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ELECTRONIC SUPPLEMENTARY INFORMATION

A General Protocol for the Reductive N-Methylation of Amines Using Dimethyl Carbonate and Molecular Hydrogen. Mechanistic Insights and Kinetic Studies

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1. GENERAL INFORMATION

All the chemicals were purchased and used without further purification. All hydrogenation reactions were set up in a 300 mL or 100 mL autoclave in the case of kinetic studies (PARR Instrument Company). In order to avoid unspecific reductions, all catalytic reactions were carried out in 8 mL glass vials, which were set in an alloy plate and placed inside the autoclave. In the case of kinetic studies a 100 mL glass inlet was used. The autoclave was then purged with 30 bar of hydrogen for three times before setting the pressure to the desired value. Conversions and yields of hydrogenation reactions were determined by GC-FID, HP 6890 with FID detector, column HP530 m x 250 mm x 0.25 µm. Mass spectra were recorded on a GC-MS Agilent 5973 Network equipped with a mass selective detector. NMR spectra were recorded using Bruker AV-300 (300 MHZ for ^{1}H) and Bruker AV-400 (400 MHz for ^{1}H) spectrometers. NMR chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to the residual proton resonance and the natural abundance ^{13}C resonance of the solvents. In all NMR experiments $CDCl_3$ was used as solvent. Coupling constants (*J*) are expressed in Hz. Abbreviations used in the reported NMR experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All measurements were carried out at room temperature unless otherwise stated. HRMS measurements of the all isolated products were performed using the electrospray ionization technique in UPLC (ultra-pressure) equipment.

2. EXPERIMENTAL PROCEDURES

General procedure for the N-methylation of aniline (1) with dimethyl carbonate: A 8 mL glass vial containing a stirring bar was sequentially charged with aniline (**1**) (46.6 mg, 0.5 mmol), *n*-hexadecane (50.0 mg) as an internal standard, $Ru(acac)_3$ (4.0 mg, 0.01 mmol, 2 mol%), Triphos (9.8 mg, 0.015 mmol, 3 mol%), THF (2 mL) as solvent, dimethyl carbonate (144.5 μL, 1.5 mmol, 3 eq) and a freshly prepared 0.2 M in THF solution of co-catalyst $HNTf_2$ (125.0 μL, 0.025 mmol, 5 mol%). Afterwards, the reaction vial was capped with a septum equipped with a syringe and set in the alloy plate, which was then placed into a 300 mL autoclave. Once sealed, the autoclave was purged three times with 30 bar of hydrogen, then pressurized to 60 bar and placed into an aluminium block, which was preheated at 150 °C. After 18 h, the autoclave was cooled in an ice bath, and the remaining gas was carefully released. Finally, the reaction mixture was diluted with ethyl acetate and analysed by GC.

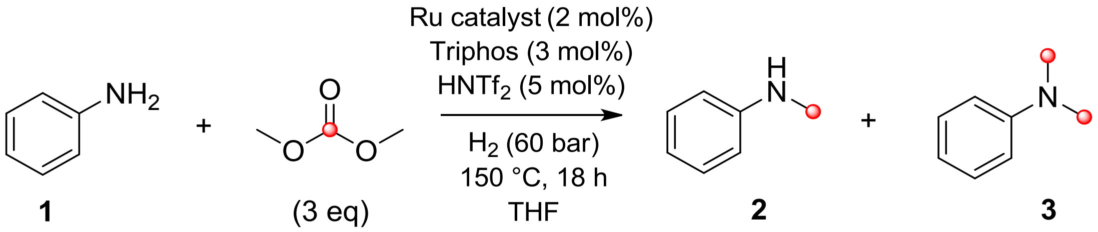
General procedure for the kinetic studies: A 100 mL glass inlet containing a stirring bar was sequentially charged with the corresponding substrate (3.0 mmol), *n*-hexadecane (250.0 mg) as an internal standard, $Ru(acac)_3$ (24.1 mg, 0.06 mmol, 2 mol%), Triphos (58.5 mg, 0.09 mmol, 3 mol%), THF (12 mL) as solvent, dimethyl carbonate (868.2 μL, 9.0 mmol, 3 eq) or methyl formate (551.5 μL, 9.0 mmol, 3 eq) and a freshly prepared 0.2 M in THF solution of co-catalyst $HNTf_2$ (750.0 μL, 0.15 mmol, 5 mol%). Afterwards, the reaction vial was then placed into a 100 mL autoclave. Once sealed, the autoclave was purged three times with 30 bar of hydrogen, then pressurized to 60 bar and placed into an aluminium block, which was preheated at 130-160 °C. Periodically, aliquots of 200 μL were taken at different times of reaction, diluted with ethyl acetate and analysed by GC.

General procedure for the N-methylation of amines with dimethyl carbonate: A 8 mL glass vial containing a stirring bar was sequentially charged with amine (0.5 mmol), *n*-hexadecane (50.0 mg) as an internal standard, $Ru(acac)_3$ (2-6 mol%), Triphos (3-9 mol%), THF (2 mL) as solvent, dimethyl carbonate (2-6 eq) and a freshly prepared 0.2 M in THF solution of co-catalyst $HNTf_2$ (5-15 mol%) for aromatic amines. In the case of aliphatic amines LiCl or $LiNTf_2$ (12.5 mol%) were used instead of $HNTf_2$. Afterwards, the reaction vial was capped with a septum equipped with a syringe and set in the alloy plate, which was then placed into a 300 mL autoclave. Once sealed, the autoclave was purged three times with 30 bar of hydrogen, then pressurized to 60 bar and placed into an aluminium block, which was preheated at 150 °C. After the corresponding time (18-40 h), the autoclave was cooled in an ice bath, and the remaining gas was carefully released. Finally, the reaction mixture was diluted with ethyl acetate and analysed by GC. To determine the isolated yield of the methylated amines, no internal standard was added and the reaction mixture was purified by silica gel column chromatography (*n*-heptane / ethyl acetate mixtures) to give the corresponding methylated products.

Procedure for the 1g-scale N-methylation of aniline (1) with dimethyl carbonate: A 300 mL containing a stirring bar was sequentially charged with aniline (**1**) (1 g, 10.72 mmol), $Ru(acac)_3$ (85.8 mg, 0.21 mmol, 2 mol%), Triphos (210.11 mg, 0.32 mmol, 3 mol%), THF (45 mL) as solvent, dimethyl carbonate (3.098 mL, 32.2 mmol, 3 eq) and a freshly prepared 0.2 M in THF solution of co-catalyst $HNTf_2$ (2.68 mL, 0.54 mmol, 5 mol%). Afterwards, the teflon inlet with the reaction was then placed into a 300 mL autoclave. Once sealed, the autoclave was purged three times with 30 bar of hydrogen, then pressurized to 60 bar and placed into an aluminium block, which was preheated at 150 °C. After 18 h, the autoclave was cooled in an ice bath, and the remaining gas was carefully released. Finally, the reaction mixture was purified by silica gel column chromatography (*n*-heptane / ethyl acetate mixtures) to give the corresponding methylated products.

3. ADDITIONAL TABLES

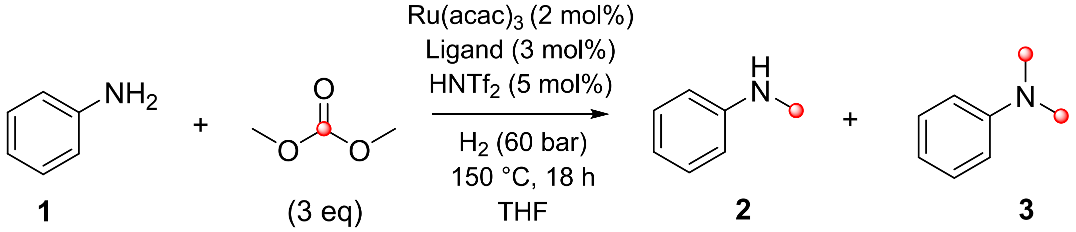
Table S1. N-Methylation of aniline (**1**) with dimethyl carbonate and hydrogen using [Ru/Triphos/$HNTf_2$] system: Influence of the ruthenium precursor

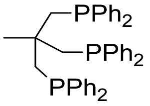
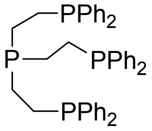
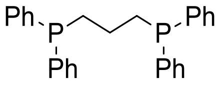
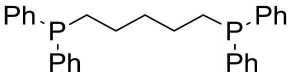
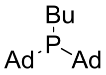
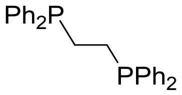
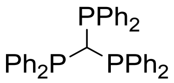


Entry[a]	Ru catalyst	Conv. (%)[b]	**2** (%)[b]	**3** (%)[b]
1	$Ru(acac)_3$	**100**	**-**	**95**
2	$[Ru(COD)(methylallyl)_2]$	100	-	92
3	$[Ru(dmso)_4Cl_2]$	3	-	-
4	$[Ru(bipy)_2Cl_2]$	2	-	-
5	$[Ru(PPh_3)_3(CO)H_2]$	14	6	-
6[c]	$[\{RuCl_2(benzene)\}_2]$	5	-	-
7	$[Ru(Cp)(p\text{-}cymene)]PF_6$	7	-	-

[a] Standard reaction conditions: aniline (**1**) (46.6 mg, 0.5 mmol), dimethyl carbonate (3 eq), Ru catalyst (2 mol%), Triphos (3 mol%), $HNTf_2$ (5 mol%), THF (2.0 mL) and H_2 (60 bar) at 150 °C during 18 h. [b] Conversion of **1** and yields of products **2** and **3** were calculated by GC using hexadecane as internal standard. [c] Run with 1 mol% of catalyst (2 mol% Ru).

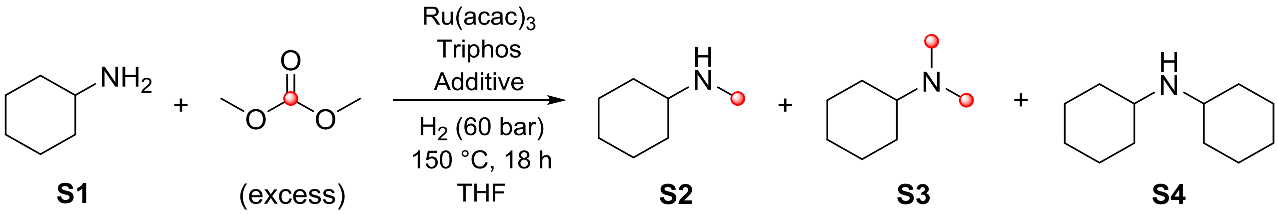
Table S2. N-Methylation of aniline (**1**) with dimethyl carbonate and hydrogen using [Ru/L/HNTf$_2$] system: Influence of the ligand



Entry[a]	Ligand	Conv. (%)[b]	**2** (%)[b]	**3** (%)[b]
1		**100**	**-**	**95**
2		8	-	-
3		10	-	-
4		12	-	-
5[c]		91	-	-
6		12	-	-
7		10	-	-

[a] Standard reaction conditions: aniline (**1**) (46.6 mg, 0.5 mmol), dimethyl carbonate (3 eq), Ru(acac)$_3$ (2 mol%), ligand (3 mol%), HNTf$_2$ (5 mol%), THF (2.0 mL) and H$_2$ (60 bar) at 150 °C during 18 h. [b] Conversion of **1** and yields of products **2** and **3** were calculated by GC using hexadecane as internal standard. [c] Cyclohexylamine in 51% and *N*-methyl cyclohexylamine in 18% were founded as by-products. (Ad = adamanthyl).

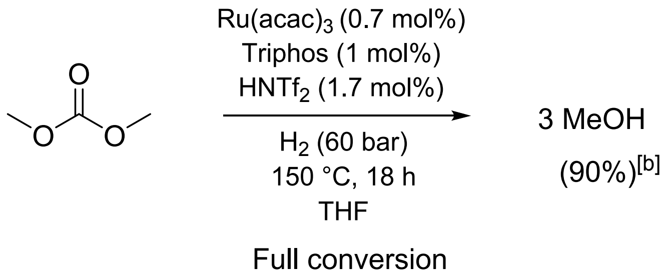
Table S3. N-Methylation of cyclohexylamine **S1** using dimethyl carbonate and molecular hydrogen: Optimization of the reaction conditions



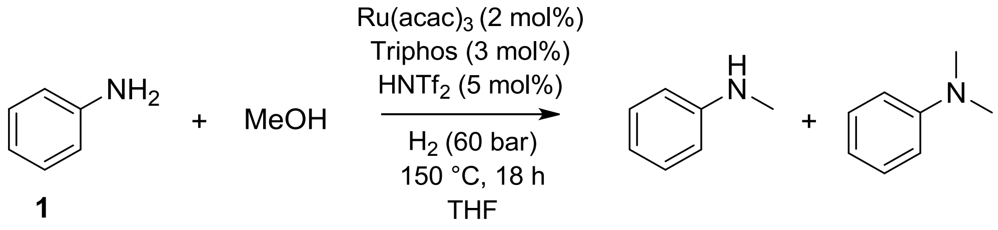
Entry[a]	t (h)	[Ru][b]	[Triphos][b]	[Additive][b]	DMC (eq)	Conv. (%)[c]	**S2** (%)[c]	**S3** (%)[c]	**S4** (%)[c]
1	18	2	3	$HNTf_2$ (5)	3	49	22	14	4
2	18	4	6	$HNTf_2$ (10)	4	62	21	14	9
3	18	5	7.5	$HNTf_2$ (12.5)	6	73	17	22	9
4	18	6	9	$HNTf_2$ (15)	10	82	14	34	6
5	18	6	9	$HNTf_2$ (15)	4	70	18	18	9
6	18	5	7.5	$LiNTf_2$ (12.5)	10	93	6	42	-
7	18	6	9	$LiNTf_2$ (15)	4	80	15	45	3
8	36	5	7.5	$LiNTf_2$ (12.5)	10	>99	-	47	-
9	18	5	7.5	LiCl (12.5)	10	>99	-	53	-
10	18	6	9	LiCl (15)	4	88	6	72	-
11	**36**	**6**	**9**	**LiCl (15)**	**4**	**>99**	**-**	**85**	**-**

[a] Standard reaction conditions: cyclohexylamine (49.6 mg, 0.5 mmol), dimethyl carbonate (3-10 eq), $Ru(acac)_3$ (2-6 mol%), Triphos (3-9 mol%), additive (5-15 mol%), THF (2.0 mL) and H_2 (60 bar) at 150 °C during 18 h. [b] [Ru] = [$Ru(acac)_3$], [Triphos] and [additive] corresponds to mol% quantities of each specie. [c] Conversion of **S1** and yields of products **S2**, **S3** and **S4** were calculated by GC using hexadecane as internal standard.

4. ADDITIONAL SCHEMES

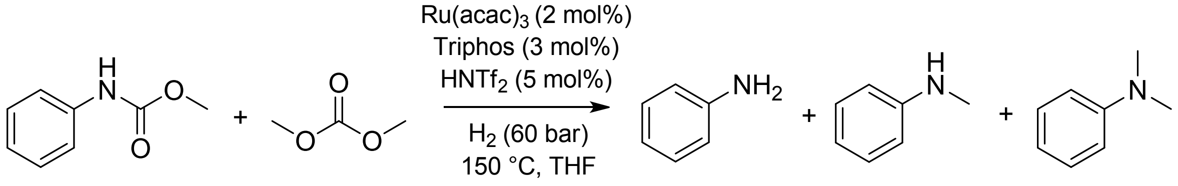


Scheme S1. Control experiment using dimethyl carbonate under catalytic conditions in the absence of aniline (**1**). [a] Standard reaction conditions: dimethyl carbonate (144.6 μL, 1.5 mmol), $Ru(acac)_3$ (0.7 mol%), Triphos (1 mol%), $HNTf_2$ (1.7 mol%), THF (2.0 mL) and H_2 (60 bar) at 150 °C during 18 h. [b] Yield of methanol was calculated by GC using hexadecane as internal standard.



(eq)	Conv. of **1** (%)[b]	**2** (%)[b]	**3** (%)[b]
3	7	2	-
4	10	7	-
8	13	11	-
6[c]	-	-	-
8[c]	-	-	-

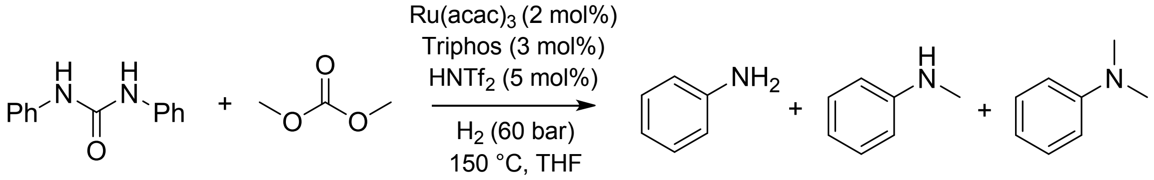
Scheme S2. Control experiments using methanol as C_1 source. [a] Standard reaction conditions: aniline (**1**) (46.6 mg, 0.5 mmol), methanol (3, 4 and 8 eq), $Ru(acac)_3$ (2 mol%), Triphos (3 mol%), $HNTf_2$ (5 mol%), THF (2.0 mL) and H_2 (60 bar) at 150 °C during 18 h. [b] Conversion of **1** and yields of products **2** and **3** were calculated by GC using hexadecane as internal standard. [c] The reaction was carried out without hydrogen at 30 bar of nitrogen.



S5

	(eq)	Conv. of **S5** (%)[b]	**1** (%)[b]	**2** (%)[b]	**3** (%)[b]
(t = 2 h)	-	17	8	3	6
	(2)	15	-	-	14
(t = 18 h)	-	44	25	9	10
	(2)	50	7	4	36

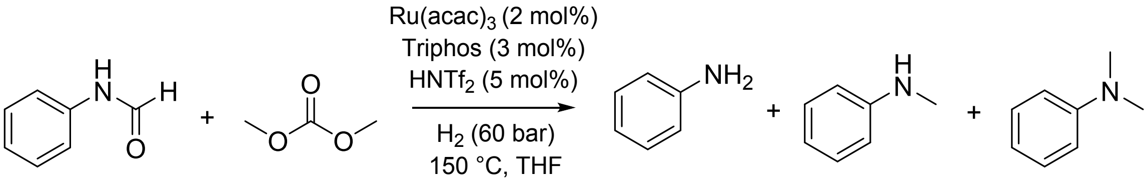
Scheme S3. Control experiments using N-phenyl methylcarbamate (**S5**) as starting material. [a] Standard reaction conditions: N-phenyl methylcarbamate (**S6**) (75.6 mg, 0.5 mmol), dimethyl carbonate (96.4 μL, 1.0 mmol) or not, Ru(acac)$_3$ (2 mol%), Triphos (3 mol%), HNTf$_2$ (5 mol%), THF (2.0 mL) and H$_2$ (60 bar) at 150 °C during 2h or 18 h. [b] Conversion of **S5** and yields of products **1**, **2** and **3** were calculated by GC using hexadecane as internal standard.



S6

	(eq)	Conv. of **S6** (%)[b]	**1** (%)[b]	**2** (%)[b]	**3** (%)[b]
(t = 2 h)	-	51	36	9	6
	(5)	54	14	6	34
(t = 18 h)	-	100	61	20	11
	(5)	100	6	6	82

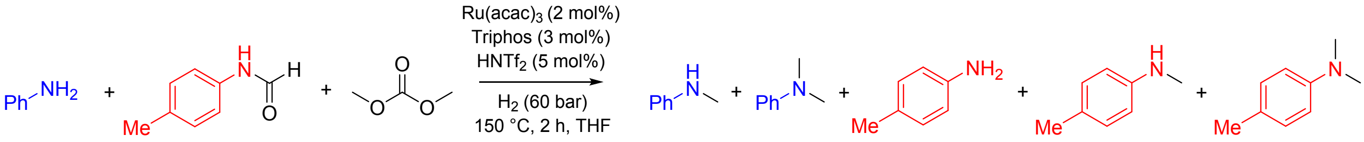
Scheme S4. Control experiments using 1,3-diphenyl urea (**S6**) as starting material. [a] Standard reaction conditions: 1,3-diphenyl urea (**S6**) (106.1 mg, 0.5 mmol), dimethyl carbonate (241.0 μL, 2.5 mmol), Ru(acac)$_3$ (2 mol%), Triphos (3 mol%), HNTf$_2$ (5 mol%), THF (2.0 mL) and H$_2$ (60 bar) at 150 °C during 18 h. [b] Conversion of **S6** and yields of products **1**, **2** and **3** were calculated by GC using hexadecane as internal standard.



