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An Efficient Metal-Free Method for the Denitrosation of Aryl *N*-Nitrosamines at Room Temperature

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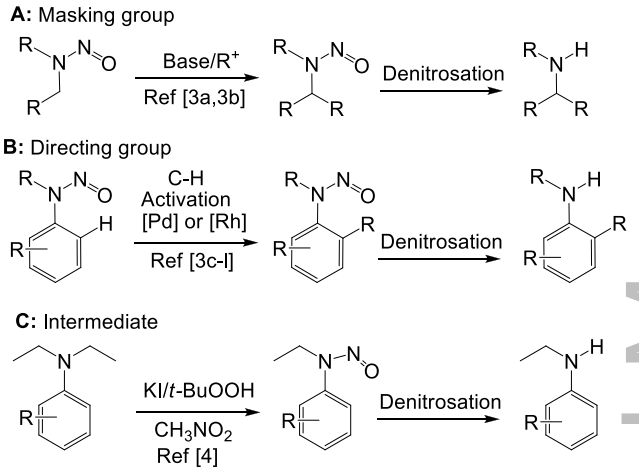
A simple and practical method for the denitrosation of aryl *N*-nitrosamines to secondary amines is reported under metal-free conditions using iodine and triethylsilane. Several reduction-susceptible functional groups such as alkene, alkyne, nitrile, nitro, aldehyde, ketone and ester were found to be very stable during the denitrosation, which is remarkable. Broad substrate scope, room temperature reactions and excellent yields are the additional features of the current methodology.

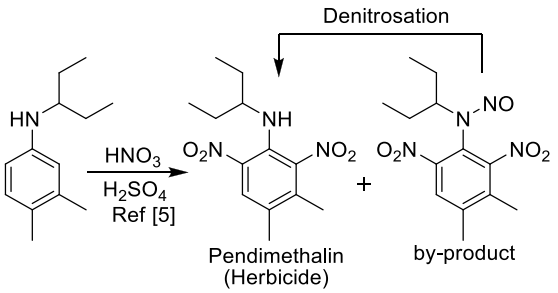
Keywords: *N*-nitrosamine, denitrosation, metal-free; triethylsilane, iodine, green chemistry

N-Nitrosamines have been known since the nineteenth century and received considerable attention in chemistry and biology.[1] In organic synthesis, *N*-nitrosamines have been used not only as synthetic intermediates[2] but also used as masking groups and directing groups (Scheme 1).[3] For example, secondary amines can be masked as *N*-nitrosamines to perform electrophilic substitutions selectively at the α-carbon (Scheme 1, **A**).[3a,b] Recently, *N*-nitrosamine directed C–H bond activation reactions have emerged as a powerful method for the synthesis of *ortho*-functionalized aniline compounds (Scheme 1, **B**).[3c-l] On the other hand, *N*-nitrosamines are the intermediate in the dealkylation of *N*, *N*-disubstituted anilines (Scheme 1, **C**).[4] While many chemical reactions employ *N*-nitrosamine intermediates, they are also often formed as major side products.[5] For instance, *N*-nitrosamine is obtained as the major side product during the synthesis of an important herbicide, pendimethalin (Scheme 2).[5a]

In all the above reactions, denitrosation of *N*-nitrosamine is the key step to generate active amine compounds for further chemical and biological applications.[3c,f,g,k,4a,b,5a] However, only a limited literature exists for the denitrosation of *N*-nitrosamines, all of which involve metal based reducing agents. For example, CuCl/HCl,[3c,6] $NiCl_2/NaBH_4$,[3c,7] $Fe(CO)_5$,[3c,8] Raney-Ni/H_2,[3c,9] Fe/NH_4Cl[3f,k] and Zn/NH_4Cl[3g] have been utilized for the denitrosation process.



Scheme 1. Applications of *N*-nitrosamines in various transformations.

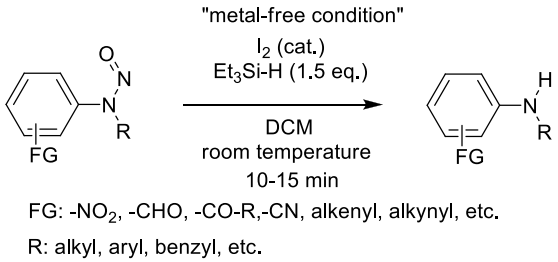


Scheme 2. Formation of *N*-nitrosamine as the by-product.

