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Selective Hydroboration of Carboxylic Acids with a Homogeneous Manganese Catalyst

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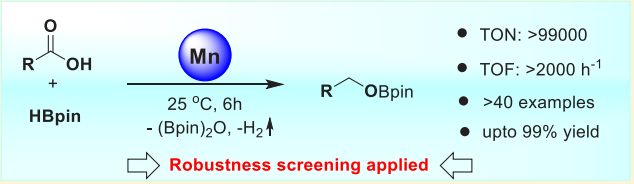
Supporting Information

ABSTRACT: Catalytic reduction of carboxylic acid to the corresponding alcohol is a challenging task of great importance for the production of a variety of value-added chemicals. Herein, a manganese-catalyzed chemoselective hydroboration of carboxylic acids has been developed with a high turnover number (>99 000) and turnover frequency (>2000 h^{-1}) at 25 °C. This method displayed tolerance of electronically and sterically differentiated substrates with high chemoselectivity. Importantly, aliphatic long-chain fatty acids, including biomass-derived compounds, can efficiently be reduced. Mechanistic studies revealed that the reaction occurs through the formation of active manganese−hydride species via an insertion and bond metathesis type mechanism.

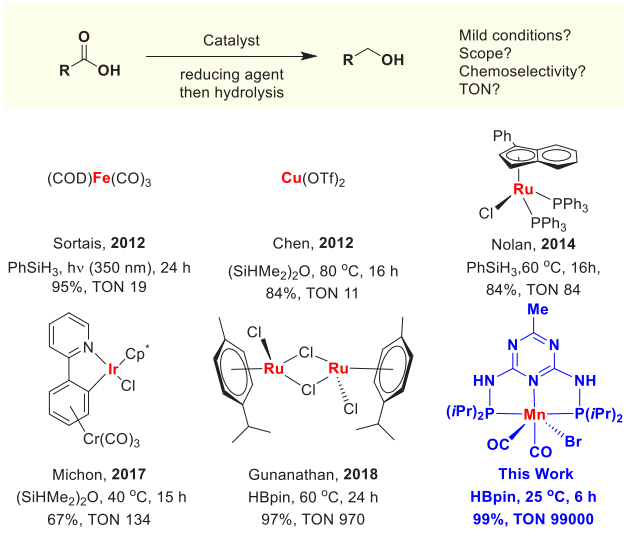


INTRODUCTION

The catalytic reduction of carboxylic acids is of great interest among the pharmaceutical and fine chemical industries for making value-added chemicals.[1] It not only allows the novel functional group manipulations in organic synthesis but also enables the utilization of the biomass feedstock to high-value oxygen-containing chemicals.[2] Traditional stoichiometric metal−hydride-based reductions of carboxylic acids are intrinsically hazardous.[3] On the other hand, the catalytic hydrogenations of carboxylic acids were executed under high temperature and pressure largely to overcome their low reactivity and/or strong interactions with the metals catalysts.[4] The catalytic hydroboration reactions of C═C[5] or C═X[5e,6] bonds are gaining attention because of their mild reaction conditions. The resulting organoborane species are often important building blocks for further synthetic manipulations.[7] Although, there are several reports available for the hydroboration and hydrosilylation of ketones[8] and esters,[8a,c,9] the transition-metal-catalyzed hydroboration of acids is largely elusive.[10] Very recently, Gunanathan and co-workers have elegantly reported the only ruthenium-catalyzed hydroboration of acids with pinacolborane with a turnover number (TON) of up to 970 (Scheme 1).[11]

Sustainable chemistry relies on strategies to avoid the use of the earth's critical resources and to utilize abundant elements in the production of ubiquitous materials. In homogeneous catalysis, where the reusability of the catalyst is challenging, catalysis with the earth's abundant first-row transition metals is a suitable alternative. In this regard, manganese is emerging as one of the appealing novel metal replacements due to its favorable properties, less toxicity, and abundance.[12] Recently, a series of homogeneous manganese catalysts were established for catalytic hydrogenation[13] and dehydrogenation[14] reactions. We have developed the manganese-catalyzed direct olefination

Scheme 1. Transition-Metal-Catalyzed Reductions of Free Carboxylic Acids



of methyl-substituted heteroarenes and α-alkylations of carbonyls and nitriles using primary alcohols.[15] Trovitch and co-workers have developed bis(imino)pyridine manganese catalysts for the hydrosilylations of aldehydes and ketones.[8e,16] Turculet and co-workers have reported an (*N*-phosphinoamidinate)manganese catalyst for the hydrosilylations of aldehydes, ketones, esters, and amides.[8c] Recently, manganese-catalyzed enantioselective hydroboration of ketones was established by Gade and co-workers.[17] Encouraged by these advancements, herein we report the manganese-

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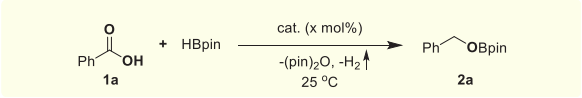
catalyzed deoxygenative hydroboration of free carboxylic acids. Notably, this robust catalyst achieves the highest turnover number (>99 000) and turnover frequency (>2000 h^{-1}) at 25 °C among the all homogeneous catalysts known for such a process (Scheme 1).

RESULTS AND DISCUSSION

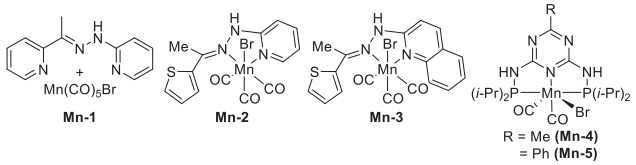
The hydroboration of benzoic acid was chosen as the model reaction to establish broadly applicable reactions condition (Table 1). In a typical reaction, a manganese catalyst (50 μL from a stock solution in toluene), benzoic acid (0.2 mmol), and pinacolborane (HBpin) (0.8 mmol) were mixed and allowed to stir at 25 °C for 6 h under argon, and the reaction mixture was analyzed by ^{1}H NMR. The hydrazone-based Mn catalysts **Mn-1−3** developed in our lab displayed very high catalytic activity, reaching a TON of up to 990 (entries 1−3).[15,18] Similarly, high catalytic activities were observed when the triazine-based PNP Mn catalysts **Mn-4,5** were used (entries 4, 5).[13e,19] Importantly, the catalyst loading could be reduced without any loss of catalytic activity [entries 6, 7 and Table S2 of the Supporting Information (SI)], and decreasing the loading to 0.001 mol % resulted in the highest TON of 99 000, with an overall turnover frequency (TOF) of 2062 h^{-1} at 25 °C.

