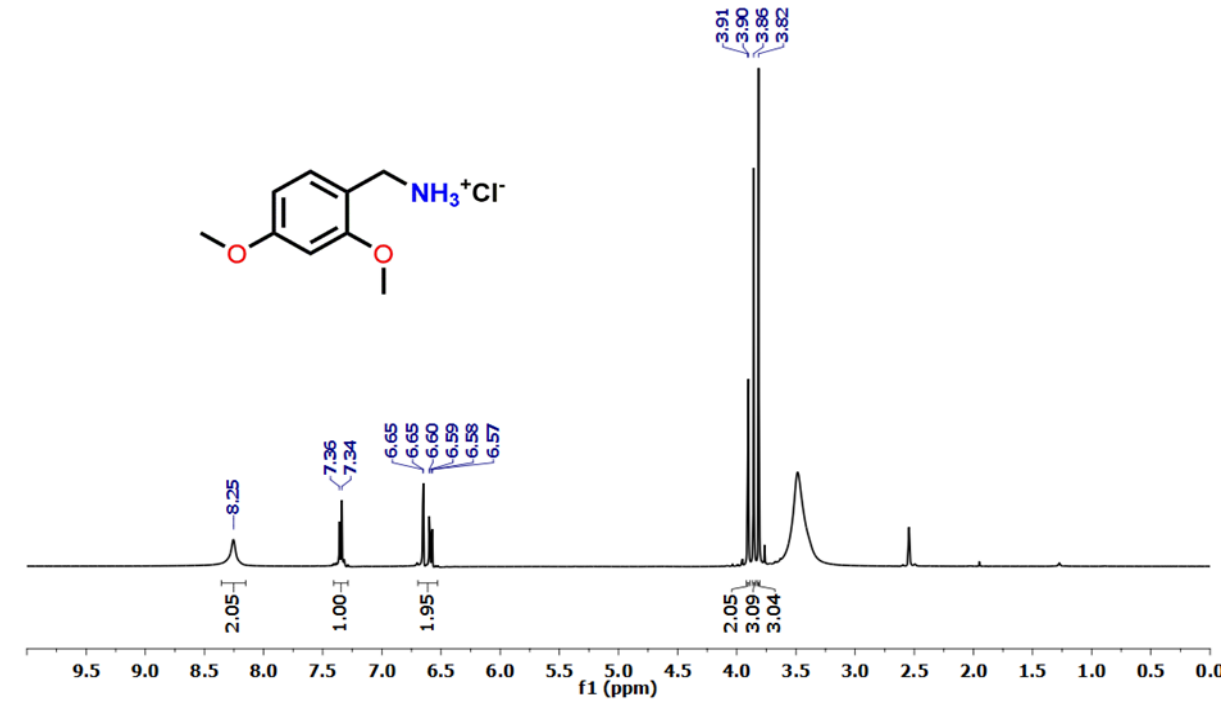


Figure S39. ^{1}H NMR spectrum (DMSO-*d*6) of (2,6-dimethoxyphenyl)methanamine hydrochloride

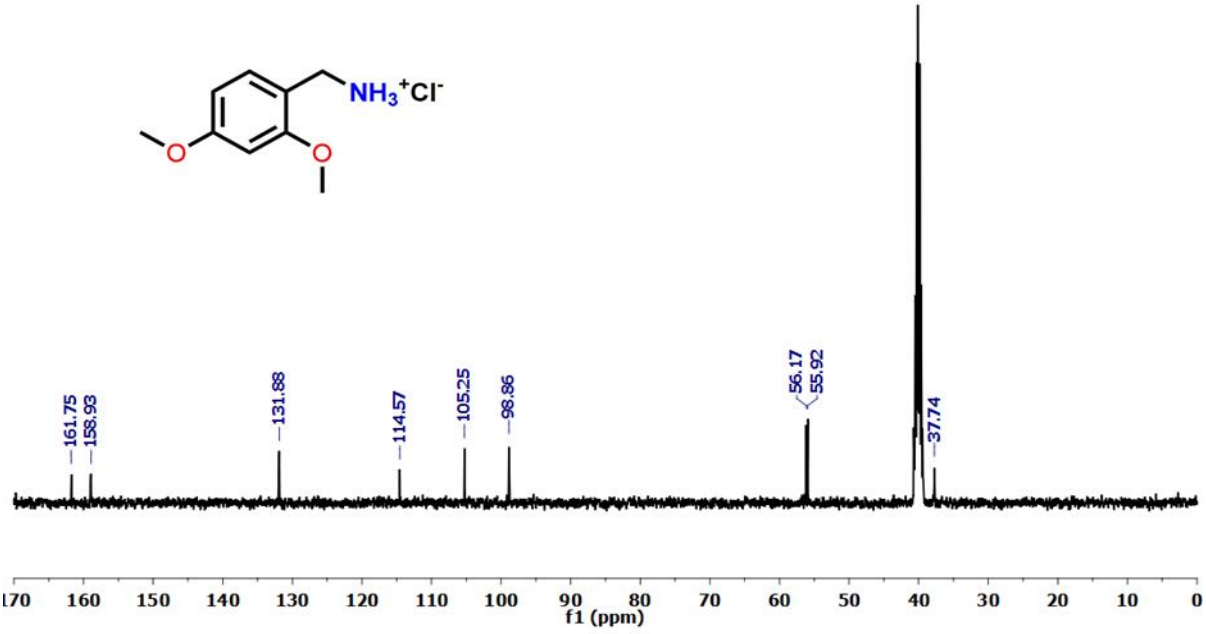


Figure S40. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (2-ethoxyphenyl)methanamine hydrochloride.

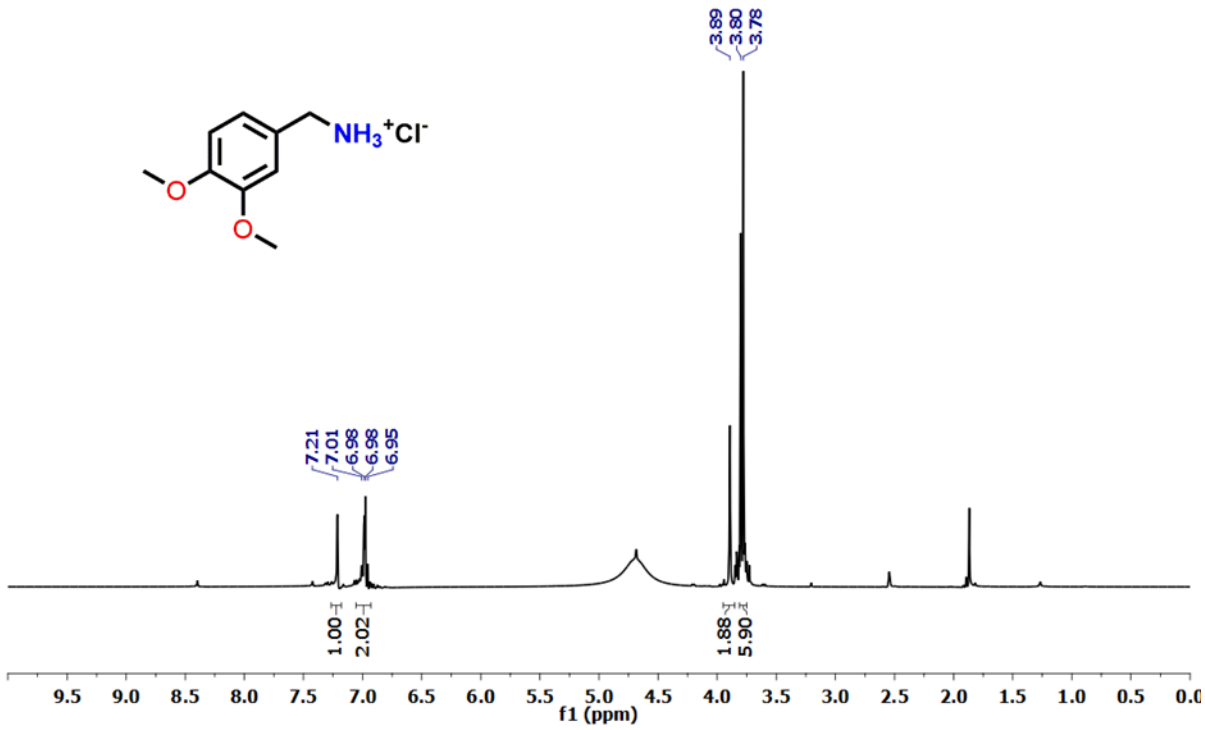


Figure S41. ^{1}H NMR spectrum (DMSO-*d*6) of (2,6-dimethoxyphenyl)methanamine hydrochloride.

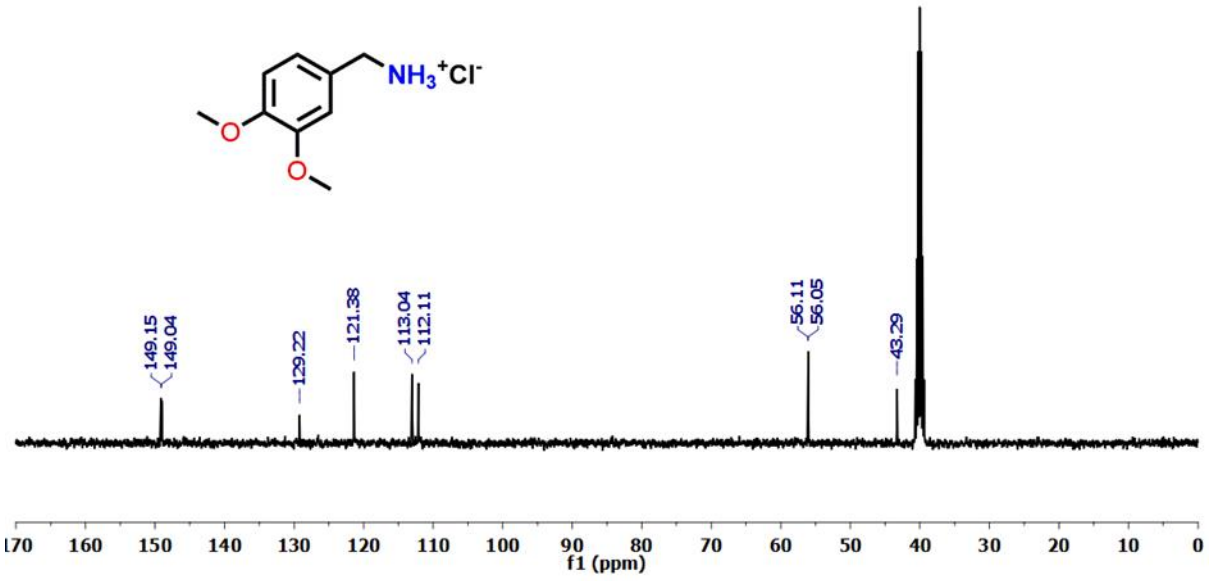


Figure S42. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (2-ethoxyphenyl)methanamine hydrochloride.

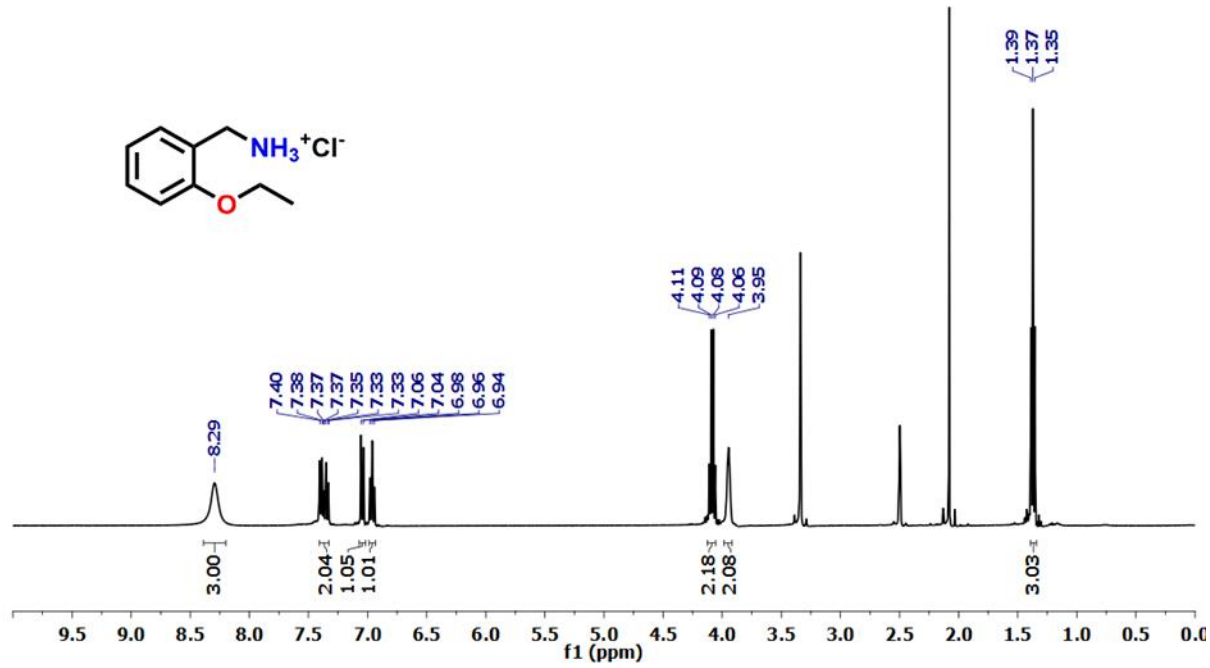


Figure S43. ^{1}H NMR spectrum (DMSO-*d*6) of (2-ethoxyphenyl)methanamine hydrochloride.

