Samarium(0) and 1,1′-Dioctyl-4,4′-Bipyridinium Dibromide: A Novel Electron-Transfer System for the Chemoselective Reduction of Aromatic Nitro Groups

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A mild and efficient electron-transfer method was developed for the chemoselective reduction of aromatic nitro groups using samarium(0) metal in the presence of a catalytic amount of 1,1′-dioctyl-4,4′-bipyridinium dibromide. This method was found to give the product aromatic amine in 79−99% yield with selectivity over a number of other functional and protecting groups such as alkene, azide, benzyl ether, nitrile, amide, halide, *p*-toluenesulfonamide, *t*-Boc, *tert*-butyldiphenylsilyl ether, and aliphatic nitro groups. Our results also indicate that samarium(0) plays an important role in the reduction process and that 1,1′-dioctyl-4,4′-bipyridinium dibromide acts as an electron-transfer catalyst and is essential in the activation of samarium(0) metal. The major active reducing agent responsible for the reduction is believed to be the radical cation species formed from 1,1′-dioctyl-4,4′-bipyridinium dibromide.

Introduction

Aromatic amines, widely used as intermediates in the preparation of important chemicals such as dyes, pharmaceuticals, and agricultural chemicals, can be obtained easily by the reduction of aromatic nitro compounds using catalytic hydrogenation[1] and a variety of other reduction conditions. Many reducing agents have been used to reduce aromatic nitro compounds with the most classic being zinc, tin, or iron in the presence of an acid.[2] Other reagents used include hydrazine,[3] $Ru_3(CO)_{12}$,[4] $TiCl_4$−dialkyl telluride,[5] $(C_2H_5O)_2PCl$,[6] metal hydride complexes[7] (e.g., $NaBH_4$−$NiCl_2$), and sulfides[8] (e.g., sodium sulfhydrate, ammonium sulfide, or polysulfides). Aromatic nitro compounds can also be reduced electrochemically[9] or enzymatically.[10] Most chemical methods, however, lack the desired chemoselectivity over other functional groups that are often present in the substrate such as alkene, azide, benzyl ether, nitrile, amide, halide, and *p*-toluenesulfonamide. In addition, reduction of aromatic nitro compounds often stops at an intermediate stage, yielding hydroxylamines,[11] hydrazines,[12] azoarenes,[13] or azoxyarenes.[14] Therefore, there is a need for the development of mild chemical methods for the selective reduction of aromatic nitro groups.

In our efforts to develop prodrugs for site-specific activation in tumor cells,[15] we were looking for a mild, selective chemical method to mimick the reduction of aromatic nitro groups in hypoxic tumor cells or by an enzyme such as *Escherichia coli* nitroreductase. It came to our attention that aliphatic nitro groups could be converted to hydoxylamines[16] and hydrazines[17] in moderate to good yields under mild conditions using samarium(II) iodide (SmI_2). As one of the most versatile single electron-transfer agents,[18] SmI_2 is capable of reducing nitro compounds to their corresponding hydroxylamines,[16]

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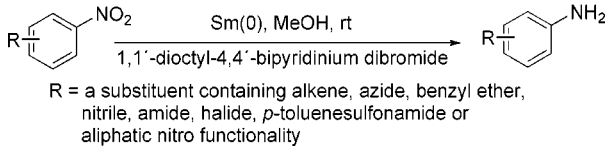
amines,[19] and azo derivatives.[19a] On the other hand, samarium(0) metal has rarely been used directly to reduce nitro groups because the samarium atom on the accessible solid surface is not sufficiently reactive.[20] To activate samarium(0) metal, additives such as $HgCl_2$,[21] TMSCl,[22] NH_4Cl (aq),[23] allyl iodide,[24] or iodine[25,26] have to be used. Samarium(0) in the presence of a catalytic amount of allyl iodide was reported to reduce nitroarenes to azoxyarenes.[24] The only method in the literature for the reduction of aromatic nitro compounds to aromatic amines and hydrazines using samarium metal was carried out in the presence of a catalytic amount of iodine in a mixed solvent of aqueous ammonium chloride and tetrahydrofuran (THF).[25] This method gave only moderate yields of their corresponding amine products (usually <74%) with significant formation of hydrazine byproducts and exhibited selectivity in reducing nitro groups over aryl halides and aryl amides. This method might also lack selectivity over common protecting groups of alcohols and amines. For a similar condition, using samarium(0) and a stoichiometric amount of iodine in methanol was reported to selectively and efficiently remove alkyloxycarbonyl protecting groups of alcohols and lactams.[26]

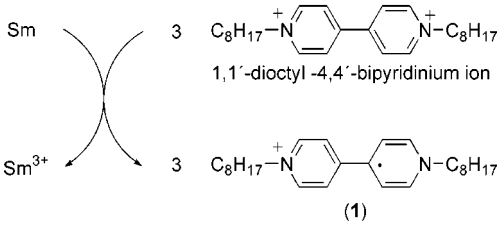
1,1′-Dialkyl-4,4′-bipyridinium halides, sometimes referred to as viologens, have been used as electron-transfer catalysts in the photoreduction of protons to produce hydrogen[27] as well as in the reduction of various organic compounds.[28] In one report, 1,1′-dioctyl-4,4′-bipyridinium dibromide was used as an electron-transfer catalyst in the sodium dithionite reduction of nitroarenes in the presence of potassium carbonate in dichloromethane (CH_2Cl_2)/water (8:1).[26i] This method was found to be selective for the reduction of aromatic nitro groups over alkene and nitrile.

