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Chiral Bicyclic Bridgehead Phosphoramidite (Briphos) Ligands for Asymmetric Rhodium-Catalyzed 1,2- and 1,4-Addition

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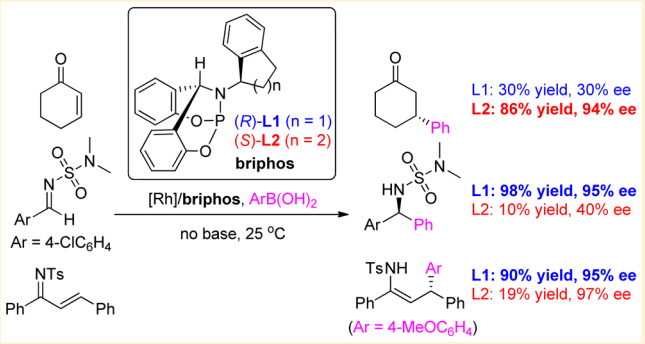
Supporting Information

ABSTRACT: A complementary solution for Rh-catalyzed enantioselective 1,2- and 1,4-arylation with two structurally related chiral ligands is reported. A chiral bicyclic bridgehead phosphoramidite (briphos) ligand derived from 1-aminoindane was efficient for the 1,2-arylation of *N*-sulfonyl imines, while that derived from 1,2,3,4-tetrahydro-1-naphthylamine was efficient for 1,4-arylation of α,β-unsaturated cyclic ketones. For α,β-unsaturated *N*-tosyl ketimines, the briphos derived from 1-aminoindane was found to selectively provide γ,γ-diaryl *N*-tosyl enamines with high yields and stereoselectivities.



INTRODUCTION

The catalytic activity of low-valent transition metals such as Co(I), Ni(0), Rh(I), Pd(0), and Ir(I) is known to be promoted by strong π-acceptor ligands when the reductive elimination is rate-determining in the catalytic cycle.[1,2] The reported π-acceptor phosphorus ligands include phosphoramidites,[3] phosphites,[4] or electron-deficient aryl phosphines.[5] For chiral ligand design, several diol-based chiral platforms such as 1,1′-bi-2-naphthol, 2,2′-biphenol, and TADDOL have been used for making efficient chiral phosphoramidite or phosphite ligands.[6] However, due to their synthetic difficulty and limited availability, chiral π-acceptor phosphorus ligands are not widely used as compared with privileged chiral phosphorus ligands. Thus, it is desirable to develop a scalable and tunable chiral π-acceptor phosphorus ligand to investigate asymmetric low-valent transition-metal catalysis. We recently developed bicyclic bridgehead phosphoramidite (briphos) ligands as a new class of π-acceptor ligands.[7] The geometrical constraints in briphos enhanced the π-acceptor ability, which resulted in significant ligand acceleration effects in Rh-catalyzed conjugate addition reactions. The simple synthetic procedure for briphos ligands allowed facile tuning of the ligand structure[7b] as well as chiral ligand design[7a] by using commercially available chiral primary amines. Here we report that two structurally related chiral briphos ligands **L1** and **L2** can efficiently promote Rh-catalyzed asymmetric 1,2- and 1,4-addition of aryl boronic acids, respectively.

Various ligand platforms including phosphorus,[8] diene,[9] sulfoxide,[10] and NHC[11] as well as its hybrid structure[12] have been creatively used to develop efficient chiral ligands for asymmetric Rh-catalyzed 1,2- or 1,4-addition of aryl boronic acid derivatives to carbonyls, imines, and alkenes.[13] As a new type of chiral ligand, we have reported chiral briphos ligand **L1** derived from 1-aminoindane which is highly efficient and selective for 1,4-addition of aryl boronic acids to α,β-unsaturated *N*,*N*-dimethyl-sulfamoyl imino esters.[7a] Chiral briphos **L1** is a unique type of chiral ligand having only one chiral carbon center, given that many efficient chiral ligands largely rely on the privileged axially chiral structures or chelating effects to achieve a high level of stereoselectivity. Moreover, the favorable ligand effect by briphos ligands allowed the reaction with aryl boronic acids to proceed under neutral conditions at ambient temperature. In order to further investigate Rh-catalyzed asymmetric arylation reactions with chiral briphos ligands, we here selected cyclohexenone (**1a**) and a *N*,*N*-dimethyl sulfamoyl imine (**3a**) as substrates for 1,4- and 1,2-addition, respectively.

RESULTS AND DISCUSSION

We investigated the asymmetric 1,4- and 1,2-addition reactions with $Rh(acac)(C_2H_4)_2$ (1−3 mol %), chiral ligands (1.1−7.5 mol %), and phenylboronic acid (2−3 equiv) at 25 °C. The results are summarized in Table 1. Chiral briphos **L1** from 1-aminoindane was selective for 1,2-addition of **3a** (95% ee) but less selective for 1,4-addition to **1a** (30% ee) (Table 1, entry 1). On the other hand, chiral briphos **L2** from 1,2,3,4-tetrahydro-1-naphthylamine was selective for 1,4-addition of **1a** (94% ee) but less selective for 1,2-addition to **3a** (40% ee) (Table 1, entry 2). A subtle structural difference between five- and six-membered rings in chiral briphos ligands is found to be crucial to control stereoselectivities of Rh-catalyzed 1,2- and 1,4-additions of aryl boronic acids. Other chiral briphos ligands prepared from acyclic chiral amines showed low to moderate enantioselectivity ranging from 16 to 81% ee (Supporting

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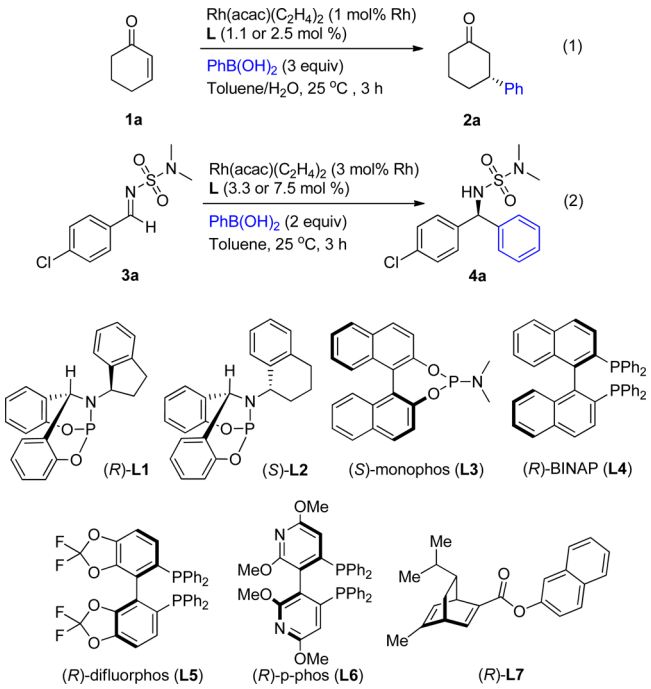
Table 1. Rh-Catalyzed Asymmetric Arylation with Various Chiral Ligands[a]



		2a		4a	
entry	L	yield (%)[b]	ee (%)[c]	yield (%)[b]	ee (%)[c]
1	**L1**	30	−30	**98**	**95** (*S*)
2	**L2**	**86**	**94** (*R*)	10	−40
3	**L3**	10	−89	<5	n.d.
4	**L4**	trace	n.d.	n.r.	n.d.
5	**L5**	trace	n.d.	n.r.	n.d.
6	**L6**	trace	n.d.	n.r.	n.d.
7	**L7**	13	87	24	96
8[d,e]	**L1**	–	–	84[f]	90
9[d,e]	**L2**	60	92	–	–
10[d,e]	**L7**	57	83	89[f]	85

[a]Conditions: (1) **1a** (0.4 mmol), $PhB(OH)_2$ (1.2 mmol), and $[Rh(acac)(C_2H_4)_2]$ (1 mol % Rh) were stirred in toluene (1.0 mL) and H_2O (0.1 mL) at 25 °C for 3 h. (2) **3a** (0.2 mmol), $PhB(OH)_2$ (0.4 mmol), and $[Rh(acac)(C_2H_4)_2]$ (3 mol % Rh) were stirred in toluene (1.0 mL) at 25 °C for 3 h. [b]Yield of isolated product. [c]Determined by chiral-phase HPLC analysis. [d]KOH (1.0 M in H_2O, 0.1 mL) was added. [e]$[Rh(C_2H_4)_2Cl]_2$ was used. [f]Decomposition of **3a** to 4-chlorobenzaldehyde was observed.

