Supplementary Information

Transition Metal-Free Transfer Hydrogenation of Aryl Azides with Alcohols: Direct Synthesis of Secondary Amines and N-Heterocycles

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1. General information

All commercially available reagents and solvents (purchased from Sigma-Aldrich, TCI, Alfa Aesar, Acros Organics) were used without further purification unless otherwise noted. All reactions were carried out in oven-dried round bottom flask & seal tube. Reactions were monitored by thin layer chromatography on silica gel 60 F254 plate (Merck, Darmstadt, Germany) using UV illumination at 254 nm (VL-4.LC, Vilber Lourmat, Eberhardzell, Germany). Column chromatography was performed on silica gel (230~400 mesh; Zeochem, Lake Zurich, Switzerland), using mixture of n-hexane and EtOAc as eluents. Nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectra were measured on JEOL JNM-ECZ400s [400 MHz (^{1}H), 100 MHz (^{13}C)] spectrometer. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm; for ^{13}C NMR: $CDCl_3$ = 77.16 ppm, DMSO-d_6 = 39.52 ppm. Coupling constants (*J*) are expressed in hertz (Hz). IR spectra were recorded on a JASCO, FT/IR-4200 Infrared spectrophotometer and are reported as cm^{-1}. High resolution mass spectra (HRMS) were acquired using Agilent 6530 Q-TOF mass spectrometer and Agilent 1290 Infinity system or fast atom bombardments (FAB) ionization method on a JMS-700 MStation mass spectrometer. Melting points were measured on a Büchi B-540 melting point apparatus.

2. General procedures for the reactions

2-1. General procedure A for the synthesis of azidobenzenes and (2-azidophenyl)ketones

Round bottom flask was charged with corresponding anilines (1.0 eq.) and 2 M HCl solution at 0 ℃ using ice bath. Sodium nitrite (1.5 eq.) dissolved in H_2O (0.1 M) was transferred to the charged round bottom flask dropwise. Reaction was proceeded at room temperature for 30 minutes. Sodium azide (2.0 eq.) was dissolved in H_2O (0.1 M) and transferred to the reaction flask dropwise. After nitrogen gas released enough, reaction was proceeded 30 minutes. Conversion was monitored using TLC. After completion of the reaction, sat. $NaHCO_3$ solution was poured into the reaction mixture carefully. Reaction mixture was diluted with EtOAc and organic layer was washed with H_2O 3 times and concentrated. The product was purified by flash column chromatography on silica gel (n-hexane/EtOAc) or filtration to afford the title compound.

2-2. General procedure B for the synthesis of azidoanilines

To an oven-dried 25 mL vial, stirring bar and copper(I) bromide (0.5 equiv.) was added and capped with rubber septum. The vial was evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous 1,4-dioxane (0.5 M), corresponding aniline (1.0 equiv.), trimethylsilyl azide (2.0 equiv.) was added to the vial. tert-Butyl hydroperoxide solution (2.0 equiv. 5.0-6.0 M in decane) was added to the vial dropwise carefully. The mixture was stirred for 3 hours and the reaction was monitored using TLC. After completion, the mixture was diluted with EtOAc and passed through a pad of celite, washed with EtOAc. The dark brown organic solution was evaporated and purified by column chromatography on silica gel (n-hexane/EtOAc) to afford the title compound.

2-3. General procedure C for the synthesis of secondary amines

Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.) and alcohol **2** (0.4 mmol, 4.0 eq., if **2** is solid) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), alcohol **2** (0.4 mmol, 4.0 eq., if **2** is liquid), azide **1** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was

capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 ℃ (dry block heater temperature, 1000 rpm). After stirring for 24 h, the reaction mixture was cooled to room temperature and diluted with sat. NH_4Cl solution (2 mL) and H_2O (8 mL). The mixture was extracted with dichloromethane (10 mL x 3) and the combined organic phase was dried over MgSO4, and concentrated using rotatory evaporator. The residue was purified by flash column chromatography on silica gel (n-hexane/EtOAc) to afford the desired product.

2-4. General procedure D for the synthesis of quinoxalines

Potassium tert-butoxide (0.025 mmol, 2.8 mg, 0.25 eq.) and 1,2-diol **6** (0.2 mmol, 2.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), 2-azidoaniline **5** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 ℃ (dry block heater temperature, 1000 rpm). After stirring for 48 h, the reaction mixture was cooled to room temperature and diluted with sat. NH_4Cl solution (2 mL) and H_2O (8 mL). The mixture was extracted with dichloromethane (10 mL x 3) and the combined organic phase was dried over MgSO4, and concentrated using rotatory evaporator. The residue was purified by flash column chromatography on silica gel (n-hexane/EtOAc) to afford the desired product.

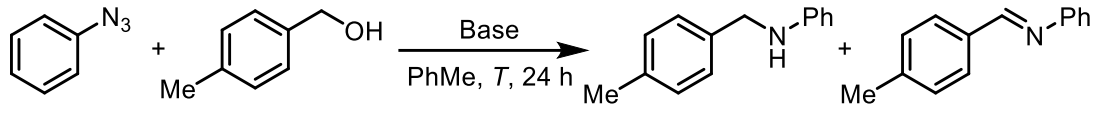
2-5. General procedure E for the synthesis of quinolines

Potassium hydroxide (0.2 mmol, 11.2 mg, 2.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), secondary benzylic alcohol **9** (0.3 mmol, 3.0 eq.) and (2-azidophenyl)ketone **8** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 ℃ (dry block heater temperature, 1000 rpm). After stirring for 24 h, the reaction mixture was cooled to room temperature and diluted with sat. NH_4Cl solution (2 mL) and H_2O (8 mL). The mixture was extracted with dichloromethane (10 mL x 3) and the combined organic phase

was dried over $MgSO_4$, and concentrated using rotatory evaporator. The residue was purified by flash column chromatography on silica gel (n-hexane/EtOAc or dichloromethane/acetone) to afford the desired product.

3. Optimization of reaction parameters

Table S1. Optimization of base: Secondary amines[a]

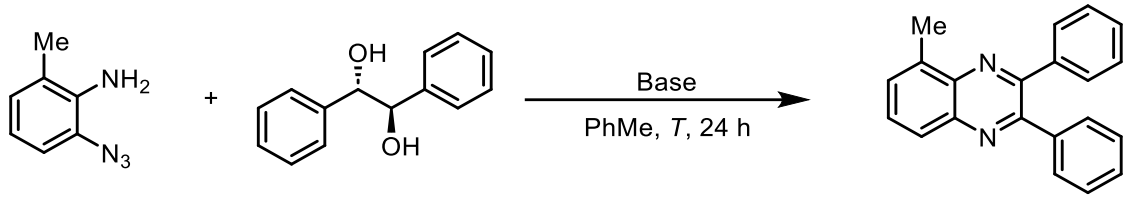


1a **2a** **3aa** **4aa**

				yield (%)	
entry	**base (equiv)**	**2a (equiv)**	**temp (°C)**	**3aa**	**4aa**
1	**KOH (2.0)**	**4.0**	**150**	**98 (97[b])**	**trace**
2	NaOH (2.0)	4.0	150	9	45
3	LiOH (2.0)	4.0	150	-	24
4	Na_2CO_3 (2.0)	4.0	150	-	trace
5	K_2CO_3 (2.0)	4.0	150	-	11
6	Cs_2CO_3 (2.0)	4.0	150	-	18
7	$K_3PO_4 \cdot H_2O$ (2.0)	4.0	150	-	14
8	NaOMe (2.0)	4.0	150	trace	43
9	NaO^{t}Bu (2.0)	4.0	150	48	49
10	**KO^{t}Bu (2.0)**	**4.0**	**150**	**99 (99[b])**	**trace**
11	**KO^{t}Bu 99.99% (2.0)**	**4.0**	**150**	**99**	**trace**

[a]Yields determined by ^{1}H NMR using dimethyl sulfone as the internal standard. [b]Isolated yield.

Table S2. Optimization of reaction parameters: Quinoxalines[a]

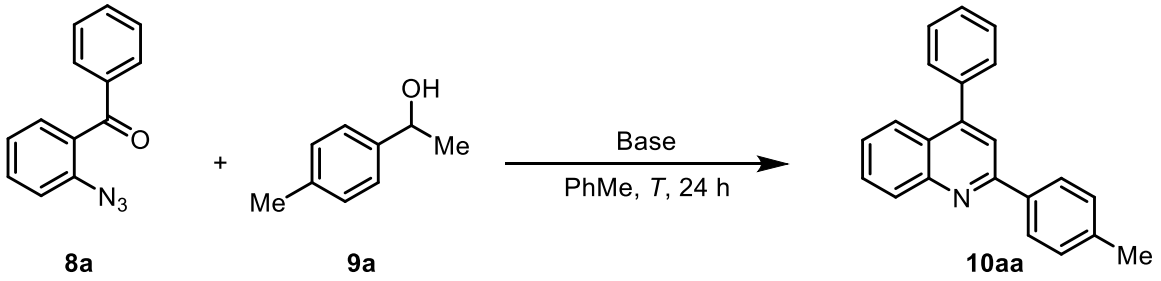


5a **6a** **7aa**

entry	base (equiv)	6a (equiv)	solvent (mL)	temp (°C)	yield 7aa (%)
1	KOtBu (2.0)	1.0	PhMe (0.5)	150	< 1
2	KOtBu (1.5)	1.0	PhMe (0.5)	150	1
3	KOtBu (1.0)	1.0	PhMe (0.5)	150	25
4	KOtBu (0.5)	1.0	PhMe (0.5)	150	42
5	KOtBu (0.25)	1.0	PhMe (0.5)	150	56
6	KOtBu (0.1)	1.0	PhMe (0.5)	150	31
7	-	1.0	PhMe (0.5)	150	-
8	KOtBu (0.25)	1.0	o-Xylene (0.5)	150	49
10	KOtBu (0.25)	1.0	PhCl (0.5)	150	50
11	KOtBu (0.25)	1.0	$PhCF_3$ (0.5)	150	50
12	KOtBu (0.25)	1.0	1,4-Dioxane (0.5)	150	53
13	KOtBu (0.25)	1.5	PhMe (0.5)	150	60
14	KOtBu (0.25)	2.0	PhMe (0.5)	150	70
15[b]	**KOtBu (0.25)**	**2.0**	**PhMe (0.5)**	**150**	**83**

[a]Yields determined by ^{1}H NMR using dibromomethane as the internal standard. [b]48 h.

Table S3. Optimization of reaction parameters: Quinolines[a]



8a **9a** **10aa**

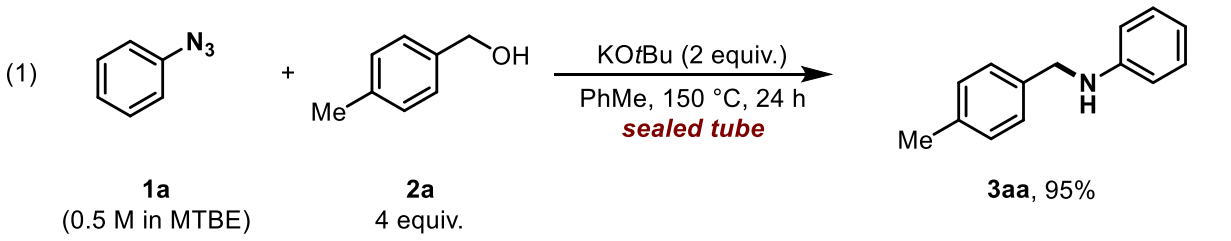
entry	base (equiv)	9a (equiv)	solvent (mL)	temp (°C)	yield 10aa (%)
1	KOtBu (0.25)	2.0	PhMe (0.5)	150	-
2	KOtBu (0.5)	2.0	PhMe (0.5)	150	-
3	KOtBu (1.0)	2.0	PhMe (0.5)	150	46
4	KOtBu (2.0)	2.0	PhMe (0.5)	150	48
5	KOtBu (2.0)	3.0	PhMe (0.5)	150	57
6	KOtBu (2.0)	4.0	PhMe (0.5)	150	51
7[b]	KOtBu (2.0)	3.0	PhMe (0.5)	150	45
8	KOtBu (1.5)	3.0	PhMe (0.5)	150	53
9	KOtBu (2.0)	3.0	PhMe (0.5)	140	49
10	KOtBu (2.0)	3.0	PhMe (0.5)	160	45
11	KOtBu (3.0)	3.0	PhMe (0.5)	150	36
12	**KOH (2.0)**	**3.0**	**PhMe (0.5)**	**150**	**63**

[a]Yields determined by ^{1}H NMR sing dibromomethane as the internal standard. [b]48 h.

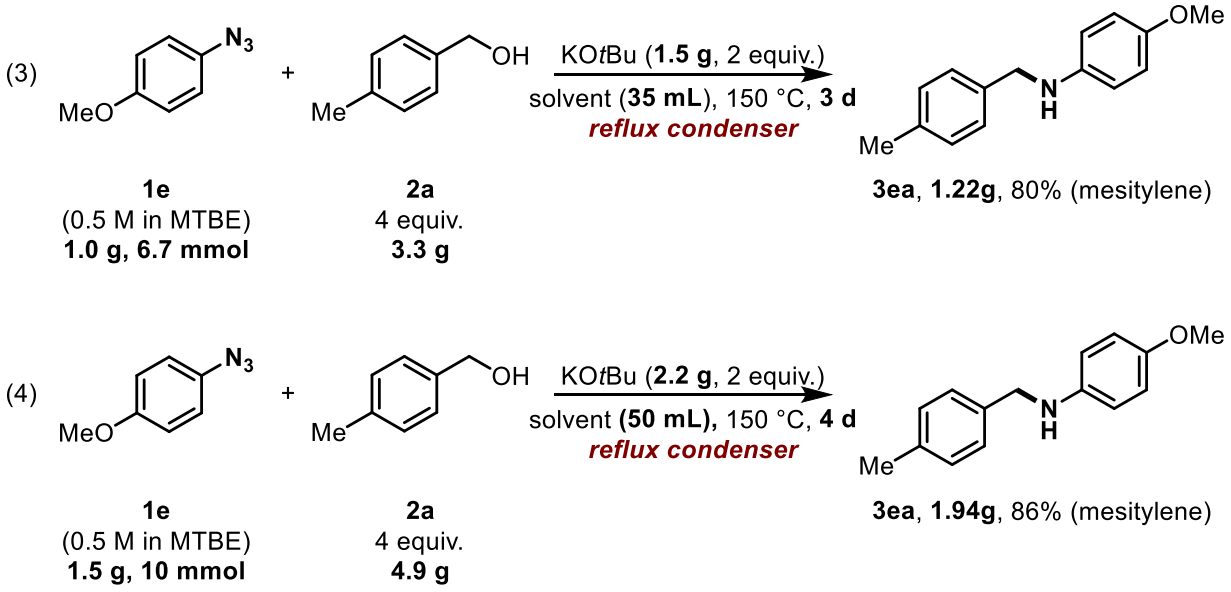
4. Large scale synthesis of secondary amines

Scheme S1. Large scale synthesis and practicability test

1 mmol scale



Gram scale



(1) Following the general procedure C, azidobenzene **1a** (1.0 mmol, 0.5 M in MTBE, 2.0 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (4.0 mmol, 488.7 mg, 4.0 eq.) were used as starting material. After purification by column chromatography on silica gel (n-hexane : EtOAc = 50 : 1), **3aa** was obtained as pale yellow solid (186.8 mg, 95% yield).

(2) Potassium tert-butoxide (2.0 mmol, 224.4 mg, 2.0 eq.) and alcohol **2a** (4.0 mmol, 488.7 mg, 4.0 eq.) was added to an oven-dried 100 mL round bottom flask and capped with rubber septum. The reaction flask was evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous solvent (5.0 mL) and azide **1e** (1.0 mmol, 0.5 M in MTBE, 2.0 mL, 1.0 eq.) was added sequentially to the flask. Reflux condenser was equipped to the flask and charged with argon balloon. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 ℃ (dry block heater temperature, 1000 rpm). After stirring for 24 h, the reaction mixture was cooled to room temperature and diluted with sat. NH_4Cl solution (20 mL) and H_2O (80 mL). The mixture was extracted with dichloromethane (50 mL x 3) and the combined organic phase was dried over MgSO4, and concentrated using rotatory evaporator. The residue was purified by flash column chromatography on silica gel (n-hexane : EtOAc = 30 : 1) to afford the desired product.

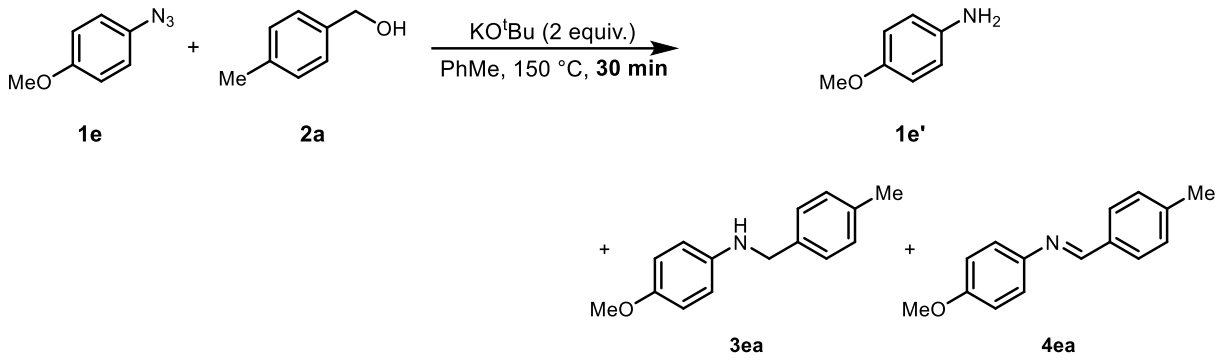
Initially, toluene was used as a solvent; however, it evaporated completely, making it unsuitable for the reflux condenser system. When o-xylene was used as a replacement, approximately half of the solvent remained, leading to the formation of the desired product **3ea** in a yield of 79% (179.8 mg). In contrast, when mesitylene was used, most of the solvent remained, resulting in the formation of the desired product **3ea** with a yield of 91% (206.4 mg).

(3) As in (2), mesitylene was used as the solvent. **1e** (6.7 mmol, 1.0 g), **2a** (26.8 mmol, 3.3 g), KOtBu (13.4 mmol, 1.5 g), Mesitylene (35 mL) using reflux condenser under Argon for 72 h at 150 ℃. After purification by column chromatography on silica gel (n-hexane : EtOAc = 30 : 1), **3ea** was obtained as orange solid (1224.4 mg, 80% yield).

(4) As in (2), mesitylene was used as the solvent. **1e** (10.0 mmol, 1.5 g), **2a** (40.0 mmol, 4.9 g), KOtBu (20.0 mmol, 2.2 g), Mesitylene (50 mL) using reflux condenser under Argon for 96 h at 150 ℃. After purification by column chromatography on silica gel (n-hexane : EtOAc = 30 : 1), **3ea** was obtained as orange solid (1944.1 mg, 86% yield).

5. Mechanistic studies

Scheme S2. Observation of aniline intermediate and requirement of KOtBu and alcohol for azide reduction



entry	deviation from the standard condition	recovery of 1e (%)	yield of 1e' (%)	yield of 3+4 (%)
1	None	3	27 (21[b])	54
2	without **2a** and KO^{t}Bu	12	trace	-
3	without **2a**	-	trace	-
4	without KO^{t}Bu	19	trace	-

Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.) and alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 ℃ (dry block heater temperature, 1000 rpm). After stirring for 30 minutes, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. The filtrate was concentrated using rotatory evaporator. Dibromomethane was added to the mixture as an internal standard and the mixture was diluted with $CDCl_3$. The mixture was analyzed using ^{1}H-NMR analysis and afforded **1e'** (27%, ^{1}H-NMR yield). The NMR spectral data of **1e'** are same as the previous report.[3] Another mixture was prepared as the same procedure above and purified by prep-TLC (n-hexane : EtOAc : triethylamine = 4 : 2 : 1) to afford **1e'** (2.6 mg, 21%) as dark brown solid.

^{1}H-NMR (400 MHz, DMSO-d_6) δ 6.63 (d, *J* = 8.7 Hz, 2H), 6.50 (d, *J* = 9.1 Hz, 2H), 4.59 (s, 2H), 3.61 (s, 3H)

HRMS (ESI) *m/z* calcd for $C_7H_{10}NO^+$ [M+H$^+$] 124.0757, found 124.0753

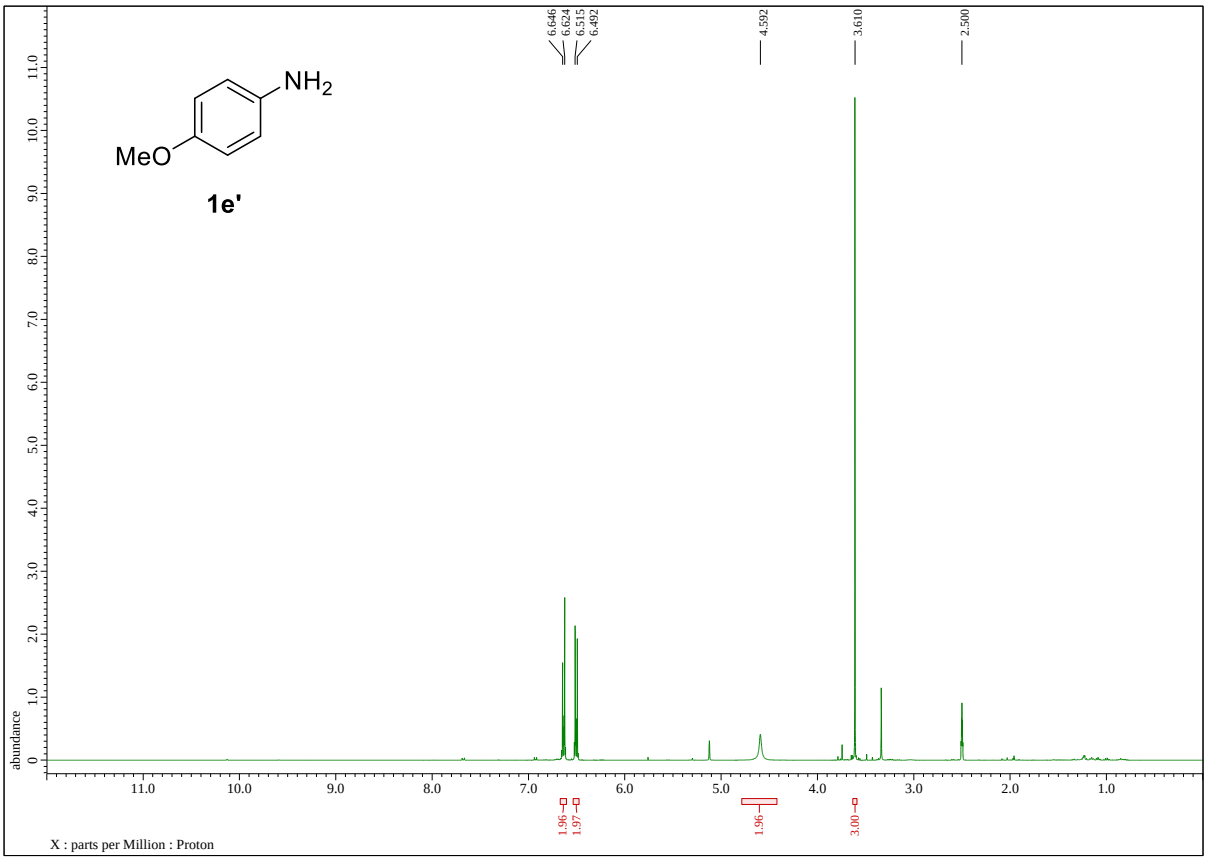


Figure S1. ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of isolated **1e'**

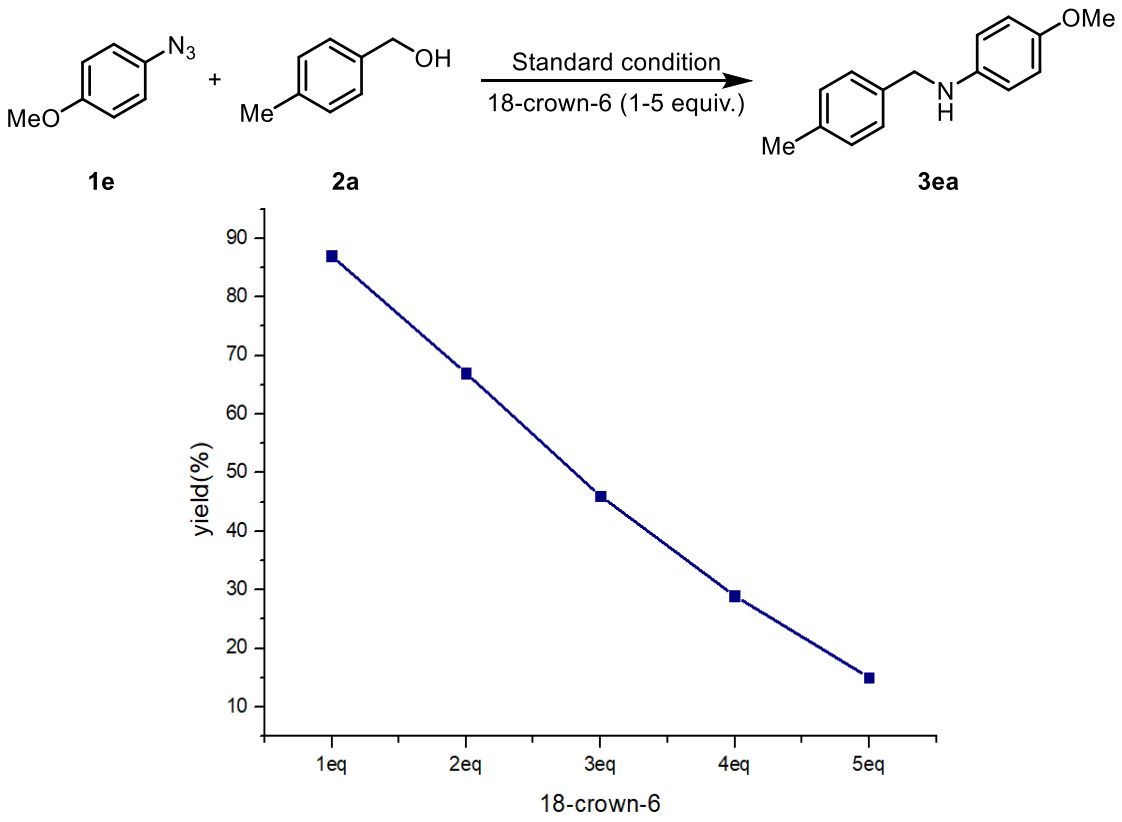
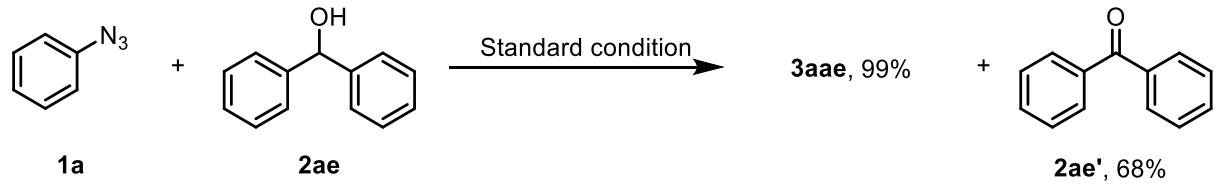


Figure S2. Potassium inhibition study using 18-crown-6 ether

Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.), alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) and 18-crown-6 ether (1.0-5.0 equiv.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 °C (dry block heater temperature, 1000 rpm). After stirring for 30 minutes, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. The filtrate was concentrated using rotatory evaporator. Dibromomethane was added to the mixture as an internal standard and the mixture was diluted with $CDCl_3$. The mixture was analyzed using ^{1}H-NMR analysis. The data was collected and shown as graph above.

Scheme S3. Observation of carbonyl intermediate



Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.) and benzhydrol **2ae** (0.4 mmol, 73.7 mg, 4.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 ℃ (dry block heater temperature, 1000 rpm). After stirring for 24 hours, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. The filtrate was concentrated using rotatory evaporator. After purification by prep-TLC (n-hexane : EtOAc = 50 : 1) to afford **2ae'** (12.3 mg, 68%) as white solid. The NMR spectral data of **2ae'** are same as the previous report.[4]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 4H), 7.59 (tt, *J* = 7.4, 1.4 Hz, 2H), 7.51-7.47 (m, 4H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.9, 137.7, 132.6, 130.2, 128.4

HRMS (ESI) *m/z* calcd for $C_{13}H_{11}O^+$ [M+H$^+$] 183.0804, found 183.0803

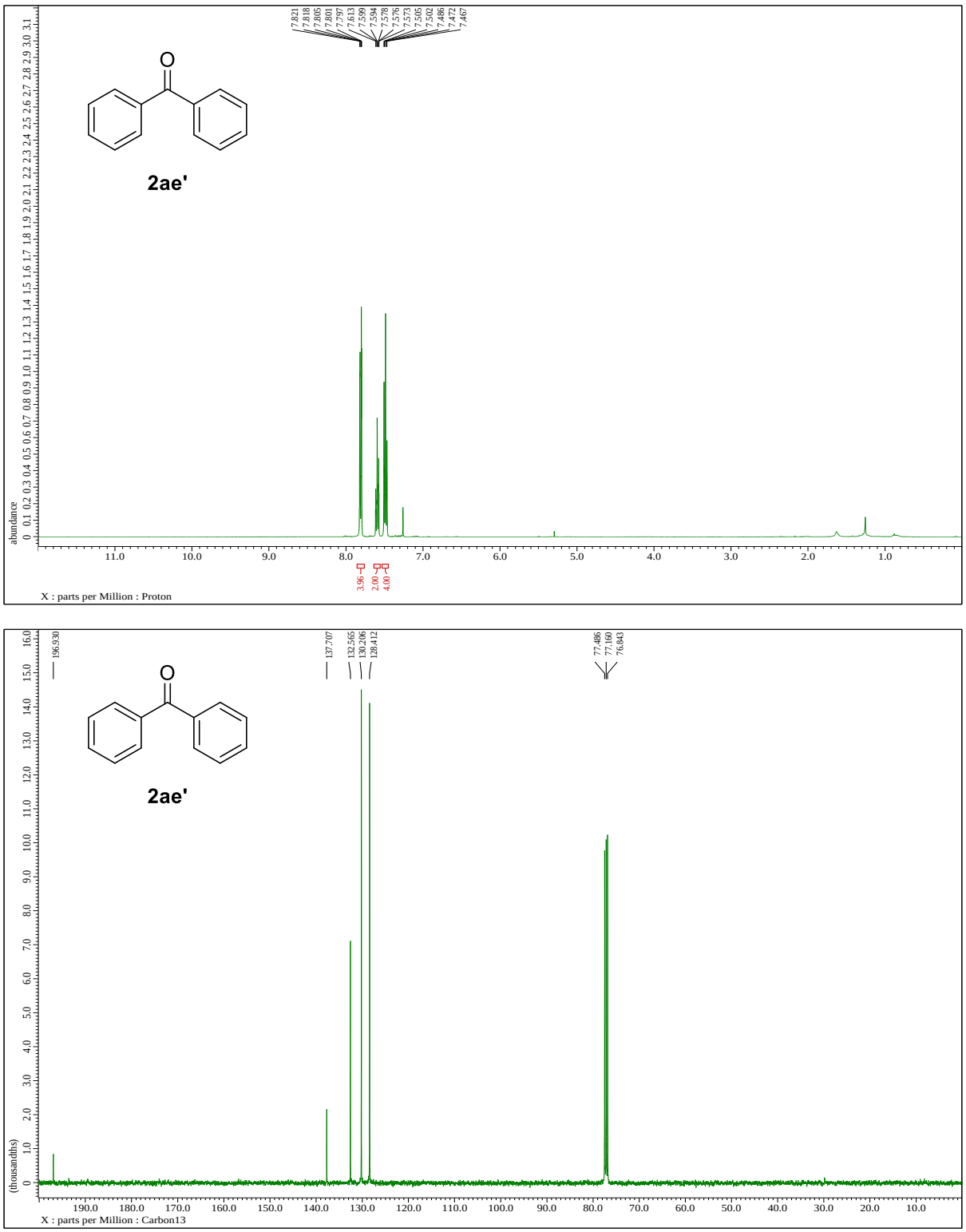
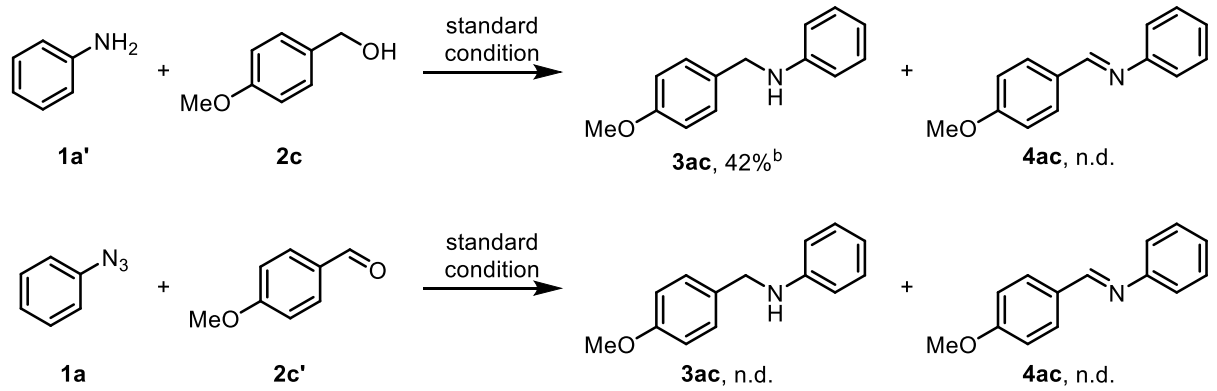


Figure S3. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, up) and ^{13}C-NMR spectrum (100 MHz, $CDCl_3$, down) of isolated **2ae'**

Scheme S4. Control experiments demonstrating the necessity of aryl azide and alcohol as redox partners



Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), aniline **1a'** or azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) and alcohol **2c** or aldehyde **2c'** (0.4 mmol, 4.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 °C (dry block heater temperature, 1000 rpm). After stirring for 24 hours, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. Dibromomethane was added to the mixture as an internal standard and the mixture was diluted with $CDCl_3$. The mixture was analyzed using ^{1}H-NMR analysis.

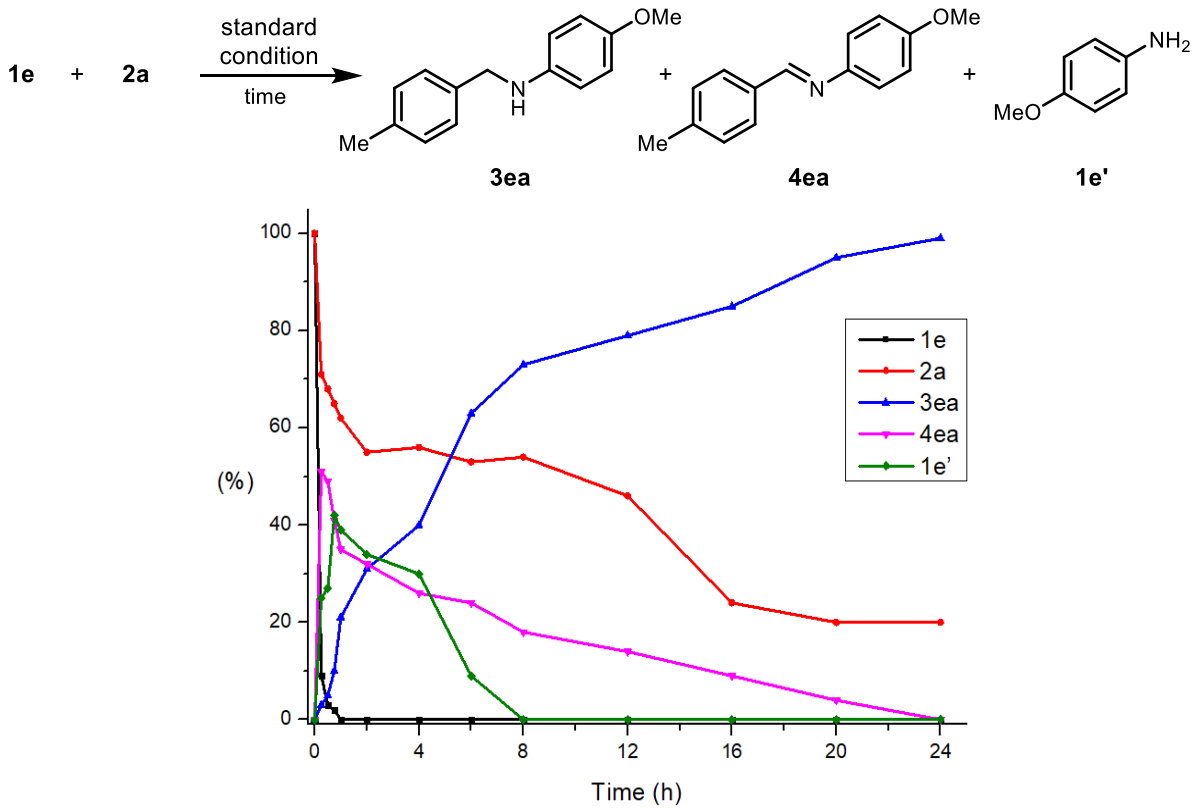
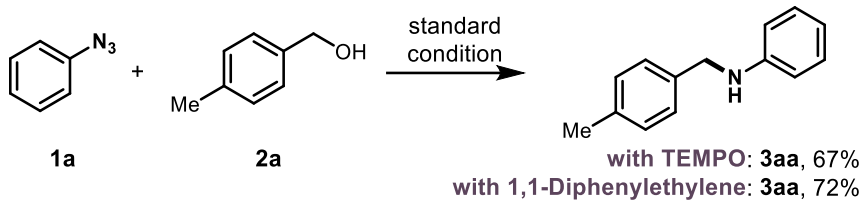


Figure S4. Time-course analysis of the reaction

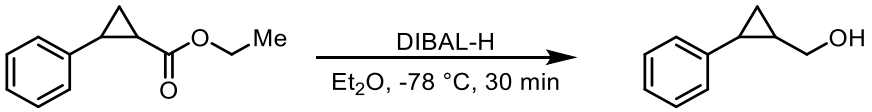
Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.) and alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 ℃ (dry block heater temperature, 1000 rpm). After stirring for suitable time, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. The filtrate was concentrated using rotatory evaporator. Dibromomethane was added to the mixture as an internal standard and the mixture was diluted with $CDCl_3$. The mixture was analyzed using ^{1}H-NMR analysis. The data was collected and shown as graph above.

Scheme S5. Radical scavenger studies for exclusion of a radical mechanism



Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.), alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) and radical scavenger (0.2 mmol, 2.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 ℃ (dry block heater temperature, 1000 rpm). After stirring for suitable time, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. The filtrate was concentrated using rotatory evaporator. Dibromomethane was added to the mixture as an internal standard and the mixture was diluted with $CDCl_3$. The mixture was analyzed using ^{1}H-NMR analysis.

Preparation of cyclopropane-containing alcohol 11



ethyl 2-phenylcyclopropane-1-carboxylate **11**

(2-Phenylcyclopropyl)methanol (11)

An oven-dried round bottom flask was capped with rubber septum, charged with argon using vacuum pump and the reaction bath was maintained to -78 ℃. Diethyl ether (4.5 mL) and diisobutylaluminum hydride solution (3.4 mL, 1 M in dichloromethane, 2.5 eq.) were added to the reaction flask at the same temperature. After ethyl 2-phenylcyclopropane-1-carboxylate (1.35 mmol, 256.8 mg, 1.0 eq.) were added to the reaction flask dropwise, the mixture was stirred for 30 minutes at -78 ℃. After the completion of the reaction was monitored using TLC, excess H_2O and dichloromethane (10 mL) were added to the mixture to quench the reaction. The organic phase was washed with H_2O, combined, and evaporated using rotatory evaporator. The residue were purified by flash column chromatography on silica gel (n-hexane : EtOAc = 5 : 1) to afford **11** (161.7 mg, 81%, trans : cis = 3 : 4) as colorless oil. The NMR spectral data of **11** are same as the previous report.[5]

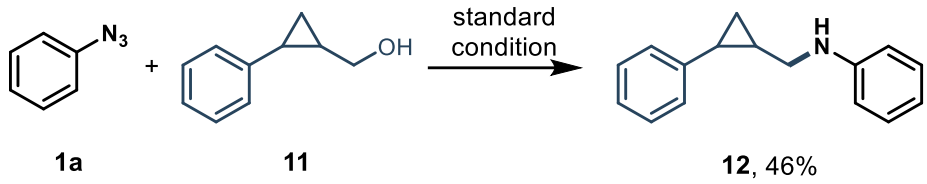
^{1}H-NMR (*trans*-11, 400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.24-7.06 (m, 3H), 3.63 (t, *J* = 6.4 Hz, 2H), 1.86-1.81 (m, 1H), 1.49-1.44 (m, 1H), 1.01-0.85 (m, 1H); **^{1}H-NMR (*cis*-11, 400 MHz, $CDCl_3$)** δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.24-7.06 (m, 3H), 3.48 (q, *J* = 6.0 Hz, 1H), 3.27 (dd, *J* = 11.5, 8.7 Hz, 1H), 2.30 (dd, *J* = 14.7, 8.7 Hz, 1H), 1.49-1.44 (m, 1H), 1.10-1.01 (m, 1H), 1.01-0.85 (m, 1H)

^{13}C-NMR (*trans*-11, 100 MHz, $CDCl_3$) δ 142.6, 128.4, 125.9, 125.7, 66.5, 25.3, 21.3, 13.9; **^{13}C-NMR (*cis*-11, 100 MHz, $CDCl_3$)** δ 138.3, 128.9, 128.3, 126.3, 62.8, 20.9, 20.8, 7.8

IR (neat) υ 3854, 3744, 3628, 2373, 2318, 1733, 1699, 1653, 1560, 1436, 1264, 749 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{10}H_{13}O^+$ [$M+H^+$] 149.0961, found 149.0957

Scheme S6. Radical clock experiment for exclusion of a radical pathway



N-((2-phenylcyclopropyl)methyl)aniline (12)

Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.) and alcohol **11** (0.4 mmol, 59.3 mg, 4.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 ℃ (dry block heater temperature, 1000 rpm). After stirring for 24 hours, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. The filtrate was concentrated using rotatory evaporator. After purification by flash column chromatography on silica gel (n-hexane : EtOAc = 30 : 1), **12** was obtained as yellow oil (10.2 mg, 46%). No ring opening product was found in the reaction mixture.

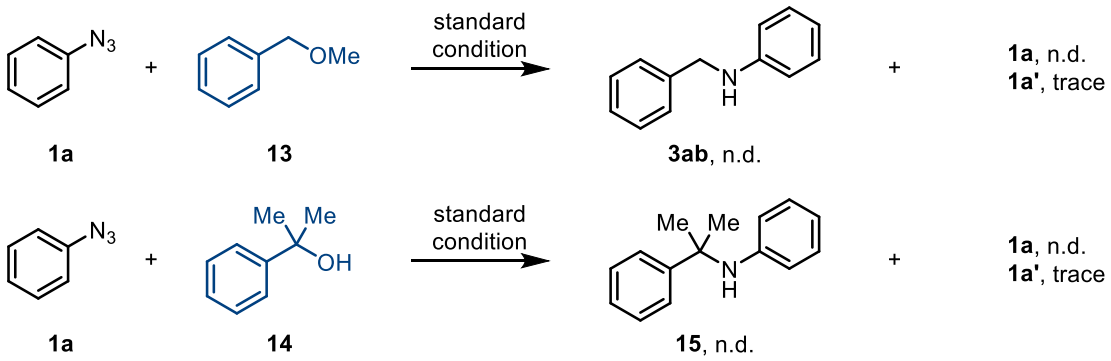
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 3H), 7.09 (d, *J* = 7.3 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 3.82 (s, 1H), 3.16 (d, *J* = 6.9 Hz, 2H), 1.88-1.84 (m, 1H), 1.52-1.44 (m, 1H), 1.04-0.96 (m, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.4, 142.8, 129.4, 128.5, 125.9, 125.8, 117.6, 112.9, 48.5, 23.0, 22.3, 14.9

IR (neat) υ 3411, 3023, 2920, 1602, 1505, 1320, 1253, 1179, 1030, 870, 749, 694 cm^{-1}

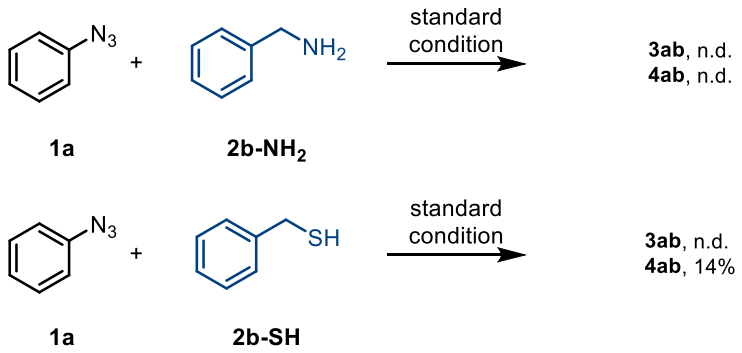
HRMS (ESI) *m/z* calcd for $C_{16}H_{18}N^+$ [M+H$^+$] 224.1434, found 224.1430

Scheme S7. Elucidation of important hydrogens of alcohols by using methyl-masked benzyl alcohols



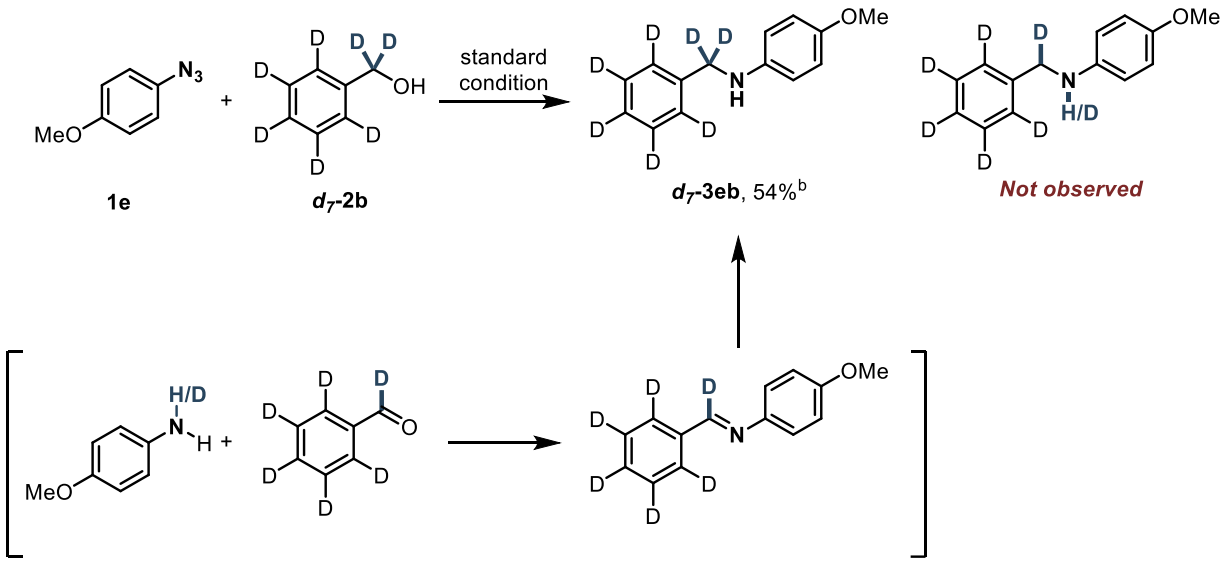
Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) and corresponding compound **13** or **14** (0.4 mmol, 4.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 °C (dry block heater temperature, 1000 rpm). After stirring for 24 hours, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. Dibromomethane was added to the mixture as an internal standard and the mixture was diluted with $CDCl_3$. The mixture was analyzed using ^{1}H-NMR analysis.

Scheme S8. Comparison of amines and thiols as hydrogen donors as possible hydrogen donors



Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) and corresponding compound **2b-NH₂** or **2b-SH** (0.4 mmol, 4.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 °C (dry block heater temperature, 1000 rpm). After stirring for 24 hours, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. Dibromomethane was added to the mixture as an internal standard and the mixture was diluted with $CDCl_3$. The mixture was analyzed using ^{1}H-NMR analysis.

Scheme S9. Use of deuterated benzyl alcohol to probe hydrogen transfer



Potassium tert-butoxide (0.2 mmol, 22.4 mg, 2.0 eq.) was added to an oven-dried Borosilicate Glass Tube and capped with rubber septum. The tube evacuated using vacuum pump and charged with argon balloon 3 times. Anhydrous toluene (0.5 mL), deuterated benzyl alcohol ***d*$_7$-2b** (0.4 mmol, 0.041 mL, 4.0 eq.) and 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.) was added sequentially to the tube. Rubber septum was removed and the tube was capped immediately with a screw cap. The reaction vessel was heated using dry block heater and the mixture was stirred at 150 °C (dry block heater temperature, 1000 rpm). After stirring for 24 hours, the reaction mixture was cooled to room temperature. The mixture was passed through celite pad and washed with dichloromethane. The filtrate was concentrated using rotatory evaporator. After purification by flash column chromatography on silica gel (n-hexane : EtOAc = 30 : 1), ***d*$_7$-3eb** was obtained as colorless oil (12.0 mg, 54%). The product and retention of the deuterium was confirmed by mass spectroscopy and ^{1}H-NMR analysis.

^{1}H-NMR (400 MHz, DMSO-*d*$_6$) δ 6.67 (td, *J* = 6.4, 4.0 Hz, 2H), 6.52 (td, *J* = 6.4, 4.0 Hz, 2H), 5.78 (s, 1H), 3.60 (s, 3H)

HRMS (ESI) *m/z* calcd for $C_{14}H_9D_7NO^+$ [M+H$^+$] 221.1666, found 221.1669

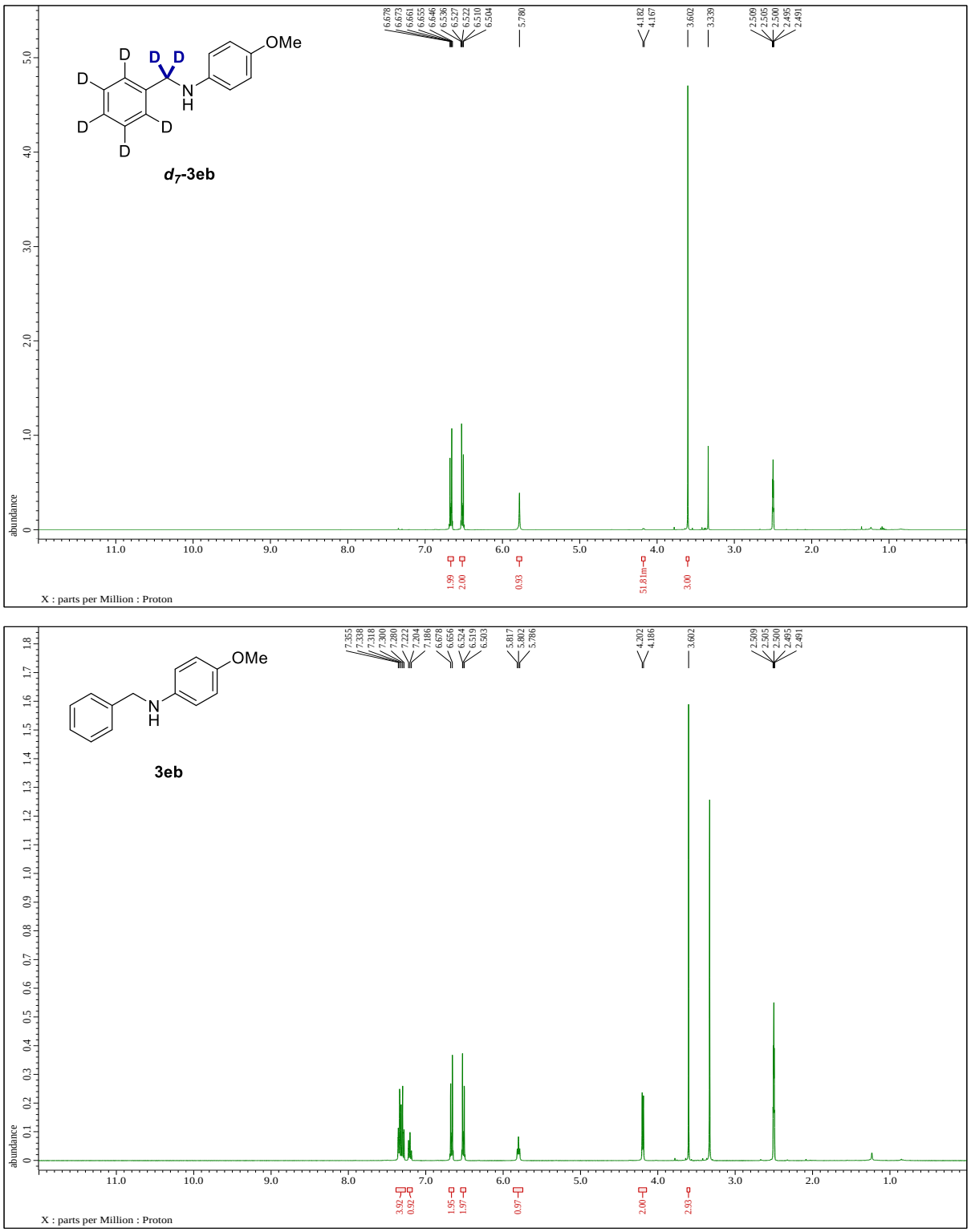
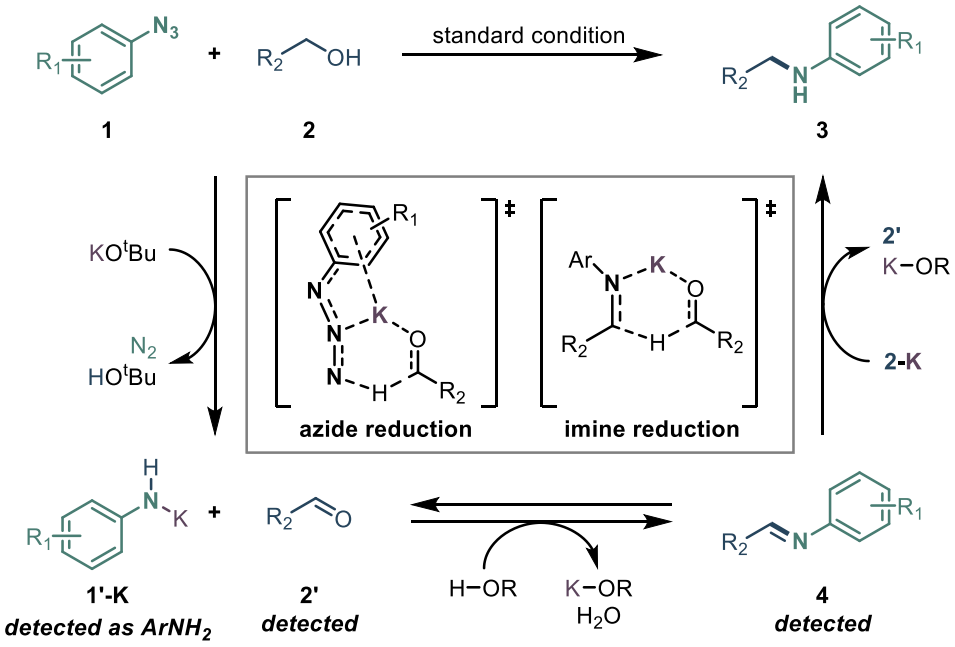


Figure S5. ^{1}H-NMR spectrum of isolated ***d*$_7$-3eb** (400 MHz, DMSO-*d*$_6$, up) and **3eb** (400 MHz, DMSO-*d*$_6$, down)

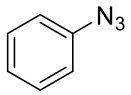
6. Proposed mechanism

Scheme S10. Plausible mechanism of the reaction

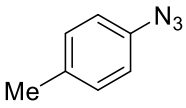


7. Synthesis of starting materials

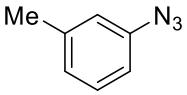
List of substrates



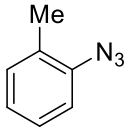
1a



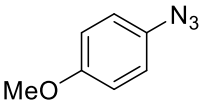
1b



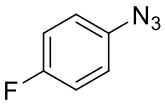
1c



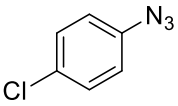
1d



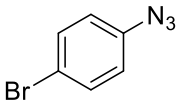
1e



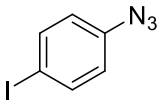
1f



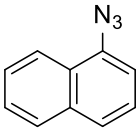
1g



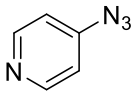
1h



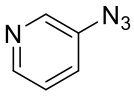
1i



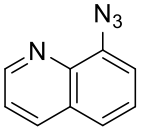
1j



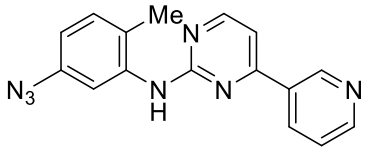
1k



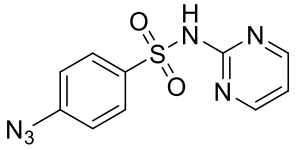
1l



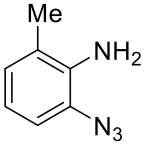
1m



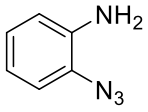
1n



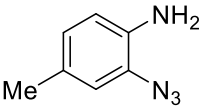
1o



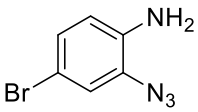
5a



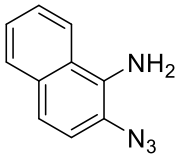
5b



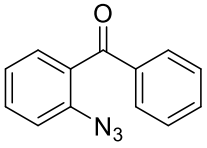
5c



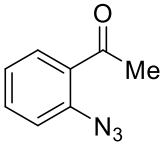
5d



5e



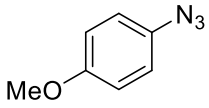
8a



8b

1a, 1b, 1c, 1d, 1f, 1g, 1h are purchased via Sigma-Aldrich. Other substrates were synthesized following the known method or modified method in literature.

7-1. Synthesis of azidobenzenes and (2-azidophenyl)ketones



1e

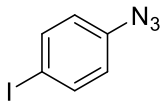
1-azido-4-methoxybenzene (1e)

: Following the general procedure A, p-anisidine (1.23 g, 10.0 mmol, 1.0 eq.), 2 M HCl solution (30.0 mL) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **1e** was obtained as orange oil (1.24 g, 83% yield). The NMR spectral data of **1e** are same as the previous report.[1]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.96 (td, *J* = 6.1, 3.4 Hz, 2H), 6.89 (td, *J* = 6.1, 3.4 Hz, 2H), 3.79 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.0, 132.3, 120.0, 115.1, 55.5

IR (neat) υ 2955, 2835, 2104, 1585, 1505, 1464, 1285, 1245, 1181, 1108, 1305, 825, 625 cm^{-1}



1i

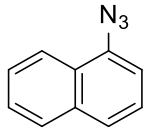
1-azido-4-iodobenzene (1i)

: Following the general procedure A, 4-iodoaniline (1.10 g, 5.0 mmol, 1.0 eq.), 2 M HCl solution (15.0 mL) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **1i** was obtained as yellow oil (1.20 g, 98% yield). The NMR spectral data of **1i** are same as the previous report.[2]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 9.5, 2.5 Hz, 2H), 6.79 (dt, *J* = 9.5, 2.5 Hz, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.1, 138.8, 121.2, 88.4

IR (neat) υ 2413, 2127, 2089, 1573, 1479, 1292, 1267, 1129, 1005, 818 cm^{-1}



1j

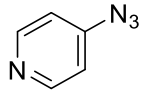
1-azidonaphthalene (1j)

: Following the general procedure A, 1-naphthylamine (715.9 mg, 5.0 mmol, 1.0 eq.), 2 M HCl solution (15.0 mL) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **1j** was obtained as red brown oil (747.0 mg, 88% yield). The NMR spectral data of **1j** are same as the previous report.[1]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13-8.09 (m, 1H), 7.83 (td, *J* = 6.4, 3.7 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.56-7.44 (3H), 7.27 (dd, *J* = 7.1, 1.1 Hz, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.6, 134.5, 127.9, 127.0, 126.5, 126.3, 125.8, 124.8, 122.7, 114.0

IR (neat) υ 3309, 2290, 2102, 1592, 1574, 1506, 1461, 1288, 1163, 1077, 1004, 791, 768, 655 cm^{-1}



1k

4-azidopyridine (1k)

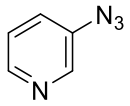
: Round bottom flask was charged with 4-chloropyridine hydrochloride (750.0 mg, 5.0 mmol, 1.0 eq.) and NaOH solution (5.0 mmol NaOH in 5.0 mL H_2O) to maintain pH of the mixture around 6. Methanol (10.0 mL) was poured into the mixture to dissolve all starting materials. Sodium azide (650.1 mg, 10.0 mmol, 2.0 eq.) was dissolved in H_2O (10.0 mL) and transferred to the reaction flask and refluxed overnight using oil bath. Conversion was monitored using TLC. After completion of the reaction, methanol was removed using rotatory evaporator and the aqueous layer was washed with ether 3 times. The organic phase was concentrated to afford the title compound **1k** (541.5 mg, 90%) as dark purple oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 6.4 Hz, 2H), 6.93 (d, *J* = 5.9 Hz, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 151.3, 148.8, 114.2

HRMS (ESI) m/z calcd for $C_5H_5N_4^+$ $[M+H]^+$ 121.0509, found 121.0510

IR (neat) υ 3272, 2138, 2113, 1582, 1565, 1494, 1415, 1300, 1214, 814, 671 cm^{-1}



1k

3-azidopyridine (1l)

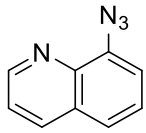
: Following the general procedure A, 3-aminopyridine (470.6 mg, 5.0 mmol, 1.0 eq.), 2 M HCl solution (15.0 mL) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 10 : 1), **1l** was obtained as yellow oil (595.8 mg, 99% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.39-8.36 (m, 2H), 7.35 (dq, *J* = 8.3, 1.4 Hz, 1H), 7.28 (dd, *J* = 8.3, 5.1 Hz, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.2, 141.5, 137.2, 126.0, 124.2

HRMS (ESI) m/z calcd for $C_5H_5N_4^+$ $[M+H]^+$ 121.0509, found 121.0510

IR (neat) υ 2428, 2135, 1572, 1475, 1422, 1305, 1238, 1140, 1020, 801, 702, 687, 817 cm^{-1}



1m

8-azidoquinoline (1m)

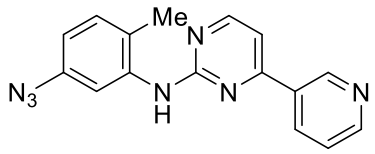
: Following the general procedure A, 8-aminoquinoline (188.2 mg, 2.0 mmol, 1.0 eq.), 2 M HCl solution (6.0 mL) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **1m** was obtained as yellow oil (309.7 mg, 91% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.92 (q, *J* = 2.0 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.59 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.52-7.44 (m, 2H), 7.40 (dd, *J* = 7.8, 1.4 Hz, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.7, 141.5, 137.3, 136.4, 129.5, 126.7, 124.3, 122.1, 118.3

HRMS (ESI) m/z calcd for $C_9H_7N_4^+$ $[M+H]^+$ 171.0665, found 171.0664

IR (neat) υ 2116, 1595, 1566, 1503, 1468, 1326, 823, 786, 758, 714 cm^{-1}



1n

N-(5-azido-2-methylphenyl)-4-(pyridin-3-yl)pyrimidin-2-amine (1n)

: Following the general procedure A, 6-methyl-N^1-(4-(pyridin-3-yl)pyrimidin-2-yl)benzene-1,3-diamine (277.3 mg, 2.0 mmol, 1.0 eq.), 2 M HCl solution (6.0 mL) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 1 : 1), **1n** was obtained as pale yellow solid (465.9 mg, 77% yield).

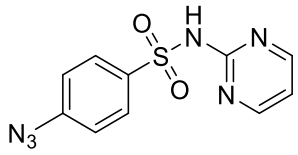
^{1}H-NMR (400 MHz, DMSO-*d*$_6$) δ 9.27 (d, *J* = 2.3 Hz, 1H), 8.98 (s, 1H), 8.71 (d, *J* = 5.0 Hz, 1H), 8.56 (d, *J* = 5.9 Hz, 1H), 8.43 (d, *J* = 8.2 Hz, 1H), 7.55 (dd, *J* = 7.5, 5.3 Hz, 2H), 7.50 (d, *J* = 4.6 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 6.82 (dd, *J* = 8.0, 2.1 Hz, 1H), 2.26 (s, 3H)

^{13}C-NMR (100 MHz, DMSO-*d*$_6$) δ 161.5, 160.6, 159.5, 151.5, 148.1, 139.2, 136.8, 134.2, 132.1, 131.5, 128.0, 123.8, 114.4, 114.0, 108.2, 17.6

HRMS (ESI) m/z calcd for $C_{16}H_{14}N_7^+$ $[M+H]^+$ 304.1305, found 304.1303

IR (neat) υ 3034, 2112, 1576, 1526, 1447, 1415, 1307, 1001, 798 cm^{-1}

m.p. 114-116 ℃



1o

4-azido-N-(pyrimidin-2-yl)benzenesulfonamide (1o)

: Following the general procedure A, sulfadiazine (750.8 mg, 3.0 mmol, 1.0 eq.), 2 M HCl solution (15.0 mL) were used as starting material. The product was purified by filtration and washed with H_2O and EA several times, affording **1o** as white solid (613.0 mg, 98% yield).

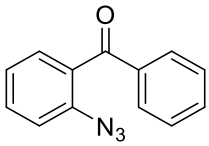
^{1}H-NMR (400 MHz, DMSO-*d*$_6$) δ 11.85 (s, 1H), 8.50 (d, *J* = 5.1 Hz, 2H), 7.98 (dt, *J* = 9.3, 2.3 Hz, 2H), 7.29 (dt, *J* = 9.2, 2.4 Hz, 2H), 7.05 (t, *J* = 5.1 Hz, 1H)

^{13}C-NMR (100 MHz, DMSO-*d*$_6$) δ 158.4, 156.8, 144.1, 136.5, 129.6, 119.4, 115.8

HRMS (ESI) m/z calcd for $C_{10}H_9N_6O_2S^+$ $[M+H]^+$ 277.0502, found 277.0509

IR (neat) υ 2138, 1582, 1492, 1442, 1414, 1306, 1306, 1291, 1165, 1090, 949, 797, 714, 616 cm^{-1}

m.p. 234-236 ℃



8a

(2-azidophenyl)(phenyl)methanone (8a)

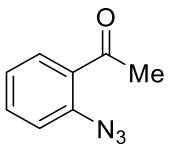
: Following the general procedure A, 2-aminobenzophenone (1.97 g, 10.0 mmol, 1.0 eq.), 2 M HCl solution (30.0 mL) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **8a** was obtained as yellow oil (1.99 g, 89% yield).

^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.80 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.62-7.57 (m, 1H), 7.54 (td, *J* = 7.8, 1.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.23 (dd, *J* = 7.8, 0.9 Hz, 1H)

^{13}C-NMR (100 MHz, CDCl$_3$) δ 195.6, 138.3, 137.2, 133.6, 131.8, 131.4, 130.2, 129.9, 128.7, 124.8, 119.0,

HRMS (ESI) m/z calcd for $C_{13}H_{10}NO^+$ $[M-N_2+H]^+$ 196.0757, found 196.0761

IR (neat) υ 3061, 2429, 2129, 1667, 1595, 1578, 1483, 1448, 927, 759, 702 cm^{-1}



8b

1-(2-azidophenyl)ethan-1-one (8b)

: Following the general procedure A, 2-aminoacetophenone (405.5 mg, 3.0 mmol, 1.0 eq.), 2 M HCl solution (9.0 mL) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **8b** was obtained as yellow oil (391.1 mg, 81%).

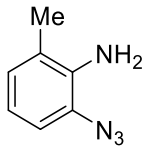
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.72-7.68 (m, 1H), 7.54-7.48 (m, 1H), 7.24-7.16 (m, 2H), 2.63 (d, *J* = 6.4 Hz, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.3, 138.8, 133.2, 131.1, 130.5, 124.9, 119.3, 31.3

HRMS (ESI) m/z calcd for $C_8H_8NO^+$ $[M-N_2+H]^+$ 134.0600, found 134.0598

IR (neat) υ 3000, 2124, 1681, 1593, 1480, 1444, 1358, 1279, 1242, 758 cm^{-1}

7-2. Synthesis of 2-azidoanilines



5a

2-azido-6-methylaniline (5a)

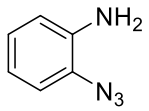
: Following the general procedure B, o-toluidine (0.106 mL, 1.0 mmol, 1.0 equiv.) was used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **5a** was obtained as brown oil (61.9 mg, 42% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.4 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 3.76 (s, 2H), 2.16 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.4, 126.8, 124.9, 123.5, 118.4, 116.0, 17.4

HRMS (ESI) m/z calcd for $C_7H_9N_2^+$ $[M-N_2+H]^+$ 121.0760, found 121.0756

IR (neat) υ 3427, 3321, 2109, 1623, 1479, 1299, 1258, 1091, 761, 727 cm^{-1}



5b

2-azidoaniline (5b)

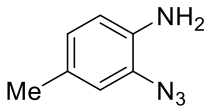
: Following the general procedure B, aniline (0.091 mL, 1.0 mmol, 1.0 equiv.) was used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **5b** was obtained as yellow oil (73.8 mg, 55% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.96 (td, *J* = 7.5, 1.4 Hz, 1H), 6.80 (td, *J* = 7.5, 1.2 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 3.70 (s, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.1, 125.7, 125.3, 119.2, 118.5, 116.0

HRMS (ESI) m/z calcd for $C_6H_7N_2^+$ $[M-N_2+H]^+$ 107.0604, found 107.0602

IR (neat) υ 3428, 3321, 2110, 1624, 1479, 1300, 1274, 1092, 761, 728 cm^{-1}



5c

2-azido-4-methylaniline (5c)

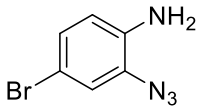
: Following the general procedure B, p-toluidine (107.2 mg, 1.0 mmol, 1.0 equiv.) was used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **5c** was obtained as yellow oil (69.6 mg, 47% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 3.59 (s, 2H), 2.28 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 135.6, 128.9, 126.3, 125.1, 118.9, 116.1, 20.6

HRMS (ESI) m/z calcd for $C_7H_9N_2^+$ $[M-N_2+H]^+$ 121.0760, found 121.0764

IR (neat) υ 3370, 2109, 1623, 1517, 1304, 1262, 809 cm^{-1}



5d

2-azido-4-bromoaniline (5d)

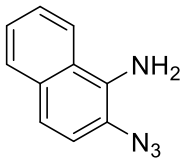
: Following the general procedure B, 4-bromoaniline (172.0 mg, 1.0 mmol, 1.0 equiv.) was used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **5d** was obtained as yellow oil (112.4 mg, 53% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 1.8 Hz, 1H), 7.05 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 1H), 3.97 (s, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) 137.2, 128.5, 126.7, 121.2, 117.1, 110.0

HRMS (ESI) m/z calcd for $C_6H_6BrN_2^+$ $[M-N_2+H]^+$ 186.9689, found 186.9686

IR (neat) υ 3431, 3321, 2115, 1620, 1488, 1410, 1276, 1257, 870, 848, 805 cm^{-1}



5e

2-azidonaphthalen-1-amine (5e)

: Following the general procedure B, 1-naphthylamine (143.2 mg, 1.0 mmol, 1.0 equiv.) was used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **5e** was obtained as yellow oil (73.7 mg, 40% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.77 (q, *J* = 8.2 Hz, 2H), 7.50-7.42 (m, 2H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.25 (d, *J* = 8.7 Hz, 1H), 4.30 (s, 2H)

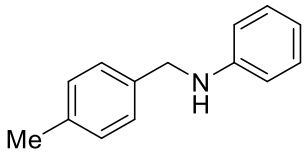
^{13}C-NMR (100 MHz, $CDCl_3$) δ 132.4, 131.7, 128.8, 125.9, 125.4, 123.9, 120.9, 119.6, 119.1, 117.1

HRMS (ESI) m/z calcd for $C_{10}H_9N_2^+$ $[M-N_2+H]^+$ 157.0760, found 157.0759

IR (neat) υ 3348, 2923, 2113, 1745, 1613, 1509, 1407, 1301, 789, 668 cm^{-1}

8. Transition-metal free transfer hydrogenation of aryl azides and alcohols

8-1. Synthesis of secondary amines



3aa

N-(4-methylbenzyl)aniline (3aa)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3aa** was obtained as pale yellow solid (19.6 mg, 99% yield).

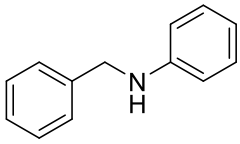
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 7.21-7.16 (m, 4H), 6.74-6.70 (m, 1H), 6.65 (dd, *J* = 8.7, 0.9 Hz, 2H), 4.30 (s, 2H), 3.99 (s, 1H), 2.36 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$ δ 148.4, 137.0, 136.5, 129.4, 129.4, 127.7, 117.6, 113.0, 48.2, 21.2

IR (neat) υ 3418, 3019, 2921, 1603, 1506, 1429, 1325, 1251, 1179, 1095, 806, 748, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{16}N^+$ $[M+H]^+$ 198.1277, found 198.1273

m.p. 39-41 ℃



3ab

N-benzylaniline (3ab)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), benzyl alcohol **2b** (0.4 mmol, 0.041 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3ab** was obtained as white solid (14.0 mg, 76% yield).

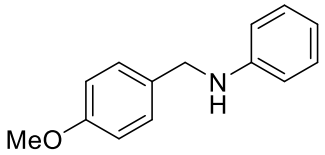
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 4H), 7.32-7.28 (m, 1H), 7.23-7.18 (m, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.67-6.65 (m, 2H), 4.35 (s, 2H), 4.05 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.3, 139.6, 129.4, 128.8, 127.6, 127.4, 117.7, 113.0, 48.5

IR (neat) υ 3820, 3648, 3613, 1748, 1704, 1647, 1601, 1508, 1489, 1338, 783, 692 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{13}H_{14}N^+$ $[M+H]^+$ 184.1121, found 184.1127

m.p. 36-38 ℃



3ac

N-(4-methoxybenzyl)aniline (3ac)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methoxybenzyl alcohol **2c** (0.4 mmol, 0.050 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **3ac** was obtained as white solid (22.1 mg, 86% yield).

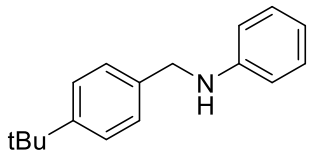
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2H), 7.18 (dd, *J* = 8.5, 7.6 Hz, 2H), 6.88 (dt, *J* = 9.2, 2.4 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.65-6.63 (m, 2H), 4.25 (s, 2H), 3.95 (s, 1H), 3.80 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.0, 148.3, 131.5, 129.4, 128.9, 117.6, 114.1, 113.0, 55.4, 47.9

IR (neat) υ 3820, 3756, 3648, 3613, 1747, 1705, 1647, 1564, 1508, 1488, 1363, 1216, 783 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO^+$ $[M+H]^+$ 214.1226, found 214.1229

m.p. 44-46 ℃



3ad

N-(4-(tert-butyl)benzyl)aniline (3ad)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-tert-butylbenzyl alcohol **2d** (0.4 mmol, 0.071 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3ad** was obtained as white solid (23.5 mg, 98% yield).

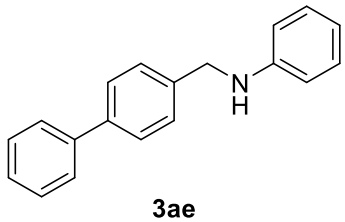
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 4H), 7.24-7.19 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.68 (dd, *J* = 8.7, 0.9 Hz, 2H), 4.32 (s, 2H), 4.01 (s, 1H), 1.36 (s, 9H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.3, 148.4, 136.5, 129.4, 127.5, 125.7, 117.6, 112.9, 48.1, 34.6, 31.5

IR (neat) υ 3820, 3756, 3648, 2962, 1748, 1670, 1647, 1603, 1507, 1429, 1363, 1324, 1267, 823, 747, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{17}H_{22}N^+$ $[M+H]^+$ 240.1747, found 240.1740

m.p. 70-72 ℃



3ae

N-[1,1'-biphenyl]4-ylmethyl)aniline (3ae)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-biphenylmethanol **2e** (0.4 mmol, 73.7 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3ae** was obtained as white solid (24.5 mg, 94% yield).

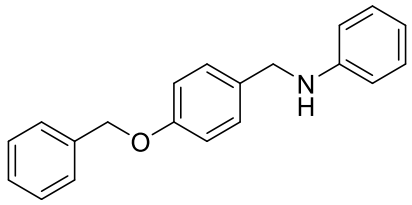
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64-7.60 (m, 4H), 7.49-7.45 (m, 4H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 8.7, 7.3 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 2H), 4.40 (s, 2H), 4.10 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.2, 140.9, 140.3, 138.6, 129.4, 128.9, 128.0, 127.5, 127.4, 127.2, 117.7, 113.0, 48.1

IR (neat) υ 3859, 3048, 2825, 2309, 1748, 1601, 1500, 1486, 1428, 1305, 1248, 1180, 872, 826, 758, 747, 689 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{19}H_{18}N^+$ $[M+H]^+$ 260.1434, found 260.1427

m.p. 83-85 ℃



3af

N-(4-(benzyloxy)benzyl)aniline (3af)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-(benzyloxy)benzyl alcohol **2f** (0.4 mmol, 85.7 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **3af** was obtained as white solid (28.5 mg, 98% yield).

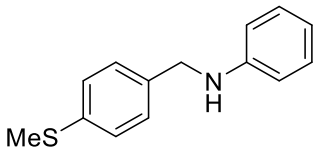
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47-7.39 (m, 4H), 7.37-7.34 (m, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.23-7.18 (m, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 2H), 5.08 (s, 2H), 4.27 (s, 2H), 3.97 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.2, 148.3, 137.1, 131.8, 129.4, 128.9, 128.7, 128.1, 127.6, 117.6, 115.1, 112.9, 70.1, 47.9

IR (neat) υ 3859, 3756, 2348, 2309, 1748, 1602, 1508, 1453, 1318, 1240, 1174, 1013, 823, 737, 693 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NNaO^+$ $[M+H]^+$ 312.1359, found 312.1351

m.p. 67-69 ℃



3ag

N-(4-(methylthio)benzyl)aniline (3ag)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-(methylthio)benzyl alcohol **2g** (0.4 mmol, 61.7 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3ag** was obtained as white solid (22.2 mg, 97% yield).

