Electronic Supporting Information
For
Controlling Catalytic Transformation of Primary Amides into Amines or Nitriles

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1. Materials and general methods

All chemicals, including primary amides, potassium tert-butoxide and $MnCl_2.4H_2O$ were purchased from commercial sources and were used as received or otherwise mentioned. The bis-phenalenyl ligand 9,9'-(ethane-1,2-diylbis(azanediyl))bis(1H-phenalen-1-one)[1] (H_2L) and substrate 1-N-phenylbenzene-1,4-dicarboxamide[2] were synthesized according to the published methods. The solvents used for metal complex synthesis were reagent grade and used as supplied. All the catalysis reactions were performed under nitrogen atmosphere in a glovebox using dry solvents. The solvents dichloromethane, acetonitrile, DMSO and DMF were distilled from calcium hydride under nitrogen; tetrahydrofuran, 1,4-dioxane, toluene, benzene, diethyl ether and hexane were distilled from Na/benzophenone under nitrogen; methanol and ethanol were refluxed over magnesium and distilled under nitrogen prior to use in catalysis. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer or on a Bruker Advance III 500 MHz spectrometer. The HRMS data were obtained using a Finnigan MAT 8230 instrument. Elemental (C, H and N) analysis were performed on a PerkinElmer 2400II analyser. Open-column chromatography and thin-layer chromatography (TLC) were performed on silica gel (Merck silica gel 100-200 mesh).

2. X-ray crystal structure details of complex 1, 2 and 3.

Suitable single crystals of **1, 2** and **3** were selected and mounted under nitrogen atmosphere using the X-TEMP2 and intensity data were collected on a Super Nova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 100 K during data collection. Atomic coordinates and isotropic and anisotropic displacement parameters of all non-hydrogen atoms were refined using Olex2,[3] and the structure was solved with the Superflip[4] structure solution program using Charge Flipping and refined with the ShelXL[5] refinement package using least-squares minimization. Crystallographic data for structural determination of **1, 2** and **3** have been deposited at the Cambridge Crystallographic Data Center (CCDC), as file no. 1889831, 1889832 and 1889830, respectively. These data can be accessed free of cost from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

2A. Table S1. X-ray structure and data of complexes **1**, **2** and **3**.

Compounds	**1**	**2**	**3**
Crystal Data	CCDC (1889831)	(CCDC 1889832)	(CCDC 1889830)
Empirical formula	$C_{28}H_{18}ClMnN_2O_2$	$C_{28}H_{18}ClMnN_2O_6$	$C_{31}H_{25}ClMnN_3O_7$
Formula weight	504.83	568.83	641.93
Temperature/K	103(5)	99.99(10)	100.00(10)
Crystal system	Monoclinic	Monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	10.0980(10)	14.9408(2)	14.1071(11)
b/Å	11.6602(7)	14.8512(3)	15.4146(7)
c/Å	18.3347(11)	20.1705(3)	14.1647(10)
α/°	90	90	90
β/°	104.276(7)	89.9800(10)	118.719(10)
γ/°	90	90	90
Volume/Å^3	2092.1(3)	4475.61(13)	2701.3(4)
Z	4	8	4
ρ_{calc}g/cm^3	1.603	1.688	1.578
μ/mm^{-1}	0.791	0.762	0.645
F(000)	1032.0	2320.0	1320.0
Crystal size/mm^3	0.2 × 0.15 × 0.1	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.228 to 50.052	3.406 to 50.054	5.286 to 50.054
Index ranges	-10 ≤ h ≤ 11, -11 ≤ k ≤ 13, -21 ≤ l ≤ 13	-17 ≤ h ≤ 17, -17 ≤ k ≤ 16, -24 ≤ l ≤ 24	-14 ≤ h ≤ 16, -18 ≤ k ≤ 17, -16 ≤ l ≤ 16
Reflections collected	5615	30597	10772
Independent reflections	3647 [R_{int} = 0.0608, R_{sigma} = 0.0881]	7897 [R_{int} = 0.0331, R_{sigma} = 0.0283]	4707 [R_{int} = 0.0398, R_{sigma} = 0.0444]
Data/restraints/parameters	3647/0/307	7897/0/697	4707/0/390
Goodness-of-fit on F^2	1.034	1.037	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0632, wR_2 = 0.1575	R_1 = 0.0287, wR_2 = 0.0735	R_1 = 0.0460, wR_2 = 0.1236
Final R indexes [all data]	R_1 = 0.0804, wR_2 = 0.1740	R_1 = 0.0323, wR_2 = 0.0758	R_1 = 0.0514, wR_2 = 0.1280
Largest diff. peak/hole / e Å^{-3}	1.30/-0.75	0.28/-0.36	1.20/-0.69

2B. Table S2. Selected X-ray crystallographic bond distances (Å) for complexes **1**, **2** and **3**.

1		**2**		**3**	
Bond distance (Å)					
Mn1–O1	1.877(3)	Mn1–O1	1.8725(13)	Mn01–O1	1.8999(18)
Mn1–O2	1.887(2)	Mn1–O2	1.9064(12)	Mn01–O2	1.8800(17)
Mn1–N1	1.955(3)	Mn1–N1	1.9520(15)	Mn01–N1	1.948(2)
Mn1–N2	1.953(4)	Mn1–N2	1.9540(15)	Mn01–N2	1.952(2)
C1–O1	1.310(4)	C1–O1	1.309(2)	C1–O1	1.330(3)
C28–O2	1.310(4)	C26–O2	1.331(2)	C13–O2	1.308(3)
C12–N1	1.339(5)	C13–N1	1.331(2)	C11–N1	1.328(3)
C16–N2	1.337(4)	C16–N2	1.331(2)	C23–N2	1.334(3)
Mn1–Cl	12.4095(12)	Mn–O3	2.2599(15)	Mn01–O3	2.2294(18)

2C. Table S3. Selected X-ray crystallographic bond angles (deg) for complexes **1**, **2** and **3**.

1		**2**		**3**	
Bond angle (deg)					
O1-Mn1-O2	87.66(11)	O1-Mn1-O2	93.71(5)	O1-Mn01-O2	92.76(7)
N1-Mn1-N2	86.16(14)	N1-Mn1-N2	85.92(6)	N1-Mn01-N2	86.47(9)
O1-Mn1-N1	90.40(13)	O1-Mn1-N1	90.82(6)	O1-Mn01-N1	89.83(8)
O2-Mn1-N2	90.08(13)	O2-Mn1-N2	89.20(6)	O2-Mn01-N2	90.90(8)
O1-Mn1-Cl1	100.46(11)	O1-Mn1- O3	87.21(6)	O3-Mn01-O1	88.61(7)
O2-Mn1-Cl1	101.78(10)	O2-Mn1- O3	86.37(6),	O3-Mn01-O2	87.76(7)
N1-Mn1-Cl1	95.97(10)	N1-Mn1-O3	104.07(6)	O3-Mn01-N1	92.83(8)
N2-Mn1-Cl1	197.98 (10)	N2-Mn1-O3	95.26(6)	O3-Mn01-N2	102.85(8)

3. Experimental Procedures

3A. Synthesis of 1

To a clear orange solution of the ligand H_2L (100 mg, 0.24 mmol) in hot DMF (9 mL), an ethanolic solution of $MnCl_2.4H_2O$ (130 mg, 0.65 mmol in 5 mL hot EtOH) was added. Subsequently, the reaction mixture was refluxed at 110 °C in air for 12h resulting in color change to deep red with precipitation of a black microcrystalline solid. The microcrystalline solid obtained was filtered at room temperature, washed with EtOH followed by Et_2O and dried in vacuum leading to pure complex [Mn^{III}(L)Cl], which was used in catalysis without further purification. Yield 68%. The single crystals of **1** suitable for X-ray diffraction analysis were obtained by layering of Et_2O into a concentrated DMF solution of the compound. Anal. Found: C, 66.49; H, 3.68; N, 5.37, Calc. for $C_{28}H_{18}N_2ClO_2Mn$: C, 66.61; H, 3.59; N, 5.55%. HRMS (ESI) Calc. for $C_{28}H_{18}MnClN_2O_2$ [M – Cl]$^+$: m/z 469.0729. Found: 469.0729 (see Figure S1).

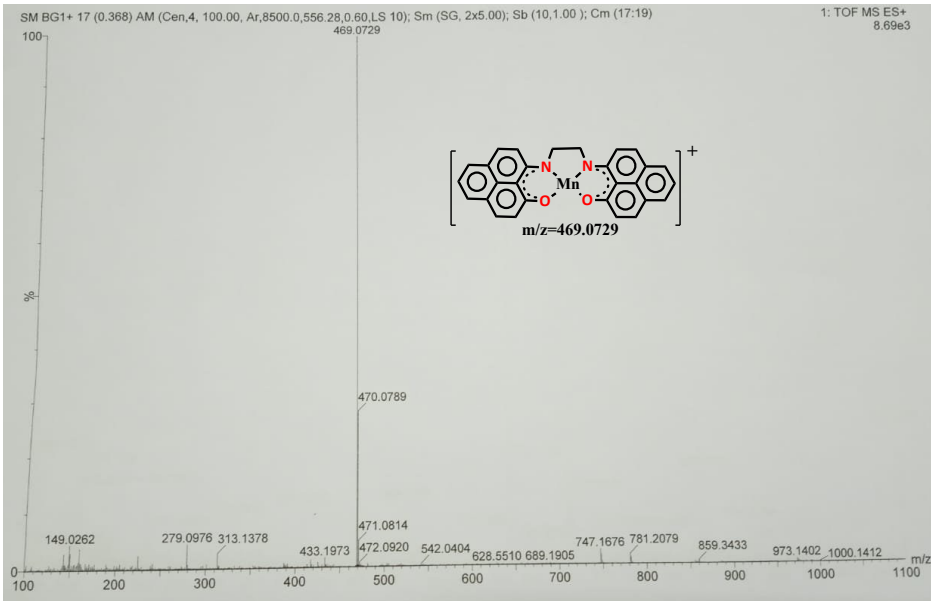


Figure S1. ESI-mass spectrum of **1** recorded in methanol.

3B. Syntheses of 2 and 3

In a Schlenk flask, **1** (50 mg, 0.1 mmol), $AgClO_4$ (30 mg, 0.12 mmol) and 15 mL THF were added under nitrogen atmosphere and stirred for 3 h resulting in magenta colored solution with white precipitate. The precipitate was filtered under nitrogen to another Schlenk flask through G4-crucible containing an activated celite bed. Evaporation of the solvent under reduced pressure afforded the complex [Mn^{III}(L)(ClO_4)], **2** with 98% yield. Single crystals for X-ray diffraction were obtained by slow diffusion of Et_2O on a solution of **2** in THF. Anal. Found: C, 58.86; H, 3.07; N, 4.79, Calc. for $C_{28}H_{18}N_2ClO_6Mn$: C, 59.12; H, 3.19; N, 4.92%. HRMS (ESI) Calc. for $C_{28}H_{18}MnClN_2O_6$ [M – ClO_4^-]$^+$: m/z 469.0729. Found:

469.0729 (see Figure S2). Slow diffusion of Et_2O on solution of **2** in DMF afforded single crystals of $[Mn^{III}(L)(DMF)](ClO_4)$ (**3**) with 87% yield. Anal. Found: C, 57.74; H, 3.68; N, 6.31, Calc. for $C_{31}H_{25}N_3ClO_7Mn$: C, 58.00; H, 3.93; N, 6.55%. HRMS (ESI) Calc. for $C_{28}H_{18}MnClN_2O_6$ $[M - ClO_4^-]^+$: m/z 469.0729. Found: 469.0729 (see Figure S3)

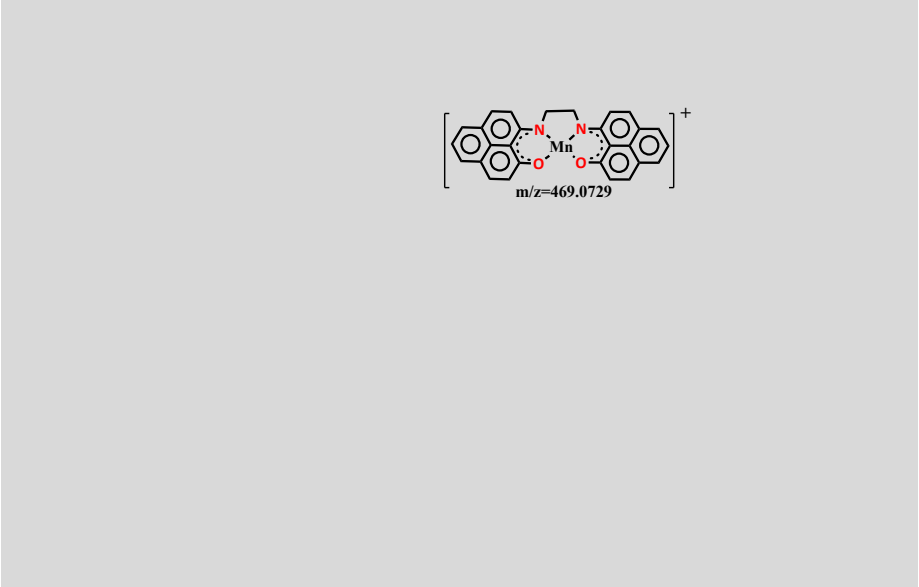


Figure S2. ESI-mass spectrum of **2** recorded in methanol.

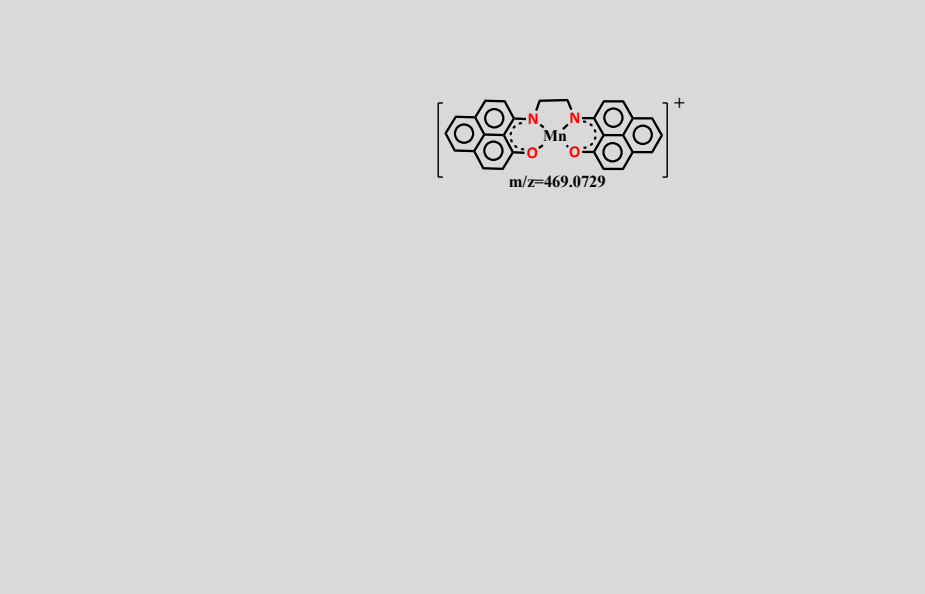


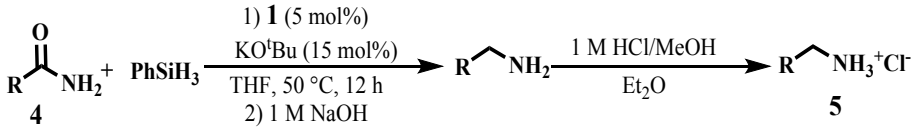
Figure S3. ESI-mass spectrum of **3** recorded in methanol.

3C. General procedure for reduction of primary amide to amine

1 (5 mol%, 13 mg) and KO^{t}Bu (15 mol%, 9 mg) were taken in a 15 mL thick-walled glass tube with 3 mL THF inside a nitrogen filled glovebox. The mixture was stirred for 5 minutes, then $PhSiH_3$ (1.2 mmol, 148μl) and primary amide (0.5 mmol) were added to the reaction mixture. The glass tube was sealed and the reaction mixture was allowed to stir for overnight at 50 °C. After completion of the reaction, 2 mL of 1 molar NaOH solution was added to the reaction mixture slowly and stirred for 3 h. The amine was extracted in 40 mL diethyl-ether (Et_2O) and dried over anhydrous sodium sulphate. The crude amine was obtained by evaporation of solvent under reduced pressure.

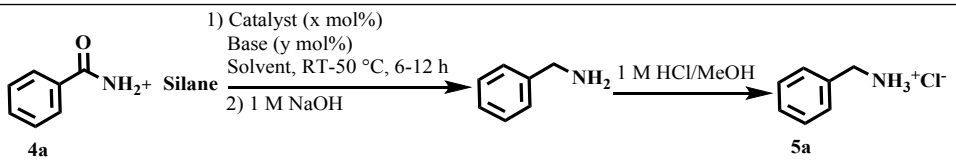
The isolated yields are based on HCl salt as unlike the free amines, the amine salts are stable, less volatile and easy to separate from the reaction mixture without performing column chromatography.

On treatment with 1 mL of 1 molar methanolic HCl followed by Et_2O addition leads to precipitation of amine salt. The precipitate was filtered off, washed with ethyl-acetate and dried in vacuum to obtain pure amine salt.



Scheme S1. General procedure for reduction of various primary amide substrates to primary amines.

3D. Table S4. Optimization of the reduction of benzamide into benzylamine[a]



4a 5a

Entry	Catalyst (x mol%)	Base (y mol%)	Solvent	Silane (equiv.)	Yield of 2a[b] (%)
1	**1** (5)	—	THF	$PhSiH_3$ (2.2)	—
2	**1** (5)	**KO^{t}Bu (15)**	**THF**	**$PhSiH_3$ (2.2)**	**81**
3	—	KO^{t}Bu (15)	THF	$PhSiH_3$ (2.2)	—
4	$MnCl_2$(5)	KO^{t}Bu (15)	THF	$PhSiH_3$ (2.2)	—
5	**1** (2.5)	KO^{t}Bu (15)	THF	$PhSiH_3$ (2.2)	65
6	**1** (5)	KO^{t}Bu (7.5)	THF	$PhSiH_3$ (2.2)	15
7[c]	**1** (5)	KO^{t}Bu (15)	THF	$PhSiH_3$ (2.2)	58
8[d]	**1** (5)	KO^{t}Bu (15)	THF	$PhSiH_3$ (2.2)	64
9	**1** (5)	KO^{t}Bu (15)	THF	Ph_2SiH_2 (3.0)	_
10	**1** (5)	KO^{t}Bu (15)	THF	Ph_3SiH (6.0)	_
11	**1** (5)	KO^{t}Bu (15)	THF	Et_3SiH (6.0)	_
12	**1** (5)	KO^{t}Bu (15)	THF	PMHS (6.0)	_
13	**1** (5)	KO^{t}Bu (15)	THF	TMDS (3.0)	_
14	**1** (5)	KO^{t}Bu (15)	THF	$PhMe_2SiH$ (6.0)	_
15	**1** (5)	KO^{t}Bu (15)	THF	$(EtO)_3SiH$ (6.0)	_
16	**1** (5)	NaO^{t}Bu(15)	THF	$PhSiH_3$ (2.2)	**78**
17	**1** (5)	NaOMe (15)	THF	$PhSiH_3$ (2.2)	_
18	**1** (5)	KOH(15)	THF	$PhSiH_3$ (2.2)	_
19	**1** (5)	$CaCO_3$(15)	THF	$PhSiH_3$ (2.2)	_
20	**1** (5)	NaOAC (15)	THF	$PhSiH_3$ (2.2)	_
21	**1** (5)	KO^{t}Bu (15)	Dioxane	$PhSiH_3$ (2.2)	62
22	**1** (5)	KO^{t}Bu (15)	DMSO	$PhSiH_3$ (2.2)	46
23	**1** (5)	KO^{t}Bu (15)	DMF	$PhSiH_3$ (2.2)	
24	**1** (5)	KO^{t}Bu (15)	MeCN	$PhSiH_3$ (2.2)	
25	**1** (5)	KO^{t}Bu (15)	EtOH	$PhSiH_3$ (2.2)	
26	**1** (5)	KO^{t}Bu (15)	MeOH	$PhSiH_3$ (2.2)	
27	**1** (5)	KO^{t}Bu (15)	Toluene	$PhSiH_3$ (2.2)	
28	**1** (5)	KO^{t}Bu (15)	Benzene	$PhSiH_3$ (2.2)	
29	**1** (5)	KO^{t}Bu (15)	Et_2O	$PhSiH_3$ (2.2)	
30	**1** (5)	KO^{t}Bu (15)	Hexane	$PhSiH_3$ (2.2)	
31	**1** (5)	KO^{t}Bu (15)	DCM	$PhSiH_3$ (2.2)	

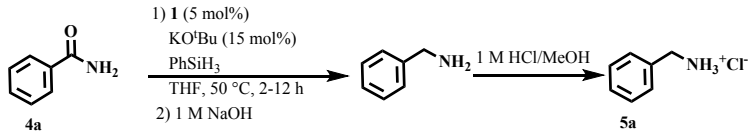
[a] $PhCONH_2$ (0.5 mmol), silane (2.2–6 equiv.), catalyst (2.5–5 mol%), base (7.5–15 mol%), solvent (3

mL) for 12 h at 50 °C followed by base hydrolysis using 1M NaOH. [b] Isolated yield of amine-hydrochloride salts. [c] Reaction performed at RT. [d] Reaction time 6 h.

4. Kinetics of catalytic reduction of amide to amine

A series of reactions was performed by taking pre-catalyst **1** (5 mol%, 13 mg) and KO^{t}Bu (15 mol%, 9 mg) in a 15 mL thick-walled glass tube with 3 mL THF inside a nitrogen filled glovebox. The mixture was stirred for 5 minutes. Next, $PhSiH_3$ (1.2 mmol, 148μl) and primary amide (0.5 mmol, 61 mg) were added to the reaction mixture. The glass tube was sealed and reaction mixtures were allowed to stir at 50 °C. In different time intervals (2, 4, 6, 8, 10 and 12 h), reaction mixture was quenched by adding 2 mL of 1 (M) NaOH solution and stirred for 3 h. The amine was extracted in 40 mL diethyl-ether (Et_2O) and dried over anhydrous sodium sulphate. The crude amine 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 amine salt. The precipitate was filtered off, washed with ethyl-acetate(5 mL x 2) and dried in vacuum to obtain pure amine salt. The yields of amine salt in each case time interval are listed in Table S5. The plot of time vs yield shows that within 10 h the reaction reaches nearly completion (Figure S4).

Table S5. Yield of benzylamine hydrochloride salt at different time intervals.



4a 5a

Entry[a]	Reaction time	Yield **5a**[b] (%)
1	2 h	28
2	4 h	53
3	6 h	65
4	8 h	76
5	10 h	80
6	12 h	81

[a] $PhCONH_2$ (0.5 mmol), $PhSiH_3$ (1.2 mmol). [b] Isolated yield of amine-hydrochloride salts.

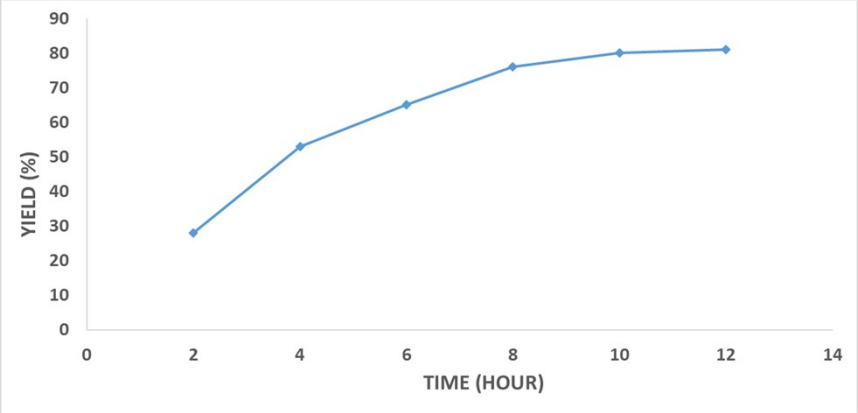
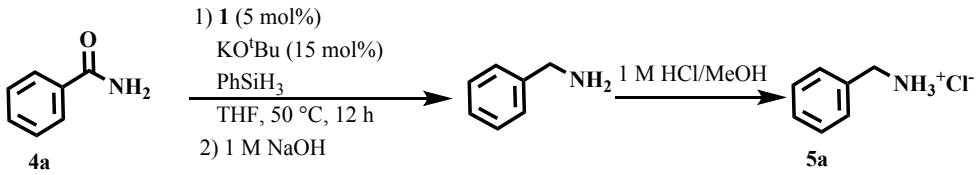


Figure S4. Graphical representation of yield of benzylamine as hydrochloride salt *vs* reaction time.

5. Procedure for gram-scale synthesis of benzylamine salt (5a):

1 (5 mol%, 215 mg) and KO^{t}Bu (15 mol%, 150 mg) were taken in a 250 mL Schlenk flask with 60 mL THF inside a nitrogen filled glovebox. The mixture was stirred for 5 minutes, then $PhSiH_3$ (19.84 mmol, 2.45 mL) and benzamide amide (1 g, 8.26 mmol) were added to the reaction mixture. After that, the Schlenk flask was connected to condenser under N_2 atmosphere and allowed to stir for 12 h at 50 °C. After completion of the reaction, 33 mL of 1 molar NaOH solution was added slowley to the reaction mixture and stirred for 3 h. The amine was extracted in 800 mL diethyl-ether (Et_2O) by using a separating funnel and dried over anhydrous sodium sulphate. The crude amine was obtained by evaporation of solvent under reduced pressure. On treatment with 20 mL of 1 molar methanolic HCl followed by Et_2O addition leads to precipitation of amine salt. The precipitate was filtered off, washed with ethyl-acetateand dried in vacuum to obtain 878 mg (74%) pure amine salt (**5a**).



Scheme S2. Reduction of benzamide to benzylamine in gram-scale.

6. Mechanistic Studies

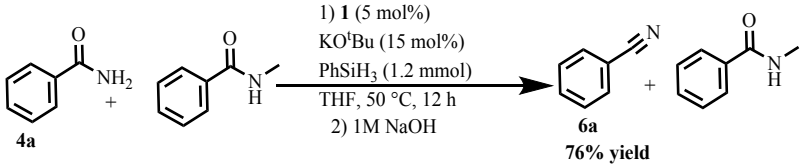
6A. Trapping the key nitrile intermediate in the amide to amine conversion using N-methyl benzamide inhibitor

To trap the nitrile intermediate, benzamide was selected as a model amide and N-methyl benzamide was used as a model inhibitor. **1** (5 mol%, 13 mg) and KO^{t}Bu (15 mol%, 9 mg) were taken in a 15 mL thick walled glass tube with 3 mL THF inside a nitrogen filled glovebox. The mixture was stirred for 5

minutes, then $PhSiH_3$ (1.2 mmol, 148 μL), $PhCONH_2$ (0.5 mmol, 61 mg) and N-methyl benzamide (0.5 mmol, 68 mg) were added to the reaction mixture successively. The glass tube was sealed and the reaction mixture was stirred for overnight at 50 ^{0}C under inert atmosphere. After completion of the reaction, 2 mL 1 molar NaOH solution was added to the reaction mixture and was stirred for 2 hours. The product was extracted in 40 mL diethyl-ether (Et_2O) and dried over anhydrous sodium sulphate. Then the crude product was obtained by evaporation of solvent under reduced pressure.^{1}H NMR spectrum of crude product suggests presence of benzonitrile in 76% yield along with N-methyl benzamide.

[6]**Benzonitrile:**^{1}H NMR(400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR(101 MHz, $CDCl_3$): δ 132.9, 132.2, 129.2, 119.0, 112.3.

[7]**N-methyl benzamide:**^{1}H NMR(400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.4 Hz, 2H), 7.42 (t, J = 7.7 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 2.93 (d,*J* = 4.6 Hz, 2H); ^{13}C NMR(101 MHz, $CDCl_3$): δ 168.5, 134.7, 131.3, 128.5, 127.0, 26.8.



Scheme S3. Trapping of nitrile intermediate by reaction of benzamide and N-methyl benzamide in presence of 5 mol% **1**, 15 mol% KO^{t}Bu and 1.2 mmol of $PhSiH_3$ at 50°C for 12 h.

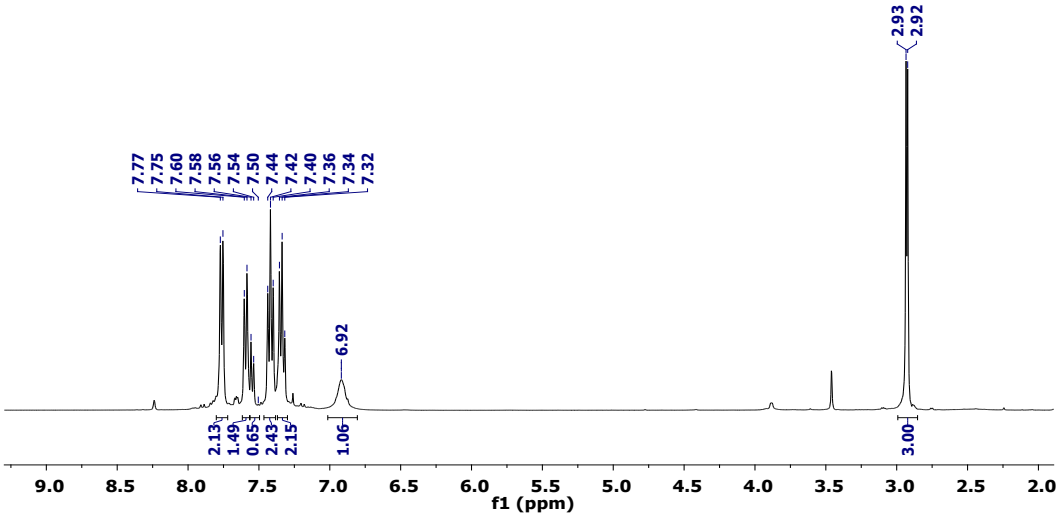


Figure S5.^{1}H NMR spectrum ($CDCl_3$) of crude reaction mixture described in Scheme S3.

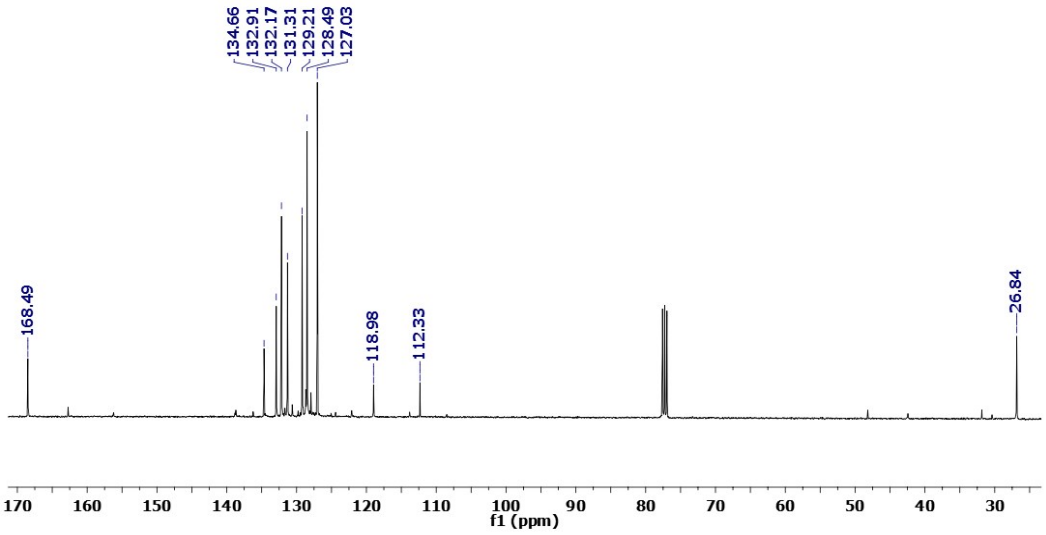
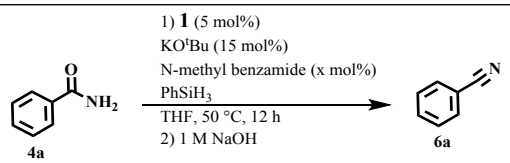


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of crude reaction mixture described in Scheme S3.

6B. Table S6. Optimization reaction study on amide reduction to nitrile.



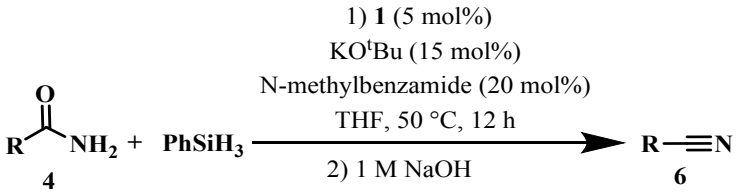
Entry[a]	N-methyl benzamide (mol%)	Yield **6a**[b] (%)
1	_	_
2	PhCONHMe (5)	_
3	PhCONHMe (10)	35
4	PhCONHMe (15)	68
5	PhCONHMe (20)	77
6	PhCONHMe (25)	79

[a]$PhCONH_2$ (0.5 mmol), $PhSiH_3$ (1.4 equiv.). [b]Isolated yield after purification by column chromatography.

6C. General procedure for reduction of amide to nitrile:

1 (5 mol%, 13 mg) and KO^{t}Bu (15 mol%, 9 mg) were taken in a 15 mL thick walled glass tube with 3 mL THF inside a nitrogen filled glovebox. The mixture was stirred for 5 minutes. Then $PhSiH_3$ (0.7 mmol, 85μl), primary amide (0.5 mmol) and N-methyl benzamide (20 mol%, 14 mg) were added to the reaction mixture. The glass tube was sealed and the reaction mixture was stirred for overnight at 50 ^{0}C under inert atmosphere. After completion of the reaction, 2 mL 1 molar NaOH solution was added to the reaction mixture and was stirred for 2 hours. The product was extracted in 40 mL diethyl-ether (Et_2O) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure

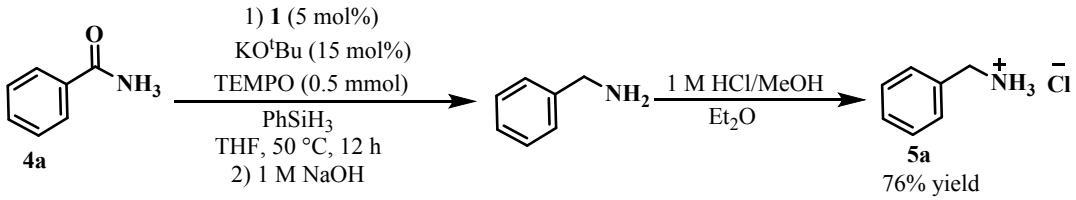
and crude product was purified by column chromatography on silica gel (100-200 mesh) by eluting with 0-2.5% ethyl acetate in hexane to yield the pure desired products.



Scheme S4. Reaction of benzamide to benzonitrile in presence of 5 mol% **2**, 15 mol% KO^{t}Bu and 1.2 mmol of $PhSiH_3$ at 50°C for 12h.

6D. Reduction of amide in presence of excess TEMPO

1 (5 mol%, 13mg) and KO^{t}Bu (15 mol%, 9 mg) in THF (3 mL) were taken in a thick walled glass tube and $PhSiH_3$ (1.2 mmol, 148 μL), benzamide (0.5 mmol, 61 mg) and TEMPO (0.5 mmol, 78 mg) were added to it inside a nitrogen filled glovebox. The glass tube was sealed and the reaction mixture was stirred at 50 °C, for 12 h and the silylated product along with excess silane was hydrolyzed with aqueous NaOH (2 mL, 1 M) solution at room temperature. The solution was extracted with Et_2O and concentrated under vacuum; finally the product was purified by salt formation.

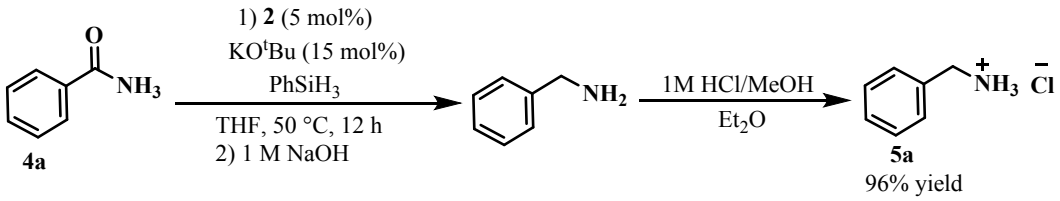


Scheme S5. Reaction of 1 equiv TEMPO with benzamide in presence of 5 mol% **1**, 15 mol% KO^{t}Bu and 1.2 mmol of $PhSiH_3$ at 50°C for 12 h.

6E. Reduction of primary amide to amine by catalyst 2

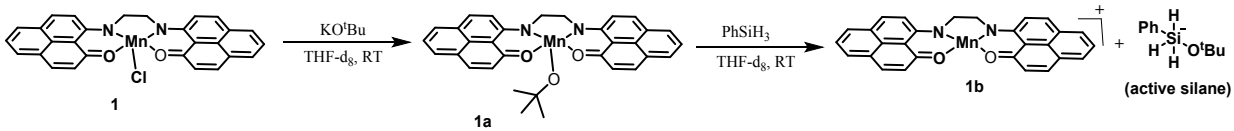
2 (5 mol%, 14 mg) and KO^{t}Bu (15 mol%, 9 mg) were taken in a 15 mL thick walled glass tube with 3 mL THF solvent inside a nitrogen filled glovebox. The mixture was stirred for 5 minutes, $PhSiH_3$ (1.2 mmol, 150 μl) and benzamide (0.5 mmol, 61 mg) were added to the reaction mixture. The glass tube was sealed and the reaction mixture was allowed to stir for overnight at 50 ^{0}C under inert atmosphere. After completion of the reaction, 2 mL 1 molar NaOH solution was added to the reaction mixture

slowly and stirred for 3 h. The amine was extracted in 40 mL diethyl-ether (Et_2O) and dried over anhydrous sodium sulphate. The crude amine was obtained by evaporation of solvent under reduced pressure. On treatment with 1 mL 1 molar methanolic HCl followed by Et_2O addition leads to precipitation of amine salt. The precipitate was filtered off, washed with ethyl-acetate and dried in vacuum to obtain pure amine salt.



Scheme S6. Reaction of benzamide in presence of 5 mol% **2**, 15 mol% KO^{t}Bu and 1.2 mmol of $PhSiH_3$ at 50°C for 12h.

6F. Identification of active silane [Ph(O^{t}Bu)SiH$_3$]$^-$ from the reaction of metal-alkoxide 1a with PhSiH$_3$. To micro-crystalline solid **1** (0.05 mmol, 25 mg) in a sample vials was added KO^{t}Bu (0.05 mmol, 6 mg) and 700 μl THF-d_8 inside a nitrogen filled glovebox resulting clear reddish-pink solution. The mixture was stirred for 10 minutes and then $PhSiH_3$ (0.06 mmol, 8 μl) was added resulting immediate color change from reddish-pink to blue and stirred again for another 10 minutes at RT followed by ^{1}H NMR measurement. ^{1}H NMR (400 MHz, THF-d_8): δ 5.08 (s, SiH signal of [Ph(^{t}BuO)SiH$_3$]K).[8]



Scheme S7. Formation of active silane by reaction of **1b** and $PhSiH_3$ in THF-d_8 at RT.

