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A Class of Benzene Backbone-Based Olefin−Sulfoxide Ligands for Rh-Catalyzed Enantioselective Addition of Arylboronic Acids to Enones

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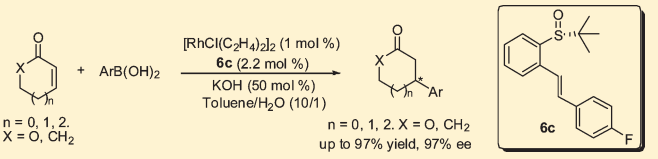
Supporting Information

ABSTRACT: A class of readily available and easily tunable benzene backbone-based olefin−sulfoxide ligands was developed for the rhodium-catalyzed asymmetric conjugate addition reaction of arylboronic acids to enones with up to 97% yield and 97% ee.



In the past few years, significant efforts have been made on the development of the highly efficient chiral ligands in Rh-catalyzed asymmetric 1,4-addition of organoboron reagents, which has rapidly developed into a powerful tool for the stereoselective formation of carbon−carbon bonds.[1−6] Pioneered by the groups of Hayashi and Carreira, chiral olefins as a new class of promising ligands have attracted great attention in recent years,[7−9] and many excellent olefin-based ligands such as diene ligands,[10−23] olefin−phosphine ligands,[24−30] and olefin−nitrogen ligands[31,32] have been successfully developed in the Hayashi−Miyaura asymmetric reactions. Meanwhile, except for a chiral auxiliary in numerous asymmetric transformations, the application of sulfoxides[33] as ligands, especially the chiral bis-sulfoxides,[34−38] has most recently been appealing in the Hayashi−Miyaura reaction.

In view of ready availability, air and moisture stability, and fine chiral environment of sulfoxides, as well as the relatively good coordination ability of alkenes and sulfoxides to transition metals, we envisioned that the combination of alkenes and sulfoxides would allow the advantages of each class to be united which provided good opportunities to find highly efficient hybrid ligands. However, examples on the combination of alkenes with inherent chiral sulfoxides into chiral olefin−sulfoxide hybrid ligands were very few;[39−43] the sulfoxides were mainly limited to *tert*-butylsulfinyl groups, and the incorporation of alkenes with different sulfinyl groups was still absent (Figure 1). Herein, we present our efforts on the development of a class of readily available and easily tunable benzene backbone-based olefin−sulfoxide ligands for the rhodium-catalyzed asymmetric addition reaction.

Inspired by recent success of olefin−oxazoline[32] and bis-sulfoxide[36] ligands based on benzene backbone in asymmetric catalysis, a benzene ring was chosen as an internal ring skeleton to strengthen the coordination ability of alkenes to transition metals. Olefin and sulfoxide frameworks attached to the benzene ring in a 1,2-fashion would be helpful for the coordination of olefins and sulfoxides to transition metals. We reasoned that the combination of η^2-binding olefins with η^1-binding sulfoxide would allow new coordination geometries and possibilities in the class of hybrid ligands. Moreover, to further examine the influence of electronic and steric modulations at the olefin−sulfoxide hybrid ligands on the reactivity and enantioselectivity of the Rh-catalyzed Hayashi−Miyaura reaction, the ligands bearing different sulfinyl moieties were also examined, and thus the highly modular and easily tunable olefin−sulfoxide ligands were formed (Scheme 1). Subsequently, a series of electronically and sterically varied benzene backbone-based olefin−sulfoxide ligands (Figure 2) were prepared in a facile two-step synthesis.

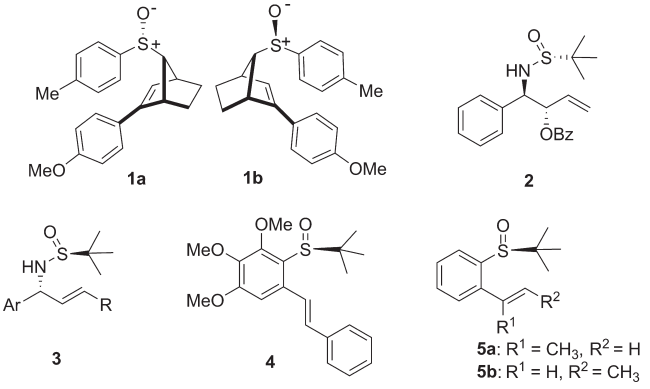


Figure 1. Very recent examples of olefin−sulfoxide ligands.

As an illustrative example, the synthesis of ligand **6c** bearing a (*R*)-*tert*-butylsulfinyl group was discussed (Scheme 2). Horner−Wadsworth−Emmons reaction of commercially available diethyl 2-bromobenzylphosphonate **9**[44] with 4-fluorobenzaldehyde provided (*E*)-1-bromo-2-(4-fluorostyryl)benzene **10c** in good yield. After standard bromo-lithium exchange of bromoarene derivative with *n*-BuLi at low temperature, the commercially available (*R*)-thiosulfinate was subsequently added and the desired product (*R*,*E*)-**6c** was obtained in 54% overall yield. It was worth noting that the Horner−Wadsworth−Emmons reaction of 3,4-dimethoxybenzaldehyde and 2,4,6-trimethoxybenzaldehyde selectively gave *Z*-isomers. Thus, the addition of (*R*)-thiosulfinate could finally afford (*R*,*Z*)-**7a** and (*R*,*Z*)-**7b** ligands.

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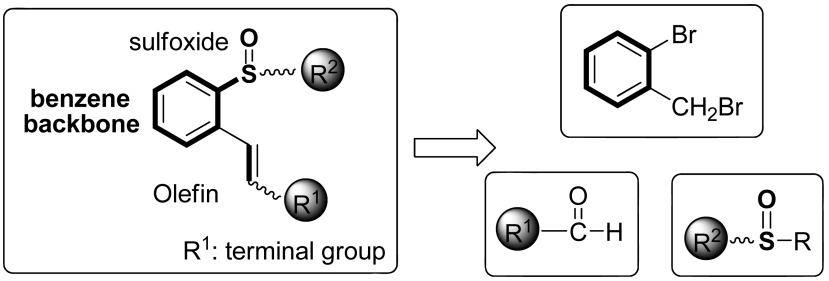
Scheme 1. Modular Olefin−Sulfoxide Ligand Assembly, Retrosynthetic Procedure