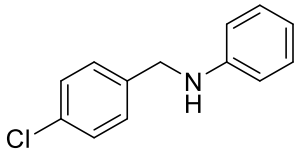
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.19 (dd, *J* = 8.7, 7.3 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.3 Hz, 2H), 4.30 (s, 2H), 4.03 (s, 1H), 2.49 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.1, 137.3, 136.5, 129.4, 128.1, 127.1, 117.7, 113.0, 48.0, 16.1

IR (neat) υ 3859, 3819, 3647, 2348, 2309, 1748, 1715, 1602, 1508, 1489, 1429, 1363, 1216, 808, 688, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NS^+$ $[M+H]^+$ 230.0998, found 230.1000

m.p. 37-39 ℃



3ah

N-(4-chlorobenzyl)aniline (3ah)

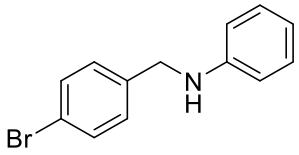
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-chlorobenzyl alcohol **2h** (0.4 mmol, 57.0 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3ah** was obtained as yellow oil (20.5 mg, 94% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 15.1 Hz, 4H), 7.18 (dd, *J* = 8.5, 7.5 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.3 Hz, 2H), 4.32 (s, 2H), 4.07 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.0, 138.1, 133.0, 129.4, 128.9, 128.8, 117.9, 113.0, 47.7

IR (neat) υ 3872, 3756, 3648, 3418, 3049, 2922, 17474, 1603, 1507, 1489, 1429, 1324, 1269, 1179, 1091, 1014, 813, 750, 692 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{13}H_{13}ClN^+$ $[M+H]^+$ 218.0731, found 218.0725



3ai

N-(4-bromobenzyl)aniline (3ai)

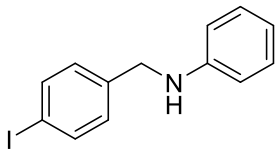
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-bromobenzyl alcohol **2i** (0.4 mmol, 74.8 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3ai** was obtained as yellow oil (19.0 mg, 72% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 2H), 4.30 (s, 2H), 4.07 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.9, 138.7, 131.8, 129.4, 129.2, 121.1, 118.0, 113.0, 47.8

IR (neat) υ 3872, 3756, 3648, 1747, 1602, 1507, 1487, 1429, 1322, 1070, 1010, 810, 749, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{13}H_{13}BrN^+$ $[M+H]^+$ 262.0226, found 262.0221



3aj

N-(4-iodobenzyl)aniline (3aj)

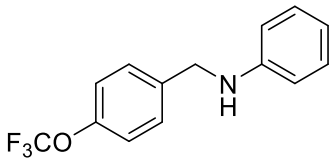
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-iodobenzyl alcohol **2j** (0.4 mmol, 93.6 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3aj** was obtained as colorless oil (8.2 mg, 27% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.19-7.15 (m, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 4.29 (s, 2H), 4.08 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ δ 147.9, 139.4, 137.8, 129.5, 129.4, 118.0, 113.0, 92.5, 47.9

IR (neat) υ 3858, 3756, 3647, 2922, 2852, 1747, 1602, 1506, 1482, 1429, 1400, 1322, 1268, 1179, 1005, 807, 748, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{13}H_{13I}N^+$ $[M+H]^+$ 310.0087, found 310.0082



3ak

N-(4-(trifluoromethoxy)benzyl)aniline (3ak)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-(trifluoromethoxy)benzyl alcohol **2k** (0.4 mmol, 0.058 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **3ak** was obtained as yellow oil (10.1 mg, 40% yield).

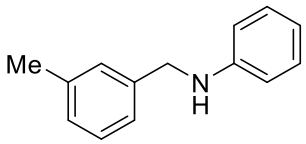
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 4H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.3 Hz, 2H), 4.35 (s, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.5, 147.4, 138.0, 129.5, 128.9, 121.9, 121.3, 118.4, 113.4, 48.0

^{19}F-NMR (375 MHz, $CDCl_3$) δ -57.8

IR (neat) υ 3859, 3756, 1646, 2348, 2309, 1748, 1602, 1508, 1374, 1227, 806, 686, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{13}F_3NO^+$ $[M+H]^+$ 268.0944, found 268.0940



3al

N-(3-methylbenzyl)aniline (3al)

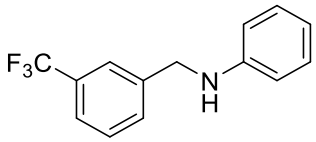
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 3-methylbenzyl alcohol **2l** (0.4 mmol, 0.048 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3al** was obtained as yellow oil (19.2 mg, 97% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28-7.18 (m, 5H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.68-6.65 (m, 2H), 4.31 (s, 2H), 4.01 (s, 1H), 2.38 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.4, 139.5, 138.4, 129.4, 128.7, 128.4, 128.1, 124.7, 117.6, 113.0, 48.5, 21.6

IR (neat) υ 3820, 3756, 3739, 1648, 3613, 2922, 1747, 1705, 1647, 1602, 1541, 1508, 1488, 1374, 1216, 781, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{16}N^+$ $[M+H]^+$ 198.1277, found 198.1280



3am

N-(3-(trifluoromethyl)benzyl)aniline (3am)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 3-(trifluoromethyl)benzyl alcohol **2m** (0.4 mmol, 0.054 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3am** was obtained as yellow oil (25.5 mg, 95% yield).

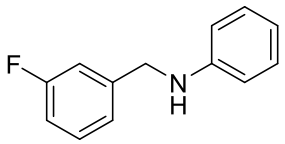
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.56 (q, *J* = 7.3 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.20 (dd, *J* = 8.5, 7.5 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 4.41 (s, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.6, 140.6, 131.1 (q, J_{C-F} = 32.0 Hz), 130.8, 129.5, 129.2, 124.3 (q, J_{C-F} = 271.5 Hz), 124.3, 118.3, 113.2, 48.2

^{19}F-NMR (375 MHz, $CDCl_3$) δ -62.4

IR (neat) υ 3859, 3756, 3647, 2348, 2309, 1748, 1603, 1508, 1328, 1164, 1123, 1072, 800, 750, 692, 670 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{13}F_3N^+$ $[M+H]^+$ 252.0995, found 252.0991



3an

N-(3-fluorobenzyl)aniline (3an)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 3-fluorobenzyl alcohol **2n** (0.4 mmol, 0.043 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3an** was obtained as brown oil (11.4 mg, 57% yield).

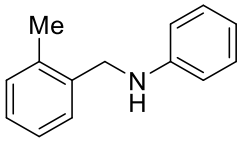
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 8.0, 5.9 Hz, 1H), 7.18 (q, *J* = 7.9 Hz, 3H), 7.10 (d, *J* = 9.6 Hz, 1H), 6.96 (td, *J* = 8.5, 2.4 Hz, 1H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.63 (dd, *J* = 8.7, 0.9 Hz, 2H), 4.35 (s, 2H), 4.12 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.2 (d, $J_{C\text{-}F}$ = 244.3 Hz), 147.9, 142.4 (d, $J_{C\text{-}F}$ = 6.7 Hz), 130.2 (d, $J_{C\text{-}F}$ = 7.7 Hz), 129.4, 122.9, 122.9, 117.9, 114.3 (d, $J_{C\text{-}F}$ = 9.6 Hz), 114.1 (d, $J_{C\text{-}F}$ = 9.6 Hz), 113.0, 47.9

^{19}F-NMR (375 MHz, $CDCl_3$) δ -112.9

IR (neat) υ 3419, 3052, 2923, 2309, 1747, 1603, 1507, 1487, 1449, 1324, 1266, 1136, 939, 915, 869, 781, 750, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{13}H_{13}FN^+$ $[M+H]^+$ 202.1027, found 202.1030



3ao

N-(2-methylbenzyl)aniline (3ao)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 2-methylbenzyl alcohol **2o** (0.4 mmol, 48.7 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3ao** was obtained as pale brown solid (17.6 mg, 89% yield).

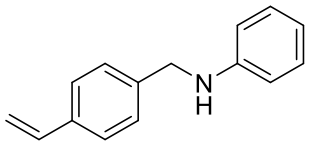
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.9 Hz, 1H), 7.23-7.17 (m, 5H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67-6.65 (m, 2H), 4.29 (s, 2H), 3.85 (s, 1H), 2.39 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.4, 137.1, 136.5, 130.5, 129.4, 128.4, 127.6, 126.3, 117.6, 112.8, 46.5, 19.1

IR (neat) υ 6417, 3049, 3019, 2923, 2854, 1746, 1601, 1505, 1428, 1321, 1251, 1179, 1090, 991, 868, 746, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{16}N^+$ $[M+H]^+$ 198.1277, found 198.1274

m.p. 37-39 ℃



3ap

N-(4-vinylbenzyl)aniline (3ap)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-vinylbenzyl alcohol **2p** (0.4 mmol, 53.7 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3ap** was obtained as pale yellow solid (11.6 mg, 55% yield).

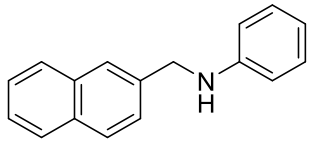
m.p. 39-41 ℃

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.17 (dd, *J* = 8.5, 7.5 Hz, 2H), 6.75-6.67 (m, 2H), 6.63 (d, *J* = 7.8 Hz, 2H), 5.74 (d, *J* = 17.4 Hz, 1H), 5.23 (d, *J* = 11.4 Hz, 1H), 4.32 (s, 2H), 4.06 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.2, 139.2, 136.7, 136.6, 129.4, 127.8, 126.6, 117.7, 113.9, 113.0, 48.2

IR (neat) υ 3647, 2348, 2309, 1748, 1647, 1602, 1508, 1489, 1363, 1228, 831, 686, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{15}H_{16}N^+$ $[M+H]^+$ 210.1277, found 210.1273



3aq

N-(naphthalen-2-ylmethyl)aniline (3aq)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 2-naphthalenemethanol **2q** (0.4 mmol, 63.3 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3aq** was obtained as yellow solid (22.3 mg, 96% yield).

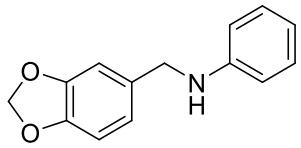
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 4H), 7.53-7.47 (m, 3H), 7.24-7.19 (m, 2H), 6.78-6.74 (m, 1H), 6.71 (dd, *J* = 8.7, 0.9 Hz, 2H), 4.51 (s, 2H), 4.16 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.3, 137.1, 133.6, 132.9, 129.4, 128.5, 127.9, 127.8, 126.3, 126.0, 125.9, 117.8, 113.1, 48.6

IR (neat) υ 3756, 3647, 2348, 2309, 1748, 1601, 1508, 1316, 1248, 815, 689, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{17}H_{16}N^+$ $[M+H]^+$ 234.1277, found 234.1274

m.p. 55-57 ℃



3ar

N-(benzo[d][1,3]dioxol-5-ylmethyl)aniline (3ar)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), piperonyl alcohol **2r** (0.4 mmol, 60.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3ar** was obtained as pale yellow solid (7.7 mg, 34% yield).

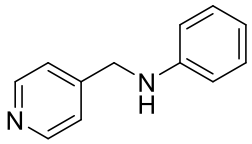
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.2, 7.3 Hz, 2H), 6.87 (s, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 5.95 (s, 2H), 4.24 (s, 2H), 3.99 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.2, 148.0, 146.9, 133.5, 129.4, 120.7, 117.8, 113.0, 108.4, 108.2, 101.1, 48.3

IR (neat) υ 3647, 2348, 2309, 1748, 1704, 1647, 1508, 1489, 1374, 1229, 806, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$ 228.1019, found 228.1013

m.p. 77-79 ℃



3as

N-(pyridine-4-ylmethyl)aniline (3as)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-pyridinemethanol **2s** (0.4 mmol, 43.7 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 4 : 1), **3as** was obtained as pale yellow solid (11.3 mg, 61% yield).

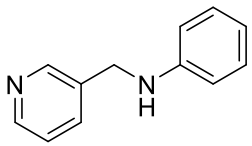
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.55 (q, *J* = 2.1 Hz, 2H), 7.29 (d, *J* = 6.0 Hz, 2H), 7.20-7.15 (m, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.58 (dt, *J* = 8.7, 1.6 Hz, 2H), 4.38 (s, 2H), 4.24 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.1, 149.1, 147.6, 129.5, 122.2, 118.2, 113.0, 47.2

IR (neat) υ 3647, 2348, 2309, 1748, 1704, 1647, 1601, 1508, 1216, 799, 670 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{12}H_{13}N_2^+$ $[M+H]^+$ 185.1073, found 185.1070

m.p. 97-99 ℃



3at

N-(pyridine-3-ylmethyl)aniline (3at)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 3-pyridinemethanol **2t** (0.4 mmol, 0.041 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 2 : 1), **3at** was obtained as white solid (11.5 mg, 62% yield).

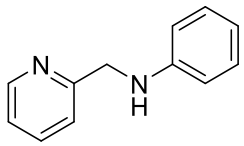
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.53 (d, *J* = 4.1 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.26 (dd, *J* = 7.8, 5.0 Hz, 1H), 7.18 (td, *J* = 7.0, 1.7 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.3 Hz, 2H), 4.37 (s, 2H), 4.08 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.3, 148.9, 147.7, 135.2, 135.0, 129.5, 123.7, 118.2, 113.1, 46.0

IR (neat) υ 3288, 3028, 2923, 1478, 1577, 1507, 1425, 1312, 1267, 1180, 1094, 1026, 989, 869, 799, 751, 712, 693 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{12}H_{13}N_2^+$ $[M+H]^+$ 185.1073, found 185.1078

m.p. 80-82 ℃



3au

N-(pyridine-2-ylmethyl)aniline (3au)

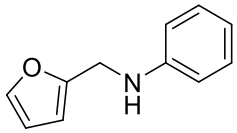
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 2-pyridinemethanol **2u** (0.4 mmol, 0.039 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 2 : 1), **3au** was obtained as white solid (10.1 mg, 55% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.1 Hz, 1H), 7.64 (td, *J* = 7.5, 1.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 8.7, 7.3 Hz, 3H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.69-6.67 (m, 2H), 4.79 (s, 1H), 4.47 (s, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.6, 149.3, 148.0, 136.7, 129.4, 122.2, 121.7, 117.7, 113.1, 49.4

IR (neat) υ 3295, 3049, 1603, 1507, 1428, 1323, 1269, 1180, 994, 869, 750, 693 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{12}H_{13}N_2^+$ $[M+H]^+$ 185.1073, found 185.1072



3av

N-(furan-2-ylmethyl)aniline (3av)

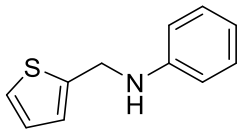
: Following the general procedure C at 160 ℃ for 48 hours, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), furfuryl alcohol **2v** (0.4 mmol, 0.035 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3av** was obtained as orange oil (10.9 mg, 63% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 1.0 Hz, 1H), 7.23-7.18 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.69 (dd, *J* = 8.7, 0.9 Hz, 2H), 6.34 (q, *J* = 1.7 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 4.33 (s, 2H), 4.03 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.9, 147.8, 142.0, 129.4, 118.1, 113.3, 110.5, 107.1, 41.6

IR (neat) υ 1647, 2348, 2309, 1748, 1704, 1603, 1507, 1319, 1216, 807, 731, 689 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{11}H_{12}NO$ $[M+H]^+$ 174.0913, found 174.0911



3aw

N-(thiophen-2-ylmethyl)aniline (3aw)

: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 2-thiophenemethanol **2w** (0.4 mmol, 0.038 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3aw** was obtained as white solid (15.0 mg, 79% yield).

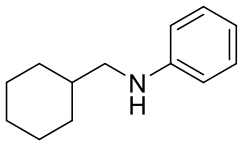
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24-7.20 (m, 3H), 7.04 (d, *J* = 2.7 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 2H), 4.53 (s, 2H), 4.07 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.7, 143.1, 129.4, 127.0, 125.2, 124.7, 118.2, 113.3, 43.6

IR (neat) υ 1647, 1348, 2309, 1748, 1704, 1647, 1602, 1507, 1429, 1312, 1251, 823, 689 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{11}H_{12}NS^+$ $[M+H]^+$ 190.0685, found 190.0681

m.p. 43-45 ℃



3ax

N-(cyclohexyllmethyl)aniline (3ax)

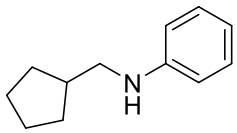
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), cyclohexanemethanol **2x** (0.4 mmol, 0.049 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-pentane : ether = 30 : 1), **3ax** was obtained as yellow oil (7.9 mg, 42% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.19-7.14 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.3 Hz, 2H), 3.72 (s, 1H), 2.96 (d, *J* = 6.9 Hz, 2H), 1.82 (d, *J* = 13.3 Hz, 2H), 1.77-1.67 (m, 3H), 1.64-1.53 (m, 1H), 1.32-1.16 (m, 3H), 0.99 (qd, *J* = 12.0, 2.9 Hz, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.8, 129.3, 117.0, 112.8, 50.7, 37.7, 31.5, 26.7, 26.1

IR (neat) υ 3419, 2922, 2850, 1602, 1507, 1448, 1322, 1259, 1179, 747, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{13}H_{20}N^+$ $[M+H]^+$ 190.1590, found 190.1587



3ay

N-(cyclopentyllmethyl)aniline (3ay)

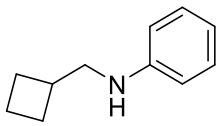
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), cyclopentanemethanol **2y** (0.4 mmol, 0.043 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-pentane : ether = 30 : 1), **3ay** was obtained as brown oil (9.5 mg, 54% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21-7.16 (m, 2H), 6.72-6.68 (m, 1H), 6.62 (dd, *J* = 8.7, 0.9 Hz, 2H), 3.69 (s, 1H), 3.04 (d, *J* = 7.3 Hz, 2H), 2.23-2.11 (m, 1H), 1.88-1.80 (m, 2H), 1.70-1.53 (m, 4H), 1.19-1.36 (m, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.7, 129.3, 117.2, 112.8, 49.6, 39.6, 30.8, 25.4

IR (neat) υ 3416, 3050, 3019, 2949, 2864, 2348, 2309, 1747, 1602, 1507, 1470, 1320, 1252, 1178, 747, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{12}H_{18}N^+$ $[M+H]^+$ 176.1434, found 176.1437



3az

N-(cyclobutyllmethyl)aniline (3az)

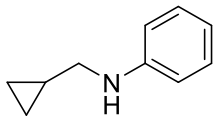
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), cyclobutanemethanol **2z** (0.4 mmol, 0.038 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-pentane : ether = 30 : 1), **3az** was obtained as brown oil (6.4 mg, 40% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.8 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 2H), 3.14 (d, *J* = 7.3 Hz, 2H), 2.66-2.55 (m, 1H), 2.18-2.09 (m, 2H), 2.02-1.87 (m, 2H), 1.80-1.71 (m, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.6, 129.3, 117.4, 113.0, 50.0, 35.1, 26.2, 18.7

IR (neat) υ 3647, 2348, 2309, 1748, 1715, 1647, 1602, 1508, 1363, 1216, 798, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{11}H_{16}N^+$ $[M+H]^+$ 162.1277, found 162.1274



3aaa

N-(cyclopropyllmethyl)aniline (3aaa)

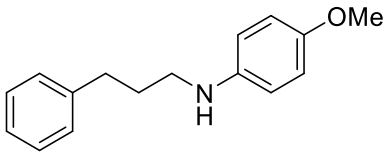
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), cyclopropylmethanol **2aa** (0.4 mmol, 0.032 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-pentane : ether = 30 : 1), **3aaa** was obtained as yellow oil (6.4 mg, 40% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21-7.16 (m, 2H), 6.71 (td, *J* = 7.3, 0.9 Hz, 1H), 6.64-6.61 (m, 2H), 3.79 (s, 1H), 2.96 (d, *J* = 7.3 Hz, 2H), 1.16-1.06 (m, 1H), 0.58-0.54 (m, 2H), 0.25 (td, *J* = 5.3, 4.3 Hz, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.6, 129.4, 117.4, 112.9, 49.2, 11.0, 3.6

IR (neat) υ 3410, 3004, 2924, 2924, 2853, 2348, 2309, 1748, 1604, 1507, 1471, 1430, 1318, 1253, 1179, 1018, 747, 691 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{10}H_{14}N^+$ $[M+H]^+$ 148.1121, found 148.1117



3aab

4-methoxy-N-(3-phenylpropyl)aniline (3eab)

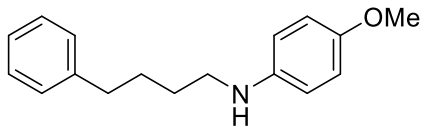
: Following the general procedure C at 160 ℃ for 48 hours, 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 3-phenyl-1-propanol **2ab** (0.8 mmol, 0.109 mL, 8.0 eq.) and KOH (0.4 mmol, 22.4 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **3eab** was obtained as brown oil (11.6 mg, 48% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.22-7.19 (m, 3H), 6.78 (td, *J* = 6.2, 4.0 Hz, 2H), 6.56 (td, *J* = 6.2, 3.7 Hz, 2H), 3.75 (s, 3H), 3.11 (t, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 1.98-1.91 (m, 2H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.2, 142.7, 141.9, 128.5, 126.1, 115.0, 114.2, 56.0, 44.6, 33.6, 31.3

IR (neat) υ 3025, 2926, 2854, 2348, 2309, 1512, 1454, 1236, 1179, 1037, 818, 700, 647 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{16}H_{20}NO^+$ $[M+H]^+$ 242.1539, found 242.1533



3aac

4-methoxy-N-(4-phenylbutyl)aniline (3eac)

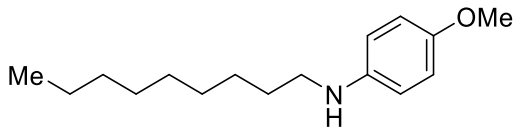
: Following the general procedure C at 160 ℃ for 48 hours, 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-phenyl-1-butanol **2ac** (0.8 mmol, 0.109 mL, 8.0 eq.) and KOH (0.4 mmol, 22.4 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **3eac** was obtained as brown oil (7.7 mg, 30% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.3 Hz, 2H), 7.21-7.18 (m, 3H), 6.79 (td, *J* = 6.3, 3.8 Hz, 2H), 6.58 (td, *J* = 6.4, 4.0 Hz, 2H), 3.75 (s, 3H), 3.09 (t, *J* = 6.9 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.79-1.62 (m, 4H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.1, 142.8, 142.4, 128.5, 128.5, 125.9, 115.0, 114.2, 56.0, 45.0, 35.8, 29.4, 29.1

IR (neat) υ 3734, 2931, 2856, 2359, 2348, 2309, 1748, 1647, 1512, 1234, 1036, 818, 699, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NO^+$ $[M+H]^+$ 256.1696, found 256.1701



3aad

4-methoxy-N-nonylaniline (3ead)

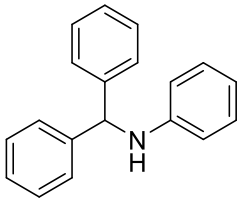
: Following the general procedure C at 170 ℃ for 48 hours, 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 1-nonanol **2ad** (0.8 mmol, 0.140 mL, 8.0 eq.) and KOH (0.4 mmol, 22.4 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **3ead** was obtained as yellow oil (11.0 mg, 44% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.79 (td, *J* = 6.2, 4.0 Hz, 2H), 6.59 (td, *J* = 6.2, 4.0 Hz, 2H), 3.75 (s, 3H), 3.06 (t, *J* = 7.1 Hz, 2H), 1.64-1.57 (m, 2H), 1.41-1.28 (m, 14H), 0.89 (t, *J* = 6.9 Hz, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.0, 143.0, 115.0, 114.1, 55.9, 45.1, 32.0, 29.8, 29.7, 29.6, 29.4, 22.8, 14.2

IR (neat) υ 3396, 2977, 2925, 2854, 1512, 1465, 1404, 1244, 1041, 817, 750 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{16}H_{28}NO^+$ $[M+H]^+$ 250.2165, found 250.2169



3aae

N-benzhydrylaniline (3aae)

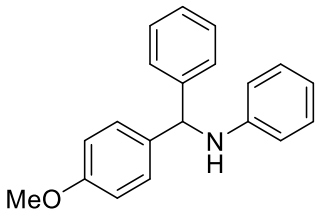
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), benzhydrol **2ae** (0.4 mmol, 73.7 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3aae** was obtained as pale yellow oil (25.8 mg, 99% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 8H), 7.32-7.28 (m, 2H), 7.16 (dd, *J* = 8.3, 7.4 Hz, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 2H), 5.55 (s, 1H), 4.28 (s, 1H)

^{13}C-NMR (100 MHz, $CDCl_3$) 13C-NMR (101 MHz, CHLOROFORM-D) δ 147.5, 143.0, 129.2, 128.9, 127.6, 127.5, 117.8, 113.6, 63.2

IR (neat) υ 3407, 3025, 2923, 2852, 2348, 2309, 1748, 1600, 1501, 1452, 1426, 1313, 1027, 746, 699 cm^{-1}

HRMS (FAB) *m/z* calcd for $C_{19}H_{17}N$ [M] 259.1361, found 259.1359



3aaf

N-((4-methoxyphenyl)(phenyl)methyl)aniline (3aaf)

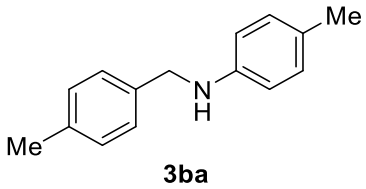
: Following the general procedure C, azidobenzene **1a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methoxybenzhydrol **2af** (0.4 mmol, 85.7 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **3aaf** was obtained as white oil (28.0 mg, 97% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 4H), 7.28 (d, *J* = 8.7 Hz, 3H), 7.14 (dd, *J* = 8.2, 7.3 Hz, 2H), 6.88 (dt, *J* = 9.3, 2.5 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.3 Hz, 2H), 5.48 (s, 1H), 4.22 (s, 1H), 3.80 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.9, 147.5, 143.3, 135.3, 129.2, 128.8, 128.7, 127.5, 127.4, 117.7, 114.2, 113.6, 62.5, 55.4

IR (neat) υ 3734, 2348, 2309, 1748, 1647, 1601, 1508, 1312, 1247, 1176, 1031, 689, 671, 648 cm^{-1}

HRMS (FAB) *m/z* calcd for $C_{20}H_{19}NO$ [M] 289.1467, found 289.1471



3ba

4-methyl-N-(4-methylbenzyl)aniline (3ba)

: Following the general procedure C, 4-azidotoluene **1b** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3ba** was obtained as white solid (20.7 mg, 98% yield).

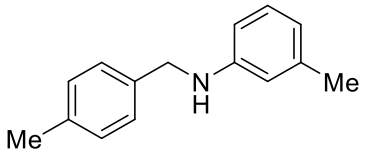
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 8.2 Hz, 2H), 4.27 (s, 2H), 3.86 (s, 1H), 2.36 (s, 3H), 2.25 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.1, 136.9, 136.7, 129.9, 129.4, 127.6, 126.8, 113.1, 48.5, 21.2, 20.5

IR (neat) υ 3756, 3734, 2379, 2359, 2348, 2309, 1748, 1647, 1541, 1516, 1489, 1374, 1216, 807, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{15}H_{18}N^+$ $[M+H]^+$ 212.1434, found 212.1437

m.p. 47-49 ℃



3ca

3-methyl-N-(4-methylbenzyl)aniline (3ca)

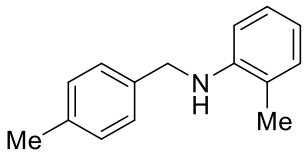
: Following the general procedure C, 3-azidotoluene **1c** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3ca** was obtained as colorless oil (19.6 mg, 93% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.49-6.45 (m, 2H), 4.28 (s, 2H), 3.92 (s, 1H), 2.36 (s, 3H), 2.29 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.4, 139.2, 137.0, 136.6, 129.4, 129.3, 127.7, 118.6, 113.7, 110.1, 48.3, 21.8, 21.2

IR (neat) υ 3734, 2379, 2359, 2348, 2309, 1748, 1704, 1679, 1647, 1541, 1509, 1489, 1374, 1216, 719, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{15}H_{18}N^+$ $[M+H]^+$ 212.1434, found 212.1431



3da

2-methyl-N-(4-methylbenzyl)aniline (3da)

: Following the general procedure C, 2-azidotoluene **1d** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 50 : 1), **3da** was obtained as white solid (20.1 mg, 93% yield).

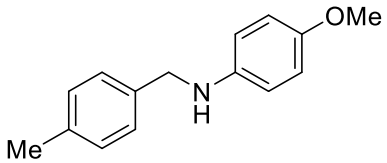
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (q, *J* = 7.9 Hz, 2H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.34 (s, 2H), 3.83 (s, 1H), 2.37 (s, 3H), 2.17 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.3, 137.0, 136.5, 130.2, 129.5, 127.7, 127.3, 122.0, 117.2, 110.0, 48.2, 21.3, 17.7

IR (neat) υ 2922, 2854, 2348, 2309, 1748, 1606, 1587, 1513, 1447, 1375, 1319, 1254, 1129, 800, 745, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{15}H_{18}N^+$ $[M+H]^+$ 212.1434, found 212.1431

m.p. 41-43 ℃



3ea

4-methoxy-N-(4-methylbenzyl)aniline (3ea)

: Following the general procedure C, 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **3ea** was obtained as dark orange solid (22.1 mg, 97% yield).

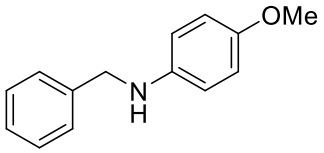
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.80 (td, *J* = 6.2, 3.8 Hz, 2H), 6.62 (td, *J* = 6.2, 3.8 Hz, 2H), 4.26 (s, 2H), 3.76 (s, 3H), 2.37 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.3, 142.7, 136.9, 136.7, 129.4, 127.7, 115.0, 114.2, 55.9, 49.1, 21.2

IR (neat) υ 3734, 2379, 2359, 2348, 2309, 1748, 1715, 1679, 1647, 1516, 1362, 1240, 1038, 823, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{15}H_{18}NO^+$ $[M+H]^+$ 228.1383, found 228.1387

m.p. 63-65 ℃



3eb

4-methoxy-N-(4-methylbenzyl)aniline (3eb)

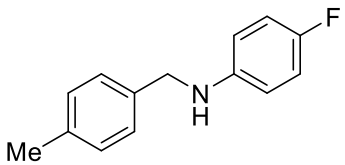
: Following the general procedure C, 1-azido-4-methoxybenzene **1e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), benzyl alcohol **2b** (0.4 mmol, 0.041 mL, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **3eb** was obtained as orange oil (17.4 mg, 82% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 4H), 7.30-7.27 (m, 1H), 6.79 (td, *J* = 6.2, 3.8 Hz, 2H), 6.62 (td, *J* = 6.3, 3.8 Hz, 2H), 4.30 (s, 2H), 3.75 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.3, 142.6, 139.8, 128.7, 127.7, 127.3, 115.0, 114.2, 55.9, 49.4

IR (neat) υ 3431, 2928, 1512, 1453, 1234, 1179, 1036, 819, 742, 698 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO^+$ $[M+H]^+$ 214.1226, found 214.1227



3fa

4-fluoro-N-(4-methylbenzyl)aniline (3fa)

: Following the general procedure C, 1-azido-4-fluorobenzene **1f** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3fa** was obtained as white solid (15.8 mg, 73% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.27-7.25 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.92-6.86 (m, 2H), 6.60-6.55 (m, 2H), 4.25 (s, 2H), 2.36 (s, 3H)

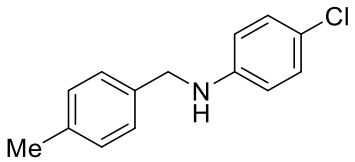
^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.0 (d, $J_{C\text{-}F}$ = 232.0 Hz), 144.6, 137.1, 136.2, 129.5, 127.6, 115.8 (d, $J_{C\text{-}F}$ = 22.0 Hz), 113.8 (d, $J_{C\text{-}F}$ = 6.7 Hz), 48.9, 21.2

^{19}F-NMR (375 MHz, $CDCl_3$) δ -127.8

IR (neat) υ 3734, 2359, 2348, 2309, 1748, 1704, 1647, 1509, 1489, 1362, 1216, 819, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{15}FN^+$ $[M+H]^+$ 216.1183, found 216.1180

m.p. 68-70 ℃



3ga

4-chloro-N-(4-methylbenzyl)aniline (3ga)

: Following the general procedure C, 1-azido-4-chlorobenzene **1g** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3ga** was obtained as white solid (22.9 mg, 99% yield).

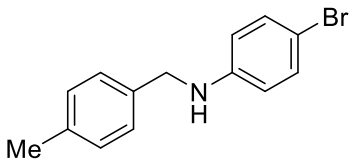
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.2 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.10 (dt, *J* = 9.5, 2.6 Hz, 2H), 6.54 (td, *J* = 6.2, 3.7 Hz, 2H), 4.25 (s, 2H), 4.02 (s, 1H), 2.35 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.8, 137.2, 136.0, 129.5, 129.2, 127.5, 122.1, 114.0, 48.2, 21.2

IR (neat) υ 3734, 2379, 2359, 2348, 2309, 1748, 1715, 1647, 1599, 1508, 1362, 1216, 810, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{15}ClN^+$ $[M+H]^+$ 232.0888, found 232.0890

m.p. 69-71 ℃



3ha

4-bromo-N-(4-methylbenzyl)aniline (3ha)

: Following the general procedure C, 1-azido-4-bromobenzene **1h** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3ha** was obtained as white solid (20.7 mg, 75% yield).

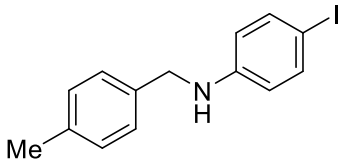
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 9.1 Hz, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.49-6.53 (m, 2H), 4.26 (s, 2H), 4.05 (s, 1H), 2.36 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.2, 137.2, 135.9, 132.0, 129.5, 127.5, 114.5, 109.1, 48.1, 21.2

IR (neat) υ 3734, 2380, 2348, 2309, 1748, 1715, 1679, 1647, 1593, 1498, 1397, 1311, 1245, 1122, 808, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{15}BrN^+$ $[M+H]^+$ 278.0363, found 278.0359

m.p. 80-82 ℃



3ia

4-iodo-N-(4-methylbenzyl)aniline (3ia)

: Following the general procedure C, 1-azido-4-iodobenzene **1i** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3ia** was obtained as yellow solid (16.5 mg, 51% yield) with **3aa** (4.9 mg, 25% yield) as side product..

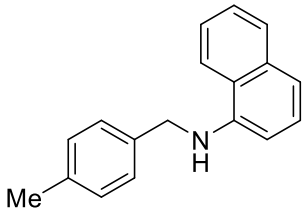
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41 (dt, *J* = 9.5, 2.5 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.41 (dt, *J* = 9.5, 2.4 Hz, 2H), 4.26 (s, 2H), 4.06 (s, 1H), 2.36 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.8, 137.9, 137.2, 135.8, 129.5, 127.5, 115.2, 78.1, 47.9, 21.2

IR (neat) υ 3734, 2380, 2359, 2348, 2309, 1748, 1704, 1647, 1508, 1489, 1374, 1216, 808, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{15}NI^+$ $[M+H]^+$ 324.0244, found 324.0238

m.p. 88-90 ℃



3ja

N-(4-methylbenzyl)naphthalen-1-amine (3ja)

: Following the general procedure C, 1-azidonaphthalene **1j** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **3ja** was obtained as purple solid (20.3 mg, 82% yield).

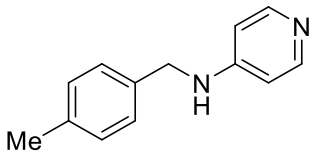
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.50-7.42 (m, 2H), 7.38-7.34 (m, 3H), 7.29-7.26 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.66 (d, *J* = 6.9 Hz, 1H), 4.67 (s, 1H), 4.47 (s, 2H), 2.39 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) 143.4, 137.2, 136.1, 134.4, 129.5, 128.8, 127.9, 126.8, 125.9, 124.8, 123.5, 120.0, 117.6, 104.8, 48.5, 21.3

IR (neat) υ 3734, 2379, 2359, 2348, 2309, 1748, 1704, 1679, 1647, 1509, 1488, 1374, 1216, 785, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{18}H_{18}N^+$ $[M+H]^+$ 248.1434, found 248.1438

m.p. 56-58 ℃



3ka

N-(4-methylbenzyl)pyridin-4-amine (3ka)

: Following the general procedure C, 4-azidopyridine **1k** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material at 160 ℃ for 48 hours. After the reaction mixture cooled down to room temperature, 2 M HCl (2 mL) was added to the mixture and washed with dichloromethane 3 times. To the aqueous phase, sat. NaHCO3 was added to neutralize and extracted with dichloromethane 3 times. After the organic phase was combined and evaporated *in vacuo*, **3ka** was obtained as white solid (15.1 mg, 76% yield).

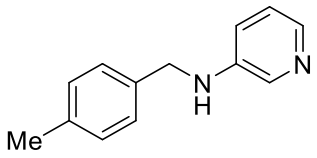
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 5.9 Hz, 2H), 7.19 (dd, *J* = 21.5, 8.2 Hz, 4H), 6.46 (d, *J* = 6.4 Hz, 2H), 4.64 (s, 1H), 4.31 (d, *J* = 5.5 Hz, 2H), 2.35 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.4, 150.1, 137.5, 134.9, 129.6, 127.5, 107.8, 46.8, 21.2

IR (neat) υ 3734, 2380, 2348, 2309, 1748, 1704, 1647, 1509, 13962, 1216, 808, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{13}H_{15}N_2^+$ $[M+H]^+$ 199.1230, found 199.1225

m.p. 120-122 ℃



3la

N-(4-methylbenzyl)pyridin-3-amine (3la)

: Following the general procedure C, 3-azidopyridine **1l** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After the reaction mixture cooled down to room temperature, 2 M HCl (2 mL) was added to the mixture and washed with dichloromethane 3 times. To the aqueous phase, sat. NaHCO3 was added to neutralize and extracted with dichloromethane 3 times. After the organic phase was combined and evaporated *in vacuo*, **3la** was obtained as white solid (15.4 mg, 78% yield).

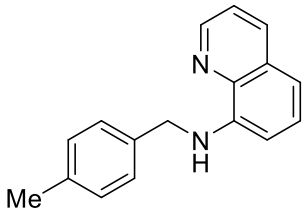
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 0.7 Hz, 1H), 7.95 (d, *J* = 4.1 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.08 (dd, *J* = 8.2, 5.0 Hz, 1H), 6.88 (dq, *J* = 8.2, 1.4 Hz, 1H), 4.30 (s, 2H), 2.34 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.4, 138.3, 137.3, 135.8, 135.4, 129.6, 127.5, 124.0, 118.9, 47.7, 21.2

IR (neat) υ 3901, 3756, 3734, 2380, 2359, 2348, 2309, 1748, 1704, 1679, 1588, 1509, 1488, 1417, 1216, 792, 671, 648 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{13}H_{15}N_2^+$ $[M+H]^+$ 199.1230, found 199.1232

m.p. 110-112 ℃



3ma

N-(4-methylbenzyl)quinolin-8-amine (3ma)

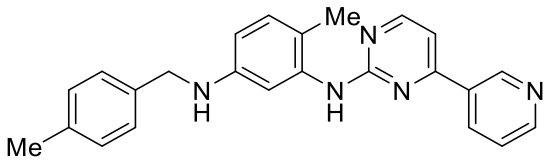
: Following the general procedure C, 8-azidoquinoline **1m** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material. After purification by column chromatography (n-hexane : EtOAc = 10 : 1), **3ma** was obtained as yellow oil (18.5 mg, 74% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.73 (t, *J* = 2.1 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.39-7.33 (m, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.58 (s, 1H), 4.53 (d, *J* = 3.2 Hz, 2H), 2.36 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.0, 144.7, 138.3, 136.8, 136.3, 136.1, 129.4, 128.7, 127.9, 127.5, 121.5, 114.2, 105.2, 47.6, 21.2

IR (neat) υ 3398, 3045, 2920, 1574, 1519, 1479, 1382, 1336, 1124, 816, 789, 743cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{17}H_{17}N_2^+$ $[M+H]^+$ 249.1386, found 249.1390



3na

4-methyl-N^1-(4-methylbenzyl)-N^3-(4-(pyridin-3-yl)pyrimidin-2-yl)benzene-1,3-diamine (3na)

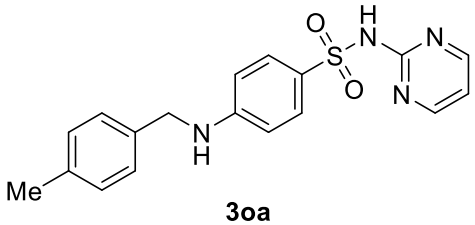
: Following the general procedure C, N-(5-azido-2-methylphenyl)-4-(pyridin-3-yl)pyrimidin-2-amine **1n** (0.1 mmol, 30.3 mg , 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as starting material at 160 ℃ for 48 hours with 1.0 mL of toluene. After the reaction mixture cooled down to room temperature, 2 M HCl (2 mL) was added to the mixture and washed with EtOAc 3 times. To the aqueous phase, sat. NaHCO3 was added to neutralize and extracted with EtOAc 3 times. After the organic phase was combined and concentrated *in vacuo*, **3na** was obtained as yellow oil (33.5 mg, 88% yield).

^{1}H-NMR (400 MHz, DMSO-*d*$_6$) δ 9.26 (d, *J* = 1.8 Hz, 1H), 8.70 (q, *J* = 2.3 Hz, 2H), 8.45 (d, *J* = 5.1 Hz, 1H), 8.40 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.53 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.36 (d, *J* = 5.1 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 2.3 Hz, 1H), 6.32 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.01 (t, *J* = 6.0 Hz, 1H), 4.19 (d, *J* = 6.0 Hz, 2H), 2.24 (s, 3H), 2.06 (s, 3H)

^{13}C-NMR (100 MHz, DMSO-*d*$_6$) δ 161.4, 161.2, 159.3, 151.3, 148.1, 147.1, 138.0, 137.4, 135.4, 134.2, 132.3, 130.3, 128.8, 127.1, 123.8, 119.3, 109.5, 109.1, 107.1, 46.6, 20.6, 17.2

IR (neat) υ 3247, 2255, 2128, 1747, 1658, 1646, 1516, 1396, 1338, 1158, 987, 824, 762 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{24}H_{24}N_5^+$ $[M+H]^+$ 382.2026, found 382.2031



3oa

4-((4-methylbenzyl)amino)-N-(pyrimidin-2-yl)benzenesulfonamide (3oa)

: Following the general procedure C, 4-azido-N-(pyrimidin-2-yl)benzenesulfonamide **1o** (0.1 mmol, 27.6 mg, 1.0 eq.), 4-methylbenzyl alcohol **2a** (0.4 mmol, 48.9 mg, 4.0 eq.) were used as

starting material at 160 ℃ for 48 hours with 1.0 mL of toluene. After the reaction mixture cooled down to room temperature, 2 M HCl (2 mL) and H_2O (10 mL) was added to the mixture and extracted with dichloromethane 3 times. After purification by column chromatography (n-hexane : EtOAc = 1 : 2), **3oa** was obtained as white solid (13.3 mg, 38% yield).

^{1}H-NMR (400 MHz, DMSO-*d*$_6$) δ 11.27 (s, 1H), 8.47 (d, *J* = 5.1 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 3H), 7.00 (t, *J* = 5.1 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.25 (d, *J* = 5.5 Hz, 2H), 2.26 (s, 3H)

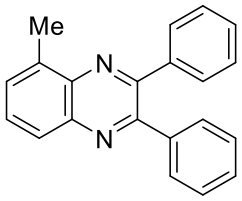
^{13}C-NMR (100 MHz, DMSO-*d*$_6$) δ 158.2, 157.2, 152.2, 136.0, 135.9, 129.6, 129.0, 127.2, 125.2, 115.5, 110.8, 45.6, 40.1, 39.9, 39.7, 39.5, 39.3, 39.1, 38.9, 20.7

IR (neat) υ 3124, 2311, 1597, 1513, 1406, 1260, 1222, 1153, 750, 630 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{18}H_{19}N_4O_2S^+$ $[M+H]^+$ 355.1223, found 355.1226

m.p. 244-246 ℃

8-2. Synthesis of quinoxalines



7aa

5-methyl-2,3-diphenylquinoxaline (7aa)

: Following the general procedure D, 2-azido-6-methylaniline **5a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), meso-hydrobenzoin **6a** (0.2 mmol, 42.9 mg, 2.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **7aa** was obtained as yellow solid (22.3 mg, 76% yield).

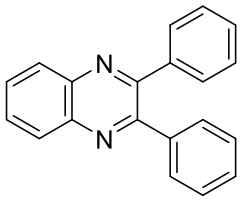
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.61-7.57 (m, 3H), 7.54 (dt, *J* = 5.3, 2.2 Hz, 2H), 7.39-7.31 (m, 6H), 2.87 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.0, 151.9, 141.3, 140.5, 139.5, 139.5, 137.8, 130.3, 129.9, 129.8, 128.8, 128.4, 128.2, 127.1, 17.3

IR (neat) 3060, 2923, 1569, 1468, 1443, 1345, 1224, 1098, 1023, 980, 791, 767, 698 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{21}H_{17}N_2^+$ $[M+H]^+$ 297.1386, found 297.1390

m.p. 112-114 ℃



7ba

2,3-diphenylquinoxaline (7ba)

: Following the general procedure D, 2-azidoaniline **5b** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), meso-hydrobenzoin **6a** (0.2 mmol, 42.9 mg, 2.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **7ba** was obtained as yellow solid (18.6 mg, 66% yield).

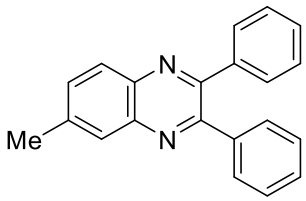
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.19 (td, *J* = 6.3, 2.9 Hz, 2H), 7.78 (td, *J* = 6.4, 3.2 Hz, 2H), 7.53 (dd, *J* = 7.5, 1.6 Hz, 4H), 7.39-7.32 (m, 6H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.6, 141.4, 139.2, 130.1, 130.0, 129.4, 128.9, 128.4

IR (neat) 3068, 1477, 1442, 1396, 1345, 1219, 1056, 1024, 976, 768, 697 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{20}H_{15}N_2^+$ $[M+H]^+$ 283.1230, found 283.1227

m.p. 126-128 ℃



7ca

6-methyl-2,3-diphenylquinoxaline (7ca)

: Following the general procedure D, 2-azido-4-methylaniline **5c** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), meso-hydrobenzoin **6a** (0.2 mmol, 42.9 mg, 2.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **7ca** was obtained as yellow solid (22.2 mg, 75% yield).

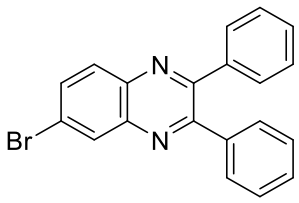
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.96 (s, 1H), 7.61 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.51 (dd, *J* = 6.4, 1.4 Hz, 4H), 7.38-7.30 (m, 6H), 2.62 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.5, 152.7, 141.4, 140.6, 139.8, 139.4, 132.5, 130.0, 128.8, 128.8, 128.4, 128.2, 22.1

IR (neat) 3057, 1745, 1620, 1485, 1444, 1345, 1204, 1057, 1024, 978, 829, 806, 772, 752, 697, 669 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{21}H_{17}N_2^+$ $[M+H]^+$ 297.1386, found 297.1382

m.p. 117-119 ℃



7da

6-bromo-2,3-diphenylquinoxaline (7da)

: Following the general procedure D, 2-azido-4-bromoaniline **5d** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), meso-hydrobenzoin **6a** (0.2 mmol, 42.9 mg, 2.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **7da** was obtained as yellow solid (16.5 mg, 46% yield).

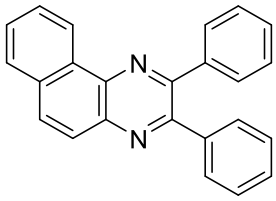
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.3 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.84 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.52-7.50 (m, 4H), 7.40-7.32 (m, 6H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.4, 153.9, 141.9, 140.1, 138.8, 138.7, 133.6, 131.6, 130.6, 130.0, 129.9, 129.3, 129.2, 128.5, 124.0

IR (neat) 3235, 2348, 2309, 1745, 1646, 1508, 1363, 1216, 1057, 1024, 978, 697 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{20}H_{14}BrN_2^+$ $[M+H]^+$ 363.0316, found 363.0320

m.p. 125-127 ℃



7ea

2,3-diphenylbenzo[f]quinoxaline (7ea)

: Following the general procedure D, 2-azidonaphthalen-1-amine **5e** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), meso-hydrobenzoin **6a** (0.2 mmol, 42.9 mg, 2.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **7ea** was obtained as yellow solid (17.3 mg, 52% yield).

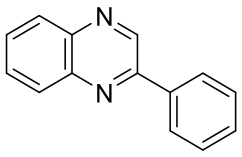
^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.34-9.32 (m, 1H), 8.05 (s, 2H), 7.97-7.95 (m, 1H), 7.79-7.72 (m, 2H), 7.68 (q, *J* = 2.3 Hz, 2H), 7.61-7.59 (m, 2H), 7.41-7.35 (m, 6H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.7, 151.4, 140.6, 139.6, 139.4, 133.5, 131.8, 131.0, 130.4, 130.0, 128.9, 128.8, 128.5, 128.3, 128.1, 127.6, 126.8, 124.9

IR (neat) 3058, 1745, 1437, 1396, 1361, 1245, 1193, 1082, 1024, 840, 810, 754, 697 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{24}H_{17}N_2^+$ $[M+H]^+$ 333.1386, found 333.1391

m.p. 142-144 ℃



7bb

2-phenylquinoxaline (7bb)

: Following the general procedure D, 2-azidoaniline **5b** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 1-phenyl-1,2-ethanediol **6b** (0.2 mmol, 27.6 mg, 2.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **7bb** was obtained as yellow solid (4.5 mg, 22% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.22-8.12 (m, 4H), 7.82-7.74 (m, 2H), 7.60-7.51 (m, 3H)

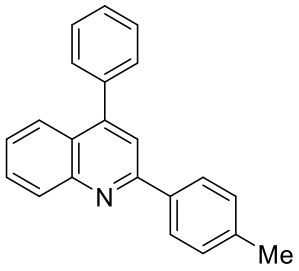
^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.0, 143.5, 142.5, 141.8, 137.0, 130.5, 130.3, 129.8, 129.7, 129.3, 129.3, 127.7

IR (neat) 3247, 2348, 1745, 1646, 1542, 1508, 1363, 1216, 1057, 1024, 978, 765, 669 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{14}H_{11}N_2^+$ $[M+H]^+$ 207.0917, found 207.0914

m.p. 79-81 ℃

8-3. Synthesis of quinolines



10aa

4-phenyl-2-(p-tolyl)quinoline (10aa)

: Following the general procedure E, (2-azidophenyl)(phenyl)methanone **8a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 1-(4-methylphenyl)ethanol **9a** (0.3 mmol, 0.041 mL, 3.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **10aa** was obtained as white solid (15.9 mg, 54% yield).

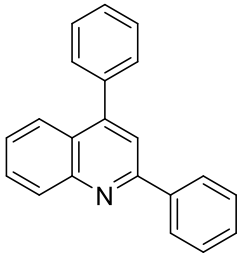
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.82 (s, 1H), 7.76-7.71 (m, 1H), 7.59-7.51 (m, 5H), 7.49-7.45 (m, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 2.45 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.9, 149.2, 148.9, 139.6, 138.6, 136.9, 130.1, 129.7, 129.6, 128.7, 128.5, 127.6, 126.3, 125.8, 125.7, 119.3, 21.5

IR (neat) 3058, 1745, 1591, 1543, 1489, 1419, 1356, 821, 771, 724, 701 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{22}H_{18}N^+$ $[M+H]^+$ 296.1434, found 296.1437

m.p. 100-102 ℃



10ab

2,4-diphenylquinoline (10ab)

: Following the general procedure E, (2-azidophenyl)(phenyl)methanone **8a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 1-phenylethanol **9b** (0.3 mmol, 0.036 mL, 3.0 eq.) were used as starting

materials. After purification by column chromatography (n-hexane : EtOAc = 30 : 1), **10ab** was obtained as white solid (17.0 mg, 60% yield).

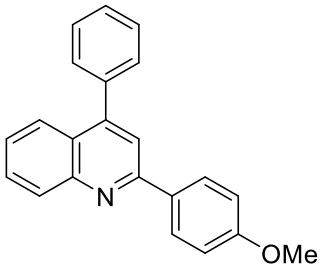
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 1H), 8.23-8.21 (m, 2H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.84 (s, 1H), 7.77-7.73 (m, 1H), 7.59-7.46 (m, 9H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.0, 149.4, 148.9, 139.7, 138.5, 130.2, 129.7, 129.5, 129.0, 128.7, 128.6, 127.7, 126.5, 125.9, 125.8, 119.5

IR (neat) 3058, 1590, 1546, 1488, 1445, 1405, 1357, 1076, 1028, 884, 769, 698 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{21}H_{16}N^+$ $[M+H]^+$ 282.1277, found 282.1279

m.p. 110-112 ℃



10ac

2-(4-methoxyphenyl)-4-phenylquinoline (10ac)

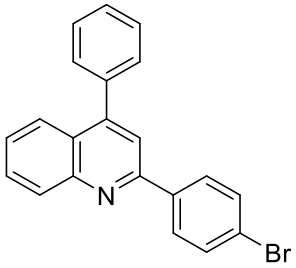
: Following the general procedure E, (2-azidophenyl)(phenyl)methanone **8a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 1-(4-methoxyphenyl)ethanol **9c** (0.3 mmol, 0.042 mL, 3.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 20 : 1), **10ac** was obtained as colorless oil (19.4 mg, 62% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 1H), 8.19 (dt, *J* = 9.6, 2.5 Hz, 2H), 7.89 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.79 (s, 1H), 7.75-7.70 (m, 1H), 7.58-7.49 (m, 5H), 7.47-7.43 (m, 1H), 7.06 (dt, *J* = 9.5, 2.5 Hz, 2H), 3.89 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.0, 156.5, 149.2, 148.8, 138.6, 132.2, 130.0, 129.7, 129.6, 129.0, 128.7, 128.5, 126.1, 125.7, 125.6, 119.0, 114.3, 55.5

IR (neat) 3058, 2834, 1590, 1543, 1516, 1489, 1457, 1423, 1357, 1250, 1176, 1030, 834, 734, 702 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{22}H_{18}NO^+$ $[M+H]^+$ 312.1383, found 312.1387



10ad

2-(4-bromophenyl)-4-phenylquinoline (10ad)

: Following the general procedure E, (2-azidophenyl)(phenyl)methanone **8a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 1-(4-bromophenyl)ethanol **9d** (0.3 mmol, 0.046 mL, 3.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **10ad** was obtained as white solid (18.4 mg, 51% yield).

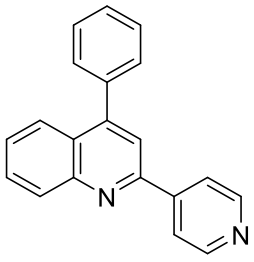
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.78 (s, 1H), 7.77-7.73 (m, 1H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.57-7.47 (m, 6H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.7, 149.6, 148.8, 138.6, 138.3, 132.1, 130.2, 129.9, 129.7, 129.2, 128.8, 128.6, 126.7, 126.0, 125.8, 124.1, 119.0, 77.5, 77.2, 76.8

IR (neat) 3058, 2348, 1745, 1589, 1542, 1486, 1416, 1356, 1071, 1008, 829, 771, 702, 669 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{21}H_{15}BrN^+$ $[M+H]^+$ 362.0364, found 362.0369

m.p. 120-122 ℃



10ae

4-phenyl-2-(pyridin-4-yl)quinoline (10ae)

: Following the general procedure E, (2-azidophenyl)(phenyl)methanone **8a** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 1-(pyridine-4-yl)ethanol **9e** (0.3 mmol, 36.9 mg, 3.0 eq.) were used as

starting materials. After purification by column chromatography (dichloromethane : acetone = 5 : 1), **10ae** was obtained as white solid (22.0 mg, 78% yield).

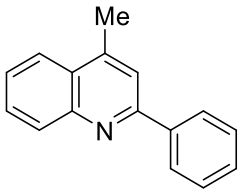
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 2H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.13 (s, 2H), 7.94 (d, *J* = 8.7 Hz, 1H), 7.84 (s, 1H), 7.79-7.75 (m, 1H), 7.57-7.52 (m, 6H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.0, 150.5, 149.9, 148.9, 146.7, 138.0, 130.4, 130.0, 129.6, 128.8, 127.4, 126.5, 125.8, 121.7, 118.9, 77.5, 77.2, 76.8

IR (neat) 3336, 2348, 1746, 1587, 1541, 1488, 1416, 1362, 1216, 827, 772, 702, 669 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{20}H_{15}N_2^+$ $[M+H]^+$ 283.1230, found 283.1228

m.p. 138-140 ℃



10bb

4-methyl-2-phenylquinoline (10bb)

: Following the general procedure E, 1-(2-azidophenyl)ethan-1-one **8b** (0.1 mmol, 0.5 M in MTBE, 0.2 mL, 1.0 eq.), 1-phenylethanol **9b** (0.3 mmol, 0.041 mL, 3.0 eq.) were used as starting materials. After purification by column chromatography (n-hexane : EtOAc = 40 : 1), **10bb** was obtained as white solid (7.6 mg, 35% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.15-8.24 (1H), 7.68-7.61 (m, 3H), 7.58-7.42 (m, 6H), 7.40 (dd, *J* = 4.6, 0.9 Hz, 2H), 7.28-7.36 (2H), 2.16 (s, 3H)

^{13}C-NMR (100 MHz, $CDCl_3$) δ 157.2, 148.1, 145.1, 139.8, 130.3, 129.5, 129.4, 128.9, 127.7, 127.4, 126.2, 123.8, 119.9, 19.2

IR (neat) 3060, 1597, 1550, 1509, 1495, 1450, 1409, 1349, 1028, 901, 862, 769, 694 cm^{-1}

HRMS (ESI) *m/z* calcd for $C_{16}H_{14}N^+$ $[M+H]^+$ 220.1121, found 220.1122

m.p. 62-64 ℃

9. Computational details

9-1. General methods

All DFT computations were carried out using Gaussian 16[6] and GaussView 6.0.[7] Geometry optimizations were performed with M06L functional[8] with Grimme's D3 dispersion correction.[9.] 6-31++G(d,p) basis set was used for all atoms. Vibrational frequency calculations were carried out at the same level of theory as the geometry optimizations to confirm the stationary points (No imaginary frequency for local minima and only one imaginary frequency for transition states) and to provide the thermal corrections for Gibbs free energy determinations. Intrinsic reaction coordinates (IRC) calculations were performed in order to confirm intermediates along the reaction pathway. The single-point energy calculations of the optimized geometries were carried out with M06L functional[8] with Grimme's D3 dispersion correction[9] and 6-311++G(d,p) basis set for all atoms with inclusion of solvation energy corrections using SMD model[10] (solvent = toluene). Structural graphics were visualized with CYLview20.[11]

9-2. Energy components of all optimized geometries

Table S4. Computed energies of the optimized geometries

	E(sol)[a] (SCF/TZ, Hartree)	Thermal correction[b] (Hartree)	G(sol) (kcal/mol)
PhN_3	-395.90254446	0.071532	-395.83101246
KOBn	-946.17868777	0.084236	-946.09445177
Int1A	-1342.09887420	0.177994	-1341.92088020
Int1A-TS	-1342.07237981	0.174577	-1341.89780281
Int1B	-1342.09830841	0.177008	-1341.92130041
Int1B-TS	-1342.05386627	0.172416	-1341.88145027
Int1C	-1342.09725976	0.173836	-1341.92342376
Int1C-TS	-1342.05116276	0.170470	-1341.88069276
Int1D	-1342.09478014	0.176017	-1341.91876314
Int1D-TS	-1342.05436779	0.171000	-1341.88336779
Int2	-1342.13500201	0.179515	-1341.95548701
BnOH	-346.82640178	0.100631	-346.72577078
PhCHO	-345.62633065	0.079100	-345.54723065
Int3	-1343.33773830	0.201982	-1343.13575630
Int3-TS	-1343.32327207	0.197963	-1343.12530907
Int4	-1343.32713910	0.201418	-1343.12572110
Int4-TS1	-1343.30336432	0.197593	-1343.10577132
Int4-TS2	-1343.29835769	0.194289	-1343.10406869
Int4-TS3	-1343.29985302	0.196663	-1343.10319002
Int5	-2289.55283529	0.309247	-2289.24358829
Int5-TS	-2289.53922857	0.307104	-2289.23212457
PhNHK	-886.98662248	0.071782	-886.91484048
N_2	-109.53850371	-0.012935	-109.55143871

[a] DFT calculation using Gaussian 16 M06L-D3/6-311++G(d,p), SMD(PhMe)
[b] DFT calculation using Gaussan 16 M06L-D3/6-31++G(d,p)

9-3. Cartesian coordinates of all optimized geometries

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PhN_3

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N	-4.787284	1.270113	4.732303
N	-3.763530	1.623020	4.351750
N	-2.706550	2.151304	3.993192
C	-1.725419	1.328105	3.386857
C	-0.544632	1.966334	2.998540
C	0.467684	1.228136	2.396603
C	0.312333	-0.140699	2.178696
C	-0.868976	-0.769678	2.568866
C	-1.891155	-0.044326	3.172504
H	-0.439734	3.032027	3.175237
H	1.384266	1.727217	2.096000
H	1.105699	-0.713223	1.708423
H	-0.999858	-1.835266	2.403601
H	-2.810991	-0.537986	3.475579

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KOBn

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K	-3.955855	2.579156	-0.028771
O	-2.764927	0.631590	-0.256967
C	-2.042530	-0.501741	-0.387747
C	-0.544184	-0.308564	-0.581043
C	0.017043	0.967548	-0.619761
C	1.389548	1.148033	-0.797074
C	2.228678	0.045243	-0.939347
C	1.680214	-1.239348	-0.902433
C	0.310593	-1.408461	-0.725299
H	-2.372116	-1.137928	-1.248498
H	-2.141212	-1.191310	0.489179
H	-0.659628	1.812569	-0.506271
H	1.808038	2.152626	-0.824692
H	3.298368	0.181140	-1.077660
H	2.325711	-2.108221	-1.012275
H	-0.113286	-2.412806	-0.696966

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Int1A

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N	-0.411892	-3.396337	-2.382724
N	-0.882050	-2.509131	-1.838431
N	-1.513485	-1.690917	-1.148403
C	-1.397513	-0.335772	-1.489570

C	-2.041811	0.573247	-0.640296
C	-2.002489	1.937835	-0.922125
C	-1.331450	2.409224	-2.052511
C	-0.689075	1.495370	-2.897063
C	-0.707113	0.133216	-2.618569
K	1.217722	1.212993	-0.307970
O	1.505040	-1.145338	-1.089018
C	1.769583	-2.044014	-0.095962
C	1.640358	-1.307131	1.224459
C	2.739477	-0.652934	1.799816
C	2.574588	0.258236	2.846101
C	1.298473	0.533409	3.342460
C	0.194073	-0.129564	2.796286
C	0.367106	-1.036937	1.752003
H	-2.564542	0.193891	0.233025
H	-2.511426	2.633225	-0.260053
H	-1.322996	3.470461	-2.283630
H	-0.163084	1.848290	-3.780497
H	-0.158289	-0.569701	-3.237493
H	2.789946	-2.493212	-0.151183
H	1.070254	-2.917587	-0.073523
H	3.734228	-0.860387	1.406148
H	3.442350	0.749030	3.281954
H	1.167204	1.237702	4.159567
H	-0.801562	0.059460	3.193030
H	-0.493603	-1.537106	1.308165

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Int1A-TS

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N	-1.883947	-0.922860	-0.171302
N	-2.037101	0.035177	-0.874325
N	-3.060776	0.744743	-1.271275
C	-2.745145	1.707110	-2.241291
C	-3.710710	2.710991	-2.446087
C	-3.498528	3.718564	-3.380042
C	-2.321095	3.756377	-4.130492
C	-1.363943	2.758679	-3.938492
C	-1.564630	1.736845	-3.012997
K	-0.831914	2.556804	-0.146868
O	0.520375	0.540081	-0.899340
C	0.645909	-0.534048	-0.179976
C	1.016128	-0.391001	1.270623
C	1.508683	0.822999	1.764126
C	1.822135	0.974454	3.114239
C	1.639805	-0.089328	3.995818

C	1.155316	-1.307159	3.514583
C	0.848403	-1.455144	2.166227
H	-4.627271	2.670311	-1.863049
H	-4.259420	4.481540	-3.523836
H	-2.158936	4.542098	-4.862269
H	-0.449480	2.764494	-4.527205
H	-0.813195	0.966194	-2.858603
H	1.129523	-1.414336	-0.659035
H	-0.526139	-1.011762	-0.086941
H	1.698547	1.627511	1.054394
H	2.225876	1.916775	3.477360
H	1.881154	0.025180	5.048778
H	1.011526	-2.140789	4.196861
H	0.457869	-2.401786	1.796215

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Int1B

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N	-2.293229	-1.088893	-0.005021
N	-2.430176	0.010771	-0.289724
N	-2.747296	1.215404	-0.372228
C	-2.514228	1.870193	-1.585220
C	-2.732380	3.256509	-1.589172
C	-2.524868	3.994125	-2.753351
C	-2.104900	3.360743	-3.926142
C	-1.903837	1.975871	-3.921275
C	-2.098598	1.227511	-2.764502
K	0.478525	2.738049	-1.883588
O	0.202580	0.458202	-1.218146
C	0.687761	-0.590918	-0.515462
C	0.854040	-0.344517	0.977646
C	0.298419	0.785446	1.581692
C	0.432130	1.010337	2.952637
C	1.134373	0.105272	3.745090
C	1.695725	-1.028963	3.153940
C	1.553559	-1.247515	1.787071
H	-3.067887	3.733447	-0.672647
H	-2.704059	5.065999	-2.745681
H	-1.960272	3.933046	-4.837872
H	-1.586687	1.470150	-4.829647
H	-1.882121	0.165134	-2.744550
H	1.678043	-0.955708	-0.885866
H	0.037621	-1.501619	-0.593019
H	-0.260114	1.475789	0.949797
H	-0.017279	1.892090	3.405207
H	1.243622	0.278069	4.812631

H	2.247141	-1.741410	3.763443
H	1.993410	-2.133898	1.329758

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Int1B-TS

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N	-3.950678	-1.504647	-1.093867
N	-3.490584	-0.458105	-1.369380
N	-2.401726	0.250492	-0.919598
C	-1.932913	1.224431	-1.795160
C	-0.892729	2.057080	-1.328877
C	-0.297889	2.985949	-2.174170
C	-0.723588	3.131103	-3.500108
C	-1.778148	2.333151	-3.955686
C	-2.376873	1.387858	-3.125695
K	0.613843	0.141667	-3.290204
O	0.567339	-0.761175	-1.025538
C	-0.171831	-0.832665	0.042075
C	0.193165	-0.063323	1.260383
C	-0.550861	-0.203185	2.441930
C	-0.232637	0.534994	3.574973
C	0.838575	1.432355	3.550714
C	1.586323	1.578509	2.382368
C	1.266043	0.839328	1.246789
H	-0.561875	1.961159	-0.298639
H	0.495016	3.619358	-1.783092
H	-0.277737	3.880902	-4.146885
H	-2.150456	2.454229	-4.970291
H	-3.204428	0.784001	-3.484922
H	-0.611551	-1.822931	0.292242
H	-1.396678	-0.284816	-0.271420
H	-1.390512	-0.897359	2.457485
H	-0.818619	0.413694	4.482422
H	1.088096	2.009594	4.436723
H	2.427111	2.268163	2.360768
H	1.845818	0.928908	0.330459

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Int1C

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N	-3.229310	6.489112	-2.102384
N	-2.632339	5.565299	-1.771552
N	-1.927609	4.654671	-1.318764
C	-2.074347	3.349096	-1.903834
C	-3.024026	3.076295	-2.891745
C	-3.112682	1.784501	-3.400659

C	-2.268384	0.780558	-2.926854
C	-1.328705	1.071984	-1.939435
C	-1.218778	2.359980	-1.419768
K	-0.184592	4.961801	1.030282
O	1.078167	3.025582	0.730693
C	1.810179	1.938207	0.392948
C	1.116007	0.598485	0.604446
C	-0.069015	0.515310	1.337317
C	-0.723251	-0.703961	1.514580
C	-0.200485	-1.868160	0.954552
C	0.986113	-1.800300	0.220223
C	1.633525	-0.579269	0.051090
H	-3.685199	3.858275	-3.257678
H	-3.848413	1.565136	-4.169189
H	-2.345071	-0.226631	-3.325448
H	-0.669849	0.295897	-1.557034
H	-0.467445	2.591279	-0.652031
H	2.778145	1.871758	0.949057
H	2.131584	1.938793	-0.680741
H	-0.467143	1.439938	1.750863
H	-1.648265	-0.746454	2.086165
H	-0.711352	-2.818828	1.084125
H	1.401342	-2.701862	-0.224980
H	2.553398	-0.528289	-0.532145

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Int1C-TS

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N	1.042788	4.573626	-2.885074
N	0.030254	4.020397	-2.662637
N	-0.441808	3.289036	-1.588094
C	-1.636554	2.579976	-1.808505
C	-2.325062	2.562781	-3.035072
C	-3.510963	1.848330	-3.158894
C	-4.041105	1.134204	-2.083600
C	-3.359154	1.146539	-0.869187
C	-2.177278	1.867374	-0.719742
K	-1.674006	4.651509	0.615170
O	-0.026710	3.088672	1.635716
C	0.754706	2.586110	0.722533
C	0.901926	1.110293	0.587649
C	0.173882	0.241549	1.410380
C	0.286709	-1.137234	1.254238
C	1.123393	-1.667464	0.272353
C	1.853661	-0.807762	-0.552343
C	1.741829	0.568138	-0.395820

H	-1.917074	3.105598	-3.881060
H	-4.024019	1.845953	-4.117144
H	-4.963554	0.572986	-2.194556
H	-3.739640	0.582749	-0.021053
H	-1.646061	1.838405	0.231032
H	1.713680	3.115344	0.517312
H	0.235335	2.883974	-0.506319
H	-0.462983	0.677436	2.176808
H	-0.275579	-1.803819	1.903856
H	1.208811	-2.743680	0.149536
H	2.507033	-1.215251	-1.319422
H	2.299741	1.242435	-1.045958

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Int1D

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N	-2.112109	2.893040	2.300052
N	-1.936263	2.925750	1.170528
N	-1.739379	3.120320	-0.040022
C	-1.948878	2.020961	-0.917347
C	-1.690893	2.256228	-2.269443
C	-1.872687	1.233322	-3.193426
C	-2.311734	-0.021919	-2.774797
C	-2.562709	-0.247681	-1.422319
C	-2.385655	0.766217	-0.488424
K	0.305920	5.123282	-0.200989
O	1.271203	3.376979	1.153804
C	1.528046	2.459317	0.210225
C	0.976466	1.061896	0.469359
C	0.420262	0.758225	1.712367
C	-0.083533	-0.517571	1.974471
C	-0.033302	-1.507520	0.994133
C	0.526658	-1.212397	-0.251907
C	1.024003	0.061402	-0.507536
H	-1.346360	3.238168	-2.585375
H	-1.666879	1.418559	-4.243678
H	-2.446712	-0.821646	-3.496430
H	-2.880315	-1.228779	-1.081053
H	-2.543095	0.572347	0.569284
H	2.620363	2.315456	-0.009786
H	1.117800	2.717816	-0.835397
H	0.404038	1.552641	2.455216
H	-0.511350	-0.741977	2.949894
H	-0.423283	-2.502401	1.196625
H	0.562015	-1.976139	-1.026436
H	1.447377	0.294818	-1.485793

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Int1D-TS

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N	-2.177503	2.874774	1.921229
N	-2.362747	2.629250	0.772155
N	-1.596221	2.526610	-0.296053
C	-2.102628	1.871796	-1.430137
C	-1.333771	1.936045	-2.601447
C	-1.745700	1.257311	-3.743057
C	-2.933025	0.526844	-3.745670
C	-3.704094	0.478068	-2.583901
C	-3.296426	1.135414	-1.428876
K	0.286603	3.632246	2.798874
O	1.588478	3.379897	0.648971
C	1.085850	2.353542	0.033741
C	1.110643	1.010627	0.709090
C	1.800468	0.837632	1.916741
C	1.798699	-0.392650	2.572691
C	1.101647	-1.471927	2.033013
C	0.424946	-1.316081	0.820350
C	0.432148	-0.090539	0.165486
H	-0.418549	2.521367	-2.605932
H	-1.136869	1.312266	-4.641294
H	-3.256354	0.006163	-4.641790
H	-4.633797	-0.084641	-2.571813
H	-3.892232	1.092404	-0.522389
H	1.291168	2.258796	-1.059392
H	-0.248409	2.506352	-0.141451
H	2.388408	1.673401	2.295312
H	2.356735	-0.515972	3.498186
H	1.094280	-2.430335	2.544370
H	-0.113000	-2.155407	0.387376
H	-0.099734	0.025457	-0.778585

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Int2

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N	-1.702777	0.266670	2.668837
N	-1.597767	-0.176524	1.454832
N	-1.567356	0.789944	0.549944
C	-1.420934	0.307159	-0.751206
C	-1.303516	1.270459	-1.772124
C	-1.103595	0.900928	-3.097219
C	-1.019999	-0.447072	-3.449665
C	-1.147725	-1.412614	-2.448264

C	-1.344833	-1.052454	-1.120414
K	-1.685194	2.907136	2.249440
O	0.881276	2.670393	1.754699
C	1.057320	1.827997	0.873151
C	1.526377	0.464355	1.090873
C	1.741355	-0.031282	2.385557
C	2.125662	-1.352281	2.561692
C	2.291552	-2.185625	1.450899
C	2.078437	-1.698239	0.161918
C	1.698776	-0.373493	-0.018751
H	-1.364981	2.322630	-1.496070
H	-1.012126	1.670322	-3.860395
H	-0.863777	-0.739480	-4.484019
H	-1.089820	-2.467983	-2.707469
H	-1.429972	-1.807791	-0.346530
H	0.873836	2.083968	-0.193696
H	-1.705351	-0.576805	3.244800
H	1.586448	0.633346	3.230819
H	2.289081	-1.744459	3.561565
H	2.583322	-3.222671	1.594314
H	2.193357	-2.352473	-0.697544
H	1.502755	0.016316	-1.016433

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BnOH

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O	-4.558378	1.118116	0.081234
C	-3.392845	1.728240	0.602823
C	-2.247623	0.757327	0.573811
C	-1.031992	1.117523	1.164709
C	0.054074	0.248866	1.140382
C	-0.063155	-0.998064	0.525920
C	-1.271962	-1.362991	-0.060633
C	-2.360249	-0.490904	-0.039432
H	-5.259039	1.775569	0.065320
H	-3.554558	2.068082	1.639364
H	-3.123797	2.623025	0.016399
H	-0.937466	2.088489	1.648892
H	0.991837	0.543059	1.603888
H	0.782693	-1.679543	0.507624
H	-1.372061	-2.333630	-0.539184
H	-3.304557	-0.771688	-0.493588

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PhCHO

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H	-3.474242	0.655364	-0.421976
C	-2.593602	1.311921	-0.625226
C	-1.439250	0.610927	-1.209432
C	-0.261859	1.305243	-1.519009
C	0.815923	0.625610	-2.069284
C	0.725488	-0.747915	-2.313391
C	-0.443219	-1.444236	-2.007555
C	-1.523977	-0.763592	-1.455999
O	-2.632136	2.500151	-0.368629
H	-0.221289	2.372229	-1.317889
H	1.730788	1.158917	-2.310920
H	1.571467	-1.276408	-2.744209
H	-0.508090	-2.511188	-2.199324
H	-2.444592	-1.290815	-1.210922

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Int3

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N	6.126494	3.021848	2.357741
N	7.404544	3.071107	2.135517
N	7.807524	2.210459	1.216472
K	5.252954	1.466740	0.368558
C	9.183504	2.266949	0.957561
C	10.069981	3.230806	1.474392
C	11.424541	3.174090	1.166179
C	11.936606	2.169665	0.342113
C	11.062843	1.214567	-0.177608
C	9.707038	1.263418	0.122604
O	6.781968	-0.348459	1.534329
C	7.243322	-0.977246	2.730977
C	8.743394	-1.037492	2.776802
C	9.469371	-0.021171	3.404598
C	10.861433	-0.014755	3.366835
C	11.543822	-1.032497	2.704826
C	10.830329	-2.054993	2.079786
C	9.438676	-2.053817	2.113935
H	5.972420	3.714573	3.091254
H	9.678735	4.011580	2.117824
H	12.093277	3.928478	1.575674
H	12.997157	2.133280	0.109234
H	11.441343	0.415308	-0.810812
H	9.031361	0.500014	-0.261101
H	6.806777	-1.981676	2.737600
H	6.860528	-0.435770	3.610521
H	8.934485	0.788817	3.898919
H	11.411479	0.796482	3.835600

H	12.629748	-1.022380	2.665038
H	11.360012	-2.849966	1.561204
H	8.878721	-2.843058	1.615079
H	7.282412	0.509199	1.461248

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Int3-TS

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N	6.184601	2.939435	2.423946
N	7.428332	3.095694	2.122499
N	7.931252	2.110945	1.405839
K	4.806725	1.111567	0.910751
C	9.278066	2.197643	1.024447
C	10.105821	3.281608	1.344361
C	11.434546	3.274315	0.933088
C	11.954885	2.202695	0.206417
C	11.124449	1.128682	-0.111668
C	9.793343	1.123250	0.286729
O	6.828556	-0.207955	1.433208
C	7.204713	-0.943729	2.549982
C	8.706694	-1.025170	2.704325
C	9.395727	-0.109029	3.503995
C	10.788240	-0.114231	3.566763
C	11.514153	-1.051198	2.834681
C	10.839533	-1.979502	2.040809
C	9.448640	-1.961684	1.976659
H	5.967013	3.761870	2.989525
H	9.702157	4.109847	1.916210
H	12.072721	4.116808	1.188081
H	12.995785	2.204026	-0.104076
H	11.516653	0.278697	-0.664292
H	9.143585	0.278839	0.068260
H	6.804026	-1.975124	2.487801
H	6.794066	-0.515320	3.493133
H	8.827093	0.631926	4.066279
H	11.307148	0.619768	4.178499
H	12.600263	-1.054238	2.876366
H	11.401133	-2.715170	1.469478
H	8.920361	-2.675552	1.346000
H	7.446516	1.074384	1.414806

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Int4

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N	-2.190581	2.430546	1.100510
N	-1.056496	2.525827	0.498454

N	-0.665973	1.433018	-0.112760
K	-3.882302	0.265539	1.242504
C	0.587991	1.418702	-0.737576
C	1.498618	2.477829	-0.639165
C	2.735461	2.377817	-1.266162
C	3.084812	1.233602	-1.984340
C	2.172534	0.184317	-2.080072
C	0.927281	0.274999	-1.469700
O	-1.963623	-0.872959	0.338528
C	-1.220178	-2.004450	0.147488
C	0.144641	-2.002838	0.818342
C	0.476310	-1.048809	1.781351
C	1.745613	-1.026174	2.359446
C	2.703707	-1.966066	1.986849
C	2.379669	-2.933352	1.033738
C	1.113196	-2.946612	0.457843
H	-2.321881	3.361327	1.501831
H	1.231039	3.359135	-0.067213
H	3.439453	3.201703	-1.182588
H	4.058427	1.160121	-2.459758
H	2.429433	-0.717104	-2.629811
H	0.213585	-0.540933	-1.543900
H	-1.035187	-2.224350	-0.932422
H	-1.751262	-2.917398	0.505066
H	-0.272106	-0.306189	2.050919
H	1.990758	-0.263818	3.095510
H	3.696692	-1.942506	2.427863
H	3.121867	-3.668391	0.731087
H	0.870375	-3.690088	-0.301929
H	-1.201930	0.498114	0.006298

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Int4-TS1

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H	-6.353170	-1.808548	-1.533171
N	-5.595550	-1.553388	-0.603991
N	-4.577285	-1.197092	-1.184645
N	-3.415636	-1.031657	-0.306846
C	-2.204723	-1.326015	-0.929178
C	-1.889585	-0.726392	-2.162063
C	-0.706375	-1.046544	-2.820391
C	0.200113	-1.945325	-2.257658
C	-0.092281	-2.515216	-1.018024
C	-1.284750	-2.222143	-0.364174
H	-3.589227	-1.517298	0.572997
H	-2.559217	0.033326	-2.558217

H	-0.474915	-0.567584	-3.769007
H	1.127651	-2.183903	-2.768675
H	0.608520	-3.208401	-0.560207
H	-1.516914	-2.692687	0.588684
K	-4.808266	-1.379832	-3.954322
O	-6.902237	-2.246572	-2.641635
C	-6.908925	-3.638032	-2.572984
C	-5.658023	-4.164038	-3.246618
C	-5.631113	-4.379792	-4.631764
C	-4.428701	-4.608873	-5.303933
C	-3.223639	-4.623542	-4.597357
C	-3.235985	-4.438660	-3.212941
C	-4.442054	-4.217652	-2.548118
H	-7.799281	-4.061208	-3.073110
H	-6.933557	-4.000911	-1.526475
H	-6.569487	-4.352877	-5.184667
H	-4.430490	-4.780684	-6.377936
H	-2.284746	-4.793444	-5.117302
H	-2.303854	-4.453937	-2.653155
H	-4.445297	-4.051977	-1.472115

