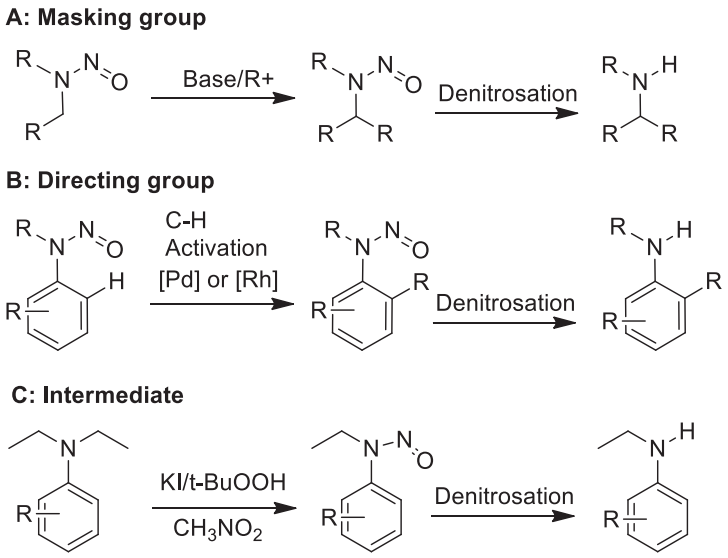
CHAPTER-3

AN EFFICIENT METAL-FREE METHOD FOR THE DENITROSATION OF ARYL *N*-NITROSAMINES AT ROOM TEMPERATURE

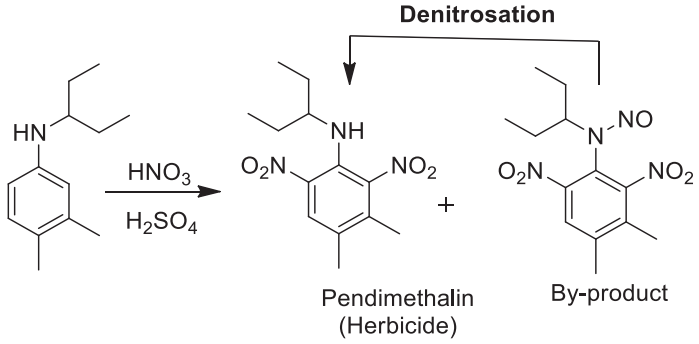
3.1 Introduction

N-Nitrosamines have been known since the nineteenth century and received considerable attention in chemistry and biology [1-3]. In organic synthesis, *N*-nitrosamines have been used not only as synthetic intermediates [4-7] but also used as masking groups and directing groups (Scheme 3.1) [8-19]. For example, secondary amines can be masked as *N*-nitrosamines to perform electrophilic substitutions selectively at the α-carbon (Scheme 3.1, **A**) [8, 9]. Recently, *N*-nitrosamine directed C-H bond activation reactions have emerged as a powerful method for the synthesis of *ortho*-functionalized aniline compounds (Scheme 4.1, **B**) [10-19]. On the other hand, *N*-nitrosamines are the intermediate in the dealkylation of *N*, *N*-disubstituted anilines (Scheme 3.1, **C**) [20-22]. While many chemical reactions employ *N*-nitrosamine intermediates, they are also often formed as major side products [23-25]. For instance, *N*-nitrosamine is obtained as the major side product during the synthesis of an important herbicide, pendimethalin (Scheme 3.2) [23].

In all the above reactions, denitrosation of *N*-nitrosamine is the key step to generate active amine compounds for further chemical and biological applications [10, 13, 15, 18, 20, 21, 23]. However, only a limited literature exists for the denitrosation of *N*-nitrosamines, all of which involve metal based reducing agents. For example, CuCl/HCl [10, 26], $NiCl_2/NaBH_4$ [10, 27], $Fe(CO)_5$ [10, 28], Raney-Ni/H_2 [10, 29], Fe/NH_4Cl [13, 18] and Zn/NH_4Cl [14] have been utilized for the denitrosation process.



Scheme 3.1 Applications of *N*-nitrosamines in various transformations.

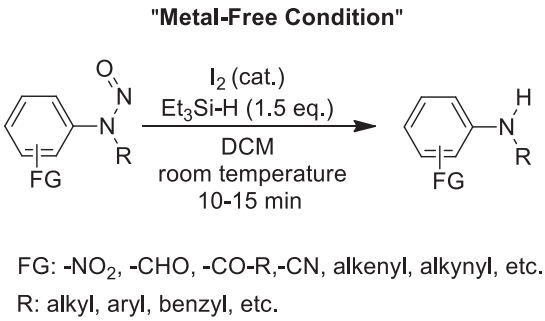


Scheme 3.2 Formation of *N*-nitrosamine as the by-product.

Besides using non eco-friendly toxic metal reagents, the existing methods also suffer from other drawbacks. One of the major setbacks with the existing reagents is "functional group intolerance". Namely, most of these reagents were known for reducing other functional groups such as nitro, nitrile, alkene, alkyne, aldehyde, ketone, etc. [30, 31]. Moreover, all these methods suffer with at least one of the following additional drawbacks such as requirement of excess of reagents, high reaction temperature, harsh reaction

conditions, longer reaction time, strong acidic media, etc. Therefore, it is important to establish a simple and efficient method for the selective denitrosation of *N*-nitrosamines under mild reaction conditions especially in the presence of other sensitive functional groups.

Triethylsilane is a mild and selective reducing agent used in combination with different metals or Lewis acids for the reduction of selected functional groups [32-35]. Triethylsilane is inexpensive, commercially available and considered to be a good alternative to other more toxic reducing agents [32, 36]. To the best of our knowledge organosilanes have not been explored in denitrosation reactions. In continuation of our second chapter [37], here we report an efficient method for the denitrosation of aryl-*N*-nitrosamines using an iodine-triethylsilane system (Scheme 3.3).



Scheme 3.3 Denitrosation of *N*-nitrosamines.

3.2 Results and Discussion

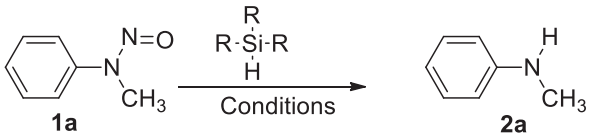
3.2.1 Optimization for denitrosation under different reaction conditions

At the outset, denitrosation of *N*-methyl *N*-nitrosoaniline **1a** was examined with one equivalent of triethylsilane in different solvents at room temperature in the absence of

catalyst (Table 3.1). A negligible amount of formation of denitrosated product was observed (*i.e.* secondary amine) in different solvents including dichloromethane, acetonitrile and methanol (Table 3.1, entries 1-3). Therefore, we have looked for a suitable catalyst which can accelerate the reaction to give the desired product in good yield.

Among the different combinations described in the literature, the iodine/triethylsilane system was found to be very mild and was explored in reductive ring opening of benzylidene acetals [38], reductive amination of acetals [39], etc. Thus, a catalytic amount of iodine (*i.e.* 10 mol %) was introduced in the denitrosation reactions with triethylsilane (Table 3.1, entries 4-6). We were delighted to see a significant conversion of *N*-nitrosamine **1a** to the corresponding secondary amine **2a** (*i.e.* 55%) in dichloromethane at room temperature (Table 3.1, entry 4). Further, the denitrosation reaction was tested with varying amounts of iodine and triethylsilane in dichloromethane (Table 3.1, entries 7-11). Finally, it was observed that a combination of 0.3 eq. of iodine and 1.5 eq. of triethylsilane would be optimum for the efficient denitrosation process which provides the desired amine in quantitative yield within 10 mins (Table 3.1, entry 9). It may also be noted that in the absence of triethylsilane no reaction was observed (Table 3.1, entry 12). In addition, we have examined the reaction with other iodine sources such as sodium iodide and tetrabutyl ammonium iodide and no reaction was observed (Table 3.1, entries 13-14).

Table 3.1 **Optimization of denitrosation under different conditions.**[a,b]



S.No.	Solvent	Silane (eq.)	Catalyst (eq.)	Time	Yield (%)[b]
1	CH_2Cl_2	TES (1.0)c	-	1 h	<5
2	CH_3CN	TES (1.0)	-	1 h	nd[d]
3	CH_3OH	TES (1.0)	-	1 h	nd[d]
4	CH_2Cl_2	TES (1.0)	I_2 (0.1)	1 h	55
5	CH_3CN	TES (1.0)	I_2 (0.1)	1h	32
6	CH_3OH	TES (1.0)	I_2 (0.1)	1 h	5
7	CH_2Cl_2	TES (1.0)	I_2 (0.2)	1 h	78
8	CH_2Cl_2	TES (1.5)	I_2 (0.2)	30 min	95
9	**CH_2Cl_2**	**TES (1.5)**	**I_2 (0.3)**	**10 min**	**95**
10	CH_2Cl_2	TES (1.5)	I_2 (0.5)	10 min	94
11	CH_2Cl_2	TES (1.5)	I_2 (1.0)	10 min	95
12	CH_2Cl_2	-	I_2 (1.0)	1 h	nd[d]
13	CH_2Cl_2	TES (1.5)	NaI (0.3)	1 h	nd[d]
14	CH_2Cl_2	TES (1.5)	Bu_4NI (0.3)	1 h	nd[d]
15	CH_2Cl_2	PS (1.5)e	I_2 (0.3)	30 min	94
16	CH_2Cl_2	DMPS (1.5)f	I_2 (0.3)	10 min	94
17	CH_2Cl_2	TES (1.5)	$B(C_6F_5)_3$ (0.3)	1 h	nd[d]
18	CH_2Cl_2	TES (1.5)	$BF_3.OEt_2$ (0.3)	1 h	nd[d]

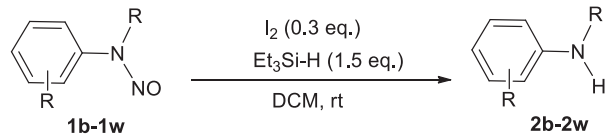
[a]Reaction conditions: *N*-Nitrosamine (1 mmol), silane and catalyst were stirred in the respective solvents (3 mL) at room temperature. [b]Isolated yields. [c]TES: Triethylsilane. [d]nd: Not detected in TLC. [e]PS: Phenylsilane. [f]DMPS: Dimethylphenylsilane.

