CHAPTER-5

DEOXYGENATION OF *TERTIARY* AMINE *N*-OXIDES UNDER METAL-FREE CONDITION USING PHENYLBORONIC ACID

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5.1 INTRODUCTION

Amine *N*-oxides have found wide application in synthetic organic chemistry as starting materials, intermediates, oxidants, ligands, organocatalysts, directing groups, etc. [1]. Besides their chemical importance, *N*-oxides have also received considerable attention in the field of biology and medicines [2]. Many findings suggest that *N*-oxides play a key role in the metabolism of drugs [2b]. Moreover, the chemistry of deoxygenation of amine *N*-oxides has attracted significant interest not only in synthetic organic chemistry [3] but also in biology [4]. Recently, fluorescent probes have been developed based on deoxygenation of *N*-oxides for sensing metal and non-metal species found in biological assays (Figure **5.1**) [4a-c].

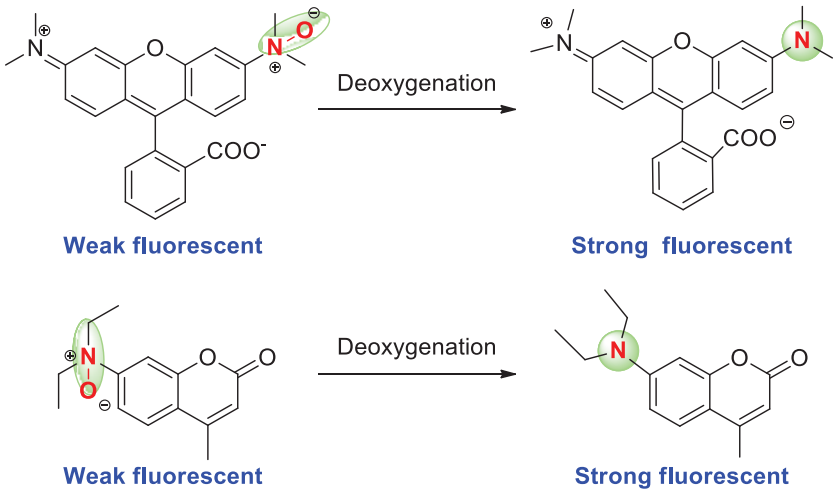


Figure 5.1 Example of *N*-oxide deoxygenation promoted turn-on fluorescent probe.

In medicine, *N*-oxides have been suggested as less toxic bio-reductive prodrugs for anticancer drugs (*i.e.* DNA intercalators) that are selectively deoxygenated to the active drug by metabolic reduction under hypoxic conditions (Figure **5.2**) [4d, 4e].

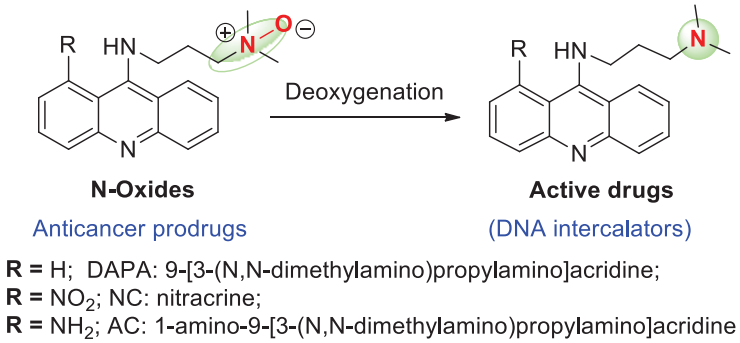
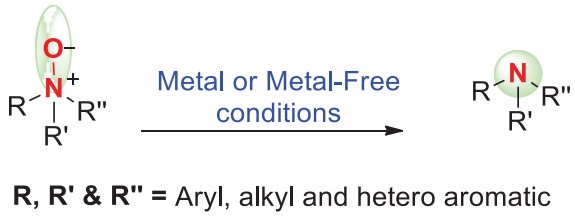


Figure 5.2 Structures of *N*-oxide based anticancer prodrugs.

Considering the importance of deoxygenation processes in chemical and biological transformations, numerous deoxygenation methods have been developed using various metal and metal-free reagents including Pd-C/$HCOONH_4$ [5], Zn/NH_4Cl [6],CuI [7], $ZrCl_4/NaBH_4$ [8], SmI_2 [9], In/NH_4Cl [10], titanium compounds [11], sulfur reagents [12], phosphorus reagents [13], diboron compounds [14], etc., (**Scheme 5.1**). The major limitations of these existing protocols are the use of toxic metals or expensive reagents or reagents that are difficult to handle (e.g. unpleasant odor, fuming, flammable or hygroscopic), requirement of harsh and dry reaction conditions, longer reaction times, functional group incompatibilities, etc.

Therefore, the development of an efficient and convenient method for the selective reduction of amine *N*-oxides using green reagents will have high significance not only in

synthetic organic chemistry but also in biological science, for example, drug metabolism studies [11c].



Scheme 5.1. Deoxygenation processes under metal or metal-free conditions.

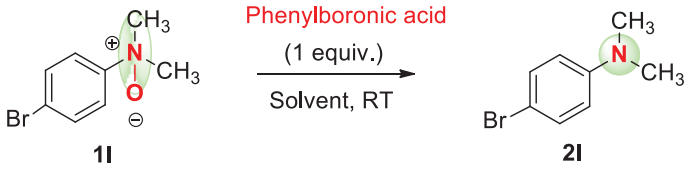
Organoboron compounds are important reagents in synthetic organic chemistry which enable many chemical transformations in an efficient manner [15]. Among the different sub-classes of organoboron compounds, arylboronic acids remain the most popular and extensively used in organic synthesis as building blocks, intermediates, reagents and catalysts [15a]. In continuation to the previous chapters [16], here we report phenylboronic acid as an efficient reagent for the deoxygenation of *tert.*-amine *N*-oxides under mild conditions.

5.2 RESULTS AND DISCUSSION

5.2.1 Optimization of reaction condition

At the outset, 4-bromo-*N*,*N*-dimethylaniline *N*-oxide (**1l**) was chosen as a model substrate for reaction optimization while phenylboronic acid was used as a deoxygenating reagent (**Table 5.1**). In order to identify a suitable solvent, the deoxygenation reactions were carried out in different protic and aprotic solvents at room temperature using equimolar amount of substrate and the reagent (**Table 5.1**, **entries 1-11**).

Table 5.1. Optimization of reaction condition in various solvents.[a,b]



1l 2l

Entry	Solvent	Time (min.)	Yield (%)[b]
1	CH_3OH	60	25
2	CH_3OH	12 h	80
3	C_2H_5OH	60	32
4	*t*-BuOH	60	50
5	H_2O	60	30
6	THF	30	89
7	2-Me THF	15	95
8	Toluene	60	46
9	CH_3CN	60	32
10	**DCM**	**5**	**95**
11	DCE	10	95

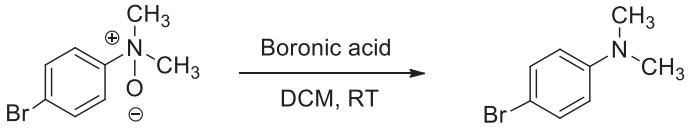
[a]**Reaction condition:** aniline *N*-oxide (1 mmol) and phenylboronic acid (1 mmol) stirred in different solvents at room temperature. [b]Isolated yield.

The protic solvents such as methanol, ethanol, *t*-butanol and water gave incomplete reactions even after prolonged reaction time (**Table 5.1**, **entries 1-5**). In the case of polar aprotic solvents (**Table 5.1**, **entries 6-11**), dichloromethane was found to be very efficient, providing a quantitative yield of the desired *tert.*-amine within 5 minutes (**Table 5.1**, **entry 10**). In addition, tetrahydrofuran, 2-methyltetrahydrofuran (2-MeTHF) as well as dichloroethane also showed comparable efficiency to that of dichloromethane (**Table 5.1**,

entries 6, 7 and **11**) while toluene and acetonitrile were found to be inefficient media (**Table 5.1**, **entries 8** and **9**).

After identifying dichloromethane as a suitable solvent, the optimization was further continued by examining the deoxygenation process with electron rich and electron deficient arylboronic acids as well as alkylboronic acids as reducing agent (**Table 5.2**, **entries 1-4**). 4-Methoxyphenylboronic acid showed equal efficiency to that of simple phenylboronic acid while 4-nitrophenylboronic acid took slightly longer time for completion of the reaction (**Table 5.2**, **entries 1** and **2**). On the other hand, alkylboronic acids such as methyl and *n*-butylboronic acid showed less efficiency than arylboronic acids in the deoxygenation process, perhaps due to migratory aptitude of alkyl groups [17] (**Table 5.2**, **entries 3** and **4**).

Table 5.2. Optimization of reaction condition with different boronicacids.[a,b]

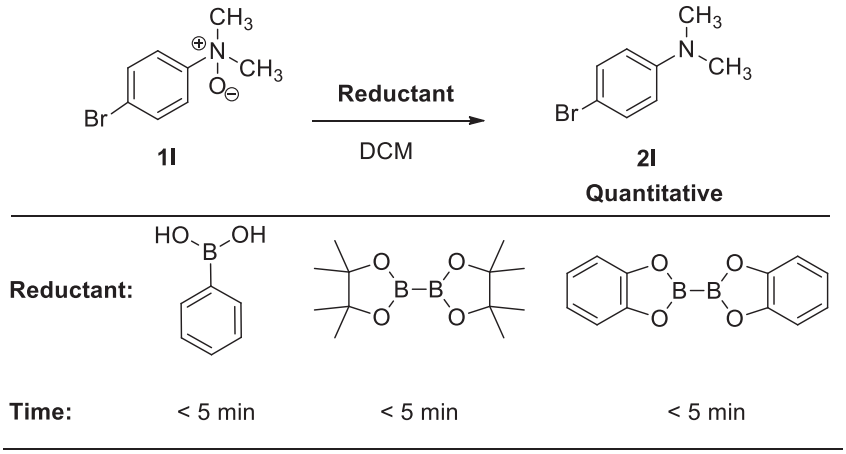


1l **2l**

S.No.	Boronic acids	Time (mins)	Yield (%)[b]
1	4-Methoxyphenylboronic acid	5	95
2	4-Nitrophenylboronic acid	60	94
3	Methylboronic acid	60	40
4	n-Butylboronic acid	60	43

[a]**Reaction condition:** aniline *N*-oxide (1 mmol) and boronic acid (1 mmol) stirred in DCM at room temperature. [b]Isolated yield.

It is important to mention here that recently diboron compounds such as bis(pinacolato)diboron [$(pinB)_2$], bis(catecholato)diboron [$(catB)_2$] and tetrahydroxydiboron have been explored as deoxygenating reagents for the amine *N*-oxides [14]. Despite the efficiency of diboron compounds, their high cost and limited availability reduce their use in organic synthesis [15a, 18]. Moreover, in the case of diboron reagents two boron atoms are required to deoxygenate one oxygen atom, while only one boron atom is utilized in the case of phenylboronic acid. Nevertheless, being an economical reagent, phenylboronic acid showed a comparable efficiency to that of diboron compounds in the deoxygenation process. For example, the deoxygenation of *N*-oxide **1l** was achieved in a quantitative yield within 5 minutes using diboron compounds as well as phenylboronic acid (**Scheme 5.2**) in dichloromethane at room temperature.



