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Structure and Reactivity of a Preactivated sp^2-sp^3 Diboron Reagent: Catalytic Regioselective Boration of α,β-Unsaturated Conjugated Compounds

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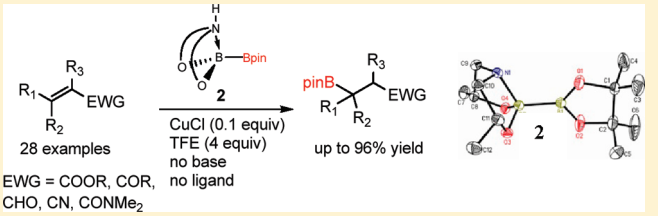
Supporting Information

ABSTRACT: A novel sp^2-sp^3 diboron reagent has been developed for the copper-catalyzed β-boration of α,β-unsaturated conjugated compounds. The reaction proceeds under mild conditions with various substrates, i.e., α,β-unsaturated esters, ketones, nitriles, ynones, amides, and aldehydes, in the absence of additives such as phosphine and sodium *tert*-butoxide to provide β-borylhomoenolates in good to excellent yields. The presence of an sp^3-hybridized boron center, unambigously confirmed by X-ray crystallography, sufficiently activates the unsymmetrical pinacolato diisopropanolaminato diboron (PDIPA diboron, **2**) to transfer the sp^2-hybridized boron moiety chemoselectively. These observations suggest that the activation of one of the boron atoms is an essential step in the Cu-catalyzed β-boration catalytic cycle.



INTRODUCTION

Organoboron compounds have emerged as versatile intermediates for the synthesis of many organic compounds.[1−4] As such, considerable effort has been committed to their preparation. Notably, transition metal-catalyzed boration with diboron compounds is particularly effective. These reactions include catalytic diboration,[5−30] C−H boration[31−42] and C−X boration,[43−50] and involve a catalytic cycle that employs a metal boryl species[51−61] generated by transmetalation or oxidative addition. Over the past decade, developing methods for the nucleophilic boration of electron-deficient alkenes has generated increasing interest. In contrast to electron-rich alkene or alkyne substrates, regioselective boration under conventional hydroboration conditions is not possible with α,β-unsaturated carbonyl compounds.[62] However, transition metal catalysis has provided a route for synthesizing organoboron derivatives.[2,4,53] Stoichiometric or catalytic reactions of metal boryl complexes have been studied with platinum,[63−65] rhodium,[66,67] nickel,[68] zinc,[69] and copper[70−80] systems. In particular, the copper-catalyzed reaction has emerged as a very convenient method for the conjugate addition of diboron reagents to α,β-unsaturated carbonyl compounds. Furthermore, enantioselective methods now exist.[74,78,79,81,82] Recently, metal-free, *N*-heterocyclic carbene (NHC)- or phosphine-promoted processes were reported by Hoveyda[83] and Fernandez,[84] respectively.

In contrast to the myriad of investigations of these catalyst systems, few studies exploring new diboron reagents have been reported. The boron source in these transformations is thus far limited to the diboron reagents B_2cat_2,[85−87] B_2neop_2,[88−90] and bis(pinacolato)diboron (B_2pin_2, **1**),[91,92] in part due to their commercial availability (Figure 1). These symmetrical reagents contain two sp^2-hybridized boron atoms. Alternative, stable diboron reagents are warranted in order to take advantage of the boronate group as an intermediate for installing other functional groups and exploiting the unique biological activities[93] of boronic acids. Differentially protected, unsymmetrical diboron compounds are expected to have the advantage of transferring boryl groups with chemoselectivity. For example, *N*-methyliminodiacetic acid (MIDA)[94−99] and 1,8-diaminonaphthalene[100−102] (dan) moieties provide a convenient protecting group strategy in

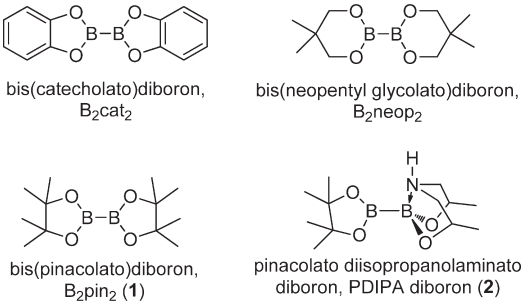


Figure 1. Structures of diboron compounds.

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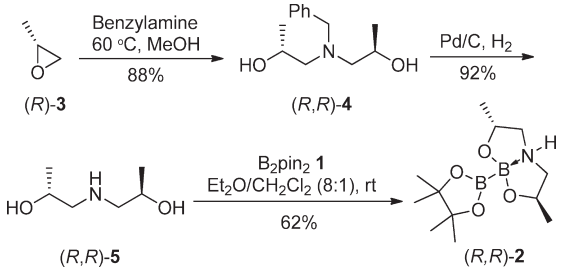
Scheme 1. Synthesis of Enantiomerically Pure PDIPA Diboron, (*R*,*R*)-2



iterative Suzuki—Miyaura coupling reactions. These protected boryl groups are inert under the coupling conditions but become reactive upon treatment with base or acid, respectively.

We recently reported an unsymmetrical, internally activated mixed sp^2—sp^3 diboron compound, pinacolato diisopropanolaminato diboron (PDIPA diboron, **2**).[103,104] This reagent, obtained as a mixture of diastereomers, enables a mild method for the Cu-catalyzed β-boration of α,β-unsaturated esters. The regioselective transfer of differentially coordinated boron atoms in pinB—Bdan to phenyl acetylene exemplifies the utility of unsymmetrical diboron compounds.[105] In this report, we disclose the synthesis, characterization, and reactivity of a single enantiomer of **2** and demonstrate that a diastereomeric mixture is sufficient to effect the boration reaction and considerably increase the substrate scope (up to 28 examples) including highly sensitive α,β-unsaturated aldehydes. In addition, we significantly increased the understanding of the mechanism of the reaction on the basis of X-ray crystal structures of PDIPA diboron; one trigonal planar boron atom is coordinated by a pinacolate moiety, and the other displays a distorted tetrahedral geometry and coordination to a diisopropanolaminate moiety. Coordination of N to B increases B—B bond length and sufficiently activates the diboron reagent for boryl group transfer to copper.

RESULTS AND DISCUSSION

Synthesis and Characterization of PDIPA Diboron (*R*,*R*)-2. In order to determine unambiguously the coordination at the boron atoms, we prepared an enantiomerically pure sample of PDIPA diboron **2**. Treatment of benzylamine with 2 equiv of (*R*)-propylene oxide **3** in methanol at 60 °C readily afforded (*R*,*R*)-**4** in 88% yield (Scheme 1).[106] The benzyl protecting group was removed by heterogeneous catalytic hydrogenation to provide (*R*,*R*)-**5** in 92% yield, which reacted with **1** under the same conditions used for racemic **5**[103] to provide (4*R*,8*R*)-PDIPA diboron ((*R*,*R*)-**2**) after filtration. The characterization (^{1}H, ^{13}C, ^{11}B NMR) of (*R*,*R*)-**2** is consistent with the presence of a single diastereomer, with the expected signals[103] at 35.5 and 9.0 ppm in the ^{11}B NMR spectrum, different from the sp^2 boron chemical shift of **1** (31.1 ppm) (Figure 2).

