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PAPER

Design of *N*-cinnamyl sulfinamides as new sulfur-containing olefin ligands for asymmetric catalysis: achieving structural simplicity with a categorical linear framework†

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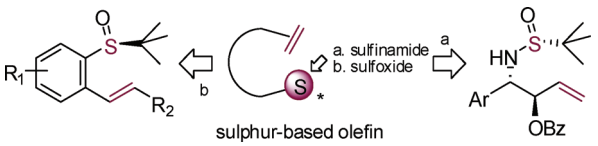
The design and development of an extraordinarily interesting new class of chiral sulfur–olefin hybrid ligands with remarkable structural simplicity were described. These unique sulfinamide–olefin ligands have been proved to be highly effective ligands in rhodium-catalyzed asymmetric 1,4-addition reactions of aryl boronic acids to α,β-unsaturated carbonyl compounds (up to 99% yield and 98% ee).

Introduction

The transition metal complex catalyzed asymmetric transformation constitutes a very important and fundamental protocol for modern organic synthesis and the pharmaceutical industry to gain access to enantioenriched compounds.[1] Despite substantial progress in developing various stereodefined metal–ligand complex catalysts, designing easily accessible, cheaper chiral ligands/catalysts with high catalytic activity and selectivity remains an eminently desirable goal and is thus a subject of great interest. In the past decades, there have been numerous chiral ligands as well as chiral catalysts reported, but most of them possess sophisticated scaffolds, which are often expensive and difficult to obtain.[1–3] Moreover, much chemistry has been based on phosphorus- or nitrogen-containing ligands.[1–3] Chiral sulphur-containing ligands, however, have received less attention in asymmetric catalysis. Nevertheless, because of the exceptional advantages of easy availability, high stability, good metal-affinity and special *S*-stereogenic control, the design and synthesis of structurally diverse chiral sulphur ligands for transition metal-catalyzed asymmetric reactions are rapidly increasing nowadays.[4]

Most recently, we discovered that simple and readily available chiral sulfinamide- or sulfoxide-olefins can display great catalytic activities and enantioselectivities in rhodium-catalyzed asymmetric 1,4-addition reactions (Scheme 1).[5] In the meantime, other research groups of Knochel,[6] Yang and Du,[7a] Liao[8a] and Wan[8b] also found that structurally appropriate sulphur-containing olefins are capable of rhodium catalysis.[9,10] These studies clearly revealed that unprecedented chiral sulfur–olefins have emerged as a significantly new and promising class of ligands. In continuation of our own exploration of chiral sulfur–olefin hybrid ligands and their application in asymmetric catalysis, we describe herein an extremely simple chiral sulfinamide-based olefin ligand that is readily accessible in a single-pot operation from commercially available cinnamaldehyde and chiral *N*-*tert*-butanesulfinamide, and its exceptional performance in rhodium–catalyzed asymmetric conjugate addition.[11]



Scheme 1 Our previous work on chiral sulphur-based olefins.

Results and discussion

In our previous studies employing *N*-sulfinyl homoallylic amine ligands, we observed that the carbon chiralities on the molecular backbone have little impact on the reaction selectivity.[5a] Inspired by these findings, we hypothesized that chiral sulfinamide–olefin **1** bearing a categorical linear framework without any pendant group should function as a ligand and form a conformationally rigid cyclic chelate upon coordination, which might promote the reaction equally in a stereoselective manner (Scheme 2). In this design, an intriguing prospect is the simplicity. The ligand only incorporates a single chiral center at the sulfur on a sulfinamide moiety, thus could be very easily synthesized.

To test this idea, we began our study by choosing readily available *N*-allyl sulfinamide **1a** (n = 1, R = H) and *N*-cinnamyl sulfinamide **1b** (n = 1, R = Ph) as two initial ligands. As shown in Scheme 3, **1a** and **1b** could be easily obtained in one single pot by *N*-allylation and condensation–reduction from

