Article

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α,β-Unsaturated *N*-Acylindoles: an Alternative Class of Michael Acceptors and Their Application in Asymmetric Borylation

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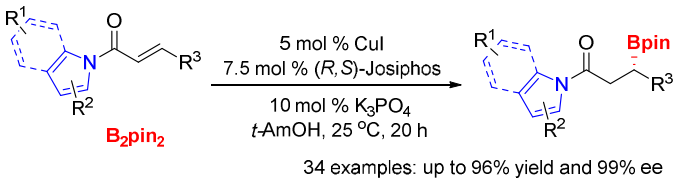


ABSTRACT: Copper(I)-catalyzed enantioselective borylation of α,β-unsaturated *N*-acylindoles as well as *N*-acylpyrroles was efficiently achieved by means of bis(pinacolato)diboron (B_2pin_2), affording the enantioenriched products in excellent yields with up to 99% ee. The present work provides an alternative class of Michael acceptors, that is, α,β-unsaturated *N*-acylindoles, for potential asymmetric transformations.

INTRODUCTION

Enantioselective conjugate additions of nucleophiles to α,β-unsaturated carbonyl compounds are among the most fundamental and important reactions in organic synthesis.[1] Numerous useful products bearing diverse functional groups can be obtained due to the broad scopes of the acceptors and donors. As compared to α,β-unsaturated ketones which have been widely used in asymmetric additions, the corresponding α,β-unsaturated esters and amides usually exhibit relatively low reactivities. Thus, a few functional groups have been brought in as ester and amide surrogates in order to improve their reactivities. In this regard, α,β-unsaturated oxazolidinones,[2] acyl imidazoles,[3] acyl pyrrazoles,[4] and acyl pyrroles[5] have been reported as the surrogates of α,β-unsaturated esters and amides in asymmetric transformations. Among the above-mentioned compounds, α,β-unsaturated *N*-acylpyrroles are monodentate coordinative acceptors, others are bidentate coordinative ones. The former has the LUMO energy similar to that of α,β-unsaturated ketones due to the delocalization of the lone electron pair of the nitrogen atom into the pyrrolyl ring and the reduced donation to the carbonyl group.[6] Therefore, α,β-unsaturated *N*-acylpyrroles can exhibit reactivity similar to that of α,β-unsaturated ketones, which is much higher than those of the corresponding esters and amides. Accordingly, α,β-unsaturated *N*-acylpyrroles have been widely investigated as the surrogates of α,β-unsaturated esters and amides in asymmetric synthesis.[5] Indole motifs are more abundant than pyrrole functionalities in bioactive compounds and natural products, and indole derivatives have become more and more

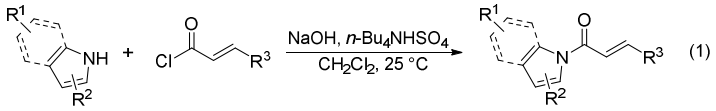
attractive in the research areas of materials, agricultural chemicals, and pharmaceuticals.[7] However, only one α,β-unsaturated *N*-acylindole, that is, *N*-cinnamoylindole, has been documented for asymmetric spirannulation to date, and such a *N*-acylindole substrate could not behave as an effective acceptor under the stated conditions.[8]

Chiral organoboron derivatives are versatile reagents in organic synthesis,[9] and have been widely used as precursors for the construction of chiral C-O, C-N, and C-C bonds with the retention of enantiopurity.[10] Enantioselective conjugate addition of diboron reagents to α,β-unsaturated carbonyls and related compounds has emerged as one of the most powerful tools for the preparation of chiral organoboron compounds due to the high reactivity and broad applicability of the substrates.[9,11] In this area, copper catalysis[12] has been widely applied for asymmetric borylation although other transition-metal-catalyzed[13] and organocatalytic[14] methods have also been documented. Herein, We disclose copper-catalyzed enantioselective borylation of α,β-unsaturated *N*-acylindoles with bis(pinacolato)diboron (B_2pin_2), and α,β-unsaturated *N*-acylpyrroles were also explored for the same transformations.

RESULTS AND DISCUSSION

Initially, the Witting[5g] and Horner–Wadsworth–Emmons (HWE)[5f] reactions were utilized to prepare α,β-unsaturated *N*-acylpyrroles by the literature methods. Unfortunately, these traditional methods usually suffer from obvious drawbacks such as use of air- and moisture-sensitive organolithium reagents, anaerobic manipulations,

time-consuming multistep procedures, and generation of stoichiometric wastes. In this communication, we used a phase transfer catalysis procedure[15] for the synthesis of α,β-unsaturated *N*-acylpyrroles and *N*-acylindoles in the presence of *n*-Bu_4NHSO_4 catalyst and NaOH base (eq 1). This method features ready availability of the starting materials and easy manipulations as compared to the Witting and HWE reactions.

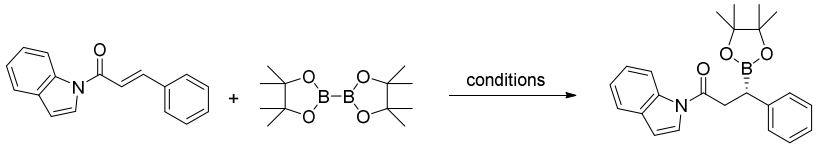


(1)

Then, the reaction of (*E*)-1-(1*H*-indol-1-yl)-3-phenylprop-2-en-1-one (**1a**) with B_2pin_2 (**2**) in a 1.0:1.1 molar ratio was carried out to screen the reaction conditions (Table 1). In the presence of 5 mol % CuI as the catalyst, and 10 mol % K_3PO_4 as the base in *t*-AmOH at ambient temperature, a range of chiral ligands were tested for the asymmetric borylation of **1a**. In the case of using an axially chiral bisphosphine ligand such as (*R*)-BINAP (**L1**), the target product **3a** was obtained in a moderate yield (41%) with a very low enantioselectivity (Table 1, entry 1). Use of both (*S,S*)-Me-Duphos (**L2**) and (*S,S,R,R*)-Tangphos (**L3**) ligands led to **3a** in 95% yield, but the ee values were not satisfactory (Table 1, entries 2 and 3). To our delight, the chiral ligand with a ferrocenyl backbone, that is, (*R,S*)-Josiphos (**L4**), promoted the reaction to afford the target product in excellent yield (95%) with 95% ee (Table 1, entry 4). Either of (*R*)-(*S*)-NMe_2-PPh_2-Mandyphos (**L5**) and (*R,R*)-Walphos (**L6**) ligands did not work well for the reaction (Table 1, entries 5 and 6). Although use of (*R,R*)-Taniaphos (**L7**) resulted in an excellent enantioselectivity (99% ee), the target product was only formed in 16% yield (Table 1, entry 7). CuI acted as the most

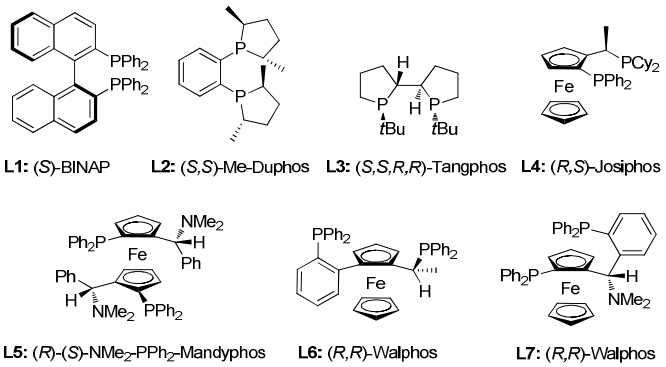
e□cient catalyst as compared to CuCl and CuBr (Table 1, entries 8 and 9). Lowering the loading of CuI catalyst to 2.5 mol % and the amount of (*R,S*)-Josiphos to 3.75 mol % obviously deteriorated the reaction e□ciency (Table 1, entry 10).

Table 1. Screening of Reaction Conditions[a]



1a (B2pin2) 2 (S)-3a

entry	[Cu] cat.	ligand	yield[b] (%)	ee[c] (%)
1	CuI	**L1**	41	-4
2	CuI	**L2**	95	-50
3	CuI	**L3**	95	-4
4	CuI	**L4**	99 (95)[d]	95
5	CuI	**L5**	22	-56
6	CuI	**L6**	25	-19
7	CuI	**L7**	16	99
8	CuCl	**L4**	0	
9	CuBr	**L4**	79	95
10[e]	CuI	**L4**	83	93

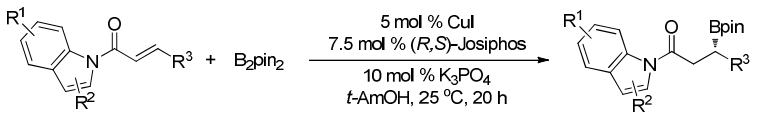


[a] Conditions: **1a** (0.2 mmol), **2** (0.22 mmol), [Cu] (5 mol %), ligand (7.5 mol %), K_3PO_4 (10 mol %), *t*-AmOH (2 mL), 0.1 MPa N_2, 25 °C, 20 h. [b] ^1H NMR yield using CH_2Br_2 as the internal standard. [c] Determined by chiral HPLC analysis using an AD-H column. [d] Isolated yield given in parentheses. [e] CuI, 2.5 mol %; ligand, 3.75 mol %; K_3PO_4, 5 mol %.

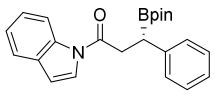
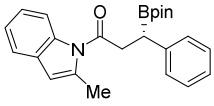
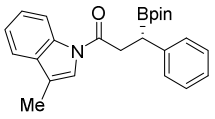
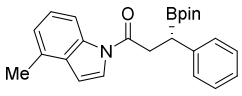
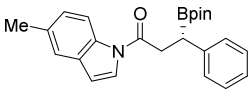
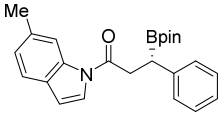
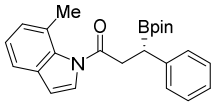
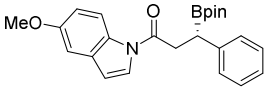
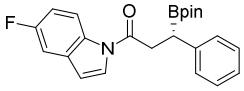
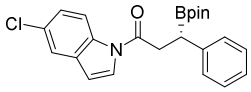
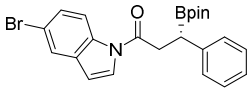
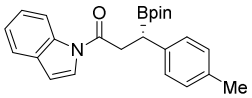
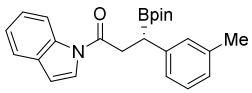
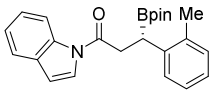
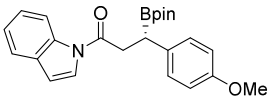
Having established the optimized reaction conditions, we tested a variety of α,β-unsaturated *N*-acylindoles (**1**) to probe into the substrate diversity (Table 2). *N*-Acylindoles bearing a methyl group at 3- to 7-positions of the indole ring showed good reactivities to react with **2**, forming the target products **3c**-**3g** in excellent yields (94-96%) with 92-99% enantioselectivities. The steric hindrance from 2-methyl group on the indole ring slightly lessened the enantioselectivity, leading to **3b** in 96% yield with 88% ee. 5-Methoxy-substituted *N*-acylindole (**1h**) efficiently reacted with **2** to give **3h** (95% yield, 92% ee). 5-Halo-bearing *N*-acylindoles (halo = F, Cl, Br) reacted to produce **3i**-**3k** in 93-95% yields with 94-95% ee, demonstrating no substituent effect from the 5-substituent on the indole ring. Next, α,β-unsaturated *N*-acylindoles with various substituents at β-position were investigated. Variation of the methyl substituent at 4-, 3-, and 2-positions of the β-aryl functionality slightly lessened the enantioselectivities of products **3l**-**3n** from 93% to 90% ee with 94-96% yields.