Scheme 5.2. Deoxygenation of 4-bromo-*N,N*-dimethylaniline *N*-oxide with diboroncompounds.

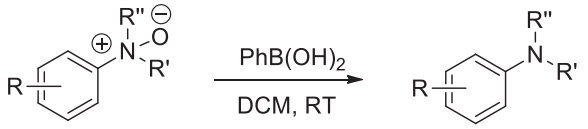
Overall, phenylboronic acid was found to be superior among the different boronic acids used in this study in terms of not only higher reactivity but also availability and cost effectiveness. Moreover, phenylboronic acid produces environmentally benign byproducts such as boric acid and phenol during the deoxygenation process which can be easily removed by simple basic workup procedures.

5.2.2 Substrates scope

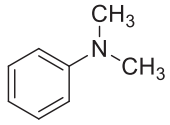
With optimized conditions in hand, the deoxygenation of various aniline *N*-oxides was studied with phenylboronic acid at room temperature (**Table 5.3**). Unsubstituted *N*,*N*-dialkylaniline *N*-oxides as well as naphthylamine *N*-oxides have been successfully reduced to corresponding amines in excellent yields within 10 mins (**Table 5.3**, **entries 2b**-**2e**).

Similarly, electron donating (e.g.methoxy and methyl) and withdrawing groups (e.g. chlorine, bromine and nitro) functionalized aniline *N*-oxides underwent deoxygenation smoothly to provide the desired products in high yield (*i.e.***> 90%**) at room temperature (**Table 5.3**, **entries 2f**-**2n**). In fact, no significant electronic effects were observed in the deoxygenation process with respect to different substituents present on the aryl ring. Moreover, sterically hindered (*i.e. ortho*- substituted) dialkylaniline *N*-oxides as well as *N*-benzyl and *N*-phenyl aniline *N*-oxides also underwent deoxygenation with same efficiency like simple aniline *N*-oxides (**Table 5.3**, **entries 2g**, **2h, 2j** and **2o**-**2r**).

Table 5.3. Deoxygenation of *N*,*N*-dialkylaniline *N*-oxides using phenylboronicacid.[a,b]

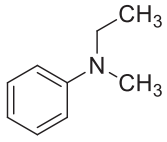


1a-s **2a-s**



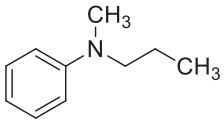
2a

(5 mins, **98%**)



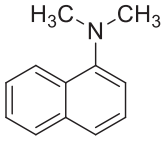
2b

(5 mins, **98%**)



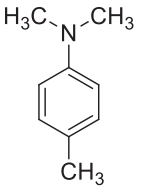
2c

(5 mins, **95%**)



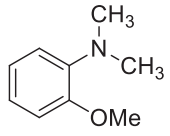
2d

(10 mins, **96%**)



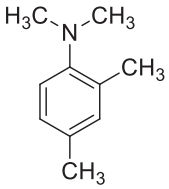
2e

(10 mins, **98%**)



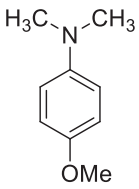
2f

(20 mins, **93%**)



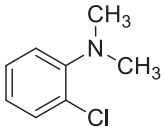
2g

(20 mins, **92%**)



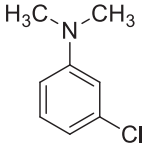
2h

(10 mins, **95%**)



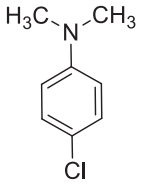
2i

(20 mins, **97%**)



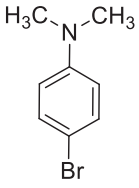
2j

(10 mins, **97%**)



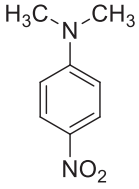
2k

(5 mins, **96%**)



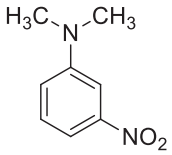
2l

(5 mins, **95%**)



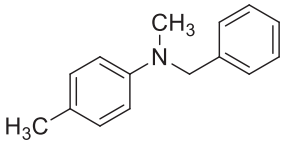
2m

(15 mins, **96%**)



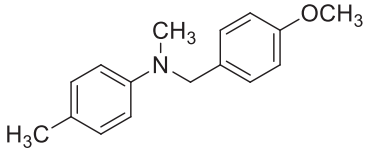
2n

(15 mins, **97%**)



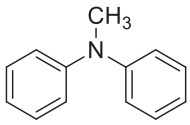
2o

(30 mins, **92%**)



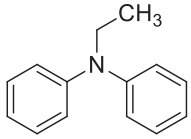
2p

(30 mins, **91%**)



2q

(20 mins, **93%**)



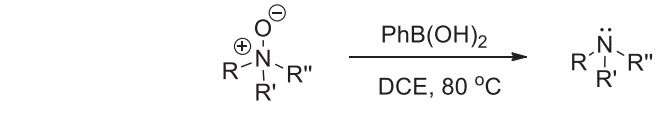
2r

(30 mins, **97%**)

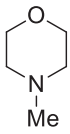
[a]**Reaction condition:** aniline *N*-oxide (1 mmol) and phenylboronic acid (1 mmol) was stirred in dichloromethane at room temperature. [b]Isolated yield.

Having successful results in hand, we have further examined the reduction of trialkylic (cyclic and acyclic) and benzylic *N*-oxides under optimized condition (**Table 5.4**). Initially, the deoxygenation of *N*-methylmorpholine*N*-oxide was performed with 1.0 equivalent of phenylboronic acid at room temperature. However, the reaction was found to be slow and the desired product was obtained only in 65% yield after 12 h (**Table 5.4**, **entry 4a**). Thus, the reaction was performed at 80 °C in 1,2-dichloroethane (DCE) using one equivalent of phenylboronic acid.

Table 5.4. Deoxygenation of trialkyl and benzylamine *N*-oxides with phenylboronicacid.[a,b]

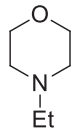


3a-g **4a-g**



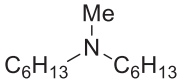
4a

(12 h, **65%**)[c]
(30 mins, **93%**)



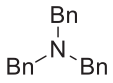
4b

(30 mins, **92%**)



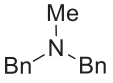
4c

(45 mins, **90%**)



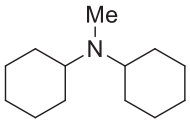
4d

(90 mins, **85%**)



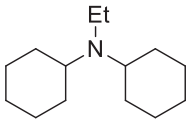
4e

(90 mins, **82%**)



4f

(15 mins, **95%**)



4g

(25 mins, **95%**)

[a]**Reaction condition:** trialkyl*N*-oxide (1 mmol) and phenylboronic acid (1 mmol) was stirred in dichloroethane at 80 °C. [b]Isolated yield. [c]Reaction was carried out at room temperature.

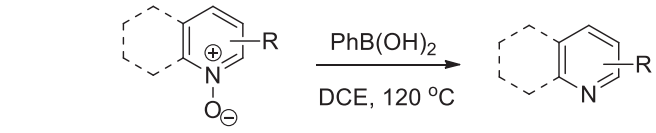
It is interesting to note that the deoxygenation of *N*-methylmorpholine *N*-oxide proceeded efficiently and gave the desired product (i.e. *N*-methylmorpholine) in 93% yield

within 30 minutes (**Table 5.4**, **entry 4a**). In addition, various cyclic, acyclic and benzylic *N*-oxides were also successfully converted to corresponding amines in excellent yields (**Table 5.4**, **entries 4b-4g**).

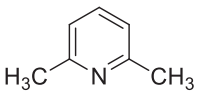
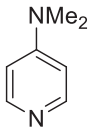
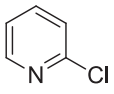
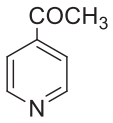
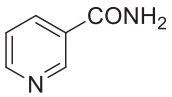
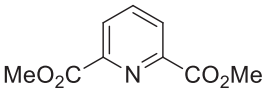
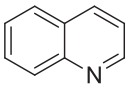
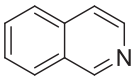
The deoxygenation of heteroaromatic *N*-oxides (e.g. pyridine *N*-oxide) has found wide scope in synthetic organic chemistry [3]. Being successful in the case of deoxygenation of aniline and alkyl *N*-oxides, we have attempted the deoxygenation of pyridine and quinoline *N*-oxides with phenylboronic acid (**Table 5.5**). The reaction provided the desired products in good to excellent yields with 1.5 equivalents of phenylboronic acid, however at high temperature (*i.e.*120 °C). Pyridine *N*-oxides are very stable because oxygen is attached with sp2-nitrogen center i.e. resonance stabilized. Pyridine *N*-oxides with electron donating groups such as 2,6-dimethyl and 4-(*N*,*N*-dimethylamino)pyridine *N*-oxides underwent smooth conversion with good yield in a short span of time (**Table 5.5**, **entries 6a** and **6b**). On the other hand, electron deficient pyridine *N*-oxides such as 2-chloro, 4-acetyl, 3-amido and 2,6-dimethyl esters functionalized pyridine *N*-oxides took slightly longer reaction time and gave the desired products in moderate yields (**Table 5.5**, **entries 6c**-**6f**). In addition, similar to pyridine *N*-oxides, quinoline and *iso*-quinoline *N*-oxides underwent deoxygenation in 70-80% yields (**Table 5.5**, **entries 6g** and **6h**). The stability of different functional groups under standard reaction conditions plays a major role in organic synthesis. It is noteworthy that many reduction susceptible functional groupssuch as ketone, amide, esters and nitro groups are well tolerated with phenylboronic acid during the deoxygenation even at high temperature

(**Table 5.3** and **5.5**). Thus, phenylboronicacid can be regarded as a chemoselective reducing agent.

Table 5.5. Deoxygenation of heteroaromatic*N*-oxides with phenylboronicacid.[a,b]



5a-h **6a-h**

			
6a	**6b**	**6c**	**6d**
(6 h, **75%**)	(10 h, **90%**)	(24 h, **61%**)	(12 h, **65%**)
			
6e	**6f**	**6g**	**6h**
(16 h, **62%**)	(18 h, **60%**)	(8 h, **80%**)	(18 h, **70%**)

[a]**Reaction condition:** *N*-oxide (1 mmol) and phenylboronic acid (1.5 mmol) was stirred in dichloroethane at 120 °C.[b]Isolated yield.

Amine functionalities were found in many drug molecules and play an important role in exerting their biological activity [19]. Drug metabolism is one of the essential biological process that limits the life time of a drug in the body [19]. In drug discovery process, drug metabolism plays a major role which determines the advantages and shortcomings of the prospective drugs [20]. Similarly, it is well known that in Phase I metabolism, drugs undergo different chemical modifications like oxidation, reduction or hydrolysis to make more water soluble compounds that can be excreted by various

processes [20]. In this context, *N*-oxides have been observed as one of the major metabolites of *tert.*-amine drugs [2b]. For example, Clozapine *N*-oxide is a major metabolite of antidepressant drug Clozapine [21] which is used in the treatment of schizophrenia and bipolar disorders (**Figure 5.3**) [22].The identification and quantification of *N*-oxide metabolites can play an important role in developing newer drugs with high potential and low toxicity [20].

