Electronic Supporting Information

For

Mimicking Transition Metals in Borrowing Hydrogen from Alcohol

Ananya Banik, Jasimuddin Ahmed, Swagata Sil and Swadhin K. Mandal*

Department of Chemical Sciences, Indian Institute of Science Education and Research-Kolkata, Mohanpur-741246, India. E-mail: swadhin.mandal@iiserkol.ac.in

Contents

1. Materials and methods.

Different phenalenyl (PLY) ligands were prepared following the reported literature procedure.[S1-S3] All solvents were distilled from Na/benzophenone or calcium hydride prior to use. All chemicals were purchased and used as received unless otherwise mentioned. Liquid anilines were distilled under vacuum before using in catalytic reactions. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on 400 and 500 MHz spectrometers in $CDCl_3$ with residual undeuterated solvent ($CDCl_3$, 7.26/77.0) as an internal standard. All chemical shifts (δ) are given in ppm using tetramethylsilane as a reference, and J values are given in Hz. Chemical shifts (δ) downfield from the reference standard were assigned positive values. Column chromatography and thin layer chromatography (TLC) were performed on silica gel (Merck silica gel 100-200 mesh). Potassium tert-butoxide was purchased from Sigma-Aldrich. High-resolution mass spectrometry (HRMS) was obtained on a Bruker maXis impact.

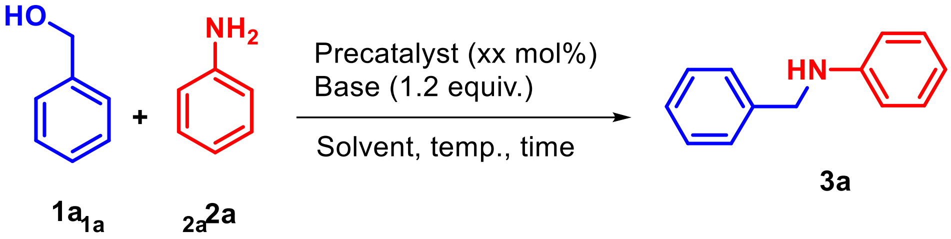
2. Synthesis of (^{Mes}N,O)-PLY.

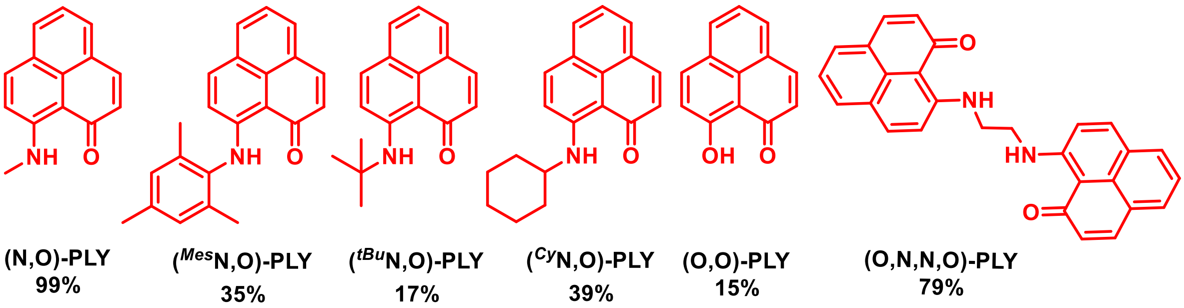
The synthesis of (^{Mes}N,O)-PLY was accomplished by the treatment of 9-methoxy-1H-phenalen-1-one (2g, 10.2 mmol) with one equiv. of 2,4,6-trimethylaniline (1.45 mL, 10.2 mmol) in 1,2-dichloroethane under reflux condition (100 ^{o}C) for 24 h. After completion of reaction, the solvent was evaporated under vacuum and reaction mixture was purified by column chromatography with neutral alumina by 25% DCM in hexane. Analytically pure orange compound was obtained in 55% yield (1.75 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 13.23 (s, 1H), 7.93-7.85 (m, 4H), 7.46 (t, 1H, J = 8.0 Hz), 7.07 (d, 1H, J = 9.6 Hz), 7.02 (s, 2H), 6.73 (d, 1H, J = 9.6 Hz), 2.36 (s, 3H), 2.19 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 184.9, 155.7, 138.7, 138.2, 137.2, 135.7, 133.0, 131.7, 131.3, 129.3, 128.8, 128.4, 125.2, 124.9, 121.9, 115.7, 108.1, 29.7, 20.9, 18.2 ppm; HRMS (TOF) calcd. for $C_{22}H_{20}NO$ $[M + H]^+$ 314.1545, found 314.1531.

3. Procedure for optimization of reaction condition for N-alkylation of aniline.

An oven dried 15 mL tube was charged with aniline, **1a** (0.3 mmol, 27.4 μL), benzyl alcohol, **2a** (0.33 mmol, 34.3 μL), different PLY ligands, and base along with 1.5 mL solvent inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. Subsequently, the reaction mixture was allowed to stir at different temperatures for different times. After completion of the reaction, internal standard, 1,4-dimethoxybenzene was added to the crude reaction mixture and passed through celite using 25 mL ethyl acetate (EtOAc) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and yields were determined from ^{1}H NMR spectroscopy. The desired product, N-benzylaniline was purified by column chromatography using neutral alumina and hexane/EtOAc mixture as eluent.

Table S1. Optimization of the reaction conditions for the N-alkylation of amine.



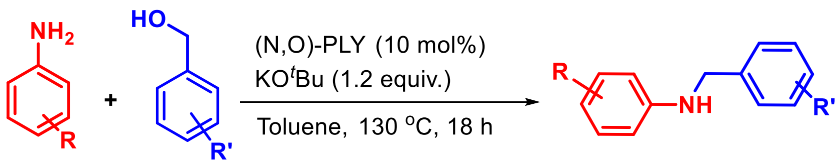


Entry	Precatalyst	Precatalyst loading (mol%)	Temp. (°C)	Base (equivalents)	Solvent	Time (h)	NMR Yield (%)
1	(N,O)-PLY	5	130	KO^{t}Bu (1.2)	Toluene	18	43
2	(N,O)-PLY	7.5	130	KO^{t}Bu (1.2)	Toluene	18	75
3	**(N,O)-PLY**	**10**	**130**	**KO^{t}Bu (1.2)**	**Toluene**	**18**	**99 (91)[a]**
4	(^{cy}N,O)-PLY	10	130	KO^{t}Bu (1.2)	Toluene	18	39
5	(^{tBu}N,O)-PLY	10	130	KO^{t}Bu (1.2)	Toluene	18	17
6	(^{Mes}N,O)-PLY	10	130	KO^{t}Bu (1.2)	Toluene	18	35
7	(O,O)-PLY	10	130	KO^{t}Bu (1.2)	Toluene	18	15
8	(O,N,N,O)-PLY	10	130	KO^{t}Bu (1.2)	Toluene	18	79
9	(N,O)-PLY	10	100	KO^{t}Bu (1.2)	Toluene	18	17
10	(N,O)-PLY	10	80	KO^{t}Bu (1.2)	Toluene	18	NR
11	(N,O)-PLY	10	130	KO^{t}Bu (1.0)	Toluene	18	73

12	(N,O)-PLY	10	130	NaO^{t}Bu (1.2)	Toluene	18	NR
14	(N,O)-PLY	10	130	LiO^{t}Bu (1.2)	Toluene	18	36
15	(N,O)-PLY	10	130	KO^{t}Bu (1.2)	THF	18	15
16	(N,O)-PLY	10	130	KO^{t}Bu (1.2)	ACN	18	NR
17	(N,O)-PLY	10	130	KO^{t}Bu (1.2)	Toluene	8	23
18	(N,O)-PLY	10	130	KO^{t}Bu (1.2)	Toluene	12	35
19	(N,O)-PLY	10	130	KO^{t}Bu (1.2)	Toluene	16	77
20	-	-	130	KO^{t}Bu (1.2)	Toluene	18	5
21	(N,O)-PLY	10	130	-	Toluene	18	NR

The reactions were carried out using aniline (0.3 mmol), benzyl alcohol (0.33 mmol), different precatalyst (xx mol%), base (xx equivalents), and solvent (1.5 mL). Parenthesis in entry 3 denotes as isolated yield. NR = No reaction.

4. General procedure for the N-alkylation of amines.

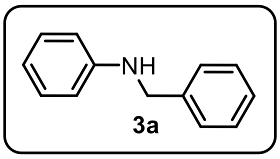


Scheme S1. N-alkylation of amines catalyzed by (N,O)-PLY.

An oven dried 15 mL tube was charged with amines, **1a-u** (0.3 mmol, 1 equiv.), alcohols, **2a-o** (0.33 mmol, 1.1 equiv.), (N,O)-PLY (6.3 mg, 0.03 mmol, 10 mol%), and KO^{t}Bu (40.4 mg, 0.36 mmol, 1.2 equivalents) along with 1.5 mL toluene inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. Then reaction mixture was stirred at 130 °C for 18 h. After completion of the reaction, the crude reaction mixture was passed through celite using 25 mL ethyl acetate (EtOAc) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using neutral alumina and hexane/EtOAc mixture as eluent to yield the pure desired product which was characterized by NMR spectroscopy. The isolated yield mentioned are average yield of two runs.

5. The analytical and spectral characterization data of N-alkylated amines.

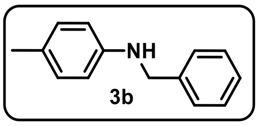
N-benzylaniline (3a):[S4, S5]



Yellow oil, yield = 91%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.39-7.32 (m, 4H), 7.28 (d, 1H, *J* = 6.8 Hz), 7.19-7.15 (m, 2H), 6.72 (t, 1H, *J* = 7.6 Hz), 6.64 (d, 2H, *J* = 7.6 Hz), 4.34 (s, 2H), 4.05 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 148.1, 139.4, 129.2, 128.6, 127.5, 127.2, 117.5, 114.8, 48.3 ppm.

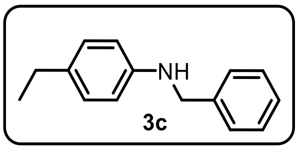
N-benzyl-4-methylaniline (3b):[S4]



Yellow oil, yield = 77%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.38-7.28 (m, 5H), 6.98 (d, 2H, *J* = 8 Hz), 6.56 (d, 2H, *J* = 8.4 Hz), 4.31 (s, 2H), 3.90 (brs, 1H), 2.24 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 145.9, 139.7, 129.7, 128.6, 127.5, 127.1, 126.8, 113.0, 48.7, 20.4 ppm.

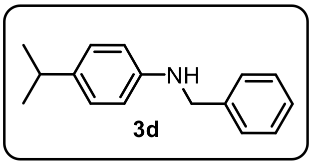
N-benzyl-4-ethylaniline (3c):[S6]



Yellow oil, yield = 75%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.39-7.32 (m, 4H), 7.28 (d, 1H, *J* = 7.2 Hz), 7.01 (d, 2H, *J* = 8.4 Hz), 6.59 (d, 2H, *J* = 8.4 Hz), 4.32 (s, 2H), 3.93 (brs, 1H), 2.54 (q, 2H, *J* = 7.6 Hz), 1.19 (t, 3H, *J* = 7.2 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 146.1, 139.7, 133.4, 128.6, 128.5, 127.5, 127.1, 112.9, 48.7, 27.9, 15.9 ppm.

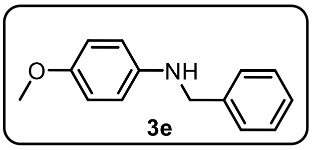
N-benzyl-4-isopropylaniline (3d):[S7]



Yellow oil, yield = 81%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.40-7.33 (m, 4H), 7.30-7.28 (m, 1H), 7.05 (d, 2H, J = 8.4 Hz), 6.60 (d, 2H, J = 8.4 Hz), 4.32 (s, 2H), 3.92 (brs, 1H), 2.81 (sept, 1H, J = 6.8 Hz), 1.21 (d, 6H, J = 7.2 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 146.2, 139.7, 138.1, 128.6, 127.5, 127.1, 127.1, 112.9, 48.7, 33.1, 24.2 ppm.

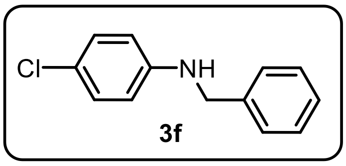
N-benzyl-4-methoxyaniline (3e):[S4]



Yellow solid, yield = 77%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.38-7.33 (m, 4H), 7.27 (d, 1H, J = 5.5 Hz), 6.78 (d, 2H, J = 8.5 Hz), 6.61 (d, 2H, J = 8.5 Hz), 4.29 (s, 2H), 3.74 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 152.3, 142.3, 139.6, 128.6, 127.6, 127.2, 114.9, 114.2, 55.8, 49.3 ppm.

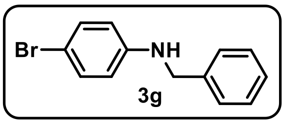
N-benzyl-4-chloroaniline (3f):[S4]



Yellow oil, yield = 71%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.35-7.34 (m, 5H), 7.11 (d, 2H, J = 8.5 Hz), 6.56 (d, 2H, J = 8.5 Hz), 4.35 (brs, 1H), 4.31 (s, 2H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 146.3, 138.7, 129.1, 128.7, 127.5, 127.4, 122.5, 114.2, 48.6 ppm.

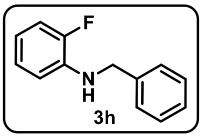
N-benzyl-4-bromoaniline (3g):[S4]



Yellow oil, yield = 74%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.38-7.28 (m, 7H), 6.53 (d, 2H, J = 8.5 Hz), 4.33 (s, 2H), 4.12 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 147.1, 138.8, 131.9, 129.2, 128.7, 127.4, 114.4, 109.1, 48.2 ppm.

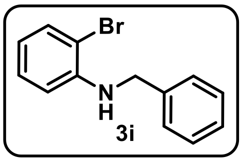
N-benzyl-2-fluoroaniline (3h):[S5]



Yellow oil, yield = 73%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.40-7.34 (m, 4H), 7.30-7.29 (m, 1H), 7.00-6.94 (m, 2H), 6.70-6.60 (m, 2H), 4.38 (s, 2H), 4.34 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 151.5 (d, J = 236.8 Hz), 138.9, 136.6 (d, J = 14 Hz), 128.7, 127.4, 127.3, 124.5 (d, J = 6 Hz), 116.8 (d, J = 6.8 Hz), 114.3 (d, J = 18.2 Hz), 112.3 (d, J = 3.2 Hz), 47.9 ppm. ^{19}F NMR ($CDCl_3$, 470 MHz, 298 K): δ -136.56 ppm.

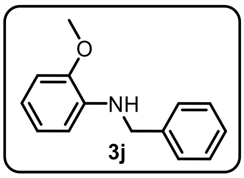
N-benzyl-2-bromoaniline (3i):[S8]



Yellow oil, yield = 73%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.39-7.28 (m, 4H), 7.20-7.16 (m, 2H), 6.73 (t, 1H, J = 7.2 Hz), 6.65 (d, 2H, J = 8 Hz), 4.34 (s, 2H), 4.03 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 148.1, 139.4, 129.2, 128.6, 127.5, 127.2, 117.6, 112.8, 48.3 ppm.

N-benzyl-2-methoxyaniline (3j):[S8]

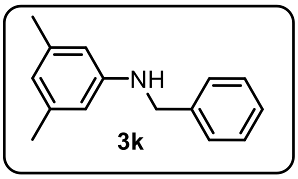


Yellow oil, yield = 71%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.39 (d, 2H, J = 7.5 Hz), 7.34 (t, 2H, J = 7.5 Hz), 7.27 (d, 1H, J = 7 Hz), 6.84 (t, 1H, J = 7.5 Hz), 6.79 (d, 1H, J = 6.5 Hz), 6.68 (t, 1H, J = 8 Hz), 6.60 (d, 1H, J = 7.5

Hz), 4.64 (brs, 1H), 4.34 (s, 2H), 3.85 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 146.8, 139.6, 138.1, 128.6, 127.5, 127.1, 121.3, 116.6, 110.1, 109.4, 55.4, 48.0 ppm.

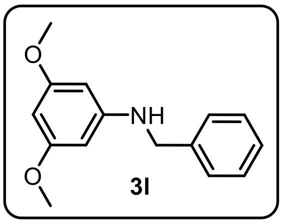
N-benzyl-3,5-dimethylaniline (3k):[S6]



Yellow oil, yield = 82%; purified by column chromatography using 2% EtOAc in hexane.

^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.38-7.33 (m, 5H), 6.39 (s, 1H), 6.29 (s, 2H), 4.31 (s, 2H), 2.90 (brs, 1H), 2.23 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 148.3, 139.7, 138.9, 128.6, 127.5, 127.1, 119.6, 110.8, 48.4, 21.5 ppm.

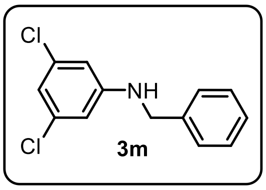
N-benzyl-3,5-dimethoxylaniline (3l):[S9]



Yellow oil, yield = 63%; purified by column chromatography using 2% EtOAc in hexane.

^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.37-7.32 (m, 4H), 7.27 (d, 1H, J = 7 Hz), 5.89 (s, 1H), 5.84 (s, 2H), 4.30 (s, 2H), 4.13 (brs, 1H), 3.73 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 161.7, 150.1, 139.3, 128.6, 127.5, 127.3, 91.6, 89.9, 55.1, 48.4 ppm.

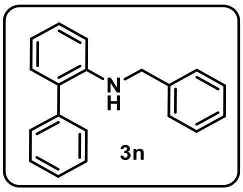
N-benzyl-3,5-dichloroaniline (3m):[S10]



Yellow oil, yield = 76%; purified by column chromatography using 2% EtOAc in hexane.

^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.41-7.30 (m, 5H), 6.67 (s, 1H), 6.48 (s, 2H), 4.28 (s, 2H), 4.19 (brs, 1H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 298 K): δ 149.7, 135.5, 128.8, 127.6, 127.4, 117.3, 110.9, 47.9 ppm.

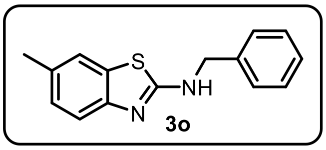
N-benzyl-[1,1'-biphenyl]-2-amine (3n):[S9]



Yellow solid, yield = 73%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.49-7.43 (m, 4H), 7.37-7.35 (m, 1H), 7.32 (d, 4H, *J* = 4.4 Hz), 7.28-7.24 (m, 1H), 7.20 (td, 1H, *J* = 8 Hz, 1.6 Hz), 7.12 (dd, 1H, *J* = 7.6 Hz, 1.6 Hz), 6.79 (td, 1H, *J* = 7.2 Hz, 0.8 Hz), 6.67 (d, 1H, *J* = 8.8 Hz), 4.35 (s, 2H), 4.35 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 144.9, 139.6, 130.3, 129.5, 129.0, 128.8, 128.7, 128.4, 127.8, 127.3, 127.1, 117.3, 110.8, 48.2 ppm.

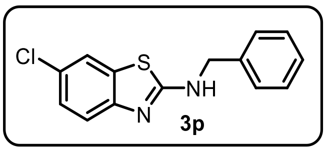
N-benzyl-6-methylbenzothiazol-2-amine (3o):[S11]



Yellow solid, yield = 65%; purified by column chromatography using 10% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.43 (d, 1H, *J* = 8.0 Hz), 7.40-7.35 (m, 5H), 7.32-7.29 (m, 1H), 7.11 (dd, 1H, *J* = 8 Hz, 8 Hz), 5.53 (brs, 1H), 4.63 (s, 2H), 2.39 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 166.5, 150.2, 137.6, 131.5, 130.6, 128.8, 127.8, 127.7, 127.1, 120.9, 118.7, 49.3, 21.2 ppm.

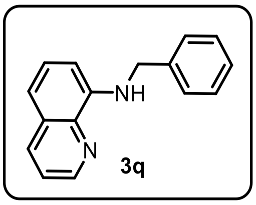
N-benzyl-6-chlorobenzothiazol-2-amine (3p):[S11]



White solid, yield = 67%; purified by column chromatography using 10% EtOAc in hexane.

^{1}H NMR (DMSO-d_6, 500 MHz, 298 K): δ 8.60 (t, 1H, *J* = 5.5 Hz), 7.79 (d, 1H, *J* = 1.5 Hz), 7.38-7.33 (m, 4H), 7.23-7.21 (m, 2H), 4.58 (d, 2H, *J* = 5 Hz) ppm. ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz, 298 K): δ 166.8, 151.3, 138.6, 132.1, 128.4, 127.4, 127.1, 125.6, 124.6, 120.6, 118.9, 47.2 ppm.

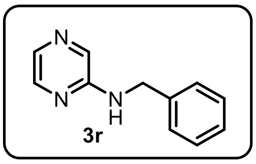
N-benzylquinolin-8-amine (3q):[S12]



Yellow oil, yield = 83%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.73 (dd, 1H, *J* = 4 Hz, 1.2 Hz), 8.34 (dd, 1H, *J* = 8.4 Hz, 1.6 Hz), 7.45 (d, 2H, *J* = 7.2 Hz), 7.40-7.32 (m, 4H), 7.29-7.28 (m, 1H), 7.06 (dd, 1H, *J* = 8 Hz, 0.8 Hz), 6.65 (dd, 1H, *J* = 8 Hz, 0.8 Hz), 6.61 (brs, 1H), 4.57 (d, 2H, *J* = 5.2 Hz) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 298 K): δ 146.9, 144.6, 139.2, 138.4, 136.0, 128.6, 127.7, 127.4, 127.1, 121.4, 114.1, 105.1, 47.7 ppm.

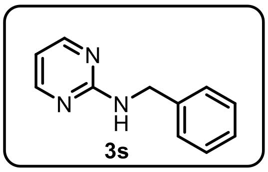
N-benzylpyrazin-2-amine (3r):[S8]



Yellow solid, yield = 85%; purified by column chromatography using 10% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.99-7.98 (m, 1H), 7.88 (d, 1H, *J* = 1 Hz), 7.81 (d, 1H, *J* = 2.5 Hz), 7.34 (d, 4H, *J* = 4 Hz), 7.30-7.27 (m, 1H), 5.03 (brs, 1H), 4.55 (d, 2H, *J* = 6 Hz) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 154.4, 141.9, 138.4, 133.1, 132.0, 128.7, 127.5, 127.5, 45.5 ppm.

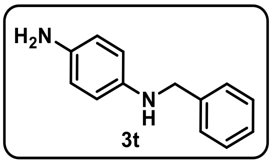
N-benzylpyrimidin-2-amine (3s):[S8]



Yellow solid, yield = 82%; purified by column chromatography using 25% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.25 (d, 2H, *J* = 4.5 Hz), 7.34-7.29 (m, 4H), 7.25-7.23 (m, 1H), 6.52 (t, 1H, *J* = 4.5 Hz), 5.55 (brs, 1H), 4.62 (d, 2H, *J* = 6 Hz) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 162.3, 158.1, 139.1, 128.6, 127.4, 127.2, 110.9, 45.4 ppm.

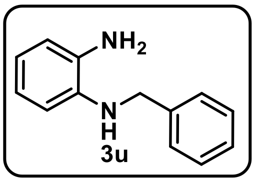
N-benzylbenzene-1,4-diamine (3t):[S13]



Brown oil, yield = 86%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.38-7.31 (m, 4H), 7.28-7.24 (m, 1H), 6.63- 6.59 (m, 2H), 6.56-6.53 (m, 2H), 4.26 (s, 2H), 3.43 (brs, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 141.4, 139.9, 137.8, 128.5, 127.6, 127.1, 116.9, 114.5, 49.4 ppm.

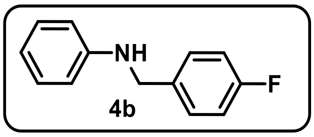
N-benzylbenzene-1,2-diamine (3u):[S14]



Brown oil, yield = 87%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.43-7.36 (m, 4H), 7.31 (t, 1H, J = 7 Hz), 6.84 (t, 1H, J = 7 Hz), 6.77- 6.70 (m, 3H), 4.34 (s, 2H), 3.47 (brs, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 139.4, 137.7, 134.1, 128.6, 127.7, 127.2, 120.7, 118.8, 115.5, 112.0, 48.6 ppm.

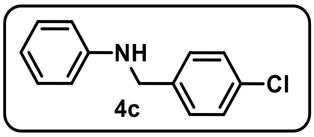
N-(4-fluorobenzyl)aniline (4b):[S5]



Yellow oil, yield = 87%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.35-7.32 (m, 2H), 7.19-7.15 (m, 2H), 7.02 (t, 2H, J = 8.8 Hz), 6.72 (t, 1H, J = 7.2 Hz), 6.62 (d, 2H, J = 7.6 Hz), 4.30 (s, 2H), 4.03 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 162.0 (d, J = 243.8 Hz), 147.9, 135.0, 129.3, 129.0 (d, J = 7.7 Hz), 117.7, 115.4 (d, J = 21.3 Hz), 112.9, 47.6 ppm. ^{19}F NMR ($CDCl_3$, 470 MHz, 298 K): δ -115.7 ppm.

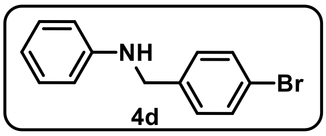
N-(4-chlorobenzyl)aniline (4c):[S4]



Yellow oil, yield = 79%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.39-7.37 (m, 3H), 7.35-7.30 (m, 1H), 7.18 (t, 2H, J = 7.6 Hz), 6.72 (t, 1H, J = 7.6 Hz), 6.34 (d, 2H, J = 8 Hz), 4.34 (s, 2H), 4.03 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 148.2, 139.4, 129.2, 128.6, 127.5, 127.2, 117.6, 112.8, 48.3 ppm.

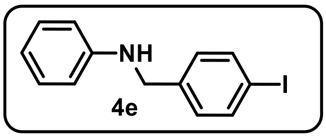
N-(4-bromobenzyl)aniline (4d):[S5]



Yellow oil, yield = 78%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.38-7.33 (m, 3H), 7.28 (d, 1H, J = 7 Hz), 7.17 (t, 2H, J = 8.5 Hz), 6.72 (t, 1H, J = 7 Hz), 6.64 (d, 2H, J = 8 Hz), 4.33 (s, 2H), 4.04 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 148.2, 139.4, 129.2, 128.6, 127.5, 127.2, 117.6, 112.8, 48.3 ppm.

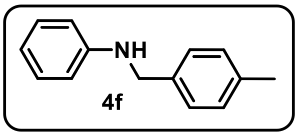
N-(4-iodobenzyl)aniline (4e):[S15]



Green oil, yield = 76%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.39-7.33 (m, 3H), 7.29 (d, 1H, J = 7 Hz), 7.18 (t, 2H, J = 8.5 Hz), 6.72 (t, 1H, J = 7.5 Hz), 6.65 (d, 2H, J = 7.5 Hz), 4.34 (s, 2H), 4.03 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 148.1, 139.4, 129.2, 128.6, 127.5, 127.2, 117.5, 112.8, 48.3 ppm.

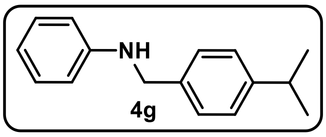
N-(4-methylbenzyl)aniline (4f):[S4]



Yellow solid, yield = 55%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.26-7.24 (m, 2H), 7.19-7.13 (m, 4H), 6.73 (t, 1H, J = 7.2 Hz), 6.65 (d, 2H, J = 8.4 Hz), 4.29 (s, 2H), 4.00 (brs, 1H), 2.34 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 147.9, 136.9, 136.1, 129.3, 129.2, 127.6, 117.7, 113.1, 48.2, 21.1 ppm.

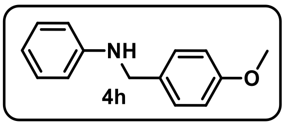
N-(4-isopropylbenzyl)aniline (4g):[S4]



Colorless oil, yield = 73%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.30 (d, 2H, J = 8 Hz), 7.22-7.16 (m, 4H), 6.71 (t, 1H, J = 7.2 Hz), 6.65 (d, 2H, J = 8.0 Hz), 4.29 (s, 2H), 3.98 (brs, 1H), 2.91 (sept, 1H, J = 6.8 Hz), 1.25 (d, 6H, J = 7.2) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 148.3, 148.0, 136.7, 129.3, 127.7, 126.7, 117.5, 112.8, 48.2, 33.9, 24.1 ppm.

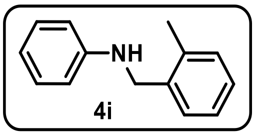
N-(4-methoxybenzyl)aniline (4h):[S4]



Yellow oil, yield = 70%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.29 (d, 2H, J = 7.5 Hz), 7.18 (t, 2H, J = 7.5 Hz), 6.88 (d, 2H, J = 7.5 Hz), 6.71 (t, 1H, J = 7 Hz), 6.64 (d, 2H, J = 8 Hz), 4.26 (s, 2H), 3.95 (brs, 1H), 3.81 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 158.9, 148.2, 131.4, 129.2, 128.8, 117.5, 114.0, 112.8, 55.3, 47.8 ppm.

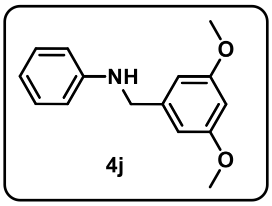
N-(2-methylbenzyl)aniline (4i):[S4]



Yellow oil, yield = 53%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.34 (d, 1H, J = 6.8 Hz), 7.22-7.16 (m, 5H), 6.73 (t, 1H, J = 7.2 Hz), 6.64 (dd, 2H, J = 8.4 Hz, 1.2 Hz), 4.28 (s, 2H), 3.85 (brs, 1H), 2.38 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 298 K): δ 148.3, 136.9, 136.3, 130.4, 129.3, 128.3, 127.4, 126.1, 117.4, 112.6, 46.4, 18.9 ppm.

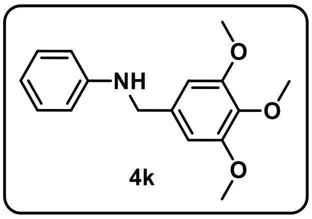
N-(3,5-dimethoxybenzyl)aniline (4j):[S16]



Yellow oil, yield = 70%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.18 (t, 2H, J = 8 Hz), 6.72 (t, 1H, J = 7.2 Hz), 6.63 (d, 2H, J = 8 Hz), 6.55 (s, 2H), 6.38 (s, 1H), 4.27 (s, 2H), 4.04 (brs, 1H), 3.78 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 161.1, 148.1, 142.0, 129.2, 117.6, 112.9, 105.3, 99.1, 55.3, 48.5 ppm.

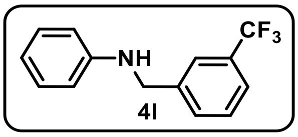
N-(3,4,5-trimethoxybenzyl)aniline (4k):[S17]



Yellow oil, yield = 62%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.19 (t, 2H, J = 8.4 Hz), 6.73 (t, 1H, J = 7.6 Hz), 6.65 (d, 2H, J = 7.6 Hz), 6.61 (s, 2H), 4.26 (s, 2H), 4.02 (brs, 1H), 3.84 (s, 9H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 153.4, 148.2, 137.0, 135.2, 129.3, 117.8, 112.9, 104.4, 60.8, 56.1, 48.3 ppm.

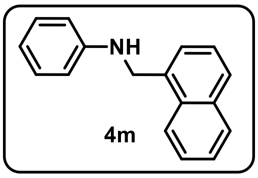
N-(3-(trifluoromethyl)benzyl)aniline (4l):[S18]



Yellow oil, yield = 78%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.65 (s, 1H), 7.57 (d, 1H, J = 7.5 Hz), 7.54 (d, 1H, J = 7.5 Hz), 7.46 (t, 1 H, J = 8.0 Hz), 7.19 (t, 2H, J = 7 Hz), 6.75 (t, 1H, J = 7.5 Hz), 6.63 (d, 2H, J = 8.5 Hz), 4.41 (s, 2H), 4.11 (brs, 1H) ppm.^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 147.7, 140.6, 131.0 (q, J = 32 Hz), 130.6, 129.3, 129.1, 124.1 (q, J = 270.5 Hz), 124.0 (q, J = 2.5 Hz), 118.0, 112.9, 47.9 ppm. ^{19}F NMR ($CDCl_3$, 470 MHz, 298 K): δ -62.6 ppm.

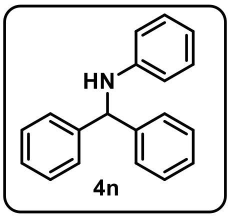
N-(naphthalen-1-ylmethyl)aniline (4m):[S4]



White solid, yield = 87%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.11-8.10 (m, 1H), 7.94-7.91 (m, 1H), 7.84 (d, 1H, J = 8.4 Hz), 7.56-7.52 (m, 3H), 7.45 (t, 1H, J = 8 Hz), 7.24 (t, 2H, J = 8 Hz), 6.79 (t, 1H, J = 7.6 Hz), 6.71 (d, 2H, J = 8 Hz), 4.75 (s, 2H), 4.00 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 148.2, 134.3, 133.8, 131.5, 129.3, 128.7, 128.1, 126.3, 126.0, 125.8, 125.5, 123.5, 117.5, 112.7, 46.8 ppm.

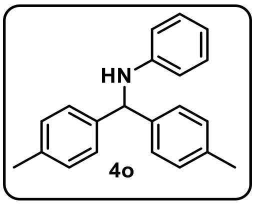
N-benzhydrylaniline (4n):[S19]



Colorless oil, yield = 89%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.39-7.32 (m, 8H), 7.29-7.25 (m, 2H), 7.13 (t, 2H, J = 8 Hz), 6.71 (t, 1H, J = 7.6 Hz), 6.56 (dd, 2H, J = 8.4 Hz, 0.8 Hz), 5.51 (s, 1H), 4.24 (brs, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 147.4, 142.9, 129.1, 128.7, 127.4, 127.3, 117.6, 113.5, 63.0 ppm.

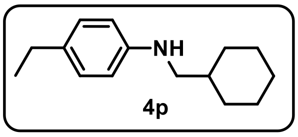
N-(di-p-tolylmethyl)aniline (4o):[S19]



White solid, yield = 85%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.26-7.24 (m, 4H), 7.14-7.10 (m, 6H), 6.69 (t, 1H, J = 7.2 Hz), 6.55 (d, 2H, J = 7.6 Hz), 5.45 (s, 1H), 4.22 (brs, 1H), 2.34 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 147.4, 140.2, 136.8, 129.4, 129.0, 127.2, 117.4, 113.4, 62.4, 21.0 ppm.

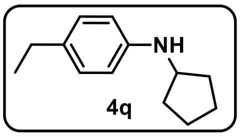
N-(cyclohexylmethyl)-4-ethylaniline (4p):



Yellow oil, yield = 71%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.00 (d, 2H, J = 8.4 Hz), 6.54 (d, 2H, J = 8.4 Hz), 3.59 (brs, 1H), 2.93 (d, 2H, J = 6.8 Hz), 2.53 (q, 2H, J = 7.6 Hz), 1.83-1.79 (m, 2H), 1.76-1.72 (m, 3H), 1.63-1.52 (m, 1H), 1.29-1.23 (m, 3H), 1.19 (t, 3H, J = 7.6 Hz), 0.97 (qd, 2H, J = 12 Hz, 3.2 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 146.7, 132.7, 128.5, 112.7, 50.9, 37.6, 31.3, 27.9, 26.6, 25.9, 15.9 ppm. HRMS (TOF) calcd. for $C_{15}H_{24}N$ $[M + H]^+$ 218.1909, found 218.1911.

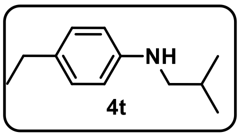
N-cyclopentyl-4-ethylaniline (4q):



Colourless oil, yield = 83%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.00 (d, 2H, J = 8.4 Hz), 6.55 (d, 2H, J = 8.4 Hz), 3.79-3.73 (m, 1H), 3.52 (brs, 1H), 2.53 (q, 2H, J = 7.6 Hz), 2.03-1.98 (m, 2H), 1.76-1.70 (m, 2H), 1.63-1.58 (m, 2H), 1.48-1.43 (m, 2H), 1.19 (t, 3H, J = 8.0 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 146.0, 132.8, 128.5, 113.3, 54.9, 33.6, 27.8, 24.1, 15.9 ppm. HRMS (TOF) calcd. for $C_{13}H_{20}N$ $[M + H]^+$ 190.1596, found 190.1587.

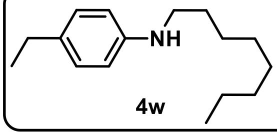
4-ethyl-N-isobutylaniline (4t):[S20]



Colourless oil, yield = 64%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.01 (d, 2H, J = 8.4 Hz), 6.55 (d, 2H, J = 8.4 Hz), 3.85 (brs, 1H), 2.91 (d, 2H, J = 6.8 Hz), 2.54 (q, 2H, J = 7.6 Hz), 1.89-1.86 (m, 1H), 1.19 (t, 3H, J = 7.6 Hz), 0.98 (d, 6H, J = 6.8 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 146.5, 132.8, 128.5, 112.8, 52.1, 28.0, 27.9, 20.5, 15.9 ppm.

4-ethyl-N-octylaniline (4w):

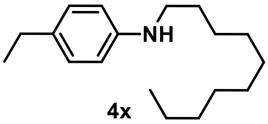


4w

Colourless oil, yield = 92%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.01 (d, 2H, J = 8.4 Hz), 6.56 (d, 2H, J = 8.4 Hz), 3.47 (brs, 1H), 3.09 (t, 2H, J = 7.2 Hz), 2.54 (q, 2H, J = 7.6 Hz), 1.63-1.59 (m, 2H), 1.39-1.29 (m, 10H), 1.19 (t, 3H, J = 8.0 Hz), 0.91-0.88 (m, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 146.5, 132.9, 128.5, 112.8, 44.3, 31.8, 29.6, 29.4, 29.2, 27.9, 27.2, 22.6, 15.9, 14.1 ppm. HRMS (TOF) calcd. for $C_{16}H_{28}N$ $[M + H]^+$ 234.2222, found 234.2233.

N-decyl-4-ethylaniline (4x):

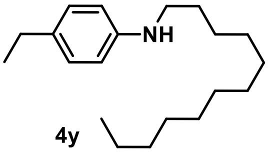


4x

Colourless oil, yield = 65%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.01 (d, 2H, J = 8.4 Hz), 6.55 (d, 2H, J = 8.4 Hz), 3.47 (brs, 1H), 3.08 (t, 2H, J = 7.2 Hz), 2.54 (q, 2H, J = 7.6 Hz), 1.64-1.59 (m, 2H), 1.31-1.27 (m, 14H), 1.19 (t, 3H, J = 8.0 Hz), 0.90-0.86 (m, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 146.5, 132.9, 128.5, 112.8, 44.3, 31.8, 29.6, 29.5, 29.3, 27.9, 27.1, 22.6, 15.9, 14.1 ppm. HRMS (TOF) calcd. for $C_{18}H_{32}N$ $[M + H]^+$ 262.2535, found 262.2551.

N-dodecyl-4-ethylaniline (4y):

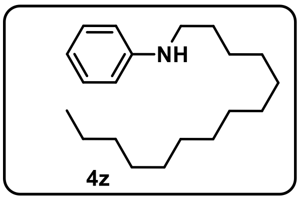


4y

Colourless oil, yield = 87%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.00 (d, 2H, J = 8.0 Hz), 6.55 (d, 2H, J = 8.4 Hz), 3.47 (brs, 1H), 3.08 (t, 2H, J = 7.2 Hz), 2.53 (q, 2H, J = 7.6 Hz), 1.64-1.58 (m, 2H), 1.30-1.26 (m, 18H), 1.19 (t, 3H, J = 8.0 Hz), 0.90-0.87 (m, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 146.5, 132.9, 128.5, 112.8, 44.3, 31.9, 29.6, 29.5, 29.3, 29.2, 27.9, 27.2, 22.6, 15.9, 14.1 ppm. HRMS (TOF) calcd. for $C_{20}H_{36}N$ $[M + H]^+$ 290.2848, found 290.2863.

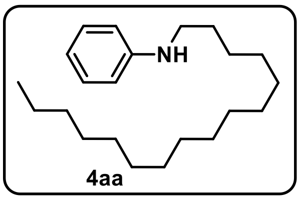
N-tetradecylaniline (4z):



Colourless oil, yield = 84%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.16 (t, 2H, J = 8.0 Hz), 6.68 (t, 1H, J = 7.2 Hz), 6.60 (d, 2H, J = 8.4 Hz), 3.59 (brs, 1H), 3.09 (t, 2H, J = 7.2 Hz), 1.63-1.60 (m, 2H), 1.41-1.22 (m, 22H), 0.89-0.86 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 148.5, 129.2, 117.0, 112.6, 43.9, 31.9, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 27.2, 22.6, 14.1 ppm. HRMS (TOF) calcd. for $C_{20}H_{36}N$ $[M + H]^+$ 290.2848, found 290.2821.

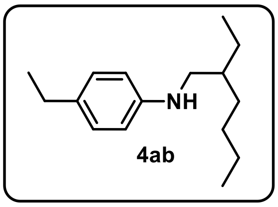
N-hexadecylaniline (4aa):



Colourless oil, yield = 83%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.16 (t, 2H, J = 8.5 Hz), 6.68 (t, 1H, J = 7.5 Hz), 6.60 (d, 2H, J = 7.5 Hz), 3.58 (brs, 1H), 3.09 (t, 2H, J = 7.5 Hz), 1.63-1.60 (m, 2H), 1.31-1.26 (m, 26H), 0.89-0.87 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 148.6, 129.2, 117.0, 112.7, 44.0, 31.9, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 27.1, 22.6, 14.1 ppm. HRMS (TOF) calcd. for $C_{22}H_{40}N$ $[M + H]^+$ 318.3161, found 318.3159.

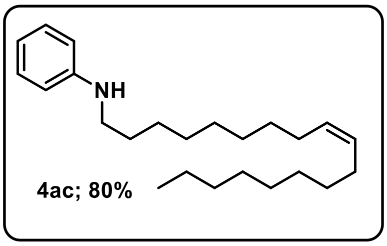
4-ethyl-N-(2-ethylhexyl)aniline (4ab):



Colourless oil, yield = 79%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.00 (d, 2H, J = 8.4 Hz), 6.55 (d, 2H, J = 8.4 Hz), 3.49 (brs, 1H), 3.00 (d, 2H, J = 7.6 Hz), 2.53 (q, 2H, J = 7.6 Hz), 1.58-1.54 (m, 1H), 1.41-1.33 (m, 8H), 1.19 (t, 3H, J = 8.0 Hz), 0.93-0.89 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ 146.7, 132.7, 128.5, 112.7, 47.3, 39.1, 31.3, 28.9, 27.9, 24.5, 23.1, 15.9, 14.0, 10.9 ppm. HRMS (TOF) calcd. for $C_{16}H_{28}N$ [M + H]$^+$ 234.2222, found 234.2240.

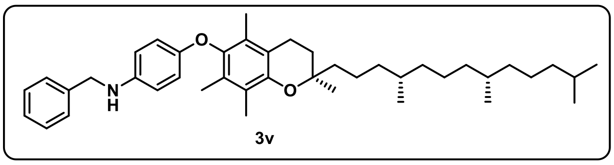
(Z)-N-(octadec-9-en-1-yl)aniline (4ac):



Colourless oil, yield = 80%; purified by column chromatography using 1% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.16 (t, 2H, *J* = 8.0 Hz), 6.68 (t, 1H, *J* = 7.6 Hz), 6.59 (d, 2H, *J* = 8.0 Hz), 5.36-5.33 (m, 2H), 3.59 (brs, 1H), 3.09 (t, 2H, *J* = 7.6 Hz), 2.02-1.99 (m, 4H), 1.65-1.58 (m, 2H), 1.30-1.27 (m, 22H), 0.89-0.86 (m, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 148.5, 129.9, 129.8, 129.2, 117.0, 112.6, 43.9, 32.6, 31.9, 29.7, 29.5, 29.4, 29.3, 29.2, 27.2, 25.9, 22.6, 14.1 ppm. HRMS (TOF) calcd. for $C_{24}H_{42}N$ [M + H]$^+$ 344.3317, found 344.3318.

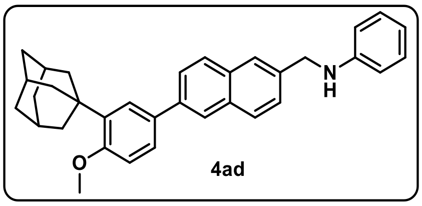
N-benzyl-4-(((R)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)aniline (3v):[S4]



Yellow oil, yield = 69%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.38-7.32 (m, 4H), 7.27 (d, 1H, *J* = 6.8 Hz), 6.57 (dd, 4H, *J* = 12.8, 8.8 Hz), 4.25 (s, 2H), 3.66 (brs, 1H), 2.59 (t, 2H, *J* = 6.8 Hz), 2.10 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.86-1.76 (m, 2H), 1.64-1.49 (m, 4H), 1.43-1.37 (m, 4H), 1.31-1.26 (m, 10H), 1.17-1.05 (m, 6H), 0.88-0.84 (m, 12H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 151.5, 148.5, 144.0, 142.4, 139.7, 128.6, 128.4, 127.6, 127.2, 126.5, 123.1, 117.7, 115.3, 114.0, 74.9, 49.4, 39.4, 37.6, 37.5, 37.4, 37.4, 37.3, 32.8, 32.7, 32.6, 28.0, 24.8, 24.4, 23.9, 22.7, 22.6, 19.7, 19.7, 19.6, 12.9, 12.0, 11.8 ppm.

N-((6-(3-((1s,3s)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)methyl)aniline (4ad):



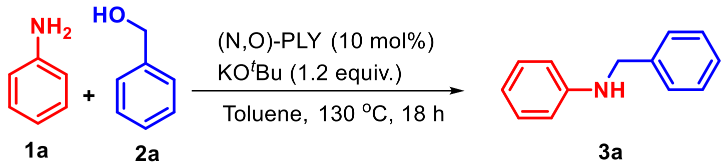
White solid, yield = 72%; purified by column chromatography using 5% EtOAc in hexane.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.99 (s, 1H), 7.89-7.83 (m, 3H), 7.74 (d, 1H, J =8.5 Hz), 7.60 (s, 1H), 7.55-7.50 (m, 2H), 7.20 (t, 2H, J = 7.5 Hz), 7.00 (d, 1H, J = 8.5 Hz), 6.74 (t, 1H, J = 7.5 Hz), 6.70 (d, 2H, J = 8 Hz), 4.51 (s, 2H), 4.15 (brs, 1H), 3.91 (s, 3H), 2.21 (s, 6H), 2.12 (s, 3H), 1.82 (s, 6H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 298 K): δ 158.6, 148.2, 138.8, 136.6, 133.1, 132.3, 129.3, 128.5, 128.1, 126.0, 126.0, 125.9, 125.6, 125.5, 124.8, 117.6, 112.9, 112.1, 55.1, 48.5, 40.6, 37.1, 29.1, 22.6 ppm. HRMS (TOF) calcd. for $C_{34}H_{36}NO$ [M + H]$^+$ 474.2797, found 474.2764.

6. Control experiments for mechanistic investigation.

To prove the mechanistic course for the alkylation of amines though transition metal free hydrogen borrowing, we performed several control experiments.

a. Investigating the radical nature for alkylation of aniline.

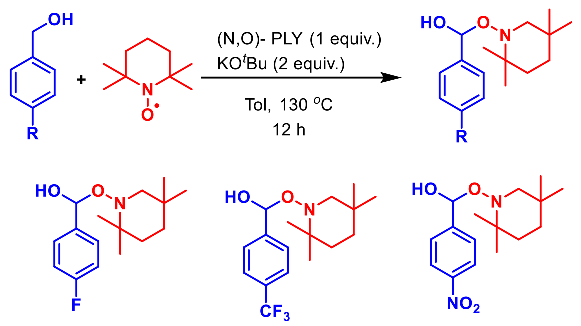


Additive	Amount	Yield
Galvinoxyl	1 equiv.	trace
TEMPO	2 equiv.	trace

Scheme S2. Inhibition of alkylation of aniline in presence of radical scavenger.

To evaluate whether the alkylation of amines proceeds through a radical pathway or not, we performed the reaction in presence of a radical scavenger (TEMPO, or galvinoxyl free radical). An oven dried 15 mL tube was charged with aniline, **1a** (27.4 µL, 0.3 mmol), benzyl alcohol, **2a** (34.3 µL, 0.33 mmol), (N,O)-PLY (6.3 mg, 0.03 mmol, 10 mol%), KO^{t}Bu (40.4 mg, 0.36 mmol, 1.2 equivalents), and TEMPO (93.6 mg, 0.6 mmol) or galvinoxyl, free radical (126.5 mg, 0.3 mmol) along with 1.5 mL toluene inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. Then the reaction mixture was allowed to stir at 130 °C for 18 h. Next, the reaction was terminated after 18 h and cooled down, then passed through a celite bed using 25 mL ethyl acetate (EtOAc) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the NMR yields were determined from ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as internal standard. In ^{1}H NMR spectroscopy, trace amount (<5%) of N-benzylaniline was observed. This reaction suggests that either 1 equiv. of galvinoxyl, free radical or 2 equiv. of TEMPO are sufficient to quench the reaction.

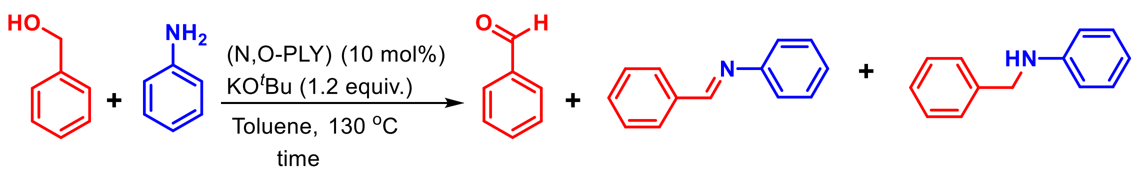
b. Ketyl radical trapping experiment *via* TEMPO adducts formation.



Scheme S3. Trapping of ketyl radical intermediate with TEMPO.

After confirming the radical mediated process is operating for N-alkylation reaction, we probed substituted benzyl alcohol to trap the ketyl radical *via* formation of TEMPO adduct. An oven dried 15 mL tube was charged with different benzyl alcohol (0.1 mmol), (N,O)-PLY (21.0 mg, 0.1 mmol), KO^{t}Bu (22.4 mg, 0.2 mmol), and TEMPO (31.2 mg, 0.2 mmol) along with 1.5 mL toluene inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. The reaction was carried out for 12h at 130 °C and cooled down. Next, the crude reaction mixture was characterized through GC-MS or HRMS spectrometry in acetonitrile (see below, figures S107-S109) and the corresponding mass of TEMPO trapped ketyl radicals were found.

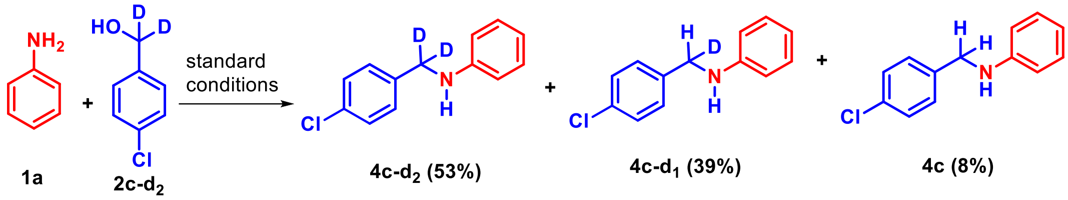
c. Time dependent *in situ* generation of intermediates.



Scheme S4. Evolution of aldehyde and imine with time.

To check the generation of intermediates with time, several time dependent NMR studies were carried out. An oven dried 15 mL tube was charged with aniline, **1a** (27.4 µL, 0.3 mmol), benzyl alcohol, **2a** (34.3 µL, 0.33 mmol), (N,O)-PLY (6.3 mg, 0.03 mmol, 10 mol%), and KO^{t}Bu (40.4 mg, 0.36 mmol, 1.2 equivalents) along with 1.5 mL toluene inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. Then the reaction mixture was allowed to stir at 130 °C for different duration. After quenching the reaction at different time interval and the crude reaction mixture was passed through celite using 25 mL ethyl acetate (EtOAc) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the yields of the *in situ* generated intermediates were determined from ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as internal standard (see below, Fig. S110). The formation of *in situ* generated intermediates such as benzaldehyde and N-benzylideneaniline clearly suggests that the reaction proceeds through borrowing hydrogen methodology.

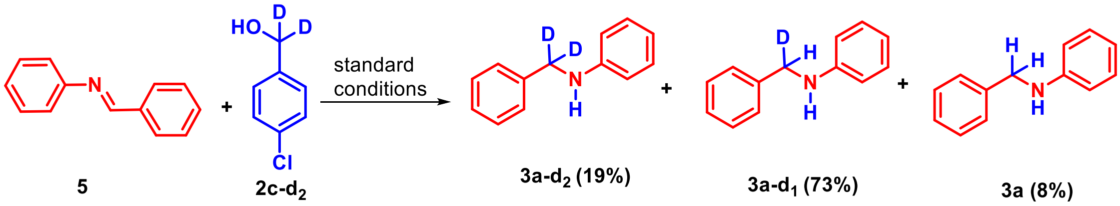
d. Deuterium labelling experiment with aniline and deuterated benzyl alcohol.



Scheme S5. Deuterium labelling experiment with aniline and deuterated benzyl alcohol.

The deuterated 4-chlorobenylalcohol **(2c-d$_2$)** was prepared by following literature methods[S22]. An oven dried 15 mL tube was charged with aniline, **1a** (27.4 μL, 0.3 mmol), 4-chlorobenzylalcohol-d$_2$**, 2c-d$_2$** (47.7 mg, 0.33 mmol), (N,O)-PLY (6.3 mg, 0.03 mmol, 10 mol%), and KO^{t}Bu (40.4 mg, 0.36 mmol, 1.2 equivalents) along with 1.5 mL toluene inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. Then the reaction mixture was allowed to stir at 130 ^{o}C for 18 h. After completion of the reaction, the crude reaction mixture was passed through celite bed using 25 mL ethyl acetate (EtOAc) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using neutral alumina and hexane/EtOAc mixture as eluent. The mixture of products was characterized through ^{1}H NMR spectroscopy and HRMS (TOF) spectrometry (see below, Fig. S111 and S112). Such observation reassures the source of hydrogen in this reaction is benzyl alcohol. However, the ratio of these three isotopomers **4c**:**4c-d$_1$**:**4c-d$_2$** (1.0:4.9:6.6), suggests the proton-deuterium scrambling during the reaction which has been observed with metal mediated alkylation of amines in borrowing hydrogen mechanism[S4].

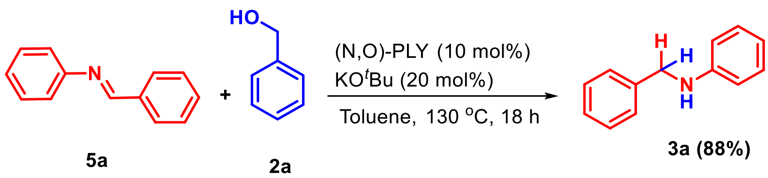
e. Deuterium labelling experiment with imine and deuterated benzyl alcohol.



Scheme S6. Deuterium labelling experiment with N-benzylideneaniline and deuterated benzyl alcohol.

The deuterated 4-chlorobenylalcohol**, 2c-d$_2$** and N-benzylideneaniline, **5a** were prepared by following literature methods[S21-S22]. An oven dried 15 mL tube was charged with N-benzylideneaniline, **5a** (54.4 mg, 0.3 mmol), 4-chlorobenylalcohol**, 2c-d$_2$** (47.7 mg, 0.33 mmol), (N,O)-PLY (6.3 mg, 0.03 mmol, 10 mol%), and KO^{t}Bu (40.4 mg, 0.36 mmol, 1.2 equivalents) along with 1.5 mL toluene inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. Then the reaction mixture was allowed to stir at 130 ºC for 18 h. After completion of the reaction, the crude reaction mixture was passed through celite using 25 mL ethyl acetate (EtOAc) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using neutral alumina and hexane/EtOAc mixture as eluent. The mixture of products was characterized through ^{1}H NMR spectroscopy and HRMS (TOF) spectrometry (see below, Fig. S113 and S114). In this case, deuterium enriched **3a-d$_1$** was obtained in higher ratio as the major isomer [**3a**:**3a-d$_1$**:**3a-d$_2$** (1.0:9.1:2.4)] along with very less amount of **3a** and **3a-d$_2$**. Such observation is in contrast with traditional borrowing hydrogen methods.

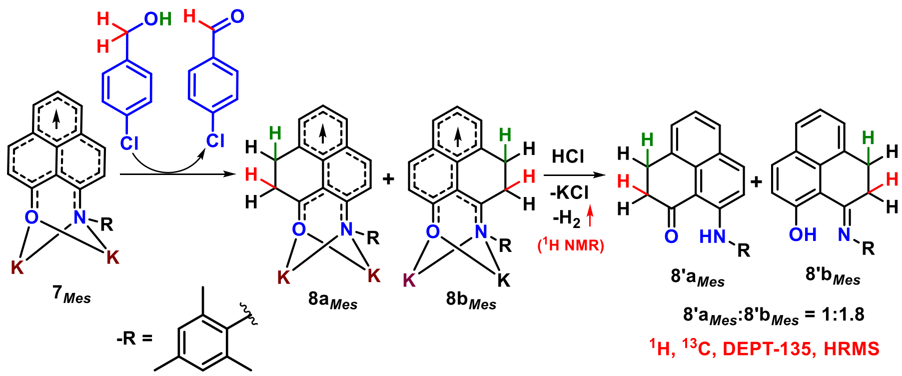
f. Reduction of imine by alcohol with catalytic amount of base.



Scheme S7. Reduction of imine by borrowed hydrogen from benzyl alcohol.

An oven dried 15 mL tube was charged with N-benzylideneaniline, **5a** (47.7 mg, 0.3 mmol), benzyl alcohol**, 2a** (34.3 μL, 0.33 mmol), (N,O)-PLY (6.3 mg, 0.03 mmol, 10 mol%), and KO^{t}Bu (6.7 mg, 0.06 mmol, 20 mol%) along with 1.5 mL toluene inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. Then reaction mixture was allowed to stir at 130 ºC for 18 h. After completion of the reaction, the crude reaction mixture was passed through celite bed using 25 mL ethyl acetate (EtOAc) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using neutral alumina and hexane/EtOAc mixture as eluent. This study unarguably suggests that catalytic amount of base, KO^{t}Bu was required to reduce the *in situ* generated imine, whereas 1.2 equivalent of base, KO^{t}Bu is needed for catalytic N-alkylation of amine.

g. Synthesis of dearomatized $((^{Mes}N,O)$-PLY**, 8′a*Mes*** and **8′b*Mes***):



Scheme S8. Leaching of the intermediates (**8a*Mes*** and **8b*Mes***) by HCl.

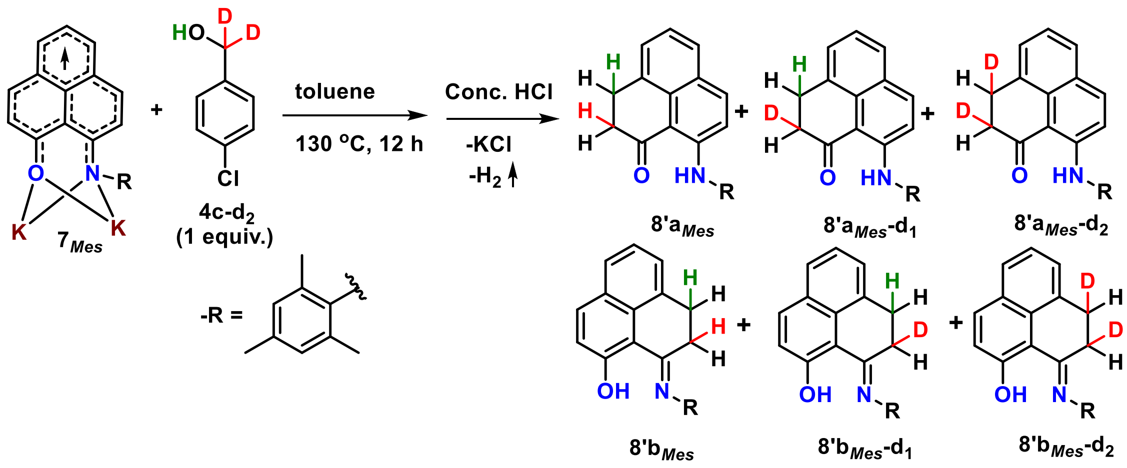
To assess whether the hydrogen atom is stored in the redox active ligand (PLY) backbone from alcohol or not, we have performed the stoichiometric reaction of mono-reduced **PLY-K** complex, **7*Mes*** with 4-chlorobenzyl alcohol. An oven dried 15 mL tube was charged with $(^{Mes}N,O)$-PLY (31.4 mg, 0.1 mmol), and KO^{t}Bu (22.4 mg, 0.2 mmol, 20 mol%) along with 1.5 mL toluene inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. Then reaction mixture was allowed to stir at 130 ^{o}C for 6 h and a sharp color change from orange to wine red was observed. After 6 hours, the reaction mixture was cooled down and the 4-chloro benzyl alcohol (14.2 mg, 0.1 mmol) was added inside a nitrogen filled glovebox. Again, the reaction mixture was stirred at 130 ^{o}C for another 8 h. After completion of the reaction, 1.0 mL of 12 (M) aqueous HCl was added dropwise to the reaction mixture and stirred at room temperature for 1 h and the crude organic product was extracted in Et_2O. The solvent was removed under reduced pressure and the dearomatized PLY (**8′a*Mes*** and **8′b*Mes***) was isolated through column chromatography using hexane: EtOAc mixture as eluent (10:1). Upon successful isolation, the oily product was characterized through NMR spectroscopy, and mass spectrometry (HRMS) (see below, Fig. S117-S122). This study indicates that the active catalyst dearomatizes to store the incoming hydrogen molecule as C-H bond.

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 15.90 (s, OH from **8′b*Mes***), 13.29 (s, NH from **8′a*Mes***), 7.89-7.85 (m), 7.63 (d, J = 7 Hz), 7.47 (d, J = 5.5 Hz), 7.35-7.24 (m), 7.05 (s), 7.00 (s), 6.81-6.76 (m, 1H), 4.28-4.17 (m, newly formed aliphatic C-H proton), 3.11 (t, J = 7.5 Hz, newly formed aliphatic C-H proton), 2.64 (t, J = 7.5 Hz, newly formed aliphatic C-H proton), 2.40–2.37 (m), 2.23–2.17 (m) ppm. The integration of protons could not be assigned as the peaks from two isomers merge in ^{1}H NMR. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298K): δ 171.2, 168.4, 138.6, 138.0, 137.1, 136.6, 135.7, 135.6, 135.3, 133.1, 131.4, 131.2, 130.7, 130.3, 130.0, 129.7, 129.5, 129.3, 129.0, 128.8, 128.6, 128.5, 127.7, 127.2, 127.0, 126.7, 126.0, 125.7, 125.1, 124.6, 122.8, 122.6, 122.0, 115.7, 107.6, 107.5, 35.7, 35.5, 27.5, 27.1, 21.0, 20.8, 18.3, 18.2 ppm.

DEPT-135 NMR (125 MHz, $CDCl_3$, 298K): δ 138.0, 136.6, 135.6, 131.2, 130.7, 130.3, 129.7, 129.3, 128.8, 128.6, 127.2, 127.0, 126.7, 125.7, 122.8, 122.6, 122.0, 115.7, 35.7, 35.5, 27.3, 27.1, 21.0, 20.8, 18.3, 18.2 ppm.

HRMS (TOF) calcd. for $C_{22}H_{22}NO$ $[M + H]^+$ 316.1701, found 316.1697.

h. Synthesis of deuterated dearomatized ((*^{Mes}*N,O)-PLY-d, 8′a*$_{Mes}$*-d and 8′b*$_{Mes}$*-d):



Scheme S9. Deuterium labelling experiment for the formation of dearomatized intermediates.