Information).[14] Thus, we found that chiral briphos **L1** and **L2** with fused bicyclic chiral amines are efficient chiral ligand structures, and they can be a complementary solution for Rh-catalyzed enantioselective 1,2- or 1,4-addition of boronic acids.

The reactivity and selectivity of chiral briphos were compared with known efficient chiral ligands **L3**−**L7**. Under the same reaction conditions, chiral phosphorus ligands including monophos (**L3**),[6,8b] BINAP (**L4**),[8c,e] difluorphos (**L5**),[5a,e] and *p*-phos (**L6**)[15] showed poor reactivity (<10%), although monophos (**L3**) showed high enantioselectivity of 89% (Table 1, entries 3−6). A chiral diene ligand **L7**[16] was found to be selective for both 1,2- and 1,4-addtion to give 96 and 87% ee but gave products with only 24 and 13% yields, respectively (Table 1, entry 7). It has been demonstrated that base additives enhance Rh-catalyzed additions of aryl boronic acids.[8c] Indeed, in the case of chiral diene **L7**, an addition of KOH increased the product yield with compatible stereoselectivity (Table 1, entry 10). However, the reactions with chiral briphos **L1** and **L2** were retarded by the addition of KOH (Table 1, entries 8 and 9). Thus, compared with existing chiral ligands, chiral briphos ligands will be useful for the Rh-catalyzed boronic acid addition under mild and neutral reaction conditions.

With two chiral briphos **L1** and **L2**, we then explored the reaction scope of the Rh-catalyzed 1,4- and 1,2-additions of aryl boronic acids. First, chiral briphos **L2** was used for 1,4-addition of aryl boronic acids to *α,β*-unsaturated ketones (Scheme 1, left). When phenylboronic acid was used with Rh/**L2**, 2-cyclohexenone provided the product **2a** with high yield (86%) and stereoselectivity (94% ee), but 2-cyclopentenone and 2-cycloheptenone provided the products **2b** and **2c** with somewhat reduced stereoselectivity of 77% and 83% ee, respectively. Aryl boronic acids substituted with electron-donating Me and OMe groups proceeded at 25 °C, while those substituted with electron-withdrawing F and CF_3 groups required elevated temperature of 50 °C due to reduced reactivity. The results showed that high enantioselectivity of 88−91% was observed for meta- or para-substituted aryl boronic acids, while reduced enantioselectivity was found for ortho-substituted ones such as 2-methylphenyl boronic acid (73% ee) and 1-naphthyl boronic acid (85% ee). An acyclic enone, 3-hepten-2-one, provided the product **2m** with moderate yield (69%) and low enantioselectivity (42% ee), whereas a heteroaromatic boronic acid, 2-thienyl boronic acid, yielded no product.

Second, chiral briphos **L1** was used for the Rh-catalyzed 1,2-addition of aryl boronic acids to *N,N*-dimethyl sulfamoyl imines (Scheme 1, right). Aryl imines with a substituent such as Cl, F, CF_3, Br, Me, and OMe at the para position reacted with phenylboronic acid to provide the products **4a**−**f** with high yields (80−98%) and good enantioselectivity (87−95% ee). In addition, the reactions with aryl imines prepared from *m*- or *o*-chlorobenzaldehyde or 2-thiophenecarboxaldehyde as well as those with *p*-methoxyphenyl, *p*-tolyl, or *m*-tolyl boronic acids gave the desired products **4g**−**l** with moderate to good yield (65−97%) and high enantioselectivity (89−96% ee). However, *o*-tolyl and 2-thienyl boronic acids provided no product.

In the Rh-catalyzed arylations with aryl boronic acids, chiral briphos **L1** was selective for 1,2-addition of *N,N*-dimethyl sulfamoyl imines and chiral briphos **L2** was selective for 1,4-addition of *α,β*-unsaturated ketones. We then expanded the reaction to *α,β*-unsaturated *N*-tosyl ketimines (**5**) in which both 1,2- and 1,4-reactions may take place. The arylation reactions were performed with [Rh] (5 mol %) and 4-methoxyphenyl boronic acid (3 equiv) at 25 °C for 30 h with chiral ligands **L1**−**L7** (5.5−12.5 mol %) (Table 2). Indeed, both chiral briphos **L1** and **L2** were selectively promoted the 1,4-addition reaction to provide *γ,γ*-diaryl *N*-tosyl enamine **6a** with good enantioselectivities (94 and 97% ee). However, chiral briphos **L1** showed high yield (90%), while chiral briphos **L2** showed low yield (19%) (Table 2, entries 1 and 2). Other chiral phosphorus ligands **L3**−**L6** were inactive (Table 2, entries 3−6). In addition, chiral diene ligand **L7** provided the product with low yield (25%) and poor selectivity (47% ee) (Table 2, entry 7). Addition of KOH was not affected to the yield and stereoselectivity (Table 2, entries 8 and 9). In consideration of reactivity and selectivity, chiral briphos **L1** was found to be the most suitable for Rh-catalyzed 1,4-addition of *α,β*-unsaturated *N*-tosyl ketimines.

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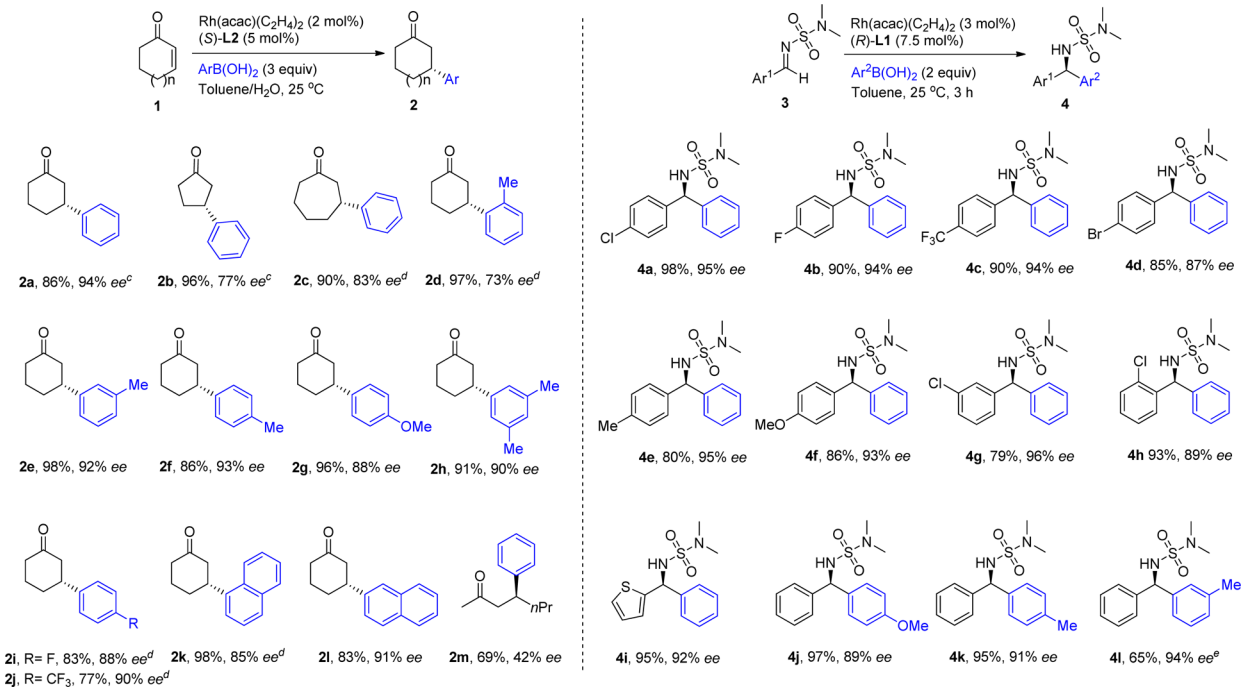
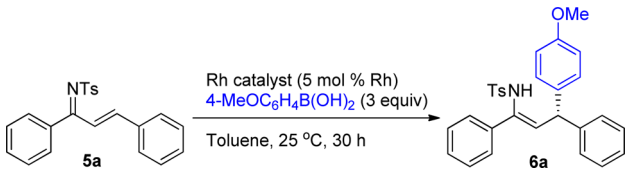
Scheme 1. Substrate Scope of Rh/Briphos-Catalyzed Asymmetric 1,4- and 1,2-Addition Reactions[a−g]



