# Highly Chemo- and Regioselective Reduction of Aromatic Nitro Compounds Using the System Silane/Oxo-Rhenium Complexes

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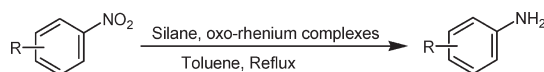
The reduction of aromatic nitro compounds to the corresponding amines with silanes catalyzed by high valent oxo-rhenium complexes is reported. The catalytic systems $PhMe_2SiH/ReIO_2(PPh_3)_2$ (5 mol %) and $PhMe_2SiH/ReOCl_3(PPh_3)_2$ (5 mol %) reduced efficiently a series of aromatic nitro compounds in the presence of a wide range of functional groups such as ester, halo, amide, sulfone, lactone, and benzyl. This methodology also allowed the regioselective reduction of dinitrobenzenes to the corresponding nitroanilines and the reduction of an aromatic nitro group in presence of an aliphatic nitro group.

Introduction

The selective reduction of aromatic nitro compounds is a useful reaction for the synthesis of amines, important intermediates in the production of many pharmaceuticals, agrochemicals, dyes, polymers, photographic and rubber materials, and chelating agents.

Numerous methods have been developed to accomplish this transformation including catalytic hydrogenation,[1] sodium borohydride/catalyst,[2] hydrazine/catalyst,[3] and metals such as iron, tin, or zinc.[4] Over the last years, a variety of other chemical systems such as $Mo(CO)_6$/DBU,[5] $Pd(OAc)_2$/PMHS,[6] Sm/I_2,[7] Sm/1,1′-dioctyl-4,4′-bipyridinium dibromide,[8] Sm/NH_4Cl,[9] Cu nanoparticles/$HCOONH_4$,[10] $S_8/NaHCO_3$,[11] and HI[12] have been reported.

Enzymatic reduction of aromatic nitro compounds with molybdoenzymes is believed to proceed by oxygen atom transfer from the nitrogen center to the $Mo^{IV}O$ center of the enzyme. The $Mo^{VI}O_2$ center thus formed is then regenerated by one of a variety of physiological reducing agents via coupled electron−proton transfers.[13]

However, most of the synthetic methods lack the desired chemoselectivity over other functional groups that are often present in the substrates such as alkene, halide, benzyl, and nitrile and also the desired regioselectivity in the reduction of

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TABLE 1. Reduction of Methyl 4-Nitrobenzoate with Dimethyl-phenylsilane Catalyzed by High-Valent Oxo-Rhenium Complexes[a]
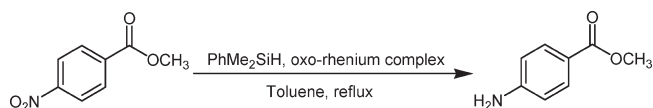
entry	catalyst	catalyst (mol %)	time	conversion[b] (%)
1	ReIO$_2$(PPh$_3$)$_2$	5	1 h	100
2	ReOCl$_3$(PPh$_3$)$_2$	5	20 min	100
3	ReIO$_2$(PPh$_3$)$_2$	1	22 h	84
4	ReOCl$_3$(dppm)	5	20 h	100
5	Re$_2$O$_7$	5	20 h	91
6	MTO	5	18 h	40
7	without catalyst		23 h	no reaction

[a]All reactions were carried out with 1.0 mmol of nitro compound and 360 mol % of silane. [b]Conversion was determined by ^{1}H NMR.

dinitro compounds. In addition, reduction of aromatic nitro compounds often stops at an intermediate stage, yielding hydroxylamine, hydrazines, and azoarenes. Due to the high importance of selective reduction of aromatic nitro compounds, the search for alternative efficient and highly chemo- and regioselective methods remains an important target in organic synthesis.

During our previous works developing novel applications of high valent oxo-complexes as catalysts for organic reductions,[14] we observed the selective reduction of the nitro group of methyl 4-nitrobenzoate with PhSiH$_3$ catalyzed by MoO$_2$Cl$_2$ (5 mol %) (eq 1).[14e] This result suggests that the system silane/high valent oxo-complexes could be appropriate for the deoxygenation of aromatic nitro compounds.
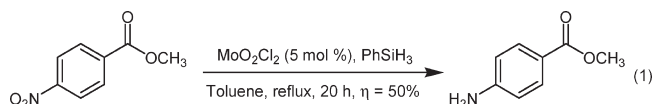

In this paper, we report a novel highly chemo- and regioselective reduction of aromatic nitro groups with silanes catalyzed by high valent oxo-rhenium complexes.