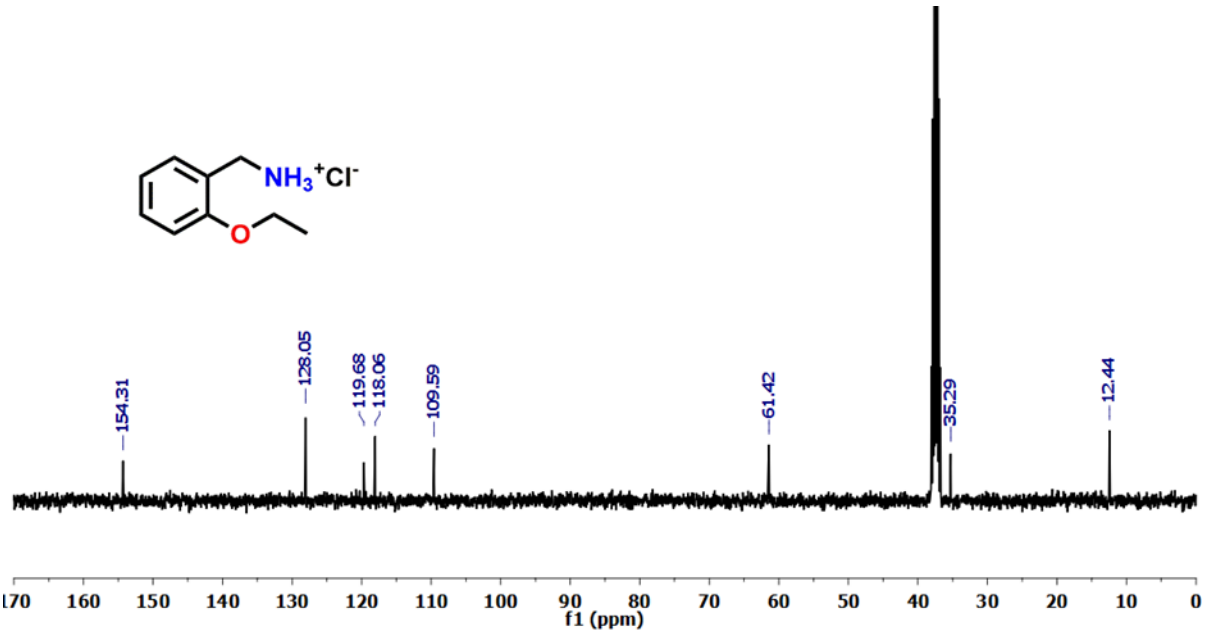


Figure S44. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (2-ethoxyphenyl)methanamine hydrochloride.

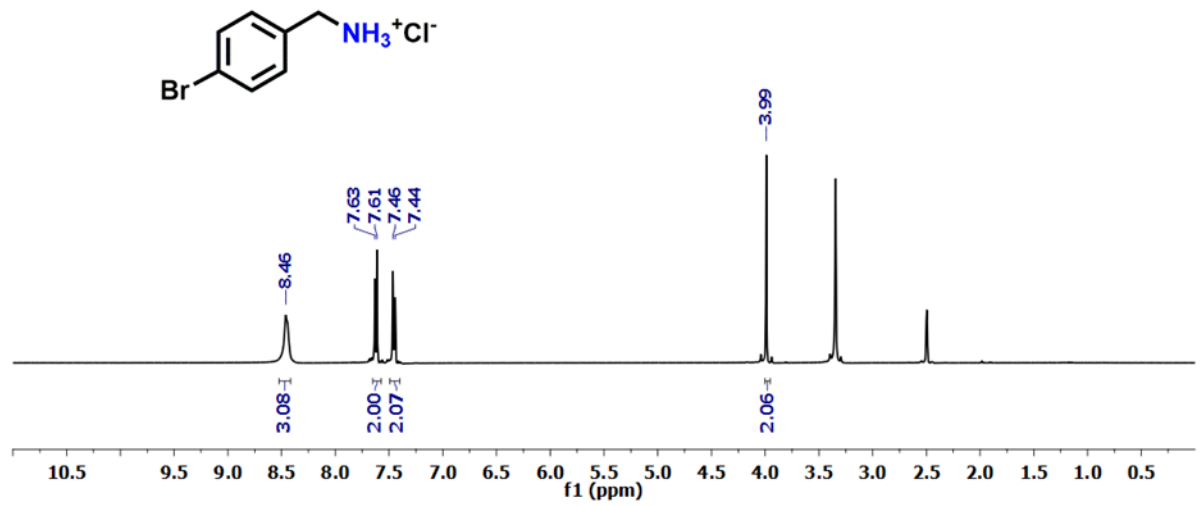


Figure S45. ^{1}H NMR spectrum (DMSO-*d*6) of (4-bromophenyl)methanamine hydrochloride.

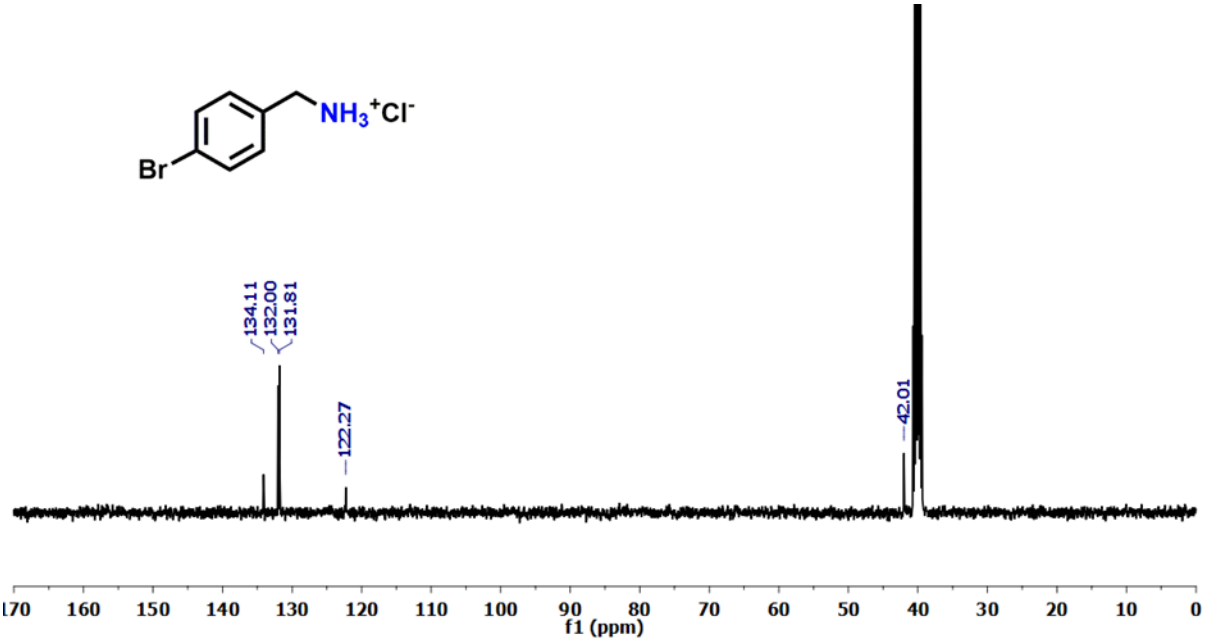


Figure S46. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (4-bromophenyl)methanamine hydrochloride.

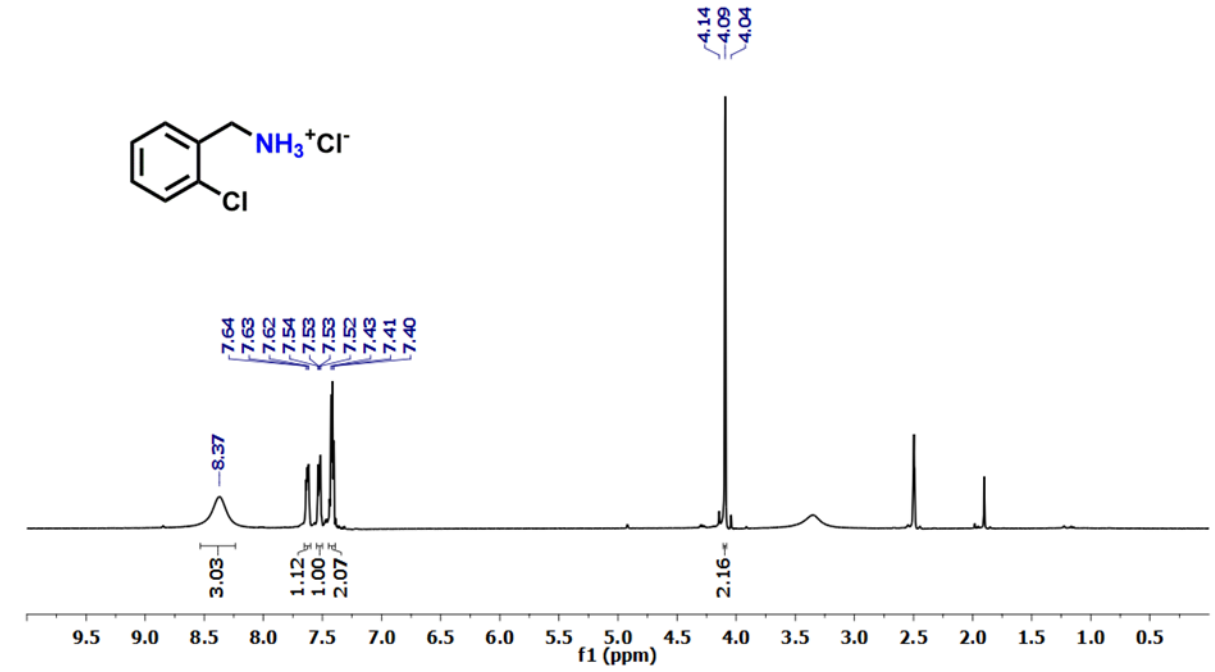


Figure S47. ^{1}H NMR spectrum (DMSO-*d*6) of (2-chlorophenyl)methanamine hydrochloride.

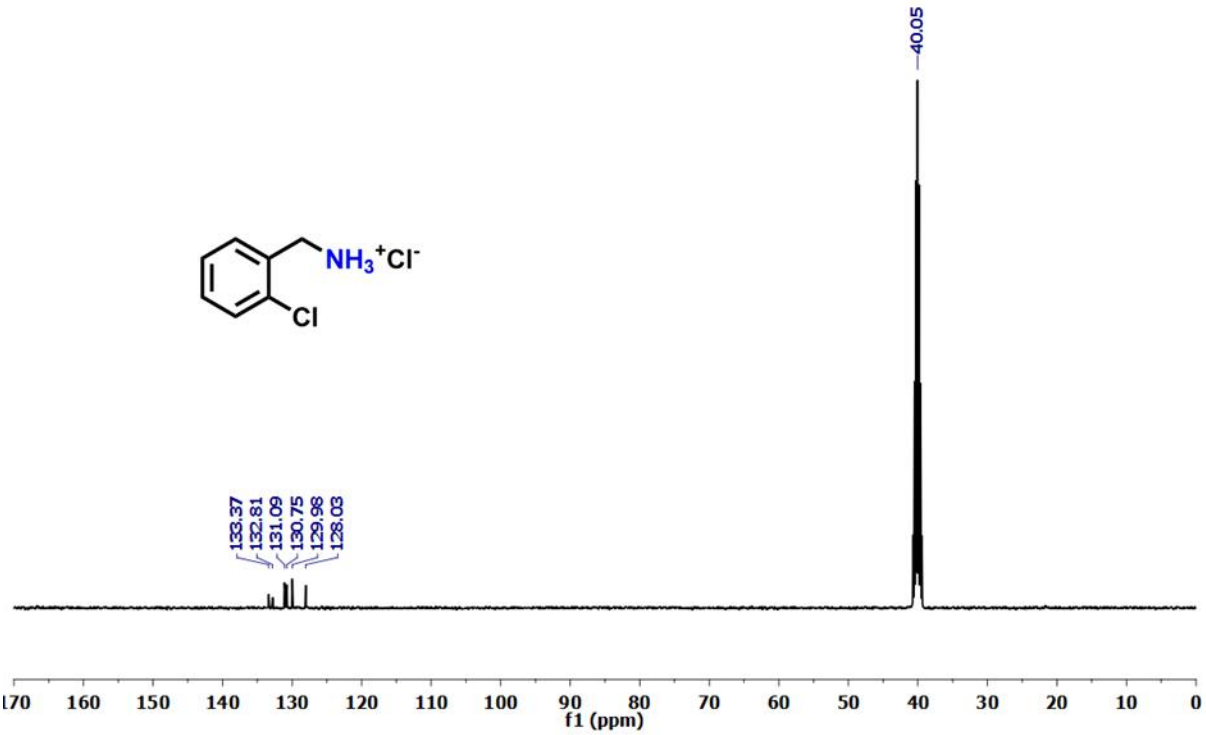


Figure S48. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (2-chlorophenyl)methanamine hydrochloride.

