Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cobalt Catalyzed Chemoselective Reduction of Nitroarenes: Hydrosilylation under Thermal and Photochemical Reaction Conditions

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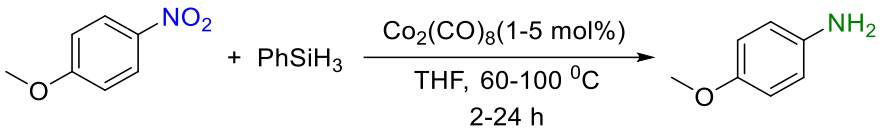
General experimental

All air and moisture-sensitive experiments such as catalytic hydrosilylation of nitroarenes were performed under dry nitrogen atmosphere using standard Schlenk or glovebox (MBraun) techniques. Hydrosilylation of nitroarenes was performed in Ace pressure tubes purchased from Sigma-Aldrich. For the air-sensitive experiments, solvents (petroleum ether, diethyl ether, *n*-pentane and THF) were distilled, degassed and stored over 3 Å molecular sieves. Solvents (acetonitrile, hexanes, pentane, ethyl acetate, DCM, MeOH and THF) were purchased from Merck, Finar and Rankem. For recording NMR spectra of air and moisture-sensitive samples, $CDCl_3$ was degasses and stored over 3 Å molecular sieves. $CDCl_3$ was purchased from Sigma Aldrich. Co_2CO_8, $PhSiH_3$, Ph_2SiH_2, Ph_3SiH, iPr_3SiH, Me_2PhSiH, Et_3SiH, PMHS, TMDS and all nitroarenes as substrates for hydrosilylation were purchased from Sigma Aldrich, Alfa Aesar and TCI Chemicals and used without further purification.

^1H and ^{13}C NMR spectra were recorded using Bruker AV-400 , AV-700 and JEOL-400 (^1H at 400 MHz and ^{13}C at 101 MHz). ^1H NMR chemical shifts are referenced in parts per million (ppm) with respect to tetramethylsilane (δ 0.00 ppm) and $^{13}C\{^1H\}$ NMR chemical shifts are referenced in ppm with respect to $CDCl_3$ (δ 77.16 ppm). The coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to describe multiplicity: s = singlet, bs = broad signal, d = doublet, t = triplet, q = quartet, m = multiplate. High resolution mass spectra were recorded on a Bruker micrOTOF-Q II Spectrometer. All the gas chromatography data were collected on Shimadzu GC-2010 Plus. All the photochemical reactions were done in Luzchem Photoreactor Model - LZC-4X. Metal impurity was determined by using an inductively coupled plasmaoptical emission spectrophotometer (iCAP 7000 ICP-OES).

General procedure for the hydrosilylation of nitroarenes

General procedure for reaction optimization (Thermal):



In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1/2/3/4/5 mol%), *p*-nitroanisole (0.077 g, 0.5 mmol), phenylsilane (0.109 g, 1.0 mmol,) and THF (2mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (60-100 °C) in a preheated oil bath for 2 to 24 h. After cooling to r.t., MeOH (1 mL) and *p*-xylene (0.053 g, 0.5 mmol) was added to the resultant mixture. The mixture was then analyzed by GC to determine the conversion of the nitroarene to the amine. Thereafter, water (3 mL) was added to the previous mixture and the mixture was extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. All volatiles were removed under high vacuum to give crude product. Occasionally, the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate as eluent.

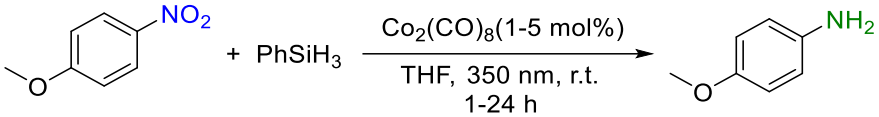
Table S1: Catalytic performance under thermal conditions

en	catalyst (mol%)	silane (2.1 eq)	**L**	temp (°C)	time (h)	yield[b] (%)
1	5	$PhSiH_3$	-	90	24	>99 (96[c])
2	5	$PhSiH_3$	-	90	18	>99
3	5	$PhSiH_3$	-	90	15	>99
4	5	$PhSiH_3$	-	90	12	>99
5	5	$PhSiH_3$	-	90	9	>99
6	5	$PhSiH_3$	-	90	6	85
7	3	$PhSiH_3$	-	90	10	>99
8	2	$PhSiH_3$	-	90	10	>99
9	2	$PhSiH_3$	-	80	10	>99
10	2	$PhSiH_3$	-	70	10	>99
11	2	$PhSiH_3$	-	60	10	72
12	2	$PhSiH_3$	-	100	10	>99

13	2	$PhSiH_3$	-	100	6	>99
14	1	$PhSiH_3$	-	100	6	>99
15	**1**	**$PhSiH_3$**	**-**	**100**	**3**	**>99 (95[c])**
16	1	$PhSiH_3$	-	100	2	88
17	1	$PhSiH_3$	-	100	3	<5[d]
18	no	$PhSiH_3$	-	100	3	<3
19	1	Et_2SiH_2	-	100	3	45
20	1	Et_3SiH	-	100	3	<10
21	1	Ph_2SiH_2	-	100	3	38
22	1	Ph_3SiH	-	100	3	<5
23	1	iPr_3SiH	-	100	3	<5
24	1	Me_2PhSiH	-	100	3	<5
25	1	PMHS	-	100	3	<5
26	1	TMDS	-	100	3	<5
27	1	$PhSiH_3$	**L_1**	100	3	<5
28	1	$PhSiH_3$	**L_2**	100	3	<5
29	1	$PhSiH_3$	**L_3**	100	3	<5
30	1	no	-	100	3	0

[a]Reactions conducted in an ace pressure tube (15 ml) with 0.5 mmol of *p*-nitroanisole, 1.00 mmol of silane, 5/3/2/1 mol% of **1**, and 1.5 mL of THF. [b]Yields were determined by GC using *p*-xylene (0.5 mmol) as standard. [c]Isolated yields. [d]Solvent-free condition. **L_1:** TMEDA, **L_2:** 1,10-phenanthroline, **L_3:** DPPE.

General procedure for reaction optimization (Photochemical):



In a dried quartz glass tube fitted with a magnetic stir bar, $Co_{2(}CO)_8$ (1/2/3/4/5 mol%), *p*-nitroanisole (0.077 g, 0.5 mmol), phenylsilane (0.109 g, 1.0 mmol) and THF (2mL) were added successively under a nitrogen atmosphere. The reaction mixture was exposed to 350 nm UV light irradiation for 1 to 24 h at r.t.. After completion of reaction, MeOH (1 mL) and *p*-xylene (0.053 g, 0.5 mmol) was added to the resultant mixture. The mixture was then

analyzed by GC to determine the conversion of the nitroarene to the amine. Thereafter, water (3 mL) was added to the previous mixture and the mixture was extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. All volatiles were removed under high vacuum to give crude product. Occasionally, the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate as eluent.

Table S2: Catalytic performance under photochemical conditions at r.t.

en	catalyst (mol%)	silane (2.1 eq)	temp (°C)	time (h)	yield[b] (%)
1	5	$PhSiH_3$	r.t.	24	>99
2	5	$PhSiH_3$	r.t.	12	>99
3	5	$PhSiH_3$	r.t.	6	>99
4	5	$PhSiH_3$	r.t.	3	>99
5	5	$PhSiH_3$	r.t.	1	>99
6	5	$PhSiH_3$	r.t.	0.5	>99 (93)[c]
7	5	$PhSiH_3$	r.t.	0.25	87
8	5	$PhSiH_3$	r.t.	0.5	<5[d]
9	3	$PhSiH_3$	r.t.	24	>99
10	3	$PhSiH_3$	r.t.	12	>99
11	3	$PhSiH_3$	r.t.	6	>99
12	3	$PhSiH_3$	r.t.	3	>99
13	**3**	**$PhSiH_3$**	**r.t.**	**2**	**>99 (92)[c]**
14	3	$PhSiH_3$	r.t.	1	90
15	2	$PhSiH_3$	r.t.	24	>99
16	2	$PhSiH_3$	r.t.	12	>99
17	2	$PhSiH_3$	r.t.	9	>99 (94)[c]
18	2	$PhSiH_3$	r.t.	6	82
19	1	$PhSiH_3$	r.t.	24	58

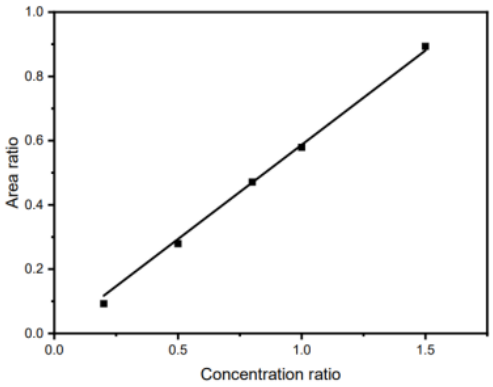
[a]Reactions conducted in a quartz tube (15 ml) with 0.5 mmol *p*-nitroanisole, 1.0 mmol silane, 5/3/2/1 mol% $Co_2(CO)_8$, in THF (1.5 mL) using 350 nm light. [b]Yields of product were

determined by GC using *p*-xylene (0.50 mmol) as standard. [c]Isolated yields. [d]Reaction conducted under solvent-free conditions.

GC Chromatogram:

Calibration Curve

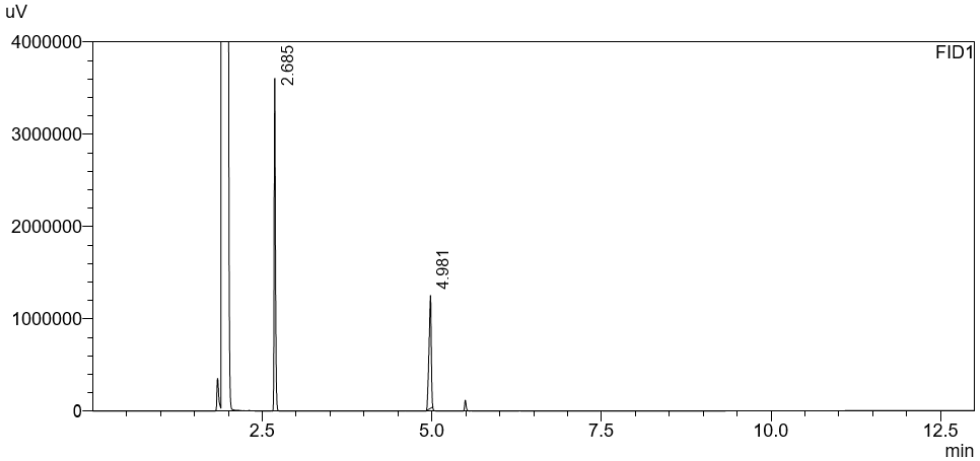
ID# 2
Name : p-anisidine
Quantitative Method : Internal Standard
Function : f(x)=0.587003*x+0
Rr1=0.9998453 Rr2=0.9996906 RSS=1.067848e-003
MeanRF: 5.565551e-001 RFSD: 5.504241e-002 RFRSD: 9.889840
FitType : Linear
ZeroThrough : Through
Weighted Regression : None
Detector Name : FID1



	Conc.(Ratio)	MeanArea Ratio	Area
1	0.2	0.0922632	465715
2	0.5	0.279222	1335206
3	0.8	0.470825	2236388
4	1	0.578916	2782658
5	1.5	0.893355	4294355

Figure S1. Calibration curve of p-anisidine with respect to p-xylene (IS)

<Chromatogram>

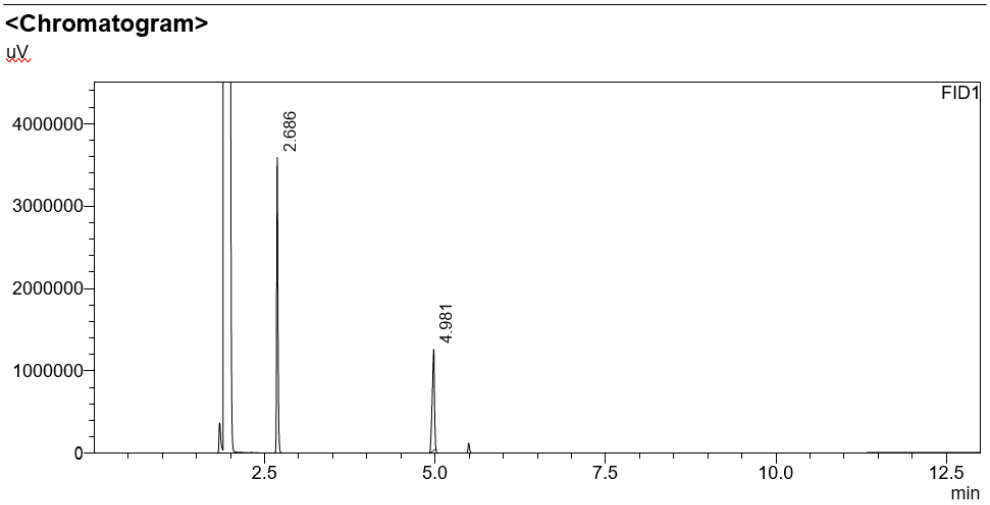


<Peak Table>

FID1

Peak#	Name	Ret. Time	Area	Area%
1	p-xylene	2.685	4835183	63.436
2	p-anisidine	4.981	2787017	36.564

Figure S2. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of $PhSiH_3$, 1 mol% of catalyst and 1.5ml of THF at 100 ^{0}C for 3 h. (Table-S1, entry 15)

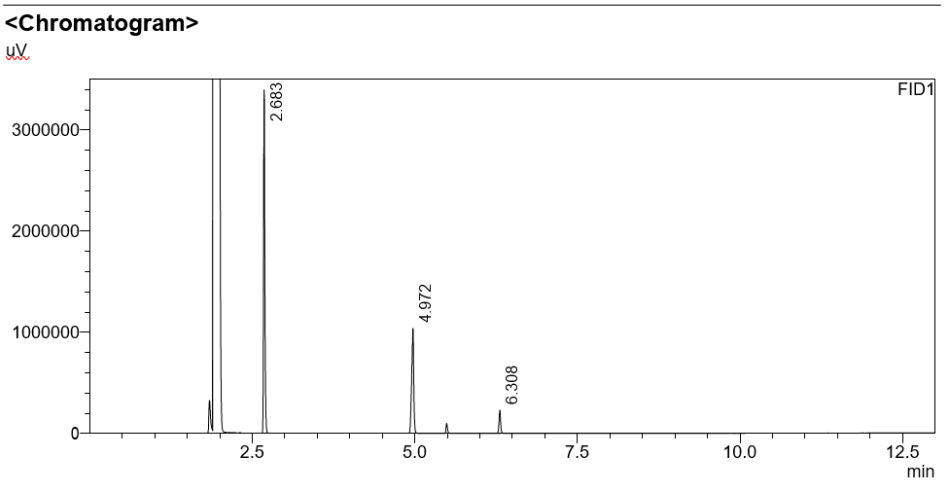


<Peak Table>

FID1

Peak#	Name	Ret. Time	Area	Area%
1	p-xylene	2.686	4795966	63.457
2	p-anisidine	4.981	2761893	36.543

Figure S3. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of $PhSiH_3$, 3 mol% of catalyst and 1.5ml of THF for 3 h at r.t. (350 nm). (Table-S2, entry 13)

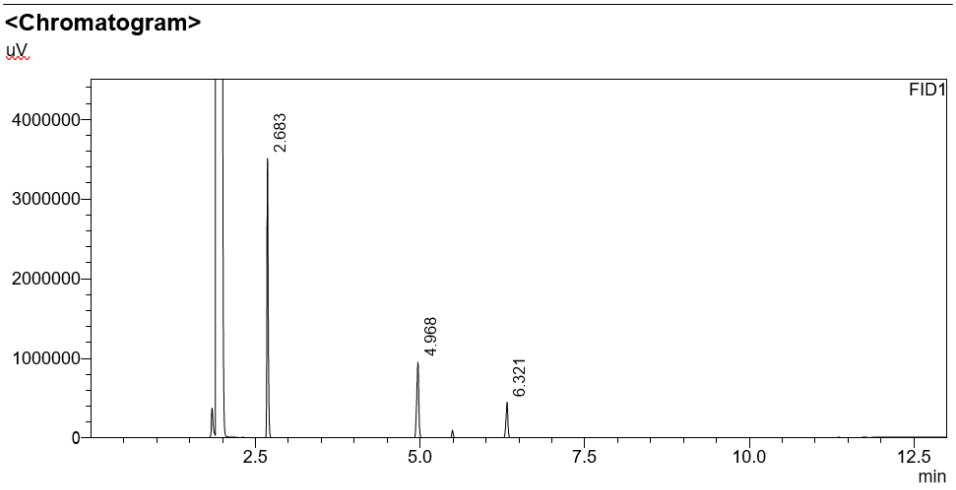


<Peak Table>

FID1

Peak#	Name	Ret. Time	Area	Height%
1	p-xylene	2.683	4582866	72.491
2	p-anisidine	4.972	2277521	22.531
3	p-nitro anisole	6.308	381417	4.978

Figure S4. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of $PhSiH_3$, 1 mol% of catalyst and 1.5ml of THF for 6 h at 90 ^{0}C. (Table-S1, entry 6)



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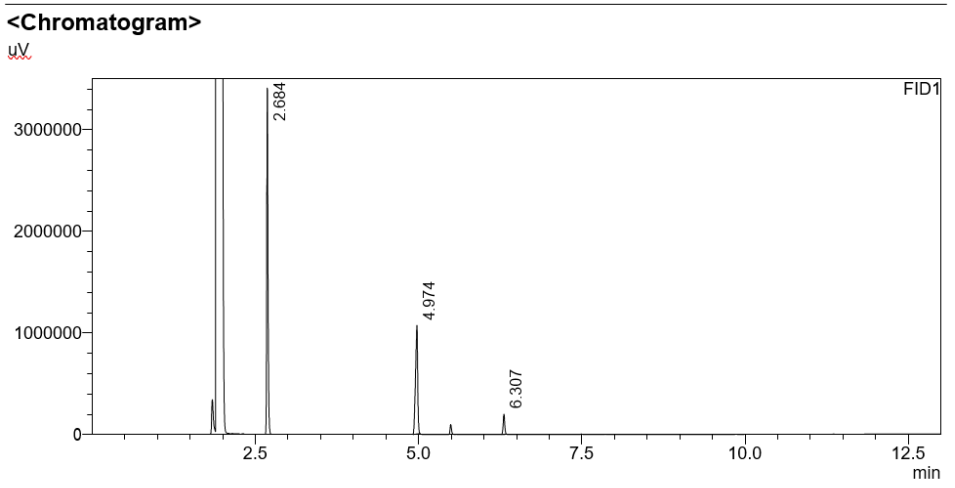
FID1

Peak#	Name	Ret. Time	Area	Area%
1	p-xylene	2.683	4724335	62.268
2	p-anisidine	4.968	1968904	25.951
3	p-nitro anisole	6.321	893907	11.782

Figure S5. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of $PhSiH_3$, 2 mol% of catalyst and 1.5ml of THF at 60 ^{0}C for 10 h. (Table-S1, entry 11)

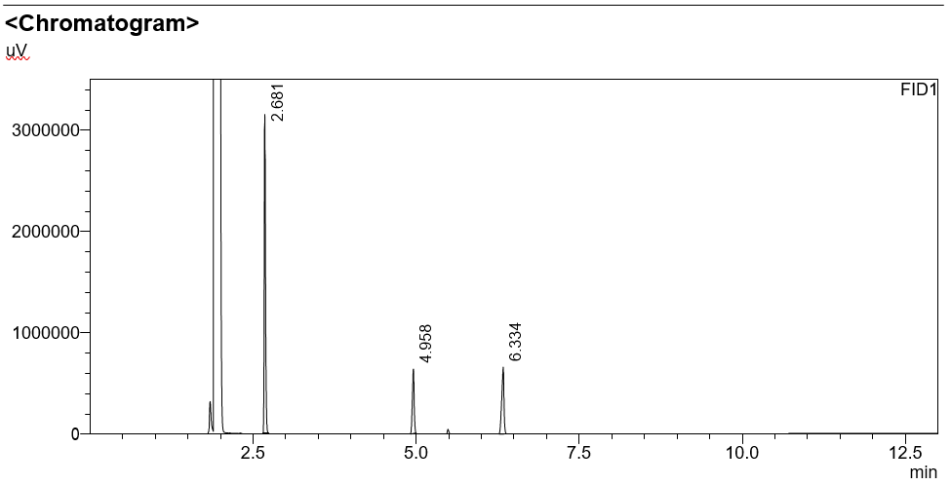


<Peak Table>

FID1

Peak#	Name	Ret. Time	Area	Area%
1	p-xylene	2.684	4579972	62.949
2	p-anisidine	4.974	2364599	32.500
3	p-nitro anisole	6.307	331149	4.551

Figure S6. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of $PhSiH_3$, 1 mol% of catalyst and 1.5ml of THF at 100 ^{0}C for 2 h. (Table-S1, entry 16)

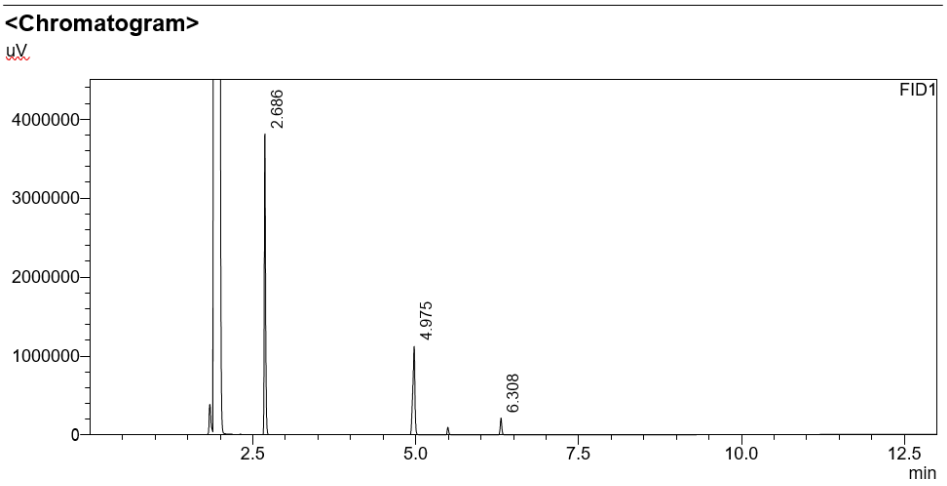


<Peak Table>

FID1

Peak#	Name	Ret. Time	Area	Area%
1	p-xylene	2.681	4281290	61.305
2	p-anisidine	4.958	1144977	16.395
3	p-nitro anisole	6.334	1557328	22.300

Figure S7. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of Et_2SiH_2, 1 mol% of catalyst and 1.5ml of THF at 100 ^{0}C for 3 h. (Table-S1, entry 19)

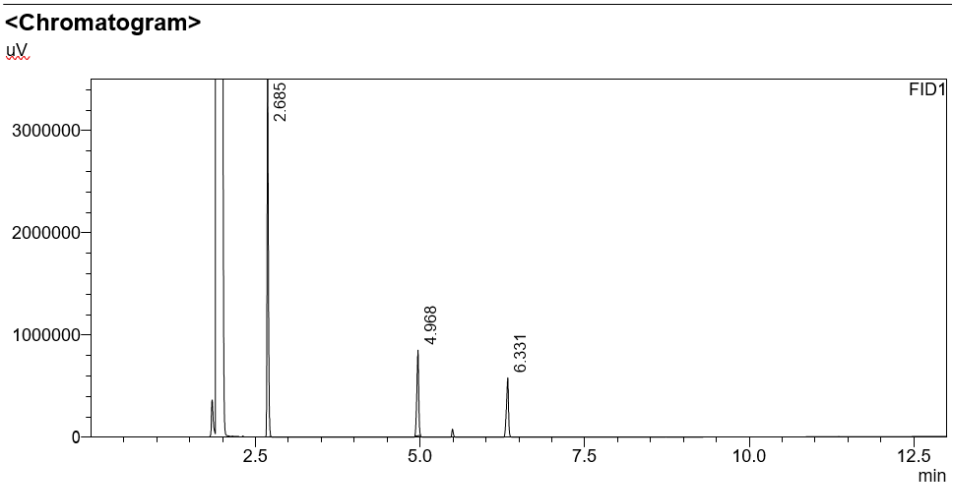


<Peak Table>

FID1

Peak#	Name	Ret. Time	Area	Area%
1	p-xylene	2.686	5129260	64.492
2	p-anisidine	4.975	2463385	30.973
3	p-nitro anisole	6.308	360659	4.535

Figure S8. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of $PhSiH_3$, 2 mol% of catalyst and 1.5ml of THF for 6 h at r.t. (350 nm). (Table-S2, entry 18)

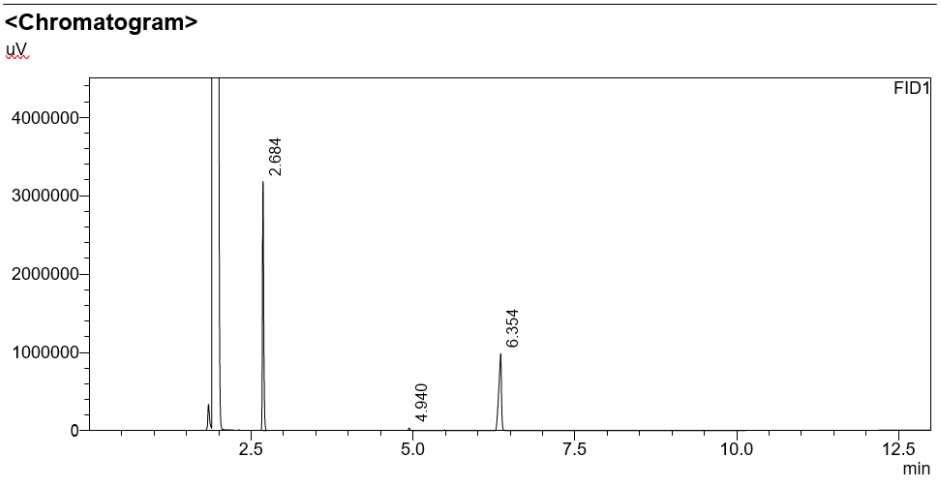


<Peak Table>

FID1

Peak#	Name	Ret. Time	Area	Area%
1	p-xylene	2.685	4804752	62.453
2	p-anisidine	4.968	1639799	21.314
3	p-nitro anisole	6.331	1248854	16.233

Figure S9. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of $PhSiH_3$, 1 mol% of catalyst and 1.5ml of THF for 24 h at r.t. (350 nm). (Table-S2, entry 19)

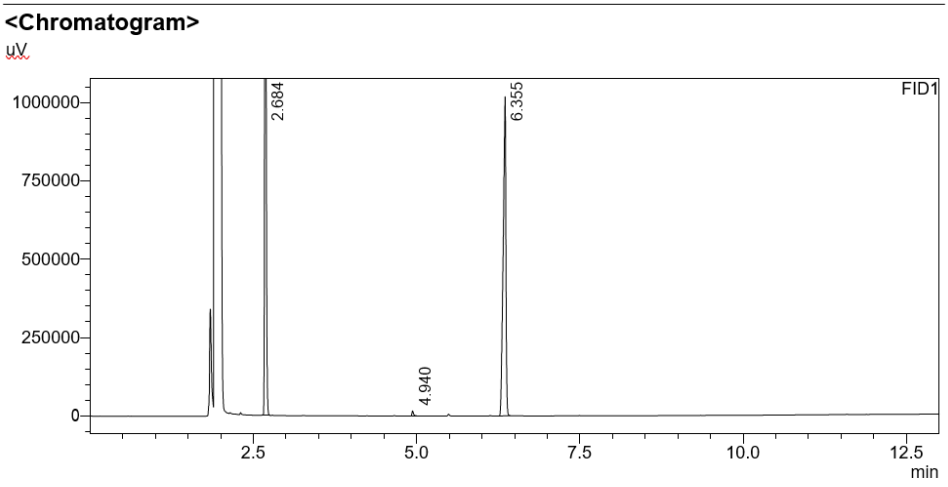


<Peak Table>

FID1

Peak#	Name	Ret. Time	Area	Area%
1	p-xylene	2.684	4305324	60.262
2	p-anisidine	4.940	51788	0.725
3	p-nitro anisole	6.354	2787289	39.014

Figure S10. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of TMDS, 1 mol% of catalyst and 1.5ml of THF at 100 ^{0}C for 3 h. (Table-S1, entry 22)



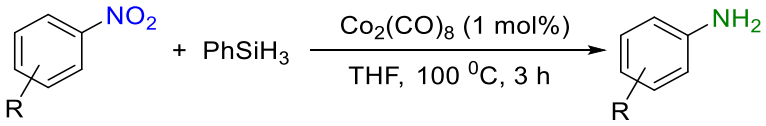
<Peak Table>

FID1

Peak#	Name	Ret. Time	Area	Area%
1	p-xylene	2.684	4593172	60.937
2	p-anisidine	4.940	27527	0.365
3	p-nitro anisole	6.355	2916924	38.698

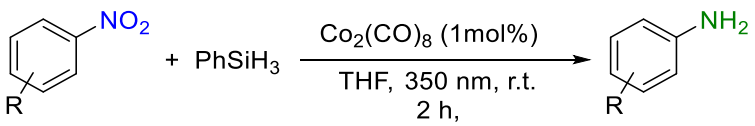
Figure S11. Representative GCMS spectrum of the crude reaction mixture from catalytic hydrosilylation of p-nitroanisole performed in presence of 2.1 eq. of $PhSiH_3$, 5 mol% of catalyst for 24 h at r.t. (350 nm) in neat condition. (Table-S2, entry 8)

General conditions for substrate screening (Thermal)[a]:



In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1 mol%, 0.0017 g), corresponding nitroarene (0.077 g, 0.5 mmol), phenylsilane (0.109 g, 1.0 mmol) and THF (2mL) were added successively under nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and water (3 mL) (occasionally 10 wt% of NaOH solution (3 mL)) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate as eluent.

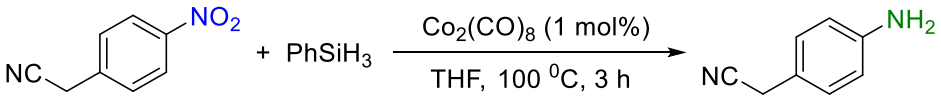
General conditions for substrate screening (Photochemical)[b]:



In a dried quartz glass tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (3 mol%, 0.0051g), corresponding nitroarene (0.077 g, 0.5 mmol), phenylsilane (0.109 g, 1.0 mmol) and THF (2mL) were added successively under nitrogen atmosphere. The reaction mixture was

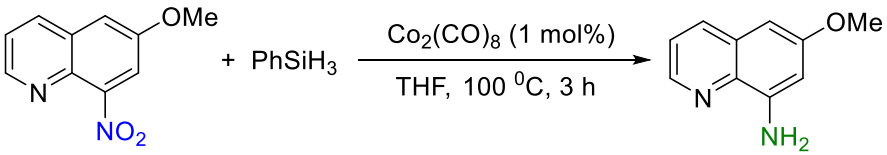
exposed to 350 nm UV light irradiation for 2 h. After completion of reaction, MeOH (1 mL) and water (3 mL) (occasionally 10 wt% of NaOH solution (3 mL)) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate as eluent.

Gram Scale synthesis of 2-(4-aminophenyl)acetonitrile (A_{4i}):



In a dried pressure tube fitted with a magnetic stir bar, $Co_{2(}CO)_8$ (1 mol%, 0.034 g), corresponding nitroarene (1.62 g, 10 mmol), phenylsilane (2.16 g, 20 mmol) and THF (10mL) were added successively under nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (10 mL) and 10 wt% of NaOH solution (30 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 15 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (9:1) as eluent. (1.05 g, 80%).

Gram Scale synthesis of 6-Methoxy-Quinolin-8-amine (A_9):



In a dried pressure tube fitted with a magnetic stir bar, $Co_{2(}CO)_8$ (1 mol%, 0.034 g), corresponding nitroarene (2.04 g, 10 mmol), phenylsilane (2.16 g, 20 mmol) and THF (10mL) were added successively under nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (10 mL) and 10 wt% of NaOH solution (30 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 15 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (9:1) as eluent. (1.22 g, 70%).

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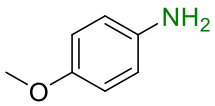
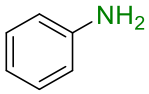
NMR data of aromatic amines

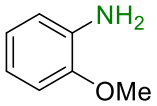
Following anilines (obtained by hydrosilylation of nitroarenes purified by column chromatography) are known compounds and they are characterized by ^{1}H and ^{13}C NMR spectroscopy.



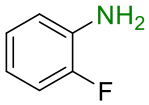
p-Anisidine (**A$_0$**):[S1] A mixture of petroleum ether, ethyl acetate, and methanol (8:1.5:0.5) was used as eluent for column chromatography. Isolated as a brown liquid [**A$_0$**: (0.058 g, 95%)[a]; (0.056 g, 92%)[b]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 – 6.72 (m, 2H), 6.67 – 6.63 (m, 2H), 3.75 (s, 3H), 3.29 (brs, 2H). $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 152.90, 140.01, 116.52, 114.90, 55.81.



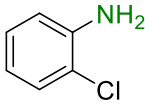
Aniline (**A$_1$**):[S1] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a yellow liquid (**A$_1$**: 0.039 g, 85%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.7 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 2H), 3.42 (brs, 2H). $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 146.42, 129.39, 118.70, 115.24.



o-Anisidine (**A$_{2a}$**):[S3] A mixture of petroleum ether, ethyl acetate, and methanol (7:2.5:0.5) was used as eluent for column chromatography. Isolated as a brown liquid (**A$_{2a}$**: 0.055 g, 90%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.78 (m, 2H), 6.74 (dt, *J* = 7.6, 1.7 Hz, 2H), 3.86 (s, 3H), 3.50 (brs, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.47, 136.16, 121.18, 118.67, 115.20, 110.54, 77.48, 77.16, 76.84, 55.54.

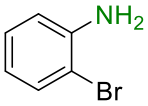


2-Fluoroaniline (**A$_{2b}$**):[S2] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a colorless oil (**A$_{2b}$**: 0.044 g, 80%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.99 (dd, *J* = 10.5, 8.8 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.77 (t, *J* = 8.1 Hz, 1H), 6.69 (d, *J* = 4.7 Hz, 1H), 3.67 (brs, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 153.09, 150.72, 134.46 (d, *J* = 12.9 Hz), 124.52 (d, *J* = 3.3 Hz), 118.80 (d, *J* = 6.7 Hz), 117.12, 115.40, 115.22.

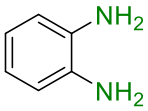


2-Chloroaniline (**A$_{2c}$**):[S1] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a brown liquid (**A$_{2c}$**: 0.052 g, 82%).^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 11.4, 3.9 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.74 – 6.71 (m, 1H), 4.07 (brs, 2H). $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 143.01, 129.50,

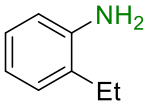
127.72, 119.37, 119.11, 115.98.



2-Bromoaniline (**A$_{2d}$**):[S2] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a brown liquid (**A$_{2d}$**: 0.073 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.11 (td, *J* = 8.0, 1.4 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.62 (td, *J* = 7.9, 1.5 Hz, 1H), 3.92 (brs, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.18, 132.71, 128.47, 119.55, 115.88, 109.46.

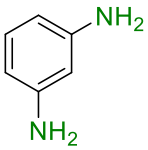


o-Phenylenediamine (**A$_{2e}$**):[S3] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a grey solid (**A$_{2e}$**: 0.045 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 – 6.69 (m, 4H), 3.25 (brs, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.83, 120.39, 116.85.

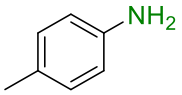


2-Ethylaniline (**A$_{2f}$**):[S4] A mixture of petroleum ether and ethyl acetate (6:4) was used as eluent for column chromatography. Isolated as a colorless oil (**A$_{2f}$**: 0.051 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 17.3, 7.8 Hz, 2H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 3.63 (brs, 2H), 2.54 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.09, 128.47, 128.20, 126.92, 118.94, 115.49, 24.10, 13.10.

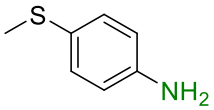
(3-Aminophenyl)methanol (**A$_{3a}$**):[S1] A mixture of petroleum ether and ethyl acetate (6:4) was used as eluent for column chromatography. Isolated as a yellow oil (**A$_{3a}$**: 0.053g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.7 Hz, 1H), 6.76 – 6.72 (m, 1H), 6.70 (s, 1H), 6.61 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.60 (s, 2H), 3.64 (brs, 2H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 146.76, 142.37, 129.65, 117.25, 114.54, 113.72, 65.46.



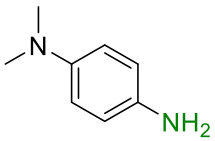
Benzene-1,3-diamine (**A$_{3b}$**):[S2] A mixture of petroleum ether and ethyl acetate (6:4) was used as eluent for column chromatography. Isolated as a brown solid (**A$_{3b}$**: 0.042 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (t, *J* = 7.9 Hz, 1H), 6.12 (dd, *J* = 7.9, 2.2 Hz, 2H), 6.04 (t, *J* = 2.1 Hz, 1H), 3.54 (brs, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.62, 130.34, 106.12, 102.05.



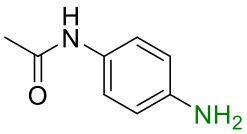
p-Toluidine (**A4a**):[S1] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a brown liquid [**A4a**: (0.048 g, 90%)[a]; (0.046 g, 87%)[b]]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 8.3 Hz, 2H), 3.43 (brs, 2H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 143.89, 129.84, 127.87, 115.37, 20.53.



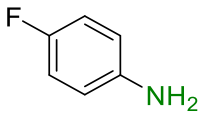
4-(Methylthio)aniline (**A4b**):[S1] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a brown solid (**A4b**: 0.056 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 3.64 (brs, 2H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.23, 131.20, 125.93, 115.87, 18.92.



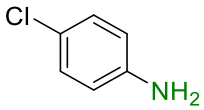
N^1,N^1-Dimethylbenzene-1,4-diamine (**A4c**):[S3] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a purple solid [**A4c**: (0.048 g, 70%)[a]; (0.043 g, 67%)[b]]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (d, *J* = 9.2Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 2.85 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.01, 138.02, 116.74, 115.73, 42.25.



N-(4-Aminophenyl)acetamide (**A4d**):[S3] A mixture of petroleum ether and ethyl acetate (7:3) was used as eluent for column chromatography. Isolated as a pale yellow solid [**A4d**: (0.060 g, 80%)[a]; (0.061 g, 82%)[b]]. ^{1}H NMR (700 MHz, DMSO-d_6) δ 9.44 (brs, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 2H), 4.80 (brs, 2H), 1.96 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, DMSO-d_6) δ 167.21, 144.47, 128.63, 120.87, 113.83, 23.60.

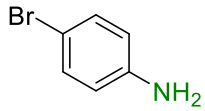


4-Fluoroaniline (**A4e**):[S1] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a brown solid (**A4e**: 0.042g, 75%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.86 (t, *J* = 8.4 Hz, 2H), 6.60 (s, 2H), 3.37 (brs, 1H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 157.23, 155.90, 142.38, 116.25, 115.67 (d, *J* = 22.3 Hz).

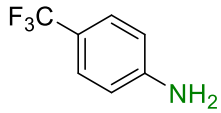


4-Chloroaniline (**A4f**):[S1] A mixture of petroleum ether and ethyl acetate (8.5:1.5) was used as eluent for column chromatography. Isolated as a pale yellow solid (**A4f**: 0.051 g, 80%). ^{1}H

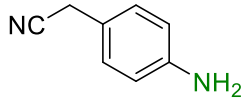
NMR (700 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 3.44 (brs, 2H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 144.91, 129.09, 123.28, 116.45.



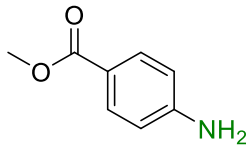
4-Bromoaniline (**A4g**):[S2] A mixture of petroleum ether and ethyl acetate (8.5:1.5) was used as eluent for column chromatography. Isolated as a white solid [**A4g**: (0.077 g, 89%)[a]; (0.070 g, 81%)[b]]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 2H), 6.69 – 6.50 (m, 2H), 3.63 (brs, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 132.14, 116.84, 111.89.



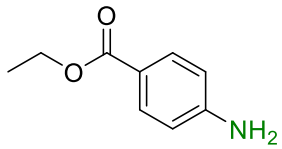
4-(trifluoromethyl)aniline (**A4h**):[S1] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a yellow liquid (**A4h**: 0.064 g, 80%).^1H NMR (700 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 3.93 (brs, 2H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 149.47, 126.82 (q, *J* = 3.7 Hz), 125.72, 124.18, 120.30 (q, *J* = 32.8 Hz), 114.32.



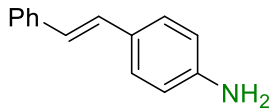
2-(4-aminophenyl)acetonitrile (**A4i**):[S5] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a yellow liquid [**A4i**: (0.055 g, 84%)[a]; (0.057 g, 87%)[b]]. ^1H NMR (700 MHz, $CDCl_3$) δ 7.08 (d, *J* = 6.7 Hz, 2H), 6.66 (d, *J* = 6.5 Hz, 2H), 3.72 (brs, 2H), 3.62 (s, 2H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 146.34, 129.05, 119.45, 118.63, 115.59, 22.92.



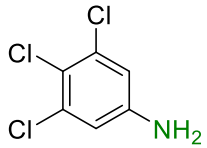
Methyl 4-aminobenzoate (**A4j**):[S1] A mixture of hexanes and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as an off-white solid (**A4j**: 0.057 g, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 167.32, 150.94, 131.74, 119.88, 113.94, 51.75.



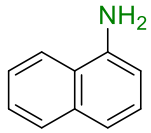
Ethyl 4-aminobenzoate (**A4k**):[S6] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a pale yellow solid [**A4k**: (0.070 g, 85%)[a]; (0.051 g, 62%)[b]]. ^1H NMR (700 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.00 (brs, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 166.86, 150.87, 131.67, 120.20, 113.90, 60.43, 14.54.



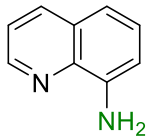
(E)-4-Styrylaniline (**A5**):[S1] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a pale yellow solid (**A5**: 0.086 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.34 (dd, *J* = 8.2, 6.7 Hz, 4H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 16.3 Hz, 1H), 6.93 (d, *J* = 16.3 Hz, 1H), 6.71 – 6.66 (m, 2H), 3.74 (brs, 2H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 146.27, 138.08, 128.81, 128.73, 128.17, 127.88, 127.02, 126.23, 125.25, 115.34.



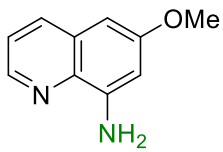
3,4,5-Trichloroaniline (**A6**):[S1] A mixture of petroleum ether and ethyl acetate (6:4) was used as eluent for column chromatography. Isolated as a brown solid (**P8**: 0.077 g, 78%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.68 (s, 2H), 3.73 (brs, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.72, 134.30, 119.97, 115.21.



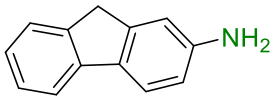
Naphthalen-1-amine (**A7**):[S2] A mixture of petroleum ether and ethyl acetate (8.5:1.5) was used as eluent for column chromatography. Isolated as a purple solid [**A7**: (0.064g, 90%)[a]; (0.060g, 84%)[b]]. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 9.0, 6.0 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.35 – 7.29 (m, 2H), 6.79 (d, *J* = 7.1 Hz, 1H), 4.14 (brs, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.17, 134.51, 128.67, 126.45, 125.96, 124.98, 123.78, 120.91, 119.11, 109.82.