Results and Discussion

Initially we studied the reduction of the test substrate methyl 4-nitrobenzoate catalyzed by high valent oxo-rhenium complexes ReIO$_2$(PPh$_3$)$_2$, ReOCl$_3$(PPh$_3$)$_2$, ReOCl$_3$-(dppm), Re$_2$O$_7$, and MTO, with different silanes, and using several solvents, in order to assess the best reaction conditions (Tables 1–3). The progress of the reactions was monitored by thin-layer chromatography and by ^{1}H NMR.

The most active catalysts were ReIO$_2$(PPh$_3$)$_2$ and ReOCl$_3$-(PPh$_3$)$_2$ and the least effective catalysts were Re$_2$O$_7$ and MTO as summarized in Table 1. The reduction of methyl 4-nitrobenzoate with dimethylphenylsilane in the presence of 5 mol % of the catalysts ReIO$_2$(PPh$_3$)$_2$ and ReOCl$_3$(PPh$_3$)$_2$

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TABLE 2. Reduction of Methyl 4-Nitrobenzoate with Different Silanes Catalyzed by ReIO$_2$(PPh$_3$)$_2$[a]
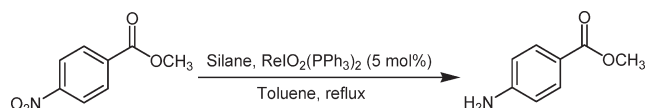
entry	silane	silane (mol %)	time	conversion[b] (%)
1	PhMe$_2$SiH	360	1 h	100
2	PhSiH$_3$	120	45 min	100
3	Et$_3$SiH	360	3 h	100
4	PMHS	390	18 h	100
5	Ph$_3$SiH	360	24 h	17

[a]All reactions were carried out with 1.0 mmol of nitro compound and 5 mol % of ReIO$_2$(PPh$_3$)$_2$. [b]Conversion was determined by ^{1}H NMR.

TABLE 3. Reduction of Methyl 4-Nitrobenzoate in Different Solvents[a]
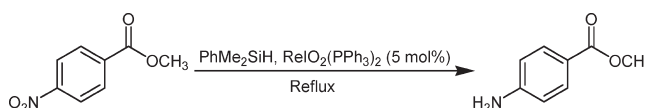
entry	solvent	time (h)	conversion[b] (%)
1	toluene	1	100
2	THF	18	100
3	heptane	12	98
4	CH$_2$Cl$_2$	24	93
5	CH$_3$CN	23	no reaction
6	neat	42	57[c]

[a]All reactions were carried out with 1.0 mmol of nitro compound, 360 mol % of silane, and 5 mol % of ReIO$_2$(PPh$_3$)$_2$. [b]Conversion was determined by ^{1}H NMR. [c]The reaction was carried out at 120 °C.

was very fast, reaching quantitative conversion within 20–60 min (Table 1, entries 1 and 2). In the presence of 1 mol % of ReIO$_2$(PPh$_3$)$_2$, the reduction of the nitro compound required significantly longer reaction time (22 h) and the amine was obtained in 84% conversion (Table 1, entry 3). The deoxygenation carried out with the catalysts ReOCl$_3$-(dppm) and Re$_2$O$_7$ afforded the amine in good conversions, but the reactions were much slower, taking 20 h (Table 1, entries 4 and 5). In the presence of MTO, the expected amine was obtained in 40% conversion only (Table 1, entry 6). Finally, in the absence of catalyst no amine formation was detected after 23 h (Table 1, entry 7).

The reduction of methyl 4-nitrobenzoate was studied with the silanes dimethylphenylsilane, phenylsilane, triethylsilane, triphenylsilane, and polymethylhydrosiloxane (PMHS). Nearly all silanes screened were able to efficiently reduce the nitro compound in the presence of ReIO$_2$(PPh$_3$)$_2$ (5 mol %). The reactions with dimethylphenylsilane and phenylsilane were very fast, reducing completely the nitro compound in 1 h at reflux temperature (Table 2, entries 1 and 2). We also found that PMHS, a stable, inexpensive, and nontoxic hydrosiloxane, was also effective for the reduction of methyl 4-nitrobenzoate, but the reaction required 18 h (Table 2, entry 4). In contrast, the deoxygenation with triphenylsilane produced the corresponding amine in only 17% conversion (Table 2, entry 5).

