Supplementary Information

Unlocking an additive-free and catalyst-free dual approach for the amide reductions to amines

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1. General Information:

All chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, Merk, Avra, Loba Chemie, and TCI at the highest purity grade and used for the amide reduction reaction without further purification. Deuterated solvents were procured from Sigma-Aldrich. Amine-boranes (unless commercially available) were synthesized as per the literature procedure.[1] Unless otherwise mentioned, all syntheses were performed in standard glassware without any special precautions taken for the removal of moisture or air. Merck precoated 0.25 mm silica gel plates (60F-254) were used to perform the analytical TLC. Visualization was achieved with shortwave UV light. NMR spectra were recorded in $CDCl_3$, DMSO-d_6, D_2O, Toluene-d_8, and TMS as internal standard on Bruker Avance 600 MHz spectrometers. Chemical shifts of ^1H NMR spectra were given in parts per million with respect to TMS, and the coupling constant (*J*) was measured in Hz. The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. GC-MS analyses were carried out on a Thermo Scientific Trace 1310 equipped with TG-17MS column (30 m x 0.25 mm x 0.25 µm).

2. General procedure for the reduction amides to amines with $Me_2NH{\cdot}BH_3$:

A 15 mL thick-wall sealed tube was charged with amine-boranes (1 mmol, 2.0 equiv.), amides (0.5 mmol, 1 equiv.), and toluene (2 mL) in a N_2 filled glove-box. The tube was sealed tightly with the PTFE screw cap, and the reaction mixture was stirred at 110 °C for 24 h. After completion of the reaction, it was quenched with the addition of methanol. The methanolic solution was evaporated and again dissolved in Et_2O, and to it, 1 mL 1(N) HCl solution in Et_2O was added to get the precipitation of amines as HCl salt. The reaction mixture was filtered, and the precipitate was washed thoroughly with Et_2O, EtOAc, and $CHCl_3$ and dried under a high vacuum.

For secondary and tertiary amides, the methanolic solution was evaporated. Then, 1 equiv. DMF (internal standard) was added to it and dissolved in $CDCl_3$ for the ^1H NMR measurement of the crude reaction mixture.

3. General procedure for the synthesis of N,N-dimethyl benzylamine derivatives from primary amides and dimethylamine-boranes:

A 15 mL thick-wall sealed tube was charged with dimethylamine-boranes (1 mmol, 2.0 equiv.), primary amides (0.5 mmol, 1 equiv.), TMEDA (as per the requirement), and toluene (2 mL) in a N_2 filled glove-box. The tube was sealed tightly with the PTFE screw cap, and the reaction

mixture was stirred at 110 °C for 60 h. After completion of the reaction, it was quenched with the addition of methanol. Subsequently, 1 equiv. mesitylene was added to it as an internal standard and a small amount of aliquot was injected in GC-MS to find out the yields of the tertiary amines.

4. The ^{11}B NMR NMR spectroscopy monitoring experiment:

A screw-capped NMR tube was charged with dimethylamine-boranes (0.25 mmol, 2.0 equiv.), amides (0.125 mmol, 1 equiv.), and toluene-d_8 (0.5 mL) in a N_2 filled glove-box. The tube was sealed tightly with the screw cap and tapes. Then, the NMR tube having the reaction mixture was heated at 110 °C for 24 h. After completion of the reaction, ^{11}B NMR was recorded.

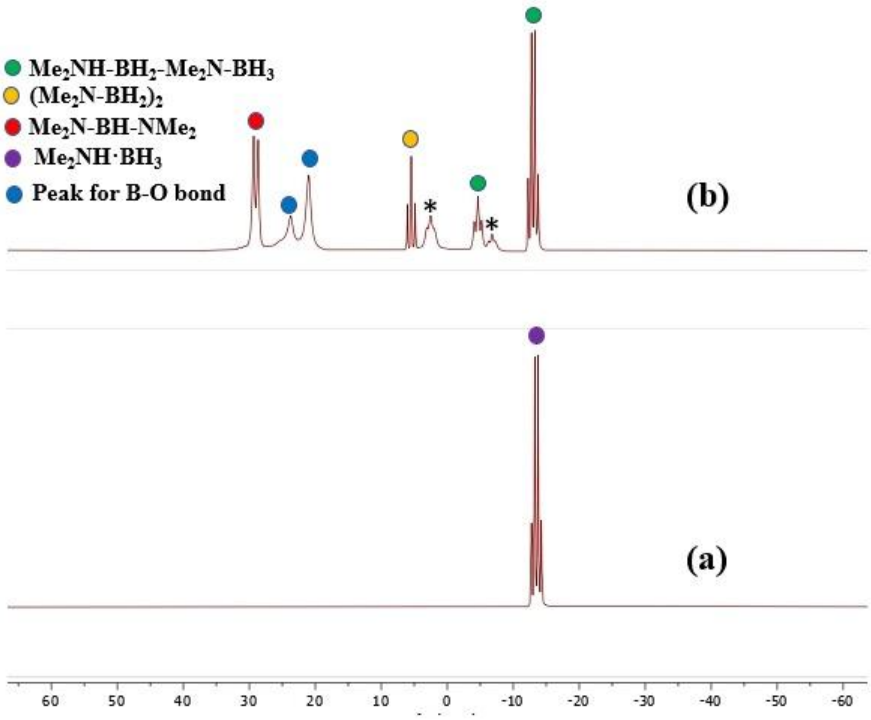


Figure S1. ^{11}B NMR of the reaction: a) at the start of the reaction and b) after 24 h heating of the crude reaction mixture. The asterisk indicates unidentified species generated in situ.

Reaction in the presence of TMEDA:

A 15 ml thick-wall sealed tube was charged with dimethylamine-boranes (0.25 mmol, 2.0 equiv.), amides (0.125 mmol, 1 equiv.), TMEDA (5/10 equiv.) and toluene (1 mL) in a N_2 filled glove-box. The tube was sealed tightly with the cap and tapes. Then, the reaction tube was heated at 110 °C for 24 h, and then a small aliquot was taken in the NMR tube, dissolved in

$CDCl_3$, and ^{11}B NMR was recorded. A broad quartet at δ –8.77 ppm was observed, which may be correlated to the formation of BH_3-TMEDA adduct.[2]

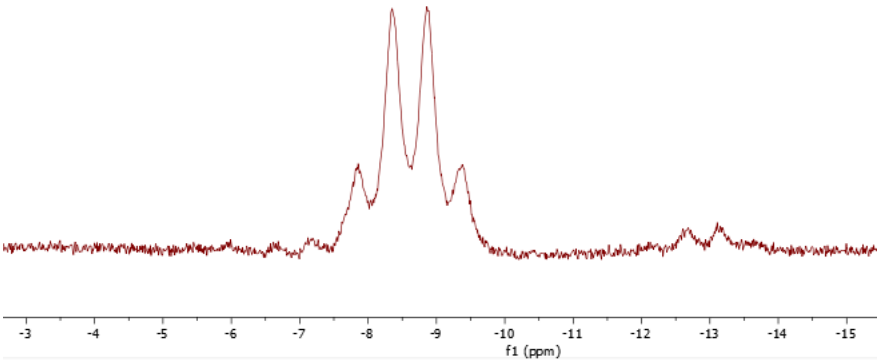


Figure S2. ^{11}B NMR of the crude reaction mixture using TMEDA as additive.

5. Kinetic studies:

The reduction of **1a** to **2a** under the optimized conditions was monitored kinetically (Figure S3). To start off, the formation of **3a** was observed as the major product. However, with the progress of time, slowly the yield of **2a** was increased with the simultaneous decrease of 1a. Notably, after 15 h, almost 54% of **2a** was obtained with 76% consumption of **1a**. When the reaction mixture was analyzed after 24 h, the formation of 67% of **2a** resulted, along with 23% of **3a**.

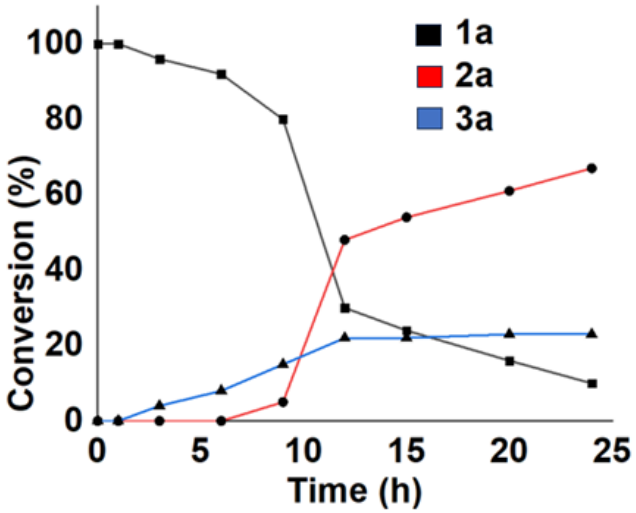
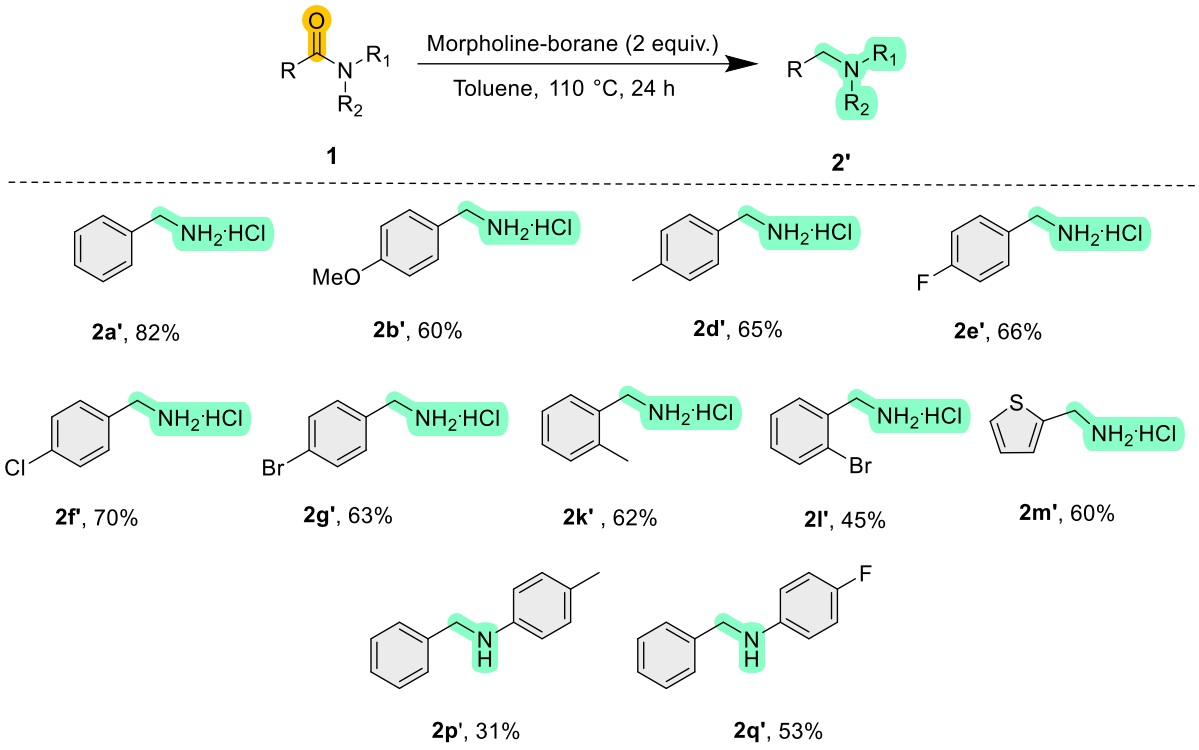


Figure S3. Reaction kinetics for the reduction of **1a** to **2a**.

6. Scope of amide reduction with morpholine-borane:

Herein, morpholine-borane was employed as the reducing agent instead of DMAB under the optimized reaction (Table S1).

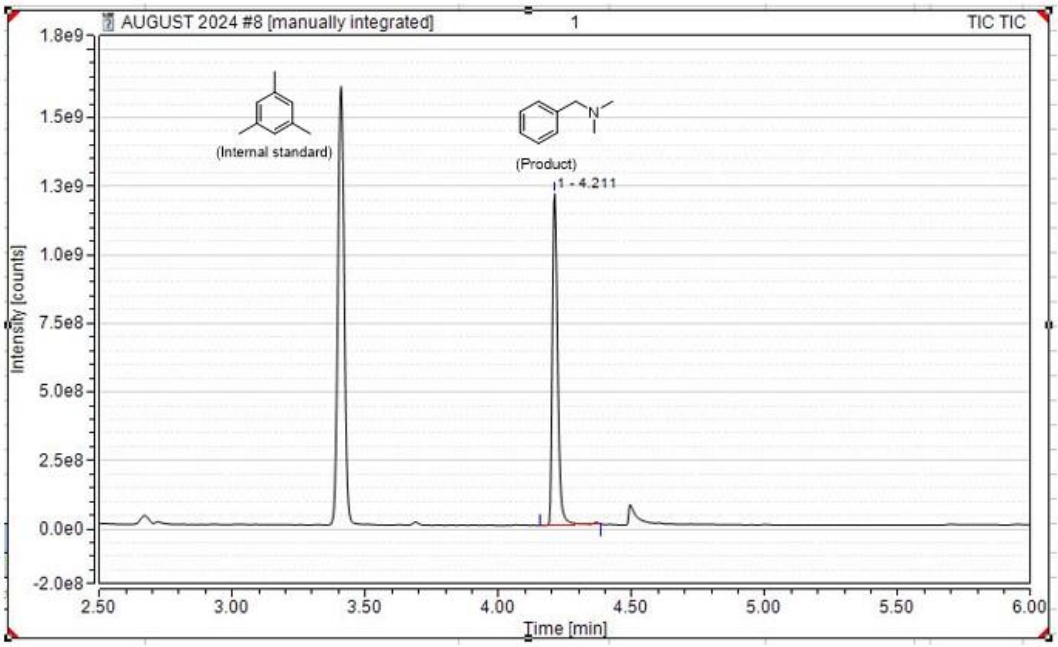
Table S1. Substrate scope of transfer hydrogenation of amides to amines with morpholine-borane.[a,b]



[a]Reaction conditions: benzamide (0.5 mmol), and morpholine borane (2 equiv.) were loaded in a thick-wall sealed tube inside the N_2-filled glove box and heated in a preheated oil-bath; [b]yield was calculated by GC-MS using mesitylene as internal standard.

7. GC chromatogram of the reaction mixture, peak reports and mass spectra of various products:

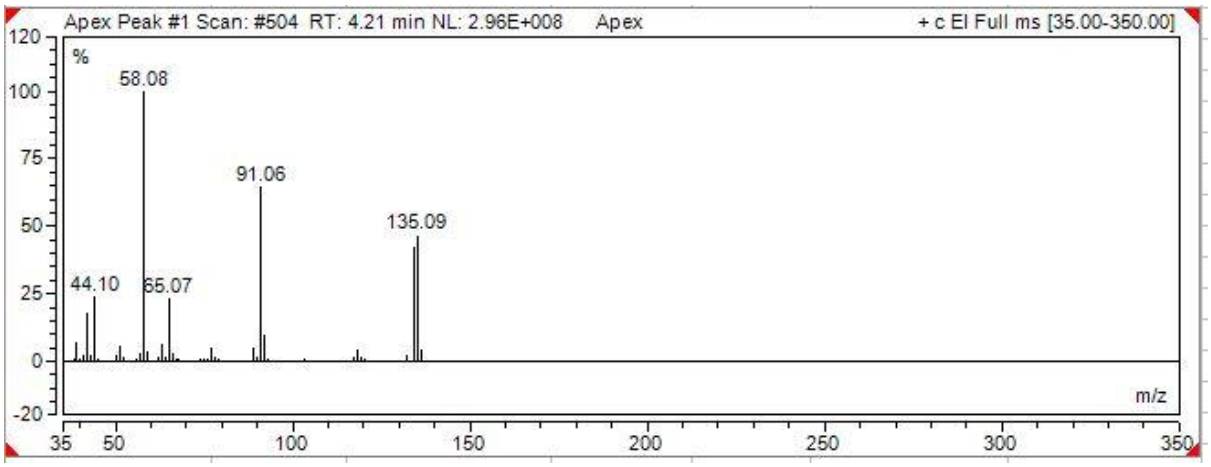
(i) GC Chromatogram of the reaction mixture of Table 3, compound 3a:



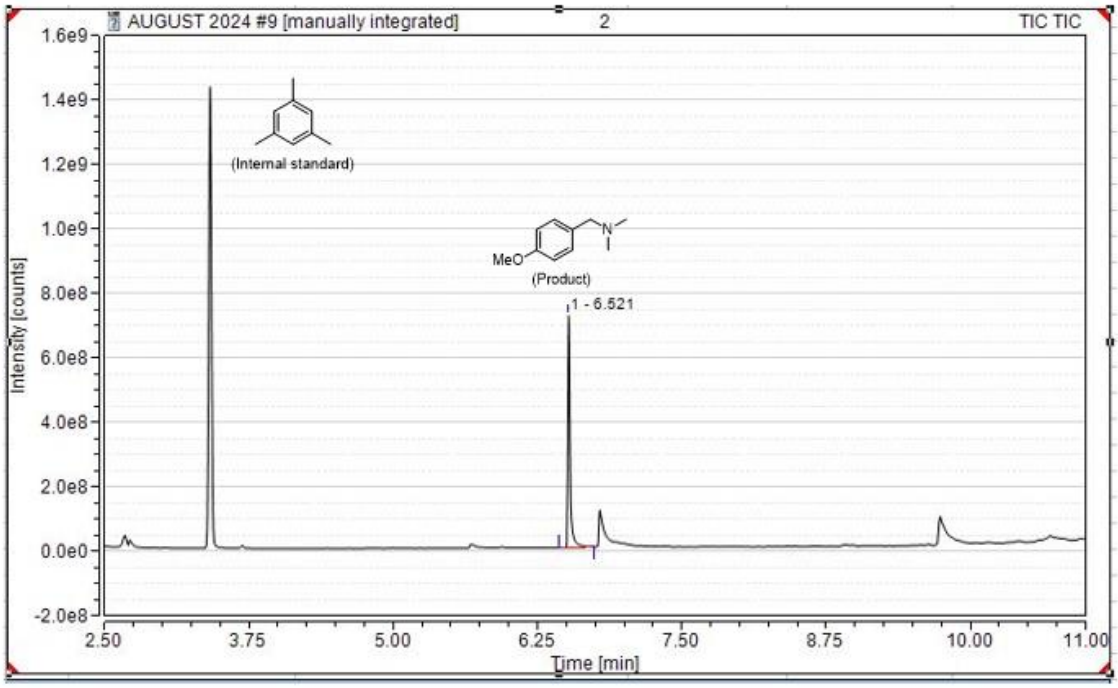
Peak Report

Peak	Retention Time (min)	Peak Area	Name
1	4.21	27975233	N,N-dimethylbenzylamine
2	3.41	44291926	Mesitylene