Additionally, the chemical shifts for **2** are markedly different from those initially reported by Hoveyda et al.,[83] for an *in situ* formed sp^2—sp^3 tetraalkoxydiboron compound, i.e., the NHC diboron adduct (NHC·**1**) wherein both the sp^2- and sp^3-hybridized boron atoms were reported to have upfield chemical shifts of δ 6.3 and 4.5 ppm. The initially reported NMR data for (NHC·**1**) were suspicious, as they are not in agreement with ^{11}B NMR data

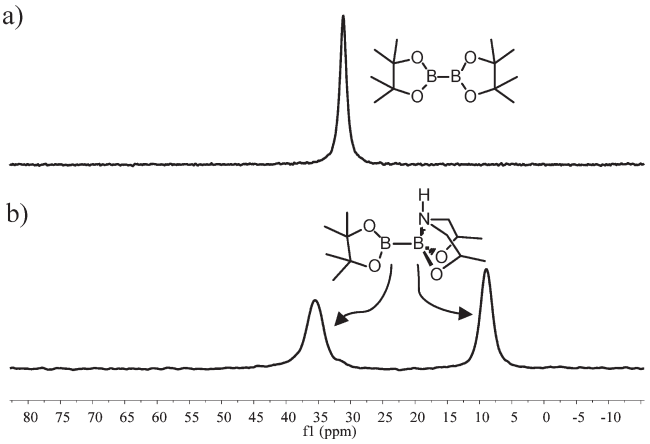


Figure 2. ^{11}B NMR spectra (160 MHz) of (a) **1** and (b) **2** in CD_3CN at room temperature.

reported for other sp^2—sp^3 diboron compounds.[107,108] This prompted us to investigate the intriguing NHC·**1** adduct. While a detailed discussion of our findings will be given elsewhere,[109] we note that in the solid state, (NHC·**1**) has, indeed, an sp^2—sp^3 diboron structure, as confirmed by single-crystal X-ray diffraction, and displays ^{11}B NMR signals at 37.3 and 2.2 ppm (at 5 °C in THF-d_8) for the sp^2 and sp^3 boron centers, respectively. The incorrect ^{11}B NMR data initially reported by Hoveyda et al.[83] are understandable considering the dynamic behavior of (NHC·**1**) in solution,[109,110] leading to an extremely broad signal at ambient temperature which is difficult to observe. Thus, the ^{11}B NMR data initially reported for (NHC·**1**) by Hoveyda et al. are likely due to impurities in the sample rather than the adduct itself.[110]

Recrystallization of (*R*,*R*)-**2** from acetonitrile yielded colorless single crystals suitable for X-ray diffraction analysis (Figure 3). The crystal structure unambiguously confirmed the presence of both 3- and 4-coordinate boron centers in the sp^2—sp^3 diboron compound. The environment of the sp^3 boron atom B2 is tetrahedral; however, it is significantly distorted, as especially apparent from the X—B2—X angles (maximum deviation from 109.47°: 10.45° (O3—B2—N1); average deviation from 109.47°: 8.21°), as a consequence of the bicyclic nature of the DIPA moiety. Although external Lewis base chelation to diboron compounds has been reported,[107,108,111] to the best of our knowledge, this is the first reported crystal structure of an internally chelated sp^2—sp^3 hybridized diboron compound. The entire structure of the B(DIPA) fragment is, not surprisingly, similar to the structures in compounds of the type R-B(deaH) (deaH = $(OCH_2CH_2)_2NH$, R = C_6H_5, $C_{10}H_7$, C_3H_5, C_8H_{11}, C_8H_7, $C_{12}H_9$, $C_{13}H_{17}O_3$).[112] Complexation of N1 to B2 pyramidalizes B2 with an N1—B2 bond length of 1.6743(19) Å, which is longer than in related trigonal tetraaminodiboranes,[113−115] and similar to those in R-B(deaH) compounds (B—N = 1.66(2) Å on average).[112] The distances O4—B2 (1.4475(19)) and O3—B2 (1.4925(19)) are significantly increased compared to O—(sp^2)B distances in related arylboronates.[50] The B—B distance in (*R*,*R*)-**2** is significantly longer (0.012 Å) than in **1** (B—B 1.710(1) Å[116]) due to the change in hybridization of one of the boron atoms, i.e. the increase in p-character, accompanied by the loss of any O—B π-bonding. This bond length change upon hybridization is found to a similar extent in all crystallized sp^2—sp^3 diboron compounds (Table 1). The result is consistent with DFT calculations on the adduct NHC·**1**.[83] The polarization of, or increased electron

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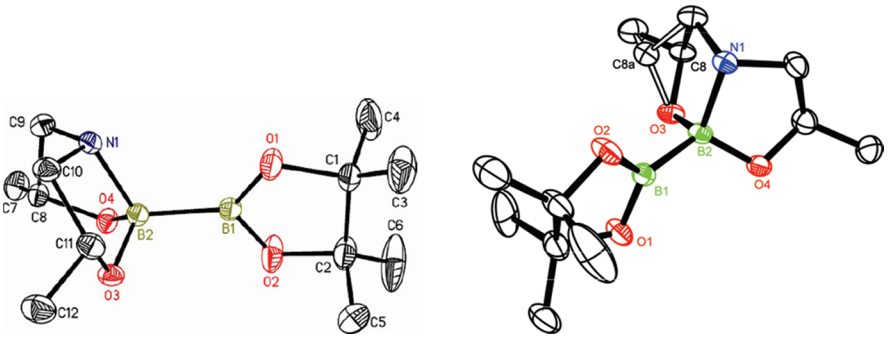

Figure 3. Anisotropic displacement ellipsoid drawings (50%) of (*R*,*R*)-**2** (left) and **2** (right). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: (*R*,*R*)-**2**: B1—B2 1.721(2), B2—N1 1.6743(19), O4—B2 1.4475(19), O3—B2 1.4925(19), B1—O1 1.367(2), B1—O2 1.3678(19), N1—B2—B1 116.16(11), O3—B2—N1 98.98(11), O4—B2—N1 102.02(11); O3—B2—O4 112.04(11), O3—B2—B1 108.82(12), O4—B2—B1 117.31(12); **2**: B1—B2 1.722(4), B2—N1 1.657(3), O4—B2 1.445(3), O3—B2 1.494(3), B1—O1 1.388(4), B1—O2 1.365(6), N1—B2—B1 117.0(2), O3—B2—N1 99.3(2), O4—B2—N1 102.1(2), O3—B2—O4 113.3(2), O3—B2—B1 108.5(2), O4—B2—B1 115.6(2).

