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β-Borylation of conjugated carbonyl compounds with silylborane or bis(pinacolato)diboron catalyzed by Au nanoparticles†

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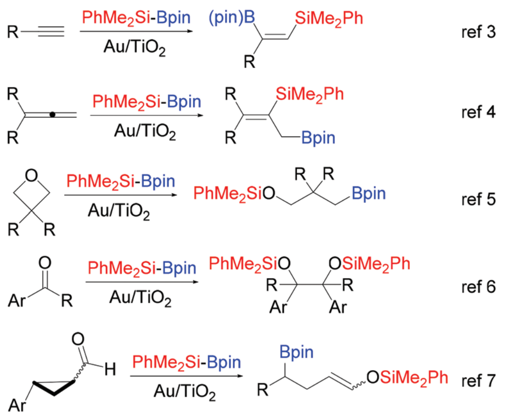
Conjugated aldehydes and ketones undergo reaction with $Me_2PhSiBpin$ (pin: pinacolato) catalyzed by Au nanoparticles supported on TiO_2 forming exclusively the β-borylation products, *via* the intermediate formation of the labile silaboration adducts. This chemoselectivity pathway is complementary to the so far known analogous reaction catalyzed by other metals, where β-silylation occurs instead. β-Borylation also occurs with pinBBpin under identical reaction conditions in a variety of conjugated carbonyl compounds, including esters and amides which are unreactive in their attempted Au-catalyzed silaboration.

Introduction

Supported gold nanoparticles (Au NPs) and other nano Au(0) materials have emerged as powerful catalytic systems in a plethora of transformations of organic substrates, beyond aerobic oxidation or transfer hydrogenation.[1] Among them, the activation and subsequent addition of interelement σ bond linkages (Si–H, Si–Si, B–B, B–Si) to alkynes, allenes and even strained σ systems represent a practical route for the synthesis of synthetically attractive organosilicon and organoboron compounds.[2] Our group was the first to establish the ability of supported Au NPs to smoothly activate the Si–B bond of the fairly stable $Me_2PhSiBpin$ (pin: pinacolato) in its reaction with alkynes.[3] Since then, a range of applications appeared using this silylborane and Au/TiO_2 as the catalyst. Thus, we have additionally shown (Scheme 1) the regioselective silaboration of allenes,[4] the regioselective ring opening of epoxides and oxetanes yielding β- or γ-silyloxy boronates respectively,[5] the pinacol-type reductive dimerization of aryl substituted carbonyl compounds promoted by the silylborane,[6] and more recently, the silaboration of 2-aryl-substituted cyclopropyl aldehydes, in which β-boronate silyl enol ethers are formed *via* ring-opening rearrangement of an intermediate α-silyloxy cyclopropyl radical.[7]

Results and discussion

Prompted by our intense interest in the Au NP-catalyzed reaction of silylboranes with organic compounds, we examined the reactivity of $Me_2PhSiBpin$ with conjugated carbonyl compounds. In our previous study regarding its reaction with simple carbonyl compounds, only aromatic benzaldehydes and acetophenones exhibited reactivity towards a radical-initiated dimerization pathway. With the exception of aryl-substituted cyclopropyl aldehydes which yield rearranged silaboration adducts,[7] all simple aliphatic aldehydes or ketones that were examined did not exhibit any kind of reactivity.[6] On the other hand, the reaction of conjugated carbonyl compounds with silylboranes in the presence of a proton source is well known[8] under various catalytic protocols, and leads to the exclusive conjugated addition of the silyl moiety as a nucleophile, forming β-silyl-substituted carbonyl compounds (Scheme 2). The group of Oestreich was the first to show that a cationic Rh(I) complex catalyzes silyl transfer from



Scheme 1 Reactivity motifs of silylborane $Me_2PhSi\text{-}Bpin$ with various organic compounds catalyzed by Au/TiO_2, previously reported by our group.

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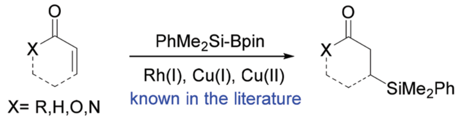
† Electronic supplementary information (ESI) available: Copies of the ^1H and ^{13}C NMR spectra of all products (PDF). See DOI: 10.1039/d0ob01806f



Scheme 2 Known chemoselectivity in the metal-catalyzed reaction of Me_2PhSi-Bpin with conjugated carbonyl compounds.