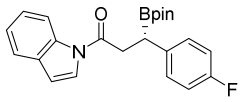
4-OMe, 4-F, and 4-Cl on the β-aryl ring ensured 94-95% ee for products **3o**-**3q**. Sterically hindered β-(1-naphthyl)-α,β-unsaturated *N*-acylindole reacted with **2** less efficiently, affording **3r** in 88% yield and 87% ee. β-(2-Thienyl), methyl, ethyl, and propyl-functionalized substrates also reacted well with **2** to give **3s**-**3v** (80-95% yields, 90-96% ee).

Table 2. Enantioselective borylation of α,β-unsaturated *N*-acyl- indoles (1) with 2[a,b,c]

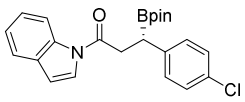


1 **2** **3**

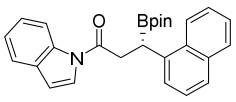
		
(*S*)-**3a**, 94%, 95% ee	(+)-**3b**, 96%, 88% ee	(-)-**3c**, 94%, 92% ee[e]
		
(-)-**3d**, 96%, 95% ee	(+)-**3e**, 94%, 96% ee	(-)-**3f**, 96%, 99% ee
		
(+)-**3g**, 94%, 92% ee	(-)-**3h**, 95%, 92% ee	(-)-**3i**, 95%, 94% ee
		
(-)-**3j**, 93%, 95% ee	(-)-**3k**, 93%, 95% ee	(-)-**3l**, 94%, 93% ee
		
(-)-**3m**, 94%, 91% ee	(-)-**3n**, 96%, 90% ee[e]	(-)-**3o**, 95%, 94% ee



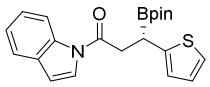
(-)-**3p**, 90%, 95% ee



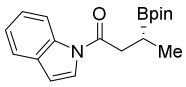
(-)-**3q**,[d] 92%, 94% ee



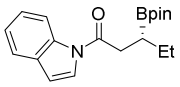
(+)-**3r**, 88%, 87% ee[e]



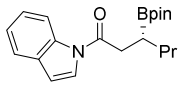
(-)-**3s**, 91%, 96% ee



(-)-**3t**, 95%, 92% ee



(-)-**3u**, 80%, 92% ee

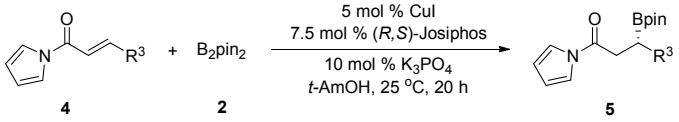


(-)-**3v**,[d] 95%, 90% ee

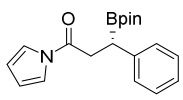
[a] Conditions: **1** (0.2 mmol), **2** (0.22 mmol), *t*-AmOH (2 mL), 25 °C, 0.1 MPa N_2, 20 h. [b] Yield refers to the isolated products. [c] The ee values were determined by chiral HPLC analysis using an AD-H column. [d] 60 °C. [e] Determined by chiral HPLC analysis of the corresponding β-hydroxy compound by oxidation with sodium perborate.

In a similar manner, α,β-unsaturated *N*-acylpyrroles (**4**) were investigated in the asymmetric borylation with **2** (Table 3). β-Aryl-*N*-acylpyrroles could efficiently react with **2** under the standard conditions, giving the target products **5a**-**5c**, and **5e**-**5g** in 83-95% yields with excellent enantioselectivities (94-96% ee). Only in the case of using the substrate bearing a β-(2-methyl)phenyl moiety (**4d**), the reaction efficiency was slightly deteriorated to form **5d** (87%) with 90% ee. The lower enantioselectivities of **3b**, **3n**, **3r**, and **5d** may be due to the steric hindrance of substrates. A minor steric effect was also observed from β-(1-naphthyl) in product **5h**. The *N*-acylpyrroles containing a β-(2-thienyl) or β-methyl functionality efficiently underwent the reactions to form **5i** (92%, 96% ee) and **5j** (93%, 92% ee), respectively. However, β-ethyl and propyl obviously lessened the reaction efficiencies to afford **5k** (73%, 84% ee) and **5l** (77%, 90% ee).

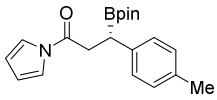
Table 3. Enantioselective borylation of α,β-unsaturated *N*-acylpyrroles (4) with 2[a,b,c]



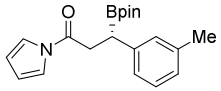
4 **2** **5**



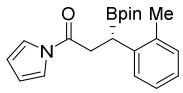
(*S*)-**5a**, 95%, 95% ee



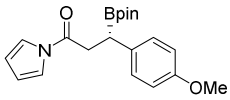
(+)-**5b**, 93%, 94% ee



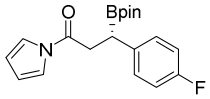
(+)-**5c**, 92%, 94% ee



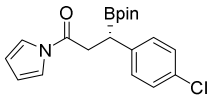
(+)-**5d**, 87%, 90% ee[e]



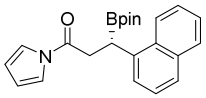
(+)-**5e**, 93%, 96% ee



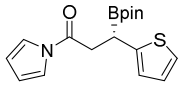
(+)-**5f**, 94%, 96% ee



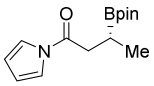
(+)-**5g**,[d] 83%, 94% ee



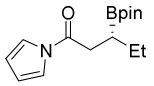
(+)-**5h**,[d] 86%, 91% ee



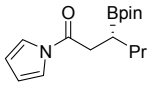
(-)-**5i**, 92%, 96% ee



(-)-**5j**, 93%, 92% ee



(-)-**5k**, 73%, 84% ee



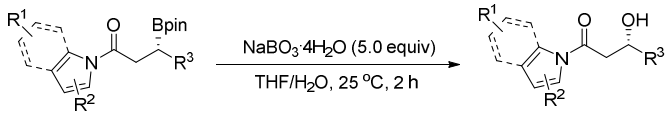
(-)-**5l**,[d] 77%, 90% ee

[a] Conditions: **4** (0.2 mmol), **2** (0.22 mmol), *t*-AmOH (2 mL), 25 °C, 0.1 MPa N_2, 20 h. [b] Yield refers to the isolated products. [c] The ee values were determined by chiral HPLC analysis using an AD-H column. [d] 60 °C. [e] Determined by chiral HPLC analysis of the corresponding β-hydroxy compound by oxidation with sodium perborate.

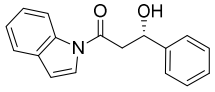
Because the enantiomers of products **3c**, **3n**, **3r**, and **5d** could not be separated on the chiral HPLC columns, they were converted to the corresponding β-hydroxy compounds through oxidation with sodium perborate in order to determine the ee values. Retention of the enantiopurity during this transformation was confirmed by oxidizing compounds **3a** to **6a,** and **5a** to **6e** (Table 4). Similar transformations were thus conducted for **3c**, **3n**, **3r**, and **5d**, affording the corresponding deborylated chiral products, that is, chiral β-hydroxy-amides **6b**-**6d** and **6f**, in good to excellent yields

(76-90%) with retention of enantiopurities (88-92%). Additional transformations were also conducted to demonstrate the utility of compounds **3** and **5** as ester and amide surrogates. However, treatment of **3a** or **5a** with NaOMe only led to trace amount of the target methyl esters through ^{1}H NMR analysis of the reaction mixtures, which is presumably attributed to the unstability of the borylated products under the strong basic conditions. To our delight, the reactions of **3a** and **5a** with pyrrolidine gave the corresponding amide **7** in good yields (71-80%) with rentention of the enantioselectivities (eq 2). Compound **7** was assigned to be (*S*)-configuration by comparison of its optical rotation with the reported data.[12j] Thus, chiral **3a** and **5a** were assigned to be (*S*)-configuration, and the configurations of other chiral products were assigned by analogy.

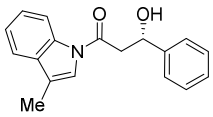
Table 4. Oxidative deborylation of compounds 3 and 5[a,b,c]



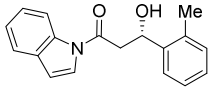
3 or **5** **6**



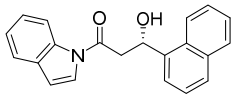
(-)-**6a** from (-)-**3a**, 90%, 95% ee



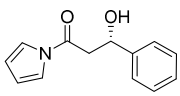
(-)-**6b** from (-)-**3c**, 89%, 92% ee



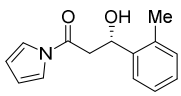
(-)-**6c** from (-)-**3n,** 76%, 90% ee



(-)-**6d** from (+)-**3r**, 90%, 87% ee

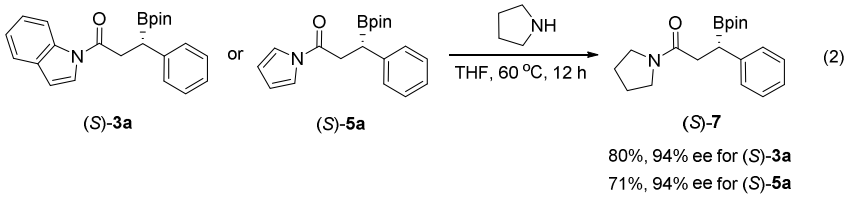


(-)-**6e** from (*S*)-**5a**, 89%, 94% ee



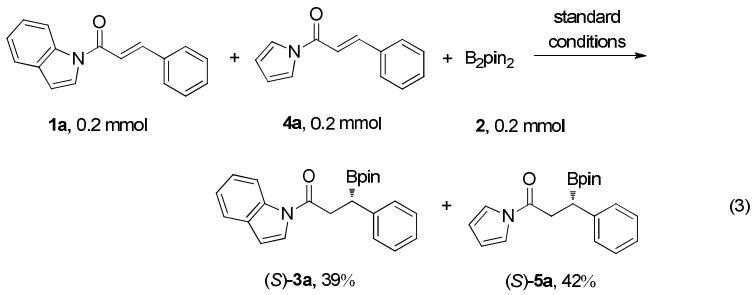
(-)-**6f** from (+)-**5d**, 87%, 90% ee

[a] Conditions: **3** or **5** (0.2 mmol), THF (1 mL), H_2O (1 mL), 25 °C, 2 h. [b] Yields refer to the isolated products. [c] The ee values were determined by chiral HPLC analysis using an AD-H column.

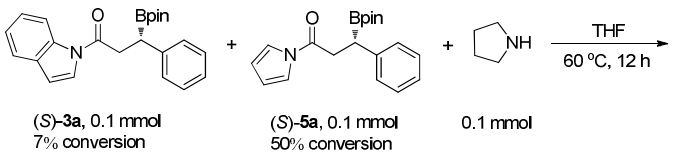


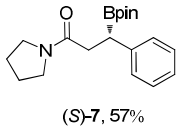
(2)

Control reactions were performed to determine the reactivity difference between α,β-unsaturated *N*-acylindoles and *N*-acylpyrroles. An equimolar mixture of **1a** and **4a** was reacted with **2** under the standard conditions to give a mixture of **3a** (39%) and **5a** (42%) (eq 3), revealing that the α,β-unsaturated *N*-acylindole and *N*-acylpyrrole have a similar reactivity in the asymmetric borylation reaction. Although **3a** reacted with pyrrolidine to afford **7** in a relative high yield (80% vs 71%) than the same reaction of **5a** did under the standard conditions (eq 2), the competition reactions of **3a** and **5a** with pyrrolidine suggested that compound **5a** reacted much faster than **3a** (eq 4). The asymmetric borylation reactions of α,β-unsaturated ketone **8** and ester **9** with **2** were also conducted under the standard conditions (eq 5), forming the target products **10** and **11** in 78-79% yields with 84-90% ee which are much lower than those from the reactions of the corresponding *N*-acylindoles and *N*-acylpyrroles (Tables 3 and 4). These results have demonstrated the unique reactivity of *N*-acylindoles and *N*-acylpyrroles as Michael acceptors.



