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V. Surzhko, T. Roisnel, B. Le Grel, P. Le Grel, C. Lalli, et al.. Synthesis of picolinohydrazides and their evaluation as ligands in the zinc-catalyzed hydrosilylation of ketones. *Tetrahedron Letters*, 2017, 58 (13), pp.1343-1347. 10.1016/j.tetlet.2017.02.062 . hal-01515172

**HAL Id: hal-01515172**

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Submitted on 4 Jul 2017

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# Synthesis of picolinohydrazides and their evaluation as ligands in the zinc-catalyzed hydrosilylation of ketones

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**Keywords**

Hydrosilylation, Zinc, Hydrazides, Ketones

**Abstract**

A set of picolinohydrazides was prepared by reaction between hydrazines and either 2-picolinic acid or ethyl pyridine-2-carboxylate, and characterized. These molecules were evaluated as ligands in the zinc-catalyzed hydrosilylation of ketones. Thus, several aromatic and aliphatic ketones were successfully reduced by diethoxymethylsilane as the hydride source in the presence of a catalytic system made of diethylzinc combined *in situ* to the picolinohydrazides described herein.

**Introduction**

In the past years the importance of zinc(II) complexes in homogeneous catalysis has increased to fulfil the need for more economical and less toxic processes in modern organic chemistry.<sup>1</sup> Among recent advances in this field, zinc-based catalysts have been successfully applied in the hydrosilylation of aldehydes and ketones,<sup>2-4</sup> but also of more challenging substrates such as imines,<sup>5</sup> amides,<sup>6</sup> esters,<sup>7</sup> or even CO<sub>2</sub>.<sup>8</sup> In the hydrosilylation of aldehydes and ketones, consisting of the addition of a hydrosilane to the carbonyl group followed by hydrolysis of the silyl ether intermediate to release the corresponding alcohol, the reduction reaction operates under very mild conditions and is therefore an attractive alternative to catalytic hydrogenation or hydrogen transfer. Thus a growing number of catalytic systems based on zinc that display excellent activities for this reaction have been described to date,<sup>2,3</sup> and this also include chiral systems that allow for high enantioselectivities in asymmetric hydrosilylation of prochiral ketones.<sup>4</sup> Apart from some limited examples of well-defined zinc complexes (or clusters) which have been reported on as active pre-catalysts in this area,<sup>3</sup> most of these catalytic systems are

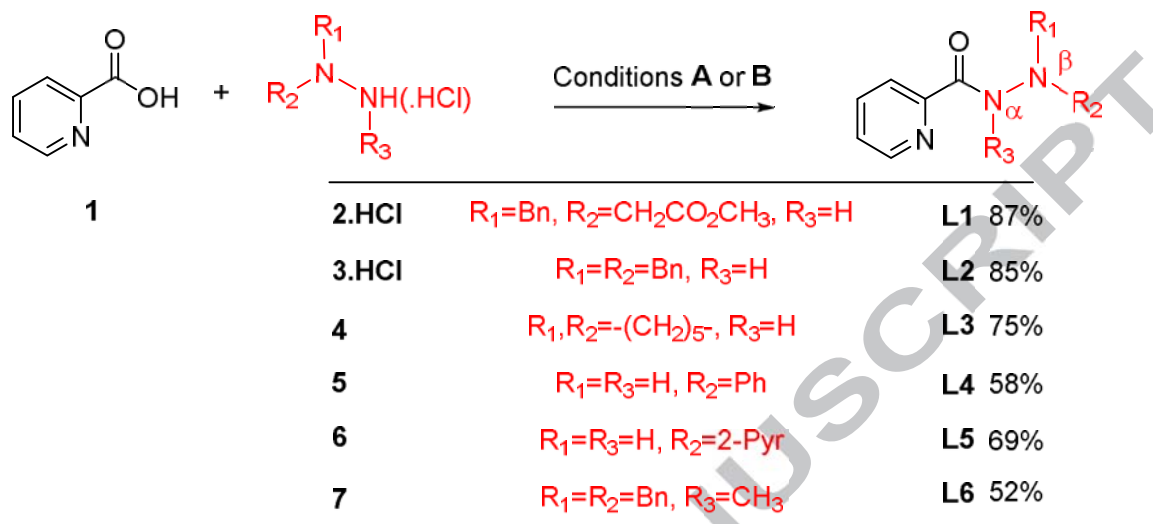
typically formed *in situ* by combining a cheap and readily available zinc precursor, namely diethylzinc or zinc(II) acetate, with various ligands. In a seminal contribution by Mimoun et al.,<sup>4a</sup> the activation of diethylzinc by diamine-type ligands was found particularly effective for the hydrosilylation reduction, and this led to the prominent use of numerous nitrogen-chelating ligands, whether or not chiral, that have contributed later on to the development of this reaction.

