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Boron-Catalyzed Silylative Reduction of Nitriles in Accessing Primary Amines and Imines

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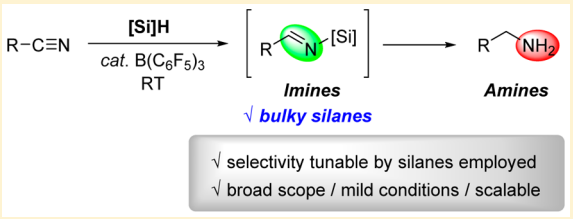
Supporting Information

ABSTRACT: Silylative reduction of nitriles was studied under transition metal-free conditions by using $B(C_6F_5)_3$ as a catalyst with hydrosilanes as a reductant. Alkyl and (hetero)aryl nitriles were efficiently converted to primary amines or imines under mild conditions. The choice of silanes was found to determine the selectivity: while a full reduction of nitriles was highly facile, the use of sterically bulky silanes allowed for the partial reduction leading to *N*-silylimines.

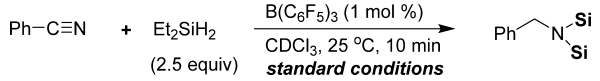


Primary amines and amino group-containing multifunctional molecules are widely present in natural products, biologically active synthetic compounds, and functional materials,[1] also serving as a key building unit in numerous fine chemicals.[2] As a result, synthetic approaches toward primary amines have actively been pursued in organic synthesis. Although primary amines can be conventionally produced by Gabriel synthesis[3a] or reductive amination,[3] substrates are required to be prepared separately for this approach. In this regard, the reduction of nitriles would be an important process to give rise to primary amines. The nitrile reduction is efficiently performed with stoichiometric amounts of metal hydrides such as those of borane and aluminum.[4] Transition metal-catalyzed hydrosilylation[5] or hydrogenation[6] is another approach with the use of Fe, Ti, Re, Co, Rh, Ru, or other metals. In recent years, tris(pentafluorophenyl)borane [B-$(C_6F_5)_3$] and its analogue have been efficiently utilized in reduction of imines, ketones, olefins, alkynes, ethers, and *N*-heteroaromatics by using hydrosilanes[7] or hydrogen[8] as the reducing agents. Beller and co-workers reported a tetra-*n*-butylammonium fluoride (TBAF)-catalyzed hydrosilylation of aryl nitriles using reactive silanes under mild conditions.[9] More recently, Stephan et al. showed that electrophilic phosphonium salts catalyze the hydrosilylation of ketones, imines, and nitriles at room temperature.[10] Recently, we have developed the silylative reduction of quinolines and conjugated nitriles to generate a new sp^3 C−Si bond *beta* to the nitrogen atom of reduced products.[11] In this context, we were curious to study the hydrosilylation of nitriles under the boron-catalyzed conditions, and reported herein are our results of this study.

We commenced our study by optimizing boron-catalyzed hydrosilylation of benzonitrile (Table 1). The reduction was completed in 10 min at room temperature in $CDCl_3$ when 2.5 equiv of diethylsilane was employed in the presence of 1 mol % of $B(C_6F_5)_3$ to afford *N*,*N*-disilylated benzylamine as determined by ^{1}H NMR analysis (entry 1). Hydrolysis of the crude reaction mixture with 1 M HCl in ether afforded the product as hydrochloride salt (**1**) that can be easily obtained by filtration. The reduction was still smooth with lower loading of borane catalyst (entry 2) or in some other solvents as well (entries 4−6). The reaction did not proceed without catalyst (entry 3). However, the efficiency of this hydrosilylation was critically varied depending on the type of silanes employed (entries 7−9). Notably, triisopropylsilane and triethoxysilane were totally ineffective for this reaction (entries 10 and 11, respectively).

With the optimal conditions in hand, we investigated the scope of aryl nitriles (Table 2). Benzonitrile derivatives bearing

Table 1. Optimization of Hydrosilylation of Benzonitrile[a]



entry	changes from the "standard conditions"	yield[a] (%)
1	none	100
2	0.5 mol % of $B(C_6F_5)_3$ instead of 1 mol % (12 h)	100
3	no catalyst	<1
4	Toluene-d_8 instead of $CDCl_3$ (20 min)	100
5	CD_2Cl_2 instead of $CDCl_3$ (20 min)	100
6	C_6D_5Cl (20 min)	100
7	Ph_2SiH_2 (2.5 equiv) instead of Et_2SiH_2 (12 h)	90
8	$PhMe_2SiH$ (3 equiv) instead of Et_2SiH_2 (12 h)	100
9	Et_3SiH (3 equiv) instead of Et_2SiH_2 (12 h)	21
10	$^iPr_3SiH$ (3 equiv) instead of Et_2SiH_2 (12 h)	<1
11	$(EtO)_3SiH$ (3 equiv) instead of Et_2SiH_2 (12 h)	<1

[a]Reactions were carried out in 0.5 mmol scale in a J. Young NMR tube and yields were determined by ^{1}H NMR (1,1,2,2-tetrachloroethane: internal standard).

