

# Electron Transfer Reduction of Nitriles Using $\text{SmI}_2$ – $\text{Et}_3\text{N}$ – $\text{H}_2\text{O}$ : Synthetic Utility and Mechanism

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### List of Known Compounds/General Methods

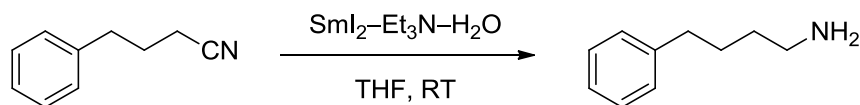
All compounds reported in the manuscript have been described in literature or are commercially available. All nitriles were purchased from commercial suppliers at the highest quality and used without further purification. Samarium(II) iodide was prepared by standard methods and titrated prior to use.<sup>1-5</sup> All experiments involving  $\text{SmI}_2$  were performed using standard techniques under argon or nitrogen atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using  $^1\text{H}$  NMR, and/or GC-MS analysis and comparison with authentic samples. All yields refer to yields determined by  $^1\text{H}$  NMR and/or GC-MS using an internal standard unless stated otherwise.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on Bruker spectrometers at 300, 400 and 500 MHz ( $^1\text{H}$  NMR) and 75, 100 and 125 MHz ( $^{13}\text{C}$  NMR). All shifts are reported in parts per million (ppm) relative to residual  $\text{CHCl}_3$  peak (7.27 and 77.2 ppm,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; br s, broad singlet. GC-MS chromatography was performed using Agilent 7890A GC System and Agilent 5975C inert XL EI/CI MSD with Triple Axis Detector equipped with Agilent HP-5MS column (19091S-433) (length 30 m, internal diameter 0.25 mm, film 0.25  $\mu\text{m}$ ) using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 40 °C or 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 25 °C/min ramp after 50 °C hold for 3 min to a final temperature of 300 °C, then hold at 300 °C for 5 min (splitless mode of injection, total run time of 18 min). All flash chromatography was performed using silica gel, 60 Å, 230–400 mesh. TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data are given for all compounds in the Supporting Experimental for characterization purposes.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR and HRMS data are reported for all new compounds.

## Effect of Additives and Additional Optimization Studies

**Table SI-1.** Effect of Additives and Additional Optimization Studies.<sup>a</sup>

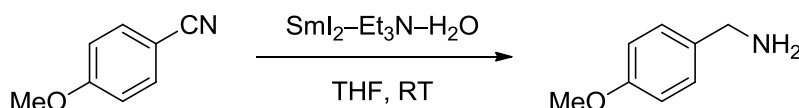
$\text{C}_{13}\text{H}_{27}\text{CN} \xrightarrow[\text{THF, RT}]{\text{SmI}_2\text{-conditions}} \text{C}_{13}\text{H}_{27}\text{NH}_2$							
entry	amine	proton source	amine (equiv)	ROH (equiv)	time <sup>b</sup>	conv. <sup>c</sup> (%)	yield <sup>c</sup> (%)
1	-	-	-	-	5 days	<2	<2
2	$\text{Et}_3\text{N}$	-	36	-	24 h	<2	<2
3	-	$\text{H}_2\text{O}$	-	36	24 h	<2	<2
4	-	$\text{H}_2\text{O}$	-	800	24 h	<2	<2
5	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	36	36	2 h	>98	94
6	pyrrolidine	$\text{H}_2\text{O}$	36	36	2 h	>98	71
7	<i>n</i> - $\text{BuNH}_2$	$\text{H}_2\text{O}$	36	36	2 h	>98	51
8	DIPA	$\text{H}_2\text{O}$	36	36	2 h	>98	86
9 <sup>d</sup>	$\text{EtN}(\text{Me})_2$	$\text{H}_2\text{O}$	36	36	5 min	>98	89
10 <sup>d,e</sup>	$\text{MeNH}_2$	$\text{H}_2\text{O}$	36	94	5 min	>98	84
11	$\text{Et}_3\text{N}$	$\text{MeOH}$	36	36	2 h	<2	<2
12	$\text{Et}_3\text{N}$	<i>t</i> - $\text{BuOH}$	36	36	2 h	<2	<2
13	$\text{Et}_3\text{N}$	$(\text{HOCH}_2)_2$	36	18	2 h	91	36
14 <sup>f</sup>	$\text{NH}_3$	$\text{H}_2\text{O}$	36	166	5 min	84	74
15 <sup>g</sup>	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	8	12	24 h	>98	26
16	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	18	18	5 min	>98	60
17 <sup>h</sup>	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	36	36	5 min	>98	95
18	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	36	144	2 h	>98	84
19	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	36	800	2 h	>98	69
20	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	36	3200	2 h	79	35
21 <sup>i</sup>	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	36	36	5 min	>98	92
22	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	72	72	5 min	>98	86
23 <sup>j</sup>	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	36	36	5 min	>98	82
24 <sup>j</sup>	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	72	72	5 min	>98	87

<sup>a</sup>All reactions carried out using standard Schlenk techniques. Conditions:  $\text{SmI}_2$  (6 equiv), THF, rt; rapid addition of ROH to the mixture of substrate,  $\text{SmI}_2$  and amine. Conversion = (100-SM). In all cases, when conversion <2%, starting material recovered in >90% after aqueous work-up. <sup>b</sup>Quenched by bubbling air through reaction mixtures. <sup>c</sup>Determined by GC-MS and/or  $^1\text{H}$  NMR. <sup>d</sup>Dodecanenitrile used as a substrate. <sup>e</sup> $\text{MeNH}_2$  (aq solution, 40%, Aldrich) was used. <sup>f</sup> $\text{NH}_3$  (aq solution, 35%, Fisher Scientific) was used. <sup>g</sup>4-Phenylbutanenitrile used as a substrate,  $\text{SmI}_2$  (4.5 equiv). <sup>h</sup>Reverse addition ( $\text{H}_2\text{O}$  first). <sup>i</sup>In situ prepared  $\text{SmI}_2$ . <sup>j</sup>Preformed  $\text{SmI}_2$ -amine-ROH system was used.

**Table SI-2.** Determination of the Effect of Reagent Stoichiometry on the Reduction of Unactivated Nitriles using SmI<sub>2</sub>.<sup>a</sup>

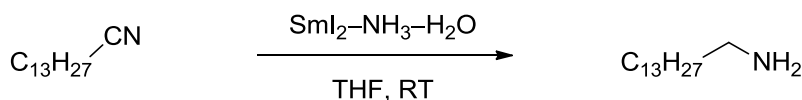
entry	SmI <sub>2</sub> (equiv)	Et <sub>3</sub> N (equiv)	H <sub>2</sub> O (equiv)	time <sup>b</sup>	conv. <sup>c</sup> (%)	yield <sup>c</sup> (%)
1	4.5	8	12	24 h	>98	26
2	6	18	18	5 min	>98	67
3	6	36	36	10 s	>98	90

<sup>a</sup>All reactions carried out using standard Schlenk techniques for handling air-sensitive reagents. <sup>b</sup>Quenched by bubbling air through reaction mixtures. <sup>c</sup>Determined by GC-MS and/or <sup>1</sup>H NMR.

**Table SI-3.** Determination of the Effect of Lewis Base on the Reduction of Activated Nitriles using SmI<sub>2</sub>.<sup>a</sup>

entry	SmI <sub>2</sub> (equiv)	Et <sub>3</sub> N (equiv)	H <sub>2</sub> O (equiv)	time <sup>b</sup>	conv. <sup>c</sup> (%)	yield <sup>c</sup> (%)
1	6	-	18	2 h	<5	<5
2	6	12	18	2 h	31	21
3	6	36	36	5 min	>95	92

<sup>a</sup>All reactions carried out using standard Schlenk techniques for handling air-sensitive reagents. <sup>b</sup>Quenched by bubbling air through reaction mixtures. <sup>c</sup>Determined by GC-MS and/or <sup>1</sup>H NMR.