[a]Conditions for **2**: **1** (0.4 mmol), $ArB(OH)_2$ (1.2 mmol), $[Rh(acac)(C_2H_4)_2]$ (2 mol %), and (*S*)-**L2** (5 mol %) were stirred in toluene (1.0 mL) and H_2O (0.1 mL) at 25 °C. [b]Conditions for **4**: **3** (0.2 mmol), $ArB(OH)_2$ (0.4 mmol), $[Rh(acac)(C_2H_4)_2]$ (3 mol %), and (*R*)-**L1** (7.5 mol %) were stirred in toluene (1.0 mL) at 25 °C for 3 h. [c]1 mol % Rh was used. [d]Reaction conducted at 50 °C. [e]Reaction conducted for 10 h. [f]Yield of isolated product. [g]ee was determined by chiral-phase HPLC analysis.

Table 2. Ligand Screening for Rh-Catalyzed Asymmetric 1,4-Addition of *α,β*-Unsaturated *N*-tosyl Ketimine[a]



entry	Rh catalyst	ligand	yield (%)[b]	ee (%)[c]
1	$Rh(acac)(C_2H_4)_2$	**L1**	90	94
2	$Rh(acac)(C_2H_4)_2$	**L2**	19	−97
3	$Rh(acac)(C_2H_4)_2$	**L3**	trace	n.d.
4	$Rh(acac)(C_2H_4)_2$	**L4**	n.r.	n.d.
5	$Rh(acac)(C_2H_4)_2$	**L5**	n.r.	n.d.
6	$Rh(acac)(C_2H_4)_2$	**L6**	n.r.	n.d.
7	$Rh(acac)(C_2H_4)_2$	**L7**	25	47
8[d]	$[Rh(C_2H_4)_2Cl]_2$	**L1**	88	94
9[d]	$[Rh(C_2H_4)_2Cl]_2$	**L7**	27	44

[a]Conditions: **5a** (0.2 mmol), $4\text{-}MeOC_6H_4B(OH)_2$ (0.6 mmol), and [Rh] (5 mol %) were stirred in toluene (1.0 mL) at 25 °C for 30 h. [b]Yield of isolated product. [c]Determined by chiral-phase HPLC analysis. [d]KOH (1.0 M in H_2O, 0.1 mL) was added.

The reaction scope of Rh-catalyzed 1,4-addition of arylboronic acids to *α,β*-unsaturated *N*-tosyl ketimines **5** was investigated with chiral briphos **L1** (Scheme 2). Aryl boronic acids substituted with *t*Bu, Me, or OMe at the meta or para positions provided the products **6a−e** with good yields (80−95%) and enantioselectivities (91−96%) at ambient temperature. In addition, aryl boronic acids substituted with electron-withdrawing groups F, Cl, or Br required the addition of KOH additive to proceed the reaction to give products **6g−j** with moderate yields (35−80%) but good enantioselectivity (91−93%). However, *o*-tolyl and 2-thienyl boronic acids provided no product. Several substituted *α,β*-unsaturated *N*-tosyl ketimines with Me, Cl, or F groups were reacted with 4-methoxyphenyl or phenylboronic acid to provide the corresponding enamines **6k−q** with good yields (70−96%) and stereoselectivities (91−97% ee), although 4-NO_2-substituted *N*-tosyl ketimine gave the product **6r** with low yield (51%) and moderate stereoselectivity (84% ee).

CONCLUSION

In summary, chiral bicyclic bridgehead phosphoramidite (briphos) ligands derived from fused bicyclic amines were successfully applied for Rh-catalyzed enantioselective 1,2- and 1,4-addition of aryl boronic acids under neutral conditions at 25−50 °C. Chiral briphos **L1** prepared from 1-aminoindane was used for 1,2-addition of *N,N*-dimethyl sulfamoyl imines to provide products **4** with 79−98% yields and 87−96% enantioselectivities. Chiral briphos **L2** prepared from 1,2,3,4-tetrahydro-1-naphthylamine was used for 1,4-addition of *α,β*-unsaturated cyclic ketones **1** to provide products **2** with 77−98% yields and 73−94% enantioselectivities. Thus, two chiral briphos **L1** and **L2** based on bicyclic fused chiral amines can be used as a complementary solution for Rh-catalyzed 1,2- and 1,4-addition of aryl boronic acids. In addition, chiral briphos **L1** was found to be selective for 1,4-addition of *α,β*-unsaturated *N*-tosyl ketimines to provide products **6** with 35−99% yields and 84−97% enantioselectivities.

EXPERIMENTAL SECTION

General Information. Commercially available compounds were used without further purification or drying. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded for characterization of

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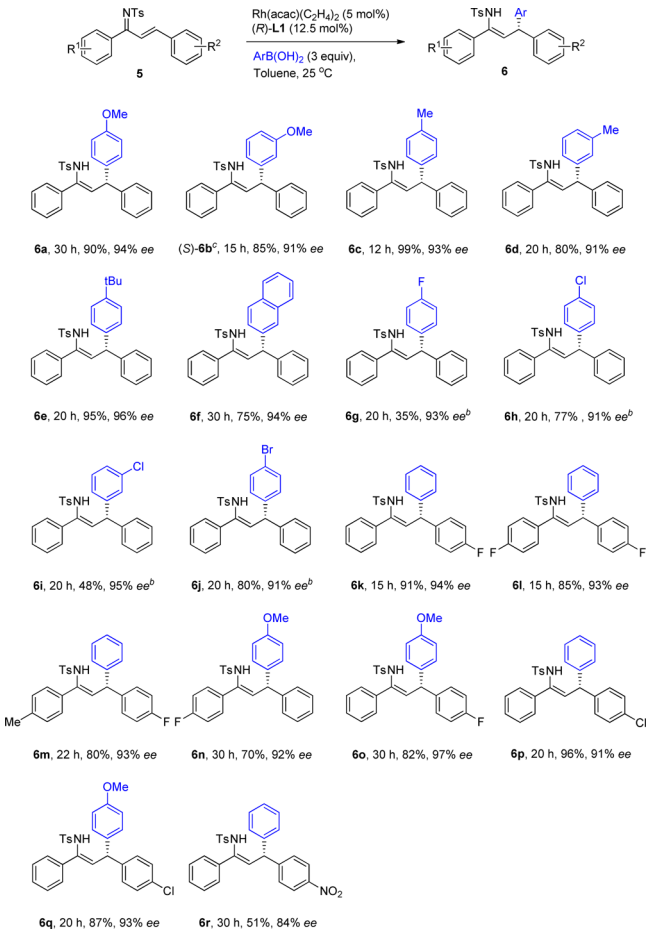
Scheme 2. Substrate Scope of Rh/L1-Catalyzed Asymmetric 1,4-Addition of α,β-Unsaturated Ketimines[a−e]



[a]Conditions: **5** (0.2 mmol), $ArB(OH)_2$ (0.6 mmol), and [Rh(acac)-$(C_2H_4)_2$] (5 mol %), and (*R*)-**L1** (12.5 mol %) were stirred in toluene (2.0 mL) at 25 °C. [b]KOH (100 mol %, 1.0 M in aq) was added. [c]The absolute configuration was determined by comparison of the specific optical rotation with literature[17] after acid hydrolysis of **6b**. [d]Yield of isolated product. [e]ee was determined by chiral-phase HPLC analysis.

compounds. Mass spectra were obtained using a TOF-Q high-resolution mass spectrometer (ESI). HPLC analysis was performed on UV detection monitored at 210, 230, or 254 nm, using Chiralpak AD-H, OD-H, OB-H, OJ-H, IA, IB, IC, and ID column (250 × 4.5 mm ID). Substrates (**3**[18] and **5**[19]) and chiral briphos (**L1** and **L2**)[7a] were prepared according to the reported procedures.