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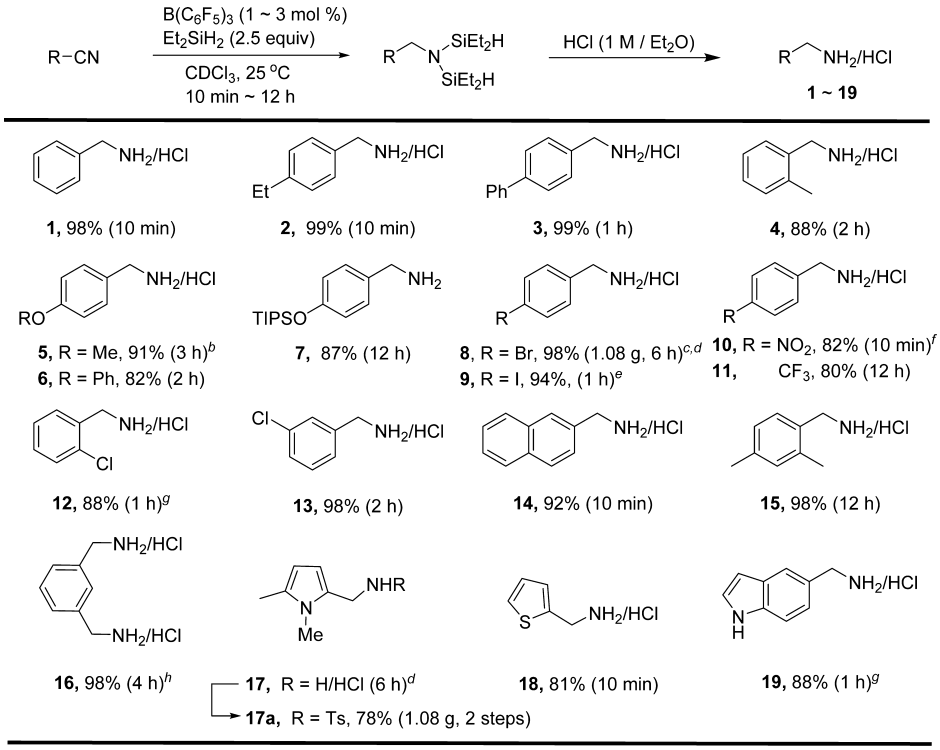
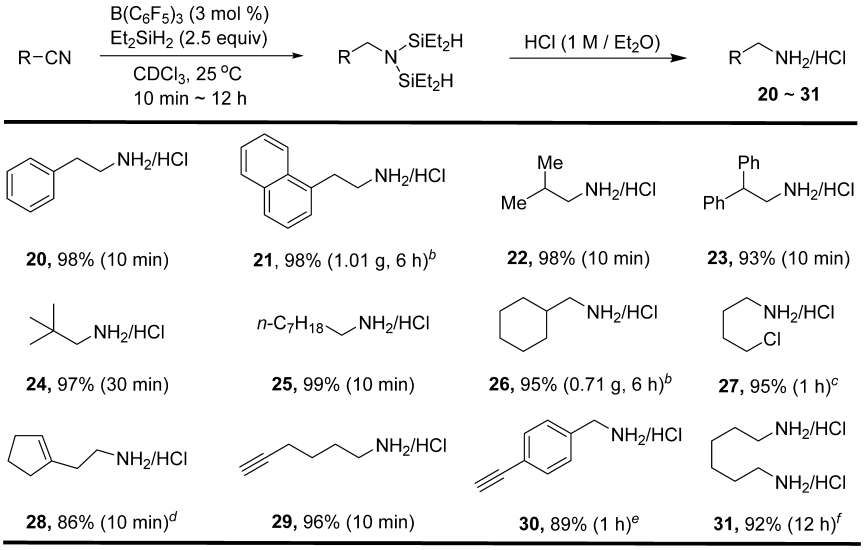
Table 2. Silylative Reduction of (Hetero)aryl Nitriles to Primary Amines[a]



[a]Nitrile (0.5 mmol), silane (2.5 equiv), and $B(C_6F_5)_3$ (1 mol %, **1**−**15**; and 3 mol %, **16**−**19**) in $CDCl_3$ (0.5 mL) at 25 °C under argon atmosphere: isolated yields. [b]$PhMe_2SiH$ (2.0 equiv) was used. [c]At 30 °C. [d]Reactions were carried out in 5 mmol scale. [e]3 mol % $B(C_6F_5)_3$. [f]At 85 °C. [g]65 °C. [h]5 Equiv of Et_2SiH_2 was used in reaction vial.

