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D. Wei, C. Netkaew, Christophe Darcel. Iron-Catalysed Switchable Synthesis of Pyrrolidines vs Pyrrolidinones by Reductive Amination of Levulinic Acid Derivatives via Hydrosilylation. Advanced Synthesis and Catalysis, 2019, 361 (8), pp.1781-1786. 10.1002/adsc.201801656 . hal-02090010

HAL Id: hal-02090010

https://univ-rennes.hal.science/hal-02090010

Submitted on 15 Apr 2019

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Iron-Catalysed Switchable Synthesis of Pyrrolidines *vs* Pyrrolidinones by Reductive Amination of Levulinic Acid Derivatives *via* Hydrosilylation

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Abstract. A selective production of pyrrolidines *vs* pyrrolidinones *via* hydrosilylation of levulinic acid and levulinates by switching of the iron complex catalyst is presented herein. The reactions proceeded efficiently with various anilines and alkylamines under both visible light irradiation and thermal conditions with 43 examples in isolated yields up to 93%. Noticeably, under similar conditions, cyclic amines such as piperidines and azepanes were efficiently synthesized with yields up to 92%, by reaction of anilines with 1,5- or 1,6-keto acids, respectively. Similarly, *N*-arylinsolidoline compounds can be prepared from 2-formylbenzoic acid in 57-93% yields.

Keywords: Iron; levulinic acid; hydrosilylation; pyrrolidines; pyrrolidinones

The selective and efficient production of inedible biomass or biomass platform derived fine chemicals, such as ethanol, hydroxymethyl-furfural (HMF), furfural, and levulinic acid (LA), has drawn much attention with the huge development of green and sustainable chemistry in the past two decades.[1] Levulinic acid or levulinate derivatives, which are easily accessible from acidic hydrolysis of carbohydrates such as lignocellulose,[2] have been extensively studied. Indeed, they are valuable fine chemicals for access to platform molecules, such as γ-valerolactone (GVL), *N*-substituted-5-methyl-2-pyrrolidones, 2-methyl-tetrahydrofuran, and 1,4-pentanediol.[3] On the other hand, the pyrrolidine ring motif is present in numerous natural alkaloids (e.g. nicotine and hygrine). It is also found in many pharmaceuticals such as procyclidine and bepridil (Figure 1a). Furthermore, pyrrolidones are usually substructure in the drug racetams such as piracetam, levetiracetam and aniracetam (Figure 1b). In this topical context, the preparation of *N*-substituted pyrrolidines and pyrrolidinones from biomass derivatives in a more sustainable way is still a challenging topic.

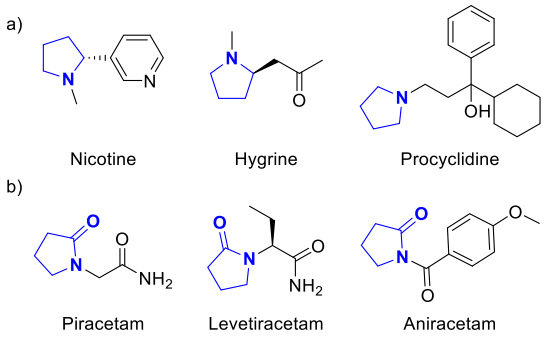

Figure 1. Selected examples for **a)** pyrrolidine functionalities in natural alkaloids and pharmaceuticals and **b)** pyrrolidone structures in racetam drugs.