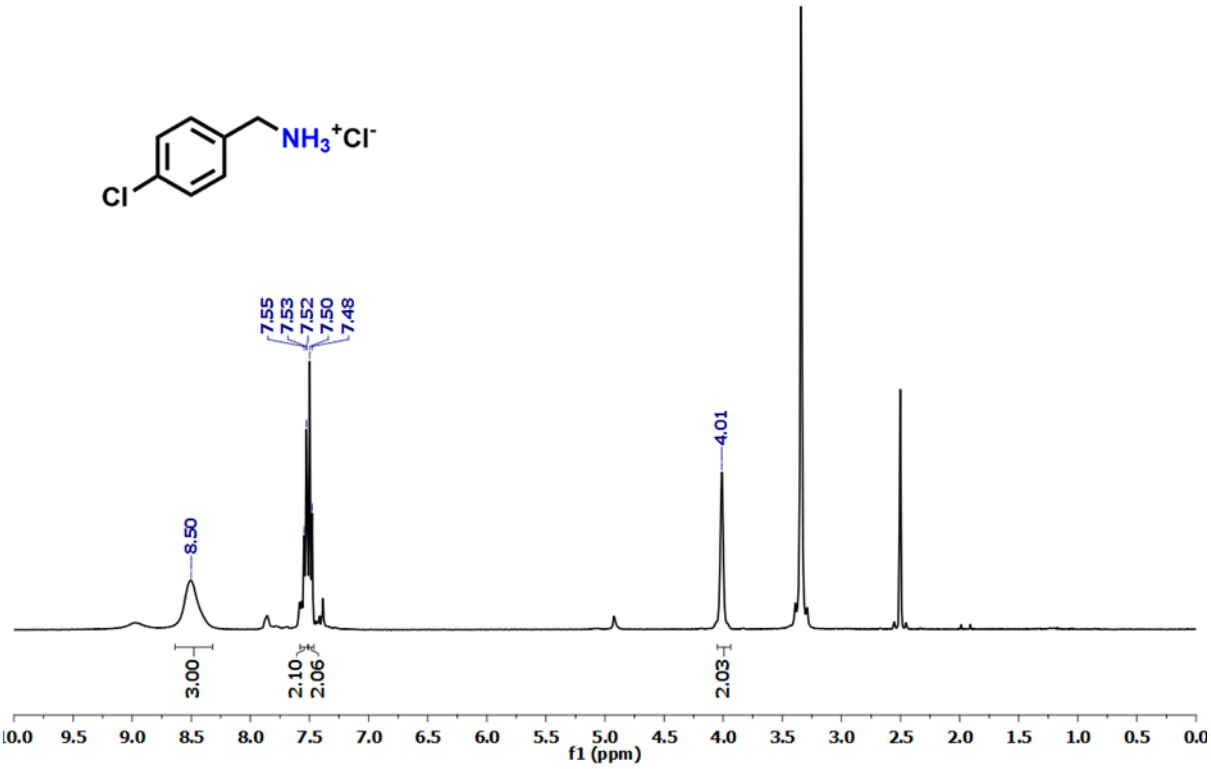


Figure S49. ^{1}H NMR spectrum (DMSO-*d*6) of (4-chlorophenyl)methanamine hydrochloride.

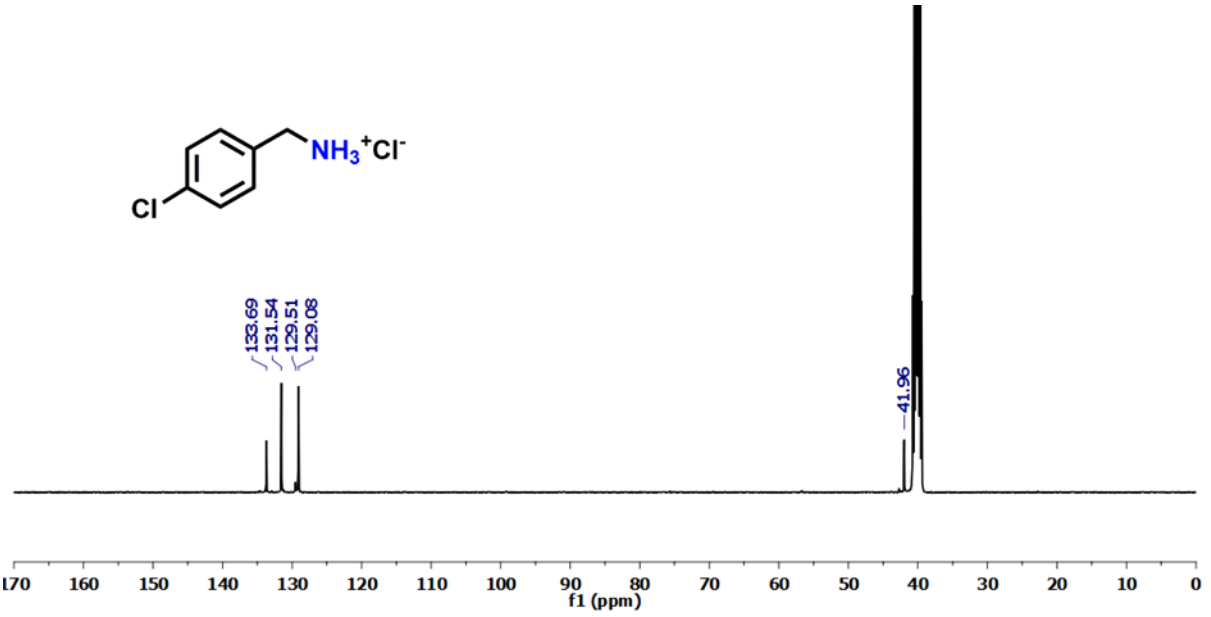


Figure S50. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (4-chlorophenyl)methanamine hydrochloride.

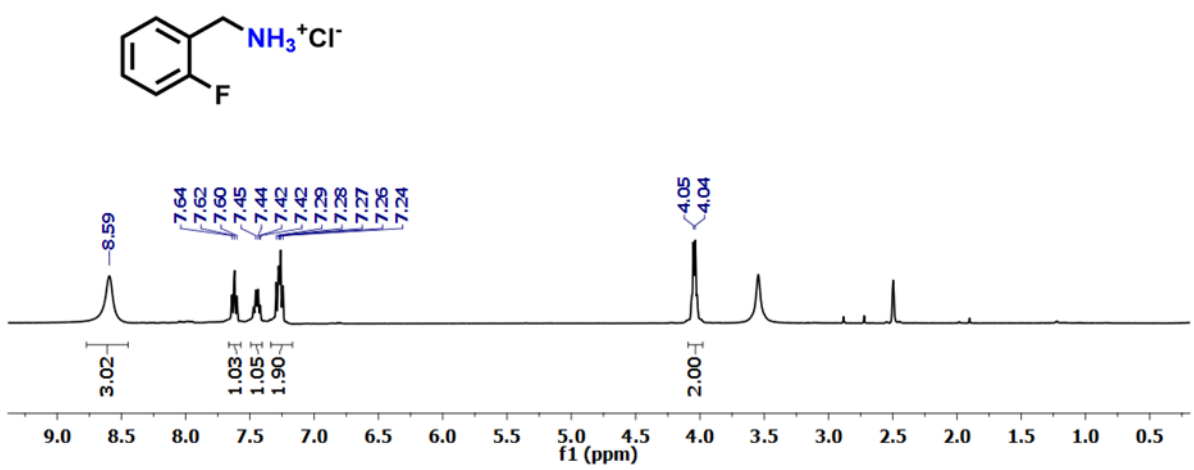


Figure S51. ^{1}H NMR spectrum (DMSO-*d*6) of (2-fluorophenyl)methanamine hydrochloride.

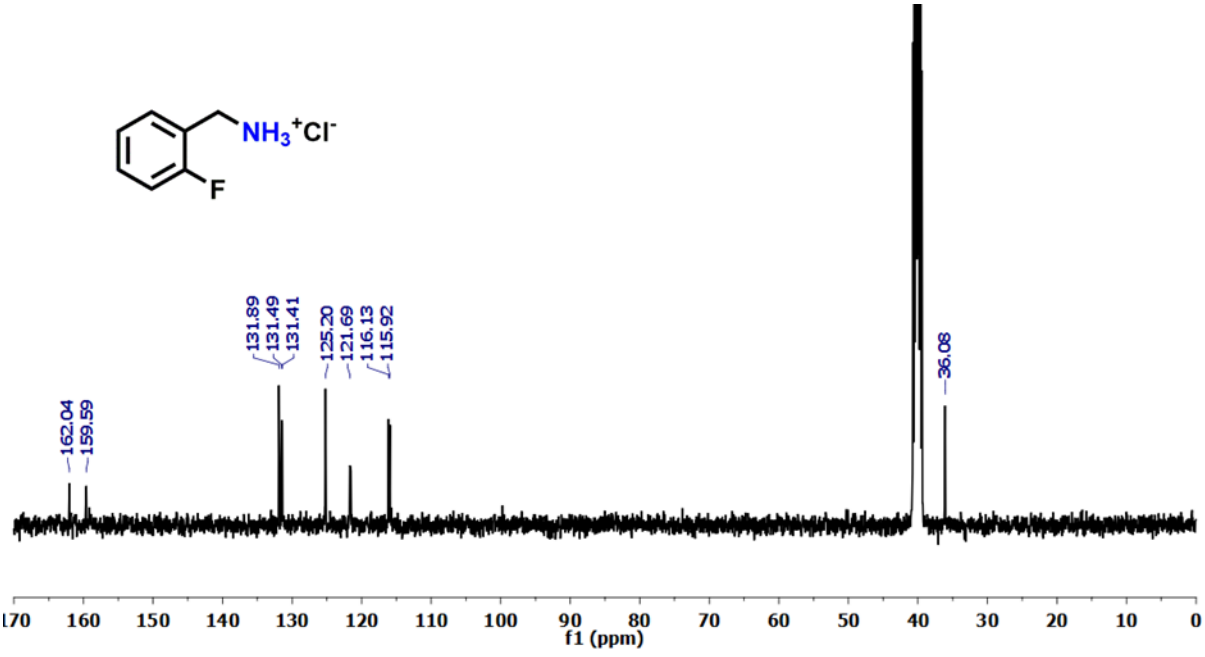


Figure S52. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (2-fluorophenyl)methanamine hydrochloride.

