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Combined KOH/BEt_3 Catalyst for Selective Deaminative Hydroboration of Aromatic Carboxamides for Construction of Luminophores

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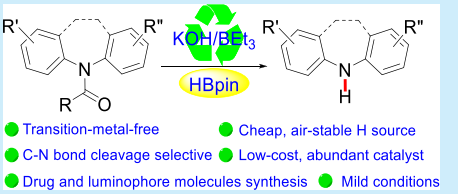
ABSTRACT: The selective catalytic C−N bond cleavage of amides into value-added amine products is a desirable but challenging transformation. Molecules containing iminodibenzyl motifs are prevalent in pharmaceutical molecules and functional materials. Here we established a combined KOH/BEt_3 catalyst for deaminative hydroboration of acyl-iminodibenzyl derivatives, including nonheterocyclic carboxamides, to the corresponding amines. This novel transition-metal-free methodology was also applied to the construction of Clomipramine and luminophores.



Iminodibenzyl and its derivatives have emerged as promising alternatives to heterocycles for use as emissive or host materials for organic light-emitting diodes (Figure 1).[1] At present, the dominant methods for synthesis of these value-added iminodibenzyl compounds include two-component cyclizations and one-pot cascade protocols.[2] Unfortunately, the reported cyclization methods require nontrivial starting materials, whereas the cascade approaches are generally narrower in substrate scope and functional group compatibility. These limitations seriously restrict the application of these two methodologies.

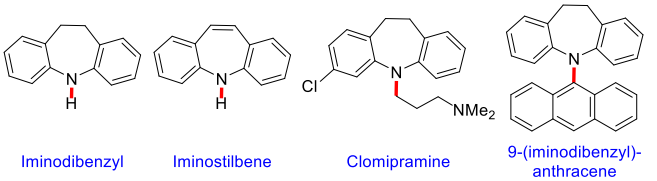
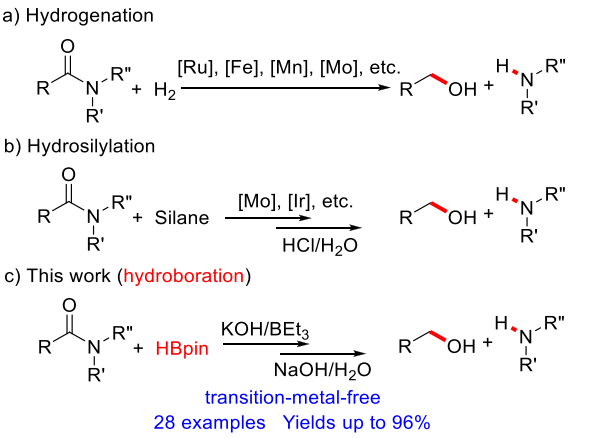


Figure 1. Representative iminodibenzyl derivatives.

As an alternative, the controlled reduction of amides to amines (hydrogenolysis) represents a valuable transformation for the synthesis of iminodibenzyl cores. However, this route remains challenging because of the relatively low electrophilicity of amide carbonyl groups and the high bond dissociation energy of C−N bonds (95−104 kcal mol^{-1}).[3] The traditional methods for the dissociation of C−N bonds in amides often suffer from terrible selectivity (C−N vs C−O cleavage), high-cost chemicals, and excess waste products.[4] Obviously, for precise and predictable control of C−N bond cleavage in catalytic amide reduction, it is of interest and necessary to continue development of synthetic strategies that are highly selective and more ecofriendly.

Catalytic hydrogenation is a significant protocol for the C−N bond cleavage of amides (Scheme 1a). During the past decade, in work pioneered by Milstein,[5] Ikariya,[6] and Bergens,[7] elegant transition-metal catalysts, dominated by the noble metal Ru[8] and involving the reductive cleavage of amide C−N bonds, have been reported. Recently, some ecofriendly and low-cost base-metal catalysts, including Fe,[9] Co,[10] Mn,[11] and Mo[12] complexes, were developed for effective catalysis in the deaminative hydrogenation of amides. While each approach

Scheme 1. Selective Cleavage of Amide C−N Bonds



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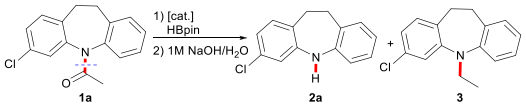
has its own merits, it is noteworthy that many hydrogenation methods involve high-pressure reactors and high temperatures, which may affect the application of these processes.