**Table SI-4.** Determination of the Effect of Ammonia Stoichiometry on the Reduction of Unactivated Nitriles using SmI<sub>2</sub>.<sup>a</sup>

entry	SmI <sub>2</sub> (equiv)	NH <sub>3</sub> (equiv)	H <sub>2</sub> O (equiv)	time <sup>b</sup>	conv. <sup>c</sup> (%)	yield <sup>c</sup> (%)
1	6	36	166	5 min	84	74
2	6	18	83	5 min	58	50
3 <sup>d</sup>	6	72	332	5 min	<5	<5

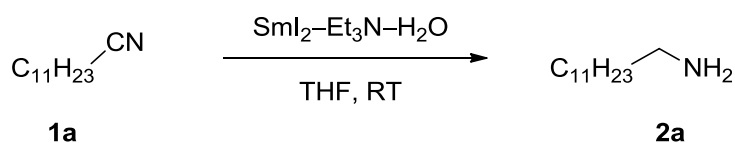
<sup>a</sup>All reactions carried out using standard Schlenk techniques for handling air-sensitive reagents. <sup>b</sup>Quenched by bubbling air through reaction mixtures. <sup>c</sup>Determined by GC-MS and/or <sup>1</sup>H NMR. NH<sub>3</sub> (aq solution, 35%, Fisher Scientific) was used.

<sup>d</sup>Reagent decomposition was observed. For a similar effect on the stability of Sm(II) systems see ref. 6-10.

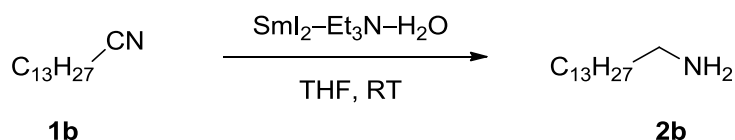
## Experimental Procedures and Characterization Data

**Procedure for the reduction of nitriles with  $\text{SmI}_2$ – $\text{Et}_3\text{N}$ – $\text{H}_2\text{O}$ .** (*Stock solutions of  $\text{SmI}_2$  in THF*). An oven-dried vial equipped with a stir bar was charged with a nitrile substrate (neat), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 6 equiv) was added followed by  $\text{Et}_3\text{N}$  (typically, 36 equiv) and  $\text{H}_2\text{O}$  (typically, 36 equiv) with vigorous stirring, which resulted in the formation of a characteristic dark brown color of the  $\text{SmI}_2$ – $\text{Et}_3\text{N}$ – $\text{H}_2\text{O}$  complex, and the reaction mixture was stirred for the indicated time. In some cases, a solution of nitrile substrate (1.0 equiv, stock solution in THF, 1.0 mL) was added to the preformed samarium(II) iodide/amine/ $\text{H}_2\text{O}$  complex, and the reaction mixture was stirred for the indicated time. The excess of  $\text{Sm}(\text{II})$  was oxidized by bubbling air through the reaction mixture, and the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  or  $\text{Et}_2\text{O}$  (20 mL) and  $\text{NaOH}$  (10 mL, 1 N) or  $\text{KOH}$  (10 mL, 10% aq). The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 20 mL), the organic layers were combined, washed with  $\text{Na}_2\text{S}_2\text{O}_3$  (5 mL, aq., sat.), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The sample was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 or 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples. Unless stated otherwise, the crude product was purified by chromatography using a short plug of silica gel. Note that reactions involving samarium(II) can typically be followed by visual observation of the color changes of the respective reaction mixtures. In the case of  $\text{Sm}(\text{II})$ /amine/ $\text{H}_2\text{O}$  complexes, the color changes from  $\text{Sm}^{\text{II}}$  (dark brown) to  $\text{Sm}^{\text{III}}$  (dark to light green: oxidized, solvated; then white and yellow: fully oxidized, characteristic of  $\text{SmI}_2\text{X}$ ).

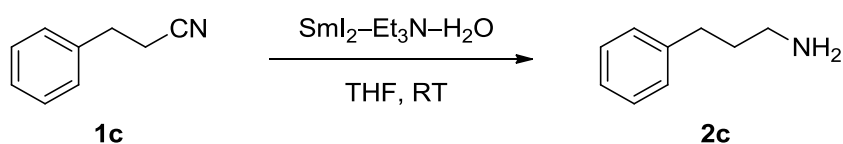
**Procedure for the reduction of nitriles with  $\text{SmI}_2$ – $\text{Et}_3\text{N}$ – $\text{H}_2\text{O}$ .** (*In situ prepared solutions of  $\text{SmI}_2$  in THF*). To a solution of samarium(II) iodide (0.10 M in THF, prepared from  $\text{Sm}$  metal and  $\text{ICH}_2\text{CH}_2\text{I}$  according to the procedure previously described),<sup>5</sup> a solution of nitrile (1.0 mmol) in THF (2.0 mL) was added, followed by amine (36 equiv) and water (36 equiv) under inert atmosphere at room temperature and stirred vigorously. After 5 min, the excess of  $\text{SmI}_2$  was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with  $\text{Et}_2\text{O}$  (100 mL) and  $\text{KOH}$  (20 mL, 10%, aq). The aqueous layer was extracted with  $\text{Et}_2\text{O}$  (2 x 100 mL), organic layers were combined, washed with  $\text{Na}_2\text{S}_2\text{O}_3$  (2 x 10 mL, aq, sat.) dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The crude product was purified by chromatography using a short plug of silica gel.

**Dodecan-1-amine** (Table 2, entry 1)

According to the general procedure, the reaction of dodecanenitrile (0.25 mmol), samarium(II) iodide (1.5 mmol, 0.080 M), water (9.0 mmol) and triethylamine (9.0 mmol) for 5 min at rt, afforded after work-up with  $\text{CH}_2\text{Cl}_2/\text{NaOH}$  (1.0 N) and chromatography (90/10/1-80/20/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ) the title compound in 93% yield. ( $R_f$  = 0.46, 90/10/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J$  = 6.9 Hz, 3 H), 1.18-1.37 (m, 18 H), 1.41-1.54 (m, 2 H), 2.22 (br, 2 H), 2.72 (t,  $J$  = 7.2 Hz, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 26.9, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9, 33.2, 42.0.

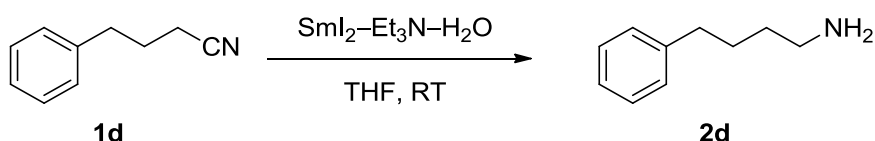
**Tetradecan-1-amine** (Table 2, entry 2)

According to the general procedure, the reaction of tetradecanenitrile (1.0 mmol), samarium(II) iodide (6.0 mmol, 0.080 M), water (36.0 mmol) and triethylamine (36.0 mmol) for 5 min at rt, afforded after work-up with  $\text{CH}_2\text{Cl}_2/\text{NaOH}$  (1.0 N) and acid-base extraction (1.0 N HCl/6.0 N NaOH,  $\text{CH}_2\text{Cl}_2$ ) the title compound in 94% yield. In another run tetradecanenitrile (1.0 mmol) was reacted with samarium(II) iodide (6.0 mmol, 0.10 M, prepared *in situ* from Sm metal, 12.0 mmol and  $\text{ICH}_2\text{CH}_2\text{I}$ , 6.0 mmol according to the procedure described in Szostak, Spain and Procter, *J. Org. Chem.*, **2012**, 77, 3049), water (36.0 mmol) and triethylamine (36.0 mmol) for 5 min at rt, to afford after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 92% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.81 (t,  $J$  = 6.9 Hz, 3 H), 1.05-1.27 (m, 22 H), 1.30-1.41 (m, 2 H), 1.47 (br, 2 H), 2.61 (t,  $J$  = 6.9 Hz, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 26.9, 29.4, 29.5, 29.7, 29.7, 31.9, 33.7, 42.2.