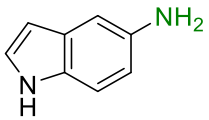
Quinolin-8-amine (**A8**):[S1] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a reddish solid [**A8**: (0.061 g, 85%)[a]; (0.055 g, 76%)[b]]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.15 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.93 (dd, *J* = 7.5, 1.2 Hz, 1H), 4.81 (brs, 2H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 147.52, 144.04, 138.49, 136.16, 128.98, 127.51, 121.45, 116.16, 110.21.



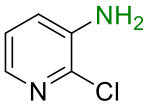
6-Methoxy-Quinolin-8-amine (**A9**):[S7] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a brown oil (**A9**: 0.061 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 4.2, 1.6 Hz, 1H), 7.95 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.31 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.58 (d, *J* = 2.6 Hz, 1H), 6.48 (d, *J* = 2.6 Hz, 1H), 4.93 (brs, 2H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.11, 134.97, 121.94, 101.78, 94.73, 55.41.



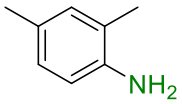
9H-Fluoren-2-amine (**A10**):[S1] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a brown yellow solid [**A10**: (0.054 g, 60%)[a]; (0.067 g, 74%)[b]]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.20 (td, *J* = 7.4, 1.0 Hz, 1H), 6.89 – 6.87 (m, 1H), 6.71 (dd, *J* = 8.0, 2.2 Hz, 1H), 3.81 (s, 2H), 3.72 (brs, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.86, 145.27, 142.38, 142.26, 133.12, 126.77, 125.20, 124.87, 120.77, 118.70, 114.10, 111.93, 36.94.



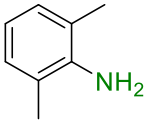
1H-Indol-5-amine (**A11**):[S8] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a yellow solid (**A10**: 0.043 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (brs, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.12 (t, *J* = 2.8 Hz, 1H), 6.96 (d, *J* = 2.2 Hz, 1H), 6.67 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.38 (ddd, *J* = 3.0, 2.0, 0.9 Hz, 1H), 3.00 (brs, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.56, 130.84, 128.90, 124.86, 113.10, 111.65, 105.73, 101.65



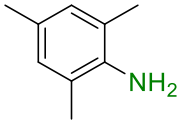
2-Chloropyridin-3-amine (**A12**):[S1] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a light yellow solid (**A12**: 0.048 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 1H), 7.05 – 7.01 (m, 2H), 4.08 (brs, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.77, 138.79, 137.11, 123.48, 122.52.



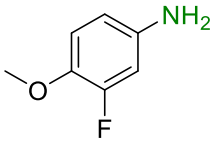
2,4-Dimethylaniline (**A13**):[S9] A mixture of petroleum ether and ethyl acetate (9:1) was used as eluent for column chromatography. Isolated as a grey brown oil (**A13**: 0.050 g, 83%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.99 – 6.94 (m, 2H), 6.66 (d, *J* = 7.9 Hz, 1H), 3.50 (brs, 2H), 2.34 (s, 3H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.99, 131.08, 127.75, 127.30, 122.44, 115.12, 20.40, 17.27.



2,6-Dimethylaniline (**A14**):[S4] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a yellow oil (**A14**: 0.045 g, 75%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.6 Hz, 2H), 6.71 (t, *J* = 7.5 Hz, 1H), 3.52 (brs, 2H), 2.24 (s, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 142.75, 128.33, 121.79, 118.10, 17.68.



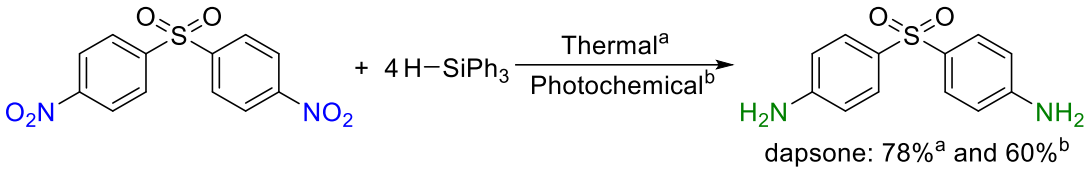
2,4,6-Dimethylaniline (**A15**):[S9] A mixture of petroleum ether and ethyl acetate (8:2) was used as eluent for column chromatography. Isolated as a yellow oil (**A15**: 0.048 g, 71%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 2H), 3.14 (brs, 2H), 2.22 (s, 3H), 2.17 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 140.12, 128.97, 127.39, 122.08, 20.49, 17.73.



3-fluoro-4-methoxyaniline (**A16**):[S7] A mixture of petroleum ether, ethyl acetate, and methanol (8:1.5:0.5) was used as eluent for column chromatography. Isolated as a brown oil (**A16**: 0.051 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (t, *J* = 9.0 Hz, 1H), 6.47 (dd, *J* = 12.7, 2.7 Hz, 1H), 6.38 (ddd, *J* = 8.6, 2.7, 1.4 Hz, 1H), 3.81 (s, 3H), 3.45 (brs, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 154.59, 152.16, 141.13, 140.48, 115.88 (d, *J* = 3.1 Hz), 110.42 (d, *J* = 3.1 Hz), 104.47, 104.26, 57.53.

Synthesis of drug molecules:

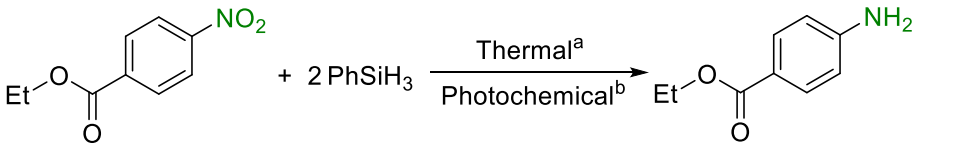
Synthesis of Dapsone:[S10]



Thermal protocol: In a dried pressure tube fitted with a magnetic stir bar, $Co_{2(}CO)_8$ (1 mol%, 0.0017 g), corresponding nitroarene (0.154 g, 0.5 mmol), phenylsilane (0.218 g, 1.05 mmol) and THF (2mL) were added successively under nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (8:2) as eluent to afford yellow hygroscopic solid as pure product (0.096 g, 78%).

Photochemical protocol: In a dried quartz glass tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (3 mol%, 0.0051g), corresponding nitroarene (0.154 g, 0.5 mmol), phenylsilane (0.218 g, 1.05 mmol) were added successively under nitrogen atmosphere. The reaction mixture was exposed to 350 nm UV light irradiation for 2 h. After completion of the reaction, MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (8:2) as eluent to afford yellow hygroscopic solid as pure product (0.075 g, 60%). ^{1}H NMR (700 MHz, DMSO-d_6) δ 7.44 (d, *J* = 8.6 Hz, 4H), 6.58 (d, *J* = 8.6 Hz, 4H), 5.93 (brs, 4H). ^{13}C{^{1}H} NMR (176 MHz, DMSO-d_6) δ 152.63, 128.42, 128.13, 112.77.

Synthesis of benzocaine:[S6]

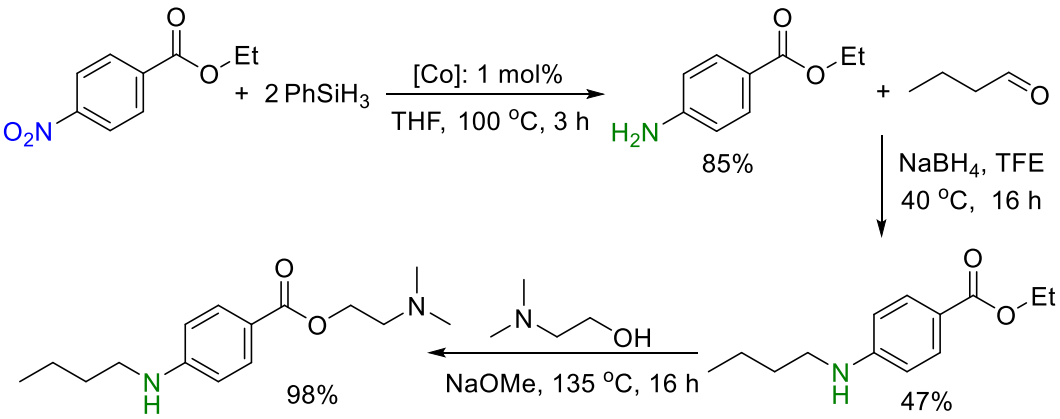


Thermal protocol: In a dried pressure tube fitted with a magnetic stir bar, $Co_{2(}CO)_8$ (1 mol%, 0.0017 g), corresponding nitroarene (0.092 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol) and THF (2mL) were added successively under nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (8:2) as eluent to afford yellow hygroscopic solid as pure product (0.070 g, 85%).

Photochemical protocol: In a dried quartz glass tube fitted with a magnetic stir bar, $Co_2(CO)_8$

(3 mol%, 0.0051g), corresponding nitroarene (0.092 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol) were added successively under nitrogen atmosphere. The reaction mixture was exposed to 350 nm UV light irradiation for 2 h. After completion of the reaction, MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (8:2) as eluent to afford yellow hygroscopic solid as pure product (0.051 g, 62%).

Synthesis of Tetracaine:[S11,S12]

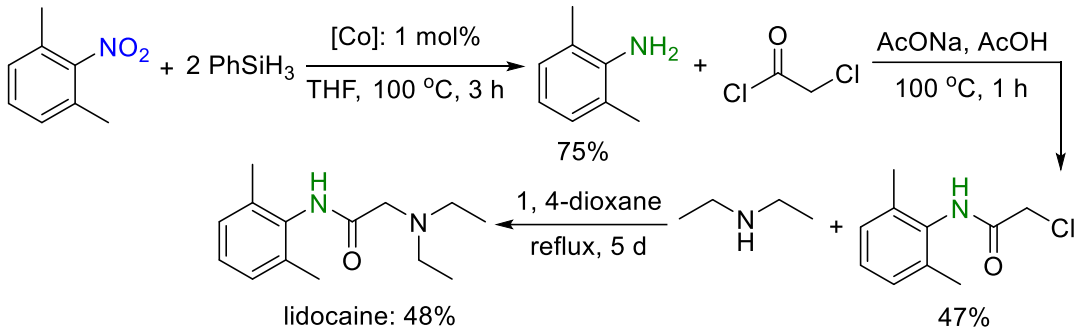


Synthesis of ethyl 4-aminobenzoate (step 1): In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1 mol%, 0.0017 g), corresponding nitroarene (0.092 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol) and THF (2mL) were added successively under nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate as eluent to afford yellow hygroscopic solid as pure product (0.070 g, 85%).

Synthesis of ethyl 4-(butylamino)benzoate (step 2): The Synthetic process was previously reported.[S11] This is a modified procedure. In a round bottom flask, a solution of the appropriate carbonyl compound (0.036 g, 0.5 mmol) and TFE (2 mL) was magnetically stirred at 40 °C. After 5 min, the ethyl 4-aminobenzoate (0.083 g, 0.5 mmol) was added, and the mixture vigorously stirred. After stirring for 5 min, $NaBH_4$ (0.023 g, 0.6 mmol) was added and the progress of the reaction conversion was followed by TLC (hexane–EtOAc, 8:2). After completion of the reaction, the mixture was filtered and the residue was washed with TFE (2 mL). The solvent was distilled off (to recover for the next run) and the pure product was obtained. the crude product was further purified by silica gel column chromatography with petroleum ether and ethyl acetate (8:2) as eluent. (0.052 g; 47%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.11 (brs, 1H), 3.15 (t, *J* = 7.1 Hz, 2H), 1.60 (dd, *J* = 14.8, 7.4 Hz, 2H), 1.43 (dt, *J* = 14.9, 7.3 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.05, 152.22, 131.61, 118.44, 111.38, 60.24, 43.18, 31.51, 20.32, 14.57, 13.95.

Synthesis of tetracaine (step 3): The Synthetic process was previously reported.[S12] This is a modified procedure. In a round bottom flask a solution of ethyl 4-(butylamino)benzoate (0.110 g, 0.5 mmol) in 2-(dimethylamino)ethan-1-ol (1.5 mL) was treated with NaOMe (5 mg, 0.1 mmol), heated to 135 ºC and stirred at the same temperature for 16 h. The mixture was cooled to room temperature and diluted with H_2O (10 mL) and CH_2Cl_2 (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. Purification by column chromatography on silica gel eluting with petroleum ether and ethyl acetate (7:3) gave pure product (0.129 g; 98%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.84 (d, *J* = 6.4 Hz, 2H), 6.51 (d, *J* = 6.7 Hz, 2H), 4.36 (s, 2H), 4.14 (s, 1H), 3.14 (d, *J* = 4.7 Hz, 2H), 2.69 (s, 2H), 2.33 (s, 6H), 1.63 – 1.56 (m, 2H), 1.42 (dt, *J* = 14.8, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 131.73, 117.97, 111.36, 62.33, 58.03, 45.89, 43.12, 31.46, 20.28, 13.92.

Synthesis of lidocaine:[S13,S14]



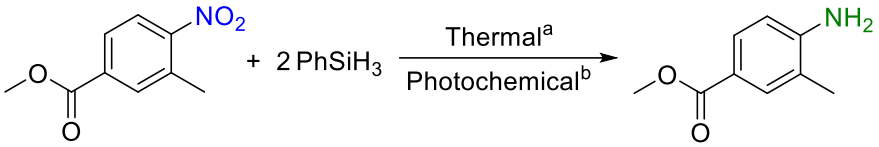
Synthesis of 2,6-dimethylaniline (step 1): In a dried pressure tube fitted with a magnetic stir bar, $Co_{2(}CO)_8$ (1 mol%, 0.0017 g), corresponding nitroarene (0.092 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol) and THF (2mL) were added successively under nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (8:2) as eluent to afford yellow hygroscopic solid as pure product (0.045 g, 75%).

Synthesis of 2-chloro-N-(2,6-dimethylphenyl)acetamide (step 2): The Synthetic process was previously reported.[S13] This is a modified procedure. In a dried round-bottom flask fitted with a magnetic stirring bar, chloroacetyl chloride (0.169 g, 1.5 mmol) and 2, 6-dimethylaniline (0.121 g, 0.5 mmol) were added and the mixture was stirred until slurry was observed. Sodium acetate (0.164 g, 2 mmol) was added into the mixture and it was allowed to run at reflux condition for 1 h. After completion of the reaction, it was cooled to 0 °C for 20 minutes. The solid material was filtered off and washed with cold water to obtain the crude. The crude was dried under vacuum to get white crystalline solid as pure compound (0.046 g, 47%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.85 (brs, 1H), 7.16 – 7.09 (m, 3H), 4.25 (d, *J* = 3.6 Hz, 2H), 2.24 (s, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 164.48, 135.48, 132.81, 128.51, 128.03, 42.92, 18.42.

Synthesis of lidocaine (step 3): The Synthetic process was previously reported.[S14] This is a modified procedure. In a dried pressure tube fitted with magnetic stirring bar, 2-chloro-N-(2,6-

dimethylphenyl)-acetamide (0.197 g, 1 mmol), diethyl amine (310 µl, 3 mmol) and triethyl amine (834 µl, 6 mmol) were taken and 1,4 dioxane (4 ml) was added into it. Then the reaction mixture was allowed to run for five days in reflux condition. After completion of the reaction, the resultant mixture was dried under high vacuum to remove all the volatiles. After drying a dark red solid was isolated as crude product. The crude product was purified by column chromatography (silica gel as stationary phase and 1:1 mixture of ethyl acetate and hexanes as eluent) to give red solid as pure product (0.113 g, 48%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.07 (s, 3H), 3.29 (s, 2H), 2.74 (d, *J* = 5.3 Hz, 4H), 2.22 (s, 6H), 1.15 (s, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 170.05, 135.22, 133.96, 128.33, 127.26, 57.12, 49.06, 18.67, 12.56.

Synthesis of intermediate A:[S7]

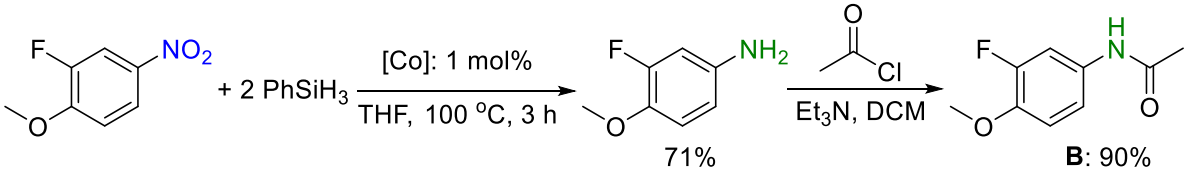


A: 72[a] and 54[b] %

Thermal protocol: In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1 mol%, 0.0017 g), corresponding nitroarene (0.083 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol) and THF (2mL) were added successively under nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (8:2) as eluent to afford yellow hygroscopic solid as pure product (0.059 g, 72%).

Photochemical protocol: In a dried quartz glass tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (3 mol%, 0.0051g), corresponding nitroarene (0.083 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol) were added successively under nitrogen atmosphere. The reaction mixture was exposed to 350 nm UV light irradiation for 2 h. After completion of the reaction, MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (8:2) as eluent to afford yellow hygroscopic solid as pure product (0.044 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 10.9, 2.6 Hz, 2H), 6.63 (d, *J* = 8.2 Hz, 1H), 3.99 (brs, 2H), 3.85 (s, 3H), 2.17 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.52, 149.27, 132.37, 129.43, 121.16, 119.76, 113.80, 51.70, 17.25.

Synthesis of intermediate B:[S7,S15]



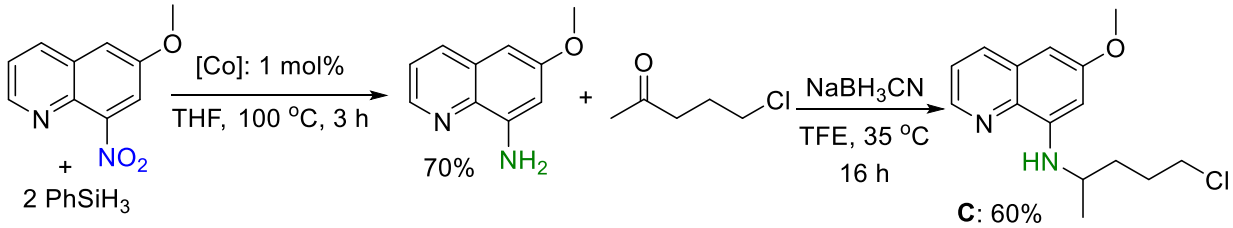
71% **B**: 90%

Synthesis of 3-fluoro-5-methoxyaniline: In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1 mol%, 0.0017 g), corresponding nitroarene (0.086 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol) and THF (2mL) were added successively under nitrogen atmosphere. The

reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether,ethyl acetate and methanol (8:1.5:0.5) as eluent to afford yellow hygroscopic solid as pure product (0.050 g, 71%).

Synthesis of N-(3-fluoro-5-methoxyphenyl)acetamide (B): The Synthetic process was previously reported.[S15] In a 50 mL round-bottom flask aniline (0.070 g, 0.5 mmol), 5 mL dry DCM and dry Et_3N (0.075 g, 1.5 equiv.) added. The reaction mixture cooled to 0 °C and stir for 15 minute. Then, CH_3COCl (0.046 g, 1.2 equiv.) added dropwise to the reaction mixture and stirred at room temperature for 12 h. After completion (judged by TLC), the resulting reaction mixture was extracted with DCM (3 x 5 mL) and dried over Na_2SO_4. Solvent evaporated and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (8:2) as eluent to afford pure product (0.082g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.38 (dd, *J* = 12.8, 2.5 Hz, 1H), 7.14 – 7.09 (m, 1H), 6.87 (t, *J* = 9.0 Hz, 1H), 3.84 (s, 3H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.70, 153.37, 150.93, 144.54 (d, *J* = 11.1 Hz), 131.50 (d, *J* = 9.3 Hz), 115.94 (d, *J* = 3.1 Hz), 113.79 (d, *J* = 2.3 Hz), 109.62, 109.50 (d, *J* = 22.6 Hz), 56.70, 24.40.

Synthesis of intermediate C:[S7]



Synthesis of 6-Methoxyquinolin-8-amine: In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1 mol%, 0.0017 g), corresponding nitroarene (0.102 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol) and THF (2mL) were added successively under nitrogen atmosphere. The reaction mixture was heated at an appropriate temperature (100 °C) in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and 10 wt% of NaOH solution (3 mL) were added to the resultant mixture. The mixture was then extracted with Et_2O (3 x 5 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and a mixture of petroleum ether and ethyl acetate (9:1) as eluent to afford yellow hygroscopic solid as pure product (0.060 g, 70%).

Synthesis of N-(5-Chloropentan-2-yl)-6-methoxyquinolin-8-amine (C): The Synthetic process was previously reported.[S7] This is a modified procedure. In a round bottom flask, a solution of the appropriate carbonyl compound (0.060 g, 0.5 mmol) and TFE (2 mL) was magnetically stirred at 40 °C. After 5 min, the 6-Methoxyquinolin-8-amine (0.087 g, 0.5 mmol) was added, and the mixture vigorously stirred. After stirring for 5 min, $NaBH_3CN$ (0.063 g, 1 mmol) was added and the progress of the reaction conversion was followed by TLC (Pet ether–EtOAc, 8:2). After completion of the reaction, the mixture was filtered and the residue was washed with TFE (2 mL). The solvent was distilled off (to recover for the next run) and the pure product was obtained. the crude product was further purified by silica gel column chromatography with petroleum ether and ethyl acetate(8:2) as eluent to get pure product

(0.083 g, 60%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.6 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.54 (s, 2H), 4.62 (dd, *J* = 12.7, 6.3 Hz, 1H), 4.04 (dd, *J* = 17.2, 8.6 Hz, 1H), 3.90 (s, 3H), 3.36 (t, *J* = 7.1 Hz, 1H), 2.26 (dt, *J* = 11.7, 9.6 Hz, 1H), 2.06 – 1.69 (m, 4H), 1.09 (d, *J* = 6.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 158.31, 144.32, 134.92, 130.75, 121.13, 105.58, 95.72, 55.38, 52.81, 33.90, 23.92, 19.22.

^{1}H and ^{13}C NMR spectra of aromatic amines:

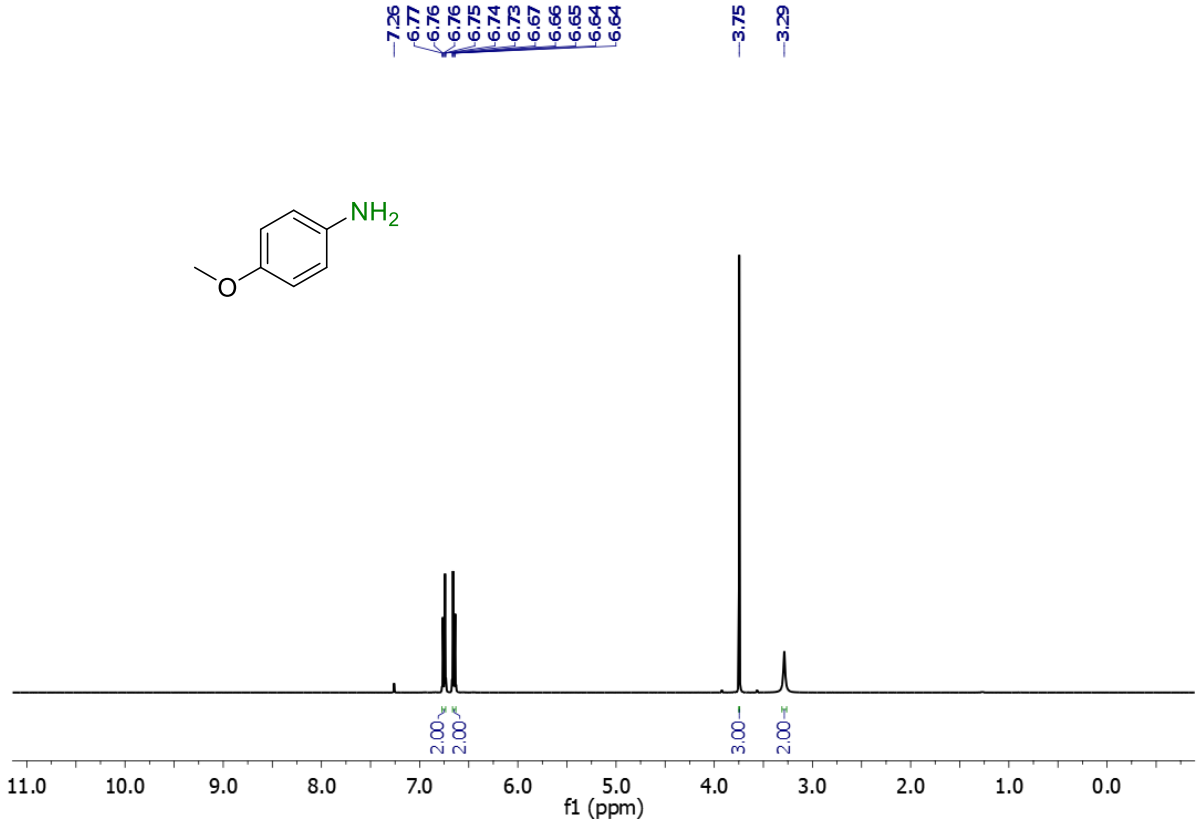


Figure S12. ^{1}H NMR (400 MHz) spectrum of *p*-Anisidine (**A$_0$**) in $CDCl_3$ at r.t.

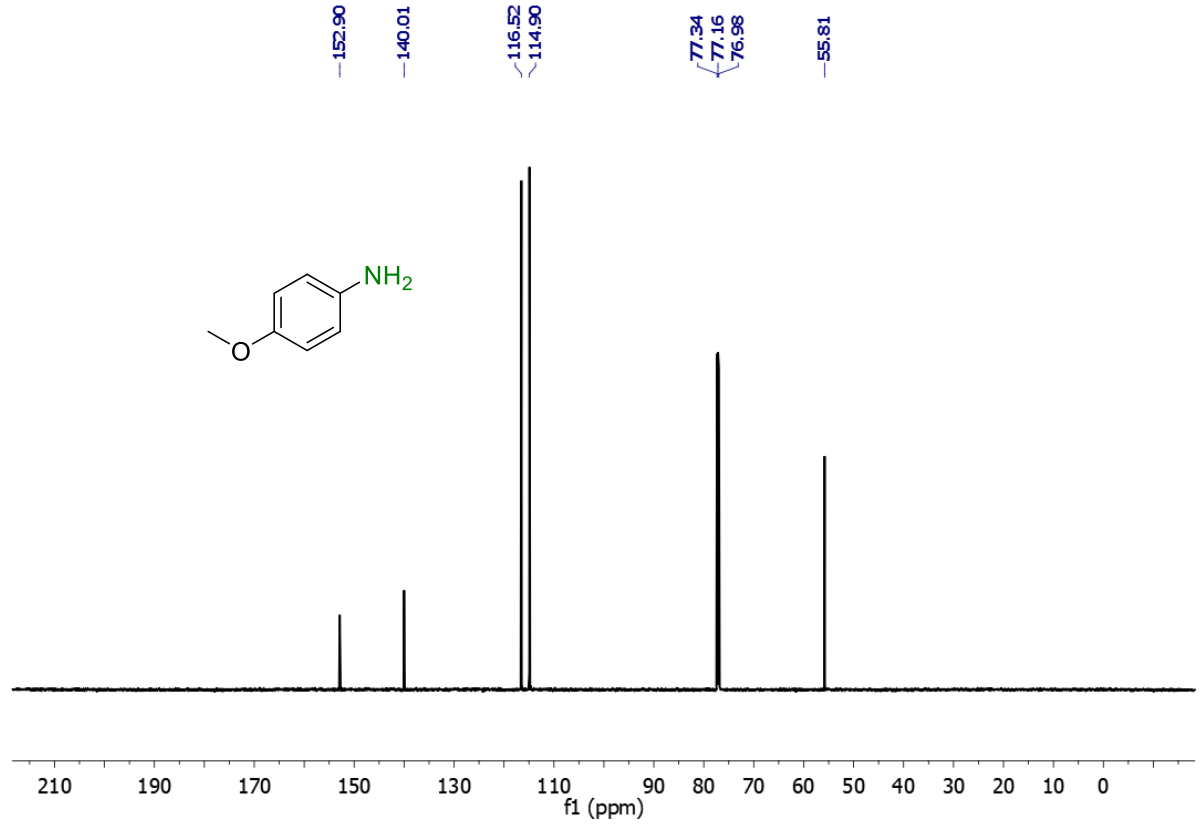


Figure S13. ^{13}C{^{1}H} NMR (176 MHz) spectrum of *p*-Anisidine (**A$_0$**) in $CDCl_3$ at r.t.

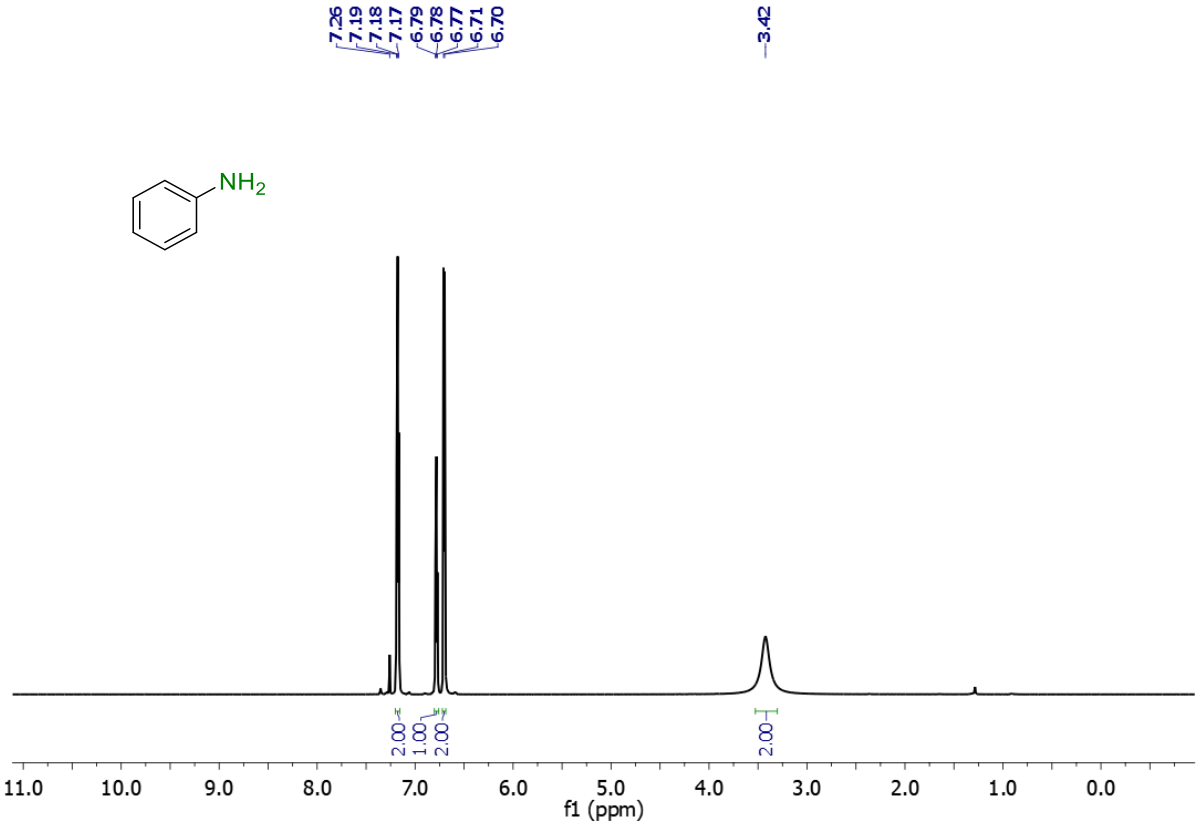


Figure S14. ^{1}H NMR (700 MHz) spectrum of Aniline (**A_1**) in $CDCl_3$ at r.t.

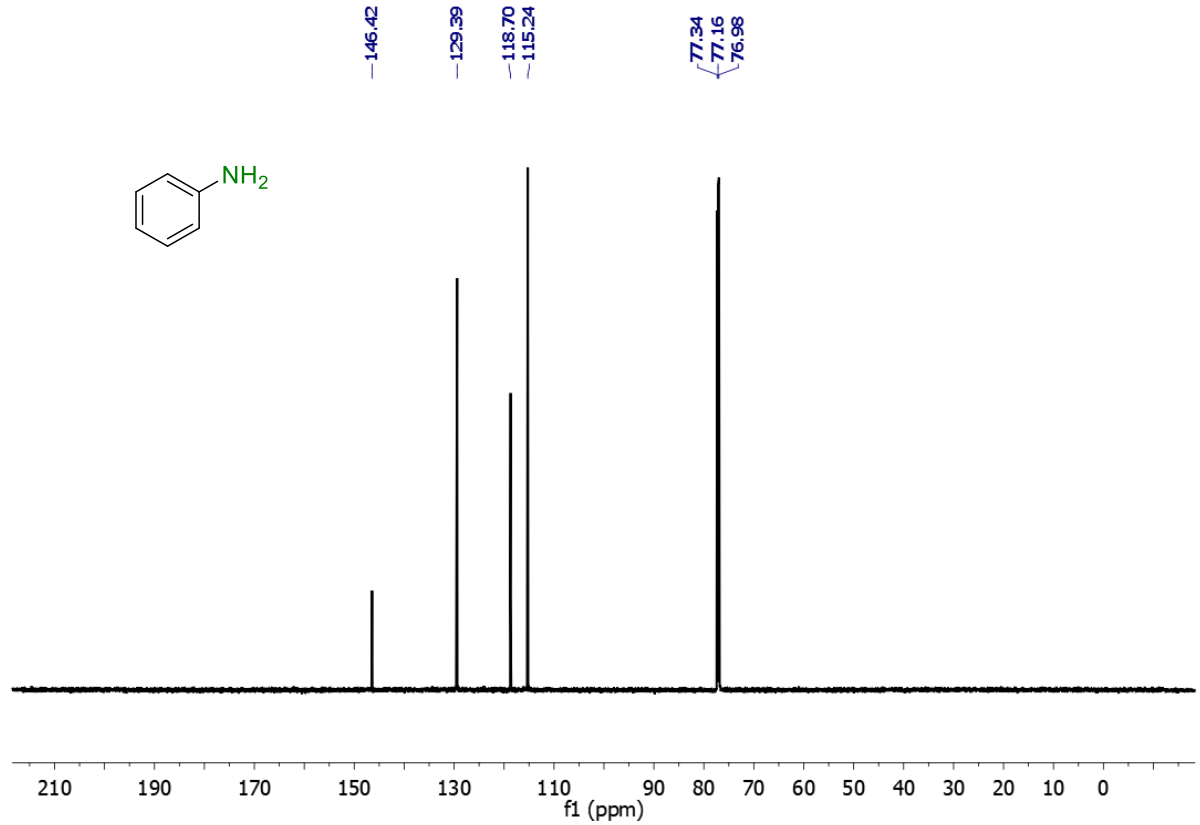


Figure S15. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of Aniline (**A_1**) in $CDCl_3$ at r.t.

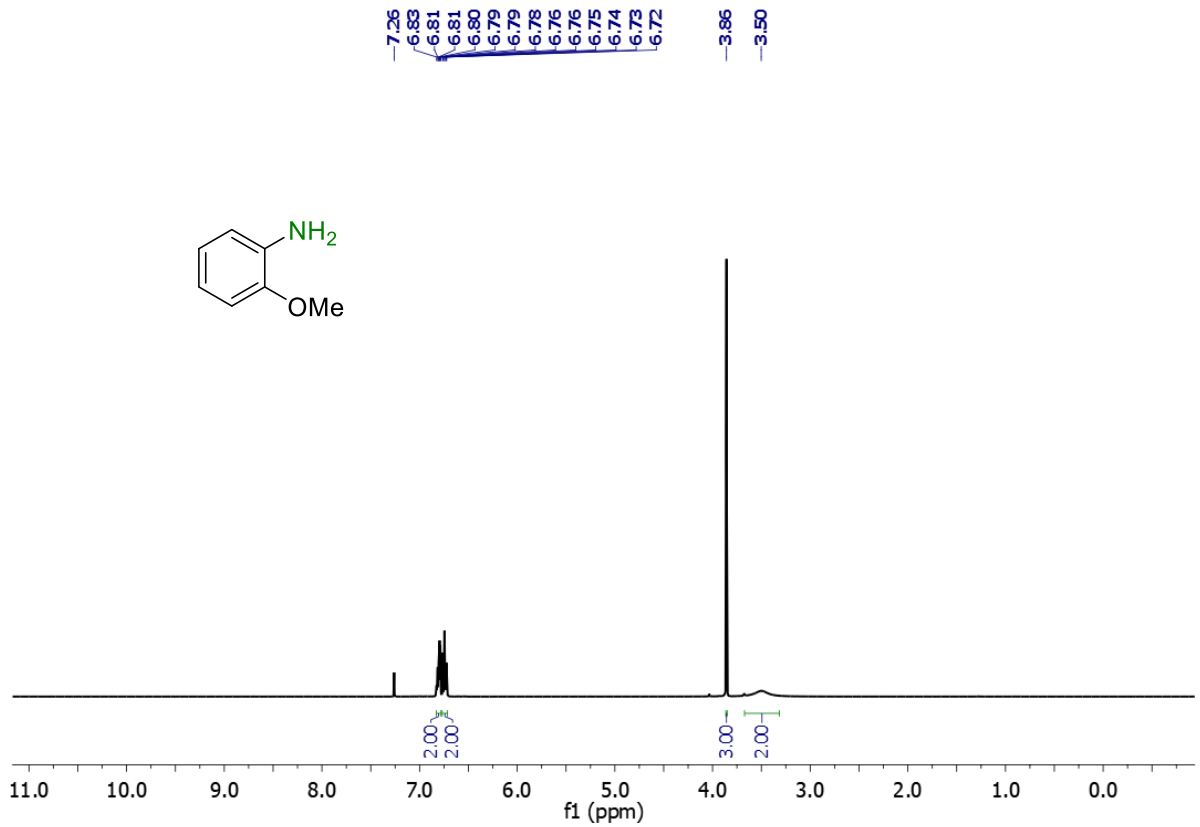


Figure S16. ^{1}H NMR (400 MHz) spectrum of *o*-Anisidine (**A$_{2a}$**) in $CDCl_3$ at r.t.

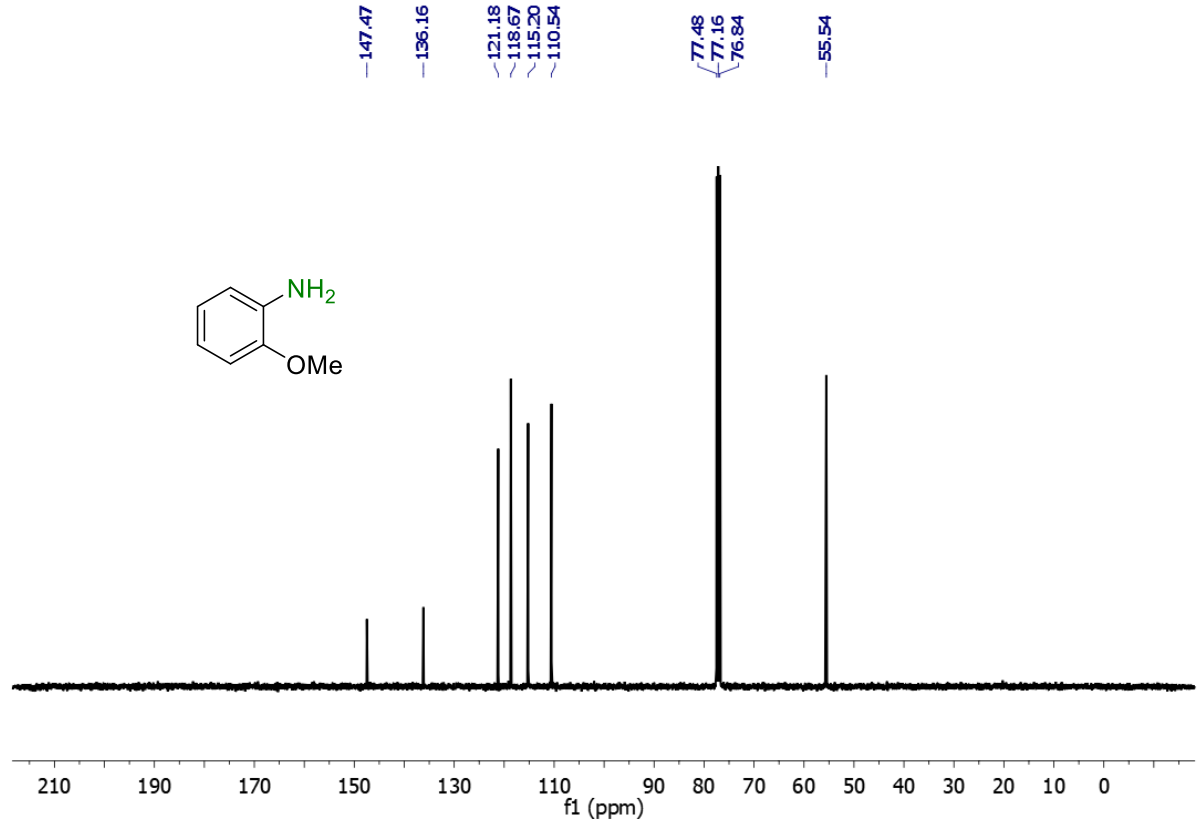


Figure S17. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of *o*-Anisidine (**A$_{2a}$**) in $CDCl_3$ at r.t.

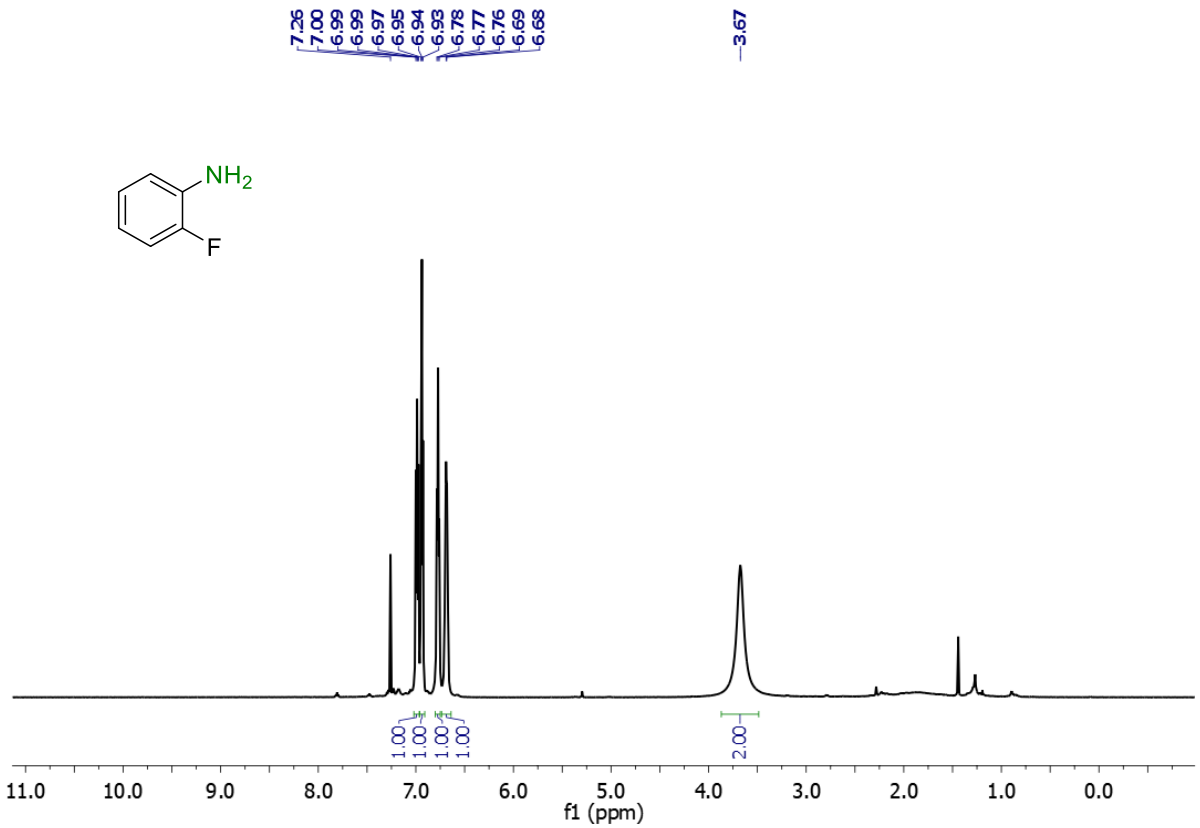


Figure S18. ^{1}H NMR (700 MHz) spectrum of 2-fluoroaniline (**A$_{2b}$**) in $CDCl_3$ at r.t.