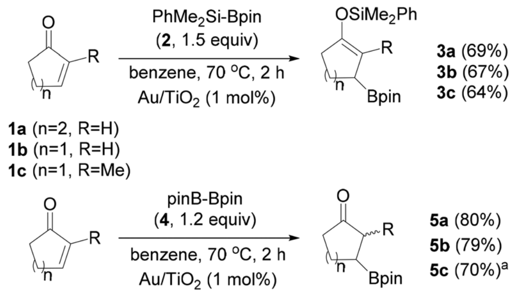
$Me_2PhSiBpin$ on cyclic conjugated ketones, obtaining additionally excellent enantioselectivity if an appropriate chiral ligand is added.[9] This concept was later applied in the enantioselective conjugate silylation of α,β-unsaturated esters.[10]

Hoveyda's and Procter's groups reported the same highly enantioselective transformation in esters, amides, dienones and dienoates using chiral NHC Cu(I) complexes as catalysts,[11] and immediately after a metal-free catalytic version using a chiral N-heterocyclic carbene.[12] A few other catalytic protocols of β-silylation of α,β-unsaturated carbonyl compounds are also known, using a Cu(I) complex in the presence of a chiral amine,[13] $CuSO_4$ in the presence of a base,[14] and more recently the Cu(I)-catalyzed reaction of silylborane with *N*-(2-iodoaryl) acrylamides forming silane-bearing oxindoles.[15] In addition, trapping of the intermediates in the β-silylation of conjugated carbonyl compounds with aldehydes generates useful synthetic motifs.[16] A common characteristic of the abovementioned metal-catalyzed procedures is the pre-activation of silylborane upon addition of a base on the B atom, which accelerates transmetallation of the silicon moiety onto the metal center, which finally delivers the silyl part as a nucleophile on the enone, in a 1,4-fashion. In general, in all metal-catalyzed reactions which make use of silylboranes, the silyl moiety behaves as a pseudo-nucleophile.[17]

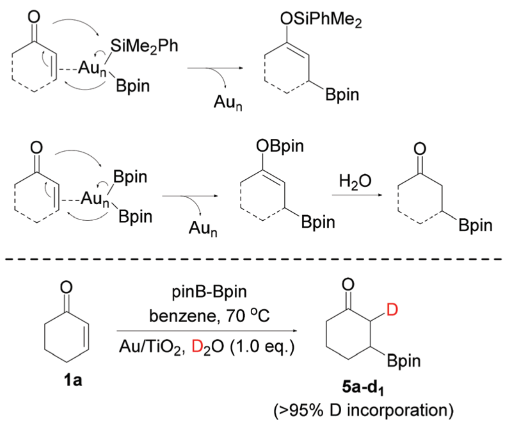
We started the exploration of the possible Au NP-catalyzed silaboration using cyclic α,β-unsaturated ketones. To our delight, the treatment of 2-cyclohexen-1-one (**1a**) with 1.5 equiv. of $Me_2PhSiBpin$ (**2**) in the presence of Au/TiO_2 (1 mol% in Au) in anhydrous benzene at 70 °C for 2 h resulted in the complete consumption of the enone and the formation of the β-boronate silyl enol ether **3a** as the sole product, in 69% isolated yield (Scheme 3). The treatment of the enone with silylborane in the absence of the catalyst does not yield any products. Surprisingly in chlorinated solvents, such as 1,2-dichloroethane (DCE), the reaction does not occur. Similarly, conjugated cyclic ketones **1b** and **1c** were also subjected to silaboration forming the corresponding products **3b** and **3c** in 67% and 64% yields, respectively. These somehow moderate yields are rather associated with the instability of the silaboration adducts under chromatographic conditions. This chemoselectivity motif of silaboration is unknown in the literature, and is complementary to the cases of using Cu or Rh catalysts, for which β-silylation occurs instead.[8]