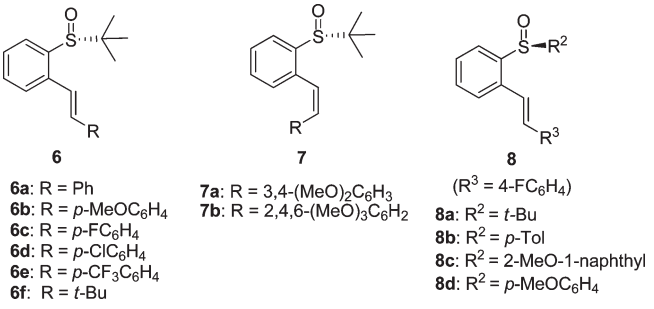
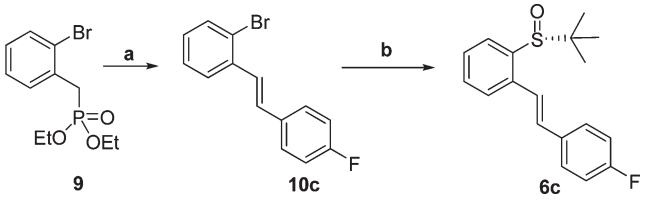


Figure 2. Olefin−sulfoxide ligands in this work.

Scheme 2. Synthesis of Olefin−Sulfoxide Ligand 6c[a]

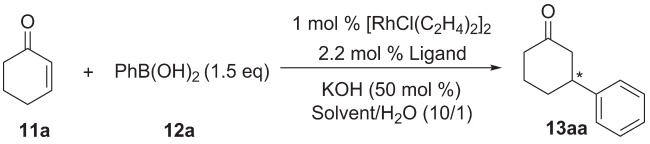


[a] Reagents and conditions: (a) NaH, THF, 0 °C to rt, 1 h; then 4-fluorobenzaldehyde, THF, 0 °C to rt, overnight, 87% yield; (b) *n*-BuLi, THF, −78 °C; then (*R*)-thiosulfinate, THF, −78 °C to rt, overnight, 62% yield.

To further enrich the electronical and sterical effect of olefin−sulfoxide ligands, ligands **8a**−**8d** (Figure 2) bearing different sulfinyl moieties were synthesized by similar procedures.

With the ligands in hand, the rhodium-catalyzed addition of phenylboronic acid to cyclohexenone was used as the model reaction to test the catalytic efficiency of this new series of ligands (Table 1). The reaction proceeded smoothly and afforded the desired product in 90% yield with 74% ee when using ligand **6a** (entry 1). Contrary to our anticipation, when ligand **6b** was employed which possesses an electron-donating *para*-methoxy group on the terminal benzene ring, both the catalytic reactivity and enantioselectivity decreased (89% yield and 41% ee, entry 2). The use of ligand **7a** with two methoxy groups on its terminal benzene ring gave a much lower ee value (8% ee, entry 3), whereas the 2,4,6-trimethoxy analogue afforded high ee value (91% ee, entry 4). When electron-withdrawing groups were screened on the *para*-position of the benzene ring, higher reactivities and enantioselectivities were obtained (entries 5−7). However, when a *tert*-butyl group was used as the terminal group instead of the aromatic group (ligand **6f**), no desired product was observed

Table 1. Screening Reaction Conditions of the Addition of Phenylboronic Acid to Cyclohexenone[a]



entry	ligand	solvent	yield[b] (%)	ee[c,d] (%)
1	**6a**	toluene	94	76 (*S*)
2	**6b**	toluene	89	41 (*S*)
3	**7a**	toluene	94	8 (*S*)
4	**7b**	toluene	78	91 (*S*)
5	**6c**	toluene	94	92 (*S*)
6	**6d**	toluene	96	87 (*S*)
7	**6e**	toluene	92	90 (*S*)
8	**6f**	toluene	trace	nd[h]
9	**8a**	toluene	94	87 (*R*)
10	**8b**	toluene	89	21 (*R*)
11	**8c**	toluene	79	48 (*S*)
12	**8d**	toluene	92	20 (*R*)
13[e]	**6c**	toluene	93	83 (*S*)
14[f]	**6c**	toluene	94	91 (*S*)
15[g]	**6c**	toluene	91	82 (*S*)
16	**6c**	DCM	93	89 (*S*)
17	**6c**	dioxane	56	82 (*S*)
18	**6c**	THF	trace	nd
19	**6c**	CH_3CN	trace	nd
20	**6c**	DMF	trace	nd

[a] The reaction was carried out with 2-cyclohexenone (0.30 mmol), arylboronic acid (0.45 mmol), $[RhCl(C_2H_4)_2]_2$ (0.003 mmol), ligand (0.0066 mmol, 1.1 equiv of Rh), and 0.75 M aq KOH (0.20 mL) in toluene (2.0 mL) at 40 °C for 0.5−3 h monitored by TLC unless otherwise stated. [b] Isolated yield based on 2-cyclohexenone. [c] Determined by HPLC analysis. [d] The configuration was determined by comparing the optical rotation with the reported one. [e] Reaction run with 2 mol % of catalyst at rt for 1 h. [f] Reaction run with 2 mol % of catalyst at 60 °C for 0.25 h. [g] Reaction run with 1 mol % catalyst at 40 °C for 0.5 h. [h] Not determined.

(entry 8). In addition to the influence of the alkene moiety with different substituents on the yield and selectivity, the change of chiral sulfinyl groups of sulfoxide moieties also obviously affected the outcome of the reaction. Compared with ligand **6c**, ligand **8a** bearing (*S*)-*tert*-butylsulfinyl groups showed decreased enantioselectivity (87% ee) with the retention of yield (94%, entry 9),

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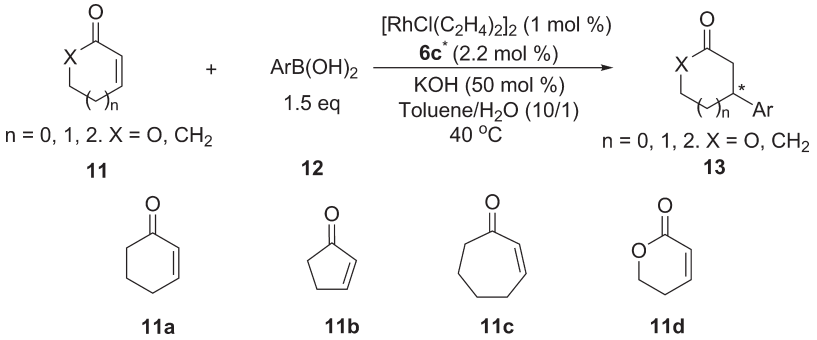
Table 2. Substrate Scope in the Addition Reaction Using 6c Ligand[a]