**3-Phenylpropan-1-amine** (Table 2, entry 3)

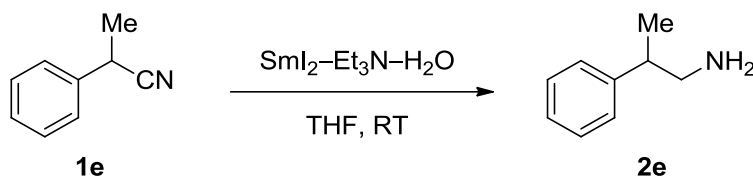
According to the general procedure, the reaction of 3-phenylpropanenitrile (0.25 mmol), samarium(II) iodide (1.5 mmol, 0.080 M), water (9.0 mmol) and triethylamine (9.0 mmol) for 5 min at rt, afforded after work-up with  $\text{CH}_2\text{Cl}_2/\text{NaOH}$  (1.0 N) and chromatography (90/10/1-80/20/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ) the title compound in 89% yield. ( $R_f$  = 0.62, 80/20/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.67-1.1.75 (m, 2 H), 1.76 (br, 2 H), 2.58 (t,  $J$  = 7.8 Hz, 2 H), 2.67 (t,  $J$  = 6.9 Hz, 2 H), 7.07-7.14 (m, 3 H), 7.17-7.24 (m, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  33.3, 35.1, 41.7, 125.8, 128.3, 128.4, 142.1.

#### 4-Phenylbutan-1-amine (Table 2, entry 4)

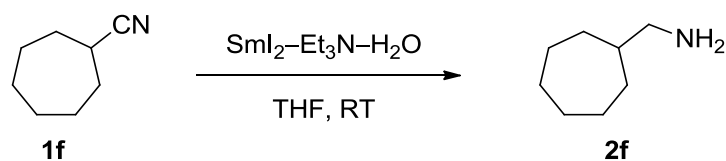


According to the general procedure, the reaction of 4-phenylbutanenitrile (1.0 mmol), samarium(II) iodide (6.0 mmol, 0.085 M), water (36.0 mmol) and triethylamine (36.0 mmol) for 5 min at rt, afforded after work-up with  $\text{CH}_2\text{Cl}_2/\text{NaOH}$  (1.0 N) and chromatography (90/10/1-80/20/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ) the title compound in 84% yield. ( $R_f$  = 0.52, 80/20/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.34 (br, 2 H), 1.36-1.43 (m, 2 H), 1.52-1.60 (m, 2 H), 2.54 (t,  $J$  = 7.6 Hz, 2 H), 2.61 (t,  $J$  = 6.8 Hz, 2 H), 7.06-7.11 (m, 3 H), 7.16-7.22 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  28.8, 33.4, 35.8, 42.1, 125.7, 128.3, 128.4, 142.5.

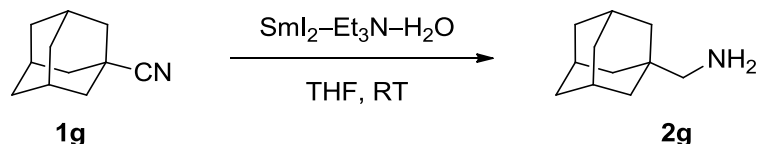
#### 2-Phenylpropan-1-amine (Table 2, entry 5)



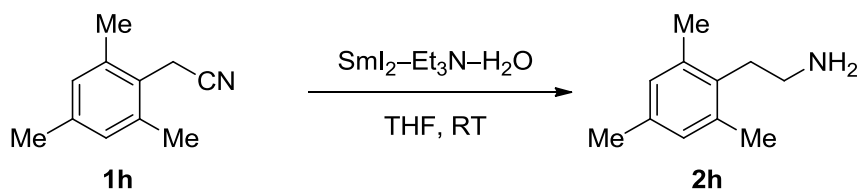
According to the general procedure, the reaction of 2-phenylpropanenitrile (0.10 mmol), samarium(II) iodide (0.32 mmol, 0.080 M), water (2.4 mmol) and triethylamine (2.4 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 98% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.26 (d,  $J$  = 6.8 Hz, 3 H), 2.69-2.80 (m, 1 H), 2.84 (s, 1 H), 2.86 (d,  $J$  = 0.8 Hz, 1 H), 7.18-7.25 (m, 3 H), 7.29-7.35 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  19.1, 43.5, 49.5, 126.2, 127.2, 128.4, 144.9.

**Cycloheptylmethanamine** (Table 2, entry 6)

According to the general procedure, the reaction of cycloheptanecarbonitrile (0.10 mmol), samarium(II) iodide (0.6 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 99% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.03-1.15 (m, 4 H), 1.31-1.46 (m, 4 H), 1.47-1.54 (m, 1 H), 1.54-1.70 (m, 4 H), 2.44 (d,  $J$  = 6.6 Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  26.4, 28.4, 31.9, 42.8, 49.1.

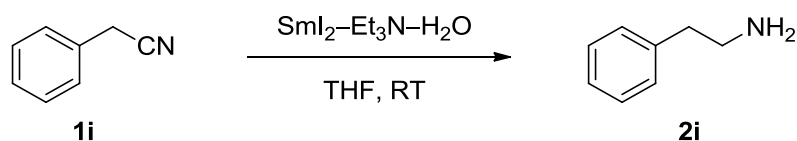
**Adamantan-1-yl-methanamine** (Table 2, entry 7)

According to the general procedure, the reaction of adamantane-1-carbonitrile (0.10 mmol), samarium(II) iodide (0.6 mmol, 0.074 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 30 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) and chromatography (90/10/1-80/20/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ) the title compound in 80% yield. ( $R_f$  = 0.66, 90/10/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.41 (m, 6 H), 1.54-1.59 (m, 3 H), 1.63-1.68 (m, 3 H), 1.92 (m, 3 H), 2.11 (br, 2 H), 2.29 (s, 2 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  28.4, 33.7, 37.2, 40.0, 54.5.

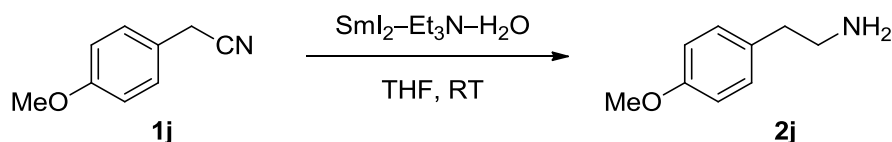
**2-Mesitylethanamine** (Table 2, entry 8)

According to the general procedure, the reaction of 2-mesitylacetonitrile (0.10 mmol), samarium(II) iodide (0.6 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 70% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.26 (s, 3 H), 2.31 (s, 6 H), 2.73-2.85 (m, 4 H), 6.85 (s, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  19.9, 20.8, 33.7, 41.5, 128.9, 133.1, 135.3, 136.3.