S7

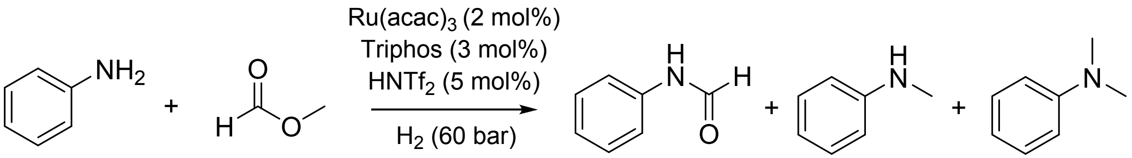
	(eq)	Conv. of **S7** (%)[b]	**1** (%)[b]	**2** (%)[b]	**3** (%)[b]
(t = 2 h)	-	100	42	17	38
	(2)	100	32	18	48
(t = 18 h)	-	100	40	16	38
	(2)	100	-	-	94

Scheme S5. Control experiments using formanilide (**S7**) as starting material. [a] Standard reaction conditions: formanilide (**S7**) (60.6 mg, 0.5 mmol), dimethyl carbonate (96.4 µL, 1.0 mmol), Ru(acac)$_3$ (2 mol%), Triphos (3 mol%), HNTf$_2$ (5 mol%), THF (2.0 mL) and H$_2$ (60 bar) at 150 °C during 18 h. [b] Conversion of **S7** and yields of products **1**, **2** and **3** were calculated by GC using hexadecane as external standard.



1	**S8**	(eq)	conversion		**2** (%)[b]	**3** (%)[b]	**1-Me** (%)[b]	**2-Me** (%)[b]	**3-Me** (%)[b]
			1 (%)[b]	**S8** (%)[b]					
0.5 mmol	0.5 mmol	(5)	20	95	16	4	48	20	24
-	0.5 mmol	(2)	-	>99	-	-	29	17	52
0.5 mmol	-	(3)	35	-	22	10	-	-	-

Scheme S6. Competitive control experiments using aniline (**1**) and 4'-methylformanilide (**S8**) as starting materials. [a] Standard reaction conditions: aniline (**1**) (46.6µL, 0.5 mmol), 4'-methylformanilide (**S8**) (68.6 mg, 0.5 mmol) or both (0.5 mmol of each one), dimethyl carbonate (2-5 eq), Ru(acac)$_3$ (2 mol%), Triphos (3 mol%), HNTf$_2$ (5 mol%), THF (2.0 mL) and H$_2$ (60 bar) at 150 °C during 2 h. [b] Conversion of **1** and **S8** and yields of products **2**, **3**, **1-Me**, **2-Me** and **3-Me** were calculated by GC using hexadecane as external standard.



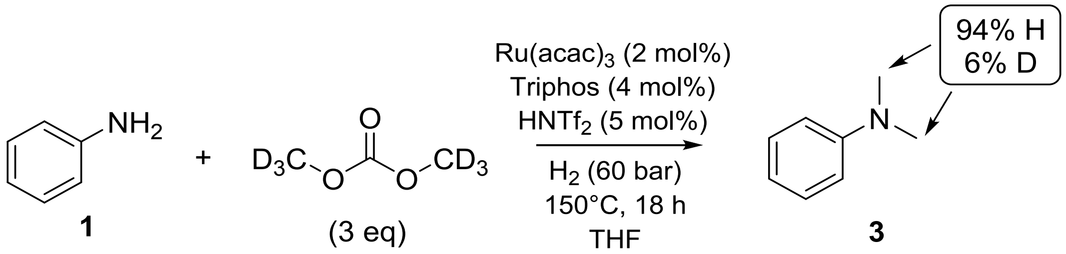
1

(3 eq)

Conv. of **1** (%)[b]	**S7** (%)[b]	**2** (%)[b]	**3** (%)[b]
>99	-	-	92
60[c]	48	-	-

Scheme S7. Control experiments using aniline (**1**) and methyl formate as starting materials. [a] Standard reaction conditions: aniline (**1**) (46.6 mg, 0.5 mmol), methyl formate (92.5 µL, 1.5 mmol), Ru(acac)$_3$ (2 mol%), Triphos (3 mol%), HNTf$_2$ (5 mol%), THF (2.0 mL) and H$_2$ (60 bar) at 150 °C during 18 h. [b] Conversion of **1** and yields of products **S7**, **2** and **3** were calculated by GC using hexadecane as internal standard. [c] The reaction was carried out without hydrogen at 30 bar of nitrogen.

5. ADDITIONAL FIGURES



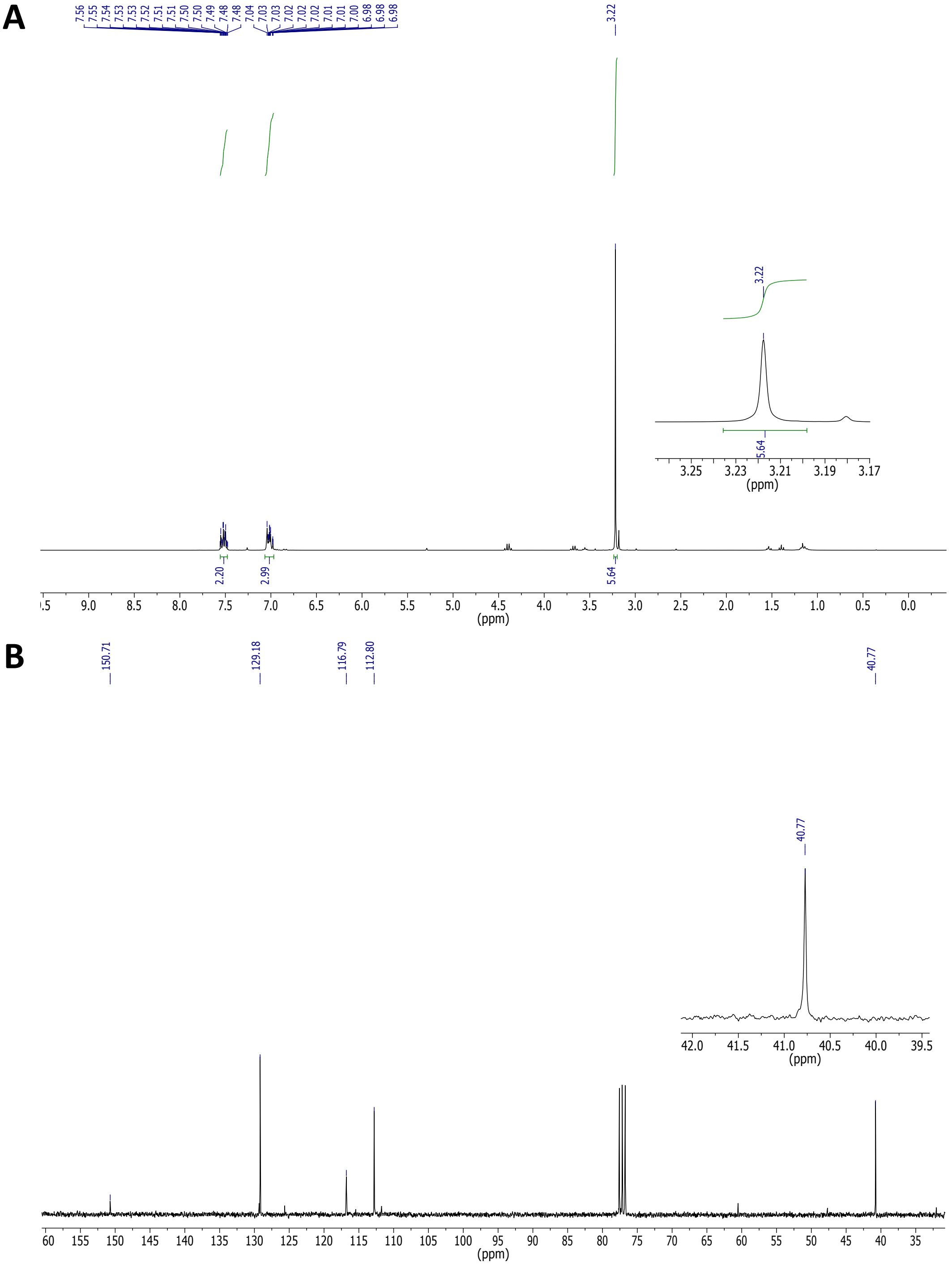


Figure S1. A) ^{1}H NMR spectra and B) ^{13}C NMR spectra for the isolated product **3** in the N-methylation of aniline (**1**) using isotopically-labeled D_6-dimethyl carbonate and molecular hydrogen catalyzed by [Ru/Triphos/$HNTf_2$]. Standard reaction conditions: aniline (**1**) (46.6 mg, 0.5 mmol), D_6-dimethyl carbonate (144.5 μL, 1.5 mmol, 3 eq), $Ru(acac)_3$ (2 mol%), Triphos (3 mol%), $HNTf_2$ (5 mol%), THF (2.0 mL) and H_2 (60 bar) at 150 °C during 18 h. Product **3** was purified by silica gel column chromatography using *n*-heptane / ethyl acetate mixtures.

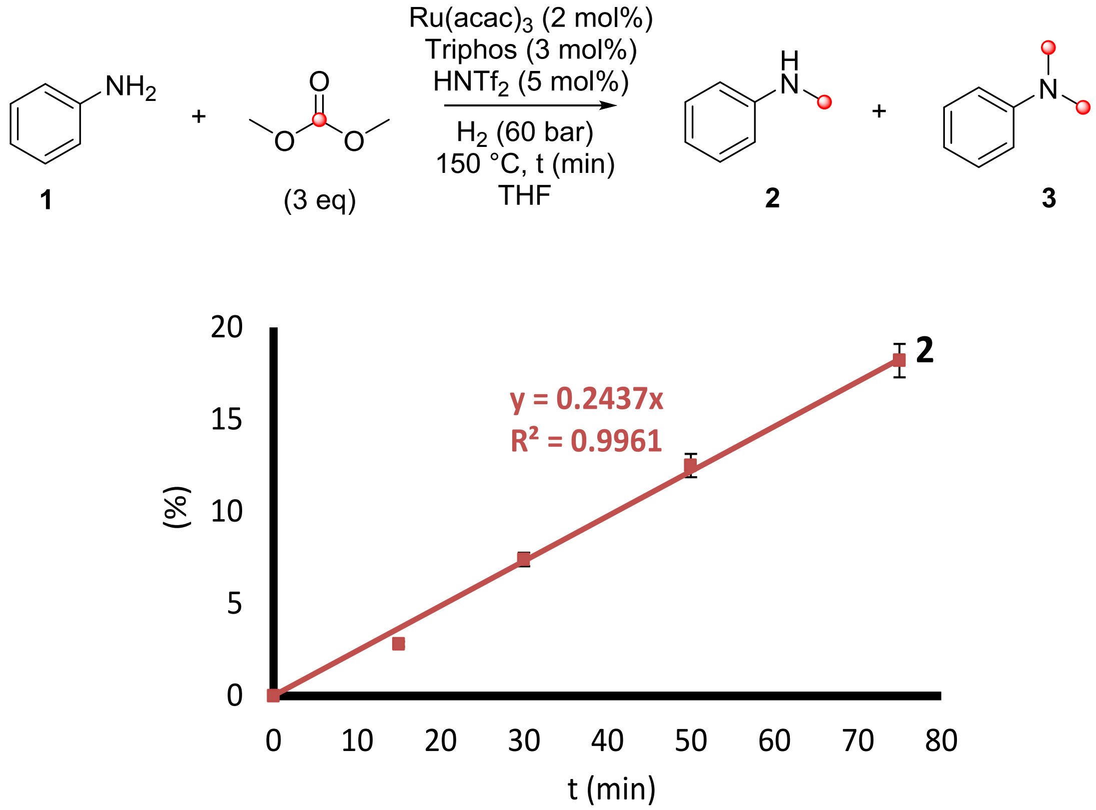


Figure S2. Yield/time kinetic profile at initial times of the reaction for the formation of N-methylaniline (**2**) in the methylation of aniline (**1**) using dimethyl carbonate and molecular hydrogen at 150 °C. Standard reaction conditions: aniline (**1**) (279.6 mg, 3.0 mmol), dimethyl carbonate (3 eq), Ru(acac)$_3$ (2 mol%), Triphos (3 mol%), HNTf$_2$ (5 mol%), THF (12.0 mL) and H_2 (60 bar) at 150 °C. Yields of product **2** were calculated by GC using hexadecane as internal standard. Vertical error bar (5%) for all data points is shown.

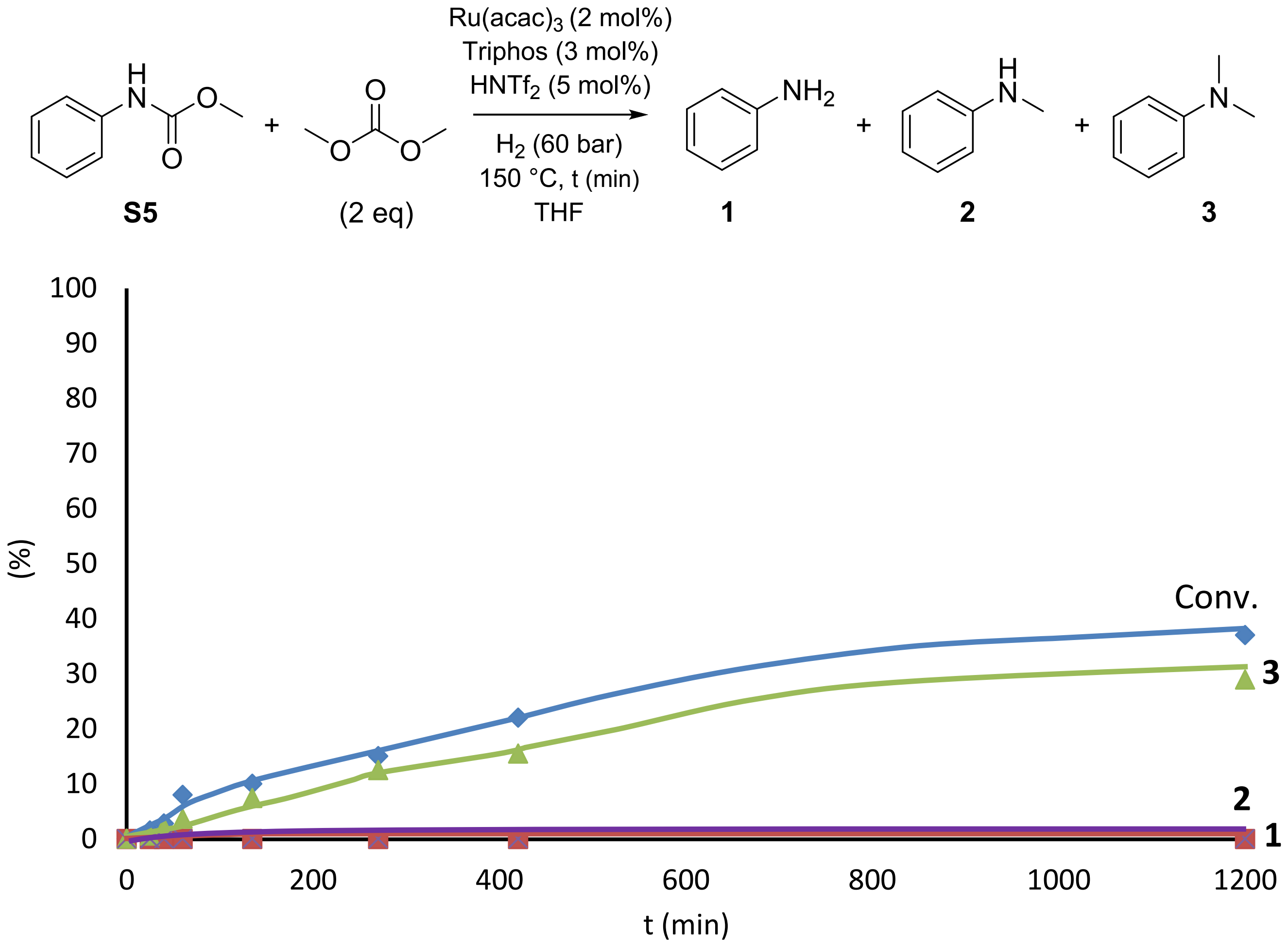


Figure S3. Yield/time kinetic profile for the formation of aniline (**1**), N-methylaniline (**2**) and N,N-dimethylaniline (**3**) from N-phenyl methylcarbamate (**S5**) using dimethyl carbonate and molecular hydrogen at 150 ºC. Standard reaction conditions: N-phenyl methylcarbamate (**S5**) (453.6 mg, 3.0 mmol), dimethyl carbonate (2 eq), Ru(acac)$_3$ (2 mol%), Triphos (3 mol%), HNTf$_2$ (5 mol%), THF (12.0 mL) and H$_2$ (60 bar) at 150 °C. Conversion of **S5** and yields of products **1** and **2**, **3** were calculated by GC using hexadecane as internal standard.

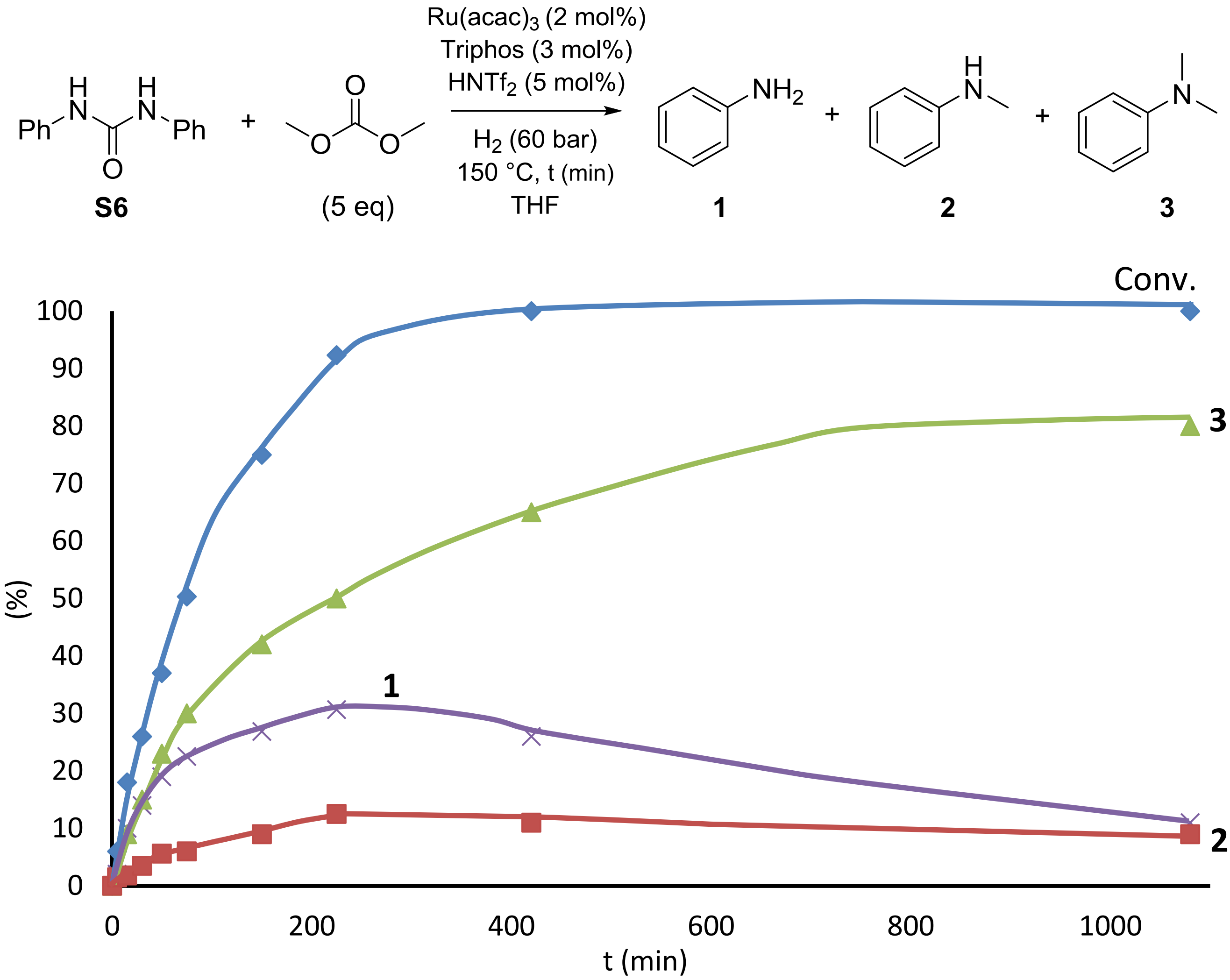


Figure S4. Yield/time kinetic profile for the formation of aniline (**1**), N-methylaniline (**2**) and N,N-dimethylaniline (**3**) from 1,3-diphenyl urea (**S6**) using dimethyl carbonate and molecular hydrogen at 150 °C. Standard reaction conditions: 1,3-diphenyl urea (**S6**) (636.7 mg, 3.0 mmol), dimethyl carbonate (5 eq), $Ru(acac)_3$ (2 mol%), Triphos (3 mol%), $HNTf_2$ (5 mol%), THF (12.0 mL) and H_2 (60 bar) at 150 °C. Conversion of **S6** and yields of products **1** and **2**, **3** were calculated by GC using hexadecane as internal standard.