ESI-MS Spectra of N,N-dimethylbenzylamine



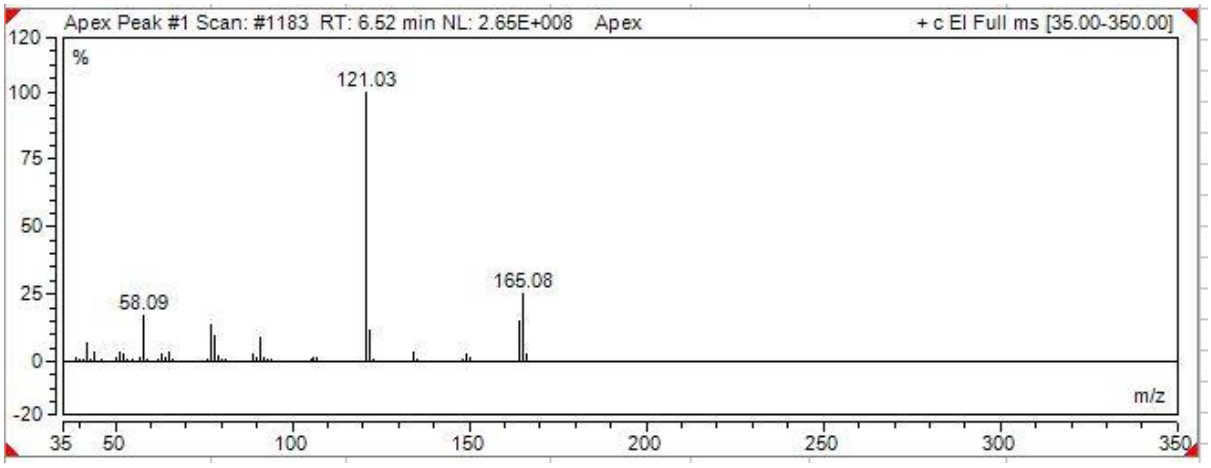
(ii) GC Chromatogram of the reaction mixture of Table 3, compound 3b:



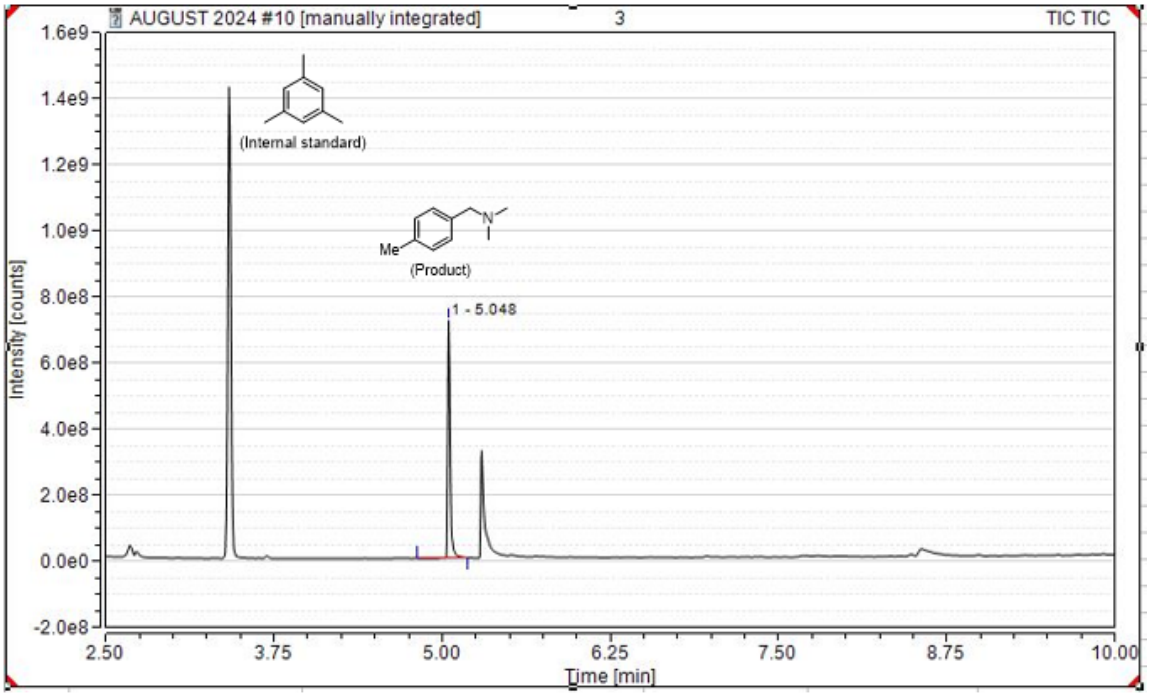
Peak Report

Peak	Retention Time (min)	Peak Area	Name
1	6.52	16450648	4-methoxy-N,N-dimethylbenzylamine
2	3.41	39248180	Mesitylene

ESI-MS Spectra of 4-methoxy-N,N-dimethylbenzylamine



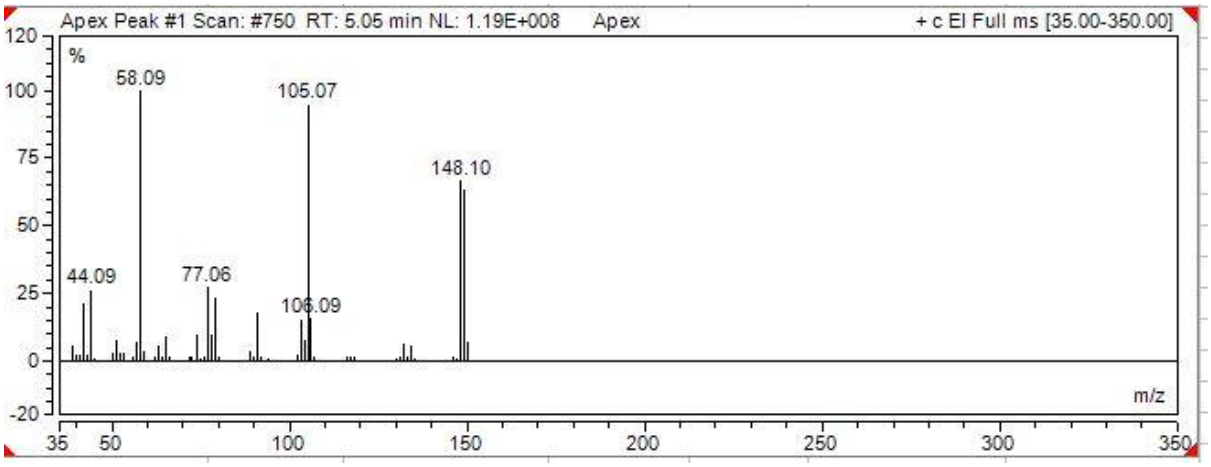
(iii) GC Chromatogram of the reaction mixture of Table 3, compound 3c:



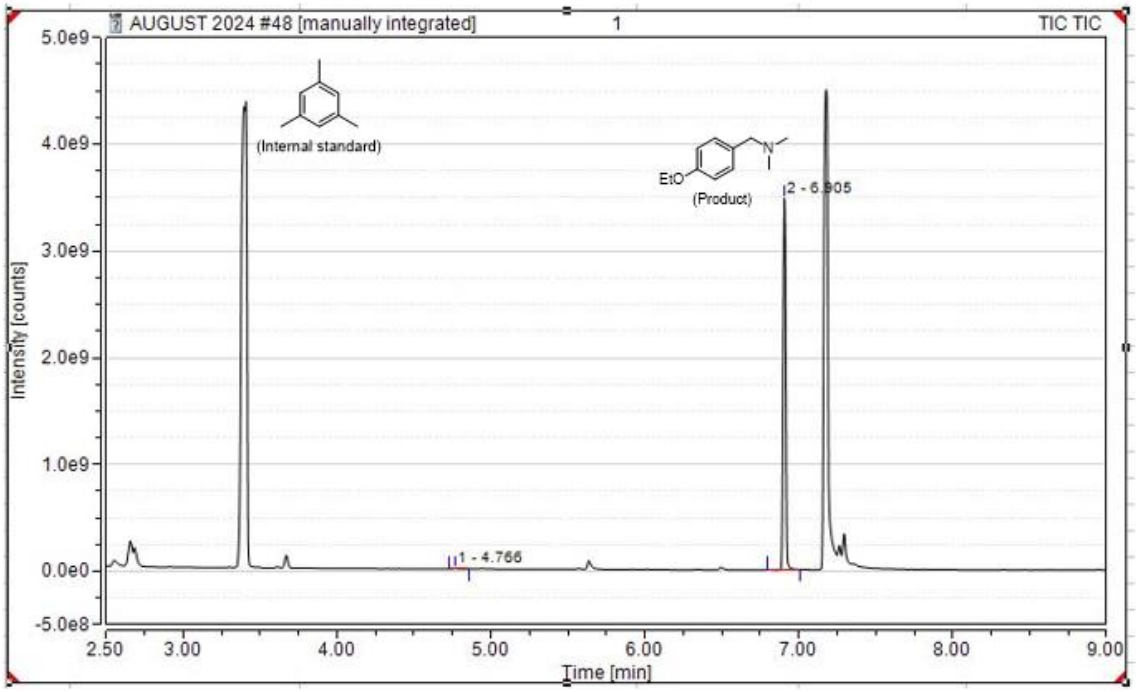
Peak Report

Peak	Retention Time (min)	Peak Area	Name
1	5.05	15081622	4-methyl-N,N-dimethylbenzylamine
2	3.42	38632783	Mesitylene

ESI-MS Spectra of 4-methyl-N,N-dimethylbenzylamine



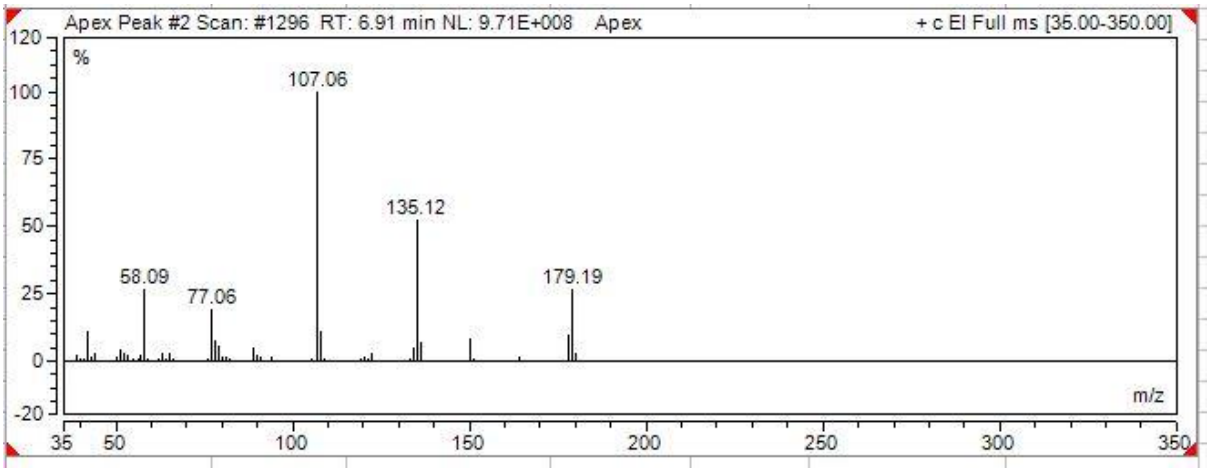
(iv) GC Chromatogram of the reaction mixture of Table 3, compound 3d:



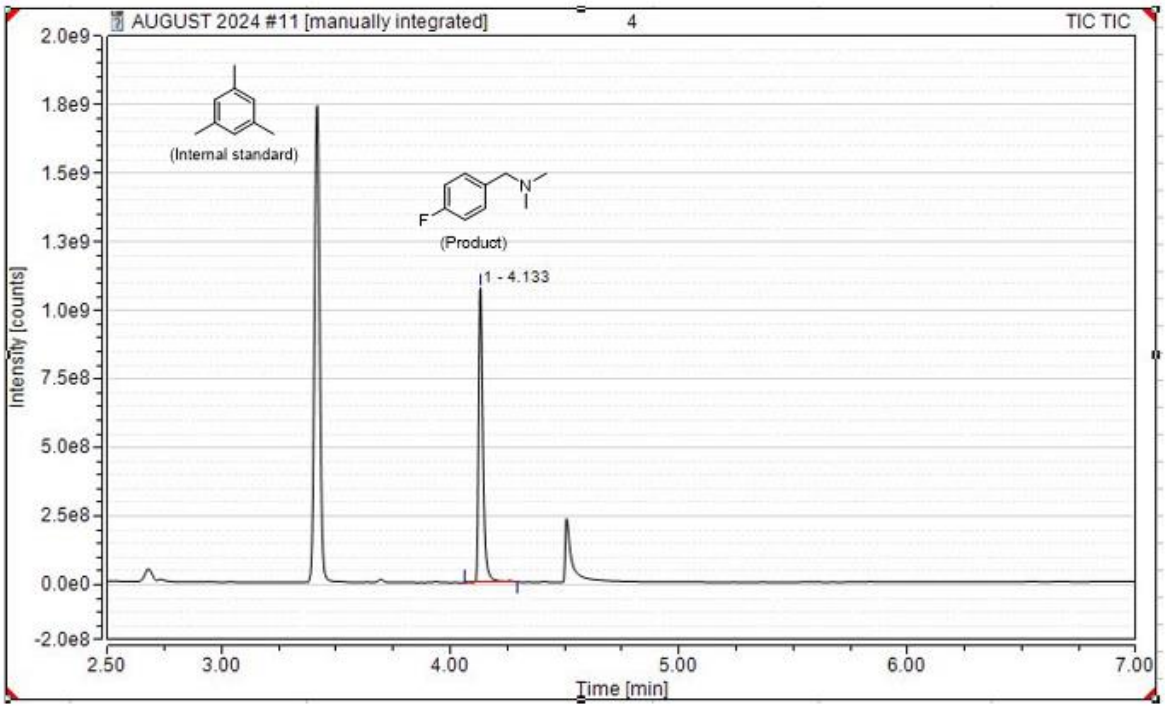
Peak Report

Peak	Retention Time (min)	Peak Area	Name
1	6.91	67396071	4-ethoxy-N,N-dimethylbenzylamine
2	3.41	178471504	Mesitylene

ESI-MS Spectra of 4-ethoxy-N,N-dimethylbenzylamine



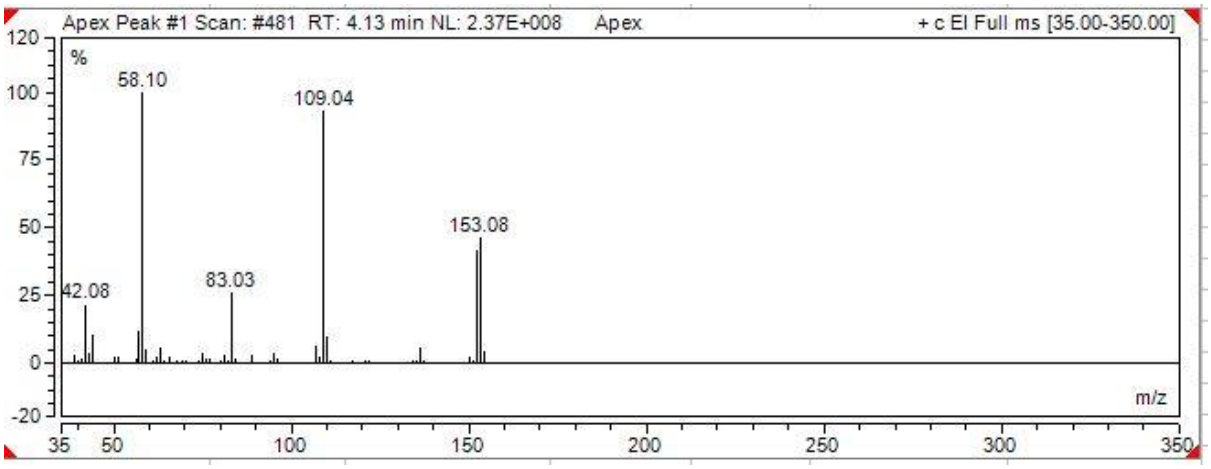
(v) GC Chromatogram of the reaction mixture of Table 3, compound 3e:



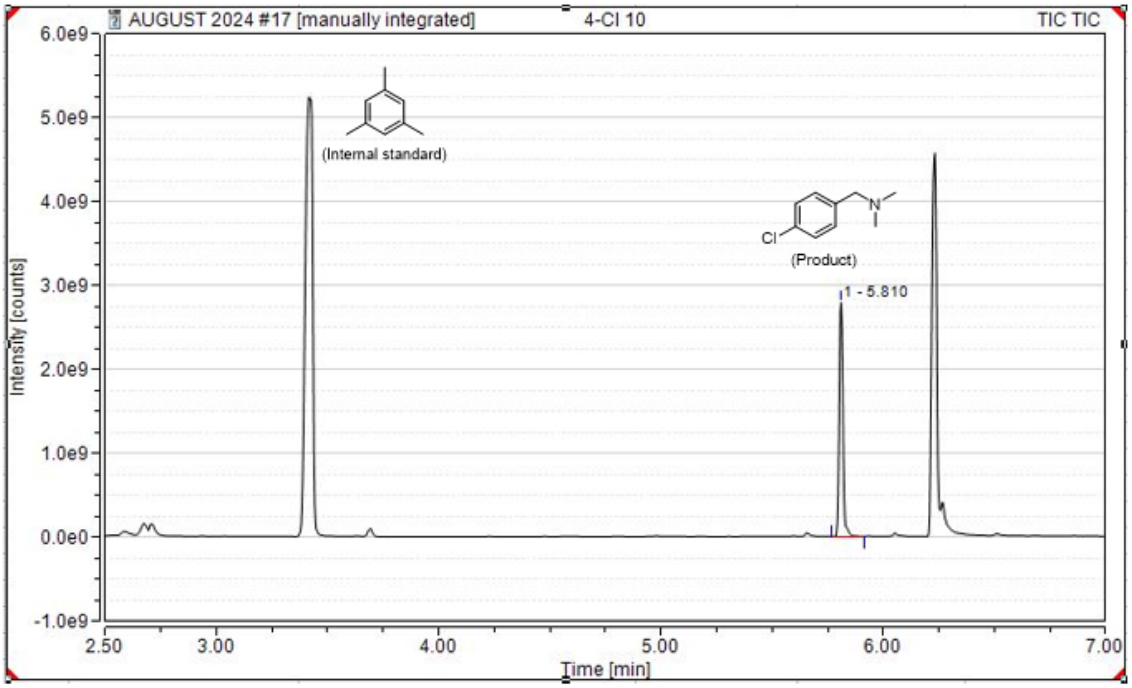
Peak Report

Peak	Retention Time (min)	Peak Area	Name
1	4.13	23363311	4-fluoro-N,N-dimethylbenzylamine
2	3.42	47012889	Mesitylene

ESI-MS Spectra of 4-fluoro-N,N-dimethylbenzylamine



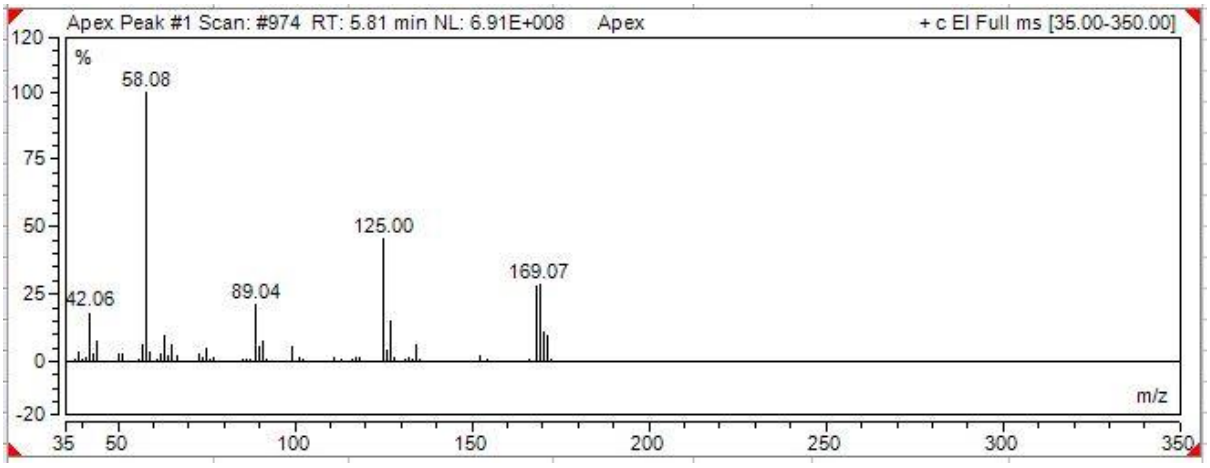
(vi) GC Chromatogram of the reaction mixture of Table 3, compound 3f:



