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# Tandem Fe/Zn or Fe/In catalysis for the selective synthesis of primary and secondary amines via selective reduction of primary amides

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Dedication ((optional))

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**Abstract:** Tandem iron/zinc or iron/indium-catalysed reductions of various primary amides to amines under hydrosilylation conditions are reported under visible light activation. By a simple modification of the nature of the co-catalyst ( $\text{Zn}(\text{OTf})_2$  vs  $\text{In}(\text{OTf})_3$ ),  $\text{Fe}(\text{CO})_4(\text{IMes})$  can promote the high chemoselective reduction of primary amides into primary amines (21 examples, up to 93% isolated yields) and secondary amines (8 examples, up to 51% isolated yields), respectively. Notably, both benzamide and alkanamide derivatives can be reduced.

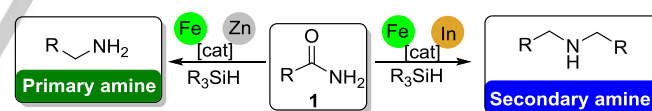
## Introduction

The reduction of carboxamides is among the most important reaction in molecular synthesis mainly for the synthesis of amines, and more particularly of primary amines.<sup>[1]</sup> Since two decades, numerous catalytic pathways to prepare efficiently amine derivatives have been developed. Representative methodologies were based on aryl halide amination with palladium or copper catalysts,<sup>[2]</sup> hydroamination of olefins,<sup>[3]</sup> imine,<sup>[4]</sup> nitro,<sup>[5]</sup> nitrile,<sup>[6]</sup> or carboxamide<sup>[7]</sup> reduction, and amination of alcohols and carbonyl derivatives.<sup>[8]</sup> It should be underlined that the reduction of carboxamides can be seen as the most difficult reaction to perform due to notably the lack of activity of the amide group and the chemoselectivity issues (C-N vs C-O bond cleavage).<sup>[7c]</sup> Indeed, using traditional stoichiometric metal hydride species, even if efficient, functional group tolerance was always the main observed drawback, associated with tedious purification procedures.<sup>[9]</sup> Additionally, when performing the reduction under hydrogenation conditions, mainly using noble metal catalysts, the main limitation is due to the drastic conditions used (elevated pressure, very high temperature...) which limited their use in larger scale.<sup>[10]</sup>

Over the last decade, progresses have been achieved with the development of metal-catalyzed chemoselective hydrosilylation, usually conducted under milder reaction conditions. Noticeably, first row transition metals can be used to perform such reduction.<sup>[11]</sup> As representative recent examples, hydrosilylation of primary amides leading to primary amines were performed with manganese<sup>[12]</sup> or nickel based catalysts.<sup>[13]</sup> It should be also underlined that over the last two decades, progresses have been made with the use of iron in homogeneous catalysis, notably in reduction area.<sup>[14]</sup> The first selective reductions of

secondary and tertiary carboxamides to their corresponding amines via deoxygenation were developed under hydrosilylation using iron salts or complexes.<sup>[15]</sup> Noticeably when performing the hydrosilylation with primary amides, the corresponding nitriles were specifically obtained.<sup>[16,15h]</sup> Only scarce contributions performing the full reduction of primary amides to primary amines were described at iron. The first one reported by Beller using two different iron complexes in a consecutive manner,  $[\text{Et}_3\text{NH}][\text{HFe}_3(\text{CO})_{11}]$  for the generation of nitriles and  $\text{Fe}(\text{OAc})_2/\text{phenanthroline}$  for the reduction of nitriles to primary amines. Similarly, Nagashima has employed an iron/cobalt catalytic system albeit with limited scope.<sup>[17]</sup>

Herein, we report iron-catalysed chemoselective and tandem methodologies to reduce primary carboxamides either to primary amines using a Zn based co-catalyst or to secondary amines with the association of an indium co-catalyst. (Scheme 1)



**Scheme 1.** Iron catalysed tandem reduction of primary carboxamides either to primary or secondary amines with Zn or In co-catalyst.

