One-pot reductive amination of araldehydes by aniline using borohydride with $CeCl_3{\cdot}7H_2O$ as catalyst

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A one-pot, two-step reductive amination of araldehydes or acetophenones with anilines using $NaBH_4$ as a cheap hydride source and catalysed by $CeCl_3{\cdot}7H_2O$ has been achieved in EtOH at room temperature in good yields.

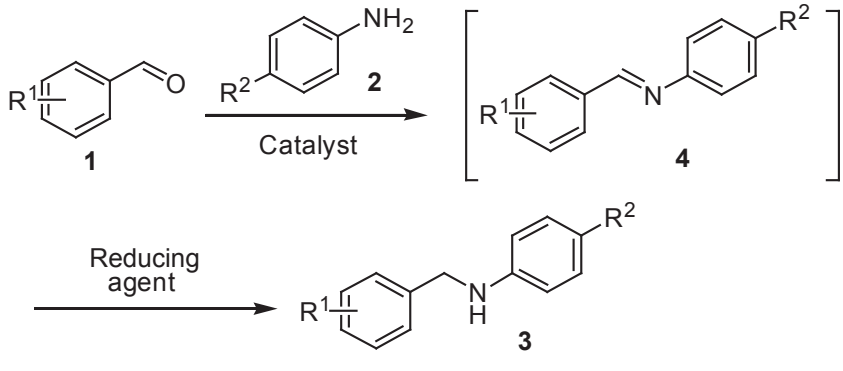
Keywords: one-pot, reductive amination, cerium(III) chloride

Substituted amines are important building blocks in a multitude of biologically active natural products and pharmaceuticals.[1,2] For example, they are used as organic intermediates for the synthesis of bactericides, drugs, herbicides, rubber accelerators, corrosion inhibitors, and surface-active agents. Owing to the immense importance of amines, their synthesis is an active field in medicinal chemistry and modern organic synthesis.[3,4] As a consequence, various methods for the efficient formation of a C–N bond have been widely investigated. As one of the most important and effective C–N bond-forming processes, reductive amination is a fundamental transformation both in laboratory synthesis and industrial production.[5-7] Direct reductive amination of carbonyl compounds remain the simplest approach.[8-10] Typically, reductive amination of aldehydes or ketones, in which a mixture of a carbonyl compound and an amine is treated with a reductant in a "one-pot" fashion, is one of the most useful methods for the preparation of secondary or tertiary amines which avoids the isolation of an unstable imine or iminium intermediate.[11-13] As shown in Scheme 1, one of the synthetic methods to *N*-benzyl-*N*-phenylamines **3** utilized condensation between aldehydes **1** and anilines **2** followed by reduction of the imine intermediate **4**. Several hydrogen sources such as sodium cyanoborohydride,[14] sodium triacetoxyborohydride,[15] sodium- or zinc borohydride[16] in the presence of Brønsted or Lewis acids[17,18] have been utilised to form the intermediate imines and to activate these C=N intermediates for a preferential reduction. However, these various borohydride derivatives suffer from limitations such as expense, high toxicity and low selectivity,[19] which limit the scope of these methods. For this reason, wide commercial availability of substrates, generally mild reaction conditions and in some cases exceptionally high functional group tolerance which promotes efficient one-pot synthesis has become an important research area in organic chemistry.[20] Several methods which effect direct reductive amination have been recently developed, such as $ZnCl_2$–$NaBH_4$,[21] $NiCl_2$–$NaBH_4$,[22] Ti(O*i*Pr)$_4$–polymethylhydrosiloxane,[23] Ti(O*i*Pr)$_4$–$NaBH_4$,[24] silica gel–$ZnBH_4$,[25] trifluoro acetic acid–Et_3SiH[26] and pyridine–BH_3.[27]

In previous work, we found that a Lewis acid can not only promote the formation of a C–C bond, but can also promote the formation of an imine.[28-30] Since imine formation is the rate-determining step for *in situ* reductive aminations, addition of a mild Lewis acid as catalyst can increase the rate. Ravishankar *et al.*[31] have recently reported a one-pot, solvent-free reductive amination of cinnamaldehydes and araldehydes by anilines using sodium borohydride and catalysed by $CeCl_3{\cdot}7H_2O$.[31] We now report that, using $NaBH_4$ with $CeCl_3{\cdot}7H_2O$ as catalyst in solvent ethanol at room temperature, aldehydes and acetophenones can be reductively aminated by anilines with higher efficiency.