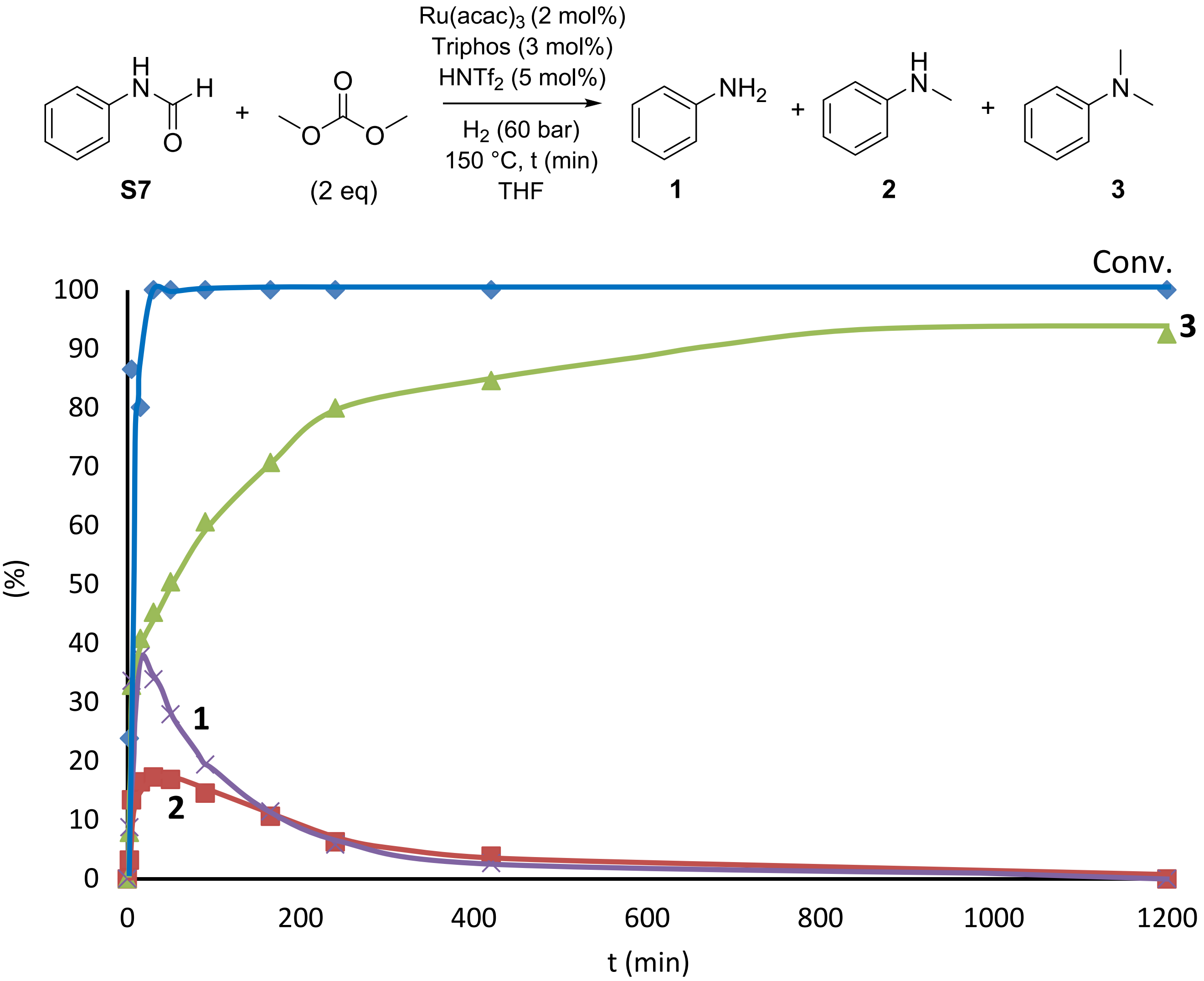


Figure S5. Yield/time kinetic profile for the formation of aniline (**1**), N-methylaniline (**2**) and N,N-dimethylaniline (**3**) from formanilide (**S7**) using dimethyl carbonate and molecular hydrogen at 150 ºC. Inset: initial times of the reaction (initial rates are given). Standard reaction conditions: formanilide (**S7**) (363.6 mg, 3.0 mmol), dimethyl carbonate (2 eq), Ru(acac)$_3$ (2 mol%), Triphos (3 mol%), HNTf$_2$ (5 mol%), THF (12.0 mL) and H$_2$ (60 bar) at 150 °C. Conversion of **S7** and yields of products **1** and **2**, **3** were calculated by GC using hexadecane as internal standard.

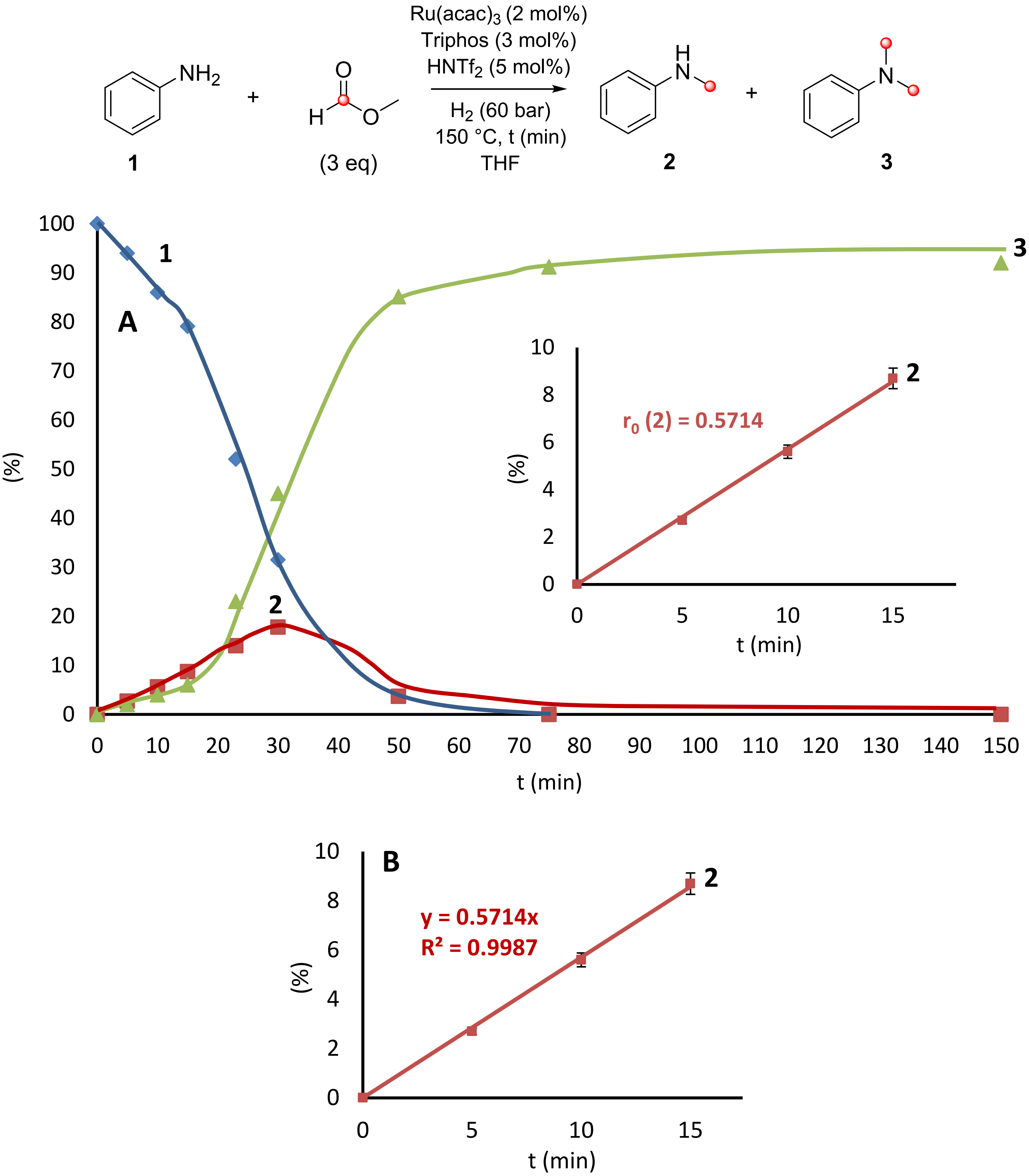


Figure S6. A) Yield/time kinetic profile for the formation of N-methylaniline (**2**) and N,N-dimethylaniline (**3**) in the methylation of aniline (**1**) using methyl formate and molecular hydrogen at 150 ºC. Inset corresponds to the initial rate plot for the formation of product **2** where (r_0) is the slope of the linear equation: [yield (%) = r_0 · time (min)] defined at initial reaction times and expressed as [yield (%) of product · t $(min)^{-1}$]. Vertical error bar (5%) for all data points in the inset is shown. B) Yield/time kinetic profile at initial times of the reaction. Standard reaction conditions: aniline (**1**) (279.6 mg, 3.0 mmol), methyl formate (3 eq), $Ru(acac)_3$ (2 mol%), Triphos (3 mol%), $HNTf_2$ (5 mol%), THF (12.0 mL) and H_2 (60 bar) at 150 °C. Percentages of compounds **1**, **2** and **3** were calculated by GC using hexadecane as internal standard.

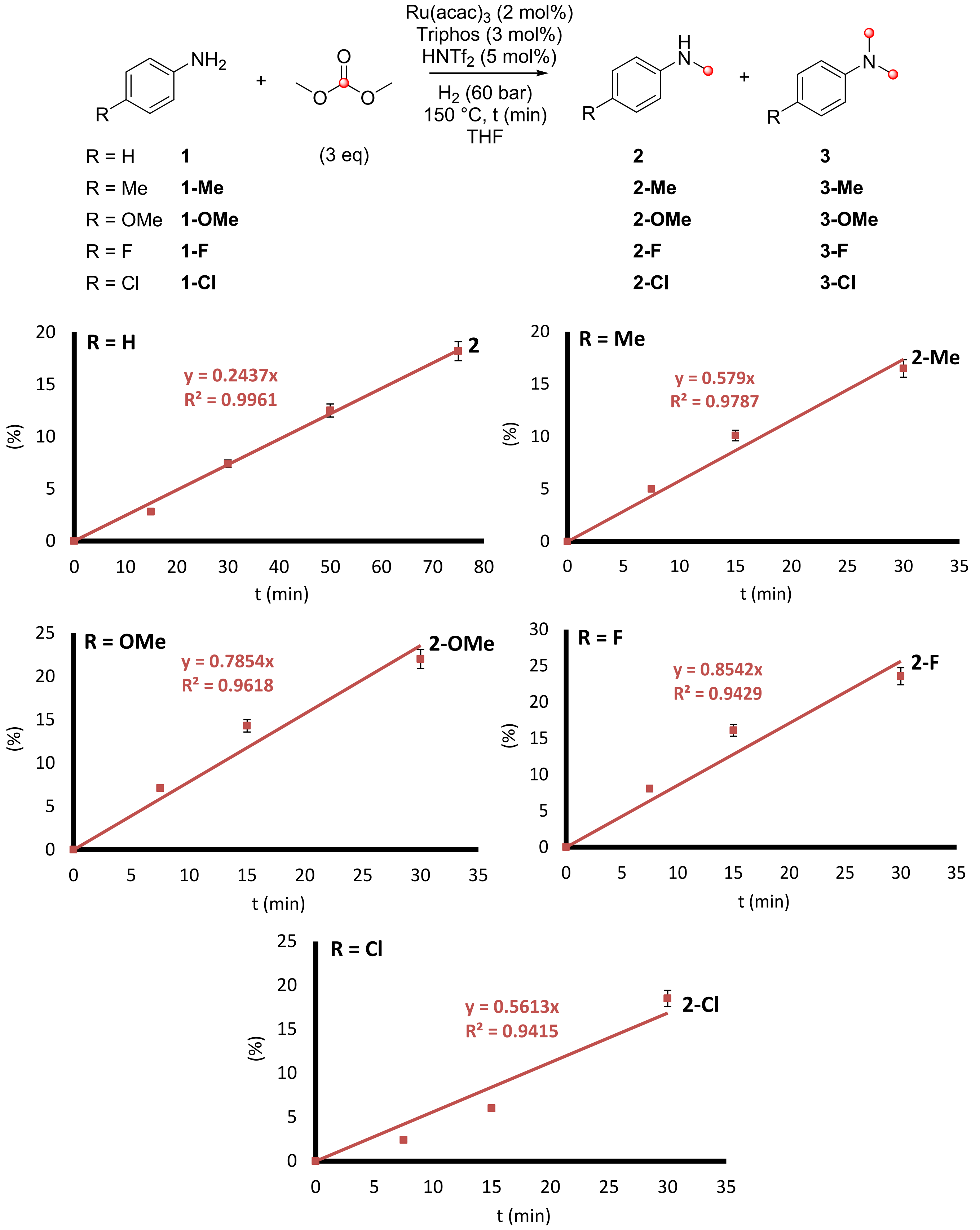
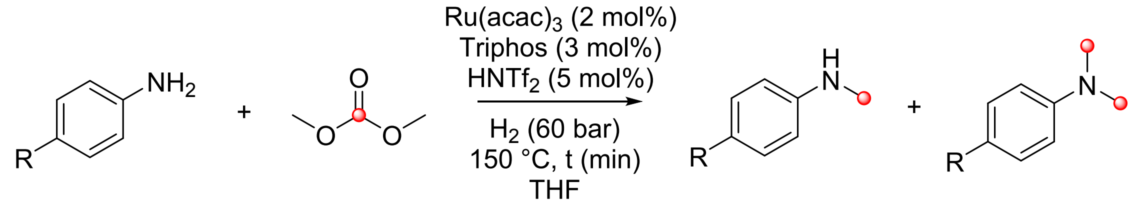


Figure S7. Yield/time kinetic profiles at initial times of the reaction for the formation of the corresponding N-methylanilines (**2**, **2-Me**, **2-OMe**, **2-F**, **2-Cl**) in the N-methylation of aniline (**1**) and different *para*-substituted anilines (**1-Me**, **1-OMe**, **1-F**, **1-Cl**) using dimethyl carbonate and molecular hydrogen at 150 °C in a separated experiments. Standard reaction conditions: aniline (3.0 mmol), dimethyl carbonate (3 eq), Ru(acac)$_3$ (2 mol%), Triphos (3 mol%), HNTf$_2$ (5 mol%), THF (12.0 mL) and H$_2$ (60 bar) at the corresponding temperature. Yields of product **2**, **2-Me**, **2-OMe**, **2-F** and **2-Cl** were calculated by GC using hexadecane as internal standard. Vertical error bar (5%) for all data points is shown.



(3 eq)

R = H	**1**	**2**	**3**
R = Me	**1-Me**	**2-Me**	**3-Me**
R = OMe	**1-OMe**	**2-OMe**	**3-OMe**
R = F	**1-F**	**2-F**	**3-F**
R = Cl	**1-Cl**	**2-Cl**	**3-Cl**

Aniline substrate	Initial rate (**r_o**) (% of product **2** ·min^{-1})	(**k_o = r_o**)	log (k_R/k_H)	σ_R (Hammett)[1]
1	0.2437	0.2437 (k_H)	0	0
1-Me	0.5790	0.5790 (k_{Me})	0.3749	-0.17
1-OMe	0.7854	0.7854 (k_{OMe})	0.5082	-0.27
1-F	0.8542	0.8542 (k_F)	0.5447	0.06
1-Cl	0.5613	0.5613 (k_{Cl})	0.3623	0.23

Hammett equation

$\log (k_R/k_H) = \rho.\sigma$

k_H = initial rate for H

k_R = initial rate for each substituent

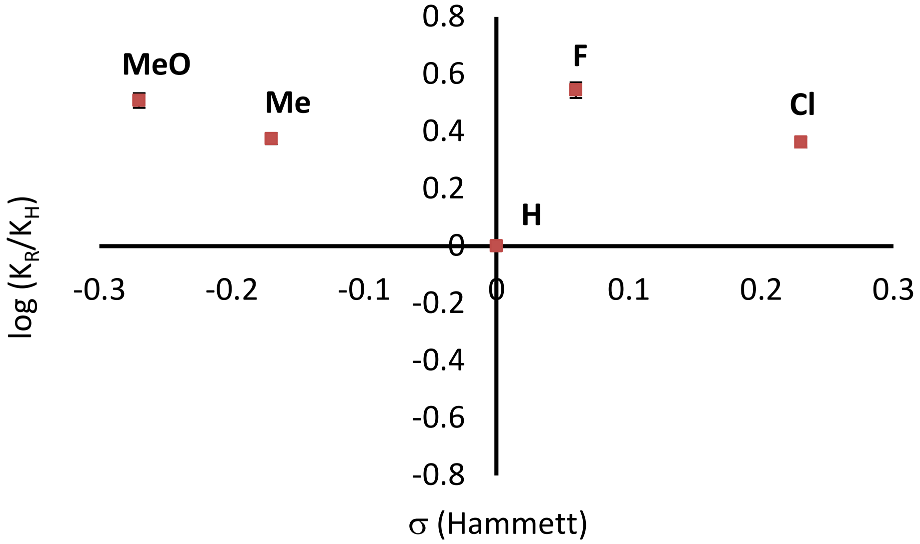
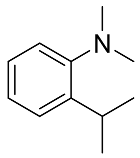
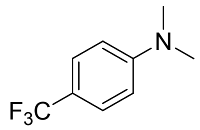


Figure S8. Hammett plot constructed with the initial rates obtained (see Figure S8) in the formation of the corresponding N-methylanilines (**2**, **2-Me**, **2-OMe**, **2-F**, **2-Cl**) by the N-methylation of aniline (**1**) and different *para*-substituted anilines (**1-Me**, **1-OMe**, **1-F**, **1-Cl**) using dimethyl carbonate and molecular hydrogen at 150 °C in a separated experiments. Vertical error bar (5%) for all data points is shown.

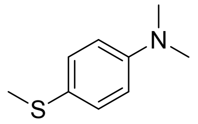
6. CHARACTERIZATION DATA OF THE ISOLATED PRODUCTS



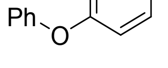
2-isopropyl-N,N-dimethylaniline. Isolated yield: 83%. GC-MS (m/z, $M^{+\cdot}$ 163), major peaks found: 163 (78%), 148 (100%), 133 (40%), 118 (35%), 91 (12%), 77 (14%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.21-7.16 (m, 1H), 7.10-7.04 (m, 2H), 7.03-6.96 (m, 1H), 3.47 (hept, *J* = 6.9, 1H), 2.60 (s, 6H), 1.15 (d, *J* = 6.9, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.99 (C), 144.30 (C), 126.58 (CH), 126.30 (CH), 124.05 (CH), 119.74 (CH), 45.95 (H_3C-N-CH_3), 26.76 (CH), 24.30 (H_3C-CH-CH_3). HRMS (ESI) [M^+; calculated for $C_{11}H_{17}N$: 163.1355] found m/z 163.1359.



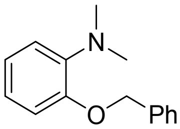
N,N-dimethyl-4-(trifluoromethyl)aniline.[2] Isolated yield: 80%. GC-MS (m/z, $M^{+\cdot}$ 188), major peaks found: 188 (100%), 172 (15%), 154 (6%), 145 (19%), 127 (5%), 118 (7%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 8.9, 2H), 6.71 (d, *J* = 8.9, 2H), 3.02 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.46 (C), 125.36 (q, J^{1}_{C-F} = 270.1, CF_3), 126.45 (q, J^{3}_{C-F} = 3.8, 2xCH), 117.64 (q, J^{2}_{C-F} = 32.6, C), 111.30 (2xCH), 40.23 (H_3C-N-CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ: -60.38 (s, CF_3). HRMS (ESI) [$M+H^+$; calculated for $C_9H_9NF_3$: 189.0759] found m/z 189.0760.



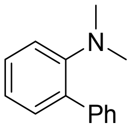
N,N-dimethyl-4-(methylthio)aniline.[3] Isolated yield: 81%. GC-MS (m/z, $M^{+\cdot}$ 167), major peaks found: 167 (75%), 152 (100%), 136 (15%), 108 (8%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.28-7.08 (m, 2H), 6.68-6.53 (m, 2H), 2.84 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.37 (C), 131.35 (2xCH), 123.76 (C), 113.36 (2xCH), 40.73 (H_3C-N-CH_3), 19.18 (S-CH_3).



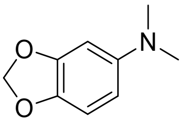
N,N-dimethyl-4-phenoxyaniline. Isolated yield: 85%. GC-MS (m/z, $M^{+\cdot}$ 213), major peaks found: 213 (100%), 197 (8%), 136 (40%), 77 (8%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.21-7.13 (m, 2H), 6.94-6.87 (m, 2H), 6.87-6.81 (m, 3H), 6.66-6.61 (m, 2H), 2.82 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.21 (C), 147.76 (C), 147.36 (C), 129.60 (2xCH), 122.02 (CH), 121.04 (2xCH), 117.23 (2xCH), 114.04 (2xCH), 41.30 (H_3C-N-CH_3). HRMS (ESI) [M^+; calculated for $C_{14}H_{15}ON$: 213.1148] found m/z 213.1143.