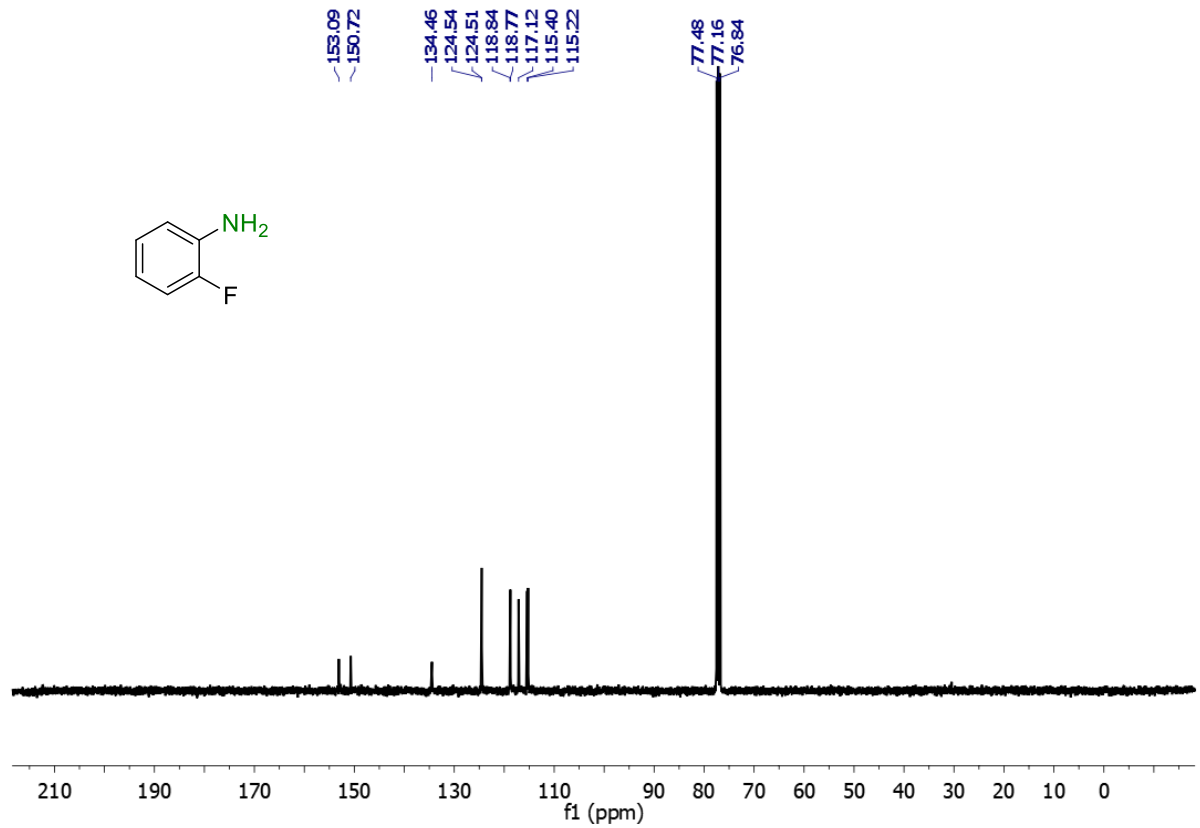


Figure S19. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 2-fluoroaniline (**A$_{2b}$**) in $CDCl_3$ at r.t.

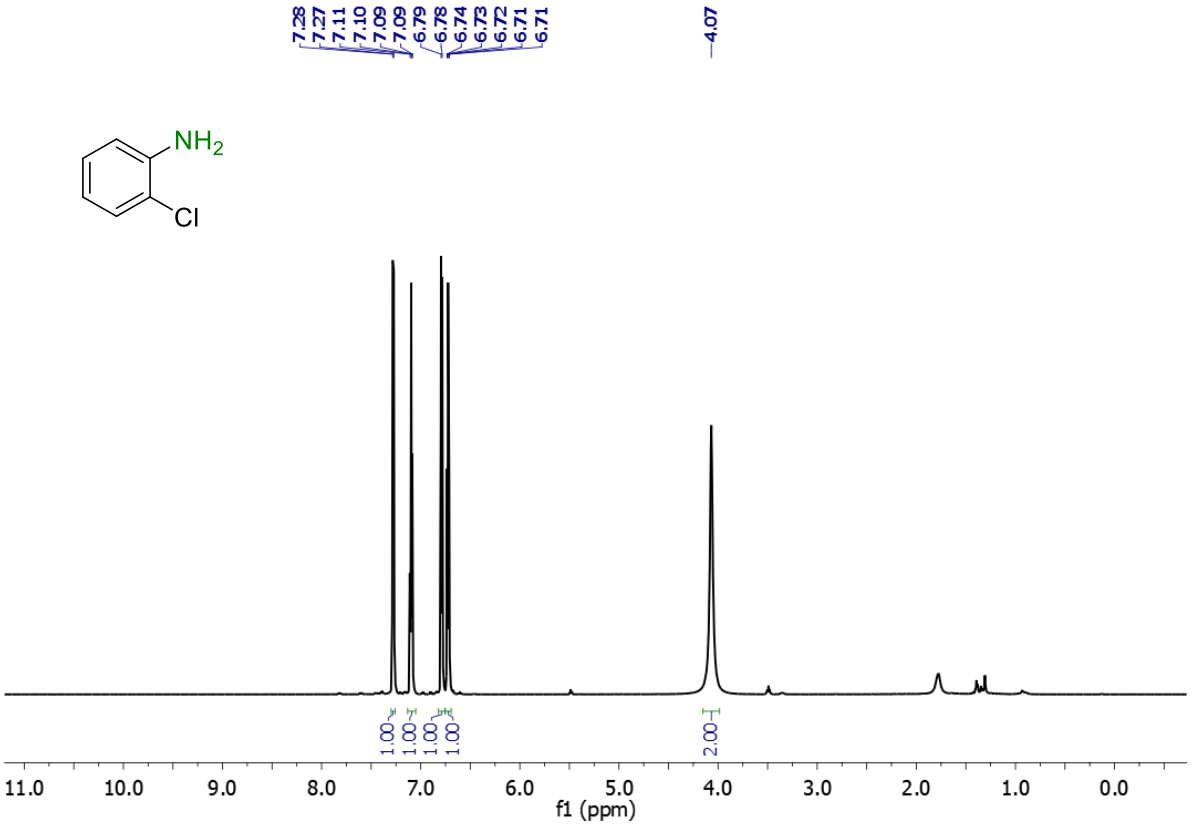


Figure S20. ^{1}H NMR (700 MHz) spectrum of 2-chloroaniline (**A$_{2c}$**) in $CDCl_3$ at r.t.

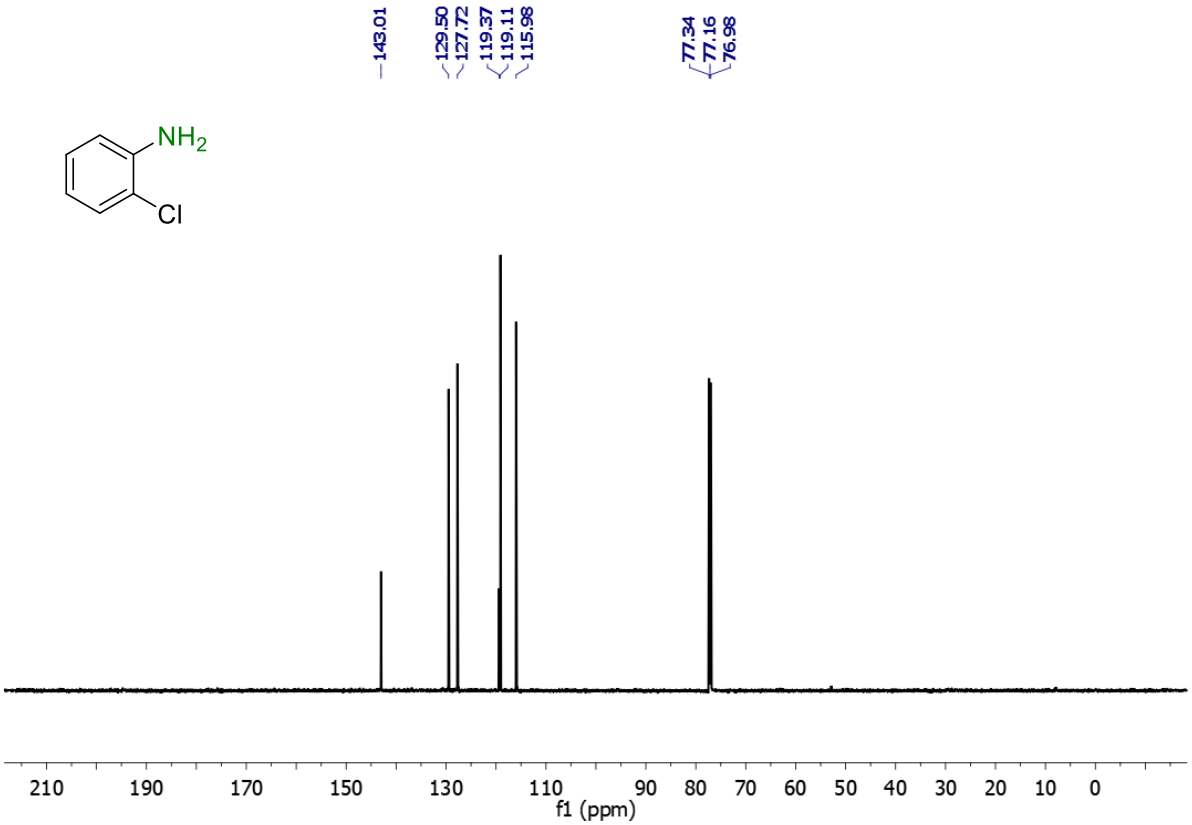


Figure S21. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of 2-chloroaniline (**A$_{2c}$**) in $CDCl_3$ at r.t.

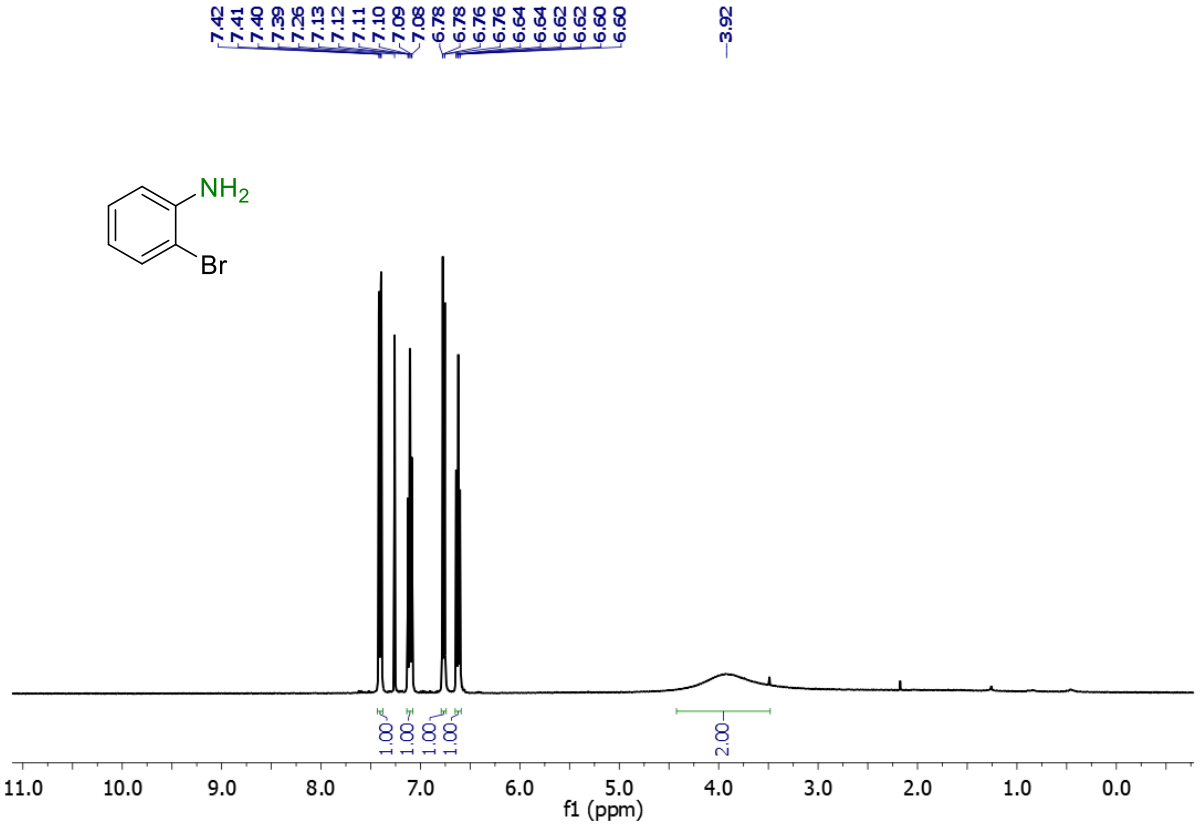


Figure S22. ^{1}H NMR (400 MHz) spectrum of 2-bromoaniline (**A_{2d}**) in $CDCl_3$ at r.t.

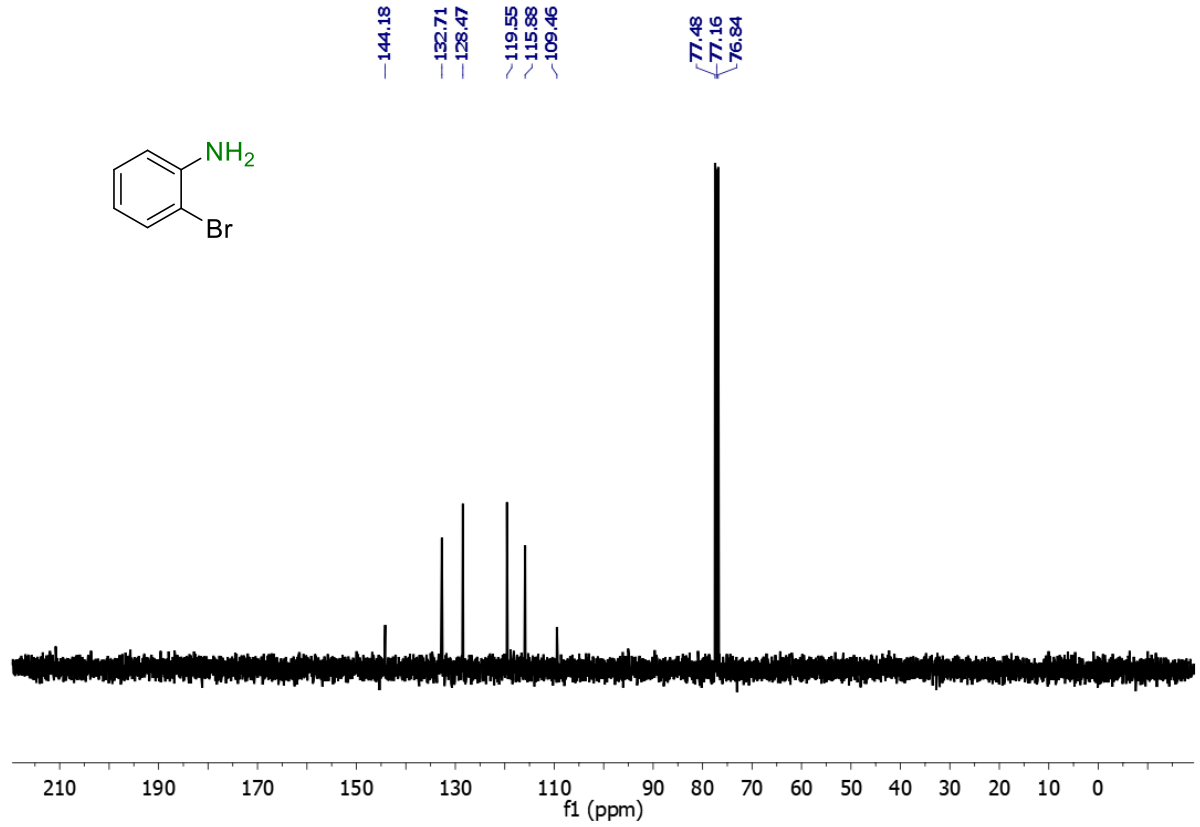


Figure S23. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 2-bromoaniline (**A_{2d}**) in $CDCl_3$ at r.t.

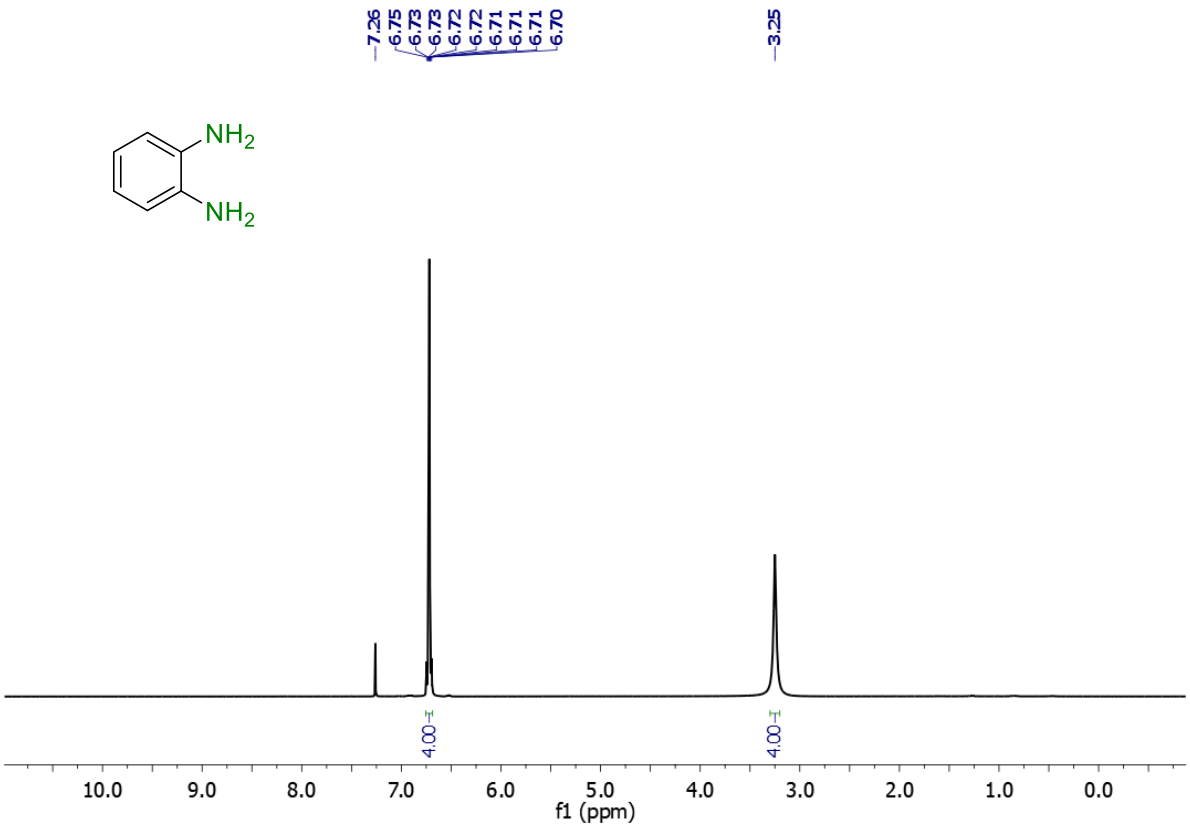


Figure S24. ^{1}H NMR (400 MHz) spectrum of Benzene-1,2-diamine (**A$_{2e}$**) in $CDCl_3$ at r.t.

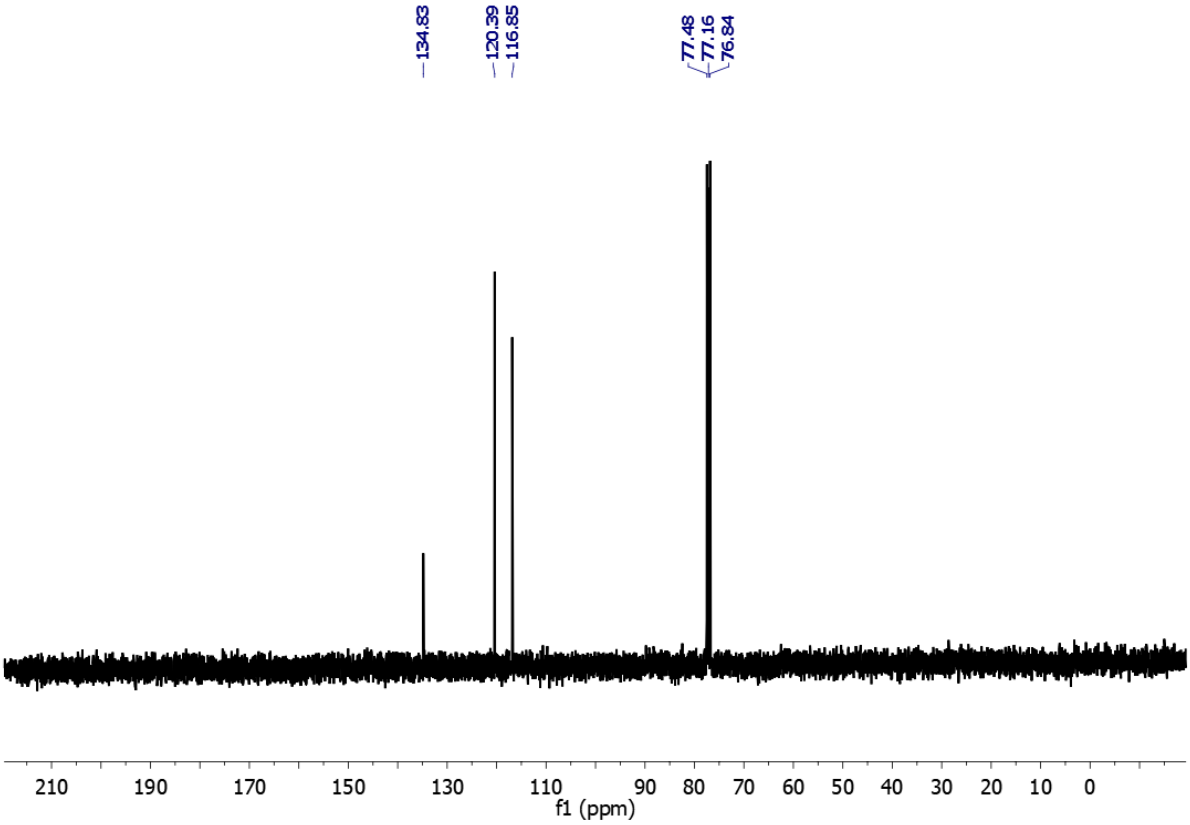


Figure S25. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of Benzene-1,2-diamine (**A$_{2e}$**) in $CDCl_3$ at r.t.

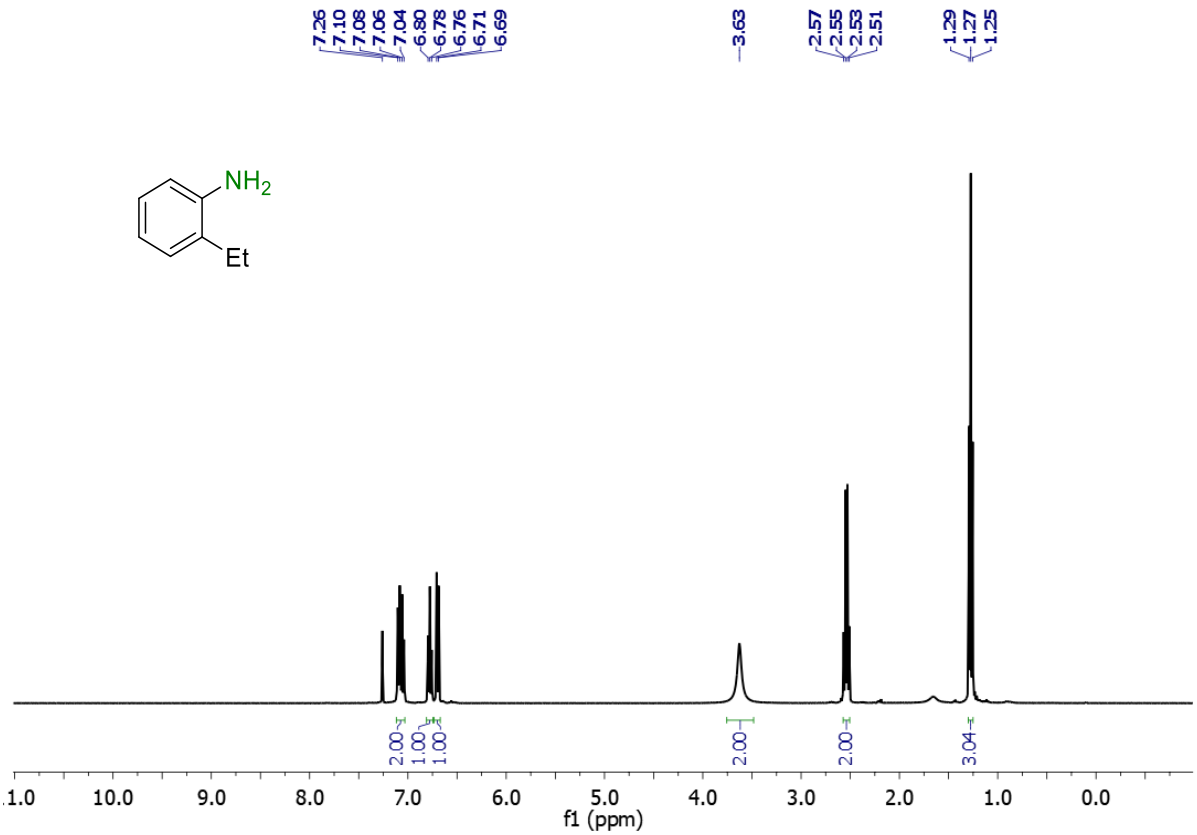


Figure S26. ^{1}H NMR (400 MHz) spectrum of 2-Ethylaniline (**A$_{2f}$**) in $CDCl_3$ at r.t.

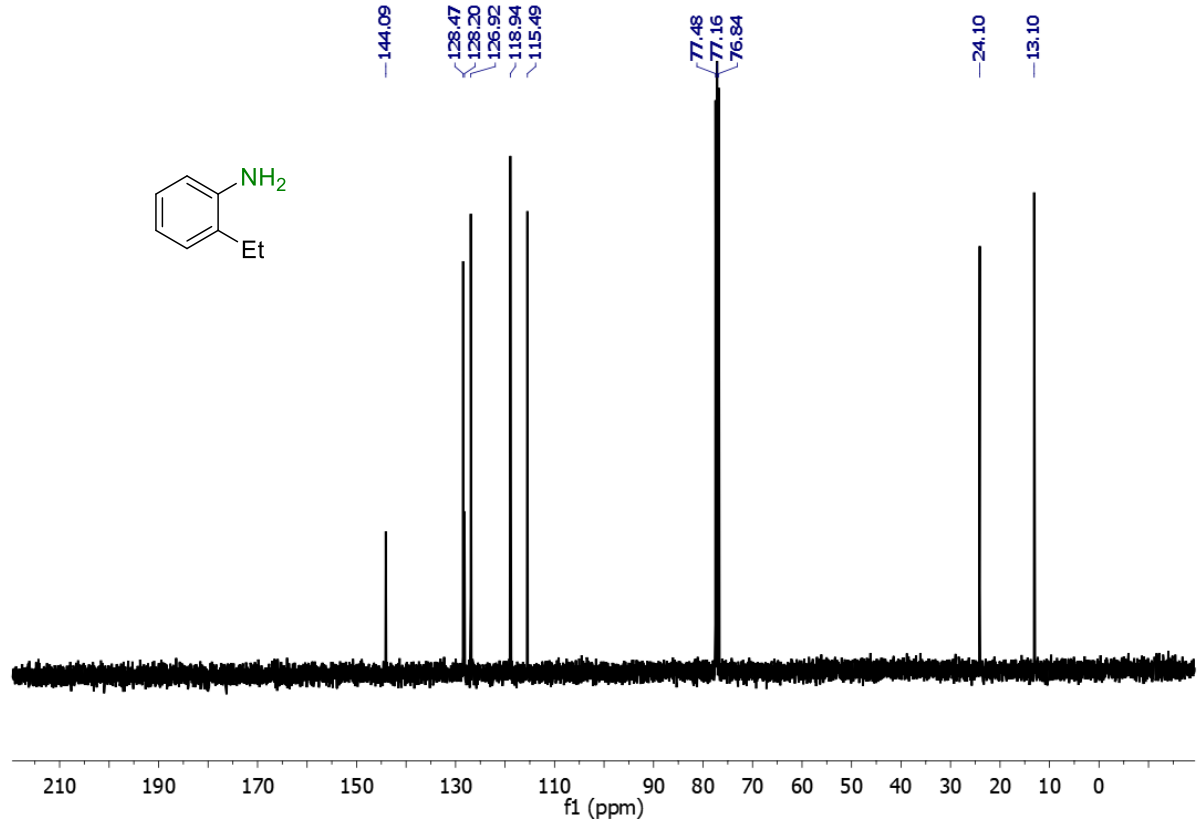


Figure S27. ^{13}C{^{1}H} NMR (101 MHz) spectrum of 2-Ethylaniline (**A$_{2f}$**) in $CDCl_3$ at r.t.

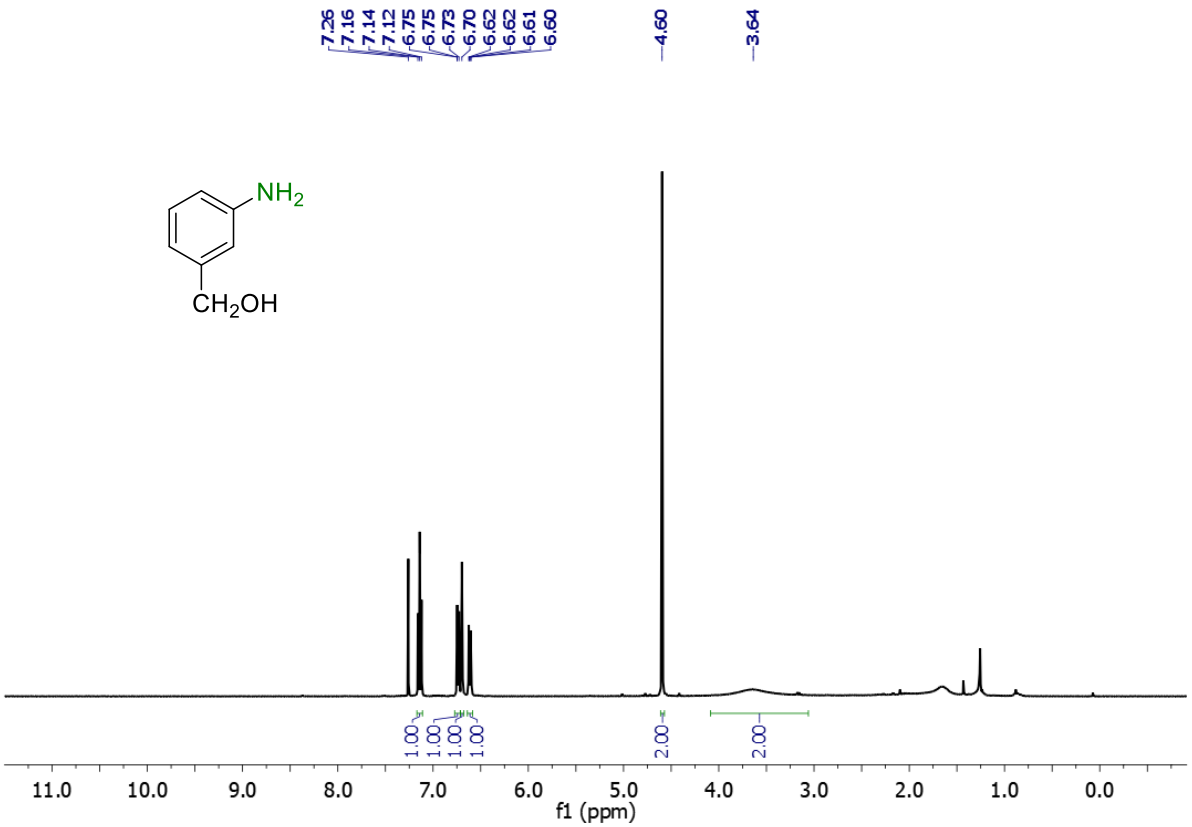


Figure S28. ^{1}H NMR (400 MHz) spectrum of (3-aminophenyl)methanol (**A_{3a}**) in $CDCl_3$ at r.t.

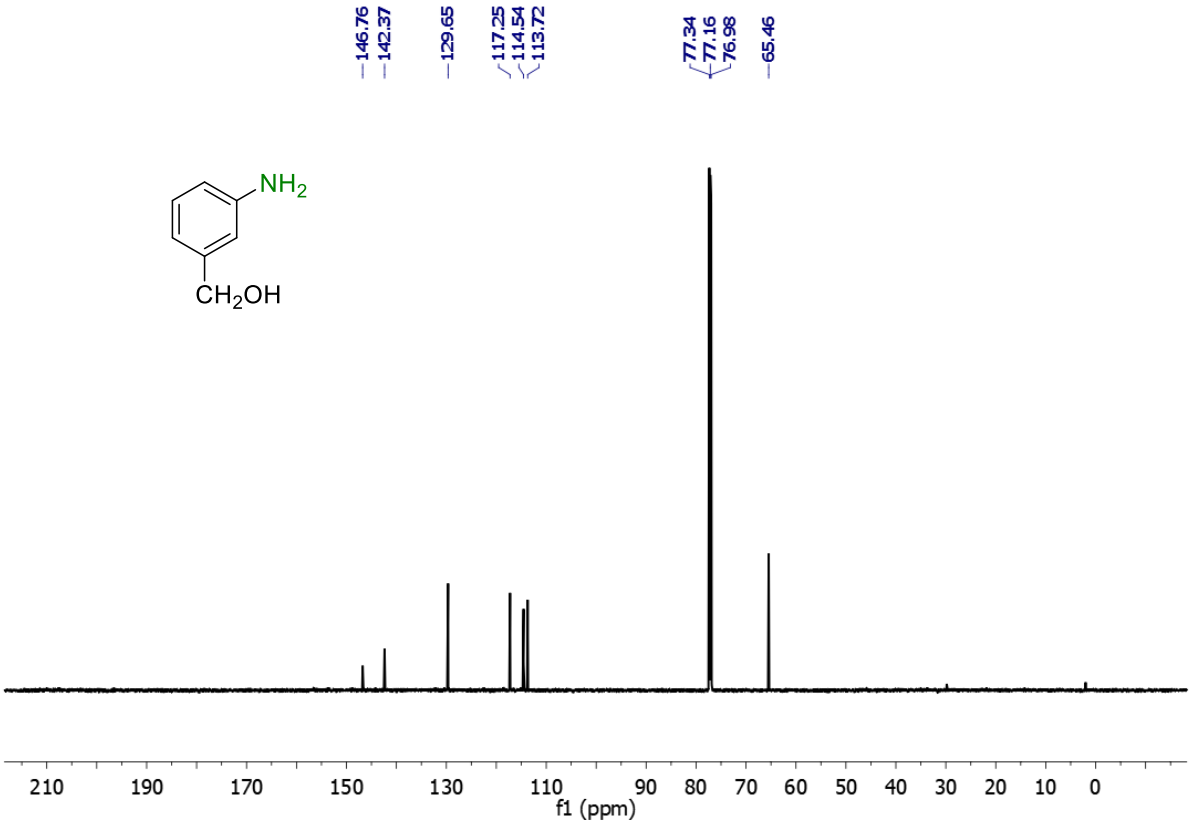


Figure S29. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of 3-aminophenylmethanol (**A_{3a}**) in $CDCl_3$ at r.t.

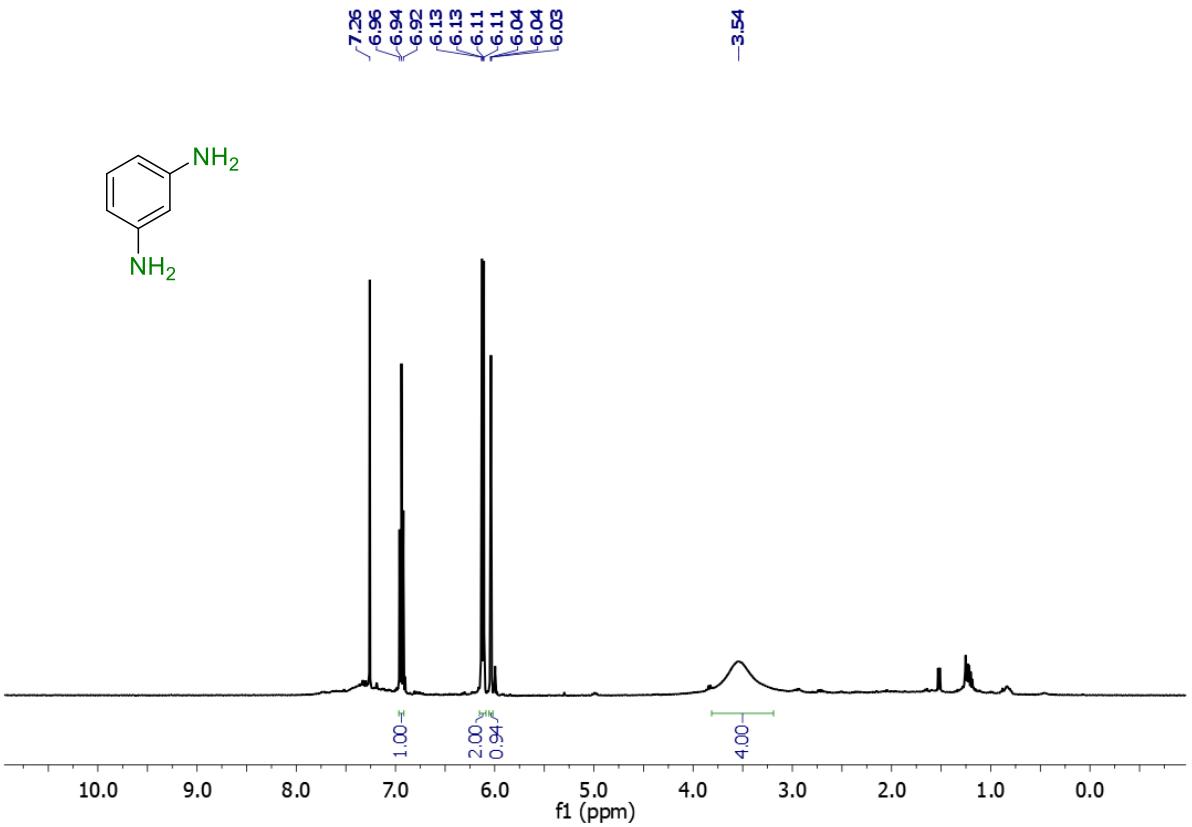


Figure S30. ^{1}H NMR (400 MHz) spectrum of Benzene-1,3-diamine (**A$_{3b}$**) in $CDCl_3$ at r.t.

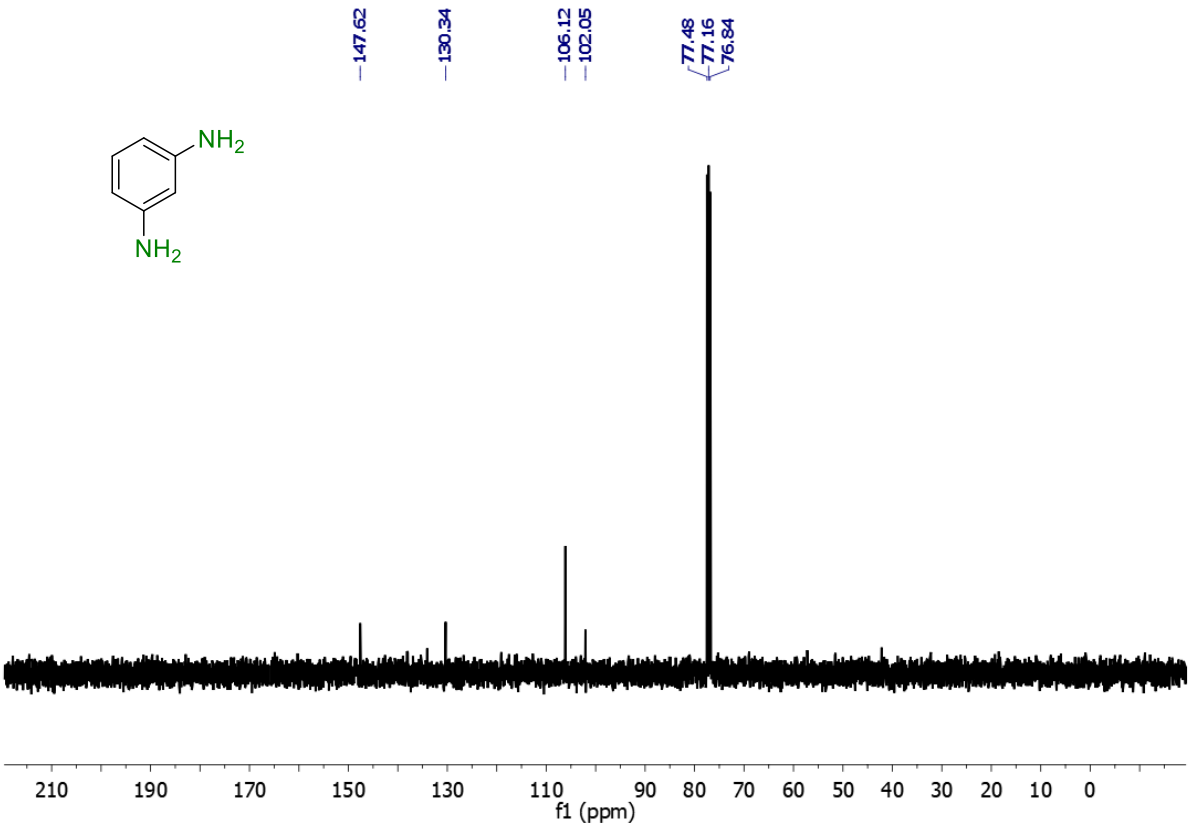


Figure S31. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of Benzene-1,3-diamine (**A$_{3b}$**) in $CDCl_3$ at r.t.