The combination of a reductive amination of levulinic acid and a subsequent intramolecular cyclization is one of the most atom economic and sustainable approaches to access pyrrolidines and pyrrolidinones, water being the sole by-product (Scheme 1a). In the area of homogeneous catalysis, in 2011, Fu *et al.* [4] reported the first example of transformation of LA to pyrrolidines with formic acid as the hydrogen source. A ruthenium catalyst generated *in situ* from [{$RuCl_2$(*p*-cymene)}$_2$] and *t*Bu_3P was efficiently used at 80 °C with alkylamines, and 120 °C with arylamines. Afterwards, Xiao[5], Zhang[6] and Fischmeister[7] developed efficient Cp*Ir based catalysts which operated in water or neat conditions at 80-110 °C, with either formic acid or H_2 as the reductants. Noticeably, production of lactams to cyclic amines in combination with $PhSiH_3$ were reported by ether switching from $In(OAc)_3$ to InI_3[8], or from $AlCl_3{\cdot}6H_2O$ to $RuCl_3{\cdot}3H_2O$[9], respectively. Furthermore, organoboron-catalysed[10] reductive aminations of LA with silanes as reducing reagents has also

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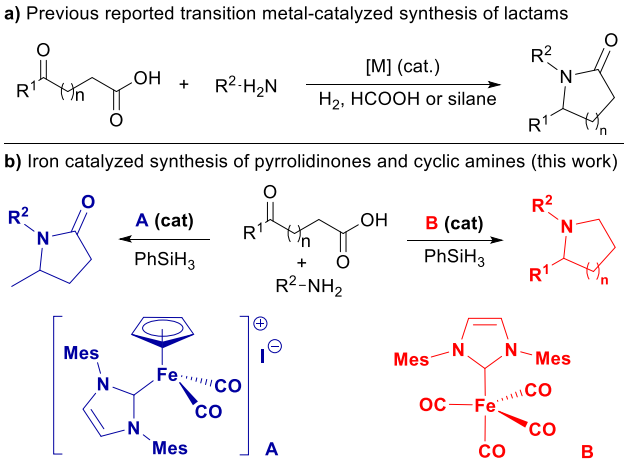
been reported. Additionally, reductive aminase from Aspergillus oryzae was also able to promote the enatioselective formation of *N*-alkylpyrrolidinones from ethyl levulinate.[11]



Scheme 1. Reductive amination of LA **a)** previous reports and **b)** iron complexes investigated for this study.

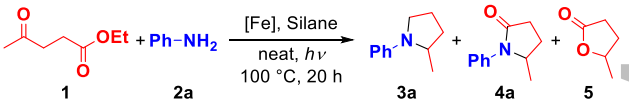
On the other hand, during the last two decades, iron has emerged as a useful substitute for precious transition metals, particularly in the reduction areas.[12] At iron, few reports deal with catalysts able to reduce levulinic acid or levulinate derivatives to γ-valerolactone under transfer hydrogenation: (i) using formic acid, $Fe(OTf)_2$ and $[P(CH_2CH_2PPh_2)_3]$ ligand (140 °C, 24 h),[13] and $Fe_3(CO)_{12}$ (water, 180 °C, 15 h),[14] and (ii) using *i*PrOH, Casey type complex ($NaHCO_3$, 100 °C, 19 h)[15] and Knölker type complexes (80-100 °C, 19-20 h).[16] Additionally, the hydrogenation of levulinic acid to GVL was performed using Knölker type complexes with TON up to 570 (EtOH, 60 bar H_2, 100 °C, 20 h). Recently, PNNNP pincer iron complex catalysed the hydrogenation of both methyl levulinate and levulinic acid leading to GVL with TOF up to 1900 h^{-1} (100 bar H_2, 100 °C).[17]

Besides hydrogenation, hydrosilanes are mild and higher selective reducing agents in terms of chemoselectivity and functional-group tolerance for the production of fine chemicals. They can be considered as interesting alternative reductants, although siloxane waste is an unavoidable by-product. To the best of our knowledge, the use of well-defined iron complexes as catalysts for transformation of levulinic acid derivatives to pyrrolidines and pyrrolidinones was scarcely explored. Only one recent contribution of Burtoloso reported the use of $Fe_3(CO)_{12}$ for catalysed transfer hydrogenation of levulinic acid using 2.2 equiv. of a mixture 1:1 of formic acid and amine in water in drastic conditions (180 °C) leading to pyrrolidones.[18]

Herein, we report efficient and selective one-pot pathways for the switchable reductive amination of levulinic acid/ levulinates *via* hydrosilylation for the selective preparation of pyrrolidines *vs* pyrrolidinones by the right choice of iron catalysts (Scheme 1b).