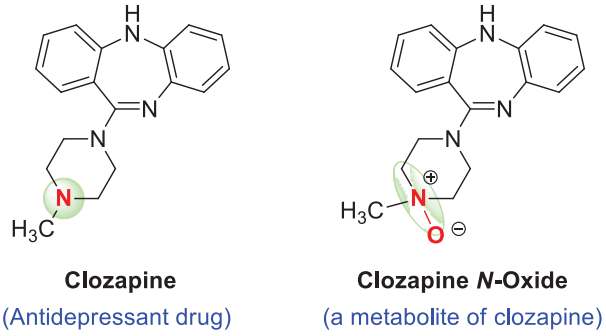


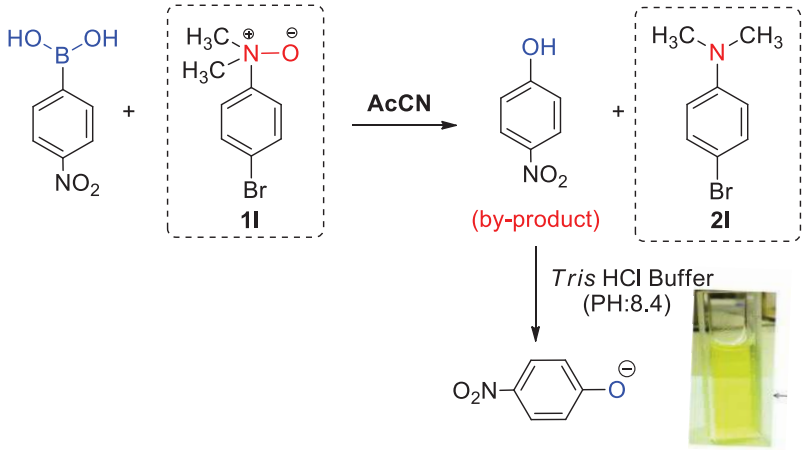
Figure 5.3 Structures of antidepressant drug Clozapine and its metabolite Clozapine *N*-oxide.

5.3 DETECTION OF *TERTIARY* AMINE *N*-OXIDES USING UV-VIS SPECTROMETRY

Recently, Kulanthaivel *et al.* have demonstrated a chemical deoxygenation method suitable for drug metabolism studies [11c]. Titanium trichloride ($TiCl_3$) has been employed as a selective deoxygenating reagent of amine *N*-oxide metabolites while there action progress and analysis were performed using liquid chromatography-mass spectrometry (LC-MS) [11c]. Nevertheless, it will be interesting to find an inexpensive method that requires simple instrumentation for a quick identification and quantification of amine *N*-oxides. In this context, we anticipated that a simple indirect method for the detection of

tert.-amine *N*-oxides is possible in UV-Vis spectrometry by using 4-nitrophenylboronic acid as a deoxygenating reagent. Because, 4-nitrophenylboronic acid will produce 4-nitrophenol as a byproduct during the deoxygenation of *N*-oxides and it is detectable even as a trace amount at 400 nm in UV-Vis spectrometer [22,23]. Based on the concentration of 4-nitrophenol, *tert.*-amine concentration can be easily calculated using *Beer-Lambert's* law which will provide a significant information regarding the concentration ofamine *N*-oxide. Moreover, other metabolites like sulfoxides and *C*-hydroxylation products can be easily distinguished from *N*-oxides since they are un-reactive with arylboronic acids.

As a case study, the deoxygenation of 4-bromo-*N,N*-dimethyl aniline *N*-oxide (**1l**) with 4-nitrophenylboronic acid was carried out in acetonitrile at room temperature (**Scheme 5.3**) [24].



Scheme 5.3. Deoxygenation of 4-bromo-*N,N*-dimethylaniline *N*-oxide (**1l**) with4-nitrophenylboronic acid.

The progress of the reaction was monitored by using UV-Vis spectrometry in every 15 minutes and observed spectra are summarized in Figure **5.4**. The spectrum clearly

shows an increase in absorption intensity at 400 nm in *Tris*-HCl buffer solution, which corresponds to the formation of 4-nitrophenol (Figure **5.4**). The rate of the reaction was calculated from absorbance *vs* time plot and found to be 1.41×10^{-4} s^{-1} (Figure **5.4 b**).The amount of p-nitrophenol (*p*-NP) formation can be directly correlated with the amount of formation of *tert.*-amine from corresponding *N*-oxide (detailed calculation is mentioned in supporting information).

Similarly, UV-Vis spectrometry studies were performed with *N,N*-dimethylaniline *N*-oxide (**1a**) with 4-nitrophenylboronic acid in acetonitrile (**Scheme 5.4**) and rate of reaction was calculated by *Lambert-Beer's* Law (Figure **5.5**).

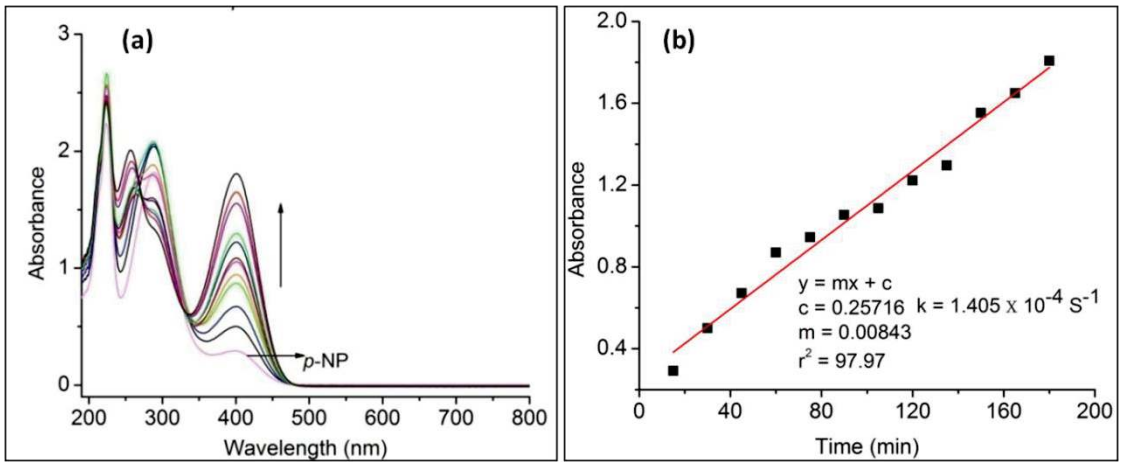
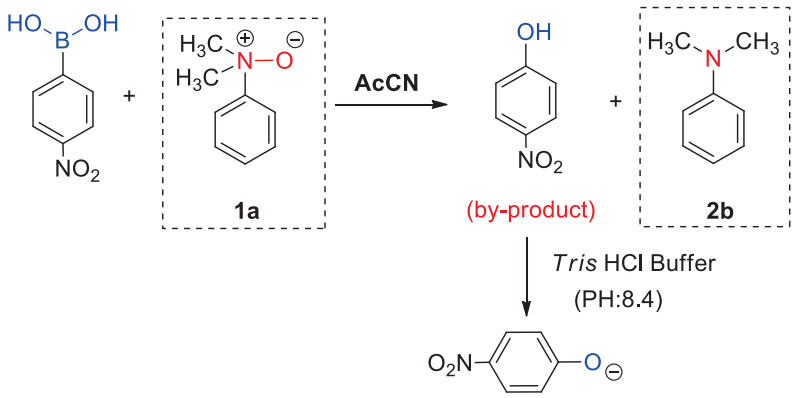


Figure5.4 (a) Spectral profile showing the increase of *p*-NP band at 400 nm with respect to time. The reaction was carried out with 4-bromo-*N,N*-dimethylaniline *N*-oxide and 4-nitrophenylboronic acid in acetonitrile and spectra were measured in *tris*-HCl buffer solution with 15 min interval. (b) Plot of absorbance *vs* time.



Scheme 5.4. Deoxygenation of *N,N*-dimethylaniline *N*-oxide (**1a**) with 4-nitrophenylboronic acid in acetonitrile.

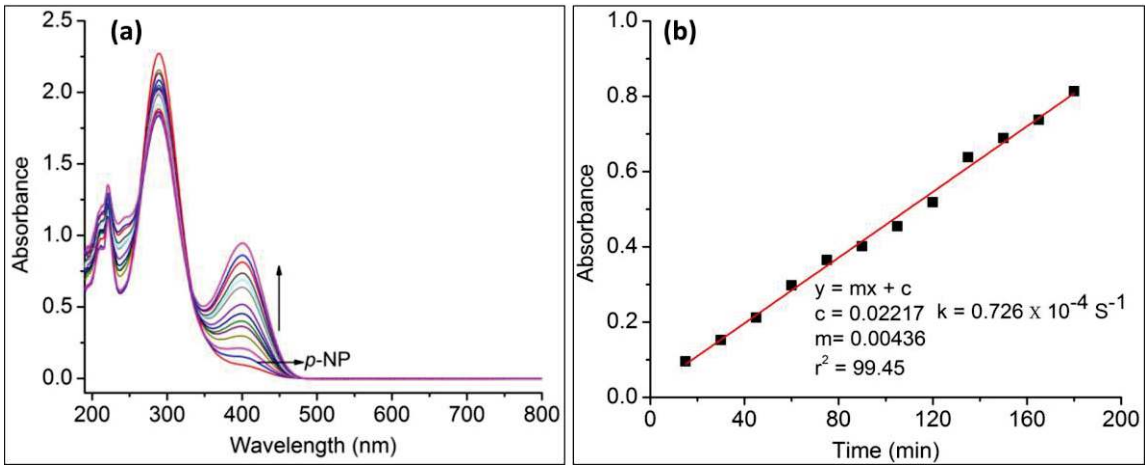
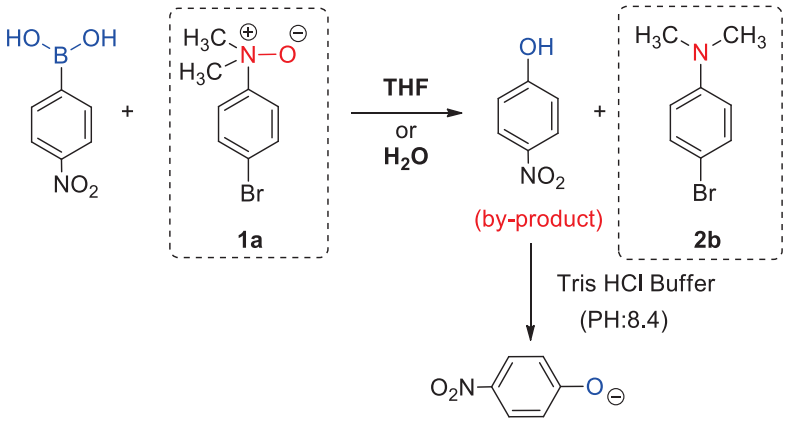


Figure 5.5 (a) Spectral profile showing the increase of *p*-NP band at 400 nm with respect to time. The reaction was carried out with *N,N*-dimethylaniline *N*-oxide and 4-nitrophenylboronic acid in acetonitrile and spectra were measured in *tris*-HCl buffer solution with 15 min interval. (b) Plot of absorbance *vs* time.