General Procedure for the Rh(I)-Catalyzed 1,4-Addition of Arylboronic Acids to α,β-Unsaturated Ketones. A 25 mL flask was flushed with nitrogen and charged with (*S*)-**L2** (7.5 mg, 0.02 mmol), Rh(acac)$(C_2H_4)_2$ (2.1 mg, 0.008 mmol), and 1 mL of degassed toluene. The mixture was stirred for 10 min at ambient temperature. The reaction mixture was mixed with 0.1 mL of degassed water, arylboronic acid (1.2 mmol), and α,β-unsaturated ketone (0.4 mmol). After stirring at 25 or 50 °C for 1−5 h, the reaction mixture was passed through a pad of silica gel with ethyl acetate, and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:5 to 1:20) to afford the corresponding product **2**.

(R)-3-Phenylcyclohexanone (**2a**).[8b] Colorless oil. (60.2 mg, 86% yield, 94% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.35−7.32 (m, 2H), 7.26−7.22 (m, 3H), 3.11−2.90 (m, 1H), 2.63−2.34 (m, 4H), 2.19−2.07 (m, 2H), 1.91−1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 211.2, 144.5, 128.8, 126.8, 126.7, 49.1, 44.9, 41.3, 32.9, 25.7. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 99/1, flow rate = 1.0 mL/min): 8.7 min (minor), 10.4 min (major).

(R)-3-Phenylcyclopentanone (**2b**).[8b] Colorless oil. (61.6 mg, 96% yield, 77% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.43−7.32 (m, 2H), 7.30−7.22 (m, 3H), 3.53−3.37 (m, 1H), 2.68 (dd, *J* = 17.8, 8.2 Hz, 1H), 2.56−2.25 (m, 4H), 2.09−1.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 218.5, 143.2, 128.8, 126.9, 45.9, 42.4, 39.0, 31.3. HPLC chromatograms (Daicel Chiralpak OB-H, Hexanes/*i*-PrOH = 99/1, flow rate = 0.6 mL/min): 34.5 min (minor), 35.8 min (major).

(R)-3-Phenylcycloheptanone (**2c**).[8b] Colorless oil. (68.0 mg, 90% yield, 83% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.30 (t, *J* = 7.4 Hz, 2H), 7.24−7.14 (m, 3H), 2.93 (m, 2H), 2.70−2.51 (m, 3H), 2.15−1.95 (m, 3H), 1.82−1.65 (m, 2H), 1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 213.5, 147.0, 128.7, 126.5, 126.4, 51.4, 44.0, 42.8, 39.3, 29.3, 24.3. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 99/1, flow rate = 1.0 mL/min): 9.5 min (minor), 10.6 min (major).

(R)-3-(o-Tolyl)cyclohexanone (**2d**).[8b] Colorless oil. (73.0 mg, 97% yield, 73% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.28−7.20 (m, 2H), 7.21−7.10 (m, 2H), 3.31−3.16 (m, 1H), 2.59−2.38 (m, 4H), 2.33 (s, 3H), 2.25−2.12 (m, 1H), 2.08−1.98 (m, 1H), 1.92−1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 211.3, 142.4, 135.2, 130.8, 126.6, 126.5, 125.2, 48.5, 41.4, 40.4, 32.2, 25.9, 19.4. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 99/1, flow rate = 1.0 mL/min): 7.8 min (minor), 9.8 min (major).

(R)-3-(m-Tolyl)cyclohexanone (**2e**).[8b] Colorless oil. (73.6 mg, 98% yield, 92% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.22 (t, *J* = 7.4 Hz, 1H), 7.08−6.99 (m, 3H), 3.06−2.89 (m, 1H), 2.63−2.36 (m, 4H), 2.35 (s, 3H), 2.20−2.11 (m, 1H), 2.11−2.04 (m, 1H), 1.91−1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 211.3, 144.5, 138.4, 128.7, 127.6, 127.5, 123.7, 49.1, 44.9, 41.4, 33.0, 25.7, 21.6. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 99/1, flow rate = 1.0 mL/min): 7.5 min (minor), 8.1 min (major).

(R)-3-(p-Tolyl)cyclohexanone (**2f**).[8b] Colorless oil. (64.5 mg, 86% yield, 93% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.19−7.08 (m, 4H), 3.04−2.93 (m, 1H), 2.63−2.36 (m, 4H), 2.34 (s, 3H), 2.20−2.04 (m, 2H), 1.90−1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 211.3, 141.5, 136.4, 129.4, 126.5, 49.2, 44.5, 41.3, 33.0, 25.7, 21.1. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 99/1, flow rate = 1.0 mL/min): 7.5 min (minor), 8.3 min (major).

(R)-3-(4-Methoxyphenyl)cyclohexanone (**2g**).[8b] Colorless oil. (78.4 mg, 96% yield, 88% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.14 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.02−2.90 (m, 1H), 2.63−2.32 (m, 4H), 2.19−2.02 (m, 2H), 1.88−1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 211.3, 158.4, 136.7, 127.6, 114.2, 55.4, 49.4, 44.1, 41.3, 33.2, 25.6. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 99/1, flow rate = 1.0 mL/min): 13.1 min (minor), 13.7 min (major).

(R)-3-(3,5-Dimethylphenyl)cyclohexanone (**2h**).[10b] Colorless oil. (73.5 mg, 91% yield, 90% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.88 (s, 1H), 6.84 (s, 2H), 3.00−2.87 (m, 1H), 2.61−2.34 (m, 4H), 2.31 (s, 6H), 2.19−2.11 (m, 1H), 2.11−2.02 (m, 1H), 1.91−1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 211.4, 144.5, 138.3, 128.5, 124.5, 49.2, 44.9, 41.4, 33.0, 25.8, 21.5. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 99/1, flow rate = 1.0 mL/min): 6.6 min (minor), 7.2 min (major).

(R)-3-(4-Fluorophenyl)cyclohexanone (**2i**).[8b] Colorless oil. (64.2 mg, 83% yield, 88% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.22−7.14 (m, 2H), 7.05−6.96 (m, 2H), 3.06−2.93 (m, 1H), 2.62−2.31 (m, 4H), 2.19−2.11 (m, 1H), 2.11−2.02 (m, 1H), 1.89−1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 210.9, 161.7 (d, *J* = 244.9 Hz), 140.2 (d, *J* = 3.0 Hz), 128.1 (d, *J* = 7.9 Hz), 115.6 (d, *J* = 21.2 Hz), 49.2, 44.1, 41.3, 33.0, 25.5. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 99/1, flow rate =1.0 mL/min): 10.0 min (minor), 13.0 min (major).

