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Chiral N-aryl tert-butanesulfinamide-olefin ligands for rhodium-catalyzed asymmetric 1,4-addition of aryl boronic acids to cyclic enones

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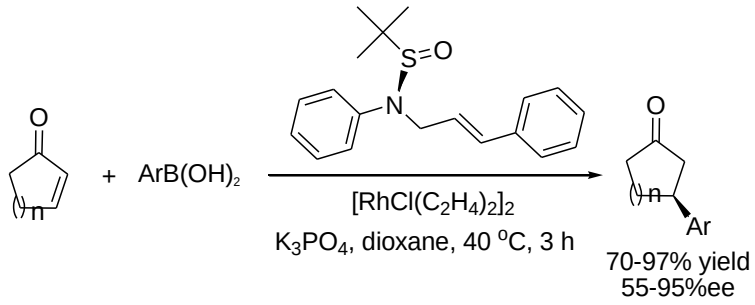
Abstract

Chiral N-aryl sulfinamide-olefins which are readily synthesized via C-N coupling and nucleophilic substitution have been used as chiral ligands, which demonstrate moderate to excellent asymmetric catalytic performance in the rhodium-catalyzed asymmetric 1,4-addition of aryl boronic acids to cyclic enones. The chiral ligands are readily synthesized via C-N coupling reaction and nucleophilic substitution. Given that chiral ligands with 97%ee produced 1,4-addition products up to 95%ee, N-aryl tert-butanesulfinamide-olefin ligands demonstrates fairly high chiral induction ability in the rhodium-catalyzed asymmetric 1,4-addition.



Keywords: Enantioselective catalysis; N-aryl sulfinamide-olefin; 1,4-addition reaction; rhodium; chiral ligands

Introduction

Chiral sulfinyl chemistry has developed fast in the recent several decades.[1-3] Chiral sulfinyl compounds have found more and more applications in organic synthesis, pharmaceuticals, agricultural chemicals and materials.[1-3] Esomeprazole, garlicin, sparsomycin and so on are the clinic chiral sulfinyl drugs, and more sulfinyl drugs are in developing.[1-4]

Chiral sulfinyl compounds are used in organic synthesis. They are extensively used as chiral intermediates and auxiliaries, chiral ligands and catalysts.[5-6] *para*-Toluenesulfinyl imines, *tert*-butanesulfinamide, *tert*-butanesulfinyl imines are the common chiral intermediates for organic synthesis and drug synthesis.[1-3]

Chiral sulfinyl ligands and catalysts now has entered rapid developing period after a long slow development.[1-3] In 1976, James, McMillan and Reimer reported the first asymmetric catalytic reaction with chiral sulfoxides as chiral ligands, namely ruthenium catalyzed asymmetric hydrogenation.[7] In 2009 the bis-sulfoxide ligands reported by Dorta group[8-9] and Liao group[10] accelerate the development of chiral sulfoxide ligands.

Not only sulfoxides are used as ligands and catalysts, sulfinamide derivatives are developed as chiral ligands pioneered by Ellman in 2001.[11] Recently chiral sulfoxide- and sulfinamide-olefins are developing as new types of chiral ligands.[12-13] Knochel,[14] Xu,[15-17] Du,[18-19] Liao,[20-21] Wan,[22] Chen,[23] Zeng[24] and so on have developed a series of chiral sulfoxide-olefin and sulfinamide-olefin ligands. Some typical chiral ligands are shown in Figure 1.