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Int4-TS2

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N	-0.818651	-0.025029	-0.646703
N	-0.062658	0.938776	-0.453706
N	0.865238	1.143440	-1.474898
K	-1.867122	-2.460999	-0.664251
C	1.712251	2.238019	-1.502355
C	1.790138	3.135811	-0.424435
C	2.665877	4.212898	-0.486721
C	3.477514	4.424255	-1.602236
C	3.398518	3.531549	-2.670069
C	2.527219	2.448942	-2.626420
O	-2.186757	-0.735784	1.333972
C	-1.316606	-1.004211	2.394899
C	-0.555148	-2.278712	2.102470
C	0.659267	-2.246395	1.402258
C	1.255293	-3.423182	0.945889
C	0.647123	-4.657084	1.182873
C	-0.554596	-4.706279	1.894150
C	-1.145952	-3.526827	2.347205
H	-1.552009	-0.237661	0.448158
H	1.159146	2.975312	0.442107
H	2.713043	4.900028	0.354400
H	4.158054	5.269363	-1.638750

H	4.019770	3.676587	-3.550238
H	2.470416	1.757442	-3.464655
H	-1.886319	-1.121577	3.331084
H	-0.598630	-0.179897	2.555766
H	1.125448	-1.284404	1.198006
H	2.198693	-3.376751	0.407675
H	1.114028	-5.573976	0.833534
H	-1.022071	-5.665232	2.105094
H	-2.085765	-3.562981	2.896735
H	0.755198	0.545116	-2.294604

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Int4-TS3

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H	1.105748	-0.901168	1.197904
N	0.805699	-1.874562	1.310204
C	-0.543291	-1.959692	1.665195
C	-1.190153	-3.206108	1.666975
C	-2.521686	-3.303502	2.056429
C	-3.228799	-2.173316	2.468441
C	-2.588977	-0.933694	2.469294
C	-1.264779	-0.821150	2.058653
K	3.210704	-2.309222	2.584341
O	3.468729	-0.622542	0.843540
H	2.733020	-1.510565	-0.116805
N	2.110005	-2.254937	-0.679574
N	1.081652	-2.592059	-0.153842
C	3.556516	0.636860	0.270389
C	2.241243	1.377305	0.393823
C	1.965428	2.175466	1.509546
C	0.720937	2.783222	1.670365
C	-0.276572	2.595352	0.713752
C	-0.019916	1.796582	-0.400413
C	1.228621	1.197053	-0.556842
H	-0.639600	-4.085110	1.343478
H	-3.011355	-4.274032	2.042808
H	-4.265644	-2.257250	2.780278
H	-3.128297	-0.041688	2.778438
H	-0.774158	0.150848	2.037292
H	3.826570	0.585097	-0.805418
H	4.349659	1.242920	0.750595
H	2.746048	2.326680	2.254374
H	0.529355	3.408066	2.539499
H	-1.248498	3.065901	0.836493
H	-0.793488	1.640835	-1.147890
H	1.427283	0.578209	-1.431328

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Int5

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K	2.215931	-0.885829	-3.324324
O	1.624945	-2.219588	-5.444624
C	2.689768	-2.158474	-6.272727
C	2.420450	-1.576289	-7.654145
C	1.154208	-1.099775	-7.995770
C	0.912942	-0.517126	-9.242414
C	1.943552	-0.409016	-10.174503
C	3.213189	-0.896181	-9.849993
C	3.442670	-1.473390	-8.605103
H	3.183584	-3.147156	-6.447969
H	3.541292	-1.527559	-5.872935
H	0.367611	-1.174863	-7.246371
H	-0.081368	-0.148621	-9.488040
H	1.761495	0.043516	-11.145588
H	4.023195	-0.821016	-10.572080
H	4.438208	-1.837840	-8.350253
N	-0.566841	0.566402	-4.979278
N	0.613007	0.983667	-4.827179
N	1.204001	1.415254	-5.951335
K	-0.742689	-2.438591	-4.796434
C	2.578519	1.669360	-5.939494
C	3.245298	1.974529	-4.744431
C	4.621214	2.180992	-4.759040
C	5.340155	2.107732	-5.952311
C	4.662770	1.833378	-7.139919
C	3.289433	1.615834	-7.142246
O	-0.428225	-1.136566	-2.673257
C	-0.671023	-0.635464	-1.417218
C	0.584564	0.036988	-0.897982
C	0.915148	1.333819	-1.315527
C	2.157790	1.892309	-1.018130
C	3.103246	1.157522	-0.298177
C	2.783745	-0.129090	0.139163
C	1.534769	-0.678624	-0.158110
H	-0.806280	0.220816	-4.026088
H	2.677370	2.063586	-3.822370
H	5.130195	2.415555	-3.827101
H	6.413646	2.269298	-5.957290
H	5.206989	1.768051	-8.078202
H	2.770860	1.365422	-8.065844
H	-0.971355	-1.418285	-0.684081
H	-1.495115	0.115640	-1.399997

H	0.188348	1.899157	-1.897304
H	2.391574	2.903323	-1.345255
H	4.072045	1.590996	-0.064865
H	3.505700	-0.700109	0.718432
H	1.286433	-1.684628	0.178822
H	0.749357	1.181210	-6.834172

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Int5-TS

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K	2.426713	-0.716864	-3.519381
O	1.778406	-2.352884	-5.377439
C	2.807100	-2.248963	-6.249047
C	2.471889	-1.643940	-7.606267
C	1.208389	-1.114308	-7.869317
C	0.912518	-0.526139	-9.101209
C	1.885970	-0.458192	-10.095272
C	3.156214	-0.985512	-9.844969
C	3.438948	-1.573102	-8.616153
H	3.316796	-3.221113	-6.460916
H	3.660925	-1.607164	-5.870522
H	0.470070	-1.121826	-7.069611
H	-0.077719	-0.111067	-9.280194
H	1.661957	0.000780	-11.054475
H	3.924466	-0.936423	-10.613306
H	4.433541	-1.975688	-8.422614
N	-0.502073	0.300894	-4.938436
N	0.517172	0.956058	-4.757885
N	1.034381	1.658399	-5.938080
K	-0.642197	-2.555382	-4.999185
C	2.415385	1.844564	-5.916623
C	3.050277	2.237784	-4.722809
C	4.436026	2.366719	-4.673559
C	5.214382	2.142050	-5.809586
C	4.581095	1.789305	-7.002581
C	3.200716	1.632816	-7.060674
O	-0.449268	-1.073738	-2.830098
C	-0.669734	-0.386927	-1.624290
C	0.634926	0.136620	-1.076290
C	1.094250	1.414725	-1.417288
C	2.367667	1.840698	-1.035863
C	3.204216	0.990722	-0.312467
C	2.753767	-0.282700	0.043605
C	1.478400	-0.701059	-0.335153
H	-0.572489	-0.353077	-3.726105
H	2.439938	2.449149	-3.849500

H	4.907556	2.668320	-3.739947
H	6.294022	2.250639	-5.769301
H	5.168182	1.609261	-7.899869
H	2.724684	1.318897	-7.987451
H	-1.132865	-1.065150	-0.890488
H	-1.368806	0.454592	-1.772095
H	0.454020	2.067437	-2.007374
H	2.710040	2.836126	-1.308726
H	4.195872	1.322049	-0.016954
H	3.393746	-0.943831	0.622347
H	1.127305	-1.695284	-0.062868
H	0.659541	1.252009	-6.796768

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PhNHK

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K	-2.549895	0.511668	-1.067707
N	-1.574858	2.212220	0.583204
H	-1.000650	3.045157	0.462056
C	-0.821907	1.255003	1.167392
C	0.592687	1.323727	1.391798
C	1.313169	0.260721	1.907853
C	0.696388	-0.953046	2.248203
C	-0.685531	-1.045845	2.086308
C	-1.425703	0.012893	1.565368
H	1.104514	2.252688	1.140098
H	2.387178	0.373619	2.050291
H	1.271052	-1.779409	2.654282
H	-1.205466	-1.952363	2.394885
H	-2.518110	-0.044711	1.577156

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N_2

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N	0.995285	-0.035772	0.072446
N	2.104946	-0.035772	0.072446

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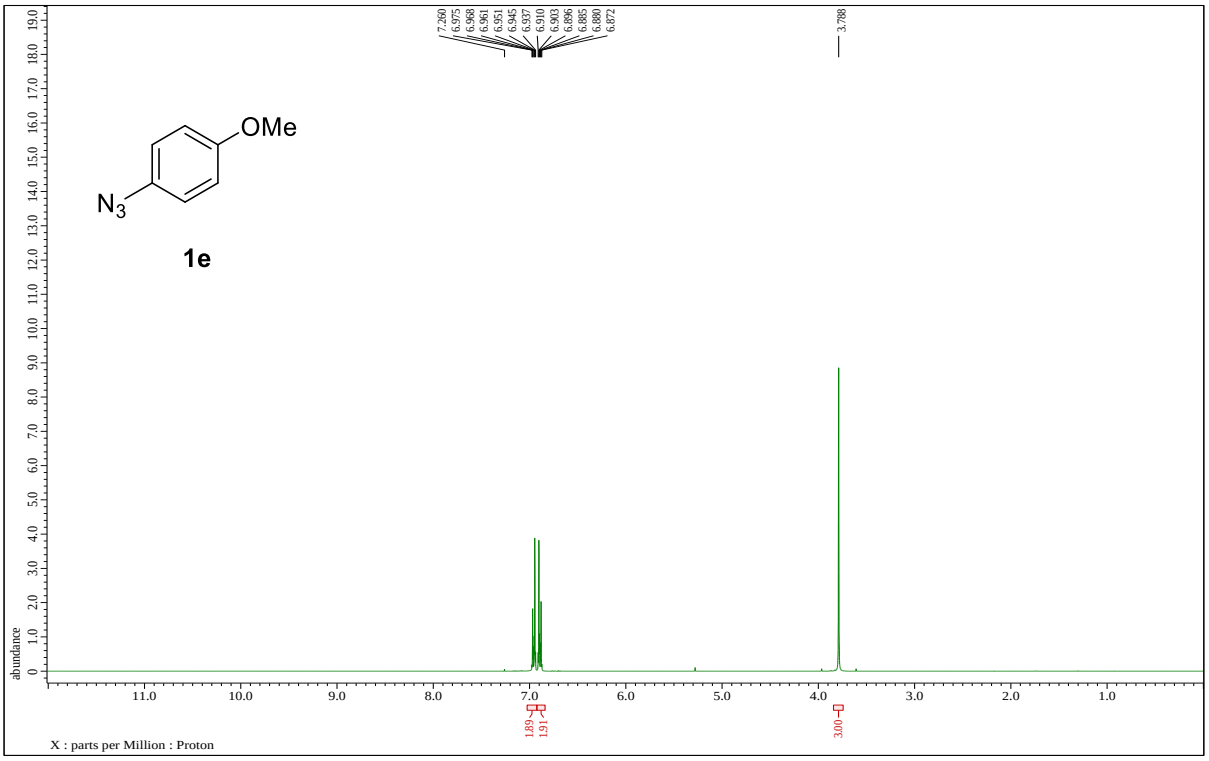
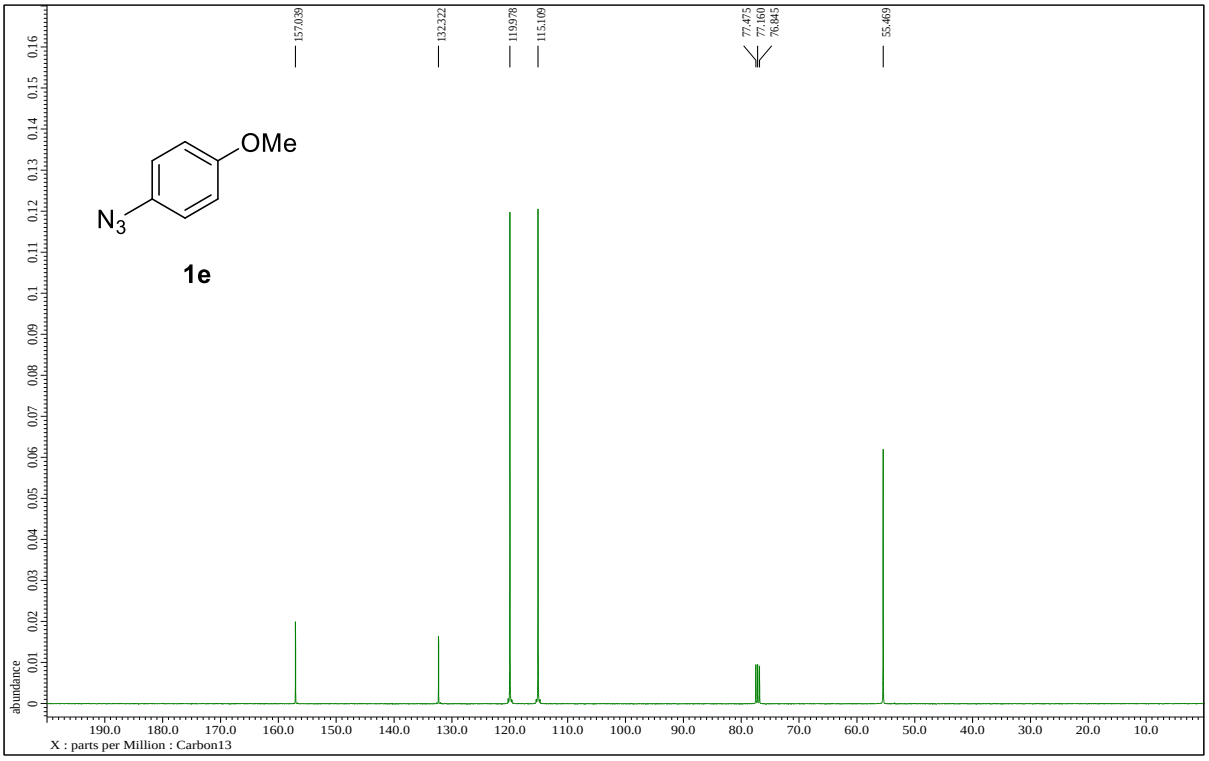
^{1}H-NMR and ^{13}C-NMR spectra of all compounds

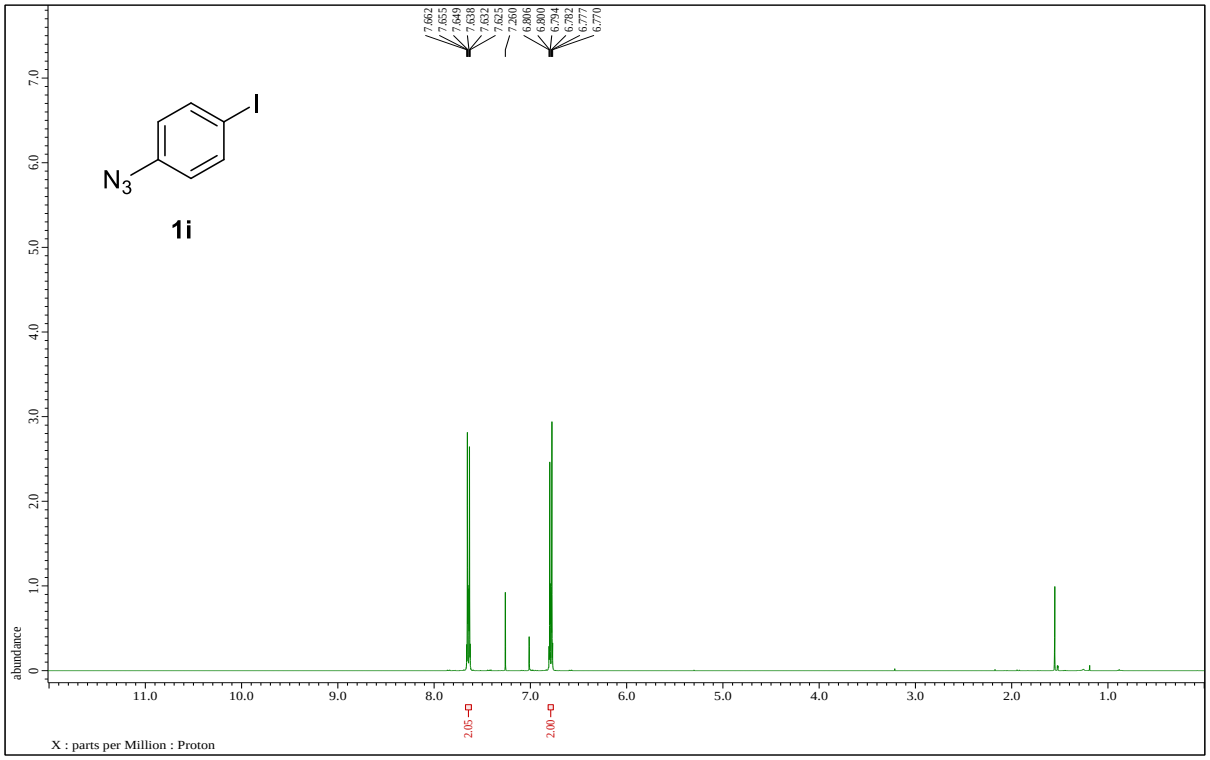
^{1}H-NMR of compound **1e** ($CDCl_3$, 400 MHz)



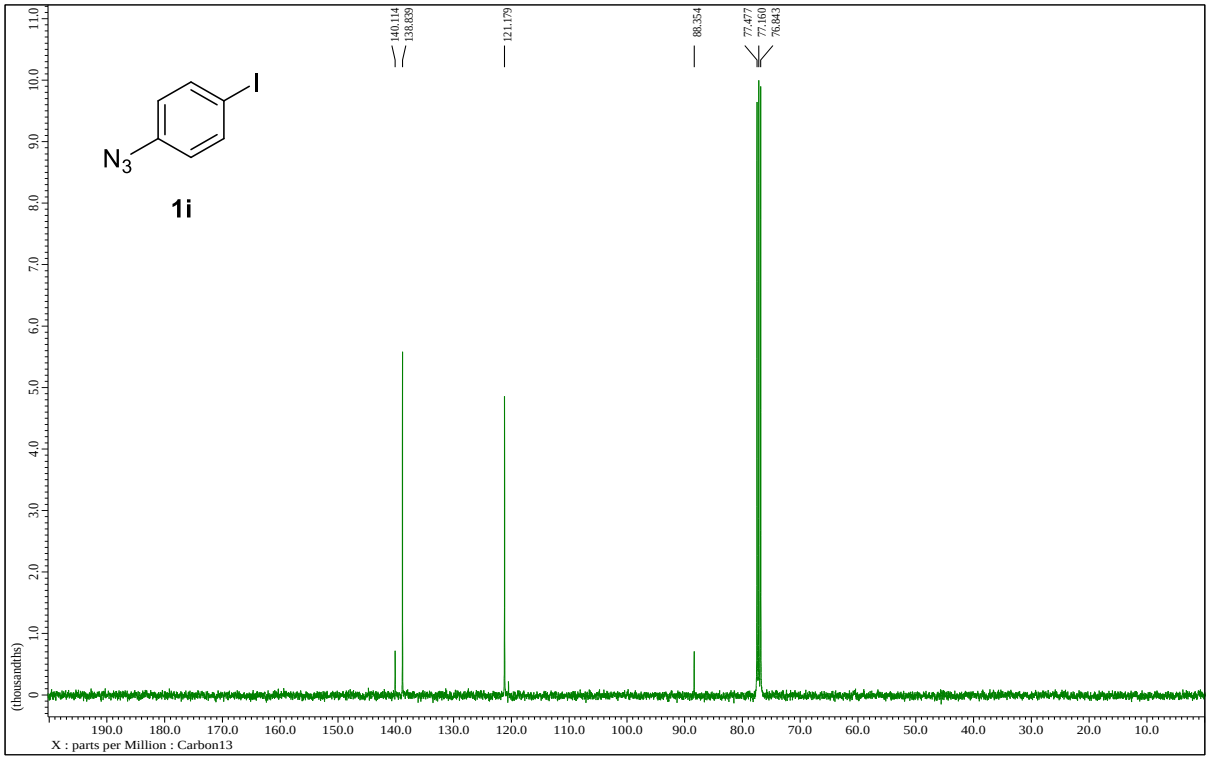
^{13}C-NMR of compound **1e** ($CDCl_3$, 100 MHz)



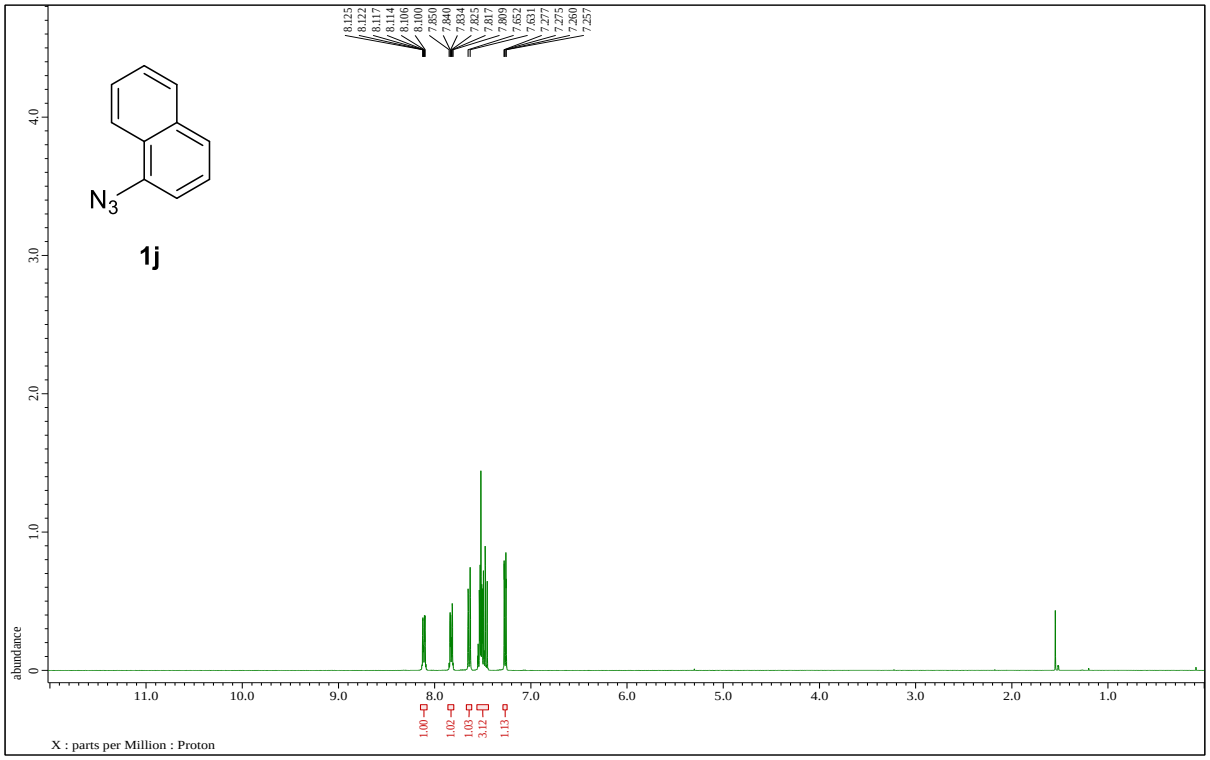
^{1}H-NMR of compound **1i** ($CDCl_3$, 400 MHz)



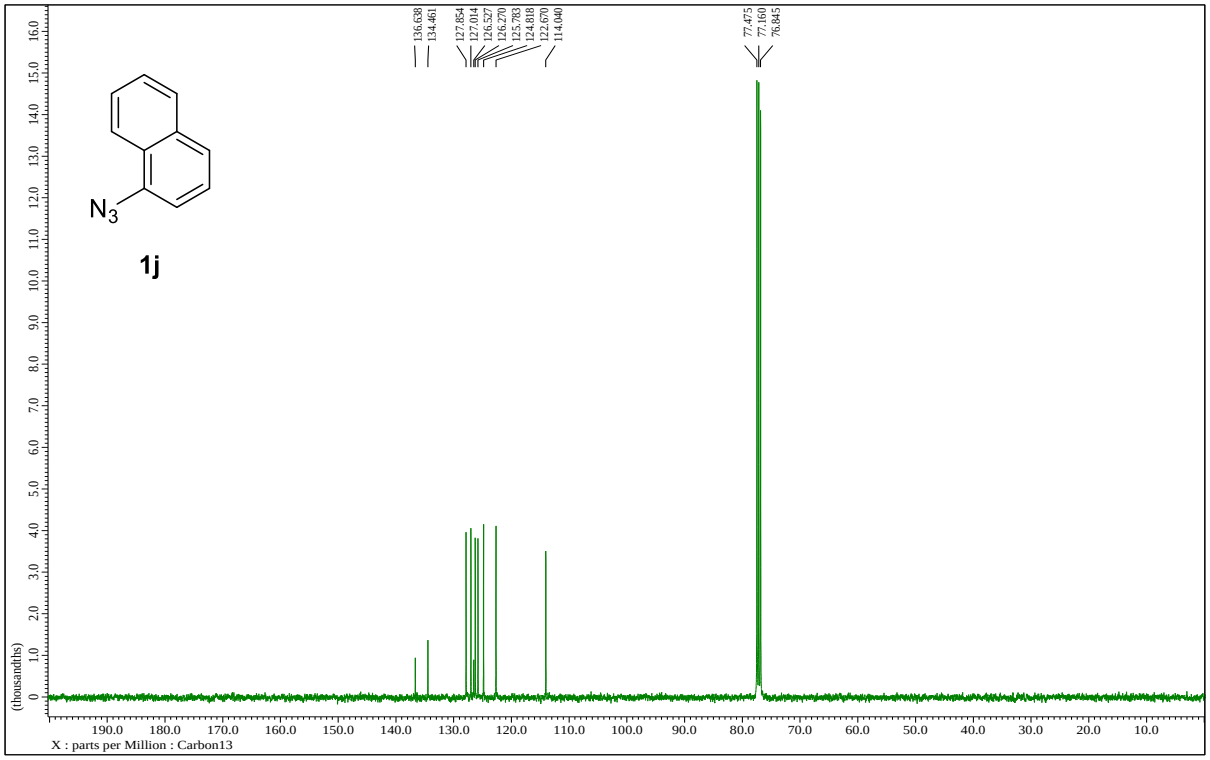
^{13}C-NMR of compound **1i** ($CDCl_3$, 100 MHz)



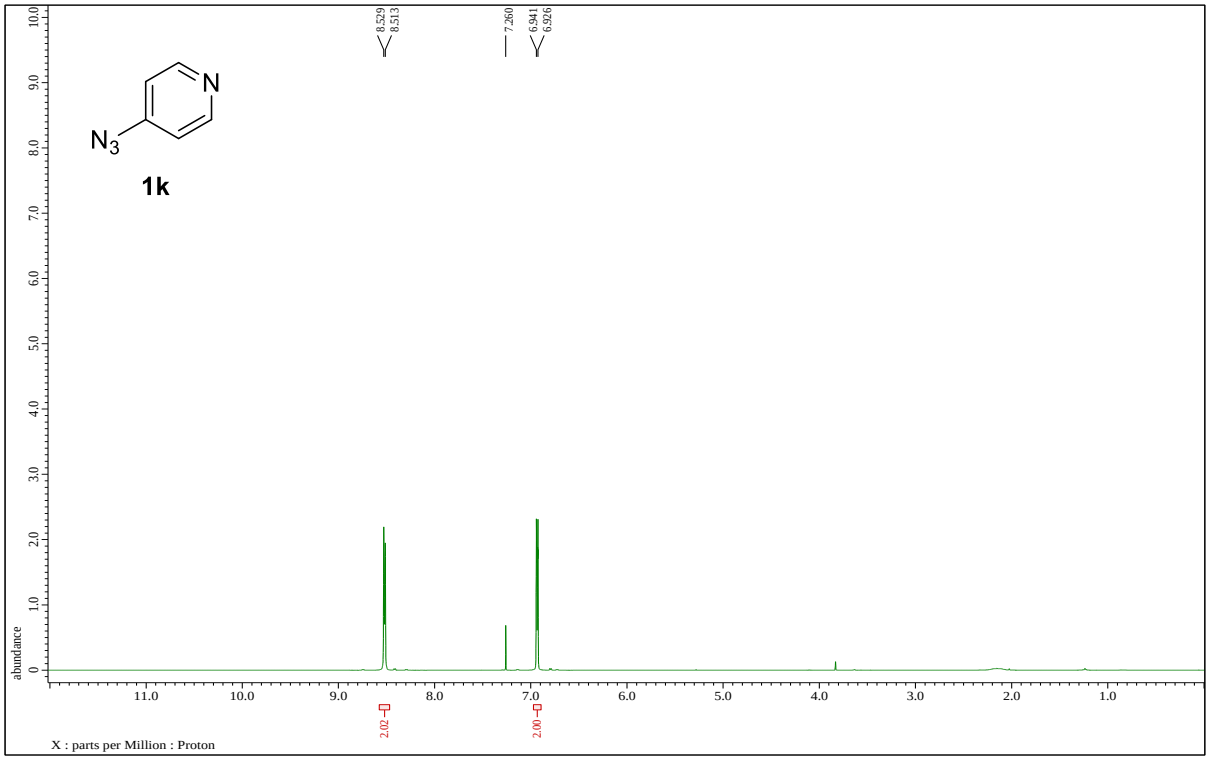
^{1}H-NMR of compound **1j** ($CDCl_3$, 400 MHz)



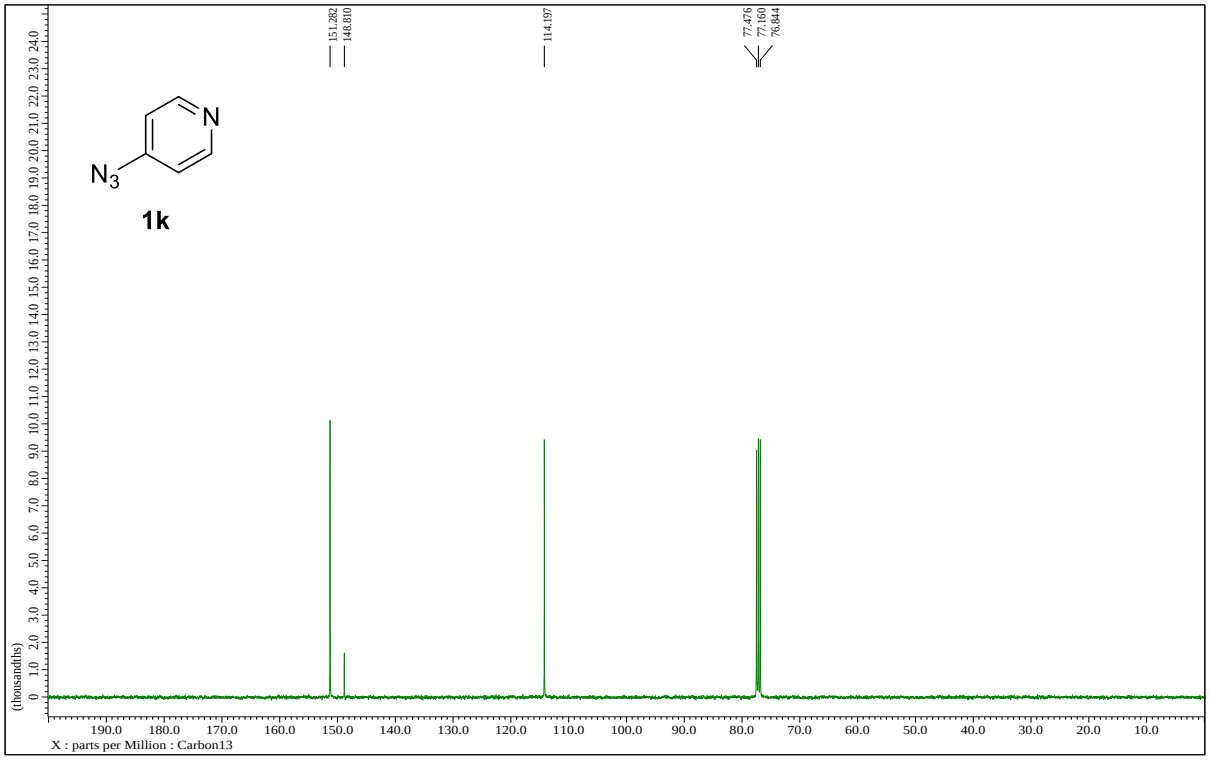
^{13}C-NMR of compound **1j** ($CDCl_3$, 100 MHz)



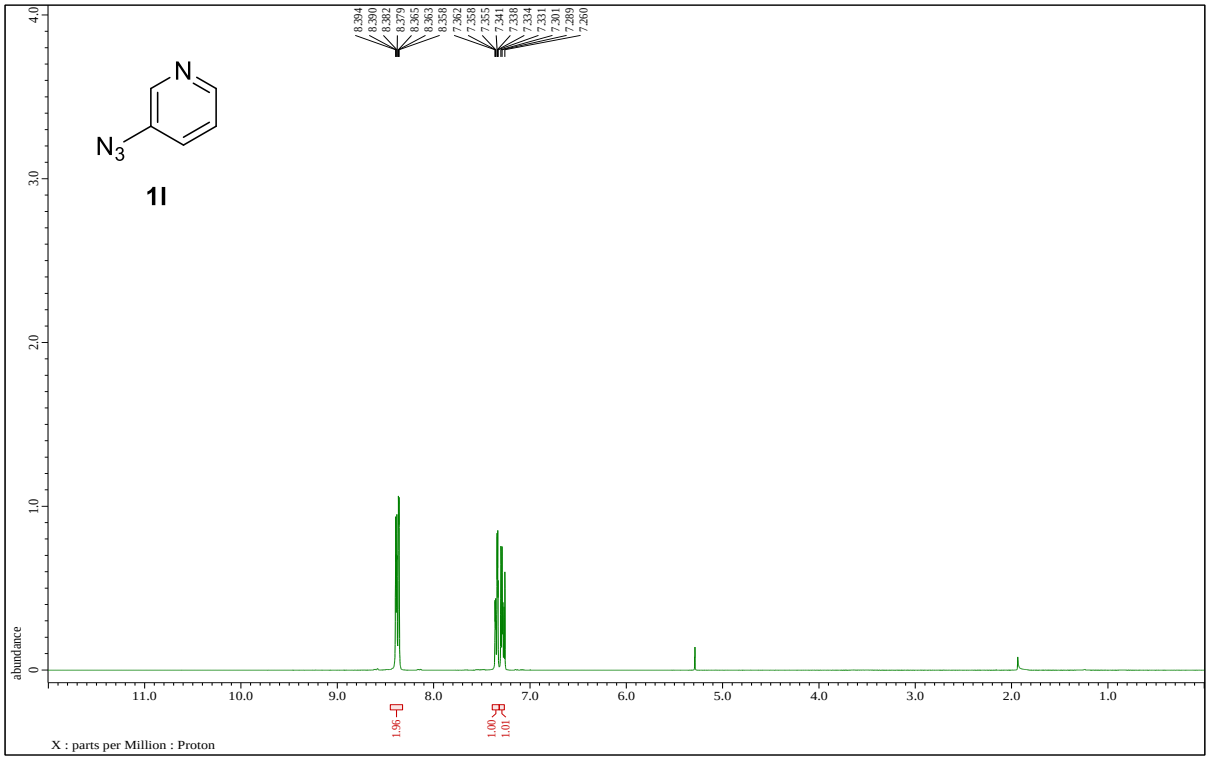
^{1}H-NMR of compound **1k** ($CDCl_3$, 400 MHz)



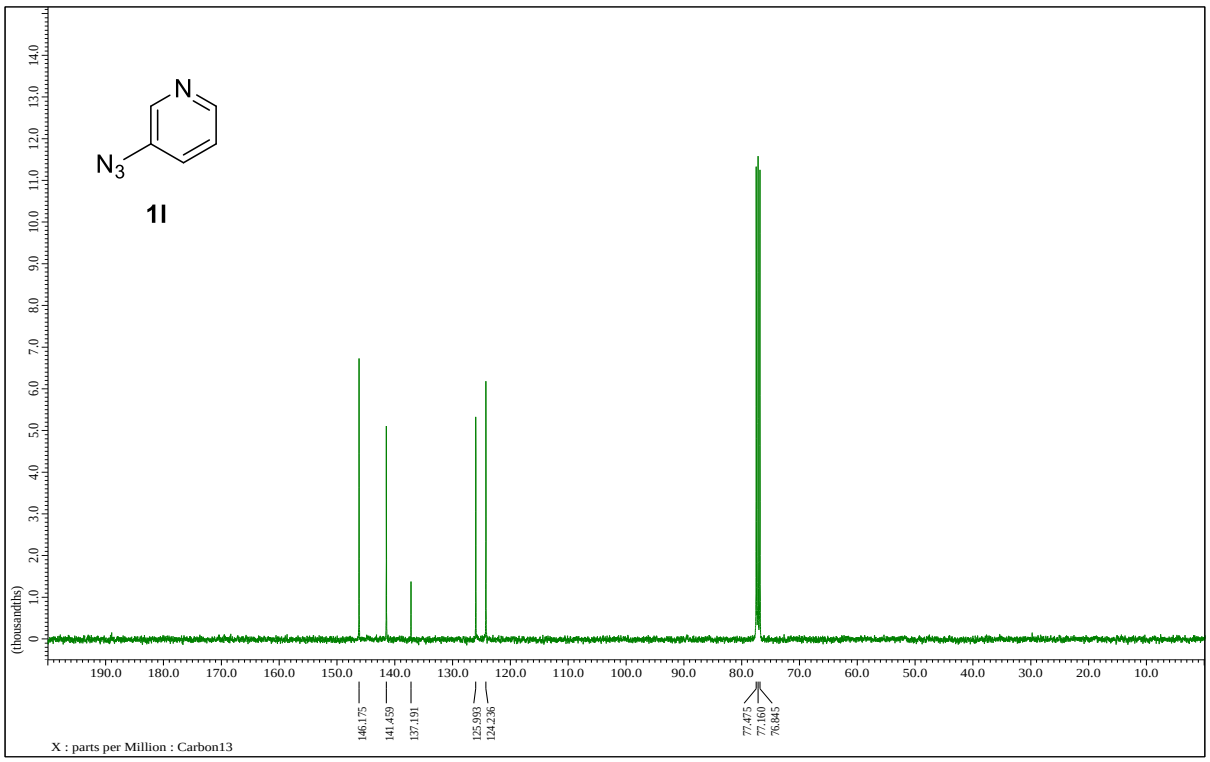
^{13}C-NMR of compound **1k** ($CDCl_3$, 100 MHz)



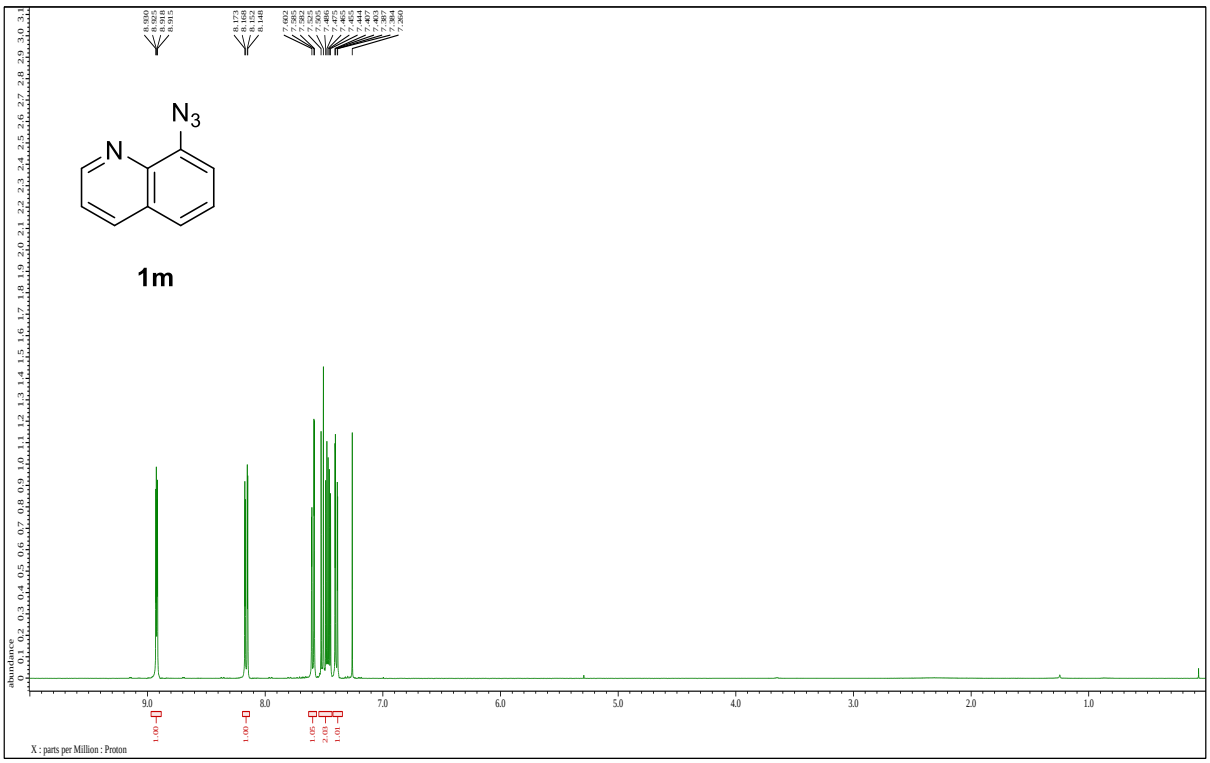
^{1}H-NMR of compound **1l** ($CDCl_3$, 400 MHz)



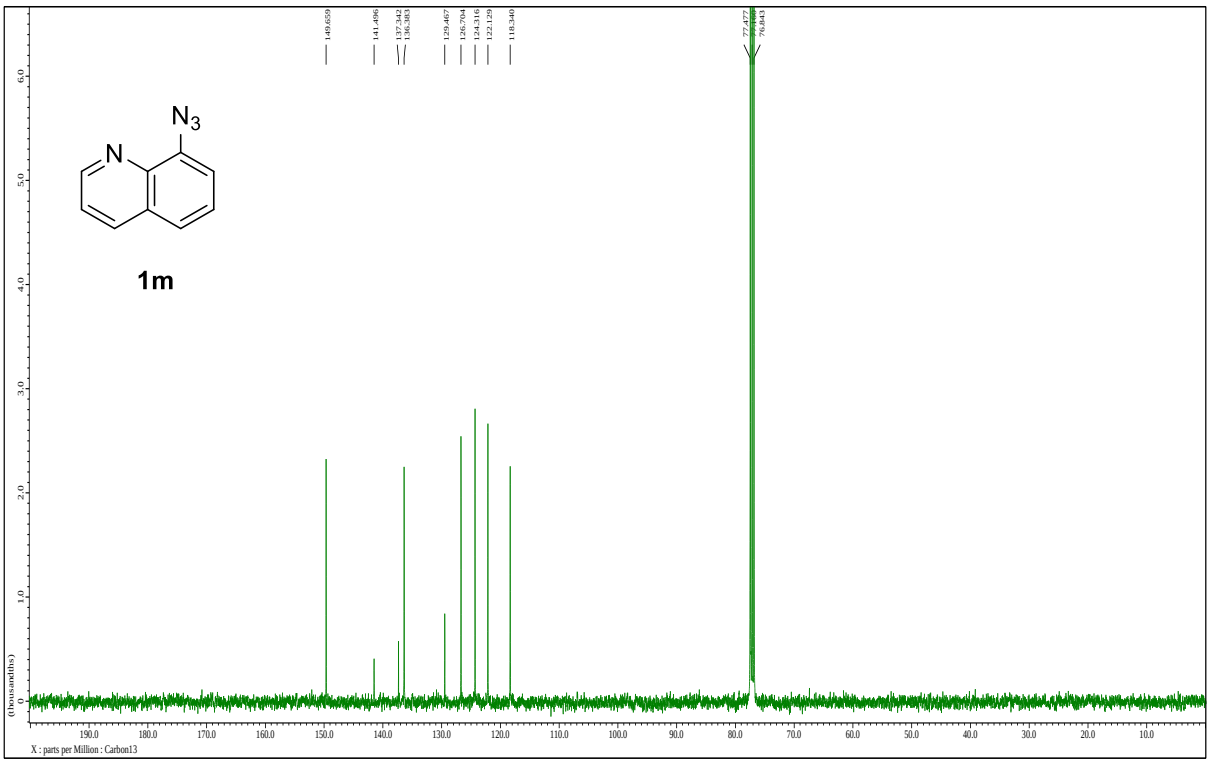
^{13}C-NMR of compound **1l** ($CDCl_3$, 100 MHz)



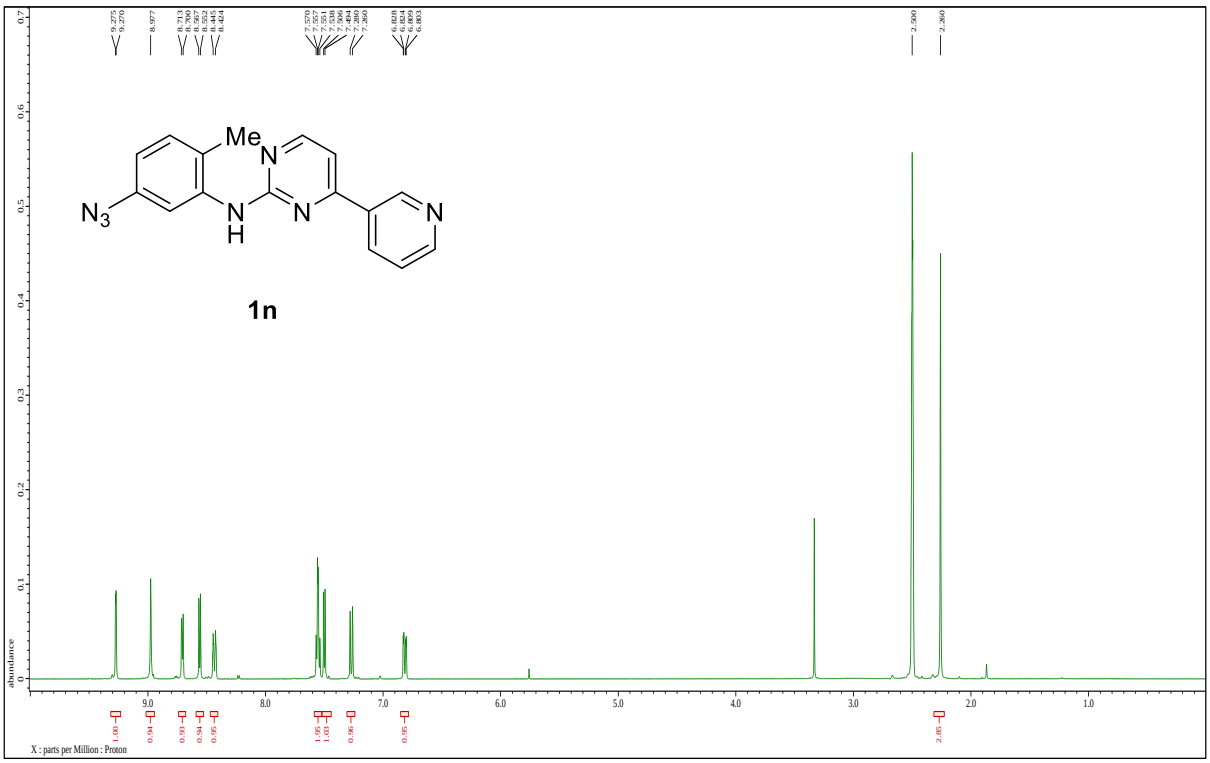
^{1}H-NMR of compound **1m** ($CDCl_3$, 400 MHz)



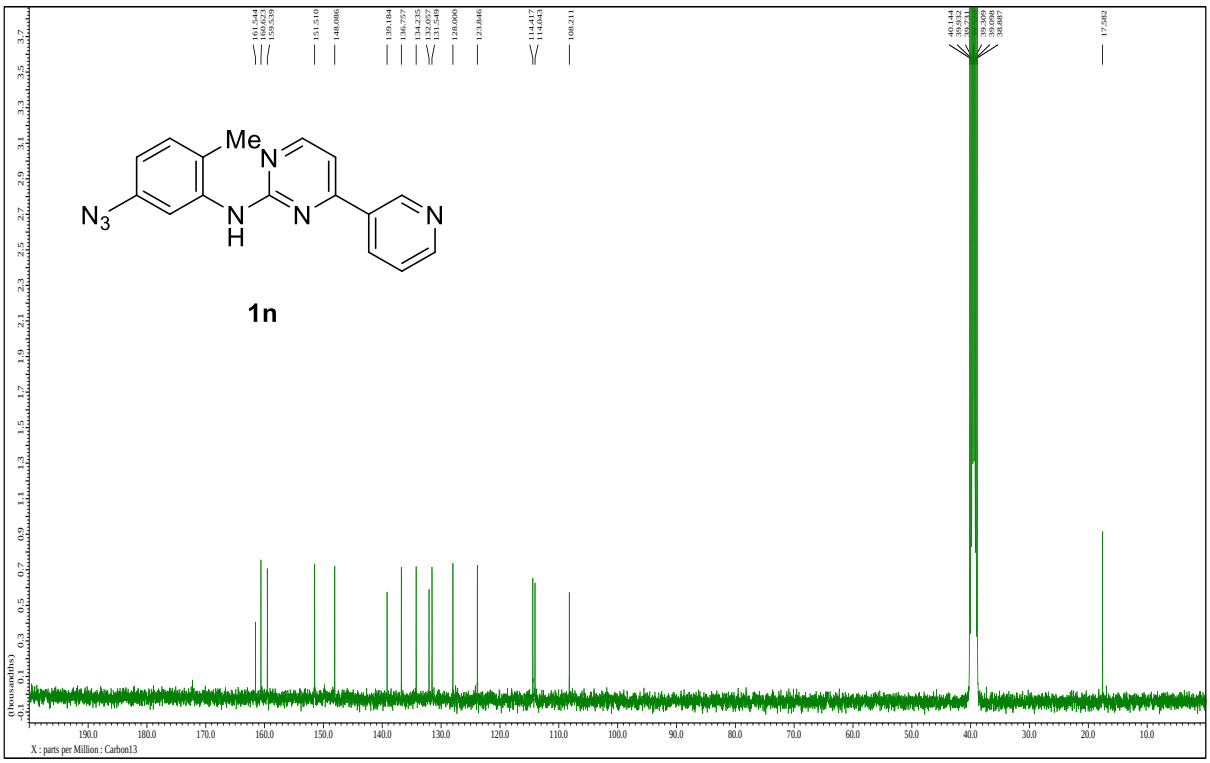
^{13}C-NMR of compound **1m** ($CDCl_3$, 100 MHz)



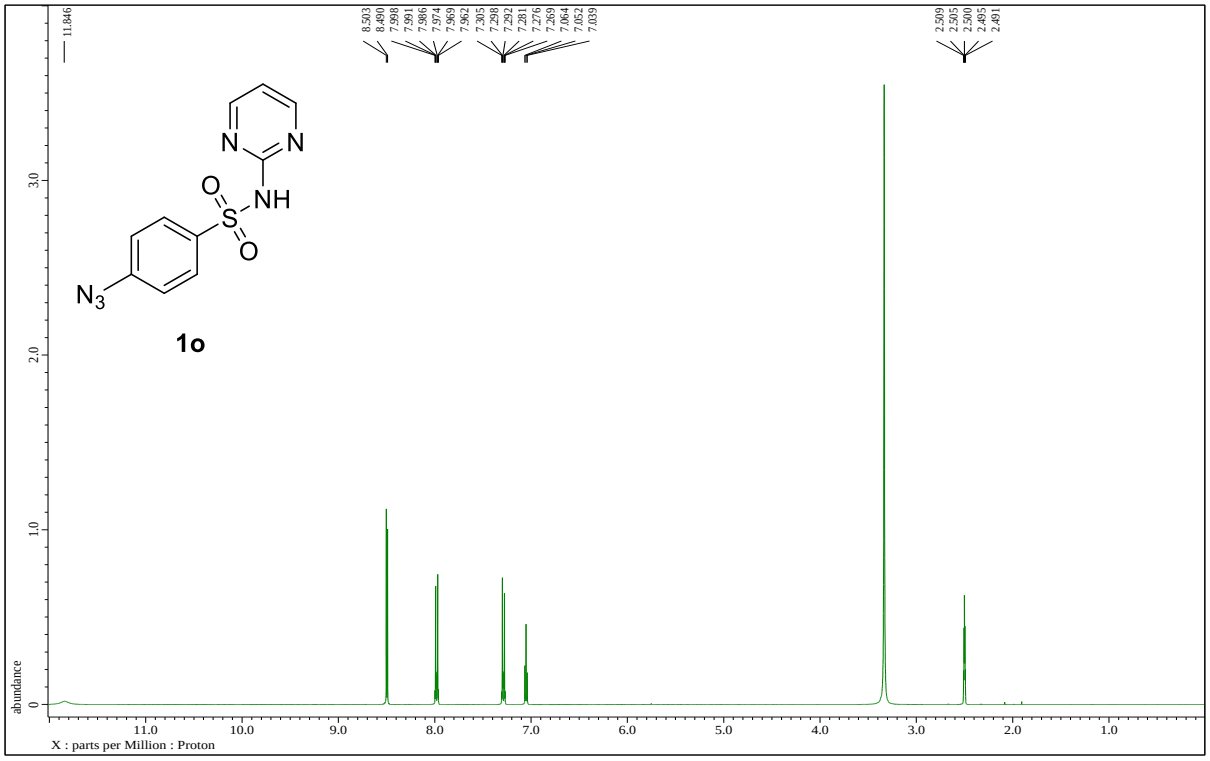
^{1}H-NMR of compound **1n** (DMSO-d_6, 400 MHz)



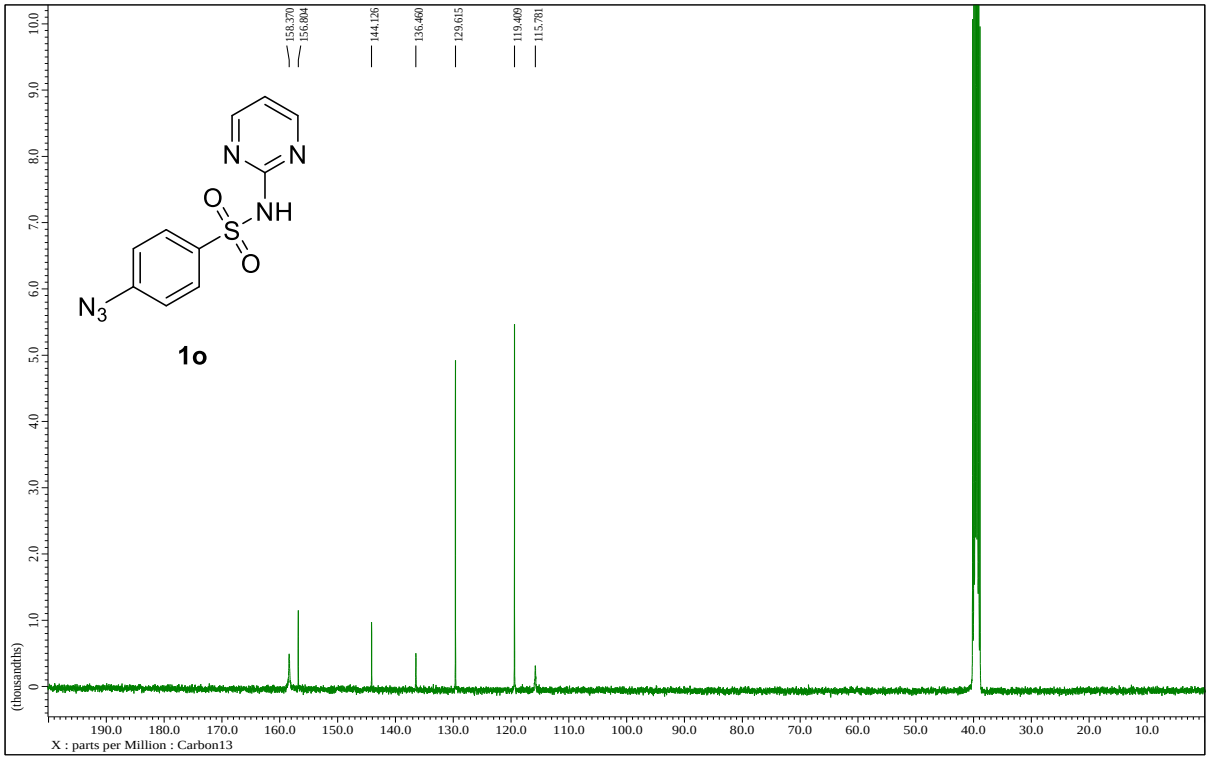
^{13}C-NMR of compound **1n** (DMSO-d_6, 100 MHz)



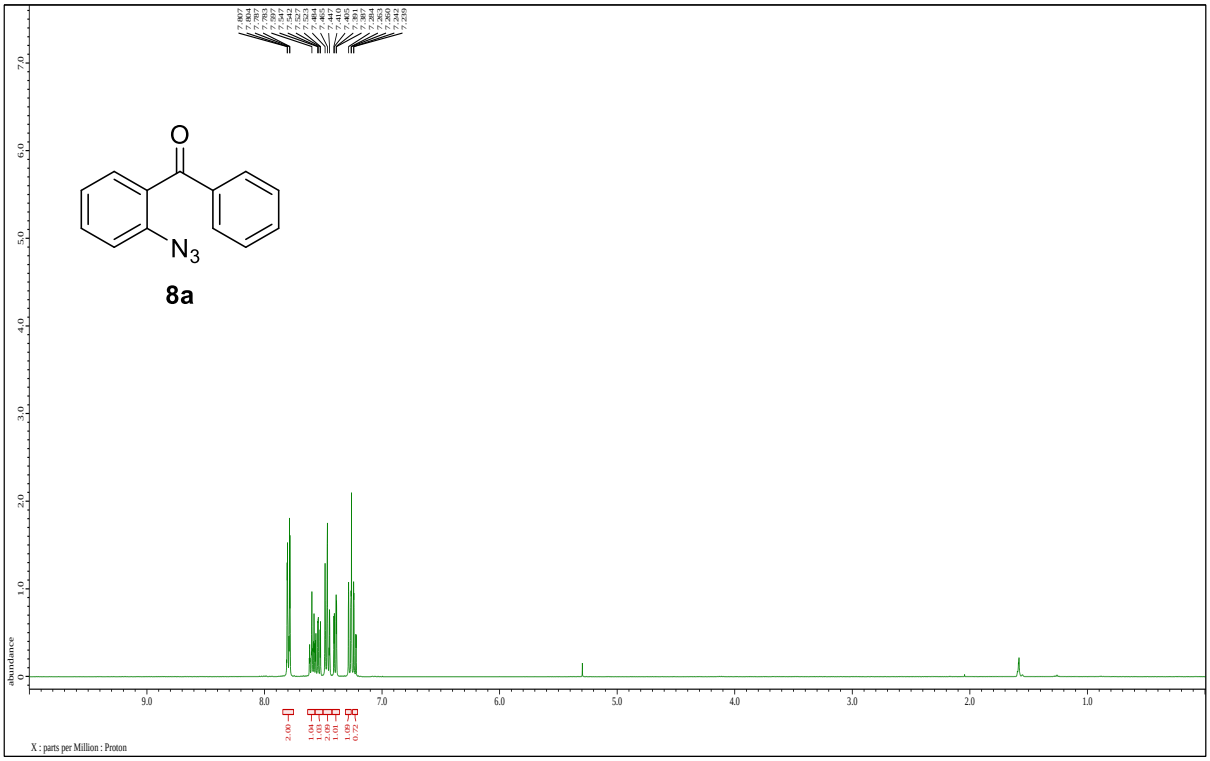
^{1}H-NMR of compound **1o** (DMSO-d_6, 400 MHz)



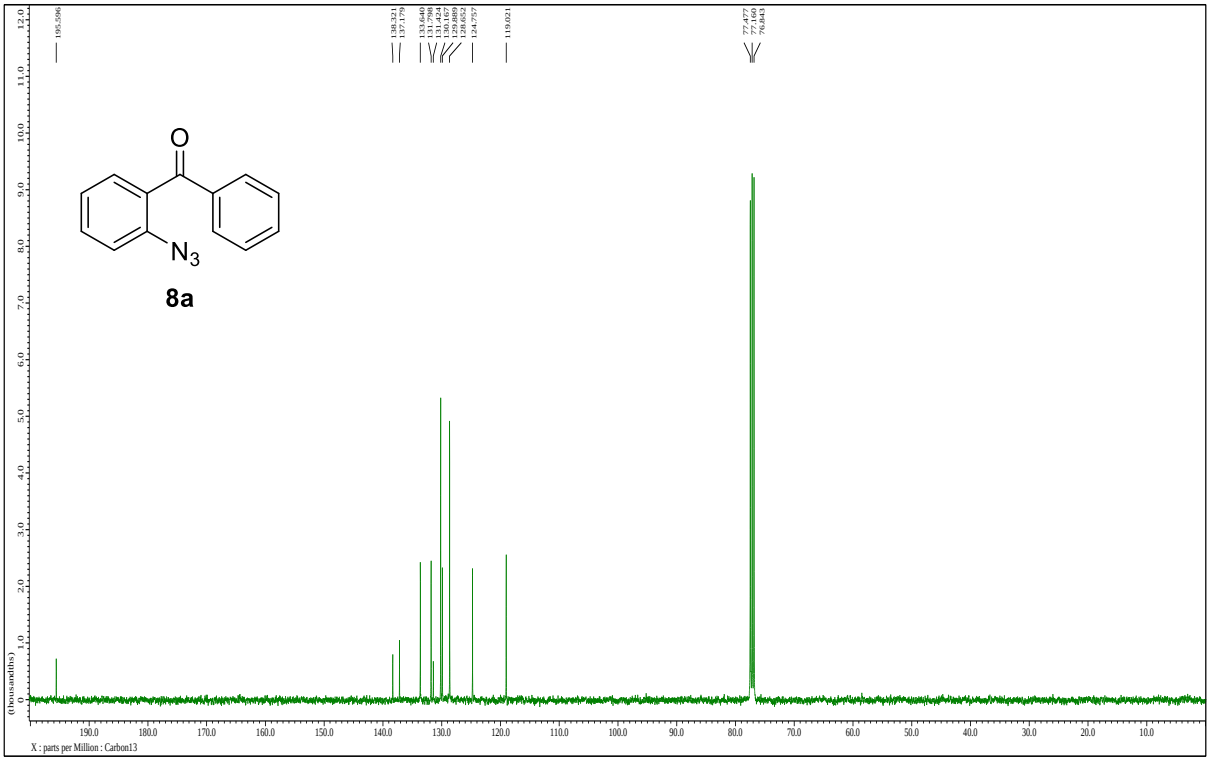
^{13}C-NMR of compound **1o** (DMSO-d_6, 100 MHz)



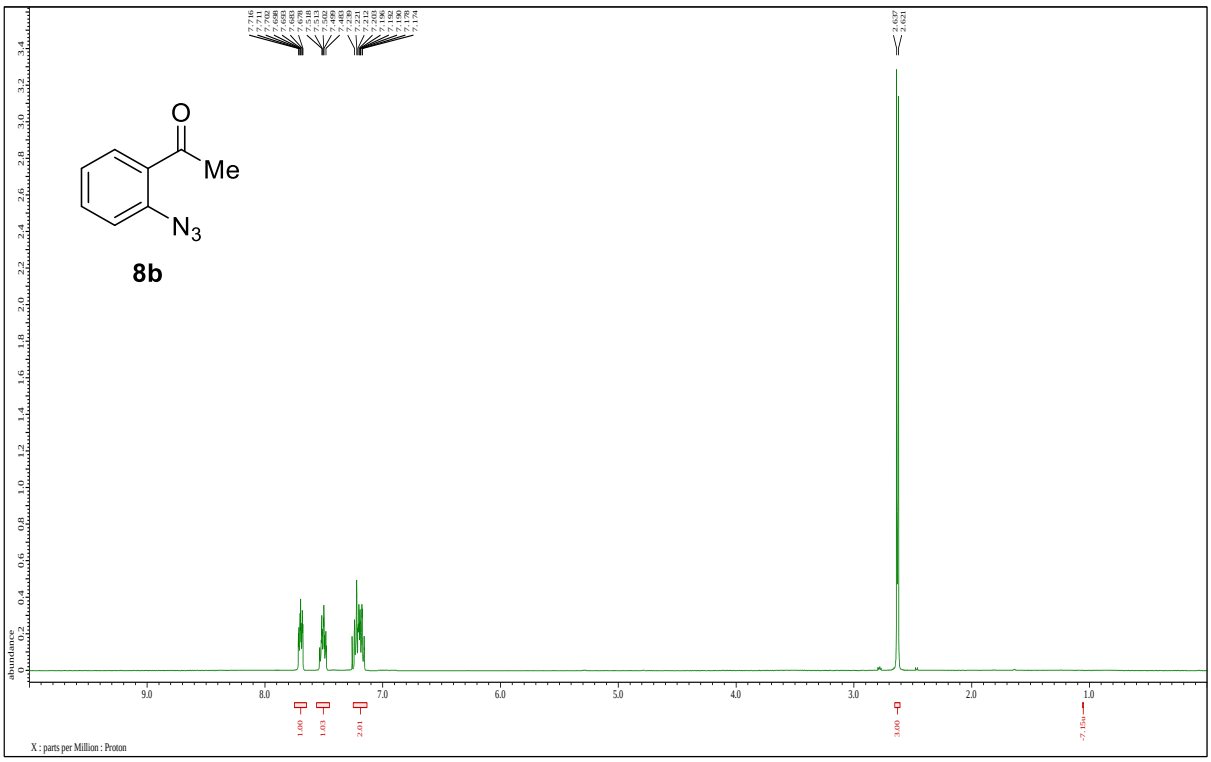
^{1}H-NMR of compound **8a** ($CDCl_3$, 400 MHz)



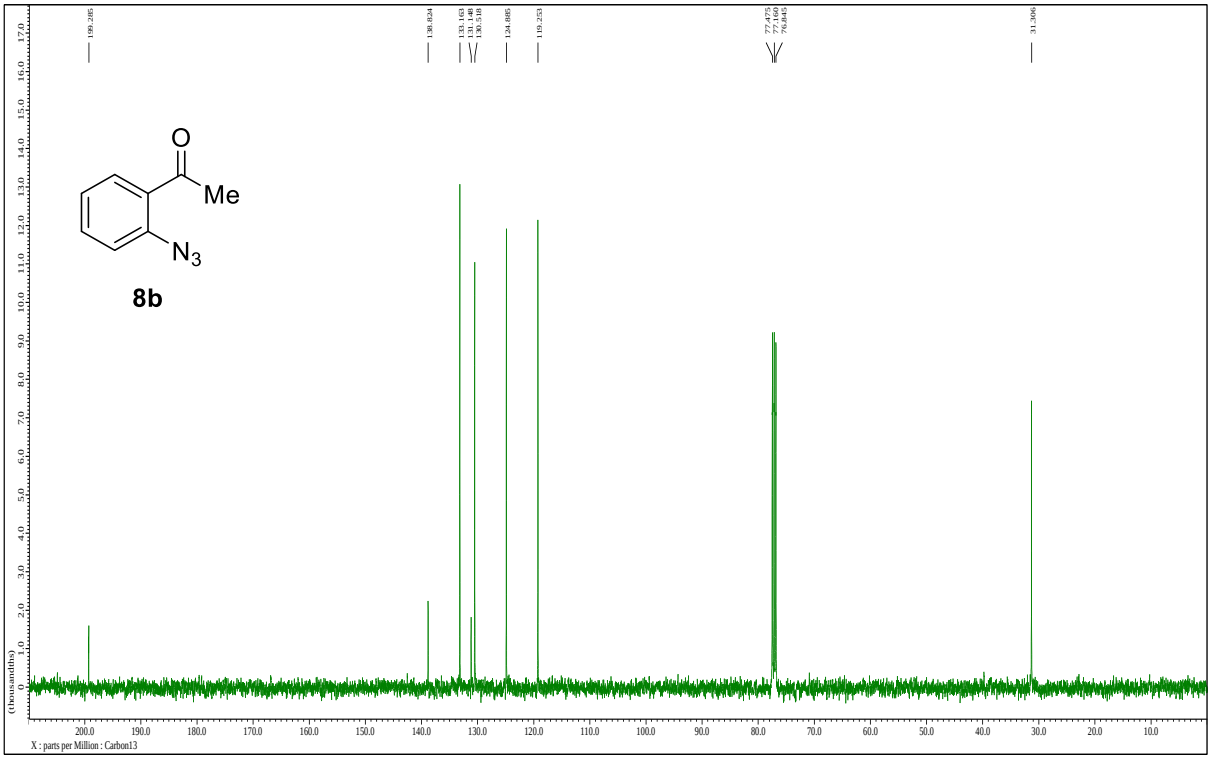
^{13}C-NMR of compound **8a** ($CDCl_3$, 100 MHz)



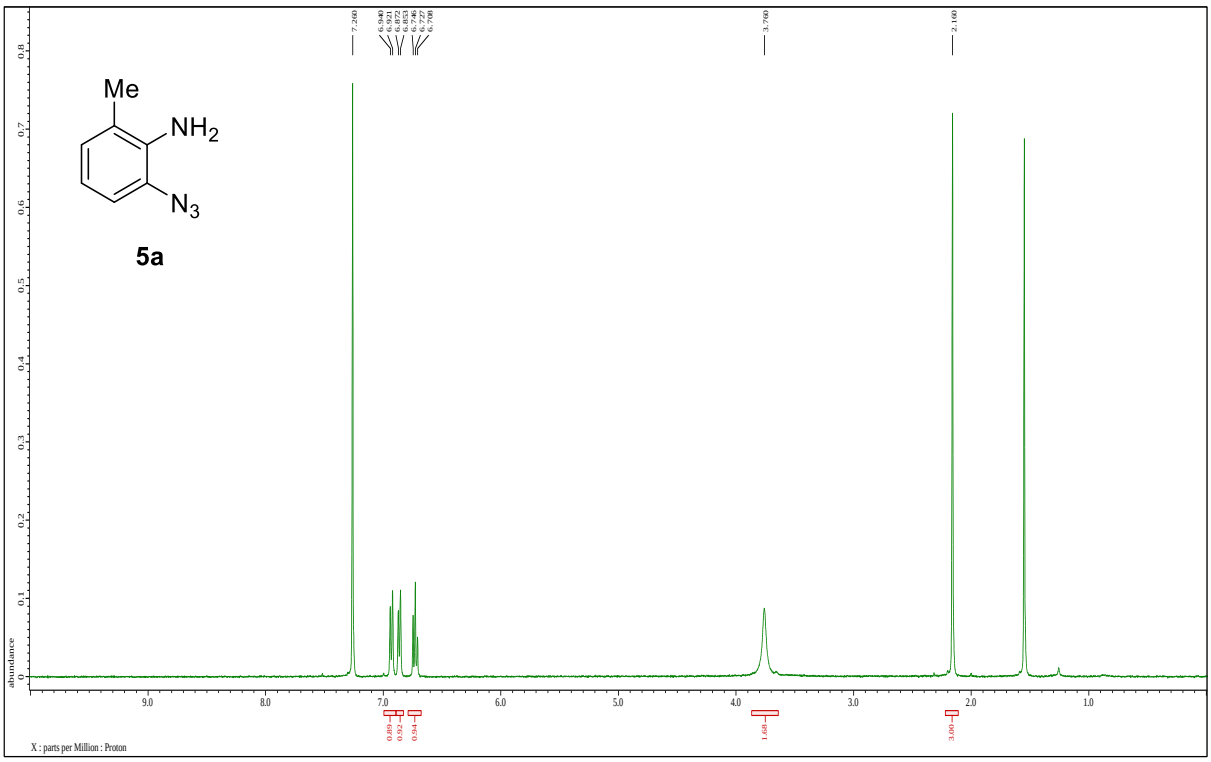
^{1}H-NMR of compound **8b** ($CDCl_3$, 400 MHz)



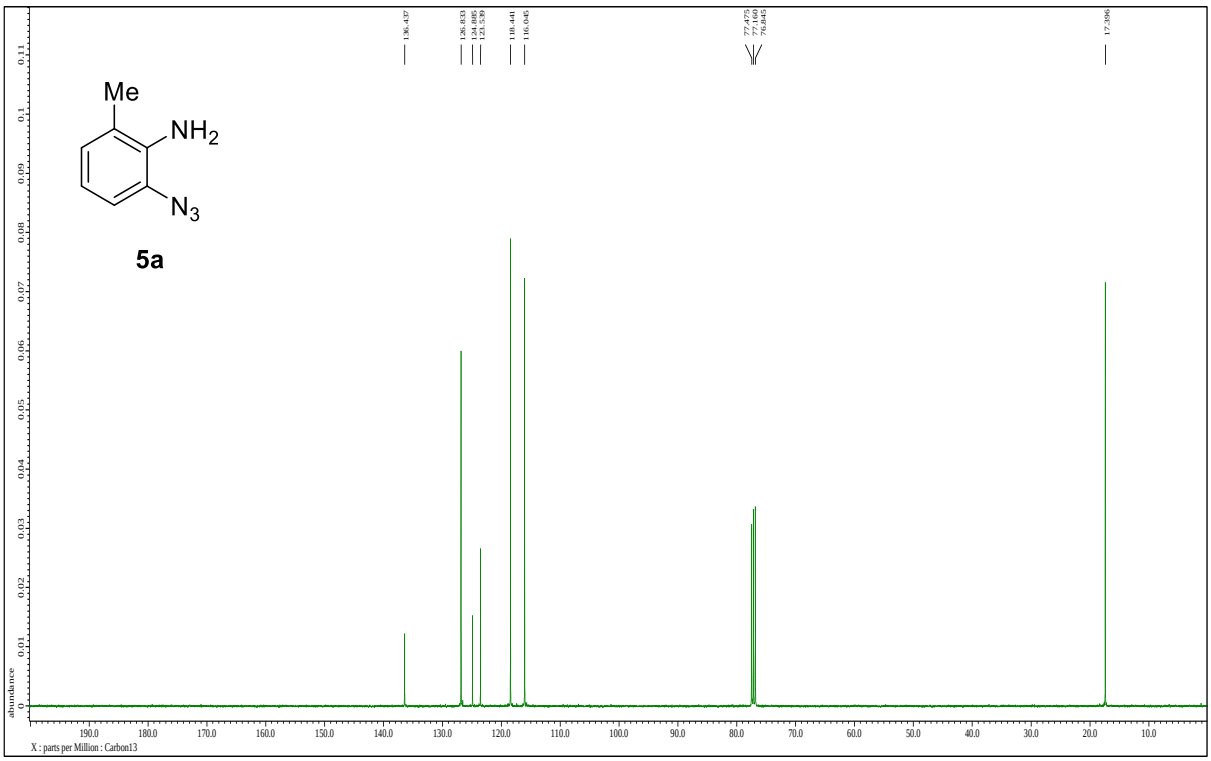
^{13}C-NMR of compound **8b** ($CDCl_3$, 100 MHz)



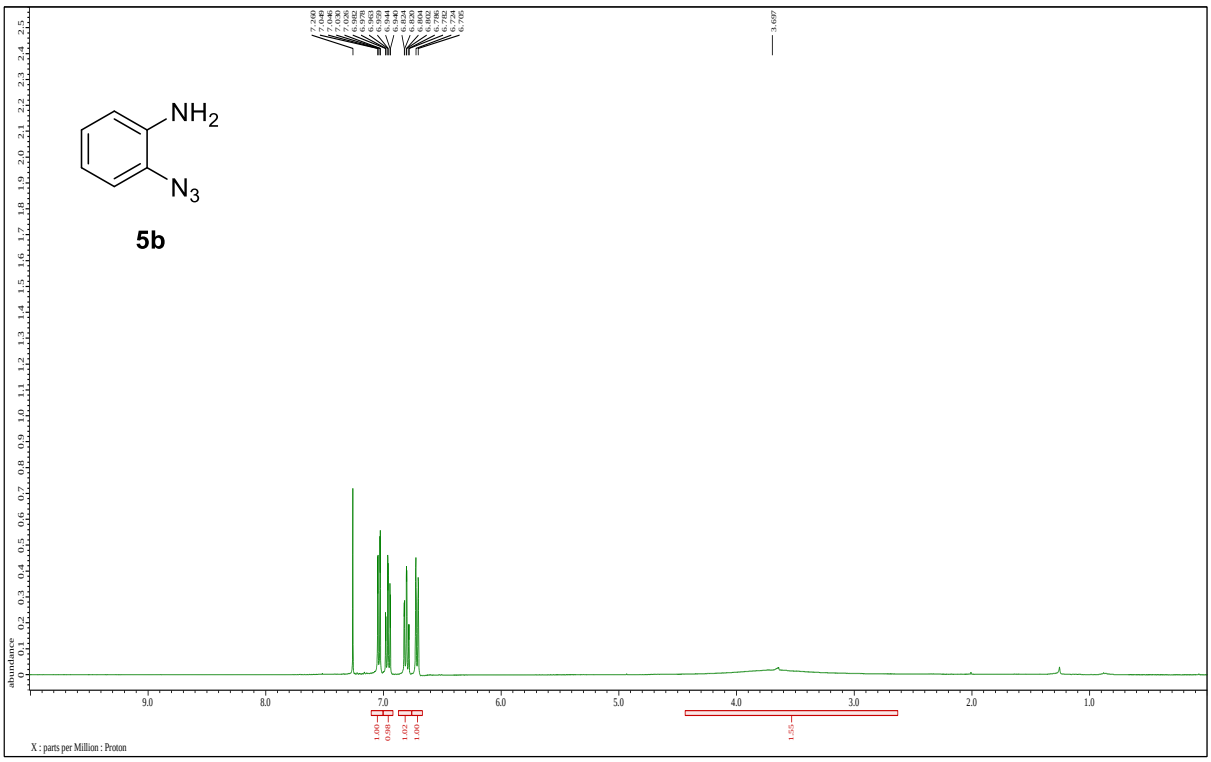
^{1}H-NMR of compound **5a** ($CDCl_3$, 400 MHz)



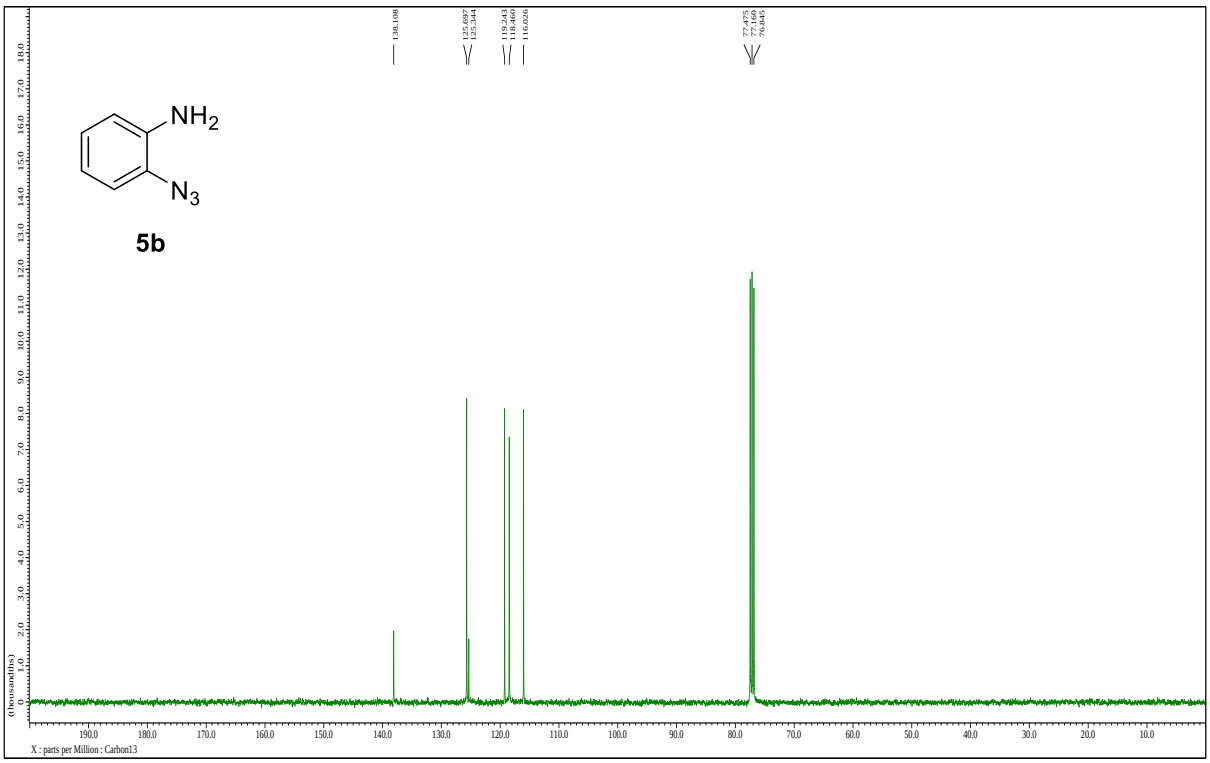
^{13}C-NMR of compound **5a** ($CDCl_3$, 100 MHz)