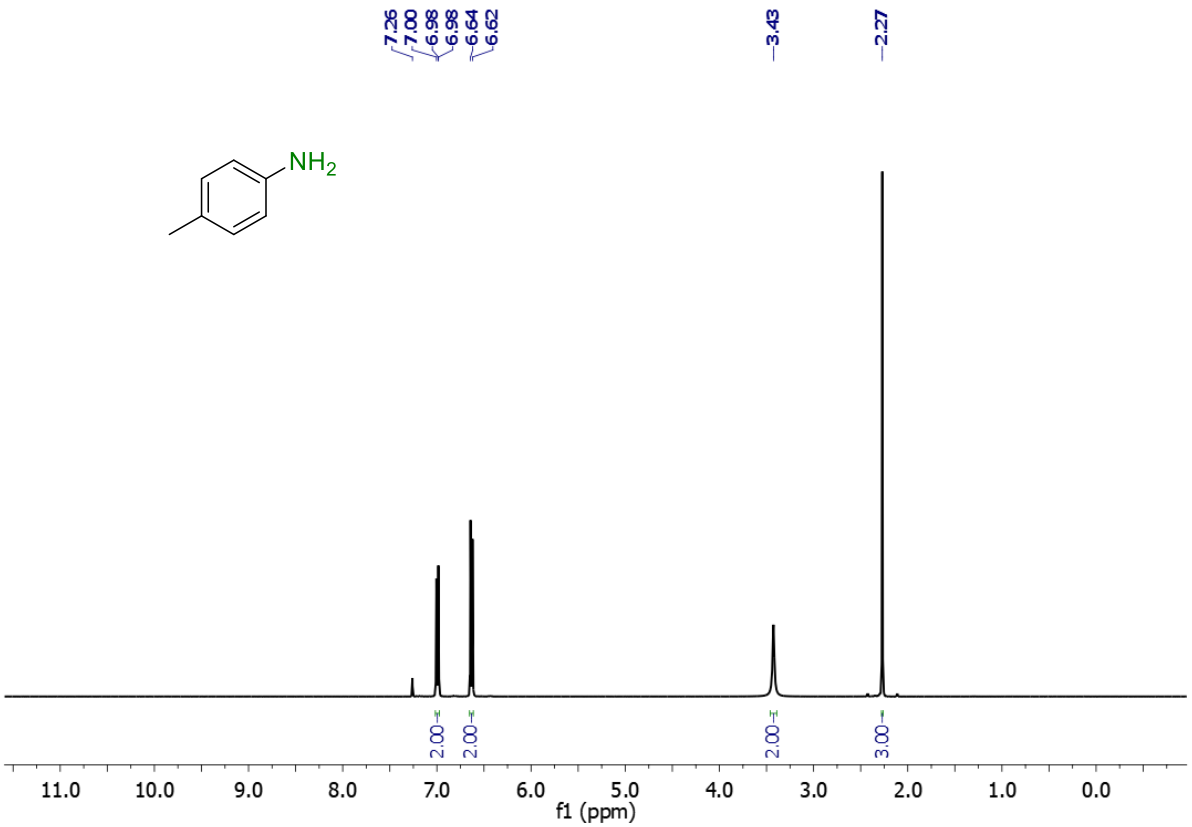


Figure S32. ^{1}H NMR (400 MHz) spectrum of *p*-toluidine (**A$_{4a}$**) in $CDCl_3$ at r.t.

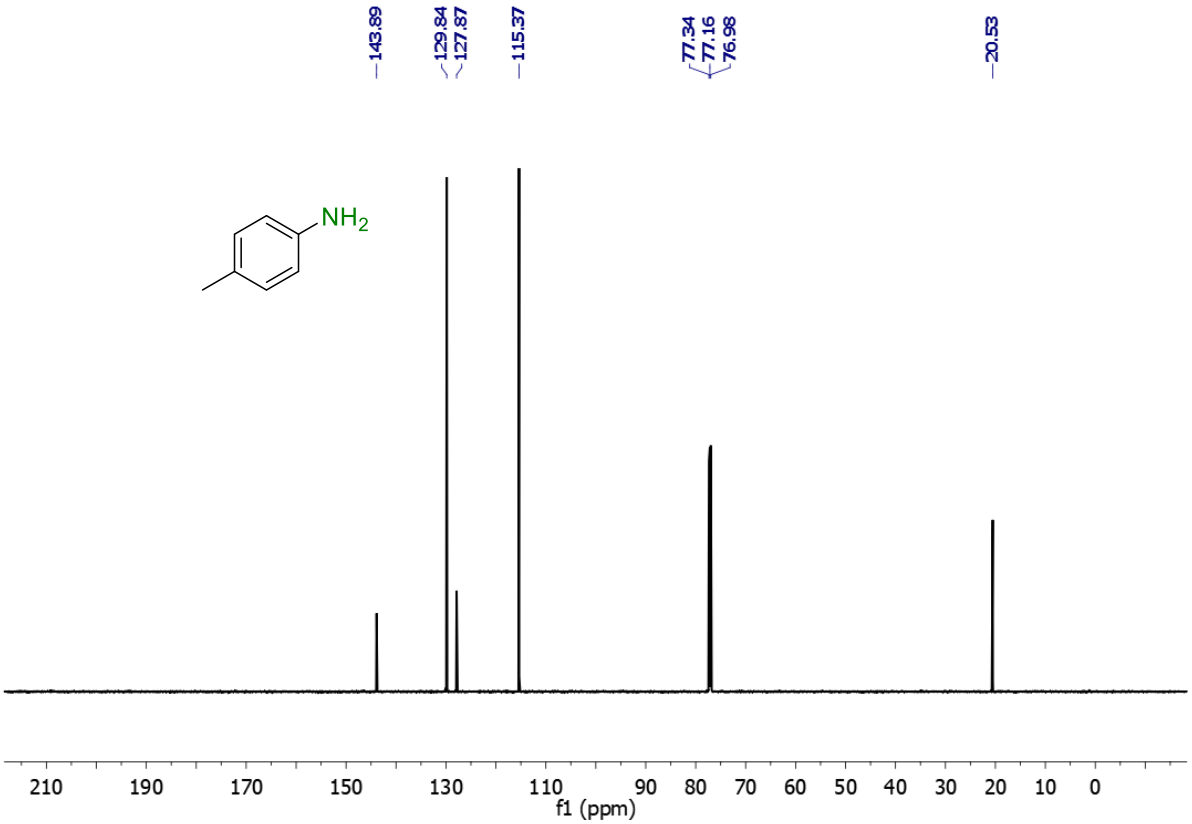


Figure S33. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of *p*-toluidine (**A$_{4a}$**) in $CDCl_3$ at r.t.

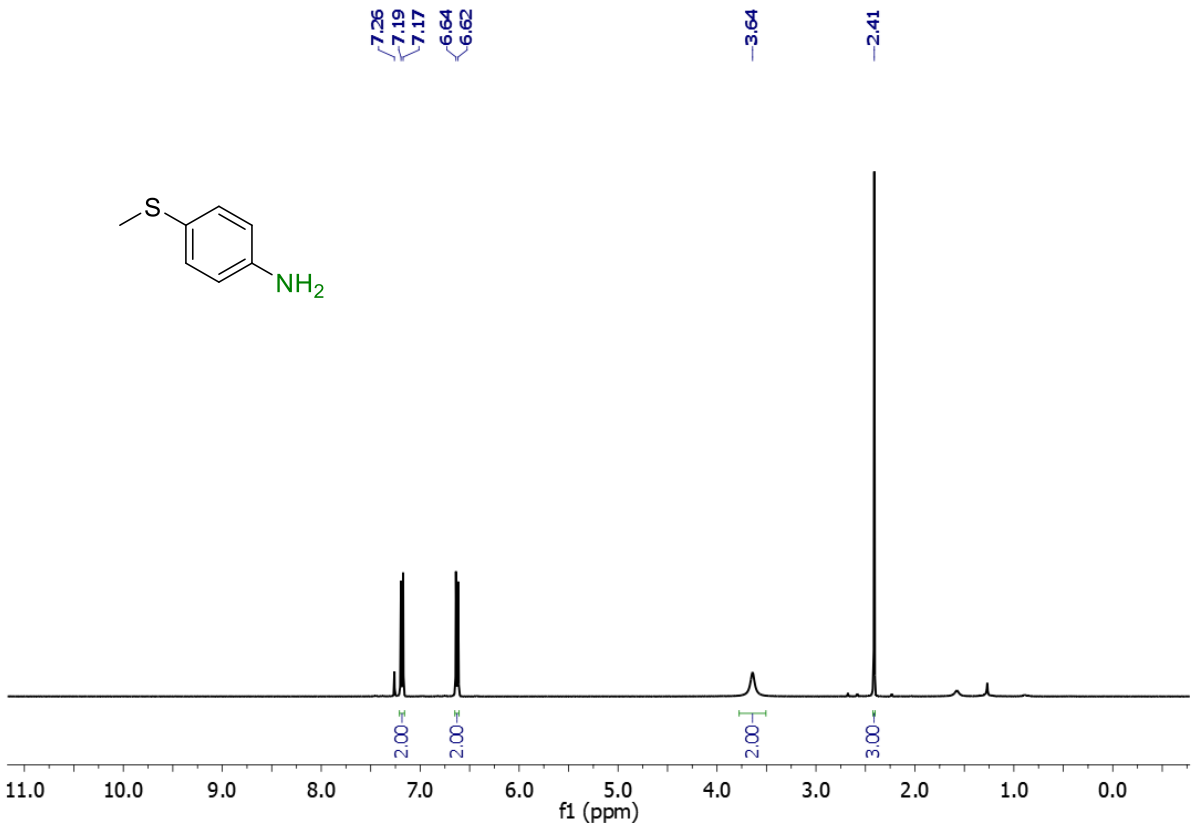


Figure S34. ^{1}H NMR (400 MHz) spectrum of 4-(methylthio)aniline (**A_{4b}**) in $CDCl_3$ at r.t.

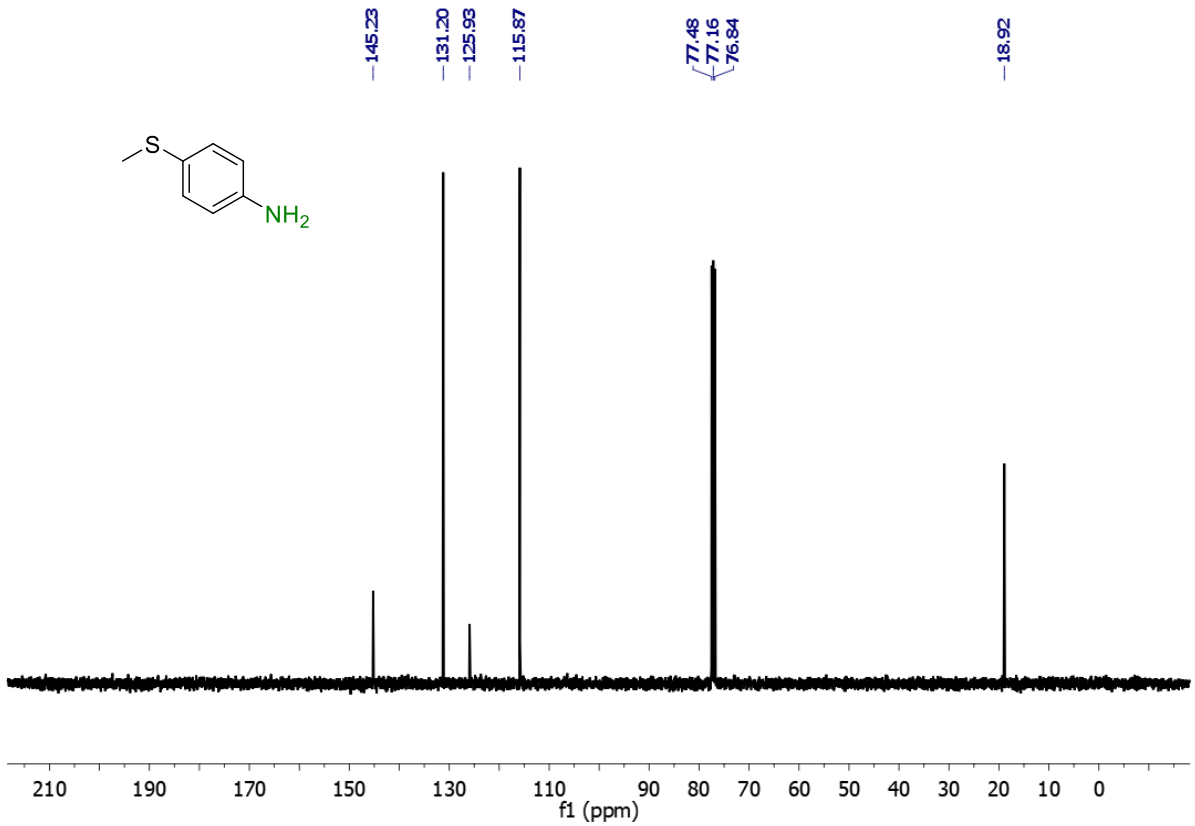


Figure S35. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 4-(methylthio)aniline (**A_{4b}**) in $CDCl_3$ at r.t.

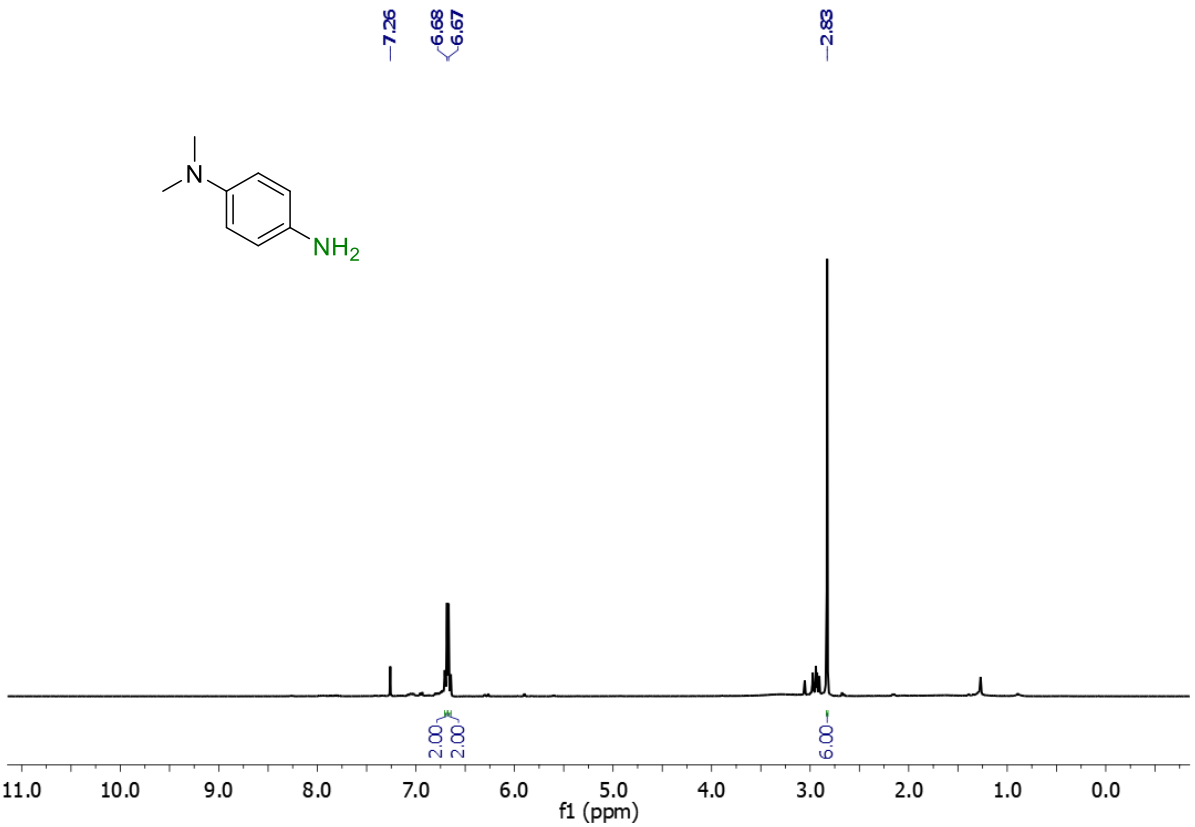


Figure S36. ^{1}H NMR (400 MHz) spectrum of N^{1},N^{1}-dimethylbenzene-1,4-diamine (**A$_{4c}$**) in $CDCl_3$ at r.t.

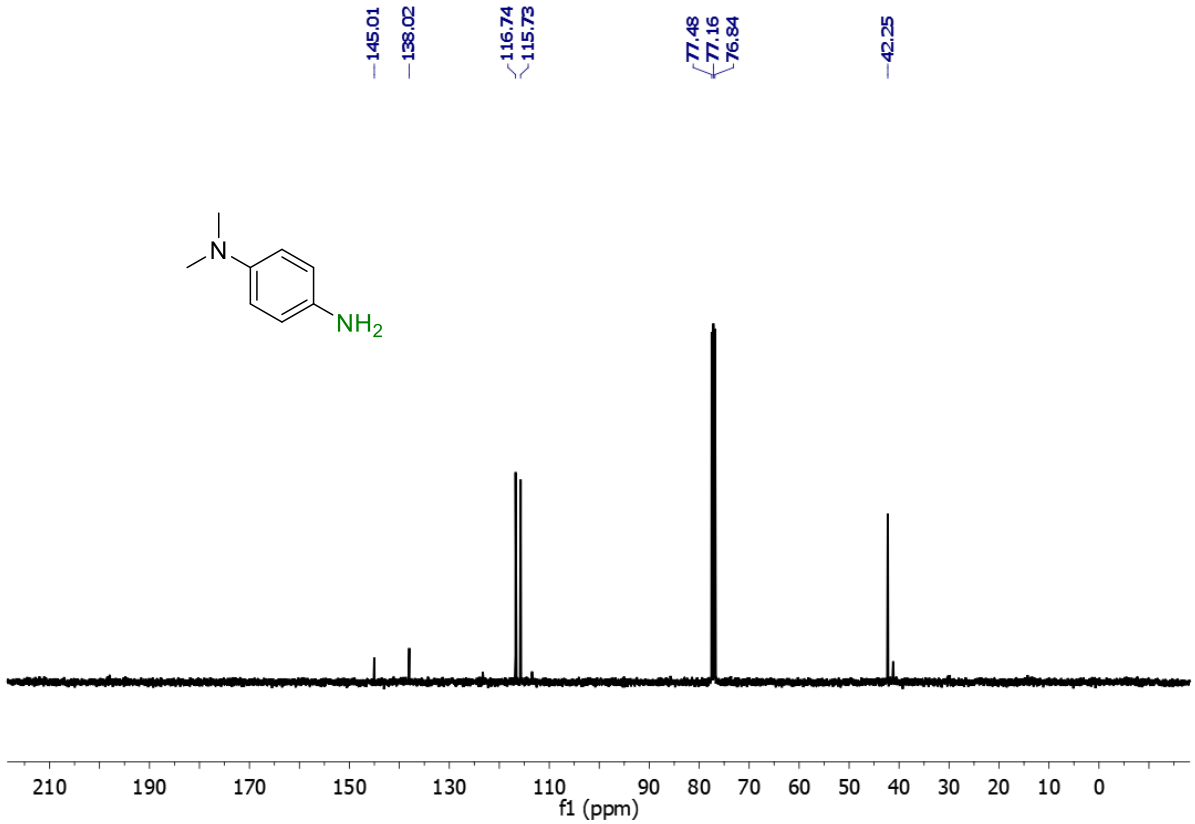


Figure S37. ^{13}C{^{1}H} NMR (101 MHz) spectrum of N^{1},N^{1}-dimethylbenzene-1,4-diamine (**A$_{4c}$**) in $CDCl_3$ at r.t.

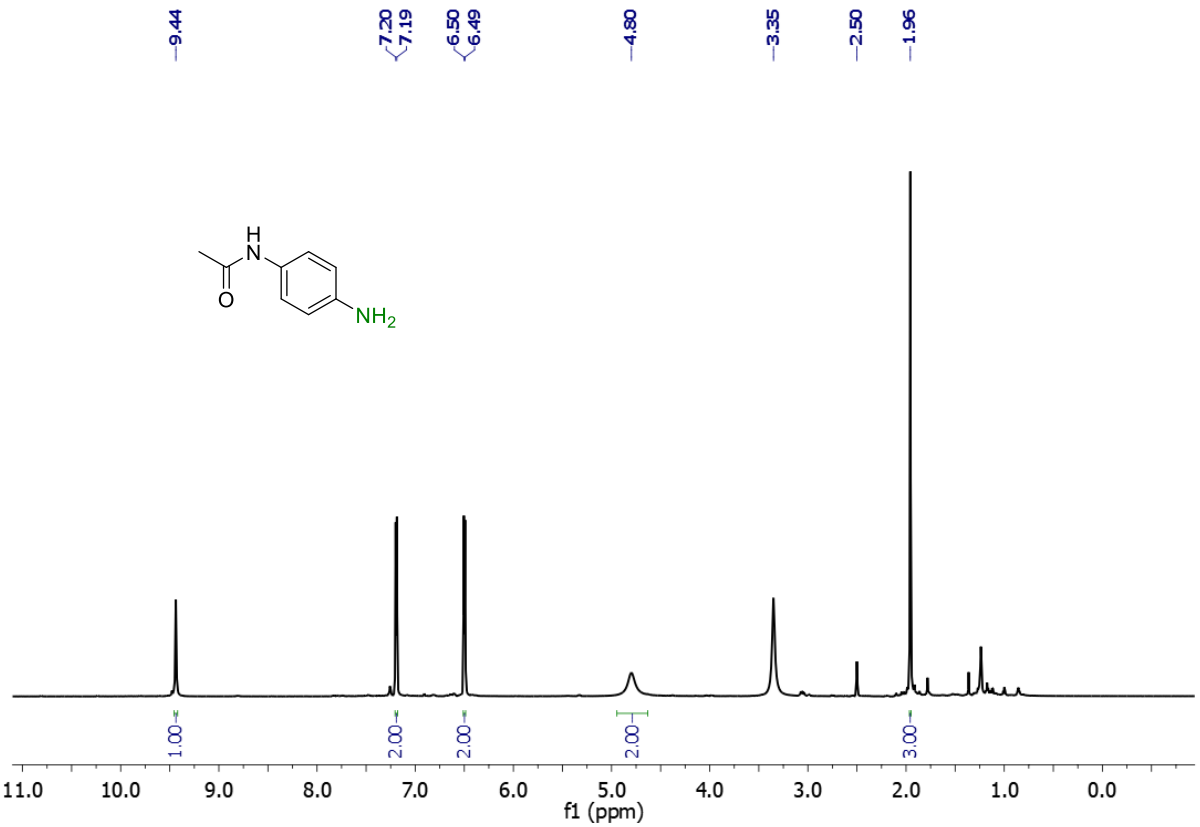


Figure S38. ^{1}H NMR (700 MHz) spectrum of N-(4-Aminophenyl)acetamide (**A$_{4d}$**) in DMSO-d$_6$ at r.t.

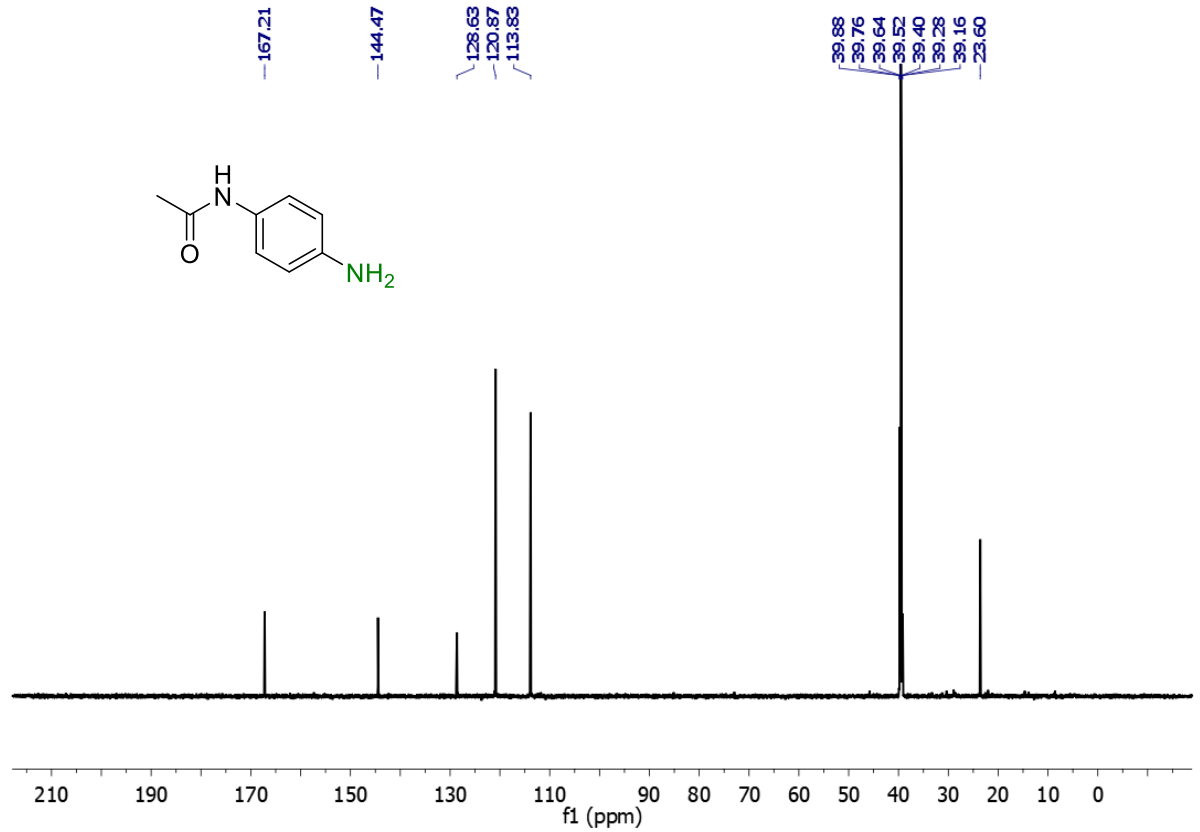


Figure S39. ^{13}C{^{1}H} NMR (176 MHz) spectrum of N-(4-Aminophenyl)acetamide (**A$_{4d}$**) in DMSO-d$_6$ at r.t.

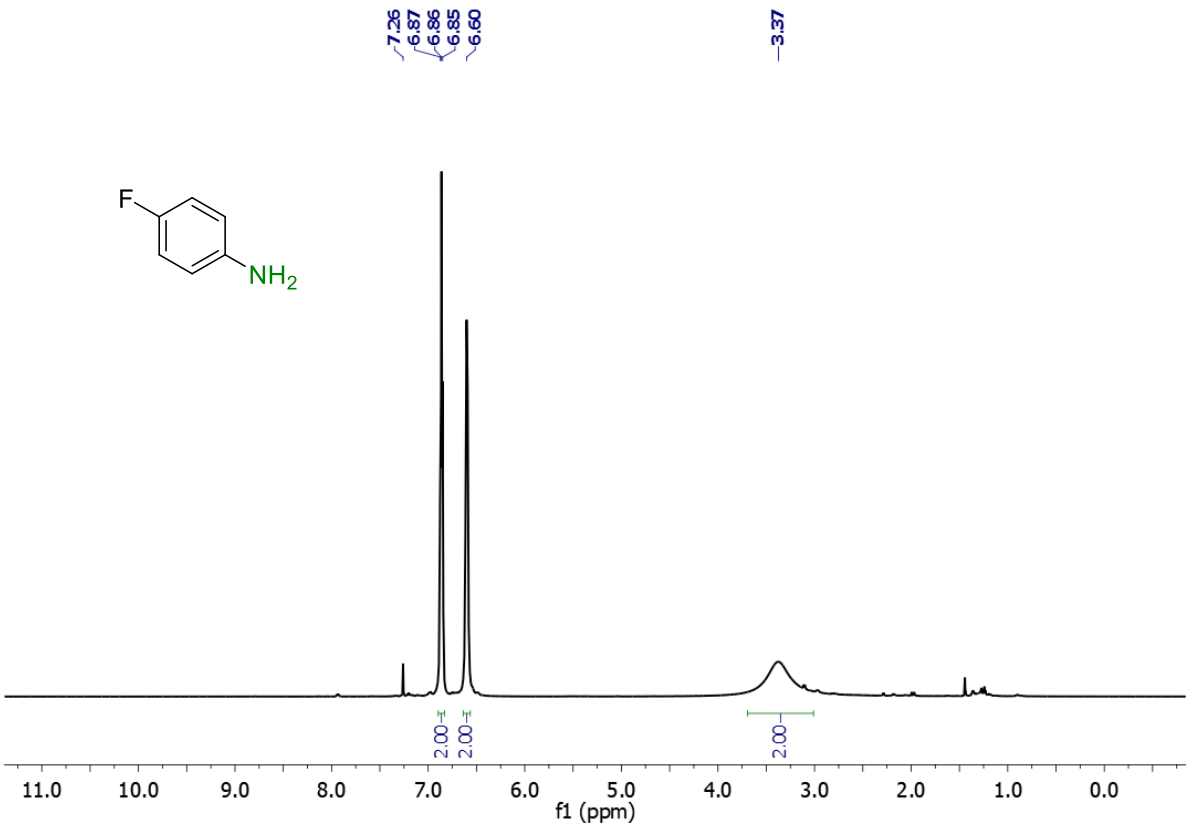


Figure S40. ^{1}H NMR (700 MHz) spectrum of 4-fluoroaniline (**A$_{4e}$**) in $CDCl_3$ at r.t.

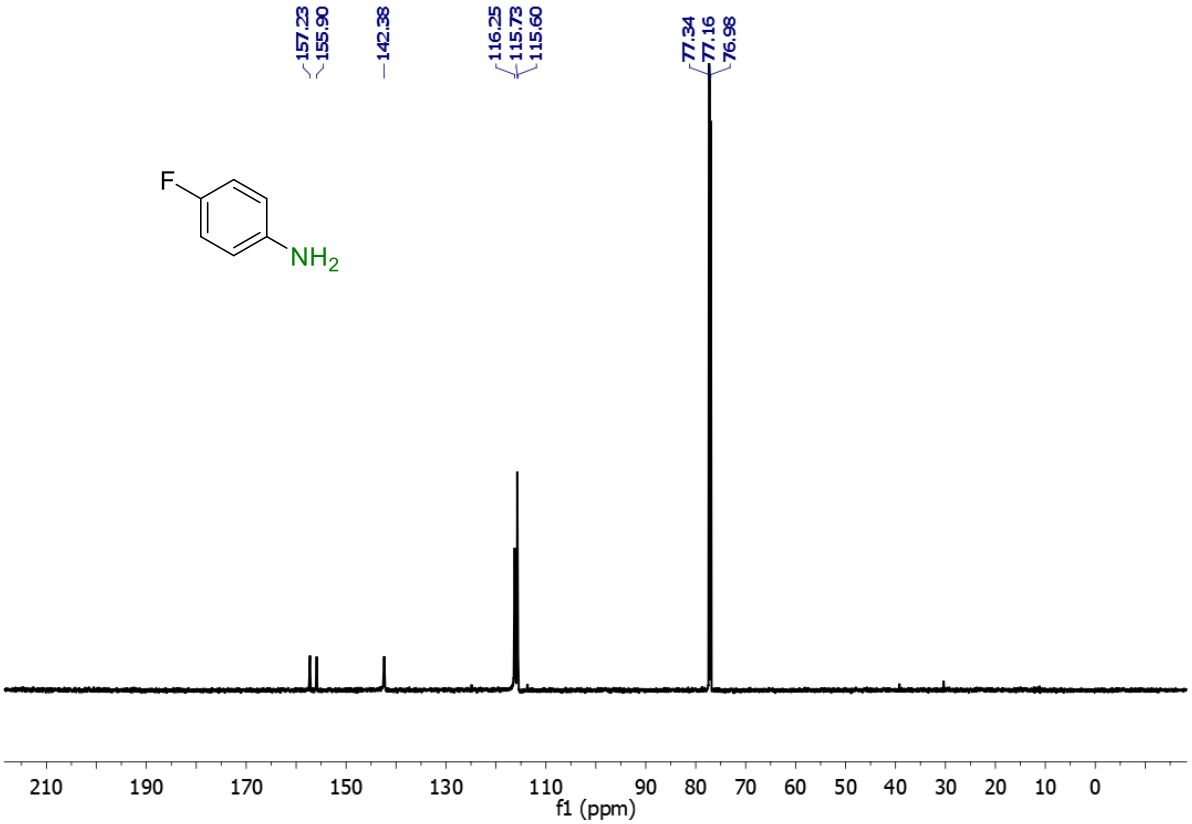


Figure S41. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of 4-fluoroaniline (**A$_{4e}$**) in $CDCl_3$ at r.t.

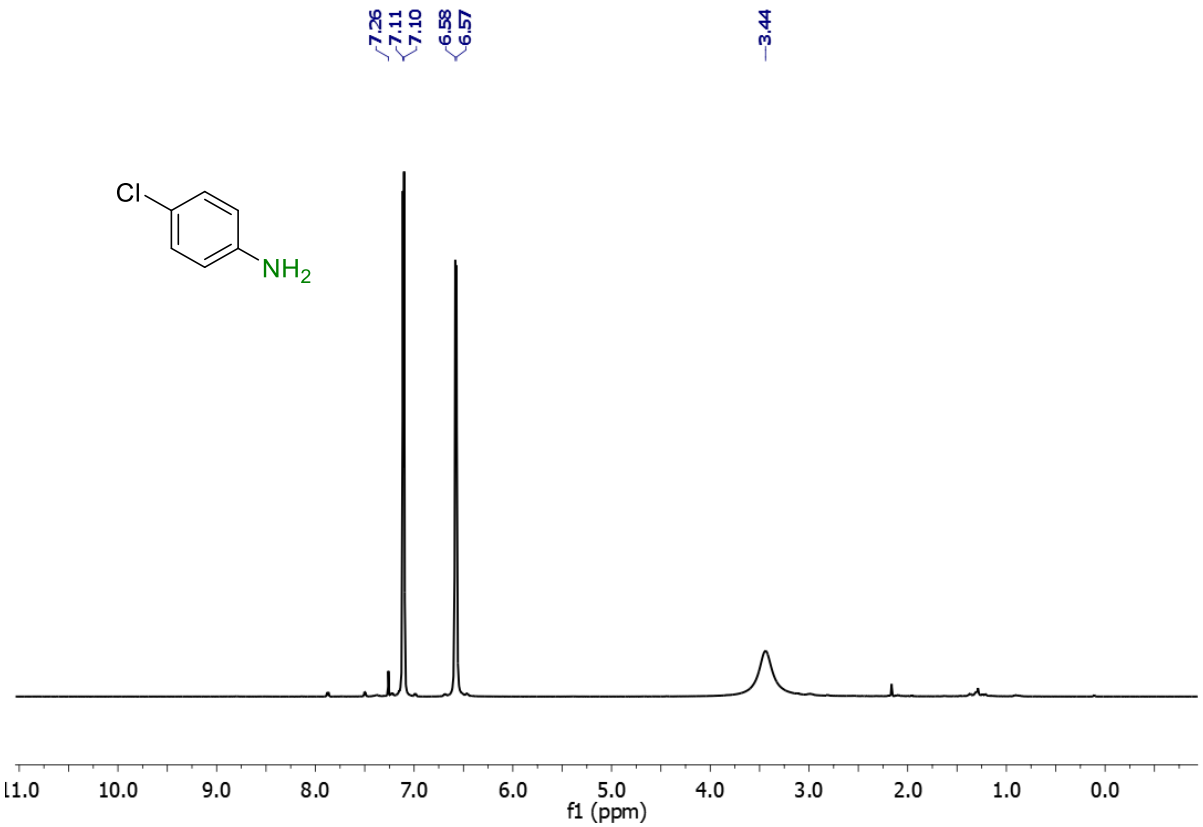


Figure S42. ^{1}H NMR (700 MHz) spectrum of 4-chloroaniline (**A_{4f}**) in $CDCl_3$ at r.t.

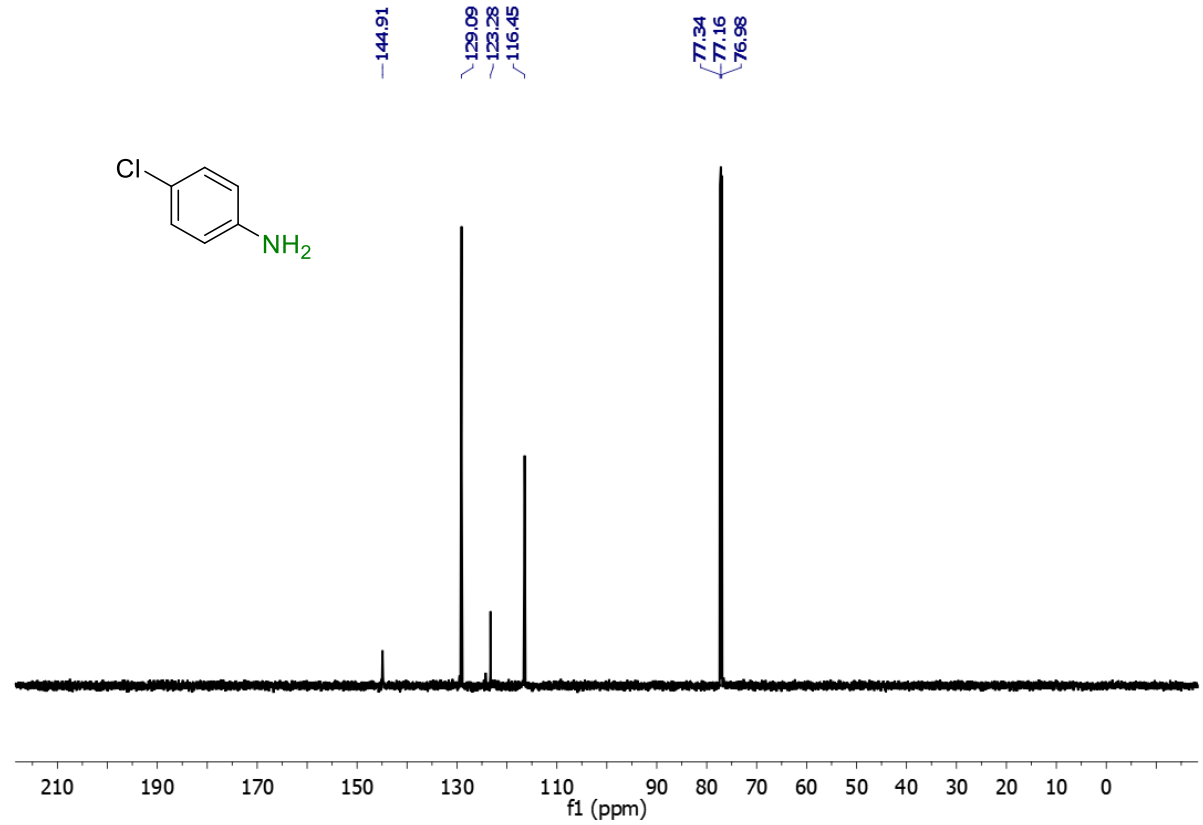


Figure S43. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of 4-chloroaniline (**A_{4f}**) in $CDCl_3$ at r.t.

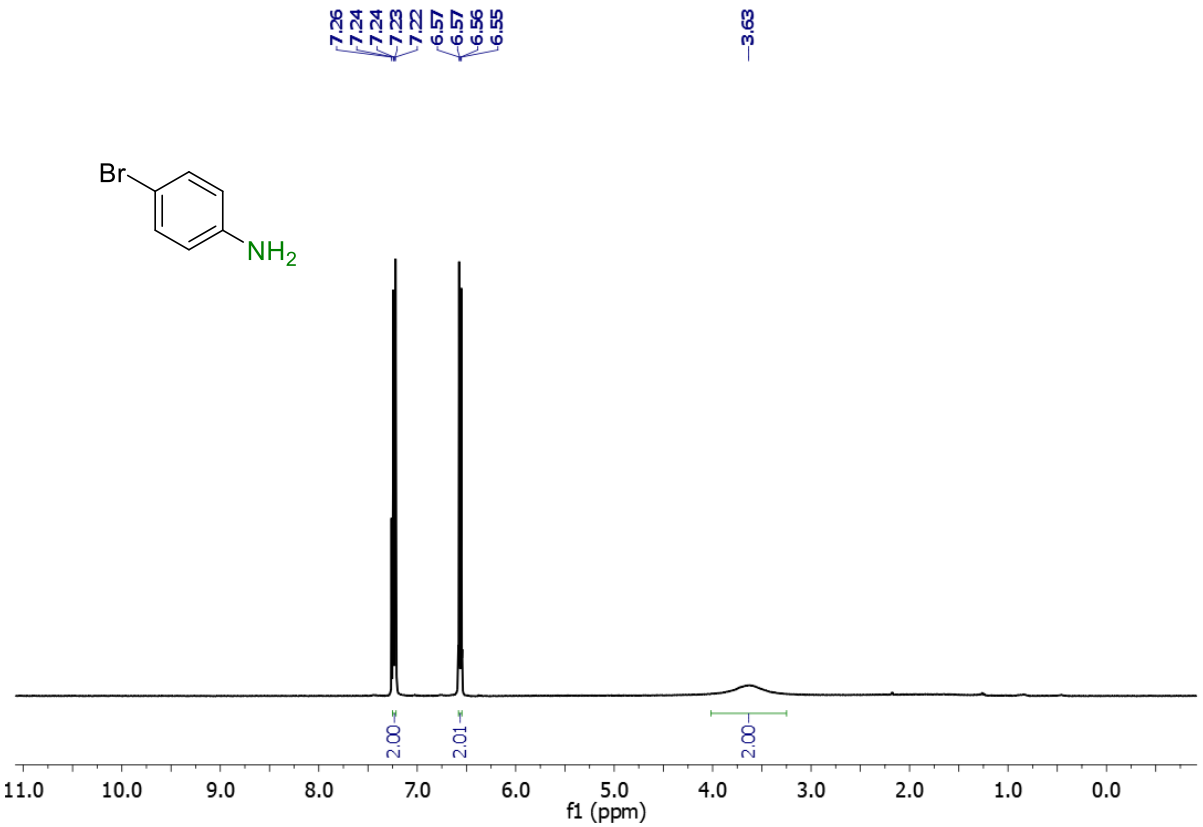


Figure S44. ^{1}H NMR (400 MHz) spectrum of 4-bromoaniline (**A$_{4g}$**) in $CDCl_3$ at r.t.