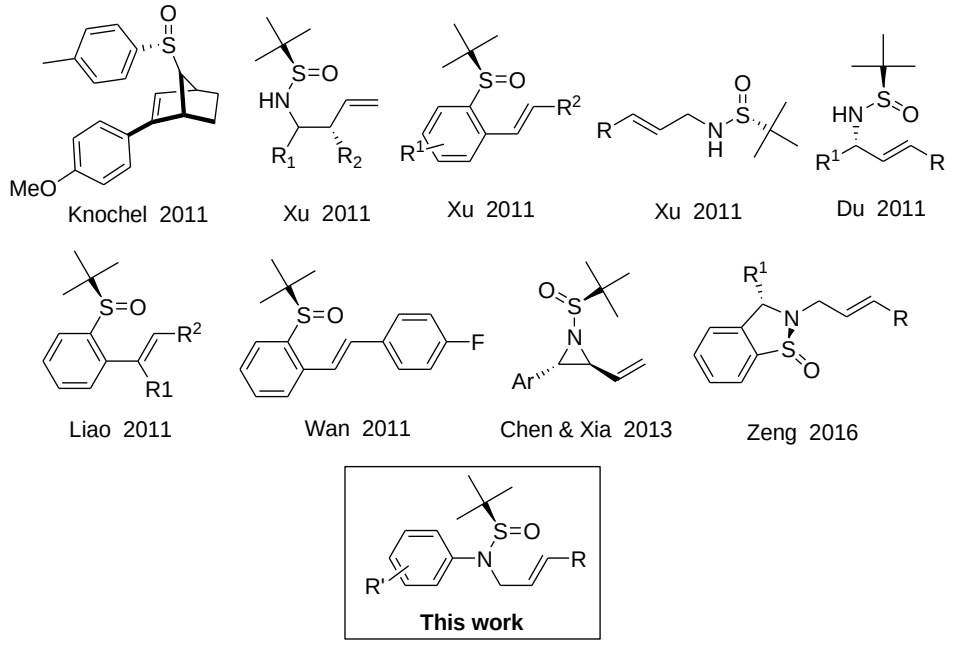
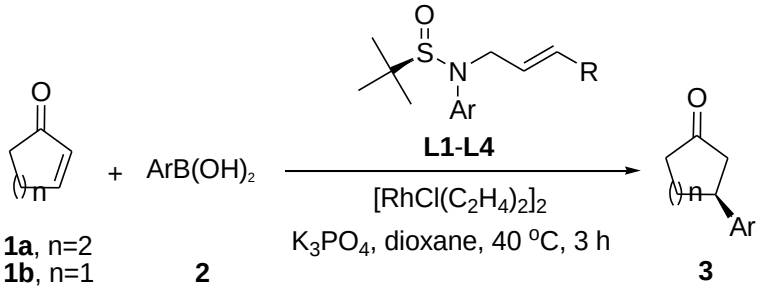


Figure 1. Some representative chiral sulfoxide/sulfinamide-olefin ligands and our designed N-aryl tert-butanesulfinamide-olefin ligands

We noticed that chiral sulfoxide-olefin ligands commonly possessed one or two aromatic rings, which often directly connect with sulfinyl groups. The reason probably is that the aromatic rings act as “chiral fences”, as afford excellent chiral induction circumstances. To the best of our knowledge, there is no chiral sulfinamide-olefin ligand with an aryl group directly connected to the nitrogen atom of the sulfinamide block. Therefore we wonder what reactivity and enantioselectivity of catalytic reactions will be if an aromatic ring was introduced on the nitrogen atom of the sulfinamide-olefin ligands (Figure 1).