To assess whether the hydrogen atom is stored in the redox active ligand (PLY) backbone from alcohol or not, we have performed the deuterium labelling experiment for stoichiometric reaction of mono-reduced ***^{Mes}*PLY-K** complex, **7*$_{Mes}$*** with dideuterated 4-chloro benzyl alcohol, **2c-d$_2$**. An oven dried 15 mL tube was charged with (^{Mes}N,O)-PLY (31.4 mg, 0.1 mmol), and KO^{t}Bu (22.4 mg, 0.2 mmol) along with 1.5 mL toluene inside a nitrogen-filled glovebox and sealed prior to bring out from the glovebox. Then the reaction mixture was allowed to stir at 130 °C for 6 h and a colour change from orange to wine red was observed. After 6 hours, the reaction mixture was cooled down and the dideuterated 4-chloro benzyl alcohol**, 2c-d$_2$** (14.4 mg, 0.1 mmol) was added inside a nitrogen filled glove box. Again, the reaction mixture was stirred at 130 °C for 8 h. After completion of the reaction, 1.0 mL of 12 (M) aqueous HCl was added dropwise at 0 °C into the reaction mixture and stirred at room temperature for an additional 1 h and the crude organic product was extracted in Et_2O. The crude reaction mixture was passed through celite using 25 mL ethyl acetate (EtOAc) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the dearomatized PLY-d (**8′a*$_{Mes}$*-d** and **8′b*$_{Mes}$*-d**) was isolated through column chromatography using hexane: EtOAc mixture as eluent (10:1).

Upon successful isolation, the oily product was characterized through ^{1}H, ^{13}C, and ^{2}H NMR spectroscopy and mass spectrometry (HRMS) (see below, Fig. S123-S127).

^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 15.85 (s, OH from **8′b*$_{Mes}$***), 13.24 (s, NH from **8′a*$_{Mes}$***), 7.86-7.80 (m), 7.65-7.57 (m), 7.45-7.41 (m), 7.16-7.13 (m), 7.01 (s), 6.96 (s), 6.74-6.72 (m), 4.33-4.12 (m), 3.09-

3.06 (m), 2.61-2.59 (m), 2.36-2.33 (m), 2.19–2.12 (m) ppm. The integration of protons could not be assigned as the peaks from two isomers merge in ^{1}H NMR.
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298K): δ 171.7, 168.4, 138.6, 138.0, 137.1, 136.6, 135.7, 135.6, 135.3, 133.1, 131.4, 131.3, 130.5, 130.3, 130.0, 129.7, 129.4, 129.3, 129.2, 128.8, 128.6, 128.5, 127.8, 127.7, 127.2, 127.0, 126.8, 126.0, 125.7, 125.1, 124.6, 124.1, 122.8, 122.6, 122.0, 115.7, 107.7, 107.6, 34.6, 34.5, 27.3, 27.1 (t, $J_{c\text{-}D}$ = 20 Hz), 21.0, 20.8,18.3, 18.2 ppm.

DEPT-135 NMR (125 MHz, $CDCl_3$, 298K): δ 138.0, 136.6, 135.6, 131.3, 130.5, 130.3, 129.9, 129.7, 129.4, 129.3, 129.2, 129.0, 128.8, 128.5, 127.7, 127.2, 127.0, 126.8, 126.0, 125.7, 124.1, 122.6, 122.0, 115.7, 35.8, 35.7, 27.3, 27.1 (t, $J_{c\text{-}D}$ = 20 Hz), 21.0, 20.8, 18.3, 18.2 ppm.
^{2}H{^{1}H} NMR (76.8 MHz, CH_2Cl_2, 298K): 4.16, 3.06, 2.58 ppm.

HRMS (TOF) calcd. for $C_{22}H_{22}NO$ $[M+H]^+$ 316.1701, found 316.1709; $C_{22}H_{21}DNO$ $[M+H]^+$ 317.1764, found 317.1765; $C_{22}H_{21}D_2NO$ $[M+H]^+$ 318.1827, found 318.1820. Ratio obtained: 1:0.98:0.4.

Interesting to note that when deuterated 4-chloro benzyl alcohol, **2c-d$_3$** was charged in order to perform stoichiometric reaction with monoreduced **PLY-K** complex, **7$_{Mes}$**, the ratio of the dearomatized protonated and deuterated PLY was observed as **8′**:**8′-d$_1$**:**8′-d$_2$** = 1:1.78:1.26, characterized through HRMS spectrometry. HRMS (TOF) calcd. for $C_{22}H_{22}NO$ $[M+H]^+$ 316.1701, found 316.1688; $C_{22}H_{21}DNO$ $[M+H]^+$ 317.1764, found 317.1747; $C_{22}H_{22}D_2NO$ $[M+H]^+$ 318.1826, found 318.1862 (see below, Fig. S128).

Table S2. Relative intensity ratio of dearomatized (^{Mes}N,O)-PLY, (^{Mes}N,O)-PLY-d and (^{Mes}N,O)-PLY-d$_2$ obtained from HRMS.

Entry	**Alcohol**	**Leaching done by**	**8′$_{Mes}$**	**8′$_{Mes}$-d$_1$**	**8′$_{Mes}$-d$_2$**
1	4-Cl-C_6H_4-CH_2-OH	HCl	1	-	-
2	4-Cl-C_6H_4-CD_2-OH	HCl	1	0.98	0.4
3	4-Cl-C_6H_4-CD_2-OH	DCl	1	0.90	0.35
4	4-Cl-C_6H_4-CD_2-OD	HCl	1	1.78	1.26

Computational details.

Theoretical calculations were performed with the Gaussian16 program suite.[S23] All theoretical calculations were carried out using the density functional theory (DFT) method with m062x method[S24] employing the 6-31+g(d) basis set[S25] for all atoms for the geometry optimization for all molecules including transition states and intermediates. The single point energy calculations were for carried out m062x method[S24] with 6-31+g(d) basis set considering SMD solvent model in toluene.[S26]

<u>Main Path:</u>

Table S3: Energies, enthalpies, and free energies (in Hartree) of the optimized structures of all transition states and intermediates.

Structure	ZPE	ΔE	ΔH	ΔG	E	H	G	IF(cm^{-1})	Infrared
7	0.20331	0.21877	0.21971	0.15907	-1868.86475	-1868.86380	-1868.92444		
8	0.22618	0.24232	0.24327	0.18132	-1870.04389	-1870.04295	-1870.10490		
2	0.13463	0.14176	0.14270	0.10118	-346.49491	-346.49397	-346.53549		
TS1	0.33558	0.35816	0.35910	0.28231	-2215.36426	-2215.36331	-2215.44011	-208.85	805.035
7_{Int}	0.33741	0.36005	0.36099	0.28380	-2215.36132	-2215.36037	-2215.43757		
TS2	0.33655	0.35970	0.36065	0.28245	-2215.36418	-2215.36324	-2215.44144	-310.48	660.298
Int2h2-Ald	0.33913	0.36258	0.36352	0.28356	-2215.40910	-2215.40815	-2215.48811		
TS3	0.42820	0.45608	0.45703	0.36713	-2426.36006	-2426.35912	-2426.44901	-1460.95	2566.4833
9	0.43165	0.45857	0.45951	0.37410	-2426.38062	-2426.37968	-2426.46509		
TS4	0.42758	0.45494	0.45588	0.36734	-2426.37345	-2426.37251	-2426.46104	-1045.18	11425.5219

Int4Amin	0.43378	0.46161	0.46255	0.37231	-2426.41672	-2426.41577	-2426.50602		
2′	0.11115	0.11746	0.11840	0.08057	-345.32500	-345.32405	-345.36188		
5	0.20482	0.21506	0.21601	0.16771	-556.32035	-556.31940	-556.36770		
3	0.22916	0.24064	0.24158	0.19002	-557.50575	-557.50481	-557.55637		

Imine preparation:

Table S4: Energies, enthalpies, and free energies (in Hartree) of the optimized structures of all transition states and intermediates.

Structure	ZPE	ΔE	ΔH	ΔG	E	H	G	IF(cm^{-1})	Infrared
TS1i	0.21792	0.23156	0.23251	0.17466	-1232.01688	-1232.01594	-1232.07378	-26.78 -20.74	6.0170 6.5524
Int1i	0.22093	0.23337	0.23431	0.18006	-1232.02944	-1232.02850	-1232.08275		
TS2i	0.21633	0.23001	0.23096	0.17393	-1231.99259	-1231.99165	-1232.04867	-1759.72	3894.3093
AnilineK	0.10559	0.11203	0.11297	0.07411	-886.67636	-886.67542	-886.71428		
KOH	0.01062	0.01410	0.01505	-0.00655	-675.67897	-675.6780	-675.69964		

Path 1 (With hydride transfer):

Table S5: Energies, enthalpies, and free energies (in Hartree) of the optimized structures of all transition states and intermediates.

Structure	ZPE	ΔE	ΔH	ΔG	E	H	G	IF(cm^{-1})	Infrared
1	0.11822	0.12397	0.12491	0.08910	-287.36601	-287.36507	-287.40088		
2	0.13463	0.14176	0.14270	0.10118	-346.49491	-346.49397	-346.53549		
Benalo-K	0.12220	0.13078	0.13172	0.08628	-945.81936	-945.81842	-945.86386		

2′	0.11115	0.11746	0.11840	0.08057	-345.32500	-345.32405	-345.36188		
5	0.20482	0.21506	0.21601	0.16771	-556.32035	-556.31940	-556.36770		
6	0.20489	0.21859	0.21954	0.16379	-1268.97830	-1268.97736	-1269.03310		
Int1a	0.32813	0.35199	0.35294	0.27172	-2214.82527	-2214.82433	-2214.90554		
TS1a	0.32385	0.34701	0.34795	0.26845	-2214.79001	-2214.78906	-2214.86856	-937.02	11456.6660
Int2a	0.21502	0.23102	0.23197	0.17075	-1869.46619	-1869.46525	-1869.52647		
TS2a	0.41754	0.44538	0.44632	0.35624	-2425.77325	-2425.77231	-2425.86239	-1101.59	14253.6225
IntAmin	0.42169	0.44875	0.44969	0.36171	-2425.82063	-2425.81969	-2425.90767		
3	0.22916	0.24064	0.24158	0.19002	-557.50575	-557.50481	-557.55637		

Alternative path (With 'O' side):

Table S6: Energies, enthalpies, and free energies (in Hartree) of the optimized structures of all transition states and intermediates.

Structure	**ZPE**	**ΔE**	**ΔH**	**ΔG**	**E**	**H**	**G**	**IF(cm^{-1})**	**Infrared**
7	0.20331	0.21877	0.21971	0.15907	-1868.86475	-1868.86380	-1868.92444		
8O	0.22653	0.24252	0.24346	0.18196	-1870.04693	-1870.04599	-1870.10748		
2	0.13463	0.14176	0.14270	0.10118	-346.49491	-346.49397	-346.53549		
TS1O	0.33589	0.35965	0.36059	0.27832	-2215.35749	-2215.35655	-2215.43882	-156.56	445.8280
7_{Int}O	0.33764	0.36140	0.36235	0.28057	-2215.39352	-2215.39257	-2215.47435		

7$_{Int}$O′	0.33722	0.35885	0.35980	0.28686	-2215.36235	-2215.36140	-2215.43434		
TS2O	0.33576	0.35852	0.35946	0.28174	-2215.35625	-2215.35531	-2215.43303	-333.89	751.3655
Int2h2-Ald	0.33902	0.36334	0.36428	0.28113	-2215.39785	-2215.39691	-2215.48006		
TS3O	0.42735	0.45479	0.45573	0.36713	-2426.35194	-2426.35100	-2426.43961	-1339.01	2545.4819
9O	0.43165	0.45857	0.45951	0.37410	-2426.38062	-2426.37968	-2426.46509		
TS4O	0.42795	0.45615	0.45709	0.36567	-2426.36526	-2426.36432	-2426.45574	-524.41	6142.4133
Int4O	0.43378	0.46161	0.46255	0.37231	-2426.41672	-2426.41577	-2426.50602		
2	0.11115	0.11746	0.11840	0.08057	-345.32500	-345.32405	-345.36188		
5	0.20482	0.21506	0.21601	0.16771	-556.32035	-556.31940	-556.36770		
3	0.22916	0.24064	0.24158	0.19002	-557.50575	-557.50481	-557.55637		

NMR spectra of N-alkylated products.

Figure S1. ^{1}H NMR spectrum of N-benzylaniline (**3a**)[S4] in $CDCl_3$.

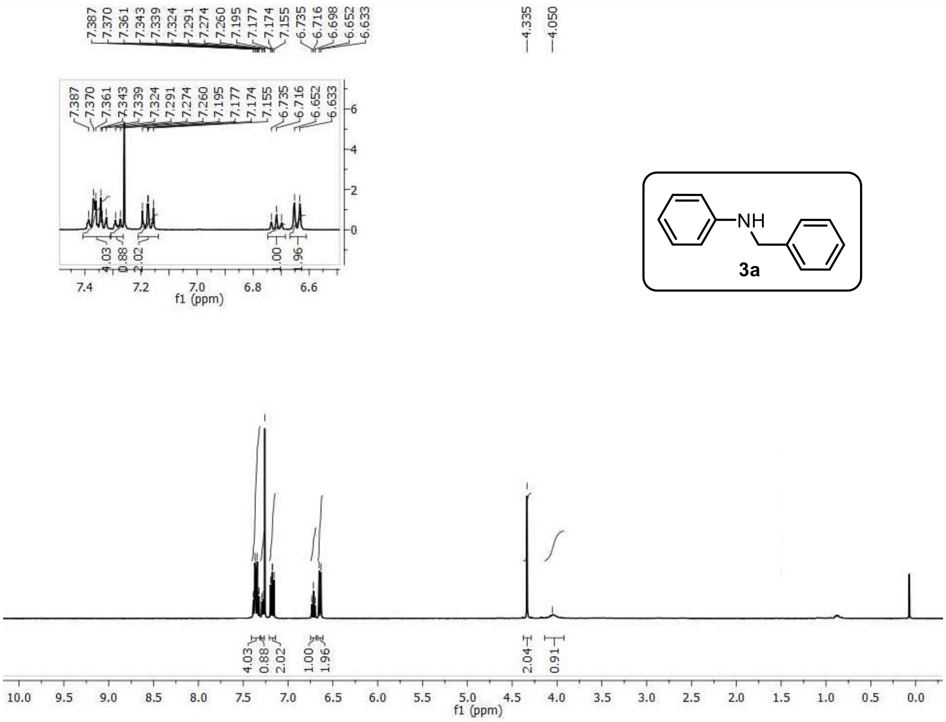


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzylaniline (**3a**)[S4] in $CDCl_3$.

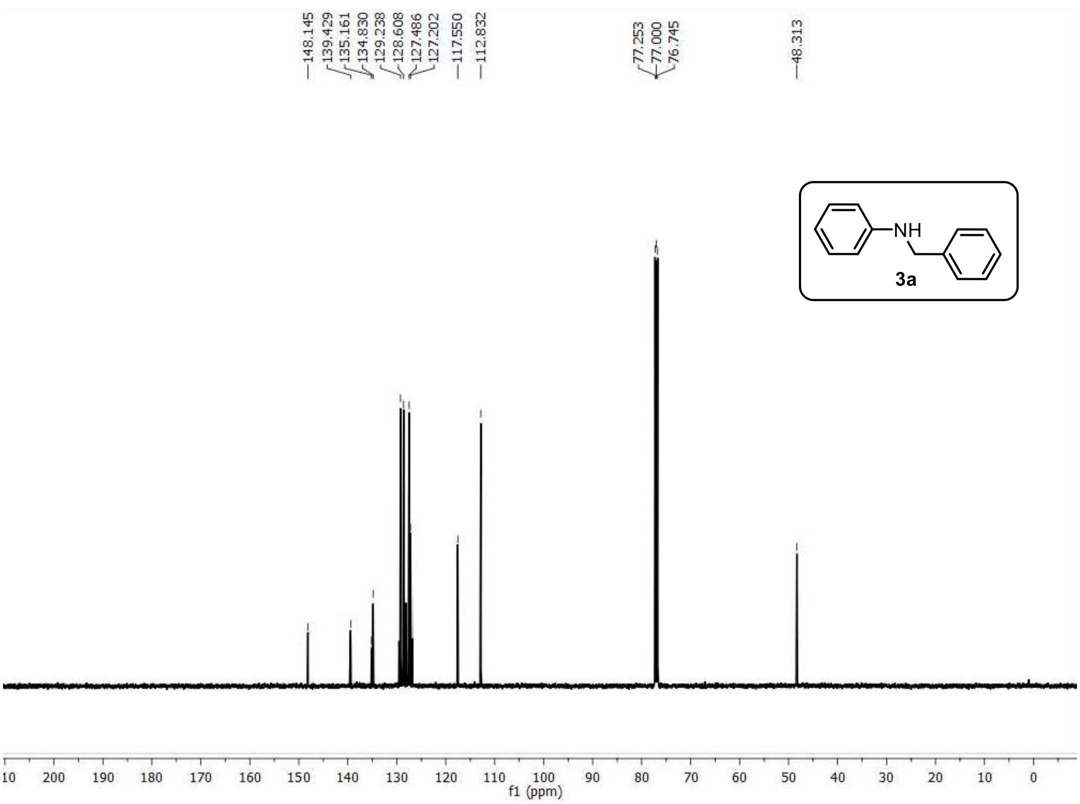


Figure S3. ^{1}H NMR spectrum of N-benzyl-4-methylaniline (**3b**)[S4] in $CDCl_3$.

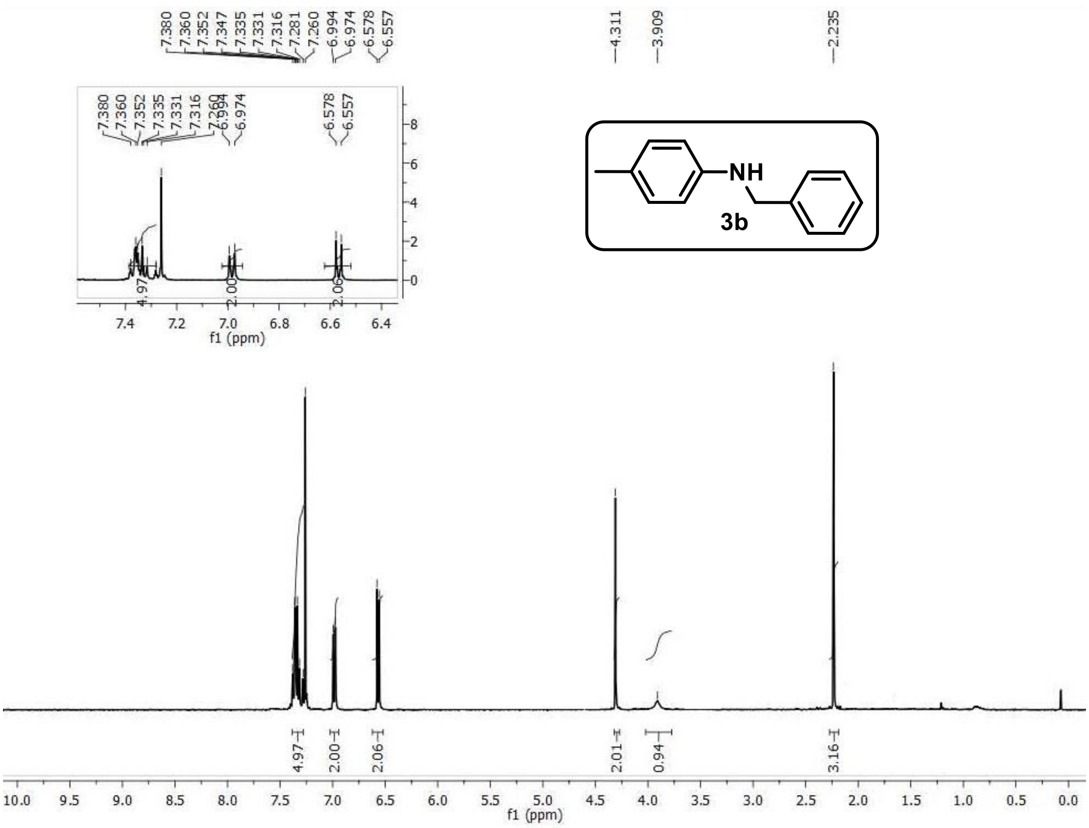


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-4-methylaniline (**3b**)[S4] in $CDCl_3$.

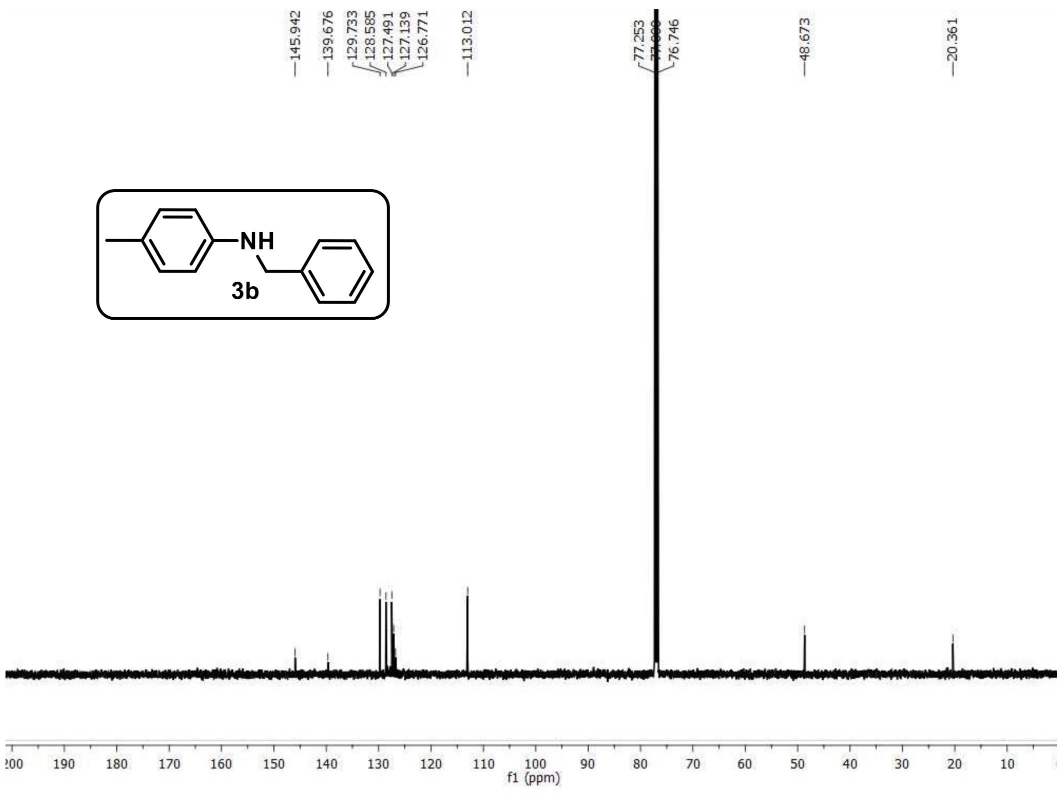


Figure S5. ^{1}H NMR spectrum of N-benzyl-4-ethylaniline (**3c**)[S6] in $CDCl_3$.

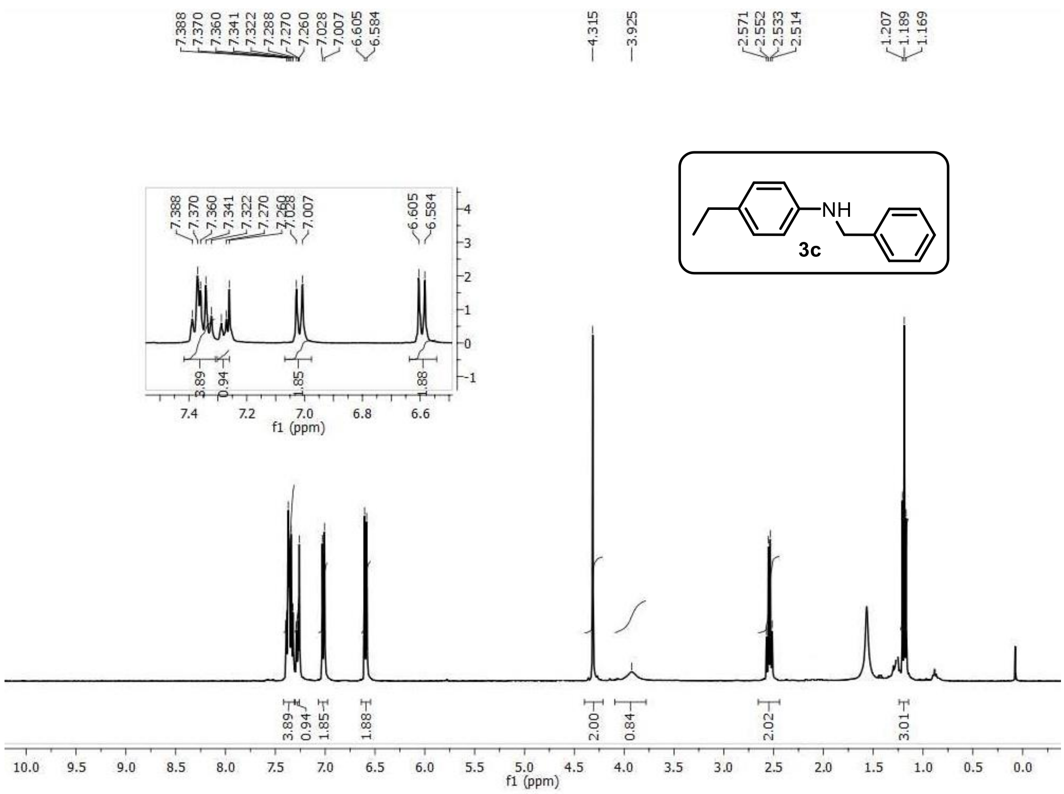


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-4-ethylaniline (**3c**)[S6] in $CDCl_3$.

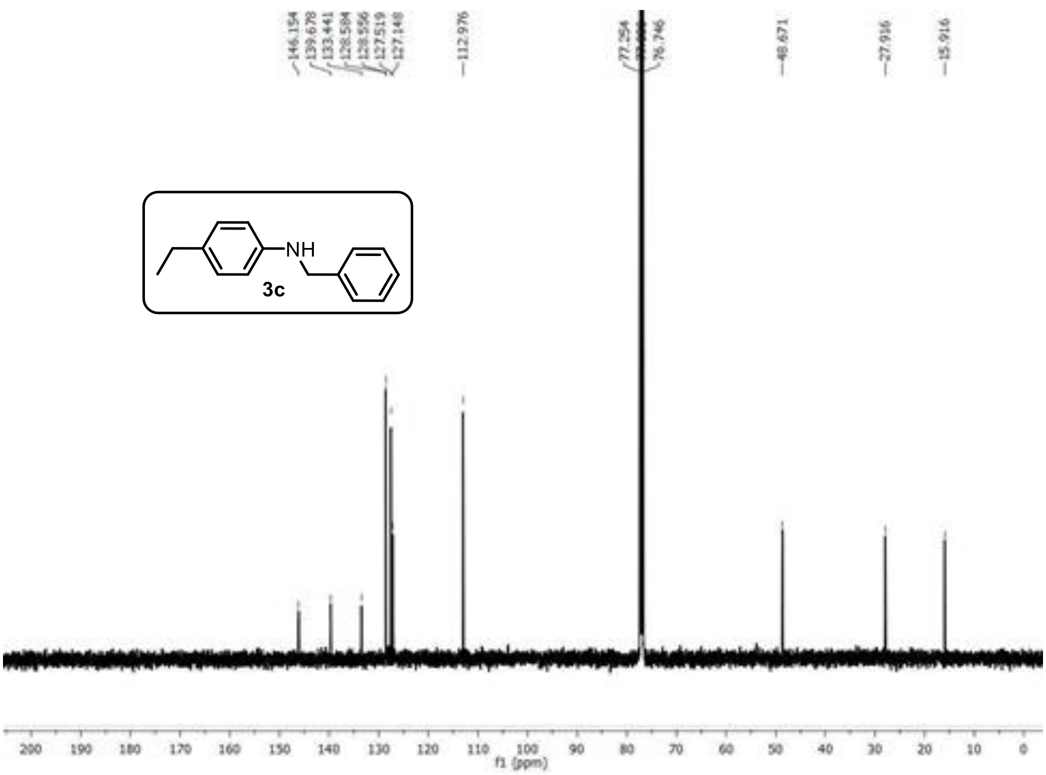


Figure S7. ^{1}H NMR spectrum of N-benzyl-4-isopropylaniline (**3d**)[S7] in $CDCl_3$.

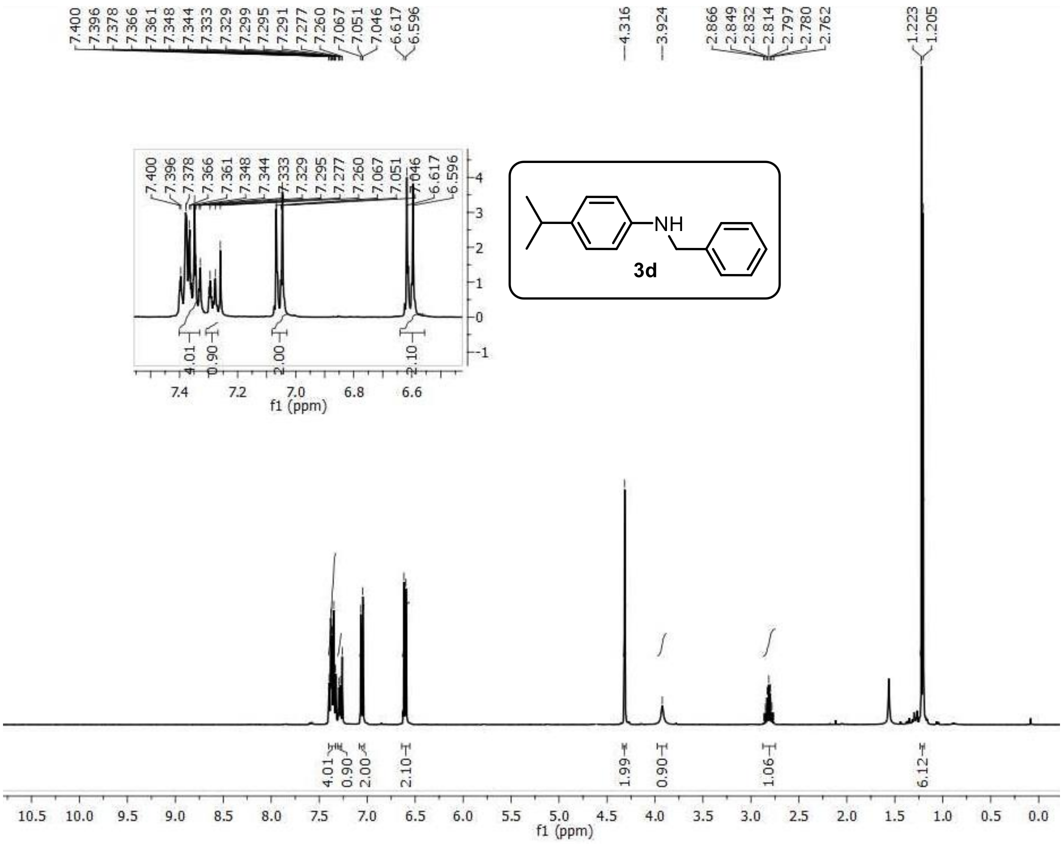


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-4-isopropylaniline (**3d**)[S7] in $CDCl_3$.

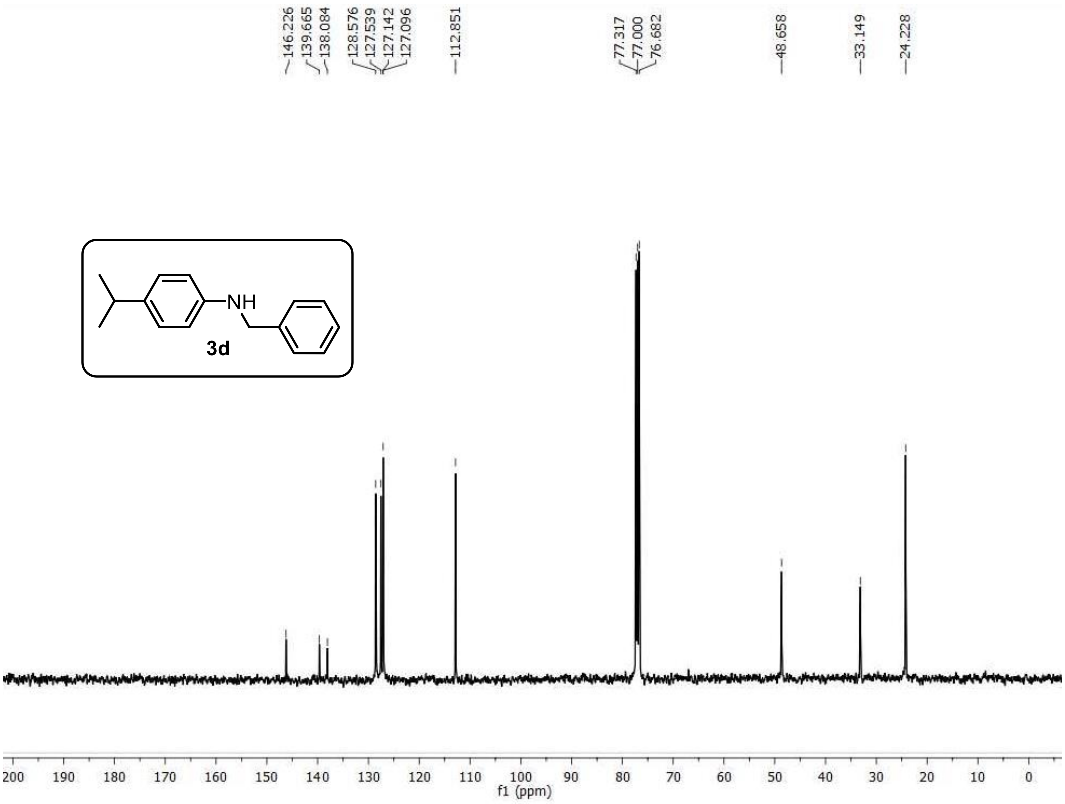


Figure S9. ^{1}H NMR spectrum of N-benzyl-4-methoxyaniline (**3e**)[S4] in $CDCl_3$.

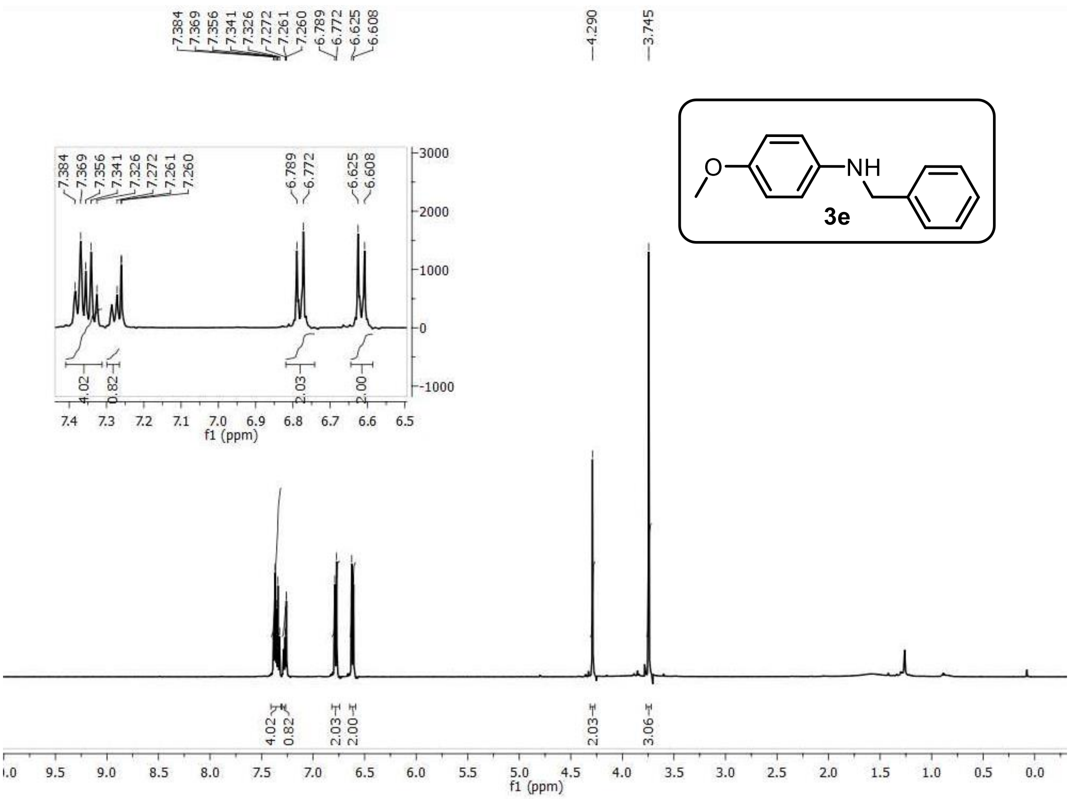


Figure S10. $^{13}C\{^1H\}$ NMR spectrum of N-benzyl-4-methoxyaniline (**3e**)[S4] in $CDCl_3$.

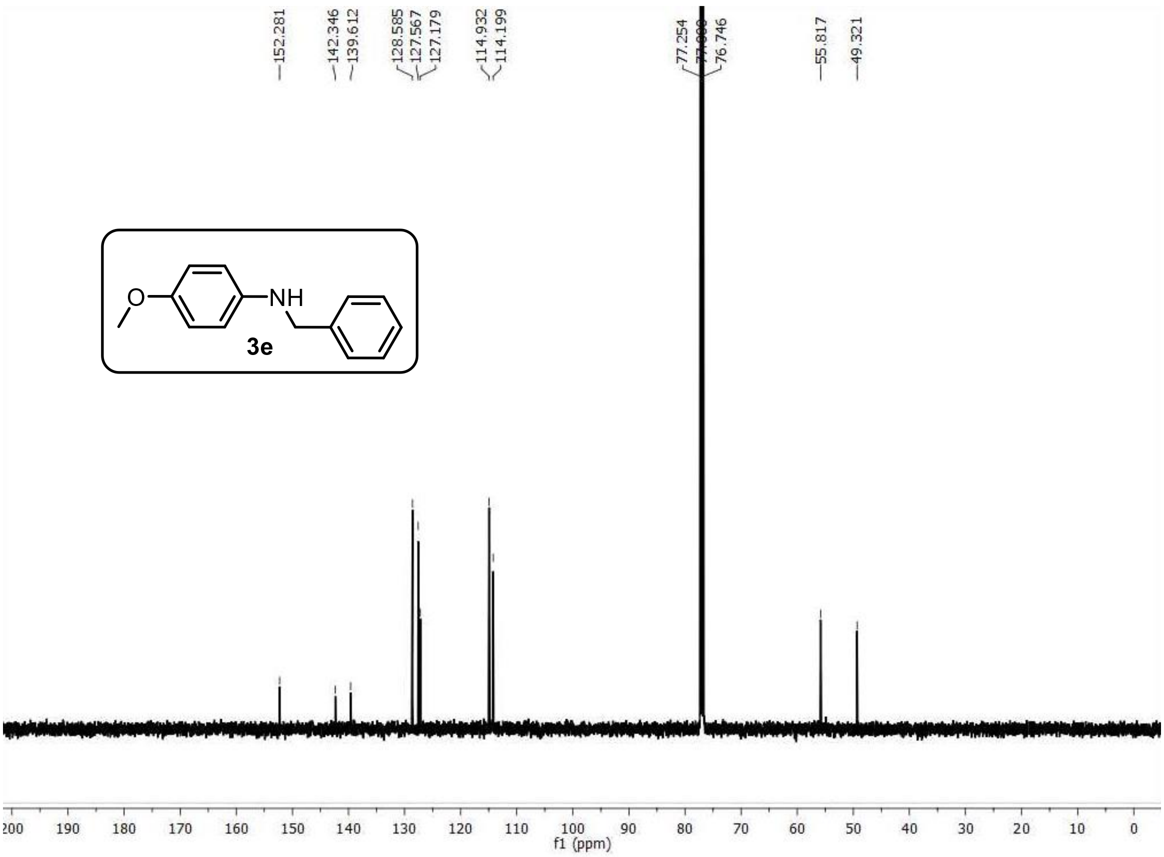


Figure S11. ^{1}H NMR spectrum of N-benzyl-4-chloroaniline (**3f**)[S4] in $CDCl_3$.

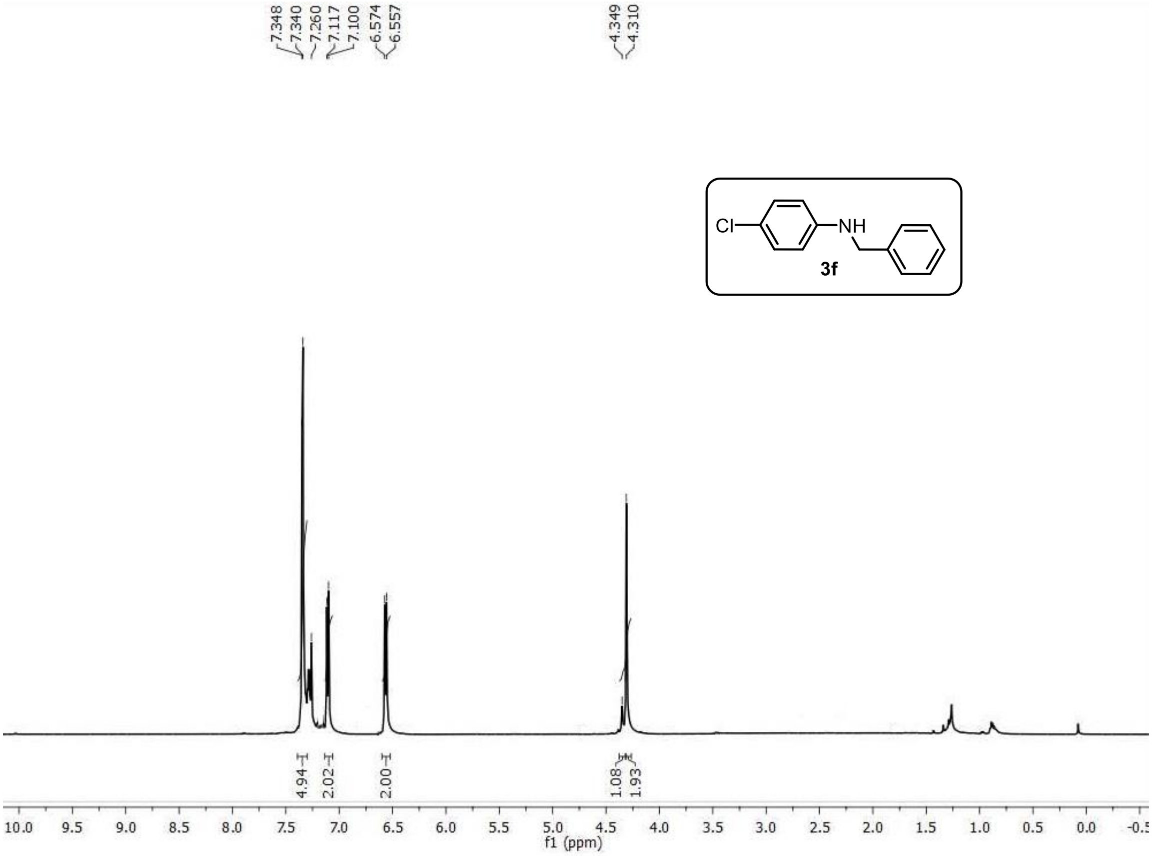


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-4-chloroaniline (**3f**)[S4] in $CDCl_3$.

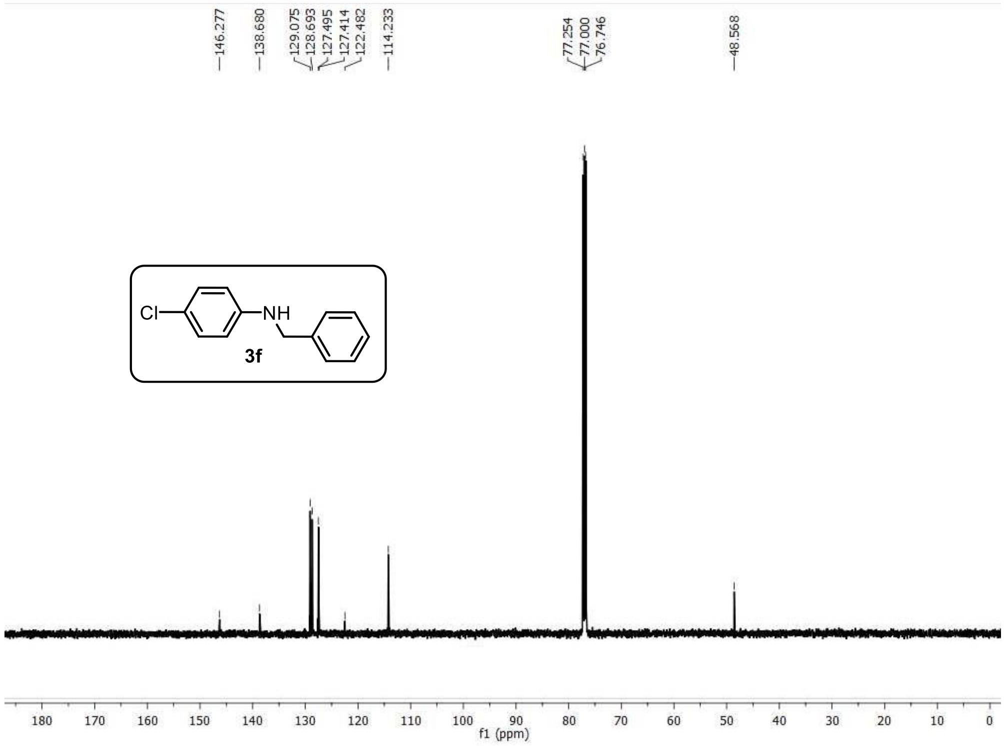


Figure S13. ^{1}H NMR spectrum of N-benzyl-4-bromoaniline (**3g**)[S4] in $CDCl_3$.

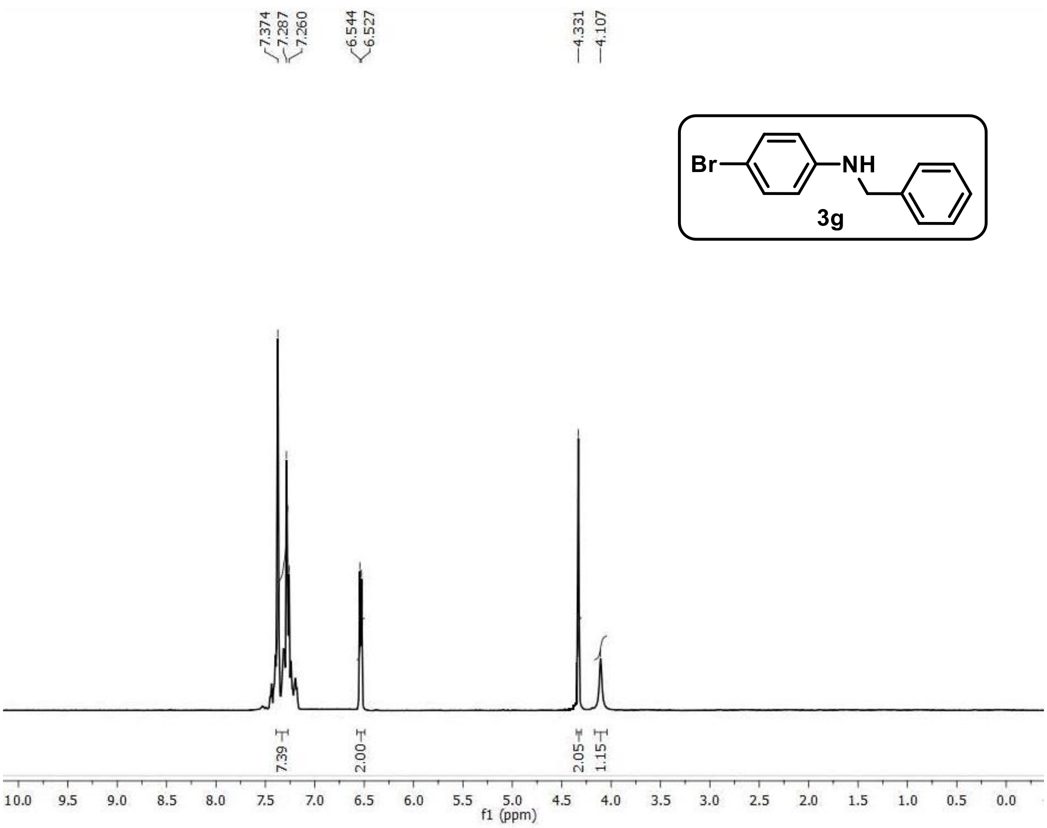


Figure S14. ^{13}C{^{1}H} NMR spectrum of N-benzyl-4-bromoaniline (**3g**)[S4] in $CDCl_3$.

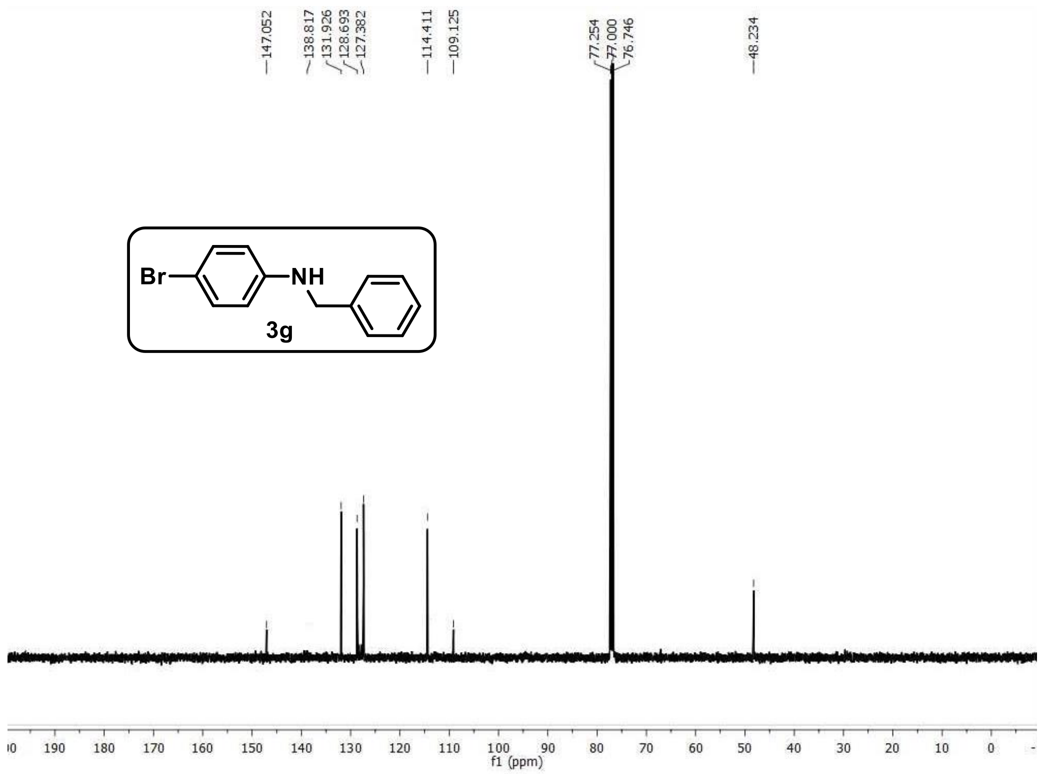


Figure S15. ^{1}H NMR spectrum of N-benzyl-2-fluoroaniline (**3h**)[S5] in $CDCl_3$.

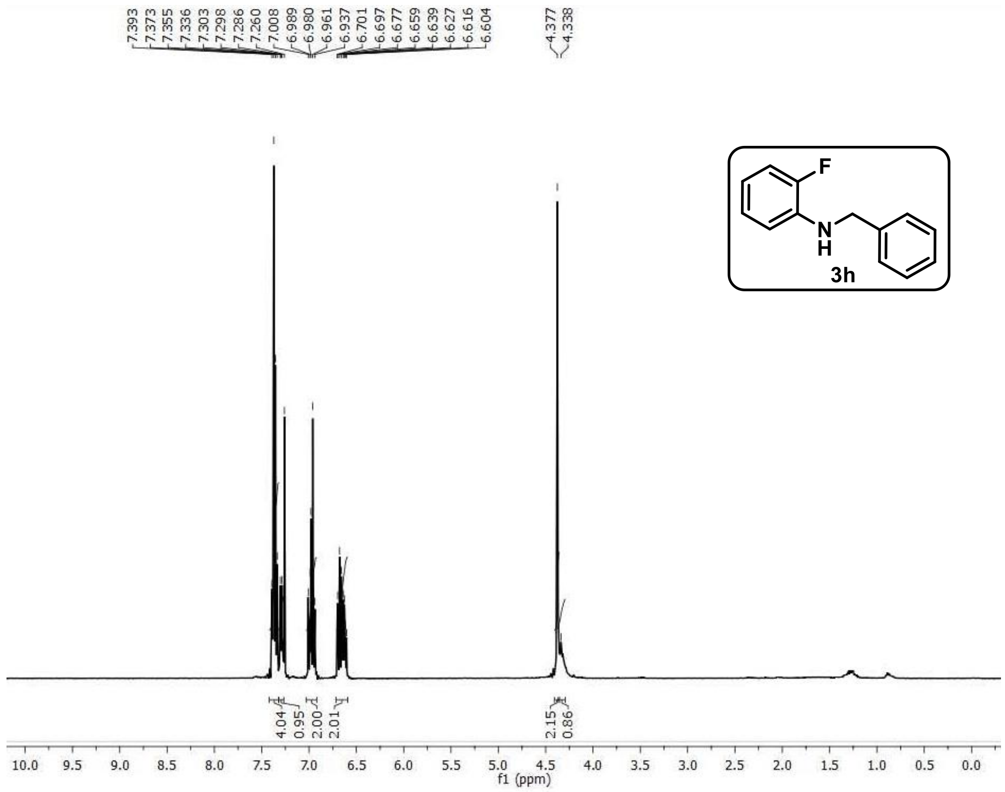


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-2-fluoroaniline (**3h**)[S5] in $CDCl_3$.

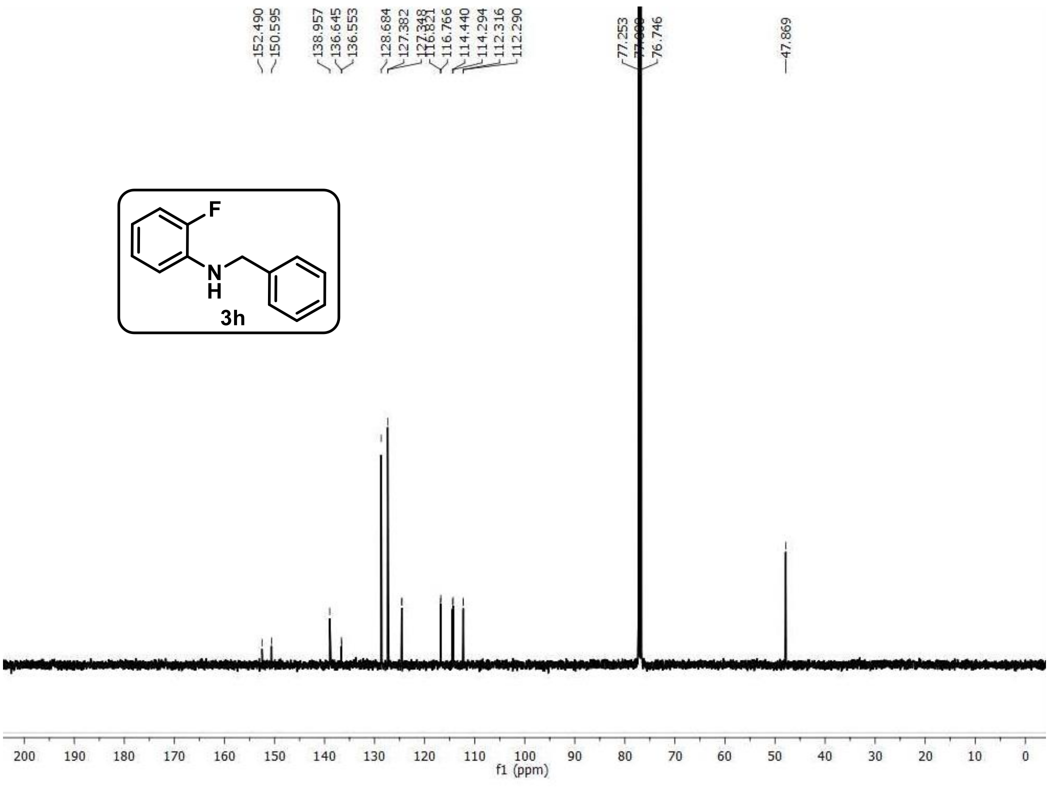


Figure S17. ^{19}F NMR spectrum of N-benzyl-2-fluoroaniline (**3h**)[S5] in $CDCl_3$.

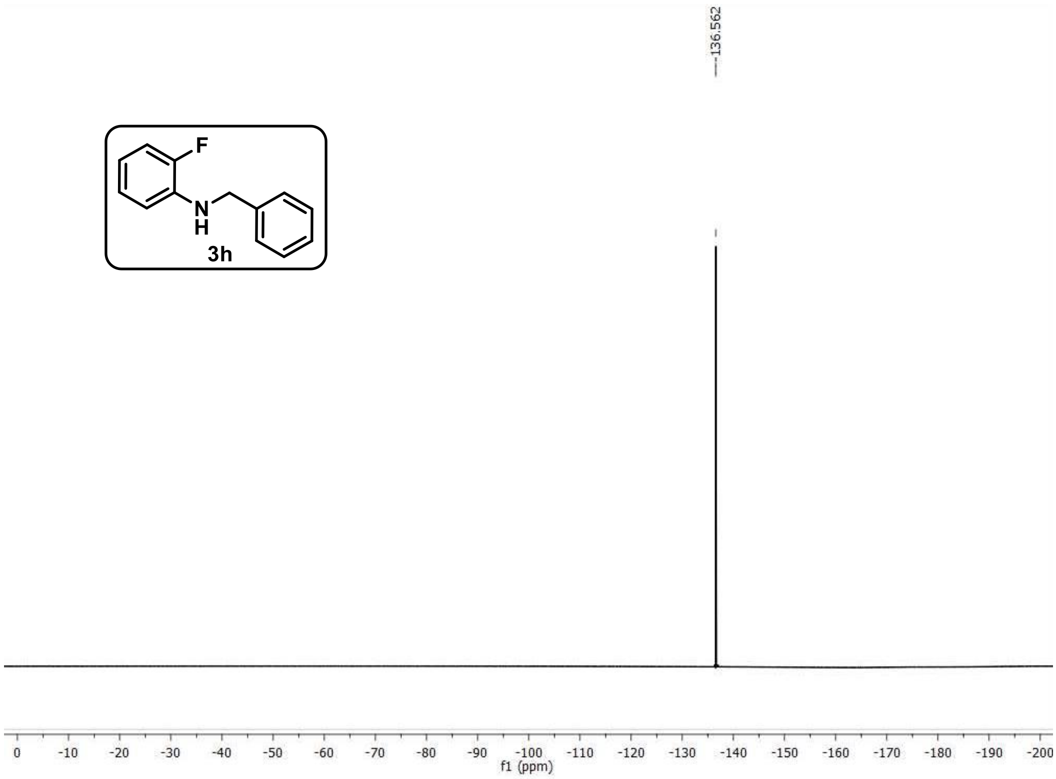


Figure S18. ^{1}H NMR spectrum of N-benzyl-2-bromoaniline (**3i**)[S8] in $CDCl_3$.

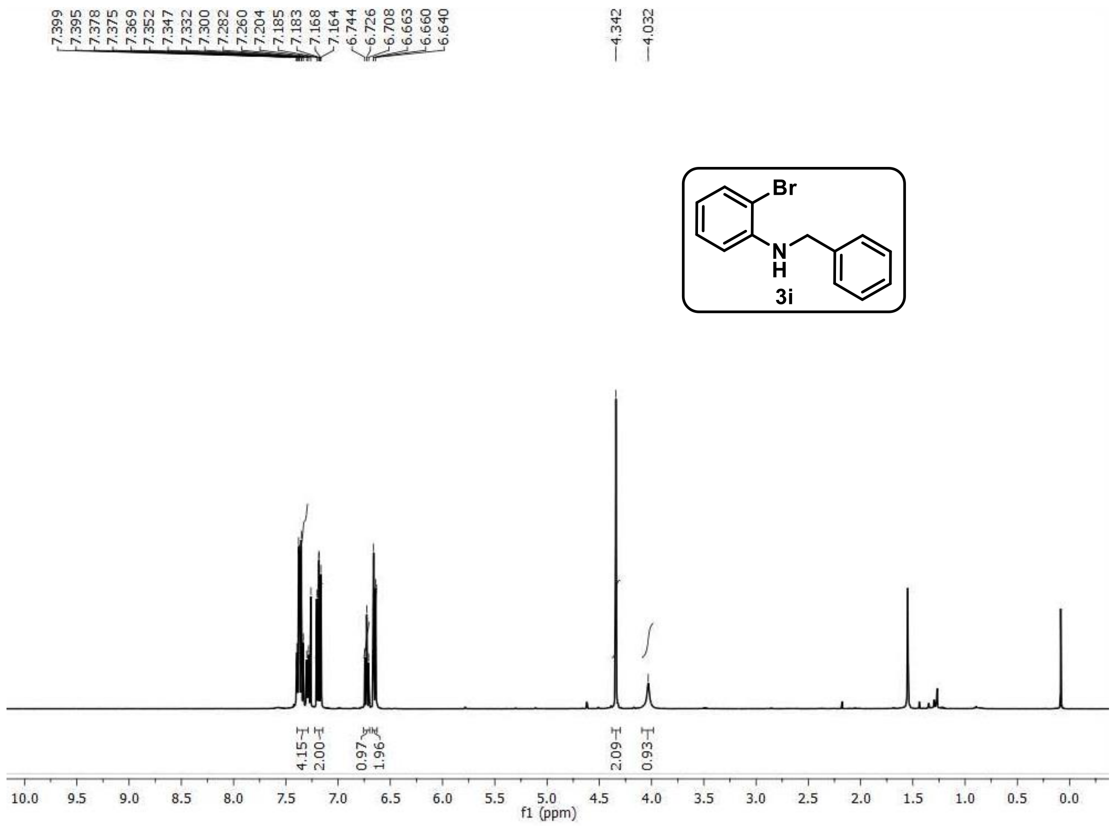


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-2-bromoaniline (**3i**)[S8] in $CDCl_3$.

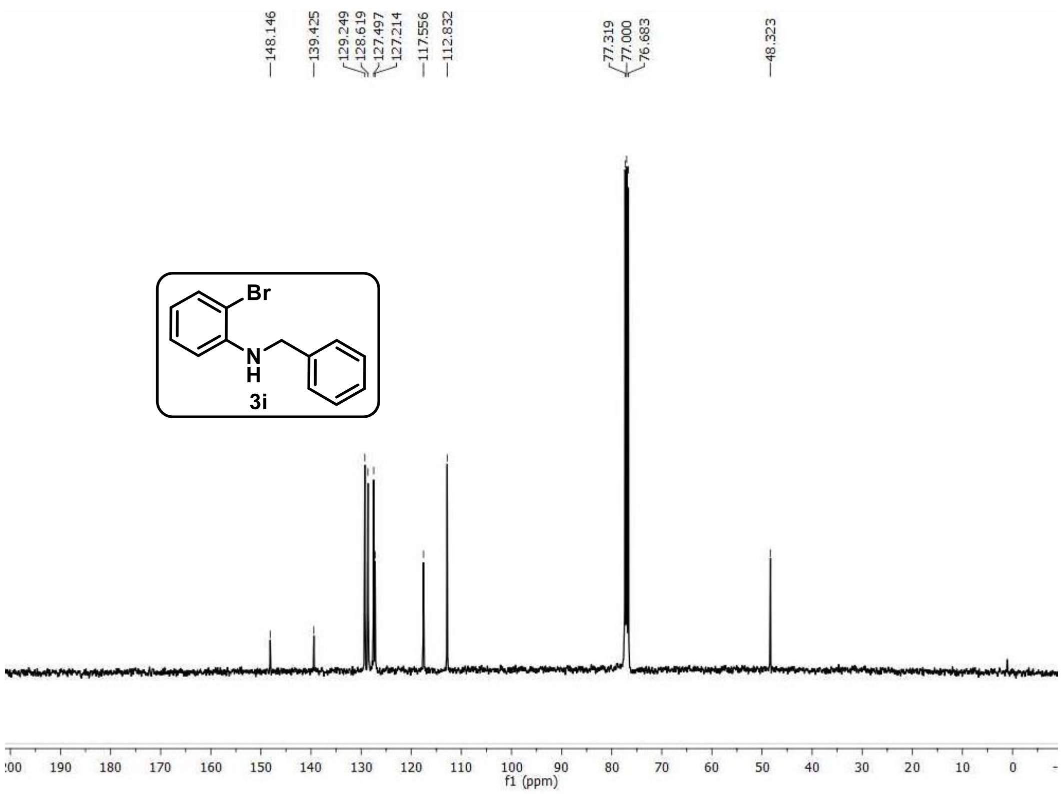


Figure S20. ^{1}H NMR spectrum of N-benzyl-2-methoxyaniline (**3j**)[S8] in $CDCl_3$.

