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Synthesis of planar chiral imidazo[1,5-*a*]pyridinium salts based on [2.2]paracyclophane for asymmetric β-borylation of enones

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ABSTRACT

Novel planar chiral *pseudo-geminal* and *pseudo-ortho*-oxazoline substituted [2.2]paracyclophanyl imidazo[1,5-*a*]pyridinium triflates were synthesized. During the synthesis of a *pseudo-ortho* imidazo[1,5-*a*]pyridinium triflate based on [2.2]paracyclophane, the diastereoisomers of 4-amino-12-oxazolinyl[2.2]paracyclophane were separated. The imidazo[1,5-*a*]pyridinium triflates were used as carbene precursors in Cu-catalyzed enantioselective conjugate β-borylation of enones. In preliminary tests of a series of ligands and substrates, we obtained up to 84% enantioselectivity.

1. Introduction

Since the first isolation of free N-heterocyclic carbenes (NHCs) by Arduengo in 1991,[1] they have been widely applied in organometallic catalysis[2] and organocatalysis.[3] Since most of the NHC complexes of the late transition metals are kinetically robust,[4] the σ-donor capacity and the molecular shape of their ligands are readily modified by varying the substituents at the *N*-atoms or on the cyclic backbone. Initial successful results in using chiral NHC ligands in organometallic catalysis were reported a decade ago.[5] Since then, chemists have designed and synthesized many chiral carbene ligands and applied them in asymmetric catalysis.[6]

Planar chiral molecules, such as ferrocene derivatives[7] and substituted [2.2]paracyclophanes[8] play an important role in asymmetric catalysis. Planar chiral substituted [2.2]paracyclophanes were first reported used as ligands in asymmetric catalysis in 1997.[9] Since then, many types of asymmetric substituted [2.2]paracyclophanes have been synthesized and applied in several asymmetric transformations such as chiral ligands.[8] In most of these ligands, the chelating groups contain *N*, *O*,[8a,d,10] *N*, *P*, or biphosphine.[9,11] Planar chiral carbene ligands derived from [2.2]paracyclophane have been rarely reported[6b,12] and oxazoline substituted planar chiral imidazo[1,5-*a*]pyridinium salts have not been synthesized to date.

Herein, we report the synthesis of *pseudo-geminal* and *pseudo-ortho* oxazoline substituted [2.2]paracyclophanyl imidazo[1,5-*a*]pyridinium triflates **1**–**2** (Fig. 1) from 4-bromo-13-oxazolinyl[2.2]paracyclophane and 4-bromo-12-oxazolinyl[2.2]paracyclophane. Then we preliminarily tested their application in the enantioselective β-borylation of enones, which is a useful method in enantioselective synthesis.[13] In recent years, several publications have focused on this transformation, but most of them used josiphos-type ligands.[14] The NHC complexes used in this work have rarely been reported.[15] Herein, we report using **1**–**2** and **14** to prepare Cu(NHC) complexes in situ[16] and the application of them in the catalytic β-borylation of enones.

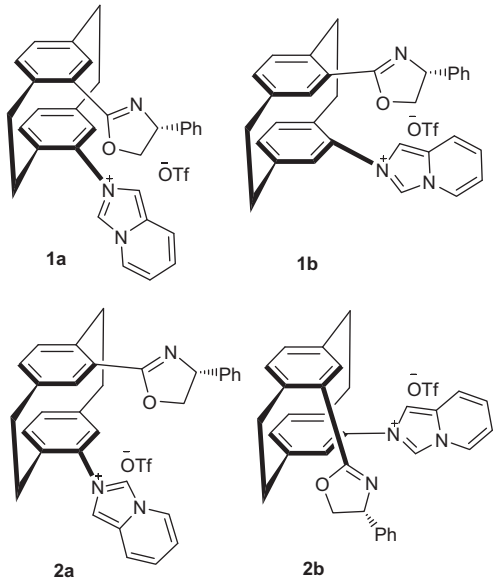

Figure 1. Regio- and diastereoisomers of *pseudo-geminal* and *pseudo-ortho*-oxazolinyl[2.2]paracyclophanyl pyridinium salts.

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2. Results and discussion

Based on the directing effects of substituted [2.2]paracyclophane, we were able to synthesize both diastereoisomers of *pseudo-geminal* and *pseudo-ortho* oxazoline substituted [2.2]paracyclophanyl imidazo[1,5-*a*]pyridinium triflates **1**–**2**. The phenyl group was chosen as the substituent on the oxazoline ring because (*R*)-phenylglycinol is inexpensive and the size of the phenyl group is large enough for resolution, but not so bulky as to inhibit reaction.

2.1. Synthesis of *pseudo-geminal* diastereoisomers

Following the literature,[8e,17] we synthesized a mixture of diasteroisomers of 4-bromo-13-oxazolinyl[2.2]paracyclophane **3a** and **3b**, which could be easily separated by column chromatography on silica gel. Compounds **3a** and **3b** were converted into **4a** and **4b** by treatment with *n*-BuLi in THF at −78 °C followed by trapping with CO_2 and acidifying with HCl. Then by using a modified Curtius process with DPPA (diphenylphosphoryl azide), we obtained the 4-amino-13-oxazolinyl[2.2]paracyclophane **5a** and **5b**.[18]

The reaction of **5a** and **5b** with 2-pyridine aldehyde in refluxing toluene resulted in the formation of imines in good yield as yellow oils. Since they were not stable, we used them directly for the formation of imidazoles **1a** and **1b** according to the method of Glorius using AgOTf and chloromethyl pivalate[12b,19] (Scheme 1).

2.2. Synthesis of *pseudo-ortho* diastereoisomers

We started the synthesis of **2a** and **2b** from 4-bromo-12-oxazolinyl[2.2]paracyclophane **7a** and **7b**, which can be prepared from racemic 4,12-dibromo[2.2]paracyclophane **6** according to the literature.[8e,12a] Compounds **7a** and **7b** were inseparable at this step. Next, 4-bromo-12-oxazolinyl[2.2]paracyclophane was reacted with benzhydrylideneamine under Pd-catalyzed amination,[20] which afforded the corresponding imines **8a** and **8b**. Fortunately, we could separate **8a** and **8b** by column chromatography on silica gel. Compound **8a** was obtained as a yellow solid, however, **8b** was a yellow oil and not stable enough for further purification. The substituted [2.2]paracyclophane imines **8a** and **8b** were easily converted into their amino analogues **9a** and **9b** by acid hydrolysis with aqueous HCl. Using the same procedure as for the *pseudo-geminal* diastereoisomers, we obtained the target products **2a** and **2b** (Scheme 2).

The absolute configurations of **1a** and **2a** were determined by comparing the specific rotation of **10** and **11** with the reported literature values.[21] Compounds **10** and **11** were obtained by hydrolysis of **5a** and **9a** (Scheme 3).