Results and discussion

Initially, we studied the influence of $CeCl_3{\cdot}7H_2O$ on the condensation reaction of benzaldehyde with aniline. The condensation reaction was carried out with $NaBH_4$ in EtOH at room temperature and the results are summarised in Table 1. Clearly $CeCl_3{\cdot}7H_2O$ plays an important role in catalysing the reaction, as without any catalyst, the yield of *N*-benzyl-*N*-phenylamine was very low and benzyl alcohol (45%) was obtained as the main product (entry 1). When $CeCl_3{\cdot}7H_2O$ was added, reduction of benzaldehyde to benzyl alcohol was observed; 1, 2, 5 and 7 mol% of catalyst was investigated (entries 2–7) and that 5 mol% of $CeCl_3{\cdot}7H_2O$ was sufficient to catalyse the reaction. Among the solvents screened, including EtOH, MeOH, CH_2Cl_2 and AcOEt, EtOH was the best solvent which afforded the amine in 93% yield using 2 equiv. $NaBH_4$ at room temperature (entry 6).



Scheme 1

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The influence of several hydride sources on the reaction outcome was studied. In general, the hydride sources were found to be most active at 70°C in EtOH (Table 2). No reaction was observed at room temperature (entry 5). By comparison of the yields when using different hydride sources, such as $NaBH_4$, $PhSiH_3$, Ph_2SiH_2 and Ph_3SiH, we found that Et_3SiH gave the *N*-benzyl-*N*-phenylamine in very low yield (entry 4). However, further studies were performed with $NaBH_4$, because of its great availability, low price and ready reaction at room temperature.

To explore the scope and limitations of the present catalyst system, reductive aminations of various carbonyl compounds and amines were performed. The reaction was in EtOH in the presence of 5 mol% of $CeCl_3{\cdot}7H_2O$ under air for 8 h, as can be seen in Table 3. Excellent yields were obtained when benzaldehydes were substituted with electron-withdrawing as well as electron-donating groups (entries 1–9), while difficulties arose with nitro groups in an *o*-position or a *m*-position (entries 10 and 11). Functional groups such as –Cl, –Br, –I, $–NO_2$, and C=C present on the aldehyde remained unaffected.

Next we investigated the influence of the amine component in combination with benzaldehyde. The reactions of an aniline containing an electron-withdrawing group decreases the reaction yield (entry 12), wheras an aniline containing an electron-donating group increased product yield slightly (entry 13).

Table 1 Optimisation of the amounts of $NaBH_4$, catalyst and solvent in the reductive amination of benzaldehyde (**1**, R^1 = H) with aniline (**2**, R^2 = H) (Scheme 1) [a]

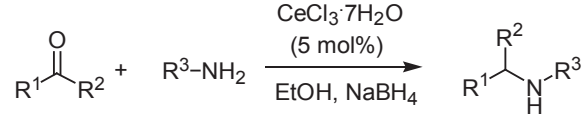
Entry	$CeCl_3{\cdot}7H_2O$ /mol%	Solvent	$NaBH_4$/equiv.	Conversion /%[b]
1	0	EtOH	1	10 (45 [c])
2	1	EtOH	1	50
3	2	EtOH	1	54
4	5	EtOH	1	60
5	5	EtOH	1.2	67
6	5	EtOH	2	93
7	7	EtOH	2	94
8	5	MeOH	2	90
9	5	CH_2Cl_2	2	78
10	5	AcOEt	2	72

[a]Reaction conditions: benzaldehyde (1 mmol), aniline (1.2 mmol), $CeCl_3{\cdot}7H_2O$ (mol%), and $NaBH_4$ in solvent (5 mL), 8 h, at room temperature.
[b]Yield determined by GC.
[c]Yield of benzyl alcohol.

One of the major advantages of the present method is that it can be used for the reductive amination of acetophenones, which are considered difficult substrates for this reaction.[24] The reductive amination of acetophenone was found to require higher quantities of the catalyst and the yields of the products are low.[32] Using our optimal conditions for the longer time of 12 h, the reductive amination of acetophenone with amines afforded the desired products in good yields (entries 14–16).