Hydrazides constitute an important class of molecules because of the high reactivity of these *N*-acylhydrazine derivatives which makes them valuable building blocks for the synthesis of many pharmaceuticals and materials.<sup>9</sup> On the other hand, contributions to catalysis in which ligands are functionalized by a CO–N–N hydrazide moiety remain scarce,<sup>10</sup> and the appealing coordination properties of this fragment, possessing the unusual nitrogen-nitrogen  $\sigma$ -bond, to transition metals stay largely under-examined. Herein, we report on the preparation of several picolinohydrazides differently substituted on the *N* <sup>$\alpha$</sup> - and *N* <sup>$\beta$</sup> -positions, some of which are new and were fully characterized. Our results on their ability to serve as efficient ligands in the zinc-catalyzed hydrosilylation of ketones are also presented.

## Results and discussion

One general approach to the synthesis of acylated hydrazines is condensation of a carboxylic acid activated by a peptide coupling reagent with a hydrazine. According to this method, the reaction between 2-picolinic acid (**1**) and various hydrazines afforded a first set of picolinohydrazide ligands **L1–L6** (Scheme 1). In the case of hydrazine hydrochlorides **2.HCl**<sup>11</sup> and **3.HCl**,<sup>12</sup> the TBTU promoted acylation in the presence of **1** was preferred because the excess of K<sub>2</sub>CO<sub>3</sub> required for this reaction can release *in situ* the corresponding free hydrazines. After reaction and purification by flash chromatography, pure compounds **L1** and **L2** were isolated in high yields. With hydrazines **4–7**, the coupling reactions were readily achieved by using CDI in CH<sub>2</sub>Cl<sub>2</sub> and gave products **L3–L6** with satisfying yields after purification by trituration or recrystallization. Compounds **L4**<sup>13</sup> and **L5**<sup>13,14</sup> have

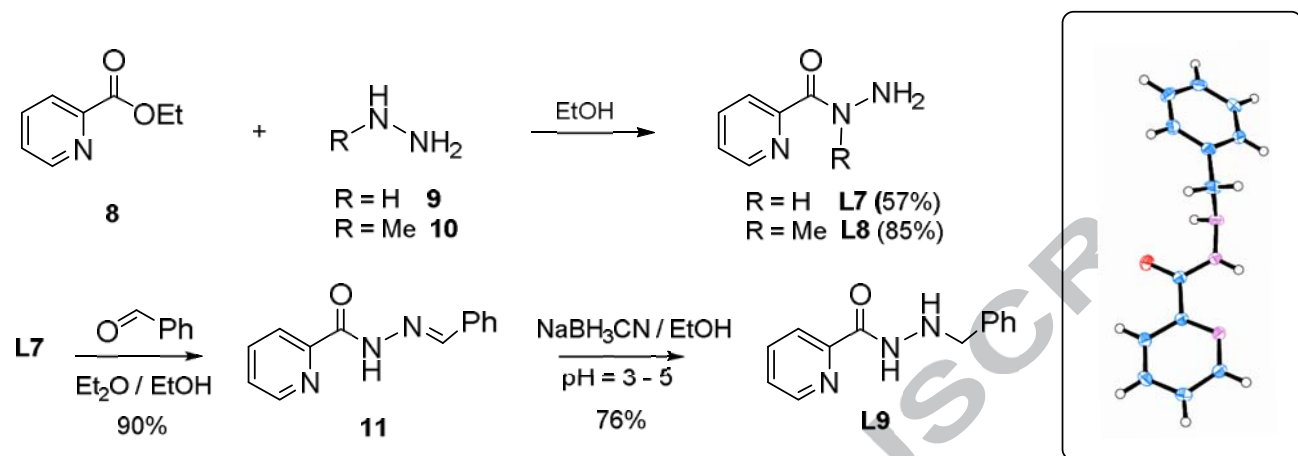
been already prepared under different reaction conditions, and the spectroscopic data that we obtained were comparable with those of the literature.