In our group, a series of *N*-heterocyclic carbene (NHC) based iron complexes have been previously developed, including $[CpFe(CO)_2(IMes)][I]$ **A** and $[Fe(CO)_4(IMes)]$ **B** [Scheme 1, *IMes* = 1,3-bis (2,4,6-trimethylphenyl)imidazol-2-ylidene], which were efficiently employed as catalysts in the hydrosilylation of carbonyl derivatives[19], imines[20], amides[21], esters[22] and also methylation of secondary amines.[23] Inspired by recent reports on the transformation of biomass, we began our initial work with ethyl levulinate **1**, aniline **2a**, phenylsilane in the absence of solvent, combined with **A** or **B** as catalysts. The preliminary experiment using **A** (5 mol%) in the presence of 4 equiv. of $PhSiH_3$ at 100 °C upon visible light irradiation (using 24 watt compact fluorescent lamp), under neat conditions exhibited a promising result for reductive amination of **1** with **2a**: 2-methyl-1-phenyl-pyrrolidine **3a** was obtained in 94% yield (Table 1, entry 1).

Table 1. Optimization for the reductive amination of ethyl levulinate with aniline.[a]



1 2a 3a 4a 5

Entry	[Fe] (mol%)	Silane (equiv.)	Conv.[b] (%)	Yield (%)[b] 3a	4a	5
1	**A** (5)	$PhSiH_3$ (4)	99	94	0	0
2	**A** (5)	Ph_2SiH_2 (6)	99	0	46	47
3	**A** (5)	Et_3SiH (12)	99	0	0	0
4[c]	**A** (5)	$PhSiH_3$ (4)	99	37	21	17
5	**A** (5)	$PhSiH_3$ (2)	99	50	27	23
6	**A** (5)	$PhSiH_3$ (1)	99	27	29	28
7[d]	**A** (5)	$PhSiH_3$ (4)	99	32	35	11
8	**B** (5)	$PhSiH_3$ (4)	99	90	0	6
9	**B** (2.5)	$PhSiH_3$ (4)	99	99	0	0
10	**B** (1)	$PhSiH_3$ (4)	99	92	0	2
11	**B** (2.5)	$PhSiH_3$ (2)	99	75	0	13
12[d]	**B** (2.5)	$PhSiH_3$ (4)	89	13	19	0

[a] Conditions: **A** or **B** (1-5 mol%), **1** (0.25 mmol), **2a** (0.25 mmol) and silane, visible light irradiation (24 watt compact fluorescent lamp), 100 °C, 20 h; then hydrolysis (THF/NaOH 2 N).

[b] Conversion and yield determined by ^1H NMR of the crude mixture. The condensation imine product from **1** and **2a** was also detected (see SI)

[c] Reaction performed at 60 °C.

[d] Reaction conducted in the absence of visible light irradiation.

The nature of the silanes was also crucial for the selectivity of the reaction. While TMDS (1,1,3,3-tetramethyldisiloxane, 6 equiv.) and PMHS (polymethylhydrosiloxane, 12 equiv.) were totally

