# Organocatalytic hydroboration of carbonyl compounds promoted by choline-based ionic liquids

Barbara Krupa[a,b], Mateusz Nowicki[a], Paweł Huninik[a,b], Jakub Szyling[a] and Jędrzej Walkowiak[a]*

[a]Center for Advanced Technology, Adam Mickiewicz University, Uniwersytetu Poznanskiego 10, 61-614 Poznan, Poland.

[b]Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznanskiego 8, 61-614 Poznan, Poland.

*E-mail: jedrzej.walkowiak@amu.edu.pl

**Abstract:**

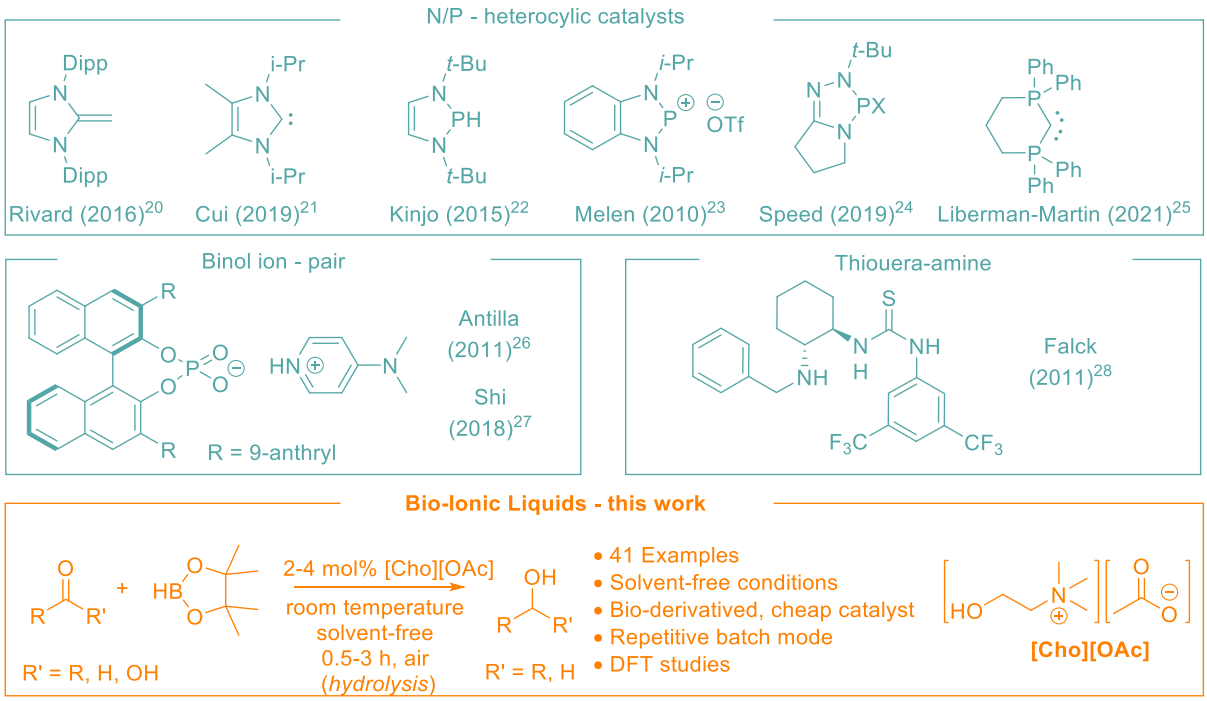
The organocatalytic activity of choline-based ionic liquids in the hydroboration of ketones, aldehydes and carboxylic acids with pinacolborane was investigated. The method employed was based on a simple, inexpensive, biobased, reusable and environmentally friendly [Cho][OAc] catalyst. Detailed studies on catalyst screening, the optimization of reaction conditions, and substrate scope were carried out. [Cho][OAc] showed excellent tolerance to various functional groups and chemoselectivity towards C=O hydroboration, which occurred under mild conditions. Furthermore, it was shown that the reaction can be carried out under repetitive batch modes, allowing effective catalyst recycling and improving process productivity.

**Introduction**

The hydroboration of carbonyl compounds is one of the most important and widely used methods not only for the synthesis of valuable boronate ethers but also for the large-scale preparation of primary or secondary alcohols that can be used, e.g., as buildings blocks for the synthesis of active pharmaceutical ingredients (APIs).[1] The process is an important alternative to the stochiometric reduction of C=O using $NaBH_4$ and $LiAlH_4$ or the application of explosive $H_2$.[2] Hydroboration has been dominated by transition metal-catalysts providing mild reaction conditions, but this very often requires them to be sacrificed in the workup procedures. Recycling them is difficult, and the amount of waste (e.g., some additives, volatile organic solvents) generated during the reaction and separation is often massive.[3] Many inorganic or organometallic compounds such as *n*-BuLi,[4] Li*O*tBu,[5] LiBr,[6] NaH,[7] NaOH,[8] NaO*t*-Bu,[9] $NaHBEt_3$,[10] KF,[11] $K_2CO_3$,[12] MeMgCl,[13] EtOMgCl,[14] and $MgI_2$,[15] have been described as effective hydroboration catalysts. However, Thomas and co-workers, proved that these simple nucleophiles can promote HBpin decomposition and generation of $BH_3$ as a hidden catalyst, responsible for process promotion.[16, 17]