## Results and Discussion

First of all, in order to evaluate the ability of iron(0) based catalysts to reduce primary amides into the corresponding primary amines under hydrosilylation conditions, we began our initial work by performing the reduction of benzamide **1a** using 3 equiv. of phenylsilane as the reducing agent in the presence of 5 mol% of  $\text{Fe}(\text{CO})_4(\text{IMes})$  [ $\text{IMes}$  = 1,3-bis (2,4,6-trimethylphenyl)imidazol-2-ylidene] upon visible light irradiation (using 24 watt compact fluorescent lamp). Even if full conversion was observed, only the dehydration derivative benzonitrile **2a** was obtained (95%, Table 1, entry 1). Such results were already described under iron-catalysed hydrosilylation conditions.<sup>[15]</sup> Thus the effect of the addition of a Lewis acid in order to promote the reduction was evaluated (Table 1). Among the tested metal salts (20 mol%), indium and zinc exhibited interesting reactivities. Whereas indium chloride favored the

formation of dibenzylamine **4a** (entry 5), zinc salts selectively led to benzylamine hydrochloride salt **5a**, resulting from the treatment of the benzylamine **3a** by a solution of dry HCl, zinc triflate being the most efficient (85% isolated yield, entry 9). Varying the quantity of  $\text{Zn}(\text{OTf})_2$  (10 and 30 mol%) had a deleterious effect on the efficiency to produce **5a** (75 and 60%, respectively, entries 10 and 11). Similarly, increasing the reaction temperature to 130 °C or decreasing to 100 °C led to **5a** in less good yields (entries 12 and 13). Importantly, when the reaction was performed in absence of iron catalyst, with 20 mol% of  $\text{Zn}(\text{OTf})_2$ , full conversion was observed but a mixture of **2a** and **3a** was obtained (73, 24%, respectively, entry 14). This result clearly demonstrated that the bimetallic association of Fe and Zn surpassed the selectivity of zinc, hydrosilylation with zinc salts being already reported with secondary and tertiary amides.<sup>[18]</sup> Additionally, different iron catalysts (5 mol%) such as  $\text{Fe}(\text{CO})_4(\text{DIPP})$  [DIPP = 1,3-bis (2,6-diisopropyl-phenyl)imidazol-2-ylidene],  $[\text{CpFe}(\text{CO})_2(\text{IMes})][\text{I}]$  or the Knölker catalyst in presence of 10 mol% of  $\text{Me}_3\text{NO}$ , were evaluated in the presence of 20 mol% of  $\text{Zn}(\text{OTf})_2$ , but lower efficiencies were obtained (79, 56 and 60% isolated yields, respectively, Table S1, SI).

Among the tested hydrosilanes, tertiary silanes gave either no conversion ( $i\text{Pr}_3\text{SiH}$ , Table 2, entry 6) or full conversion, but led only to the dehydrated benzonitrile **2a** (entries 8-11). By contrast, the use of secondary silanes such as diethylsilane permitted to selectively obtained benzylamine hydrochloride salt **5a** with moderate isolated yields up to 64% (entry 5). Finally, the best identified silane was  $\text{PhSiH}_3$  with an optimized amount of 3 equiv. which permitted to obtain up to 85% of **5a**. (entries 1-3).

Additionally, the nature of the solvents was evaluated for this reaction under similar conditions in the presence of 3 equiv. of  $\text{PhSiH}_3$  (Table S2, SI). Whereas lower conversions were obtained in *n*-BuOH (10%) and 2-MeTHF (30%), with all the other tested solvents including cyclopentylmethylether, dioxane, and cyclohexane, full conversions were detected and benzylamine **3a** were selectively produced. The best efficiency was observed in cyclohexane, **5a** being isolated in 93% yield, thus exhibiting higher efficiencies in non-polar solvents.

**Table 1.** Optimization of the parameters for the selective reduction of benzamide **1a** to benzylamine **3a**.<sup>[a]</sup>

