

# Rhodium-Catalyzed Asymmetric Arylation of Allyl Sulfones under the Conditions of Isomerization into Alkenyl Sulfones

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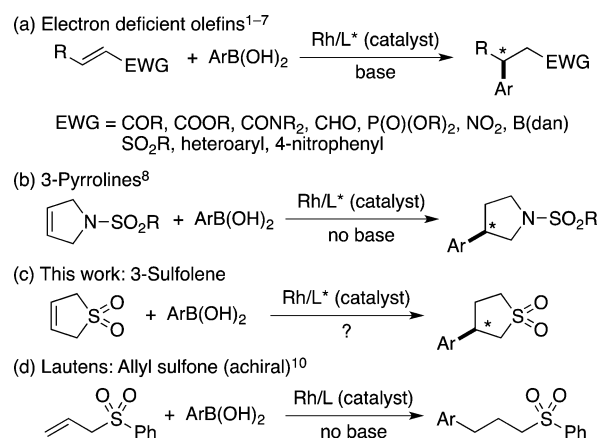
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**S** Supporting Information

**ABSTRACT:** The reaction of 3-sulfolene with arylboronic acids in the presence of a chiral diene-rhodium catalyst under highly basic conditions (10 equiv of KOH) gave high yields of 3-arylsulfolanes with high enantioselectivity, where 3-sulfolene is in equilibration with 2-sulfolene by base-catalyzed isomerization and the more reactive 2-sulfolene undergoes the rhodium-catalyzed asymmetric arylation.

It has been well documented that the rhodium-catalyzed asymmetric arylation of olefins with arylboronic acids is one of the most convenient and reliable methods of creating benzylic stereocenters with high enantioselectivity.<sup>1</sup> The olefinic substrates successfully applied for the asymmetric arylation are mostly electron-deficient olefins including  $\alpha,\beta$ -unsaturated carbonyl compounds,<sup>2</sup> alkenylphosphonates,<sup>3</sup> nitroalkenes,<sup>4</sup> borylalkenes,<sup>5</sup> alkenyl sulfones,<sup>6</sup> and some alkenylarenes<sup>7</sup> (Scheme 1a). The reactions are usually carried

## Scheme 1. Rhodium-Catalyzed Asymmetric Hydroarylation of Alkenes



out in the presence of a substoichiometric amount (10–100 mol %) of inorganic bases, typically KOH.<sup>1</sup> Recently, we reported a 3-pyrroline as a new type of substrate whose asymmetric arylation is catalyzed by a bisphosphine-rhodium complex under nonbasic conditions<sup>8</sup> (Scheme 1b). As a cyclic olefin substrate analogous to 3-pyrroline, we have focused our attention on 3-sulfolene, which is industrially manufactured and is therefore abundant and inexpensive,<sup>9</sup> for the

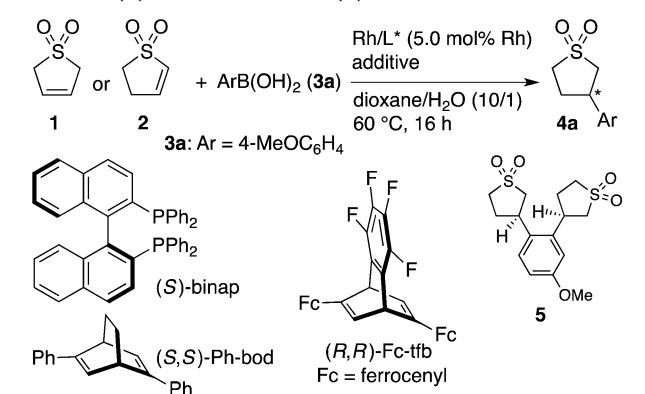
rhodium-catalyzed asymmetric arylation (Scheme 1c). As structurally relevant compounds with 3-sulfolene, linear allyl sulfones have been used by Lautens<sup>10</sup> for the rhodium-catalyzed arylation (Scheme 1d), in addition to the alkenyl sulfone substrates for the asymmetric conjugate arylation.<sup>6,11–13</sup>