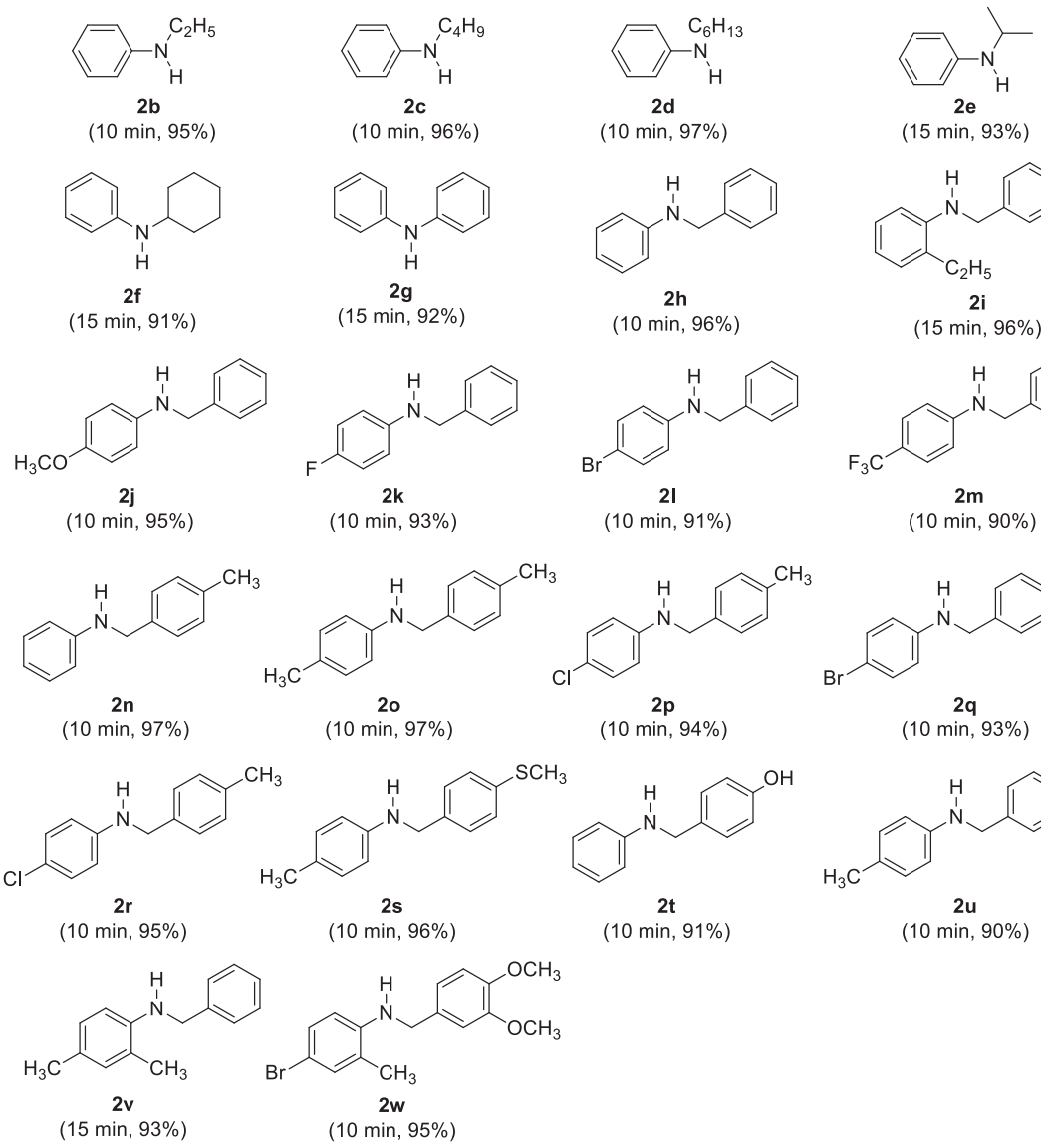
It is also interesting to note that other expensive silanes such as phenylsilane (PS) and dimethylphenylsilane (DMPS) showed a comparable efficiency to that of triethylsilane in presence of iodine (Table 3.1, entries 15-16). However, when tris(pentafluorophenyl)borane and trifluoroborane diethyl etherate was used as a catalyst in the presence of triethylsilane, no reaction was detected (Table 3.1, entries 17-18).

3.2.2 Substrate scope

With optimized conditions in hand, the investigation of denitrosation of various *N*-nitrosamines was undertaken using I_2/Et_3SiH at room temperature (Table 3.2). Denitrosation of *N*-nitroso *N*-alkyl/aryl anilines were achieved in excellent yields (*i.e.* 95-97%) within 10 min at room temperature (Table 3.2, **2b**-**2d**). Sterically hindered *N*-isopropyl, *N*-cyclohexyl and *N*-phenyl aniline derivatives also denitrosated with similar efficiency and provided >91% yield (Table 3.2, **2e**-**2g**). Further, denitrosation of various *N*-nitroso *N*-benzyl anilines with electron donating and withdrawing substituents was attempted under optimized conditions (Table 3.2, **2h**-**2w**). It is interesting to note that irrespective of the substituents present on the substrate, the reaction gave the desired amines in excellent yields, i.e. 90-97% (Table 3.2, **2h-2w**) in a short span of time. It was also observed that *N*-nitrosamines with *ortho*-substituents took a slightly longer time, i.e. 15 min, for completion of the reaction (Table 3.2, **2i** and **2v**). It is worth noting that we haven't observed any debenzylation or dehalogenation products during the denitrosation, which signals the broad scope of this methodology.

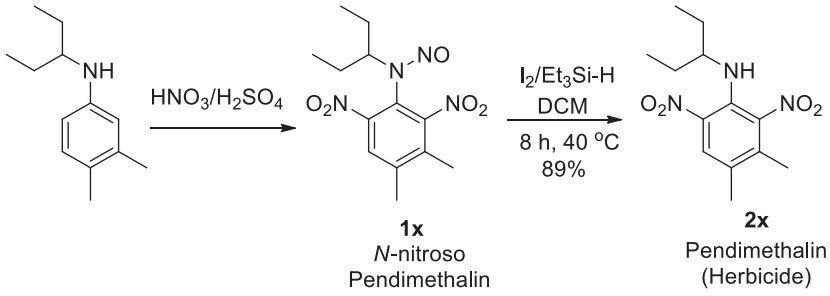
Table 3.2 Denitrosation of *N*-nitrosamines using iodine-triethylsilane.[a,b]





[a]Reaction conditions: *N*-nitrosamine (1 mmol), triethylsilane (1.5 eq.) and iodine (0.3 eq.) were stirred in dichloromethane (3 mL) at room temperature. [b]Isolated yields.

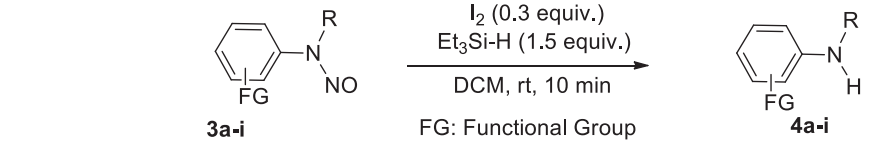
As mentioned in the introduction, *N*-nitrosamine is formed as the byproduct during preparation of herbicide pendimethalin [23, 24]. To investigate the efficiency of our method, we have synthesized the *N*-nitroso pendimethalin and attempted for the denitrosation using I_2 and Et_3SiH. To our delight, the denitrosation underwent smoothly to provide pendimethalin **2x** in 89% yield (Scheme 3.4). Perhaps, due to steric hindrance, denitrosation of *N*-nitroso pendimethalin required slightly longer time (8 h) and elevated temperature, i.e. 40 °C.

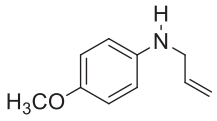


Scheme 3.4 Synthesis of Pendimethalin using Iodine and triethylsilane in DCM.

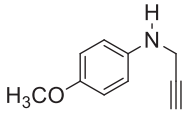
An investigation of functional group tolerance is an important aspect in methodology development. For this study, we have subjected a series of *N*-nitrosamines containing reduction susceptible functional groups such as nitro, alkenyl, alkynyl, nitrile, aldehyde, ketone and ester with iodine-triethylsilane under optimized conditions (Table 3.3).

Table 3.3 Denitrosation of functionalized *N*-nitrosamines using iodine-triethylsilane.[a,b]

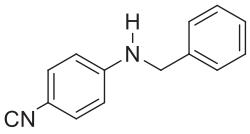




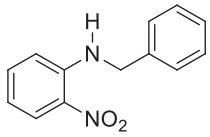
4a: 91%



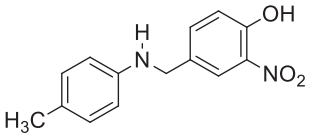
4b: 89%



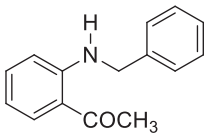
4c: 89%



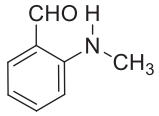
4d: 89%



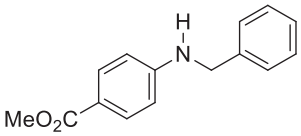
4e: 91%



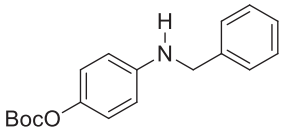
4f: 90%



4g: 85%



4h: 92%



4i: 95%

[a]Reaction conditions: *N*-nitrosamine (1 mmol), triethylsilane (1.5 eq.) and iodine (0.3 eq.) were stirred in dichloromethane (3 mL) at room temperature. [b]Isolated yields.

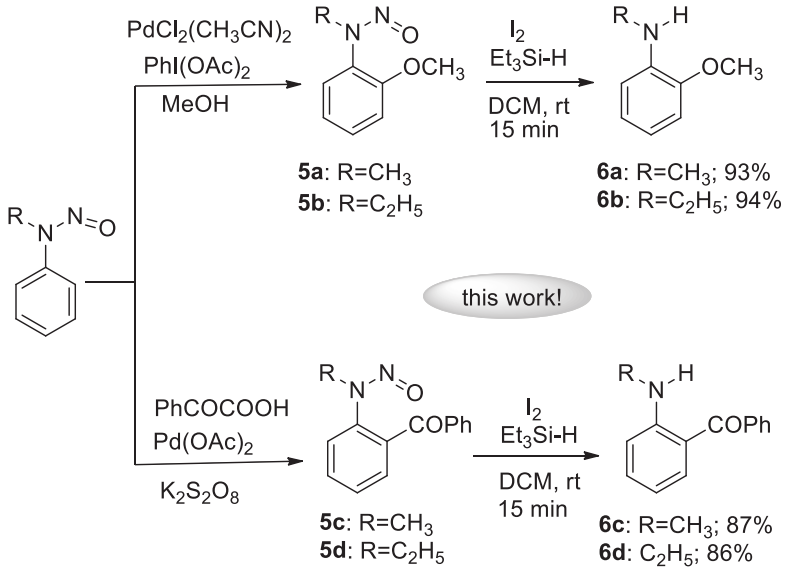
Olefin, alkyne and nitrile functionalized *N*-nitrosamines underwent denitrosation efficiently without affecting double bond and triple bonds (Table 3.3, **4a-4c**). It may be noted that previously used reagent such as Raney-Ni/H_2 is well known for the reduction of these functional groups [31] Similarly, the nitro group is susceptible to reduction [30, 31] with Raney-Ni/H_2, Zn/NH_4Cl and Fe/NH_4Cl while found to be intact during the denitrosation with I_2-Et_3SiH (Table 3.3, **4d** and **4e**), which is remarkable. The carbonyl functionalities such as aldehyde and ketone are prone to reduction in the presence of

various reducing agents (e.g. sodium borohydride). Indeed, reduction of aldehyde was previously achieved with organosilanes in the presence of different catalysts [40-42]. Therefore, denitrosation of carbonyl groups functionalized *N*-nitrosamines was investigated with triethylsilane-iodine system under optimized condition.

Remarkably, aldehyde, ketone and ester functional groups found to be intact while selective denitrosation was achieved in high yields (Table 3.3, **4f-4h**). Further, we have also tested the stability of acid labile protecting group such as *tert*-butyl carbonate (Boc). Interestingly, Boc group was preserved during the denitrosation of Boc containing *N*-nitrosamine derivative (Table 3.3, **4i**).