entry	enone (**11**)	boronic acid (**12**)	product (**13**)	yield[b] (%)	ee[c,d] (%)
1	**11a**	Ph (**12a**)	**13aa**	94	92 (*S*)
2	**11a**	2-MeOC$_6$H$_4$ (**12b**)	**13ab**	91	95 (*S*)
3	**11a**	3-MeOC$_6$H$_4$ (**12c**)	**13ac**	84	96 (*S*)
4	**11a**	4-MeOC$_6$H$_4$ (**12d**)	**13ad**	89	97 (*S*)
5	**11a**	2-MeC$_6$H$_4$ (**12e**)	**13ae**	85	90 (*S*)
6	**11a**	4-MeC$_6$H$_4$ (**12f**)	**13af**	89	91 (*S*)
7	**11a**	4-CF$_3$C$_6$H$_4$ (**12g**)	**13ag**	90	84 (*S*)
8	**11a**	3-CF$_3$C$_6$H$_4$ (**12h**)	**13ah**	97	88 (*S*)
9	**11a**	2-FC$_6$H$_4$ (**12i**)	**13ai**	84	95 (*S*)
10	**11a**	4-FC$_6$H$_4$ (**12j**)	**13aj**	96	96 (*S*)
11	**11a**	4-ClC$_6$H$_4$ (**12k**)	**13ak**	97	90 (*S*)
12	**11a**	4-*t*-BuC$_6$H$_4$ (**12l**)	**13al**	91	83 (*S*)
13	**11a**	1-naphthyl (**12m**)	**13am**	86	91 (*S*)
14	**11a**	2-naphthyl (**12n**)	**13an**	83	86 (*S*)
15	**11b**	Ph (**12a**)	**13ba**	91	93 (*S*)
16	**11c**	Ph (**12a**)	**13ca**	89	65 (*S*)
17	**11d**	Ph (**12a**)	**13da**	95	91 (*S*)

[a] The reaction was carried out with enone (0.30 mmol), arylboronic acid (0.45 mmol), [RhCl(C$_2$H$_4$)$_2$]$_2$ (0.003 mmol), ligand **6c** (0.0066 mmol, 1.1 equiv of Rh), and 0.75 M aq KOH (0.20 mL) in toluene (2.0 mL) at 40 °C for 0.5−3 h. [b] Isolated yield was based on enone. [c] Determined by HPLC analysis. [d] The configuration was determined by comparing the optical rotation with the reported one.

whereas the ligands with other aryl sulfinyl groups resulted in a drastic decrease in ee value (entries 10−12). When 2 mol % of catalyst derived from the optimal ligand **6c** was employed, product **13aa** was obtained with high reactivity (94% yield, entry 5) and enantioselectivity (92% ee) at 40 °C. Increasing or decreasing the reaction temperature resulted in a slight decrease in enantioselectivities (entries 13 and 14). Decreasing the catalyst loading to 1 mol % also led to a loss in yield and enantioselectivity (entry 15). Furthermore, the reaction worked well in CH_2Cl_2 or dioxane, albeit with slightly lower yields and ee values (entries 16 and 17). However, when the reaction was conducted in THF, CH_3CN, or DMF, no desired product was found (entries 18−20). Finally, a single sulfoxide ligand (*R*)-*tert*-butylsulfinylbenzene was employed in the model reaction, but no reaction took place. This verified the fact that the alkene moiety was indispensable in our olefin−sulfoxide ligands.

With the optimized reaction conditions in hand, we tested the scope of the reaction using representative enones and boronic acids, and the results are summarized in Table 2. To our delight, both electron-rich and electron-deficient arylboronic acids reacted efficiently to produce the desired products in good yields (83−97%) and high enantioselectivities (83−97% ee). It was worth noting that the position of the substituent on the phenyl ring had little influence on the enantioselectivities (entries 2−10). When five-membered cyclicenone **11b** (entry 15) and α,β-unsaturated cyclic ester **11d** (entry 17) were subjected to this

Table 3. Other Arylboronic Reagents in the Addition Reaction Using 6c Ligand[a]

entry	enone (**11**)	arylboronic reagents	product (**13**)	yield[b] (%)	ee[c,d,e] (%)
1	**11a**	PhBF$_3$K (**14a**)	**13aa**	92	91 (*S*)
2	**11a**	4-MeOC$_6$H$_4$BF$_3$K (**14b**)	**13ad**	90	94 (*S*)
3	**11b**	PhBF$_3$K (**14a**)	**13ba**	90	90 (*S*)
4	**11c**	PhBF$_3$K (**14a**)	**13ca**	90	68 (*S*)
5	**11d**	PhBF$_3$K (**14a**)	**13da**	89	90 (*S*)
6	**11a**	(PhBO)$_3$ (**15**)	**13aa**	92	44 (*S*)
7	**11b**	(PhBO)$_3$ (**15**)	**13ba**	89	75 (*S*)
8	**11c**	(PhBO)$_3$ (**15**)	**13ca**	56	5 (*S*)
9	**11d**	(PhBO)$_3$ (**15**)	**13da**	87	77 (*S*)
10	**11a**	Ph$_4$BNa (**16**)	**13aa**	trace	nd[f]

[a] General procedure: see Table 2. [b] Isolated yield was based on enone. [c] Determined by HPLC analysis. [d] The configuration was determined by comparing the optical rotation with the reported one. [e] See the Supporting Information for details. [f] Not determined.

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reaction, good enantioselectivities were also obtained. Unfortunately, lower ee was observed for the seven-membered cyclic-enone **11c** (65% ee, entry 16).

To further examine the reactivity of this catalyst, the reaction of different cyclic enones (**11**) with trifluoroborate salts (**14**), boronate ester (**15**), and tetraarylborate salts (**16**) were studied under the optimal reaction conditions (Table 3). To our delight, moderate to good yields and enantioselectivities were also obtained by the reaction of cyclic enones with potassium trifluoroborate salts (89−92% yield, 68−94% ee, entries 1−5). However, drastic decrease of the enantioselectivity was observed when phenyl boronate ester was employed (5−77% ee, entries 6−9), and sodium tetraarylborate (**16**) only gave a trace amount of product (entry 10).