The reaction of 3-sulfolene (**1**) with 4-MeOC<sub>6</sub>H<sub>4</sub>B(OH)<sub>2</sub> (**3a**) (3.0 equiv) in the presence of 5 mol % of a rhodium catalyst generated from [Rh(OH)(coe)<sub>2</sub>]<sub>2</sub><sup>14</sup> and (*S*)-binap<sup>15</sup> in dioxane/H<sub>2</sub>O at 60 °C for 16 h, which is one of the best conditions for the addition to 3-pyrrolines,<sup>8</sup> gave a low yield (8%) of the arylation product, (*S*)-3-arylsulfolane **4a**, with 37% ee, 92% of **1** being recovered unreacted (entry 1 in Table 1). The asymmetric arylation of its olefin isomer, 2-sulfolene (**2**), under the same conditions gave a higher yield (38%) of the product **4a** which is an *R* isomer of 91% ee (entry 2). The higher yield in the reaction of 2-sulfolene (**2**) is easily understood because this substrate is an alkenyl sulfone, which is classified as an electron-deficient olefin.<sup>1,6</sup> A Rh/cod complex showed higher catalytic activity than Rh/binap for the arylation of 2-sulfolene (**2**) to give the product **4a** with complete conversion (entry 4), while the activity is similar to the Rh/binap catalyst in the reaction of 3-sulfolene (**1**) (entry 3). The use of (*R,R*)-Fc-tfb,<sup>16,17</sup> which is one of the best chiral diene ligands in terms of both catalytic activity and enantioselectivity for some of the rhodium-catalyzed asymmetric addition reactions,<sup>18</sup> brought about 100% conversion of **2** to produce 66% yield of (*R*)-**4a** with 99% ee, which was accompanied by the formation of a minor amount of ortho-phenylene bis(sulfolene)<sup>19</sup> **5** (entry 6). The arylation of 3-sulfolene (**1**) with the Rh/(*R,R*)-Fc-tfb catalyst gave a low yield of (*R*)-**4a** with 10% ee (entry 5).

To simply summarize the results obtained for asymmetric arylation of **1** and **2** with boronic acid **3a** catalyzed by rhodium complexes coordinated with binap and diene ligands under a neutral condition (entries 1–6 in Table 1), 3-sulfolene (**1**) is less reactive than 2-sulfolene (**2**), and the enantioselectivity is much higher for 2-sulfolene (**2**) than for 3-sulfolene (**1**). On the other hand, it has been reported that the isomerization between allyl sulfone **1** and alkenyl sulfone **2** takes place in the presence of a transition metal<sup>20</sup> or base catalyst<sup>21</sup> and the equilibrated ratio of **1**:**2** is 60/40–50/50 (Scheme 2). Because the arylation of 2-sulfolene (**2**) is faster than that of 3-sulfolene (**1**) ( $k_2 \gg k_1$  in Scheme 2) particularly with diene ligands, if the isomerization of **1** into **2** is much faster than the arylation of **1** ( $k_i \gg k_1$ ) and the reaction condition for the isomerization is

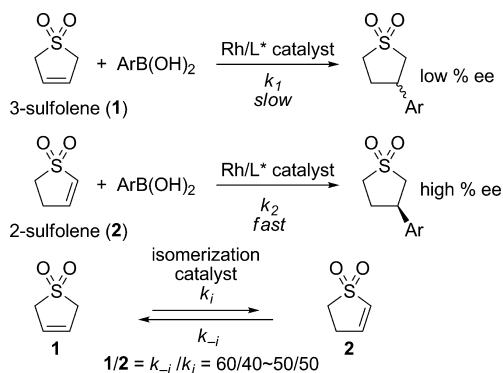
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**Table 1. Rhodium-Catalyzed Asymmetric Arylation of 3-Sulfolene (1) and 2-Sulfolene (2)<sup>a</sup>**