Table 3. Silylative Reduction of Alkyl Nitriles to Primary Amines[a]



[a]Nitrile (0.5 mmol), silane (2.5 equiv), and $B(C_6F_5)_3$ (3 mol %) in $CDCl_3$ (0.5 mL) at 25 °C under argon atmosphere: isolated yields. [b]Reactions were carried out in 5 mmol scale. [c]$PhMe_2SiH$ (2.0 equiv) was used. [d]2 Equiv of Et_2SiH_2 used. [e]Ph_2SiH_2 (2.5 equiv). [f]5 Equiv of Et_2SiH_2 and 6 mol % boron were used, at 85 °C.

substituents at the 4-position such as 4-ethyl and 4-phenyl were quantitatively reduced with diethylsilane to the corresponding benzylamines (**2**−**3**). Benzonitrile substituted at the 2-position smoothly underwent the hydrosilylation albeit at a longer reaction time (**4**). Importantly, an ether bond was compatible with the present conditions as evidenced by the successful reduction of methoxy-, phenoxy-, and silyloxy-substituted benzonitriles (**5**, **6**, and **7**, respectively).[12] However, the silylative reduction of substrates bearing the dialkyl ether or ester functional groups was not compatible to the present conditions, and failed to give the desired products. High functional group tolerance was additionally demonstrated in the reduction of substrates having such diverse groups as halide, nitro, and trifluoromethyl (**8**−**13**). It should be mentioned that the hydrosilylation was scalable as proven by a successful gram scale reaction run in a flask in $CHCl_3$ (**8**). Again, the position of

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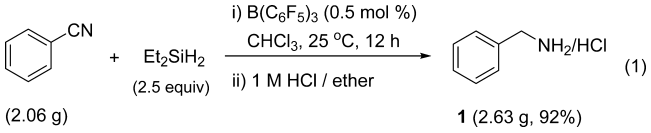
substituents was not critical to the reaction efficiency (**12**–**13**). However, the reaction of 4-nitrobenzonitrile was rather sluggish to require more demanding conditions (85 °C for 10 min) to obtain satisfactory product yield (**10**, 82%). 4-(Trifluoromethyl)benzonitrile was also hydrosilylated rather slowly (12 h) to give 80% product yield (**11**). 2-Cyanonaphthalene was readily reduced under the optimized conditions (10 min at 25 °C) in good yield (**14**).

2,4-Dimethylbenzonitrile was converted to the desired product in good yield (**15**) and the hydrosilylation of 1,3-dicyanobenzene was also efficient leading to a diamine product (HCl salt, **16**) with the use of 5 equiv of diethylsilane. Nitriles of heterocycles such as pyrrole, thiophene, or indole were smoothly reduced to the corresponding primary amines in good yields (**17**–**19**).[13a] In particular, 5 mmol scale reaction of 2-cyano-1,5-dimethylpyrrole was also efficient to afford **17** (HCl salt) that was next converted to its tosylate (**17a**) for the convenience of isolation. The fact that no reaction was detected at the heterocyclic rings was noteworthy, considering that quinoline was readily reduced under the same conditions as shown in our previous study.[11a]

We were pleased to further observe that the borane-catalyzed silylative reduction procedure was readily extended to more challenging alkyl nitriles (Table 3). Although slightly higher loading of $B(C_6F_5)_3$ catalyst (3 mol %) was applied, the reduction took place smoothly still at room temperature in 10 min to 12 h to give excellent product yields. Acetonitrile derivatives monosubstituted with phenyl or 1-naphthyl groups were reacted in high efficiency even on gram scale (**20** and **21**, respectively). α,α-Disubstituted acetonitriles were also reactive in reduction to give the desired β,β-disubstituted primary alkylamines in quantitative yields (**22**–**23**). Reaction of a sterically more demanding substrate such as pivalonitrile took place smoothly (**24**). In addition, caprylonitrile and cyanocyclohexane underwent the reduction in high yields even in large scale (**25** and **26**, respectively).

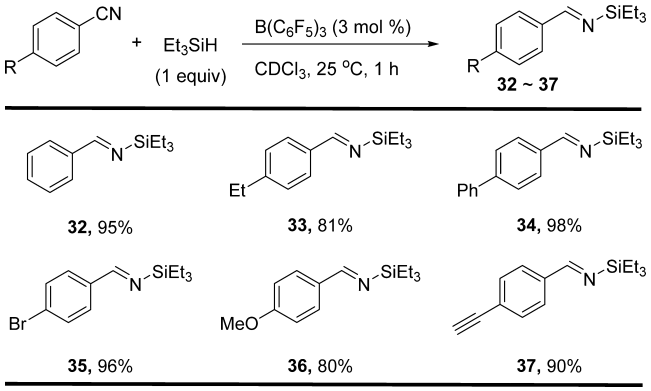
Functional group tolerance was maintained high as evidenced by some representative substrates. For instance, chloro substituent and isolated double bond were completely compatible with the present conditions (**27** and **28**, respectively).[14] In addition, an alkynyl group was tolerated, and substrates containing either aliphatic or aryl triple bonds[15] were reduced highly selectively to afford primary amines without reacting at the labile acetylenic moiety (**29**–**30**) when diphenylsilane was used in the latter case. Hydrosilylation of industrially important adipodinitrile proceeded successfully at 85 °C to give hexane-1,6-diamine dihydrochloride in good yield (92%, **31**).

As shown above, the present hydrosilylation procedure was convenient to carry out in large scale, and a reaction of benzonitrile (20 mmol) was performed successfully using 0.5 mol % of $B(C_6F_5)_3$ to give benzylamine as HCl salt in 92% yield (**1**, 2.63 g, TON ~200) at 25 °C in chloroform (eq 1).