(R)-3-(4-Trifluoromethylphenyl)cyclohexanone (**2j**).[10c] Colorless oil. (74.6 mg, 77% yield, 90% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.58 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 3.14−3.02 (m, 1H), 2.64−2.34 (m, 4H), 2.22−2.13 (m, 1H), 2.13−2.06 (m, 1H), 1.94−1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 210.4,

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J. Org. Chem. 2016, 81, 3520−3527

148.3, 129.2 (q, J = 32.4 Hz), 125.8 (q, J = 3.8 Hz), 124.3 (q, J = 271.8 Hz), 48.6, 44.6, 41.2, 32.6, 25.5. HPLC chromatograms (Daicel Chiralpak OJ-H, Hexanes/*i*-PrOH = 99/1, flow rate = 1.0 mL/min): 13.9 min (minor), 17.5 min (major).

*(R)-3-(1-Naphthyl)cyclohexanone (**2k**).*[10b] White solid. (87.9 mg, 98% yield, 85% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.04 (d, J = 8.8 Hz, 1H), 7.92−7.85 (m, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.57−7.38 (m, 4H), 3.93−3.79 (m, 1H), 2.83−2.41 (m, 4H), 2.30−2.15 (m, 2H), 2.08−1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 211.4, 140.2, 134.1, 131.0, 129.2, 127.4, 126.4, 125.8, 125.7, 122.8, 122.6, 48.7, 41.6, 39.5, 32.4, 25.7. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 98/2, flow rate = 1.0 mL/min): 9.9 min (minor), 10.4 min (major).

*(R)-3-(2-Naphthyl)cyclohexanone (**2l**).*[10b] White solid. (74.6 mg, 83% yield, 91% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.89−7.77 (m, 3H), 7.69−7.62 (m, 1H), 7.53−7.42 (m, 2H), 7.37 (dd, J = 8.6, 1.7 Hz, 1H), 3.26−3.13 (m, 1H), 2.75−2.59 (m, 2H), 2.55−2.37 (m, 2H), 2.24−2.12 (m, 2H), 2.04−1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 211.1, 141.9, 133.7, 132.5, 128.5, 127.8, 127.7, 126.3, 125.8, 125.4, 124.9, 49.0, 44.9, 41.4, 32.8, 25.7. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 1.0 mL/min): 6.4 min (minor), 6.8 min (major).

*(S)-4-Phenylheptan-2-one (**2m**).*[10b] Colorless oil. (52.6 mg, 69% yield, 42% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.33−7.25 (m, 2H), 7.23−7.13 (m, 3H), 3.19−3.07 (m, 1H), 2.79−2.64 (m, 2H), 2.01 (s, 3H), 1.67−1.48 (m, 2H), 1.28−1.05 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 208.1, 144.7, 128.5, 127.6, 126.4, 51.0, 41.2, 38.8, 30.7, 20.6, 14.1. HPLC chromatograms (Daicel Chiralpak IA, Hexanes/*i*-PrOH = 99/1, flow rate = 0.5 mL/min): 10.2 min (major), 10.7 min (minor).

General Procedure for the Rh(I)-Catalyzed 1,2-Addition of Arylboronic Acids to *N*,*N*-Dimethylsulfamoyl Aldimines. A 25 mL flask was flushed with nitrogen and charged with (*R*)-**L1** (5.4 mg, 0.015 mmol), Rh(acac)$(C_2H_4)_2$ (1.55 mg, 0.006 mmol), and 1 mL of degassed toluene. The mixture was stirred for 10 min at ambient temperature. The reaction mixture was mixed with arylboronic acid (0.4 mmol) and aldimine (0.2 mmol). After stirring at 25 °C for 3 h, the reaction mixture was passed through a pad of silica gel with ethyl acetate, and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1:4 to 1:10) to afford the corresponding product **4**.

*N′-[(S)-(4-Chlorophenyl)phenylmethyl]-N,N-dimethylsulfamide (**4a**).*[18] White solid. (63.6 mg, 98% yield, 95% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.42−7.27 (m, 9H), 5.60 (d, J = 6.8 Hz, 1H), 4.87 (d, J = 6.7 Hz, 1H), 2.58 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 141.0, 140.0, 133.8, 129.1, 129.0, 128.9, 128.2, 127.5, 61.2, 37.8. HPLC chromatograms (Daicel Chiralpak OD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 0.8 mL/min): 10.4 min (major), 13.2 min (minor).

*N′-[(S)-(4-Fluorophenyl)phenylmethyl]-N,N-dimethylsulfamide (**4b**).*[18] White solid. (55.8 mg, 90% yield, 94% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39−7.33 (m, 2H), 7.33−7.27 (m, 5H), 7.07−6.99 (m, 2H), 5.61 (d, J = 6.7 Hz, 1H), 4.87 (d, J = 6.8 Hz, 1H), 2.58 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 162.4 (d, J = 246.8 Hz), 141.3, 137.4 (d, J = 3.2 Hz), 129.3 (d, J = 8.1 Hz), 129.0, 128.1, 127.5, 115.7 (d, J = 21.5 Hz), 61.1, 37.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −114.4. HPLC chromatograms (Daicel Chiralpak OD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 0.8 mL/min): 10.2 min (major), 12.0 min (minor).

*N′-[(S)-(4-Trifluoromethylphenyl)phenylmethyl]-N,N-dimethylsulfamide (**4c**).*[18] White solid. (64.5 mg, 90% yield, 94% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.61 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.39−7.27 (m, 5H), 5.67 (d, J = 7.0 Hz, 1H), 5.05 (d, J = 7.0 Hz, 1H), 2.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.5, 140.7, 130.1 (q, J = 32.5 Hz), 129.2, 128.4, 127.9, 127.5, 125.8 (q, J = 3.8 Hz), 61.4, 37.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −62.6. HPLC chromatograms (Daicel Chiralpak OD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 0.8 mL/min): 8.9 min (major), 12.9 min (minor).

*N′-[(S)-(4-Bromophenyl)phenylmethyl]-N,N-dimethylsulfamide (**4d**).* Off white solid. (62.5 mg, 85% yield, 87% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.48 (d, J = 8.2 Hz, 2H), 7.39−7.27 (m, 5H), 7.21 (d, J = 8.6 Hz, 2H), 5.58 (d, J = 6.9 Hz, 1H), 4.78 (d, J = 7.2 Hz, 1H), 2.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 141.0, 140.6, 132.0, 129.3, 129.1, 128.3, 127.5, 122.0, 61.2, 37.8. HRMS (ESI) calcd for $C_{15}H_{17}BrN_2O_2S$ $[M + Na]^+$: 391.0092, Found: 391.0090. HPLC chromatograms (Daicel Chiralpak OD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 0.8 mL/min): 10.5 min (major), 13.6 min (minor).

*N′-[(S)-(p-Tolyl)phenylmethyl]-N,N-dimethylsulfamide (**4e**).*[18] White solid. (48.9 mg, 80% yield, 95% ee for **4e** and 58.1 mg, 95% yield, −91% ee for **4k**) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.37−7.26 (m, 5H), 7.20 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 5.59 (d, J = 6.6 Hz, 1H), 4.81 (d, J = 6.8 Hz, 1H), 2.57 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 141.7, 138.6, 137.7, 129.6, 128.8, 127.8, 127.5, 127.4, 61.5, 37.8, 21.2. HPLC chromatograms (Daicel Chiralpak OD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 0.8 mL/min): 9.5 min (major), 11.6 min (minor).

*N′-[(S)-(4-Methoxyphenyl)phenylmethyl]-N,N-dimethylsulfamide (**4f**).*[18] White solid. (54.9 mg, 86% yield, 93% ee for **4f** and 62.0 mg, 97% yield, −89% ee for **4j**) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39−7.27 (m, 5H), 7.23 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.58 (d, J = 6.6 Hz, 1H), 4.89 (d, J = 6.7 Hz, 1H), 3.79 (s, 3H), 2.56 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 159.2, 141.8, 133.7, 128.8, 128.8, 127.8, 127.5, 114.2, 61.2, 55.4, 37.7. HPLC chromatograms (Daicel Chiralpak OD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 0.8 mL/min): 15.2 min (major), 18.8 min (minor).