entry	1 or 2	ligand on Rh	additive (equiv) <sup>b</sup>	ratio of 1:2:4a <sup>c</sup>	yield (%) <sup>d</sup> 4a	% ee 4a
1	1	(S)-binap <sup>e</sup>	—	92:0:8	8	37 (S)
2	2	(S)-binap <sup>e</sup>	—	0:60:40	38	91 (R)
3	1	cod <sup>f</sup>	—	94:0:6	—	—
4	2	cod <sup>f</sup>	—	0:0:100	90	—
5	1	(R,R)-Fc-tfb <sup>g</sup>	—	89:0:11	10	10 (R)
6	2	(R,R)-Fc-tfb <sup>g</sup>	—	0:0:100	66 <sup>h</sup>	99 (R)
7	1	(R,R)-Fc-tfb <sup>i</sup>	KOH (1.0)	85:1:14	14	40 (R)
8	1	(R,R)-Fc-tfb <sup>i</sup>	KOH (3.0)	77:8:15	13	66 (R)
9	1	(R,R)-Fc-tfb <sup>i</sup>	KOH (5.0)	4:4:92	87	94 (R)
10	1	(R,R)-Fc-tfb <sup>i</sup>	KOH (10.0)	0:0:100	91	98 (R)
11 <sup>j</sup>	1	(R,R)-Fc-tfb <sup>i</sup>	KOH (10.0)	0:0:100	90	98 (R)
12 <sup>j</sup>	2	(R,R)-Fc-tfb <sup>i</sup>	KOH (10.0)	0:0:100	79 <sup>h</sup>	99 (R)
13 <sup>j</sup>	1	(S,S)-Ph-bod <sup>k</sup>	KOH (10.0)	— <sup>l</sup>	39	23 (R)
14 <sup>j</sup>	1	(S)-binap <sup>m</sup>	KOH (10.0)	— <sup>l</sup>	30	67 (R)

<sup>a</sup>Reaction conditions: 3- or 2-sulfolene (0.15 mmol), ArB(OH)<sub>2</sub> (0.45 mmol unless otherwise noted), Rh catalyst (5 mol % of Rh), dioxane/H<sub>2</sub>O (1.0/0.1 mL). <sup>b</sup>Equivalents to sulfolene. <sup>c</sup>Determined by <sup>1</sup>H NMR of the reaction mixture. <sup>d</sup>Isolated yield. <sup>e</sup>[Rh(OH)(coe)<sub>2</sub>]<sub>2</sub>/(S)-binap. <sup>f</sup>[Rh(OH)(cod)]<sub>2</sub>. <sup>g</sup>[Rh(OH)((R,R)-Fc-tfb)]<sub>2</sub>. <sup>h</sup>As a side product, the formation of 3,3'-(4-methoxy-1,2-phenylene)-bis(tetrahydrothiophene 1,1-dioxide) (5) was observed. <sup>i</sup>[RhCl((R,R)-Fc-tfb)]<sub>2</sub>. <sup>j</sup>ArB(OH)<sub>2</sub> (0.23 mmol). <sup>k</sup>[RhCl(coe)<sub>2</sub>]<sub>2</sub>/(S,S)-Ph-bod. <sup>l</sup>Not determined. <sup>m</sup>[RhCl(coe)<sub>2</sub>]<sub>2</sub>/(S)-binap.

**Scheme 2. Rhodium-Catalyzed Asymmetric Arylation of 3- and 2-Sulfolenes**

For the high % ee of the product:  $k_2 \gg k_1$  and  $k_i \gg k_{-i}$

compatible with the rhodium-catalyzed asymmetric arylation of 2, we have a chance to obtain a high yield of the arylation product 4a with high enantioselectivity.