During the course of our study on the silylative reaction of nitriles, a partial reduction was observed to occur highly selectively when 1 equiv of *bulky* trialkylsilanes was employed as a reducing reagent. In fact, with the use of triethylsilane (1 equiv), benzonitrile and its derivatives were converted to *N*-silylimines in excellent yields determined by ^{1}H NMR analysis of the crude reaction mixture (Table 4, **32**–**34**). Functional group tolerance was briefly examined by the successful partial reduction of benzonitriles containing bromo, alkoxy, and acetylenic groups (**35**–**37**). Although reported herein are crude product yields since *N*-silylimines were unstable to purify by column chromatography, purity of the crude products was high (>95%) indicating that the partial reduction was clean and highly selective.[16]

Table 4. Selective Hydrosilylation of Nitriles to Imines



In summary, we have developed the facile $B(C_6F_5)_3$-catalyzed hydrosilylation of nitriles to afford primary amines and *N*-silylimines depending on the type of silanes employed. The reaction was highly mild, efficient, and scalable enabling a convenient synthetic tool to access amines and imines starting from readily available nitriles including both (hetero)aryl and alkyl derivatives.

EXPERIMENTAL SECTION

General Methods. All solvent, nitriles, silanes, and reagents were directly used as purchased without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm), exposure to treatment with acidic anisaldehyde, phosphomolybdic acid, ninhydrin, or ceric ammonium molydate stain followed by heating. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak. $^{13}C\{^1H\}$ NMR was recorded after broad band proton decoupling. Infrared (IR) spectra of new products are given in wave numbers (cm^{-1}), and only selected peaks are reported.

General Procedure of the $B(C_6F_5)_3$-Catalyzed Reduction of Nitriles to Primary Amines (Tables 2 and 3). Silane (2.5 equiv) was added to a solution of $B(C_6F_5)_3$ (1.0 mol % for aryl nitriles and 3.0 mol % for heteroaryl and aliphatic nitriles) in $CDCl_3$ (0.5 mL) in a J. Young NMR tube under argon atmosphere, and the solution was shaken briefly and nitrile (0.50 mmol) [for solids, dissolved in $CDCl_3$] was then added and the reaction mixture was continued at required temperature for 10 min ~12 h. After indicated time, volatiles were removed by reduced pressure and 1 M HCl solution in ether (3 mL) was added, stirred it for 1 h at room temperature to give the desired primary amines as HCl salts as white solid upon filtration washing with ether.

Phenylmethanamine Hydrochloride (Table 2, 1).[13a] Colorless solid (70 mg, 98%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.70 (s, 3H), 7.51 (d, J = 7.3 Hz, 2H), 7.40–7.31 (m, 3H), 3.97 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 134.5, 129.4 (2C), 128.9 (2C), 128.7, 42.5; HRMS (FAB-TOF): Calculated for $C_7H_{10}N$ [M-Cl]$^+$: 108.0813, Found: 108.0810.

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(4-Ethylphenyl)methanamine Hydrochloride (Table 2, 2).[17] Colorless solid (84.6 mg, 99%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.66 (s, 3H), 7.42 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 7.7 Hz, 2H), 3.92 (s, 2H), 2.56 (q, J = 7.6 Hz, 2H), 1.13 (t, J = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 144.4, 131.8, 129.5 (2C), 128.2 (2C), 42.3, 28.3, 16.1; HRMS (FAB-TOF): Calculated for $C_9H_{14}N$ [M-Cl]$^+$: 136.1126, Found: 136.1128.

[1,1′-Biphenyl]-4-ylmethanamine Hydrochloride (Table 2, 3).[13a] Colorless solid (108.4 mg, 99%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.75 (s, 3H), 7.75−7.55 (m, 6H), 7.44 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 4.03 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 140.5, 139.9, 133.7, 130.1 (2C), 129.4 (2C), 128.1, 127.1 (2C), 127.1 (2C), 42.2; HRMS (FAB-TOF): Calculated for $C_{13}H_{14}N$ [M-Cl]$^+$: 184.1126, Found: 184.1125.

***o*-Tolylmethanamine Hydrochloride (Table 2, 4).**[18] Colorless solid (69.1 mg, 88%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 3H), 7.43 (d, J = 7.2 Hz, 1H), 7.30−7.16 (m, 3H), 3.98 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.1, 132.8, 130.7, 129.7, 128.9, 126.5, 39.9, 19.3; HRMS (FAB-TOF): Calculated for $C_8H_{12}N$ [M-Cl]$^+$: 122.0970, Found: 122.0970.

(4-Methoxyphenyl)methanamine Hydrochloride (Table 2, 5).[13a] Colorless solid (78.7 mg, 91%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.59 (s, 3H), 7.43 (d, J = 8.2 Hz, 2H), 6.91 (d, J = 8.3 Hz, 2H), 3.88 (d, J = 5.8 Hz, 2H), 3.71 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.7, 131.0 (2C), 126.4, 114.3 (2C), 55.6, 42.0; HRMS (FAB-TOF): Calculated for $C_8H_{12}NO$ [M-Cl]$^+$: 138.0919, Found: 138.0917.

