Supplementary Material (ESI) for Chemical Communications
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**Supporting Information**

# Title: Solvent-Free One-Pot Reductive Amination by catalytic use of tin reagent incorporated on ionic liquid

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## Experimental

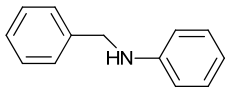
### I. General

All moisture-sensitive reactions were carried out in oven-dried glassware (100°C) under $N_2$. Commercially available reagents and solvents were purified and dried, when necessary, by standard methods prior to use. IR spectra were scanned on a Nicolet Avatar 370 DTGS FTIR spectrophotometer. $^1$H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm. TMS was used as the internal standard for $CDCl_3$. $^{13}$C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) with complete proton decoupling. High resolution mass spectra measurements were recorded on Waters-Micromass GCT Premier spectrometers. Analytical thin layer chromatography was performed on pre-coated silica gel 60-$F_{254}$ plates. For preparative chromatography silica gel 60 (230-400 mesh) was used. Reagents were purchased from commercial suppliers and were used without purification unless otherwise noted.

### II. Representative Procedure for the Reductive Amination of Benzaldehyde with Aniline

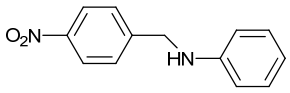
To a solution of benzaldehyde (0.362 mL, 3.56 mmol, 1.0 equiv) were added at room temperature, aniline (0.325 mL, 3.56 mmol, 1.0 equiv) and 1-((dibutylchlorostannyl)hexyl)-3-methyl-*1H*-imidazol-3-ium iodide (**1**) (2 mg, $3.56 \times 10^{-3}$ mmol, 0.001 equiv). The resulting yellow solution was allowed to stir for 10 min, and treated with phenylsilane (0.482 mL, 3.92 mmol, 1.1 equiv). After 2 h, thin layer chromatography showed no remaining aniline. The colorless reaction was evaporated by rotavaporation in other to remove maximum of phenylsilane and the mixture was distilled by short path distillation (90°C, $3 \times 10^{-2}$ mbar) to afford the product (84% yield).

***N*-Benzylaniline (4a)**[1]



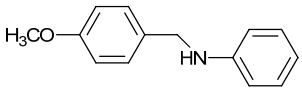
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 3.99 (br s, 1H, NH), 4.31 (s, 2H), 6.61-6.63 (m, 2H), 6.69-6.73 (m, 1H), 7.14-7.37 (m, 7H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 48.4, 112.9, 117.6, 127.3, 127.6, 128.7, 129.4, 139.5, 148.2

***N*-(4-Nitrobenzyl)benzenamine (4b)**[2,3,4]



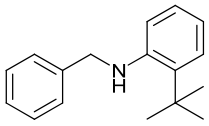
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 4.25 (br s, 1H, NH), 4.46 (s, 3H), 6.56-6.58 (m, 2H), 6.72-6.76 (m, 1H), 7.14-7.18 (m, 2H), 7.51-7.53 (m, 2H), 8.16-8.19 (m, 2H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 47.7, 112.9, 118.3, 123.9, 127.7, 129.4, 147.2, 147.3, 147.8.

***N*-(4-Methoxybenzyl)benzenamine (4c)**[2]



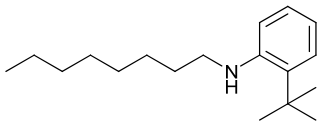
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 3.79 (s, 3H), 3.95 (br s, 1H, NH), 4.24 (s, 2H), 6.59-6.74 (m, 3H), 6.83-6.91 (m, 2H), 7.13-7.32 (m, 4H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 47.8, 55.4, 112.9, 114.1, 117.6, 128.9, 129.3, 131.5, 148.3, 158.9.

***N*-Benzyl-2-*tert*-butylaniline (4d)**[5]



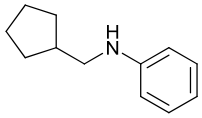
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 1.43 (s, 9H), 4.40 (s, 2H), 6.65-6.73 (m, 2H), 7.08-7.23 (m, 1H), 7.25-7.41 (m, 6H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 29.9, 34.2, 48.9, 111.9, 117.2, 126.2, 127.2, 127.5, 128.7, 133.2, 139.6, 146.1.

