Catalyst-Free Approach for Hydroboration of Carboxylic Acids under Mild Conditions

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ABSTRACT: Herein, we present a facile method for deoxygenative hydroboration of a broad range of carboxylic acids under very mild conditions. The most striking feature of this attractive hydroboration is that this elusive and challenging transformation was realized without catalyst and solvent. The investigation of solvent effect showed that tetrahydrofuran was also suitable for this kind of reaction. Moreover, a successful gram-scale trial may provide a very promising toolkit for carboxylic acid reduction at a large scale.

INTRODUCTION

Alcohols are basic building blocks in organic synthesis because of their versatile reactivity for the generation of a wide range of products for fine chemical, agrichemical, and pharmaceutical industries.1 Reduction of carboxylic acids into corresponding alcohols is a straightforward procedure. Traditionally, two classical reduction methods utilizing stoichiometric quantities of strong metal hydride/borane agents and pressurized hydrogen gas have been developed.2−4 Although metal hydrides/boranes are common and reliable, safe handling of highly reactive or even pyrophoric agents would be a major concern. Moreover, the disposal of large amounts of waste stream may pose a cumbersome environment problem.2a,b

Hydrogen gas reduction represents an atom-efficient procedure. However, intrinsic extreme flammability of hydrogen gas, the harsh requirement of special high-pressure and high-temperature withstanding equipment, and the lack of reactivity toward certain substrates prohibit its widespread application.4a−a In this regard, to develop a more convenient alternative protocol for the reduction of biomass-abundant carboxylic acids into alcohols is of significant importance for the valorization of carbon feedstock.

Carbonyl hydroboration is a key and prevalent transformation in organic chemistry because it offers a useful functional group manipulation method to obtain corresponding alcohols via hydrolysis from boric esters in both academic and industrial perspectives. During the past years, a lot of progress has been made in carbonyl hydroboration involving aldehydes and ketones by employing a variety of catalysts including main group elements,5−11 transition metals,12−22 and lanthanide complexes.23,24 Interestingly, catalyst- and solvent-free methodologies for the hydroboration of aldehydes were reported by Hreczycho’s group recently.25 Among these well-developed hydroboration manifolds, it is not difficult to find that the research concerning the hydroboration of carboxylic acids is seriously lagging behind that related to carbonyl counterparts. Only a few examples have been covered to date.26,27 Very recently, Gunanathan and co-workers reported an efficient deoxygenative hydroboration of carboxylic acids catalyzed by a ruthenium complex for both aromatic and aliphatic carboxylic acids under neat conditions.26 Later, Leitner’s and Maji’s groups reported that manganese complexes could enable the reduction of a wide range of carboxylic acids with low catalyst loadings under mild conditions, respectively.27 Almost at the same time, our group archived a very interesting patent discovery regarding the deoxygenative hydroboration of carboxylic acids under catalyst- and solvent-free conditions.28 Soon, in the course of preparation of this work, we noticed that Panda’s team also documented similar findings.29 On the one hand, in the continuation of our group’s work on the hydroboration of various unsaturated carbonyl, imine, and alkyne compounds,30 on the other hand, to further broaden the substrate scope of our carboxylic acid hydroboration patent and exploring the potential scalability in commercial scale, we would like to present this work for the direct hydroboration of pinacolborane (HBpin) toward carboxylic acids without catalyst under very mild conditions.