(4-Phenoxyphenyl)methanamine Hydrochloride (Table 2, 6). Colorless solid (96.3 mg, 82%); mp 251−253 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (s, 3H), 7.54 (d, J = 8.6 Hz, 2H), 7.47−7.31 (m, 2H), 7.23−7.09 (m, 1H), 7.08−6.87 (m, 4H), 4.09−3.88 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.3, 156.8, 131.5 (2C), 130.6 (2C), 129.6, 124.2, 119.2 (2C), 118.9 (2C), 42.0; IR (cm^{-1}): 2950, 2875, 1588, 1507, 1487, 1250, 1171, 964, 872, 689; HRMS (FAB-TOF): Calculated for $C_{13}H_{14}NO$ [M-Cl]$^+$: 200.1075, Found: 200.1074.

[4-(Triisopropylsilyloxy)phenyl]methanamine (Table 2, 7). The general procedure was applied and the product was isolated by flash column chromatography on silica gel (ethyl acetate/*n*-hexane, 3:7): colorless liquid (126.4 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 6.5 Hz, 2H), 3.76 (s, 2H), 2.02−1.70 (m, 2H), 1.29−1.20 (m, 3H), 1.09 (d, J = 7.6 Hz, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 135.6, 128.1 (2C), 119.8 (2C), 45.9, 17.9 (6C), 12.6 (3C); ^{29}Si NMR (120 MHz, $CDCl_3$) δ 14.9; IR (cm^{-1}): 3331, 3228, 2943, 2865, 1669, 1607, 1508, 1460, 1261, 1167, 1071, 911, 672; HRMS (ESI-TOF): Calculated for $C_{16}H_{29}NOSiNa$ [M + Na]$^+$: 302.1916, Found: 302.1890.

(4-Bromophenyl)methanamine Hydrochloride (Table 2, 8).[13a] Colorless solid (1.08 g/5 mmol, 98%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.70 (s, 3H), 7.57 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 3.96 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 133.9, 131.8 (2C), 131.7 (2C), 122.1, 41.8; HRMS (FAB-TOF): Calculated for C_7H_9BrN [M-Cl]$^+$: 185.9918, Found: 185.9921.

(4-Iodophenyl)methanamine Hydrochloride (Table 2, 9).[19] Colorless solid (126.4 mg, 94%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.69 (s, 3H), 7.76 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 3.96 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.7 (2C), 134.3, 131.8 (2C), 95.3, 42.0.

(4-Nitrophenyl)methanamine Hydrochloride (Table 2, 10).[4c] Brown solid (77.1 mg, 82%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 3H), 8.27 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 4.17 (d, J = 5.7 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.8, 142.2, 130.7 (2C), 123.9 (2C), 41.8; HRMS (FAB-TOF): Calculated for $C_7H_9N_2O_2$ [M-Cl]$^+$: 153.0664, Found: 153.0660.

[4-(Trifluoromethyl)phenyl]methanamine Hydrochloride (Table 2, 11).[13a] Colorless solid (84.4 mg, 80%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 3H), 7.80 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 4.12 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 139.3, 130.3 (2C), 129.3 (q, J = 32 Hz), 125.7 (q, J = 3.8 Hz, 2C), 124.6 (q, J = 272.7 Hz), 42.0; ^{19}F NMR (376 MHz, DMSO-d_6) δ −61.5; HRMS (FAB-TOF): Calculated for $C_8H_9NF_3$ [M-Cl]$^+$: 176.0687, Found: 176.0689.

(2-Chlorophenyl)methanamine Hydrochloride (Table 2, 12). Colorless solid (78 mg, 88%); mp 222−224 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 3H), 7.81−7.63 (m, 1H), 7.58−7.47 (m, 1H), 7.46−7.30 (m, 2H), 4.10 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 133.3, 132.1, 131.1, 130.7, 129.8, 127.9, 40.0; IR (cm^{-1}): 2892, 1598, 1535, 1438, 1381, 1205, 1050, 890, 746; HRMS (FAB-TOF): Calculated for C_7H_9ClN [M-Cl]$^+$: 142.0424, Found: 142.0425.

(3-Chlorophenyl)methanamine Hydrochloride (Table 2, 13). Colorless solid (86.7 mg, 98%); mp 307−309 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.72 (s, 3H), 7.65 (s, 1H), 7.59−7.25 (m, 3H), 4.00 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 136.9, 133.4, 130.7, 129.4, 128.6, 128.2, 41.9; IR (cm^{-1}): 2960, 2903, 1598, 1576, 1458, 1216, 1111, 1083, 969, 788; HRMS (FAB-TOF): Calculated for C_7H_9ClN [M-Cl]$^+$: 142.0424, Found: 142.0422.

Naphthalen-2-ylmethanamine Hydrochloride (Table 2, 14).[4d] Colorless solid (88.8 mg, 92%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (s, 3H), 8.10−7.81 (m, 4H), 7.77−7.63 (m, 1H), 7.62−7.43 (m, 2H), 4.18 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 133.0, 132.2, 128.6, 128.4, 128.2, 128.1, 127.1 (2C), 127.0, 127.0 (2C); HRMS (FAB-TOF): Calculated for $C_{11}H_{12}N$ [M-Cl]$^+$: 158.0970, Found: 158.0969.