Table 1. B—B Distances in Selected Diboron Compounds

compound	B—B dist. /Å	Δ(B—B)[a] /Å
B_2pin_2[116]	1.710(5)	
PDIPA B_2 ((*R*,*R*)-**2**)	1.721(2)	0.012[b]
([PDIPA B_2][K(thf)])$_2$ (((**10**)thf)$_2$)	1.735(2)	0.025[b]
B_2pin_2(CyNHC)[109]	1.743(2)	0.033
$B_2(1,2\text{-}O_2C_6H_4)_2$[88]	1.678(3)	
$B_2(1,2\text{-}O_2C_6H_4)_2(4\text{-}MeC_5H_4N)$[108]	1.706(3)	0.028
$B_2(1,2\text{-}O_2C_6H_4)_2(4\text{-}MeC_5H_4N)_2$[108]	1.713(4)	0.035
$B_2(1,2\text{-}S_2C_6H_4)_2$[90]	1.673(4)[c]	
$B_2(1,2\text{-}S_2C_6H_4)_2(4\text{-}MeC_5H_4N)$[107]	1.701(7)	0.028
$B_2(1,2\text{-}S_2C_6H_4)_2(PMe_2Ph)$[107]	1.689(5)	0.016
$B_2(1,2\text{-}S_2C_6H_4)_2(PEt_3)$[107]	1.707(3)	0.034
$B_2(1,2\text{-}S_2C_6H_4)_2$(phen)[111]	1.707(13)	0.034
$B_2(1,2\text{-}S_2C_6H_4)_2$(bpy)[111]	1.63(5)[c]	0.043
$B_2Cl_3(MeNCH_2CH_2NMe_2)$[117]	1.699(4)	
(1-mesityl-5,7-dimethyl-9*H*-10- (mesityl-(methoxy)boryl)-10-boraphenanthrenyl)lithium[118]	1.725(6)	
(1-mesityl-5,7-dimethyl-9-methoxy-9′- (methyl-(methoxy)boryl)-9-borafluorenyl)lithium[118]	1.720(7)	
B,P;B′,P′-bi(bis(dimethylamino)boryl-1,3- bis(isopropyl)-4,5-benzo-1,3,2-diphosphaborolane)[119]	1.744(9)	
tert-butyl(trichloro)dimethylammoniodiborane[120]	1.704(5)	
2,5-bis(dimethylamino)-2,3,5,6- tetrakis(3,5-bis(trifluoromethyl)phenoxy)-2,3,5,6-tetrabora-1,4-dioxane[121]	1.737(6)	

[a] Change in the B—B distance compared to parent compound. [b] Comparison with B_2pin_2; this work. [c] Averaged value.

density in, the B—B bond in **2** should increase its propensity to undergo transmetalation to copper,[103] enhancing the rates of Cu-catalyzed boration reactions.

Copper-Catalyzed Selective Boration and Additive Screening. In the initial disclosure of our copper-catalyzed boration methodology,[103] we demonstrated the efficient conversion of benzylacrylate to the corresponding borated product **7e** in the presence of catalytic amounts of CuCl and methanol (Figure 4). In the process, we established the chemoselective transfer of the pinacolate protected, sp^2-hybridized boron from **2**. No product is formed in the absence of CuCl. However, we were delighted to discover that copper-stabilizing additives (DPEphos (bis(2-diphenylphosphinophenyl)ether) and trialkylphosphines) and boron-activating agents (NaO^{t}Bu and N-heterocyclic carbene) were not required. This is noteworthy not only because these additives are expensive but also because PDIPA diboron is predicted to be useful for reactions of base-sensitive substrates. As shown in Figure 4, a variety of ester substituents were tolerated, affording the corresponding products **7a**—**e** in excellent yields (91—96%). However, when additional groups are present at the α- or β-position (**7g**—**f**), the reactions yields were lower, presumably as a result of a combination of steric and electronic effects.[122]

In order to improve the reaction conditions and expand the scope of the reaction to other α,β-unsaturated compounds, we studied the effect of additives on the yield and efficiency of the β-boration reaction. The critical importance of MeOH as an additive, initially disclosed by Yun et al.[73] and supported by DFT calculations,[122] was substantiated by our recent work.[103] We investigated whether the identity of the protic additive had a significant effect on the reaction rate and conversion yield (Figure 5). First, we monitored the conversion of 2-cyclohexenone to β-borated cyclohexanone **9h** following addition of **2** (2 equiv), protic additive (2 equiv), and CuCl (5 mol %) in CH_2Cl_2. As expected, MeOH and EtOH accelerated the boration to a

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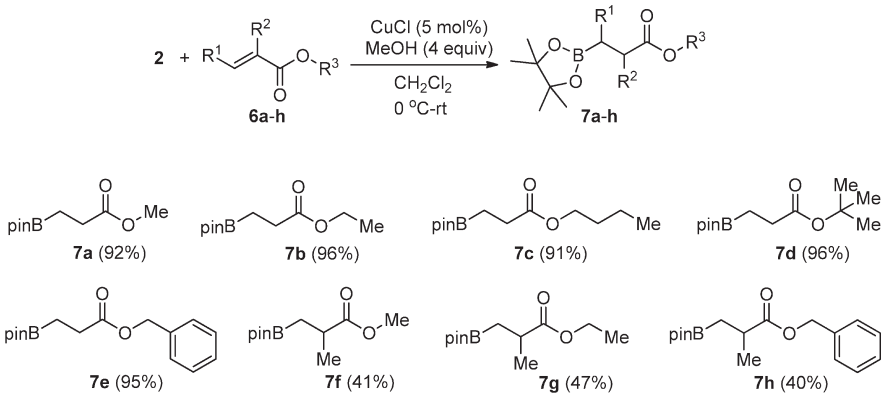

Figure 4. Copper-catalyzed β-boration of various α,β-unsaturated esters.

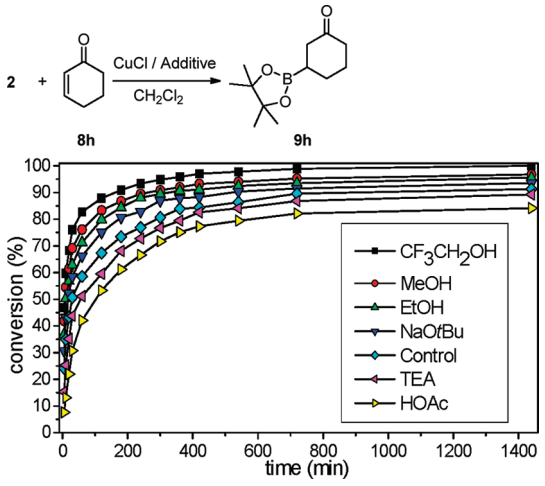

Figure 5. Boration of 2-cyclohexenone in the presence of various additives.

similar degree with >90% conversion after 5 h compared to 81% for the control reaction (no additive). We next investigated the effect of acetic acid and found the reaction to be sluggish, which is not surprising given that **2** rapidly decomposes under acidic conditions. To our delight, however, CF_3CH_2OH (TFE) was found to be the best additive, affording the desired boronate **9h** in >90% conversion in slightly over 3 h.

Next, we examined the effect of base, noting that a catalytic amount of NaO^{t}Bu did enhance the reaction rate.[103] We hypothesized that the addition of a stoichiometric amount of base such as triethylamine or NaO^{t}Bu might accelerate the reaction via removal of the NH proton in **2** providing an anionic diboron reagent in which lengthening of the B−B bond and the anionic charge could further facilitate boryl group transfer to copper. To our disappointment, neither provided a significant improvement. This is explained by the finding that reaction of **2** with a stoichiometric amount of KO^{t}Bu indeed leads to the deprotonation of **2**. However, the initial deprotonation product rearranges to an isomeric species, **10**, wherein one of the alkoxy groups of the DIPA moiety migrates to the neighboring boron atom (Figure 6). This rearrangement is understandable considering the superior π-donor capabilities (to boron) of the NR_2 group compared to the alkoxy group. Hence, the sp^2 boron atom is bound to one NR_2 and one alkoxy group, while the sp^3 boron atom is bound to three alkoxy groups. Compound **10** crystallizes as a potassium-bridged centrosymmetric dimer containing two molecules of THF ((**10**)thf)$_2$. As compound **10** was obtained from a mixture of diastereomers of **2** (1:1.2 by ^{1}H NMR), it too consists of a mixture of diastereomers, resulting in a disorder of the atom pairs O4/O4a, C11/C11a, and C12/C12a (Figure 6). Despite the connectivity in **10** being different from that in **2**, similar principal structural features can be found, namely a virtually planar environment at one boron atom (B2) and a (distorted) tetrahedral environment at the other boron atom (B1). The distance of the NR_2 nitrogen atom N1 to the boron atom B2 is, as expected, much shorter than the N−B distance in the NR_2H adduct **2**, accounting for the stronger N−B bond in **10**, in accordance with N−B distances found in related trigonal tetraaminodiboranes.[113−116] However, the initially suggested lengthening of the B−B bond compared to **2** (Figure 6, Table 1) is indeed observed. Nonetheless, formation of **10** is detrimental to the catalytic reaction as with the two boron centers now being bridged, transmetalation of one of the boron moieties to Cu is less effective.