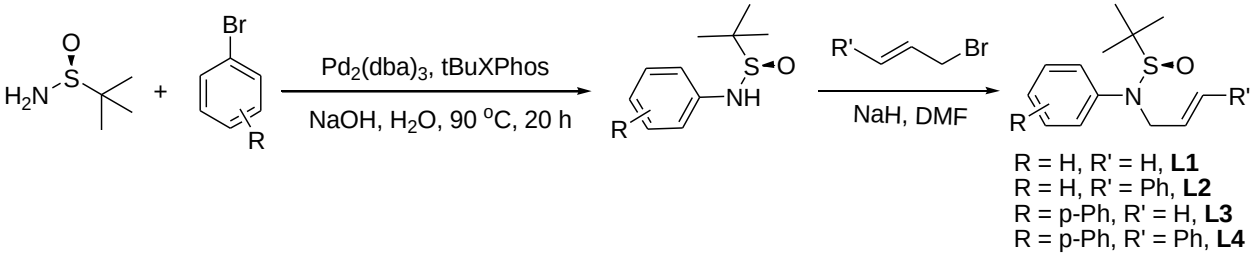
Our group has done a series of researches on chiral organic sulfur chemistry,[24-27] especially we have reported synthesis of a sulfinamide-olefin compound, namely, *N*-allyl-*N*-phenyl-tert-butanesulfinamide, via C-N coupling reaction and S_N2 nucleophilic substitution.[28] As we know, sulfinamide-olefin compounds are recently used as chiral ligand in highly enantioselective rhodium-catalyzed asymmetric 1,4-addition reaction of arylboronic acids to α,β-unsaturated carbonyl compounds,[29-30] which has extensive applications in medicinal synthesis and natural synthesis,[31] and has achieved great progress.[32-39] Furthermore, the C-N coupling reaction products are seldom directly used as chiral ligands.[40-41] Therefore we would like to explore the application of the C-N coupling products chiral N-aryl tert-butanesulfinamide-olefin ligands in rhodium-catalyzed asymmetric 1,4-addition reaction of arylboronic acids to cyclic enones (Scheme 1).



Scheme 1. Rhodium-catalyzed asymmetric addition with N-aryl tert-butanesulfinamide-olefin ligands as chiral ligands

Results and Discussion

We started our research by preparing chiral sulfinamide-olefin ligands (Scheme 2). Firstly, (R)-N-aryl-tert-butanesulfinamides are prepared according to our group's C-N coupling protocol (Scheme 2).[28] It is a little pity that slight racemization occurred during the C-N coupling reaction and N-phenyl-tert-butanesulfinamide with 97%ee was obtained.[28] And then chiral *N*-allyl and *N*-cinnamyl *N*-aryl-tert-butanesulfinamides were synthesized via S_N2 nucleophilic substitution of N-aryl-tert-butanesulfinamide with allyl or cinnamyl bromide (Scheme 2). To our delight, no any racemization occurred during the substitution.



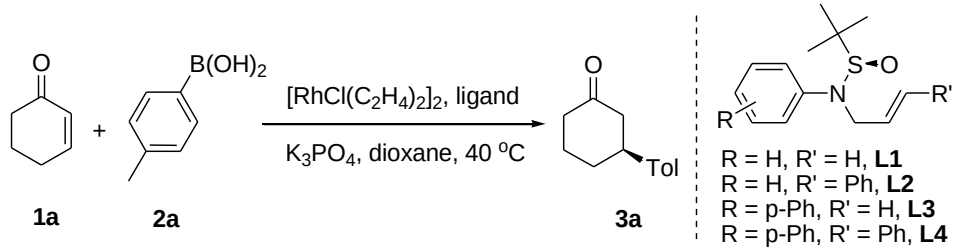
Scheme 2. Synthesis of chiral sulfinamide-olefin ligands *N*-allyl and *N*-cinnamyl-*N*-aryl-tert-butanesulfinamides **L1**-**L4**.

With chiral *N*-allyl and *N*-cinnamyl *N*-aryl-tert-butanesulfinamides in hand, we chose Rh-catalyzed 1,4-addition of phenylboronic acid to cyclohexenone as the model reaction to evaluate their catalytic performance (Table 1).

First of all, (*R*)-*N*-allyl-*N*-phenyl-tert-butanesulfinamide was used as the chiral ligand to examine the reaction (Table 1). To our delight, moderate enantioselectivity (63%ee) was obtained for the ligand (Entry 1), but it is much better than that (only 5%ee) of the reported ligand *N*-allyl-tert-butanesulfinamide without the N-phenyl group.[17] This result encouraged us to study further.

When allyl group was placed with cinnamyl group and thus (*R*)-*N*-cinnamyl-*N*-phenyl-tert-butanesulfinamide (**L2**) was used as ligand, enantioselectivity and yield increased obviously (Entry 2). Ligands (**L3** and **L4**) with another phenyl substitution at the *para*-position of *N*-phenyl of ligands **L1** and **L2**, but no better results were obtained (Entries 3 and 4).