UV-Vis spectrometry study was further continued in THF and water to check role of solvent on the rate of reaction (**Scheme 5.5**). Deoxygenation of 4-bromo-*N,N*-dimethylaniline *N*-oxide in water required 70 °C to carry out reaction in UV-Vis spectroscopy. The rate of reaction was observed better in acetonitrile solvent in comparison

to others. The spectra of reactions carried out in THF (Figure **5.6**) and in water (Figure **5.7**) wereshown below.



Scheme 5.5. Deoxygenation of 4-bromo-*N,N*-dimethylaniline *N*-oxide (**1l**) with 4-nitrophenylboronic acid in THF or water.

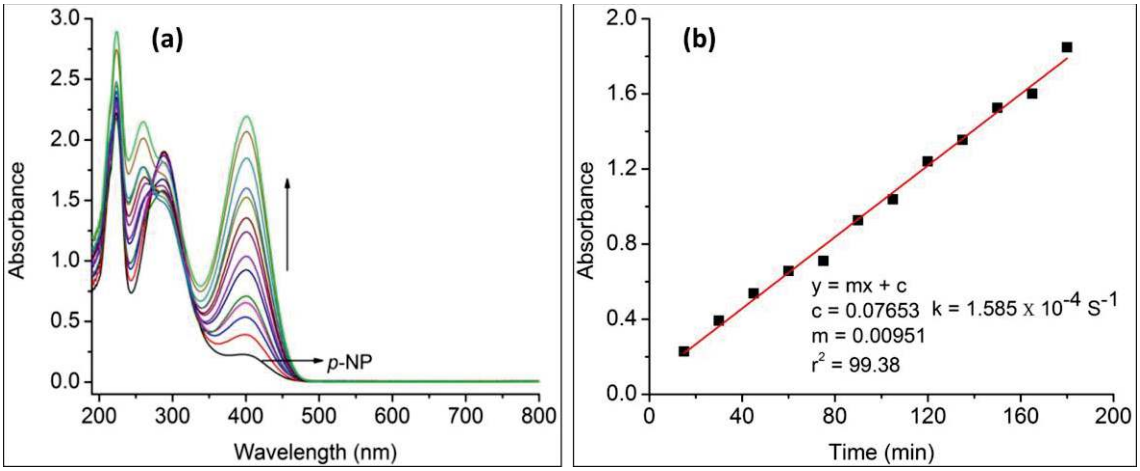


Figure 5.6 (a) Spectral profile showing the increase of *p*-NP band at 400 nm with respect to time. The reaction was carried out with 4-bromo-*N,N*-dimethylaniline *N*-oxide and 4-nitrophenylboronic acid in THF and spectra were measured in *tris*-HCl buffer solution with 15 min interval. (b) Plot of absorbance *vs* time.

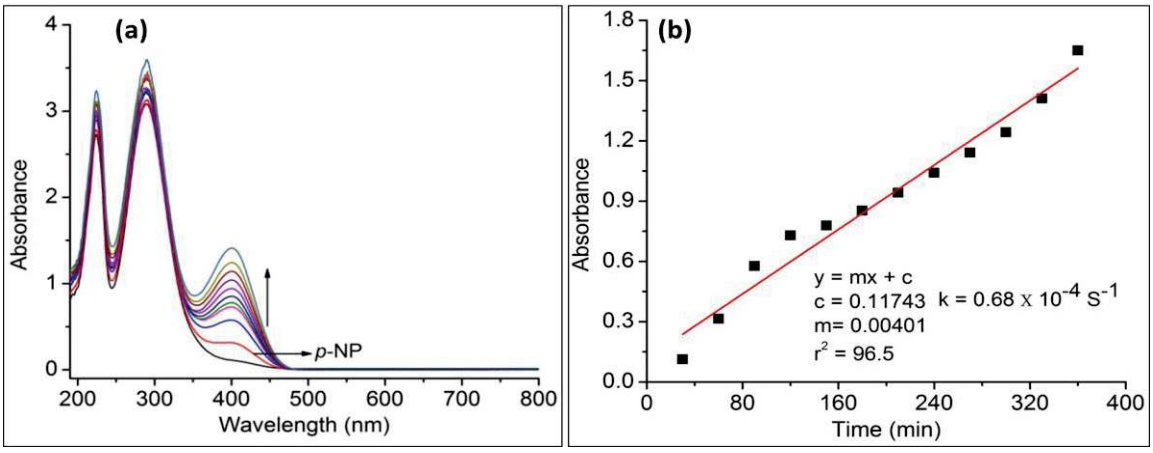


Figure 5.7(a) Spectral profile showing the increase of *p*-NP band at 400 nm with respect to time. The reaction was carried out with 4-bromo-*N,N*-dimethylaniline *N*-oxide and 4-nitrophenylboronic acid in H_2O at 70 °C and spectra were measured in *tris*-HCl buffer solution with 30 min interval. (b) Plot of absorbance *vs* time.

It can be seen from **Table 5.6** that isolated yield of *tert.*-amine approximately matches with the calculated yield of *tert.*-amine from UV experiment. For example, after 60 minutes the isolated yield was about 34% while the calculated UV yield was 39% (**Table 5.6, entry 1**). Similarly, the yields obtained in various intervals, for example, after two hours and three hours (in both isolated as well as UV-Vis experiment) were found to be similar (**Table 5.6**, **entries 2** and **3**), which confirms our preliminary assumption.

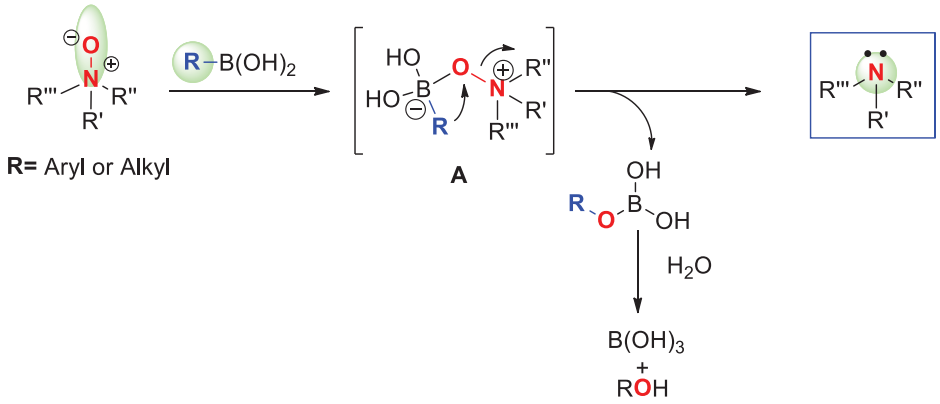
Table 5.6. Yield comparison between isolated and calculated values from UV for the deoxygenation reaction of 4-bromo-*N,N*-dimethylaniline *N*-oxide (**1l**) with 4-nitrophenylboronic acid.[a,b]

Entry	Time	UV yield (%)[a]	Isolated yield (%)[b]
1	1 h	39	34
2	2 h	54	46
3	3 h	81	70

[a]Yield was calculated using *Beer-Lambert's* law (A=Ɛcl) (Refer supporting information). [b]Yield from batch reaction in 1.0 mmol scale.

5.4 PLAUSIBLE REACTION MECHANISM

A plausible mechanism for the deoxygenation of amine *N*-oxide is shown in **Scheme 5.6**. At first, *N*-oxide attacks the electrophilic aryl/alkylboronic acid and forms an unstable *Amino-Borate complex*(**A**) [15a]. Further, the aryl/alkyl group migrates from boron to *N*-oxide oxygen which results in formation of *tert.*-amine and borate ester. The unstable borate ester further undergoes degradation to boric acid and alcohol in the presence of water.



Scheme 5.6. Plausible mechanism for the deoxygenation of amine *N*-oxides to corresponding amines.

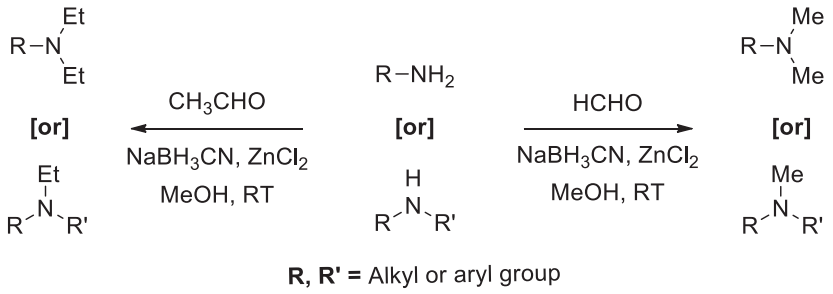
5.5CONCLUSION

In conclusion, we have demonstrated a simple and efficient method for the deoxygenation of amine *N*-oxides to corresponding amines using the green and economical reagent phenylboronic acid. The *N*,*N*-dialkylaniline *N*-oxides, trialkylamine *N*-oxides and pyridine *N*-oxides underwent deoxygenation smoothly to provide the desired amines in good to excellent yields. The reduction susceptible functional groups such as ketone,

amide, ester, nitro and arylhalides are well tolerated with phenylboronic acid during the deoxygenation process even at high temperature. An indirect method for identification and quantification of *tert*-amine *N*-oxide in UV-Vis spectrometry is demonstrated by using 4-nitrophenylboronic acid as a deoxygenating reagent. We believe that this technique will be useful for drug metabolism studies.

5.6 EXPERIMENTAL SECTION

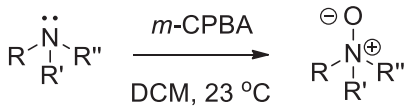
5.6.1 Experimental procedure for the preparation of *tertiary* amines



R, R' = Alkyl or aryl group

Amine (1.0 g) and respective aldehyde (8.0 equiv.) was stirred in methanol (15 mL) to which pre-prepared methanol (5 mL) solution of sodium cyanoborohydride (1.0 equiv.) and zinc chloride (0.5 equiv.) was added at room temperature. The resulted reaction mixture was stirred for overnight at room temperature and basified with 0.1 N NaOH (20 mL). Methanol was evaporated and aqueous layer was extracted with ethylacetate (3×50 mL). The combined organic layer was washed with water and brine, dried over anhydrous sodium sulfate. Further, the organic layer was evaporated to dryness and subjected for silica gel column chromatography using ethyl acetate:hexane mixture as an eluent. Yield of *tert.*-amines were approx. 80-90%.

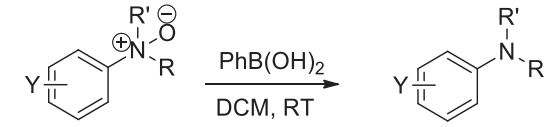
5.6.2 Experimental procedure for the preparation of amine *N*-oxides



To a stirred solution of *tert.*-amines in dichloromethane (10 ml), *m*-chloroperbenzoic acid (70% w/w, 1.5 equiv) was added portion wise at room temperature. The resultant solution was stirred for 4 h and the progress of reaction was monitored using TLC. After completion, the reaction mixture was directlyloaded on basic alumina column chromatography and purified using methanol:chloroform solvent mixture as an eluent. The combined filtrates were concentrated to give corresponding amine *N*-oxides with approx. 90-95% isolated yield.