**Scheme 1.** Synthesis of picolinohydrazides **L1–L6** using peptide coupling reagents. Conditions **A** for **L1** and **L2**: **1** (1 equiv.), hydrazine hydrochloride (1 equiv.), TBTU (1 equiv.),  $\text{K}_2\text{CO}_3$  (4 equiv.), DMF, THF, rt, 12 h. Conditions **B** for **L3–L6**: **1** (1.2 equiv.), hydrazine (1 equiv.), CDI (1.2 equiv.),  $\text{CH}_2\text{Cl}_2$ , rt, 12 h.

Another standard procedure to prepare carboxylic acid hydrazides is hydrazinolysis of esters in alcoholic solutions. Using this method, the reaction of ethyl pyridine-2-carboxylate (**8**) with an excess of hydrazine (**9**) or methylhydrazine (**10**) in ethanol gave hydrazides **L7** and **L8** (Scheme 2). The new compound **L8** was isolated in pure form as a white solid with 85% yield, and was readily identified by the usual analytical techniques. Noteworthy is the regioselectivity of this condensation since no acylation reaction took place on the  $\text{NH}_2$  position of methylhydrazine presumably because of its lower nucleophilicity if compared to the one at the  $\text{NHMe}$  terminus. On the other hand, picolinohydrazide **L7** is a commercially available building block extensively used in various fields of synthesis, ranging from pharmaceuticals to photoswitches or sensors.<sup>15</sup> In the presence of benzaldehyde, this reactive molecule was easily converted into the intermediate hydrazone **11** that underwent reduction with  $\text{NaBH}_3\text{CN}$  to