Table 1. Evaluation of chiral ligands **L1** to **L4** in Rh-catalyzed asymmetric 1,4-addition



1a **2a** **3a**

Entry	Ligand	Yield (%)	ee (%)
1	**L1**	75	63
2	**L2**	96	89
3	**L3**	66	59
4	**L4**	64	83

All the reactions were carried out with 2-cyclohexenone (1.00 mmol), p-tolylboronic acid (1.5 mmol), K_3PO_4 (0.5 mmol), $[RhCl(C_2H_4)_2]_2$ (0.015 mmol), 97%ee chiral ligand (0.035 mmol) in 1,4-dioxane (3.0 mL) at 40 °C under argon for 3 h. The ee values were determined by chiral HPLC.

Next, we examined bases and solvents in Rh-catalyzed 1,4-addition of phenylboronic acid to cyclohexenone with **L2** as chiral ligand (Table 2). The results shows that all of the tested solvents may carried out the addition reaction, and 1,4-dioxane was the best one (Entries 1-4). The evaluation of the bases confirmed that K_3PO_4 is the preferred base (Entries 4-10).

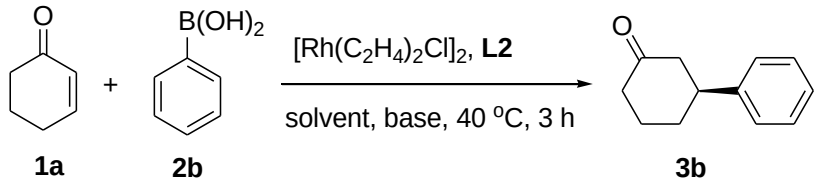
With the optimized conditions in hand, we examined various arylboronic acids to react with cyclohexenone in the presence of $[RhCl(C_2H_4)_2]_2$ and chiral ligand **L2** (Table 3). All of the reactions gave moderate to very high yields (Entries 1-13).

Except that 4-fluorophenylboronic acid gave lower ee value (Entry 13), arylboronic acids all afforded moderate to high enantioselectivities (Entries 1-12). Compared with phenylboronic acid (Entry 1), *para*-alkyl substitution favored the addition reaction (Entries 2 and 5), and *para*-tert-butylphenylboronic acid afforded the highest enantioselectivity of 93%ee (Entry 5). In view of the chiral ligand **L2** only with 97%ee, this is an excellent enantioselectivity. Among methyl-substituted arylboronic acids, *para*-methyl one gave the highest ee value, and meta-methyl one achieved the lowest.

However, for chloro-substituted arylboronic acids, *para*-chlorophenylboronic acid exhibited poorer enantioselectivity than the meta- and ortho-phenylboronic acids (Entries 9 vs 10-11). It seems that arylboronic acids with *para*-electron-donating groups, such as alkyl, methoxyl, were more beneficial to enantioselectivity

than that with *para*-electron-withdrawing groups, such as chloro, bromo, fluoro (Entries 2, 5, 8 vs. 9, 12, 13). To our delight, halo and vinyl groups are compatible for this reaction (Entries 6 and 9-13).

Table 2. Screening of bases and solvents of Rh-catalyzed 1,4-addition of phenylboronic acid to cyclohexanone

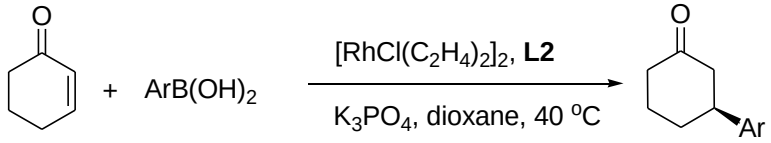


1a **2b** **3b**

Entry	solvent	base	Yield (%)	Ee (%)[b]
1	EtOH	K_3PO_4	43	70
2	DCE	K_3PO_4	46	71
3	THF	K_3PO_4	41	55
4	dioxane	K_3PO_4	90	93
5	dioxane	KF	75	68
6	dioxane	KOH	71	67

All the reactions were carried out with cyclohexenone (1.00 mmol), phenylboronic acid (1.5 mmol), base (0.5 mmol), $[RhCl(C_2H_4)_2]_2$ (0.015 mmol), 97%ee **L2** as chiral ligand (0.035 mmol) in solvent (3.0 mL) at 40 °C under argon for 3 h. The ee was determined by chiral HPLC.

