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 N₂. 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. ¹H 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 CDCl₃. ¹³C 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-F₂₅₄ 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)-1H-imidazol-3-ium iodide (I) (2 mg, 3.56x10⁻³ 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, 3x10⁻² mbar) to afford the product (84% yield).
$N$-Benzylaniline (4a)$^1$

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\begin{array}{c}
\text{H} \\
\text{N} \\
\text{N} \\
\end{array}
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$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 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) $\delta$ 48.4, 112.9, 117.6, 127.3, 127.6, 128.7, 129.4, 139.5, 148.2

$N$-(4-Nitrobenzyl)benzenamine (4b)$^{2,3,4}$

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\begin{array}{c}
\text{O} \\
\text{N} \\
\text{N} \\
\end{array}
\]

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 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) $\delta$ 47.7, 112.9, 118.3, 123.9, 127.7, 129.4, 147.2, 147.3, 147.8.

$N$-(4-Methoxybenzyl)benzenamine (4c)$^2$

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\begin{array}{c}
\text{H} \\
\text{O} \\
\text{N} \\
\end{array}
\]

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 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) $\delta$ 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)$^5$

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\begin{array}{c}
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\text{N} \\
\end{array}
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$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 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) $\delta$ 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)

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\begin{array}{c}
\text{H} \\
\text{N} \\
\end{array}
\]

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 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) $\delta$ 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)$^6$
**1H NMR (CDCl$_3$, 400 MHz)** $\delta$ 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); **13C NMR (CDCl$_3$, 100 MHz)** $\delta$ 26.1, 26.7, 31.4, 37.7, 50.7, 112.7, 116.9, 129.3, 148.7.

**Dibenzylamine (4g)**

**1H NMR (CDCl$_3$, 400 MHz)** $\delta$ 1.71 (br s, 1H), 3.80 (s, 4H), 7.21-7.34 (m, 10H); **13C NMR (CDCl$_3$, 100 MHz)** $\delta$ 53.2, 127.1, 128.3, 128.5, 140.4.

**N-(Furan-2-ylmethyl)benzenamine (4h)**

**1H NMR (CDCl$_3$, 400 MHz)** $\delta$ 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); **13C NMR (CDCl$_3$, 100 MHz)** $\delta$ 41.5, 107.1, 110.5, 113.3, 118.1, 129.4, 142.0, 147.8, 152.9.

**N-Cinnamylaniline (4i)**

**1H 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); **13C NMR (CDCl$_3$, 100 MHz)** $\delta$ 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)**

**1H NMR (CDCl$_3$, 400 MHz)** $\delta$ 2.43-2.45 (m, 4H), 3.50 (s, 2H), 3.69-3.72 (m, 4H), 7.23-7.34 (m, 5H); **13C NMR (CDCl$_3$, 100 MHz)** $\delta$ 53.6, 63.5, 67.0, 127.2, 128.3, 129.2, 137.8.

**1-Benzylpiperidine (5b)**

**1H NMR (CDCl$_3$, 400 MHz)** $\delta$ 1.54-1.59 (m, 2H), 2.37 (br s, 4H), 3.43-3.47 (m, 4H), 7.20-7.33 (m, 5H); **13C NMR (CDCl$_3$, 100 MHz)** $\delta$ 24.4, 26.0, 26.2, 54.5, 63.9, 126.8, 128.1, 129.3, 138.7.

**N-Benzyl-N-methylaniline (5c)**
$^1$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)$^9$
III. Synthesis of tin reagent supported on ionic liquid (1)

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

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)-1H-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 CH2Cl2 (100 mL) was added and the organic phase was successively washed with H2O (20 mL) and brine (10 mL). The aqueous layer was extracted with CH2Cl2 (3 × 20 mL), and the organic combined phase was dried dried over MgSO4, 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%). ^1H NMR (CDCl3, 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); ^13C NMR (CDCl3, 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; ^119Sn NMR (149 MHz, CDCl3): 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 C23H39N2120Sn 463.2135. Found 463.2138.

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

In a dried sealed tube, crude 1-{3-[dibutyl(phenyl)stannyl]hexyl}-1H-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. ^1H NMR (CDCl3, 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); ^13C NMR (CDCl3, 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, 141.7; ^119Sn NMR (149 MHz, CDCl3): δ –43.8; IR (neat): 447, 503, 596, 662, 698, 725, 808, 1074, 1228, 1282, 1427, 1462, 1504, 2850, 2922, 2955 cm⁻¹; HRMS calcd. for C24H41N2120Sn 477.2291. Found 477.2296.
1-{6-[Dibutyl(chloro)stannyl]hexyl}-3-methyl-\textit{iH}-imidazolium iodide (1)$^{11}$

To a solution of 1c (1.25 g, 2.07 mmol) in CH$_2$Cl$_2$ (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$_2$O (10 mL). To this mixture CH$_2$Cl$_2$ (20 mL) was added and the organic phase was washed with H$_2$O (3x20 mL), and the aqueous phase was washed CH$_2$Cl$_2$ (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): $\delta$ 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): $\delta$ 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$_3$): $\delta$ +105.7; IR (neat): 519, 678, 1166, 1462, 1579, 2853, 2920, 2953, 3082 cm$^{-1}$; HRMS calcd. for C$_{18}$H$_{36}$N$_2$Cl$_2$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.


