**Zn-Catalyzed Regioselective and Chemoselective Reduction of Aldehydes, Ketones and Imines**

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**Abstract:** An operationally convenient Zn-catalyzed synthesis of alcohols by the reduction of aldehydes, ketones, and α,β-unsaturated aldehydes/ketones is reported. It is a rare example of using mild and sustainable HBpin as a reductant for catalytic reduction of carbonyl compounds in the absence of acid or base as hydrolysis reagent. The reaction is upscalable and proceeds in high selectivity without the formation of boronate ester by-products, and tolerates sensitive functionalities, such as iodo, bromo, chloro, fluoro, nitro, trifluoromethyl, aminomethyl, alkynyl, and amide. The Zn(OAc)$_2$/HBpin combination has been also proved to be chemoselective for the C=N reduction of imine analogs.

**Keywords:** zinc; reduction; aldehydes; ketones; imines

1. **Introduction**

Selective reduction is one of the most efficient reactions in modern synthetic chemistry because of its importance in the manufacture of chemicals and basic raw materials [1–4]. The reduction of carbonyl compounds is a straightforward method to prepare alcohols, which are widely used as chemical intermediates for the synthesis of natural products, pharmaceuticals, agrochemicals, and functional materials [5,6]. Traditionally, the reduction of carbonyl compounds was usually accomplished by using stoichiometric amounts of metal hydrides (NaBH$_4$) and Lewis acid [7,8]. Alternatively, transition-metal-catalyzed hydrogenation of C=O bond in the presence of hydrogen (as the reductant) could also provide corresponding alcohol [9–12]. In the past two decades, pinacolborane (HBpin=4,4,5,5-tetramethyl-1,3,2-dioxaborolane), as a mild and sustainable carbonyl reductant, has attracted considerable interest [13–23]. Metal-catalyzed hydroboration of polarized C=O bonds for the preparation of alcohols has been developed [24–26]; however, certain special reagents are required for the hydrolysis reaction, such as HCl [27,28], NaOH [29,30], H$_2$O$_2$ [31], SiO$_2$ [32–36] (Scheme 1a). In 2019, the commercially available MgBu$_2$-catalyzed reduction of α,β-unsaturated ketones for the synthesis of alcohols was reported; however, the sensitive functional groups could not survive under the reported conditions [37].

To develop cost-effective hydrogenation protocols, the replacement of precious transition metals with earth-abundant, low-cost, first-row metals is contemporary and highly desirable in terms of sustainability [38–43]. Zinc, as a typical first-row transition metal, is abundant, inexpensive, and nontoxic, having been applied in a wide range of chemical reactions [44–47]. In 2006, an efficient ZnCl$_2$-catalyzed selective alkylation of ketones for the synthesis of tertiary alcohol in the presence of RMgCl (1.3 equiv.) was reported [48]. Zn-catalyzed hydrogenation of carbonyl in the presence of NH$_4$Cl was also reported with a wide range of substrates bearing various sensitive groups, but excessive amounts of metallic zinc were necessary [49]. Recently, Panda’s group reported that zinc(II) complexes catalyzed chemoselective hydroboration of aldehydes and ketones to achieve corresponding primary and secondary alcohols, requiring the necessary SiO$_2$/MeOH as hydrolysis
reported with a wide range of substrates bearing various sensitive groups, but excessive amounts of metallic zinc were necessary [49]. Recently, Panda’s group reported that series of parasubstituted aromatic aldehydes were investigated. The results showed that aldehydes gave the corresponding primary alcohols in good yields and selectivity, it can be concluded that the position (ortho, meta, para) and substituent effect (electron donating vs. electron withdrawing) have no obvious influence on the efficiency of hydrogenation.

In this work, we present Zn(OAc)₂-catalyzed chemoselective reduction of aldehydes, ketones, and imines.

In this work, we present Zn(OAc)₂-catalyzed chemoselective reduction of aldehydes, ketones, and α,β-unsaturated ketones for the synthesis of corresponding alcohols dispensed with special hydrolysis steps. In addition, Zn(OAc)₂/HBpin was not only active for C=O reduction, but also chemoselective for the C=N reduction of imine under optimized conditions (Scheme 1b).