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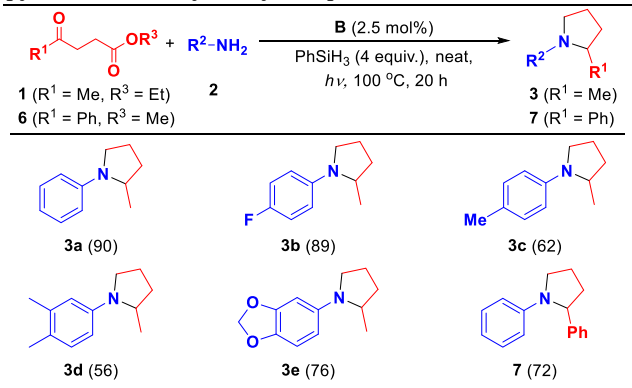
inactive, diphenylsilane (6 equiv.) led to the pyrrolidinone (**4a**, 46%) and GVL (**5**, 47%) (Table 1, entry 2). Using 12 equiv. of Et_3SiH, led only to the condensation imine product generated from **1** and **2a** (Table 1, entry 3). Decreasing the temperature to 60 °C or the amount of $PhSiH_3$ led to a deteriorative selectivity (entries 4-6) as **3a** was obtained in mixture with **4a** and **5**.

Compared with **A**, **B** exhibited a better activity. Indeed, at lower catalyst loading of **B** (2.5 mol% and even at 1 mol%), excellent yields of **3a**, 99 and 92%, respectively, were achieved (Table 1, entries 8-10). Furthermore, lowering the $PhSiH_3$ amount to 2 equiv. led to a mixture of **3a** and **5**. Noticeably, the catalytic reaction performed in the absence of visible light irradiation led to unsatisfactory selectivity under catalysis of **A** or **B** (Table 1, entries 7 and 12). In absence of catalyst, no reduction reaction occurs, as only the condensation imine product from **1** and **2a** was detected.

The substrate scope for the catalysed reductive amination of levulinate into pyrrolidines was then explored using 2.5 mol% of **B** in the presence of 4 equiv. of phenylsilane in solvent-free conditions at 100 °C for 20 h (Table 2).

Table 2. Scope of reductive amination of levulinates into pyrrolidines catalysed by complex **B**.[a]

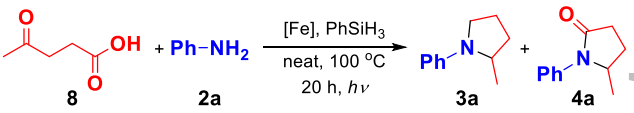


[a] Conditions: **B** (2.5 mol%), **1** or **6** (0.5 mmol), **2** (0.5 mmol) and $PhSiH_3$ (4 equiv.), visible light irradiation, 100 °C, 20 h; then hydrolysis (THF/NaOH 2 N). Isolated yields in parenthesis.

Aromatic amines bearing substituents such as methyl, methoxy or fluoro **2b-2d**, as well as aniline **2a**, were smoothly converted into corresponding pyrrolidines in moderate to good isolated yields (56-90%). Notably, important building blocks for pharmaceuticals such as 5-amino-1,3-benzodioxole was effectively transformed to **3e** in 76%. Additionally, methyl 3-benzoylpropanoate **6** can be also transformed into 1,2-diphenylpyrrolidine **7** in 72% yield.

The direct transformation of levulinic acid to pyrrolidines and pyrrolidinones is also another interesting target. The feasibility of the catalytic reductive amination of levulinic acid with aniline **2a** was conducted with **A** (5 mol%) under similar conditions: 4 equiv. of $PhSiH_3$, 100 °C, 24 h upon visible light irradiation. Levulinic acid was quantitatively converted to a mixture with pyrrolidinone **4a** as the major product (**3a**:**4a** = 28:72, Table 3, entry 1). Increasing the quantity of $PhSiH_3$ to 6 equiv. gave a 7:3 mixture of **3a** and **4a** (entry 2). Noticeably, lowering the amount of $PhSiH_3$ to 2 equiv. led to a remarkable improvement in selectivity as **4a** was obtained specifically with 99% yield (entry 3).