We next investigated ways to obtain high yields using a smaller excess of **2** and TFE as the additive (Table 2). With CuCl (5%) and **2** (2 equiv), 2-cylohexenone **8h** underwent the β-boration reaction to afford product **9h** in good conversion (entry 1). To confirm that the β-boration reaction was unaffected by the optical purity of the diboron reagent, we employed enantiopure (*R*,*R*)-**2** or **2** and found the same reactivity and conversion yields (entries 1−4). As a result, **2** was used in all subsequent reactions. Slightly increasing the reaction temperature to 40 °C gave higher conversion (entry 5). We next tried to decrease the number of equivalents of **2**, but a change from 2 to 1.5 (entry 6) or 1.2 (entry 7) equiv resulted in slightly decreased yields of **9h**. To our delight, increasing the catalyst loading to 10 mol % CuCl, with 1.2 equiv of **2** gave excellent conversion after 2 h (entry 8). As expected, the reaction was slightly less efficient when the reaction was run at room temperature (entry 9). Changing the catalyst to CuOAc or [Rh(cod)Cl]$_2$ also afforded the desired product in excellent yield (entries 10−11). However, when we surveyed other metals as catalysts including zinc, nickel, and platinum complexes, only poor conversions were observed (entries 12−14).

Copper-Catalyzed β-Boration of α,β-Unsaturated Ketones. With the optimal reaction conditions determined (entry 8, Table 2), we tested the β-boration conditions with more reactive α,β-unsaturated ketones (Table 3). As shown in entries 1−3, simple acyclic vinyl ketones with methyl **8a**, ethyl **8b**, and propyl **8c** groups afforded the corresponding products **8a**−**c** in up to

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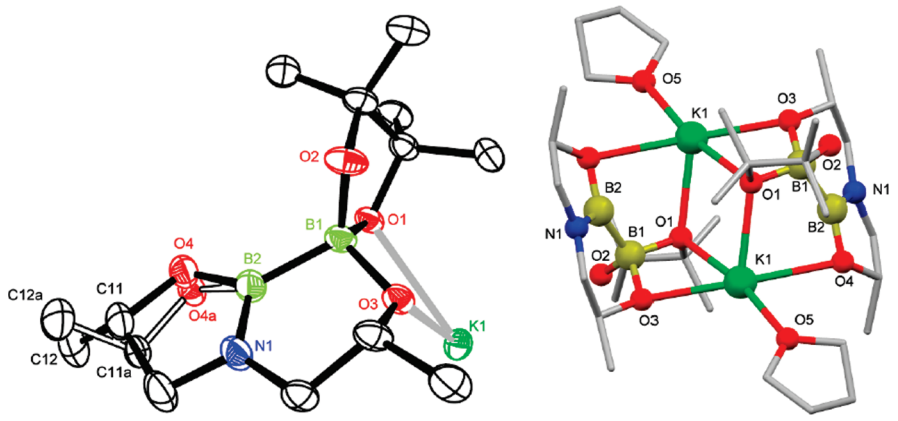
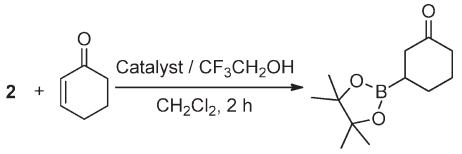


Figure 6. Perspective view of one formula unit of **10** (left) and a view of the potassium-bridged dimer of (**(10)**thf)$_2$ (right). Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms and disorder of the THF moiety are omitted for clarity. Selected bond distances (Å) and angles (deg): B1−B2 1.735(2), O1−B1 1.498(2), O2−B1 1.486(2), O3−B1 1.524(2), O4−B2 1.400(4), N1−B2 1.408(2), O1−B1−O2 104.1(1), O1−B1−O3 107.8(1), O2−B1−O3 108.9(1), O1−B1−B2 115.8(1), O2−B1−B2 116.2(1), O3−B1−B2 103.8(1).

Table 2. Addition of 2 to 2-cyclohexenone under various conditions.[a]

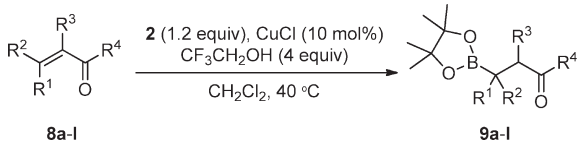


entry	catalyst, loading (mol %)	equiv of **2**	t (°C)	convn[b] (%)
1	CuCl, 5	2	rt	87.8
2[c]	CuCl, 5	2	rt	87.1
3	CuCl, 5	1.2	rt	73.1
4[c]	CuCl, 5	1.2	rt	73.7
5	CuCl, 5	2	40	91.3
6	CuCl, 5	1.5	40	88.4
7	CuCl, 5	1.2	40	82.3
8	**CuCl, 10**	**1.2**	**40**	**89.0**
9	CuCl, 10	1.2	rt	82.9
10	CuOAc, 10	1.2	40	85.1
11	[Rh(cod)Cl]$_2$, 10	1.2	40	80.1
12	ZnCl$_2$, 10	1.2	40	17.3
13	Ni(cod)$_2$, 10	1.2	40	16.2
14	Pt(cod)Cl$_2$, 10	1.2	40	21.6

[a] General procedure: **2** in CH_2Cl_2 was added to a solution of metal catalyst in CH_2Cl_2 at rt followed by **8h** (1 equiv) and CF_3CH_2OH (4 equiv). Then the mixture was stirred at the indicated temperature. [b] Conversion was determined by GC analysis. [c] (*R*,*R*)-**2** was used instead of **2**.