Notably, the reaction of cyclic ketones **1a–1c** with bis(pinacolato)diboron (pinBBpin, **4**, pin: pinacolato) also proceeds smoothly under the same catalytic conditions, and yields the β-boronate substituted ketones **5a–5c** in very good yields (Scheme 3). Apparently, analogous to the enol silyl ethers **3a–3c**, boron enolates are extremely labile and undergo hydrolysis under the reaction conditions to yield the single-borylation products **5a–5c**. In the case of borylation of **1a** with pinBBpin, the catalyst was separated after the end of the reaction from the slurry by filtration, and after washing with an organic solvent and drying in an oven it was reused without any loss in its activity. This is a typical characteristic of Au/TiO_2 in a series of reactions involving silylboranes or bis(pinacolato) diboron.[3–7] The activation of the diboron reagent pinBBpin with nano Au(0) materials has been well established in its reaction with alkynes,[18] allenes[4] and methylene cyclopropanes.[19] The β-borylation of conjugated carbonyl compounds using pinBBpin as the boron source is also known in the literature applying several catalytic protocols.[20] These include transition metals such as Rh(I),[21] Ni(0),[22,23a] and Pd(0),[23] primarily Cu(I) catalysts,[24] Cu(II),[25] Cu NPs or Cu(0),[26] as well as organocatalysts.[27]

In Scheme 4, we propose that after the insertion of $Me_2PhSiBpin$ on Au NPs (denoted as Au_n), primarily at its low coordinated Au atoms (corners and edges)[2] to form $Me_2PhSi-(Au_n)-Bpin$ species, and coordination of the substrate on them, the boron and silicon moieties are selectively delivered on the C and O atoms, respectively, forming the silaboration



Scheme 3 Silaboration of cyclic enones **1a–1c** with Me_2PhSi-Bpin, and their β-borylation with pinB-Bpin catalyzed by Au/TiO_2. [a] A mixture of diastereomers in a relative ratio of 1.1/1.



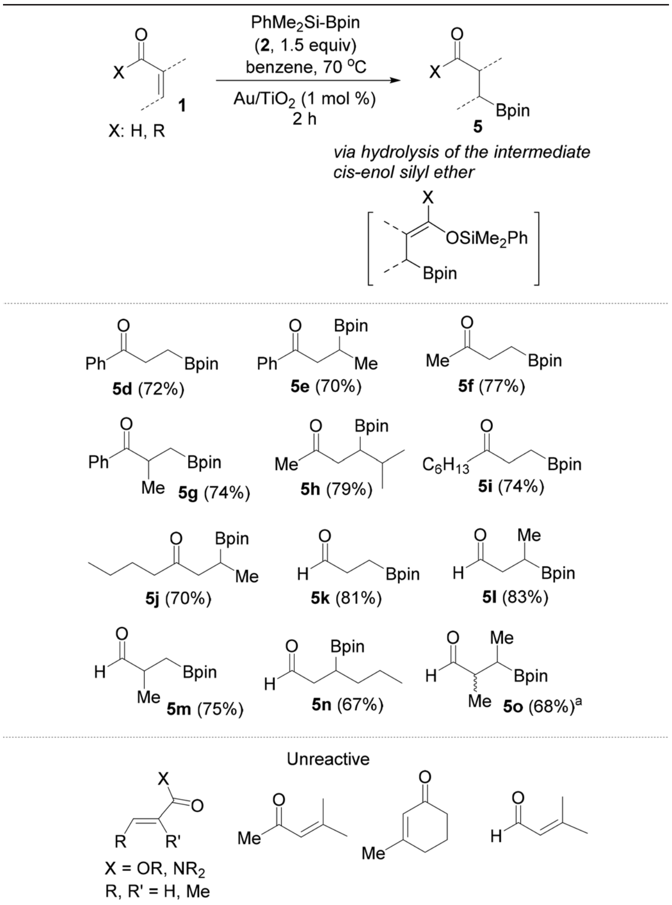
Scheme 4 Proposed mechanisms of the Au NP-catalyzed silaboration/borylation.