In recent years, the use of organocatalysts has been a growing trend in the field of catalysis.[18, 19] Among several transformations catalyzed by organocatalysts, the hydroboration of carbonyl compounds is limited to a few examples (Scheme 1). Catalysts such as N-heterocyclic olefins (NCO)[20] or N-heterocyclic carbenes (NHC)[21] have proved to be efficient organocatalysts for the hydroboration of ketones and aldehydes, leading to borylated ethers in 5 min to 24 hours with 0.5–5.0 mol% catalyst loading. Similarly, P-containing heterocycles such as 1,3,2-diazaphospholene,[22] phosphenium triflate,[23] triazaphospholene halides (TAP)[24] or carbodiphosphorane[25] have been applied in boron-hydrogen bond addition to C=O bonds. Moreover, the use of binol-derived phosphoric acids[26, 27] or thiourea-amine complex[28] allows the enantioselective reduction of ketones. However, in most cases of

organocatalytic hydroboration of carbonyl compounds, the catalysts were not commercially available, their preparation was not trivial, or the process itself had to be carried out in an inert atmosphere.




**Scheme 1.** Organocatalysts applied in the hydroboration of carbonyl compounds.

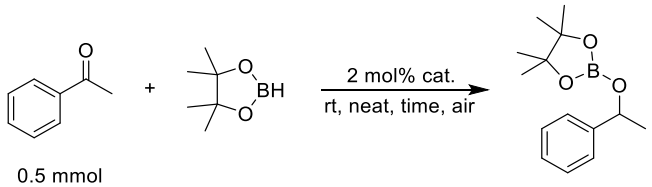
Inspired by the unique and tunable properties of ionic liquids (ILs), and based on our experience with hydroboration reactions,[29-33] in particular our recent work on IL-catalyzed hydroboration of olefins in the presence of [EMPyrr][OTf][34] as a proof concept, we decided to use bio-ionic liquids as potential organocatalysts for the hydroboration of carbonyl compounds. ILs are defined as salts with a melting point below 100 °C.[35] Due to the possibility of changing their properties by anion and cation exchange, low vapor pressure, non-flammability and electrical conductivity, ionic liquids have a wide range of applications, e.g., in organic synthesis and catalysis, electrochemical applications, extraction and separation, and biomass conversion, and are considered to be green solvents for chemical processes.[36-38] Among the various classes of ionic liquids, the bio-ILs have attracted particular attention due to their biodegradability and non-cytotoxicity, as they only contain naturally derived compounds as components.[39, 40] In particular, choline-based ionic liquids, e.g., [Cho][OAc], have been used in various organic transformations, such as Knoevenagel reactions,[41] cyclizations,[42, 43] polymerization/depolymerization,[44-46] etherification[47] and oxidations.[48] Moreover, choline is an essential nutrient for human health,[49] consequently choline-based ionic liquids are considered a safer alternative to the other ILs and can be applied in drug delivery or the synthesis of biomaterials.[50] Despite the extensive use of traditional ionic liquids in hydroboration reactions as solvents or immobilization media for TM-metal catalysts,[29, 31, 51-53] their application as organocatalysts in the hydroboration reaction has been almost entirely neglected.[34, 54-56] Therefore, the search for a novel and selective method for the hydroboration of carbonyl compounds with a simple, cheap, reusable and environmentally-friendly catalyst is of great importance.

Herein, we report for the first time an efficient and chemoselective protocol for the hydroboration of ketones, aldehydes and carboxylic acids by employing simple and cheap bio-ILs [Cho][OAc] in single and repetitive batch mode. The subsequent one-pot hydrolysis process yielded primary and secondary alcohols in high yields.

## Results and discussion

We started our investigations with the screening of several ionic liquids based on choline or simple *n*-alkyl quaternary ammonium cations and carboxylic acids or bis(trifluoromethylsulfonyl)imide anions (**IL1**–**9**) (see ESI, Fig S1) in the model reaction of acetophenone (**1a**) with pinacolborane (**2**). This was carried out under solvent-free conditions at room temperature with 2 mol% catalyst loading. Initially, the hydroboration of the ketone was examined in the absence of an IL to exclude the non-catalytic pathway. After 2 h, only trace conversion of substrate **1a** was observed (Table 1, entry 1). Subsequently, choline-based ILs with various anions were screened as potential organocatalysts in the reduction of carbonyl groups. High yields were obtained for the hydroboration of **1a** with HBpin (**2**) using basic ionic liquids. Almost quantitative yields were observed for choline ionic liquids with both $[OAc]^-$ (**IL1** ) and $[Bz]^-$ (**IL2**) anions (Table 1, entries 2–5). A slightly lower but still satisfactory conversion of **1a** was observed when $[Cho]_2[Oxa]$ (**IL5**) was applied (Table 1, entry 8). Contrary to previous findings, [Cho][TFA] (**IL3**) had a poor catalytic effect (Table 1, entry 6). Similarly, IL with amphoteric [Cho][Oxa] (**IL4**) or the neutral anion $[Cho][NTf_2]$ (**IL6**) showed no catalytic activity (Table 1, entries 7 and 9). Thus, we assumed that the nucleophilicity of the anion plays an important role in the catalytic process.[57] Moreover, it should be noted that excellent selectivity towards **3a** was observed for the hydroboration of acetophenone (**1a**) with **2** in the presence of all tested ILs. The competitive aldol condensation of **1a** promoted by basic ionic liquids was not observed.[58] In the next step of our study, we investigated the influence of the cation on the catalytic activity of acetate-based ionic liquids. Changing the cation from $[Cho]^+$ (**IL1**) to $[TBA]^+$ (**IL7**) resulted in a lower conversion of **1a** (Table 1, entry 10). A similar trend was observed for [TBA][TFA] (Table 1, entry 11). A significant decrease in **1a** conversion was visible when a simple and much smaller tetramethylammonium cation was used (Table 1, entry 12).