95% isolated yield within 12 h. The lower isolated yield in the case of **8a** may be due, in part, to its volatility. β-Substituted enones containing methyl and ethyl groups also provided the desired products **9d**−**e** in excellent yields (entries 4−5). In addition, β-phenyl-substituted enones **8f**−**g** provided products **9f**−**g** in good yields (entries 7−8). The decrease in reactivity of these substrates might arise from a combination of steric and electronic effects of the phenyl ring. Cyclohexenone **8h** and cyclopentenone **8i** were also converted to their respective β-borated

Table 3. Copper-Catalyzed β-Boration of α,β-Unsaturated ketones



entry	substrate	R^1	R^2	R^3	R^4	time (h)	% yield[a] (%)[b]
1	**8a**	H	H	H	Me	12	74
2	**8b**	H	H	H	Et	12	87
3	**8c**	H	H	H	Pr	12	95
4	**8d**	Me	H	H	Me	16	90
5	**8e**	Me	H	H	Et	16	92
6	**8f**	Ph	H	H	Me	36	80
7	**8g**	Ph	H	H	Ph	36	83
8	**8h**	2-cyclohexenone				24	82
9	**8i**	2-cyclopentenone				24	82
10	**8j**	Me	Me	H	Me	48	41(55)
11	**8k**[c]	Me	H	Me	Me	48	35(48)
12	**8l**[d]	H	$(CH_2)_4$		Me	48	61

[a] Isolated yield. [b] 2 equiv of **2** was used. [c] dr = 6.7:1. [d] dr = 4.3:1.

products in good yields (entries 10−11). Additionally, sterically encumbered **8j** resulted in a boronate with a quaternary carbon center, and the disubstituted enones **8k**−**l** were converted to the desired products **9j**−**l** in moderate yields (entries 10−12). Interestingly, the disubstituted ketones **8k** and **8l** resulted in products with good diastereoselectivity (6.7:1 and 4.3:1, respectively). Enone **8l** shows improved selectivity in comparison to that of the NHC-catalyzed case.[83] It should be noted that, compared with our previous studies,[103] the improved β-boration protocol gave faster rates with similar yields and required only 1.2 equiv of **2**.

Copper-catalyzed β-boration of other α,β-unsaturated conjugated compounds. Perhaps the most challenging substrates for metal-catalyzed boron addition reactions are α,β-unsaturated aldehydes (Scheme 2). Aromatic aldehydes have been shown to react in a 1,2-fashion using a Cu-NHC catalyst

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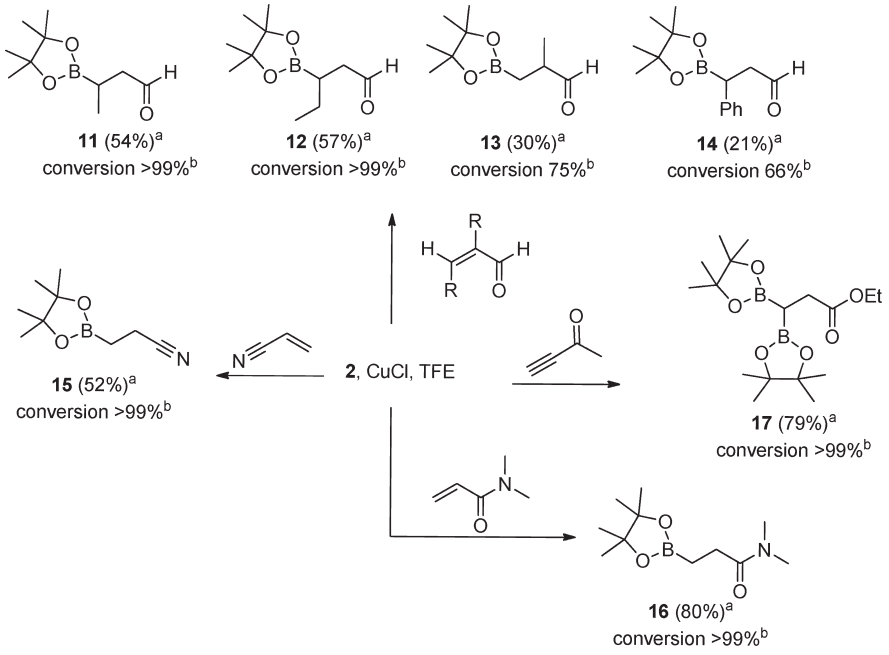
Scheme 2. Copper-Catalyzed β-Boration of Other α,β-Unsaturated Conjugated Compounds



[a] Isolated yield. [b] Conversion after 3 h as determined by GC analysis.

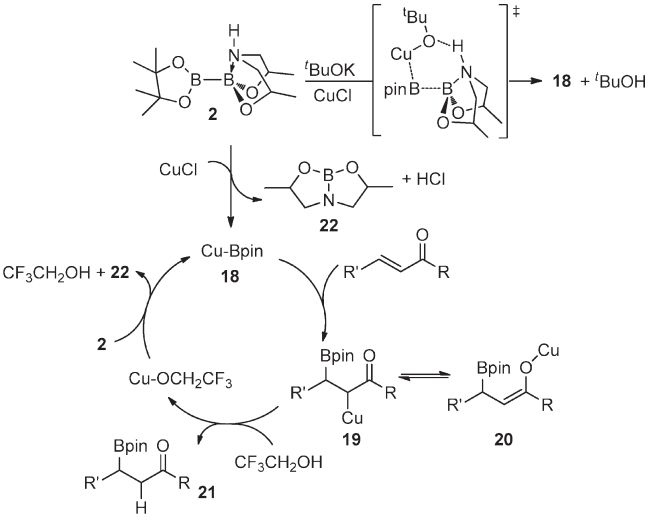
system.[123,124] Thus, in addition to the 1,4-selective diboration of α,β-unsaturated aldehydes, there can be a competing 1,2-diboron addition reaction. To date, there have only been three reported cases of boron addition to α,β-unsaturated aldehydes, using Pt,[64] Rh[66] and Cu[78] as catalysts. However, some of these methods require harsh reaction condition such as high reaction temperature;[64,66] some only reported GC[66,78] yields.

Taking advantage of our milder reaction conditions, we examined the borylation of a series of α,β-unsaturated aldehydes. As shown in Scheme 2, crotonaldehyde was readily converted into the boronate **11** in >99% conversion after 3 h with moderate isolated yield. 2-Ethylacrolein and methacrolein also proceeded in moderate yields affording compounds **12** and **13**, respectively. Not surprisingly for cinnamaldehyde as substrate, the reaction proceeded to 66% conversion after 3 h (or 97% after 24 h), affording a 21% yield of **14**. In comparison, the CuCl/DPEphos/NaO*t*Bu system[73] with **1** as the boron source and cinnamaldehyde as substrate via Yun's method gave only 73% conversion after 24 h and <10% isolated yield. Thus, the mild reaction conditions using **2** offer a significant advantage relative to previously reported protocols.

In order to demonstrate further the synthetic utility of **2**, we investigated the β-boration of conjugated compounds bearing other functional groups. For example, acrylonitrile and *N*,*N*-dimethylacrylamide underwent β-boration to yield **15** and **16** in good yields and excellent conversions (>99%). 3-Butyn-2-one, which was also smoothly borated, furnished the interesting β,β-diborated product **17** in 79% yield.