2. Results

We began our catalytic studies by using HBpin as a reducing agent in THF and 2-naphthaldehyde 1a as a model substrate (Table 1). Different zinc salts were tested at 45 °C for 24 h (Table 1, entries 1–3). Treatment of 2-naphthaldehyde 1a in the presence of HBpin (1.5 equiv.) and Zn(O Tf)₂ (10 mol%) in THF at 45 °C for 24 h gave the hydrogenated product naphthalen-2-ylmethanol 2a in 44% yield. We found that directly hydrogenated products were obtained in the absence of acid or base as hydrolysis reagent, and the undesired hydroboration products of carbonyl groups were not observed. The hydrogenated product was isolated in 80% and 94% with ZnCl₂ and Zn(OAc)₂, respectively (entries 2–3). Under the same conditions, the reduction products were not detected when silane was used as a reducing agent (entries 4). It is surprising to find out that there was no influence on the catalytic activity with significantly lowered temperature (rt) and shortened time (1 h), which is a huge advantage of the Zn-HBpin system (entries 5). Further optimization revealed that the loading of Zn(OAc)₂ could be cut to 1 mol % while maintaining the yield of product 2a at 93% (entries 6). Various solvents, including EtOH, toluene, DCM, and CH₃CN, were found to be unsatisfactory (entries 7–10). The hydrogenation of 1a was also successful with other transition metal catalysts, such as FeCl₂, CoBr₂, NiBr₂, and MnBr(CO)₅; however, the yield of 2a was much lower (41–80%) under standard conditions (entries 11–14). Moreover, CrCl₂ and CuCl₂ failed to give any hydrogenation product (entries 15 and 16). It is worth noting that the Zn-catalyzed hydrogenation of 1a proceeded smoothly in the presence of a huge excess of Hg (0) (100 equiv., entry 6, footnote d), indicating that it is highly likely to be a homogeneous catalytic system.

With the optimized reaction conditions in hand, the scope of the zinc-catalyzed reduction of aldehydes was examined. As shown in Scheme 2, all substrates were well tolerated under optimal conditions, and the desired hydrogenation products were isolated in good to excellent yields. Since the hydrogenation of o-nitro (2b), o-methoxy (2c), and m-nitro (2d) aldehydes gave the corresponding primary alcohols in good yields and selectivity, it can be concluded that the position (ortho, meta, para) and substituent effect (electron donating vs. electron withdrawing) have no obvious influence on the efficiency of hydrogenation. A series of parasubstituted aromatic aldehydes were investigated. The results showed that

![Scheme 1. Zn(OAc)₂-catalyzed chemoselective reduction of aldehydes, ketones, and imines.](image-url)
various electron-donating and electron-withdrawing groups (e.g., halogen, nitro, trifluoromethyl, and aminomethyl) were all well tolerated (2e–2m). Remarkably, the substrates bearing an alkenyl and amido group were well tolerated as well. The corresponding reduction products were obtained in 65% and 93%, respectively (2n–2o). Interestingly, the subjection of 4-acetyl benzaldehyde under the optimal condition gave a reduction of a formyl group. However, increasing the loading of the hydrogen source could easily boost the efficiency to 87% with the reduction of both carbonyl groups (2p). The treatment of p-dibenzaldehyde with 1.5 equiv. of HBpin for 12 h gave product 2q with the selective reduction of one carbonyl group. In addition, various heavily functionalized aromatic, ferrocene complex and polycyclic aromatic hydrocarbons bearing an aldehyde group were explored as well. All the reduced primary alcohol products were obtained in high yields (77–89%, 2r–2v). Inspired by the promising results, the feasibility of Zn(OAc)$_2$/HBpin for catalytic reduction of heteroaromatic aldehydes was further examined. As expected, various thiophene, furan, pyridine, quinoline aldehyde analogues can be regioselectively reduced and gave the corresponding primary alcohols in good yields (65–92%, 2w–2ab).

Table 1. Reaction optimization for the Zn-catalyzed reduction of 2-naphthaldehyde.

| Entry | Metal Salt | Reductant | Solvent | Time/h | Yield of 2a/% |
|-------|------------|-----------|---------|--------|--------------|
| 1 b   | Zn(OAc)$_2$ | HBpin     | THF     | 24     | 44           |
| 2 b   | ZnCl$_2$    | HBpin     | THF     | 24     | 80           |
| 3 b   | Zn(OAc)$_2$ | HBpin     | THF     | 24     | 94           |
| 4 b   | Zn(OAc)$_2$ | PhSiH$_3$ | THF     | 24     | nd           |
| 5     | Zn(OAc)$_2$ | HBpin     | THF     | 1      | 94           |
| 6     | Zn(OAc)$_2$ | HBpin     | THF     | 1      | nd           |
| 7     | Zn(OAc)$_2$ | HBpin     | EtOH    | 1      | 93 (88) d    |
| 8     | Zn(OAc)$_2$ | HBpin     | Toluene | 1      | 41           |
| 9     | Zn(OAc)$_2$ | HBpin     | DCM     | 1      | 48           |
| 10    | Zn(OAc)$_2$ | HBpin     | CH$_3$CN| 1      | trace        |
| 11    | FeCl$_2$    | HBpin     | THF     | 1      | 58           |
| 12    | CoBr$_2$    | HBpin     | THF     | 1      | 71           |
| 13    | NiBr$_2$    | HBpin     | THF     | 1      | 41           |
| 14    | MnBr(CO)$_5$| HBpin     | THF     | 1      | 80           |
| 15    | CrCl$_2$    | HBpin     | THF     | 1      | nd c         |
| 16    | CuCl$_2$    | HBpin     | THF     | 1      | nd c         |