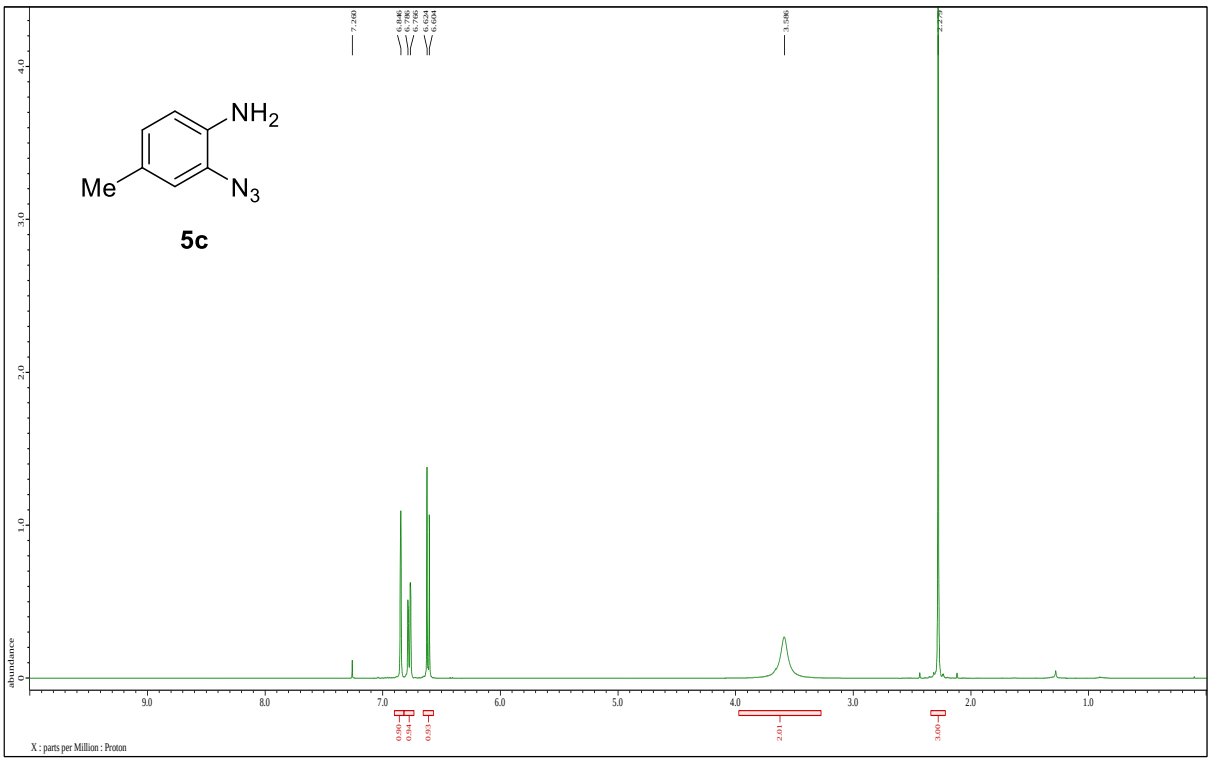
^{1}H-NMR of compound **5b** ($CDCl_3$, 400 MHz)



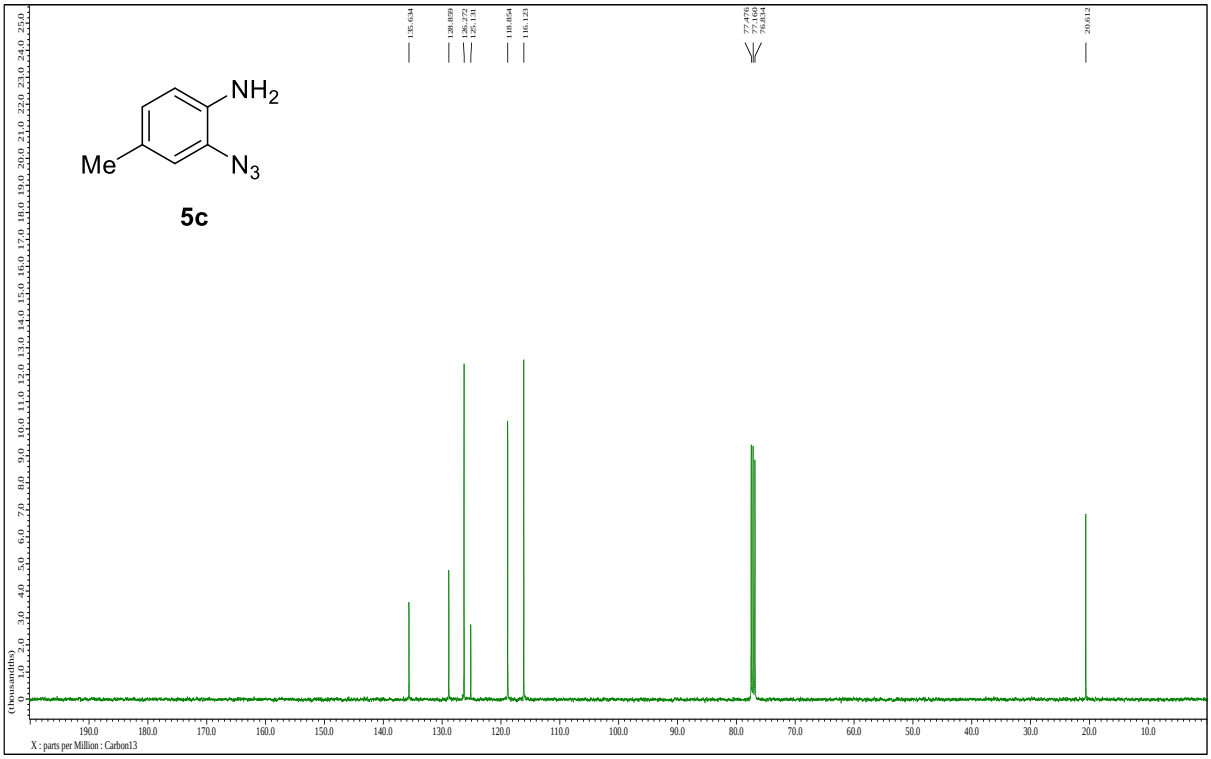
^{13}C-NMR of compound **5b** ($CDCl_3$, 100 MHz)



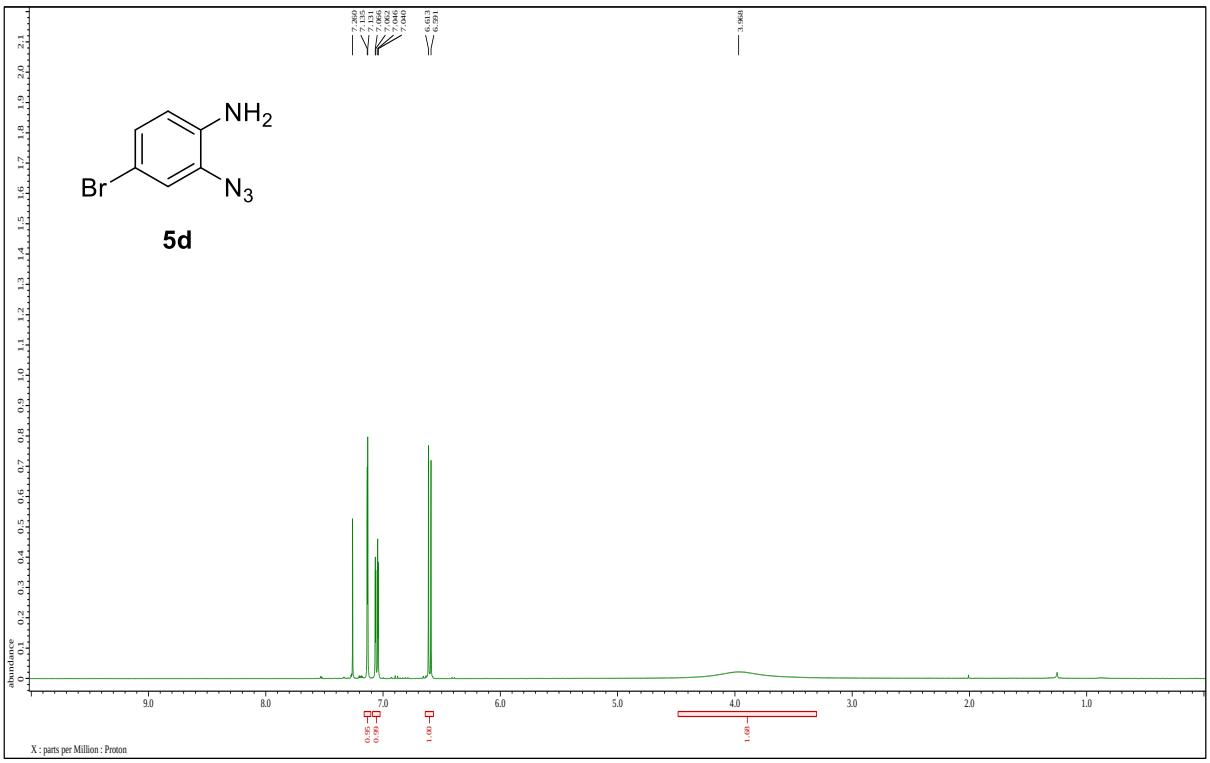
^{1}H-NMR of compound **5c** ($CDCl_3$, 400 MHz)



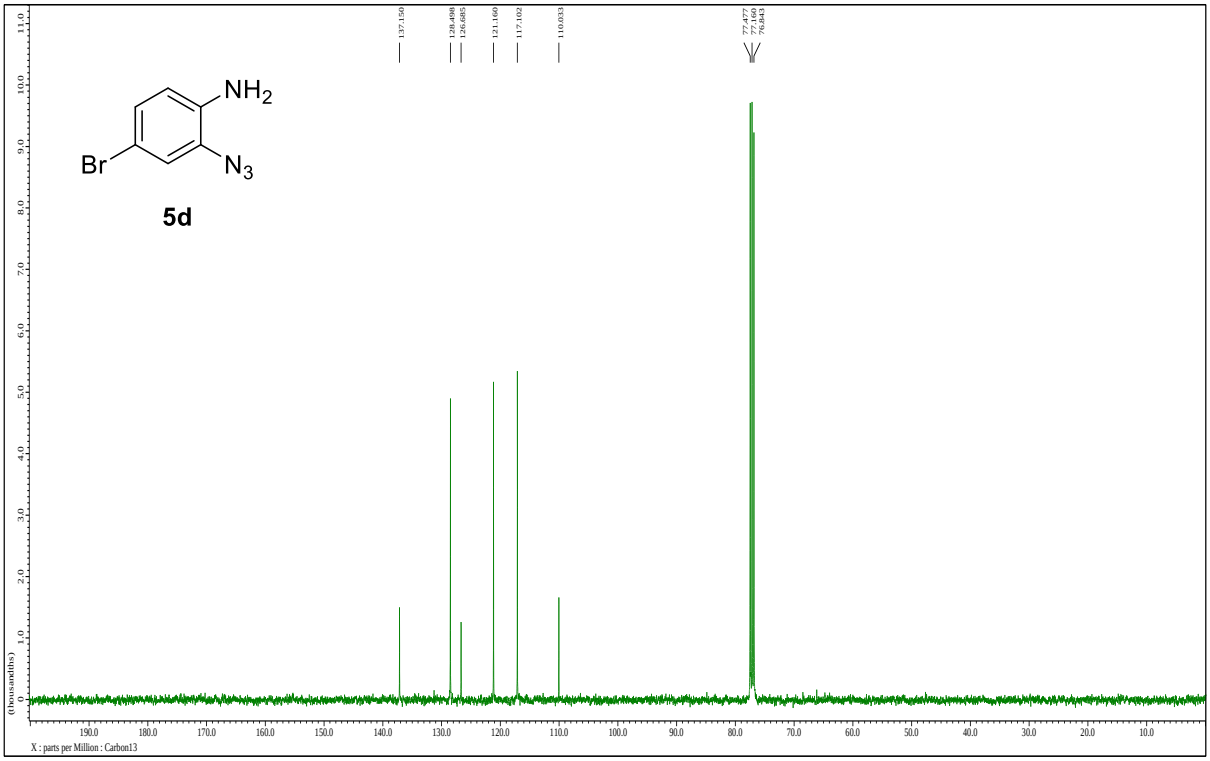
^{13}C-NMR of compound **5c** ($CDCl_3$, 100 MHz)



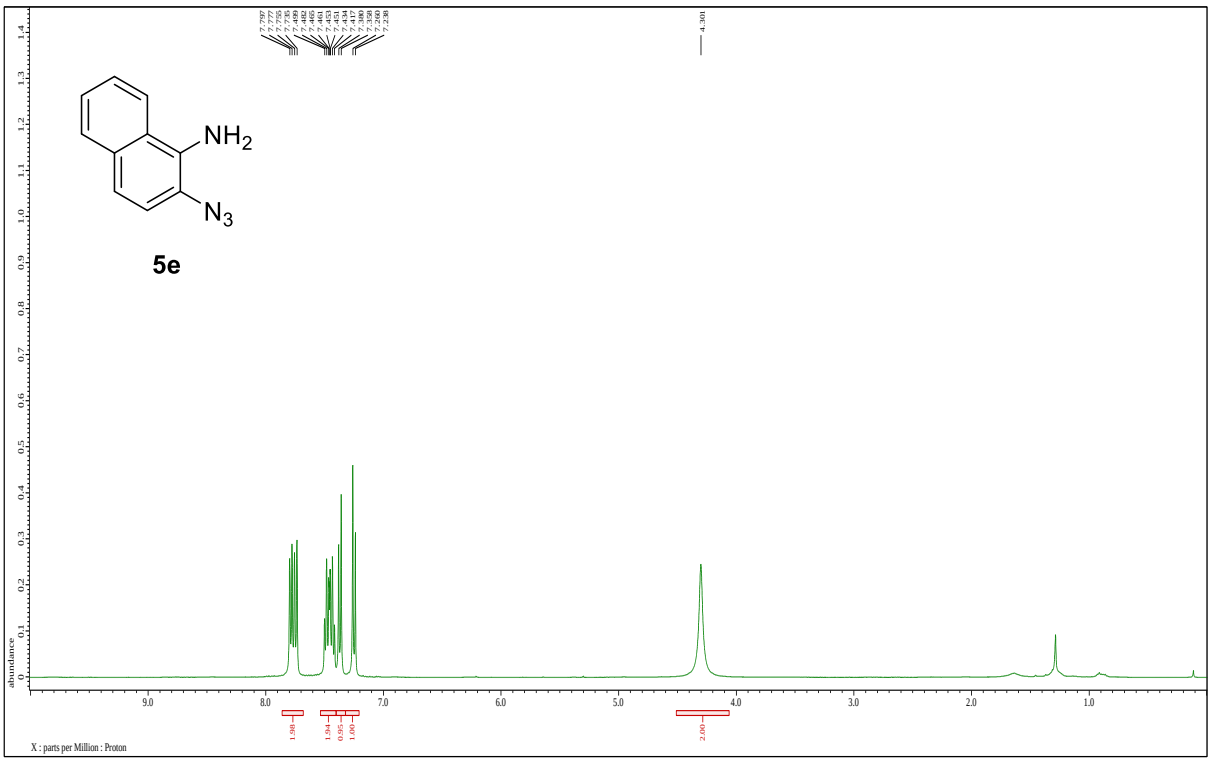
^{1}H-NMR of compound **5d** ($CDCl_3$, 400 MHz)



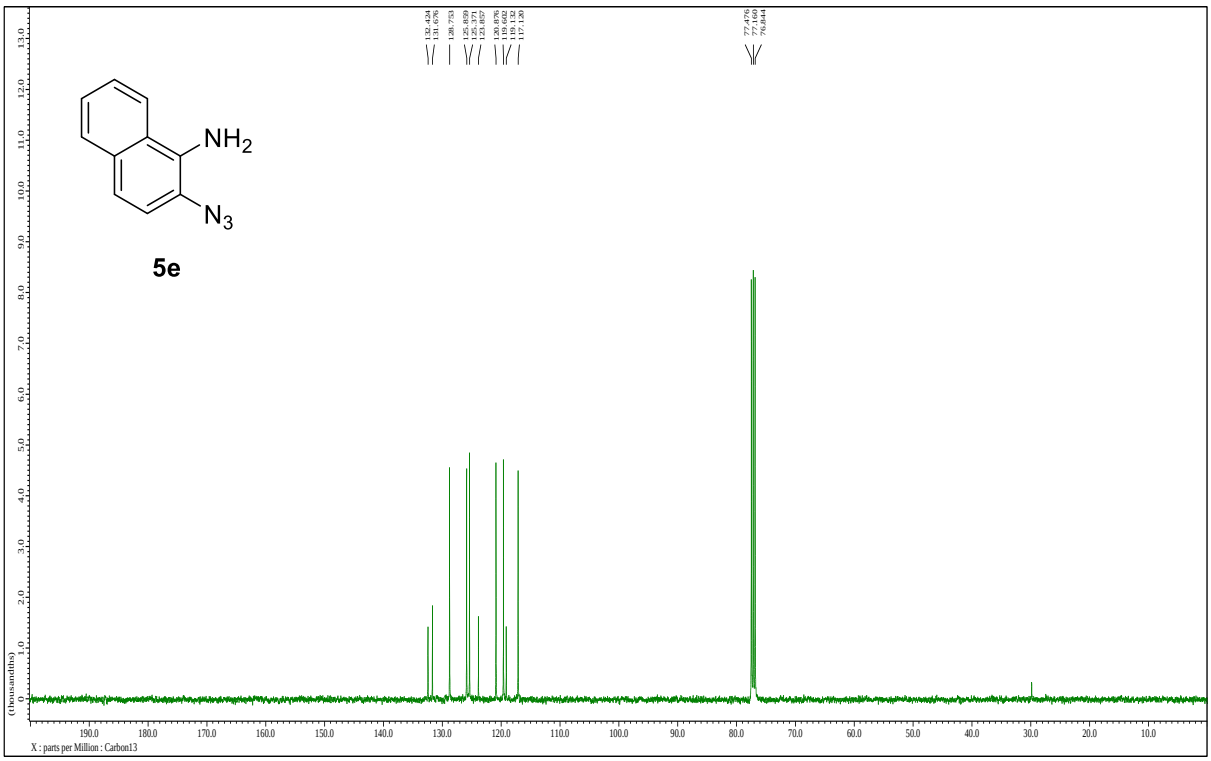
^{13}C-NMR of compound **5d** ($CDCl_3$, 100 MHz)



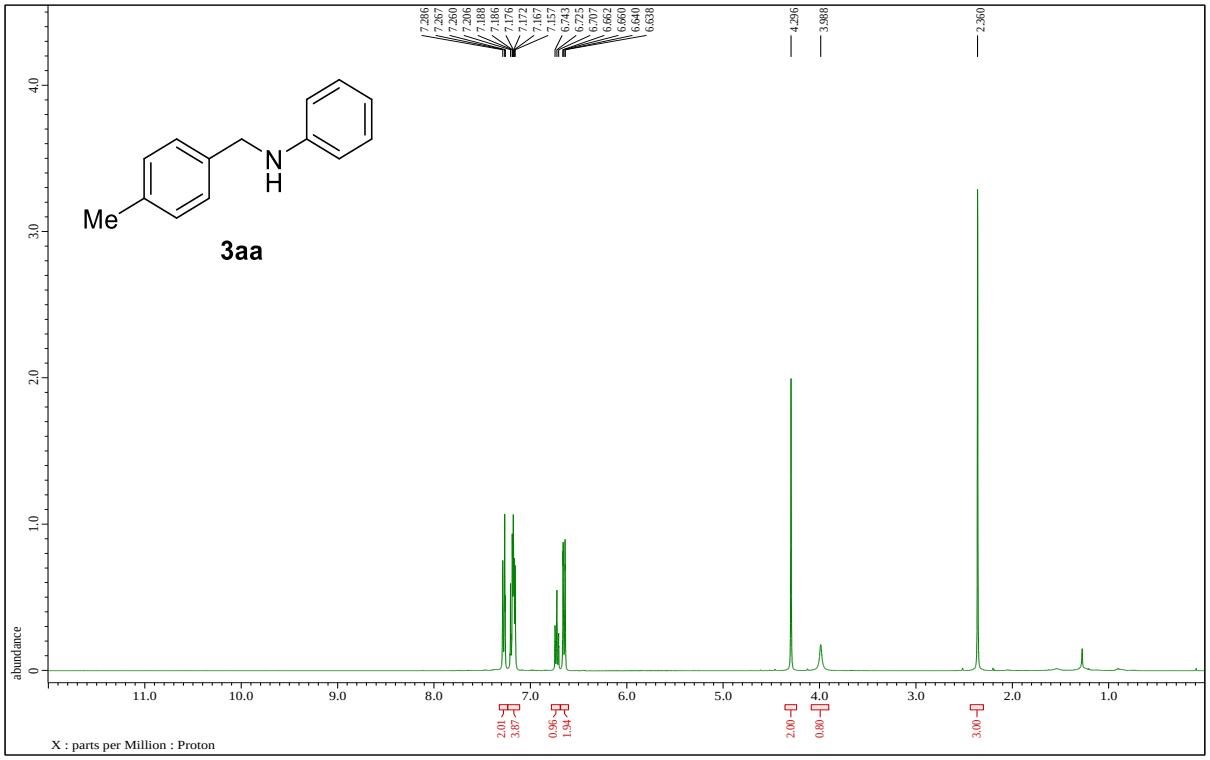
^{1}H-NMR of compound **5e** ($CDCl_3$, 400 MHz)



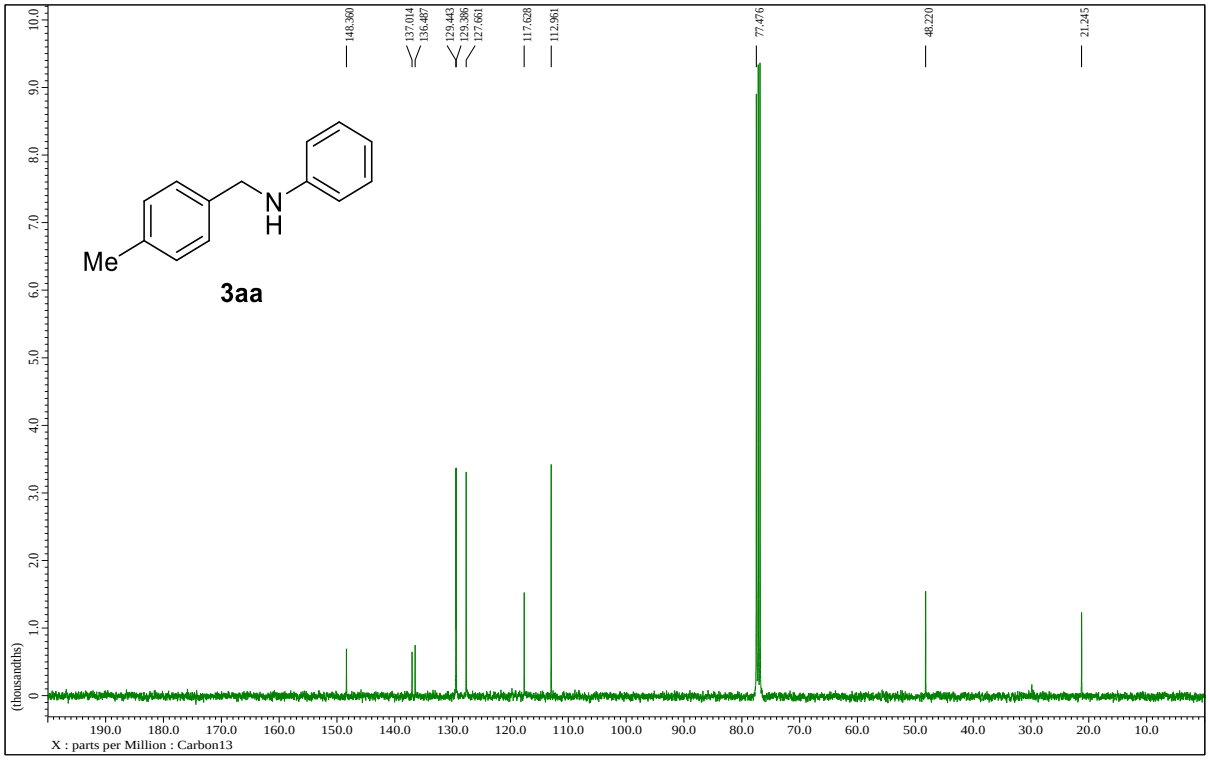
^{13}C-NMR of compound **5e** ($CDCl_3$, 100 MHz)



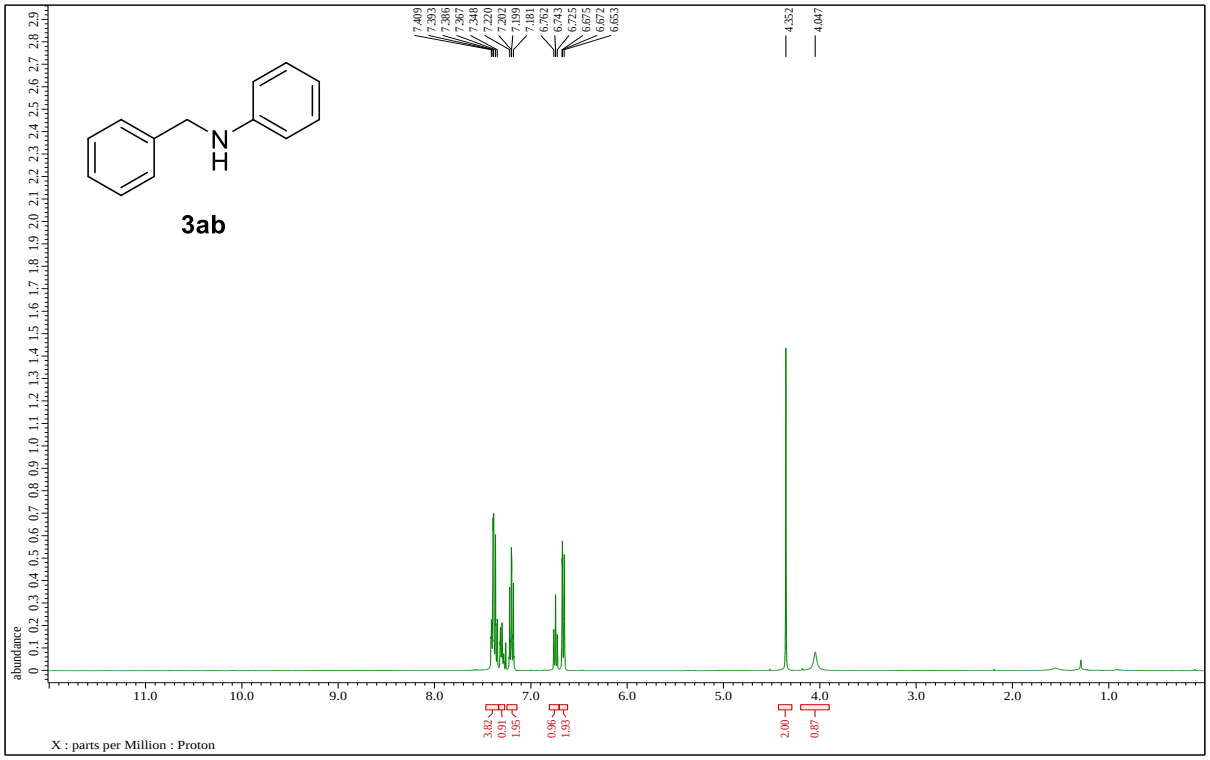
^{1}H-NMR of compound **3aa** ($CDCl_3$, 400 MHz)



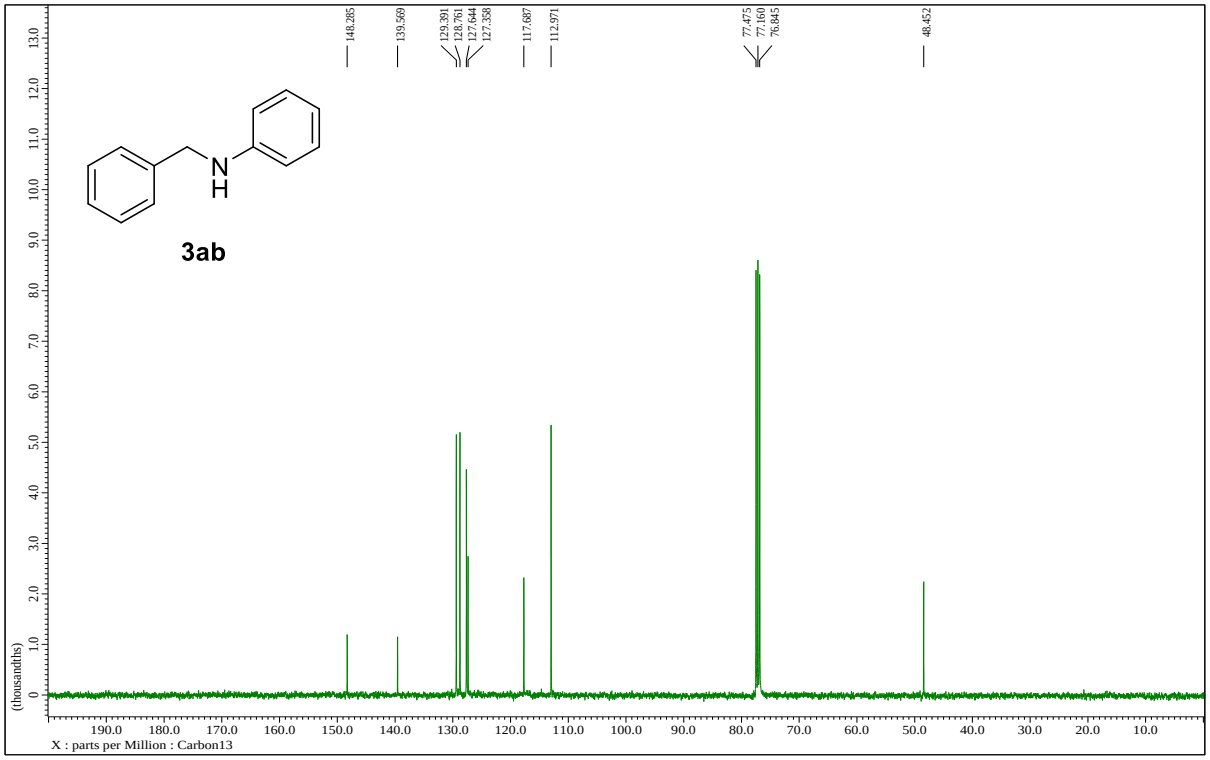
^{13}C-NMR of compound **3aa** ($CDCl_3$, 100 MHz)



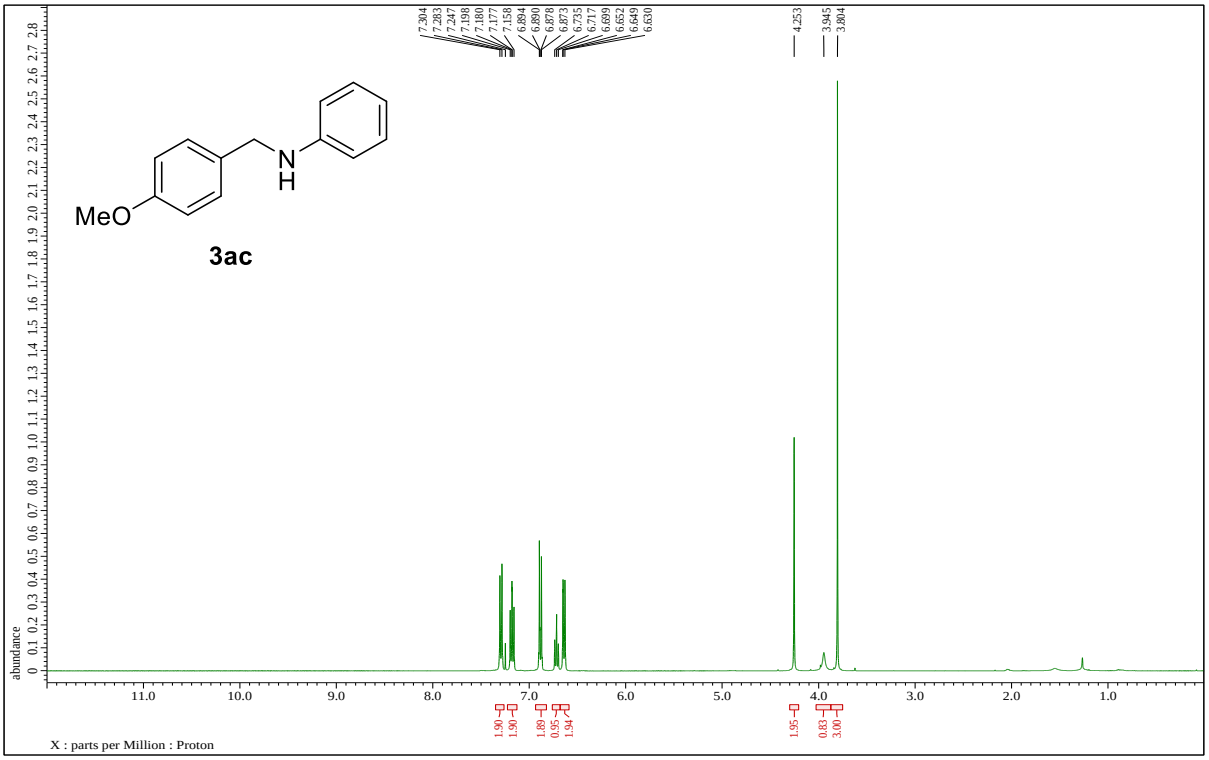
^{1}H-NMR of compound **3ab** ($CDCl_3$, 400 MHz)



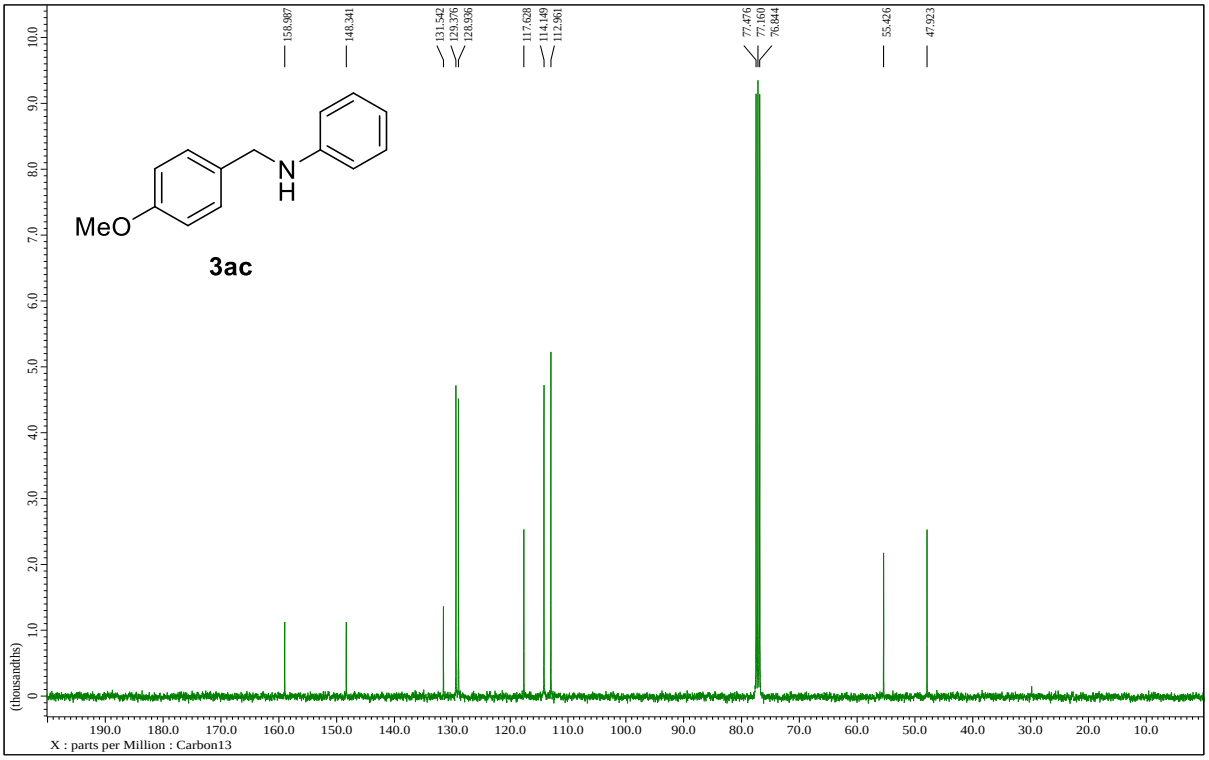
^{13}C-NMR of compound **3ab** ($CDCl_3$, 100 MHz)



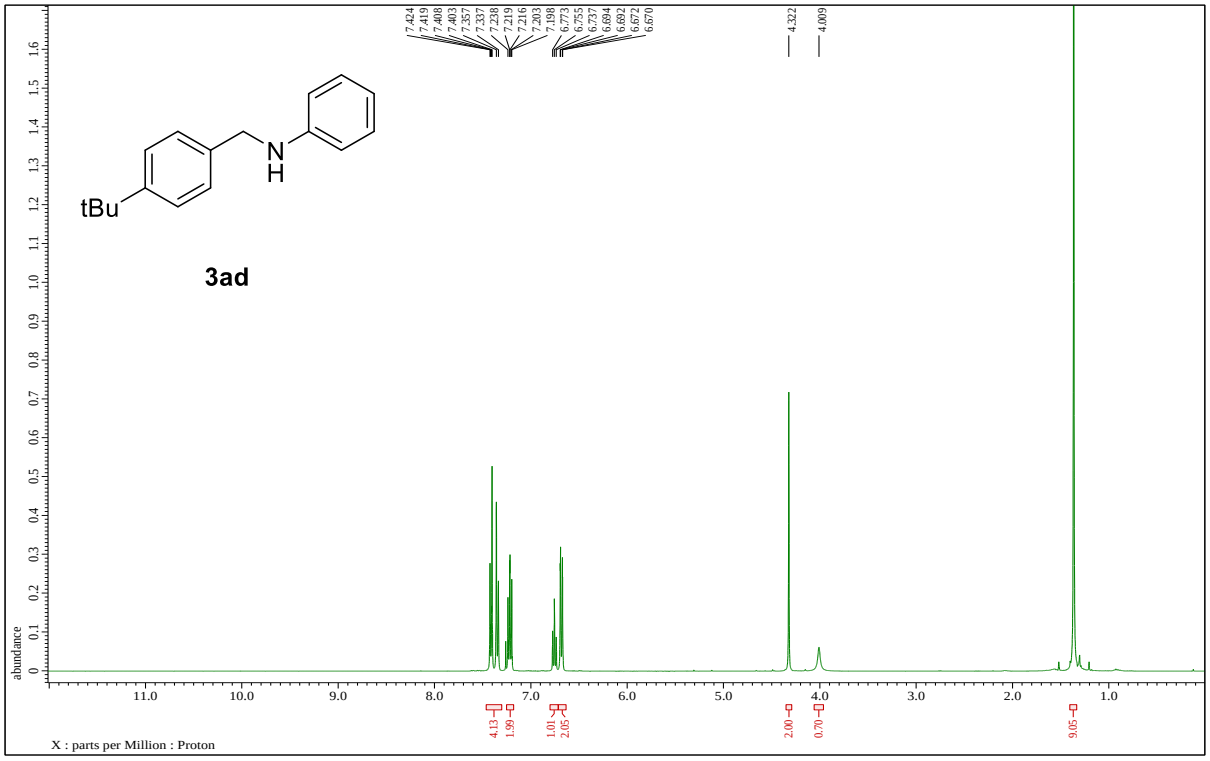
^{1}H-NMR of compound **3ac** ($CDCl_3$, 400 MHz)



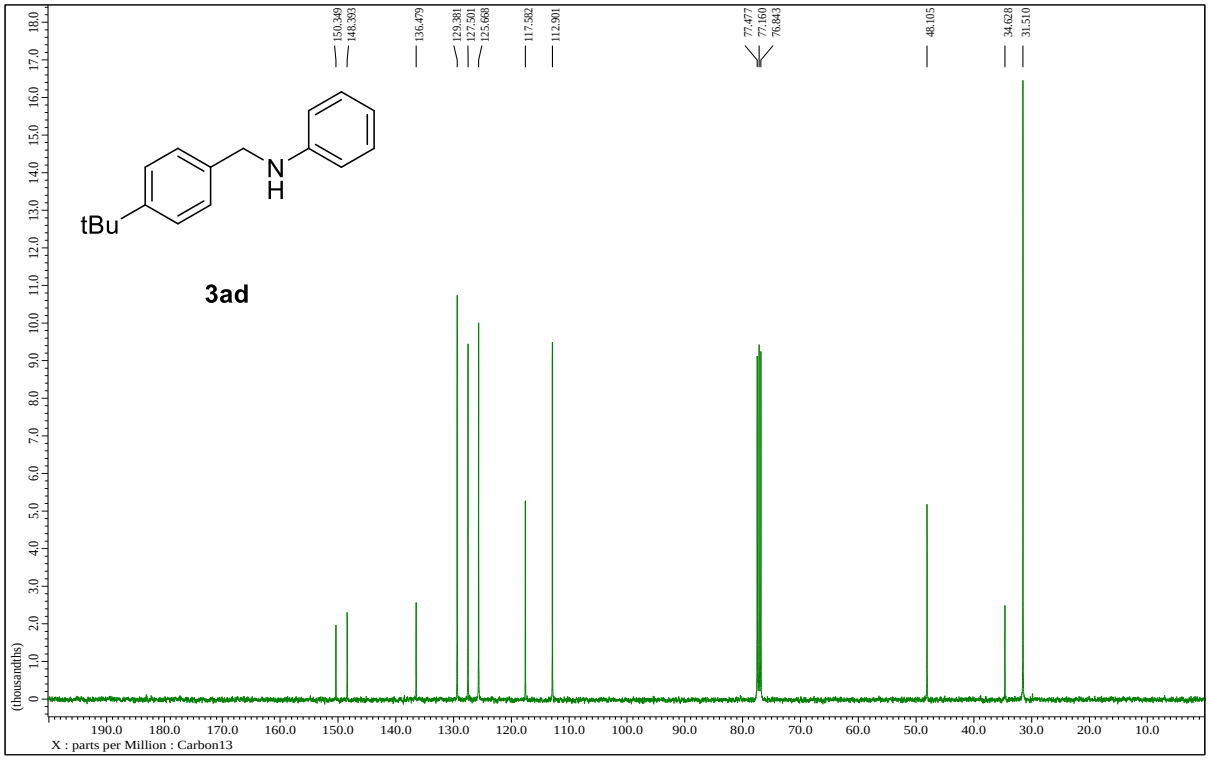
^{13}C-NMR of compound **3ac** ($CDCl_3$, 100 MHz)



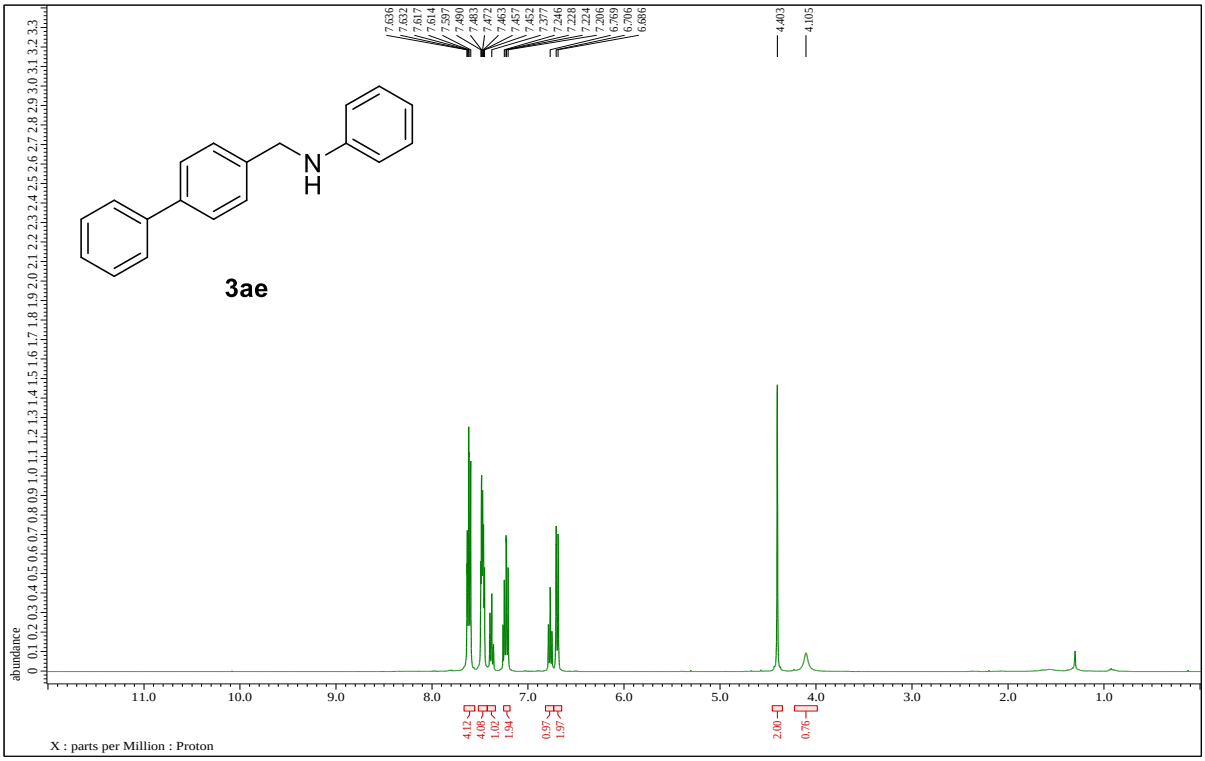
^{1}H-NMR of compound **3ad** ($CDCl_3$, 400 MHz)



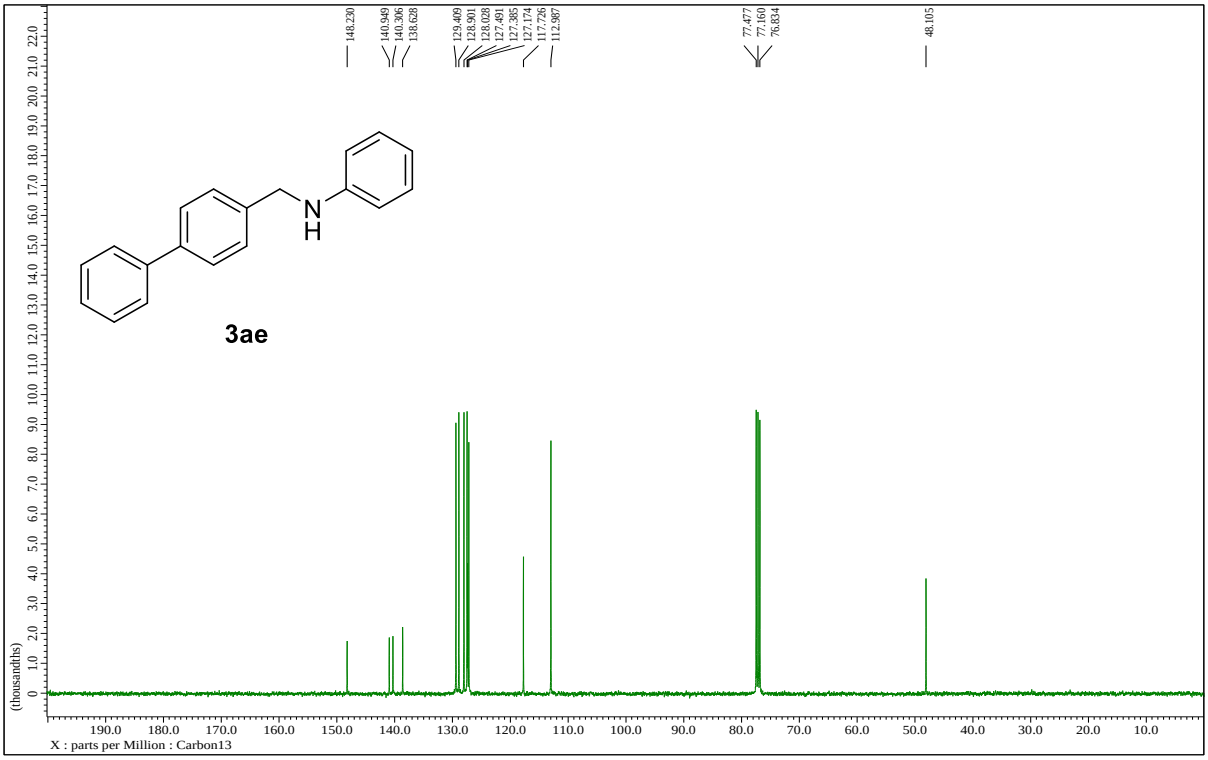
^{13}C-NMR of compound **3ad** ($CDCl_3$, 100 MHz)



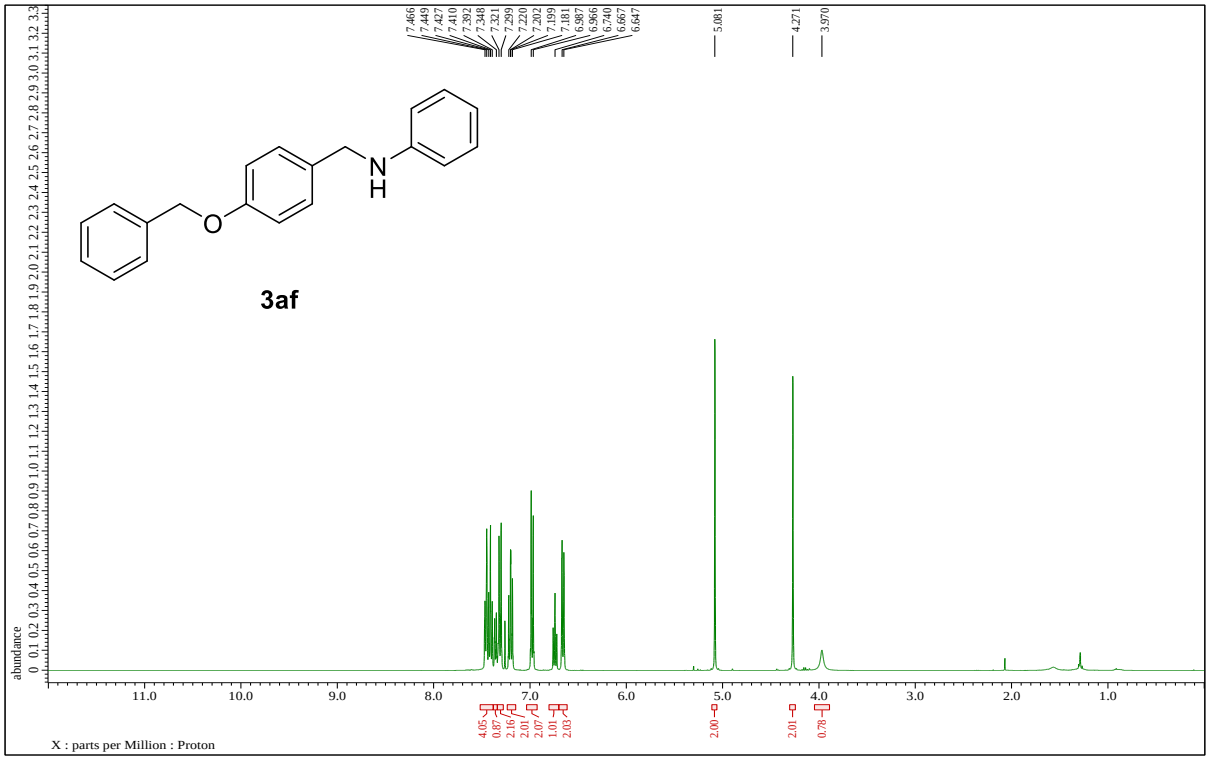
^{1}H-NMR of compound **3ae** ($CDCl_3$, 400 MHz)



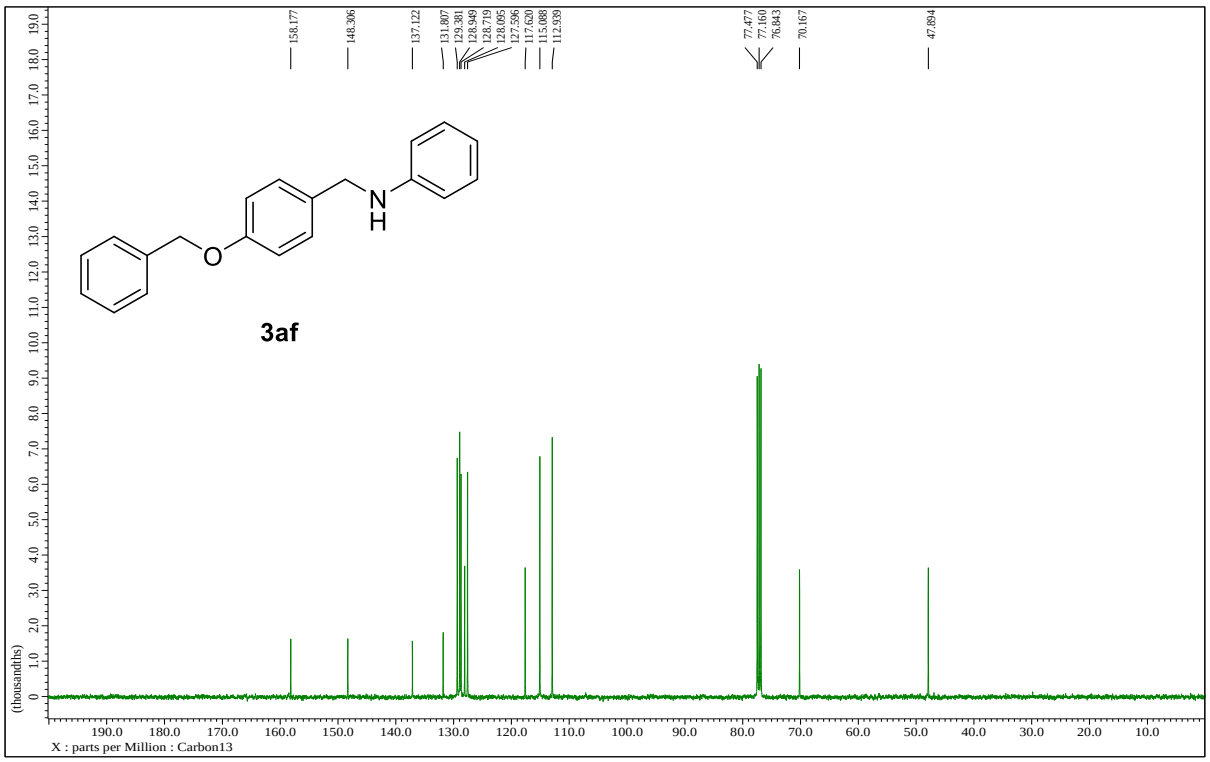
^{13}C-NMR of compound **3ae** ($CDCl_3$, 100 MHz)



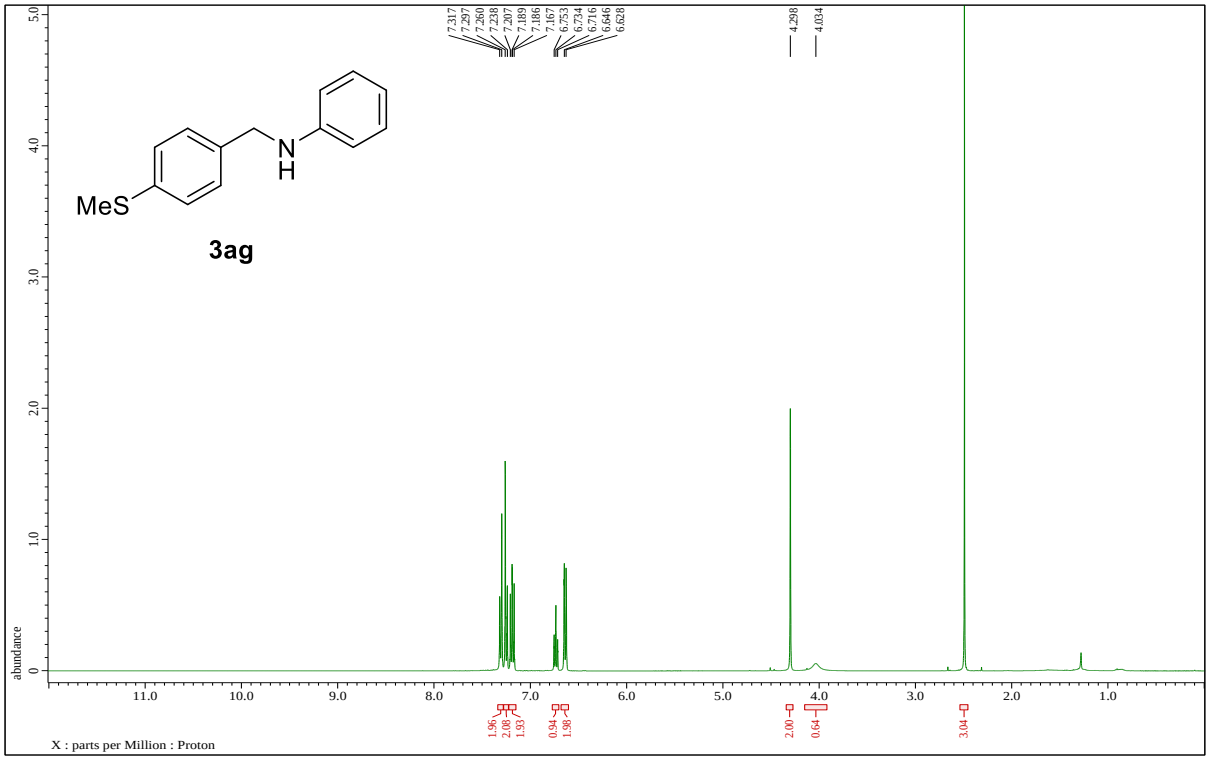
^{1}H-NMR of compound **3af** ($CDCl_3$, 400 MHz)



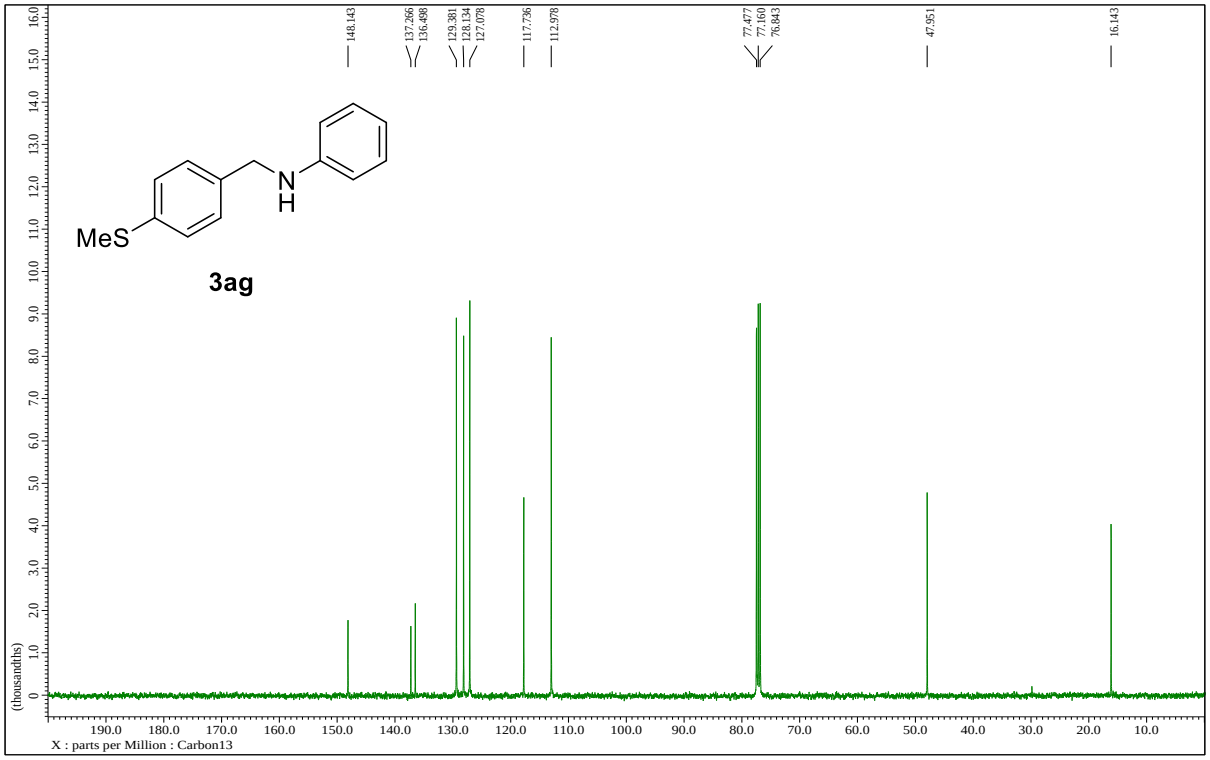
^{13}C-NMR of compound **3af** ($CDCl_3$, 100 MHz)



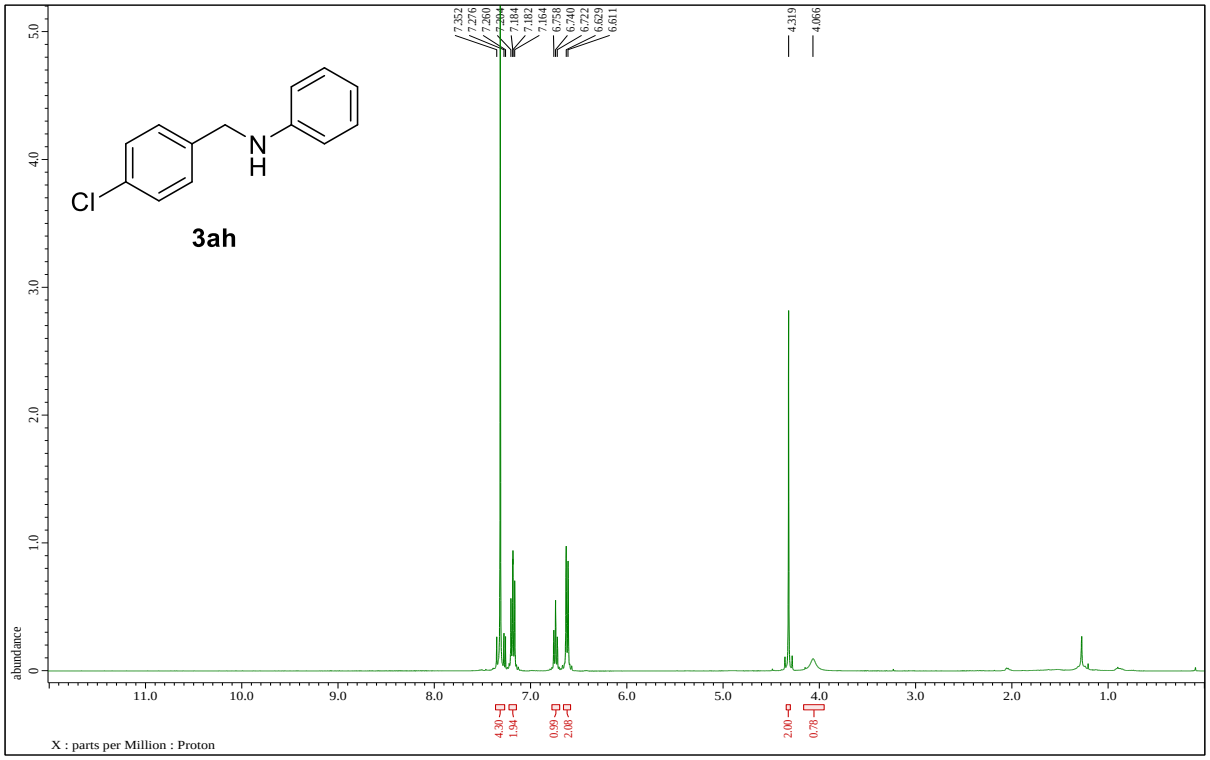
^{1}H-NMR of compound **3ag** ($CDCl_3$, 400 MHz)



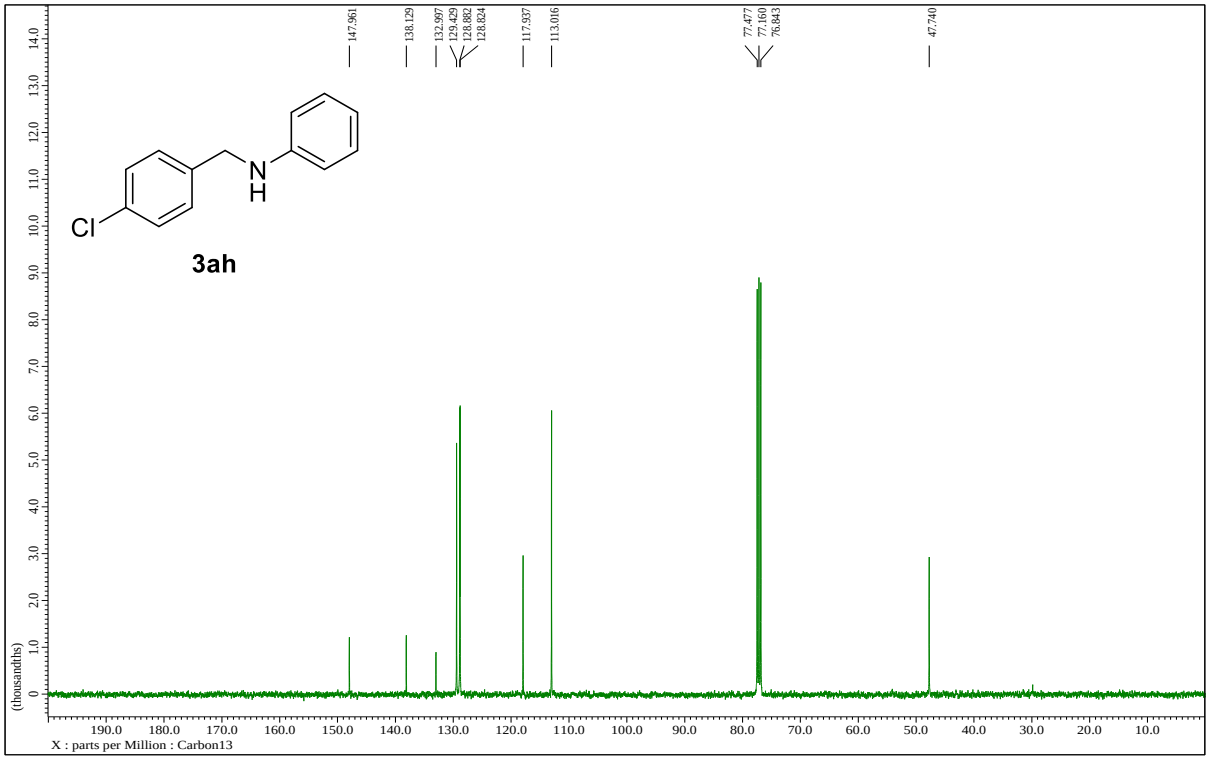
^{13}C-NMR of compound **3ag** ($CDCl_3$, 100 MHz)



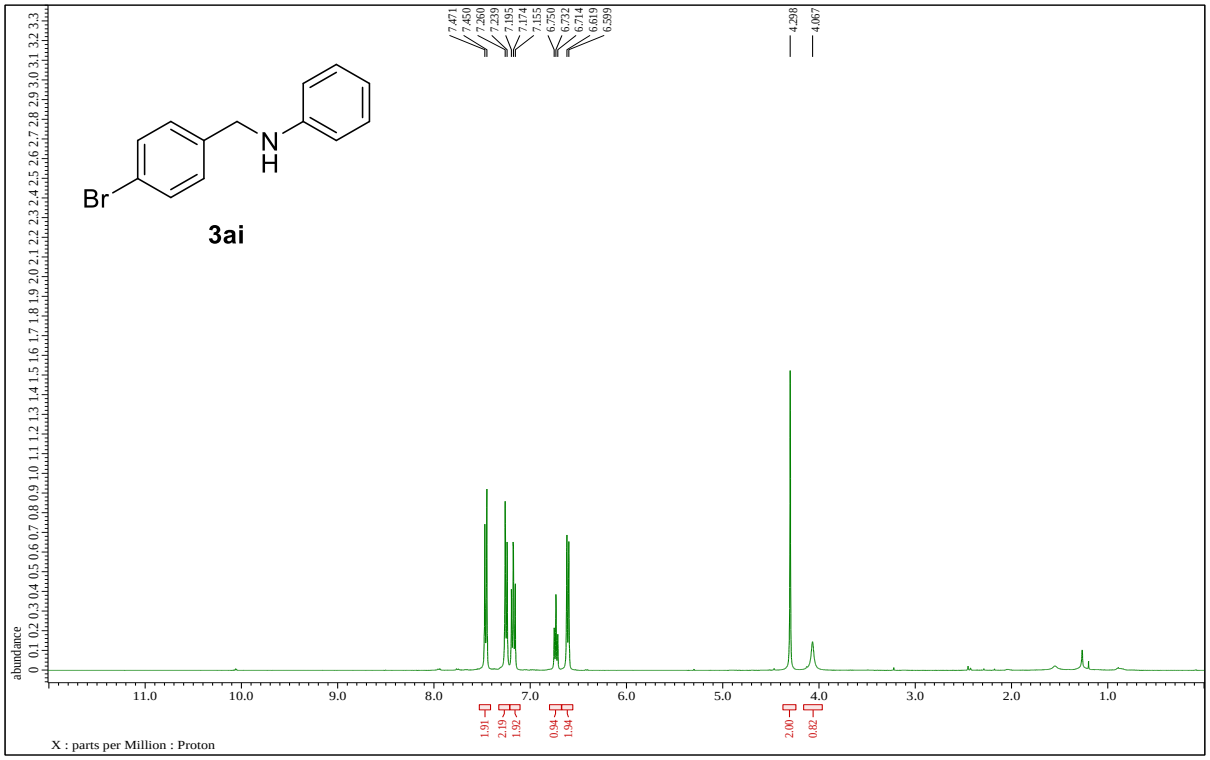
^{1}H-NMR of compound **3ah** ($CDCl_3$, 400 MHz)



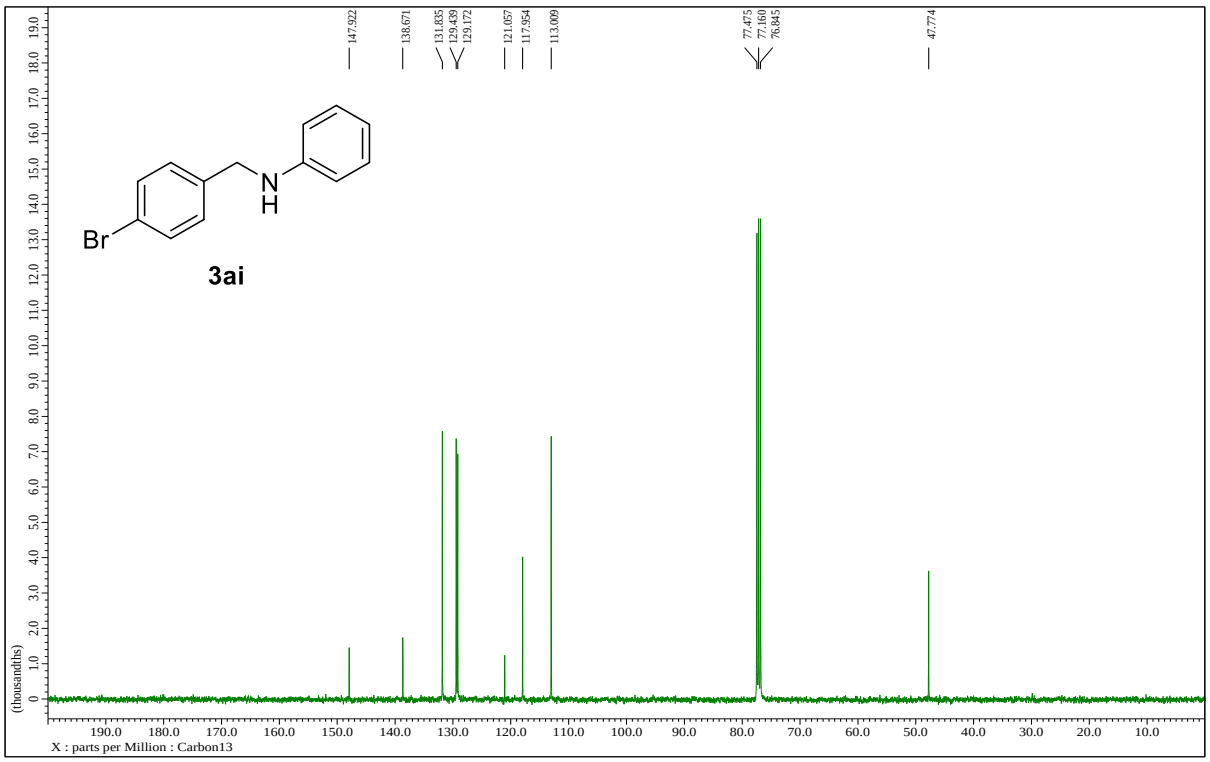
^{13}C-NMR of compound **3ah** ($CDCl_3$, 100 MHz)



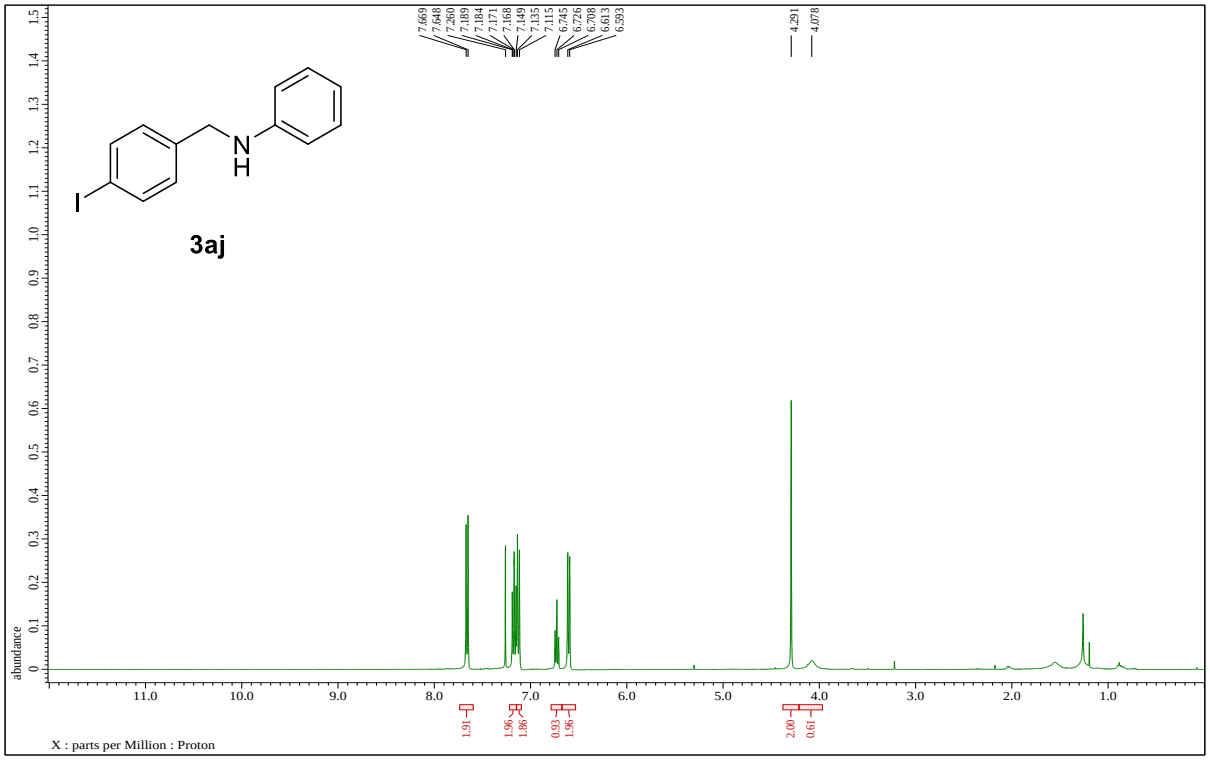
^{1}H-NMR of compound **3ai** ($CDCl_3$, 400 MHz)



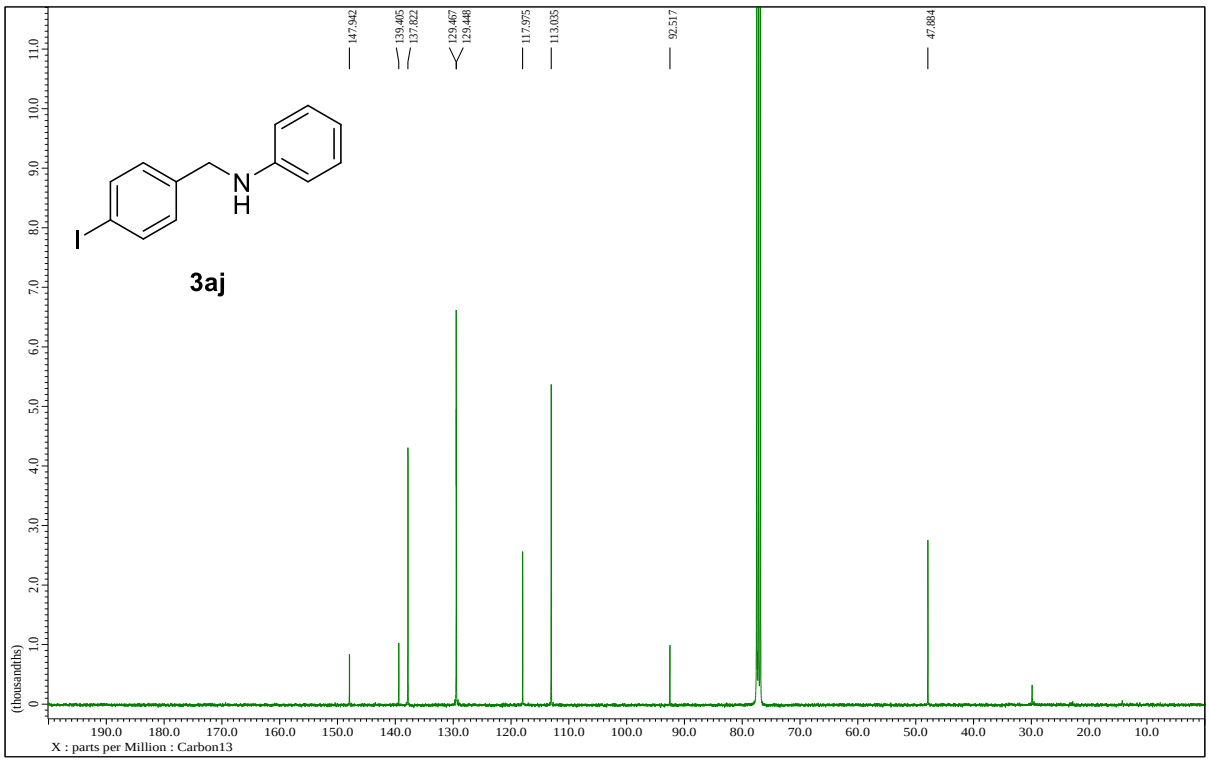
^{13}C-NMR of compound **3ai** ($CDCl_3$, 100 MHz)