**2-*tert*-Butyl-*N*-octylbenzenamine (4e)**



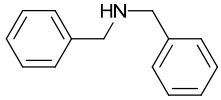
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 1.43 (s, 9H), 4.40 (s, 2H), 6.65-6.73 (m, 2H), 7.08-7.12 (m, 1H), 7.25-7.41 (m, 6H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 14.1, 22.7, 24.8, 27.5, 29.3, 29.4, 29.6, 29.9, 31.9, 44.4, 111.6, 116.6, 126.1, 127.2, 132.9, 146.7; **HRMS** calcd. for $C_{18}H_{31}N$ 261.2457. Found 261.2473 (6.1 ppm).

***N*-(Cyclopentylmethyl)benzenamine (4f)**[6]



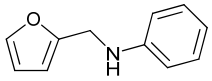
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 0.92-1.82 (m, 9H), 3.52-3.60 (d, *J*=6.7 Hz, 2H), 6.56-6.58 (m, 2H), 6.63-6.68 (m, 1H), 7.13-7.17 (m, 2H); **$^{13}$C NMR** ($CDC1_3$, 100 MHz) δ 26.1, 26.7, 31.4, 37.7, 50.7, 112.7, 116.9, 129.3, 148.7.

**Dibenzylamine (4g)**[7]



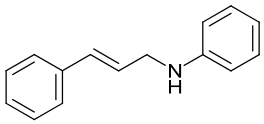
**$^1$H NMR** ($CDC1_3$, 400 MHz) δ 1.71 (br s, 1H), 3.80 (s, 4H), 7.21-7.34 (m, 10H); **$^{13}$C NMR** ($CDC1_3$, 100 MHz) δ 53.2, 127.1, 128.3, 128.5, 140.4.

***N*-(Furan-2-ylmethyl)benzenamine (4h)**[1]



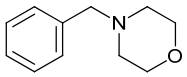
**$^1$H NMR** ($CDC1_3$, 400 MHz) δ 4.00 (br s, 1H), 4.31 (s, 2H), 6.22-6.23 (m, 1H), 6.31-6.32 (m, 1H), 6.66-6.68 (m, 2H), 6.72-6.76 (m, 1H), 7.16-7.21 (m, 2H), 7.35-7.36 (m, 1H); **$^{13}$C NMR** ($CDC1_3$, 100 MHz) δ 41.5, 107.1, 110.5, 113.3, 118.1, 129.4, 142.0, 147.8, 152.9.

***N*-Cinnamylaniline (4i)**[1,4]



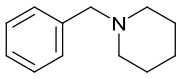
**$^1$H NMR** ($CDCl_3$, 400 MHz) 3.85 (br s, 1H), 3.94 (d, *J*=5.6 Hz, 2H), 6.34 (dt, *J*=5.8, *J*=15.9 Hz, 1H), 6.61-6.69 (m, 3H), 6.70-6.75 (m, 1H), 7.17-7.38 (m, 7H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) 46.3, 113.1, 117.7, 126.4, 127.1, 127.6, 128.6, 129.3, 131.6, 136.9, 148.1.

**4-Benzylmorpholine (5a)**[7]



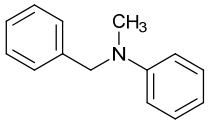
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 2.43-2.45 (m, 4H), 3.50 (s, 2H), 3.69-3.72 (m, 4H), 7.23-7.34 (m, 5H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 53.6, 63.5, 67.0, 127.2, 128.3, 129.2, 137.8.

**1-Benzylpiperidine (5b)**[7]



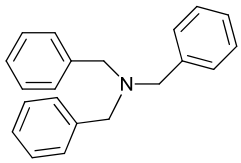
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 1.54-1.59 (m, 2H), 2.37 (br s, 4H), 3.43-3.47 (m, 4H), 7.20-7.33 (m, 5H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 24.4, 26.0, 26.2, 54.5, 63.9, 126.8, 128.1, 129.3, 138.7.

***N*-Benzyl-*N*-methylaniline (5c)**[7]



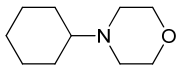
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 2.99 (s, 3H), 4.51 (s, 2H), 6.68-6.75 (m, 3H), 7.19-7.32 (m, 7H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 41.8, 58.1, 114.2, 121.8, 127.1, 127.9, 128.4, 129.7, 133.2; 138.9.