3.3 Applications of Current Methodology to Multi-Step Synthesis

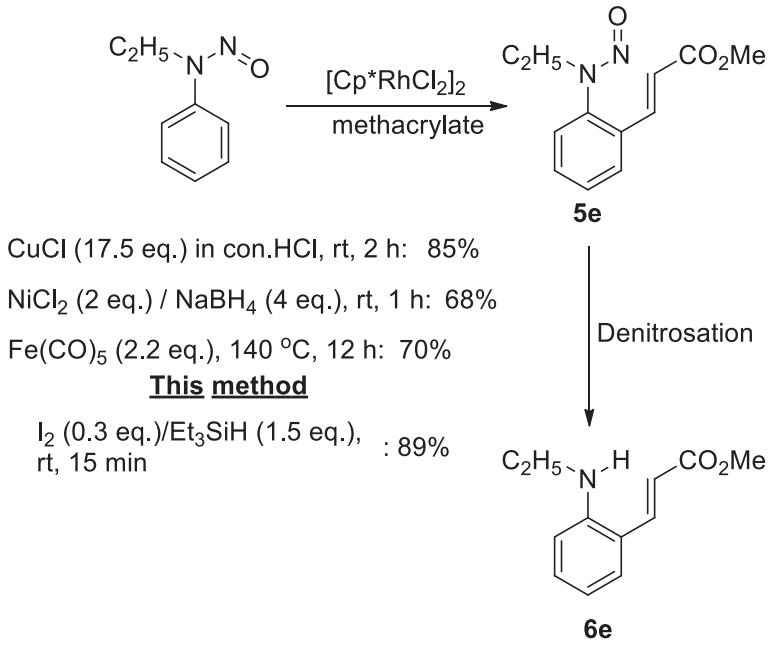
3.3.1 Palladium catalyzed C-H activation followed by denitrosation



Scheme 3.5 Palladium catalyzed C-H activation followed by denitrosation.

After an extensive study of denitrosation with a variety of substrates, we utilized the current methodology in different useful reactions. Palladium catalysed *N*-nitrosamine directed *ortho*-methoxylation and *ortho*-acylation of anilines have been recently reported (Scheme 3.5) [13, 18]. The resulting *N*-nitroso intermediates were successfully denitrosated using the present method *i.e.* I_2/Et_3SiH in >86% yield at room temperature within 15 minutes. In contrast, original reports require excess amount of reagent, *i.e.* Fe (4.0 eq.)/NH_4Cl (3.0 eq.), high temperature (80 °C) and longer reaction time (6 h) for the denitrosation. [13, 18]

3.3.2 Rhodium catalyzed C-H activation followed by denitrosation



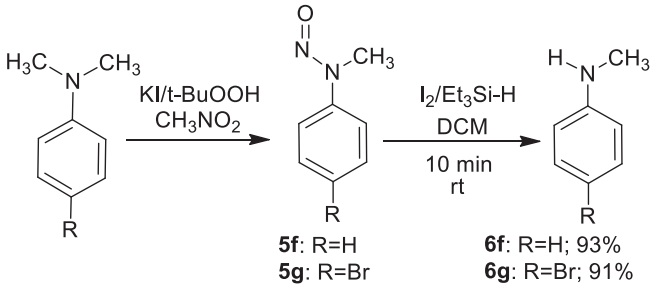
Scheme 3.6 Rhodium catalyzed C-H activation followed by denitrosation.

Recently, *N*-nitroso directed C-H olefination was demonstrated using rhodium(III) catalysts. In this report, CuCl/HCl, $NiCl_2/NaBH_4$ and $Fe(CO)_5$ have been utilized for the

denitrosation purpose (Scheme 3.6) [10]. However, this process requires either an excess of reagents or strong acidic medium or high reaction temperature. Nevertheless, the current protocol, *i.e.* I_2/Et_3SiH gave the desired denitrosated product in 89% yield within 15 min at room temperature.

3.3.3 Nitrosative dealkylation of *tert*-amines followed by denitrosation

The current methodology was further applied in nitrosative dealkylation process of *N,N*-disubstituted anilines. Dealkylated *N*-nitroso intermediates **5f** and **5g** were prepared using the reported method [22] (Scheme 3.7) and subjected to denitrosation with I_2/Et_3SiH. The reaction yielded the corresponding secondary amines **6f** and **6g** in >91% yields in 10 min. We believe that this new process will be an efficient alternative route for the previously reported oxidative dealkylation methods [43, 44].

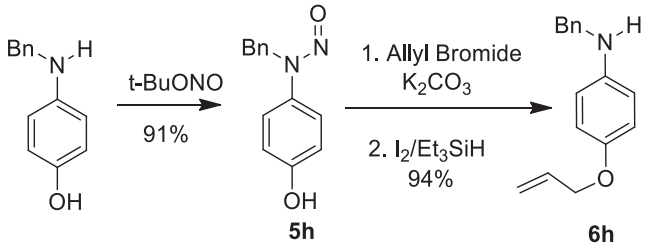


Scheme 3.7 Nitrosative dealkylation of *tert*-amines.

3.4 Nitroso as Protecting Group

Further, we utilized the nitroso moiety as a "protecting group" for secondary amines. For this study, we have synthesized *N*-benzyl 4-hydroxy aniline and attempted for *O*-allylation. At first, secondary amine was selectively converted to *N*-nitrosamine **5h** in

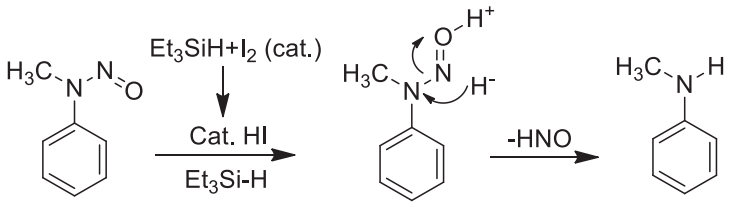
high yield using *tert*-butyl nitrite (Scheme 3.8). The resulted phenolic compound was allylated using allyl bromide in a quantitative yield which was subsequently denitrosated using I_2/Et_3SiH to obtain the desired product in 94% yield (for two steps). It shows that the "NO" moiety can be used as an alternative protecting group to acetate or Boc for the protection of secondary amines in organic synthesis [45, 46].



Scheme 3.8 *N*-Nitroso moiety as protecting group in organic synthesis.

3.5 Plausible Mechanism

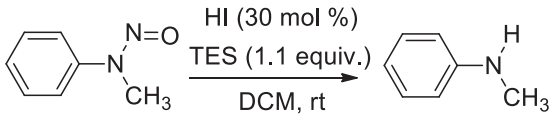
Although, the mechanism of the denitrosation reaction is unclear, we believe that the reaction may proceed through following mechanism as shown in Scheme 3.9. Iodine reacts with triethylsilane to form hydroiodic acid (HI), [47, 48] which is expected to catalyse the reaction actively. The H^+ ion coordinates with the nitroso group while triethylsilane delivers the hydride ion to form a secondary amine [40]. It may be noted that the reaction proceeds faster when the concentration of iodine is increased from 0.1 equiv. to 0.3 equiv. (Table 3.1, entries 4, 8 and 9).



Scheme 3.9 Proposed mechanism for the denitrosation reaction.

This may be due to increase in the concentration of hydroiodic acid (HI) in the reaction. Further to confirm the participation of HI in the denitrosation process, denitrosation of *N*-nitrosamine **1a** was performed with 30 mol % of HI in the presence of 1.1 equiv. of triethylsilane (Table 3.4, entry 1). The reaction proceeds smoothly to yield the desired product **2a** in 95% yield in 15 min. However, other acids such as hydrobromic acid (HBr) and hydrochloric acid (HCl) provide the desired product in a low yield.

Table 3.4 Denitrosation of *N*-methyl *N*-nitroso aniline catalyzed by haloacids.



1a **2a**

S.No.	Catalyst	Time (min)	Yield(%)
1.	HI	15	95
2.	HBr	15	43
3.	HCl	15	36

[a]Reaction conditions: *N*-nitrosamine (1 mmol), triethylsilane (1.5 eq.) and iodine (0.3 eq.) were stirred in dichloromethane (3 mL) at room temperature. [b]Isolated yields.

3.6 Conclusion

In conclusion, we have developed an efficient and practical method for the denitrosation of *N*-nitrosamines using iodine and triethylsilane. The reaction proceeds at room temperature in a short span of time and provides typical yields of 85-97%. Reduction susceptible functionalities such as alkene, alkyne, nitrile, nitro, aldehyde, ketone and ester were found to be stable under the standard reaction conditions. Applications of the current methodology were demonstrated in different multistep organic synthesis. In addition, the nitroso moiety was explored as a protecting group for secondary amines. Overall, we found the current methodology will have a wide of scope in organic synthesis.

3.7 Experimental Section

3.7.1 General experimental procedure for the denitrosation of *N*-nitrosamines

N-nitrosamine (1.0 mmol, 1.0 equiv.) was allowed to stir in dichloromethane (3 mL) approximately for 2 min at room temperature to which iodine (76 mg, 0.3 equiv.) and triethylsilane (0.24 mL, 1.5 equiv.) was added. The reaction was further allowed to stir for 10-15 minutes and the progress of the reaction was monitored by TLC. After completion, the reaction mixture was quenched with saturated solution of sodium thiosulfate (20 mL) extracted with ethyl acetate (2 × 25 mL). The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (SiO_2, eluent: Hexane/ethyl acetate) to obtain corresponding pure substituted secondary amines (Scheme 3.3).

3.7.2 Denitrosation of *N*-methyl *N*-nitrosaniline using Triethylsilane with hydroiodic acid (HI), hydrobromic acid (HBr) and hydrochloric acid (HCl).

N-methyl *N*-nitrosaniline (137 mg, 1 equiv.) was stirred in dichloromethane (3 mL) approximately for 2 min at room temperature to which triethylsilane (0.17 mL, 1.1 equiv.) and hydroiodic acid (0.01 mL, 0.1 equiv.) was added *via* syringe and allowed to stir for 15 minutes. After completion, the reaction mixture was quenched with saturated solution of sodium thiosulfate (20 mL) and extracted with ethyl acetate (2 × 25 mL). The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (SiO_2, eluent: Hexane/ethyl acetate) to obtain *N*-methyl aniline in 95% yield (101 mg). Similarly, the denitrosation reaction was performed with hydrobromic and hydrochloric acid (Table 3.4).