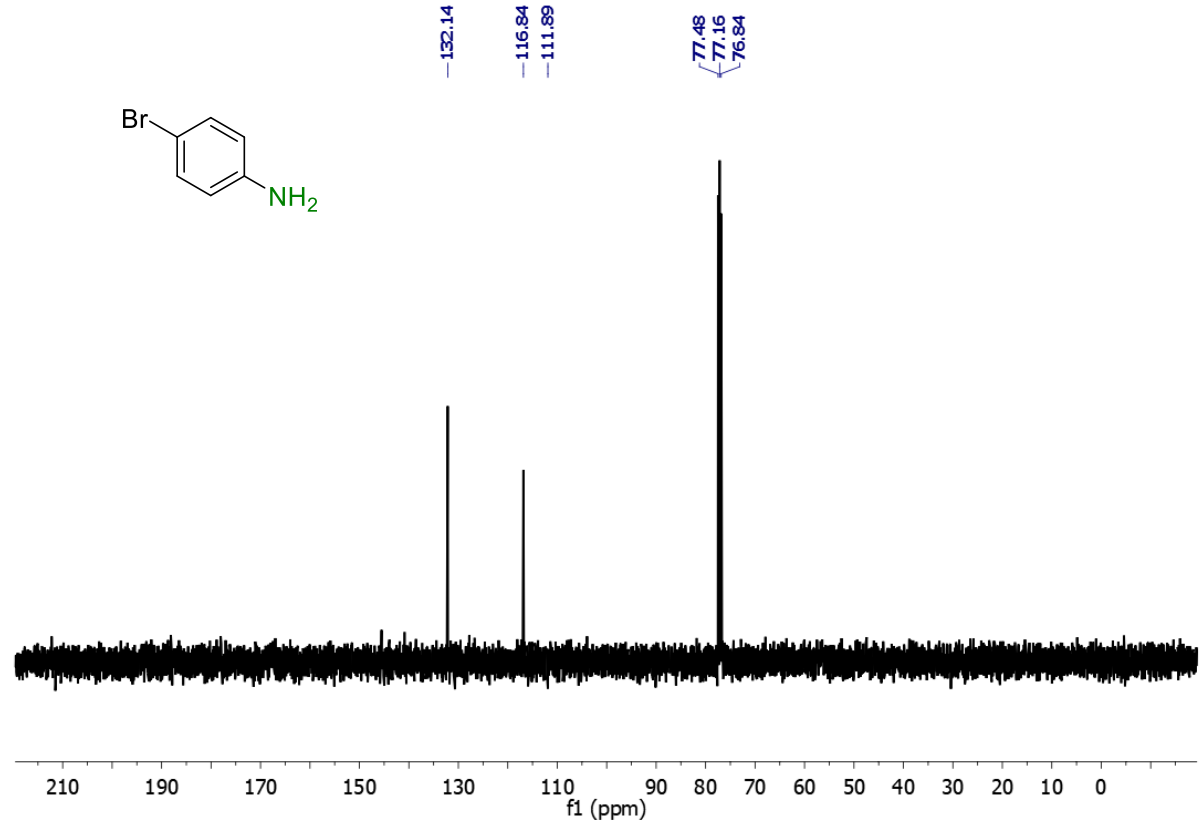


Figure S45. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 4-bromoaniline (**A$_{4g}$**) in $CDCl_3$ at r.t.

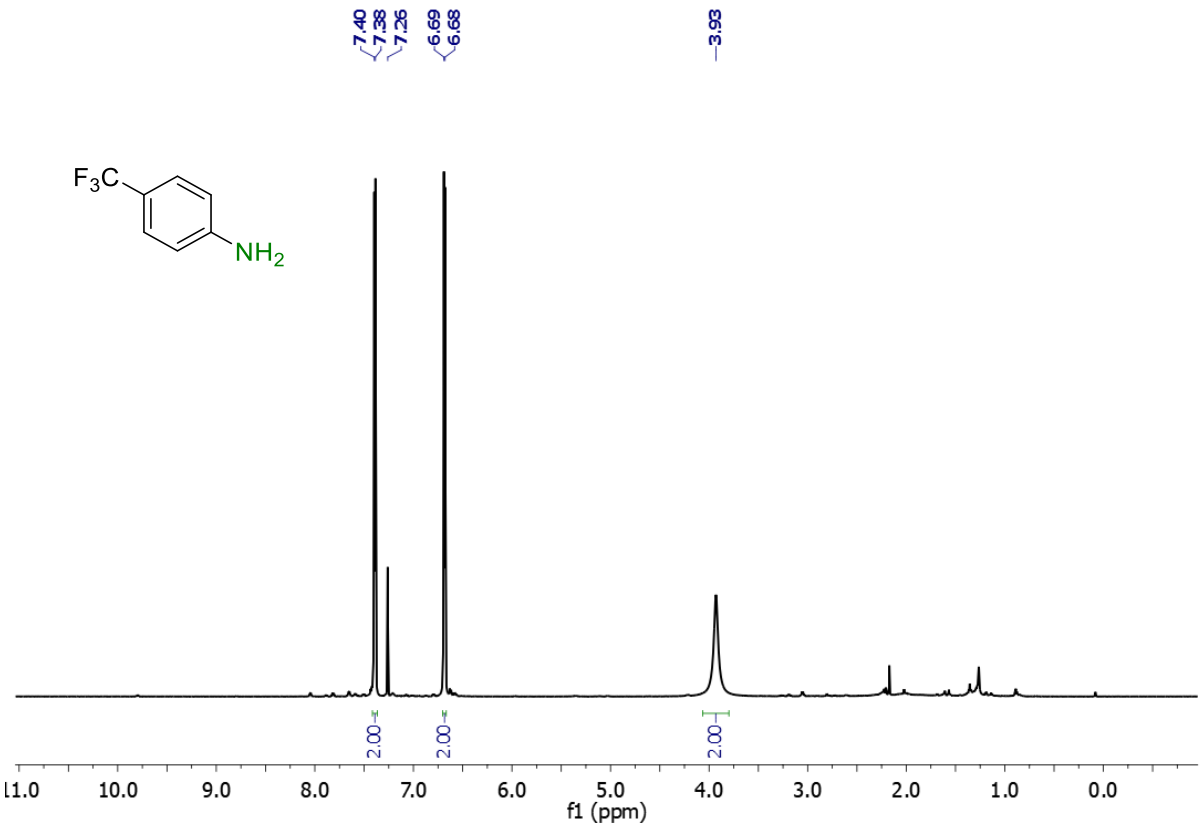


Figure S46. ^{1}H NMR (700 MHz) spectrum of 4-(trifluoromethyl)aniline (**A$_{4h}$**) in $CDCl_3$ at r.t.

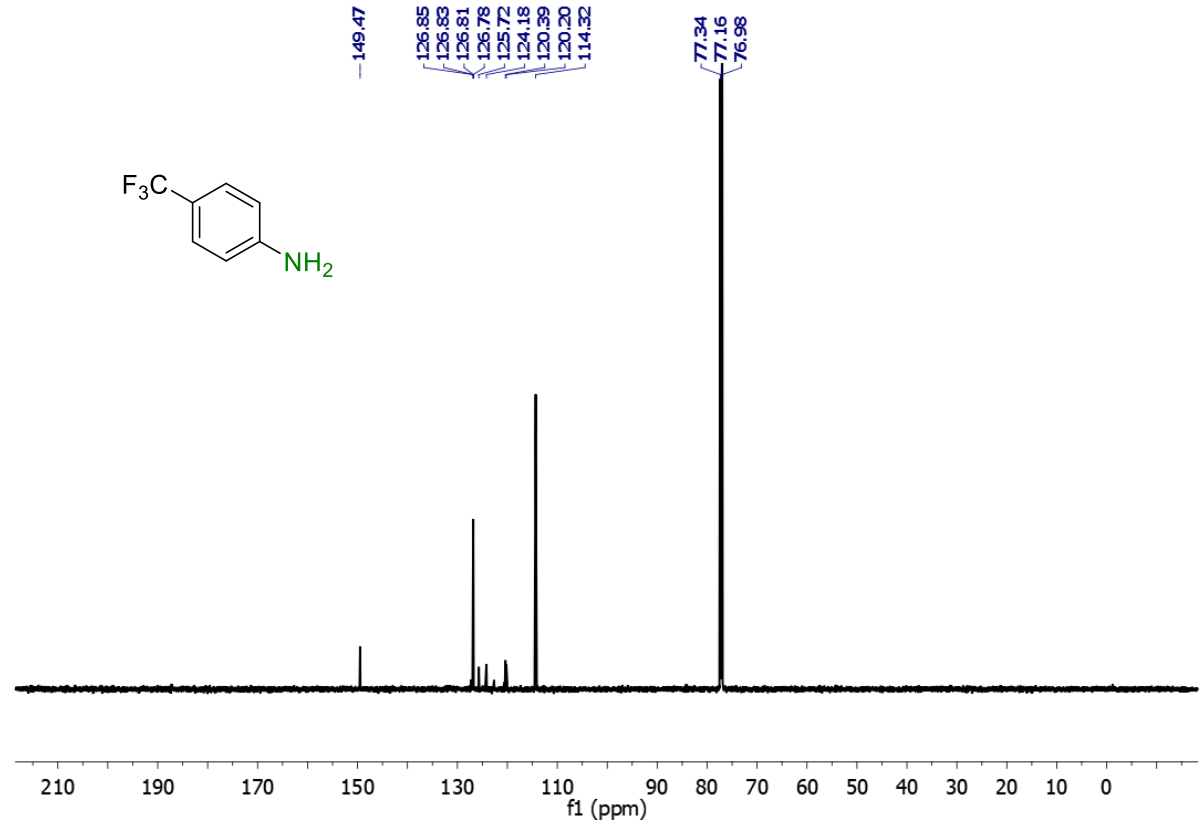


Figure S47. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of 4-(trifluoromethyl)aniline (**A$_{4h}$**) in $CDCl_3$ at r.t.

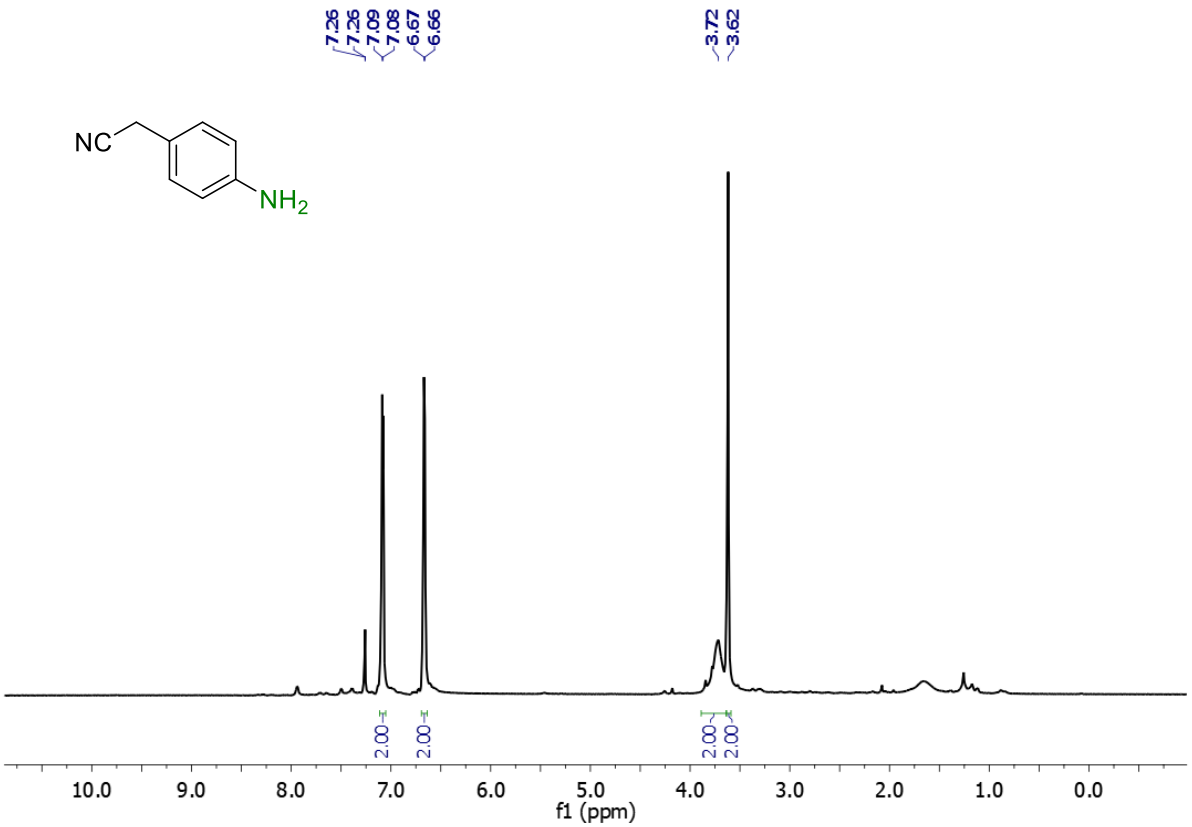


Figure S48. ^{1}H NMR (700 MHz) spectrum of 2-(4-aminophenyl)acetonitrile (**A$_{4i}$**) in $CDCl_3$ at r.t.

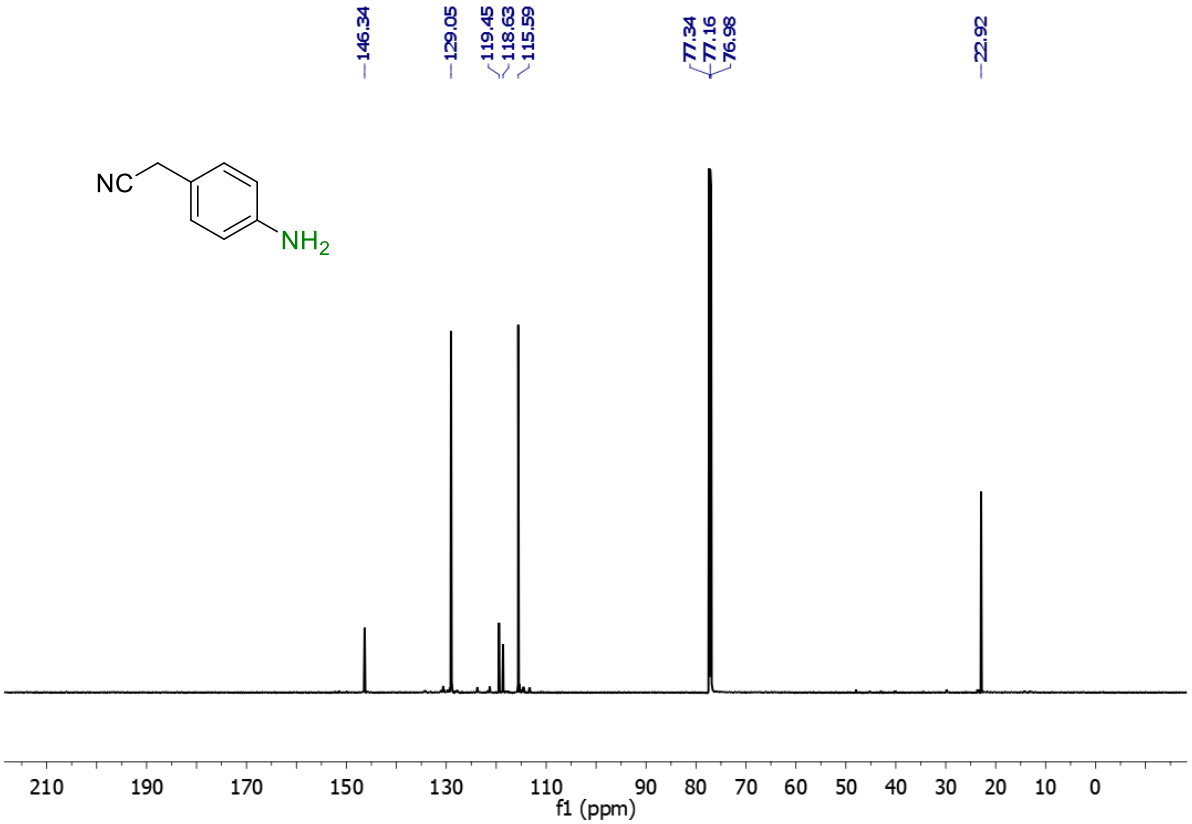


Figure S49. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of 2-(4-aminophenyl)acetonitrile (**A$_{4i}$**) in $CDCl_3$ at r.t.

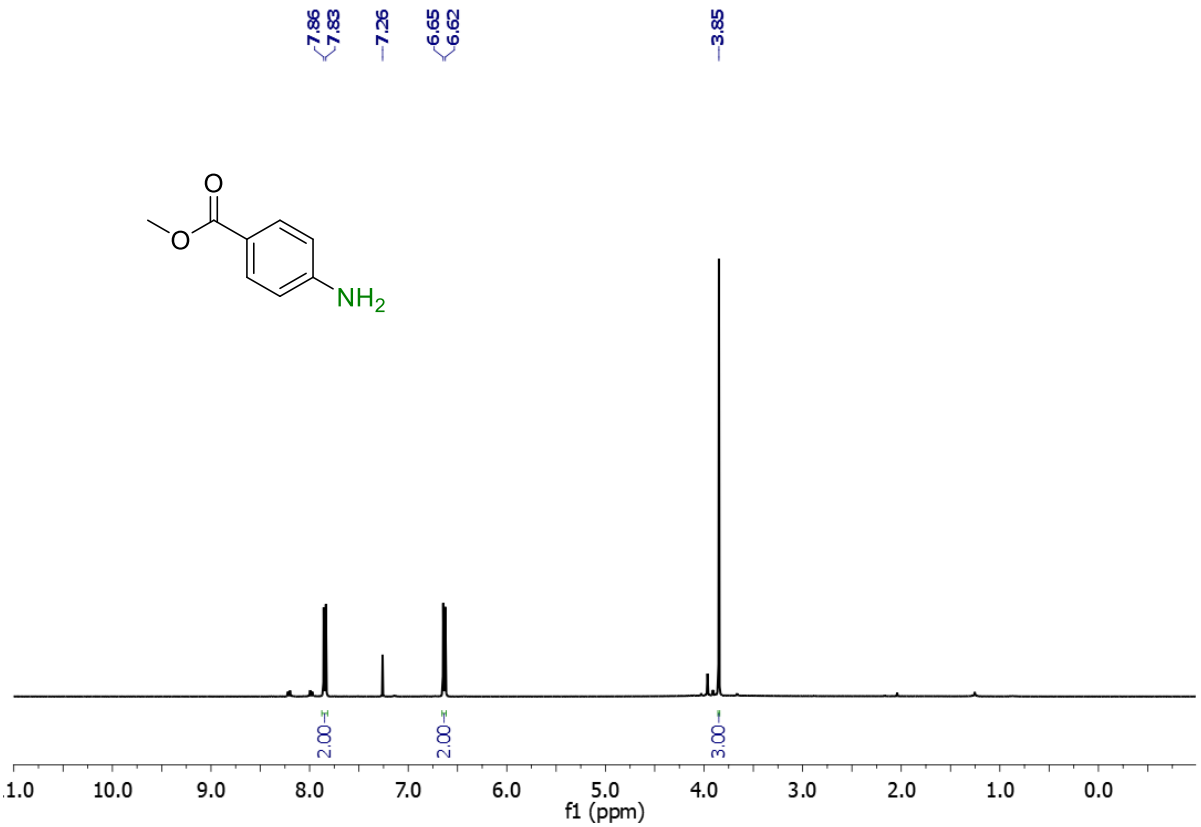


Figure S50. ^{1}H NMR (400 MHz) spectrum of methyl 4-aminobenzoate (**P$_{4j}$**) in $CDCl_3$ at r.t.

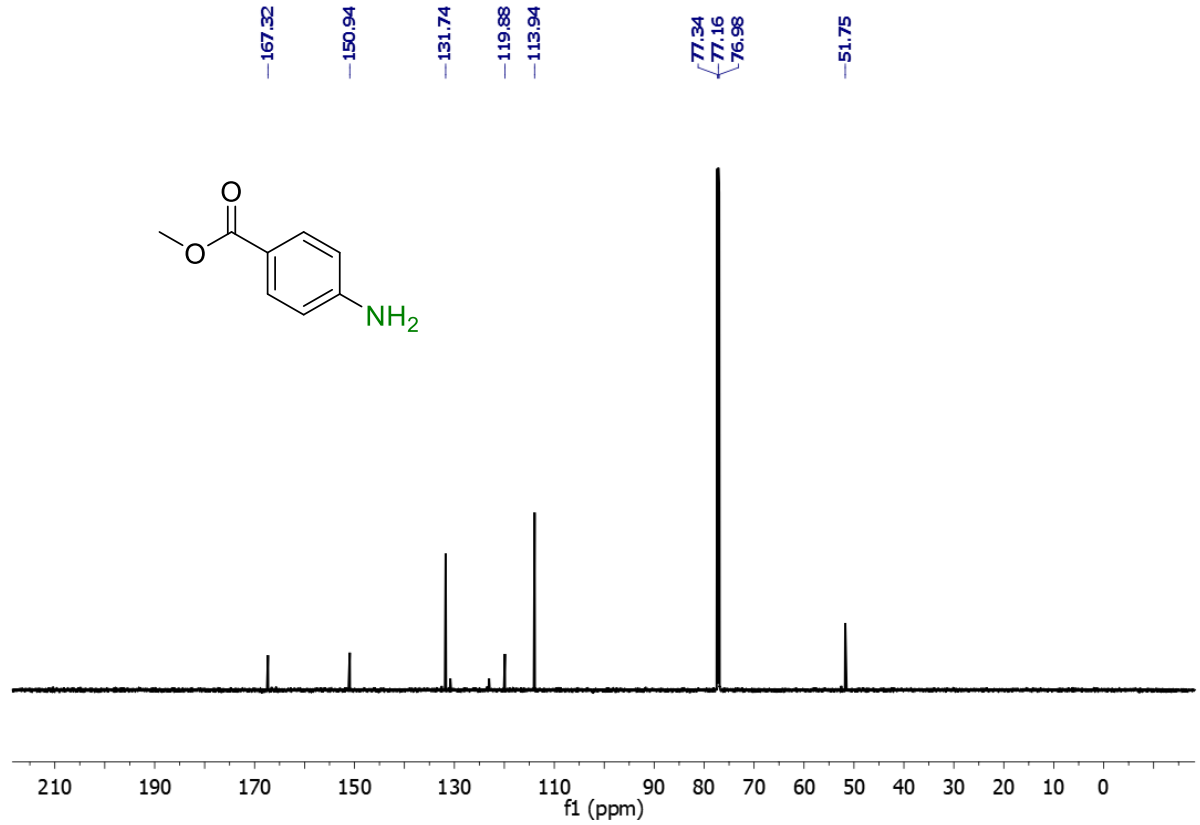


Figure S51. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of methyl 4-aminobenzoate (**P$_{4j}$**) in $CDCl_3$ at r.t.

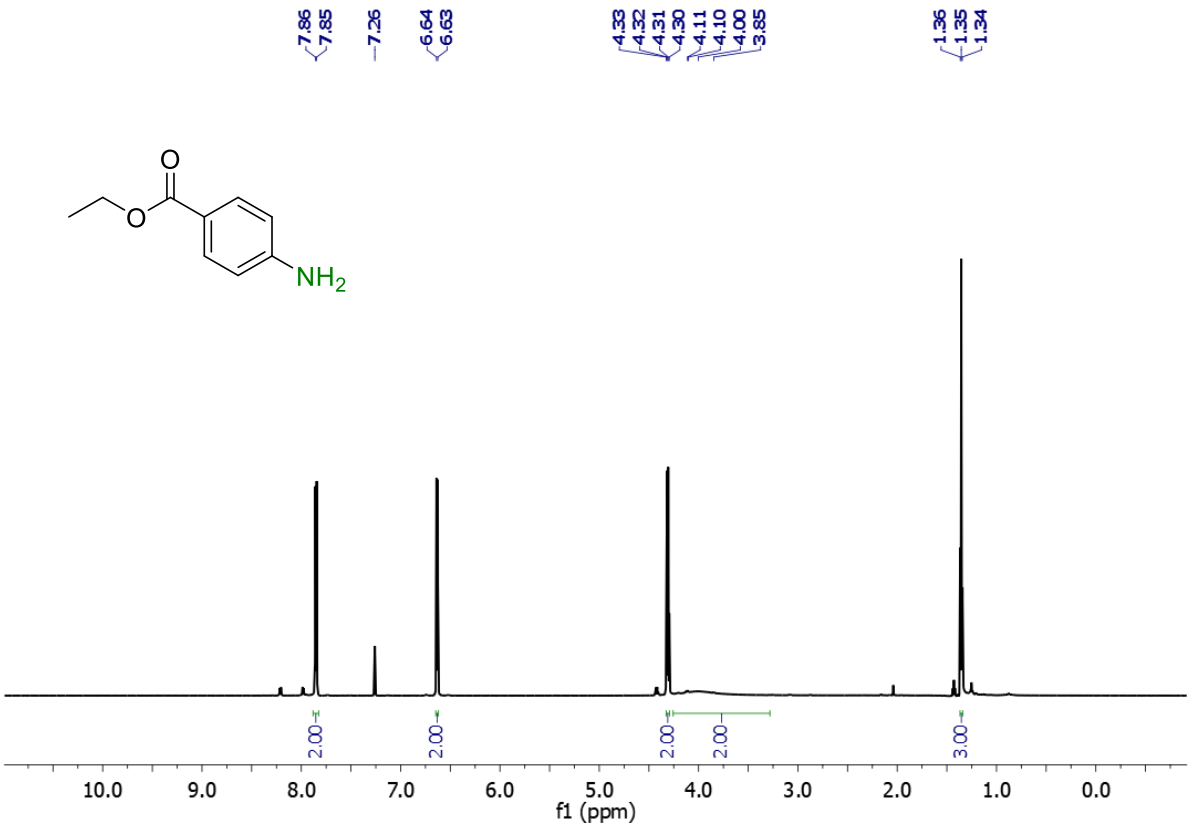


Figure S52. ^{1}H NMR (700 MHz) spectrum of Ethyl 4-aminobenzoate (**P_{4k}**) in $CDCl_3$ at r.t.

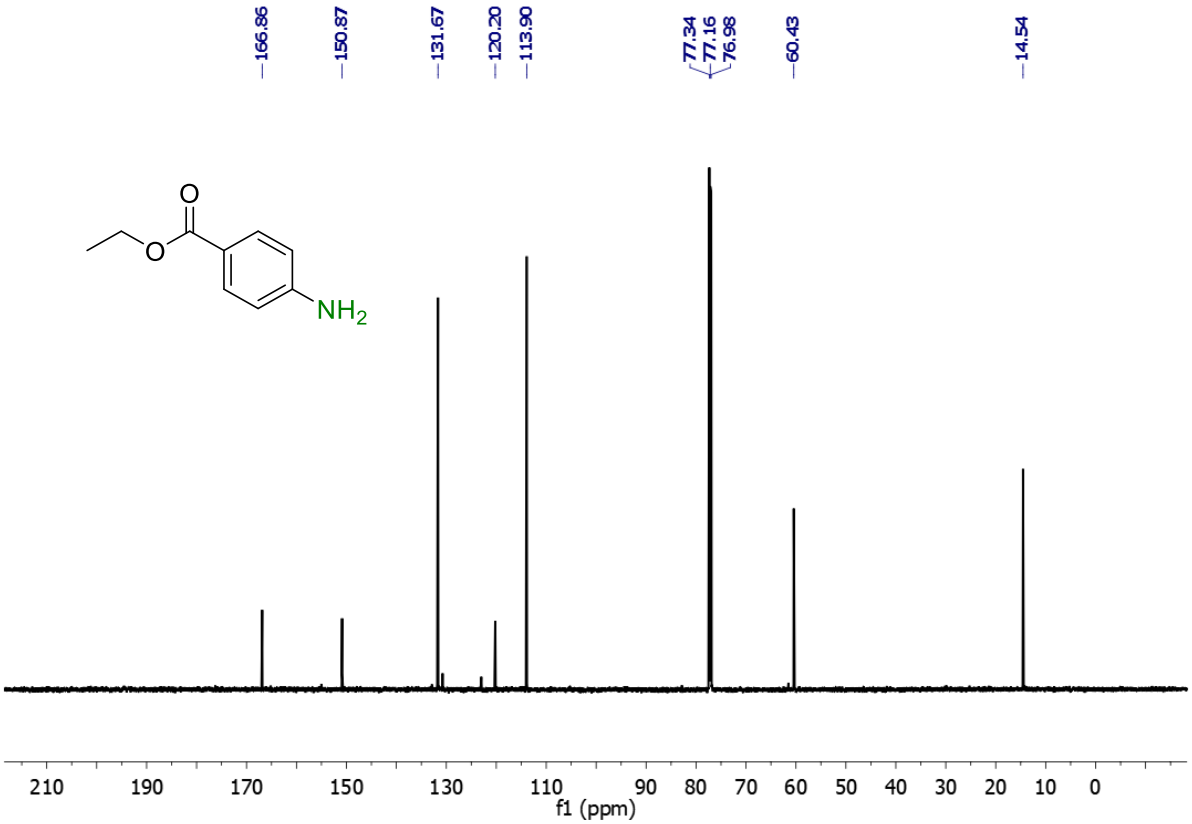


Figure S53. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of Ethyl 4-aminobenzoate (**P_{4k}**) in $CDCl_3$ at r.t.

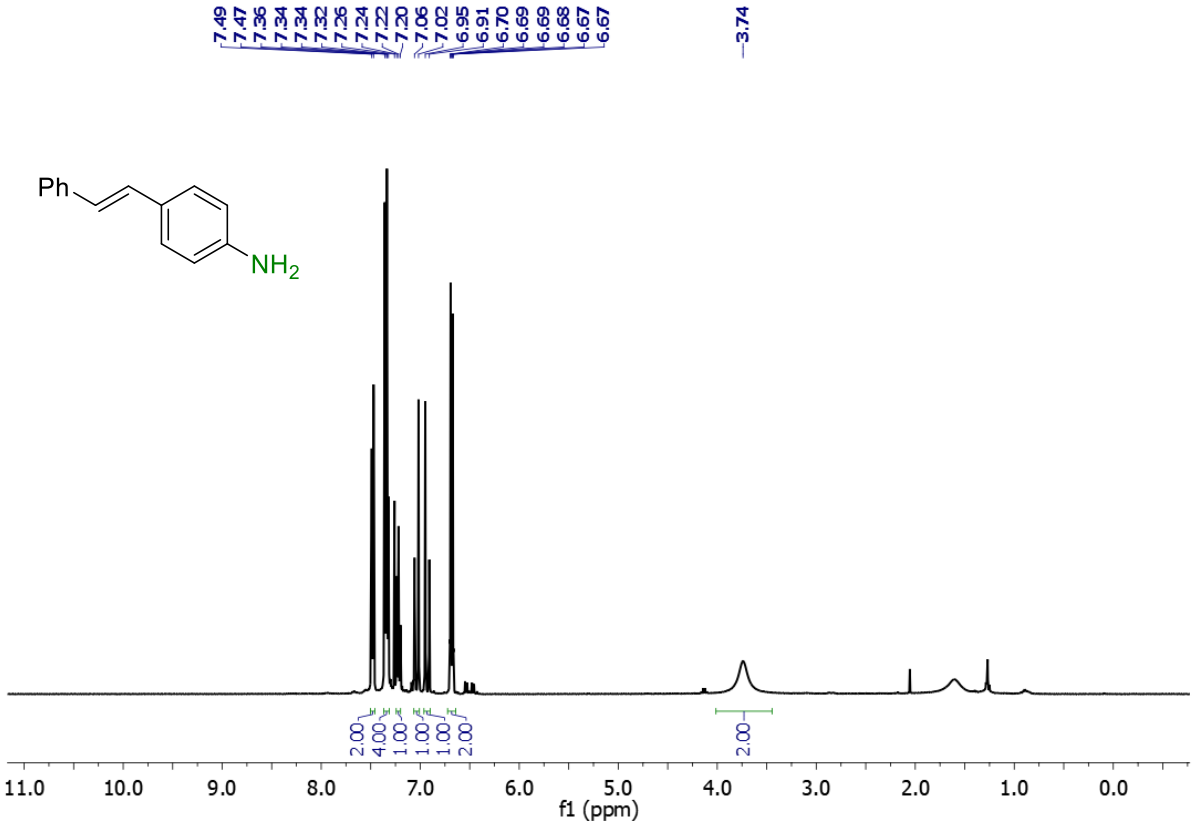


Figure S54. ^{1}H NMR (400 MHz) spectrum of (E)-4-styrylaniline (**A**$_5$) in $CDCl_3$ at r.t.

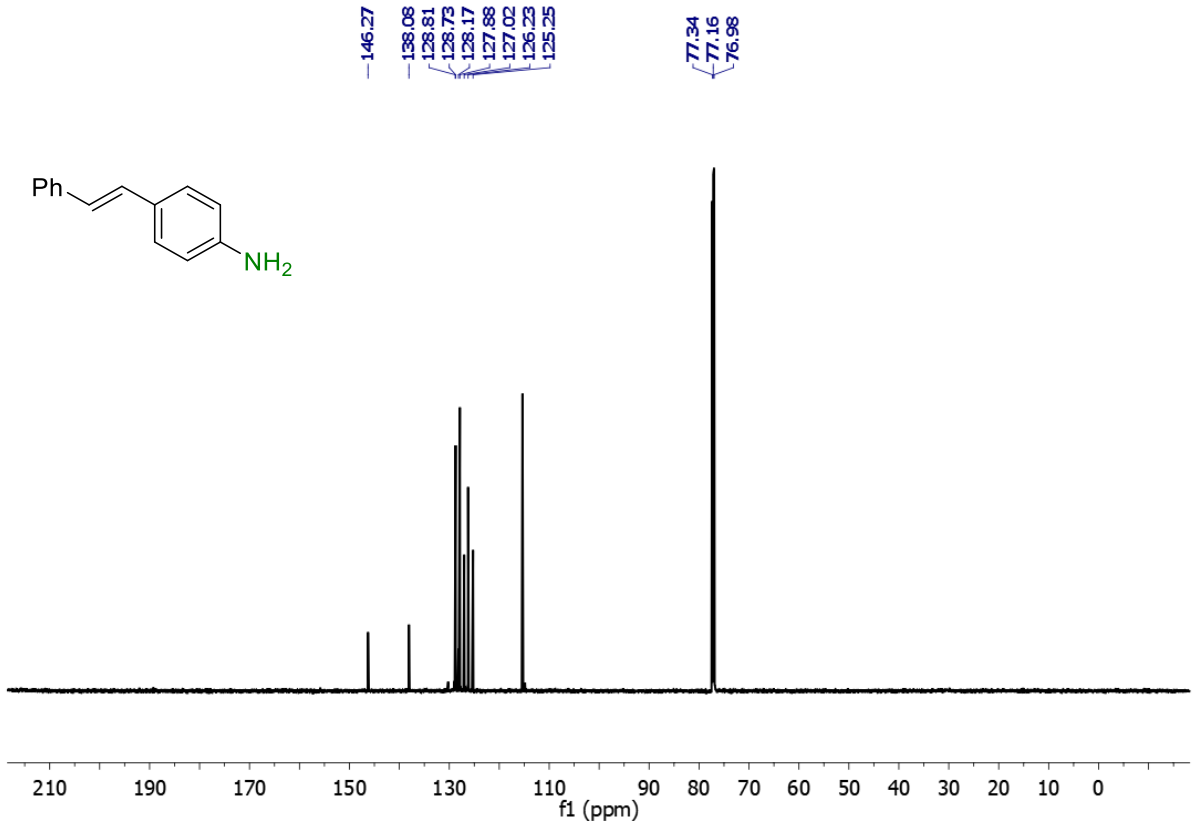


Figure S55. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of (E)-4-styrylaniline (**A**$_5$) in $CDCl_3$ at r.t.

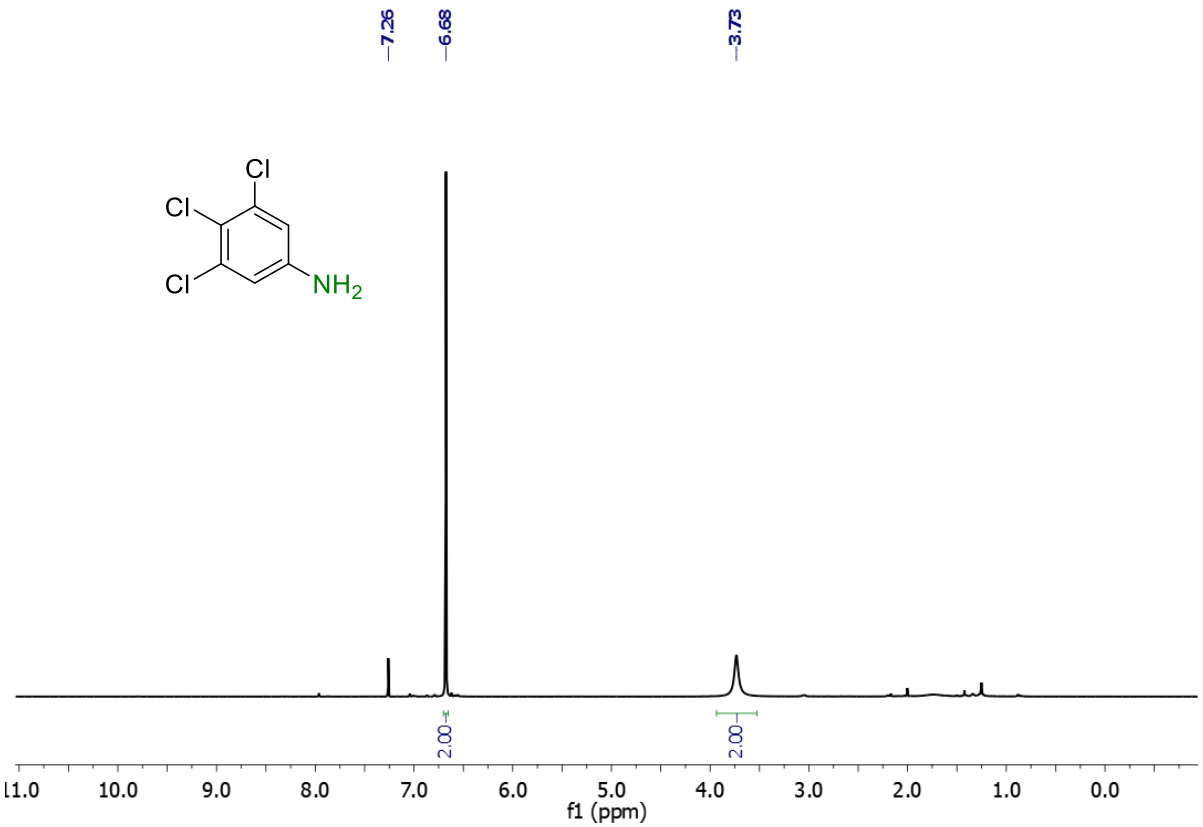


Figure S56. ^{1}H NMR (700 MHz) spectrum of 3,4,5-trichloroaniline (**A$_6$**) in $CDCl_3$ at r.t.

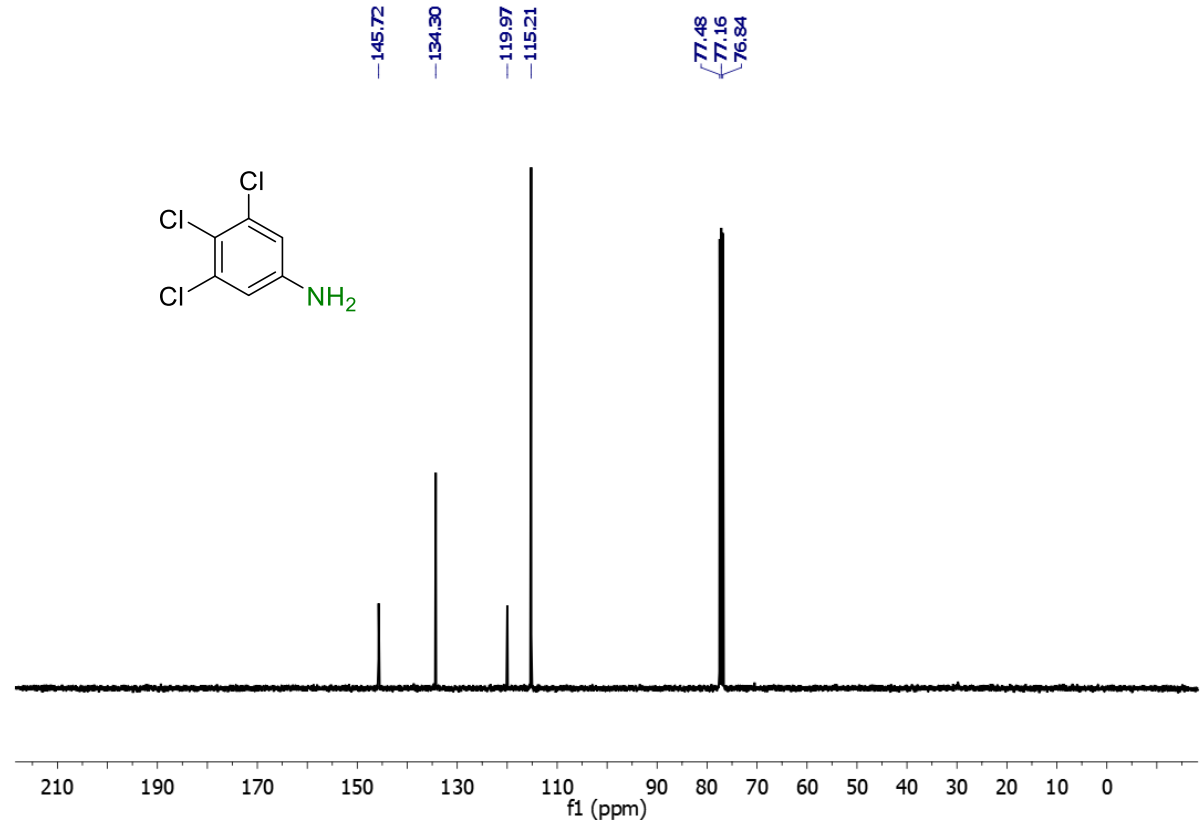


Figure S57. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 3,4,5-trichloroaniline (**A$_6$**) in $CDCl_3$ at r.t.

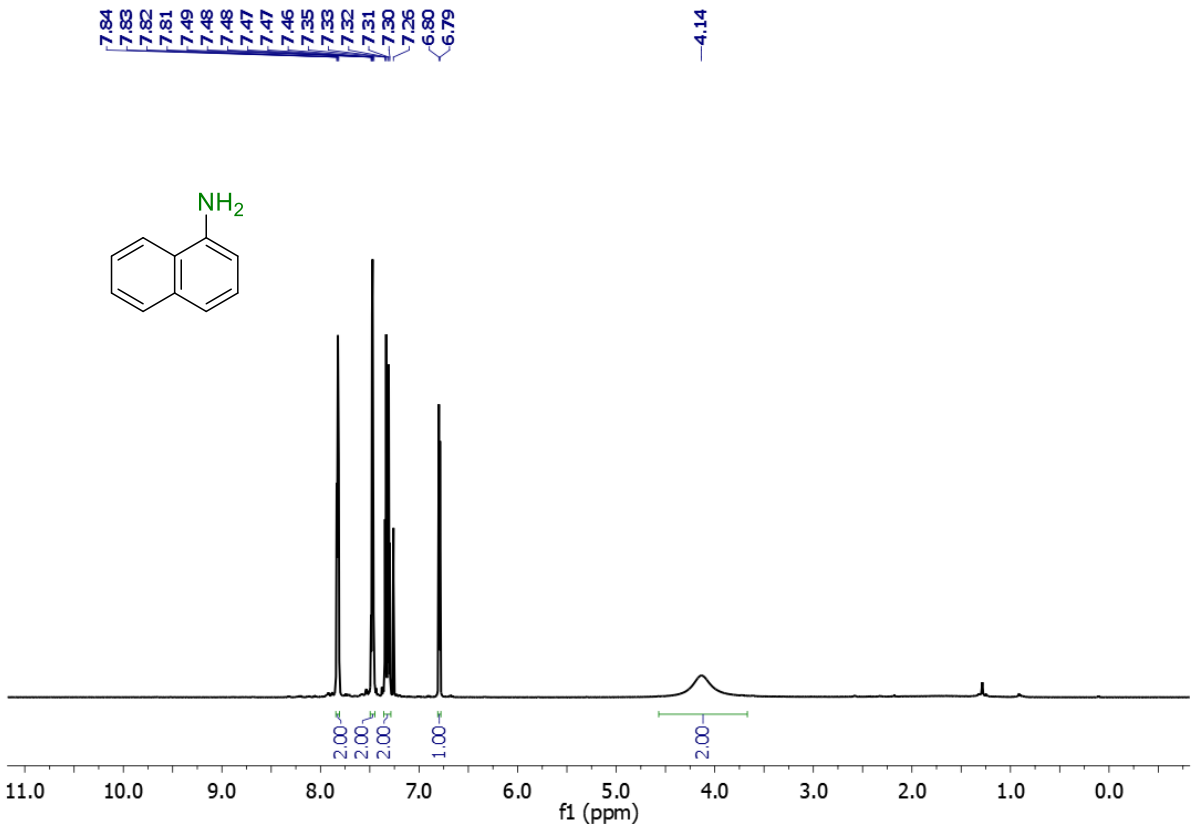


Figure S58. ^{1}H NMR (700 MHz) spectrum of Naphthalen-1-amine (**A**$_7$) in $CDCl_3$ at r.t.