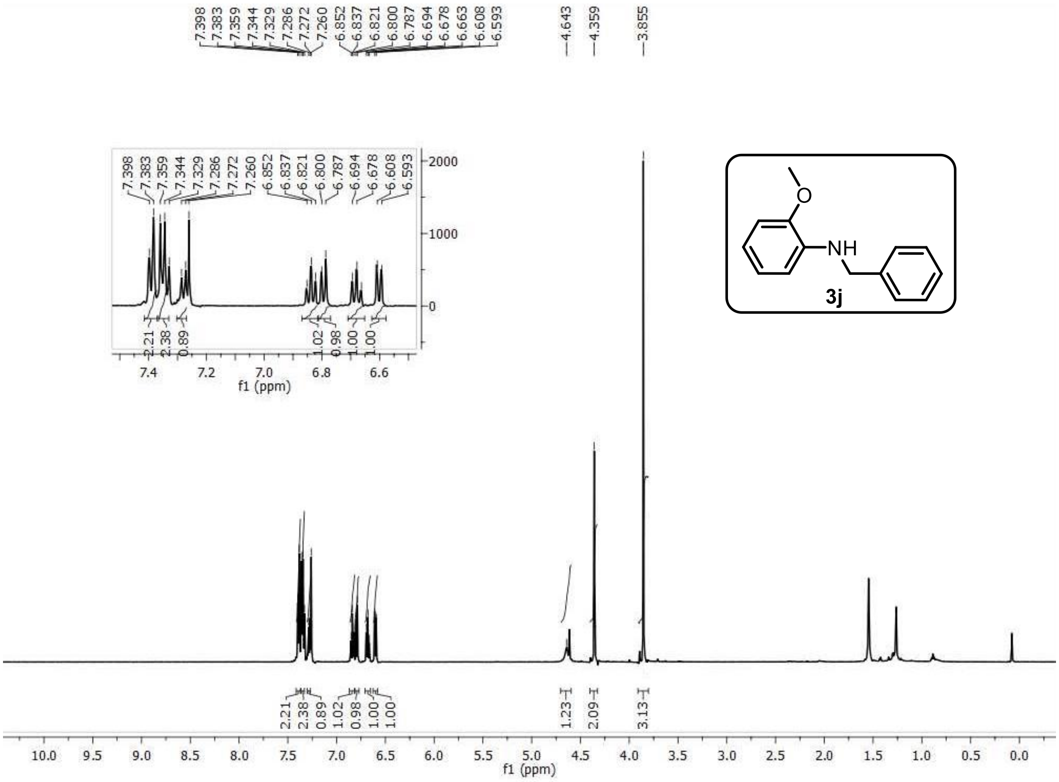


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-2-methoxyaniline (**3j**)[S8] in $CDCl_3$.

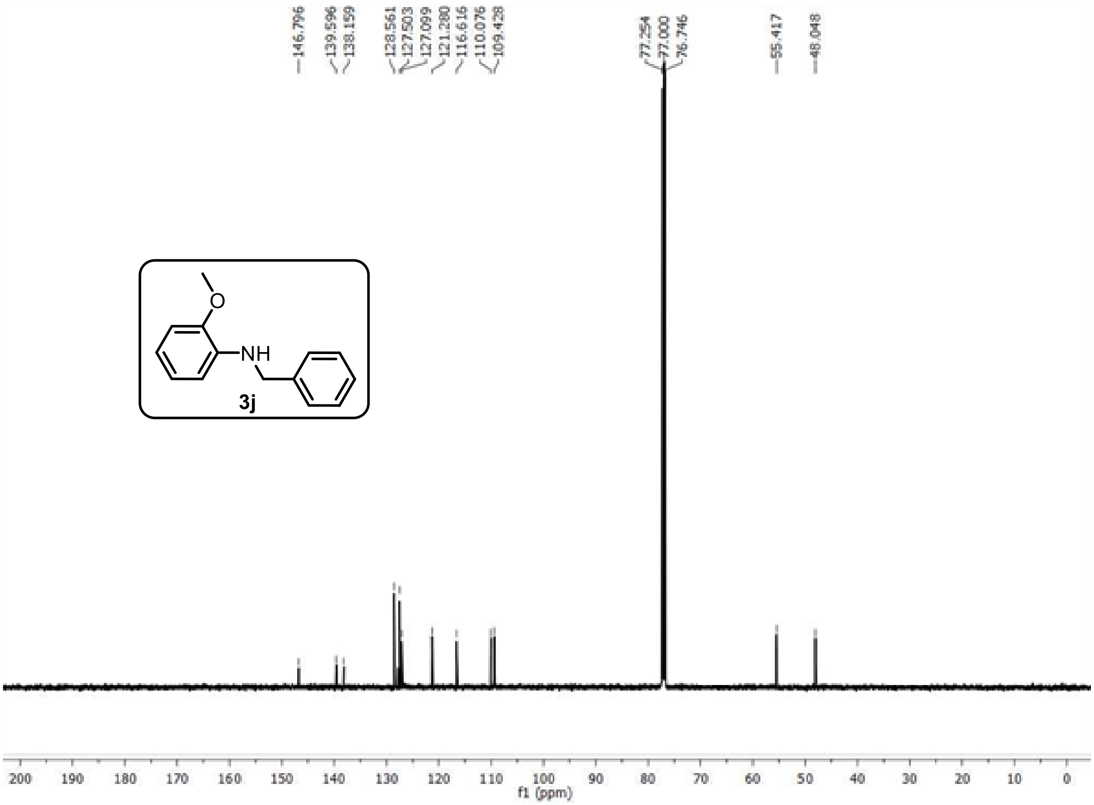


Figure S22. ^{1}H NMR spectrum of N-benzyl-3,5-dimethylaniline (**3k**)[S6] in $CDCl_3$.

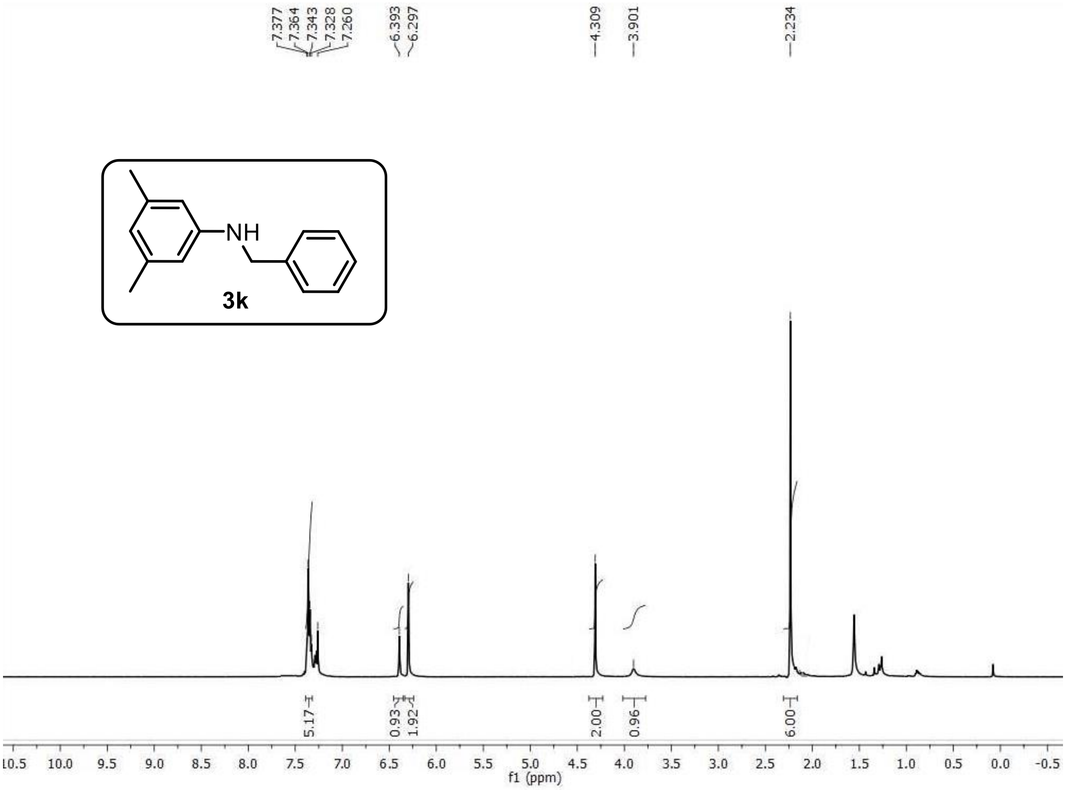


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-3,5-dimethylaniline (**3k**)[S6] in $CDCl_3$.

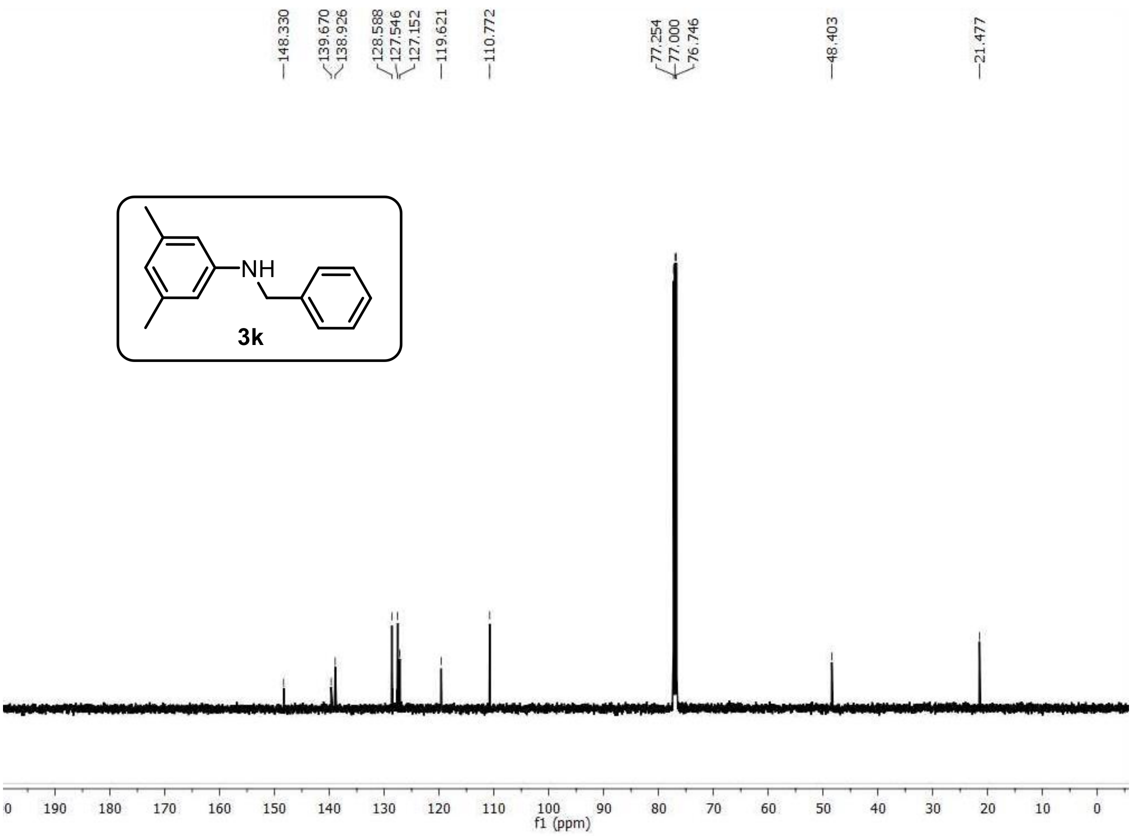


Figure S24. ^{1}H NMR spectrum of N-benzyl-3,5-dimethoxyaniline (**3l**)[S9] in $CDCl_3$.

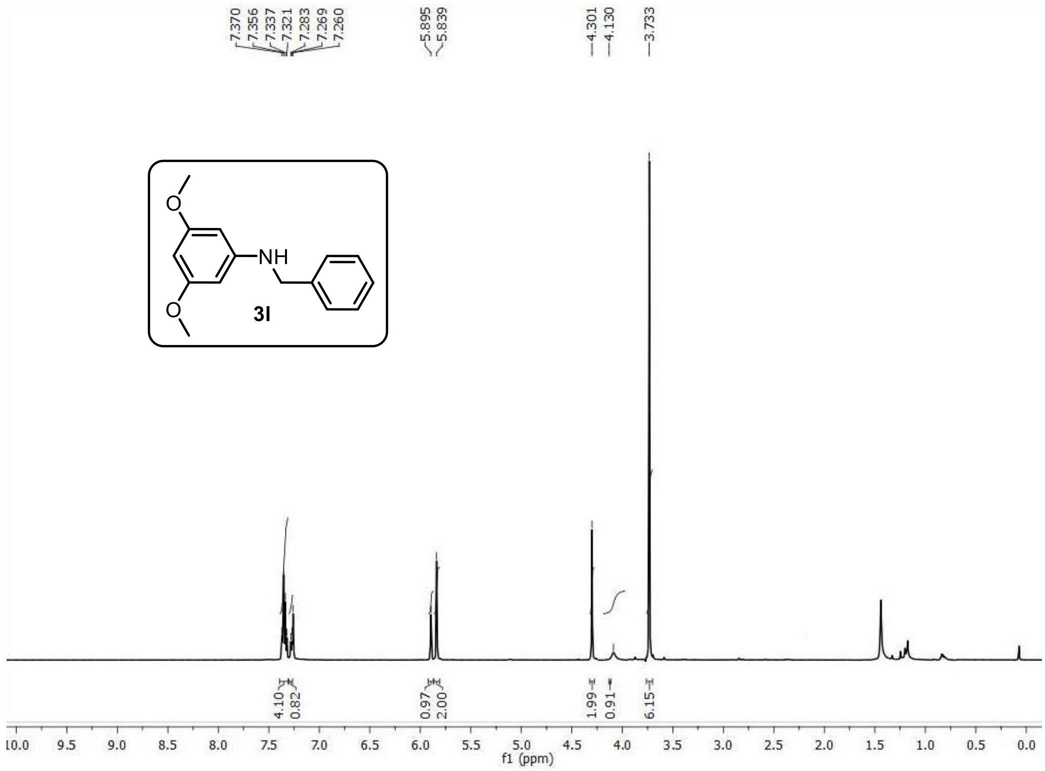


Figure S25. $^{13}C\{^1H\}$ NMR spectrum of N-benzyl-3,5-dimethoxyaniline (**3l**)[S9] in $CDCl_3$.

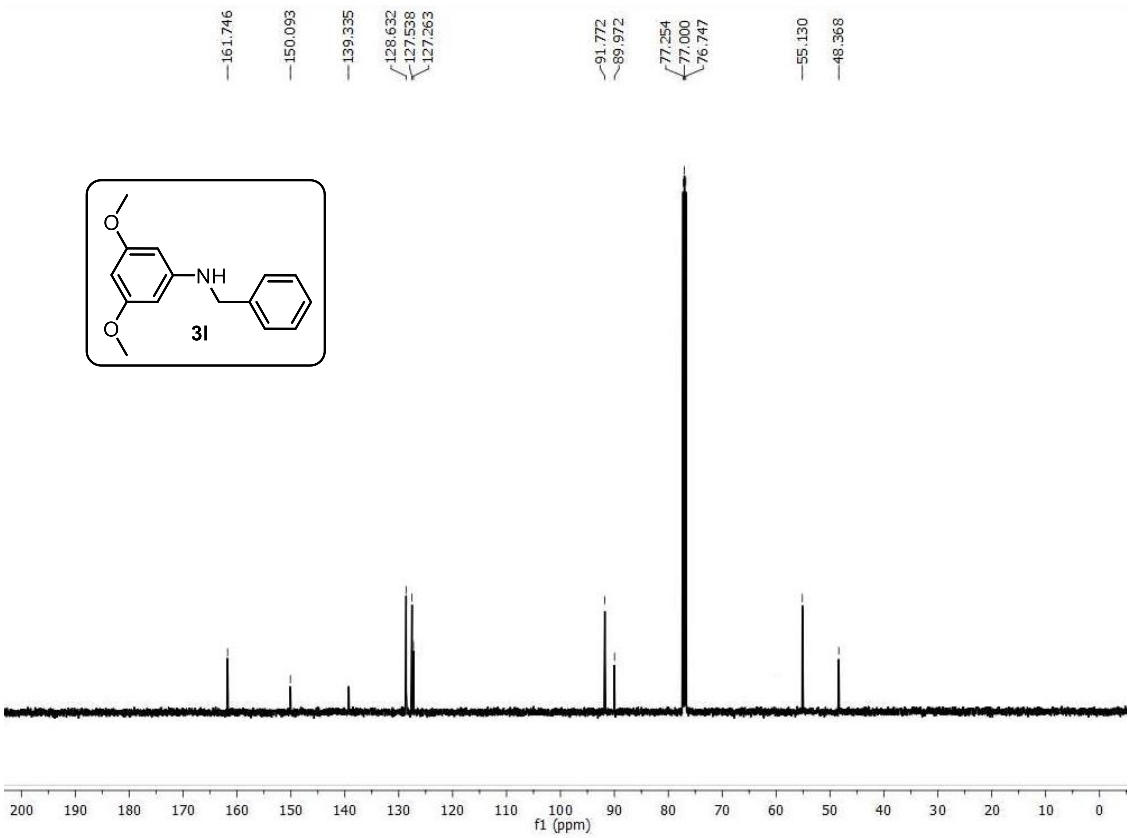


Figure S26. ^{1}H NMR spectrum of N-benzyl-3,5-dichloroaniline (**3m**)[S10] in $CDCl_3$.

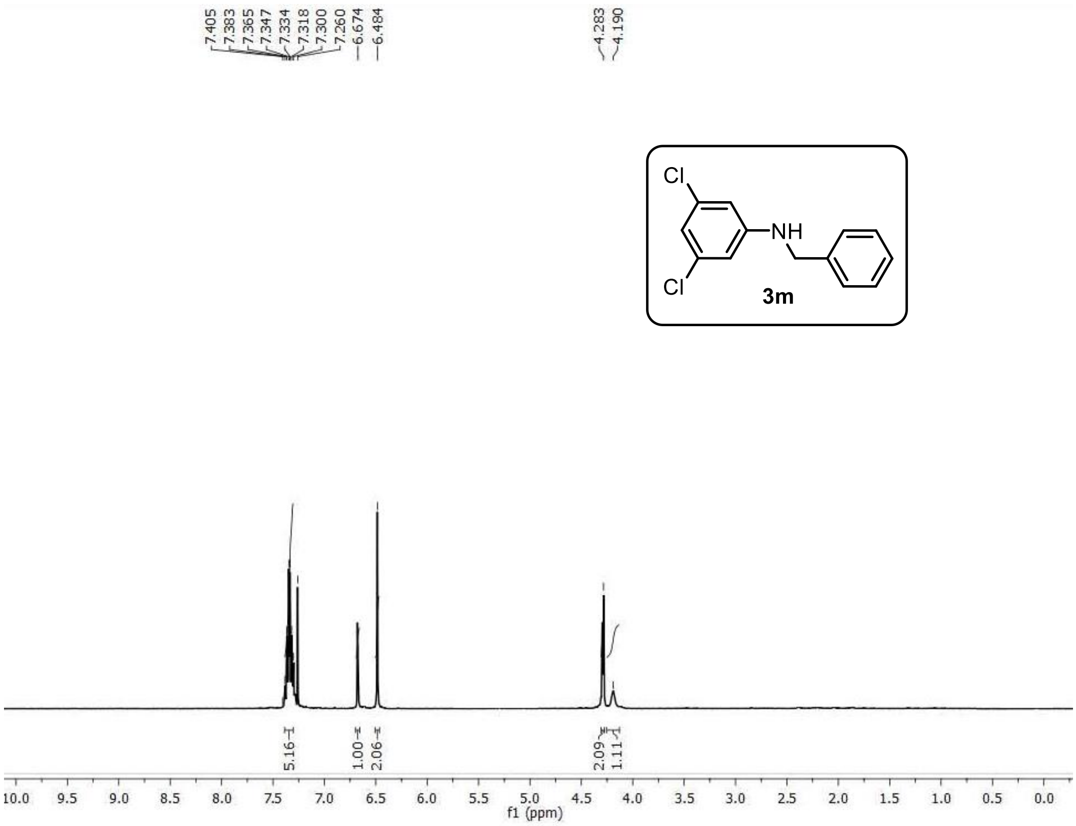


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-3,5-dichloroaniline (**3m**)[S10] in $CDCl_3$.

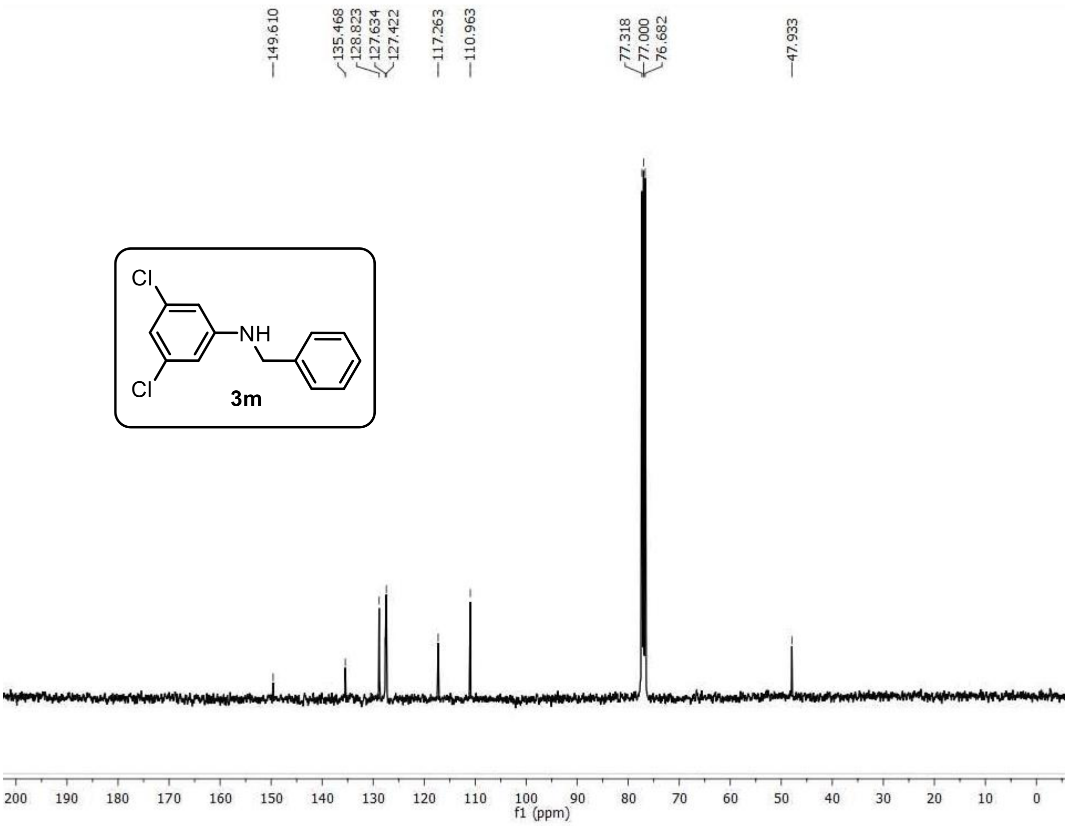


Figure S28. ^{1}H NMR spectrum of N-benzyl-[1,1'-biphenyl]-2-amine (**3n**)[S9] in $CDCl_3$.

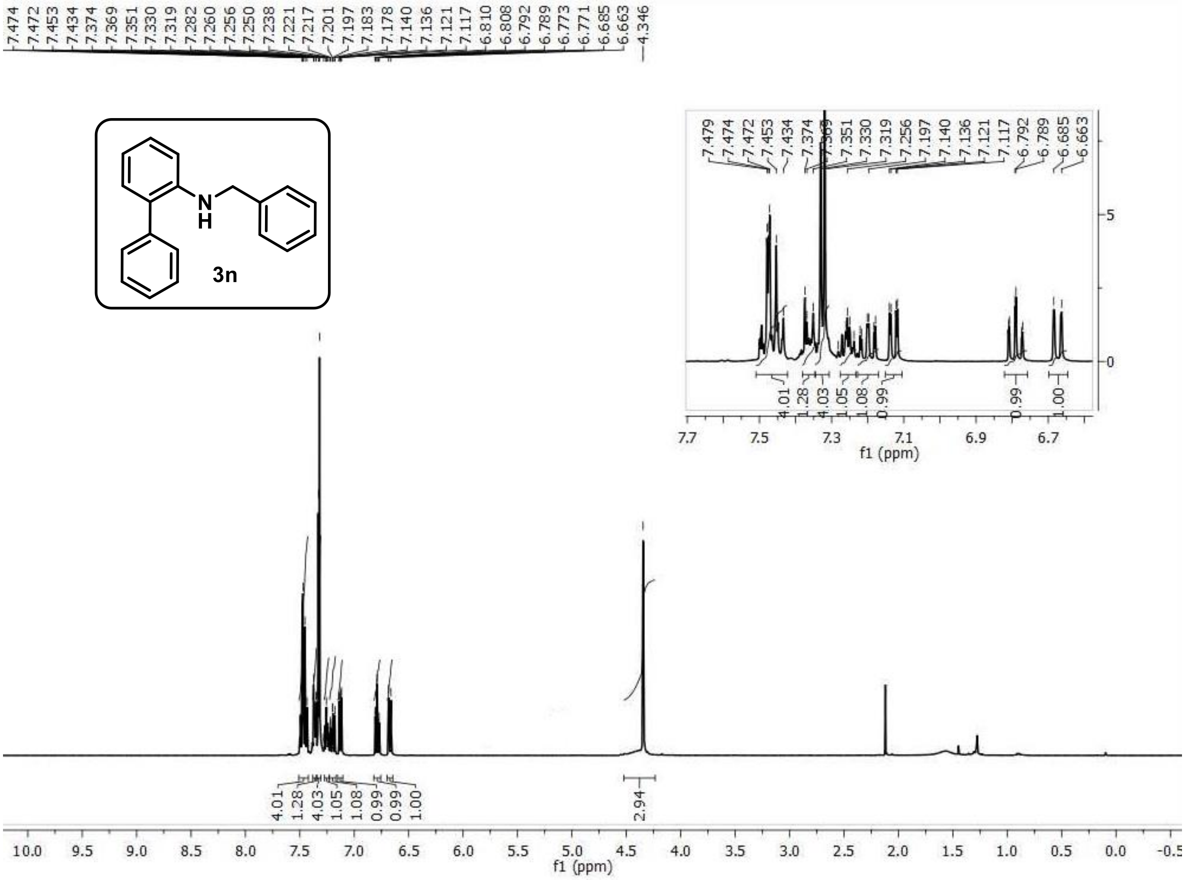


Figure S29. $^{13}C\{^1H\}$ NMR spectrum of N-benzyl-[1,1'-biphenyl]-2-amine (**3n**)[S9] in $CDCl_3$.

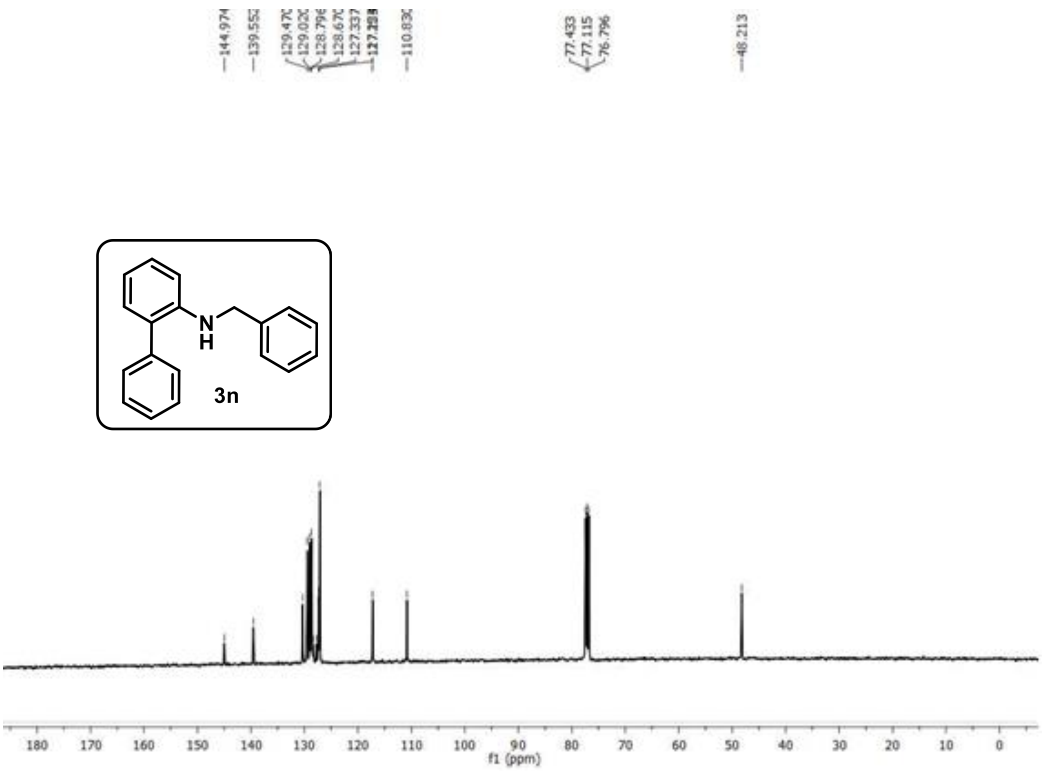


Figure S30. ^{1}H NMR spectrum of N-benzyl-6-methylbenzothiazol-2-amine (**3o**)[S11] in $CDCl_3$.

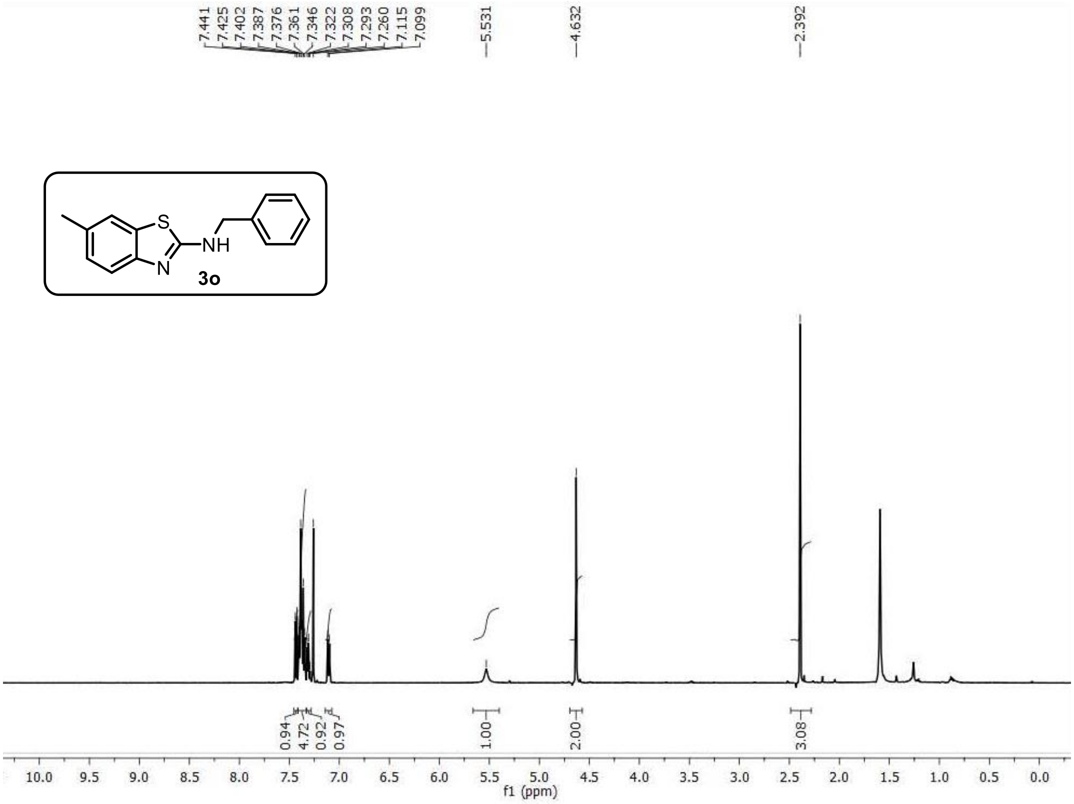


Figure S31. ^{13}C{^{1}H} NMR spectrum of N-benzyl-6-methylbenzothiazol-2-amine (**3o**)[S11] in $CDCl_3$.

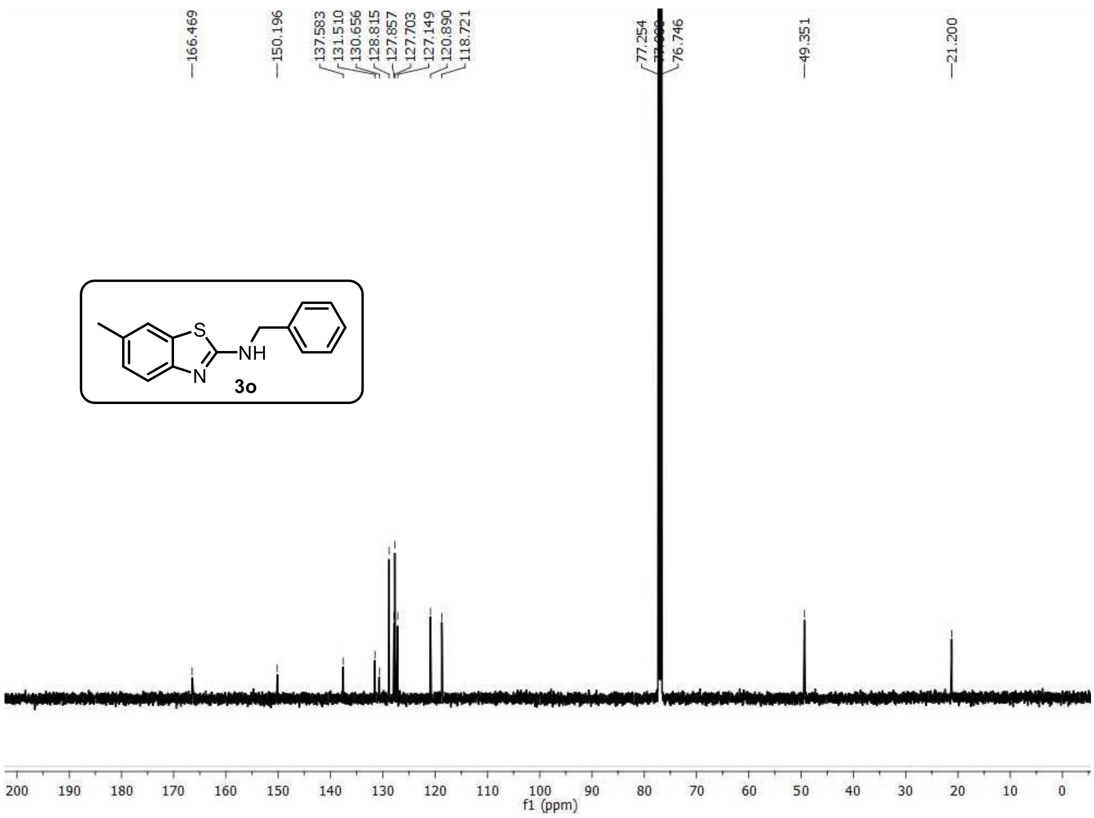


Figure S32. ^{1}H NMR spectrum of N-benzyl-6-chlorobenzothiazol-2-amine (**3p**)[S11] in DMSO-d$_6$.

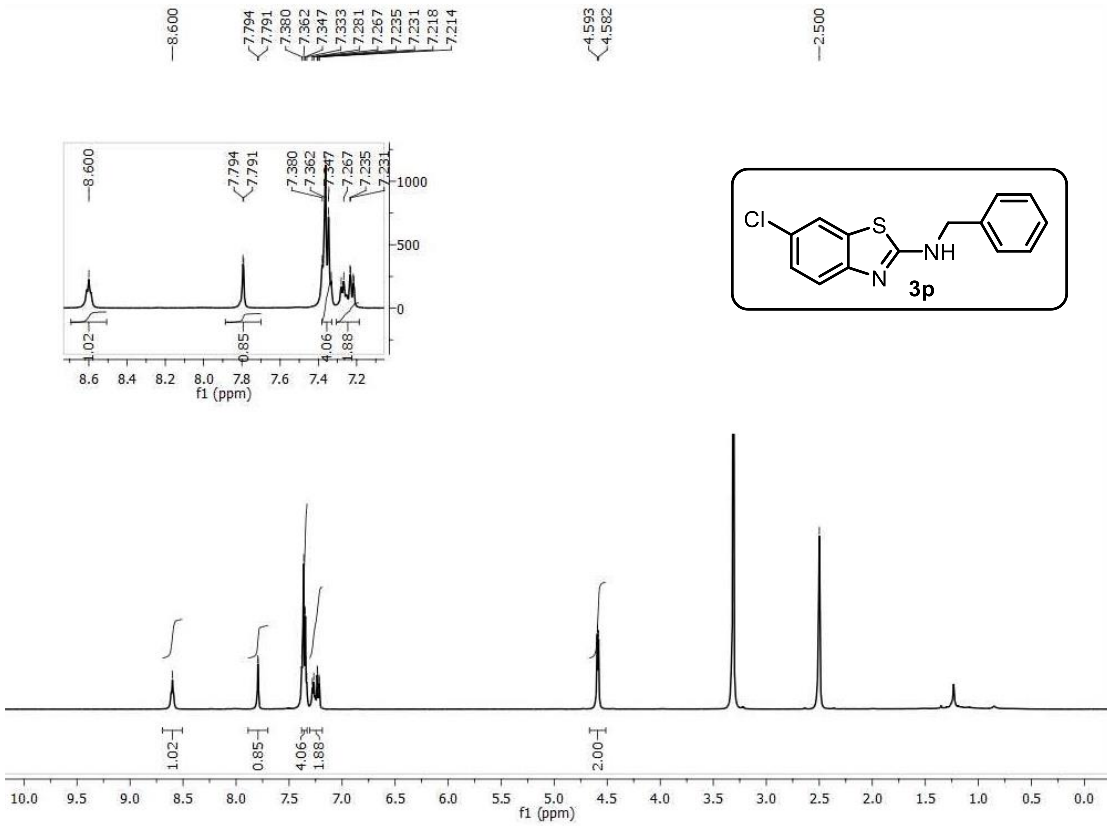


Figure S33. ^{13}C{^{1}H} NMR spectrum of N-benzyl-6-chlorobenzothiazol-2-amine (**3p**)[S11] in DMSO-d$_6$.

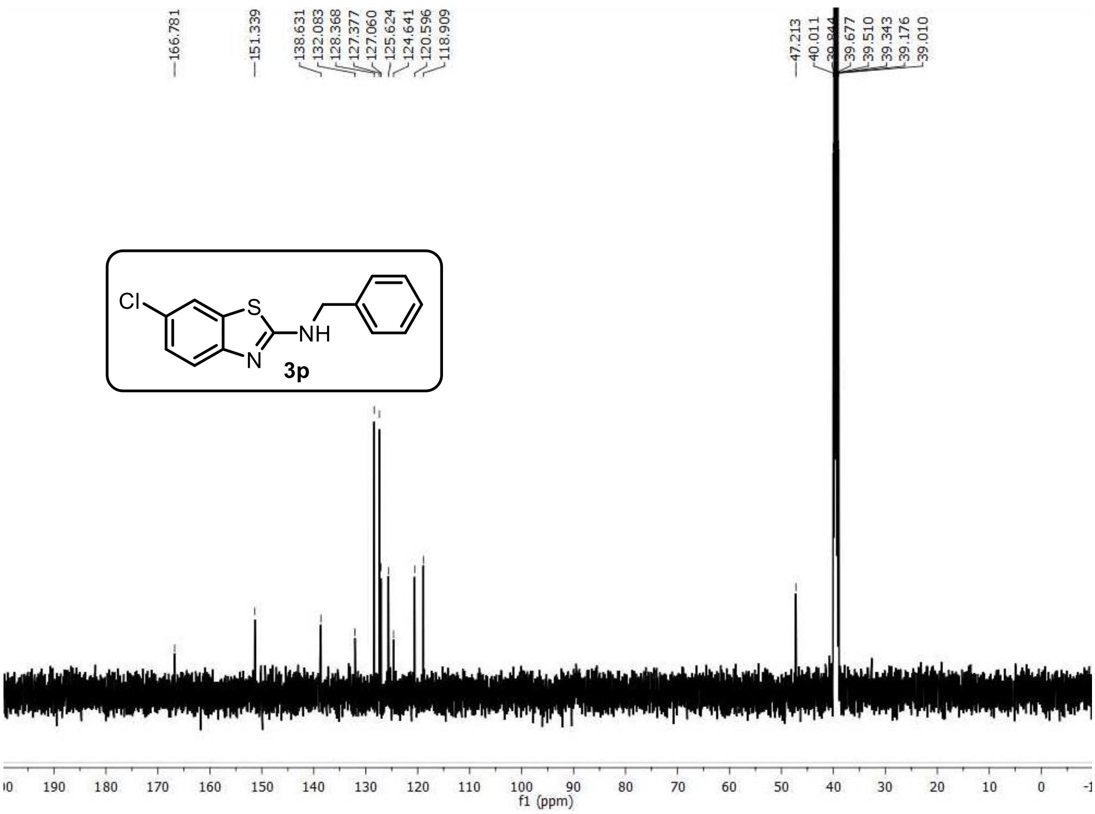


Figure S34. ^{1}H NMR spectrum of N-benzylquinolin-8-amine (**3q**)[S12] in $CDCl_3$.

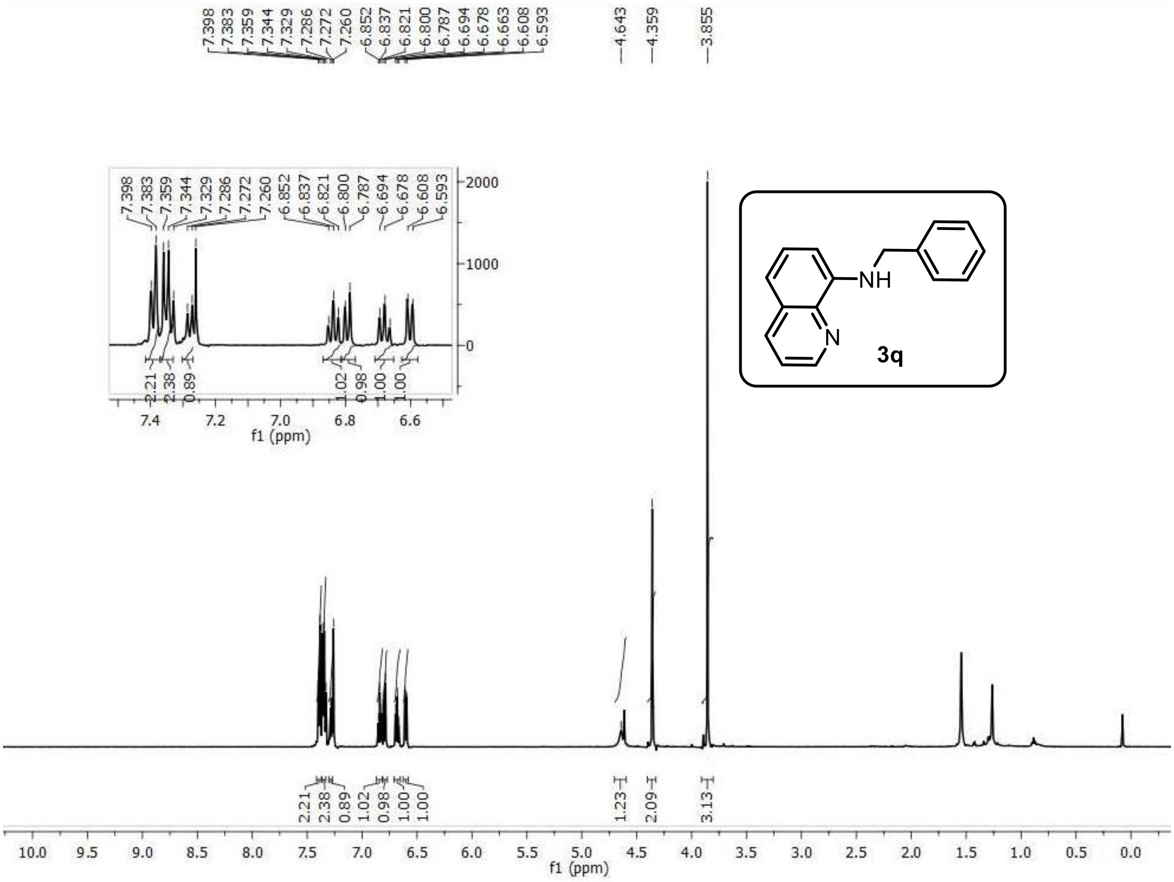


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzylquinolin-8-amine (**3q**)[S12] in $CDCl_3$.

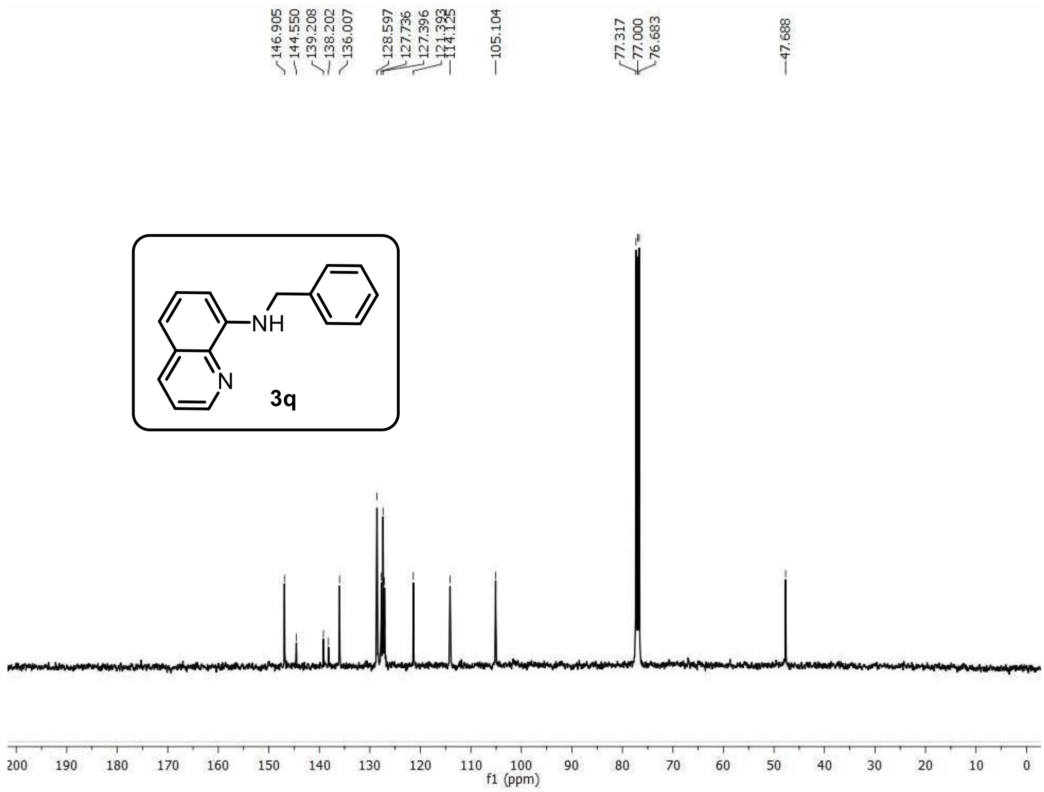


Figure S36. ^{1}H NMR spectrum of N-benzylpyrazin-2-amine (**3r**)[S8] in $CDCl_3$.

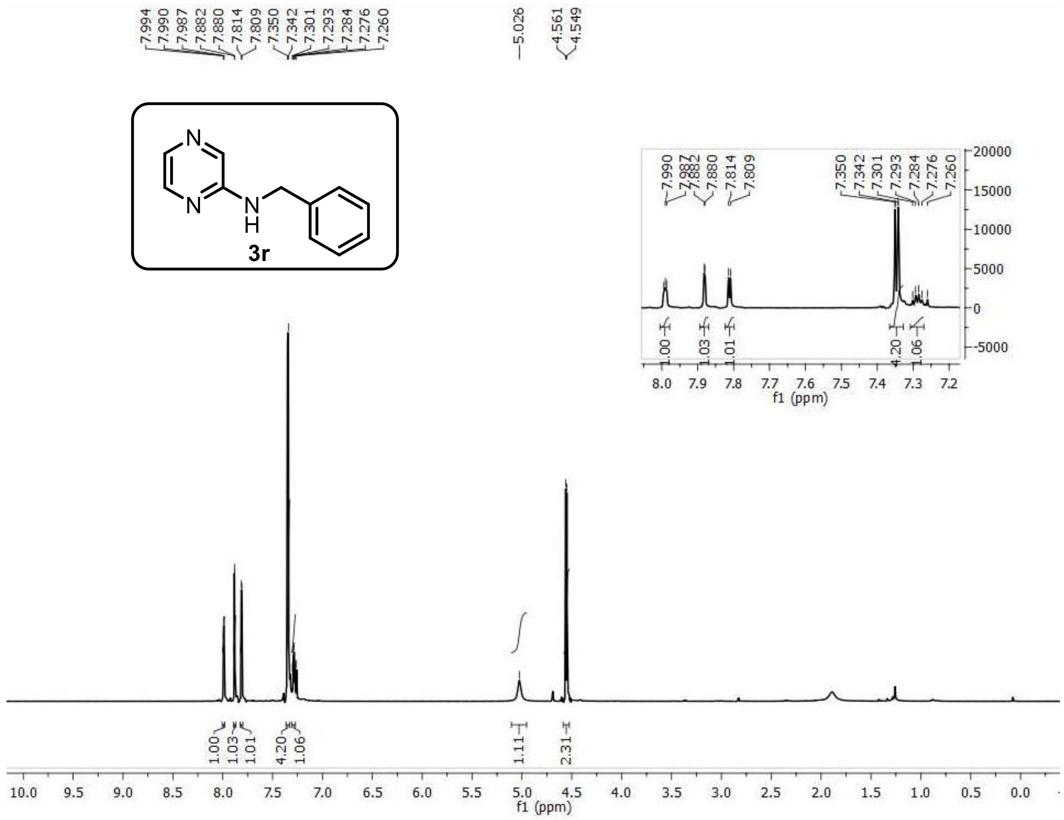


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzylpyrazin-2-amine (**3r**)[S8] in $CDCl_3$.

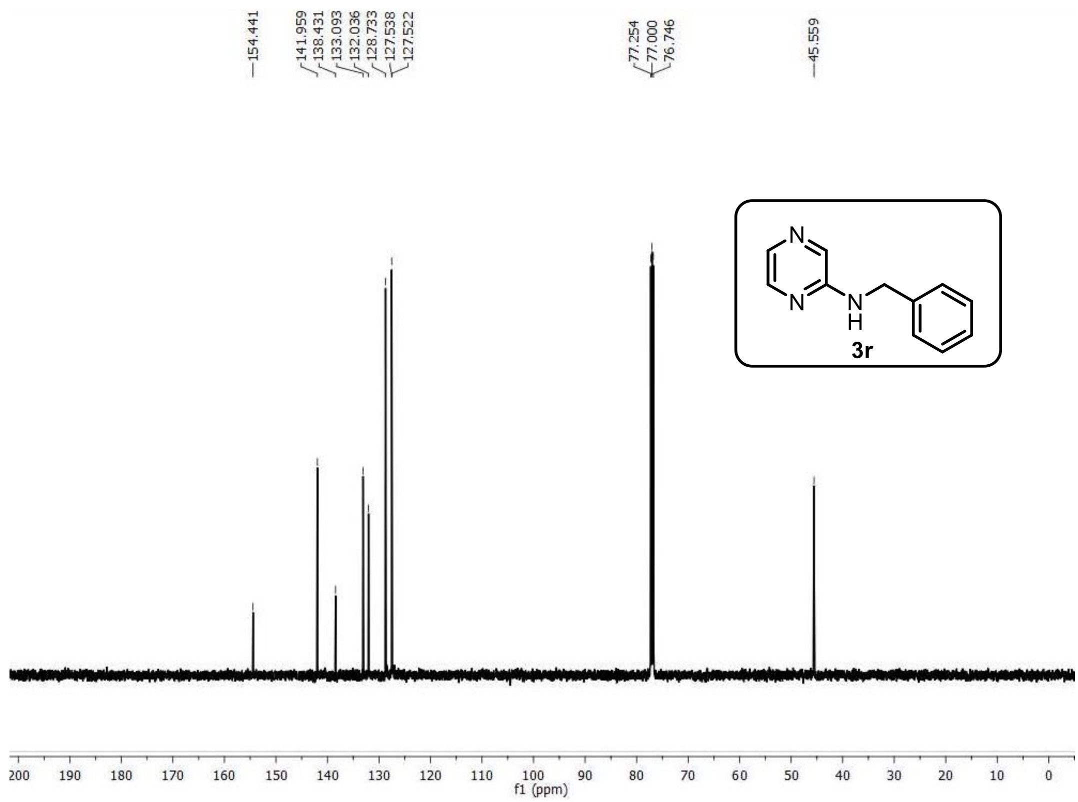


Figure S38. ^{1}H NMR spectrum of N-benzylpyrimidin-2-amine (**3s**)[S8] in $CDCl_3$.

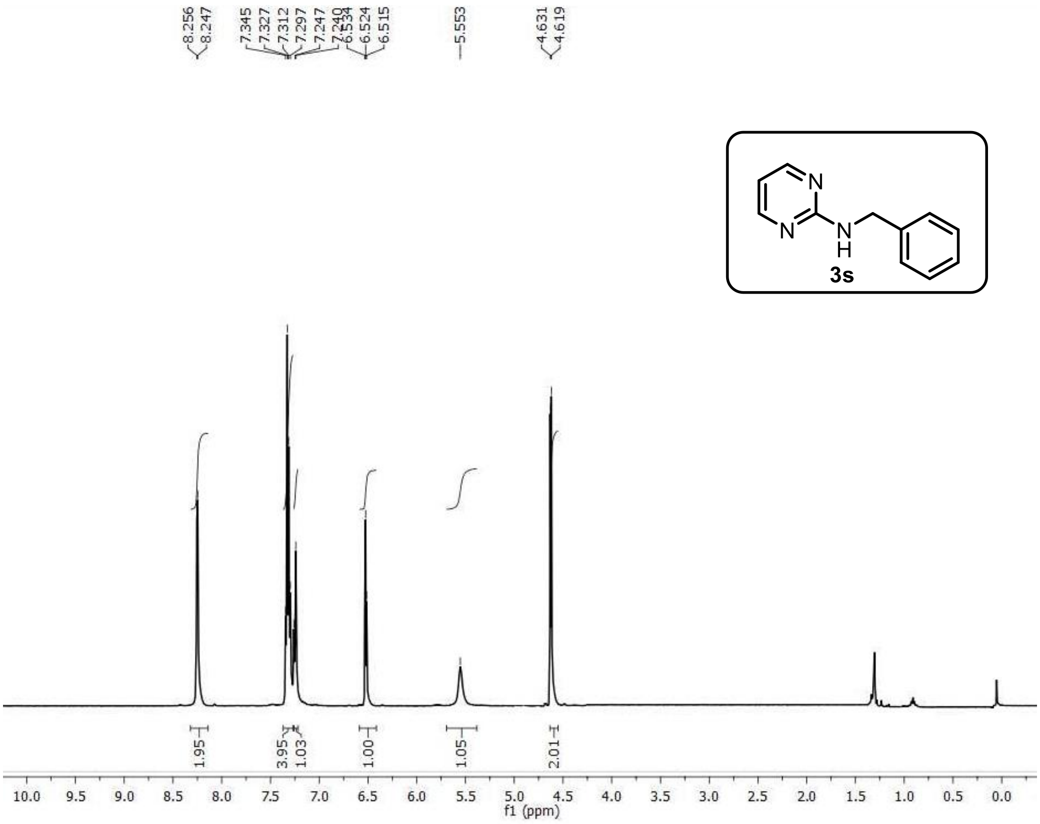


Figure S39. ^{13}C{^{1}H} NMR spectrum of N-benzylpyrimidin-2-amine (**3s**)[S8] in $CDCl_3$.

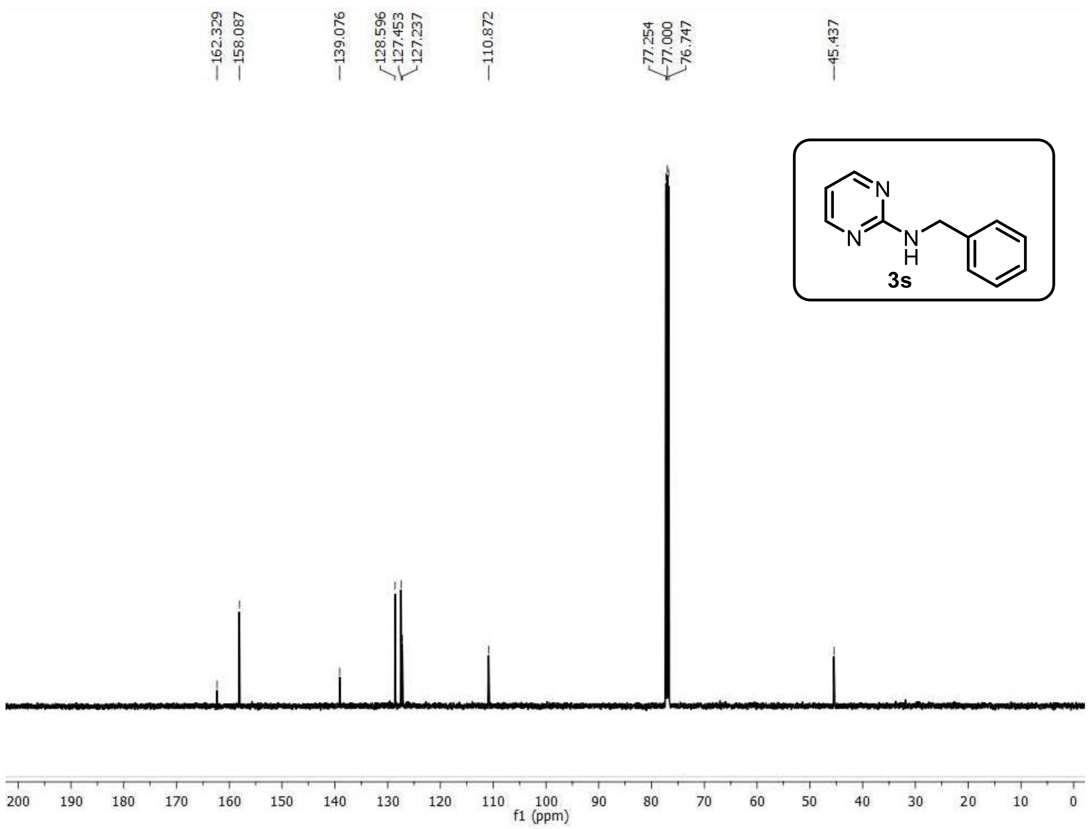


Figure S40. ^{1}H NMR spectrum of N-benzylbenzene-1,4-diamine (**3t**)[S13] in $CDCl_3$.

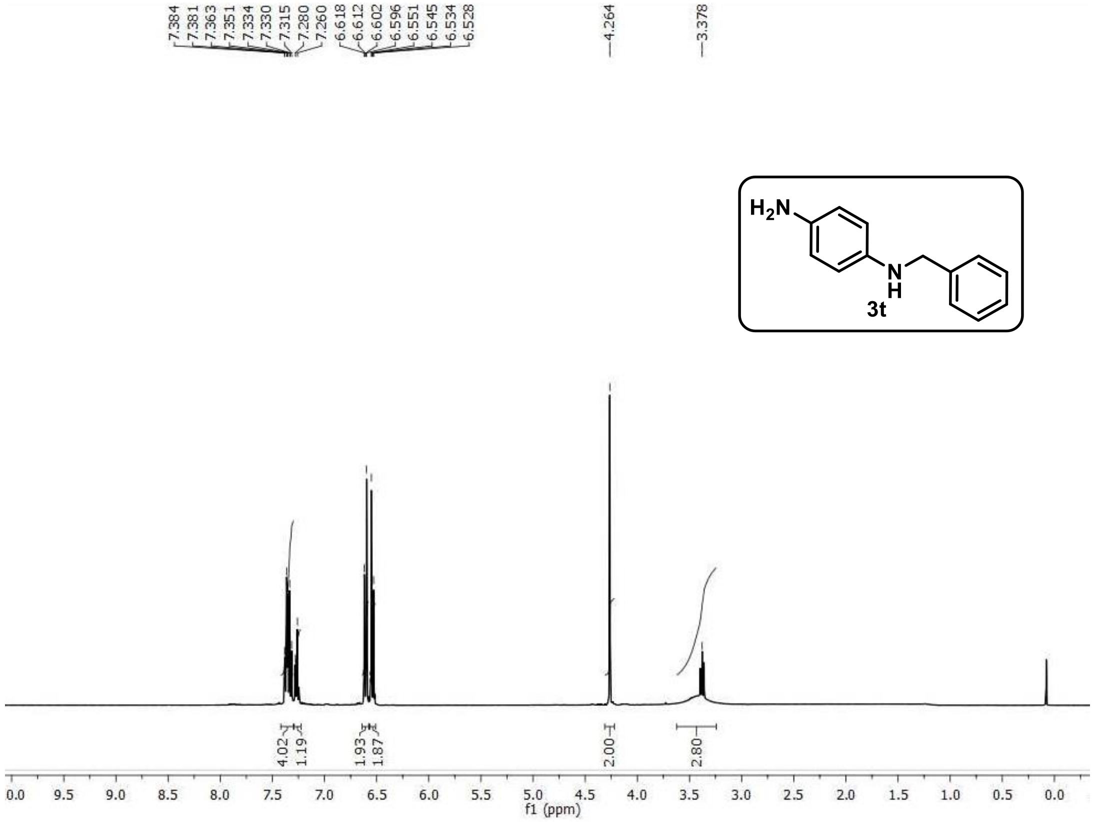


Figure S41. ^{13}C{^{1}H} NMR spectrum of N-benzylbenzene-1,4-diamine (**3t**)[S13] in $CDCl_3$.