Table 1. Optimization of the Reaction Condition for Manganese Catalyzed Hydroboration of Carboxylic Acid[a]



entry	cat.[b]	mol %	time (h)	yield (%)	TON
1	**Mn-1**	0.1	6	92	920
2	**Mn-2**	0.1	6	97	970
3	**Mn-3**	0.1	6	99	990
4	**Mn-4**	0.1	6	99	990
5	**Mn-5**	0.1	6	99	990
6	**Mn-4**	0.01	24	99	9900
7	**Mn-4**	0.001	48	99	99000
8[c]	–	0.1	6	trace	
9	$Mn(CO)_5Br$[d]	1.0	12	37	37

[a]Reaction conditions: catalyst (*x* mol %, 50 μL from stock solution in toluene), benzoic acid (0.2 mmol), HBpin (0.8 mmol), 6 h at 25 °C. The yield of **3a** was determined by ^{1}H NMR using cyclohexane as an internal standard. TON = number of moles of desired product formed/number of moles of catalyst used. TOF = TON/time of reaction. [b]Structure of catalysts:



[c]From ref 11a. [d]In 0.2 mL of toluene.

Control experiments demonstrated that $Mn(CO)_5Br$ gave only 37% of the desired product with 1 mol % catalyst loading after 12 h (entry 9). Alternative organic solvents such as benzene, toluene, and THF were also employed instead of neat conditions with different molar concentrations, but no major effect on the reactivity was observed (see Table S3, SI). Further screenings in terms of HBpin loading and the effects of concentration, time, and temperature are listed in Tables S4−S7 (SI).

After the optimization of the reaction parameters, the conditions in entry 4 of Table 1 were conveniently used to explore the scope and limitations of this catalytic system. As shown in Table 2, a broad range of aromatic, as well as aliphatic, carboxylic acids underwent efficient hydroboration with excellent yields and selectivities. Aromatic carboxylic acid derivatives bearing electron-donating or -withdrawing group such as methoxy (**1b**), ethoxy (**1c**), *tert*-butyl (**1d**), halogens (**1e−1i**), nitro (**1h**), cyano (**1j**), and ester (**1m**) groups at different positions underwent successful hydroboration in excellent yields (Table 2, **1a−1n**). Corresponding alcohols have been isolated after hydrolysis of the boronate esters in SiO_2/methanol at 60 °C. Interestingly, the heteroaromatic carboxylic acids, such as furan (**1k**) and thiophene (**1l**) carboxylic acids, were also hydroborated in high yields and selectivities.

The manganese-catalyzed hydroboration reactions of aliphatic carboxylic acids underwent smoothly to give the corresponding boronate esters (Table 2, **1o−1an**). Phenylacetic acid (**1o**), phenylpropionic acid (**1p**), and diphenylacetic acid (**1q**) displayed similar reactivity, and the reduced products were obtained quantitatively (**1o−1q**). The hydroboration reaction of 2-(1*H*-indol-3-yl)acetic acid **1r** yielded the desired boronated alcohol in 86% yield. In the case of conjugated cinnamic acid **1s**, some C=C hydroboration product (22%) was observed along with 78% of the desired product. Moreover, cyclic aliphatic carboxylic acids such as the cyclobutane carboxylic acid **1t** and cyclopropane carboxylic acid **1u** also underwent a smooth hydroboration reaction to the corresponding boronated products in 99% and 91% yields, respectively, and the strained cyclopropane ring is retained under such conditions. Sterically hindered pivalic acid **1v**, unhindered acetic acid **1w**, and even the C1 compound formic acid **1x** reacted smoothly with HBpin in quantitative yields.

Long-chain fatty acids comprise an attractive class of renewable feedstocks for the productions of lubricants, fuels, polymers, surfactants, etc.[2] The manganese catalyst developed in this work displayed excellent catalytic activity for the conversion of short-chain to long-chain carboxylic acids (**1ab−1ak**).

The hydroboration of different drug molecules and bile acid were also successful under these conditions. The anti-inflammatory drug naproxen (**1al**) and ibuprofen (**1am**) were quantitatively reacted with HBpin under the standard conditions. Similarly, lithocholic acid **1an** was effectively converted to its respective boronated product in quantitative yields.

Being one of the least reactive functional group, the carboxylic acids reductions often suffer from the chemoselectivity issue. In this regard, we have demonstrated that our catalyst system could efficiently be employed for the chemoselective hydroboration of acid in the presence of other reducible functional groups (Table 2). Intramolecular competition experiments demonstrated that the halogens (F, Cl, Br, and I) at different position of the aryl ring and alkyl bromides were tolerated under the reaction conditions (**1e−1n**, Table 2). Similarly, the reducible nitro (**1h**), nitrile (**1j**, **1am**), and ester (**1m**, **1n**) groups could also be retained under these conditions without compromising the reactivity. While the carboxylic acid **1ae** with a terminal double bond got reduced, the carboxylic acids containing internal *Z*-olefins (**1aj**,