*N′-[(S)-(3-Chlorophenyl)phenylmethyl]-N,N-dimethylsulfamide (**4g**).* White solid. (51.5 mg, 79% yield, 96% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39−7.20 (m, 9H), 5.59 (d, J = 6.6 Hz, 1H), 4.87 (d, J = 6.8 Hz, 1H), 2.59 (s, 6H) ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 143.5, 140.8, 134.8, 130.2, 129.1, 128.3, 128.1, 127.7, 127.5, 125.7, 61.3, 37.8. HRMS (ESI) calcd for $C_{15}H_{17}ClN_2O_2S$ $[M + Na]^+$: 347.0597, Found: 347.0609. HPLC chromatograms (Daicel Chiralpak IC, Hexanes/*i*-PrOH = 90/10, flow rate = 0.8 mL/min): 22.3 min (major), 23.6 min (minor).

*N′-[(S)-(2-Chlorophenyl)phenylmethyl]-N,N-dimethylsulfamide (**4h**).* White solid. (60.2 mg, 93% yield, 89% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.56 (d, J = 8.2 Hz, 1H), 7.45−7.27 (m, 8H), 6.02 (d, J = 7.5 Hz, 1H), 4.94 (d, J = 7.8 Hz, 1H), 2.64 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 140.1, 138.9, 133.1, 130.3, 129.2, 128.9, 128.0, 127.5, 127.3, 58.7, 37.8. HRMS (ESI) calcd for $C_{15}H_{17}ClN_2O_2S$ $[M + Na]^+$: 347.0597, Found: 347.0604. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 80/20, flow rate = 0.5 mL/min): 13.4 min (major), 16.6 min (minor).

*N′-[(S)-(2-Thienyl)phenylmethyl]-N,N-dimethylsulfamide (**4i**).*[18] White solid. (56.1 mg, 95% yield, 92% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.42−7.30 (m, 5H), 7.27−7.24 (m, 1H), 6.94 (dd, J = 5.1, 3.6 Hz, 1H), 6.91−6.86 (m, 1H), 5.83 (d, J = 6.9 Hz, 1H), 4.90 (d, J = 6.9 Hz, 1H), 2.61 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.6, 141.3, 128.9, 128.4, 127.3, 127.1, 126.2, 125.8, 58.0, 37.8. HPLC chromatograms (Daicel Chiralpak OJ-H, Hexanes/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): 18.5 min (minor), 27.3 min (major).

*N′-[(R)-(m-Tolyl)phenylmethyl]-N,N-dimethylsulfamide (**4l**).* White solid. (39.6 mg, 65% yield, 94% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.38−7.30 (m, 4H), 7.30−7.25 (m, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.15−7.06 (m, 3H), 5.58 (d, J = 6.5 Hz, 1H), 4.82 (d, J = 6.8 Hz, 1H), 2.57 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 141.6, 141.5, 138.6, 128.8, 128.8, 128.7, 128.2, 127.9, 127.5, 124.5, 61.8, 37.7, 21.6. HRMS (ESI) calcd for $C_{16}H_{20}N_2O_2S$ $[M + Na]^+$: 327.1143, Found: 327.1132. HPLC chromatograms (Daicel Chiralpak IC, Hexanes/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): 13.1 min (minor), 13.8 min (major).

General Procedure for the Rh(I)-Catalyzed 1,4-Addition of Arylboronic Acids to α,β-Unsaturated *N*-Tosyl Ketimines. A 25 mL flask was flushed with nitrogen and charged with (*R*)-**L2** (9.0 mg, 0.025 mmol), Rh(acac)$(C_2H_4)_2$ (2.6 mg, 0.01 mmol), and 2.0 mL of degassed toluene. The mixture was stirred for 10 min at ambient temperature. The reaction mixture was mixed with arylboronic acid (0.6 mmol) and α,β-unsaturated *N*-tosyl ketimine (0.2 mmol). After stirring at 25 °C, the reaction mixture was passed through a pad of silica gel with ethyl acetate, and the filtrate was concentrated under

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vacuum. The residue was purified by flash chromatography on silica gel (Et_2O/hexane =1:1 to 1:5) to afford the corresponding product **6**.

*(Z)-N-[(3S)-3-(4-Methoxyphenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6a**).*[7b] White solid (84.2 mg, 90% yield, 94% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.60 (d, J = 8.3 Hz, 2H), 7.45 (dd, J = 7.5, 2.1 Hz, 2H), 7.31−7.19 (m, 8H), 6.94−6.76 (m, 6H), 6.06 (s, 1H), 5.90 (dd, J = 8.8, 0.7 Hz, 2H), 4.33 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.5, 144.0, 143.4, 137.3, 137.0, 135.4, 134.9, 129.8, 129.1, 128.9, 128.7, 128.2, 128.0, 127.7, 127.6, 127.5, 126.9, 114.3, 55.4, 48.1, 21.7. HRMS (ESI) calcd for $C_{29}H_{27}NO_3S$ [M + Na]$^+$: 492.1609, Found: 492.1631. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): 12.1 min (major), 13.3 min (minor).

*(Z)-N-[(3S)-3-(3-Methoxyphenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6b**).* White solid (79.4 mg, 85% yield, 91% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.60 (d, J = 8.3 Hz, 2H), 7.46−7.44 (m, 2H), 7.32−7.27 (m, 3H), 7.26−7.15 (m, 6H), 6.94 (d, J = 7.0 Hz, 1H), 6.74 (dd, J = 8.8, 2.2 Hz, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.49 (s, 1H), 6.03 (s, 1H), 5.92 (d, J = 9.6 Hz, 1H), 4.33 (d, J = 8.8 Hz, 1H), 3.75 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 160.0, 144.5, 144.0, 142.8, 137.3, 137.0, 135.6, 129.9, 129.8, 128.9, 128.7, 128.2, 128.1, 127.6, 127.4, 127.3, 127.0, 120.5, 114.4, 111.8, 55.3, 48.9, 21.7. HRMS (ESI) calcd for $C_{29}H_{27}NO_3S$ [M + Na]$^+$: 492.1609, Found: 492.1639. HPLC chromatograms (Daicel Chiralpak IB, Hexanes/*i*-PrOH = 95/5, flow rate = 1.0 mL/min): 13.9 min (major), 14.8 min (minor).

*(Z)-N-[(3S)-3-(4-Methylphenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6c**).* White solid (89.8 mg, 99% yield, 93% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.61 (d, J = 8.2 Hz, 2H), 7.48−7.45 (m, 2H), 7.32−7.17 (m, 8H), 7.06 (d, J = 7.9 Hz, 2H), 6.92 (d, J = 6.9 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 6.03 (s, 1H), 5.92 (d, J = 8.8 Hz, 1H), 4.31 (d, J = 8.8 Hz, 1H), 2.43 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.0, 143.2, 139.9, 137.4, 136.9, 136.6, 135.4, 129.7, 129.6, 128.8, 128.7, 128.2, 128.0, 128.0, 127.7, 127.6, 127.4, 126.8, 48.5, 21.7, 21.1. HRMS (ESI) calcd for $C_{29}H_{27}NO_2S$ [M + Na]$^+$: 476.1660, Found: 476.1671. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): 8.7 min (minor), 10.3 min (major).