products. Similar arguments have been invoked in the Au NP-catalyzed silaboration of strained cyclic ethers[5] and cyclopropyl aldehydes[7] by our group, with the Bpin part of silylborane acting as a pseudo-nucleophile. The driving force of this specific mode of addition is the formation of the thermodynamically stable O–Si and C–B[28] bonds, and the fact that boron is more electronegative compared to silicon. Contrary to this mode of addition, in all other metal catalyzed reactions as already mentioned,[17] between silylborane and enones, the silicon moiety acts as a pseudo-nucleophile, being bound on the metal after an external basic reagent is bonded by the boron atom of silylborane, breaking therefore the Si–B bond. Analogous is the proposed mechanistic scenario of using pinBBpin (Scheme 4). The O–B bond of the diborylation products is extremely labile and *via* hydrolysis under the reaction conditions/work up, β-borylated ketones are formed. If in the borylation of **1a** one equiv. of D_2O is added along with B_2pin_2, >95% single deuteration is observed on the α-carbon (product **5a-d$_1$**), indicative of the reaction between the transient boron enolate and D_2O. Note that no D-incorporation was detected when any of the single borylated products **5a–5c** was treated with D_2O under the same reaction conditions. Unfortunately, any other electrophile added, such as aldehydes or allyl halides, was inefficient in trapping this putative enol intermediate.

Following these very interesting results, we extended our silaboration studies with a series of acyclic α,β-unsaturated aldehydes and ketones (Table 1). With this kind of substrate the reaction proceeds smoothly, just as with the cyclic ketones shown in Scheme 3. Yet, no silaboration products could be seen. Instead, the corresponding β-borylated carbonyl compounds were isolated in good yields. The acyclic silaboration adducts can be detected by GC-MS in samples taken directly from the reaction flask. For example in the silaboration of crotonaldehyde (**1l**) in benzene-d_6, the labile silaboration product **3l** was detected having a *cis*-configuration because the $^3J_{HH}$ of the olefinic protons is 6.0 Hz (see page S22 of the ESI†). The *cis*-silaboration adducts appear to be more prone towards hydrolysis under the reaction conditions/workup more possibly because the Lewis-acidic boron moiety interacts intramolecularly with the silyl enol ether facilitating thus its hydrolysis. As a limitation, the more sterically hindered β,β-disubstituted conjugated aldehydes and ketones are completely unreactive against silylborane, as well as a series of the less electron deficient α,β-unsaturated esters and an amide.

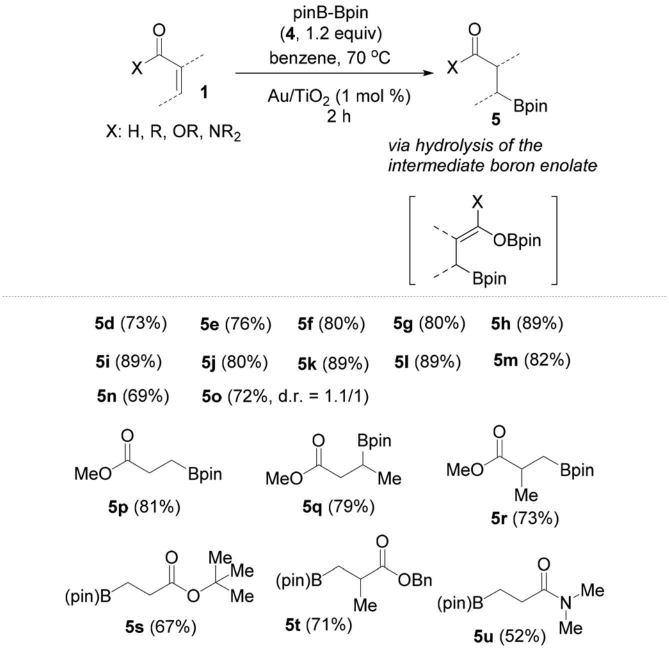
Contrary, however, to the unachieved reaction between $Me_2PhSiBpin$ and conjugated esters or amides (Table 1), their β-borylation occurs in good to excellent isolated yields using pinBBpin. In addition, all conjugated aldehydes and ketones whose reaction with silylborane was studied, as given in Table 1, afforded the borylated products **5d–5o** in slightly higher yields relative to the use of $Me_2PhSiBpin$. The additional results from the borylation of the rest of the conjugated carbonyl compounds are summarized in Table 2. Amide **1u** reacts slowly and requires excess borylating reagent (2–3 equiv.) and a prolonged reaction time (overnight).