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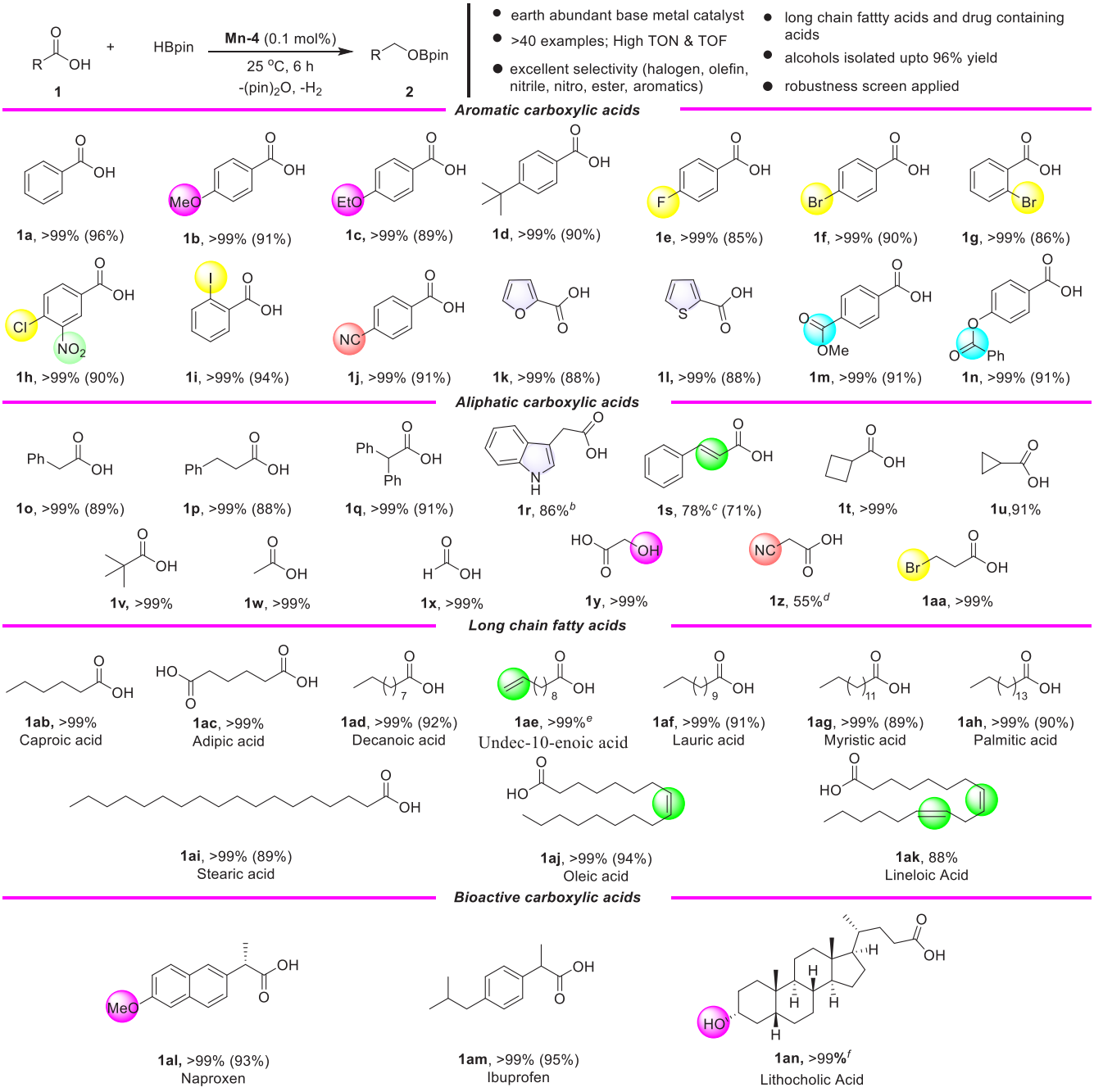
Table 2. Substrate Scope Studies



[a]Reaction conditions: **Mn-4** (0.1 mol %, 50 μL from stock solution in toluene), HBpin (0.8 mmol), carboxylic acid (0.2 mmol), 6 h at 25 °C under Ar. The yield was determined by ^{1}H NMR using cyclohexane as an internal standard. The isolated yield of the alcohols after hydrolysis with MeOH/SiO_2 (cat.) at 60 °C for 3 h is in the parentheses. [b]Side product (14%) was detected. [c]C=C hydroboration product (22%) was detected. [d]**1z** (45%) remains unreacted. [e]Reduced product formed. [f]At 60 °C, 12 h.

1ak) were uneffected in terms of the integrity and stereochemistry of the double bonds.

To further investigate the functional group tolerance of this manganese catalyst system, we have performed an intermolecular robustness screen as previously described by the Glorius group.[20] In such an experiment, hydroboration of **1a** was carried out in the presence of an additive, and after the reaction, the yields of **2a** and the additive were calculated by ^{1}H NMR analysis using cyclohexane as an internal standard, and the results are summarized in Table 3. We found that aryl halides (chlorides, bromides, iodides), cyanides, nitro, ester, amide, internal and terminal alkynes, and sulfones were tolerated. However, aldehydes and ketones got reduced under such conditions and aniline, pyridine, and imidazole deteriorate the reaction outcome.

Then to get insight into the reaction mechanism, the following experiments were performed. As it has previously been observed by Gunanathan and co-workers, benzoic acid reacts rapidly with HBpin to form the corresponding boryl ester.[11a] The overall progress of this manganese-catalyzed reaction was monitored by ^{1}H NMR. As shown in the Supporting Information, the initially formed boryl ester of

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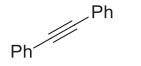
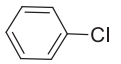
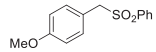
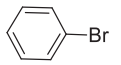
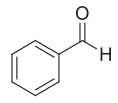
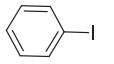
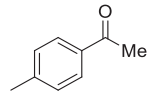
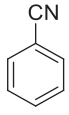
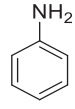
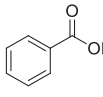
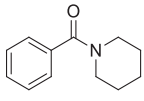
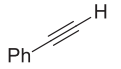
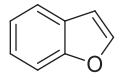
Table 3. Robustness Screening[a]

Entry	Additive	Yield of **2a**	Additive remaining	Entry	Additive	Yield of **2a**	Additive remaining
1	None	>99 √	-	10		95 √	95
2		95 √	>95	11		99 √	99
3		90 √	>95	12		55 —	0
4		90 √	>95	13		55 —	0
5		99 √	99	14		10 ×	90
6		99 √	99	15		10 ×	90
7		>99 √	100	16		10 ×	
8		>99 √	100	17		56 —	68
9		90 √	95	18		84 √	95