(2,4-Dimethylphenyl)methanamine Hydrochloride (Table 2, 15).[20] Colorless solid (83.8 mg, 98%); mp 215−216 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.57 (s, 3H), 7.30 (d, J = 7.8 Hz, 1H), 7.01 (s, 1H), 7.00 (d, J = 8.5 Hz, 1H), 3.90 (s, 2H), 2.30 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 138.1, 136.9, 131.3, 129.8, 129.7, 126.9, 39.6, 21.1, 19.2.

1,3-Phenylenedimethanamine Dihydrochloride (Table 2, 16).[21] Colorless solid (102 mg, 98%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.73 (s, 6H), 7.66−7.46 (m, 3H), 7.41 (s, 1H), 3.95 (s, 4H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 134.7 (2C), 130.2, 129.2, 129.1 (2C), 42.4 (2C).

(1,5-Dimethyl-1*H*-pyrrol-2-yl)methanamine Hydrochloride (Table 2, 17). Brown solid; mp 203−205 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.41 (s, 3H), 6.18−5.90 (d, J = 2.8 Hz, 1H), 5.75 (d, J = 3.5 Hz, 1H), 3.95 (d, J = 5.6 Hz, 2H), 3.48 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 130.2, 124.3, 109.4, 105.9, 34.4, 30.8, 12.7; IR (cm^{-1}): 2972, 1603, 1466, 1412, 1385, 1315, 1109, 1079, 990, 754.

***N*-[(1,5-Dimethyl-1*H*-pyrrol-2-yl)methyl]-4-methylbenzenesulfonamide (Table 2, 17a).** To a flame-dried 50 mL round-bottom flask were added $B(C_6F_5)_3$ (77 mg, 0.3 mmol, 3 mol %), diethylsilane (1.62 mL, 12.5 mmol, 2.5 equiv), and chloroform (5 mL) under argon atmosphere. Benzonitrile (0.60 g, 5 mmol) was then added and the reaction mixture was stirred at room temperature for 6 h. After removing volatiles by rotary evaporator, 1 M HCl solution in ether (30 mL) was added and the reaction mixture stirred for 1 h at room temperature to form the desired product **17** (HCl salt) as brown solid. To a flame-dried round-bottom flask were added **17**/HCl (5 mmol) and dichloromethane (25 mL). After the dropwise addition of triethylamine (2.1 mL, 15 mmol) at 0 °C, it was stirred for 15 min at 0 °C. *p*-Toluenesulfonyl chloride (1.14 g, 6 mmol) was added and the reaction mixture was stirred at room temperature for 12 h. Water was added and the reaction mixture was extracted with dichloromethane (15 mL × 3). The combined organic layers were dried over Na_2SO_4, evaporated under reduced pressure, and purified by flash column chromatography on silica gel (ethyl acetate/*n*-hexane, 3:7) to afford the corresponding product **17a** (1.08 g, 78% over two steps): Brown solid (1.08 g/5 mmol, 78%); mp 107−108 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.83 (d, J = 3.4 Hz, 1H), 5.73 (d, J = 3.3 Hz 1H), 4.45 (t, J = 5.8 Hz, 1H), 4.03 (d, J = 5.8 Hz, 2H), 3.42 (s, 3H), 2.45 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 136.5, 130.8 (2C), 129.7, 127.1 (2C), 125.1, 108.2, 105.3, 39.9, 30.3, 21.5, 12.3; IR (cm^{-1}): 3270, 2924, 1685, 1584, 1511, 1433, 1324, 1305, 1157, 1091, 1034, 832, 667; HRMS (ESI-TOF): Calculated for $C_{14}H_{18}N_2NaO_2S$ [M + Na]$^+$: 301.0987, Found: 301.0983.

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Thiophen-2-ylmethanamine Hydrochloride (Table 2, 18). White solid (60.3 mg, 81%); mp 292−294 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 (s, 3H), 7.56 (dd, J = 5.1, 1.3 Hz, 1H), 7.30 (dd, J = 3.4, 1.3 Hz, 1H), 7.06 (dd, J = 5.1, 3.5 Hz, 1H), 4.20 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.8, 129.6, 127.7 (2C), 37.0; IR (cm^{-1}): 3339, 3082, 2910, 1617, 1589, 1508, 1275, 1241, 958, 719; HRMS (FAB-TOF): Calculated for C_5H_8NS [M-Cl]$^+$: 114.0377, Found: 114.0378.

(1*H*-Indol-5-yl)methanamine Hydrochloride (Table 2, 19).[22] Brown solid (80.1 mg, 88%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.31 (s, 1H), 8.44 (s, 3H), 7.65 (s, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.37 (t, J = 2.8 Hz, 1H), 7.21 (dd, J = 8.4, 1.7 Hz, 1H), 6.45−6.41 (m, 1H), 4.03 (q, J = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.1, 128.0, 126.7, 124.7, 122.5, 121.4, 111.9, 101.5, 43.4; HRMS (FAB-TOF): Calculated for $C_9H_{11}N_2$ [M-Cl]$^+$: 147.0922, Found: 147.0925.