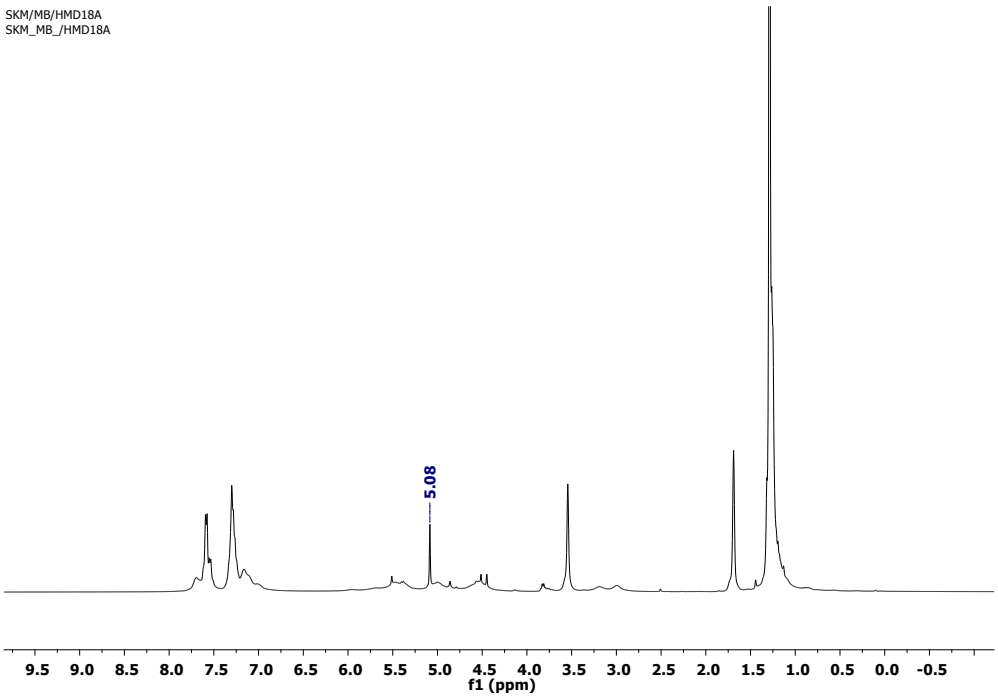


Figure S7. ^{1}H NMR spectrum (THF-d_8) of crude reaction mixture described in Scheme S7.

6G. Detection of molecular hydrogen during amide to amine catalytic reaction

Pre-catalyst **1** (5 mol%, 8 mg) and KO^{t}Bu (15 mol%, 5 mg) were taken in a 15 mL thick-walled glass tube with 1.5 mL DMSO-d_6 inside a nitrogen filled glovebox. The mixture was stirred for 5 minutes, then $PhSiH_3$ (0.72 mmol, 89 μL) and primary amide (0.3 mmol, 36 mg) were added to the reaction mixture and the reaction mixture was taken in a screw cap NMR tube, sealed and heated for 4 h at 50 °C. Then the NMR tube was cooled to RT and analysed with ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.61 (s, H_2).[9]

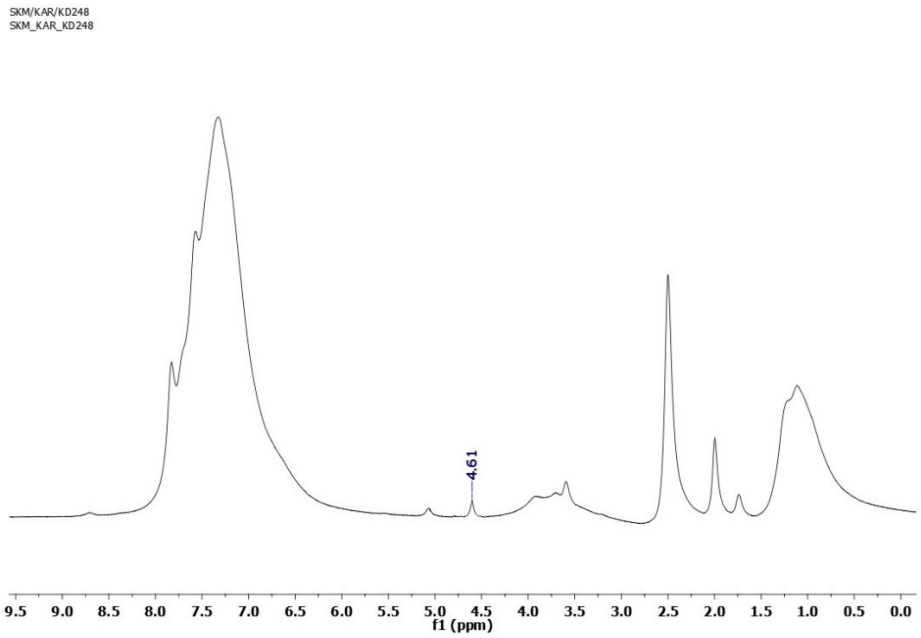
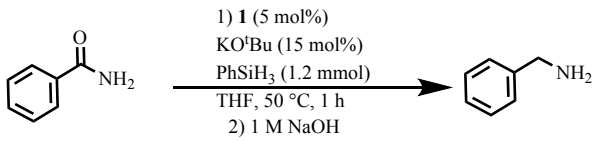


Figure S8. ^{1}H NMR spectrum (DMSO-d_6) of reaction mixture after 4 h reaction in a screw cap NMR tube.

6H. Detection of imine intermediate during amide to amine catalytic reaction

To trap the reaction key intermediates, we stopped our catalytic reaction prematurely. **1** (5 mol%, 13 mg) and KO^{t}Bu (15 mol%, 9 mg) were taken in a 15 mL thick walled glass tube with 3 mL THF inside a nitrogen filled glovebox. The mixture was stirred for 5 minutes, $PhSiH_3$ (1.2 mmol, 148 μL) and $PhCONH_2$ (0.5 mmol, 61 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 1 h by adding 2 mL 1 molar NaOH solution followed by stirring for 2 hours. The reaction mixture was extracted in 40 mL diethyl-ether (Et_2O) and dried over anhydrous sodium sulphate. Then the crude product was obtained by evaporation of solvent under reduced pressure. ^{1}H NMR and HRMS mass of crude product was measured. The analysis of ^{1}H NMR and HRMS spectrum of crude product suggest the formation of imine intermediate in our catalytic reaction.[10]



Scheme S8: Stopping the reduction prematurely after 1 h during conversion of benzamide to benzyl amine.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, PhC*H*=NH) (see Figure S9).[10]

HRMS (ESI) Calcd for PhC*H*=NH: m/z 105.0578. Found: 105.0327 (see Figure S10)

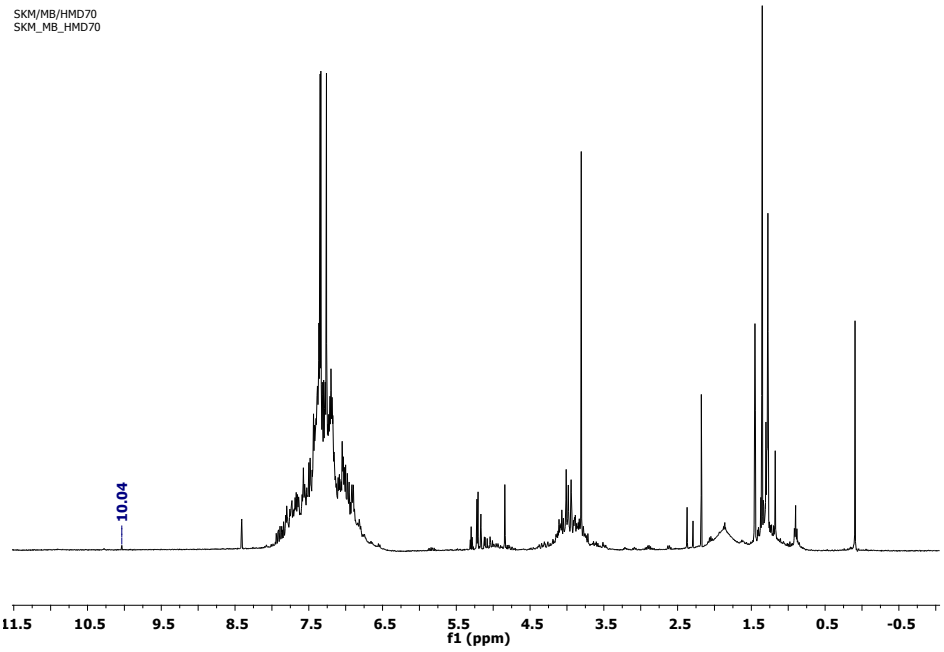


Figure S9. ^{1}H NMR spectrum ($CDCl_3$) of crude reaction mixture obtained after 1 h reaction.

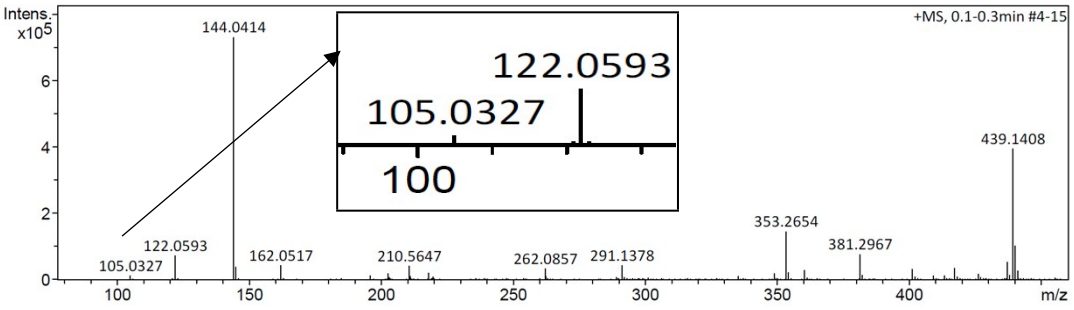


Figure S10. HRMS (ESI, m/z) mass spectrum of crude reaction mixture obtained after 1 h reaction.

6I. Stability of catalyst 1 under reducing conditions

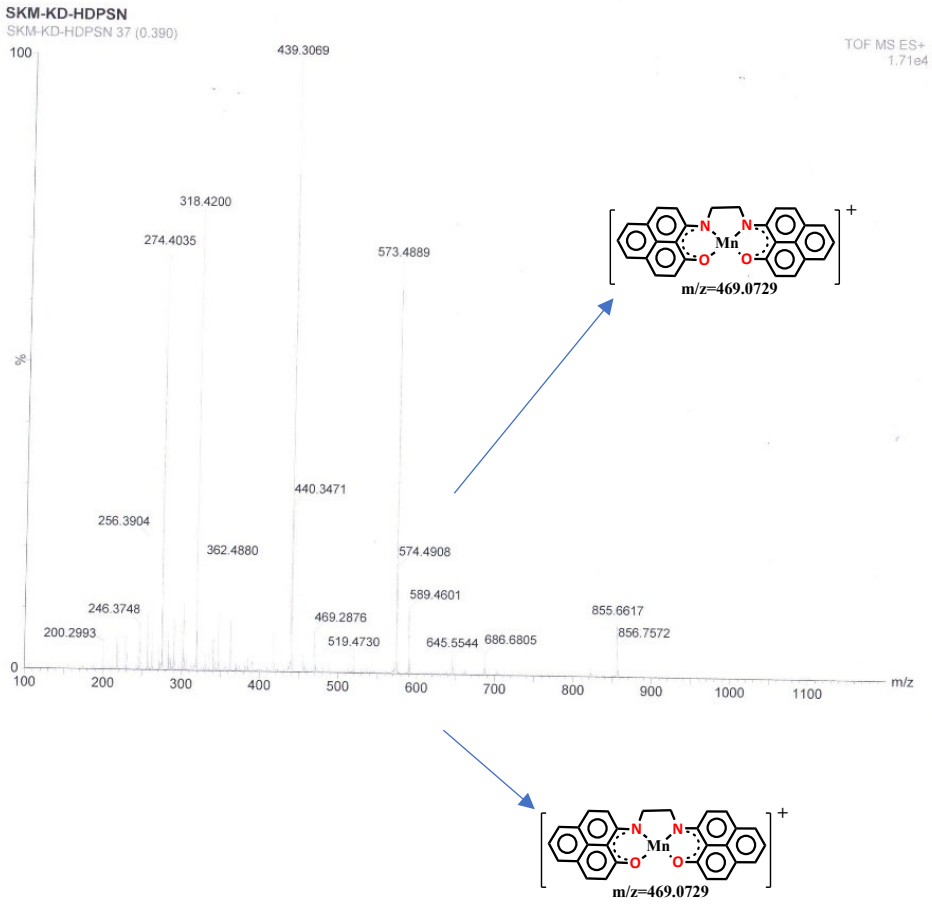
The mass spectroscopic studies were carried out to understand the stability of the paramagnetic complex **1** under reducing conditions. For the mass spectroscopic study, two samples were prepared as follows: Sample-1 was prepared by treating the complex **1** (5 mol%, 13 mg) with a reducing agent such as $PhSiH_3$ (1.2 mmol, 148 μL) in 300 μL DMSO in a 15 mL sealed tube inside the glovebox. It was kept for 12 h and analysed by mass spectrometry.

Similarly, Sample-2 was prepared by dissolving complex **1** (5 mol%, 13 mg) in 300 μL DMSO in a 25 mL Schlenk flask inside a nitrogen filled glovebox. After that, the reaction mixture was taken out of the

glovebox and subjected to two cycles of freeze pump thaw process and filled with H_2 (1 atm.) gas and kept for 12 h followed by mass spectrometric investigation.

In each case (Sample-1 and Sample-2), the mass spectrum analysis shows molecular ion peak at which confirms the stability of complex **1** under reducing atmosphere (Figure S11). It may be concluded that the catalyst is stable under reducing environment (in presence of $PhSiH_3$ or H_2).

(a)


SKM-KD-HDPSN
SKM-KD-HDPSN 37 (0.390)
TOF MS ES+
1.71e4
100
%
0
439.3069
318.4200
274.4035
573.4889
440.3471
256.3904
362.4880
574.4908
589.4601
246.3748
469.2876
855.6617
200.2993
519.4730
645.5544
686.6805
856.7572
100
200
300
400
500
600
700
800
900
1000
1100
m/z
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+
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N
N
Mn
O
O
+
m/z=469.0729

(b)

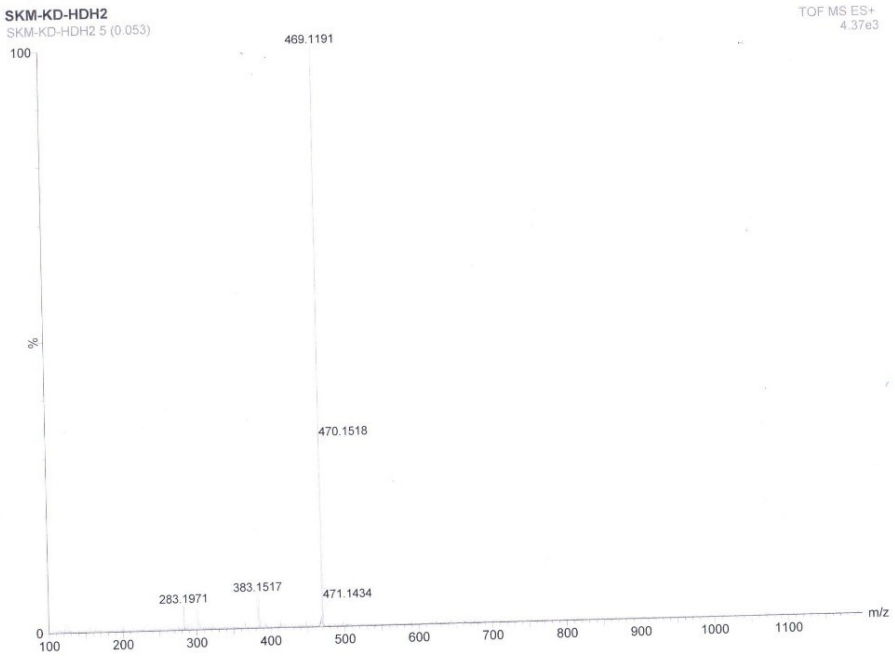
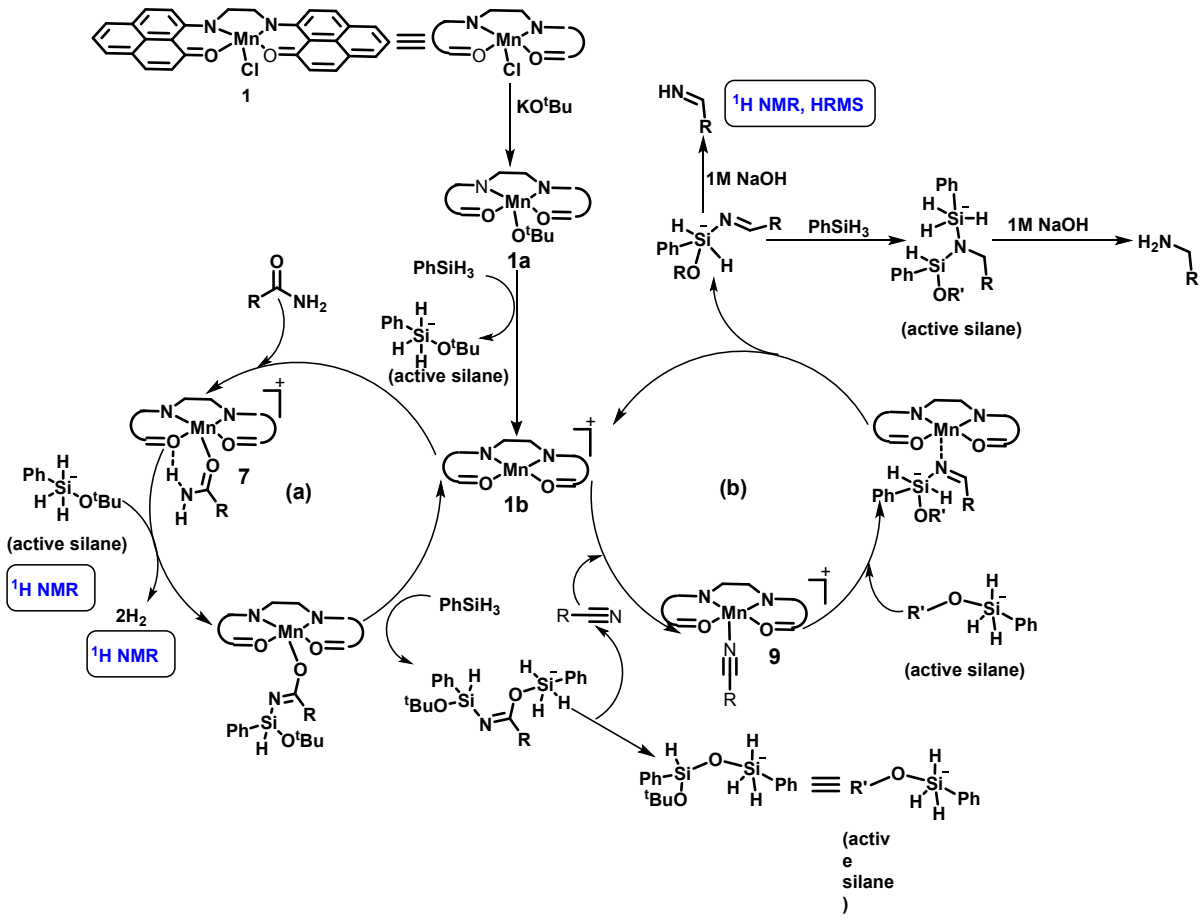


Figure S11. (a) ESI-MS spectrum of Sample-1. (b) ESI-MS spectrum of Sample-2 after exposing to reducing .

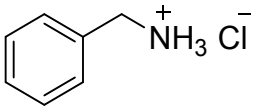
6j. Proposed catalytic cycle for reduction of primary amide to nitrile and amine



Scheme S9. Proposed catalytic cycle of primary amide to amine transformation.

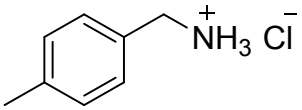
7. Characterization Data

7A. Characterization data of amine salts



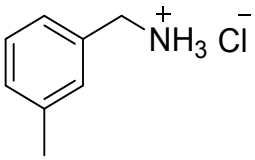
Phenylmethanamine hydrochloride, 5a[11,12,13]

Colourless solid, Yield: 81%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.56 (br s, 3H), 7.47 (d, J = 6.6 Hz, 2H), 7.39-7.29 (m, *3*H), 3.95 (q, J = 5.5 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 134.1, 129.0, 128.6, 128.4, 42.2.



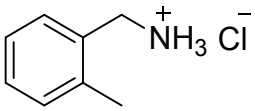
***p*-Tolylmethanamine Hydrochloride, 5b**[13]

Colourless solid, Yield: 87%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.48 (br s, 3H), 7.34 (d, J = 7.3 Hz, 2H), 7.16 (d, J = 7.3 Hz, 2H), 3.89 (q, J = 4.5 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 137.6, 131.0, 129.0, 128.9, 41.8, 20.7.



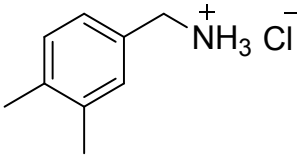
***m*-Tolylmethanamine Hydrochloride, 5c**[11]

Colourless solid, Yield: 85%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.42 (br s, 3H), 7.28-7.22 (m, 3H), 7.17-7.11 (m,1H), 3.91 (q, J = 5.4 Hz, 2H) 2.27 (s,3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 137.8, 134.0, 129.6, 129.1, 128.5, 126.0, 42.2, 21.0.



***o*-Tolylmethanamine Hydrochloride, 5d**[13]

Colourless solid, Yield: 84%.**^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.50 (br s, 3H), 7.41-7.36 (m, 1H), 7.25-7.16 (m, *3*H), 3.94 (q, J = 5.8 Hz, 2H), 2.31 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 136.7, 132.6, 130.3, 129.3, 128.4, 126.0, 39.4, 18.9.



(3,4-Dimethylphenyl)-methanamine Hydrochloride, 5e

Colourless solid, Yield: 90%.**^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.44 (br s, 3H), 7.22 (s, 1H), 7.18-7.16 (m,1H), 7.11 (d, J = 7.7 Hz, 1H) 3.86 (q, J = 5.7 Hz, 2H), 2.17 (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 136.9, 136.8, 131.9, 130.6, 130.1, 126.9, 42.4, 19.8, 19.6. (HRMS): m/z (%) calcd for $[C_9H_{11}\text{-Cl-}NH_3]^+$: 119.087; found: 119.087.

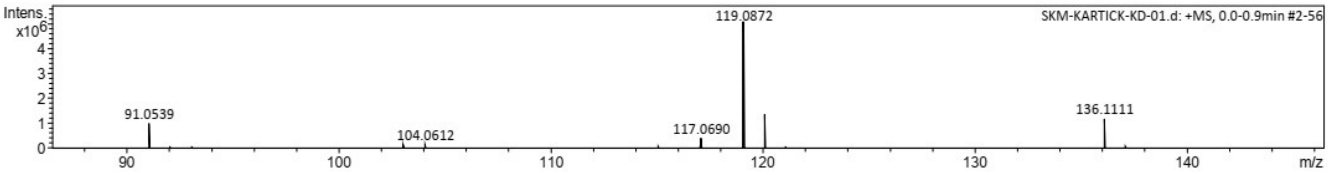
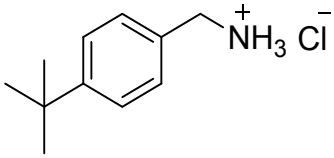
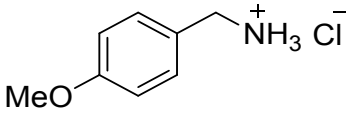


Figure S12. HRMS spectrum of **5e** recorded in methanol.



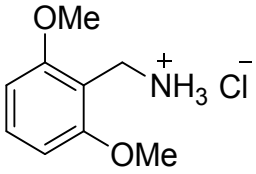
4-(1,1-dimethylethyl)-Benzenemethanamine Hydrochloride, 5f[14]

Colourless solid, Yield: 95%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.43 (br s, 3H), 7.38 (s, 4H), 3.91 (q, J = 5.7 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 150.9, 131.2, 128.8, 125.3, 41.8, 34.4, 31.1.



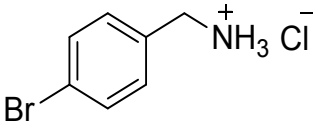
(4-Methoxyphenyl)methanamine Hydrochloride, 5g[11]

Colourless solid, Yield: 83%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.45 (br s, 3H), 7.39 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 3.87 (q, J = 5.7 Hz, 2H) 3.70 (s, J = 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 159.4, 130.7, 126.1, 113.9, 55.3, 41.7.



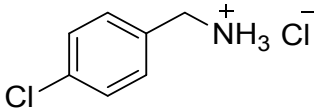
(2,6-Dimethoxyphenyl)methanamine Hydrochloride, 5h[15]

Colourless solid, Yield: 87%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.52 (br s, 3H), 6.69 (d, J = 2.2 Hz, 2H), 6.44 (t, J = 2.2 Hz, 1H), 3.88 (q, J = 5.7 Hz, 2H), 3.70 (s,6H);**^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 160.5, 136.3, 106.9, 100.0, 55.4, 42.2.



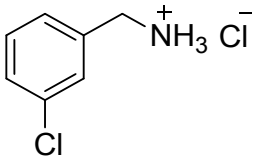
(4-Bromophenyl)methanamine Hydrochloride, 5i[11]

Colourless solid, Yield: 74%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.54 (br s, 3H), 7.57 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 3.94 (q, J = 5.6 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 134.5, 132.4, 132.3, 112.7, 42.4.



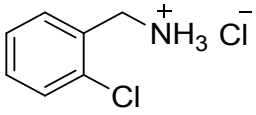
(4-Chlorophenyl)methanamine Hydrochloride, 5j[13]

Colourless solid, Yield: 75%. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.54 (s, 3H), 7.53 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 4.00 (q, J = 5.8 Hz, 2H).**^{13}C{^{1}H} NMR** (101 MHz, DMSO- d_6) δ 133.1, 133.0, 131.0, 128.4, 41.3.



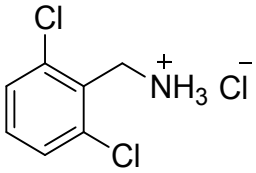
(3-Chlorophenyl)methanamine Hydrochloride, 5k[11,13]

Colourless solid, Yield: 80%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.64 (br s, 3H), 7.61 (s, 1H), 7.45 (m,1H), 7.41-7.36 (m,2H), 3.98 (q, J = 5.6 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 137.6, 134.1, 131.5, 130.0, 129.3, 128.8, 42.5.



(2-Chlorophenyl)methanamine Hydrochloride, 5l[11,13]

Colourless solid, Yield: 67%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.59 (br s, 3H), 7.60 (m, 1H), 7.49 (m, 1H), 7.41-7.35 (m, 2H), 4.08 (q, J = 4.4 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 132.9, 131.7, 130.8, 130.4, 129.5, 127.5, 39.3.



(2,6-Dichlorophenyl)methanamine Hydrochloride, 5m

Colourless solid, Yield: 78%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.60 (br s, 3H), 7.53 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 4.20 (q, J = 4.2 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 135.8, 131.8, 129.8, 128.7, 37.4. (HRMS): m/z (%) calcd for $[C_7H_5Cl_2\text{-}Cl\text{-}NH_3]^+$: 158.975; found: 158.975.

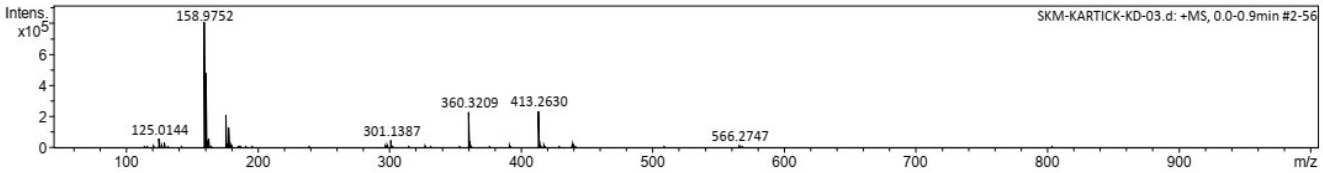
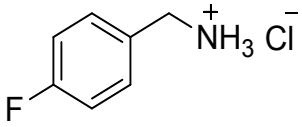
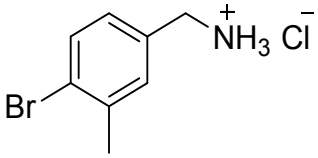


Figure 13. HRMS-spectrum of **5m** recorded in methanol.



(4-Fluorophenyl)methanamine Hydrochloride, 5n[14]

Colourless solid, Yield: 64%.**^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.40 (s, 3H), 7.57 – 7.50 (m, 2H), 7.28 – 7.21 (m, 1H), 4.00 (q, J = 5.7 Hz, 1H).**^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ 162.0 (d, J = 244.5 Hz), 131.4 (d, J = 8.4 Hz), 130.4 (d, J = 2.7 Hz), 115.3 (d, J = 21.4 Hz), 41.3 (s).



(4-bromo-3-methylphenyl)methanamine Hydrochloride, 5o

Colourless solid, Yield: 76%.**^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.51 (br s, 3H), 7.58 (d, J = 8.3 Hz, 1H), 7.46 (s,1H), 7.24 (m, 1H) 3.90 (m, 2H), 2.30 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 137.3, 133.8,

132.2, 131.8, 128.5, 124.1, 41.4, 22.4. (HRMS): m/z (%) calcd for $[C_8H_8Br\text{-}Cl\text{-}NH_3]^+$: 182.978(51%) and 184.976 (49%); found: 182.978(51%) and 184.976 (49%).

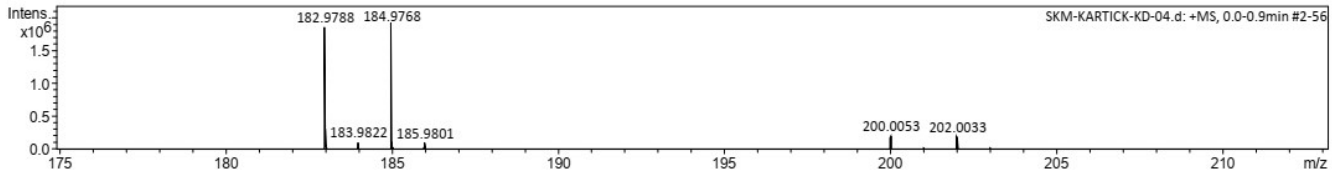
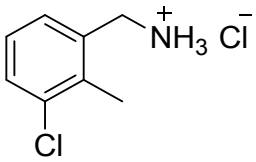


Figure S13. HRMS-spectrum of **5o** recorded in methanol.



(3-chloro-2-methyl)methanamine Hydrochloride, 5p

Colourless solid, Yield: 81%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.57 (br s, 3H), 7.41 (d, J = 8.2 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H) 4.02 (q, J = 5.5 Hz, 2H), 2.34 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 135.2, 135.1, 134.5, 129.8, 128.9, 127.7, 40.6, 16.3. (HRMS): m/z (%) calcd for $[C_8H_8Cl\text{-}Cl\text{-}NH_3]^+$: 139.030 found: 139.030.

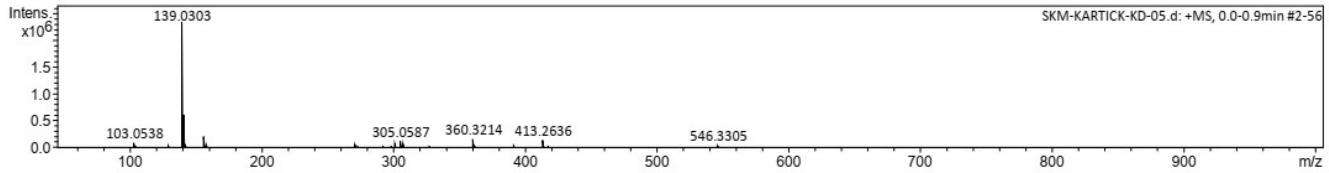
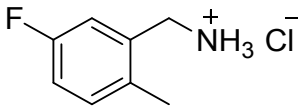


Figure S14. HRMS-spectrum of **5p** recorded in methanol.



(5-fluoro-2-methyl)methanamine Hydrochloride, 5q,

Colourless solid, Yield: 80%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.63 (br s, 3H), 7.30 (dd, J = 10.1 Hz, J = 2.7 Hz, 1H), 7.22 (dd, J = 8.3 Hz, J = 6.2 Hz, 1H), 7.05 (td, J = 8.6 Hz, J = 2.7 Hz, 1H), 3.95 (q, J = 5.3 Hz, 2H) 2.27 (s,3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 161.76, 159.4, 134.6, 134.5, 132.9, 132.8, 132.2, 132.1, 116.1, 115.8, 115.2, 115.0, 39.5, 18.3. (HRMS): m/z (%) calcd for $[C_8H_8F\text{-}Cl\text{-}NH_3]^+$: 123.059 found: 123.059.

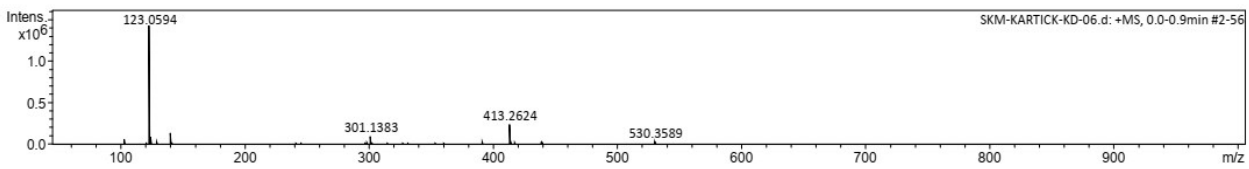
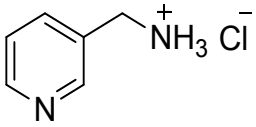


Figure S15. HRMS-spectrum of **5q** recorded in methanol.



3-Pyridinemethanamine Hydrochloride, 5r

White solid, Yield: 63%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 9.04 (s, 1H), 8.90 (br s, 3H), 8.86 (d, J = 5.5 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.01 (dd, J = 8.0 Hz, J = 9.3 Hz, 1H) 4.21 (q, J = 5.3 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 145.4, 143.5, 142.5, 133.5, 126.4, 39.0. (HRMS): m/z (%) calcd for $[C_6H_9N_2\text{-}Cl]^+$: 109.075 found: 109.075.

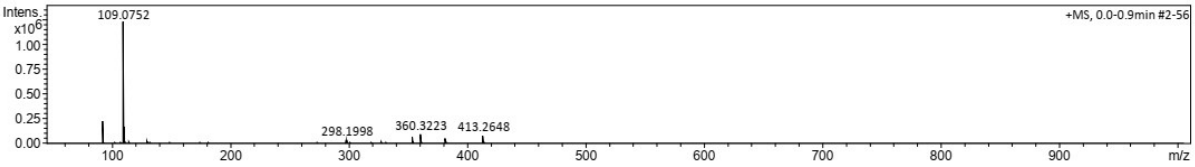
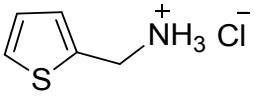
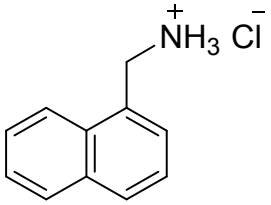


Figure S16**.** HRMS-spectrum of **5r** recorded in methanol.



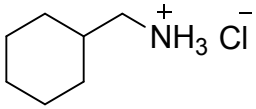
Thiophen-2-ylmethanamine Hydrochloride, 5s[11]

White solid, Yield: 61%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.61 (br s, 3H), 7.52 (d, J = 4.7 Hz, 1H), 7.25 (d, J = 3.2 Hz, 1H), 7.01 (dd, J = 4.8 Hz, J = 3.7 Hz, 1H), 4.15 (q, J = 5.4 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 135.3, 129.2, 127.3, 36.7.



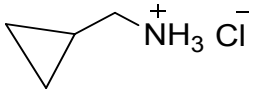
Naphthalen-1-ylmethanamine Hydrochloride, 5t[12]

Off-white solid, Yield: 74%.**^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.66 (br s, 3H), 8.11 (d, J = 8.2 Hz, 1H), 8.00-7.90 (m,2H), 7.65-7.61 (m,1H), 7.61-7.49 (m,3H), 4.47 (q, J = 5.4 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 133.2, 130.7, 130.0, 129.0, 128.7, 127.3, 126.8, 126.2, 125.4, 123.5, 39.1.



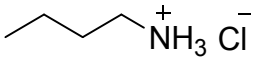
Cyclohexylmethanamine Hydrochloride, 5u[11]

Colourless solid, Yield: 89%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.10 (br s, 3H), 2.55 (m, 2H), 1.74-1.46 (m,6H), 1.21-1.00 (m,3H), 0.93-0.80 (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 45.4, 36.3, 30.8, 26.7, 26.1.



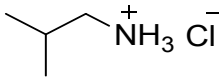
Cyclopropylmethanamine Hydrochloride, 5v[16]

Colourless solid, Yield: 77%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.17 (br s, 3H), 2.62-2.52 (m, 2H), 1.05-0.91 (m,1H), 0.50-0.40 (m, 2H) 0.30-0.22 (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 43.4, 8.6, 3.9.



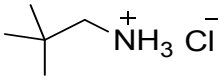
***n*-butylamine Hydrochloride, 5w**[17]

Colourless solid, Yield: 65%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.11 (br s, 3H), 2.67 (m, 2H), 1.57-1.40 (m,1H), 1.26 (dq, J = 14.4 Hz, J = 7.2 Hz, 1H), 0.81 (t, J = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 38.9, 29.5, 19.7, 14.1.



2-Methylpropan-1-amine Hydrochloride, 5x[11]

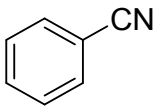
Colourless solid, Yield: 62%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.06 (br s, 3H), 2.55 (p, J = 5.7 Hz, 2H), 1.84 (m,1H), 0.87 (d, J = 6.8 Hz, 6H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 45.7, 30.8, 26.4, 19.8.



2,2-Dimethylpropan-1-amine Hydrochloride, 5y[11]

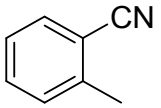
Colourless solid, Yield: 82%. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.05 (br s, 3H), 2.54 (q, J = 5.9 Hz, 1H), 0.90 (s,9H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 49.7, 30.2, 27.0.

7 B. Characterization data of nitrile products



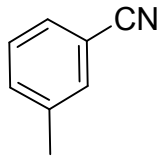
Benzonitrile, 6a [18]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; colorless liquid, Yield: 75%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.1 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 132.6, 131.9, 128.9, 118.6, 112.1.



