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Synthesis of Quaternary Carbon Stereocenters by Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Arylboronates

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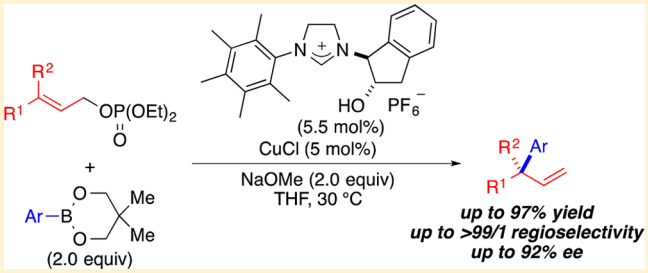
Supporting Information

ABSTRACT: A copper-catalyzed asymmetric allylic substitution of γ,γ-disubstituted allyl phosphates with arylboronates has been developed for the construction of quaternary stereocenters. High regio- and enantioselectivities have been achieved by employing a hydroxy-bearing chiral *N*-heterocyclic carbene ligand, and both *E* and *Z* substrates provide the same enantiomer as the major product. The mechanistic aspect of this catalysis has also been investigated to find that a 1:1 copper/ligand complex is most likely responsible for the present asymmetric catalysis, and the reaction proceeds with almost perfect 1,3-*anti* stereochemistry with respect to the allylic electrophile.



INTRODUCTION

Enantioselective construction of quaternary carbon stereocenters is a subject of great importance in modern asymmetric catalysis.[1] Among the various approaches to this end, copper-catalyzed asymmetric allylic substitution with organometallic reagents is one of the attractive methods through the formation of a new carbon−carbon bond.[2] Although various effective protocols have been developed for the construction of *tertiary* stereocenters by using γ-monosubstituted allylic electrophiles,[3] only a limited number of publications have been made for the construction of *quaternary* stereocenters. A pioneering work by Hoveyda and co-workers employed dialkylzincs as the nucleophile,[4] and since then, alkylmetals based on zinc[5] or magnesium[6] have been most widely utilized for the copper-catalyzed construction of quaternary carbon stereocenters by allylic substitution reactions. In contrast, the use of aryl nucleophiles has been much less explored, and only arylaluminum reagents had been successfully employed[7−9] when we reported our preliminary results using air-stable, easily handled arylboronic acid esters as the nucleophile for the first time in 2011.[10] After this report, allenyl- and alkenylboronates were also utilized by Hoveyda and co-workers.[11] In this paper, we describe an overview of the copper-catalyzed asymmetric allylic substitution of γ,γ-disubstituted allyl phosphates with arylboronates to create quaternary carbon stereocenters with high regio- and enantioselectivities.

RESULTS AND DISCUSSION

In 2010, Lalic and co-workers reported that a copper complex coordinated with *N*-heterocyclic carbene (NHC) ligand IMes (1,3-dimesitylimidazol-2-ylidene) could effectively catalyze the allylic substitution of γ-monosubstituted allyl chlorides with arylboronates with high γ-selectivity.[12] When we initially employed related NHC ligand salt **L1** for a nonasymmetric reaction of γ,γ-disubstituted allyl phosphate (*E*)-**1a** with 4-methoxyphenylboronate **2a** under the conditions shown in eq 1, an almost 1:1 mixture of γ-substitution product **3aa** and α-substitution product **4aa** was obtained in 50% combined yield. In contrast, the replacement of one of the methyl groups on **L1** by hydroxy group (**L2**) led to a dramatic improvement of regioselectivity, leading to exclusive formation of **3aa** in 70% yield under otherwise identical conditions. As a control experiment, the use of **L3** having methoxy group instead of hydroxy group also provided compound **3aa** as the major product, but the regioselectivity became somewhat lower (**3aa**/**4aa** = 90/10). These results clearly indicate the positive effect of hydroxy group on the regioselectivity for the present allylic substitution to construct a quaternary carbon stereocenter.[13,14]

Based on the results in eq 1 and the recent report by Crévisy, Mauduit, and co-workers on the related asymmetric allylic substitution with Grignard reagents using hydroxy-bearing

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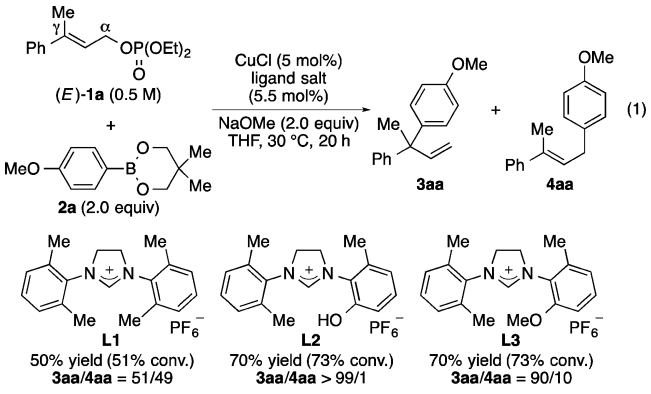
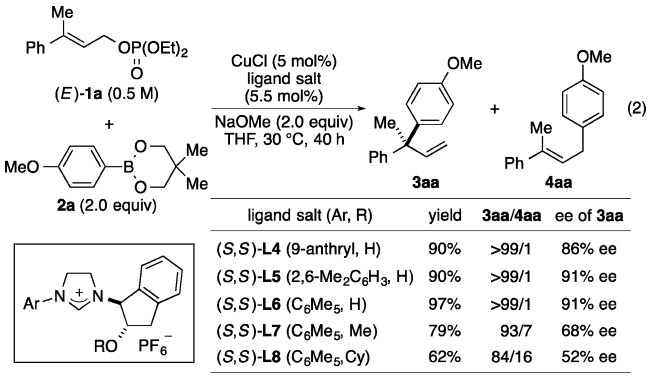


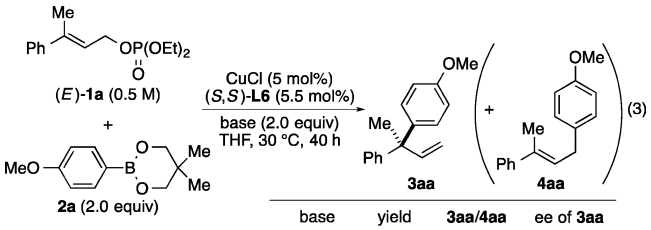
chiral NHCs,[6c] we turned our attention to the development of its asymmetric variant by employing (*S*,*S*)-**L4**[15] and found that **3aa** was obtained in 90% yield with 86% ee without the formation of **4aa** (eq 2).[10] Changing the ligand substituent



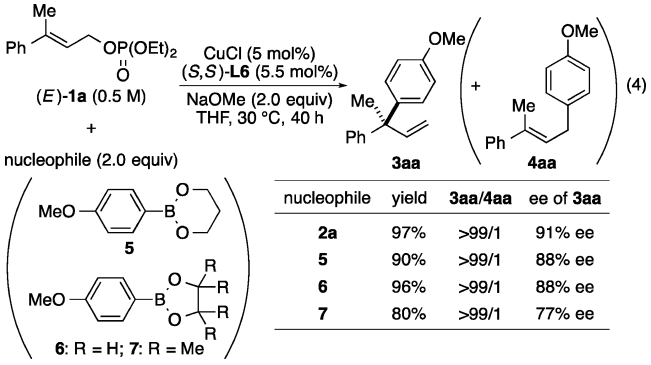
ligand salt (Ar, R)	yield	3aa/4aa	ee of 3aa
(*S*,*S*)-**L4** (9-anthryl, H)	90%	>99/1	86% ee
(*S*,*S*)-**L5** (2,6-$Me_2C_6H_3$, H)	90%	>99/1	91% ee
(*S*,*S*)-**L6** (C_6Me_5, H)	97%	>99/1	91% ee
(*S*,*S*)-**L7** (C_6Me_5, Me)	79%	93/7	68% ee
(*S*,*S*)-**L8** (C_6Me_5,Cy)	62%	84/16	52% ee

from 9-anthryl to 2,6-dimethylphenyl ((*S*,*S*)-**L5**)[15] gave somewhat improved enantioselectivity (91% ee), and the best result was obtained with newly synthesized (*S*,*S*)-**L6** having pentamethylphenyl on the nitrogen (97% yield, 91% ee).[16] The absolute configuration of **3aa** thus obtained was determined to be *S* by comparing the value of its optical rotation with the literature value.[17] As was the case for the nonasymmetric variant (eq 1), the presence of a hydroxy group in the ligand substituent was found to be crucial for achieving high reactivity and selectivity. Thus, the use of *O*-methylated ligand salt (*S*,*S*)-**L7** resulted in the formation of **3aa** in lower yield of 79% with 68% ee, and the regioselectivity also became somewhat lower (93/7). An even lower yield of **3aa** with lower regio- and enantioselectivities was observed by employing ligand salt (*S*,*S*)-**L8** with a bulkier cyclohexyl group on oxygen.

In the presence of (*S*,*S*)-**L6**, the effect of base was briefly examined, and we found that the use of NaOH, which was highly effective for the related copper-catalyzed asymmetric allylic substitution with a silylboronate,[18] showed much lower reactivity, although the regio- and enantioselectivities were identical to those with NaOMe (eq 3). When NaO-*t*-Bu was used as the base instead, high yield and excellent regioselectivity were observed, but the enantioselectivity of **3aa** became slightly lower (88% ee). The enantioselectivity was also affected by the boronic ester portion of 4-methoxyphenylboronate, and neopentyl glycol ester **2a** gave the best result among those tested (eq 4). Thus, 1,3-propanediol ester **5** or ethylene glycol ester **6** gave a high yield of **3aa** exclusively as well, but the enantioselectivity was somewhat lower (88% ee), and pinacol



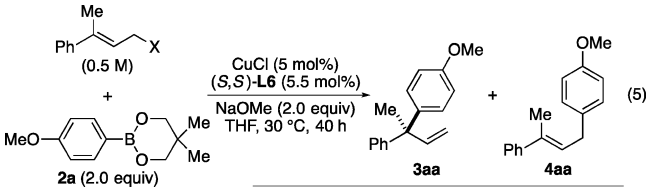
base	yield	3aa/4aa	ee of 3aa
NaOMe	97%	>99/1	91% ee
NaOH	21%	>99/1	91% ee
NaO*t*-Bu	92%	>99/1	88% ee



nucleophile	yield	3aa/4aa	ee of 3aa
2a	97%	>99/1	91% ee
5	90%	>99/1	88% ee
6	96%	>99/1	88% ee
7	80%	>99/1	77% ee

ester **7** resulted in the formation of **3aa** with significanty lower enantioselectivity (77% ee) in 80% yield.

It is worth noting that the present reaction was best catalyzed with diethyl phosphate as the leaving group, although chloride could also be used as the leaving group, giving **3aa** with comparable yield and regioselectivity, albeit with slightly lower enantioselectivity (eq 5). In contrast, much lower yield was observed by using other leaving groups such as picolinate (35% yield),[19] methyl carbonate (26% yield), or benzoate (<1% yield).



X	yield	3aa/4aa	ee of 3aa
$OP(O)(OEt)_2$	97%	>99/1	91% ee
Cl	97%	>99/1	88% ee
OC(O)(2-Py)	35%	>99/1	90% ee
OC(O)OMe	26%	99/1	88% ee
OC(O)Ph	<1%	—	—

Under the conditions using (*S*,*S*)-**L6** as the ligand precursor and NaOMe as the base, various para- or meta-substituted arylboronic acid neopentyl glycol esters **2a**–**g** can efficiently react with substrate (*E*)-**1a** with high regio- and enantioselectivities (**3**/**4** ≥ 90/10, 87–92% ee; Table 1, entries 1–7). The reaction also smoothly proceeds with ortho-substituted arylboronates such as 2-methoxyphenylboronate **2h**, although moderate regio- and enantioselectivities are observed (entry 8). In addition to these simple aryl nucleophiles, 2-naphthylboronate **2i**, 1-methyl-5-indolylboronate **2j**, and 3-thienylboronate **2k** are also suitable nucleophiles to give the corresponding γ-substitution products **3ai**–**ak** in 85–93% yield with similar efficiency (**3**/**4** ≥ 97/3, 88–91% ee; entries 9–11).

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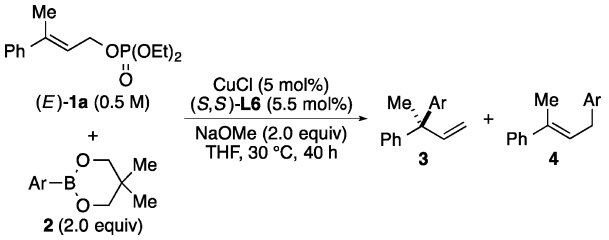
Table 1. Copper-Catalyzed Asymmetric Allylic Substitution of (*E*)-1a with Arylboronates 2



Entry	Ar	Product	Yield (%)[a]	3/4[b]	ee of 3 (%)[c]
1	 (2a)	(*S*)-3aa	97	>99/1	91
2	 (2b)	(*S*)-3ab	87	>99/1	87
3	 (2c)	(*S*)-3ac	84	96/4	89
4	 (2d)	(*S*)-3ad	87	90/10	87
5	 (2e)	(*S*)-3ae	96	>99/1	91
6	 (2f)	(*S*)-3af	92	99/1	92
7	 (2g)	(*S*)-3ag	83	97/3	89
8	 (2h)	(*S*)-3ah	94	87/13	75
9	 (2i)	(*S*)-3ai	93	>99/1	91
10[d]	 (2j)	(*S*)-3aj	89	99/1	88
11	 (2k)	(*S*)-3ak	85	97/3	88

[a]Combined isolated yield of **3** and **4**. [b]Determined by ^{1}H NMR. [c]Determined by chiral HPLC with hexane/2-propanol after converting **3** to alcohol **8** by a hydroboration–oxidation sequence. [d]The reaction was conducted at 0.2 M concentration.

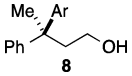
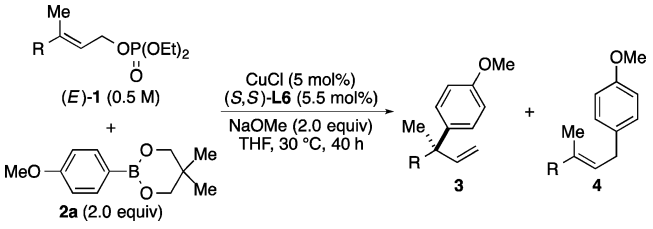
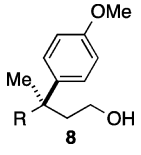


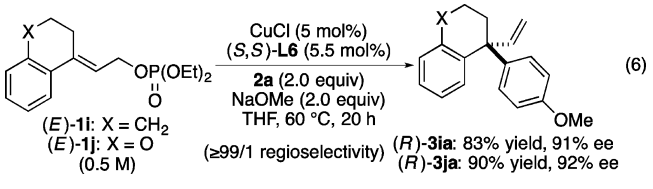
Table 2. Copper-Catalyzed Asymmetric Allylic Substitution of (*E*)-1 with Arylboronate 2a



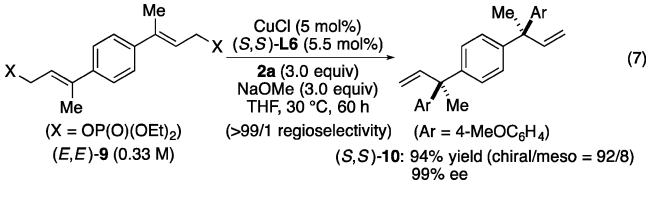
Entry	R	Product	Yield (%)[a]	3/4[b]	ee of 3 (%)[c]
1	 (1a)	(*S*)-3aa	97	>99/1	91
2	 (1b)	(*R*)-3ba	90	>99/1	84
3	 (1c)	(*S*)-3ca	94	>99/1	86
4	 (1d)	(*R*)-3da	81	>99/1	83
5	 (1e)	(*R*)-3ea	95	>99/1	85
6	 (1f)	(*R*)-3fa	72	99/1	89
7	 (1g)	(*R*)-3ga	98	>99/1	64
8	 (1h)	(*S*)-3ha	91	>99/1	76[d]

[a]Combined isolated yield of **3** and **4**. [b]Determined by ^{1}H NMR. [c]Determined by chiral HPLC with hexane/2-propanol after converting **3** to alcohol **8** by a hydroboration–oxidation sequence. [d]Determined by chiral HPLC with hexane/2-propanol.





