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Boron-Catalyzed O−H Bond Insertion of *α*-Aryl *α*-Diazoesters in Water

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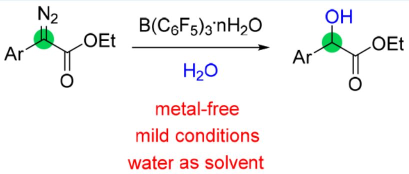
Supporting Information

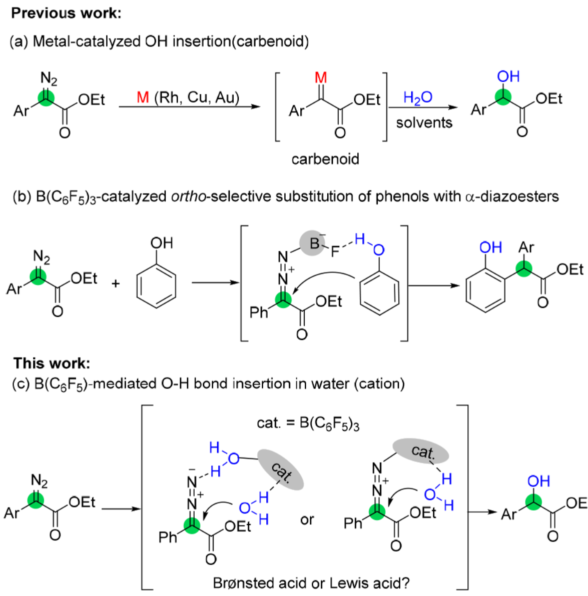
ABSTRACT: A catalytic, metal-free O−H bond insertion of *α*-diazoesters in water in the presence of $B(C_6F_5)_3{\cdot}nH_2O$ (2 mol %) was developed, affording a series of *α*-hydroxyesters in good to excellent yields. The reaction features easy operation and wide substrate scope, and importantly, no metal is needed as compared with the conventional methods. Significantly, this approach further expands the applications of $B(C_6F_5)_3$ under water-tolerant conditions.



The strong Lewis acid, tris(pentafluorophenyl)-borane, $B(C_6F_5)_3$, and other related electron-deficient boron catalysts have recently drawn much attention for their broad applications in many useful transformations,[1] including reduction of unsaturated substances,[2] dehydrogenations,[3] hydrosilylations,[4] hydroaminations,[5] hydroborations,[6] dehydrogenative cross couplings,[7] polymerizations,[8] and other reactions.[9] $B(C_6F_5)_3$ has also emerged as one of the most important components in Frustrated Lewis Pair (FLP) chemistry[10] after the seminal work reported by Stephan and Erker.[11] To date, the aim of developing more practical and widely applicable synthetic methods using the $B(C_6F_5)_3$ catalyst becomes increasingly important. One of the major concerns is that $B(C_6F_5)_3$ always faces the dilemma of water hydrolysis via B−C bond protonolysis due to its strong Lewis acidity. Such shortcomings have seriously hampered the development of $B(C_6F_5)_3$ or FLP-involving chemistry.[12] Thus, many efforts have been devoted to applying $B(C_6F_5)_3$-catalyzed reactions under water-tolerant conditions.[13,14] For example, Shibuya reported a boron-catalyzed intramolecular double hydrofunctionalization reaction of alkynes using water as a proton source.[14a] Moran disclosed that $B(C_6F_5)_3{\cdot}H_2O$ could be used as a Brønsted acid in the azidation of tertiary aliphatic alcohols[14e] and the Friedel−Crafts reactions of tertiary aliphatic fluorides.[14b] The groups of Stephan,[14l] Ashley,[14k] and Soós[14f] also independently discovered that $B(C_6F_5)_3$/ethers were efficient FLP catalysts in the challenging hydrogenation of ketones/aldehydes to alcohols. In addition, the groups of Fu[14h] and Ingleson[14c] also developed reductive aminations of carboxylic acids and aldehydes catalyzed by $B(C_6F_5)_3$, respectively. Despite those advances, the performance of $B(C_6F_5)_3$ in reactions using water as the solvent is still unknown to the best of our knowledge.