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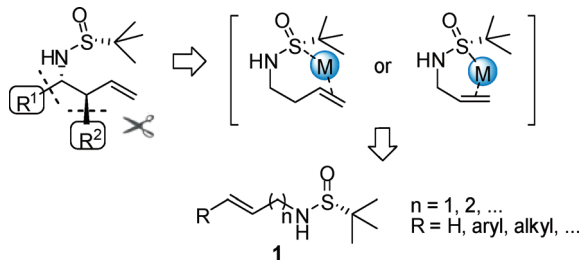
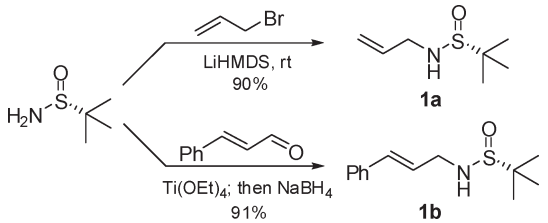
†Electronic supplementary information (ESI) available: Experimental details including copies of ^{1}H and ^{13}C NMR and HPLC spectra. See DOI: 10.1039/c2ob06723d



Scheme 2 New chiral sulfinamide–olefin ligand proposal.



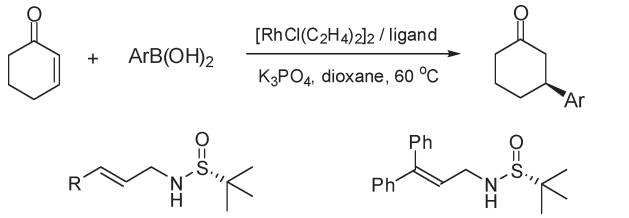
Scheme 3 Synthesis of simple sulfinamide–olefin ligands **1a** and **1b**.

enantiopure (*R*)-*N*-*tert*-butanesulfinamide in 90% and 91% yield, respectively.

To examine the catalytic potential of the designed ligands, reaction of Rh-catalyzed conjugate addition of phenyl boronic acid to 2-cyclohexenone was performed using 3 mol% of **1a** and **1b** under aqueous K_3PO_4/dioxane at 60 °C, respectively. Interestingly, both reactions proceeded smoothly as expected and went to completion in 1 h, giving the corresponding product in 99% yield. To our great delight, an excellent enantioselectivity (96% ee) was observed with the use of *N*-cinnamyl sulfinamide ligand **1b**, although *N*-allyl sulfinamide **1a** afforded a very low enantioselectivity (5% ee). These results clearly demonstrate that the above proposed simple sulfinamide–olefins indeed can be suitable chiral ligands for asymmetric catalysis.

Being aware of the stereoinduction importance of the R substituent attached to the terminal double bond, we then focused our efforts on exploring *N*-cinnamyl sulfinamide analogues containing different R groups. Following the one-pot condensation–reduction procedure in Scheme 3, a series of structurally simple sulfinamide–olefin compounds **1c–i** were prepared. Table 1 outlines the evaluation of these compounds as chiral ligands in the reaction of phenyl boronic acid with 2-cyclohexenone under the same conditions. In most cases, except for **1f** bearing a sterically very bulky 1-naphthyl (entry 6), complexes of **1b–e** and **1g**, **1h** with $[RhCl(C_2H_4)_2]_2$ exhibited an equally high catalytic activity with the same excellent enantiomeric excess of 96–97% (entries 1–5, 7–8 and 10–11), suggesting that changing the R group of the ligand has almost no influence on the activity and enantioselectivity. In particular, the electronic properties of substituents on the aryl ring had no impact on the ee of the products. However, similar to **1f**, **1i** with an additional phenyl group on the olefin moiety completely lost its catalytic activity, giving no product of the reaction presumably due to the coordination difficulty raised by the increased steric hindrance (entry 9). Given the high availability of cinnamaldehyde for ligand preparation, we chose **1b** instead of the others as the ideal ligand for further intensive study.

Table 1 Ligand screening[a]



1a R = H
1b R = Ph
1c R = 4-$MeOC_6H_4$
1d R = 4-$CF_3C_6H_4$
1e R = 3,4,5-$(MeO)_3C_6H_2$
1f R = 1-Naphthyl
1g R = 2-Naphthyl
1h R = cyclohexyl