On the basis of these earlier reports, we decided to test the hypothesis that 1,1′-dialkyl-4,4′-bipyridinium dibromide might act as an electron-transfer catalyst to activate samarium(0) metal and that this combination might provide a mild chemical method for the selective reduction of aromatic nitro groups. In this paper, we report the development and the chemical selectivity of such an efficient electron-transfer system using samarium(0) and 1,1′-dioctyl-4,4′-bipyridinium dibromide.

Scheme 1



Scheme 2



Results and Discussion

In a typical experiment, 1,1′-dioctyl-4,4′-bipyridinium dibromide (5% mol) and samarium(0) powder (2 equiv)[29] were added sequentially to a solution of aromatic nitro substrate (1 mmol) in anhydrous methanol (MeOH). The reaction mixture was stirred at room temperature, and the reaction progress was monitored by TLC. Our experiments indicated that the combination of samarium(0) powder and 1,1′-dioctyl-4,4′-bipyridinium dibromide effectively reduced at room-temperature aromatic nitro compounds to their corresponding amines and that the reduction was selective over a number of common functional groups that might be present in a substrate (Scheme 1). Other functional groups unaffected by this process include alkene, azide, benzyl ether, nitrile, amide, halide, *p*-toluenesulfonamide, *t*-Boc, *tert*-butyldiphenylsilyl ether, and aliphatic nitro groups.

The addition of samarium(0) powder to a solution of 1,1′-dioctyl-4,4′-bipyridinium dibromide in methanol gave instantly a deep blue suspension, a phenomenon similar to mixing sodium dithionite ($Na_2S_2O_4$) with a biphasic solution of 1,1′-dioctyl-4,4′-bipyridinium dibromide in $CH_2Cl_2-H_2O$.[28i] The deep blue color of the suspension is also similar to that of SmI_2 in THF. Both solutions of dithionite-1,1′-dioctyl-4,4′-bipyridinium and SmI_2 in THF were believed to contain a blue radical species that acts as a reducing agent. On the basis of our observation of the formation of the blue suspension, we concluded that the reaction occurring on the surface of samarium(0) metal was an electron-transfer reaction. As shown in Scheme 2, electron transfer from samarium(0) to the pyridine rings in 1,1′-dioctyl-4,4′-bipyridinium dibromide led to the formation of a hyperconjugated radical cation (**1**) that is responsible for the blue color. This is consistent with an earlier mechanistic study by Okawara et al. that demonstrated the immediate formation of a similar blue

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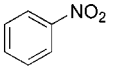
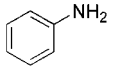
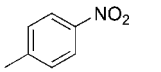
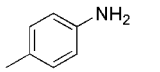
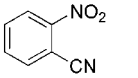
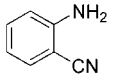
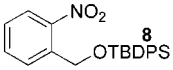
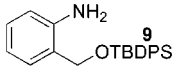
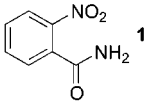
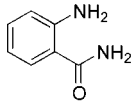
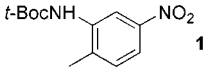
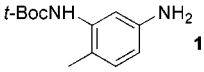
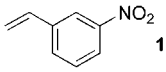
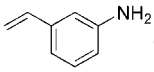
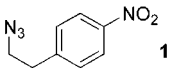
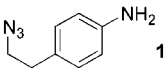
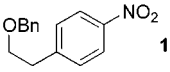
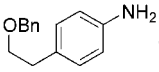
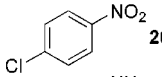
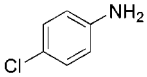
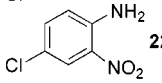
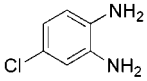
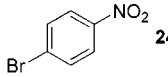
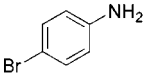
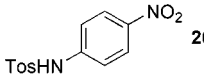
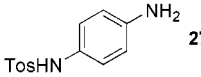
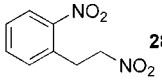
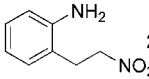
(29) It should also be noted that excess samarium(0) (up to 3−7 equiv) did not adversely affect the reduction and could help offset the samarium(0) loss caused by oxidation during storage. Therefore, a little excess samarium(0) could increase the yield of product isolated if old samarium(0) powder was used.