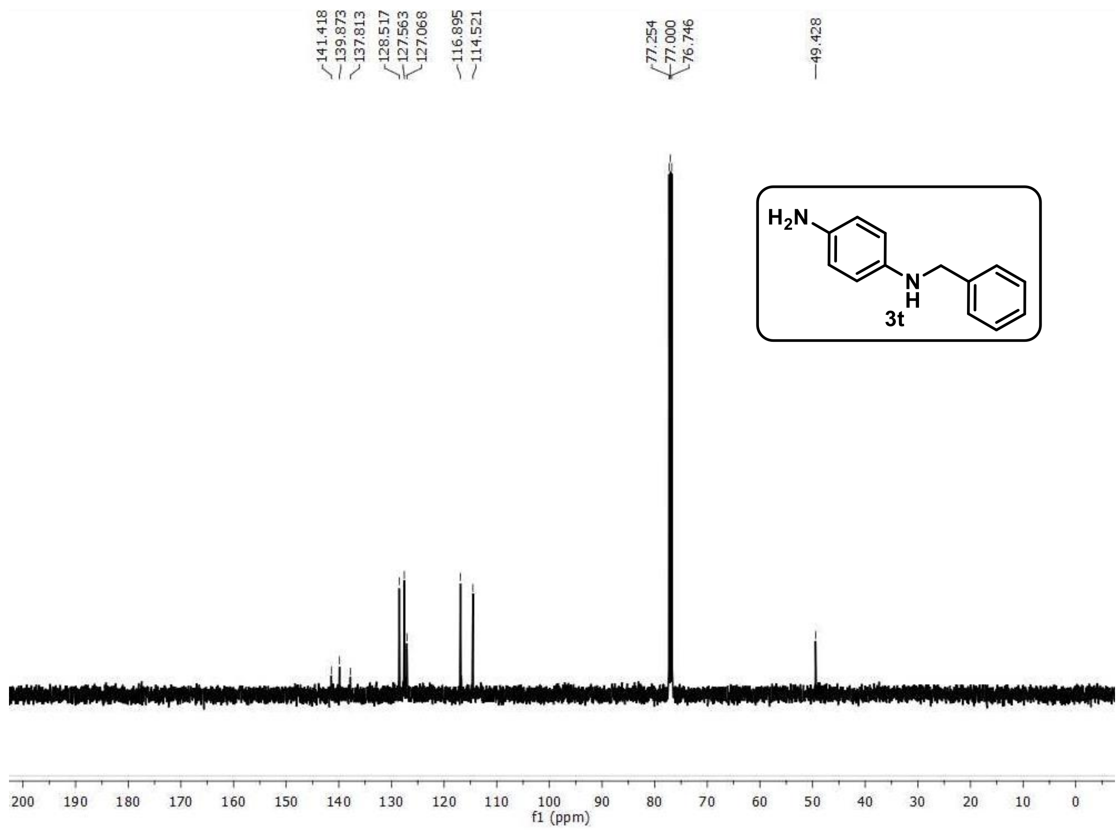


Figure S42. ^{1}H NMR spectrum of N-benzylbenzene-1,2-diamine (**3u**)[S14] in $CDCl_3$.

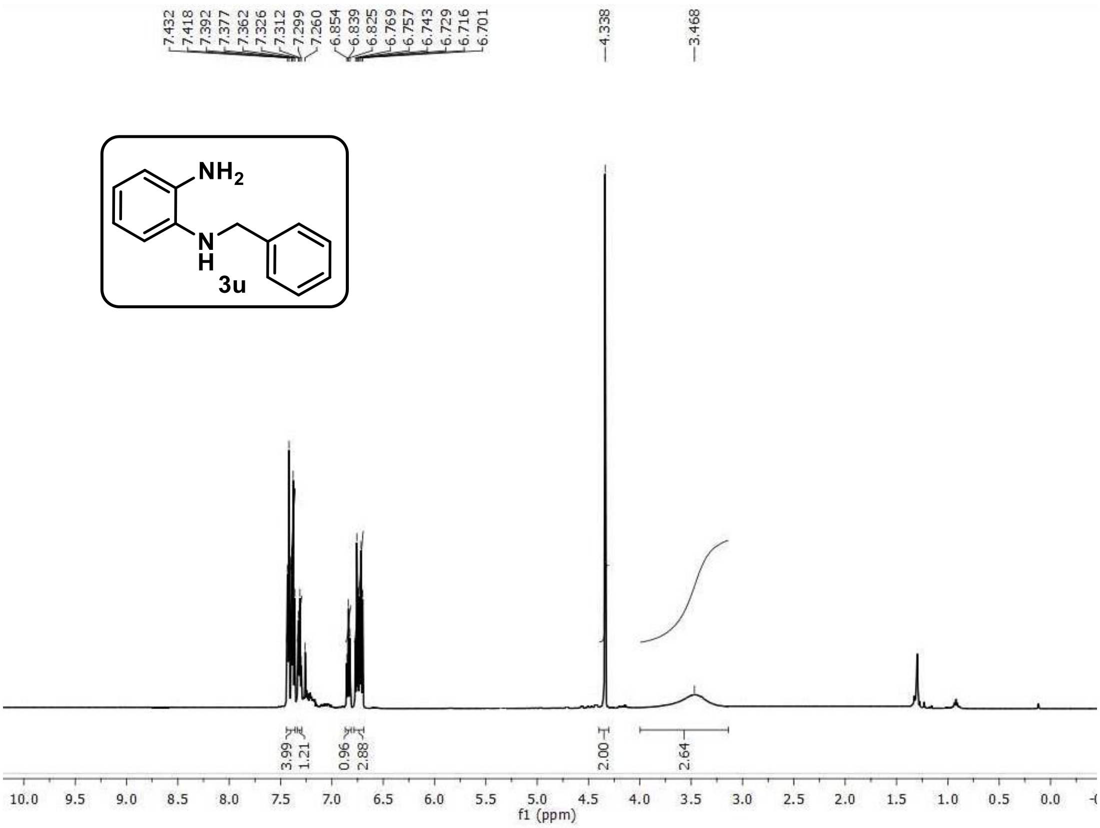


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzylbenzene-1,2-diamine (**3u**)[S14] in $CDCl_3$.

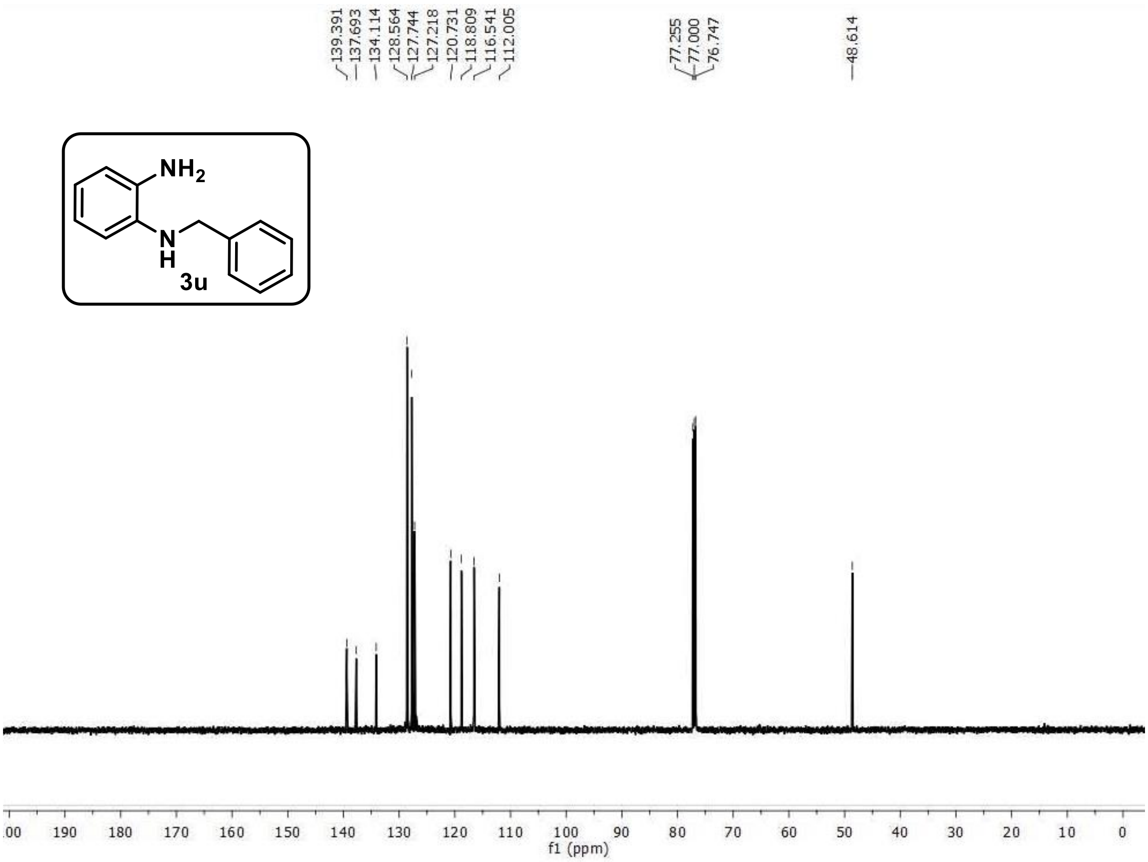


Figure S44. ^{1}H NMR spectrum of N-(4-fluorobenzyl)aniline (**4b**)[S5] in $CDCl_3$.

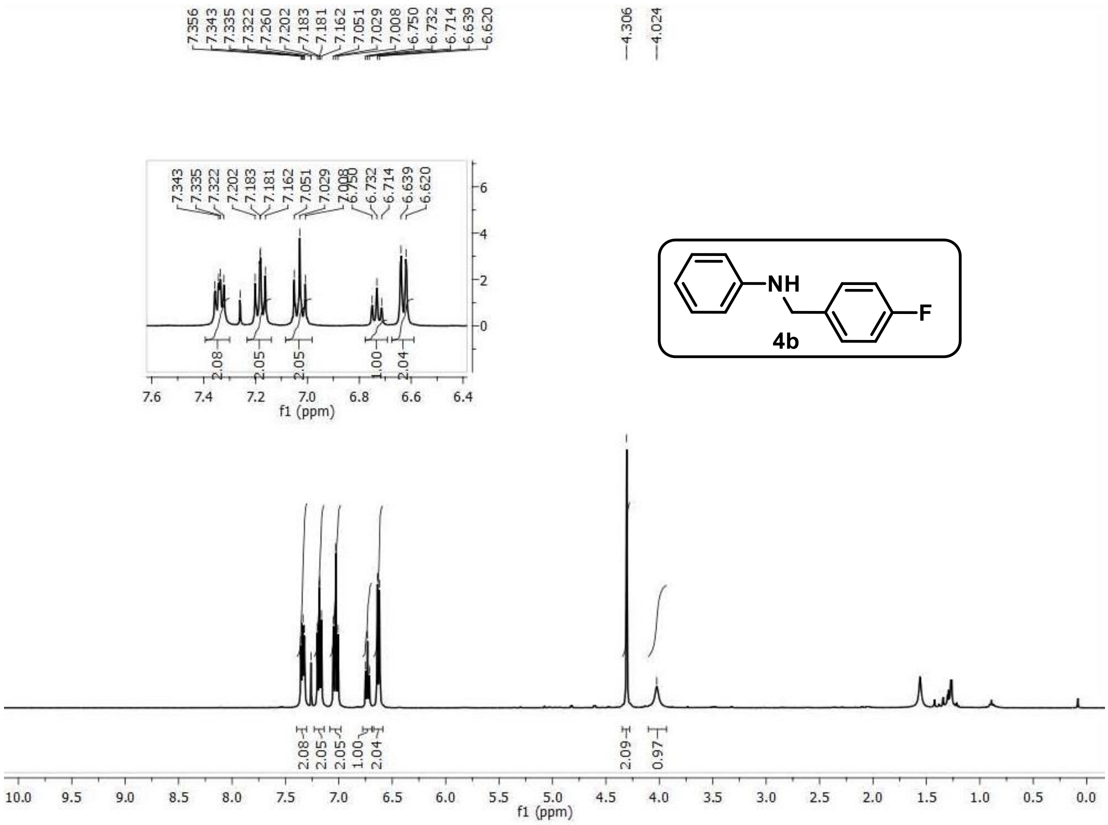


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of N-(4-fluorobenzyl)aniline (**4b**)[S5] in $CDCl_3$.

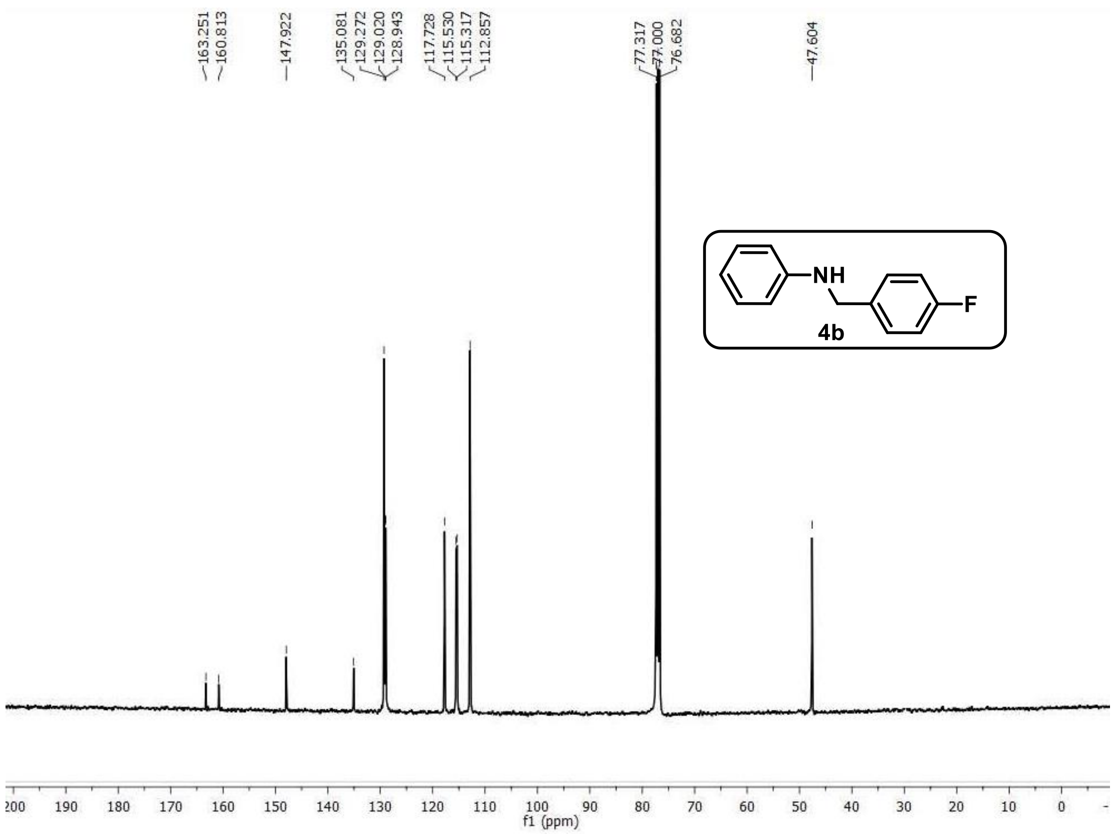


Figure S46. ^{19}F NMR spectrum of N-(4-fluorobenzyl)aniline (**4b**)[S5] in $CDCl_3$.

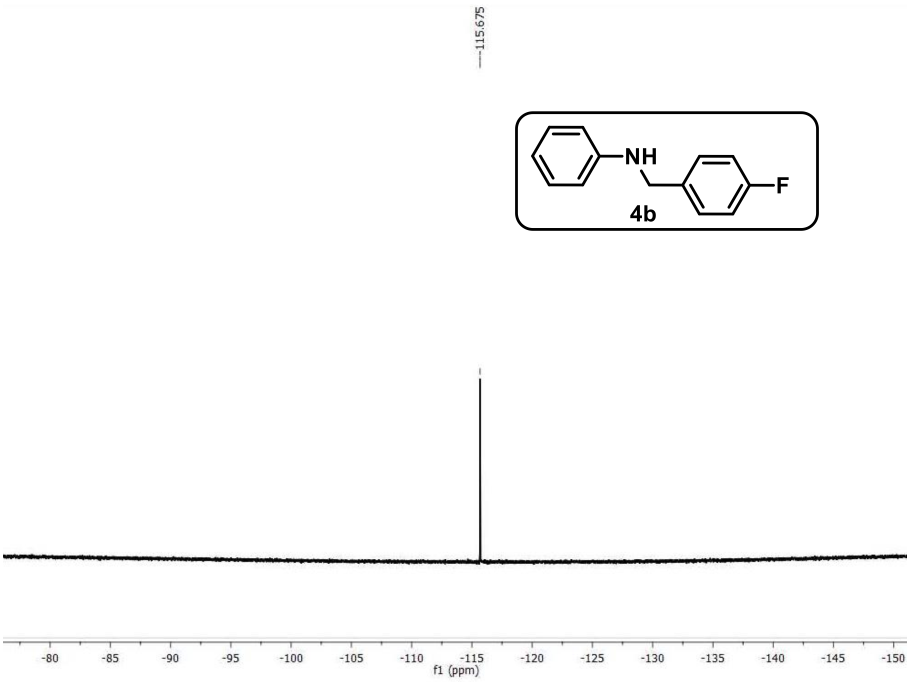


Figure S47. ^{1}H NMR spectrum of N-(4-chlorobenzyl)aniline (**4c**)[S4] in $CDCl_3$.

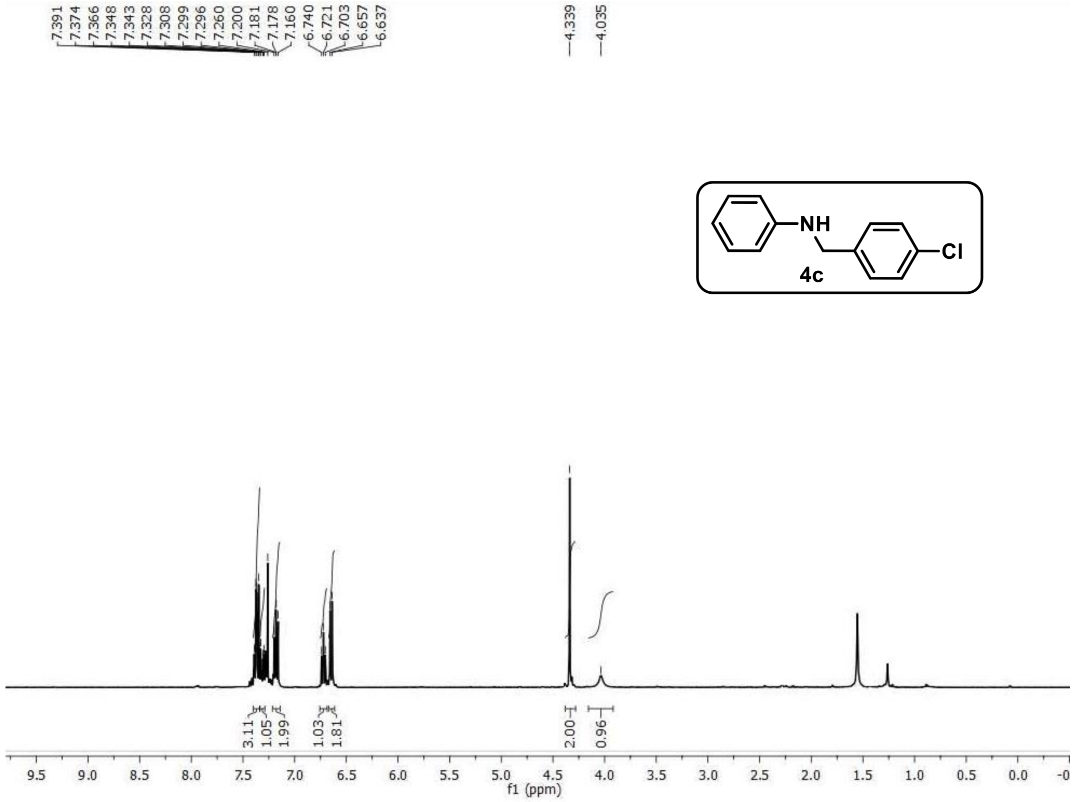


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of N-(4-chlorobenzyl)aniline (**4c**)[S4] in $CDCl_3$.

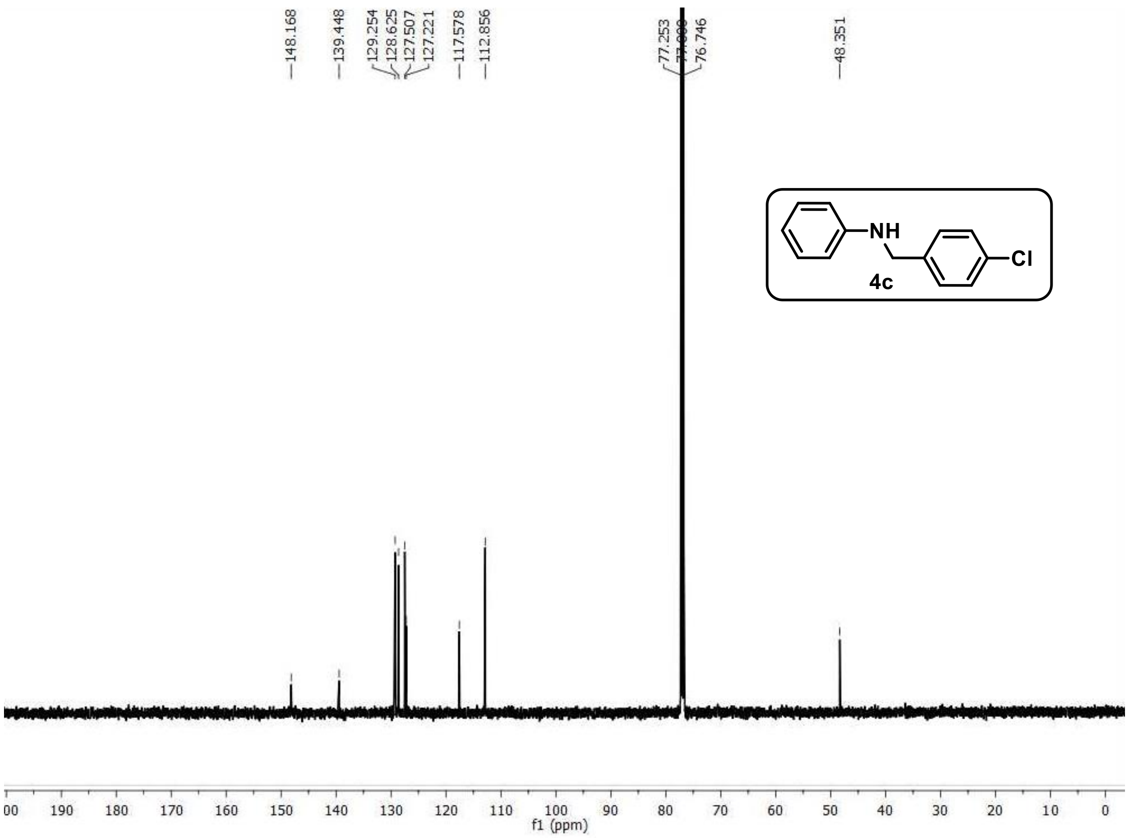


Figure S49. ^{1}H NMR spectrum of N-(4-bromobenzyl)aniline (**4d**)[S5] in $CDCl_3$.

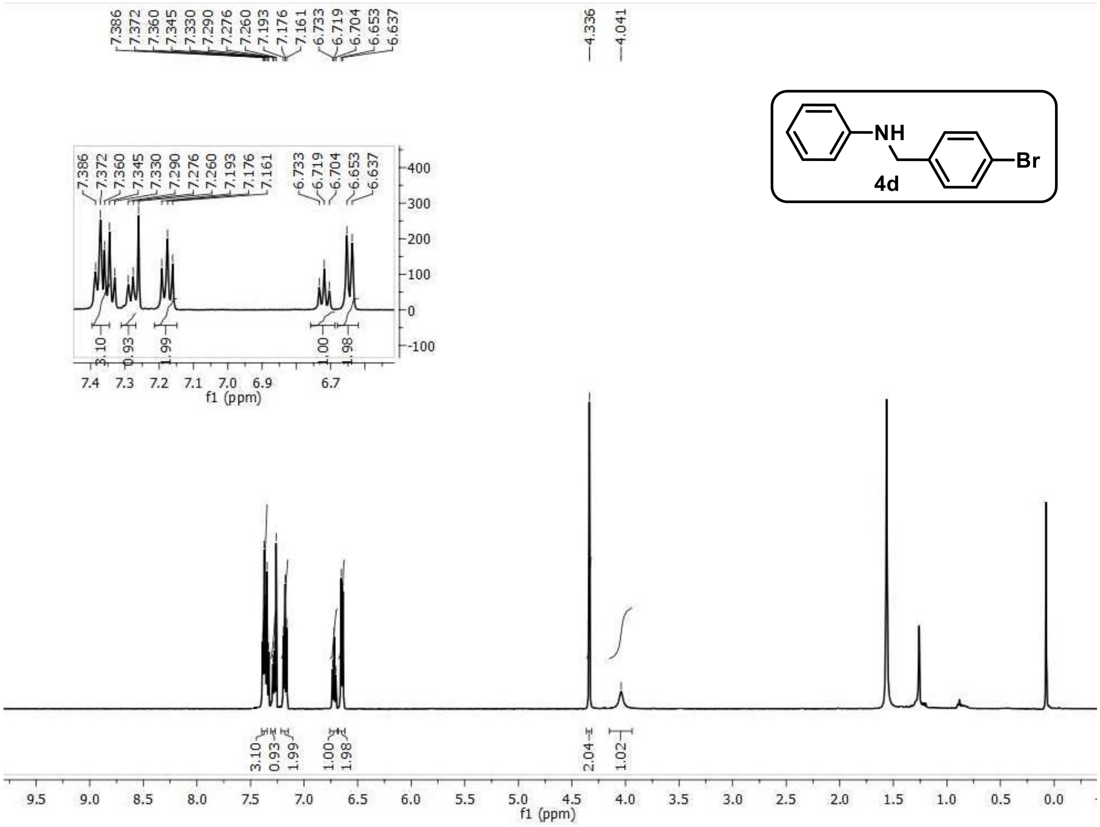


Figure S50. $^{13}C\{^1H\}$ NMR spectrum of N-(4-bromobenzyl)aniline (**4d**)[S5] in $CDCl_3$.

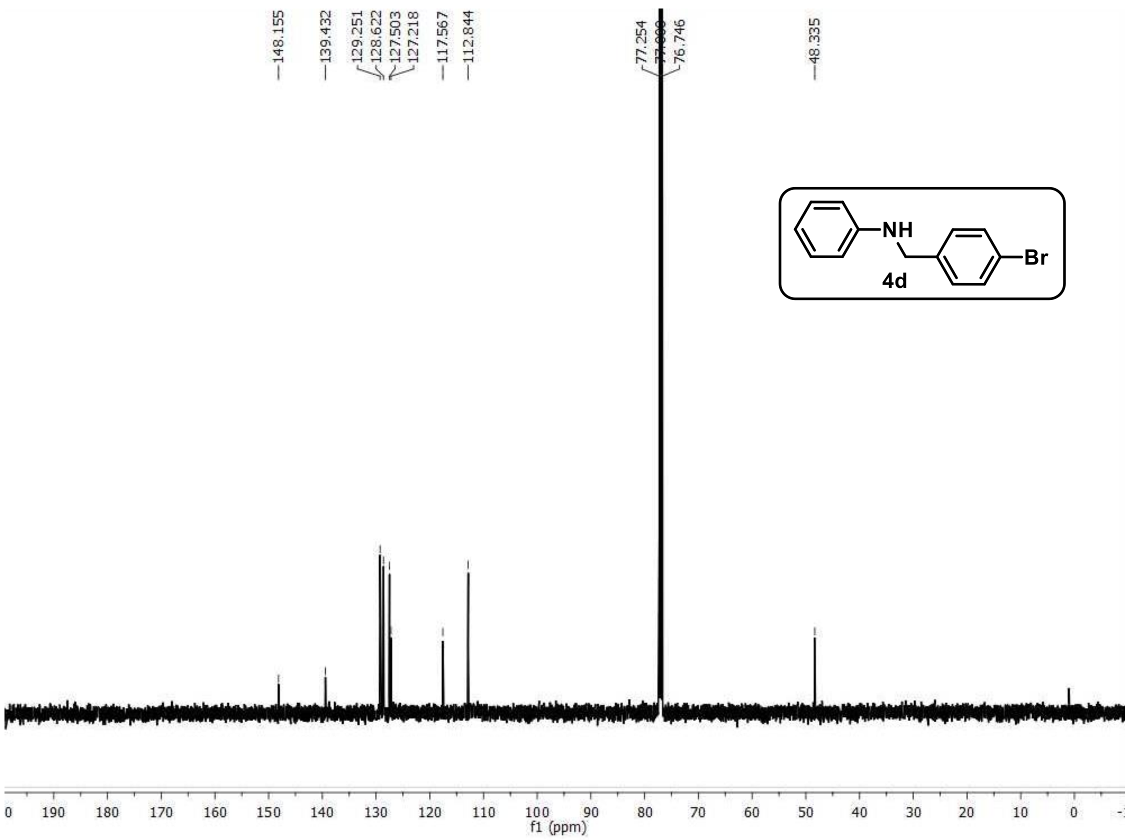


Figure S51. ^{1}H NMR spectrum of N-(4-iodobenzyl)aniline (**4e**)[S15] in $CDCl_3$.

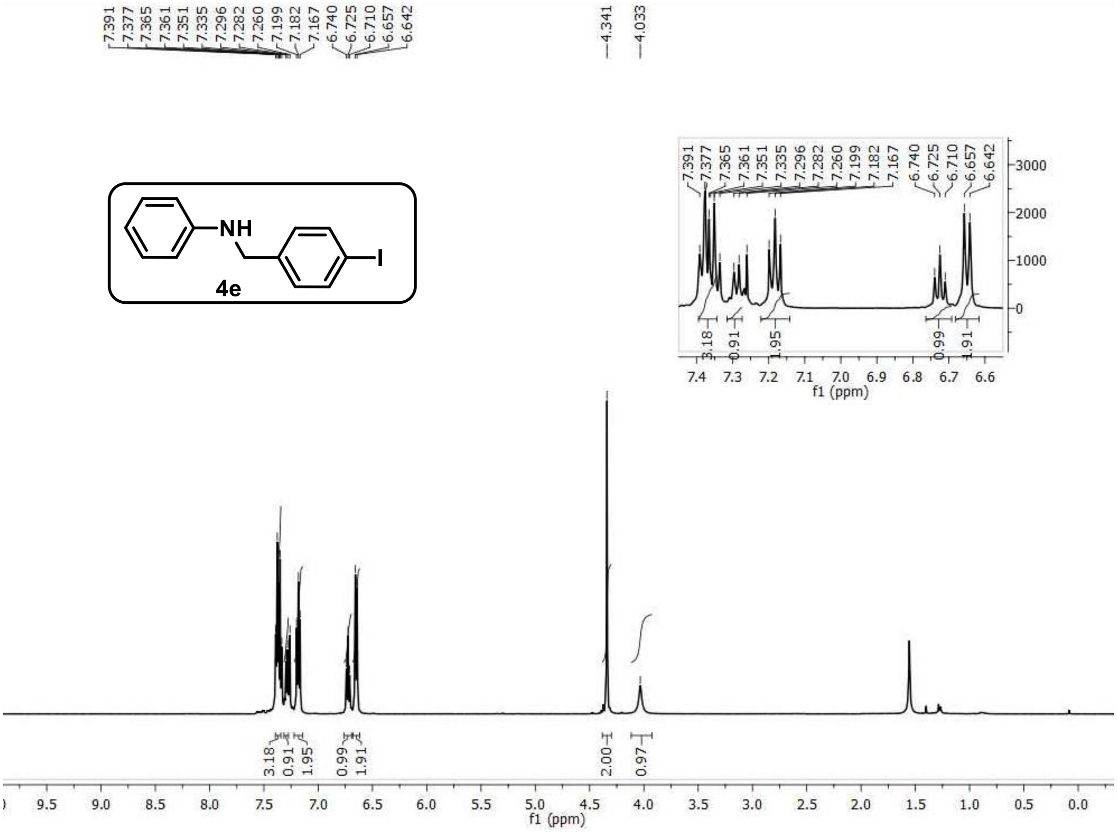


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of N-(4-iodobenzyl)aniline (**4e**)[S15] in $CDCl_3$.

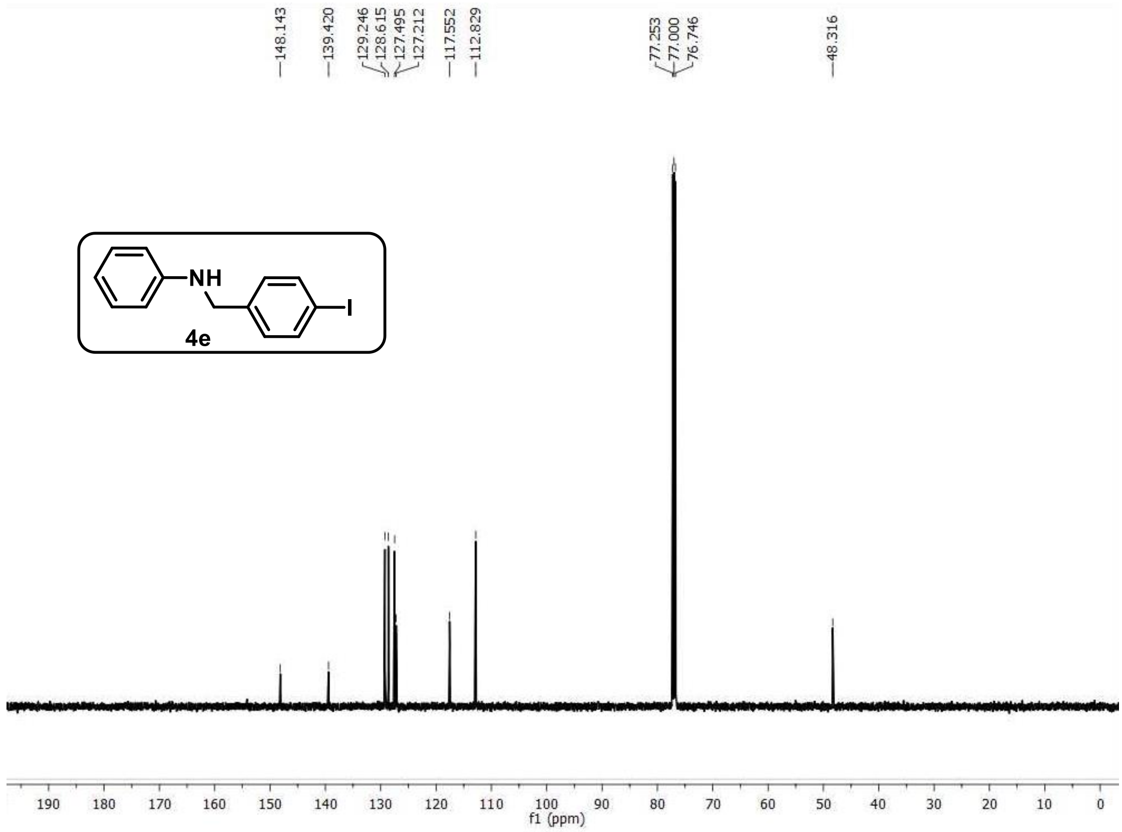


Figure S53. ^{1}H NMR spectrum of N-(4-methylbenzyl)aniline (**4f**)[S4] in $CDCl_3$.

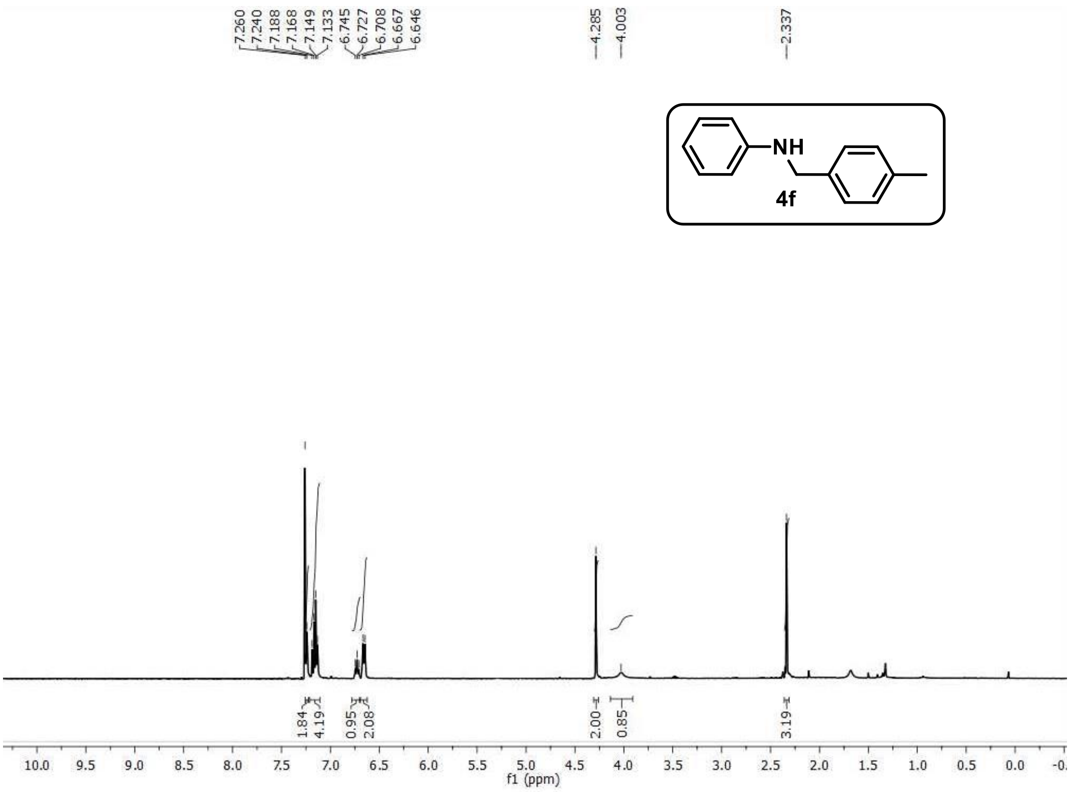


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of N-(4-methylbenzyl)aniline (**4f**)[S4] in $CDCl_3$.

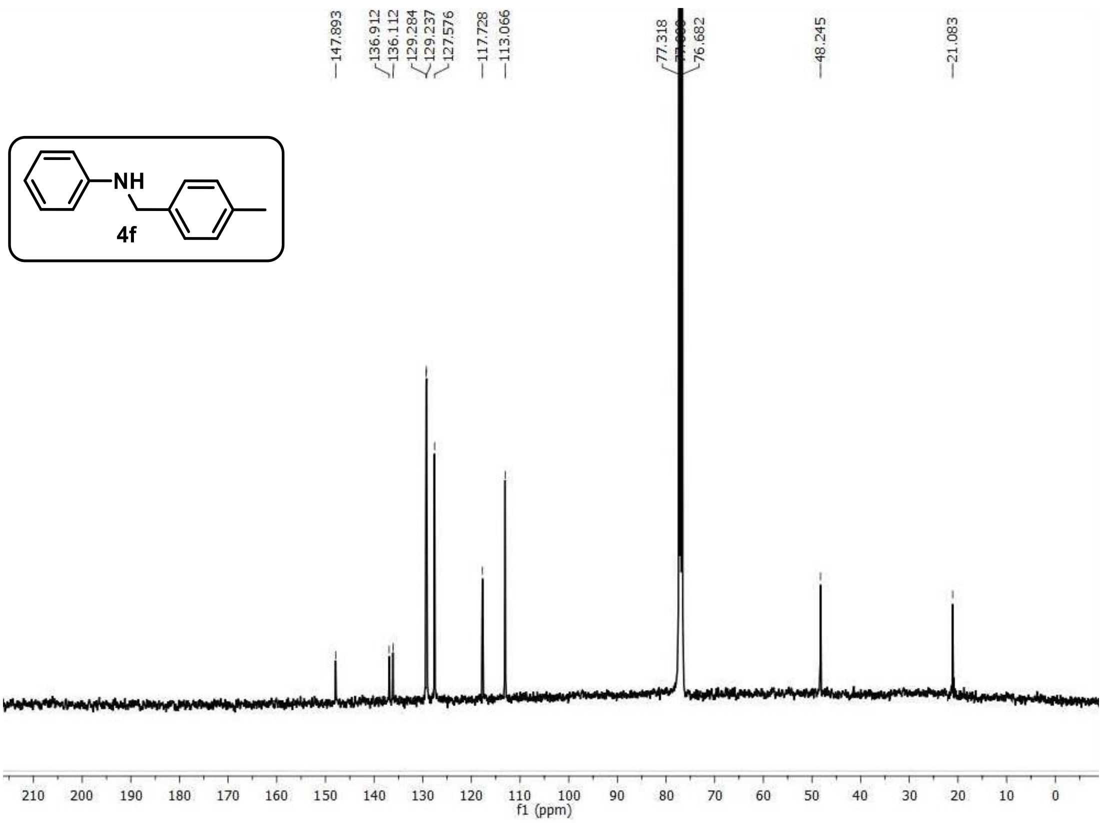


Figure S55. ^{1}H NMR spectrum of N-(4-isopropylbenzyl)aniline (**4g**)[S4] in $CDCl_3$.

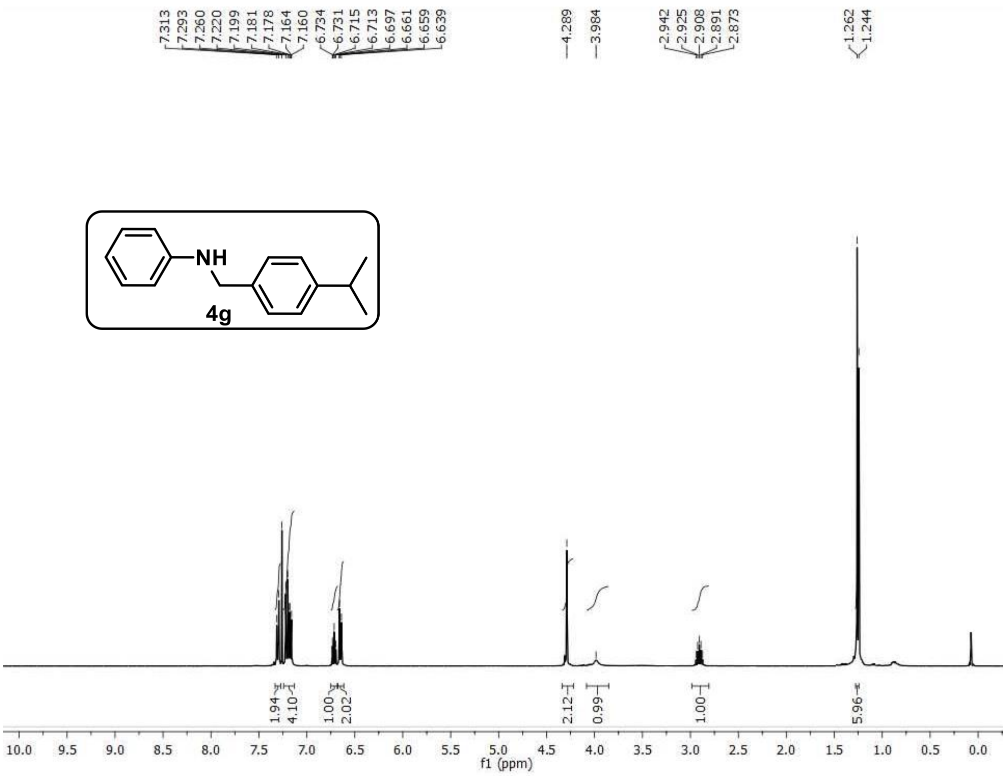


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of N-(4-isopropylbenzyl)aniline (**4g**)[S4] in $CDCl_3$.

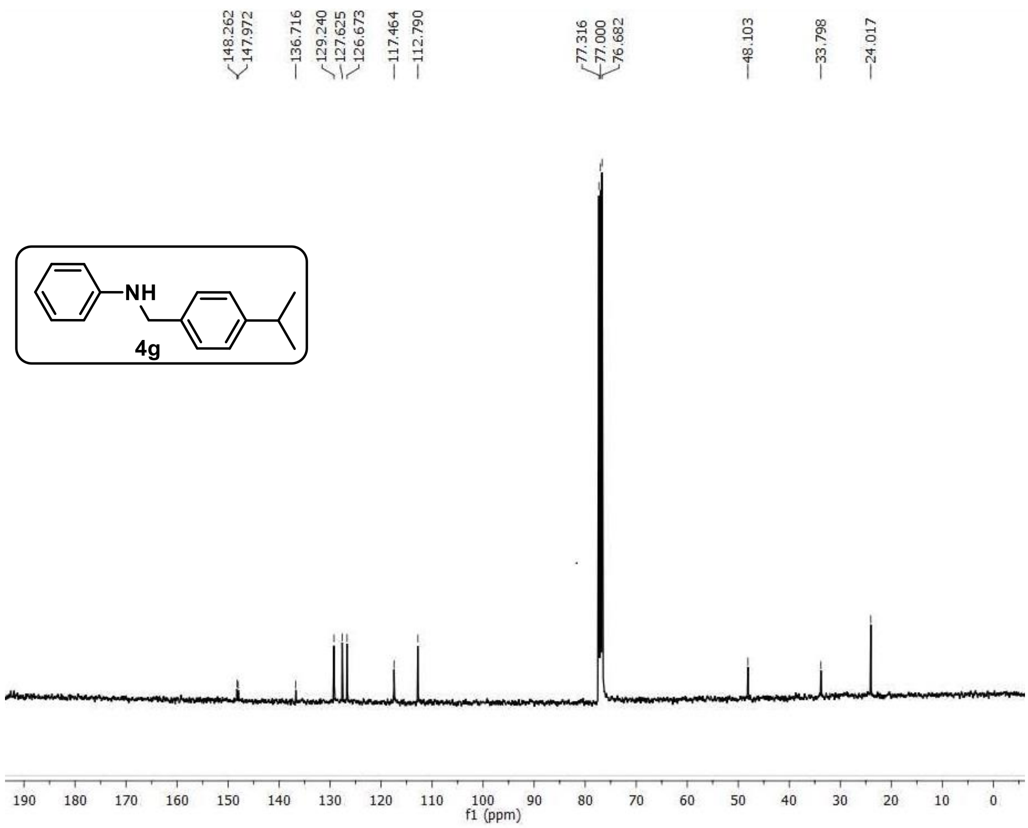


Figure S57. ^{1}H NMR spectrum of N-(4-methoxybenzyl)aniline (**4h**)[S4] in $CDCl_3$.

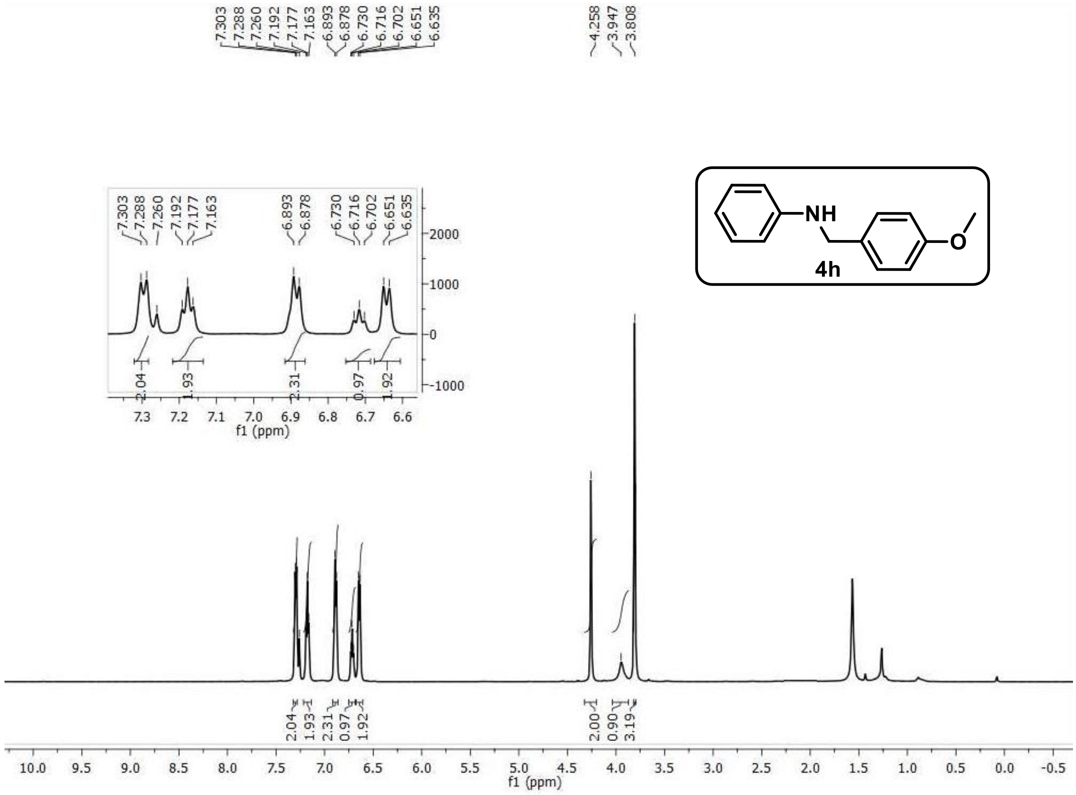


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of N-(4-methoxybenzyl)aniline (**4h**)[S4] in $CDCl_3$.

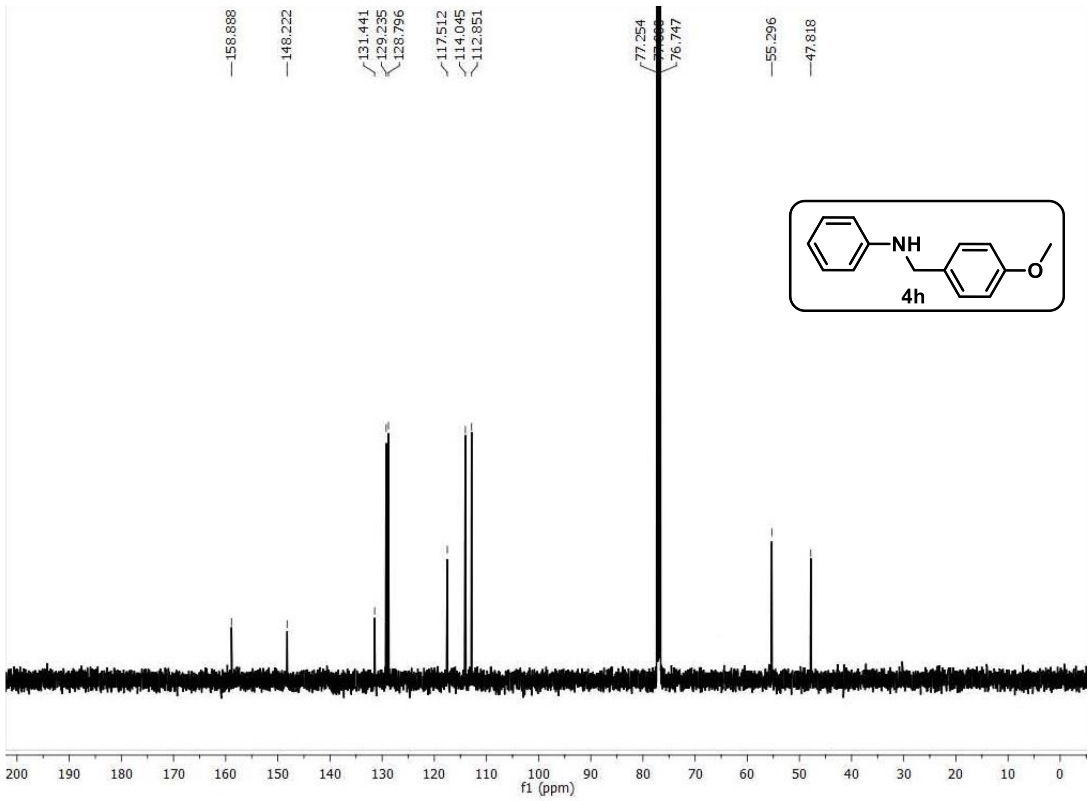


Figure S59. ^{1}H NMR spectrum of N-(2-methylbenzyl)aniline (**4i**)[S4] in $CDCl_3$.

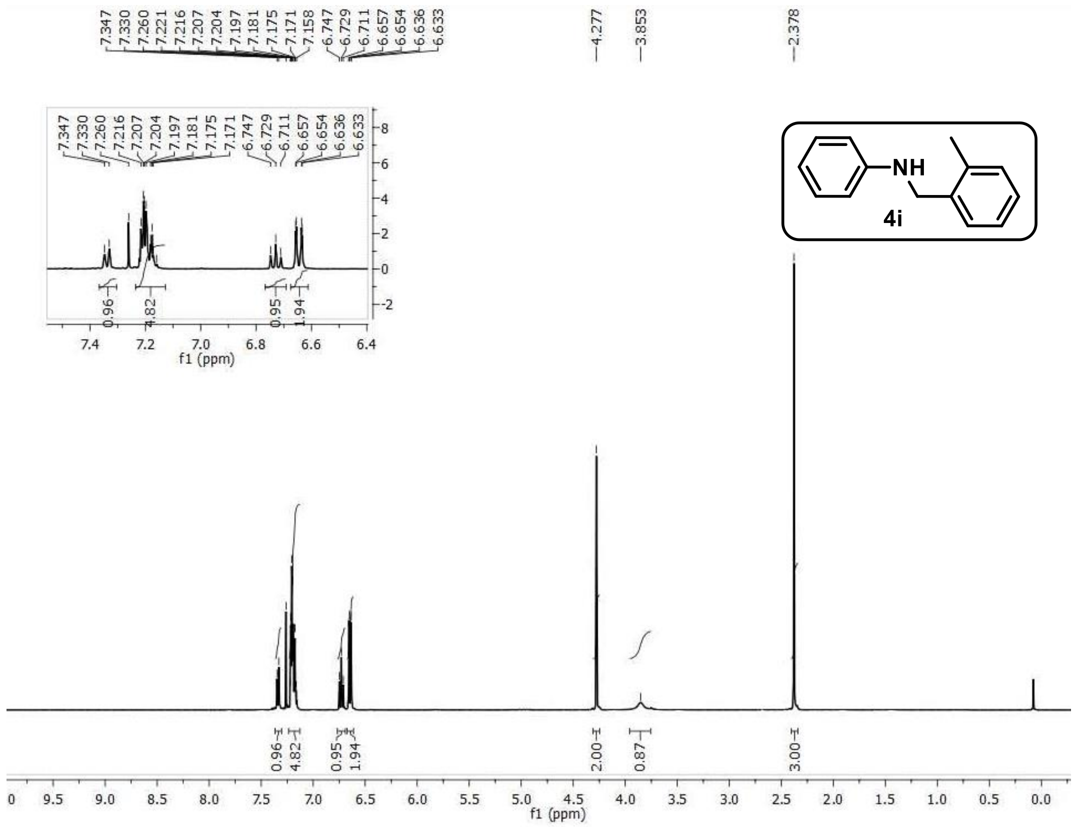


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of N-(2-methylbenzyl)aniline (**4i**)[S4] in $CDCl_3$.

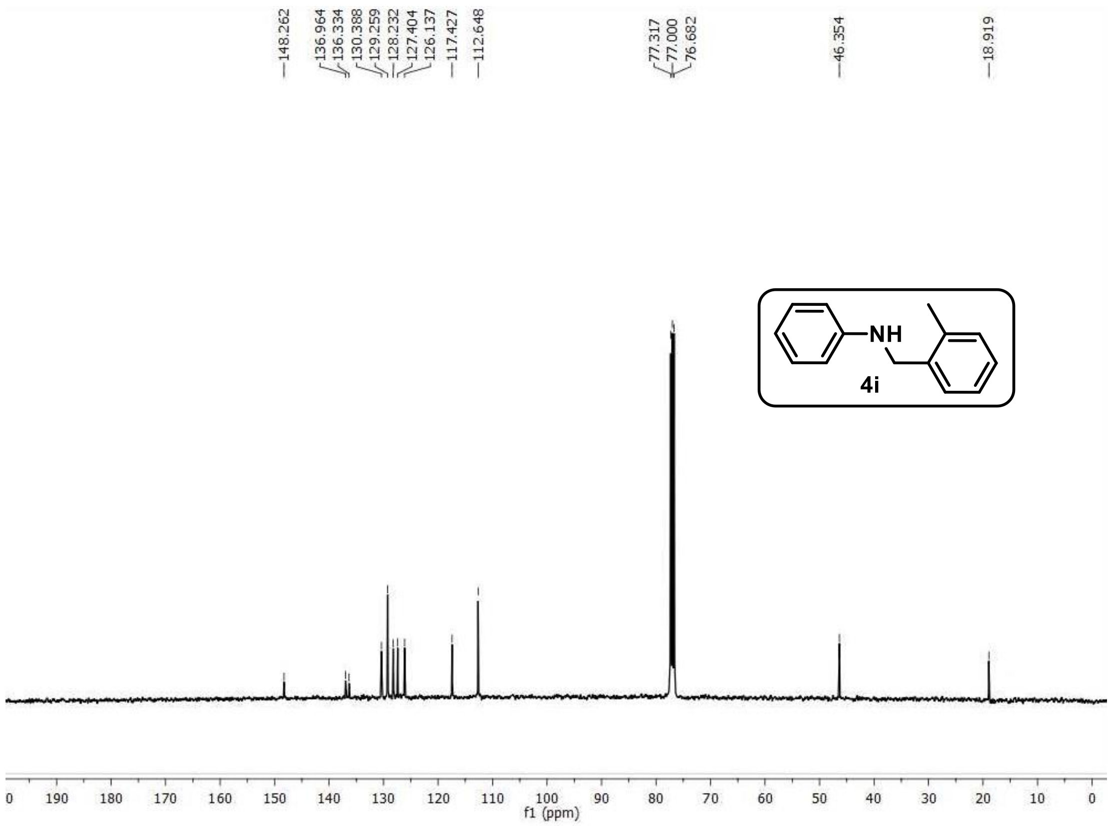


Figure S61. ^{1}H NMR spectrum of N-(3,5-dimethoxybenzyl)aniline (**4j**)[S16] in $CDCl_3$.

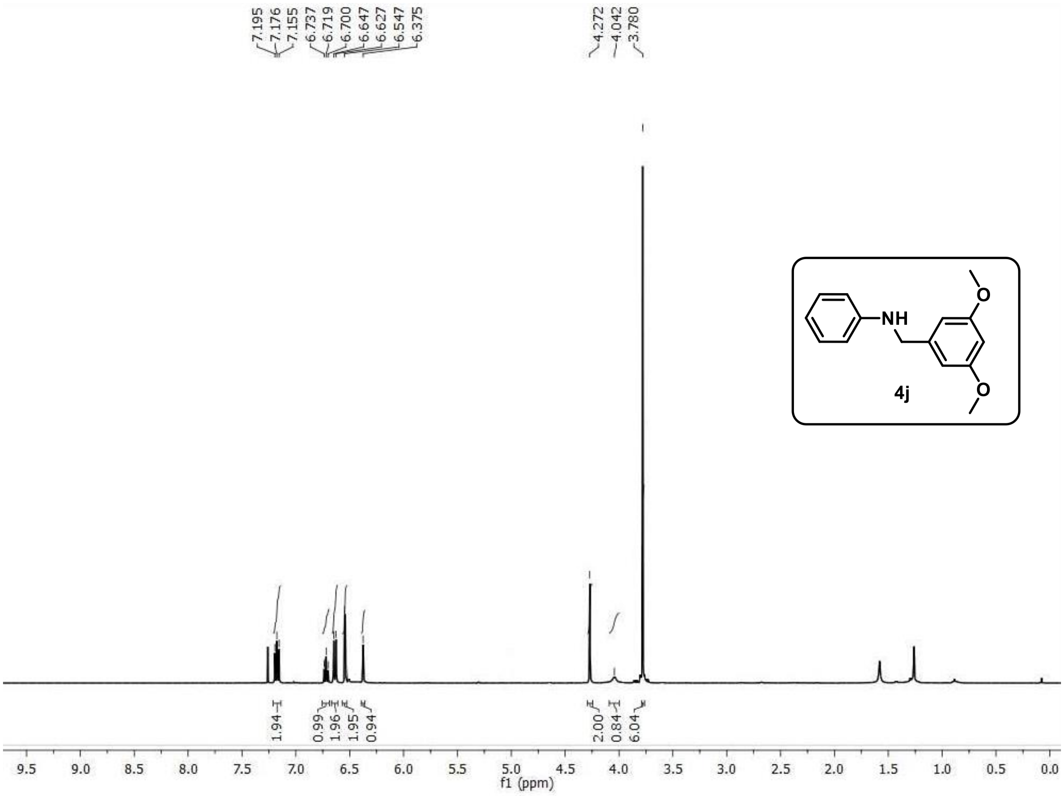


Figure S62. ^{13}C{^{1}H} NMR spectrum of N-(3,5-dimethoxybenzyl)aniline (**4j**)[S16] in $CDCl_3$.

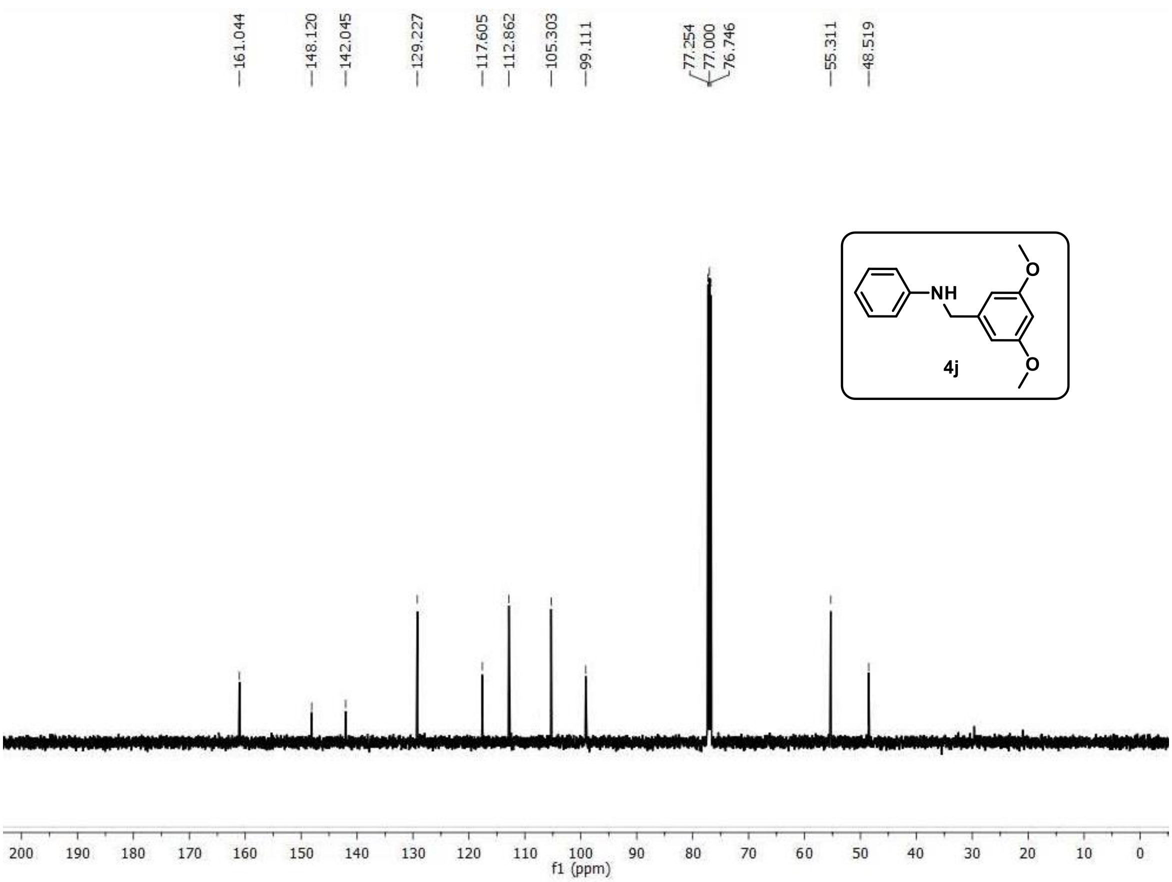


Figure S63. ^{1}H NMR spectrum of N-(3,4,5-trimethoxybenzyl)aniline (**4k**)[S17] in $CDCl_3$.