Transition metal-catalyzed insertion of *α*-diazoesters into C−H[15] or X−H (X = heteroatoms)[16] bonds is a powerful method for easy construction of C−C and C−X bonds. In particular, the O−H bond insertion of *α*-diazoesters with water is of great importance not only because water is one of the most abundant and green resources for C−O bond construction but also due to its high simplicity for the direct synthesis of free *α*-hydroxyesters in an atom-economical way.[17] Indeed, numerous efforts have been devoted to developing efficient metal catalysts for this important reaction, including those based on Cu(I),[17a,d] Au(I),[17b] Fe(II),[17c] and Rh(II)[17e] (Scheme 1, a). In light of the importance of developing green

Scheme 1. Transition Metal-Catalyzed or Metal-Free OH Insertions with *α*-Diazoesters



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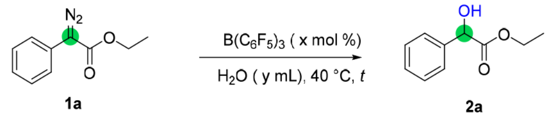
processes and also continuing our research interests in insertion reactions,[18] it is highly desirable to perform this important reaction in water (Scheme 1, b). However, this could be very challenging owing to the low solubility of α-hydroxyesters in water.

To solve the problem described above, we envisaged that a bifunctional catalyst that could activate α-hydroxyesters and also pull a water molecule closer via hydrogen bonding would facilitate the desired water insertion (Scheme 1, c). Recently, an elegant *ortho*-selective substitution reaction of phenols with α-aryl α-diazoesters was reported by Zhang and co-workers[19] in which $B(C_6F_5)_3$ acted as a bifunctional hydrogen-bonding catalyst. Inspired by this work, we tested our hypothesis by conducting the desired reaction in water in the presence of $B(C_6F_5)_3{\cdot}nH_2O$.

Upon treatment of **1a** in 2 mL of water in the presence of 2 mol % of $B(C_6F_5)_3{\cdot}nH_2O$ at 40 °C for 2 h, the reaction gave the corresponding water insertion product **2a** in 68% yield (Table 1, entry 1). Considering that alcohol **2a** could also take part in the reaction as a nucleophile, we performed the reaction in diluted solution; however, the yield of **2a** slightly decreased to 65% after 4 h (Table 1, entry 2). When performing the reaction in 0.5 mL of H_2O, the reaction proceeded much faster and delivered **2a** in 80% yield (Table 1, entry 3). Increasing or decreasing the loadings of $B(C_6F_5)_3{\cdot}nH_2O$, the reactions furnished product **2a** in 71 and 75% yields, respectively (Table 1, entries 4 and 5). Higher concentration did not increase the efficiency of this reaction (Table 1, entry 6). $MeNO_2$ was demonstrated by Moran and co-workers to have a cocatalytic effect in the $B(C_6F_5)_3{\cdot}H_2O$-catalyzed azidation of tertiary aliphatic alcohols.[14e] Therefore, different amounts of $MeNO_2$ were added to the reaction system, but the yields of **2a** were not increased (Table 1, entries 7–10). Meanwhile, the reaction was also performed in mixed solvent (*t*BuOH/H_2O), and **2a** was obtained in 75 and 56% yields, respectively (Table 1, entries 11 and 12).

Table 1. Screening of the Reaction Conditions[a]