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 are known for reducing other functional groups such as nitro, nitrile, alkene, alkyne, aldehyde, ketone, etc.[10] Moreover, all these methods suffer from at least one of the following additional drawbacks such as the requirement for excess reagents, high reaction

temperatures, harsh reaction conditions, longer reaction times, 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.[11] Triethylsilane is inexpensive, commercially available and considered to be a good alternative to other more toxic reducing agents.[11a,12] To the best of our knowledge organosilanes have not been explored in denitrosation reactions. In continuation of our previous works on *N*-nitrosamine chemistry [2b,13], here we report an efficient method for the denitrosation of aryl-*N*-nitrosamines using an iodine-triethylsilane system (Scheme 3).

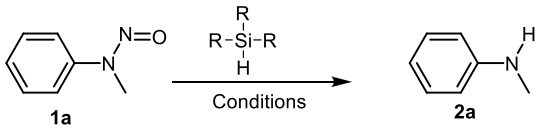


Scheme 3. Denitrosation of *N*-nitrosamines.

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 1). A negligible amount of formation of denitrosated product was observed (*i.e.* secondary amine) in different solvents including dichloromethane, acetonitrile and methanol (Table 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,[14] reductive amination of acetals,[15] etc.[16,17] Thus, a catalytic amount of iodine (*i.e.* 10 mol%) was introduced in the denitrosation reactions with triethylsilane (Table 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 1, entry 4). Further, the denitrosation reaction was tested with varying amounts of iodine and triethylsilane in dichloromethane (Table 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 1, entry 9). It may also be noted that in the absence of triethylsilane no reaction was observed (Table 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 1, entries 13-14). 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 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 1, entries 17-18).

Table 1. Optimization of denitrosation under different conditions.[a]



1a **2a**

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.

With optimized conditions in hand, the investigation of denitrosation of various *N*-nitrosamines was undertaken using I_2/Et_3SiH at room temperature (Table 2). Denitrosation of *N*-nitroso *N*-alkyl/aryl anilines was achieved in excellent yields (*i.e.* 95-97%) within 10 mins at room temperature (Table 2, entries **2b**-**2d**). Sterically hindered *N*-isopropyl, *N*-

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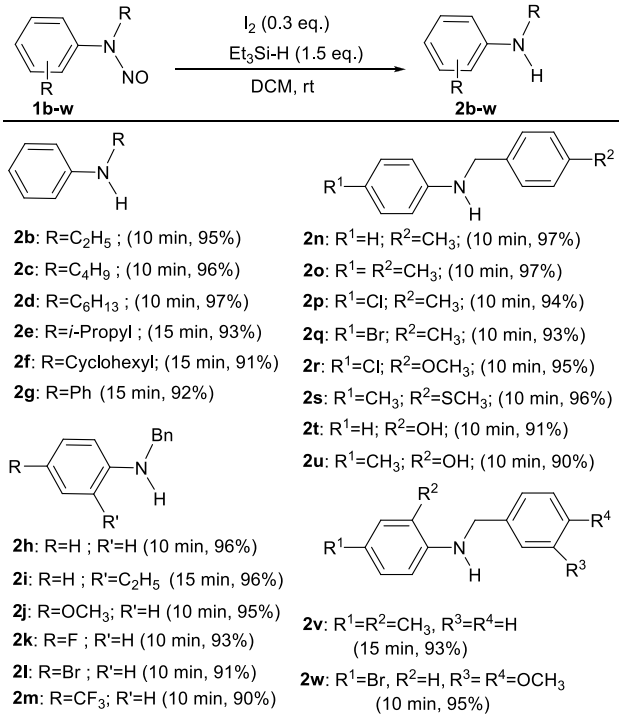
cyclohexyl and *N*-phenyl aniline derivatives also denitrosated with similar efficiency and provided >91% yield (Table 2, **2e**-**2g**). Further, denitrosation of various *N*-nitroso *N*-benzyl anilines with electron donating and withdrawing substituents was attempted under optimized conditions (Table 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 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 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.