**Table 1**. Catalyst screening for the model reaction of acetophenone (**1a**) and pinacolborane (**2**).




0.5 mmol **1a** | **2** | **3a**

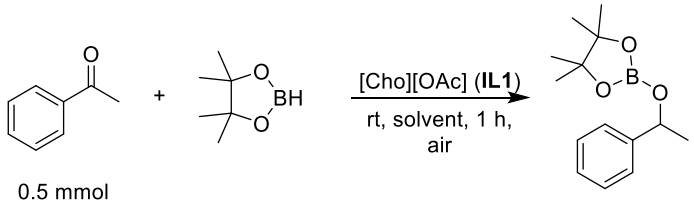
| Entry | Cat. | | Time [h] | Yield of 3a[a)] |
|---|---|---|---|---|
| **1** | - | - | 2 | trace |
| **2** | [Cho][OAc] | **IL1** | 0,5 | 93 |
| **3** | | | 1 | 97 |
| **4** | | | 2 | 99 |
| **5** | [Cho][Bz] | **IL2** | 1 | 97 |
| **6** | [Cho][TFA] | **IL3** | 1 | 20 |
| **7** | [Cho][Oxa] | **IL4** | 1 | 4 |
| **8** | $[Cho]_2[Oxa]$ | **IL5** | 1 | 89 |
| **9** | $[Cho][NTf_2]$[b)] | **IL6** | 2 | 0 |
| **10** | [TBA][OAc] | **IL7** | 2 | 87 |
| **11** | [TBA][TFA][b)] | **IL8** | 2 | 89 |
| **12** | [TBA][OAc] | **IL9** | 2 | 10 |

[a)] Yield of **3a** (= conversion of **1a**) was determined based on GC-MS and $^1$H NMR analyzes; [b)] 8 mol% of catalyst.

Next, we studied the catalytic activity of precursors used for the synthesis of the applied ionic liquids, carboxylic acids (e.g., HOAc, HBz, $H_2$Oxa) and salts (ChoCl, KOAc, and KBz), to verify whether both the cation and the anion of the IL are necessary for its catalytic activity. The hydroboration of **1a**

in the presence of all the carboxylic acids used was not selective and led to a mixture of hydroboration and aldol condensation products. On the other hand, when potassium salts were employed as catalysts, the hydroboration reactions were completely selective to product **3a**, but the yields were significantly lower than for ionic liquid catalysts with the same anions. Choline chloride did not catalyze the reaction even at a high catalyst loading (8 mol%) and prolonged reaction time (18 hours) (for details see ESI, Table S1).

**Table 2**. Optimization of conditions for the model reaction of acetophenone (**1a**) and pinacolborane (**2**)




0.5 mmol
**1a** **2** **3a**

| Entry | HBpin [equiv.] | Solvent | IL1 [mol%] | Yield of 3a [%][a)] |
|---|---|---|---|---|
| 1 | 1.2 | neat | 4 | 97 (97)[b)] |
| 2 | 1.1 | neat | 4 | 95 |
| 3 | 1.0 | neat | 4 | 85 |
| 4 | 1.2 | toluene | 4 | 86 |
| 5 | 1.2 | ethyl acetate | 4 | 85 |
| 6 | 1.2 | THF | 4 | 79 |
| 7 | 1.2 | DCM | 4 | 90 |
| 8[c)] | 1.2 | neat | 4 | 0 |
| 9 | 1.2 | neat | 8 | >99 |
| 10 | 1.2 | neat | 2 | 96 |
| 11 | 1.2 | neat | 1 | 92 |
| 12 | 1.2 | neat | 0.5 | 14 |