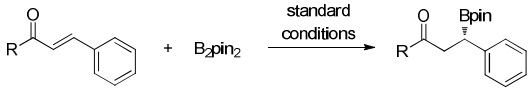
(3)





(4)

(S)-7, 57%



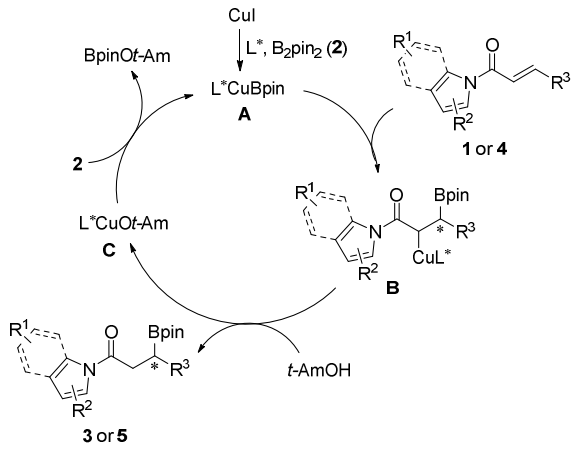
(5)

R =: Ph (8), OBn (9) 2

(S)-10 from 8, 79%, 90% ee
(S)-11 from 9, 78%, 84% ee

A plausible mechanism is proposed in Scheme 1.[16] The copper(I) salt initially reacts with B_2pin_2 (**2**) in the presence of a chiral phosphine ligand to generate Cu(I)-Bpin species **A**. Addition of **A** to α,β-unsaturated *N*-acylindole (**1**) or *N*-acypyrrole (**4**) leads to the organocopper(I) intermediate **B**. Subsequent protonation of **B** with the alcohol solvent *t*-AmOH affords the target product **3** or **5** with release of copper(I) alkoxide **C**. Interaction of species **C** with **2** regenerates the catalytically active species **A** to accomplish the catalytic cycle.

Scheme 1. Proposed mechanism



In conclusion, copper-catalyzed enantioselective borylation of α,β-unsaturated *N*-acylindoles and *N*-acylpyrroles with bis(pinacolato)diboron has been developed. Under the mild conditions, chiral organoboron compounds were obtained in high yields and enantioselectivities. This work provides an alternative class of Michael acceptors for conjugate additions.

EXPERIMENTAL SECTION

General Considerations. The solvents were dried and distilled prior to use by the literature methods. ^{1}H and ^{13}C spectra were recorded on a 400 MHz NMR spectrometer. In the ^{13}C NMR data, for many of the B-containing compounds, the signal to noise ratio was low for the carbon atom bound to Boron, which appear as broad signals likely due to quadrupolar relaxation.[12j] As a result, we have not assigned a value for the chemical shift in the tabulated ^{13}C NMR data below. HRMS data was obtained by ESI on a Q-TOF mass spectrometer. Enantiomeric excess was determined by chiral HPLC analysis. Optical rotations were measured by an olarimeter. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compounds **1a**,[17] **1c**,[18] **1e**,[17] **1h**-**1k**,[17] **1o**,[17] **1t**,[19] **4a**,[5g] **4b**,[5g] **4c**,[20] **4d**,[20] **4e**,[5g] **4f**,[5e] **4g**,[5g] **4h**,[5g] **4i**,[5g] **4j**,[21] **4k**,[22] **4l**,[5f] ,**7**[12j] ,**10**[23] ,**11**[24] were known and their spectroscopic features are in good agreement with those reported in the literatures.

General Procedure for the Synthesis of α,β-unsaturated *N*-acylindoles 1 and

pyrroles 4. Indole or pyrrole (2.0 mmol) and *n*-Bu_4NHSO_4 (340 mg, 1.0 mmol) were dissolved in CH_2Cl_2 (10 mL). Powdered NaOH (200 mg, 5.0 mmol) was added, and then α,β-unsaturated acyl chloride (3.0 mmol) in CH_2Cl_2 (5 mL) was introduced dropwise to the vigorously stirring solution. Stirring was continued at ambient temperature for 12 h. All the volatiles were evaporated under reduced pressure. The resulting residue was purification by silica gel column chromatography to afford the desired product **1** or **4**.

*(E)-1-(2-Methyl-1H-indol-1-yl)-3-phenylprop-2-en-1-one (**1b**).* 256 mg, 49% yield; yellow solid, mp 112-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 15.7 Hz, 1 H, 7.78-7.75 (m, 1 H), 7.65-7.63 (m, 2 H), 7.52-7.50 (m, 1 H), 7.47-7.45 (m, 3 H), 7.28-7.21 (m, 3 H), 6.42 (s, 1 H), 2.67 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 145.7, 137.7, 136.2, 134.6, 130.9, 129.9, 129.2, 128.5, 123.1, 122.9, 121.4, 120.2, 114.4, 108.6, 16.3; HRMS (ESI) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1230.

*(E)-1-(4-Methyl-1H-indol-1-yl)-3-phenylprop-2-en-1-one (**1d**).* 256 mg, 49% yield; yellow solid, mp 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.3 Hz, 1 H), 7.99 (d, *J* = 15.4 Hz, 1 H), 7.62-7.60 (m, 3 H), 7.45-7.40 (m, 3 H), 7.37-7.33 (m, 1 H), 7.19 (d, *J* = 15.4 Hz, 1 H), 7.15 (d, *J* = 7.3 Hz, 1 H, aromatic CH), 6.71 (d, *J* = 3.5 Hz, 1 H), 2.57 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 146.1, 135.5, 134.2, 130.5, 130.1, 128.8, 128.2, 124.9, 124.1, 124.0, 117.0, 114.3, 107.3, 18.4; HRMS (ESI) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1232.

*(E)-1-(6-Methyl-1H-indol-1-yl)-3-phenylprop-2-en-1-one (**1f**).* 219 mg, 42% yield;

yellow solid, mp 63-65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1 H), 8.00 (d, *J* = 15.4 Hz, 1 H), 7.64-7.62 (m, 2 H), 7.56 (d, *J* = 3.8 Hz, 1 H), 7.50 (d, *J* = 7.9 Hz, 1 H), 7.45-7.44 (m, 3 H), 7.22 (d, *J* = 15.4 Hz, 1 H), 7.17 (d, *J* = 7.9 Hz, 1 H), 6.66 (d, *J* = 3.7 Hz, 1 H), 2.55 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 146.3, 136.3, 135.1, 134.4, 130.7, 129.0, 128.4, 125.3, 124.0, 120.5, 117.3, 117.1, 109.1, 22.0; HRMS (ESI) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1235.

*(E)-1-(7-Methyl-1H-indol-1-yl)-3-phenylprop-2-en-1-one (**1g**)*. 282 mg, 54% yield; yellow solid, mp 105-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 15.6 Hz, 1 H), 7.65 (s, 2 H), 7.55-7.47 (m, 5 H), 7.30-7.26 (m, 1 H), 7.23-7.16 (m, 2 H), 6.69 (s, 1 H), 2.62 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 146.6, 135.2, 134.3, 132.2, 130.9, 129.1, 126.2, 128.5, 127.8, 126.8, 124.0, 119.4, 118.8, 108.4, 22.1; HRMS (ESI) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1233.

*(E)-1-(1H-indol-1-yl)-3-(p-tolyl)prop-2-en-1-one (**1l**)*. 480 mg, 92% yield; yellow solid, mp 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.3 Hz, 1 H), 7.98 (d, *J* = 15.4 Hz, 1 H), 7.64-7.61 (m, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.23 (d, *J* = 7.9 Hz, 2 H), 7.18 (d, *J* = 15.4 Hz), 6.69 (d, *J* = 3.7 Hz), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 146.5, 141.3, 136.0, 131.7, 130.6, 129.8, 128.4, 124.9, 124.7, 123.7, 120.9, 116.9, 116.1, 109.0, 21.5; HRMS (ESI) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1228.

*(E)-1-(1H-indol-1-yl)-3-(m-tolyl)prop-2-en-1-one (**1m**)*. 433 mg, 83% yield; pale yellow solid, mp 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.2 Hz, 1 H), 7.98 (d, *J* = 15.4 Hz, 1 H) 7.65-7.62 (m, 2 H), 7.43-7.41 (m, 3 H), 7.33 (td, *J* = 7.5,

2.6 Hz, 2 H), 7.26 (s, 1 H), 7.21 (d, *J* = 15.4 Hz, 1 H), 6.70 (d, *J* = 3.5 Hz, 1 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 146.6, 138.6, 135.9, 134.3, 131.6, 130.6, 129.0, 128.9, 125.6, 124.9, 124.7, 123.7, 120.9, 116.89, 116.86, 109.0, 21.3; HRMS (ESI) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1232.

*(E)-1-(1H-indol-1-yl)-3-(o-tolyl)prop-2-en-1-one (**1n**).* 277 mg, 53% yield; yellow solid, mp 58-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.3 Hz, 1 H), 8.31 (d, *J* = 15.3 Hz, 1 H), 7.69 (d, *J* = 7.7 Hz, 1 H), 7.66 (d, *J* = 3.8 Hz, 1 H), 7.62 (d, *J* = 7.7 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 7.35-7.30 (m, 2 H), 7.27 (d, *J* = 7.2 Hz, 2 H), 7.17 (d, *J* = 15.3 Hz, 1 H), 6.71 (d, *J* = 3.7 Hz, 1 H), 2.52 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 144.4, 138.3, 136.1, 133.6, 131.1, 130.7, 130.6, 126.5, 125.2, 124.7, 123.9, 121.0, 118.5, 116.9, 109.3, 20.0; HRMS (ESI) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1234.

*(E)-3-(4-Fluorophenyl)-1-(1H-indol-1-yl)prop-2-en-1-one (**1p**).* 445 mg, 84% yield; white solid, mp 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.1 Hz, 1 H), 7.93 (d, *J* = 15.4 Hz, 1 H), 7.62-7.57 (m, 4 H), 7.41-7.37 (m, 1 H), 7.31 (td, *J* = 7.6, 1.0 Hz, 1 H), 7.15-7.07 (m, 3 H), 6.68 (d, *J* = 3.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (d, *J* = 250.6 Hz), 164.1 (Cq, C=O), 145.2, 136.0, 130.73 (d, *J* = 3.3 Hz), 130.69, 130.4 (d, *J* = 8.7 Hz), 125.1, 124.6, 123.9, 121.0, 116.9, 116.2 (d, *J* = 21.8 Hz), 109.3, 117.0 (d, *J* = 2.0 Hz); HRMS (ESI) calcd for $C_{17}H_{13}FNO$ $[M+H]^+$: 266.0976, found 266.0985.