*(Z)-N-[(3S)-3-(3-Methylphenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6d**).* White solid (72.7 mg, 80% yield, 91% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.61 (d, J = 8.3 Hz, 2H), 7.48−7.45 (m, 2H), 7.32−7.18 (m, 8H), 7.14 (t, J = 7.9 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H) 6.93 (d, J = 7.0 Hz, 1H), 6.75−6.74 (m, 2H), 6.02 (s, 1H), 5.92 (d, J = 8.7 Hz, 1H), 4.30 (d, J = 8.7 Hz, 1H), 2.43 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.0, 143.1, 142.9, 138.6, 137.4, 137.0, 135.5, 129.8, 128.9, 128.9, 128.8, 128.7, 128.2, 128.1, 127.8, 127.6, 127.6, 127.4, 126.9, 125.2, 48.9, 21.7, 21.6. HRMS (ESI) calcd for $C_{29}H_{27}NO_2S$ [M + Na]$^+$: 476.1660, Found: 476.1677. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 1.0 mL/min): 12.8 min (major), 14.1 min (minor).

*(Z)-N-[(3S)-3-(4-(tert-Butyl)phenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6e**).* White solid. (93.7 mg, 95% yield, 96% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.64−7.59 (m, 2H), 7.49−7.45 (m, 2H), 7.32−7.18 (m, 11H), 6.96−6.91 (m, 2H), 6.89−6.84 (m, 2H), 6.06 (s, 1H), 5.94 (dd, J = 8.7, 0.8 Hz, 1H), 4.31 (d, J = 8.8 Hz, 1H), 2.44 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 144.0, 143.2, 139.8, 137.4, 137.0, 135.4, 129.8, 128.9, 128.7, 128.2, 128.1, 127.7, 127.7, 127.6, 127.5, 126.9, 125.8, 48.5, 34.5, 31.5, 21.7. HRMS (ESI) calcd for $C_{32}H_{33}NO_2S$ [M + Na]$^+$: 518.2130, Found: 518.2175. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): 6.6 min (minor), 7.4 min (major).

*(Z)-N-[(3S)-3-(2-Naphthyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6f**).* White solid (73.3 mg, 75% yield, 94% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.77−7.68 (m, 3H), 7.58 (d, J = 8.2 Hz, 2H), 7.46−7.40 (m, 4H), 7.38 (s, 1H), 7.29−7.16 (m, 8H), 7.03 (dd, J = 8.5, 1.7 Hz, 1H), 6.96 (d, J = 7.2 Hz, 2H), 6.17 (s, 1H), 5.99 (d, J = 9.0 Hz, 1H), 4.58 (d, J = 9.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.0, 142.9, 140.3, 137.3, 136.9, 135.7, 133.5, 132.4, 129.7, 128.9, 128.8, 128.7, 128.2, 127.9, 127.8, 127.6, 127.5, 127.2, 127.0, 126.6, 126.4, 126.3, 126.0, 49.0, 21.6. HRMS (ESI) calcd for $C_{32}H_{27}NO_2S$ [M + Na]$^+$: 512.1660, Found: 512.1697. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 1.0 mL/min): 21.5 min (minor), 26.3 min (major).

*(Z)-N-[(3S)-3-(4-Fluorophenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6g**).* White solid (30.7 mg, 35% yield, 93% ee for **6g** and 80.3 mg, 91% yield, −94% ee for **6k**) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.58 (d, J = 8.3 Hz, 2H), 7.42 (dd, J = 7.7, 1.8 Hz, 2H), 7.32−7.20 (m, 8H), 6.96−6.89 (m, 6H), 6.07 (s, 1H), 5.90 (d, J = 9.2 Hz, 1H), 4.48 (d, J = 9.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 161.7 (d, J = 245.6 Hz), 144.0, 142.8, 138.8 (d, J = 3.3 Hz), 137.2, 136.9, 135.5, 129.7, 129.6 (d, J = 7.9 Hz), 129.0, 128.8, 128.2, 128.1, 127.6, 127.4, 127.3, 127.0, 115.6 (d, J = 21.3 Hz), 48.0, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −115.9. HRMS (ESI) calcd for $C_{28}H_{24}FNO_2S$ [M + Na]$^+$: 480.1409, Found: 480.1428. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 95/5, flow rate = 1.0 mL/min): 30.6 min (minor), 33.6 min (major).

*(Z)-N-[(3S)-3-(4-Chlorophenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6h**).* White solid (73.4 mg, 77% yield, 91% ee for **6h** and 90.9 mg, 96% yield, −91% ee for **6p**) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.57 (d, J = 8.1 Hz, 2H), 7.42−7.38z (m, 2H), 7.28−7.16 (m, 10H), 6.95 (d, J = 7.2 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 6.03 (s, 1H), 5.88 (d, J = 9.2 Hz, 1H), 4.47 (d, J = 9.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.0, 142.5, 141.6, 137.2, 136.9, 135.6, 132.7, 129.7, 129.5, 129.0, 128.9, 128.8, 128.2, 128.1, 127.6, 127.4, 127.1, 127.0, 48.1, 21.7. HRMS (ESI) calcd for $C_{28}H_{24}ClNO_2S$ [M + Na]$^+$: 496.1114, Found: 496.1135. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 1.0 mL/min): 15.8 min (minor), 20.4 min (major).

*(Z)-N-[(3S)-3-(3-Chlorophenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6i**).* White solid. (45.7 mg, 48% yield, 95% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.63−7.57 (m, 2H), 7.47−7.42 (m, 2H), 7.32−7.26 (m, 5H), 7.26−7.21 (m, 3H), 7.19−7.15 (m, 2H), 6.97 (m, 2H), 6.83 (m, 2H), 6.06 (s, 1H), 5.89 (d, J = 9.1 Hz, 1H), 4.41 (d, J = 9.1 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.2, 144.2, 142.1, 137.1, 136.9, 135.9, 134.6, 130.1, 129.8, 129.1, 128.9, 128.3, 128.3, 128.1, 127.6, 127.4, 127.3, 127.1, 126.6, 126.2, 48.6, 21.7. HRMS (ESI) calcd for $C_{28}H_{24}ClNO_2S$ [M + Na]$^+$: 496.1114, Found: 496.1139. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 95/5, flow rate = 1.0 mL/min): 25.7 min (major), 27.4 min (minor).

*(Z)-N-[(3S)-3-(4-Bromophenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6j**).* White solid. (83.3 mg, 80% yield, 91% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.57 (d, J = 8.3 Hz, 2H), 7.44−7.39 (m, 2H), 7.38−7.34 (m, 2H), 7.31−7.18 (m, 8H), 6.98−6.92 (m, 2H), 6.82 (d, J = 8.4 Hz, 2H), 6.11 (s, 1H), 5.88 (d, J = 9.6 Hz, 1H), 4.48 (d, J = 9.1 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.1, 142.4, 142.2, 137.1, 136.9, 135.7, 131.9, 129.9, 129.7, 129.0, 128.9, 128.2, 128.1, 127.6, 127.4, 127.2, 126.9, 120.8, 48.3, 21.7. HRMS (ESI) calcd for $C_{28}H_{24}BrNO_2S$ [M + Na]$^+$: 540.0609, Found: 540.0622. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): 8.9 min (minor), 11.4 min (major).

*(Z)-N-[(3R)-3-Phenyl-1,3-bis(4-fluorophenyl)-1-propen-1-yl]-4-methylbenzenesulfonamide (**6l**).* White solid (80.9 mg, 85% yield, 93% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.58−7.56 (m, 2H), 7.42−7.38 (m, 2H), 7.29−7.19 (m, 5H), 6.99−6.87 (m, 8H), 6.07 (s, 1H), 5.81 (d, J = 9.1 Hz, 1H), 4.42 (d, J = 9.1 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 163.7 (d, J = 143.7 Hz), 161.2 (d, J = 141.3 Hz), 144.2, 142.7, 138.7 (d, J = 3.3 Hz), 136.8, 134.6, 133.3 (d, J = 3.2 Hz), 129.8, 129.6 (d, J = 7.9 Hz), 129.4 (d, J = 8.2 Hz), 129.0, 128.1, 127.4, 127.1, 126.8, 115.7 (d, J = 21.3 Hz), 115.2 (d, J = 21.7 Hz), 48.0, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −112.8, −115.8. HRMS (ESI) calcd for $C_{28}H_{23}F_2NO_2S$ [M + Na]$^+$: 498.1315, Found: 498.1333. HPLC chromatograms (Daicel Chiralpak AD-H,

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J. Org. Chem. 2016, 81, 3520−3527

Hexanes/*i*-PrOH = 95/5, flow rate = 1.0 mL/min): 29.0 min (major), 31.6 min (minor).