Table 1 β-Borylation of acyclic conjugated aldehydes and ketones with Me_2PhSi-Bpin catalyzed by Au/TiO_2



[a] Mixture of diastereomers in a relative ratio of 1.1/1.

Table 2 β-Borylation of acyclic conjugated carbonyl compounds with pinB-Bpin catalyzed by Au/TiO_2



Conclusions

In conclusion, we report herein the so far unrecognized ability of supported Au(0) nanoparticles on TiO_2 in catalyzing the silaboration of conjugated aldehydes and ketones with $Me_2PhSiBpin$ and the quite general β-borylation of α,β-unsaturated carbonyl compounds with pinBBpin. In contrast to all of the known metal-catalyzed analogous reactions with silylborane, in which the silyl moiety acts as a pseudo-nucleophile, under our Au NP-catalyzed conditions, the boryl moiety behaves as a nucleophile, leading to conjugate β-borylation. These results, exemplify once more the unique potency of supported Au nanoparticles in catalyzing organic transformations of high synthetic utility.

Experimental section

The reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (60F-254). Benzene was passed though silica gel and kept over 4 Å molecular sieves. NMR spectra were recorded on a Bruker Avance-500 instrument. HRMS spectra were recorded on an Agilent Q-TOF mass spectrometer, G6540B model with the Dual AJS ESI-MS instrument. GC analyses were performed on a Shimadzu GC-17A model equipped with a 60 m HP-5 capillary column. Flash column chromatography for the purification of compounds was carried out on SiO_2 (silica gel 60, particle size 0.040–0.063 mm) using mixtures of hexane or petroleum ether/ethyl acetate as the eluent. Au/TiO_2 (1 wt% in Au) was provided by Strem Chemicals and has an average gold crystallite size of ~2–3 nm.

Conjugated carbonyl compounds **1a–1c**, **1e–1f**, **1h**, and **1k–1u** are commercially available. Enones **1d**, **1g**, **1i** and **1j** were synthesized as described in the ESI.†

General procedure of the Au/TiO_2-catalyzed β-borylation

To a tube containing a solution of 0.2 mmol of the conjugate carbonyl compound in benzene (0.5 mL) were added 0.30 mmol of $Me_2PhSiBpin$ or 0.24 mmol of pinBBpin followed by the addition of 47.3 mg of Au/TiO_2 (1.0 mol% in Au) and the mixture was heated to 70 °C for a certain period of time until the reaction was complete (TLC and GC-MS). The slurry was filtered with the aid of dichloromethane under a low pressure through a short pad of silica gel and the filtrate was evaporated. The desired product was isolated after column chromatography, using petroleum ether/ethyl acetate (typically ~15/1). The borylation was also performed on a larger scale using 96.1 mg (1.0 mmol) of enone **1a**, 305 mg of bis(pinacolato)diboron (**4**, 1.2 mmol), 3 mL of benzene and 236.4 mg of Au/TiO_2 (2.4 mg of Au, as the catalyst contains 1 w/w% Au). After 2 h at 70 °C the reaction was complete and following the above workup, compound **5a** was isolated in 76% yield (170 mg) after column chromatography, using petroleum ether/ethyl acetate = 15/1 as an eluent.

Spectroscopic data of silaboration products

Dimethyl(phenyl)((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-en-1-yl)oxy)silane (3a). Light pale yellow oil (49.3 mg, 69% yield); ^1H NMR (500 MHz, $CDCl_3$): 7.61 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 2H), 7.38–7.34 (m, 3H), 4.93 (br m, 1H), 1.96–1.93 (m, 2H), 1.76–1.46 (m, 5H), 1.21 (s, 12H), 0.43 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 149.1, 138.2, 133.4, 129.5, 127.7, 83.0, 29.7, 24.7, 24.7, 23.6, 23.1, −1.0, −1.1; MS (EI): 358 (M^+, 15%), 135 (100%), 55 (59%), 40 (100%); HRMS (ESI-Orbit trap) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{31}BO_3Si$ + H, 359.2214; found 359.2206.