(6)



(7)

With regard to the scope of allyl phosphates, several (*E*)-3-(hetero)aryl-2-butenyl diethyl phosphates **1b–f** as well as (*E*)-**1a** can be employed in the reaction with 4-methoxyphenylboronate **2a**, and γ-substitution products **3** are obtained almost exclusively with relatively high enantioselectivity (**3**/**4** ≥ 99/1, 83–91% ee; Table 2, entries 1–6).[20] (*E*)-3-Alkyl-2-butenyl diethyl phosphates **1g** and **1h** are also smoothly converted to γ-substitution products **3ga** and **3ha** in high yield with perfect regioselectivity, but the enantioselectivities become significantly lower under the present reaction conditions (64–76% ee; entries 7 and 8).[21] In addition to (*E*)-3-substituted 2-butenyl phosphates, exocyclic allyl phosphates **1i** and **1j** are also successfully employed to give the corresponding γ-substitution products **3ia** and **3ja** with a high level of enantioselectivity (eq 6; 91–92% ee).[22] Furthermore, the reaction of bis(allyl phosphate) (*E*,*E*)-**9** gives double allylic substitution product **10** in 94% combined yield of chiral and meso isomers (ratio = 92/8) with 99% ee for the chiral isomer (eq 7).

In contrast to the (*E*)-substrates employed so far, the use of (*Z*)-**1a** led to the formation of **3aa** with lower enantioselectivity (56% ee), and the absolute configuration of the major enantiomer turned out to be the same as the one obtained from (*E*)-**1a** (eq 8; see Table 2, entry 1, for comparison).[23] Alkyl-substituted (*Z*)-**1g** also showed the same trend (see Table 2, entry 6 for comparison), indicating that the reacting enantioface of the allyic substrates is primarily determined by the γ-substituents in the present asymmetric catalysis.

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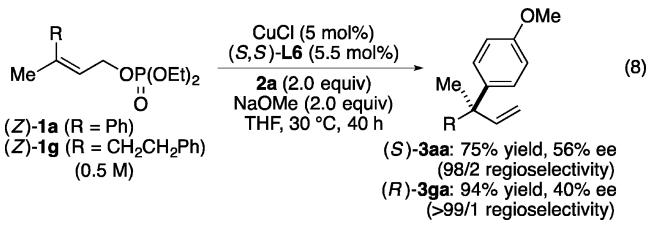
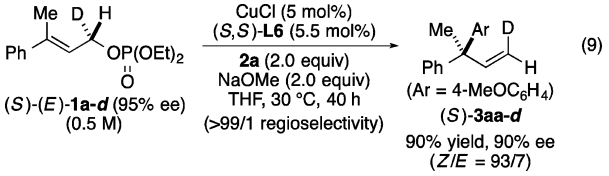
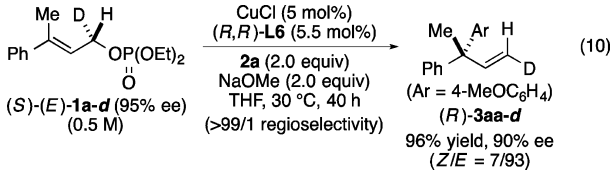


To probe the sterochemical course of the present catalysis more in detail, we prepared enantioenriched monodeuterated substrate (*S*)-(*E*)-**1a-*d*** (95% ee) and subjected it to the reaction with 4-methoxyphenylboronate **2a** as shown in eq 9.



Under these conditions, (*S*)-**3aa-*d*** was selectively obtained in 90% yield with 90% ee, and the *Z*/*E* ratio was 93/7. This result can be explained by the 1,3-*anti* stereochemical course of this overall S_N'-type substitution reaction. Thus, if the reaction proceeds with perfect 1,3-*anti* stereochemistry from (*S*)-(*E*)-**1a-*d*** with 95% ee (er = 97.5/2.5) to (*S*)-**3aa-*d*** with 90% ee (er =95/5), the *Z*/*E* ratio should be (97.5 × 0.95 + 2.5 × 0.05)/(97.5 × 0.05 + 2.5 × 0.95) ≈ 93/7. The calculated *Z*/*E* ratio matches very well with the observed one, indicating the present catalysis proceeds with almost perfect 1,3-*anti* selectivity. This 1,3-*anti* stereochemistry was also confirmed by employing (*R*,*R*)-**L6**, the opposite enantiomer of the ligand salt, for the reaction of (*S*)-(*E*)-**1a-*d*** with **2a**, which gave (*R*)-**3aa-*d*** in 96% yield with 90% ee, and the *Z*/*E* ratio became 7/93 as expected (eq 10). In addition, as shown in Figure 1, a linear correlation



between the ee of ligand salt **L6** and the ee of product **3aa** was observed, indicating that a 1:1 copper/ligand complex is most likely responsible for the present asymmetric catalysis.[24]

As demonstrated in eqs 1 and 2, the regioselectivity in the present catalysis is highly dependent on the existence of the hydroxy group in the ligand. In addition, as shown in eqs 2−4, both the reactivity and the enantioselectivity are influenced by the ligand substituent, metal alkoxide base, and the ester portion of arylboronate nucleophile. Although further evidence is still needed for conclusive elucidation of the reaction mechanism, on the basis of these experimental data and the result in Figure 1 as well as the literature precedents for the mechanistic insights of the copper-catalyzed asymmetric allylic substitutions,[3h,11a] a possible catalytic cycle for the reaction of (*E*)-**1a** with **2a** catalyzed by Cu/(*S*,*S*)-**L6** in the presence of NaOMe is shown in Scheme 1. At first, chelated 1:1 copper(I)/NHC complex **A** is generated from CuCl and (*S*,*S*)-**L6** in the presence of NaOMe.[25] Complex **A** then undergoes transmetalation with arylboronate to give arylcopper(I) **B**.[12,15,26] Interaction of NaOMe with the pendant tricoordinated neutral

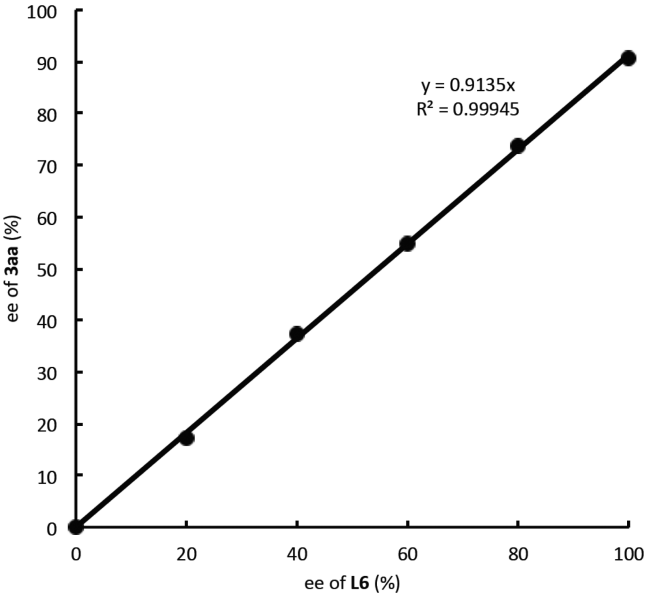
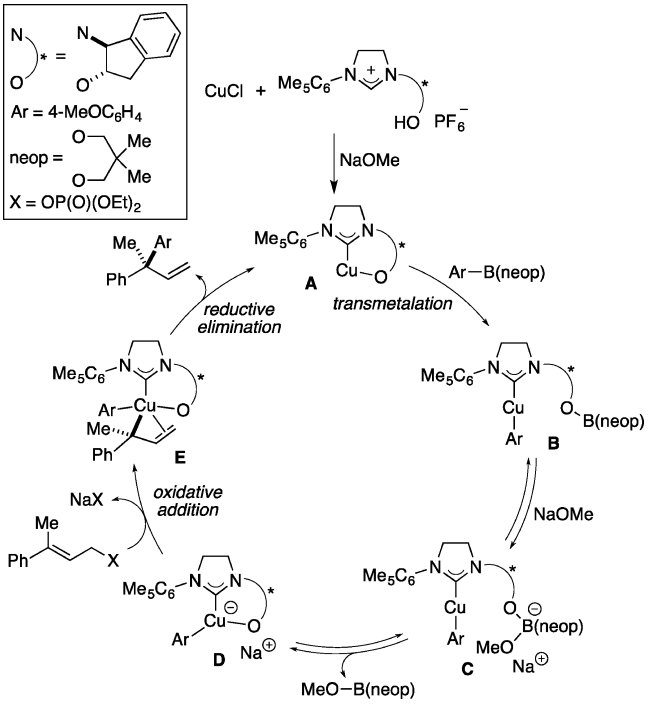


Figure 1. Relationship between ee of **L6** and ee of **3aa** in the copper-catalyzed asymmetric allylic substitution of (*E*)-**1a** with **2a**.

Scheme 1. Possible Catalytic Cycle for the Cu/(*S*,*S*)-L6-Catalyzed Allylic Substitution of 1a with 2a



boron of intermediate **B** would form anionic borate-containing intermediate **C**, which could undergo elimination of trialkoxyborane to generate arylcuprate **D**.[11a] Subsequent oxidative addition of allyl phosphate (*E*)-**1a** to **D** gives allyl(aryl)copper(III) **E** along with the formation of sodium diethyl phosphate. Reductive elimination of **E** then provides the substitution product and copper(I) complex **A** is regenerated. The formation of **E** from **B** through **C** and **D** presumably determines the regio- and stereoselectivities, and this scheme can explain why these selectivities are dependent on the ligand substituent,[27] the boronic ester, and the base. Furthermore, based on the 1,3-*anti* stereochemistry observed in eq 9, the

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oxidative addition of (*E*)-**1a** to complex **D** could go through a pathway illustrated in Figure 2 via a preferential coordination of the *γ-si* face of (*E*)-**1a** with the *anti* geometry of the phosphate group (X), although the precise mechanism of enantioinduction is still unclear.

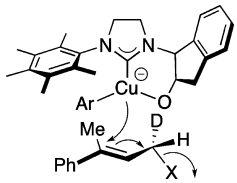

Figure 2. Possible stereochemical course of the oxidative addition step using (*S*)-(*E*)-**1a-*d*** in Scheme 1 (Ar = 4-MeOC$_6$H$_4$, X = OP(O)-(OEt)$_2$).

CONCLUSION

We have described that a Cu/NHC complex derived from CuCl, and newly synthesized (*S*,*S*)-**L6** can efficiently catalyze the asymmetric allylic substitution of *γ*,*γ*-disubstituted allyl phosphates with air-stable and easily handled arylboronates to construct quaternary carbon stereocenters with high enantioselectivities. We have found that the pendant hydroxy group on the chiral NHC ligand is essential for the induction of high regio- and enantioselectivities, and the stereochemical course of the reaction has also been monitored by employing a deuterium-labeled substrate. Future studies will be directed toward further expansion of the present catalysis as well as more insight into the mechanistic aspect.

EXPERIMENTAL SECTION

General Methods. All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glovebox under argon. CH_2Cl_2, THF, toluene, and Et_2O were purified by passing through neutral alumina columns under nitrogen. 1,2-Dichloroethane was distilled over CaH_2 under nitrogen. Et_3N and pyridine were distilled over KOH under nitrogen. CuCl was washed with HCl(aq) and dried under vacuum prior to use. NaOH was ground into a powder and dried under vacuum prior to use. (*E*)-**1a**,[10] (*E*)-**1b**,[18] (*E*)-**1e**,[18] (*E*)-**1g**,[18] (*E*)-**1h**,[9b] (*Z*)-**1g**,[18] (*E*)-3-phenyl-2-butenol,[28] ethyl (*E*)-3-(4-trifluoromethylphenyl)-2-butenoate,[29] (*E*)-3-(3-methylphenyl)-2-butenol,[30] (*Z*)-3-phenyl-2-butenol,[30] (*S*)-(*E*)-1-deuterio-3-phenyl-2-butenol,[31] (*E*)-1-chloro-3-phenyl-2-butene,[32] methyl (*E*)-3-phenyl-2-buten-1-yl carbonate,[33] (*S*,*S*)-**L4**,[15] (*S*,*S*)-**L5**,[15] ethyl 2,6-dimethylphenyloxamate,[15] and 2,3,4,5,6-pentamethylaniline[34] were synthesized following the literature procedures. Arylboronates **2a**−**k** and **5**−**7** were synthesized by esterification of the corresponding arylboronic acids with diols.[26a,35] All other commercial chemicals and solvents were used as received.

(*E*)-3-Phenyl-2-butenyl Picolinate. *N*,*N*′-Dicyclohexylcarbodiimide (1.34 g, 6.50 mmol) and 4-dimethylaminopyridine (305 mg, 2.50 mmol) were added to a suspension of picolic acid (739 mg, 6.00 mmol) in CH_2Cl_2 (15 mL) at 0 °C, and the mixture was stirred for 30 min at 0 °C. (*E*)-3-Phenyl-2-butenol (741 mg, 5.00 mmol) in CH_2Cl_2 (10 mL) was added, and the mixture was stirred for 5 h at 0 °C. The precipitate that formed was filtered through Celite with Et_2O, and the resulting solution was concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 1/1 to afford (*E*)-3-phenyl-2-butenyl picolinate as a yellow oil (1.19 g, 4.70 mmol; 94% yield). ^{1}H NMR ($CDCl_3$): δ 8.77 (ddd, $^3J_{HH}$ = 4.6 Hz, $^4J_{HH}$ = 1.7 Hz, and $^5J_{HH}$ = 1.0 Hz, 1H), 8.16 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.85 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 7.48 (ddd, $^3J_{HH}$ = 7.6 and 4.7 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 7.45−7.41 (m, 2H), 7.32 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.26 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.07 (tq, $^3J_{HH}$ = 7.0 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 5.14 (d, $^3J_{HH}$ = 7.1 Hz, 2H), 2.20 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 165.2, 149.9, 148.2, 142.5, 140.7, 137.0, 128.3, 127.6, 126.9, 125.9, 125.2, 121.1, 63.1, 16.4. HRMS (ESI-TOF): calcd for $C_{16}H_{15}NO_2Na$ (M + Na$^+$) 276.0995, found 276.0992.