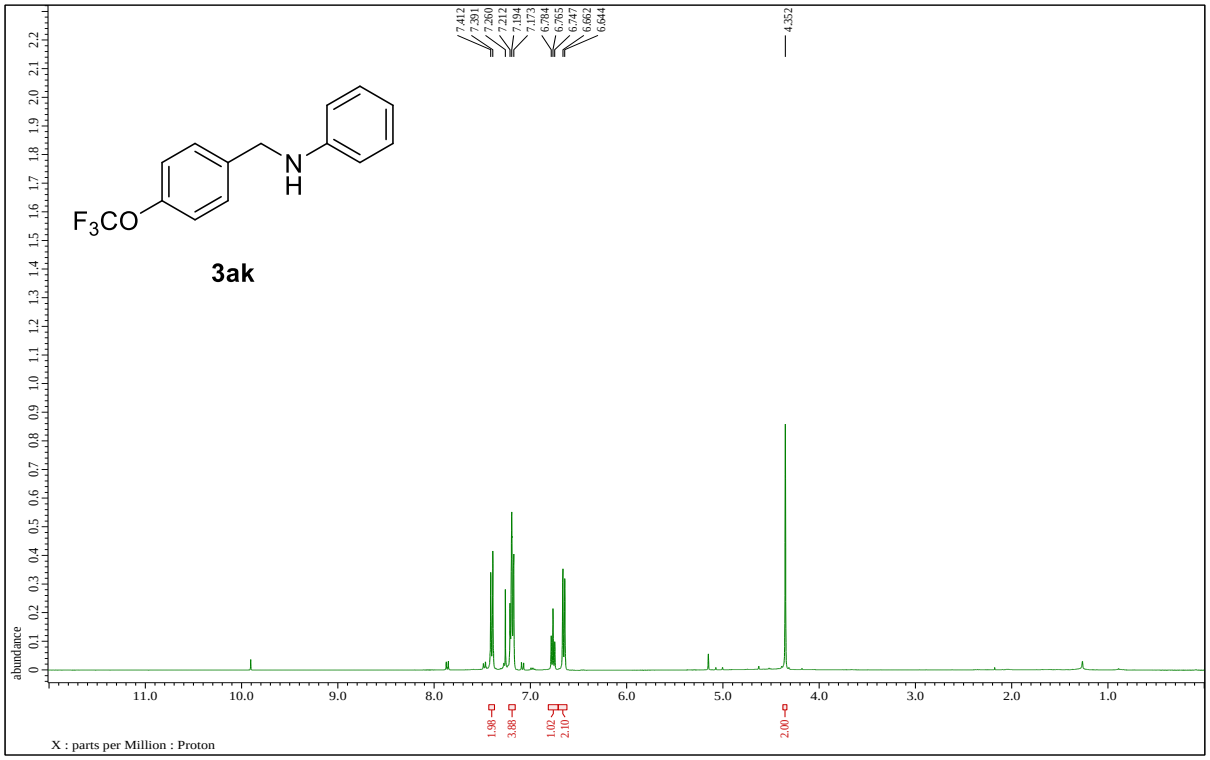
^{1}H-NMR of compound **3aj** ($CDCl_3$, 400 MHz)



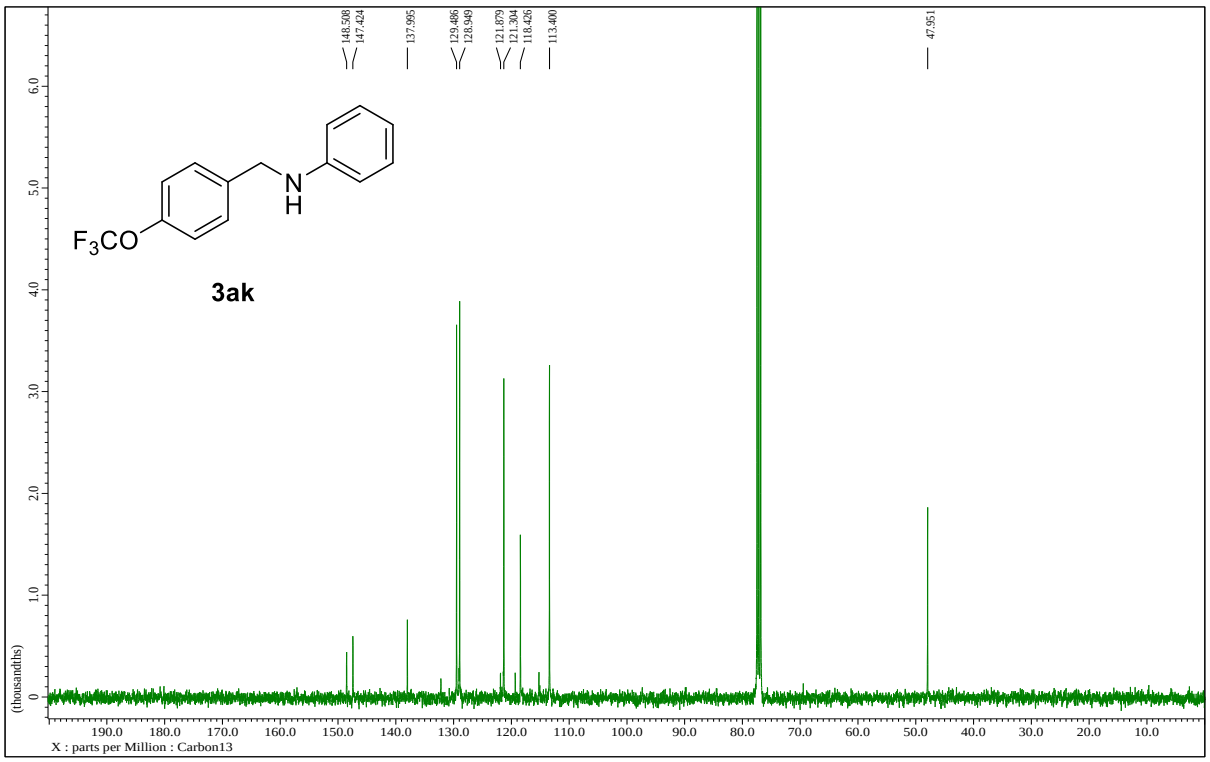
^{13}C-NMR of compound **3aj** ($CDCl_3$, 100 MHz)



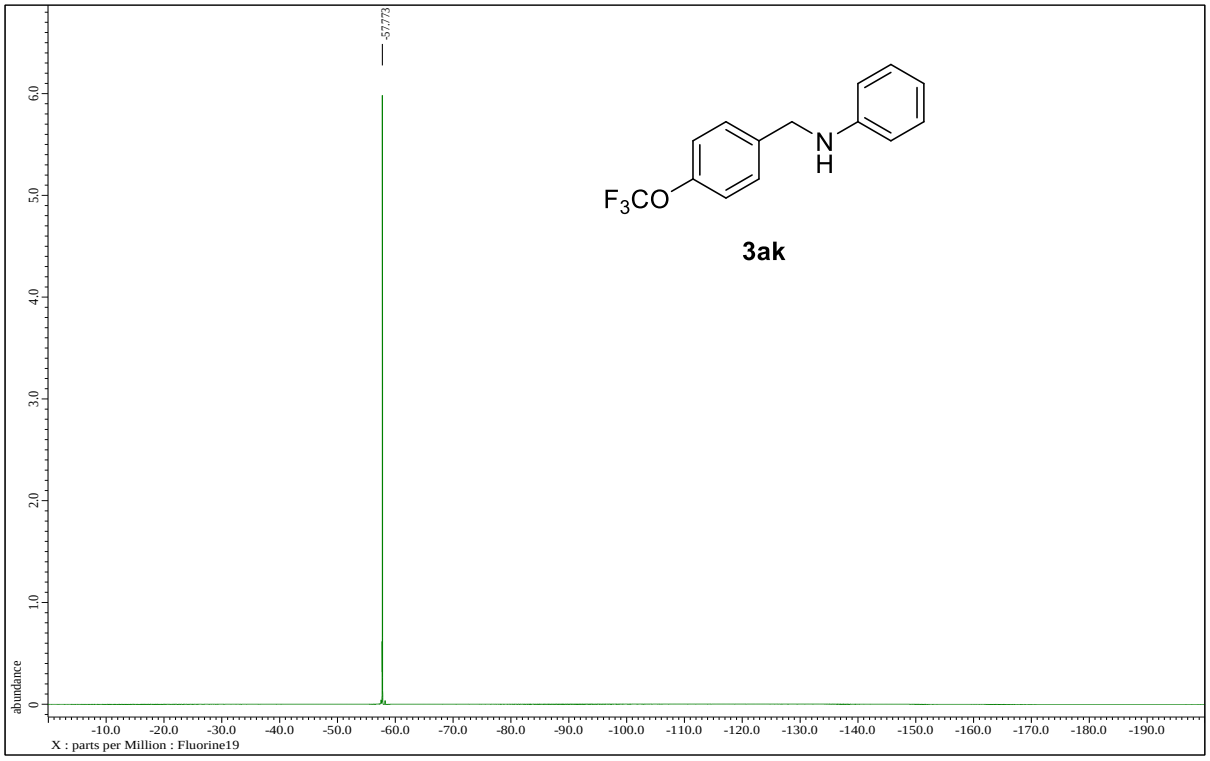
^{1}H-NMR of compound **3ak** ($CDCl_3$, 400 MHz)



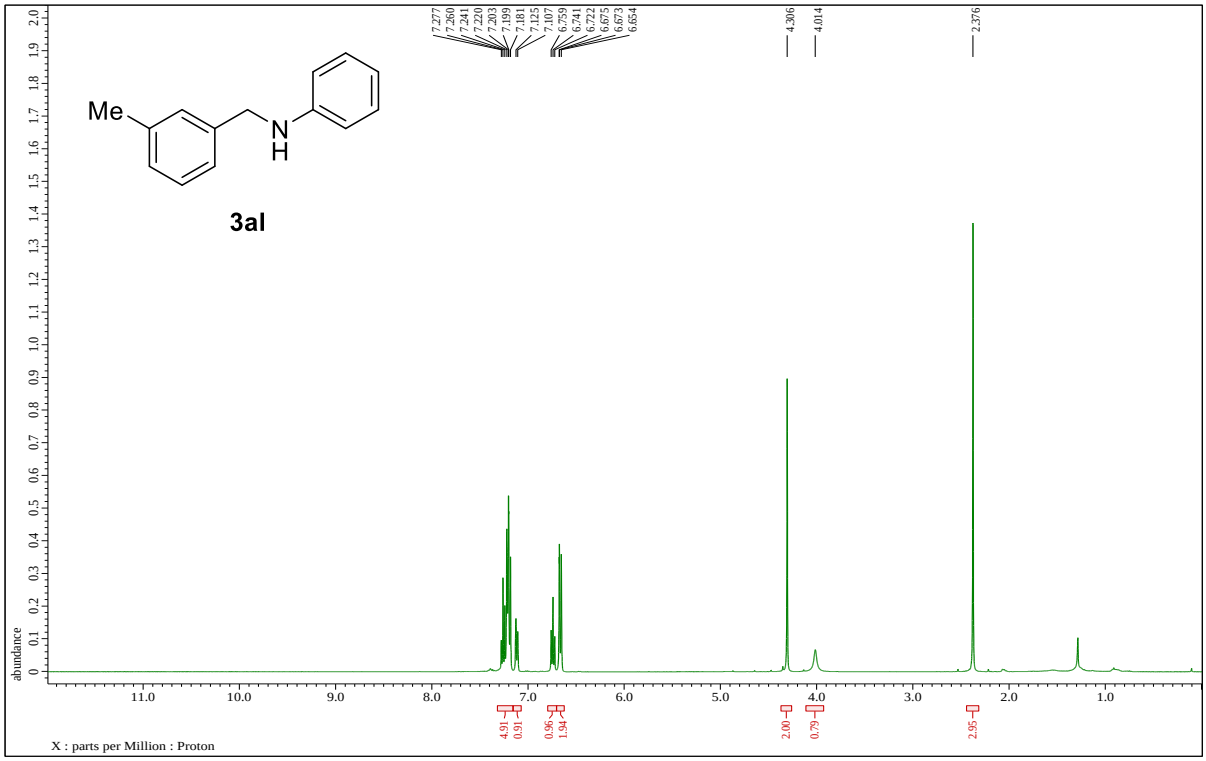
^{13}C-NMR of compound **3ak** ($CDCl_3$, 100 MHz)



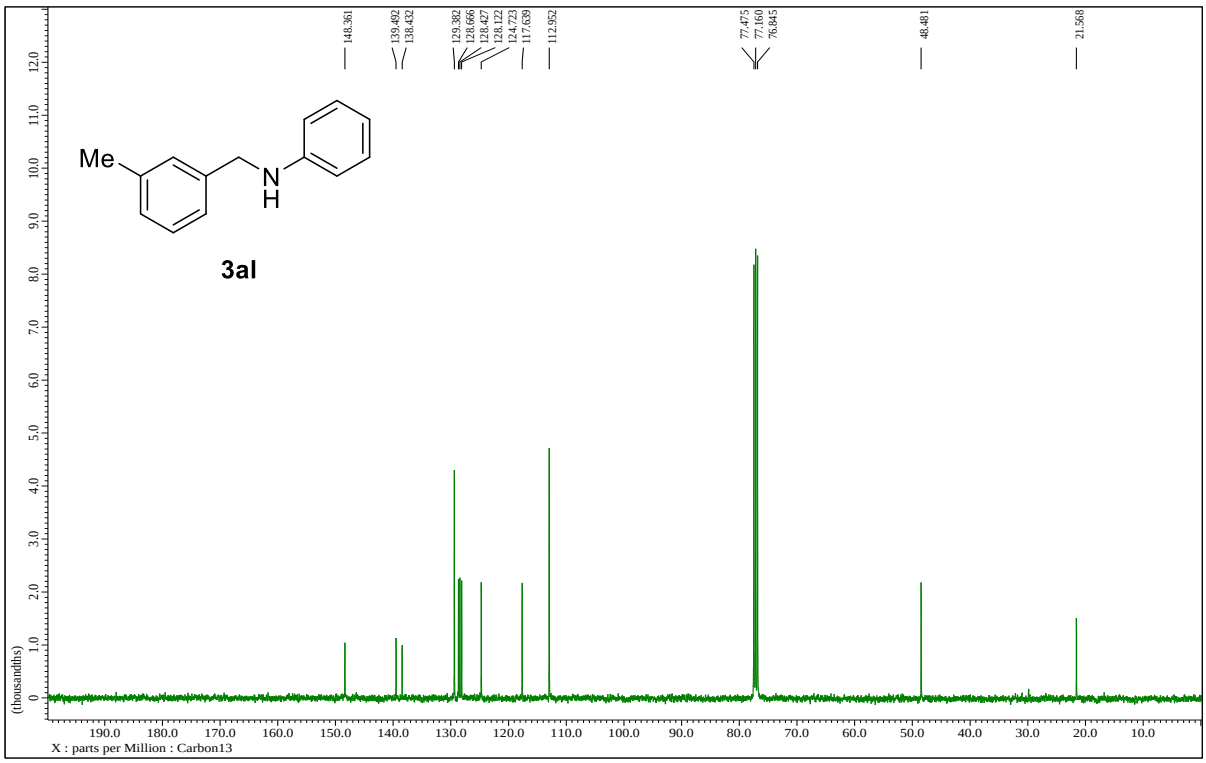
^{19}F-NMR of compound **3ak** ($CDCl_3$, 375 MHz)



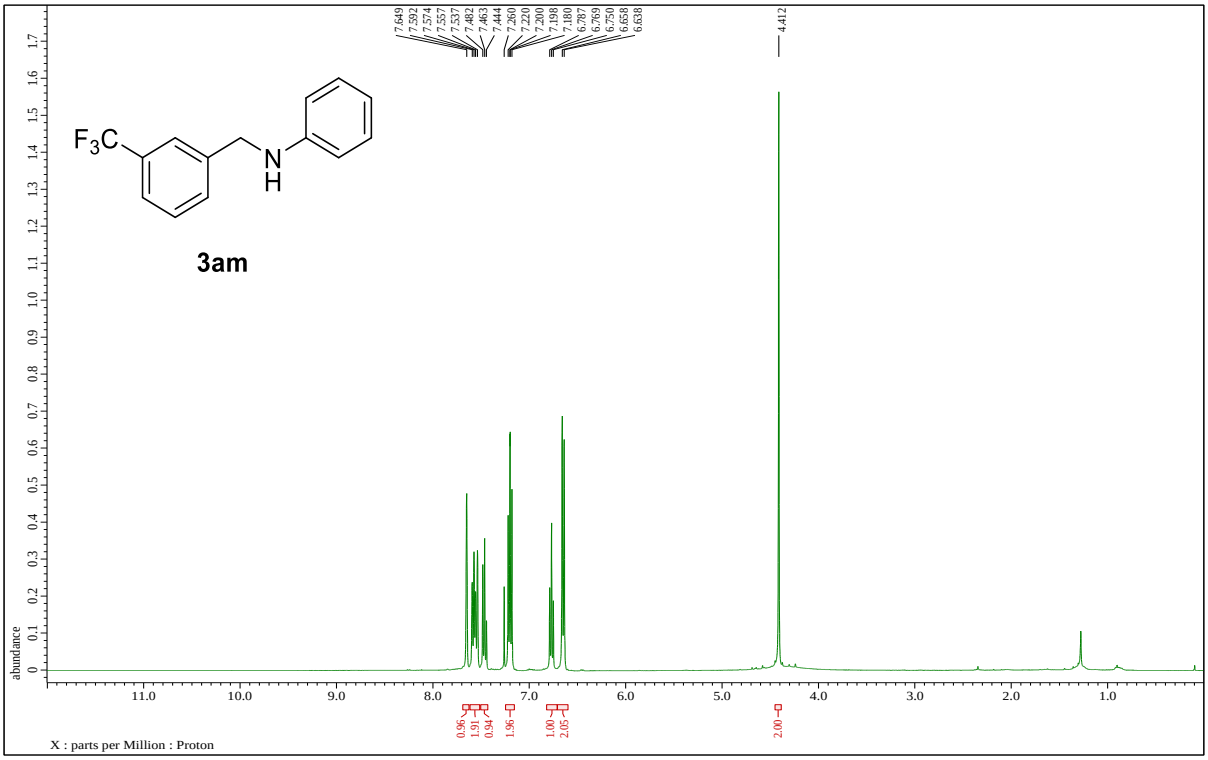
^{1}H-NMR of compound **3al** ($CDCl_3$, 400 MHz)



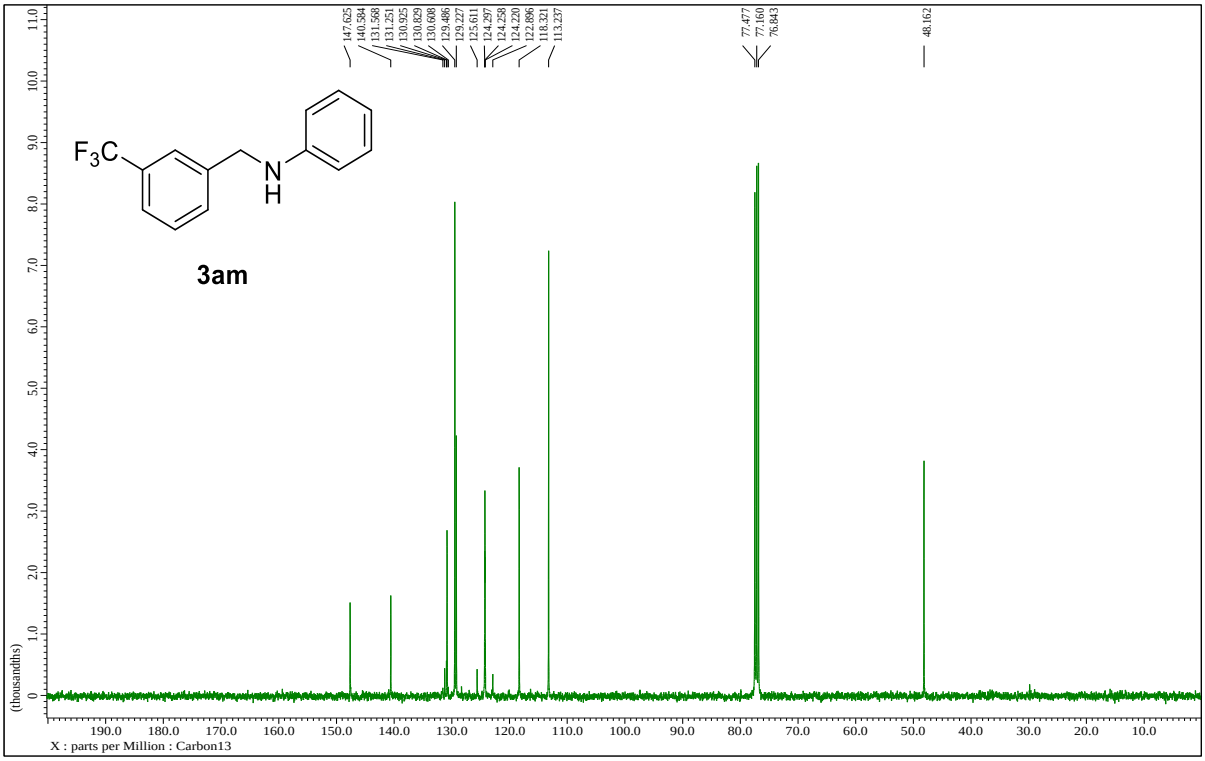
^{13}C-NMR of compound **3al** ($CDCl_3$, 100 MHz)



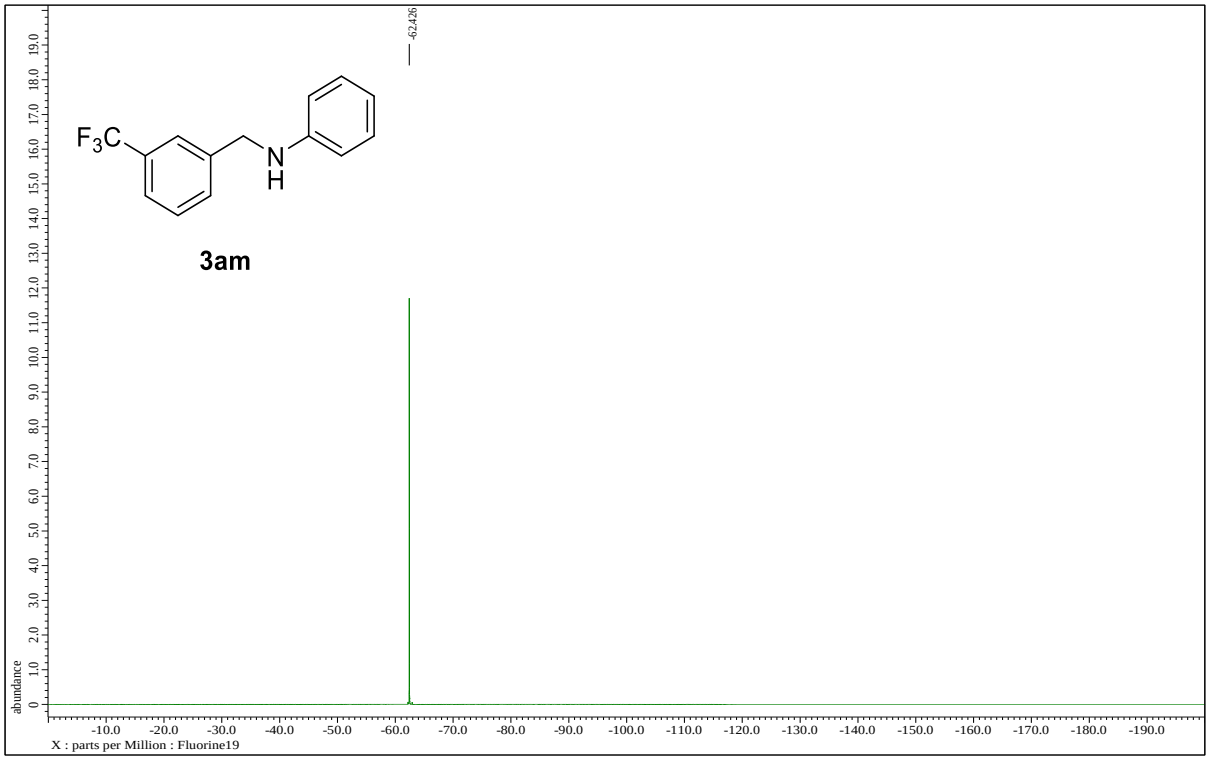
^{1}H-NMR of compound **3am** ($CDCl_3$, 400 MHz)



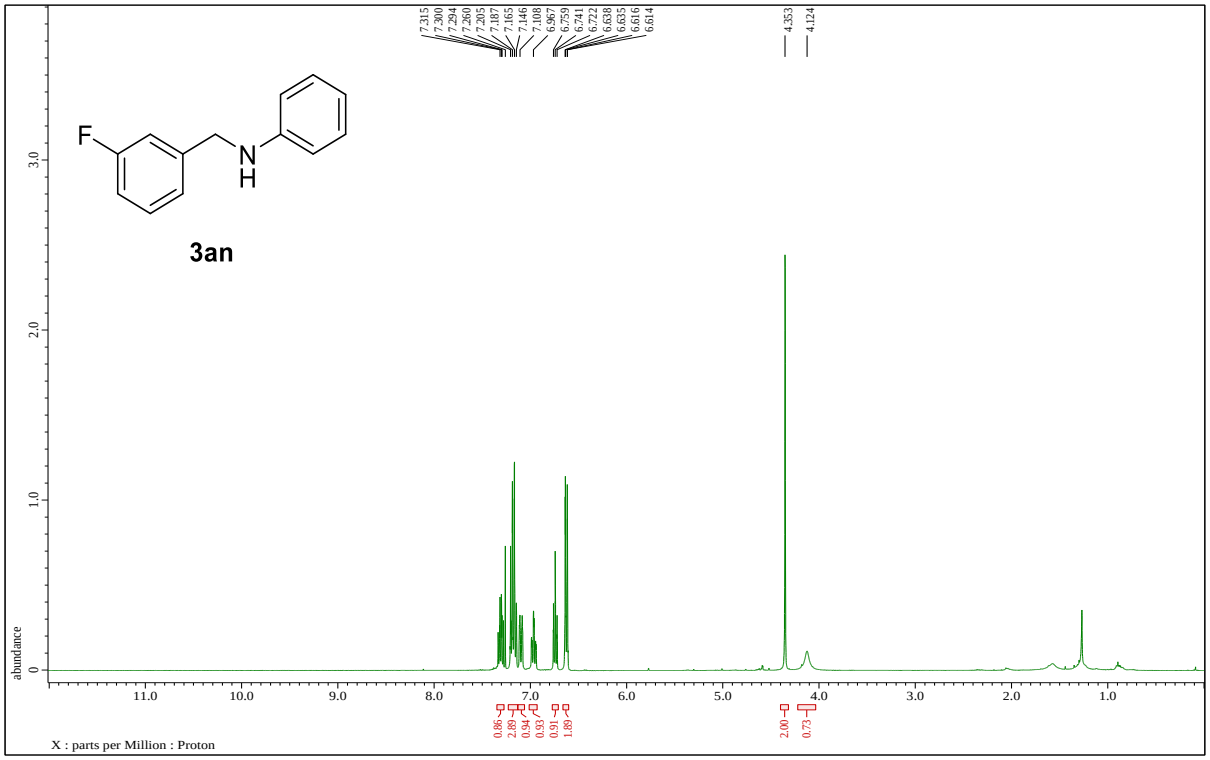
^{13}C-NMR of compound **3am** ($CDCl_3$, 100 MHz)



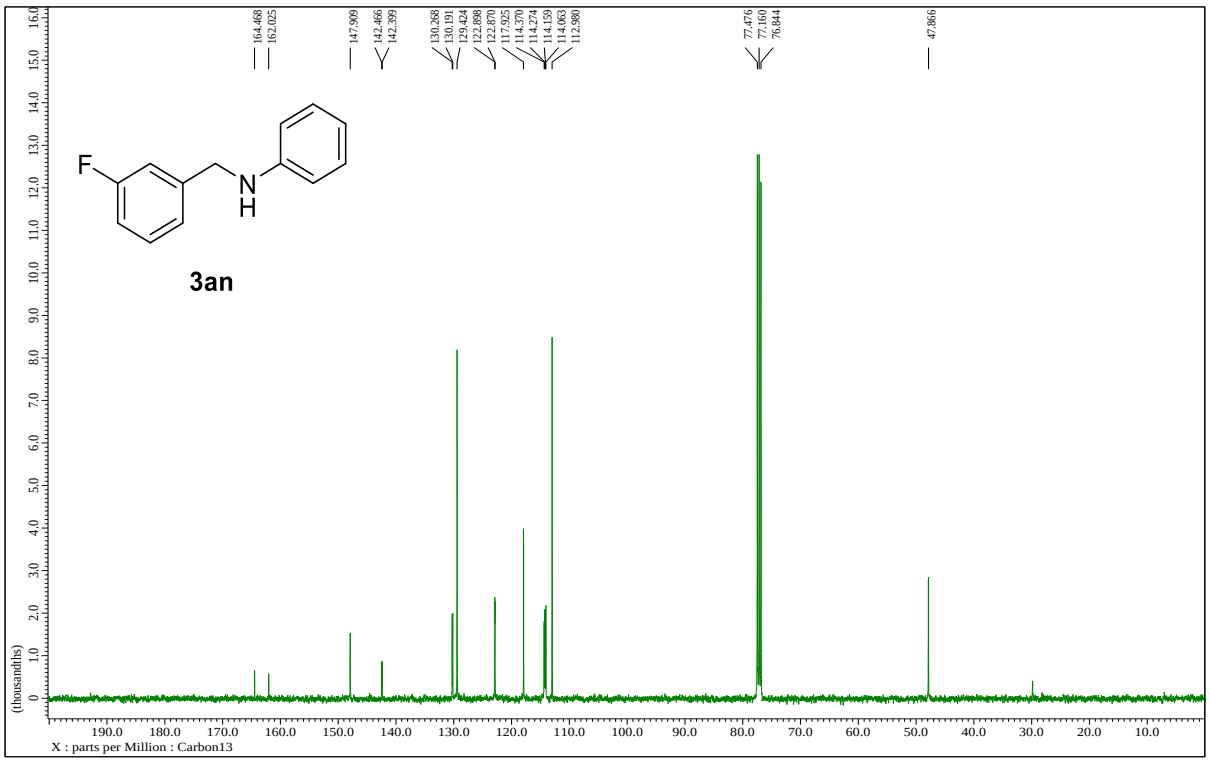
^{19}F-NMR of compound **3am** ($CDCl_3$, 375 MHz)



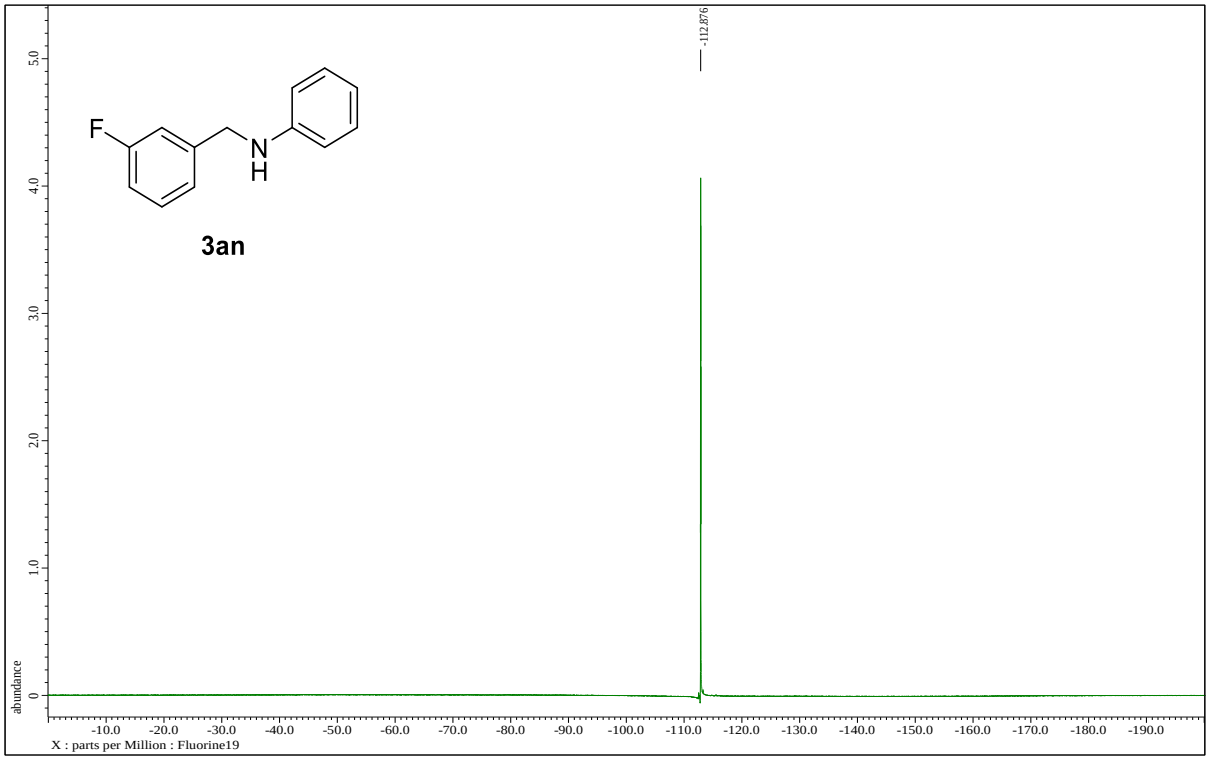
^{1}H-NMR of compound **3an** ($CDCl_3$, 400 MHz)



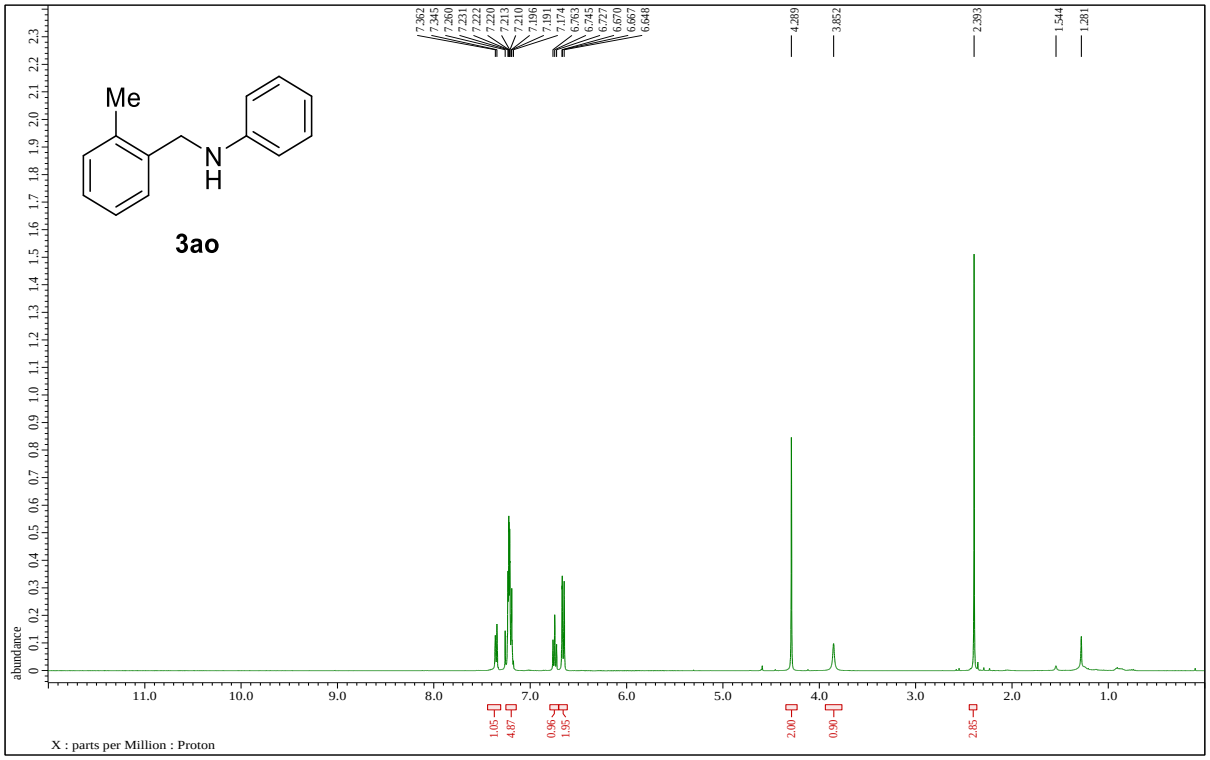
^{13}C-NMR of compound **3an** ($CDCl_3$, 100 MHz)



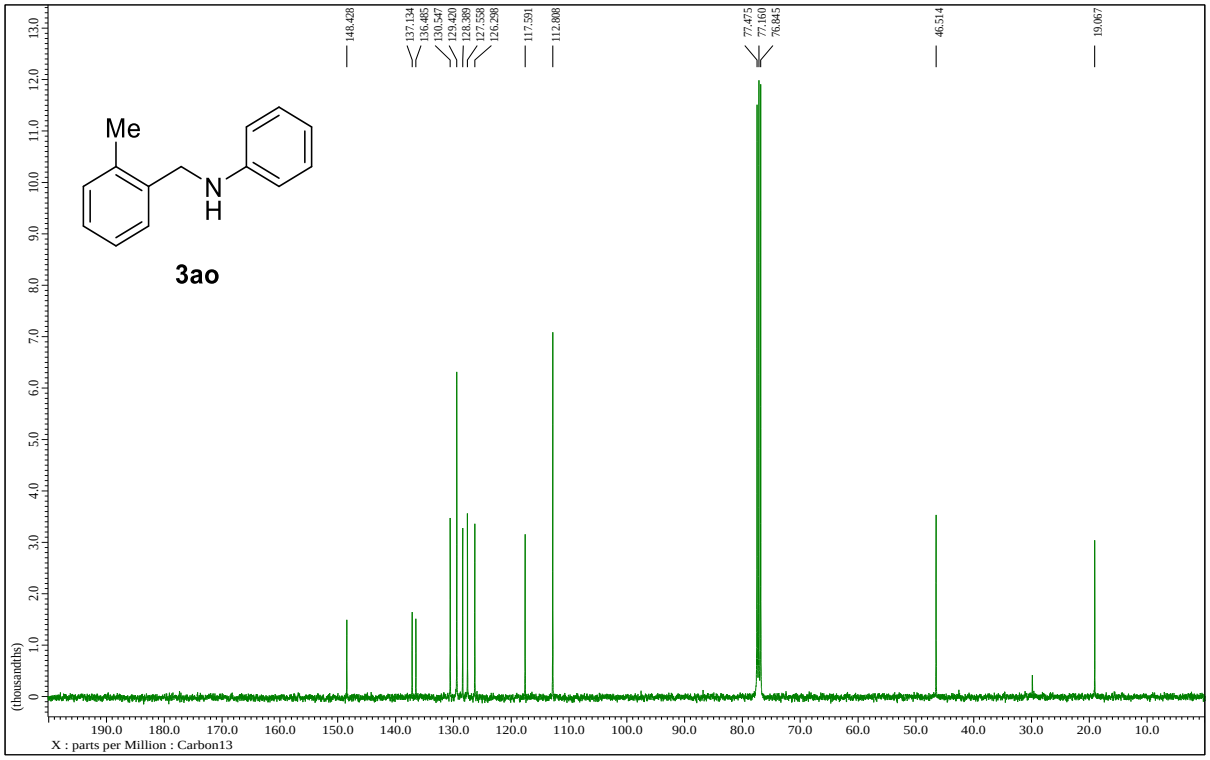
^{19}F-NMR of compound **3an** ($CDCl_3$, 375 MHz)



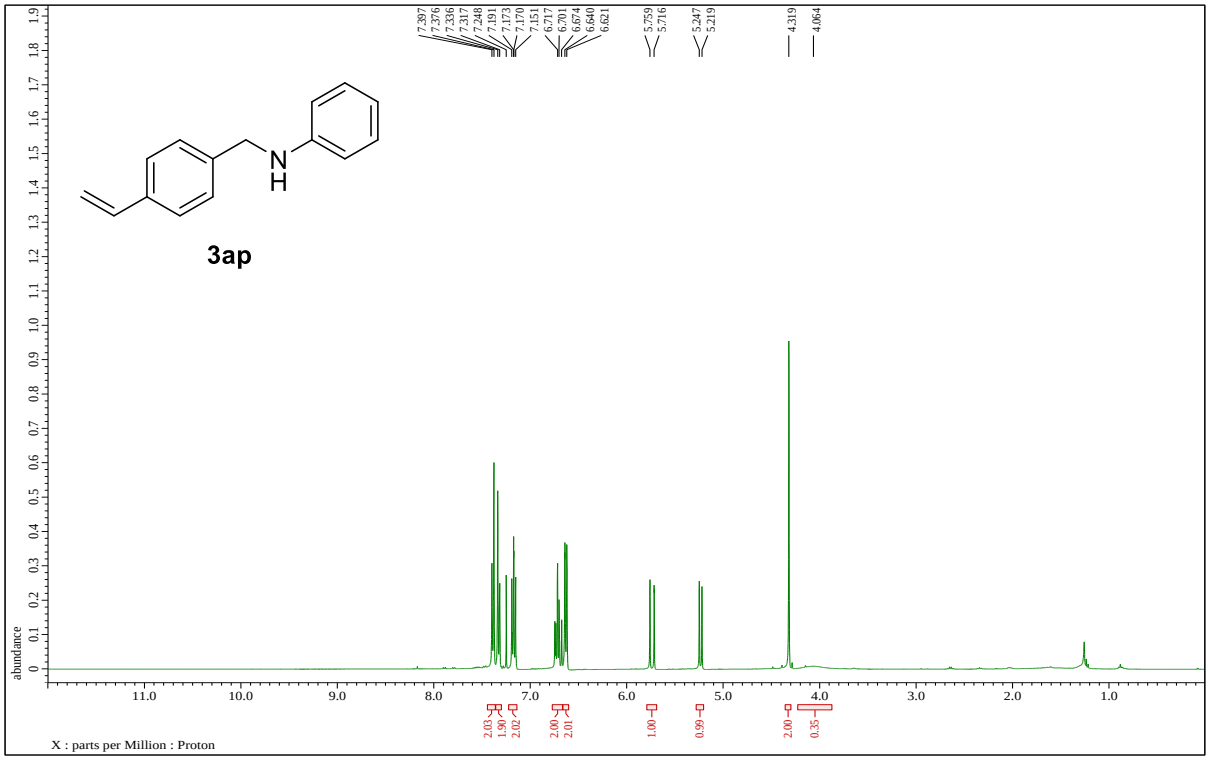
^{1}H-NMR of compound **3ao** ($CDCl_3$, 400 MHz)



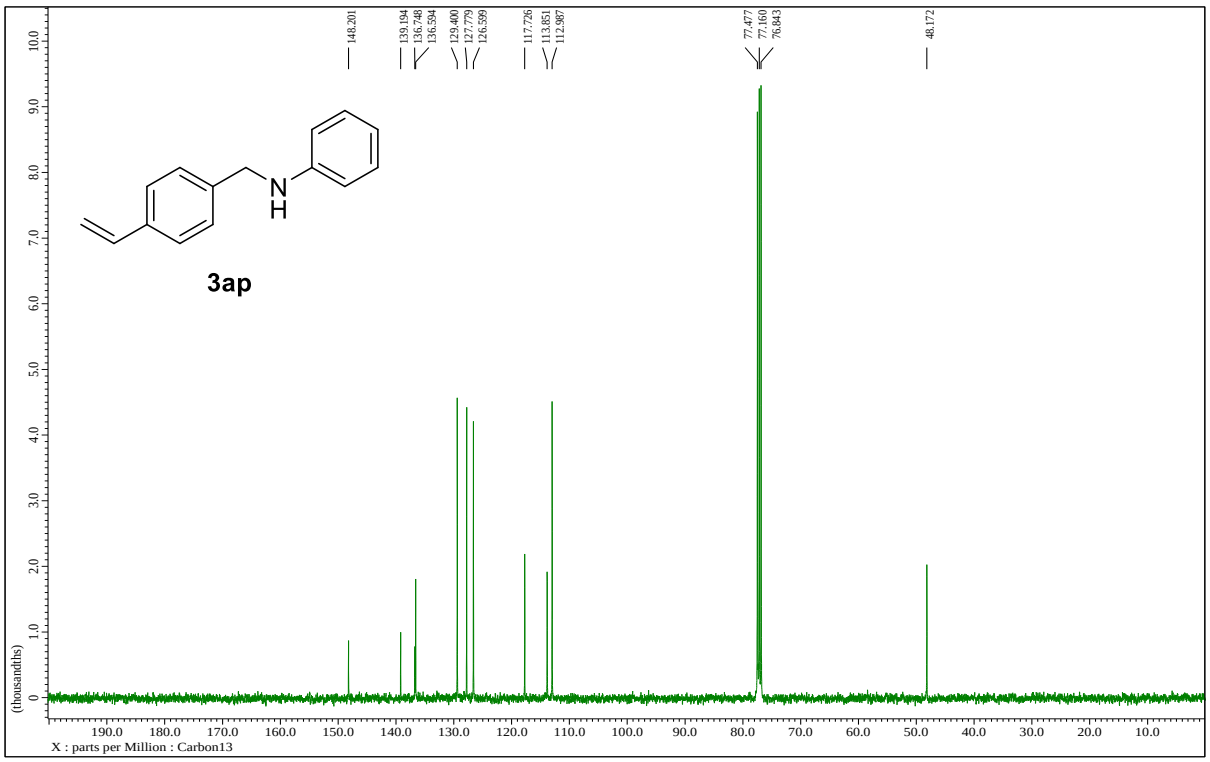
^{13}C-NMR of compound **3ao** ($CDCl_3$, 100 MHz)



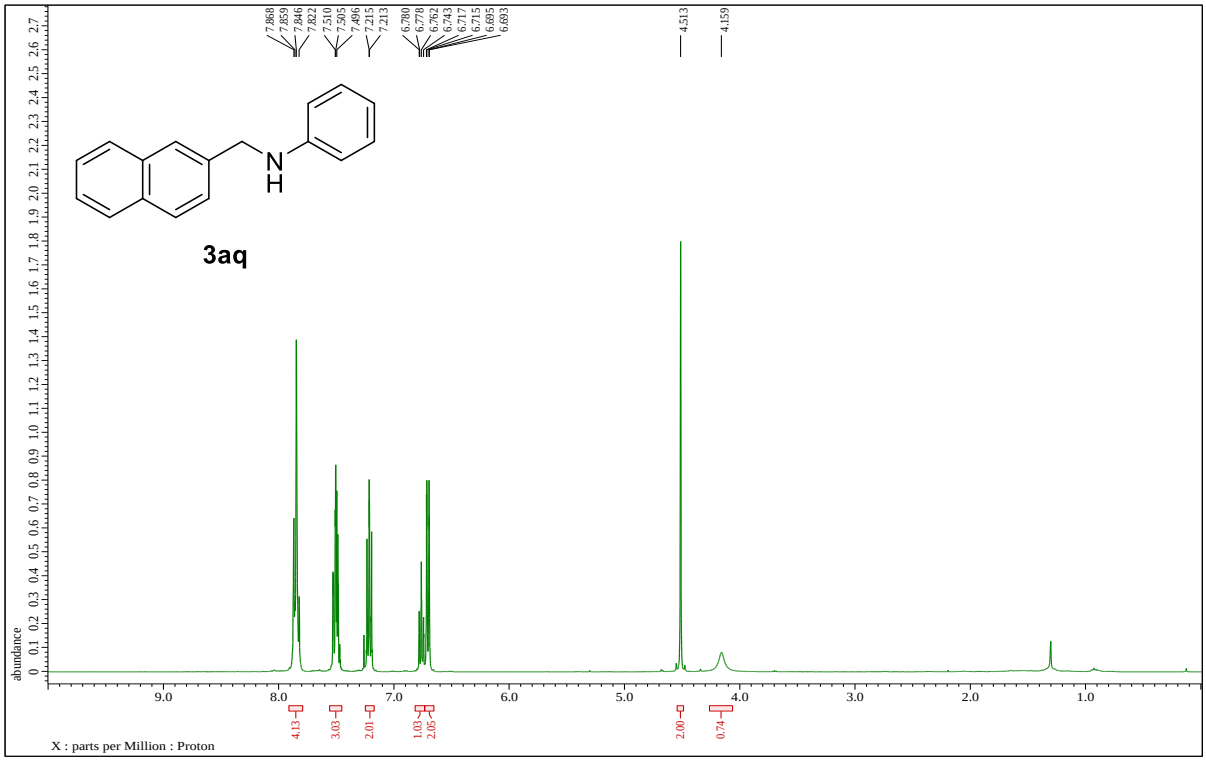
^{1}H-NMR of compound **3ap** ($CDCl_3$, 400 MHz)



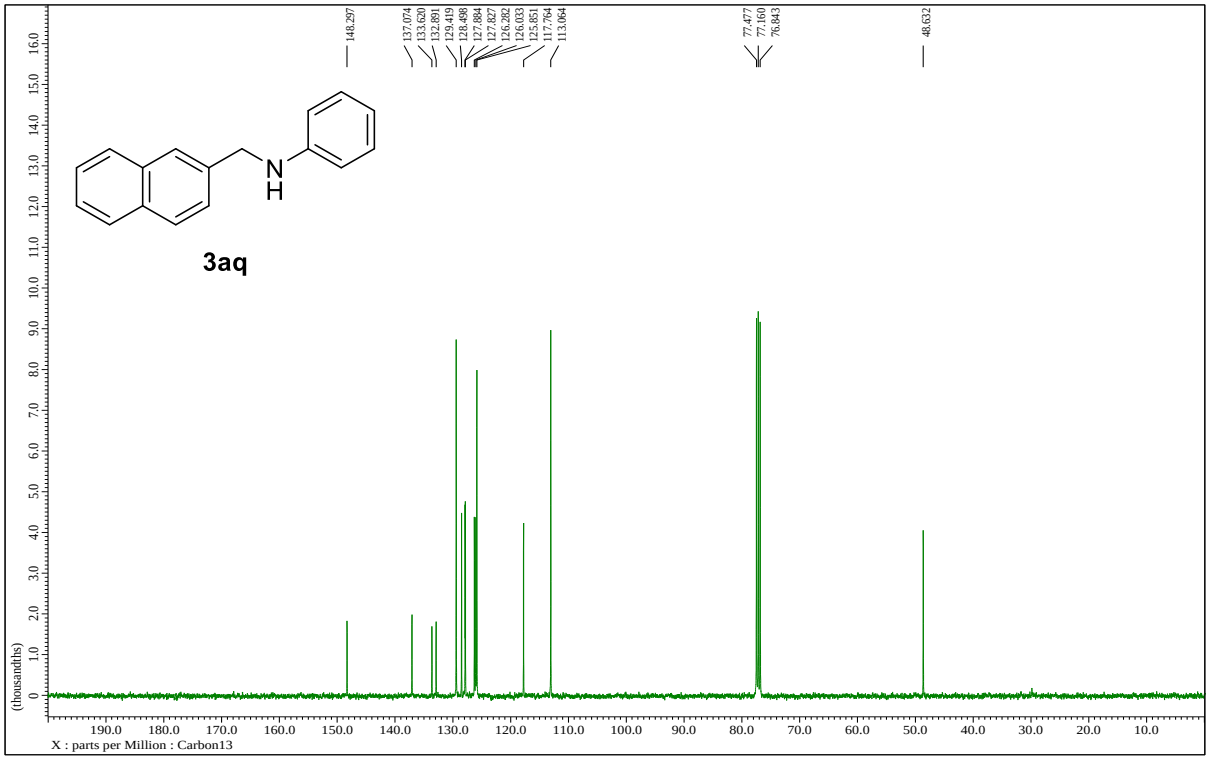
^{13}C-NMR of compound **3ap** ($CDCl_3$, 100 MHz)



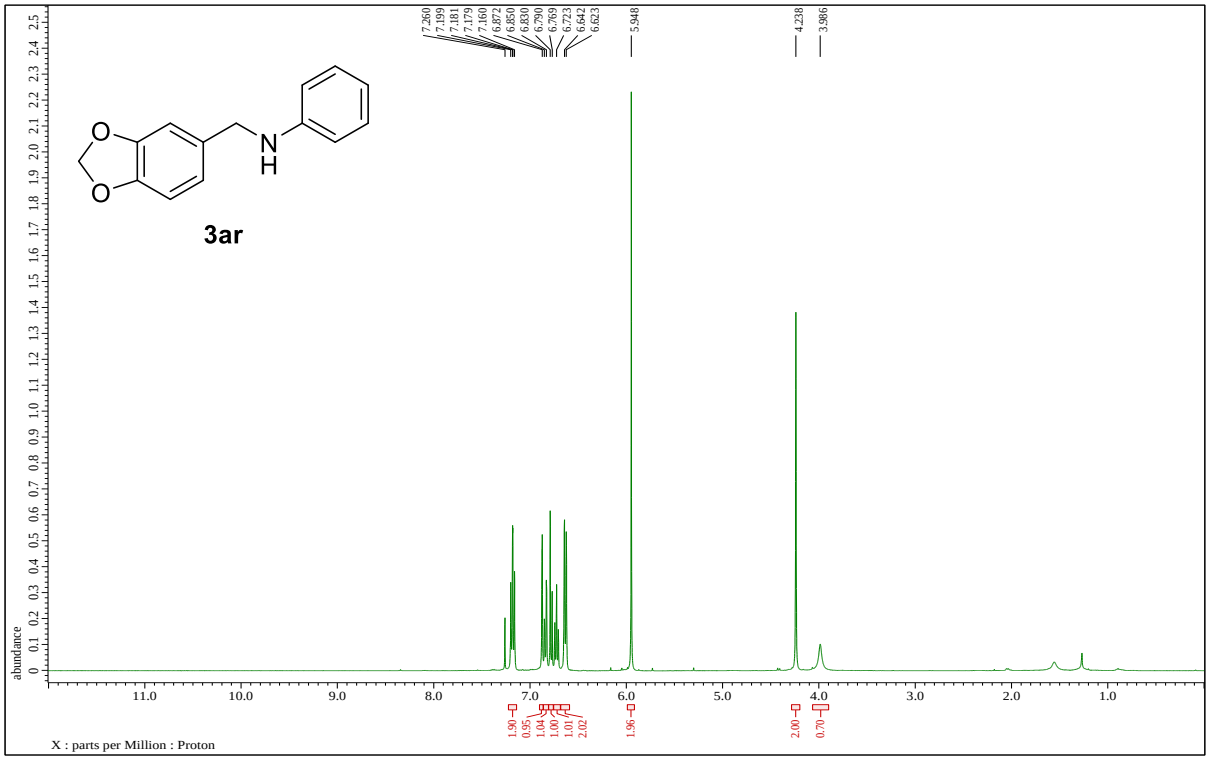
^{1}H-NMR of compound **3aq** ($CDCl_3$, 400 MHz)



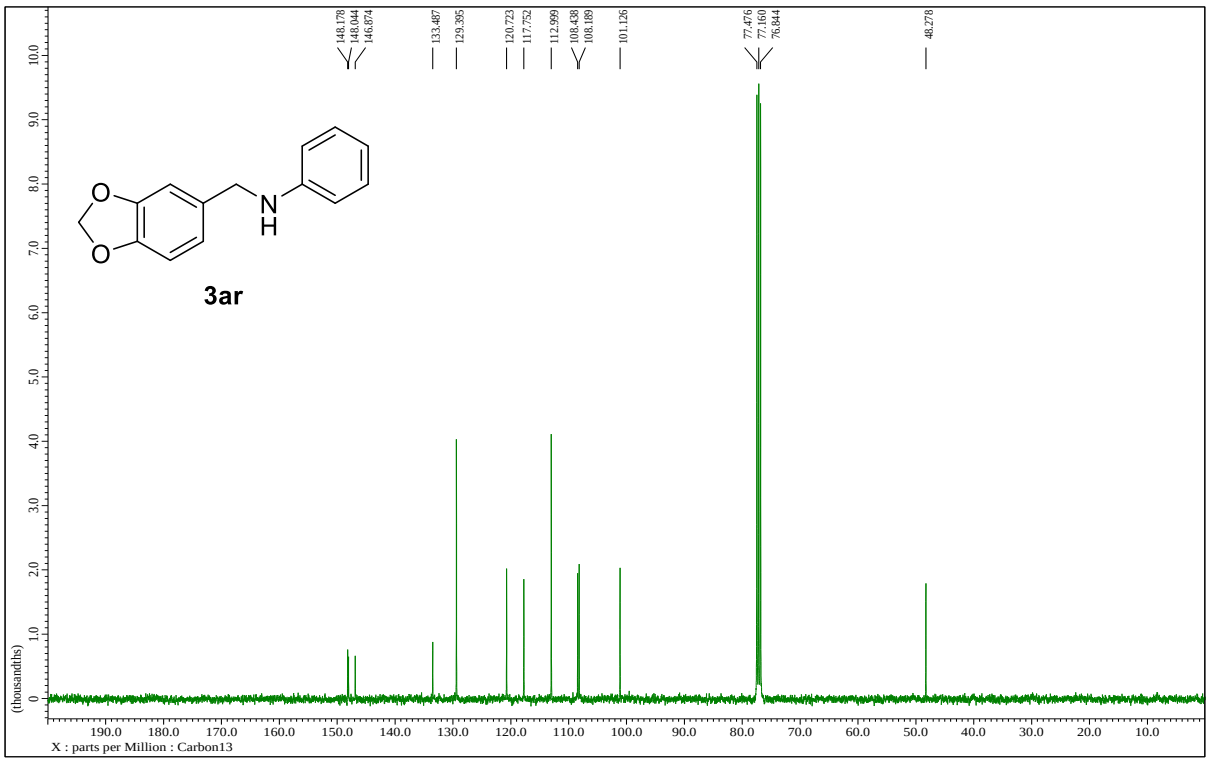
^{13}C-NMR of compound **3aq** ($CDCl_3$, 100 MHz)



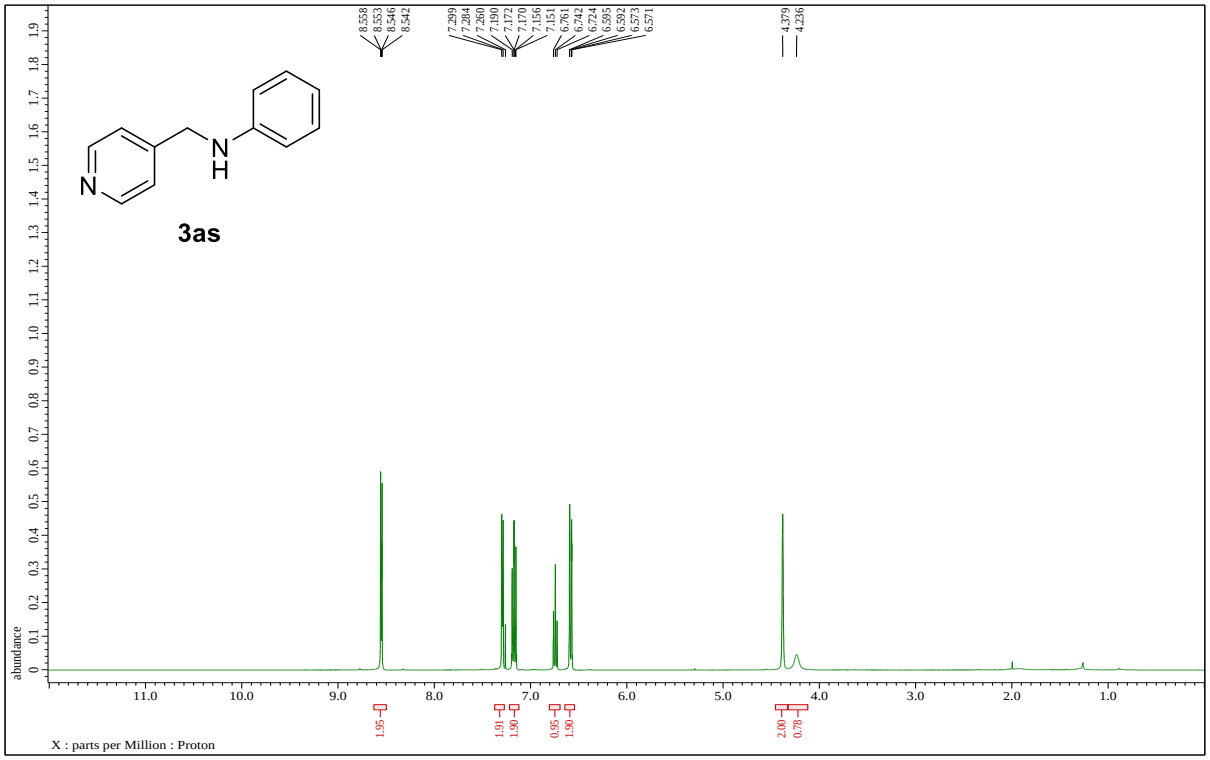
^{1}H-NMR of compound **3ar** ($CDCl_3$, 400 MHz)



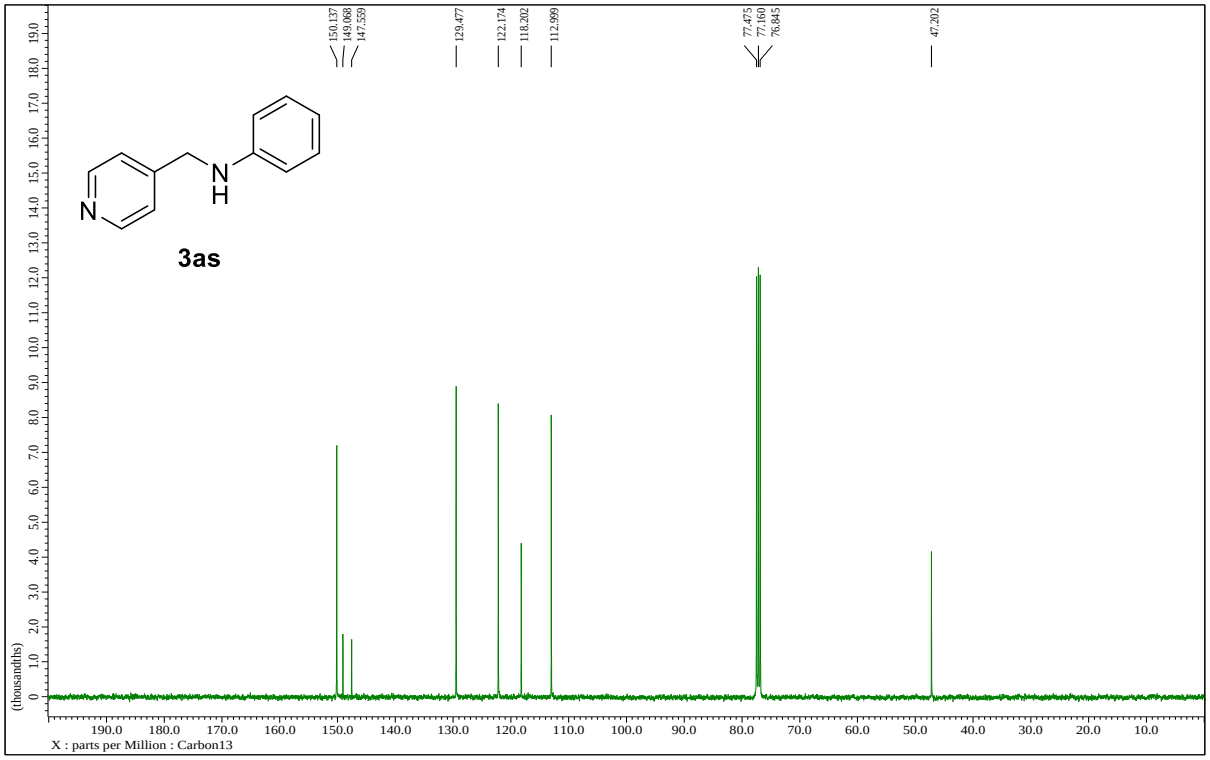
^{13}C-NMR of compound **3ar** ($CDCl_3$, 100 MHz)



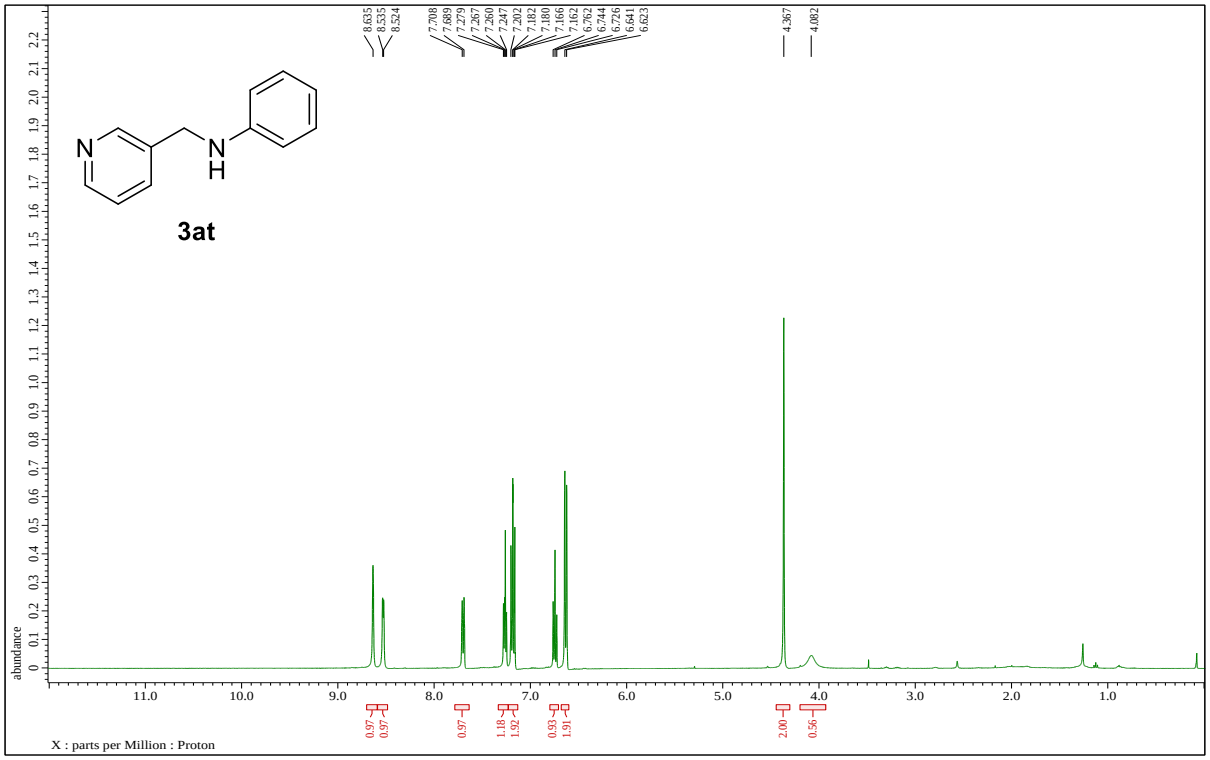
^{1}H-NMR of compound **3as** ($CDCl_3$, 400 MHz)



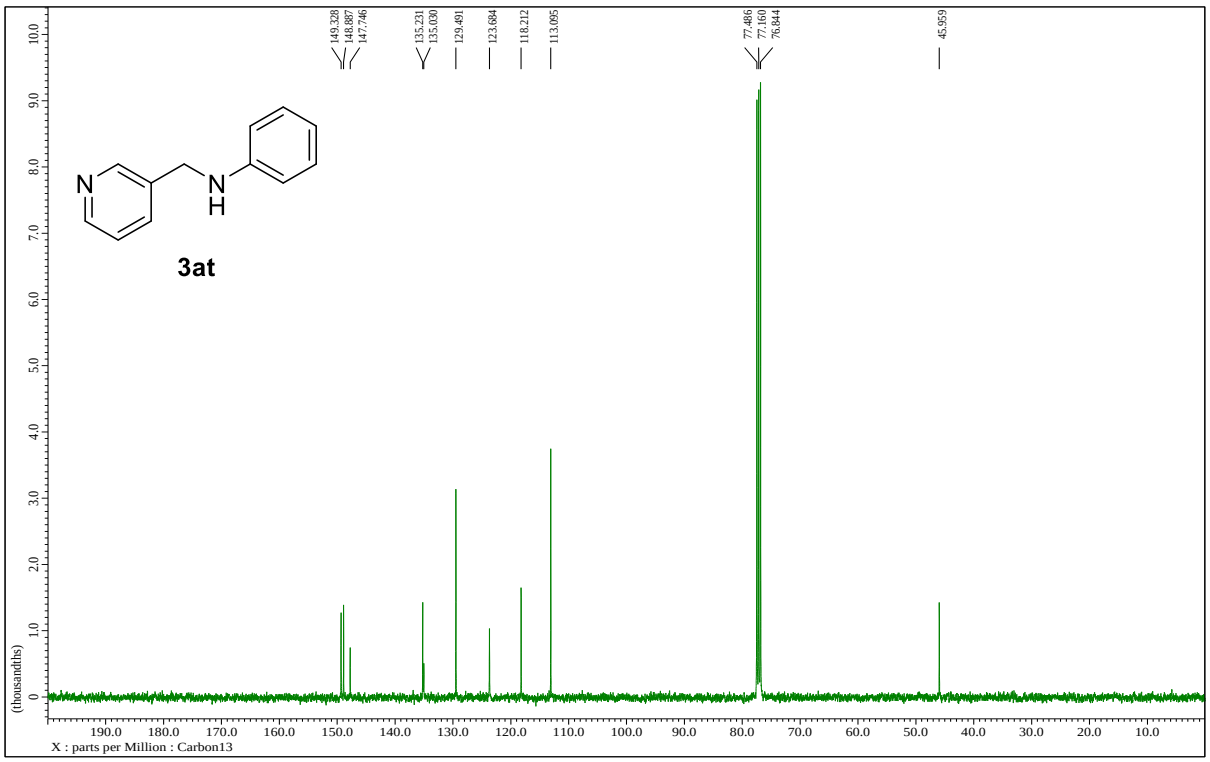
^{13}C-NMR of compound **3as** ($CDCl_3$, 100 MHz)



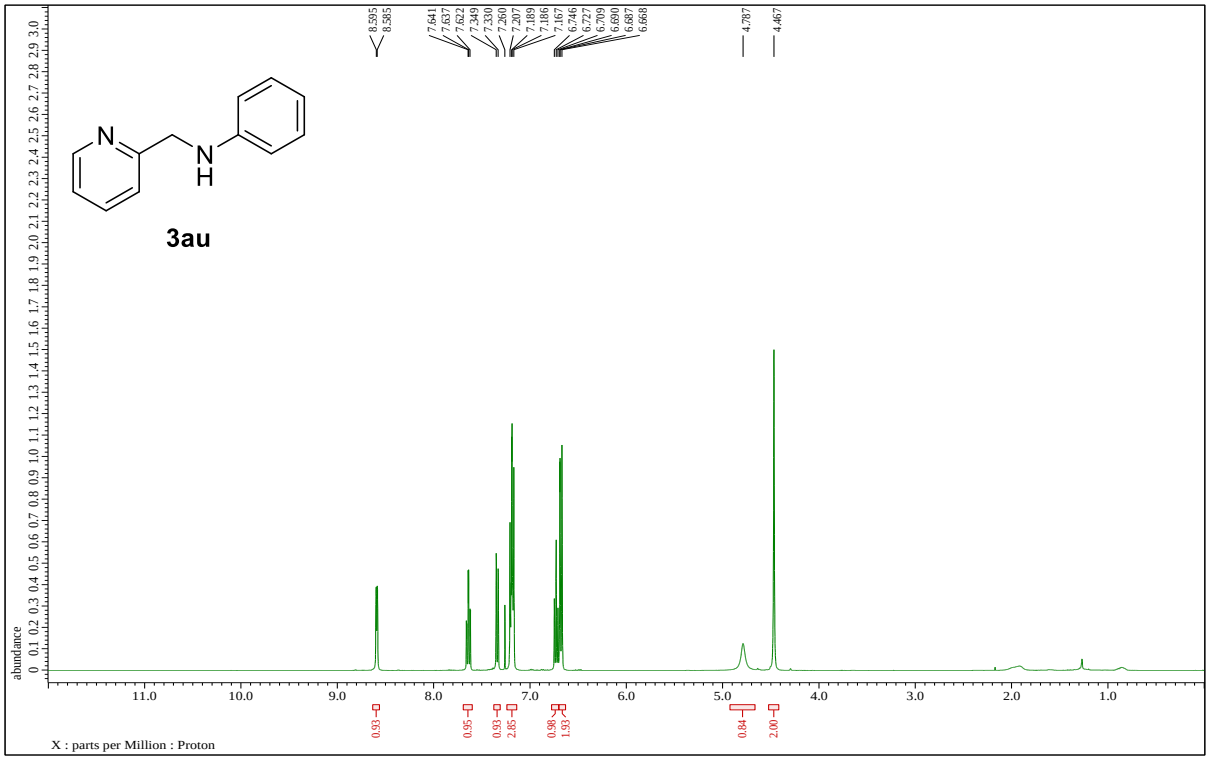
^{1}H-NMR of compound **3at** ($CDCl_3$, 400 MHz)



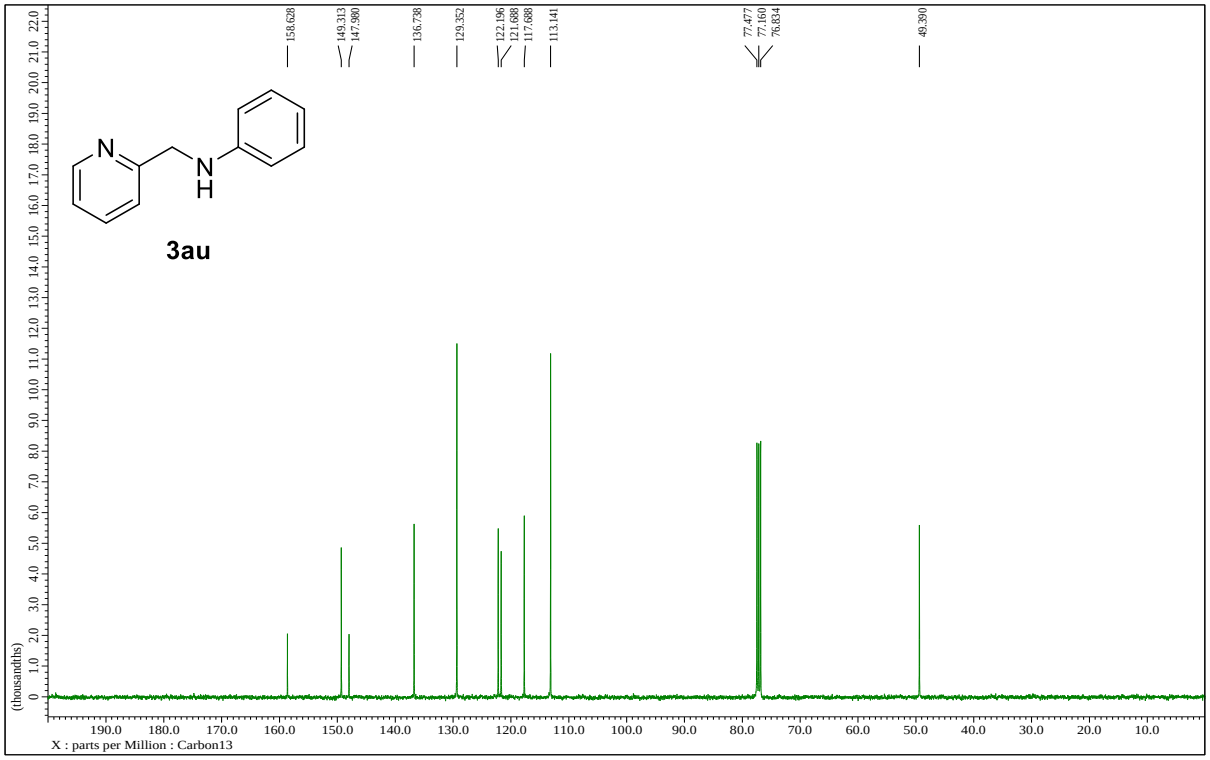
^{13}C-NMR of compound **3at** ($CDCl_3$, 100 MHz)



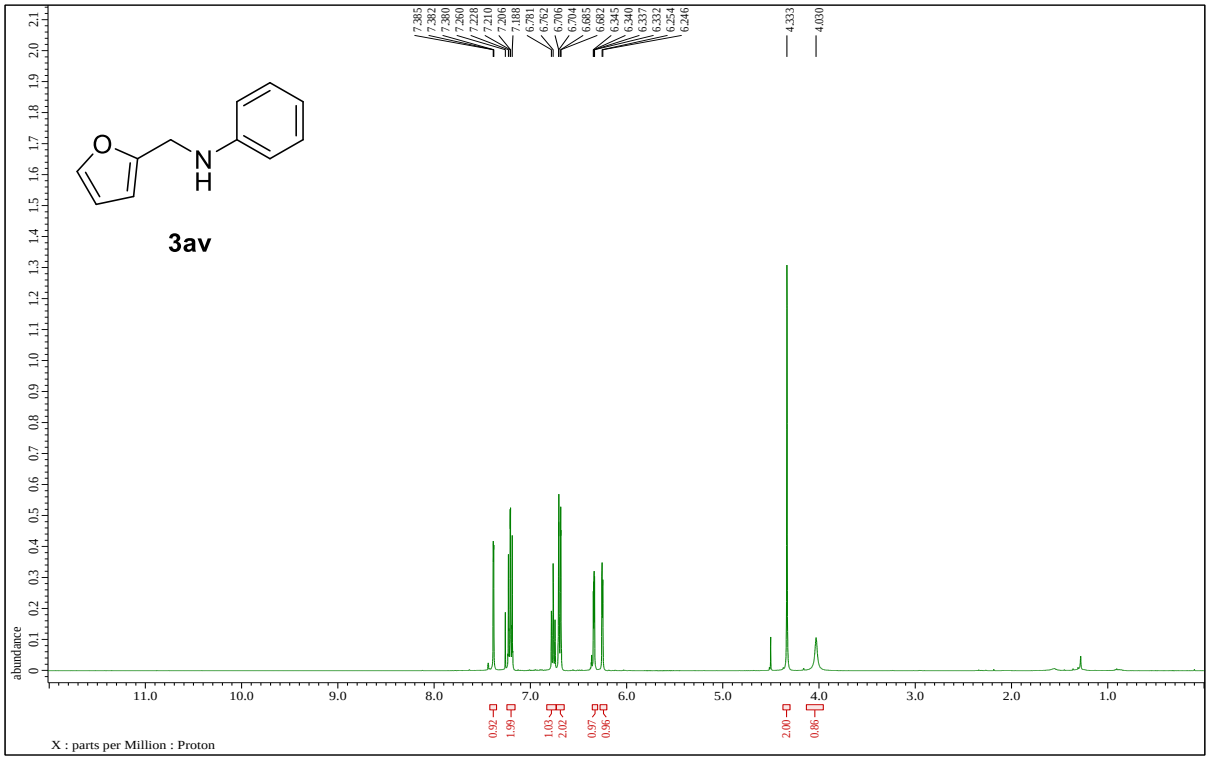
^{1}H-NMR of compound **3au** ($CDCl_3$, 400 MHz)