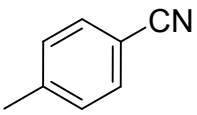
2-Methylbenzonitrile, 6b[18]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; colorless liquid, Yield: 93%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, J = 7.7 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.31 (d, J = 7.8 Hz,1H), 7.26 (t, J = 7.6 Hz, 1H), 2.54 (s, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 141.8, 132.6, 132.4, 130.2, 126.2, 118.1, 112.7, 20.4.



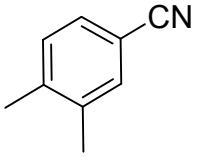
3-Methylbenzonitrile 6c[18]

The compound was purified by column chromatography using silica gel (10c0-200 mesh) with 2.5% of EtOAc in hexane; colorless liquid, Yield: 84%.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (t, J = 9.1 Hz, 3H), 7.31 (t, J = 7.7 Hz, 1H), 2.34 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 139.1, 133.6, 132.3, 129.1, 128.9, 118.9, 112.1, 21.0.



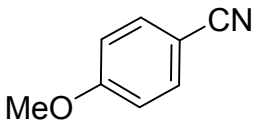
4-Methylbenzonitrile 6d[17]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; colourless liquid, Yield: 90%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.7 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 2H), 2.41 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 143.7, 131.9, 129.8, 119.1, 109.2, 21.7.



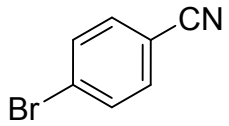
(3,4-Dimethylphenyl)-carbonitrile 6e[18]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; colorless liquid, Yield: 95%.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.37 (m, 2H), 7.21 (d, J = 7.7 Hz, 1H), 2.31 (s, 3H), 2.28 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 142.6, 138.0, 133.0, 130.4, 129.8, 119.4, 109.7, 20.3, 19.7.



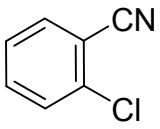
4-Methoxybenzonitrile, 6f[18]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; white solid, Yield 72%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 163.0, 134.1, 119.3, 114.7, 104.1, 55.7.



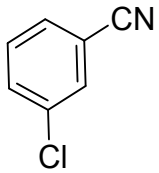
4-Bromobenzonitrile, 6g[19]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; white solid, Yield: 74%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 133.5, 132.7, 128.1, 118.1, 111.3.



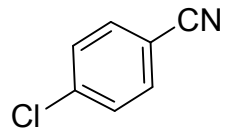
2-Chlorobenzonitrile, 6h[18]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; white solid, Yield: 73%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, J = 7.6 Hz, 1H), 7.57-7.51 (m, 2H), 7.38 (td, J_1= 7.1 Hz, J_2 = 1.4 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 136.9, 134.1, 124.0, 130.1, 127.3, 116.0, 113.5.



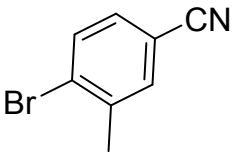
3-Chlorobenzonitrile, 6i[20]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; white solid, Yield: 82%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.61-7.55(m, 2H), 7.45-7.41 (m, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 135.4, 133.4, 132.1, 130.6, 130.4, 117.6, 114.1.



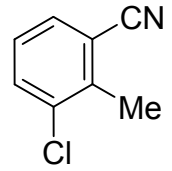
4-Chlorobenzonitrile 6j[18]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; white solid, Yield: 71.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 139.7, 133.5, 129.8, 118.1, 110.9.



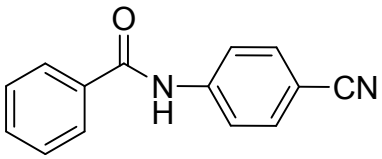
4-Bromo-3-methylbenzonitrile 6k[21]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; white solid Yield: 87%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.1 Hz, 1H), 7.51 (s, 1H), 7.34-7.32 (m, 1H), 2.44 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 139.8, 133.9, 133.5, 130.7, 130.6, 118.3, 111.5, 23.0.



(3-Chloro-2-methylphenyl)-carbonitrile, 6l[22]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; colorless solid, Yield: 89%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.24-7.20 (m, 1H), 2.57 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 139.9, 135.6, 133.6, 131.1, 127.5, 117.4, 114.7, 18.7.



N-(4-carbamoylphenyl)benzamide, 6m

The crude product was almost pure and characterized analytically without further purification; White solid, Yield: 94%.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.61 (s, 1H), 7.97 – 7.91 (m, 4H), 7.80 (d, J = 8.7 Hz, 2H),

7.58 (d, J = 7.5 Hz, 1H) 7.52 (t, J = 7.4 Hz, 2H); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ 166.3, 143.5, 134.4, 133.2, 132.1, 128.5, 127.9, 120.2, 119.1, 105.4. (HRMS): m/z (%) calcd for $[C_{14}H_{10}N_2O+Na]^+$: 245.067 found: 245.067.

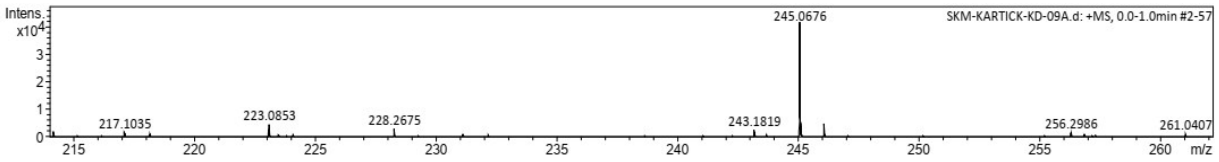
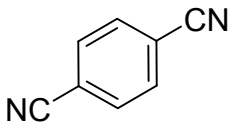
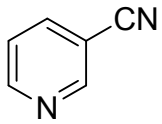


Figure S17. HRMS-spectrum of **6m** recorded in acetonitrile.



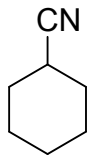
1,4-Dicyanobenzene,6n[23]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; White solid, Yield: 81%.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (s, 4H); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ 132.9, 117.1, 116.9.



3-Pyridinecarbonitrile, 6o[24]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; colorless liquid, Yield: 81%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.82 (d, J = 4.7 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.44 (m, 1H); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ 153.0, 152.5, 139.3, 123.7, 116.5, 110.1.



Cyclohexylcarbonitrile, 6p[25]

The compound was purified by column chromatography using silica gel (100-200 mesh) with 2.5% of EtOAc in hexane; colorless liquid, Yield: 81%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.62-2.58 (m, 1H), 1.82-1.81 (m, 2H), 1.68-1.66 (m, 4H), 1.49-1.40 (m, 4H); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ 122.6, 29.5, 27.9, 25.2, 24.0.

8. ^{1}H NMR and ^{13}C NMR spectra of the products

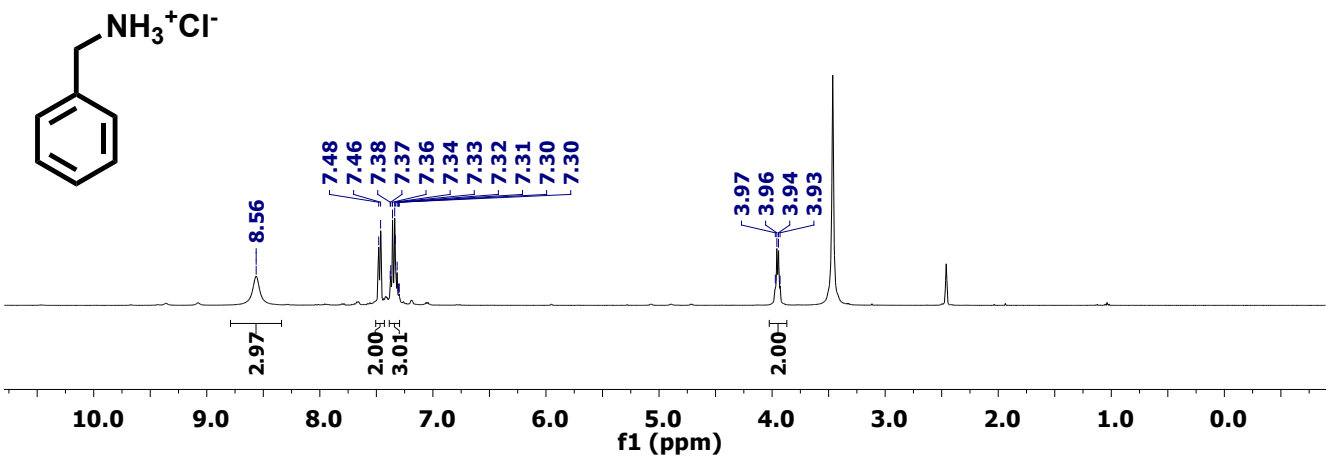


Figure S18.[1]H NMR spectrum (DMSO-d_6) of phenylmethanaminium chloride.

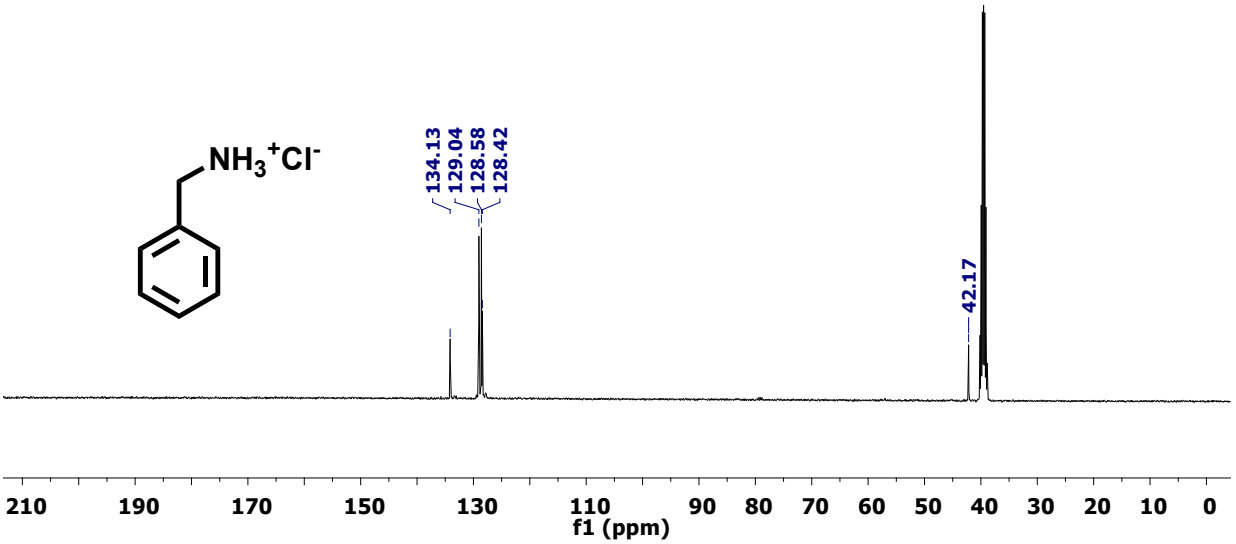


Figure S19. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of phenylmethanaminium chloride.

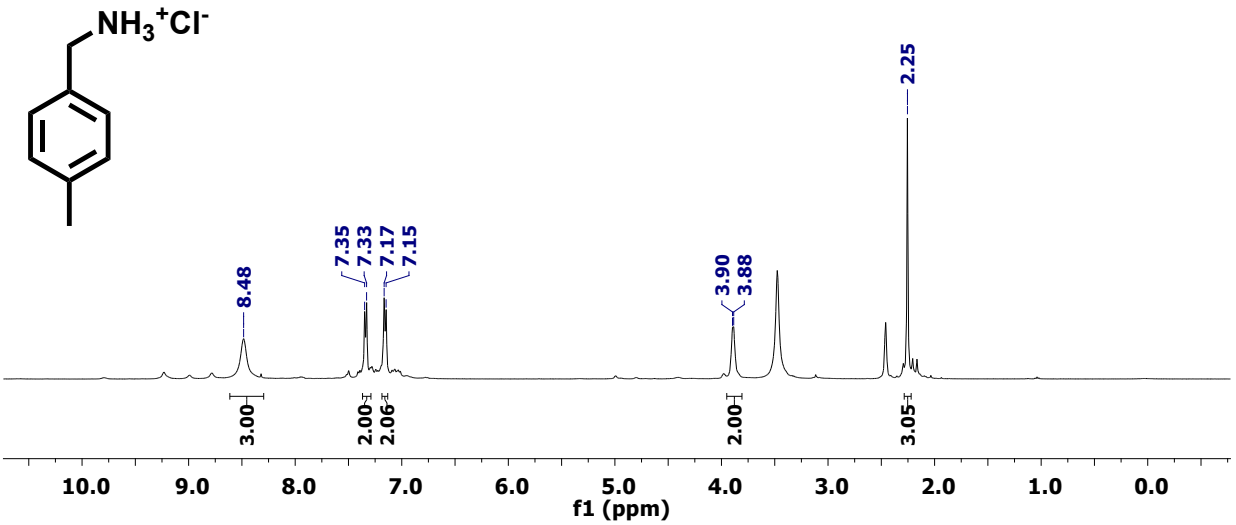


Figure S20.^{1}H NMR spectrum (DMSO-d_6) of p-tolylmethanaminium chloride.

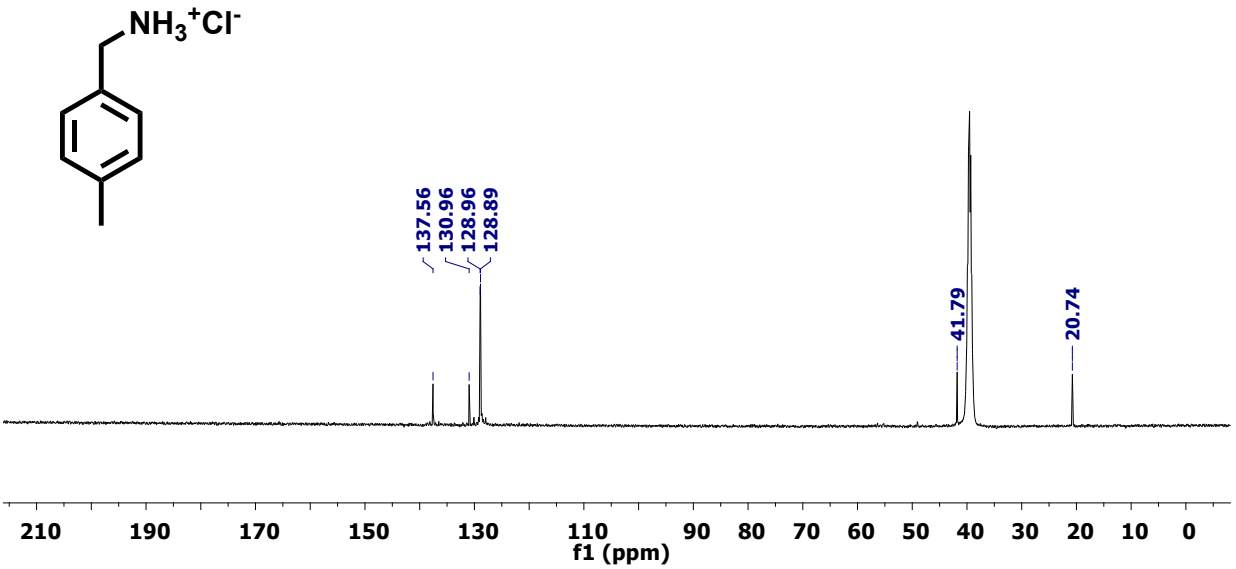


Figure S21. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of p-tolylmethanaminium chloride.

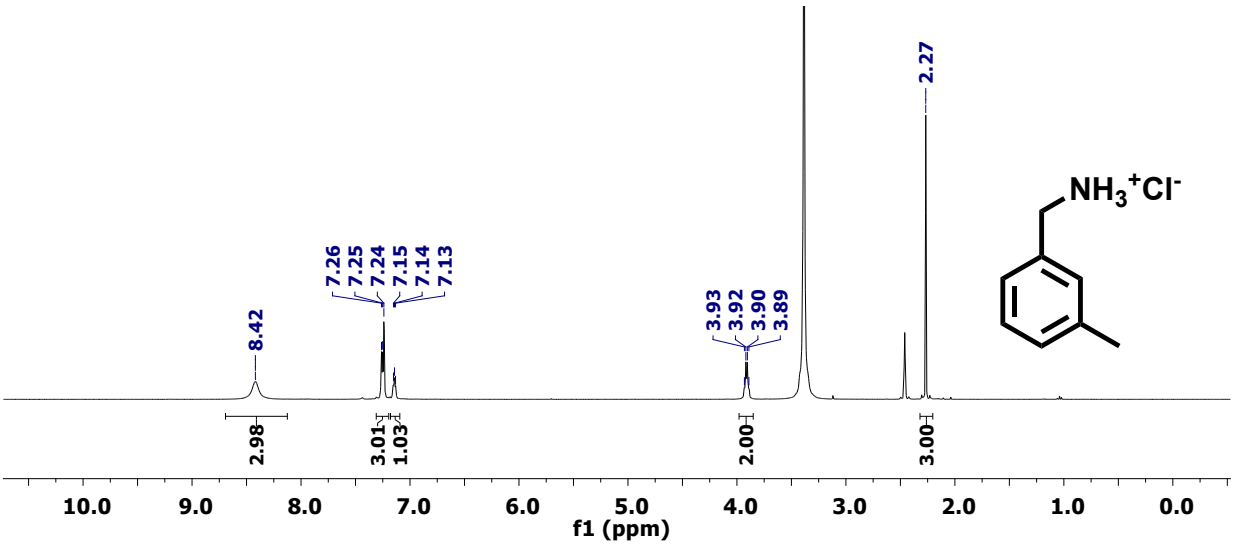


Figure S22.[1]H NMR spectrum (DMSO-d_6) of m-tolylmethanaminium chloride

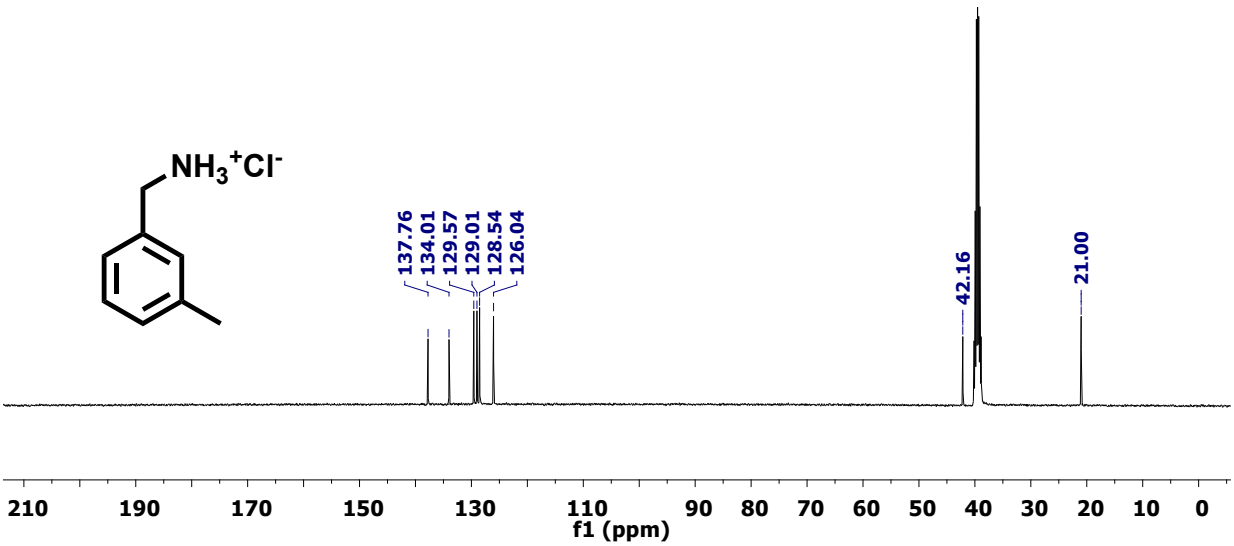


Figure S23. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of m-tolylmethanaminium chloride

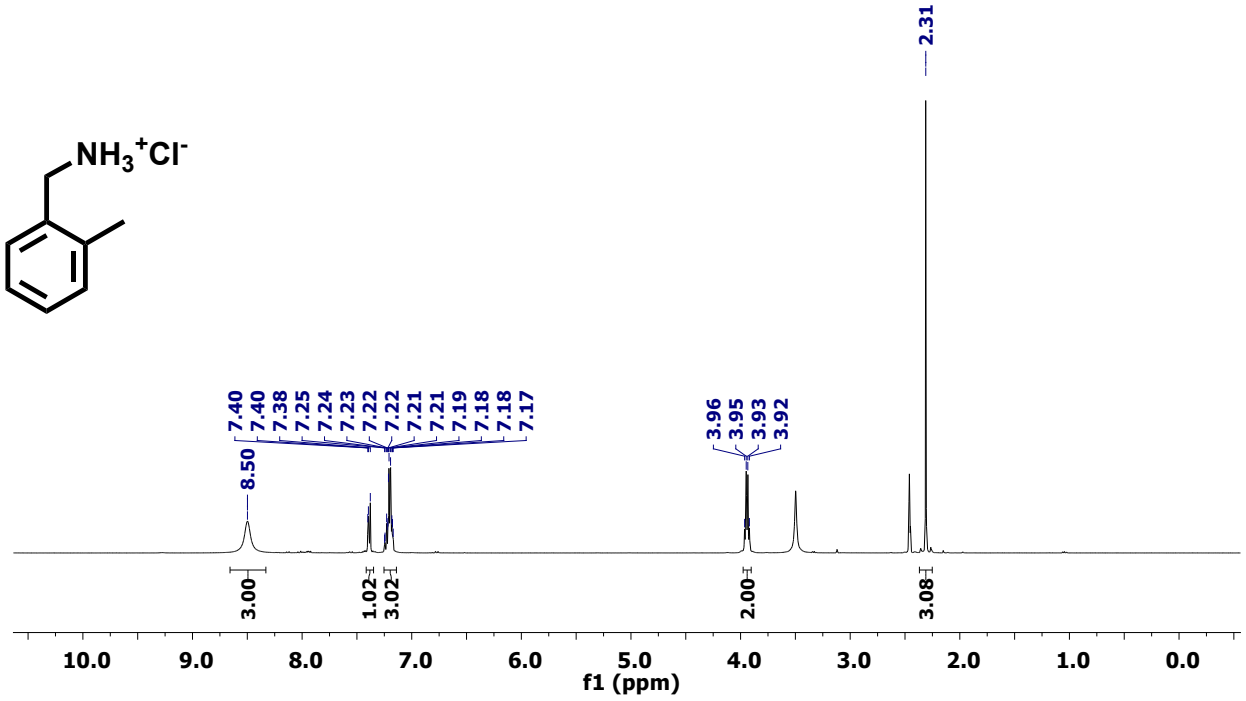


Figure S24.[1]H NMR spectrum (DMSO-d_6) of o-tolylmethanaminium chloride.

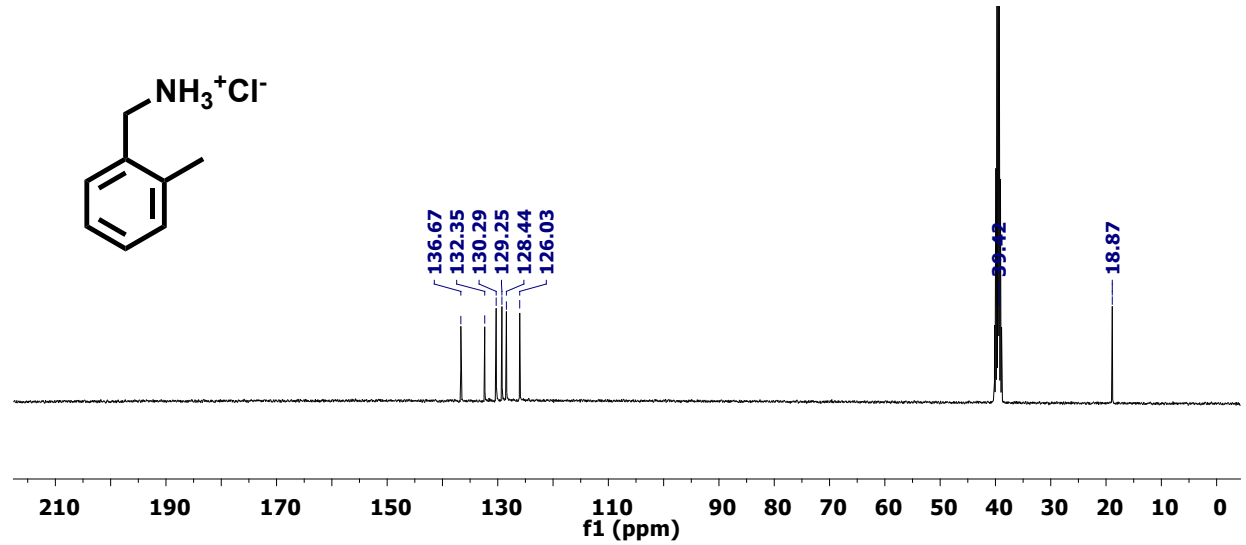


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) of o-tolylmethanaminium chloride.

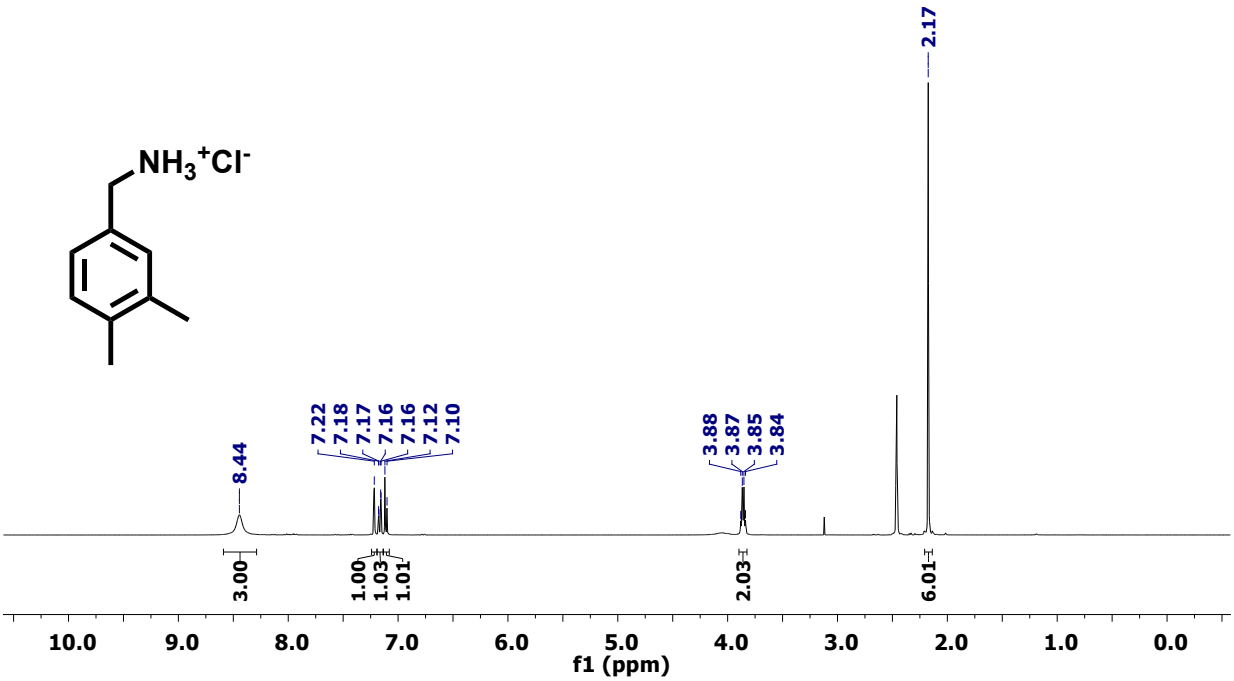


Figure S26.^{1}H NMR spectrum (DMSO-d_6) of (3,4-dimethylphenyl)methanaminium chloride.

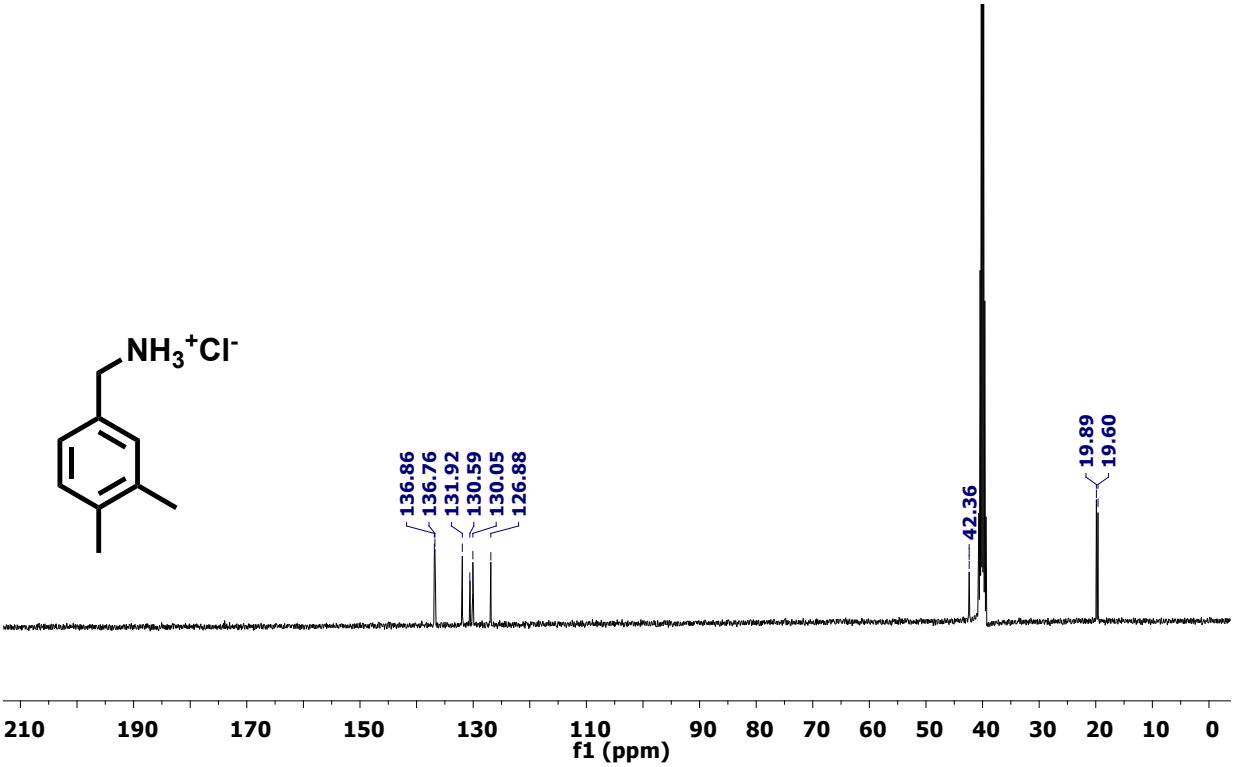


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) of (3,4-dimethylphenyl)-methanaminium chloride.

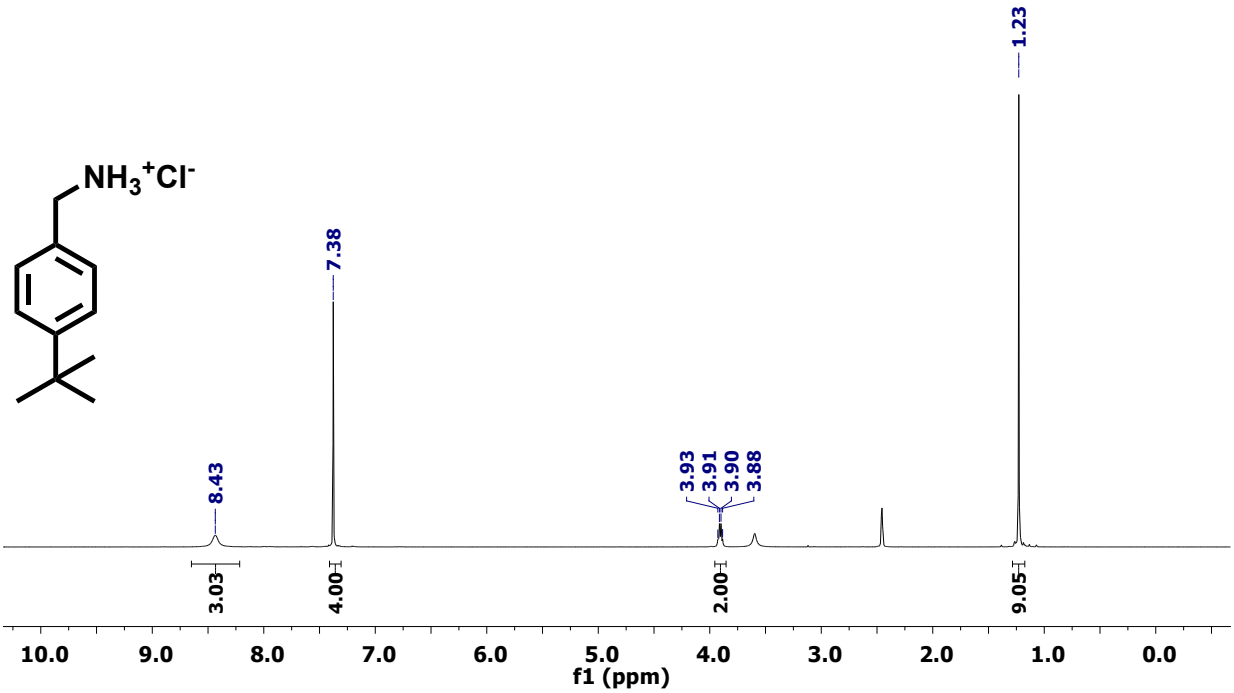


Figure S28.[1]H NMR spectrum (DMSO-d_6) of (4-(tert-butyl)phenyl)methanaminium chloride.

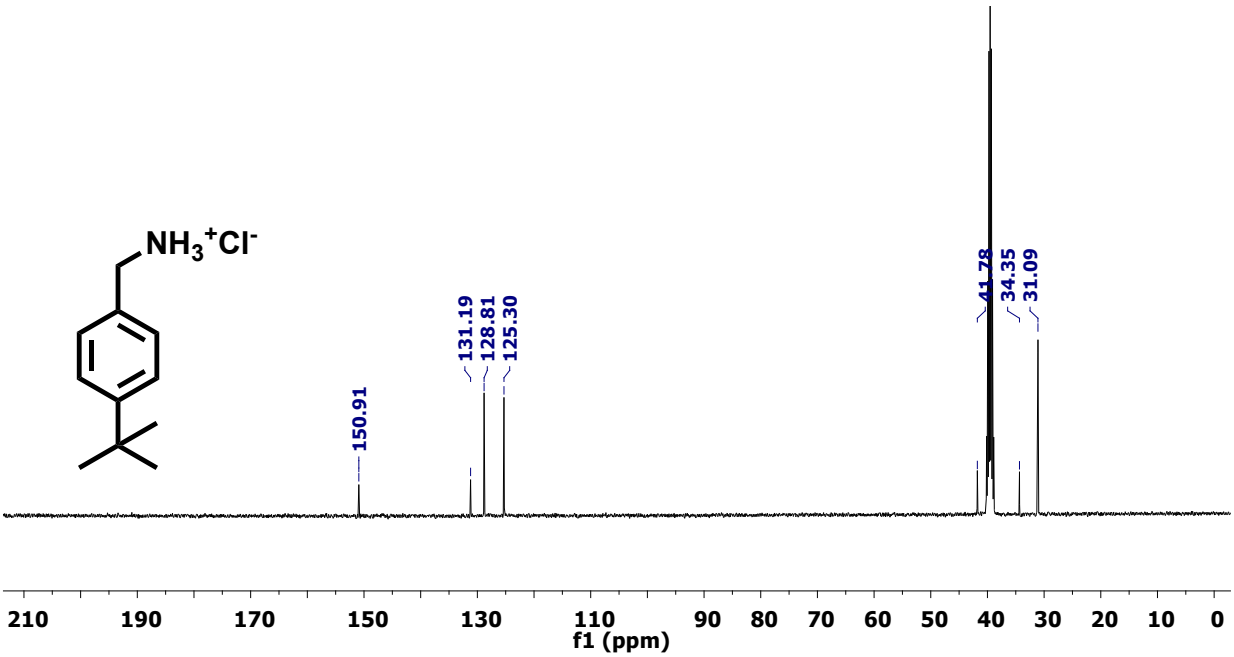


Figure S29. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of (4-(tert-butyl)phenyl)methanaminium chloride.

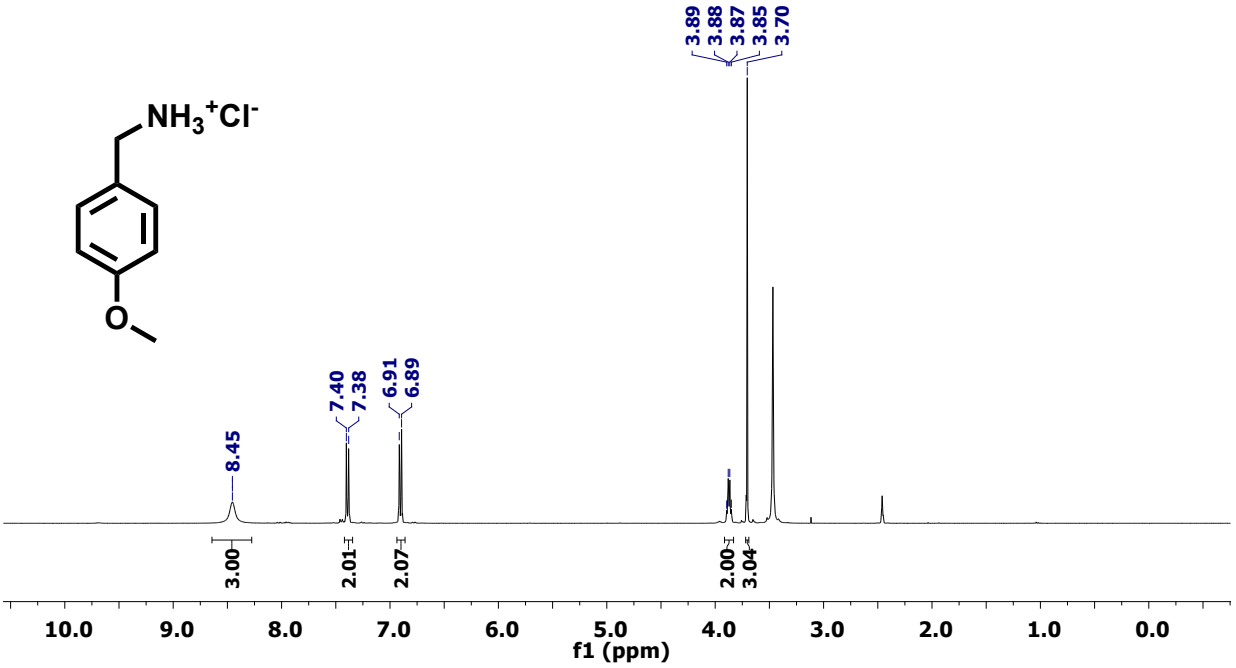


Figure S30. ^{1}H NMR spectrum (DMSO-d_6) of (4-methoxyphenyl)methanaminium chloride.