3.7.3 Experimental procedure for the synthesis of *O*-allyl *N*-benzyl (4-hydroxyaniline) (6h) *via* nitrosation and denitrosation:

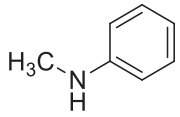
N-Benzyl (4-hydroxyaniliine) (398 mg, 2.0 mmol, 1.0 equiv.) was stirred with *tert*-butyl nitrite (1.2 equiv., 0.16 mL) under solvent-free condition at room temperature to obtain *N*-nitroso *N*-benzyl (4-hydroxyaniliine) **5h** as yellow solid in 91% (414 mg). Further, the nitrosamine **5h** (230 mg, 1 mmol) was stirred with allyl bromide (180 mg, 1.5 mmol) and potassium carbonate (830 mg, 6 mmol) in acetone (12 mL) under refluxed condition for 10 h. After completion, the reaction mixture was filtered, washed with acetone and concentrated to obtain pale yellow solid. *N*-nitroso *N*-benzyl (4-hydroxyaniliine) (**5h**) : ^{1}H NMR (500 MHz, DMSO) δ 9.87 (s, 1H), 7.41-7.37 (d, J = 8.5 Hz, 2H), 7.30-7.25 (m, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.10-7.00 (m, 2H), 6.90-6.78 (m, 2H),

5.26 (s, 2H).^{13}C NMR (125 MHz, DMSO) δ 157.3, 135.1, 133.3, 129.0, 127.7, 127.6, 122.8, 116.2, 47.4.

Without further purification, the pale yellow solid product was subjected for denitrosation using iodine (76 mg, 0.3 equiv.) and triethylsilane (0.24 mL, 1.5 equiv.) in dichloromethane (3 mL) was added and allowed to stir for 15 minutes. After completion, the reaction mixture was quenched with saturated solution of sodium thiosulfate extracted with ethyl acetate (2 × 10 mL). The organic layer was dried over anhydrous sodium sulphate, concentrated and followed by column chromatography purification as described in general procedure to obtain **6h** in 94% yield (0.224 g) (for two steps) (Scheme 3.7).

3.8 Analytical Data for Products

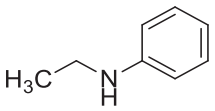
3.8.1 *N*-Methyaniline (2a)



2a

The title compound was obtained as yellow liquid. Yield: 95% (101 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc 95:5, R_f = 0.66. IR (neat): 3498, 1567, 1550, 1320, 667 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.30 (m, 2H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 2H), 3.71 (brs, 1H), 2.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 129.0, 117.0, 112.2, 30.5; HRMS: Calc. for $C_7H_{10}N$ $[M+H]^+$: 108.0813, Obser. 108.0818.

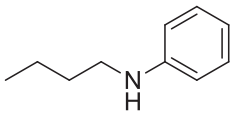
3.8.2 *N*-Ethylaniline (2b)



2b

The title compound was obtained as yellow liquid. Yield: 95% (114 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.68. IR (neat): 3401, 2968, 1596, 1504, 1256, 745, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.7 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 3.37 (brs, 1H), 3.03 (q, *J* = 7.1 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 129.1, 117.0, 112.6, 38.3, 14.7. HRMS: Calc. for $C_8H_{12}N$ $[M+H]^+$: 122.0970, Obser. 122.0967.

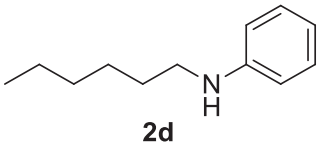
3.8.3 *N*-Butylaniline (2c)



2c

The title compound was obtained as yellow liquid. Yield: 96% (143 mg); The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.66. IR (neat): 3413, 3046, 1599, 1474, 1250, 995, 740 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.9 Hz, 2H), 6.76 (t, *J* = 6.8 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 2H), 3.60 (brs, 1H), 3.17 (t, *J* = 7.1 Hz, 2H), 1.69-1.52 (m, 2H), 1.51-1.48 (m, 2H), 1.06-1.02 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 129.1, 117.0, 112.6, 43.6, 31.6, 20.2, 13.8. HRMS: Calc. for $C_{10}H_{16}N$ $[M+H]^+$: 150.1283, Obser. 150.1280.

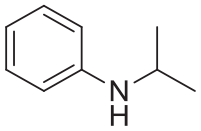
3.8.4 *N*-Hexylaniline (2d)



2d

The title compound was obtained as pale yellow liquid. Yield: 97% (171 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.67. IR (neat): 3400, 2985, 1508, 1470, 1243, 990, 737 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (t, *J* =5 Hz , 2H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 2H), 3.67 (brs, 1H), 3.21 (t, *J* = 7.1 Hz, 2H), 1.73-1.54 (m, 2H), 1.53-1.45 (m, 6H), 1.06-1.03 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 129.1, 116.9, 112.5, 43.9, 31.5, 29.4, 26.7, 22.5, 13.9. HRMS: Calc. for $C_{12}H_{20}N$ $[M+H]^+$: 178.1596, Obser. 178.1597.

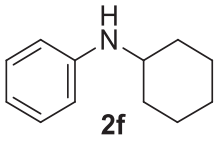
3.8.5 *N*-Isopropylaniline (2e)



2e

The title compound was obtained as yellow liquid. Yield: 93% (125 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.60. IR (neat): 3399, 3045, 1603, 1503, 1255, 1173, 689 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.9 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.71-6.64 (m, 2H), 3.72 (m, 1H), 3.50 (brs, 1H), 1.30 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 129.1, 116.8, 113.1, 44.0, 22.9. HRMS: Calc. for $C_9H_{14}N$ $[M+H]^+$: 136.1126, Obser. 136.1132.

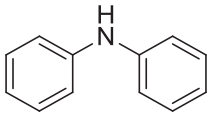
3.8.6 N-Cyclohexylaniline (2f)



2f

The title compound was obtained as dark yellow liquid. Yield: 91% (159 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.62. IR (neat): 3410, 3046, 2843, 1588, 1253, 748, 691 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, *J* = 6.9 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 2H), 3.48 (brs, 1H), 3.28-3.21 (m, 2H), 2.05 (m, 2H), 1.78-1.76 (m, 2H), 1.67-1.63 (m, 1H), 1.41-1.32 (m, 2H), 1.26-1.11 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 129.2, 116.8, 113.1, 51.7, 33.4, 25.9, 25.0. HRMS: Calc. for $C_{12}H_{18}N$ $[M+H]^+$: 176.1439, Obser. 176.1437.

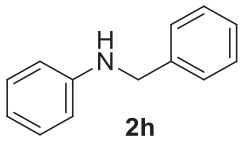
3.8.7 Diphenylamine (2g)



2g

The title compound was obtained as dark yellow solid. M.p. 54 °C. Yield: 92% (155 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.69. IR (neat): 3378, 3023, 3011, 1455, 1310, 1248, 1022, 878, 668 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.31 (m, 4H), 7.13 (d, *J* = 7.5 Hz, 4H), 6.99 (t, *J* = 7.3 Hz, 2H), 5.73 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 129.3, 121.0, 117.8. HRMS: Calc. for $C_{12}H_{12}N$ $[M+H]^+$: 170.0970, Obser. 170.0977.

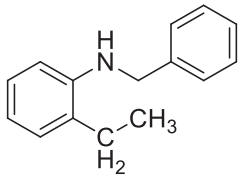
3.8.8 *N*-Benzyl aniline (2h)



2h

The title compound was obtained as pale yellow solid. M.p. 37.5 °C. R_f = 0.69; Yield: 96% (175 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5). IR (neat): 3419, 3073, 3064, 1594, 1500, 692 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.24 (m, 4H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.09 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 2H), 4.23 (s, 2H), 3.94 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 139.4, 129.2, 128.6, 127.4, 127.1, 117.5, 112.8, 48.2. HRMS: Calc. for $C_{13}H_{14}N$ $[M+H]^+$: 184.1126, Obser. 184.1126.

3.8.9 *N*-Benzyl 2-ethylaniline (2i)

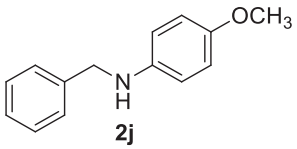


2i

The title compound was obtained was dark yellow liquid. Yield: 96% (202 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.59. IR (neat): 3430, 3063, 3054, 1580, 1478, 675 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.24 (m, 4H), 7.21 (d, *J* = 6.9 Hz, 1H), 7.02 (t, *J* = 6.4 Hz, 2H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 1H), 4.29 (s, 2H), 3.89 (brs, 1H), 2.44 (q, *J* = 7.5 Hz, 2H), 1.19 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 139.5, 128.6, 127.8, 127.5, 127.5, 127.2, 126.9, 117.3, 110.2, 48.3, 23.8, 12.8. HRMS: Calc. for $C_{15}H_{18}N$ $[M+H]^+$:

212.1439, Obser. 212.1440.

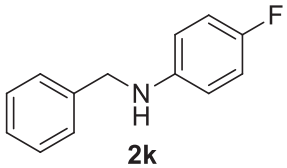
3.8.10 *N*-Benzyl 4-methoxyaniline (2j)



2j

The title compound was obtained as white solid. M.p. 52 °C. Yield: 95% (202 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.72. IR (neat): 3408, 3012, 1899, 1600, 1300, 1237, 1170, 815, 678 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.25 (m, 4H), 7.20 (d, *J* = 7.1 Hz, 1H), 6.70 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 8.9 Hz, 2H), 4.21 (s, 2H), 3.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 142.4, 139.5, 128.5, 127.5, 127.1, 114.9, 114.1, 55.8, 49.3. HRMS: Calc. for $C_{14}H_{16}NO$ $[M+H]^+$: 214.1232, Obser. 214.1231.

3.8.11 *N*-Benzyl 4-fluoroaniline (2k)

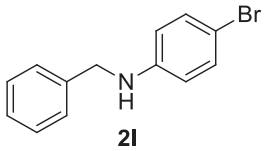


2k

The title compound was obtained as dark yellow liquid. Yield: 93% (186 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.70. IR (neat): 3405, 2922, 1600, 1512, 1450, 1231, 1032 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.36 (m, 4H), 7.31-7.28 (m, 1H), 6.89 (t, *J* = 8.8 Hz, 2H), 6.57 (m, 2H), 4.29 (s, 2H), 3.93 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7 (d, $J_{C\text{-}F}$ = 233.6 Hz), 154.9, 144.4, 139.2, 128.6, 127.4, 127.2, 115.7 (d, $J_{C\text{-}F}$ = 22.9 Hz), 113.6 (d, $J_{C\text{-}F}$ = 7.6 Hz), 48.8. HRMS: Calc. for

$C_{13}H_{13}FN$ $[M+H]^+$: 202.1032, Obser. 202.1026.

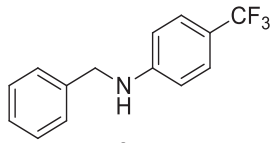
3.8.12 *N*-Benzyl 4-bromoaniline (2l)



2l

The title product was obtained as yellow solid. M.p. 52 °C. Yield: 91% (238 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.68. IR (neat): 3427, 2820, 1612, 1502, 1423, 1343, 1042, 757 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.4 Hz, 4H), 7.28-7.26 (m, 1H), 7.25-7.21 (m, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 4.29 (s, 2H), 4.05 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 138.8, 131.9, 128.6, 127.3, 127.3, 114.4, 109.1, 48.2. HRMS: Calc. for $C_{13}H_{13}BrN$ $[M+H]^+$: 262.0231, Obser. 262.0229.