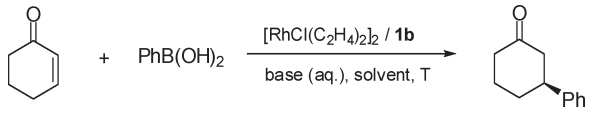
Entry	Ar	Ligand	Yield (%)[b]	ee (%)[c]
1	Ph	**1a**	99	5
2	Ph	**1b**	99	96 (*S*)
3	Ph	**1c**	99	96 (*S*)
4	Ph	**1d**	99	96 (*S*)
5	Ph	**1e**	99	96 (*S*)
6	Ph	**1f**	trace	—
7	Ph	**1g**	99	97 (*S*)
8	Ph	**1h**	99	96 (*S*)
9	Ph	**1i**	N.R	—
10	4-MeC_6H_4	**1b**	99	96 (*S*)
11	4-MeC_6H_4	**1g**	99	96 (*S*)

[a] Reaction conditions: $ArB(OH)_2$ (0.5 mmol), 2-cyclohexenone (0.25 mmol), $[RhCl(C_2H_4)_2]_2$ (3 mol%), ligand (3 mol%), and K_3PO_4 (1.5 M aq., 0.5 eq) in dioxane (0.5 mL) at 60 °C for 0.5 h. [b] Isolated yield. [c] Determined by HPLC analysis on a Daicel Chiralcel OJ-H column; the absolute configuration was determined by comparison with known data.

Encouraged by the above results, we proceeded to further optimize the reaction parameters using **1b** as the ligand. A survey of solvents indicated that the use of dioxane, THF, or MeOH provided the same high enantioselectivity (96% ee) while a non-coordinating solvent such as toluene or $(CH_2)_2Cl_2$ would lead to diminished enantioselectivities (90% ee) (Table 2, entries 1–5). A very slight improvement of the ee was achieved by lowering the reaction temperature to 40 °C (97% ee, entry 6). Subsequent examination of other base additives including Na_2CO_3, K_2CO_3, KF, KOH, LiOH and Et_3N did not give better results (for selected examples, see entries 7–9). Notably, the catalyst loading can be reduced to 1 mol% or even 0.5 mol% without compromising the enantioselectivity (entries 10–11). The reaction can also be performed at room temperature to afford the addition product with 96% ee, but the yield decreases to 80% (entry 12).

Having identified the optimal conditions, we turned our attention to investigate the reaction substrate scope of this rhodium-catalyzed asymmetric 1,4-addition using **1b** as a chiral ligand. Gratifyingly, unlike the use of previous reported chiral sulfinamide–olefin ligand *N*-sulfinyl homoallylic amine,[5a] the reaction generality disclosed herein appears to be quite broad. As illustrated in Table 3, a wide range of arylboronic acids with varying electronic and steric demands were successfully reacted with α,β-unsaturated carbonyl compounds including not only common cyclic enones such as 2-cyclohexenone (**2a**), 2-cyclopentenone (**2b**), but also cyclic ester 5,6-dihydro-2-pyranone (**2c**) and amide 1-benzyl-5,6-dihydropyridin-2(1*H*)-one (**2d**), giving the corresponding addition products **3** in very good yields

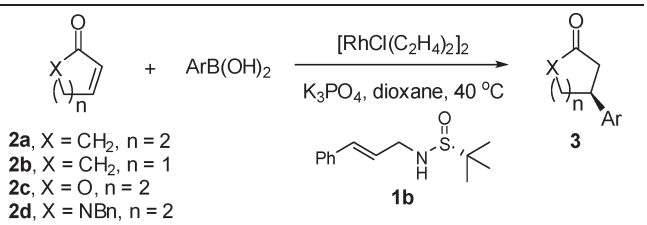
Table 2 Optimization of the reaction conditions[a]



Entry	Solvent	T (°C)	Base	Yield (%)[b]	ee (%)[c]
1	dioxane	60	K_3PO_4	99	96
2	THF	60	K_3PO_4	99	96
3	MeOH	60	K_3PO_4	98	96
4	toluene	60	K_3PO_4	99	90
5	DCE	60	K_3PO_4	99	90
6	dioxane	40	K_3PO_4	99	97
7	dioxane	40	Na_2CO_3	99	97
8	dioxane	40	KF	99	96
9	dioxane	40	K_2CO_3	99	97
10[d]	dioxane	40	K_3PO_4	98	97
11[e]	dioxane	40	K_3PO_4	80	97
12	dioxane	rt	K_3PO_4	80	96

[a] The reaction was carried out with 0.25 mmol of 2-cyclohexenone, 0.5 mmol of arylboronic acid in the presence of 3 mol % of $[RhCl(C_2H_4)_2]_2$ and ligand **1b**, 1.5 M aq base (0.5 eq) in solvent (0.5 mL) for 0.5–1 h, unless otherwise noted. [b] Isolated yield. [c] Determined by HPLC analysis on a Daicel Chiralcel OJ-H column. [d] 1 mol% of Rh/**1b** was used. [e] 0.5 mol% of Rh/**1b** was used, for 2 h.