Table 1. Chemoselective Reduction of Nitro Compounds to Corresponding Amines[a]

Substrate		Time (h)	Major Product		yield (%)[b]
	**2**	3		**3**	83
	**4**	0.5		**5**	85
	**6**	1		**7**	88
	**8**	16		**9**	92
	**10**	4		**11**	93
	**12**	1.6		**13**	79
	**14**	2		**15**	82
	**16**	2.2		**17**	92
	**18**	28		**19**	80
	**20**	1.5		**21**	78
	**22**	5.5		**23**	99
	**24**	4		**25**	85
	**26**	10		**27**	96
	**28**	5		**29**	83

[a] Reduction condition: Sm (2 equiv), 1,1′-dioctyl-4,4′-bipyridinium dibromide (5% mol), MeOH, rt; [b] Isolated yield.

radical cation when zinc powder was mixed with 1,1′-dipropyl-4,4′-bipyridinium dibromide in acetonitrile/water (49:1).[28c] In our method, the strong reduction potential of Sm(0) ($E°$ (Sm^{2+}/Sm^0) = −2.68 V, $E°$ (Sm^{3+}/Sm^0) = −2.30 V) and Sm(II) ($E°$ (Sm^{3+}/Sm^{2+}) = −1.55 V) favors the electron-transfer process from samarium(0) to bipyridinium ion, leading to the formation of the radical cation.[19a]

The scope of this reduction reaction is illustrated in Table 1, where we examined a series of aromatic nitro compounds with a variety of substituents. Electron-withdrawing groups such as cyano (in **6**), amide (in **10**, **12**, and **26**), alkenyl (in **14**), chloro (in **20** and **22**), and bromo (in **24**) did not adversely affect the reduction of nitro groups. In general, the time required for the reduction as monitored by TLC ranges from 30 min to about 28 h depending on the substrate. The rate of reduction is limited by the solubility of the substrate in MeOH, which is the solvent of choice in this process. As shown in Table 1, *tert*-butyl-(2-nitrobenzyloxy)diphenylsilane (**8**) and 1-(2-benzyloxyethyl)-4-nitrobenzene (**18**) were reduced slowly relative to the other substrates because of their poor solubility in MeOH. When a less polar solvent such as THF, diethyl ether (Et_2O), or CH_2Cl_2 was added as a cosolvent to increase the solubility of these substrates, the formation of the deep blue species was rather slow, and the reduction of nitro compounds was adversely affected. While mixed solvents of THF and MeOH were often the solvent of choice in reductions employing SmI_2,[19a] the addition of a less polar solvent such as THF inhibited the electron-transfer process between samarium(0) and 1,1′-dioctyl-4,4′-bipyridinium dibromide.

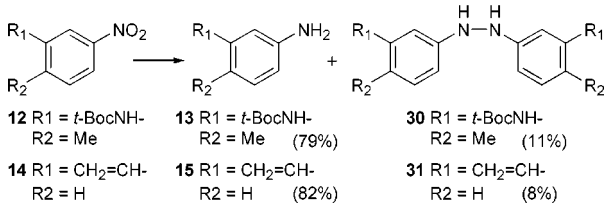
As shown in Table 1, our method selectively reduced aromatic nitro compounds to their corresponding amines in satisfactory yields (79−99%) in the presence of other functional groups such as cyano (**6**), amide (**10**, **12**, and **26**), alkenyl (**14**), azido (**16**), benzyl ether (**18**), halide (**20**, **22**, and **24**), and aliphatic nitro (**28**), groups which might otherwise be reduced using other reduction conditions. The chemoselectivity in the reduction of aromatic nitro group versus cyano group in compound **6** using our process is the opposite of that reported using $NaBH_4$−$AlCl_3$ complex in diglyme.[30] Protecting groups, such as *tert*-butyldiphenylsilyl (TBDPS) (in **8**), *tert*-butoxycarbonyl (*t*-Boc) (in **12**), and *p*-toluenesulfonyl (Tos) (in **26**), are unaffected under the slightly basic condition (pH 7−8) in this procedure. The cleavage of TBDPS that was reported under basic conditions[31] was not observed using our method. It should also be noted that *t*-Boc was not affected under our condition while Sm(0)−I_2/MeOH could remove this protecting group in almost quantitative yield.[26] The *p*-toluenesulfonamides that could be removed using samarium(II) iodide[32] was stable under our condition. Furthermore, the fact that reduction of 1-nitro-2-(2-nitroethyl)benzene **28** affords only the 2-(2-nitroethyl)-aniline product **29** in good yield (83%) indicates that our reduction condition is selective for the aromatic over the aliphatic nitro groups. To compare the mildness and selectivity of our method with classical hydrogenation, we examined reductions of compounds **22** and **28** using atmospheric hydrogenation at room temperature in the presence of 5% Pd−C. This hydrogenation procedure was found to produce a complex product mixture within 1.5 h for each of the two compounds examined. This result indicates that our condition is superior to hydrogenation and should be useful in the selective reduction of aromatic nitro groups over halides or aliphatic nitro groups. In comparison with the method using Sm(0)−I_2(cat.)/THF−NH_4Cl (aq) for the reduction of aromatic nitro compounds, our method gave better product yields for the same substrates (78−85% versus 56−74%). The differences in yield and selectivity could be attributed to a unique mechanism of action where the hyperconjugated radical cation (**1**) formed by Sm(0) and 1,1′-dioctyl-4,4′-bipyridinium dibromide is the real, active reducing agent rather than Sm(II) species. This was further supported by the reduction of **26** and **28**, where both the tosyl protecting group in **26** and aliphatic nitro group in **28**

(30) Brown, H. C.; Rao, B. C. S. *J. Am. Chem. Soc.* **1956**, *78*, 2582−2588.