RESULTS AND DISCUSSION

We began our investigation by adopting HBpin and benzoic acid as modular substrates.1H NMR was used to monitor the reaction progress and representative results are displayed in Table 1. Initially, we were gratified that 85% deoxygenative hydroboration product was obtained with a molar ration of 1:3 (benzoic acid/HBpin) in catalyst- and solvent-free manners in...
suitable solvent conditions: homogeneous reaction and mitigation of safety concern in neat reaction.\textsuperscript{31} Further, a very detailed investigation by using dioxane as a solvent was examined for inspecting the possible toxic effect of solvent on this reaction. Interestingly, the reactivity in dioxane dropped down sharply when increasing the solvent amount (entries 15–18). Noticeably, trace amount of desired product was detected once 500 \( \mu \text{L} \) dioxane was added to the reaction mixture. On the basis of above laboratory trials and in consideration of the green chemistry principle, the optimized reaction condition was defined as a reactant molar ratio of 1:3.3 and solvent-free under ambient temperature. To facilitate the complete transformation of the subsequent substrates selected below, the reaction time for most aromatic carboxylic acid substrates was set at 12 h in conformity with entry 7 in Table 1.

With the optimized reaction conditions in hand, the applicability of this promising transformation with a broad range of carboxylic acids was exploited. Typical results are listed in Table 2. We are delighted that all selected commercially available aromatic and aliphatic carboxylic acids have been successfully transformed into targeted deoxygenative hydroboration products with satisfactory to excellent yields based on \(^1\text{H} \) NMR analysis. As shown in Table 2, under solvent-free condition, either the carboxylic acids with electron-withdrawing group, \( p\)-F, \( o\)-Br, \( p\)-I, and \( m\)-Br (1b–1f), or electron-donating group, \( p\)-Bu, \( p\)-OEt, and \( o\)-OMe (1g–1i), could afford quantitative yields of borate esters at ambient temperature in 12 h. Inspiringly, the catalyst- and solvent-free systems showcased good tolerability with functionality-carboxylic acids. For example, \( m\)-NO\(_2\) and \( p\)-CN benzoic acids accomplished 98 and 81\% yields, respectively (1j and 1k). Remarkably, 1-naphthoic acid also achieved a full conversion (1l). It is worth pointing out that no hydroboration product was detected for 6-Br-2-naphthoic acid; nevertheless, 99\% conversion was obtained by adjusting the temperature to 60 °C (1m). This phenomenon may be attributed to the slighter reaction activity of the \( \alpha \) position than that of the \( \beta \) position of the naphthalene cycle. Subsequently, we shifted our interest to aliphatic carboxylic acids, as this transformation is of enormous potential for the valorization of nonfossil feedstocks. In general, the hydroboration of aliphatic acids is more challenging than those of aromatic acids.\textsuperscript{27a} In our catalyst- and solvent-free systems, all selected low- to medium-chain aliphatic carboxylic acids underwent smooth hydroboration conversion, demonstrating a competent capability of aliphatic carboxylic acids to be reduced to pertinent alkyl borate esters (1p–1y). Noticeably, hydroboration of aliphatic acids was more effective as shortened reaction periods were evidenced. For example, within 1 h, 97\% conversion was finished for acetic acid (1t). Octodecanoic acid, a biologically available long-chain fatty acid, could offer quantitative conversion within 6 h (1y). It is presumed that the more excellent performance of the aliphatic acids in comparison to those of aromatics may be due to the better solubility of aliphatic acids, which provides the space for reaction homogeneity. Remarkably, formic acid gave 99\% yield under room temperature within 6 h, showing a much higher reactivity in comparison with the 29% yield in the reported system.\textsuperscript{27a} Diacids such as \( \text{O}-\text{carboxyphenylacetic} \) and adipic acids also achieved satisfactory outcomes (1n and 1o). Apart from the reported substrates by Panda and co-workers,\textsuperscript{29} a further broad range of substrates were proven to be applicable for this transformation, affirming that this catalyst-
free approach is suitable for carboxylic acid substrates with structural diversity. As mentioned before, the resultant borates could be derivatized into alcohols via hydrolysis. A handful of representative boric esters were selected to undergo hydrolysis to afford the corresponding alcohols. As expected, all boric esters presented in Table 3 were successfully hydrolyzed with satisfactory yields of related primary alcohols.

Furthermore, intermolecular chemical selectivity by using benzoic acid and methyl benzoate or benzyl benzoate was explored (Scheme 1). Under our current reaction conditions, the reaction exhibited exclusive chemical selectivity toward carboxylic acid with the yield of 99%, whereas methyl benzoate or benzyl benzoate remained intact.