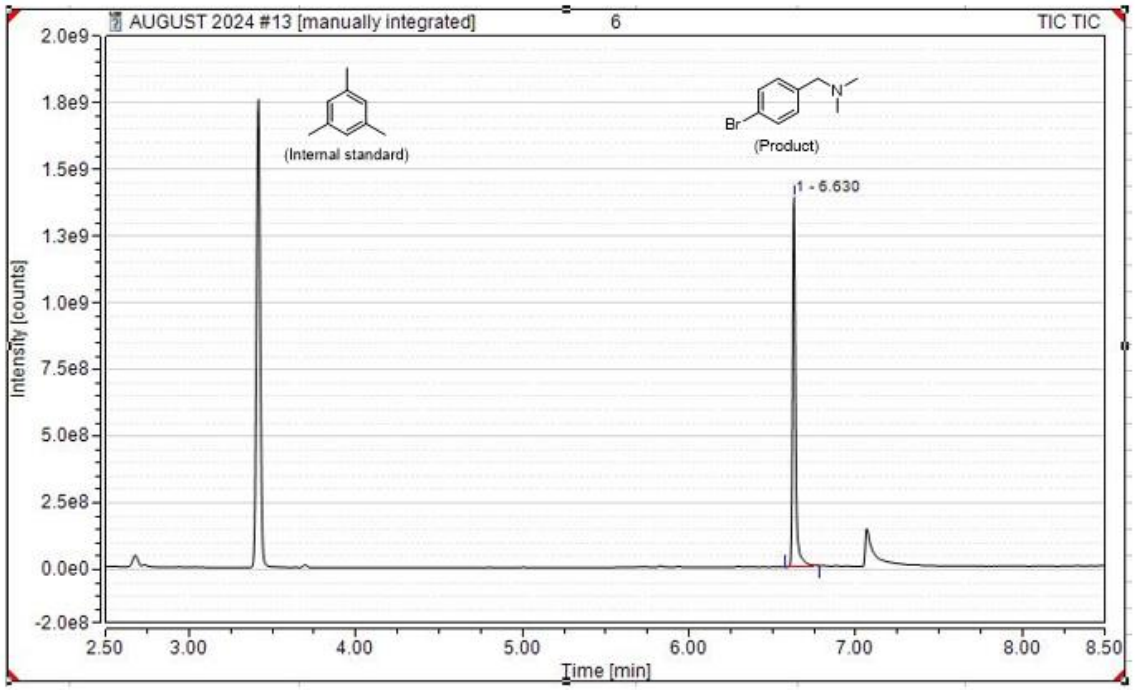
Peak Report

Peak	Retention Time (min)	Peak Area	Name
1	5.81	53708021	4-chloro-N,N-dimethylbenzylamine
2	3.42	203425639	Mesitylene

ESI-MS Spectra of 4-chloro-N,N-dimethylbenzylamine



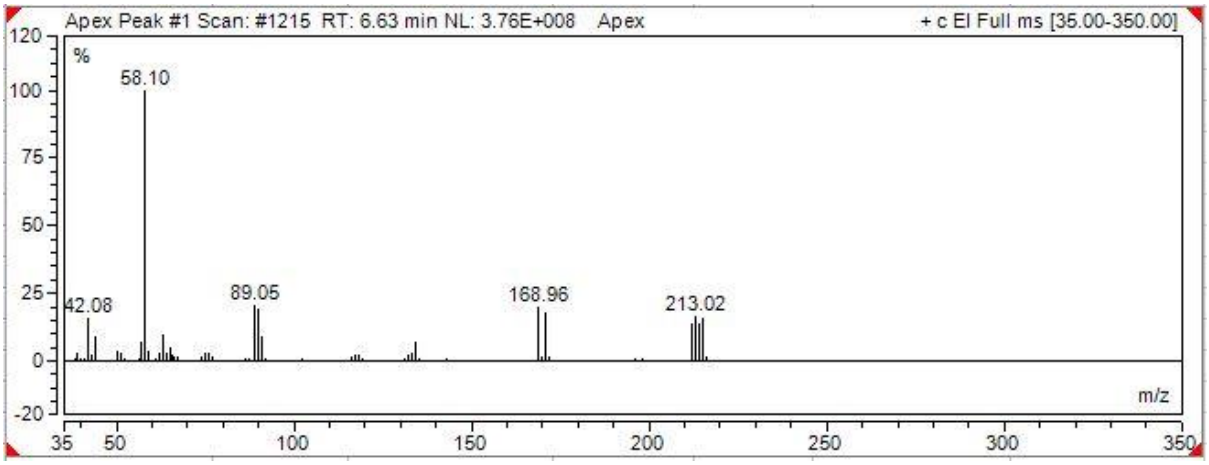
(vii) GC Chromatogram of the reaction mixture of Table 3, compound 3g:



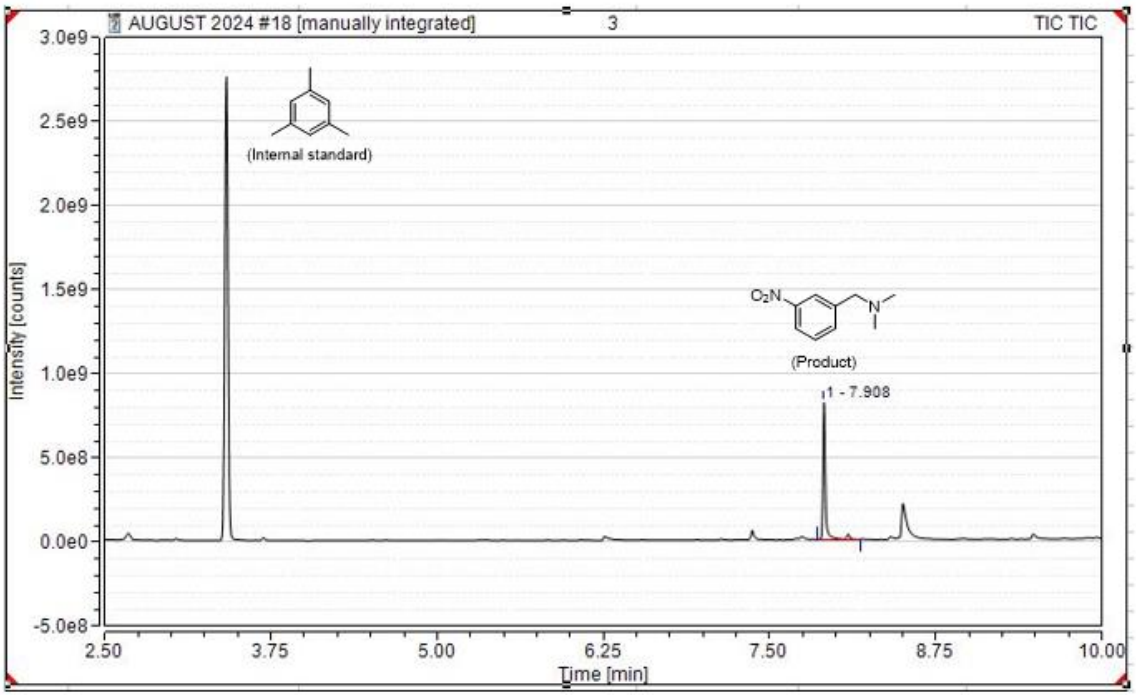
Peak Report

Peak	Retention Time (min)	Peak Area	Name
1	6.63	29040441	4-bromo-N,N-dimethylbenzylamine
2	3.42	46592324	Mesitylene

ESI-MS Spectra of 4-bromo-N,N-dimethylbenzylamine



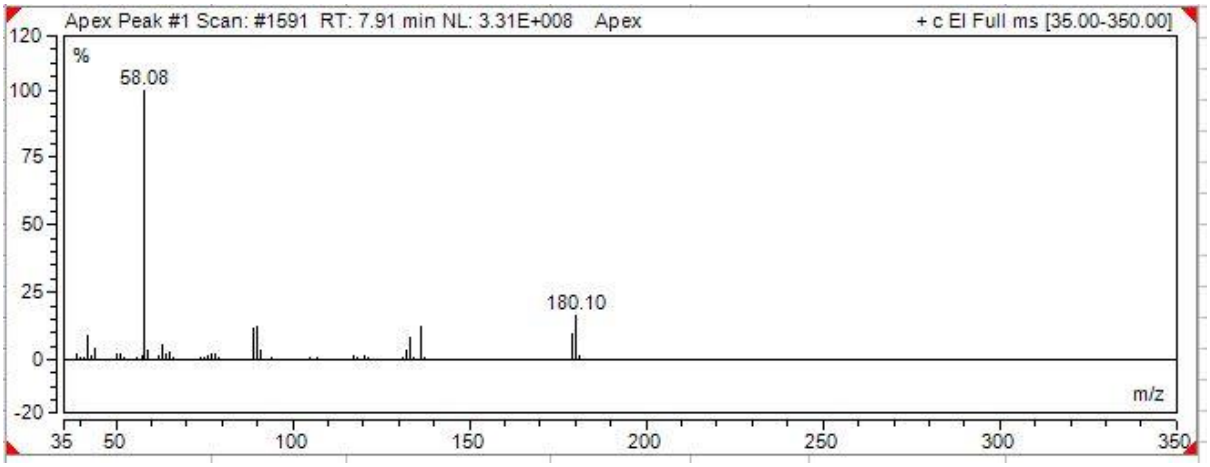
(viii) GC Chromatogram of the reaction mixture of Table 3, compound 3h:



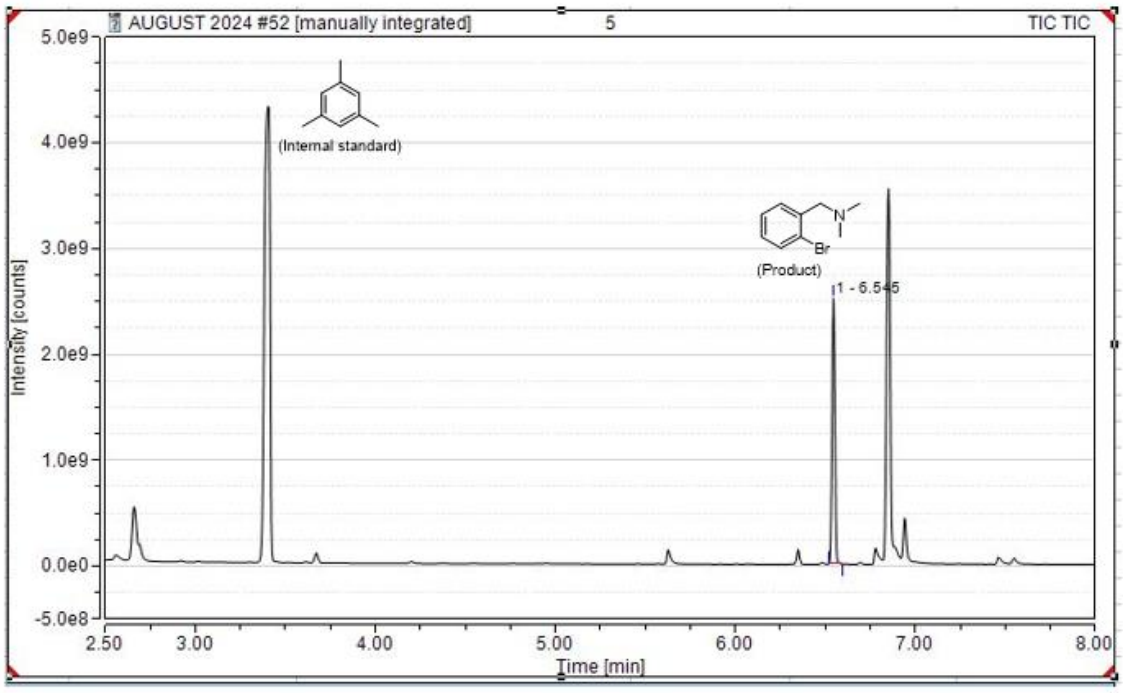
Peak Report

Peak	Retention Time (min)	Peak Area	Name
1	7.91	16466598	3-nitro-N,N-dimethylbenzylamine
2	3.42	78178739	Mesitylene

ESI-MS Spectra of 3-nitro-N,N-dimethylbenzylamine



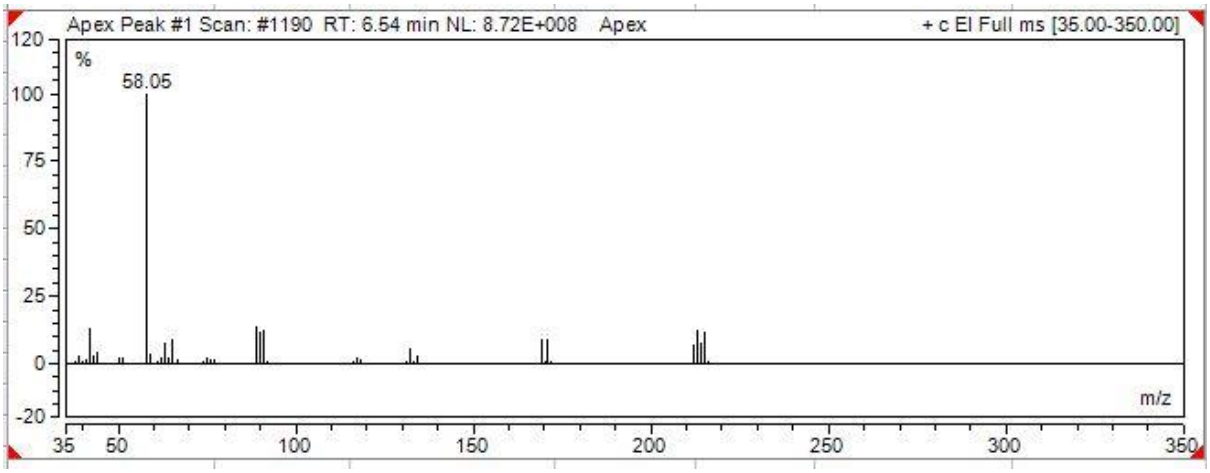
(ix) GC Chromatogram of the reaction mixture of Table 3, compound 3i:



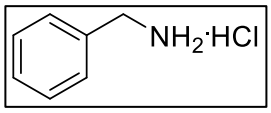
Peak Report

Peak	Retention Time (min)	Peak Area	Name
1	6.54	46321725	2-bromo-N,N-dimethylbenzylamine
2	3.41	154347569	Mesitylene

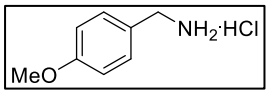
ESI-MS Spectra of 2-bromo-N,N-dimethylbenzylamine



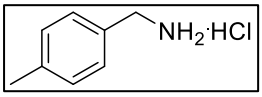
8. ^{1}H and ^{13}C NMR spectra of the isolated products:



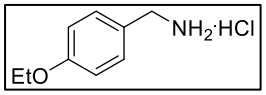
Phenylmethanamine hydrochloride[3]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.57 (s, 1H), 7.50 (d, *J* = 7.1 Hz, 2H), 7.37 (ddd, *J* = 10.9, 9.7, 5.8 Hz, 3H), 3.99 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 134.53, 129.41, 129.02, 128.86, 42.60.



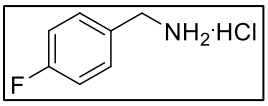
(4-methoxyphenyl)methanamine hydrochloride[3]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.52 (s, 3H), 7.44 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 3.92 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.78, 131.04, 126.43, 114.35, 55.66, 42.09.



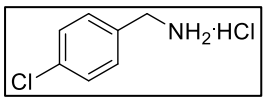
***p*-tolylmethanamine hydrochloride**[3]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.53 (s, 3H), 7.47 (t, *J* = 9.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.06 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 138.22, 131.54, 129.54, 129.38, 42.37, 21.21.



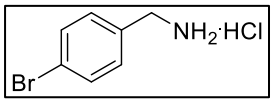
(4-ethoxyphenyl)methanamine hydrochloride: ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.33 (s, 3H), 7.40 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.93 (s, 2H), 1.33 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.10, 130.98, 126.28, 114.87, 63.56, 42.16, 15.05. HRMS (ESI) calcd for $[M\text{-}Cl]^{+}$: 152.1070, found: 152.1053



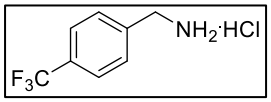
(4-fluorophenyl)methanamine hydrochloride[3]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.55 (s, 4H), 7.74 – 7.56 (m, 3H), 7.41 – 7.29 (m, 3H), 4.09 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.37, 131.79, 130.87, 115.92, 41.87.



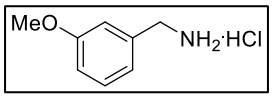
(4-chlorophenyl)methanamine hydrochloride[3]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.64 (s, 3H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 4.01 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 133.57, 133.5, 131.47, 128.94, 41.85.



(4-bromophenyl)methanamine hydrochloride[3]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.62 (s, 3H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 3.99 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 134.02, 131.88, 131.77, 122.15, 41.90.

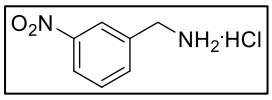


(4-(trifluoromethyl)phenyl)methanamine hydrochloride[4]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.63 (s, 3H), 7.93 (dd, *J* = 21.4, 8.2 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 4.24 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 139.28, 130.20, 129.57 – 129.44 (m), 125.90, 42.09.

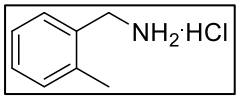


(3-methoxyphenyl)methanamine hydrochloride[5]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.52 (d, *J* = 58.8 Hz, 3H), 7.32 (td, *J* = 8.0, 4.2 Hz, 1H), 7.23 – 7.12 (m, 1H), 7.08 – 7.04 (m, 1H), 6.94 (dd, *J* = 8.2, 2.6 Hz,

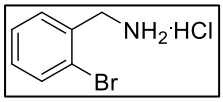
1H), 3.98 (d, *J* = 3.8 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.80, 136.04, 130.16, 121.40, 114.95, 114.39, 55.66, 42.54.



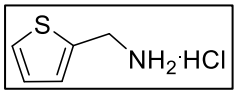
(3-nitrophenyl)methanamine hydrochloride: ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.68 (s, 3H), 8.45 (t, *J* = 1.8 Hz, 1H), 8.27 – 8.20 (m, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.75 – 7.67 (m, 1H), 4.18 (d, *J* = 5.3 Hz, 2H). HRMS (ESI) calcd for [M-Cl]$^{+}$: 153.0659, found: 153.0638.



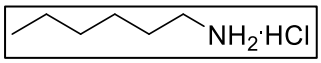
o-tolylmethanamine hydrochloride[6]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.48 (s, 3H), 7.41 (dd, *J* = 6.0, 2.9 Hz, 1H), 7.25 (dtd, *J* = 12.7, 7.4, 1.6 Hz, 3H), 3.99 (d, *J* = 18.1 Hz, 2H), 2.34 (s, 3H), ^{13}C NMR (151 MHz, DMSO-d_6) δ 137.13, 132.77, 130.78, 129.63, 128.95, 126.52, 19.27.



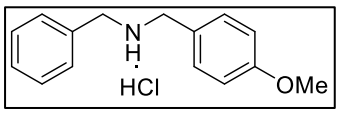
(2-bromophenyl)methanamine hydrochloride[6]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.77 (s, 3H), 7.73 – 7.63 (m, 2H), 7.54 – 7.41 (m, 1H), 7.39 – 7.28 (m, 1H), 4.12 – 4.07 (m, 2H).



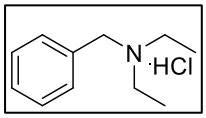
Thiophen-2-ylmethanamine hydrochloride[3]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.54 (s, 3H), 7.59 (ddd, *J* = 30.3, 5.1, 1.2 Hz, 1H), 7.36 – 7.20 (m, 1H), 7.15 – 7.02 (m, 1H), 4.20 (s, 2H).^{13}C NMR (151 MHz, DMSO-d_6) δ 135.77, 129.58, 127.75, 127.71, 37.12.