5.6.3 Experimental procedure for deoxygenation of amine *N*-oxides

a) Deoxygenation of aromatic amine *N*-oxides

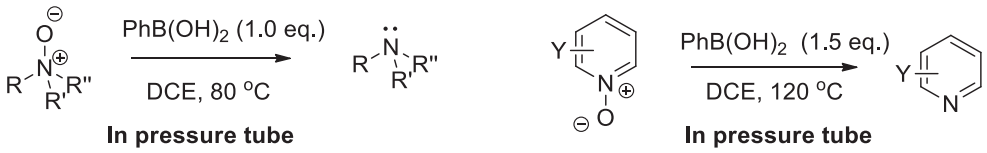


R= Ph, Me and Et
R'= Me or Et

Phenylboronic acid (1 mmol) was added to a stirred solution of *tert.*-amine *N*-oxide (1 mmol) in dichloromethane (3 mL) at room temperature. After completion, the reaction mixture was diluted with ethyl acetate (25 mL) and washed with NaOH solution (1 N, 3×5 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated to dryness to obtain *tert.*-amines which is pure enough. On the other hand, the crude compound was

subjected to column chromatography (silica gel using ethyl acetate/hexane) to obtain the products in high purity.

b) Deoxygenation of aliphatic and hetero-aromatic amine *N*-oxides

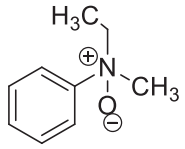


Phenylboronic acid (1.0 equiv. for aliphatic *N*-oxides and 1.5 equiv. for pyridine *N*-oxides) and *tert.*-amine *N*-oxide (1 mmol) was stirred in dichloroethane (2 mL) at appropriate temperature (80 °C and 120 °C respectively) in a pressure tube. The progress of the reaction was monitored by using TLC. After completion, the reaction mixture was diluted with ethylacetate and washed with water and NaOH solution (1 normal, 3×5 mL). The organic layer was dried over anhydrous sodium sulfate, evaporated and subjected to the column chromatography to obtain pure products.

5.7 ANALYTICAL DATA FOR THE *N*-OXIDES

N-Oxides of **1a**, **1c**, **1d**, **1e**, **1h,1k, 1l**, **1m**, **1o**, **1p**, **3a**, **3d**, **3e**, **3f**, **3g**, **5a**, **5b**, **5c**, **5d**, **5e**, **5f**, **5g** & **5f** are already found in the literature, whereas *N*-oxides of **1b**, **1f**, **1g**, **1i**, **1j**, **1n**, **1q**, **1r**, **3b** and **3c** are given below.

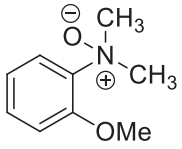
5.7.1 *N*-Ethyl-*N*-methylaniline *N*-oxide (1b):



1b

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 3.70 (m, 2H), 3.54 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.94, 129.24, 128.93, 121.06, 68.30, 61.71, 8.99. **HRMS:** Calc. for $C_9H_{14}NO$ $[M+H]^+$: 152.1075, Obser. 152.1064.

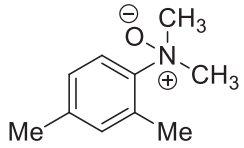
5.7.2 2-Methoxy-*N*,*N*-dimethylaniline *N*-oxide (1f):



1f

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.39 (td, *J* = 8.0, 1.7 Hz, 1H), 7.15–7.07 (m, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H), 3.66 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.34, 142.35, 130.78, 124.39, 121.62, 111.93, 61.11, 55.94. **HRMS:** Calc. for $C_9H_{14}NO_2$ $[M+H]^+$: 168.1024, Obser. 168.1019.

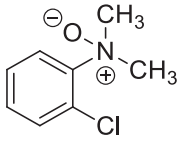
5.7.3 *N*,*N*,2,4-Tetramethylaniline *N*-oxide (1g):



1g

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.10–7.03 (m, 2H), 3.64 (s, 6H), 2.75 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.28, 139.11, 134.87, 129.63, 127.61, 120.88, 61.89, 22.40, 20.69. **HRMS:** Calc. for $C_{10}H_{16}NO$ $[M+H]^+$: 166.1232, Obser. 166.1225

5.7.4 2-Chloro-*N*,*N*-dimethylaniline *N*-oxide (1i):

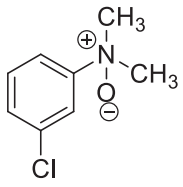


1i

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (d, *J* = 8.3 Hz, 1H), 7.51–7.35 (m, 3H), 3.80 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.75, 131.78,

130.96, 128.67, 125.55, 124.32, 60.89. **HRMS:** Calc. for $C_8H_{11}ClNO$ $[M+H]^+$:172.0529, Obser. 172.0523.

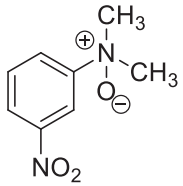
5.7.5 3-Chloro-*N*,*N*-dimethylaniline *N*-oxide (1j):



1j

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.81 (dt, *J* = 7.2, 2.1 Hz, 1H), 7.44–7.38 (m, 2H), 3.59 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.73, 135.32, 130.30, 129.46, 121.27, 118.27, 63.60. **HRMS:** Calc. for $C_8H_{11}ClNO$ $[M+H]^+$:172.0529, Obser. 172.0525.

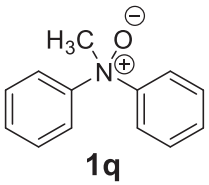
5.7.6 *N*,*N*-Dimethyl-3-nitroaniline *N*-oxide (1n):



1n

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (m, 1H), 8.53 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.32 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.73 (t, *J* = 8.2 Hz, 1H), 3.67 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.11, 148.46, 130.63, 126.77, 124.29, 116.06, 63.88. **HRMS:** Calc. for $C_8H_{11}N_2O_3$ $[M+H]^+$: 183.0769, Obser. 183.0762.

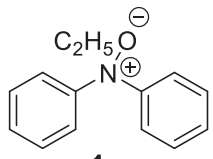
5.7.7 *N*-Methyl-*N*-phenylaniline *N*-oxide (1q):



1q

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 4H), 7.48–7.23 (m, 6H), 3.94 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.68, 129.18, 128.75, 121.24, 62.24. **HRMS:** Calc. for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1075, Obser. 200.1071.

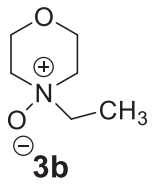
5.7.8 *N*-Ethyl-*N*-phenylaniline *N*-oxide (1r):



1r

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 4H), 7.39–7.24 (m, 6H), 4.14 (q, *J* = 6.9 Hz, 2H), 1.27 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.07, 128.93, 128.42, 121.83, 65.90, 9.05. **HRMS:** Calc. for $C_{14}H_{16}NO$ $[M+H]^+$: 214.1232, Obser. 214.1227.

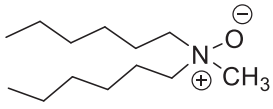
5.7.9 4-Ethylmorpholine *N*-oxide (3b):



3b

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 (m, 2H), 3.78 (m, 2H), 3.34–3.21 (m, 2H), 3.08 (d, *J* = 5.7 Hz, 4H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 67.01, 63.87, 61.82, 7.42. **HRMS:** Calc. for $C_6H_{14}NO_2$ $[M+H]^+$: 132.1024, Obser. 132.1021.

5.7.10 *N*-Hexyl-*N*-methylhexan-1-amine *N*-oxide (3c):

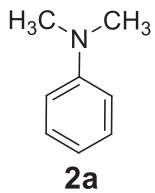


3c

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.17 (m, 4H), 3.07 (s, 3H), 1.80 (d, *J* = 6.6 Hz, 4H), 1.33 (m, 12H), 0.90 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 69.25, 55.98, 31.67, 26.63, 23.72, 22.64, 14.11. **HRMS:** Calc. for $C_{13}H_{30}NO$ $[M+H]^+$: 216.2327, Obser. 216.2320.

5.8 ANALYTICAL DATA FOR THE PRODUCTS

5.8.1 *N,N*-Dimethylaniline (2a)

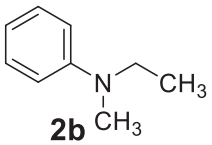


2a

(Yield= 118 mg, 98%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.21 (m, 2H), 6.73 (m, 3H), 2.94 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.87, 129.27, 116.84, 112.87,

40.84. **HRMS:** Calc. for $C_8H_{11}N$ $[M+H]^+$: 122.0970, Obser. 122.0967

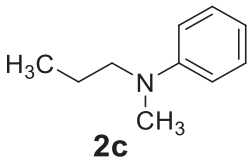
5.8.2 *N*-Ethyl-*N*-methylaniline (2b)



2b

(Yield= 132 mg, 98%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (m,2H), 6.72–6.66 (m, 3H), 3.39 (q, *J* = 7.1 Hz, 2H), 2.89 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.33, 129.35, 116.23, 112.60, 47.00, 37.62, 11.39. **HRMS:** Calc. for $C_9H_{14}N$ $[M+H]^+$: 136.1126, Obser. 136.1117.

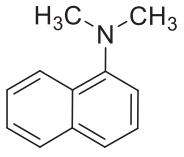
5.8.3 *N*-Methyl-*N*-propylaniline (2c)



2c

(Yield= 141 mg, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.9 Hz, 2H), 6.67 (m, 3H), 3.26 (t, *J* = 7.5 Hz, 2H), 2.92 (s, 3H), 1.60 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.60, 129.32, 115.98, 112.25, 54.75, 38.52, 20.13, 11.72. **HRMS:** Calc. for $C_9H_{16}N$ $[M+H]^+$: 150.1283, Obser. 150.1276.

5.8.4 *N,N*-Dimethylnaphthalen-1-amine (2d)

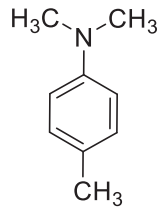


2d

(Yield= 164 mg, 96%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.53–7.35 (m, 4H), 7.06 (d, *J* = 7.3 Hz, 1H), 2.89 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.06 , 135.01, 129.00,

128.53, 125.96, 125.89, 125.32, 124.33, 123.07, 114.10, 45.42. **HRMS:** Calc. for $C_{12}H_{14}N$ $[M+H]^+$: 172.1126, Obser. 172.1114.

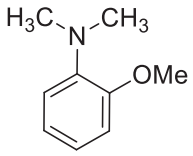
5.8.5 *N,N*,4-Trimethylaniline (2e)



2e

(Yield= 132 mg, 98%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.6 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 2H), 2.89 (s, 6H), 2.25 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.06, 129.78, 126.30, 113.43, 41.26, 20.44. **HRMS:** Calc. for $C_9H_{14}N$ $[M+H]^+$: 136.1126, Obser. 136.1120.

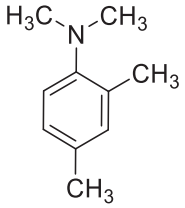
5.8.6 2-Methoxy-*N,N*-dimethylaniline (2f)



2f

(Yield= 140 mg, 93%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00–6.95 (m, 2H), 6.91–6.89 (m, 1H), 6.86 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.88 (s, 3H), 2.79 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.60, 142.63, 122.67, 120.96, 118.36, 111.11, 55.47, 43.56. **HRMS:** Calc. for $C_9H_{14}NO$ $[M+H]^+$: 152.1075, Obser. 152.1069.