Table 3. Asymmetric 1,4-addition reaction of various arylboronic acids and cyclohexenone in the presence of rhodium and chiral ligand **L2**



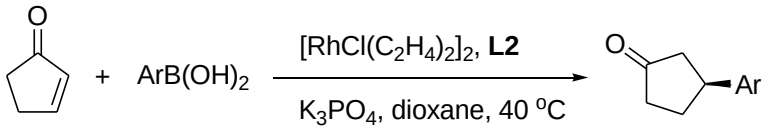
1a **2** **3**

Entry	Ar	Product	Yield (%)	Ee (%)
1	Ph	**3b**	93	83
2	4-MeC_6H_4	**3a**	96	89
3	3-MeC_6H_4	**3c**	90	75
4	2-MeC_6H_4	**3d**	91	81
5	4-$(CH_3)_3CC_6H_4$	**3e**	89	93
6	4-$(CH_2{=}CH)C_6H_4$	**3f**	81	85
7	2-naphthyl	**3g**	90	79
8	4-$MeOC_6H_4$	**3h**	97	85
9	4-ClC_6H_4	**3i**	88	73
10	3-ClC_6H_4	**3j**	81	83
11	2-ClC_6H_4	**3k**	83	83
12	4-BrC_6H_4	**3l**	83	83
13	4-FC_6H_4	**3m**	70	55

All the reactions were carried out with cyclohexenone (1.00 mmol), arylboronic acid (1.5 mmol), base (0.5 mmol), $[RhCl(C_2H_4)_2]_2$ (0.015 mmol), 97% ee **L2** as chiral ligand (0.035 mmol) in solvent (3.0 mL) at 40 °C under argon for 3 h. The ee was determined by chiral HPLC.

After evaluation of cyclohexenone, we continued to investigate cyclopentenone to react with several arylboronic acids in the presence of $[RhCl(C_2H_4)_2]_2$ and chiral ligand **L2** (Table 4). Phenylboronic acid afforded good yield and high enantioselectivity of 93%ee (Entry 1). Moreover, ortho-methylphenylboronic acid even gave better result with 95%ee (Entry 3), which is a very high enantioselectivity in consideration of 97%ee **L2** as chiral ligand. Except 4-tert-butylphenylboronic acid with much poorer result, arylboronic acids with electron-donating groups afforded good to high enantioselectivities (Entries 1-5). For 2-naphthylboronic acid, cyclopentenone gave poorer result cyclohexenone (Table 4, entry 6 vs. Table 3, entry 7).

Table 4. Asymmetric 1,4-addition reaction of various arylboronic acids and cyclopentenone in the presence of rhodium and chiral ligand **L2**



1b **2** **3**

Entry	Ar	Product	Yield (%)	Ee (%)
1	Ph	**3n**	82	93
2	4-MeC_6H_4	**3o**	90	83
3	2-MeC_6H_4	**3p**	86	95
4	4-$(CH_3)_3CC_6H_4$	**3q**	77	55
5	4-$MeOC_6H_4$	**3r**	89	83
6	2-Naphthyl	**3s**	80	55

All the reactions were carried out with cyclopentenone (1.00 mmol), arylboronic acid (1.5 mmol), base (0.5 mmol), $[RhCl(C_2H_4)_2]_2$ (0.015 mmol), 97%ee **L2** as chiral ligand (0.035 mmol) in solvent (3.0 mL) at 40 °C under argon for 3 h. The ee was determined by chiral HPLC.