Table 3 $[RhCl(C_2H_4)_2]_2$/**1b**-catalyzed asymmetric conjugated addition[a]



2a, X = CH_2, n = 2
2b, X = CH_2, n = 1
2c, X = O, n = 2
2d, X = NBn, n = 2

Entry	**2**	Ar	**3**	Yield (%)[b]	ee (%)[c]
1	**2a**	C_6H_5	**3a**	99	97
2	**2a**	4-MeC_6H_4	**3b**	99	96
3	**2a**	4-MeOC_6H_4	**3c**	94	96
4	**2a**	4-FC_6H_4	**3d**	99	97
5	**2a**	4-ClC_6H_4	**3e**	99	96
6	**2a**	3-MeC_6H_4	**3f**	98	97
7	**2a**	2-MeC_6H_4	**3g**	57	97
8	**2a**	2-MeOC_6H_4	**3h**	90	94
9	**2a**	1-naphthyl	**3i**	99	97
10	**2a**	2-naphthyl	**3j**	99	96
11	**2b**	C_6H_5	**3k**	99	97
12	**2b**	4-MeC_6H_4	**3l**	98	96
13	**2b**	4-ClC_6H_4	**3m**	99	96
14	**2b**	2-MeOC_6H_4	**3n**	88	97
15	**2b**	1-naphthyl	**3o**	99	98
16	**2c**	C_6H_5	**3p**	80	97
17	**2c**	2-MeOC_6H_4	**3q**	72	96
18	**2c**	3-MeC_6H_4	**3r**	85	97
19	**2c**	1-naphthyl	**3s**	84	97
20	**2d**	C_6H_5	**3t**	87	95
21	**2d**	4-FC_6H_4	**3u**	76	97
22	**2d**	4-ClC_6H_4	**3v**	81	97

[a] The reaction was carried out with 0.25 mmol of substrate **2**, 0.5 mmol of arylboronic acid in the presence of 3 mol % of $[RhCl(C_2H_4)_2]_2$ and ligand **1b**, 1.5 M aq K_3PO_4 (0.5 eq) in dioxane (0.5 mL) at 40 °C for 0.5–1 h. [b] Isolated yield. [c] Determined by HPLC analysis on Daicel chiral columns.

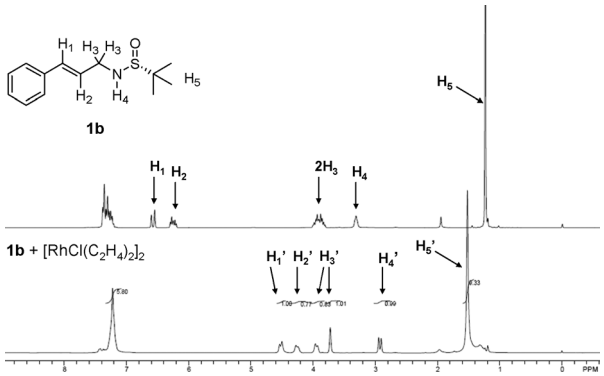


Fig. 1 Comparison of ^{1}H NMR chemical shifts.

(72–99% yield except entry 7) and with excellent enantioselectivities (94–98% ee) in all cases.

To demonstrate the scalability of the procedure, the reaction of substrate **2d** with phenyl boronic acid was carried out on a 5 mmol scale (*vs* 0.25 mmol scale in Table 3) in the presence of only 1 mol% of Rh/**1b**. As expected, the addition product **3t** was isolated in 75% yield with comparable enantioselectivity (95% ee), suggesting the practicality of the reaction. In addition, this catalytic system is also applied to asymmetric addition of α,β-unsaturated acyclic substrate. When linear ester *tert*-butyl cinnamate was subjected to react with 4-methoxyphenyl boronic acid in THF, both modest yield (65%) and enantioselectivity (80% ee) were afforded.