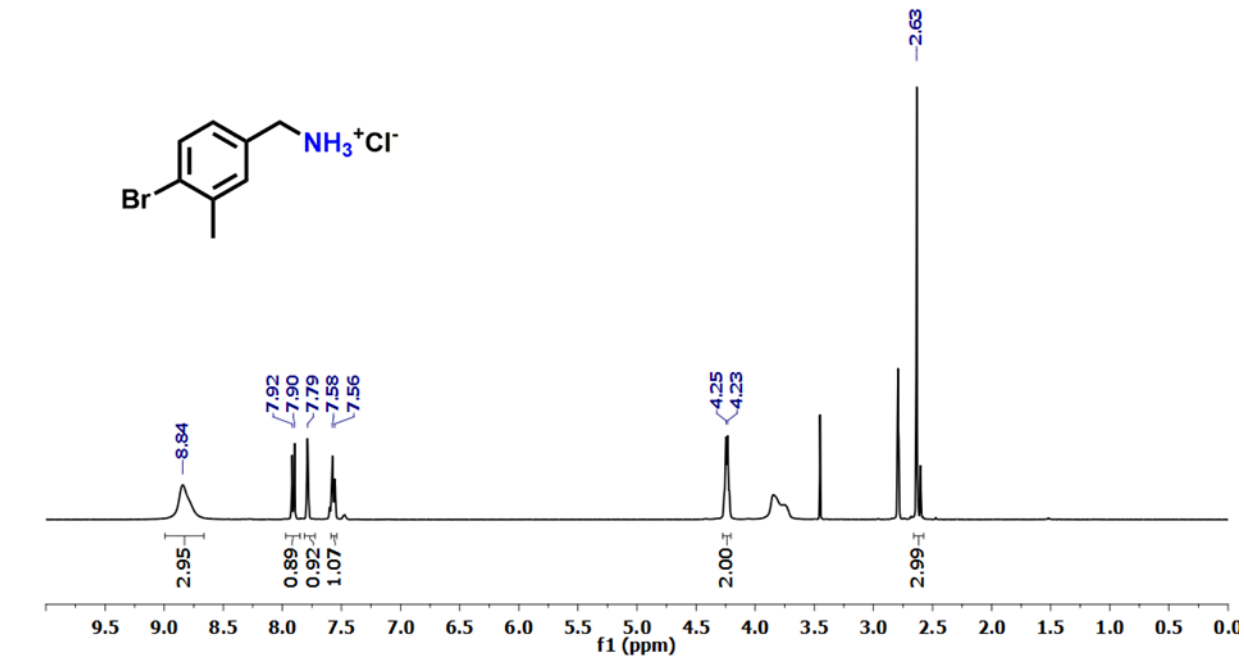


Figure S53. ^{1}H NMR spectrum (DMSO-*d*6) of (4-bromo-3-methylphenyl)methanamine hydrochloride.

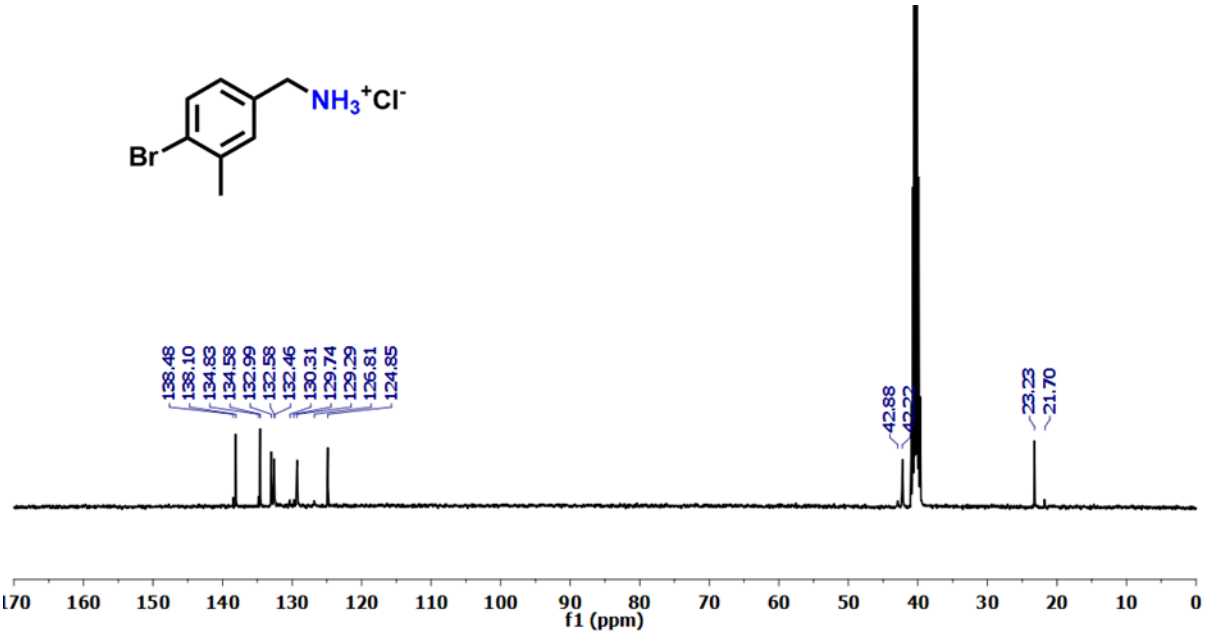


Figure S54. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (4-bromo-3-methylphenyl)methanamine hydrochloride

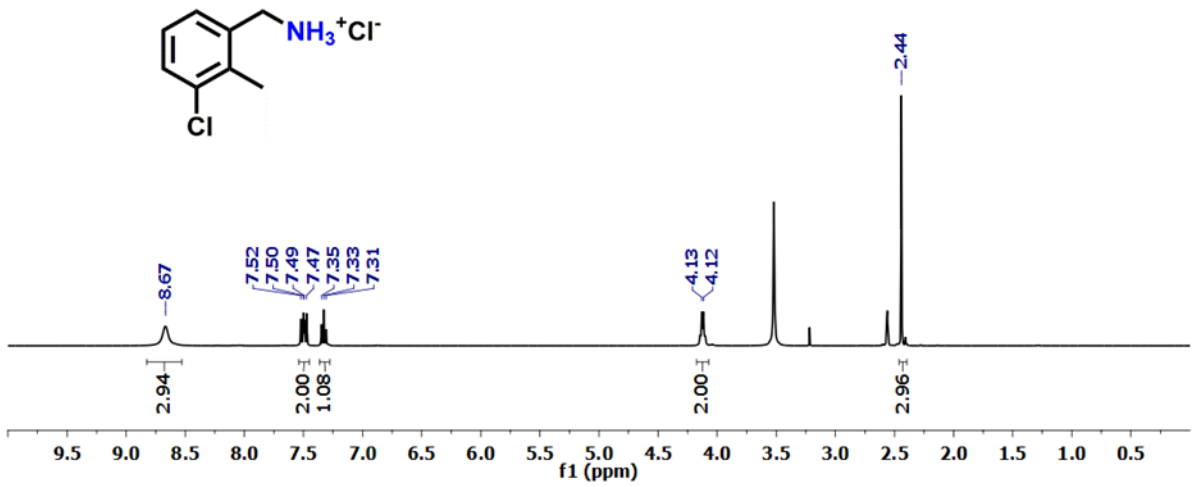


Figure S55. ^{1}H NMR spectrum (DMSO-*d*6) of (3-chloro-2-methylphenyl)methanamine hydrochloride.

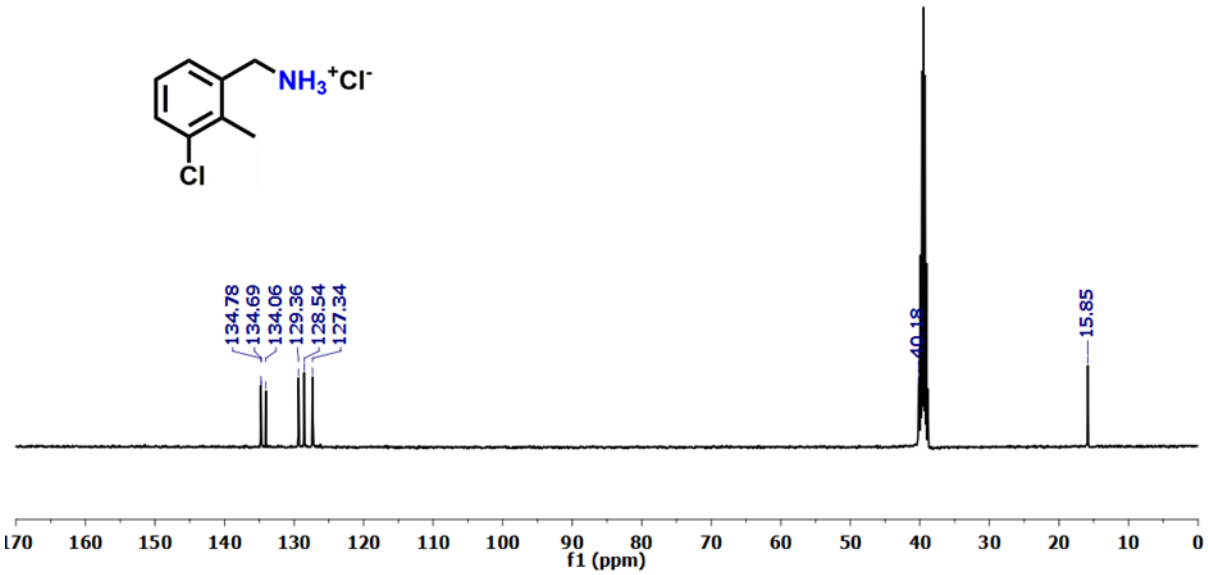


Figure S56. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (3-chloro-2-methylphenyl)methanamine hydrochloride.

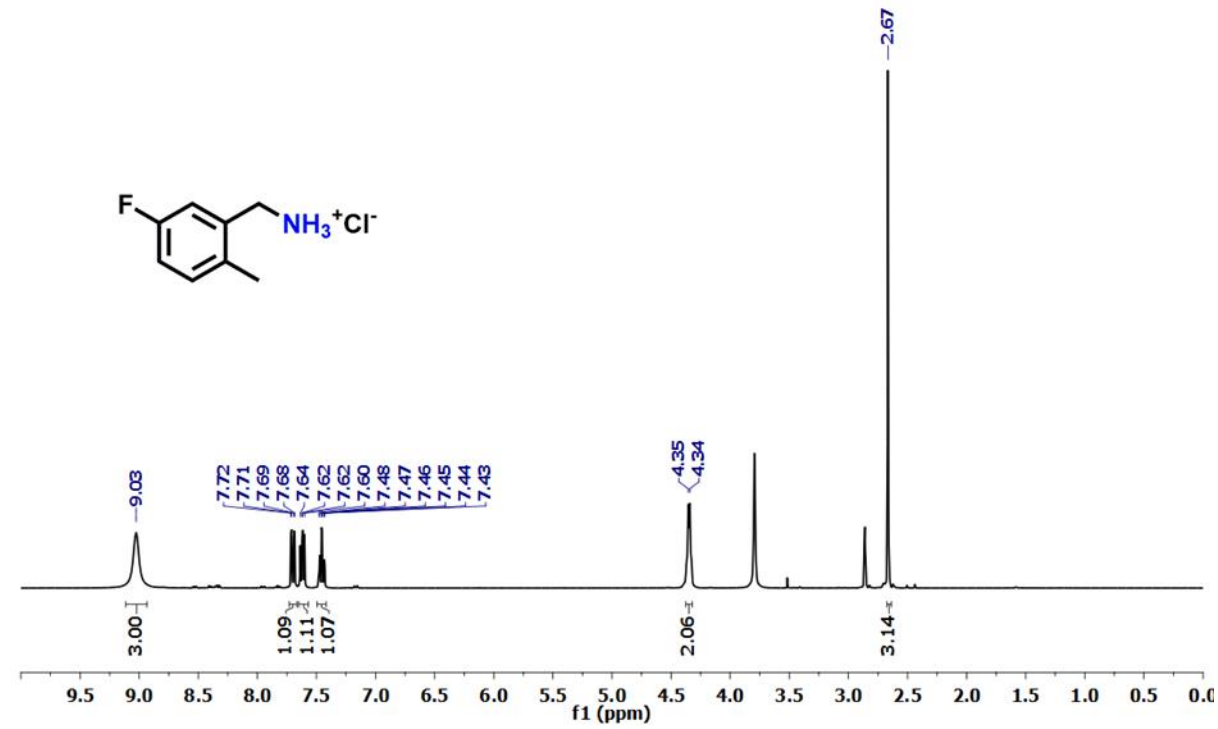


Figure S57. ^{1}H NMR spectrum (DMSO-*d*6) of (5-fluro-2-methylphenyl)methanamine hydrochloride.

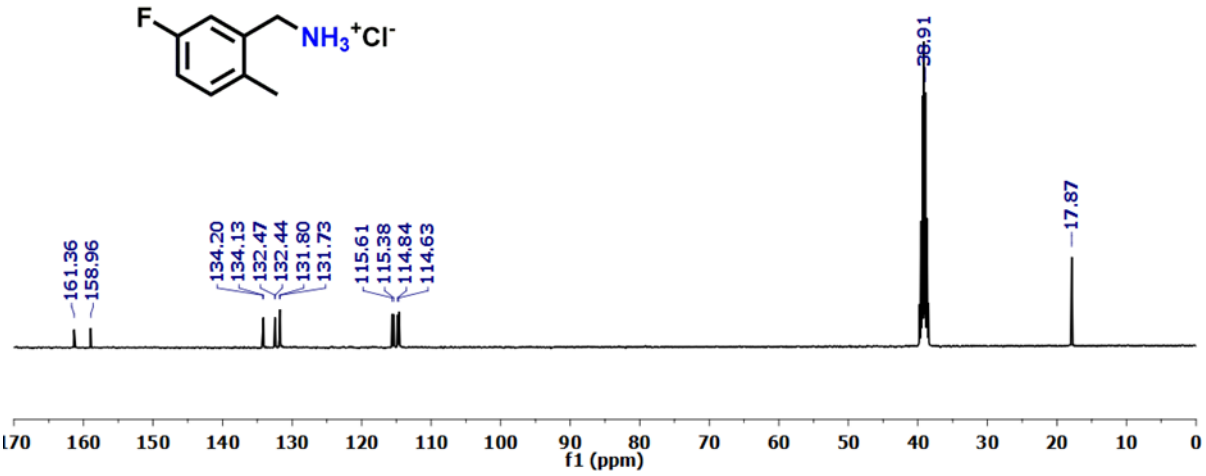


Figure S58. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of (5-fluro-2-methylphenyl)methanamine hydrochloride.