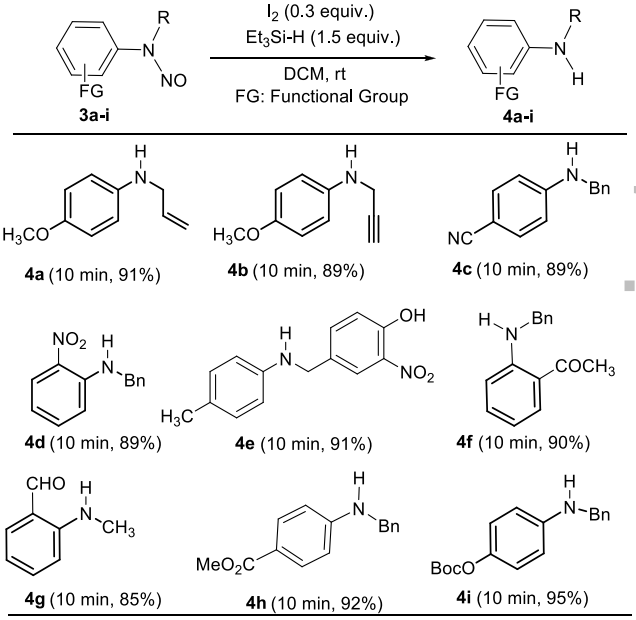
Table 2. Denitrosation of *N*-nitrosamines using iodine-triethylsilane.[a,b]



[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.

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). Olefin, alkyne and nitrile functionalized *N*-nitrosamines underwent denitrosation efficiently without affecting double bond and triple bonds (Table 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.[10b] Similarly, the nitro group is susceptible to reduction[10] 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, **4d** and **4e**), which is remarkable.

Table 3. Denitrosation of functionalized *N*-nitrosamines using iodine-triethylsilane.[a,b]



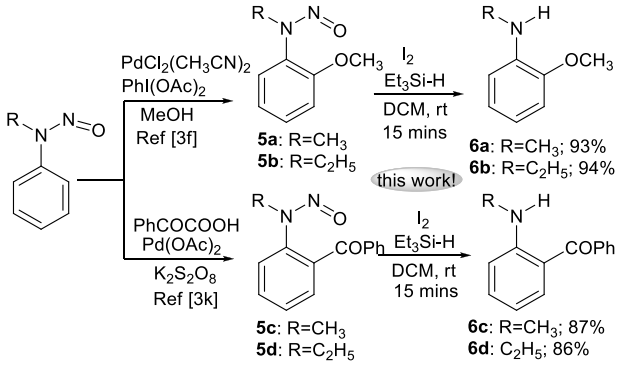
[a]Reaction conditions: *N*-nitrosamine (1 mmol), triethylsilane (1.5 eq.) and iodine (0.3 eq.) were stirred in dichloromethane (3 mL) at room temperature. [b]Isolated yields.

Carbonyl functionalities such as those in aldehydes and ketones 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.[18] Therefore, denitrosation of carbonyl-functionalized *N*-nitrosamines was investigated with the triethylsilane-iodine system under optimized conditions.

Remarkably, aldehyde, ketone and ester functional groups found to be intact while selective denitrosation was achieved in high yields (Table 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, **4i**).

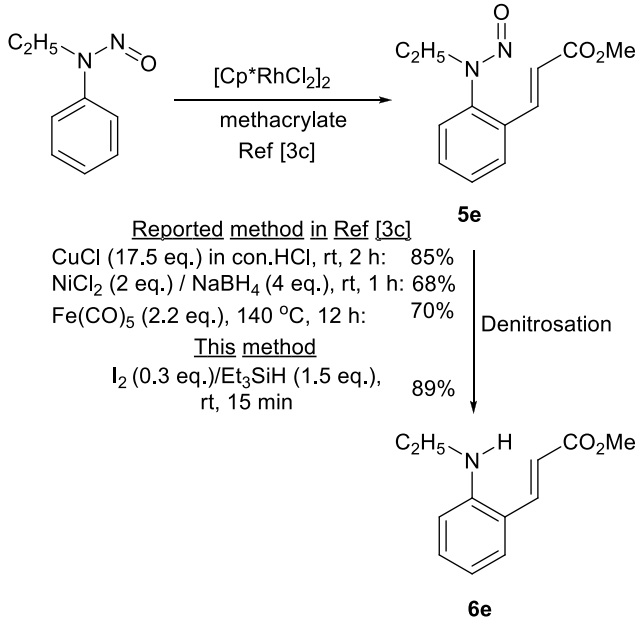
After an extensive study of denitrosation with a variety of substrates, we utilized the current methodology in different useful reactions. Palladium catalyzed *N*-nitrosamine directed *ortho*-methoxylation and *ortho*-acylation of anilines have been recently reported (Scheme 4).[3f,3k] The resulting *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.[3f,3k]