**Tribenzylamine (5d)**[7]



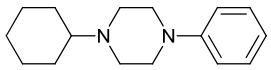
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 3.88 (s, 6H), 7.30-7.48 (m, 15H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 53.0, 127.1, 128.3, 128.5, 139.9.

**4-Cyclohexylmorpholine (7a)**[7]



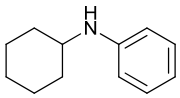
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 1.09-1.94 (m, 10H), 2.18-2.25 (m, 1H), 2.58-2.61 (m, 4H), 3.75-3.77 (m, 4H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 25.8, 26.3, 28.9, 49.7, 63.8, 67.5.

**1-Cyclohexyl-4-phenylpiperazine (7b)**[8]



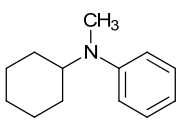
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 1.09-1.93 (m, 10H), 2.26-2.33 (m, 1H), 2.72-2.74 (m, 4H), 3.19-3.21 (m, 4H), 6.82-6.87 (m, 1H), 6.92-6.94 (m, 2H), 7.23-7.28 (m, 3H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 25.9, 26.4, 29.0, 49.1, 49.7, 63.6, 116.1, 119.6, 129.1, 151.5.

***N*-Cyclohexylaniline (7c)**[7]



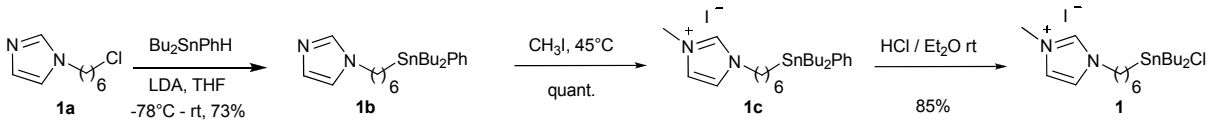
**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 1.07-1.39 (m, 5H), 1.60-1.66 (m, 1H), 1.71-1.76 (m, 2H), 2.02-2.05 (m, 2H), 3.19-3.26 (m, 1H), 3.46 (s, 1H), 6.55-6.57 (m, 2H), 6.62-6.67 (m, 1H), 7.12-7.16 (m, 2H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 25.2, 26.1, 35.6, 51.8, 113.5, 116.9, 129.8, 147.5.

***N*-Cyclohexyl-*N*-methylbenzenamine (7d)**[9]



**$^1$H NMR** ($CDCl_3$, 400 MHz) δ 1.08-1.85 (m, 10H), 2.76 (s, 3H), 3.52-3.60 (m, 1H), 6.65-6.69 (m, 1H), 6.76-6.78 (m, 2H), 7.18-7.24 (m, 2H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz) δ 26.1, 26.3, 30.1, 30.2, 58.2, 113.3, 116.3, 129.2, 150.3.

## III. Synthesis of tin reagent supported on ionic liquid (1)




### 1-{6-[Dibutyl(phenyl)stannyl]hexyl}-1*H*-imidazole (1b)[10]

To a solution of lithium diisopropylamide (11.3 mmol) in dry THF (40 mL), dibutylphenyltin hydride (3.45 g, 11.1 mmol) was slowly added at –78 °C. The resulting mixture was stirred for 1 h at –50 °C and subsequently added to a solution of 1-(6-chlorohexyl)-1*H*-imidazole (1.57 g, 8.5 mmol) in dry THF (20 mL) at –50 °C. Then the mixture was allowed to warm up to r.t. and stirred for 18 h. Water (5 mL) was slowly added and the mixture was stirred for additional 15 min at r.t.. To this mixture $CH_2Cl_2$ (100 mL) was added and the organic phase was successively washed with $H_2O$ (20 mL) and brine (10 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 × 20 mL), and the organic combined phase was dried dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude product (4.69 g) was then purified by column chromatography (silica gel with solvent: AcOEt:Cyclohexane (80:20) to yield the pure product **1b** as a colorless oil (2.86 g, 6.2 mmol, 73%). **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 0.88 (t, *J*=7.2 Hz, 6H), 0.89–1.07 (m, 5H), 1.27–1.37 (m, 8H), 1.50–1.57 (m, 5H), 1.64 (br s, 2H), 1.68–1.75 (m, 2H), 3.87 (t, *J*=7.2 Hz, 2H), 6.87 (s, 1H), 7.05 (s, 1H), 7.29–7.45 (m, 6H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ 9.5, 9.6, 13.7, 26.0, 26.6, 27.4, 29.1, 31.0, 33.7, 47.0, 118.8, 128.0, 128.1, 129.3, 136.5, 137.1, 141.8; **$^{119}$Sn NMR** (149 MHz, $CDCl_3$): δ –43.9; **IR** (neat): 446, 503, 596, 662, 698, 725, 808, 1074, 1228, 1282, 1427, 1462, 1504, 2850, 2922, 2955 $cm^{-1}$; **HRMS** calcd. for $C_{23}H_{39}N_2{}^{120}Sn$ 463.2135. Found 463.2138.