We have also investigated the formation of Rh/**1b** complex by NMR spectroscopy. After treatment of *N*-cinnamyl sulfinamide ligand **1b** with $[RhCl(C_2H_4)_2]_2$ (0.5 equiv) in $CDCl_3$ at rt for 30 min, several new ^{1}H signals appeared that were assigned to a dimeric rhodium complex. Upon coordination, two olefinic protons move upfield from 6.59 and 6.27 to 4.52 and 4.26 ppm, and the *tert*-butyl protons close to sulfur shifted downfield from 1.25 to 1.52 ppm (Fig. 1). In addition, the ^{13}C NMR spectra also indicated large chemical shifts of olefin carbons and quaternary *tert*-butyl carbon.† Unfortunately, attempts to obtain the X-ray crystal structure have been unsuccessful so far.

When considering the stereochemical outcome of the reaction, we assume that the transition state after transmetalation[12] exists in a preferred conformation with a specific geometry in which the aryl substituent is positioned *trans* to the olefin ligand and the *tert*-butyl moiety is staggered. To avoid the steric repulsion, rhodium coordination to the α,β-unsaturated substrate is favored in such a manner that the ring is oriented away from the bulky R substituent attached to the double bond (Fig. 2).

Conclusion

In summary, we have designed a novel, unique and extremely simple sulfinamide–olefin class of ligands for asymmetric catalysis, and their great catalytic activity and enantioselectivity as chiral ligands has been revealed through highly enantioselective rhodium-catalyzed asymmetric conjugate addition. The key advantage of these chiral sulfur-based olefin ligands over other known ligands lies in their extraordinary structural simplicity. It offers not only remarkable synthetic and economic benefits but

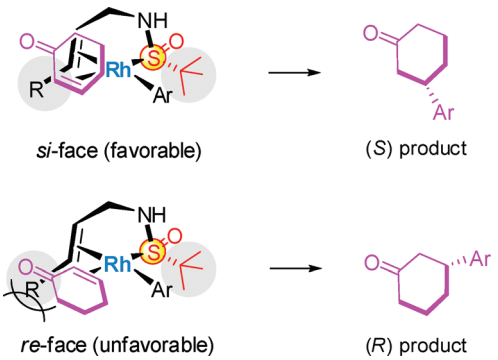


Fig. 2 Proposed reaction transition state model.

also promising opportunities for future ligand design and catalytic applications. Further studies are underway in our laboratory to extend their use in other catalytic asymmetric transformations.

Experimental

General

NMR spectra were recorded on Varian spectrometers (300 MHz for ^{1}H, and 100 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-*d* (δ 77.16) for ^{13}C NMR. HPLC was performed on a JASCO 2000 instrument by using Daicel chiral columns with 2-propanol/hexane as the eluent at 214 nm.

Procedure for preparation of ligand 1a

Under a N_2 atmosphere, 2 mL of LiHMDS (1 M in THF, 2 mmol) was added to a solution of (*R*)-*tert*-butanesulfinamide (121 mg, 1 mmol) in 5 mL THF at room temperature. After 15 min, allyl bromide (1.6 mL, 2 mmol) was added to the mixture and the reaction was stirred for 2 h at room temperature. When the reaction was complete, 10 mL of water was added. The solution was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography gave the product **1a** as colorless oil (145 mg, 90% yield).

Typical procedure for preparation of ligand 1b

A solution of cinnamaldehyde (1.9 mL, 15 mmol), (*R*)-*tert*-butanesulfinamide (1.21 g, 10 mmol) and $Ti(OEt)_4$ (4.1 mL, 20 mmol) in 30 mL THF was heated to reflux for 4 h. Then the reaction was cooled to room temperature and $NaBH_4$ (1.52 g, 40 mmol). The mixture was stirred at room temperature for additional 2 h. When the reaction was complete, methanol was added dropwise until there was no bubble. The mixture was poured to 30 mL of brine, stirred for a while and filtered. The filtrate was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography gave the product **1b** as a white solid (2.15 g, 91% yield).