Table 3. Optimization for reductive amination of LA.[a]



Entry	[Fe] (mol%)	$PhSiH_3$ (equiv.)	Conv. [b] (%)	Yield (%)[b] **3a**	**4a**
1	**A** (5)	4	99	28	72
2	**A** (5)	6	99	69	31
3	**A** (5)	2	99	0	99
4	**A** (2.5)	4	99	18	82
5	**B** (5)	5	99	90	9
6	**B** (5)	6	99	99	0
7	**B** (2.5)	6	99	72	27
8	**B** (5)	2	82	0	80
9	**B** (2.5)	2	80	0	75

[a] Conditions: **A** or **B** (2.5-5 mol%), **8** (0.25 mmol), **2a** (0.25 mmol) and $PhSiH_3$ (2-6 equiv.), visible light irradiation, 100 °C, 20 h; then hydrolysis (THF/NaOH 2 N).

[b] Conversion and yield determined by ^1H NMR of the crude mixture. GVL **5** was not observed under these conditions.

The use of **B** as the catalyst permitted to switch the selectivity of the reaction. Indeed, using 5 mol% of **B** led to **3a** as the sole product (99%) when the reaction was conducted with 6 equiv. of $PhSiH_3$ (Table 3, entry 6). Further lowering the catalyst loading of **A** or **B** from 5 to 2.5 mol% result in the drop of the selectivity with mixtures of **3a** and **4a** (entries 4 and 7). Furthermore, with 2 equiv. of $PhSiH_3$, **4a** can be formed in lower NMR-yield 80 and 75% with 5 and 2.5% of **B**, respectively (Table 3, entries 8 and 9). Similarly to methyl levulinate, the reaction did not proceeded using 6 equiv. of TMDS or PMHS.

We then explored the substrates scope in regard of levulinic acid. To prepare pyrrolidinones **4**, a variety of anilines **2** were employed for the annulation of LA catalysed by **A** (5 mol%), with $PhSiH_3$ (2 equiv.) at 100 °C under visible light irradiation (Table 4).

The reactions of aniline **2a**, 3,4-(methylenedioxy) aniline **2e** as well as 4-methoxyaniline **2f** afforded the corresponding *N*-arylpyrrolidinones **4a**, **4e** and **4f** in 60-87% yields. Notably, anilines bearing reducible functional group such as halogen substituents, boronate ester, acetyl, cyano, carboxylic ester and primary amide also provided the corresponding products **4b**, **4g-h**, **4l-4p** in 30-68% yields, highlighting the good group tolerance of the

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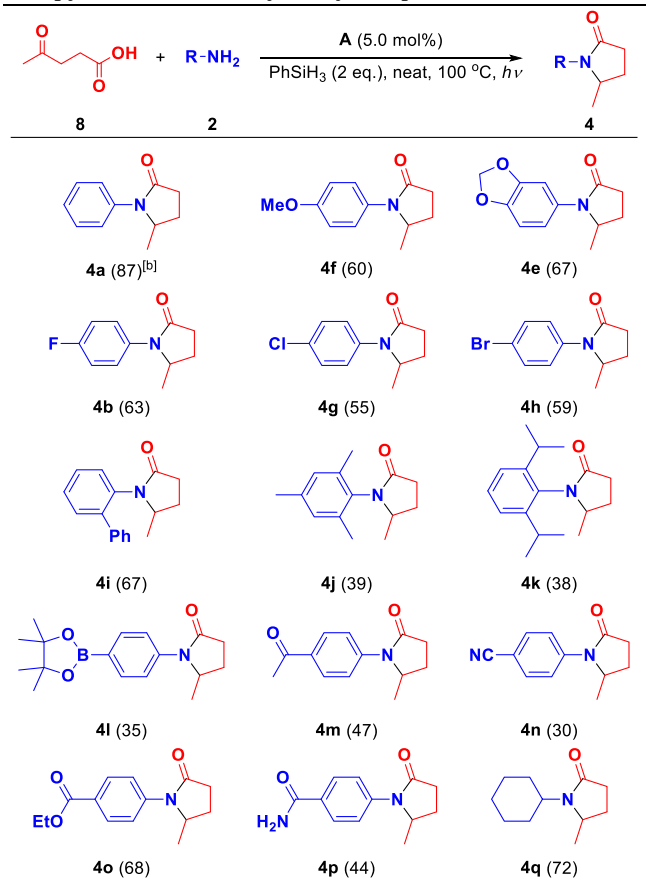
transformation. Noticeably, the reaction can be performed with hindered amines leading to the pyrrolidones **4i-4k** in moderate yields up to 67%. Indeed, alkylamines such as cyclohexylamine can be used giving the pyrrolidinone **4q** in 72% yield (Table 4).