$\text{Ph}-\text{C}(=\text{O})\text{NH}_2 \xrightarrow[\text{110 } ^\circ\text{C, 20 h, hv}]{\text{Fe}(\text{CO})_4\text{IMes (5 mol\%)} \text{ Additive PhSiH}_3 \text{ (3 equiv.)}} \text{Ph}-\text{CN} + \text{Ph}-\text{CH}_2\text{NH}_2 + (\text{Ph})_2\text{NH}$					
			<b>2a</b>	<b>3a</b>	<b>4a</b>
Entry	Additive (mol%)	Conv. (%) <sup>[b]</sup>	Yield (%)		
			<b>2a</b> <sup>[b]</sup>	<b>5a</b> <sup>[c]</sup>	<b>4a</b> <sup>[b]</sup>
1	-	>99	95	0	0
2	$\text{FeCl}_2$ (20)	>99	82	0	17
3	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (20)	33	0	0	20
4	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (20)	90	67	0	8
5	$\text{InCl}_3$ (20)	90	13	15	41
6	$\text{ZnF}_2$ (20)	>99	0	68	trace
7	$\text{ZnBr}_2$ (20)	>99	0	82	trace
8	$\text{Zn}(\text{OAc})_2$ (20)	>99	0	50	trace
9	$\text{Zn}(\text{OTf})_2$ (20)	>99	0	<b>85</b>	6
10	$\text{Zn}(\text{OTf})_2$ (10)	>99	0	75	5
11	$\text{Zn}(\text{OTf})_2$ (30)	>99	0	60	12
12 <sup>[d]</sup>	$\text{Zn}(\text{OTf})_2$ (20)	>99	0	71	10
13 <sup>[e]</sup>	$\text{Zn}(\text{OTf})_2$ (20)	>99	13	56	14
14 <sup>[f]</sup>	$\text{Zn}(\text{OTf})_2$ (20)	>99	73	24	0

[a] Conditions: Benzamide (0.3 mmol), additive (10-30 mol%),  $\text{Fe}(\text{CO})_4\text{IMes}$  (5 mol%),  $\text{PhSiH}_3$  (3 equiv.), toluene (1 mL), 110 °C for 20 h under argon and visible light activation (using 24 watt compact fluorescent lamp). [b] Conversion and yields of **2a** and **4a** determined by GC using dodecane as an internal standard; [c] Isolated yield of **5a** after acidification of **3a** with HCl solution (0.5 M in dioxane). [d] 130 °C. [e] 100 °C. [f] Reaction without iron catalyst.

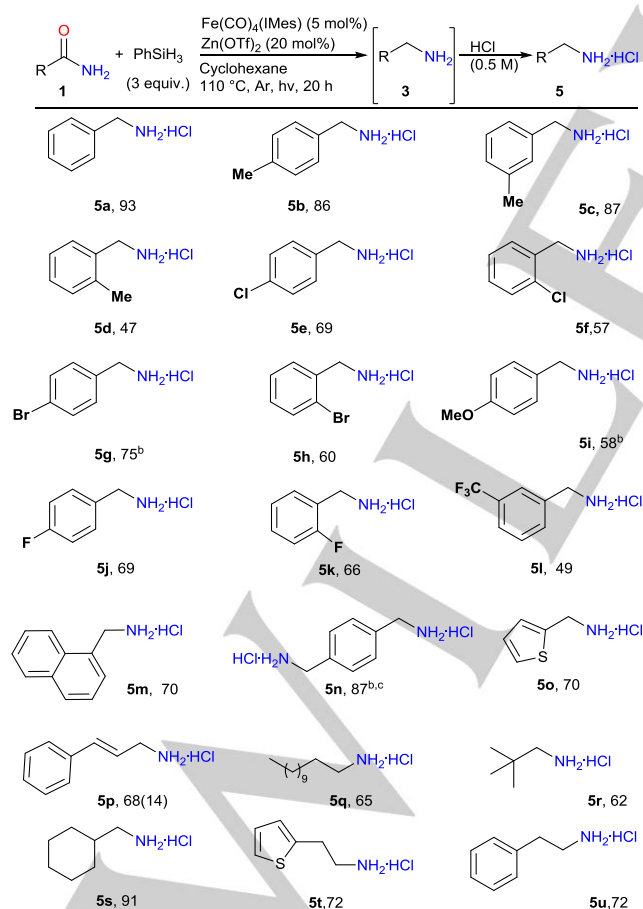
**Table 2.** Influence of the nature of the hydrosilane on the reduction of benzamide **1a**.<sup>[a]</sup>