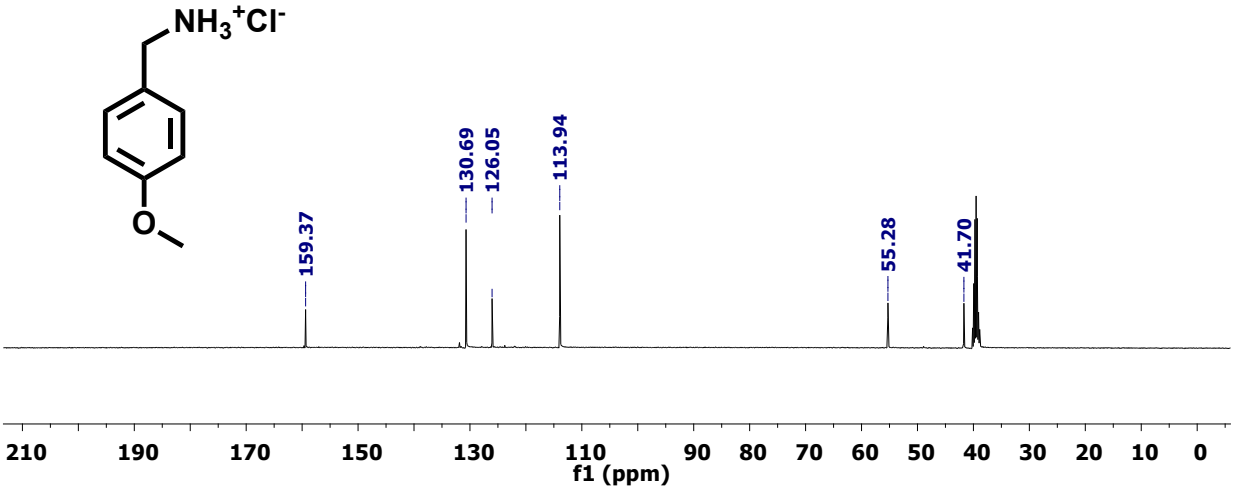


Figure S31. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (4-methoxyphenyl)methanaminium chloride.

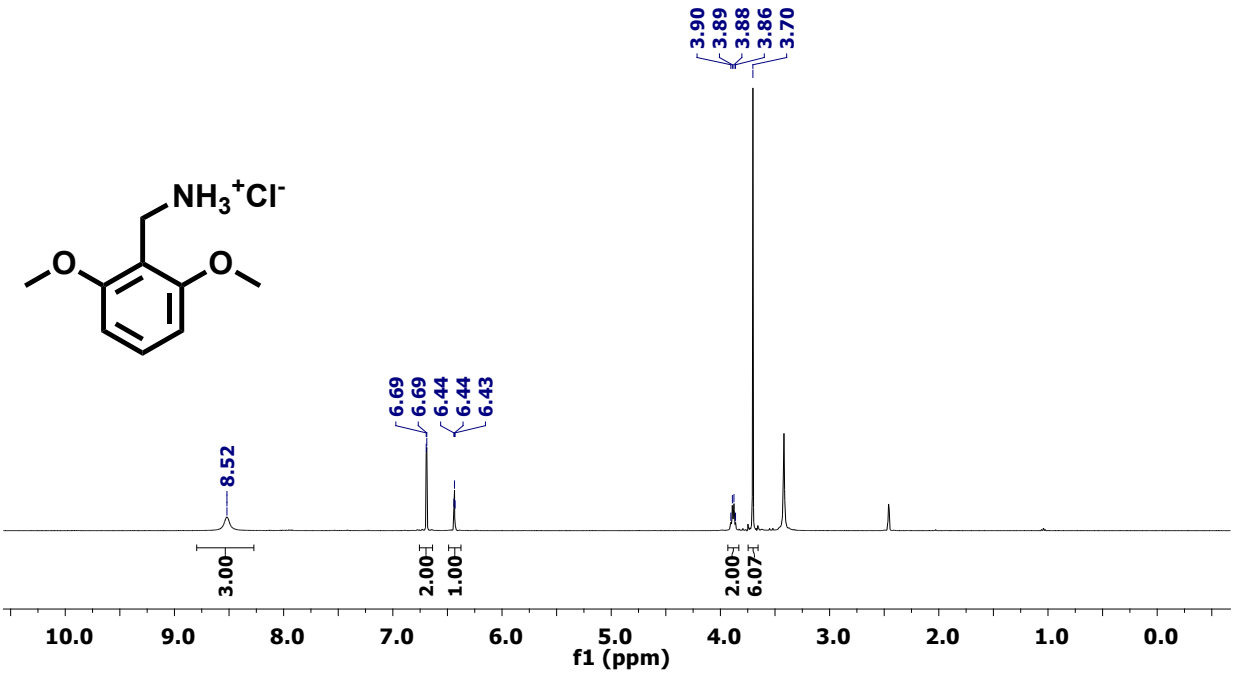


Figure S32. ^{1}H NMR spectrum (DMSO-d_6) of (2,6-dimethoxyphenyl)methanaminium chloride.

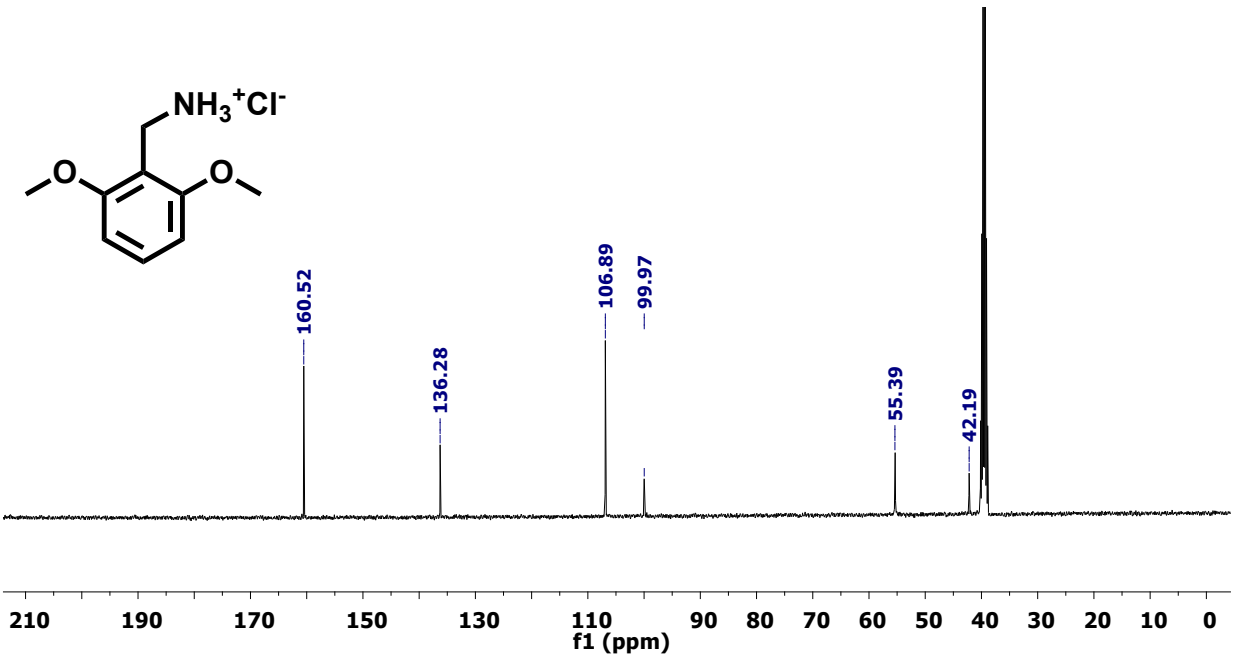


Figure S33. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (2,6-dimethoxyphenyl)methanaminium chloride.

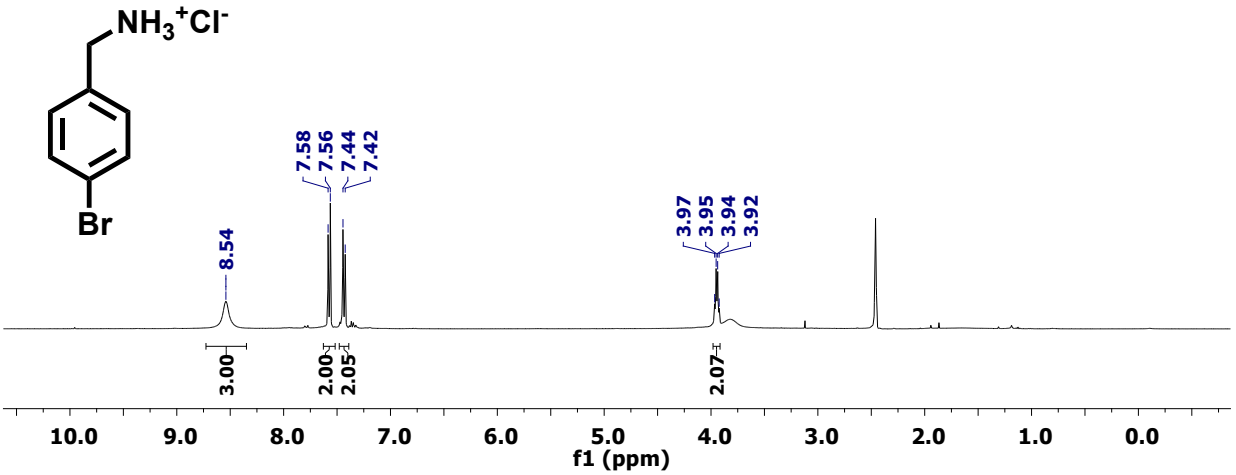


Figure S34. ^{1}H NMR spectrum (DMSO-d_6) of (4-bromophenyl)methanaminium chloride.

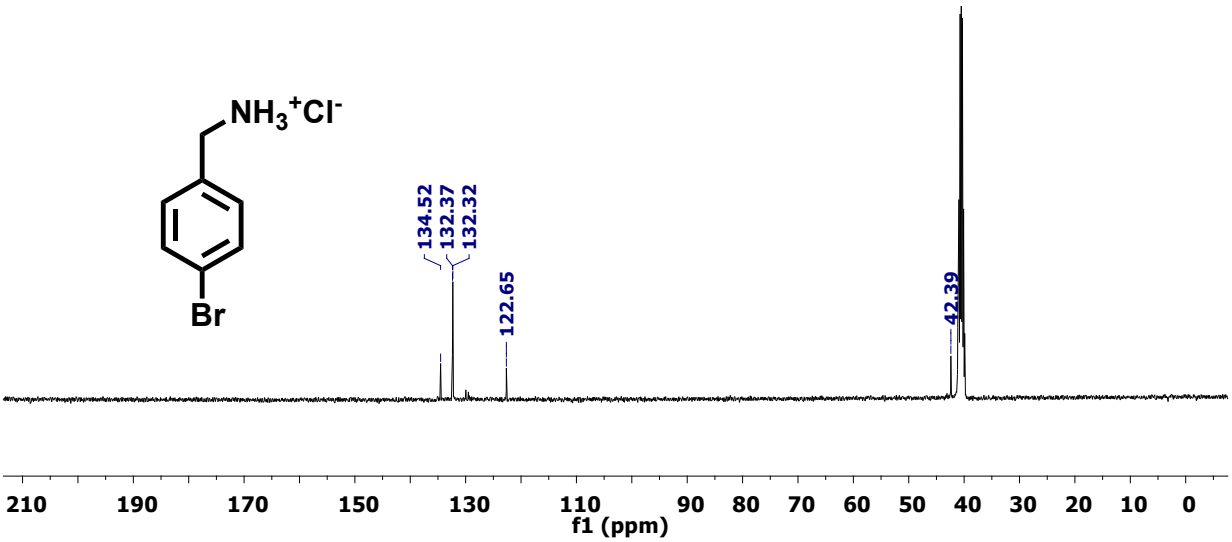


Figure S35. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (4-bromophenyl)methanaminium chloride.

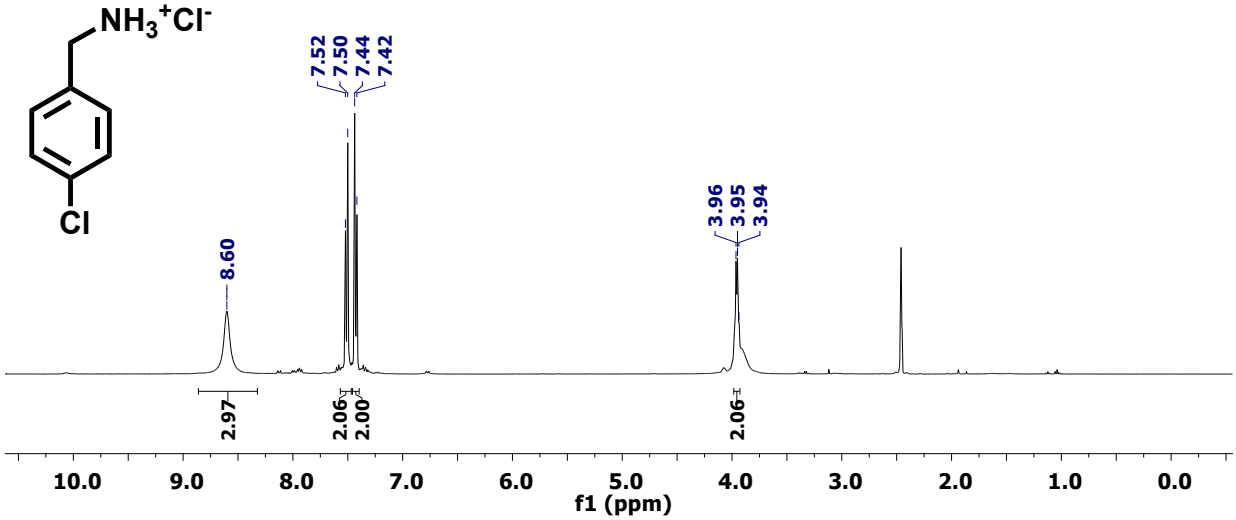


Figure S36. ^{1}H NMR spectrum (DMSO-d_6) of (4-chlorophenyl)methanaminium chloride.

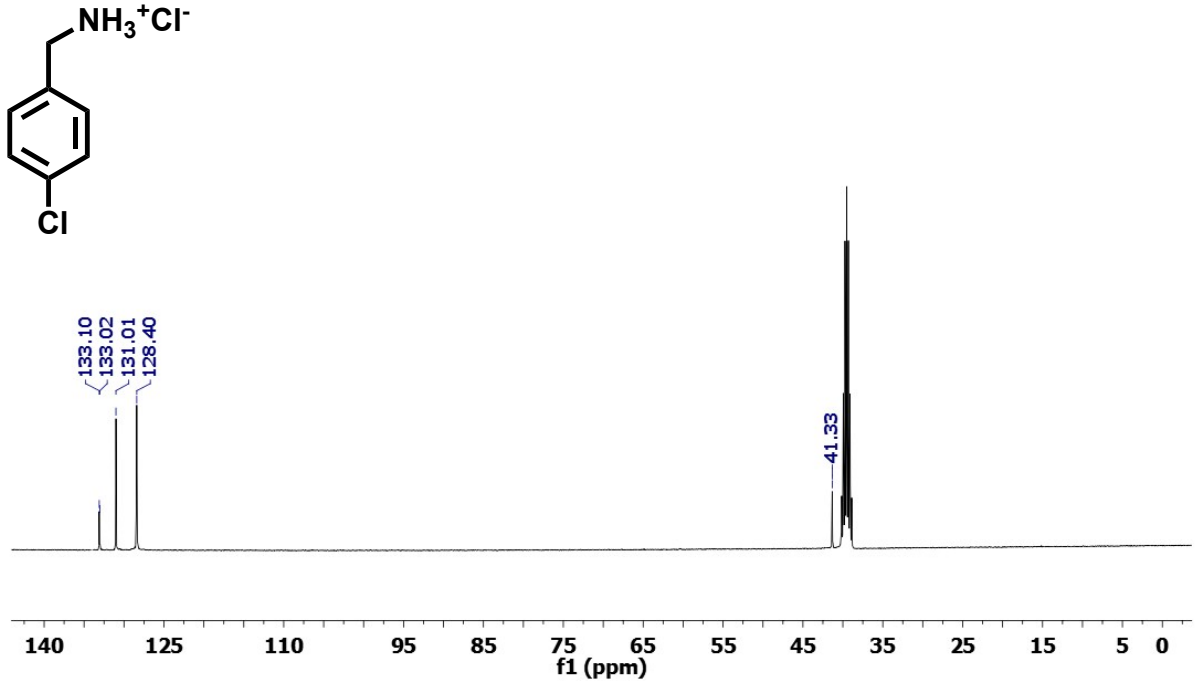


Figure S37. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (4-chlorophenyl)methanaminium chloride.

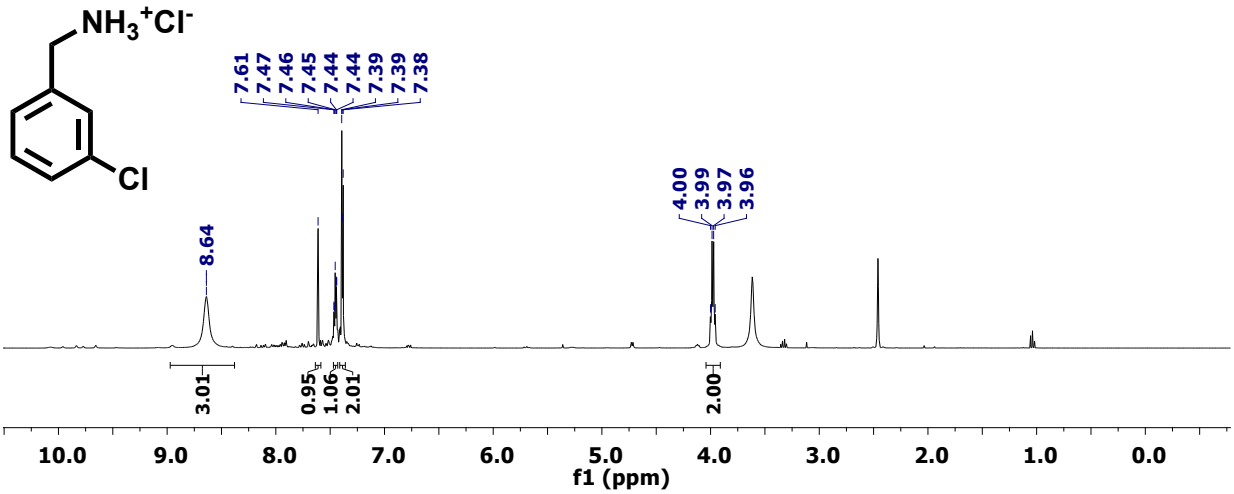


Figure S38. ^{1}H NMR spectrum (DMSO-d_6) of (3-chlorophenyl)methanaminium chloride.

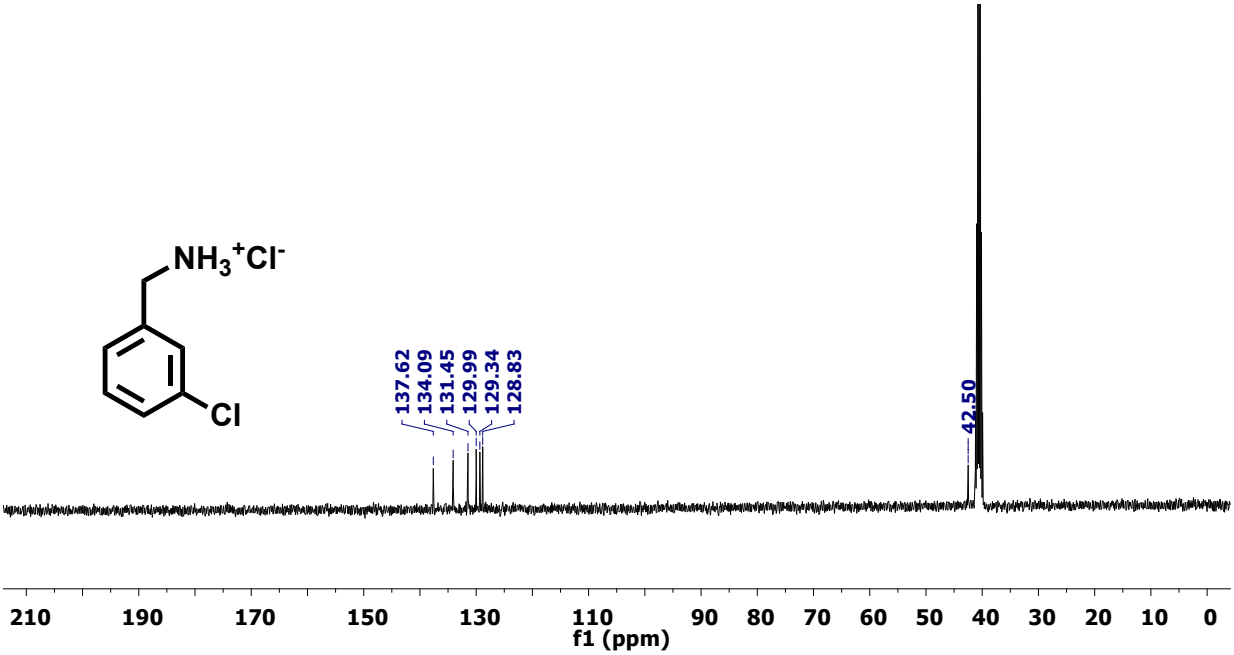


Figure S39. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (3-chlorophenyl)methanaminium chloride.

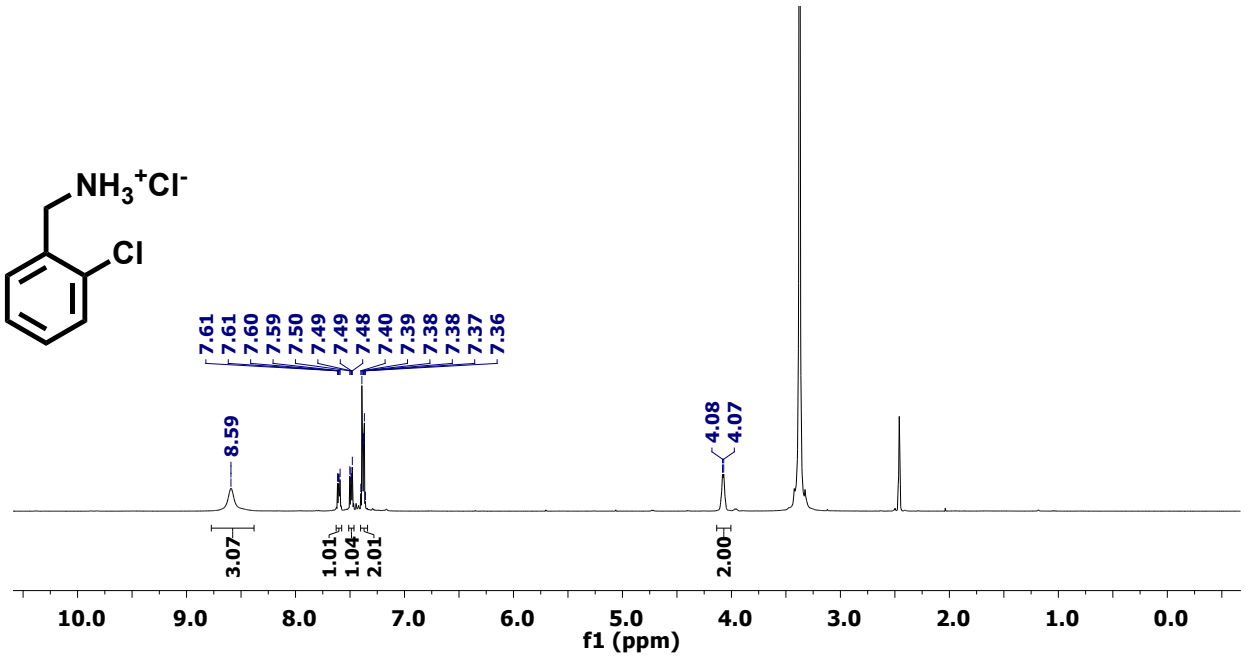


Figure S40. ^{1}H NMR spectrum (DMSO-d_6) of (2-chlorophenyl)methanaminium chloride.

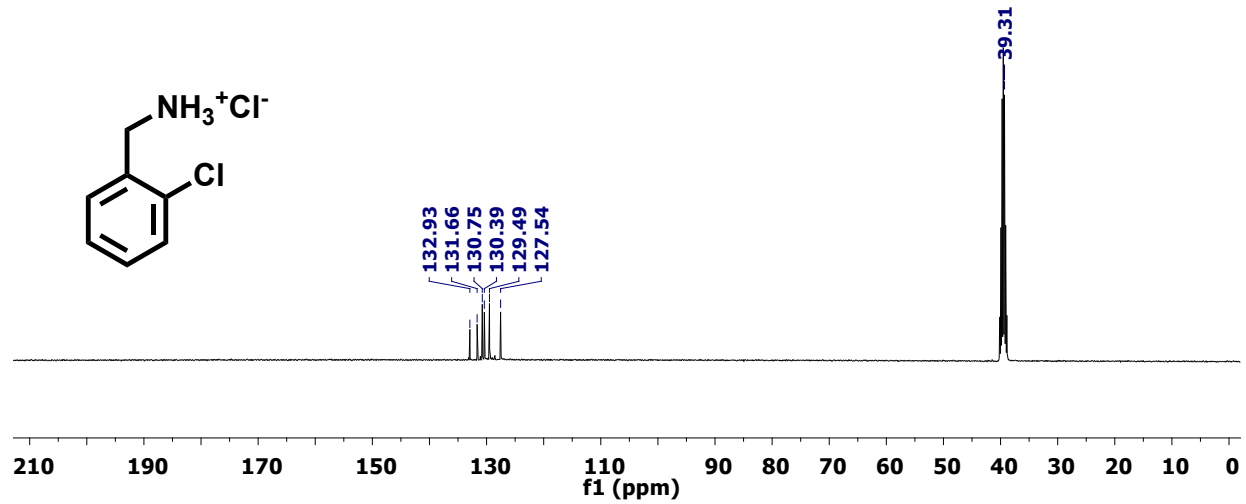


Figure S41. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (2-chlorophenyl)methanaminium chloride.

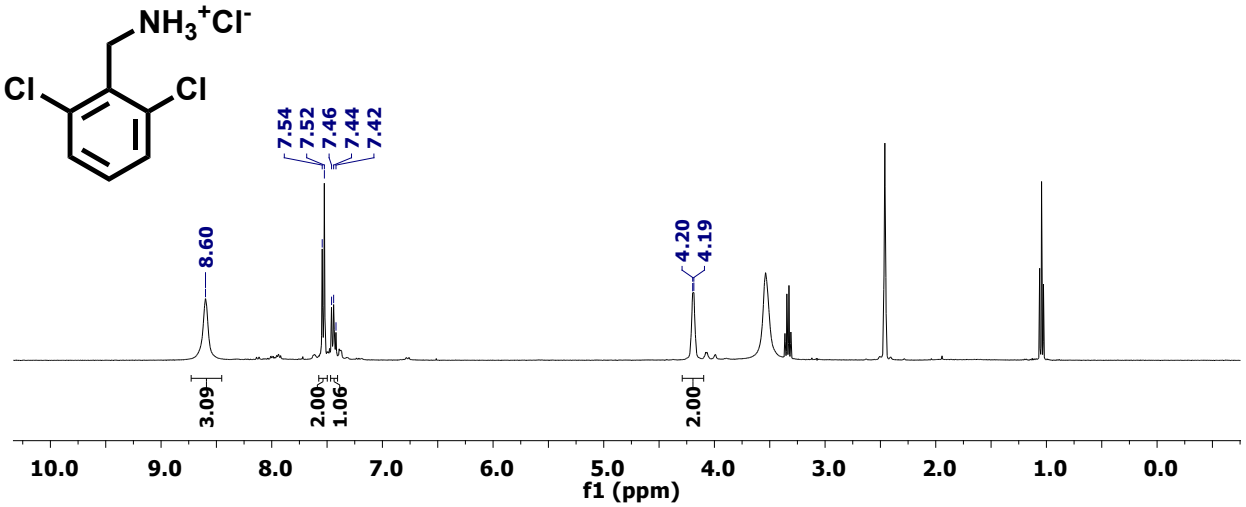


Figure S42. ^{1}H NMR spectrum (DMSO-d_6) of (2,6-dichlorophenyl)methanaminium chloride.

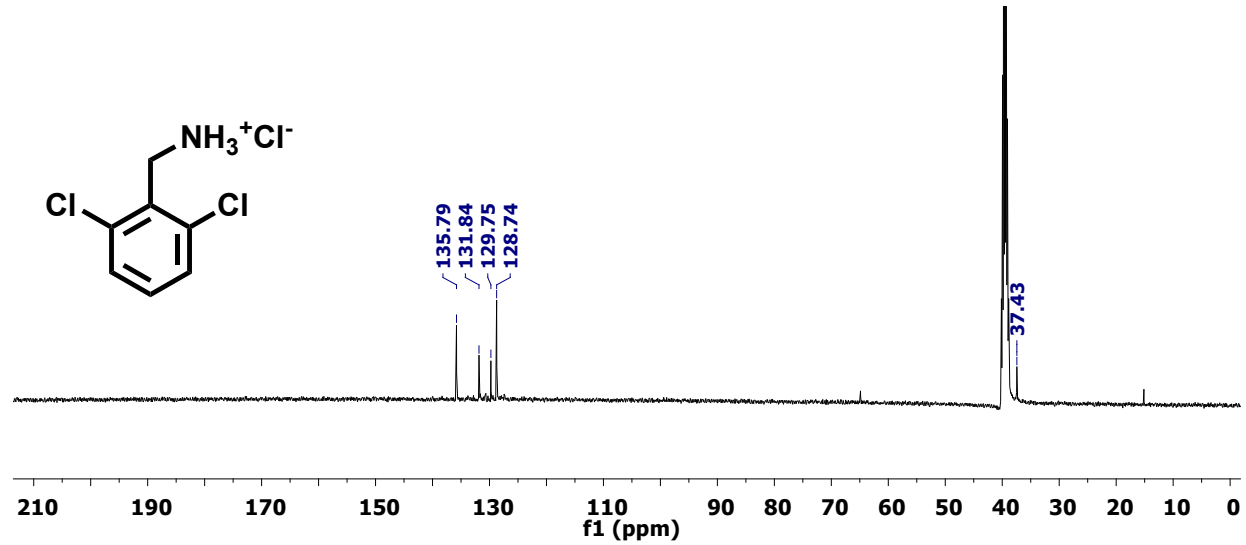


Figure S43. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (2,6-dichlorophenyl)methanaminium chloride.

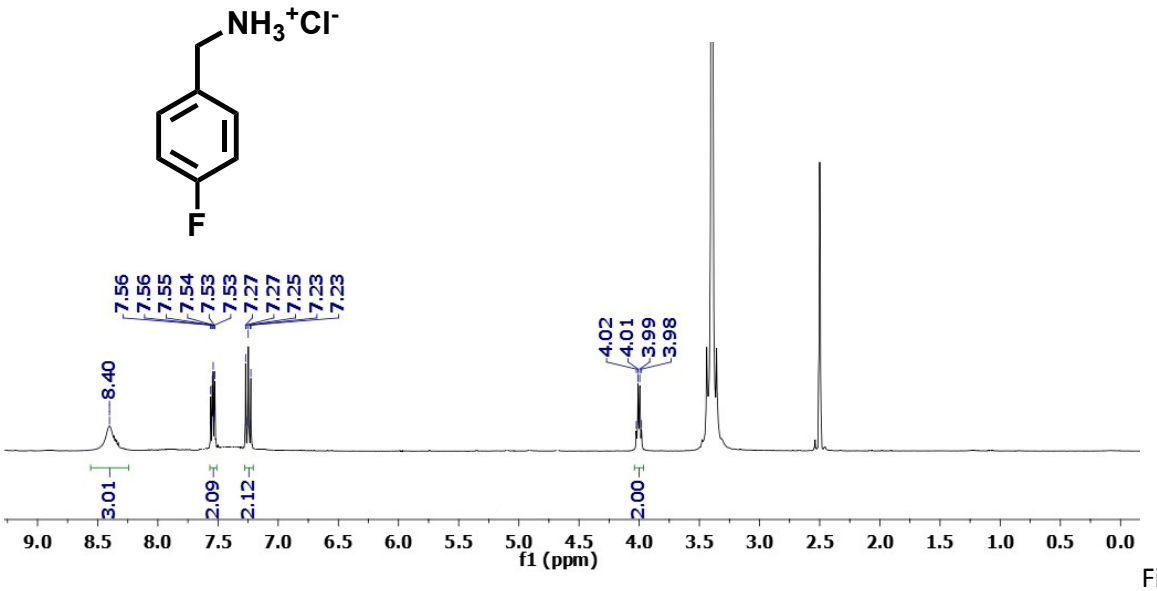


Figure S44. ^{1}H NMR spectrum (DMSO-d_6) of (4-fluorophenyl)methanaminium chloride.

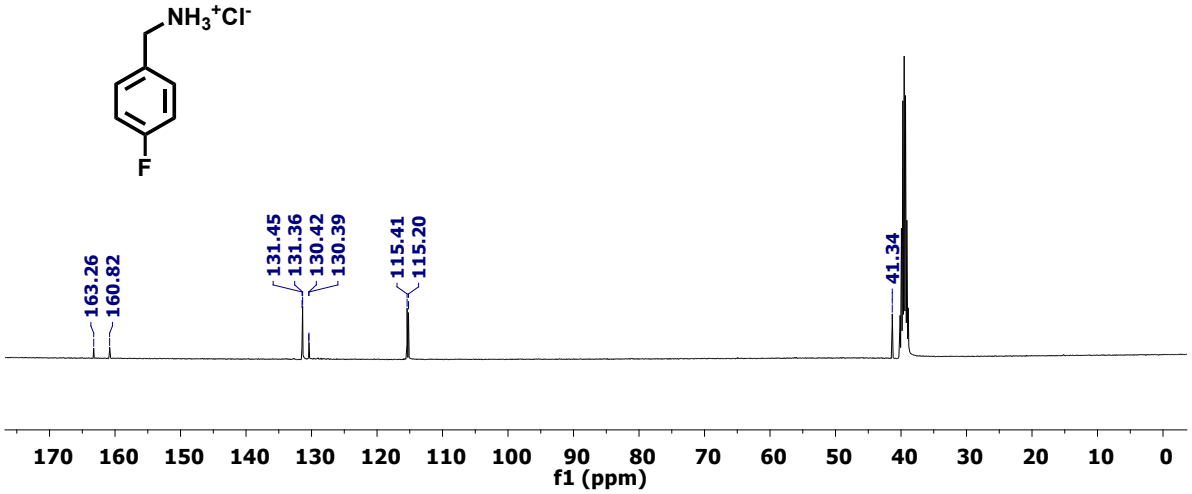


Figure S45. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (4-fluorophenyl)methanaminium chloride.

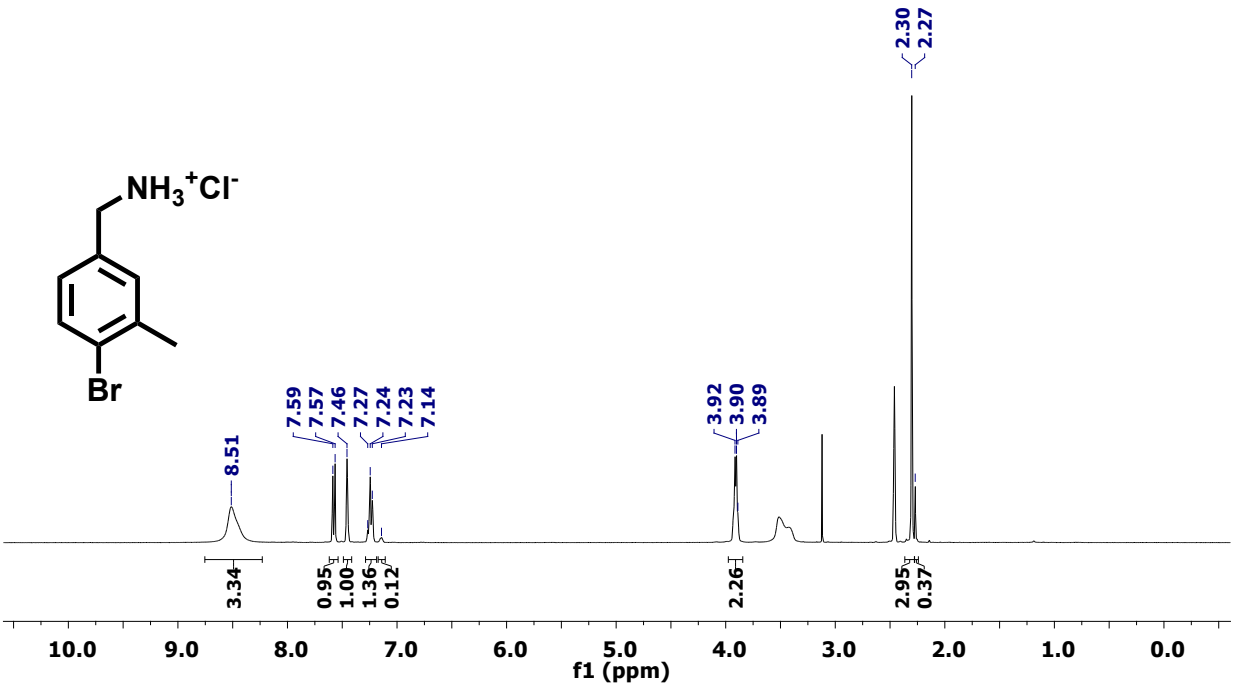


Figure S46. ^{1}H NMR spectrum (DMSO-d_6) of (4-bromo-3-methylphenyl)methanaminium chloride.