*(E)-3-(4-Chlorophenyl)-1-(1H-indol-1-yl)prop-2-en-1-one (**1q**).* 337 mg, 60% yield; white solid, mp 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.2 Hz,

1 H), 7.87 (d, *J* = 15.4 Hz, 1 H), 7.57-7.54 (m, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 7.36-7.32 (m, 3 H), 7.28-7.21 (m, 1 H), 7.15 (d, *J* = 15.4 Hz, 1 H), 6.65 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 145.1, 136.8, 136.0, 133.0, 130.7, 129.6, 129.4, 125.2, 124.6, 124.0, 121.1, 117.9, 116.9, 109.4; HRMS (ESI) calcd for $C_{17}H_{13}ClNO$ $[M+H]^+$ 282.0680, found 282.0677.

*(E)-1-(1H-indol-1-yl)-3-(naphthalen-1-yl)prop-2-en-1-one (**1r**).* 315 mg, 53% yield; yellow solid, mp 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 15.2 Hz, 1 H), 8.63 (d, *J* = 8.2 Hz, 1 H), 8.28 (d, *J* = 8.3 Hz, 1 H), 7.96-7.86 (m, 3 H), 7.68 (d, *J* = 3.6 Hz, 1 H), 7.64-7.52 (m, 4 H), 7.43 (t, *J* = 7.7 Hz, 1 H), 7.35-7.26 (m, 2 H), 6.72 (d, *J* = 3.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 143.7, 136.1, 133.8, 132.0, 131.7, 131.1, 130.8, 128.9, 127.2, 126.5, 125.5, 125.3, 125.2, 124.7, 124.0, 123.5, 121.1, 120.1, 117.0, 109.4; HRMS (ESI) calcd for $C_{21}H_{16}NO$ $[M+H]^+$ 298.1226, found 298.1229.

*(E)-1-(1H-indol-1-yl)-3-(thiophen-2-yl)prop-2-en-1-one (**1s**).* 364 mg, 72% yield. pale yellow solid, mp 107-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.3 Hz, 1 H), 8.11 (d, *J* = 15.1 Hz, 1 H), 7.63-7.59 (m, 2 H), 7.45 (d, *J* = 5.0 Hz), 7.40-7.37 (m, 2 H), 7.30 (t, *J* = 7.4 Hz), 7.11 (t, *J* = 4.3 Hz), 7.03 (d, *J* = 15.1 Hz), 6.70 (d, *J* = 3.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 139.8, 139.1, 136.0, 132.2, 130.8, 129.1, 128.5, 125.1, 124.7, 123.9, 121.0, 117.0, 115.9, 109.2; HRMS (ESI) calcd for $C_{15}H_{12}NOS$ $[M+H]^+$ 254.0634, found 254.0637.

*(E)-1-(1H-indol-1-yl)pent-2-en-1-one (**1u**).* 115 mg, 29% yield; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.3 Hz, 1 H), 7.45 (d, *J* = 7.7 Hz, 1 H), 7.41 (d,

J = 3.7 Hz, 1 H), 7.26-7.13 (m, 3 H), 6.53-6.49 (m, 2 H), 2.29-2.22 (m, 2 H), 1.05 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 153.0, 136.0, 130.7, 125.0, 124.8, 123.8, 120.9, 120.0, 116.9, 109.0, 26.0, 12.4; HRMS (ESI) calcd for $C_{13}H_{14}NO$ $[M+H]^+$ 200.1070, found 200.1074.

*(E)-1-(1H-indol-1-yl)hex-2-en-1-one (**1v**)*. 256 mg, 60% yield; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.3 Hz, 1 H), 7.60 (d, *J* = 7.7 Hz, 1 H), 7.57 (d, *J* = 3.8 Hz, 1 H), 7.41-7.37 (m, 1 H), 7.33-7.28 (m, 2 H), 6.70-6.66 (m, 2 H), 2.37 (qd, *J* = 7.2, 1.5 Hz, 2 H), 1.67-1.57 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 151.6, 136.0, 130.7, 125.0, 124.8, 123.8, 121.1, 120.9, 116.9, 109.0, 34.9, 21.6, 13.9; HRMS (ESI) calcd for $C_{14}H_{16}NO$ $[M+H]^+$ 214.1226, found 214.1222.

A typical procedure for the enantioselective borylation of α,β-unsaturated *N*-acylindoles (1) and *N*-acylpyrroles (4) with B_2pin_2 (2) − Synthesis of (*S*)-3a. Under a nitrogen atmosphere, a mixture of CuI (1.9 mg, 0.01 mmol), (*R,S*)-JosiPhos (9.6 mg, 0.015 mmol), and K_3PO_4 (4.2 mg, 0.02 mmol) in *t*-AmOH (1 mL) was stirred at ambient temperature for 30 min, followed by the addition of B_2pin_2 (**2**) (56 mg, 0.22 mmol) in *t*-AmOH (0.5 mL). After the mixture was stirred at ambient temperature for 10 min, (*E*)-1-(1*H*-indol-1-yl)-3-phenylprop- 2-en-1-one (**1a**) (49 mg, 0.2 mmol) in *t*-AmOH (0.5 mL) was added. The resultant mixture was stirred at ambient temperature for 20 h, filtered through a short pad of celite, and rinsed with 20 mL EtOAc. All the volatiles were removed under reduced pressure, the resulting residue was purified by silica gel column chromatography (eluent: petroleum ether

(60-90 °C)/EtOAc = 50:1, v/v) to afford (*S*)-**3a** as a white solid (71 mg, 95%).

*(S)-1-(1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (**3a**)*. 71 mg, 95% yield; 95% ee, $[\alpha]^{20}_{D}$ = -23.4 (*c* 1.0 $CHCl_3$); white solid, mp 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.2 Hz, 1 H), 7.59 (d, *J* = 7.7 Hz, 1 H), 7.46 (d, *J* = 3.5 Hz, 1 H), 7.40-7.25 (m, 7 H), 6.63 (d, *J* = 3.6 Hz, 1 H), 3.55 (dd, *J* = 17.2, 11.2 Hz, 1 H), 3.32 (dd, *J* = 17.2, 5.1 Hz, 1 H), 2.97 (dd, *J* = 11.1, 5.0 Hz, 1 H, CH), 1.32 and 1.24 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 141.2, 135.7, 130.4, 128.7, 128.5, 126.0, 125.0, 124.7, 123.6, 120.8, 116.6, 109.0, 83.7, 40.1, 24.7, 24.5; HRMS (ESI) calcd for $C_{23}H_{27}BNO_3$ $[M+H]^+$ 376.2079, found 376.2084; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 220 nm, flow rate: 0.7 mL/min), t_1 = 7.3 min (maj.), t_2 = 8.0 min.

*(+)-1-(2-Methyl-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (**3b**)*. 75 mg, 96% yield; 88% ee, $[\alpha]^{20}_{D}$ = +5.0 (*c* 1.0 $CHCl_3$); white solid, mp 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 1 H), 7.47-7.45 (m, 1 H), 7.36-7.31 (m, 4 H), 7.24-7.21 (m, 3 H), 6.37 (s, 1 H), 3.59 (dd, *J* = 17.0, 11.4 Hz, 1 H), 3.38 (dd, *J* = 17.0, 4.9 Hz, 1 H), 2.93 (dd, *J* = 11.3, 4.8 Hz, 1 H), 2.65 (s, 3 H), 1.27 and 1.20 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 141.3, 137.7, 136.4, 129.9, 128.7, 128.5, 125.9, 123.5, 123.0, 119.8, 115.6, 109.6, 83.5, 43.4, 24.6, 24.5, 17.9; HRMS (ESI) calcd for $C_{24}H_{29}BNO_3$ $[M+H]^+$ 390.2235, found 390.2243; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.5 mL/min), t_1 = 13.2 min (maj.), t_2 = 14.6 min.

(-)-1-(3-Methyl-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborola

*n-2-yl)propan-1-one (**3c**)*. 73 mg, 94% yield; 92% ee, $[\alpha]^{20}_{D}$ = -20.2 (*c* 1.0 $CHCl_3$); white solid, mp 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.5 Hz, 1 H), 7.51 (d, *J* = 7.5 Hz, 1 H), 7.38-7.28 (m, 6 H), 7.25-7.20 (m, 2 H), 3.50 (dd, *J* = 17.1, 11.2 Hz, 1 H), 3.28 (dd, *J* = 17.2, 5.2 Hz, 1 H), 2.94 (dd, *J* = 11.1, 5.1 Hz, 1 H), 2.28 (s, 3 H), 1.29 and 1.21 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 141.4, 136.0, 131.4, 128.7, 128.5, 125.9, 125.1, 123.3, 121.7, 118.8, 118.2, 116.7, 83.7, 40.2, 24.7, 24.6, 9.8; HRMS (ESI) calcd for $C_{24}H_{29}BNO_3$ $[M+H]^+$ 390.2235, found: 390.2238; enantioselectivity was determined by chiral HPLC analysis of the corresponding β-hydroxy compound (-)-**6a** by oxidation of (-)-**3c** with sodium perborate.

*(-)-1-(4-Methyl-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborola n-2-yl)propan-1-one (**3d**)*. 75 mg, 96% yield; 95% ee, $[\alpha]^{20}_{D}$ = -7.2 (*c* 1.0 $CHCl_3$); white solid, mp 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1 H), 7.47 (d, *J* = 3.8 Hz, 1 H), 7.37-7.19 (m, 6 H), 7.09 (d, *J* = 7.3 Hz, 1 H), 6.67 (d, *J* = 3.8 Hz, 1 H), 3.53 (dd, *J* = 17.2, 11.2 Hz, 1 H), 3.31 (dd, *J* = 17.2, 5.1 Hz, 1 H), 2.94 (dd, *J* = 11.2, 5.1 Hz, 1 H), 2.54 (s, 3 H), 1.28 and 1.20 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 141.3, 135.5, 130.3, 130.0, 128.8, 128.5, 126.0, 125.2, 124.2, 124.0, 114.2, 107.4, 83.7, 40.2, 24.7, 24.6, 18.6; HRMS (ESI) calcd for $C_{24}H_{29}BNO_3$ $[M+H]^+$ 390.2235, found 390.2239; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99.2/0.8, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 13.1 min, t_2 = 14.3 min (maj.).

*(+)-1-(5-Methyl-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborola n-2-yl)propan-1-one (**3e**)*. 73 mg, 94% yield; 96% ee, $[\alpha]^{20}_{D}$ = +33.9 (*c* 1.0 $CHCl_3$);

white solid, mp 142-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.2 Hz, 1 H), 7.43 (d, *J* = 3.2 Hz, 1 H), 7.36-7.32 (m, 5 H), 7.24-7.17 (m, 2 H), 6.55 (d, *J* = 3.6 Hz, 1 H), 3.52 (dd, *J* = 17.1, 11.2 Hz, 1 H), 3.30 (dd, *J* = 17.2, 5.1 Hz, 1 H), 2.95 (dd, *J* = 11.1, 5.0 Hz, 1 H), 2.47 (s, 3 H), 1.29 and 1.21 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 141.3, 133.9, 133.1, 130.6, 128.8, 128.6, 126.4, 126.0, 124.8, 120.8, 116.3, 108.8, 83.7, 40.0, 24.7, 24.6, 21.5; HRMS (ESI) calcd for $C_{24}H_{29}BNO_3$ $[M+H]^+$ 390.2235, found 390.2243; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 9.3 min (maj.), t_2 = 11.0 min.