* Conditions: 1a (0.2 mmol), metal salt (0.002 mmol, 1 mol %), HBpin (1.5 equiv.), THF (2.0 mL), rt, 1 h. isolated yield. b Metal salt (0.02 mmol, 10 mol %), 45 °C. c Not detected. d Hg(0) (100 equiv.) was added.

Next, a series of aromatic and aliphatic ketones were examined (Scheme 3). It is important to mention that Zn(OAc)$_2$-catalyzed reduction of ketones would only proceed at an elevated temperature (60 °C). As expected, the boronate ester was not observed during the reaction (analyzed by $^1$H NMR).

Both the diaryl ketone 4c and aryl alkyl ketones 4a, 4b, and 4d–4l were efficiently converted to the corresponding secondary alcohols under optimal conditions. Various electron-donating and electron-withdrawing groups, such as bromide, chloride, fluoride, trifluoromethyl, cyano, nitro, and amino, were well tolerated. Furthermore, the efficiency of the demonstrated catalytic system was not compromised in the presence of heteroatom (4l). Last but not least, dialkyl ketones were also examined, and the corresponding secondary alcohols were obtained in moderate yields (79–90%, 4m–4o).
Scheme 2. Scope for the Zn-catalyzed reduction of aldehydes a. a All reactions were performed with substrate 1 (0.2 mmol), Zn(OAc)$_2$ (0.002 mmol), HBpin (1.5 equiv.) in THF (2 mL) at 25 °C for 1 h under N$_2$. Isolated yield. b HBpin (3 equiv.), 45 °C for 24 h.

Scheme 3. Scope for the Zn-catalyzed reduction of ketones a. a All reactions were performed with substrate 3 (0.2 mmol), Zn(OAc)$_2$ (1 mol %), HBpin (1.5 equiv.) in THF (2 mL) at 60 °C for 24 h under N$_2$, isolated yield.

Scheme 4. Scope for the Zn-catalyzed reduction of α,β-unsaturated aldehyde/ketones a. a All reactions were performed with substrate 5 (0.2 mmol), Zn(OAc)$_2$ (2 mol %), HBpin (1.5 equiv.) in THF (2 mL) at 45 °C for 24 h under N$_2$, isolated yield.

In order to check the generality of the demonstrated Zn(OAc)$_2$/HBpin system, the subjection of the gram scale of 1a (1.56 g, 10 mmol) to the optimal conditions with an extended reaction time (8 h) gave 2a in 94% (Scheme 5).
Inspired by these results, the feasibility of Zn(OAc)$_2$/HBpin-catalyzed reduction of $\alpha,\beta$-unsaturated aldehyde/ketones was examined (Scheme 4). The carbonyl group of $\alpha,\beta$-unsaturated aldehydes/ketones can be regioselectively reduced at an elevated temperature (45 °C) by the formation of allylic alcohols in good yields. We found that the C=C bond reduction was not observed according to the $^1$H NMR analysis. The efficiency and selectivity were not significantly affected by the type and location of substituents in the aromatic ring, and all the corresponding allylic alcohols were obtained in fair to good yields (81–95%, 6a–6m). Moreover, fluoride, chloride, bromide, iodide, trifluoromethyl, and heteroatom, which are usually sensitive to catalytic hydrogenation, were intact (6g–6m). Lastly, the subjection of alkynone to the optimal conditions gave the corresponding product 6n in 74% with the preservation of the alkyne group.

![Scheme 4](https://example.com/scheme4.png)

**Scheme 4.** Scope for the Zn-catalyzed reduction of $\alpha,\beta$-unsaturated aldehyde/ketones. All reactions were performed with substrate 5 (0.2 mmol), Zn(OAc)$_2$ (2 mol %), HBpin (1.5 equiv.) in THF (2 mL) at 60 °C for 24 h under N$_2$, isolated yield.

In order to check the generality of the demonstrated Zn(OAc)$_2$/HBpin system, the subjection of the gram scale of 1a (1.56 g, 10 mmol) to the optimal conditions with an extended reaction time (8 h) gave 2a in 94% (Scheme 5).