3.8.13 *N*-Benzyl 4-trifluoromethylaniline (2m)

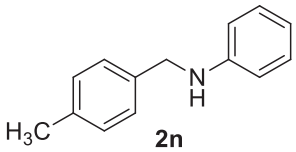


2m

The title compound was obtained as orange-coloured liquid. Yield: 90% (225 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.42. IR (neat): 3415, 2800, 1597, 1497, 1323, 1400, 964, 934, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 3H), 7.44 (t, *J* = 7.3 Hz, 3H), 7.40 (d, *J* = 6.5 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 2H), 4.43 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 138.5, 128.8, 127.6, 127.4, 126.7 (q, J_{C-F} = 3.8 Hz), 124.0, 119.4 (q, J_{C-F} = 32.8 Hz), 112.0, 47.8.

HRMS: Calc. for $C_{14}H_{13}F_3N$ $[M+H]^+$: 252.1000, Obser. 252.0999.

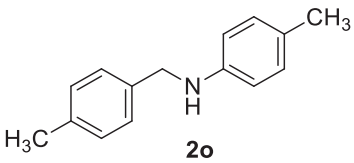
3.8.14 *N*-(4-Methylbenzyl)aniline (2n)



2n

The title compound was obtained as yellow solid. M.p. 47 °C. Yield: 97% (191 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.70. IR (neat): 3434, 3024, 2912, 2755, 1906, 1609, 1513, 1450, 1323, 1120, 980, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (s 1H), 7.21-7.17 (m, 4H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 4.31 (s, 2H), 4.06 (brs, 1H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 136.8, 136.3, 129.3, 129.2, 127.5, 117.5, 112.7, 48.1, 21.0. HRMS: Calc. for $C_{14}H_{16}N$ $[M+H]^+$: 198.1283, Obser. 198.1283.

3.8.15 *N*-(4-Methylbenzyl) 4-methylaniline (2o)

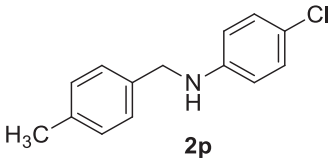


2o

The title compound was obtained as yellow solid. M.p. 56 °C. Yield: 97% (204 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.72. IR (neat): 3452, 3033, 2910, 2753, 1900, 1599, 1453, 1320, 1111, 978, 667 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 6.1 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 4.17 (s, 2H), 3.76 (brs, 1H), 2.26 (s, 3H), 2.15 (s, 3H). ^{13}C

NMR (125 MHz, $CDCl_3$) δ 145.9, 136.7, 136.5, 129.7, 129.2, 127.4, 126.6, 112.9, 48.3, 21.0, 20.3. HRMS: Calc. for $C_{15}H_{18}N$ $[M+H]^+$: 212.1439, Obser. 212.1434.

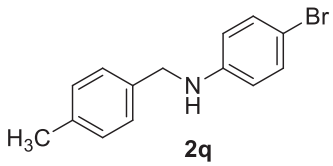
3.8.16 *N*-(4-Methylbenzyl) 4-chlogroaniline (2p)



2p

The title compound was obtained as yellow liquid. Yield: 94% (217 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.71. IR (neat): 3445, 3021, 2907, 1899, 1450, 1306, 989, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.22-7.18 (m, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 4.21 (s, 2H), 3.90 (brs, 1H), 2.16 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 138.1, 132.7, 129.7, 128.6, 127.0, 125.8, 113.0, 47.9, 20.3. HRMS: Calc. for $C_{14}H_{15}ClN$ $[M+H]^+$: 232.0893, Obser. 232.0894.

3.8.17 *N*-(4-Methylbenzyl) 4-bromoaniline (2q)

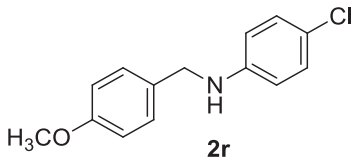


2q

The title compound was obtained as yellow solid. M.p.78-79 °C. Yield: 93% (256 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.72. IR (neat): 3443, 3033, 2934, 1897, 1309, 987, 692 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.16-7.12 (m, 4H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.41 (d, *J* = 8.8 Hz, 2H), 4.16 (s, 2H), 3.94 (brs, 1H), 2.26 (s, 3H). ^{13}C NMR

(125 MHz, $CDCl_3$) δ 147.0, 137.0, 135.7, 131.8, 129.3, 127.3, 114.3, 108.9, 47.9, 21.0. HRMS: Calc. for $C_{14}H_{15}BrN$ $[M+H]^+$: 276.0388, Obser. 276.0389.

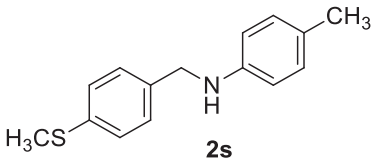
3.8.18 *N*-(4-Methoxylbenzyl) 4-chloroaniline (2r)



2r

The title compound was obtained as yellow solid. M.p. 81 °C. Yield: 95% (278 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.69. IR (neat): 3450, 3031, 2810, 2752, 1876, 1556, 1444, 1334, 967, 670 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 4.14 (s, 2H), 3.90 (brs, 1H), 3.72 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 146.6, 130.8, 129.0, 128.7, 122.0, 114.0, 113.8, 55.2, 47.8. HRMS: Calc. for $C_{14}H_{15}ClNO$ $[M+H]^+$: 248.0842, Obser. 248.0842.

3.8.19 *N*-(4-(Methylthio)benzyl) 4-methylaniline (2s)

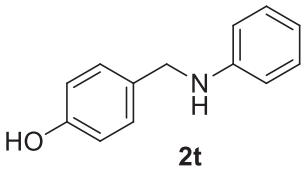


2s

The title compound was obtained as dark yellow liquid. Yield: 96% (233 mg,). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.65. IR (neat): 3429, 3031, 2758, 1865, 1458, 1367, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.17-7.10 (m, 4H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.43

(d, *J* = 8.3 Hz, 2H), 4.13 (s, 2H), 3.73 (brs, 1H), 2.35 (s, 3H), 2.13 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 136.9, 136.5, 129.6, 127.8, 126.8, 126.6, 112.9, 48.0, 20.3, 15.9. HRMS: Calc. for $C_{15}H_{18}NS$ $[M+H]^+$: 244.1160, Obser. 244.1157.

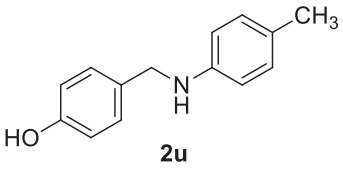
3.8.20 *N*-Phenyl-4-hydroxybenzylamine (2t)



2t

The title compound was obtained as yellow solid. M.p.114-116 °C. Yield: 91% (181 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.69. IR (neat): 3378, 1583, 1508, 1283, 890 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.36 (m, 3H), 7.34-7.28 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 4.43 (brs, 1H), 4.30 (s, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 141.9, 139.4, 128.5, 127.5, 127.1, 116.2, 114.7, 49.4. HRMS: Calc. for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1075, Obser. 200.1071.

3.8.21 4-((*p*-Tolylamino) methyl)phenol (2u)

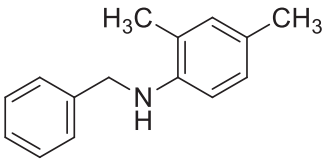


2u

The title compound was obtained as yellow solid. M.p. 90 °C. Yield: 90% (191 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.67. IR (neat): 3348, 1680,

1595, 1284, 892, 592 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 4.53 (brs, 1H), 4.25 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 145.7, 131.3, 129.8, 129.7, 128.9, 127.0, 115.9, 115.4, 113.3, 48.3, 20.3. HRMS: Calc. for $C_{14}H_{16}NO$ $[M+H]^+$: 214.1232. Obser. 214.1228.

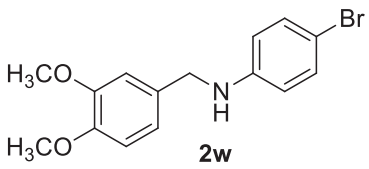
3.8.22 *N*-Benzyl-2, 4-dimethylaniline (2v)



2v

The title compound was obtained as pale yellow liquid. Yield: 93% (196 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.70. IR (neat): 3457, 3009, 2767, 1872, 1458, 1365, 667 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.56-7.43 (m, 5H), 7.08 (t, *J* = 8.2 Hz, 2H), 6.70 (t, *J* = 9.4 Hz, 1H), 4.50 (d, *J* = 7.9 Hz, 2H), 3.88 (brs, 1H), 2.40 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 139.6, 130.9, 128.5, 127.4, 127.3, 127.0, 126.2, 121.9, 110.1, 48.4, 20.2, 17.4. HRMS: Calc. for $C_{15}H_{18}N$ $[M+H]^+$: 212.1439, Obser. 212.1435.

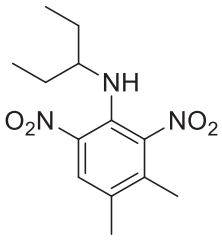
3.8.23 *N*-(4-Bromobenzyl)-3, 4-dimethoxyaniline (2w)



2w

The title compound was obtained as yellow solid. M.p. 108 °C. Yield: 95% (230 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.59. IR (neat) 3432, 2987, 2778, 1890, 1445, 1345, 1080 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.16-7.14 (m, 2H), 6.7 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.42 (d, *J* = 8.8 Hz, 2H), 4.13 (s, 2H), 3.94 (brs, 1H), 3.78 (s, 3H), 3.77(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 148.2, 147.0, 131.8, 131.2, 119.5, 114.3, 111.2, 110.6, 109.0, 55.8, 55.8, 48.0. HRMS: Calc. for $C_{15}H_{17}BrNO_2$ $[M+H]^+$: 322.0443. Obser. 322.0440.

3.8.24 3,4-dimethyl-2,6-dinitro-*N*-(pentan-3-yl)aniline (2x)

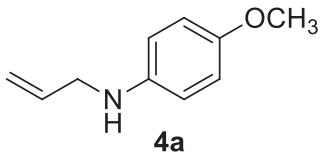


2x

The title compound was obtained as pale yellow solid. M.p. 56-57 °C. Yield: 82% (230 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (85:15), R_f = 0.45. IR (neat) 3345, 2997, 2889, 1683, 1397, 1321 cm^{-1}. ^1H NMR (500 MHz, CDCl3) δ 7.99 (s, 1H), 7.55 (brs, 1H), 3.13-3.01 (m, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 1.51-1.34 (m, 4H), 0.80 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 138.3, 136.9, 134.2,

128.3, 125.5, 57.3, 28.0, 19.3, 15.3, 9.7. HRMS: Calc. for $C_{13}H_{20}N_3O_4$ $[M+H]^+$: 282.1454. Obser. 282.1452.

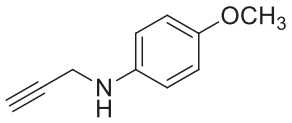
3.8.25 *N*-Allyl 4-methoxyaniline (4a)



4a

The title compound was obtained as yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.58; Yield: 91% (148 mg). IR (neat): 3548, 3474, 1637, 1210, 928, 617 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 6.70 (d, *J* = 8.9 Hz, 2H), 6.52 (d, *J* = 8.9 Hz, 2H), 5.90-5.85 (m, 1H), 5.19 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.07 (dd, *J* = 10.3, 1.4 Hz, 1H), 3.66 (s, 3H), 3.65-3.63 (m, 2H), 3.24 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 142.2, 135.7, 116.0, 114.8, 114.2, 55.7, 47.5. HRMS: Calc. for $C_{10}H_{14}NO$ $[M+H]^+$: 164.1075, Obser. 164.1075.