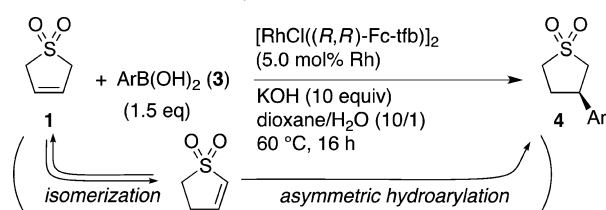
Several basic conditions were examined by changing the amount of KOH (entries 7–10 in Table 1). With 1.0 equiv

(to 1) of KOH, which is one of the standard conditions for asymmetric hydroarylation of  $\alpha,\beta$ -unsaturated ketones,<sup>1,2</sup> the product (R)-4a of 40% ee was formed in a slightly higher yield (14%) (entry 7), and with 3.0 equiv of KOH the % ee of (R)-4a was increased to 66% ee (entry 8). The higher % ee (40% and 66% ee vs 10% ee in entry 5) indicates that a part of 4a is produced by the asymmetric arylation of 2 under these conditions, but the isomerization of 1 into 2 is not fast enough to supply 2 for the catalytic arylation to produce a high yield of 4a. The recovery of unreacted sulfolene as 3-sulfolene (1) is consistent with this slow isomerization. The addition of 5.0 equiv of KOH greatly improved the result (entry 9). The reaction gave (R)-4a of 94% ee in 87% yield. Finally, with 10 equiv of KOH, (R)-4a of 98% ee was produced in 91% yield (entry 10). The amount of boronic acid 3a was decreased from 3.0 to 1.5 equiv (to 1) without loss of yield or selectivity (entry 11). The high enantiomeric purity (98% ee) of 4a produced with 10 equiv of KOH for the reaction starting with 3-sulfolene (1) (entries 10 and 11) is almost the same as 99% ee observed for the reaction starting with 2-sulfolene (2) (entry 6). Interestingly, the yield of 4a is higher in the reaction of 3-sulfolene (1) under the basic conditions than that in the reaction of 2-sulfolene (2) (entries 6 and 12) where the formation of side product 5<sup>19</sup> is accompanied. It should be noted that the yield and % ee of 4a are low with other ligands, for example, Ph-bod<sup>22</sup> and binap (entries 13 and 14). It is likely that the Rh-catalyzed arylation of 2-sulfolene (2) is not fast enough with other chiral ligands to produce a high yield of 4a.

Under the optimized conditions found for the reaction of 3-sulfolene (1) with 4-MeOC<sub>6</sub>H<sub>4</sub>B(OH)<sub>2</sub> (3a) (entry 11 in Table 1), the Rh/(R,R)-Fc-tfb catalyst was examined for its scope in the asymmetric hydroarylation of 1 with several other arylboronic acids 3. The results summarized in Table 2 show that the reaction in the presence of 10 equiv of KOH is applicable to a variety of arylboronic acids. Thus, the phenylboronic acids substituted with methyl and alkoxy groups at para, meta, and ortho positions all gave the corresponding products with high % ee ranging between 98% and 99% ee except for 2-MeC<sub>6</sub>H<sub>4</sub> (entries 3–8). The enantioselectivity was higher (>99% ee) in the arylation with boronic acids bearing electron-withdrawing groups, halides and trifluoromethyl, on the para position (entries 9–12). The asymmetric introduction of 3-cyclopentyloxy-4-methoxyphenyl group provided us with one step synthesis of enantiomerically enriched (S)-4o which is of pharmaceutical interest<sup>23</sup> (entry 15).