5.8.7 *N,N*,2,4-Tetramethylaniline (2g)

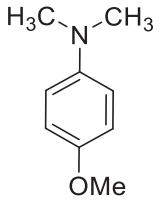


2g

(Yield= 137 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, *J* = 6.2 Hz, 1H), 6.94 (t, *J* = 5.9 Hz, 2H), 2.66 (s, 6H), 2.29 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.51, 132.31, 132.21, 132.09, 127.09, 118.53,

44.69, 20.83, 18.35. **HRMS:** Calc. for $C_{10}H_{16}N$ $[M+H]^+$: 150.1283, Obser. 150.1274.

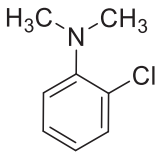
5.8.8 4-Methoxy-*N*,*N*-dimethylaniline (2h)



2h

(Yield= 141 mg, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 2.86 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.22, 145.95, 115.15, 114.83, 55.96, 42.06. **HRMS:** Calc. for $C_9H_{14}NO$ $[M+H]^+$: 152.1075, Obser. 152.1064.

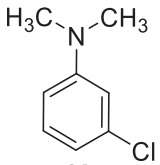
5.10.9 2-Chloro-*N*,*N*-dimethylaniline (2i)



2i

(Yield= 150 mg, 97%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 2.81 (s, 6H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.65, 130.89, 128.47, 127.63, 123.42, 120.22, 44.01. **HRMS:** Calc. for $C_8H_{11}ClN$ $[M+H]^+$: 156.0580, Obser. 156.0566.

5.8.10 3-Chloro-*N*,*N*-dimethylaniline (2j)

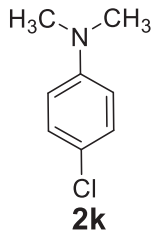


2j

(Yield= 150 mg, 97%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.4 Hz, 1H), 6.67 (d, *J* = 6.3 Hz, 2H), 6.59–6.57 (m, 1H), 2.94 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.70, 135.18, 130.18, 116.37, 112.40, 110.67, 40.58. **HRMS:** Calc. for $C_8H_{11}ClN$ $[M+H]^+$: 156.0580, Obser.

156.0575.

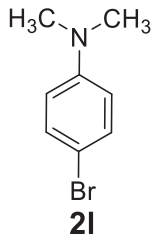
5.8.11 4-Chloro-*N*,*N*-dimethylaniline (2k)



2k

(Yield= 148 mg, 96%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 2.90 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.36, 128.97, 121.56, 113.81, 40.82. **HRMS:** Calc. for $C_8H_{11}ClN$ $[M+H]^+$: 156.0580, Obser. 156.0568.

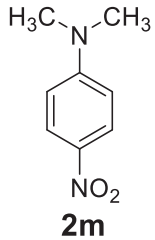
5.8.12 4-Bromo-*N*,*N*-dimethylaniline (2l)



2l

(Yield= 194 mg, 97%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 7.9 Hz, 2H), 2.91 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.72, 131.88, 114.31, 108.71, 40.76. **HRMS:** Calc. for $C_8H_{11}BrN$ $[M+H]^+$: 200.0075, Obser. 200.0067.

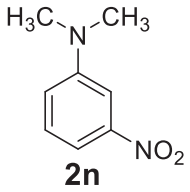
5.8.13 *N*,*N*-Dimethyl-4-nitroaniline (2m)



2m

(Yield= 159 mg, 96%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 3.11 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.41, 137.15, 126.31, 110.41, 40.45. **HRMS:** Calc. for $C_8H_{11}N_2O_2$ $[M+H]^+$: 167.0821, Obser. 167.0815.

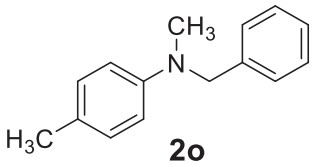
5.8.14 *N*,*N*-Dimethyl-3-nitroaniline (2n)



2n

(Yield= 161 mg, 97%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.33 (t, *J* = 8.2 Hz, 1H), 6.96 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.04 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.01, 129.75, 128.19, 117.82, 110.91, 106.37, 40.58. **HRMS:** Calc. for $C_8H_{11}N_2O_2$ $[M+H]^+$: 167.0821, Obser. 167.0814.

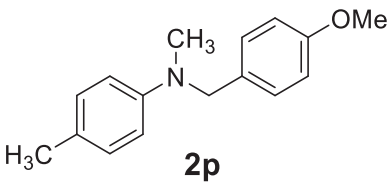
5.8.15 *N*-Benzyl-*N*,4-dimethylaniline (2o)



2o

(Yield= 194 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 6.7 Hz, 2H), 7.22 (d, *J* = 7.0 Hz, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H), 4.47 (s, 2H), 2.95 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.00, 139.44, 129.89, 128.70, 127.04, 126.98, 125.96, 112.91, 57.19, 38.81, 20.43. **HRMS:** Calc. for $C_{15}H_{18}N$ $[M+H]^+$: 212.1439, Obser. 212.1434.

5.8.16 *N*-(4-Methoxybenzyl)-*N*,4-dimethylaniline (2p)

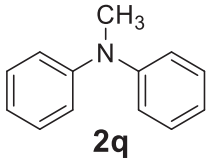


2p

(Yield= 193 mg, 91%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 4.41 (s, 2H), 3.78 (s, 3H), 2.92 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.75, 148.09, 131.32, 129.87, 128.29,

126.01, 114.09, 113.11, 56.65, 55.47, 38.64, 20.44.**HRMS:** Calc. for $C_{16}H_{20}NO$ $[M+H]^+$: 242.1545, Obser. 242.1546.

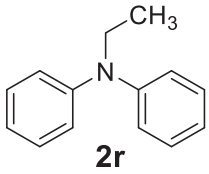
5.8.17 *N*-Methyl-*N*-phenylaniline (2q)



2q

(Yield= 170 mg, 93%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.02 (d, *J* = 7.7 Hz, 4H), 6.95 (t, *J* = 7.2 Hz, 2H), 3.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.23, 129.40, 121.50, 120.67, 40.46. **HRMS:** Calc. for $C_{13}H_{14}N$ $[M+H]^+$: 184.1126, Obser. 184.1124.

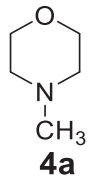
5.8.18 *N*-Ethyl-*N*-phenylaniline (2r)



2r

(Yield= 191 mg, 97%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 4H), 6.99 (d, *J* = 8.2 Hz, 4H), 6.93 (t, *J* = 7.3 Hz, 2H), 3.77 (q, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.93, 129.45, 121.28, 121.11, 46.60, 12.88. **HRMS:** Calc. for $C_{14}H_{16}N$ $[M+H]^+$: 198.1283, Obser. 198.1280.

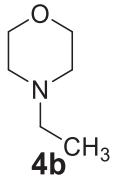
5.8.19 4-Methylmorpholine (4a)



4a

(Yield= 94 mg, 93%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.72 (t,*J* = 4 Hz, 4H), 2.41 (m, 4H), 2.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 67.08, 55.59, 46.61. **HRMS:** Calc. for $C_5H_{12}NO$ $[M+H]^+$: 102.0919, Obser. 102.0917.

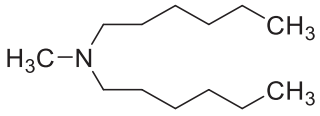
5.8.20 4-Ethylmorpholine (4b)



4b

(Yield= 105 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 (t, *J* = 4 Hz, 4H), 2.44–2.39 (m, 6H), 1.09 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 67.20, 53.56, 52.95, 11.88. **HRMS:** Calc. for $C_6H_{14}NO$ $[M+H]^+$: 116.1075, Obser. 116.1071.

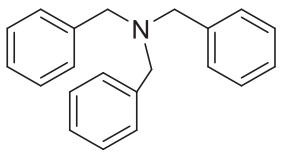
5.8.21 *N*-Hexyl-*N*-methylhexan-1-amine (4c)



4c

(Yield= 179 mg, 90%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31–2.28 (m, 4H), 2.20 (s, 3H), 1.45 (m, 4H), 1.28 (m, 12H), 0.88 (t, 6H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 58.20, 54.43, 42.60, 32.08, 27.54, 22.86, 14.27. **HRMS:** Calc. for $C_{13}H_{30}N$ $[M+H]^+$: 200.2378, Obser. 200.2378.

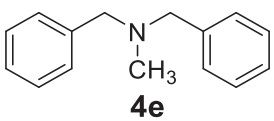
5.8.22 Tribenzylamine (4d)



4d

(Yield= 243 mg, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.4 Hz, 6H), 7.30 (t, *J* = 7.5 Hz, 6H), 7.21 (m, 3H), 3.55 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.85, 128.94, 128.42, 127.06, 58.13. **HRMS:** Calc. for $C_{12}H_{22}N$ $[M+H]^+$: 288.1752, Obser. 288.1750.

5.8.23 *N*-Benyl-*N*-methyl-1-phenylmethanamine (4e)

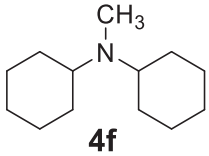


4e

(Yield= 173 mg, 82%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.29 (m, 8H), 7.24 (t, *J* = 7.2 Hz, 2H), 3.52 (s, 4H),

2.18 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.54, 129.13, 128.42, 127.12, 62.07, 42.45. **HRMS:** Calc. for $C_{15}H_{18}N$ $[M+H]^+$: 212.1439, Obser. 212.1433.

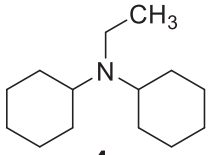
5.8.24 *N*-Cyclohexyl-*N*-methylcyclohexanamine (4f)



4f

(Yield= 182 mg, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.49 (m, 2H), 2.24 (m, 3H), 1.77 (m, 8H), 1.61 (m, 2H), 1.28-1.19 (m, 8H), 1.09 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 59.54, 33.06, 30.76, 26.53, 26.42. **HRMS:** Calc. for $C_{13}H_{26}N$ $[M+H]^+$: 196.2065, Obser. 196.2064.

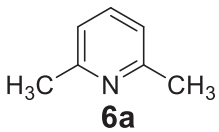
5.8.25 *N*-Cyclohexyl-*N*-ethylcyclohexanamine (4g)



4g

(Yield= 198 mg, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.57 (m, 4H), 1.74 (m, 8H), 1.60 (m, 2H), 1.22 (m, 10H), 1.00 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 58.32 , 40.53, 34.50, 31.70, 26.62, 25.54. **HRMS:** Calc. for $C_{14}H_{28}N$ $[M+H]^+$: 210.2222, Obser. 210.2206.

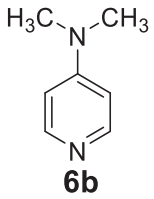
5.8.26 2,6-Lutidine (6a)



6a

(Yield= 80 mg, 75%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 2.52 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.87, 136.70, 120.33, 24.70. **HRMS:** Calc. for C_7H_9N $[M+H]^+$: 108.0813, Obser. 108.0812.

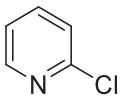
5.8.27 *N,N*-Dimethylpyridin-4-amine (6b)



6b

(Yield= 109 mg, 90%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.9 Hz, 2H), 6.49 (d, *J* = 7.9 Hz, 2H), 3.00 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.43, 149.99, 106.78, 39.22. **HRMS:** Calc. for $C_7H_{10}N_2$ $[M+H]^+$: 123.0922, Obser. 123.0911.