In conclusion, a class of simple and readily available benzene backbone-based chiral olefin−sulfoxide ligands was developed and successfully applied in the rhodium-catalyzed asymmetric conjugate addition reaction of arylboronic acids to enones with high yields and great enantioselectivities. Such a kind of ligands with both modularity and versatility can be easily varied on its steric and electronic properties over a wide range, thus making these types of ligands attractive and promising for asymmetric catalysis.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under nitrogen using standard Schlenk techniques. Commercially available reagents were used without further purification. Solvents were dried according to the standard procedure.

General Procedure for the Synthesis of 10. To a suspension of NaH (60% in oil, 0.44 mg, 11.0 mmol) in THF (5 mL) at 0 °C was slowly added diethyl 2-bromobenzylphosphonate **9**[44] (3.07 g, 10.0 mmol). The resulting suspension was stirred for an additional 1 h at room temperature. The reaction mixture was cooled to 0 °C, and then a solution of aldehyde (10.0 mmol) in THF (5 mL) was added dropwise and slowly warmed to room temperature. After stirring overnight, the reaction was quenched with ice water and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by silica gel flash column chromatography to give product **10**.

*(E)-1-Bromo-2-styrylbenzene (**10a**) (ref 45):* following general procedure with benzaldehyde, colorless oil, 89% yield; ^{1}H NMR (400 MHz, acetone) δ 7.80 (d, J = 7.8 Hz, 1H), 7.62 (dd, J = 7.8, 2.5 Hz, 3H), 7.51 (d, J = 16.3 Hz, 1H), 7.39 (q, J = 7.2 Hz, 3H), 7.31 (t, J = 7.3 Hz, 1H), 7.25−7.15 (m, 2H); ^{13}C NMR (100 MHz, acetone) δ 137.2 (d, J = 6.2 Hz), 133.2, 131.9, 129.4, 128.9, 128.4, 128.1, 127.1, 126.9, 123.8.

*(E)-1-Bromo-2-(4-methoxystyryl)benzene (**10b**) (ref 46):* following general procedure with 4-methoxybenzaldehyde, white solid, 88% yield, mp 65−67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.36−7.22 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 16.2 Hz, 1H), 6.90 (d, J = 8.3 Hz, 2H), 3.81 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 137.5, 133.2, 131.1, 129.9, 128.5, 128.2, 127.6, 126.6, 125.4, 124.1, 114.3, 55.5.

*(E)-1-Bromo-2-(4-fluorostyryl)benzene (**10c**):* following general procedure with 4-fluorobenzaldehyde, white solid, 87% yield, mp 55−57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.50 (dd, J = 8.2, 5.6 Hz, 2H), 7.36 (d, J = 16.2 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.08 (dt, J = 17.2, 8.0 Hz, 3H), 6.97 (d, J = 16.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.5,137.1, 133.2, 130.4, 128.9, 128.5 (d, J = 7.4 Hz), 127.9, 127.5 (d, J = 35.2 Hz), 126.8, 124.2, 115.85 (d, J = 21.7 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −113.98 (s, 1F); HRMS (EI, m/z) calcd for $C_{14}H_{10}BrF$ $[M]^+$ 275.9950, found 275.9944.

*(E)-1-Bromo-2-(4-chlorostyryl)benzene (**10d**):* following general procedure with 4-chlorobenzaldehyde, white solid, 93% yield, mp 67−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 13.1 Hz, 3H), 7.31 (dd, J = 15.2, 8.0 Hz, 3H), 7.16−7.09 (m, 1H), 6.97 (d, J = 16.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 135.7, 133.8, 133.3, 130.2, 129.1 (d, J = 10.5 Hz), 128.1, 127.7, 126.8, 124.3; HRMS (EI, m/z) calcd for $C_{14}H_{10}BrCl$ $[M]^+$ 291.9654, found 291.9665.

*(E)-1-Bromo-2-(4-(trifluoromethyl)styryl)benzene (**10e**):* following general procedure with 4-(trifluoromethyl)benzaldehyde, white solid, 85% yield, mp 44−46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (t, J = 6.3 Hz, 1H), 7.63−7.58 (m, 5H), 7.54 (d, J = 16.2 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 16.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 136.6, 133.3, 130.1 (d, J = 10.8 Hz), 129.6, 127.8, 127.0 (d, J = 6.0 Hz), 125.8 (d, J = 2.8 Hz), 124.5, 122.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ −63.07 (s, 3F); HRMS (EI, m/z) calcd for $C_{15}H_{10}BrF_3$ $[M]^+$ 325.9918, found 325.9910.

*(E)-1-Bromo-2-(3,3-dimethylbut-1-enyl)benzene (**10f**):* following general procedure with pivalaldehyde, colorless oil, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 12.0, 7.9 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.13−6.95 (m, 1H), 6.64 (d, J = 16.0 Hz, 1H), 6.17 (d, J = 16.0 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 137.9, 132.8, 128.1, 127.4, 126.9, 124.1, 123.7, 33.8, 29.6; HRMS (EI, m/z) calcd for $C_{12}H_{15}Br$ $[M]^+$ 238.0357, found 238.0353.

*(Z)-4-(2-Bromostyryl)-1,2-dimethoxybenzene (**10g**):* following general procedure with 3,4-dimethoxybenzaldehyde, white solid, 80% yield, mp 98−101 °C; ^{1}H NMR (400 MHz, acetone) δ 7.84−7.72 (m, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.37 (dd, J = 15.9, 9.4 Hz, 2H), 7.26−7.14 (m, 4H), 6.97 (d, J = 8.3 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, acetone) δ 150.9, 150.1, 133.9, 132.9, 129.7, 128.9, 127.7, 125.6, 121.2, 112.9, 110.9, 56.2; HRMS (ESI, m/z) calcd for $C_{16}H_{15}BrO_2Na$ $[M + Na]^+$ 341.0153, found 341.0160.

*(Z)-2-(2-Bromostyryl)-1,3,5-trimethoxybenzene (**10h**):* following general procedure with 2,4,6-trimethoxybenzaldehyde, light yellow solid, 78% yield, mp 104−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 16.5 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.37−7.24 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.17 (s, 2H), 3.90 (s, 6H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, acetone) δ160.9, 133.9, 128.9 (d, J = 16.3 Hz), 128.5, 126.9, 124.3, 123.7, 91.9, 56.4, 55.8; HRMS (ESI, m/z) calcd for $C_{17}H_{17}BrO_3Na$ $[M + Na]^+$ 371.0259, found 371.0252.