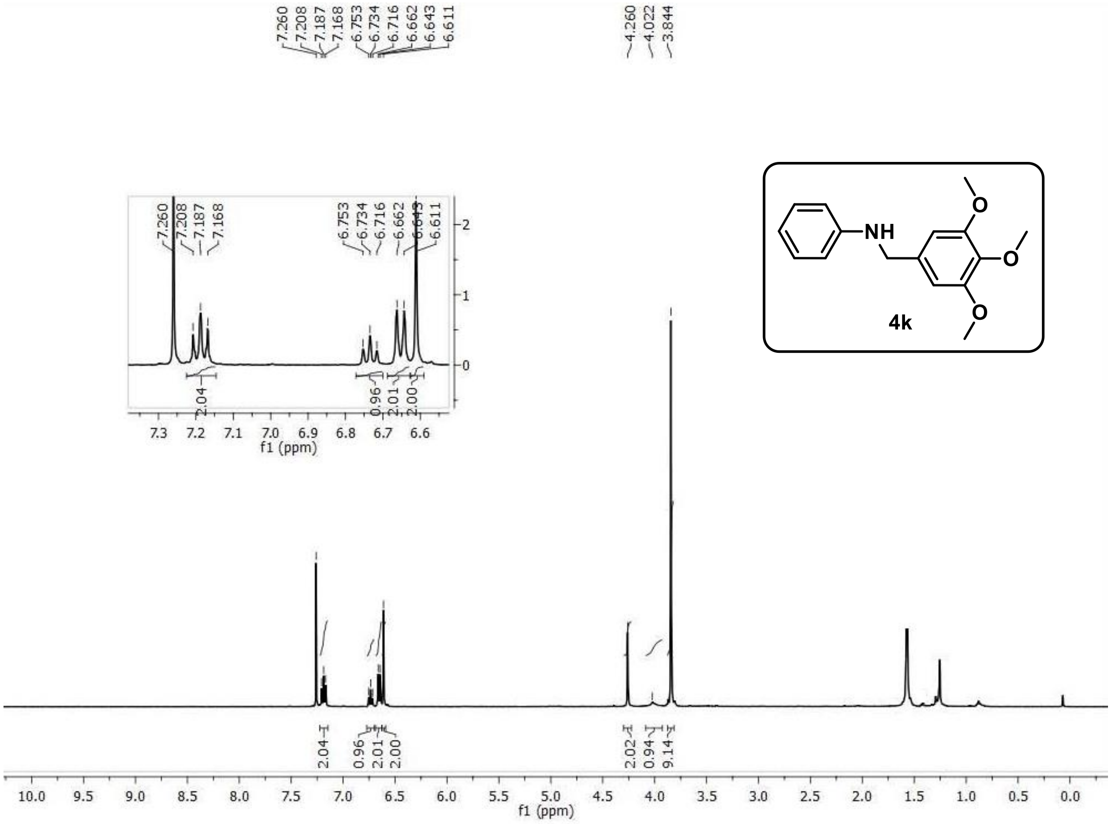


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of N-(3,4,5-trimethoxybenzyl)aniline (**4k**)[S17] in $CDCl_3$.

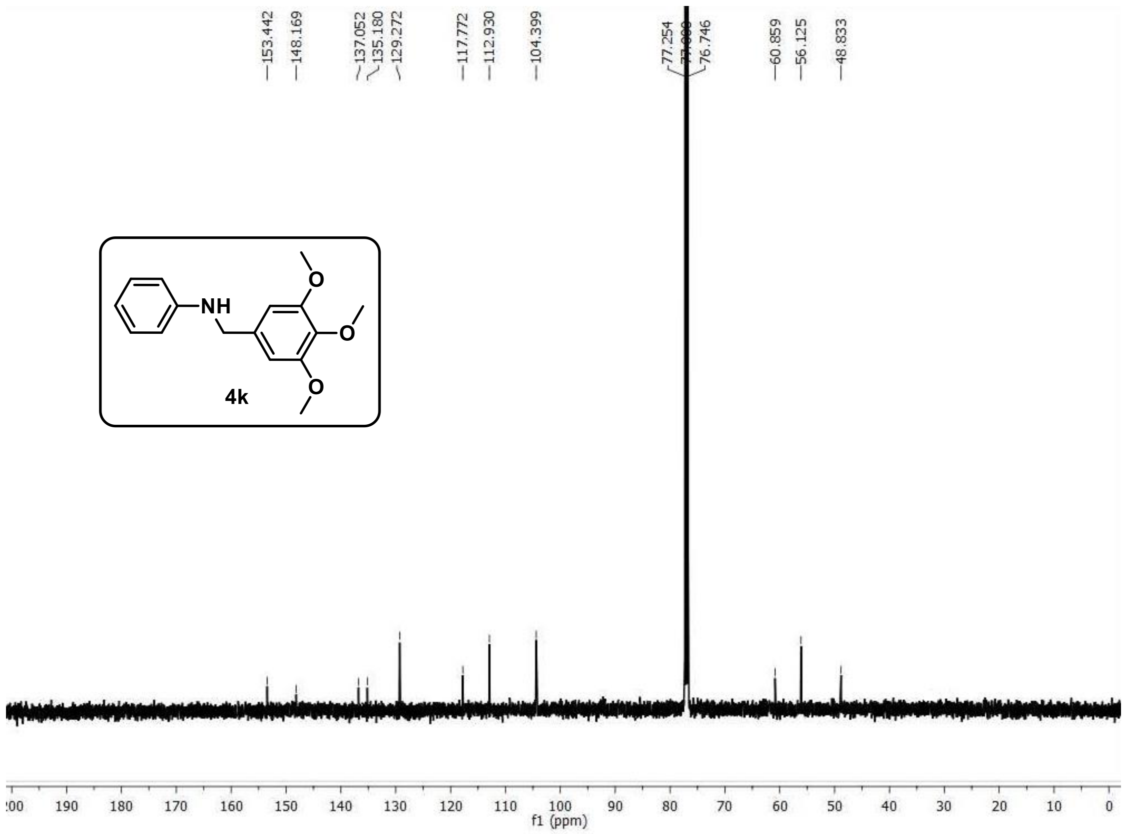


Figure S65. ^{1}H NMR spectrum of N-(3-(trifluoromethyl)benzyl)aniline (**4l**)[S18] in $CDCl_3$.

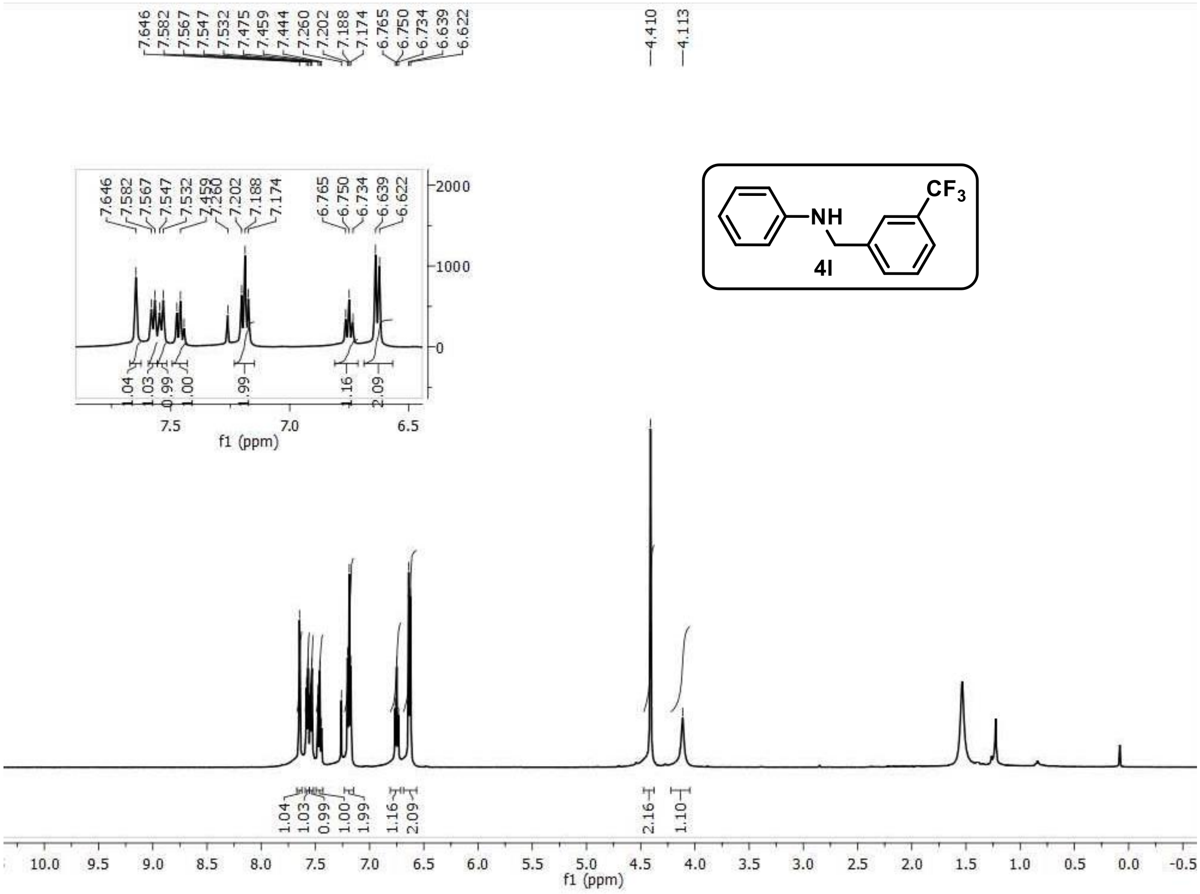


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of N-(3-(trifluoromethyl)benzyl)aniline (**4l**)[S18] in $CDCl_3$.

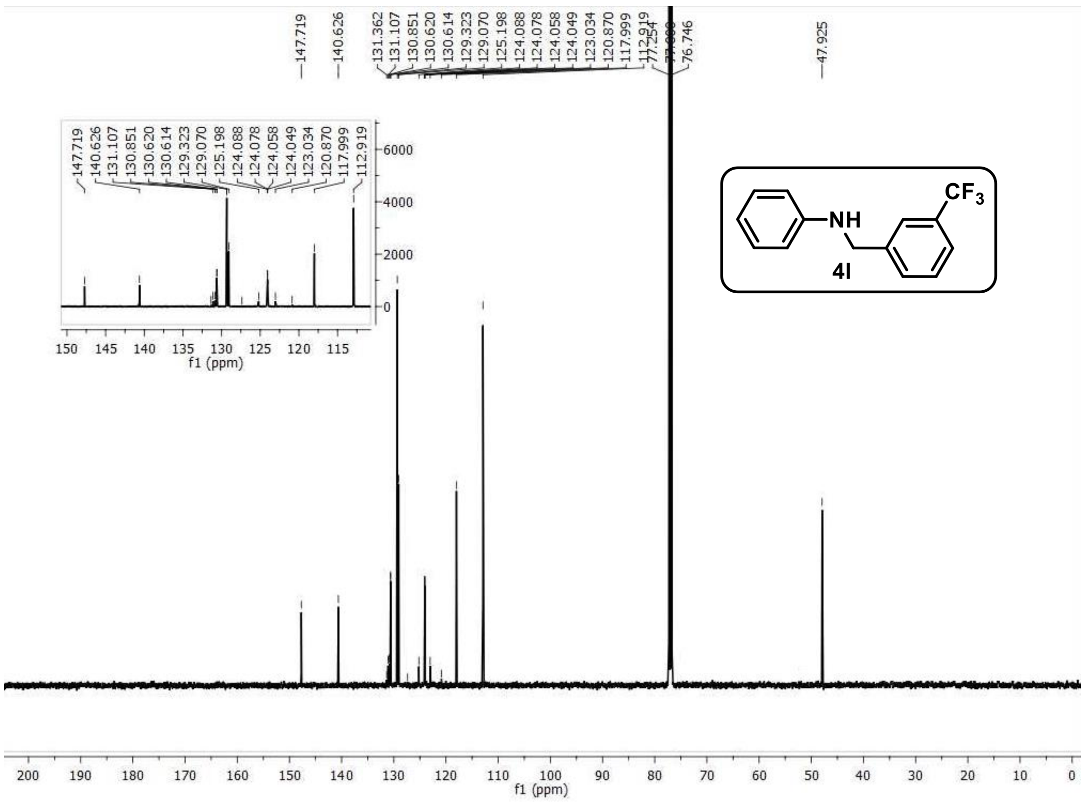


Figure S67. ^{19}F NMR spectrum of N-(3-(trifluoromethyl)benzyl)aniline (**4l**)[S18] in $CDCl_3$.

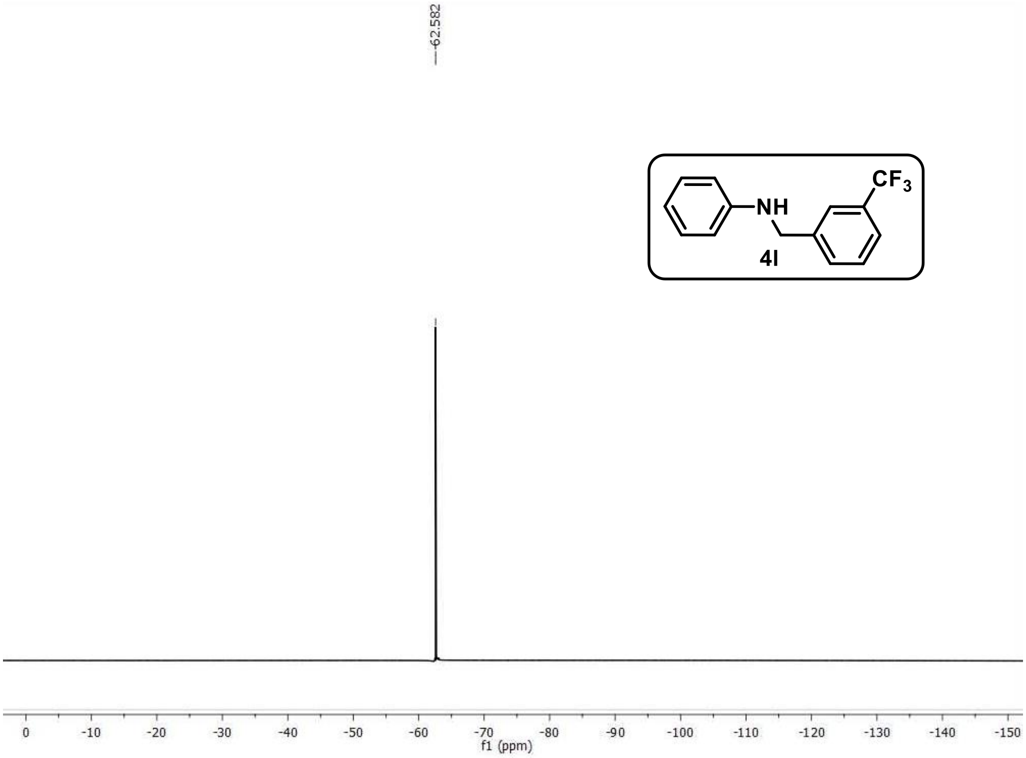


Figure S68. ^{1}H NMR spectrum of N-(naphthalen-1-ylmethyl)aniline (**4m**)[S4] in $CDCl_3$.

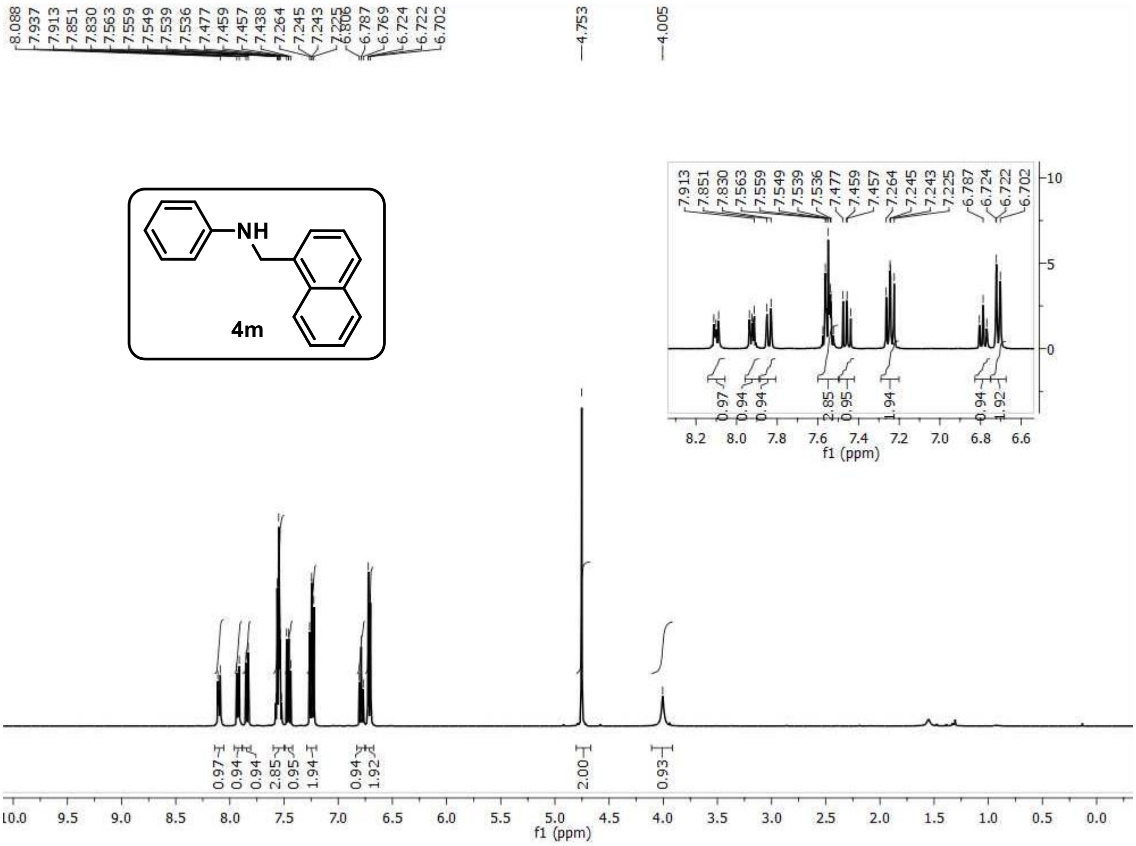


Figure S69. ^{13}C{^{1}H} NMR spectrum of N-(naphthalen-1-ylmethyl)aniline (**4m**)[S4] in $CDCl_3$.

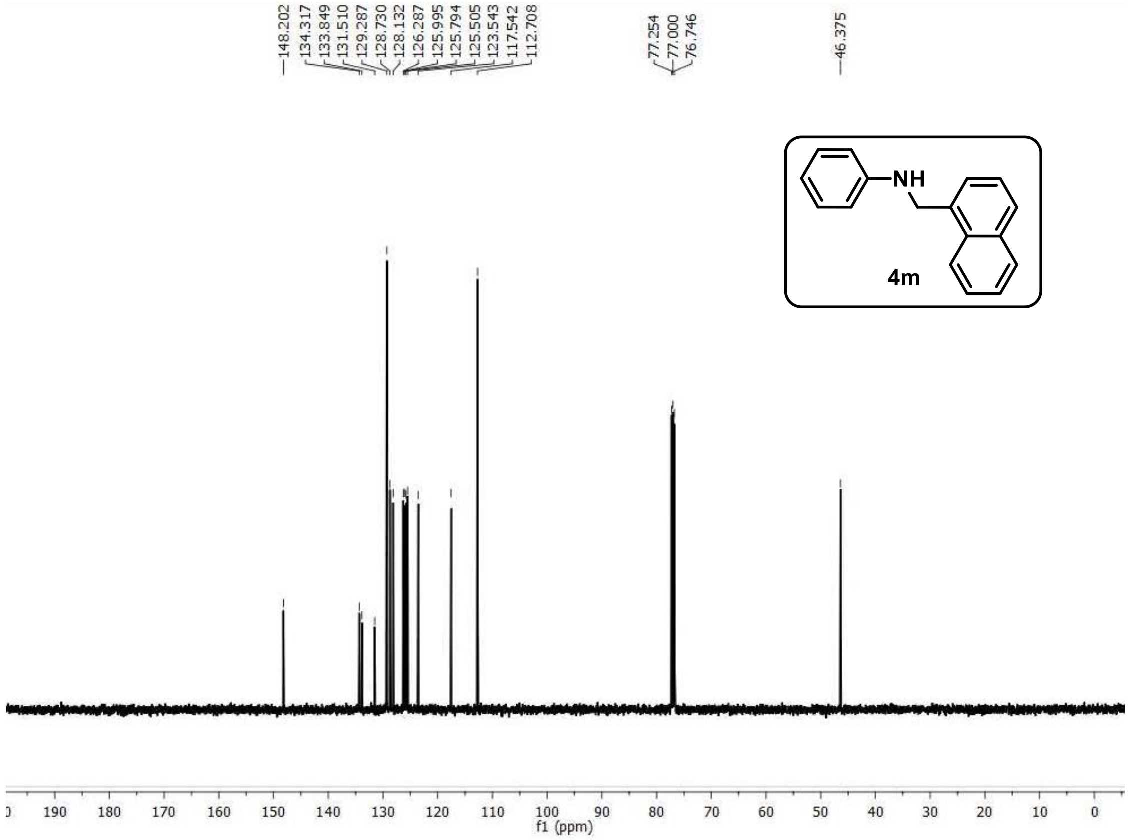


Figure S70. ^{1}H NMR spectrum of N-benzhydrylaniline (**4n**)[S19] in $CDCl_3$.

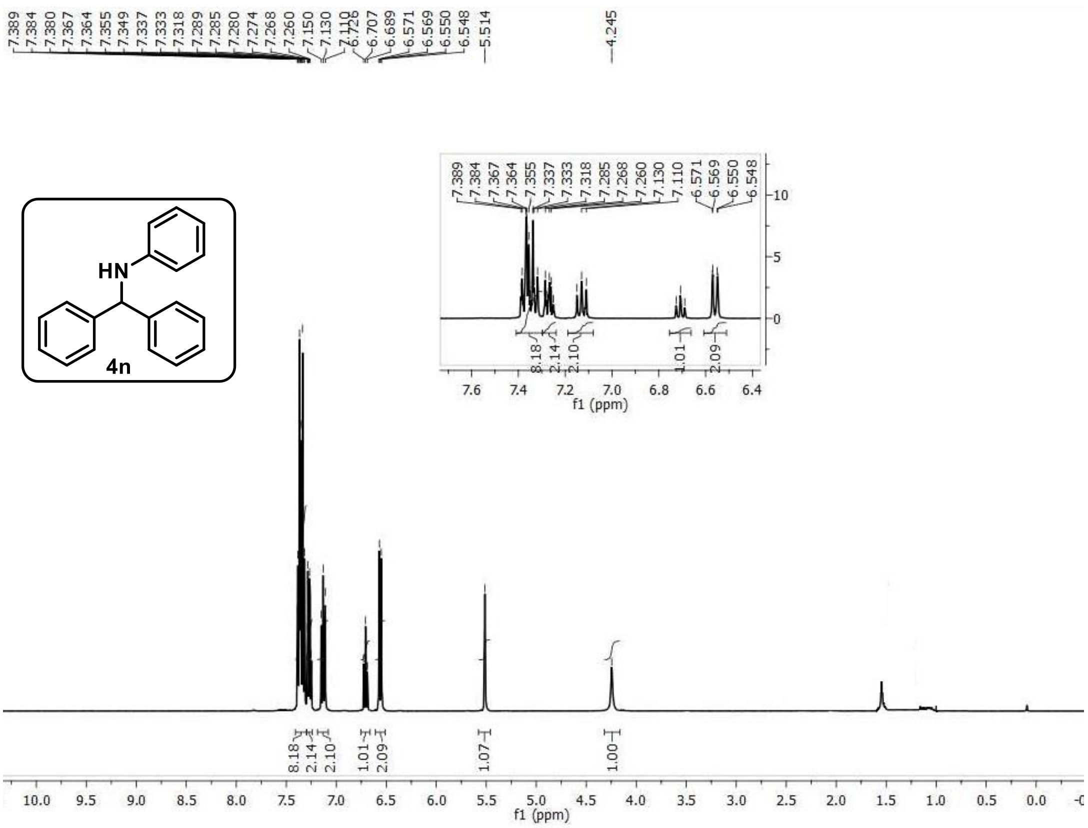


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzhydrylaniline (**4n**)[S19] in $CDCl_3$.

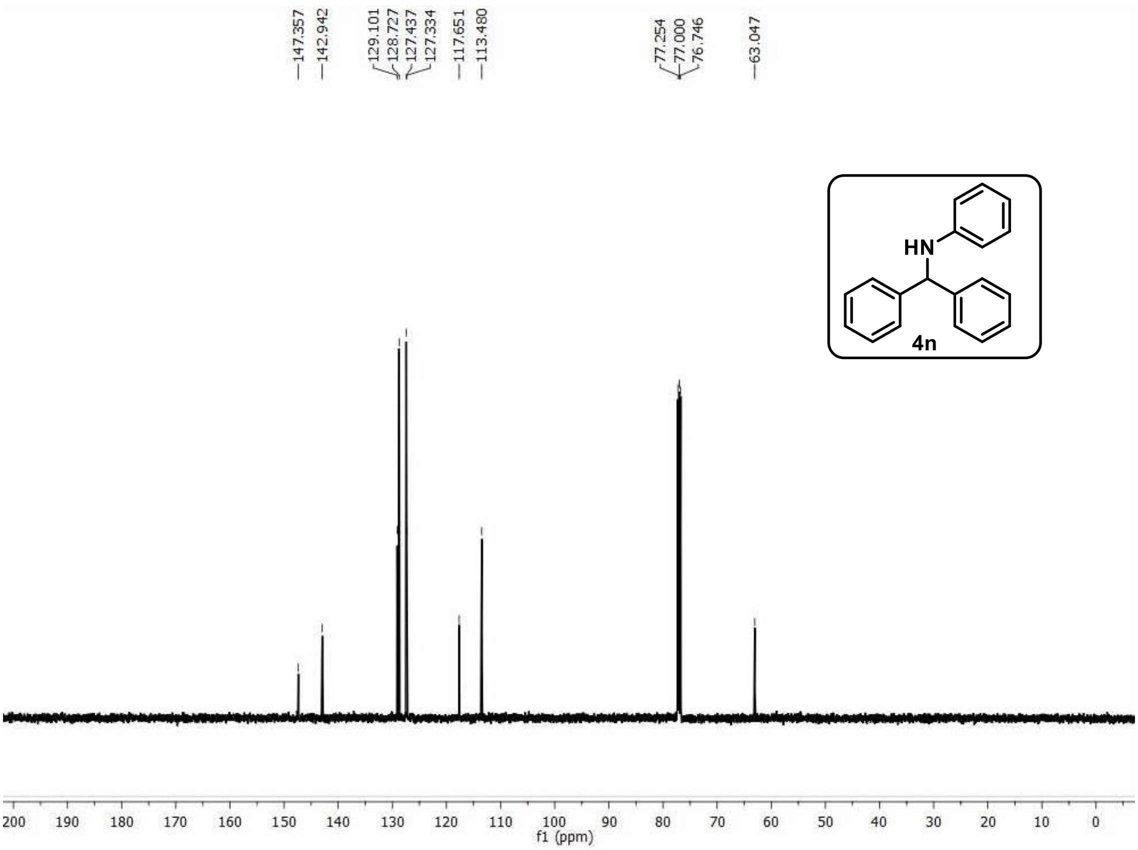


Figure S72. ^{1}H NMR spectrum of N-(di-p-tolylmethyl)aniline (**4o**)[S19] in $CDCl_3$.

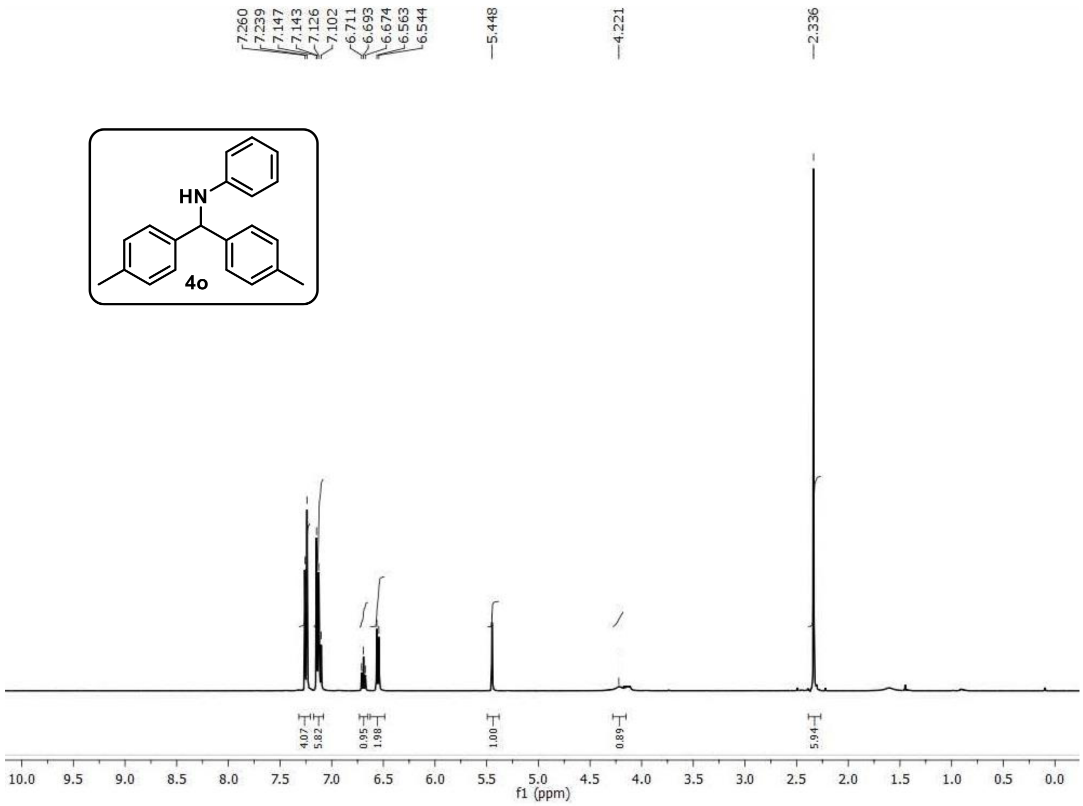


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of N-(di-p-tolylmethyl)aniline (**4o**)[S19] in $CDCl_3$.

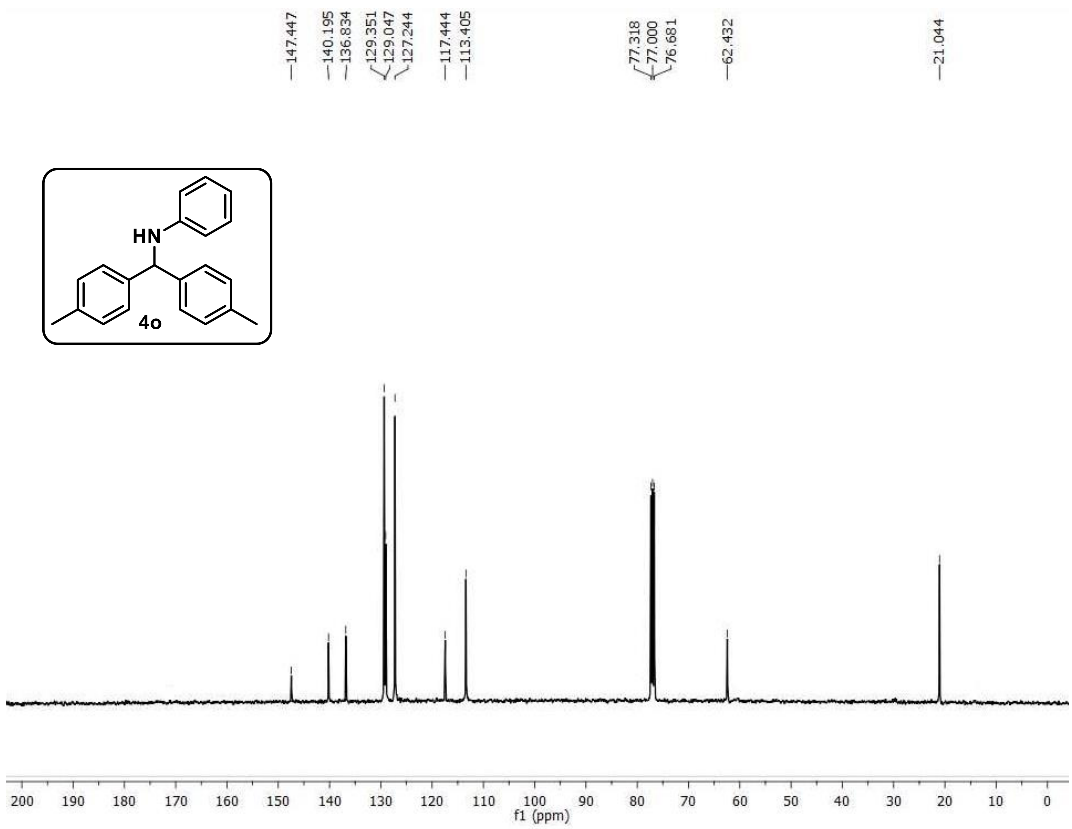


Figure S74. ^{1}H NMR spectrum of N-(cyclohexylmethyl)-4-ethylaniline (**4p**) in $CDCl_3$.

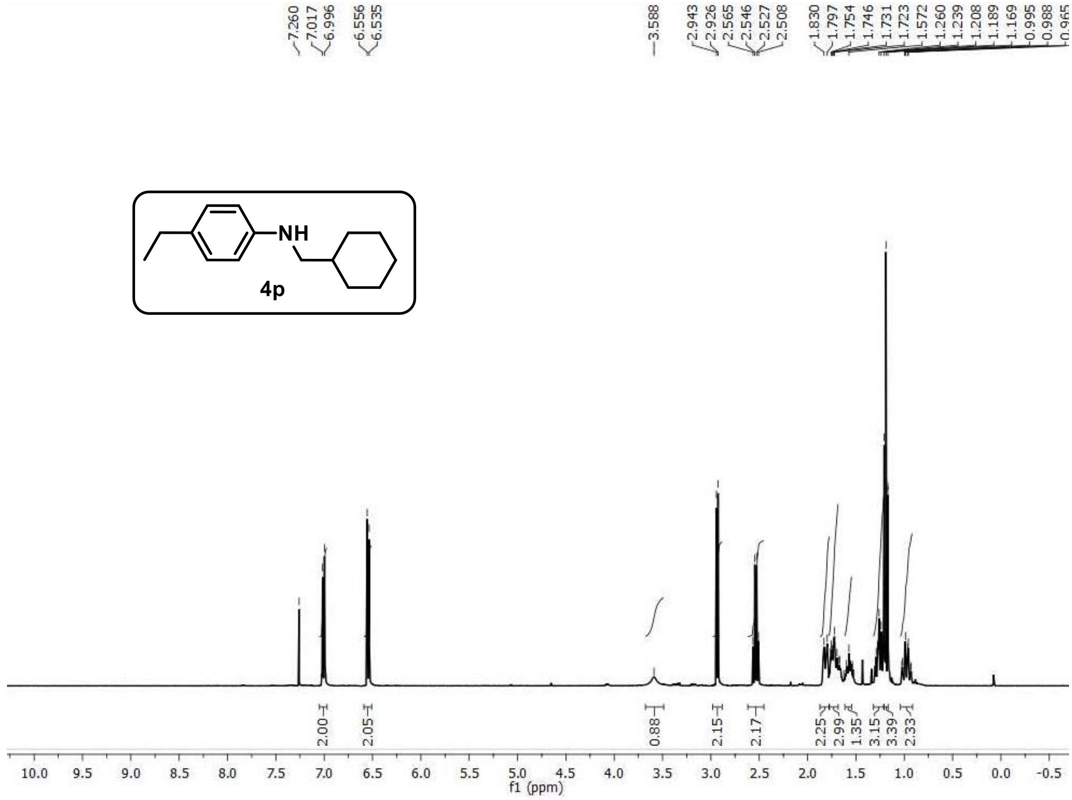


Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum of N-(cyclohexylmethyl)-4-ethylaniline (**4p**) in $CDCl_3$.

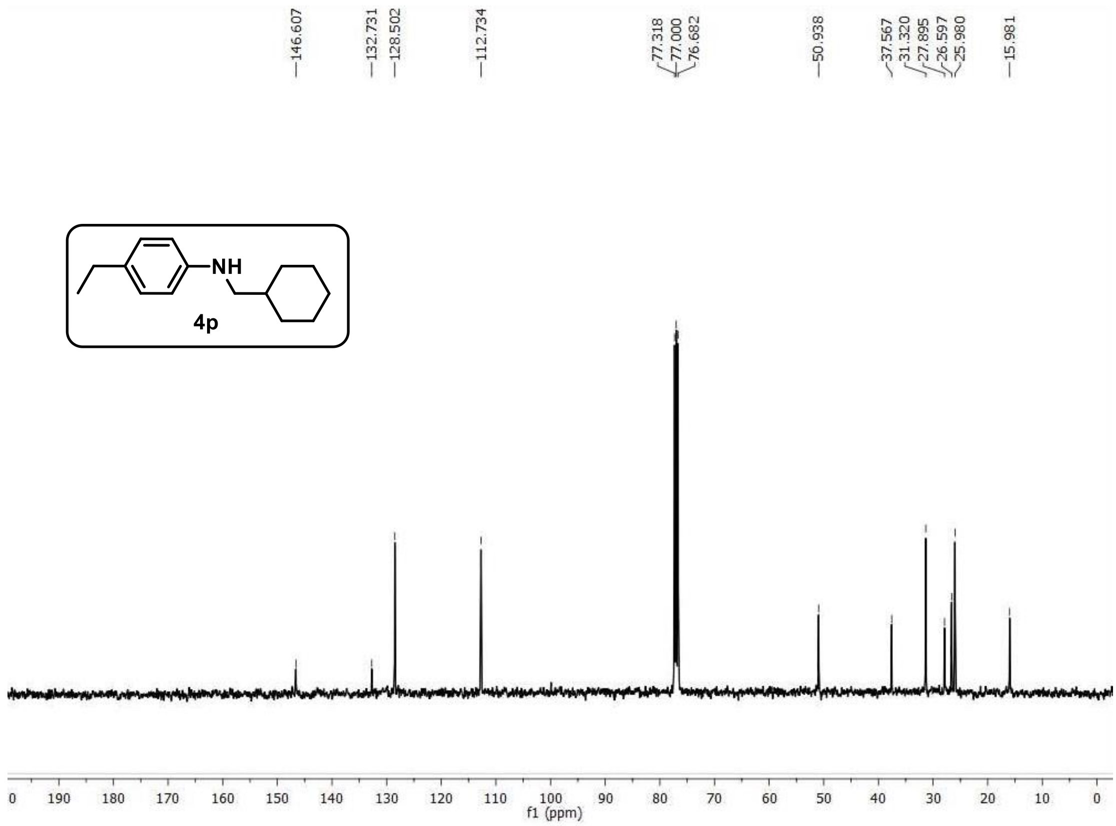


Figure S76. GC-MS of N-cyclopentyl-4-ethylaniline **(4q)**.

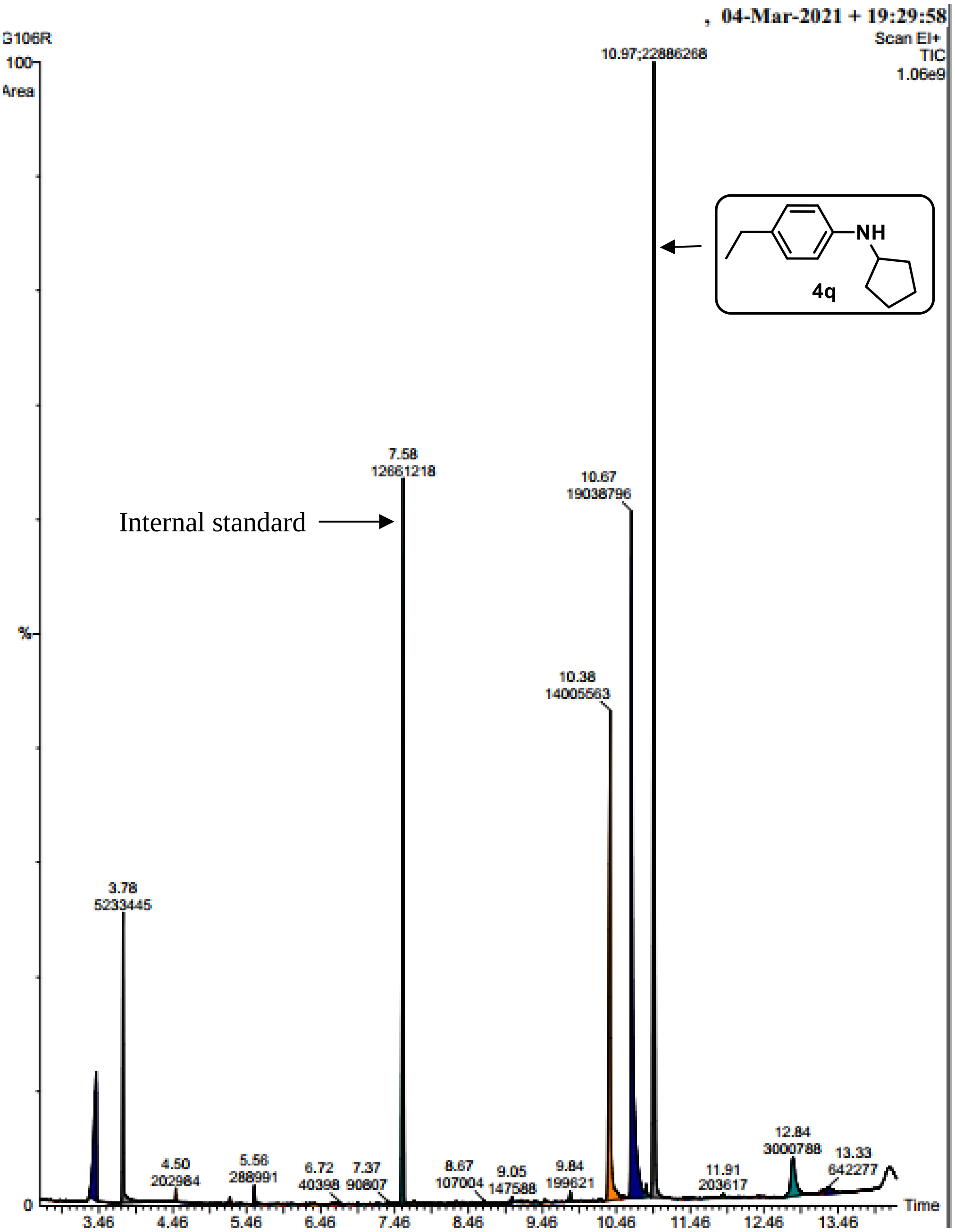


Figure S77. ^{1}H NMR spectrum of N-cyclopentyl-4-ethylaniline (**4q**) in $CDCl_3$.

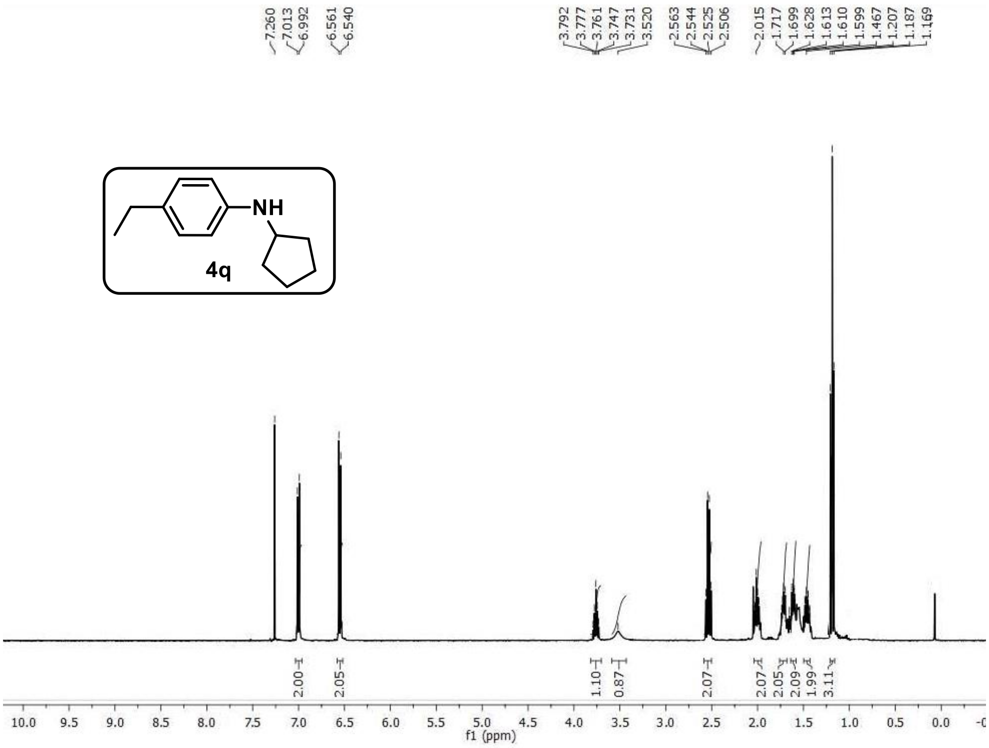


Figure S78. $^{13}C\{^1H\}$ NMR spectrum of N-cyclopentyl-4-ethylaniline (**4q**) in $CDCl_3$.

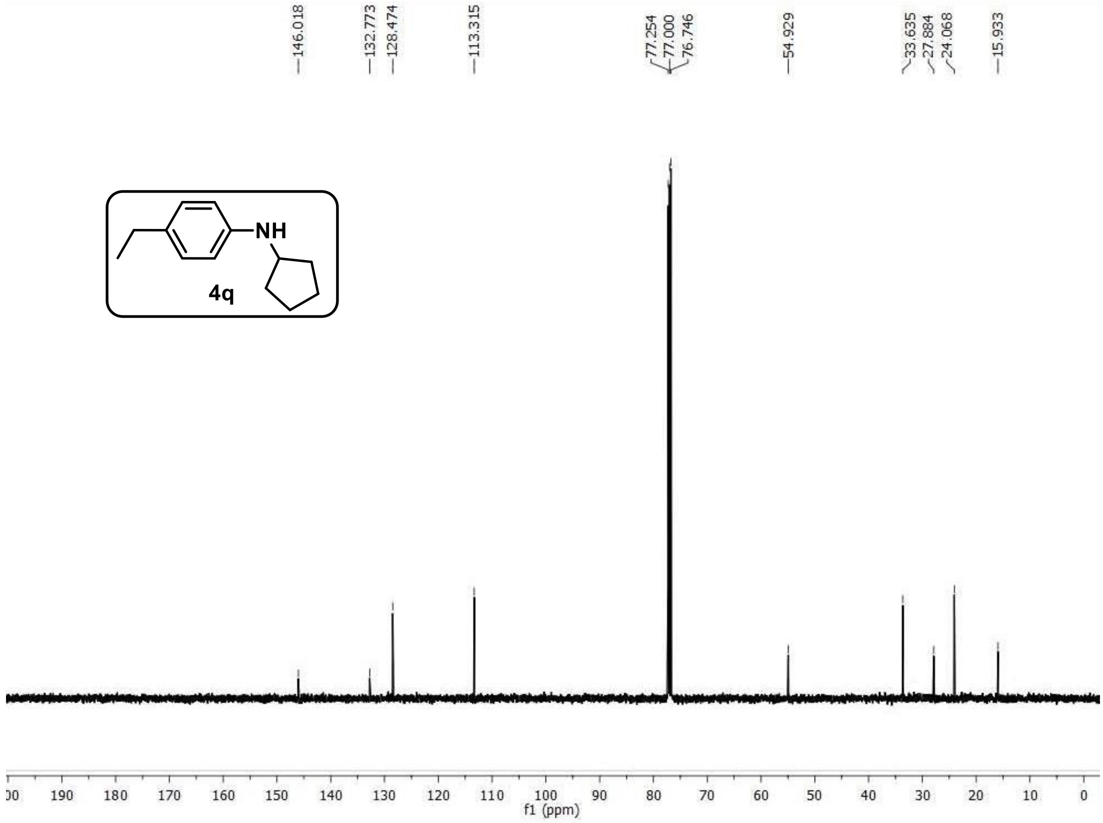


Figure S79. GC-MS of N-cyclohexyl-4-ethylaniline (**4r**).

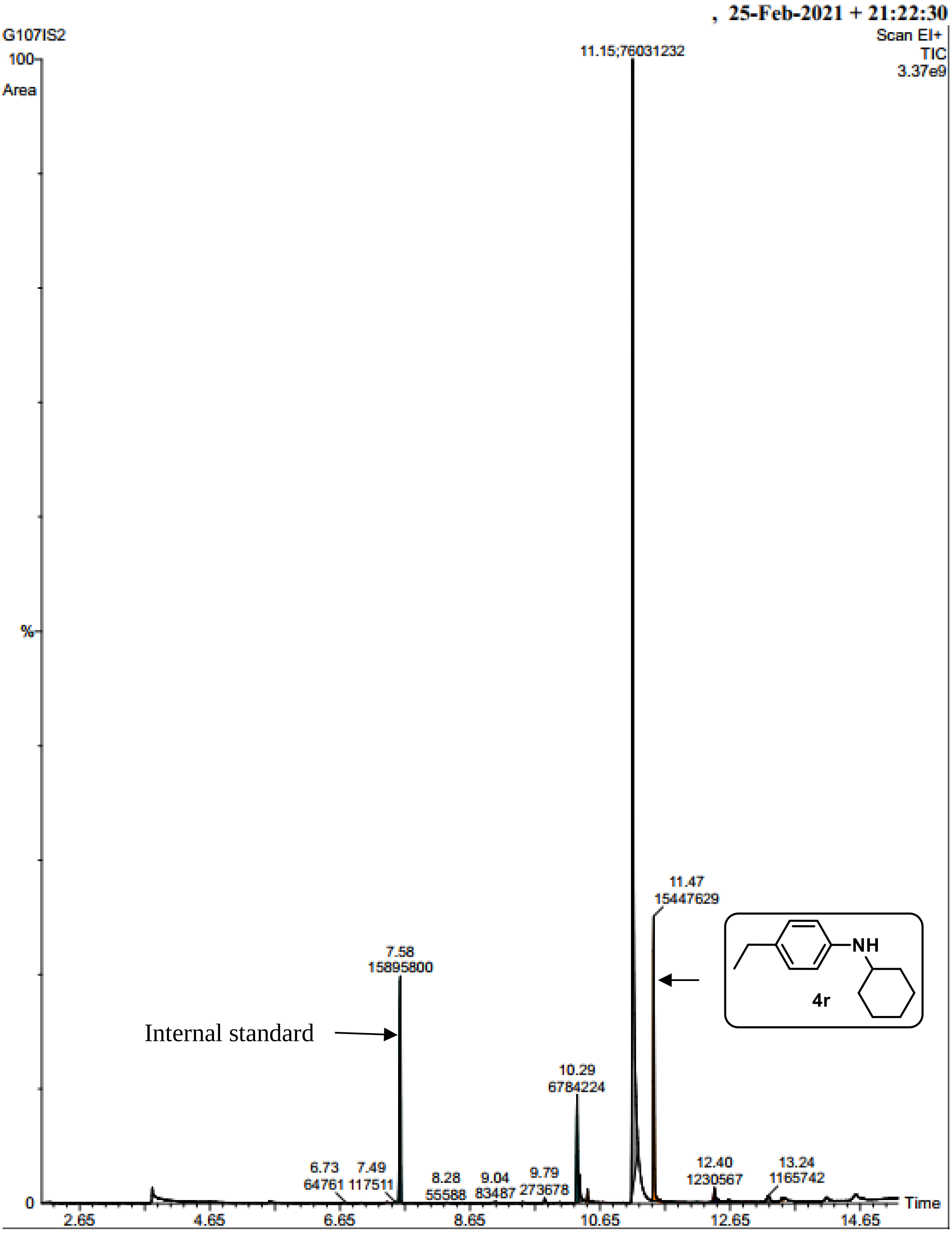


Figure S80. GC-MS of N-(4-ethylphenyl)cycloheptanamine (**4s**).

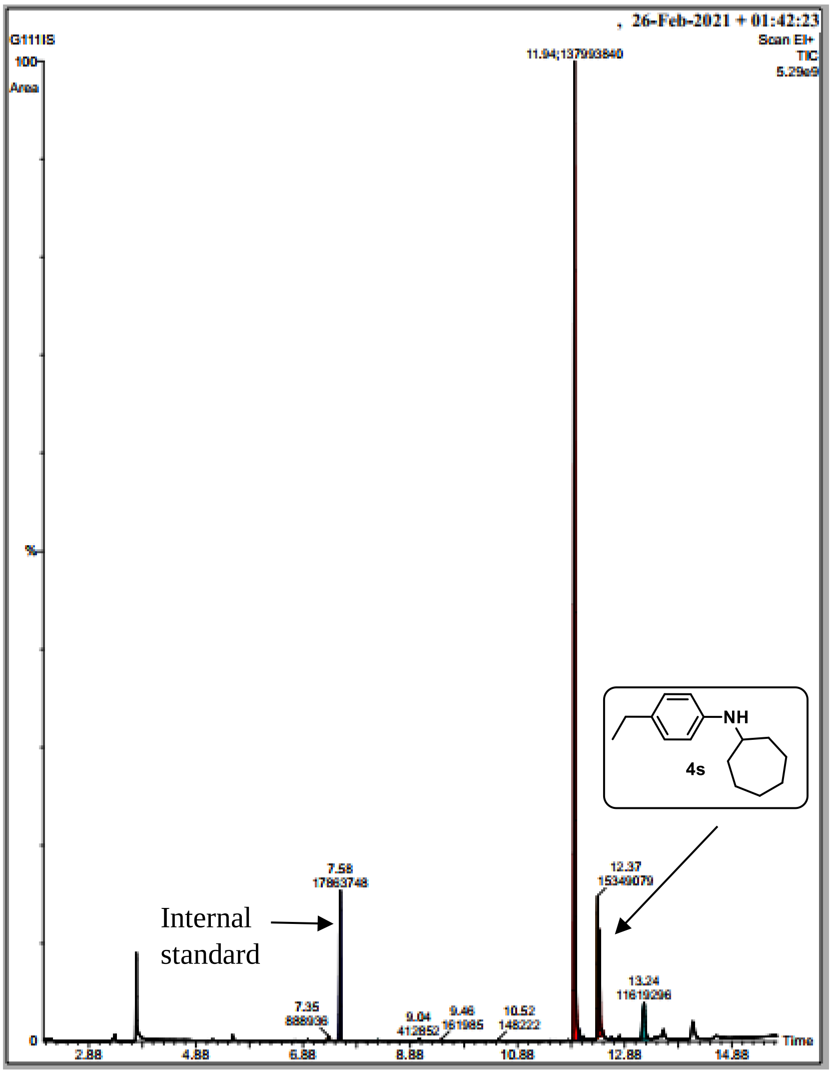


Figure S81. GC-MS of 4-ethyl-N-isobutylaniline **(4t)**.

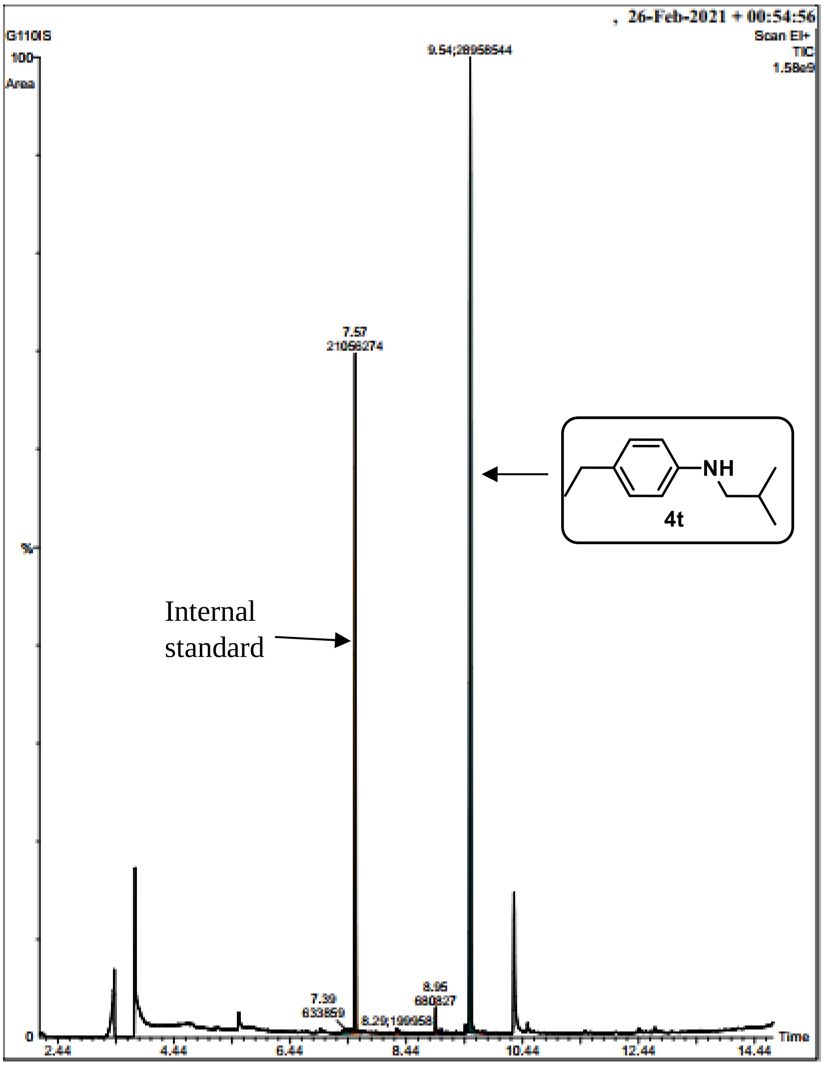


Figure S82. ^{1}H NMR spectrum of 4-ethyl-N-isobutylaniline (**4t**)[S20] in $CDCl_3$.

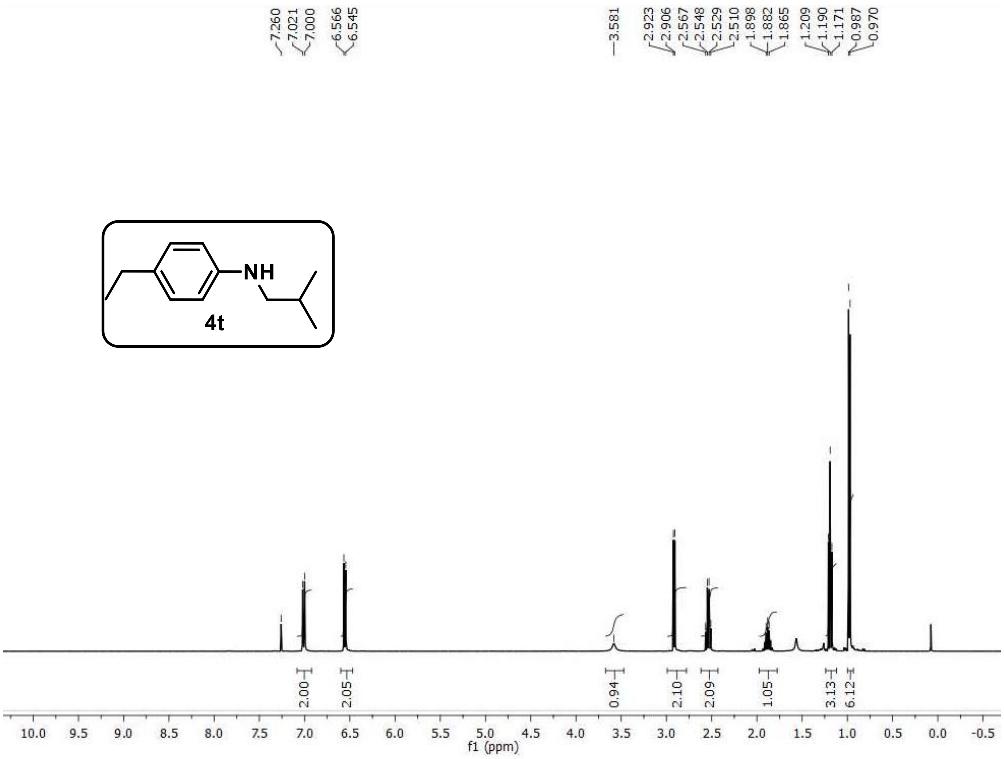


Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum of 4-ethyl-N-isobutylaniline (**4t**)[S20] in $CDCl_3$.

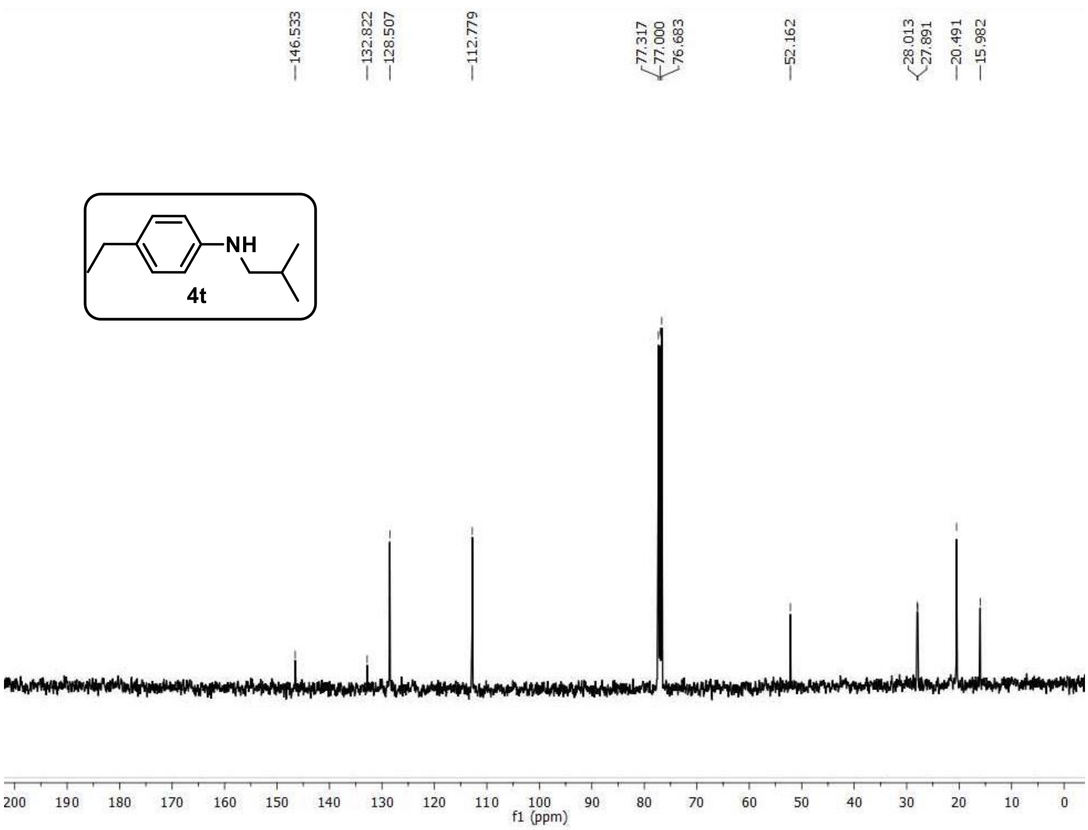


Figure S84. GC-MS of N-butyl-4-ethylaniline (**4u**).

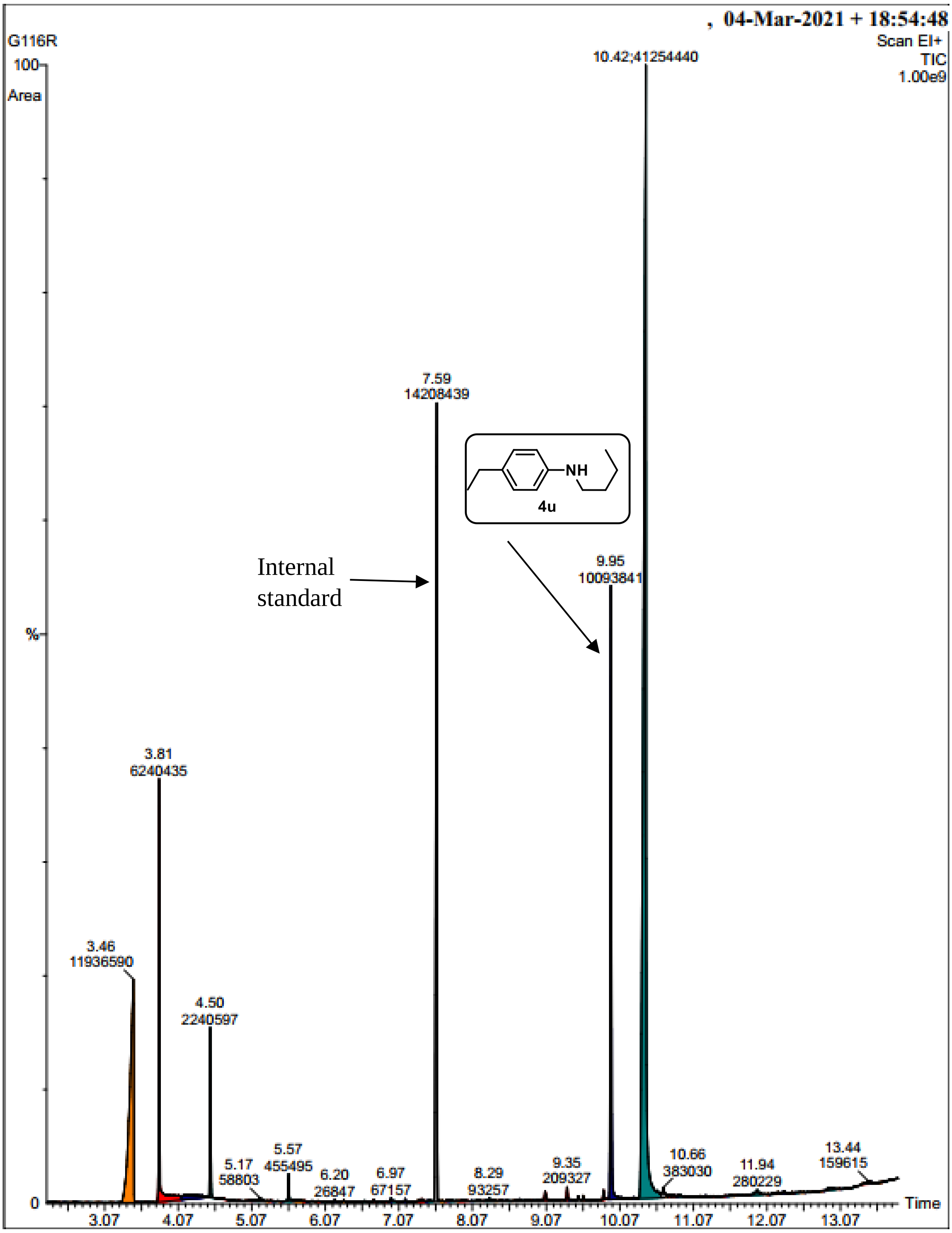


Figure S85. GC-MS of 4-ethyl-N-hexylaniline (**4v**).