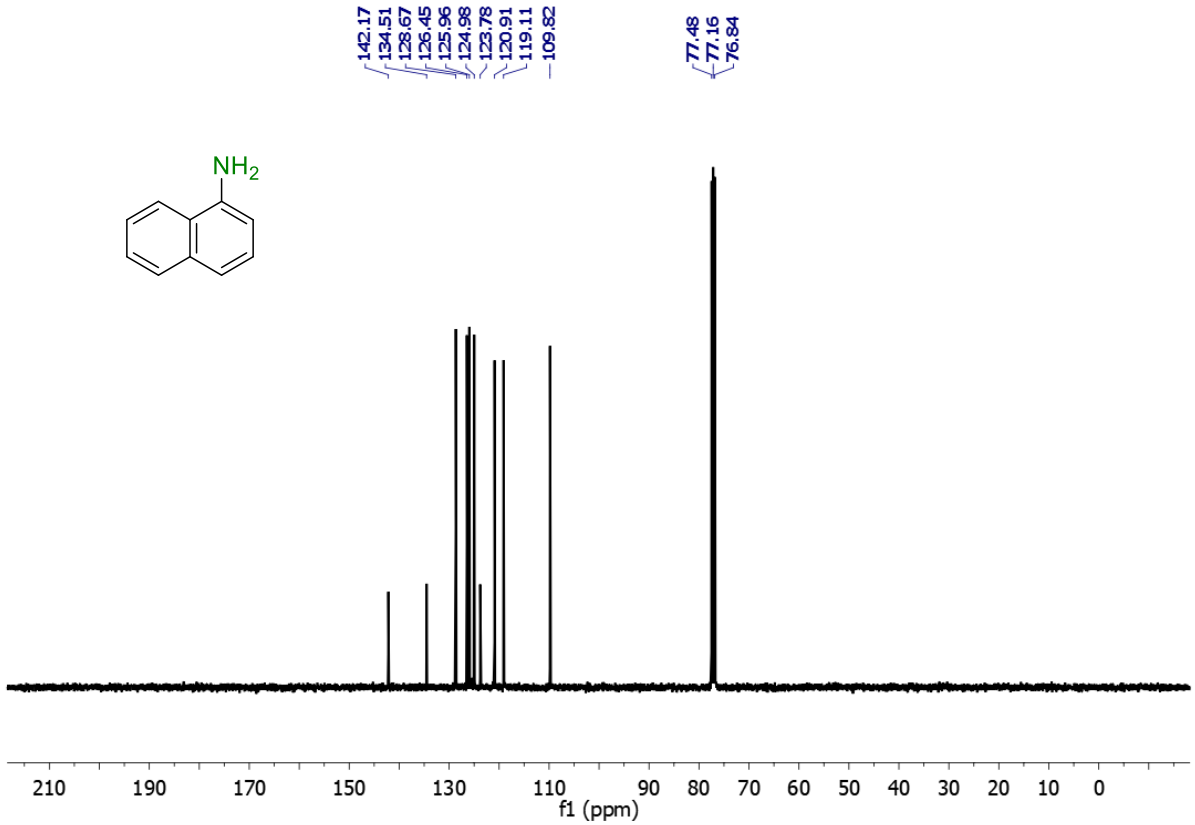


Figure S59. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of Naphthalen-1-amine (**A**$_7$) in $CDCl_3$ at r.t.

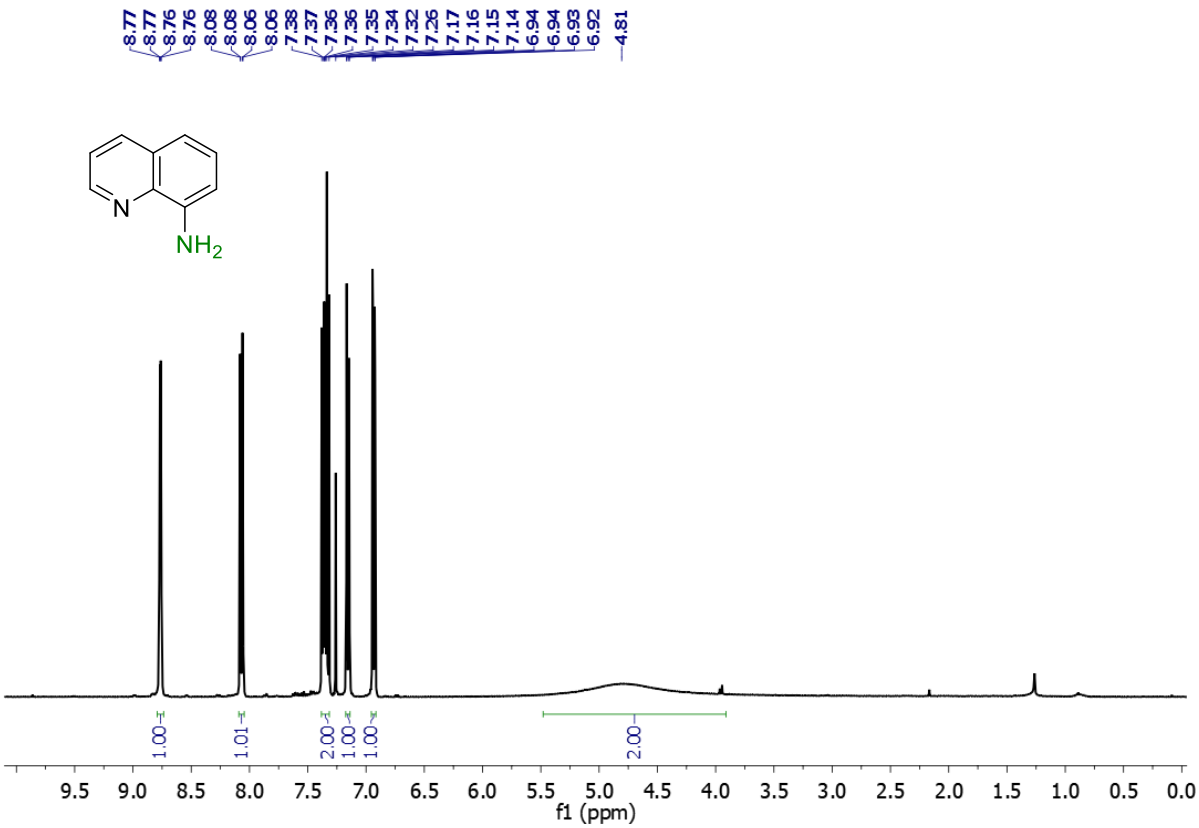


Figure S60. ^{1}H NMR (400 MHz) spectrum of quinolin-8-amine (**A8**) in $CDCl_3$ at r.t.

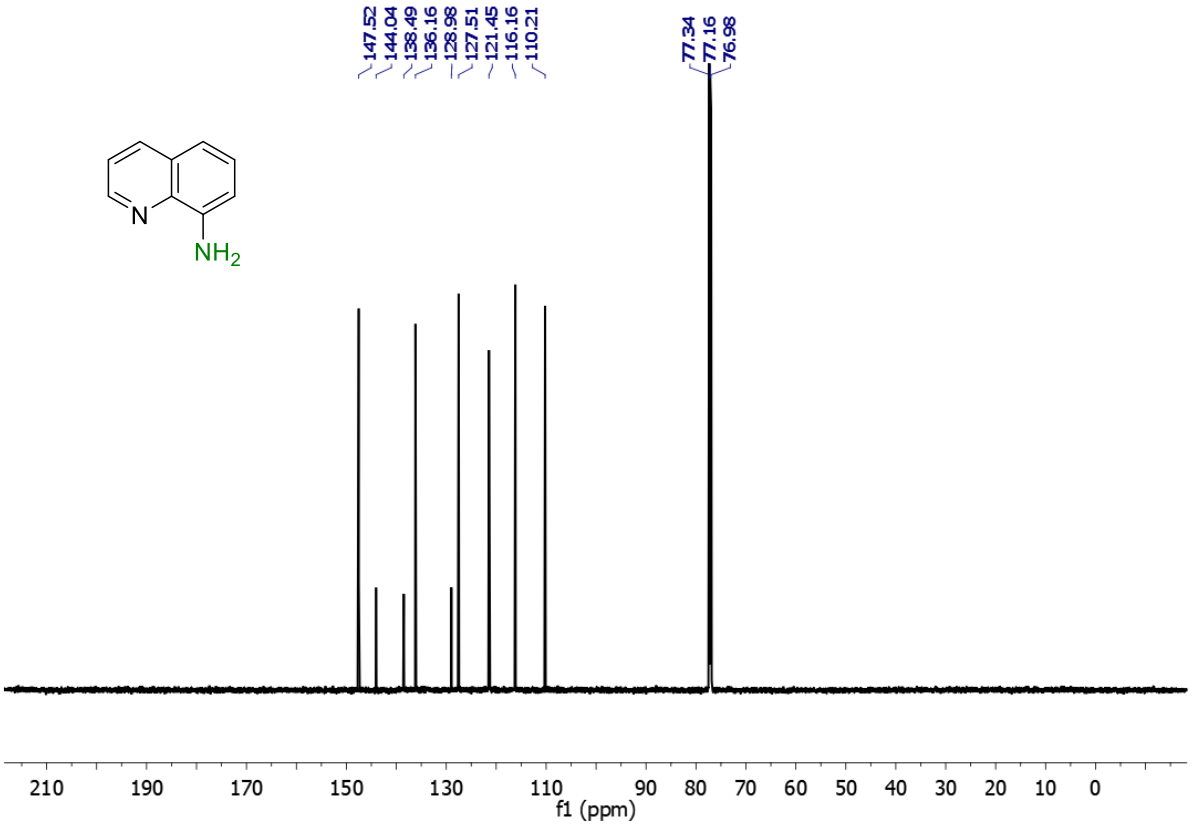


Figure S61. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of quinolin-8-amine (**A8**) in $CDCl_3$ at r.t.

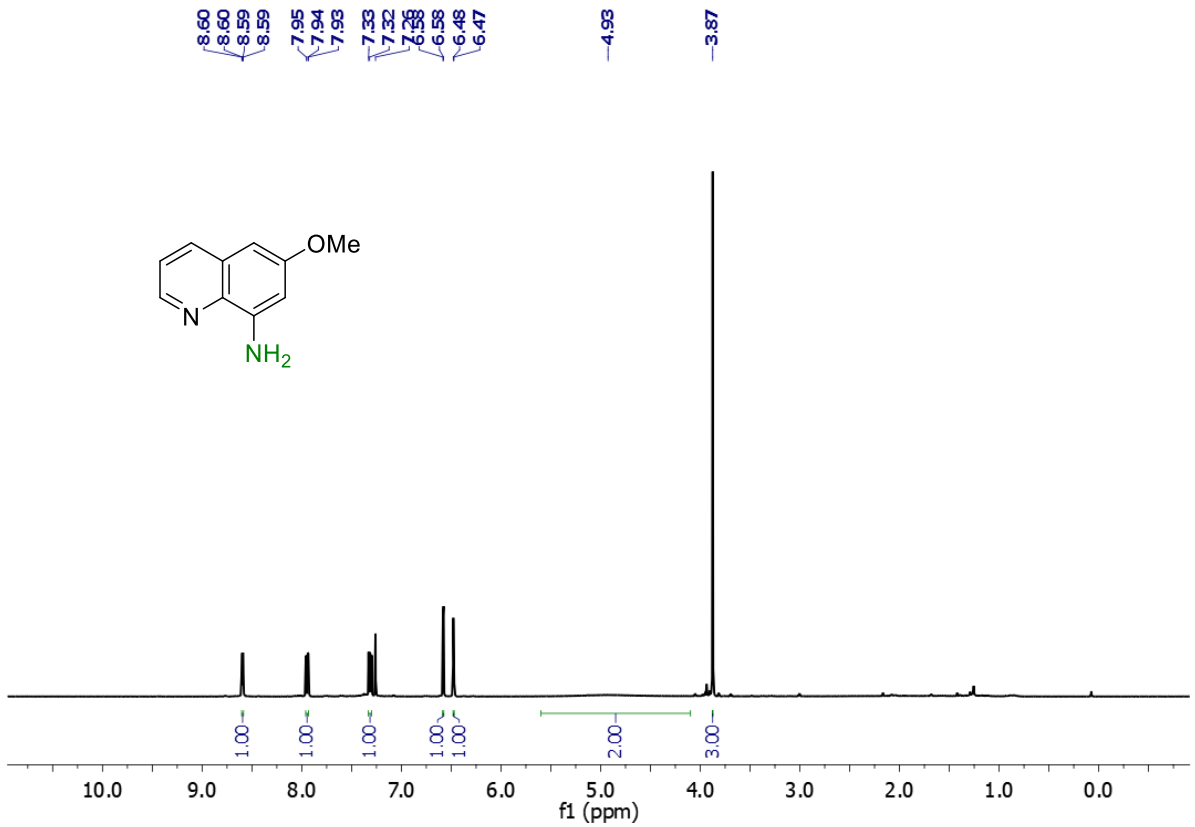


Figure S62. ^{1}H NMR (400 MHz) spectrum of 6-methoxy-quinolin-8-amine (**A9**) in $CDCl_3$ at r.t.

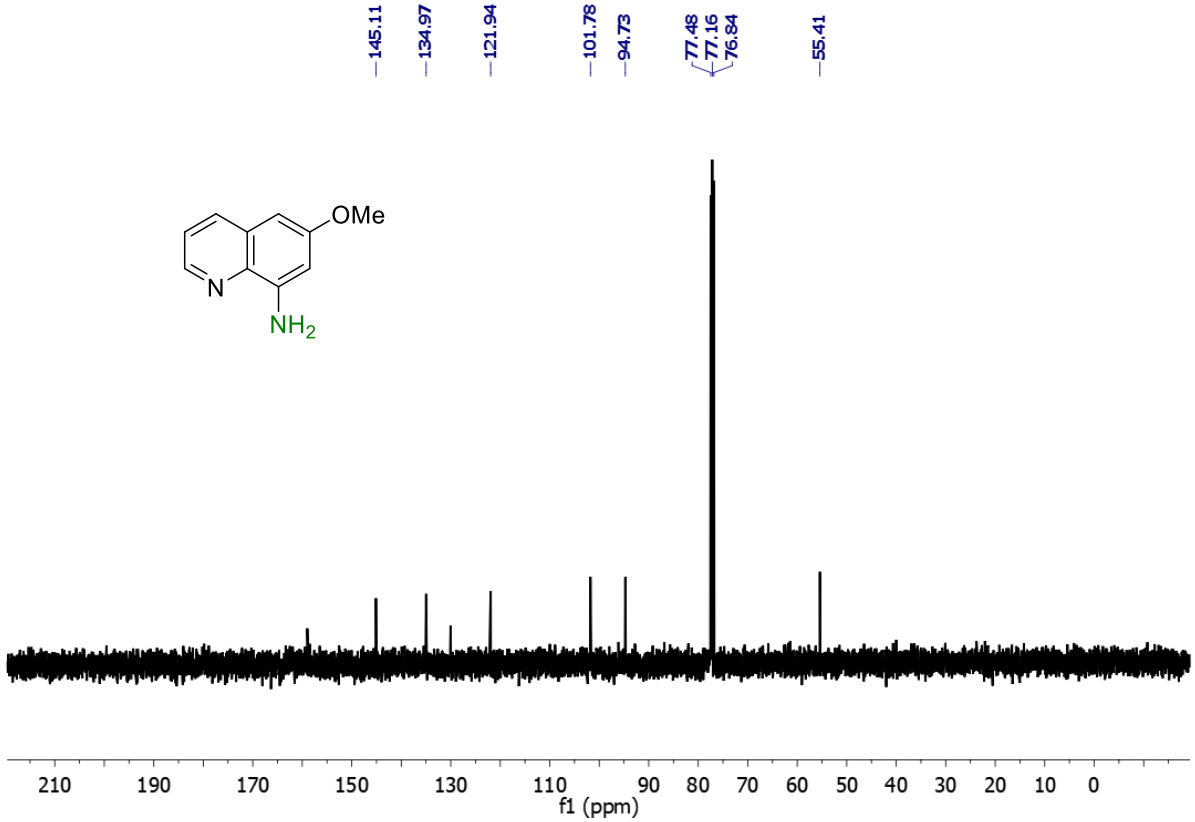


Figure S63. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 6-methoxy-quinolin-8-amine (**A9**) in $CDCl_3$ at r.t.

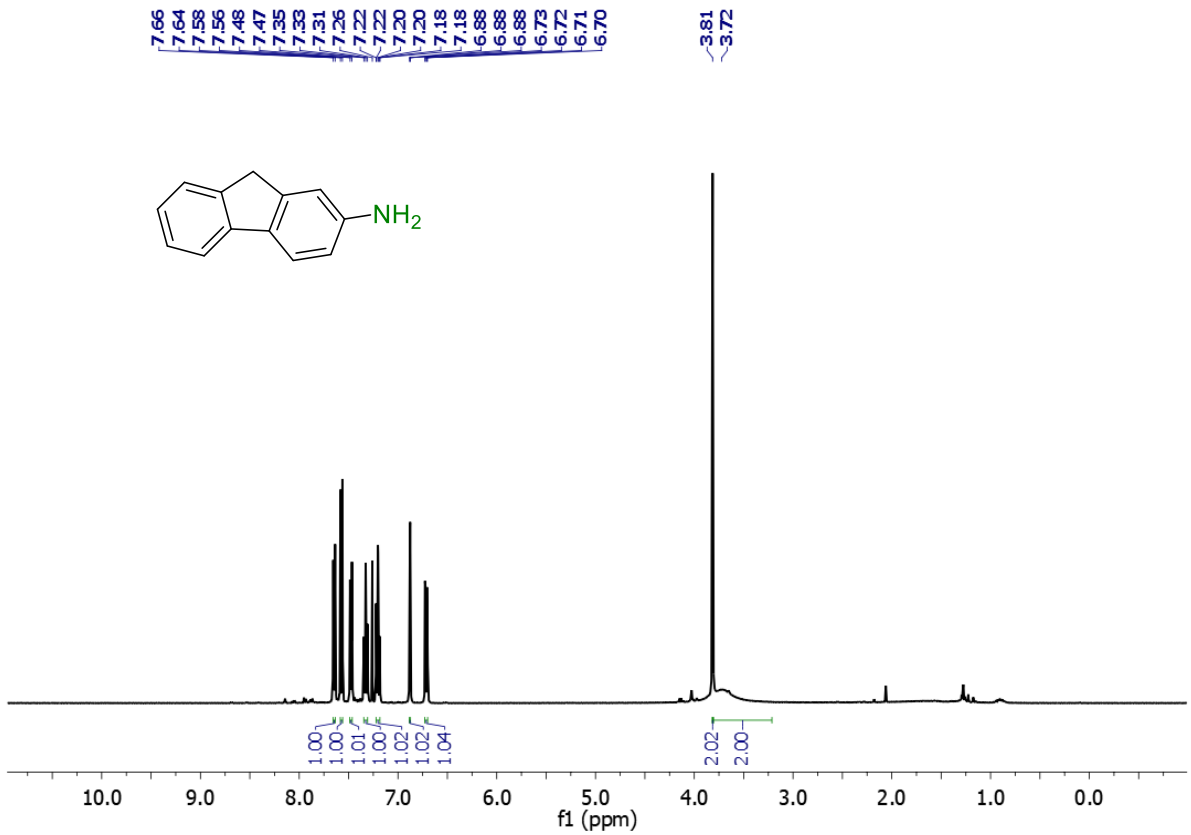


Figure S64. ^{1}H NMR (400 MHz) spectrum of 9*H*-fluoren-2-amine (**A$_{10}$**) in $CDCl_3$ at r.t.

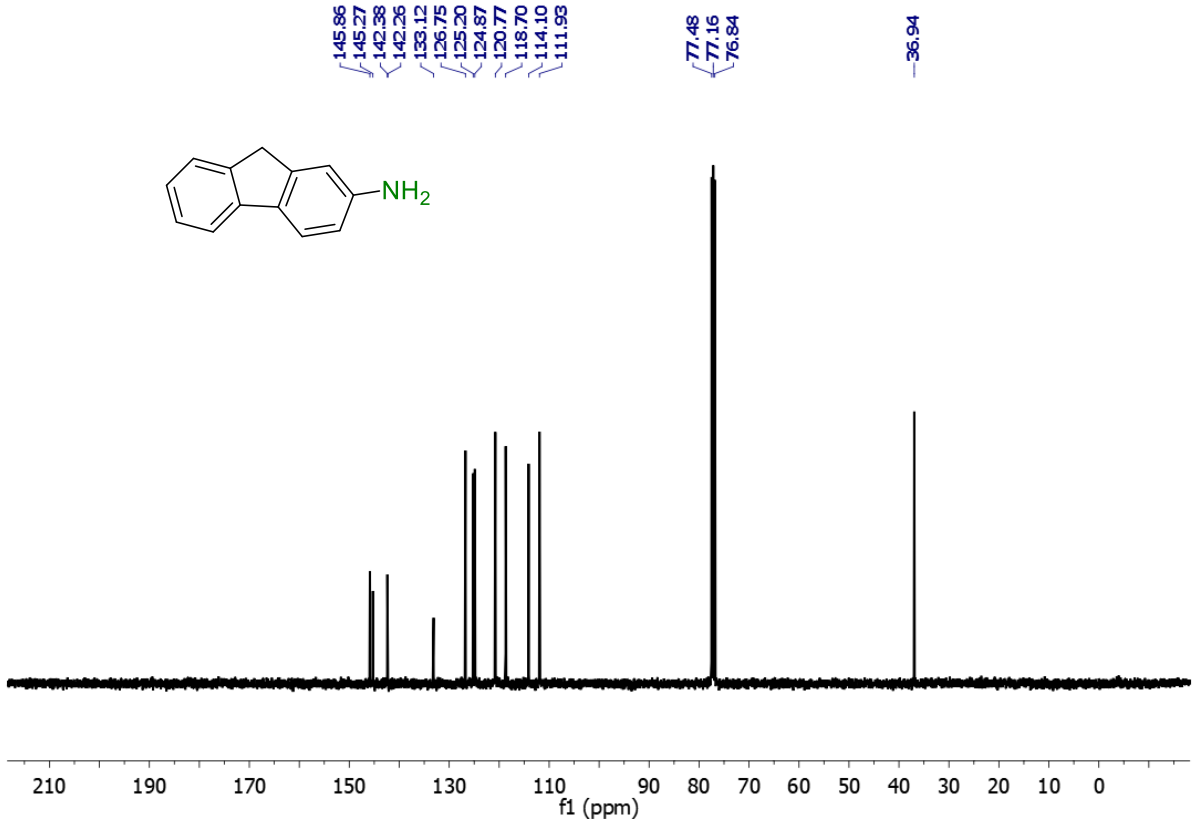


Figure S65. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 9*H*-fluoren-2-amine (**A$_{10}$**) in $CDCl_3$ at r.t.

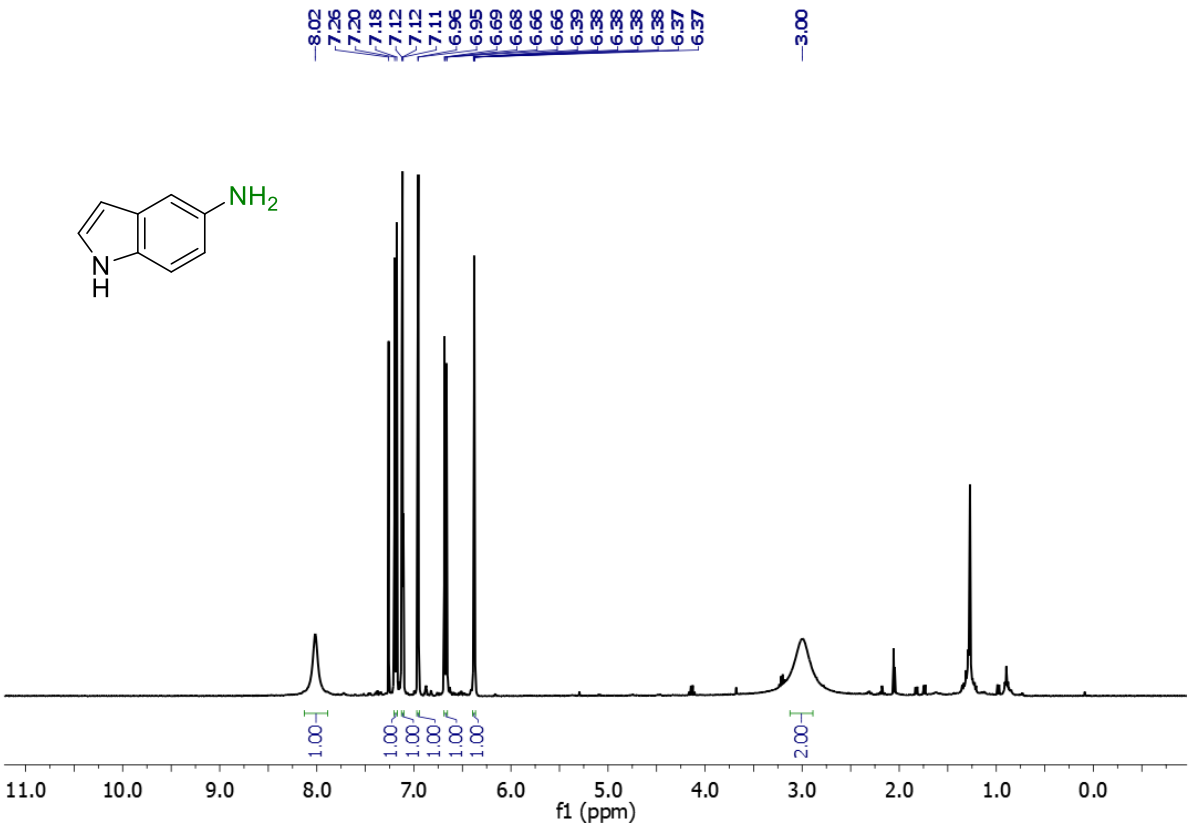


Figure S66. ^{1}H NMR (400 MHz) spectrum of 1*H*-indol-6-amine (**A$_{11}$**) in $CDCl_3$ at r.t.

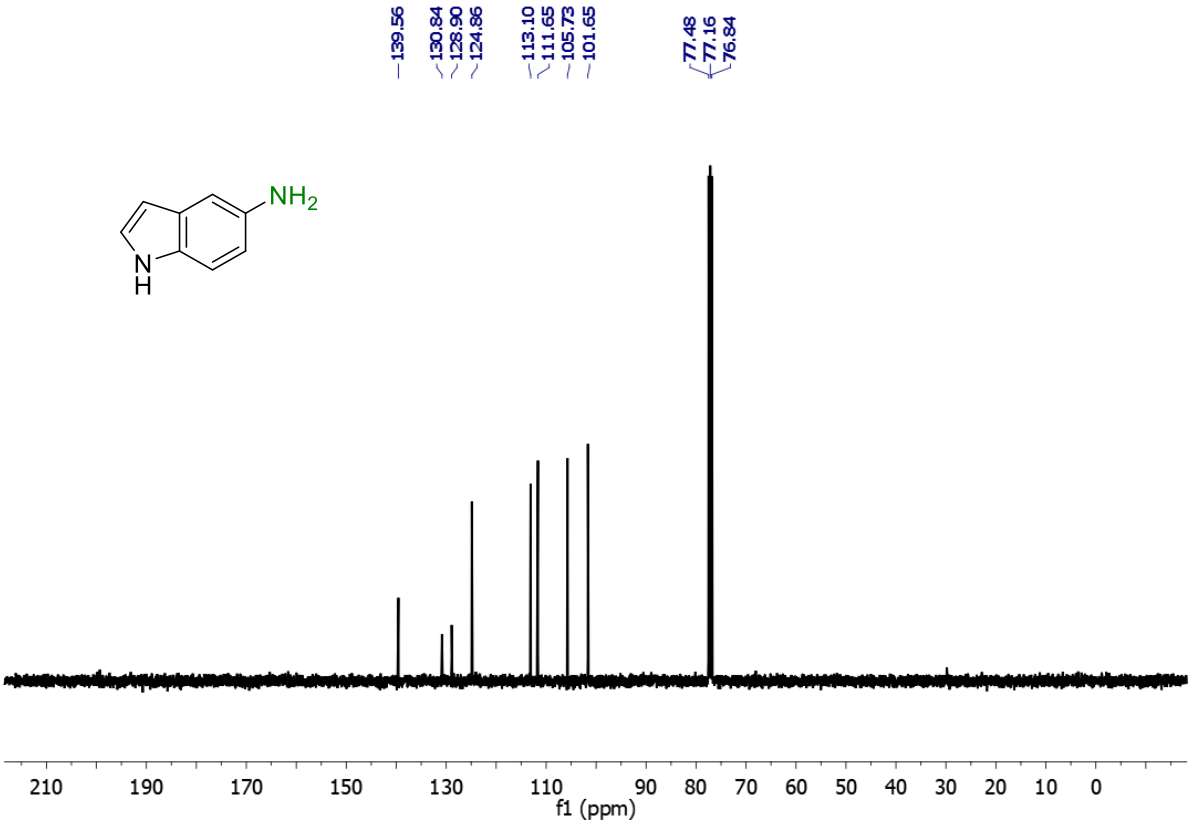


Figure S67. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 1*H*-indol-6-amine (**A$_{11}$**) in $CDCl_3$ at r.t.

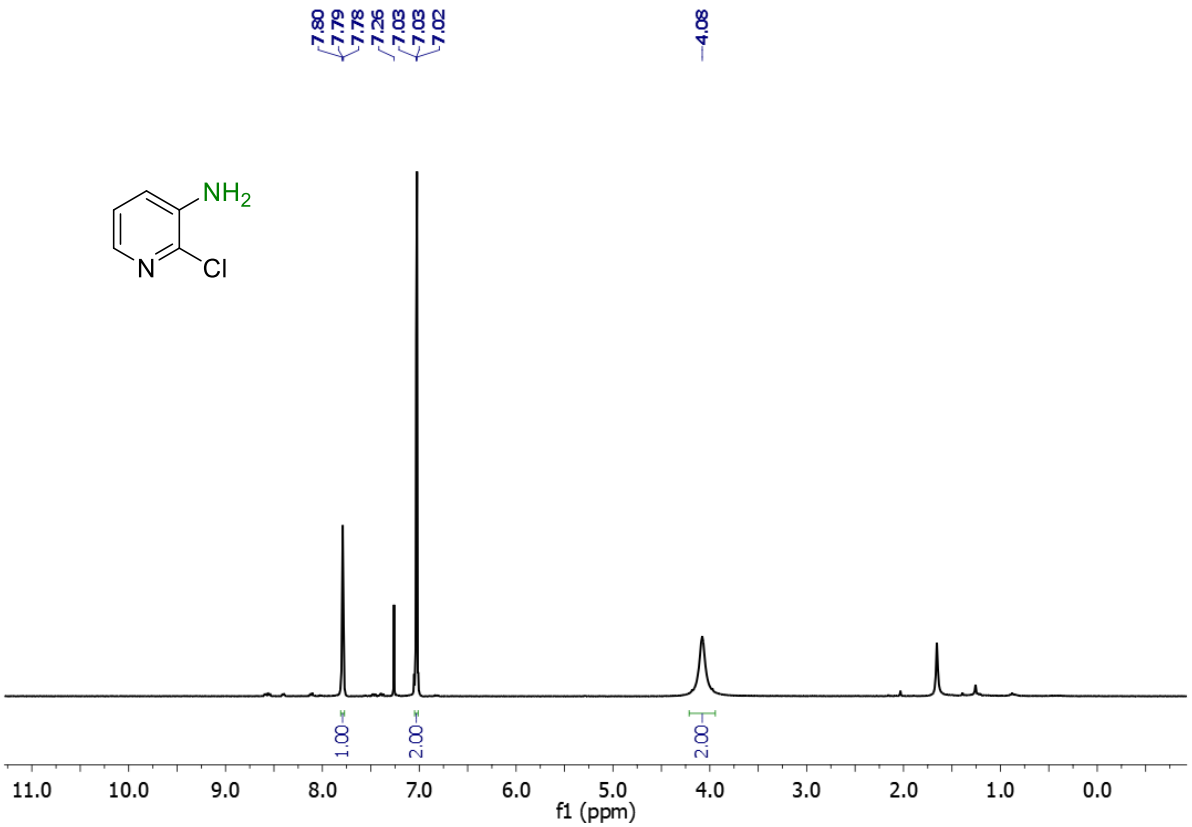


Figure S68. ^{1}H NMR (400 MHz) spectrum of 2-chloropyridin-3-amine (**A_{12}**) in $CDCl_3$ at r.t.

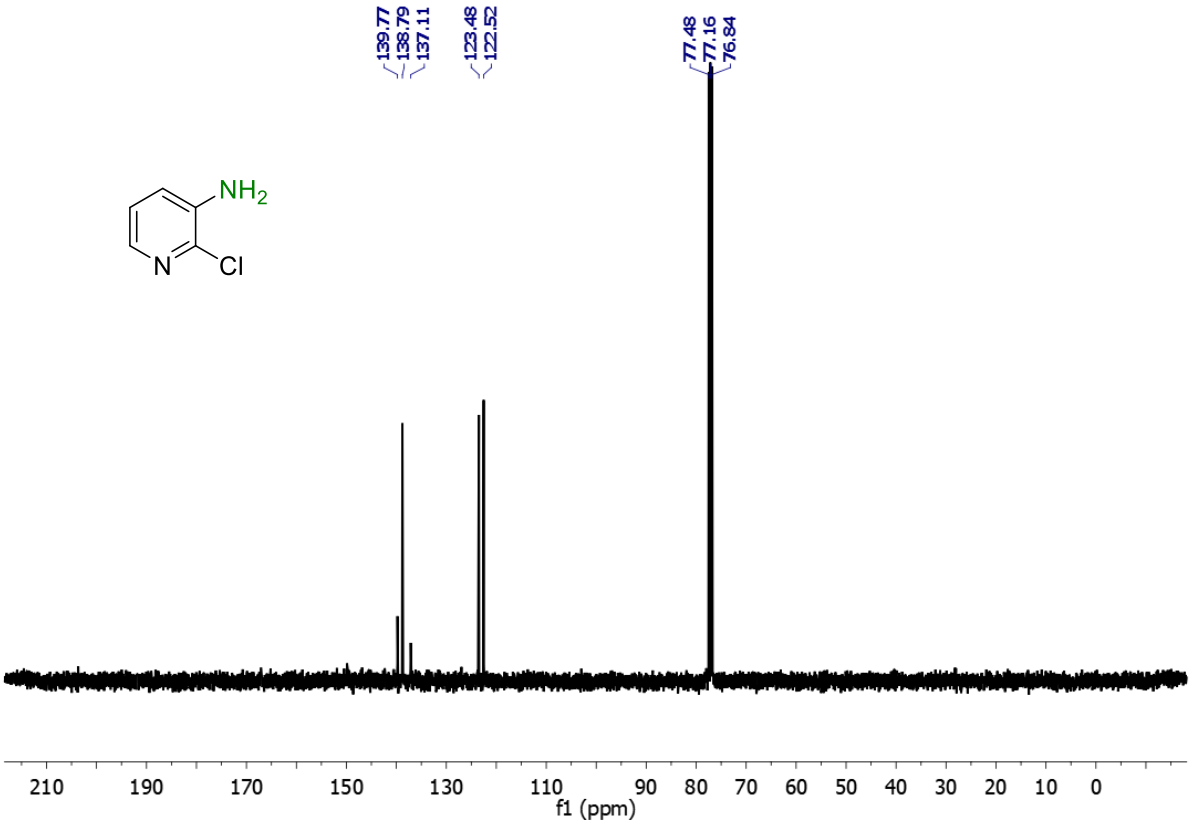


Figure S69. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 2-chloropyridin-3-amine (**A_{12}**) in $CDCl_3$ at r.t.

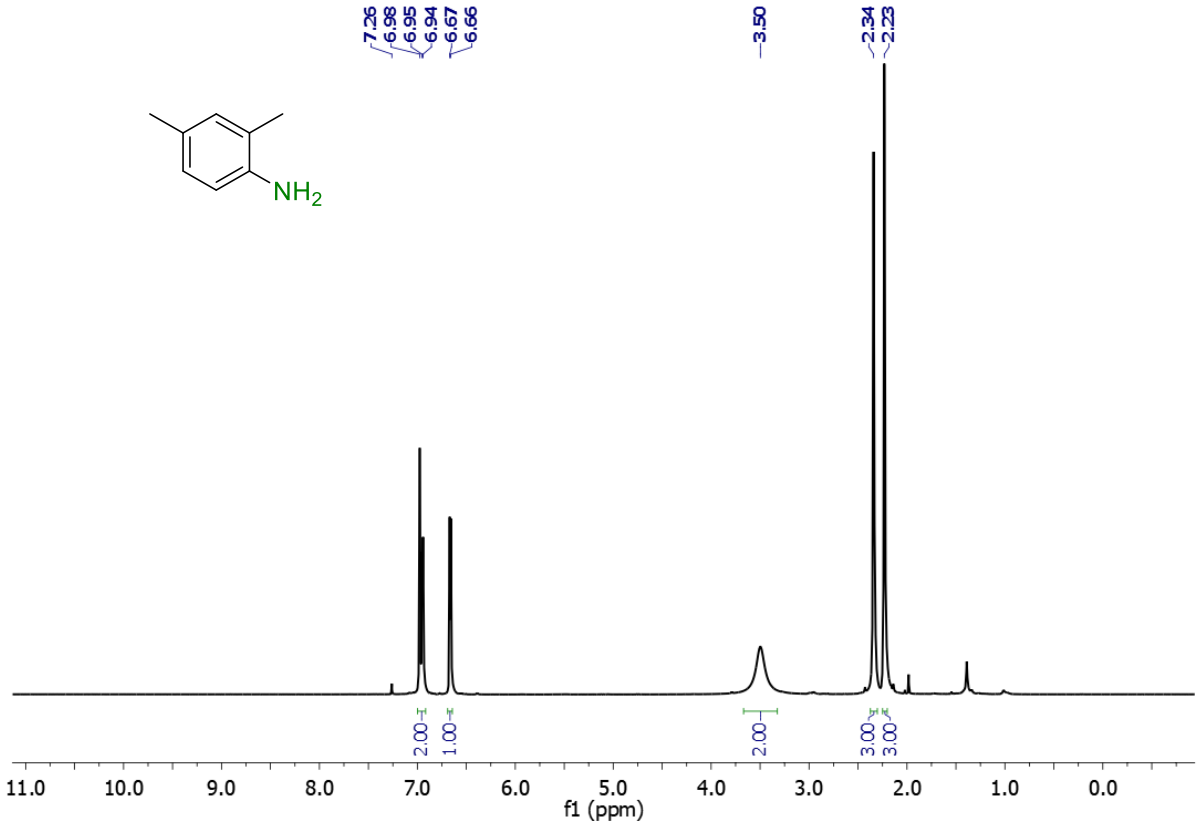


Figure S70. ^{1}H NMR (700 MHz) spectrum of 2,4-Dimethylaniline (**A$_{13}$**) in $CDCl_3$ at r.t.

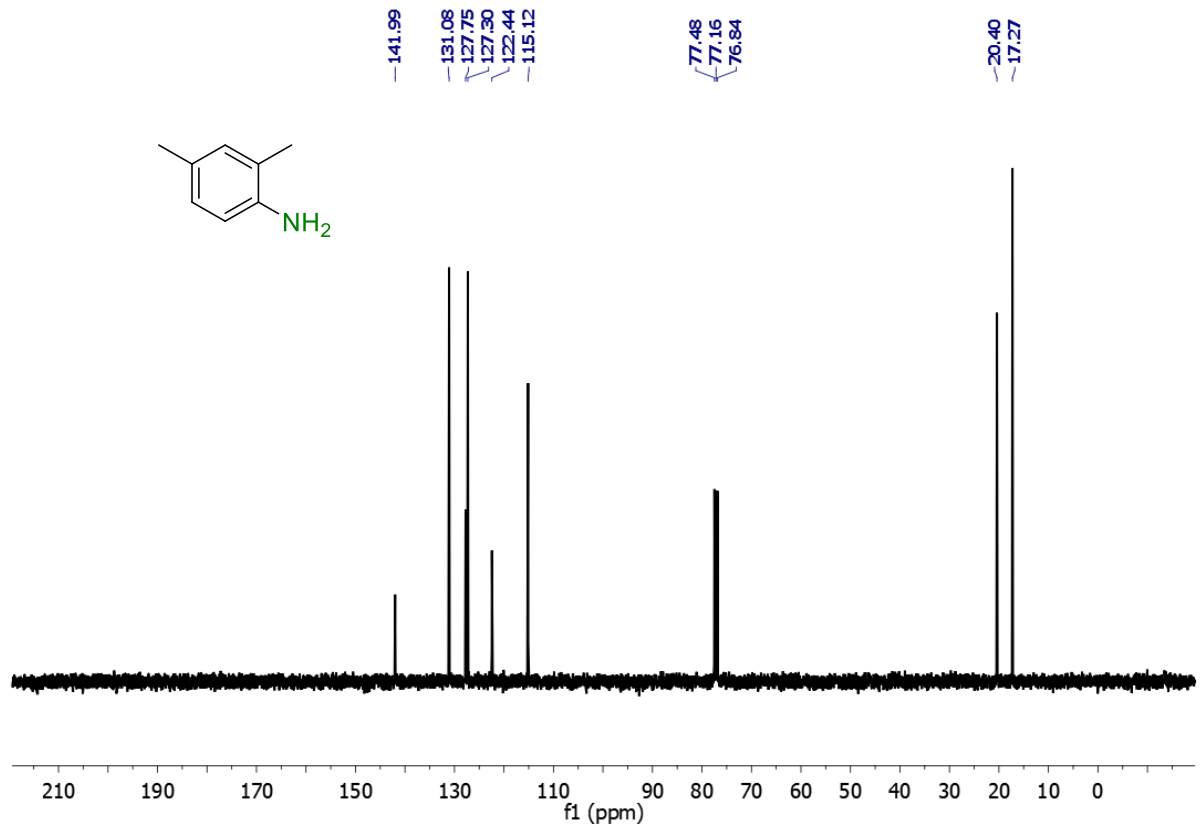


Figure S71. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 2,4-Dimethylaniline (**A$_{13}$**) in $CDCl_3$ at r.t.