According to the structure of (*R*)-*N*-cinnamyl-*N*-phenyl-tert-butanesulfinamide **(L2**) and the former study on the rhodium-catalyzed 1,4-addition mechanism,[33,38-39] we propose a Rh-catalyzed enantioselective 1,4-addition model during the transition state. There will exist a most stable conformation with Si face selectivity, which produce S form addition product (S)-3-phenylcyclohexanone (Figure 2). While there is large repulsion between cinnamyl's phenyl group and cyclohexenone perpendicular coordination to rhodium in the Re face transition state, so (R) form product is the minor component (Figure 2). The model well explains high S form enantioselectivity when (R)-**L2** is used.

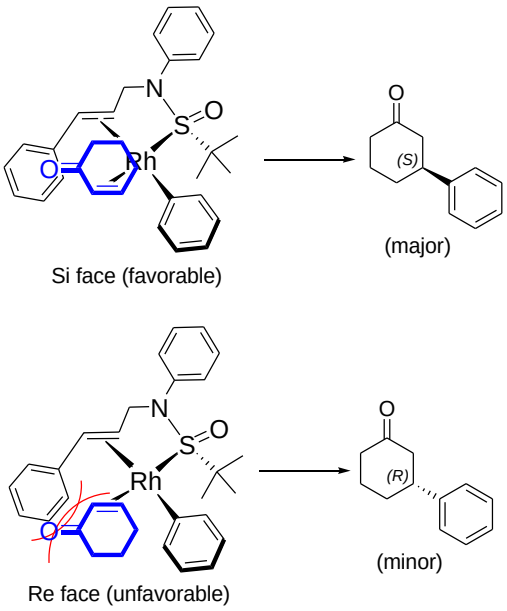


Figure 2. Enantioselective model for the addition to 2-cyclohexenone (**1a**) catalyzed by the Rh(I)/(R)-**L2** complex.

Conclusions

We have developed a new type of chiral *N*-aryl tert-butanesulfinamide-olefin ligand as chiral ligands in rhodium-catalyzed asymmetric 1,4-addition of aryl boronic acids to cyclic enones. The chiral ligands are readily synthesized via C-N coupling reaction and nucleophilic substitution, but only 97%ee chiral ligands were obtained due to the slight racemization during the C-N coupling reaction. Given that chiral ligands with 97%ee produced 1,4-addition products up to 95%ee, *N*-aryl tert-butanesulfinamide-olefin ligands demonstrates fairly high chiral induction ability in the rhodium-catalyzed asymmetric 1,4-addition.

Experimental Section

General. All chemicals were purchased from Aldrich, Aladdin, Alfa Aesar, Adamas, and Kelong Chemical Company and used as received. Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. All reactions were carried out under argon atmosphere. All glassware used was dried in electric oven at 120 °C. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, HR-MS and IR spectroscopy, unless otherwise mentioned. Nuclear magnetic resonance spectra were recorded on a 300MHz instrument or 400 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), DMSO (2.50 ppm) or acetone (2.05 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.2 ppm), DMSO-d_6 (39.5 ppm) or acetone-d_6 (206.7 ppm for C=O) unless otherwise stated, and all were obtained with ^{1}H decoupling. All IR spectra were taken on an infrared spectrometer. High-resolution mass spectra are recorded on an LCMS-IT-TOF instrument. Chiral HPLC analyses were performed on

a Shimadzu liquid chromatography with a Chiralcel OD-H, AD-H, AS-H chiral column (4.6 mm × 250 mm × 5 μm). All rotation data are recorded on an auto rotation (Na D line, cell long 10 cm, λ 589 nm).

Procedure for synthesis of chiral ligands L1 to L4. An oven-dried round-bottom flask with a magnetic stir bar and fitted with a rubber septum, was charged with (R)-tert-butanesulfinamide (13.0 mmol), $Pd_2(dba)_3$ (0.26 mmol), tBu-XPhos (0.45 mmol), NaOH (26 mmol), bromobenzene (10.0 mmol), toluene (20 mL), and degassed water (3.0 mL).The vessel was evacuated and backfilled with argon for three times. The solution was stirred at 90 °C for 20 h. when cooled to room temperature, quenched by water, and extracted with ethyl acetate (35 mL) for three times. The combined organic layer was dried over anhydrous $MgSO_4$. The filtrate was condensed under vacuum. The resulting residual was purified with silica gel column chromatography with a solution of petroleum ether and ethyl acetate (5:1 (v:v)) as an eluent to afford N-aryl tert-butanesulfinamide.