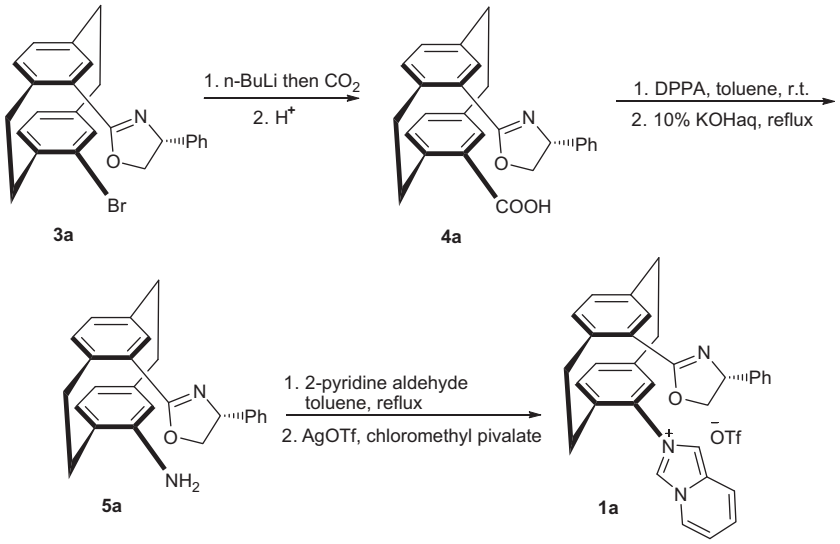
2.3. Catalytic asymmetric reaction

With these imidazo[1,5-*a*]pyridinium triflates in hand, we briefly examined their application in the asymmetric β-borylation of enones. The combination of the planar chirality of [2.2]paracyclophane with the central chirality of oxazoline gives rise to interesting interactions between the two chiral elements (Table 1).

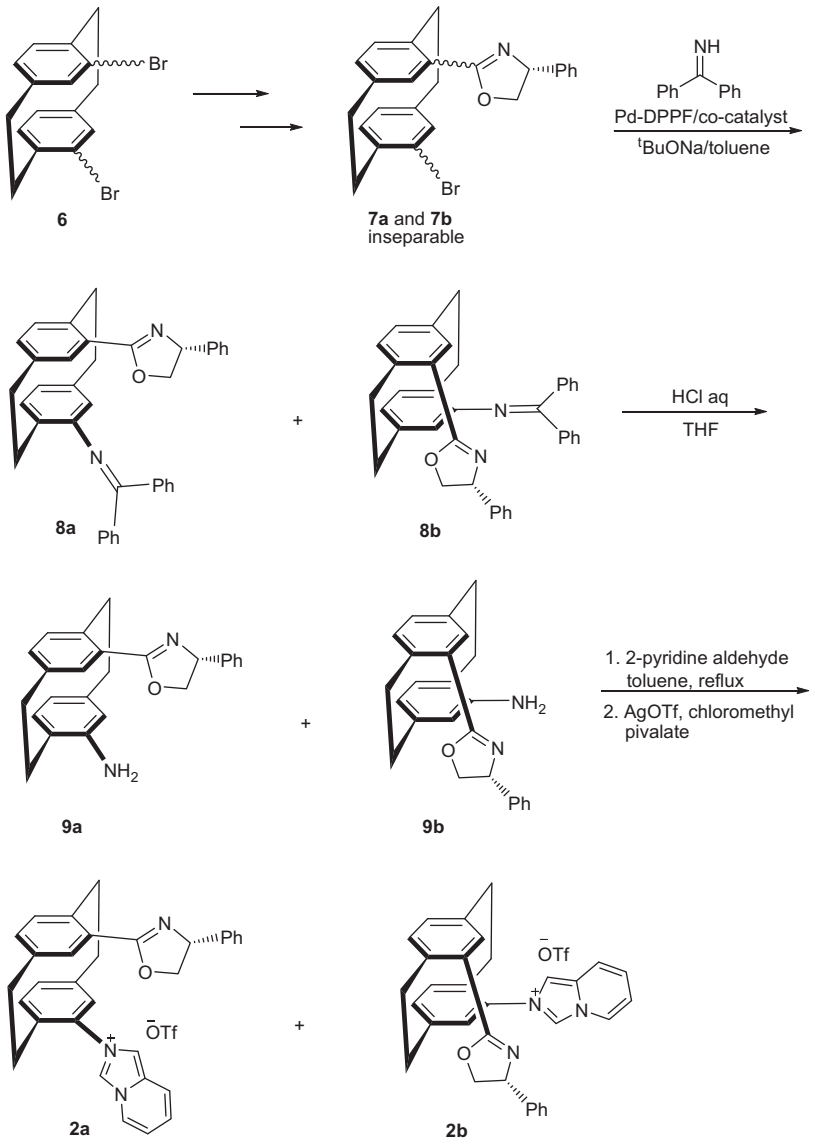
The Cu(NHC) complexes were prepared in situ by incubating a mixture of Cu_2O, KI, and imidazo[1,5-*a*]pyridinium triflate in solvent at 60 °C under an Ar atmosphere.[16] Next, Cs_2CO_3, bis(pinacolato)diboron, chalcone, and MeOH were added consecutively. In the presence of catalytic imidazo[1,5-*a*]pyridinium triflate (5 mol %), the reaction proceeded smoothly to afford the addition products.

When we tested the effects of different imidazo[1,5-*a*]pyridinium triflates in the β-borylation of chalcone, the best result was obtained by using *pseudo-ortho* ligand **2a** (entry 3), in which the planar chirality and central chirality have a cooperative effect. However, the lowest ee was given by its diastereoisomer **2b** with a mismatched pair of chiralites (entry 4). Since the substituted functional groups were the same in these four imidazo[1,5-*a*]pyridinium triflates, the different results show that the substituted positions on the [2.2]paracyclophane scaffold play an important role in the asymmetric catalysis. We ascribe the poor ee obtained from the *pseudo-geminal* ligands to their structures, in which the coordinating atoms point in opposite directions and cannot chelate the metal well (Fig. 2). Among the solvents tested, THF gave the best yields and enantiomeric excess. Although the reaction rates were much faster in isopropanol and *t*-butanol, the enantioselectivity was not good.

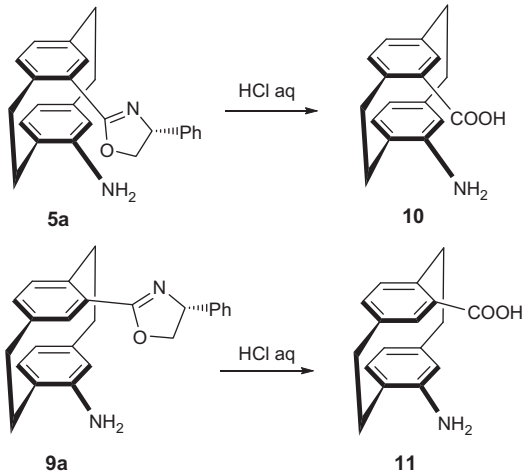
In an attempt to improve the catalytic enantioselectivity, we modified ligand **2a** by synthesis of the *tert*-butyl analogue **14** from (S,S_p)-4-bromo-12-(4-*t*-butyloxazolin-2-yl)[2.2]paracyclophane (Scheme 4).[12,20] By using imidazo[1,5-*a*]pyridinium triflate **14**, the enantioselectivity when using chalcone as substance was



Scheme 1. Synthesis of *pseudo-geminal* diastereoisomers.