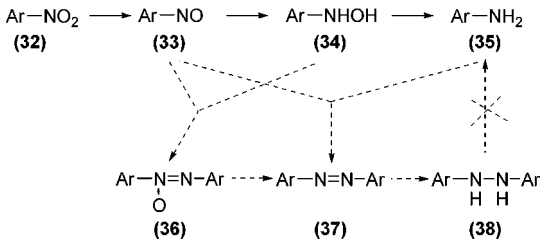
(31) (a) Torisawa, Y.; Shibasaki, M.; Ikegami, S. *Chem. Pharm. Bull.* **1983**, *31*, 2607−2615. (b) Wood, W. W.; Rashid, A. *Tetrahedron Lett.* **1987**, *28*, 1933−1936. (c) Malik, A. A.; Cormier, R. J.; Sharts, C. M. *Org. Prep. Proced. Int.* **1986**, *18*, 345−352. (d) Shekhani, M. S.; Khan, K. M.; Mahmood, K.; Shah, P. M.; Malik, S. *Tetrahedron Lett.* **1990**, *31*, 1669−1670.

(32) Vedejs, E.; Lin, S. *J. Org. Chem.* **1994**, *59*, 1602−1603.

Scheme 3



Scheme 4



were not affected using our method but could be removed or reduced by Sm(II) reducing agents.[16,32]

Reduction of *N*-*t*-Boc-5-nitro-*o*-toluidine (**12**) not only afforded the desired amine **13** as the major product, but also gave as a minor product symmetrical hydrazine **30** in 11% yield. Similarly, reduction of 3-nitrostyrene (**14**) gave the desired amine **15** as the major product and *N*,*N*′-bis(3-vinylphenyl)hydrazine **31** as the minor product in 8% yield (Scheme 3).

The formation of these hydrazine intermediates is often observed in the reduction of nitro groups. Nitro group reduction is believed to involve several intermediates including nitroso compounds and hydroxylamines.[33] Similarly, under our condition using samarium(0) powder and 1,1′-dioctyl-4,4′-bipyridinium dibromide, a nitro compound (**32**) could be reduced to the corresponding amine (**35**) through the nitroso (**33**) and the hydroxylamine (**34**) intermediates as shown in Scheme 4. Condensation of the reduced intermediates and the amine product followed by subsequent reduction could explain the formation of the hydrazine byproduct under our condition as well as conditions reported by others.[11a,19a]

As outlined in Scheme 4, the product amine (**35**) could condense under certain conditions with nitrosoarene intermediate (**33**) to produce azoarene intermediate (**37**), which could be further reduced to the hydrazine byproduct (**38**).[11a] Alternatively azoarene (**37**) could be produced from the reduction of azoxyarene intermediate (**36**),[19a] which is formed by condensation of nitrosoarene (**33**) with *N*-arenylhydroxylamine (**34**). The fact that we did not isolate any azoxyarene intermediate (**36**) suggests that the latter pathway is less likely to occur or that the azoxyarene intermediate formed is readily reduced further. However, prolonged treatment of the hydrazine compounds **30** and **31** with samarium(0) and 1,1′-dioctyl-4,4′-bipyridinium dibromide failed to convert them to their corresponding amine products. These results indicate that once the N−N bond is formed, it is stable under our reduction condition. This is consistent with our observation that the azido group in compound **16** could survive the reduction condition we developed. It should also be noted that we could not exclude the formation of the byproduct hydrazines through other mechanisms. For example, the Sm(II) species could be formed in the activation process of samarium(0) metal. Rather than transferring its electron to dioctyl bipyridinium ion, the Sm(II) formed could reduce directly the nitro groups or their reduced intermediates to the hydrazine byproducts as has been reported in the literature.[17]

Table 2. Effect of Metal in the Reduction of Nitro Compound 8[a]

metal	equivalents[b]	time (h)	yield (%)[c]
Sm	2	16	92
Zn	3	24	0
Zn−Cu	3	18	61
Mg	3	14	45
In	3	24	5
Fe	3	24	0
Sn	3	24	10

[a] All the reactions were carried out with *tert*-butyl-(2-nitrobenzyloxy)diphenylsilane **8** (0.2 mmol), 1,1′-dioctyl-4,4′-bipyridinium dibromide (5 mol %) and the given metal in MeOH (10 mL) at room temperature. [b] Equivalents of metal were calculated based on the substrate **8**. [c] Isolated yield of amine product **9**.

To study the role of samarium(0) in our method, we examined the effect of several other metals in the reduction of *tert*-butyl-(2-nitrobenzyloxy)diphenylsilane **8** under the same condition. As shown in Table 2, using samarium(0) metal in the presence of 1,1′-dioctyl-4,4′-bipyridinium dibromide, compound **8** was reduced to the amine product **9** in 92% yield. Among the other metals tested, only magnesium turning and zinc−copper couple were sufficiently reactive to reduce compound **8** to give the amine product **9** in 45% and 61% yield, respectively. While the other metals including zinc, indium, iron, and tin failed to reduce **8** in the presence of 1,1′-dioctyl-4,4′-bipyridinium dibromide. This result suggests that samarium(0) metal plays an important role in this reduction system. Also, we found that samarium(0) in MeOH in the absence of 1,1′-dioctyl-4,4′-bipyridinium dibromide would not effect the reduction of aromatic nitro compounds, suggesting that a catalytic amount of 1,1′-dioctyl-4,4′-bipyridinium dibromide is essential in the activation of samarium(0) metal.