In Table 3 are summarized the results of the search for the appropriate solvent. We found that toluene was the best

TABLE 4. Reduction of Aromatic Nitro Compounds with the System PhMe₂SiH/ReIO₂(PPh₃)₂[a]

Reaction scheme: Ar–NO₂ + PhMe₂SiH, ReIO₂(PPh₃)₂ (5 mol%), Toluene, reflux → Ar–NH₂

Entry	Substrate	Product	Time	Yield (%)[b]
1	4-bromonitrobenzene	4-bromoaniline	1 h	94[c]
2	4-chloronitrobenzene	4-chloroaniline	1.5 h	91[c]
3	4-iodonitrobenzene	4-iodoaniline	1.5	86[c]
4	4-fluoronitrobenzene	4-fluoroaniline	24 h	50[c]
5			40 min	98[c,e]
6	methyl 4-nitrobenzoate	methyl 4-aminobenzoate	1 h	97[c]
7	4-nitro-N-(4-bromophenyl)benzamide	4-amino-N-(4-bromophenyl)benzamide	23 h	95[d]
8	4-(methylsulfonyl)nitrobenzene	4-(methylsulfonyl)aniline	5.5 h	84[c]
9	5-nitrophthalide	5-aminophthalide	24 h	78[d]
10	4-(benzyloxy)nitrobenzene	4-(benzyloxy)aniline	24 h	71[c]
11	4-nitrobenzonitrile	4-aminobenzonitrile	23 h	35[d] (53)[f]
12	2-nitrobiphenyl	2-aminobiphenyl	17 h	98[d]
13	4-phenoxynitrobenzene	4-phenoxyaniline	8 h	71[c]
14	nitrobenzene	aniline	24 h	95[c]
15	1,2-dinitrobenzene	2-nitroaniline	24 h	76[d]
16	1,3-dinitrobenzene	3-nitroaniline	38 h	56[c]
17	1,4-dinitrobenzene	4-nitroaniline	24 h	58[c] (38)[f]
18	4-nitro-(2-nitroethyl)benzene	4-amino-(2-nitroethyl)benzene	48 h	50[g,h]
19	3-nitrostyrene	3-aminostyrene (51%); 3-ethylaniline (20%)	24 h	71[c]
20	ethyl 4-nitrocinnamate	ethyl 4-aminocinnamate (47%); ethyl 3-(4-aminophenyl)propanoate (11%)	24 h	58[c]

[a] All reactions were carried out with 1.0 mmol of nitro compound, 360 mol % of silane, and 5 mol % of ReIO₂(PPh₃)₂. [b] Isolated yield. [c] Isolated as hydrochloride salt. [d] Isolated by column chromatography. [e] Phenylsilane was used instead of dimethylphenylsilane. [f] Yield of aromatic nitro compound recovered. [g] This reaction was carried out with 10 mol % of ReIO₂(PPh₃)₂ in dioxane at reflux temperature. [h] The yield was determined by ¹H NMR.

TABLE 5. Reduction of Aromatic Nitro Compounds with the System PhMe₂SiH/ReOCl₃(PPh₃)₂[a]

Reaction scheme: Ar–NO₂ + PhMe₂SiH, ReOCl₃(PPh₃)₂ (5 mol%), Toluene, reflux → Ar–NH₂

Entry	Substrate	Product	Time	Yield (%)[b]
1	4-bromonitrobenzene	4-bromoaniline	1 h	87[c]
2	4-chloronitrobenzene	4-chloroaniline	1.5 h	79[c]
3	4-iodonitrobenzene	4-iodoaniline	1.5 h	76[c]
4	4-fluoronitrobenzene	4-fluoroaniline	24 h	50[c]
5			75 min	96[c,e]
6	methyl 4-nitrobenzoate	methyl 4-aminobenzoate	20 min	89[c]
7	4-nitro-N-(4-bromophenyl)benzamide	4-amino-N-(4-bromophenyl)benzamide	21 h	96[d]
8	4-(methylsulfonyl)nitrobenzene	4-(methylsulfonyl)aniline	3 h	66[c]
9	5-nitrophthalide	5-aminophthalide	24 h	45[d]
10	4-(benzyloxy)nitrobenzene	4-(benzyloxy)aniline	22 h	67[c]
11	4-nitrobenzonitrile	4-aminobenzonitrile	29 h	34[d] (56)[f]
12	2-nitrobiphenyl	2-aminobiphenyl	5 h	91[d]
13	4-phenoxynitrobenzene	4-phenoxyaniline	8 h	78[c]
14	nitrobenzene	aniline	24 h	94[c]
15	1,2-dinitrobenzene	2-nitroaniline	24 h	51[d] (41)[f]
16	1,3-dinitrobenzene	3-nitroaniline	36 h	45[c] (22)[f]
17	1,4-dinitrobenzene	4-nitroaniline	24 h	60[c] (22)[f]