Complementary to the direct hydrogenolysis of amide derivatives is the use of hydrosilanes as hydrogen donors, providing a promising alternative method because of its safety and operational simplicity (Scheme 1b). The elegant works of Enthaler[13] and Fernández-Alvarez[14] using Mo-catalyzed or Ir-catalyzed hydrosilylation of amides allow access to the hydrolyzed products. However, current hydrosilylation approaches frequently suffer from using complex metal catalysts, noble/air-sensitive silanes (Ph_2SiH_2 and $HSiMe_2Ph$), and non-ideal selectivity.

As a reducing agent, pinacolborane (HBpin) is a relatively low-cost, bench-stable hydrogen source that exhibits high functional group tolerance.[15] Therefore, catalytic reduction of carboxamide moieties using HBpin is highly desirable. Surprisingly, the hydroboration reduction of amide substrates (C−O cleavage) is very rare.[15,16] Moreover, the reductive cleavage of C−N bonds in amide functions by employing hydroboration protocols was disclosed by Findlater only using a lanthanum catalyst.[16a] To date, no transition-metal-free catalyst has been realized for the selective C−N bond cleavage of amides utilizing hydroborons.

Hence, the development of non-transition-metal catalysts for selective deaminative hydroboration of amides, especially the iminodibenzyl amide derivatives of the broad-spectrum amine luminophores, is of great interest. Among the various non-transition-metal catalysts investigated, boron Lewis acids are especially attractive because of their high Lewis acid strength and low environmental impact, and significant progress has been made in recent years. Notably, since the ground-breaking finding that the strong boron Lewis acid $B(C_6F_5)_3$ can activate Si−H bonds through η^1-coordination, this Lewis acid has emerged as a powerful tool for cleavage of carbon−heteroatom bonds.[17] However, as a catalyst, $B(C_6F_5)_3$ is relatively expensive. In contrast, BEt_3 is more air-stable and at least 100 times less expensive than $B(C_6F_5)_3$. Inspired by previous works,[18,19] we herein report KOH/BEt_3-catalyzed hydrogenolysis of C−N bonds in acyl-iminodibenzyl derivatives to produce iminodibenzyl luminophores in good yield and high selectivity (Scheme 1c), high Lewis acid strength, and low environmental impact, and significant progress has been made in recent years. Notably, since the ground-breaking finding that the strong boron Lewis acid $B(C_6F_5)_3$ can activate Si−H bonds through η^1-coordination, this Lewis acid has emerged as a powerful tool for cleavage of carbon−heteroatom bonds.[17] However, as a catalyst, $B(C_6F_5)_3$ is relatively expensive. In contrast, BEt_3 is more air-stable and at least 100 times less expensive than $B(C_6F_5)_3$. Inspired by previous works,[18,19] we herein report KOH/BEt_3-catalyzed hydrogenolysis of C−N bonds in acyl-iminodibenzyl derivatives to produce iminodibenzyl luminophores in good yield and high selectivity (Scheme 1c). 3-Chloro-iminodibenzyl (**2a**) is an important precursor for the construction of highly valuable Clomipramine, which is used as a treatment for depression. Thus, we commenced the selective cleavage of the C−N bond in 3-chloro-iminodibenzyl amide (**1a**) with HBpin by evaluating the catalytic activities of non-transition-metal catalysts. As shown in Table 1, the reaction in the presence of 5.0 mol % KOH/BEt_3 and 2.5 equiv of HBpin at room temperature selectively formed **2a** in the best yield after 16 h (entry 1). Notably, the same reaction using BEt_3 or KOH alone did not