Scheme 2. Synthesis of *pseudo-ortho* diastereoisomers.



Scheme 3. Synthesis of enantiopure *pseudo-geminal* and *pseudo-ortho* amino acids based on [2.2]paracyclophane.

enhanced from 64% to 76% ee. Finally, several other enones were tested in order to evaluate the effect of different substrates. The best result was obtained when using *p*-chlorochalcone.

3. Conclusion

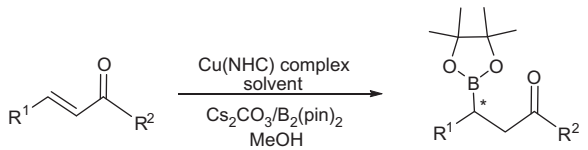
In conclusion, a series of planar chiral bidentate NHC precursors based on [2.2]paracyclophane were designed and synthesized. They were successfully applied to a copper-catalyzed asymmetric β-borylation, which was convenient and effective, revealing moderate to good enantioselectivity for this reaction.

4. Experimental section

4.1. General methods

Enones were prepared by the standard method reported in the literature.[22] The commercially available reagents were used as received without further purification. The solvents were purified by standard methods. Reactions were magnetically stirred under an Ar atmosphere and monitored by thin layer chromatography

Table 1
Asymmetric β-borylation of chalcones by Cu(NHC) complexes[a]



15a-g

	L	R^1	R^2	Solvent	Product	Yield[b] (%)	ee (%) (Config.)[c]
1	**1a**	Ph	Ph	THF	**15a**	88	16 (*R*)
2	**1b**	Ph	Ph	THF	**15a**	93	6 (*R*)
3	**2a**	Ph	Ph	THF	**15a**	97	64 (*R*)
4	**2b**	Ph	Ph	THF	**15a**	87	4 (*S*)
5	**2a**	Ph	Ph	1,4-dioxane	**15a**	91	42 (*R*)
6	**2a**	Ph	Ph	DME	**15a**	44	46 (*R*)
7[d]	**2a**	Ph	Ph	Isopropanol	**15a**	96	60 (*R*)
8[d]	**2a**	Ph	Ph	*t*-BuOH	**15a**	78	46 (*R*)
9	**14**	Ph	Ph	THF	**15a**	93	76 (*S*)
9	**14**	*p*-ClC_6H_4	Ph	THF	**15b**	90	84 (–)
10	**14**	*p*-$MeOC_6H_4$	Ph	THF	**15c**	87	80 (–)
11	**14**	*p*-MeC_6H_4	Ph	THF	**15d**	96	78 (+)
12	**14**	1-Naph	Ph	THF	**15e**	73	78 (–)
13	**14**	Me	Ph	THF	**15f**	92	72 (*R*)
14	**14**	Ph	Me	THF	**15g**	91	62 (*S*)

[a] The complex was formed in solvent with **L** (5 mol %), Cu_2O (2.3 mol %), and KI (6 mol %) at 60 °C. The reaction was carried out at room temperature using Cs_2CO_3 (5 mol %), 40 mg chalcone, 54 mg $B_2(pin)_2$ (1.1 equiv) and MeOH (2 equiv) after preparing the Cu complex.
[b] Isolated yield.
[c] Enantiomeric excesses were determined by chiral HPLC analysis (Chiralpak IA column). The absolute configuration of **15** was determined by comparison of the specific rotation with the literature value.[14c]
[d] Without adding MeOH.

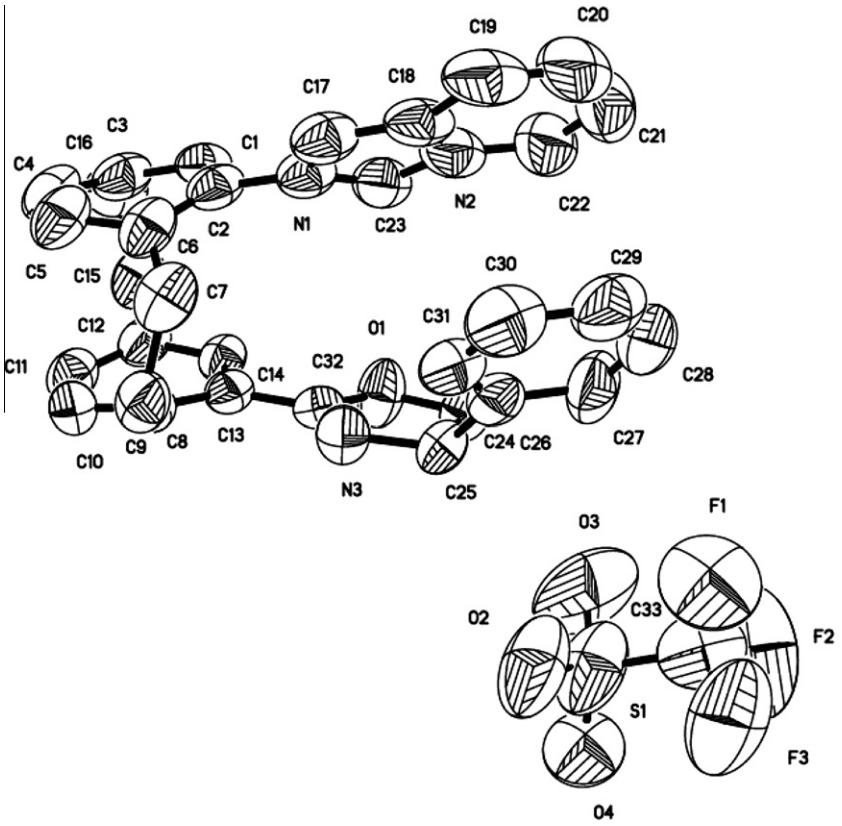
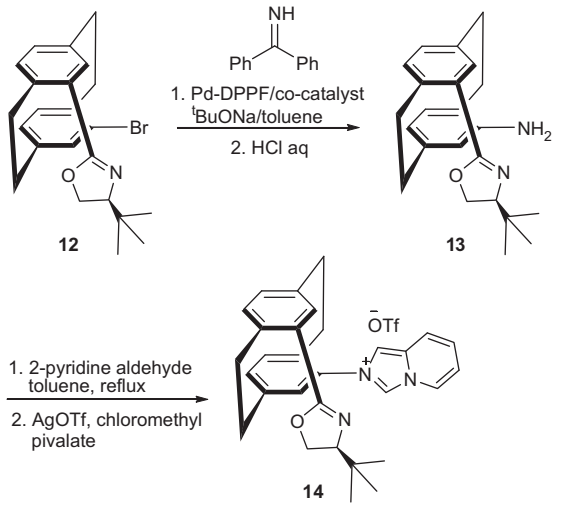


Figure 2. ORTEP diagram of the molecular structure of **1b**. Ellipsoids are drawn at the 50% probability level. The solvent molecules have been omitted. Hydrogen atoms have been removed for clarity.