(*E*)-3-Phenyl-2-butenyl Benzoate. Benzoyl chloride (665 μL, 5.72 mmol) was added dropwise to a solution of (*E*)-3-phenyl-2-butenol (707 mg, 4.77 mmol) and Et_3N (799 μL, 5.72 mmol) in CH_2Cl_2 (10 mL) at 0 °C, and the mixture was stirred for 3 h at room temperature. The reaction was quenched with 1 M HCl(aq), and this was extracted with CH_2Cl_2. The organic layer was washed with saturated NH_4Cl(aq), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/50 to afford (*E*)-3-phenyl-2-butenyl benzoate as a colorless oil (1.07 g, 4.24 mmol; 89% yield). ^{1}H NMR ($CDCl_3$): δ 8.08 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.56 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.47−7.42 (m, 4H), 7.34 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.28 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.04 (tq, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 5.05 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 166.7, 142.7, 140.4, 133.0, 130.4, 129.7, 128.43, 128.39, 127.6, 126.0, 121.5, 62.3, 16.4. HRMS (ESI-TOF) calcd for $C_{17}H_{16}O_2Na$ (M + Na$^+$) 275.1043, found 275.1041.

Diethyl (*E*)-3-(4-Trifluoromethylphenyl)-2-butenyl Phosphate ((*E*)-1c) (CAS no. 768392-44-5). Diisobutylaluminum hydride (11.2 mL, 11.2 mmol; 1.0 M solution in hexane) was added dropwise over 5 min to a solution of ethyl (*E*)-3-(4-trifluoromethylphenyl)-2-butenoate (1.31 g, 5.07 mmol) in toluene (20 mL) at −78 °C. The mixture was stirred for 12 h while the temperature was gradually raised to room temperature. The reaction was quenched with 1 M HCl(aq) at 0 °C, and the white precipitate was filtered off through Celite with EtOAc. After extraction with EtOAc, the organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/2 to afford (*E*)-3-(4-trifluoromethylphenyl)-2-butenol (CAS 273377-09-6) as a colorless oil (973 mg, 4.50 mmol: 89% yield). ^{1}H NMR ($CDCl_3$): δ 7.58 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.50 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 6.03 (tq, $^3J_{HH}$ = 6.5 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 4.39 (d, $^3J_{HH}$ = 6.5 Hz, 2H), 2.09 (d, $^4J_{HH}$ = 1.2 Hz, 3H), 1.45 (bs, 1H).

4-Dimethylaminopyridine (55.5 mg, 0.455 mmol) and Et_3N (380 μL, 2.73 mmol) were added to a solution of (*E*)-3-(4-trifluoromethylphenyl)-2-butenol (541 mg, 2.50 mmol) in CH_2Cl_2 (15 mL), and the resulting solution was cooled to 0 °C. Diethyl chlorophosphate (327 μL, 2.27 mmol) was added dropwise, and the mixture was stirred for 20 h at room temperature. The reaction was quenched with H_2O, and this was extracted with EtOAc. The organic layer was washed with saturated NH_4Cl(aq), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was passed through a pad of alumina with EtOAc and then purified by GPC with $CHCl_3$ to afford (*E*)-**1c** as a colorless oil (629 mg, 1.79 mmol; 71% yield). ^{1}H NMR ($CDCl_3$): δ 7.59 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.49 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.00 (tq, $^3J_{HH}$ = 6.8 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 4.77 (t, $^3J_{HH}$ = $^3J_{HP}$ = 7.6 Hz, 2H), 4.14 (dq, $^3J_{HP}$ = 7.8 Hz and $^3J_{HH}$ = 7.1 Hz, 4H), 2.12 (s, 3H), 1.35 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HP}$ = 0.9 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 146.0 (q, $^5J_{CF}$ = 1.0 Hz), 139.0, 129.6 (q, $^2J_{CF}$ = 32.6 Hz), 126.2, 125.3 (q, $^3J_{CF}$ = 3.6 Hz), 124.2 (q, $^1J_{CF}$ = 272 Hz), 124.1 (d, $^3J_{CP}$ = 6.7 Hz), 64.1 (d, $^2J_{CP}$ = 5.7 Hz), 63.9 (d, $^2J_{CP}$ = 6.2 Hz), 16.2 (d, $^3J_{CP}$ = 6.7 Hz). HRMS (ESI-TOF): calcd for $C_{15}H_{20}O_4F_3PNa$ (M + Na$^+$) 375.0944, found 375.0939.

Diethyl (*E*)-3-(3-Methylphenyl)-2-butenyl Phosphate ((*E*)-1d). This was synthesized from (*E*)-3-(3-methylphenyl)-2-butenol, following the procedure for compound (*E*)-**1c**. Colorless oil. 62% yield (1.43 g). ^{1}H NMR ($CDCl_3$): δ 7.25−7.18 (m, 3H), 7.12−7.08 (m, 1H), 5.93 (tq, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 4.76 (t, $^3J_{HH}$ = $^3J_{HP}$ = 7.7 Hz, 2H), 4.13 (quint, $^3J_{HH}$ = $^3J_{HP}$ = 7.3 Hz, 4H), 2.36 (s, 3H), 2.11−2.08 (m, 3H), 1.34 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HP}$ = 0.9 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 142.5 140.6 (d, $^4J_{CP}$ = 1.0 Hz), 137.9, 128.5, 128.3, 126.7, 123.1, 121.8 (d, $^3J_{CP}$ = 6.7 Hz), 64.4 (d, $^2J_{CP}$ = 5.2 Hz), 63.8 (d, $^2J_{CP}$ = 6.2 Hz), 21.5, 16.3, 16.2 (d, $^3J_{CP}$ = 6.7 Hz). HRMS (ESI-TOF) calcd for $C_{15}H_{23}O_4PNa$ (M + Na$^+$) 321.1226, found 321.1221.

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Diethyl (*E*)-3-(3-Thienyl)-2-butenyl Phosphate ((*E*)-1f). Triethyl phosphonoacetate (4.40 mL, 22.0 mmol) was added to a suspension of NaH (840 mg, 21.0 mmol; 60 wt % in mineral oil) in THF (25 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. 3-Acetylthiophene (2.52 g, 20.0 mmol) was then added with additional THF (5 mL), and the resulting mixture was stirred for 24 h at room temperature. The reaction was quenched with H_2O at 0 °C, and this was extracted with EtOAc. The organic layer was washed with saturated NaCl(aq), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/60→1/30 to afford ethyl (*E*)-3-(3-thienyl)-2-butenoate (CAS no. 65121-25-7) as a colorless oil (2.41 g, 12.2 mmol; 61% yield). ^{1}H NMR ($CDCl_3$): δ 7.48 (dd, $^4J_{HH}$ = 2.7 and 1.6 Hz, 1H), 7.32 (dd, $^3J_{HH}$ = 5.1 Hz and $^4J_{HH}$ = 2.7 Hz, 1H), 7.30 (dd, $^3J_{HH}$ = 5.2 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 6.22 (q, $^4J_{HH}$ = 1.2 Hz, 1H), 4.21 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 2.57 (d, $^4J_{HH}$ = 1.2 Hz, 3H), 1.32 (t, $^3J_{HH}$ = 7.1 Hz, 3H).

(*E*)-**1f** was synthesized from ethyl (*E*)-3-(3-thienyl)-2-butenoate, following the procedure for compound (*E*)-**1c**. Pale brown oil. 60% yield over two steps (1.05 g). ^{1}H NMR ($CDCl_3$): δ 7.28 (dd, $^3J_{HH}$ = 5.1 Hz and $^4J_{HH}$ = 2.8 Hz, 1H), 7.25 (dd, $^3J_{HH}$ = 5.1 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.23 (d, $^4J_{HH}$ = 2.8 and 1.4 Hz, 1H), 6.05 (tq, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 4.76 (tq, $^3J_{HH}$ = $^3J_{HP}$ = 7.7 Hz and $^5J_{HH}$ = 0.5 Hz, 2H), 4.12 (dq, $^3J_{HP}$ = 7.7 Hz and $^3J_{HH}$ = 7.4 Hz, 4H), 2.11−2.08 (m, 3H), 1.34 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HP}$ = 0.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 143.6, 135.1, 125.8, 125.1, 121.0, 120.4 (d, $^3J_{CP}$ = 6.7 Hz), 64.1 (d, $^2J_{CP}$ = 5.7 Hz), 63.8 (d, $^2J_{CP}$ = 5.7 Hz), 16.2 (d, $^3J_{CP}$ = 6.7 Hz), 15.9. HRMS (ESI-TOF): calcd for $C_{12}H_{19}O_4PSNa$ (M + Na^+) 313.0634, found 313.0628.

Diethyl (*Z*)-3-Phenyl-2-butenyl phosphate ((*Z*)-1a) (CAS 853658-20-5). This was synthesized from (*Z*)-3-phenyl-2-butenol, following the procedure for compound (*E*)-**1c**. Colorless oil. 94% yield (1.16 g). ^{1}H NMR ($CDCl_3$): δ 7.34 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.30−7.26 (m, 1H), 7.19−7.15 (m, 2H), 5.71 (tq, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 4.46 (t, $^3J_{HH}$ = $^3J_{HP}$ = 7.4 Hz, 2H), 4.07 (quint, $^3J_{HH}$ = $^3J_{HP}$ = 7.2 Hz, 4H), 2.11 (s, 3H), 1.30 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HP}$ = 1.4 Hz, 6H), ^{13}C NMR ($CDCl_3$): δ 143.0, 140.3, 128.4, 127.8, 127.6, 121.8 (d, $^3J_{CP}$ = 7.2 Hz), 65.1 (d, $^2J_{CP}$ = 5.2 Hz), 63.7 (d, $^2J_{CP}$ = 6.2 Hz), 25.5, 16.2 (d, $^3J_{CP}$ = 6.7 Hz).

Diethyl (*E*)-2-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)ethyl Phosphate ((*E*)-1i). This was synthesized from 1-tetralone, following the procedure for compound (*E*)-**1f**. Colorless oil. 12% yield over three steps (1.10 g). For storage, it is kept in a freezer under inert atmosphere to prevent decomposition. ^{1}H NMR ($CDCl_3$): δ 7.62−7.57 (m, 1H), 7.20−7.13 (m, 2H), 7.13−7.07 (m, 1H), 6.15 (t, $^3J_{HH}$ = 7.0 Hz, 1H), 4.78 (t, ^3J = 7.6 Hz, 2H), 4.13 (quint, ^3J = 7.3 Hz, 4H), 2.79 (t, $^3J_{HH}$ = 6.2 Hz, 2H), 2.59−2.53 (m, 2H), 1.85 (quint, $^3J_{HH}$ = 6.3 Hz, 2H), 1.34 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HP}$ = 0.9 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 139.5, 138.0, 134.7, 128.9, 127.7, 126.1, 124.1, 117.5 (d, $^3J_{CP}$ = 6.7 Hz), 64.1 (d, $^2J_{CP}$ = 5.7 Hz), 63.7 (d, $^2J_{CP}$ = 5.7 Hz), 30.2, 26.6, 22.9, 16.1 (d, $^3J_{CP}$ = 6.7 Hz). HRMS (ESI-TOF): calcd for $C_{16}H_{23}O_4PNa$ (M + Na^+) 333.1226, found 333.1222.

Diethyl (*E*)-2-(Chroman-4-ylidene)ethyl Phosphate ((*E*)-1j). This was synthesized from 4-chromanone, following the procedure for compound (*E*)-**1f**. Yellow oil. 27% yield over three steps (873 mg). For storage, it is kept in a freezer under inert atmosphere to prevent decomposition. ^{1}H NMR ($CDCl_3$): δ 7.55 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 1.6 Hz, 1H), 7.18 (ddd, $^3J_{HH}$ = 8.1 and 7.3 Hz and $^4J_{HH}$ = 1.6 Hz, 1H), 6.93−6.88 (m, 1H), 6.85 (dd, $^3J_{HH}$ = 8.1 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 6.20 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 4.75 (dd, $^3J_{HP}$ = 8.8 Hz and $^3J_{HH}$ = 7.3 Hz, 2H), 4.22 (t, $^3J_{HH}$ = 5.8 Hz, 2H), 4.12 (quint, ^3J = 7.3 Hz, 4H), 2.77−2.71 (m, 2H), 1.34 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 0.9 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 155.2, 134.2, 129.9, 124.3, 121.5, 121.0, 117.7, 115.4 (d, $^3J_{CP}$ = 6.2 Hz), 65.9, 63.9 (d, $^2J_{CP}$ = 5.7 Hz), 63.4 (d, $^2J_{CP}$ = 5.2 Hz), 25.9, 16.2 (d, $^3J_{CP}$ = 6.7 Hz). HRMS (ESI-TOF): calcd for $C_{15}H_{21}O_5PNa$ (M + Na^+) 335.1019, found 335.1013.

Tetraethyl (2*E*,2′*E*)-1,4-Phenylenebis(2-butene-3,1-diyl) Bis(phosphate) ((*E*,*E*)-9). Triethyl phosphonacetate (7.74 mL, 39.0 mmol) was added to a suspension of NaH (1.44 g, 36.0 mmol; 60 wt % in mineral oil) in THF (40 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. 1,4-Diacetylbenzene (2.43 g, 20.0 mmol) was then added with additional THF (10 mL), and the resulting mixture was stirred for 48 h at room temperature. The reaction was quenched with H_2O at 0 °C and extracted with EtOAc. The organic layer was washed with saturated NaCl(aq), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/30→1/20, and the solid thus obtained was washed with cold pentane to afford diethyl (2*E*,2′*E*)-3,3′-(1,4-phenylene)bis(2-butenoate) as a white solid (2.15 g, 7.09 mmol; 47% yield). ^{1}H NMR ($CDCl_3$): δ 7.48 (s, 4H), 6.16 (q, $^4J_{HH}$ = 1.2 Hz, 2H), 4.22 (q, $^3J_{HH}$ = 7.1 Hz, 4H), 2.58 (d, $^4J_{HH}$ = 1.2 Hz, 6H), 1.32 (t, $^3J_{HH}$ = 7.1 Hz, 6H).

Diisobutylaluminum hydride (34.0 mL, 34.0 mmol; 1.0 M solution in hexane) was added dropwise over 15 min to a solution of diethyl (2*E*,2′*E*)-3,3′-(1,4-phenylene)bis(2-butenoate) (2.15 g, 7.09 mmol) in toluene (20 mL) at −78 °C, and the mixture was stirred for 24 h at room temperature. The reaction was quenched with 1 M HCl(aq) at 0 °C, and the white precipitate was filtered off through Celite with EtOAc. After extraction with EtOAc, the organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was passed through a pad of silica gel with EtOAc/hexane = 1/1, and the solid thus obtained was washed with Et_2O to afford (2*E*,2′*E*)-3,3′-(1,4-phenylene)bis(2-buten-1-ol) as a white solid (1.03 g, 4.71 mmol; 66% yield). ^{1}H NMR ($CDCl_3$): δ 7.38 (s, 4H), 6.01 (t, $^3J_{HH}$ = 6.7 Hz, 2H), 4.37 (t, $^3J_{HH}$ = 5.9 Hz, 4H), 2.09 (s, 6H), 1.35 (bs, 2H).

4-Dimethylaminopyridine (83.0 mg, 0.682 mmol) and Et_3N (570 μL, 4.09 mmol) were added to a solution of (2*E*,2′*E*)-3,3′-(1,4-phenylene)bis(2-buten-1-ol) (372 mg, 1.71 mmol) in CH_2Cl_2 (10 mL) and the resulting solution was cooled to 0 °C. Diethyl chlorophosphate (588 μL, 4.09 mmol) was added dropwise, and the mixture was stirred for 16 h at room temperature. The reaction was quenched with H_2O, and this was extracted with CH_2Cl_2. The organic layer was washed with saturated NH_4Cl(aq), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was passed through a pad of alumina with EtOAc and then purified by GPC with $CHCl_3$ to afford (*E*,*E*)-**9** as a colorless oil (710 mg, 1.45 mmol; 85% yield). ^{1}H NMR ($CDCl_3$): δ 7.38 (s, 4H), 5.97 (t, $^3J_{HH}$ = 6.8 Hz, 2H), 4.76 (t, $^3J_{HH}$ = $^3J_{HP}$ = 7.7 Hz, 4H), 4.13 (quint, $^3J_{HH}$ = $^3J_{HP}$ = 7.3 Hz, 8H), 2.10 (s, 6H), 1.34 (t, $^3J_{HH}$ = 7.1 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 141.6, 139.8, 125.8, 121.9 (d, $^3J_{CP}$ = 6.7 Hz), 64.3 (d, $^2J_{CP}$ = 5.2 Hz), 63.8 (d, $^2J_{CP}$ = 5.7 Hz), 16.1 (d, $^3J_{CP}$ = 6.2 Hz), 16.0. HRMS (ESI-TOF): calcd for $C_{22}H_{36}O_8P_2Na$ (M + Na^+) 513.1778, found 513.1780.