In our kinetics studies, the empirical rate law for carboxylic acid hydroboration was monitored and determined by $^1$H NMR spectroscopy. Representative first-order linear plots were found in [carboxylic acid] and [HBpin] (eq 1). Details of kinetics are displayed in the Supporting Information (Figure S6A,B).

$$\text{rate} = k[\text{carboxylic acid}]^1[\text{HBpin}]^1$$  (1)

In addition, a gram-scale experiment was performed under the same solvent-free condition. Interestingly, at a molar ratio of

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### Table 2. Hydroboration of Various Carboxylic Acids with HBpin$^c$

| Product | Yield$^b$ (%) | Product | Yield$^b$ (%) | Product | Yield$^b$ (%) |
|---------|--------------|---------|--------------|---------|--------------|
| 1a      | 99$^c$       | 1j      | 98           | 1s      | 99$^c$       |
| 1b      | 99           | 1k      | 81$^c$       | 1t      | 97$^c$       |
| 1c      | 99           | 1l      | 99           | 1u      | 99$^a$       |
| 1d      | 99           | 1m      | 99$^c$       | 1v      | 97$^h$       |
| 1e      | 99           | 1n      | 92$^c$       | 1w      | 99$^b$       |
| 1f      | 99           | 1o      | 99$^c$       | 1x      | 99$^c$       |
| 1g      | 99           | 1p      | 99           | 1y      | 99$^c$       |
| 1h      | 98           | 1q      | 99           |         |              |
| 1i      | 99           | 1r      | 99           |         |              |

$^a$Condition: carboxylic acid (0.5 mmol) and HBpin (1.65 mmol) were stirred for 12 h. $^b$Yields were determined by $^1$H NMR spectroscopy using mesitylene as an internal standard. $^c$The reaction was conducted for 6 h. $^d$The reaction was conducted for 24 h. $^e$The reaction was conducted at 60 °C for 12 h. $^f$HBpin (3.5 mmol) was used. $^g$The reaction was conducted for 1 h. $^h$The reaction was conducted for 4 h.

### Table 3. Hydrolysis of Boric Esters to Alcohols$^c$

| Reaction conditions: carboxylic acid (1.0 mmol) and HBpin (3.3 mmol) were stirred at rt for 12 h; isolated yields and products were purified by column chromatography.

| Product | Yield (%) |
|---------|-----------|
| 2a      | 93%       |
| 2b      | 92%       |
| 2c      | 90%       |
| 2d      | 91%       |

$^c$Reaction conditions: carboxylic acid (1.0 mmol) and HBpin (3.3 mmol) were stirred at rt for 12 h; isolated yields and products were purified by column chromatography.
15 (benzoic acid)/49.5 (HBpin) in 12 h, nearly a quantitative hydroboration product was obtained (Scheme 2). This demonstration may provide a promising pathway for the hydroboration of carboxylic acids at a large scale.

Scheme 2. Large-Scale Reaction of Carboxylic Acid with HBpin

Except the mechanism of this catalyst-free system described in the literature,29 we proposed another possible reaction pathway according to the reported documents.25−27 As shown in Scheme 3, a Lewis adduct could be formed in the course of the reaction. An aldehyde intermediate was generated accompanied by boron ether releasing, and the subsequent process was similar to that of the known literature.25 A thorough experimental demonstration of the mechanism study and more interesting findings related to hydroboration transformation are being undertaken in our laboratory.

■ CONCLUSIONS
In summary, we have disclosed catalyst- and solvent-free protocols for the deoxigenative hydroboration under very mild conditions. This transformation with high efficiency has been realized with a wide range of aromatic and aliphatic carboxylic acids. Excellent chemical selectivity and good functional group tolerance were also achieved. A gram-scale trial proved the feasibility and scalability of this protocol without compromising the reaction conversion rate.