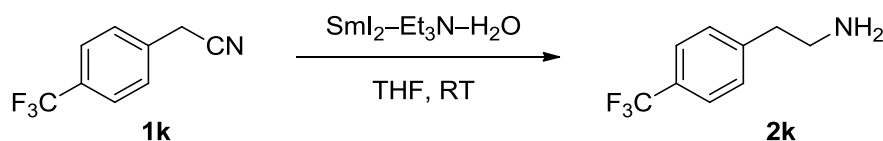


**2-Phenylethanamine** (Table 2, entry 9)

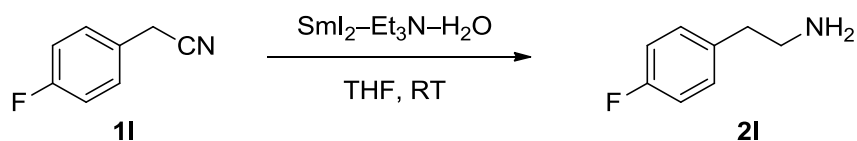
According to the general procedure, the reaction of 2-phenylacetonitrile (0.10 mmol), samarium(II) iodide (0.6 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 84% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.63 (t,  $J = 6.8$  Hz, 2 H), 2.85 (m,  $J = 6.3, 7.3$  Hz, 2 H), 7.07-7.14 (m, 3 H), 7.16-7.24 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  39.9, 43.4, 125.9, 128.2, 128.6, 139.6.

**2-(4-Methoxyphenyl)ethanamine** (Table 2, entry 10)

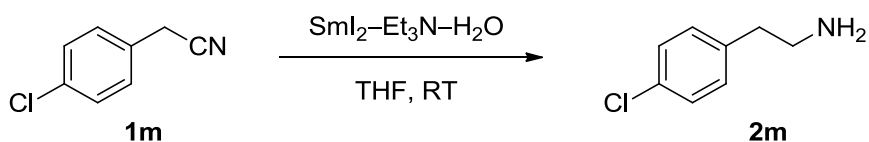
According to the general procedure, the reaction of 2-(4-methoxyphenyl)acetonitrile (0.10 mmol), samarium(II) iodide (0.6 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 89% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.52 (br, 2 H), 2.72 (t,  $J = 7.2$  Hz, 2 H), 2.95 (t,  $J = 6.8$  Hz, 2 H), 3.82 (s, 3 H), 6.87 (d,  $J = 8.8$  Hz, 2 H), 7.14 (d,  $J = 8.8$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  39.7, 43.7, 55.3, 113.9, 129.8, 131.9, 158.1.

**2-(4-(Trifluoromethyl)phenyl)ethanamine** (Table 2, entry 11)

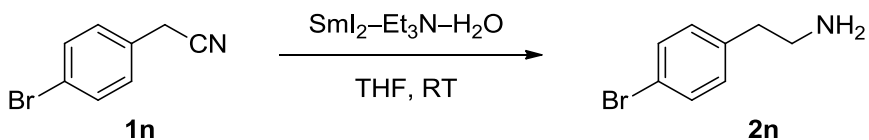
According to the general procedure, the reaction of 2-(4-(trifluoromethyl)phenyl)acetonitrile (0.10 mmol), samarium(II) iodide (0.32 mmol, 0.080 M), water (2.4 mmol) and triethylamine (2.4 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 74% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.80 (t,  $J = 6.9$  Hz, 2 H), 2.97 (t,  $J = 6.9$  Hz, 2 H), 7.26 (d,  $J = 8.0$  Hz, 2 H), 7.49 (d,  $J = 8.0$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  38.9, 42.9, 122.9, 125.5 (q,  $J^3 = 3.7$  Hz), 129.1 (q,  $J^2 = 32.0$  Hz), 129.2, 143.4;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9.

**2-(4-Fluorophenyl)ethanamine** (Table 2, entry 12)

According to the general procedure, the reaction of 2-(4-fluorophenyl)acetonitrile (0.10 mmol), samarium(II) iodide (0.60 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 79% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.74 (t,  $J = 6.9$  Hz, 2 H), 2.96 (t,  $J = 6.9$  Hz, 2 H), 6.96-7.03 (m, 2 H), 7.13-7.19 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  39.0, 43.5, 115.3 (d,  $J^2 = 21.3$  Hz), 130.2 (d,  $J^3 = 8.1$  Hz), 135.3 (d,  $J^4 = 2.9$  Hz), 161.5 (d,  $J^1 = 243.6$  Hz);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.7.

**2-(4-Chlorophenyl)ethanamine** (Table 2, entry 13)

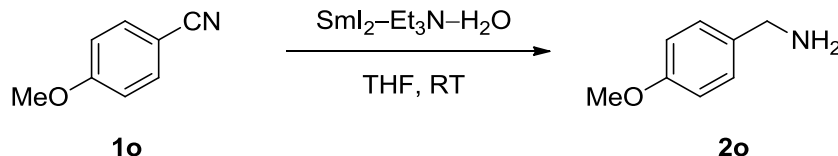
According to the general procedure, the reaction of 2-(4-chlorophenyl)acetonitrile (0.10 mmol), samarium(II) iodide (0.32 mmol, 0.080 M), water (2.4 mmol) and triethylamine (2.4 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 86% yield (based on unreacted nitrile).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.72 (t,  $J = 6.7$  Hz, 2 H), 2.95 (t,  $J = 6.7$  Hz, 2 H), 7.11-7.15 (m, 2 H), 7.24-7.29 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  39.3, 43.3, 128.5, 130.1, 131.9, 138.2.

**2-(4-Bromophenyl)ethanamine** (Table 2, entry 14)

According to the general procedure, the reaction of 2-(4-bromophenyl)acetonitrile (0.10 mmol), samarium(II) iodide (0.32 mmol, 0.080 M), water (2.4 mmol) and triethylamine (2.4 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 83% yield (based on unreacted nitrile), 84:16 ratio of **2n** to 2-phenylethanamine.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.70 (t,  $J = 6.8$  Hz, 2 H), 2.94 (t,  $J = 6.8$  Hz, 2 H), 7.08 (d,  $J = 8.3$  Hz, 2

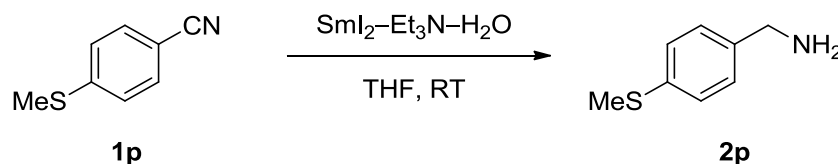
H), 7.42 (d,  $J = 8.3$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  39.4, 43.3, 119.9, 130.5, 131.5, 138.8.

**(4-Methoxyphenyl)methanamine** (Table 2, entry 15)



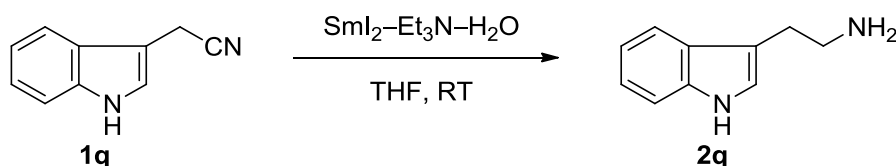
According to the general procedure, the reaction of 4-methoxybenzonitrile (0.10 mmol), samarium(II) iodide (0.6 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 92% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.42 (br, 2 H), 3.81 (s, 5 H), 6.88 (d,  $J = 8.7$  Hz, 2 H), 7.24 (d,  $J = 8.7$  Hz, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  45.9, 55.3, 113.9, 128.3, 135.6, 158.5.