![Scheme 5](https://example.com/scheme5.png)

**Scheme 5.** Gram-scale reduction of 1a.

Since it has been demonstrated that more than two carbonyl groups could be reduced with increased loading of a Zn catalyst (Scheme 2, 2p), it is important to find out the reactivity of different carbonyls in aldehydes, ketones, esters, and amides. Hence, the chemose-
lectivity of the Zn-catalyzed hydrogenation reaction was further explored (Scheme 6). The treatment of an equal molar of aldehyde (1 mmol) and ketone (1 mmol) with Zn(OAc)$_2$ (1 mol%) and HBpin (1.5 equiv.) in THF at ambient temperature for 2 h gave naphthalen-2-ylmethanol as a major reduction product (92%) with the recovery of naphthalen-2-yl methyl ketone (Scheme 6a). A similar chemoselectivity was also observed for the pair of 4-methylbenzaldehyde and 4-methylacetophenone. Most of the 4-methylbenzaldehyde was reduced, while the 4-methylacetophenone was successfully recovered (Scheme 6b). The treatment of acetophenone along with ethyl benzoate and HBpin catalysts showed a clear positive correlation, suggesting that the catalytic concentration of 2-naphthaldehyde, Zn(OAc)$_2$, and HBpin determined the initial rate (Figure 1b–d).

Scheme 6. Intermolecular chemoselective reduction of carbonyl substrate: (a) Intermolecular chemoselective of 2-naphthaldehyde and 2-acetonaphthone; (b) Intermolecular chemoselective of 4-methylbenzaldehyde and 4-methylacetophenone; (c) Intermolecular chemoselective of acetophenone and ethyl benzoate; (d) Intermolecular chemoselective of acetophenone and N,N′-dimethylbenzamide.

Out of curiosity, the reactivity of imines was explored at the optimal conditions. It is surprising to find out that the hydrogenation products 8 were obtained in excellent yields (Scheme 7). Additionally, the electron-withdrawing groups did not affect reduction efficiency at all. Thus, it is an excellent alternative method for the preparation of secondary amine.

To have an insight of the reaction mechanism, the kinetic behavior associated with Zn-catalyzed hydrogenation of 2-naphthaldehyde was explored. The hydrogenation proceeded rapidly at the first 0.5 h to give 2a in 88% yield (Figure 1a). The yield was increased to 94% in the next half an hour. There was a significant improvement in the next hour, as the reaction was almost finished in the first hour. The dependence of the initial reaction rate on the substrate, catalyst, and HBpin was investigated. The initial reaction rate ($\Delta[2a]/\Delta t$) for the initial concentration of 1a, Zn(OAc)$_2$ and HBpin catalysts showed a clear positive correlation, suggesting that the catalytic concentration of 2-naphthaldehyde, Zn(OAc)$_2$, and HBpin determined the initial rate (Figure 1b–d).
Scheme 7. The substrate scope of Zn(OAc)₂–catalyzed reduction of imines with HBpin a. a All reactions were performed with substrate 7 (0.2 mmol), Zn(OAc)₂ (1 mol %), HBpin (1.5 equiv.) in THF (2 mL) at 25 °C for 5 h under N₂. Isolated yield.

To have an insight of the reaction mechanism, the kinetic behavior associated with Zn-catalyzed hydrogenation of 2-naphthaldehyde was explored. The hydrogenation proceeded rapidly at the first 0.5 h to give 2a in 88% yield (Figure 1a). The yield was increased to 94% in the next half an hour. There was a significant improvement in the next hour, as the reaction was almost finished in the first hour. The dependence of the initial reaction rate on the substrate, catalyst, and HBpin was investigated. The initial reaction rate (Δ[2a]/Δt) for the initial concentration of 1a, Zn(OAc)₂ and HBpin catalysts showed a clear positive correlation, suggesting that the catalytic concentration of 2-naphthaldehyde, Zn(OAc)₂, and HBpin determined the initial rate (Figure 1b–d).

Figure 1. Kinetic profiles for Zn-catalyzed reduction of 1a: (a) reaction profile of Zn-catalyzed reduction of 2-naphthaldehyde, (b) initial reaction rate against the concentration of 1a, (c) initial reaction rate against the concentration of catalyst of Zn(OAc)₂, (d) initial reaction rate against the concentration of HBpin.