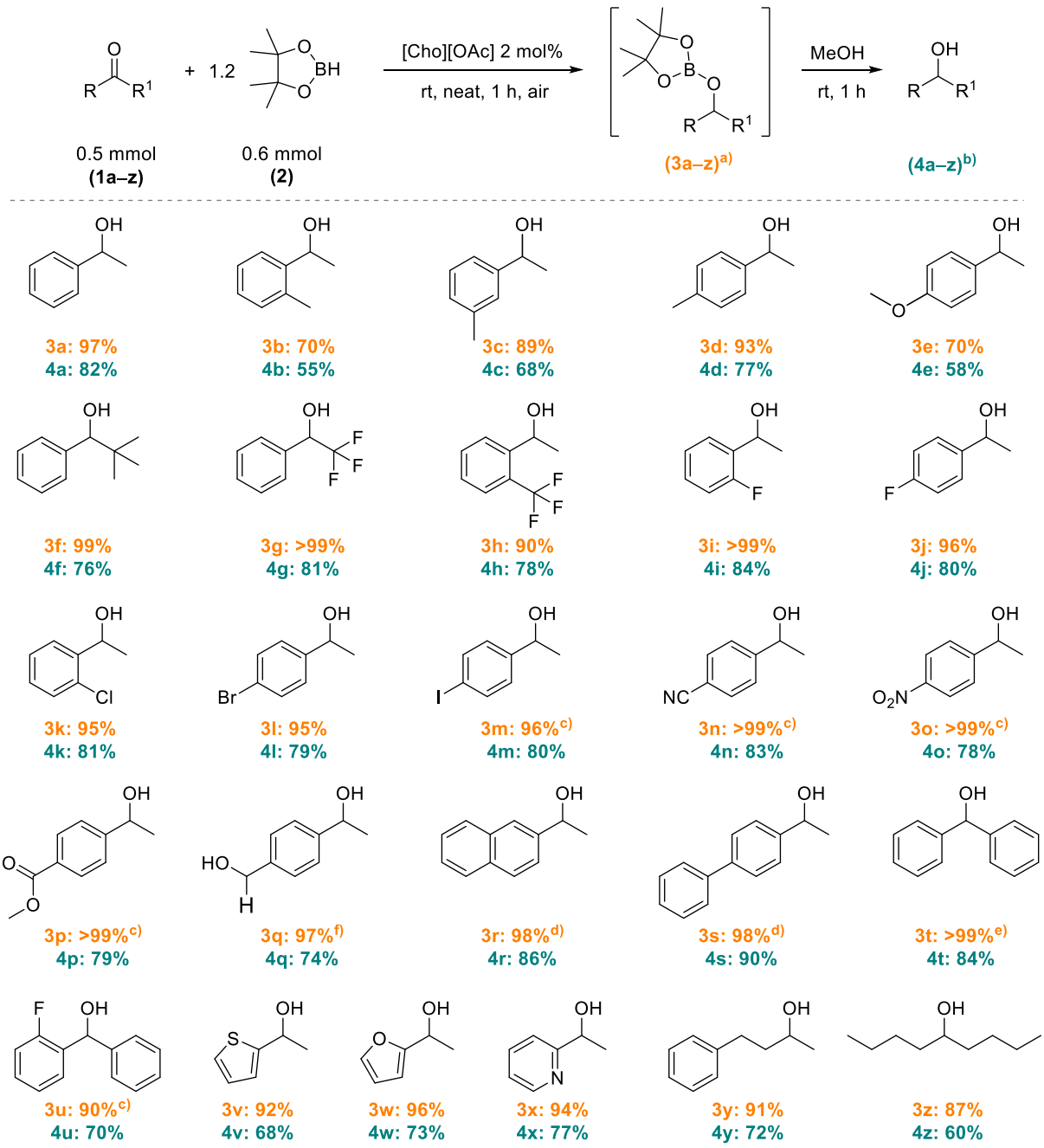
[a)] Yield of **3a** (= conversion of **1a**) was determined based on GC-MS and $^1$H NMR analyzes; [b)] under argon atmosphere. [c)] 20 µL of water was added.

Selecting [Cho][OAc] (**IL1**) as the most active catalyst, we carried out the process optimization (Table 2). Reducing the HBpin excess (1.2 to 1.0 equiv.) resulted in a slight decrease in the yield of **3a** (Table 2, entries 1–3). The process proceeded smoothly in air or in an argon atmosphere (Table 2, entry 1) and under solvent-free conditions. Slightly lower yields of **3a** were observed when toluene, ethyl acetate or THF were used as the reaction medium. A better yield was achieved when DCM was employed as the solvent (Table 2, entries 4–7). Moreover, the effect of the presence of moisture on the reaction efficiency was determined. The addition of 20 µL of water to the reaction mixture completely stopped the process (Table 2, entry 8). Quantitative conversion of **1a** was observed under solvent-free conditions with 8 mol% of **IL1** in 1 h at room temperature (Table 2, entry 9). Reducing the catalyst loading to 2 and 1 mol% resulted in a slight decrease in **1a** conversion, but the further reduction of the catalyst concentration (0.5 mol%) caused a significant drop in reagent conversion after 1 hour (Table 2, entries 10–12).

The optimized reaction conditions were applied for the hydroboration of various ketones (Scheme 2). The yields for borylated ethers (**3b**–**e**) with electron-donating groups were slightly lower than for the model reaction. Replacement of the methyl group in the acetophenone core with the sterically hindered *t*-Bu substituent (**1f**) or the trifluoromethyl group (**1g**) led to an almost quantitative conversion of the substrates. High catalytic activity of **IL1** was also observed for *ortho*- and *meta*-halogen substituted acetophenones (**1h**–**m**). Only for the more crowded -$CF_3$ group in the *ortho*

position (**1h**) was the process efficiency slightly lower (90%). It is worth noting that the [Cho][OAc]-catalyzed hydroboration of ketones possessing nitrile, nitro and ester groups attached to the phenyl ring (**1n**–**p**) was chemoselective, leading only to the reduction of the carbonyl group. However, in the presence of an aldehyde group (**1q**), both groups were reduced when 2.2 equiv. of HBpin (**2**) was applied. Ketones with 2-naphthyl (**1r**) or 4-biphenyl (**1s**) substituents and benzophenone (**1t**) gave an almost quantitative or quantitative conversion when 2 equiv. of **2** were used to provide sufficient mixing of the reaction mixture. A very good result was also obtained for the hydroboration of *o*-fluorobenzophenone (**1u**) under standard reaction conditions, but the conversion of **1u** was not complete. Subsequently, a series of heterocyclic ketones (**3v**–**x**) containing S, O and N atoms were tested, leading to hydroboration products with excellent yields. The developed protocol was also effective for the reaction of aliphatic ketones such as 4-phenylbutan-2-one (**1y**) or 5-nonanone (**1z**), with HBpin (**2**) easily providing the corresponding products with high yields (87–91%). However, 3'-aminoacetophenone, 2-acetylpyrrole and 4,4'-dibromobenzophenone could not be converted to hydroboration products.