**(4-Methylthiophenyl)methanamine** (Table 2, entry 16)



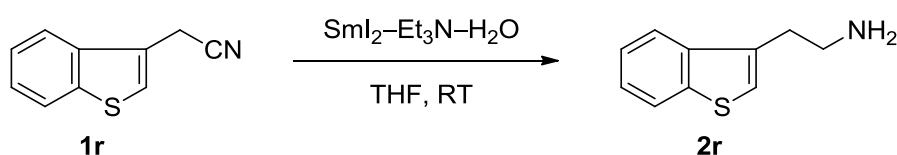
According to the general procedure, the reaction of 4-(methylthio)benzonitrile (0.10 mmol), samarium(II) iodide (0.6 mmol, 0.080 M), water (3.6 mmol) and triethylamine (3.6 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 81% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.52 (br, 2 H), 2.50 (s, 3 H), 3.85 (s, 2 H), 7.24-7.27 (m, 4 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  16.2, 46.1, 127.1, 127.7, 136.6, 140.4. Note that the reduction of benzonitrile proceeded in lower yield, most likely due to volatility of the amine product. The reduction of aromatic nitriles with  $\text{SmI}_2$  has been previously reported.<sup>10</sup> In addition, the reduction of 4-nitrobenzonitrile was unselective. The reduction of nitro group with  $\text{SmI}_2$  is the easiest among all standard functional group transformations.<sup>27</sup>

**2-(1H-Indol-3-yl)ethanamine** (Table 2, entry 17)

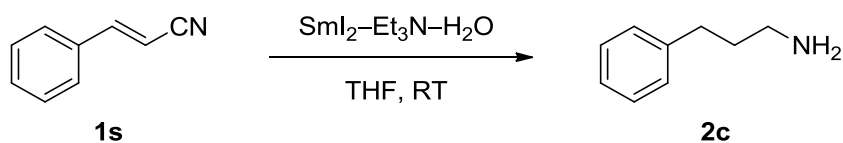


According to the general procedure, the reaction of 2-(1*H*-indol-3-yl)acetonitrile (0.10 mmol), samarium(II) iodide (0.32 mmol, 0.080 M), water (2.4 mmol) and triethylamine (2.4 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 74% yield (based on reacted unreacted nitrile).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.94 (t,  $J$  = 6.8 Hz, 2 H), 3.04–3.10 (m, 2 H), 7.02 (d,  $J$  = 2.0 Hz, 1 H), 7.15 (ddd,  $J$  = 1.0, 7.1, 8.1 Hz, 1 H), 7.22 (ddd,  $J$  = 1.0, 7.1, 8.1 Hz, 1 H), 7.37 (d,  $J$  = 8.1 Hz, 1 H), 7.65 (d,  $J$  = 7.8 Hz, 1 H), 8.58 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  29.4, 42.3, 111.1, 113.5, 118.8, 119.1, 121.8, 122.1, 127.4, 136.4.

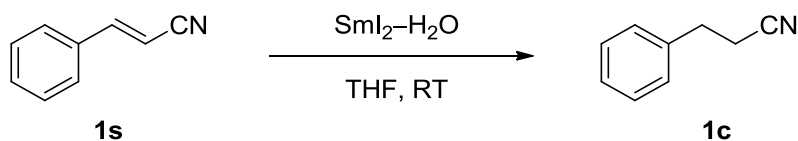
**2-(Benzo[*b*]thiophen-3-yl)ethanamine** (Table 2, entry 18)



According to the general procedure, the reaction of 2-(benzo[*b*]thiophen-3-yl)acetonitrile (0.10 mmol), samarium(II) iodide (0.32 mmol, 0.080 M), water (2.4 mmol) and triethylamine (2.4 mmol) for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 90% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.98–3.05 (m, 2 H), 3.06–3.12 (m, 2 H), 7.17 (s, 1 H), 7.33–7.43 (m, 2 H), 7.74–7.80 (m, 1 H), 7.85–7.91 (m, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  32.8, 41.5, 121.6, 122.1, 122.9, 123.9, 124.2, 134.1, 138.9, 140.5.

**Divergent Selectivity in the Reduction of  $\alpha,\beta$ -Unsaturated Nitriles****3-Phenylpropan-1-amine (Scheme 1)**

According to the general procedure, the reaction of 3-phenylpropionitrile (0.10 mmol), samarium(II) iodide (0.80 mmol, 0.080 M), water (7.2 mmol) and triethylamine (7.2 mmol) using reverse addition protocol of substrate to the preformed  $\text{Sm}(\text{II})$  complex for 5 min at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 78% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.67-1.75 (m, 2 H), 1.76 (br, 2 H), 2.58 (t,  $J = 7.8$  Hz, 2 H), 2.67 (t,  $J = 6.9$  Hz, 2 H), 7.07-7.14 (m, 3 H), 7.17-7.24 (m, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  33.3, 35.1, 41.7, 125.8, 128.3, 128.4, 142.1.

**3-Phenylpropanenitrile (Scheme 1)<sup>10-12</sup>**

According to the general procedure, the reaction of 3-phenylpropionitrile (0.10 mmol), samarium(II) iodide (0.40 mmol, 0.080 M) and water (1.8 mL, 1000 equiv) for 2 h at rt, afforded after work-up with  $\text{Et}_2\text{O}/\text{KOH}$  (10%, aq) the title compound in 99% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.59 (2 H, t,  $J = 7.4$  Hz), 2.94 (2 H, t,  $J = 7.4$  Hz), 7.20-7.30 (3 H, m), 7.31-7.37 (2 H, m);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  19.2, 31.4, 119.1, 127.1, 128.1, 128.7, 137.9.

Studies on Stability of the Iminium Intermediate<sup>13-15</sup>**Table SI-5.** Determination of the Role of Water Concentration on Stability of the Iminium Intermediate.<sup>a</sup>

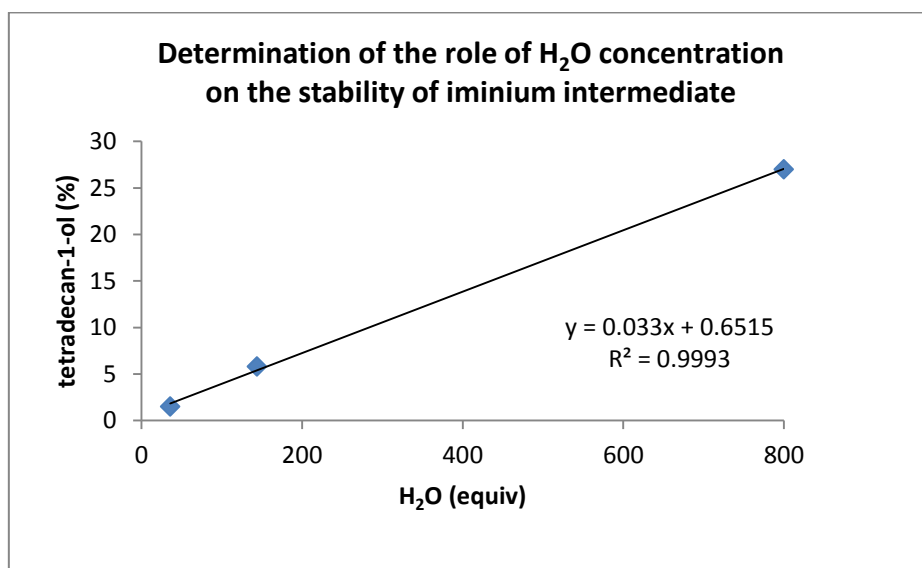
$  \begin{array}{ccc}  \text{C}_{13}\text{H}_{27}\text{CN} & \xrightarrow[\text{THF, RT}]{\text{SmI}_2\text{-Et}_3\text{N-H}_2\text{O}} & \text{C}_{13}\text{H}_{27}\text{CH}_2\text{OH} \\  \mathbf{1b} & & \mathbf{2b\text{-alcohol}}  \end{array}  $						
Entry	SmI <sub>2</sub> (equiv)	NH <sub>3</sub> (equiv)	H <sub>2</sub> O (equiv)	time <sup>b</sup>	conv. <sup>c</sup> (%)	yield <sup>c</sup> (%)
1	6	36	36	2 h	>98	1.5
2	6	36	144	2 h	>98	5.8
3	6	36	800	2 h	>98	27
3	6	36	3200	2 h	79	55

<sup>a</sup>All reactions carried out using standard Schlenk techniques for handling air-sensitive reagents. <sup>b</sup>Quenched by bubbling air through reaction mixtures. <sup>c</sup>Determined by GC-MS and/or <sup>1</sup>H NMR.