■ EXPERIMENTAL SECTION

General Methods. All reactions were carried out in a glovebox under nitrogen atmosphere. Hexane, THF, toluene, and 1,4-dioxane were dried by heating to reflux over sodium benzenophene ketyl and then distilled under nitrogen prior to use. Chemicals were purchased from Acros, Sigma-Aldrich, Alfa-Aesar, and Spectrochem, and used without further purification. Mesitylene was used for the clarification of product yield. The progress of reactions was monitored by Bruker AV-400 (1H: 400 MHz, 13C: 101 MHz) using CDCl3 as the solvent.

General Procedure for Catalytic Hydroboration of Carboxylic Acids. In the glovebox, carboxylic acid (0.5 mmol) and pinacolborane (1.65 mmol) were added in a reaction vial with a magnetic bead. The reaction mixture was allowed to run at room temperature for 1−12 h. Then, the reaction was removed from the glovebox and mesitylene (0.5 mmol) was added as an internal standard. The reaction mixture was subjected to 1H NMR spectroscopy to confirm the yield in alkyl boric ester.

Spectral Data for Boric Esters.

2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a).23a Colorless oil; 1H NMR (400 MHz, CDCl3) δ 7.33−7.21 (m, 5H, ArCH), 4.90 (s, 2H, CH2OCH2), 1.24 (s, 36H, CH3OBOpin & pinBOBpin); 13C NMR (101 MHz, CDCl3) δ 138.68 (quat-C, ArC), 127.76 (ArCH), 126.85 (ArCH), 126.20 (ArCH), 82.54 (quat-C, pinBOBpin), 82.48 (quat-C, OBpin), 66.15 (CH2, OCH2), 24.07 (CH3, OBpin), 23.96 (CH3, pinBOBpin).

2-((4-Fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1b).23b Colorless oil; 1H NMR (400 MHz, CDCl3) δ 7.31−7.28 (t, 2H, J = 8.4 MHz, ArCH), 7.00−6.96 (t, 2H, J = 8.7 MHz, ArCH), 4.85 (s, 2H, OCH2), 1.25 (s-overlap, 36H, CH3, OBpin & pinBOBpin); 13C NMR (101 MHz, CDCl3) δ 161.64 (d,quat-C, C-F, ArC), 134.46 (d,quat-C, C-CH2O, ArC), 128.11 (d, ArCH), 114.54 (d, ArCH), 82.53 (quat-C, pinBOBpin), 82.50 (quat-C, OBpin), 65.49 (CH2, OCH2), 24.02 (CH3, OBpin), 23.91 (CH3, pinBOBpin).

2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1c). Colorless oil; 1H NMR (400 MHz, CDCl3) δ 7.42−7.40 (d, 2H, J = 8.4 MHz, ArCH), 7.20−7.18 (d, 2H, J = 8.5 MHz, ArCH), 4.84 (s, 2H, OCH2), 1.24 (s, 36H, CH3, OBpin & pinBOBpin); 13C NMR (101 MHz, CDCl3) δ 137.68 (quat-C, C-CH2, ArC), 130.83 (ArCH), 120.65 (quat-C, C-Br, ArC), 82.63 (quat-C, pinBOBpin), 82.57 (quat-C, OBpin), 65.42 (CH2, OCH2), 24.04 (CH3, OBpin), 23.93 (CH3, pinBOBpin).

2-((4-Iodophenethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1d).27a Colorless oil; 1H NMR (400 MHz, CDCl3) δ 7.63−7.61 (d, 2H, J = 8.1 MHz, ArCH), 7.08−7.06 (d, 2H, J = 8.0 MHz, ArCH), 4.84 (s, 2H, OCH2), 1.25 (s, 36H, CH3, OBpin & pinBOBpin); 13C NMR (101 MHz, CDCl3) δ...
138.44 (quat-C, C=CH₂, ArC), 136.80 (ArCH), 128.11 (ArCH), 92.22 (quat-C, C-I, ArC), 82.64 (quat-C, OBPin), 82.59 (quat-C, pinBOBpin), 65.49 (CH₂, OCH₂), 24.06 (CH₃, OBPin), 23.95 (CH₃, pinBOBpin).