[a] All reactions were carried out with 1.0 mmol of nitro compound, 36% of silane, and 5 mol % of ReIO₂(PPh₃)₂. [b] Isolated yield. [c] Isolated as hydrochloride salt. [d] Isolated by column chromatography. [e] Phenylsilane was used instead of dimethylphenylsilane. [f] Yield of aromatic nitro compound recovered.

solvent for this reaction (Table 3, entry 1). Tetrahydrofuran, dichloromethane, and heptane proved to be good solvents, but the reductions required extended periods of time (12−24 h) (Table 3, entries 2−4). When the reaction was conducted in CH₃CN, the reduction did not proceed (Table 3, entry 5). Finally, the deoxygenation of methyl 4-nitrobenzoate in the

absence of solvent afforded the amine in 54% conversion after 42 h (Table 3, entry 6).

We decided to study the reduction of a series of aromatic nitro compounds with both systems $PhMe_2SiH/ReIO_2$-$(PPh_3)_2$ (5 mol %) and $PhMe_2SiH/ReOCl_3(PPh_3)_2$ (5 mol %) at reflux temperature under air atmosphere to evaluate the scope and limitations of these catalytic systems. The results presented in Tables 4 and 5 indicate the generality of the method and the efficacy of these new catalytic systems. The deoxygenation of 4-bromo-, 4-chloro-, and 4-iodo-1-nitrobenzenes was completed within 1−1.5 h, and the amines were isolated as their hydrochloride salts in high yields (Tables 4 and 5, entries 1−3). The reduction of 4-fluoro-1-nitrobenzene with these systems afforded the corresponding amine in only 50% yield after 24 h (Tables 4 and 5, entry 4). However, the complete deoxygenation of this substrate was possible in only 40−75 min when phenylsilane was used instead of dimethylphenylsilane (Tables 4 and 5, entry 5). Of particular importance is the tolerance of halo substituents on the aromatic ring observed under our catalytic conditions, contrary to the dehalogenation or decomposition which was often encountered with several methods such as hydrogenation[1d] or $Pd(OAc)_2/PMHS$[6a] and S_8/mild base.[11]

A series of aromatic nitro substrates containing other functional groups such as ester, amide, sulfone, lactone, and benzyl were also successfully reduced with these two catalytic systems (Tables 4 and 5, entries 6−10), showing the good chemoselectivity of this novel methodology. It is interesting to note the tolerance of benzyl group under our reaction conditions, which is often cleaved with other methods such as hydrogenation. The selective reduction of 4-nitrobenzonitrile was also carried out with the systems $PhMe_2SiH/ReIO_2(PPh_3)_2$ (5 mol %) and $PhMe_2SiH/ReOCl_3(PPh_3)_2$ (5 mol %), but the 4-aminobenzonitrile was isolated in low yield (Tables 4 and 5, entry 11). The deoxygenation of 2-nitro-1,1′-biphenyl to the corresponding amine was achieved in excellent yield (Tables 4 and 5, entry 12), without reductive cyclization observed with the catalytic system MoO_2Cl_2/PPh_3.[15] The analysis of the results of the Tables 4 and 5 shows that the best yields were obtained with substrates containing electron-withdrawing groups. However, the presence of electron-donating groups such as benzyloxy and phenyloxy also conducted to good yields of amine (Tables 4 and 5, entries 10 and 13).