**Table SI-6.** Determination of the Role of Reaction Conditions on Stability of the Iminium Intermediate.<sup>a</sup>

$  \begin{array}{ccccccc}  \text{C}_{13}\text{H}_{27}\text{CN} & \xrightarrow[\text{THF, RT}]{\text{SmI}_2\text{-R}_3\text{N-H}_2\text{O}} & \text{C}_{13}\text{H}_{27}\text{CH}_2\text{NH}_2 & \text{C}_{13}\text{H}_{27}\text{CH}_2\text{NR}_2 & \text{C}_{13}\text{H}_{27}\text{CH}_2\text{OH} \\  \mathbf{1b} & & \mathbf{2b} & \mathbf{2b\text{-amine}} & \mathbf{2b\text{-alcohol}}  \end{array}  $						
entry	R <sub>3</sub> N	time <sup>b</sup>	conv. <sup>b</sup> (%)	<b>2b</b> , yield <sup>c</sup> (%)	<b>2b-NR<sub>2</sub></b> , yield <sup>c</sup> (%)	<b>2b-OH</b> , yield <sup>c</sup> (%)
1	Et <sub>3</sub> N	2 h	>95	94	<2	<2
2	pyrrolidine	2 h	>95	71	24	4.4
3	<i>n</i> -BuNH <sub>2</sub>	2 h	>95	51	48	<2
4	DIPA	2 h	>95	86	<2	13

<sup>a</sup>All reactions carried out using standard Schlenk techniques for handling air-sensitive reagents. <sup>b</sup>Quenched by bubbling air through reaction mixtures. <sup>c</sup>Determined by GC-MS and/or <sup>1</sup>H NMR. All reactions carried out with SmI<sub>2</sub>/R<sub>3</sub>N/H<sub>2</sub>O (6-36-36).

**Figure SI-1.** Effect of Water Concentration on the Formation of Tetradecan-1ol using  $\text{SmI}_2$ – $\text{Et}_3\text{N}$ – $\text{H}_2\text{O}$ .

## Selectivity Studies – Carboxylic Acid Derivatives

**General Procedure.** An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, 0.20 mmol, 2.0 equiv, 0.10 M) was added followed by triethylamine (2.4 mmol) and H<sub>2</sub>O (2.4 mmol) with vigorous stirring, which resulted in the formation of a characteristic dark-brown color of the SmI<sub>2</sub>–Et<sub>3</sub>N–H<sub>2</sub>O complex. A preformed solution of two substrates (each 0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred until decolorization to white had occurred. The reaction mixture was diluted with Et<sub>2</sub>O (30 mL) and KOH (20 mL, 10%, aq). The aqueous layer was extracted with Et<sub>2</sub>O (2 x 30 mL), organic layers were combined, washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2 x 5 mL, sat., aq) dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The sample was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

**Table SI-7.** Selectivity Study in the Reduction of Unactivated Nitriles using SmI<sub>2</sub>–amine–H<sub>2</sub>O (Reduction of Carboxylic Acid Derivatives).<sup>a</sup>

$\text{R-CN} + \text{R'-FG} \xrightarrow[\text{THF, RT}]{\text{SmI}_2\text{-Et}_3\text{N-H}_2\text{O}}$		$\text{R-CH}_2\text{NH}_2 + \text{R'-CH}_2\text{OH}$	
(1:1 ratio)		I-red	II-red
entry	Substrate I	Substrate II	<i>k</i> <sub>I</sub> / <i>k</i> <sub>R-FG</sub>
1	C <sub>13</sub> H <sub>27</sub> -CN		48:52
2	C <sub>13</sub> H <sub>27</sub> -CN		63:36
3	C <sub>13</sub> H <sub>27</sub> -CN		76:24
4	C <sub>13</sub> H <sub>27</sub> -CN		>98:2
5	C <sub>13</sub> H <sub>27</sub> -CN		<2:98
6	C <sub>13</sub> H <sub>27</sub> -CN		11:89
7	C <sub>13</sub> H <sub>27</sub> -CN		<2:98
8	C <sub>13</sub> H <sub>27</sub> -CN		95:5




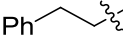

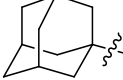
<sup>a</sup>Conditions: SmI<sub>2</sub> (2 equiv), Et<sub>3</sub>N (24 equiv), H<sub>2</sub>O (24 equiv), THF, room temperature, 10 s to 1 min. All reactions carried out using standard Schlenk techniques. <sup>b</sup>Determined by <sup>1</sup>H NMR (500 MHz) and/or GC-MS. Conversion = (100-SM). In all cases, rapid injection of substrate (THF solution) to the preformed SmI<sub>2</sub>–Et<sub>3</sub>N–H<sub>2</sub>O complex was applied.



## Selectivity Studies – Nitriles

**General Procedure.** An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, 0.20 mmol, 2.0 equiv, 0.10 M) was added followed by triethylamine (2.4 mmol) and H<sub>2</sub>O (2.4 mmol) with vigorous stirring, which resulted in the formation of a characteristic dark-brown color of the SmI<sub>2</sub>–Et<sub>3</sub>N–H<sub>2</sub>O complex. A preformed solution of two substrates (each 0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred until decolorization to white had occurred. The reaction mixture was diluted with Et<sub>2</sub>O (30 mL) and KOH (20 mL, 10%, aq). The aqueous layer was extracted with Et<sub>2</sub>O (2 x 30 mL), organic layers were combined, washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2 x 5 mL, sat., aq) dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The sample was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

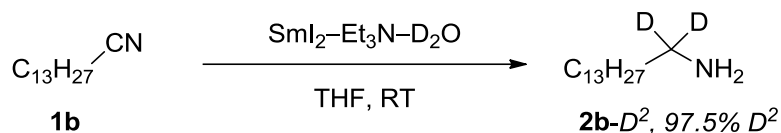
**Table SI-8.** Selectivity Study in the Reduction of Unactivated Nitriles using SmI<sub>2</sub>–amine–H<sub>2</sub>O (Reduction of Nitriles).<sup>a</sup>

$\text{R}-\text{C}\equiv\text{N} \xrightarrow[\text{THF, RT}]{\text{SmI}_2\text{-Et}_3\text{N-H}_2\text{O}} \text{R}-\text{CH}_2\text{NH}_2$		
entry		RV <sup>a</sup>
1		47.63
2		5.00
3		4.17
4		1.00
5		0.36

<sup>a</sup>Relative reactivity values determined from product distribution by <sup>1</sup>H NMR and/or GC of crude reaction mixtures. Conditions: SmI<sub>2</sub> (2 equiv), Et<sub>3</sub>N (24 equiv) H<sub>2</sub>O (24 equiv), THF, room temperature, 10 s to 1 min. All reactions carried out using standard Schlenk techniques.

Deuterium Incorporation Study<sup>16-20</sup>

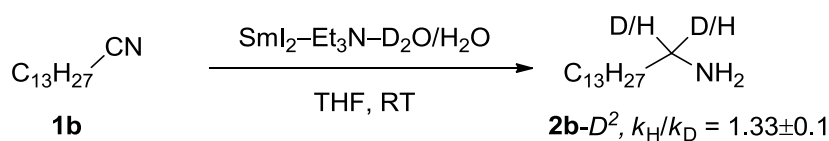
**Scheme SI-1.** Determination of Deuterium Incorporation in the Reduction of Nitriles using  $\text{SmI}_2$ –amine– $\text{H}_2\text{O}$ .