Table 4. Scope of reductive amination of levulinic acid into pyrrolidinones catalysed by complex **A**.[a]



[a] Conditions: **A** (5 mol%), **8** (0.5 mmol), **2** (0.5 mmol) and $PhSiH_3$ (2 equiv.), visible light irradiation, 100 °C, 20 h; then hydrolysis (THF/NaOH 2 N). Isolated yields in parenthesis.

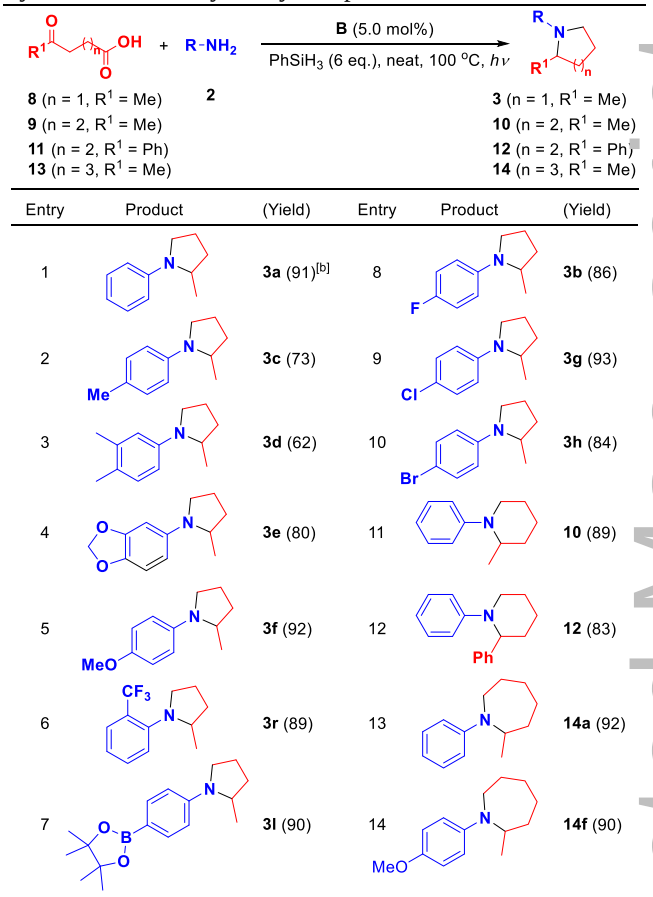
[b] 84% isolated yield on gram scale (10 mmol) reaction.

On the other hand, the reaction scope can be extended to pyrrolidines **3** using **B** (5 mol%) as the catalyst: indeed, the reaction of various keto acids with amines to give cyclic amines were performed in the presence of $PhSiH_3$ (6 equiv.) at 100 °C for 20 h under visible light irradiation (Table 5).

Interestingly, by reaction with LA, aniline **2a**, methyl-substituted anilines **2c-2d**, 3,4-(methylenedioxy)aniline **2e**, as well as 4-methoxyaniline **2f** afforded the corresponding pyrrolidines **3a**, **3c-f** in 62%-92% yields. Notably, the boronate ester **2l** and trifluoromethyl **2r** substituted anilines led also to **3l** and **3r** in 90% and 89% yields, respectively. Additionally, halogen-containing anilines **2b**, **2g-2h** were converted to the corresponding pyrrolidines **3b**, **3g-3h** in yields up to 93% (Table 5, entries 8-10). Even if the reaction showed a broad functional group tolerance including reducible functional groups, no reaction occurred with 4-nitroaniline. By contrast, functional groups such as ester and ketone were reduced under such conditions, and primary amides were dehydrated to nitriles.[21]

It must be underlined that this methodology can be extended to the synthesis of cyclic amines like piperidines **10**, **12** and azepane (**14a** and **14f**) which can be obtained efficiently by reaction of anilines with 1,5- or 1,6-keto acids with yields up to 92%.