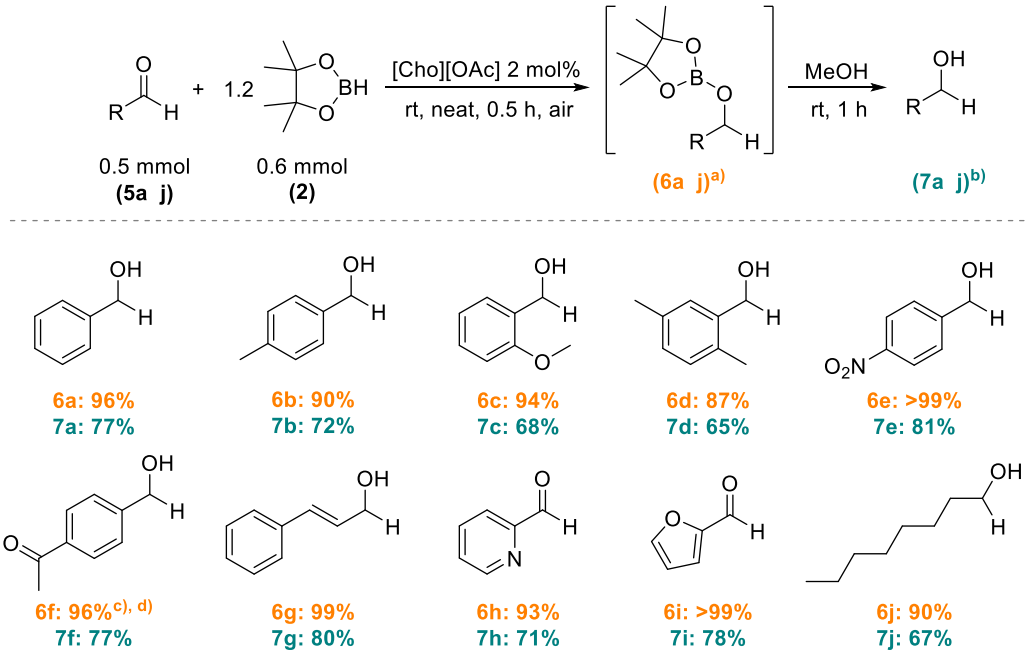
All O-borylated ethers (**3a**–**z**) were readily converted to the corresponding alcohols (**4a**–**z**) in a one-pot procedure *via* simple hydrolysis with methanol, without the isolation of borylated intermediates (**3a**–**z**). This approach eliminated a time-consuming separation step of the intermediates and reduced the amount of volatile organic solvents used for additional purification procedures. The final products were purified by column chromatography. All obtained products **3** and **4** were characterized by nuclear magnetic resonance ($^1$H NMR) and mass spectroscopy (GC-MS).




**Scheme 2.** Hydroboration of ketones (**1a–z**) catalyzed by [Cho][OAc]. [a] Yields were based on $^1$H NMR analysis. [b] Isolated yields; [c] HBpin 1.5 equiv.; [d] HBpin 2.0 equiv.; [e] HBpin 4.0 equiv.; [f] HBpin 2.2 equiv.

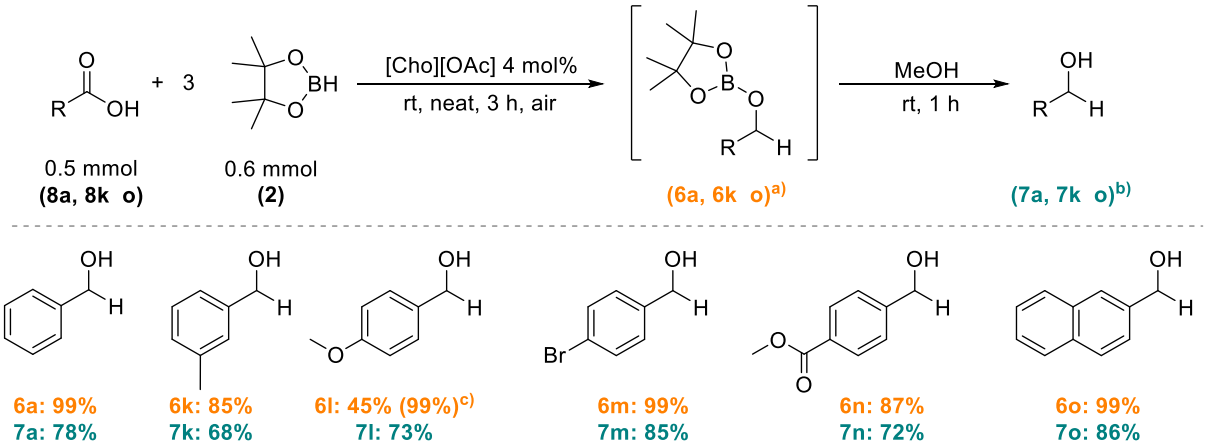
The successful organocatalytic hydroboration of ketones prompted us to extend the scope of the reagents to include other carbonyl compounds (aldehydes and acids). The process optimization is presented in ESI (Table S3).[59] A very high yield was observed in the hydroboration of benzaldehyde (**5a**) with pinacolborane (**2**) after just 30 minutes in analogous reaction conditions for ketones, showing the higher reactivity of aldehydes. Various aldehydes (**5**) were converted to the corresponding O-borylated ethers (**6**) and primary alcohols (**7**) in a one-pot procedure using the same process conditions (Scheme 3). The effect of electron-donating and electron-withdrawing substituents is similar to that observed in the hydroboration of ketones. For aromatic aldehydes with methyl and methoxy groups (**5b–d**), lower yields of the expected products were observed. On the other hand, compounds with electron-withdrawing groups, such as nitro or acetyl (**6e–f**) had a positive effect on reaction yields. However, to

ensure chemoselectivity towards the aldehyde group in 4-acetylbenzaldehyde (**6f**), 1.02 equiv. of HBpin was used. Furthermore, for cinnamaldehyde (**5g**) only the reduction of the C=O bond was observed whereas the C=C bond was unreactive. The heteroaromatic and aliphatic substrates (**5h–j**) could also be successfully applied, furnishing the corresponding boryl ethers and alcohols with excellent yields.