Scheme 4. Synthesis of (S,S_p)-3-{12-(4-*t*-butyloxazolin-2-yl)[2.2]paracyclophane-4-yl}imidazo[1,5-*a*]pyridinium triflate.

(TLC). Purification of reaction products was carried out by column chromatography on silica gel. Melting points were recorded on a melting point apparatus and are uncorrected. Optical rotations were measured on a polarimeter and are reported in degrees (*c* g/100 mL, solvent). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-300 at 298 K. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to the internal standard for ^{1}H NMR and ^{13}C NMR spectra. HRMS spectra were recorded on an Agilent 100 ABI-API4000 spectrometer. Enantiomeric excess was determined using HPLC on a Chiralpak IA chiral column.

4.2. Synthesis of *pseudo-geminal* and *pseudo-ortho* ligands

4.2.1. (*R*,4*R*$_p$,13*S*$_p$)-4-Carboxy-13-(4-phenyloxazolin-2-yl)[2.2]paracyclophane 4a

At first, (*R*,4*S*$_p$,13*R*$_p$)-4-bromo-13-(4-phenyloxazolin-2-yl)[2.2]paracyclophane **3a** (5.00 g, 11.56 mmol) was placed in a Schlenk flask under an argon atmosphere and dissolved in anhydrous THF (80 mL). After cooling to −78 °C, a solution of *n*-BuLi in pentane (9.40 mL, 15.04 mmol) was added slowly. The solution was stirred at −78 °C for another 1 h and was bubbled with CO_2 for 30 min. The solution was allowed to warm to room temperature while continuing the bubbling of CO_2, then acidified with 2 M HCl to pH 5–6, and extracted with dichloromethane (3 × 100 mL). The organic phase was dried with Na_2SO_4 and concentrated to give crude product, which was purified with column chromatography on silica gel (EtAc/petroleum = 2:8 to 5:5) yielding 3.73 g (81.1%) of **4a** as a white solid. Mp 182–184 °C; $[\alpha]_D^{20} = -22.8$ (*c* 0.3, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 3.05–3.21 (m, 6H), 3.95–4.01 (m, 1H), 4.30–4.40 (m, 1H), 4.44–4.54 (m, 1H), 4.64 (dd, *J* = 10.2, 8.4 Hz, 1H), 5.34 (t, *J* = 9.6 Hz, 1H), 6.66–6.77 (m, 4H), 7.11–7.14 (m, 3H), 7.16–7.26 (m, 3H), 7.35–7.38 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 34.5, 34.7, 34.8, 34.9, 70.8, 73.6, 126.8, 127.3, 128.2, 128.5, 128.8, 133.2, 134.8, 135.0, 135.7, 136.4, 137.5, 139.2, 139.7, 141.7, 142.4, 144.1, 163.9, 172.9; HRMS(ESI): calcd for $C_{26}H_{24}NO_3$ (M+H)$^+$ 398.1756, found 398.1760.

4.2.2. (*R*,4*R*$_p$,13*S*$_p$)-4-Amino-13-(4-phenyloxazolin-2-yl)[2.2]paracyclophane 5a

At first, (*R*,4*S*$_p$,13*R*$_p$)-4-carboxy-13-(4-phenyloxazolin-2-yl)[2.2]paracyclophane **4a** (2.10 g, 5.29 mmol) was dissolved in toluene (120 mL) at room temperature. Then NEt_3 (1.53 mL, 10.58 mmol) and DPPA (1.41 mL, 10.58 mmol) were added. The solution was stirred at room temperature for 30 min and then refluxed for 2 h. Next, KOH aq (10%, 50 mL) was added and the mixture was refluxed for another 3 h. Finally, the solution was cooled to room temperature, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The organic phase was combined and concentrated. The crude product was purified by column chromatography on silica gel (hexane/EtAc = 1:2), giving 1.61 g (83%) of **5a** as a white solid. Mp 187–188 °C; $[\alpha]_D^{20} = +41.0$ (*c* 0.3, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 2.69–2.80 (m, 1H), 2.88–2.95 (m, 2H), 2.97–3.24 (m, 4H), 3.50 (br s, 2H), 4.22 (t, *J* = 8.4 Hz, 1H), 4.31–4.41 (m, 1H), 4.74 (dd, *J* = 10.2, 8.4 Hz, 1H), 5.29–5.40 (m, 1H), 5.51 (d, *J* = 1.8 Hz, 1H), 6.18 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 6.64 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.23–7.26 (m, 1H), 7.27–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 31.2, 32.2, 34.7, 34.8, 70.6, 74.0, 121.3, 122.5, 124.4, 125.0, 126.9, 127.6, 128.8, 132.4, 134.6, 134.9, 136.0, 138.5, 140.5, 140.6, 142.4, 146.3, 166.1; HRMS(ESI): calcd for $C_{25}H_{25}N_2O$ (M+H)$^+$ 369.1967, found 369.1963.

4.2.3. (*R*,4*R*$_p$,13*S*$_p$)-3-{13-(4-Phenyloxazolin-2-yl)[2.2]paracyclophane-4-yl}imidazo[1,5-*a*]pyridinium triflate 1a