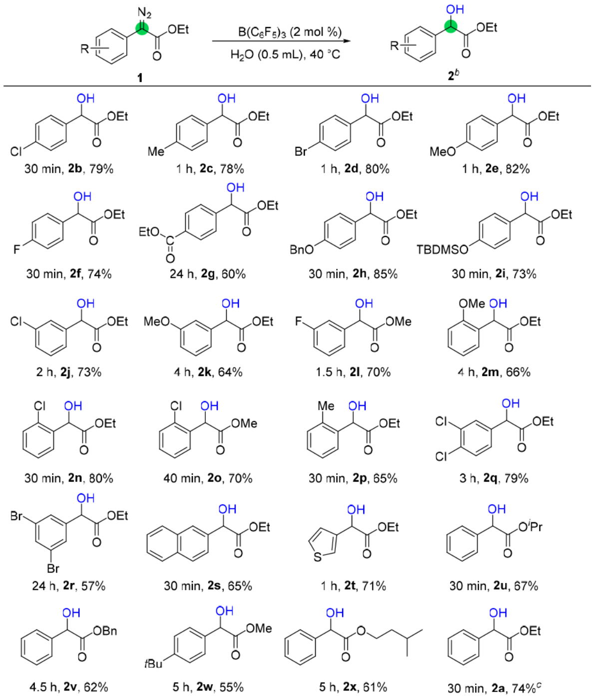


entry	*x*	*y* (mL)	time (min)	yield (%)[b]
1	2	2	180	68 (55)[c]
2	2	4	240	65
3	2	0.5	30	80
4	5	0.5	30	71
5	1	0.5	30	75
6	2	0.1	30	70
7[d]	2	0.5	50	62
8[e]	2	0.5	50	70
9[f]	2	0.5	50	74
10[g]	2	0.5	30	68
11[h]	2	0.9	30	75
12[i]	2	0.5	30	56

[a] Reactions were carried out on a 0.2 mmol scale under air in deionized water. [b] Isolated yields. [c] Reaction temperature of 25 °C. [d] With 0.4 mL of $MeNO_2$. [e] With 0.3 mL of $MeNO_2$. [f] With 0.2 mL of $MeNO_2$. [g] With 0.1 mL of $MeNO_2$. [h] With 0.1 mL of *t*BuOH. [i] With 0.5 mL of *t*BuOH.

With the optimal reaction conditions in hand (Table 1, entry 3), we next turned our interest to evaluating the substrate scope of the reaction by varying the structure of diazoesters. As can be seen in Scheme 2, the reactions of *para*-substituted substrates **1** all went smoothly to give the corresponding products **2b**–**2i** in good yields, and the electronic properties of the substituents did not have a significant effect on the reaction outcomes. For substrates with *meta*-substituents, the reaction also furnished products **2j**–**2l** in moderate yields. When *ortho*-substituted diazoesters were treated under the standard reaction conditions, products **2m**–**2p** were obtained in 65–80% yields, respectively. As for disubstituted diazoesters, products **2q** and **2r** were obtained in 79 and 57% yields, respectively. It is worth noting that naphthyl and thienyl groups were also compatible with this reaction, and products **2s** and **2t** were produced in 65 and 71% yields. In addition, changing the ethyl group of the diazoesters to methyl, isopropyl, benzyl, and isopentyl groups, corresponding products **2o**–**2u** and **2v**–**2x** were delivered in moderate yields. Notably, upon conducting the reaction of **1a** on a 1.0 mmol scale, **2a** could still be produced in 74% yield.

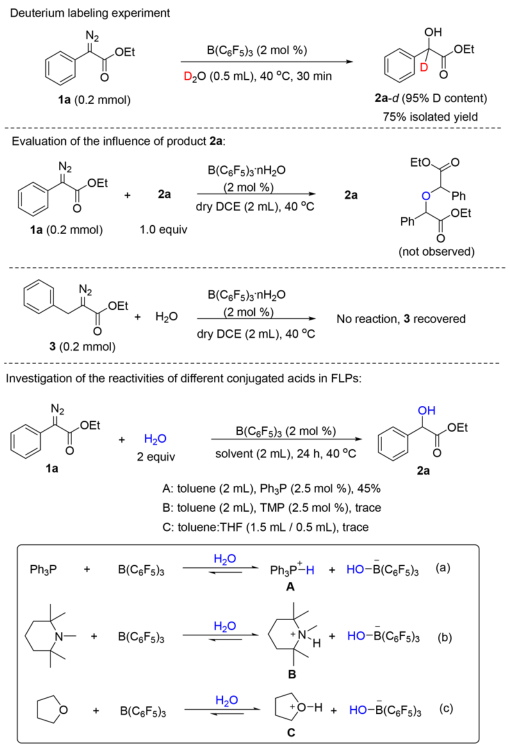
Scheme 2. Substrate Scope[a]



[a] Reactions were carried out on a 0.2 mmol scale under air at 40 °C in deionized water. [b] Isolated yields. [c] On a 1.0 mmol scale.