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	HBpin (equiv)	solute	yield of **2a** (%)	yield of **3** (%)
1	KOH/BEt_3	2.5	MTBE	31	2
2	KOTMS/BEt_3	2.5	MTBE	15	2
3	CH_3ONa/BEt_3	2.5	MTBE	7	3
4	NaOH/BE_3	2.5	MTBE	17	5
5	KOAc/BEt_3	2.5	MTBE	3	<1
6	BEt_3	2.5	MTBE	0	0
7	KOH	2.5	MTBE	0	0
8	$B(C_6F_5)_3$	2.5	MTBE	<1	<1
9	BPh_3	2.5	MTBE	<1	<1
10	KOH/BEt_3	2.5	THF	50	4
11	KOH/BEt_3	2.5	Et_2O	30	2
12	KOH/BEt_3	2.5	PhMe	19	3
13	KOH/BEt_3	2.0	THF	51	1
14[b]	KOH/BEt_3	2.0	THF	82 (80)	<1

[a]Reaction conditions: **1a** (1.0 mmol), HBpin (2.5 mmol), catalyst (5.0 mol %), solvent (2 mL), rt, 16 h; then 1 M NaOH/H_2O, rt, 1 h. The GC yield is based on **1a** with 1,2-dimethoxybenzene as an internal standard, and the isolated yield is in parentheses. [b]At 100 °C for 24 h.

proceed (entry 6 or 7, respectively). To our surprise, the use of electrophilic $B(C_6F_5)_3$ or Lewis acidic BPh_3 also failed to generate any desired product under standard conditions despite having enabled various reductions of amides (entries 8 and 9).[17,20] Subsequent optimization revealed that use of a tetrahydrofuran (THF) solvent, which has a moderate dielectric constant, suppressed the formation of **3** and provided **2a** as the primary product in 50% yield (entry 10). Pleasingly, the selectivity of the C−N bond cleavage was efficiently improved using 2.0 equiv of HBpin (entry 13). Remarkably, extending the temperature and reaction time further improved the yield and selectivity of **2a** (entry 14).

Utilizing the optimized conditions, we explored the substrate scope concerning amide starting materials for the selective C−N bond cleavage (Scheme 2). Pleasingly, a variety of acyl-iminodibenzyl and acyl-iminostilbene derivatives bearing halogen (**1a**, **1j**, **1k**, and **1v**), alkenyl (**1f**), alkoxy (**1h** and **1y**), trifluoromethyl (**1p**), or sulfhydryl (**1q**) substituents were all well tolerated in hydroboration reactions, selectively providing the valuable iminodibenzyl analogues in moderate to excellent yields. However, substrates bearing steric substituents such as isopropyl (**1d**), *tert*-butyl (**1t**), and phenyl (**1u** and **1v**) groups decreased the reactivities. To our delight, acetyl-protected carbazole (**1i**−**1l**) and 9,10-dihydroacridine derivatives (**1m**−**1q**) similarly gave ideal yields of the nitrogen-containing luminophores at room temperature.

Encouraged by the success of C−N bond cleavage of acyl-iminodibenzyl analogues, we continued to evaluate the deaminative hydroboration of nonheterocyclic amides. Pleasingly, when the reactions were performed at room temperature, the diarylamine carbonyl substrates, including alkyl (**1r**−**1t** and **1w**−**1ab**) and aryl amides (**1u** and **1v**), were all smoothly transformed to give the corresponding amine luminophores in moderate to excellent yields with exclusive selectivity.