Representative Procedure for the Synthesis of Chiral Olefin−Sulfoxide Ligand 6c. At −78 °C, n-BuLi (5.25 mmol) was added dropwise to a solution of (*E*)-1-bromo-2-(4-fluorostyryl)benzene **10c** (1.38 g, 5.0 mmol) in THF (15 mL). The resulting mixture was stirred for 1 h at −78 °C, and a solution of (*R*)-*tert*-butyl *tert*-butanethiosulfinate (1.02 g, 5.25 mmol) in THF (10 mL) was slowly added. After stirring for an additional 1 h at −78 °C, the solution was allowed to warm to room temperature and stirred for another 1 h, then quenched with cold saturated aqueous NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by flash chromatography to afford (*R*,*E*)-**6c** as a white solid: 0.94 g, 62% yield.

*(R,E)-1-(tert-Butylsulfinyl)-2-styrylbenzene (**6a**):* white solid, 62% yield, mp 77−80 °C; $[\alpha]^{20}_D$ = 209.4 (c = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.1 Hz, 1H), 7.71 (dd, J = 7.5, 1.0 Hz, 1H), 7.54−7.45 (m, 5H), 7.39 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 16.1 Hz, 1H), 1.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 136.9, 131., 131.3, 129.0, 128.5, 127.8, 126.9, 126.7, 125.6, 124.4, 64.7, 23.5; HRMS (ESI, m/z) calcd for $C_{18}H_{20}OSNa$ $[M + Na]^+$ 307.1133, found 307.1133.

*(R,E)-1-(tert-Butylsulfinyl)-2-(4-methoxystyryl)benzene (**6b**):* colorless oil, 66% yield, $[\alpha]^{20}_D$ = 186.5 (c = 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.52−7.39 (m, 4H), 7.36 (d, J = 16.1 Hz, 1H), 7.01 (d, J = 16.1 Hz, 1H), 6.92 (d, J =

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8.5 Hz, 2H), 3.83 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 138.1 (d, J = 7.1 Hz), 131.3 (d, J = 15.3 Hz), 131.0, 130.1, 129.6, 128.1, 127.3, 126.5, 125.2, 122.1, 114.4, 58.3, 55.4, 23.4; HRMS (ESI, m/z) calcd for $C_{19}H_{22}O_2SNa$ $[M + Na]^+$ 337.1238, found 337.1241.

*(R,E)-1-(tert-Butylsulfinyl)-2-(4-fluorostyryl)benzene (**6c**):* white solid, 62% yield, mp 87−90 °C; $[\alpha]^{20}_D$ = 237.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.6, 1.5 Hz, 1H), 7.71−7.66 (m, 1H), 7.52−7.45 (m, 4H), 7.42 (d, J = 16.1 Hz, 1H), 7.08 (t, J = 8.6 Hz, 2H), 7.02 (d, J = 16.1 Hz, 1H), 1.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 161.9, 138.5, 137.8, 133.1, 131.3, 130.3, 128.4 (d, J = 8.0 Hz), 127.8, 126.7, 125.5, 124.2, 116.1, 115.9, 58.4, 23.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −113.53 (s, 1F); HRMS (ESI, m/z) calcd for $C_{18}H_{19}FOSNa$ $[M + Na]^+$ 325.1038, found 325.1044.

*(R,E)-1-(tert-Butylsulfinyl)-2-(4-chlorostyryl)benzene (**6d**):* white solid, 60% yield, mp 113−116 °C; $[\alpha]^{20}_D$ = 220.5 (c = 1.0, $CDCl_3$) ^{1}H NMR (400 MHz, acetone) δ 7.88 (dd, J = 10.2, 8.0 Hz, 2H), 7.67−7.62 (m, 3H), 7.61−7.52 (m, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 16.2 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, acetone) δ 140.5, 138.4, 136.9, 134.3,132.1, 130.9, 129.9, 129.4, 128.7, 127.5, 126.4, 125.8, 58.5, 23.5; HRMS (ESI, m/z) calcd for $C_{18}H_{19}ClOSNa$ $[M + Na]^+$ 341.0743, found 341.0737.

*(R,E)-1-(tert-Butylsulfinyl)-2-(4-(trifluoromethyl)styryl)benzene (**6e**):* white solid, 61% yield, mp 77−79 °C; $[\alpha]^{20}_D$ = 183.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97−7.91 (m, 1H), 7.75−7.70 (m, 1H), 7.68−7.57 (m, 5H), 7.51 (p, J = 7.3 Hz, 2H), 7.08 (d, J = 16.1 Hz, 1H), 1.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3 138.9 137.3 131.4 130.2, 129.9 (q, $J_{C,F}$ = 32.6 Hz), 128.3, 126.9, 125.9 (q, $J_{C,F}$ = 3.5 Hz), 125.7, 123.2, 58.5 23.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −63.15 (s, 3F); HRMS (ESI, m/z) calcd for $C_{19}H_{19}F_3OSNa$ $[M + Na]^+$ 375.1006, found 375.1009.

*(R,E)-1-(tert-Butylsulfinyl)-2-(3,3-dimethylbut-1-enyl)benzene (**6f**):* white solid, 57% yield, mp 47−50 °C; $[\alpha]^{20}_D$ = 138.1 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, acetone) δ 7.81 (d, J = 9.1 Hz, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.53−7.43 (m, 2H), 6.77 (d, J = 16.0 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 1.14 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, acetone) δ145.3 139.3 131.9, 127.8, 127.2 126.5 122.2 58.7, 34.5, 23.6; HRMS (ESI, m/z) calcd for $C_{16}H_{24}OSNa$ $[M + Na]^+$ 287.1446, found 287.1448.

*(R,Z)-4-(2-(tert-Butylsulfinyl)styryl)-1,2-dimethoxybenzene (**7a**):* light yellow oil, 82% yield; $[\alpha]^{20}_D$ = 124.2 (c = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, acetone) δ 7.85 (d, J = 7.8 Hz, 2H), 7.58−7.49 (m, 2H), 7.46 (d, J = 16.0 Hz, 1H), 7.22 (dd, J = 9.0, 7.0 Hz, 2H), 7.17 (dd, J = 8.3, 1.8 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, acetone) δ 151.1 150.7, 139.9, 139.1132.3 132.0, 131.1 127.9, 127.3, 126.1 122.8, 121.1 112.9, 111.1 56.3 30.6 23.6; HRMS (ESI, m/z) calcd for $C_{20}H_{24}O_3SNa$ $[M + Na]^+$ 367.1344, found 367.1344.