Diethyl (*S*)-(*E*)-1-Deuterio-3-phenyl-2-butenyl Phosphate ((*S*)-(*E*)-1a-*d*). This was synthesized from (*S*)-(*E*)-1-deuterio-3-phenyl-2-butenol (95% ee) following the procedure for compound (*E*)-**1c**. Colorless oil. 72% yield (285 mg). $[\alpha]^{30}_D$ −0.9 (*c* 2.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.42−7.38 (m, 2H), 7.36−7.31 (m, 2H), 7.30−7.25 (m, 1H), 5.94 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 4.74 (t, ^3J = 7.6 Hz, 1H), 4.17−4.09 (m, 4H), 2.13−2.09 (m, 3H), 1.344 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 1.342 (t, $^3J_{HH}$ = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 142.5, 140.6, 128.4, 127.7, 125.9, 121.9 (d, $^3J_{CP}$ = 6.7 Hz), 64.1 (td, $^1J_{CD}$ = 22.7 Hz and $^2J_{CP}$ = 5.7 Hz), 63.8 (d, $^2J_{CP}$ = 6.1 Hz), 16.3, 16.2 (d, $^3J_{CP}$ = 6.7 Hz). HRMS (ESI-TOF): calcd for $C_{14}H_{20}DO_4PNa$ (M + Na^+) 308.1132, found 308.1131.

1,3-Bis(2,6-dimethylphenyl)imidazolinium Hexafluorophosphate (L1). Oxalyl chloride (430 μL, 5.00 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of 2,6-dimethylaniline (1.33 g, 11.0 mmol) and pyridine (967 μL, 12.0 mmol) in CH_2Cl_2 (20 mL) at 0 °C, and the resulting solution was stirred for 12 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 and washed successively with 1 M HCl(aq) and saturated $NaHCO_3$(aq). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The resulting solid was washed with hexane and dried under vacuum to afford *N*,*N*′-bis(2,6-dimethylphenyl)oxalamide (CAS 91325-47-2) as a white solid (1.45 g, 4.90 mmol; 98% yield). ^{1}H NMR ($CDCl_3$): δ 8.86(bs, 2H),7.20−7.15 (m, 2H), 7.15−7.11 (m, 4H), 2.29 (s, 12H). ^{13}C NMR (DMSO-d_6): δ 158.9, 135.1, 134.2, 127.8, 127.0, 18.0.

$LiAlH_4$ (744 mg, 19.6 mmol) was added to a solution of *N*,*N*′-bis(2,6-dimethylphenyl) oxalamide (1.45 g, 4.90 mmol) in THF (25 mL) at 0 °C, and the mixture was stirred for 48 h at 70 °C. The

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reaction was diluted with Et_2O at 0 °C and slowly quenched with H_2O. The resulting suspension was filtered through Celite with THF, and the solution was concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/5 to afford *N*,*N*′-bis(2,6-dimethylphenyl)ethane-1,2-diamine (CAS 72991-60-7) as a colorless oil (494 mg, 1.85 mmol; 38% yield). ^{1}H NMR ($CDCl_3$): δ 7.01(d, $^3J_{HH}$ = 7.3 Hz, 4H), 6.84 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 3.39 (bs, 2H), 3.22 (s, 4H), 2.32 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 146.0, 129.6, 129.0, 122.2, 49.0, 18.7.

HCl (2.22 mL, 2.22 mmol; 1.0 M solution in Et_2O) was added to a solution of *N*,*N*′-bis(2,6-dimethylphenyl)ethane-1,2-diamine (494 mg, 1.85 mmol) in Et_2O (20 mL), and the mixture was stirred for 15 min at room temperature. The precipitate was collected by filtration and washed with Et_2O/hexane to afford a white solid. Toluene (10 mL) and trimethyl orthoformate (1.01 mL, 9.25 mmol) were successively added to this solid, and the mixture was stirred for 16 h at 90 °C. After being cooled to room temperature, the resulting precipitate was collected by filtration and washed with Et_2O. The solid thus obtained was then suspended in H_2O (10 mL) and MeOH (10 mL), and KPF_6 (682 mg, 3.70 mmol) was added. The mixture was stirred for 2 h at room temperature, and this was diluted with H_2O. After extraction with CH_2Cl_2, the organic layer was concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/EtOAc = 10/1, and the solid thus obtained was triturated with CH_2Cl_2 and washed with $CHCl_3$ to afford compound **L1** as a white solid (490 mg, 1.15 mmol; 62% yield). ^{1}H NMR (acetone-d_6): δ 8.96 (s, 1H), 7.39 (dd, $^3J_{HH}$ = 8.3 and 6.8 Hz, 2H), 7.34−7.29 (m, 4H), 4.80 (s, 4H), 2.53 (s, 12H). ^{13}C NMR (acetone-d_6): δ 161.2, 136.9, 134.3, 131.3, 130.2, 52.3, 17.8. HRMS (ESI-TOF): calcd for $C_{19}H_{23}N_2$ ($M - PF_6^-$) 279.1856, found 279.1855.

1-(2,6-Dimethylphenyl)-3-(2-hydroxy-6-methylphenyl)-imidazolinium Hexafluorophosphate (L2). A solution of ethyl 2,6-dimethylphenyloxamate (1.11 g, 5.00 mmol), 2-amino-*m*-cresol (616 mg, 5.00 mmol), and 4-(dimethylamino)pyridine (30.5 mg, 0.25 mmol) in CH_2Cl_2 (25 mL) was refluxed for 48 h. After the solution was cooled to room temperature, the solvent was removed under vacuum and the residue was chromatographed on silica gel with $CHCl_3$/EtOAc = 20/1 to afford *N*-(2,6-dimethylphenyl)-*N*′-(2-hydroxy-6-methylphenyl)oxalamide as a white solid (1.02 g, 3.43 mmol; 69% yield). ^{1}H NMR ($CDCl_3$): δ 9.50 (bs, 1H), 8.81 (bs, 1H), 8.19 (s, 1H), 7.22−7.17 (m, 1H), 7.17−7.10 (m, 3H), 6.97 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.83 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 2.37 (s, 3H), 2.29 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 158.4, 157.2, 150.2, 135.1, 132.0, 131.4, 128.6, 128.5, 128.3, 122.9, 122.7, 118.6, 18.6, 18.1.

$LiAlH_4$ (357 mg, 9.40 mmol) was added to a solution of *N*-(2,6-dimethylphenyl)-*N*′-(2-hydroxy-6-methylphenyl)oxalamide (1.02 g, 3.43 mmol) in THF (15 mL) at 0 °C, and the mixture was stirred for 12 h at 70 °C. The reaction was diluted with Et_2O at 0 °C and slowly quenched with H_2O. The resulting suspension was filtered through Celite with THF, and the solution was concentrated under vacuum. Et_2O (20 mL) and HCl (5.15 mL, 5.15 mmol; 1.0 M solution in Et_2O) were added to the residue, and the mixture was stirred for 15 min at room temperature. The precipitate was collected by filtration and washed with Et_2O/hexane to afford a brown solid. Toluene (25 mL) and trimethyl orthoformate (1.88 mL, 17.2 mmol) were successively added to this solid, and the mixture was stirred for 18 h at 90 °C. After being cooled to room temperature, the resulting precipitate was collected by filtration and washed with Et_2O. The solid thus obtained was suspended in H_2O (10 mL) and MeOH (10 mL), and KPF_6 (1.26 g, 6.86 mmol) was added. The mixture was stirred for 2 h at room temperature, and this was diluted with H_2O. After extraction with CH_2Cl_2, the organic layer was concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/EtOAc = 10/1, and the solid thus obtained was triturated with CH_2Cl_2 and washed with $CHCl_3$ to afford compound **L2** as a white solid (540 mg, 1.27 mmol; 73% yield). ^{1}H NMR (acetone-d_6): δ 8.87 (s, 1H), 7.38 (dd, $^3J_{HH}$ = 8.3 and 6.7 Hz, 1H), 7.32−7.25 (m, 3H), 6.99 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.92 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 4.72 (s, 4H), 2.87 (bs, 1H), 2.494 (s, 6H), 2.490 (s, 3H). ^{13}C NMR (acetone-d_6): δ 162.3, 154.0, 137.8, 136.9, 134.3, 131.8, 131.2, 130.1, 123.4, 123.0, 115.0, 52.4, 52.3, 17.7, 17.6. HRMS (ESI-TOF): calcd for $C_{18}H_{21}N_2O$ ($M - PF_6^-$) 281.1648, found 281.1648.

1-(2,6-Dimethylphenyl)-3-(2-methoxy-6-methylphenyl)-imidazolinium Hexafluorophosphate (L3). Trimethylsilyldiazomethane (2.00 mL, 4.00 mmol; 2.0 M solution in Et_2O) was added dropwise to a solution of compound **L2** (213 mg, 0.500 mmol) and HBF_4(aq) (80.0 μL, 0.500 mmol; 42 wt %) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred for 15 min at 0 °C, and it was poured into H_2O. After extraction with CH_2Cl_2, the organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was washed with $CHCl_3$ to afford compound **L3** as a white solid (176 mg, 0.40 mmol; 80% yield). ^{1}H NMR (acetone-d_6): δ 8.86 (s, 1H), 7.44 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.38 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.31 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 7.13 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.03 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.77−4.64 (m, 4H), 3.99 (s, 3H), 2.51 (s, 9H). ^{13}C NMR (acetone-d_6): δ 162.5, 156.1, 138.0, 136.9, 134.3, 132.0, 131.2, 130.1, 124.3, 123.8, 110.9, 56.9, 52.5, 52.4, 17.6, 17.5. HRMS (ESI-TOF): calcd for $C_{19}H_{23}N_2O$ ($M-PF_6^-$) 295.1805, found 295.1806.

1-((1*S*,2*S*)-2-Hydroxyindan-1-yl)-3-pentamethylphenylimidazolinium Hexafluorophosphate ((*S*,*S*)-L6). Ethyl chloroglyoxylate (1.09 mL, 9.77 mmol) was added dropwise to a solution of 2,3,4,5,6-pentamethylaniline (1.75 g, 10.8 mmol) and pyridine (1.02 mL, 12.7 mmol) in CH_2Cl_2 (11 mL) at 0 °C, and the resulting solution was stirred for 18 h at room temperature. The reaction mixture was diluted with EtOAc and washed successively with 1 M HCl(aq) and saturated $NaHCO_3$(aq). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The resulting solid was washed with hexane and dried under vacuum to afford ethyl 2,3,4,5,6-pentamethylphenyloxamate as a white solid (1.90 g, 7.24 mmol; 74% yield). ^{1}H NMR ($CDCl_3$): δ 8.41 (bs, 1H), 4.43 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 2.23 (s, 3H), 2.22 (s, 6H), 2.15 (s, 6H), 1.45 (t, $^3J_{HH}$ = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 162.5, 156.1, 138.0, 136.9, 134.3, 132.0, 131.2, 130.1, 124.3, 123.8, 110.9, 56.9, 52.5, 52.4, 17.6, 17.5. HRMS (ESI-TOF): calcd for $C_{15}H_{21}NO_3Na$ ($M + Na^+$) 286.1414, found 286.1412.

A solution of ethyl 2,3,4,5,6-pentamethylphenyloxamate (1.05 g, 4.00 mmol) and (1*S*,2*S*)-*trans*-1-amino-2-indanol (597 mg, 4.00 mmol) in CH_2Cl_2 (20 mL) was refluxed for 60 h. After the solution was cooled to room temperature, the solvent was removed under vacuum and the residue was chromatographed on silica gel with $CHCl_3$/EtOAc/hexane = 4/2/1 to afford *N*-(2,3,4,5,6-pentamethylphenyl)-*N*′-((1*S*,2*S*)-2-hydroxy-1-indanyl)oxalamide as a white solid (861 mg, 2.35 mmol; 59% yield). $[\alpha]^{20}_D$ +8.4 (*c* 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.81 (bs, 1H), 7.94 (d, $^3J_{HH}$ = 5.8 Hz, 1H), 7.33−7.23 (m, 4H), 5.24 (t, $^3J_{HH}$ = 6.2 Hz, 1H), 4.58 (td, $^3J_{HH}$ = 7.7 and 6.2 Hz, 1H), 3.80 (bs, 1H), 3.37 (dd, $^2J_{HH}$ = 15.7 Hz and $^3J_{HH}$ = 7.6 Hz, 1H), 3.00 (dd, $^2J_{HH}$ = 15.7 Hz and $^3J_{HH}$ = 7.8 Hz, 1H), 2.24 (s, 3H), 2.23 (s, 6H), 2.17 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 161.7, 158.1, 140.4, 138.3, 135.3, 133.4, 130.5, 129.7, 129.1, 127.6, 125.4, 123.7, 80.8, 64.0, 38.8, 17.0, 16.8, 15.7. HRMS (ESI-TOF): calcd for $C_{22}H_{26}N_2O_3Na$ ($M + Na^+$) 389.1836, found 389.1833.

$LiAlH_4$ (357 mg, 9.40 mmol) was added to a solution of *N*-(2,3,4,5,6-pentamethylphenyl)-*N*′-((1*S*,2*S*)-2-hydroxy-1-indanyl)-oxalamide (861 mg, 2.35 mmol) in THF (10 mL) at 0 °C, and the mixture was stirred for 16 h at 70 °C. The reaction was diluted with Et_2O at 0 °C and slowly quenched with H_2O. The resulting suspension was filtered through Celite with THF, and the solution was concentrated under vacuum. Et_2O (40 mL) and HCl (2.05 mL, 2.05 mmol; 1.0 M solution in Et_2O) were added to the residue, and the mixture was stirred for 15 min at room temperature. The precipitate was collected by filtration and washed with Et_2O/hexane to afford a brown solid. Toluene (15 mL) and trimethyl orthoformate (1.12 mL, 10.3 mmol) were successively added to this solid, and the mixture was stirred for 17 h at 90 °C. After being cooled to room temperature, the resulting precipitate was collected by filtration and washed with Et_2O. The solid thus obtained was suspended in H_2O (40 mL), and KPF_6 (757 mg, 4.11 mmol) was added. The mixture was stirred for 2 h at room temperature, and this was diluted with H_2O. After extraction with CH_2Cl_2, the organic layer was concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/acetone = 4/

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1, and the solid thus obtained was triturated with CH_2Cl_2 and washed with $CHCl_3$ to afford compound (*S*,*S*)-**L6** as a white solid (736 mg, 1.49 mmol; 73% yield). $[\alpha]^{20}_D$ +40.8 (*c* 1.00, acetone). ^{1}H NMR (acetone-d_6): δ 8.77 (s, 1H), 7.49 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.41−7.32 (m, 3H), 5,40 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 5.00 (d, $^3J_{HH}$ = 5.2 Hz, 1H), 4.91−4.84 (m, 1H), 4.55−4.30 (m, 4H), 3.37 (dd, $^2J_{HH}$ = 15.8 Hz and $^3J_{HH}$ = 7.2 Hz, 1H), 2.93 (dd, $^2J_{HH}$ = 15.9 Hz and $^3J_{HH}$ = 7.3 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (acetone-d_6): δ 160.0, 141.7, 138.2, 136.1, 135.0, 132.2, 131.93, 131.87, 130.4, 128.3, 126.5, 125.4, 76.2, 71.4, 52.7, 47.1, 39.2, 17.0, 16.7, 15.5, 15.4. HRMS (ESI-TOF): calcd for $C_{23}H_{29}N_2O$ (M − PF_6^-) 349.2274, found 349.2269.