In conclusion, we developed a novel electron-transfer system using a combination of samarium(0) and 1,1′-dioctyl-4,4′-bipyridinium dibromide in the chemoselective reduction of aromatic nitro compounds. In comparison with SmI_2 reduction of nitro groups, our method is superior in terms of both chemoselectivity and efficiency. SmI_2 is known to reduce alkyne, alkene,[18b] and halides[34] and cleave *p*-toluenesulfonamide and *t*-Boc protecting groups. In addition, SmI_2 is difficult to handle because of its high sensitivity to air and moisture and its poor solubility in THF. Our method using samarium(0) as a reducing agent not only avoids the cumbersome preparation required in the case of SmI_2, but also takes full advantage of the reduction potential of samarium(0) metal. Furthermore, the use of 1,1′-dioctyl-4,4′-bipyridinium dibromide as an electron-transfer catalyst makes our method more selective and mild; protecting groups such as silyl ether, amide, Tos and *t*-Boc are not cleaved in our condition. Furthermore, our method is selective for the reduction of aromatic, not aliphatic, nitro groups. Thus, the method that we developed represents a mild,

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(34) Molander, G. A.; Harris, C. R. In *Handbook of Reagents for Organic Synthesis*; Burke, S. D., Danheiser, R. L., Eds., Wiley Press: New York, 1999; pp 354−358.

efficient, and economical condition that should prove useful in functional group transformation in organic synthesis.

Experimental Section

General Methods. All glassware used in our experiments was evacuated, flame-dried, and flushed with argon before use. Reactions were performed under argon, unless otherwise noted. Solvents were either ACS reagent grade or HPLC grade and were subjected to the following purification procedures before use. Et_2O and THF were freshly distilled from sodium/benzophenone under argon. MeOH was redistilled from sodium methoxide and stored over 4 Å molecular sieves. CH_2Cl_2 was freshly distilled from calcium hydride. Triethylamine (Et_3N) was distilled from calcium hydride and stored over potassium hydroxide. $CDCl_3$ was stored over magnesium turning and filtered through a short column packed with basic aluminum oxide. *N*,*N*-Dimethylformamide (DMF) was stored over anhydrous 4 Å molecular sieves for at least one week before use. Pyridine was dried over potassium hydroxide for 24 h at room temperature followed by distillation over CaH_2 under nitrogen and then stored over 4 Å molecular sieves in the darkness. *p*-Toluenesulfonyl chloride was recrystallized from hexanes before use. 1,1′-Dioctyl-4,4′-bipyridinium dibromide was purchased from TCI America (Portland, OR). Samarium(0) powder and other commercially available compounds were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

Unless otherwise stated, all reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using 0.25 mm Whatman precoated silica gel plates. TLC plates were visualized using either 7% (w/w) ethanolic phosphomolybdic acid or 1% (w/w) aqueous potassium permagnate containing 1% (w/w) $NaHCO_3$. Flash column chromatography was performed using silica gel (Merck 230−400 mesh). Yields were based on the chromatographically and spectroscopically pure compounds.

Melting points were determined using a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer model 1600 series FTIR spectrometer using polystyrene as an external standard. Infrared absorbance is reported in reciprocal centimeters (cm^{-1}). All ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer at ambient temperature. Chemical shifts (200 MHz for ^1H and 50 MHz for ^{13}C) are reported in parts per million (δ) relative to $CDCl_3$ (δ 7.24 for ^1H and 77.0 for ^{13}C) or DMSO-d_6 (δ 2.49 for ^1H and 39.5 for ^{13}C). Coupling constants (*J* values) are given in hertz (Hz). Mass spectral data were obtained from the University of Kansas Mass Spectrometry Laboratory (Lawrence, KS).

General Procedures for the Reduction of Nitro Compounds. A flame-dried, 50 mL, round-bottomed, two-neck flask equipped with a Teflon-coated magnetic stirring bar was flushed with dried argon and charged with substrate (1 mmol) in anhydrous MeOH (30 mL). To the well-stirred clear solution were added sequentially a catalytic amount of 1,1′-dioctyl-4,4′-bipyridinium dibromide (22 mg, 0.05 mmol) and Sm (301 mg, 2 mmol). The deep blue suspension formed was stirred vigorously at room temperature until TLC showed disappearance of the starting material. At the end of reaction, saturated aqueous NH_4Cl (50 mL) and Et_2O (100 mL) were added to partition the reaction mixture. The aqueous phase was separated and extracted with Et_2O (2 × 50 mL). The combined ether phase was washed with brine (50 mL) and dried over anhydrous $MgSO_4$. After filtration and removal of organic solvent under reduced pressure, the residue was purified by flash column chromatography using ethyl acetate (EtOAc)/hexanes (0.5% Et_3N) to give the desired aromatic amine product.[35] Compounds **3**, **5**, **7**, **11**, **21**, **23**, and **25** are known compounds and their spectroscopic data and melting points matched those of commercially available material.