Proposed Catalytic Cycle. A possible catalytic cycle for the copper-catalyzed boration with **2** is shown in Scheme 3. On the basis of the above experimental results and the X-ray structure of (*R*,*R*)-**2**, the catalytic cycle starts with an activated diboron compound. In our view, the formation of an sp^2-sp^3 hybridized diboron compound is critical for the transmetalation of the (sp^2)-Bpin moiety to copper to form the active

Scheme 3. Proposed Catalytic Cycle



boryl copper complex **18**. This is consistent with the use of stoichiometric amounts of *tert*-butoxide (i.e., excess with respect to the amount of the copper catalyst)[73−75,79] in reactions employing **1** as the boron source and related to the activation of **1** with NHC ligand in the copper-free diboration of α,β-unsaturated compounds.[83] With a catalytic amount of *tert*-butoxide present (*vide supra*), a Cu−O^{t}Bu species can be formed, which can deprotonate **2** and transmetalate faster than CuCl to form **18**, resulting in more rapid catalyst initiation.[125] Following insertion of the substrate into the Cu−Bpin bond, the resulting copper enolate[126] **19**/**20** undergoes protolytic cleavage by MeOH or TFE to form the product **21** and a copper alkoxide species, which regenerates **18** in the presence of **2**.[73]

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CONCLUSIONS

In summary, using a preactivated sp^2-sp^3 hybridized diboron, we developed a mild method for the installation of a boryl group at the β-carbon of α,β-unsaturated conjugated compounds in up to 95% yield. The PDIPA diboron compound is unique in that it is the first example of a mixed-hybrid diboron reagent; all previously reported diboron reagents are sp^2-hybridized. We have expanded the scope of the reaction to a variety of α,β-unsaturated ketones, highly reactive aldehydes and substrates containing other functional groups. The sp^3-hybridized, pyramidal DIPA-coordinated boron atom was unambiguously identified on the basis of ^{11}B NMR spectroscopic and X-ray crystallographic data and indicates the critical role of an activating nucleophile, such as *tert*-butoxide, for the reaction of diboron compounds. These results provide mechanistic insights into the activation of related reactions involving N-heterocyclic carbene-Cu catalysts. Finally, our results demonstrate the chemoselective transfer of a Bpin moiety to the β-carbon of conjugated substrates. In principle, chiral nonracemic sp^2-sp^3 diboron compounds could induce enantioselective β-boration of α,β-unsaturated conjugated compounds. The synthesis of other unsymmetrical diboron compounds and examinations of their utility in catalyzed borylation reactions are currently under investigation.

EXPERIMENTAL SECTION

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or in a glovebox filled with nitrogen. CuCl, bis(pinacolato)diboron, and other commercial compounds were purchased and used as received. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded either on 400, 500, or 700 MHz spectrometers. ^{1}H NMR chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, THF-d_8: 1.73, 3.58 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and assignment. ^{13}C NMR chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm, THF-d_8: 67.57, 25.37 ppm). ^{11}B NMR chemical shifts are reported in ppm with boron trifluoride diethyl etherate as an external standard ($BF_3O(C_2H_5)_2$: 0 ppm).

(2*R*,2′*R*)-1,1′-(Benzylazanediyl)bis(propan-2-ol) (*R*,*R*)-4. To a one-neck round-bottomed flask was added *R*-(+)-propylene oxide **3** (1.21 mL, 17.22 mmol), and benzylamine (0.86 mL, 7.83 mmol). The reaction mixture was diluted with methanol (5 mL) and heated to 60 °C. After 8 h, the reaction mixture was concentrated via rotary evaporator and purified by silica gel column chromatography to provide the product as a yellow oil (1.54 g, 88%). TLC (alumina, EtOAc): R_f = 0.44. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36−7.26 (m, 5H), 3.9−3.80 (m, 3H), 3.50 (d, J = 13.6 Hz, 1H), 2.78 (s, 2H, OH), 2.45 (d, J = 5.2 Hz, 2H), 2.44 (d, J = 7.5 Hz, 2H), 1.09 (d, J = 6.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.6, 129.1, 128.6, 127.5, 64.1, 62.2, 59.9, 20.4.

(2*R*,2′*R*)-1,1′-Azanediylbis(propan-2-ol) (*R*,*R*)-5. To a 25-mL round-bottomed flask was added 10% Pd/C (32 mg, 0.297 mmol) and (*R*,*R*)-**4** (1.328 g, 5.95 mmol) in methanol (6 mL) to give a black suspension. The reaction mixture was stirred under a hydrogen atmosphere at room temperature for 6 h. After completion of the reaction, the suspension was filtered through a pad of Celite and concentrated to give the product as light-yellow oil (729 mg, 92%). TLC (alumina, 5% MeOH/EtOAc): R_f =0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.84−3.78 (m, 2H), 2.67 (dd, J = 12.1, 3.0 Hz, 2H), 2.49 (dd, J = 12.1, 9.0 Hz, 2H), 1.16 (d, J = 6.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 66.2, 56.8, 20.7.

(4*R*,8*R*)-4,8-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,6,2-dioxazaborocane, (4*R*,8*R*)-2. To a solution of bis(pinacolato)diboron **1** (1 g, 3.94 mmol) in diethyl ether (16 mL) was added (*R*,*R*)-**5** (573 mg, 4.33 mmol) in CH_2Cl_2 (2 mL). After 5 min, a white precipitate appeared, and the reaction mixture was stirred at room temperature for 24 h. The white solid was collected by filtration and washed with a copious amount of diethyl ether to provide the desired product (4*R*,8*R*)-**2** (660 mg, 62%), which was sufficiently pure to perform the β-boration experiments. Recrystallization from acetonitrile yielded colorless single crystals suitable for X-ray diffraction analysis. ^{1}H NMR (500 MHz, CD_3CN) δ = 5.14 (s, br, 1H), 4.11−4.04 (m, 1H), 3.70−3.63 (m, 1H), 3.32−3.27 (m, 1H), 2.69 (dd, J = 11.5, 3.7 Hz, 1H), 2.28−2.22 (m, 1H), 1.92−1.86 (m, 1H), 1.16 (s, 12H), 1.13 (d, J = 6.2 Hz, 3H), 1.12 (d, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ = 81.4, 67.5, 66.8, 58.0, 56.4, 24.7, 24.7, 19.0, 18.3; ^{11}B NMR (160 MHz, CD_3CN) δ = 35.51 (sp^2-B), 8.95 (sp^3-B); IR (NaCl) 3074, 2971, 2929, 2883, 1368, 1251, 1114, 1024, 971, 854, 804 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{12}H_{26}B_2NO_4$ $[M + H]^+$: 270.2048, Found: 270.2047.

General Procedure for the β-Boration of Compounds: Typical Example: 9h. To a 25-mL two-neck round-bottom flask was added copper(I) chloride (7.36 mg, 0.074 mmol). CH_2Cl_2 (0.5 mL) was added, and the suspension was stirred for 2 min. PDIPA diboron **2** (240 mg, 0.892 mmol) in CH_2Cl_2 (7.2 mL) was added by syringe, and the suspension was stirred for another 5 min (the solution turned brown). Cyclohexen-2-one **8h** (71.5 mg, 0.744 mmol) followed by CF_3CH_2OH (0.214 mL, 2.97 mmol) was added by syringe. The solution was heated to 40 °C and stirred until no starting material was detected by TLC. The reaction mixture was filtered through a pad of Celite, concentrated, and purified by silica gel chromatography.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one 9a: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.57 (t, J = 7.1 Hz, 2H), 2.11 (s, 3H), 1.22 (s, 12H), 0.88 (t, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 209.3, 83.2, 38.5, 29.4, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.47; IR (NaCl) 2980, 1717, 1379, 1315, 1146, 968, 849 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{10}H_{20}BO_3$ $[M + H]^+$: 199.1506, Found: 199.1497.

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-3-one 9b: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.54 (t, J = 7.2 Hz, 2H), 2.40 (q, J = 7.4 Hz, 2H), 1.22 (s, 12H), 1.04 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 212.1, 83.2, 37.1, 35.4, 24.8, 8.1; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.58; IR (NaCl) 2978, 1715, 1377, 1315, 1148, 968, 837 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{11}H_{22}BO_3$ $[M + H]^+$: 213.1662, Found: 213.1662.