3.8.26 *N*-Propargyl 4-methoxyaniline (4b)

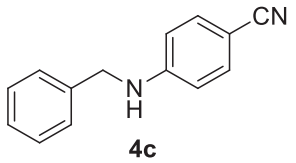


4b

The title compound was obtained as yellow liquid. Yield: 89% (143 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.55. IR (neat): 3200, 2908, 1890, 1540, 1231, 890 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 6.88-6.84 (m, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 2H), 3.76 (s, 3H), 3.72

(brs) 2.27 (t, J = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7, 140.7, 114.9, 114.6, 81.3, 71.1, 55.4, 34.3. HRMS: Calc. for $C_{10}H_{12}NO$ $[M+H]^+$: 162.0919, Obser. 162.0914.

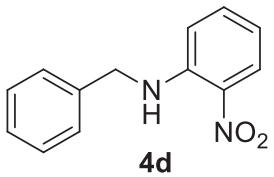
8.27 *N*-(Benzylamino) 4-benzonitrile (4c)



4c

The title compound was obtained as yellow solid. M.p. 62 °C. Yield: (185 mg, 89%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.64. IR (neat): 3330, 2250, 1657, 1090, 658 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.41-7.30 (m, 5H), 6.61 (d, J = 8.8 Hz, 2H), 4.66 (brs, 1H), 4.40 (d, J = 3.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 137.7, 133.6, 128.8, 127.6, 127.2, 120.3, 112.3, 99.0, 47.4. HRMS: Calc. for $C_{14}H_{13}N_2$ $[M+H]^+$: 209.1079, Obser. 209.1075.

3.8.28 *N*-(Benzylamino) 4-nitroaniline (4d)

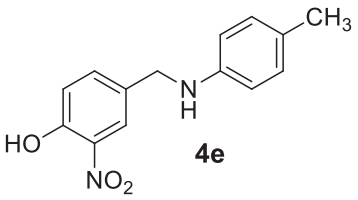


4d

The title compound was obtained as yellow solid. M.p.73-74 °C Yield: 89% (202 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.54. IR (neat): 3470, 1680, 1500, 1230, 720 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (brs, 1H), 8.12-8.10 (m, 1H), 7.29-7.27 (m, 5H), 7.22-7.17

(m, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.59-6.56 (m, 1H), 4.46 (d, *J* = 5.7 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 137.3, 136.1, 132.2, 128.8, 127.6, 126.9, 126.7, 115.6, 114.1, 47.0. HRMS: Calc. for $C_{13}H_{13}N_2O_2$ $[M+H]^+$: 229.0977, Obser. 229.0975.

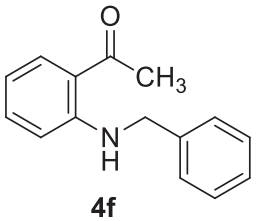
3.8.29 2-Nitro-4-((p-tolylamino)methyl)phenol (4e)



4e

The title compound was obtained as yellow solid. M.p. 132 °C. Yield: 91% (234 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.61. IR (neat): 3386, 1577, 1510, 1385, 567, 750 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.02 (d, *J* = 2.1 Hz, 1H), 7.54-7.51 (m, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.46–6.43 (m, 2H), 4.23 (s, 2H), 3.94 (brs, 1H), 2.16 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 145.0, 136.6, 133.4, 132.3, 129.8, 127.4, 123.2, 120.2, 113.1, 47.2, 20.3. HRMS: Calc. for $C_{14}H_{16}N_2O_3$ $[M+H]^+$: 259.1083. Obser. 259.1079.

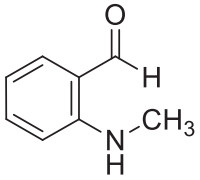
3.8.30 *N*-Benzyl (2-acetoxyaniline) (4f)



4f

The title compound was obtained as yellow solid. M.p. 74 °C. Yield: 90% (202 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.53. IR (neat): 3458, 1695, 1456, 1253, 780 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 9.36 (brs, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.43-7.21 (m, 5H), 6.72-6.68 (m, 2H), 4.50 (d, *J* = 5.7 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.9, 150.8, 138.6, 134.9, 132.6, 128.6, 127.0, 126.9, 117.8, 114.3, 112.1, 46.7, 27.8. HRMS: Calc. for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1232, Obser. 226.1235.

3.8.31 2-Methylamino benzaldehyde (4g)

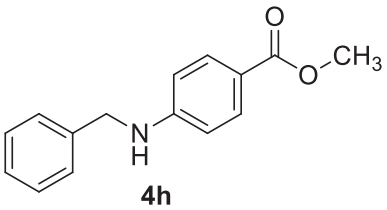


4g

The title compound was obtained as yellow oil. Yield: 85% (114 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.54. IR (neat): 3489, 2823, 2190, 1756, 890 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.27 (brs, 1H), 7.48 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.43-7.28 (m, 1H), 6.72-6.68 (m, 2H), 2.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 151.5, 136.5, 135.7, 118.3, 114.6, 110.3,

29.0. HRMS: Calc. for $C_8H_{10}NO$ $[M+H]^+$: 136.0762, Obser. 136.0759.

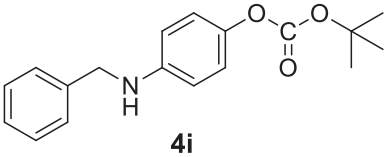
3.8.32 Methyl 4-(benzylamino) benzoate (4h)



4h

The title compound was obtained as pale yellow solid. M.p. 52 °C. Yield: 92% (221 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.62. IR (neat): 3890, 2923, 1740, 1100, 977 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.41-7.36 (m, 4H), 7.34-7.30 (m, 1H), 6.61 (d, *J* = 8.5 Hz, 2H), 4.57 (brs, 1H), 4.41 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 151.7, 138.3, 131.5, 128.7, 127.4, 127.3, 118.6, 111.6, 51.4, 47.6. HRMS: Calc. for $C_{15}H_{16}NO_2$ $[M+H]^+$: 242.1181, Obser. 242.1179.

3.8.33 *N*-[4-(*Tert*-Butoxycarbonyloxy)benzyl] aniline (4i)

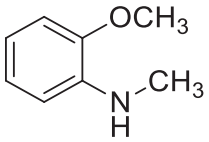


4i

The title compound was obtained as yellow liquid. Yield: 95% (284 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.62. IR (neat): 3356, 2820, 1845, 1890, 1689, 1001 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.23-7.17 (m, 4H), 6.76 (d, *J* = 7.3 Hz, 1H), 6.67-

6.65 (m, 2H), 4.35 (s, 2H), 4.07 (brs, 1H), 1.60 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 150.1, 147.9, 136.9, 129.2, 128.3, 121.3, 117.6, 112.8, 83.5, 47.6, 27.6. HRMS: Calc. for $C_{18}H_{22}NO_3$ $[M+H]^+$: 300.1600. Obser. 300.1598.

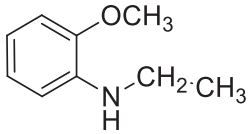
3.8.34 2-Methoxy-*N*-methyl aniline (6a)



6a

The title compound was obtained as yellow liquid. Yield: 93% (127 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.54. IR (neat): 3310, 2923, 1560, 1254, 1102 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.60 (t, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 4.17 (brs, 1H), 3.77 (d, *J* = 0.5 Hz, 3H), 2.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 139.3, 121.3, 116.2, 109.3, 109.2, 55.3, 30.3. HRMS: Calc. for $C_8H_{12}NO$ $[M+H]^+$: 138.0919, Obser. 138.0919.

3.8.35 2-Methoxy-*N*-ethyl aniline (6b)

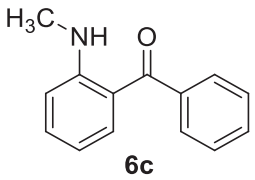


6b

The title compound was obtained as yellow liquid. Yield: (141 mg, 94%). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (90:10), R_f = 0.53. IR (neat): 3330, 2925, 1453, 1566, 1243, 1002, 980 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (t, *J* = 8.3 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.59 (t, *J* = 7.7 Hz,

1H), 6.54 (d, *J* = 7.8 Hz, 1H), 4.03 (brs, 1H), 3.77 (s, 3H), 3.10 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 138.4, 121.3, 116.2, 109.8, 109.3, 55.3, 38.1, 14.8. HRMS: Calc. for $C_9H_{14}NO$ $[M+H]^+$: 152.1075, Obser. 152.1073.

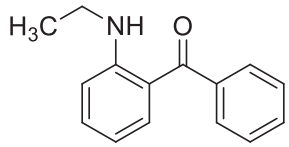
3.8.36 (2-Methylamino) phenyl)(phenyl) methanone (6c)



6c

The title compound was obtained as yellow liquid. Yield: 87% (183 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.63. IR (neat): 3449, 2972, 1675, 1533, 899 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 7.63-7.61 (m, 2H), 7.55-7.48 (m, 2H), 7.47-7.41 (m, 3H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.60-6.53 (m, 1H), 3.00 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 152.7, 140.6, 135.4, 135.0, 130.6, 128.9, 128.0, 117.2, 113.6, 111.0, 29.4. HRMS: Calc. for $C_{14}H_{14}NO$ $[M+H]^+$: 212.1075, Obser. 212.1077.

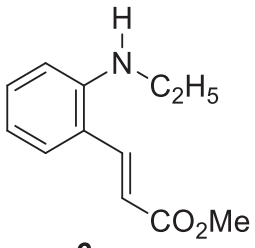
3.8.37 (2-Ethylamino) phenyl)(phenyl) methanone (6d)



6d

The title compound was obtained as yellow liquid. Yield: 86% (195 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.65. IR (neat): 3452, 2980, 1680, 1567, 980 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 7.64-7.63 (m, 2H), 7.55-7.44 (m, 4H), 7.42-7.39 (m, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.55 (t, *J* = 7.5 Hz, 1H), 3.33 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 151.7, 140.5, 135.4, 134.9,130.5, 128.9, 127.9, 116.9, 113.4, 111.4, 37.2, 14.4. HRMS: Calc. for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1232, Obser. 226.1233.

3.8.38 (*E*)-Methyl 3-(2-(ethylamino)phenyl)acrylate (6e)

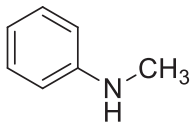


6e

The title compound was obtained as dark brown liquid. Yield: 89% (182 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.58. IR (neat): 3450, 2980, 1675, 1750, 1278, 899 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 15.7 Hz, 1H), 7.37 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.27 (td, *J* = 8.0,1.6 Hz, 1H), 6.73-6.65 (m, 2H), 6.34 (d, *J* = 15.7 Hz, 1H), 3.93 (brs, 1H), 3.81 (s, 3H), 3.21 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* =

7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 146.8, 140.4, 131.6, 128.1, 119.5, 117.6, 117.1, 111.3, 51.6, 38.4, 14.7. HRMS: Calc. for $C_{12}H_{16}NO_2$ $[M+H]^+$: 206.1181, Obser. 205.1178.