Reductive amination of propinaldehyde with aniline reactions was carried out in the presence of 5 mol% $CeCl_3{\cdot}7H_2O$ affording the corresponding secondary amine in a moderate yield (entry 17). An excellent yields was obtained when benzaldehyde was reductively aminated with an aliphatic amines (entry 18).

Table 3 Yields of reductive aminations of various araldehydes and acetophenones by anilines using $NaBH_4$ and $CeCl_3{\cdot}7H_2O$ under the optimised conditions[a]



1 **2** **3**

Entry	R^1	R^2	R^3	Product	Yield/%[b]
1	*p*-$NO_2C_6H_5$	H	C_6H_5	**3a**	92
2	*p*-ClC_6H_5	H	C_6H_5	**3b**	92
3	*p*-BrC_6H_5	H	C_6H_5	3c	89
4	*p*-IC_6H_5	H	C_6H_5	**3d**	88
5	C_6H_5CH=CH	H	C_6H_5	**3e**	91
6	*p*-$CH_3C_6H_5$	H	C_6H_5	**3f**	85
7	C_6H_5	H	C_6H_5	**3g**	88
8	*p*-$OCH_3C_6H_5$	H	C_6H_5	**3h**	82
9	*p*-HOC_6H_5	H	C_6H_5	**3i**	83
10	*m*-$NO_2C_6H_5$	H	C_6H_5	**3j**	62
11	*o*-$NO_2C_6H_5$	H	C_6H_5	**3k**	70
12	C_6H_5	H	*p*-BrC_6H_5	**3l**	83
13	C_6H_5	H	*p*-$OCH_3C_6H_5$	**3m**	90
14	C_6H_5	CH_3	C_6H_5	**3n**	75 [c]
15	C_6H_5	CH_3	*p*-BrC_6H_5	**3o**	70 [c]
16	C_6H_5	CH_3	*p*-$OCH_3C_6H_5$	**3p**	79 [c]
17	C_3H_7	H	C_6H_5	**3q**	60
18	C_6H_5	H	C_4H_9	**3r**	91

[a]Reaction conditions: araldehyde (1 mmol), aniline (1.2 mmol), $CeCl_3{\cdot}7H_2O$ (5 mol%), and $NaBH_4$ (2 mmol) in EtOH (5 mL), 8 h, at room temperature.
[b] Yield of isolated product.
[c] Reaction time was 12 h.

Table 2 Influence of the hydride source and the Lewis acid on the yield of the reductive amination of benzaldehyde (1, R^1 = H) with aniline (2, R^2 = H) (Scheme 1)

Entry	Lewis acid		Hydride source	Time /h	Temp /°C	Solvent	Yield/%[a]
1	$CeCl_3{\cdot}7H_2O$	(5 mol%)	$PhSiH_3$ (2 equiv.)	4	0	EtOH	95
2	$CeCl_3{\cdot}7H_2O$	(5 mol%)	Ph_2SiH_2 (2 equiv.)	4	70	EtOH	92
3	$CeCl_3{\cdot}7H_2O$	(5 mol%)	Ph_3SiH (2 equiv.)	4	70	EtOH	67
4	$CeCl_3{\cdot}7H_2O$	(5 mol%)	Et_3SiH (2 equiv.)	4	70	EtOH	35
5	$AlCl_3$	(5 mol%)	Poly (methylhydro-siloxane) (2 equiv.)	12	rt	EtOH	NR [33]
6	$AlCl_3$	(5 mol%)	Poly (methylhydro-siloxane) (2 equiv.)	12	70	EtOH	99 [33]
7	$Zn(OTf)_2$	(5 mol%)	$PhSiH_3$ (1.5 equiv.)	4	60	THF	95 [17]
8	$ZnCl_2$	(5 mol%)	NH_3BH_3 (1.5 equiv.)	10	rt	THF	88 [19]
9	$CeCl_3{\cdot}7H_2O$	(5 mol%)	$NaBH_4$ (2 equiv.)	8	rt	EtOH	93

[a]Yield was determined by GC-MS. NR= less than 5% conversion.