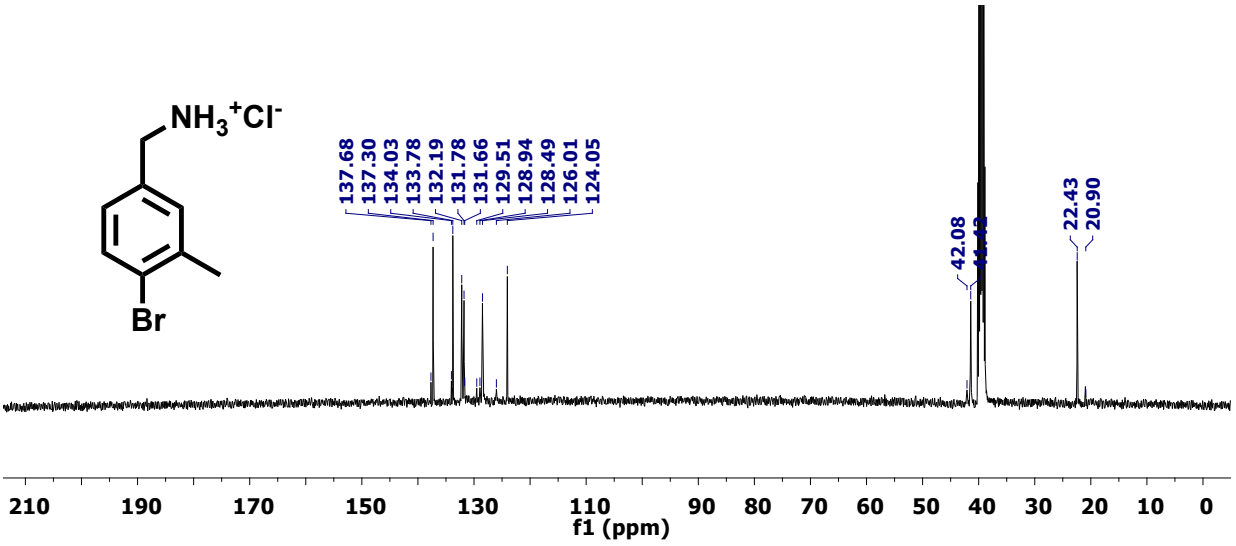


Figure S47. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (4-bromo-3-methylphenyl)methanaminium chloride.

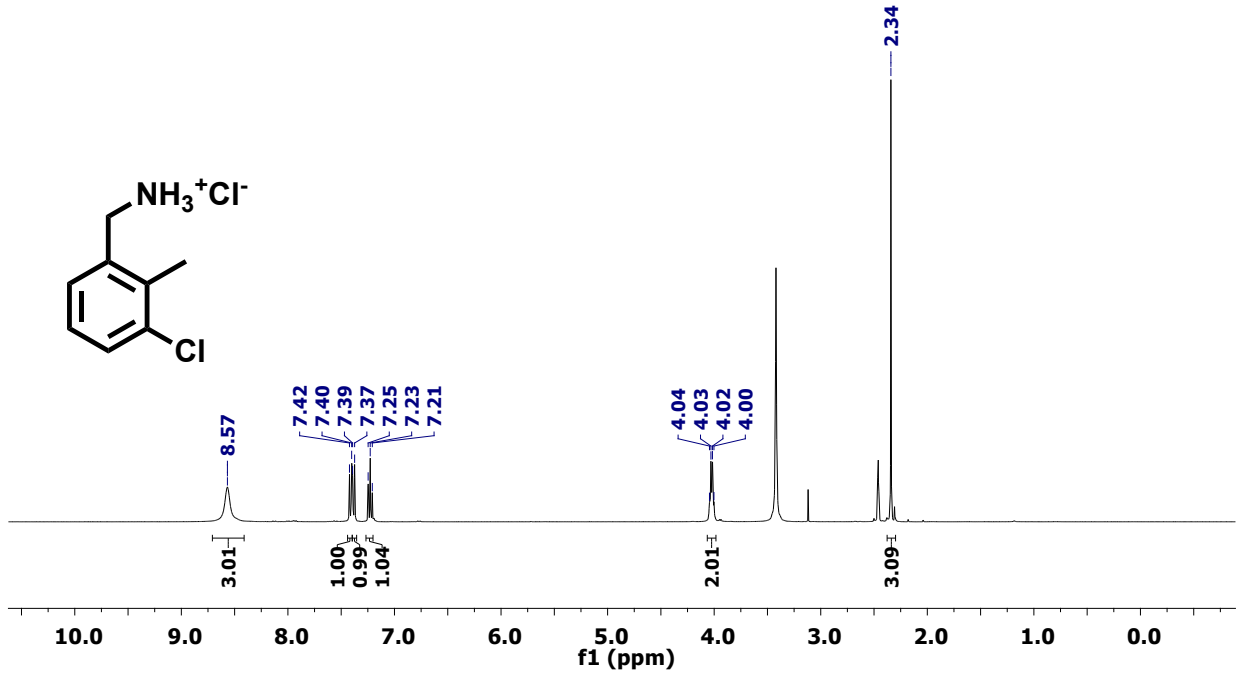


Figure S48. ^{1}H NMR spectrum (DMSO-d_6) of (3-chloro-2-methylphenyl)methanaminium chloride.

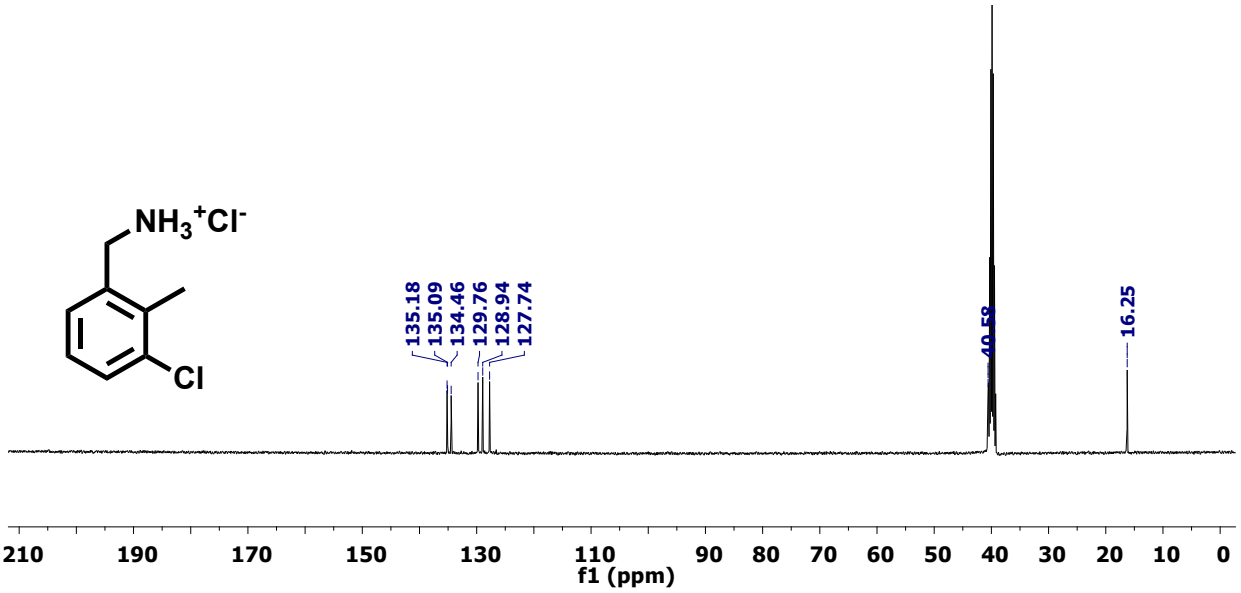


Figure S49. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (3-chloro-2-methylphenyl)methanaminium chloride.

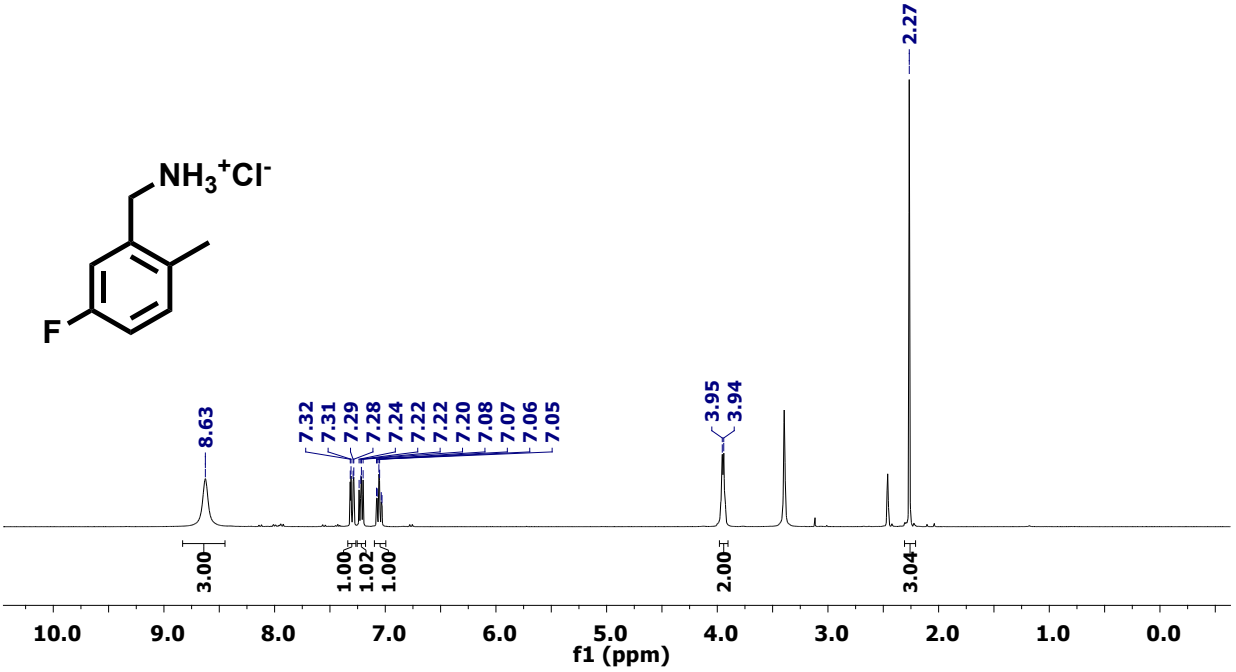


Figure S50. ^{1}H NMR spectrum (DMSO-d_6) of (5-fluoro-2-methylphenyl)methanaminium chloride.

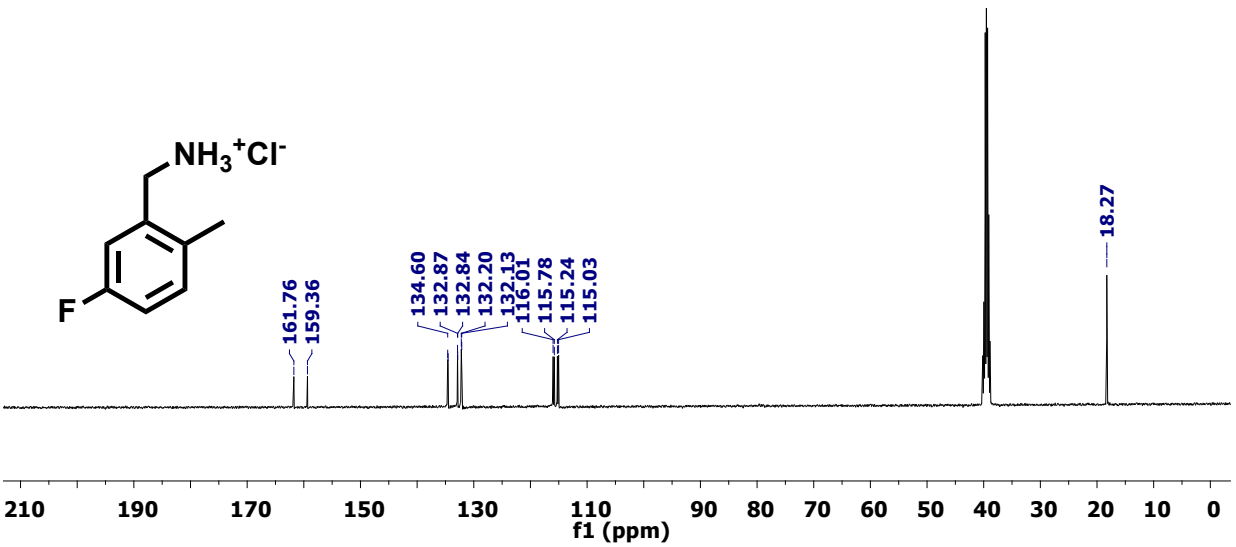


Figure S51. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of (5-fluoro-2-methylphenyl)methanaminium chloride.

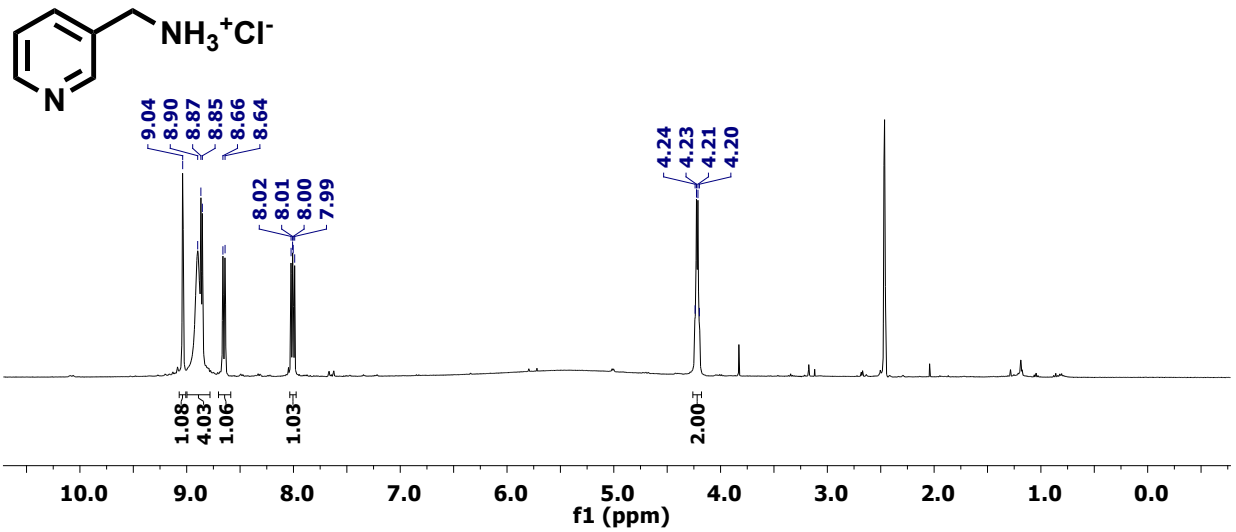


Figure S52. ^{1}H NMR spectrum (DMSO-d_6) of pyridin-3-ylmethanaminium chloride.

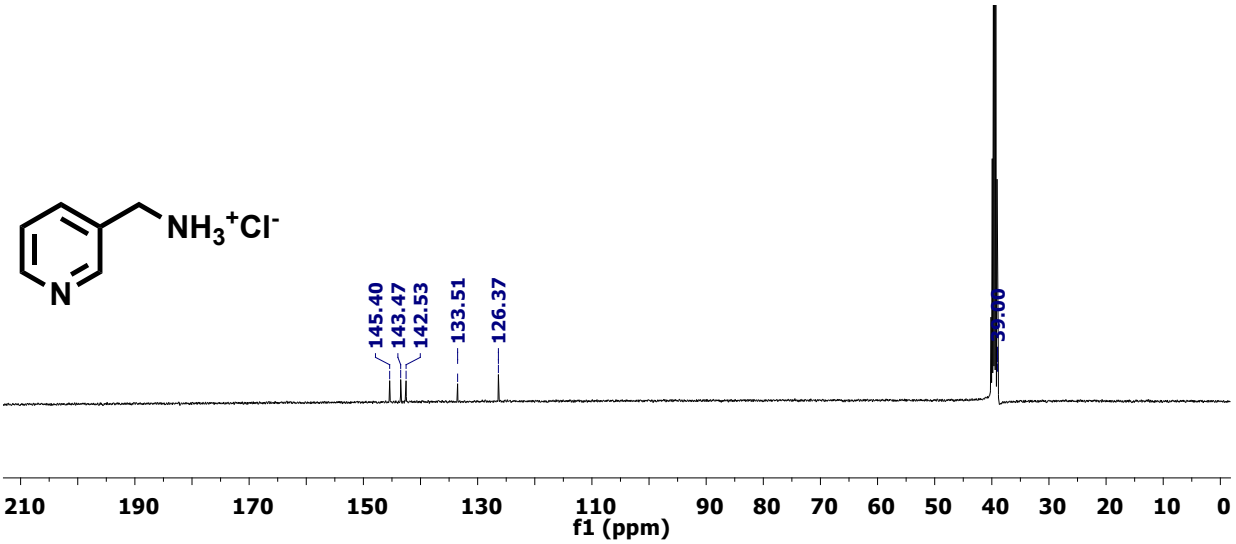


Figure S53. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of pyridin-3-ylmethanaminium chloride.

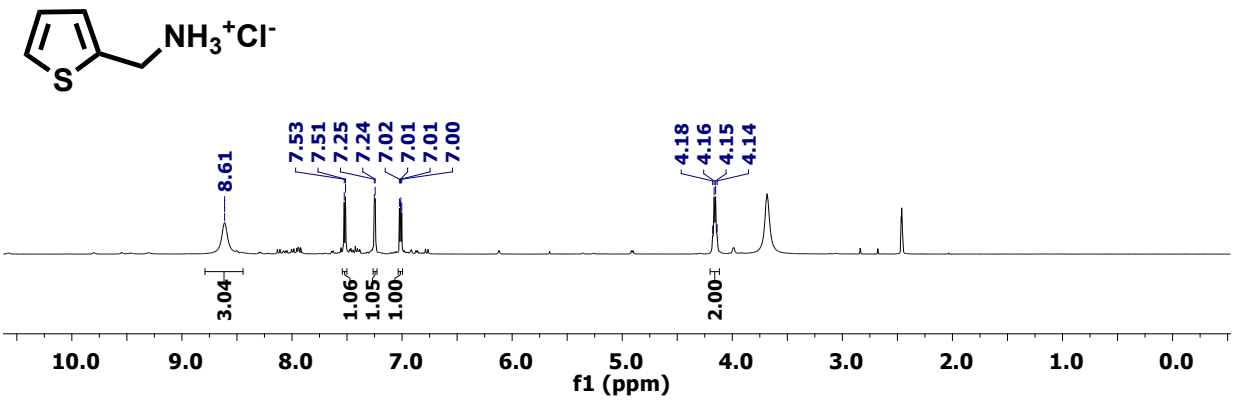


Figure S54. ^{1}H NMR spectrum (DMSO-d_6) of thiophen-2-ylmethanaminium chloride.

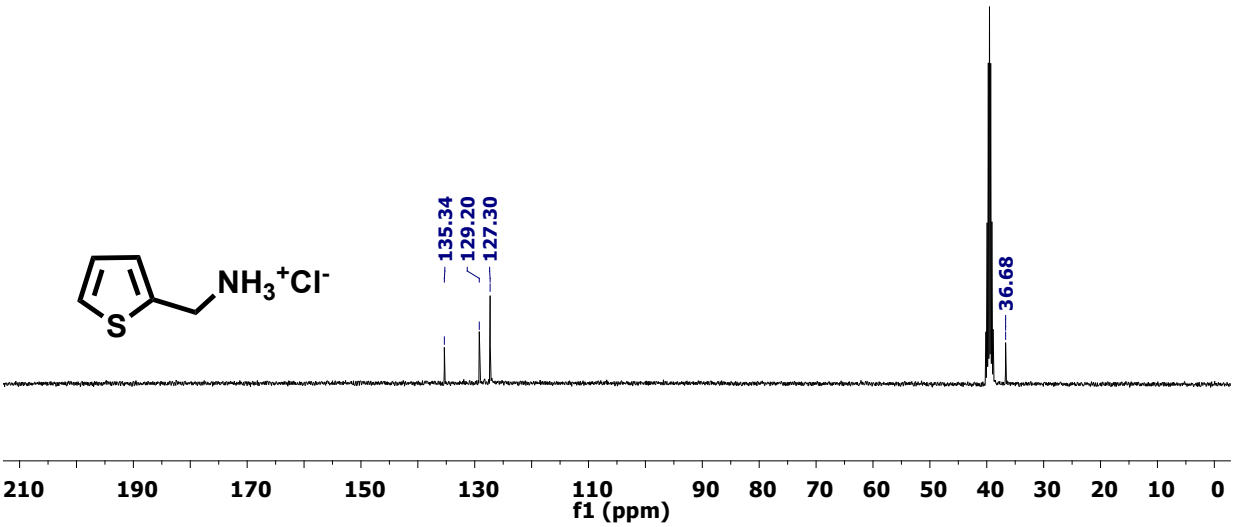


Figure S55. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of thiophen-2-ylmethanaminium chloride.

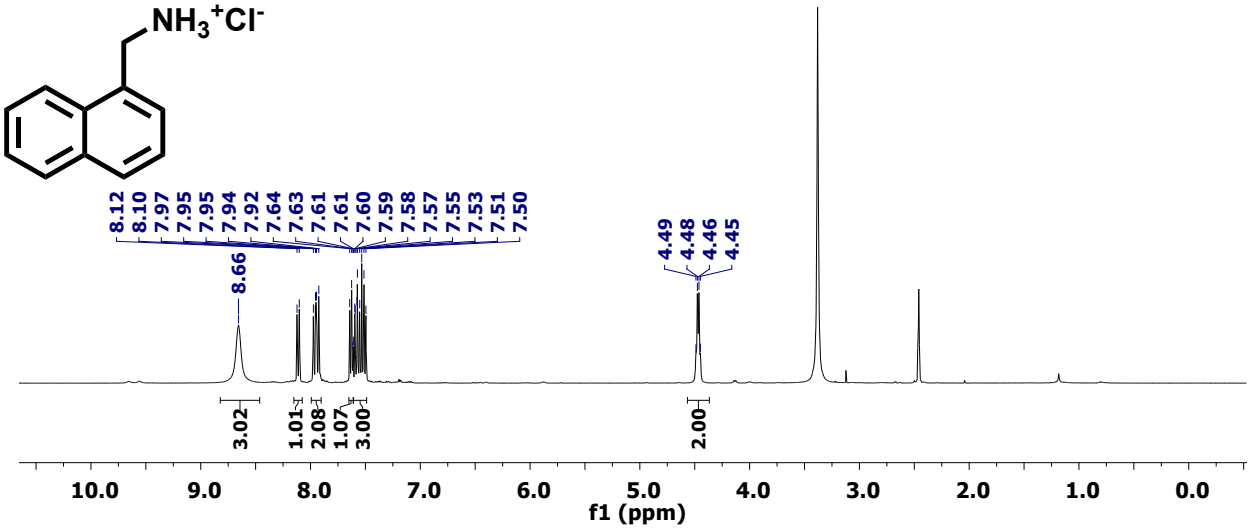


Figure S56.[1]H NMR spectrum (DMSO-d_6) of naphthalen-1-ylmethanaminium chloride.

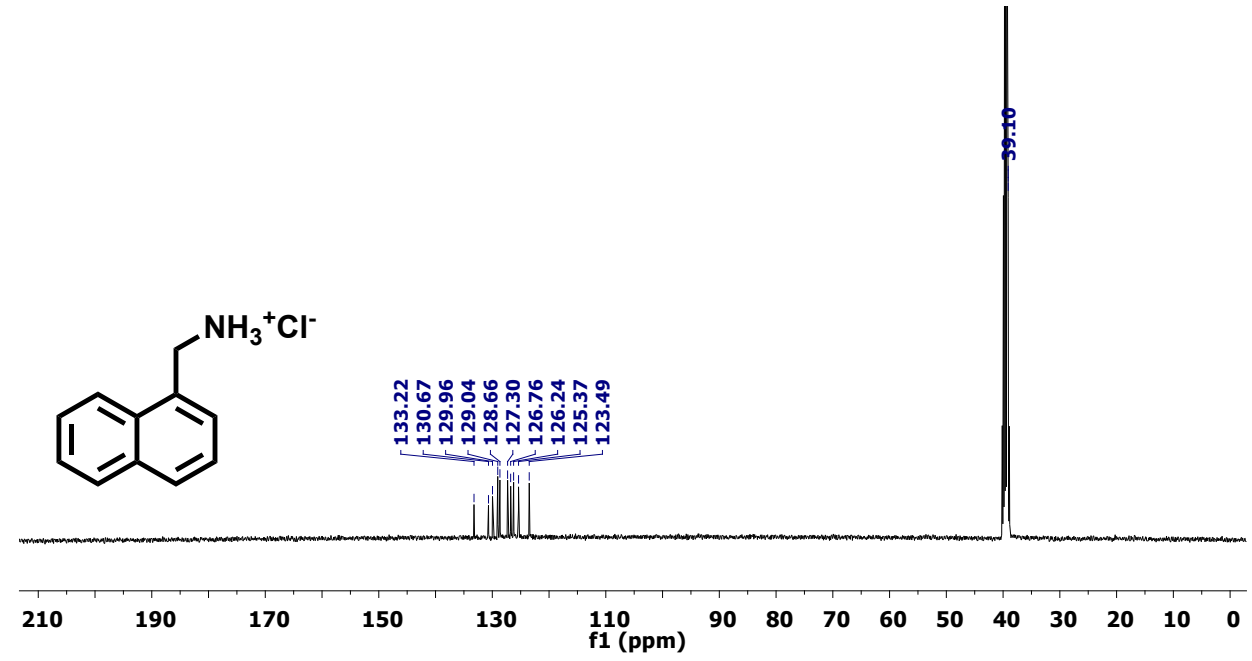


Figure S57. $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of naphthalen-1-ylmethanaminium chloride.

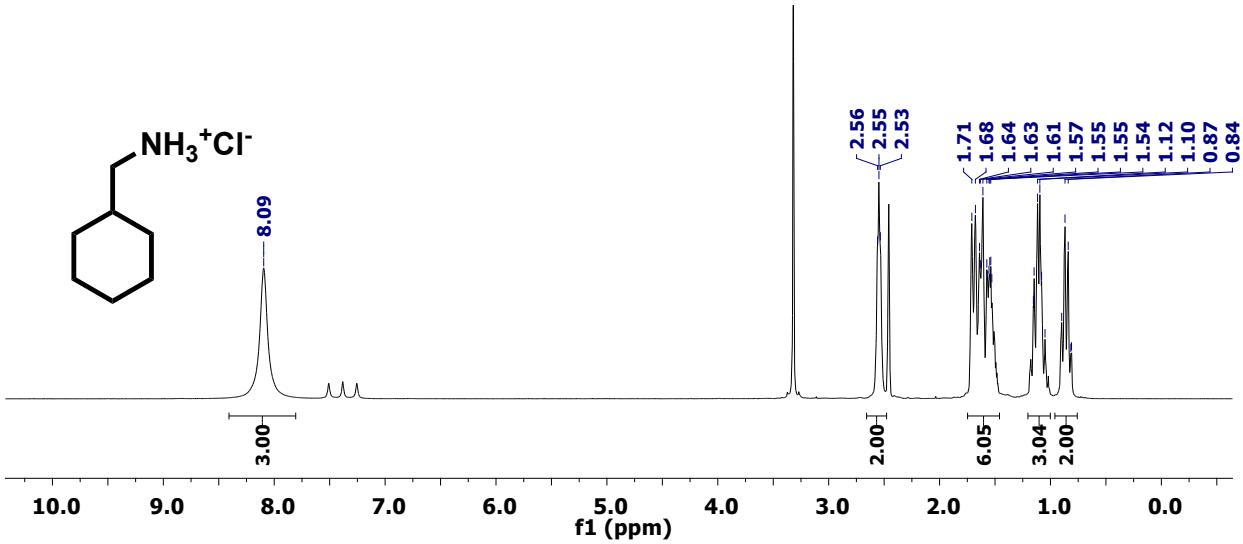


Figure S58. ^{1}H NMR spectrum (DMSO-d_6) of cyclohexylmethanaminium chloride.

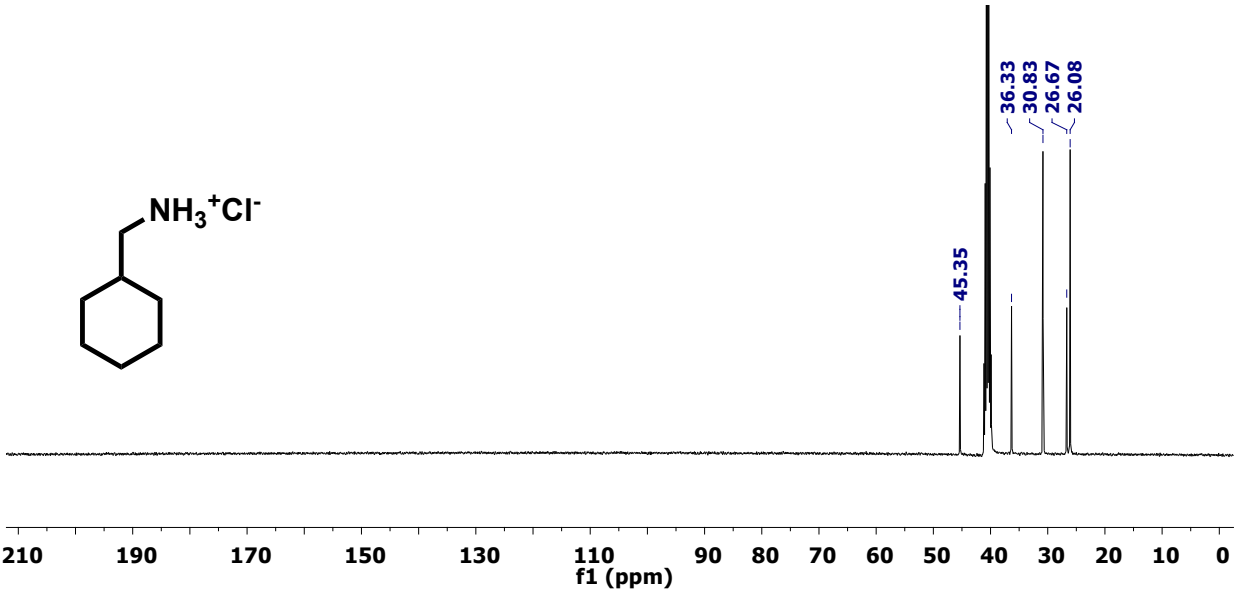


Figure S59. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of cyclohexylmethanaminium chloride.

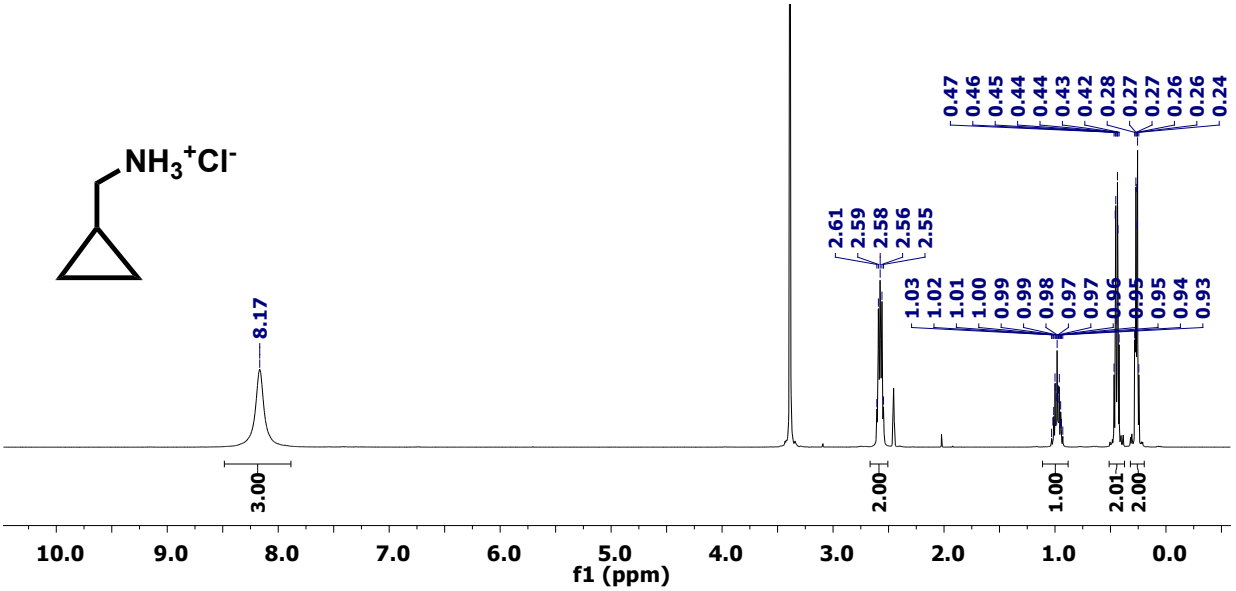


Figure S60. ^{1}H NMR spectrum (DMSO-d_6) of cyclopropylmethanaminium chloride.

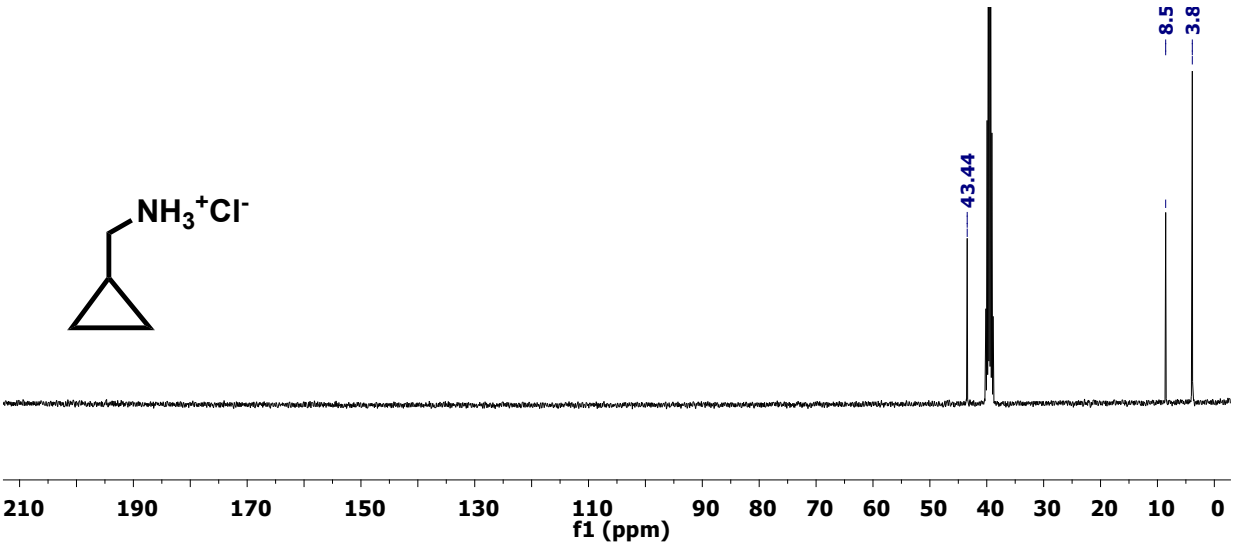


Figure S61. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of cyclopropylmethanaminium chloride.

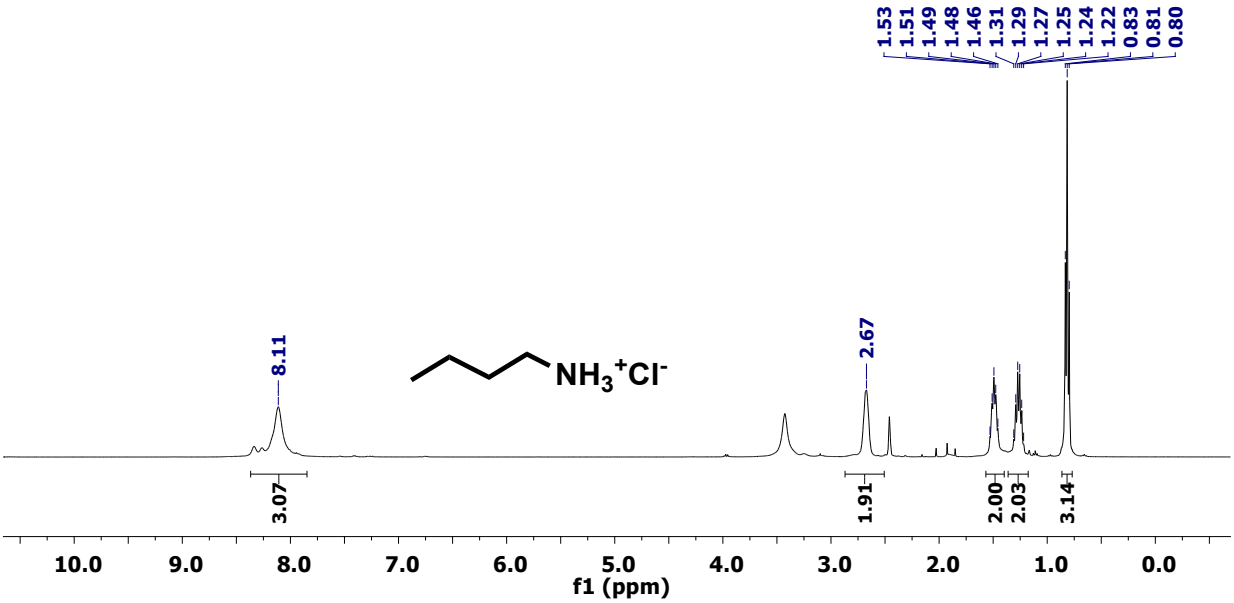


Figure S62. ^{1}H NMR spectrum (DMSO-d_6) of butan-1-aminium chloride.

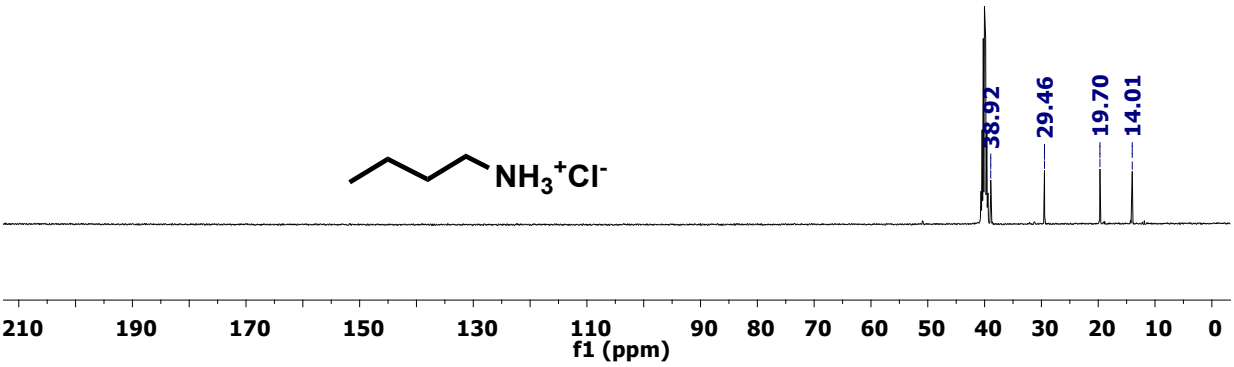


Figure S63. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of butan-1-aminium chloride.