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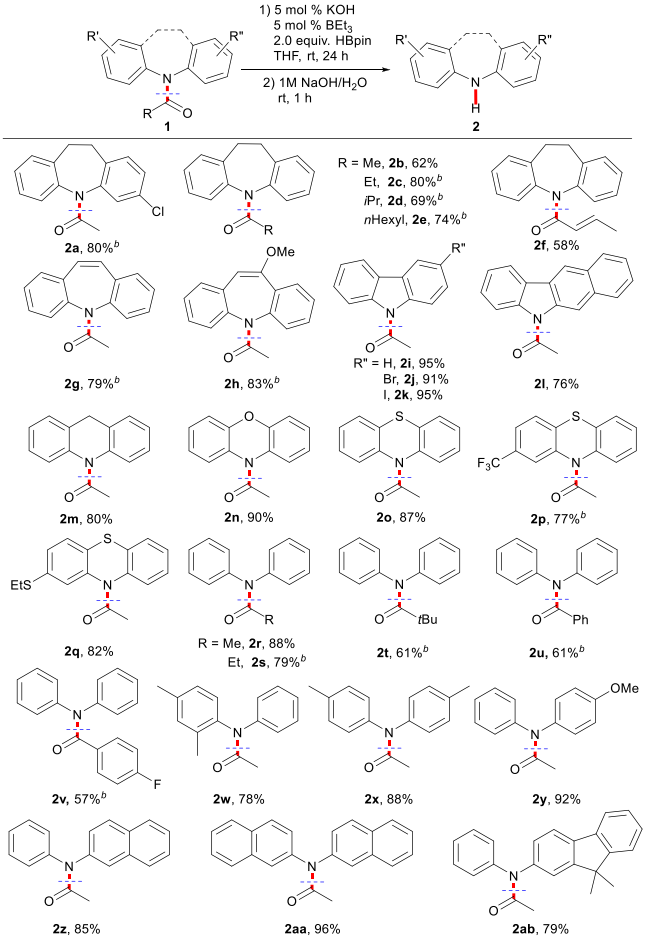
Scheme 2. KOH/BEt_3-Catalyzed Selective Hydrogenolysis of Acyl-iminodibenzyl Derivatives[a]

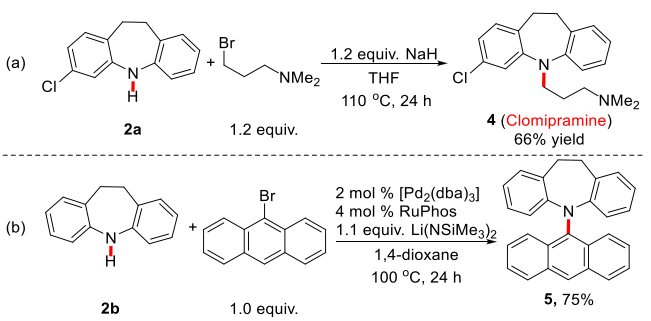


[a]Reaction conditions: **1** (1.0 mmol), HBpin (2.0 mmol), BEt_3 (5.0 mol %), KOH (5.0 mol %), THF (2 mL), rt, 24 h; then 1 M NaOH/H_2O, rt, 1 h. Yields are of isolated products. [b]At 100 °C for 24 h.

However, the attempted C−N bond cleavage of *N*-aryl-*N*-alkyl amides or *N*,*N*-dialkyl amides did not proceed (see page S4 of the Supporting Information).

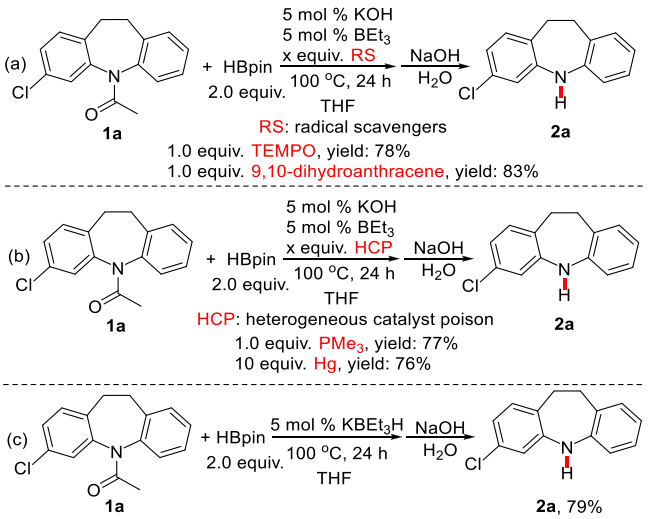
The transition-metal-free-catalyzed C−N cleavage of amides was further applied in the synthesis of Clomipramine **4** (Scheme 3a), while compound **5**, which can provide derivatives as promising emissive or host materials for organic light-emitting diodes, was also smoothly prepared from hydrolyzed product **2b** (Scheme 3b).