Table 5. Scope of reductive amination of keto acids into cyclic amines catalysed by complex **B**.[a]



Entry	Product	(Yield)	Entry	Product	(Yield)
1		**3a** (91)[b]	8		**3b** (86)
2		**3c** (73)	9		**3g** (93)
3		**3d** (62)	10		**3h** (84)
4		**3e** (80)	11		**10** (89)
5		**3f** (92)	12		**12** (83)
6		**3r** (89)	13		**14a** (92)
7		**3l** (90)	14		**14f** (90)

[a] Conditions: **B** (2.5 mol%), **1** or **6** (0.5 mmol), **2** (0.5 mmol) and $PhSiH_3$ (4 equiv.), visible light irradiation, 100 °C, 20 h; then hydrolysis (THF/NaOH 2 N). Isolated yields in parenthesis.

[b] 89% isolated yield on gram scale (10 mmol) reaction.

In order to show the generality of the catalysed transformation, the use of 2-formylbenzoic acid **15** rather than keto acids for this transformation was next investigated under similar conditions (Scheme 5). Several *N*-arylisoindoline derivatives **16** were then synthesized starting from anilines bearing halogen atoms **2b**, **2g-2h**, trifluoromethyl **2r**, boronate ester **2l**, as well as *o*-phenyl group **2i** (57-93% isolated yields). Notably, under similar conditions, benzylamine **2t** gave also the 2-benzylisoindoline **16t** in 86% yield. It is particularly worth mentioning that this

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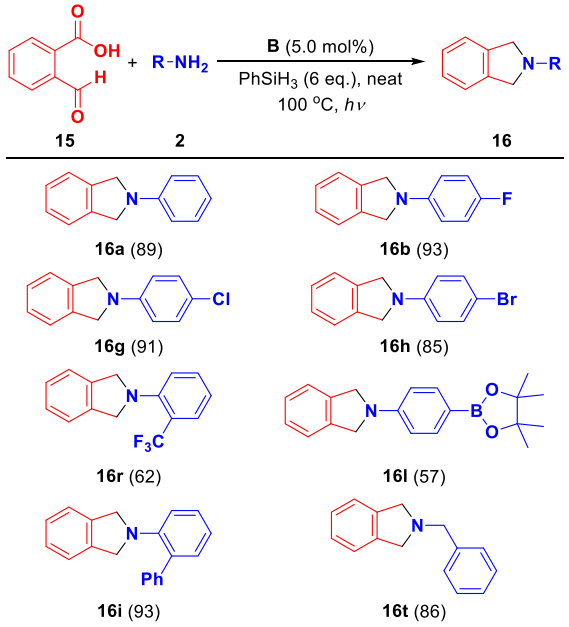
methodology permitted to tolerate halogen and boronate ester functionality and the corresponding products could be applied for further elaboration of complex molecules *via* catalysed cross-coupling reactions.

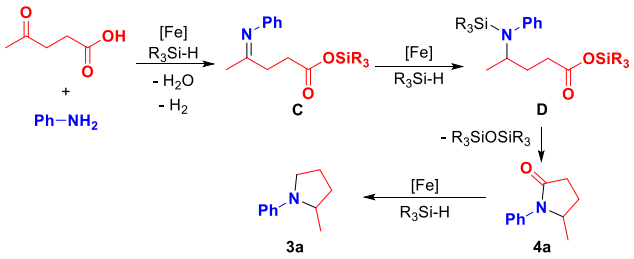
Table 6. Scope of reductive amination of **15** into isoindolines catalysed by complex **B**.[a]



[a] Conditions: **B** (5 mol%), **15** (0.5 mmol), **2** (0.5 mmol) and $PhSiH_3$ (6 equiv.) visible light irradiation, 100 °C, 24 h; then hydrolysis (THF/NaOH 2 N). Isolated yields in parenthesis.