To an oven-dry round-bottom flask with a magnetic stir bar was added N-phenyl (R)-tert-butanesulfinamide (4.0 mmol), 60% NaH (8 mmol), and THF (15 mL). The vessel was evacuated and backfilled with argon for three times. Then the mixture was stirred in an ice water bath for 1 h, and then added cinnamyl bromide (1.2 mmol) by syringe to the flask. The reaction mixture was stirred overnight. Then quenched by saturated NH_4Cl solution, the reaction mixture was extracted with ethyl acetate (20 mL) three times. The combined organic layer was washed with saturated NaCl solution and then dried over anhydrous $MgSO_4$. The filtrate was condensed under vacuum. The residual was purified with a silica gel column chromatography with a mixed solution of petroleum ether and ethyl acetate (5:1(v:v)) as an eluent to afford (R)-*N*-cinnamyl-2-methyl-*N*-phenylpropane-2-sulfinamide (**L2**).

The same synthetic method as **L2** was adopted for synthesis of chiral ligands **L1**, **L3**, **L4**.

(*R*)-*N*-cinnamyl-2-methyl-*N*-phenylpropane-2-sulfinamide (**L2**). White solid. Yield: 25.3 mg (81%). mp 94-97 °C. $[\alpha]_D^{20.5}$ +105°(c 0.21, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.39 (m, 2H), 7.35 – 7.21 (m, 4H), 7.07 (dd, *J* 16.2, 8.0 Hz, 2H), 6.58 (dt, *J* 14.4, 7.6 Hz, 4H), 6.36 (dt, *J* 16.0, 5.6 Hz, 1H), 3.89 – 3.81 (m, 2H), 1.05 (s, 7H). ^{13}C NMR (101 MHz, DMSO): δ 137.19 (s), 136.68 (s), 132.66 (s), 130.63 (s), 129.43 (d, *J* 17.0 Hz), 129.08 (s), 128.42 (s), 128.07 (s), 127.78 (s), 126.60 (d, *J* 6.9 Hz), 126.34 (s), 123.67 (s), 121.68 (s), 59.99 (s), 55.73 (s), 23.44 (s), 21.51 (s). IR (KBr), ν (cm^{-1}): 3056, 3025, 2936, 2593, 2154, 1927, 1702, 1655, 1592, 1472, 1363, 1298, 1246, 1176, 1075, 968, 852, 781. ESI-MS (positive mode), *m/z* 336 [M + Na] $^+$. HR-MS (ESI-TOF) *m/z* calcd for $C_{19}H_{23}NNaOS$ [M+Na^+] 336.1393; found 336.1379. Chiral HPLC: Chiralcel OD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol 95:5; flow rate: 0.7 ml/min; retention time: 12.7 min (minor), 15.2 min (major). Measured ee value 97 %.

(*R*)-*N*-([1,1'-biphenyl]-4-yl)-*N*-allyl-2-methylpropane-2-sulfinamide (**L3**). White solid. Yield: 21.0 mg (80%). mp 72-75 °C. $[\alpha]_D^{21.0}$ +88.98° (c 0.12, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.51 (m, 4H), 7.45 – 7.40 (m, 2H), 7.32 (ddt, *J* 9.5, 8.2, 4.1 Hz, 1H), 7.25 – 7.21 (m, 2H), 5.88 – 5.76 (m, 1H), 5.25 – 5.12 (m, 2H), 4.38 – 4.25 (m, 1H), 4.14 – 4.00 (m, 1H), 1.26 (d, *J* 11.7 Hz, 9H). ^{13}C NMR (101 MHz, DMSO): δ 141.01 (s), 129.29 (d, *J* 18.4 Hz), 127.60 (s), 126.74 (s), 126.22 (s), 125.89 (s), 113.35 (s), 60.09 (s), 55.73 (s), 23.32 (s), 21.50 (s). IR (KBr), ν (cm^{-1}): 3417, 3050, 2959, 1601, 1519, 1484, 1450, 1364, 1295, 1251, 1204, 1142, 1091, 1055, 995, 918, 827, 757, 692. ESI-MS (positive mode), *m/z* 336 [M + Na] $^+$. HR-MS (ESI-TOF) *m/z* calcd for $C_{19}H_{23}NOS$ [M+Na^+] 336.1393; found 336.1405. Chiral HPLC: Chiralcel OD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol 95:5; flow rate: 0.7 ml/min; retention time: 5.5 min (minor), 10.6 min (major).