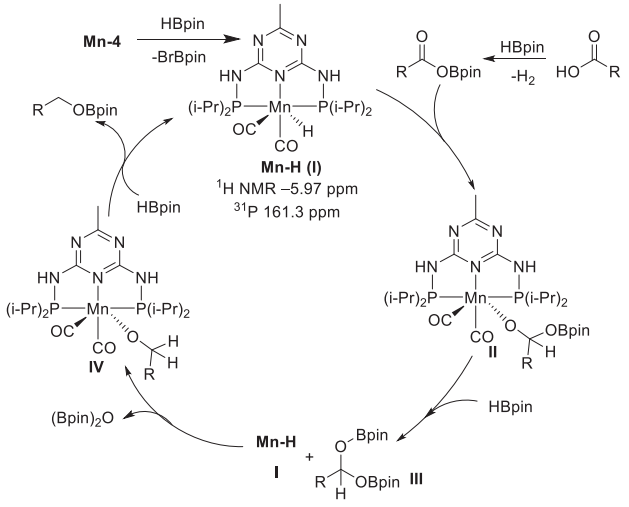
[a]Reaction conditions: **1a** (0.1 mmol) and corresponding additive (0.1 mmol), **Mn-4** (0.1 mol %, 50 μL from 2 mL stock solution, stock solution was prepared in toluene), HBpin (0.4 mmol), 6 h, 25 °C, The yield was determined by ^{1}H NMR using cyclohexane as an internal standard.

benzoic acid disappears with time with the concurrent appearance of the benzylboronate ester (the characteristic singlet signal appeared at δ 4.9 ppm). Further, several 30 min experiments with **1a** and HBpin were performed in order to gain insight into the concentration dependence of each component. The yield of **2a** was found to be independent of the initial concentration of **1a** while the other components were kept constant, whereas the yield increased with the increased **Mn-4** and HBpin loading. A logarithmic plot of yield (after 30 min) vs concentration of the individual components is found to be linear, from which the approximate partial order with respect to **1a**, **Mn-4**, and HBpin were determined to be 0, 1, and 2, respectively (see the Supporting Information).

Then the reactivity of the manganese complex toward HBpin was investigated. Thus, the manganese complex **Mn-4** was treated with a 10-fold excess of HBpin in THF-d_8 at room temperature. After 2 h, we obtained a yellow solution that revealed a new signal at δ −5.97 ppm and −161.3 ppm in ^{1}H and ^{31}P{^{1}H} NMR (see the Supporting Information for details). This can be attributed to the **Mn-4** hydride complex, as previously reported by Kempe and co-workers.[19a]

On the basis of the recent studies on the ruthenium-catalyzed reduction of carboxylic acids,[11a] on manganese catalysis,[17] and on our experimental findings, herewith we are proposing an insertion/bond metathesis type mechanism (Scheme 2). The initial reaction of the manganese precatalyst with HBpin led to the formation of a Mn−hydride complex **I**,

Scheme 2. Proposed Mechanism for the Hydroboration of Carboxylic Acid



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as detected by ^{1}H and ^{31}P NMR. The hydride complex **I** then could react with the boryl ester PhC(O)OBpin (derived from noncatalytic reaction of carboxylic acid with HBpin) to form the alkoxy intermediate **II**. The resulting intermediate **II** then underwent a σ-bond metathesis with HBpin to produce the manganese hydride **I** and the diboronated intermediate **III**, which subsequently converted to the alkoxy intermediate **IV** with the release of $(Bpin)_2O$ as a byproduct. Alternatively, the intermediate **III** could produce an aldehyde with the release of $(Bpin)_2O$ and that aldehyde could undergo hydroboration with the manganese hydride **I** to generate the intermediate **IV**. Finally, the alkoxy intermediate **IV** underwent another σ-bond metathesis with HBpin to release the product **2a** and to close the catalytic cycle.

CONCLUSION

In summary, we have developed an unprecedented base-metal-catalyzed hydroboration of carboxylic acids which proceeded with excellent yields and selectivities. The catalyst operates under very mild reaction conditions, reaching the highest TON (99 000), with TOF >2000 h^{-1}, achieved up to date. Successful catalytic studies showed more than 40 substrates bearing different functional groups, different short- and long-chain fatty acids, drugs, and bile acids. More importantly, intra- and intermolecular chemoselectivities have been demonstrated effectively. On the basis of the kinetic studies and in situ NMR experiments, a possible insertion/bond metathesis type mechanism is proposed. The synthetic protocol and mechanistic understanding of this work will help for future research on base-metal catalysis for the sustainable reduction of unsaturated compounds.

EXPERIMENTAL SECTION

General. Unless otherwise noted, all reactions were carried out under an atmosphere of argon/nitrogen in oven-dried glassware, using a standard Schlenk line or nitrogen-filled glovebox. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Analytics. ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR spectra were recorded on Bruker (^{1}H, 500 MHz; $^{13}C\{^{1}H\}$, 126 MHz) and JEOL (^{1}H, 400 MHz; $^{13}C\{^{1}H\}$, 101 MHz; $^{11}B\{^{1}H\}$, 161 MHz; $^{31}P\{^{1}H\}$, 202 MHz) instruments and were referenced to the resonances of the solvent used. Multiplicities are indicated as br (broad), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), or m (multiplet). Coupling constants (J) are reported in hertz (Hz). For thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm).

Chemicals. Commercially available chemicals were purchased and used without further purification. Dry solvents were prepared according to the standard procedure and degassed by freeze–pump–thaw cycles prior to use. Catalysts (**Mn-1**–**Mn-5**) were prepared according to the literature procedures.[13h,15,18,19a,b]

General Procedure for the Hydroboration of Carboxylic Acid. In a 5 mL reaction tube, carboxylic acid (0.2 mmol), **Mn-4** (0.1 mol %, 50 μL from 2 mL stock solution, stock solution was prepared in toluene), and HBpin (0.8 mmol) were added under an argon atmosphere. The reaction tube was closed and stirred at room temperature (25 °C) for 6 h. After completion of the reaction, cyclohexane (0.2 mmol) and $CDCl_3$ were added, and the reaction stirred for 5 min before ^{1}H NMR spectra were collected. Further, the reaction mixture was evaporated to remove the cyclohexane, any solvent, and unreacted HBpin and was characterized by ^{1}H and ^{13}C spectroscopy.