### 1-{6-[Dibutyl(phenyl)stannyl]hexyl}-3-methyl-1*H*-imidazolium iodide (1c)[10]

In a dried sealed tube, crude 1-{3-[dibutyl(phenyl)stannyl]hexyl}-1*H*-imidazole (**1b**) (1.02 g, 2.2 mmol) was dissolved in methyl iodide (0.5 mL) and stirred over night at 40 °C. The mixture was cooled down to r.t. and the excess methyl iodide was evaporated under reduced pressure to yield **1c** (1.33 g, 2.2 mmol, 99%) as a pale yellow oil. **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 0.88 (t, *J*=7.2 Hz, 6H), 0.98–1.57 (m, 20H), 1.83–1.90 (m, 2H), 4.11 (s, 3H), 4.25 (t, *J*=7.5 Hz, 2H), 7.20 (s, 1H), 7.29–7.46 (m, 6H), 10.17 (s, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ 9.4, 9.5, 13.6, 25.6, 26.5, 27.3, 29.0, 30.1, 33.5, 37.1, 50.1, 121.8, 123.6, 128.0, 136.4, 136.8, 136.8, 141.7; **$^{119}$Sn NMR** (149 MHz, $CDCl_3$): δ –43.8; **IR** (neat): 447, 505, 617, 656, 700, 727, 862, 1072, 1165, 1375, 1427, 1462, 1568, 2848, 2922, 2953, 3061 $cm^{-1}$; **HRMS** calcd. for $C_{24}H_{41}N_2{}^{120}Sn$ 477.2291. Found 477.2296.

**1-{6-[Dibutyl(chloro)stannyl]hexyl}-3-methyl-*1H*-imidazolium iodide (1)**[11]

To a solution of **1c** (1.25 g, 2.07 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise at 0–5 °C over a period of 5 min, a solution of HCl 2M in ether (1.1 mL, 2.2 mmol). The mixture was stirred for 2 h at rt, then treated with $H_2O$ (10 mL). To this mixture $CH_2Cl_2$ (20 mL) was added and the organic phase was washed with $H_2O$ (3x20 mL), and the aqueous phase was washed $CH_2Cl_2$ (3x10 mL), the combined organic phase was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield **1** (988 mg, 85%) as a yellow viscous oil. **$^1$H NMR** ($CDCl_3$, 400 MHz): δ 0.92 (t, *J*=7.3 Hz, 6H), 1.31–1.99 (m, 22 H), 4.12 (s, 3H), 4.34 (t, *J*=7.3 Hz, 2H), 7.42–7.40 (m, 2H), 10.10 (s, 1H); **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ 13.7, 18.1, 18.5, 25.4, 25.9, 26.8, 28.6, 29.9, 32.6, 37.1, 50.2, 123.4, 123.7, 136.6; **$^{119}$Sn NMR** (149 MHz, $CDCl_3$): δ +105.7; IR (neat): 519, 678, 1166, 1462, 1579, 2853, 2920, 2953, 3082 $cm^{-1}$ ; **HRMS** calcd. for $C_{18}H_{36}N_2Cl^{120}Sn$ 435.1589. Found 435.1595.

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[7] $^1$H NMR and $^{13}$C NMR of **4g** (CAS [103-49-1]), **5a** (CAS [92-53-5]), **5b** (CAS [4096-20-2]), **5c** (CAS [614-30-2]), **5d** (CAS [620-40-6]), **7a** (CAS [6425-41-8]), **7c** (CAS [1821-36-9]) and the commercially available products were identical.
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