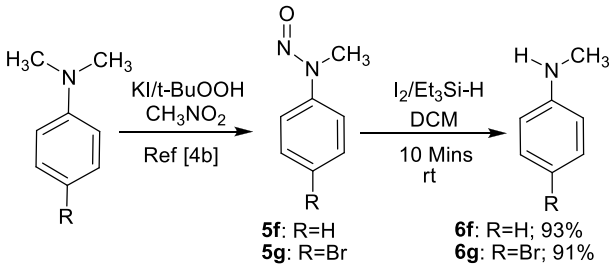
Scheme 4. Palladium catalyzed C-H activation followed by denitrosation.

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 5).[3c] 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 mins at room temperature.



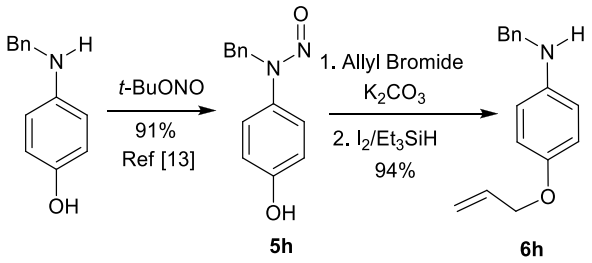
Scheme 5. Rhodium catalyzed C-H activation followed by denitrosation.

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[4b] (Scheme 6) and subjected to denitrosation with I_2/Et_3SiH. The reaction yielded the corresponding secondary amines **6f** and **6g** in >91% yields in 10 mins. We believe that this new process will be an efficient alternative route for the previously reported oxidative dealkylation methods.[19]



Scheme 6. Nitrosative dealkylation of *tert*-amines.

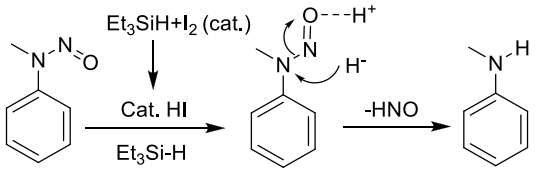
Further, we utilized the nitroso moiety as a "protecting group" for secondary amines. For this study, we have synthesized *N*-benzyl 4-hydroxy aniline and attempted for *O*-allylation. At first, secondary amine was selectively converted to *N*-nitrosamine **5h** in high yield using *tert*-butyl nitrite (Scheme 7). 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.[20]



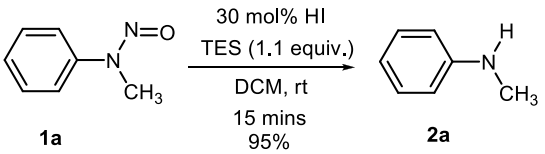
Scheme 7. *N*-Nitroso moiety as protecting group in organic synthesis.

Although, the mechanism of the denitrosation reaction is unclear, we believe that the reaction may proceed through following mechanism as shown in Scheme 8. Iodine reacts with triethylsilane to form hydroiodic acid (HI),[16,17] which is expected to catalyze the reaction actively. The H^+ ion coordinates with the nitroso group while triethylsilane delivers the hydride ion to form a secondary amine.[18a] 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 1, entries 4, 8 and 9). This may be due to increase in the concentration of hydroiodic acid (HI) in the reaction. To further 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 (Scheme 9). The reaction proceeds smoothly to yield the desired product **2a** in 95% yield in 15 mins. However, other acids such as

hydrobromic acid (HBr) and hydrochloric acid (HCl) provide the desired product in low yields (see the Supporting Information).



Scheme 8. Proposed mechanism for the denitrosation reaction.



Scheme 9. Denitrosation reaction catalyzed by hydroiodic acid.

In summary, 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.

Experimental Section

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 x 25 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated and subjected for column chromatography (SiO_2, eluent: Hexane/ethyl acetate) to obtain corresponding pure substituted secondary amines.

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