*2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a**).*[2] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 6.4 Hz, 5H), 4.92 (s, 2H), 1.26 (s, 36H).

*2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b**).*[6e] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 4.82 (s, 2H), 3.77 (s, 3H), 1.25 (s, 24H), 1.24 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 131.6, 128.6, 113.8, 83.3, 83.0, 66.6, 55.4, 24.7, 24.6.

*2-((4-Ethoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2c**).*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 7.3 Hz, 2H), 6.82 (d, J = 7.0 Hz, 2H), 4.81 (s, 2H), 4.02–3.97 (m, 2H), 1.37 (t, J = 6.9 Hz, 3H), 1.24 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5, 131.4, 128.6, 114.4, 83.2, 83.0, 66.6, 63.5, 24.7, 24.6, 14.9.

*2-((4-(tert-Butyl)benzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2d**):*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 4.90 (s, 2H), 1.31 (s, 9H), 1.26 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.4, 136.3, 126.7, 125.2, 83.1, 82.9, 66.6, 34.5, 31.4, 24.6, 24.5.

*2-((4-Fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**).*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.26 (m, 2H), 6.99 (dd, J = 12.0, 5.4 Hz, 2H), 4.86 (s, 2H), 1.25 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.3 (d, J = 246.4 Hz), 135.07 (d, J = 2.9 Hz), 128.7 (d, J = 8.0 Hz), 115.2 (d, J = 21.6 Hz), 83.2, 83.1, 66.1, 24.7, 24.6.

*2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2f**).*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 4.87 (s, 2H), 1.27 (s, 24H), 1.26 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.4, 131.5, 128.5, 121.32, 83.3, 83.2, 66.1, 24.7, 24.6.

*2-((2-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2g**).*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 7.9 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 4.97 (s, 2H), 1.27 (s, 24H), 1.26 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.5, 132.4, 128.7, 127.9, 127.5, 121.6, 83.3, 83.2, 66.4, 24.7, 24.6.

*2-((4-Chloro-3-nitrobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2h**).* NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.45 (s, 2H), 4.90 (s, 2H), 1.22 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 139.8, 131.8, 131.1, 125.7, 123.6, 83.6, 83.2, 64.9, 24.6, 24.5.

*2-((2-Iodobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2i**).* NMR yield: >99%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 7.7 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 6.95 (t, J = 7.3 Hz, 1H), 4.85 (s, 2H), 1.25 (S, 36H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.1, 138.9, 128.9, 128.2, 127.6, 96.3, 83.2, 83.1, 70.8, 24.6, 24.5.

*4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)-benzonitrile (**2j**).*[21] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 2H), 7.41 (s, 2H), 4.93 (s, 2H), 1.22 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.6, 132.2, 126.9, 118.9, 111.1, 83.4, 83.1, 65.8, 24.6, 24.5.

*2-(Furan-2-ylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2k**).*[21] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 6.26 (s, 2H), 4.78 (s, 2H), 1.23 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 142.5, 110.3, 108.3, 83.2, 83.1, 59.2, 24.6, 24.5.

*4,4,5,5-Tetramethyl-2-(thiophen-2-ylmethoxy)-1,3,2-dioxaborolane (**2l**).*[6e] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 4.8 Hz, 1H), 6.99 (s, 1H), 6.93 (d, J = 3.2 Hz, 1H), 5.02 (s, 2H), 1.24 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.0, 126.6, 125.9, 125.6, 83.2, 83.1 61.7, 24.7, 24.6.

*Methyl 4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)-methyl)benzoate (**2m**).* NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 4.94 (s, 2H), 3.86 (s, 3H), 1.22 (s, 36H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.0, 144.4, 129.7, 129.2, 126.2, 83.2, 83.1, 66.1, 52.1, 24.6, 24.5.

*4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)-phenyl Benzoate (**2n**).* NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 4.94 (s, 2H), 1.26 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.3, 150.3,

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136.99, 133.7, 130.2, 129.6, 128.6, 127.9, 121.6, 83.2, 83.1, 66.2, 24.7, 24.6.

*4,4,5,5-Tetramethyl-2-phenethoxy-1,3,2-dioxaborolane (**2o**).*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.15 (m, 5H), 4.03 (t, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 6.6 Hz, 2H), 1.24 (s, 24H), 1.16 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.5, 129.2, 128.3, 126.3, 83.2, 82.7, 65.7, 38.1, 24.6.

*4,4,5,5-Tetramethyl-2-(3-phenylpropoxy)-1,3,2-dioxaborolane (**2p**).*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J* = 6.9 Hz, 2H), 7.17 (d, *J* = 6.6 Hz, 3H), 3.85 (t, *J* = 5.7 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.90−1.83 (m, 2H), 1.24 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.9, 128.6, 128.4, 125.8, 83.2, 82.8, 64.2, 33.2, 31.9, 24.7, 24.6.

*2-(2,2-Diphenylethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2q**).*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.22 (m, 8H), 7.22−7.12 (m, 2H), 4.39 (d, *J* = 7.1 Hz, 2H), 4.22 (t, *J* = 7.2 Hz, 1H), 1.26 (s, 24H), 1.13 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.9, 128.6, 128.5, 126.6, 83.3, 82.8, 67.9, 52.6, 24.6.

*3-(2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)-1H-indole (**2r**).*[11a] NMR yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 4.22 (t, *J* = 7.0 Hz, 7H), 3.06 (t, *J* = 6.9 Hz, 8H), 1.31 (s).

*2-(Cyclobutylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2t**).* NMR yield: >99%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 (d, *J* = 6.3 Hz, 2H), 2.54−2.48 (m, 1H), 1.97 (d, *J* = 6.4 Hz, 2H), 1.86−1.72 (m, 4H), 1.25 (s, 24H), 1.23 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 83.3, 82.8, 68.9, 36.5, 24.6, 24.30, 18.4.

*2-(Cyclopropylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2u**).* NMR yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (d, *J* = 6.9 Hz, 2H), 1.39 (d, *J* = 4.5 Hz, 1H), 0.49−0.41 (m, 2H), 0.20 (q, *J* = 5.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 83.1, 83.0, 82.6, 69.3, 24.5, 12.3, 2.7.