Dimethyl(phenyl)((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopent-1-en-1-yl)oxy)silane (3b). Light pale yellow oil (44.0 mg, 67% yield); ^1H NMR (500 MHz, $CDCl_3$): 7.59 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 2H), 7.40–7.34 (m, 3H), 4.60 (br q, J = 2.0 Hz, 1H), 2.28–2.25 (m, 2H), 2.09–2.04 (m, 1H), 1.98–1.84 (m, 2H), 1.20 (s, 12H), 0.45 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 153.9, 137.5, 133.4, 129.6, 127.8, 103.9, 83.0, 33.8, 24.7, 24.7, 23.5, −1.2, −1.3; MS (EI): 344 (M^+, 2%), 329 (M^+–Me, 1%), 135 (28%), 84 (35%), 40 (100%); HRMS (ESI-Orbit trap) *m*/*z*: $[M + H]^+$ calcd for $C_{19}H_{29}BO_3Si$ + H, 345.2057; found 345.2049.

Dimethyl((2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopent-1-en-1-yl)oxy)(phenyl)silane (3c). Light pale yellow oil (43.7 mg, 64% yield); ^1H NMR (500 MHz, $CDCl_3$): 7.61 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 2H), 7.39–7.35 (m, 3H), 2.29–2.15 (m, 2H), 1.95–1.77 (m, 3H), 1.56 (d, J = 1.0 Hz, 3H), 1.22 (s, 12H), 0.43 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 145.7, 138.1, 133.3, 129.6, 127.7, 114.2, 82.9, 33.7, 24.8, 24.8, 22.5, 11.9, −0.7; MS (EI): 358 (M^+, 3%), 329 (M^+–Me, 1%), 135 (14%), 84 (16%), 40 (100%); HRMS (ESI-Orbit trap) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{31}BO_3Si$ + H, 359.2214; found 359.2206.

Spectroscopic data of β-borylated products

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-one (5a).[27a] Colorless oil (35.8 mg, 80% yield); ^1H NMR (500 MHz, $CDCl_3$): 2.38–2.26 (m, 4H), 2.08–2.04 (m, 1H), 1.88–1.84 (m, 1H), 1.77–1.69 (m, 1H), 1.65–1.57 (m, 1H), 1.46–1.43 (m, 1H), 1.22 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): 212.3, 83.4, 42.5, 41.8, 28.4, 26.5, 24.7, 24.7.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentan-1-one (5b).[27a] Colorless oil (31.1 mg, 79% yield); ^1H NMR (500 MHz, $CDCl_3$): 2.32–2.22 (m, 2H), 2.16–2.07 (m, 3H), 1.89–1.80 (m, 1H), 1.68–1.61 (m, 1H), 1.25 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): 221.1, 83.5, 40.2, 38.9, 25.2, 24.7.

2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentan-1-one (5c, a mixture of diastereomers).[29] Colorless oil (31.3 mg, 70% yield); ^1H NMR (500 MHz, $CDCl_3$): 2.39–1.70 (m, 6H from each diastereomer), 1.25 (s, 12H, major diastereomer), 1.22 (s, 12H, minor diastereomer), 1.08 (d, J = 7.5 Hz, 3H, major diastereomer), 1.07 (d, J = 7.5 Hz, 3H, minor diastereomer); ^{13}C NMR (75 MHz, $CDCl_3$): 222.5 and 222.1 (2 diastereomers), 83.4, 46.5 and 45.2 (2 diastereomers), 38.1 and 37.3 (2 diastereomers), 24.8, 24.8, 24.8, 24.7 and 22.7 (2 diastereomers), 22.7 and 22.5 (2 diastereomers), 14.0 and 13.2 (2 diastereomers).

1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (5d).[30] Colorless oil (33.2 mg, 72% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 7.97 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 2H), 7.54 (t, J = 7.0 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 3.16 (d, J = 7.0 Hz, 2H), 1.25 (m, 12H), 1.07 (d, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): 200.6, 137.0, 132.7, 128.4, 128.0, 83.1, 33.7, 24.8.