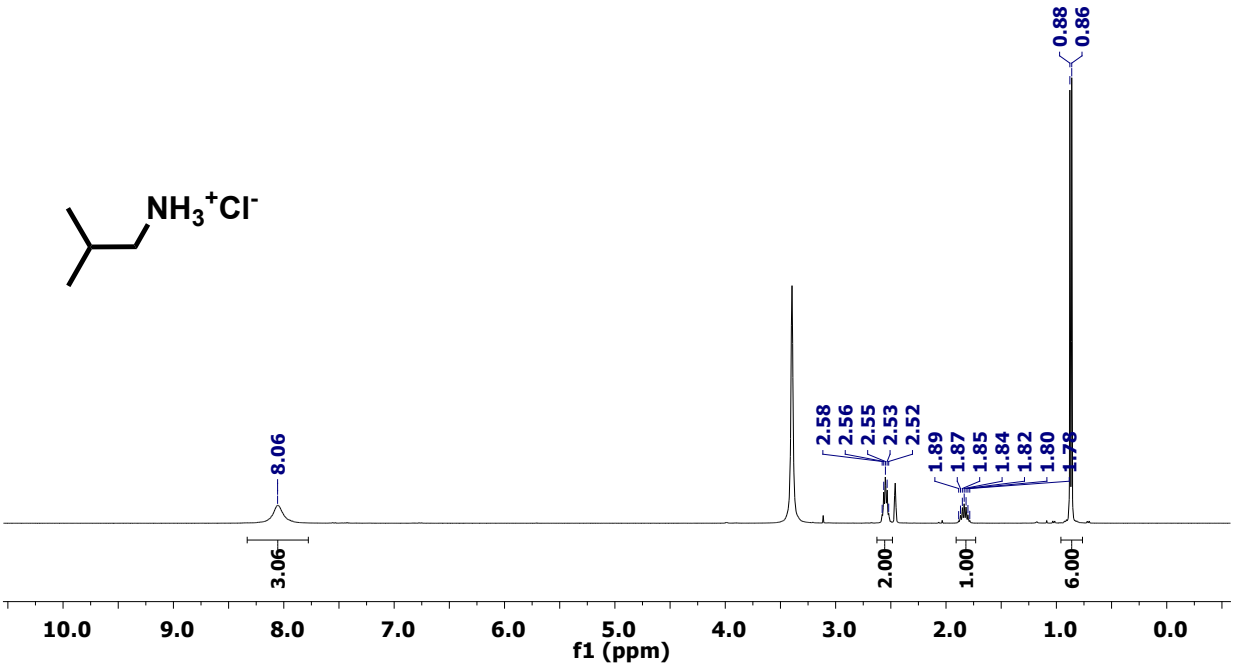


Figure S64. ^{1}H NMR spectrum (DMSO-d_6) of 2-methylpropan-1-aminium chloride.

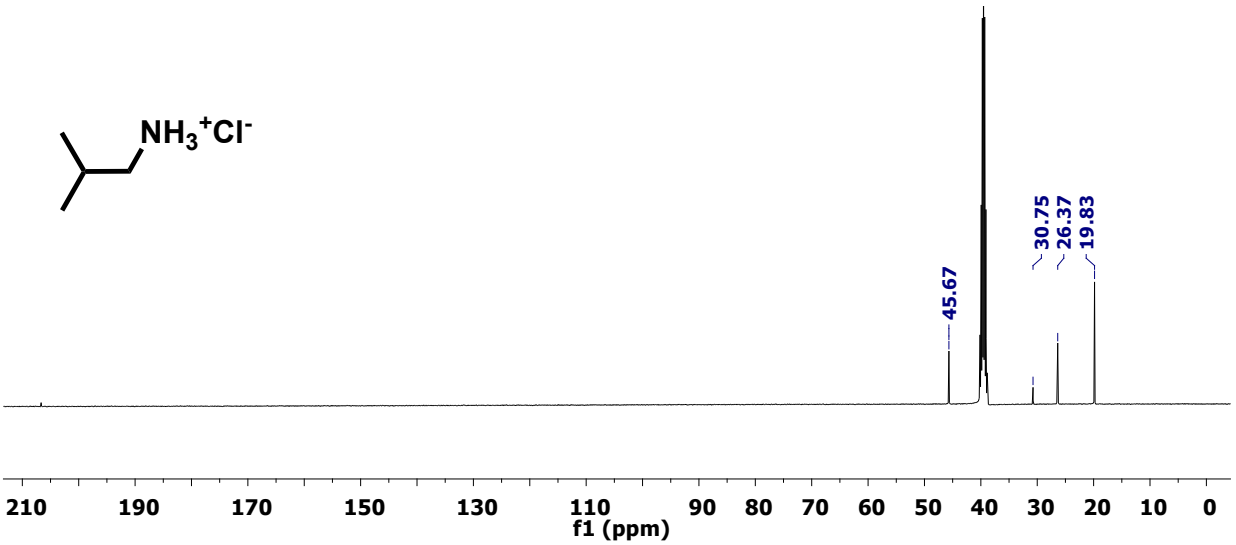


Figure S65. ^{13}C{^{1}H} NMR spectrum (DMSO-d_6) of 2-methylpropan-1-aminium chloride.

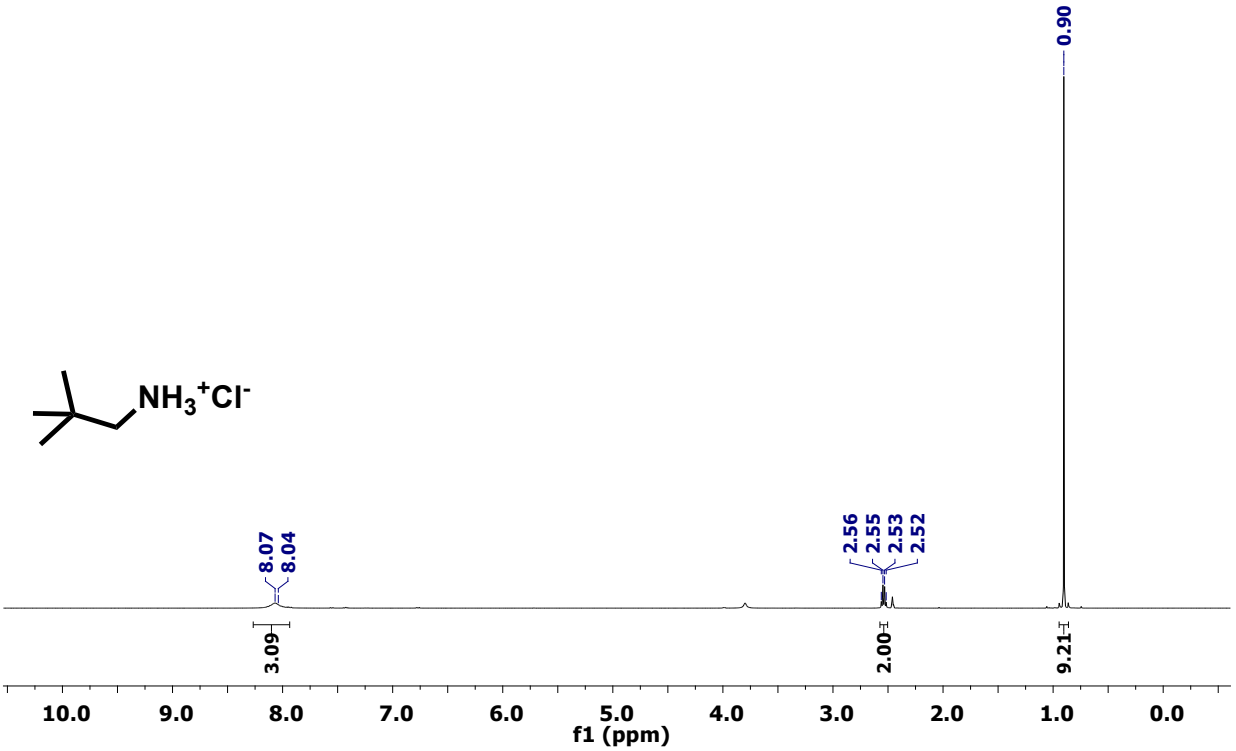


Figure S66. ^{1}H NMR spectrum (DMSO-d_6) of 2,2-dimethylpropan-1-aminium chloride.

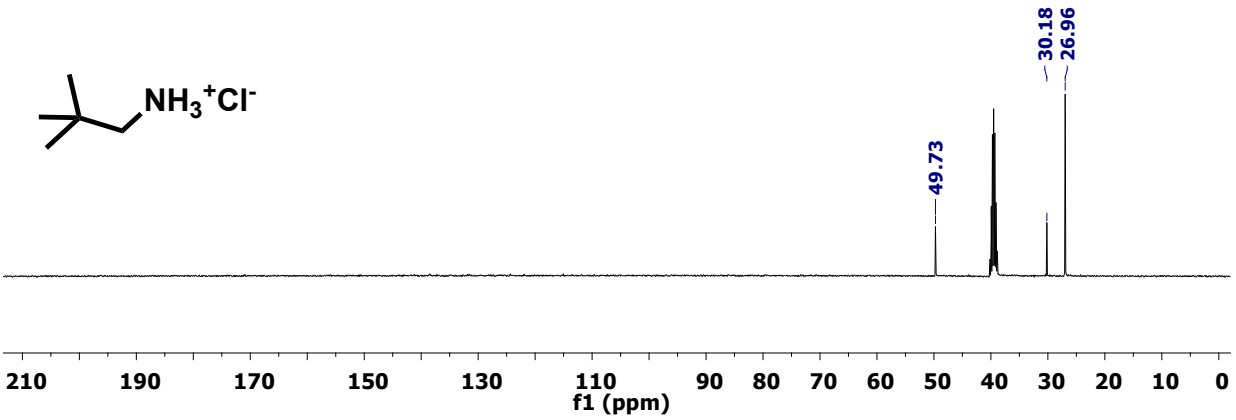


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) of 2,2-dimethylpropan-1-aminium chloride.

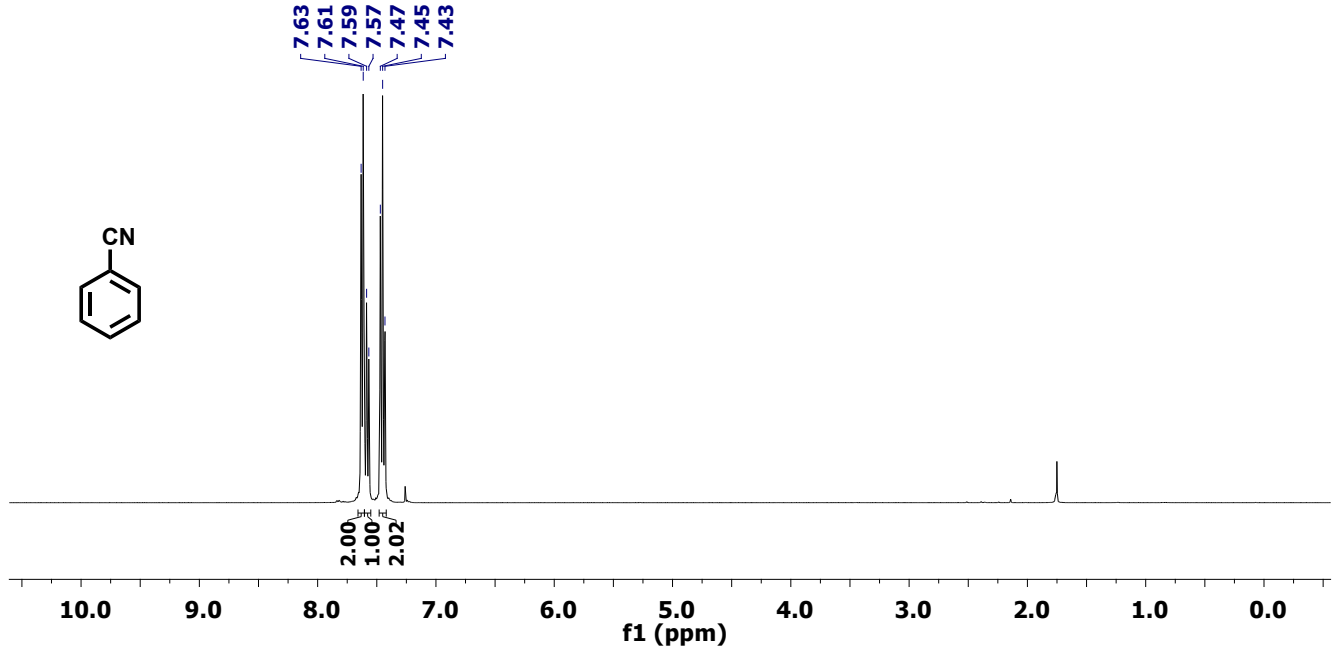


Figure S68. ^{1}H NMR spectrum ($CDCl_3$) of benzonitrile.

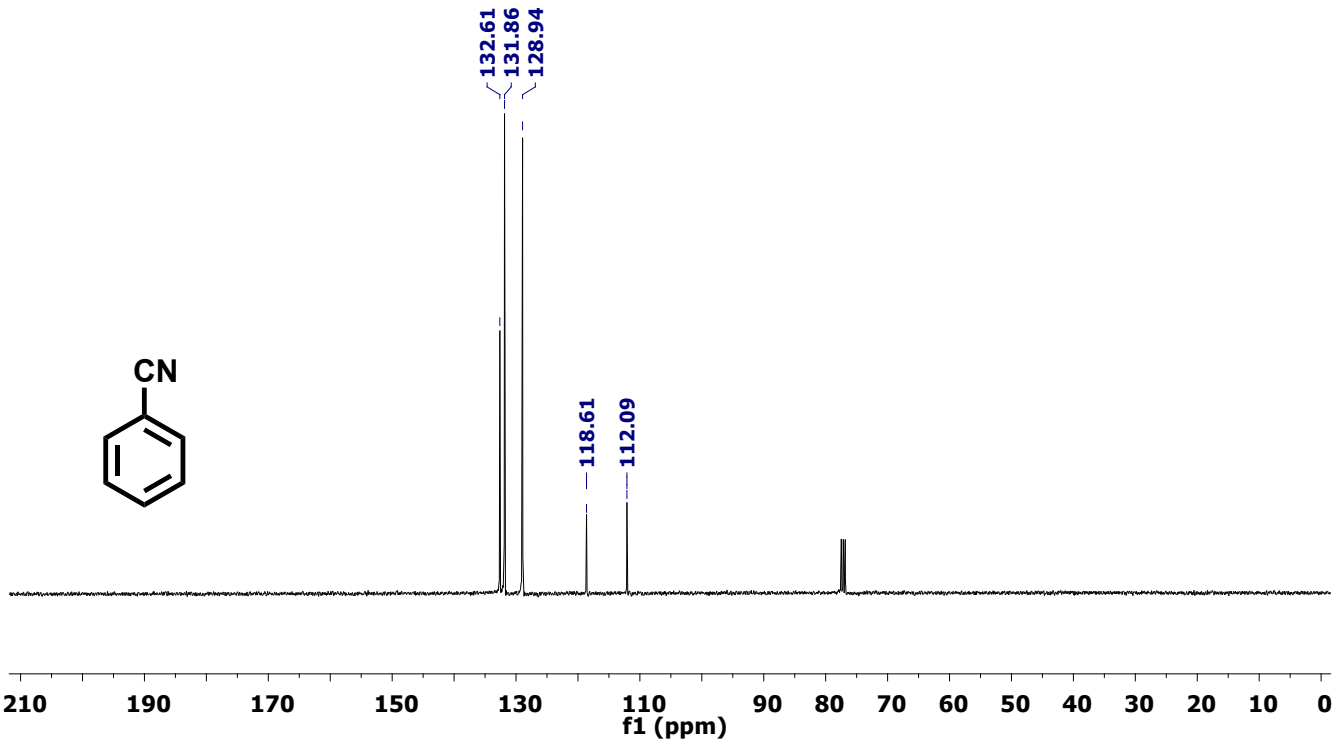


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum (spectrum ($CDCl_3$) of benzonitrile.

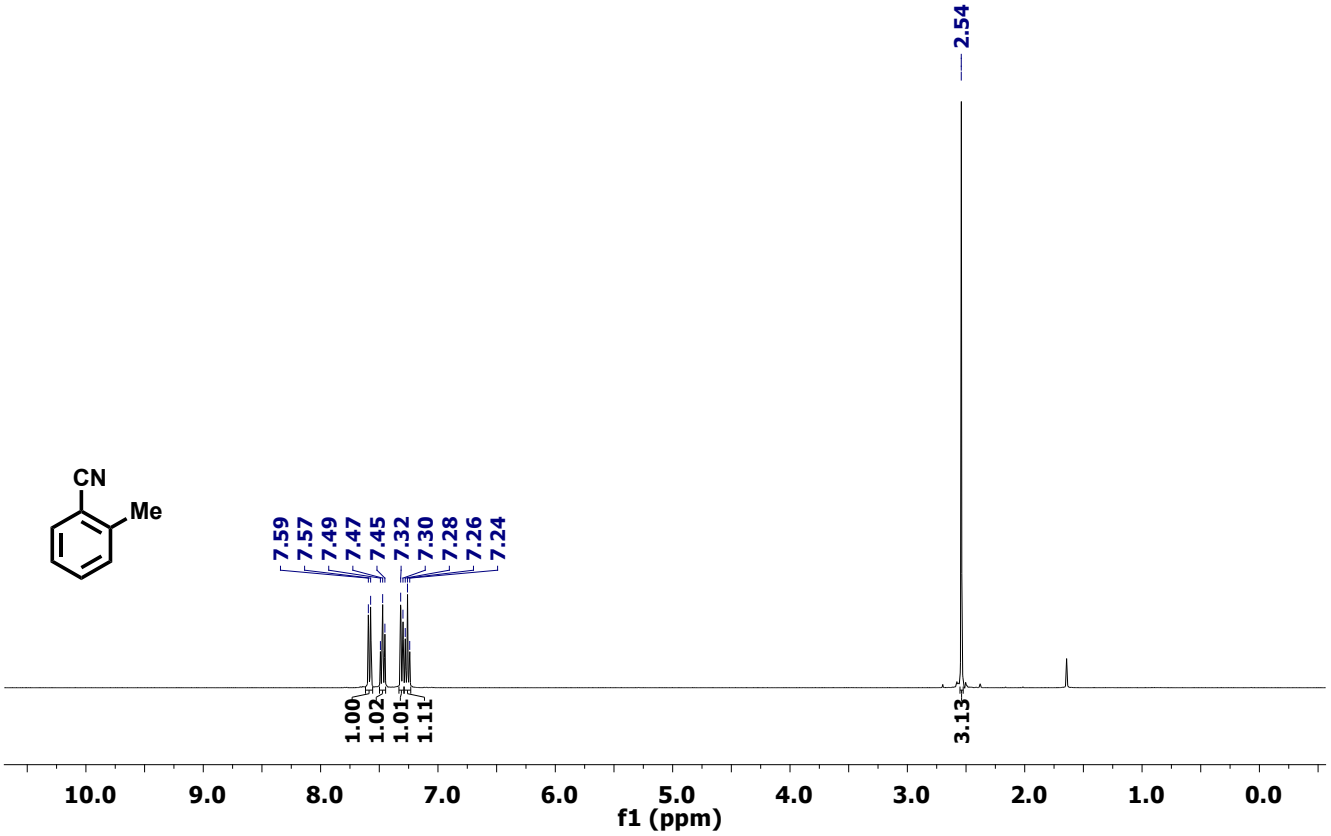


Figure S70.^{1}H NMR spectrum ($CDCl_3$) of 2-methylbenzonitrile.

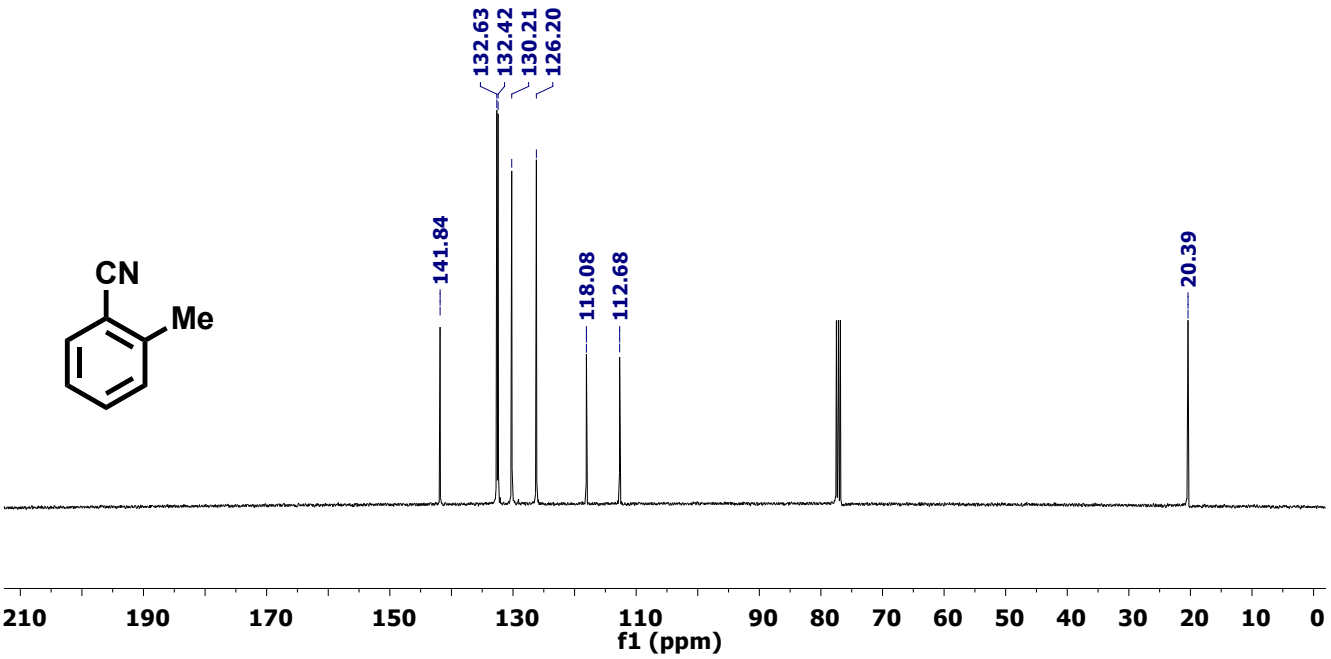


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum (spectrum ($CDCl_3$) of 2-methylbenzonitrile.

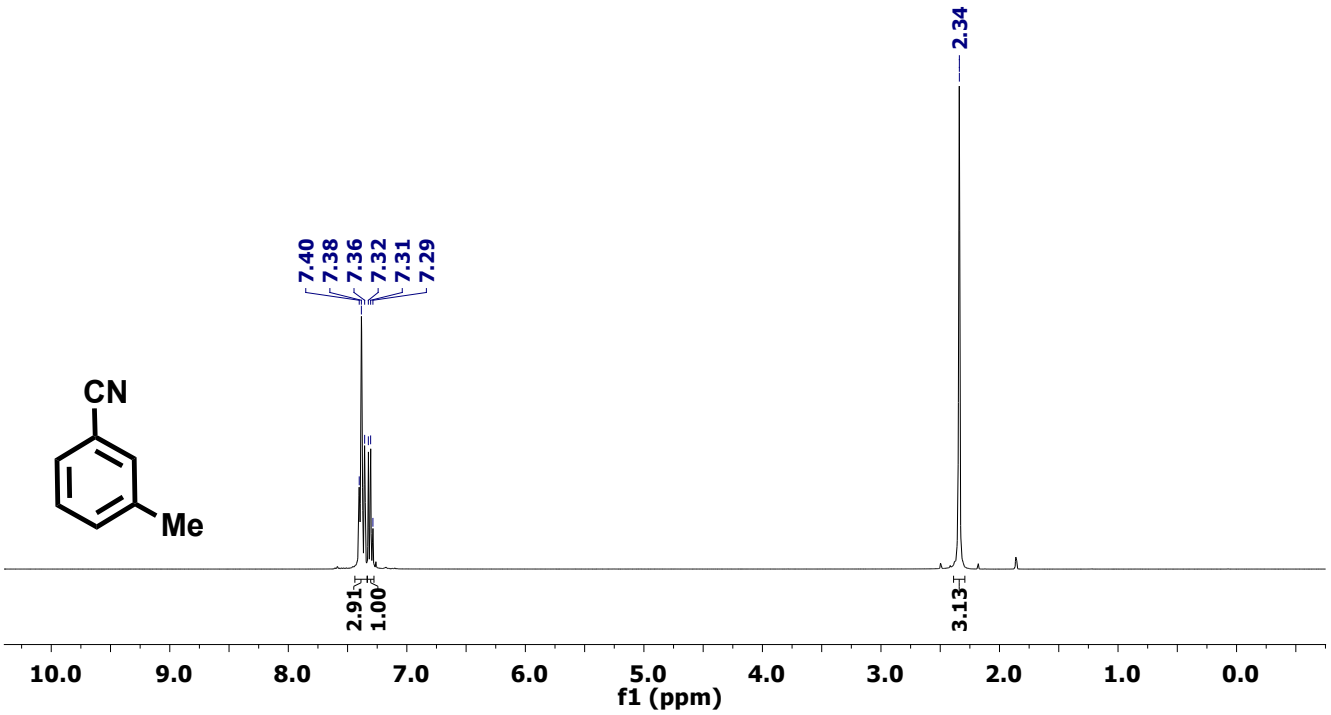


Figure S72. ^{1}H NMR spectrum ($CDCl_3$) of 3-methylbenzonitrile.

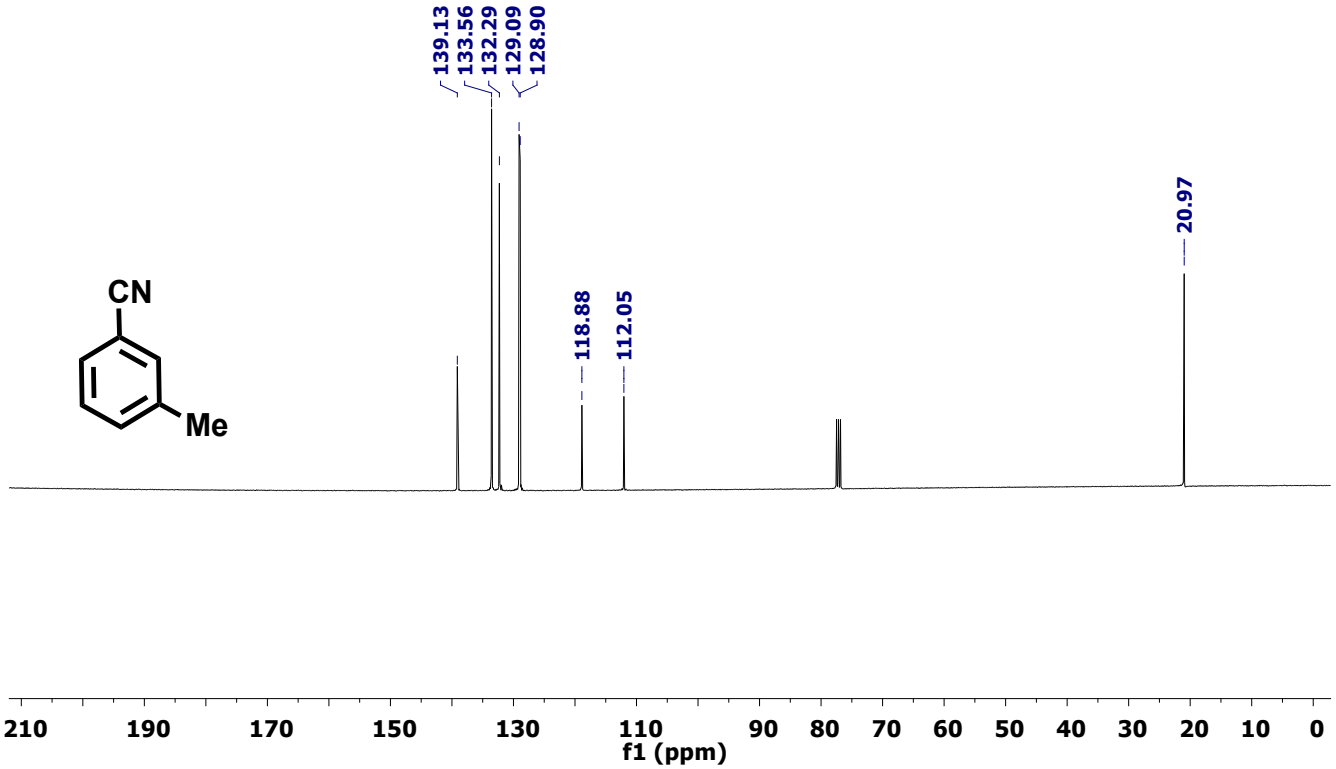


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 3-methylbenzonitrile.

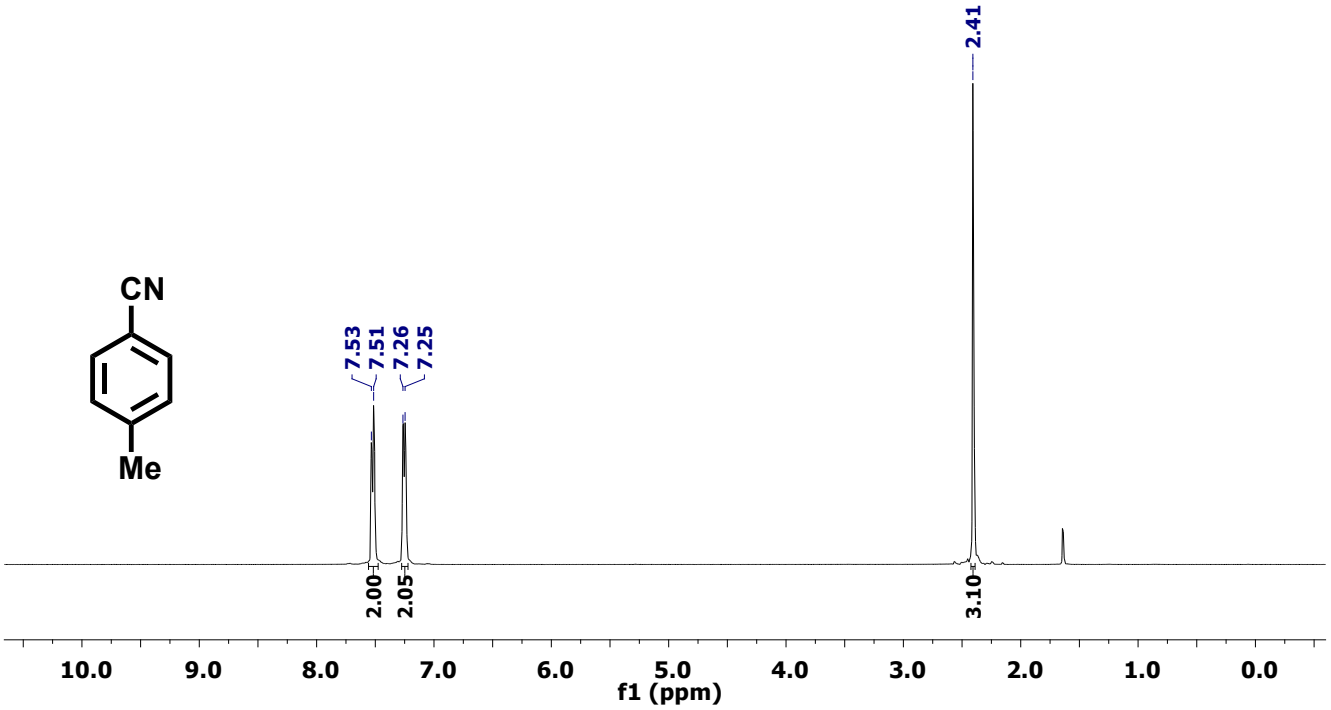


Figure S74. ^{1}H NMR spectrum ($CDCl_3$) of 4-methylbenzonitrile.

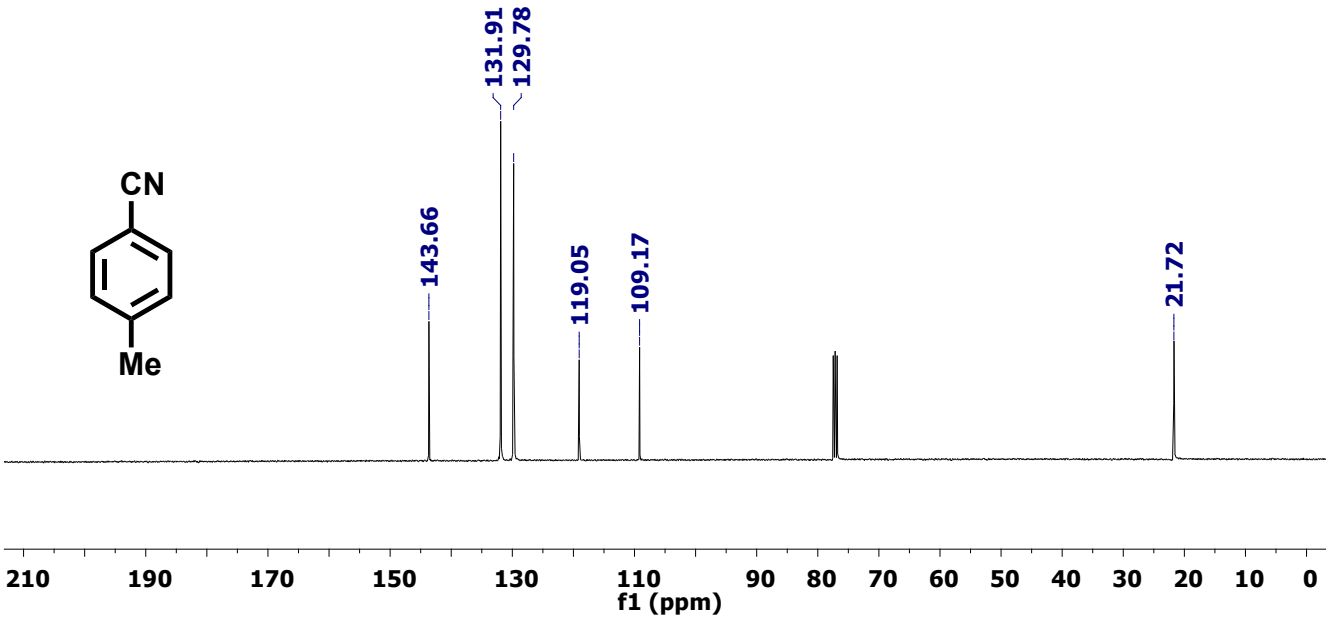


Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 4-methylbenzonitrile.

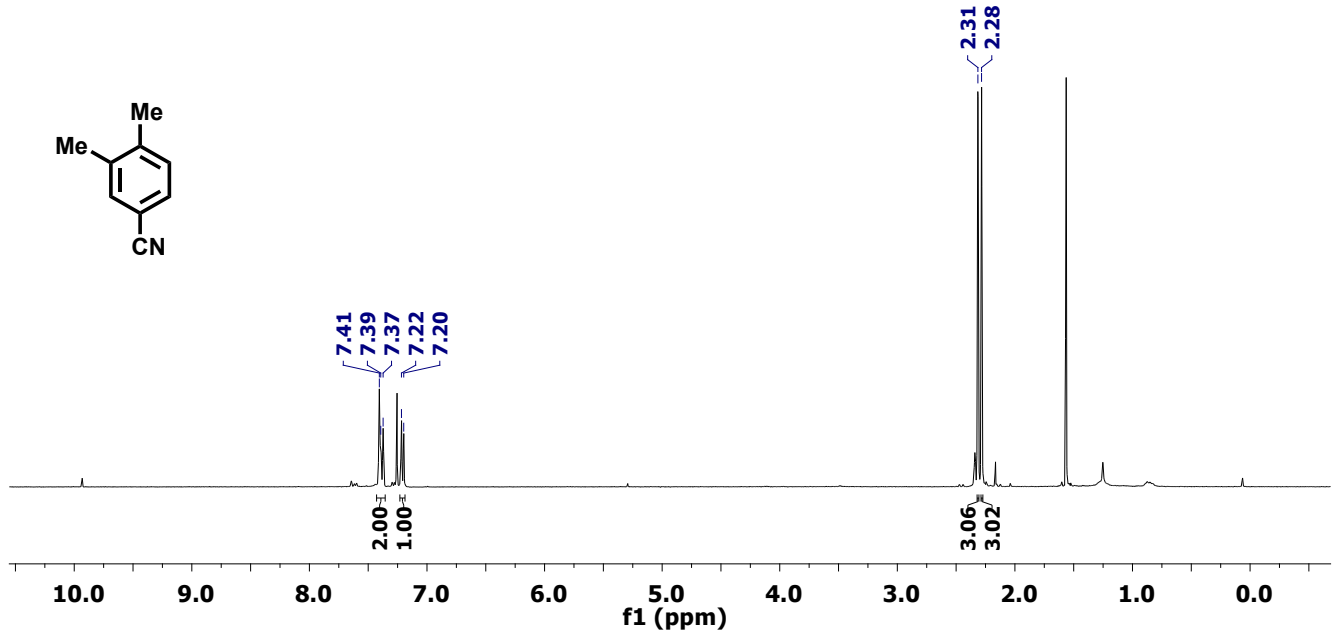


Figure S76. ^{1}H NMR spectrum ($CDCl_3$) of 3,4-dimethylbenzonitrile.

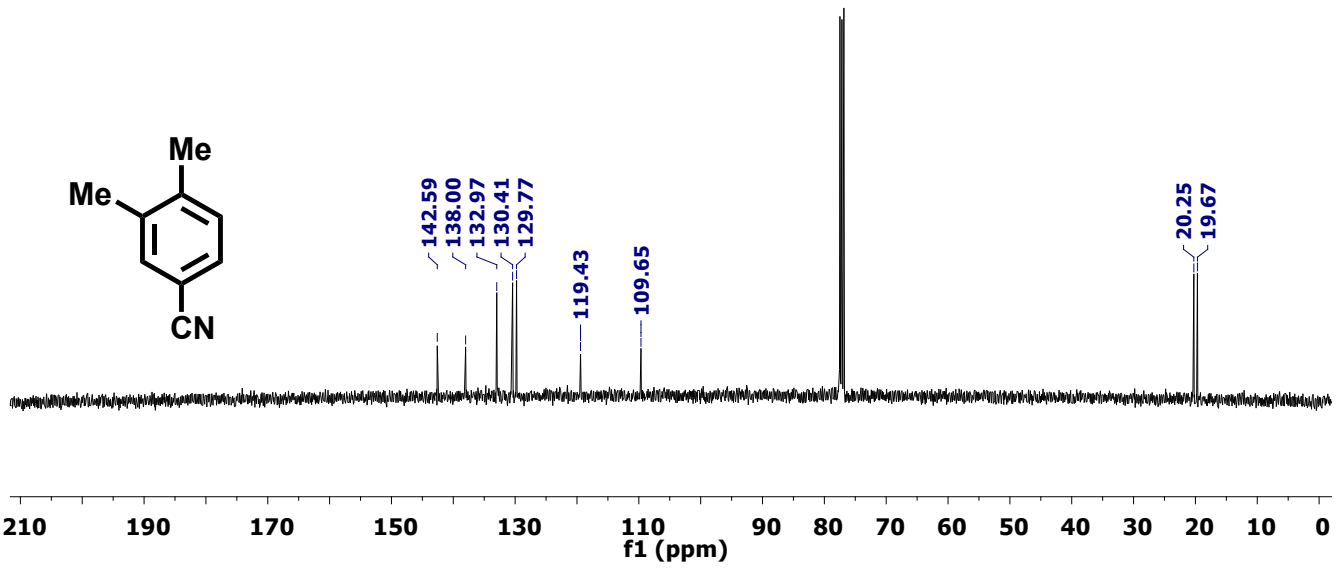


Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 3,4-dimethylbenzonitrile.