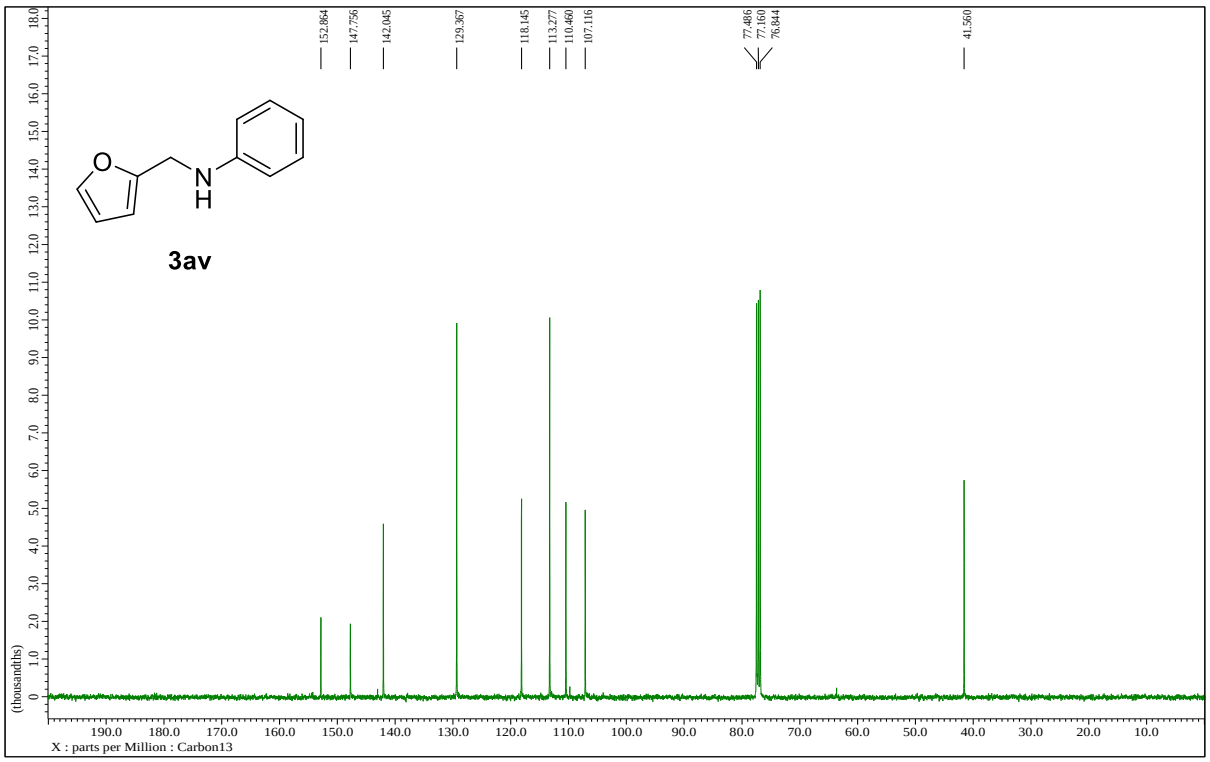
^{13}C-NMR of compound **3au** ($CDCl_3$, 100 MHz)



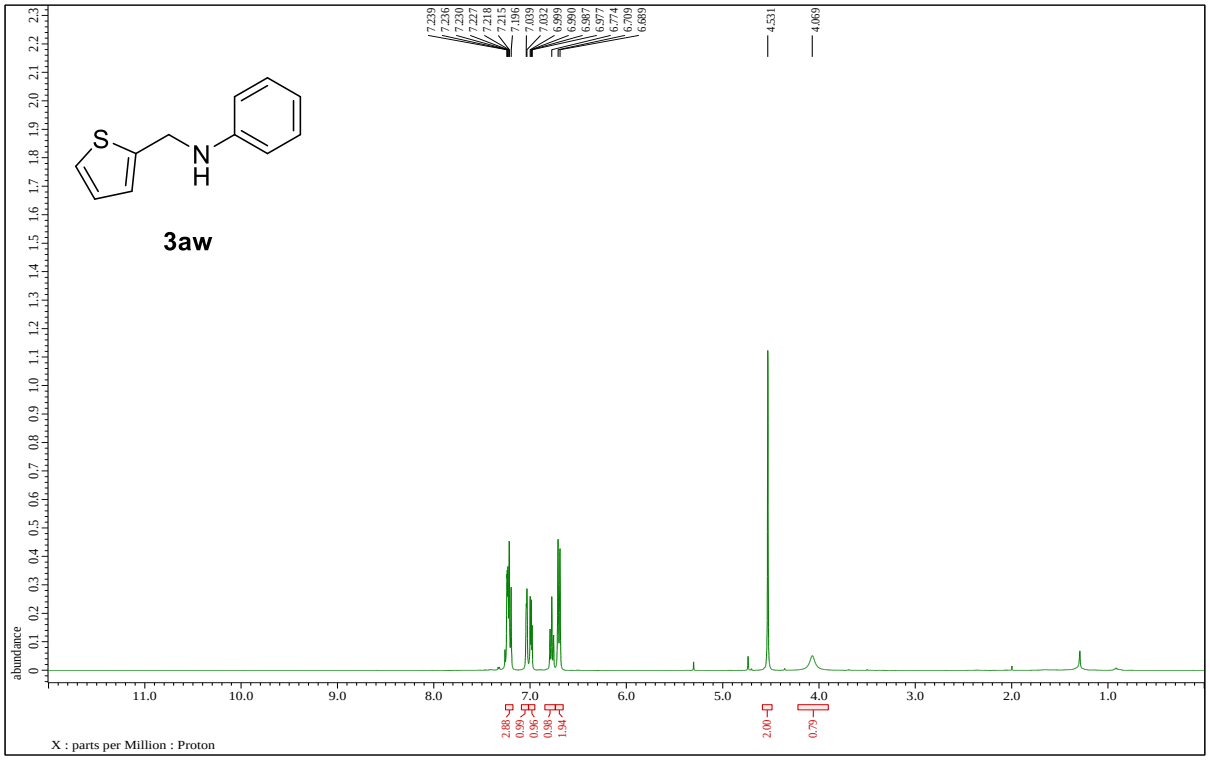
^{1}H-NMR of compound **3av** ($CDCl_3$, 400 MHz)



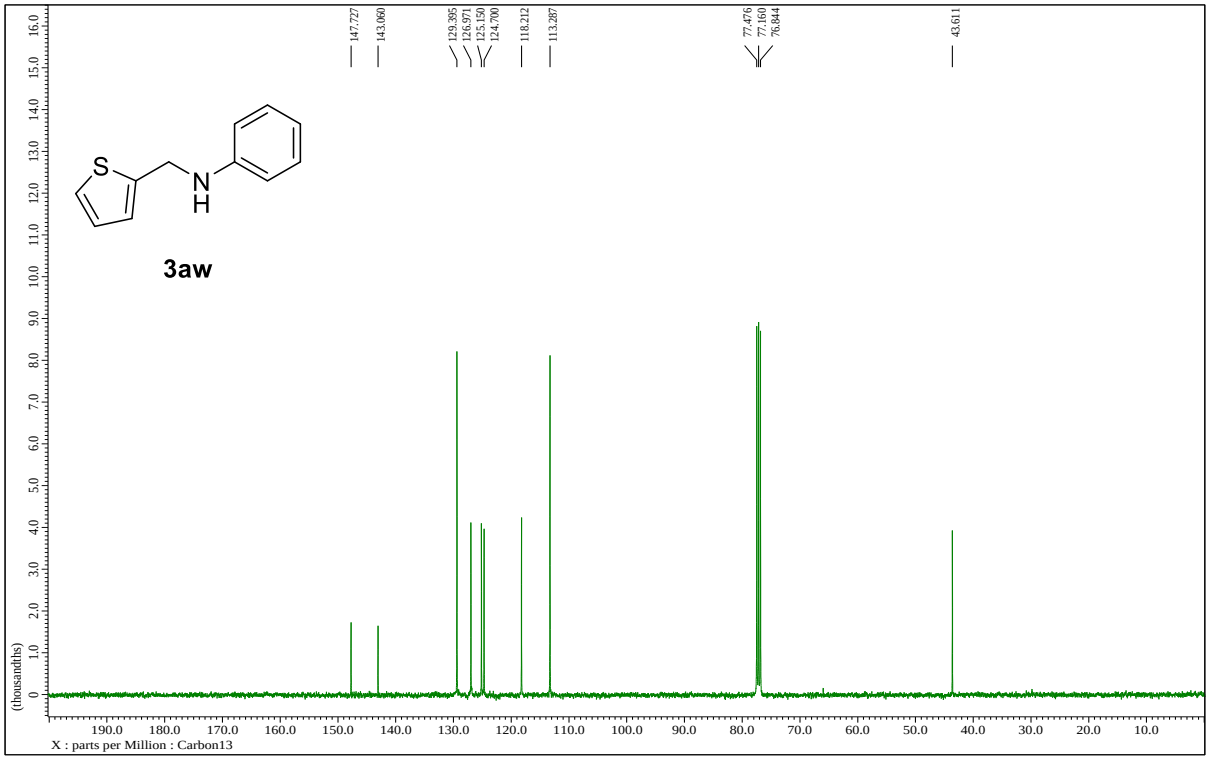
^{13}C-NMR of compound **3av** ($CDCl_3$, 100 MHz)



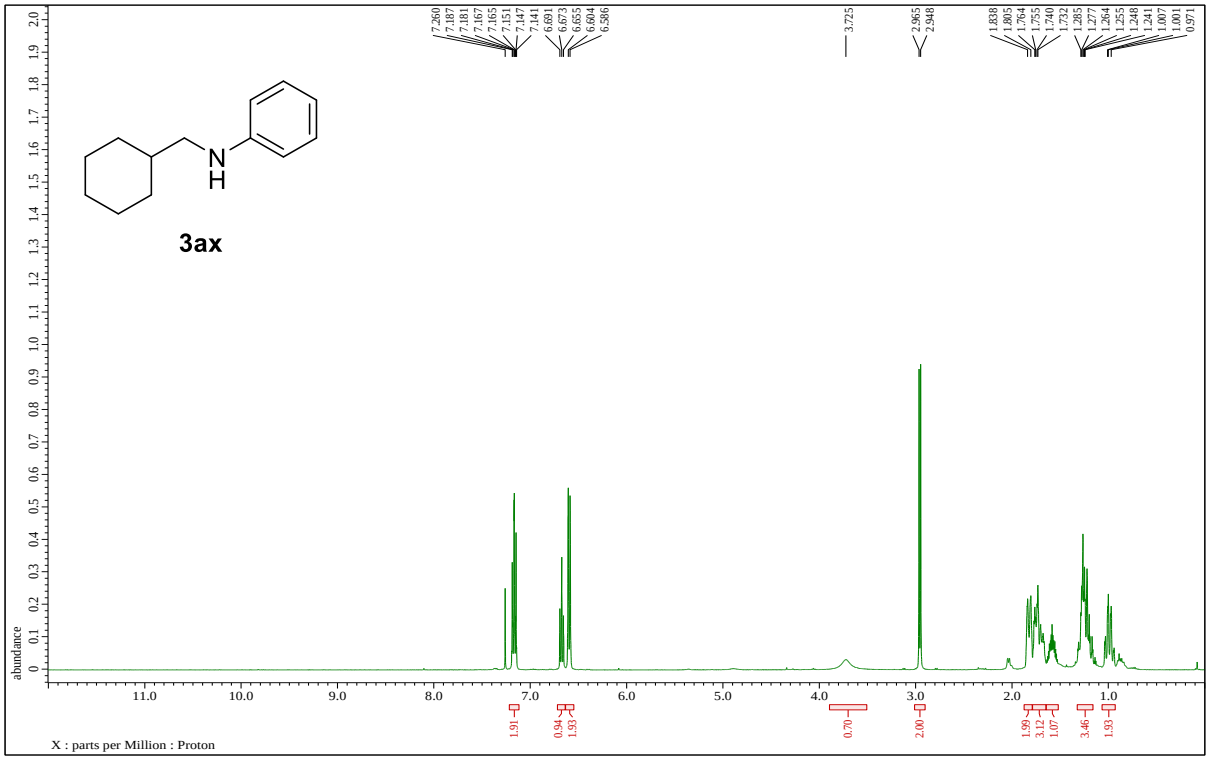
^{1}H-NMR of compound **3aw** ($CDCl_3$, 400 MHz)



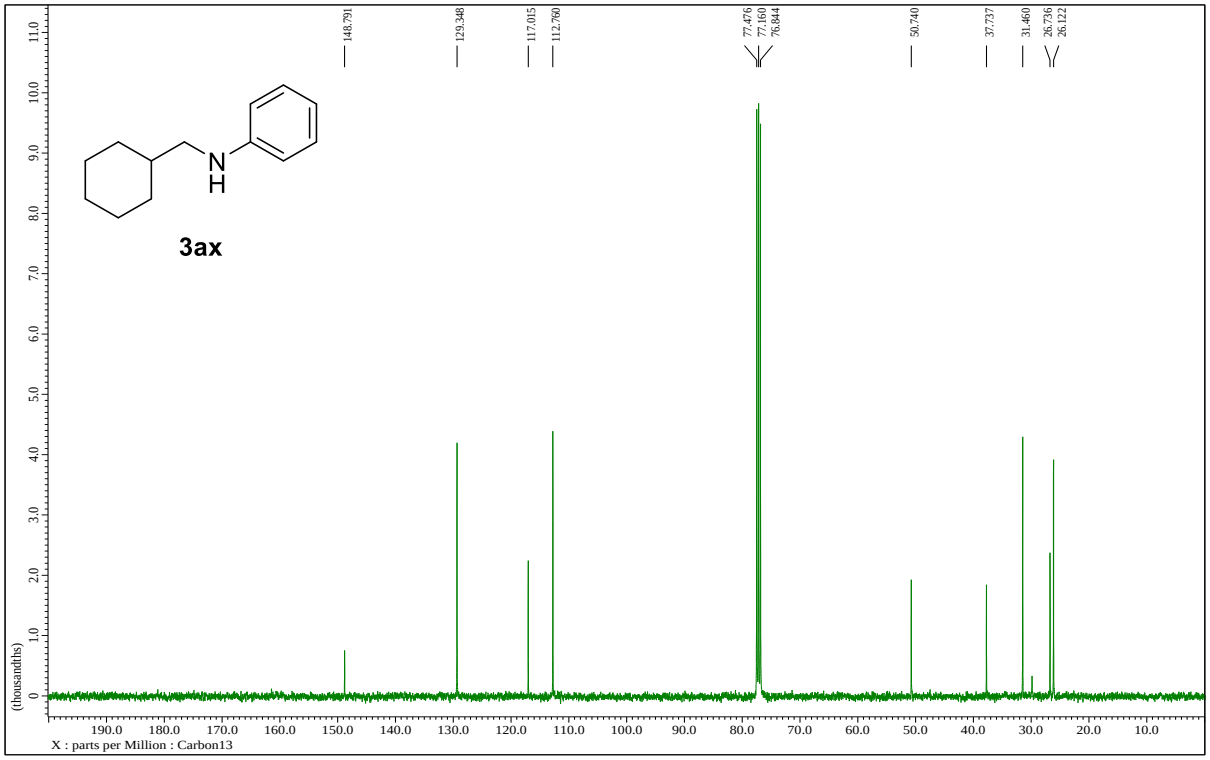
^{13}C-NMR of compound **3aw** ($CDCl_3$, 100 MHz)



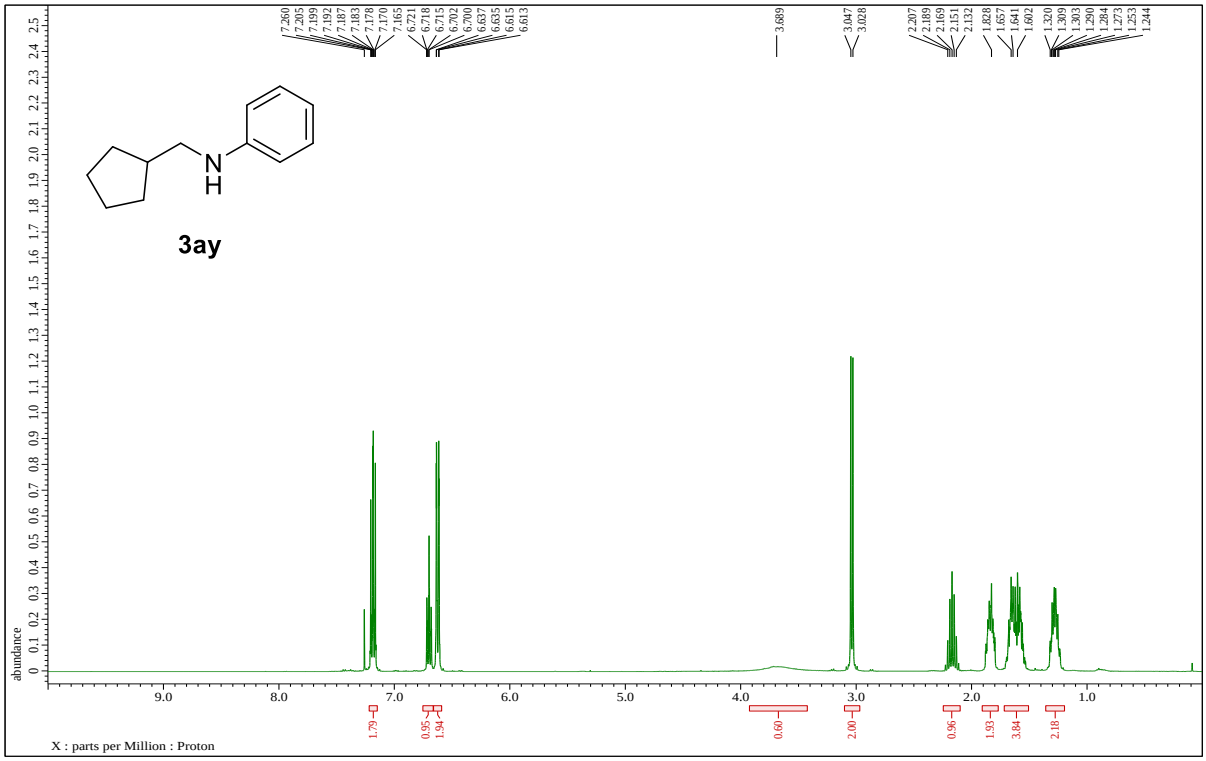
^{1}H-NMR of compound **3ax** ($CDCl_3$, 400 MHz)



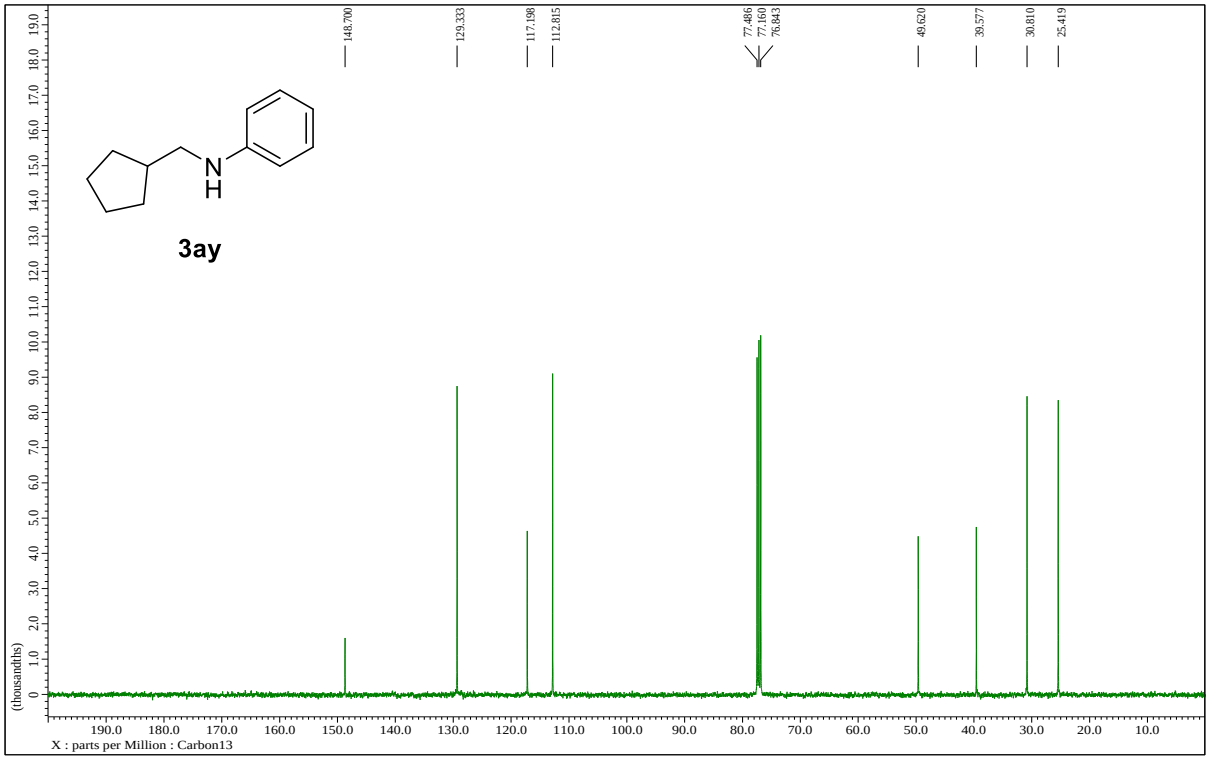
^{13}C-NMR of compound **3ax** ($CDCl_3$, 100 MHz)



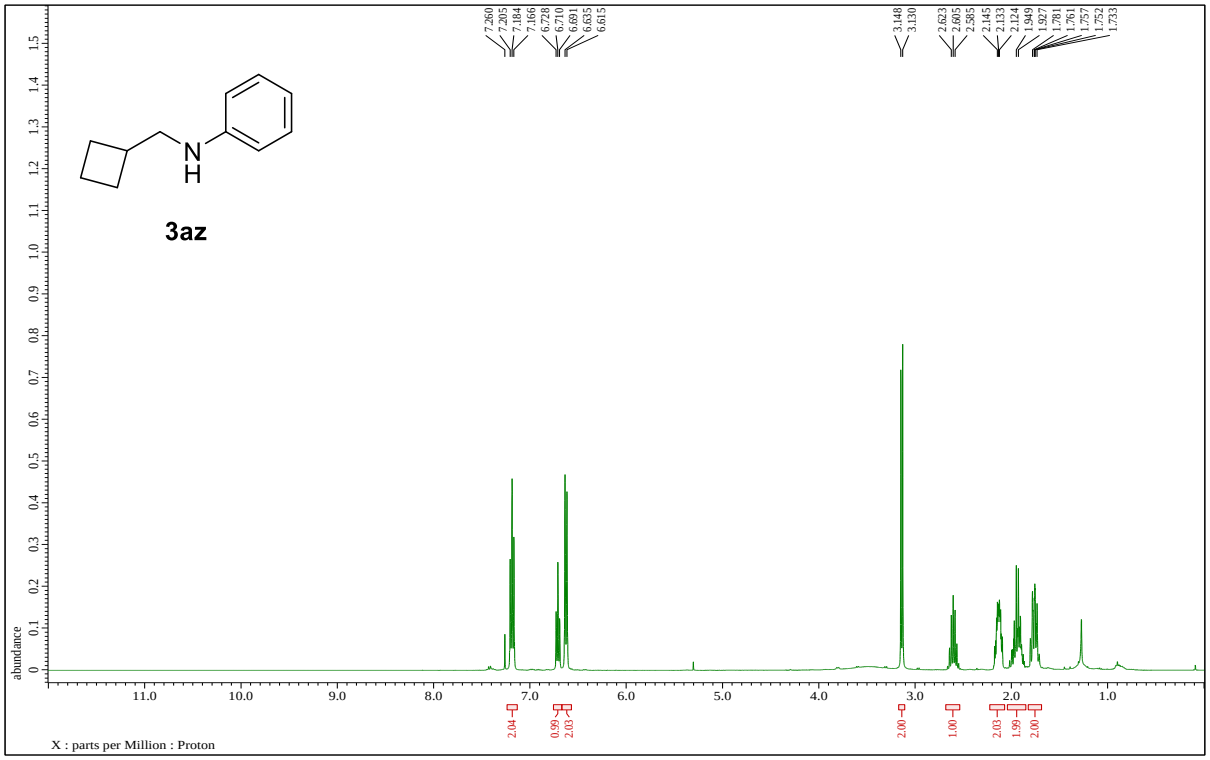
^{1}H-NMR of compound **3ay** ($CDCl_3$, 400 MHz)



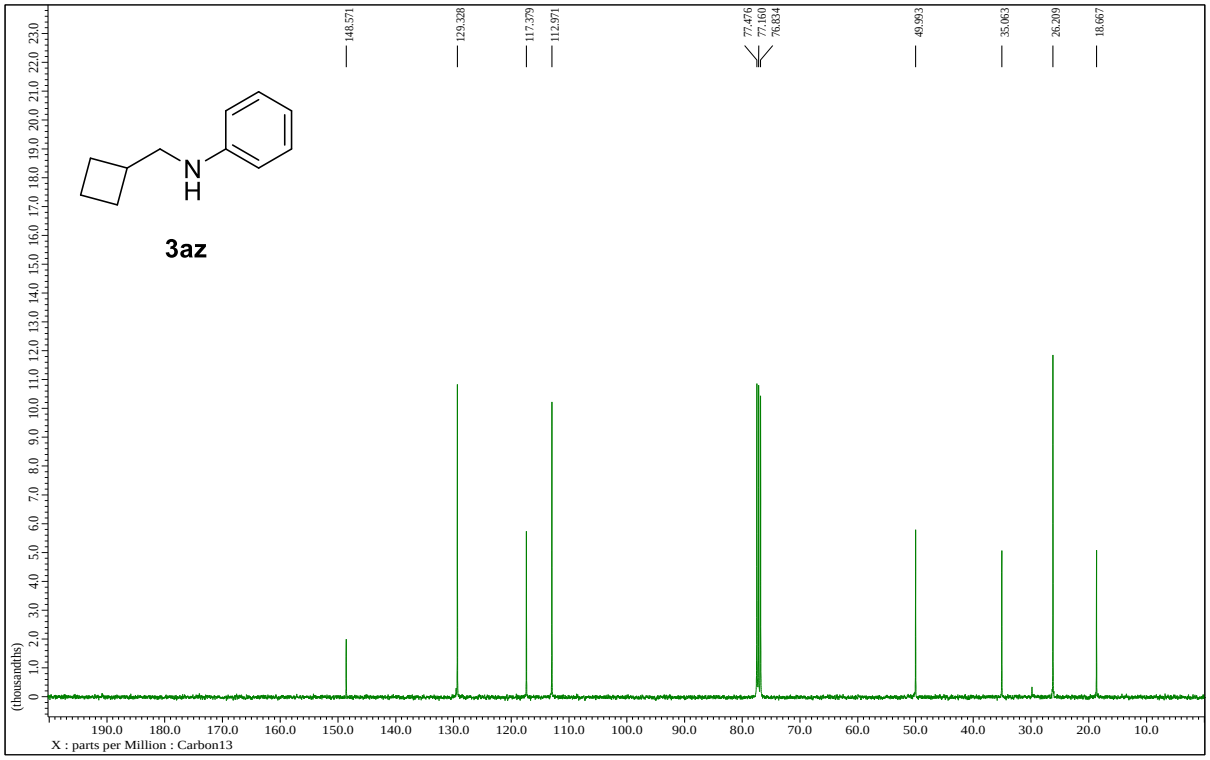
^{13}C-NMR of compound **3ay** ($CDCl_3$, 100 MHz)



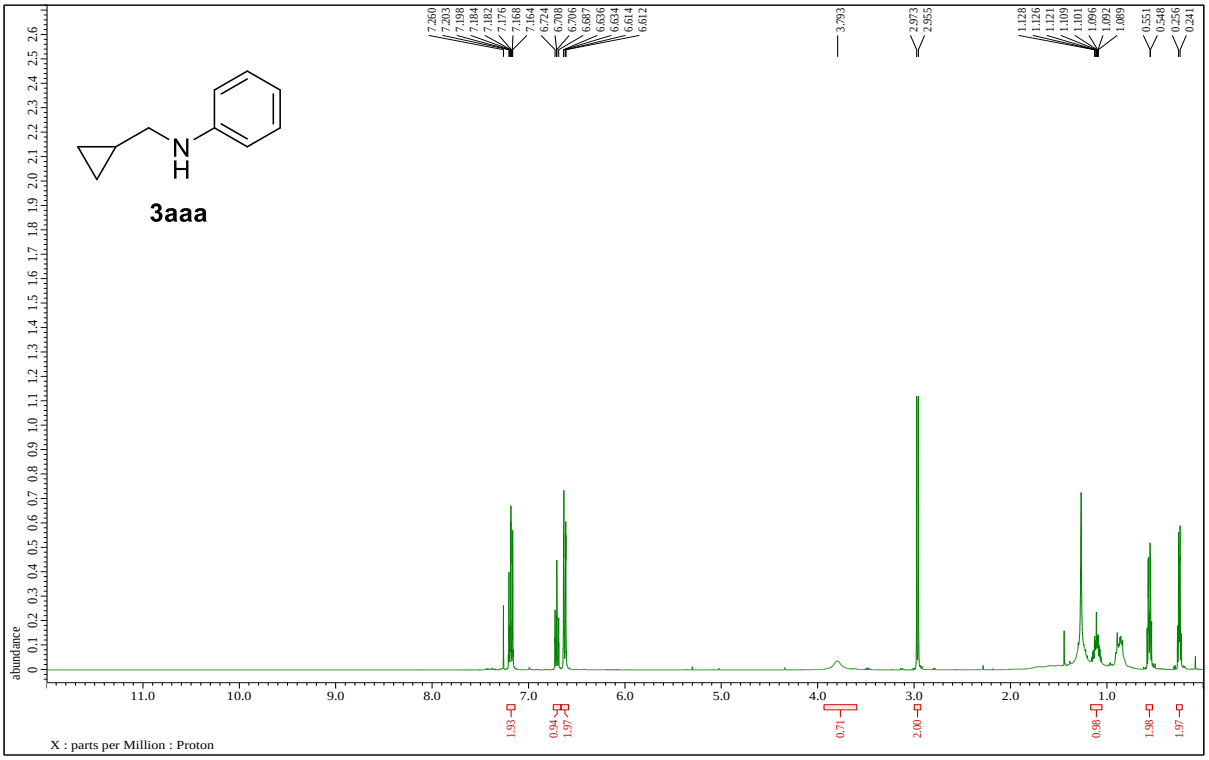
^{1}H-NMR of compound **3az** ($CDCl_3$, 400 MHz)



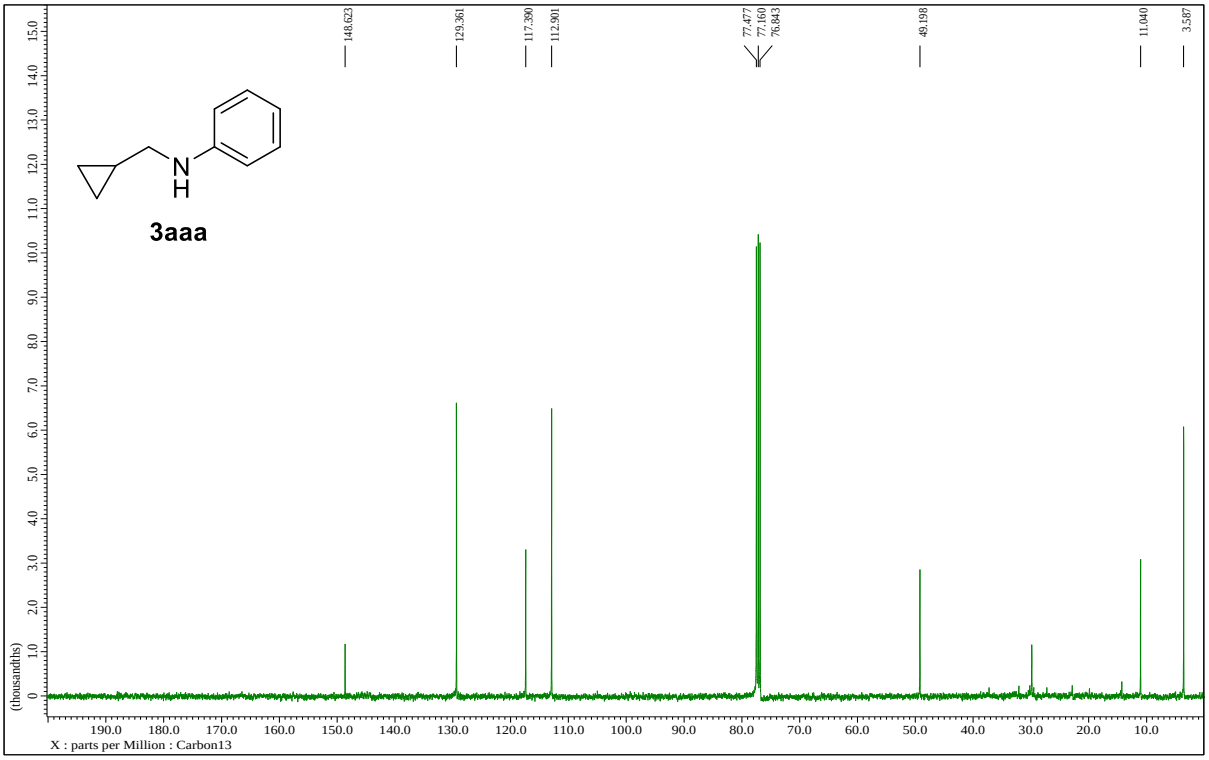
^{13}C-NMR of compound **3az** ($CDCl_3$, 100 MHz)



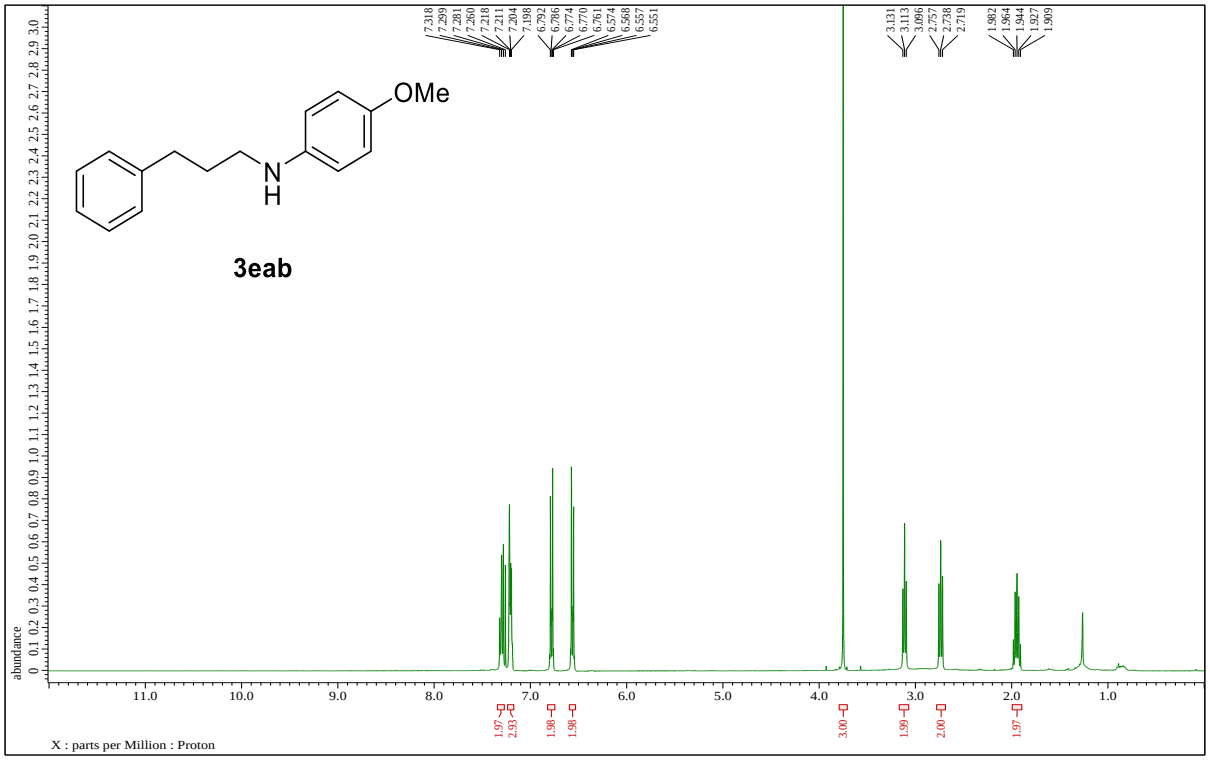
^{1}H-NMR of compound **3aaa** ($CDCl_3$, 400 MHz)



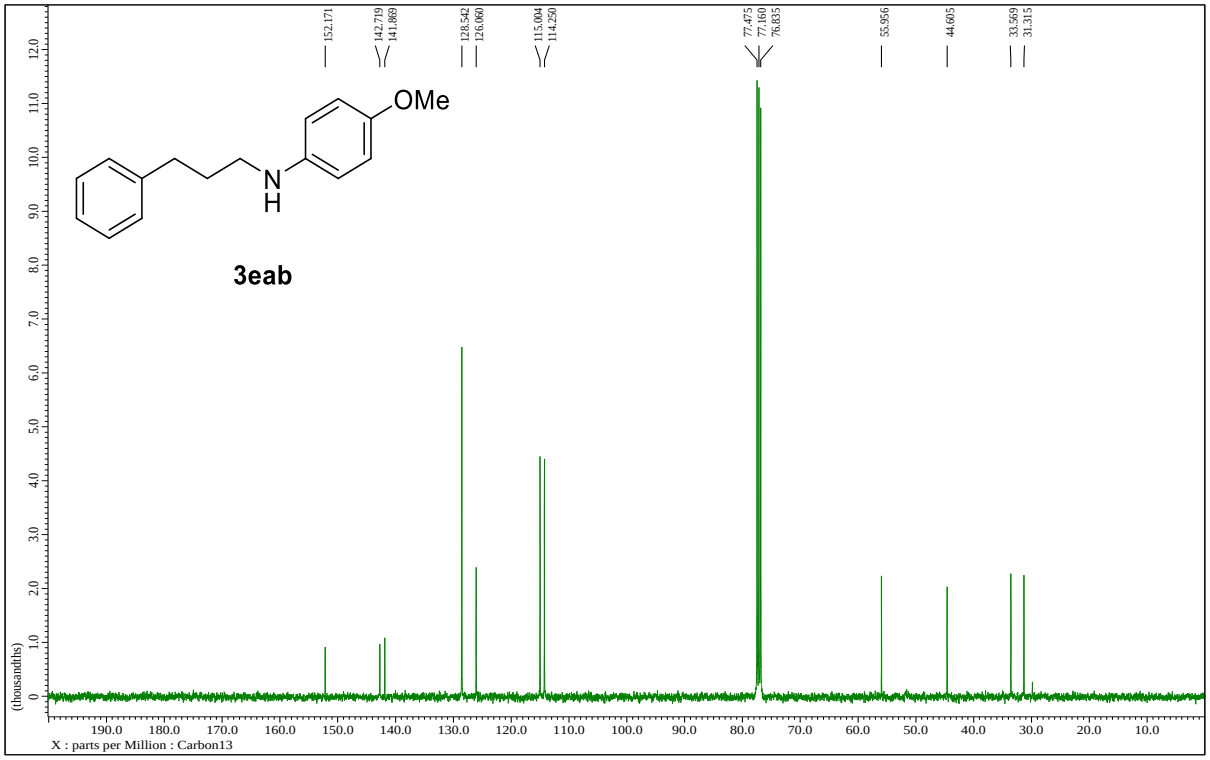
^{13}C-NMR of compound **3aaa** ($CDCl_3$, 100 MHz)



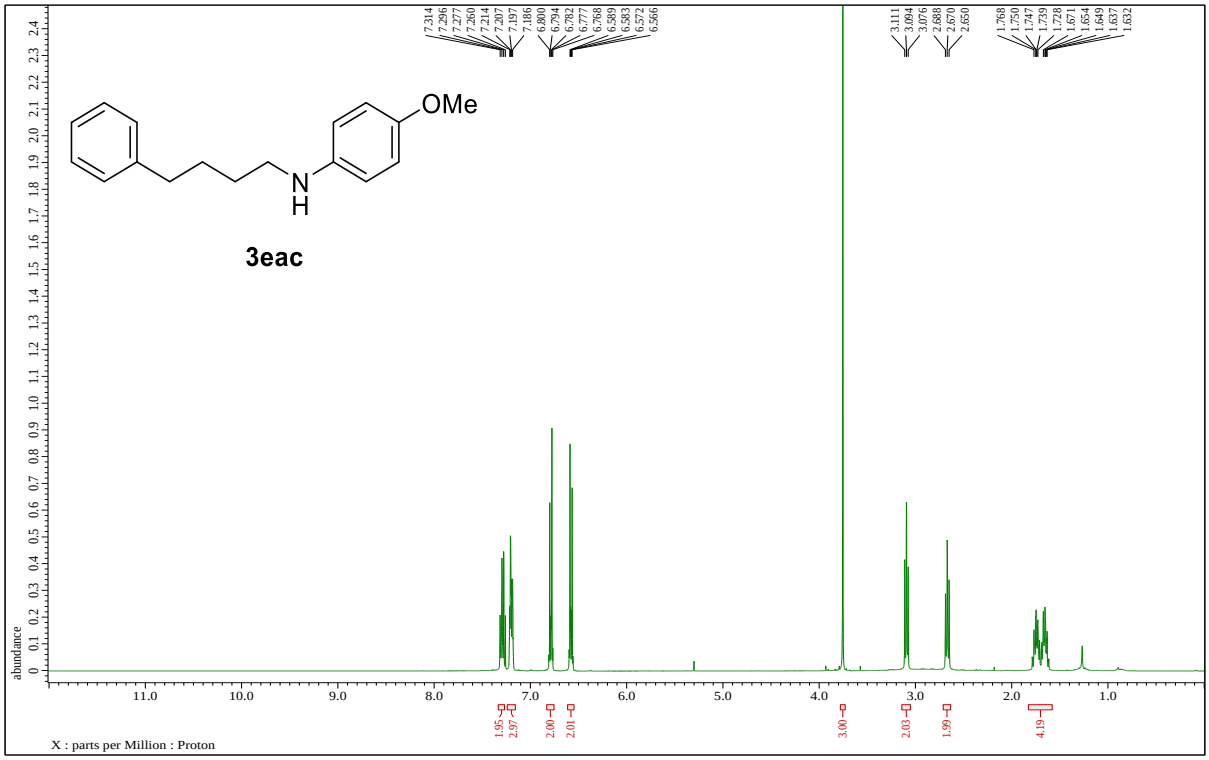
^{1}H-NMR of compound **3eab** ($CDCl_3$, 400 MHz)



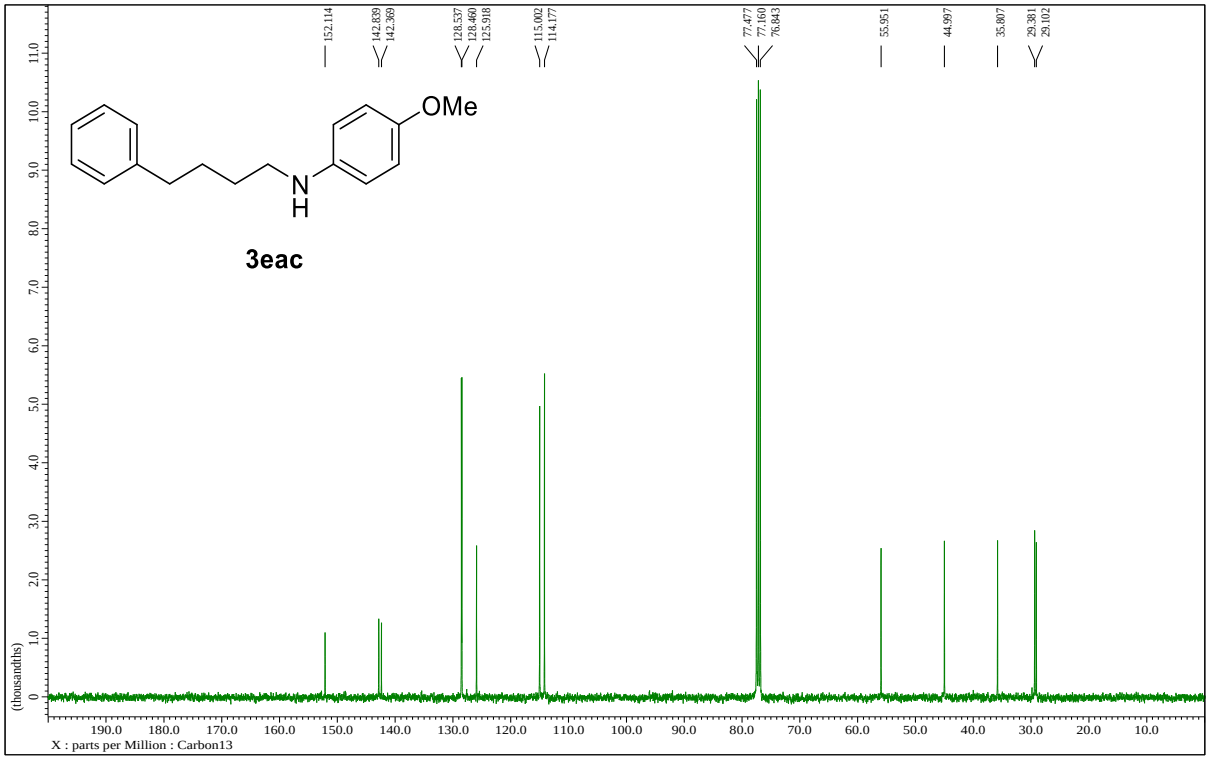
^{13}C-NMR of compound **3eab** ($CDCl_3$, 100 MHz)



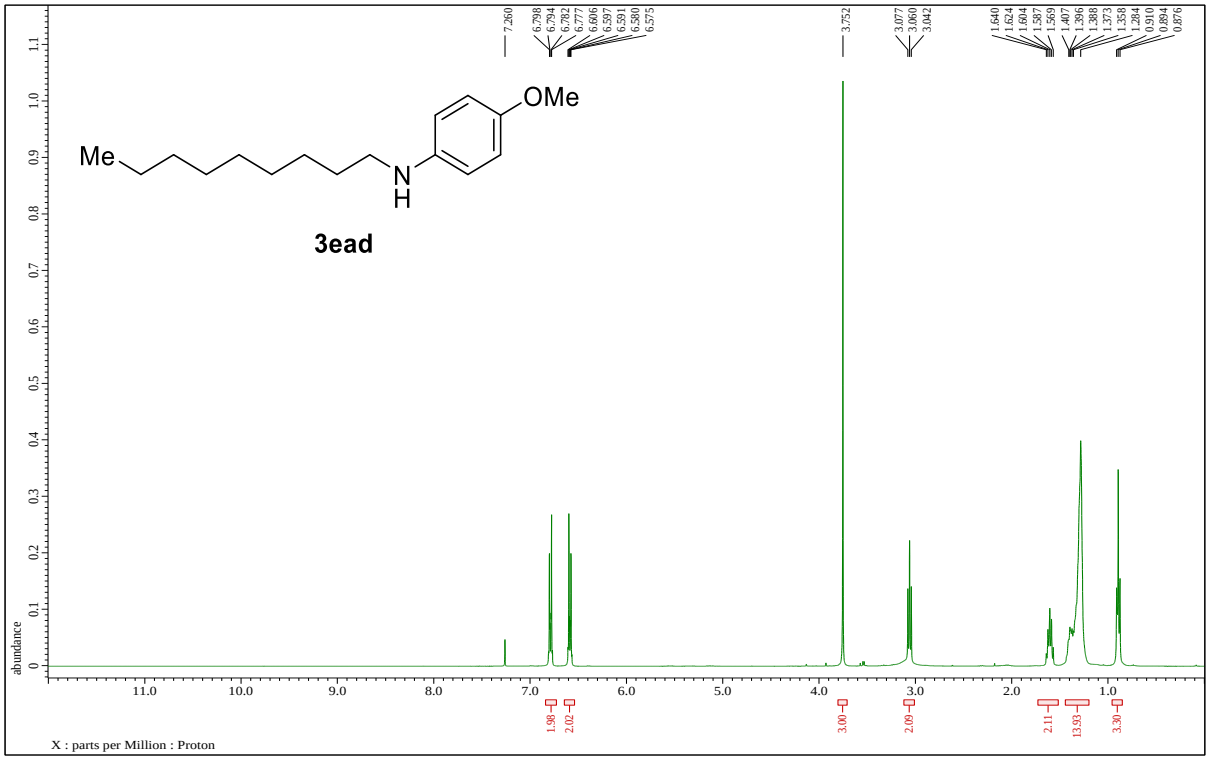
^{1}H-NMR of compound **3eac** ($CDCl_3$, 400 MHz)



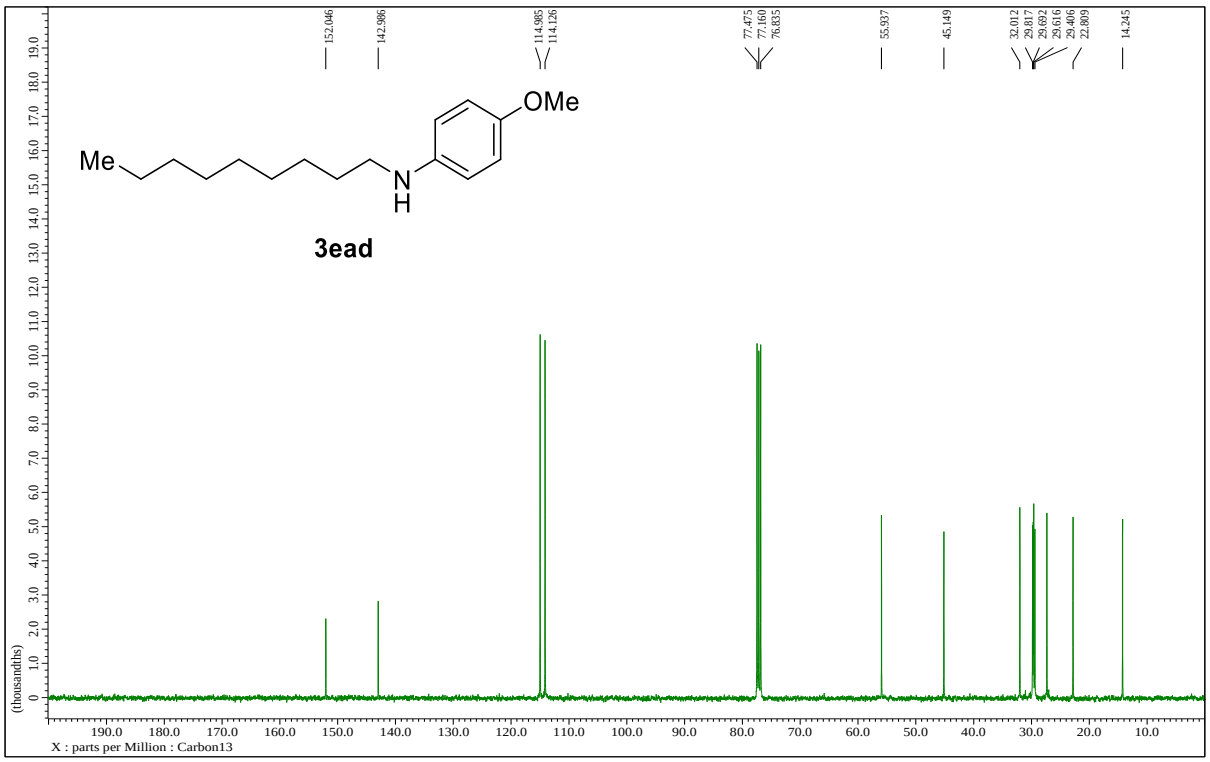
^{13}C-NMR of compound **3eac** ($CDCl_3$, 100 MHz)



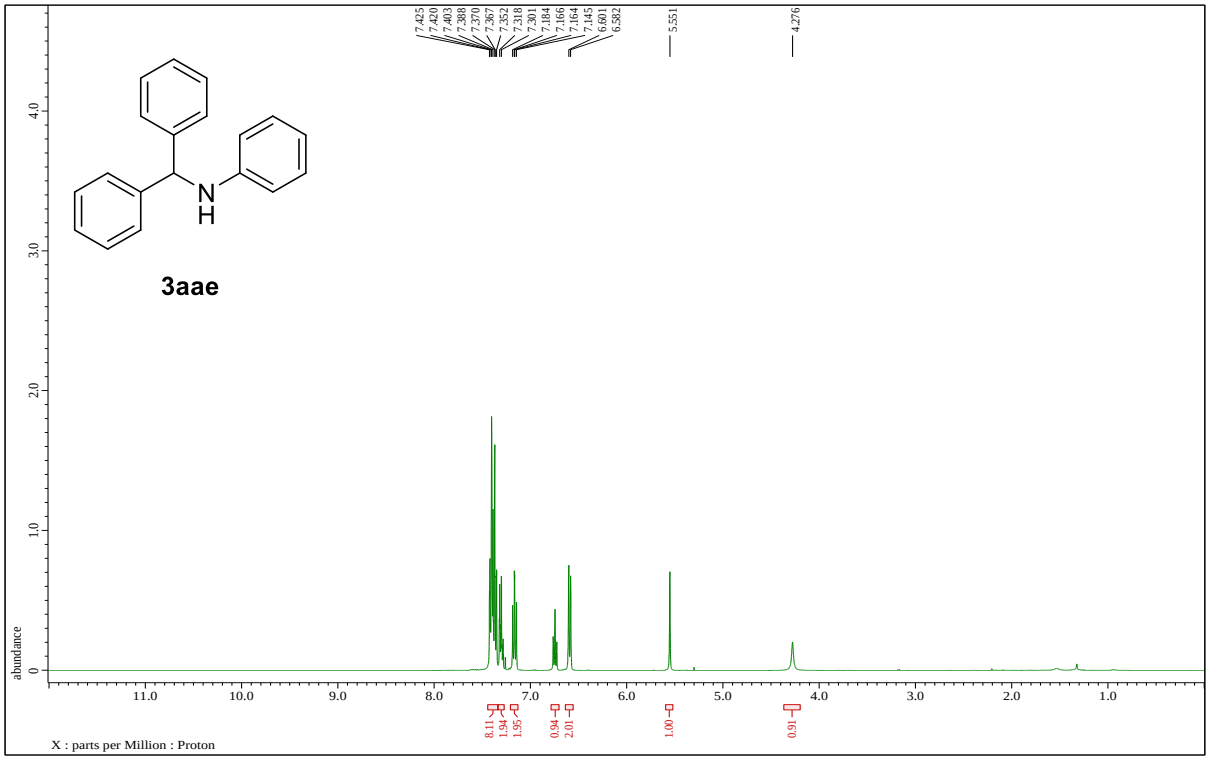
^{1}H-NMR of compound **3ead** ($CDCl_3$, 400 MHz)



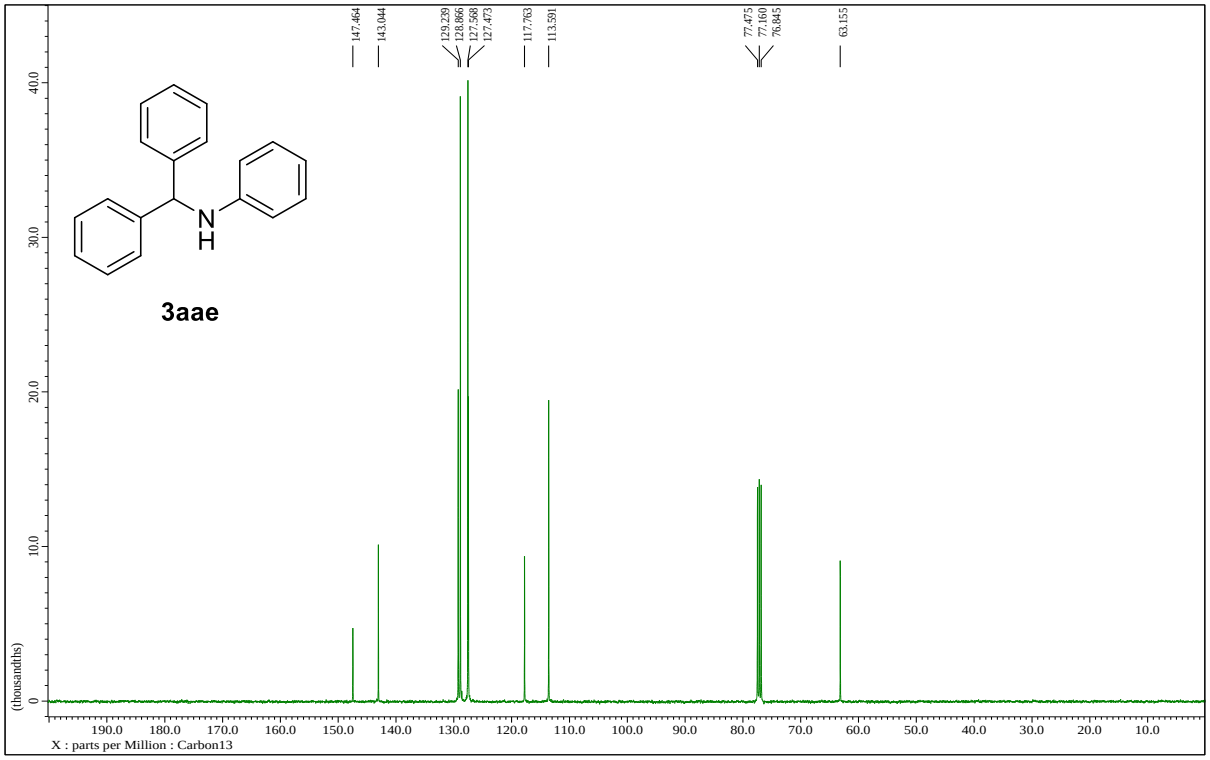
^{13}C-NMR of compound **3ead** ($CDCl_3$, 100 MHz)



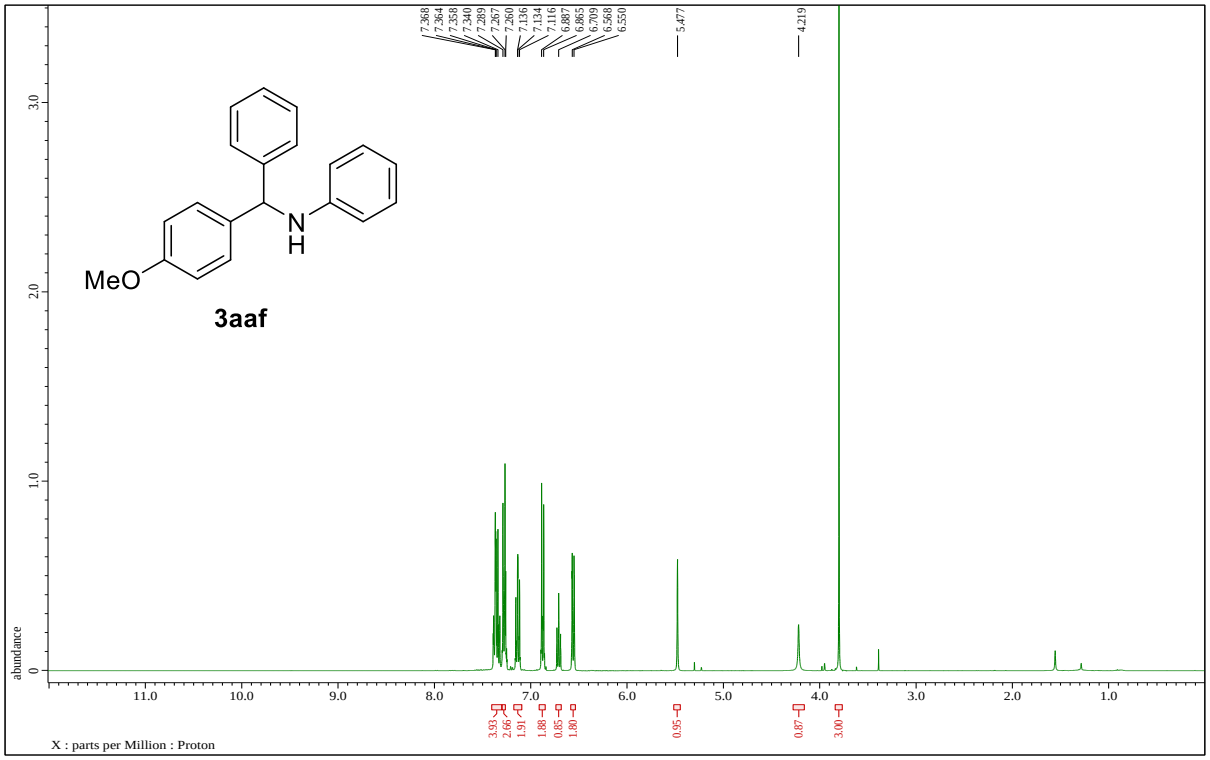
^{1}H-NMR of compound **3aae** ($CDCl_3$, 400 MHz)



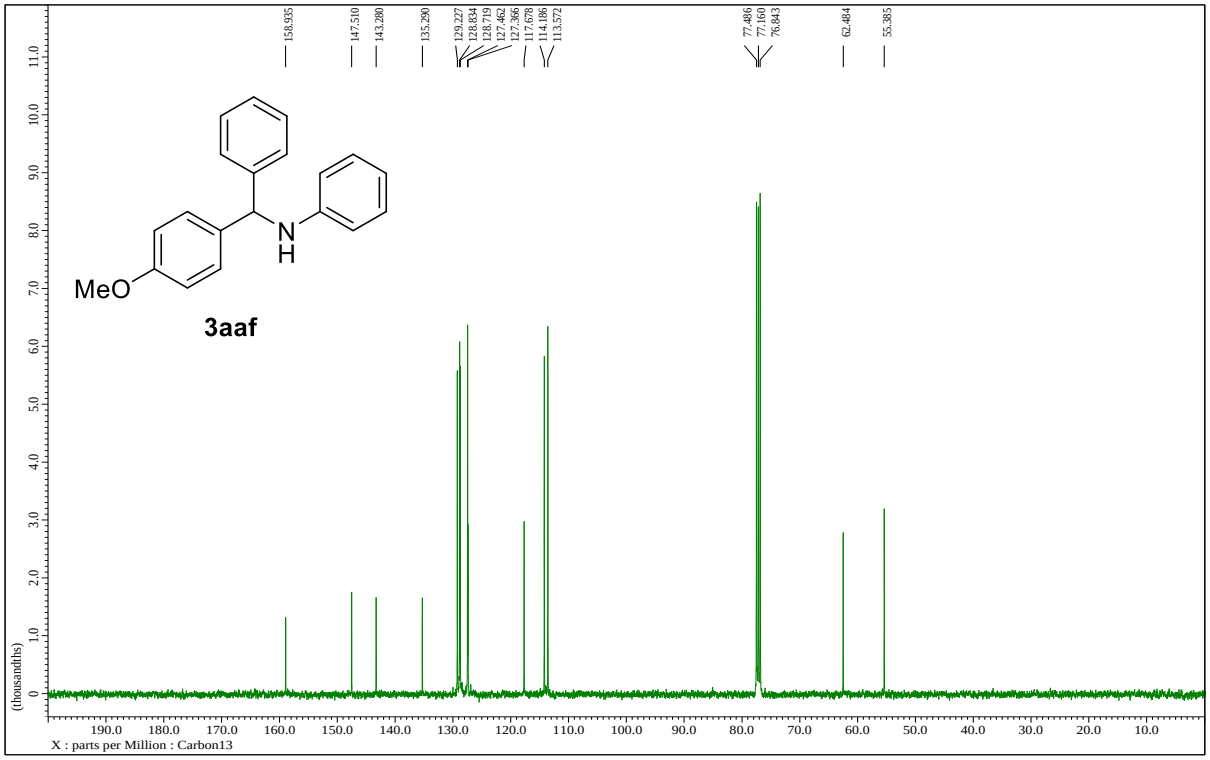
^{13}C-NMR of compound **3aae** ($CDCl_3$, 100 MHz)



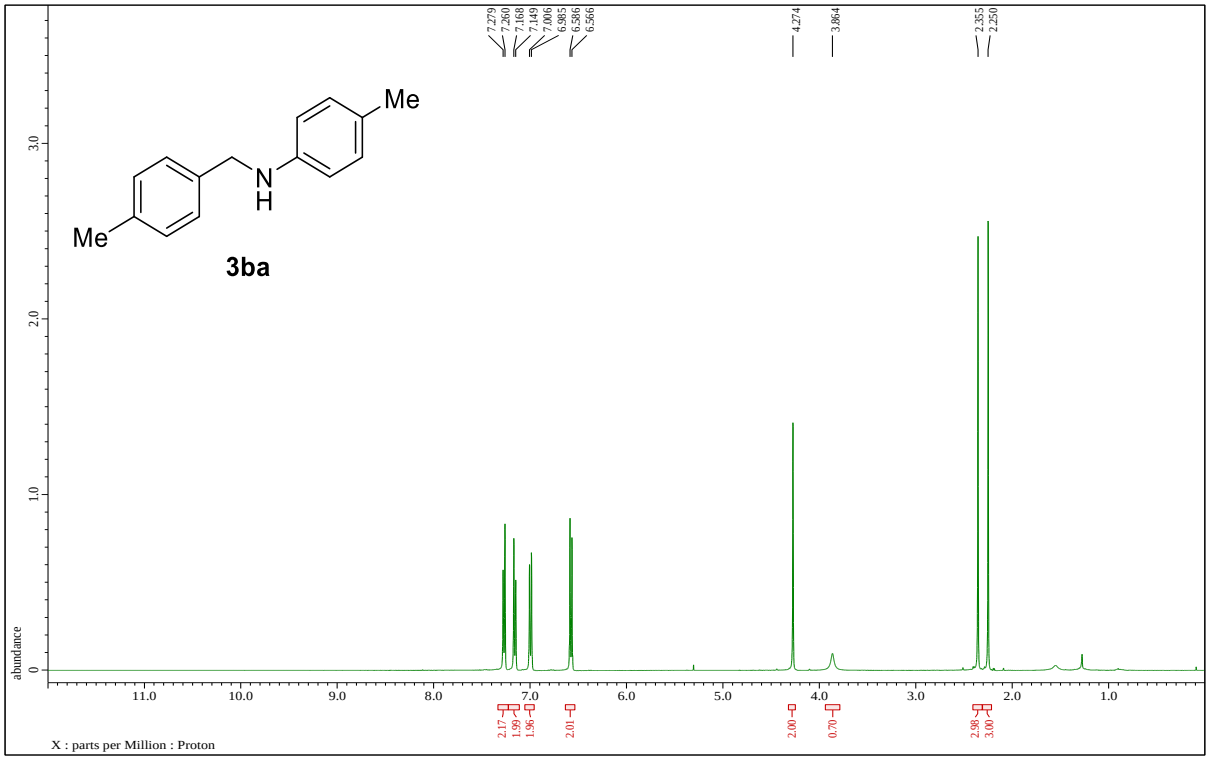
^{1}H-NMR of compound **3aaf** ($CDCl_3$, 400 MHz)



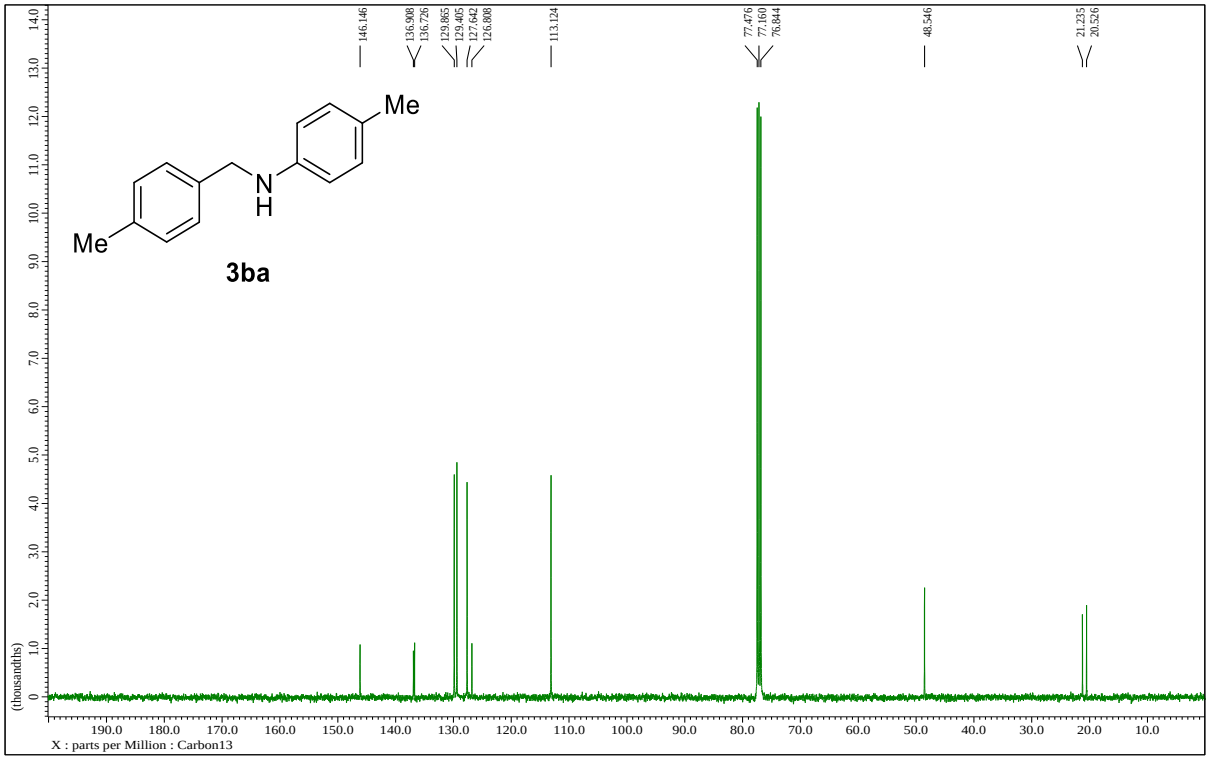
^{13}C-NMR of compound **3aaf** ($CDCl_3$, 100 MHz)



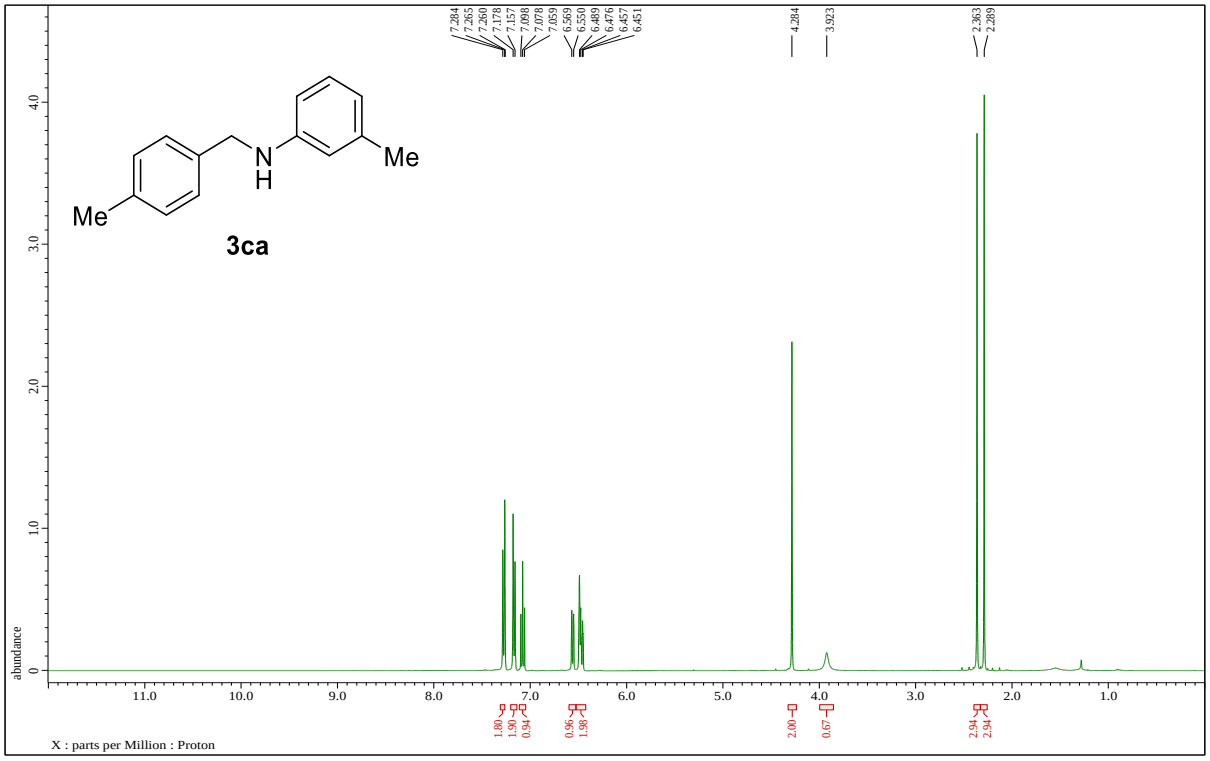
^{1}H-NMR of compound **3ba** ($CDCl_3$, 400 MHz)



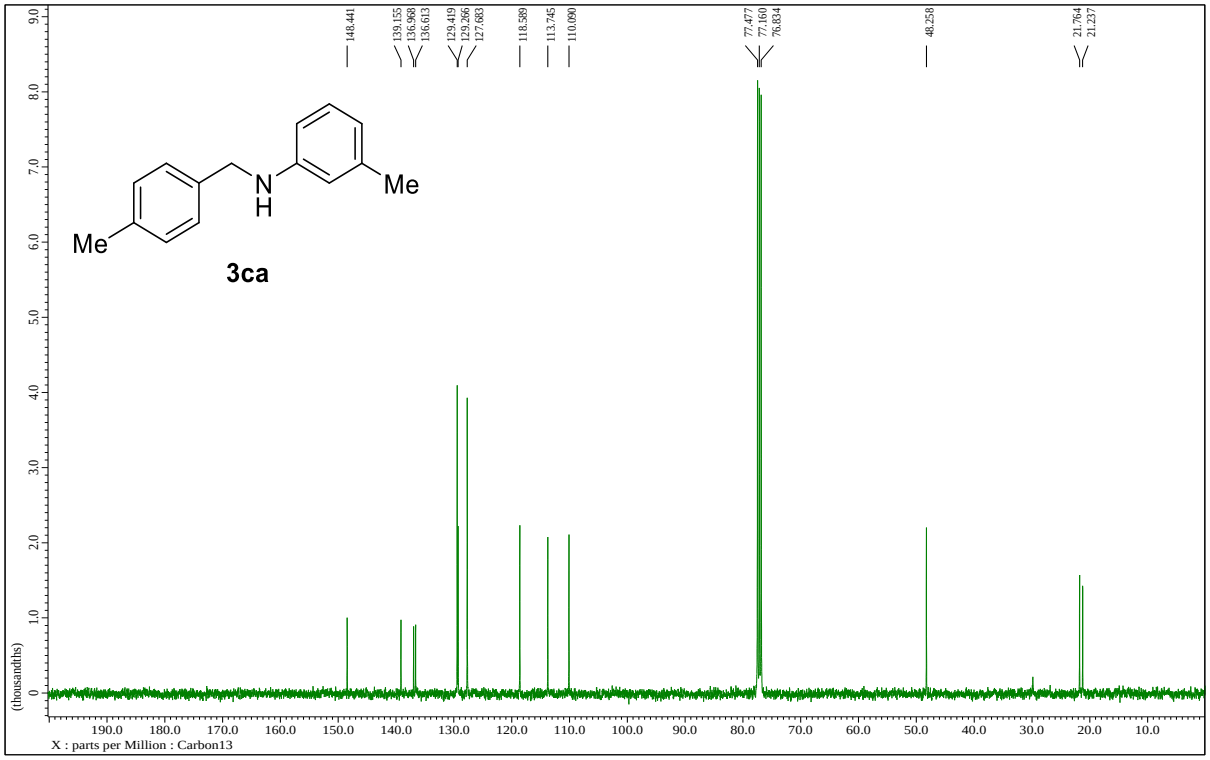
^{13}C-NMR of compound **3ba** ($CDCl_3$, 100 MHz)



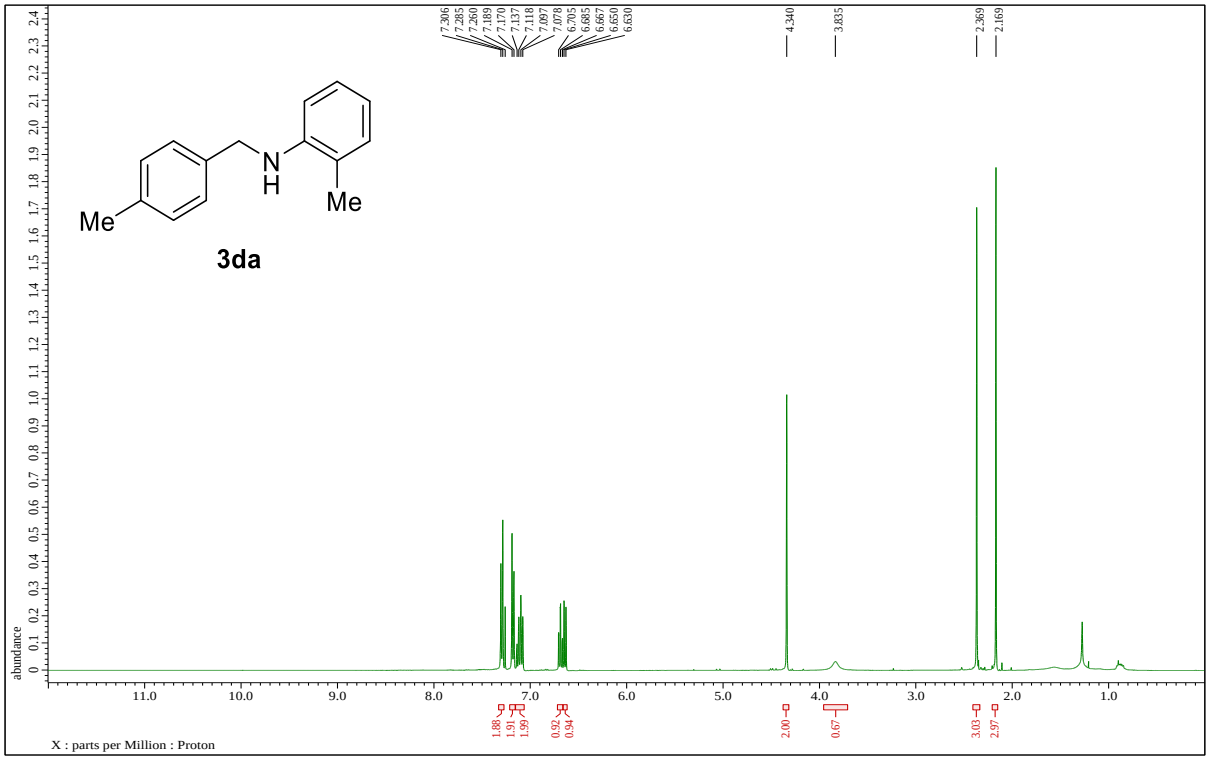
^{1}H-NMR of compound **3ca** ($CDCl_3$, 400 MHz)



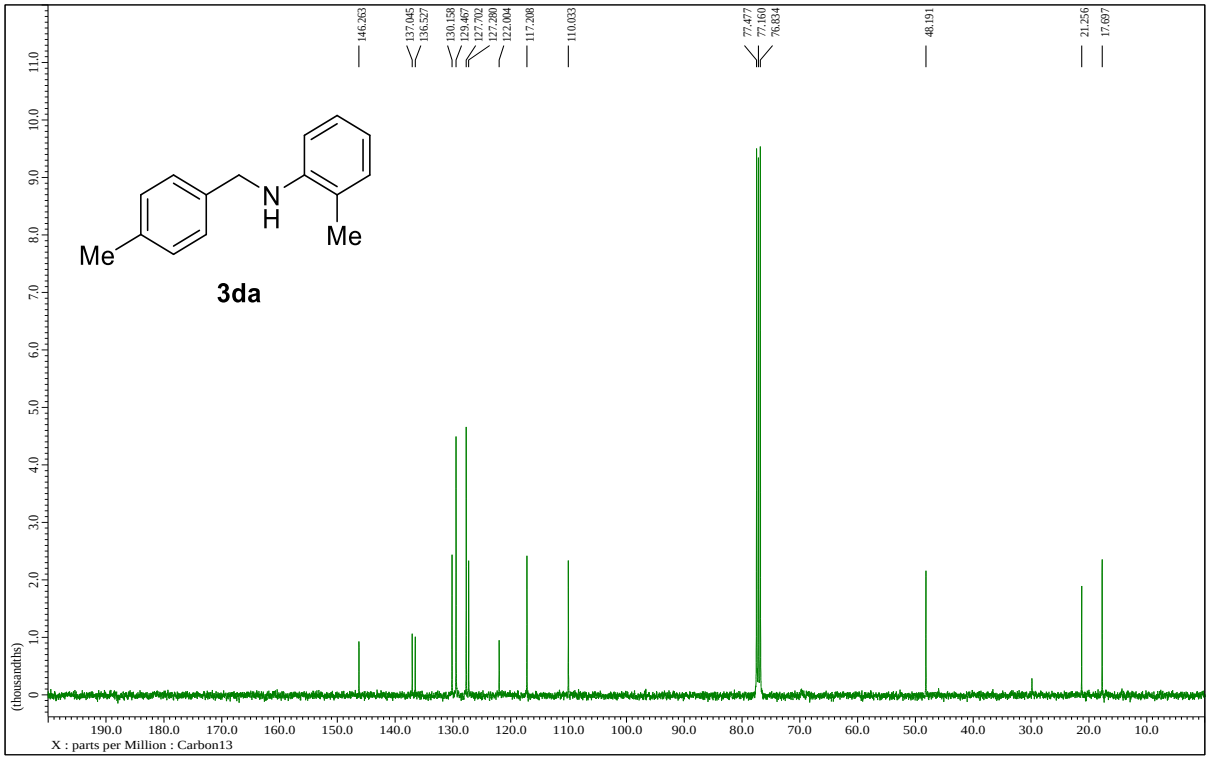
^{13}C-NMR of compound **3ca** ($CDCl_3$, 100 MHz)