***tert*-Butyl-(2-nitrobenzyloxy)diphenylsilane 8.** To a solution of 2-nitrobenzyl alcohol (5.32 g, 33.6 mmol) in anhydrous DMF (60 mL) were added imidazole (2.74 g, 40.3 mmol) and TBDPSCl (8.6 mL, 33.6 mmol). The reaction mixture was stirred at room temperature for 2 h, quenched with water (50 mL), and extracted with Et_2O (3 × 60 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered through a pad of cotton, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with EtOAc and hexanes as the eluent (hexanes:ethyl acetate = 11:1 → 10:1 → 9:1) to give **8** as a white solid (12.86 g, 98%). R_f = 0.35 (hexanes:ethyl acetate = 9:1); mp 75−77 °C; ^1H NMR ($CDCl_3$) δ 8.16−8.10 (m, 2H), 7.79−7.71 (m, 5H), 7.52−7.28 (m, 7H), 5.21 (s, 2H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.0, 135.7, 134.1, 133.1, 130.1, 128.2, 128.0, 127.7, 124.8, 63.1, 27.1, 19.6; IR (KBr): 3056.4, 2964.1, 2923.1, 1517.9, 1333.3 cm^{-1}; FABMS (in 3-nitrobenzyl alcohol matrix) *m*/*z* (relative intensity) 392 (6, MH^+), 334 (100), 314 (29), 197 (42).

2-(*tert*-Butyldiphenylsilanyloxymethyl)phenylamine 9. Yield, 92%; R_f = 0.3 (hexanes:ethyl acetate = 3:1); ^1H NMR ($CDCl_3$) δ 7.80−7.76 (m, 4H), 7.52−7.41 (m, 6H), 7.18 (t, *J* = 7.1 Hz, 1H), 6.96 (dd, *J* = 7.3, 1.5 Hz, 1H), 6.79−6.70 (m, 2H), 4.80 (s, 2H), 4.30 (br s, 2H, N−H), 1.13 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 146.2, 135.8, 133.4, 130.0, 128.8, 128.7, 127.9, 125.0, 118.1, 115.8, 65.6, 27.0, 19.4; IR (neat): 3456.4, 3374.3 cm^{-1}; FABMS (in 3-nitrobenzyl alcohol matrix) *m*/*z* (relative intensity) 361 (32, M^+), 304 (100); HRMS (FAB) (in 3-nitrobenzyl alcohol matrix) *m*/*z* calcd for $C_{23}H_{27}NOSi$ (M^+) 361.1862, found 361.1862.

(2-Methyl-5-nitrophenyl)carbamic Acid *tert*-Butyl Ester 12. A solution of 5-nitro-*o*-toluidine (350 mg, 2.3 mmol) in MeOH (20 mL) was charged with $NaHCO_3$ (396 mg, 4.6 mmol) and (*t*-Boc)$_2$O (510 mg, 2.3 mmol). The reaction mixture was sonicated for 4 h and evaporated in vacuo to remove most of the solvent. The residue was diluted with EtOAc (200 mL) and brine (60 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered through a pad of cotton, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with EtOAc and hexanes as the eluent (hexanes:EtOAc = 7:1 → 6:1 → 5:1) to give **12** as a brownish crystal (487 mg, 85%). R_f = 0.45 (hexanes:EtOAc = 3:1); mp 143−144 °C;^1H NMR ($CDCl_3$) δ 8.81 (d, *J* = 2.6 Hz, 1H), 7.82 (dd, *J* = 16.4, 2.6 Hz, 1H), 7.30−7.26 (m, 2H), 6.51 (br s, 1H), 2.35 (s, 3H), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.5, 147.2, 137.6, 133.7, 130.9, 118.0, 114.9, 81.8, 28.4, 18.2; IR (KBr): 3342.5, 1697.5 cm^{-1}; FABMS (in 3-nitrobenzyl alcohol matrix) *m*/*z* (relative intensity) 252 (47, M^+), 197 (100), 180 (9).

(5-Amino-2-methylphenyl)carbamic Acid *tert*-Butyl Ester 13. Yield, 79%; R_f = 0.25 (hexanes:ethyl acetate = 3:1); ^1H NMR ($CDCl_3$) δ 7.34 (d, *J* = 1.6 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.33 (dd, *J* = 2.6, 8.0 Hz), 6.28 (br s, 1H), 3.58 (br s, 2H), 2.13 (s, 3H), 1.52 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 153.0, 145.5, 137.2, 131.0 116.2, 110.3, 107.2, 80.5, 28.6, 17.0; IR (KBr): 3425.6, 3333.3, 3312.8, 1692.3 cm^{-1}; FABMS (in 3-nitrobenzyl alcohol matrix) *m*/*z* (relative intensity) 222 (80, M^+), 166 (100); HRMS (FAB) (in 3-nitrobenzyl alcohol matrix) *m*/*z* calcd for $C_{12}H_{18}N_2O_2$ (M^+) 222.1368, found 222.1368; ***N, N′*-Bis-[3-(*t*-Boc-amino)-4-methylphenyl]hydrazine 30.** Yield, 11%; R_f = 0.5 (hexanes:ethyl acetate = 3:1); mp 114−116 °C; ^1H NMR ($CDCl_3$) δ 8.30 (s, 1H), 7.73 (dd, *J* = 15.8, 2.2 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 6.45 (s, 1H), 2.35 (s, 3H), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 166.1, 152.7, 137.7, 135.1, 131.1, 118.1, 111.3, 81.5, 28.5, 18.5; IR (neat): 3333.3, 2974.3, 1692.3 cm^{-1}; FABMS (in 3-nitrobenzyl alcohol matrix) *m*/*z* (relative intensity) 442 (3, M^+), 327 (21), 316 (50), 222 (2), 181 (100); HRMS (FAB) (in 3-nitrobenzyl alcohol matrix) *m*/*z* calcd for $C_{24}H_{34}N_4O_4$ (M^+) 442.2580, found 442.2608.