In order to have evidences of the pathway of the transformation, the reduction of pyrrolidinone **4a** with 2 equiv. of $PhSiH_3$ was then carried out in the presence of [Fe(CO)$_4$(*IMes*)] **B** (5.0 mol%) at 100 °C for 20 h upon visible light irradiation: the 2-methyl-1-phenylpyrrolidine **3a** was then obtained in 95% NMR-yield (Scheme S1). This result indicates that in the reaction of aniline with LA, the resulting pyrrolidinone **4a** could be further converted into pyrrolidine **3a** catalysed by **B** under similar reductive conditions.

In a mechanism point of view, based on the previous reaction pathway proposed with indium,[8] an imine intermediate **C** could be firstly generated from the condensation of LA with amine and dehydrogenative silylation of carboxylic acid with hydrosilanes. (Scheme 2) Then the imine moiety of **C** was reduced under catalytic hydrosilylation conditions leading to silylamine species **D**[20,24] which underwent transamidation generating **4a**. Finally, **4a** could be further reduced into **3a** under catalytic hydrosilylation conditions. Noticeably, as already shown with iron(0) complex **B**, visible light is crucial to generate a 16 electron active iron(0) species able to promote the oxidative addition of silanes.[22,25]



Scheme 2. Possible reaction pathway.

In summary, this contribution described a switchable and efficient iron catalysed synthesis of *N*-substituted pyrrolidinones and pyrrolidines starting from levulinic acid and esters and a variety of amines, *via* reductive amination using phenylsilane as the reducing agent. Notably, two well-defined NHC iron complexes were employed, each of them being able to conduct specifically to a single derivative: pyrrolidones or pyrrolidines. Noticeably, under similar conditions, cyclic amines such as piperidines and azepanes were efficiently synthesized by reaction of anilines with 1,5- or 1,6-keto acids, respectively. Additionally, this methodology can be applied for the preparation of isoindolines starting from 2-formylbenzoic acid.

Experimental Section

Typical procedure for the catalytic reductive amination reactions: in an argon filled glove box, a 20 mL Schlenk tube was charged with [Fe(CO)$_4$(*IMes*)] (**B**, 2.5 mol%), ethyl levulinate (0.5 mmol), aniline (0.5 mmol) and $PhSiH_3$ (4 equiv.) in this order. Then the reaction mixture was stirred upon visible light irradiation (using 24 watt compact fluorescent lamp) at 100 °C for 20 h. After cooling to room temperature, the reaction was quenched by adding 2 mL THF and 2 mL NaOH (aq.) 2 N, stirred for 2 h at room temperature and then extracted with 3×10 mL of ethyl acetate. The combined fractions were dried over anhydrous Na_2SO_4 for 0.5 h. After filtrate through degreasing cotton, the crude mixture was dried under reduced pressure. The residue was then purified by silica gel column chromatography using a mixture of heptane/ethyl acetate as the eluent to afford the desired product.

Acknowledgements

We thank the Université de Rennes 1 and the Centre National de la Recherche Scientifique (CNRS). C. N. thanks French Embassy in Thailand for a grant.

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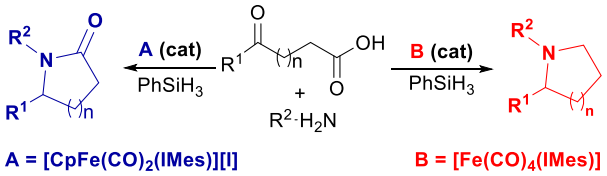

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