(*R*)-*N*-([1,1'-biphenyl]-4-yl)-*N*-cinnamyl-2-methylpropane-2-sulfinamide (**L4**). Yellow solid. Yield: 23.3 mg (81%). mp 116-119 °C. $[\alpha]_D^{21.2}$ +116.20° (c 0.14, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.49 (m, 4H), 7.44 – 7.38 (m, 2H), 7.30 (ddd, *J* 8.8, 7.4, 2.0 Hz, 6H), 7.21 (ddd, *J* 6.8, 3.8, 1.6 Hz, 1H), 6.51 (d, *J* 16.0 Hz, 1H), 6.19

(dt, *J* 16.0, 5.9 Hz, 1H), 4.45 (ddd, *J* 16.8, 6.2, 1.5 Hz, 1H), 4.24 (ddd, *J* 16.8, 5.6, 1.5 Hz, 1H), 1.28 (d, *J* 11.9 Hz, 8H). ^{13}C NMR (101 MHz, DMSO): δ 144.88 (s), 139.88 (s), 137.18 (s), 136.66 (s), 135.07 (s), 132.66 (s), 130.58 (s), 129.46 – 128.95 (m), 128.42 (s), 128.09 (s), 127.66 (t, *J* 13.6 Hz), 126.86 – 126.49 (m), 126.27 (d, *J* 18.1 Hz), 125.86 (s), 121.46 (s), 113.17 (s), 60.17 (s), 55.73 (s), 23.44 (s), 21.51 (s). IR (KBr), ν (cm^{-1}): 3432, 3041, 2938, 1602, 1519, 1486, 1364, 1305, 1254, 1203, 1083, 1050, 962, 845, 733, 694. ESI-MS (positive mode), *m/z* 412 ([M + Li]$^+$). HR-MS (ESI-TOF) *m/z* calcd for $C_{25}H_{27}NNaOS$ [M+Na$^+$] 412.1706; found 412.1715. Chiral HPLC: Chiralcel OD-H Column (Particle Size: 5 μm, dimensions: 4.6 mm×250 mm); detected at 254 nm; n-hexane: 2-propanol 95:5; flow rate: 0.7 ml/min; retention time: 15.3 min (minor), 20.3 min (major).

Procedure of rhodium-catalyzed 1,4-addition reaction. To an oven-dry test tube with a ground joint neck with a magnetic stir bar were added enone (1.00 mmol), arylboronic acid (1.5 mmol), $[RhCl(C_2H_4)_2]_2$ (0.015 mmol, 1.32 mg), Ligand (0.035 mmol) in 1,4-dioxane (3.0 mL). The vessel was evacuated and backfilled with argon for three times. The solution was stirred at 40 °C for 30 min, and then aqueous K_3PO_4 (0.5 mmol, 106 mg) was added by syringe to the flask. After being stirred at 40 °C for 3 h, the reaction mixture was then cooled to room temperature, quenched by water, and extracted with ethyl acetate (15 mL) for three times. The combined organic layer was dried over anhydrous $MgSO_4$. The filtrate was condensed in vacuum. The residual was purified with silica gel column chromatography with a solution of petroleum ether and ethyl acetate as an eluent to afford the product. The ee value was determined by chiral HPLC.

Acknowledgements

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Supplementary Material

Full experimental details, ^{1}H and ^{13}C NMR spectra.

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