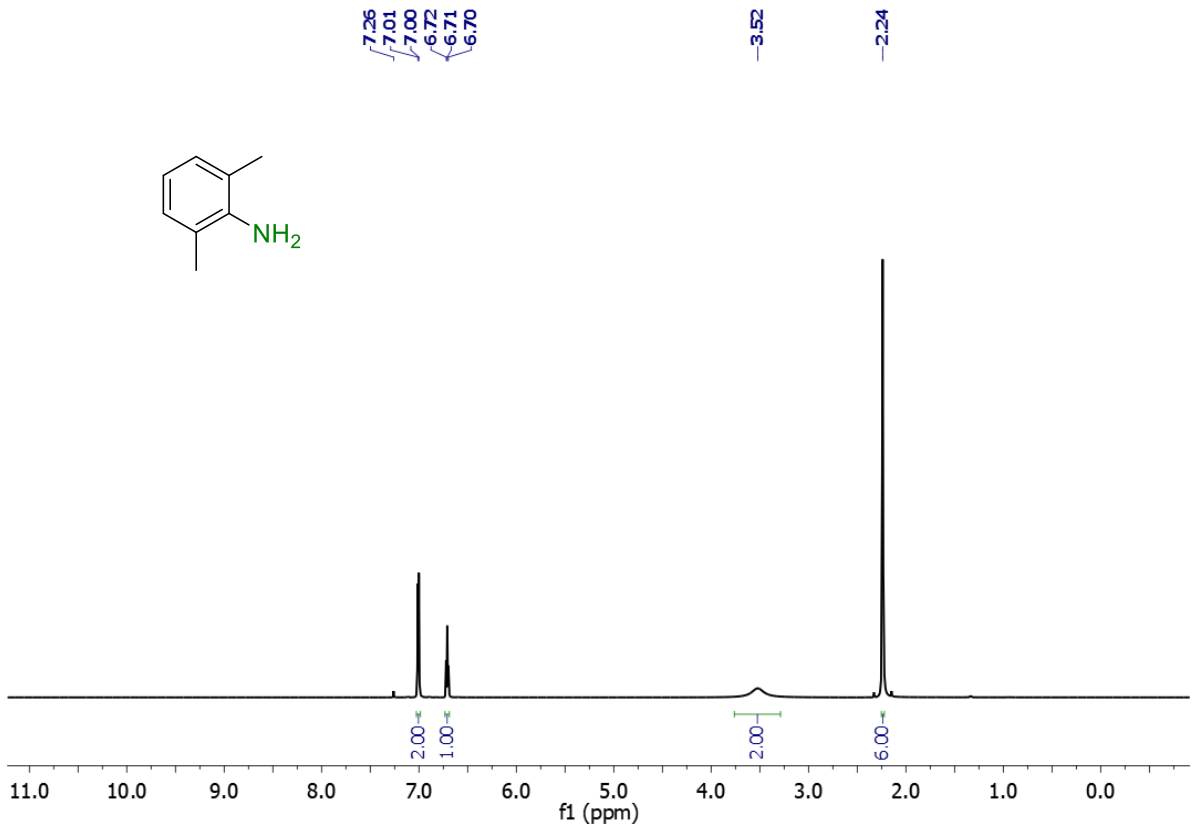


Figure S72. ^{1}H NMR (700 MHz) spectrum of 2,6-dimethylaniline (**A$_{14}$**) in $CDCl_3$ at r.t.

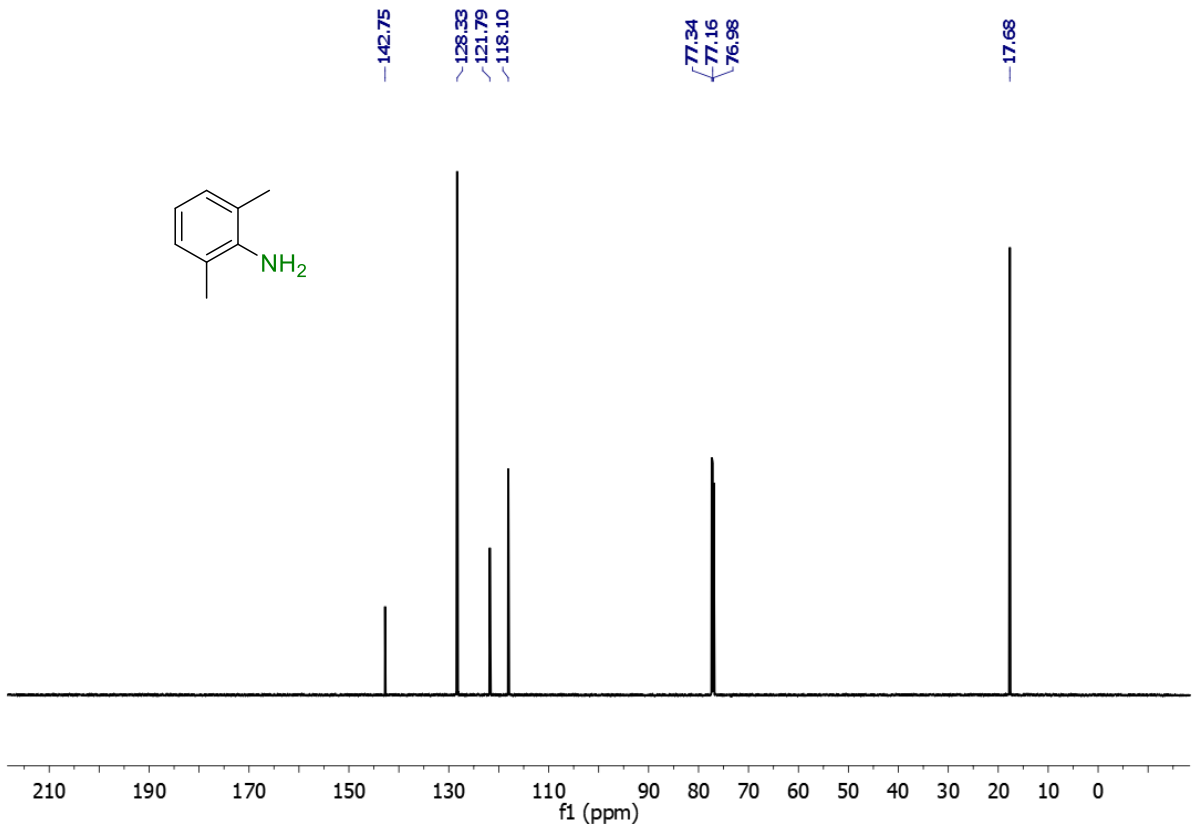


Figure S73. ^{13}C{^{1}H} NMR (176 MHz) spectrum of 2,6-dimethylaniline (**A$_{14}$**) in $CDCl_3$ at r.t.

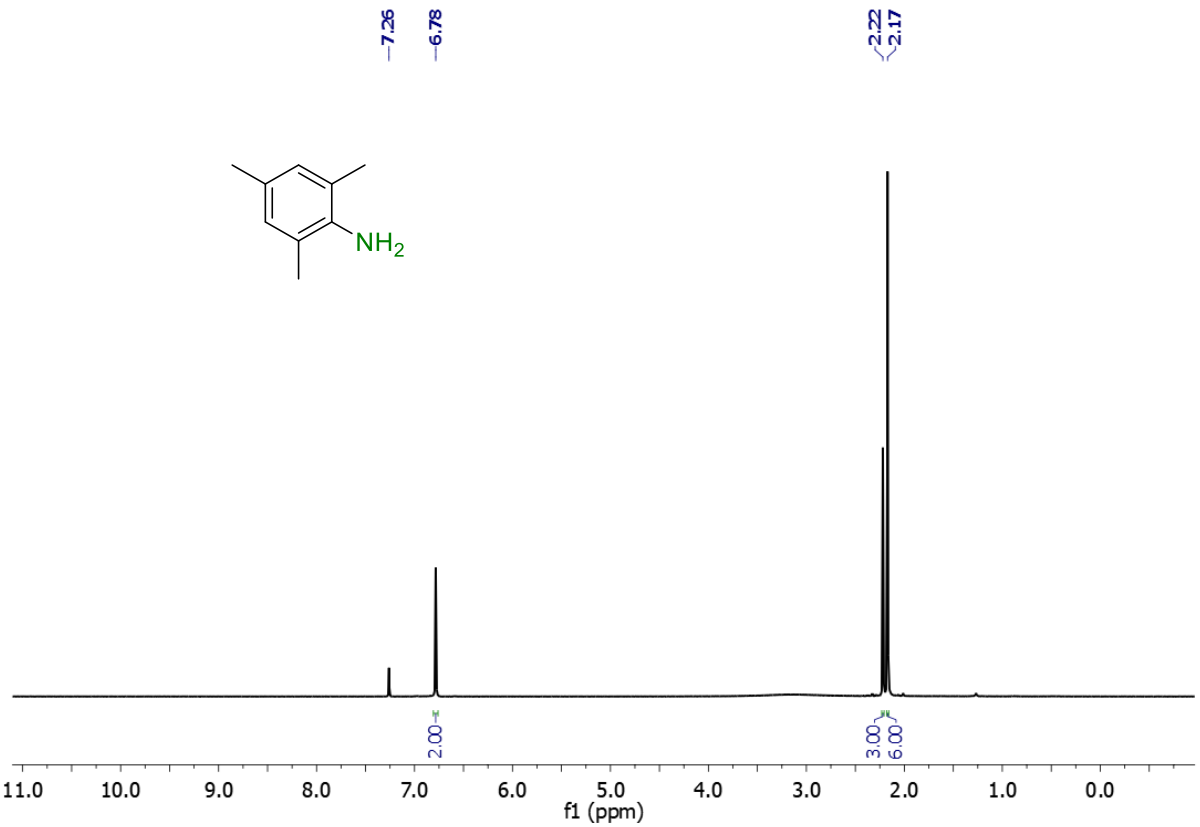


Figure S74. ^{1}H NMR (400 MHz) spectrum of 2,4,6-trimethylaniline (**A_{15}**) in $CDCl_3$ at r.t.

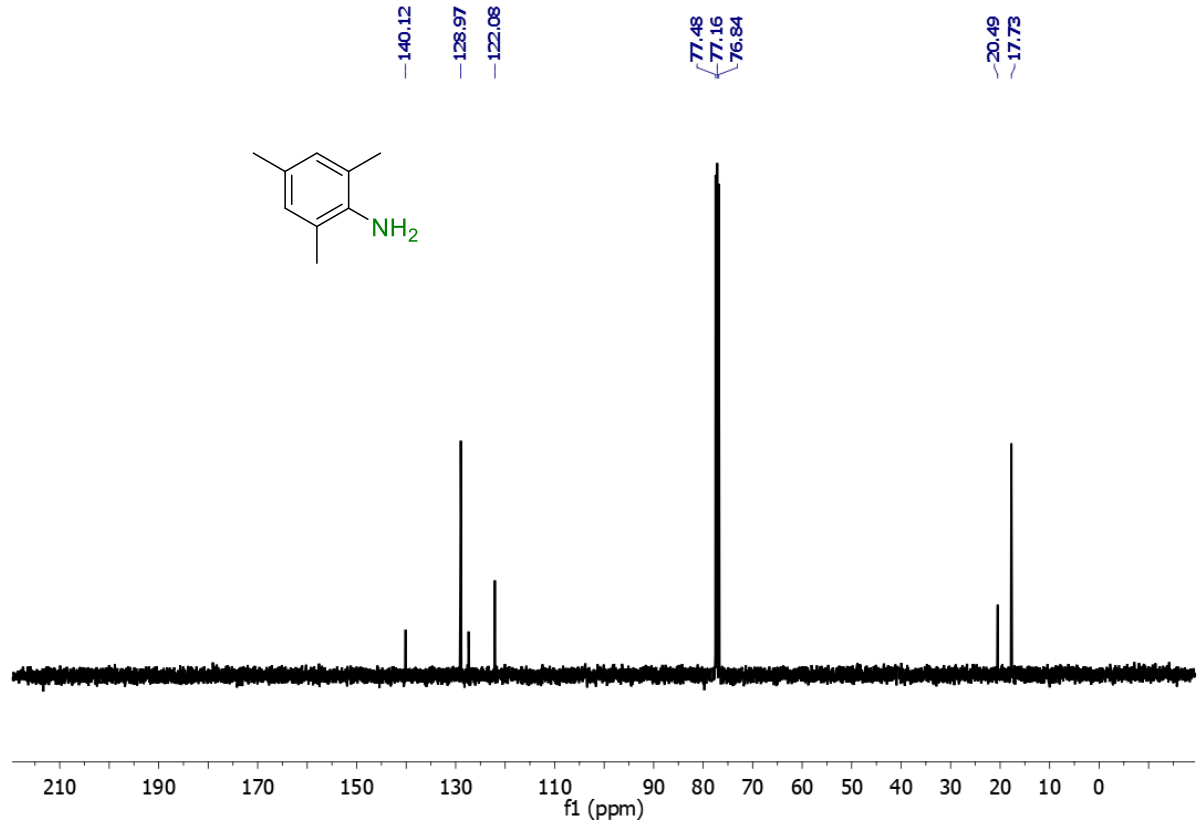


Figure S75. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 2,4,6-trimethylaniline (**A_{15}**) in $CDCl_3$ at r.t.

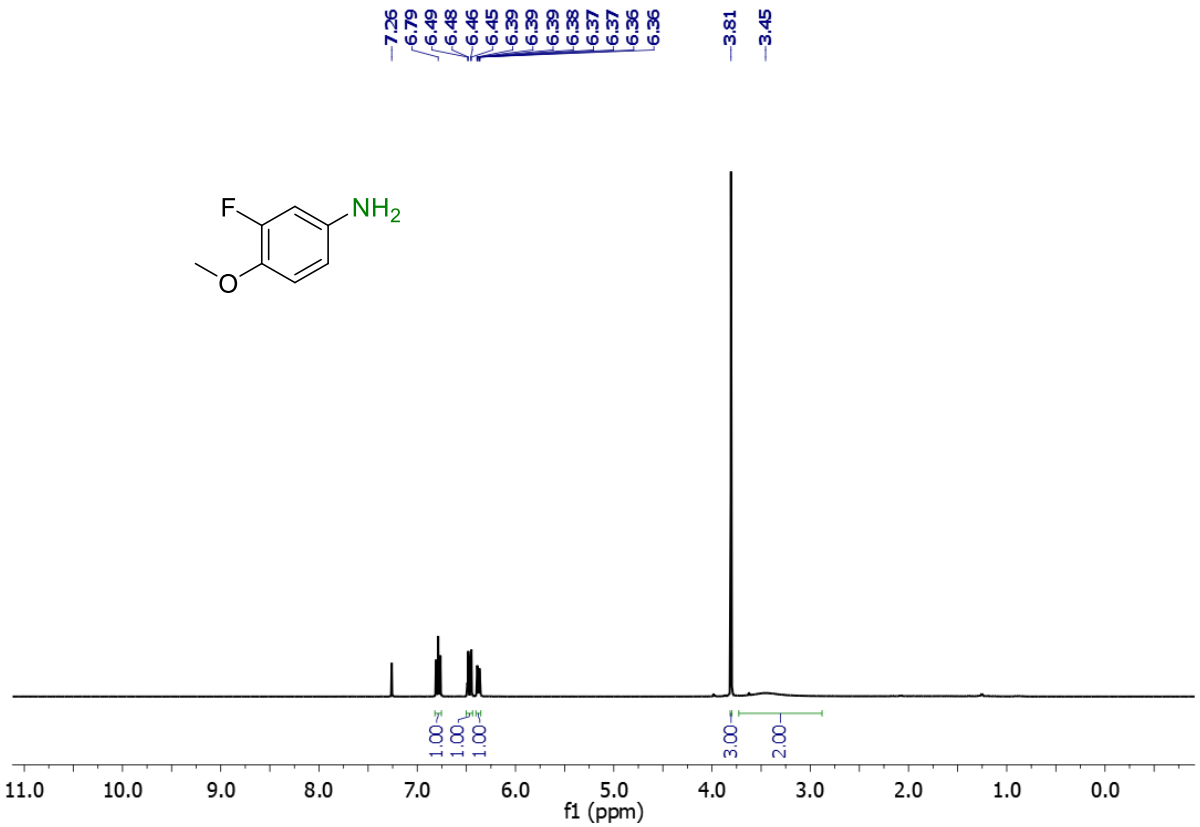


Figure S76. ^{1}H NMR (400 MHz) spectrum of 3-fluoro-4-methoxyaniline (**A_{16}**) in $CDCl_3$ at r.t.

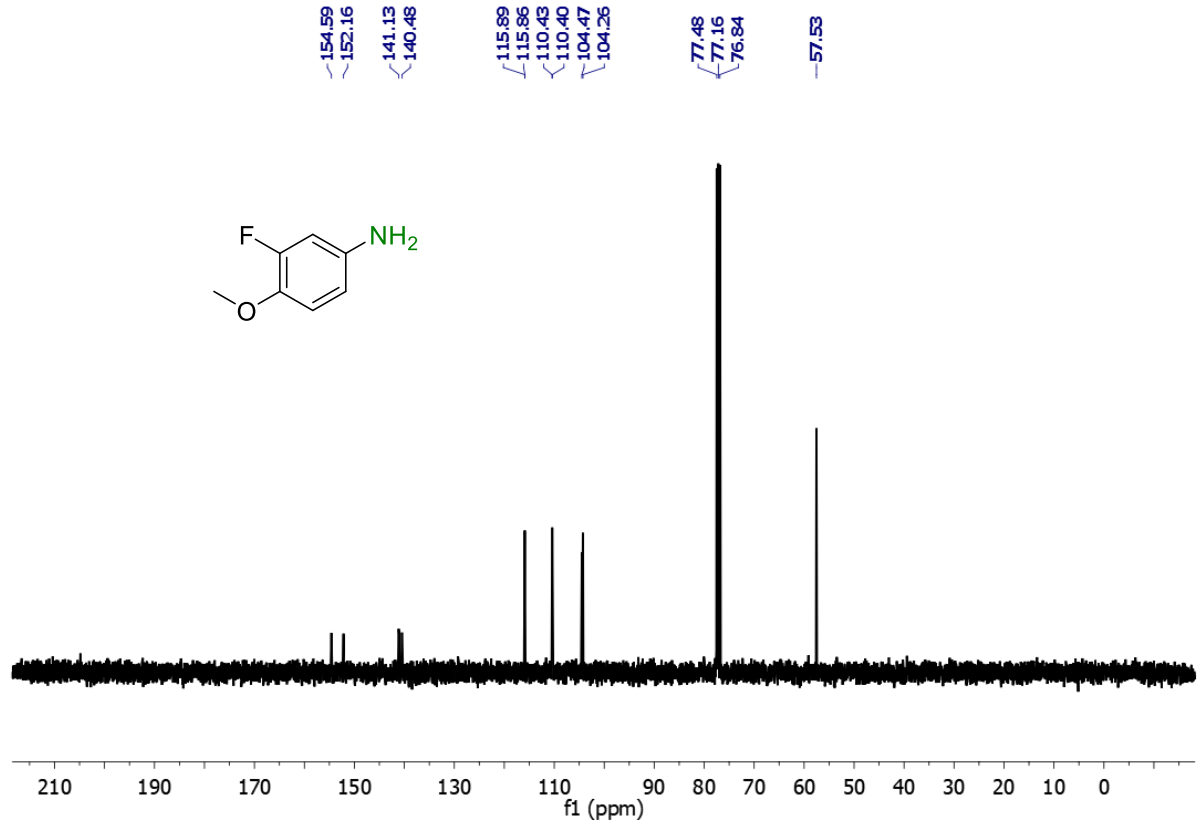


Figure S77. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 3-fluoro-4-methoxyaniline (**A_{16}**) in $CDCl_3$ at r.t.

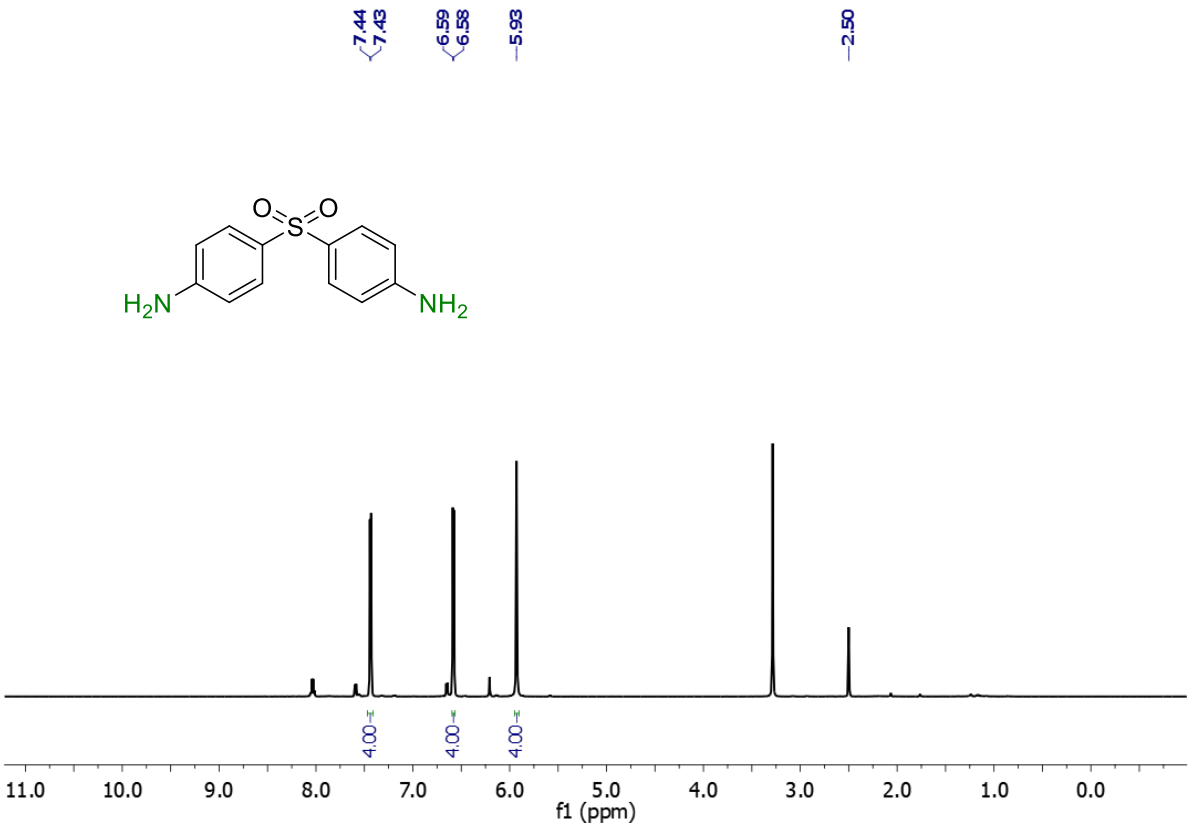


Figure S78. ^{1}H NMR (700 MHz) spectrum of Dapsone in DMSO-d_6 at r.t.

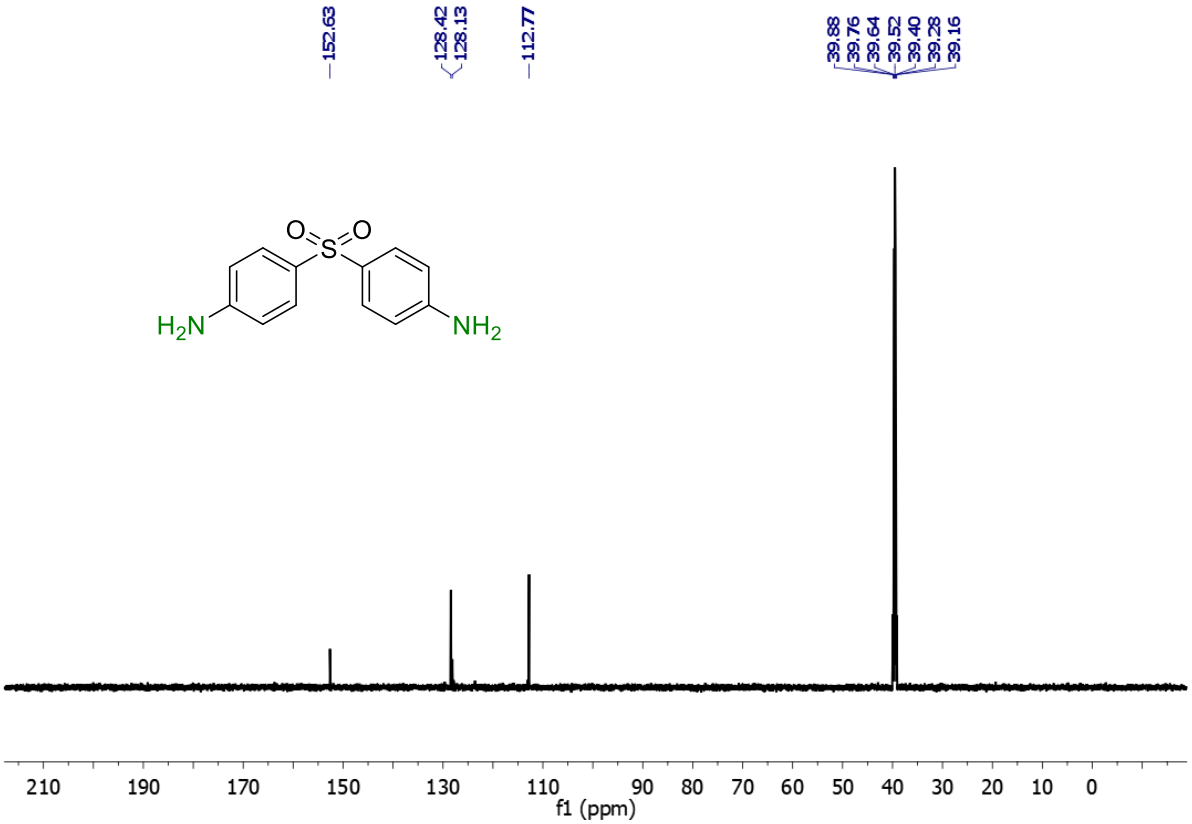


Figure S79. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of Dapsone in DMSO-d_6 at r.t.

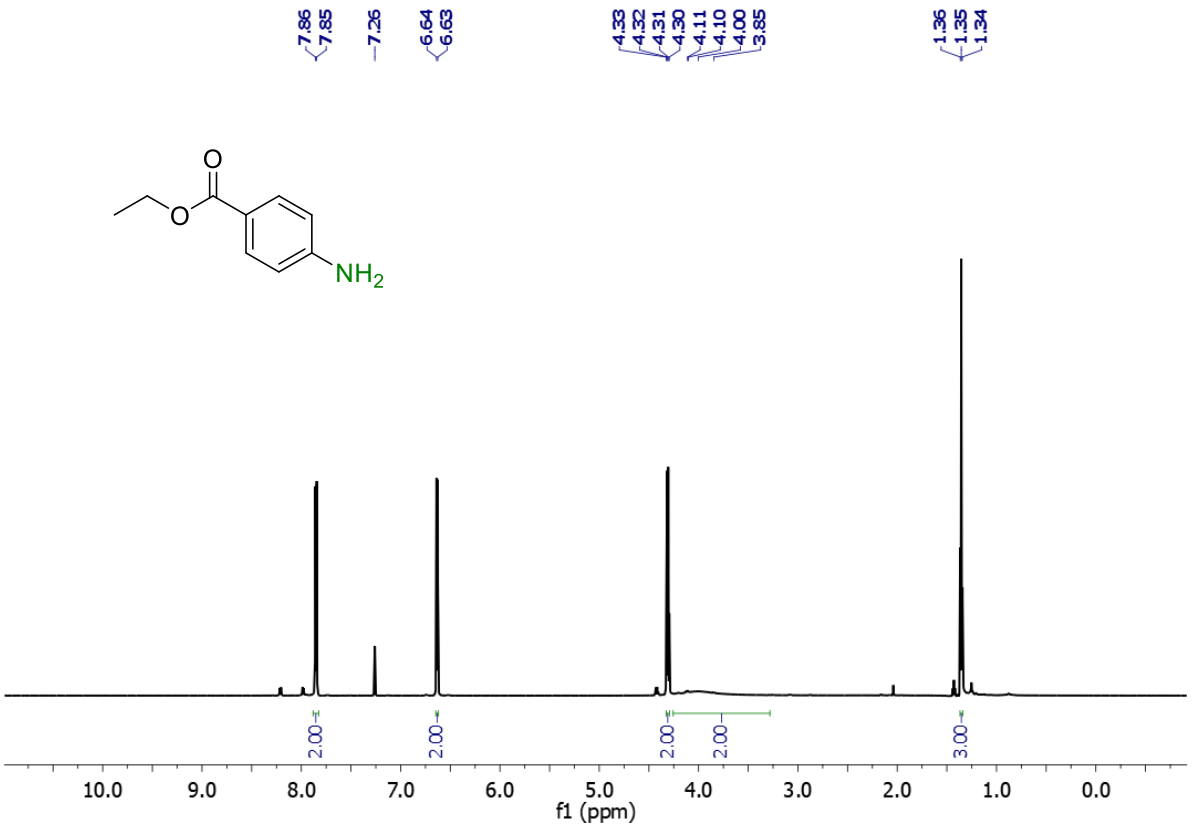


Figure S80. ^{1}H NMR (700 MHz) spectrum of Benzocaine (**P$_{4k}$**) in $CDCl_3$ at r.t.

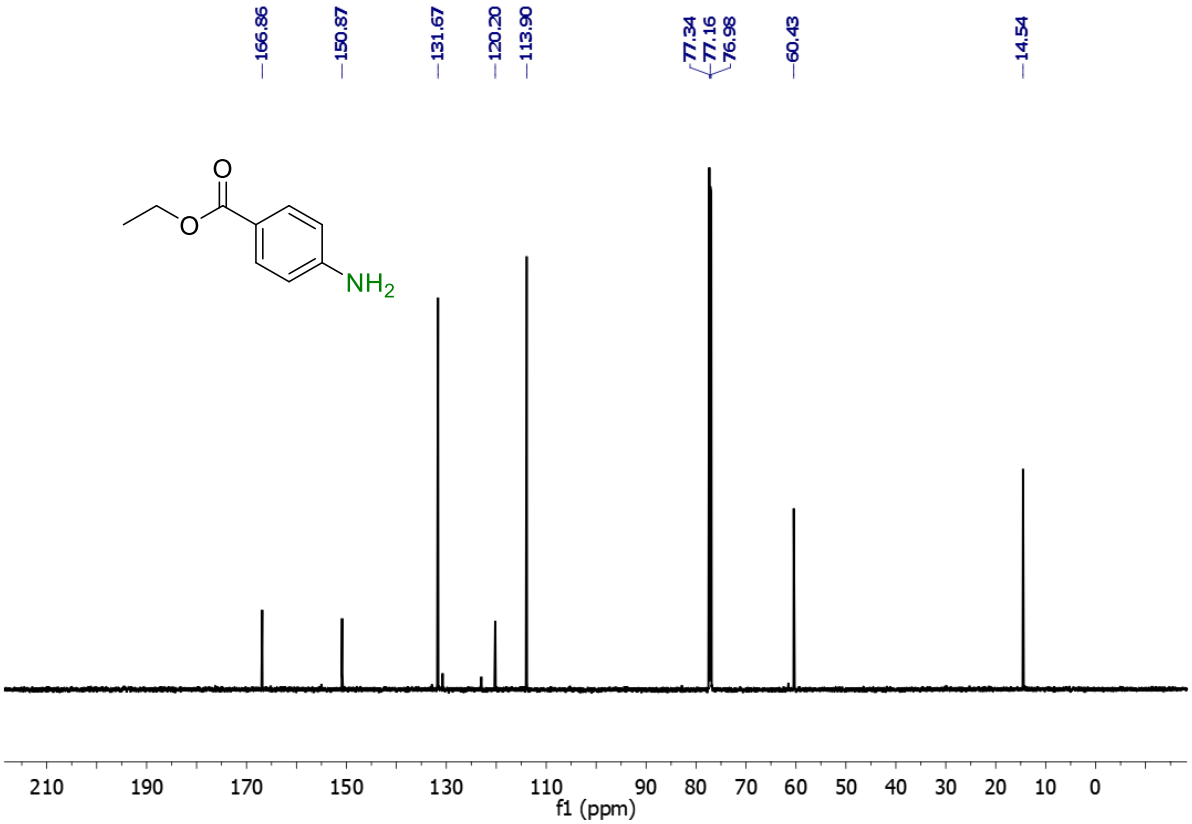


Figure S81. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of Benzocaine (**P$_{4k}$**) in $CDCl_3$ at r.t.

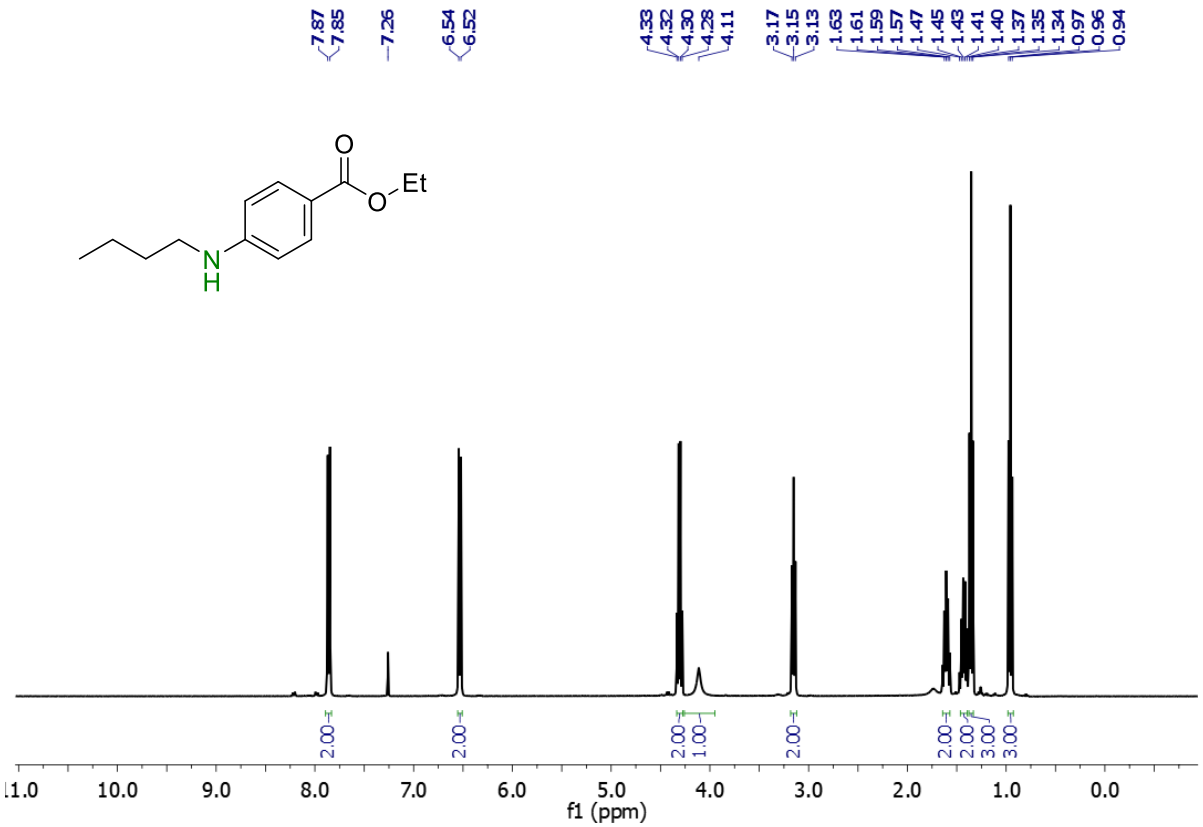


Figure S82. ^{1}H NMR (400 MHz) spectrum of ethyl 4-(butylamino)benzoate $CDCl_3$ at r.t.

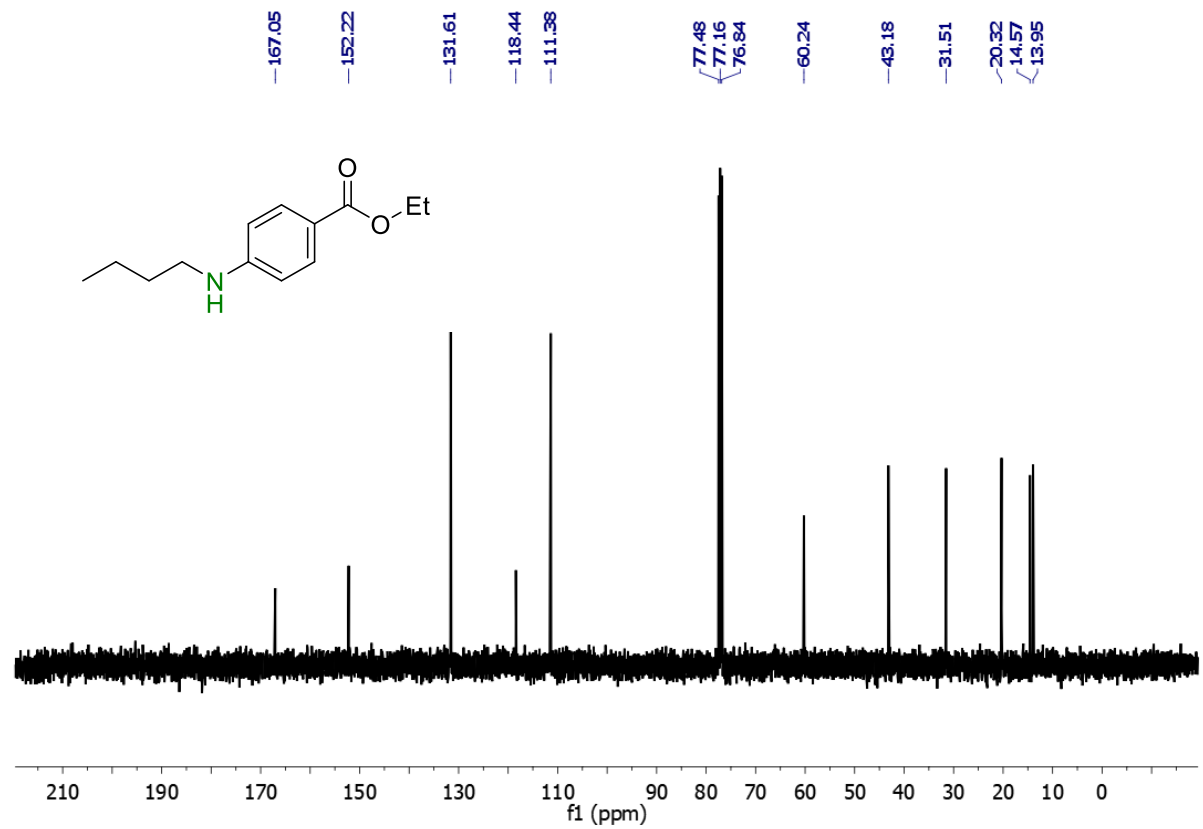


Figure S83. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of ethyl 4-(butylamino)benzoate in $CDCl_3$ at r.t.

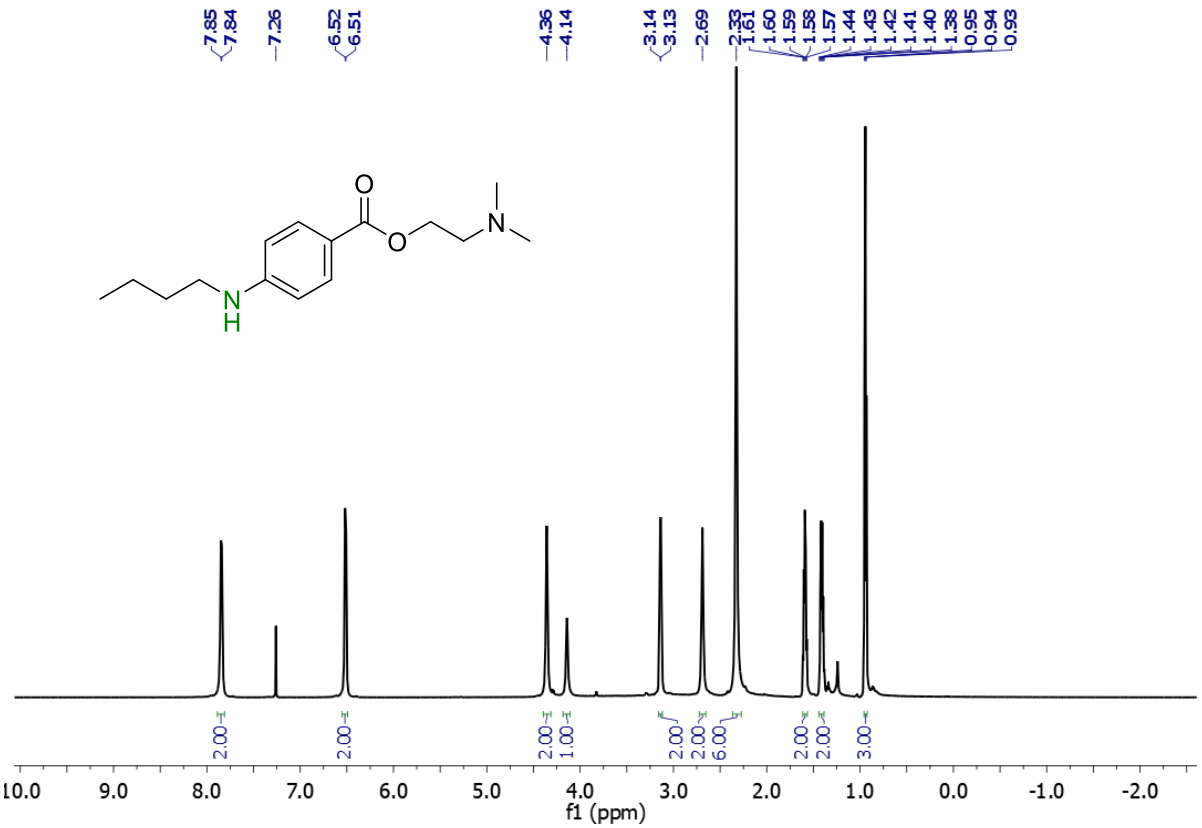


Figure S84. ^{1}H NMR (700 MHz) spectrum of tetracaine in $CDCl_3$ at r.t.

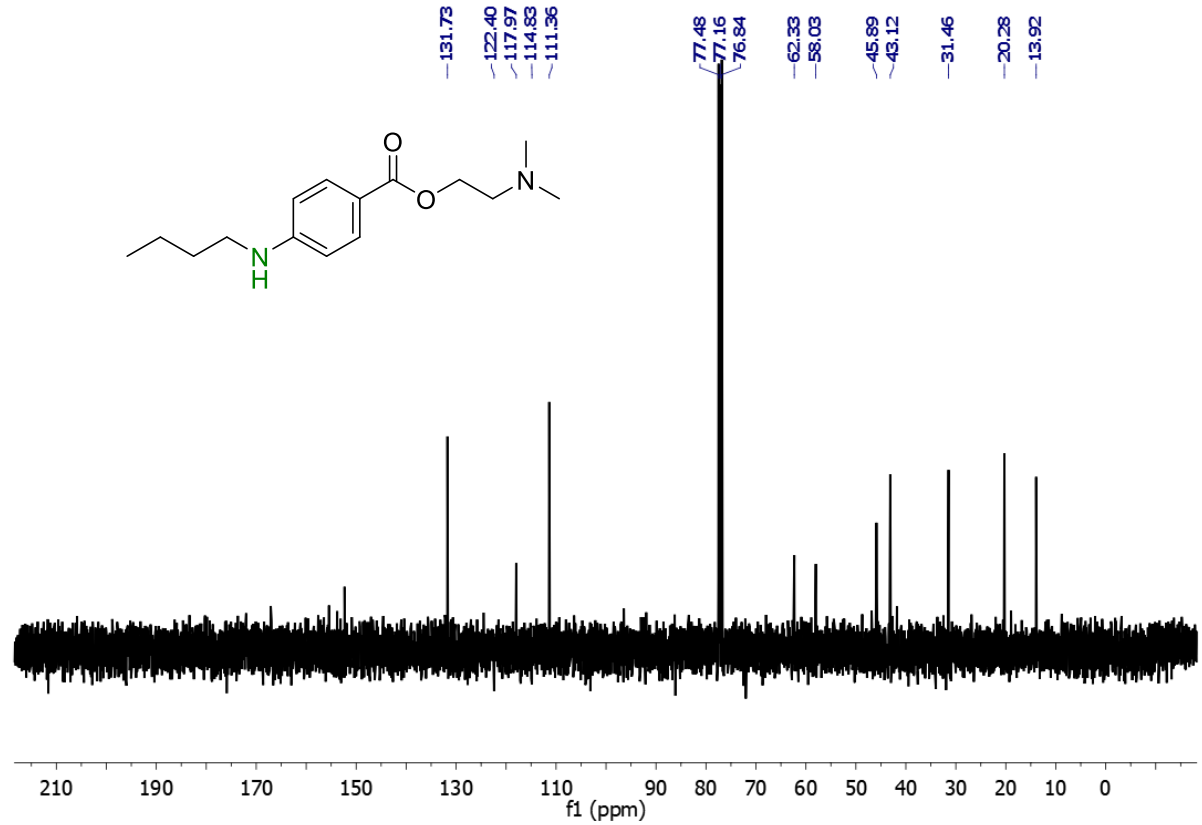


Figure S85. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of tetracaine in $CDCl_3$ at r.t.