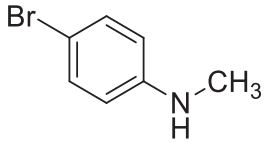
3.8.39 *N*-Methyl aniline (6f)



6f

The title compound was obtained as yellow liquid. Yield: 93% (99 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.66. IR (neat): 3467, 1598, 1578, 1315, 668 cm^{-1} cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.9 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 2H), 3.54 (brs, 1H), 2.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 129.1, 117.1, 112.3, 30.6. HRMS: Calc. for $C_7H_{10}NO$ $[M+H]^+$: 108.0813, Obser. 108.0807.

3.8.40 4-Bromo *N*-methyl aniline (6g)

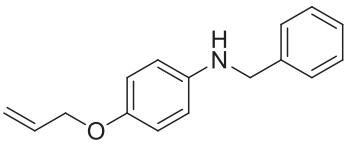


6g

The title compound was obtained as yellow solid**.** M.p. 181 °C. Yield: 91% (169 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.64. IR (neat): 3450, 2943, 1592, 1470, 1181, 813 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.1 Hz, 2H), 6.51 (d, *J* = 8.9 Hz, 2H), 3.76 (brs, 1H), 2.83

(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 131.8, 113.9, 108.7, 30.6. HRMS: Calc. for C_7H_9BrN $[M+H]^+$: 185.9918, Obser. 185.9913.

3.8.41 *N*-(4-(4(Allyloxy)benzyl)aniline (6h)



6h

The title compound was obtained as yellow liquid. Yield: 94% (224 mg). The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.66. IR (neat): 3385, 2900, 2856, 1468, 1460, 1294, 1021 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.7 Hz, 2H), 7.23 (t, *J* = 8.5, 7.4 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.69 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.15-6.07 (m, 1H), 5.47 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.36-5.33 (m, 1H), 4.58 (dt, *J* = 5.3, 1.5 Hz, 2H), 4.29 (s, 2H), 3.98 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 148.1, 133.3, 131.5, 129.2, 128.7, 117.6, 117.5, 114.8, 112.8, 68.8, 47.8. HRMS: Calc. for $C_{16}H_{19}NO$ $[M+H]^+$: 240.1388, Obser. 240.1385.

3.9 Spectral Data for Few Products

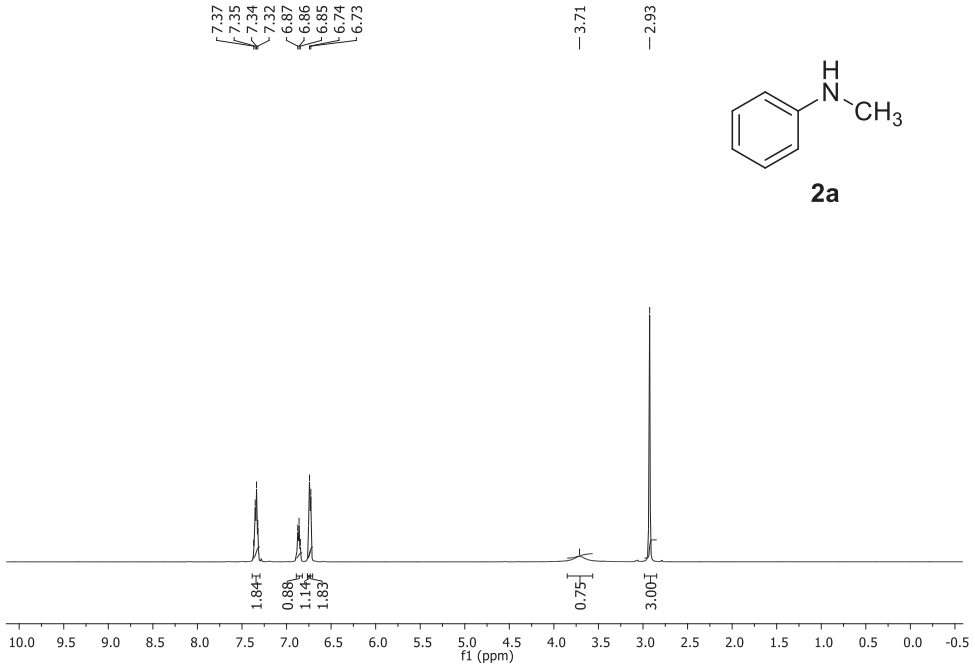


Figure 3.1 ^{1}H NMR of product **2a** in $CDCl_3$.

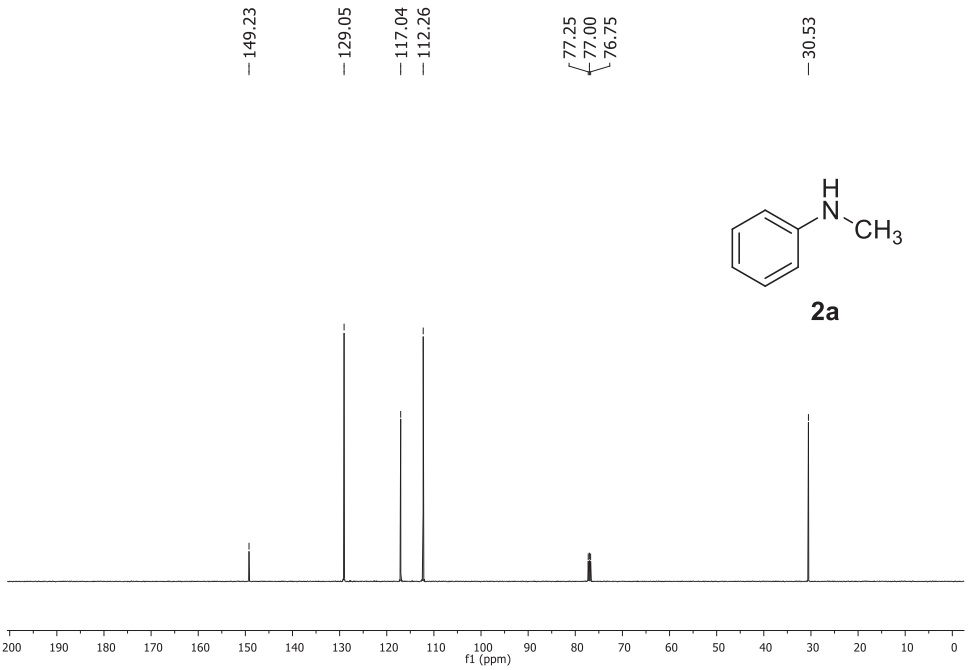


Figure 3.2 ^{13}C NMR of product **2a** in $CDCl_3$.

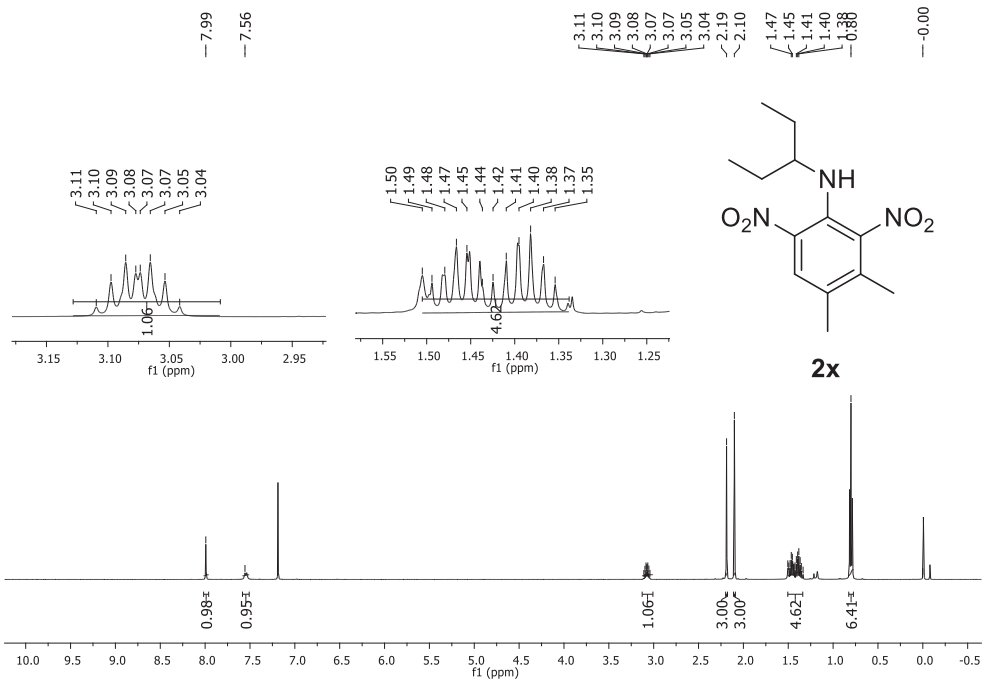


Figure 3.3 ^{1}H NMR of product **2x** in $CDCl_3$.

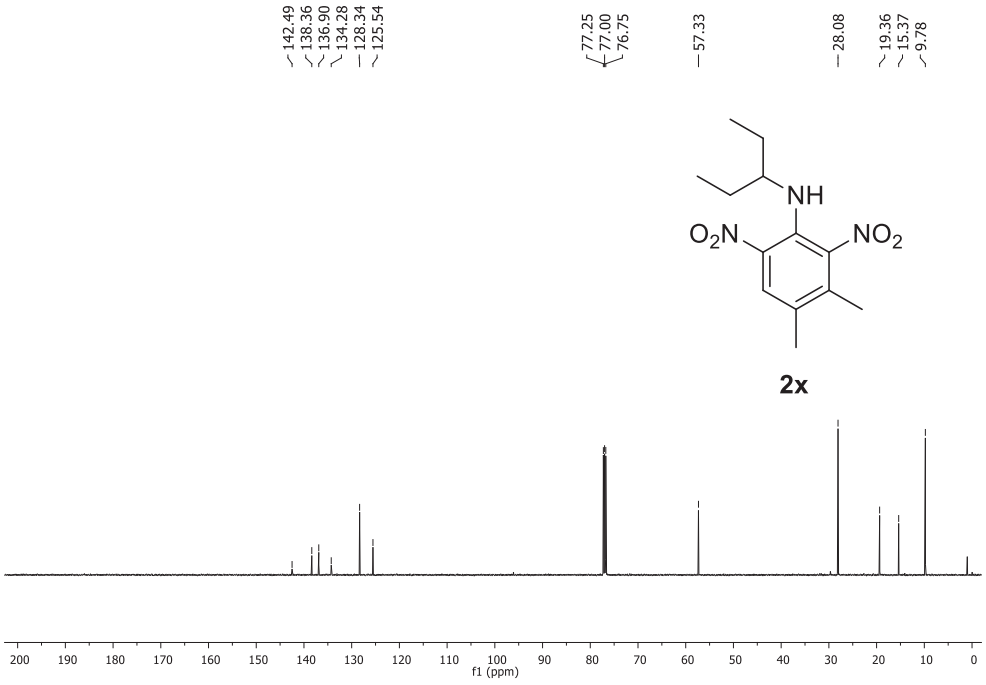


Figure 3.4 ^{13}C NMR of product **2x** in $CDCl_3$.

3.10 References

[1] J.-P. Anselme, The organic chemistry of *N*-nitrosamines: A brief review, ACS, Washington, DC, 1979**.**

[2] R. N. Loeppky, C. J. Michejda, Nitrosamines and related *N*-nitroso compounds: chemistry and biochemistry, ACS, Washington, DC 1994

[3] R. N. Loeppky, J. R. Outram, *N*-nitroso compounds: Occurrence and biological Effects, IARC Scientific Publishers: Lyon, 1982.