2-[(2-Bromobenzyl)oxy]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1f). Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.53–7.49 (t, 2H, J = 6.8 MHz, ArCH), 7.33–7.29 (t, 1H, J = 7.5 MHz, ArCH), 7.14–7.10 (m, 1H, ArCH), 4.99 (s, 2H, OCH₂), 1.27 (s-overlap, 36H, CH₃, OBPin & pinBOBpin); ¹³C NMR (101 MHz, CDCl₃) δ 136.77 (quat-C, C=OCH₂ ArC), 131.70 (ArCH), 128.12 (ArCH), 127.27 (ArCH), 126.82 (ArCH), 120.96 (quat-C, C-Br, ArC), 82.63 (quat-C, pinBOBpin), 82.48 (quat-C, OBPin), 65.72 (CH₂, OCH₂), 24.03 (CH₃, OBPin), 23.92 (CH₃, pinBOBpin).

- (4-Bromophenyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j). Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.01–7.99 (d, 1H, J = 7.8 MHz, ArCH), 7.81–7.79 (d, 1H, J = 8.8 MHz, ArCH), 7.74–7.72 (d, 1H, J = 8.2 MHz, ArCH), 7.56–7.54 (d, 1H, J = 7.0 MHz, ArCH), 7.47–7.38 (m, 3H, ArCH), 5.37 (s, 2H, CH₂, OCH₂), 1.24 (s, 36H, CH₃, OBPin & pinBOBpin); ¹³C NMR (101 MHz, CDCl₃) δ 136.45 (quat-C, C=CH₂ ArC), 130.09 (quat-C, ArC), 130.34 (quat-C, ArC), 128.08 (ArCH), 127.70 (ArCH), 126.62 (ArCH), 125.19 (ArCH), 124.87 (ArCH), 122.97 (ArCH), 82.61 (quat-C, pinBOBpin), 82.57 (quat-C, OBPin), 64.54 (CH₂, OCH₂), 24.15 (CH₃, OBPin), 24.00 (CH₃, pinBOBpin).

- (4-Vinyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1l). Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.37 (m, 2H, ArCH), 7.06–7.00 (m, 2H, ArCH), 5.04 (s, 2H, CH₂, OCH₂), 1.24 (s-overlap, 36H, CH₃, OBPin & pinBOBpin); ¹³C NMR (101 MHz, CDCl₃) δ 136.76 (quat-C, C=CH₂ ArC), 133.31 (quat-C, ArC), 131.18 (quat-C, ArC), 129.15 (ArCH), 129.04 (ArCH), 128.84 (ArCH), 126.56 (ArCH), 125.37 (ArCH), 124.50 (ArCH), 119.06 (quat-C, C-Br, ArC), 82.60 (quat-C, pinBOBpin), 82.47 (quat-C, OBPin), 66.00 (CH₂, OCH₂), 24.09 (CH₃, OBPin), 24.00 (CH₃, pinBOBpin).

- (3,4,5,6-Tetramethyl-2-naphthalen-1-ylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1m). Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H, ArCH), 7.74 (s, 1H, ArCH), 7.65–7.60 (m, 2H, ArCH), 7.48–7.41 (m, 2H, ArCH), 5.04 (s, 2H, CH₂, OCH₂), 1.24 (s-overlap, 36H, CH₃, OBPin & pinBOBpin); ¹³C NMR (101 MHz, CDCl₃) δ 136.79 (quat-C, C=CH₂ ArC), 135.52 (quat-C, ArC), 131.23 (quat-C, ArC), 129.40 (ArCH), 127.30 (ArCH), 126.98 (ArCH), 125.87 (ArCH), 124.50 (ArCH), 119.06 (quat-C, C-Br, ArC), 82.60 (quat-C, pinBOBpin), 82.47 (quat-C, OBPin), 66.00 (CH₂, OCH₂), 24.09 (CH₃, OBPin), 24.00 (CH₃, pinBOBpin).