1-((1*R*,2*R*)-2-Hydroxyindan-1-yl)-3-pentamethylphenylimidazolinium Hexafluorophosphate ((*R*,*R*)-L6). This was synthesized from (1*R*,2*R*)-*trans*-1-amino-2-indanol and ethyl 2,6- dimethylphenyloxamate, following the procedure for compound (*S*,*S*)-**L6**. White solid. 46% yield (313 mg). $[\alpha]^{20}_D$ −40.1 (*c* 0.50, acetone).

1-((1*S*,2*S*)-2-Methoxyindan-1-yl)-3-pentamethylphenylimidazolinium Hexafluorophosphate ((*S*,*S*)-L7). Trimethylsilyldiazomethane (0.60 mL, 1.20 mmol; 2.0 M solution in Et_2O) was added dropwise to a solution of compound (*S*,*S*)-**L6** (74.2 mg, 0.150 mmol) and HBF_4(aq) (24.0 μL, 0.150 mmol; 42 wt %) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was stirred for 15 min at 0 °C, and it was poured into H_2O. After extraction with CH_2Cl_2, the organic layer was concentrated under vacuum. The resulting solid was suspended in MeOH/H_2O (25 mL; 4/1), and KPF_6 (28.2 mg, 0.150 mmol) was added. The mixture was stirred for 1 h at room temperature, and this was diluted with H_2O. After extraction with CH_2Cl_2, the organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with acetone/CH_2Cl_2 = 1/10, and the resulting solid was dissolved in CH_2Cl_2 and triturated with hexane. The precipitate that formed was collected by filtration and dried under vacuum to afford compound (*S*,*S*)-**L7** as a white solid (65.4 mg, 0.129 mmol; 85% yield). $[\alpha]^{20}_D$ +27.6 (*c* 0.72, acetone). ^{1}H NMR (acetone-d_6): δ 8.77 (s, 1H), 7.53 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.44−7.32 (m, 3H), 5.52 (d, $^3J_{HH}$ = 6.0 Hz, 1H), 4.61−4.55 (m, 1H), 4.55−4.30 (m, 4H), 3.54 (s, 3H), 3.50 (dd, $^2J_{HH}$ = 15.9 Hz and $^3J_{HH}$ = 7.1 Hz, 1H), 2.92 (dd, $^2J_{HH}$ = 16.0 Hz and $^3J_{HH}$ = 6.6 Hz, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (acetone-d_6): δ 160.1, 141.6, 138.2, 135.7, 135.04, 135.03, 132.2, 131.9, 131.8, 130.6, 128.5, 126.7, 125.6, 84.8, 69.3, 57.7, 52.8, 47.2, 36.6, 17.0, 16.74, 16.71, 15.5, 15.4. HRMS (ESI-TOF): calcd for $C_{24}H_{31}N_2O$ (M − PF_6^-) 363.2431, found 363.2426.

1-((1*S*,2*S*)-2-Cyclohexyloxyindan-1-yl)-3-pentamethylphenylimidazolinium Hexafluorophosphate ((*S*,*S*)-L8). 3-Bromocyclohexene (524 μL, 4.53 mmol) was added to a suspension of *N*-(2,3,4,5,6-pentamethylphenyl)-*N*′-((1*S*,2*S*)-2-hydroxy-1-indanyl)-oxalamide (632 mg, 2.27 mmol) and silver oxide (1.04 g, 4.53 mmol) in 1,2-dichloroethane (30 mL) at room temperature. The mixture was stirred for 24 h at 80 °C while 3-bromocyclohexene (262 μL, 2.27 mmol) and silver oxide (502 mg, 2.27 mmol) were added after 8 and 16 h. After the mixture was cooled to room temperature, the precipitate was filtered off through Celite with CH_2Cl_2 and concentrated under vacuum. The residue (starting oxalamide/product oxalamide ∼3.5/1) was chromatographed on silica gel with $CHCl_3$ and then with $CHCl_3$/EtOAc = 10/1 to afford *N*-((1*S*,2*S*)-2-(2-cyclohexen-1-yloxy)-1-indanyl)-*N*′-(2,3,4,5,6-pentamethylphenyl)oxalamide as a yellow solid after washing with Et_2O/pentane (218 mg, 0.488 mmol; 21% yield), and *N*-(2,3,4,5,6-pentamethylphenyl)-*N*′-((1*S*,2*S*)-2-hydroxy-1-indanyl)oxalamide was recovered as a yellow solid. This process was repeated two more times with the recovered starting material to afford *N*-((1*S*,2*S*)-2-(2-cyclohexen-1-yloxy)-1-indanyl)-*N*′-(2,3,4,5,6-pentamethylphenyl)oxalamide in 58% overall yield (584 mg, 1.31 mmol; 1/1 mixture of diastereomers). $[\alpha]^{25}_D$ +69.2 (*c* 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.85 (bs, 1H), 7.73−7.64 (m, 1H), 7.30−7.20 (m, 4H), 5.91−5.83 (m, 1H), 5.83−5.77 (m, 1H), 5.41 (t, $^3J_{HH}$ = 5.8 Hz, 0.5H), 5.39 (t, $^3J_{HH}$ = 5.6 Hz, 0.5H), 4.37−4.31 (m, 1H), 4.25−4.19 (m, 0.5H), 4.17−4.11 (m, 0.5H), 3.34 (dd, $^2J_{HH}$ = 16.0 Hz and $^3J_{HH}$ = 6.8 Hz, 0.5H), 3.33 (dd, $^2J_{HH}$ = 15.6 Hz and $^3J_{HH}$ = 6.8 Hz, 0.5H), 3.02−2.92 (m, 1H), 2.24 (s, 3H), 2.23 (s, 6H), 2.17 (s, 6H), 2.11−1.92 (m, 2H), 1.92−1.83 (m, 1H), 1.83−1.69 (m, 2H), 1.62−1.51 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 160.2, 160.1, 158.54, 158.53, 140.6, 140.3, 139.4, 139.3, 135.1, 133.3, 131.2, 131.0, 130.5, 129.9, 128.8, 128.7, 128.2, 127.9, 127.3, 125.2, 124.7, 124.6, 84.04, 84.00, 72.6, 72.5, 61.2, 61.0, 38.2, 37.8, 29.2, 29.0, 25.30, 25.26, 19.32, 19.29, 16.9, 16.8, 15.62, 15.60.

A mixture of palladium on carbon (41.7 mg, 39.2 μmol; 10 wt % Pd) and *N*-((1*S*,2*S*)-2-(2-cyclohexen-1-yloxy)-1-indanyl)-*N*′-(2,3,4,5,6-pentamethylphenyl)oxalamide (584 mg, 1.31 mmol) in EtOH (10 mL) and CH_2Cl_2 (10 mL) was stirred for 12 h at room temperature under H_2 (1 atm). The catalyst was filtered off through Celite with CH_2Cl_2, and the solvent was removed under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 3/1 to afford *N*-((1*S*,2*S*)-2-cyclohexyloxy-1-indanyl)-*N*′-(2,3,4,5,6-pentamethylphenyl)-oxalamide as a white solid (470 mg, 1.05 mmol; 80% yield). $[\alpha]^{25}_D$ +30.4 (*c* 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.85 (bs, 1H), 7.68 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 7.30−7.19 (m, 4H), 5.38 (dd, $^3J_{HH}$ = 8.8 and 5.6 Hz, 1H), 4.30 (q, $^3J_{HH}$ = 6.2 Hz, 1H), 3.54 (tt, $^3J_{HH}$ = 9.1 and 4.0 Hz, 1H), 3.30 (dd, $^2J_{HH}$ = 16.0 Hz and $^3J_{HH}$ = 7.2 Hz, 1H), 2.93 (dd, $^2J_{HH}$ = 16.0 Hz and $^3J_{HH}$ = 5.9 Hz, 1H), 2.24 (s, 3H), 2.23 (s, 6H), 2.17 (s, 6H), 1.98−1.88 (m, 2H), 1.80−1.70 (m, 2H), 1.57−1.50 (m, 1H), 1.40−1.16 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 160.2, 158.6, 140.5, 139.4, 135.2, 133.4, 130.5, 129.9, 128.8, 127.3, 125.2, 124.6, 83.7, 61.1, 38.0, 32.9, 32.8, 25.9, 24.3, 17.0, 16.9, 15.6. HRMS (ESI-TOF): calcd for $C_{28}H_{36}N_2O_3Na$ (M + Na^+) 471.2618, found 471.2618.

N-((1*S*,2*S*)-2-Cyclohexyloxy-1-indanyl)-*N*′-(2,3,4,5,6-pentamethylphenyl)oxalamide was converted to (*S*,*S*)-**L8** following the procedure for compound (*S*,*S*)-**L6**. The final purification was performed by silica gel chromatography with hexane/EtOAc = 1/1, and the solid thus obtained was washed with Et_2O to afford compound (*S*,*S*)-**L8** as a pale brown solid (272 mg, 0.472 mmol; 45% yield). $[\alpha]^{25}_D$ +212 (*c* 1.20, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.70 (s, 1H), 7.40−7.35 (m, 1H), 7.33−7.26 (m, 2H), 7.25−7.20 (m, 1H), 5.23 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 4.49 (q, $^3J_{HH}$ = 6.8 Hz, 1H), 4.31−4.18 (m, 4H), 3.56−3.46 (m, 1H), 3.35 (dd, $^2J_{HH}$ = 15.6 Hz and $^3J_{HH}$ = 7.1 Hz, 1H), 2.86 (dd, $^2J_{HH}$ = 15.8 Hz and $^3J_{HH}$ = 6.7 Hz, 1H), 2.24 (s, 3H), 2.23 (s, 3H), 2.22 (s, 3H), 2.21 (s, 6H), 1.98−1.86 (m, 2H), 1.79−1.67 (m, 2H), 1.59−1.50 (m, 1H), 1.39−1.14 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 157.6, 140.4, 137.9, 134.7, 134.5, 133.8, 131.1, 130.6, 130.5, 129.9, 128.0, 125.8, 124.8, 80.2, 77.5, 69.4, 52.0, 46.2, 37.3, 33.3, 32.5, 25.7, 24.0, 17.0, 16.8, 16.7, 15.3, 15.2. HRMS (ESI-TOF): calcd for $C_{29}H_{39}N_2O$ (M − PF_6^-) 431.3057, found 431.3061.

General Procedure for Tables 1 and 2 and eqs 8−10. A solution of CuCl (1.5 mg, 15 μmol), (*S*,*S*)-**L6** (8.2 mg, 17 μmol), and NaOMe (32.4 mg, 0.600 mmol) in THF (0.40 mL) was stirred for 15 min at room temperature. Organoboronate **2** (0.600 mmol) was added, and the mixture was stirred for 5 min at room temperature. Allyl phosphate **1** (0.300 mmol) was then added with additional THF (0.20 mL), and the resulting mixture was stirred for 40 h at 30 °C. After dilution with EtOAc, the reaction mixture was passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane to afford compounds **3** and **4**. Further purification by GPC with $CHCl_3$ was carried out when necessary.

For ee analysis, compound **3** was converted to the corresponding alcohol **8** through a hydroboration−oxidation sequence: BH_3·SMe_2 (0.15 mL, 0.30 mmol; 2.0 M solution in THF) was added to a solution of compound **3** in THF (1.0 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. NaOH(aq) (1 M, 0.45 mL) and 30 wt % H_2O_2(aq) (61 μL, 0.600 mmol) were successively added at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated NaCl(aq) and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane to afford compound **8**.

((*S*)-3-(4-Methoxyphenyl)-3-phenyl-1-butene ((*S*)-3aa)) (Table 1, Entry 1) (CAS 1301717-33-8 for (*S*)). Colorless oil. 97% yield (69.0 mg, **3aa**/**4aa** > 99/1). $[\alpha]^{30}_D$ −12.1 (*c* 0.94, $CHCl_3$). The absolute configuration was determined by comparison of the

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optical rotation with the literature value.[17] ^{1}H NMR ($CDCl_3$): δ 7.29 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.24−7.18 (m, 3H), 7.13 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.83 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.39 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.18 (d, $^3J_{HH}$ = 10.5 Hz, 1H), 4.91 (d, $^3J_{HH}$ = 17.3 Hz, 1H), 3.80 (s, 3H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.9, 148.5, 146.9, 140.4, 129.0, 128.1, 127.9, 126.1, 113.4, 112.9, 55.4, 49.7, 27.5.

(*S*)-3-(4-Methoxyphenyl)-3-phenyl-1-butanol ((*S*)-8aa) (CAS 1334512-30-9 for (*S*)). Colorless oil. 53% yield (39.4 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 9.0 min (major enantiomer), 13.1 min (minor enantiomer). 91% ee. $[\alpha]^{30}_D$ −3.2 (*c* 0.92, C_6H_6). ^{1}H NMR ($CDCl_3$): δ 7.27 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.22−7.15 (m, 3H), 7.12 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.82 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 3.79 (s, 3H), 3.53 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 2.42 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 1.65 (s, 3H), 1.07 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 157.7, 149.6, 141.4, 128.3, 128.2, 127.2, 126.0, 113.6, 60.3, 55.3, 44.6, 44.4, 28.4.

((*S*)-3-(4-Methylphenyl)-3-phenyl-1-butene ((*S*)-3ab)) (Table 1, Entry 2). Colorless oil. 87% yield (58.2 mg, **3ab**/**4ab** > 99/1). $[\alpha]^{25}_D$ −5.5 (*c* 1.06, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.30−7.25 (m, 2H), 7.23−7.17 (m, 3H), 7.12−7.06 (m, 4H), 6.39 (dd, $^3J_{HH}$ = 17.4 and 10.6 Hz, 1H), 5.17 (dd, $^3J_{HH}$ = 10.6 Hz and $^2J_{HH}$ = 1.2 Hz, 1H), 4.91 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 1.2 Hz, 1H), 2.32 (s, 3H), 1.77 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 148.5, 146.8, 145.3, 135.6, 128.9, 128.1, 127.9, 127.8, 126.0, 113.0, 50.0, 27.3, 21.1. HRMS (APCI-TOF): calcd for $C_{17}H_{19}$ (M + H^+) 223.1481, found 223.1487.

(*S*)-3-(4-Methylphenyl)-3-phenyl-1-butanol ((*S*)-8ab). Colorless oil. 34% yield (21.2 mg). The ee was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 90/10, flow = 0.8 mL/min. Retention times: 19.6 min (minor enantiomer), 22.6 min (major enantiomer). 87% ee. $[\alpha]^{25}_D$ +0.8 (*c* 1.06, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.27 (t, $^3J_{HH}$ = 7.1 Hz, 2H), 7.23−7.19 (m, 2H), 7.17 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.13−7.05 (m, 4H), 3.54 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 2.43 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 2.31 (s, 3H), 1.66 (s, 3H), 0.99 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 149.5, 146.3, 135.5, 129.0, 128.2, 127.2, 127.1, 126.0, 60.3, 44.9, 44.3, 28.3, 21.0. HRMS (ESI-TOF) calcd for $C_{17}H_{20}ONa$ (M + Na^+) 263.1406, found 263.1406.