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-3-one 9c: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.54 (t, J = 7.1 Hz, 2H), 2.36 (t, J = 7.3 Hz, 2H), 1.59 (sextet, J = 7.3 Hz, 2H), 1.22 (s, 12H), 0.89 (t, J = 7.4 Hz, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 211.7, 83.1, 44.2, 37.6, 24.8, 17.6, 13.8; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.54; IR (NaCl) 2976, 1712, 1379, 1315, 1148, 968, 845 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{12}H_{24}BO_3$ $[M + H]^+$: 227.1819, Found: 227.1805.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-one 9d: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.55−2.53 (m, 2H), 2.10 (s, 3H), 1.28−1.24 (m, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 0.94 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 209.1, 83.1, 47.7, 29.8, 24.8, 24.7, 15.1; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.79; IR (NaCl) 2978, 1715, 1369, 1315, 1146, 968, 862 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{11}H_{22}BO_3$ $[M + H]^+$: 213.1662, Found: 213.1639.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-3-one 9e: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.53−2.51 (m, 2H), 2.38 (qd, J = 3.7, 7.4 Hz, 2H), 1.30−1.26 (m, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.04 (t, J = 7.4 Hz, 3H), 0.95 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 211.8, 83.0, 46.3, 35.8, 24.8, 24.7, 15.1, 8.0; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.58; IR (NaCl) 2976, 2934, 1713, 1369, 1315, 1146, 968, 860 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{12}H_{24}BO_3$ $[M + H]^+$: 227.1819, Found: 227.1796.

4-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-butan-2-one 9f: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.27−7.17 (m,

4H), 7.15−7.10 (m, 1H), 3.03 (dd, J = 18.3, 10.8 Hz, 1H), 2.82 (dd, J = 18.3, 5.3 Hz, 1H), 2.63 (dd, J = 10.8, 5.3 Hz, 1H), 2.12 (s, 3H), 1.21 (s, 6H), 1.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 208.4, 141.8, 128.6, 128.3, 125.6, 83.5, 47.6, 29.7, 27.0, 24.6, 24.6; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.16; IR (NaCl) 2978, 1713, 1366, 1319, 1144, 966, 854, 702 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{16}H_{24}BO_3$ [M + H]: 275.1819, Found: 275.1819; Calcd for $C_{16}H_{27}BNO_3$ [M + NH_4]$^+$: 292.2084, Found: 292.2091.

1,3-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one 9g: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97−7.95 (m, 2H), 7.59−7.50 (m, 1H), 7.45−7.42 (m, 2H), 7.34−7.24 (m, 4H), 7.21−7.13 (m, 1H), 3.55 (dd, J = 10.9, 18.3 Hz, 1H), 3.42 (dd, J = 5.0, 18.3 Hz, 1H), 2.80 (dd, J = 5.0, 10.9 Hz, 1H), 1.24 (s, 6H), 1.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 199.8, 142.0, 136.9, 133.0, 128.6, 128.6, 128.5, 128.1, 125.7, 83.5, 43.4, 27.3, 24.7, 24.6; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.63; IR (NaCl) 2978, 1682, 1367, 1321, 1142, 754, 698 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{21}H_{26}BO_3$ [M + H]$^+$: 337.1975, Found: 337.1981.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexanone 9h: oil; TLC (20% EtOAC/hexanes): R_f = 0.37. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.39−2.25 (m, 4H), 2.11−2.01 (m, 1H), 1.89−1.82 (m, 1H), 1.79−1.68 (m, 1H), 1.67−1.59 (m, 1H), 1.49−1.40 (m, 1H), 1.22 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 212.4, 83.5, 42.6, 41.9, 28.5, 26. 6, 25.1, 24.8, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.11; IR (NaCl) 2978, 1711, 1383, 1327, 1144, 980, 851 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{12}H_{22}BO_3$ [M + H]$^+$: 225.1662, Found: 225.1639.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentanone 9i: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.34−2.17 (m, 2H), 2.16−2.04 (m, 3H), 1.88−1.77 (m, 1H), 1.69−1.55 (m, 1H), 1.23 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 221.1, 83.6, 40.5, 39.0, 25.3, 24.8, 24.8, 19.7; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.48; IR (NaCl) 2978, 1742, 1385, 1323, 1144, 968, 858 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{11}H_{20}BO_3$ [M + H]: 211.1506, Found: 211.1492; Calcd for $C_{11}H_{23}BNO_3$ [M + NH_4]$^+$: 228.1771, Found: 228.1762.

4-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pentan-2-one 9j: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.48 (s, 2H), 2.07 (s, 3H), 1.23 (s, 12H), 0.91 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 208.8, 83.0, 55.8, 30.1, 24.7; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 34.10; IR (NaCl) 2976, 2934, 1715, 1367, 1308, 1140, 968, 858 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{12}H_{24}BO_3$ [M + H]$^+$: 227.1819, Found: 227.1814.

3-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pentan-2-one 9k: oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.59 (m, 1.21H), 2.14 (s, 0.63H, minor diastereomer), 2.11 (s, 3H, major diastereomer), 1.26 (m, 1.21H), 1.23 (s, 12H, major diastereomer), 1.21 (s, 2.52H, minor diastereomer), 1.13 (d, J = 7.2 Hz, 3H, major diastereomer), 1.12 (d, J = 7.2 Hz, 0.63H, minor diastereomer), 0.91 (d, J = 7.5 Hz, 3H, major diastereomer), 0.89 (d, J = 8.5 Hz, 0.63H, minor diastereomer); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 213.1, 83.1, 83.0, 50.1, 49.8, 28.2, 28.1, 24.8, 24.8, 15.7, 14.8, 13.0, 12.3; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.63; IR (NaCl) 2976, 1711, 1369, 1317, 1146, 968, 856 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{12}H_{24}BO_3$ [M + H]$^+$: 227.1819.

1-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)ethanone 9l: oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.57 (dt, J = 4.5, 7.5 Hz, 1H, major diastereomer), 2.49 (dt, J = 6.5, 13.5 Hz, 0.1H, minor diastereomer), 2.12 (s, 3.3H), 1.88−1.78 (m, 2.2H), 1.69−1.65 (m, 1.1H), 1.55−1.50 (m, 1.1H), 1.48−1.42 (m, 2.2H), 1.41−1.34 (m 2.2H), 1.29−1.26 (m, 1.1H), 1.22 (d, J = 4.3 Hz, 13.2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 212.1, 83.2, 82.8, 53.0, 52.2, 29.9, 27.9, 27.6, 27.6, 26.7, 26.7, 26.5, 25.8, 25.4, 25.2, 25.1, 24.9, 24.8, 24.8, 24.6, 24.6; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.22; IR (NaCl) 2928, 2855, 1707, 1377, 1311, 1146, 970, 852 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{14}H_{26}BO_3$ [M + H]$^+$: 253.1975, Found: 253.1993.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pentanal 12: oil; TLC (5% EtOAc/hexanes): R_f = 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.76 (s, 1H), 2.58 (dd, J = 7.2, 18.0 Hz, 1H), 2.51 (dd, J = 7.2, 18.0 Hz, 1H), 1.53−1.46 (m, 1H), 1.43−1.36 (m, 1H), 1.32−1.26 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 203.0, 83.3, 45.6, 24.9, 24.7, 23.6, 13.3; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.74; IR (NaCl) 2977, 1725, 1368, 1318, 1146, 968, 854 cm^{-1}; HRMS (ESI$^+$): Calcd for $C_{11}H_{21}BNaO_3$ [M + Na]$^+$: 235.1481, Found: 235.1484.