*(-)-1-(6-Methyl-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborola n-2-yl)propan-1-one (**3f**)*. 75 mg, 96% yield; 99% ee, $[\alpha]^{20}_D$ = -3.0 (*c* 1.0 $CHCl_3$); white solid, mp 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1 H), 7.43 (d, *J* = 7.9 Hz, 1 H), 7.39 (d, *J* = 3.6 Hz, 1 H), 7.35-7.29 (m, 4 H), 7.22-7.18 (m, 1 H), 7.10 (d, *J* = 7.9 Hz, 1 H), 6.56 (d, *J* = 3.6 Hz, 1 H), 3.50 (dd, *J* = 17.1, 11.0 Hz, 1 H), 3.29 (dd, *J* = 17.2, 5.2 Hz, 1 H), 2.93 (dd, *J* = 10.9, 5.1 Hz, 1 H), 2.49 (s, 3 H), 1.27 and 1.19 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 141.3, 136.1, 135.1, 128.7, 128.5, 128.1, 126.0, 125.0, 124.1, 120.4, 116.9, 108.9, 83.7, 40.0, 24.7, 24.6, 22.0; HRMS (ESI) calcd for $C_{24}H_{29}BNO_3$ $[M+H]^+$ 390.2235, found 390.2242; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 10.0 min, t_2 = 12.6 min (maj.).

*(+)-1-(7-Methyl-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborola n-2-yl)propan-1-one (**3g**)*. 73 mg, 94% yield; 92% ee, $[\alpha]^{20}_D$ = +7.8 (*c* 1.0 $CHCl_3$); white solid, mp 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 3.7 Hz, 1 H),

7.41 (d, *J* = 7.5 Hz, 1 H), 7.36-7.31 (m, 4 H), 7.24-7.14 (m, 3 H), 6.60 (d, *J* = 3.6 Hz, 1 H), 3.54 (dd, *J* = 16.8, 10.6 Hz, 1 H), 3.35 (dd, *J* = 16.8, 5.5 Hz, 1 H), 2.97 (dd, *J* = 10.5, 5.5 Hz, 1 H), 2.57 (s, 3 H), 1.28 and 1.23 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 141.3, 135.3, 132.0, 128.8, 128.6, 128.1, 126.8, 126.2, 126.0, 124.0, 118.5, 108.9, 83.8, 40.6, 24.8, 24.5, 23.0; HRMS (ESI) calcd for $C_{24}H_{29}BNO_3$ $[M+H]^+$ 390.2235, found 390.2243; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 220 nm, flow rate: 0.7 mL/min), t_1 = 14.4 min, t_2 = 16.6 min (maj.).

*(-)-1-(5-Methoxy-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (**3h**).* 77 mg, 95% yield; 92% ee, $[\alpha]^{20}_D$ = -35.2 (*c* 1.0 $CHCl_3$); white solid, mp 156-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.8 Hz, 1 H), 7.43 (d, *J* = 3.3 Hz, 1 H), 7.35-7.29 (m, 4 H), 7.22-7.19 (m, 1 H), 7.03 (d, *J* = 2.1 Hz, 1 H), 6.96 (dd, *J* = 9.0, 2.2 Hz, 1 H), 6.54 (d, *J* = 3.6 Hz, 1 H), 3.86 (s, 3 H), 3.49 (dd, *J* = 17.1, 11.2 Hz, 1 H), 3.28 (dd, *J* = 17.1, 5.1 Hz, 1 H), 2.92 (dd, *J* = 11.1, 5.1 Hz, 1 H), 1.27 and 1.19 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 156.5, 141.3, 131.4, 130.5, 128.8, 128.5, 126.0, 125.4, 117.4, 113.5, 108.9, 103.6, 83.7, 55.8, 39.9, 24.7, 24.6; HRMS (ESI) calcd for $C_{24}H_{29}BNO_4$ $[M+H]^+$ 406.2184, found 406.2187; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 10.4 min (maj.), t_2 = 12.2 min.

*(-)-1-(5-Fluoro-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (**3i**).* 75 mg, 95% yield; 94% ee, $[\alpha]^{20}_D$ = -12.8 (*c* 0.5 $CHCl_3$); white solid, mp 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 8.9, 4.7 Hz, 1 H), 7.50 (d, *J* = 3.7 Hz, 1 H), 7.34-7.29 (m, 4 H), 7.22-7.20 (m, 2 H), 7.08-7.03 (m,

1 H), 6.57 (d, *J* = 3.7 Hz, 1 H), 3.50 (dd, *J* = 17.2, 11.1 Hz, 1 H), 3.29 (dd, *J* = 17.2, 5.2 Hz, 1 H), 2.91 (dd, *J* = 11.0, 5.1 Hz, 1 H), 1.26 and 1.18 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 159.6 (d, *J* = 238.4 Hz), 141.1, 132.1, 131.3 (d, *J* = 10.0 Hz), 128.8, 128.5, 126.2, 126.0, 117.6 (d, *J* = 9.0 Hz), 112.7 (d, *J* = 24.6 Hz), 108.6 (d, *J* = 3.9 Hz), 106.3 (d, *J* = 23.7 Hz), 83.7, 39.8, 24.6, 24.5; HRMS (ESI) calcd for $C_{23}H_{26}BFNO_3$ $[M+H]^+$ 394.1984, found: 394.1989; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 220 nm, flow rate: 0.7 mL/min), t_1 = 6.6 min (maj.), t_2 = 7.2 min.

*(-)-1-(5-Chloro-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborola n-2-yl)propan-1-one (**3j**)*. 76 mg, 93% yield; 95% ee, $[\alpha]^{20}_D$ = -14.7 (*c* 1.0 $CHCl_3$); white solid, mp 121-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.8 Hz, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 7.47 (d, *J* = 3.7 Hz, 1 H), 7.33-7.28 (m, 5 H), 7.23-7.19 (m, 1 H), 6.55 (d, *J* = 3.7 Hz, 1 H), 3.50 (dd, *J* = 17.2, 11.1 Hz, 1 H), 3.28 (dd, *J* = 17.3, 5.2 Hz, 1 H), 2.92 (dd, *J* = 11.0, 5.2 Hz, 1 H, CH), 1.27 and 1.19 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 141.1, 134.1, 131.6, 129.2, 128.8, 128.5, 126.1, 126.0, 125.2, 120.5, 117.7, 108.3, 83.8, 40.0, 24.7, 24.6; HRMS (ESI) calcd for $C_{23}H_{26}BClNO_3$ $[M+H]^+$ 410.1689, found 410.1698; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 14.8 min (maj.), t_2 = 21.0 min.

*(-)-1-(5-Bromo-1H-indol-1-yl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborola n-2-yl)propan-1-one (**3k**)*. 84 mg, 93% yield; 95% ee, $[\alpha]^{20}_D$ = -15.9 (*c* 1.0 $CHCl_3$); white solid, mp 132-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.8 Hz, 1 H),

7.69 (d, *J* = 1.9 Hz, 1 H), 7.46 (d, *J* = 3.8 Hz, 1 H), 7.43 (dd, *J* = 8.8, 1.9 Hz, 1 H), 7.33-7.29 (m, 4 H), 7.20 (ddd, *J* = 8.5, 5.9, 2.9 Hz, 1 H), 6.55 (d, *J* = 3.7 Hz, 1 H), 3.49 (dd, *J* = 17.2, 11.0 Hz, 1 H), 3.28 (dd, *J* = 17.3, 5.2 Hz, 1 H), 2.91 (dd, *J* = 11.0, 5.2 Hz, 1 H), 1.26 and 1.18 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 141.1, 134.5, 132.1, 128.8, 128.5, 127.9, 126.1, 125.9, 123.6, 118.1, 116.9, 108.2, 83.8, 40.0, 24.7, 24.6; HRMS (ESI) calcd for $C_{23}H_{26}BBrNO_3$ $[M+H]^+$ 454.1184, found 454.1187; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 9.0 min (maj.), t_2 = 10.6 min.

*(-)-1-(1H-indol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl)propan-1-one (**3l**).* 73 mg, 94% yield; 93% ee, $[\alpha]^{20}_D$ = -8.3 (*c* 1.0 $CHCl_3$); white solid, mp 132-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.2 Hz, 1 H), 7.59 (d, *J* = 7.6 Hz, 1 H), 7.47 (d, *J* = 3.8 Hz, 1 H), 7.39-7.35 (m, 1 H), 7.29-7.26 (m, 3 H), 7.16 (d, *J* = 7.8 Hz, 2 H), 6.63 (d, *J* = 3.6 Hz, 1 H), 3.52 (dd, *J* = 17.2, 11.1 Hz, 1 H), 3.30 (dd, *J* = 17.2, 5.2 Hz, 1 H), 2.93 (dd, *J* = 11.1, 5.1 Hz, 1 H), 2.36 (s, 3 H), 1.31 and 1.23 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 138.1, 135.8, 135.4, 130.4, 129.5, 128.4, 125.0, 124.7, 123.6, 120.9, 116.7, 109.0, 83.7, 40.3, 24.7, 24.6, 21.1; HRMS (ESI) calcd for $C_{24}H_{29}BNO_3$ $[M+H]^+$ 390.2235, found 390.2237; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.5 mL/min), t_1 = 11.5 min (maj.), t_2 = 12.9 min.

*(-)-1-(1H-indol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)propan-1-one (**3m**).* 73 mg, 94% yield; 91% ee, $[\alpha]^{20}_D$ = -2.7 (*c* 1.0 $CHCl_3$); white solid, mp 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.2 Hz, 1 H), 7.58 (d, *J* =

7.6 Hz, 1 H), 7.48 (d, *J* = 3.8 Hz, 1 H), 7.38-7.34 (m, 1 H), 7.30-7.26 (m, 1 H), 7.25-7.21 (m, 1 H), 7.17-7.15 (m, 2 H), 7.04 (d, *J* = 7.4 Hz, 1 H), 6.63 (d, *J* = 3.8 Hz, 1 H), 3.52 (dd, *J* = 17.2, 11.3 Hz, 1 H), 3.30 (dd, *J* = 17.2, 5.1 Hz, 1 H), 2.91 (dd, *J* = 11.3, 5.1 Hz, 1 H), 2.37 (s, 3 H), 1.29 and 1.21 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 141.1, 138.3, 135.8, 130.4, 129.4, 128.7, 126.8, 125.5, 125.1, 124.8, 123.6, 120.9, 116.7, 109.0, 83.7, 40.2, 24.7, 24.6, 21.6; HRMS (ESI) calcd for $C_{24}H_{29}BNO_3$ $[M+H]^+$ 390.2235, found 390.2228; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 8.1 min (maj.), t_2 = 8.9 min.

*(-)-1-(1H-indol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(o-tolyl)propan-1-one (**3n**).* 75 mg, 94% yield; 90% ee, $[\alpha]^{20}_D$ = -8.8 (*c* 1.0 $CHCl_3$); white solid, mp 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.2 Hz, 1 H), 7.58 (d, *J* = 7.7 Hz, 1 H), 7.47 (d, *J* = 3.7 Hz, 1 H), 7.38-7.34 (m, 2 H), 7.30-7.27 (t, *J* = 7.5 Hz, 1 H), 7.21-7.17 (t, *J* = 7.7 Hz, 2 H), 7.14-7.11 (t, *J* = 7.1 Hz, 1 H), 6.63 (d, *J* = 3.7 Hz, 1 H), 3.51 (dd, *J* = 17.0, 10.9 Hz, 1 H), 3.24 (dd, *J* = 17.0, 4.8 Hz, 1 H), 3.18 (dd, *J* = 10.9, 4.8 Hz, 1 H), 2.44 (s, 3 H), 1.29 and 1.21 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 139.6, 136.6, 135.8, 130.8, 130.4, 127.9, 126.3, 125.9, 125.1, 124.8, 123.6, 120.9, 116.7, 109.0, 83.7, 39.5, 24.8, 24.6, 20.2. HRMS (ESI) calcd for $C_{24}H_{29}BNO_3$ $[M+H]^+$ 390.2235, found 390.2238; enantioselectivity was determined by chiral HPLC analysis of the corresponding β-hydroxy compound (-)-**6b** by oxidation of (-)-**3n** with sodium perborate.