$\text{Ph}-\text{C}(=\text{O})\text{NH}_2 \xrightarrow[\text{110 } ^\circ\text{C, 20 h, hv}]{\text{Fe}(\text{CO})_4\text{IMes (5 mol\%)} \text{ Zn}(\text{OTf})_2 \text{ (20 mol\%)} \text{ silane (3 equiv.)}} \text{Ph}-\text{CN} + \text{Ph}-\text{CH}_2\text{NH}_2 + (\text{Ph})_2\text{NH}$					
			<b>2a</b>	<b>3a</b>	<b>4a</b>
Entry	Silane (equiv.)	Conv. (%) <sup>[b]</sup>	Yield (%)		
			<b>2a</b> <sup>[b]</sup>	<b>5a</b> <sup>[c]</sup>	<b>4a</b> <sup>[b]</sup>
1	<b><math>\text{PhSiH}_3</math> (3)</b>	<b>&gt;99</b>	<b>0</b>	<b>85</b>	<b>6</b>
2	$\text{PhSiH}_3$ (2)	>99*	10	45	12
3	$\text{PhSiH}_3$ (4)	>99	0	82	16
4	$\text{Ph}_3\text{SiH}$ (3)	9	7	trace	0
5	$\text{Et}_2\text{SiH}_2$ (3)	>99*	0	64	5
6	$i\text{Pr}_3\text{SiH}$ (3)	<5	0	0	0
7	$(\text{EtO})_3\text{SiH}$ (3)	82	78	0	0
8	$\text{Et}_3\text{SiH}$ (3)	98	94	0	0
9	$\text{PhMe}_2\text{SiH}$ (3)	>99	74	0	25
10	$\text{Ph}_2\text{MeSiH}$ (3)	>99	92	0	8
11	$(\text{EtO})_2\text{MeSiH}$ (3)	>99	71	0	28

[a] Conditions: Benzamide (0.3 mmol),  $\text{Zn}(\text{OTf})_2$  (20 mol%),  $\text{Fe}(\text{CO})_4\text{IMes}$  (5 mol%), silane (2-4 equiv.), toluene (1 mL), 110 °C for 20 h under argon and visible light activation. [b] Conversion and yields of **2a** and **4a** determined by GC using dodecane as an internal standard; [c] Isolated yield of **5a** after acidification of **3a** with HCl solution (0.5 M in dioxane). \*Numerous unidentified by-products were also detected.

With these optimized conditions in hands, we then evaluated the substrate scope and limitation of this transformation. Noticeably, the primary amines **3** were isolated as their chloride ammonium salts **5** by simple

addition of a HCl solution (0.5 M in dioxane) at the end of the reaction (Scheme 2). The reduction was successfully conducted with substituted benzamide derivatives bearing electron-donating groups such as methoxy, methyl, or halides, leading to the corresponding  $\text{ArNH}_2\cdot\text{HCl}$  salts **5b-i** in 47-87% isolated yields. It must be underlined that the steric hindrance due to the *ortho*-substitution of the benzamide derivatives has a significant influence on the reactivity lowering the yields (47-66%, **5d**, **5f**, **5h**, and **5k**). In the case of *o*-iodobenzamide, even if the full conversion was observed, the main product obtained was the corresponding nitrile compound, with trace amount of amine. The reduction can also be conducted with benzamide derivatives bearing an electron-withdrawing group such as trifluoromethyl thus leading to **5l** in 49% yield. Interestingly, terephthamide was efficiently reduced leading to the salt **5n** derived from 1,4-phenylenediamine **3n** in 87% isolated yield. Additionally, heteroaromatic derivatives such as 2-thiophenecarboxamide led to the corresponding ammonium salt **5o** in 70% yield. The reaction can be selectively conducted with cinnamamide: the corresponding salt **5p** derived from cinnamylamine was isolated in 68% associated to the fully reduced one derived from 3-phenylpropanamine (14%) showing that under such conditions, the conjugated  $\text{C}=\text{C}$  bond can be also reduced.



**Scheme 2.** Scope for the hydrosilylation of primary amides leading to primary amines. <sup>a</sup> Isolated yield. <sup>b</sup> In toluene. <sup>c</sup>  $\text{Fe}(\text{CO})_4\text{IMes}$  (7.5 mol%),  $\text{Zn}(\text{OTf})_2$  (30 mol%).