- (4-Vinyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1n). Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.46 (d, 1H, J = 7.0 MHz, CH), 1.23 (s, 24H, CH₃, OBPin & pinBOBpin).

- (4,5,5-Tetramethyl-2-(3-nitrobenzyl)oxy)-1,3,2-dioxaborolane (1p). Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H, ArCH), 8.10–8.08 (d, 1H, J = 8.2 MHz, ArCH), 7.65–7.64 (d, 1H, J = 7.6 MHz, ArCH), 7.50–7.46 (t, 1H, J = 7.9 MHz, ArCH), 4.99 (s, 2H, OCH₂), 1.25 (s-overlap, 36H, CH₃, OBPin & pinBOBpin); ¹³C NMR (101 MHz, CDCl₃) δ 148.26 (quat-C, C=OCH₂ ArC), 141.25 (ArCH), 132.59 (ArCH), 129.28 (ArCH), 122.35 (ArCH), 121.49 (quat-C, C=NO₂ ArC), 83.37 (quat-C, pinBOBpin), 83.06 (quat-C, OBPin), 65.48 (CH₂, OCH₂), 24.53 (CH₃, OBPin), 24.42 (CH₃, pinBOBpin).

- (4-Cyanobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1k). White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.60–7.58 (d, 2H, J = 8.0 MHz, ArCH), 7.43–7.41 (d, 2H, J = 8.0 MHz, ArCH), 4.96 (s, 2H, OCH₂), 1.25 (s-overlap, 36H, CH₃, OBPin & pinBOBpin).

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25.01 (CH₃), 24.01 (CH₃, OBPin), 23.92 (CH₃, pinBOBpin), 22.05 (CH₃), 13.53 (CH₃).

4,4,5,5-Tetramethyl-2-(nonepentyl)-1,3,2-dioxaborolane (1x).2⁶ Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 3.50 (s, 2H, OCH₂), 1.24 (s-overlap, 36H, CH₃, OBPin & pinBOBpin), 0.88 (s, 9H, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 82.55 (quat-C, pinBOBpin), 82.08 (quat-C, OBPin), 74.34 (CH₂, OCH₂), 31.77 (quat-C, ‘Bu), 25.45 (CH₃, ‘Bu), 23.98 (CH₃, OBPin), 23.93 (CH₃, pinBOBpin).

4,4,5,5-Tetramethyl-2-(octadecyloxy)-1,3,2-dioxaborolane (1y).2⁶ Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 3.83–3.80 (t, 2H, J = 6.5 MHz, OCH₂), 1.56–1.36 (m, 4H, CH₂), 1.24 (s-overlap, 64H, CH₂, OBPin & pinBOBpin), 0.89–0.86 (t, 3H, J = 6.8 MHz, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 82.97 (quat-C, pinBOBpin), 82.46 (quat-C, OBPin), 64.86 (CH₂, OCH₂), 31.88 (CH₃), 31.41 (CH₃), 29.65 (CH₃), 29.61 (CH₃), 29.56 (CH₃), 29.31 (CH₃), 29.27 (CH₂), 25.55 (CH₂), 24.49 (CH₃, OBPin), 24.45 (CH₃, pinBOBpin), 22.62 (CH₃), 14.03 (CH₃).

**General Procedure for Hydrolysis of Boric Esters to Alcohols.** Upon completion of the reaction, the resulting boric ester residue was refluxed with silica gel (1g) and methanol for 6 h. Then, the aliquot is evaporated under vacuum and extracted with dichloromethane. The combined organic layers were dried, evaporated, and purified by column chromatography over silica gel (100–200 mesh) using ethyl acetate/hexane (1:5) mixture as an eluent to obtain pure primary alcohols (2a–g).