(-)-1-(1H-indol-1-yl)-3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboro

*lan-2-yl)propan-1-one (**3o**)*. 77 mg, 95% yield; 94% ee, $[\alpha]^{20}_{D}$ = -12.5 (*c* 1.0 $CHCl_3$); White solid, mp 147-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.2 Hz, 1 H), 7.57 (d, *J* = 7.7 Hz, 1 H), 7.46 (d, *J* = 3.7 Hz, 1 H), 7.37-7.33 (m, 1 H), 7.29-7.26 (m, 3 H), 6.88 (d, *J* = 8.6 Hz, 2 H), 6.61 (d, *J* = 3.7 Hz, 1 H), 3.80 (s, 3 H), 3.48 (dd, *J* = 17.2, 11.0 Hz, 1 H), 3.28 (dd, *J* = 17.2, 5.3 Hz, 1 H), 2.89 (dd, *J* = 10.9, 5.2 Hz, 1 H), 1.29 and 1.21 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 158.0, 135.7, 133.1, 130.4, 129.4, 125.0, 124.7, 123.5, 120.8, 116.7, 114.2, 108.9, 83.7, 55.3, 40.4, 24.7, 24.6; HRMS (ESI) calcd for $C_{24}H_{29}BNO_4$ $[M+H]^+$ 406.2184, found 406.2183; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 254 nm, flow rate: 0.5 mL/min), t_1 = 13.8 min (maj.), t_2 = 14.9 min.

*(-)-3-(4-Fluorophenyl)-1-(1H-indol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborola n-2-yl)propan-1-one (**3p**)*. 71 mg, 90% yield; 95% ee, $[\alpha]^{20}_{D}$ = -13.5 (*c* 0.2 $CHCl_3$); white solid, mp 130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.2 Hz, 1 H), 7.57 (d, *J* = 7.7 Hz, 1 H), 7.45 (d, *J* = 3.7 Hz, 1 H), 7.38-7.25 (m, 4 H), 7.04-6.99 (m, 4 H), 6.62 (d, *J* = 3.8 Hz, 1 H), 3.47 (dd, *J* = 17.2, 10.8 Hz, 1 H), 3.28 (dd, *J* = 17.2, 5.4 Hz, 1 H), 2.92 (dd, *J* = 10.7, 5.3 Hz, 1 H), 1.29 and 1.21 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 161.4 (d, *J* = 242.3 Hz), 136.9 (d, *J* = 3.2 Hz), 135.7, 130.4, 129.9 (d, *J* = 7.7 Hz), 125.1, 124.7, 123.6, 120.9, 116.7, 115.5 (d, *J* = 21.0 Hz), 109.1, 83.8, 40.1, 24.7, 24.6; HRMS (ESI) calcd for $C_{23}H_{26}BFNO_3$ $[M+H]^+$ 394.1984, found 394.1990; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 8.7 min (maj.), t_2 = 9.7 min.

(-)-3-(4-Chlorophenyl)-1-(1H-indol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborola

*n-2-yl)propan-1-one (**3q**)*. 75 mg, 92% yield; 94% ee, $[\alpha]^{20}_{D}$ = -6.4 (*c* 0.5 $CHCl_3$); white solid, mp 135-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.2 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 3.8 Hz, 1 H), 7.37-7.33 (m, 1 H), 7.30-7.26 (m, 5 H), 6.63 (d, *J* = 3.7 Hz, 1 H), 3.48 (dd, *J* = 17.2, 10.7 Hz, 1 H), 3.29 (dd, *J* = 17.2, 5.4 Hz, 1 H), 2.90 (dd, *J* = 10.7, 5.4 Hz, 1 H), 1.27 and 1.20 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 139.8, 135.8, 131.8, 130.4, 129.9, 128.9, 125.2, 124.6, 123.7, 121.0, 116.7, 109.2, 83.9, 39.9, 24.7, 24.6; HRMS (ESI) calcd for $C_{23}H_{26}BClNO_3$ $[M+H]^+$ 410.1689, found 410.1700; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 16.0 min (maj.), t_2 = 18.0 min.

*(+)-1-(1H-indol-1-yl)-3-(naphthalen-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborol an-2-yl)propan-1-one (**3r**)*. 75 mg, 88% yield; 87% ee, $[\alpha]^{20}_{D}$ = +18.9 (*c* 1.0 $CHCl_3$); white solid, mp 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.2 Hz, 1 H), 8.30 (d, *J* = 8.3 Hz, 1 H), 7.90 (d, *J* = 7.8 Hz, 1 H), 7.77 (d, *J* = 8.1 Hz, 1 H), 7.60-7.46 (m, 5 H), 7.41-7.38 (m, 2 H), 7.32-7.28 (m, 1 H), 6.59 (d, *J* = 3.7 Hz, 1 H), 3.79 (dd, *J* = 10.9, 4.5 Hz, 1 H), 3.67 (dd, *J* = 17.0, 10.9 Hz, 1 H), 3.40 (dd, *J* = 17.0, 4.5 Hz, 1 H), 1.35 and 1.24 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 137.9, 135.8, 134.3, 132.1, 130.4, 129.0, 126.9, 126.1, 125.9, 125,74, 125,68 125.1, 124.7, 124.0, 123.6, 120.9, 116.7, 109.0, 83.9, 39.8, 24.8, 24.6; HRMS (ESI) calcd for $C_{27}H_{29}BNO_3$ $[M+H]^+$ 426.2235, found 426.2238; enantioselectivity was determined by chiral HPLC analysis of the corresponding β-hydroxy compound (-)-**6c** by oxidation of (+)-**3r** with sodium perborate.

*(-)-1-(1H-indol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(thiophen-2-yl)propan-1-one (**3s**).* 69 mg, 91% yield; 96% ee, $[\alpha]^{20}_{D}$ = -56.0 (*c* 0.1 $CHCl_3$); white solid, mp 99-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.1 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.47 (d, *J* = 3.4 Hz, 1 H), 7.37-7.34 (m, 1 H), 7.29-7.26 (m, 1 H), 7.14 (d, *J* = 4.7 Hz, 1 H), 6.97-6.95 (m, 2 H), 6.63 (d, *J* = 3.6 Hz, 1 H), 3.51 (dd, *J* = 17.1, 10.6 Hz, 1 H), 3.41 (dd, *J* = 17.2, 5.1 Hz, 1 H), 3.22 (dd, *J* = 10.4, 5.1 Hz, 1 H), 1.31 and 1.25 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 143.9, 135.8, 130.4, 127.1, 125.2, 124.7, 123.7, 123.4, 120.9, 116.7, 109.2, 84.1, 40.9, 24.8, 24.6; HRMS (ESI) calcd for $C_{21}H_{25}BNO_3S$ $[M+H]^+$ 382.1643, found 382.1646; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 9.5 min (maj.), t_2 = 10.6 min.

*(-)-1-(1H-indol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (**3t**).* 59 mg, 95% yield; 92% ee, $[\alpha]^{20}_{D}$ = -27.5 (*c* 0.1 $CHCl_3$); white solid, mp 96-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.2 Hz, 1 H), 7.56 (d, *J* = 7.7 Hz, 1 H), 7.48 (d, *J* = 3.8 Hz, 1 H), 7.37-7.32 (m, 1 H), 7.28-7.24 (m, 1 H), 6.61 (d, *J* = 3.7 Hz, 1 H), 3.09-2.98 (m, 2 H), 1.63-1.53 (m, 1 H), 1.29 and 1.27 (s each, 6:6 H), 1.15 (d, *J* = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 135.7, 130.4, 125.0, 124.8, 123.5, 120.8, 116.7, 108.7, 83.3, 39.8, 24.8, 24.7, 15.2. HRMS (ESI) calcd for $C_{18}H_{25}BNO_3$ $[M+H]^+$ 314.1922, found 314.1926; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 6.8 min (maj.), t_2 = 7.6 min.

(-)-1-(1H-indol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one

*(**3u**)*. 52 mg, 80% yield; 92% ee, $[\alpha]^{20}_{D}$ = -37.3 (*c* 1.0 $CHCl_3$); white solid, mp 75-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.2 Hz, 1 H), 7.56 (d, *J* = 7.7 Hz, 1 H), 7.51 (d, *J* = 3.7 Hz, 1 H), 7.36-7.32 (m, 1 H), 7.28-7.24 (m, 1 H), 6.62 (d, *J* = 3.8 Hz, 1 H), 3.11-3.00 (m, 2 H), 1.69-1.58 (m, 1 H), 1.56-1.46 (m, 2 H), 1.28 and 1.26 (s each, 6:6 H), 1.02 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 135.8, 130.4, 125.0, 124.9, 123.5, 120.8, 116.7, 108.8, 83.3, 37.7, 24.9, 24.8, 23.6, 13.6; HRMS (ESI) calcd for $C_{19}H_{27}BNO_3$ $[M+H]^+$ 328.2079, found 328.2087; HPLC (two AD-H series, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 22.1 min (maj.), t_2 = 27.2 min.

*(-)-1-(1H-indol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (**3v**)*. 65 mg, 95% yield; 90% ee, $[\alpha]^{20}_{D}$ = -38.2 (*c* 1.0 $CHCl_3$); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.2 Hz, 1 H), 7.57 (d, *J* = 7.7 Hz, 1 H), 7.51 (d, *J* = 3.8 Hz, 1 H), 7.36-7.32 (m, 1 H), 7.28-7.24 (m, 1 H), 6.62 (d, *J* = 3.8 Hz, 1 H), 3.22-2.89 (m, 2 H), 1.63-1.51 (m, 2 H), 1.50-1.38 (m, 3 H), 1.28 and 1.25 (s each, 6:6 H), 0.95 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 135.8, 130.4, 125.0, 124.9, 123.5, 120.8, 116.7, 108.8, 83.3, 37.9, 32.8, 24.9, 24.8, 22.2, 14.4. HRMS (ESI) calcd for $C_{20}H_{29}BNO_3$ $[M+H]^+$ 342.2235, found 342.2230; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 7.9 min (maj.), t_2 = 9.2 min.

*(+)-3-Phenyl-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (**5a**)*. 62 mg, 95% yield; 95% ee, $[\alpha]^{20}_{D}$ = +18.4 (*c* 0.5 $CHCl_3$); white solid, mp 65-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 6 H), 7.23-7.16 (m,

1 H), 6.28-6.27 (m, 2 H), 3.42 (dd, *J* = 17.5, 10.9 Hz, 1 H), 3.21 (dd, *J* = 17.5, 5.3 Hz, 1 H), 2.87 (dd, *J* = 10.8, 5.2 Hz, 1 H), 1.25 and 1.18 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 141.2, 128.8, 128.5, 126.1, 119.1, 113.0, 83.8, 38.7, 24.7, 24.6; HRMS (ESI) calcd for $C_{19}H_{25}BNO_3$ $[M+H]^+$ 326.1922, found: 326.1928; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 220 nm, flow rate: 0.7 mL/min), t_1 = 6.6 min (maj.), t_2 = 7.2 min.