**General Procedure.** According to the general procedure, tetradecanenitrile (0.10 mmol), was reacted with samarium(II) iodide (0.6 mmol, 0.085 M, THF solution),  $\text{D}_2\text{O}$  (3.6 mmol) and triethylamine (3.6 mmol) for 2 h at rt to give the title compound with 97.5%  $\text{D}^2$  incorporation (determined by  $^1\text{H}$  NMR, 500 MHz and GC-MS). Purification by chromatography (90/10/1-80/20/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ) afforded the title product in 92% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.81 (t,  $J = 6.9$  Hz, 3 H), 0.91-1.33 (m, 22 H), 1.34-1.49 (m, 2 H), 3.37 (br, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.2, 22.7, 26.8, 29.4, 29.6, 29.6, 29.7, 29.7, 31.9, 32.0, 40.9 (m,  $J^1 = 21.9$  Hz).

Kinetic Isotope Effect Study<sup>17-20</sup>

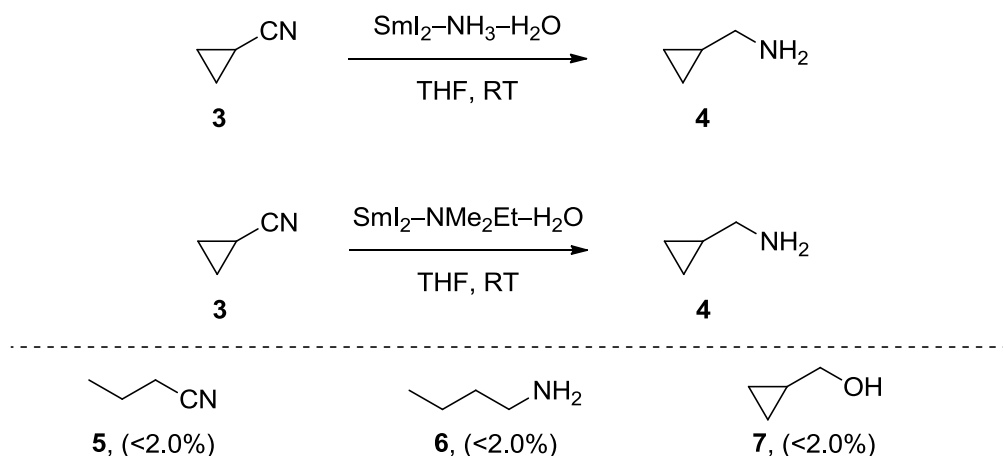
**Scheme SI-2.** Determination of Kinetic Isotope Effect in the Reduction of Nitriles using  $\text{SmI}_2$ –amine– $\text{H}_2\text{O}$ .



**General Procedure.** According to the general procedure, tetradecanenitrile (0.10 mmol), was reacted with samarium(II) iodide (0.6 mmol, 0.085 M, THF solution),  $\text{H}_2\text{O}/\text{D}_2\text{O}$  (1:1, 3.6 mmol) and triethylamine (3.6 mmol) for 2 h at rt to afford tetradecan-1-amine and 1,2- $\text{D}^2$ -tetradecan-1-amine in 99% yield. The amount of each species was determined by a combination of  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and GC-MS analysis. Kinetic isotope effect,  $k_{\text{H}}/k_{\text{D}} = 1.35 \pm 0.1$  (NMR);  $k_{\text{H}}/k_{\text{D}} = 1.31 \pm 0.1$  (GC-MS), average  $1.33 \pm 0.1$ .

### Radical Clock Experiments<sup>21-24</sup>

**Scheme SI-3.** Summary of the Radical Clock Experiments in the Reduction of Nitriles using  $\text{SmI}_2$ –amine– $\text{H}_2\text{O}$ .



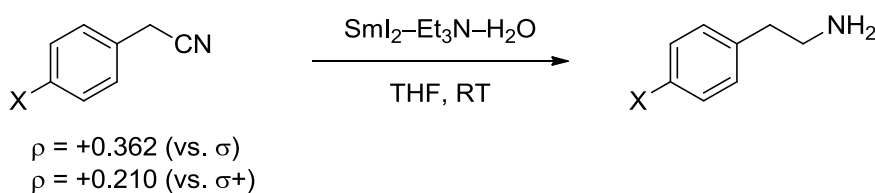
**Method 1.** According to the general procedure, the reaction of cyclopropanecarbonitrile (0.20 mmol), samarium(II) iodide (0.3 mmol, 1.5 equiv), water (83 equiv) and ammonia (18 equiv) for 2 h at rt, afforded cyclopropylmethanamine (33.7% conv.). Butyronitrile, butan-1-amine and cyclopropylmethanol were not detected in the reaction mixture (<2.0%). The amount of each species was determined by GC-MS analysis after basic work-up as described above.

**Method 2.** According to the general procedure, the reaction of cyclopropanecarbonitrile (0.10 mmol), samarium(II) iodide (0.8 mmol, 8 equiv), water (166 equiv) and ammonia (36 equiv) for 2 h at rt, afforded cyclopropylmethanamine (>98.0% conv.). Butyronitrile, butan-1-amine and cyclopropylmethanol were not detected in the reaction mixture (<2.0%). The amount of each species was determined by GC-MS analysis after basic work-up as described above.

**Method 3.** To demonstrate that the fast reduction/fragmentation rate of cyclopropanecarbonitrile is not specific to ammonia-water reagent system, the reduction was performed using *N,N*-dimethylethanamine-water as Lewis base-proton donor system. *N,N*-dimethylethanamine was used instead of triethylamine to facilitate analysis of the reaction mixture by GC-MS. According to the general procedure, the reaction of cyclopropanecarbonitrile (0.20 mmol), samarium(II) iodide (0.3 mmol, 1.5 equiv), water (1.8 mmol, 9.0 equiv) and *N,N*-dimethylethanamine (1.8 mmol, 9.0 equiv) for 2 h at rt, afforded cyclopropylmethanamine (23.7% conv.). Butyronitrile, butan-1-amine and cyclopropylmethanol were not detected in the reaction mixture (<2.0%). The amount of each species was determined by GC-MS analysis after basic work-up as described above.