At first, (*R*,4*R*$_p$,13*S*$_p$)-4-amino-13-(4-phenyloxazolin-2-yl)[2.2]paracyclophane **5a** (0.50 g, 1.36 mmol) was dissolved in toluene, then 2-pyridine aldehyde (0.130 mL, 1.36 mmol) was added. The solution was stirred and refluxed overnight. After cooling to room temperature, the solution was subjected to column chromatography on silica gel (CH_2Cl_2/EtAc/NEt_3 = 10:1:0.01) and the corresponding imine was obtained as a yellow oil, which was not stable enough for further purification and so was used to prepare **1a** directly. To a suspension of AgOTf (0.56 g, 2.18 mmol) in CH_2Cl_2 (3.0 mL) was added chloromethyl pivalate (0.32 mL, 2.18 mmol) and the resulting suspension was sealed and stirred for 30 min in the dark. Then the above imine in CH_2Cl_2 (2.0 mL) was added and the solution was stirred in a sealed tube in the dark at 40 °C for 12 h. After the solution was cooled to room temperature, EtOH (2.0 mL) was added and filtered. The solvent was removed from the filtrate in vacuo and **1a** was obtained as a white solid by chromatographing the crude product on a silica gel column (CH_2Cl_2/MeOH = 30:1) (yield: 0.59 g, 70.0%). Mp 107–108 °C; $[\alpha]_D^{20} = +43.9$ (*c* 0.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 2.82–2.93 (m, 1H), 2.97–3.03 (m, 1H), 3.22–3.40 (m, 4H), 3.47–3.56 (m, 1H), 3.83 (t, *J* = 8.7 Hz, 1H), 4.05–4.13 (m, 1H), 4.34 (t, *J* = 9.6 Hz, 1H), 4.61–4.68 (m, 1H), 6.71–6.89 (m, 4H), 6.95–6.98 (m, 2H), 7.05–7.13 (m, 2H), 7.18–7.29 (m, 4H), 7.50–7.53 (m, 2H), 7.68 (s, 1H), 8.96 (s, 1H), 10.32 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 30.1, 34.5, 34.7, 36.6, 70.5, 73.5, 113.4, 117.8, 118.2, 120.8 (q, *J* = 318 Hz), 124.5, 125.3, 125.4, 125.5, 125.6, 126.2, 127.6, 128.7, 129.6, 132.6, 133.5, 134.5, 135.2, 136.1, 136.3, 137.4, 140.5, 140.6, 142.05, 143.3, 163.8; HRMS(ESI): calcd for $C_{32}H_{28}N_3O$ (M−OTf)$^+$ 470.2232, found 470.2435.

4.2.4. (*R*,4*S*$_p$,13*R*$_p$)-3-{13-(4-Phenyloxazolin-2-yl)[2.2]paracyclophane-4-yl}imidazo[1,5-*a*]pyridinium triflate 1b

Compound **1b** was obtained by the same procedure as for **1a** as white crystals (76.1%). Mp 198–200 °C; $[\alpha]_D^{20} = +16.7$ (*c* 0.3, CH_2Cl_2); ^{1}H NMR (300 MHz, DMSO, rt) δ 2.95–3.29 (m, 5H), 3.37–3.48 (m, 2H), 3.71 (dd, *J* = 9.9, 8.4 Hz, 1H), 4.17–4.25 (m, 1H), 4.61 (dd, *J* = 10.5, 8.4 Hz, 1H), 5.14 (t, *J* = 10.2 Hz, 1H), 6.73–6.77 (m, 2H), 6.88–6.70 (m, 3H), 7.04–7.14 (m, 7H), 7.36 (d, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 8.40–8.43 (m, 2H), 9.97 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (75 MHz, DMSO, rt) δ 30.4, 34.5, 34.6, 36.6, 69.4, 72.9, 113.7, 118.4, 118.9, 120.8 (q, *J* = 318 Hz), 124.2, 125.5,

125.7, 126.0, 126.7, 127.2, 128.9, 130.0, 132.7, 133.3, 135.0, 135.8, 136.4, 137.1, 137.7, 140.2, 141.4, 142.4, 142.7, 162.6; HRMS(ESI): calcd for $C_{32}H_{28}N_3O$ $(M-OTf)^+$ 470.2232, found 470.2415.

4.2.5. (R,R_p)-4-Benzhydrylideneamino-12-(4-phenyl oxazolin-2-yl)[2.2]paracyclophane 8a

In a glovebox, a diastereomeric mixture of 4-bromo-12-(4-phenyloxazolin-2-yl)[2.2]paracyclophane (1.05 g, 2.43 mmol), 4,12-bis(benzhydry lideneamino)[2.2]paracyclophane (30.8 mg, 0.073 mmol), Pd–DPPF (59.5 mg, 0.073 mmol), benzhydrylideneamine (0.66 g, 3.64 mmol), and sodium *tert*-butoxide (0.35 g, 3.64 mmol) were placed in an oven-dried Schlenk flask, then toluene (2.0 mL) was added. The mixture was stirred at 110 °C under Ar for 12 h. Then the mixture was allowed to cool to room temperature and water (10 mL) was added. The solution was extracted with CH_2Cl_2 (3×10 mL). The organic phase was combined and distilled in vacuo. A yellow oil was obtained and subjected to column chromatography on silica gel (CH_2Cl_2/NEt_3 = 99.8:0.2). Compound **8a** was separated from the diastereomeric mixture as a yellow semisolid and could be further purified by recrystallization from EtOH to afford a yellow solid (0.61 g, 47%). Mp 187–188 °C; $[\alpha]_D^{20} = +188.7$ (c 0.3, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 2.55–2.63 (m, 1H), 2.74–2.84 (m, 3H), 3.05–3.13 (m, 1H), 3.37–3.48 (m, 2H), 4.11 (t, J = 8.4 Hz, 1H), 4.18–4.22 (m, 1H), 4.64–4.70 (m, 1H), 5.33–5.40 (m, 2H), 6.27–6.30 (m, 1H), 6.68 (d, J = 7.8 Hz, 1H), 6.61 (s, 2H), 6.92–6.96 (m, 2H), 7.11–7.20 (m, 3H), 7.25–7.34 (m, 5H), 7.40–7.47 (m, 3H), 7.89 (dd, J = 8.4, 1.8 Hz, 2H), 8.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 32.9, 33.2, 33.8, 35.2, 70.8, 73.4, 124.4, 126.8, 127.2, 127.4, 127.7, 128.0, 128.1, 128.3, 128.7, 129.4, 129.5, 130.2, 131.2, 134.0, 135.1, 135.7, 136.8, 140.1, 140.4, 140.6, 140.7, 143.0, 148.5, 164.6, 164.7; HRMS(ESI): calcd for $C_{38}H_{33}N_2O$ $(M+H)^+$ 533.2593, found 533.2583.

4.2.6. (R,R_p)-4-Amino-12-(4-phenyloxazolin-2-yl)[2.2]paracyclophane 9a

To a solution of (R,R_p)-4-benzhydry lideneamino-12-(4-phenyloxazolin-2-yl)[2.2]paracyclophane **8a** (0.50 g, 0.94 mmol) in THF (5 mL) was added 2 M HCl aq (1.41 mL, 2.82 mmol). The solution was stirred at room temperature for 2 h. After the yellow color had faded, 1 M NaOH aq was added dropwise into the solution until the pH reached 9, and the product was extracted with CH_2Cl_2 (3×5 mL). The organic phase was combined and dried with $MgSO_4$, then concentrated in vacuo, and subjected to column chromatography on silica gel to give **9a** (0.34 g, 98.1%) as a white solid. Mp 176–177 °C; $[\alpha]_D^{20} = +34.9$ (c 0.3, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 2.62–2.70 (m, 1H), 2.75–3.01 (m, 3H), 3.05–3.21 (m, 3H), 3.89 (br s, 2H), 3.98–4.07 (m, 1H), 4.32 (t, J = 7.8 Hz, 1H), 4.77–4.83 (m, 1H), 5.45 (dd, J = 10.5, 7.5 Hz, 1H), 5.61 (d, J = 1.5 Hz, 1H), 6.16–6.19 (m, 1H), 6.32 (d, J = 7.8 Hz, 1H), 6.51–6.54 (m, 1H), 6.66 (d, J = 7.8 Hz, 1H), 7.29–7.44 (m, 5H), 7.82 (d, J = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 32.1, 32.3, 34.4, 35.1, 70.1, 74.2, 120.4, 122.6, 124.3, 126.7, 127.6, 127.7, 128.6, 128.8, 135.1, 135.8, 139.0, 140.3, 141.4, 142.9, 145.6, 165.6; HRMS(ESI): calcd for $C_{25}H_{25}N_2O$ $(M+H)^+$ 369.1967, found 369.1961.