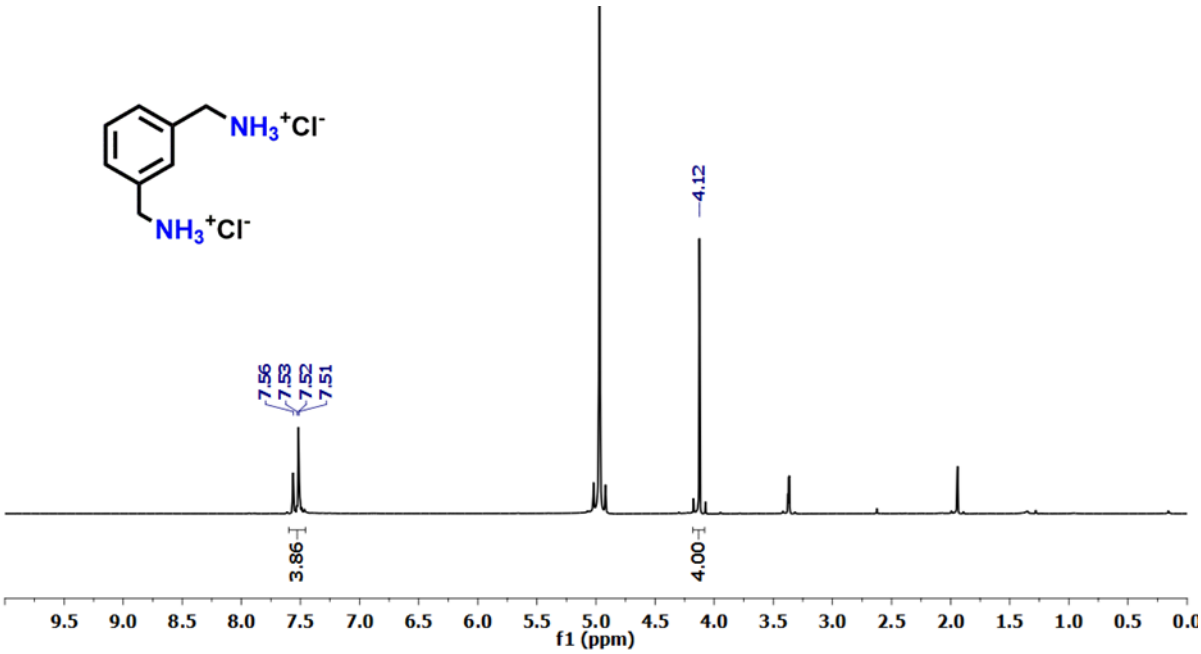


Figure S59. ^{1}H NMR spectrum (CD_3OD) of 1, 3-phenylenedimethanamine hydrochloride.

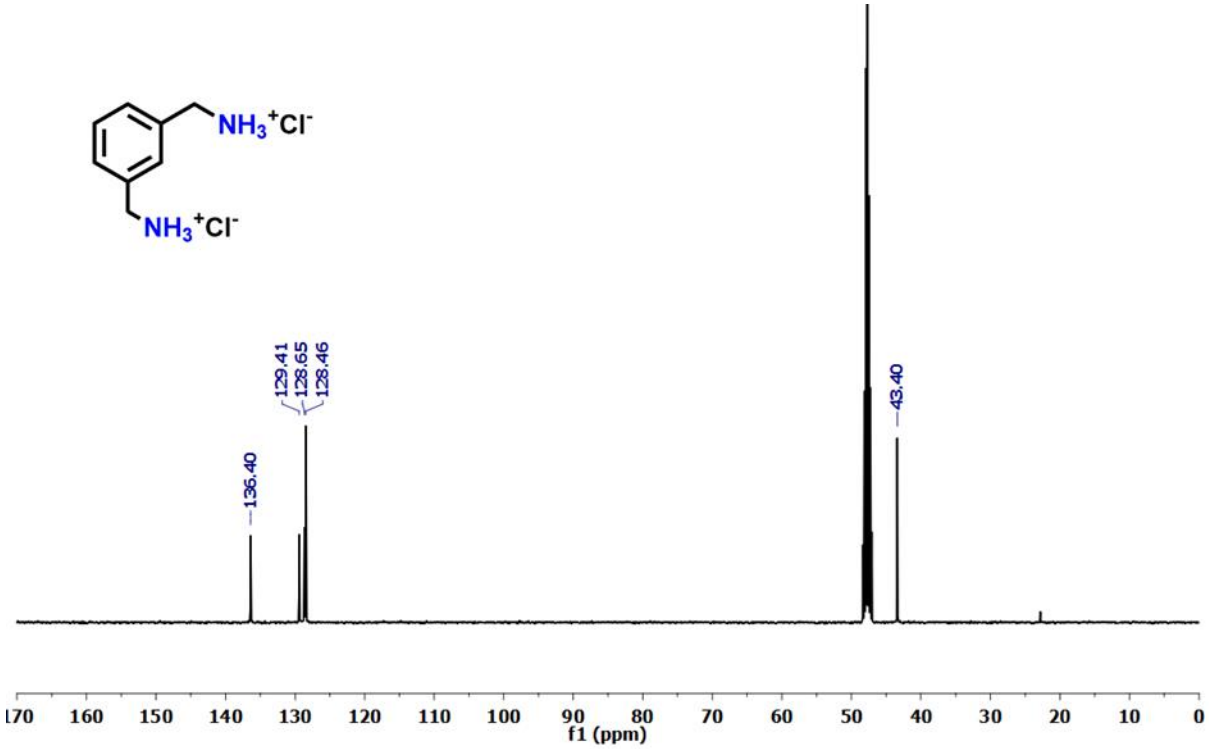


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD) of 1, 3-phenylenedimethanamine hydrochloride.

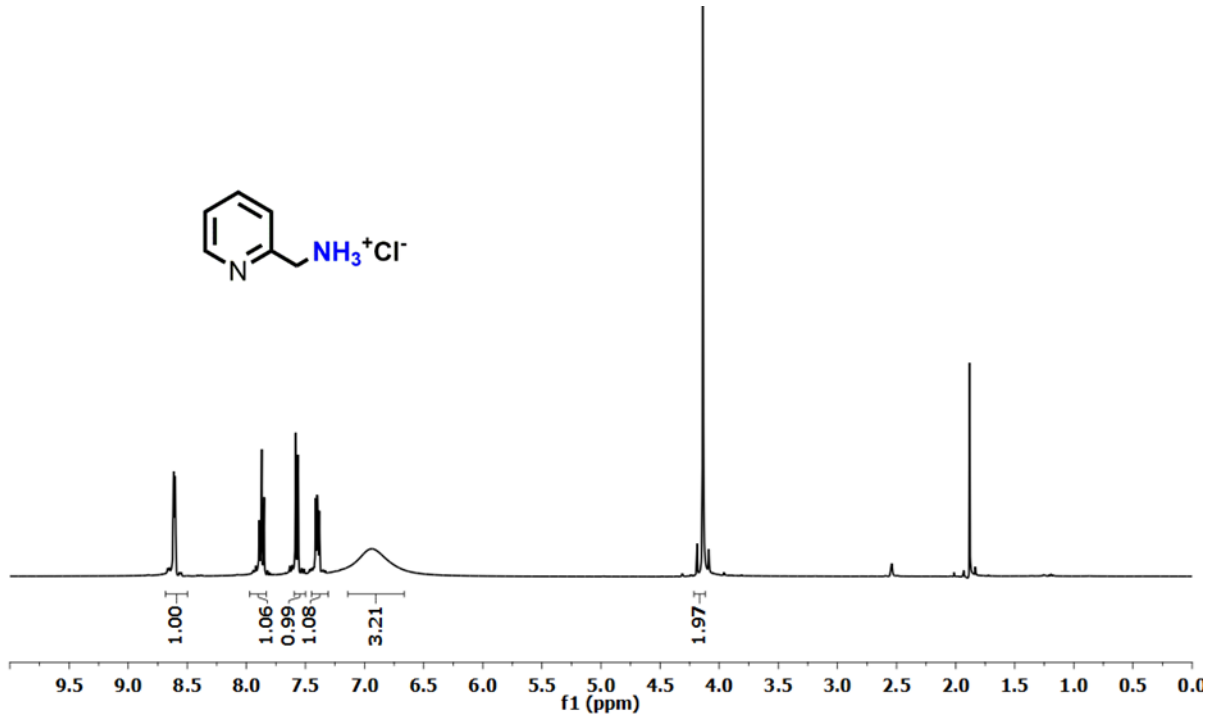


Figure S61. ^{1}H NMR spectrum (DMSO-d_6) of pyridin-2-ylmethanaminium hydrochloride.

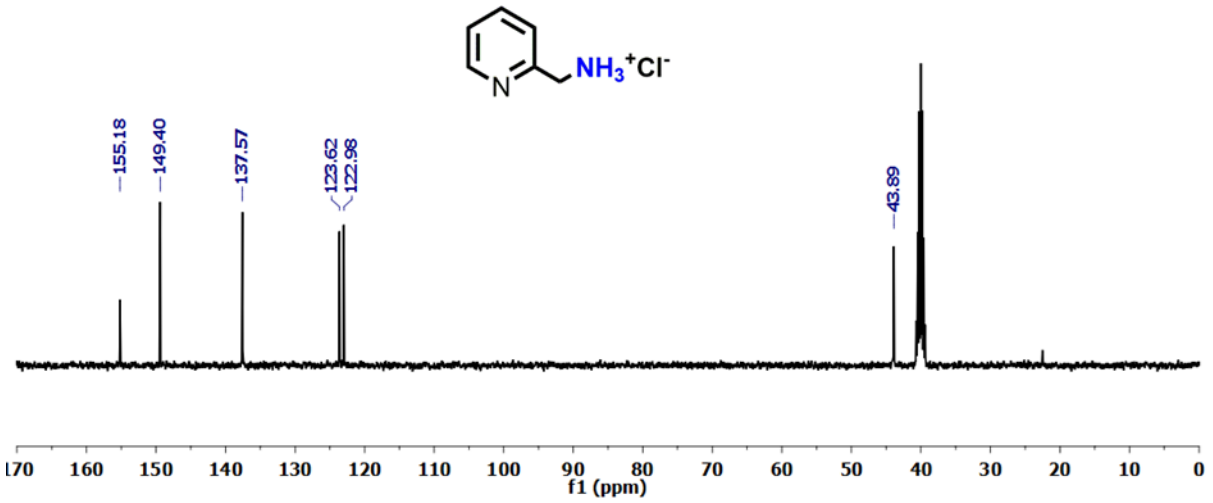


Figure S62. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of pyridin-2-ylmethanaminium hydrochloride.

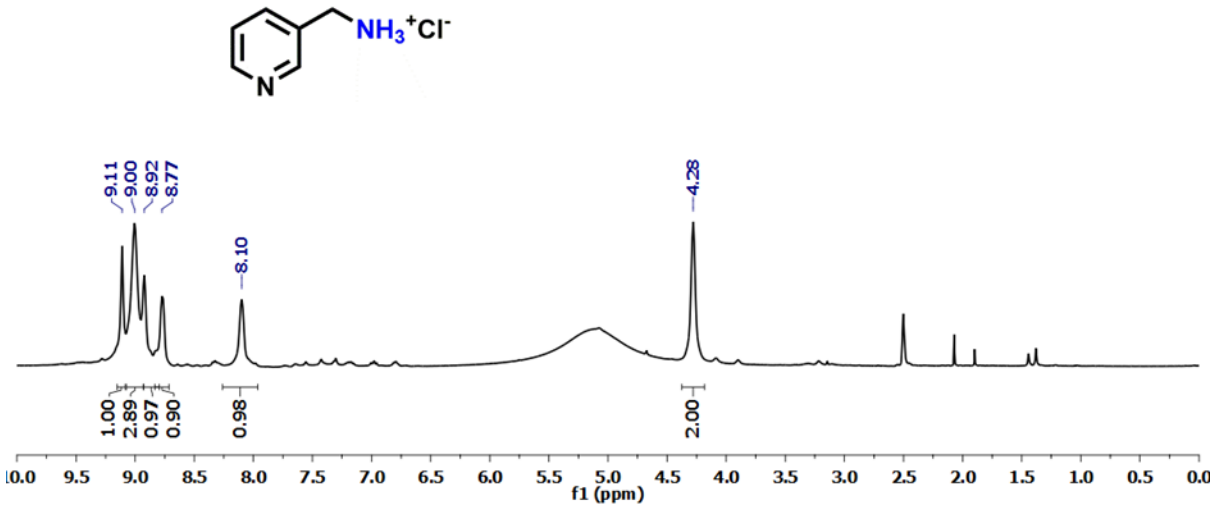


Figure S63. ^{1}H NMR spectrum (DMSO-d_6) of pyridin-3-ylmethanaminium hydrochloride.