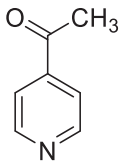
5.8.28 2-Chloropyridine (6c)



6c

(Yield= 68 mg, 61%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 4.2 Hz, 1H), 7.67–7.64 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, *J* = 7.0, 5.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.75, 149.96, 138.86, 124.62, 122.40. **HRMS:** Calc. for C_5H_4ClN $[M+H]^+$: 114.0111, Obser. 114.0163.

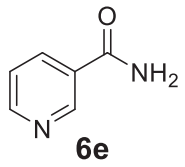
5.8.29 1-(Pyridine-4-yl)ethanone (6d)



6d

(Yield= 78 mg, 65%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 2.63 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.50, 151.16, 142.89, 121.38, 26.81. **HRMS:** Calc. for C_7H_7NO $[M+H]^+$: 122.0606, Obser. 122.0601.

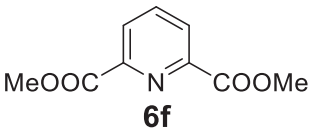
5.8.30 Nicotinamide (6e)



6e

(Yield= 75 mg, 62%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.73 (m, 1H), 8.20 (m, 1H), 7.43 (dd, *J* = 7.9, 4.9 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.82, 152.60, 148.41, 135.96, 129.49, 123.86. **HRMS:** Calc. for $C_6H_6N_2O$ $[M+H]^+$: 123.0558, Obser. 123.0045.

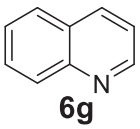
5.8.31 Dimethylpyridine-2,6-dicarboxylate (6f)



6f

(Yield= 117 mg, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.8 Hz, 2H), 7.97 (t, *J* = 7.8 Hz, 1H), 3.97 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.23, 148.41, 138.55, 128.21, 53.36. **HRMS:** Calc. for $C_9H_9NO_4$ $[M+H]^+$: 196.0610, Obser. 195.9961.

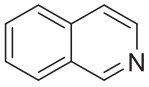
5.8.32 Quinoline (6g)



6g

(Yield= 103 mg, 80%):^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87–8.86 (m, 1H), 8.07 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.66 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 8.2, 4.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.61, 148.51, 136.23, 129.68 ,129.64, 128.49, 127.98 , 126.73, 121.26. **HRMS:** Calc. for C_9H_7N $[M+H]^+$: 130.0657, Obser. 130.0649.

5.8.33 Isoquinoline (6h)



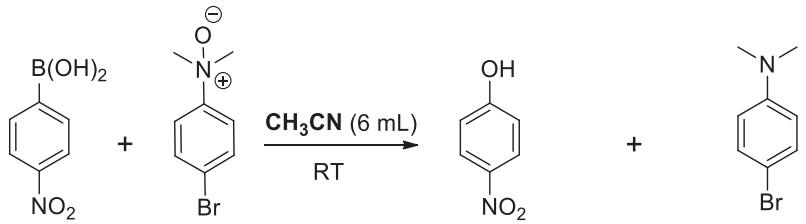
6h

(Yield= 90 mg, 70%):^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.51 (d, *J* = 5.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 5.7 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.75, 143.22, 136.01, 130.55, 128.91, 127.85, 127.45, 126.68, 120.67. **HRMS:** Calc. for C_9H_7N $[M+H]^+$: 130.0657, Obser. 130.0644.

5.9 PROCEDURE FOR UV-VIS EXPERIMENTS

4-bromo-*N,N*-dimethylaniline *N*-oxide (0.039 g, 0.185 mmol) and 4-nitro-phenylboronic acid (0.031 g, 0.185 mmol) (1:1 ratio) was allowed to stir in 6 mL of acetonitrile at room temperature. The reaction was monitored every 15 minutes in UV-Vis spectrometer as follows: 10 μL of reaction mixture was taken by using micro pipette and added to the 2.5 mL of *Tris*-HCl buffer solution (pH 8.4), the spectrum was recorded by UV-Vis spectrophotometer.

YIELD CALCULATION FROM UV-VIS DATA



Wt.:	0.031 g	0.040 g	0.0258 g (expected yield)	0.037g (expected yield
M.Wt.:	166.92	216.08	139.11	200.08
moles:	1.857×10^{-4}	1.857×10^{-4}	1.857×10^{-4}	1.857×10^{-4}

S. No.	T (h)	Absor-bance (A)	[*p*-NP]/ M	[*Tert.* amine]/ M	Wt. of *p*-NP (g)	Yield of *p*-NP(%)	Wt. of *Tert.* Amine (g)	Yield of *Tert.* Amine(%)
1	1	0.8704	0.012	0.012	0.01	38.75	0.014	37.83
2	2	1.223	0.0169	0.0169	0.014	54.26	0.02	54.05
3	3	1.808	0.0251	0.0251	0.0209	81.00	0.03	81.08

CALCULATION:

Acc. to *Beer-Lambert's* Law: **A= εcl**

Where,

A = Absorbance from the spectrum at 400 nm wavelength
c = Concentration of the solution
l = path length of the cuvette = 1 cm

A=0.8704 (1hr); ε = 18000 M^{-1} cm^{-1} *p*-NP

time = 1 hr

0. 8704 =18000xCx1

C = 4. 83 x 10^{-5} M

4. 83 x 10^{-5} Mx 2.5 mL = 0.01 mL x X1

X_1= 0. 012 M (*p*-nitrophenol in 6 mL solvent)

amount of of *p*-nitrophenol in 6 mL solvent = Y_1

$$[X_1] = \frac{Wt}{M.Wt} \times \frac{1000}{V}$$

$$0.012\ M = \frac{Y1}{139.11} \times \frac{1000}{6\ mL}$$

Y_1 =0. 01015 gram

$$\%\ \text{yield of } p\text{- Nitrophenol} = \frac{0.010}{0.0258} \times 100$$

= 38.75%

SIMILARLY

T= 2 hrs: A=1.223; $[X_2]$=0.0169 M; Y_2=0.014 gram; % yield=54.26

T= 3 hrs: A=1.808; $[X_3]$=0.0251 M; Y_3=0.0209 gram; % yield = 81%

Similarly, Calculation Of % Yield Of Tert.Amine Is As Follows:

T= 1 hrs: $[X_1]$=0.012 M; A_1=0.014 gram; % yield=37.83

$$[X_1] = \frac{Wt}{M.Wt} \times \frac{1000}{V}$$

$$0.012\ M = \frac{A_1}{200.08} \times \frac{1000}{6\ mL}$$

A1 = 0.014 grams

$$\%\ \text{yield of tert.amine} = \frac{0.014}{0.037} \times 100$$

= 37.83%

T= 2 hrs: $[X_2]$=0.0169 M; A_2=0.02 gram; % yield=54.05

T= 3 hrs: $[X_3]$=0.0251 M; A_3=0.03 gram; % yield=81.08

5.10 SPECTRAL DATA FOR FEW PRODUCTS

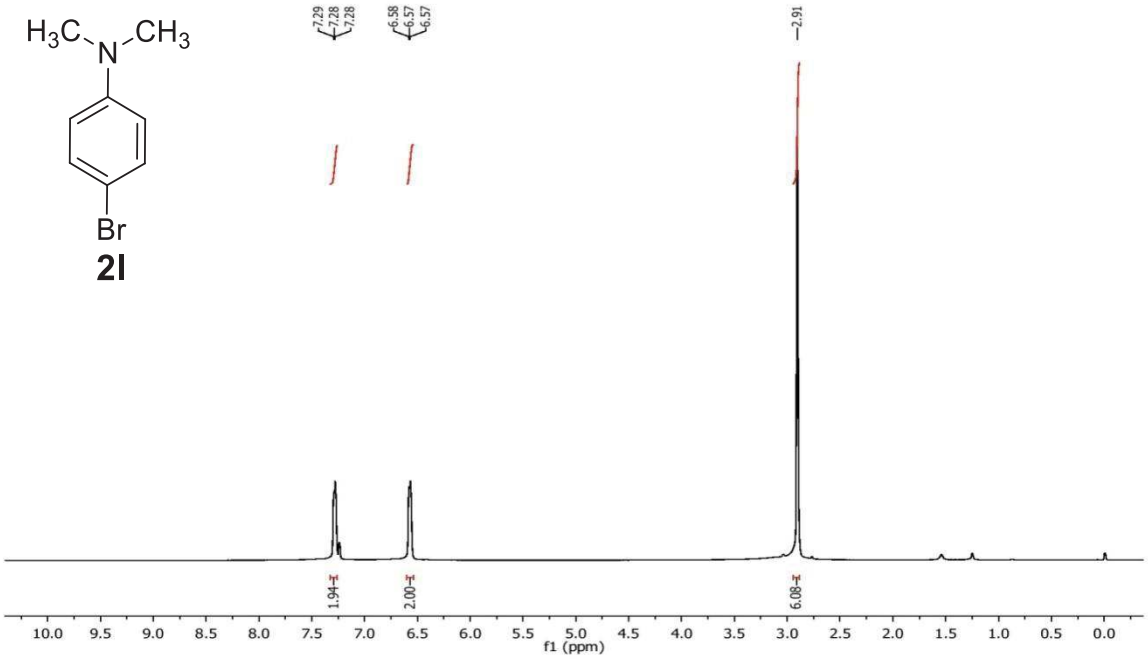


Figure 5.8 ^{1}H NMR of 4-bromo-*N,N*-dimethylaniline(**2l**)

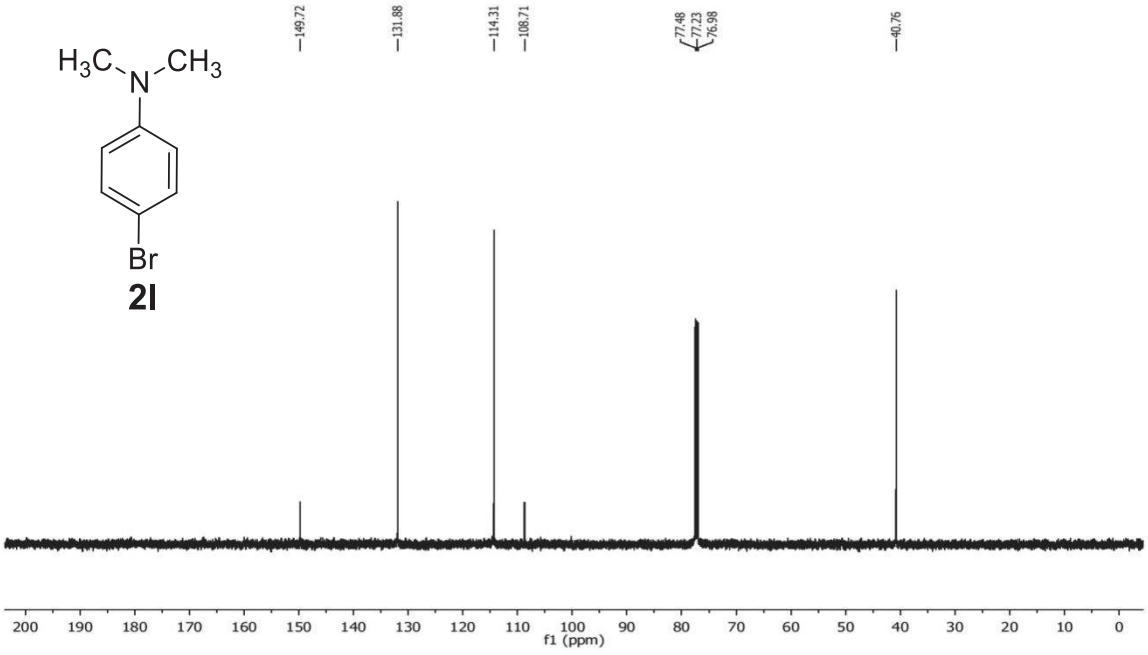


Figure 5.9 ^{13}C NMR of 4-bromo-*N,N*-dimethylaniline (**2l**)