*(+)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl) propan-1-one (**5b**).* 63 mg, 93% yield; 94% ee, $[\alpha]^{20}_D$ = +14.0 (*c* 1.0 $CHCl_3$); white solid, mp 77-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 7.9 Hz, 2 H), 6.29-6.28 (m, 2 H), 3.40 (dd, *J* = 17.5, 10.8 Hz, 1 H), 3.19 (dd, *J* = 17.5, 5.3 Hz, 1 H), 2.84 (dd, *J* = 10.8, 5.2 Hz, 1 H), 2.34 (s, 3 H), 1.27 and 1.20 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 138.0, 135.4, 129.5, 128.3, 119.1, 112.9, 83.7, 38.9, 24.63, 24.62, 21.1; HRMS (ESI) calcd for $C_{20}H_{27}BNO_3$ $[M+H]^+$ 340.2079, found 340.2087; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.5 mL/min), t_1 = 10.1 min (maj.), t_2 = 11.0 min.

*(+)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl) propan-1-one (**5c**).* 62 mg, 92% yield; 94% ee, $[\alpha]^{20}_D$ = +12.9 (*c* 1.0 $CHCl_3$); white solid, mp 58-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2 H), 7.22-7.19 (m, 1 H), 7.11 (d, *J* = 8.8 Hz, 2 H), 7.02 (d, *J* = 7.5 Hz, 1 H), 6.29-6.28 (m, 2 H), 3.42 (dd, *J* = 17.5, 11.0 Hz, 1 H), 3.20 (dd, *J* = 17.5, 5.2 Hz, 1 H), 2.84 (dd, *J* = 11.0, 5.1 Hz, 1 H), 2.35 (s, 3 H), 1.27, 1.20 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 141.0,

138.3, 129.3, 128.6, 126.8, 125.4, 119.1, 112.9, 83.7, 38.8, 24.61, 24.59, 21.5; HRMS (ESI) calcd for $C_{20}H_{27}BNO_3$ $[M+H]^+$ 340.2079, found 340.2082; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 7.0 min (maj.), t_2 = 7.5 min.

*(+)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(o-tolyl) propan-1-one (**5d**).* 59 mg, 87% yield; 90% ee, $[\alpha]^{20}_D$ = +0.4 (*c* 1.0 $CHCl_3$); Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 2 H), 7.29-7.27 (m, 1 H), 7.18-7.14 (m, 2 H), 7.12-7.08 (m, 1 H), 6.28-6.27 (m, 2 H), 3.40 (dd, *J* = 16.9, 10.2 Hz, 1 H), 3.14 (dd, *J* = 17.0, 5.0 Hz, 1 H), 3.09 (dd, *J* = 10.1 Hz, 5.0 Hz, 1 H), 2.40 (s, 3 H), 1.26 and 1.18 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 139.6, 136.5, 130.8, 127.8, 126.3, 126.0, 119.1, 113.0, 83.7, 38.1, 24.7, 24.6, 20.1; HRMS (ESI) calcd for $C_{20}H_{27}BNO_3$ $[M+H]^+$ 340.2079, found 340.2082; enantioselectivity was determined by chiral HPLC analysis of the corresponding β-hydroxy compound (-)-**6e** by oxidation of (+)-**5d** with sodium perborate.

*(+)-3-(4-Methoxyphenyl)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxabo rolan-2-yl)propan-1-one (**5e**).* 66 mg, 93% yield; 96% ee, $[\alpha]^{20}_D$ = +15.2 (*c* 0.5 $CHCl_3$); white solid, mp 70-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 2 H), 7.21 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 6.27-6.26 (m, 2 H), 3.78 (s, 3 H), 3.36 (dd, *J* = 17.5, 10.7 Hz, 1 H), 3.17 (dd, *J* = 17.5, 5.4 Hz, 1 H), 2.80 (dd, *J* = 10.6, 5.3 Hz, 1 H), 1.24 and 1.18 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 158.0, 133.1, 129.4, 119.1, 114.2, 113.0, 83.7, 55.3, 39.0, 24.7, 24.6; HRMS (ESI) calcd for $C_{20}H_{27}BNO_4$ $[M+H]^+$ 356.2028, found 356.2034; HPLC (AD-H, elute:

Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 11.5 min (maj.), t_2 = 13.0 min.

*(+)-3-(4-Fluorophenyl)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (**5f**).* 64 mg, 94% yield; 96% ee, $[\alpha]^{20}_D$ = +8.5 (*c* 0.4 $CHCl_3$); white solid, mp 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 2 H), 7.25 (dd, *J* = 8.0, 5.1 Hz, 2 H), 7.00-6.96 (m, 2 H), 6.28-6.27 (m, 2 H), 3.36 (dd, *J* = 17.5, 10.4 Hz, 1 H), 3.18 (dd, *J* = 17.5, 5.5 Hz, 1 H), 2.84 (dd, *J* = 10.3, 5.5 Hz, 1 H), 1.24 and 1.18 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$ δ 170.3, 161.4 (d, *J* = 242.2 Hz), 136.8 (d, *J* = 3.3 Hz), 129.9 (d, *J* = 7.7 Hz), 119.1, 115.5 (d, *J* = 21.0 Hz), 113.1, 83.9, 38.7, 24.7, 24.6; HRMS (ESI) calcd for $C_{19}H_{24}BFNO_3$ $[M+H]^+$ 344.1828, found 344.1835; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 8.9 min (maj.), t_2 = 11.5 min.

*(+)-3-(4-Chlorophenyl)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (**5g**).* 60 mg, 83% yield; 94% ee, $[\alpha]^{20}_D$ = +7.6 (*c* 0.5 $CHCl_3$); white solid, mp 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.19 (m, 6 H), 6.28-6.27 (m, 2 H), 3.37 (dd, *J* = 17.5, 10.3 Hz, 1 H), 3.19 (dd, *J* = 17.5, 5.5 Hz, 1 H), 2.84 (dd, *J* = 10.3, 5.5 Hz, 1 H), 1.24 and 1.18 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 139.8, 131.8, 129.8, 128.9, 119.1, 113.1, 84.0, 38.4, 24.7, 24.6; HRMS (ESI) calcd for $C_{19}H_{24}BClNO_3$ $[M+H]^+$ 360.1532, found 360.1532; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 11.8 min (maj.), t_2 = 14.2 min.

(+)-3-(Naphthalen-1-yl)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxabor

*olan-2-yl)propan-1-one (**5h**)*. 65 mg, 86% yield; 91% ee, $[\alpha]^{20}_{D}$ = +3.5 (*c* 1.0 $CHCl_3$); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.3 Hz, 1 H), 7.88-7.85 (m, 1 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.55-7.46 (m, 3 H), 7.45-7.41 (m, 1 H), 7.31 (s, 2 H), 6.27-6.26 (m, 2 H), 3.67 (dd, *J* = 10.5, 4.7 Hz, 1 H), 3.55 (dd, *J* = 17.4, 10.5 Hz, 1 H), 3.29 (dd, *J* = 17.3, 4.8 Hz, 1 H), 1.29 and 1.19 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 137.8, 134.4, 132.1, 129.0, 126.9, 126.1, 126.0, 125.74, 125.70, 124.0, 119.2, 113.0, 84.0, 38.4, 24.8, 24.7; HRMS (ESI) calcd for $C_{23}H_{27}BNO_3$ $[M+H]^+$ 376.2079, found 376.2070; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 98/2, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 11.9 min, t_2 = 12.9 min (maj.).

*(-)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(thiophen -2-yl)propan-1-one (**5i**)*. 61 mg, 92% yield; 96% ee, $[\alpha]^{20}_{D}$ = -25.0 (*c* 0.1 $CHCl_3$); pale yellow solid, mp 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 2 H), 7.12 (d, *J* = 5.1 Hz, 1 H), 6.94-6.90 (m, 2 H), 6.28 (s, 2 H), 3.40 (dd, *J* = 17.4, 10.3 Hz, 1 H), 3.30 (dd, *J* = 17.5, 5.1 Hz, 1 H), 3.15 (dd, *J* = 10.2, 5.1 Hz, 1 H), 1.27 and 1.22 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 143.8, 127.1, 124.7, 123.5, 119.1, 113.1, 84.1, 39.5, 24.7, 24.6; HRMS (ESI) calcd for $C_{17}H_{23}BNO_3S$ $[M+H]^+$ 332.1486, found 332.1491; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 8.0 min (maj.), t_2 = 8.7 min.

*(-)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (**5j**)*. 49 mg, 92% yield; 93% ee, $[\alpha]^{20}_{D}$ = -4.8 (*c* 1.0 $CHCl_3$); white solid, mp 46-48 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 2 H), 6.27-6.25 (m, 2 H), 2.99-2.87 (m, 2 H), 1.55-1.45 (m, 1 H), 1.24 and 1.23 (s each, 6:6 H), 1.08 (d, *J* = 7.5 Hz, 3 H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 170.9, 119.1, 112.8, 83.4, 38.4, 24.8, 24.7, 15.2; HRMS (ESI) calcd for $C_{14}H_{23}BNO_3$ $[M+H]^+$ 264.1766, found 264.1771; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 5.9 min (maj.), t_2 = 6.3 min.

*(-)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one (**5k**)*. 40 mg, 73% yield; 84% ee, $[\alpha]^{20}_D$ = -7.3 (*c* 0.4 $CHCl_3$); yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 2 H), 7.27-7.26 (m, 2 H), 3.01-2.89 (m, 2 H), 1.61-1.54 (m, 1 H), 1.51-1.39 (m, 2 H), 1.25 and 1.23 (s each, 6:6 H), 0.97 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 119.2, 112.8, 83.4, 36.2, 24.9, 24.8, 23.6, 13.5; HRMS (ESI) calcd for $C_{15}H_{25}BNO_3$ $[M+H]^+$ 278.1922, found 278.1926; HPLC (two AD-H series, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 22.6 min (maj.), t_2 = 23.5 min.

*(-)-1-(1H-pyrrol-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (**5l**)*. 45 mg, 77% yield; 90% ee, $[\alpha]^{20}_D$ = -9.6 (*c* 0.5 $CHCl_3$); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 2 H), 6.27-6.25 (m, 2 H), 2.99-2.89 (m, 2 H), 1.55-1.45 (m, 2 H), 1.43-1.33 (m, 3 H), 1.24 and 1.22 (s each, 6:6 H), 0.91 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 119.2, 112.8, 83.3, 36.5, 32.8, 24.9, 24.8, 22.1, 14.4; HRMS (ESI) calcd for $C_{16}H_{27}BNO_3$ $[M+H]^+$ 292.2079, found 292.2073; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.5 mL/min), t_1 = 11.4 min (maj.), t_2 = 11.9 min.

A typical procedure for the Oxidation of the borylated products − Oxidation of (*S*)-(5a). By means of a modified procedure as reported in reference 25, a mixture

of (*S*)-**5a** (65 mg, 0.2 mmol) and sodium perborate (154 mg, 1.0 mmol) in THF/water (2 mL, v/v = 1:1) was stirred at ambient temperature for 2 h. The mixture was then concentrated in vacuo, and the resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 ^{o}C)/EtOAc = 10:1, v/v) to afford (-)-**6e** as a white solid (38 mg, 89%).

*(-)-3-hydroxy-1-(1H-indol-1-yl)-3-phenylpropan-1-one (**6a**).* 48 mg, 90% yield; ee 95%, $[\alpha]^{20}_{D}$ = -66.2 (*c* 1.0 $CHCl_3$); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.8 Hz, 1 H), 7.58 (d, *J* = 7.7 Hz, 1 H), 7.49-7.47 (m, 2 H), 7.43-7.29 (m, 6 H), 6.64 (d, *J* = 3.8 Hz, 1 H), 5.41 (d, *J* = 8.8 Hz, 1 H), 3.72 (s, 1 H), 3.56-3.22 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 142.4, 135.6, 130.5, 128.8, 128.0, 125.9, 125.5, 124.4, 124.1, 121.1, 116.8, 110.0, 70.1, 45.0; HRMS (ESI) calcd for $C_{17}H_{14}NO$ $[M\text{-}OH]^+$ 248.1070, found 280.1064; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 34.1 min, t_2 = 36.9 min (maj.).