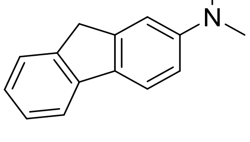
2-(benzyloxy)-N,N-dimethylaniline. Isolated yield: 83%. GC-MS (m/z, $M^{+\cdot}$ 227), major peaks found: 227 (10%), 136 (100%), 120 (8%), 108 (7%), 91 (10%), 65 (8%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51 (m, 2H), 7.46-7.31 (m, 3H), 7.04-6.92 (m, 4H), 5.20 (s, 2H), 2.89 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.45 (C), 142.95 (C), 137.47 (C), 128.57 (2xCH), 127.78 (CH), 127.30 (2xCH), 122.12 (CH), 121.41 (CH), 118.26 (CH), 113.33 (CH), 70.39 (CH_2), 43.40 (H_3C-N-CH_3). HRMS (ESI) [M^+; calculated for $C_{15}H_{17}ON$: 227.1304] found m/z 227.1303.



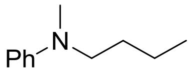
N,N-dimethyl-[1,1'-biphenyl]-2-amine.[4] Isolated yield: 86%. GC-MS (m/z, $M^{+\cdot}$ 197), major peaks found: 197 (100%), 180 (55%), 167 (20%), 152 (25%), 131 (16%), 91 (17%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51-7.47 (m, 2H), 7.34-7.26 (m, 2H), 7.23-7.11 (m, 3H), 6.97-6.89 (m, 2H), 2.45 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.37 (C), 142.14 (C), 134.27 (C), 131.83 (CH), 128.79 (2xCH), 128.42 (2xCH), 128.18 (CH), 126.59 (CH), 121.57 (CH), 117.69 (CH), 43.48 (H_3C-N-CH_3). HRMS (ESI) [M^+; calculated for $C_{14}H_{15}N$: 197.1199] found m/z 197.1193.



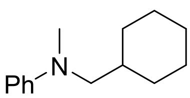
N,N-dimethylbenzo[d][1,3]dioxol-5-amine. Isolated yield: 83%. GC-MS (m/z, $M^{+\cdot}$ 165), major peaks found: 165 (100%), 149 (10%), 136 (9%), 107 (10%), 92 (30%), 82 (9%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.73 (d, *J* = 8.5, 1H), 6.44 (d, *J* = 2.5, 1H), 6.18 (dd, *J* = 8.5, 2.5, 1H), 5.88 (s, 2H), 2.87 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.42 (C), 147.37 (C), 139.51 (C), 108.43 (CH), 105.31 (CH), 100.72 (H_2C-O-CH_2), 96.60 (CH), 41.96 (H_3C-N-CH_3). HRMS (ESI) [M^+; calculated for $C_9H_{11}O_2N$: 165.0784] found m/z 165.0781.



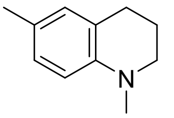
N,N-dimethyl-9H-fluoren-2-amine.[5] Isolated yield: 98%. GC-MS (m/z, $M^{+\cdot}$ 209), major peaks found: 209 (100%), 194 (10%), 165 (50%), 152 (5%), 104 (5%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 8.4, 2H), 7.51-7.45 (m, 1H), 7.33 (td, *J* = 7.5, 1.0, 1H), 7.19 (td, *J* = 7.4, 1.2, 1H), 6.99-6.93 (m, 1H), 6.80 (dd, *J* = 8.5, 2.4, 1H), 3.87 (s, 2H), 3.03 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.41 (C), 145.11 (C), 142.50 (C), 142.42 (C), 131.20 (C), 126.72 (CH), 124.88 (CH), 124.80 (CH), 120.52 (CH), 118.61 (CH), 111.75 (CH), 109.37 (CH), 41.17 (H_3C-N-CH_3), 37.23 (CH_2). HRMS (ESI) [M^+; calculated for $C_{15}H_{15}N$: 209.1199] found m/z 209.1195.



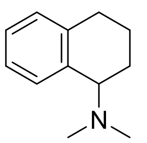
N-butyl-N-methylaniline.[6] Isolated yield: 92%. GC-MS (m/z, $M^{+\cdot}$ 163), major peaks found: 163 (15%), 120 (100%), 104 (10%), 77 (14%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.17-7.08 (m, 2H), 6.63-6.53 (m, 3H), 3.20 (t, *J* = 7.4, 2H), 2.81 (s, 3H), 1.53-1.40 (m, 2H), 1.25 (td, *J* = 14.8, 7.3, 2H), 0.85 (t, *J* = 7.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.50 (C), 129.22 (2xCH), 115.91 (CH), 112.19 (2xCH), 52.63 (N-CH_2), 38.35 (N-CH_3), 28.98 (CH_2), 20.49 (CH_2), 14.13 (CH_3). HRMS (ESI) [M^+; calculated for $C_{11}H_{17}N$: 163.1355] found m/z 163.1355.



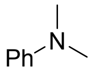
N-(cyclohexylmethyl)-N-methylaniline.[7] Isolated yield: 90%. GC-MS (m/z, $M^{+\cdot}$ 203), major peaks found: 203 (14%), 120 (100%), 104 (5%), 77 (8%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.27-7.02 (m, 2H), 6.66-6.45 (m, 3H), 3.03 (d, *J* = 6.7, 2H), 2.86 (s, 3H), 1.77-1.48 (m, 6H), 1.24-1.00 (m, 3H), 0.94-0.74 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.73 (C), 129.18 (2xCH), 115.53 (CH), 111.77 (2xCH), 59.84 (N-CH_2), 39.72 (CH), 37.03 (N-CH_3), 31.46 (CH_2), 26.73 (CH_2), 26.18 (CH_2). HRMS (ESI) [M^+; calculated for $C_{14}H_{21}N$: 203.1668] found m/z 203.1670.



1,6-dimethyl-1,2,3,4-tetrahydroquinoline.[8] Isolated yield: 88%. GC-MS (m/z, $M^{+\cdot}$ 160), major peaks found: 160 (100%), 144 (25%), 131 (15%), 117 (9%), 91 (12%), 79 (11%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.98-6.91 (m, 1H), 6.85 (s, 1H), 6.59 (d, *J* = 8.2, 1H), 3.22 (t, *J* = 5.8, 2H), 2.91 (s, 3H), 2.80 (t, *J* = 6.5, 2H), 2.28 (s, 3H), 2.14-1.95 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 144.85 (C), 129.73 (CH), 127.50 (CH), 125.64 (C), 123.17 (C), 111.53 (CH), 51.59 (CH_2), 39.56 (N-CH_3), 27.81 (CH_2), 22.77 (CH_2), 20.35 (CH_3). HRMS (ESI) [M^+; calculated for $C_{11}H_{14}N$: 160.1120] found m/z 160.1121.



N,N-dimethyl-1,2,3,4-tetrahydronaphthalen-1-amine.[9] Isolated yield: 87%. GC-MS (m/z, $M^{+\cdot}$ 175), major peaks found: 175 (9%), 146 (75%), 130 (100%), 115 (30%), 91 (30%), 46 (33%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.66-7.60 (m, 1H), 7.22-7.03 (m, 2H), 3.81 (t, *J* = 7.0, 1H), 2.89-2.64 (m, 2H), 2.30 (s, 6H), 2.10-1.86 (m, 2H), 1.79-1.62 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.48 (C), 138.30 (C), 128.84 (CH), 128.60 (CH), 126.39 (CH), 125.77 (CH), 62.87 (CH), 40.91 (H_3C-N-CH_3), 29.86 (CH_2), 21.64 (CH_2), 20.40 (CH_2). HRMS (ESI) [$M+H^+$; calculated for $C_{12}H_{17}N$: 176.1433] found m/z 176.1437.



N,N-dimethylaniline.[10] Isolated yield: 85% (from 1g-scale reaction). GC-MS (m/z, $M^{+\cdot}$ 167), major peaks found: 120 (100%), 105 (12%), 91 (8%), 77 (30%). (The NMR spectrum is consistent with the reported data). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.39-7.33 (m, 2H), 6.88-6.85 (m, 3H), 3.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.71 (C), 129.14 (2xCH), 116.72 (CH), 112.74 (2xCH), 40.68 (CH_3).

7. REFERENCES

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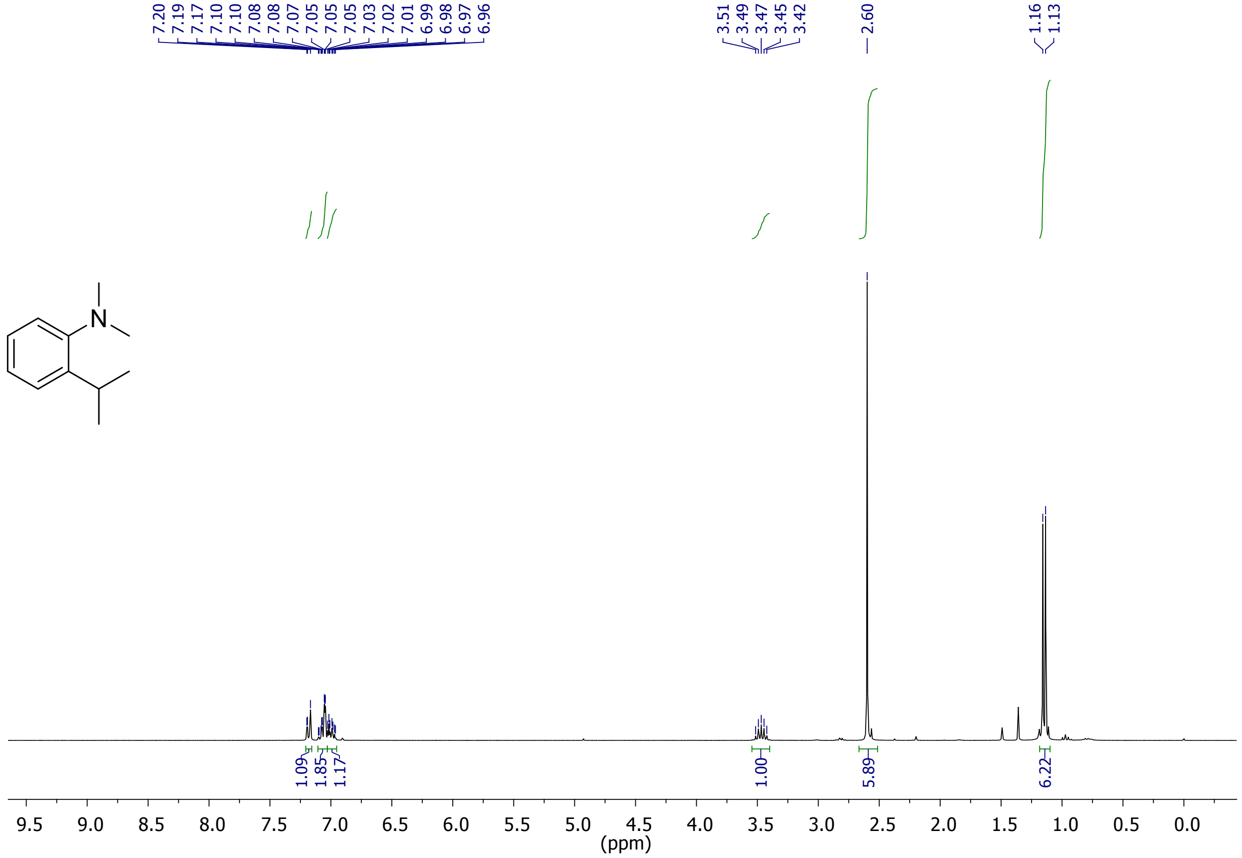
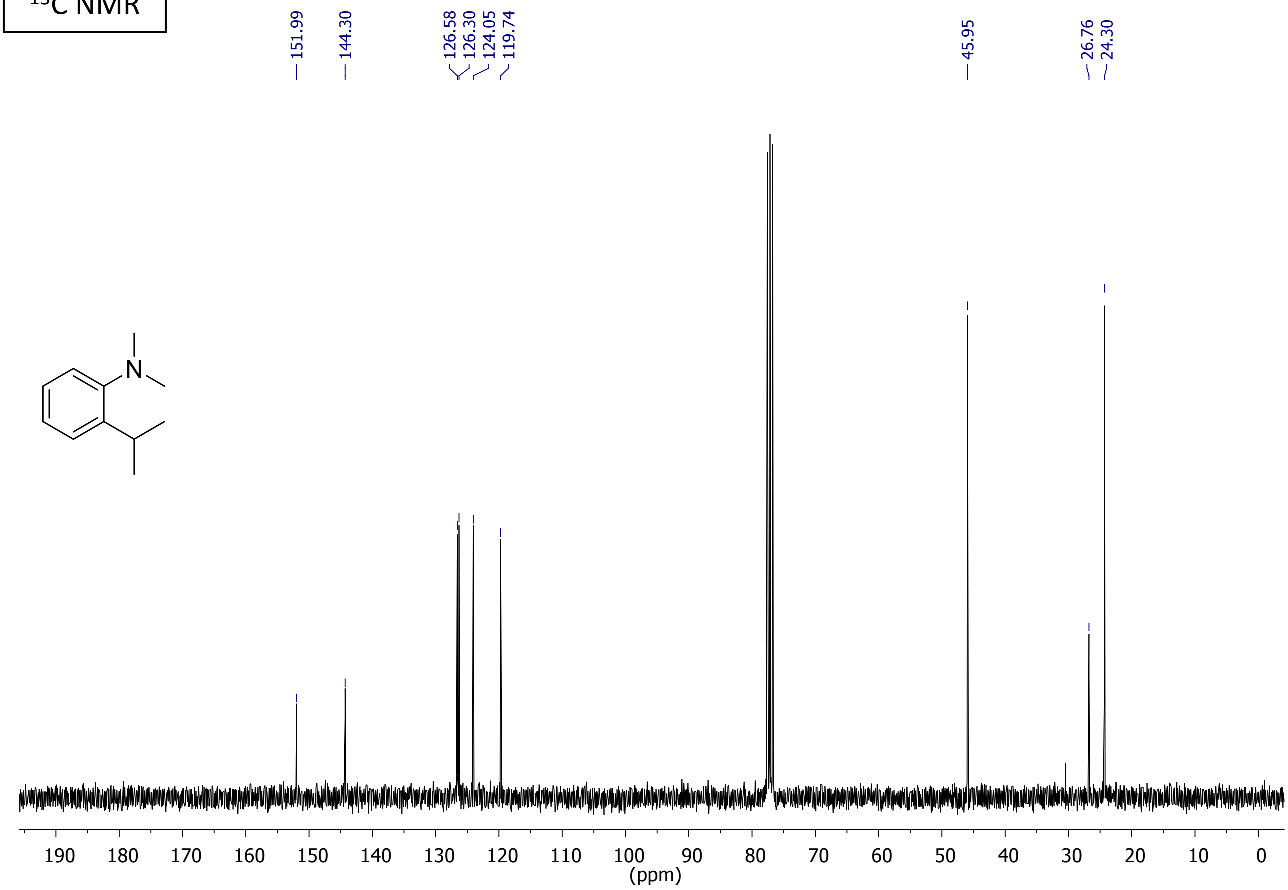
8. NMR SPECTRA OF THE ISOLATED PRODUCTS