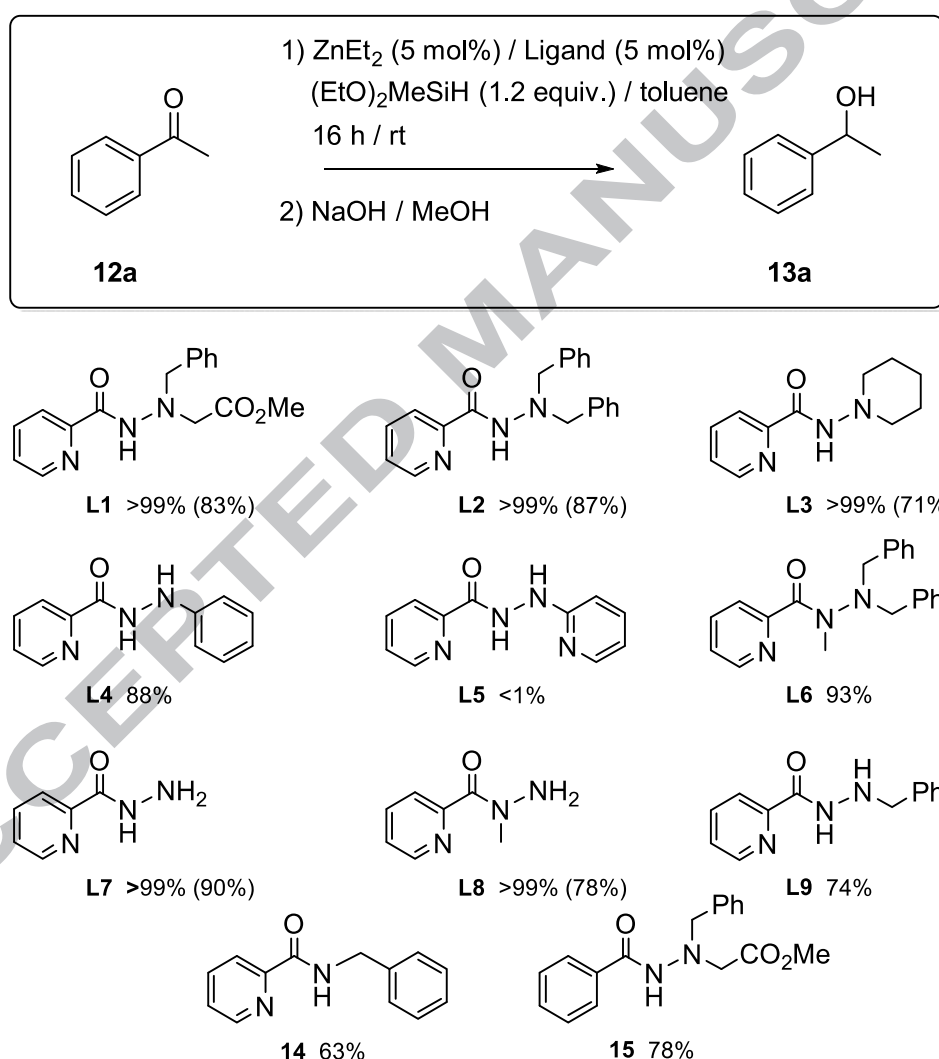
give ligand **L9** which was fully characterized.<sup>16</sup> In addition, the crystal structure of **L9** was unequivocally determined by X-ray diffraction analyses.<sup>17</sup>



**Scheme 2.** Synthesis of picolinohydrazides **L7-L9** and molecular diagram of ligand **L9** at the 50% probability level.

After preparation and characterization of picolinohydrazides **L1-L9**, and in connection with some of our earlier work,<sup>18</sup> we were interested in the catalytic performance of this ligand class in the zinc-catalyzed hydrosilylation of carbonyl compounds. Typical reaction conditions for our initial screening on acetophenone (**12a**) as the model substrate were chosen with the relatively cheap diethoxymethylsilane as the reducing agent, toluene as the solvent, and 5 mol% of an *in situ* generated zinc catalyst composed of diethylzinc and the ligand in a ratio of 1:1 (Scheme 3). After 16 h of reaction at room temperature, the generated silyl ether was hydrolyzed under basic conditions to release the corresponding 1-phenylethanol (**13a**). Overall, the above results have shown that the degree of substitution of the ligand had a major influence on the outcome of the reaction. Thus, when hydrazides **L1-L3** bearing two substituents at the *N*<sup>β</sup>-position were first tested, near-quantitative conversions were obtained. Despite their very different functionalization, the *N*<sup>β</sup>-unsubstituted ligands **L7** and **L8** also gave a complete conversion of acetophenone. On the contrary, for hydrazides **L4** and **L9** possessing only one substituent at the *N*<sup>β</sup>-position, significantly lower conversions were observed (88% and 74%,

respectively). A reduced conversion of 93% was found with the fully substituted hydrazide **L6**, probably for steric reasons. Finally, in the case of **L5** incorporating two pyridine moieties, almost no reduction occurred presumably because of its specific ligation to the zinc precluding any access of the reactants to the metal center. In those reactions, when complete conversions were reached, **13a** was purified by column chromatography and the average isolated yields were 82%. This rather low value may be attributed to some loss during the treatment, as no other product derived from **12a** could be detected by NMR after hydrolysis (see Supporting Information for an example).



**Scheme 3.** Evaluation of the picolinohydrazides in the zinc-catalyzed hydrosilylation of acetophenone. Conversions determined by  $^1\text{H}$  NMR spectroscopy after basic hydrolysis are provided for each ligand, and isolated yields are given in parentheses.