Hexan-1-amine hydrochloride[4]**:** ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.10 (s, 3H), 2.72 (dd, *J* = 16.7, 9.8 Hz, 2H), 1.62 – 1.47 (m, 2H), 1.37 – 1.19 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H).^{13}C NMR (151 MHz, DMSO-d_6) δ 39.16, 31.19, 27.31, 26.00, 22.35, 14.30.



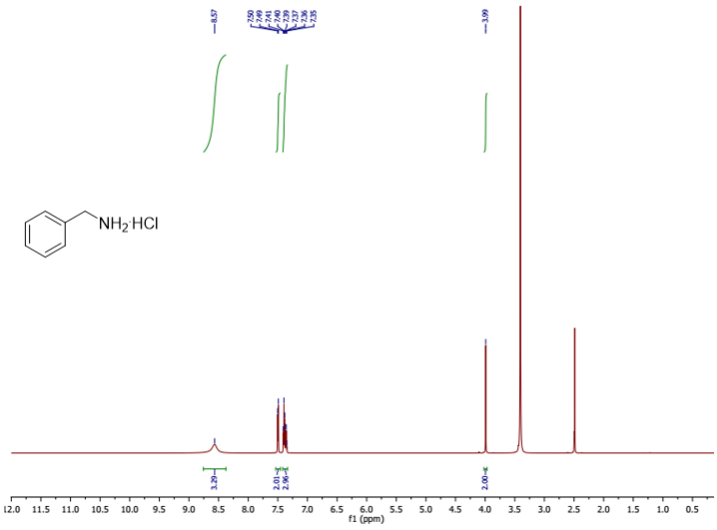
N-benzyl-1-(4-methoxyphenyl)methanamine: ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.72 (d, *J* = 105.1 Hz, 2H), 7.58 (d, *J* = 5.7 Hz, 2H), 7.50 (t, *J* = 10.3 Hz, 2H), 7.42 (d, *J* = 2.2 Hz, 3H), 7.03 – 6.94 (m, 2H), 4.08 (d, *J* = 17.6 Hz, 4H), 3.77 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.13, 132.46, 132.24, 130.59, 129.29, 129.04, 124.1, 114.39, 55.68, 49.65. HRMS (ESI) calcd for [M-Cl]$^{+}$: 212.3155, found: 212.3149



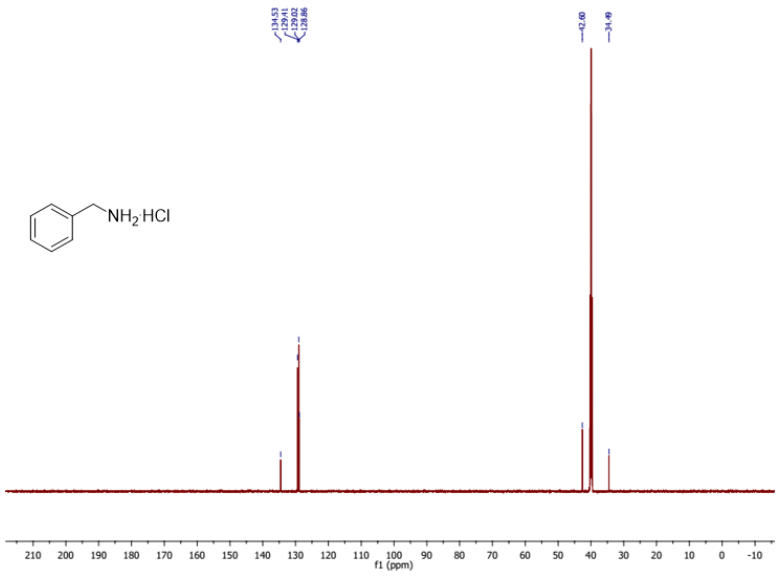
N-benzyl-N-ethylethanamine[4]**:** ^{1}H NMR (600 MHz, D_2O) δ 7.41 – 7.31 (m, 5H), 4.17 (s, 2H), 3.05 (q, *J* = 7.3 Hz, 4H), 1.18 – 1.13 (m, 6H).^{13}C NMR (151 MHz, D_2O) δ 130.79, 129.99, 129.37, 129.31, 55.94, 46.74, 8.03.

9. Copies of ^{1}H and ^{13}C NMR spectra of the isolated products:

(i) ^{1}H and ^{13}C spectra of 2a:

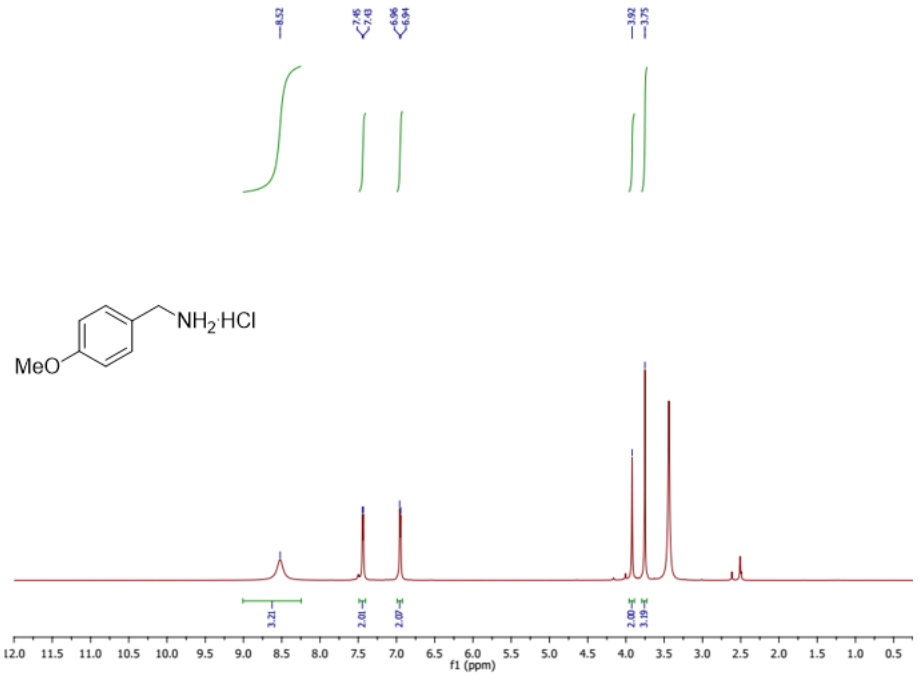


^{1}H spectrum of 2a in DMSO-d_6

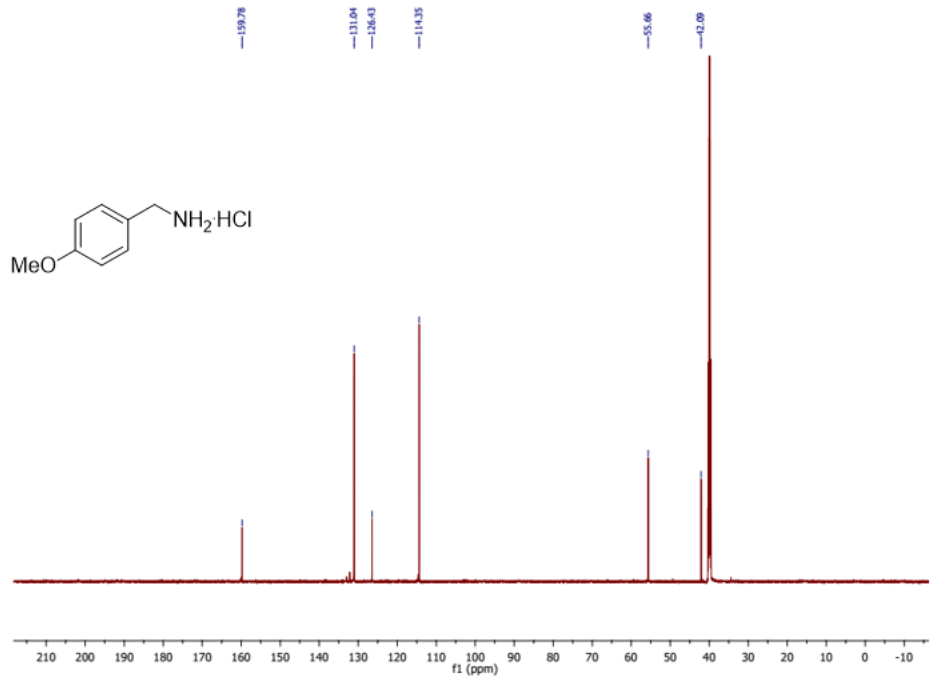


^{13}C spectrum of 2a in DMSO-d_6

(ii) ^{1}H and ^{13}C spectra of 2b:

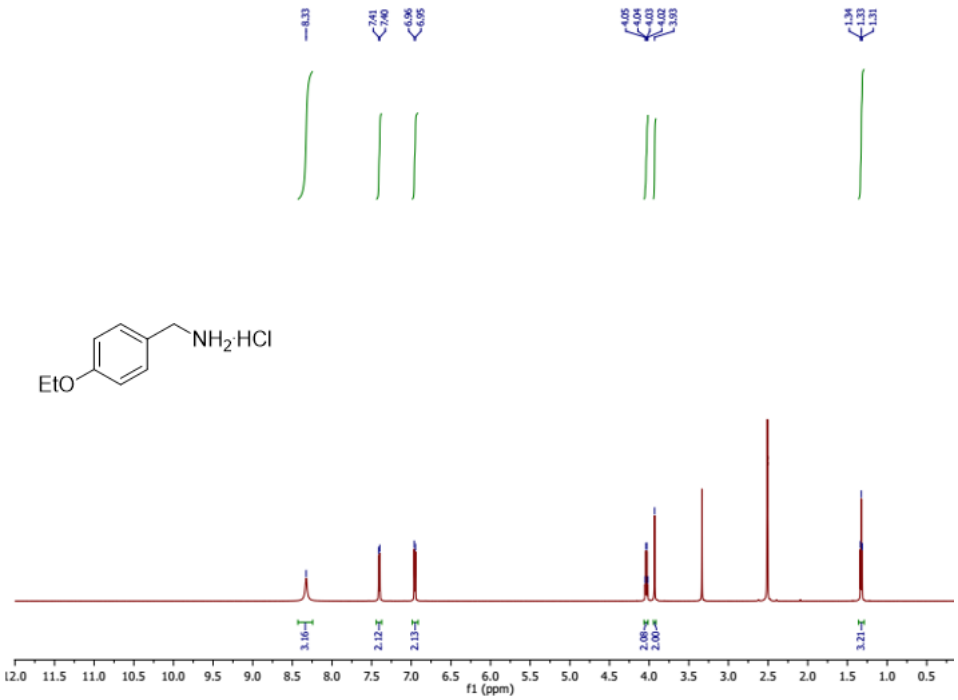


^{1}H spectrum of 2b in DMSO-d$_6$

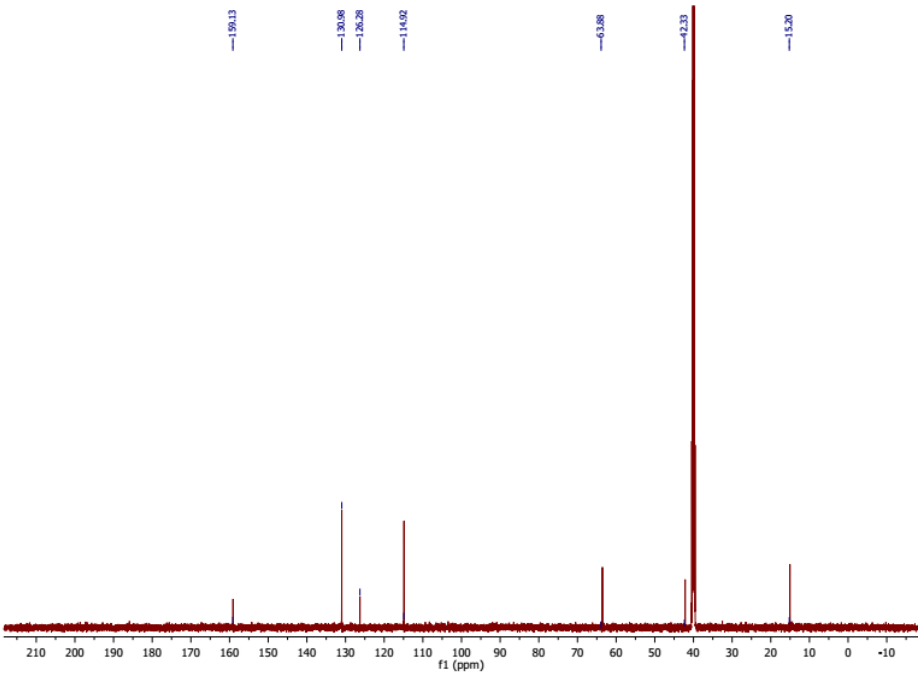


^{13}C spectrum of 2b in DMSO-d$_6$

(iii) ^{1}H and ^{13}C spectra of 2c:

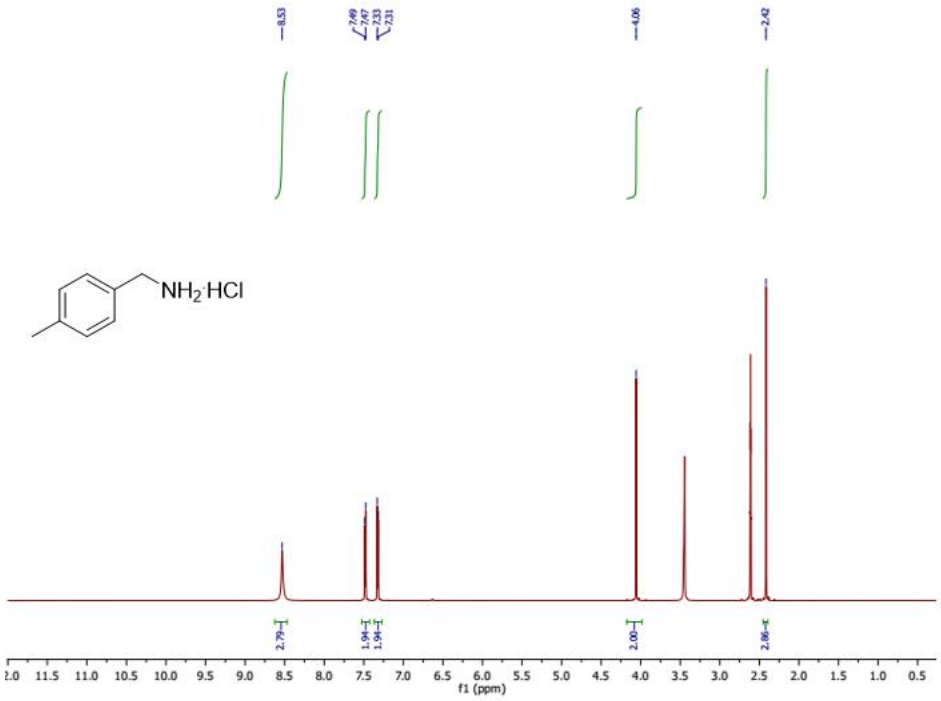


^{1}H spectrum of 2c in DMSO-d$_6$

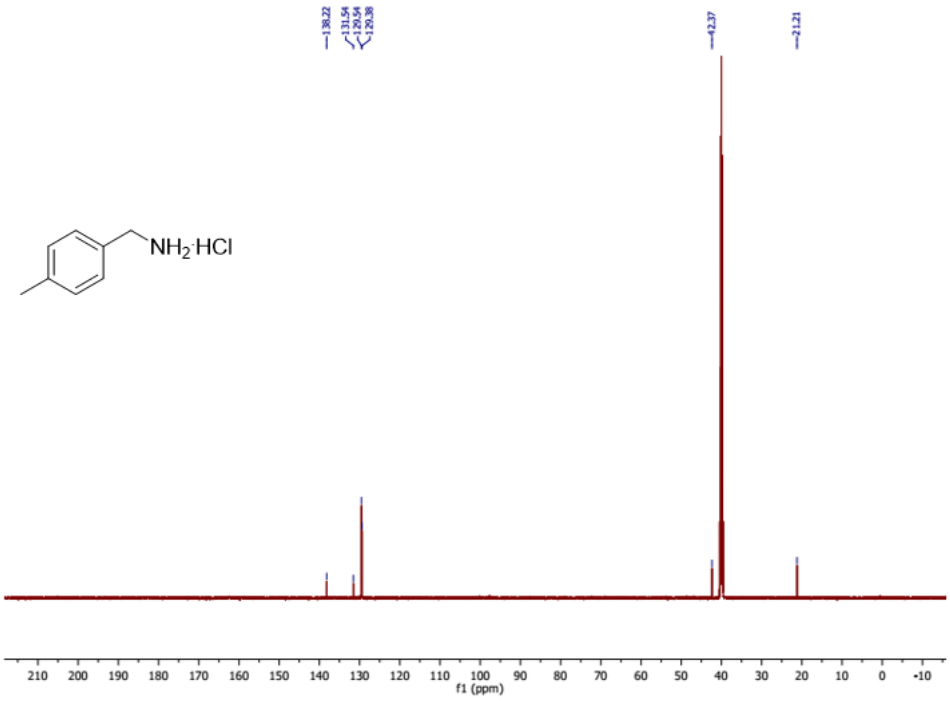


^{13}C spectrum of 2c in DMSO-d$_6$

(iv) ^{1}H and ^{13}C spectra of 2d:

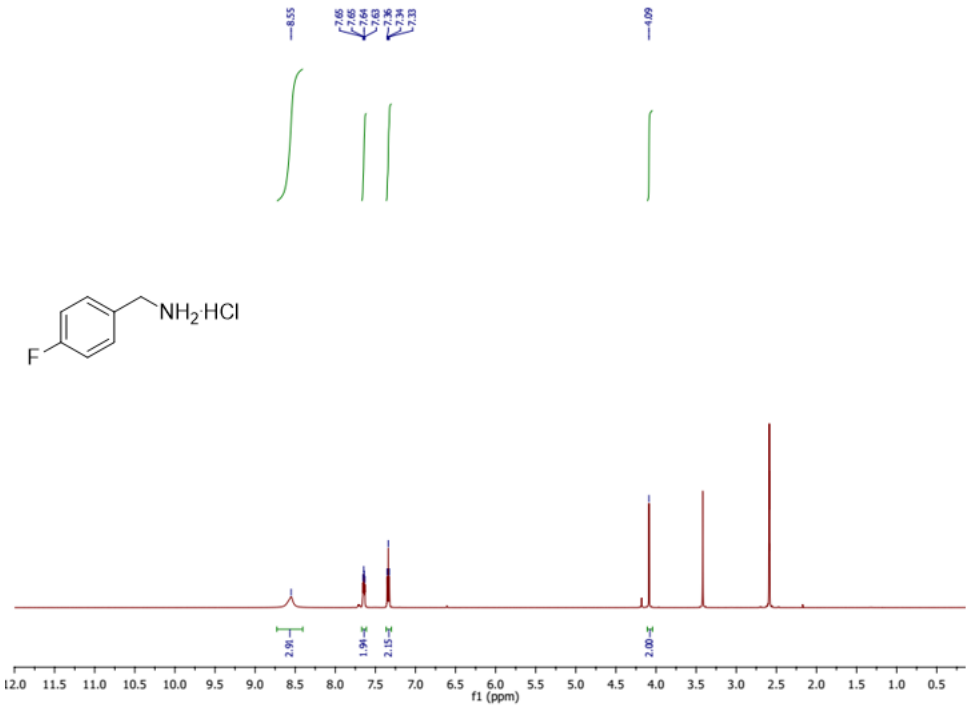


^{1}H spectrum of 2d in DMSO-d$_6$

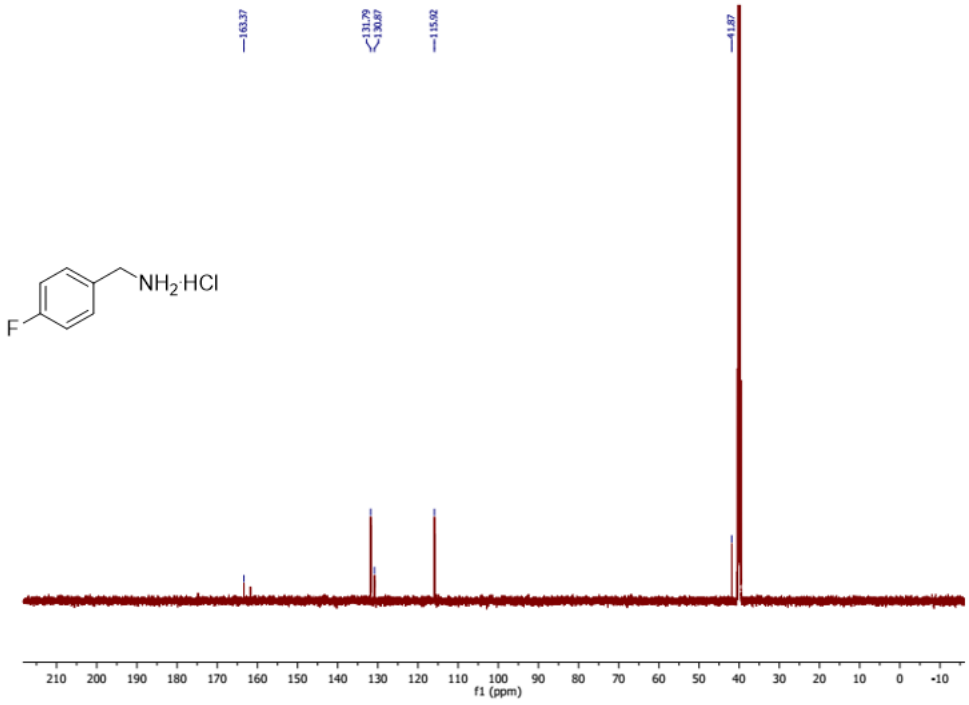


^{13}C spectrum of 2d in DMSO-d$_6$

(v) ^{1}H and ^{13}C spectra of 2e:

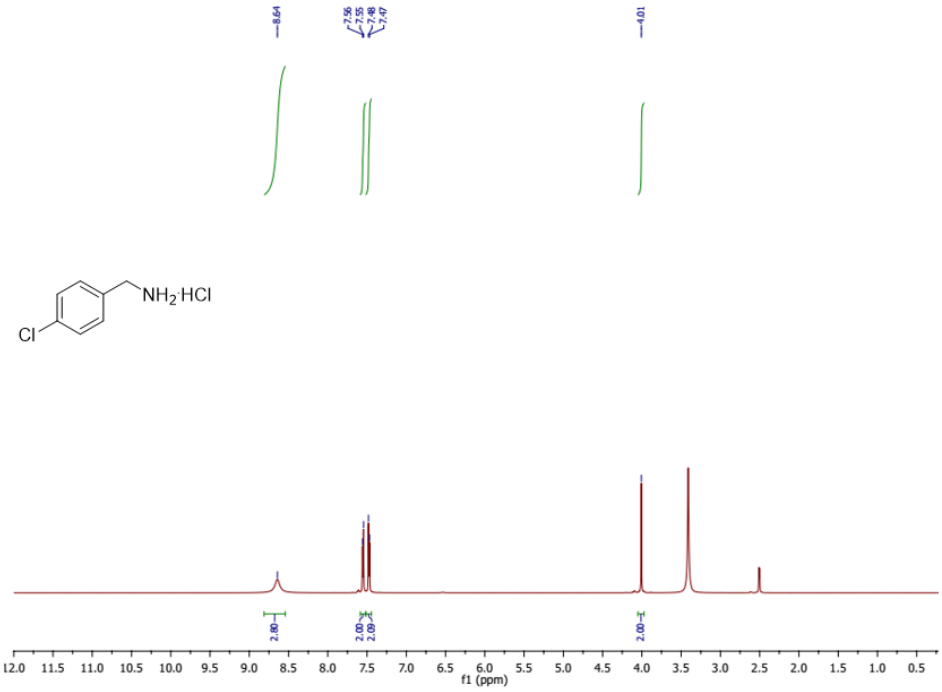


^{1}H spectrum of 2e in DMSO-d$_6$

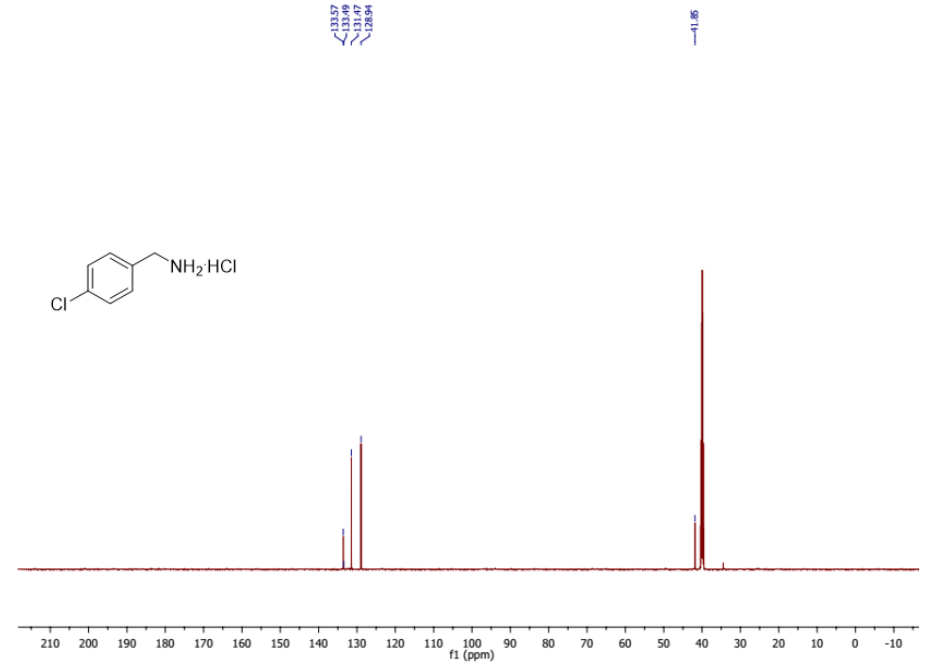


^{13}C spectrum of 2e in DMSO-d$_6$

(vi) ^{1}H and ^{13}C spectra of 2f:

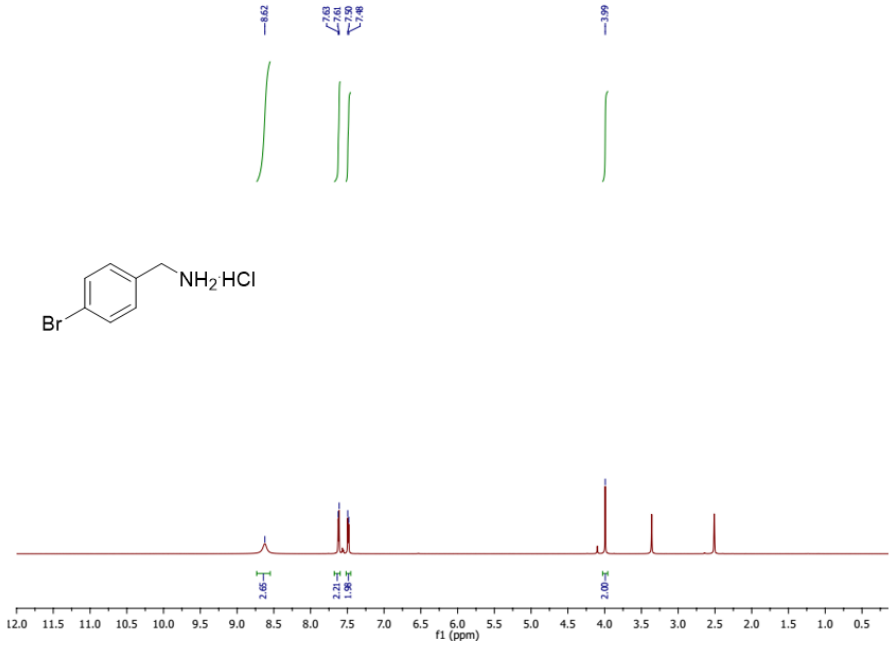


^{1}H spectrum of 2f in DMSO-d$_6$

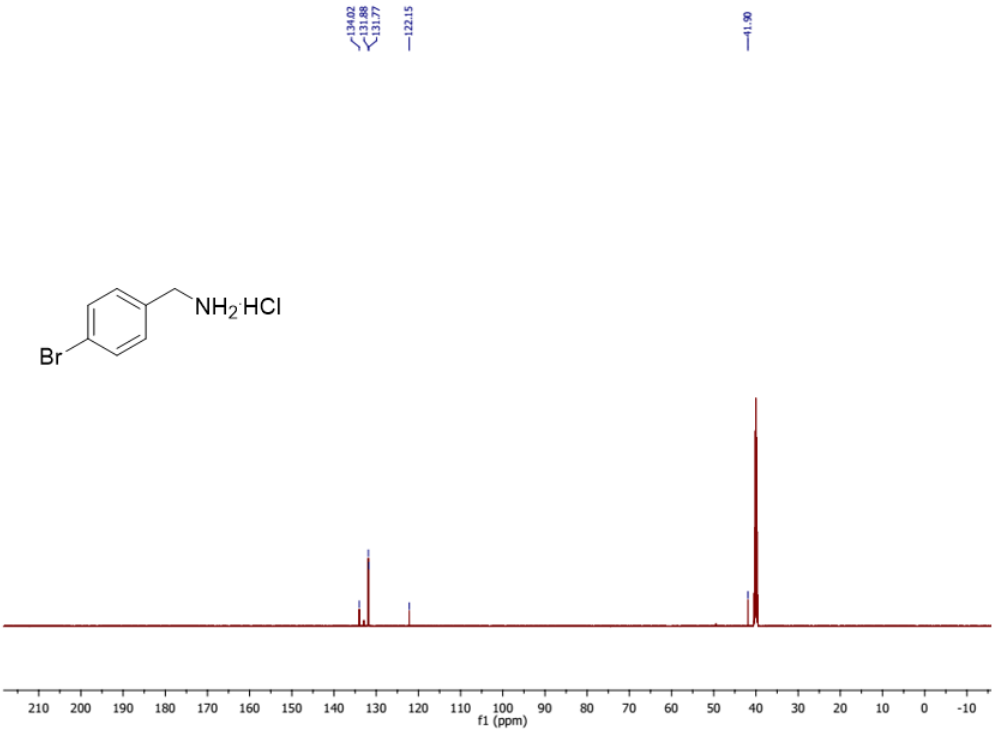


^{13}C spectrum of 2f in DMSO-d$_6$

(vii) ^{1}H and ^{13}C spectra of 2g:

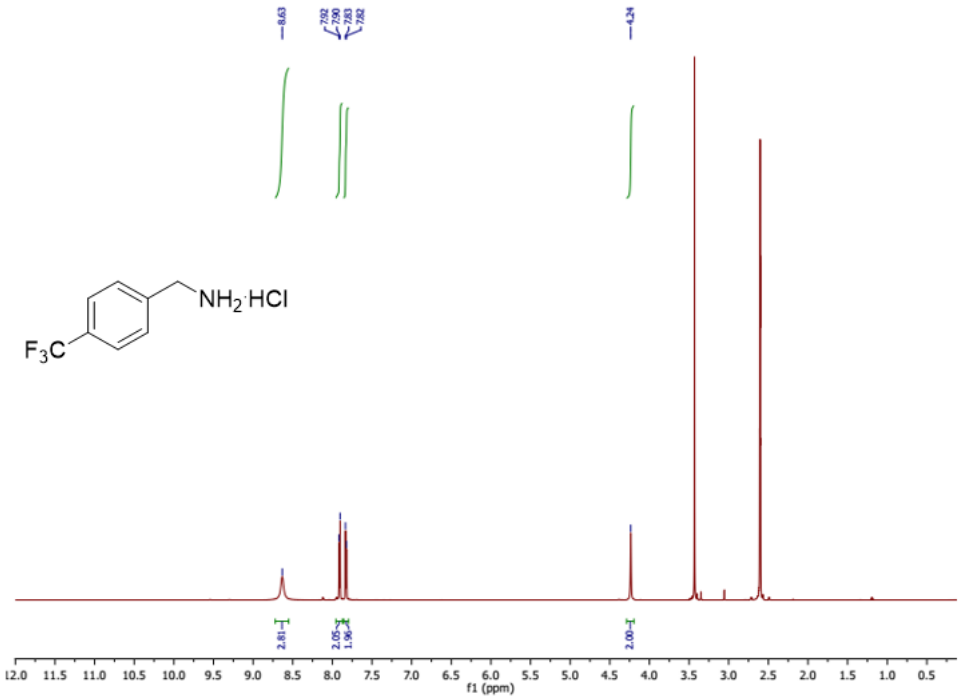


^{1}H spectrum of 2g in DMSO-d$_6$

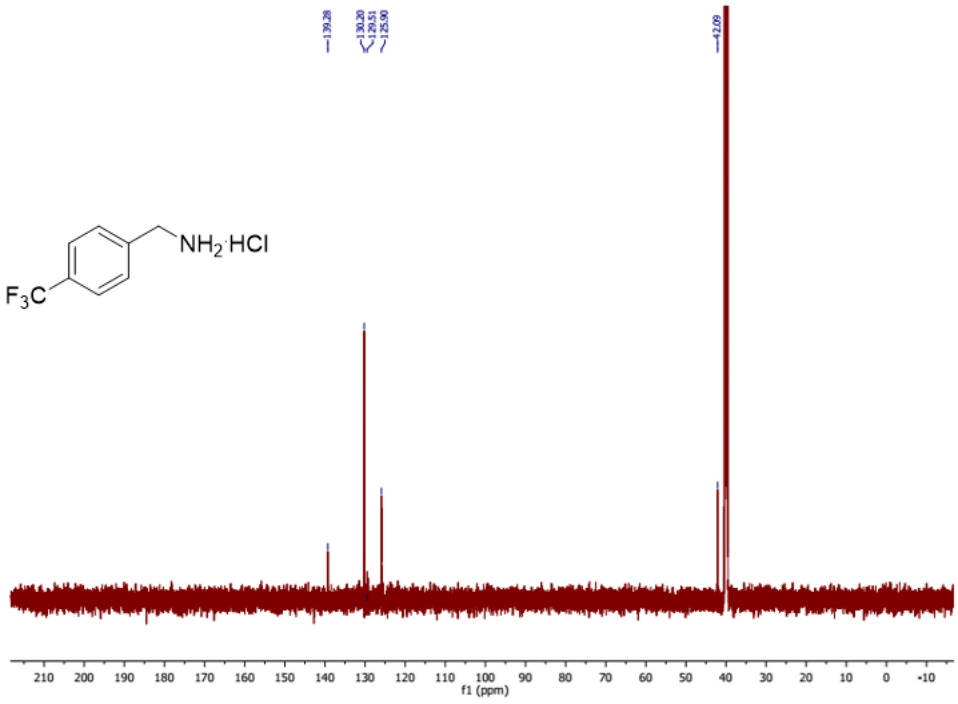


^{13}C spectrum of 2g in DMSO-d$_6$

(viii) ^{1}H and ^{13}C spectra of 2h:

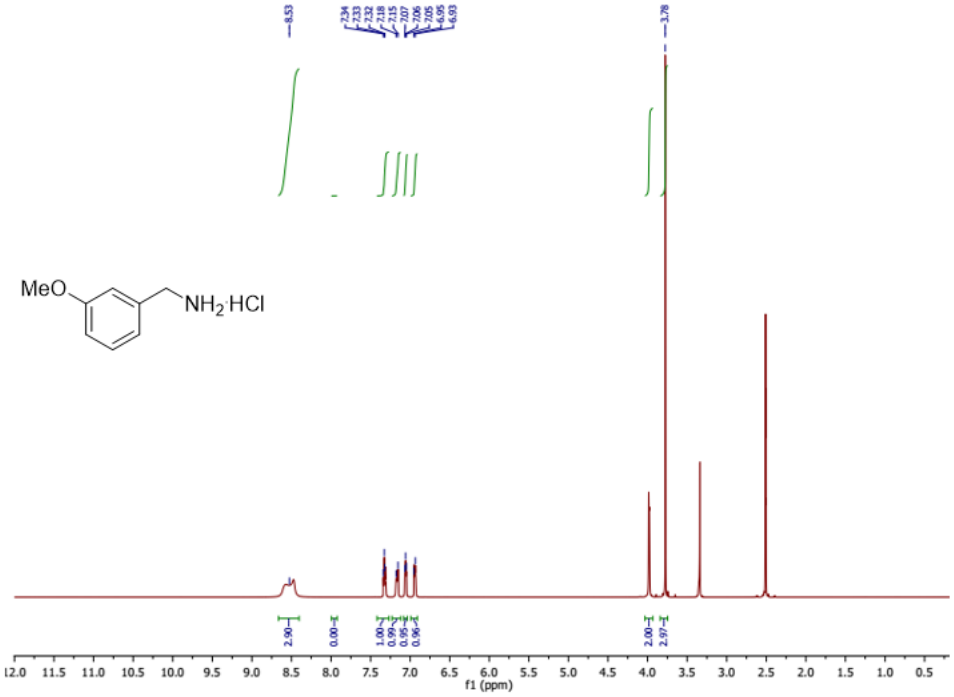


^{1}H spectrum of 2h in DMSO-d$_6$

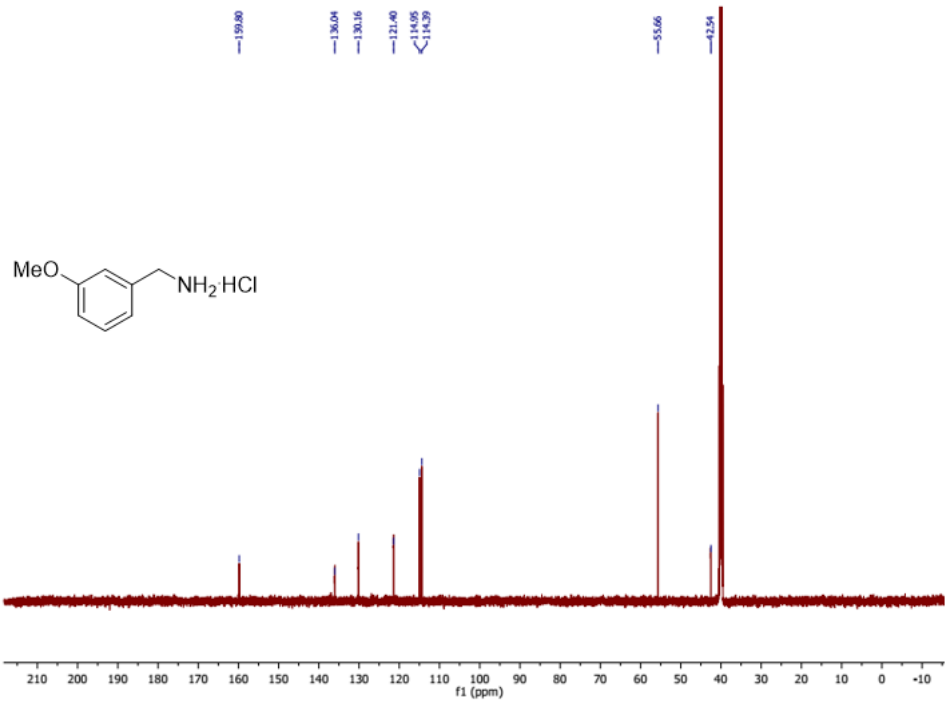


^{13}C spectrum of 2h in DMSO-d$_6$

(ix) ^{1}H and ^{13}C spectra of 2i:

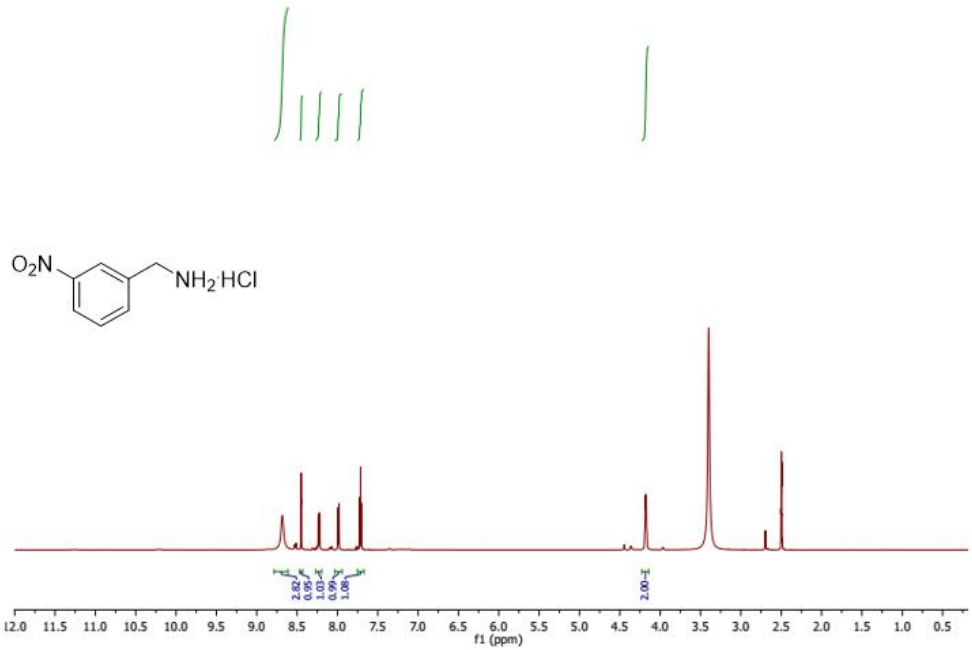


^{1}H spectrum of 2i in DMSO-d$_6$



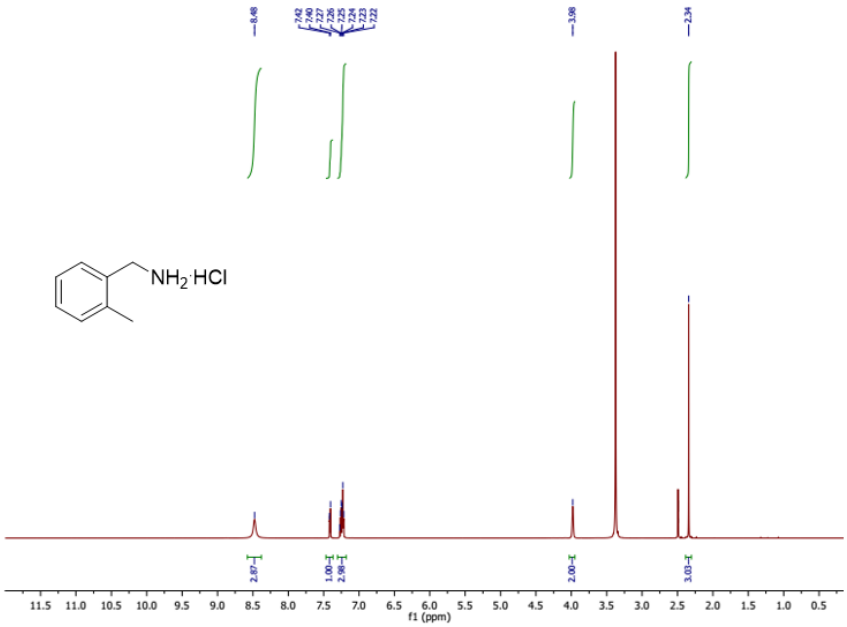
^{13}C spectrum of 2i in DMSO-d$_6$

(x) ^{1}H spectra of 2j:

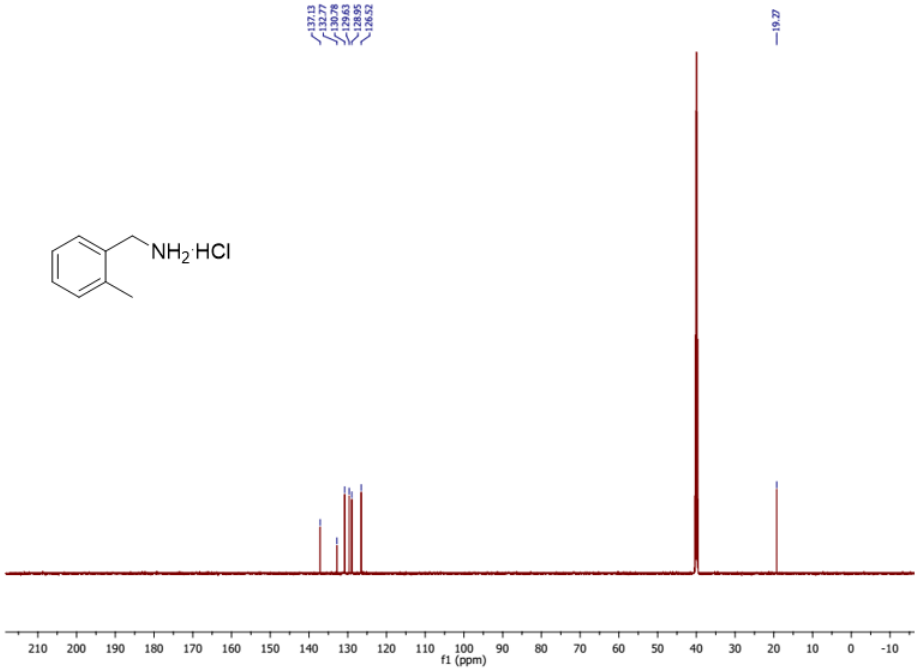


^{1}H spectrum of 2j in DMSO-d$_6$

(xi) ^{1}H and ^{13}C spectra of 2k:

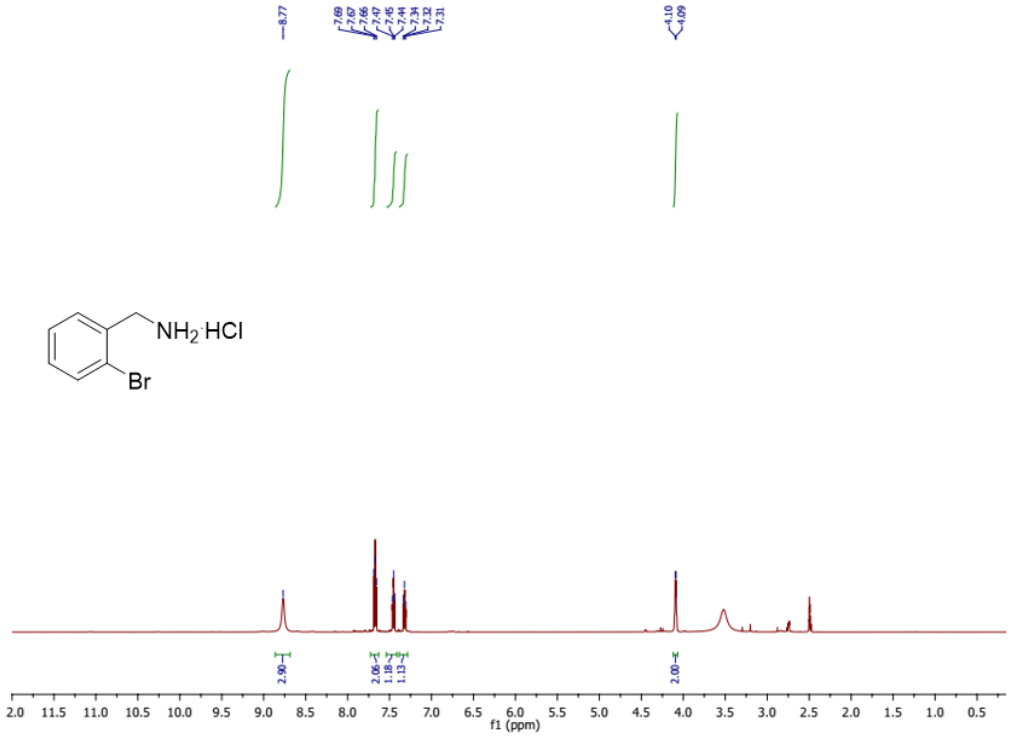


^{1}H spectrum of 2k in DMSO-d$_6$



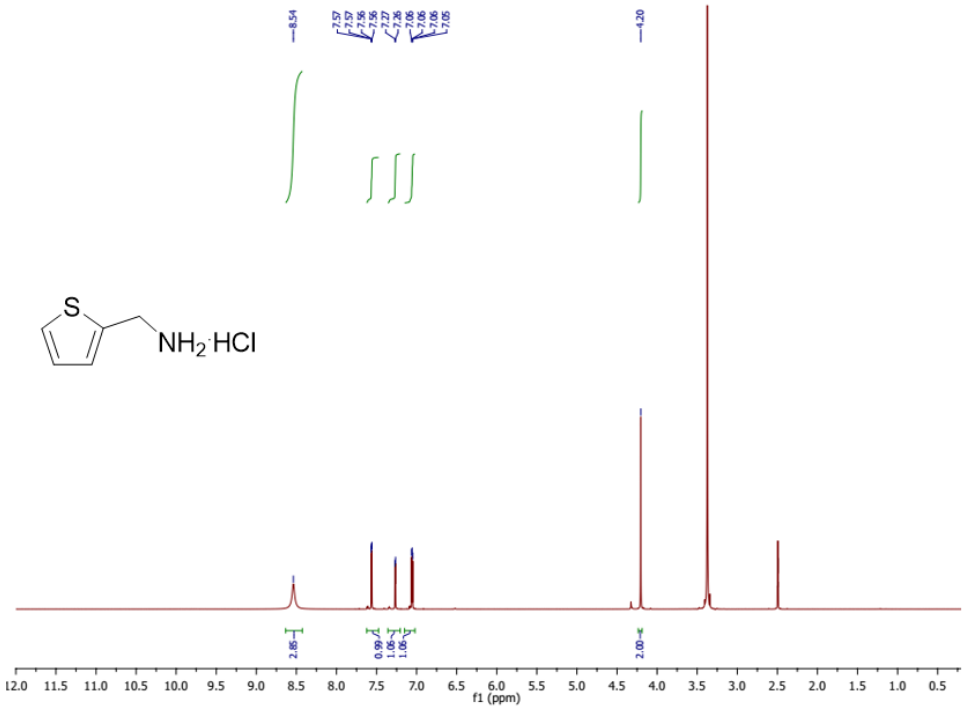
^{13}C spectrum of 2k in DMSO-d$_6$

(xii) ^{1}H spectra of 2l:

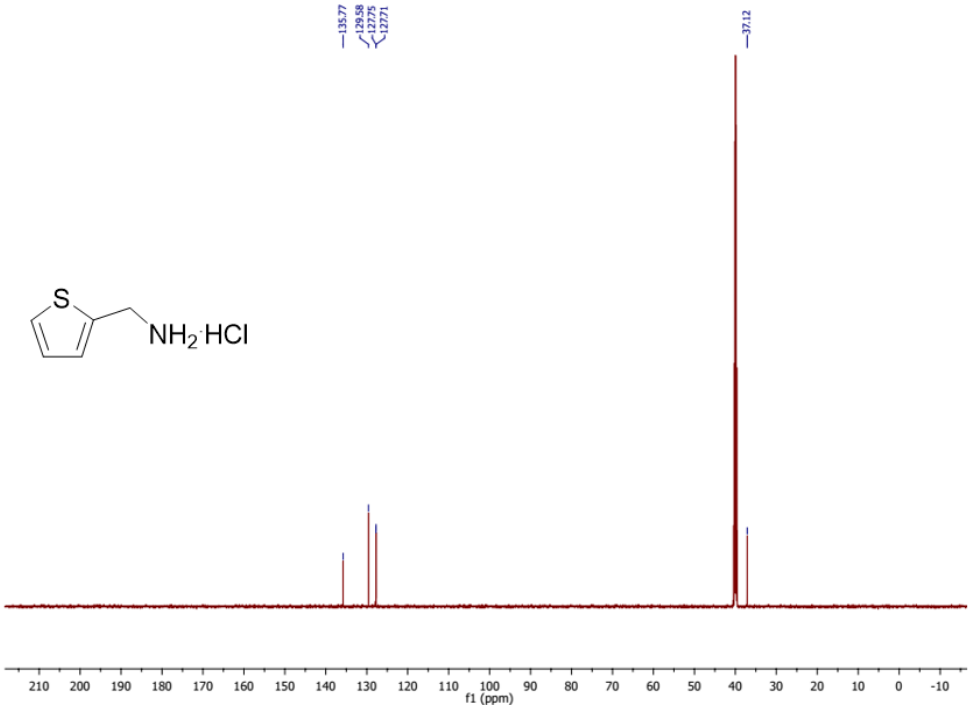


^{1}H spectrum of 2l in DMSO-d$_6$

(xiii) ^{1}H and ^{13}C spectra of 2m:

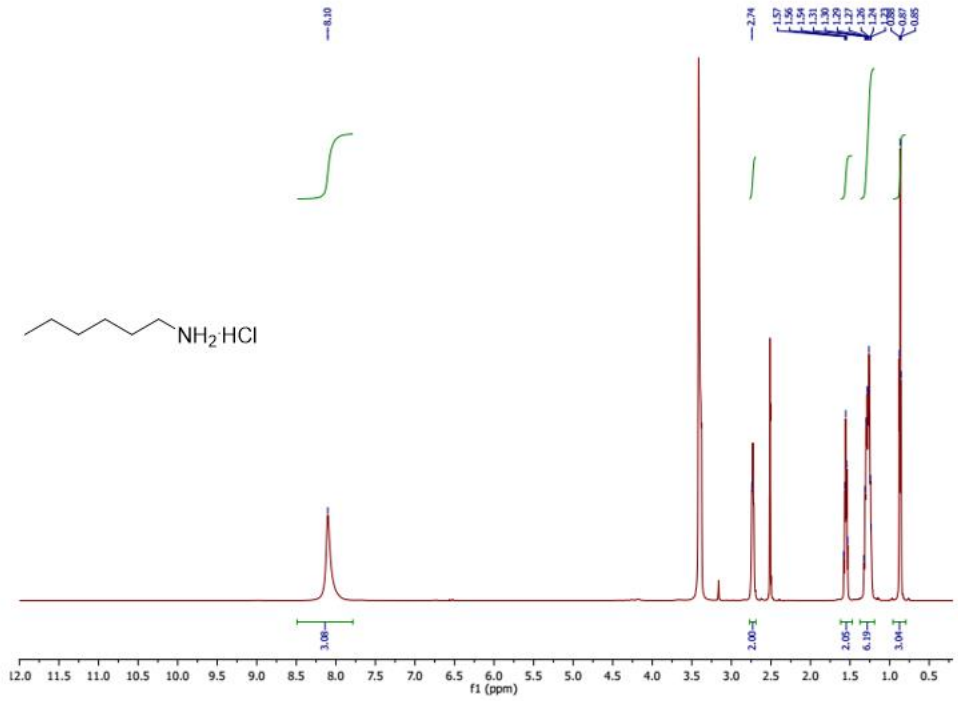


^{1}H spectrum of 2m in DMSO-d$_6$

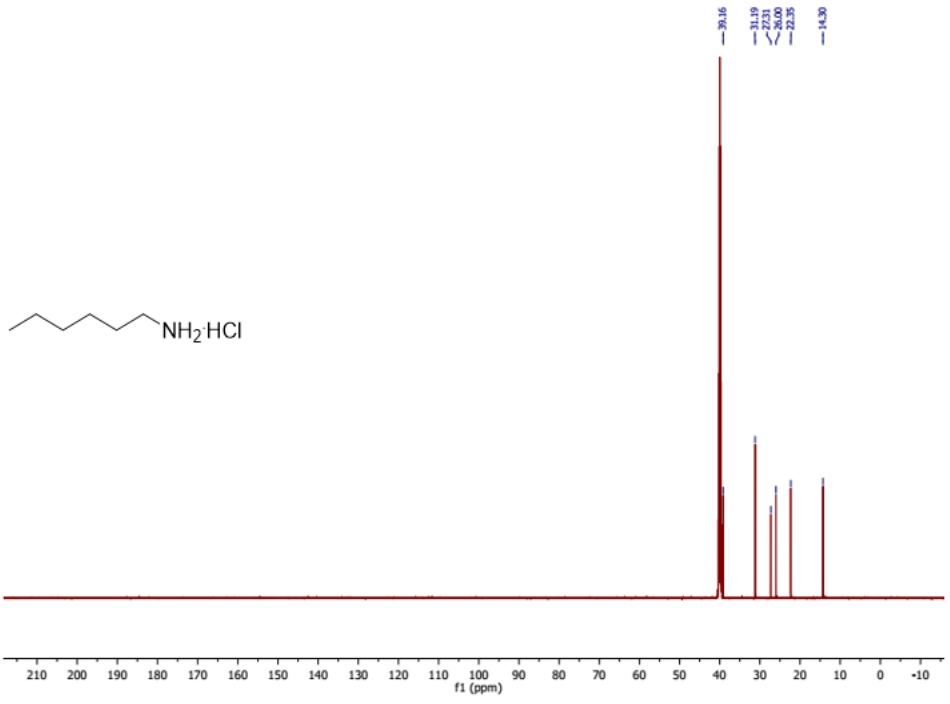


^{13}C spectrum of 2m in DMSO-d$_6$

(xiv) ^{1}H and ^{13}C spectra of 2n:

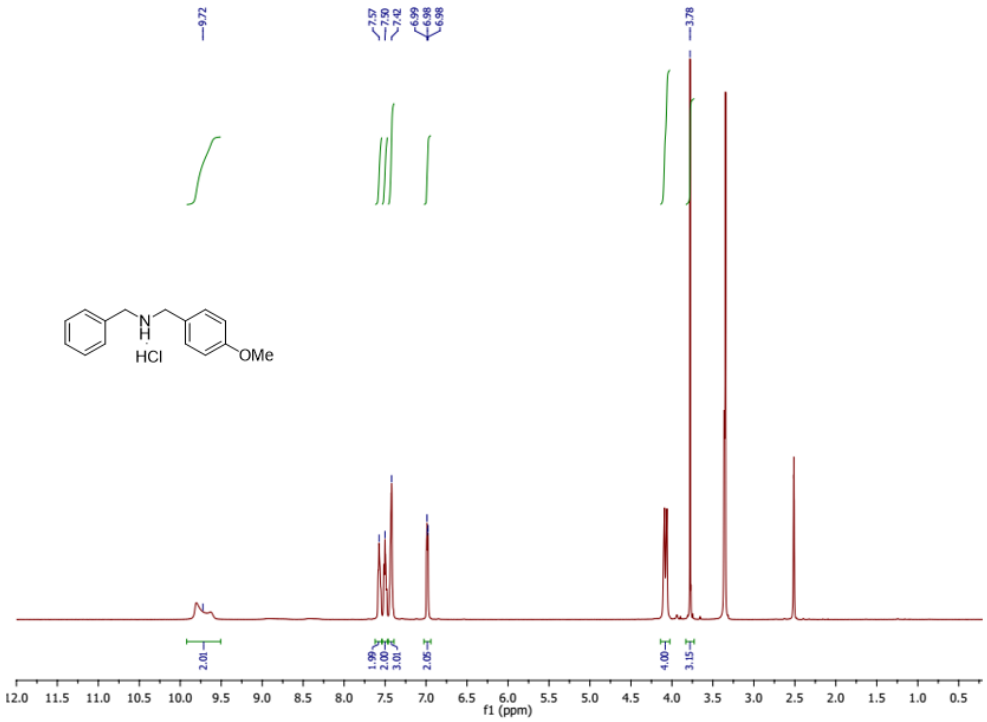


^{1}H spectrum of 2n in DMSO-d$_6$

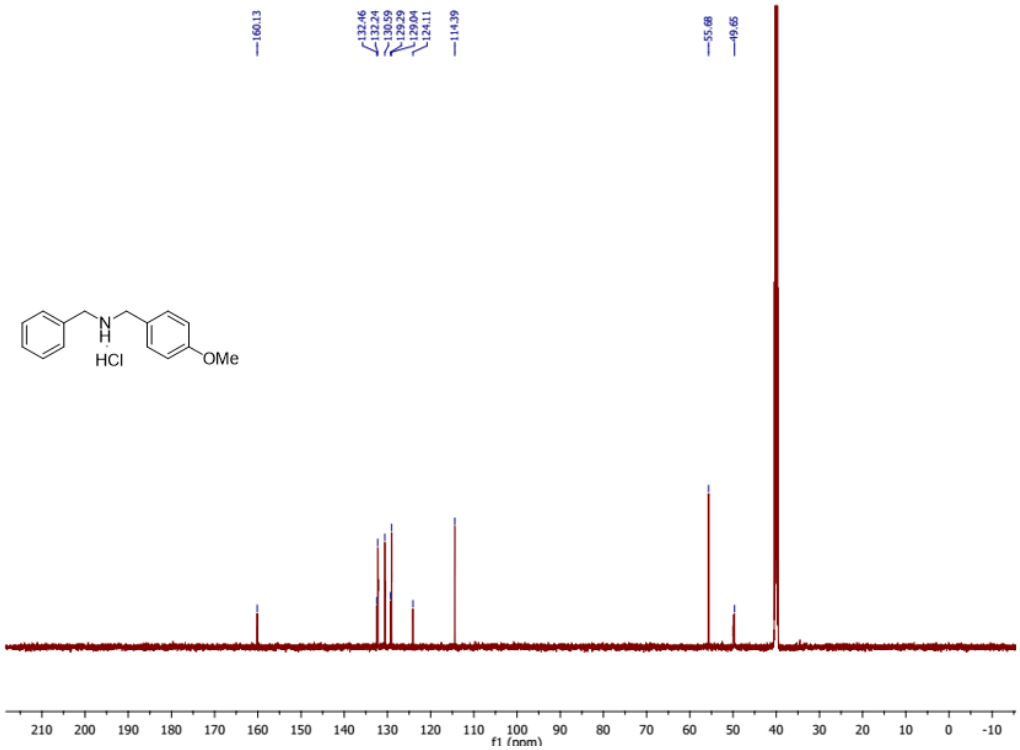


^{13}C spectrum of 2n in DMSO-d$_6$

(xv) ^{1}H and ^{13}C spectra of 2t:

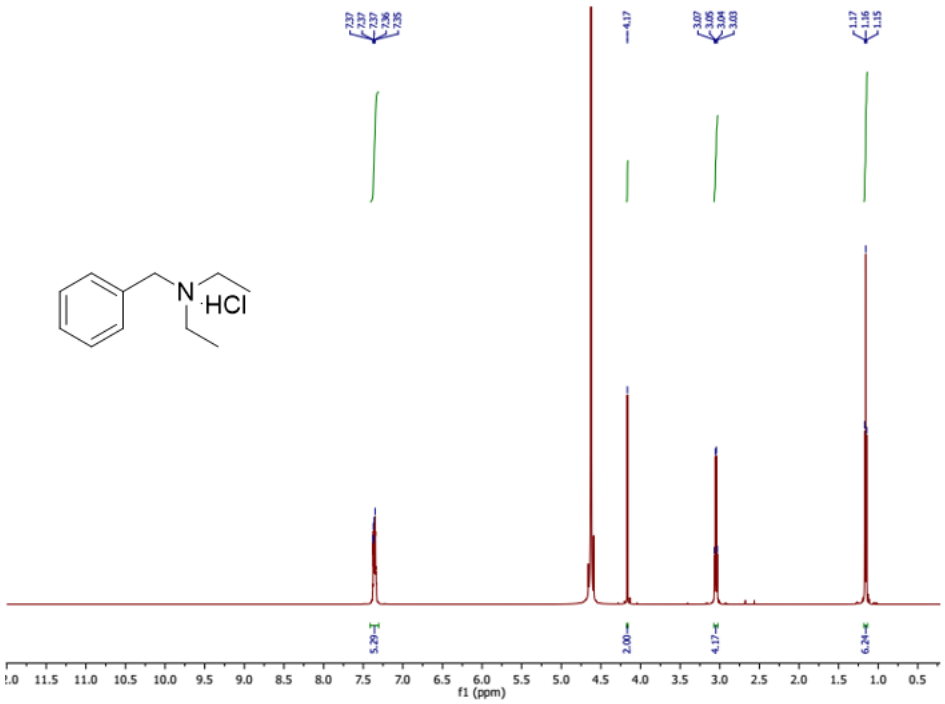


^{1}H spectrum of 2t in DMSO-d_6

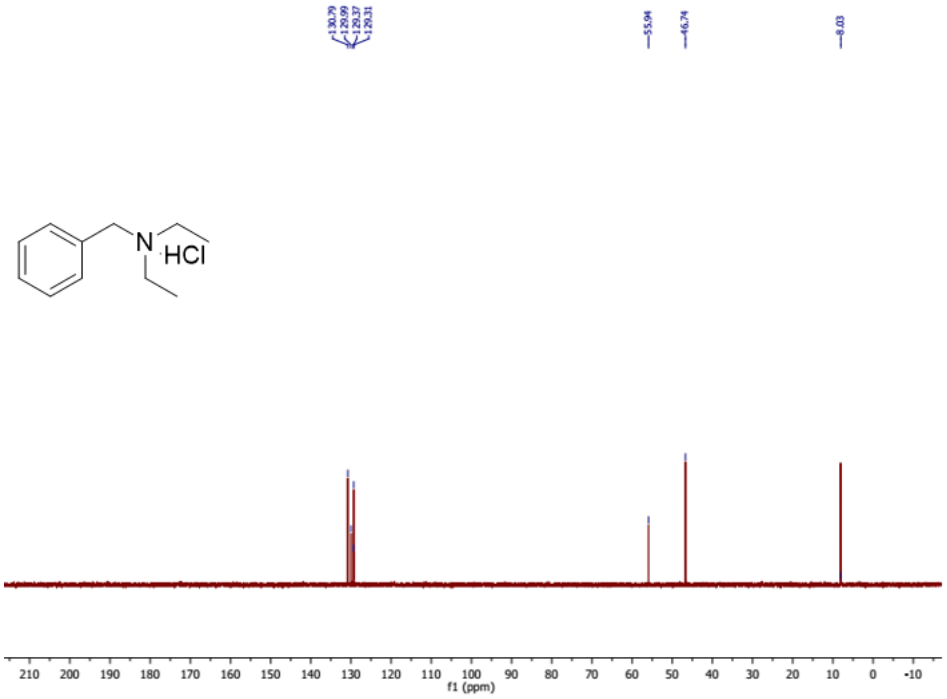


^{13}C spectrum of 2t in DMSO-d_6

(xvi) ^{1}H and ^{13}C spectra of 2y:



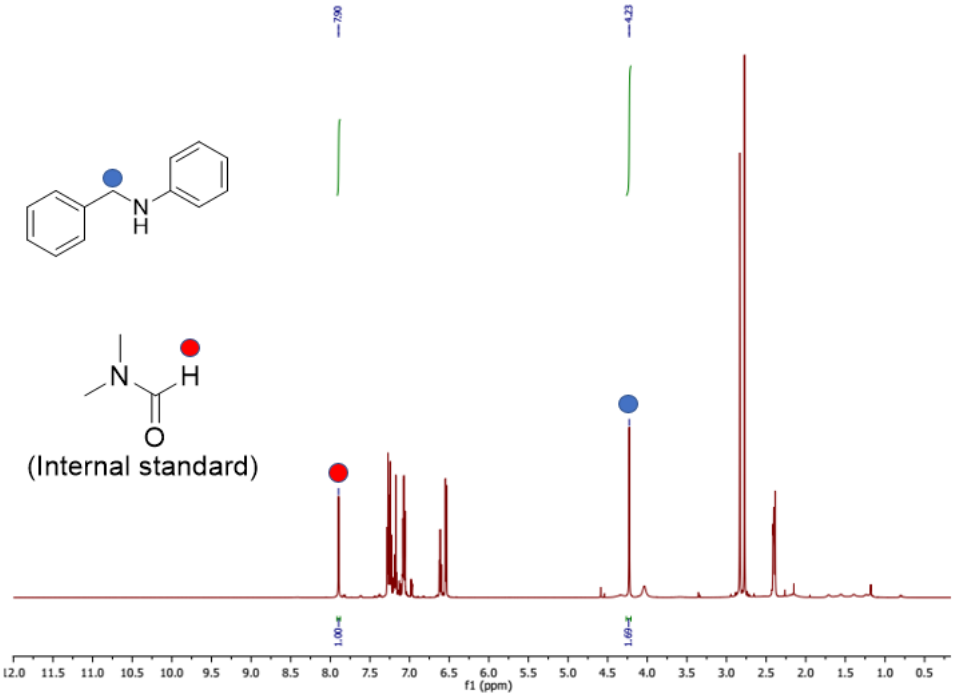
^{1}H spectrum of 2y in D_2O



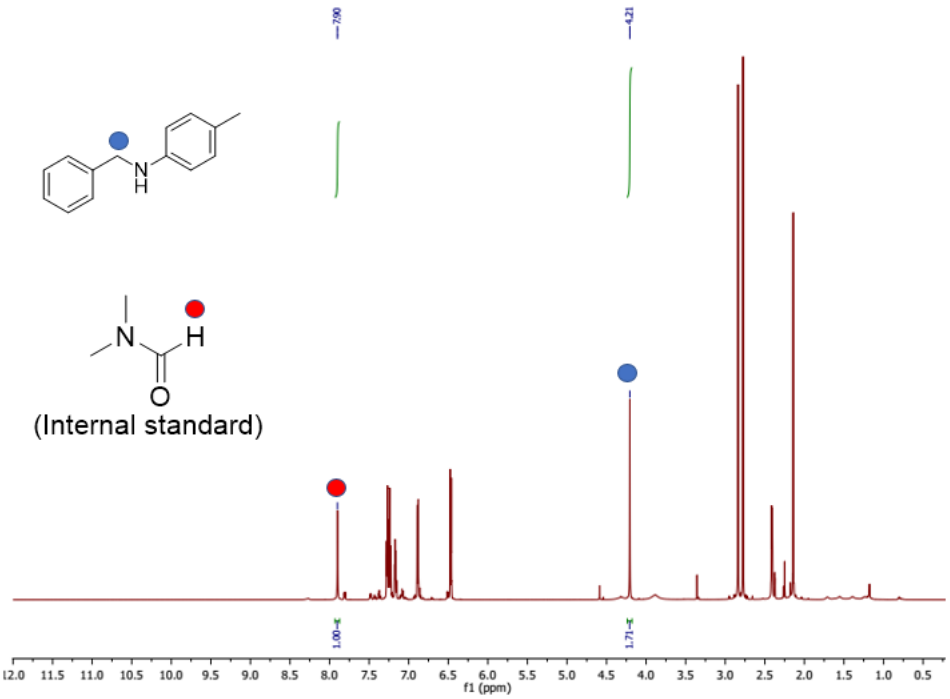
^{13}C spectrum of 2y in D_2O

10. Copies of ^{1}H NMR spectra of crude reaction mixture of secondary and tertiary amides

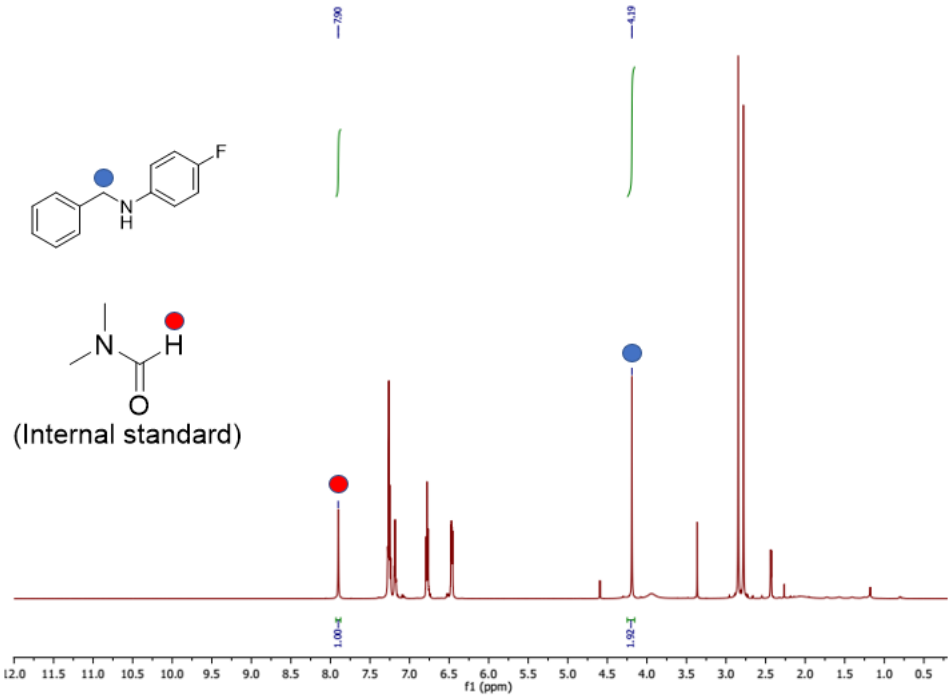
(i) ^{1}H NMR of the reaction mixture of Table 2, compound 2o':



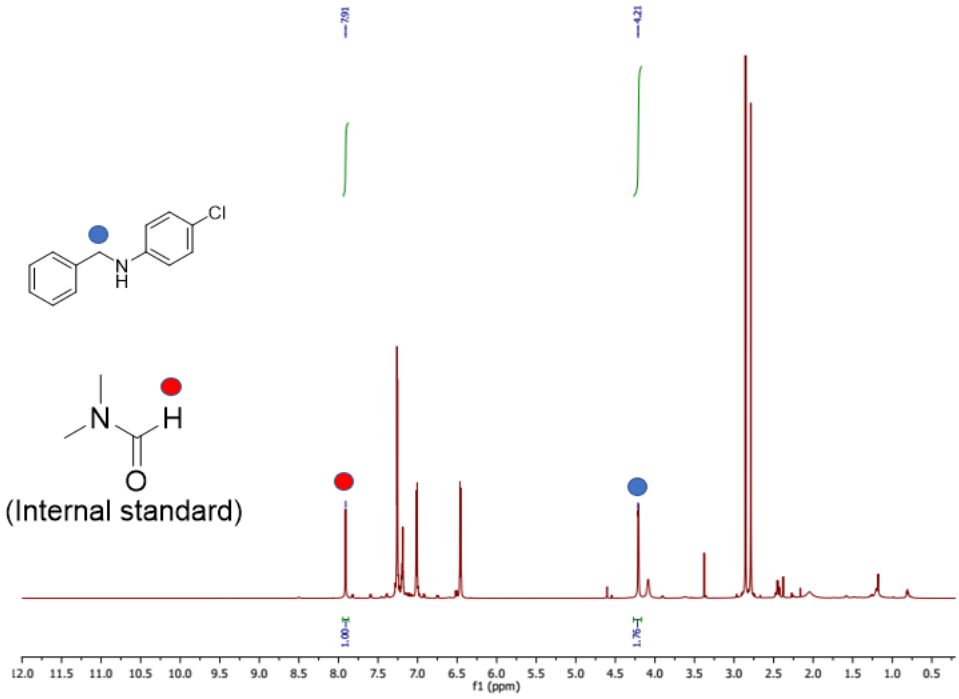
(ii) ^{1}H NMR of the reaction mixture of Table 2, compound 2p':



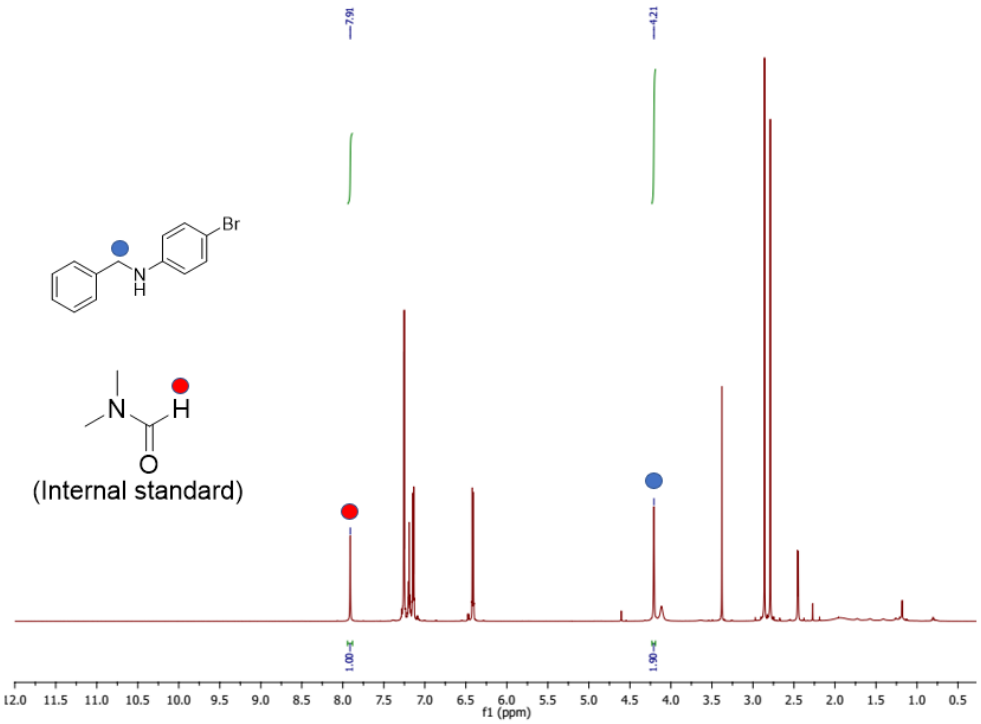
(iii) ^{1}H NMR of the reaction mixture of Table 2, compound 2q':



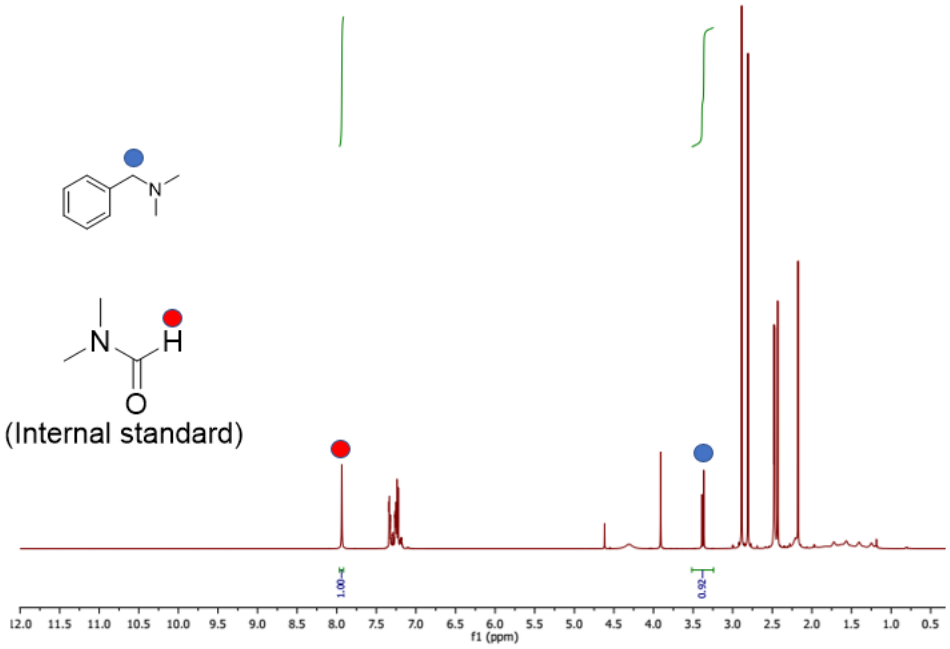
(iv) ^{1}H NMR of the reaction mixture of Table 2, compound 2r':