These conditions can be also efficiently applied to alkanamides, and the corresponding ammonium salts **5q-5t** were isolated in 62-91% yields. The reduction of 4-hydroxybenzamide and 4-aminobenzamide led to a mixtures of products with small amount of the expected amines. Additionally, 2-phenylethylamine **3u**, a monoaminergic neuro-modulator and a neurotransmitter in the human central nervous system (CNS) can be efficiently prepared from its corresponding amide and the corresponding salt **5u** was obtained in 72% yield. By contrast, when starting from 2-phenylpropanamide, no corresponding product was obtained under such conditions. To demonstrate the synthetic usefulness of this methodology, a gram scale reaction starting from 10 mmol of benzamide **1a** led to the benzylamine hydrochloride salt **5a** in 79% isolated yield.

During the optimization of the reaction, it was observed that when 20 mol% of  $\text{InCl}_3$  was used, 90% conversion was detected and the selectivity was switched as 41% of dibenzylamine **4a** was obtained as the main product in addition to 13% of benzonitrile **2a** and 15% of benzylamine **3a** (Table 3, entry 1). Noticeably,  $\text{InBr}_3$  was described as a catalyst specifically for the reductive deoxygenation of tertiary and secondary amines, but only one example of primary amide was reported.<sup>[19]</sup> The optimization of the reaction performing a screening of salts and conditions was illustrated in Table 3. The decrease of the amount of  $\text{InCl}_3$  to 10 mol% had a deleterious effect, whereas its increase to 30 mol% did not give better results (Table 3, Entries 2 and 3). Noticeably, when performing the reaction at 130 °C, even if full conversion was observed, only 50% of dibenzylamine **4a** was obtained. (Table 3, entry 4).

**Table 3.** Optimization of the parameters for the selective preparation of dibenzylamine **4a** from benzamide **1a**.<sup>[a]</sup>

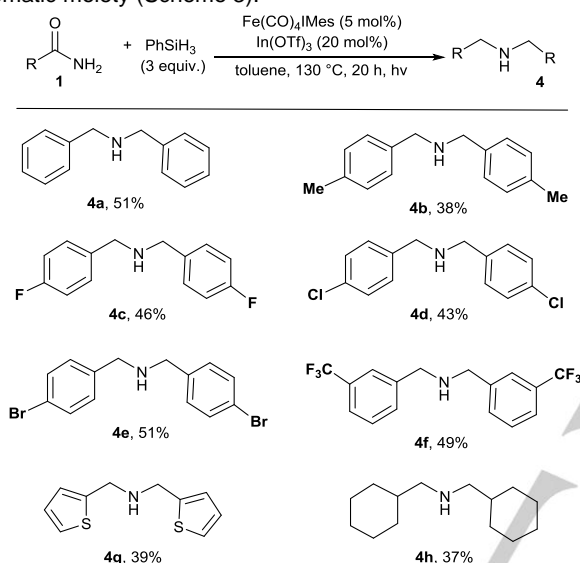
Entry	Additive (mol%)	Conv. (%) <sup>[b]</sup>	Yield (%)		
			<b>2a</b> <sup>[b]</sup>	<b>3a</b> <sup>[b]</sup>	<b>4a</b> <sup>[b]</sup>
1	$\text{InCl}_3$ (20)	90	13	15	41
2	$\text{InCl}_3$ (10)	90	31	0	21
3 <sup>[c]</sup>	$\text{InCl}_3$ (30)	88	17	13	36
4 <sup>[d,e]</sup>	$\text{InCl}_3$ (20)	>99	5	Trace	50
5 <sup>[d,e]</sup>	$\text{InBr}_3$ (20)	>99	0	32	42
6 <sup>[d]</sup>	$\text{In}(\text{OTf})_3$ (20)	99	0	Trace	<b>55(51)</b>
7 <sup>[e]</sup>	$\text{InCl}_3$ (20)	90	37	0	29

[a] Conditions: Benzamide (0.3 mmol), indium salt (10-30 mol%),  $\text{Fe}(\text{CO})_4\text{IMes}$  (5 mol%),  $\text{PhSiH}_3$  (3 equiv.), toluene (1 mL), 110 °C for 20 h under argon and visible light activation (using 24 watt compact fluorescent lamp). [b] Conversion and yields determined by GC; in parenthesis, isolated yield of **4a**. [c] Several by-products were also



detected including one corresponding to the formation of secondary amides. [d] 130 °C. [e] Reaction without iron catalyst.