2-Phenylethan-1-amine Hydrochloride (Table 3, 20).[13] Colorless solid (77 mg, 98%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.37 (s, 3H), 7.54−6.90 (m, 5H), 3.20−2.60 (m, 4H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 137.9, 129.0 (4C), 127.1, 40.3, 33.3; HRMS (FAB-TOF): Calculated for $C_8H_{12}N$ [M-Cl]$^+$: 122.0970, Found: 122.0967.

2-(Naphthalen-1-yl)ethan-1-amine Hydrochloride (Table 3, 21).[23] Colorless solid (1.01 g/5 mmol, 98%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.39 (s, 3H), 8.21 (dd, J = 8.5, 1.2 Hz, 1H), 7.95 (dd, J = 8.3, 1.3 Hz, 1H), 7.84 (dd, J = 7.6, 1.9 Hz, 1H), 7.62−7.51 (m, 2H), 7.49−7.41 (m, 2H), 3.49−3.38 (m, 2H), 3.12−3.04 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 134.0, 133.9, 131.8, 129.2, 127.9, 127.4, 126.8, 126.3, 126.1, 124.0, 40.0, 30.6; HRMS (FAB-TOF): Calculated for $C_{12}H_{14}N$ [M-Cl]$^+$: 172.1126, Found: 172.1128.

2-Methylpropan-1-amine Hydrochloride (Table 3, 22).[24] Colorless solid (53.4 mg, 98%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.17 (s, 3H), 2.55 (d, J = 7.0 Hz, 2H), 1.93−1.80 (m, 1H), 0.88 (d, J = 6.8 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 46.1, 26.7, 20.3 (2C); HRMS (FAB-TOF): Calculated for $C_4H_{12}N$ [M-Cl]$^+$: 74.0970, Found: 74.0971.

2,2-Diphenylethan-1-amine Hydrochloride (Table 3, 23).[18] Colorless solid (108.3 mg, 93%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.28 (s, 3H), 7.62−6.81 (m, 10H), 4.42 (s, 1H), 3.49 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 141.6 (2C), 129.2 (4C), 128.3 (4C), 127.4 (2C), 48.8, 42.8; HRMS (FAB-TOF): Calculated for $C_{14}H_{16}N$ [M-Cl]$^+$: 198.1283, Found: 198.1280.

2,2-Dimethylpropan-1-amine Hydrochloride (Table 3, 24).[18] Colorless solid (59.6 mg, 97%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.17 (s, 3H), 2.54 (s, 2H), 0.92 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 50.1, 30.6, 27.4 (3C); HRMS (FAB-TOF): Calculated for $C_5H_{14}N$ [M-Cl]$^+$: 88.1126, Found: 88.1125.

***n*-Octan-1-amine Hydrochloride (Table 3, 25).**[24] Colorless solid (81.7 mg, 99%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.17 (s, 3H), 2.79−2.57 (m, 2H), 1.53 (t, J = 7.5 Hz, 2H), 1.37−1.05 (m, 10H), 0.82 (t, J = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 39.1, 31.6, 28.9, 28.9, 27.3, 26.4, 22.5, 14.3; HRMS (FAB-TOF): Calculated for $C_8H_{20}N$ [M-Cl]$^+$: 130.1596, Found: 130.1595.

Cyclohexylmethanamine Hydrochloride (Table 3, 26).[13a] Colorless solid (0.71 g/5 mmol, 95%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.19 (s, 3H), 2.56 (s, 2H), 1.87−1.34 (m, 6H), 1.11 (m, 3H), 0.87 (q, J = 12.1, 11.6 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 44.8, 35.7, 30.3 (2C), 26.1, 25.5 (2C); HRMS (FAB-TOF): Calculated for $C_7H_{16}N$ [M-Cl]$^+$: 114.1283, Found: 114.1284.

4-Chlorobutylamine Hydrochloride (Table 3, 27).[25] Colorless solid (68 mg, 95%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (s, 3H), 3.57 (t, J = 5.4 Hz, 2H), 3.22−2.86 (m, 2H), 2.06−1.75 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 44.3, 39.5, 29.4, 24.9.

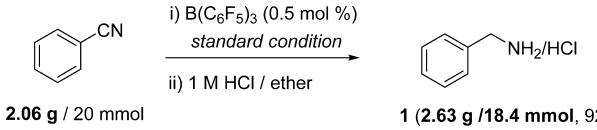
2-(Cyclopent-1-en-1-yl)ethan-1-amine Hydrochloride (Table 3, 28). Brown solid (63.2 mg, 86%); mp 220−222 °C: ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.22 (s, 3H), 5.40 (s, 1H), 2.83 (d, J = 11.3 Hz, 2H), 2.46−2.28 (m, 2H), 2.29−2.08 (m, 4H), 1.94−1.60 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 140.2, 125.6, 37.5, 35.0, 32.5, 28.9, 23.1; IR (cm^{-1}): 3299, 2954, 1595, 1477, 1336, 1217, 1075, 1009, 837; HRMS (FAB-TOF): Calculated for $C_7H_{14}N$ [M-Cl]$^+$: 112.1126, Found: 112.1124.