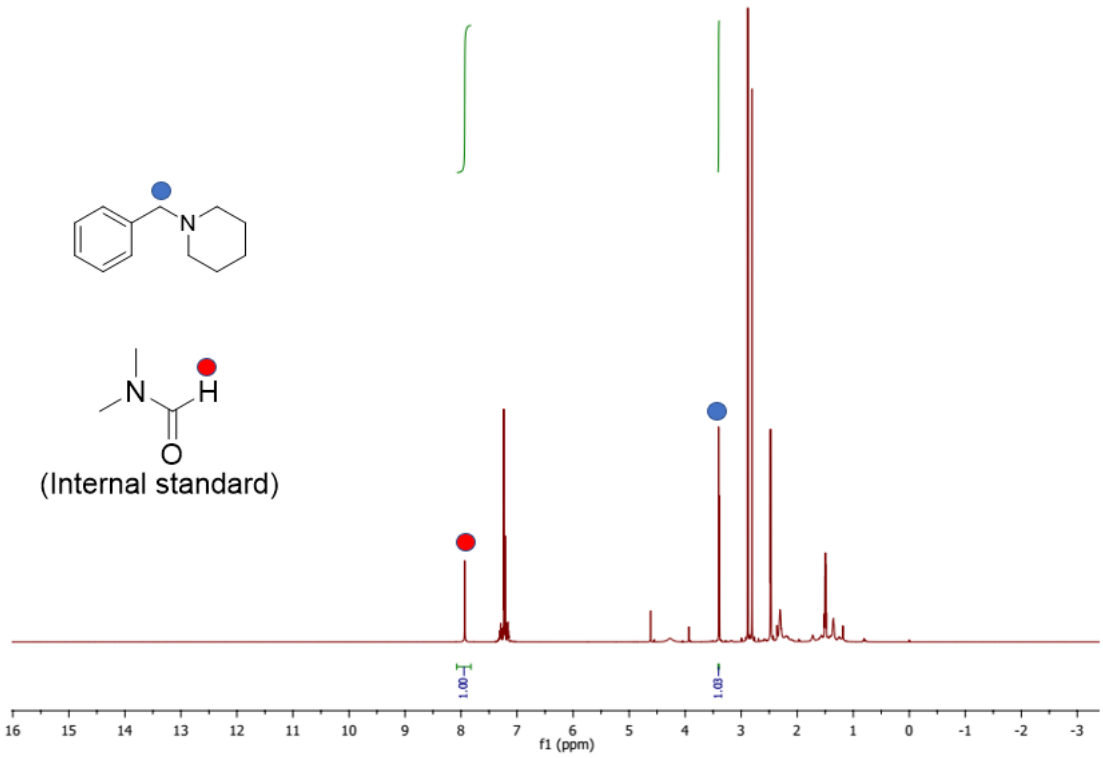
(v) ^{1}H NMR of the reaction mixture of Table 2, compound 2s':



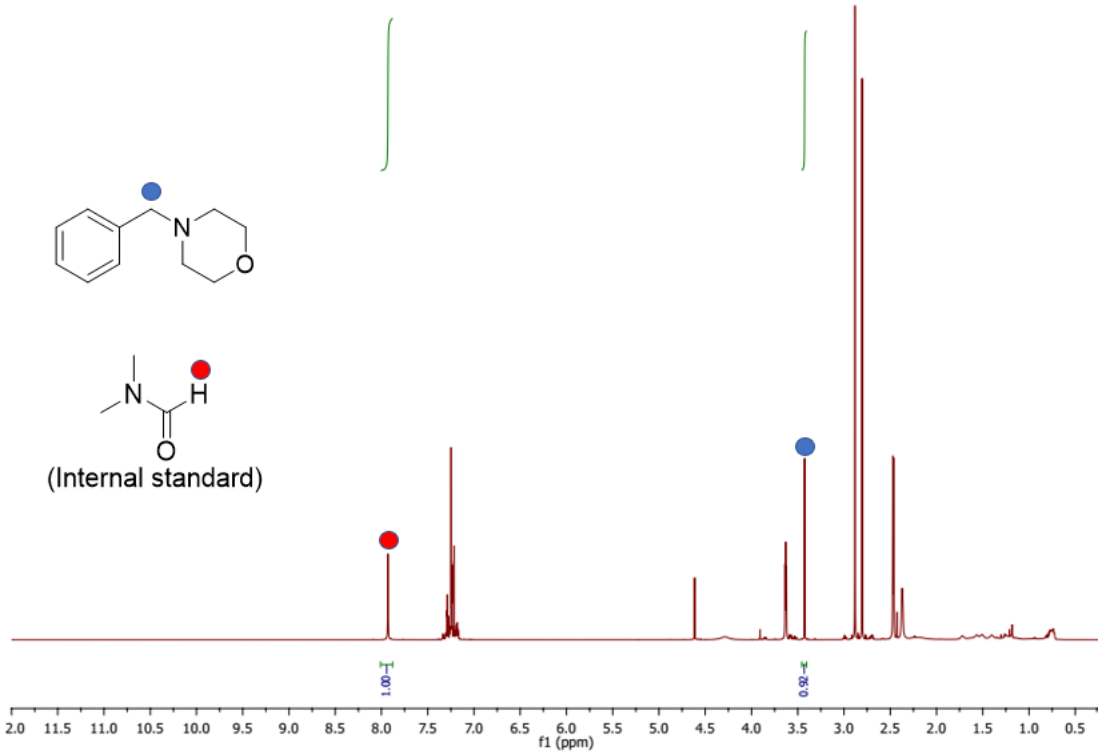
(vi) ^{1}H NMR of the reaction mixture of Table 2, compound 2u':



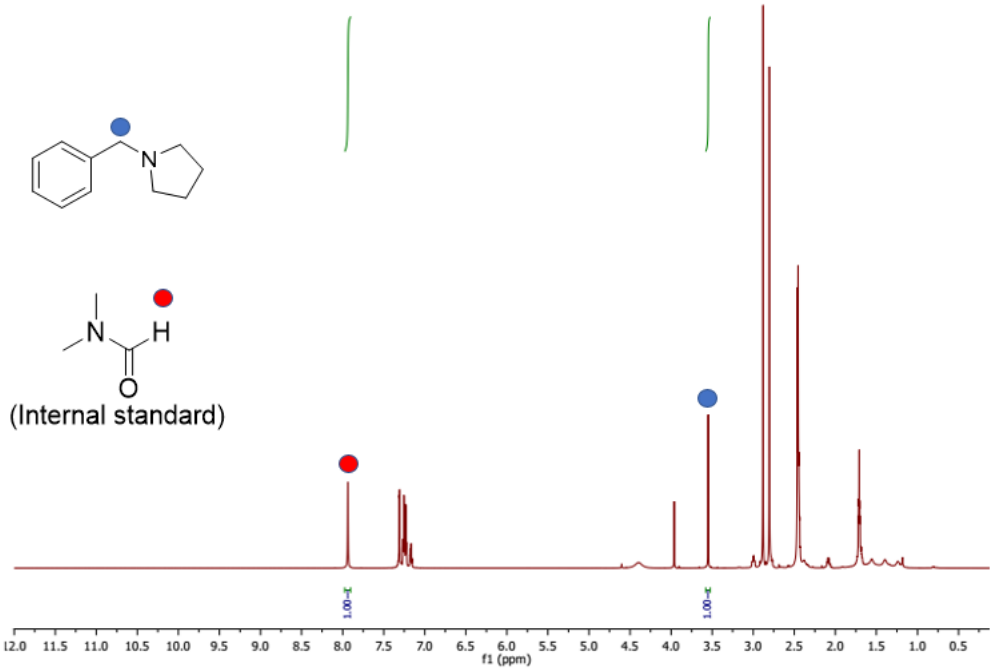
(vii) ^{1}H NMR of the reaction mixture of Table 2, compound 2v':



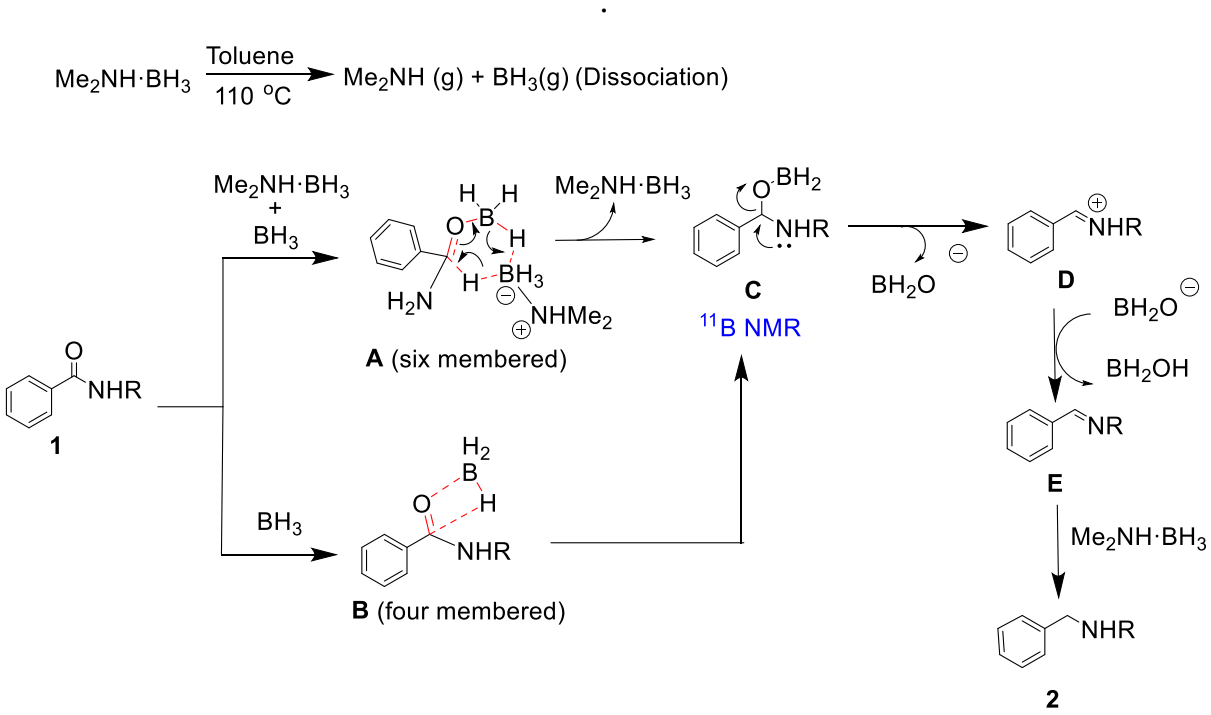
(viii) ^{1}H NMR of the reaction mixture of Table 2, compound 2w':



(ix) ^{1}H NMR of the reaction mixture of Table 2, compound 2x':



11. Plausible mechanism and Computational details:

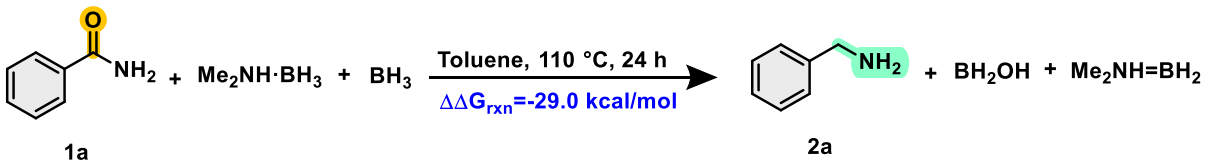


Scheme S1. Plausible reaction mechanism for the reduction of amides with DMAB.

Based on the preliminary NMR studies and previous reports[7], a plausible mechanism is proposed in Scheme S1 (other possibilities cannot be ruled out). At the outset, DMAB

could undergo the decomposition to dimethylamine (Me_2NH) and BH_3. Following this, the activation of the carbonyl group of the less electrophilic amide moieties could take place in the presence of the Lewis acidic BH_3 via a 6-member (**A**) or a 4-member (**B**) intermediate to facilitate the hydride transfer. Notably, both processes could lead to the formation of the same intermediate (**C**), having a B–O bond. The formation of such a bond has been detected through ^{11}B NMR spectroscopy. Subsequently, intermediate **C** could lead to the formation of **E** via the iminium ion intermediate (**D**). In the last step, intermediate **D** could undergo a spontaneous reduction[8] in the presence of DMAB to form the desired primary amine.

Additionally, we have calculated the energy associated with the amide reduction in the present protocol and found that the reaction is facile and exothermic in nature and releases 29 kcal/mole energy.



Scheme S2. Energy associated with the transformation of benzamide (**1a**) to benzylamine (**2a**).

The DFT calculations were carried out using the Gaussian 16 software package.[9] Geometric structures were optimized by employing wB97X-D functional.[10] Frequency analysis was performed to verify the minima or saddle point. The free energy reported in this study is at SMD $_{(toluene)}$/wb97X-D /def2TZVPP// SMD $_{(toluene)}$/wb97X-D /def2SVP.

BH_3

Number of imaginary frequencies : 0 Electronic energy : HF=-26.5770859

Zero-point correction= 0.025992 (Hartree/Particle)

Thermal correction to Energy= 0.028885

Thermal correction to Enthalpy= 0.029829

Thermal correction to Gibbs Free Energy= 0.008408

Sum of electronic and zero-point Energies= -26.551094

Sum of electronic and thermal Energies= -26.548201

Sum of electronic and thermal Enthalpies= -26.547257

Sum of electronic and thermal Free Energies= -26.568678

.....

Cartesian Coordinates

.....

5	0.000000	0.000000	0.000000
1	0.000000	1.205395	0.000000
1	-1.043903	-0.602698	0.000000
1	1.043903	-0.602698	-0.000000

BH_2OH

Number of imaginary frequencies : 0 Electronic energy : HF=-101.8014026

Zero-point correction= 0.035529 (Hartree/Particle)

Thermal correction to Energy= 0.038574

Thermal correction to Enthalpy= 0.039519

Thermal correction to Gibbs Free Energy= 0.013341

Sum of electronic and zero-point Energies= -101.765874

Sum of electronic and thermal Energies= -101.762828

Sum of electronic and thermal Enthalpies= -101.761884

Sum of electronic and thermal Free Energies= -101.788061

.....

Cartesian Coordinates

.....

5	-0.709418	0.031629	0.000077
1	-1.376684	-0.975670	-0.000349
1	-1.207229	1.137380	-0.000010

8 0.627082 -0.127884 0.000048

1 1.114349 0.703219 -0.000414

1a

Number of imaginary frequencies : 0 Electronic energy : HF=-400.5455797

Zero-point correction= 0.129153 (Hartree/Particle)

Thermal correction to Energy= 0.136570

Thermal correction to Enthalpy= 0.137514

Thermal correction to Gibbs Free Energy= 0.097050

Sum of electronic and zero-point Energies= -400.416427

Sum of electronic and thermal Energies= -400.409009

Sum of electronic and thermal Enthalpies= -400.408065

Sum of electronic and thermal Free Energies= -400.448529

.....

Cartesian Coordinates

.....

6 0.513714 1.205360 0.126188

6 1.904923 1.170234 0.151850

6 2.575583 -0.046536 0.021068

6 1.850097 -1.226486 -0.138804

6 0.456760 -1.192240 -0.155524

6 -0.221578 0.023794 -0.013235

1 -0.028027 2.149058 0.213329

1 2.470455 2.097157 0.270318

1 3.667594 -0.074358 0.036703

1 2.371177 -2.178863 -0.258818

1 -0.097572 -2.121534 -0.308364

6 -1.724539 0.134615 -0.037085

8 -2.281838 1.181285 -0.313117

7 -2.410517 -0.999655 0.260852

1 -1.964877 -1.798046 0.690847

1 -3.420192 -0.938553 0.308210

$Me_2N=BH_2$

Number of imaginary frequencies : 0 Electronic energy : HF=-160.488621

Zero-point correction= 0.105051 (Hartree/Particle)

Thermal correction to Energy= 0.110413

Thermal correction to Enthalpy= 0.111358

Thermal correction to Gibbs Free Energy= 0.077790

Sum of electronic and zero-point Energies= -160.383570

Sum of electronic and thermal Energies= -160.378208

Sum of electronic and thermal Enthalpies= -160.377263

Sum of electronic and thermal Free Energies= -160.410831

.....

Cartesian Coordinates

.....

5 -0.000212 1.537186 0.000000

1 -0.000300 2.129032 -1.055797

1 -0.000300 2.129032 1.055797

7 0.000056 0.147351 0.000000

6 0.000056 -0.648440 1.211832

6 0.000056 -0.648440 -1.211832

1 -0.000679 0.002187 -2.095141

1 0.890843 -1.299022 -1.256673

1 -0.889864 -1.300246 -1.255933

1 -0.889864 -1.300246 1.255933

1 0.890843 -1.299022 1.256673

1 -0.000679 0.002187 2.095141

$Me_2NH{\cdot}BH_3$

Number of imaginary frequencies : 0 Electronic energy : HF=-161.6771859

Zero-point correction= 0.127477 (Hartree/Particle)

Thermal correction to Energy= 0.133362

Thermal correction to Enthalpy= 0.134306

Thermal correction to Gibbs Free Energy= 0.099568

Sum of electronic and zero-point Energies= -161.549709

Sum of electronic and thermal Energies= -161.543824

Sum of electronic and thermal Enthalpies= -161.542880

Sum of electronic and thermal Free Energies= -161.577618

.....

Cartesian Coordinates

.....

5 0.103719 -1.565308 0.000000

1 -0.371627 -2.060190 1.018716

1 1.332812 -1.586000 0.000000

1 -0.371627 -2.060190 -1.018716

7 -0.331973 -0.003429 -0.000000

1 -1.354101 -0.012118 -0.000000

6 0.103719 0.698182 -1.218331

6 0.103719 0.698182 1.218331

1 -0.291488 0.174605 2.096807

1 1.200703 0.679801 1.262062

1 -0.246645 1.741023 1.216214

1 -0.246645 1.741023 -1.216214

1 1.200703 0.679801 -1.262062

1 -0.291488 0.174605 -2.096807

2a

Number of imaginary frequencies : 0 Electronic energy : HF=-326.5777048

Zero-point correction= 0.147429 (Hartree/Particle)

Thermal correction to Energy= 0.154494

Thermal correction to Enthalpy= 0.155438

Thermal correction to Gibbs Free Energy= 0.115785

Sum of electronic and zero-point Energies= -326.430276

Sum of electronic and thermal Energies= -326.423211

Sum of electronic and thermal Enthalpies= -326.422267

Sum of electronic and thermal Free Energies= -326.461920

.....

Cartesian Coordinates

.....

6 0.427878 0.267221 -0.093385

6 -0.022378 -1.056530 -0.128764

6 -1.384446 -1.346872 -0.051216

6 -2.318251 -0.317493 0.060970

6 -1.879006 1.006128 0.100114

6 -0.517071 1.293235 0.027417

1 0.716006 -1.856452 -0.213173

1 -1.718634 -2.387071 -0.079296

1	-3.385108	-0.545082	0.122217
1	-2.601586	1.820525	0.194188
1	-0.180505	2.333616	0.067406
6	1.901999	0.596904	-0.218198
1	2.118352	0.796466	-1.282534
1	2.088360	1.554108	0.310003
7	2.755987	-0.495235	0.210286
1	3.730229	-0.283271	0.008221
1	2.688631	-0.621753	1.219333

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