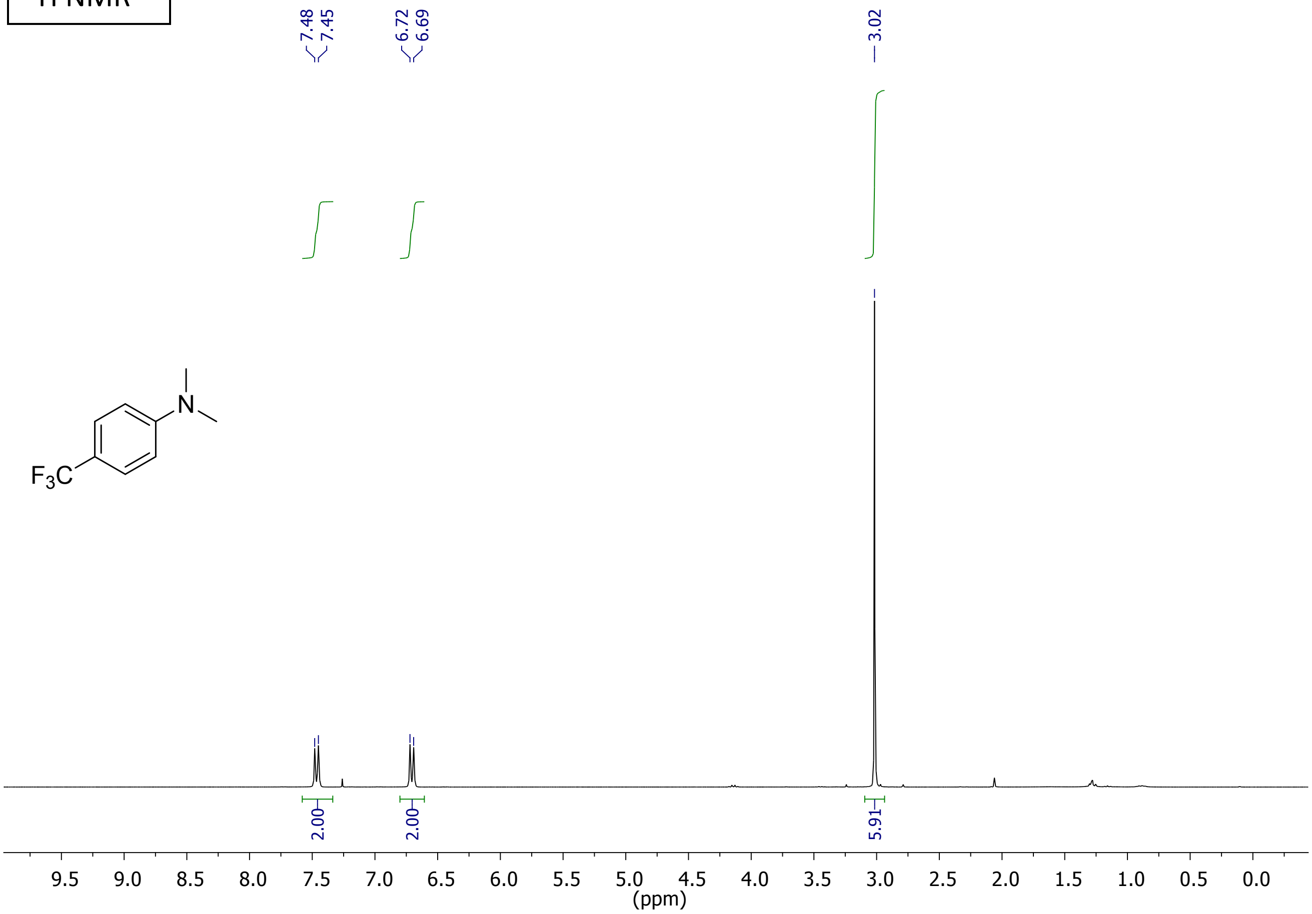
^{1}H NMR



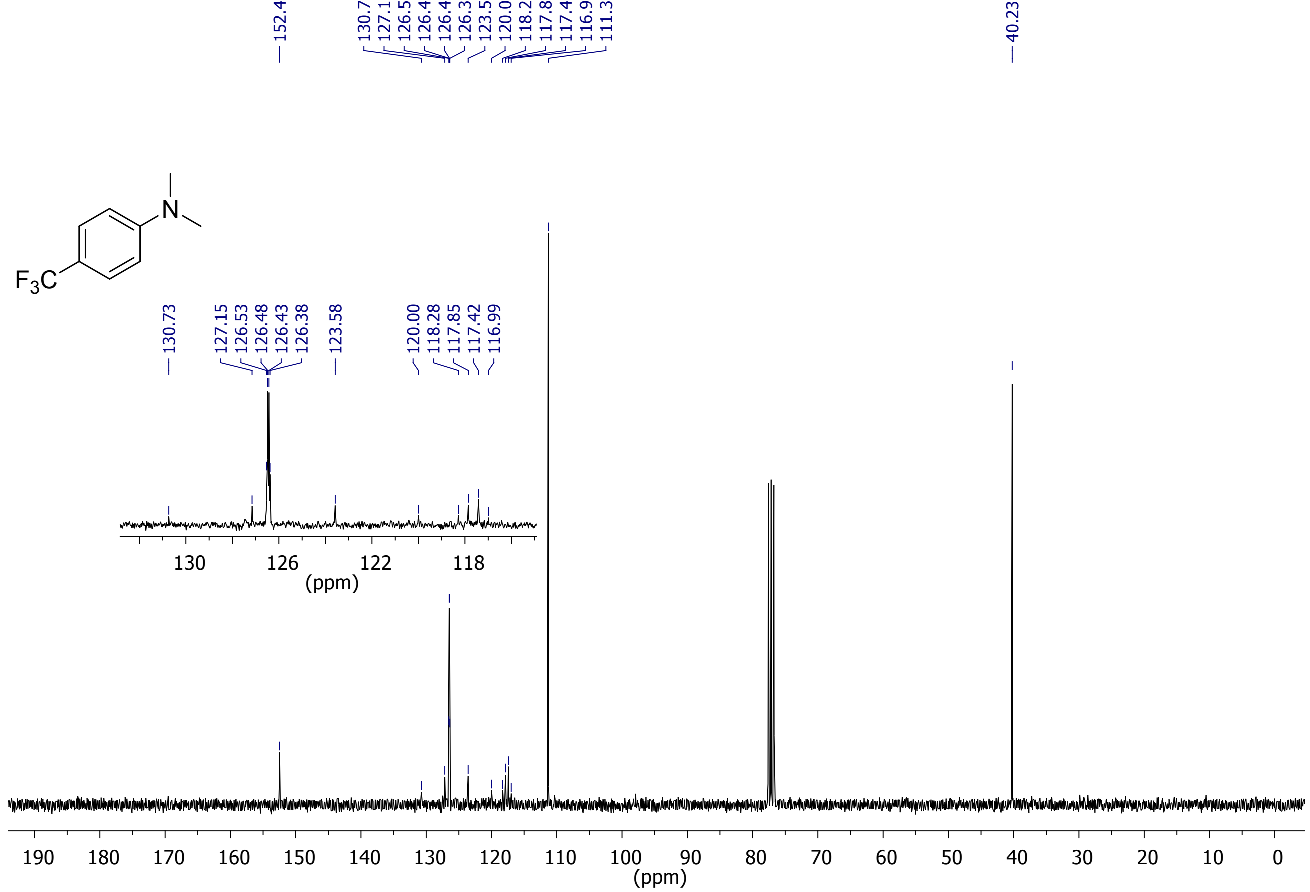
^{13}C NMR



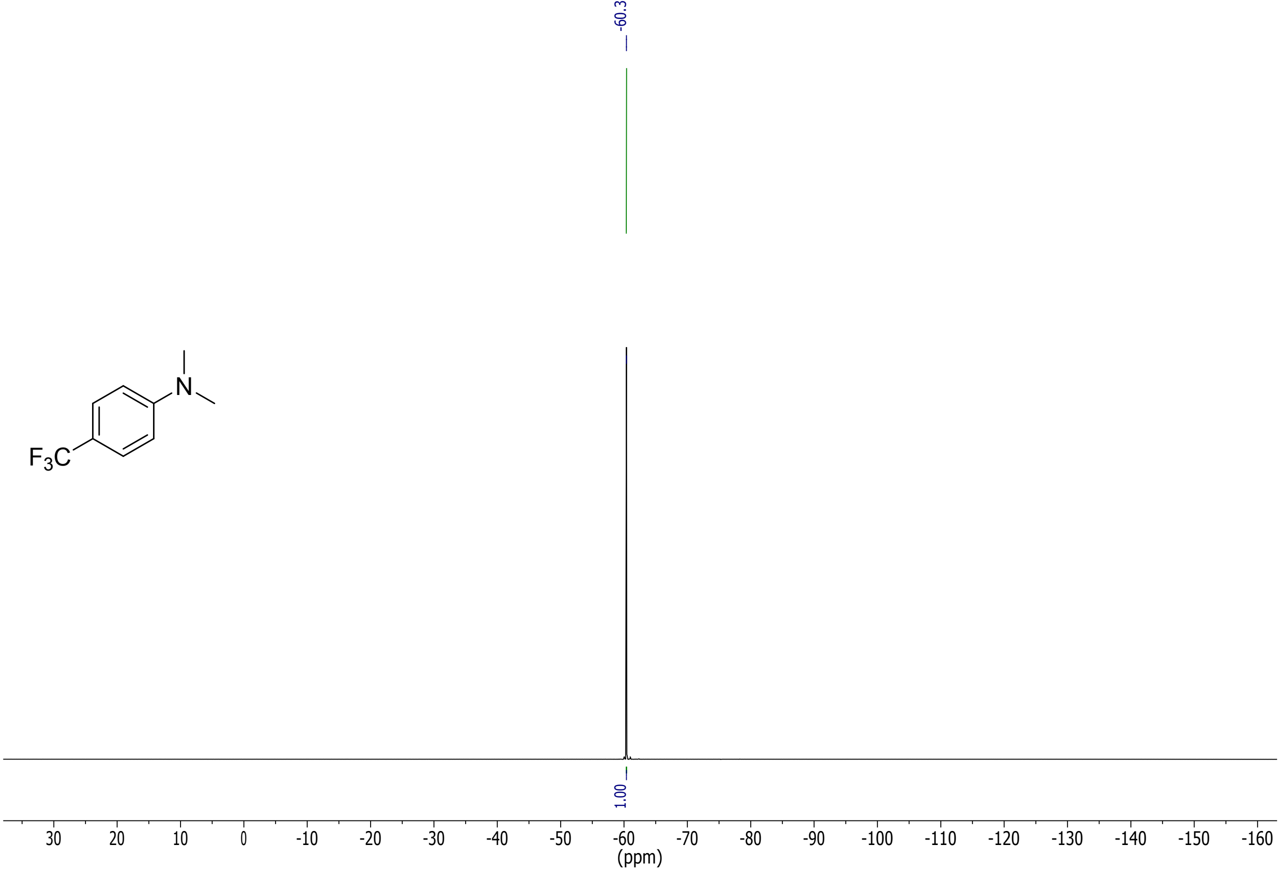
^{1}H NMR



^{13}C NMR



^{19}F NMR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F3C
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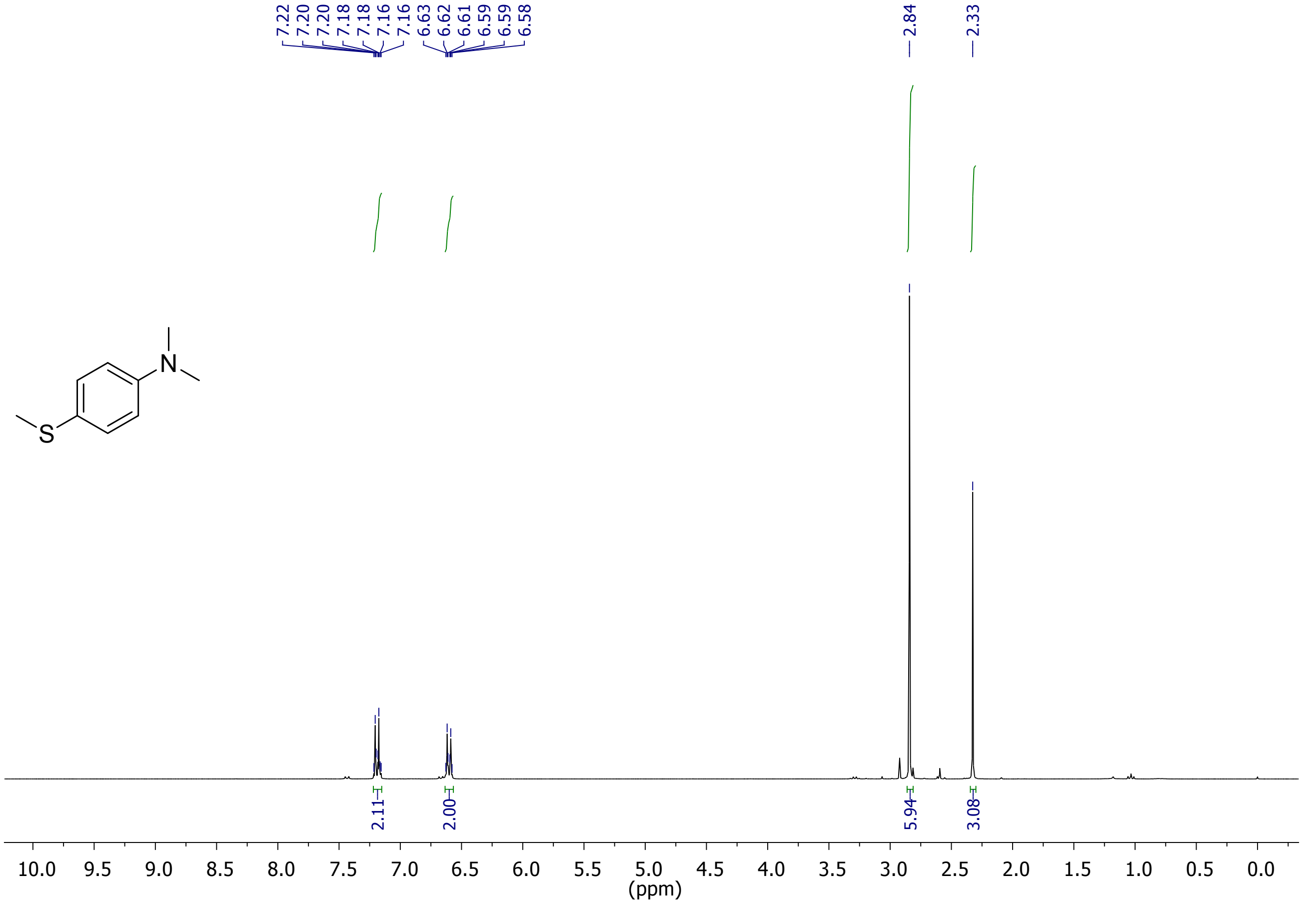
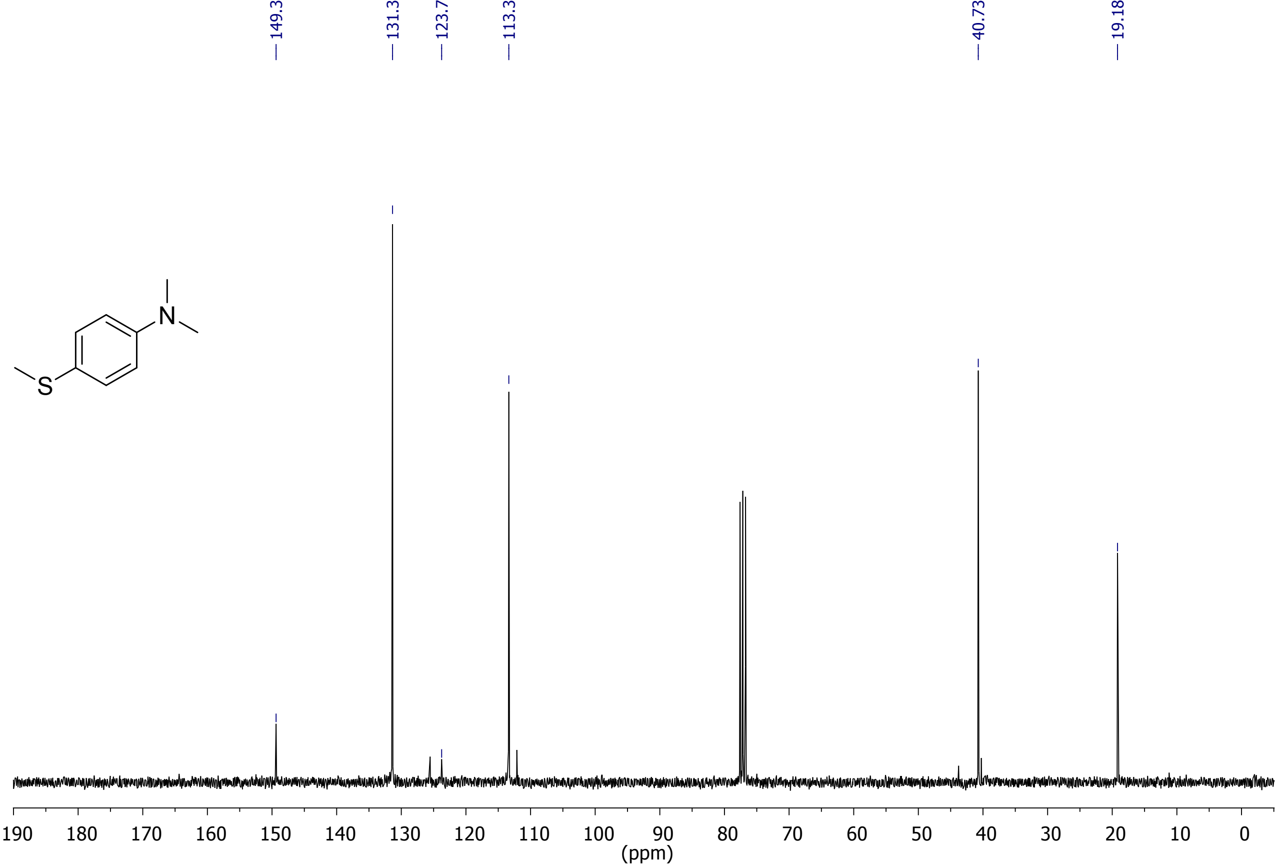
(ppm)