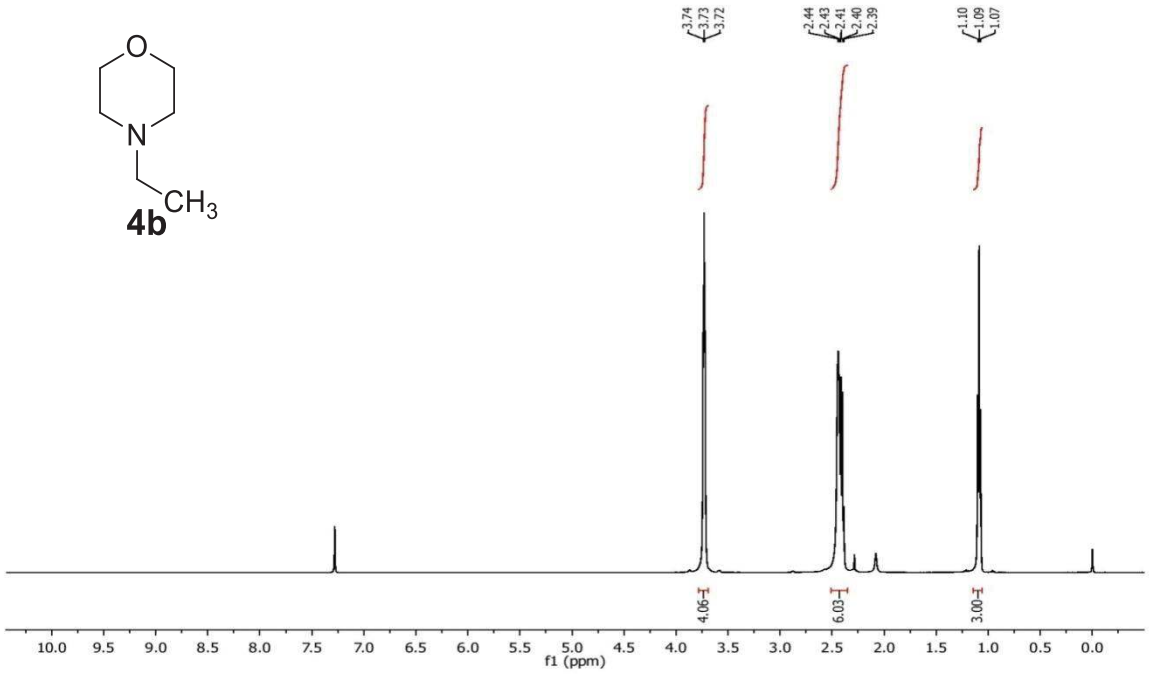


Figure 5.10 ^{1}H NMR of 4-ethylmorpholine (**4b**)

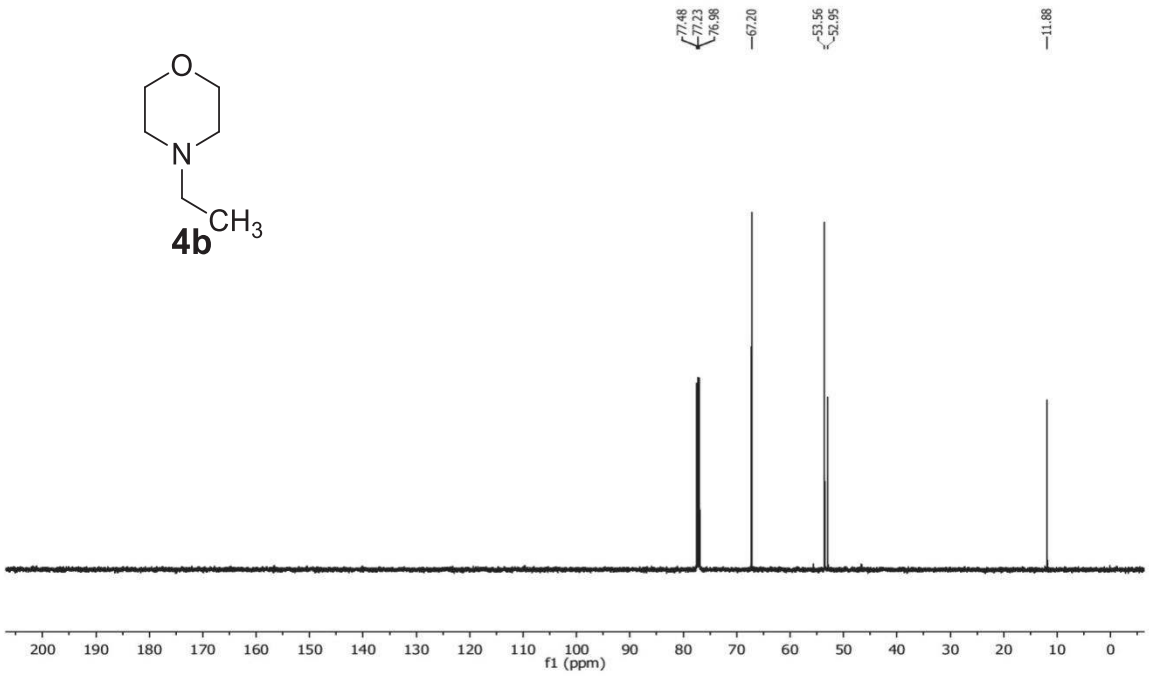


Figure 5.11 ^{13}C NMR of 4-ethylmorpholine (**4b**)

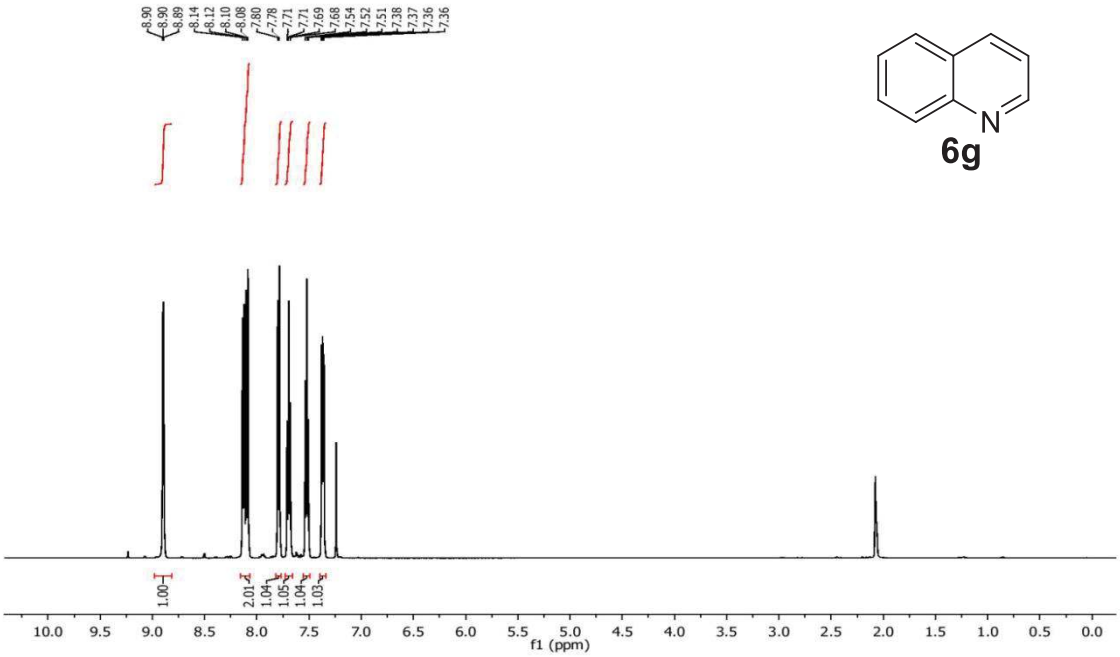


Figure 5.12 ^{1}H NMR of Quinoline (**6g**)

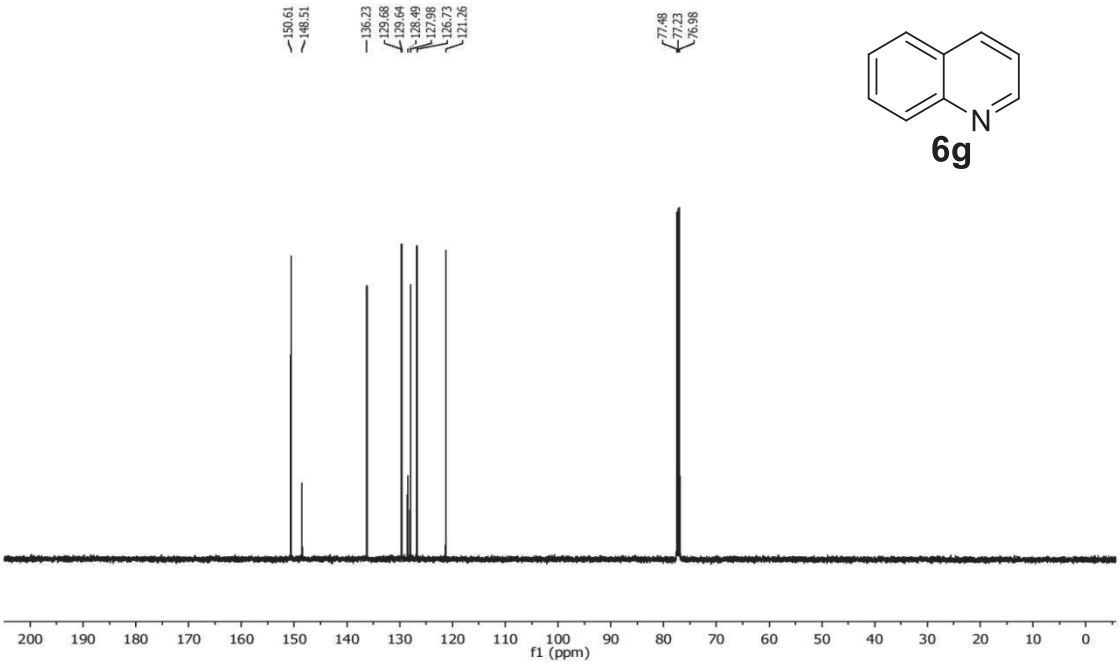


Figure 5.13 ^{13}C NMR of Quinoline (**6g**)

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[17] As per mechanism (see **Scheme 5.6**), migration of aryl or alkyl group is necessary to obtain the desired amine. In general migration efficiency of alkyl groups are relatively less when compare to aryl groups. We belive it may be a reason for less reactivity of alkylboronic acid in the deoxygenation.

[18] Cost of the organoboron compounds in Sigma Aldrich: Phenylboronic acid 50 g is 73 $; Bis(pinacolato)diboron [$(pinB)_2$] 5g is 101 $; Bis(catecholato)diboron [$(catB)_2$] 5g is 481$; and Tetrahydroxydiboron 5g is 103 $.

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