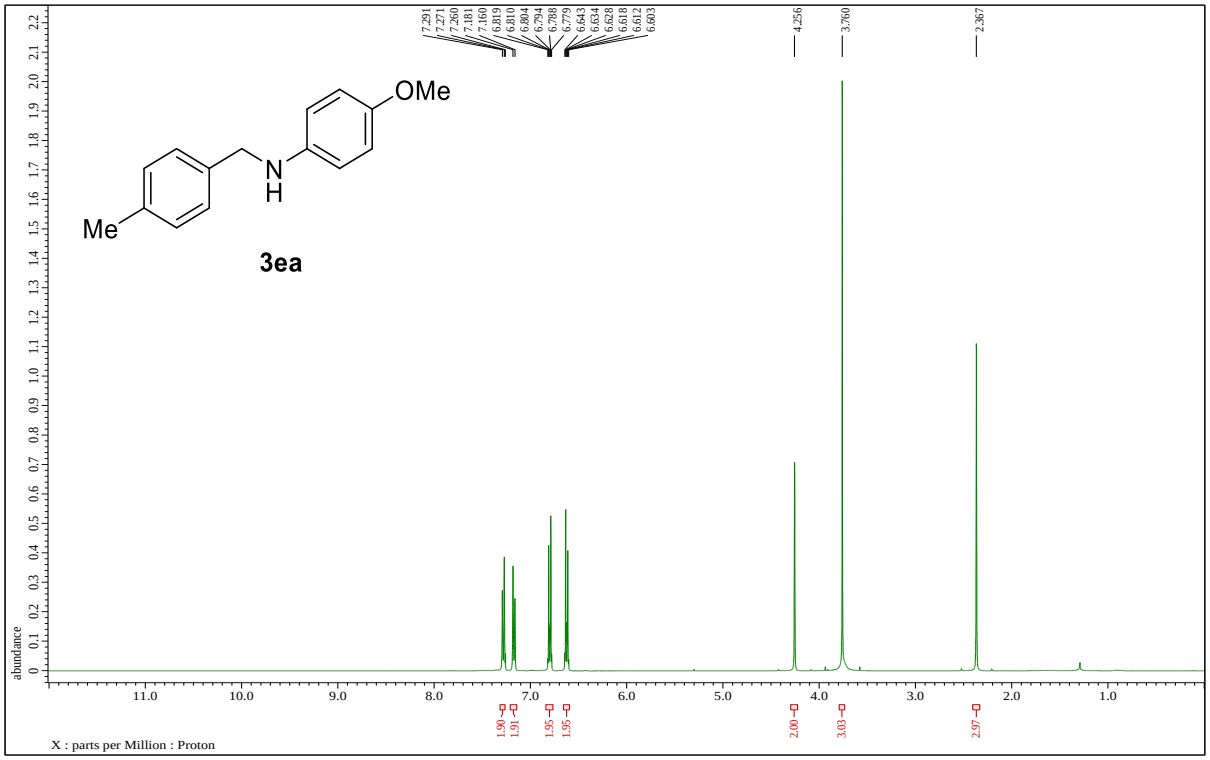
^{1}H-NMR of compound **3da** ($CDCl_3$, 400 MHz)



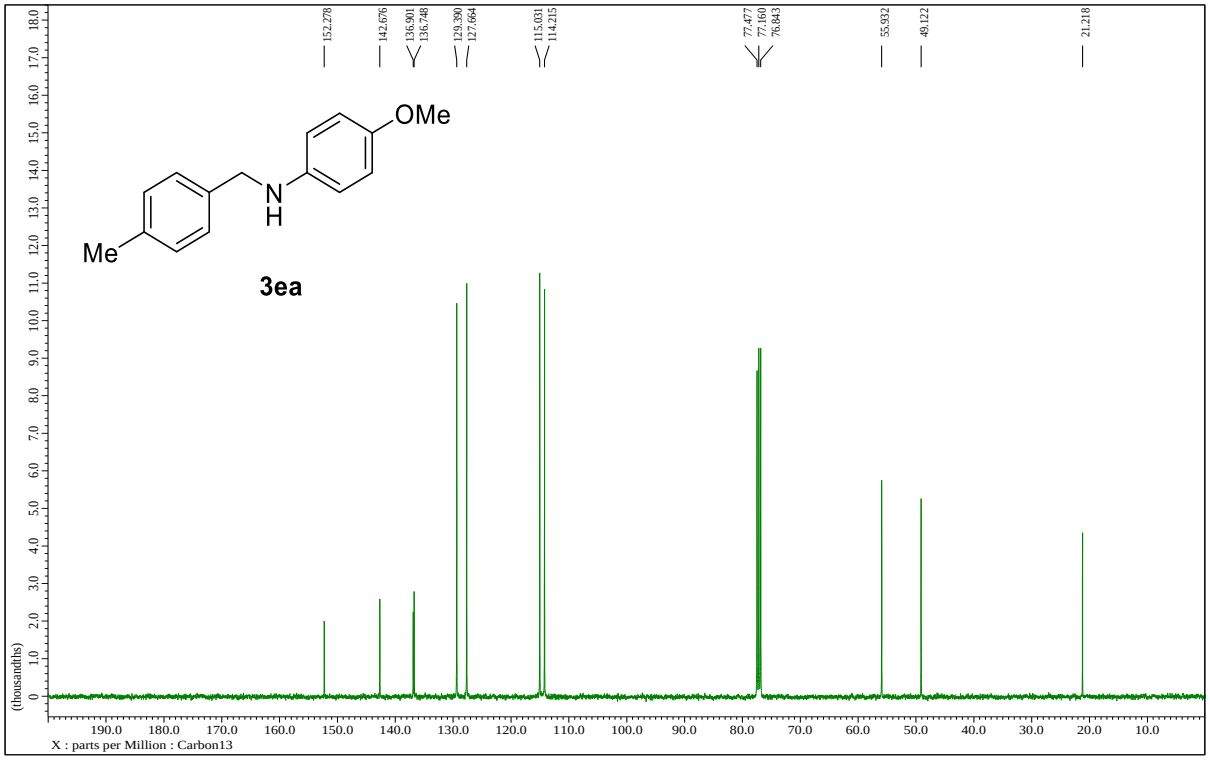
^{13}C-NMR of compound **3da** ($CDCl_3$, 100 MHz)



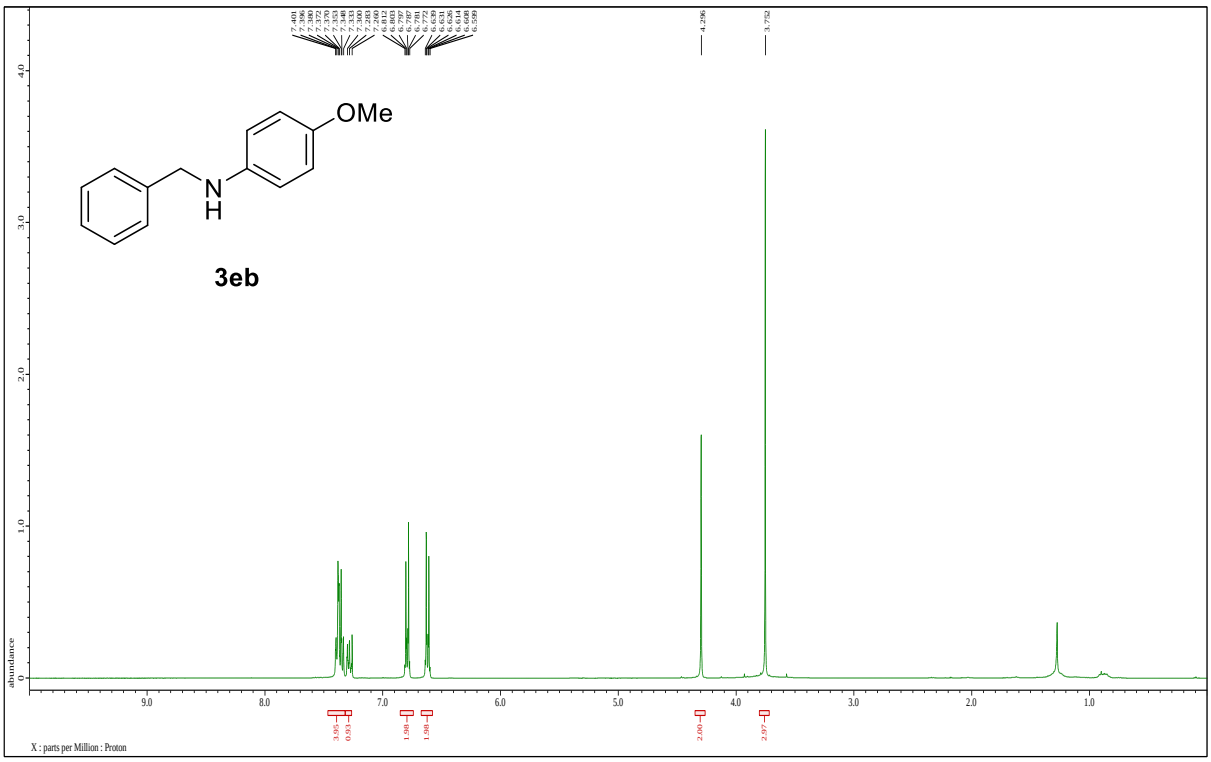
^{1}H-NMR of compound **3ea** ($CDCl_3$, 400 MHz)



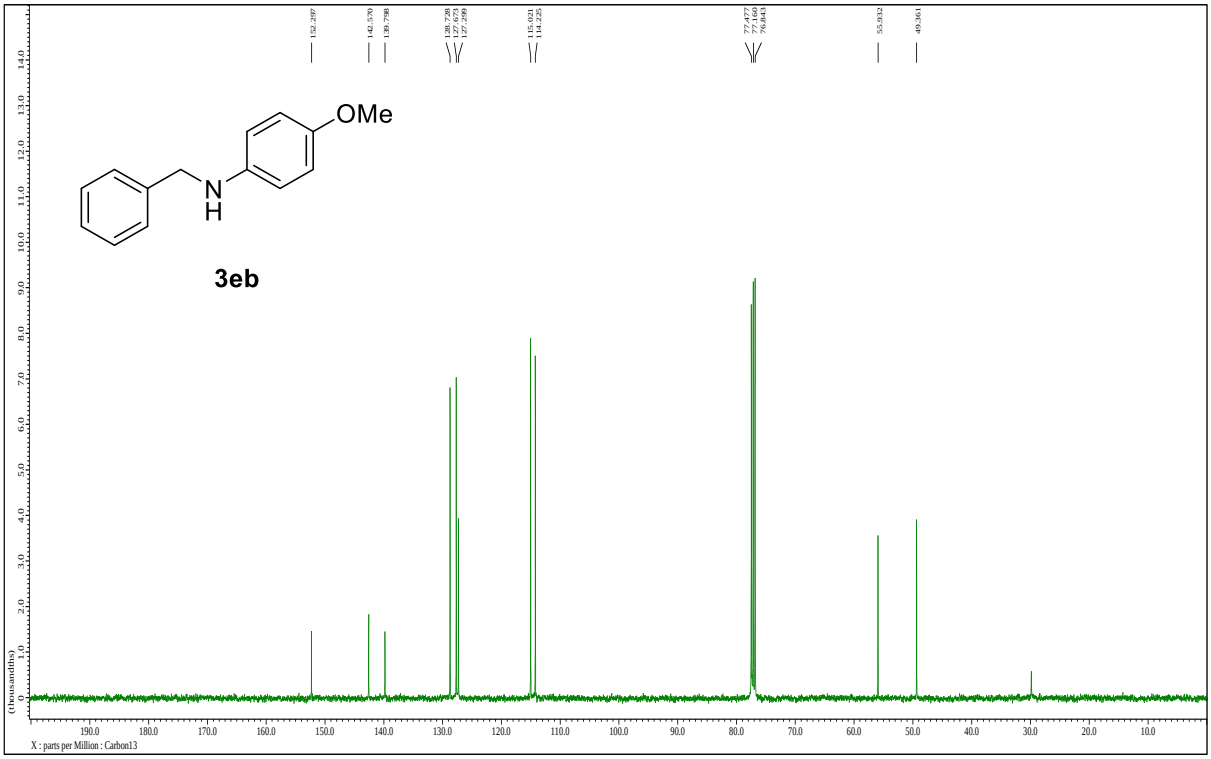
^{13}C-NMR of compound **3ea** ($CDCl_3$, 100 MHz)



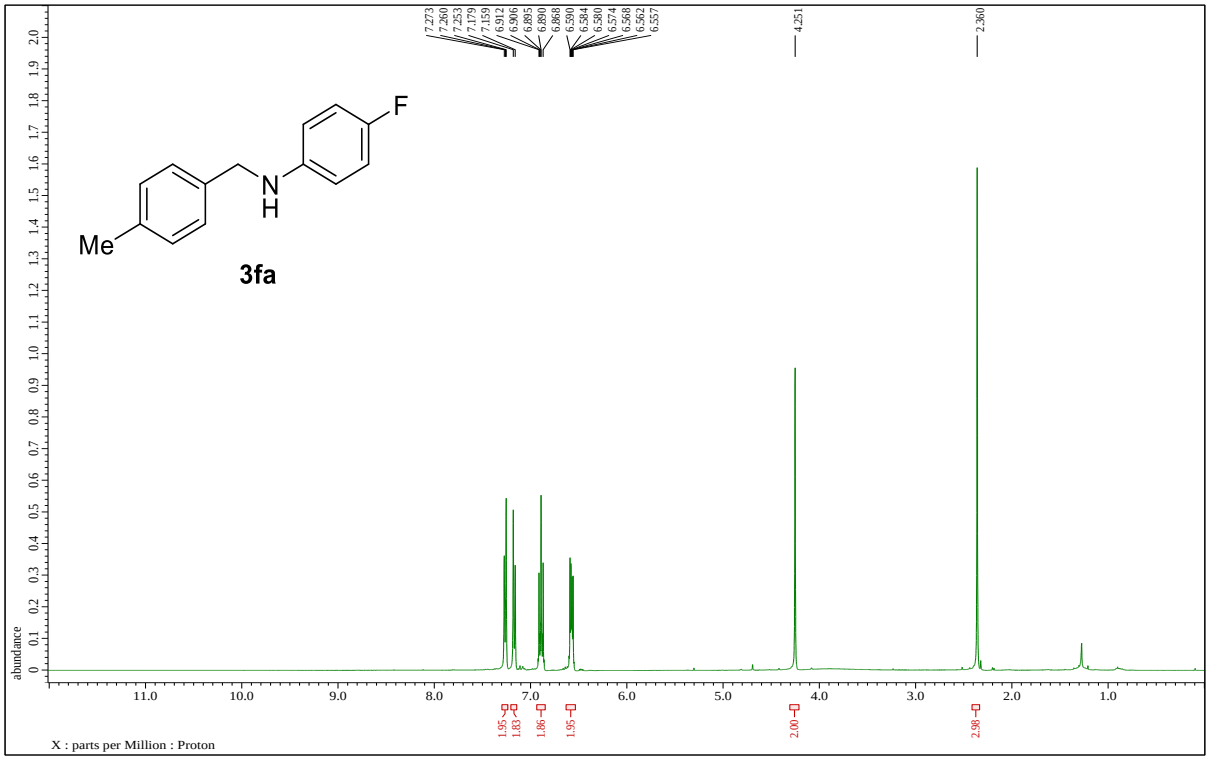
^{1}H-NMR of compound **3eb** ($CDCl_3$, 400 MHz)



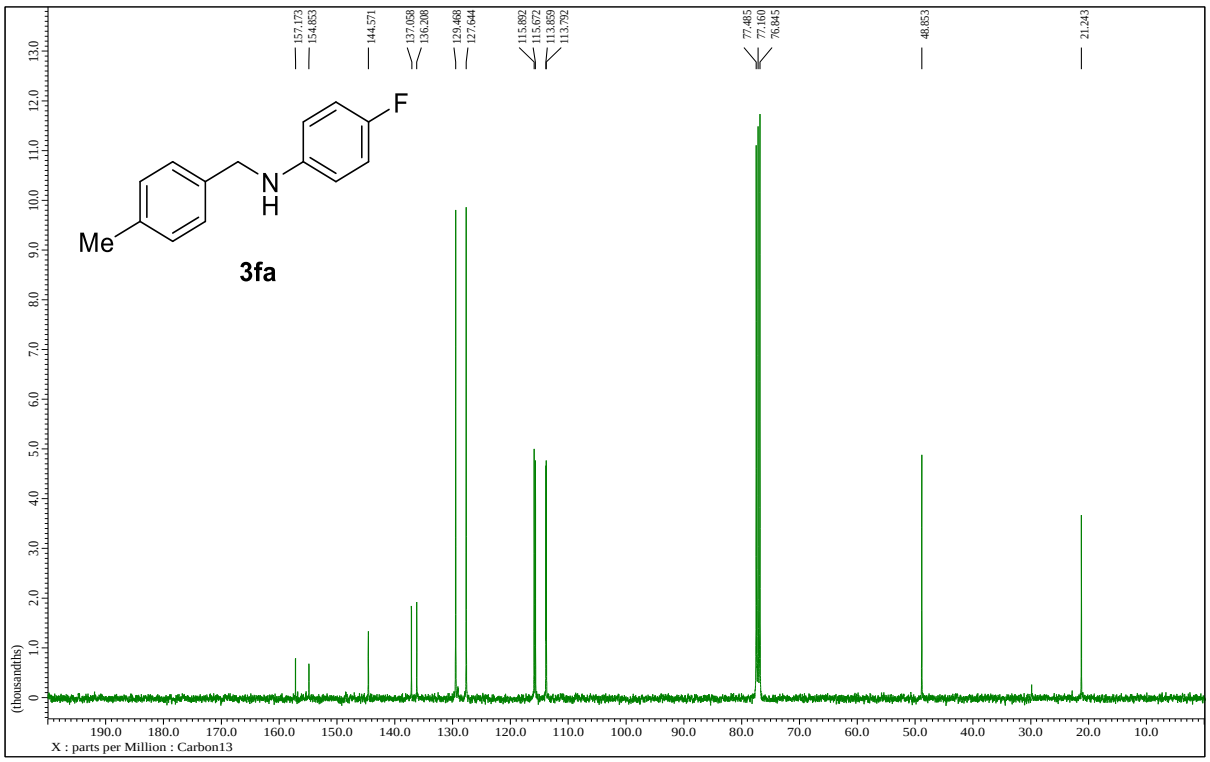
^{13}C-NMR of compound **3eb** ($CDCl_3$, 100 MHz)



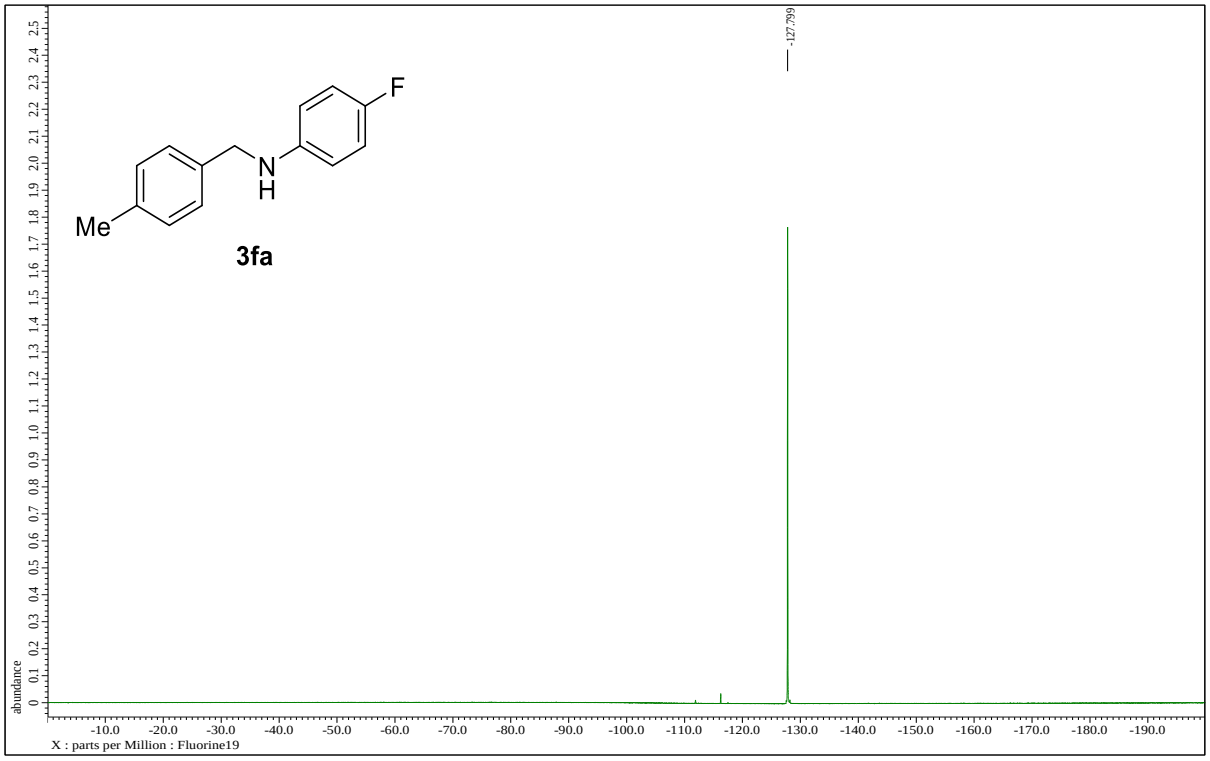
^{1}H-NMR of compound **3fa** ($CDCl_3$, 400 MHz)



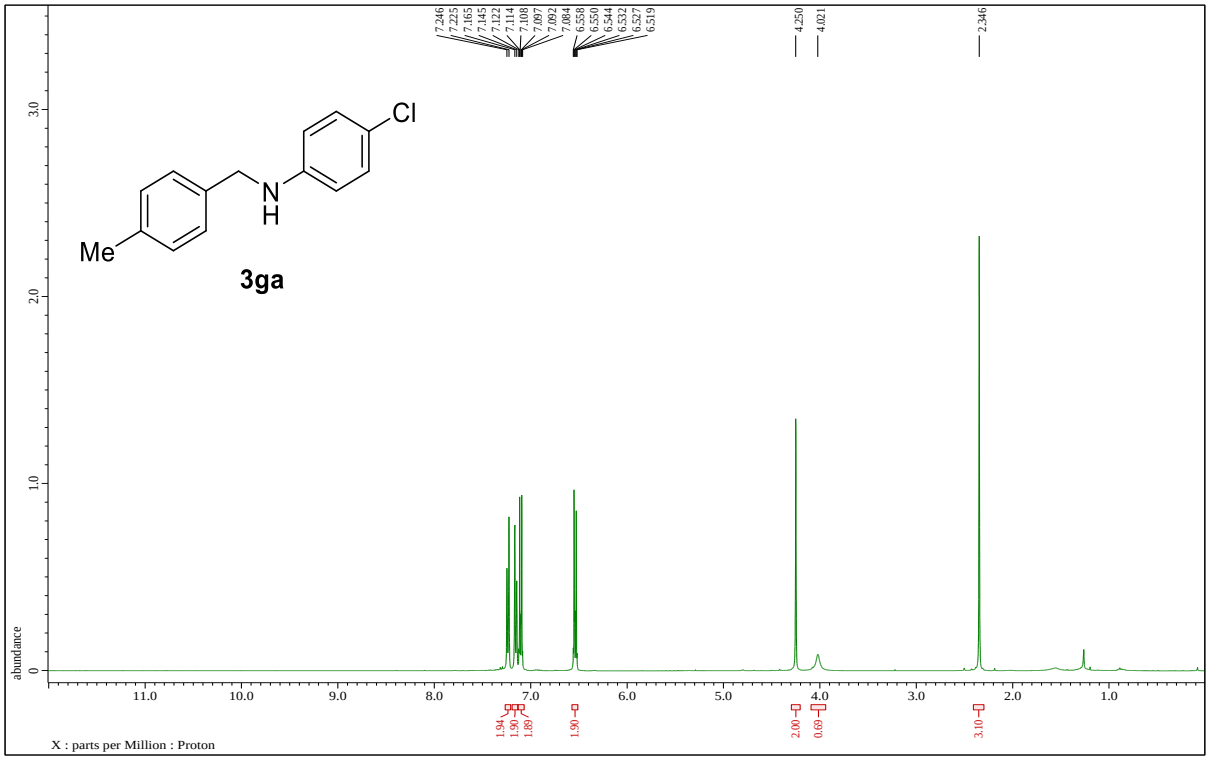
^{13}C-NMR of compound **3fa** ($CDCl_3$, 100 MHz)



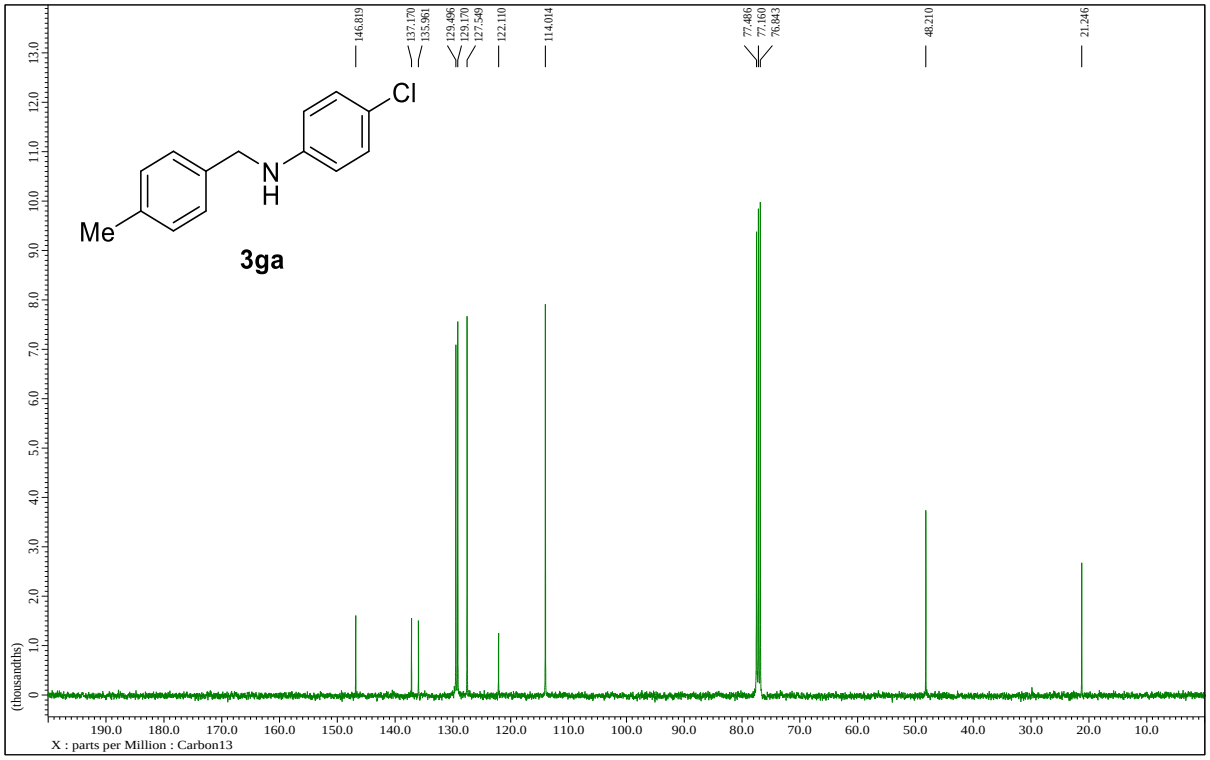
^{19}F-NMR of compound **3fa** ($CDCl_3$, 400 MHz)



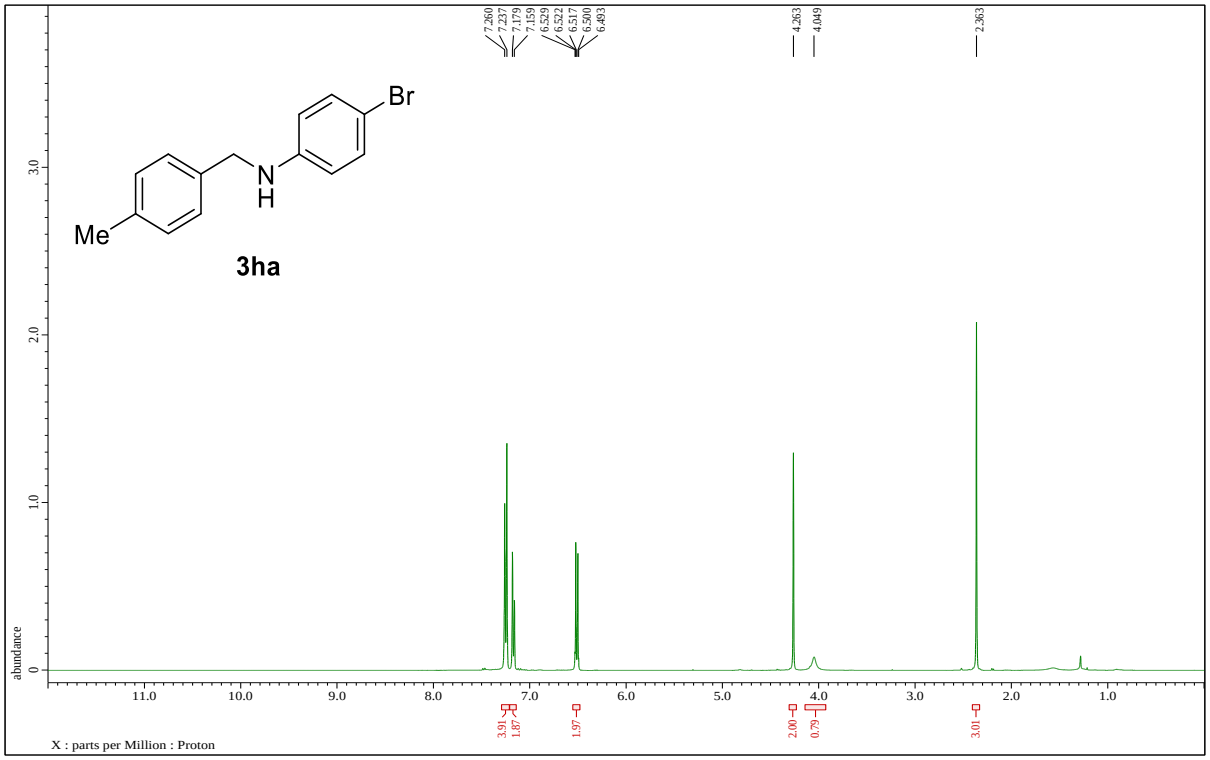
^{1}H-NMR of compound **3ga** ($CDCl_3$, 400 MHz)



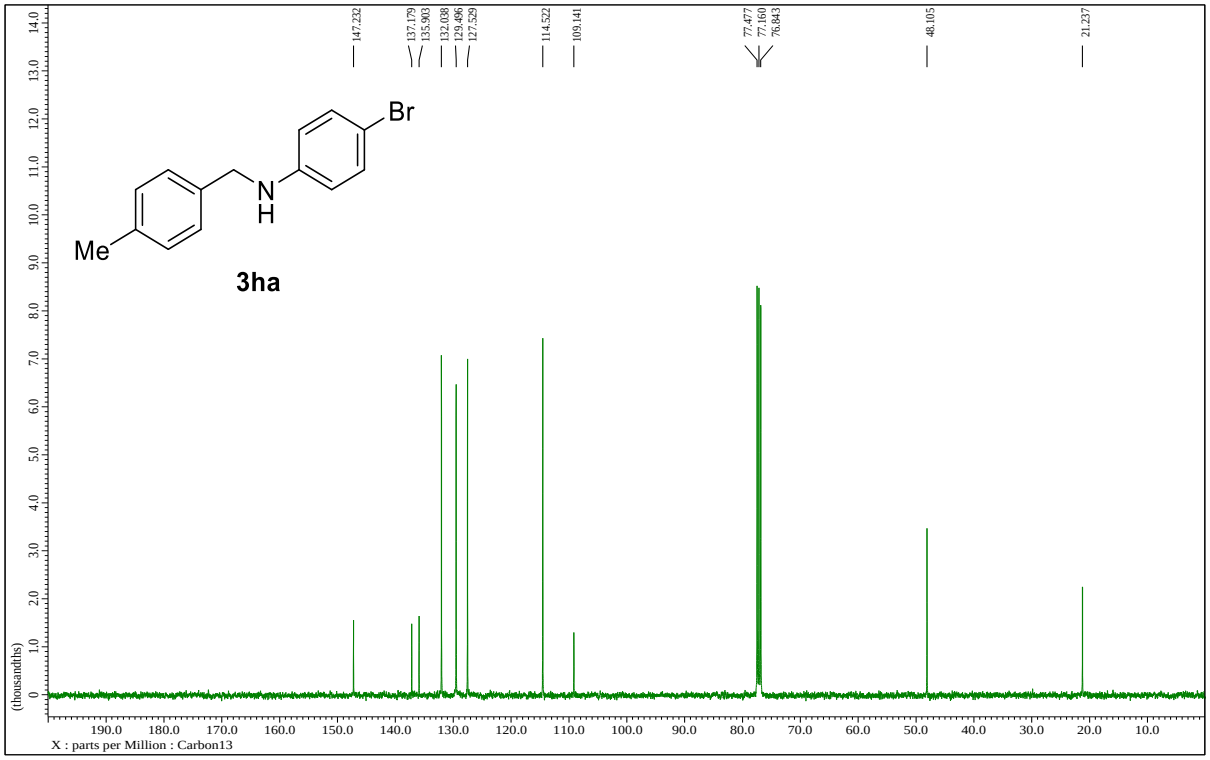
^{13}C-NMR of compound **3ga** ($CDCl_3$, 100 MHz)



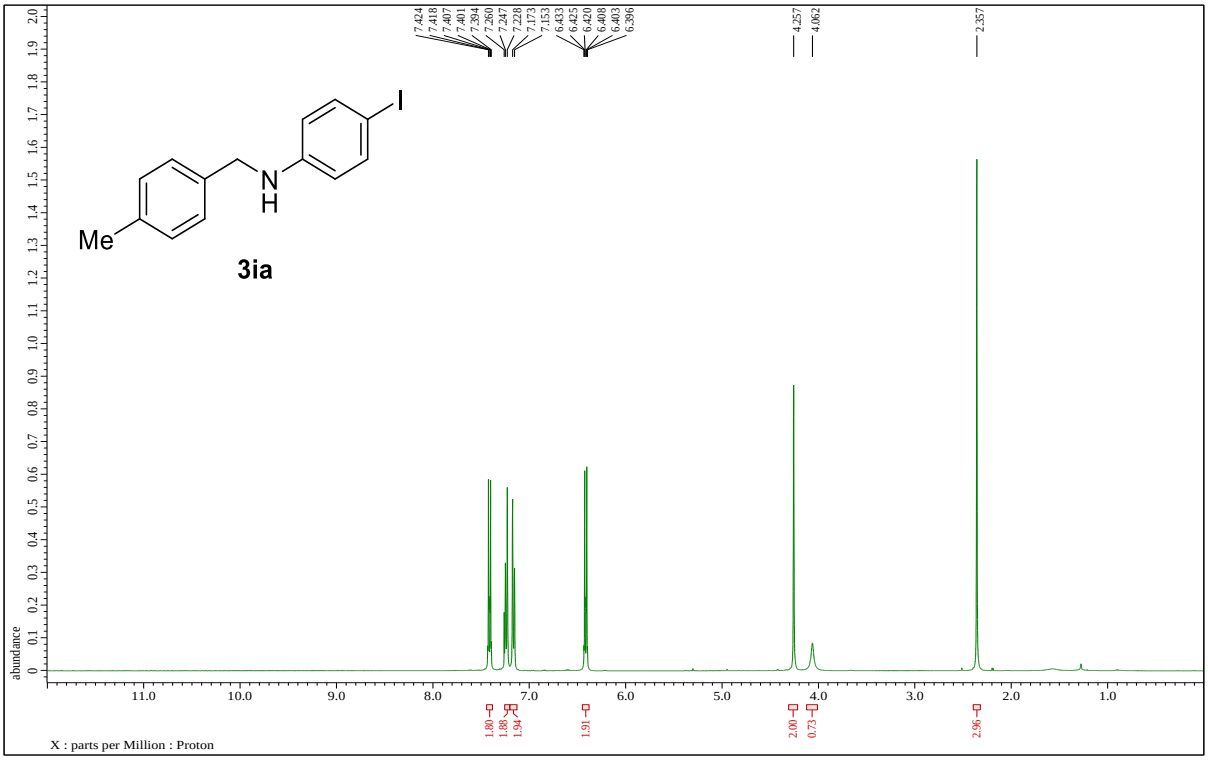
^{1}H-NMR of compound **3ha** ($CDCl_3$, 400 MHz)



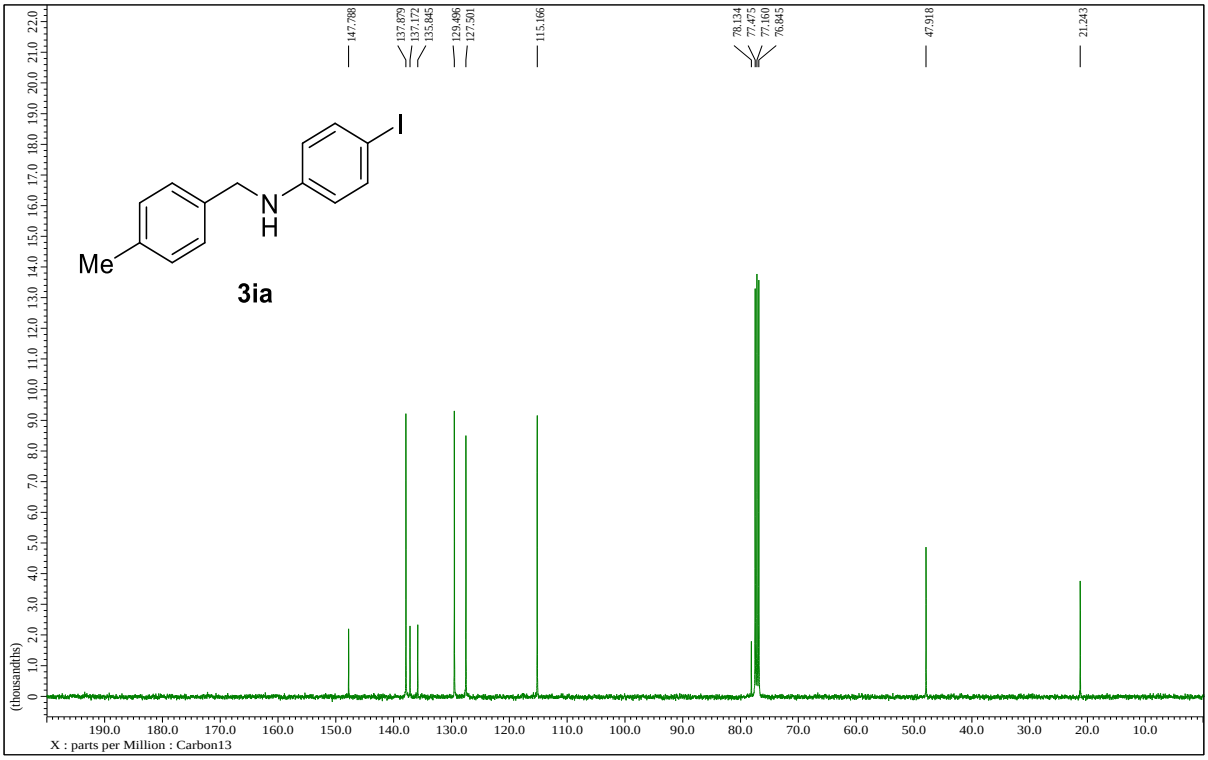
^{13}C-NMR of compound **3ha** ($CDCl_3$, 100 MHz)



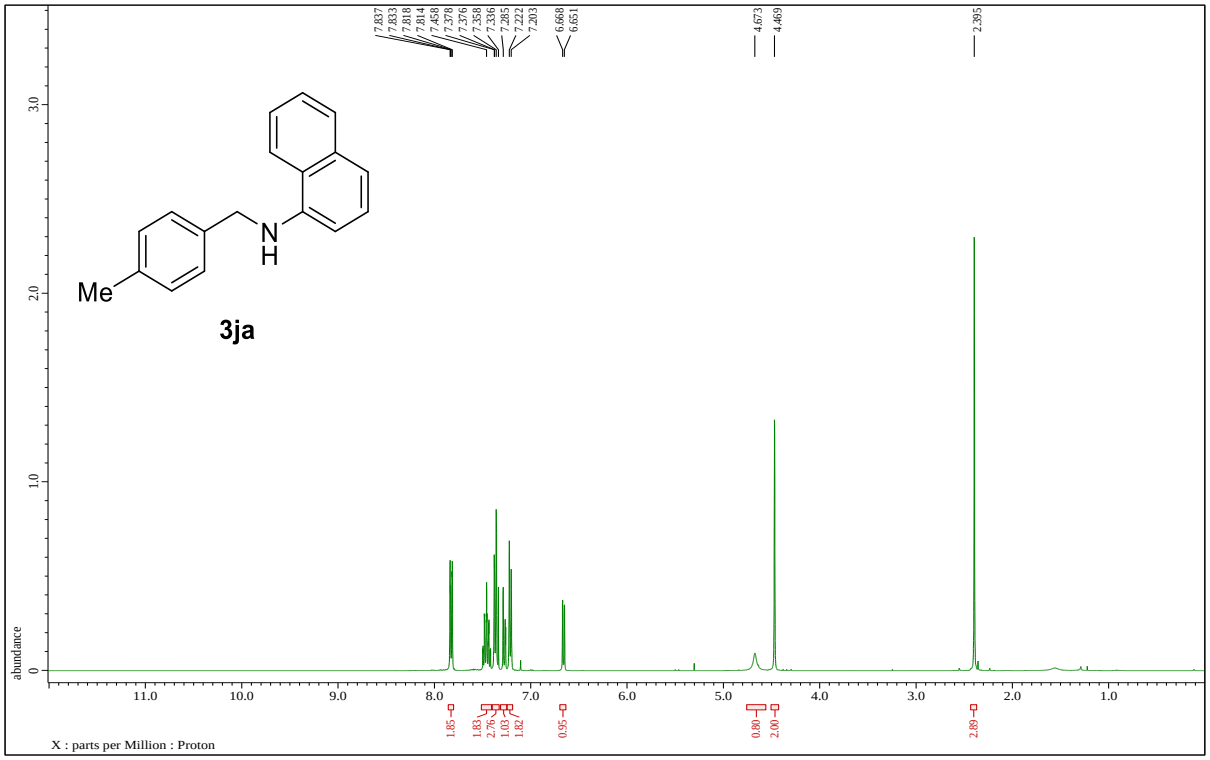
^{1}H-NMR of compound **3ia** ($CDCl_3$, 400 MHz)



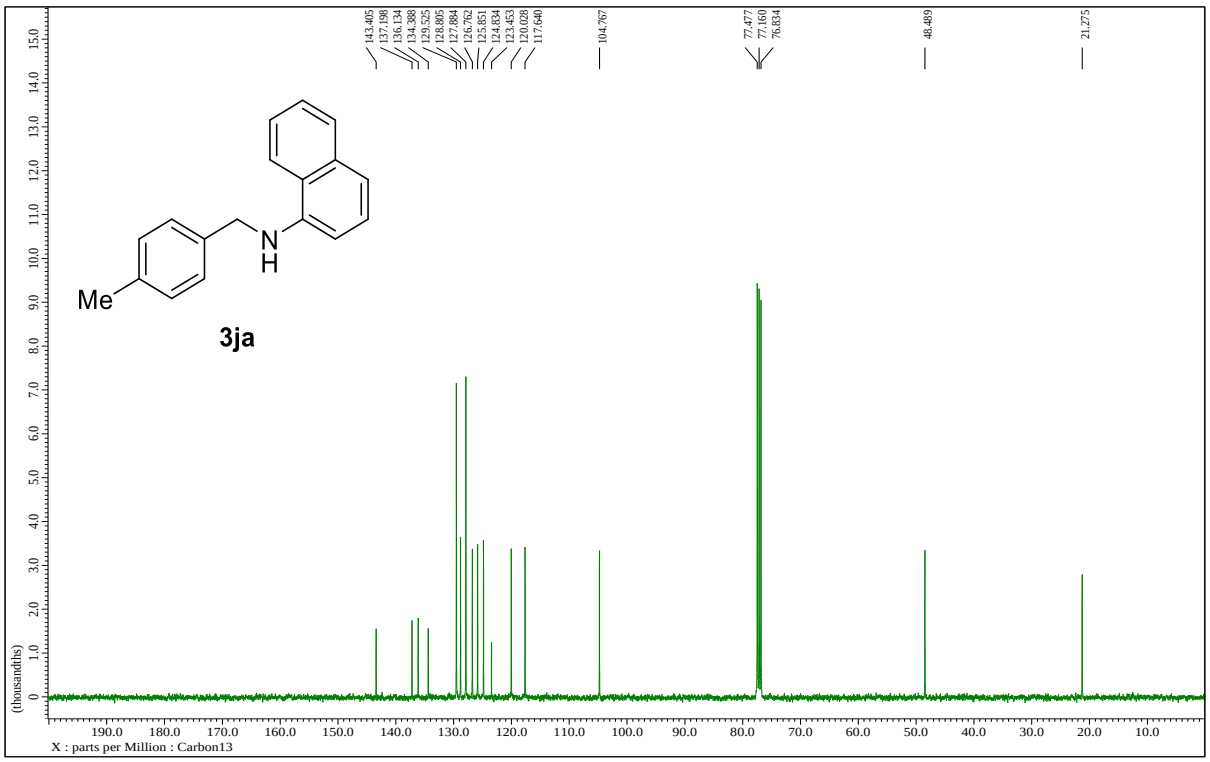
^{13}C-NMR of compound **3ia** ($CDCl_3$, 100 MHz)



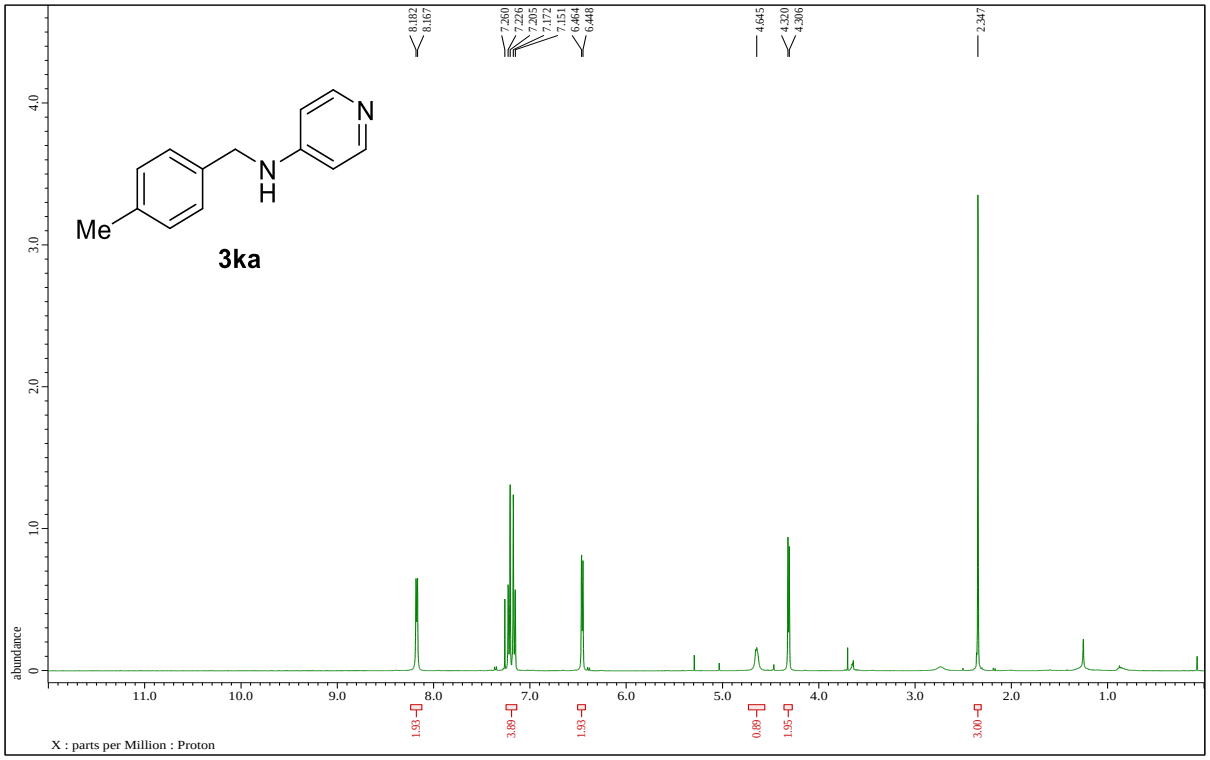
^{1}H-NMR of compound **3ja** ($CDCl_3$, 400 MHz)



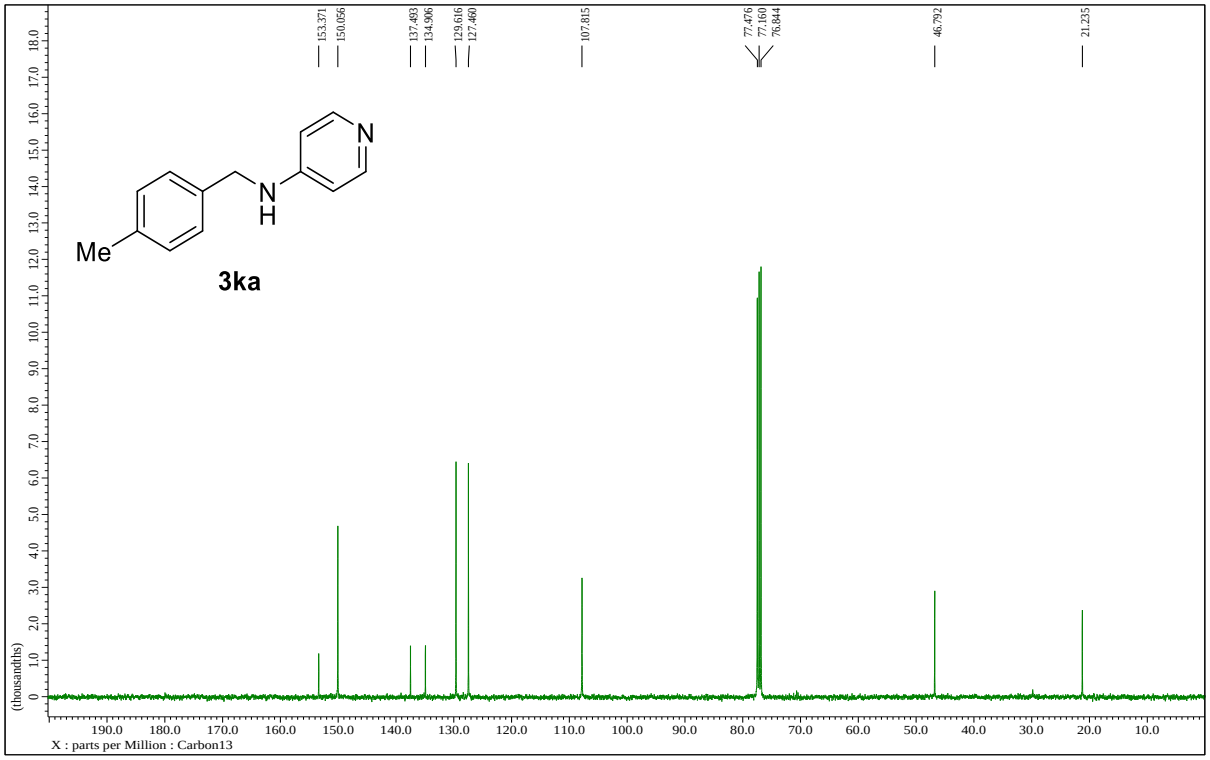
^{13}C-NMR of compound **3ja** ($CDCl_3$, 100 MHz)



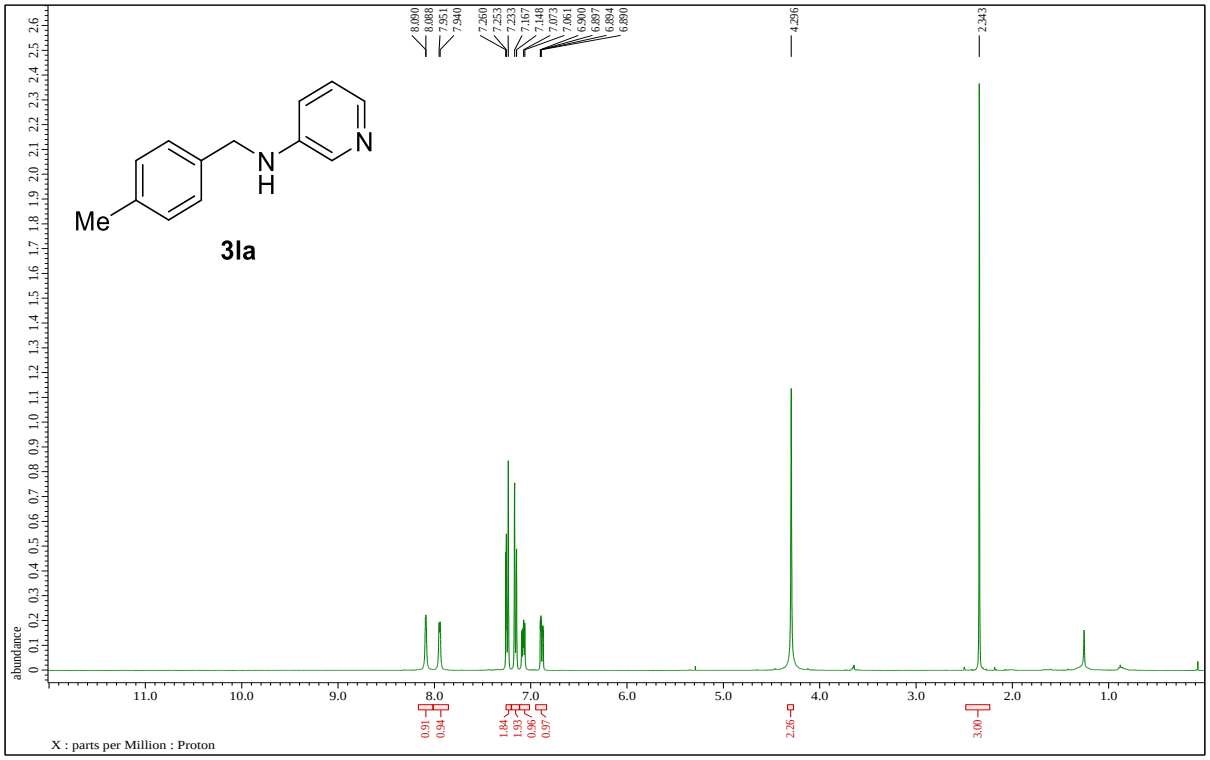
^{1}H-NMR of compound **3ka** ($CDCl_3$, 400 MHz)



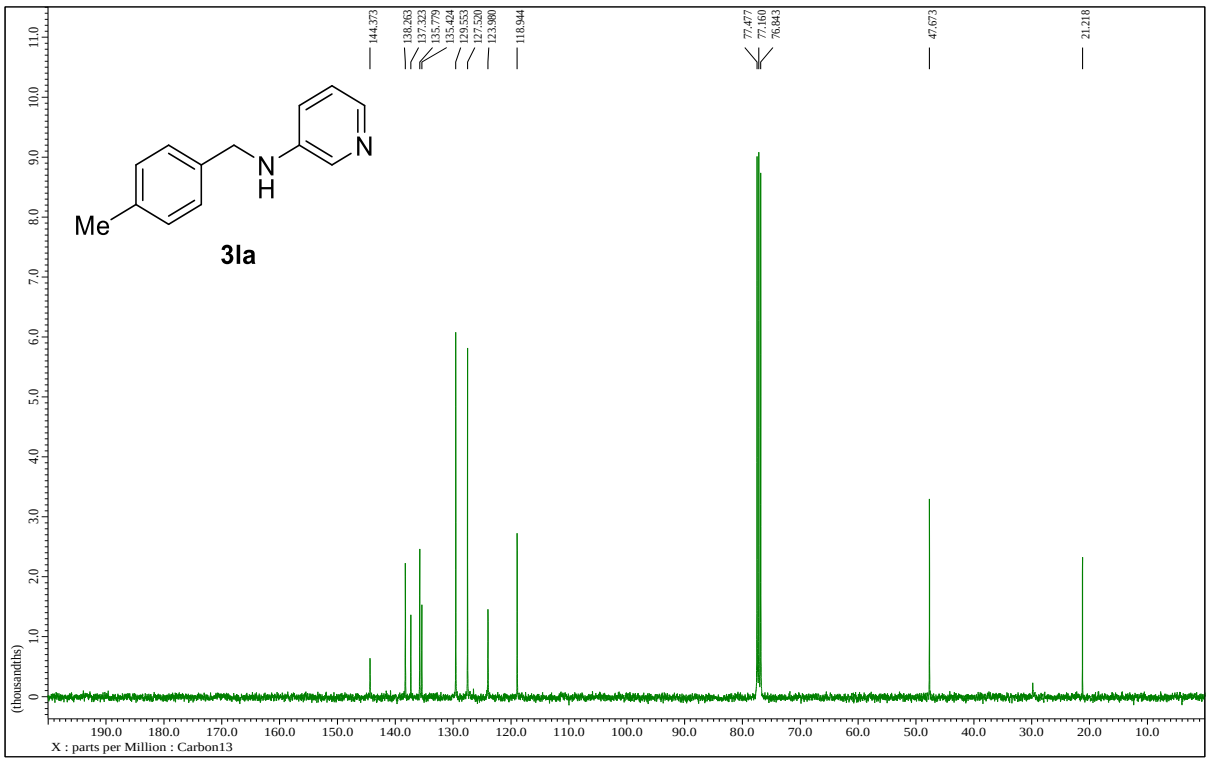
^{13}C-NMR of compound **3ka** ($CDCl_3$, 100 MHz)



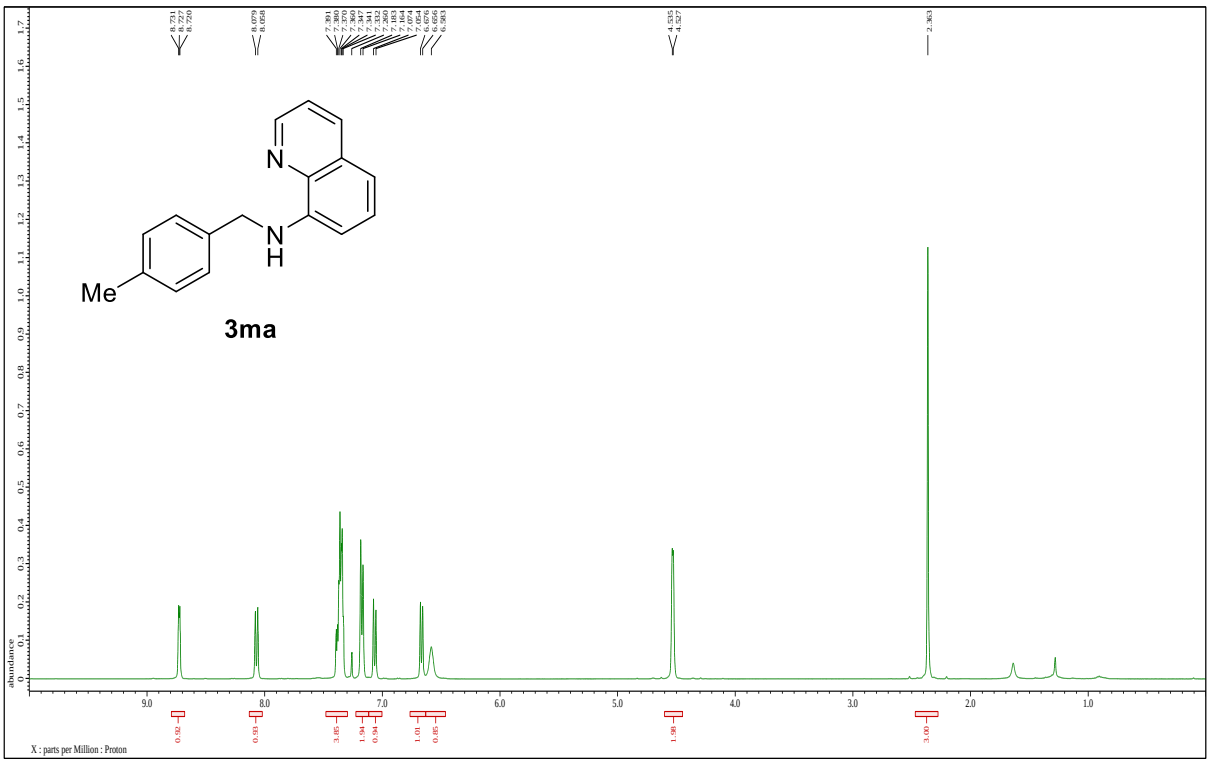
^{1}H-NMR of compound **3la** ($CDCl_3$, 400 MHz)



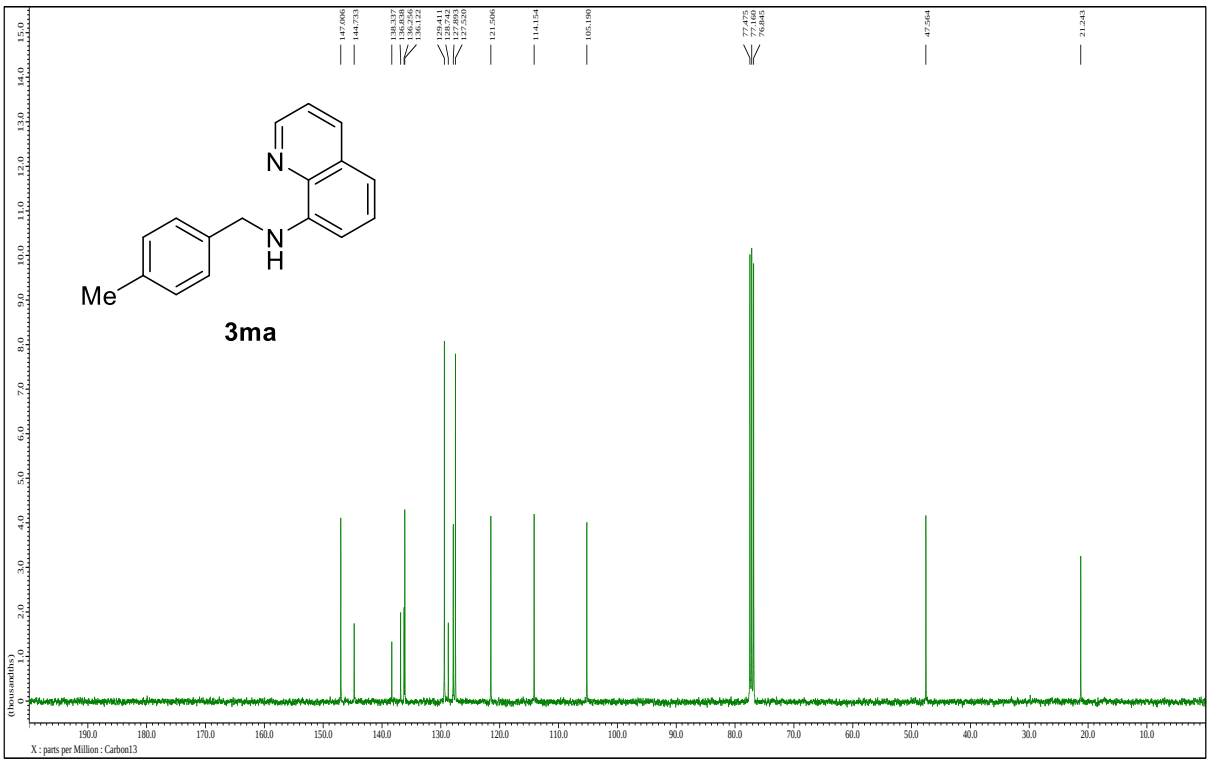
^{13}C-NMR of compound **3la** ($CDCl_3$, 100 MHz)



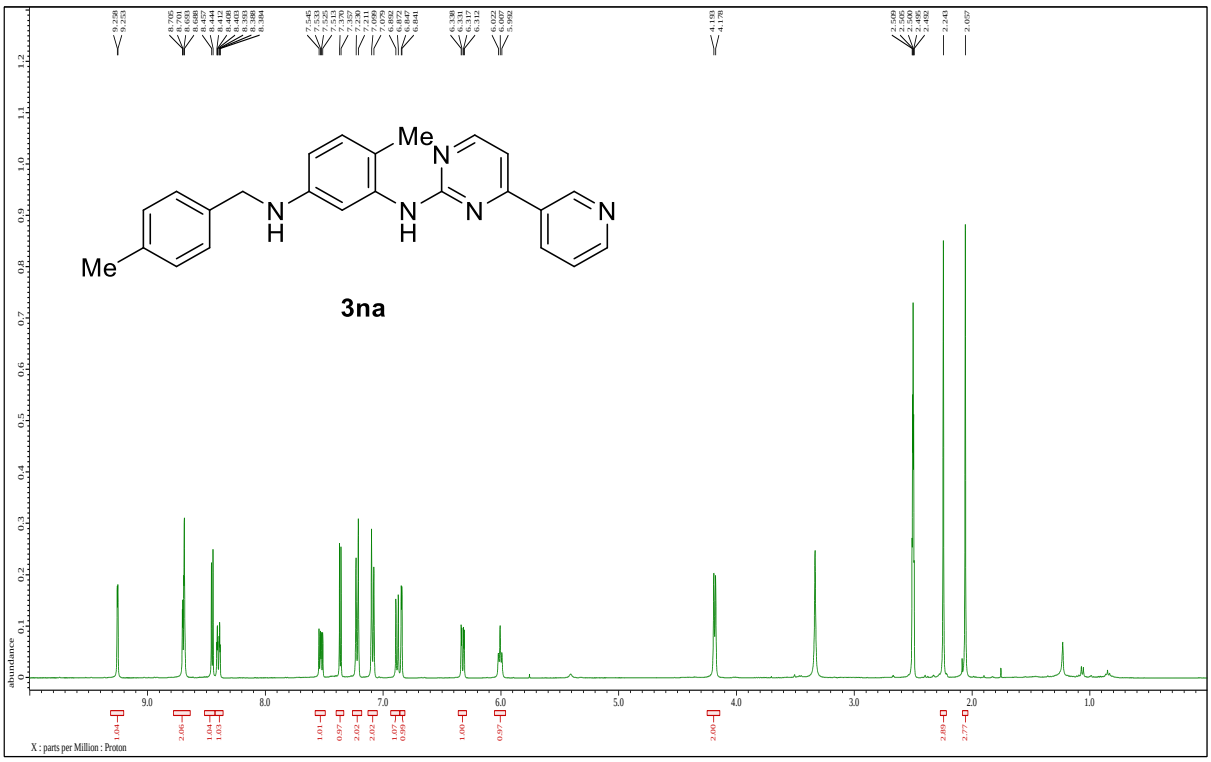
^{1}H-NMR of compound **3ma** ($CDCl_3$, 400 MHz)



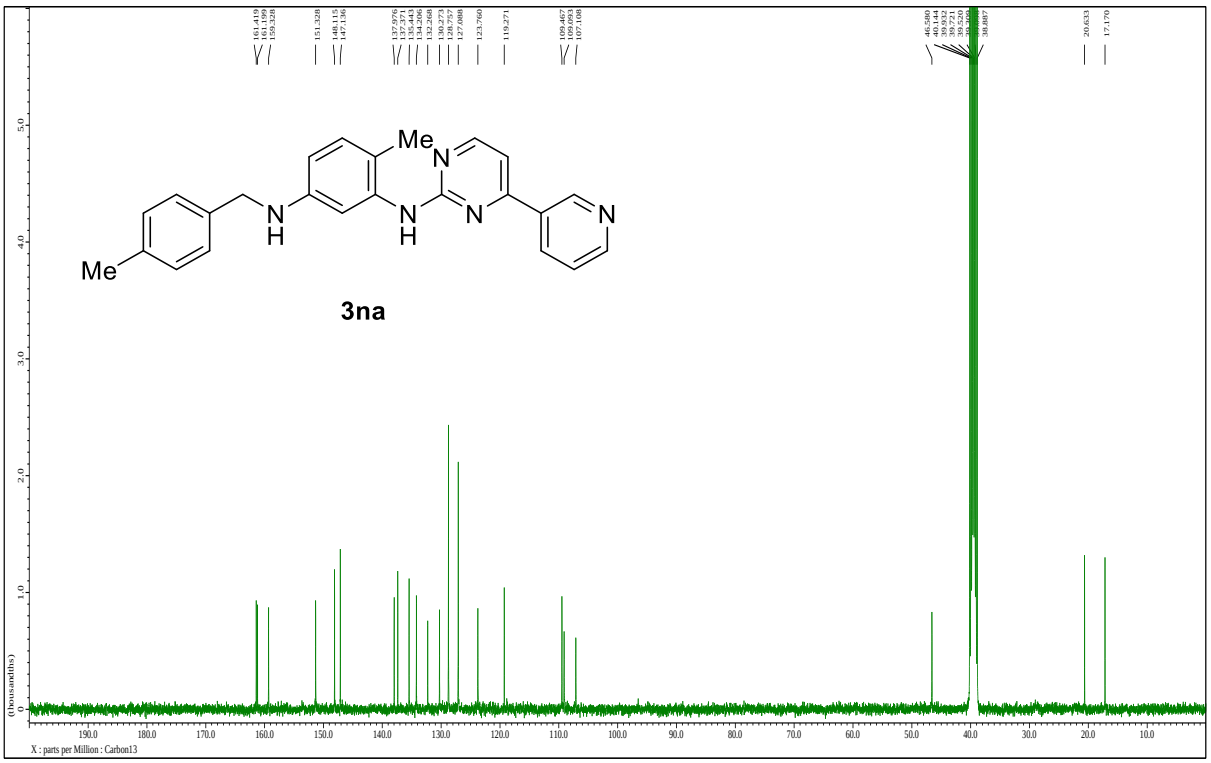
^{13}C-NMR of compound **3ma** ($CDCl_3$, 100 MHz)



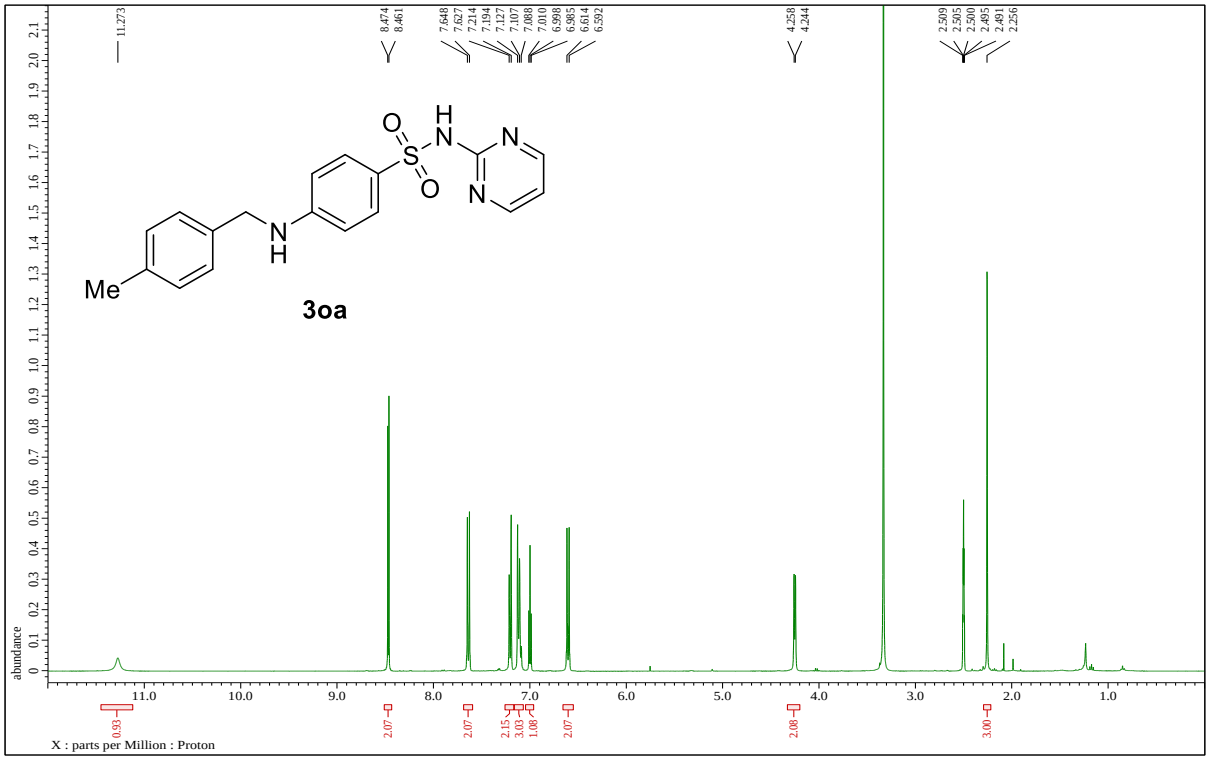
^{1}H-NMR of compound **3na** (DMSO-d_6, 400 MHz)



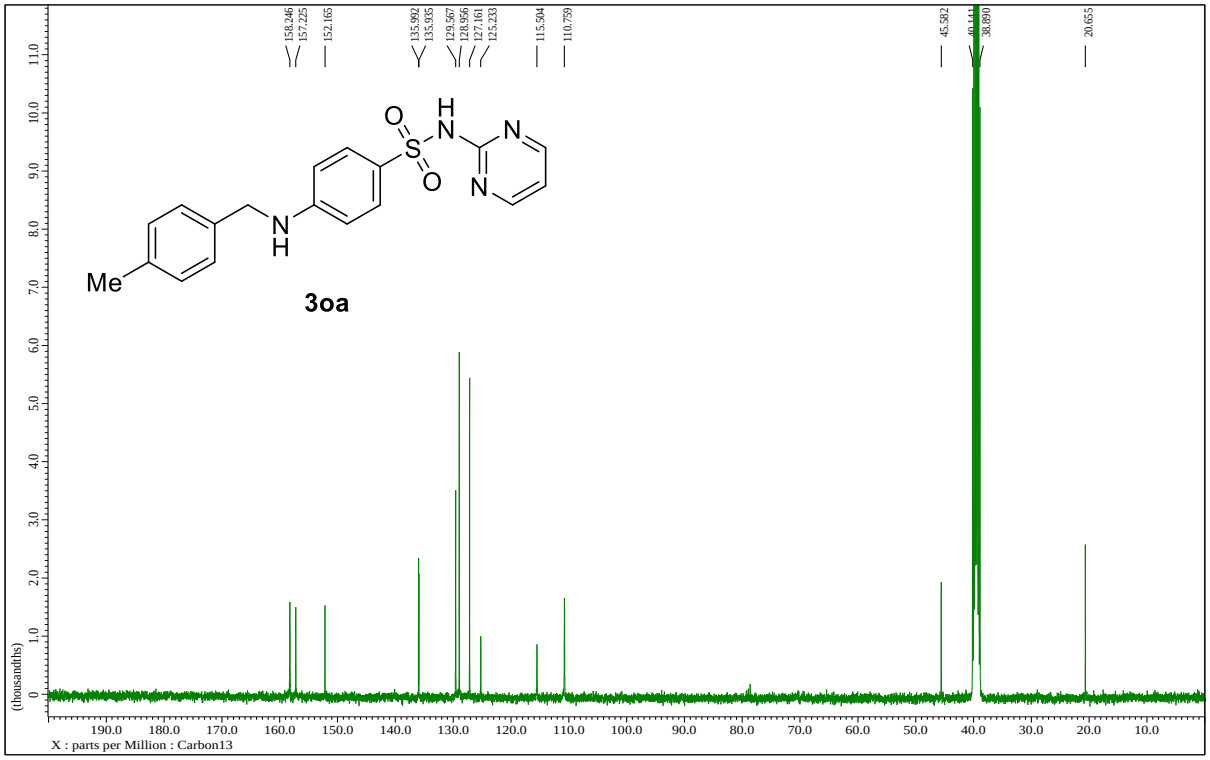
^{13}C-NMR of compound **3na** (DMSO-d_6, 100 MHz)



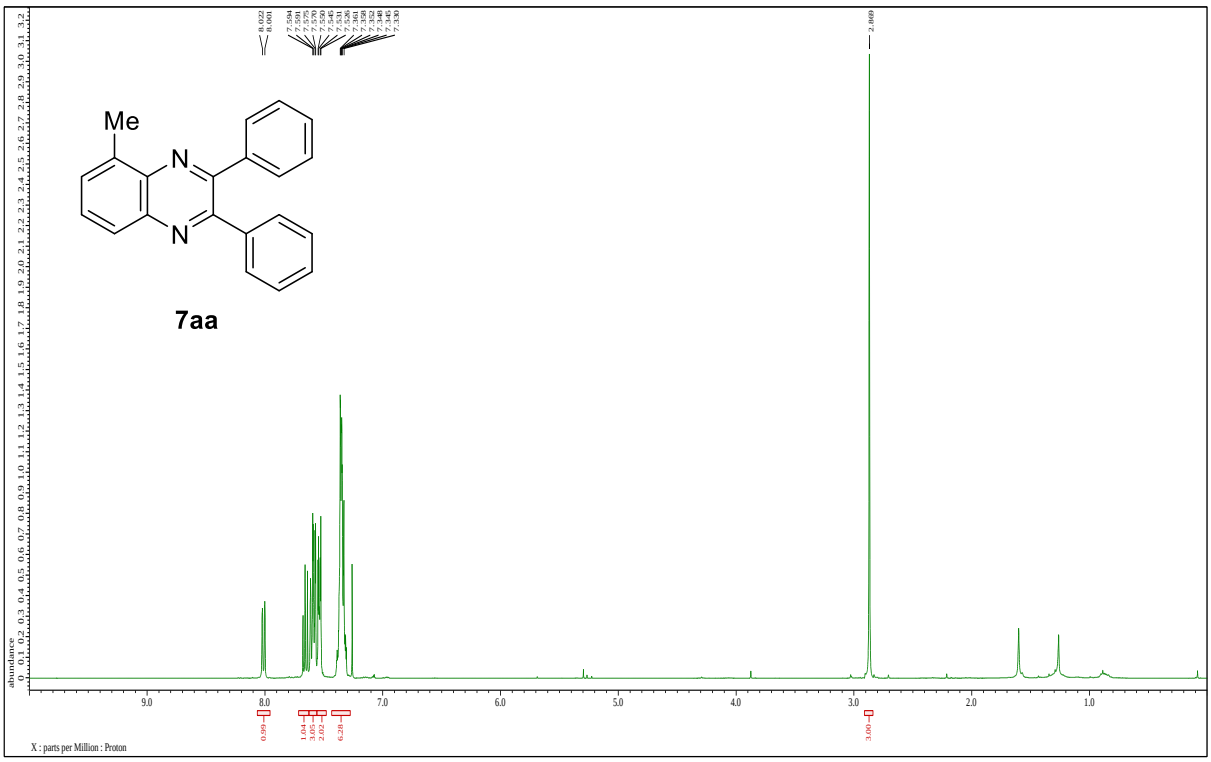
^{1}H-NMR of compound **3oa** (DMSO-*d*$_6$, 400 MHz)