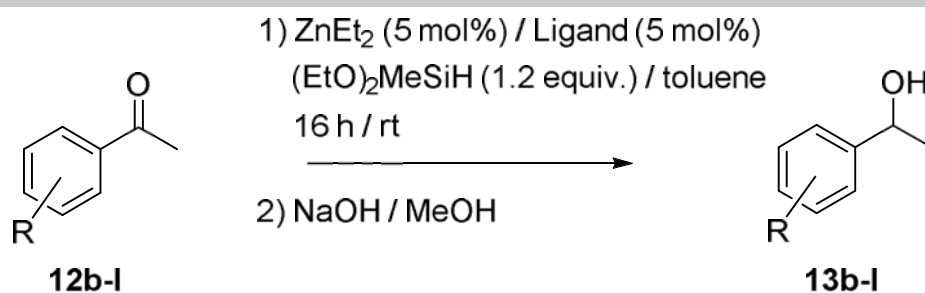
In order to further extend this preliminary study, other hydrosilylation trials were made on the model substrate. In particular, a very low conversion was observed in the absence of ligand, which was consistent with previous observations.<sup>4a</sup> Some attempts to decrease the catalyst loading were also conducted with **L2** and proved to be detrimental to the acetophenone consumption since the use of 2.5 mol% and 1 mol% catalyst led to 92% and 74% conversion, respectively. When *N*-benzylpicolinamide (**14**)<sup>19</sup> or the benzohydrazide-type compound **15** were applied to the reaction, rather low conversions were obtained, highlighting the beneficial role of suitably substituted picolinohydrazide functionalities to the reaction. At last, one may also wonder if acetophenone could condense onto ligand **L7** (or **L8**) in the course of the reaction to form the corresponding hydrazone that could act as the active ligand. Actually, control experiments between stoichiometric amounts of hydrazide **L7** and this ketone in toluene solutions, in the presence or not of ZnEt<sub>2</sub>, were run and monitored by <sup>1</sup>H NMR spectroscopy, but no trace of condensation product could be detected in the reaction medium.

A series of representative acetophenone derivatives were next hydrosilylated with the combination of diethylzinc and selected picolinohydrazides **L1**, **L2**, and **L7**, to study the scope and limitations of the reaction (Table 1). Regardless the electron-withdrawing group present within the *para*-substituted ketones **12b–12f**, high conversions as well as good yields were obtained with either **L1** or **L2** (entries 1–5). For 4'-methylacetophenone (**12g**), the conversion was only of 79% with **L2** (entry 6), but could be satisfyingly raised over 99% using **L7** (entry 7). With stronger electron-donating substituents, decent conversions were attained for **12h** (91%, entry 8) and **12i** (81%, entry 9). Complete reduction was also observed with ketones **12j–12l** (entries 10–13), although the latter was an *ortho*-substituted acetophenone.

**Table 1**

Scope of zinc-catalyzed hydrosilylation of acetophenone derivatives with **L1**, **L2**, and **L7**<sup>a</sup>





Entry	Substrate	R	Ligand	Conv. <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1	<b>12b</b>	4-Cl	<b>L1</b>	>99	89
2	<b>12c</b>	4-F	<b>L2</b>	>99	84
3	<b>12d</b>	4-CN	<b>L2</b>	>99	65
4	<b>12e</b>	4-NO <sub>2</sub>	<b>L2</b>	97	89
5	<b>12f</b>	4-Br	<b>L1</b>	>99	85
6	<b>12g</b>	4-CH <sub>3</sub>	<b>L2</b>	79	—
7	<b>12g</b>	4-CH <sub>3</sub>	<b>L7</b>	>99	90
8	<b>12h</b>	4-OCH <sub>3</sub>	<b>L2</b>	91	—
9	<b>12i</b>	4-NEt <sub>2</sub>	<b>L7</b>	81	—
10	<b>12j</b>	4-Ph	<b>L1</b>	>99	91
11	<b>12j</b>	4-Ph	<b>L7</b>	>99	78
12	<b>12k</b>	3-OCH <sub>3</sub>	<b>L7</b>	>99	91
13	<b>12l</b>	2-Cl	<b>L7</b>	>99	85

<sup>a</sup> Typical conditions: substrate (1 mmol), diethoxymethylsilane (1.2 mmol), diethylzinc (0.05 mmol), ligand (0.05 mmol), toluene (2 mL), 16 h, rt.