Nitrobenzene was effectively reduced with both catalytic systems after 24 h at reflux temperature (Tables 4 and 5, entry 14). Regioselective reductions of *o-*, *m-*, and *p-*dinitrobenzene were also possible, producing the corresponding nitroanilines in moderate to good yields (Tables 4 and 5, entries 15−17). In all cases, the formation of the diamine was not detected. These results show a high regioselectivity in the reduction of dinitro compounds under our reaction conditions. Many conventional procedures involving hydride reducing agents or hydrogenation failed to give such high regioselectivity.[1b]

Another interesting result was the regioselective reduction of the aromatic nitro group over the aliphatic nitro group in the reaction of 1-nitro-4-(2-nitroethyl)benzene with the catalytic system $PhMe_2SiH/ReIO_2(PPh_3)_2$ (5 mol %) affording

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TABLE 6. Reduction of Nitrosobenzene, Phenylhydroxyamine, Azoxybenzene, And Diazobenzene with the Catalytic System $PhMe_2SiH/ReIO_2(PPh_3)_2$[a]

entry	substrate	product	time	conversion[b] (%)
1	Ph-NO	Ph-NH$_2$	50 min	100
2	Ph-NHOH	Ph-NH$_2$	30 min	100
3	Ph-N(O)=N-Ph	Ph-NH$_2$	7 h	60
4	Ph-N=N-Ph	Ph-NH$_2$	24 h	65

[a]All reactions were carried out with 1.0 mmol of substrate, 360 mol % of silane, and 5 mol % of $ReIO_2(PPh_3)_2$. [b]Conversion was determined by ^{1}H NMR.

the 4-(2-nitroethyl)aniline (Table 4, entry 18) in moderate yield.

The deoxygenation of nitro group was also examined with two substrates containing a double bond using the catalytic system $PhMe_2SiH/ReIO_2(PPh_3)_2$ (5 mol %) (Table 4, entries 19 and 20). The reaction of *m*-nitrostyrene afforded the 3-vinylaniline as the major product and the *m*-ethylaniline as the minor product (Table 4, entry 19). Similar reduction of ethyl 3-(4-nitrophenyl)-2-propenoate gave ethyl 3-(4-aminophenyl)-2-propenoate in 47% yield along with 12% yield of ethyl 3-(4-aminophenyl)propanoate (Table 4, entry 20). In both cases, the reduction of the nitro group is apparently favored over the double bond.

Finally, we decided to test this novel methodology in the reduction of an aliphatic nitro compound. The reaction of 2-nitroethylbenzene was monitored by ^{1}H NMR, and after 36 h, we observed the complete reduction of the substrate. After purification by chromatography, the corresponding nitrile was isolated in 38% yield (eq 2). This result is in agreement with other methods reported in the literature for the reduction of primary nitro compounds which gave the corresponding nitriles.[16]

$$\text{PhMe}_2\text{SiH, ReIO}_2(\text{PPh}_3)_2 \text{ (5 mol\%)} \qquad \text{Toluene, reflux, 36 h, } \eta = 38\% \qquad (2)$$
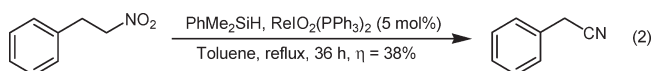
The reusability of $ReIO_2(PPh_3)_2$ was evaluated using 4-fluoro-1-nitrobenzene as test substrate. We carried out successive reactions by sequential addition of fresh substrate and phenylsilane to the reaction mixture. The results showed that the catalytic activity of $ReIO_2(PPh_3)_2$ did not decrease after three cycles. However, the deoxygenation of the substrate was not complete in the fourth cycle.

The reduction of nitro group is believed to involve several intermediates including nitroso, hydroxylamine, azoxy, and diazo. However, all attempts to detect these intermediates under our catalytic conditions by thin-layer chromatography and by ^{1}H NMR were unsuccessful. Only the final product could be observed. Most likely the intermediates are converted into the final amines very rapidly without building sufficient concentration.

The formation of these intermediates was investigated by independent reduction of nitrosobenzene, phenylhydroxylamine, azoxybenzene, and diazobenzene with the catalytic system $PhMe_2SiH/ReIO_2(PPh_3)_2$ (5 mol %) (Table 6). The deoxygenation of nitrosobenzene and phenylhydroxylamine was very fast, requiring only 50 and 30 min, respectively

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(Table 6, entries 1 and 2). In contrast, the reduction of azoxybenzene and diazobenzene took long reaction times and gave moderate conversions into amine (Table 6, entries 3 and 4). The formation of aniline was not detected in the reduction of nitrosobenzene with dimethylphenylsilane in the absence of catalyst, and only a trace amount of amine was observed in similar reduction of hydroxylamine. These experiments led us to conclude the existence of these intermediates in the nitro reduction, under our catalytic conditions, and that the catalyst plays an active role in the deoxygenation of the intermediates. The rapid reduction of nitroso and hydroxylamine suggests that the route involving the sequence nitro → nitroso → hydroxylamine → amine is the more probable pathway and that the rate-determining step of this reduction is the deoxygenation of nitro compound to the corresponding nitroso derivative.