(*R*)-*N*-Allyl-2-methylpropane-2-sulfinamide (1a)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 9H), 3.29 (s, 1H), 3.67–3.86 (m, 2H), 5.16 (dd, J = 10.2, 1.2 Hz, 1H), 5.27 (dd, J = 17.1, 1.5 Hz, 1H), 5.85–5.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.67, 48.20, 55.78, 117.12, 135.30; IR (KBr): ν 3442, 3210, 2956, 2867, 1643, 1475, 1363, 1058, 918, 596 cm^{-1}; ESI-MS: 162.0 $[M + H]^+$, 322.9 $[2M + H]^+$; HRMS (ESI) for $C_7H_{15}NOSNa$ $[M + Na]^+$: calcd 184.0772, found 184.0764.

(*R*)-*N*-Cinnamyl-2-methylpropane-2-sulfinamide (1b)

$[\alpha]_D^{20}$: − 23.4 (c 0.90, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 9H), 3.35 (t, J = 5.7 Hz, 1H), 3.82–4.01 (m, 2H), 6.25 (dt, J = 15.9, 6.6 Hz, 1H), 6.58 (d, J = 15.9 Hz, 1H), 7.24–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.74, 47.97, 55.88, 126.55, 127.89, 128.67, 132.66, 136.51; ESI-MS: 238.0 $[M + H]^+$, 475.0 $[2M + H]^+$; HRMS (ESI) for $C_{13}H_{19}NOSNa$ $[M + Na]^+$: calcd 260.1085, found 260.1070.

(*R*)-*N*-(3-(4-Methoxyphenyl)allyl)-2-methylpropane-2-sulfinamide (1c)

$[\alpha]_D^{20}$: − 18.6 (c 0.83, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 9H), 3.34 (t, J = 5.4 Hz, 1H), 3.80 (s, 3H), 3.83–3.98 (m, 2H), 6.11 (dt, J = 15.6, 6.6 Hz, 1H), 6.52 (d, J = 15.6 Hz, 1H), 6.85 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.75, 48.13, 55.37, 55.86, 114.07, 124.26, 127.76, 129.29, 132.22, 159.43; ESI-MS: 267.9 $[M + H]^+$, 535.0 $[2M + H]^+$; HRMS (ESI) for $C_{14}H_{22}NO_2S$ $[M + H]^+$: calcd 268.1371, found 268.1360.

(*R*)-2-Methyl-*N*-(3-(4-(trifluoromethyl)phenyl)allyl)propane-2-sulfinamide (1d)

$[\alpha]_D^{20}$: − 18.1 (c 1.05, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 9H), 3.72 (t, J = 5.4 Hz, 1H), 3.85–4.03 (m, 2H), 6.36 (dt, J = 15.6, 6.3 Hz, 1H), 6.61 (d, J = 15.6 Hz, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.59, 47.65, 55.89, 125.39, 125.43, 125.46, 126.60, 129.51, 130.86, 140.00; ESI-MS: 306.0 $[M + H]^+$, 610.9 $[2M + H]^+$; HRMS (ESI) for $C_{14}H_{19}F_3NOS$ $[M + H]^+$: calcd 306.1139, found 306.1124.

(*R*)-2-Methyl-*N*-(3-(3,4,5-trimethoxyphenyl)allyl)propane-2-sulfinamide (1e)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 9H), 3.47 (s, 1H), 3.84 (s, 3H), 3.87 (s, 6H), 3.84–4.00 (m, 2H), 6.19 (dt, J = 15.6, 6.6 Hz, 1H), 6.50 (d, J = 15.6 Hz, 1H), 6.61 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.62, 47.88, 55.79, 56.02, 60.85, 103.47, 126.01, 132.18, 132.46, 137.84, 153.23; IR (KBr): ν 3415, 3218, 2940, 2838, 1672, 1583, 1506, 1328, 1126, 1010, 848 cm^{-1}; ESI-MS: 327.9 $[M + H]^+$, 655.1 $[2M + H]^+$; HRMS (ESI) for $C_{16}H_{25}NO_4SNa$ $[M + Na]^+$: calcd 350.1402, found 350.1381.