<sup>b</sup> Conversion determined by <sup>1</sup>H NMR spectroscopy after basic hydrolysis.

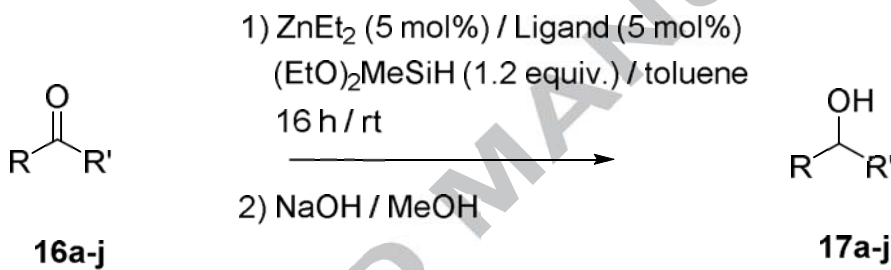
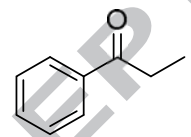
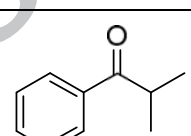
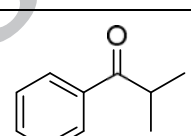
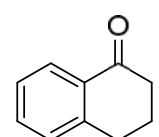
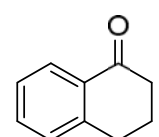
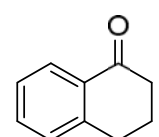
<sup>c</sup> Isolated yield after purification by column chromatography.

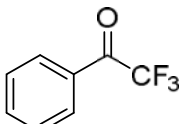
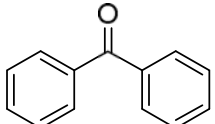
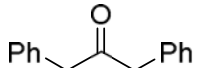
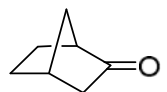
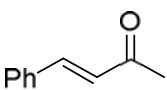
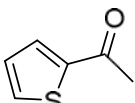
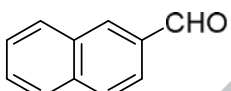
Encouraged by the good results obtained with acetophenone and its congeners, we decided to try in turn more challenging carbonyl substrates (Table 2). First, the ability of the catalytic system to reduce

bulky ketones was probed by using propiophenone (**16a**), isobutyrophenone (**16b**), and  $\alpha$ -tetralone (**16c**). These compounds underwent complete transformation provided that the right ligand was employed. For instance, **L1** was efficient on **16a** (entry 1) but found its limit with **16c** (entry 4), whereas **L2** gave a clean reduction of **16c** (entry 5) but a partial conversion of **16b** (entry 2). Nevertheless, when the hydrosilylation of **16b** was carried out with **L7**, alcohol **17b** was formed quantitatively (entry 3). No problem was encountered in the reduction of the activated ketone **16d** with either **L1** or **L2** (entries 7 and 8).

**Table 2**

Scope of zinc-catalyzed hydrosilylation of various carbonyl compounds with **L1**, **L2**, and **L7**<sup>a</sup>

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Entry	Substrate	Ligand	Conv. <sup>b</sup> (%)	Yield <sup>c</sup> (%)	
1	 <b>16a</b>	<b>L1</b>	>99	75	
2	 <b>16b</b>	<b>L2</b>	82	–	
3	 <b>16b</b>	<b>L7</b>	>99	93	
4	 <b>16c</b>	<b>L1</b>	89	–	
5	 <b>16c</b>	<b>L2</b>	>99	78	
6	 <b>16c</b>	<b>L7</b>	>99	92	