Mechanistically, we suggest that the reduction of aromatic nitro compounds with the system silane/oxo-rhenium complexes initiates with the coordination of the nitro group to the rhenium with liberation of the phosphines. While monitoring the reaction between $ReIO_2(PPh_3)_2$ and 2 equiv of 4-fluoro-1-nitrobenzene by ^{31}P NMR, it was possible to see the displacement of the phosphines by the disappearance of the peak at δ 4.0 ppm corresponding to the PPh_3 of the catalyst and the detection of a new peak at δ −5 ppm assigned to free PPh_3. Similar coordination was also suggested by other authors.[17] Since triphenylphosphine is liberated in solution in catalytic amounts, the reduction of nitro compound by PPh_3 is negligible. When the reduction of methyl 4-nitrobenzoate is started by the addition of the silane to the $ReIO_2(PPh_3)_2$, followed by addition of the nitro compound, the reduction is much slower.

According to previous works about the activation of Si−H[18] and B−H[19] bonds by $ReIO_2(PPh_3)_2$, that produced hydride species, we believe that after addition of the silane to the complex containing the nitro compound, a hydride species is formed, followed by the reduction of the nitro compound to the corresponding nitroso derivative with liberation of R_3SiOH. In the next two steps, the nitroso intermediate is rapidly deoxygenated to the hydroxylamine, which is then reduced to the amine by addition of 2 equiv of silane. The precise mechanism by which these intermediates/products are formed and subsequently reduced is not entirely clear.

Conclusion

In conclusion, we have demonstrated that the catalytic system silane/high valent oxo-rhenium complexes is very efficient for the reduction of aromatic nitro compounds.

This novel methodology is highly chemoselective, tolerating a large range of functional groups such as ester, halo, amide, sulfone, lactone, benzyl, and nitrile. In comparison to other methods reported in the literature, this novel methodology is more chemoselective than some hydrogenation systems in the reduction of aromatic nitro compounds bearing halo and benzyl groups. Furthermore, our method is also highly regioselective allowing the synthesis of o-, m-, p-nitroanilines from the corresponding dinitro compounds and the selective reduction of an aromatic group over an aliphatic nitro group.

Other remarkable advantages of this methodology include high isolated yields, clean reactions, easy workup, reusability of the catalyst and stability of oxo-rhenium complexes toward air and moisture, allowing the reaction to be carried out under air atmosphere. All these features make this method an attractive and useful alternative in organic synthesis.

The reduction of aliphatic nitro compound to the corresponding nitrile suggests a future application for the catalytic system silane/oxo-rhenium complexes as novel method for the synthesis of nitrile compounds.

Further mechanistic studies of this catalytic reduction and applications of this methodology toward the synthesis of compounds of biological interest are now in progress in our group.

Experimental Section

General Procedure for the Reduction of Aromatic Nitro Compounds with Silanes Catalyzed by Oxo-Rhenium Complexes. To a mixture of nitro compound (1 mmol) and catalyst (5 mol %) in toluene (5 mL) was added dimethylphenylsilane (360 mol %). The reaction solution was stirred at reflux temperature under air atmosphere and the progress of the reaction was monitored by TLC (silica gel; hexane/ethyl acetate 8:2). Upon completion, the reaction mixture was cooled to ambient temperature, filtered through a plug of alumina/Celite/charcoal.

Workup A. To the filtrate was added an ethereal solution of HCl followed by addition of n-hexane to induce the precipitation of the amine hydrochloride salt. The solid was isolated upon filtration through a fritted funnel and then washed with ether and n-hexane.

Workup B. The volatiles were removed under reduced pressure, and the residue was purified by flash chromatography (alumina; n-hexane/ethyl acetate mixture) to afford the amine product. All products obtained are known compounds.

Supporting Information Available: Experimental details. ^{1}H NMR and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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