The reduction of 2-naphthaldehyde (1a) with 1.5equiv. of DBpin showed that deuterium was introduced mainly at the C2 positions of naphthalen-2-ylmethanol (92%, Figure 2a). On the basis of the experimental results and literature report [30,37,51], the proposed Zn-catalyzed reduction of carbonyl compounds is shown in Figure 2b. First of all, commercially available Zn(OAc)₂ reacts with HBpin to in situ generate active ZnH(OAc) species [52–54], and the (OAc)Bpin intermediate was observed by ¹¹B NMR, followed by the addition of C=O bonds of substrate 1 or 3 or 5 to provide the corresponding Zn
alkoxide species. Finally, HBpin reproduces active ZnH(OAc) species by the formation of the corresponding boronic esters and provides corresponding alcohols.

Figure 2. Plausible mechanism for the hydroboration of carbonyl compounds: (a) control experiment; (b) proposed mechanism for the Zn-catalyzed regioselective and chemoselective reduction of aldehydes, ketones and α,β-unsaturated aldehydes/ketones.

3. Materials and Methods

3.1. Chemicals and Reagents

Unless otherwise noted, materials and solvents were purchased from Tokyo Chemical Industry, Aldrich Inc., Alfa Aesar, Adamas-beta, and other commercial suppliers and used as received. Zn(OAc)₂ (99.5%) and ZnCl₂ (98%) were purchased from Innochem and used as received. CuCl₂ (98%) and Zn(OTf)₂ (99%) were purchased from Adamas-beta and used as received. CoBr₂ (97%), Mn(CO)₅Bri (98%), CrCl₃ (99%), and NiBr₂ (99%) were purchased from Aldrich Inc. and used as received. FeCl₂ (99.5%) was purchased from Aladdin and used as received. Aldehyde and ketone derivatives were purchased or were prepared according the known procedures.

All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60 N (spherical and neutral, 140–325 mesh), as described by Still. NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. ¹H NMR spectra were recorded at 400 MHz in CDCl₃, or DMSO-d₆ was referenced internally to tetramethylsilane as a standard, and ¹³C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Supplementary Materials: Characterization spectra (¹HNMR and ¹³CNMR) of compounds 2, 4, 6 and 8.

3.2. General Procedure for Zn-Catalyzed Reduction of Aldehydes

A mixture of corresponding aldehyde derivatives (0.2 mmol) and Zn(OAc)₂ (0.002 mmol) was added to a Schlenk tube. Then HBpin (1.5 equiv.) and THF (2 mL) were added by syringe under an atmosphere of nitrogen. The reaction mixture was stirred at 25 °C for 1 h. After quenching with saturated NH₄Cl/H₂O (10 mL), the crude product was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous...
Na₂SO₄ and concentrated under vacuum, and the crude product was purified by column chromatography to afford the desired hydrogenation compound.

3.3. General Procedure for Zn-Catalyzed Reduction of Ketones

A mixture of corresponding ketone derivatives (0.2 mmol) and Zn(OAc)₂ (0.002 mmol) was added to a Schlenk tube. Then HBpin (1.5 equiv.) and THF (2 mL) were added by syringe under an atmosphere of nitrogen. The reaction mixture was stirred at 60 °C for 24 h. After quenching with saturated NH₄Cl/H₂O (10 mL), the crude product was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated under vacuum, and the crude product was purified by column chromatography to afford the desired hydrogenation compound.

3.4. General Procedure for Zn-Catalyzed Reduction of Imines

A mixture of corresponding imines (0.2 mmol) and Zn(OAc)₂ (0.002 mmol) was added to a Schlenk tube. Then HBpin (1.5 equiv.) and THF (2 mL) were added by syringe under an atmosphere of nitrogen. The reaction mixture was stirred at 25 °C for 5 h. After quenching with saturated NH₄Cl/H₂O (10 mL), the crude product was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated under vacuum, and the crude product was purified by column chromatography to afford the desired hydrogenation compound.

4. Conclusions

In summary, we successfully demonstrated a method for the synthesis of various alcohols and related derivatives by using low-cost HBpin with commercially available Zn(OAc)₂ in THF. Good yields and chemoselectivity were obtained for a wide range of substrates, including aldehydes, ketones, α,β-unsaturated aldehydes/ketones, and imines, showing the great versatility and group tolerance. The current protocol operates under mild conditions and enables the reduction of C=O in good yields and selectivity without the requirement of a hydrolysis reagent (acid or base). Mechanistic studies indicated the formation of active ZnH(OAc) species. Further studies on the mechanism and enantioselective reducing ketones and α,β-unsaturated ketones using Zn(OAc)₂/HBpin are undergoing. We believe that the catalytic system is expected to be used for asymmetric hydrogenation of carbonyl compounds.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijms232012679/s1, Characterization spectra (¹HNMR and ¹³CNMR) of compounds 2, 4, 6 and 8.

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