(*R*)-2-Methyl-*N*-(3-(naphthalen-1-yl)allyl)propane-2-sulfinamide (1f)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (s, 9H), 3.45 (t, J = 5.4 Hz, 1H), 3.93–4.15 (m, 2H), 6.28 (dt, J = 15.6, 6.3 Hz, 1H), 7.34 (d, J = 15.3 Hz, 1H), 7.40–7.59 (m, 4H), 7.77 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.78, 48.17, 55.94, 123.76, 124.08, 125.66, 125.91, 126.25, 128.24, 128.62, 129.81, 129.83, 131.16, 133.65, 134.30; IR (KBr): ν 3450, 3360, 3218, 2919, 1625, 1429, 1343, 1061, 942, 863, 732 cm^{-1}; ESI-MS: 288.0 $[M + H]^+$, 575.0 $[2M + H]^+$; HRMS (ESI) for $C_{17}H_{21}NOSNa$ $[M + Na]^+$: calcd 310.1242, found 310.1224.

(*R*)-2-Methyl-*N*-(3-(naphthalen-2-yl)allyl)propane-2-sulfinamide (1g)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (s, 9H), 3.37 (s, 1H), 3.90–4.05 (m, 2H), 6.38 (dt, J = 15.6, 6.6 Hz, 1H), 6.74 (d, J = 15.6 Hz, 1H), 7.44–7.46 (m, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.73–7.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.80, 48.18, 55.99, 123.63, 126.11, 126.44, 126.64, 126.96, 127.78, 128.11, 128.38, 132.80, 133.17, 133.64, 134.00; IR (KBr): ν 3453, 3359, 3226, 3057, 1628, 1411, 1363, 1041, 962, 809, 744 cm^{-1}; ESI-MS: 287.9 $[M + H]^+$, 575.0 $[2M + H]^+$; HRMS (ESI) for $C_{17}H_{22}NOS$ $[M + H]^+$: calcd 288.1422, found 288.1409.

(*R*)-*N*-(3-Cyclohexylallyl)-2-methylpropane-2-sulfinamide (1h)

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99–1.28 (m, 6H), 1.22 (s, 9H), 1.62–1.72 (m, 4H), 1.91–2.00 (m, 2H), 3.18 (t, J = 5.4 Hz, 1H), 3.58–3.78 (m, 2H), 5.45 (dt, J = 15.3, 6.3 Hz, 1H), 5.61 (dd, J = 15.3, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.72, 26.04, 26.18, 32.80, 32.81, 40.41, 47.99, 55.69, 124.27, 140.17; IR (KBr): ν 3208, 2923, 2850, 1475, 1448, 1363, 1180, 1056, 970, 601 cm^{-1}; ESI-MS: 244.1 $[M + H]^+$, 487.1 $[2M + H]^+$; HRMS (ESI) for $C_{13}H_{26}NOS$ $[M + H]^+$: calcd 244.1735, found 244.1722.

(*R*)-*N*-(3,3-Diphenylallyl)-2-methylpropane-2-sulfinamide (1i)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 9H), 3.42 (t, J = 4.5 Hz, 1H), 3.73–3.92 (m, 2H), 6.14 (t, J = 6.6 Hz, 1H), 7.16–7.39 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.65, 44.93, 55.79, 125.63, 127.52, 127.60, 128.18, 128.36, 129.67, 138.89, 141.66, 144.41; IR (KBr): ν 3500, 3342, 3147, 2923, 1597, 1444, 1363, 1143, 1049, 756, 700 cm^{-1}; ESI-MS: 314.0 $[M + H]^+$, 627.0 $[2M + H]^+$; HRMS (ESI) for $C_{19}H_{24}NOS$ $[M + H]^+$: calcd 314.1579, found 314.1564.

General procedures for Rh-Catalyzed 1,4-additions

Under a N_2 atmosphere, a solution of $[RhCl(C_2H_4)_2]_2$ (1.5 mg, 0.00375 mmol of Rh), **1b** (1.8 mg, 0.0075 mmol), and arylboronic acid (0.60 mmol) in 0.5 mL of dioxane was stirred at 40 °C for 30 min. To this mixture were added the α,β-unsaturated carbonyl compounds (0.25 mmol) and then aqueous K_3PO_4 (83 μL, 1.5 M, 0.125 mmol). After being stirred at 40 °C for 0.5–1 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding addition product **3**.

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