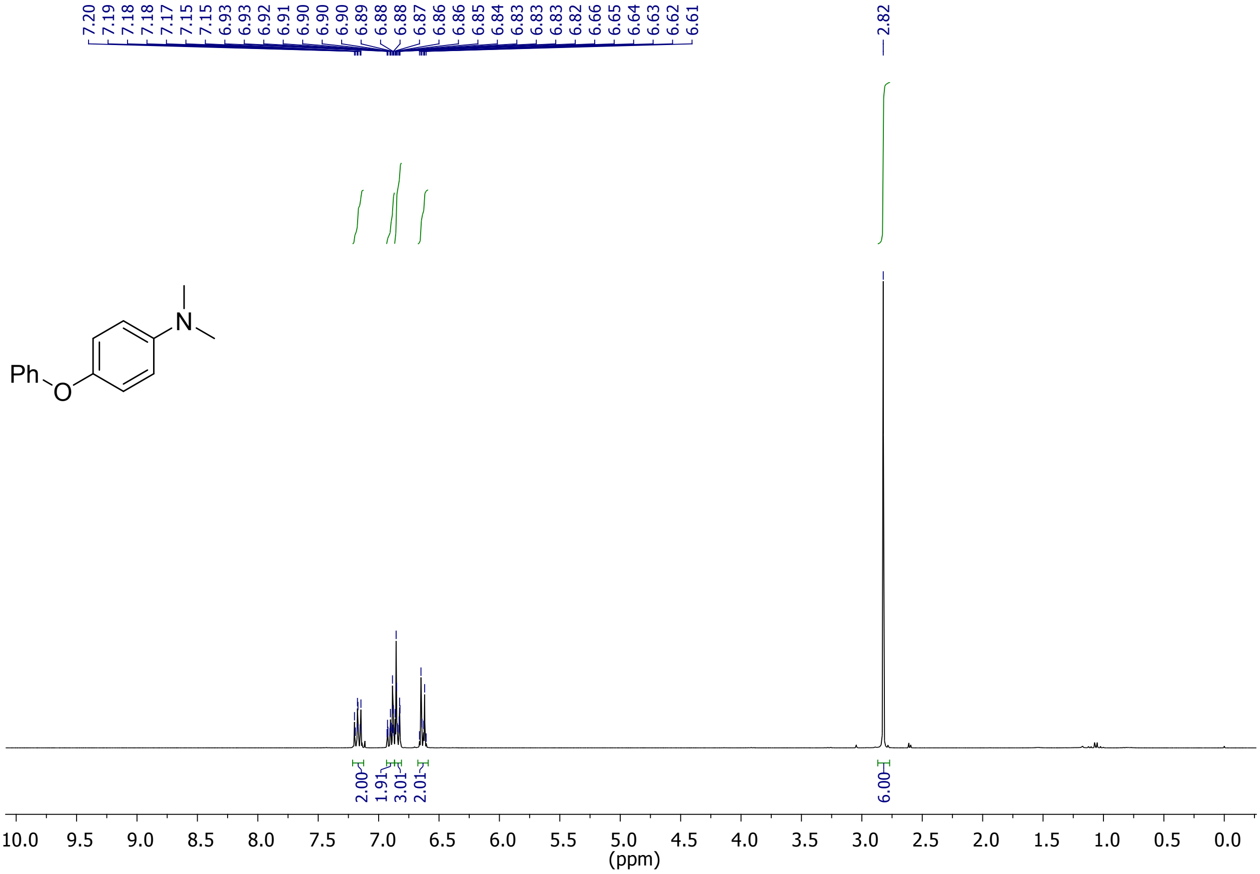
^{1}H NMR



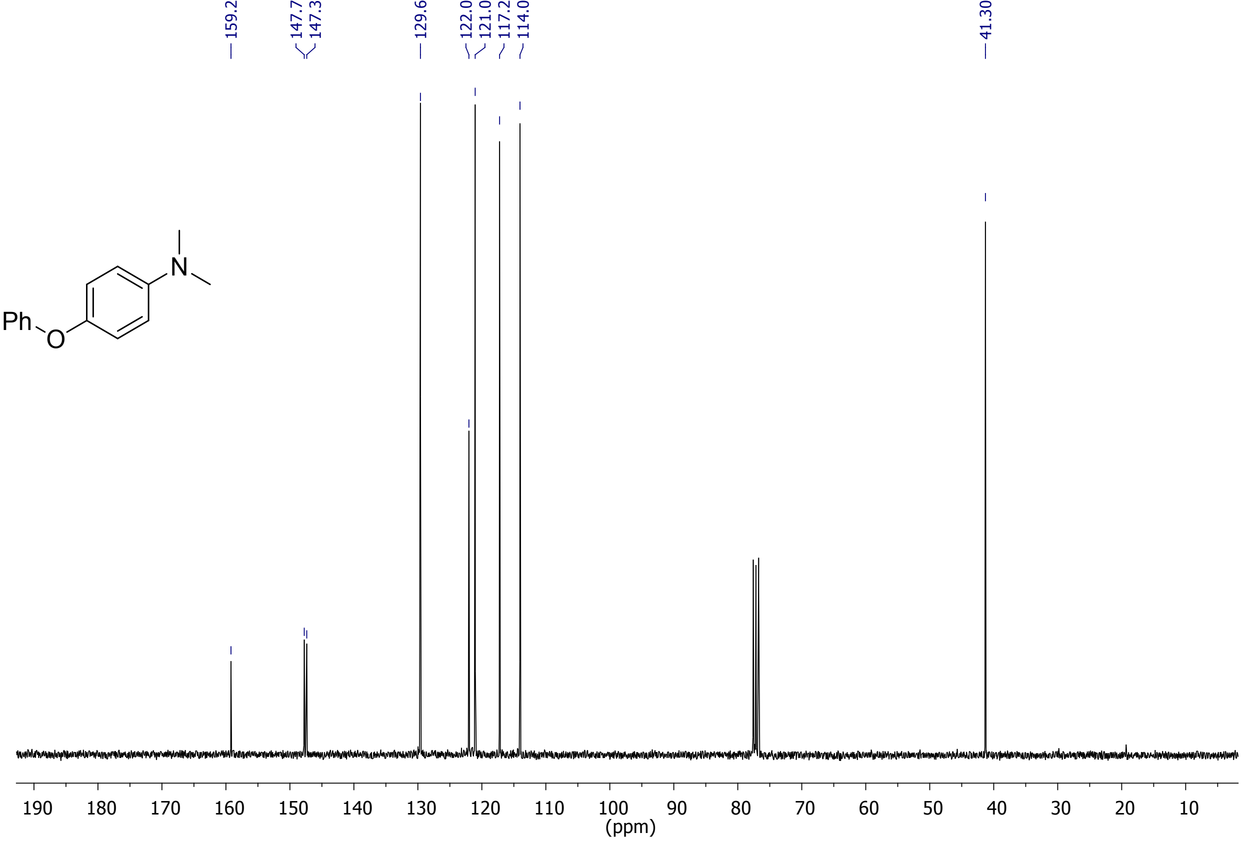
^{13}C NMR

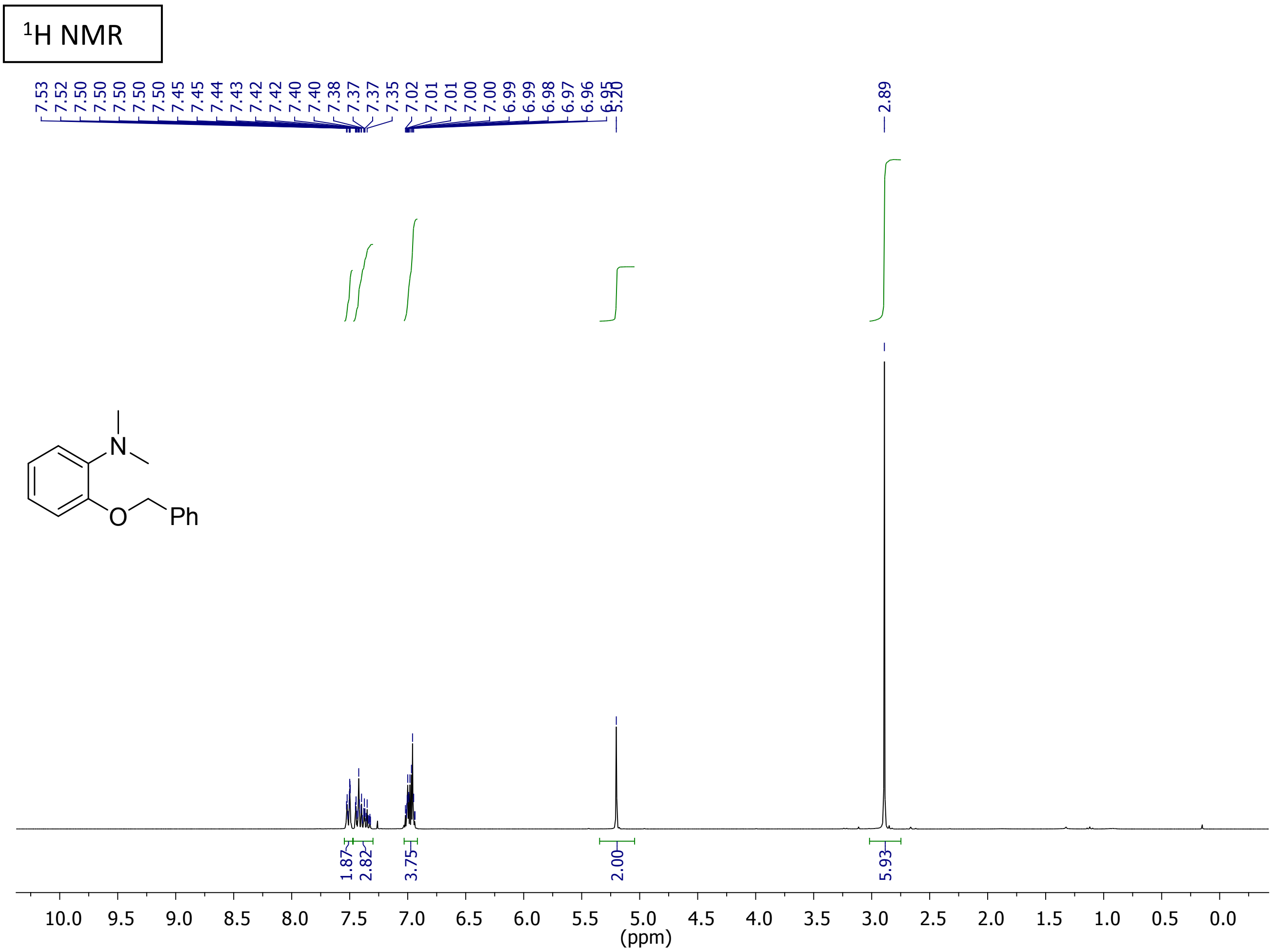


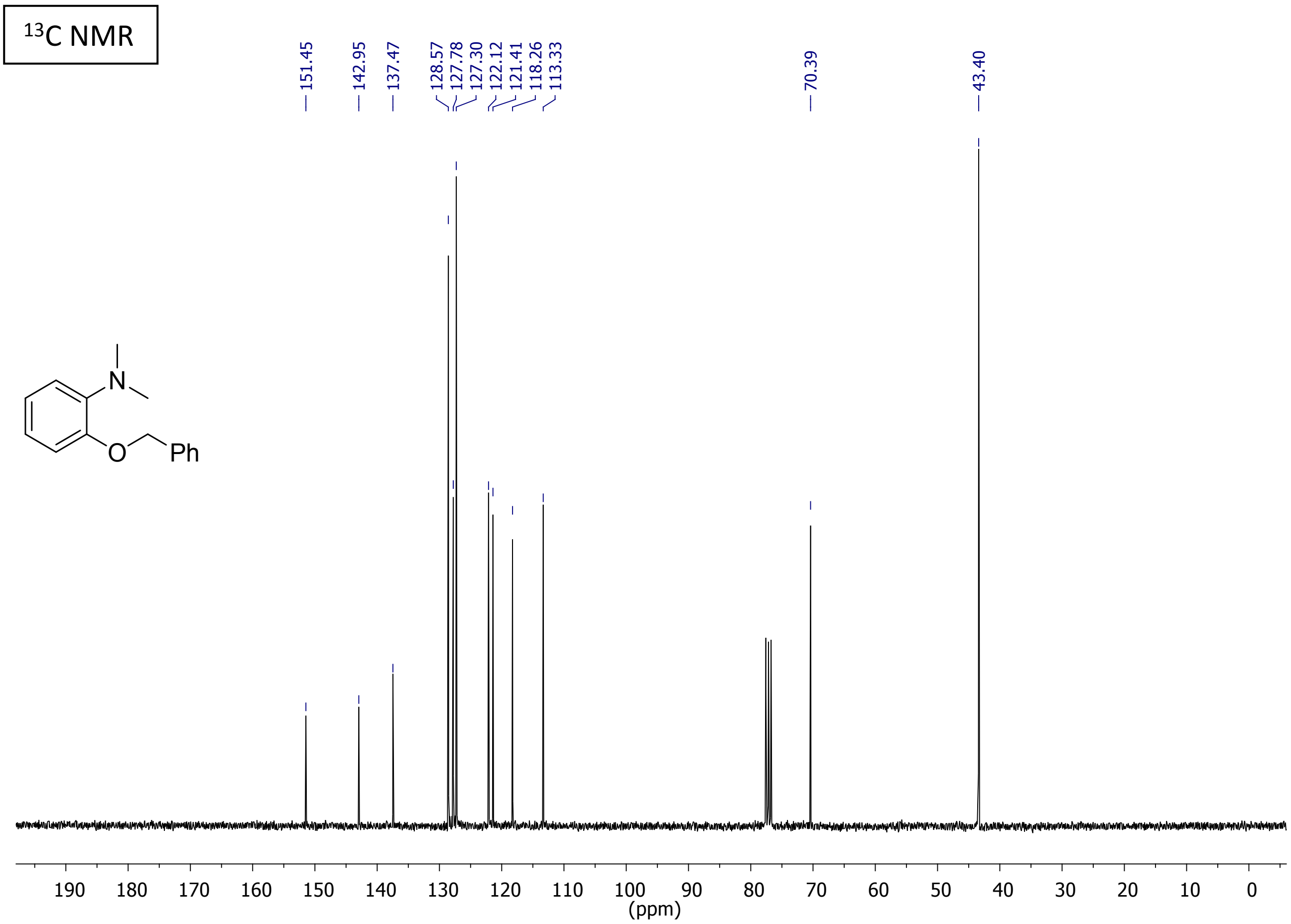
^{1}H NMR



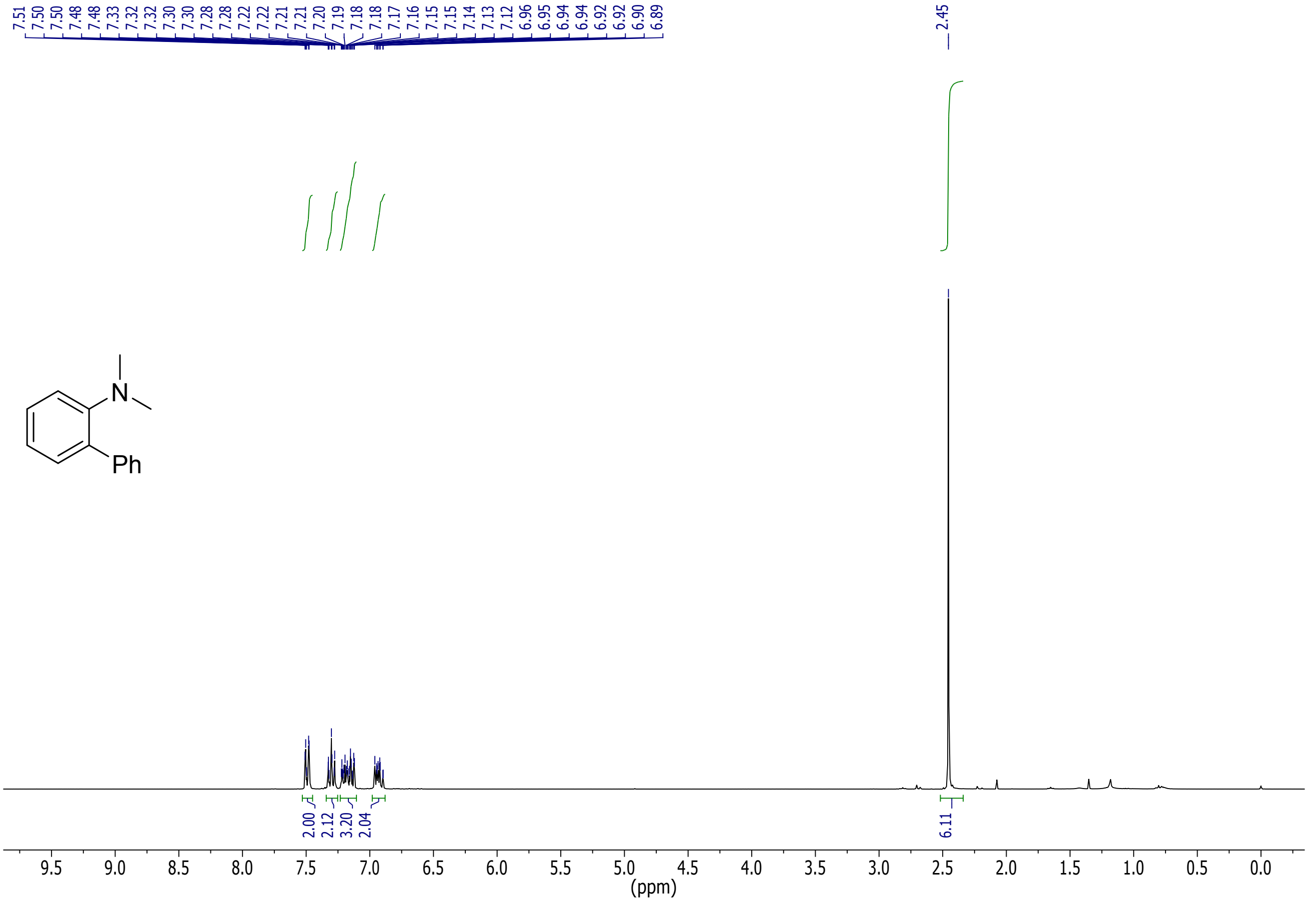
^{13}C NMR



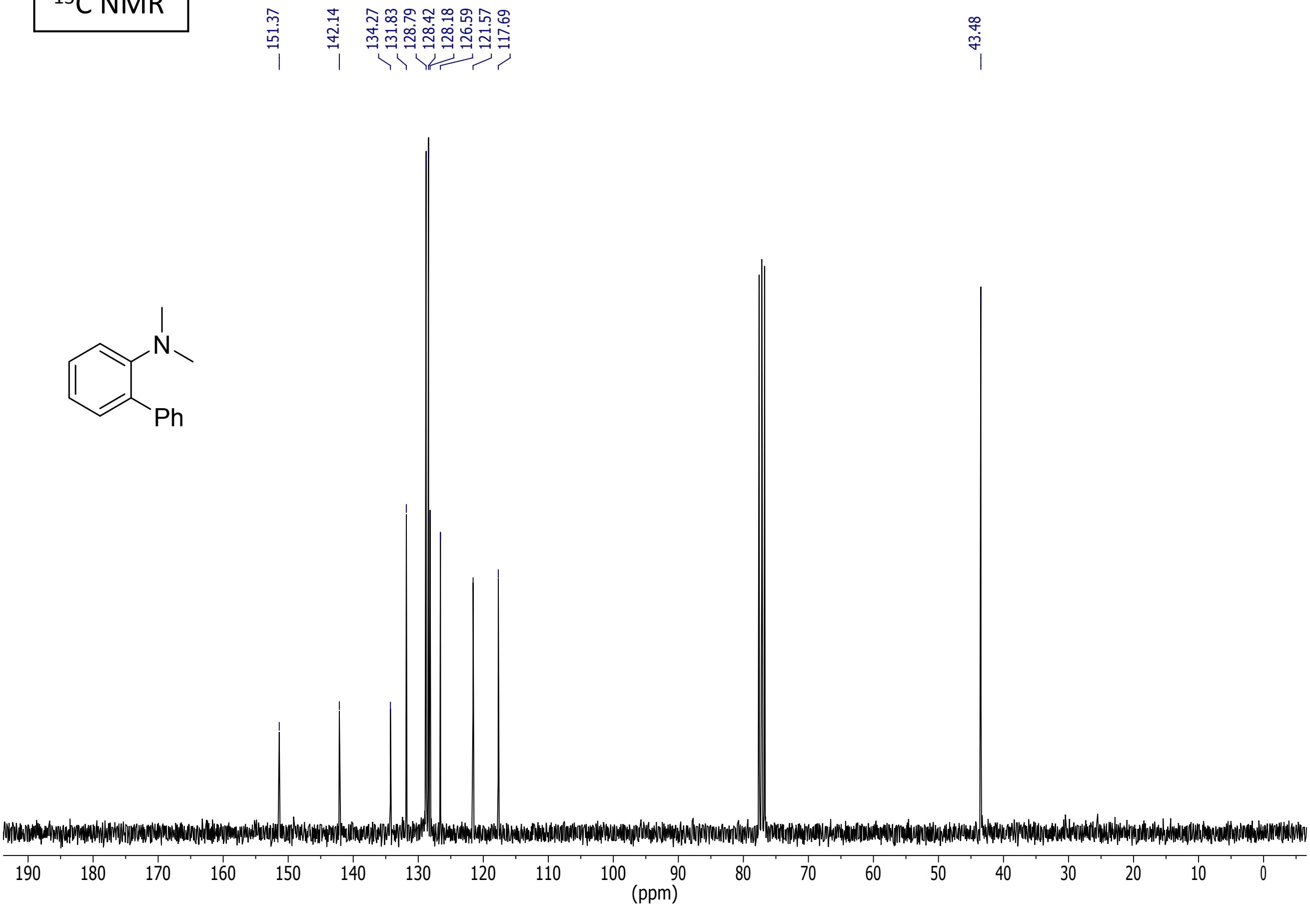

^{1}H NMR
7.53
7.52
7.50
7.50
7.50
7.50
7.45
7.45
7.44
7.43
7.42
7.42
7.40
7.40
7.38
7.37
7.37
7.35
7.02
7.01
7.01
7.00
7.00
6.99
6.99
6.98
6.97
6.96
6.95
5.20
2.89
N
O
Ph
1.87
2.82
3.75
2.00
5.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

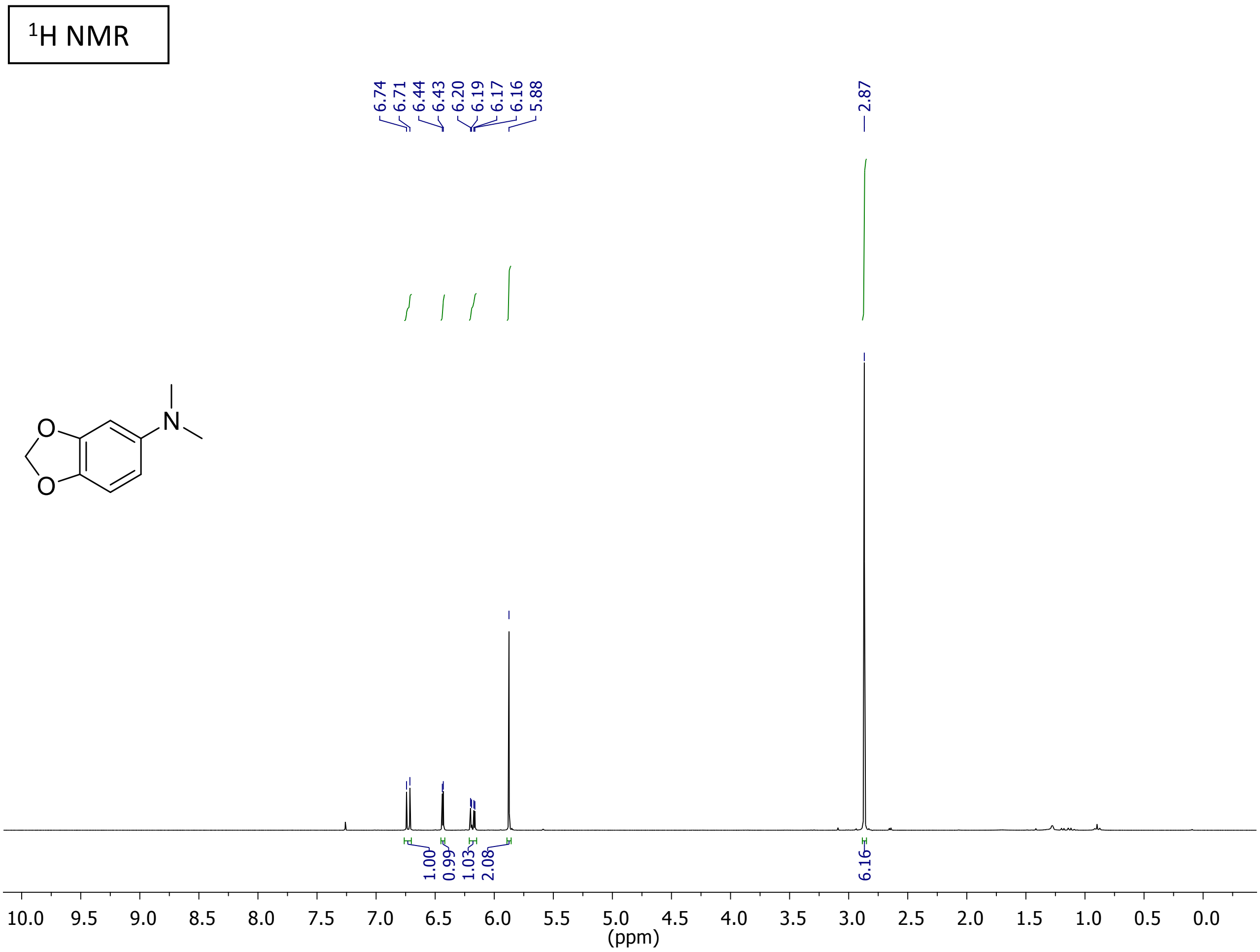

^{13}C NMR
151.45
142.95
137.47
128.57
127.78
127.30
122.12
121.41
118.26
113.33
70.39
43.40
N
O
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