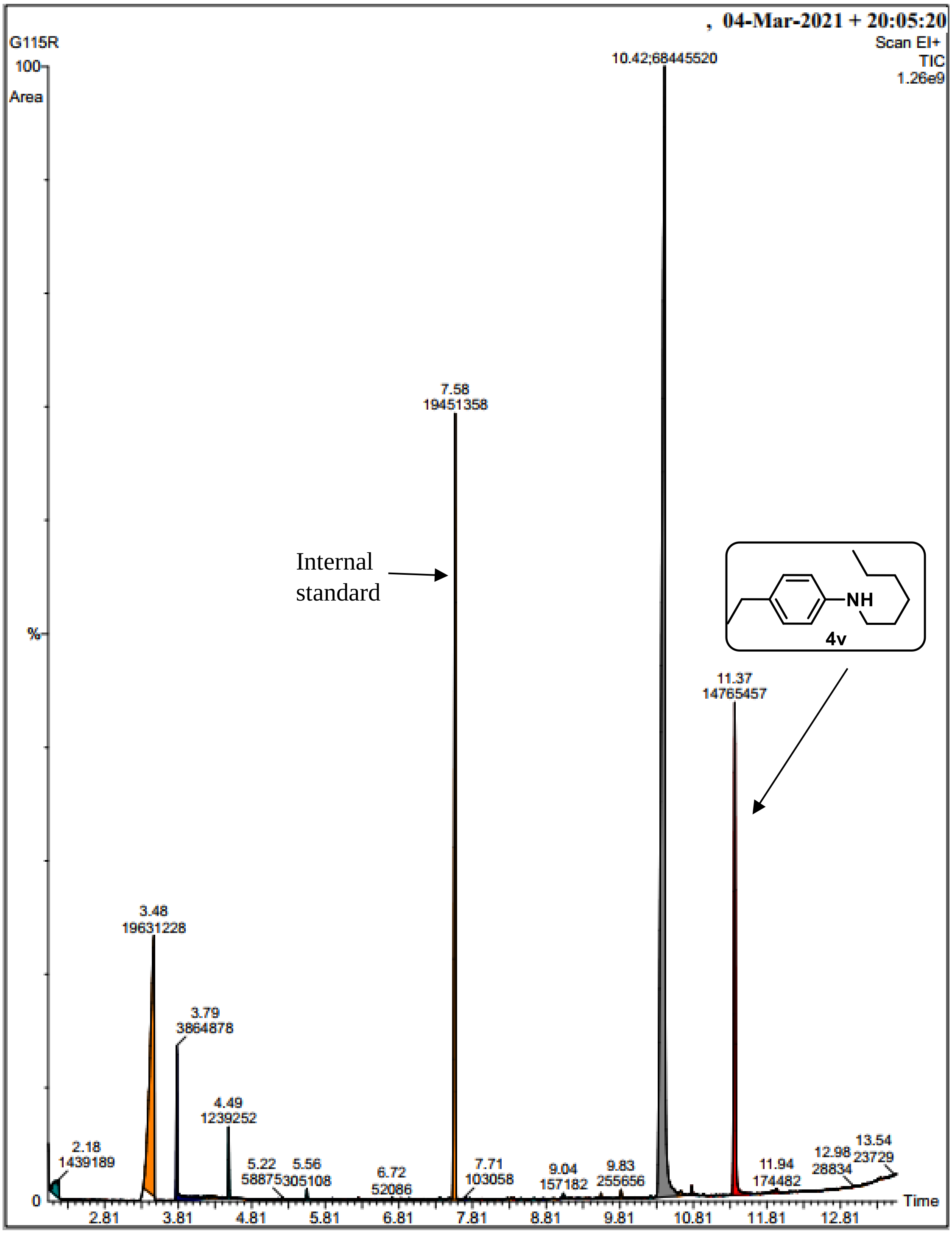


Figure S86. GC-MS of 4-ethyl-N-octylaniline **(4w)**.

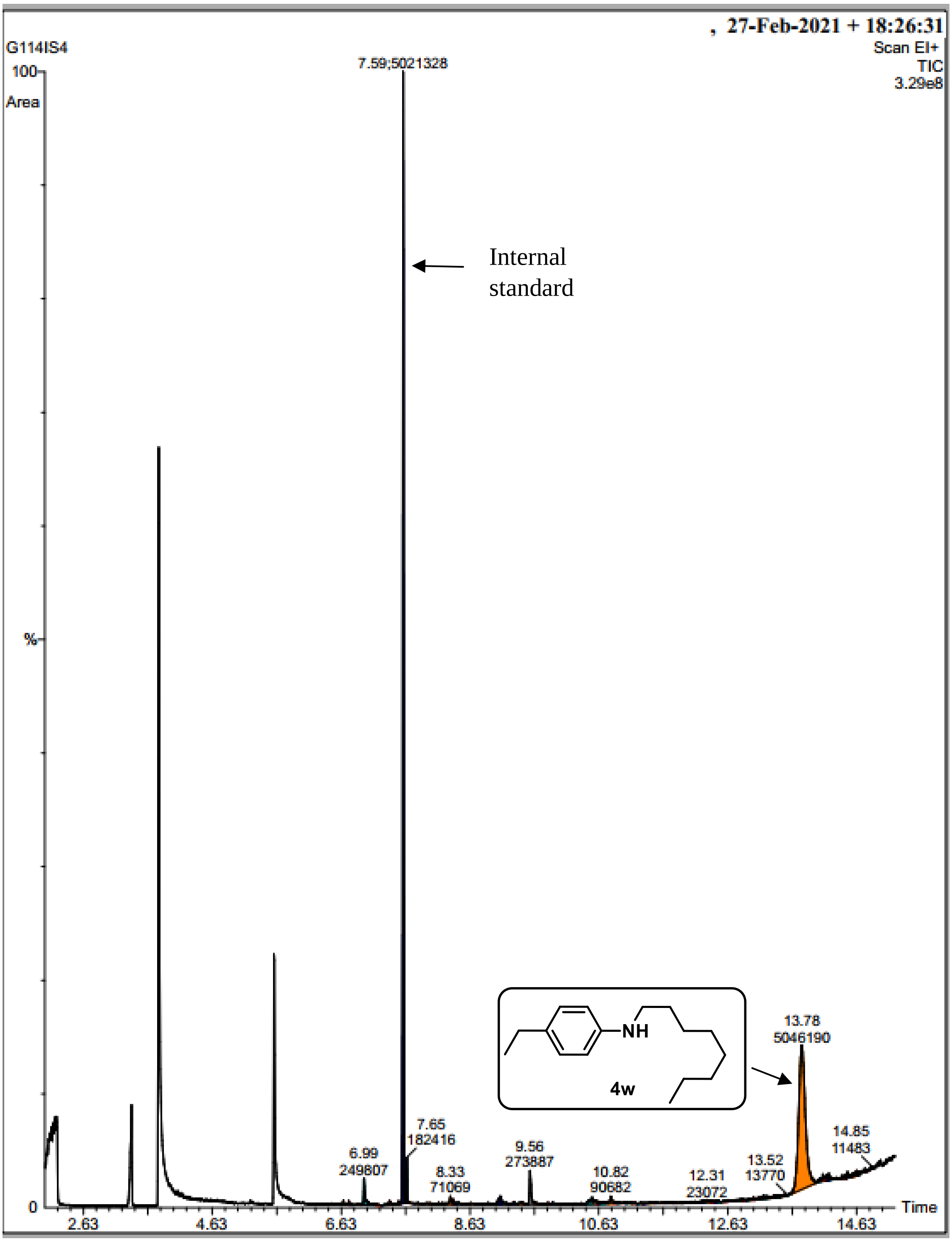


Figure S87. ^{1}H NMR spectrum of 4-ethyl-N-octylaniline **(4w)** in $CDCl_3$.

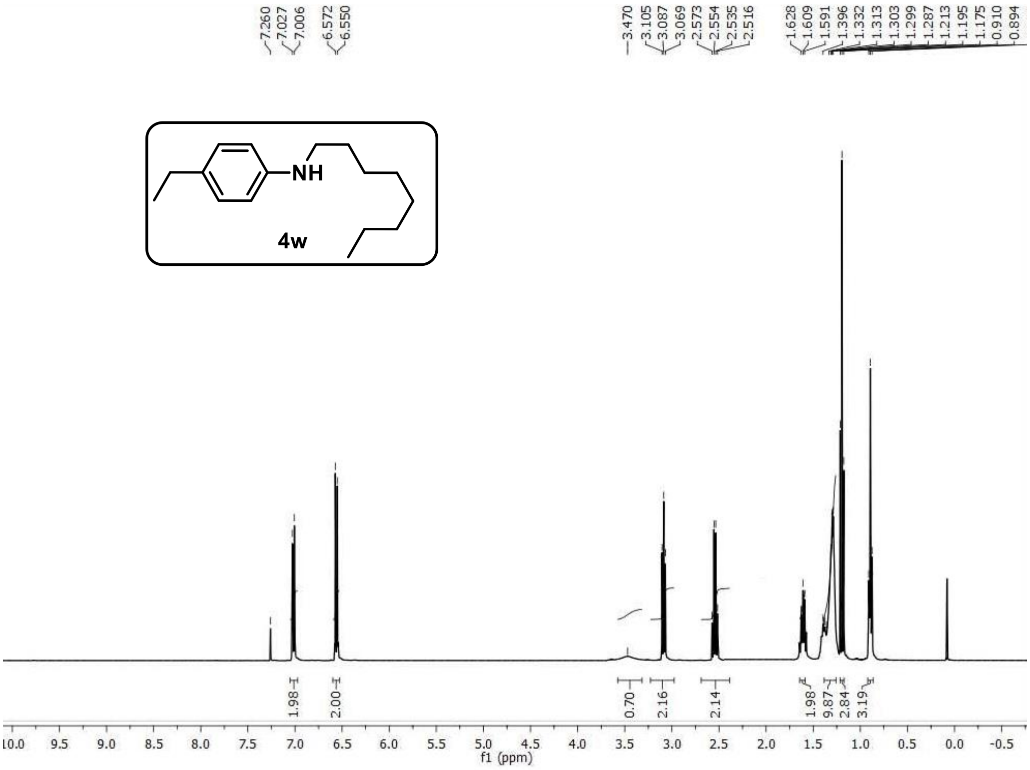


Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum of 4-ethyl-N-octylaniline **(4w)** in $CDCl_3$.

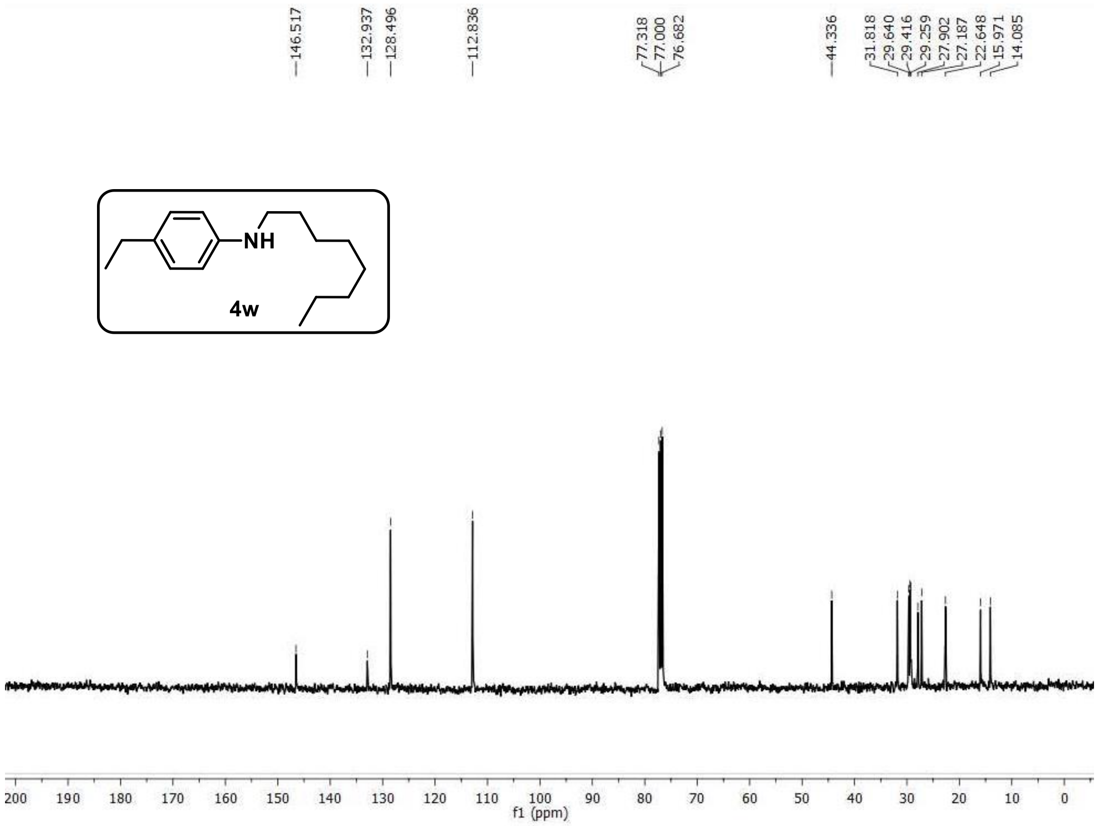


Figure S89. GC-MS of 4-ethyl-N-decylaniline **(4x)**.

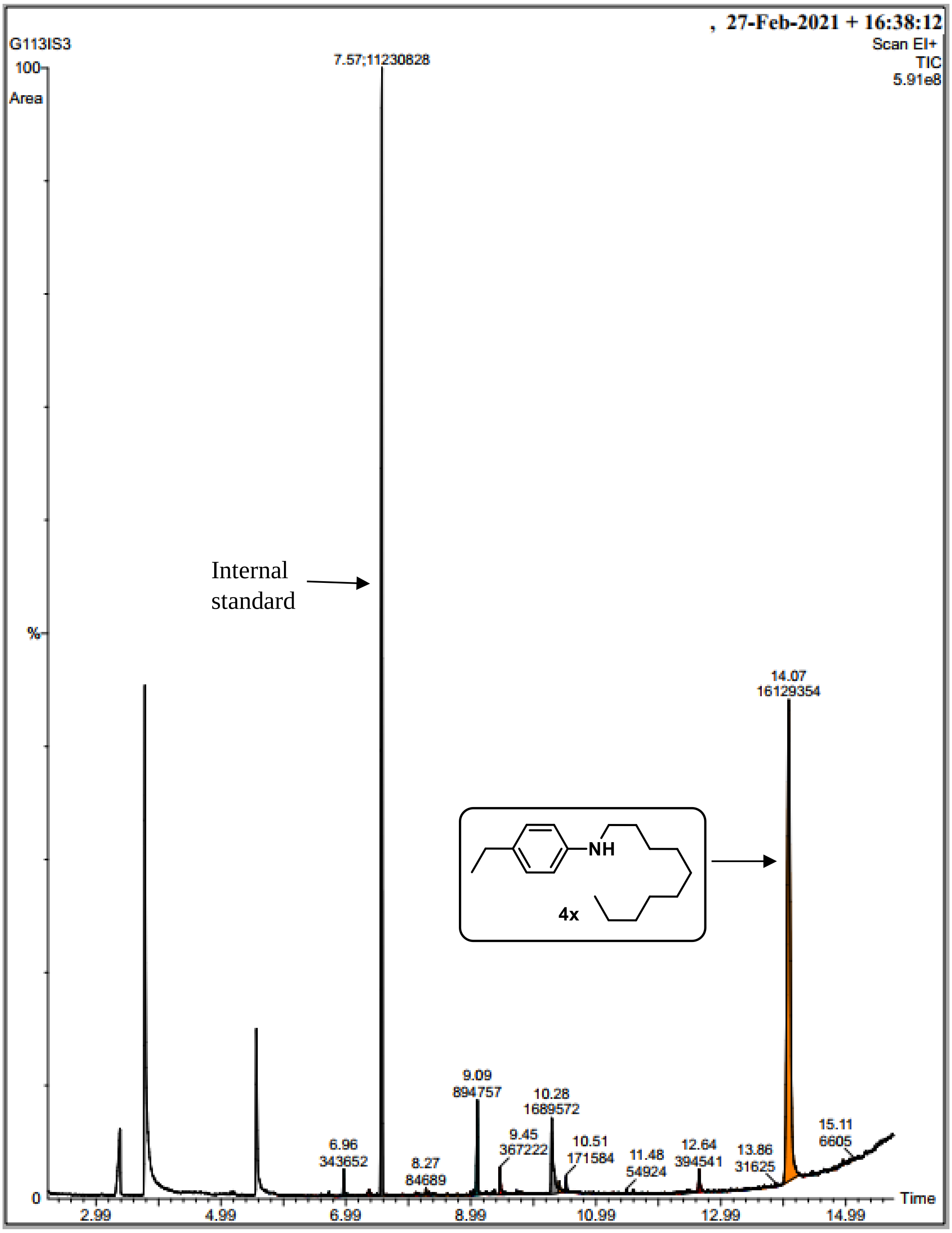


Figure S90. ^{1}H NMR spectrum of 4-ethyl-N-decylaniline **(4x)** in $CDCl_3$.

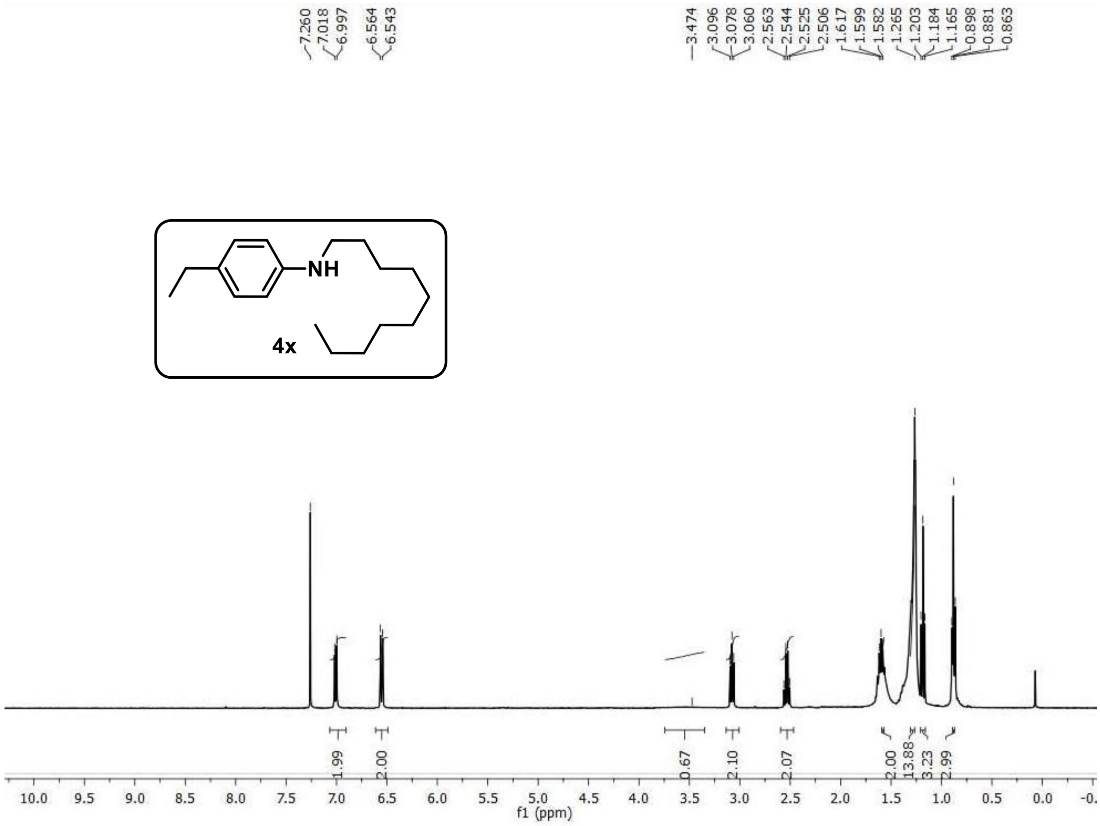


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of 4-ethyl-N-decylaniline **(4x)** in $CDCl_3$.

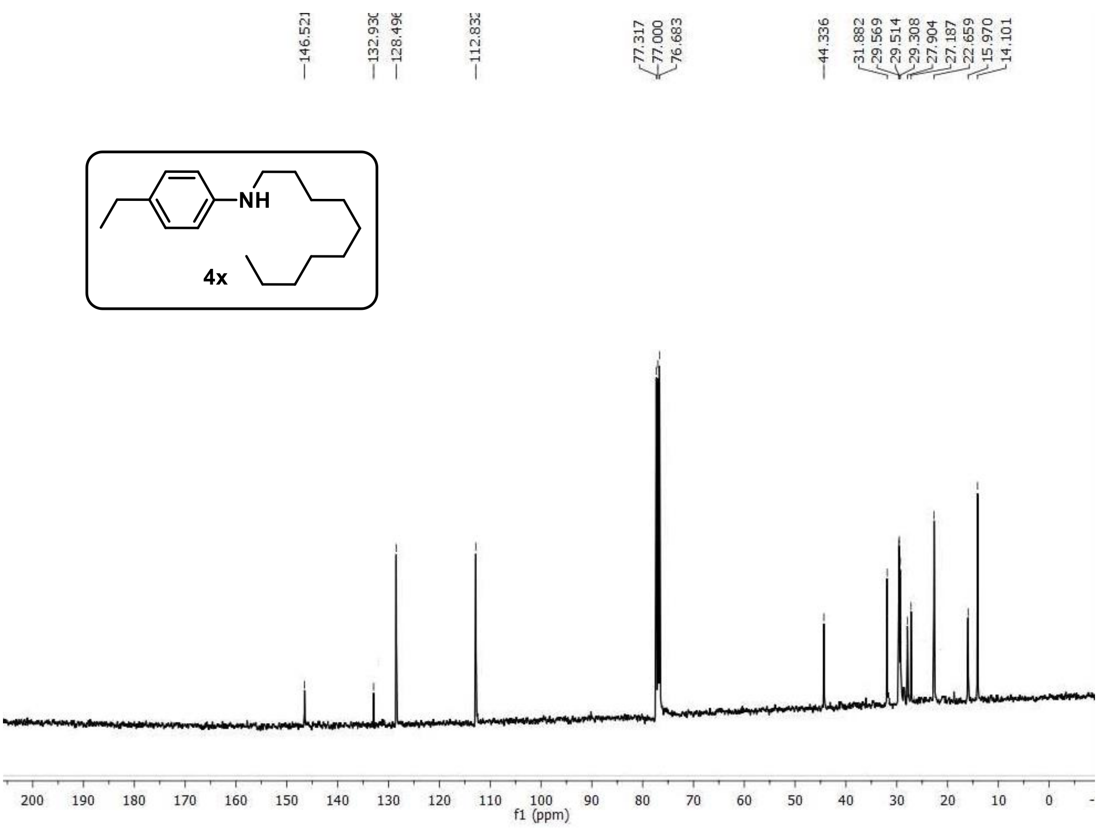


Figure S92. ^{1}H NMR spectrum of N-dodecyl-4-ethylaniline **(4y)** in $CDCl_3$.

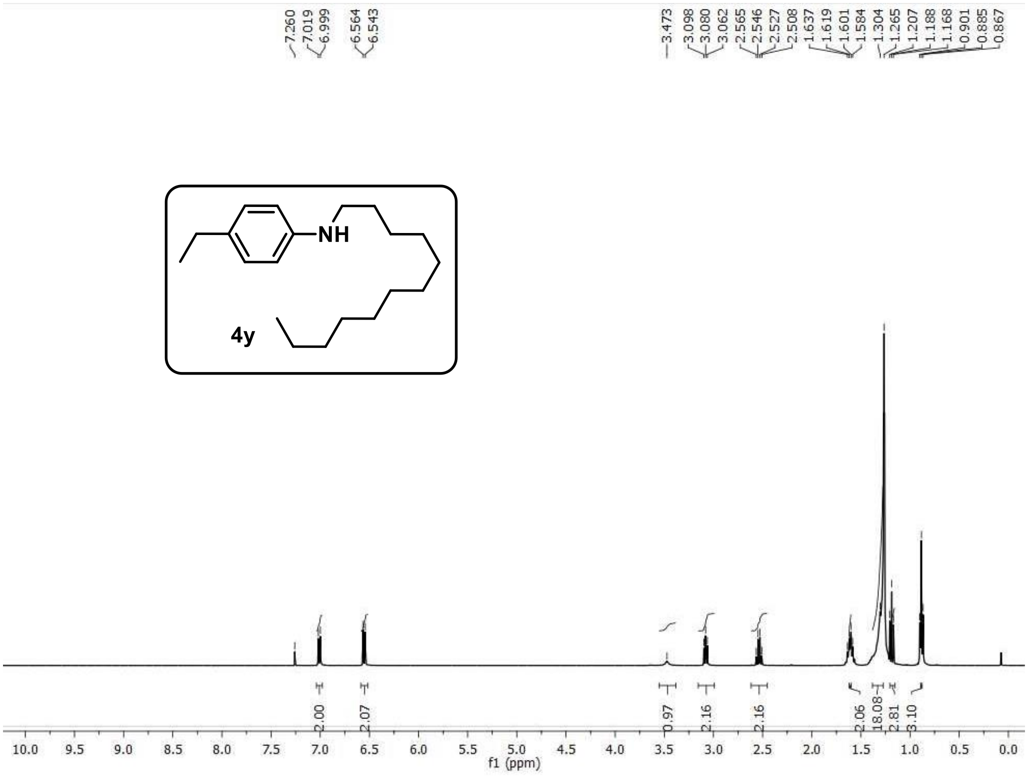


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of 4-ethyl-N-dodecylaniline **(4y)** in $CDCl_3$.

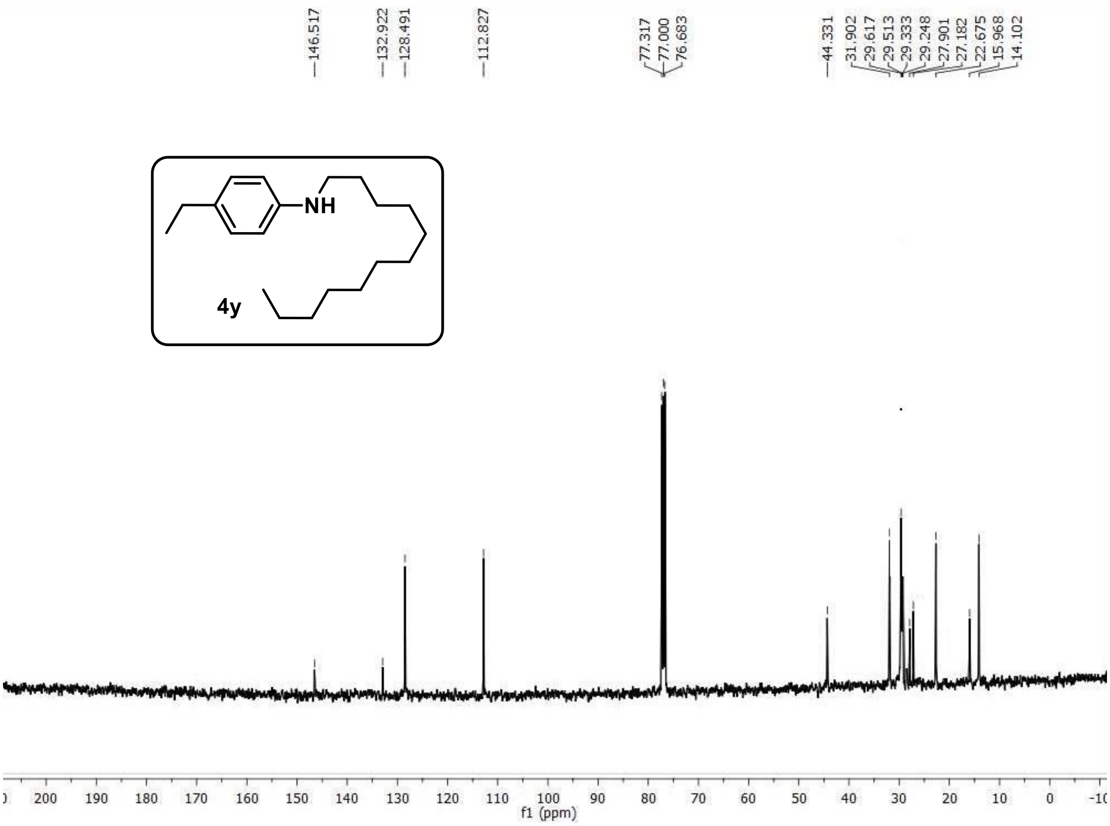


Figure S94. ^{1}H NMR spectrum of N-tetradecylaniline **(4z)** in $CDCl_3$.

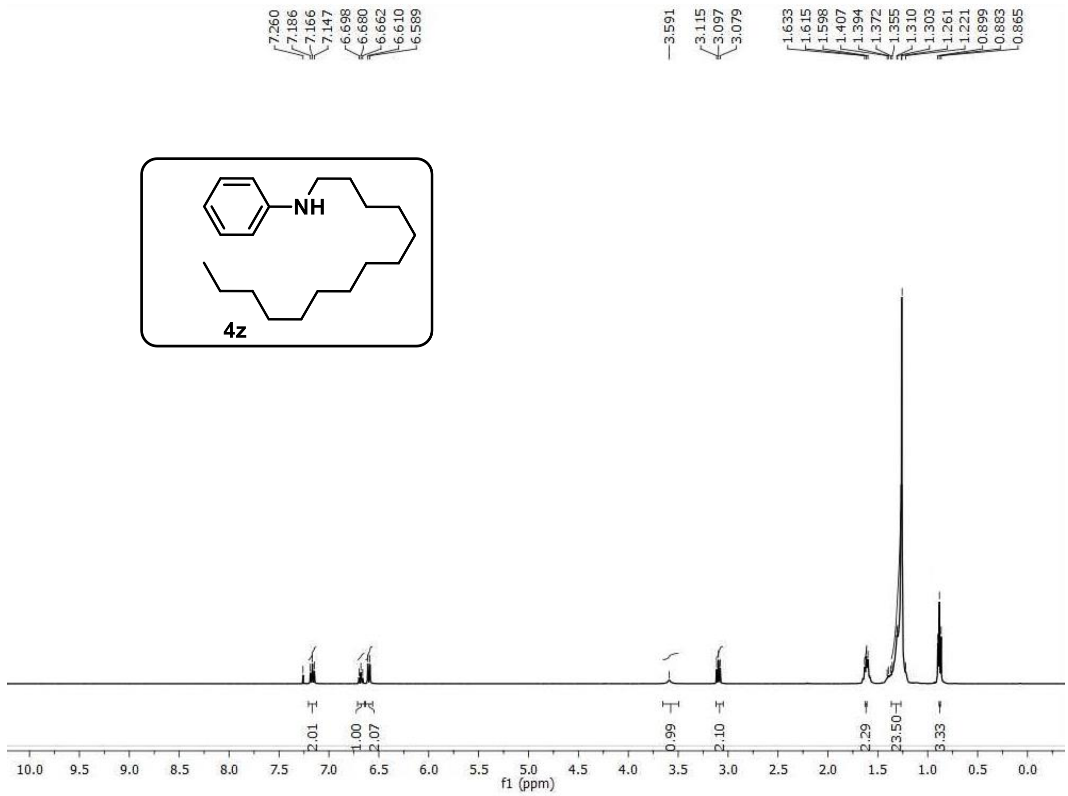


Figure S95. $^{13}C\{^{1}H\}$ NMR spectrum of 4-ethyl-N-tetradecylaniline **(4z)** in $CDCl_3$.

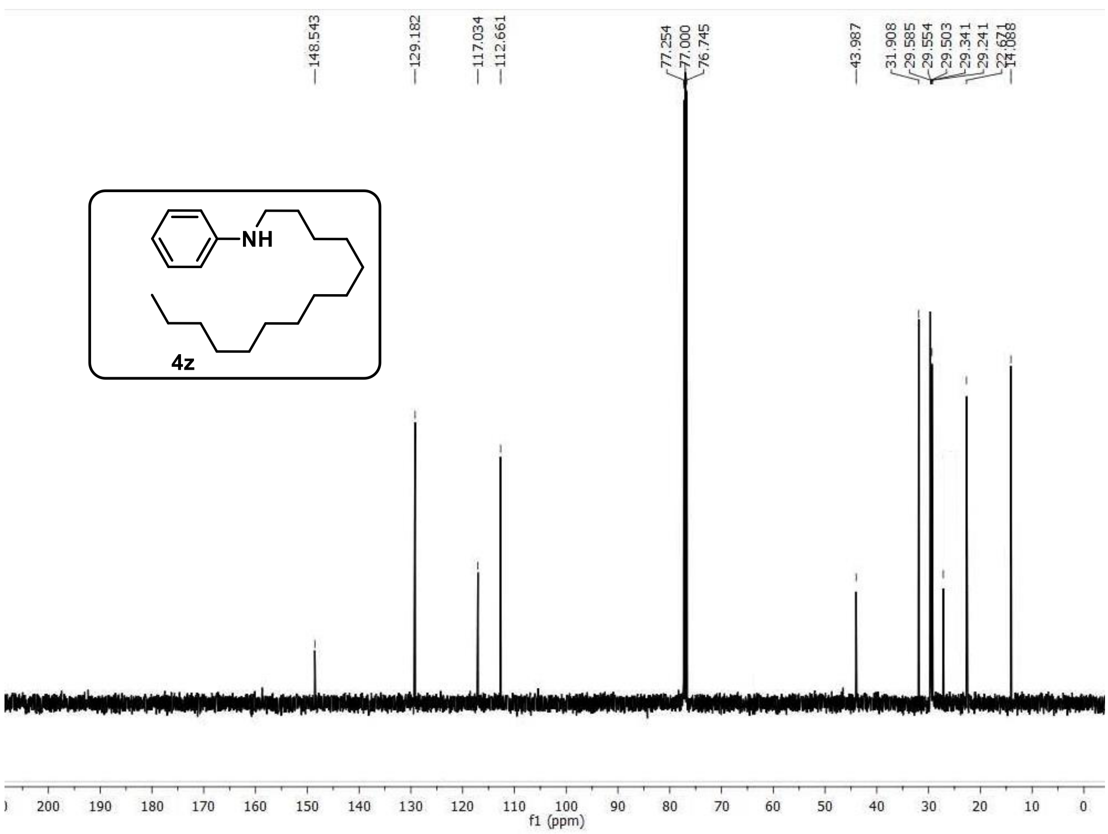


Figure S96. ^{1}H NMR spectrum of N-hexadecylaniline **(4aa)** in $CDCl_3$.

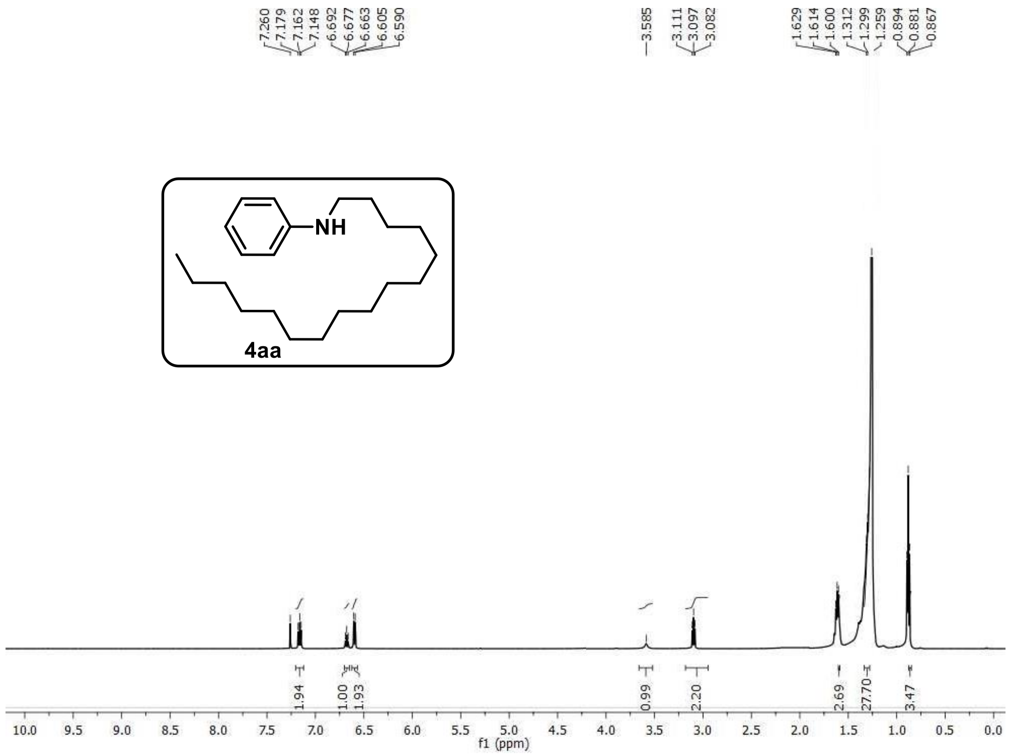


Figure S97. $^{13}C\{^{1}H\}$ NMR spectrum of N-hexadecylaniline **(4aa)** in $CDCl_3$

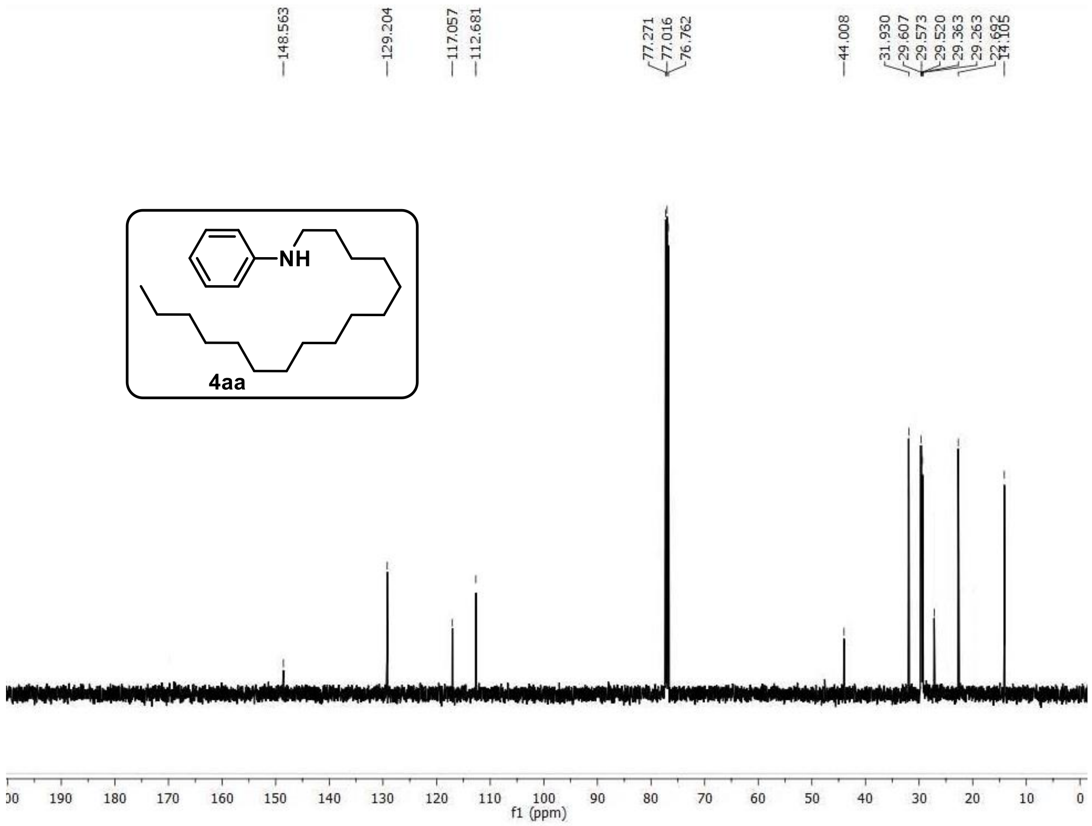


Figure S98. GC-MS of 4-ethyl-N-(2-ethylhexyl)aniline (**4ab**).

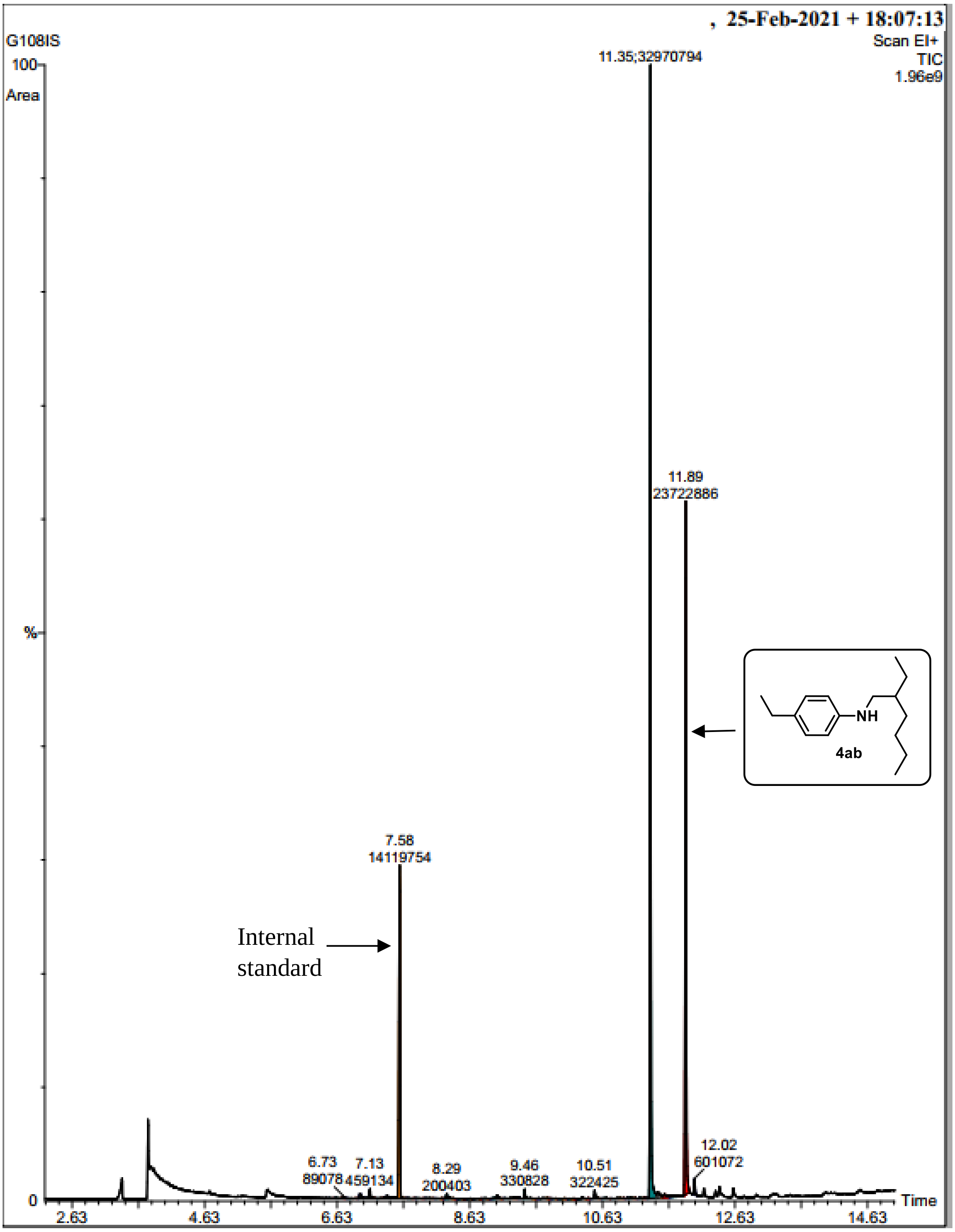


Figure S99. ^{1}H NMR spectrum of 4-ethyl-N-(2-ethylhexyl)aniline **(4ab)** in $CDCl_3$.

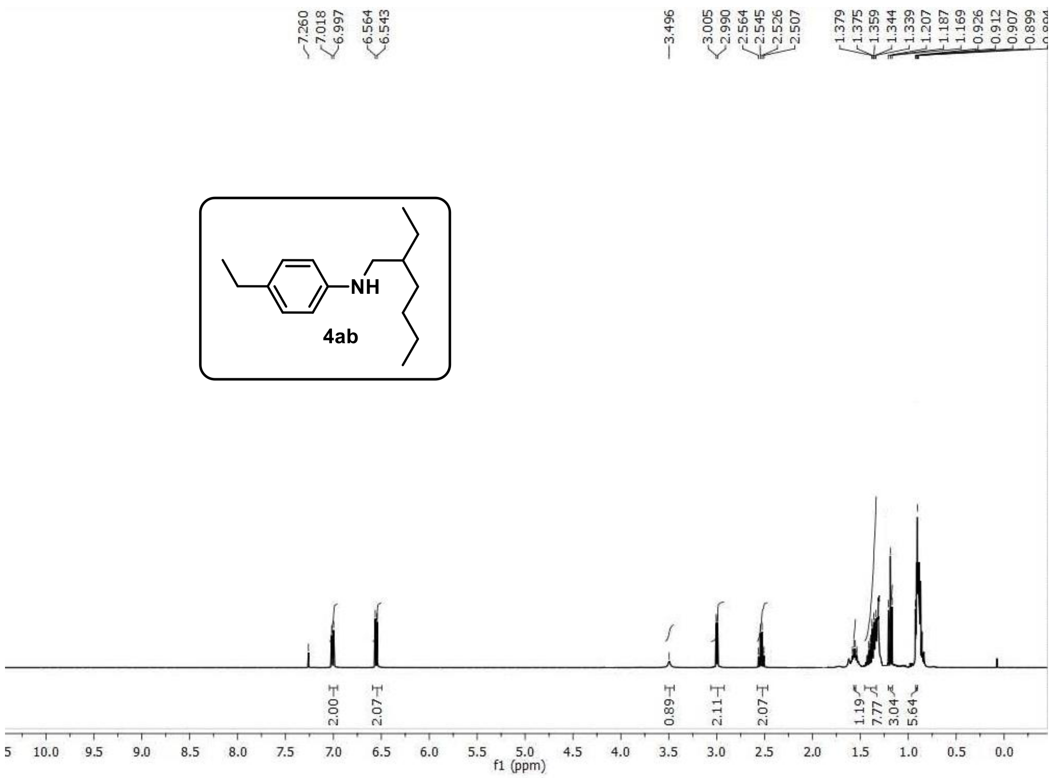


Figure S100. $^{13}C\{^{1}H\}$ NMR spectrum of 4-ethyl-N-(2-ethylhexyl)aniline **(4ab)** in $CDCl_3$.

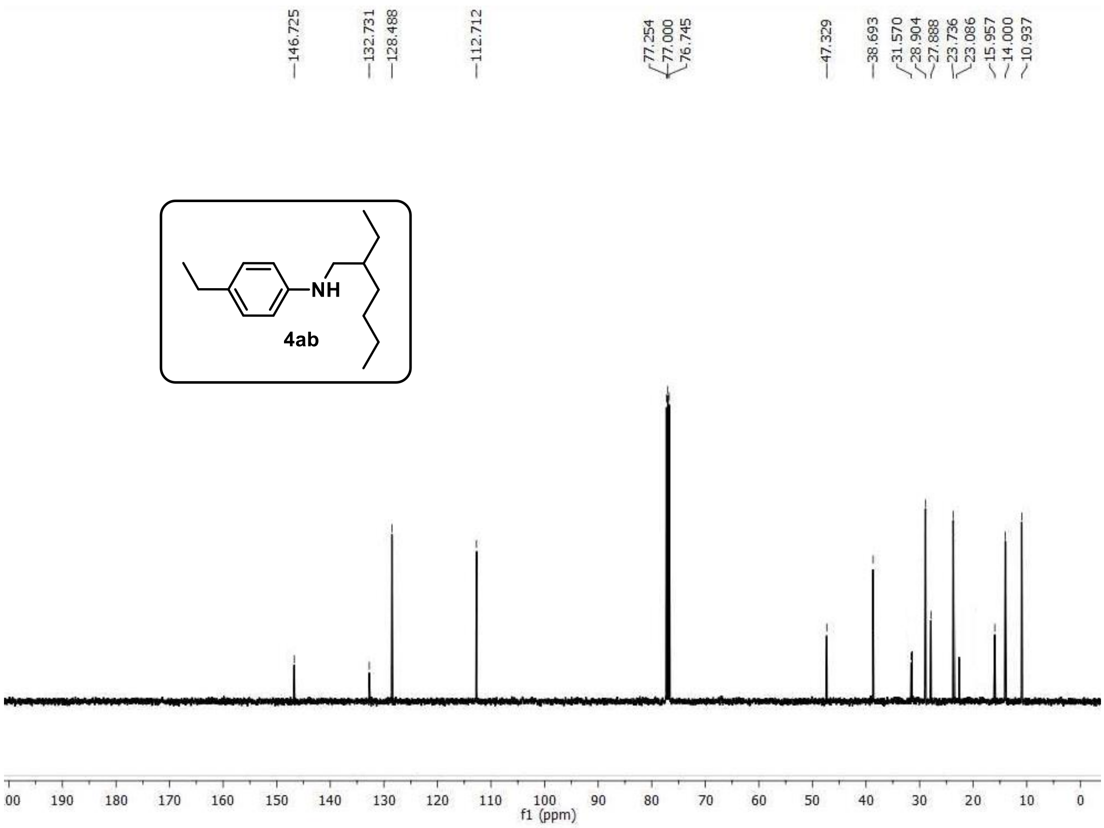


Figure S101. ^{1}H NMR spectrum of (Z)-N-(octadec-9-en-1-yl)aniline (**4ac**) in $CDCl_3$.

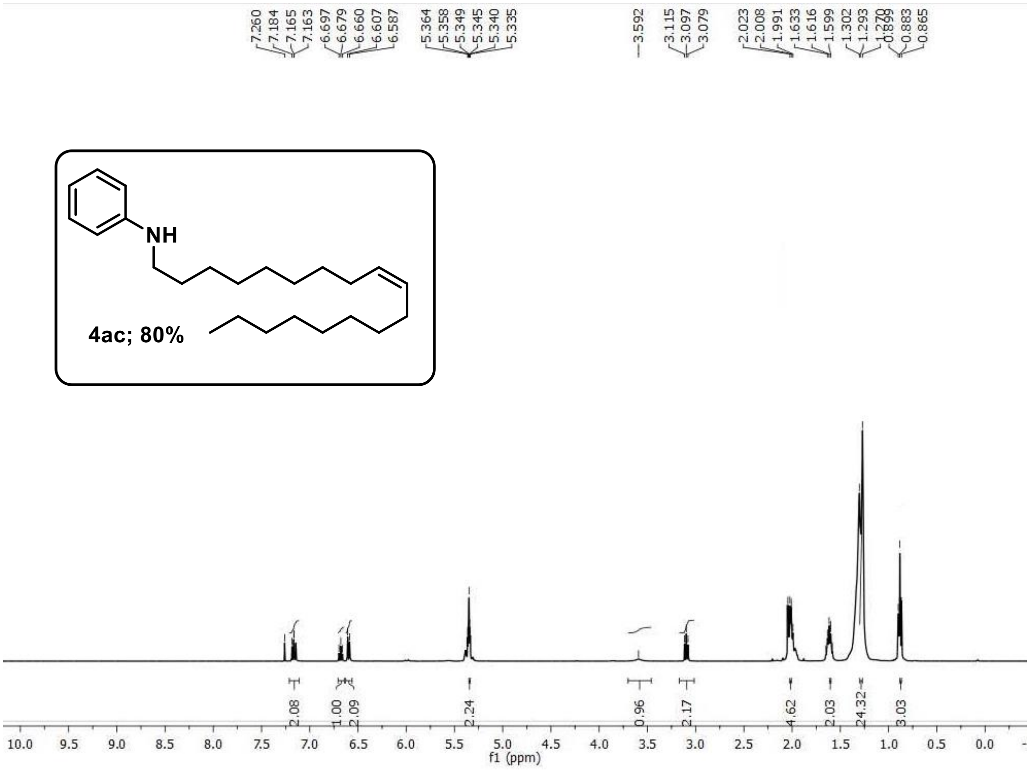


Figure S102. ^{13}C{^{1}H} NMR spectrum of (Z)-N-(octadec-9-en-1-yl)aniline (**4ac**) in $CDCl_3$.

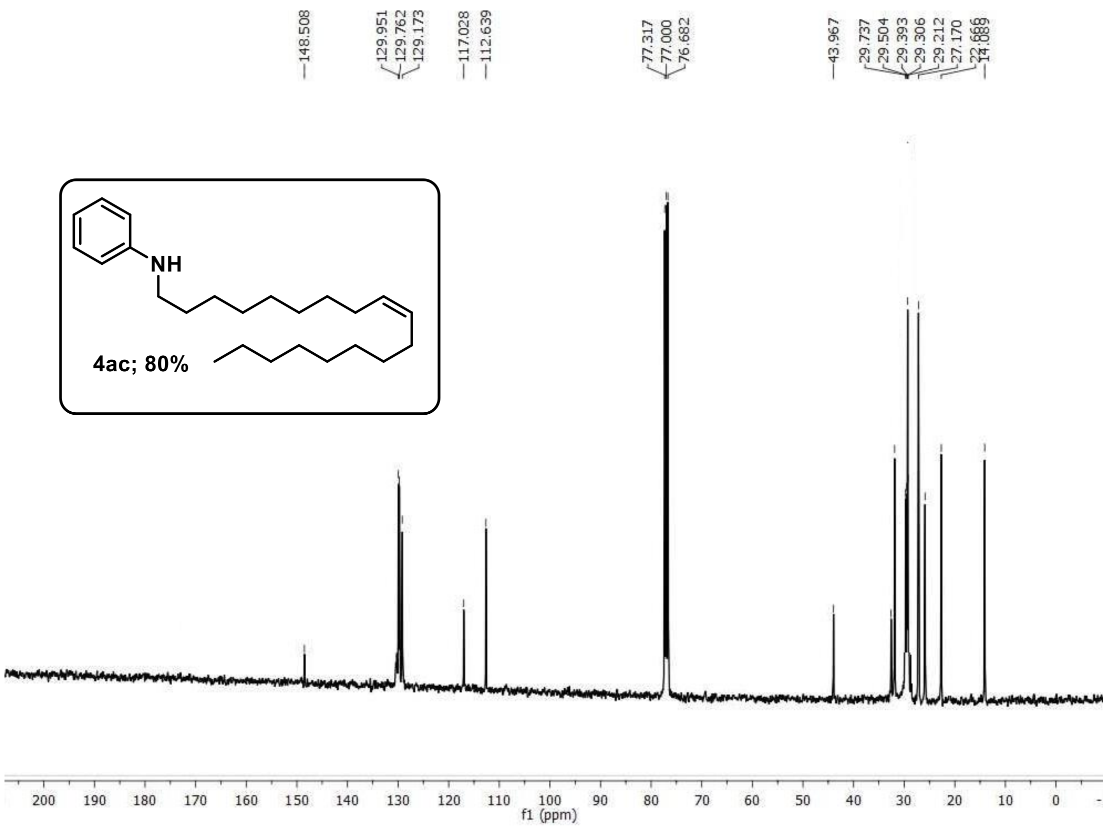


Figure S103. ^{1}H NMR spectrum of N-benzyl-4-(((R)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)aniline (**3v**)[S4] in $CDCl_3$.

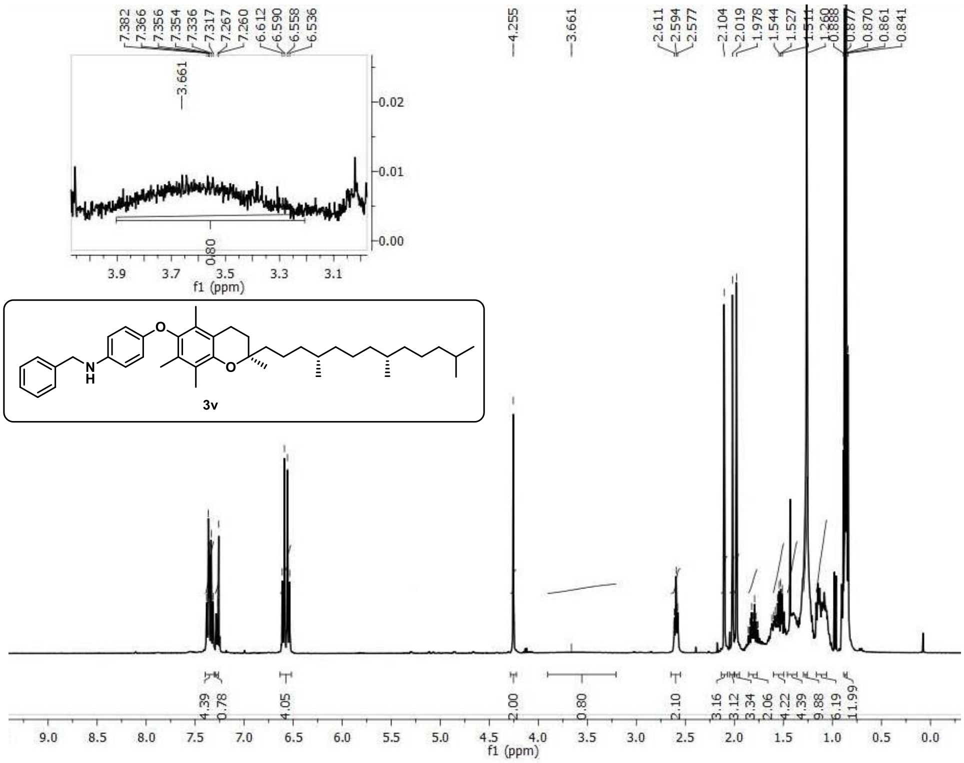


Figure S104. $^{13}C\{^{1}H\}$ NMR spectrum of N-benzyl-4-(((R)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)aniline (**3v**)[S4] in $CDCl_3$.

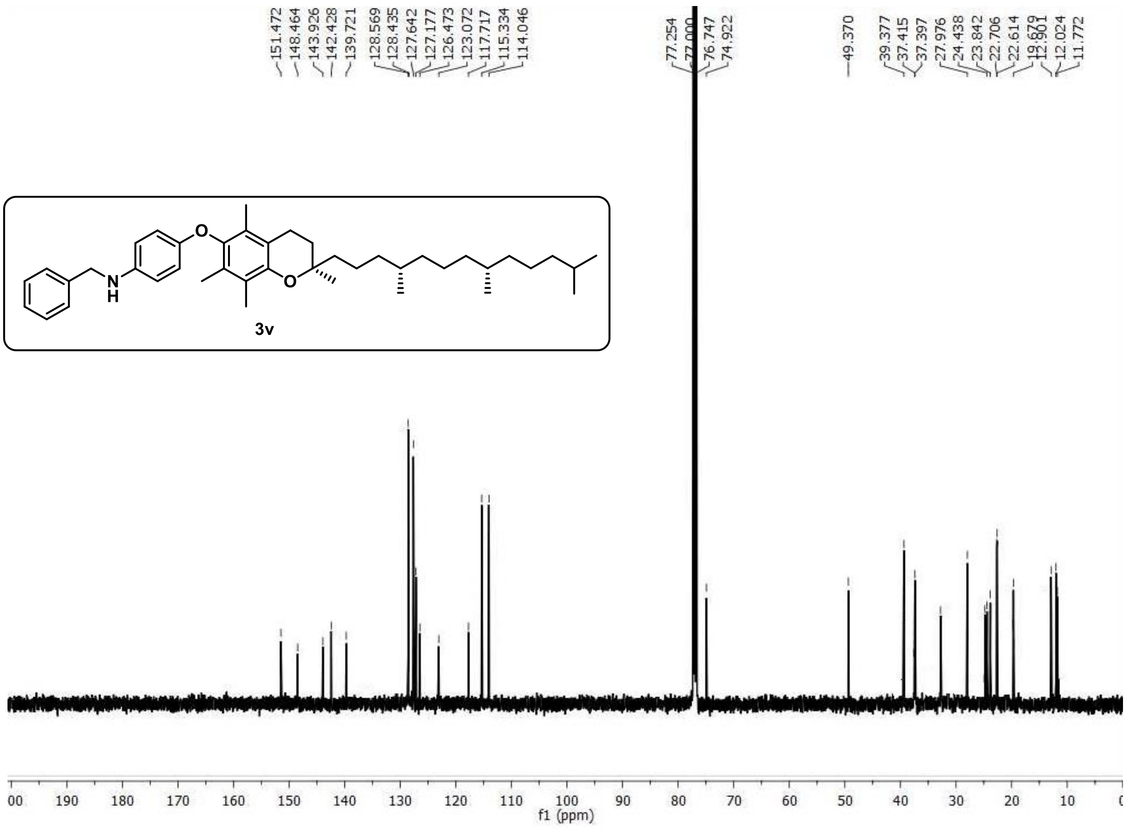


Figure S105. [1]H NMR spectrum of N-((6-(3-((1s,3s)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)methyl)aniline (**4ad**) in $CDCl_3$.