4.2.7. (R,R_p)-3-{12-(4-Phenyloxazolin-2-yl)[2.2]paracyclo phane-4-yl}imidazo[1,5-a]pyridinium triflate 2a

Compound **2a** was prepared by the same procedure as for **1a** from (R,R_p)-4-amino-12-(4-phenyloxazolin-2-yl)[2.2]paracyclophane **9a** as a white solid (74.5%). Mp 215–216 °C; $[\alpha]_D^{20} = +187.5$ (c 0.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 2.39–2.44 (m, 1H), 2.83–3.08 (m, 4H), 3.22–3.40 (m, 2H), 3.93–4.00 (m, 1H), 4.41 (t, J = 7.8 Hz, 1H), 5.00 (t, J = 9.6 Hz, 1H), 5.81 (dd, J = 9.9, 7.8 Hz, 1H), 6.79 (m, 4H), 6.95–7.00 (m, 2H), 7.04–7.11 (m, 1H), 7.16 (s, 1H), 7.34–7.50 (m, 6H), 8.34 (d, J = 7.2 Hz, 1H), 8.81 (s, 1H), 10.78 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 32.3, 33.6, 34.2, 35.3, 68.7, 75.5, 113.6, 117.9, 118.2, 120.8 (q, J = 318 Hz), 124.6, 124.9, 126.3, 126.8, 127.2, 127.9, 128.2, 129.0, 130.2, 130.5, 132.8, 134.0, 135.4, 135.6, 136.0, 137.4, 139.4, 140.7, 142.4, 142.7, 166.7; HRMS(ESI): calcd for $C_{32}H_{28}N_3O$ $(M-OTf)^+$ 470.2232, found 470.2227.

4.2.8. (R,S_p)-4-Amino-12-(4-phenyloxazolin-2-yl)[2.2]paracyclophane 9b

Compound **9b** was synthesized by the same method as for **9a** from 4-bromo-12-(4-phenyloxazolin-2-yl)[2.2]paracyclophane (1.05 g, 2.43 mmol) as a white solid (0.40 g, 44.8%). Mp 122–123 °C; $[\alpha]_D^{20} = +64.0$ (c 0.3, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 2.66–2.72 (m, 1H), 2.75–3.05 (m, 3H), 3.09–3.23 (m, 3H), 3.92–4.01 (m, 1H), 4.22–4.35 (m, 3H), 4.85 (dd, J = 10.2, 8.4 Hz, 1H), 5.45 (dd, J = 10.2, 8.7 Hz, 1H), 5.63 (s, 1H), 6.17–6.20 (m, 1H), 6.33 (d, J = 7.8 Hz, 1H), 6.53–6.56 (m, 1H), 6.66 (d, J = 7.8 Hz, 1H), 7.29–7.44 (m, 5H), 7.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 32.1, 32.3, 34.5, 35.2, 70.2, 74.5, 120.3, 122.6, 124.3, 126.8, 127.6, 127.7, 128.6, 128.9, 135.0, 135.1, 135.8, 139.1, 140.2, 141.4, 142.5, 145.5, 166.0; HRMS(ESI): calcd for $C_{25}H_{25}N_2O$ $(M+H)^+$ 369.1967, found 369.1962.

4.2.9. (R,S_p)-3-{12-(4-Phenyloxazolin-2-yl)[2.2]paracyclo phane-4-yl}imidazo[1,5-a]pyridinium triflate 2b

Compound **2b** was prepared by the same procedure as **1a** from (R,S_p)-4-amino-12-(4-phenyloxazolin-2-yl)[2.2]paracyclophane **9b** as a white solid (76.3%). Mp 202–203 °C; $[\alpha]_D^{20} = -122.4$ (c 0.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 2.43–2.53 (m, 1H), 2.86–2.96 (m, 1H), 2.99–3.12 (m, 3H), 3.33–3.44 (m, 2H), 4.09–4.17 (m, 1H), 4.58 (t, J = 9.0 Hz, 1H), 4.97 (dd, J = 9.9, 9.0 Hz, 1H), 5.49 (t, J = 9.6 Hz, 1H), 6.64 (s, 1H), 6.81–6.84 (m, 4H), 7.02–7.06 (m, 1H), 7.12–7.17 (m, 1H), 7.23 (s, 1H), 7.31–7.36 (m, 1H), 7.38–7.41 (m, 1H), 7.42–7.48 (m, 2H), 7.54–7.57 (m, 2H), 8.57 (d, J = 6.6 Hz, 1H), 9.00 (s, 1H), 10.28 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 32.1, 33.7, 34.3, 35.6, 69.8, 74.8, 113.9, 118.3, 120.8 (q, J = 318 Hz), 124.5, 125.1, 126.1, 126.2, 127.0, 127.7, 128.4, 129.3, 130.5, 130.9, 133.2, 133.7, 135.6, 135.8, 136.3, 137.9, 139.6, 140.8, 141.7, 142.4, 166.0; HRMS(ESI): calcd for $C_{32}H_{28}N_3O$ $(M-OTf)^+$ 470.2232, found 470.2239.

4.2.10. ($4R_p$,$13S_p$)-4-Amino-13-carboxy[2.2]paracyclo phane 10

At first, (R,$4R_p$,$13S_p$)-4-amino-13-(4-phenyloxazolin-2-yl)[2.2]paracyclophane **5a** (0.60 g, 1.63 mmol) was placed in a flask, then 6 M HCl aq (30.0 mL) was added and the solution was refluxed for 24 h. After cooling to room temperature, 6 M NaOH aq was added dropwise into the solution until pH 5–6. The white solid precipitated from the water and was extracted with CH_2Cl_2 (3×30 mL). The organic phase was combined, concentrated, and then subjected to column chromatography on silica gel to afford compound **10** 0.36 g (82.7%) as a white solid. Mp >224 °C (dec); $[\alpha]_D^{20} = +84.0$ (c 0.1, CH_3OH); ^{1}H NMR (300 MHz, DMSO, rt) δ 2.46–2.56 (m, 1H), 2.69–3.00 (m, 5H), 3.19–3.26 (m, 1H), 4.27 (ddd, J = 13.2, 9.6, 6.0 Hz, 1H), 5.25 (d, J = 1.5 Hz, 1H), 5.97 (dd, J = 7.5, 1.5 Hz, 1H), 6.25 (d, 7.8 Hz, 1H), 6.34 (d, J = 7.8 Hz, 1H), 6.64 (dd, J = 7.5, 1.8 Hz, 1H), 7.11 (d, J = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO, rt) δ 30.7, 32.1, 34.7, 120.4, 120.5, 123.7, 128.4, 133.5, 134.6, 134.8, 136.2, 138.1, 139.9, 142.3, 147.9, 169.5; HRMS(ESI): calcd for $C_{17}H_{18}NO_2$ $(M+H)^+$ 268.1338, found 268.1336.