((*S*)-3-(4-Chlorophenyl)-3-phenyl-1-butene ((*S*)-3ac)) (Table 1, Entry 3) (CAS 1334512-27-4 for (*S*)). Colorless oil. 84% yield (61.4 mg, **3ac**/**4ac** = 96/4). $[\alpha]^{30}_D$ −12.1 (*c* 1.01, $CHCl_3$). The absolute configuration was assigned analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.30 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.25 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.24−7.18 (m, 3H), 7.15 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.37 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.21 (dd, $^3J_{HH}$ = 10.6 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 4.92 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 147.7, 146.8, 146.2, 132.0, 129.4, 128.3, 128.2, 127.8, 126.3, 113.6, 50.0, 27.3.

(*S*)-3-(4-Chlorophenyl)-3-phenyl-1-butanol ((*S*)-8ac) (CAS 1334512-31-0 for (*S*)). Colorless oil. 55% yield (36.4 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 14.9 min (major enantiomer), 20.4 min (minor enantiomer). 89% ee. $[\alpha]^{30}_D$ +2.9 (*c* 0.84, C_6H_6). ^{1}H NMR ($CDCl_3$): δ 7.28 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.24 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.22−7.16 (m, 3H), 7.13 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 3.51 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 2.44 (dt, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 7.2 Hz, 1H), 2.40 (dt, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 7.2 Hz, 1H), 1.65 (s, 3H), 1.05 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 148.7, 148.0, 131.8, 128.7, 128.39, 128.36, 127.2, 126.3, 60.1, 45.0, 44.2, 28.2.

((*S*)-3-(4-Methoxycarbonylphenyl)-3-phenyl-1-butene ((*S*)-3ad)) (Table 1, Entry 4) (CAS 527744-57-6 for racemate). Colorless oil. 88% yield (70.5 mg, **3ad**/**4ad** = 96/4). $[\alpha]^{30}_D$ −8.0 (*c* 1.16, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.94 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.31−7.26 (m, 4H), 7.24−7.16 (m, 3H), 6.39 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.22 (d, $^3J_{HH}$ = 10.6 Hz, 1H), 4.92 (d, $^3J_{HH}$ = 17.3 Hz, 1H), 3.90 (s, 3H), 1.80 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 167.1, 153.7, 147.5, 145.9, 129.5, 128.3, 128.1, 128.0, 127.8, 126.4, 113.8, 52.1, 50.5, 27.1.

(*S*)-3-(4-Methoxycarbonylphenyl)-3-phenyl-1-butanol ((*S*)-8ad). Colorless oil. 51% yield (36.3 mg). The ee was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 80/20, flow = 0.8 mL/min. Retention times: 15.4 min (major enantiomer), 21.2 min (minor enantiomer). 87% ee. $[\alpha]^{30}_D$ +1.1 (*c* 1.08, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.94 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.31−7.25 (m, 4H), 7.22−7.16 (m, 3H), 3.90 (s, 3H), 3.52 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 2.48 (dt, $^2J_{HH}$ = 13.4 Hz and $^3J_{HH}$ = 7.4 Hz, 1H), 2.45 (dt, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 7.3 Hz, 1H), 1.69 (s, 3H), 1.54 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 167.1, 154.9, 148.4, 129.6, 128.4, 128.0, 127.3, 127.2, 126.3, 60.0, 52.1, 45.6, 44.1, 28.1. HRMS (ESI-TOF): calcd for $C_{18}H_{20}O_3Na$ (M + Na^+) 307.1299, found 307.1305.

((*S*)-3-(3-Methoxyphenyl)-3-phenyl-1-butene ((*S*)-3ae)) (Table 1, Entry 5). Colorless oil. 96% yield (68.6 mg, **3ae**/**4ae** > 99/1). $[\alpha]^{25}_D$ +1.7 (*c* 1.29, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.30−7.25 (m, 2H), 7.24−7.17 (m, 4H), 6.81−6.78 (m, 2H), 6.75 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 2.3 Hz, 1H), 6.39 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.19 (d, $^3J_{HH}$ = 10.6 Hz, 1H), 4.93 (d, $^3J_{HH}$ = 17.3 Hz, 1H), 3.76 (s, 3H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.5, 150.0, 148.1, 146.5, 129.0, 128.1, 127.9, 126.1, 120.6, 114.5, 113.2, 110.8, 55.2, 50.3, 27.2. HRMS (APCI-TOF): calcd for $C_{17}H_{19}O$ (M + H^+) 239.1430, found 239.1428.

(*S*)-3-(3-Methoxyphenyl)-3-phenyl-1-butanol ((*S*)-8ae). Colorless oil. 48% yield (34.9 mg). The ee was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 80/20, flow = 0.8 mL/min. Retention times: 19.3 min (minor enantiomer), 22.7 min (major enantiomer). 91% ee. $[\alpha]^{20}_D$ −3.9 (*c* 1.24, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.30−7.24 (m, 2H), 7.23−7.16 (m, 4H), 6.80−6.76 (m, 2H), 6.75−6.71 (m, 1H), 3.76 (s, 3H), 3.57−3.49 (m, 2H), 2.43 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 1.66 (s, 3H), 1.02 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 159.5, 151.0, 149.1, 129.2, 128.3, 127.1, 126.0, 119.9, 113.9, 110.6, 60.2, 55.2, 45.2, 44.2 28.2. HRMS (ESI-TOF): calcd for $C_{17}H_{20}O_2Na$ (M + Na^+) 279.1356, found 279.1354.

((*S*)-3-(3-Methylphenyl)-3-phenyl-1-butene ((*S*)-3af)) (Table 1, Entry 6) (CAS 1334512−28−5 for (*S*)). Colorless oil. 92% yield (61.3 mg, **3af**/**4af** = 99/1). $[\alpha]^{30}_D$ +4.2 (*c* 0.91, C_6H_6). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.31−7.26 (m, 2H), 7.24−7.16 (m, 4H), 7.06−6.99 (m, 3H), 6.41 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.19 (dd, $^3J_{HH}$ = 10.6 Hz and $^2J_{HH}$ = 1.2 Hz, 1H), 4.93 (dd, $^3J_{HH}$ = 17.5 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 2.32 (s, 3H), 1.79 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 148.4, 148.3, 146.8, 137.6, 128.6, 128.1, 128.02, 127.95, 126.9, 126.1, 125.1, 113.0, 50.2, 27.2, 21.8.

(*S*)-3-(3-Methylphenyl)-3-phenyl-1-butanol ((*S*)-8af) (CAS 1334512-32-1 for (*S*)). Colorless oil. 52% yield (34.5 mg). The ee was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 90/10, flow = 0.8 mL/min. Retention times: 11.9 min (minor enantiomer), 13.7 min (major enantiomer). 92% ee. $[\alpha]^{30}_D$ +1.1 (*c* 0.98, C_6H_6). ^{1}H NMR ($CDCl_3$): δ 7.28 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.24−7.17 (m, 3H), 7.16 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.04−6.98 (m, 3H), 3.53 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 2.44 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 2.31 (s, 3H), 1.66 (s, 3H), 1.33 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 148.4, 148.3, 146.8, 137.6, 128.6, 128.1, 128.02, 127.95, 126.9, 126.1, 125.1, 113.0, 50.2, 27.2, 21.8.

((*S*)-3-(3-Chlorophenyl)-3-phenyl-1-butene ((*S*)-3ag)) (Table 1, Entry 7). Colorless oil. 83% yield (60.2 mg, **3ag**/**4ag** = 97/3). $[\alpha]^{25}_D$ −1.1 (*c* 1.04, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.30 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.24−7.16 (m, 6H), 7.10−7.05 (m, 1H), 6.36 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.22 (d, $^3J_{HH}$ = 10.5 Hz, 1H), 4.93 (d, $^3J_{HH}$ = 17.3 Hz, 1H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 150.5, 147.5, 145.9, 134.1, 129.4, 128.3, 128.1, 127.8, 126.40, 126.36, 126.3, 113.8, 50.3, 27.2. HRMS (APCI-TOF): calcd for $C_{16}H_{15}Cl$ ($^{M+}$) 242.0857, found 242.0862.

(*S*)-3-(3-Chlorophenyl)-3-phenyl-1-butanol ((*S*)-8ag). Colorless oil. 42% yield (27.3 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.7 mL/min. Retention times: 26.9 min (major enantiomer), 29.1 min (minor enantiomer). 89% ee. $[\alpha]^{20}_D$ +0.8 (*c* 1.01, $CHCl_3$). ^{1}H NMR

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($CDCl_3$): δ 7.29 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.23−7.14 (m, 6H), 7.06 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 3.55−3.47 (m, 2H), 2.44 (dt, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 7.2 Hz, 1H), 2.40 (dt, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 7.3 Hz, 1H), 1.66 (s, 3H), 1.08 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 151.7, 148.4, 134.2, 129.5, 128.4, 127.4, 127.1, 126.31, 126.25, 125.6, 60.0, 45.3, 44.0, 28.1. HRMS (ESI-TOF): calcd for $C_{16}H_{17}ClONa$ (M + Na^+) 283.0860, found 283.0858.

((*S*)-3-(2-Methoxyphenyl)-3-phenyl-1-butene ((*S*)-3ah)) (Table 1, Entry 8). Colorless oil. 94% yield (67.4 mg, **3ah**/**4ah** = 87/13). $[\alpha]^{20}_D$ −12.5 (*c* 1.37, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.41 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 7.28−7.18 (m, 3H), 7.15−7.10 (m, 3H), 6.98 (td, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 6.84 (dd, $^3J_{HH}$ = 8.0 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 6.62 (dd, $^3J_{HH}$ = 17.4 and 10.6 Hz, 1H), 5.14 (dd, $^3J_{HH}$ = 10.7 Hz and $^2J_{HH}$ = 1.0 Hz, 1H), 4.99 (dd, $^3J_{HH}$ = 17.5 Hz and $^2J_{HH}$ = 1.0 Hz, 1H), 3.37 (s, 3H), 1.79 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.8, 149.4, 145.7, 136.5, 128.0, 127.9, 127.8, 126.2, 125.3, 120.6, 113.0, 112.4, 55.3, 49.0, 26.0. HRMS (APCI-TOF): calcd for $C_{17}H_{19}O$ (M + H^+) 239.1430, found 239.1426.

(*S*)-3-(2-Methoxyphenyl)-3-phenyl-1-butanol ((*S*)-8ah). Colorless oil. 52% yield (38.0 mg). The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 90/10, flow = 0.8 mL/min. Retention times: 9.9 min (minor enantiomer), 12.0 min (major enantiomer). 75% ee. $[\alpha]^{25}_D$ −22.2 (*c* 0.96, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.43 (dd, $^3J_{HH}$ = 7.7 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.28−7.18 (m, 3H), 7.16−7.09 (m, 3H), 6.99 (td, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 0.6 Hz, 1H), 6.80 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 3.57−3.48 (m, 1H), 3.48−3.40 (m, 1H), 3.31 (s, 3H), 2.79 (ddd, $^2J_{HH}$ = 13.0 Hz and $^3J_{HH}$ = 8.6 and 6.1 Hz, 1H), 2.31 (ddd, $^2J_{HH}$ = 13.1 Hz and $^3J_{HH}$ = 8.4 and 5.7 Hz, 1H), 1.66 (s, 3H), 1.01 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 158.3, 151.1, 136.8, 128.3, 128.1, 127.7, 125.9, 125.4, 120.8, 113.3, 60.9, 55.6, 44.3, 42.3, 28.5. HRMS (ESI-TOF): calcd for $C_{17}H_{20}O_2Na$ (M + Na^+) 279.1356, found 279.1355.

((*S*)-3-(2-Naphthyl)-3-phenyl-1-butene ((*S*)-3ai)) (Table 1, Entry 9) (CAS 1334512-29-6 for (*S*)). Colorless oil. 93% yield (72.3 mg, **3ai**/**4ai** > 99/1). $[\alpha]^{30}_D$ +5.1 (*c* 1.06, $CHCl_3$). The absolute configuration was assigned analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.82−7.77 (m, 2H), 7.75 (d, $^4J_{HH}$ = 0.9 Hz, 1H), 7.72 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.49−7.42 (m, 2H), 7.31−7.19 (m, 6H), 6.51 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.24 (dd, $^3J_{HH}$ = 10.6 Hz and $^2J_{HH}$ =1.0 Hz, 1H), 4.98 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 1.0 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 148.1, 146.4, 145.7, 133.4, 132.1, 128.23, 128.16, 128.0, 127.7, 127.6, 127.2, 126.2, 126.1, 125.8, 125.6, 113.5, 50.5, 27.2.

(*S*)-3-(2-Naphthyl)-3-phenyl-1-butanol ((*S*)-8ai) (CAS 1334512-31-0 for (*S*)). Colorless oil. 56% yield (43.3 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 12.8 min (major enantiomer), 19.4 min (minor enantiomer). 91% ee. $[\alpha]^{30}_D$ −1.7 (*c* 0.90, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.85 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.83 (d, $^4J_{HH}$ = 1.7 Hz, 1H), 7.80 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.72 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.53−7.45 (m, 2H), 7.32−7.24 (m, 4H), 7.24−7.17 (m, 2H), 3.62−3.51 (m, 2H), 2.63−2.52 (m, 2H), 1.79 (s, 3H) 1.40 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 149.1, 146.5, 133.3, 132.0, 128.3, 128.1, 128.0, 127.6, 127.3, 126.9, 126.2, 126.1, 125.8, 124.6, 60.3, 45.4, 44.0, 28.1.

((*S*)-3-(1-Methyl-5-indolyl)-3-phenyl-1-butene ((*S*)-3aj)) (Table 1, Entry 10). The reaction was conducted in 1.5 mL of THF (instead of 0.60 mL). Colorless oil. 89% yield (69.8 mg, **3aj**/**4aj** = 99/1). $[\alpha]^{20}_D$ −5.2 (*c* 1.05, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.54 (d, $^4J_{HH}$ = 1.7 Hz, 1H), 7.30−7.24 (m, 4H), 7.22 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.21−7.17 (m, 1H), 7.05−7.01 (m, 2H), 6.51 (dd, $^3J_{HH}$ = 17.4 and 10.6 Hz, 1H), 6.44 (d, $^3J_{HH}$ = 3.1 Hz, 1H), 5.18 (dd, $^3J_{HH}$ = 10.5 Hz and $^2J_{HH}$ = 1.2 Hz, 1H), 4.94 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 3.77 (s, 3H), 1.86 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 149.3, 147.5, 139.3, 135.3, 129.0, 128.2, 128.04, 128.01, 125.8, 122.6, 119.6, 112.6, 108.9, 101.2, 50.2, 32.9, 27.7. HRMS (ESI-TOF): calcd for $C_{19}H_{19}NNa$ (M + Na^+) 284.1410, found 284.1407.