1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (5e).[27b] Colorless oil (31.5 mg, 70% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 7.97 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 3.11 (d, J = 7.0 Hz, 2H), 1.48–1.40 (m, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 1.05 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): 200.2, 137.1, 132.7, 128.4, 128.0, 83.0, 42.9, 24.7, 24.6, 15.1.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one (5f).[23b] Colorless oil (30.4 mg, 77% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 2.58 (t, J = 7.0 Hz, 2H), 2.12 (s, 3H), 1.23 (s, 12H), 0.90 (t, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): 209.2, 83.1, 38.4, 29.3, 24.7.

2-Methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (5g). Colorless oil (32.4 mg, 74% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 7.95 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 3.70–3.63 (m, 1H), 1.23 (t, J = 7.5 Hz, 3H) 1.23 (s, 6H), 1.21 (s, 6H), 1.19 (dd, J_1 = 16.0 Hz, J_2 = 7.0 Hz, 1H), 0.97 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): 204.9, 136.3, 132.5, 128.4, 128.4, 83.1, 37.3, 24.8, 24.7, 19.8; HRMS (ESI-Orbit trap) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{23}BO_3$ + H, 275.1819; found 275.1816.

5-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (5h).[31] Colorless oil (35.0 mg, 79% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 2.62 (dd, J_1 = 18.0 Hz, J_2 = 11.0 Hz, 1H), 2.51 (dd, J_1 = 18.0 Hz, J_2 = 5.0 Hz, 1H), 2.12 (s, 3H), 1.74–1.66 (m, 1H), 1.25 (s, 6H), 1.21 (s, 6H), 1.19–1.68 (m, 1H), 0.93 (d, J = 7.0 Hz, 3H), 0.91 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): 209.5, 83.0, 43.8, 29.7, 28.9, 24.9, 24.7, 22.1, 21.6.

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)nonan-3-one (5i). Colorless oil (34.7 mg, 74% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 2.55 (t, J = 7.0 Hz, 2H), 2.37 (t, J = 7.5 Hz, 2H), 1.58–1.52 (m, 2H), 1.27–1.24 (m, 6H), 1.22 (s, 12H), 0.89 (t, J = 7.0 Hz, 2H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): 211.7, 83.0, 42.3, 37.4, 31.6, 28.9, 24.7, 24.1, 22.5, 14.0; HRMS (ESI-Orbit trap) *m*/*z*: $[M + H]^+$ calcd for $C_{15}H_{29}BO_3$ + H, 269.2288; found 269.2280.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)octan-4-one (5j). Colorless oil (32.2 mg, 70% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 2.52 (d, J = 7.0 Hz, 2H), 2.41–2.31 (m, 2H), 1.57–1.51 (m, 2H), 1.33–1.26 (m, 4H), 1.23 (s, 6H), 1.22 (s, 6H), 0.94 (d, J = 7.5 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): 211.4, 82.9, 46.7, 42.3, 26.2, 24.7, 24.6, 22.3, 15.0, 13.8; HRMS (ESI-Orbit trap) *m*/*z*: $[M + H]^+$ calcd for $C_{14}H_{27}BO_3$ + H, 255.2131; found 255.2122.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propanal (5k).[23b] Colorless oil (29.5 mg, 81% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 9.79 (t, J = 1.0 Hz, 1H), 2.60 (dd, J_1 = 7.0 Hz, J_2 = 1.0 Hz, 2H), 1.24 (s, 12H), 0.97 (t, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): 202.8, 83.3, 38.8, 24.7.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butanal (5l).[23b] Colorless oil (32.2 mg, 83% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 9.75 (s, 1H), 2.58 (dd, J_1 = 18.0 Hz, J_2 = 7.0 Hz, 1H), 2.50 (dd, J_1 = 18.0 Hz, J_2 = 6.5 Hz, 1H), 1.39–1.35 (m, 1H), 1.23 (s, 6H), 1.23 (s, 6H), 1.00 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): 202.8, 83.3, 47.7, 24.7, 24.6, 15.1.