4.2.11. (R_p)-4-Amino-12-carboxy[2.2]paracyclophane 11

Compound **11** was prepared by the same procedure as for **10** as a white solid (86.7%). Mp >212 °C (dec); $[\alpha]_D^{20} = -31.3$ (c 0.2, CH_3OH); ^{1}H NMR (300 MHz, DMSO, rt) δ 2.41–2.49 (m, 1H), 2.62–2.76 (m, 2H), 2.82–2.98 (m, 2H), 3.05–3.24 (m, 2H), 3.85–3.93 (m, 1H), 5.24 (d, J = 1.5 Hz, 1H), 5.94 (dd, J = 7.5, 1.5 Hz, 1H), 6.15 (d, J = 7.5 Hz, 1H), 6.53 (dd, J = 7.8, 1.5 Hz, 1H), 6.60 (d,

J = 7.8 Hz, 1H), 7.70 (d, J = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO, rt) δ 31.9, 32.4, 34.5, 35.8, 120.1, 123.2, 129.6, 130.8, 135.2, 135.3, 137.0, 139.6, 140.8, 141.3, 147.2; HRMS(ESI): calcd for $C_{17}H_{18}NO_2$ $(M+H)^+$ 268.1338, found 268.1314.

4.2.12. (S,S_p)-4-Amino-12-(4-*t*-butyloxazolin-2-yl)[2.2] paracyclophane 13

Compound **12** was prepared by the same procedure as for **9a** from (S,S_p)-4-bromo-12-(4-*t*-butyloxazolin-2-yl)[2.2]paracyclophane as colorless crystals (83.1%). Mp = 175–176 °C; $[\alpha]_D^{20}$ = +17.5 (c 0.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 1.05 (s, 9H), 2.62–2.72 (m, 1H), 2.79–2.97 (m, 3H), 3.08–3.22 (m, 5H), 3.97–4.07 (m, 1H), 4.13 (dd, J = 10.2, 7.5 Hz, 1H), 4.26–4.31 (m, 1H), 4.36–4.43 (m, 1H), 5.52 (d, J = 1.8 Hz, 1H), 6.16 (dd, J = 7.8, 1.8 Hz, 1H), 6.31 (d, J = 7.8 Hz, 1H), 6.49 (dd, J = 7.8, 1.8 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 7.73 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 26.2, 32.1, 32.3, 34.3, 34.4, 34.6, 68.3, 76.0, 120.6, 122.7, 124.4, 127.7, 128.2, 134.9, 135.7, 138.9, 140.1, 141.4, 145.6, 164.3; HRMS(ESI): calcd for $C_{23}H_{29}N_2O$ $(M+H)^+$ 349.2280, found 349.2276.

4.2.13. (S,S_p)-3-{12-(4-*t*-Butyloxazolin-2-yl)[2.2]paracyclophane-4-yl}imidazo[1,5-*a*]pyridinium triflate 14

Compound **14** was prepared by the same procedure as for **1a** from **13** as a white solid (41.2%). Mp = 196–198 °C; $[\alpha]_D^{20}$ = −235.7 (c 0.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 1.07 (s, 9H), 2.36–2.39 (m, 1H), 2.76–2.80 (m, 1H), 2.86–2.93 (m, 1H), 2.96–3.09 (m, 2H), 3.27 (m, 1H), 3.39–3.47 (m, 1H), 3.99 (dd, J = 13.2, 9.6 Hz, 1H), 4.35–4.38 (m, 2H), 4.52 (m, 1H), 6.77–6.84 (m, 5H), 7.07–7.15 (m, 2H), 7.20–7.26 (m, 1H), 7.68 (d, J = 9.3 Hz, 1H), 8.79 (d, J = 7.2 Hz, 1H), 9.47 (s, 1H), 10.32 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 25.9, 32.5, 33.6, 34.1, 34.4, 35.5, 69.4, 75.2, 113.8, 118.0, 118.1, 120.8 (q, J = 318 Hz), 125.1, 125.2, 126.0, 127.0, 127.1, 128.5, 130.5, 133.1, 133.8, 135.2, 135.4, 136.1, 137.6, 139.4, 140.7, 142.5, 165.5; HRMS(ESI): calcd for $C_{30}H_{32}N_3O$ $(M-f)^+$ 450.2545, found 450.2543.

4.3. General experimental procedure for the enantioselective β-borylation of chalcones

The imidazo[1,5-*a*]pyridinium triflate (5.8 mg, 9.7×10^{-3} mmol), Cu_2O (0.6 mg, 4.2×10^{-3} mmol), and KI (2.4 mg, 14.4×10^{-3} mmol) were added to 1.0 mL anhydrous THF in a Schlenk flask under an atmosphere of Ar. The suspension was stirred at 60 °C overnight to give a yellow solution of the Cu complex. The solution was cooled to room temperature. Next, Cs_2CO_3 (3.5 mg, 10.7×10^{-3} mmol) and bis(pinacolato)diboron (54.1 mg, 0.21 mmol) were added consecutively. The solution was stirred for 5 min after which chalcone (40.3 mg, 0.19 mmol) and then MeOH (7.8 μl, 0.38 mmol) were added. The reaction mixture was stirred until no chalcone was detected by TLC. The solvent was removed in vacuo and the product was purified by column chromatography on silica gel. The enantiomeric excess was determined using HPLC on a Chiralpak IA chiral column, with UV detection at 254 nm.

4.3.1. (*S*)-1,3-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one 15a

Using the general procedure, compound **15a** was obtained as a colorless oil (93%) with **14** as the ligand. The ^{1}H NMR (300 MHz, $CDCl_3$, rt) results are in good agreement with those reported in the literature.[14c] The ee (76% ee) was obtained by chiral HPLC analysis of **15a** using a Chiralpak IA chiral column (*i*-PrOH/hexane = 1:10, flow 0.5 mL min^{-1}, 20 °C), t_{major} = 9.53 min; t_{minor} = 12.15 min; $[\alpha]_D^{20}$ = −69.4 (c 0.2, CH_2Cl_2); The specific rotation of the corresponding hydroxyl ketone was $[\alpha]_D^{20}$ = −74.3 (c 0.2, CH_2Cl_2). The absolute configuration was determined by comparing this value with the reported literature[14c] {$[\alpha]_D^{20}$ = −107.3(c 0.2, $CHCl_3$), 95% ee (*S*)}.