To gain some insight into the reaction mechanism, we conducted several control experiments (Scheme 3). Treating diazoester **1a** in D_2O, the reaction gave isolated **2a**-*d* in 75% yield with 95% D content. In the presence of **2a**, the water insertion of **1a** was not inhibited, and no alcohol insertion product was observed, indicating that the binding between **2a** and $B(C_6F_5)_3{\cdot}nH_2O$ cannot be too strong. Substrate **3** with a benzyl group could not undergo such water insertion, presumably due to the fact that the putative cation intermediate could not be stabilized by the benzyl group. It was reported by Wasa and co-workers[20] that the conjugated acids in FLPs could act as Brønsted acids; therefore, PPh_3 and

Scheme 3. Control Experiments



TMP were added to the mixture of **1a** and $B(C_6F_5)_3$ in toluene, respectively. In the presence of PPh_3, the reaction was very slow, and **2a** was formed in 45% yield, whereas the reaction with TMP only gave trace amount of product after 24 h. In addition, if conducting the reaction in mixed solvent (THF/toluene), the reaction was also inhibited. These results indicated that $B(C_6F_5)_3{\cdot}nH_2O$ is more active than corresponding conjugated acids **A**−**C**, probably because these conjugated acids cannot serve as bifunctional hydrogen bonding catalysts.

To probe the real catalyst of this water insertion further, we performed several NMR experiments (Figure 1). No obvious chemical shifts changed when the first two equiv of **1a** were added (Figure 1, 1−3); however, all three peaks shifted downfield when another 3.0 equiv of **1a** was added (Figure 1, 4). As water was consumed, all three peaks, which were not identical with anhydrous $B(C_6F_5)_3$,[21] showed no significant changes (Figure 1, 4−6), suggesting that **1a** may coordinate with $B(C_6F_5)_3$ in the absence of water.

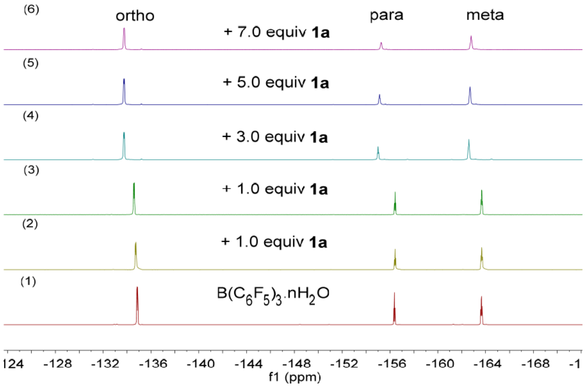


Figure 1. ^{19}F-NMR titration experiments of **1a** with $B(C_6F_5)_3{\cdot}nH_2O$. (1) $B(C_6F_5)_3{\cdot}nH_2O$ (10.0 mg, 1.0 equiv) in 0.6 mL of toluene-d_8. (2) **1a** (4.0 mg, 1.0 equiv) was added; (3) another 4.0 mg of **1a** (1.0 equiv) was added; (4) 12.0 mg of **1a** (3.0 equiv) was added; (5) 20.0 mg of **1a** (5.0 equiv) was added; and (6) 28.0 mg of **1a** (7.0 equiv) was added.

A considerable amount of **2a** was formed in the above titration experiments because the addition of **1a** into the NMR tube would introduce moisture.[22] For further excluding the influence of alcohol product, 20.0 equiv of **1f** was added in one portion to the solution of $B(C_6F_5)_3{\cdot}nH_2O$ in an NMR tube to avoid moisture interruption. As can be seen in Figure 2, the set of three peaks also shifted downfield (Figure 2, 2) and were almost identical with the final ^{19}F NMR spectrum of **1a** with $B(C_6F_5)_3$ obtained in the above titration experiments (Figure 1, 4−6). We also tested the NMR again after 1 h. No obvious chemical shift was observed, and a large amount of **1f** remained unreacted (Figure 2, 3). These results further confirmed that **1f** could coordinate with $B(C_6F_5)_3$ in the absence of water.

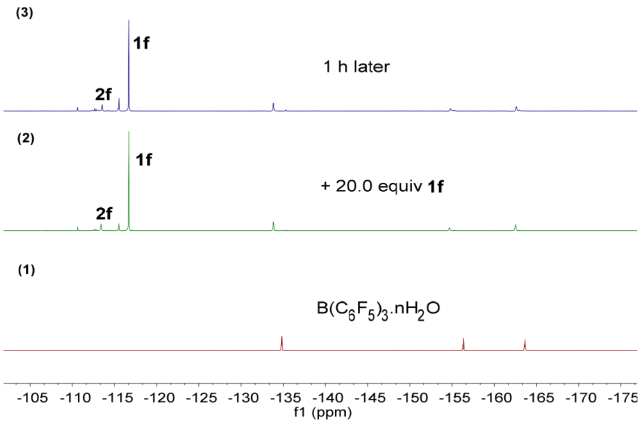
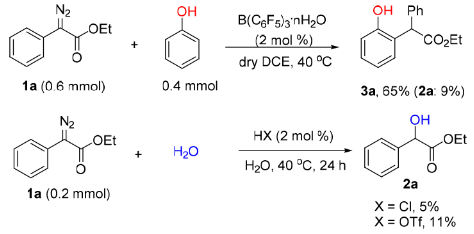