(*S*)-3-(1-Methyl-5-indolyl)-3-phenyl-1-butanol ((*S*)-8aj). Colorless oil. 78% yield (54.5 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.8 mL/min. Retention times: 17.9 min (major enantiomer), 41.8 min (minor enantiomer). 88% ee. $[\alpha]^{20}_D$ −16.3 (*c* 1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.58 (d, $^4J_{HH}$ = 1.6 Hz, 1H), 7.28−7.22 (m, 4H), 7.20 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.19−7.14 (m, 1H), 7.03 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 6.97 (dd, $^3J_{HH}$ = 8.6 Hz and $^4J_{HH}$ = 1.9 Hz, 1H), 6.44 (dd, $^3J_{HH}$ = 3.0 Hz and $^4J_{HH}$ = 0.7 Hz, 1H), 3.76 (s, 3H), 3.62−3.52 (m, 2H), 2.58−2.46 (m, 2H), 1.73 (s, 3H), 0.95 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 150.6, 140.0, 135.1, 129.1, 128.2, 128.1, 127.3, 125.7, 122.2, 118.7, 109.1, 101.2, 60.5, 45.1, 44.7, 32.9, 28.8. HRMS (ESI-TOF): calcd for $C_{19}H_{21}NONa$ (M + Na^+) 302.1515, found 302.1513.

((*S*)-3-Phenyl-3-(3-thienyl)-1-butene ((*S*)-3ak)) (Table 1, Entry 11) (CAS 1259553-77-9 for (*S*)). Colorless oil. 85% yield (52.9 mg, **3ak**/**4ak** = 97/3). $[\alpha]^{25}_D$ −15.9 (*c* 0.89, C_6H_6). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.31−7.26 (m, 2H), 7.25 (dd, $^3J_{HH}$ = 5.1 Hz and $^4J_{HH}$ = 2.9 Hz, 1H), 7.23−7.18 (m, 3H), 6.96 (dd, $^4J_{HH}$ = 3.0 and 1.3 Hz, 1H), 6.84 (dd, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 6.36 (dd, $^3J_{HH}$ = 17.3 and 10.5 Hz, 1H), 5.17 (dd, $^3J_{HH}$ = 10.5 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 4.92 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 149.1, 147.6, 146.1, 128.19, 128.18, 127.5, 126.3, 125.3, 120.9, 113.1, 48.3, 27.6. HRMS (APCI-TOF): calcd for $C_{14}H_{15}S$ (M + H^+) 215.0889, found 215.0884.

(*S*)-3-Phenyl-3-(3-thienyl)-1-butanol ((*S*)-8ak). Colorless oil. 44% yield (26.0 mg). The ee was determined on two Daicel Chiralcel OD-H columns with hexane/2-propanol = 90/10, flow = 0.8 mL/min. Retention times: 25.6 min (major enantiomer), 29.6 min (minor enantiomer). 88% ee. $[\alpha]^{25}_D$ +5.5 (*c* 0.98, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.28 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.24−7.21 (m, 3H), 7.21−7.16 (m, 1H), 7.05−7.03 (m, 1H), 6.79−6.76 (m, 1H), 3.62−3.52 (m, 2H), 2.44 (dt, $^2J_{HH}$ = 13.7 Hz and $^3J_{HH}$ = 7.1 Hz, 1H), 2.39 (dt, $^2J_{HH}$ = 13.4 Hz and $^3J_{HH}$ = 6.8 Hz, 1H), 1.68 (s, 3H), 1.50 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 150.6, 148.4, 128.3, 127.8, 126.7, 126.2, 125.6, 119.9, 60.2, 44.6, 43.4, 28.1. HRMS (ESI-TOF): calcd for $C_{14}H_{16}OSNa$ (M + Na^+) 255.0814, found 255.0811.

((*R*)-3-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1-butene ((*R*)-3ba)) (Table 2, Entry 2). Colorless oil. 90% yield (75.3 mg, **3ba**/**4ba** > 99/1). $[\alpha]^{25}_D$ −1.1 (*c* 1.35, C_6H_6). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.23 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.13 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.10 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.82 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.33 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.17 (dd, $^3J_{HH}$ = 10.6 Hz and $^2J_{HH}$ = 1.0 Hz, 1H), 4.88 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 0.9 Hz, 1H), 3.79 (s, 3H), 1.74 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 158.0, 147.1, 146.4, 139.7, 131.9, 129.4, 128.9, 128.2, 113.6, 113.4, 55.4, 49.4, 27.5. HRMS (APCI-TOF): calcd for $C_{17}H_{18}ClO$ (M + H^+) 273.1041, found 273.1044.

(*R*)-3-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1-butanol ((*R*)-8ba). Colorless oil. 56% yield (36.4 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 11.9 min (major enantiomer), 15.8 min (minor enantiomer). 84% ee. $[\alpha]^{30}_D$ −2.0 (*c* 1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.23 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.13 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.09 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.82 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 3.79 (s, 3H), 3.51 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 2.44−2.33 (m, 2H), 1.62 (s, 3H), 1.06 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 157.9, 148.3, 140.7, 131.7, 128.6, 128.3, 128.2, 113.7, 60.1, 55.3, 44.33, 44.31, 28.4. HRMS (ESI-TOF): calcd for $C_{17}H_{19}ClO_2Na$ (M + Na^+) 313.0966, found 313.0973.

((*S*)-3-(4-Methoxyphenyl)-3-(4-trifluoromethylphenyl)-1-butene ((*S*)-3ca)) (Table 2, Entry 3). Colorless oil. 94% yield (86.0 mg, **3ca**/**4ca** > 99/1). $[\alpha]^{20}_D$ −3.7 (*c* 1.00, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.52 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.32 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.10 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.84 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.35 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.21 (d, $^3J_{HH}$ = 10.5 Hz, 1H), 4.91 (d, $^3J_{HH}$ = 17.5 Hz, 1H), 3.80 (s 3H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 158.2, 152.7, 146.1, 139.4, 128.9, 128.4 (q, $^2J_{CF}$ = 32.6 Hz), 128.3, 125.1 (q, $^3J_{CF}$ = 4.1 Hz), 124.5 (q, $^1J_{CF}$ = 272 Hz), 113.71, 113.70,

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55.3, 49.8, 27.4. HRMS (APCI-TOF): calcd for $C_{18}H_{17}OF_3$ ($^{M+}$) 306.1226, found 306.1228.

(*S*)-3-(4-Methoxyphenyl)-3-(4-trifluoromethylphenyl)-1-butanol ((*S*)-8ca). Colorless oil. 57% yield (52.3 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 10.4 min (major enantiomer), 14.6 min (minor enantiomer). 86% ee. $[\alpha]^{25}_D$ −5.0 (*c* 0.87, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.52 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.31 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.10 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.83 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.79 (s, 3H), 3.52 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 2.48−2.38 (m, 2H), 1.66 (s, 3H), 1.07 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 158.0, 154.0 (q, $^5J_{CF}$ = 1.4 Hz), 140.2, 128.24 (q, $^2J_{CF}$ = 32.6 Hz), 128.23, 127.5, 125.2 (q, $^3J_{CF}$ = 3.8 Hz), 124.4 (q, $^1J_{CF}$ = 272 Hz), 113.8, 60.0, 55.3, 44.8, 44.2, 28.2. HRMS (ESI-TOF): calcd for $C_{18}H_{19}O_2F_3Na$ (M + Na^+) 347.1229, found 347.1228.

((*R*)-3-(4-Methoxyphenyl)-3-(3-methylphenyl)-1-butene ((*R*)-3da)) (Table 2, Entry 4). Colorless oil. 81% yield (65.8 mg, **3da**/**4da** > 99/1). $[\alpha]^{20}_D$ −13.5 (*c* 1.25, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.17 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.12 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 7.05−7.03 (m, 1H), 7.03−6.98 (m, 2H), 6.82 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.38 (dd, $^3J_{HH}$ = 17.3 and 10.6 Hz, 1H), 5.16 (dd, $^3J_{HH}$ = 10.6 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 4.90 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 1.1 Hz, 1H), 3.80 (s 3H), 2.31 (s, 3H), 1.76 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.8, 148.5, 147.0, 140.5, 137.6, 129.0, 128.6, 128.0, 126.8, 125.0, 113.4, 112.8, 55.3, 49.5, 27.4, 21.7. HRMS (APCI-TOF): calcd for $C_{18}H_{21}O$ (M + H^+) 253.1587, found 253.1587.

(*R*)-3-(4-Methoxyphenyl)-3-(3-methylphenyl)-1-butanol ((*R*)-8da). Colorless oil. 53% yield (35.0 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 8.5 min (major enantiomer), 12.3 min (minor enantiomer). 83% ee. $[\alpha]^{25}_D$ +3.9 (*c* 1.16, C_6H_6). ^{1}H NMR ($CDCl_3$): δ 7.16 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.12 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.03−6.97 (m, 3H), 6.81 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 3.79 (s, 3H), 3.57−3.49 (m, 2H), 2.45−2.36 (m, 2H), 2.30 (s, 3H), 1.63 (s, 3H), 1.01 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 157.7, 149.5, 141.5, 137.7, 128.2, 128.1, 127.9, 126.7, 124.3, 113.5, 60.3, 55.3, 44.4, 28.4, 21.8. HRMS (ESI-TOF): calcd for $C_{18}H_{22}O_2Na$ (M + Na^+) 293.1512, found 293.1513.

((*R*)-3-(4-Methoxyphenyl)-3-(2-naphthyl)-1-butene ((*R*)-3ea)) (Table 2, Entry 5). Colorless oil. 95% yield (82.3 mg, **3ea**/**4ea** > 99/1). $[\alpha]^{25}_D$ −12.0 (*c* 1.25, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.81−7.77 (m, 2H), 7.74−7.70 (m, 2H), 7.48−7.41 (m, 2H), 7.26 (dd, $^3J_{HH}$ = 8.5 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 7.15 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.83 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.48 (dd, $^3J_{HH}$ = 17.4 and 10.6 Hz, 1H), 5.22 (d, $^3J_{HH}$ = 10.6 Hz, 1H), 4.95 (d, $^3J_{HH}$ = 17.3 Hz, 1H), 3.80 (s, 3H), 1.86 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.9, 146.7, 145.9, 140.1, 133.3, 132.0, 129.0, 128.1, 127.7, 127.5, 127.2, 126.0, 125.7, 125.6, 113.5, 113.3, 55.3, 49.8, 27.4. HRMS (APCI-TOF): calcd for $C_{21}H_{21}O$ (M + H^+) 289.1587, found 289.1592.

(*R*)-3-(4-Methoxyphenyl)-3-(2-naphthyl)-1-butanol ((*R*)-8ea). Colorless oil. 63% yield (55.4 mg). The ee was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol =80/20, flow =0.9 mL/min. Retention times: 22.1 min (minor enantiomer), 27.7 min (major enantiomer). 85% ee. $[\alpha]^{20}_D$ +0.8 (*c* 1.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.82 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.81−7.75 (m, 2H), 7.70 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.51−7.42 (m, 2H), 7.18 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.15 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.82 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.79 (s, 3H), 3.62−3.51 (m, 2H), 2.59−2.48 (m, 2H), 1.75 (s, 3H), 1.10 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 157.8, 146.8, 141.2, 133.3, 131.9, 128.3, 128.1, 127.9, 127.5, 126.8, 126.1, 125.8, 124.5, 113.6, 60.3, 55.3, 44.7, 44.1, 28.2. HRMS (ESI-TOF): calcd for $C_{21}H_{22}O_2Na$ (M + Na^+) 329.1512, found 329.1512.

((*R*)-3-(4-Methoxyphenyl)-3-(3-thienyl)-1-butene ((*R*)-3fa)) (Table 2, Entry 6). Colorless oil. 72% yield (52.9 mg, **3fa**/**4fa** = 99/1). $[\alpha]^{25}_D$ +10.5 (*c* 1.04, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.25 (dd, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 2.9 Hz, 1H), 7.14 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.97−6.94 (m, 1H), 6.86−6.83 (m, 1H), 6.83 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.35 (dd, $^3J_{HH}$ = 17.3 and 10.5 Hz, 1H), 5.15 (d, $^3J_{HH}$ = 10.5 Hz, 1H), 4.91 (d, $^3J_{HH}$ = 17.3 Hz, 1H), 3.80 (s, 3H), 1.77 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 158.0, 149.3, 146.3, 139.7, 128.5, 128.2, 125.3, 120.7, 113.5, 112.9, 55.3, 47.6, 27.7. HRMS (APCI-TOF): calcd for $C_{15}H_{17}OS$ (M + H^+) 245.0995, found 245.0992.

(*R*)-3-(4-Methoxyphenyl)-3-(3-thienyl)-1-butanol ((*R*)-8fa). Colorless oil. 52% yield (29.6 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 11.4 min (major enantiomer), 15.5 min (minor enantiomer). 89% ee. $[\alpha]^{25}_D$ −6.2 (*c* 1.07, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.22 (dd, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 2.9 Hz, 1H), 7.14 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.03−7.00 (m, 1H), 6.82 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.78 (dd, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 3.78 (s, 3H), 3.60−3.53 (m, 2H), 2.44−2.32 (m, 2H), 1.65 (s, 3H), 1.05 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 157.9, 151.0, 140.5, 127.7, 125.6, 119.7, 113.6, 60.2, 55.3, 44.7, 42.8, 28.2. HRMS (ESI-TOF): calcd for $C_{15}H_{18}O_2SNa$ (M + Na^+) 285.0920, found 285.0917.

((*R*)-3-(4-Methoxyphenyl)-3-methyl-5-phenyl-1-pentene ((*R*)-3ga)) (Table 2, Entry 7). Colorless oil. 98% yield (78.2 mg, **3ga**/**4ga** > 99/1). $[\alpha]^{20}_D$ −7.7 (*c* 0.91, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.28 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 7.26 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.16 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.14 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 6.88 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.08 (dd, $^3J_{HH}$ = 17.4 and 10.7 Hz, 1H), 5.13 (d, $^3J_{HH}$ = 10.7 Hz, 1H), 5.08 (d, $^3J_{HH}$ = 17.5 Hz, 1H), 3.81 (s, 3H), 2.50 (ddd, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 12.5 and 5.0 Hz, 1H), 2.42 (ddd, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 12.7 and 5.0 Hz, 1H), 2.09 (ddd, $^2J_{HH}$ = 13.1 Hz and $^3J_{HH}$ = 12.7 and 4.9 Hz, 1H), 2.00 (ddd, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 12.6 Hz, 1H), 1.44 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.8, 147.1, 143.2, 139.3, 128.5, 128.4, 127.8, 125.8, 113.7 111.9, 55.3, 44.0, 43.5, 31.3, 25.3. HRMS (APCI-TOF): calcd for $C_{19}H_{23}O$ (M + H^+) 267.1743, found 267.1744.

(*R*)-3-(4-Methoxyphenyl)-3-methyl-5-phenyl-1-pentanol ((*R*)-8ga). Colorless oil. 62% yield (52.0 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 13.3 min (major enantiomer), 19.6 min (minor enantiomer). 64% ee. $[\alpha]^{25}_D$ −21.2 (*c* 1.16, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.28 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.24 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.15 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.11−7.06 (m, 2H), 6.89 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 3.81 (s, 3H), 3.64−3.53 (m, 1H), 3.53−3.44 (m, 1H), 2.46 (td, J_{HH} = 13.0 Hz and $^3J_{HH}$ = 5.0 Hz, 1H), 2.25 (td, J_{HH} = 13.0 Hz and $^3J_{HH}$ = 4.4 Hz, 1H), 2.12−1.97 (m, 2H), 1.92−1.81 (m, 2H), 1.41 (s, 3H), 0.96 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 157.7, 143.0, 138.8, 128.42, 128.36, 127.3, 125.7, 113.8, 59.8, 55.3, 46.2, 46.1, 39.5, 30.7, 24.2. HRMS (ESI-TOF): calcd for $C_{19}H_{24}O_2Na$ (M + Na^+) 307.1669, found 307.1663.