*(R,Z)-2-(2-(tert-Butylsulfinyl)styryl)-1,3,5-trimethoxybenzene (**7b**):* light yellow solid, 89% yield, mp 110−113 °C; $[\alpha]^{20}_D$ = 224.7 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 16.4 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 9.7 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 6.16 (s, 2H), 3.89 (s, 6H), 3.83 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.26,158.6 139.7 138.1 130.9, 129.8127.5, 126.9, 126.6 126.0 (t, J = 18.7 Hz), 125.3, 124.7 123.2 122.1, 107.4 90.9 90.6 58.3 55.9, 55.4, 55.3, 23.5; HRMS (ESI, m/z) calcd for $C_{21}H_{26}O_4SNa$ $[M + Na]^+$ 397.1450, found 397.1437.

*(S,E)-1-(tert-Butylsulfinyl)-2-(4-fluorostyryl)benzene (**8a**):* following the general procedure with (*S*)-*tert*-butyl *tert*-butanethiosulfinate in place of (*R*)-*tert*-butyl *tert*-butanethiosulfinate, gray-white solid, 63% yield, mp 66−68 °C; $[\alpha]^{20}_D$ = −199.7 (c = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.3, 1.9 Hz, 1H), 7.68 (dd, J = 7.5, 1.5 Hz, 1H), 7.50−7.45 (m, 4H), 7.43 (d, J = 16.1 Hz, 1H), 7.13−7.06 (m, 2H), 7.02 (d, J = 16.1 Hz, 1H), 1.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9 161.9 138.6, 137.8, 133.1, 131.3 130.3 128.4 (d, J = 8.1 Hz), 127.8, 126.8 125.5, 124.3 116.1, 115.9, 58.4, 23.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −113.53 (s, 1F); HRMS (ESI, m/z) calcd for $C_{18}H_{19}FOSNa$ $[M + Na]^+$ 325.1038, found 325.1039.

*(S,E)-1-(4-Fluorostyryl)-2-(p-tolylsulfinyl)benzene (**8b**):* following the general procedure with (1*S*,2*R*,5*S*)-(+)-menthyl-(*S*)-*p*-Tol-sulfinate in place of (*R*)-*tert*-butyl *tert*-butanethiosulfinate, white solid, 55% yield, mp 82−85 °C; $[\alpha]^{20}_D$ = −115.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01−7.96 (m, 1H), 7.61 (dd, J = 5.9, 3.1 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.47−7.43 (m, 7H), 7.24 (d, J = 8.1 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.07 (t, J = 8.6 Hz, 2H), 6.94 (d, J = 16.1 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 161.9, 143.1, 142.2,141.5,136.1, 132.9, 131.3 (d, J = 13.1 Hz), 130.1, 128.7, 128.5 (d, J = 8.1 Hz), 126.1, 125.4, 124.9 (d, J = 9.6 Hz), 123.0, 115.9 (d, J = 21.8 Hz), 21.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −113.31 (s, 1F); HRMS (ESI, m/z) calcd for $C_{21}H_{17}FOSNa$ $[M + Na]^+$ 359.0882, found 359.0890.

*(R,E)-1-(2-(4-Fluorostyryl)phenylsulfinyl)-2-methoxynaphthalene (**8c**):* following the general procedure with (*S*)-L-menthyl 2-methoxy-1-naphthalensulfinate[47] in place of (*R*)-*tert*-butyl *tert*-butanethiosulfinate, white solid, 50% yield, mp 95−97 °C; $[\alpha]^{20}_D$ = −162.2 (c = 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (dd, J = 8.7, 0.7 Hz, 1H), 8.36 (dd, J = 8.0, 1.2 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.74 (dd, J = 8.2, 0.5 Hz, 1H), 7.57−7.50 (m, 2H), 7.47 (d, J = 7.2 Hz, 1H), 7.42−7.36 (m, 2H), 7.07 (d, J = 9.1 Hz, 1H), 6.96−6.83 (m, 5H), 6.63 (d, J = 15.9 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 161.4, 157.6, 141.7, 135.1, 134.6, 132.8, 132.4, 130.1, 129.9, 129.2, 128.9, 128.5, 128.23, 127.3, 126.6, 125.6, 124.4, 123.7, 123.0, 122.6, 115.4, 115.3, 113.4, 56.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.09 (s, 1F); HRMS (ESI, m/z) calcd for $C_{25}H_{19}FO_2SNa$ $[M + Na]^+$ 425.0987, found 425.0977.

*(S,E)-1-(4-Fluorostyryl)-2-(4-methoxyphenylsulfinyl)benzene (**8d**):* following the general procedure for the preparation with (*S*)-L-menthyl *p*-methoxybenzenesulfinate[48] instead of (*R*)-*tert*-butyl *tert*-butanethiosulfinate, white solid, 63% yield, mp 80−82 °C; $[\alpha]^{20}_D$ = −291.1 (c = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06−8.01 (m, 1H), 7.59−7.53 (m, 1H), 7.51−7.40 (m, 6H), 7.37 (d, J = 16.0 Hz, 1H), 7.10−7.04 (m, 2H), 6.91 (d, J = 16.0 Hz, 1H), 6.89−6.85 (m, 2H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 161.8, 142.9, 136.3, 135.7, 132.9, 131.2, 131.0, 128.6, 128.36 (d, J = 8.1 Hz), 127.48 (s), 126.1, 124.5, 122.8, 115.9, 115.8, 114.76, 55.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −113.38 (s, 1F); HRMS (ESI, m/z) calcd for $C_{21}H_{17}FO_2SNa$ $[M + Na]^+$ 375.0831, found 375.0839.

Asymmetric 1,4-Addition of Arylboronic Acids to Enones. Under nitrogen atmosphere, a mixture of $[RhCl(C_2H_4)_2]_2$ (1.2 mg, 0.003 mmol) and **6c** (2.0 mg, 0.0066 mmol) in 1 mL toluene was stirred at room temperature for 1 h, at which time arylboronic acid (0.45 mmol) was added, followed by enone (0.30 mmol), aqueous KOH (0.75 M in H_2O, 0.20 mL, 0.15 mmol), and toluene (1 mL). The reaction was stirred at 40 °C and monitored by TLC. When the reaction was over, the reaction mixture was concentrated in vacuo and purified by silica gel flash column chromatography to afford the product.