Hex-5-yn-1-amine Hydrochloride (Table 3, 29).[26] Brown solid (64 mg, 96%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.19 (s, 3H), 2.78 (s, 1H), 2.72 (q, J = 6.7 Hz, 2H), 2.21−2.08 (m, 2H), 1.68−1.56 (m, 2H), 1.53−1.39 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 84.4, 71.9, 38.6, 26.5, 25.3, 17.7; HRMS (FAB-TOF): Calculated for $C_6H_{12}N$ [M-Cl]$^+$: 98.0970, Found: 98.0971.

(4-Ethynylphenyl)methanamine Hydrochloride (Table 3, 30).[27] Brown solid (74.3 mg, 89%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.70 (s, 3H), 7.54 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 4.27 (s, 1H), 4.01 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.4, 132.2 (2C), 129.7 (2C), 122.1, 83.5, 81.8, 42.2; HRMS (FAB-TOF): Calculated for $C_9H_{10}N$ [M-Cl]$^+$: 132.0813, Found: 132.0813.

Hexane-1,6-diamine Dihydrochloride (Table 3, 31).[13a] Colorless solid (86.5 mg, 92%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.20 (s, 6H), 2.69 (q, J = 7.2, 6.7 Hz, 4H), 1.63−1.40 (m, 4H), 1.27 (t, J = 5.5 Hz, 4H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 38.9, 27.1, 25.8.

Synthetic Applications (eq 1): Gram Scale Reduction of Benzonitrile. To a flame-dried 50 mL round-bottom flask were added



2.06 g / 20 mmol — **1** (**2.63 g /18.4 mmol**, 92%)

$B(C_6F_5)_3$ (51 mg, 0.5 mol %), diethylsilane (6.5 mL, 2.5 equiv), and chloroform (20 mL) under argon atmosphere. Benzonitrile (2.06 g, 20 mmol) was then added and the reaction mixture was stirred at room temperature for 12 h. Volatiles were removed by reduced pressure and 1 M HCl solution in ether (120 mL) was added, and the mixture stirred for 1 h at room temperature to give the desired primary amine as HCl salt form as a white solid (**1**, 92%, 2.63 g) upon filtration washing with ether.

$B(C_6F_5)_3$-Catalyzed Silylative Reduction of Nitriles to Imines (Table 4). Triethylsilane (1.0 equiv) was added to a solution of $B(C_6F_5)_3$ (3.0 mol %) in $CDCl_3$ (0.5 mL) in a J. Young NMR tube, and the solution was shaken briefly followed by the addition of the corresponding nitrile (0.5 mmol) and dibromomethane (0.5 equiv: internal standard) under argon atmosphere. After 1 h, the reaction mixture was subjected to ^{1}H NMR spectroscopy and crude NMR yields were measured on the basis of an internal standard.

1-Phenyl-*N*-(triethylsilyl)methanimine (Table 4, 32).[28] ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.93−7.78 (m, 2H), 7.50−7.43 (m, 3H), 1.05 (t, J = 8.0 Hz, 9H), 0.81 (q, J = 7.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 139.1, 131.1, 128.5 (2C), 128.4 (2C), 7.0 (3C), 3.6 (3C).

1-(4-Ethylphenyl)-*N*-(triethylsilyl)methanimine (Table 4, 33). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 2.71 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.7 Hz, 3H), 1.04 (t, J = 8.0 Hz, 9H), 0.80 (q, J = 7.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 147.8, 137.0, 128.5 (2C), 128.0 (2C), 28.9, 15.5, 7.0 (3C), 3.7 (3C).

1-[(1,1′-Biphenyl)-4-yl]-*N*-(triethylsilyl)methanimine (Table 4, 34). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.97 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 7.6 Hz, 2H), 7.54−7.50 (m, 2H), 7.44 (t, J = 7.4 Hz, 1H), 1.13 (t, J = 8.0 Hz, 9H), 0.89 (q, J = 8.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 144.0, 140.6, 138.1, 128.9 (2C), 128.9 (2C), 127.8, 127.3 (2C), 127.3 (2C), 7.1 (3C), 3.8 (3C).

1-(4-Bromophenyl)-*N*-(triethylsilyl)methanimine (Table 4, 35). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 1.02 (t, J = 8.0 Hz, 9H), 0.77 (q, J = 8.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.1, 137.8, 131.7 (2C), 129.7 (2C), 125.7, 7.0 (3C), 3.6 (3C).

1-(4-Methoxyphenyl)-*N*-(triethylsilyl)methanimine (Table 4, 36). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.78 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 3.84 (s, 3H), 1.03 (t, J = 8.1 Hz, 9H), 0.77 (q, J = 8.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 162.1, 132.5, 130.0 (2C), 113.8 (2C), 55.3, 7.0 (3C), 3.7 (3C).

1-(4-Ethynylphenyl)-*N*-(triethylsilyl)methanimine (Table 4, 37). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.76 (d, J = 8.1

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Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 3.19 (s, 1H), 1.00 (t, J = 8.0 Hz, 9H), 0.76 (q, J = 8.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 138.9, 132.3 (2C), 128.1 (2C), 124.7, 83.4, 79.0, 6.9 (3C), 3.6 (3C).

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra data for all compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00941.

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Notes

The authors declare no competing financial interest.

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