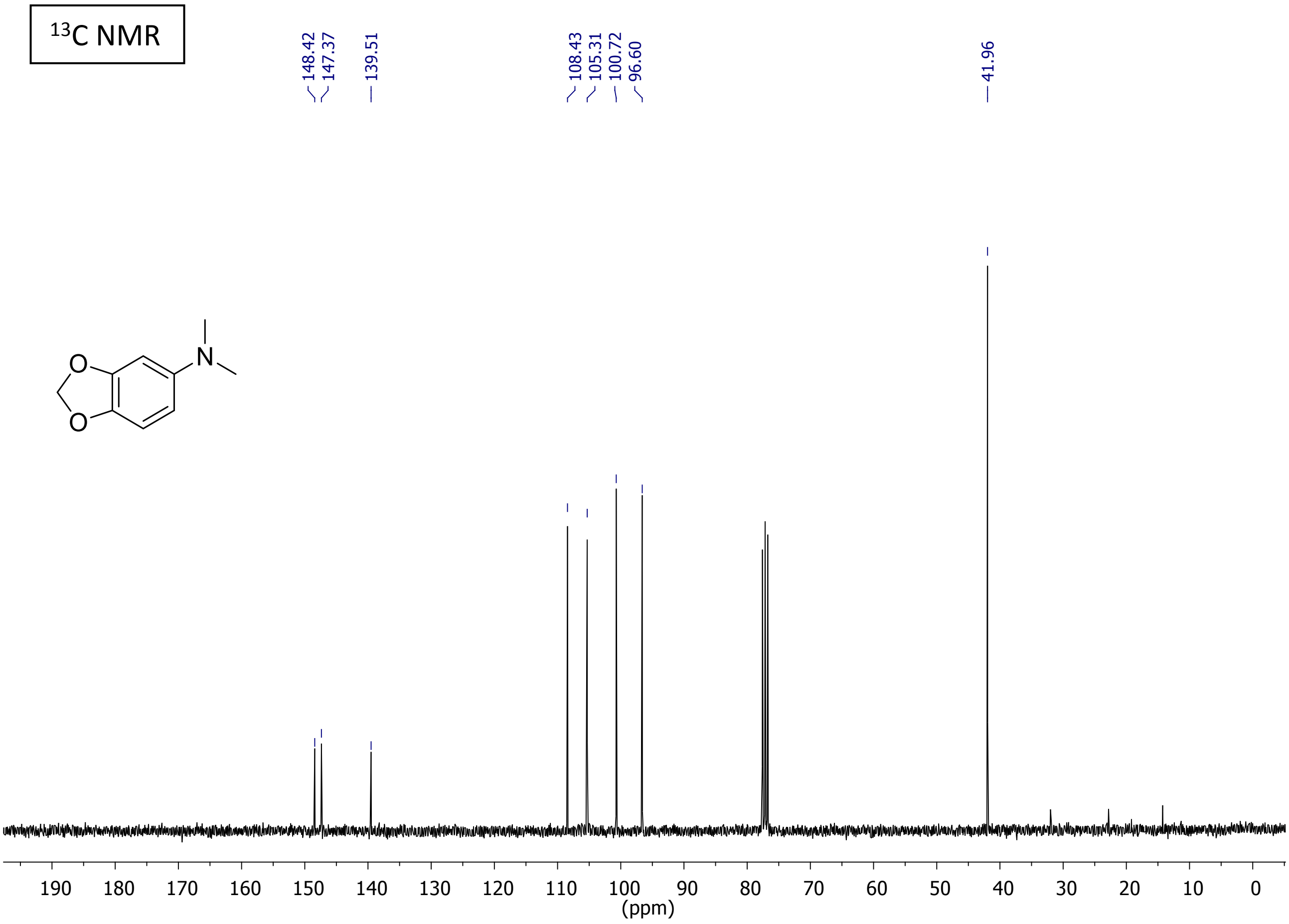
^{1}H NMR



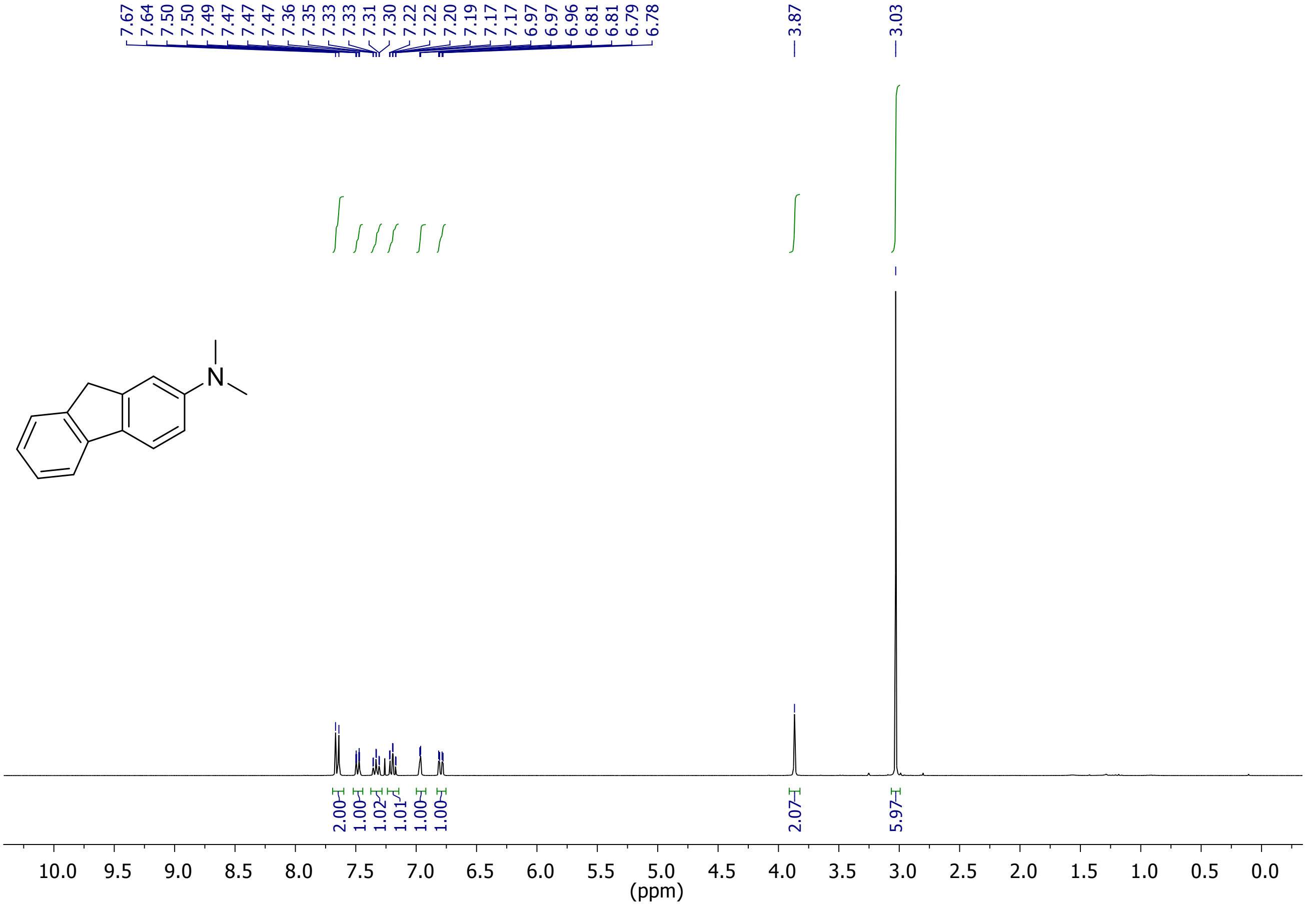
^{13}C NMR



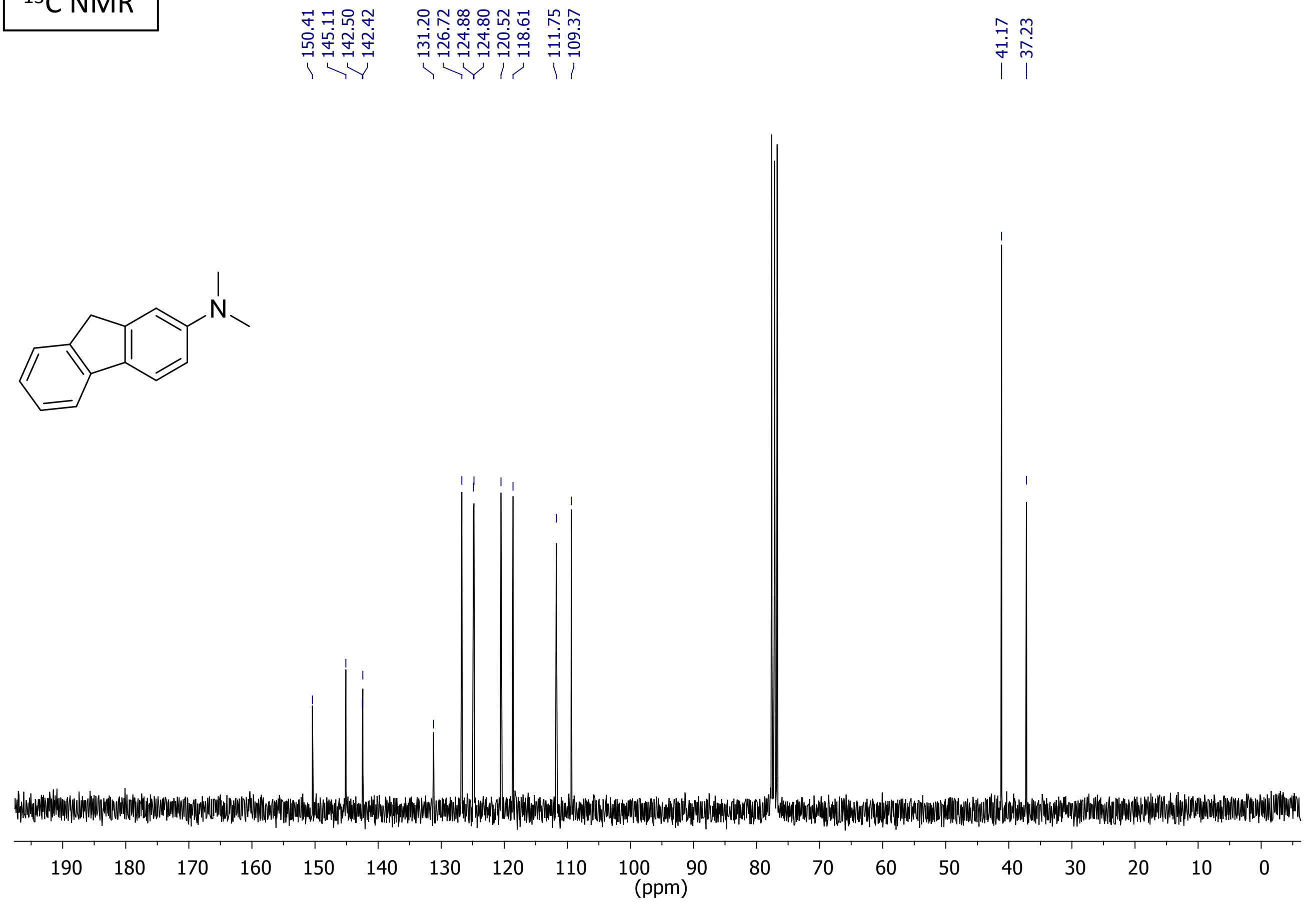

^{1}H NMR
6.74
6.71
6.44
6.43
6.20
6.19
6.17
6.16
5.88
2.87
O
O
N
1.00
0.99
1.03
2.08
6.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


^{13}C NMR
148.42
147.37
139.51
108.43
105.31
100.72
96.60
41.96
O
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