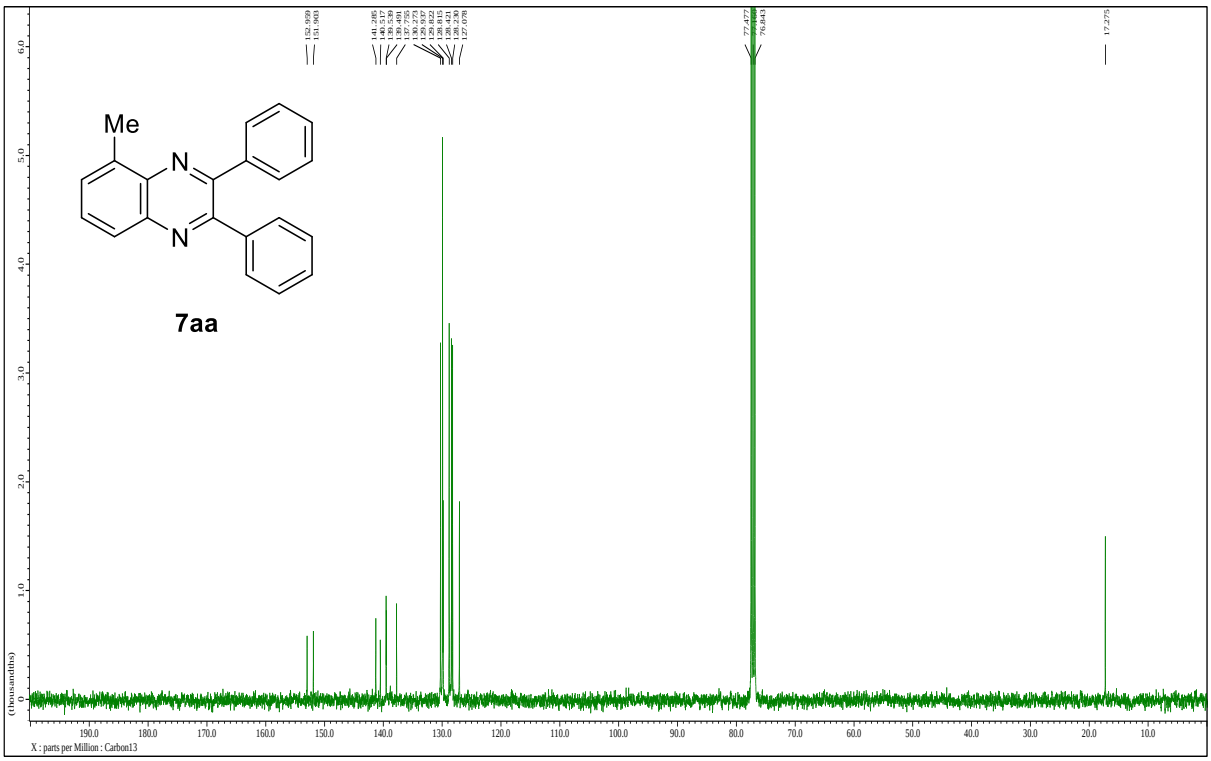
^{13}C-NMR of compound **3oa** (DMSO-*d*$_6$, 100 MHz)



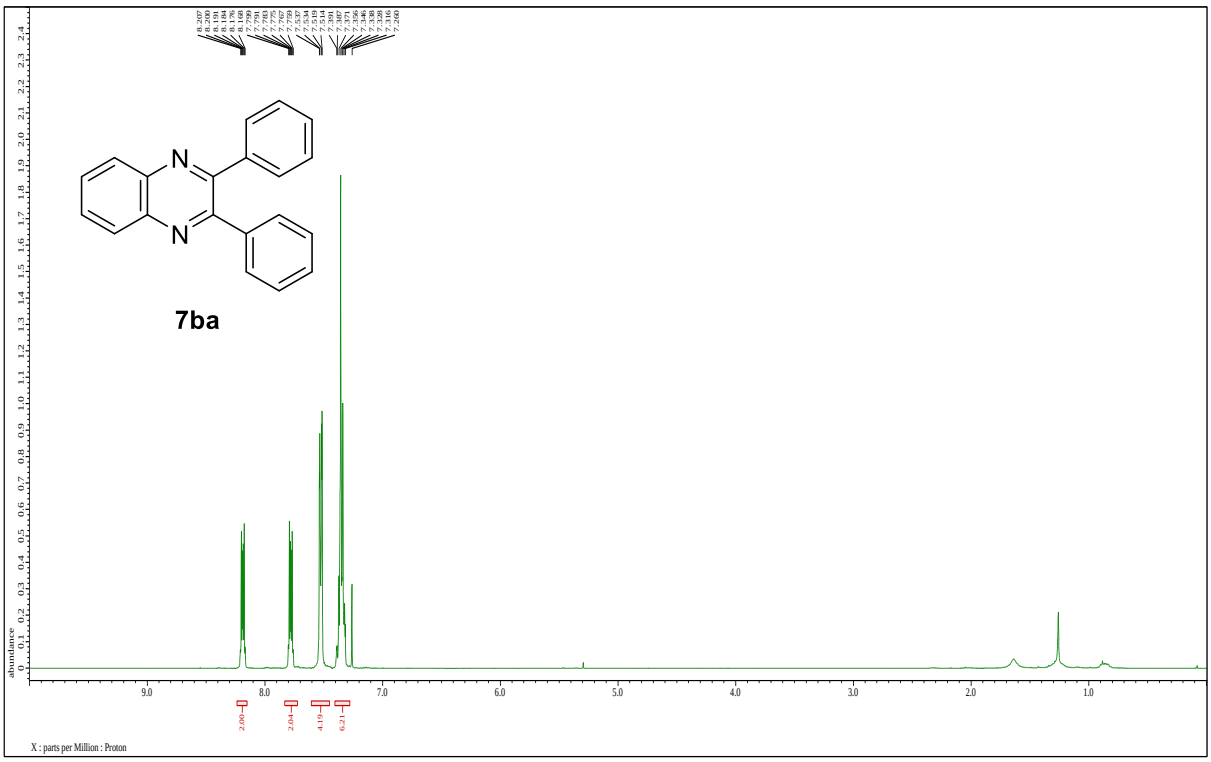
^{1}H-NMR of compound **7aa** ($CDCl_3$, 400 MHz)



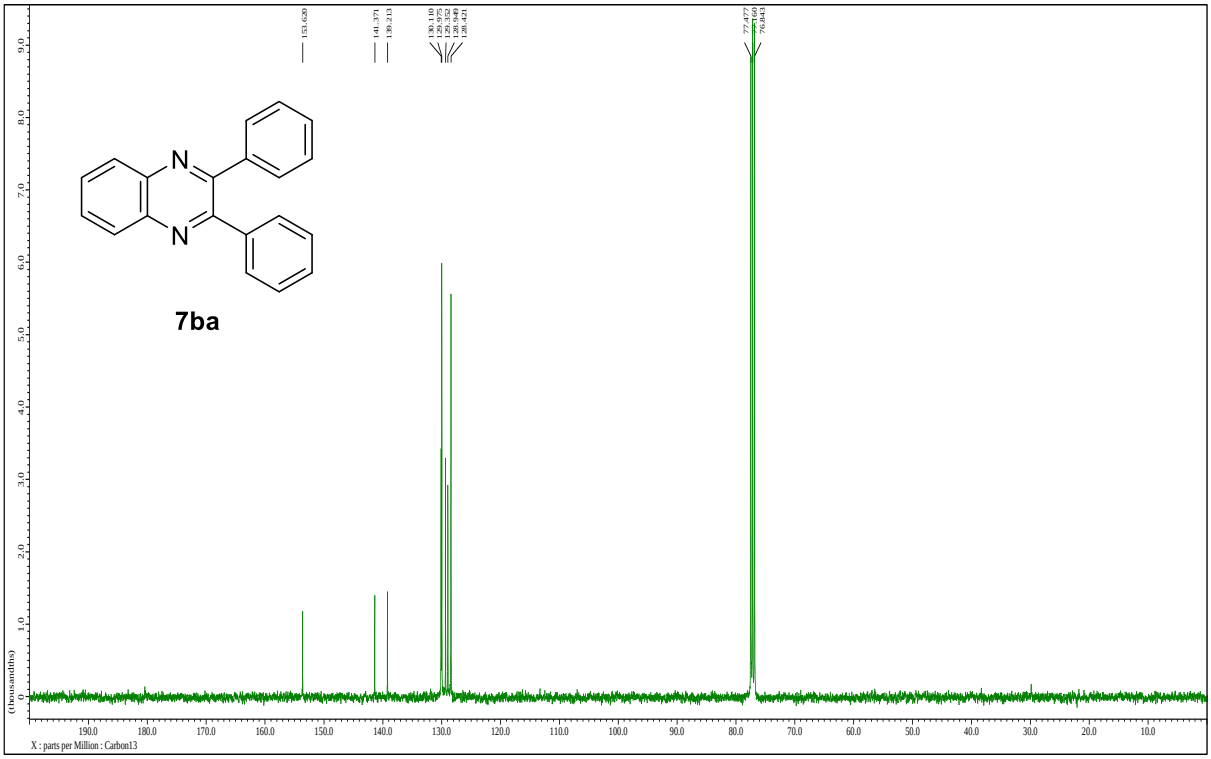
^{13}C-NMR of compound **7aa** ($CDCl_3$, 100 MHz)



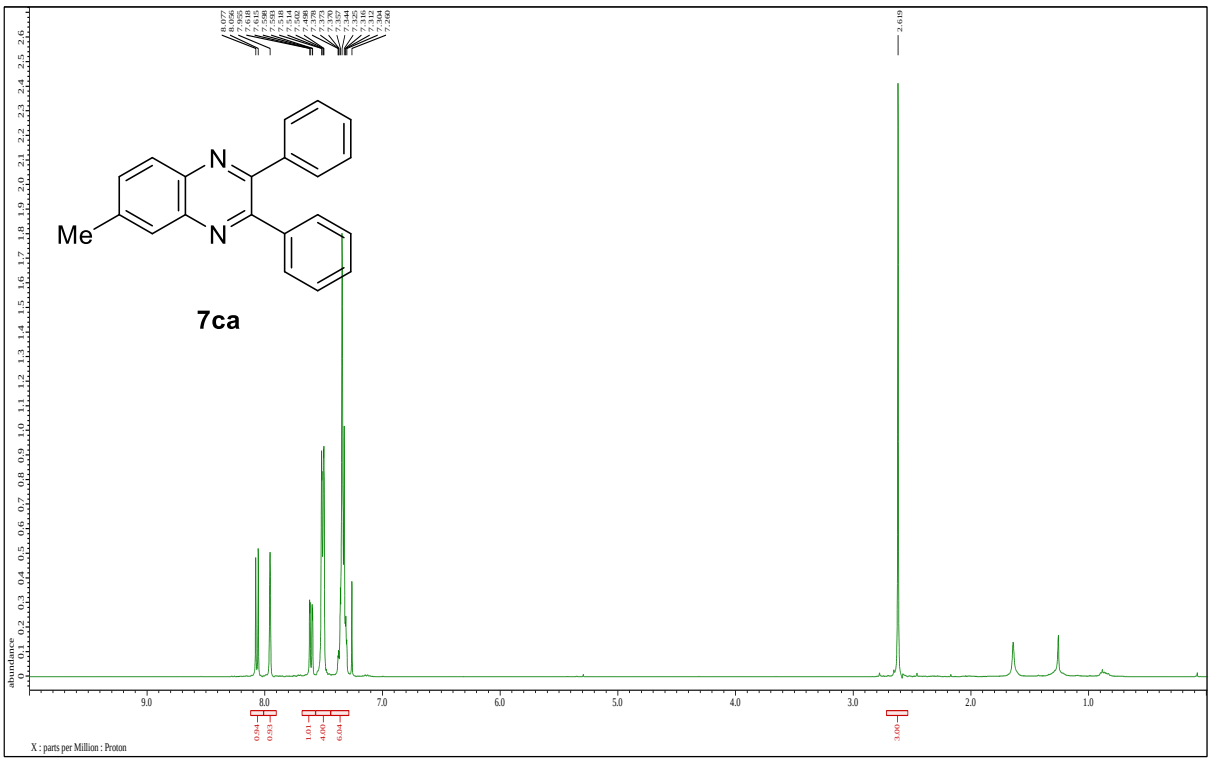
^{1}H-NMR of compound **7ba** ($CDCl_3$, 400 MHz)



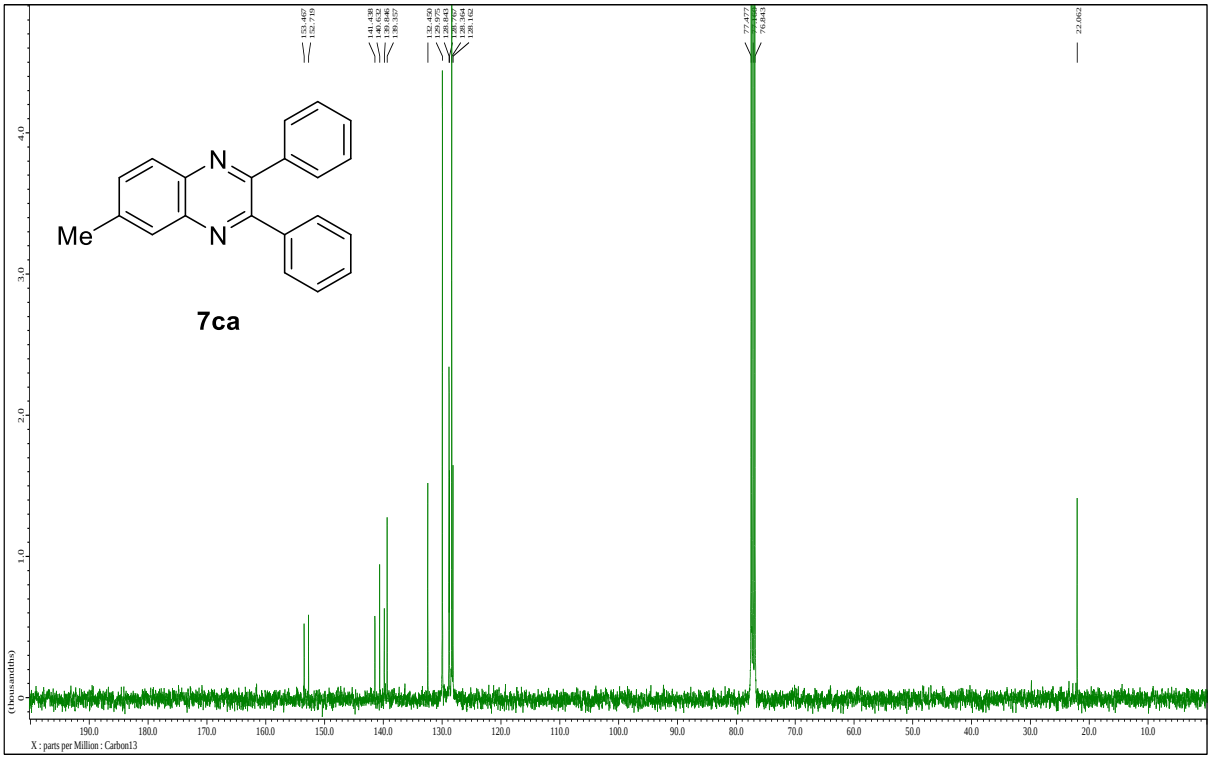
^{13}C-NMR of compound **7ba** ($CDCl_3$, 100 MHz)



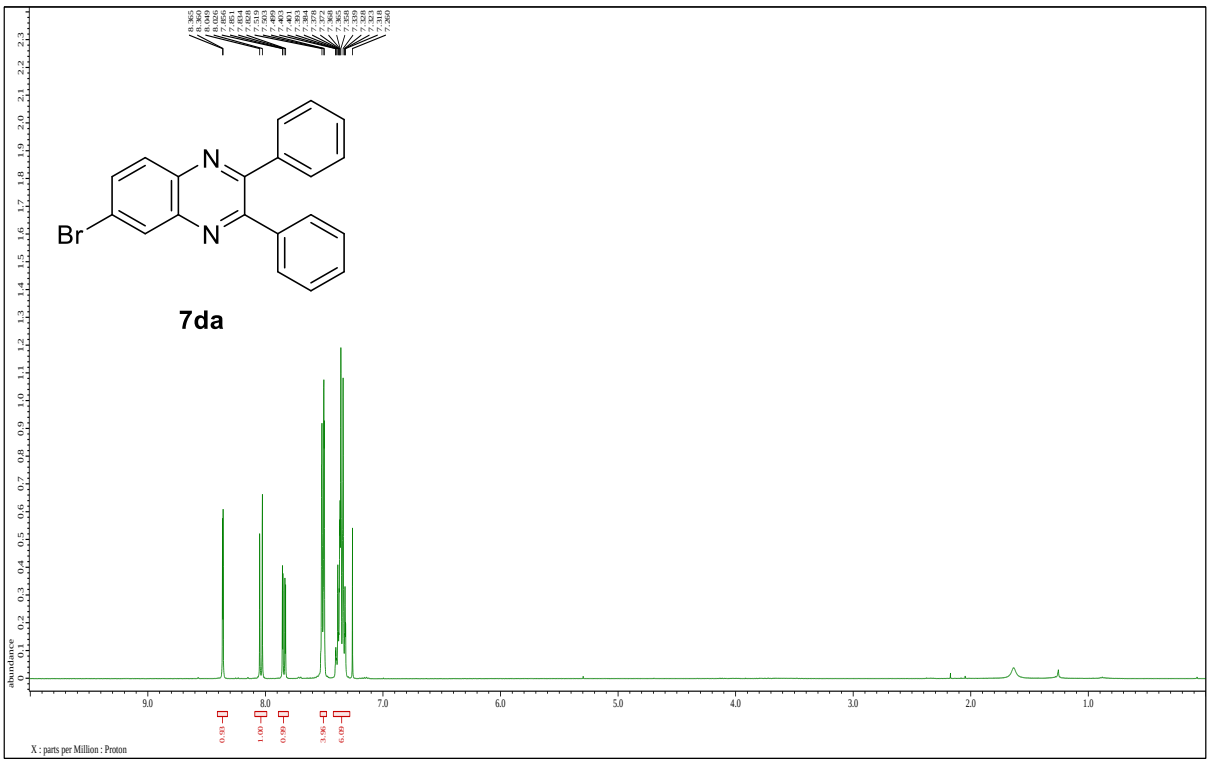
^{1}H-NMR of compound **7ca** ($CDCl_3$, 400 MHz)



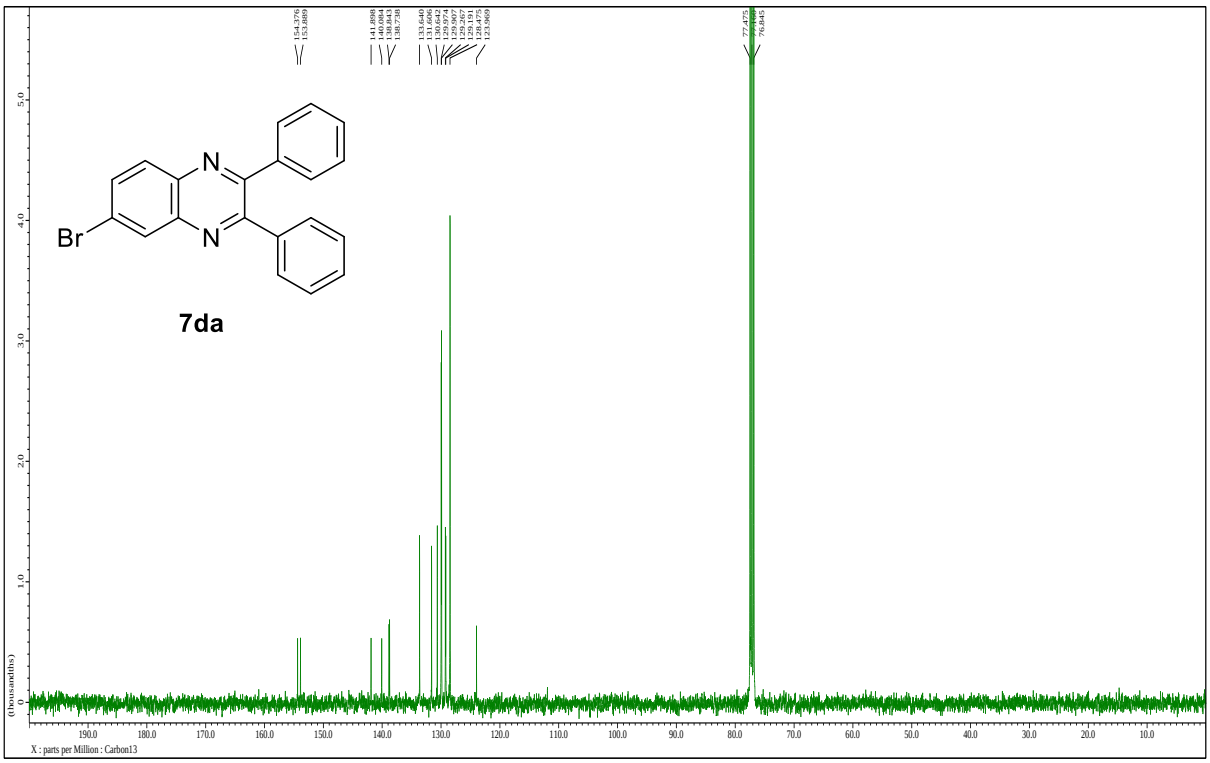
^{13}C-NMR of compound **7ca** ($CDCl_3$, 100 MHz)



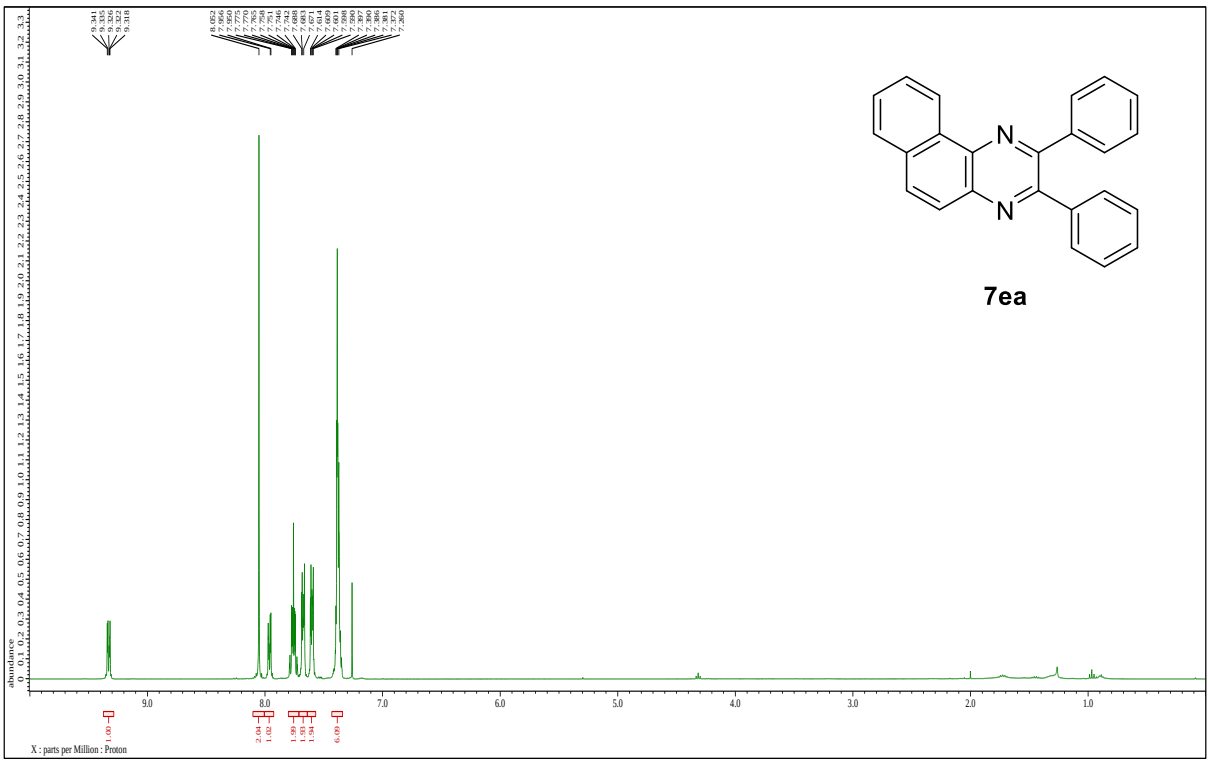
^{1}H-NMR of compound **7da** ($CDCl_3$, 400 MHz)



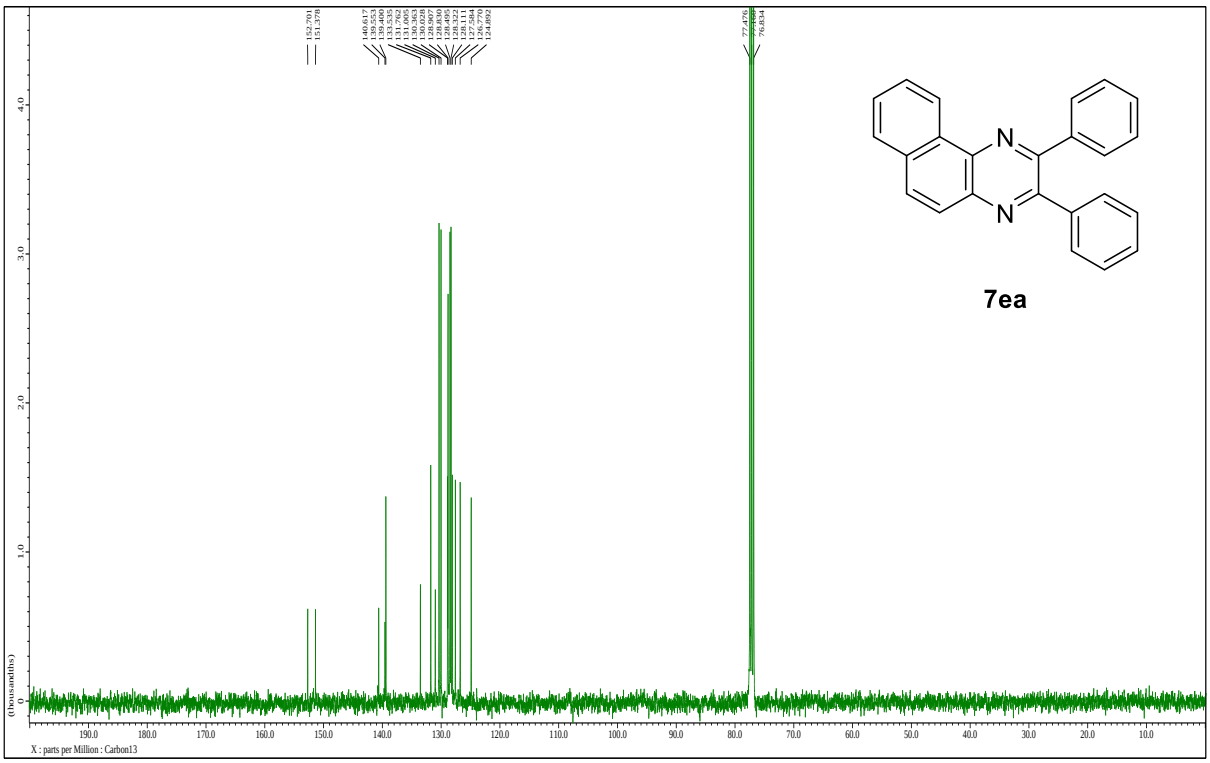
^{13}C-NMR of compound **7da** ($CDCl_3$, 100 MHz)



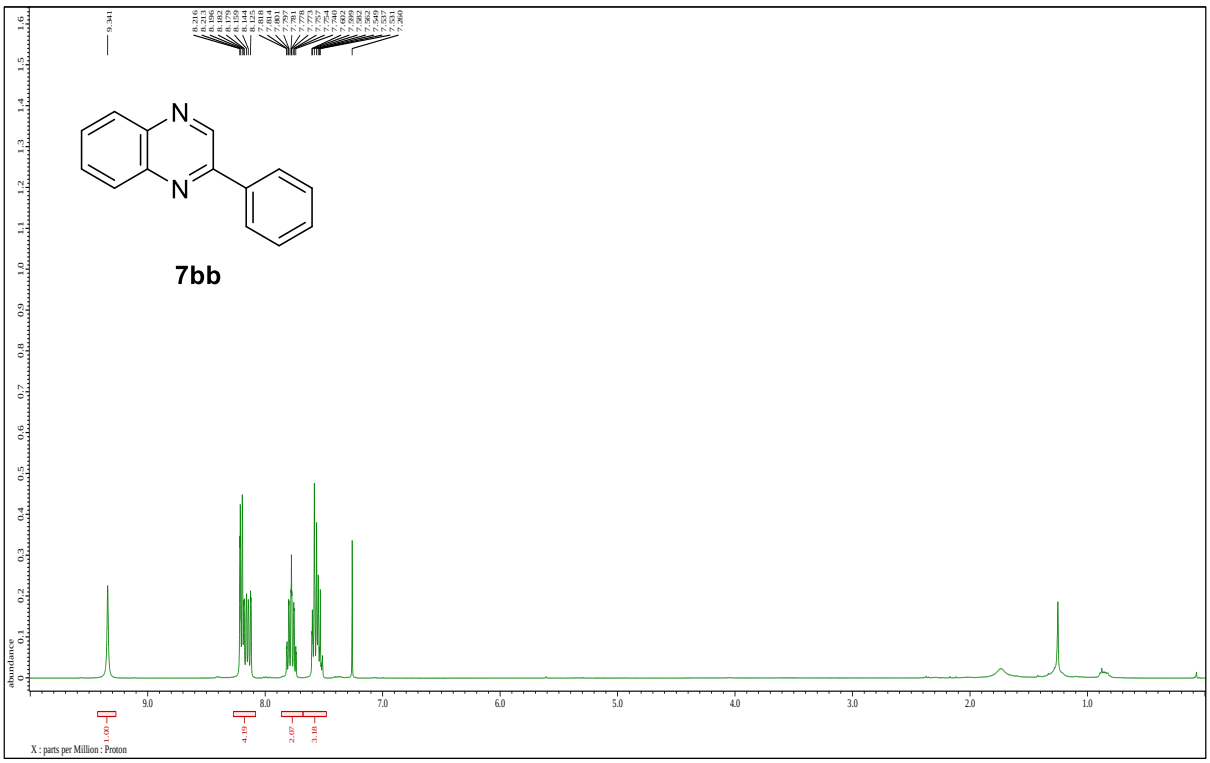
^{1}H-NMR of compound 7**ea** ($CDCl_3$, 400 MHz)



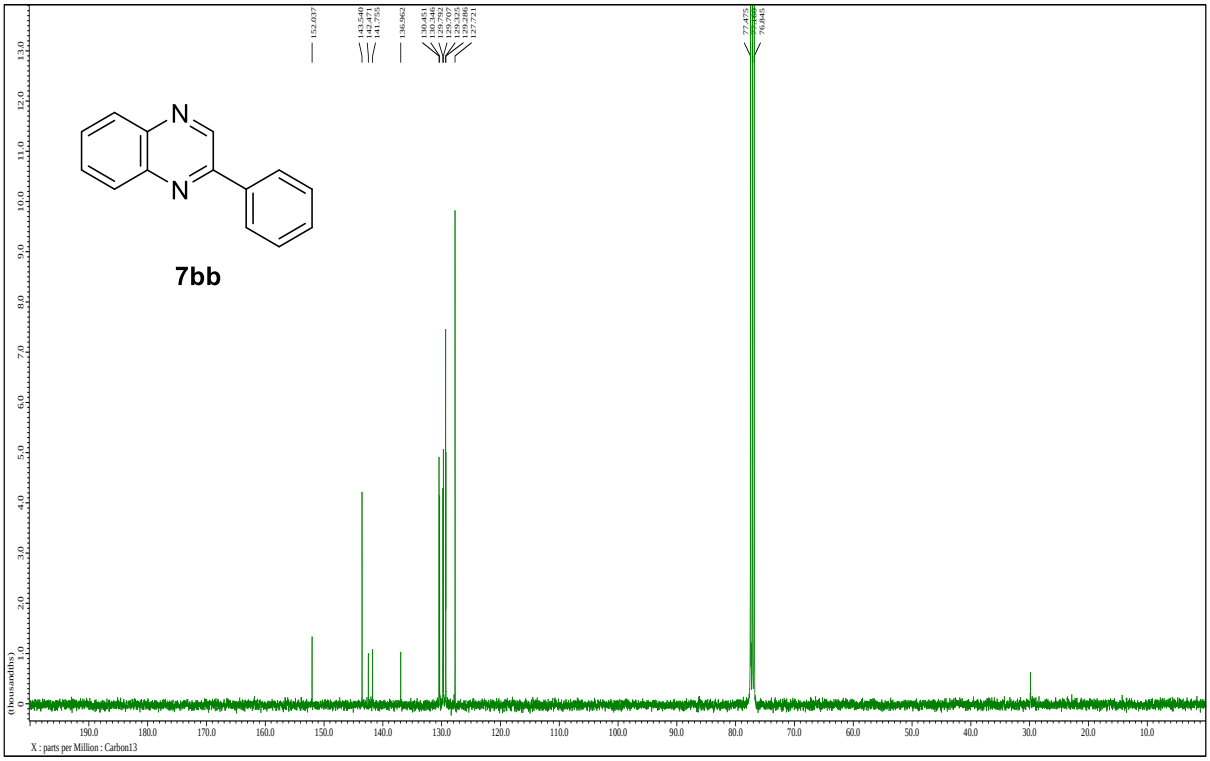
^{13}C-NMR of compound **7ea** ($CDCl_3$, 100 MHz)



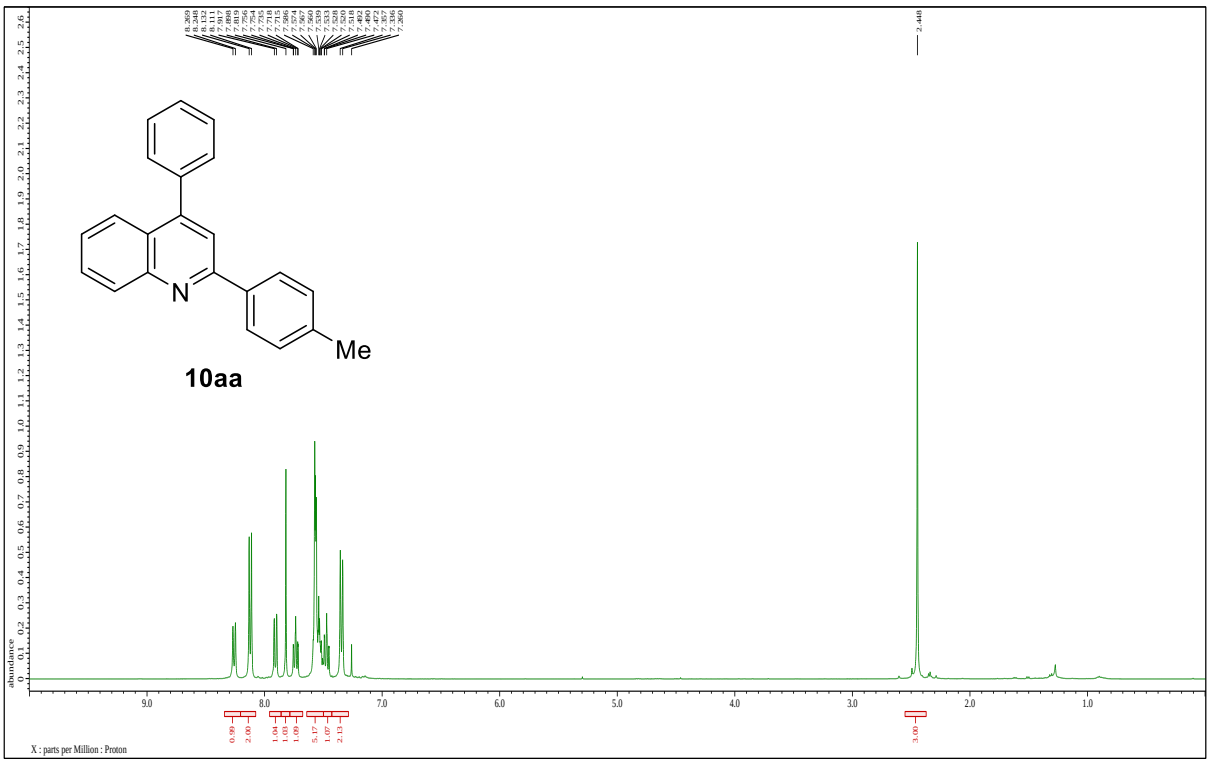
^{1}H-NMR of compound 7**bb** ($CDCl_3$, 400 MHz)



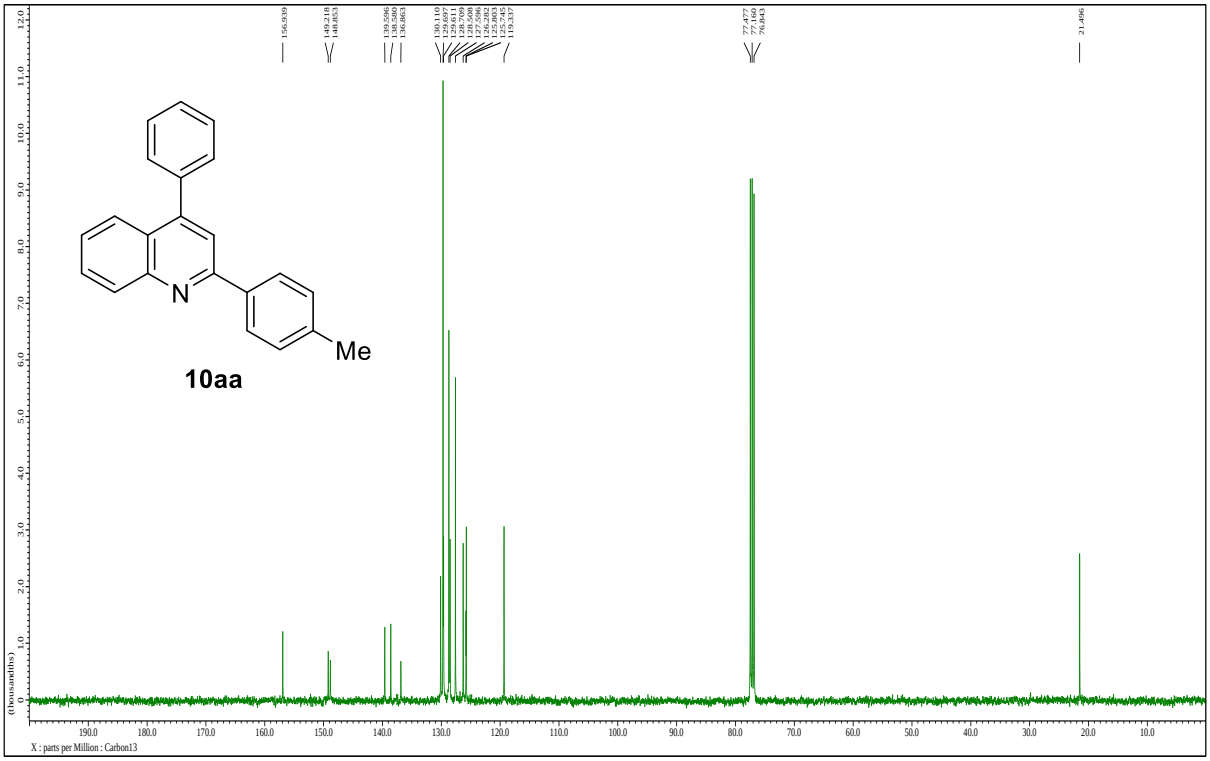
^{13}C-NMR of compound **7bb** ($CDCl_3$, 100 MHz)



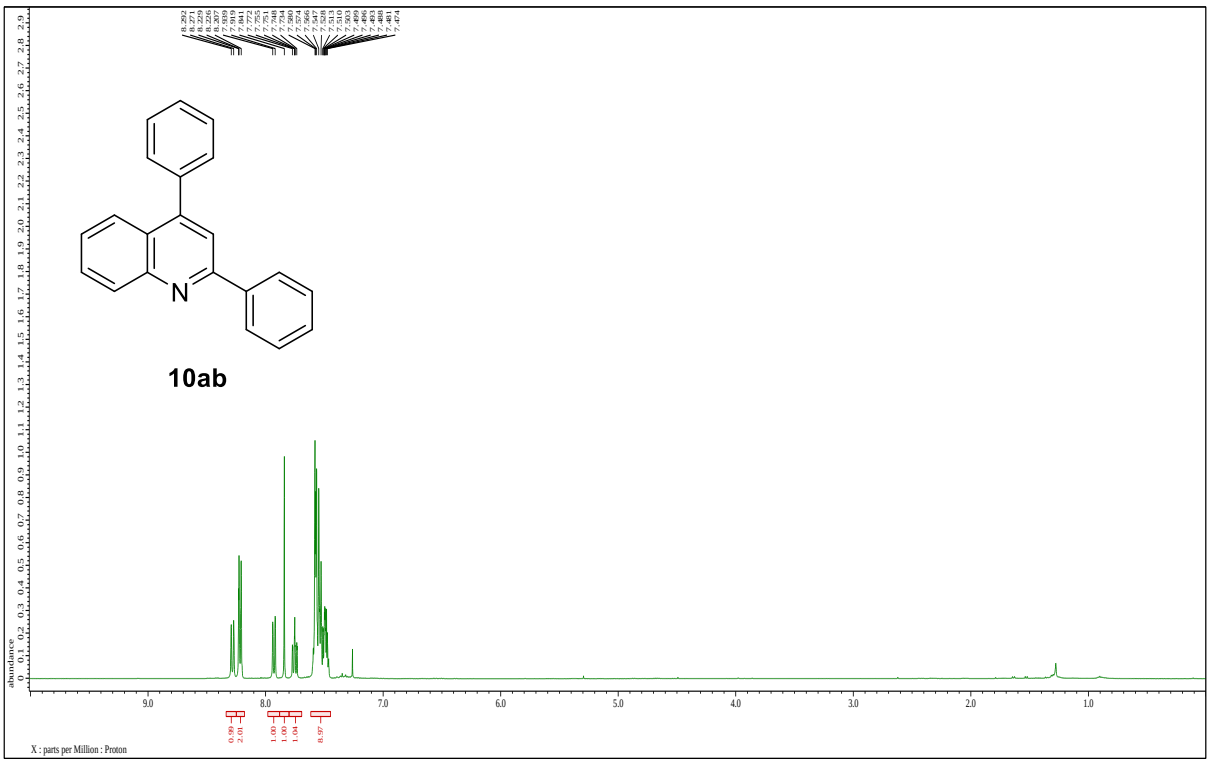
^{1}H-NMR of compound **10aa** ($CDCl_3$, 400 MHz)



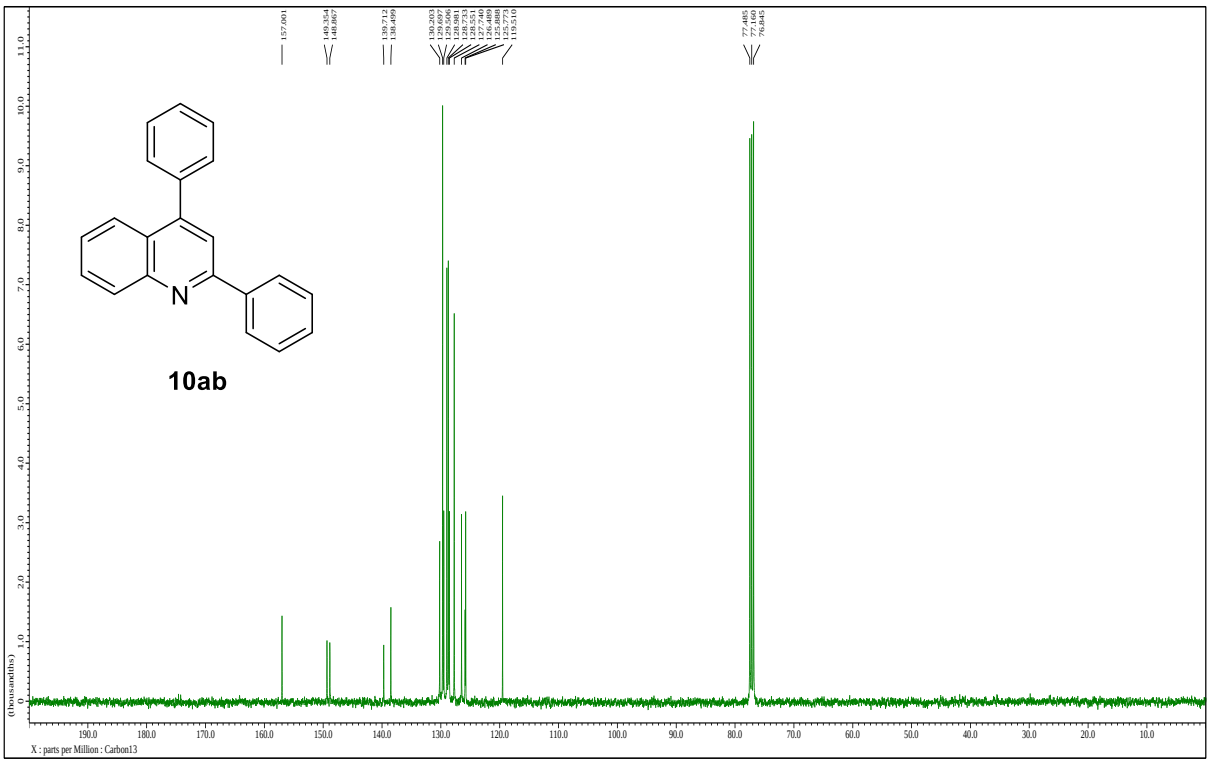
^{13}C-NMR of compound **10aa** ($CDCl_3$, 100 MHz)



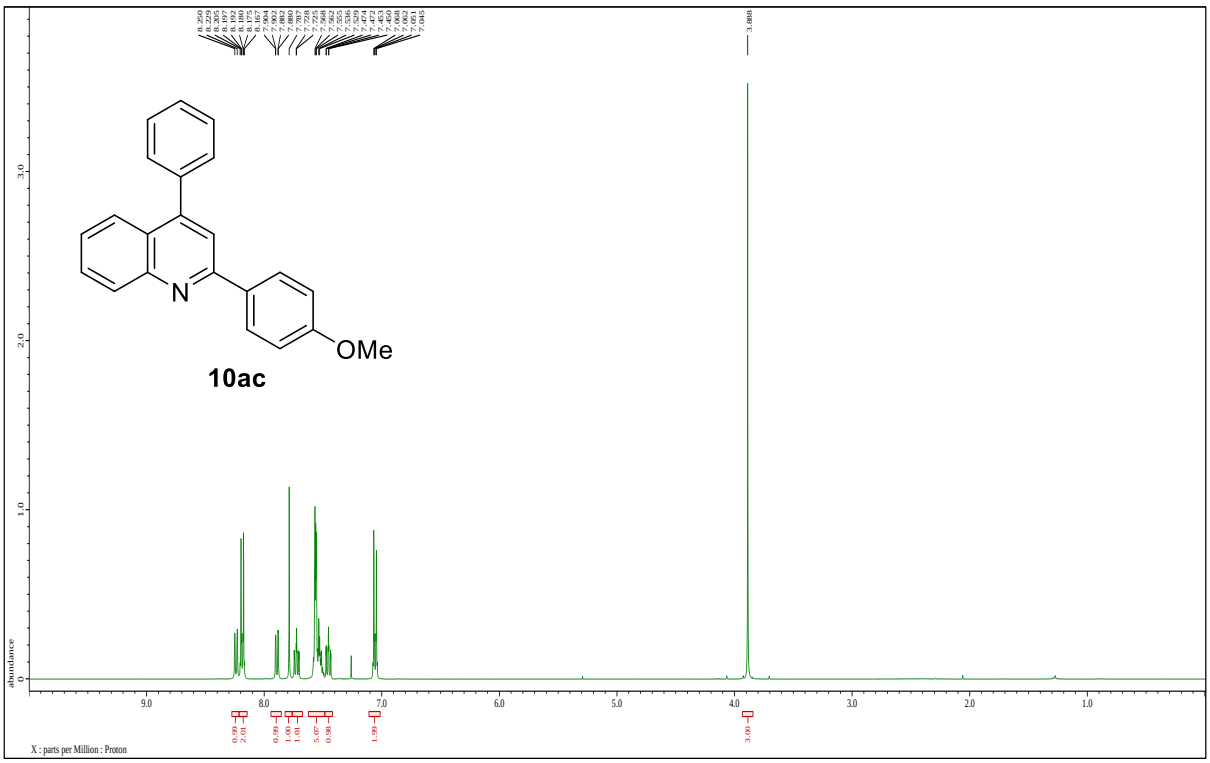
^{1}H-NMR of compound **10ab** ($CDCl_3$, 400 MHz)



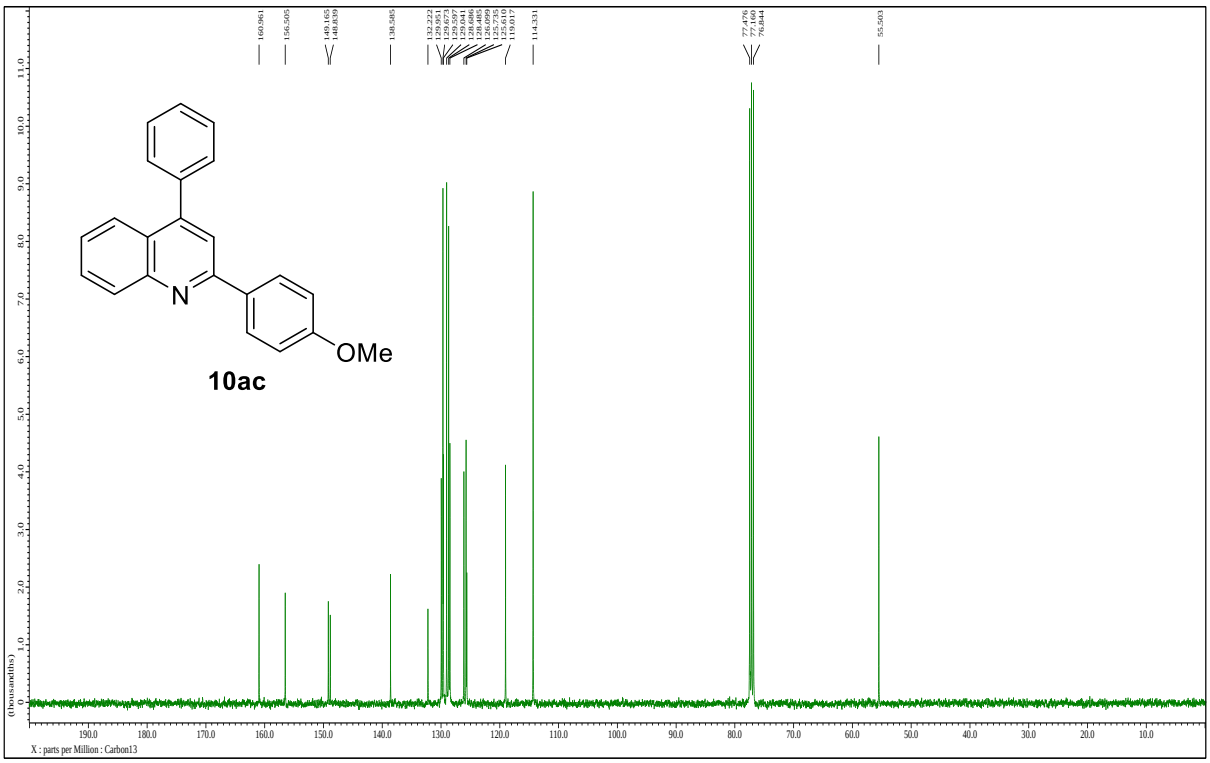
^{13}C-NMR of compound **10ab** ($CDCl_3$, 100 MHz)



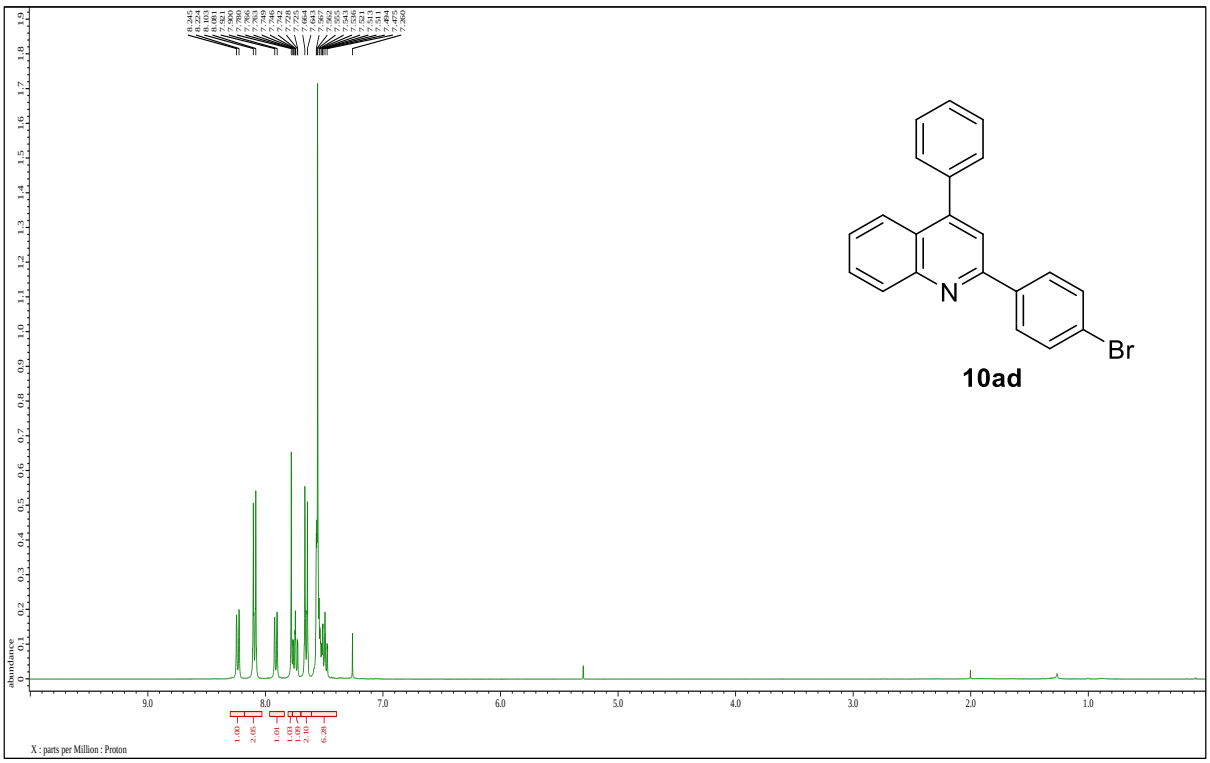
^{1}H-NMR of compound **10ac** ($CDCl_3$, 400 MHz)



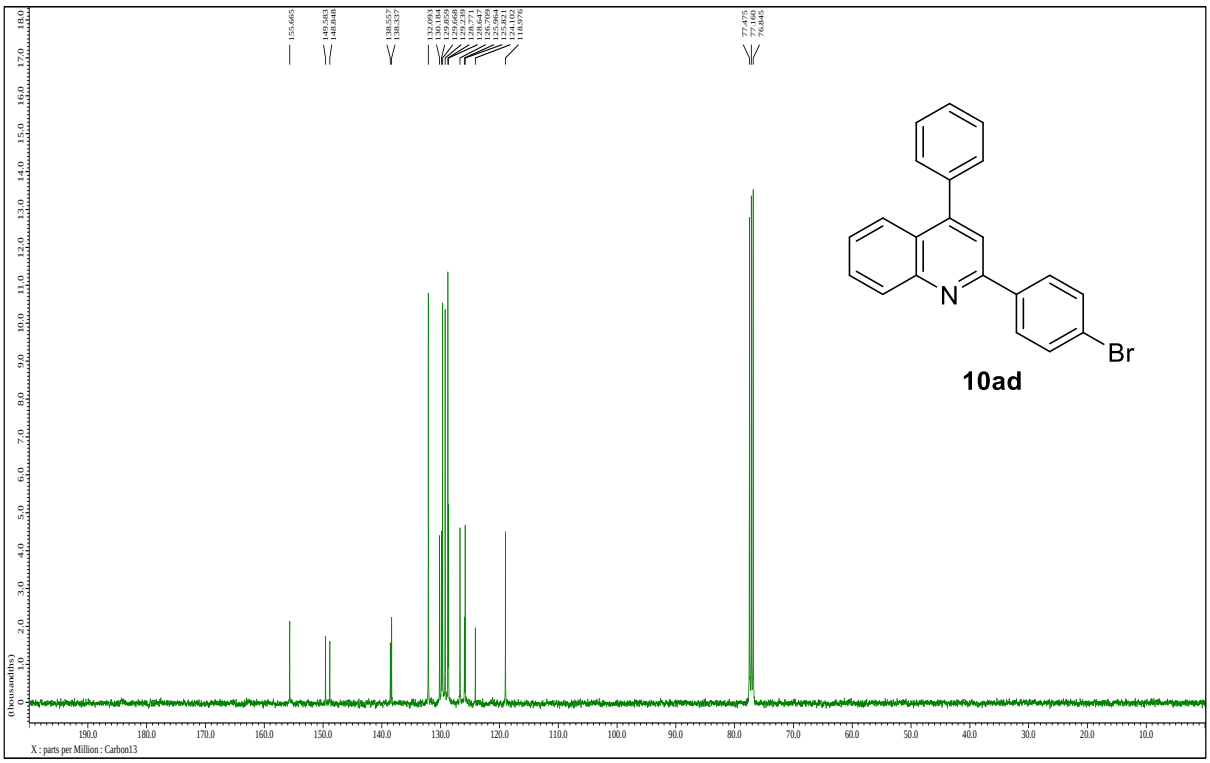
^{13}C-NMR of compound **10ac** ($CDCl_3$, 100 MHz)



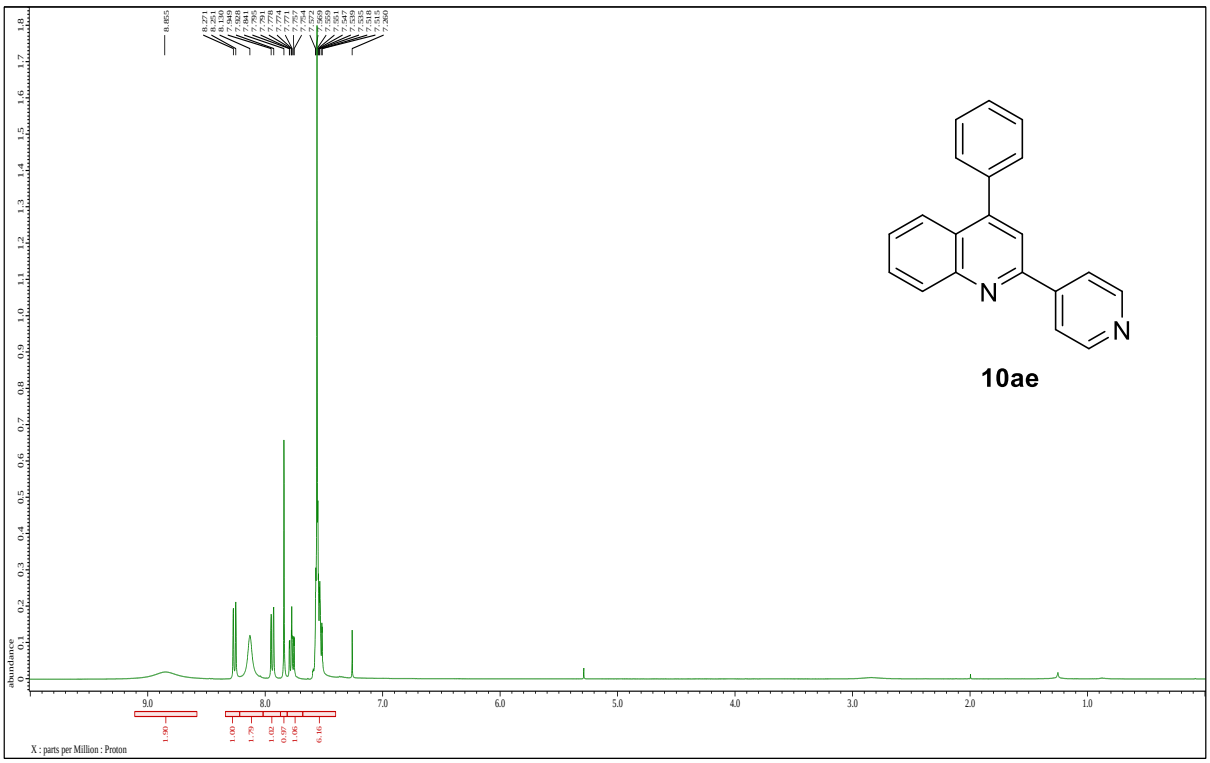
^{1}H-NMR of compound **10ad** ($CDCl_3$, 400 MHz)



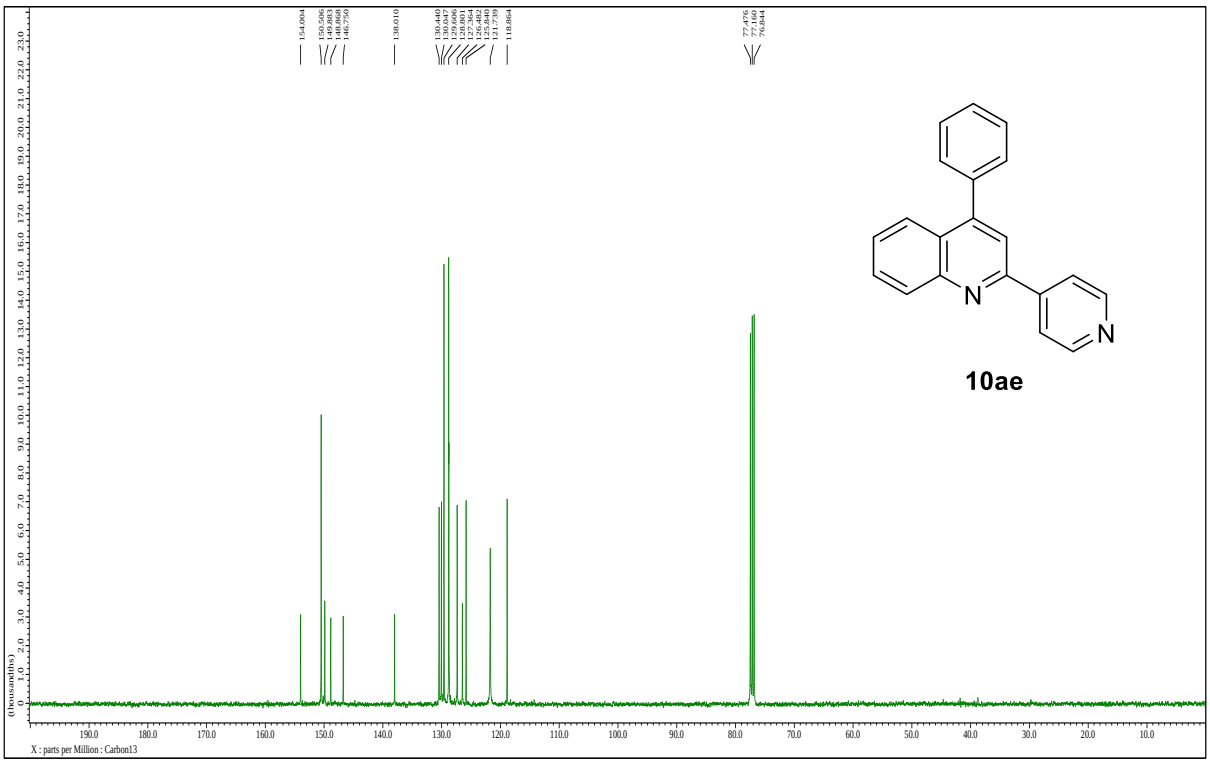
^{13}C-NMR of compound **10ad** ($CDCl_3$, 100 MHz)



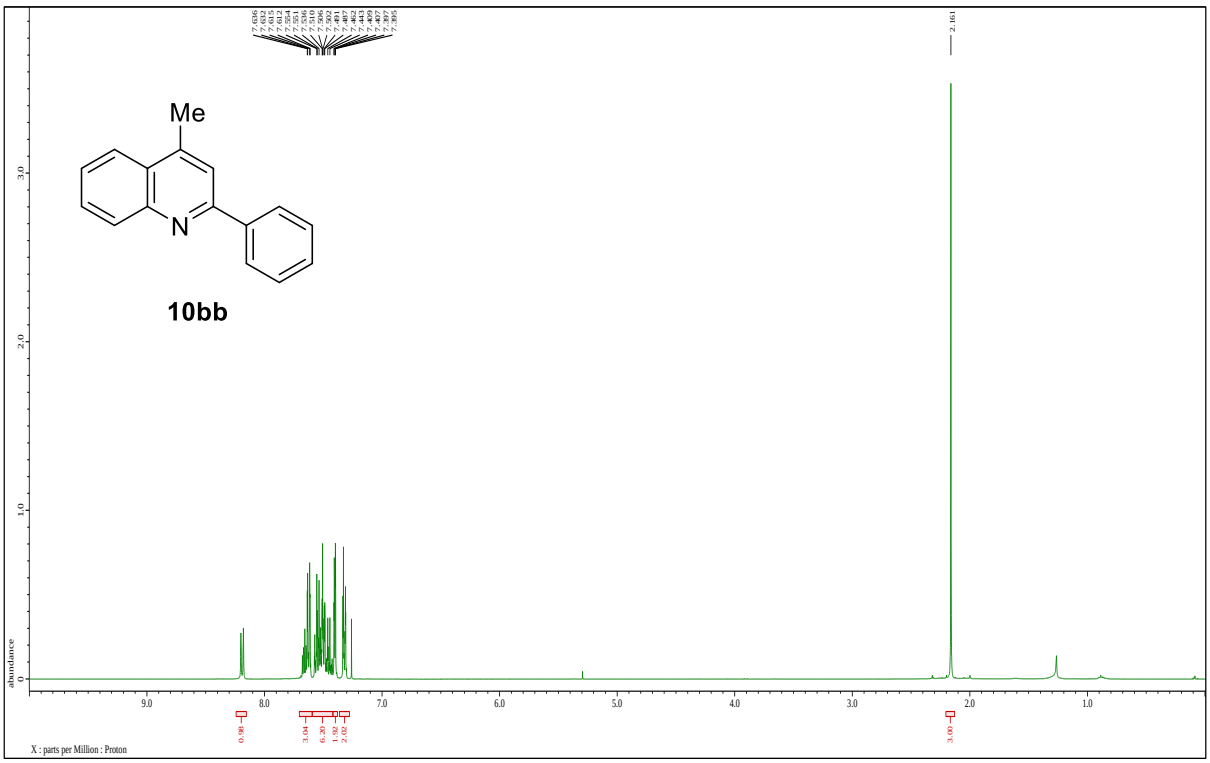
^{1}H-NMR of compound **10ae** ($CDCl_3$, 400 MHz)



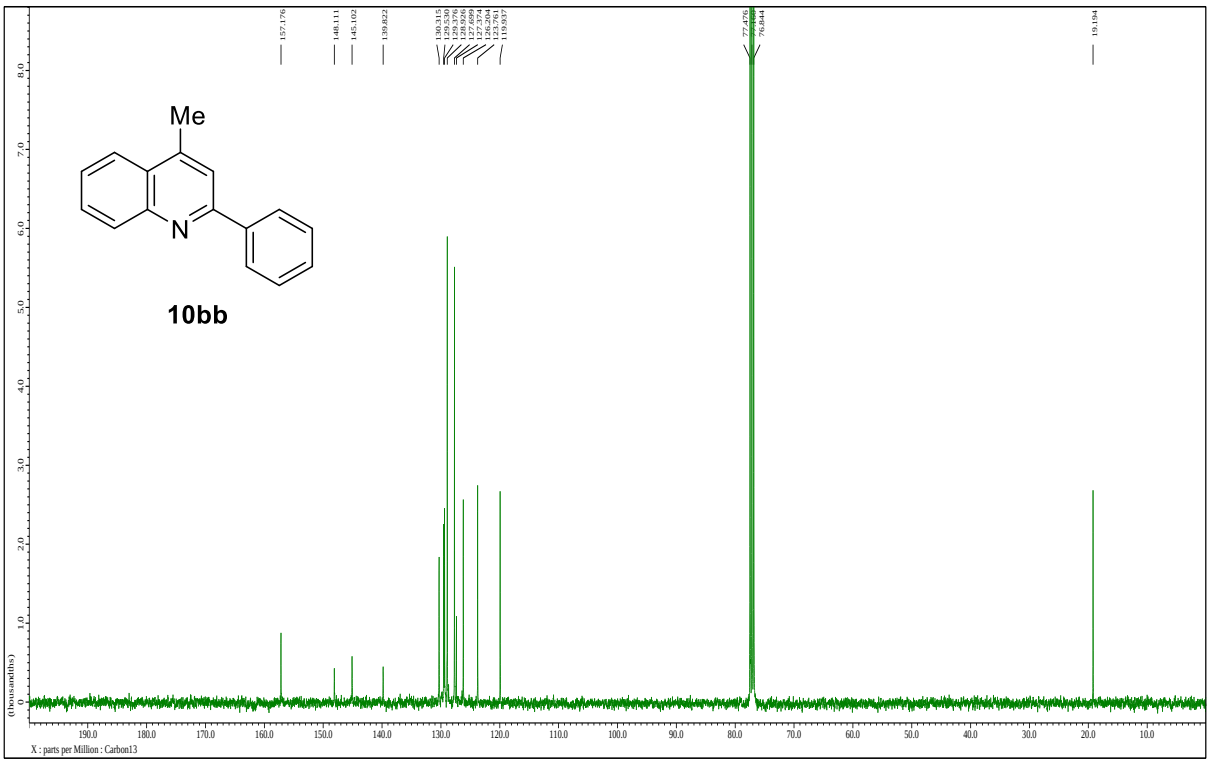
^{13}C-NMR of compound **10ae** ($CDCl_3$, 100 MHz)



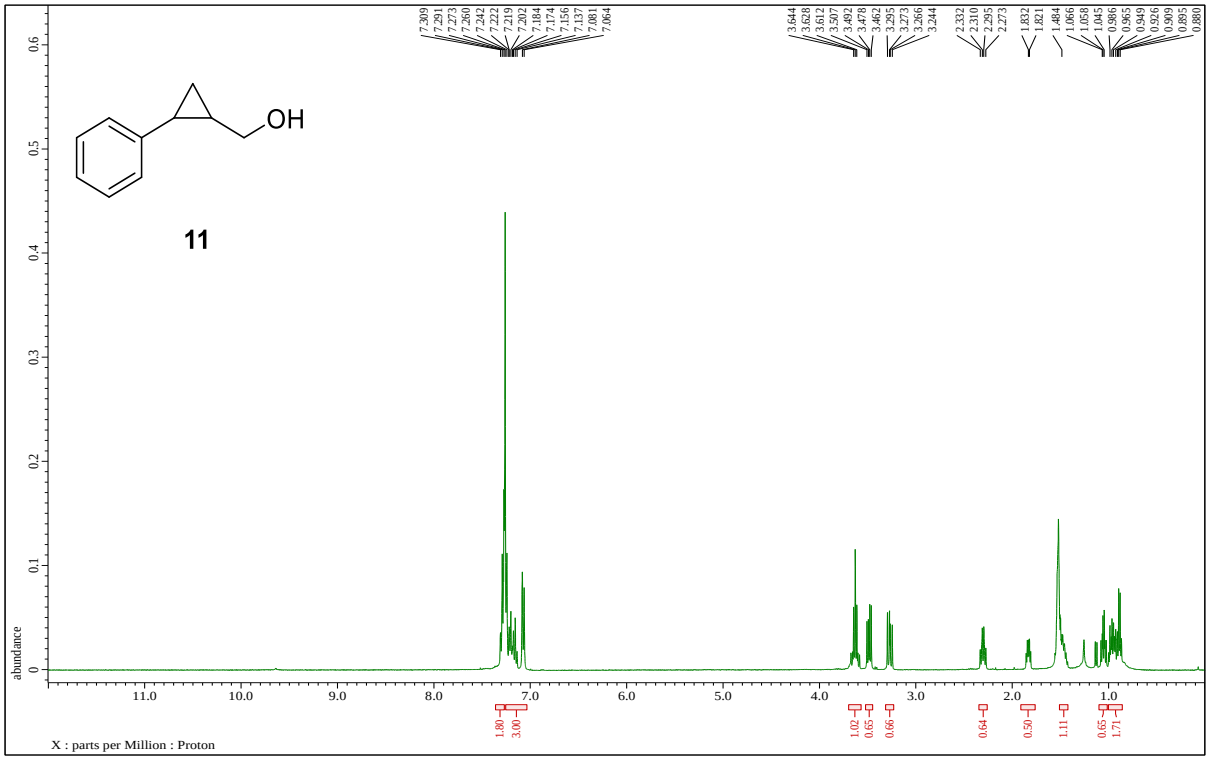
^{1}H-NMR of compound **10bb** ($CDCl_3$, 400 MHz)



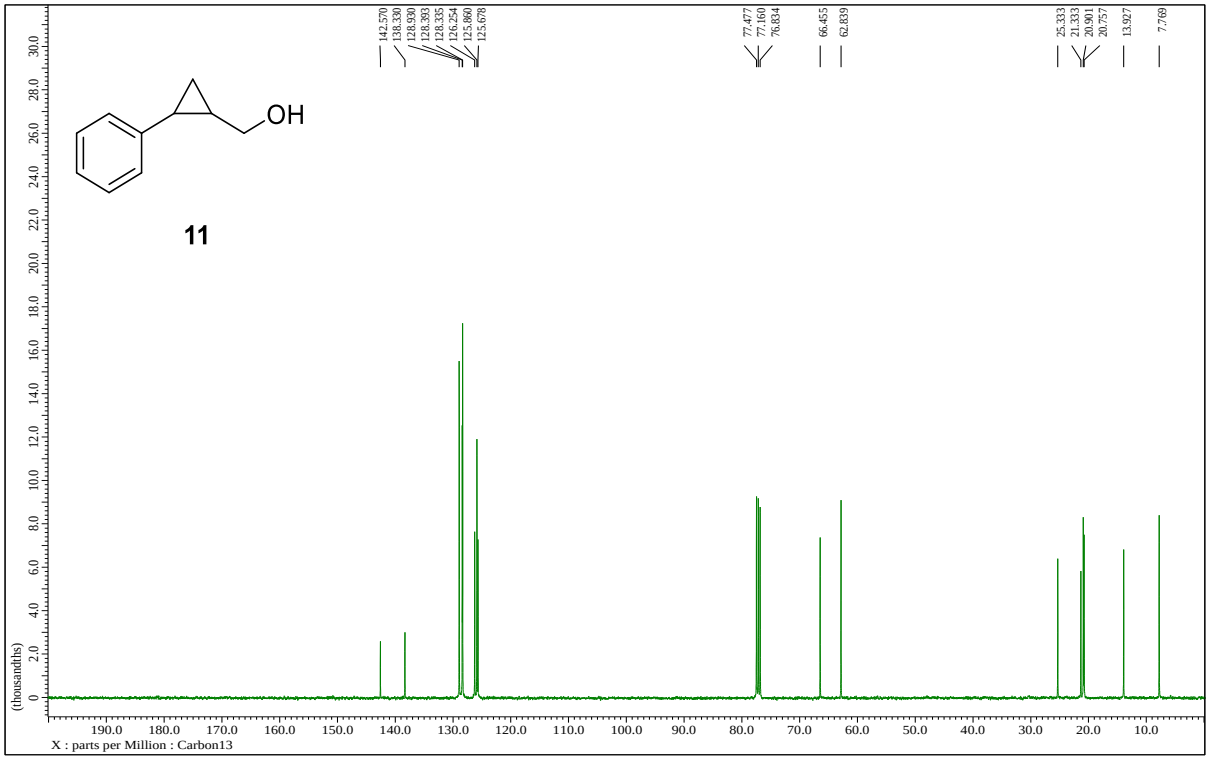
^{13}C-NMR of compound **10bb** ($CDCl_3$, 100 MHz)



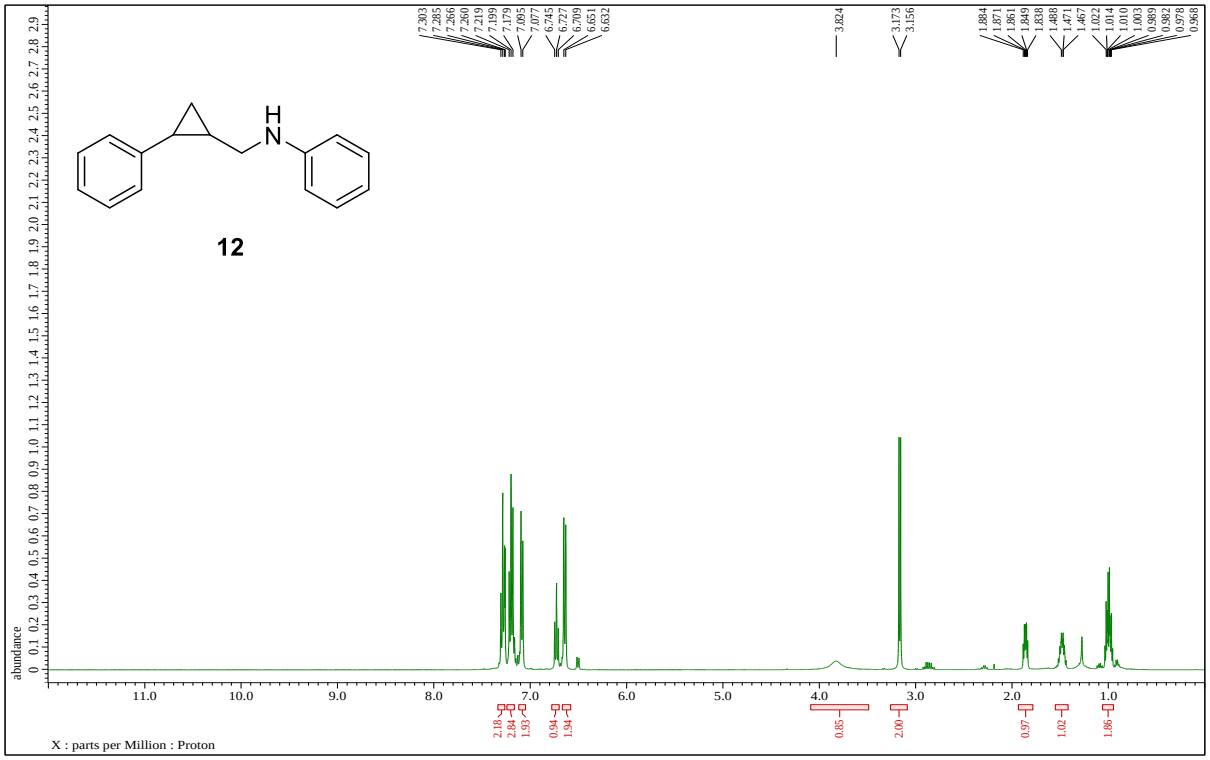
^{1}H-NMR of compound **11** ($CDCl_3$, 400 MHz)



^{13}C-NMR of compound **11** ($CDCl_3$, 100 MHz)



^{1}H-NMR of compound **12** ($CDCl_3$, 400 MHz)



^{13}C-NMR of compound **12** ($CDCl_3$, 100 MHz)