*4,4,5,5-Tetramethyl-2-(neopentyloxy)-1,3,2-dioxaborolane (**2v**).*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.50 (s, 2H), 1.25 (s, 36H), 0.88 (s, 9H).

*2-Ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2w**):*[11a] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (q, *J* = 7.0 Hz, 1H), 1.24 (s, 36H), 1.20 (t, *J* = 6.9 Hz, 2H).

*2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2x**).*[22] NMR yield: >99%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.61 (s, 3H), 1.27 (s, 36H).

*1,2-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethane (**2y**).* NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 4H), 1.18 (s, 48H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 83.0, 82.7, 64.9, 24.4.

*3-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)-propanenitrile (**2z**).* NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 (t, *J* = 6.0 Hz, 2H), 2.60 (t, *J* = 6.1 Hz, 2H), 1.24 (s, 48H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 117.3, 83.6, 83.3, 59.9, 24.6, 20.5. ^{11}B NMR (161 MHz, $CDCl_3$): δ 22.5 (−CH_2OBpin), 21.4 (($Bpin)_2$O).

*2-(3-Bromopropoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2aa**).* NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95 (t, *J* = 5.7 Hz, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 2.10−2.04 (m, 2H), 1.24 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 83.2, 83.0, 62.6, 34.4, 29.9, 24.6, 24.5. ^{11}B NMR (161 MHz, $CDCl_3$): δ 22.3 (−CH_2OBpin), 21.3 (($Bpin)_2$O).

*2-(Hexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2ab**).*[9b] NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (t, *J* = 6.5 Hz, 2H), 1.57−1.51 (m, 2H), 1.26 (s, 30H), 1.24 (s, 12H), 0.87 (t, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 83.3, 82.7, 65.1, 31.6, 31.5, 25.4, 24.7, 24.6, 22.7, 14.2.

*1,6-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)hexane (**2ac**).*[11a] NMR yield: >99%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.82 (t, *J* = 6.5 Hz, 4H), 1.58−1.53 (m, 4H), 1.37−1.32 (m, 4H), 1.27 (s, 48H), 1.24 (s, 24H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 83.4, 82.8, 65.0, 31.6, 25.5, 24.7, 24.6.

*2-(Decyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2ad**).*[6e] Reaction time: 12 h. NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (t, *J* = 6.5 Hz, 2H), 1.56−1.40 (m, 2H), 1.20 (s, 38H), 1.19 (s, 12H), 0.81 (t, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 83.1, 82.6, 64.9, 31.9, 31.5, 29.6, 29.5, 29.3, 25.6, 24.5, 24.4, 22.7, 14.1.

*2-(Dodecyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2af**).* Reaction time: 12 h. NMR yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (t, *J* = 6.5 Hz, 2H), 1.50−1.46 (m, 2H), 1.24 (s, 42H), 1.22 (s, 12H), 0.85 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 83.2, 82.7, 65.1, 32.0, 31.5, 29.7, 29.6, 29.4, 25.7, 24.64, 24.60, 24.5, 22.8, 14.2. ^{11}B NMR (161 MHz, $CDCl_3$): δ 22.4 (−CH_2OBpin), 21.3 (($Bpin)_2$O).

*4,4,5,5-Tetramethyl-2-(tetradecyloxy)-1,3,2-dioxaborolane (**2ag**).* Reaction time: 12 h. NMR yield: 99%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.82 (br, 2H), 1.56 (br, 2H), 1.26 (br, 58H), 0.88 (br, 3H). ^{11}B NMR (161 MHz, $CDCl_3$): δ 22.4 (−CH_2OBpin), 21.3 (($Bpin)_2$O).

*2-(Hexadecyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2ah**).*[7] Reaction time: 12 h. NMR yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (t, *J* = 6.6 Hz, 2H), 1.58−1.53 (m, 2H), 1.27 (s, 50H), 1.24−1.23 (m, 12H), 0.87 (t, *J* = 6.6 Hz, 3H).

*4,4,5,5-Tetramethyl-2-(octadecyloxy)-1,3,2-dioxaborolane (**2ai**).*[11b] Reaction time: 12 h. NMR yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (t, *J* = 6.5 Hz, 2H), 1.56−1.52 (m, 2H), 1.27 (s, 24H), 1.25 (s, 42H), 0.88 (d, *J* = 6.2 Hz, 3H).

*(Z)-4,4,5,5-Tetramethyl-2-(octadec-9-en-1-yloxy)-1,3,2-dioxaborolane (**2aj**).*[11b] Reaction time: 12 h. NMR yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (br, 2H), 3.81 (br, 2H), 1.99 (br, 4H), 1.54 (br, 2H), 1.25 (br, 59H), 0.86 (br, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 129.9, 83.3, 82.7, 65.1, 32.0, 31.6, 29.9, 29.8, 29.7, 29.6. 29.4, 29.3, 27.3, 25.7, 25.6, 24.6, 22.8, 14.2.

*2-((8Z,11Z)-Heptadeca-8,11-dien-1-yloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2ak**).* Reaction time: 12 h. NMR yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.38−5.37 (m, 4H), 3.82 (t, 2H), 2.76 (t, 2H), 2.07−2.0 (m, 4H), 1.63−1.5 (m, 3H), 1.36−1.28 (m, 20H), 1.25 (br, 36H), 0.88 (t, 3H). ^{11}B NMR (161 MHz, $CDCl_3$): δ 22.4 (−CH_2OBpin), 21.3 (($Bpin)_2$O).

*(S)-2-(2-(6-Methoxynaphthalen-2-yl)propoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2al**).* NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 8.5, 4.3 Hz, 2H), 7.58 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.11−7.06 (m, 2H), 4.03 (dd, *J* = 10.2, 6.5 Hz, 1H), 3.93 (dd, *J* = 10.2, 7.1 Hz, 1H), 3.87 (s, 3H), 3.10 (h, *J* = 6.9 Hz, 1H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.25 (s, 24H), 1.12 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.3, 138.9, 133.5, 129.2, 129.1, 126.8, 126.7, 125.7, 118.6, 105.6, 83.2, 82.7, 70.4, 55.3, 41.3, 24.6, 24.5, 17.7. ^{11}B NMR (161 MHz, $CDCl_3$): δ 22.5 (−CH_2OBpin), 21.3 (($Bpin)_2$O).