[4] D. L. Browne, J. P. A. Harrity, "Recent developments in the chemistry of sydnones," *Tetrahedron*, **66**(2010**)** 553-568.

[5] R. L. Hinmap, K. L. Hamm, "Synthesis of some 1,1-dibenzylhydrazines," *Journal of Organic Chemistry,* **23(**1958**)** 529-531.

[6] F. W. Schueler, C. Hanna, "A synthesis of unsymmetrical dimethyl hydrazine using lithium aluminum hydride," *Journal of American Chemical Society*, **73**(1951**)** 4996.

[7] F. H. C. Stewart, "The chemistry of the sydnones," *Chemical Reviews,* **64**(1964) 129-147.

[8] D. Seebach, D. Enders, "Umpolung of amine reactivity. Nucleophilic α-(secondary amino)-alkylation *via* metalated nitrosamines," *Angewandte Chemie International Edition,* **14**(1975**)** 15-32.

[9] L. K. Keefer, C. H. Fodor, "Facile hydrogen isotope exchange as evidence for an alpha-nitrosamino carbanion," *Journal of American Chemical Society,* **92**(1970**)** 5747-5748.

[10] B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, "Rhodium (III)-catalyzed *N*-nitroso-directed C-H olefination of arenes. High-yield, versatile coupling under mild conditions," *Journal of American Chemical Society*, 135(**2013)** 468-473.

[11] J. Chen, P. Chen, C. Song, J. Zhu, "Rhodium(III)-catalyzed *N*-nitroso-directed C-H addition to ethyl 2-oxoacetate for cycloaddition/fragmentation synthesis of indazoles," *Chemistry: A European Journal*, **20**(2014) 14245-14249.

[12] J. W. Dong, Z. J. Wu, Z. Y. Liu, P. Liu, P. Sun, "Rhodium(III)-catalyzed direct cyanation of aromatic C-H bond to form 2-(alkylamino)benzonitriles using *N*-nitroso as directing group," *Journal of Organic Chemistry* , **80**(2015) 12588-12593.

[13] T. Gao, P. Sun, "Palladium-catalyzed *N*-nitroso-directed C-H alkoxylation of arenes and subsequent formation of 2-alkoxy-*N*-alkylarylamines," *Journal of Organic Chemistry,* **79**(2014) 9888- 9893.

[14] D. D. Li, Y. X. Cao, G. W. Wang, "Palladium-catalyzed *ortho*-acyloxylation of *N*-nitrosoanilines *via* direct sp^2 C-H bond activation," *Organic and Biomolecular Chemistry*, **13**(2015) 6958-6964.

[15] J. Wang, M. Wang, K. Chen, S. Zha, C. Song, J. Zhu, "C-H activation-based traceless synthesis *via* electrophilic removal of a directing group. Rhodium(III)-catalyzed entry into indoles from *N*-Nitroso and α-Diazo-β-keto compounds," *Organic Letters*, **18**(2016**)** 1178-1181.

[16] B. Liu, C. Song, C. Sun, S. Zhou, J. Zhu, "Rhodium(III)-catalyzed indole synthesis using *N*-*N* bond as an internal oxidant," *Journal of American Chemical Society*, **135**(2013) 16625-16631.

[17] Y. N. Wu, L.-J. Feng, X. Lu, F. Y. Kwong, H.-B. Luo, "Palladium-catalyzed oxidative C-H bond acylation of *N*-nitrosoanilines with toluene derivatives: A traceless approach to synthesize *N*-alkyl-2-aminobenzophenones," *Chemical Communications,* **50**(2014) 15352-15354.

[18] Y. Wu, L. Sun, Y. Chen, Q. Zhou, J.-W. Huang, H. Miao, H.-B. Luo, "Palladium-catalyzed decarboxylative acylation of *N*-nitrosoanilines with α-oxocarboxylic acids," *Journal of Organic Chemistry*, **81**(2016) 1244-1250.

[19] F. Xie, Z. Qi, S. Yu, X. Li, "Rh(III)- and Ir(III)-Catalyzed C-H alkynylation of arenes under chelation assistance," *Journal of American Chemical Society*, **136**(2014**)** 4780-4787.

[20] E. L. Teuten, R. N. Loeppky, "The mechanistic origin of regiochemical changes in the nitrosative *N*-dealkylation of *N*,*N*-dialkyl aromatic amines," *Organic and Biomolecular Chemistry,* **3**(2005) 1097-1108.

[21] J. Zhang, J. Jiang, Y. Li, X. Wan, "Iodide-catalyzed synthesis of *N*-nitrosamines *via* C-N cleavage of nitromethane," *Journal of Organic Chemistry,* **78(**2013) 11366-11372.

[22] R. N. Leoppky, W. Tomasik, "Stereoelectronic effects in tertiary amine nitrosation: nitrosative cleavage *vs* aryl ring nitration," *Journal of Organic Chemistry*, **48**(1983**)** 2751-2757.

[23] Y. Z. Chen, Y. C. Zhao, M. Han, C. B. Ye, M. H. Dang, G. W. Chen, "Safe, efficient and selective synthesis of dinitro herbicides *via* a multifunctional continuous-flow microreactor: One-step dinitration with nitric acid as agent," *Green Chemistry*, **15**(2013) 91-94.

[24] X.-H. Du, D.-W. Luo, Z.-Y. Xu, "A novel synthesis of pendimethalin," *Organic Preparations and Procedures International***, 41** (2009**)** 249-252.

[25] B. P. Cho, L. R. Blankenship, J. D. Moody, D. R. Doerge, F. A. Beland, S. J. Culp, "Synthesis and characterization of 4′-amino and 4′-nitro derivatives of 4-*N*,*N*-dimethylaminotriphenylmethane as precursors for a proximate malachite green metabolite," *Tetrahedron*, **56**(2000) 7379-7388.

[26] E. C. S. Jones, J. Kenner, "The analogy between the benzidine change and the dissociation of oxides of nitrogen. A new reagent for the recovery of secondary bases from nitrosoamines and for purifying amines," *Journal of the Chemical Society,* (1932) **7**11-715.

[27] S. Kano, Y. Tanaka, E. Sugino, S. Shibuya, S. Hibino, "Reductive denitrosation of nitrosamines to secondary amines with metal halide/sodium borohydride," *Synthesis,* **9**(1980) 741-742.

[28] H. Alper, J. T. Edward, "Reactions of iron pentacarbonyl with compounds containing the N-O linkage," *Canadian Journal of Chemistry,* **48**(1970) 1543-1549.

[29] D. Enders, T. Hassel, R. Pieter, B. Renger, D. Seebach, "Reductive denitrosation of nitrosamines to secondary amines with Hydrogen/Raney nickel," *Synthesis,* (1976) 548-550.
[30] P. G. Andersson, I. J. Munslow, Modern Reduction Methods; WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008**.**
[31] M. Hudlicky, Reductions in Organic Chemistry; Ellis Horwood Limited, England, 1984.
[32] G. L. Larson, Silicon-Based Reducing Agents in Gelest/Silicon Compounds in Silanes and Silicones Handbook, 2013**.**
[33] L. Benati, G. Bencivenni, R. Leardini, D. Nanni, M. Minozzi, P. Spagnolo, R. Scialpi, G. Zanardi, "Reaction of azides with dichloroindium hydride: Very mild production of amines and pyrrolidin-2-imines through possible Indium-aminyl radicals," *Organic Letters,* **8**(2006) 2499-2502.
[34] R. J. Rahaim, R. E. Maleczka, "Pd-catalyzed silicon hydride reductions of aromatic and aliphatic nitro groups," *Organic Letters,* **7**(2005**)** 5087-5090.
[35] O. Y. Lee, K. L. Law, C. Y. Ho, D. Yang, "Highly chemoselective reductive amination of carbonyl compounds promoted by $InCl_3/Et_3SiH$/MeOH system," *Journal of Organic Chemistry,* **73**(2008**)** 8829-8837.
[36] A. Sugie, T. Somete, K. Kanie, A. Muramatsu, A. Mori, "Triethylsilane as a mild and efficient reducing agent for the preparation of alkane thiol-capped gold nanoparticles," *Chemical Communications,* (2008) 3882-3884.
[37] P. Chaudhary, S. Gupta, N. Muniyappan, S. Sabiah J. Kandasamy, "An efficient synthesis of *N*-nitrosamines under solvent, metal and acid free conditions using *tert*-butyl nitrite," *Green Chemistry,* **18**(2016) 2323-2330.
[38] R. Panchadhayee, A. K. Misra, "Regioselective reductive ring opening of benzylidene acetals using triethylsilane and iodine," *Synlett,* **8**(2010**)** 1193-1196.
[39] X. L. Zhang, P. Yu, Y. W. Wu, Q. P. Wu, Q. S. Zhang, "Reductive amination of acetals by anilines in the presence of triethylsilane and iodine," *Journal of Chemical Research.* **38**(2014) 261-264.
[40] D. N. Kursanov, Z. N. Parnes, N. M. Loim, "Applications of ionic hydrogenation to organic synthesis," *Synthesis*, **9**(1974**)** 633-651.
[41] W. P. Weber, Silicon Reagents for Organic Synthesis, 1st Edition, Springer, New York, 1983**.**
[42] Z. Jia, M. Liu, X. Li, A. S. C. Chan, C.-J. Li, "Highly efficient reduction of aldehydes with silanes in water catalyzed by silver," *Synlett*, **24**(2013**)** 2049-2056.
[43] V. Botla, C. Barreddi, R. V. Daggupati, C. Malapaka, "Base-oxidant promoted metal-free *N*-demethylation of arylamines," *Journal of Chemical Research***,** **128**(2016) 1469-1473.
[44] Z. Ling, L. Yun, L. Liu, B. Wu, X. Fu, "Aerobic oxidative *N*-dealkylation of tertiary amines in aqueous solution catalyzed by rhodium porphyrins," *Chemical Communications,* **49**(2013) 4214-4216.

[45] A. Vlasceanu, M. Jessing, J. P. Kilburn, "BN/CC isosterism in borazaronaphthalenes towards phosphodiesterase 10A (PDE10A) inhibitors," *Bioorganic and Medicinal Chemistry,* **23**(2015) 4453-4461.

[46] B. Alcaide, P. Almendros, J. M. Alonso, "Ruthenium catalyzed chemoselective *N*-allyl cleavage: Novel Grubbs carbene mediated deprotection of allylic amines," *Chemistry: A European Journal*, **9**(2003) 5793-5799.

[47] M. Adinolfi, A. Iadonisi, A. Ravida, M. Schiattarella, "Efficient and direct synthesis of saccharidic 1,2-ethylidenes, orthoesters, and glycals from peracetylated sugars *via* the *in situ* generation of glycosyl iodides with I_2/Et_3SiH," *Tetrahedron Letters*, **44**(2003) 7863-7866.

[48] M. Adinolfi, G. Barone, A. Iadonisi M. Schiattarella, "Iodine/Triethylsilane as a convenient promoter system for the activation of disarmed glycosyl trichloro- and *N*-(phenyl)trifluoroacetimidates," *Synlett*, **2**(2002) 269-270.