4.3.2. (−)-3-(4-Chlorophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one 15b

Compound **15b** was prepared according to the general procedure using **14** as the ligand to afford a waxy white solid (90%). The ee (84% ee) was obtained by chiral HPLC analysis of **15b** using a Chiralpak IA chiral column (*i*-PrOH/hexane = 1:10, flow 0.5 mL min^{-1}, 20 °C), t_{major} = 10.55 min; t_{minor} = 13.85 min; $[\alpha]_D^{20}$ = −62.3 (c 0.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 1.17 (s, 6H), 1.24 (s, 6H), 2.77 (dd, J = 10.2, 5.7 Hz, 1H), 3.40 (dd, J = 18.3, 5.4 Hz, 1H), 3.51 (dd, J = 18.3, 10.2 Hz, 1H), 7.24–7.26 (m, 4H), 7.41–7.46 (m, 2H), 7.52–7.58 (m, 1H), 7.94–7.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 24.5, 24.6, 43.0, 83.5, 128.0, 128.5, 128.6, 129.7, 131.3, 133.0, 136.6, 140.5, 199.4.

4.3.3. (−)-3-(4-Methoxyphenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one 15c

Compound **15c** was prepared according to the general procedure using **14** as the ligand to afford a white semisolid (87%). The ee (80% ee) was obtained by chiral HPLC analysis of **15c** using a Chiralpak IA chiral column (*i*-PrOH/hexane = 1:10, flow 0.5 mL min^{-1}, 20 °C), t_{major} = 11.96 min; t_{minor} = 15.21 min; $[\alpha]_D^{20}$ = −37.3 (c 0.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 1.17 (s, 6H), 1.24 (s, 6H), 2.74 (dd, J = 10.5, 5.4 Hz, 1H), 3.50 (dd, J = 18.3, 10.5 Hz, 1H), 3.78 (s, 3H), 6.80–6.85 (m, 2H), 7.19–7.26 (m, 2H), 7.41–7.46 (m, 2H), 7.51–7.56 (m, 1H), 7.94–7.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 24.5, 24.6, 43.5, 55.2, 83.3, 114.0, 128.0, 128.5, 129.3, 132.9, 133.9, 136.8, 157.6, 199.8.

4.3.4. (+)-3-(4-Methylphenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one 15d

Compound **15d** was prepared according to the general procedure using **14** as the ligand to afford a white solid (96%). The ee (78% ee) was obtained by chiral HPLC analysis of **15c** using a Chiralpak IA chiral column (*i*-PrOH/hexane = 1:50, flow 0.5 mL min^{-1}, 20 °C), t_{major} = 12.81 min; t_{minor} = 16.49 min; $[\alpha]_D^{20}$ = +88.2 (c 0.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 1.17 (s, 6H), 1.24 (s, 6H), 2.31 (s, 3H), 2.76 (dd, J = 10.8, 5.1 Hz, 1H), 3.38 (dd, J = 18.3, 5.1 Hz, 1H), 3.53 (dd, J = 18.3, 10.8 Hz, 1H), 7.07–7.10 (m, 2H), 7.18–7.20 (m, 2H), 7.40–7.45 (m, 2H), 7.50–7.56 (m, 1H), 7.93–7.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 21.0, 24.5, 24.6, 43.5, 83.3, 128.0, 128.3, 128.4, 129.2, 132.8, 135.0, 136.9, 138.8, 199.7.

4.3.5. (−)-3-(Naphthalen-1-yl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one 15e

Compound **15d** was prepared according to the general procedure using **14** as the ligand to afford a colorless oil (73%). The ee (78% ee) was obtained by chiral HPLC analysis of **15d** using a Chiralpak IA chiral column (*i*-PrOH/hexane = 1:200, flow 1.0 mL min^{-1}, 20 °C), t_{major} = 14.93 min; t_{minor} = 19.18 min; $[\alpha]_D^{20}$ = −31.3 (c 0.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 1.17 (s, 6H), 1.27 (s, 6H), 3.48 (dd, J = 15.6, 2.4 Hz, 1H), 3.60–3.74 (m, 2H), 7.38–7.55 (m, 7H), 7.69 (d, 8.1 Hz, 1H), 7.82–7.85 (m, 1H), 7.94–7.96 (m, 2H), 8.21–8.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 24.6, 24.7, 43.1, 83.6, 124.1, 125.4, 125.6, 125.7, 125.8, 126.4, 128.1, 128.5, 128.8, 132.1, 132.9, 134.2, 136.8, 138.7, 199.8.

4.3.6. (*R*)-1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one 15f

Compound **15f** was prepared according to the general procedure using **14** as the ligand to afford a colorless oil. The ^{1}H NMR (300 MHz, $CDCl_3$, rt) results are in good agreement with those reported in the literature.[14c] The ee (72% ee) was obtained by chiral

HPLC analysis of **15f** using a Chiralpak IA chiral column (*i*-PrOH/hexane = 1:50, flow 0.5 mL min^{-1}, 20 °C), t_{major} = 9.58 min; t_{minor} = 11.33 min; $[\alpha]_D^{20} = -29.8$ (*c* 0.1, CH_2Cl_2); The absolute configuration was determined by comparing this value with the reported literature value[14c] {$[\alpha]_D^{20} = -58.1$ (*c* 1.0, $CHCl_3$), 97% ee (*R*)}.

4.3.7. (*S*)-4-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one 15g

Compound **15g** was prepared according to the general procedure using **14** as the ligand to afford a colorless oil. The ^1H NMR (300 MHz, $CDCl_3$, rt) results are in good agreement with those reported in the literature.[14c] The ee (62% ee) was obtained by chiral HPLC analysis of **15g** using a Chiralpak IA chiral column (*i*-PrOH/hexane = 1:50, flow 0.5 mL min^{-1}, 20 °C), t_{major} = 10.49 min; t_{minor} = 11.89 min; $[\alpha]_D^{20} = -35.4$ (*c* 0.1, CH_2Cl_2); The absolute configuration was determined by comparing this value with the reported literature[14c] {$[[\alpha]_D^{20} = -49.0$ (*c* 1.0, $CHCl_3$), 79% ee (*S*)}.

4.4. Crystallographic analysis of 1b

Colorless, needle-like crystals were grown from ethanol, $C_{33}H_{30}F_3N_3O_{4.75}S$, M = 633.66, a = 16.9887(2) Å, b = 16.9887(2) Å, c = 21.0226(4) Å, v = 6067.43(16) $Å^3$, T = 291(2) K, Z = 8, 1.387 Mg/m^3. Final R indices [$I > 2\sigma(I)$], R_1 = 0.0931, wR_2 = 0.2739; R indices (all data), R_1 = 0.1067, wR_2 = 0.2985.

Crystallographic data (excluding structure factors) for **1b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 821397. Copies of the data can be obtained, free of charge, on application to CCDC, 12Union Road, Cambridge, CB2 1EZ, UK [fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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