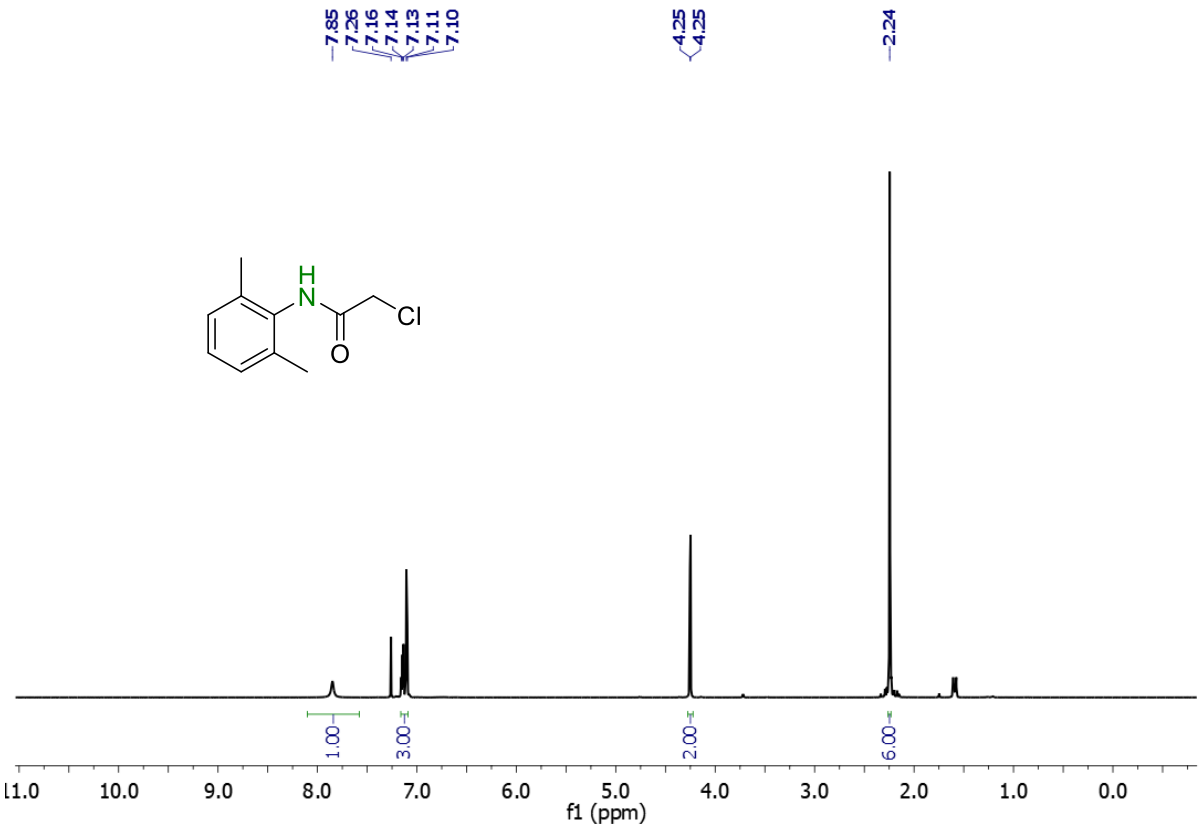


Figure S86. ^{1}H NMR (700 MHz) spectrum of lidocaine intermediate in $CDCl_3$ at r.t.

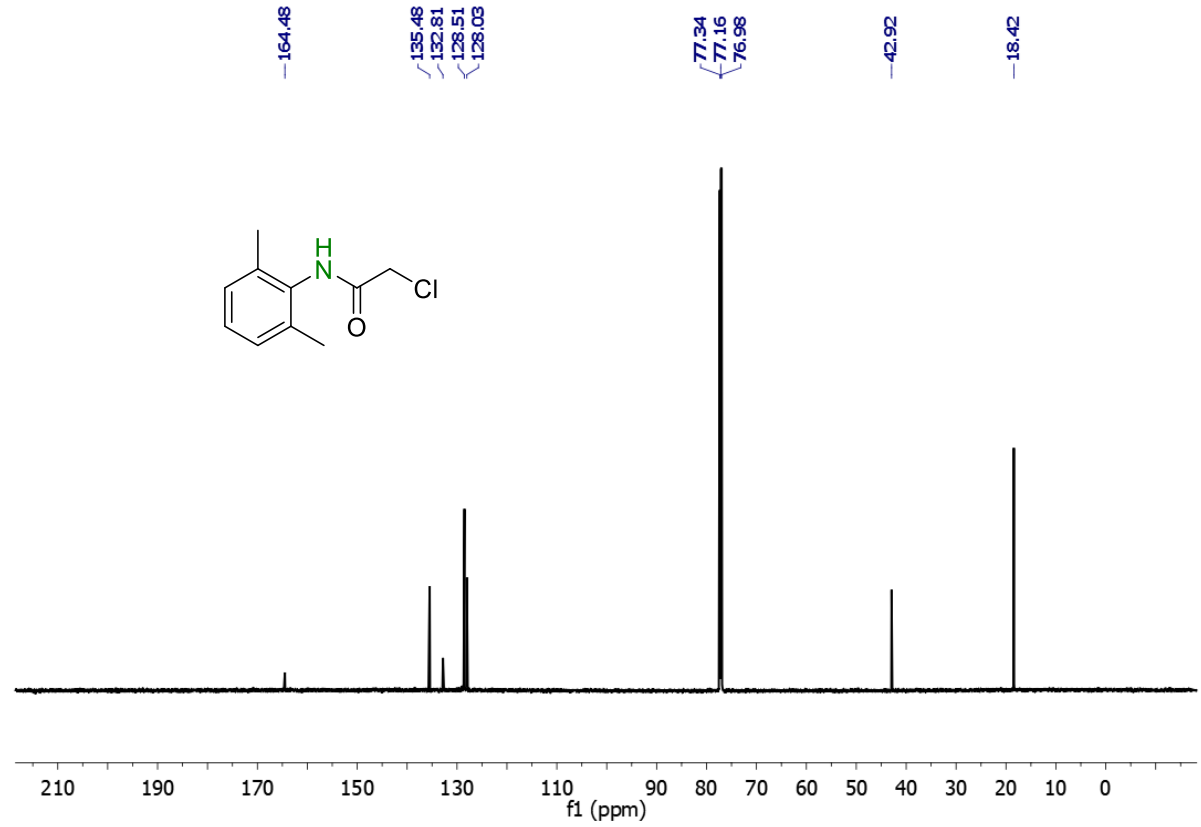


Figure S87. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of lidocaine intermediate in $CDCl_3$ at r.t.

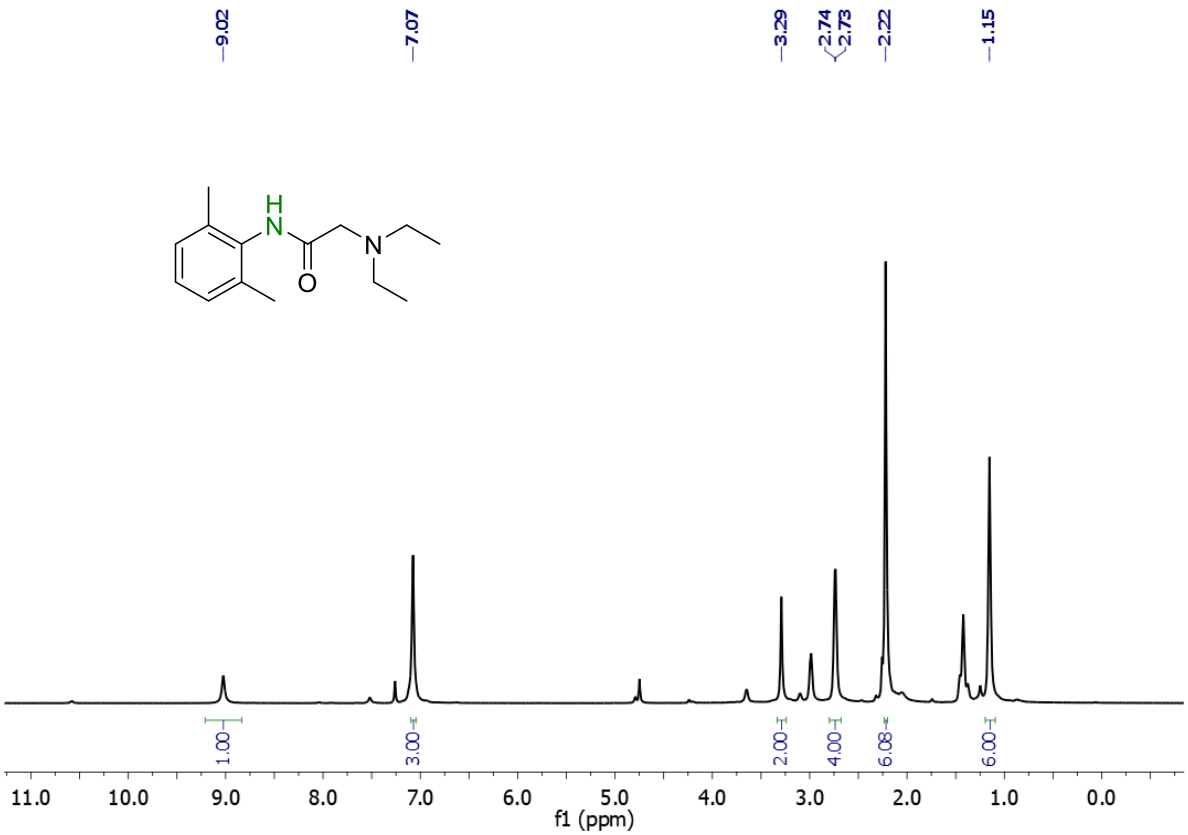


Figure S88. ^{1}H NMR (700 MHz) spectrum of lidocaine in $CDCl_3$ at r.t.

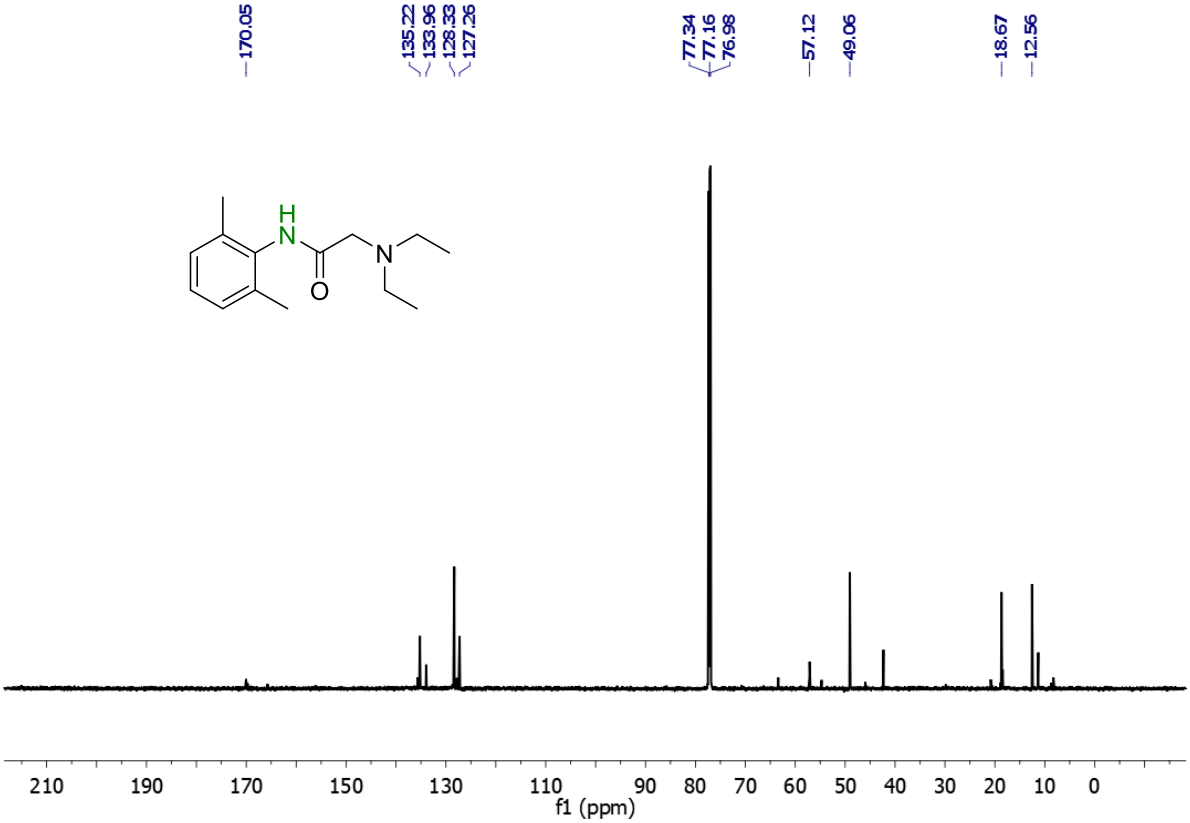


Figure S89. $^{13}C\{^{1}H\}$ NMR (176 MHz) spectrum of lidocaine in $CDCl_3$ at r.t.

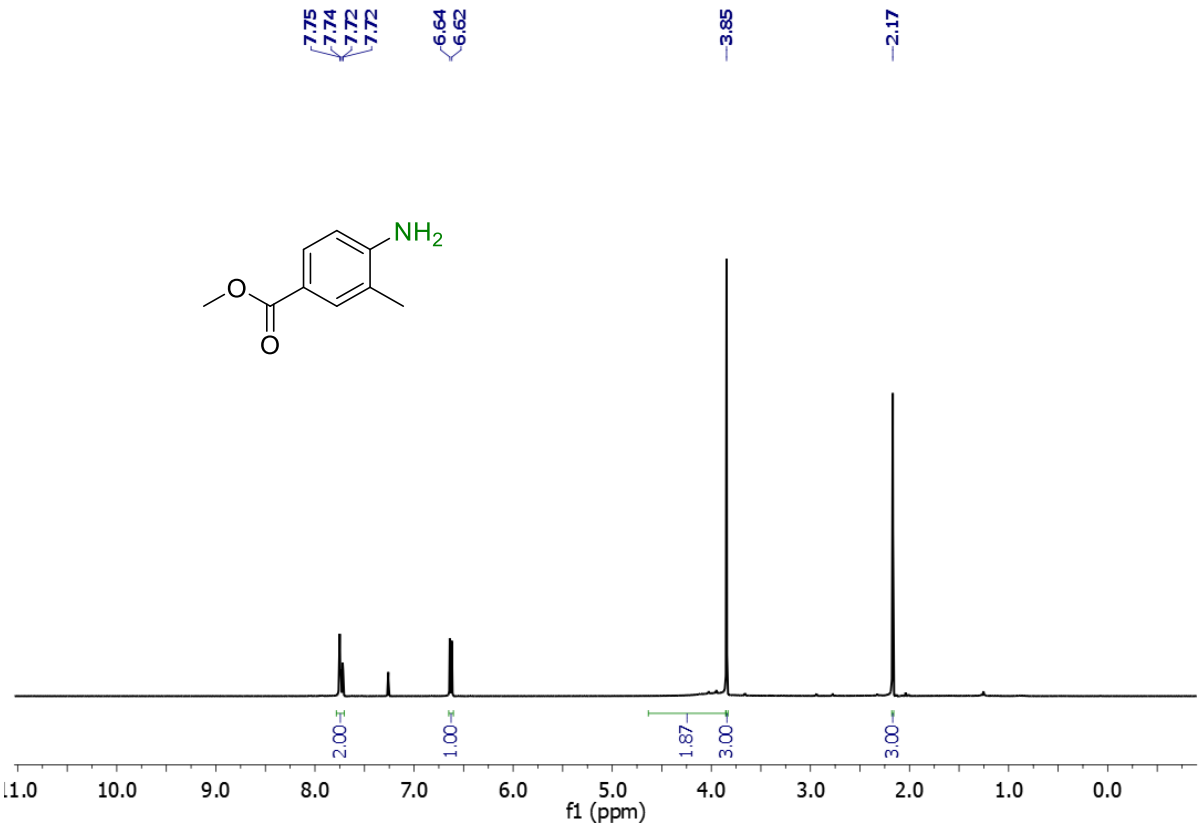


Figure S90. ^{1}H NMR (400 MHz) spectrum of compound **A** in $CDCl_3$ at r.t.

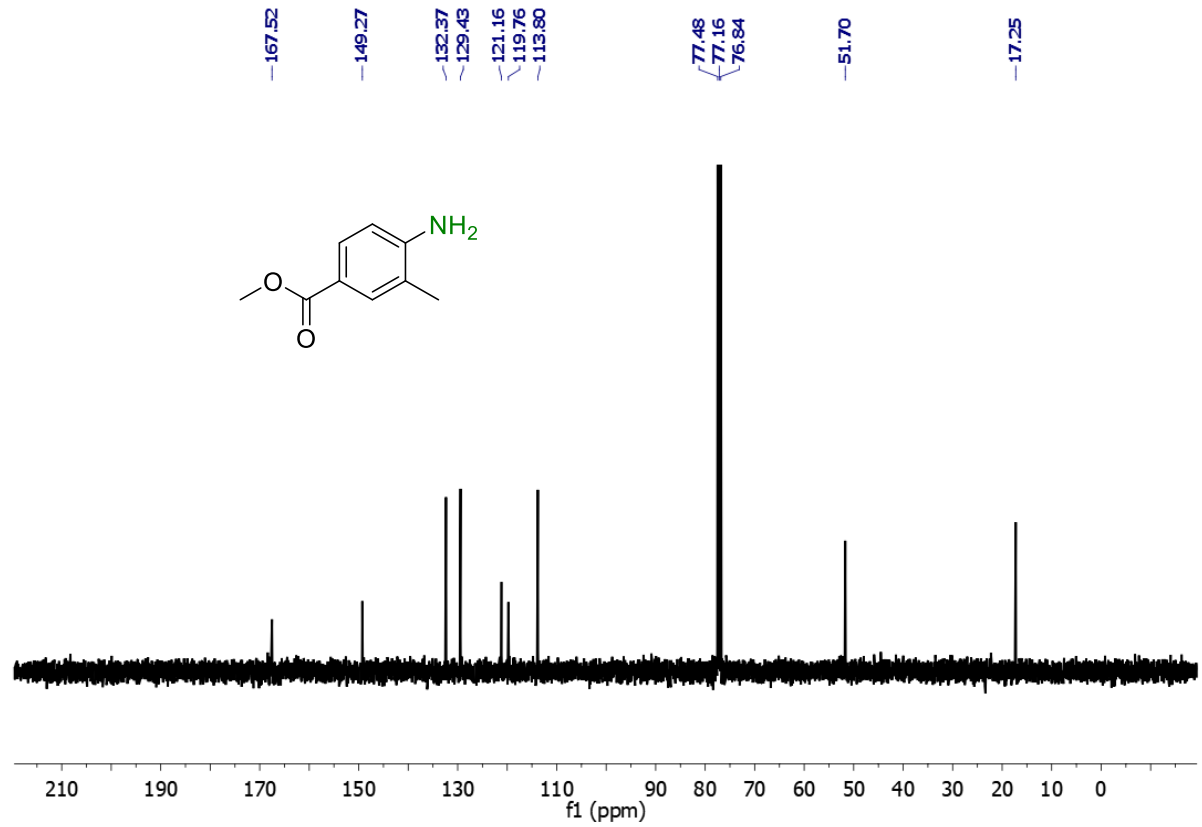


Figure S91. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **A** in $CDCl_3$ at r.t.

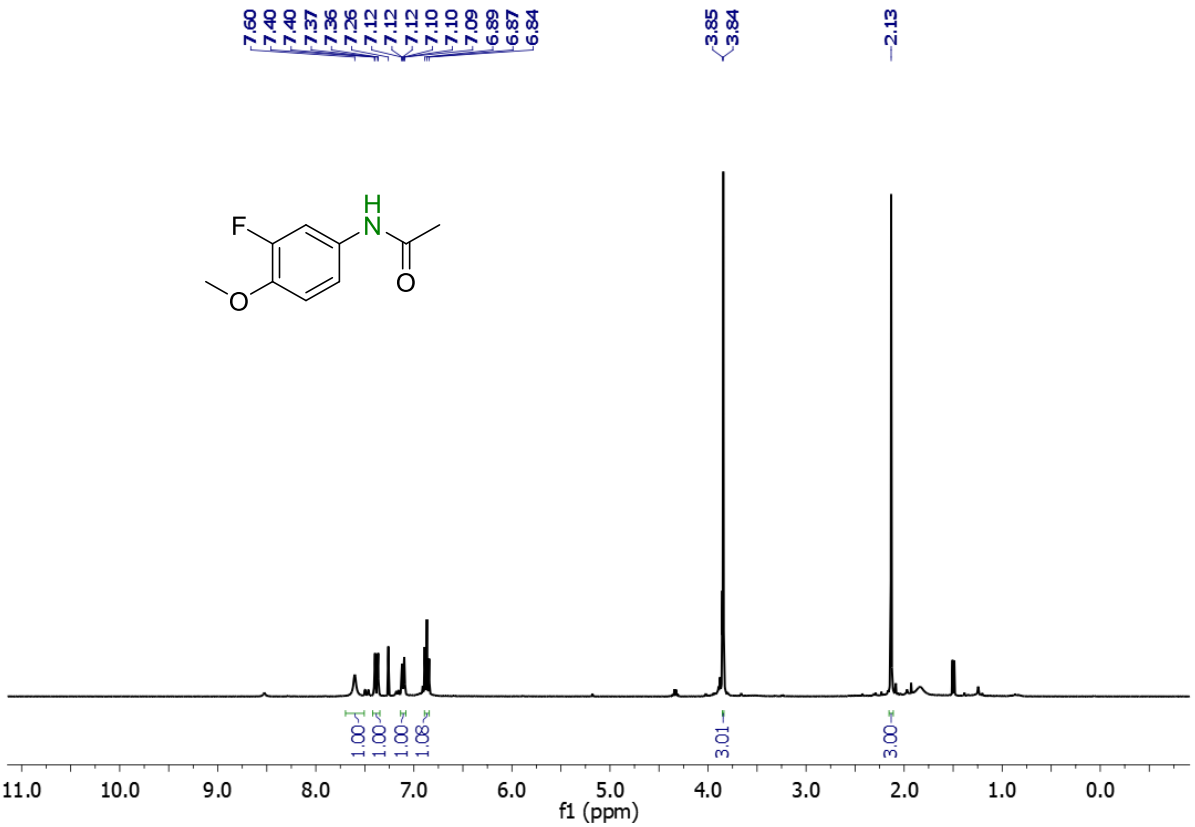


Figure S92. ^{1}H NMR (400 MHz) spectrum of compound **B** in $CDCl_3$ at r.t.

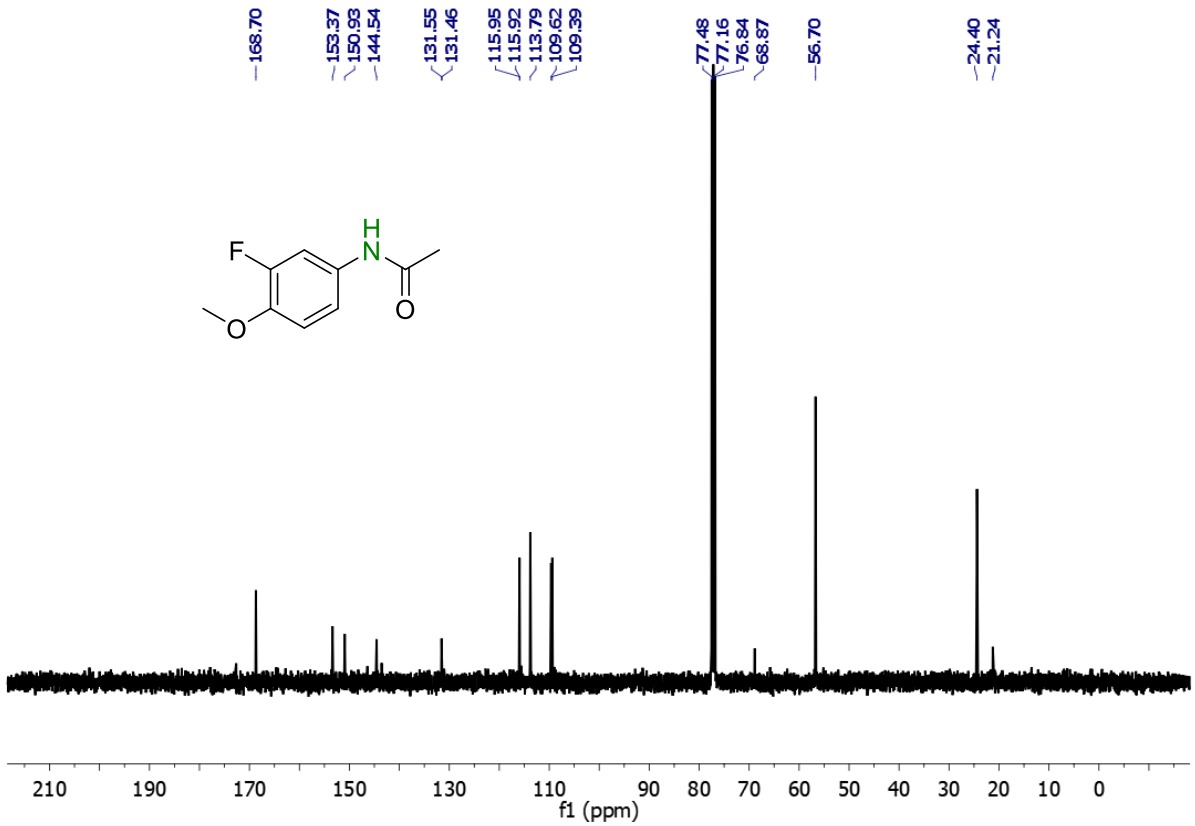


Figure S93. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **B** in $CDCl_3$ at r.t.

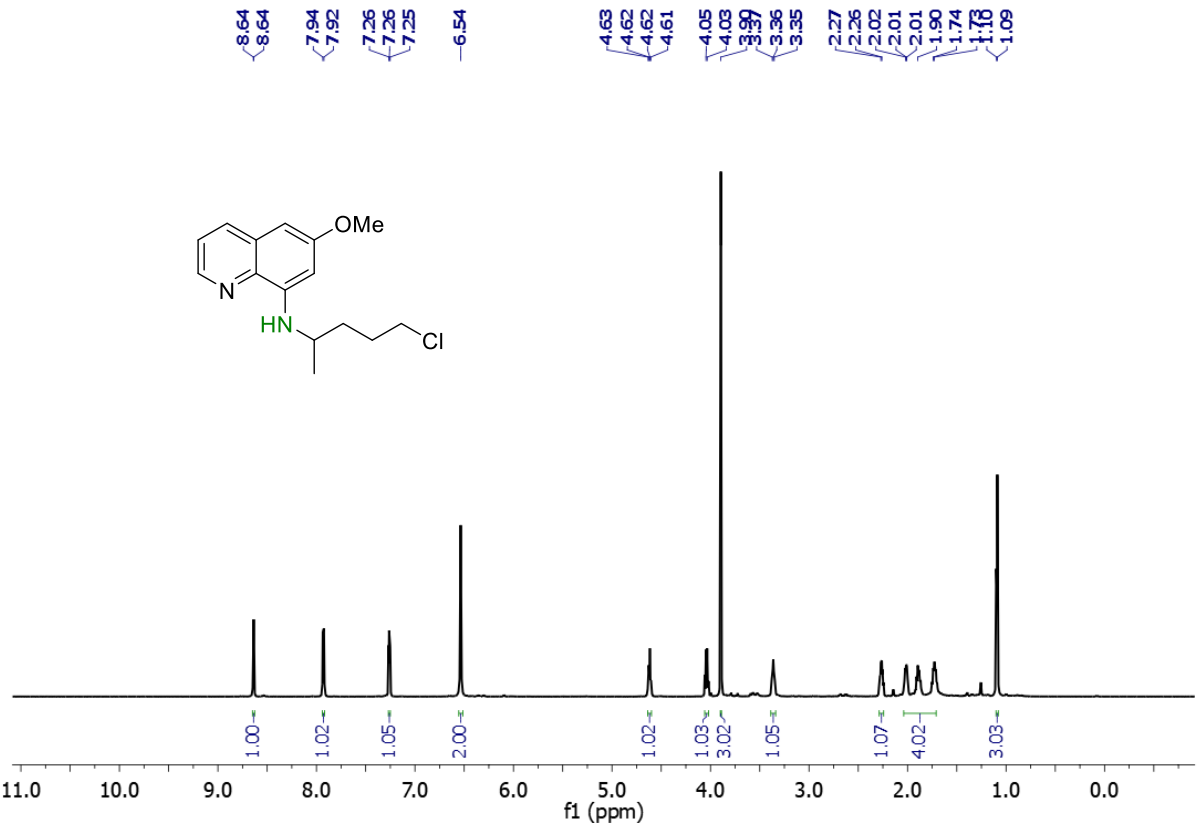


Figure S94. ^{1}H NMR (700 MHz) spectrum of compound **C** in $CDCl_3$ at r.t.

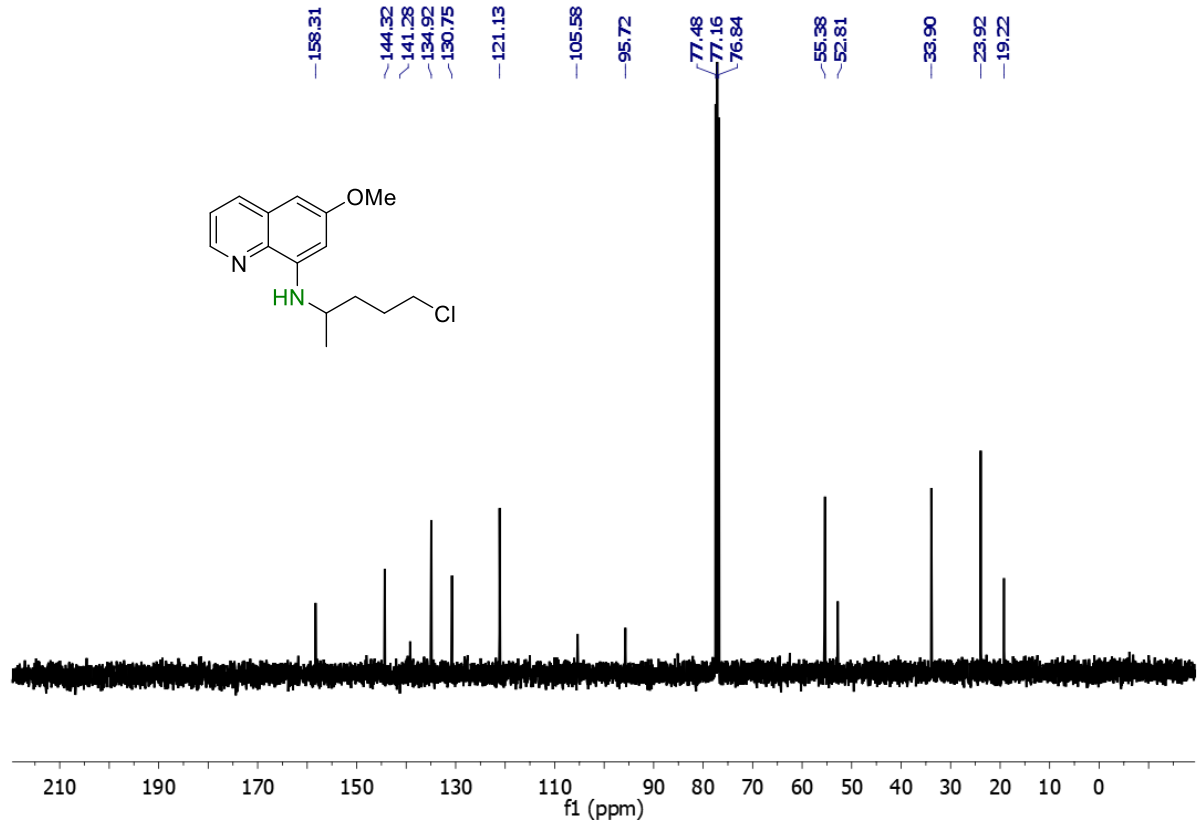
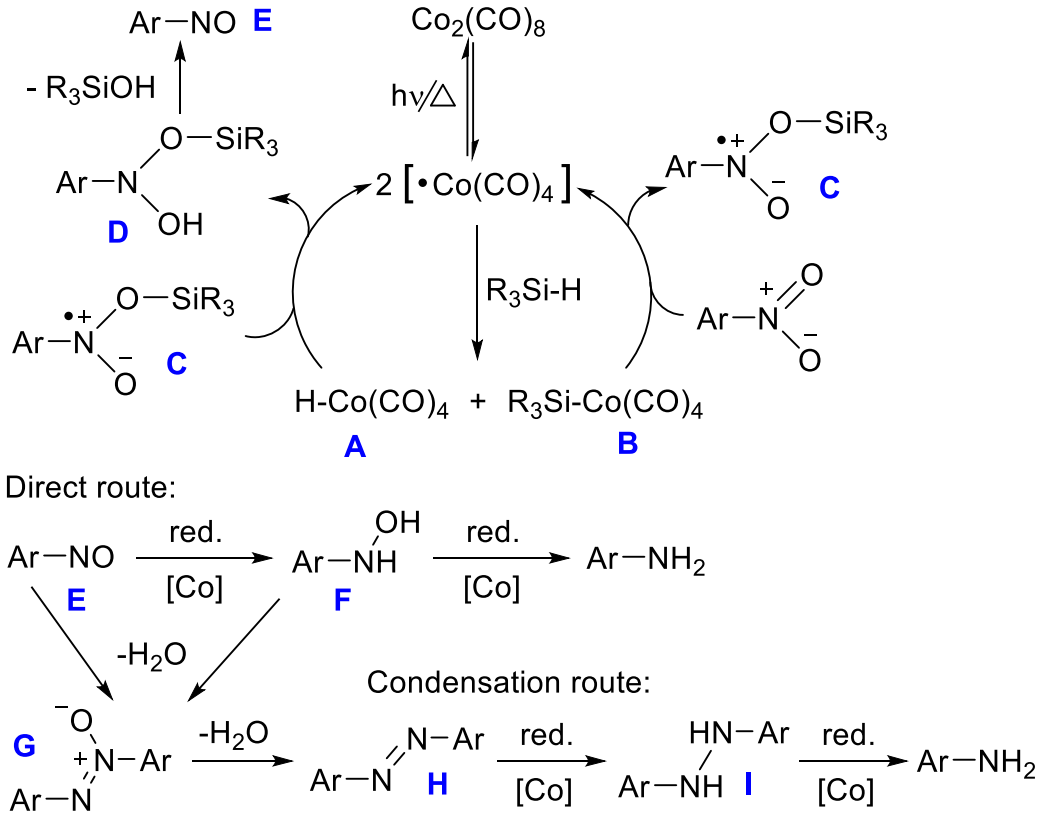


Figure S95. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **C** in $CDCl_3$ at r.t.

Mechanistic study:

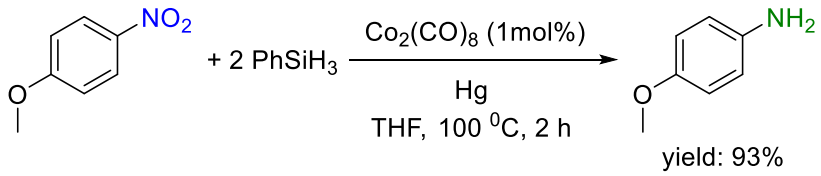
Plausible reaction mechanism:



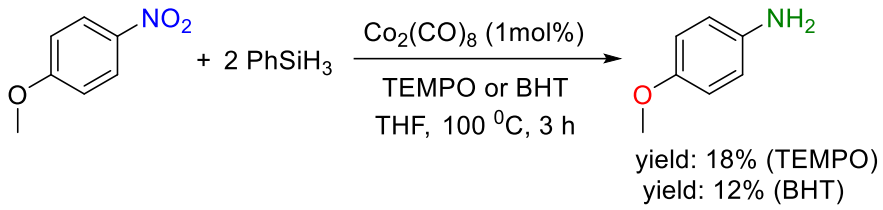
Proposed reaction pathway: A plausible catalytic pathway involves the homoleptic cleavage of the metal-metal bond in $Co_2(CO)_8$ under photochemical or thermal reaction condition to generate two 17-electron radical species $(CO)_4Co^{\bullet}$. Thereafter, two $(CO)_4Co^{\bullet}$ species react with phenyl silane to give highly reactive tetracarbonyl cobalt hydride (**A**) and tetracarbonyl(silyl) cobalt(I) (**B**) intermediate. It is believed that tetracarbonyl cobalt hydride species will decomposes to give hydrogen and dicobalt octacarbonyl in absence of any substrate[S16]. However, in presence of nitroarene, tetracarbonyl(silyl) cobalt(I) (**B**) reacts with nitroarene and leads to the formation of **C** and regenerate one $(CO)_4Co^{\bullet}$. Thereafter, tetracarbonyl cobalt hydride (**A**) reacts with **C** to produce Ar-N($OSiR_3$)OH (**D**) and regenerate another $(CO)_4Co^{\bullet}$. Finally, elimination of silanol results in the formation of nitrosoarene (**E**). At this stage, there are two available pathways towards the formation of the corresponding aromatic amine from nitrosoarene.[S4] The direct route involves the stepwise reduction of nitrosoarene to N-hydroxylamine (**F**) and finally aromatic amine. The condensation route involvess the formation of azoxyarene (**G**) by the condensation of arylnitroso and N-hydroxylamine. Azoxyarene forms azo compound (**H**) which further reduce to amine through hydrazine intermediate (**I**).

Control Experiments:

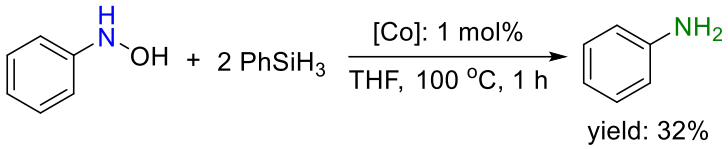
a) Mercury drop test:



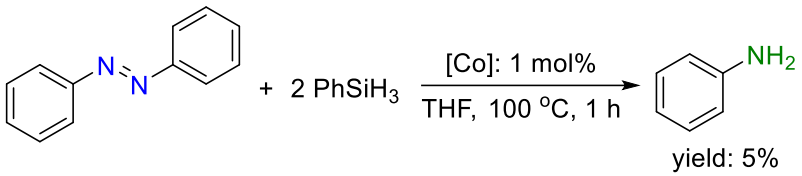
b) Radical trapping test:



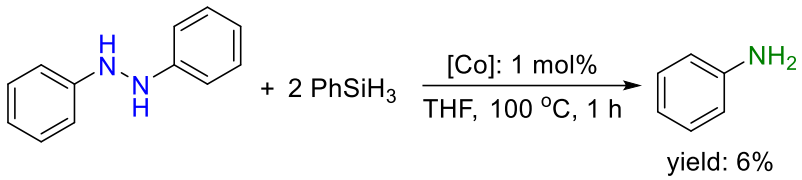
c) Catalytic hydrosilylation of N-hydroxyaniline:



d) Catalytic hydrosilylation of diazobenzene:



e) Catalytic hydrosilylation of 1,2-diphenylhydrazine:



Proposed reaction pathway supported by control experiments: At first, the homogeneity of this catalytic hydrosilylation was established through the mercury drop experiment where the nitroarene was successfully reduced to the corresponding aromatic amine (equation-a in the above scheme). Thereafter, the catalytic hydrosilylation of nitroarene was carried out in presence of radical-scavengers such as TEMPO and BHT (equation-b in the above scheme). The progress of the reaction was hindered and very low yields of the corresponding aromatic amine were obtained, hence indicating a radical pathway is in action. Several experiments were conducted to identify the plausible intermediates. HRMS analysis of the reaction mixture revealed the presence of the diazoarene intermediate [HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}N_2O_2$, 243.1134; found, 243.1177], however, we were unable to detect the presence of the N-hydroxylamine intermediate. This advocates that the reaction might proceed through condensation route. However, Rueping *et al.* previously suggested the direct route for

manganese catalysed catalytic hydrogenation of nitroarenes. To obtain more clarity, we performed the catalytic hydrosilylation of N-hydroxyaniline, diazobenzene and 1,2-diphenylhydrazine. While hydrosilylation of N-Phenylhydorxylamine gave corresponding amine in 32% yield, the hydrosilylation of diazobenzene and 1,2-diphenylhydrazine produced roughly 5% of yield of amine. This clearly suggets that direct route is the favourable path for this cobalt carbonyl catalyzed hydrosilylation of nitroarene; however, the condensation route cannot be ruled out.

Procedure for control experiments:

Mercury drop test: In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1 mol%), *p*-nitroanisole (0.077 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol), mercury (100 eq) and THF (2mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at 100 °C in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and *p*-xylene (0.053 g, 0.5 mmol) was added to the resultant mixture. The mixture was filtered and the filtrate was analyzed by GC to determine the conversion of the nitroarene to the amine.

Radical trapping test: In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1 mol%), *p*-nitroanisole (0.077 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol,), TEMPO (0.078 g, 0.5 mmol) or BHT (0.110 g, 0.5 mmol) and THF (2mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at 100 °C in a preheated oil bath for 3 h. After cooling to r.t., MeOH (1 mL) and *p*-xylene (0.053 g, 0.5 mmol) was added to the resultant mixture. The mixture was then analyzed by GC to determine the conversion of the nitroarene to the amine.

Catalytic hydrosilylation of N-hydroxyaniline: In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1.7 mg, 1 mol%), N-hydroxyaniline (0.054 g, 0.5 mmol) (0.077 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol and THF (2mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at 100 °C in a preheated oil bath for 1 h. After cooling to r.t., MeOH (1 mL) and *p*-xylene (0.053 g, 0.5 mmol) as standard was added to the resultant mixture. The mixture was then analyzed by GC to determine the conversion of the nitroarene to the amine.

Catalytic hydrosilylation of diazobenzene: In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1.7 mg, 1 mol%), diazobenzene (0.091 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol and THF (2mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at 100 °C in a preheated oil bath for 1 h. After cooling to r.t., MeOH (1 mL) and *p*-xylene (0.053 g, 0.5 mmol) as standard was added to the resultant mixture. The mixture was then analyzed by GC to determine the conversion of the nitroarene to the amine.

Catalytic hydrosilylation of 1,2-diphenylhydrazine: In a dried pressure tube fitted with a magnetic stir bar, $Co_2(CO)_8$ (1.7 mg, 1 mol%), 1,2-diphenylhydrazine (0.092 g, 0.5 mmol), phenylsilane (0.109 g, 1.05 mmol and THF (2mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at 100 °C in a preheated oil bath for 1 h. After cooling to r.t., MeOH (1 mL) and *p*-xylene (0.053 g, 0.5 mmol) as standard was added to the resultant mixture. The mixture was then analyzed by GC to determine the conversion of the nitroarene to the amine.

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