2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propanal 13: oil; TLC (5% EtOAc/hexanes): R_f = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.64 (s, 1H), 2.56 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.15 (d, J = 7.2 Hz, 3H), 1.05 (dd, J = 6.9, 15.9 Hz, 1H), 0.83 (dd, J = 7.7, 15.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 205.3, 83.4, 42.7, 24.8, 15.7; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.38; IR (NaCl) 2979, 1723, 1369, 1319, 1147, 968, 852 cm^{-1}; HRMS (ESI+): Calcd for $C_{10}H_{19}BNaO_3$ [M+Na]$^+$: 221.1325, Found: 221.1311.

([PDIPA B_2][K(thf)])$_2$, ((10)thf)$_2$. Under an atmosphere of nitrogen **2** (70 mg, 260 μmol) and KO^{t}Bu (41 mg, 365 μmol, 1.4 equiv) were combined in 2 mL of dry THF. After 3 d, X-ray quality crystals separated, which were washed with n-hexane (2 × 2 mL) and dried *in vacuo* to give 27 mg (36 μmol, 27%) of a colorless solid. mp: > 160 °C dec; ^{1}H NMR (700 MHz, THF-d_8): δ = 4.43−4.38 (m, 1 H, OCH(A)), 4.37−4.31 (m, 1 H, OCH(A′)), 4.15−4.09 (m, 1 H, OCH(B)), 3.63−3.60 (m, 4 H, CH_2O(THF)), 3.14 (t, J = 8 Hz, 1 H, CH_2N(A)), 3.09 (t, J = 8 Hz, 1 H, CH_2N(A′)), 2.76−2.66 (m, 2 H, CH_2N(A, B)), 2.59−2.55 (m, 2 H, CH_2N(A′, B)), 1.79−1.76 (m, 4 H, CH_2O(THF)), 1.30 (d, J_{HH} = 6 Hz, 3 H, CH_3(A′)), 1.19 (d, J = 6 Hz, 3 H, CH_3(A′)), 1.09, 1.07, 1.06 (two signals) (s, 6 H, CH_3(pin)), 1.04 (d, J = 6 Hz, 3 H, CH_3(B)), 0.99 (two signals) (s, 3 H, CH_3(pin)), 0.95 (s, 3 H, CH_3(pin)); ^{13}C NMR (175 MHz, THF-d_8): δ = 78.5, 78.4, 77.2, 77.0, 74.7, 74.1, 68.4, 66.1, 65.9, 58.2, 57−7, 57.4, 57.3, 27.6, 27.5, 27.3, 27.1 (two signals), 26.7 (two signals), 26.6, 24.6, 23.1, 22.6; ^{11}B NMR (224 MHz, THF-d_8): δ = 38.1 (v br s), 5.4 (br s); Anal. Calcd for: $C_{32}H_{64}O_{10}N_2B_4K_2$: C, 50.68; H, 8.51; N, 3.67%. Found: C, 50.84; H, 8.58; N, 3.61%.

X-ray Crystallographic Analysis. Crystals were centered on the goniometer of an Oxford Diffraction SuperNova equipped with an Eos detector and operating with Cu Kα radiation (*R,R*)-**2** or a Bruker SMART 1000 ((**10**)thf)$_2$ diffractometer using Mo Kα radiation, respectively. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro ((*R,R*)-**2**)[127] or SMART,[128] SAINT[129] and SADABS[130] (((**10**)K·thf)$_2$). The structures were solved by direct methods and refined using SHELXTL NT or SHELXTL 6.14.[131] The final refinement model involved anisotropic displacement parameters for all non-hydrogen atoms and a riding model for all hydrogen atoms. In the case of (*R,R*)-**2**, the anisotropic displacement parameters of the pinacol group suggest disorder, but attempts to model 2-position disorder did not improve the overall model and were abandoned. In the structure of ((**10**)thf)$_2$, the THF molecule is partly disordered; two positions were refined (ratio of occupancies: 54:46). Additionally, a part of the diisopropanolamine moiety is disordered (see text). The absolute configuration of (*R,R*)-**2** was established from anomalous dispersion effects (Flack x = −0.07(18);[132] Hooft P2(true) = 1.000, P3(true) = 1.000, P3(rac-twin) = 0.4 × 1015; P3(false) = 0.000, y = −0.05(7)[133]). CCDC-750196 ((4*R*,8*R*)-**2**), CCDC-784473 (**2**) and CCDC-784472 (((**10**)thf)$_2$)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray data for (*R,R*)-2: $C_{12}H_{25}B_2NO_4$, M_r = 268.95, crystal dimensions 0.211 × 0.072 × 0.066 mm^3, orthorhombic, $P2_12_12_1$, a = 9.5436(2) Å, b = 11.7206(3) Å, c = 13.6397(3) Å, V = 1525.69(6) Å^3, Z = 4, Z' = 1, ρ_{calcd} = 1.171 g/cm^3, μ = 0.673 mm^{-1}, Cu K_α radiation (1.5418 Å), T = 100(2) K, $2\theta_{max}$ = 144.5°, 9951 reflections with 2992 unique [R(int) = 0.0274], R1= 0.0365 (for 2852 unique data with I > 2σ(I)), wR2 = 0.994 (all data), max peak/hole = 0.246/−0.205 e$^-$/Å^3.

X-ray data for 2: $C_{12}H_{25}B_2NO_4$, M_r = 268.95, crystal dimensions 0.51 × 0.24 × 0.21 mm^3, orthorhombic, $P2_12_12_1$, a = 9.5091(3) Å, b = 11.8200(3) Å, c = 13.6947(4) Å, V = 1539.25(8) Å^3, Z = 4, Z' = 1, ρ_{calcd} = 1.161 g/cm^3, μ = 0.082 mm^{-1}, Mo Kα radiation (0.71073 Å), T = 120(2) K, $2\theta_{max}$ = 54.0°, 17150 reflections with 1927 unique [R(int) = 0.0652], R1= 0.0495 (for 1708 unique data with $I > 2\sigma(I)$), wR2 = 0.1433 (all data), max peak/hole = 0.469/−0.216 e$^-$/Å^3.

X-ray data for ((10)thf)$_2$: $C_{16}H_{32}B_2KNO_5$, M_r =379.15, crystal dimensions 0.42 × 0.31 × 0.29 mm^3, triclinic, $P\bar{1}$, a = 9.8528(3) Å, b = 10.1429(3) Å, c = 10.9177(3) Å, α = 86.801(1)°, β = 83.170(1)°, γ = 69.752(1)°, V = 1018.12(5) Å^3, Z = 2, Z' = 1, ρ_{calcd} = 1.237 g/cm^3, μ = 0.285 mm^{-1}, Mo K_α radiation (0.71073 Å), T = 120(2) K, $2\theta_{max}$ = 56.0°, 13552 reflections with 4906 unique [R(int) = 0.0356], R1 = 0.0378 (for 4272 unique data with $I > 2\sigma(I)$), wR2 = 0.1030 (all data), max peak/hole = 0.327/−0.360 e$^-$/Å^3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. GC analysis of **9k** and **9l**, ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR spectra of all of the products prepared in this study, and crystallographic information for (4*R*, 8*R*)-**2**, **2**, and ((**10**)thf)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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