*(-)-3-Hydroxy-1-(3-methyl-1H-indol-1-yl)-3-phenylpropan-1-one (**6b**).* 50 mg, 89% yield; 92% ee, $[\alpha]^{20}_{D}$ = -70.8 (*c* 0.5 $CHCl_3$); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1 H), 7.51-7.46 (m, 3 H), 7.42-7.30 (m, 5 H), 7.13 (s, 1 H), 5.40 (dd, *J* = 8.8, 3.1 Hz, 1 H), 3.80 (br, 1 H), 3.31-3.19 (m, 2 H), 2.26 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 142.5, 135.9, 131.6, 128.8, 128.0, 125.9, 125.5, 123.9, 121.3, 119.3, 119.1, 116.8, 70.1, 45.0, 9.8; HRMS (ESI) calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.1332, found 280.1339; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 15.2 min, t_2 = 16.7 min (maj.).

*(-)-3-Hydroxy-1-(1H-indol-1-yl)-3-(o-tolyl)propan-1-one (**6c**).* 42 mg, 76% yield;

90% ee, $[\alpha]^{20}_D$ = -76.9 (*c* 0.2 $CHCl_3$); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.8 Hz, 1 H), 7.63 (d, *J* = 7.6 Hz, 1 H), 7.58 (d, *J* = 7.7 Hz, 1 H), 7.41-7.37 (m, 2 H), 7.31 (t, *J* = 7.7 Hz, 2 H), 7.21 (dd, *J* = 16.6, 7.0 Hz, 2 H), 6.65 (d, *J* = 3.8 Hz, 1 H), 5.65 (d, *J* = 9.4 Hz, 1 H), 3.56 (d, *J* = 2.5 Hz, 1 H), 3.29 (dd, *J* = 17.0, 9.4 Hz, 1 H), 3.19 (dd, *J* = 17.0, 2.5 Hz, 1 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 140.5, 135.7, 135.0, 134.3, 130.7, 127.9, 126.7, 125.6, 125.5, 124.4, 124.2, 121.1, 116.8, 110.1, 66.7, 43.8, 19.3; HRMS (ESI) calcd for $C_{18}H_{17}NNaO_2$ $[M+Na]^+$ 302.1151, found 302.1151; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 16.8 min, t_2 = 24.6 min (maj.).

*(-)-3-Hydroxy-1-(1H-indol-1-yl)-3-(naphthalen-1-yl)propan-1-one (**6d**)*. 57 mg, 90% yield; 87% ee, $[\alpha]^{20}_D$ = -53.0 (*c* 0.1 $CHCl_3$); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 6.9 Hz, 1 H), 8.09 (d, *J* = 7.7 Hz, 1 H), 7.93-7.91 (m, 1 H), 7.84 (d, *J* = 7.6 Hz, 2 H), 7.58-7.50 (m, 4 H), 7.40 (t, *J* = 7.7 Hz, 1 H), 7.33-7.26 (m, 2 H), 6.60 (d, *J* = 3.6 Hz, 1 H), 6.22 (dd, *J* = 8.5, 2.7 Hz, 1 H), 3.84 (br, 1 H), 3.46-3.35 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 138.0, 135.7, 133.9, 130.6, 129.9, 129.2, 128.4, 126.6, 125.80, 125.76, 125.5, 124.4, 124.2, 123.4, 122.8, 121.1, 116.8, 110.0, 67.0, 44.4; HRMS (ESI) calcd for $C_{21}H_{16}NO$ $[M-OH]^+$ 298.1226, found 298.1233; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 20.7 min, t_2 = 26.9 min (maj.).

*(-)-3-Hydroxy-3-phenyl-1-(1H-pyrrol-1-yl)propan-1-one (**6e**)*. 38 mg, 89% yield; 94% ee, $[\alpha]^{20}_D$ = -85.6 (*c* 0.5 $CHCl_3$); white solid, mp 76-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.37 (m, 4 H), 7.34-7.26 (m, 3 H), 6.31-6.30 (m, 2 H), 5.35 (dd, *J* = 9.1,

3.2 Hz, 1 H), 3.44 (br, 1 H), 3.26 (dd, *J* = 17.1, 9.1 Hz, 1 H), 3.17 (dd, *J* = 17.1, 3.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 142.4, 128.8, 128.1, 125.8, 119.1, 113.8, 70.0, 43.9; HRMS (ESI) calcd for $C_{13}H_{12}NO$ $[M\text{-}OH]^+$ 198.0913, found 198.0913; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 19.7 min (maj.), t_2 = 21.9 min.

*(-)-3-Hydroxy-1-(1H-pyrrol-1-yl)-3-(o-tolyl)propan-1-one (**6f**)*. 40 mg, 87% yield; 90% ee, $[\alpha]^{20}_D$ = -96.5 (*c* 0.2 $CHCl_3$); white solid, mp 63-65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 1 H), 7.34-7.29 (m, 3 H), 7.22 (t, *J* = 8.6 Hz, 1 H), 6.36-6.35 (m, 2 H), 5.60 (dd, *J* = 9.4, 2.5 Hz, 1 H), 3.43 (br, 1 H), 3.24 (dd, *J* = 17.1, 9.4 Hz, 1 H) and 3.13 (dd, *J* = 17.1, 2.6 Hz, 1 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 140.4, 134.2, 130.7, 127.9, 126.6, 125.5, 119.1, 113.8, 66.5, 42.7, 19.2; HRMS (ESI) calcd for $C_{14}H_{15}NNaO_2$ $[M+Na]^+$ 252.0995, found 252.0998; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 16.8 min, t_2 = 19.2 min (maj.).

Derivations of the borylated products

A solution of NaOMe (12 mg, 0.22 mmol) in MeOH (1 mL) was added to a stirred solution of (*S*)-**3a** (75 mg, 0.2 mmol) in dry THF (1 mL) at 0 °C. After the reaction mixture was stirred at 0 °C for 30 min, aqueous NH_4Cl (10 mL) was added to quench the reaction and the mixture was extracted with Et_2O (3×10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The corresponding methyl ester was observed in <10% yield with 100% conversion of (*S*)-**3a** by ^{1}H NMR analysis using CH_2Br_2 as the internal standard. Compound (*S*)-**5a**

was treated in a similar fashion.

Pyrrolidine (71 mg, 1.0 mmol) was added to a stirred solution of (*S*)-**3a** (38 mg, 0.1 mmol) in dry THF (2 mL), and the mixture was then stirred at 60 ^{o}C for 12 h. After cooled to ambient temperature, all the volatiles were removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 ^{o}C)/EtOAc = 15:1, v/v) to afford (*S*)-**7** as a pale yellow solid (26 mg, 80%). Compound (*S*)-**5a** was treated in a similar fashion to afford (*S*)-**7** (23 mg, 71%).

*(+)-3-Phenyl-1-(pyrrolidin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) propan-1-one (**7**).*[12j] 26 mg, 80% yield; 94% ee, $[\alpha]^{20}_{D}$ = +7.5 (*c* 0.2 CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.21 (m, 4 H), 7.13-7.09 (m, 1 H), 3.50 (t, *J* = 6.8 Hz, 2 H), 3.43-3.29 (m, 2 H), 2.81 (dd, *J* = 16.6, 10.7 Hz, 1 H), 2.73 (dd, *J* = 16.6, 6.7 Hz, 1 H_2), 2.62 (dd, *J* = 10.7, 6.7 Hz, 1 H), 1.96-1.83 (m, 4 H), 1.13 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 143.3, 128.4, 128.2, 125.1, 82.3, 46.8, 46.3, 39.2, 26.0, 24.5, 24.82, 24.79; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 220 nm, flow rate: 0.7 mL/min), t_1 = 18.5 min, t_2 = 20.1 min (maj.).

Control reactions

Under a nitrogen atmosphere, a mixture of CuI (1.9 mg, 0.01 mmol), (*R,S*)-JosiPhos (9.6 mg, 0.015 mmol), and K_3PO_4 (4.2 mg, 0.02 mmol) in *t*-AmOH (1 mL) was stirred at ambient temperature for 30 min, followed by the addition of B_2pin_2 (**2**) (51 mg, 0.2 mmol) in *t*-AmOH (0.5 mL). After the mixture was stirred at ambient temperature for 10 min, (*E*)-1-(1*H*-indol-1-yl)-3-phenylprop- 2-en-1-one (**1a**)

(49 mg, 0.2 mmol) and (*E*)-3-phenyl-1-(1H-pyrrol-1-yl)prop-2-en-1-one (**4a**) (39 mg, 0.2 mmol) in *t*-AmOH (0.5 mL) was added. The resultant mixture was stirred at ambient temperature for 20 h, filtered through a short pad of celite, and rinsed with 20 mL EtOAc. All the volatiles were removed under reduced pressure, the yield of (*S*)-**3a** and (*S*)-**5a** was determined by ^{1}H NMR analysis using CH_2Br_2 (0.2 mmol) as the internal standard.

Pyrrolidine (7.1 mg, 0.1 mmol) was added to a stirred solution of (*S*)-**3a** (38 mg, 0.1 mmol) and (*S*)-**5a** (32.5 mg, 0.1 mmol) in dry THF (2 mL), and the resultant mixture was then stirred at 60 ^{o}C for 12 h. After cooled to ambient temperature, all the volatiles were removed under reduced pressure. The conversion of (*S*)-**3a** and (*S*)-**5a** was determined by ^{1}H NMR analysis using CH_2Br_2 (0.2 mmol) as the internal standard.

(S)-1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one ***(10)***.[23] 53 mg, 79% yield; 90% ee, $[\alpha]^{20}_D$ = +2.8 (*c* 0.5 $CHCl_3$); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.97 (m, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.36-7.29 (m, 4 H), 7.21-7.17 (m, 1H), 3.59 (dd, *J* = 18.3, 10.9 Hz, 1 H), 3.44 (dd, *J* = 18.3, 5.0 Hz, 1 H), 2.84 (dd, *J* = 10.9, 5.0 Hz, 1 H), 1.28 and 1.20 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 142.0, 136.8, 133.0, 128.6, 128.5, 128.4, 128.1, 125.6, 83.4, 43.3, 24.63, 24.59; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 254 nm, flow rate: 0.7 mL/min), t_1 = 15.3 min (maj.), t_2 = 26.4 min.

(S)-benzyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***(11)***.[24] 57 mg, 78% yield; 84% ee, $[\alpha]^{20}_D$ = +17.0 (*c* 1.0 $CHCl_3$); colorless liquid; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.37-7.21 (m, 10 H), 7.18-7.13 (m, 1 H), 5.16-5.06 (m, 2 H), 2.96 (dd, *J* = 15.3, 8.8 Hz, 1 H), 2.81-2.71 (m, 2 H), 1.20 and 1.15 (s each, 6:6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 141.4, 136.2, 128.60, 128.57, 128.3, 128.20, 128.16, 125.8, 83.7, 66.2, 37.4, 24.7, 24.6; HPLC (two AD-H series, elute: Hexanes/*i*-PrOH = 99/1, detector: 220 nm, flow rate: 0.7 mL/min), t_1 = 34.1 min (maj.), t_2 = 36.9 min.

ASSOCIATED CONTENT

Supporting Information Available

NMR spectra of the substrates and products, and HPLC analysis for racemic and chiral products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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