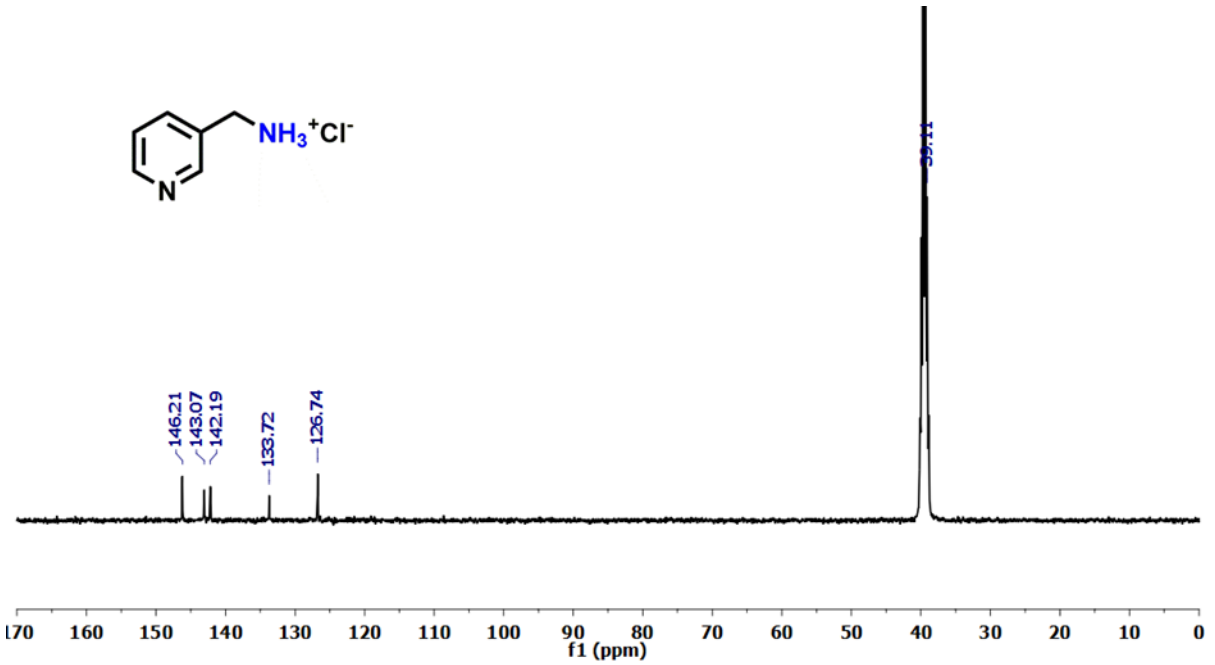


Figure S64. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of pyridin-3-ylmethanaminium hydrochloride.

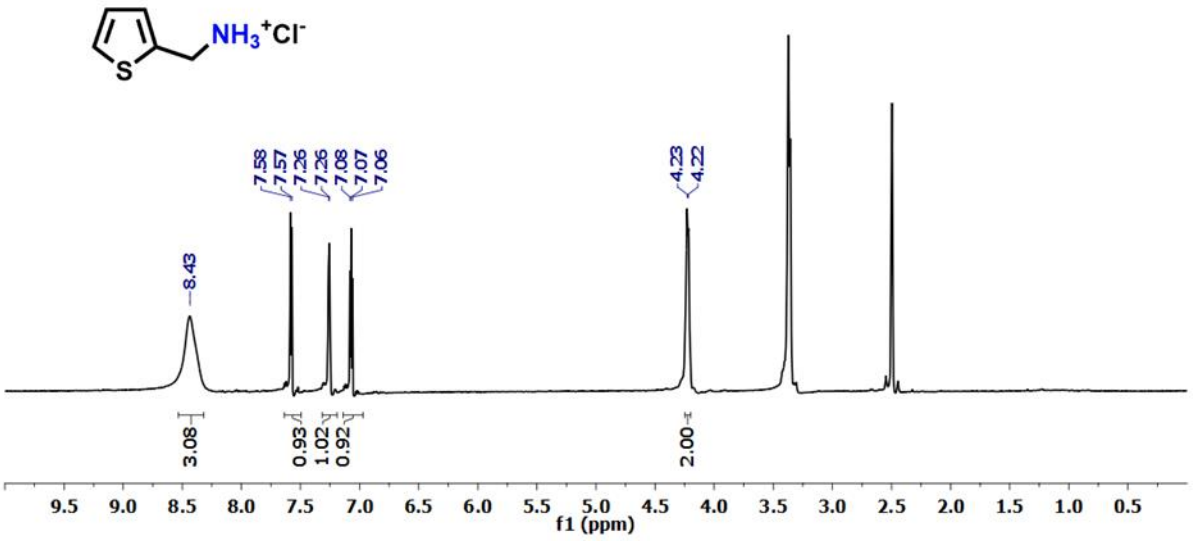


Figure S65. ^{1}H NMR spectrum (DMSO-d_6) of thiophen-2-ylmethanaminium hydrochloride.

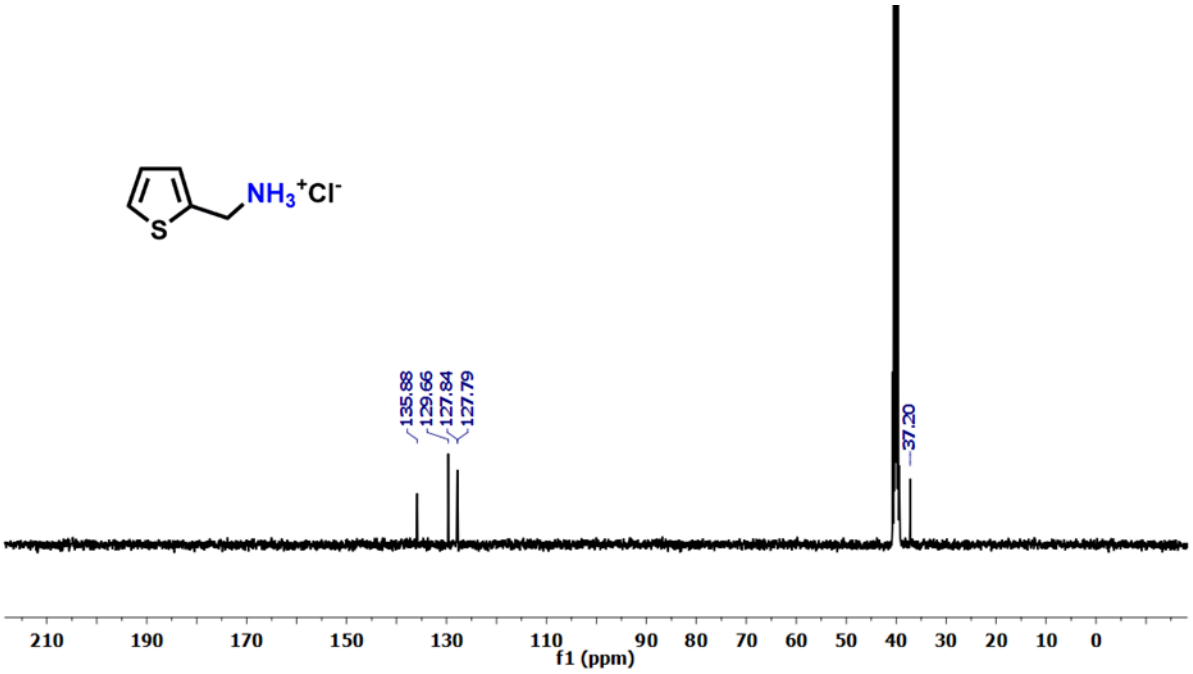


Figure S66. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of thiophen-2-ylmethanaminium hydrochloride.

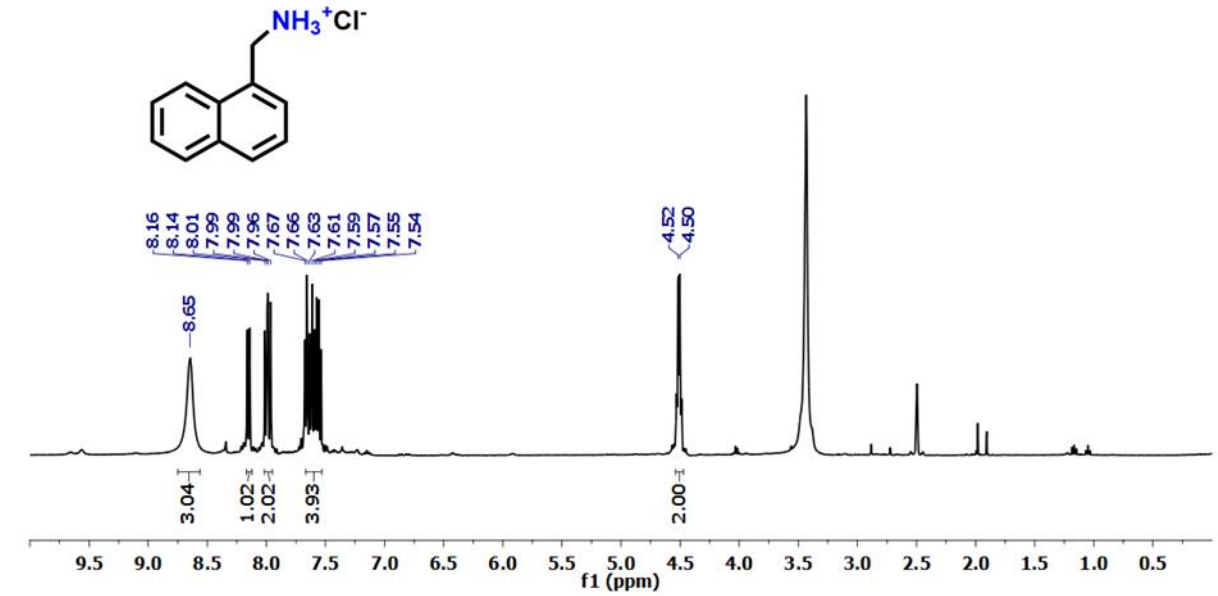


Figure S67. ^{1}H NMR spectrum (DMSO-*d*6) of naphthalene-1-ylmethanamine hydrochloride.

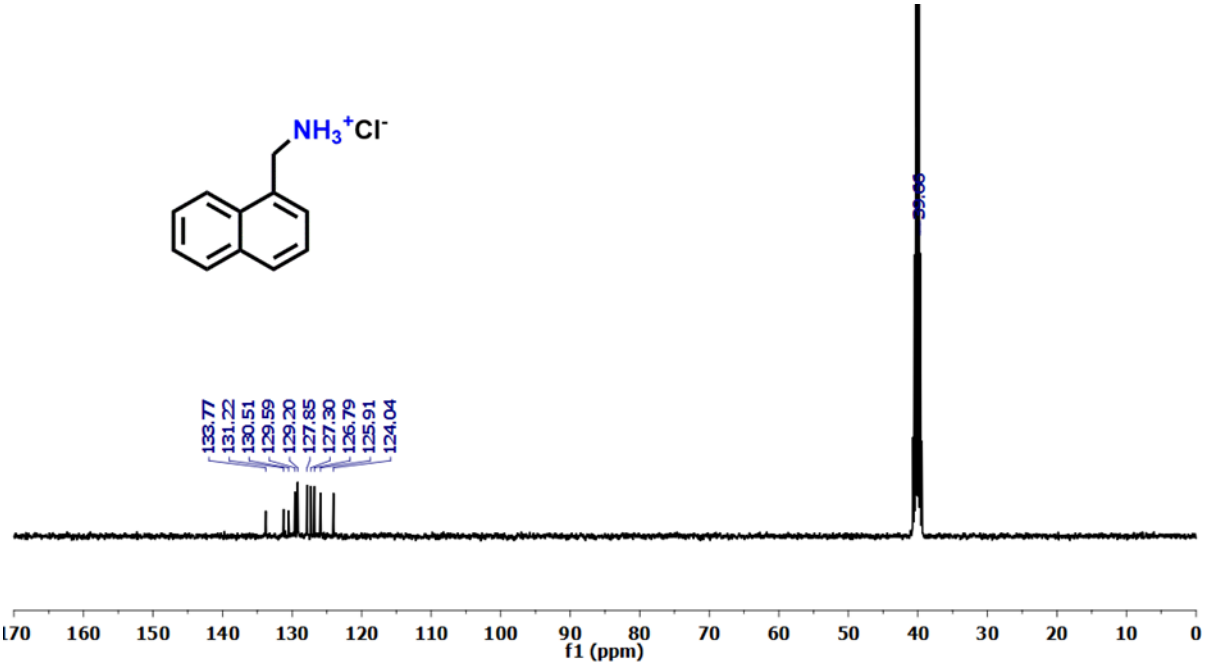


Figure S68. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of naphthalene-1-ylmethanamine hydrochloride.