*2-(2-(4-Isobutylphenyl)propoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2am**).* NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (br, 4H), 3.91 (br, 2H), 2.96 (br, 1H), 2.40 (br, 2H), 1.84 (br, 1H), 1.44 (br, 3H), 1.29 (s, 24H), 1.20 (s, 12H), 0.91 (br, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.0, 139.7, 129.1, 127.3, 83.2, 82.7, 70.6, 45.2, 41.0, 30.3, 27.0, 24.6, 22.5, 17.7. ^{11}B NMR (161 MHz, $CDCl_3$): δ 22.5 (−CH_2OBpin), 21.3 (($Bpin)_2$O).

*2-(((3R,8R,9S,10S,13R,14S,17R)-10,13-Dimethyl-17-((R)-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentan-2-yl)-hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2an**).* NMR yield: >99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.97−3.92 (m, 1H), 3.77−3.71(m, 2H), 1.93−1.91 (m, 1H), 1.85−1.79 (m, 4H), 1.64−1.56 (m, 2H), 1.45−1.36 (m, 8 H), 1.24 (s, 10 H), 1.22 (s, 24H), 1.13−0.94 (m, 6H), 0.87 (s, 3H), 0.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 83.0, 82.5, 82.4, 74.2, 65.4, 56.4, 56.2, 42.6, 41.8, 40.2, 40.1, 35.8, 35.4, 35.1, 34.9, 34.4, 31.6, 29.1, 28.2, 28.0, 27.1, 26.3, 24.54, 24.5, 24.1, 23.3, 20.7, 18.5, 12.0. ^{11}B NMR (161 MHz, $CDCl_3$): δ 22.5 (−CH_2OBpin), 21.3 (($Bpin)_2$O).

General Procedure for the Hydrolysis of 2. After completion of the hydroboration reaction, the solvent and unreacted HBpin were removed in a vacuum, and the resulted boronate ester residue was hydrolyzed with silica gel (1 g)/methanol (5 mL) for 3−5 h at 60 °C. An aliquot was then removed in a vacuum and the residue was purified by column chromatography over silica gel (100−200 mesh) with a hexane/ethyl acetate (8:2) mixture as eluent, which provided the pure primary alcohol.

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(4-Methoxyphenyl)methanol (**3b**).[6e] Yield: 25.1 mg (0.182 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.21 (m, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.58 (s, 2H), 3.78 (s, 3H), 1.86 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.3, 133.2, 128.8, 114.1, 65.1, 55.4.

(4-Ethoxyphenyl)methanol (**3c**).[11a] Yield: 27.1 mg (0.178 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 4.58 (s, 2H), 4.01 (q, J = 7.0 Hz, 2H), 1.79 (br, 1H, OH), 1.40 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 133.1, 128.8, 114.7, 65.2, 63.6, 14.9.

(4-(tert-Butyl)phenyl)methanol (**3d**).[23] Yield: 29.6 mg (0.180 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.37 (m, 2H), 7.31 (d, J = 6.5 Hz, 2H), 4.66 (s, 2H), 1.73 (br, 1H, OH), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.9, 138.1, 127.1, 125.6, 65.3, 34.7, 31.5.

(4-Fluorophenyl)methanol (**3e**).[6e] Yield: 21.4 mg (0.170 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.28 (m, 2H), 7.07−6.99 (m, 2H), 4.63 (s, 2H), 2.10 (br, 1H, OH). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.4 (d, J = 245.7), 136.7 (d, J = 3.0 Hz), 128.9 (d, J = 8.2 Hz), 115.5 (d, J = 21.4 Hz), 64.7.

(4-Bromophenyl)methanol (**3f**).[6e] Yield: 33.7 mg (0.180 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 4.59 (s, 2H), 2.38 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.8, 131.7, 128.7, 121.5, 64.5.

(4-Methoxyphenyl)methanol (**3g**).[11a] Yield: 32.2 mg (0.172 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 4.73 (s, 2H), 2.28 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.8, 132.7, 129.2, 128.9, 127.8, 122.7, 65.1.

(4-Chloro-3-nitrophenyl)methanol (**3h**).[24] Yield: 33.8 mg (0.180 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.53−7.47 (m, 2H), 4.75 (s, 2H), 2.34 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 141.5, 131.9, 131.2, 125.8, 123.5, 63.3.

(2-Iodophenyl)methanol (**3i**).[25] Yield: 44 mg (0.188 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.01−6.97 (m, 1H), 4.66 (s, 2H), 2.32 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.7, 139.3, 129.4, 128.6, 128.5, 97.6, 69.4.

4-(Hydroxymethyl)benzonitrile (**3j**).[21] Yield: 24.2 mg (0.182 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 4.76 (s, 2H), 2.29 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.4, 132.4, 127.1), 119.0, 111.2, 64.3.

Furan-2-ylmethanol (**3k**).[6e] Yield: 17.3 mg (0.176 mmol, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (s, 1H), 6.31 (d, J = 25.2 Hz, 2H), 4.60 (s, 2H), 2.07 (br, 1H, OH). ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.1, 142.7, 110.5, 107.9, 57.6.

Thiophen-2-ylmethanol (**3l**).[21] Yield: 20.1 mg (0.176 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 4.0 Hz, 1H), 7.02 (d, J = 2.9 Hz, 1H), 7.00−6.96 (m, 1H), 4.83 (s, 2H), 1.92 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.1, 127.0, 125.8, 125.6, 60.2.

Methyl 4-(Hydroxymethyl)benzoate (**3m**).[26] Yield: 30.2 mg (0.182 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 4.70 (s, 2H), 3.87 (s, 3H), 2.58 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.2, 146.2, 129.9, 129.2, 126.5, 64.6, 52.2.

4-(Hydroxymethyl)phenyl benzoate (**3n**).[27] Yield: 41.5 mg (0.182 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 4.69 (s, 2H), 2.13 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 150.4, 138.7, 133.8, 130.3, 129.6, 128.7, 128.2, 121.9, 64.8.