Hammett Correlation Study<sup>25-26</sup>

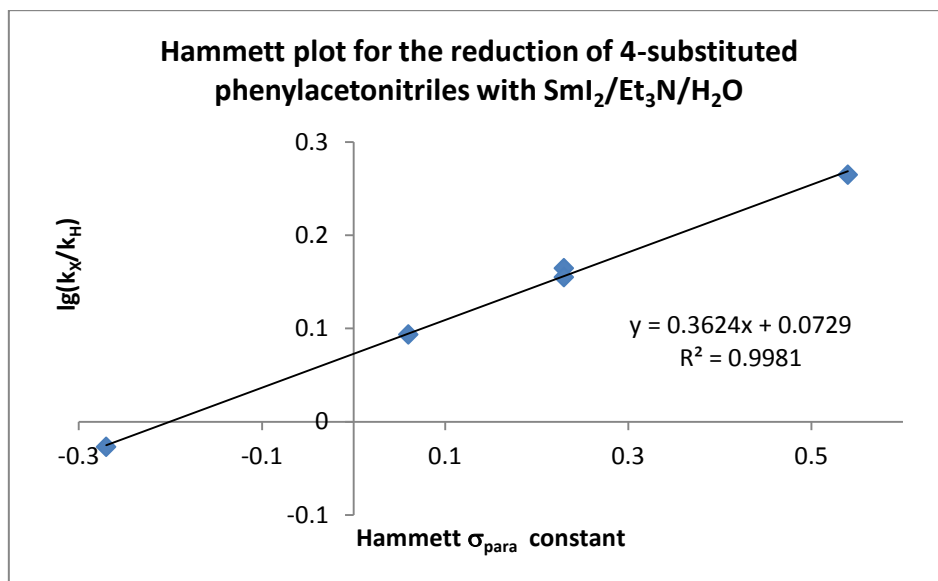
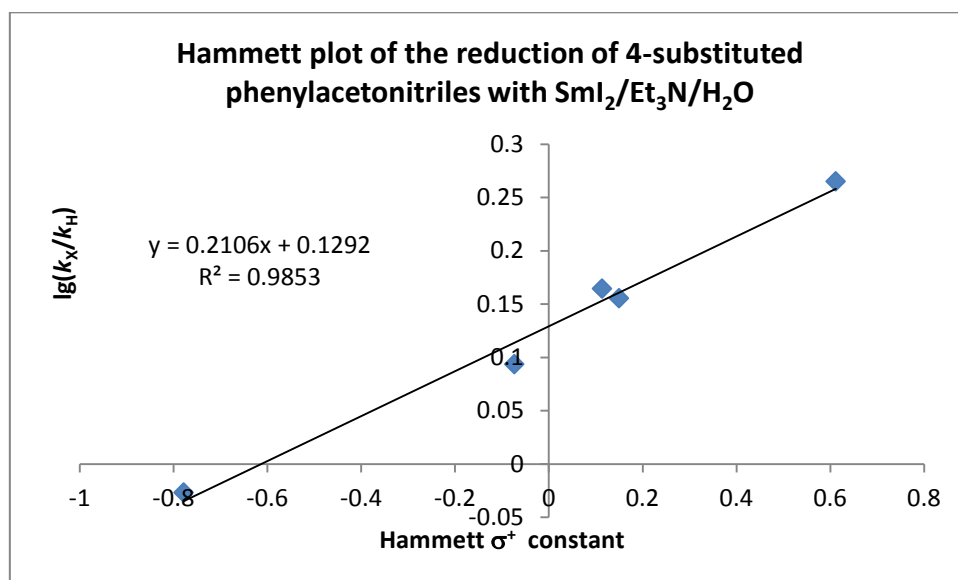
**General Procedure.** An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 0.20 mmol, 2.0 equiv, 0.10 M) was added followed by Et<sub>3</sub>N (0.33 mL, 24 equiv) and H<sub>2</sub>O (0.043 mL, 24 equiv) with vigorous stirring, which resulted in the formation of a characteristic dark brown color of the SmI<sub>2</sub>–Et<sub>3</sub>N–H<sub>2</sub>O complex. A preformed solution of two substrates (each 0.10 mmol, 1.0 equiv, stock solution in THF) was added and the reaction mixture was stirred until decolorization to white had occurred. The reaction mixture was diluted with Et<sub>2</sub>O (30 mL) and KOH (20 mL, 10%, aq). The aqueous layer was extracted with Et<sub>2</sub>O (2 x 30 mL), organic layers were combined, washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2 x 5 mL, sat., aq) dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The sample was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

**Table SI-9.** Relative Rates for the Reduction of Nitriles using SmI<sub>2</sub> – Hammett.<sup>a</sup>

entry	X	$k_X/k_H^a$	$\sigma_{\text{para}}$	$\sigma^+_{\text{para}}$
1	CF <sub>3</sub>	1.84	0.54	0.612
2	Cl	1.46	0.23	0.114
3 <sup>b</sup>	Br	1.43	0.23	0.150
4	F	1.24	0.06	-0.073
5	H	1.00	0	0
6	MeO	0.94	-0.27	-0.778

<sup>a</sup>Relative reactivity values determined from product distribution by <sup>1</sup>H NMR and/or GC of crude reaction mixtures.

<sup>b</sup>Calculated from  $k_X/k_H = 1.20$  based on the relative rate for debromination of 84:16. Hammett correlation w/o X = Br,  $\rho = 0.362$ ,  $R^2 = 0.998$  and  $\rho = 0.211$ ,  $R^2 = 0.985$  for Hammett  $\sigma$  and  $\sigma^+$  parameters, respectively. The  $\rho$  values can be compared with  $\rho = 0.43$  (Hammett  $\sigma$  parameters) and  $\rho = 0.25$  (Hammett  $\sigma^+$  parameters) for the reduction of 4-phenylacetic methyl esters with SmI<sub>2</sub>/Et<sub>3</sub>N/H<sub>2</sub>O.

**Figure SI-2.** Hammett  $\sigma$  Correlation Study in the Reduction of 4-Substituted Phenylacetonitriles  $\text{SmI}_2$ .**Figure SI-3.** Hammett  $\sigma^+$  Correlation Study in the Reduction of 4-Substituted Phenylacetonitriles  $\text{SmI}_2$ .

## References

1. P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, **1980**, *102*, 2693.
2. T. Imamoto and M. Ono, *Chem. Lett.*, **1987**, 501.
3. A. Dählen and G. Hilmeresson, *Eur. J. Inorg. Chem.*, **2004**, 3020.
4. J. A. Teprovich, Jr., P. K. S. Antharjanam, E. Prasad, E. N. Pesciotta and R. A. Flowers, II, *Eur. J. Inorg. Chem.*, **2008**, 5015.
5. M. Szostak, M. Spain and D. J. Procter, *J. Org. Chem.*, **2012**, *77*, 3049.
6. Y. Kamochi and T. Kudo, *Chem. Lett.*, **1991**, 893.
7. Y. Kamochi and T. Kudo, *Tetrahedron Lett.*, **1991**, *32*, 3511.
8. Y. Kamochi and T. Kudo, *Bull. Chem. Soc. Jpn.*, **1992**, *65*, 3049.
9. Y. Kamochi and T. Kudo, *Tetrahedron*, **1992**, *48*, 4301.
10. Y. Kamochi and T. Kudo, *Chem. Lett.*, **1993**, 1495.
11. J. M. Concellón and H. Rodríguez-Solla, *Chem. Eur. J.*, **2001**, *7*, 4266.
12. J. M. Concellón and H. Rodríguez-Solla, *Chem. Eur. J.*, **2002**, *8*, 4493.
13. B. M. Trost and I. Fleming, *Comprehensive Organic Synthesis*, Pergamon Press: 1991.
14. A. Dahlén and G. Hilmeresson, *Chem. Eur. J.*, **2003**, *9*, 1123.
15. M. Kim, B. W. Knettle, A. Dahlén, G. Hilmeresson and R. A. Flowers, II, *Tetrahedron*, **2003**, *59*, 10397.
16. L. A. Duffy, H. Matsubara and D. J. Procter, *J. Am. Chem. Soc.*, **2008**, *130*, 1136.
17. D. Parmar, L. A. Duffy, D. V. Sadasivam, H. Matsubara, P. A. Bradley, R. A. Flowers, II and D. J. Procter, *J. Am. Chem. Soc.*, **2009**, *131*, 15467.
18. M. Szostak, M. Spain and D. J. Procter, *Chem. Commun.*, **2011**, *47*, 10254.
19. M. Szostak, M. Spain and D. J. Procter, *Org. Lett.*, **2012**, *14*, 840.
20. E. M. Simmons and J. F. Hartwig, *Angew. Chem. Int. Ed.*, **2012**, *51*, 3066.
21. M. Newcomb, *Tetrahedron*, **1993**, *49*, 1151.
22. E. Hasegawa and D. P. Curran, *Tetrahedron Lett.*, **1993**, *34*, 1717.
23. D. P. Curran, T. L. Fevig, C. P. Jasperse and M. J. Tottleben, *Synlett*, **1992**, 943.
24. C. Chatgililoglu and A. Studer, *Encyclopedia of Radicals in Chemistry, Biology and Materials*, Wiley-Blackwell: 2012.
25. H. H. Jaffé, *Chem. Rev.*, **1953**, *53*, 191.
26. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, **1991**, *91*, 165.
27. M. Szostak, M. Spain, D. J. Procter, *Chem. Soc. Rev.*, **2013**, *42*, 9155.