Interestingly, when using  $\text{InBr}_3$ , similar results were obtained, with a significant amount of primary benzylamine **3a** (entry 5). The more efficient identified co-catalyst was  $\text{In}(\text{OTf})_3$ , leading selectively to the dibenzylamine **4a** with 51% isolated yield (entry 6). Noticeably, without iron catalyst, even if the conversion can reach 90%, and 29% of **4a** can be obtained, several by-products including *N*-benzylbenzamide were detected (Entry 7). In order to illustrate the applicability of this tandem iron/indium catalyzed reactions of primary amides, using the optimized conditions (Table 3, entry 6), various symmetrical secondary amines **4** were prepared in moderate yields from primary amides bearing either electron donating or deficient groups on the aromatic moiety (Scheme 3).



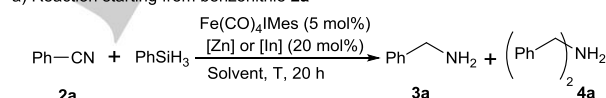
**Scheme 3.** Selective preparation of symmetrical secondary amines by hydrosilylation of primary amides catalyzed by  $\text{In}/\text{Fe}$  catalysts (Isolated yield).

We then conducted preliminary mechanistic studies to gain insights into these  $\text{Fe}/\text{Zn}$  and  $\text{Fe}/\text{In}$  catalyzed transformations, performing a series of control experiments. (Scheme 4) First of all, benzamide **1a** was not selectively reduced by the sole iron catalyst and by the sole zinc or indium additive under light activation (Table 1, entries 1 and 14; Table 3, entry 7). Additionally, the dehydration of primary amide **1** leading to nitrile **2**, already described under iron catalyzed hydrosilylation conditions,<sup>[15h,16]</sup> proceeded efficiently using  $\text{Fe}(\text{CO})_4\text{IMes}$  under light activation (Table 1, entry 1). Thus, the obtained nitrile **2** should then react with the hydrosilane to lead to the *N*-silylimine **A**, and the disilylated amine **B**, both  $\text{Zn}(\text{OTf})_2$  and  $\text{In}(\text{OTf})_3$  possibly playing a role in activating the amide moiety. Noticeably these two reactions did not proceed in the absence of light activation.<sup>[18,20–22]</sup> It should be underlined that benzonitrile **2a** was not reduced to the corresponding amine **3a** using either  $\text{Zn}(\text{OTf})_2$  or  $\text{In}(\text{OTf})_3$  as the sole catalyst. (Scheme 4b) It should be underlined that there are only scarce reports dealing with zinc-catalyzed hydrosilylation of benzonitrile derivatives, and that only the formation of silylated imines was described when using well defined zinc hydride complexes.<sup>[20b,c]</sup>

Noticeably, the reaction of benzonitrile in the presence of 5 mol% of  $\text{Fe}(\text{CO})_4\text{IMes}$ , 20 mol% of  $\text{Zn}(\text{OTf})_2$  or  $\text{In}(\text{OTf})_3$  and 3 equiv. of  $\text{PhSiH}_3$  led exclusively to benzylamine **3a** with only trace amount of **4a**. (Scheme 4a)<sup>[21,22]</sup> Importantly, no reaction occurred without light activation. (Scheme 4a) This result with  $\text{In}(\text{OTf})_3$  as a co-catalyst thus excludes the formation of the secondary amine **4** through a pathway involving the generation of the aldimine **C** resulting of the condensation of **A** with **B**. (Scheme 5)<sup>[23, 19a]</sup> Additionally, as already described with  $\text{Fe}(0)$  catalyst in reduction of esters, and highlighted in Scheme 5, visible light activation is a crucial process to generate a 16 e<sup>-</sup> iron(0) species able to promote the oxidative addition of hydrosilane.<sup>[24]</sup>

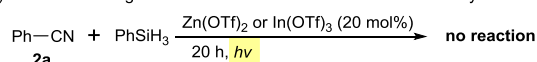
In order to rationalize the difference of selectivity when using indium co-catalyst in comparison to zinc one, a plausible pathway through the formation of secondary amide and its subsequent reduction was evaluated. The formation of the secondary amide **D** from benzylamine **3a** and benzamide **1a** was catalysed only by the indium salt, even if under the optimized conditions, the efficiency is moderate (22% yield) which may suggest that the species **D** can be efficiently obtained by the direct condensation of **1a** with the disilylated species **B**. (Scheme 4c) The obtained secondary amide was then efficiently reduced by the  $\text{Fe}/\text{In}$  under hydrosilylation, both catalysts being described as efficient in such transformation. (Scheme 4d)<sup>[15,19]</sup>