*3-Phenylcyclohexanone (**13aa**) (ref 16):* colorless oil, 94% yield, 92% ee, $[\alpha]^{20}_D$ = −12.6 (c = 1.0, $CHCl_3$); Chiracel AD-H column, 210 nm, *n*-hexane/*i*-propanol = 97/3, flow = 0.8 mL/min, t_R = 9.9 and 11.8 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.28 (m, 2H), 7.26−7.19 (m, 3H), 3.01 (tt, J = 11.8, 3.9 Hz, 1H), 2.62−2.34 (m, 4H), 2.18−2.05 (m, 2H), 1.90−1.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.1, 144.5, 128.8, 126.7, 49.0, 44.9, 41.3, 32.9, 25.6.

*3-(2-Methoxyphenyl)cyclohexanone (**13ab**) (ref 16):* colorless oil, 91% yield, 95% ee, $[\alpha]^{20}_D$ = −31.3 (c = 1.0, $CHCl_3$); Chiracel OJ-H column, 210 nm, *n*-hexane/*i*-propanol = 98/2, flow = 1.0 mL/min, t_R = 13.4 and 14.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.13 (m, 2H), 6.94 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 3.81 (s, 3H), 3.49−3.36 (m, 1H), 2.65−2.31 (m, 4H), 2.20−1.97 (m, 2H), 1.92−1.73 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9, 156.8, 138.2, 132.2,127.6, 126.6, 120.7, 110.8, 55.3, 47.7, 41.5, 38.0, 31.1, 25.7.

*3-(3-Methoxyphenyl)cyclohexanone (**13ac**) (ref 16):* colorless oil, 84% yield, 96% ee, $[\alpha]^{20}_D = -10.4$ (c = 0.8, $CHCl_3$); Chiracel AD-H column, 210 nm, *n*-hexane/*i*-propanol = 95/5, flow = 0.6 mL/min, t_R = 16.6 and 18.1 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 7.6 Hz, 1H), 6.79 (dd, J = 14.9, 7.4 Hz, 3H), 3.80 (s, 3H), 3.09−2.88 (m, 1H), 2.66−2.27 (m, 4H), 2.22−1.99 (m, 2H), 1.94−1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 159.9, 146.1, 129.7, 118.9, 112.8, 111.7, 55.2, 48.9, 44.8, 41.2, 32.7, 25.6.

*3-(4-Methoxyphenyl)cyclohexanone (**13ad**) (ref 49):* white solid, 89% yield, 97% ee, $[\alpha]^{20}_D = -14.3$ (c = 1.0, $CHCl_3$); Chiracel OJ-H column, 210 nm, *n*-hexane/*i*-propanol = 98/2, flow =1.0 mL/min, t_R = 33.8 and 40.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 3.09−2.82 (m, 1H), 2.66−2.22 (m, 4H), 2.17−1.94 (m, 2H), 1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 158.5, 136.6, 127.6, 114.1, 55.3, 49.3, 44.0, 41.2, 33.1, 25.6.

*3-o-Tolylcyclohexanone (**13ae**) (ref 49):* colorless oil, 85% yield, 90% ee, $[\alpha]^{20}_D = -32.6$ (c = 1.0, $CHCl_3$); Chiracel AD-H column, 210 nm, *n*-hexane/*i*-propanol = 95/5, flow = 0.6 mL/min, t_R = 10.0 and 11.8 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26−7.18 (m, 2H), 7.17−7.10 (m, 2H), 3.28−3.15 (m, 1H), 2.54−2.41 (m, 4H), 2.32 (s, 3H), 2.17 (m,1H), 2.04−1.97 (m, 1H), 1.86−1.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.2, 142.4, 135.2, 130.8, 126.52, 125.2, 48.4, 41.4, 40.4, 32.1, 25.9, 19.4.

*3-p-Tolylcyclohexanone (**13af**) (ref 16):* white solid, 89% yield, 91% ee, $[\alpha]^{20}_D = -12.6$ (c = 1.0, $CHCl_3$); Chiracel AD-H column, 210 nm, *n*-hexane/*i*-propanol = 95/5, flow = 0.6 mL/min, t_R = 9.9 and 11.1 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14−7.09 (m, 4H), 3.07−2.87 (m, 1H), 2.60−2.33 (m, 4H), 2.32 (s, 3H), 2.13−2.01 (m, 2H), 1.87−1.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.1, 141.5, 136.3, 129.4, 126.5, 49.1, 44.5, 41.3, 32.9, 25.6, 21.0.

*3-(4-(Trifluoromethyl)phenyl)cyclohexanone (**13ag**) (ref 16):* white solid, 90% yield, 84% ee, $[\alpha]^{20}_D = -8.1$ (c = 1.0, $CHCl_3$); Chiracel AS-H column, 210 nm, *n*-hexane/*i*-propanol = 90/10, flow = 0.7 mL/min, t_R = 12.6 and 13.9 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 3.08 (m, 1H), 2.68−2.32 (m, 4H), 2.25−2.03 (m, 2H), 1.96−1.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2, 148.4, 129.2 (q, $J_{C,F}$ = 32.1 Hz), 127.1, 125.8 (q, J = 3.7 Hz), 124.3 (d, $J_{C,F}$ = 271.4 Hz), 48.6, 44.6, 41.2, 32.6, 25.5.

*3-(3-(Trifluoromethyl)phenyl)cyclohexanone (**13ah**) (ref 34):* colorless oil, 97% yield, 88% ee, $[\alpha]^{20}_D = -9.5$ (c = 1.0, $CHCl_3$); Chiracel OJ-H column, 210 nm, *n*-hexane/*i*-propanol = 99.5/0.5, flow = 0.5 mL/min, t_R = 41.7 and 45.4 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61−7.35 (m, 4H), 3.08 (tt, J = 12.0, 3.9 Hz, 1H), 2.69−2.35 (m, 4H), 2.23−2.06 (m, 2H), 1.96−1.73 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2, 145.3, 131.2 (q, $J_{C,F}$ = 31.7 Hz), 130.2, 129.3, 124.2 (d, $J_{C,F}$ = 270.7 Hz), 123.7 (q, $J_{C,F}$ = 3.75 Hz), 123.4 (q, $J_{C,F}$ = 3.64 Hz), 48.8, 44.6, 41.2, 32.7, 25.5.

*3-(2-Fluorophenyl)cyclohexanone (**13ai**) (ref 34):* colorless oil, 84% yield, 95% ee, $[\alpha]^{20}_D = -8.8$ (c = 1.0, $CHCl_3$); Chiracel AD-H column, 210 nm, *n*-hexane/*i*-propanol = 95/5, flow = 0.8 mL/min, t_R = 8.8 and 10.3 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34−7.16 (m, 2H), 7.16−6.99 (m, 2H), 3.42−3.24 (m, 1H), 2.65−2.32 (m, 4H), 2.20−2.00 (m, 2H), 1.97−1.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.6, 161.6, 159.7, 131.1 (d, J = 14.0 Hz), 128.3 (d, J = 8.4 Hz), 127.7 (d, J = 4.7 Hz), 124.4 (d, J = 3.4 Hz), 115.9, 115.7, 47.3, 41.3, 38.2, 31.3, 25.5.