Scheme 3. Synthetic Applications



To disclose a plausible reaction mechanism, several control tests were performed. First, addition of typical radical scavengers, such as TEMPO and 9,10-dihydroanthracene, did not obviously affect the hydroboration transformations (Scheme 4a), rendering a free radical mechanism unlikely.

Scheme 4. Control Tests



Moreover, addition of commonly used heterogeneous catalyst poisons such as PMe_3 or Hg showed no adverse effect on the yield of **2a** (Scheme 4b), which indicated that the combined KOH/BEt_3 catalyst was likely to be homogeneous under the described conditions.

Subsequently, the control experiment with 5 mol % $KHBEt_3$ afforded the desired product **2a** in a result that was very similar to the reaction catalyzed by the combined KOH/BEt_3 catalyst (Scheme 4c). This result suggested that $KHBEt_3$ itself may serve as a catalyst for amide C−N bond cleavage. This result is consistent with the original mechanism unveiled by Huang for the BEt_3-catalyzed reduction of carbonyl compounds to alcohols.[19]

In addition, the treatment of various aldehydes with 1.0 equiv of HBpin using 5 mol % catalyst at room temperature conveniently gave alcohol products in high yields (Scheme 5), indicating aldehydes as possible intermediates in the current hydroboration protocol.

Next, we studied the generation of **2a** and **3** on the basis of the amount of HBpin. A presentation of HBpin-dependent yields for the catalytic C−N bond cleavage of **1a** in THF is given in Figure 2. We found that hydrogenolysis of **1a** by treatment with 2.0 equiv of HBpin offered the best selectivity and yield of **2a**. This result partly contributed to the explanation of the catalytic cycle reported below.

Simultaneously, we performed kinetic studies to explore the roles of the catalyst, amide, and HBpin at the RDS (see pages S7−S14 of the Supporting Information). Measurements of the initial rates (k_{in}) for the protocols of different concentrations of substrates and KOH/BEt_3 catalyst exhibited a corresponding increase in the rates of the reactions. Plots of k_{in} versus the concentrations of amide, HBpin, and the combined catalyst offered linear curves (slopes of 3.05×10^{-4}, 2.03×10^{-4}, and 5.94×10^{-3} M s^{-1}), indicating a first-order rate dependence on both amide, HBpin, and the catalyst.

On the basis of previous reports[15,19,21] and our control tests and kinetic studies, we proposed a plausible mechanism for the

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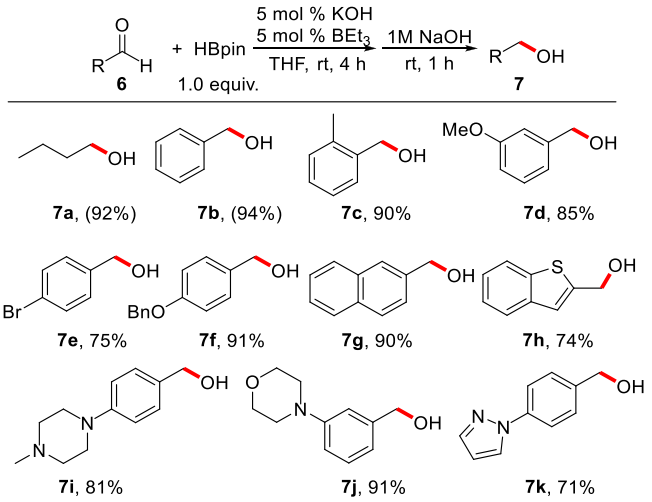
Scheme 5. KOH/BEt_3-Catalyzed Hydroboration Reduction of Aldehydes[a]



[a]Reaction conditions: aldehyde (1.0 mmol), HBpin (1.0 mmol), BEt_3 (5.0 mol %), KOH (5.0 mol %), THF (2 mL), rt, 4 h; then 1 M $NaOH/H_2O$, rt, 1 h. Yields are of isolated products. The yields in parentheses are GC yields.