**Spectral Data for Synthesized Alcohols.**

**Phenylmethanol (2a).**2⁶ Colorless oil; 100.6 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.79–7.22 (m, 5H, ArCH), 4.61 (s, 2H, CH₂, OCH₂), 1.87 (brs, 1H, OH); ¹³C NMR (101 MHz, CDCl₃) δ 140.86 (quat-C, ArC), 128.58 (ArCH), 127.68 (ArCH), 127.00 (ArCH), 65.42 (CH₂, OCH₂).

**(4-Bromophenyl)methanol (2b).**2⁶ White solid; 172.1 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.45 (d, 2H, J = 8.4 MHz, ArCH), 7.20–7.18 (d, 2H, J = 8.4 MHz, ArCH), 4.59 (s, 2H, OCH₂), 2.26 (brs, 1H, OH); ¹³C NMR (101 MHz, CDCl₃) δ 139.74 (quat-C, C-Br, ArC), 131.60 (quat-C, C–CH₂O, ArC), 128.59 (ArCH), 124.12 (ArCH), 64.46 (CH₂, OCH₂).

**(2-Methoxyphenyl)methanol (2c).**2⁶ Colorless oil; 124.4 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.29–7.24 (m, 2H, ArCH), 6.95–6.86 (m, 2H, ArCH), 4.68–4.66 (d, 2H, J = 6.0 MHz, OCH₂), 3.85 (s, 3H, OCH₃), 2.46 (brs, 1H, OH); ¹³C NMR (101 MHz, CDCl₃) δ 135.74 (quat-C, C–OCH₂, ArC), 129.08 (ArCH), 128.94 (quat-C, C–OCH₂, ArC), 128.73 (ArCH), 120.66 (ArCH), 110.21 (ArCH), 62.04 (CH₂, OCH₂), 55.27 (CH₃, OCH₃).

**((4-tert-Butyl)phenyl)methanol (2d).**2⁶ Colorless oil; 149.5 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.28 (d, 2H, J = 8.4 MHz, ArCH), 7.20–7.18 (d, 2H, J = 8.5 MHz, ArCH), 4.51 (s, 2H, OCH₂), 2.12 (brs, 1H, OH), 1.23 (s, 9H, CH₃, ‘Bu); ¹³C NMR (101 MHz, CDCl₃) δ 150.17 (quat-C, C–CH₂Bu, ArC), 137.48 (quat-C, C–CH₂Bu, ArC), 126.45 (ArCH), 124.99 (ArCH), 64.56 (CH₂, OCH₂), 34.09 (quat-C, ‘Bu), 30.92 (CH₃, ‘Bu).

**Naphthalen-1-ylmethanol (2e).**2⁶ Colorless oil; 145.5 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.03–8.00 (d, 1H, J = 7.8 MHz, ArCH₃), 7.84–7.81 (d, 1H, J = 8.8 MHz, ArCH₃), 7.76–7.74 (d, 1H, J = 8.2 MHz, ArCH₃), 7.50–7.35 (m, 4H, ArCH₃), 5.00 (s, 2H, CH₂, OCH₂), 2.33 (brs, 1H, OH); ¹³C NMR (101 MHz, CDCl₃) δ 135.80 (quat-C, C–CH₃), 133.30 (quat-C, C–CH₃).
ArC), 130.73 (quart-C, ArC), 128.19 (ArCH), 128.04 (ArCH), 125.85 (ArCH), 125.40 (ArCH), 124.95 (ArCH), 124.81 (ArCH), 123.18 (ArCH), 63.00 (CH₂, OCH₂).

3-Phenylpropan-1-ol (2f).²² Colorless oil; 118.4 mg; 1H NMR spectrum of 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure S1) (PDF).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00406.

Solvent effect; experiments of benzoic acid with different batches of HBpin from different suppliers; copies of NMR spectra for all compounds; solvent THF effect (Table S1); 1H NMR spectrum of 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (PDF)

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**Notes**

The authors declare no competing financial interest.

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