3-Vinylphenylamine 15.[36] Yield, 82%; R_f = 0.35 (hexanes:ethyl acetate = 4:1); ^1H NMR ($CDCl_3$) δ 7.13 (t, *J* = 18 Hz, 1H), 6.83 (d, *J* = 8 Hz, 1H), 6.73 (s, 1H), 6.70−6.55 (m, 2H), 5.70 (d, *J* = 18 Hz, 1H), 5.20 (d, *J* = 11 Hz, 1H), 3.85 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 146.4, 138.1, 136.7, 128.9, 116.2,

(35) Because aromatic amine products are known to be unstable upon exposure to air and light, all products should be handled with care and stored under argon at low temperature.

114.3, 113.1, 112.2; IR (neat): 3435.9, 3353.8, 3210.2, 1620.5, 1600 cm^{-1}; ***N, N′*-Bis-(3-vinylphenyl)hydrazine 31.**[37] Yield, 8%; R_f = 0.5 (hexanes:ethyl acetate = 4:1); mp 95−97 °C; ^1H NMR ($CDCl_3$) δ 7.20 (t, J = 8.0 Hz, 1H), 6.95−6.92 (m, 2H), 6.81−6.77 (m, 1H), 6.74−6.60 (m, 1H), 5.76 (d, J = 1.0 Hz, 1H), 5.68−5.66 (m, 1H), 5.23 (dd, J = 11.6, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 149.3, 138.9, 137.1, 129.7, 118.3, 114.1, 112.1, 110.2; IR (KBr): 3343.6, 3087.2, 1605.1, 1574.3.

1-(2-Azidoethyl)-4-nitrobenzene 16.[38] To a solution of 4-nitrophenethyl alcohol (1.23 g, 7.4 mmol) in anhydrous DMF (50 mL) were added with stirring sodium azide (1.91 g, 29.6 mmol) and 4-(dimethylamino)pyridine (899 mg, 7.4 mmol) followed by bis(2,4-dichlorophenyl) chlorophosphate (2.99 g, 7.4 mmol). The reaction mixture was stirred for 24 h at room temperature and quenched with water (60 mL). The aqueous reaction mixture was extracted with Et_2O (3 × 60 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered through a pad of cotton, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with EtOAc and hexanes as the eluent (hexanes:ethyl acetate = 6:1 → 5:1 → 4:1) to give **16** as an oil (1.17 g, 83%). R_f = 0.2 (hexanes:ethyl acetate = 6:1); ^1H NMR ($CDCl_3$) δ 8.20−8.15 (m, 2H), 7.41 (dd, J = 17.6, 0.8 Hz, 2H), 3.60 (dd, J = 15.2, 6.4 Hz, 2H), 3.00 (t, J = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 147.1, 146.1, 129.9, 124.0, 51.9, 35.3; IR (neat): 2092.3, 1517.9 cm^{-1}; FABMS (in 3-nitrobenzyl alcohol matrix) m/z (relative intensity) 193 (17, MH^+), 165 (7), 154 (100).

4-(2-Azidoethyl)phenylamine 17. Yield, 92%; R_f = 0.3 (hexanes:ethyl acetate = 4:1); ^1H NMR ($CDCl_3$) δ 7.03 (dd, J = 12.8, 2.0 Hz, 2H), 6.71−6.65 (m, 2H), 3.64 (br s, 2H), 3.46 (t, J = 7.4 Hz, 2H), 2.81 (t, J = 7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 145.3, 129.8, 128.0, 115.5, 53.0, 34.7; IR (neat): 3446.2, 3364.1, 2102.6 cm^{-1}; FABMS (in 3-nitrobenzyl alcohol matrix) m/z (relative intensity) 162 (85, M^+), 120 (19), 106 (100); HRMS (FAB) (in 3-nitrobenzyl alcohol matrix) m/z calcd for $C_8H_{10}N_4$ (M^+) 162.0905, found 162.0905.

1-(2-Benzyloxyethyl)-4-nitrobenzene 18.[39] R_f = 0.4 (hexanes:ethyl acetate = 9:1); mp 46−48 °C; ^1H NMR ($CDCl_3$) δ 8.17 (d, J = 8.8 Hz, 2H), 7.44−7.28 (m, 7H), 4.54 (s, 2H), 3.76 (t, J = 6.4 Hz, 2H), 3.05 (t, J = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 147.4, 138.1, 129.9, 128.5, 127.8, 127.7, 123.6, 73.2, 70.0, 36.3; IR (neat): 2851.3, 1600.0, 1512.8 cm^{-1}; FABMS (in 3-nitrobenzyl alcohol matrix) m/z (relative intensity) 258 (49, MH^+), 212 (2), 165 (6), 150 (31), 154 (100).