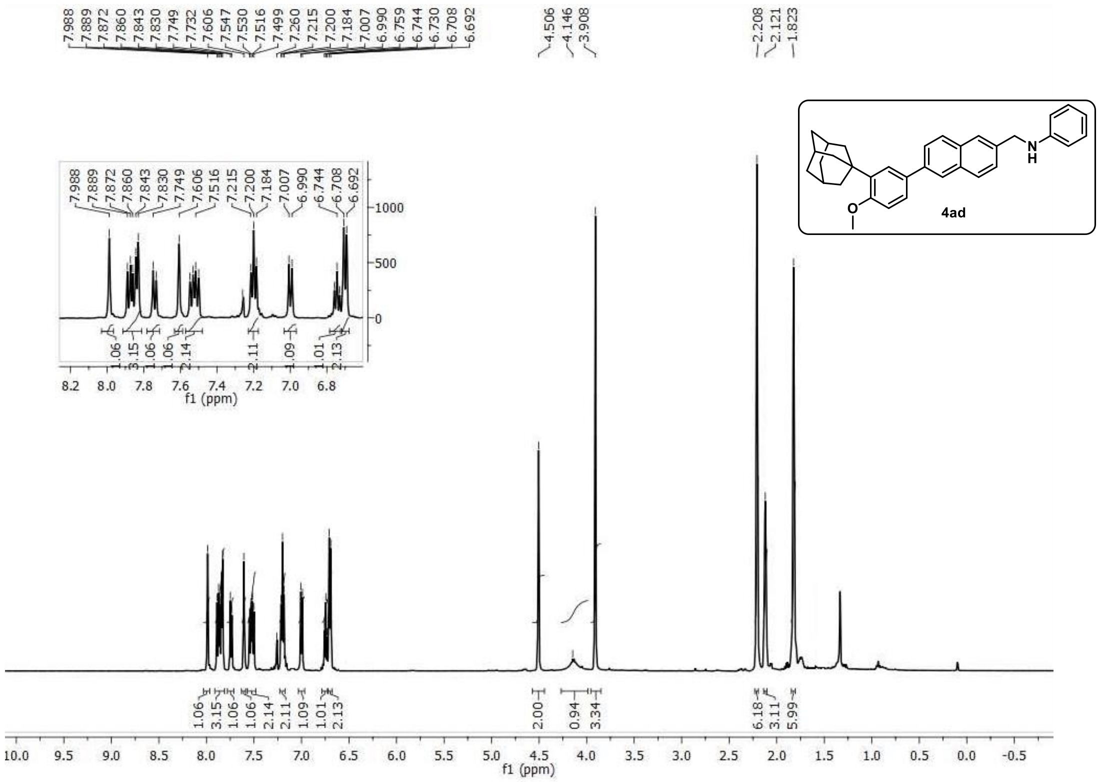
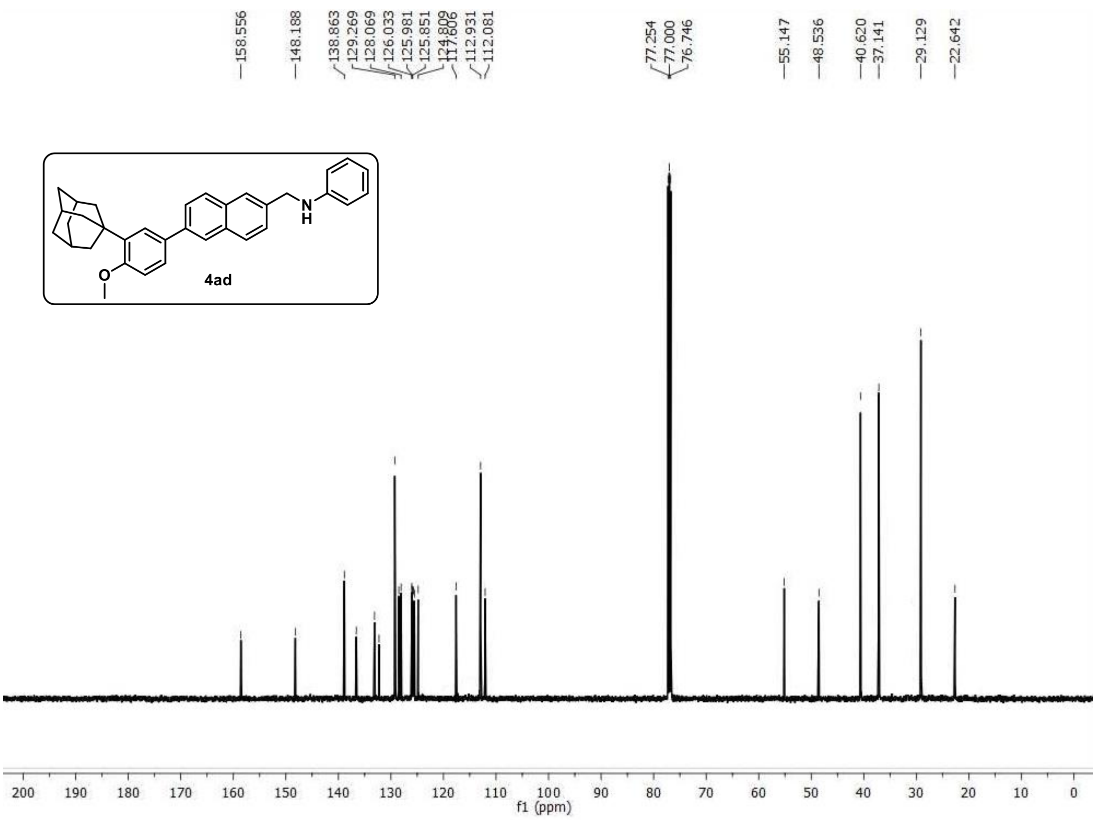


Figure S106. $^{13}C\{^1H\}$ NMR spectrum of N-((6-(3-((1s,3s)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)methyl)aniline (**4ad**) in $CDCl_3$.



Spectroscopic Characterization of stoichiometric reactions.

Radical trapping experiment through TEMPO adducts formation.

Figure S107. HRMS of TEMPO trapped product with 4-fluorobenzyl alcohol.

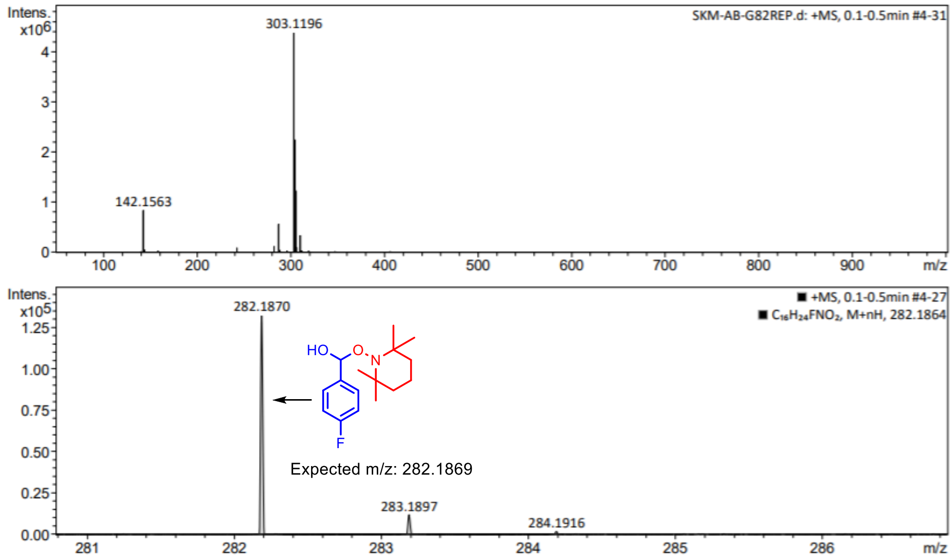


Figure S108. GC-MS of TEMPO trapped product with 4-nitrobenzyl alcohol.

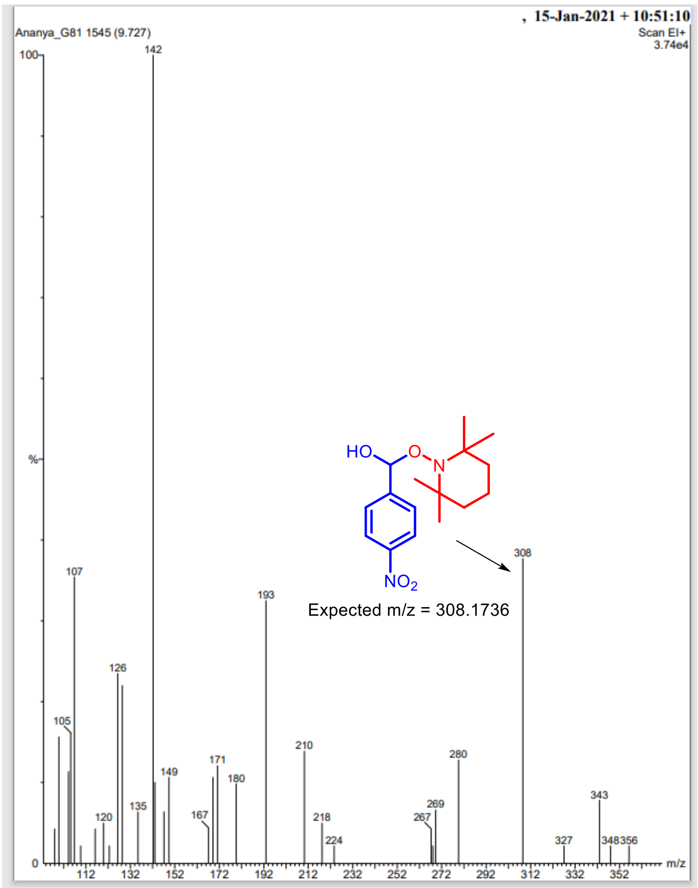


Figure S109. GC-MS of TEMPO trapped product with 4-trifluoromethylbenzyl alcohol.

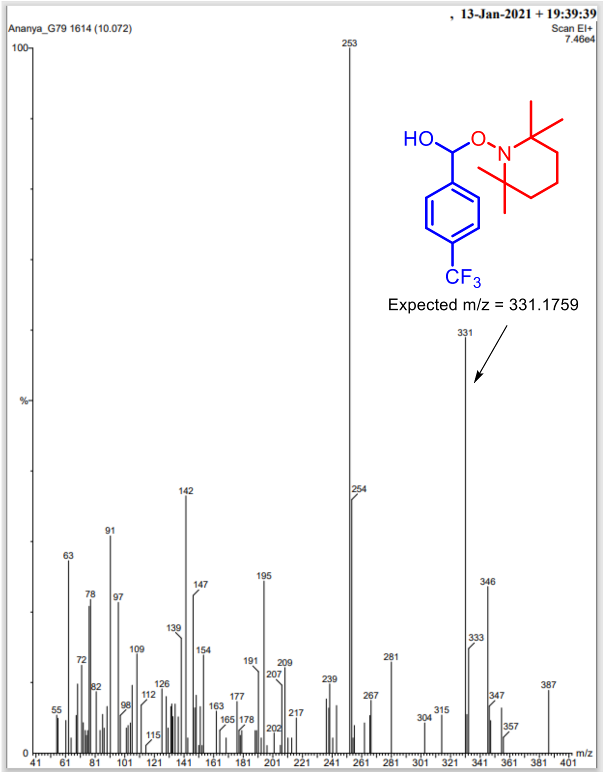
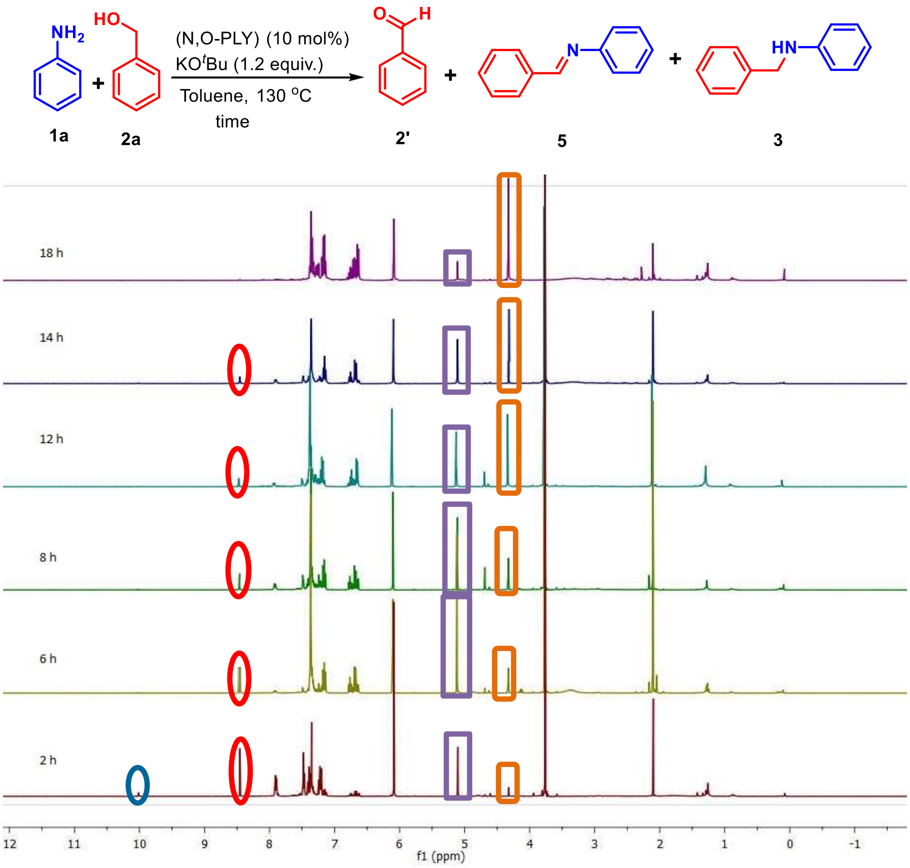


Figure S110. Evolution of aldehyde and imine with time.



Deuterium labelling experiment: with aniline and deuterated 4-chloro benzyl alcohol (2c-d_2).

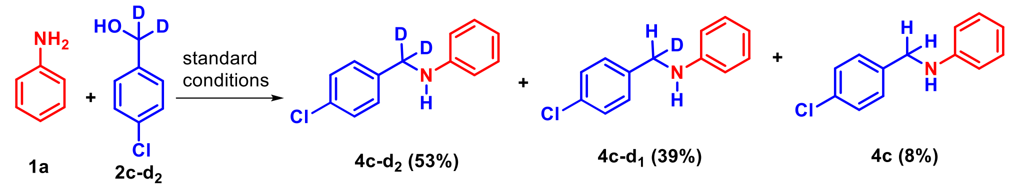


Figure S111. [1]H NMR spectrum of alkylated amines obtained using deuterium labelled alcohol (**4c**, **4c-d_1**, and **4c-d_2**).in $CDCl_3$.

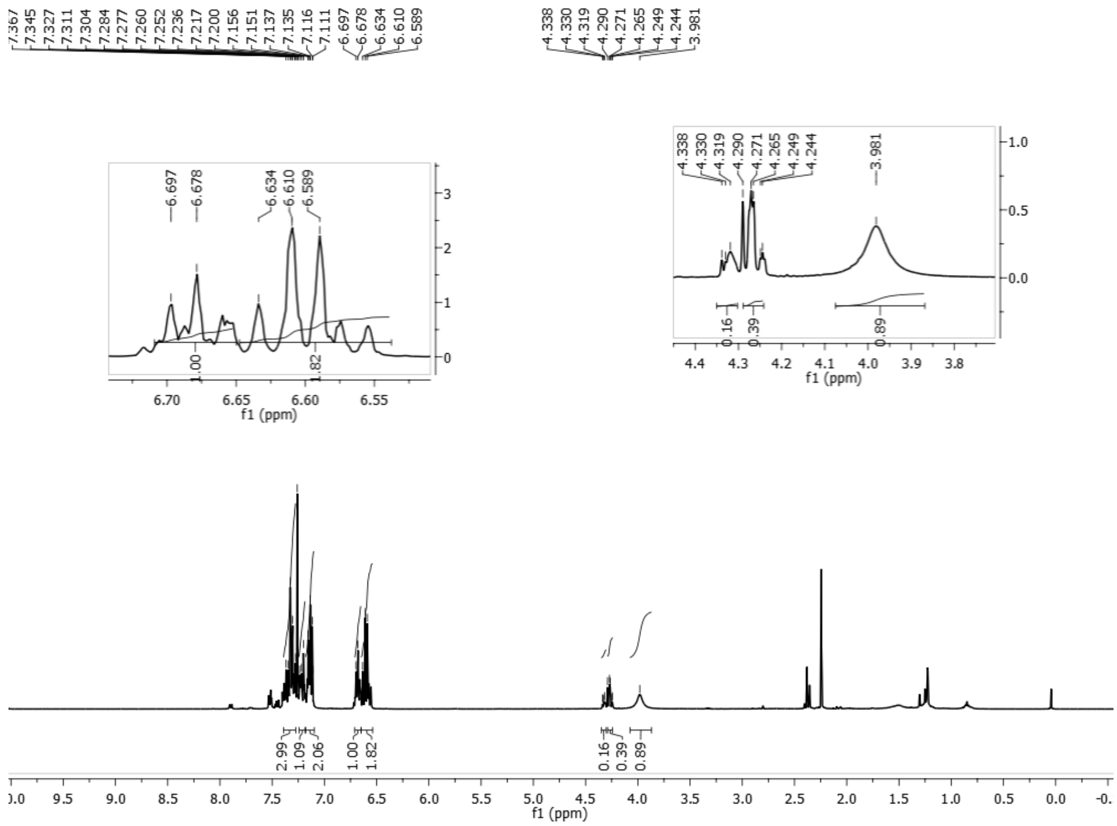
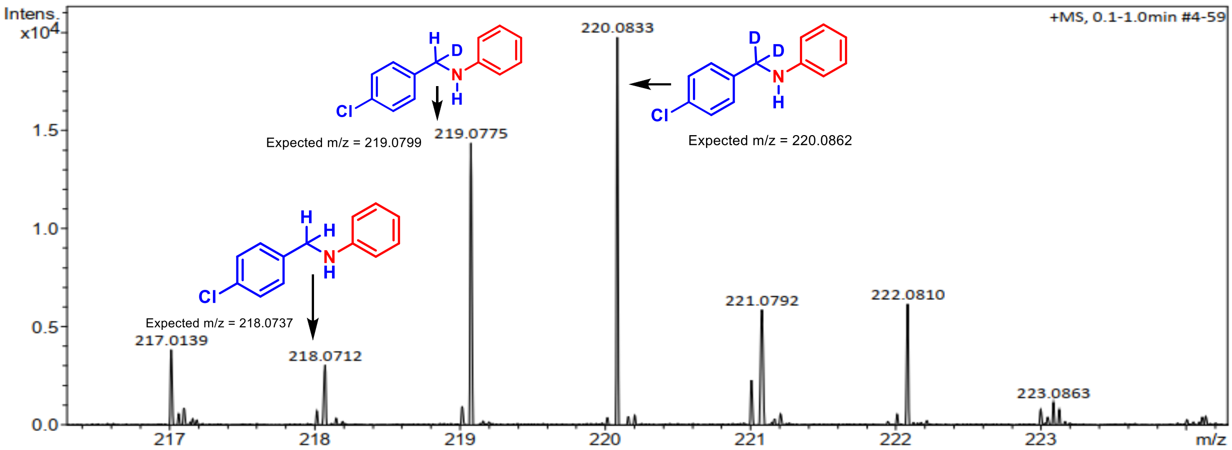


Figure S112: HRMS of alkylated amines obtained using deuterium labelled alcohol (**4c**, **4c-d_1**, and **4c-d_2**).



Deuterium labelling experiment: Performed with N-benzylideneaniline and deuterated 4-chloro benzyl alcohol (**2c-d₂**).

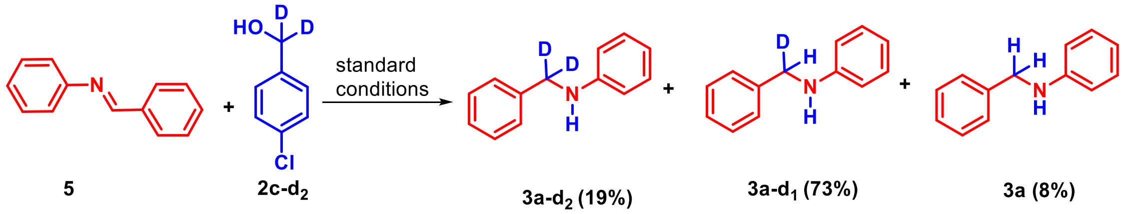


Figure S113. [1]H NMR spectrum of alkylated amines (**3a**, **3a-d₁**, and **3a-d₂**) obtained by reduction of imine using deuterium labelled alcohol in $CDCl_3$.

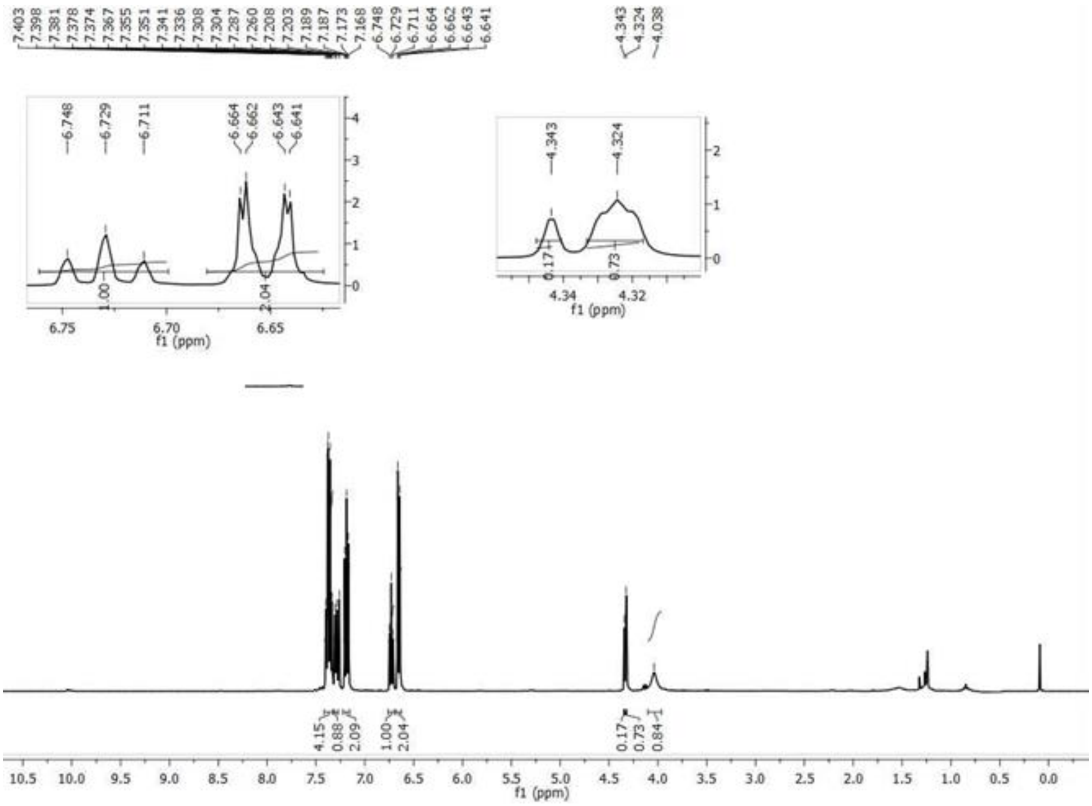


Figure S114: HRMS of alkylated amines (**3a**, **3a-d₁**, and **3a-d₂**) obtained by reduction of imine using deuterium labelled alcohol.

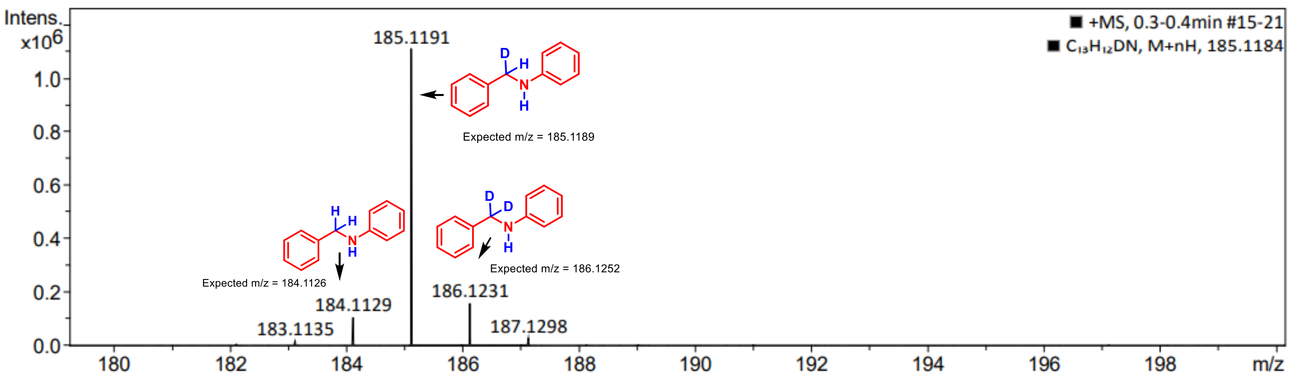


Figure S115. ^{1}H NMR spectrum of 9-(mesitylamino)-1H-phenalen-1-one ((*Mes*N,O)-PLY) in $CDCl_3$.

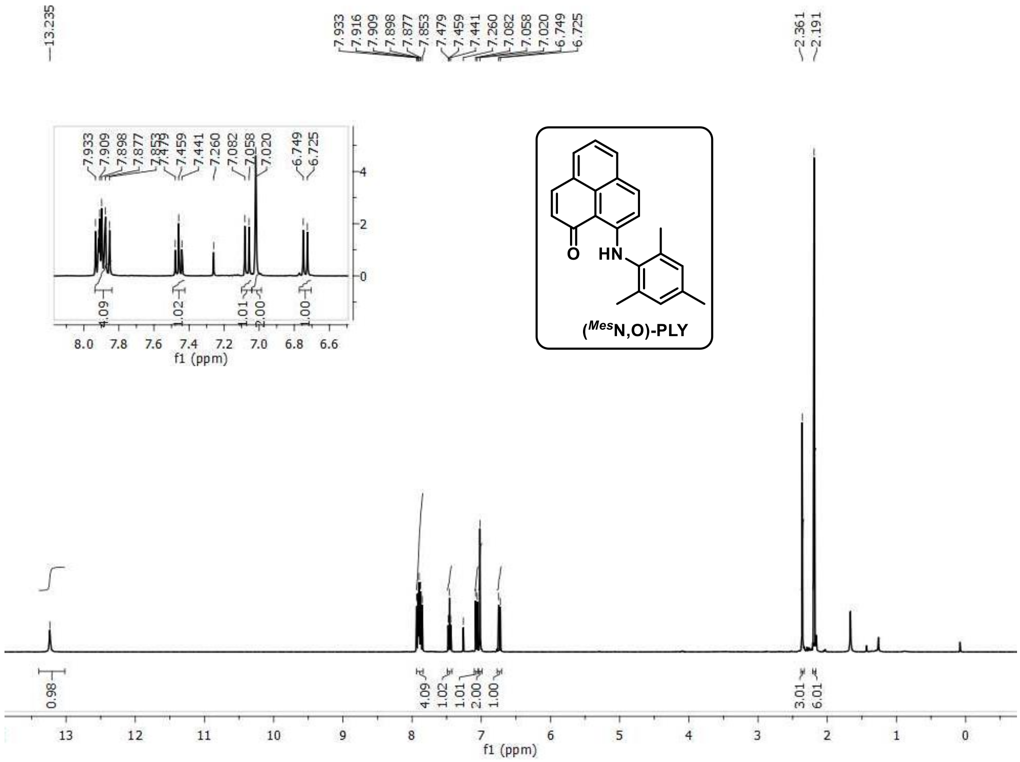


Figure S116. $^{13}C\{^{1}H\}$ NMR spectrum of 9-(mesitylamino)-1H-phenalen-1-one ((*Mes*N,O)-PLY) in $CDCl_3$.

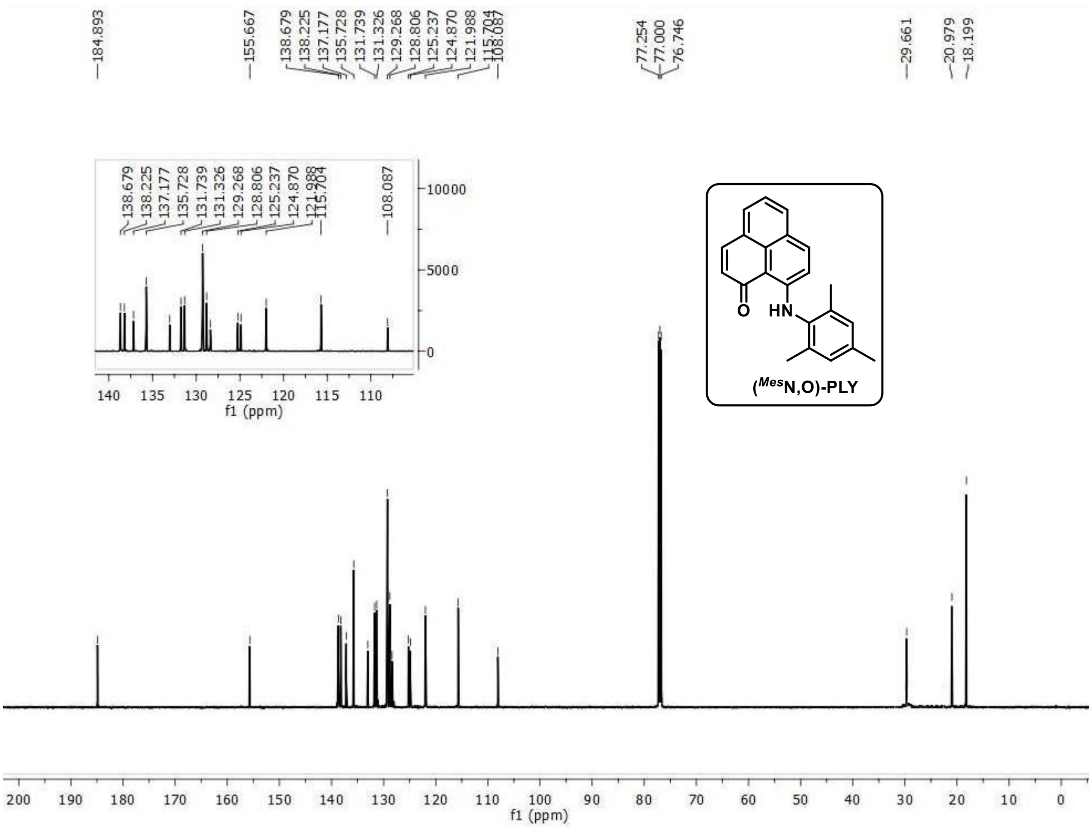


Figure S117. ^{1}H NMR spectrum of dearomatized (^{Mes}N,O)-PLY (**8′a**$_{Mes}$ and **8′b**$_{Mes}$) in $CDCl_3$ after storing borrowed hydrogen.

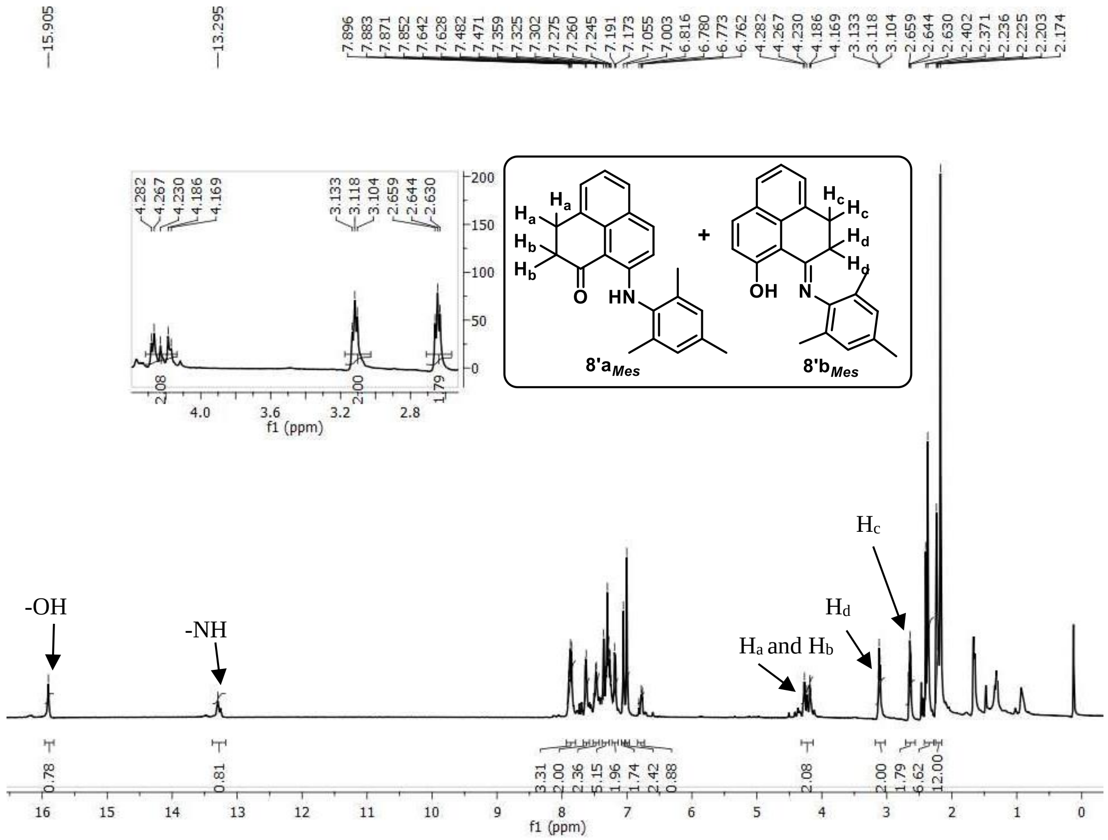


Figure S118. ^{13}C{^{1}H} NMR spectrum of dearomatized (^{Mes}N,O)-PLY (**8′a**$_{Mes}$ and **8′b**$_{Mes}$) in $CDCl_3$ after storing borrowed hydrogen.

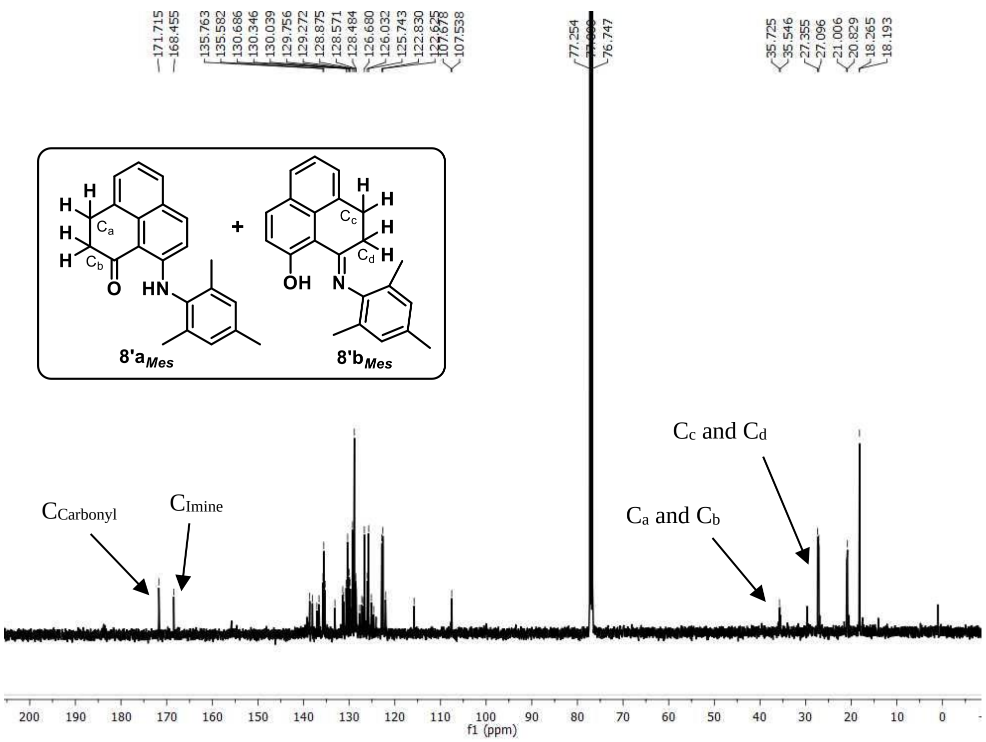


Figure S119. DEPT-135 NMR spectrum of dearomatized (^{Mes}N,O)-PLY (**8′a**$_{Mes}$ and **8′b**$_{Mes}$) after storing borrowed hydrogen in $CDCl_3$.

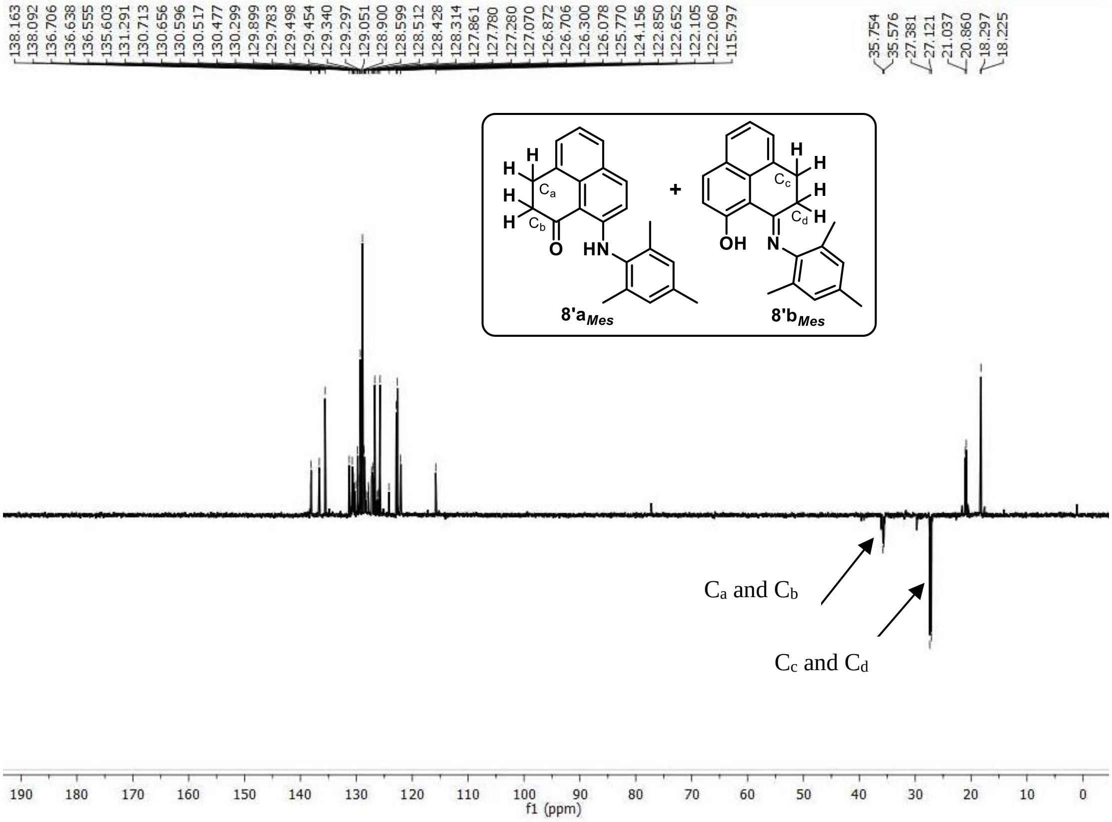


Figure S120. COSY NMR spectrum of dearomatized (^{Mes}N,O)-PLY (**8′a**$_{Mes}$ and **8′b**$_{Mes}$) after storing borrowed hydrogen in $CDCl_3$.

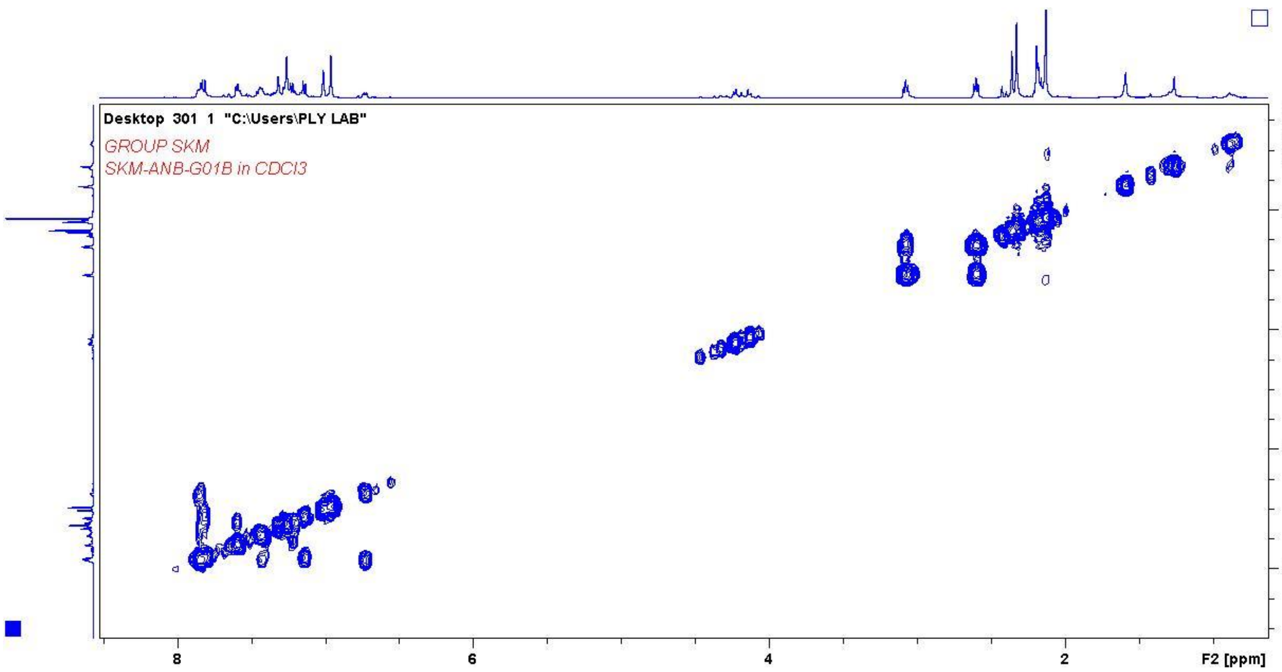


Figure S121. HSQC NMR spectrum of dearomatized (^{Mes}N,O)-PLY (**8′a*Mes*** and **8′b*Mes***) after storing borrowed hydrogen in $CDCl_3$.

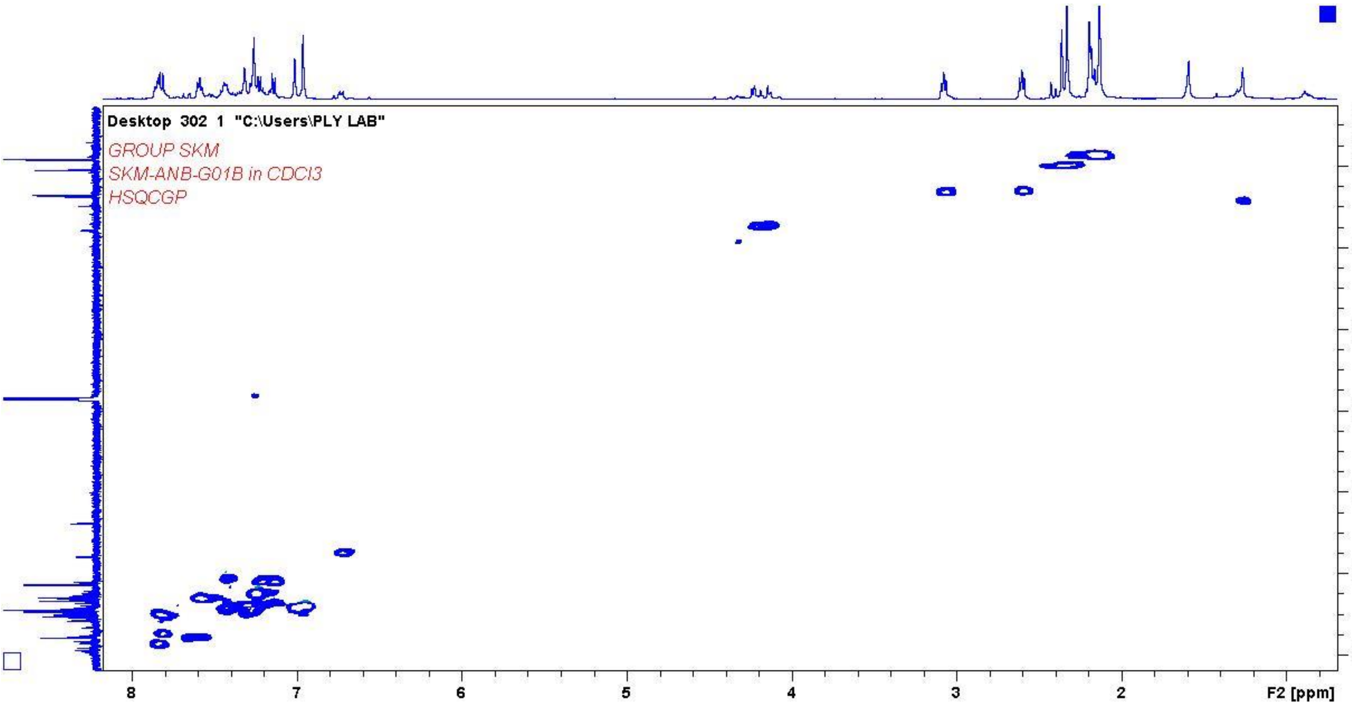
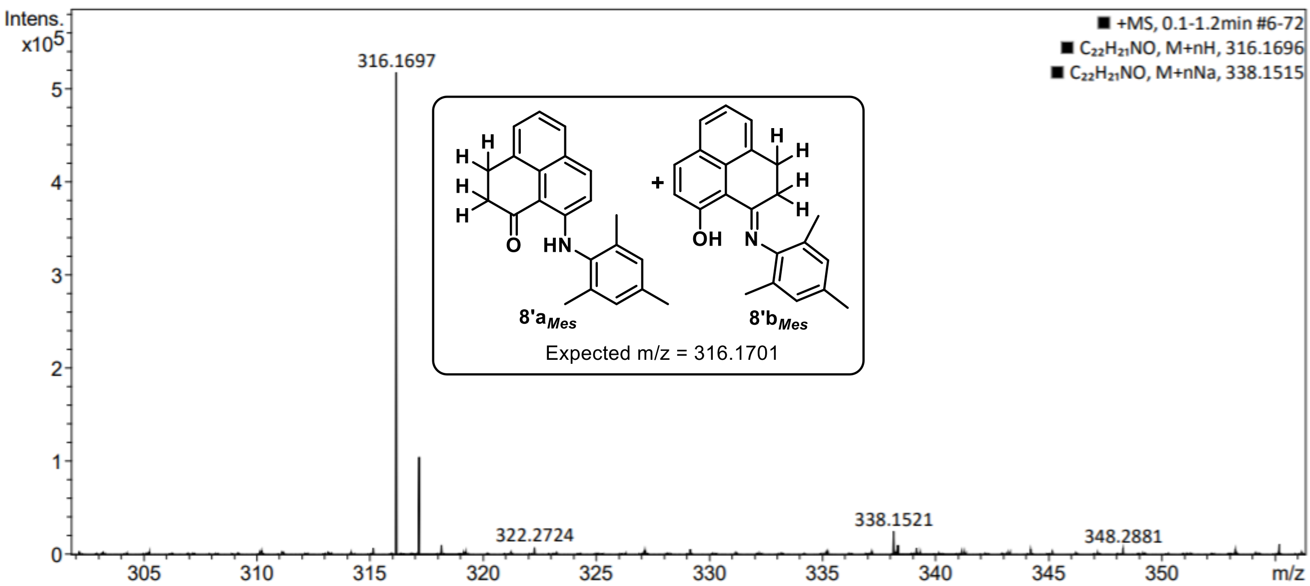


Figure S122. HRMS of dearomatized (^{Mes}N,O)-PLY (**8′a*Mes*** and **8′b*Mes***) after storing borrowed hydrogen.



Note: Only one major peak 316.1697 implies that two isomers with same m/z is present in the mixture.

Figure S123. ^{1}H NMR spectrum of dearomatized (^{Mes}N,O)-PLY (**8′a$_{Mes}$-d** and **8′b$_{Mes}$-d**) in $CDCl_3$ after storing borrowed hydrogen/D_2/HD.

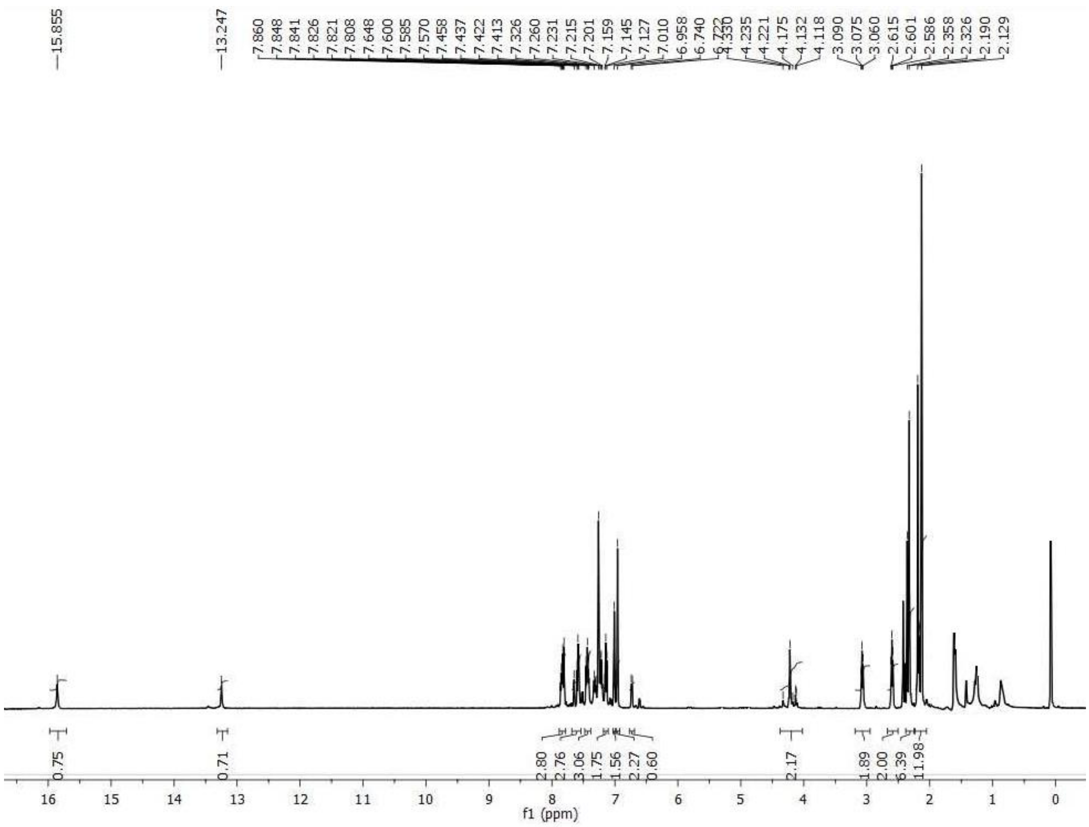


Figure S124. ^{13}C{^{1}H} NMR spectrum of dearomatized (^{Mes}N,O)-PLY (**8′a$_{Mes}$-d** and **8′b$_{Mes}$-d**) in $CDCl_3$ after storing borrowed hydrogen/D_2/HD.

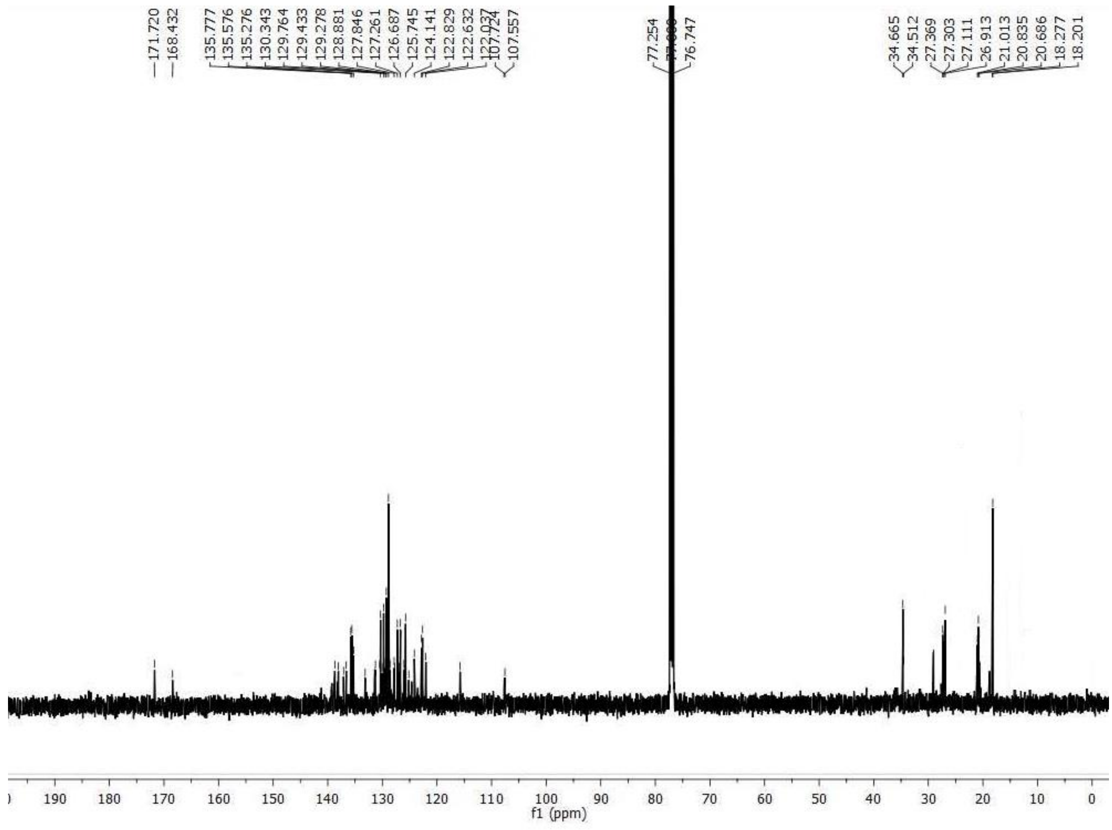


Figure S125. DEPT-135 NMR spectrum of dearomatized (^{Mes}N,O)-PLY (**8′a$_{Mes}$-d** and **8′b$_{Mes}$-d**) in $CDCl_3$ after storing borrowed hydrogen/D_2/HD.

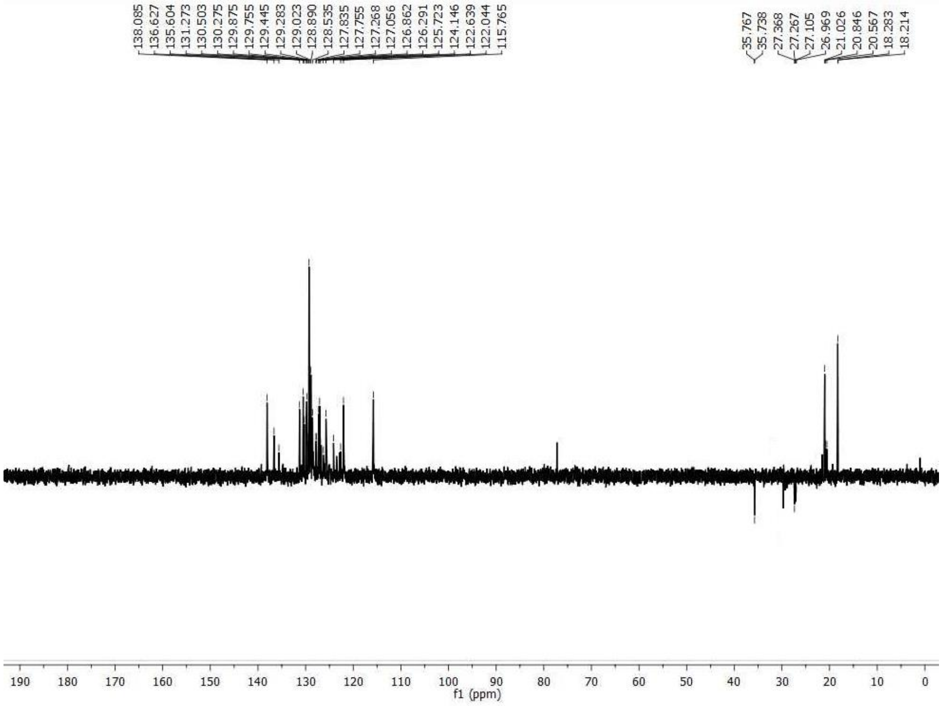
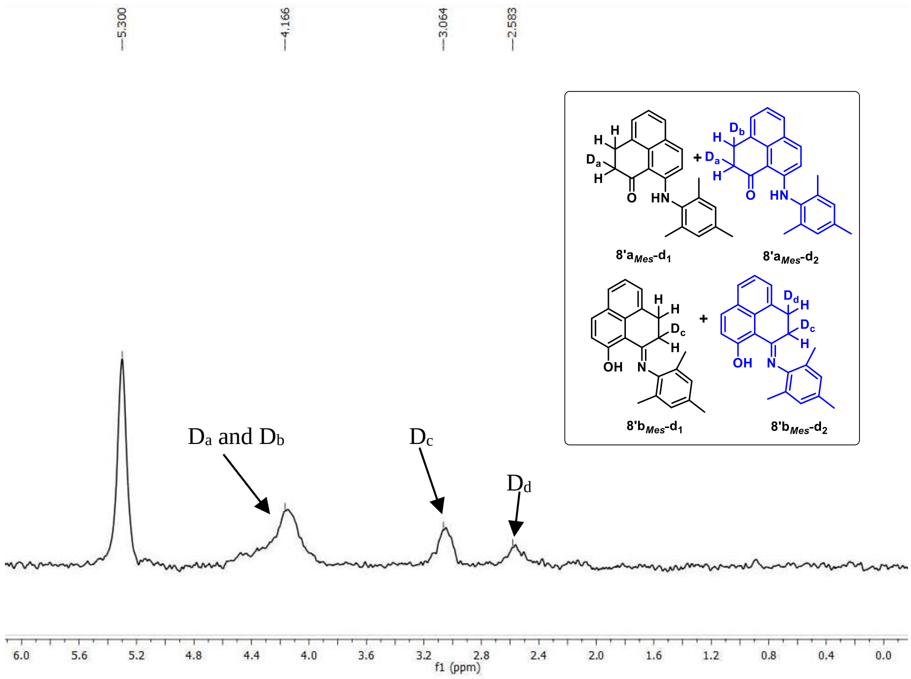
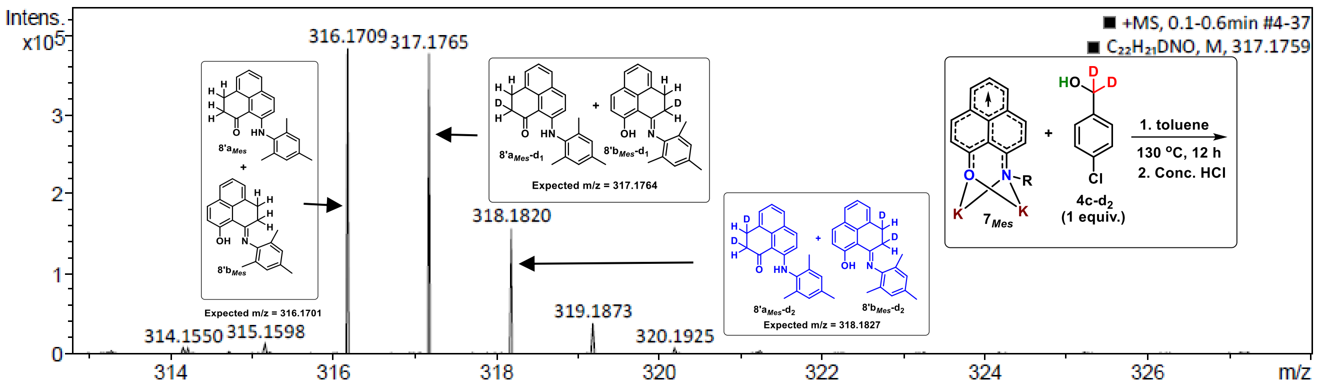


Figure S126. ^{2}H NMR spectrum of deuterated dearomatized (^{Mes}N,O)-PLY (**8′a$_{Mes}$-d** and **8′b$_{Mes}$-d**) in DCM after storing borrowed D_2/HD.



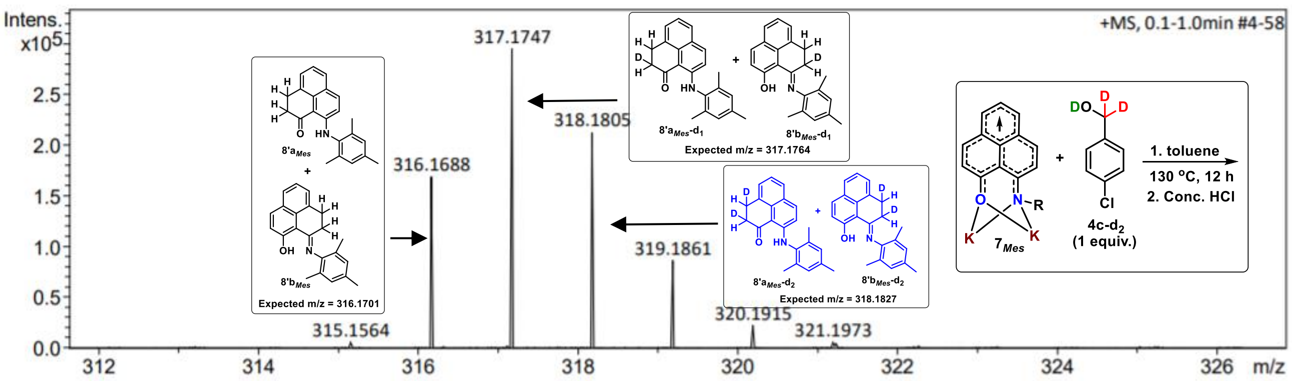
Note: The peak at δ 4.16 ppm consists of one D from **8′a$_{Mes}$-d$_1$** and two D from **8′a$_{Mes}$-d$_2$**. The other peaks i.e., peak at δ 3.06 ppm consists of one D from monodeuterated **8′b$_{Mes}$-d$_1$** and same D from dideuterated **8′b$_{Mes}$-d$_2$** whereas peak at δ 2.58 ppm consists of one D from dideuterated **8′b$_{Mes}$-d$_2$**.

Figure S127. HRMS of dearomatized (^{Mes}N,O)-PLY (**8′a$_{Mes}$-d** and **8′b$_{Mes}$-d**) after storing borrowed hydrogen/D_2/HD.



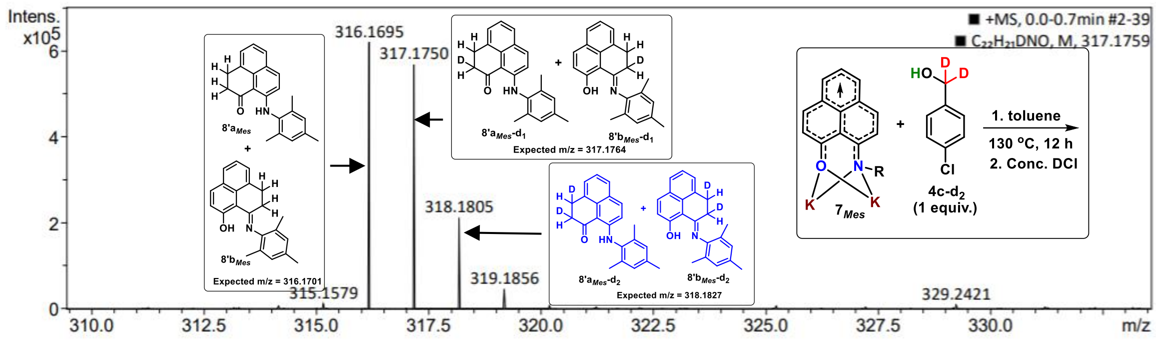
Note: Each pair of isomer resembles of same m/z. The ratio between **8′$_{Mes}$:8′$_{Mes}$-d$_1$:8′$_{Mes}$-d$_2$** obtained as 1:0.98:0.4.

Figure S128. HRMS of dearomatized deuterated dearomatized (^{Mes}N,O)-PLY (**8′a$_{Mes}$-d** and **8′b$_{Mes}$-d**) after storing borrowed hydrogen/D_2/HD when 4-chlorobenzyl alcohol (**4c-d$_3$**) is used.



Note: Each pair of isomer resembles of same m/z. The ratio between **8′$_{Mes}$:8′$_{Mes}$-d$_1$:8′$_{Mes}$-d$_2$** obtained as 1:1.78:1.26.

Figure S129. HRMS of dearomatized deuterated dearomatized (^{Mes}N,O)-PLY (**8′a$_{Mes}$-d** and **8′b$_{Mes}$-d**) after storing borrowed hydrogen/D_2/HD using 4-chlorobenzyl alcohol (**4c-d$_2$**) and DCl.



Note: Each pair of isomer resembles of same m/z. The ratio between **8′$_{Mes}$**:**8′$_{Mes}$-d$_1$**:**8′$_{Mes}$-d$_2$** obtained as 1:0.9:0.35.

Figure S130. ^{1}H NMR spectrum of reaction mixture showing evolution of hydrogen gas when HCl was charged to **8′$_{Mes}$**.