Experimental

All chemicals (AR grade) were obtained from commercial sources and used without further purification. Gas chromatography analysis was performed on an Agilent GC-6820 chromatograph equipped with a 30 m×0.32 mm×0.5 μm HP-Innowax capillary column and a flame ionisation detector. GC-MS spectra were recorded on Thermo Trace DSQ GC-MS spectrometer using TRB-5MS (30 m×0.25 mm×0.25 μm) column. Melting points were determined using a XT-4 apparatus and are not corrected. ^{1}H NMR spectra were obtained on a Bruker Avance III 400 (400 MHz) spectrometer in DMSO-d_6 using TMS as internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Progress of the reactions was followed by TLC using silica-gel polygrams SIL G/UV 254 plates. Column chromatography was performed using Silicycle (40–60 mm) silica gel. All products are known compounds and were characterised by comparison of their physical and spectral properties with literature data.

Synthesis of secondary amines catalysed by the $CeCl_3{\cdot}7H_2O$–$NaBH_4$ system; general procedure

Benzaldehyde (1.0 mmol), amine (1.2 mmol) and $CeCl_3{\cdot}7H_2O$ (0.02 mmol) in ethanol (5 mL) were stirred for 20 min at room temperature, then $NaBH_4$ (2 mmol) was added. On completion of the reaction (as monitored by TLC), the reaction mixture was dried under vacuum and the product was extracted with ethyl acetate (3 × 10 mL). Evaporation of the solvent gave a crude product which was purified on a small silica gel column with EtOAc: petroleum ether (10:1) as eluent.

N-*(4-Nitrobenzyl)-aniline* (**3a**): White solid (209 mg, 92%), m.p. 66–68 °C (EtOH) (lit.[13] 67–68 °C); ^{1}H NMR: δ 7.78–7.74 (m, 2H),7.66–7.62 (m, 2H), 6.77–6.73 (m, 2H), 6.63–6.61 (m, 2H), 6.56–6.52 (m, 1H), 6.26 (s, 1H), 4.26 (s, 2H).

N-*(4-Chlorobenzyl)-aniline* (**3b**): Yellow oil (200 mg, 92%); ^{1}H NMR: δ 7.30–7.30 (m, 4H), 7.07–7.03 (m, 2H), 6.58–6.51 (m, 3H), 6.26 (s, 1H), 4.26 (s, 2H).

N-*(4-Bromobenzyl)-aniline* (**3c**): Yellow solid (224 mg, 89%), m.p. 51–53 °C (EtOH) (lit.[38] 51–52 °C). ^{1}H NMR: δ 7.40–7.35 (m, 4H), 7.07–7.03 (m, 2H), 6.58–6.51 (m, 3H), 6.26 (s, 1H), 4.26 (s, 2H).

N-*(4-Iodobenzyl)-aniline* (**3d**): Yellow solid (253 mg, 88%), m.p. 52–54 °C (EtOH) (lit.[37] 52–53 °C); ^{1}H NMR: δ 7.58–7.49 (m, 4H), 7.07–7.03 (m, 2H), 6.58–6.51 (m, 3H), 6.26 (s, 1H), 4.26 (s, 2H).

N-*Styryl-aniline* (**3e**): White solid (190 mg, 91%), m.p. 135–138 °C (EtOH) (lit.[13] 137–138 °C); ^{1}H NMR: δ 7.40–7.38 (m, 2H), 7.31–7.29 (m, 2H), 7.20–7.18 (m, 1H), 6.98–6.96 (m, 2H), 6.62 (s, 1H), 6.50–6.43(m, 3H), 6.27 (s, 1H), 6.11 (s, 1H), 4.41 (d, J=8 Hz, 2H).

N-*(4-Methylbenzyl)-aniline* (**3f**): Colourless oil (167 mg, 85%); ^{1}H NMR: δ 7.41–7.31 (m, 4H), 7.08–7.05 (m, 2H), 6.62–6.61 (m, 2H), 6.56–6.52 (m, 1H), 6.24 (s, 1H), 4.29 (s, 2H), 2.20 (s, 3H).

N-*Benzyl-aniline* (**3g**): Colourless oil (161 mg, 88%); ^{1}H NMR: δ 7.40–7.38 (m, 2H), 7.35–7.31 (m, 2H), 7.25–7.22 (m, 1H), 7.09–7.04 (m, 2H), 6.63–6.61 (m, 2H), 6.56–6.52 (m, 1H), 6.24 (s, 1H), 4.29 (s, 2H).