**Scheme 3.** Hydroboration of aldehydes (**5a–j**) catalyzed by [Cho][OAc]. [a] Yields were based on $^1$H NMR analysis; [b] Isolated yields; [c] 45 min; [d] 1.02 equiv. of HBpin.

Reduction of carboxylic acids with pinacolborane followed by hydrolysis with methanol gave primary alcohols, similar to aldehydes (Scheme 4). However, an extension of the reaction time to 3 hours and increased catalyst loading to 4 mol% were necessary to achieve full conversion of benzoic acid (**8a**) (see ESI, Table S5). The benzoic acids substituted with electron-donating methyl and methoxy (**8k–l**) required a much longer reaction time (18 h) to obtain the satisfactory conversion of these reagents. On the other hand, carboxylic acids with electron-withdrawing substituents, e.g., bromo (**8m**) or bulky 2-naphthoic acid (**8o**), reacted with HBpin with almost quantitative yields. High efficiency and chemoselectivity towards the carboxyl group in the presence of the ester group was observed for substrate **8n**.




**Scheme 4.** Substrate scope for hydroboration of carboxylic acids (**8a** and **8k–o**) catalyzed by [Cho][OAc]. [a)] Yields were based on $^1$H NMR analysis; [b)] Isolated yields; [c)] 18 h.

In the next stage of our study, bearing in mind green chemistry principles and our previous research on catalyst recycling in the synthesis of organoboron compounds,[31-33, 60-62] we tested the possibility of recycling the catalyst, carrying out our reaction in a repetitive batch mode. Hydroboration of acetophenone (**1a**) was performed under standard conditions (1 h, rt, 2 mol% of **IL1**, neat). After the process, *n*-heptane was added to the post-reaction mixture, causing precipitation of [Cho][OAc]. The catalyst was washed three times (3 x 2 mL) with *n*-heptane to remove the product and then dried under vacuum for one hour to evaporate the residual of the solvent before a new portion of substrates was added. This strategy allowed us to efficiently reuse **IL1** up to 5 times. After the 5$^{th}$ cycle, the product yield dropped drastically (see ESI, Figure S2). This probably happened due to the mechanical loss of the suspended catalyst during the extraction process, which was visible from the milky color of the filtrate. To minimize the effect of accidental sediment removal from the reaction vessel, it was decided to increase the catalyst loading in the next experiment. When an 8 mol% catalyst was used, 13 runs were carried out with stable and high reagent conversion (Figure 1). After that, the catalyst was transferred to a vial and exposed to ambient conditions for 6 weeks. In the 14th and 15$^{th}$ runs, a high conversion of **1a** (72 and 81%) was observed; however, product **3a** was formed in 53–75% yield. This experiment showed that catalyst aging has a negative influence on process selectivity.

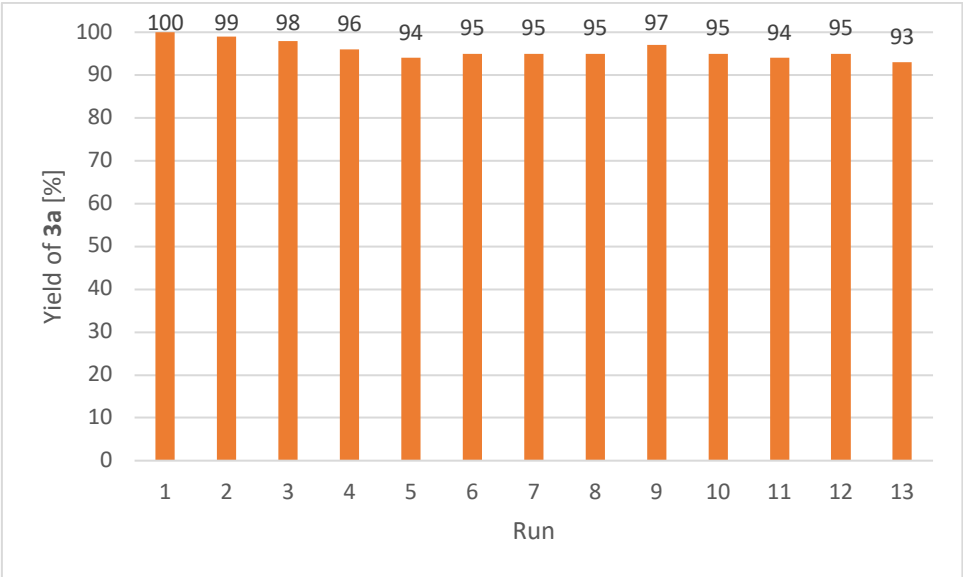



**Figure 1**. The repetitive batch hydroboration of **1a** (1 mmol) with **2** (1.2 mmol) using 8 mol% of [Cho][OAc] at room temperature for 1 h in air. Yields of **3a** were determined by GC-MS analysis.