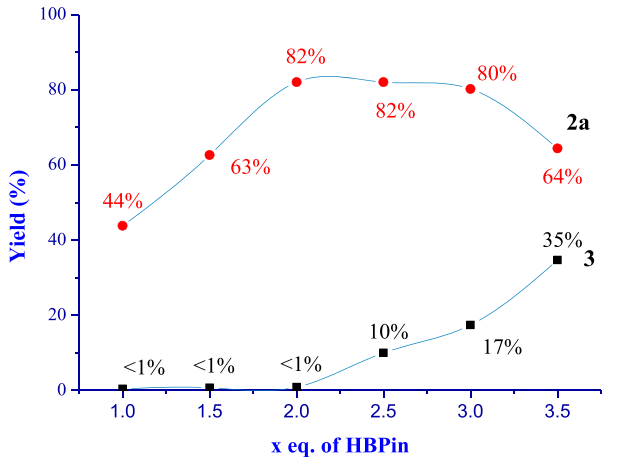
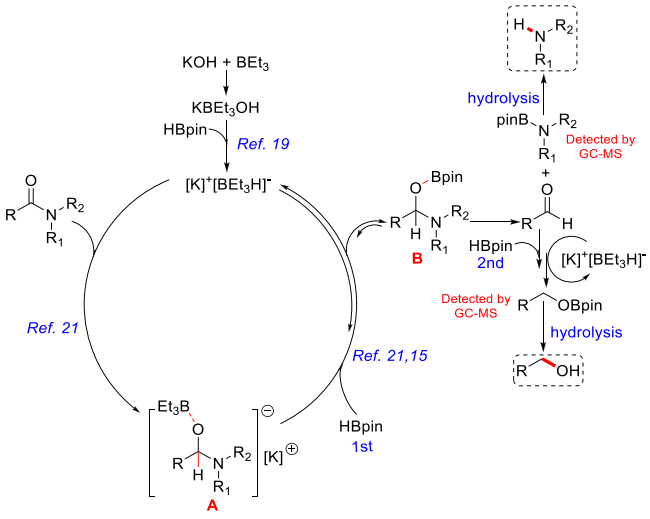


Figure 2. Time course for hydrogenolysis of **1a** (1.0 mmol), HBpin (1.0–3.5 mmol), BEt_3 (5.0 mol %), KOH (5.0 mol %), and THF (2 mL) at 100 °C for 24 h and then 1 M $NaOH/H_2O$ at rt for 1 h. The GC yield based on **1a** with 1,2-dimethoxybenzene as an internal standard.

selective hydroboration reduction (Scheme 6). Initially, BEt_3 is converted by KOH to form a borate that rapidly reacts with HBpin to generate $KBEt_3H$.[19] Subsequently, $KBEt_3H$ reacts with the *tert*-amide to generate an intermediate ion pair **A**. Reactions of hydrides with HBpin through ion pair **A** analogues have been described by Shao,[15] Crabtree,[21a] and Findlater.[21b] The further reaction of this ion pair with 1 equiv of HBpin gives borate **B** and regenerates the catalyst. Importantly, the density functional theory (DFT)-calculated enthalpy and entropy of reactions using DFT-B3LYP/3-21+G* also demonstrated the possible generation of species **A** and **B** (page S14 of the Supporting Information and Tables S8 and S9). Indeed, with the electron density of the N atom being decreased by the conjugation effect, borate **B** undergoes facile conversion to aldehyde and ammonia borane. Thereafter, upon addition of an additional 1 equiv of HBpin, alkoxyborane

Scheme 6. Plausible Mechanism



is released with concomitant regeneration of $KBEt_3H$ after repeating the catalytic cycle likewise. The subsequent hydrolysis of ammonia borane and alkoxyborane allows the facile formation of amine and alcohol.

In conclusion, a transition-metal-free approach for the selective catalytic cleavage of inert C–N bonds in acyl-iminodibenzyl molecules with HBpin, using a low-cost and abundant combined KOH/BEt_3 catalyst, has been disclosed. The notable advantages of the developed method are high efficiency, mild conditions, operational simplicity, and excellent selectivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03033.

General considerations, typical reaction procedures, DFT calculations, kinetic studies, NMR spectra, and spectra for pure products (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Qizhong Zhou on the occasion of his 48th birthday.

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