((*S*)-3-Cyclohexyl-3-(4-methoxyphenyl)-1-butene ((*S*)-3ha)) (Table 2, Entry 8). Colorless oil. 91% yield (66.4 mg, **3ha**/**4ha** > 99/1). The ee was determined on two Daicel Chiralcel OJ-H columns with hexane/2-propanol = 97/3, flow = 0.7 mL/min. Retention times: 15.0 min (major enantiomer), 22.9 min (minor enantiomer). 76% ee. $[\alpha]^{20}_D$ −41.8 (*c* 1.12, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.22 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.84 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.15 (dd, $^3J_{HH}$ = 17.5 and 10.9 Hz, 1H), 5.12 (d, $^3J_{HH}$ = 10.8 Hz, 1H), 5.00 (d, $^3J_{HH}$ = 17.5 Hz, 1H), 3.79 (s, 3H), 1.76−1.59 (m, 5H), 1.51−1.43 (m, 1H), 1.31 (s, 3H), 1.25−1.01 (m, 3H), 1.00−0.84 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 157.5, 145.8, 140.3, 127.8, 113.4, 112.6, 55.3, 47.5, 46.8, 28.3, 28.0, 27.4, 27.3, 26.9, 21.1. HRMS (APCI-TOF): calcd for $C_{17}H_{25}O$ (M + H^+) 245.1900, found 245.1897.

Equation 8 ((*S*)-3aa: R = Ph) (CAS 1301717-33-8 for (*S*)). Colorless oil. 75% yield (53.8 mg, **3aa**/**4aa** = 98/2). $[\alpha]^{30}_D$ −6.2 (*c* 1.18, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[17]

(*S*)-8aa (CAS 1334512-30-9 for (*S*)). Colorless oil. 65% yield (37.4 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 8.7 min (major enantiomer), 12.7 min (minor enantiomer). 56% ee. $[\alpha]^{25}_D$ −1.6 (*c* 0.95, C_6H_6).

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Equation 8 ((*R*)-3ga: R = CH_2CH_2Ph). Colorless oil. 94% yield (75.3 mg, **3ga**/**4ga** > 99/1). $[\alpha]^{25}_D$ −6.8 (*c* 1.40, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1.

(*R*)-8ga. Colorless oil. 29% yield (23.2 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 13.0 min (major enantiomer), 19.3 min (minor enantiomer). 40% ee. $[\alpha]^{25}_D$ −26.9 (*c* 1.02, $CHCl_3$).

Equation 9 ((*S*)-(*Z*)-3aa-*d*). Colorless oil. 90% yield (64.9 mg, **3aa**/**4aa** > 99/1, *Z*/*E* = 93/7). $[\alpha]^{30}_D$ −11.6 (*c* 1.08, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.30−7.25 (m, 2H), 7.23−7.16 (m, 3H), 7.12 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.82 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.37 (d, $^3J_{HH}$ = 10.5 Hz, 1H), 5.15 (d, $^3J_{HH}$ = 10.6 Hz, 0.93H), 4.88 (d, $^3J_{HH}$ = 17.3 Hz, 0.07H), 3.79 (s, 3H), 1.77 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.9, 148.5, 146.8, 140.3, 129.0, 128.1, 127.9, 126.0, 113.5, 112.7 (t, $^1J_{CD}$ = 23.8 Hz), 55.3, 49.6, 27.5. HRMS (APCI-TOF): calcd for $C_{17}H_{18}DO$ (M + H^+) 240.1493, found 240.1489.

(*S*)-8aa-*d*. Colorless oil. 53% yield (36.8 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 8.6 min (major enantiomer), 13.0 min (minor enantiomer). 90% ee. $[\alpha]^{30}_D$ −3.1 (*c* 0.88, C_6H_6). ^{1}H NMR ($CDCl_3$): δ 7.27 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.22−7.15 (m, 3H), 7.12 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.81 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.79 (s, 3H), 3.55−3.48 (m, 1H), 2.41 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 1.65 (s, 3H), 1.02 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 157.7, 149.6, 141.4, 128.3, 128.2, 127.2, 126.0, 113.6, 59.9 (t, $^1J_{CD}$ = 21.7 Hz), 55.3, 44.6, 44.3, 28.4. HRMS (ESI-TOF): calcd for $C_{17}H_{19}DO_2Na$ (M + Na^+) 280.1418, found 280.1414.

Equation 10 ((*R*)-(*E*)-3aa-*d*). Colorless oil. 96% yield (68.9 mg, **3aa**/**4aa** > 99/1, *Z*/*E* = 7/93). $[\alpha]^{20}_D$ +11.3 (*c* 1.02, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.31−7.24 (m, 2H), 7.24−7.17 (m, 3H), 7.13 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.82 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.38 (d, $^3J_{HH}$ = 17.5 Hz, 1H), 5.15 (d, $^3J_{HH}$ = 10.6 Hz, 0.07H), 4.89 (d, $^3J_{HH}$ = 17.3 Hz, 0.93H), 3.79 (s, 3H), 1.77 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.9, 148.5, 146.8, 140.3, 128.9, 128.1, 127.9, 126.0, 113.5, 112.6 (t, $^1J_{CD}$ = 24.0 Hz), 55.3, 49.6, 27.4. HRMS (APCI-TOF): calcd for $C_{17}H_{18}DO$ (M + H^+) 240.1493, found 240.1489.

(*R*)-8aa-*d*. Colorless oil. 58% yield (43.2 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol =90/10, flow =1.0 mL/min. Retention times: 9.1 min (minor enantiomer), 13.1 min (major enantiomer). 90% ee. $[\alpha]^{30}_D$ +2.4 (*c* 0.90, C_6H_6).

Procedure for Equation 6. A solution of CuCl (1.5 mg, 15 μmol), (*S*,*S*)-**L6** (8.2 mg, 17 μmol), and NaOMe (32.4 mg, 0.600 mmol) in THF (0.40 mL) was stirred for 15 min at room temperature. Compound **2a** (132.0 mg, 0.600 mmol) was added, and the mixture was stirred for 5 min at room temperature. Allyl phosphate **1** (0.300 mmol) was then added with additional THF (0.20 mL), and the resuting mixture was stirred for 20 h at 60 °C. After dilution with EtOAc, the reaction mixture was passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane to afford compounds **3** and **4**.

For ee analysis, compound **3** was converted to the corresponding alcohol **8** through a hydroboration−oxidation sequence: BH_3·SMe_2 (0.15 mL, 0.30 mmol; 2.0 M solution in THF) was added to a solution of compound **3** in THF (1.0 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. NaOH(aq) (1 M, 0.45 mL) and 30 wt % H_2O_2(aq) (61 μL, 0.600 mmol) were successively added at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated NaCl(aq) and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane to afford compound **8**.

(*R*)-1-Ethenyl-1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene ((*R*)-3ia: X = CH_2). Colorless oil. 83% yield (67.8 mg, **3ia**/**4ia** > 99/1). $[\alpha]^{25}_D$ +33.9 (*c* 0.90, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.15−7.10 (m, 2H), 7.07 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 7.07−7.04 (m, 1H), 6.93 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 6.80 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.26 (dd, $^3J_{HH}$ = 17.4 and 10.6 Hz, 1H), 5.28 (dd, $^3J_{HH}$ = 10.5 Hz and $^2J_{HH}$ = 1.3 Hz, 1H), 4.76 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 1.3 Hz, 1H), 3.78 (s, 3H), 2.90−2.78 (m, 2H), 2.17 (ddd, $^2J_{HH}$ = 13.4 Hz and $^3J_{HH}$ = 9.5 and 2.9 Hz, 1H), 2.06 (ddd, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 7.9 and 2.9 Hz, 1H), 1.86−1.76 (m, 1H), 1.73−1.63 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 157.8, 146.7, 141.1, 140.8, 137.6, 130.9, 129.6, 129.2, 126.1, 125.4, 115.5, 113.3, 55.3, 50.5, 37.9, 30.0, 19.4. HRMS (APCI-TOF): calcd for $C_{19}H_{21}O$ (M + H^+) 265.1587, found 265.1581.

(*R*)-2-(1-(4-Methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)ethanol ((*R*)-8ia). Colorless oil. 31% yield (22.3 mg). The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 11.9 min (major enantiomer), 17.5 min (minor enantiomer). 91% ee. $[\alpha]^{20}_D$ +13.9 (*c* 1.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.17−7.08 (m, 4H), 6.96 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.77 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.76 (s, 3H), 3.71−3.62 (m, 1H), 3.61−3.52 (m, 1H), 2.84−2.71 (m, 2H), 2.52−2.41 (m, 2H), 2.08−1.96 (m, 2H), 1.75−1.67 (m, 1H), 1.62−1.52 (m, 1H), 1.12 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 157.5, 143.0, 141.1, 138.3, 129.5, 129.1, 128.5, 126.1, 125.9, 113.3, 60.5, 55.3, 44.7, 44.4, 37.9, 30.2, 19.2. HRMS (ESI-TOF): calcd for $C_{19}H_{22}O_2Na$ (M + Na^+) 305.1512, found 305.1511.

(*R*)-4-Ethenyl-4-(4-methoxyphenyl)chromane ((*R*)-3ja: X = O). Colorless oil. 90% yield (72.8 mg, **3ja**/**4ja** = 99/1). $[\alpha]^{25}_D$ +12.5 (*c* 1.02, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.14 (ddd, $^3J_{HH}$ = 8.4 and 7.2 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 7.10 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.90 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 6.85 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 6.82 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.83−6.80 (m, 1H), 6.23 (dd, $^3J_{HH}$ = 17.3 and 10.5 Hz, 1H), 5.36 (dd, $^3J_{HH}$ = 10.6 Hz and $^2J_{HH}$ = 0.9 Hz, 1H), 4.86 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 0.8 Hz, 1H), 4.18 (ddd, $^2J_{HH}$ = 10.9 Hz and $^3J_{HH}$ = 7.8 and 3.0 Hz, 1H), 4.03 (ddd, $^2J_{HH}$ = 11.0 Hz and $^3J_{HH}$ = 7.4 and 2.9 Hz, 1H), 3.79 (s, 3H), 2.38 (ddd, $^2J_{HH}$ = 13.9 Hz and $^3J_{HH}$ = 7.7 and 2.9 Hz, 1H), 2.20 (ddd, $^2J_{HH}$ = 13.9 Hz and $^3J_{HH}$ = 7.5 and 2.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 158.1, 154.8, 145.3, 138.6, 131.0, 129.6, 128.1, 126.3, 120.0, 117.0, 116.7, 113.5, 63.0, 55.3, 47.0, 36.1. HRMS (APCI-TOF): calcd for $C_{18}H_{19}O_2$ (M + H^+) 267.1380, found 267.1375.

(*S*)-2-(4-(4-Methoxyphenyl)chroman-4-yl)ethanol ((*S*)-8ja). Colorless oil. 56% yield (43.4 mg). The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 80/20, flow = 0.8 mL/min. Retention times: 9.8 min (major enantiomer), 11.1 min (minor enantiomer). 92% ee. $[\alpha]^{25}_D$ −11.0 (*c* 0.97, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.17 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.11 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.04 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.90 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.87 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 6.81 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 4.14 (dt, $^2J_{HH}$ = 11.0 Hz and $^3J_{HH}$ = 3.9 Hz, 1H), 3.84 (td, J_{HH} = 11.1 Hz and $^3J_{HH}$ = 1.8 Hz, 1H), 3.77 (s, 3H), 3.72−3.64 (m, 1H), 3,64−3.57 (m, 1H), 2.53−2.41 (m, 2H), 2.38 (ddd, $^2J_{HH}$ = 13.9 Hz and $^3J_{HH}$ = 11.1 and 3.4 Hz, 1H), 2.08 (ddd, $^2J_{HH}$ = 13.9 Hz and $^3J_{HH}$ = 3.3 and 2.3 Hz, 1H), 1.23 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 157.9, 155.4, 141.3, 129.2, 128.5, 128.1, 126.1, 120.4, 117.5, 113.6, 62.8, 60.0, 55.3, 43.3, 41.6, 35.8. HRMS (ESI-TOF): calcd for $C_{18}H_{20}O_3Na$ (M + Na^+) 307.1305, found 307.1302.

Procedure for Equation 7. A solution of CuCl (1.5 mg, 15 μmol), (*S*,*S*)-**L6** (8.2 mg, 17 μmol), and NaOMe (48.6 mg, 0.900 mmol) in THF (0.40 mL) was stirred for 15 min at room temperature. Compound **2a** (198 mg, 0.900 mmol) and THF (0.20 mL) were added, and the mixture was stirred for 5 min at room temperature. (*E*,*E*)-**9** (147 mg, 0.300 mmol) was then added with additional THF (0.30 mL), and the resuting mixture was stirred for 60 h at 30 °C. After dilution with EtOAc, the reaction mixture was passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/20 to afford 1,4-bis(2-(4-methoxyphenyl)-3-buten-2-yl)benzene **10** as a colorless oil (113 mg, 0.283 mmol; 94% yield, regioselectivity: >99/1). $[\alpha]^{30}_D$ +5.4 (*c* 2.00, $CHCl_3$). The absolute configuration was assigned by analogy with Table 1, entry 1. ^{1}H NMR ($CDCl_3$): δ 7.13 (d, $^3J_{HH}$ = 8.9 Hz, 4H), 7.10 (s, 4H), 6.82 (d, $^3J_{HH}$ = 8.8 Hz, 4H), 6.36 (dd, $^3J_{HH}$ = 17.3 and 10.5 Hz, 2H), 5.15 (dd, $^3J_{HH}$ =

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10.6 Hz and $^2J_{HH}$ = 0.9 Hz, 2H), 4.89 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 1.0 Hz, 2H), 3.79 (s, 6H), 1.75 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 157.8, 147.1, 145.9, 140.4, 129.0, 127.4, 113.4, 112.8, 55.3, 49.3, 27.4. HRMS (APCI-TOF): calcd for $C_{28}H_{31}O_2$ (M + H^+) 399.2319, found 399.2318.

For ee and diastereoselectivity analyses, compound **10** was converted to 3,3′-(1,4-phenylene)bis(3-(4-methoxyphenyl)butanol) **11** through a hydroboration−oxidation sequence: BH_3·SMe_2 (0.30 mL, 0.60 mmol; 2.0 M solution in THF) was added to a solution of compound **10** (113 mg, 0.283 mmol) in THF (1.0 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. NaOH(aq) (1 M, 0.60 mL) and 30 wt % H_2O_2(aq) (82 μL, 0.80 mmol) were successively added at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated NaCl(aq) and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/1 to afford compound **11** as a colorless oil (61.6 mg, 0.142 mmol; 50% yield). The ee and diastereoselectivity were determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 16.2 min (major enantiomer), 21.6 min [meso isomer], and 28.7 min (minor enantiomer). 99% ee, chiral/meso = 92/8. $[\alpha]^{25}_D$ −2.0 (*c* 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.11 (d, $^3J_{HH}$ = 8.8 Hz, 4H), 7.09 (s, 4H), 6.81 (d, $^3J_{HH}$ = 8.8 Hz, 4H), 3.78 (s, 6H), 3.55−3.46 (m, 4H), 2.38 (t, $^3J_{HH}$ = 7.3 Hz, 4H), 1.62 (s, 6H), 1.03 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ 157.7, 146.9, 141.3, 128.2, 126.8, 113.5, 60.3, 55.3, 44.4, 44.2, 28.3. HRMS (ESI-TOF): calcd for $C_{28}H_{34}O_4Na$ (M + Na^+) 457.2349, found 457.2354.

■ ASSOCIATED CONTENT

Supporting Information

HPLC data for asymmetric reactions, X-ray crystal structure of compound (*S*,*S*)-**L6**, and ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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