a) Reaction starting from benzonitrile **2a**

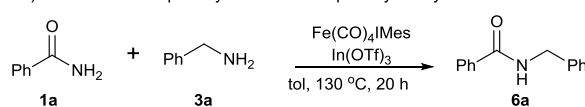


$\text{Zn}(\text{OTf})_2$ , cyclohexane, 110 °C, **3a**, 95% GC-yield, (91% isolated yield); **4a**, trace  
 $\text{In}(\text{OTf})_3$ , Toluene, 130 °C, **3a**, 95% GC-yield, (90% isolated yield); **4a**, trace  
 without light activation: no reaction

b) Reaction starting from benzonitrile **2a** with zinc or indium catalyst

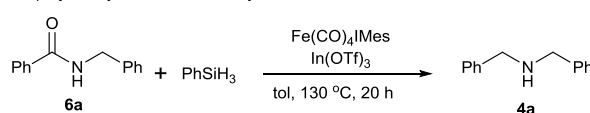


c) Condensation of primary amide **1a** with primary benzylamine **3a**



No catalyst, **6a**, 2% <sup>1</sup>H-NMR yield  
 $\text{Fe}(\text{CO})_4\text{IMes}$  (5 mol%), **6a**, trace amount  
 $\text{In}(\text{OTf})_3$  (20 mol%), **6a**, 22% <sup>1</sup>H-NMR yield  
**6a**, 21% <sup>1</sup>H-NMR yield (without light activation)  
 $\text{Fe}(\text{CO})_4\text{IMes}$  (5 mol%),  $\text{In}(\text{OTf})_3$  (20 mol%),  
**6a**, 22% <sup>1</sup>H-NMR yield (with light activation)

d) Hydrosilylation of secondary amide **6a**

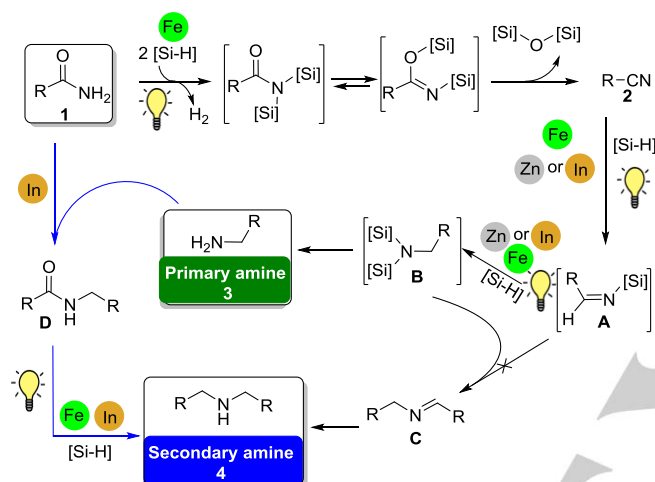


$\text{Fe}(\text{CO})_4\text{IMes}$  (5 mol%), **4a**, 67% GC yield (with light activation)  
**4a**, 9% GC yield (without light activation)  
 $\text{In}(\text{OTf})_3$  (20 mol%), **4a**, 95% GC yield (with light activation)  
**4a**, 73% GC yield (without light activation)  
 $\text{Fe}(\text{CO})_4\text{IMes}$  (5 mol%),  $\text{In}(\text{OTf})_3$  (20 mol%), **4a**, 99% GC yield (with light activation)  
**4a**, 89% GC yield (without light activation)

**Scheme 4.** Mechanistic studies. Reactions performed using light activation are highlighted in yellow. Results conducted in the absence of light activation are highlighted in grey.

From a mechanistic point of view, based on the above investigations, plausible pathways are shown in Scheme 5. The pathway explaining the selective formation of primary amines from primary amides involved a dehydration step leading to the nitrile **2** which is reduced thanks to the synergic combination of the iron catalyst and the zinc salt under light activation.

An alternative pathway for the formation of the secondary amine **4** is proposed through the formation of secondary amide **D** via the  $\text{In}(\text{OTf})_3$  promoted transamidation of **1** by the produced benzylamine **3** or its disilylated precursor **B**,<sup>[25]</sup> reaction which is more difficult with  $\text{Zn}(\text{OTf})_2$ . Finally, the amide **D** is reduced.