Figure 2. ^{19}F-NMR experiments of **1a** with $B(C_6F_5)_3{\cdot}nH_2O$. (1) $B(C_6F_5)_3{\cdot}nH_2O$ (5.0 mg, 1.0 equiv) in 0.6 mL of toluene-d_8; (2) **1f** (41.6 mg, 0.2 mmol, 20.0 equiv) was added; and (3) tested by ^{19}F NMR 1 h later.

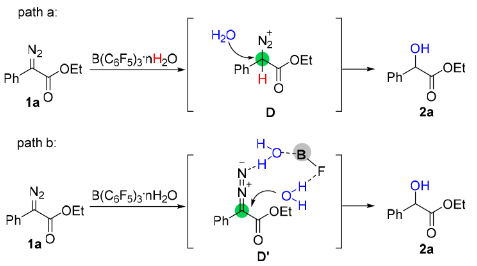
On the basis of the discovery presented above, we believed that the reaction of phenol with **1a** could also occur under our reaction conditions. Indeed, upon treatment of phenols with α-aryl α-diazoester **1a** in dry DCE in the presence of a catalytic amount of $B(C_6F_5)_3{\cdot}nH_2O$, the reaction also proceeded smoothly to give *ortho*-substituted product **3a** in 65% yield together with **2a** as a minor product. We assumed that water insertion would take place first. After water was consumed, the Friedel−Crafts reaction then occurred. This result also provides good support for bifunctional hydrogen-bonding catalyst of $B(C_6F_5)_3$ proposed by Zhang.[19] Furthermore, classic Brønsted acids were used as catalysts in the reaction of **1a** with water. It was found that both HCl and HOTf were less effective than $B(C_6F_5)_3{\cdot}nH_2O$, indicating hydrogen bonding may have a significant influence on the reaction outcome (Scheme 4).

On the basis of the results presented above and reported literature,[14a,19] two mechanisms are proposed in Scheme 5. First, diazoester **1a** can be protonated by $B(C_6F_5)_3{\cdot}nH_2O$ to form intermediate **D** followed by nucleophilic attack by H_2O to furnish the desired product **2a** (path a). On the other hand, we assume that $B(C_6F_5)_3{\cdot}nH_2O$ acts as a bifunctional catalyst in the reaction. $B(C_6F_5)_3{\cdot}nH_2O$ can protonate **1a** to generate activated cationic intermediate **D′**. Meanwhile, water is pulled closer to **1a** via hydrogen bonding and then attacks the carbon

Scheme 4. Evaluation of Hydrogen Bonding



Scheme 5. Plausible Mechanism



cation center of **1a**. Finally, the product is formed after the elimination of N_2 and regeneration of catalyst (path b). According to Norton's report and others,[23] no evidence has been reported for a HO−H···F interaction of water and $B(C_6F_5)_3$; thus, path a should be more reliable. However, taking Zhang's report into consideration, path b cannot be excluded at this stage.

In conclusion, we have discovered that $B(C_6F_5)_3 \cdot nH_2O$ catalyzes α-diazoester insertion into the O−H bond in water, affording various α-hydroxyesters under mild and metal-free conditions. Our preliminary mechanistic studies revealed that α-diazoesters can coordinate with $B(C_6F_5)_3$ under anhydrous conditions. However, the catalyst $B(C_6F_5)_3 \cdot nH_2O$ in fact acted as a Brønsted acid in the presence of water. This discovery demonstrates the feasibility of developing a unique approach for $B(C_6F_5)_3$-catalyzed reactions under water-tolerated conditions. Further efforts are in progress to understand the mechanism more deeply and its applications in organic synthesis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01988.

> Control experiments, NMR monitoring for mechanistic investigation, experimental details, characterization of new compounds, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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