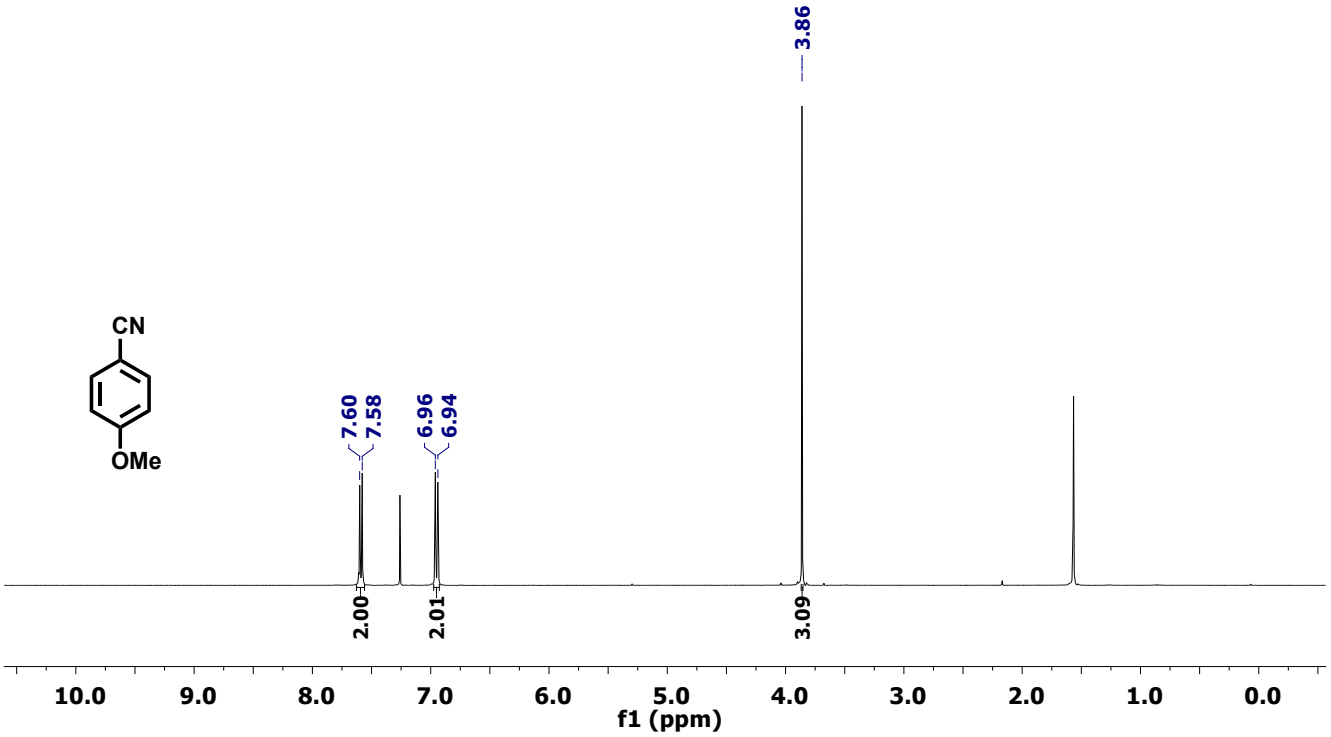


Figure S78. ^{1}H NMR spectrum ($CDCl_3$) of 4-methoxybenzonitrile.

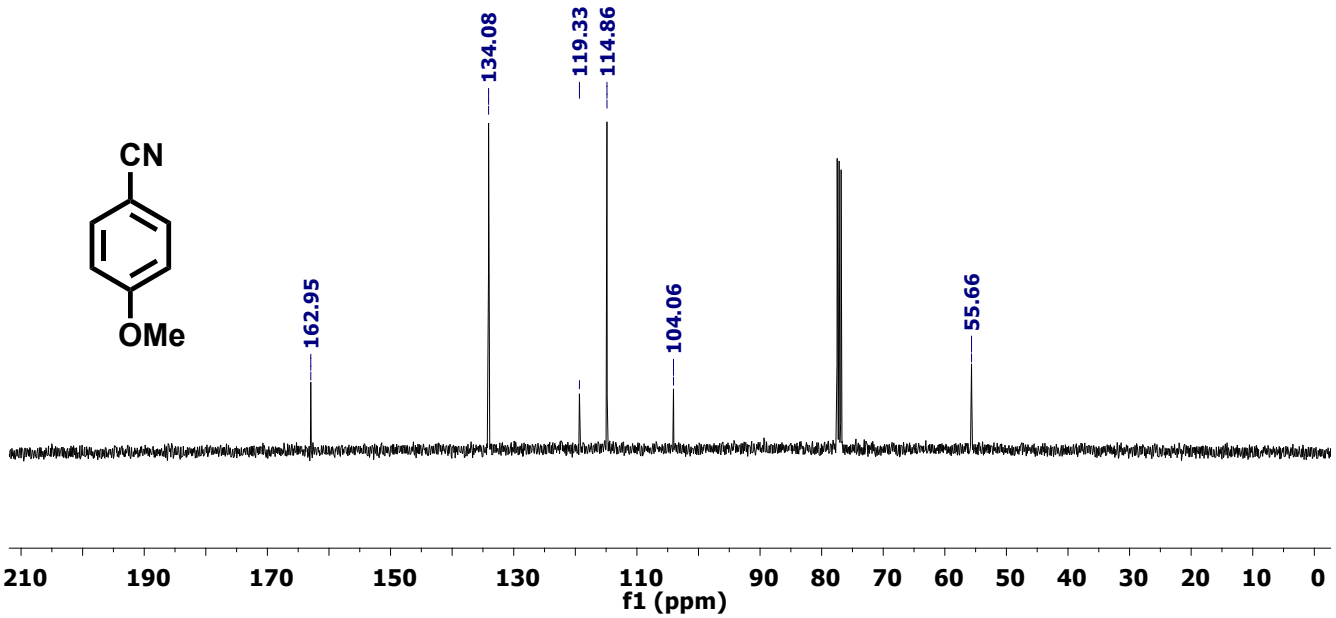


Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 4-methoxybenzonitrile.

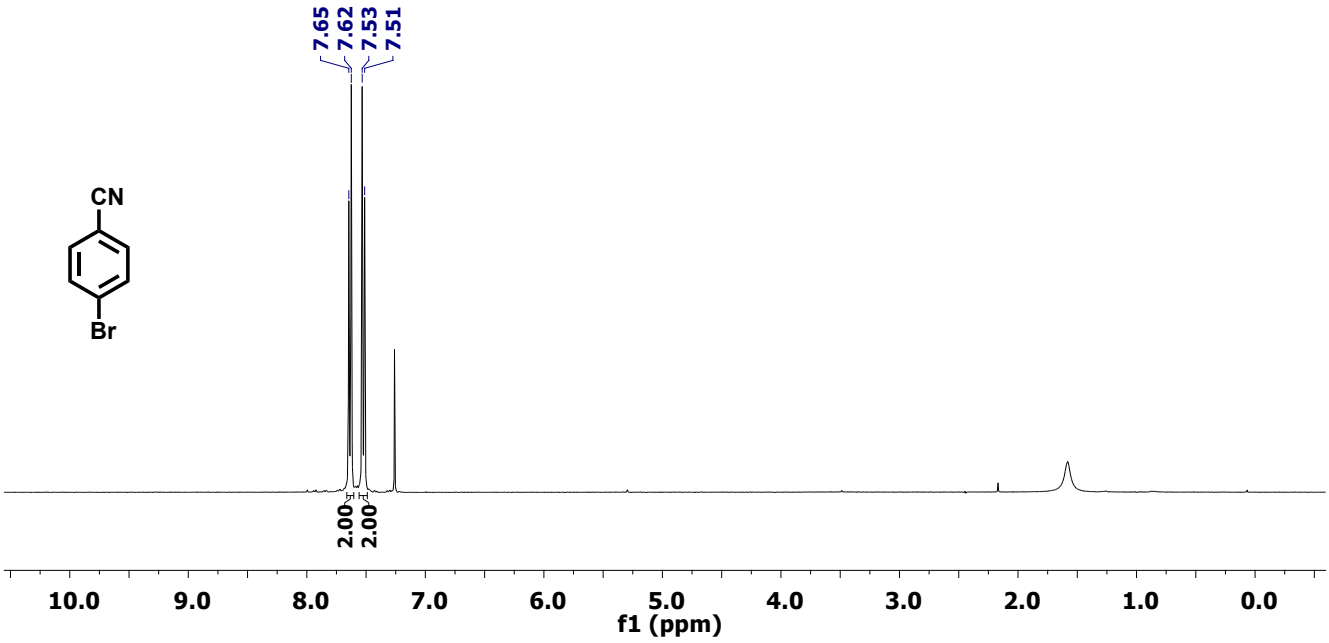


Figure S80. ^{1}H NMR spectrum ($CDCl_3$) of 4-bromobenzonitrile

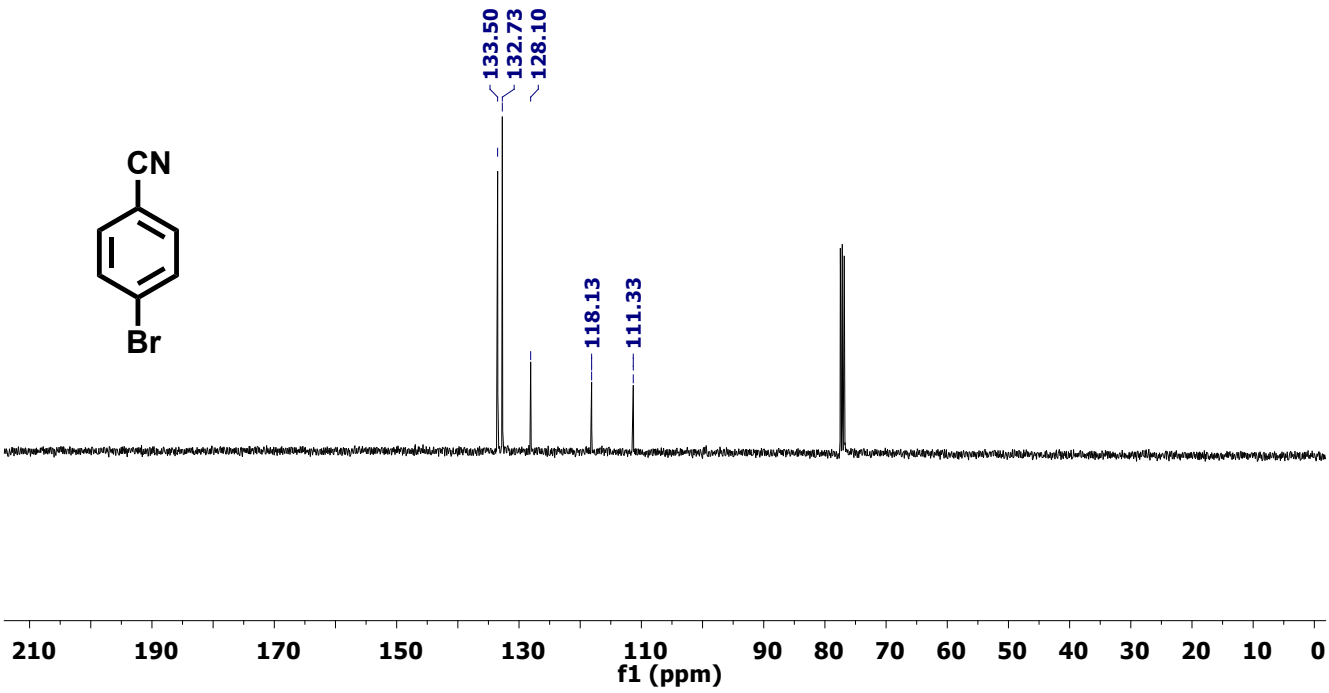


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 4-bromobenzonitrile

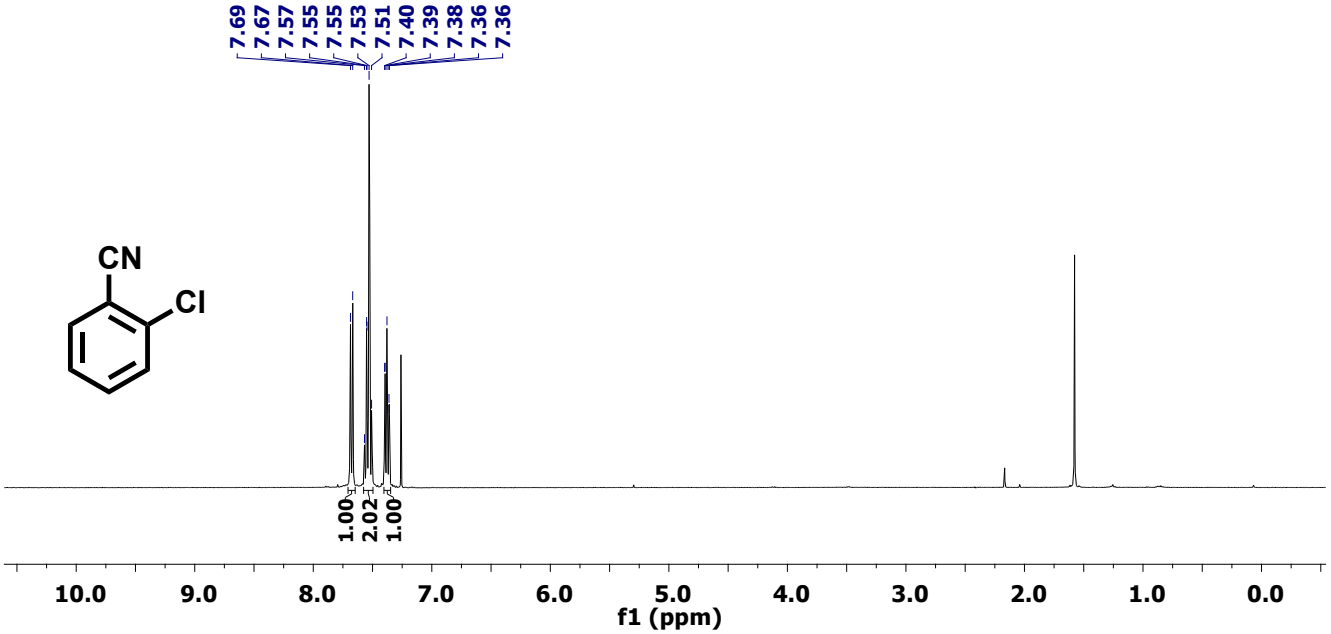


Figure S82. ^{1}H NMR spectrum ($CDCl_3$) of 2-chlorobenzonitrile.

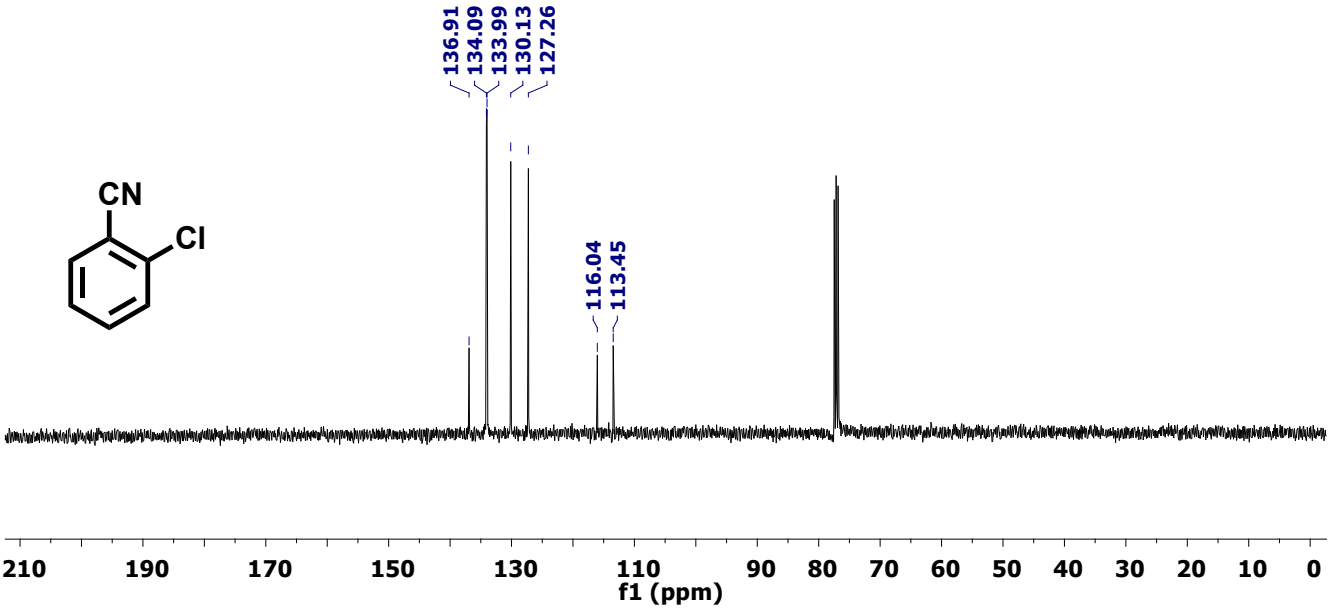


Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 2-chlorobenzonitrile.

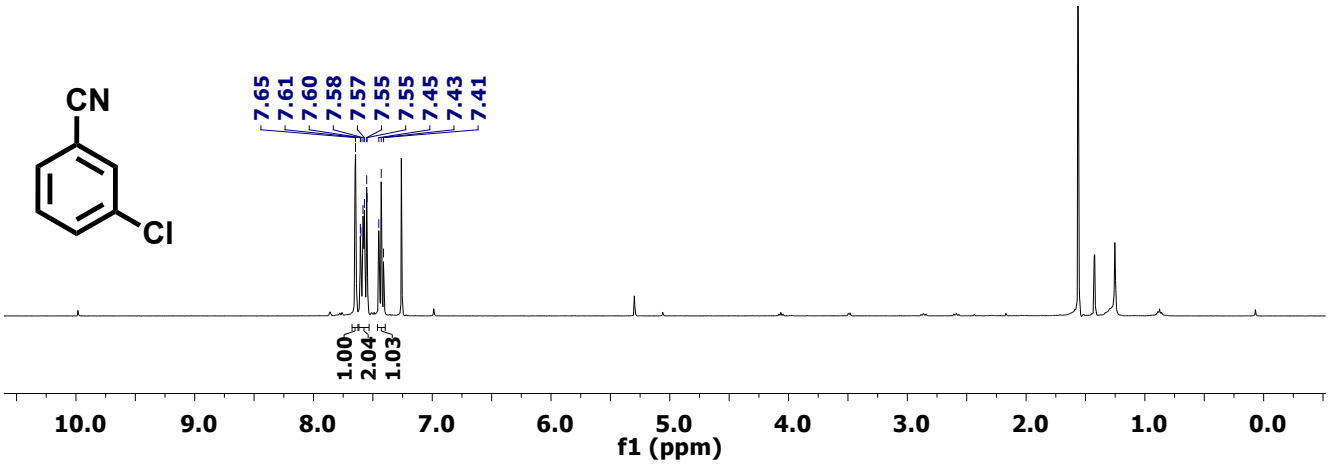


Figure S84. ^{1}H NMR spectrum ($CDCl_3$) of 3-chlorobenzonitrile.

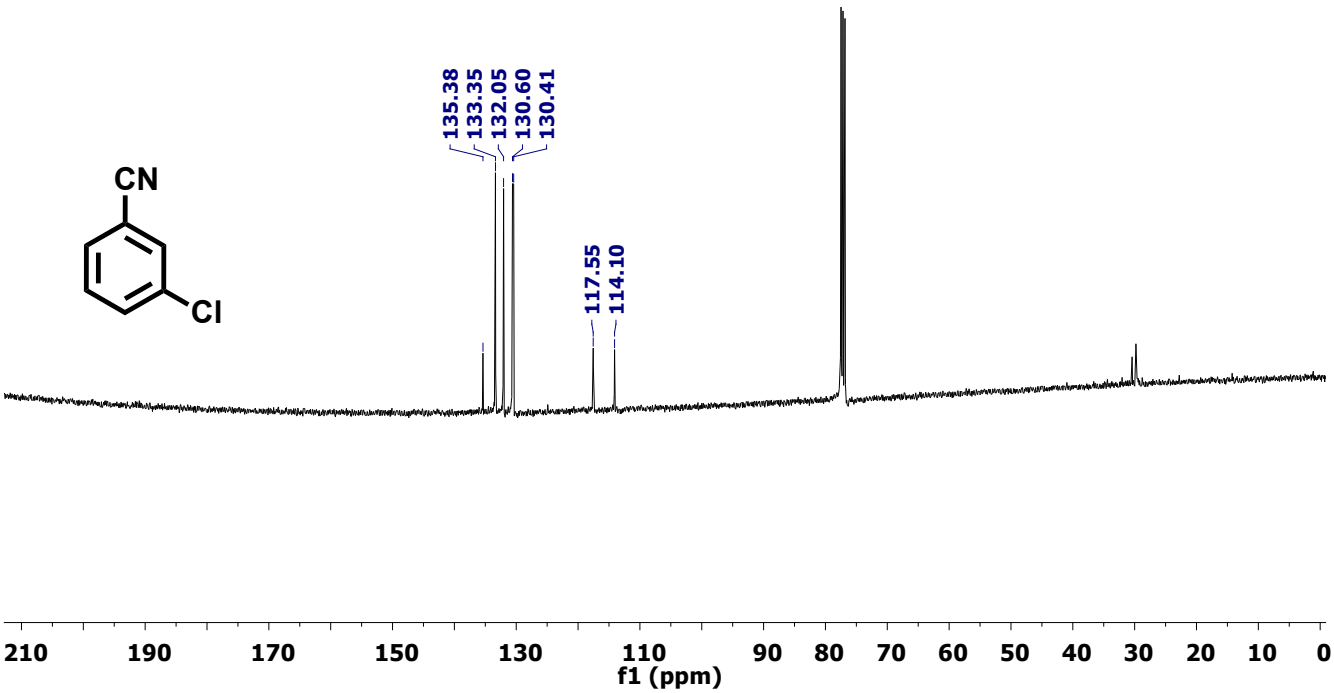


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 3-chlorobenzonitrile.

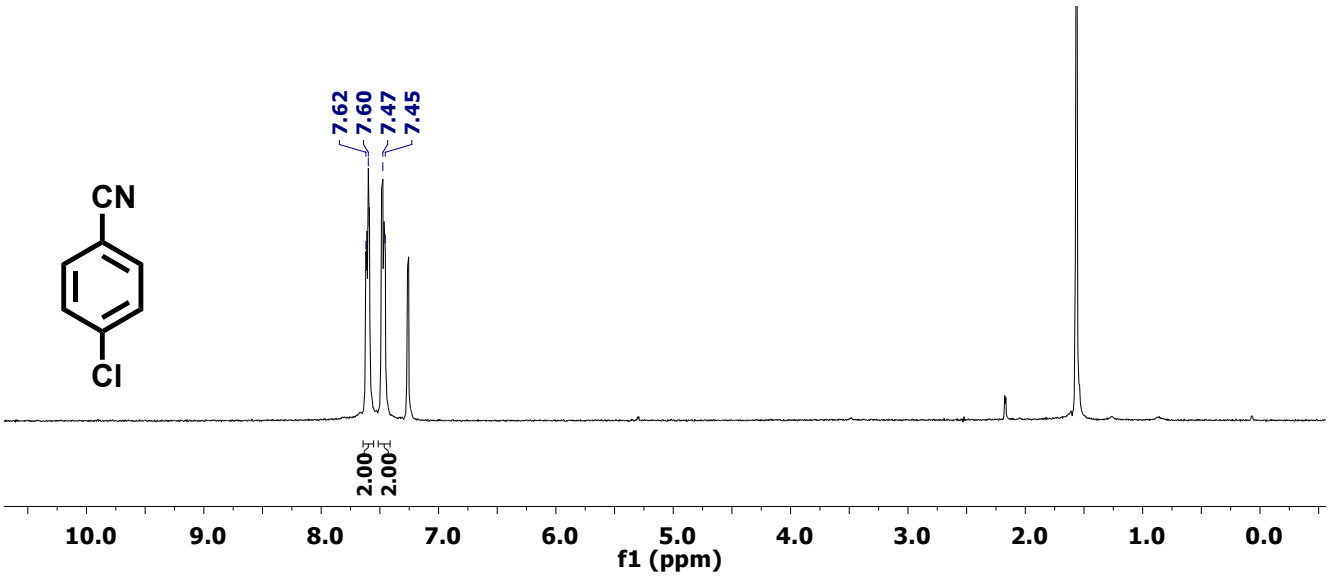


Figure S86.^{1}H NMR spectrum ($CDCl_3$) of 4-chlorobenzonitrile.

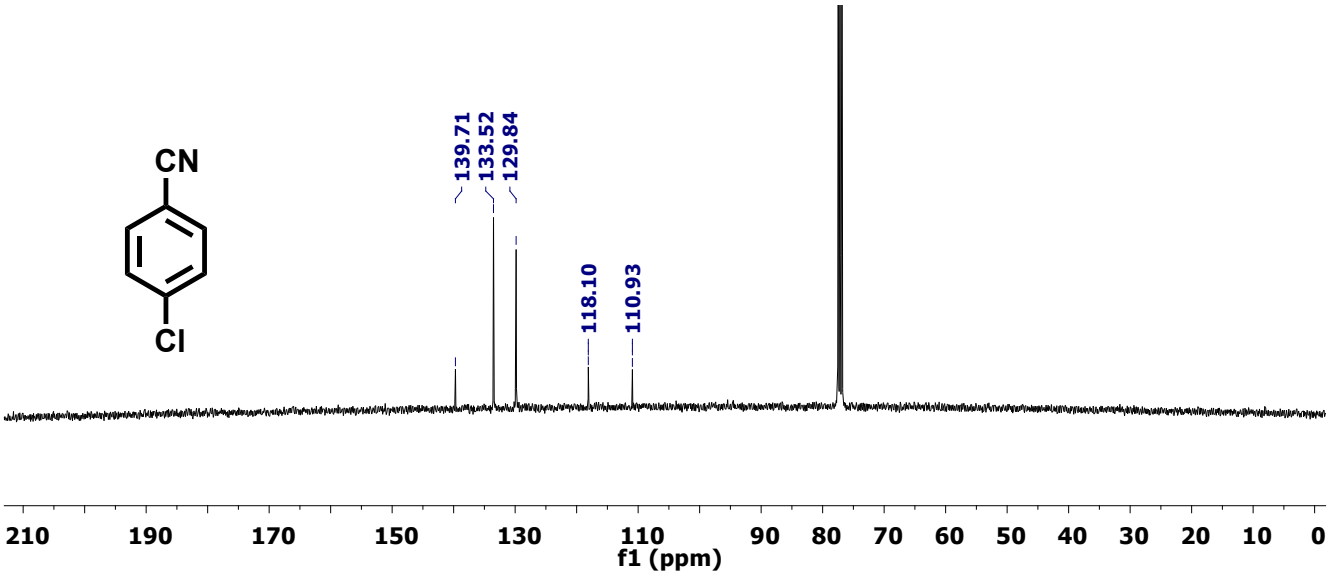


Figure S87. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 4-chlorobenzonitrile.

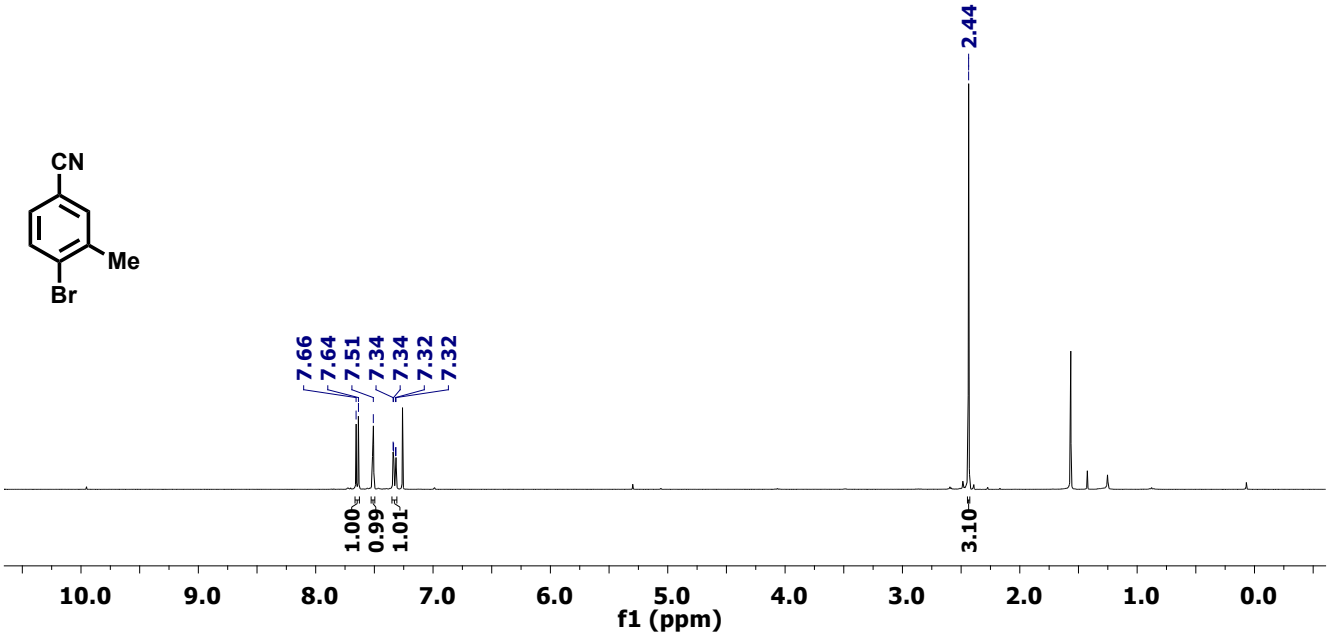


Figure S88. ^{1}H NMR spectrum ($CDCl_3$) of 4-bromo-3-methylbenzonitrile.

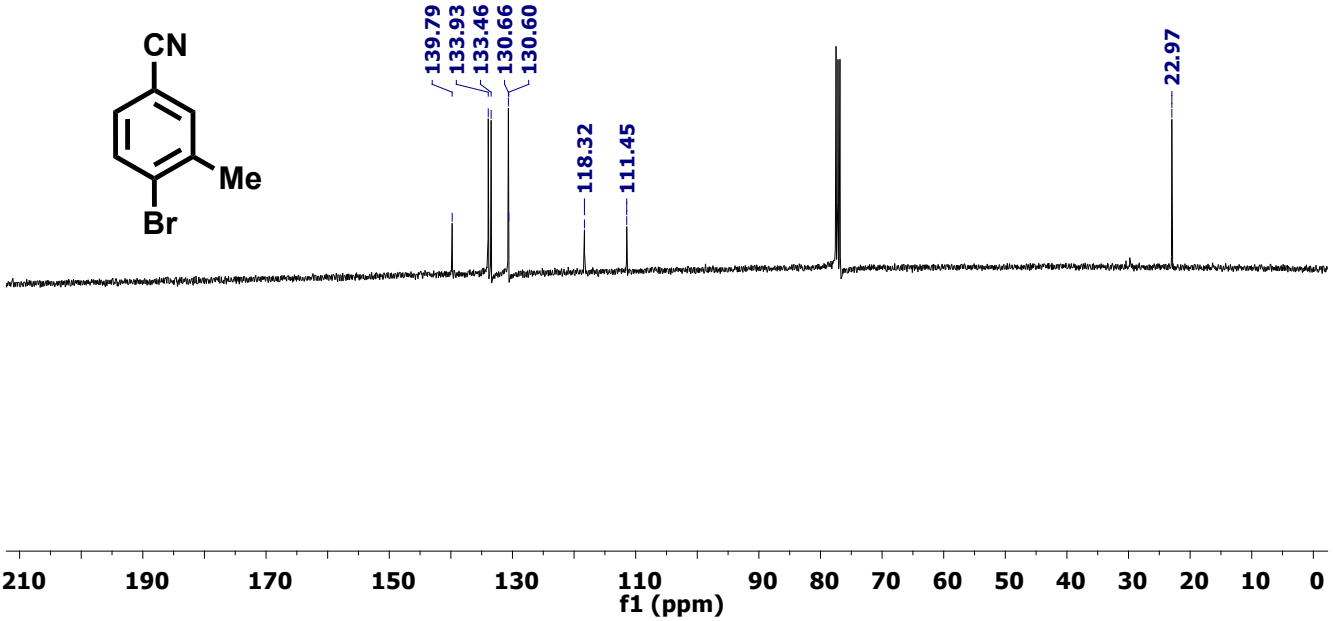


Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 4-bromo-3-methylbenzonitrile.

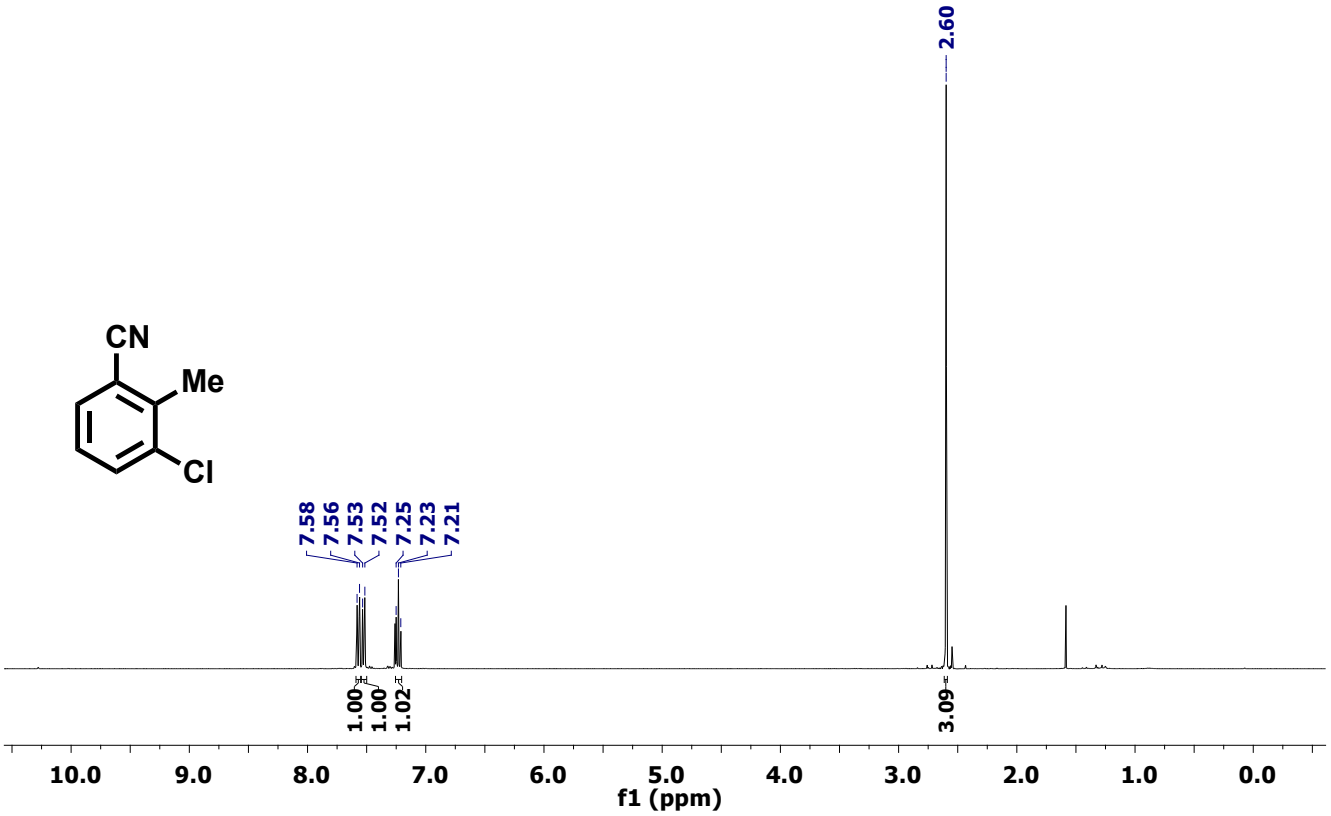


Figure S90. ^{1}H NMR spectrum ($CDCl_3$) of 3-chloro-2-methylbenzonitrile.

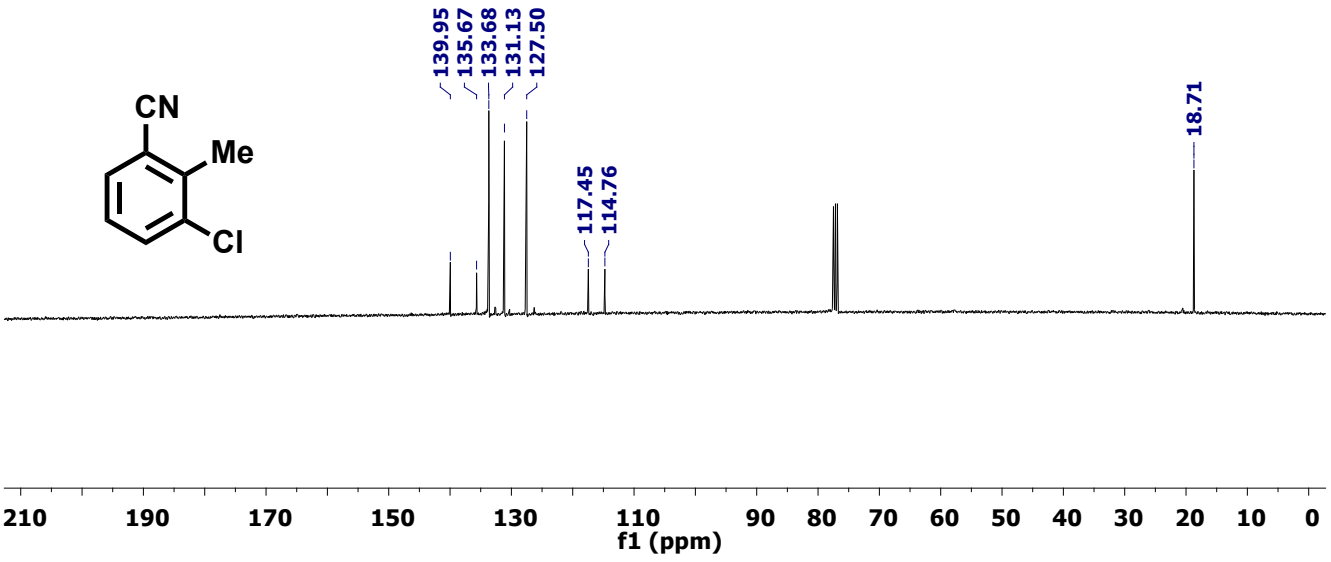


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of 3-chloro-2-methylbenzonitrile.