2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanal (5m).[31] Colorless oil (28.1 mg, 75% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 9.63 (d, J = 0.5 Hz, 1H), 2.59–2.52 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.14 (d, J = 7.0 Hz, 3H), 1.05 (dd, J_1 = 16.0 Hz, J_2 = 7.0 Hz, 1H), 0.82 (dd, J_1 = 16.0 Hz, J_2 = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): 205.2, 83.3, 42.6, 24.7, 15.6.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexanal (5n).[32] Colorless oil (24.4 mg, 67% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 9.76 (t, J = 1.0 Hz, 1H), 2.58 (dd, J_1 = 19.0 Hz, J_2 = 8.0 Hz, 1H), 2.51 (dd, J_1 = 19.0 Hz, J_2 = 7.0 Hz, 1H), 1.46–1.44 (m, 1H), 1.36–1.31 (m, 1H), 1.24 (s, 16H), 1.22 (s, 16H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): 203.0, 83.2, 45.8, 32.7, 24.8, 24.6, 21.9, 14.2.

2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanal (5o, mixture of diastereomers).[31] Colorless oil (24.7 mg, 68% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 9.65 (d, J = 1.0 Hz, 1H, minor diastereomer), 9.60 (d, J = 1.5 Hz, 1H, major diastereomer), 2.50–2.43 (m, 1H from each diastereomer), 1.38–1.31 (m, 1H from one diastereomer), 1.30–1.27 (m, 1H from one diastereomer), 1.24 (s, 6H), 1.23 (s, 12H), 1.23 (s, 6H), 1.18 (d, J = 6.5 Hz, 3H from one diastereomer), 1.11 (d, J = 6.5 Hz, 3H from one diastereomer), 0.96 (d, J = 7.5 Hz, 3H from major diastereomer), 0.94 (d, J = 7.5 Hz, 3H from minor diastereomer); ^{13}C NMR (125 MHz, CDCl$_3$): 205.8 and 205.6 (2 diastereoisomers), 83.3 and 83.2 (2 diastereoisomers), 48.8 and 48.6 (2 diastereoisomers), 24.7, 24.7, 24.5, 12.3, 11.8 and 11.7 (2 diastereoisomers).

Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (5p).[33] Colorless oil (34.0 mg, 81% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 3.65 (s, 3H), 2.44 (t, J = 7.5 Hz, 2H), 1.24 (s, 2H), 1.02 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): 175.1, 83.2, 51.5, 28.6, 24.7.

Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5q).[24] Colorless oil (33.3 mg, 79% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 3.65 (s, 3H), 2.46–2.35 (m, 2H), 1.39–1.35 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 0.99 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): 174.3, 83.2, 51.3, 37.5, 24.7, 24.6, 15.1.

Methyl 2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (5r).[33] Colorless oil (28.7 mg, 73% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 3.65 (s, 3H), 2.72–2.65 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.19 (d, J = 7.0 Hz, 3H), 1.12 (dd, J_1 = 16.0 Hz, J_2 = 7.5 Hz, 1H), 0.93 (dd, J_1 = 16.0 Hz, J_2 = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$): 117.7, 83.2, 51.5, 35.3, 24.8, 24.7, 19.4.

***t*-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (5s).**[33] Colorless oil (29.5 mg, 67% yield); ^{1}H NMR (500 MHz, CDCl$_3$): 2.35 (t, J = 7.5 Hz, 2H), 1.43 (s, 9H), 1.23 (s, 12H), 0.96 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): 174.0, 83.1, 79.8, 29.9, 28.1, 24.8.

Benzyl 2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (5t).[33] Colorless oil (34.5 mg, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$): 7.35–7.30 (m, 5H), 5.13 (d, J = 13.0 Hz, 1H), 5.08 (d, J = 13.0 Hz, 1H), 2.76–2.72 (m, 1H), 1.22 (d, J = 7.0 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H), 1.17 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 0.96 (dd, J_1 = 16.0 Hz, J_2 = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 177.0, 136.4, 128.4, 127.9, 127.9, 83.1, 65.9, 35.4, 24.7, 19.3.

***N*,*N*-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propenamide (5u).**[23b] Colorless oil (22.0 mg, 52% yield); ^{1}H NMR (500 MHz, $CDCl_3$): 2.98 (s, 3H), 2.93 (s, 3H), 2.45 (t, J = 7.5 Hz, 2H), 1.24 (s, 2H), 0.95 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 174.3, 82.7, 37.0, 35.6, 28.3, 24.8.

Conflicts of interest

There are no conflicts to declare.

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