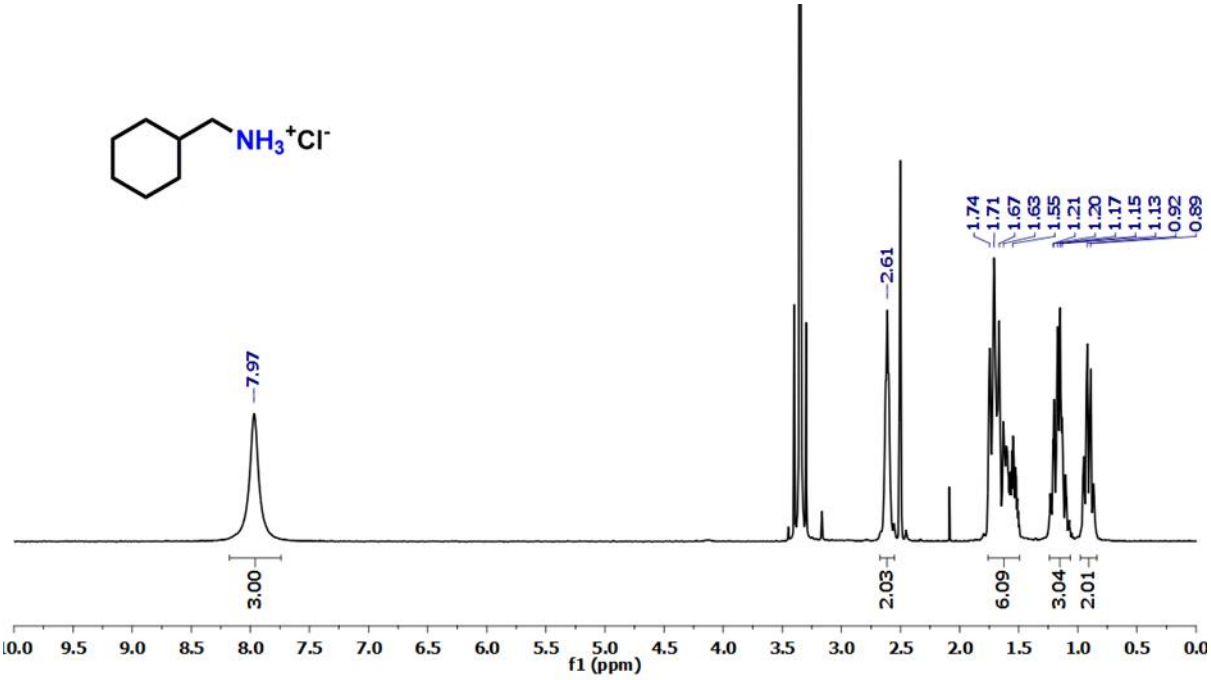


Figure S69. ^{1}H NMR spectrum (DMSO-*d*6) of cyclohexaylmethanamine hydrochloride.

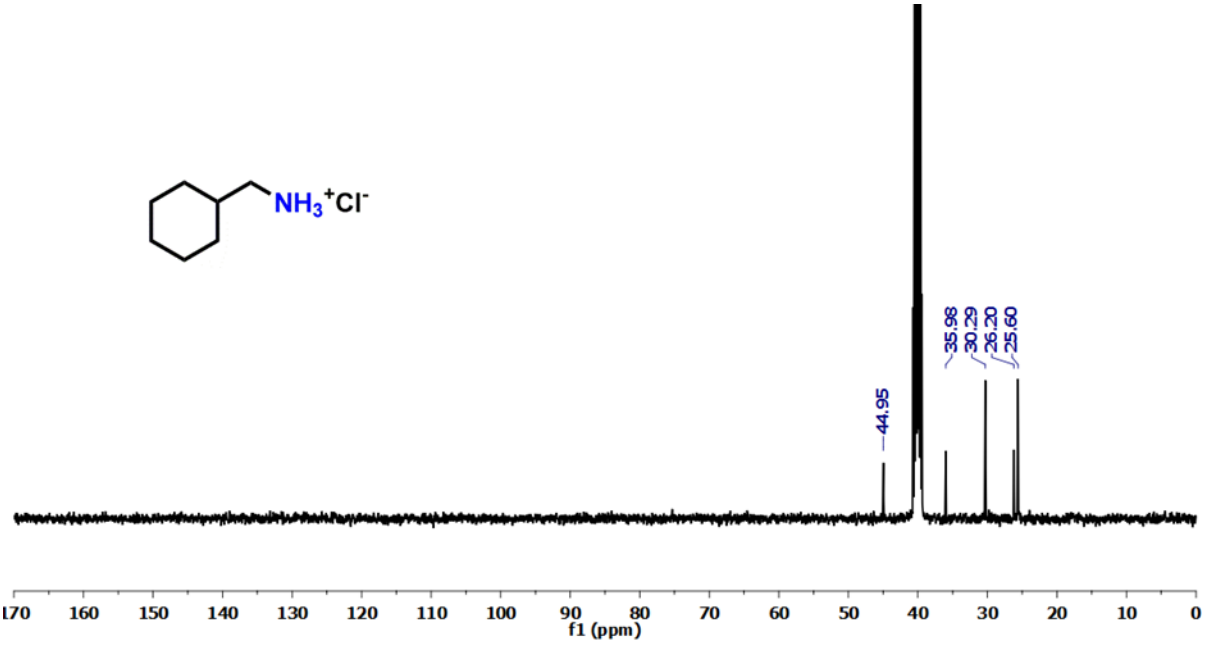


Figure S70. ^{13}C{^{1}H} NMR spectrum (DMSO-*d*6) of cyclohexaylmethanamine hydrochloride.

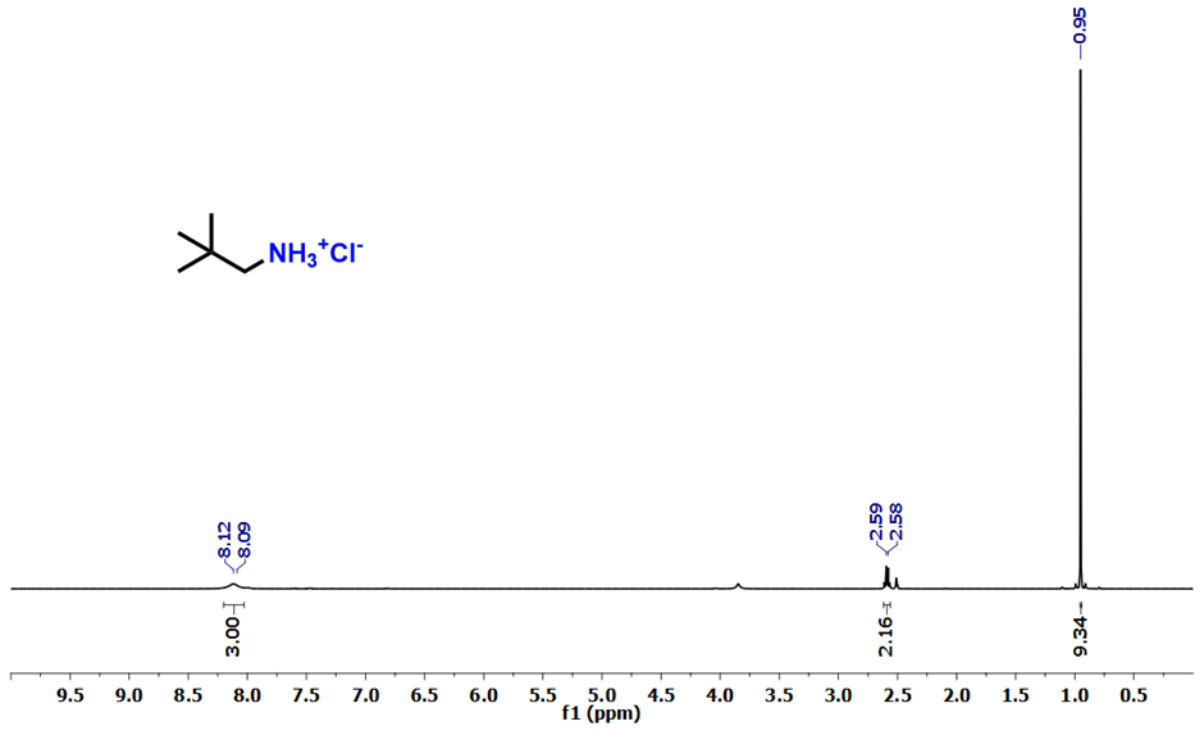


Figure S71. ^{1}H NMR spectrum (DMSO-d_6) of 2,2-dimethylpropan-1-aminium hydrochloride.

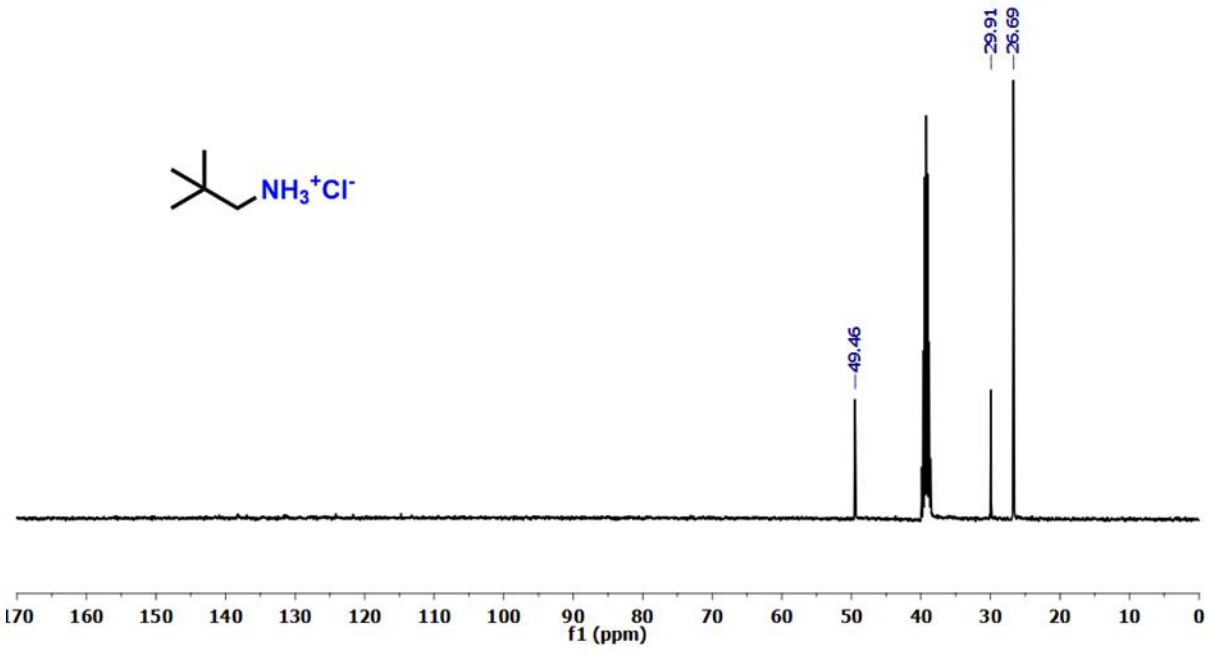


Figure S72. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of 2,2-dimethylpropan-1-aminium hydrochloride.