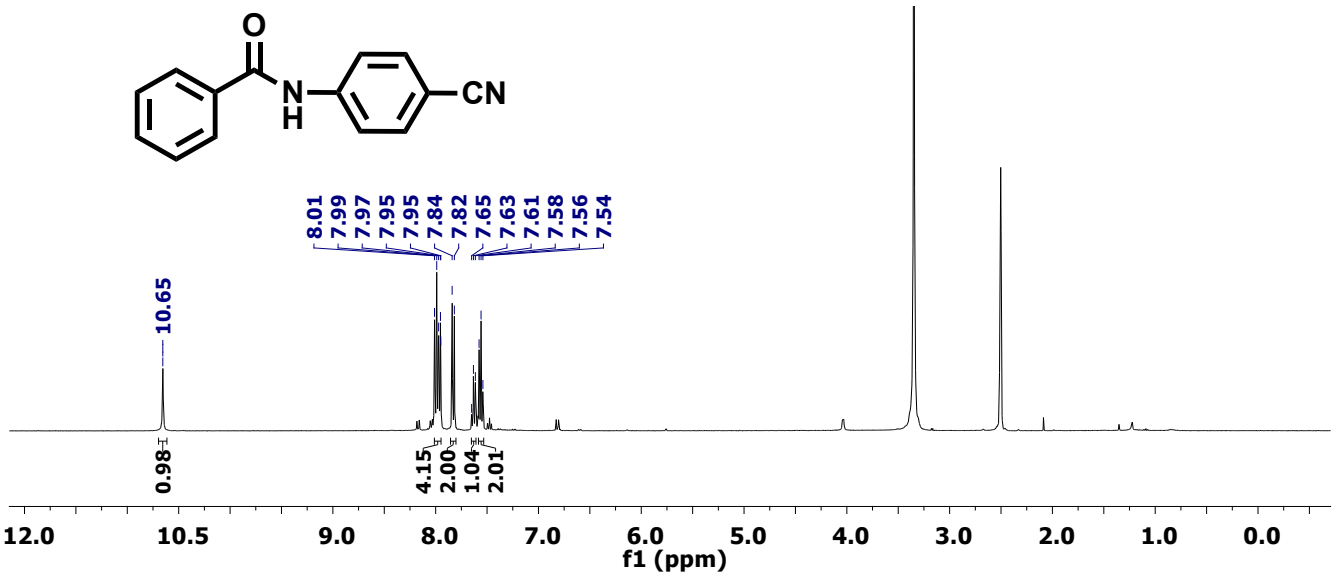


Figure S92.[1]H NMR spectrum (DMSO-d6) of N-(4-cyanophenyl)benzamide.

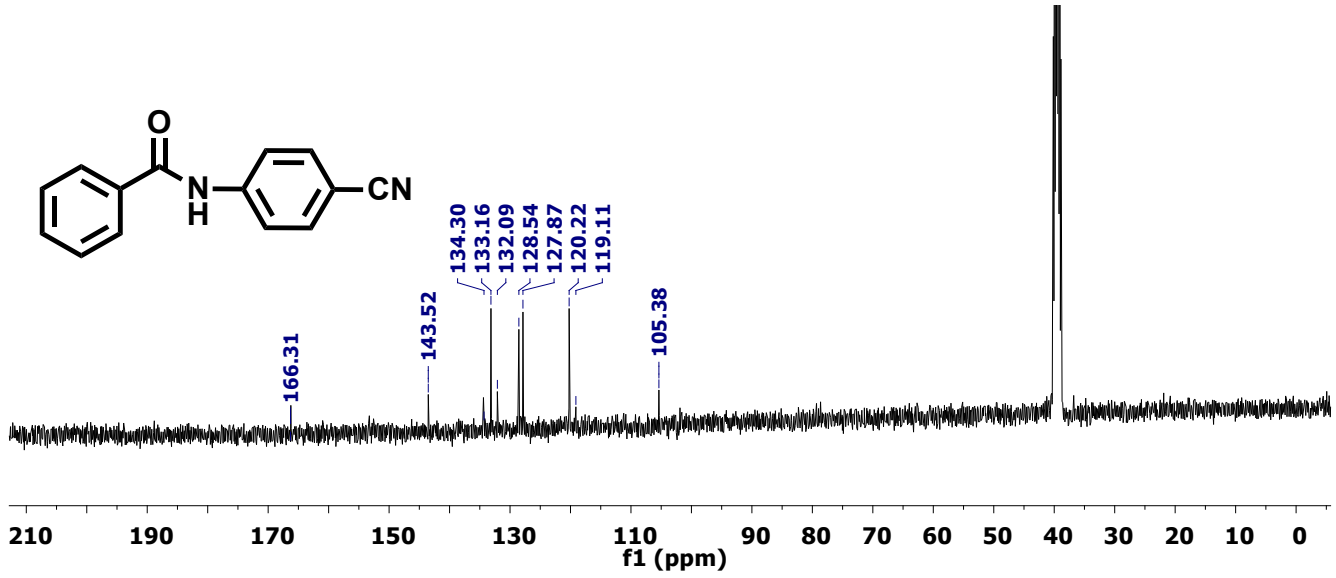


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d6) of N-(4-cyanophenyl)benzamide.

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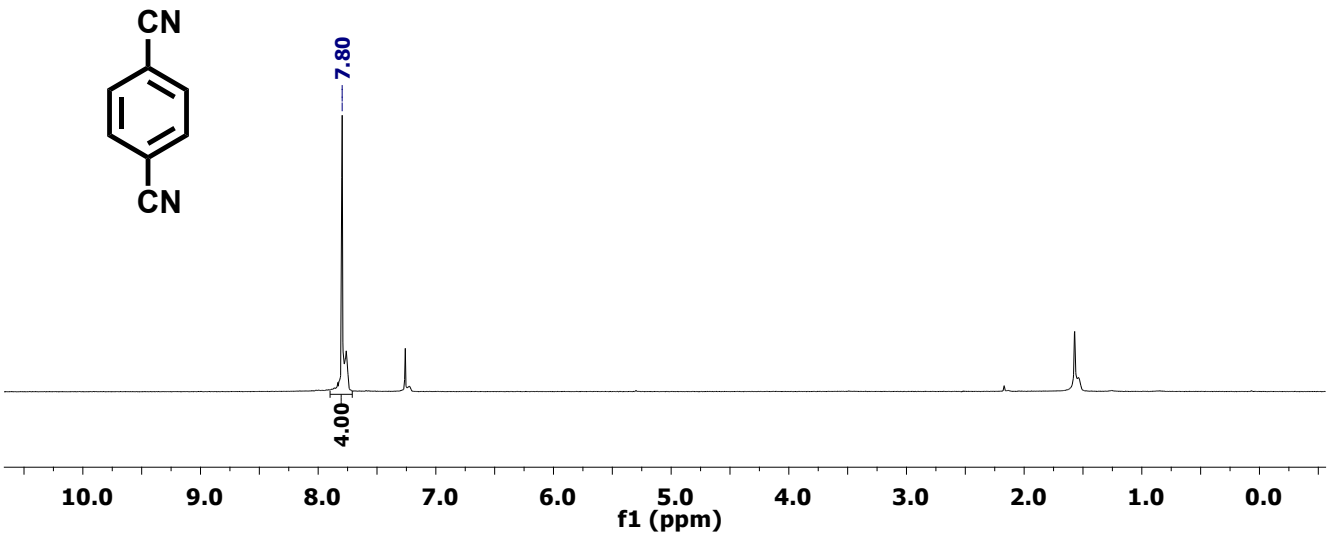


Figure S94. ^{1}H NMR spectrum ($CDCl_3$) of terephthalonitrile.

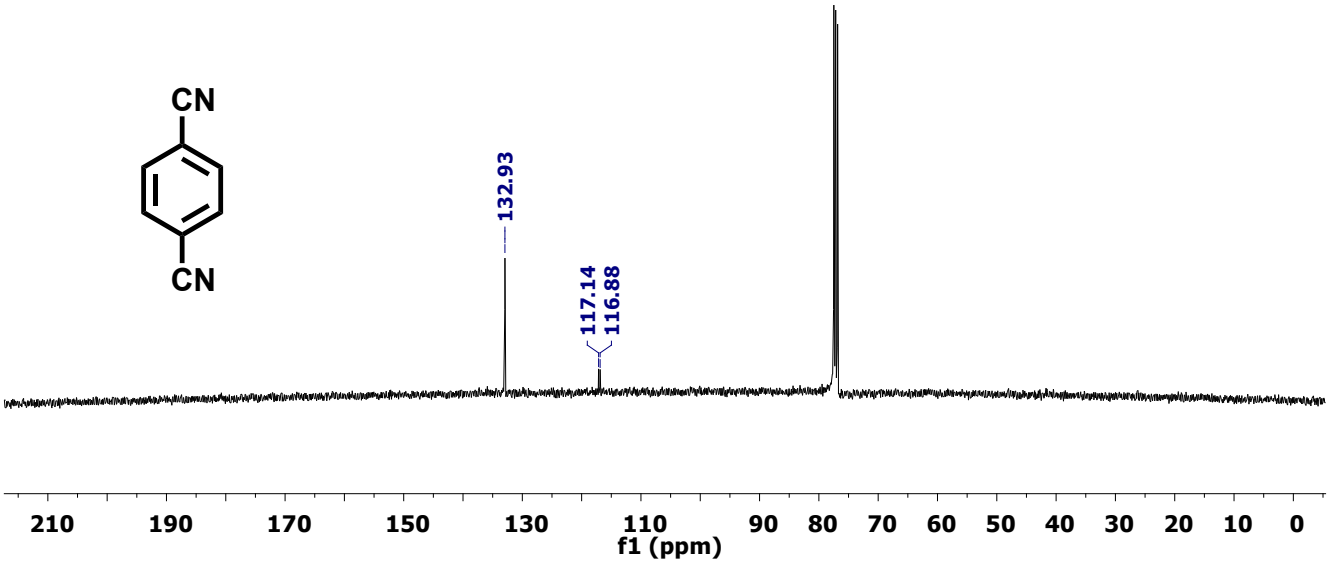


Figure S95. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of terephthalonitrile.

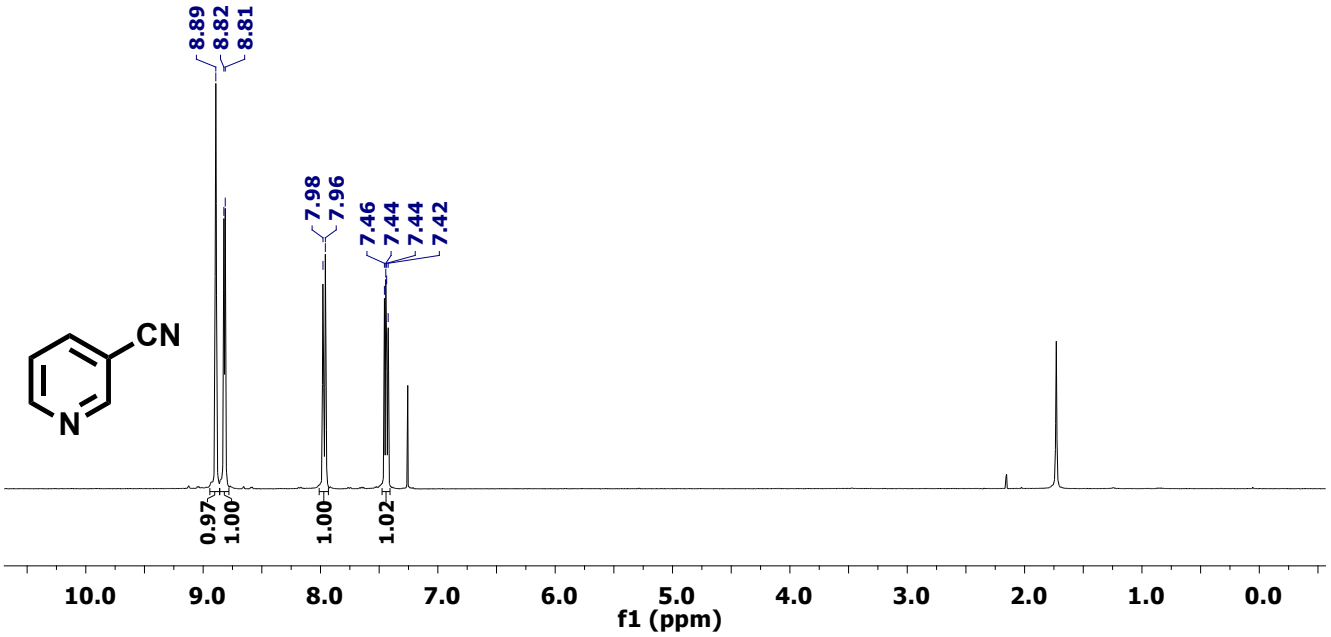


Figure S96. ^{1}H NMR spectrum ($CDCl_3$) of nicotinonitrile.

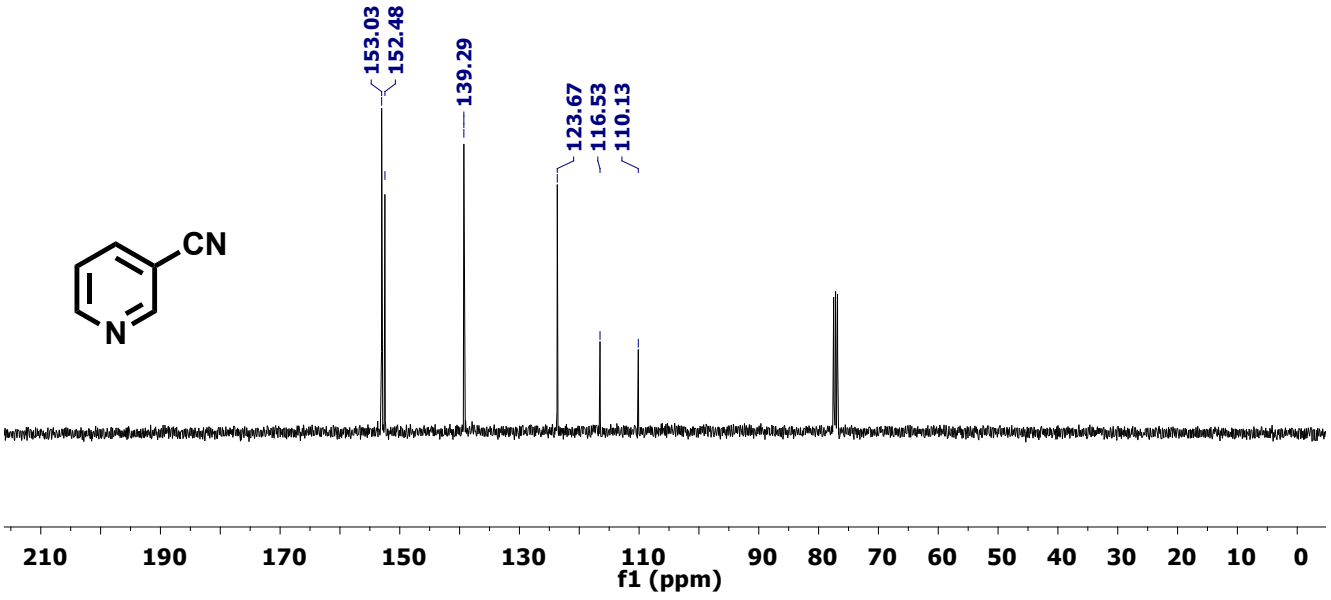


Figure S97. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of nicotinonitrile.

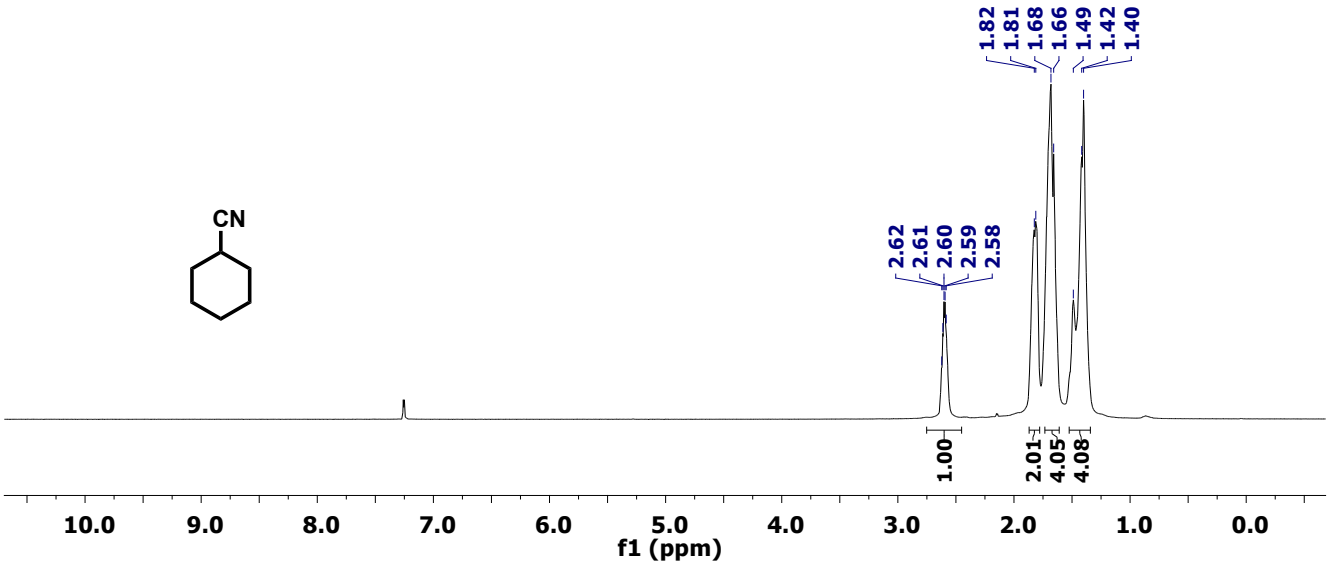


Figure S98. ^{1}H NMR spectrum ($CDCl_3$) of cyclohexanecarbonitrile.

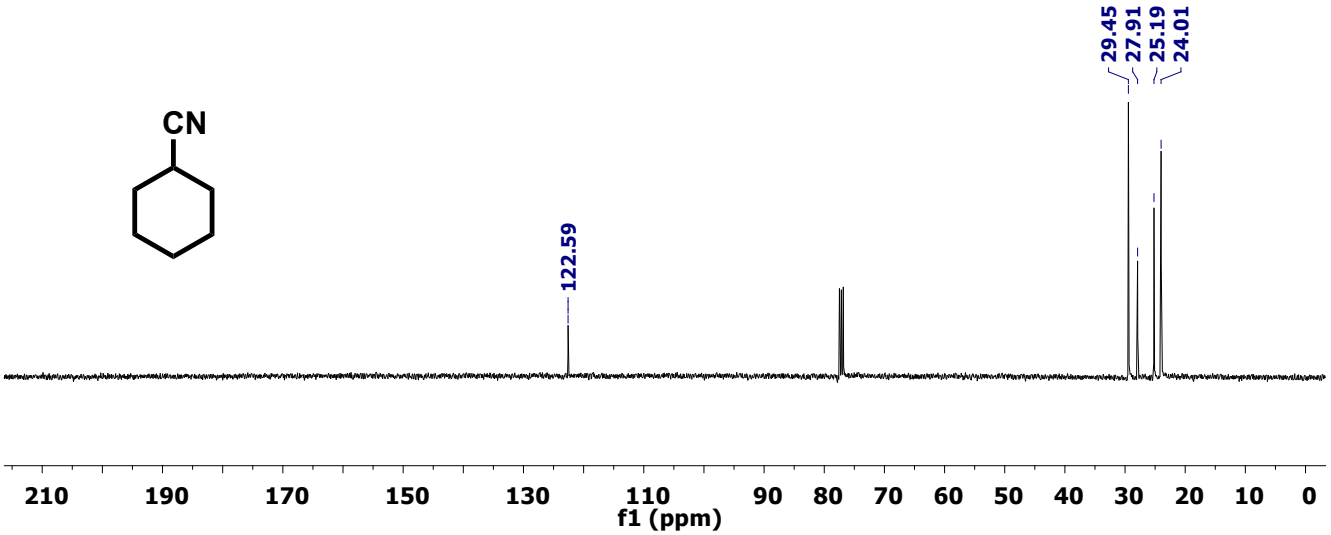
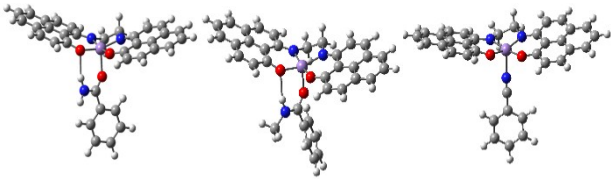


Figure S99. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of cyclohexanecarbonitrile.

9. Computational Details

Theoretical calculation:

The binding energies of benzamide, N-methyl benzamide and benzonitrile to Mn(III) centre were theoretically calculated with the help of Gaussian16[26] at B3LYP level of theory with basis set lanl2dz for Mn and 6-31g(d) for other elements.



7 **8** **9**

Binding energy: -8.5 (Kcal/mol) **-3.8 (Kcal/mol)** **-3.1 (Kcal/mol)**

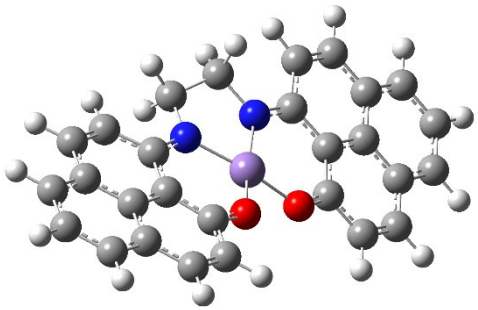
Figure S100. Binding energies in DFT-optimized structures of primary amide, secondary amide, nitrile bound intermediates.

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	IF (cm^{-1})	Infrared
Cationic Mn-complex	0.393304	0.416890	0.417835	0.338930	-1441.233934	-1441.232989	-1441.311894		
7	0.522672	0.555486	0.556431	0.454089	-1842.079304	-1842.078360	-1842.180701		
Benzamide	0.128070	0.135528	0.136473	0.095879	-400.815528	-400.814584	-400.855177		
8	0.551250	0.585612	0.586557	0.480673	-1881.353853	-1881.352909	-1881.458792		
SecAmide	0.156235	0.165483	0.166427	0.120805	-440.096187	-440.095243	-440.140865		
9	0.493378	0.525239	0.526183	0.423868	-1765.638642	-1765.637697	-1765.740013		
Benzonitrile	0.099431	0.105534	0.106478	0.069154	-324.386675	-324.385731	-324.423054		

Coordinates of all the optimized geometries:

Cationic Mn-Complex:



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C	3.34087800	-0.13693200	-0.02550400
C	-2.66963400	1.12391800	-0.20276200
C	2.62103200	-1.34393800	-0.27270400
C	-3.34095700	-0.13694000	0.02541700
C	4.77147300	-0.19664700	-0.01561500
C	2.66964300	1.12399800	0.20271800
C	5.45436400	-1.41975400	-0.28600300
C	-4.77153400	-0.19665100	0.01545200
C	-2.62114400	-1.34383300	0.27270600
C	5.54823300	0.96228700	0.26958700
C	-5.45438400	-1.41974600	0.28594500
C	4.68708400	-2.59022400	-0.56035900
H	5.20690900	-3.52150200	-0.76954000
C	-5.54825400	0.96225800	-0.26992700
C	-3.32049400	-2.55581500	0.55200600
H	-2.72221300	-3.43975200	0.74395800
C	3.32052100	-2.55593000	-0.55181300
H	2.72226400	-3.43991200	-0.74364500
C	-6.86292200	-1.45013700	0.27584800
H	-7.36659300	-2.38923900	0.48944400
C	-4.85806700	2.17401000	-0.55940800
H	-5.43863000	3.05745000	-0.81320400
C	6.86288000	-1.45013500	-0.27601600
H	7.36655100	-2.38925700	-0.48952200
C	-3.49411900	2.25626200	-0.53088000
H	-3.03094800	3.20131500	-0.77809500
C	6.95265300	0.88923600	0.27702700
H	7.52486300	1.78557300	0.50146300

C	3.49417100	2.25632000	0.53070900
H	3.03106100	3.20137200	0.77802900
C	-4.68708600	-2.59014600	0.56052000
H	-5.20688200	-3.52140800	0.76983600
C	7.60928400	-0.30852000	0.00234100
H	8.69338500	-0.35188000	0.00781500
C	-7.60929400	-0.30857200	-0.00272000
H	-8.69339500	-0.35193200	-0.00829100
C	-0.69875200	2.57228000	-0.30638300
H	-1.28050700	3.36659500	0.17163700
H	-0.64171900	2.79669100	-1.38090600
C	-6.95265300	0.88918800	-0.27748900
H	-7.52487000	1.78548300	-0.50207500
C	4.85812600	2.17405400	0.55907000
H	5.43873700	3.05748700	0.81278300
C	0.69857500	2.57228000	0.30691000
H	0.64147500	2.79650900	1.38147800
H	1.28023700	3.36676600	-0.17092000
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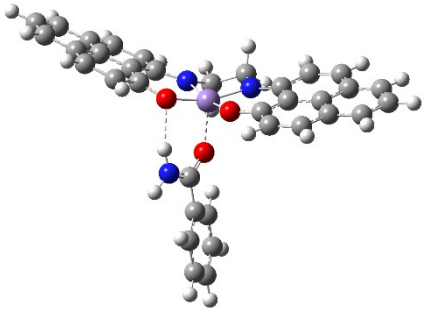
O	1.31783200	-1.41867800	-0.24224700

Mn-Benzamide:



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N	-1.44007700	-0.71498900	1.31236400
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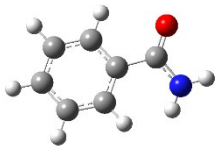
C	-2.76765600	-0.82588300	1.16781900
C	2.53106600	-0.68432500	-1.30884600
C	-3.39779500	-0.85460400	-0.14350600
C	4.57267100	-1.56521800	-0.27412500
C	2.47965200	-1.47185900	1.07996100
C	5.29460000	-1.31479400	-1.47945500
C	-4.79927700	-1.13731400	-0.25455800
C	-2.67227400	-0.58803400	-1.34064600
C	5.27018900	-2.16338600	0.81482100
C	-5.43437600	-1.21804400	-1.52995300
C	4.60297900	-0.74111000	-2.58706000
H	5.15121800	-0.55074800	-3.50620800
C	-5.60133900	-1.33153300	0.90689300
C	-3.32739600	-0.67531600	-2.60779800
H	-2.72275600	-0.48939300	-3.48938500
C	3.27285100	-0.44316500	-2.50787600
H	2.72928500	-0.02125100	-3.34634300
C	-6.81098900	-1.51374800	-1.61178700
H	-7.27249900	-1.57985900	-2.59364400
C	-4.97378100	-1.19863900	2.18244500
H	-5.58586700	-1.29908400	3.07548800
C	6.66264500	-1.64218400	-1.55798700
H	7.19539000	-1.43916400	-2.48344000
C	-3.64135900	-0.94677200	2.31224800
H	-3.23534800	-0.84009800	3.30824000
C	6.63314800	-2.48052200	0.69555200

H	7.14190300	-2.93911000	1.53955900
C	3.21675000	-2.12609400	2.13430800
H	2.71347900	-2.37601800	3.05797300
C	-4.65434400	-0.98754200	-2.69974400
H	-5.13330500	-1.05573800	-3.67315100
C	7.33101100	-2.21802100	-0.48256300
H	8.38455500	-2.46558000	-0.56136100
C	-7.57511500	-1.71362800	-0.46869400
H	-8.63372800	-1.93793400	-0.54890500
C	-0.78473900	-0.64239500	2.62497200
H	-1.38152300	-1.08456000	3.42510800
H	-0.61061700	0.41279800	2.87426400
C	-6.97013000	-1.61385900	0.78504100
H	-7.56061600	-1.75316600	1.68692300
C	4.53689300	-2.44330200	2.00586800
H	5.05153200	-2.92785200	2.83209200
C	0.54476600	-1.38990600	2.55500000
H	0.36994800	-2.47073500	2.65425700
H	1.16599600	-1.06903000	3.39912600
C	0.36691600	4.10107700	0.05298200
C	0.61490500	5.14910200	-0.84845200
C	0.51414000	4.32652800	1.42978900
C	0.98952100	6.40524600	-0.37624000
H	0.55826900	4.98503000	-1.92120200
C	0.87957100	5.58570000	1.89889800
H	0.33295700	3.50795000	2.11758500
C	1.11575800	6.62691800	0.99743700
H	1.19024100	7.20781300	-1.07947100
H	0.98205800	5.75608400	2.96646900

H	1.40467200	7.60779100	1.36359800
O	-1.41116500	-0.23504500	-1.36582200
O	1.26214300	-0.39304000	-1.34938200
C	-0.03924600	2.74216900	-0.39776600
O	0.12464400	1.75090100	0.35660600
N	-0.58091300	2.60372500	-1.62043200
H	-0.89732400	1.68086000	-1.90976400
H	-0.84184600	3.40571800	-2.17353200

Benzamide:



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C	-1.85509600	1.22967800	-0.12286600
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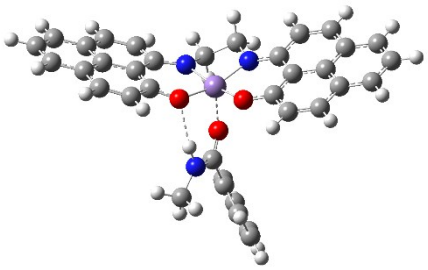
C	0.22029300	-0.02216700	-0.01868200
C	-0.51506900	-1.20784600	0.10963200
C	-1.90701900	-1.17386300	0.13752200
C	-2.57998900	0.04557300	0.02401700
H	-2.37473900	2.17799100	-0.22974900
H	0.09143400	2.12075300	-0.29418300
H	0.02858200	-2.14387200	0.18436900
H	-2.46889900	-2.09775300	0.24460500
H	-3.66627000	0.07221600	0.04230900
C	1.71853400	-0.13664100	-0.03418100
O	2.28763100	-1.19446300	-0.27233500
N	2.42115900	1.02370100	0.20735800
H	1.99657500	1.76936600	0.73993800
H	3.41799400	0.90037300	0.32890600

Mn-SecAmide:



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Mn	-0.06533800	-0.43609600	-0.00082100
N	1.19644800	-1.23093600	1.26957200
N	-1.43933000	-0.82083000	1.34062600
C	3.16540300	-1.34074900	-0.18594800
C	-2.76611300	-0.93557200	1.19731000
C	2.51408100	-0.74029300	-1.30423600
C	-3.40192600	-0.91270000	-0.11183900
C	4.54718600	-1.69562700	-0.31965500
C	2.46787500	-1.61017400	1.05629200
C	5.26328600	-1.41904500	-1.52278400
C	-4.80315400	-1.19497100	-0.22859400
C	-2.68229600	-0.59423300	-1.30015600
C	5.24318700	-2.34211400	0.74242500
C	-5.44438700	-1.22234300	-1.50325800
C	4.57320500	-0.79545200	-2.60397300

H	5.11666900	-0.58581600	-3.52178700
C	-5.59918100	-1.44243400	0.92694900
C	-3.34431800	-0.62738400	-2.56671500
H	-2.74395900	-0.40272500	-3.44219500
C	3.25026700	-0.47382400	-2.50162800
H	2.70762400	-0.01399500	-3.32059000
C	-6.82044200	-1.51874400	-1.59144000
H	-7.28646500	-1.54346300	-2.57309200
C	-4.96586800	-1.36389700	2.20433000
H	-5.57309300	-1.50780200	3.09475500
C	6.62399000	-1.76980900	-1.62536500
H	7.15207400	-1.54661000	-2.54885500
C	-3.63426000	-1.11156000	2.33916000
H	-3.22385000	-1.04953100	3.33712000
C	6.59852300	-2.68074700	0.59974900
H	7.10602600	-3.17598500	1.42356600
C	3.20327300	-2.30977400	2.08271800
H	2.70402700	-2.57922100	3.00307800
C	-4.67080500	-0.93876900	-2.66573300
H	-5.15447700	-0.96637700	-3.63883800
C	7.29074100	-2.39329400	-0.57600900
H	8.33854200	-2.65820600	-0.67296400
C	-7.57832800	-1.77112200	-0.45466500
H	-8.63656100	-1.99553000	-0.53957300
C	-0.77398000	-0.78762700	2.64970500
H	-1.36876600	-1.24062000	3.44505300
H	-0.58511600	0.25958500	2.92046900
C	-6.96744900	-1.72421300	0.79935100
H	-7.55295200	-1.90518200	1.69708400

C	4.51593600	-2.64629100	1.93144900
H	5.02943600	-3.16577400	2.73690000
C	0.54722000	-1.54664300	2.55000900
H	0.36174900	-2.62802100	2.61996400
H	1.17767400	-1.25573000	3.39818800
C	0.50470700	3.99230500	0.32295700
C	1.21004400	4.91771200	-0.46176500
C	0.33186900	4.23858300	1.69384200
C	1.72089100	6.07960900	0.11658700
H	1.39035900	4.71877400	-1.51358900
C	0.82375000	5.41067400	2.26238900
H	-0.19265600	3.50800900	2.30085100
C	1.51950300	6.33245500	1.47493500
H	2.27828300	6.78447600	-0.49310700
H	0.67173300	5.60338100	3.32028800
H	1.91016900	7.24240700	1.92111900
O	-1.42169900	-0.24100400	-1.31757600
O	1.25164200	-0.42029400	-1.32296100
C	-0.00096500	2.70305600	-0.22849900
O	0.13255600	1.65768800	0.46488000
N	-0.58691300	2.64860600	-1.43675000
C	-1.04356300	3.74690800	-2.28398100
H	-1.13278300	4.66480900	-1.70270100
H	-0.36126100	3.92113800	-3.12351800
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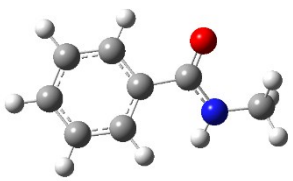
N-Methylbenzamide:



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C	2.17708900	-1.35772700	-0.13933300
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C	0.24302400	0.10589200	-0.05066500
C	1.09683200	1.19961400	0.14392600
C	2.47555000	1.01479700	0.21397100
C	3.01889300	-0.26511100	0.07558300
H	2.59563800	-2.35229900	-0.26788600
H	0.15569500	-2.02825400	-0.40738100
H	0.65455200	2.18626600	0.23436100
H	3.12832600	1.86885900	0.37315900
H	4.09486600	-0.40929100	0.12620000
C	-1.23427100	0.38633500	-0.11081100
O	-1.66824300	1.50199900	-0.38451800
N	-2.05972800	-0.67727000	0.14878500
H	-1.65970700	-1.49109000	0.59227900
C	-3.50271700	-0.51677900	0.19891900
H	-3.98947900	-1.44738700	-0.10835600
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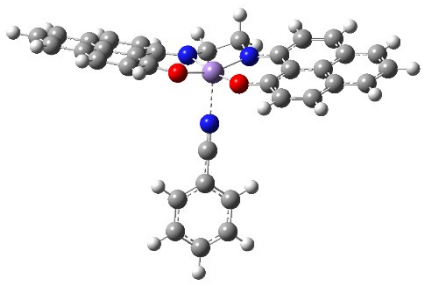
Mn-Benzonitrile:



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Mn	0.02893000	-0.59789500	-0.12367300
N	1.36203400	-1.19261100	1.18164800
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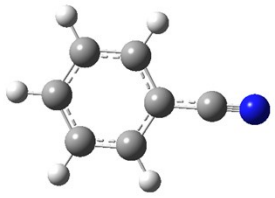
C	-2.64813800	-1.08151300	1.09526400
C	2.66320700	-0.47985400	-1.34641900
C	-3.29952800	-1.06930400	-0.19902700
C	4.79270200	-1.10950500	-0.30455800
C	2.68417300	-1.37796400	1.00197500
C	5.49092200	-0.69962300	-1.47996900
C	-4.71844800	-1.24512600	-0.28725500
C	-2.56505200	-0.89993700	-1.41196000
C	5.54910400	-1.66162200	0.76903500
C	-5.37366000	-1.29742100	-1.55415500
C	4.74232600	-0.17615400	-2.57643200
H	5.27325300	0.13485600	-3.47257400
C	-5.51482400	-1.36688100	0.88765900
C	-3.23997400	-0.97003600	-2.67226700
H	-2.63092400	-0.85323700	-3.56216000
C	3.38220200	-0.07667100	-2.51631300
H	2.79604200	0.30169600	-3.34679500
C	-6.76886900	-1.47945100	-1.61326900
H	-7.24845100	-1.52423100	-2.58770000
C	-4.85682700	-1.28892500	2.15048800
H	-5.45841700	-1.33938200	3.05486600
C	6.89206300	-0.82719800	-1.54187300
H	7.40603000	-0.50512700	-2.44388700
C	-3.50379300	-1.14987400	2.25536400

H	-3.07039100	-1.07731500	3.24315000
C	6.94549000	-1.77829700	0.66641500
H	7.49980000	-2.20646300	1.49762700
C	3.48713000	-1.98567600	2.03561100
H	3.00961200	-2.35960300	2.93041700
C	-4.58960300	-1.16350500	-2.73919900
H	-5.08704700	-1.20995000	-3.70465300
C	7.61785200	-1.35859500	-0.47997600
H	8.69688900	-1.45186800	-0.54675100
C	-7.53252000	-1.59994300	-0.45606300
H	-8.60684200	-1.73809600	-0.52112100
C	-0.67297200	-1.06987400	2.54694200
H	-1.23187200	-1.68265200	3.25968800
H	-0.62212700	-0.04750300	2.94798300
C	-6.90553000	-1.53896200	0.78720200
H	-7.49188200	-1.62554300	1.69836600
C	4.84133900	-2.10842800	1.92345800
H	5.40365400	-2.56473600	2.73458300
C	0.72923000	-1.65825000	2.42531600
H	0.67504000	-2.75626900	2.42452500
H	1.30492400	-1.35186400	3.30583400
C	-0.13833600	4.27757100	0.34908900
C	-1.20190500	4.95506300	-0.27552600
C	0.88928100	4.99150200	0.99288300
C	-1.23007500	6.34613900	-0.25117700
H	-1.98662600	4.39175200	-0.76995500
C	0.84516000	6.38226400	1.00822500
H	1.70432200	4.45643900	1.46939400
C	-0.21063800	7.05771600	0.38855700

H	-2.04667400	6.87594500	-0.73144400
H	1.63414500	6.94004400	1.50278000
H	-0.23877100	8.14319100	0.40382400
O	-1.28769400	-0.66175600	-1.45522000
O	1.36845400	-0.37746200	-1.40270200
C	-0.10162000	2.84962500	0.32686600
N	-0.07434500	1.68821700	0.31053500

Benzonitrile:



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C	-1.48394300	1.21094600	0.00000700
C	-2.18060800	0.00002400	-0.00001400
H	-2.02614900	-2.15197100	-0.00001400
H	0.45875900	-2.15286000	0.00001300
H	0.45889900	2.15278300	0.00000400
H	-2.02607400	2.15201600	0.00000200
H	-3.26698200	0.00007600	-0.00001600
C	2.04497200	-0.00002600	-0.00000800
N	3.20841100	0.00001100	-0.00000400

10. References

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