## Conclusions

In conclusion, [Cho][OAc] is an efficient, inexpensive and bio-based organocatalyst for the hydroboration of various carbonyl compounds (aldehydes, ketones and carboxylic acids). The process occurred very quickly (30 min for aldehydes, 1 hour for ketones and 3 hours for carboxylic acids) under mild conditions in air atmosphere. This metal-free hydroboration is feasible for aromatic compounds with electron-donating and electron-withdrawing substituents, and also with sterically hindered, heteroaromatic and aliphatic reagents. The system based on [Cho][OAc] is tolerant to many functional groups (e.g., nitro, nitrile, ester, and acetyl groups). Moreover, the recyclability of the catalyst was successfully demonstrated, running up to 13 cycles with excellent reaction yields. This result, as well as the elimination of transition metal catalysts, which are commonly used in this transformation, and the reduction of the amount of organic solvents are in line with the rules of green chemistry. Studies to determine the mechanism of the reaction are under investigation and will be published soon.

## Acknowledgments

The authors thank for the financial support from the National Science Centre (Poland), grant no. UMO-2019/34/E/ST4/00068.

## References

1. J. Magano and J. R. Dunetz, *Org. Process Res. Dev.*, 2012, **16**, 1156-1184.
2. J. Seyden-Penne, *Reductions by the Alumino- and Borohydrides in Organic Synthesis*, Wiley-VCH, Inc, 1997.
3. S. J. Geier, C. M. Vogels, J. A. Melanson and S. A. Westcott, *Chem. Soc. Rev.*, 2022, **51**, 8877-8922.
4. S. J. Yang, A. K. Jaladi, J. H. Kim, S. Gundeti and D. K. An, *Bull. Korean Chem. Soc.*, 2019, **40**, 34-38.
5. J. H. Kim, A. K. Jaladi, H. T. Kim and D. K. An, *Bull. Korean Chem. Soc.*, 2019, **40**, 971-975.
6. H. Kim, H. L. Shin, J. Yi, H. S. Choi, J. H. Lee, H. Hwang and D. K. An, *Bull. Korean Chem. Soc.*, 2020, **41**, 1009-1018.
7. W. K. Shin, H. Kim, A. K. Jaladi and D. K. An, *Tetrahedron*, 2018, **74**, 6310-6315.
8. Y. Wu, C. Shan, J. Ying, J. Su, J. Zhu, L. L. Liu and Y. Zhao, *Green Chem.*, 2017, **19**, 4169-4175.
9. I. P. Query, P. A. Squier, E. M. Larson, N. A. Isley and T. B. Clark, *J. Org. Chem.*, 2011, **76**, 6452-6456.
10. K. Kuciński and G. Hreczycho, *Green Chem.*, 2019, **21**, 1912-1915.
11. K. Kuciński and G. Hreczycho, *Eur. J. Org. Chem.*, 2020, **2020**, 552-555.
12. D. H. Ma, A. K. Jaladi, J. H. Lee, T. S. Kim, W. K. Shin, H. Hwang and D. K. An, *ACS Omega*, 2019, **4**, 15893-15903.
13. W. Wang, K. Lu, Y. Qin, W. Yao, D. Yuan, S. A. Pullarkat, L. Xu and M. Ma, *Tetrahedron*, 2020, **76**, 131145.
14. H. J. Han, H. T. Kim, J. Kim, A. K. Jaladi and D. K. An, *Tetrahedron*, 2023, **142**, 133500.
15. J. Shi, M. Luo, X. Zhang, T. Yuan, X. Chen and M. Ma, *Org. Biomol. Chem.*, 2023, **21**, 3628-3635.
16. A. D. Bage, T. A. Hunt and S. P. Thomas, *Org. Lett.*, 2020, **22**, 4107-4112.
17. A. D. Bage, K. Nicholson, T. A. Hunt, T. Langer and S. P. Thomas, *ACS Catal*, 2020, **10**, 13479-13486.
18. V. d. G. Oliveira, M. F. d. C. Cardoso and L. d. S. M. Forezi, *Catalysts*, 2018, **8**, 605.
19. I. R. Shaikh, *J. Catal.*, 2014, **2014**.