2-Phenylethan-1-ol (**3o**).[6e] Yield: 21.7 mg (0.178 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.32 (m, 2H), 7.26 (t, J = 6.5 Hz, 3H), 3.87 (t, J = 6.6 Hz, 2H), 2.89 (t, J = 6.6 Hz, 2H), 1.65 (br, 1H, OH). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.6, 129.2, 128.7, 126.6, 63.8, 39.3.

3-Phenylpropan-1-ol (**3p**).[13j] Yield: 24 mg (0.176 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.27 (m, 2H), 7.24−7.17 (m, 3H), 3.68 (t, J = 6.4 Hz, 2H), 2.72 (t, J = 6.4 Hz, 2H), 1.91 (m, 2H), 1.69 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.9, 128.53, 128.51, 125.9, 62.3, 34.3, 32.2.

2,2-Diphenylethan-1-ol (**3q**).[11a] Yield: 36.1 mg (0.182 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.29 (m, 4H), 7.29−7.21 (m, 6H), 4.21 (dd, J = 8.4, 5.9 Hz, 1H), 4.16 (d, J = 6.1 Hz, 2H), 1.66 (br, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.5, 128.8, 128.4, 126.9, 66.2, 53.7.

(E)-3-Phenylprop-2-en-1-ol (**3s**).[25] Yield: 19.1 mg (0.142 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.23 (dd, J = 8.7, 4.9 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 6.35 (dt, J = 15.8, 5.6 Hz, 1H), 4.30 (d, J = 5.5 Hz, 2H), 1.86 (br, 1H, OH). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.8, 131.3, 128.7, 128.6, 127.8, 126.6, 63.8.

Decan-1-ol (**3ad**).[6e] Yield: 29.1 mg (0.184 mmol, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.61 (t, J = 6.7 Hz, 2H), 1.75 (br, 1H, OH), 1.58−1.51 (m, 2H), 1.34−1.24 (m, 14H), 0.86 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 63.1, 32.9, 32.0, 29.8, 29.7, 29.6, 29.4, 25.9, 22.8, 14.20.

Dodecan-1-ol (**3af**).[28] Yield: 33.9 mg (0.182 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (t, J = 6.7 Hz, 2H), 1.65 (br, 1H, OH), 1.59−1.52 (m, 2H), 1.33−1.24 (m, 18H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 63.2, 32.9, 32.1, 29.8, 29.77, 29.75, 29.6, 29.5, 25.9, 22.8, 14.2.

Tetradecan-1-ol (**3ag**).[28] Yield: 38.2 mg (0.178 mmol, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.64 (t, J = 6.6 Hz, 2H), 1.59−1.55 (m, 2H), 1.43 (br, 1H, OH), 1.26 (s, 22H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 63.3, 33.0, 32.1, 29.84, 29.81, 29.8, 29.7, 29.6, 29.5, 25.9, 22.8, 14.3.

Hexadecan-1-ol (**3ah**).[28] Yield: 43.7 mg (0.180 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.60 (t, J = 6.7 Hz, 2H), 1.56−1.50 (m, 2H), 1.22 (s, 26H), 0.84 (t, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 63.2, 32.9, 32.1, 29.84, 29.8, 29.76, 29.75, 29.6, 29.5, 25.9, 22.8, 14.3.

Octadecan-1-ol (**3ai**).[28] Yield: 48.1 mg (0.178 mmol, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.64 (t, J = 6.6 Hz, 2H), 1.59−1.54 (m, 2H), 1.26 (s, 30H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 63.3, 33.0, 32.1, 29.9, 29.8, 29.77, 29.75, 29.6, 29.5, 25.9, 22.8, 14.3.

(Z)-Octadec-9-en-1-ol (**3aj**).[29] Yield: 50.5 mg (0.188 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42−5.27 (m, 2H), 3.63 (t, J = 6.7 Hz, 2H), 2.01 (dd, J = 12.3, 6.5 Hz, 4H), 1.58−1.54 (m, 2H), 1.37−1.22 (m, 23H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 130.1, 129.9, 63.2, 32.9, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 27.4, 27.3, 25.9, 22.8, 14.3.

(S)-2-(6-Methoxynaphthalen-2-yl)propan-1-ol (**3al**).[13j] Yield: 40.2 mg (0.186 mmol, 93%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (t, J = 7.9 Hz, 2H), 7.61 (s, 1H), 7.35 (dd, J = 8.5, 1.4 Hz, 1H), 7.18−7.10 (m, 2H), 3.92 (s, 3H), 3.77 (d, J = 6.6 Hz, 2H), 3.08 (h, J = 6.9 Hz, 1H), 1.56 (br, 1H, OH), 1.36 (d, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.6, 138.8, 133.7, 129.2, 129.1, 127.3, 126.4, 126.0, 119.0, 105.8, 68.7, 55.4, 42.5, 17.8. Optical rotation: $[\alpha]_D^{22}$ −9.80 (c = 0.255, $CHCl_3$), lit. $[\alpha]_D^{22}$ −8.23 (c = 0.255, $CHCl_3$).[30]

2-(4-Isobutylphenyl)propan-1-ol (**3am**).[4b] Yield: 36.5 mg (0.190 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 3.69 (d, J = 6.8 Hz, 2H), 2.97−2.88 (m, 1H), 2.45 (d, J = 7.2 Hz, 2H), 1.90−1.80 (m, 1H), 1.61 (br, 1H, OH), 1.27 (d, J = 7.0 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H).

General Procedure for the Robustness Screening. To a 5 mL reaction tube were added carboxylic acid (0.1 mmol) and corresponding additive (0.1 mmol), catalyst **Mn-4** (0.1 mol %, 50 μL from 2 mL stock solution; stock solution was prepared in toluene), and pinacolborane (0.4 mmol) under an argon atmosphere. The reaction tube was closed and stirred at room temperature for 6 h. ^{1}H NMR was recorded in $CDCl_3$, and yields were calculated using cyclohexane as an internal standard.

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■ ASSOCIATED CONTENT

Supporting Information

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Detailed optimizations, NMR spectra of the products, and procedures for mechanistic experiments (PDF)

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Notes

The authors declare no competing financial interest.

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