**Scheme 5.** Proposed pathways for the selective formation of primary and secondary amines from primary amides.<sup>[26]</sup> The yellow light bulb indicated the steps promoted by light activation.

## Conclusion

In conclusion, we have developed tandem iron/zinc and iron/indium-catalyzed reductions of primary amides to primary and secondary amines under hydrosilylation conditions. Depending of the nature of the co-catalyst, the selectivity of the reduction was controlled: by using  $\text{Zn}(\text{OTf})_2$ , primary amines were selectively and efficiently produced (21 examples, 47–93% isolated yields) whereas with  $\text{In}(\text{OTf})_3$ , secondary amines can be obtained in moderate yields up to 51%. The potential synthetic application of the preparation of primary amines was demonstrated by a gram-scale reaction.

## Experimental Section

### Typical procedure for the synthesis of primary amine hydrochloride salts **5**.

In a dried Schlenk tube with a magnetic bar,  $\text{Fe}(\text{CO})_4(\text{IMes})$  (11.8 mg, 0.025 mmol, 5 mol%),  $\text{Zn}(\text{OTf})_2$  (36.3 mg, 0.1 mmol, 20 mol%), primary amide (0.5 mmol, 1 equiv.), phenylsilane (162.3 mg, 1.5 mmol, 3 equiv.) and cyclohexane (1.5 mL) were added successively under an argon atmosphere. Then the mixture was stirred upon visible light irradiation (using 24 watt compact fluorescent lamp) at 110 °C for 20 h. After cooling to the room temperature, the mixture was diluted with ethyl acetate and

filtrated through aluminum oxide. Then, 0.5 M HCl in dioxane solution was added and a precipitation occurred immediately, which was filtered and washed with diethyl ether to obtain the corresponding amine hydrochloride salt **5**.

### Typical procedure for the synthesis of secondary amines **4**.

In a dried Schlenk tube with a magnetic bar,  $\text{Fe}(\text{CO})_4(\text{IMes})$  (11.8 mg, 0.025 mmol, 5 mol%),  $\text{In}(\text{OTf})_3$  (56.2 mg, 0.1 mmol, 20 mol%), primary amide (0.5 mmol, 1 equiv.), phenylsilane (162.3 mg, 1.5 mmol, 3 equiv.) and toluene (1.5 mL) were added successively under an argon atmosphere. Then the mixture was stirred upon visible light irradiation (using 24 watt compact fluorescent lamp) at 130 °C for 20 h. After cooling to the room temperature, the mixture was diluted with ethyl acetate and filtrated through aluminum oxide. The residue was purified by silica gel column chromatography using a mixture of heptane and ethyl acetate as the eluent to afford the desired products **4**.

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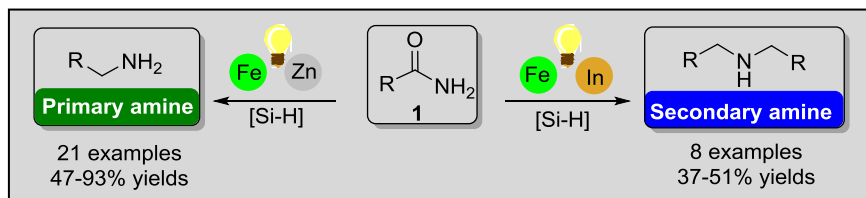
**Keywords:** Iron • zinc • indium • primary amides • hydrosilylation

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- [26] It should be noted that siloxane O[Si<sub>2</sub>Ph<sub>2</sub>(OMe)<sub>2</sub>(OH)<sub>2</sub>] was detected by GC-MS analysis of the crude mixture obtained after quenching the reaction with NaOH in methanol (0.1M).

## Entry for the Table of Contents

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Insert text for Table of Contents here. Tandem iron/zinc or iron/indium-catalysed hydrosilylation primary amides is reported under visible light activation. The nature of the co-catalyst (Zn(OTf)<sub>2</sub> vs In(OTf)<sub>3</sub>) played a crucial role for the selectivity of the Fe(CO)<sub>4</sub>(IMes) catalyzed reduction of primary amides: Zn promoted the formation of primary amines whereas secondary amines were obtained using indium co-catalyst.

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