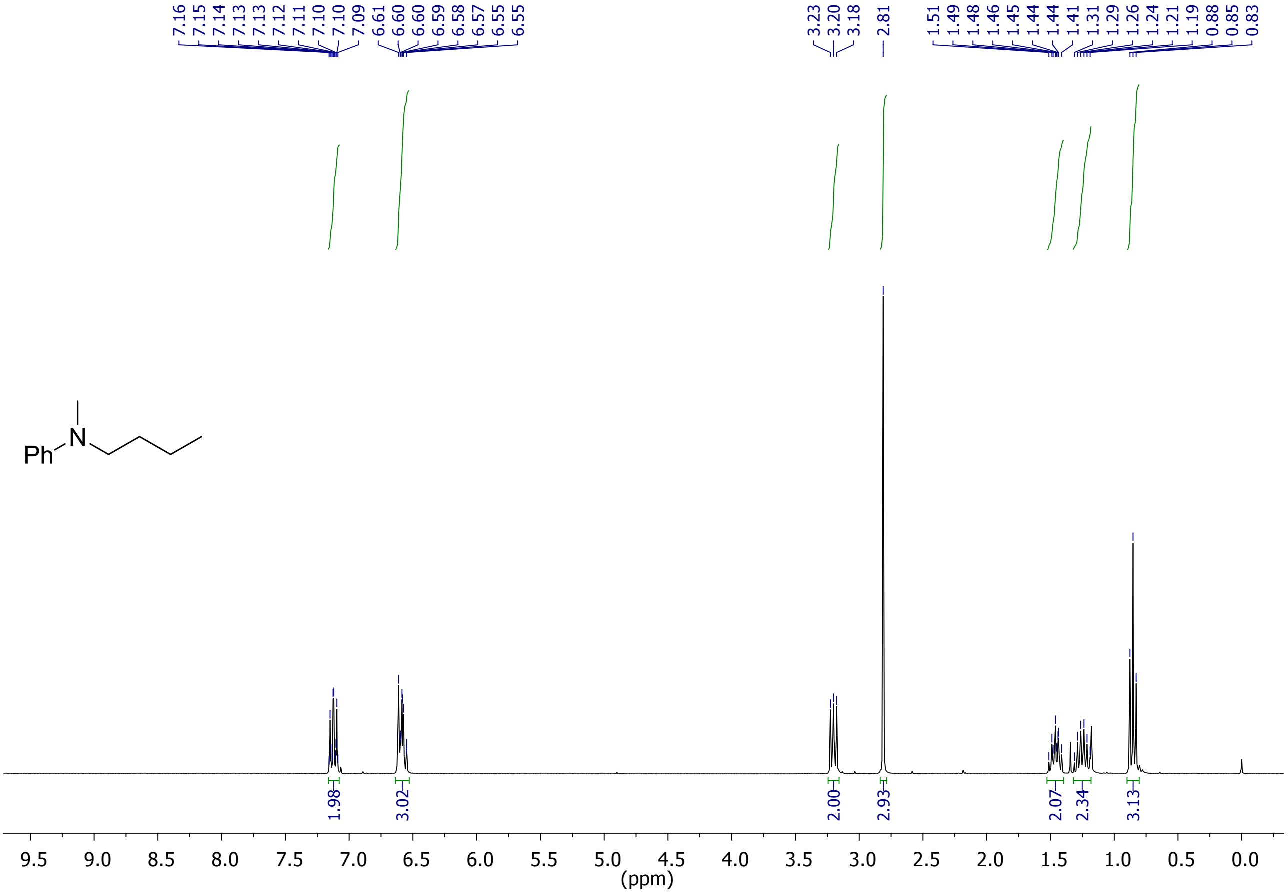
^{1}H NMR



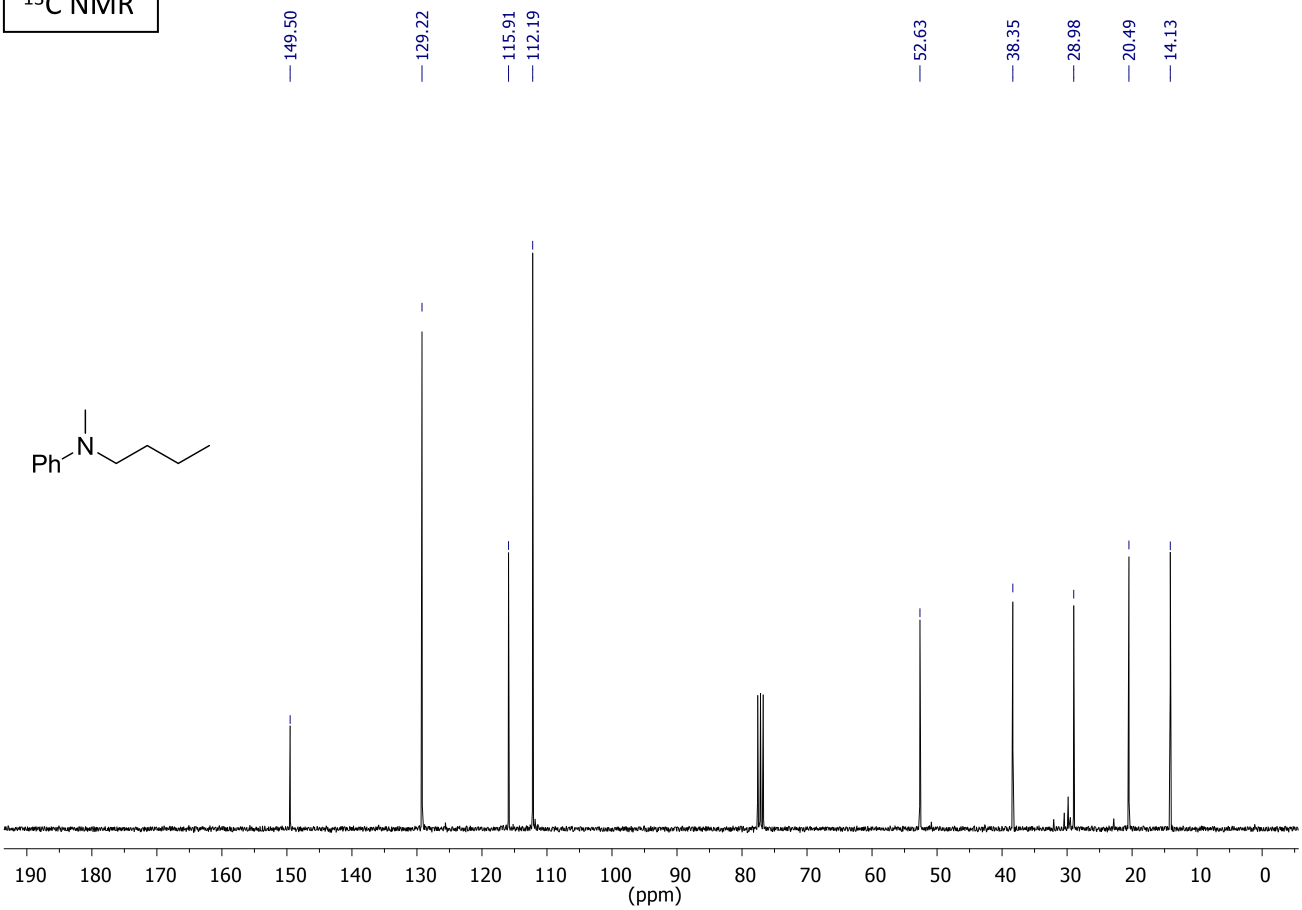
^{13}C NMR



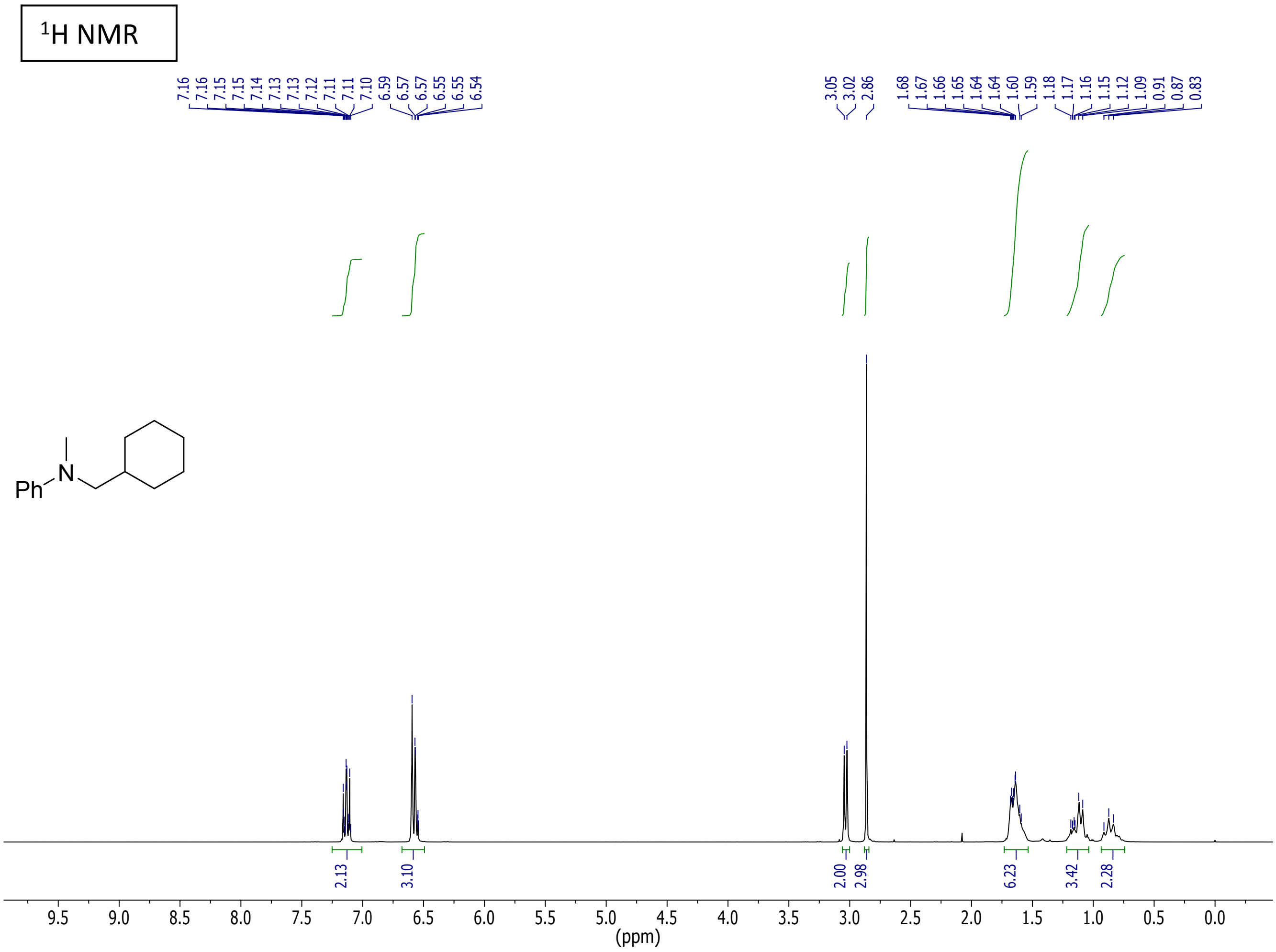
^{1}H NMR



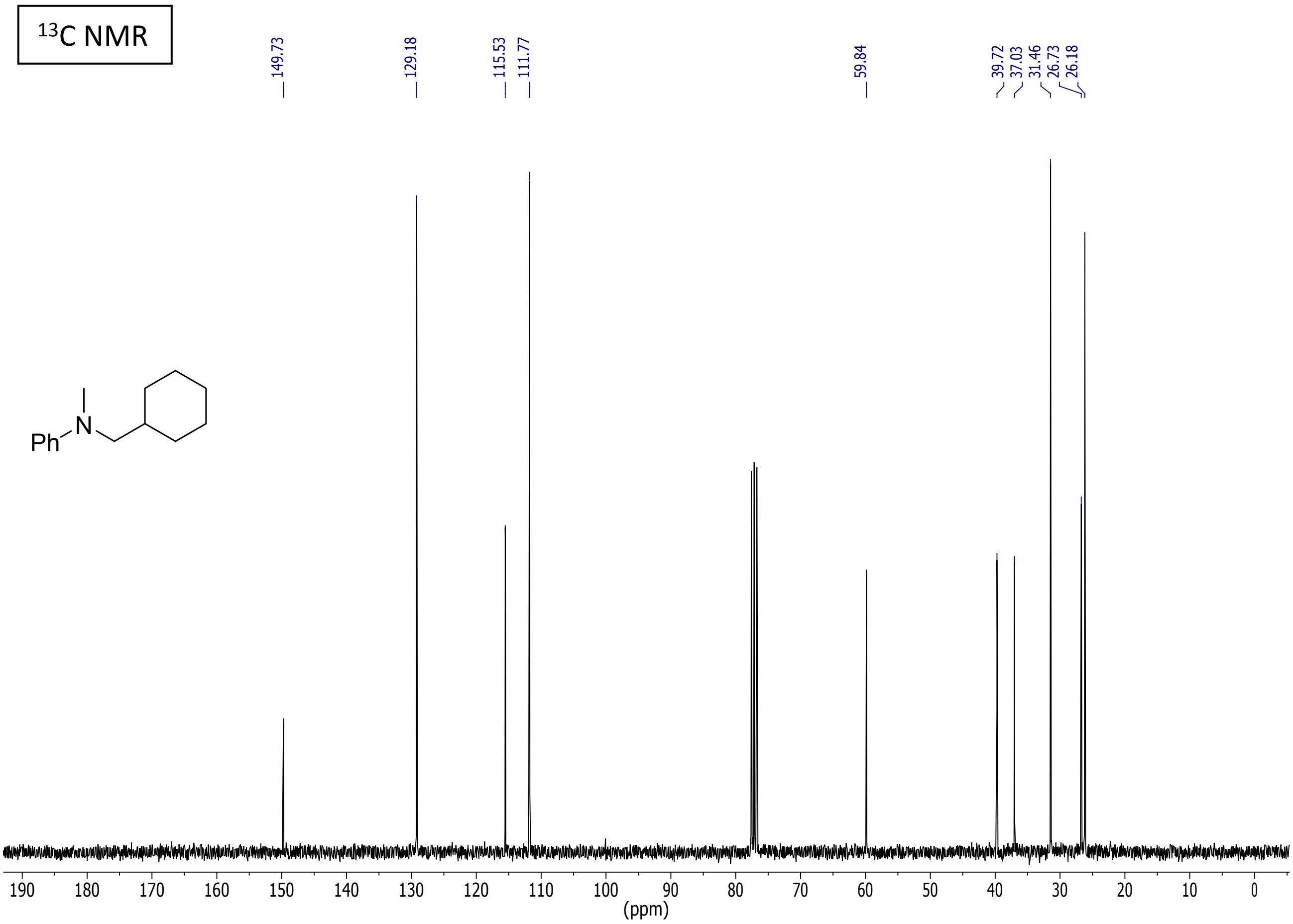
^{13}C NMR



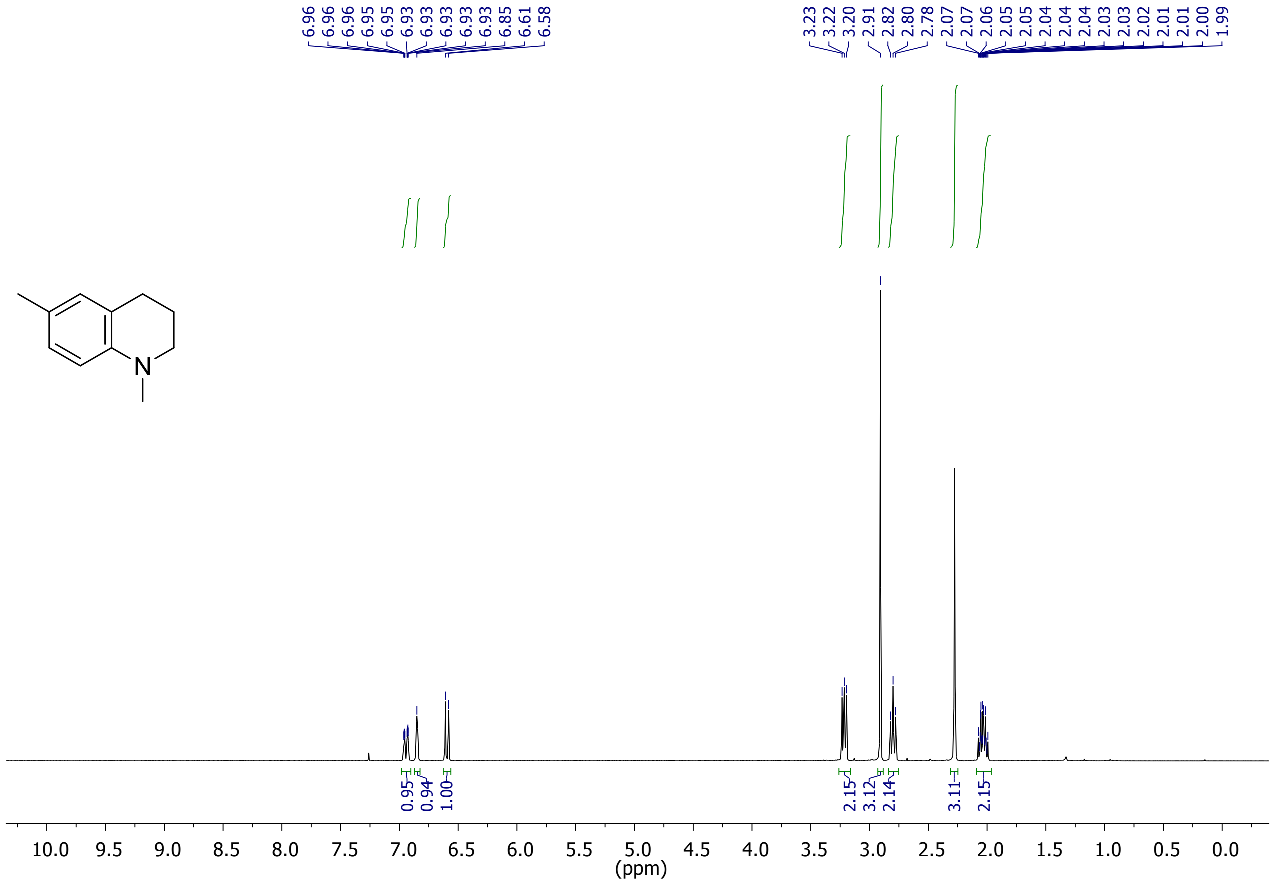
^{1}H NMR



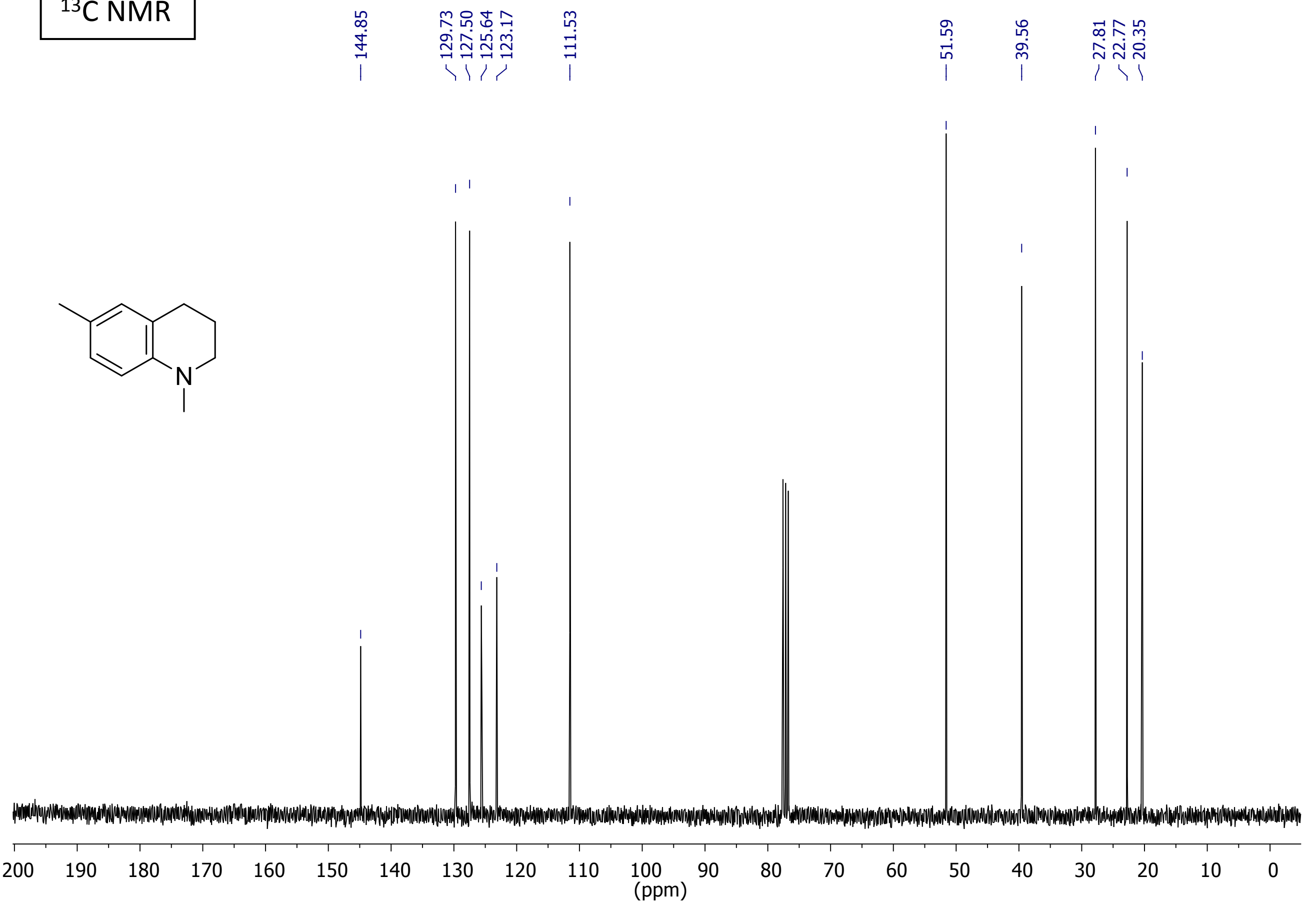
^{13}C NMR



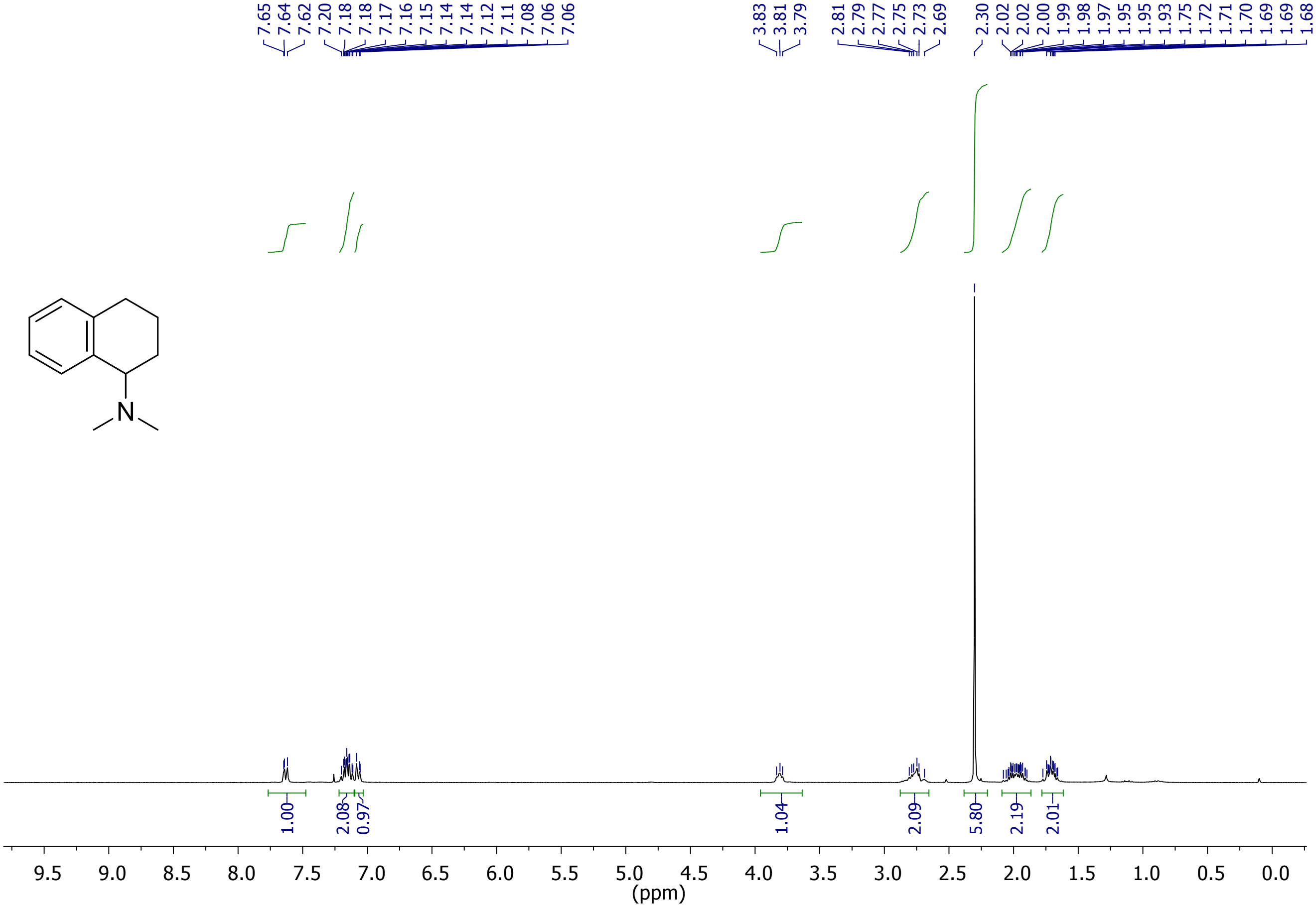
^{1}H NMR



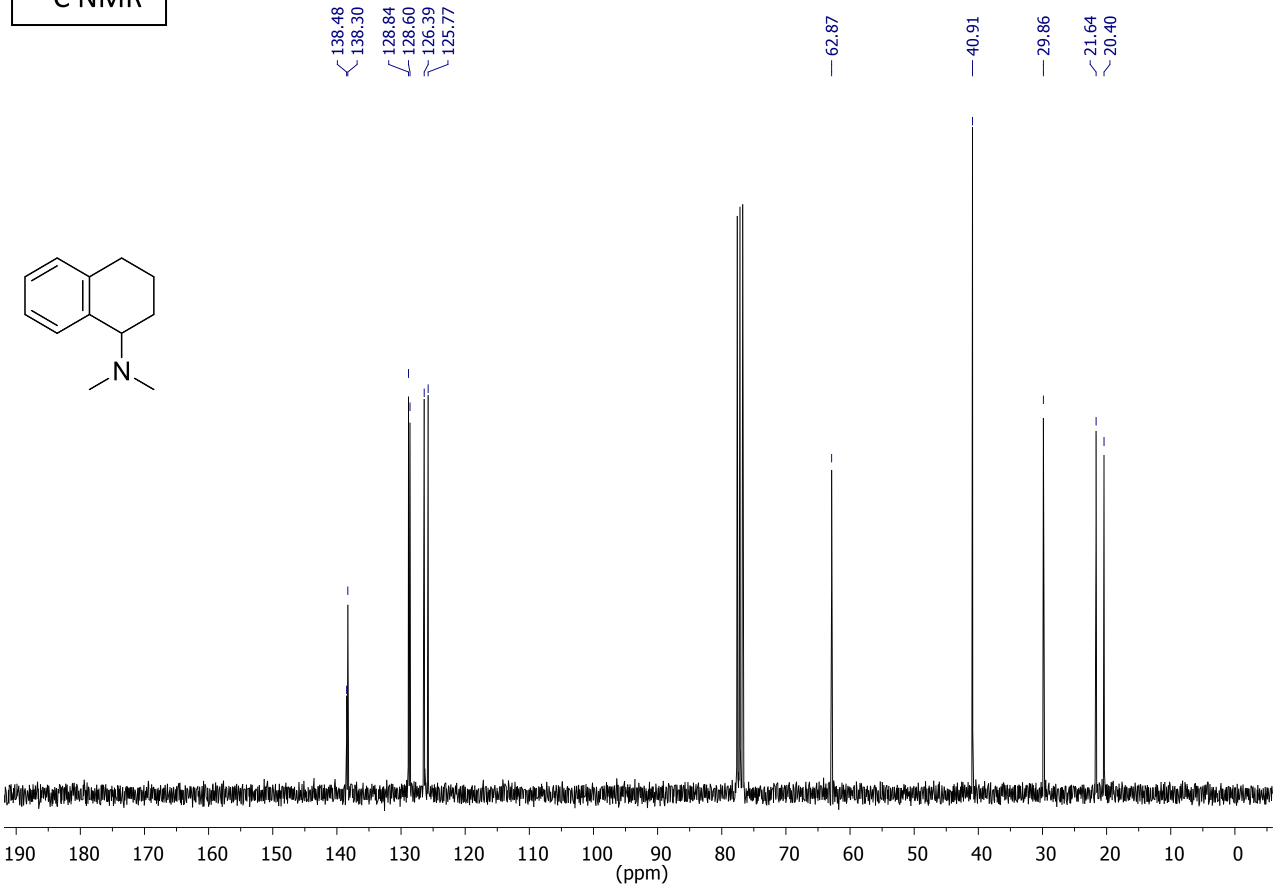
^{13}C NMR



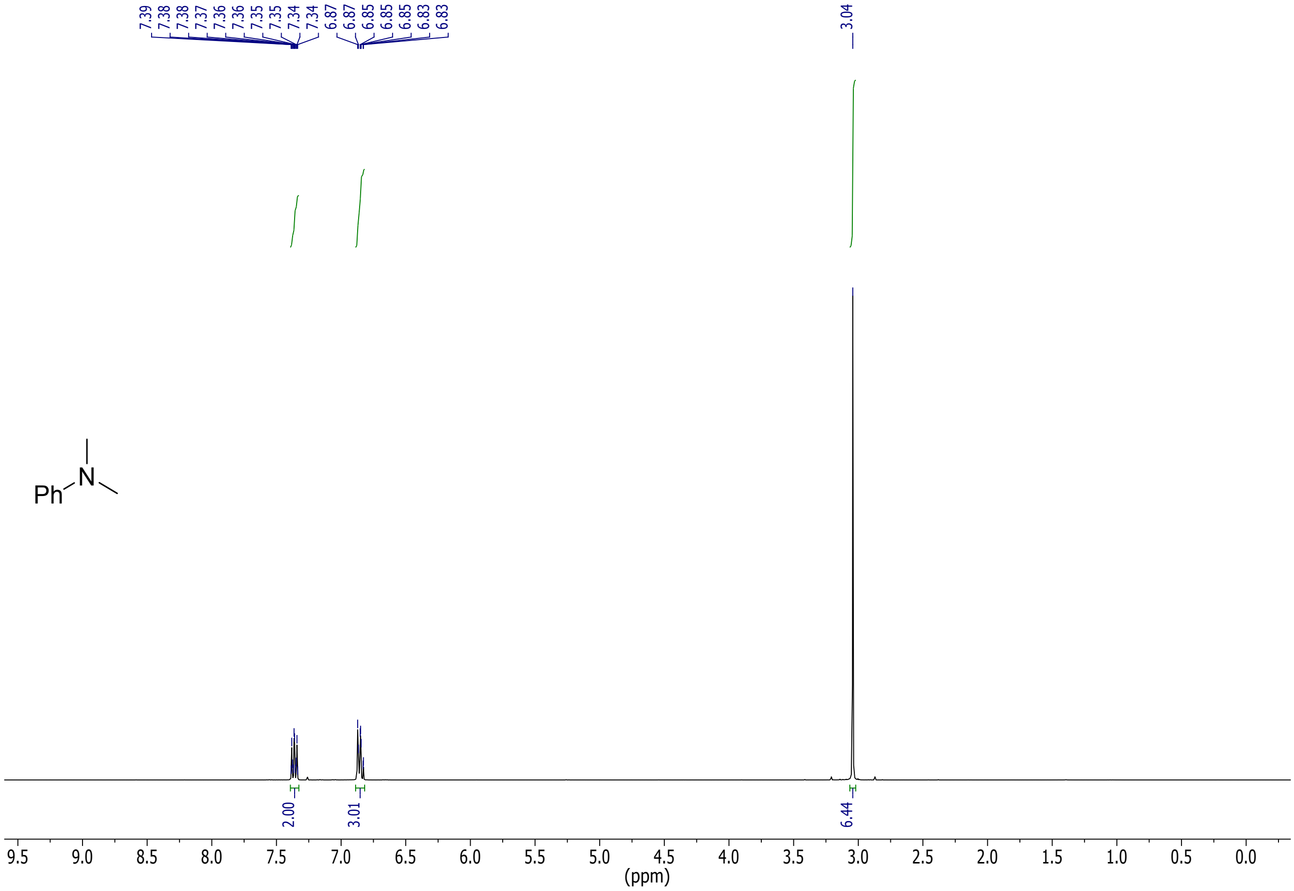
^{1}H NMR



^{13}C NMR



^{1}H NMR



^{13}C NMR