20. C. Hering-Junghans, I. C. Watson, M. J. Ferguson, R. McDonald and E. Rivard, *Dalton Trans.*, 2017, **46**, 7150-7153.
21. T. Li, J. Zhang and C. Cui, *Chin. J. Chem.*, 2019, **37**, 679-683.
22. C. C. Chong, H. Hirao and R. Kinjo, *Angew. Chem.*, 2015, **54**, 190-194.
23. D. M. C. Ould, T. T. P. Tran, J. M. Rawson and R. L. Melen, *Dalton Trans.*, 2019, **48**, 16922-16935.
24. C.-H. Tien, M. R. Adams, M. J. Ferguson, E. R. Johnson and A. W. H. Speed, *Org. Lett.*, 2017, **19**, 5565-5568.
25. C. R. Aversa-Fleener, D. K. Chang and A. L. Liberman-Martin, *Organometallics*, 2021, **40**, 4050-4054.
26. Z. Zhang, P. Jain and J. C. Antilla, *Angew. Chem.*, 2011, **50**, 10961-10964.
27. Y. Zhang, L. He and L. Shi, *Adv. Synth. Catal.*, 2018, **360**, 1926-1931.
28. D. R. Li, A. He and J. R. Falck, *Org. Lett.*, 2010, **12**, 1756-1759.
29. B. Krupa, J. Szyling and J. Walkowiak, *Sci. Rep.*, 2023, **13**, 20237.
30. T. Sokolnicki, J. Szyling, A. Franczyk and J. Walkowiak, *Adv. Synth. Catal.*, 2020, **362**, 177-183.
31. J. Szyling, A. Franczyk, K. Stefanowska, H. Maciejewski and J. Walkowiak, *ACS Sustain. Chem. Eng.*, 2018, **6**, 10980-10988.
32. J. Szyling, A. Franczyk, K. Stefanowska, M. Klarek, H. Maciejewski and J. Walkowiak, *ChemCatChem*, 2018, **10**, 531-539.
33. J. Szyling, A. Franczyk, K. Stefanowska and J. Walkowiak, *Adv. Synth. Catal.*, 2018, **360**, 2966-2974.
34. P. Huninik, J. Szyling, A. Czapik and J. Walkowiak, *Green Chem.*, 2023, **25**, 3715-3722.
35. L. K. S. Gujjala, D. Kundu, D. Dutta, A. Kumar, M. Bal, A. Kumar, E. Singh, R. Mishra, S. Kumar and D.-V. N. Vo, J. Mol. Liq., 2024, **396**, 123896.
36. M. Eqbalpour, A. Andooz, E. Kowsari, S. Ramakrishna, Z. A. Cheshmeh and A. Chinnappan, *WIREs Energy and Environment*, 2023, **12**, e473.
37. G. Kaur, H. Kumar and M. Singla, *J. Mol. Liq.*, 2022, **351**, 118556.
38. J. Bailey, E. L. Byrne, P. Goodrich, P. Kavanagh and M. Swadźba-Kwaśny, *Green Chem.*, 2024, **26**, 1092-1131.
39. I. F. Mena, E. Diaz, J. Palomar, J. J. Rodriguez and A. F. Mohedano, *Chemosphere*, 2020, **240**, 124947.
40. Y. Fukaya, Y. Iizuka, K. Sekikawa and H. Ohno, *Green Chem.*, 2007, **9**, 1155-1157.
41. A. Zhu, R. Liu, L. Li, L. Li, L. Wang and J. Wang, *Catal. Today*, 2013, **200**, 17-23.
42. A. Zhu, D. Fan, Y. You, H. Wang, Y. Zhao, J. Wang and L. Li, *Green Chem.*, 2022, **24**, 8466-8476.
43. H. Hu, F. Qiu, A. Ying, J. Yang and H. Meng, *Int. J. Mol. Sci.,* 2014, **15**, 6897-6909.
44. W. Zheng, C. Liu, X. Wei, W. Sun and L. Zhao, *Chem. Eng. Sci.*, 2023, **267**, 118329.
45. D. Bura, L. Pedrini, C. Trujillo and S. J. Connon, *RSC Sustain.*, 2023, **1**, 2197-2201.
46. Y. Liu, X. Yao, H. Yao, Q. Zhou, J. Xin, X. Lu and S. Zhang, *Green Chem.*, 2020, **22**, 3122-3131.
47. S. Chen, R. Liu, Y. Li, R. Zhang, C. Zhao, H. Tang, C. Qiao and S. Zhang, *Catal. Commun.*, 2017, **96**, 69-73.
48. A. J. Kunov-Kruse, P. L. Thomassen, A. Riisager, S. Mossin and R. Fehrmann, *Chem. Eur. J.*, 2016, **22**, 11745-11755.
49. S. H. Zeisel and K.-A. da Costa, *Nutr. Rev.*, 2009, **67**, 615-623.
50. X. Li, N. Ma, L. Zhang, G. Ling and P. Zhang, *Int. J. Pharm.*, 2022, **612**, 121366.
51. S. Aubin, F. Le Floch, D. Carrié, J. P. Guegan and M. Vaultier, in *Ionic Liquids*, American Chemical Society, 2002, vol. 818, ch. 26, pp. 334-346.
52. A. M. Scurto and W. Leitner, *Chem. Commun.*, 2006, 3681-3683.
53. Y. Zhu, S. H. A. Jang, Y. H. Tham, O. B. Algin, J. A. Maguire and N. S. Hosmane, *Organometallics*, 2012, **31**, 2589-2596.
54. U. Kusari, P. J. Carroll and L. G. Sneddon, *Inorg. Chem.*, 2008, **47**, 9203-9215.
55. Z. Lin, Z. Zhang, J. Mai, Z. Huang, S. Lv, D. Wu, F. Xie and B. Li, *ACS Sustain. Chem. Eng.*, 2022, **10**, 13742-13749.

56. Y. C. A. Sokolovicz, O. Nieto Faza, D. Specklin, B. Jacques, C. S. López, J. H. Z. dos Santos, H. S. Schrekker and S. Dagorne, *Catal. Sci. Technol.*, 2020, **10**, 2407-2414.
57. D. Xu, Q. Yang, B. Su, Z. Bao, Q. Ren and H. Xing, *The Journal of Physical Chemistry B*, 2014, **118**, 1071-1079.
58. P. McNeice, P. C. Marr and A. C. Marr, *Catal. Sci. Technol.*, 2021, **11**, 726-741.
59. M. L. Shegavi and S. K. Bose, *Catal. Sci. Technol.,* 2019, **9**, 3307-3336.
60. J. Szyling, J. Walkowiak, T. Sokolnicki, A. Franczyk, K. Stefanowska and M. Klarek, *J. Catal.*, 2019, **376**, 219-227.
61. J. Szyling, T. Sokolnicki, A. Franczyk and J. Walkowiak, *Catalysts*, 2020, **10**, 762.
62. M. Ludwiczak, J. Szyling, A. Garbicz, T. Sokolnicki, J. Pyziak and J. Walkowiak, *Inorg. Chem.*, 2020, **59**, 17555-17564.