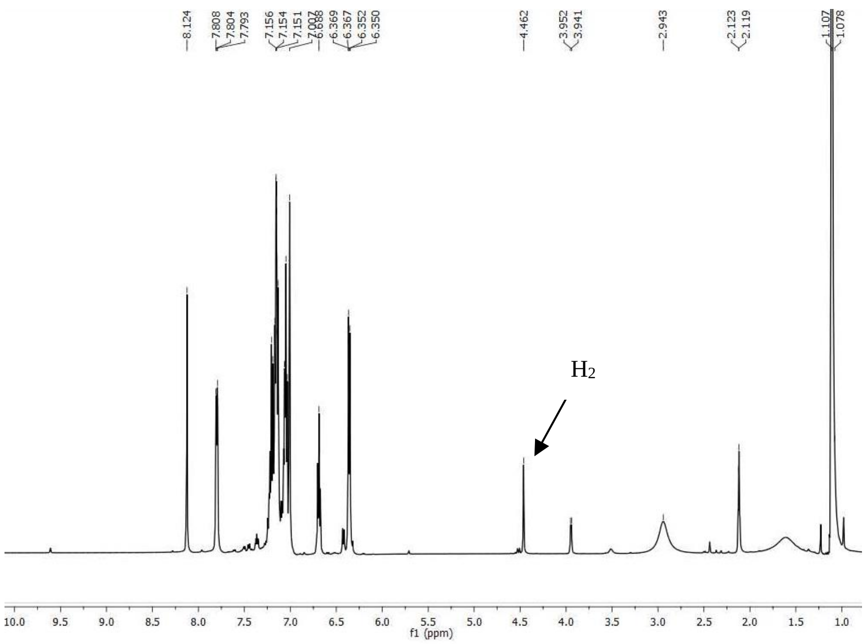


Figure S131. GC-MS of reaction mixture showing evolution of hydrogen gas when HCl was charged **8′**$_{Mes}$.

Page 1 of 1

Software Version	: 6.3.4.0700	Date	: 10-02-2021 18:58:30
Sample Name	:	Data Acquisition Time	: 10-02-2021 14:41:15
Instrument Name	: Clarus 590	Channel	: B
Rack/Vial	: 0/0	Operator	: IISER
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : C:\TurboMass\TcWS\Ver6.3.4\Examples\Installation\Sample H2 check1.rst
Sequence File : C:\TurboMass\TcWS\Ver6.3.4\Examples\Sample H2 check1.seq

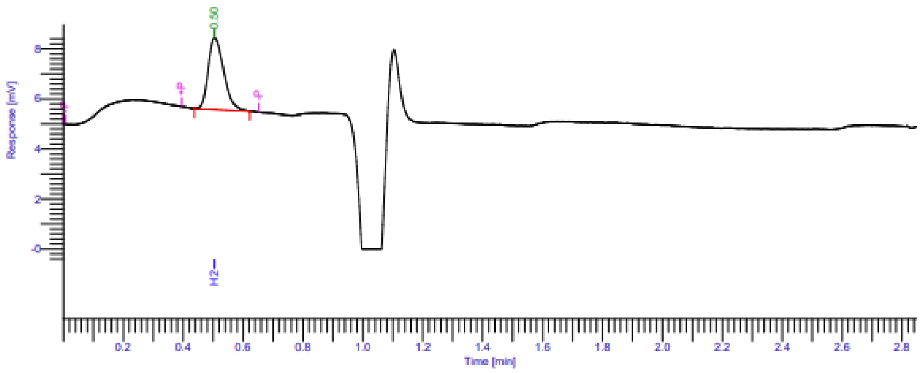


Figure S132. Reaction coordinate by DFT calculations for hydride mechanism (polar mechanism):

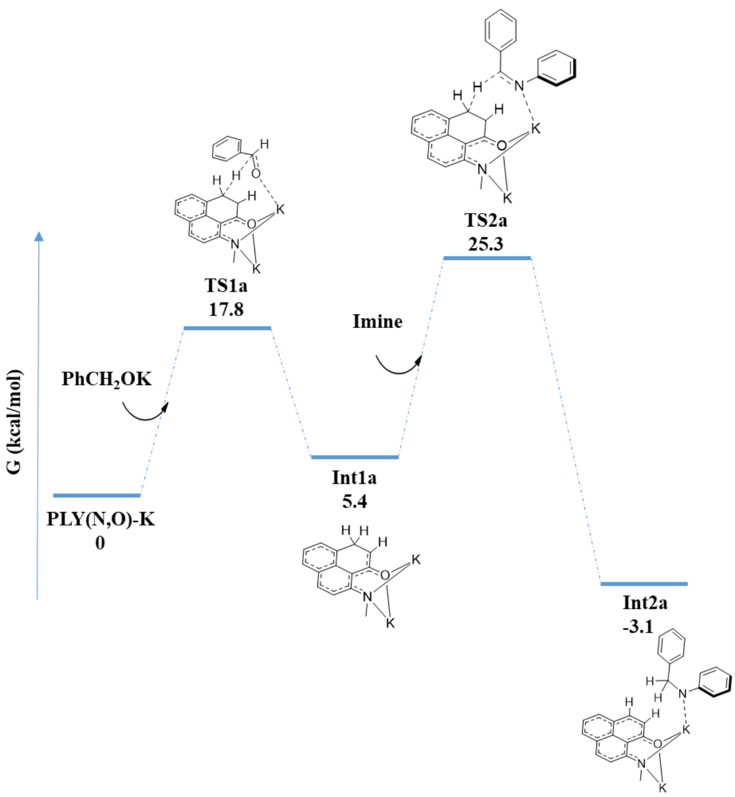
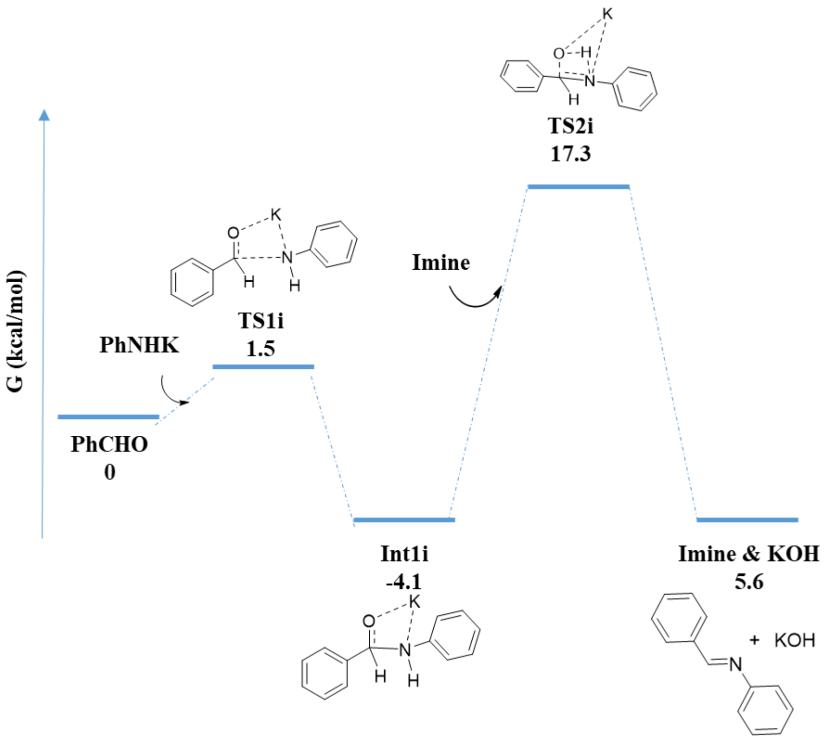
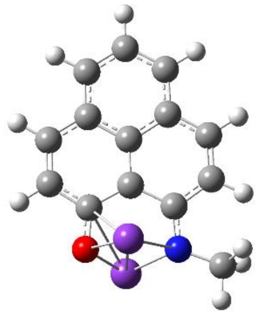


Figure S133. Reaction coordinate for the formation of N-benzylideneaniline assisted by KO^{t}Bu from DFT:



Co-ordinates:

7

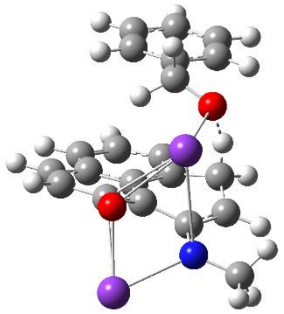


0 2

C	4.34245400	0.41313700	-0.00069700
C	3.79619800	-0.86168800	-0.00034700
C	2.39179600	-1.05534100	0.00001900
C	1.49932400	0.06635600	-0.00015900
C	2.09680600	1.37092800	-0.00018500
C	3.50331000	1.52029800	-0.00054800
C	1.84450600	-2.36120400	0.00072300
C	0.05918400	-0.10756600	-0.00010100
C	-0.45184800	-1.47661500	0.00004200
C	0.48506000	-2.54781500	0.00088000
C	-0.79696800	1.10413100	-0.00006100
C	-0.12579700	2.36347000	0.00052200
C	1.24436500	2.49806400	0.00031300
H	1.69013000	3.49085700	0.00055900
H	-0.72147700	3.26868800	0.00087200
H	2.52015000	-3.21434000	0.00117200
H	5.42131000	0.54559500	-0.00101300
H	4.43757800	-1.73982600	-0.00030100
H	3.91539300	2.52672600	-0.00065300
H	0.05339600	-3.54612700	0.00136900
O	-1.72862800	-1.79087100	-0.00016900
N	-2.16006200	1.01847800	-0.00035900
C	-2.87305600	2.27583300	0.00043600
H	-2.66252200	2.91322800	0.88188000
H	-2.66239500	2.91446200	-0.88007000
H	-3.95102700	2.07320100	0.00019900

K	-2.13675400	-0.55926300	-2.12764500
K	-2.13604000	-0.55898800	2.12737300

TS1

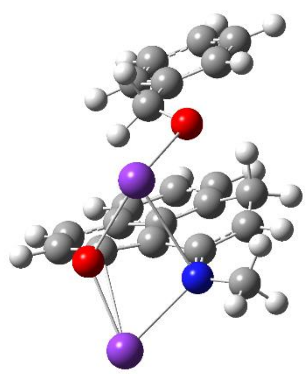


0 2

C	-2.46857700	2.10532800	1.54718800
C	-2.07612900	0.81321800	1.94813800
C	-0.89137000	0.25782600	1.50743400
C	-0.02941900	0.99421000	0.64826300
C	-0.48810200	2.24505800	0.15787400
C	-1.69582600	2.79889700	0.64451400
C	-0.53968600	-1.17064300	1.75646800
C	1.24325200	0.45046400	0.23135900
C	1.80419000	-0.68598200	1.01884900
C	0.89118900	-1.42647900	1.81822200
C	1.88464200	1.01796700	-0.90700800
C	1.35925700	2.27006700	-1.41102300
C	0.26412400	2.87776500	-0.87560000
H	-0.08337700	3.83287400	-1.26627300
H	1.89397800	2.70403800	-2.25277700
H	-1.11315200	-1.63138800	2.56453000
H	-3.40727300	2.51898400	1.90379700
H	-2.73752500	0.22020100	2.57578800
H	-2.01623100	3.76733300	0.26586700
H	1.24228100	-2.28730200	2.37528200
K	4.55515700	1.12849000	0.21900300
K	1.64400000	-1.81834400	-1.72760100
O	-0.70221500	-2.12925900	-0.88920800
H	-0.80787100	-1.70466500	0.74309900

C	-1.43755900	-1.23151500	-1.62445700
H	-1.66496500	-1.61918400	-2.64497900
H	-0.90422200	-0.26135500	-1.79516300
C	-2.78350100	-0.85957300	-1.00758400
C	-3.41677500	-1.74020200	-0.12699000
C	-3.40763100	0.35246000	-1.30918600
C	-4.64609000	-1.41304300	0.44325200
H	-2.91589500	-2.67591300	0.10802400
C	-4.63893400	0.68285100	-0.74577800
H	-2.90732500	1.05764300	-1.97232400
C	-5.26247500	-0.19845300	0.13719500
H	-5.12634900	-2.10584600	1.13051300
H	-5.10268200	1.63834300	-0.97922900
H	-6.21837900	0.05997600	0.58530900
O	2.90488900	0.49436400	-1.52156500
N	3.10851500	-0.95037300	0.97952000
C	3.58639800	-2.06527900	1.77693100
H	4.66333200	-2.18296700	1.61789100
H	3.42329400	-1.91846900	2.85618800
H	3.11152000	-3.02293900	1.50898700

7_{Int}

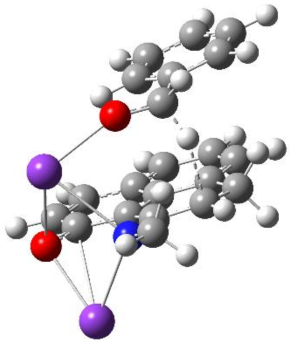


C	-2.55847900	2.34551600	1.35367500
C	-2.16182600	1.11657200	1.91117200
C	-0.98457700	0.50066800	1.53608000
C	-0.12397300	1.10589100	0.57898500
C	-0.57664300	2.30345000	-0.03964500
C	-1.77970900	2.91818100	0.37585700

C	-0.66550300	-0.87705600	2.03374000
C	1.14975700	0.51833000	0.21156200
C	1.67180800	-0.59215400	1.05057200
C	0.76336600	-1.22136100	1.95081500
C	1.82044800	1.00864100	-0.94808500
C	1.29259500	2.20273900	-1.57581800
C	0.18145500	2.83991400	-1.12244600
H	-0.17138800	3.74941700	-1.60591400
H	1.84478100	2.56451400	-2.43963200
H	-1.06217400	-1.04782100	3.04138700
H	-3.49332900	2.80501600	1.66036700
H	-2.81391200	0.61387100	2.62249600
H	-2.08811300	3.84005000	-0.11302700
H	1.10446000	-2.06464700	2.53806900
K	4.41459500	1.16557200	0.33037400
K	1.79744700	-1.90309500	-1.65846700
O	-0.47263800	-2.25433800	-0.74683700
C	-1.20480200	-1.42472700	-1.54353500
H	-1.41174400	-1.86006800	-2.55559800
H	-0.69794600	-0.44401100	-1.76630500
C	-2.57704300	-1.04182200	-0.98677700
C	-3.23321300	-1.90833800	-0.10846900
C	-3.20687700	0.15348300	-1.34071900
C	-4.48519700	-1.58310800	0.41185200
H	-2.72747000	-2.83316300	0.15971400
C	-4.46214000	0.48154400	-0.83047600
H	-2.69207600	0.84783700	-2.00474200
C	-5.10587300	-0.38466000	0.05306800
H	-4.98238800	-2.26593600	1.09737100
H	-4.92896300	1.42490600	-1.10460900
H	-6.08031600	-0.12769700	0.46056000
O	2.87816400	0.47632100	-1.48338000
N	2.94888700	-0.95295600	0.98407800
C	3.39025200	-2.06051200	1.81601000
H	4.44665800	-2.25824100	1.60816300
H	3.29796200	-1.85180000	2.89303500
H	2.83783900	-2.99222700	1.61938400

H	-1.16007000	-1.59940000	1.35172400

TS2

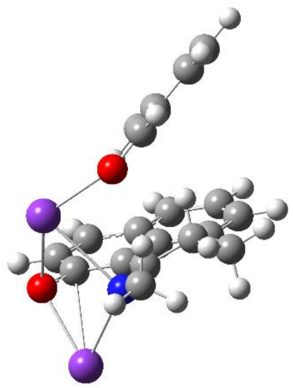


0 2

C	-3.07483600	2.51172900	0.82170800
C	-2.61421200	1.45428600	1.62314000
C	-1.35707200	0.90595300	1.46032800
C	-0.47655200	1.38255800	0.44731500
C	-0.96386300	2.44571300	-0.36705500
C	-2.24747100	2.99835000	-0.16172600
C	-0.94299700	-0.20279700	2.38663000
C	0.83737900	0.80349500	0.21299600
C	1.24214500	-0.37895500	1.03903500
C	0.33316700	-0.86575700	2.01128600
C	1.62994100	1.32461700	-0.85742300
C	1.08069700	2.40326600	-1.65336100
C	-0.14361800	2.93764600	-1.42435000
H	-0.52356100	3.74597200	-2.04690400
H	1.71919300	2.75894800	-2.45785700
H	-1.74859500	-0.95129600	2.43610200
H	-4.06991300	2.92045300	0.96985400
H	-3.26537800	1.03966000	2.39090600
H	-2.57089900	3.80849500	-0.81212000
H	0.67553400	-1.63870900	2.68962400
K	3.87280700	1.25955800	1.02355300
K	2.25444800	-1.48294800	-1.91940600
C	-0.61308100	-2.77000800	-0.10948300
H	-0.30184200	-2.31033900	0.91420100

O	0.37878300	-2.65323500	-0.98411700
C	-1.89717300	-2.00379300	-0.41045800
C	-1.91188600	-0.98589300	-1.36407100
C	-3.06523400	-2.25741000	0.31624100
C	-3.06202300	-0.22818400	-1.58122700
H	-0.99844200	-0.79096500	-1.92041700
C	-4.21895400	-1.50478100	0.10443100
H	-3.06612500	-3.05718500	1.05745600
C	-4.21898800	-0.48271400	-0.84641300
H	-3.05036700	0.57503600	-2.31411100
H	-5.11877900	-1.71547000	0.67749800
H	-5.11231100	0.11486100	-1.00791900
H	-0.88103800	-3.81749800	0.16162900
H	-0.85436700	0.19181300	3.41366500
O	2.82346100	0.92966200	-1.18910900
N	2.42476800	-0.96747100	0.84624700
C	2.66899000	-2.21698300	1.54483400
H	3.63848000	-2.61367000	1.22429600
H	2.71143200	-2.10721800	2.64212000
H	1.90166900	-2.96962200	1.31100300

Int2h2-Ald



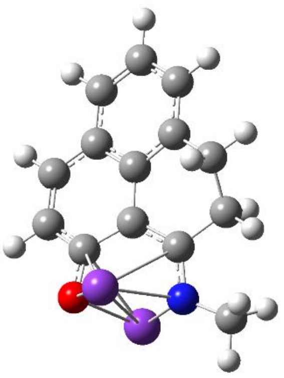
0 2

C	-2.10241200	3.57711900	0.71644600
C	-1.79492300	2.60644000	1.68797400
C	-0.76150400	1.70890300	1.51377400
C	0.01752300	1.72370800	0.32261900

C	-0.29191600	2.71673300	-0.64483400
C	-1.34844500	3.63132800	-0.43171900
C	-0.43623700	0.69103100	2.56929500
C	1.08853800	0.76493200	0.09520400
C	1.19329400	-0.39297900	1.02118300
C	0.00012500	-0.61924100	1.92373000
C	1.85203900	0.86215300	-1.11390500
C	1.49050900	1.89424700	-2.06439300
C	0.47518500	2.76749900	-1.84726900
H	0.22803800	3.52338300	-2.59068400
H	2.08086100	1.91951000	-2.97644500
H	-1.30750800	0.52006800	3.20936800
H	-2.92646800	4.26604800	0.87433200
H	-2.38961700	2.55019600	2.59703000
H	-1.55863100	4.37052700	-1.20167500
H	0.22818400	-1.35997400	2.69049100
K	4.21753900	0.52796900	0.57287300
K	1.48093800	-2.11748800	-1.64896900
C	-1.54798300	-3.10521600	0.01194600
O	-0.28715500	-3.02501600	-0.24095500
C	-2.49265200	-2.07891700	-0.26278300
C	-2.11268500	-0.83372200	-0.85111700
C	-3.87229300	-2.23403000	0.06880800
C	-3.03724900	0.18034100	-1.05204000
H	-1.06891500	-0.66560300	-1.10967600
C	-4.78417800	-1.21943900	-0.14735200
H	-4.19930000	-3.17495600	0.50903500
C	-4.38263800	0.00986300	-0.70503600
H	-2.70352800	1.12663800	-1.47482200
H	-5.82703200	-1.37286100	0.12191100
H	-5.10089200	0.80883800	-0.86148900
H	-1.93465200	-4.02728200	0.47462300
H	0.36907800	1.07093500	3.21822000
O	2.83681900	0.08781300	-1.44313200
N	2.23314900	-1.17176400	1.02670800
C	2.18943900	-2.39375100	1.82838500
H	3.10223800	-2.96607800	1.63345000

H	2.15458500	-2.19208600	2.90803700
H	1.32347500	-3.01287800	1.55757400
H	-0.81952300	-1.02559500	1.31879400

8b

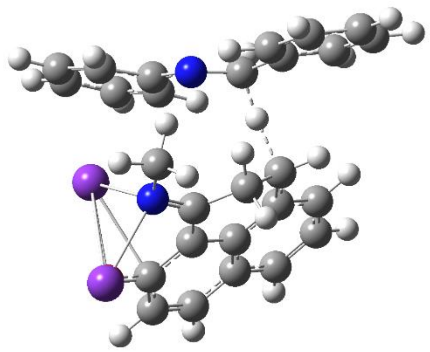


0 2

C	-4.32821000	0.30042000	-0.14354900
C	-3.50001800	1.43336800	-0.07000900
C	-2.12294400	1.29543900	0.01795300
C	-1.50124200	0.02223800	0.02077500
C	-2.35434800	-1.12509100	0.00351200
C	-3.75826600	-0.95252500	-0.09862100
C	-1.23305700	2.49309900	0.16593700
C	-0.03286000	-0.11249600	0.07658200
C	0.78100700	1.02819200	-0.26865600
C	0.03449700	2.29975500	-0.64867400
C	0.47873900	-1.46022900	0.37067400
C	-0.42439800	-2.55018800	0.33486000
C	-1.78534200	-2.41916000	0.12568900
H	-2.43411700	-3.29140800	0.10403000
H	0.01943300	-3.52822800	0.51181800
H	-1.75798700	3.40817600	-0.13160400
H	-5.40623000	0.41402700	-0.22063800
H	-3.93436000	2.43089500	-0.07650500
H	-4.38280200	-1.84333100	-0.12583900
H	-0.23635800	2.25228700	-1.71874500
K	2.16078800	-1.27919800	-1.81218500
K	2.14682900	0.17034200	2.16368500

H	0.67711900	3.17501200	-0.52993300
H	-0.95186900	2.61098100	1.22653500
N	2.13325600	0.97143100	-0.41094700
O	1.75040500	-1.70825000	0.62052600
C	2.82676500	2.19458700	-0.76006300
H	2.74883800	2.98953600	0.01017000
H	3.89503000	1.97106300	-0.86774400
H	2.50060100	2.66079100	-1.70608800

TS3



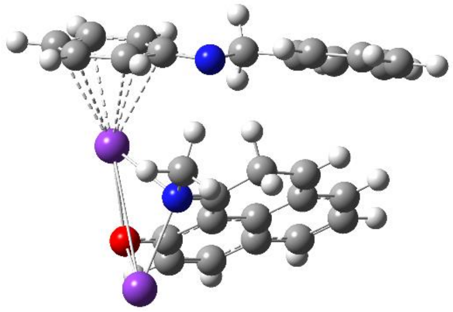
0 2

C	-0.49462400	4.53604500	1.28683900
C	0.48210500	3.69801500	0.73671000
C	0.15102200	2.52388900	0.05102200
C	-1.22989400	2.14527700	-0.07542100
C	-2.20398100	3.01811500	0.47732200
C	-1.82687500	4.20541700	1.15140000
C	1.17428200	1.69026900	-0.50896600
C	-1.62371400	0.90207600	-0.71176800
C	-0.56571900	0.03090900	-1.27286000
C	0.77742700	0.68141500	-1.54337400
C	-3.01467300	0.57016000	-0.78646400
C	-3.96487900	1.51673900	-0.25309000
C	-3.58125200	2.67194100	0.35110500
H	-4.32614200	3.35236300	0.76036600
H	-5.01190600	1.24129800	-0.34717600
H	2.13534400	2.17243800	-0.69440500
H	-0.20124500	5.44331300	1.80718300

H	1.53426100	3.96071000	0.82574400
H	-2.60663300	4.84280600	1.56106200
H	0.70381200	1.15343600	-2.54187100
K	-2.76225000	-1.61851000	-3.31737600
K	-2.19617300	-1.65523400	0.81182800
C	2.46493300	-0.24898900	0.95445500
H	1.74069900	0.70318300	0.48824400
H	2.58281400	0.10306700	1.99476600
C	3.72934200	-0.06699000	0.17782000
C	4.49935500	1.09015300	0.36371900
C	4.14647400	-0.99610400	-0.78297300
C	5.64981200	1.31596300	-0.38657700
H	4.18652700	1.81857100	1.11122100
C	5.29764100	-0.77093500	-1.53650700
H	3.56165700	-1.90303300	-0.90488400
C	6.05382300	0.38529500	-1.34563100
H	6.23456000	2.21723300	-0.22222900
H	5.61196900	-1.50731100	-2.27209600
H	6.95220300	0.55755100	-1.93164700
C	0.85215700	-1.79714800	1.63107800
C	0.21459900	-0.90905800	2.56681200
C	0.35525100	-3.14629900	1.62640600
C	-0.74127900	-1.37154000	3.46837200
H	0.49436700	0.14049900	2.58585500
C	-0.59657700	-3.58404600	2.53225200
H	0.81768400	-3.83966100	0.92752700
C	-1.16865300	-2.70564600	3.47412300
H	-1.16880400	-0.66904500	4.18170400
H	-0.89444800	-4.63118700	2.52343900
H	-1.88828600	-3.05997900	4.20533600
N	1.84233600	-1.48065100	0.78811300
H	1.56089400	-0.07823900	-1.61529700
O	-3.49125300	-0.53778100	-1.26045700
N	-0.78565000	-1.21521200	-1.57155100
C	0.31656900	-2.02812800	-2.08450300
H	-0.07320100	-3.02141800	-2.34203500
H	0.79035000	-1.60638000	-2.98322900

H	1.09076100	-2.15657200	-1.31226800

9

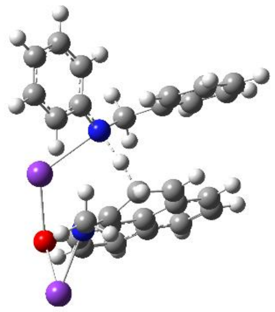


0 2

C	-3.35632100	3.27181200	-1.36955500
C	-3.33373300	2.25774900	-0.41788800
C	-2.11884700	1.76402400	0.11813000
C	-0.85875000	2.31952100	-0.33644300
C	-0.92080500	3.34309300	-1.31444500
C	-2.16227200	3.81205900	-1.81637600
C	-2.13372400	0.74117400	1.05780000
C	0.41127500	1.84935300	0.17493300
C	0.41237800	0.78016800	1.19701000
C	-0.89722100	0.14688200	1.60356000
C	1.62237100	2.41436900	-0.36212200
C	1.50010100	3.44992900	-1.35978800
C	0.29730100	3.89517200	-1.80619900
H	0.24509000	4.67959400	-2.55916700
H	2.43570100	3.85168300	-1.73917400
H	-3.08074500	0.31035200	1.37339400
H	-4.30326600	3.62992400	-1.76271400
H	-4.26007800	1.80977000	-0.06660900
H	-2.15393200	4.59991200	-2.56524800
H	-0.94816100	0.11806700	2.70348700
K	2.97647600	2.47545800	2.39504500
K	2.70300300	-0.44362400	-0.71890300
C	-1.23564300	-2.29275400	-0.89752400
H	-1.04536500	-1.31990300	-1.40492900
H	-1.35901100	-3.02223500	-1.72237400

C	-2.57736800	-2.17992900	-0.19995000
C	-3.63714700	-1.52609800	-0.83831000
C	-2.78943400	-2.71165000	1.07341400
C	-4.87872900	-1.39853200	-0.22104800
H	-3.47705200	-1.09220300	-1.82439600
C	-4.02929000	-2.57634700	1.70131500
H	-1.95981200	-3.21560000	1.56118300
C	-5.07823200	-1.91866900	1.05943500
H	-5.68762800	-0.88352600	-0.73325200
H	-4.17779200	-2.98993100	2.69575700
H	-6.04285700	-1.81526300	1.54887300
C	1.00255800	-2.89358800	-0.59189600
C	1.30140200	-2.75554200	-2.00089500
C	2.13221600	-3.28717000	0.22163000
C	2.59125400	-2.93617600	-2.49794300
H	0.50551300	-2.51816100	-2.69877700
C	3.40247600	-3.44571900	-0.29678600
H	1.93970600	-3.47941900	1.27425300
C	3.67403100	-3.24259900	-1.66743700
H	2.75447400	-2.82881100	-3.56954900
H	4.20864500	-3.75085500	0.36880800
H	4.66871700	-3.39805400	-2.07218800
N	-0.16657900	-2.66090500	-0.00714000
H	-0.82483800	-0.91867500	1.30913700
O	2.82265100	2.06624500	-0.02797200
N	1.51163000	0.34074300	1.74506900
C	1.40694900	-0.78161100	2.67400900
H	2.41634600	-1.11110800	2.93955300
H	0.88536800	-0.50888600	3.60498400
H	0.87353600	-1.63385500	2.23072400

TS4

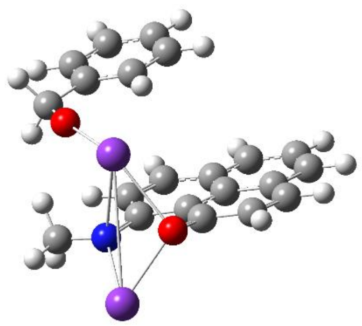


0 2

C	1.63403600	4.38937200	-0.32581300
C	0.84374900	3.69258300	0.58291100
C	0.94841400	2.28688700	0.73439500
C	1.90711000	1.55363800	-0.07009900
C	2.67252500	2.29305800	-1.01085000
C	2.53706500	3.70302400	-1.12180000
C	0.10241900	1.58789800	1.58996800
C	2.06774900	0.12603600	0.06612800
C	1.31175200	-0.56111900	1.15120800
C	0.11941000	0.13493300	1.66280800
C	2.93427000	-0.56421400	-0.85169600
C	3.68083200	0.23028300	-1.79091700
C	3.57038000	1.58725900	-1.85685200
H	4.15817100	2.15207900	-2.57858200
H	4.33631300	-0.31985300	-2.46145600
H	-0.65971200	2.12965800	2.14471400
H	1.52985900	5.46671300	-0.42079700
H	0.10419000	4.21562400	1.18433100
H	3.14884000	4.22807300	-1.85100000
H	-0.27100600	-0.25212500	2.60348000
K	4.24038600	-2.14267600	1.25955000
K	0.58507100	-2.35583100	-1.27307500
C	-1.64029300	0.61203200	-1.13482100
H	-0.66144500	1.08325400	-1.30891700
H	-2.10308600	0.50627200	-2.13220500
C	-2.46543400	1.60290900	-0.31915000
C	-2.42093200	2.96146200	-0.64955100

C	-3.22920300	1.20744300	0.78106500
C	-3.12100400	3.90486600	0.09823500
H	-1.80200200	3.28490500	-1.48529100
C	-3.93498800	2.14894000	1.53147300
H	-3.25848100	0.15808400	1.06176900
C	-3.88302400	3.50061900	1.19534100
H	-3.06212300	4.95725900	-0.16723200
H	-4.52409200	1.82337100	2.38481000
H	-4.42790200	4.23360200	1.78375700
C	-2.38509200	-1.61834400	-0.56641000
C	-3.63395000	-1.48595500	-1.23580700
C	-2.15397200	-2.87249900	0.07089200
C	-4.53759500	-2.54044300	-1.29363500
H	-3.89935800	-0.53771200	-1.69334900
C	-3.07256700	-3.91387900	0.01156400
H	-1.24660900	-2.98992700	0.66431800
C	-4.27404000	-3.76974100	-0.68406800
H	-5.47875900	-2.39312700	-1.81882000
H	-2.85089700	-4.84694000	0.52553800
H	-4.99222800	-4.58176300	-0.73213700
N	-1.40115800	-0.67382500	-0.51635000
H	-0.68799100	-0.30009700	0.77802600
O	3.08533900	-1.85586000	-0.91093800
N	1.63571800	-1.77203500	1.53702100
C	0.86511400	-2.36016600	2.62490000
H	1.23591600	-3.37337400	2.81370000
H	0.95704100	-1.78747500	3.56060500
H	-0.20932000	-2.43823600	2.40802600

Int1a

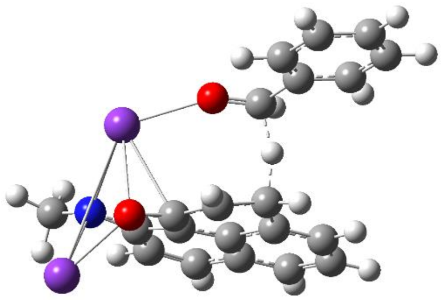


0 1

C	-1.37716100	4.15639700	-0.57806100
C	-0.20215900	4.26183300	0.14606000
C	0.67167100	3.16635100	0.28251000
C	0.37708300	1.92087300	-0.34298300
C	-0.84448900	1.83484200	-1.07563300
C	-1.69503600	2.93289500	-1.17707500
C	1.85960700	3.27085600	1.07055300
C	1.25767400	0.78954600	-0.22379700
C	2.41082200	0.90780800	0.62955400
C	2.67191500	2.19843000	1.24250600
C	0.92102900	-0.45410100	-0.94694900
C	-0.40057200	-0.50798800	-1.57641600
C	-1.20902300	0.56632400	-1.65510400
H	-2.18475600	0.48168800	-2.13077900
H	-0.74094500	-1.45413400	-1.97907300
H	2.09028600	4.22345300	1.54427800
H	-2.04917000	5.00416700	-0.66954000
H	0.06109500	5.19816200	0.63397700
H	-2.62790200	2.81850000	-1.72520800
H	3.56496300	2.25533500	1.85937800
O	3.21738900	-0.04766000	0.91408900
N	1.75305500	-1.46300300	-1.01135600
C	1.29350100	-2.68572000	-1.65873100
H	0.44415100	-3.11931600	-1.10943900
H	1.00582700	-2.53880000	-2.71014100
H	2.10847900	-3.42069000	-1.64592300
K	4.39431100	-1.28123900	-0.90680700
K	1.25204500	-1.70077000	1.81211700
C	-1.92086200	-2.98730200	0.36968900
H	-1.83037800	-3.27106000	-0.71282300
H	-2.44529100	-3.86110600	0.82765200
O	-0.72882900	-2.71675100	0.94848800
C	-2.93533700	-1.83670200	0.39210700
C	-4.15822000	-1.94270500	-0.28196000
C	-2.65267400	-0.64704800	1.06248600

C	-5.06861500	-0.88745400	-0.29387000
H	-4.39308900	-2.86579000	-0.81281100
C	-3.55814200	0.41599600	1.05839500
H	-1.69234700	-0.56525900	1.56526000
C	-4.76998200	0.30171900	0.37768100
H	-6.01107300	-0.98859000	-0.82719300
H	-3.31102100	1.34029800	1.57619100
H	-5.47566000	1.12853500	0.36841500

TS1a

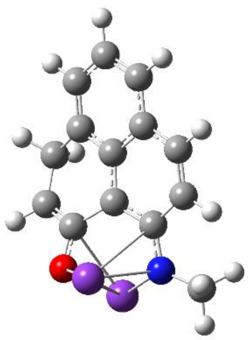


0 1

C	-0.40870000	4.22101800	0.41110700
C	-1.03397000	3.07945200	0.93831200
C	-0.43352700	1.83053900	0.88257800
C	0.85496400	1.66557500	0.28688200
C	1.45084000	2.82541000	-0.28753800
C	0.81938900	4.08206600	-0.20645500
C	-1.15273800	0.62787400	1.33647000
C	1.51166900	0.38745500	0.26532200
C	0.91829900	-0.69312100	1.08887800
C	-0.36997200	-0.51410600	1.62638600
C	2.70506400	0.22169900	-0.54423700
C	3.27895600	1.44703500	-1.09515600
C	2.70098800	2.66781900	-0.95630500
H	3.18274400	3.54939200	-1.37694700
H	4.21689000	1.38102000	-1.63437100
H	-2.02625100	0.81597100	1.96655700
H	-0.89369200	5.19059200	0.47368700

H	-2.02061800	3.16339600	1.39093800
H	1.31729400	4.94340700	-0.64782800
H	-0.78239700	-1.33868400	2.20004500
O	1.55306200	-1.79133900	1.31387600
N	3.25525200	-0.97236800	-0.80039800
C	4.39639500	-1.00002000	-1.69757700
H	4.19100200	-0.56633200	-2.69113500
H	5.28927400	-0.47372100	-1.31087200
H	4.69068900	-2.04348800	-1.86146300
K	3.99762000	-1.80362100	1.63480400
K	0.84386500	-2.33297300	-1.19205300
C	-2.21198100	-0.31959100	-0.92611000
H	-1.83940800	0.31536800	0.22622100
H	-2.03993000	0.56842500	-1.56963400
O	-1.43935900	-1.32919300	-1.05904400
C	-3.65534000	-0.51357700	-0.56465700
C	-4.55418800	0.55839000	-0.62861300
C	-4.10648800	-1.75634700	-0.11078300
C	-5.88344600	0.39019400	-0.25043000
H	-4.20180600	1.52820400	-0.97816000
C	-5.43750100	-1.92519500	0.26943400
H	-3.39760500	-2.57873500	-0.06926500
C	-6.32986500	-0.85465200	0.20077000
H	-6.57455900	1.22702100	-0.30918500
H	-5.78192900	-2.89529400	0.61891800
H	-7.36739400	-0.98792900	0.49467700

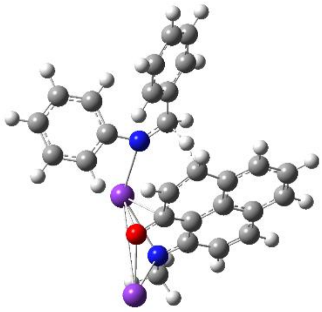
Int2a



0 1

C	-4.37126300	0.34900000	0.07004100
C	-3.76475900	-0.92901900	0.11300300
C	-2.39907000	-1.08963400	0.02434100
C	-1.54324400	0.05793900	-0.06437300
C	-2.16984000	1.33357100	-0.18961900
C	-3.57888400	1.45805000	-0.10444500
C	-1.78636500	-2.46162900	-0.13099300
C	-0.11603100	-0.07931200	-0.04382200
C	0.42600000	-1.40304900	0.45447600
C	-0.37079500	-2.50984500	0.37188200
C	0.70338700	1.03693300	-0.43537700
C	0.01716800	2.31383700	-0.56080100
C	-1.33293800	2.45768200	-0.41449200
H	-1.78722000	3.44440200	-0.49587800
H	0.60433200	3.20020300	-0.77552200
H	-2.40696800	-3.20050100	0.39204400
H	-5.45128100	0.44224900	0.14262000
H	-4.39419500	-1.81512900	0.18149600
H	-4.01912100	2.45037300	-0.18562100
H	0.00588100	-3.43460000	0.80536900
O	1.63306000	-1.44410700	0.98016300
N	2.03839200	0.92949900	-0.64428300
C	2.72896200	2.13366400	-1.05092600
H	2.34169300	2.58451500	-1.98322300
H	2.71504700	2.94963700	-0.29716900
H	3.78528900	1.89684400	-1.22803300
H	-1.85300300	-2.73379600	-1.20090700
K	2.15574900	0.70842800	2.08206900
K	2.50069100	-1.58984700	-1.39364100

TS2a

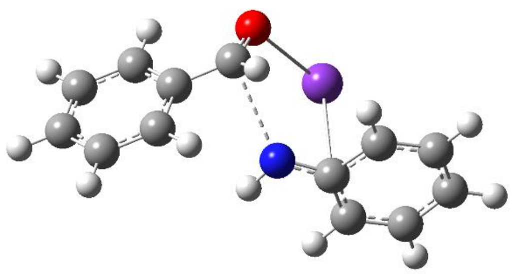


0 1

C	1.26705600	4.69362400	0.35997400
C	0.39036400	3.75700900	0.92888600
C	0.65035500	2.39431700	0.88708400
C	1.83452300	1.89555200	0.26015400
C	2.69395200	2.86020600	-0.34086000
C	2.40476300	4.23776600	-0.27641100
C	-0.33234500	1.43052800	1.40412000
C	2.14337000	0.48815000	0.24183700
C	1.29466400	-0.40276100	1.06889800
C	0.12457200	0.11710800	1.65888400
C	3.27637000	0.02379000	-0.54138300
C	4.12166100	1.06095500	-1.12593100
C	3.85707600	2.38740400	-1.01707900
H	4.53314300	3.11548800	-1.46317100
H	5.01162200	0.75860900	-1.66502300
H	-1.08881800	1.84632600	2.07473800
H	1.04425900	5.75529400	0.41050700
H	-0.52732700	4.09571100	1.40656600
H	3.09675000	4.93628200	-0.74292200
H	-0.46351700	-0.56760800	2.26344500
O	1.60068600	-1.63992100	1.25991500
N	3.54478200	-1.27242100	-0.75198900
C	4.66900000	-1.59043600	-1.61455300
H	4.58308200	-1.17151800	-2.63189500
H	5.64711900	-1.25405700	-1.22457200
H	4.72935400	-2.67991800	-1.72646300
K	3.90693000	-2.41659600	1.63590200

K	0.91667000	-1.92882700	-1.31236500
C	-1.78587200	0.71124700	-0.74044700
H	-1.13551900	1.27539900	0.32616000
H	-1.32386700	1.36683200	-1.49029200
C	-3.17030900	1.14466500	-0.36377500
C	-3.83867700	2.10017700	-1.13665600
C	-3.79679900	0.65968500	0.79419600
C	-5.11078300	2.54769700	-0.77790000
H	-3.35769700	2.49253600	-2.03038700
C	-5.06442100	1.10598400	1.15411400
H	-3.28303900	-0.07423900	1.41135200
C	-5.72970800	2.04924500	0.36673900
H	-5.61692100	3.28601700	-1.39427200
H	-5.53660700	0.71754200	2.05251000
H	-6.72069400	2.39451000	0.64798100
C	-2.13887800	-1.65972400	-0.45530200
C	-3.40031800	-1.88620500	-1.05691000
C	-1.62957900	-2.68569200	0.37397700
C	-4.10602800	-3.06230300	-0.82995100
H	-3.81155100	-1.12590600	-1.71563500
C	-2.34286800	-3.86394100	0.58986700
H	-0.68174800	-2.51712400	0.88634600
C	-3.58734200	-4.06603500	-0.00683500
H	-5.07250900	-3.20086100	-1.30920000
H	-1.92497500	-4.62473900	1.24573300
H	-4.14382200	-4.98256800	0.16588800
N	-1.34098500	-0.56296100	-0.75548600

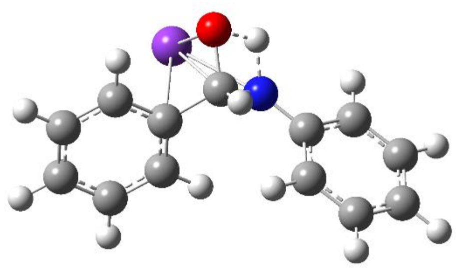
TS1i



0 1

C	-4.59119100	-1.01494600	-0.58871900
C	-4.28064300	0.29073300	-0.97214300
C	-3.16648900	0.92619100	-0.43041100
C	-2.36552300	0.25512700	0.49659000
C	-2.67976100	-1.05005500	0.88419800
C	-3.79102800	-1.68552200	0.33837500
H	-5.46047700	-1.51052500	-1.01177700
H	-4.91101700	0.81156700	-1.68702200
H	-4.03232400	-2.70355300	0.62917700
H	-2.91340400	1.94708000	-0.70327200
H	-2.02163100	-1.56382100	1.58036700
C	-1.19653700	0.93701400	1.10504900
H	-0.79858600	0.48263100	2.02136400
N	0.35406000	-0.89145700	0.23966900
H	-0.06489300	-1.39719800	-0.54589600
C	1.69583600	-0.90881400	0.14771900
C	2.44737300	-1.35592700	-0.98977100
C	2.47761200	-0.29473800	1.18337000
C	3.82023000	-1.16044200	-1.09007100
H	1.91391200	-1.86430200	-1.79224800
C	3.84755300	-0.10217600	1.06030400
H	1.95753900	0.01410300	2.08852900
C	4.54564300	-0.51304400	-0.08299500
H	4.33729500	-1.51956300	-1.97804000
H	4.38746800	0.37043100	1.87877400
H	5.61703700	-0.36679600	-0.16929800
O	-0.77026800	2.01634800	0.70131600
K	1.32075500	1.65626100	-0.73514900

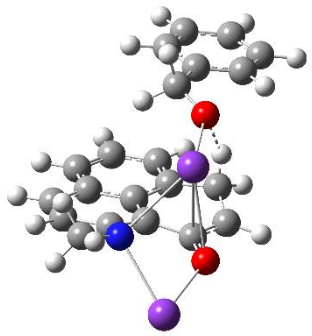
TS2i



0 1

C	-3.57278800	-1.80219500	-0.61868600
C	-2.29354600	-1.89459900	-1.16621400
C	-1.23389300	-1.18281600	-0.59813200
C	-1.44315600	-0.37548800	0.52574200
C	-2.73092400	-0.28669100	1.06841600
C	-3.78927200	-0.99679100	0.50129000
H	-4.39654300	-2.35611600	-1.05982200
H	-2.11790600	-2.52215100	-2.03579300
H	-4.78412300	-0.92247500	0.93214900
H	-0.23559100	-1.24316300	-1.02731500
H	-2.88625000	0.35535300	1.93181400
C	-0.31261100	0.44418300	1.13310700
H	0.11659300	-0.11503800	1.98443200
O	-0.71765200	1.74164400	1.51713400
K	-1.41487800	2.08692800	-0.98231500
N	0.72581100	0.87847600	0.18484700
H	0.37355800	1.91984700	0.89097200
C	1.93939200	0.21984700	0.10263800
C	3.05345400	0.89938800	-0.43719000
C	2.12912100	-1.11947400	0.50185700
C	4.28625400	0.27630100	-0.56276100
H	2.92415200	1.93429600	-0.74567800
C	3.37394800	-1.73538600	0.37356100
H	1.29429500	-1.68393600	0.90980600
C	4.46331400	-1.05103100	-0.15822700
H	5.12371000	0.83248500	-0.97707600
H	3.48631000	-2.76840200	0.69384300
H	5.42926200	-1.53630400	-0.25676300

TS1O

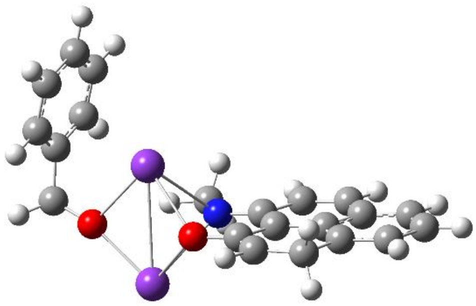


0 2

C	2.22944900	2.66625800	-0.99936400
C	2.13593100	1.34343800	-1.45646500
C	0.96772700	0.61177900	-1.31279500
C	-0.16742000	1.18324700	-0.67589000
C	-0.04283100	2.50572900	-0.17664100
C	1.14723100	3.23710800	-0.36031400
C	0.92213200	-0.83244000	-1.66213100
C	-1.39231700	0.42797700	-0.49539300
C	-1.54878200	-0.82490100	-1.23205900
C	-0.41906800	-1.34874500	-1.90150100
C	-2.39860600	0.93472100	0.42149000
C	-2.23353800	2.31319000	0.86321200
C	-1.13919400	3.05409500	0.55682600
H	-1.06674100	4.08329400	0.90488500
H	-3.01829900	2.76858900	1.45558700
H	1.67108300	-1.13219200	-2.39992100
H	3.15588300	3.21919900	-1.12314200
H	3.00568700	0.86062700	-1.89822900
H	1.20323400	4.25103900	0.03009500
H	-0.56464400	-2.28865400	-2.42718900
O	-2.64524200	-1.50071000	-1.25077100
N	-3.40500700	0.17432900	0.87539800
C	-4.26296700	0.76310900	1.88984400
H	-3.71578700	1.11552600	2.77929500
H	-4.85551900	1.62410100	1.53044500
H	-4.97574700	0.00356100	2.23498000

K	-4.95442700	-0.82129600	-1.01924000
K	-1.41619700	-1.94104000	1.35449100
O	1.01385600	-1.62991000	1.10967400
H	1.18619500	-1.33692600	-0.65396800
C	1.89025400	-0.71450200	1.63207600
H	2.06948500	-0.87879100	2.71903700
H	1.51586200	0.33357000	1.55775200
C	3.27066100	-0.70688300	0.97450400
C	3.69336800	-1.78275500	0.19326400
C	4.13290300	0.38385700	1.13088900
C	4.94432600	-1.76701400	-0.42739400
H	3.01357500	-2.62291100	0.07591000
C	5.38355700	0.40479700	0.51909600
H	3.80277700	1.23860500	1.72067100
C	5.79407100	-0.67303900	-0.26933800
H	5.25716200	-2.61145000	-1.03722700
H	6.03620200	1.26534900	0.64560300
H	6.76624200	-0.65764900	-0.75485200

7_{Int}O

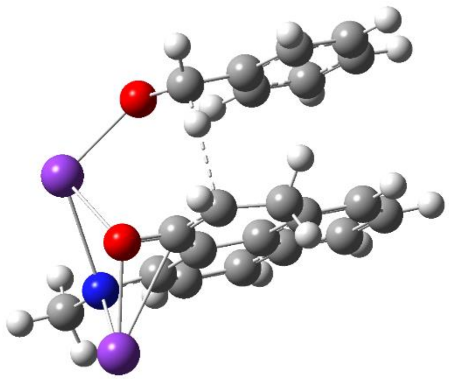


0 2

C	-6.20474500	0.68151400	-0.86756400
C	-5.63037400	-0.55973300	-1.16123900
C	-4.30564600	-0.84287600	-0.86187200
C	-3.47665100	0.12810700	-0.23991500
C	-4.07653300	1.38562200	0.05203900
C	-5.42000300	1.64489600	-0.26260600
C	-3.76505100	-2.20161200	-1.20514700
C	-2.08256800	-0.12389000	0.09006700

C	-1.50040100	-1.40940400	-0.25998600
C	-2.33371700	-2.37851400	-0.88281500
C	-1.30526800	0.91932800	0.75187400
C	-1.98623500	2.18860300	1.00699000
C	-3.27820300	2.40012700	0.67931900
H	-3.74475700	3.36087300	0.89051000
H	-1.42823600	2.98729900	1.48045500
H	-4.35893600	-2.97409900	-0.68636700
H	-7.24359800	0.88032400	-1.11164500
H	-6.23169300	-1.33231400	-1.63794300
H	-5.83179900	2.62206200	-0.02001400
H	-1.85418000	-3.32282000	-1.12449500
O	-0.27974700	-1.73321800	-0.04780000
N	-0.04715100	0.73645100	1.11060000
C	0.65995400	1.82385800	1.76684300
H	0.74511700	2.72661200	1.13922500
H	0.19271200	2.13672700	2.71481300
H	1.67600400	1.47726300	1.99096500
K	0.85996900	-1.59832400	2.26092100
K	1.75958700	-0.28667500	-0.72422300
O	3.04011200	-0.89321900	1.46651100
H	-3.93301400	-2.40563100	-2.27585300
C	4.36979300	-0.55545700	1.39788100
H	5.04363700	-1.43126100	1.50307100
H	4.67150400	0.16248000	2.18976000
C	4.65658100	0.09482700	0.04816600
C	4.95716000	-0.68988300	-1.07163500
C	4.41422800	1.46034600	-0.14736200
C	4.99422600	-0.13530100	-2.35263600
H	5.14672600	-1.75266500	-0.93108500
C	4.44880800	2.02393400	-1.42397400
H	4.17906800	2.08018800	0.71630300
C	4.73088900	1.22412100	-2.53399800
H	5.23105400	-0.76076800	-3.20955500
H	4.25902700	3.08615900	-1.55502000
H	4.75948100	1.65923900	-3.52887200

TS2O

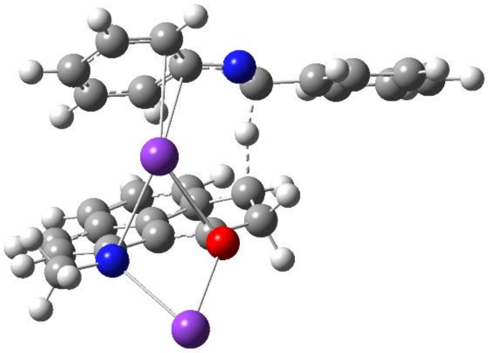


0 2

C	-2.80496900	2.69216200	0.58913000
C	-2.51541200	1.64041200	1.46937200
C	-1.32194400	0.94208200	1.41296000
C	-0.33781300	1.26295200	0.43734300
C	-0.65625600	2.31817300	-0.45966100
C	-1.87405200	3.02087400	-0.37014200
C	-1.09520300	-0.15998900	2.40980000
C	0.93105400	0.55172300	0.33290700
C	1.14005500	-0.60030200	1.21657100
C	0.11657900	-0.96657800	2.12925500
C	1.89587800	0.96165200	-0.67885600
C	1.46970000	2.00907100	-1.59783300
C	0.28011700	2.64517400	-1.48603800
H	0.01652100	3.42992000	-2.19344000
H	2.13667800	2.30043300	-2.39946500
H	-1.98438000	-0.80804100	2.43912000
H	-3.75452400	3.21492200	0.65108400
H	-3.25310100	1.34475500	2.21334600
H	-2.06731600	3.81798100	-1.08506800
H	0.35266100	-1.80724800	2.77623600
O	2.21097900	-1.31221800	1.21203100
N	3.12320200	0.43052700	-0.77982800
C	3.97072000	0.90114000	-1.86048200
H	3.55038000	0.72047300	-2.86521400
H	4.20092100	1.97975700	-1.81192000
H	4.92640300	0.36654100	-1.81368700

K	3.80699300	0.51464100	1.76608300
K	2.22381800	-2.18142300	-1.25613000
C	-1.09873100	-2.63713700	-0.14475300
H	-0.71907900	-2.25274800	0.87773400
O	-0.13276000	-2.58931500	-1.06062900
C	-2.32352800	-1.76699100	-0.40956800
C	-2.28440400	-0.78869800	-1.40427300
C	-3.48349500	-1.89794500	0.36025500
C	-3.37948600	0.04592800	-1.62187100
H	-1.37297700	-0.70365400	-1.99099100
C	-4.58155000	-1.06468600	0.14869200
H	-3.52629700	-2.66893300	1.13060300
C	-4.53156700	-0.08740600	-0.84649400
H	-3.33241900	0.81136700	-2.39313200
H	-5.47843600	-1.18150800	0.75274400
H	-5.38353400	0.56678800	-1.01381500
H	-1.45642300	-3.66487300	0.10222900
H	-1.02279900	0.27183000	3.42420100

TS3O



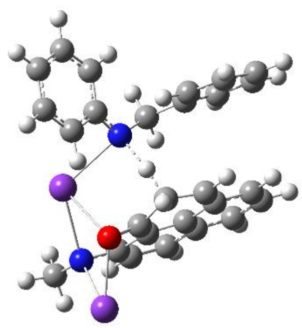
0 2

C	0.11745600	4.32396800	1.00484900
C	0.93254500	3.47941300	0.24928600
C	0.44561800	2.30347200	-0.34603000
C	-0.93634300	1.95620900	-0.17701700
C	-1.73275000	2.81343400	0.61402700
C	-1.21146600	3.99328400	1.19202200
C	1.33666000	1.40179100	-1.00748400

C	-1.49355700	0.73176100	-0.74902600
C	-0.64980900	-0.06347600	-1.59643100
C	0.75847100	0.38199900	-1.93243700
C	-2.87585500	0.35652900	-0.44314200
C	-3.62866800	1.29256200	0.37921900
C	-3.09254300	2.44222300	0.85384000
H	-3.70520700	3.10900400	1.45912900
H	-4.66063600	1.06743400	0.61658500
H	2.30764100	1.80359800	-1.29953000
H	0.53057700	5.22543700	1.44792900
H	1.98492000	3.72067200	0.11460800
H	-1.86811800	4.62042600	1.78969100
H	0.72184900	0.74739200	-2.97589800
O	-0.99983200	-1.15442900	-2.13560200
N	-3.43453200	-0.77787000	-0.87045500
C	-4.79297100	-1.05954700	-0.43075000
H	-4.89546000	-1.11322600	0.66499600
H	-5.53620300	-0.32383400	-0.78182600
H	-5.09429900	-2.03765800	-0.82492800
K	-3.08355500	-1.17446300	-3.45666600
K	-1.29913100	-2.14928900	0.36452300
C	2.66140200	-0.20475900	0.84708200
H	1.91866400	0.48107700	0.06988500
H	2.74057800	0.54674200	1.65667700
C	3.92746500	-0.28803400	0.05850400
C	4.71651400	0.85627000	-0.12073600
C	4.32188600	-1.47580700	-0.56885600
C	5.86653900	0.81991200	-0.90543600
H	4.42468400	1.78307300	0.37229900
C	5.47252900	-1.51385600	-1.35405100
H	3.71577100	-2.36231600	-0.40881800
C	6.24947200	-0.36804500	-1.52951900
H	6.46831500	1.71709400	-1.02556300
H	5.76984900	-2.44600500	-1.82827100
H	7.14793600	-0.40151800	-2.13948000
C	1.01817400	-1.39499000	1.99867000
C	0.19049400	-0.24743000	2.24048100

C	0.57083800	-2.62010000	2.60264700
C	-1.01539500	-0.35469500	2.92711400
H	0.47850800	0.71811000	1.83512300
C	-0.62053600	-2.69965500	3.30502600
H	1.21428100	-3.48945100	2.49075000
C	-1.45829000	-1.57646700	3.45077200
H	-1.62767600	0.53826300	3.04372900
H	-0.90989000	-3.64818100	3.75422400
H	-2.39083200	-1.64266800	4.00230900
N	2.10464100	-1.42436500	1.21200800
H	1.37640500	-0.52686700	-1.96471100

TS4O



0 2

C	1.29359700	4.48348900	-0.30489900
C	0.52596300	3.76597400	0.60362100
C	0.70735000	2.37086400	0.80318000
C	1.72926200	1.67416100	0.04427100
C	2.47765900	2.43766500	-0.88527800
C	2.26250700	3.82985300	-1.05152000
C	-0.10998000	1.66165100	1.67781100
C	1.98031700	0.25789100	0.22195600
C	1.18248500	-0.44101600	1.22753800
C	-0.01904700	0.21236400	1.76776200
C	2.97378100	-0.41550000	-0.61493600
C	3.69025800	0.42840500	-1.55053000
C	3.45903600	1.76417100	-1.66399600
H	4.03557300	2.34777700	-2.38038300

H	4.44284100	-0.01914700	-2.18788800
H	-0.90506100	2.18014200	2.20753700
H	1.12506600	5.54858400	-0.43708100
H	-0.25894200	4.25946200	1.17136200
H	2.86624400	4.36794500	-1.77781200
H	-0.33489100	-0.24001500	2.71152600
O	1.38929100	-1.64138800	1.57471400
N	3.21451600	-1.73575600	-0.54445800
C	4.17420900	-2.27953400	-1.48864800
H	3.90166000	-2.11134100	-2.54496500
H	5.19760400	-1.87865300	-1.37047500
H	4.23686100	-3.36354700	-1.34075600
K	3.83662900	-1.74617200	2.03125500
K	0.56852000	-2.54780000	-0.82791900
C	-1.70576300	0.38957700	-1.16361100
H	-0.73238400	0.86804100	-1.35266000
H	-2.13528800	0.18661300	-2.16166500
C	-2.57467400	1.43327700	-0.46632800
C	-2.51261000	2.76634500	-0.88550500
C	-3.39854700	1.11086100	0.61456100
C	-3.25511600	3.75573300	-0.24583200
H	-1.84641100	3.03538300	-1.70414800
C	-4.14712000	2.09841300	1.25651000
H	-3.44157700	0.08346700	0.96545300
C	-4.07828200	3.42411800	0.83115100
H	-3.18070100	4.78788500	-0.57874400
H	-4.78327800	1.82944900	2.09574000
H	-4.65679400	4.19295500	1.33590200
C	-2.40824900	-1.79679700	-0.40034900
C	-3.59682500	-1.82602700	-1.18377100
C	-2.19555600	-2.92500800	0.44963300
C	-4.45027600	-2.92356100	-1.15931500
H	-3.85505700	-0.97002700	-1.80015600
C	-3.06404000	-4.00924500	0.46529700
H	-1.36029400	-2.88476500	1.15178300
C	-4.19678500	-4.03554100	-0.35248600
H	-5.34450100	-2.90343200	-1.77880400

H	-2.86438700	-4.83854900	1.14117200
H	-4.87613700	-4.88171700	-0.33900500
N	-1.45987000	-0.81994900	-0.41382900
H	-0.78616800	-0.26551300	0.94326100

References

S1. S. K. Mandal, M. E. Itkis, X. Chi, S. Samanta, D. Lidsky, R. W. Reed, R. T. Oakley, F. S. Tham and R. C. Haddon, *J. Am. Chem. Soc.*, 2005, **127**, 8185-8196.

S2. R. Paira, B. Singh, P. K. Hota, J. Ahmed, S. C. Sau, J. P. Johnpeter and S. K. Mandal, *J. Org. Chem.*, 2016, **81**, 2432−2441.

S3. A. Banik, R. Paira, B. K. Shaw, G. Vijaykumar and S. K. Mandal, *J. Org. Chem.*, 2018, **83**, 3236−3244.

S4. M. Vellakkaran, K. Singh and D. Banerjee, *ACS Catal.*, 2017, **7**, 8152−8158.

S5. L. Homberg, A. Roller and K. C. Hultzsch, *Org lett*., 2019, **21**, 3142-3147.

S6. R. Fertig, T. Irrgang, F. Freitag, J. Zander and R. Kempe, *ACS Catal.*, 2018, **8**, 8525−8530.

S7. G. Zhang, Z. Yin and S. Zheng, *Org lett.*, 2016, **18**, 300-303.

S8. R. Pothikumar, V. T. Bhat and K. Namitharan, *Chem. Commun.*, 2020, **56**, 13607—13610.

S9. S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel and M. Beller, *Nat. Commun.*, 2016, **7**, 12641.

S10. S. Ruch, T. Irrgang and R. Kempe, *Chem. Eur. J.*, 2014, **20**, 13279-13285.

S11. F. Li, S. Shan, Q. Kang and L. Chen, *Chem. Commun.*, 2011, **47**, 5058-5060.

S12. V. G. Landge, A. Mondal, V. Kumar, A. Nandakumar and E. Balaraman, *Org. Biomol. Chem.*, 2018, **16**, 8175-8180.

S13. J. R. Cabrero-Antonino, E. Alberico, K. Junge, H. Jungea and M. Beller, *Chem. Sci.*, 2016, **7**, 3432-3442.

S14. G. Singh, A. Singh, V. Singh, R. K. Verma1, J. Tomar and R. Mall, *Med. Chem. Res.*, 2020, **29**, 1846-1866.

S15. F. Kallmeier, R. Fertig, T. Irrgang and R. Kempe, *Angew. Chem., Int. Ed.*, 2020, **59**, 11789 – 11793.

S16. H. Chung and Y. K. Chung, *J. Org. Chem.*, 2018, **83**, 8533-8542.

S17. P. T. K. Arachchige, H. Lee and C. S. Yi, *J. Org. Chem.*, 2018, **83**, 4932-4947.

S18. M. Huang, Y. Li, Y. Li, J. Liu, S. Shu, Y. Liu and Z. Ke, *Chem. Commun.*, 2019, **55**, 6213−6216.

S19. M. Subaramanian, S. P. Midya, P. M. Ramar, and E. Balaraman, *Org. Lett.*, 2019, **21**, 8899-8903.

S20. G. A. Barcan, J. J. Conde, M. K. Mokhallalati, M. G. Nilson, S. Xie, C. L. Allen, Y. W. Andemichael, N. A. Calandra, C. David, D. C. Leitch, L. Li and M. J. Morris, *Org. Process Res. Dev.*, 2019, **23**, 1396−1406.

S21. C. G. Swain, A. L. Powell, T. J. Lynch, S. R. Alpha and R. P. Dunlap, *J. Am. Chem. Soc.*, 1979, **101**, 3584–3587.

S22. J. J. Pesek and J. H. Frost, *Synth. Commun.*, 1974, **14**, 367-372.

S23. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Gaussian Inc., Wallingford, CT, 2010.

S24. M. Walker, A. J. A. Harvey, A. Sen and C. E. H. Dessent, *J. Phys. Chem. A*, 2013, **117**, 12590-12600.

S25. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.

S26. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.