4-(2-Benzyloxyethyl)phenylamine 19. Yield, 80%; R_f = 0.3 (hexanes:ethyl acetate = 4:1); ^1H NMR ($CDCl_3$) δ 7.37−7.29 (m, 5H), 7.05 (d, J = 8.4 Hz, 2H), 6.66 (dd, J = 6.6, 1.8 Hz, 2H), 4.56 (s, 2H), 3.67 (t, J = 7.2 Hz, 2H), 3.60 (br s, 2H), 2.86 (t, J = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 144.8, 138.7, 129.9, 129.0, 128.5, 127.8, 127.7, 115.4, 73.1, 71.9, 35.7; IR (neat): 3446.2, 2253.8, 1620.5, 1512.8 cm^{-1}; FABMS (in 3-nitrobenzyl alcohol matrix) m/z (relative intensity) 227 (100, M^+), 210 (10), 136 (78); HRMS (FAB) (in 3-nitrobenzyl alcohol matrix) m/z calcd for $C_{15}H_{17}NO$ (M^+) 227.1310, found 227.1311.

4-Methyl-*N*-(4-nitrophenyl)benzenesulfonamide 26.[40] To a solution of *p*-nitroaniline (138 mg, 1 mmol) in dry pyridine (10 mL) were added *p*-toluenesulfonyl chloride (191 mg, 1 mmol) and 4-(dimethylamino)pyridine (12 mg, 0.1 mmol) at room temperature. The reaction mixture was heated to 80 °C and stirred at this temperature for 2 h. Ethyl ether (100 mL) and saturated aqueous $CuSO_4$ solution (50 mL) were added to partition the reaction mixture. The organic phase was washed with saturated aqueous $CuSO_4$ solution (2 × 50 mL) and brine (2 × 50 mL), dried over anhydrous $MgSO_4$, filtered through a pad of cotton, and concentrated in vacuo. The crude product was pure without any further purification. mp (ethanol): 189−190 °C; [lit. 189−190 °C (ethanol)]; ^1H NMR (DMSO-d_6) δ 11.21 (br s, 1H), 8.15−8.10 (m, 2H), 7.76 (dd, J = 10.0, 1.8 Hz, 2H), 7.40−7.28 (m, 4H), 2.33 (s, 3H).

***N*-(4-Aminophenyl)-4-methylbenzenesulfonamide 27.**[40] Yield, 96%; R_f = 0.25 (hexanes:ethyl acetate = 3:2); mp (ethanol): 185−186 °C; [lit. 185−186 °C (ethanol)]; ^1H NMR (DMSO-d_6) δ 9.37 (br s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 6.36 (d, J = 8.8 Hz, 2H), 4.90 (br s, 2H), 2.32 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 147.1, 143.3, 137.9, 130.1, 127.6, 126.6, 125.3, 114.8, 21.8.

1-Nitro-2-(2-nitroethyl)benzene 28.[41] To a cooled solution of β,2-dinitrostyrene (843 mg, 4.34 mmol) in methanol (20 mL) in ice−water bath was added sodium borohydride (0.4 g, 10.57 mmol) in one portion. The reaction mixture was stirred at room temperature for 45 min before ethyl ether (100 mL) and saturated aqueous NH_4Cl solution (30 mL) were added to quench the reaction. The aqueous phase was extracted by ethyl ether (2 × 30 mL). The combined organic phase was washed with brine (40 mL), dried over anhydrous $MgSO_4$, filtered through a pad of cotton, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with EtOAc and hexanes as the eluent (hexanes:ethyl acetate = 5:1 → 4:1) to give **28** as an oil (638 mg,75%). R_f = 0.5 (hexanes:ethyl acetate = 2:1); ^1H NMR ($CDCl_3$) δ 8.09 (dd, J = 8.1, 1.5 Hz, 1H), 7.63−7.40 (m, 3H), 4.80 (t, J = 6.7 Hz, 2H), 3.63 (t, J = 6.7 Hz, 2H).

2-(2-Nitroethyl)phenylamine 29. Yield, 83%; R_f = 0.3 (hexanes:ethyl acetate = 2:1); ^1H NMR ($CDCl_3$) δ 7.17−7.03 (m, 2H), 6.76 (dd, J = 13.3, 7.5 Hz, 2H), 4.65 (t, J = 7.6 Hz, 2H), 3.71 (br s, 2H), 3.25 (t, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 144.5, 130.2, 128.9, 120.1, 119.6, 116.7, 74.1, 29.6; IR (neat): 3446.2, 3382.4, 1628.3, 1550.8, 1498.6, 1379.8 cm^{-1}; MS (ESI) m/z (relative intensity) 167.14 (100, MH^+); HRMS (FAB) (in 3-nitrobenzyl alcohol matrix) m/z calcd for $C_8H_{10}N_2O_2$ (M^+) 166.0742, found 166.0736.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra for compounds **8**, **9**, **12**, **13**, **16**, **17**, **19**, **29**, **30**, and **31**. This material is available free of charge via the Internet at http://pubs.acs.org.

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