*3-(4-Fluorophenyl)cyclohexanone (**13aj**) (ref 34):* colorless oil, 96% yield, 96% ee, $[\alpha]^{20}_D = -12.6$ (c = 0.9, $CHCl_3$); Chiracel AD-H column, 210 nm, *n*-hexane/*i*-propanol = 95/5, flow = 0.8 mL/min, t_R = 9.5 and 11.7 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23−7.10 (m, 2H), 7.07−6.94 (m, 2H), 3.00 (m, 1H), 2.67−2.30 (m, 4H), 2.23−2.02 (m, 2H), 1.88−1.66 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.7, 162.7, 160.8, 140.2, 128.1, 115.6, 115.5, 49.2, 44.1, 41.2, 33.0, 25.5.

*3-(4-Chlorophenyl)cyclohexanone(**13ak**) (ref 49):* colorless oil, 97% yield, 90% ee, $[\alpha]^{20}_D = -7.3$ (c = 1.1, $CHCl_3$); Chiracel AD-H column, 210 nm, *n*-hexane/*i*-propanol = 95/5, flow = 0.8 mL/min, t_R = 9.8 and 10.7 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.24 (m, 2H), 7.20−7.07 (m, 2H), 3.09−2.92 (m, 1H), 2.69−2.30 (m, 4H), 2.26−2.00 (m, 2H), 1.85−1.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.5, 142.9, 132.5, 128.9, 128.1, 48.9, 44.2, 41.2, 32.8, 25.5.

*3-(4-tert-Butylphenyl)cyclohexanone (**13al**) (ref 49):* white solid, 91% yield, 83% ee, $[\alpha]^{20}_D = -9.9$ (c = 0.9, $CHCl_3$); Chiracel AS-H column, 210 nm, *n*-hexane/*i*-propanol = 98/2, flow = 0.6 mL/min, t_R = 21.4 and 24.3 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41−7.33 (m, 2H), 7.20−7.12 (m, 2H), 3.03−2.95 (m, 1H), 2.66−2.30 (m, 4H), 2.19−2.05 (m, 2H), 1.86−1.73 (m, 2H), 1.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.3, 149.6, 141.4, 126.3, 125.6, 49.1, 44.4, 41.3, 34.5, 32.9, 31.5, 25.7.

*3-(Naphthalen-1-yl)cyclohexanone (**13am**) (ref 16):* white solid, 86% yield, 91% ee, $[\alpha]^{20}_D = -48.4$ (c = 0.8, $CHCl_3$); Chiracel AD-H column, 210 nm, *n*-hexane/*i*-propanol = 98/2, flow = 0.6 mL/min, t_R = 19.2 and 21.5 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 11.1 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.59−7.38 (m, 4H), 3.85−3.80 (m, 1H), 2.78−2.40 (m, 4H), 2.26−2.13 (m, 2H), 2.03−1.86 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.2, 140.2, 134.1, 131.0, 129.2, 127.4, 126.3, 125.7, 122.8, 122.6, 48.7, 41.5, 39.5, 32.4, 25.7.

*3-(Naphthalen-2-yl)cyclohexanone (**13an**) (ref 49):* white solid, 83% yield, 86% ee, $[\alpha]^{20}_D = -6.3$ (c = 1.0, $CHCl_3$); Chiracel AD-H column, 210 nm, *n*-hexane/*i*-propanol = 98/2, flow = 0.6 mL/min, t_R = 20.8 and 23.1 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87−7.76 (m, 3H), 7.64 (dd, J = 5.8, 5.4 Hz, 1H), 7.52−7.33 (m, 3H), 3.27−3.11 (m, 1H), 2.75−2.58 (m, 2H), 2.54−2.35 (m, 2H), 2.24−2.11 (m, 2H), 2.02−1.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.9, 141.9, 133.7, 132.5, 128.5, 127.8, 126.3, 125.8, 125.4, 124.9, 48.9, 44.9, 41.4, 32.9, 25.7.

*3-Phenylcyclopentanone (**13ba**) (ref 16):* colorless oil, 91% yield, 93% ee, $[\alpha]^{20}_D = -78.8$ (c = 0.9, $CHCl_3$); Chiracel GC (β-DEX-GAMA-225, 1.0 mL H_2/min, 120 °C isotherm); t_R = 19.8 and 20.8 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.22 (m, 5H), 3.46−3.37 (m, 1H), 2.67 (m, 1H), 2.54−2.22 (m, 4H), 2.09−1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.5, 143.2, 128.8, 126.8, 45.9, 42.3, 38.9, 31.3.

*3-Phenylcycloheptanone (**13ca**) (ref 49):* colorless oil, 89% yield, 65% ee, $[\alpha]^{20}_D = -19.9$ (c = 0.9, $CHCl_3$); Chiracel OD-H column, 210 nm, *n*-hexane/*i*-propanol = 98/2, flow =1.0 mL/min, t_R = 11.7 and 13.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.12 (m, 5H), 3.01−2.85 (m, 2H), 2.70−2.55 (m, 3H), 2.09−1.95 (m, 3H), 1.86−1.73 (m, 2H), 1.56−1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.6, 147.0, 128.8, 126.5, 126.5, 51.4, 44.1, 42.9, 39.3, 29.4, 24.3.

*4-Phenyltetrahydro-2H-pyran-2-one (**13da**) (ref 49):* colorless oil, 95% yield, 91% ee, $[\alpha]^{20}_D = 17.8$ (c = 0.9, $CHCl_3$); Chiracel AS-H column, 210 nm, *n*-hexane/*i*-propanol = 70/30, flow = 0.6 mL/min, t_R = 29.4 and 33.0 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.15 (m, 5H), 4.53−4.35 (m, 2H), 3.24 (m, 1H), 2.92 (dd, J = 17.6, 5.9 Hz, 1H), 2.63 (dd, J = 17.6, 10.7 Hz, 1H), 2.25−2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 142.9, 138.2, 129.1, 127.3, 126.6, 68.9, 37.6, 30.4.

■ ASSOCIATED CONTENT

Supporting Information. Copies of NMR, HRMS, HPLC for racemic and chiral compound spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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