N-*(4-Methoxybenzyl)-aniline* (**3h**): White solid (174 mg, 82%), m.p. 60–62 °C (EtOH) (lit.[40] 61–62 °C); ^{1}H NMR: δ 7.29–7.21(m, 4H), 7.08–7.06 (m, 2H), 6.63–6.61 (m, 2H), 6.54–6.52 (m, 1H), 6.24 (s, 1H), 4.29 (s, 2H), 3.59 (s, 3H).

N-*(4-Hydroxylbenzyl)-aniline* (**3i**): White solid (165 mg, 83%), m.p. 112–115 °C (EtOH) (lit.[38] 51–52 °C); ^{1}H NMR: δ 7.37–7.30 (m, 4H), 7.08–7.04 (m, 2H), 6.63–6.52 (m, 3H), 6.24 (s, 1H), 5.81 (s, 1H), 4.29 (s, 2H).

N-*(2-Nitrobenzyl)-aniline* (**3j**): Yellow oil (166 mg, 73%); ^{1}H NMR: δ 7.63–7.61 (m, 1H), 7.52–7.50 (m, 2H), 7.38–7.34 (m, 1H)), 7.04–7.02 (m, 2H), 6.91–6.90 (m, 2H), 6.70–6.66 (m, 1H), 6.21 (s, 1H), 4.22 (s, 2H).

N-*(3-Nitrobenzyl)-aniline* (**3k**): White solid (159 mg, 70%), m.p. 83–85 °C (EtOH) (lit.[39] 82–84 °C); ^{1}H NMR: δ 7.41–7.35 (m, 4H), 7.25–7.23 (m, 2H), 6.77–6.66 (m, 3H)), 5.90 (s, 1H), 4.25 (s, 2H).

N-*Benzyl-4-bromoaniline* (**3l**): Yellow solid (209 mg, 83%), m.p. 51–53 °C (EtOH) (lit.[34] 52–53 °C]; ^{1}H NMR: δ 7.40–7.35 (m, 4H), 7.18–7.14 (m, 1H), 6.74–6.72 (m, 2H), 6.58–6.56 (m, 2H), 6.26 (s, 1 H), 4.26 (s, 2H).

N-*Benzyl-4-methoxyanilines* (**3m**): White solid (191 mg, 90%), m.p. 47–50 °C (EtOH) (lit.[35] 48–50 °C); ^{1}H NMR: δ 7.40–7.38 (m, 2H), 7.35–7.31 (m, 2H), 7.25–7.22 (m, 1H), 6.69–6.61 (m, 4H), 6.24 (s, 1 H), 4.29 (s, 2H), 3.55 (s, 3H).

N-*(1-Phenylethyl) aniline* (**3n**): Colourless oil (147 mg, 75%); ^{1}H NMR: δ 7.38–7.36 (m, 2H), 7.31–7.27 (m, 2H), 7.19–7.16 (m, 1H), 6.99–6.95 (m, 2H), 6.50–6.43 (m, 3H), 6.11 (s, 1H), 4.46–4.44 (t, J=8 Hz, 1H), 1.42 (d, J=8 Hz, 3H).

4-Bromo-N-*(1-phenylethyl) aniline* (**3°**): Yellow oil (162 mg, 70%); ^{1}H NMR: δ 7.39–7.35 (m, 2H), 7.30–7.26 (m, 2H), 7.20–7.16 (m, 2H), 7.08–7.00 (m, 3H), 6.11 (s, 1H), 4.45–4.43 (t, J=8 Hz, 1H), 1.42 (d, J=8 Hz, 3H).

4-Methoxy-N-*(1-phenylethyl) aniline* (**3p**): White solid (179 mg, 79%), m.p. 61–63 °C (EtOH) (lit.[36] 61–62 °C); ^{1}H NMR: δ 7.38–7.27(m, 5H), 6.77–6.73 (m, 2H), 6.65–6.62 (m, 2H), 6.11 (s, 1H), 4.45–4.45 (m, 1H), 3.57 (s,3H), 1.42 (d, J=8 Hz, 3H).

N-*Butyl-anilines* (**3q**): Colourless oil (0.089 mg, 60%); ^{1}H NMR: δ 7.09–7.06 (m, 2H), 6.81–6.78 (m, 1H), 6.63–6.60 (m, 2H), 6.08 (s, 1H), 4.08–4.06 (t, J=8 Hz, 2H), 2.81 (m, 2H), 1.99–1.91 (m, 2H), 1.10 (t, J=8 Hz, 3H).

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