*(Z)-N-[(3R)-3-(4-Fluorophenyl)-3-phenyl-1-(p-tolyl)-1-propen-1-yl]-4-methylbenzenesulfonamide (**6m**).* White solid (75.3 mg, 80% yield, 93% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.59 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.28−7.19 (m, 5H), 7.09 (d, J = 7.9 Hz, 2H), 6.95−6.86 (m, 6H), 6.00 (s, 1H), 5.84 (d, J = 9.7 Hz, 1H), 4.40 (d, J = 9.2 Hz, 1H), 2.42 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 161.7 (d, J = 245.5 Hz), 143.9, 142.9, 138.9 (d, J = 3.2 Hz), 138.8, 136.9, 135.4, 134.4, 129.7, 129.6 (d, J = 8.0 Hz), 128.9, 128.1, 127.5, 127.4, 127.0, 126.3, 115.6 (d, J = 21.3 Hz), 47.9, 21.6, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −116.0. HRMS (ESI) calcd for $C_{29}H_{26}FNO_2S$ $[M + Na]^+$: 494.1566, Found: 494.1577. HPLC chromatograms (Daicel Chiralpak IB, Hexanes/*i*-PrOH = 95/5, flow rate = 1.0 mL/min): 13.4 min (major), 14.5 min (minor).

*(Z)-N-[1-(4-Fluorophenyl)-(3S)-3-(4-methoxyphenyl)-3-phenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6n**).* White solid. (68.0 mg, 70% yield, 92% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.60 (d, J = 8.3 Hz, 2H), 7.43 (dd, J = 8.8, 5.4 Hz, 2H), 7.28−7.17 (m, 5H), 7.00−6.77 (m, 8H), 6.14 (s, 1H), 5.83 (d, J = 8.8 Hz, 1H), 4.32 (d, J = 8.8 Hz, 1H), 3.78 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 163.1 (d, J = 248.0 Hz), 158.6, 144.1, 143.3, 136.9, 134.8, 134.4, 133.4 (d, J = 3.1 Hz), 129.8, 129.4 (d, J = 8.2 Hz), 129.1, 128.9, 128.0, 127.4, 127.3, 126.9, 115.1 (d, J = 21.7 Hz), 114.3, 55.4, 48.0, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −113.1. HRMS (ESI) calcd for $C_{29}H_{26}FNO_3S$ $[M + Na]^+$: 510.1515, Found: 510.1541. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 1.0 mL/min): 20.2 min (minor), 21.7 min (major).

*(Z)-N-[(3R)-3-(4-Fluorophenyl)-3-(4-methoxyphenyl)-1-phenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6o**).* White solid. (80.2 mg, 82% yield, 97% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.59 (d, J = 8.3 Hz, 2H), 7.45−7.40 (m, 2H), 7.32−7.26 (m, 3H), 7.24−7.18 (m, 2H), 6.96−6.84 (m, 6H), 6.82−6.77 (m, 2H), 6.15 (s, 1H), 5.87 (dd, J = 9.0, 0.7 Hz, 1H), 4.44 (d, J = 9.0 Hz, 1H), 3.78 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 161.7 (d, J = 245.4 Hz), 158.6, 144.0, 139.2 (d, J = 3.2 Hz), 137.2, 137.0, 135.3, 134.7, 129.7, 129.5 (d, J = 7.9 Hz), 129.1, 128.7, 128.2, 127.6, 127.6, 127.4, 115.6 (d, J = 21.3 Hz), 114.4, 55.4, 47.2, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −116.1. HRMS (ESI) calcd for $C_{29}H_{26}FNO_3S$ $[M + Na]^+$: 510.1515, Found: 510.1527. HPLC chromatograms (Daicel Chiralpak ID, Hexanes/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): 20.3 min (major), 22.6 min (minor).

*(Z)-N-[(3R)-3-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1-phenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6q**).* White solid. (87.9 mg, 87% yield, 93% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.58 (d, J = 8.3 Hz, 2H), 7.42 (dd, J = 7.8, 1.7 Hz, 2H), 7.31−7.26 (m, 3H), 7.23−7.18 (m, 4H), 6.87 (t, J = 9.2 Hz, 4H), 6.82−6.77 (m, 2H), 6.12 (s, 1H), 5.85 (d, J = 9.1 Hz, 1H), 4.43 (d, J = 9.0 Hz, 1H), 3.78 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.7, 144.0, 142.0, 137.1, 136.9, 135.5, 134.4, 132.6, 129.7, 129.4, 129.1, 128.9, 128.8, 128.2, 127.6, 127.4, 127.3, 114.4, 55.4, 47.4, 21.7. HRMS (ESI) calcd for $C_{29}H_{26}ClNO_3S$ $[M + Na]^+$: 526.1220, Found: 526.1263. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 90/10, flow rate = 1.0 mL/min): 22.2 min (major), 27.0 min (minor).

*(Z)-N-[(3R)-3-(4-Nitrophenyl)-1,3-diphenyl-1-propen-1-yl]-4-methylbenzenesulfonamide (**6r**).* Pale yellow solid. (49.2 mg, 51% yield, 84% ee) ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.08 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.41−7.34 (m, 2H), 7.32−7.23 (m, 6H), 7.16 (dd, J = 8.7, 2.2 Hz, 4H), 7.04−6.97 (m, 2H), 6.41 (s, 1H), 5.93 (d, J = 9.6 Hz, 1H), 4.86 (d, J = 9.6 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 150.9, 146.8, 144.1, 141.6, 136.9, 136.9, 136.1, 129.7, 129.2, 129.1, 129.0, 128.3, 128.2, 127.5, 127.5, 127.4, 126.1, 123.9, 48.6, 21.6. HRMS (ESI) calcd for $C_{28}H_{24}N_2O_4S$ $[M + Na]^+$: 507.1354, Found: 507.1377. HPLC chromatograms (Daicel Chiralpak AD-H, Hexanes/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): 15.7 min (major), 17.5 min (minor).

Procedure for Acid Hydrolysis of 6b. A 5 mL reaction vial was charged with (*S*)-**6b** (47.0 mg, 0.1 mmol), THF (0.8 mL), and conc. HCl (0.2 mL). The resulting solution was stirred at 100 °C for 1 h. After cooling to ambient temperature, saturated $NaHCO_3$ solution (5 mL) was poured into the flask, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude was purified by chromatography on silica gel (diethyl ether/hexane = 1:5) to give (*S*)-3-(3-methoxyphenyl)-1,3-diphenylpropan-1-one[17] as white solid (27.6 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.99−7.88 (m, 2H), 7.58−7.50 (m, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.30−7.24 (m, 4H), 7.22−7.12 (m, 2H), 6.91−6.78 (m, 2H), 6.72 (dd, J = 8.0, 2.2 Hz, 1H), 4.80 (t, J = 7.2 Hz, 1H), 3.78−3.68 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 198.1, 159.8, 145.9, 144.1, 137.2, 133.2, 129.7, 128.7, 128.7, 128.2, 127.9, 126.5, 120.4, 114.2, 111.5, 55.3, 46.1, 44.8. $[\alpha]_D^{25}$ = +7.7 (*c* 1.00, $CHCl_3$) for 91% ee.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00033.

Additional chiral briphos ligands experimental data, copies of ^{1}H and ^{13}C NMR spectra, and HPLC chromatograms (PDF)

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Notes

The authors declare no competing financial interest.

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