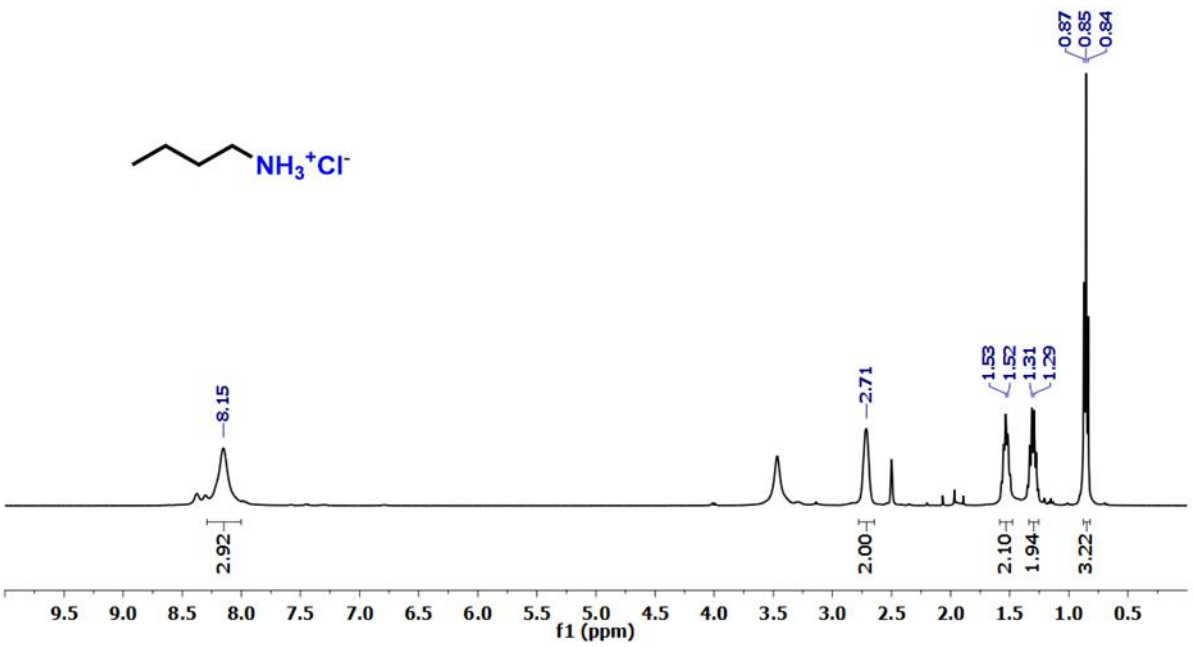


Figure S73. ^{1}H NMR spectrum (DMSO-d_6) of butan-1-aminium hydrochloride.

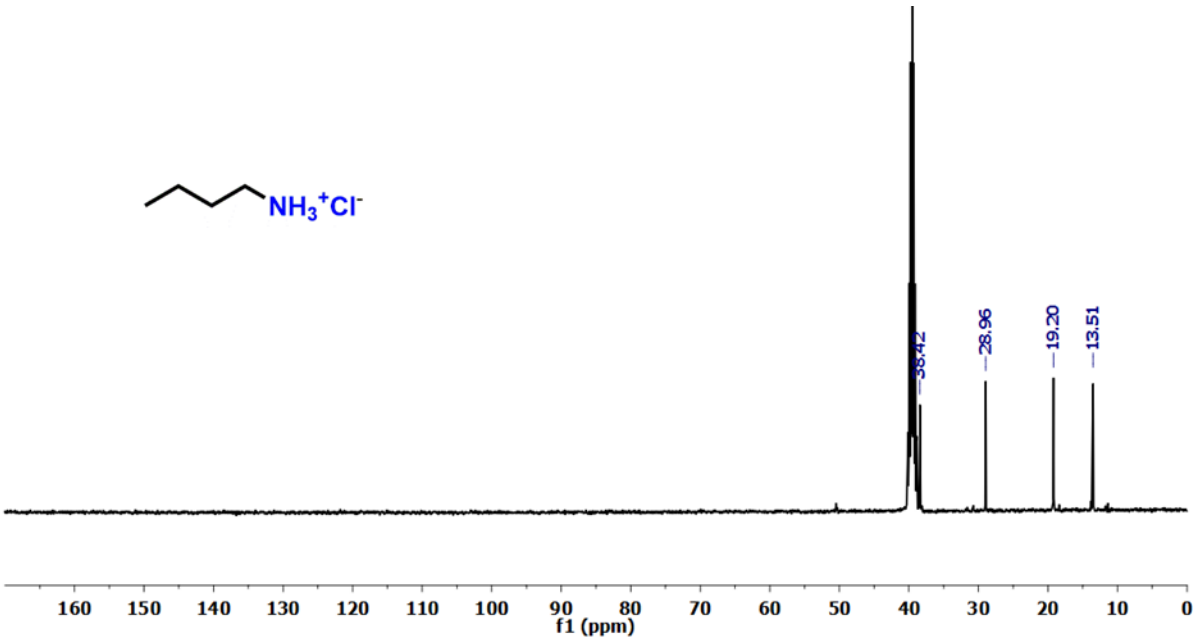
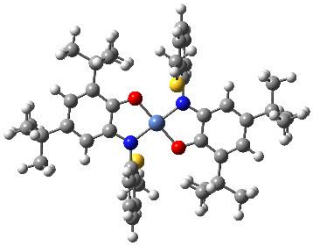


Figure S74. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of butan-1-aminium hydrochloride.

X. Coordinates of all the optimized geometries:

Complex 1:



Ni	-0.000028	0.000063	-0.000101
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O	1.180953	-1.401090	0.164291
N	1.492768	1.065359	-0.354994
C	3.525615	-1.935665	0.145044
C	3.296970	-3.445049	0.301936
C	4.783586	-1.334143	0.021976
H	5.519726	-1.901082	0.072293
C	5.050429	0.018607	-0.168257
C	6.493783	0.561468	-0.180037
C	2.423747	-1.021594	0.047228
C	1.525630	2.559593	-0.700431
C	4.629509	-4.229631	0.361944
H	5.101162	-4.126032	-0.467497
H	4.448440	-5.160857	0.511722
H	5.169236	-3.889419	1.079740
C	2.675550	0.351087	-0.258757
C	1.336272	4.783625	0.106745
C	1.215125	5.403153	0.790288
C	3.992187	0.897532	-0.323252
H	4.134349	1.804584	-0.460993

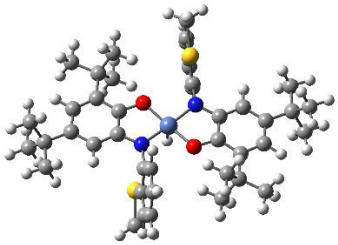
C	1.445945	5.154537	-1.124574
H	1.476805	6.067275	-1.305923
C	2.513709	-3.964689	-0.909540
H	1.778641	-3.376011	-1.092761
H	2.179409	-4.844460	-0.721205
H	3.093800	-3.998799	-1.674433
C	1.408572	3.392196	0.371322
C	1.670631	2.659571	-2.061347
H	1.812342	2.009177	-2.710752
C	2.521198	-3.708218	1.611915
H	3.040803	-3.401137	2.357808
H	2.352538	-4.648848	1.702333
H	1.683881	-3.234604	1.587727
C	1.517596	4.286283	-2.180411
H	1.477989	4.649901	-3.035091
C	7.479136	-0.476537	-0.608274
H	7.589269	-1.122322	0.092539
H	8.323754	-0.057936	-0.792413
H	7.159502	-0.914839	-1.399849
C	6.799048	1.028759	1.248872
H	6.875427	1.985865	1.261132
H	7.622434	0.635953	1.545504
H	6.085856	0.757025	1.831998
C	6.627774	1.745331	-1.094066
H	6.346403	1.497389	-1.979648
H	7.543653	2.028565	-1.117437
H	6.077010	2.461822	-0.771573

C	1.270683	4.103392	3.050730
H	0.715532	3.892254	3.805964
H	0.892918	4.843794	2.571198
H	2.150641	4.335032	3.354860
S	-1.367870	-2.696845	-1.981530
O	-1.180569	1.400380	-0.164167
N	-1.492825	-1.065233	0.354792
C	-3.525672	1.935792	-0.145246
C	-3.297027	3.445176	-0.302138
C	-4.783643	1.334269	-0.022178
H	-5.519343	1.900372	-0.072170
C	-5.050486	-0.018480	0.168055
C	-6.493840	-0.561342	0.179835
C	-2.423804	1.021720	-0.047430
C	-1.525686	-2.559466	0.700229
C	-4.629566	4.229758	-0.362146
H	-5.100778	4.125322	0.467620
H	-4.448497	5.160983	-0.511924
H	-5.169293	3.889545	-1.079942
C	-2.675811	-0.350700	0.259499
C	-1.336329	-4.783498	-0.106947
C	-1.215182	-5.403026	-0.790490
C	-3.992244	-0.897405	0.323050
H	-4.134169	-1.805033	0.462060
C	-1.446002	-5.154410	1.124371
H	-1.476862	-6.067148	1.305721
C	-2.513766	3.964815	0.909338

H	-1.778698	3.376137	1.092558
H	-2.179670	4.844847	0.721946
H	-3.093857	3.998926	1.674231
C	-1.408629	-3.392069	-0.371525
C	-1.670892	-2.659184	2.062089
H	-1.812603	-2.008790	2.711494
C	-2.521459	3.708605	-1.611173
H	-3.040860	3.401263	-2.358010
H	-2.352358	4.648398	-1.701266
H	-1.683938	3.234731	-1.587930
C	-1.517653	-4.286157	2.180208
H	-1.477605	-4.650611	3.035214
C	-7.479193	0.476664	0.608072
H	-7.588886	1.121612	-0.092416
H	-8.323811	0.058063	0.792211
H	-7.159559	0.914966	1.399647
C	-6.798664	-1.029469	-1.248748
H	-6.875483	-1.985738	-1.261334
H	-7.622491	-0.635826	-1.545706
H	-6.085472	-0.757735	-1.831874
C	-6.627831	-1.745205	1.093864
H	-6.346020	-1.498099	1.979771
H	-7.543710	-2.028439	1.117235
H	-6.076626	-2.462532	0.771696
C	-1.270944	-4.103005	-3.049988
H	-0.715793	-3.891867	-3.805222
H	-0.892975	-4.843668	-2.571401

H	-2.150698	-4.334906	-3.355062

Complex 1-H:



Ni	0.000057	0.000460	0.003310
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N	1.515613	1.053644	-0.249288
C	3.592098	-1.947449	0.216119
C	3.372919	-3.446502	0.507943
C	4.858759	-1.381863	0.047774
H	5.722138	-2.031855	0.129627
C	5.099394	0.011387	-0.227028
C	6.558179	0.495179	-0.381356
C	2.480097	-1.050230	0.099214
C	1.524265	2.459213	-0.535451
C	4.709121	-4.225420	0.602462
H	5.278281	-4.181927	-0.335988
H	4.495183	-5.281553	0.810758
H	5.346709	-3.850281	1.414374
C	2.692315	0.351307	-0.178898
C	1.514478	4.787323	0.192240
H	1.499100	5.536519	0.977150

C	4.009726	0.868875	-0.339168
H	4.134927	1.925195	-0.540048
C	1.529726	5.209399	-1.149655
H	1.528713	6.272980	-1.376127
C	2.524628	-4.076068	-0.637310
H	1.557760	-3.574782	-0.729248
H	2.346898	-5.140139	-0.427033
H	3.052626	-3.999357	-1.597890
C	1.513518	3.414965	0.512369
C	1.535324	2.892388	-1.875217
H	1.528917	2.140058	-2.659687
C	2.621242	-3.608909	1.862744
H	3.209438	-3.182573	2.687011
H	2.458724	-4.675082	2.073702
H	1.648412	-3.111656	1.832971
C	1.539339	4.262138	-2.189174
H	1.543017	4.582299	-3.227724
C	7.236828	-0.263017	-1.561375
H	7.241165	-1.348005	-1.402399
H	8.279856	0.064181	-1.671060
H	6.712747	-0.063502	-2.504988
C	7.342657	0.207312	0.933861
H	6.892098	0.741676	1.780077
H	8.385271	0.538523	0.832407
H	7.353026	-0.861522	1.178745
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H	6.136446	2.280926	-1.604810

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H	-8.279847	-0.062915	1.677386
H	-6.712800	0.065053	2.511388
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H	-6.891815	-0.741418	-1.773448
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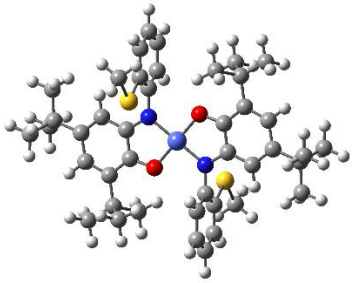

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H	1.545546	3.470804	-1.482332
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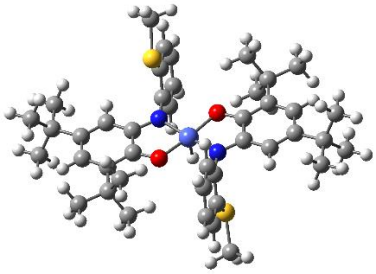
Complex 2$_{-H}$:



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H	-1.530085	2.140211	-2.662180
H	0.105675	-0.354449	-1.100377

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