7		<b>16d</b>	<b>L1</b>	>99	74
8			<b>L2</b>	>99	–
9		<b>16e</b>	<b>L7</b>	>99	65
10		<b>16f</b>	<b>L7</b>	>99	77
11		<b>16g</b>	<b>L7</b>	>99	70 <sup>d</sup>
12		<b>16h</b>	<b>L7</b>	>99	88 <sup>c</sup>
13		<b>16i</b>	<b>L7</b>	>99	70
14		<b>16j</b>	<b>L7</b>	>99	82

<sup>a</sup> Typical conditions: substrate (1 mmol), diethoxymethylsilane (1.2 mmol), diethylzinc (0.05 mmol), ligand (0.05 mmol), toluene (2 mL), 16 h, rt.

<sup>b</sup> Conversion determined by <sup>1</sup>H NMR spectroscopy after basic hydrolysis.

<sup>c</sup> Isolated yield after purification by column chromatography.

<sup>d</sup> *Endo/exo* = 85/15.

<sup>e</sup> Mixture of products: 4-phenylbut-3-en-2-ol (80%) and 4-phenylbutan-2-ol (20%).

On the basis of the foregoing and given its availability, ligand **L7** was retained for the following assays. Excellent conversions were obtained for benzophenone (**16e**), dibenzyl ketone (**16f**), 2-norbornanone (**16g**), and 2-acetylthiophene (**16i**) (entries 9–11 and 13). The  $\alpha,\beta$ -unsaturated ketone **16h**

was also investigated (entry 12), and in this case the expected allylic alcohol **17h** together with 4-phenylbutan-2-ol were present in the final product in a ratio 4:1. As expected with the more reactive aldehydes, when the reaction was carried out on 2-naphthaldehyde (**16j**) as a representative example, a complete conversion was reached (entry 14).

## Conclusion

In the present study, we have demonstrated the high catalytic performance of diethylzinc combined with picolinohydrazides in the hydrosilylation of carbonyl compounds under mild conditions. This novel *in situ* system allowed the efficient reduction of a wide variety of (hetero)aromatic and aliphatic ketones with broad functional group tolerance, and when some steric limitations arose they could be circumvented. Aldehydes and enone-containing substrates were also readily transformed, although for these latter some loss in selectivity was observed. In short, picolinohydrazides constitute a class of easily accessible molecules able to serve as efficient ligands for zinc-catalyzed hydrosilylation. It would be now worth devoting future work in the direction of enantioselective hydrosilylation of prochiral ketones based on zinc catalysts of chiral hydrazides.

## Acknowledgments

We thank Université de Rennes 1 and CNRS for financial support, and FEDER funds for acquisition of single crystal equipment.

## Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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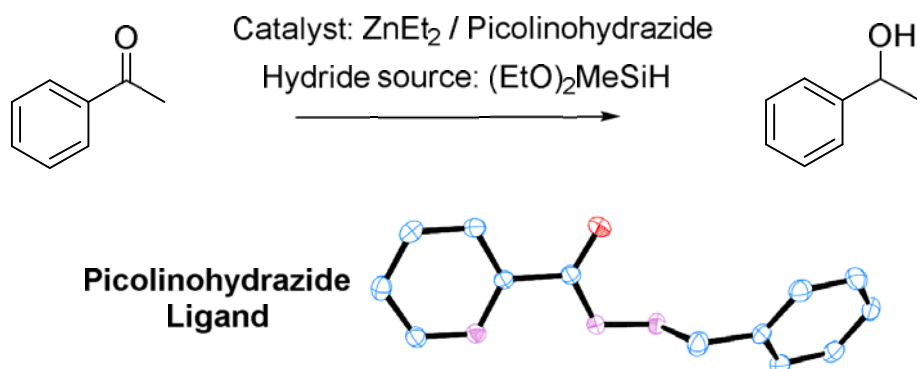
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- Novel picolinohydrazides were readily prepared and characterized.
- They were combined with diethylzinc and used in hydrosilylation of ketones.
- Over 20 ketones were reduced by diethoxymethylsilane and this catalytic system.

ACCEPTED MANUSCRIPT