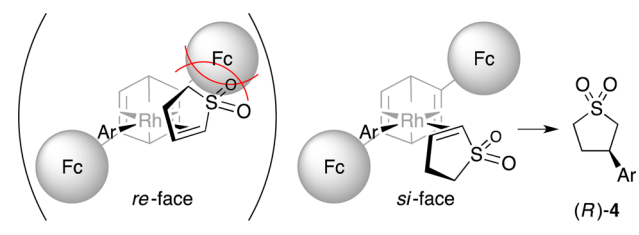
The absolute configuration of the product 4k (Ar = 4-Br-C<sub>6</sub>H<sub>4</sub>) was determined to be (R) by its X-ray crystallographic analysis.<sup>24</sup> The R configuration obtained with (R,R)-Fc-tfb is rationalized by the coordination of 2-sulfolene to an aryl-rhodium intermediate with its *si* face. The coordination with the other face is much less favorable due to the steric repulsions between the cyclic alkyl chain of 2-sulfolene and one of the ferrocenyl groups on the diene ligand<sup>25</sup> (Scheme 3). All the products under the present conditions with (R,R)-Fc-tfb ligand are predicted to have the same absolute configuration (R).

For six-membered ring sulfone, the Rh-catalyzed asymmetric arylation under the isomerization condition is more difficult and challenging, because equilibration of the isomerization between allyl sulfone 6 and alkenyl sulfone 7 is heavily on the allyl sulfone side.<sup>26</sup> In our experiments with DBU as a base in THF at 25 °C, the equilibrated ratio was 97/3 for 6/7.<sup>27</sup> Under the standard conditions (1.5 equiv ArB(OH)<sub>2</sub>, 10 equiv KOH,

**Table 2. Rhodium-Catalyzed Asymmetric Hydroarylation of 3-Sulfolene (1) with Arylboronic Acids 3<sup>a</sup>**

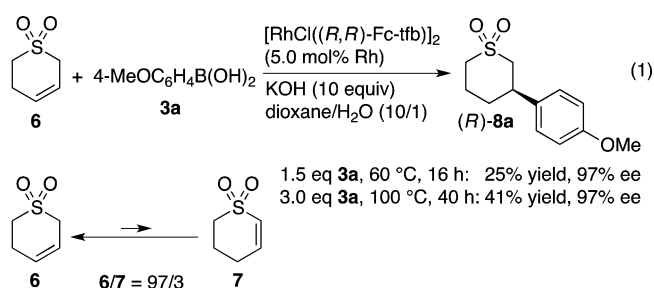
entry	ArB(OH) <sub>2</sub> (3): Ar	product 4	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	3a: 4-MeOC <sub>6</sub> H <sub>4</sub>	4a	90	98 ( <i>R</i> )
2	3b: C <sub>6</sub> H <sub>5</sub>	4b	80 <sup>d</sup>	97 ( <i>R</i> )
3	3c: 4-MeC <sub>6</sub> H <sub>4</sub>	4c	67 <sup>d</sup>	>99 ( <i>R</i> )
4	3d: 3-MeC <sub>6</sub> H <sub>4</sub>	4d	89	98 ( <i>R</i> )
5	3e: 2-MeC <sub>6</sub> H <sub>4</sub>	4e	97	93 ( <i>R</i> )
6	3f: 4-PhOC <sub>6</sub> H <sub>4</sub>	4f	87	99 ( <i>R</i> )
7 <sup>e</sup>	3g: 3-MeOC <sub>6</sub> H <sub>4</sub>	4g	95	98 ( <i>R</i> )
8	3h: 2-MeOC <sub>6</sub> H <sub>4</sub>	4h	84	>99 ( <i>R</i> )
9	3i: 4-FC <sub>6</sub> H <sub>4</sub>	4i	89	>99 ( <i>R</i> )
10	3j: 4-ClC <sub>6</sub> H <sub>4</sub>	4j	90	>99 ( <i>R</i> )
11	3k: 4-BrC <sub>6</sub> H <sub>4</sub>	4k	94	>99 ( <i>R</i> )
12	3l: 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4l	87	>99 ( <i>R</i> )
13	3m: 2-naphthyl	4m	97	97 ( <i>R</i> )
14 <sup>f</sup>	3n:	4n	93	95 ( <i>S</i> ) <sup>g</sup>
15	3o:	4o	61	91 ( <i>S</i> ) <sup>g</sup>

<sup>a</sup>Reaction conditions: 3-sulfolene (0.15 mmol), ArB(OH)<sub>2</sub> (0.23 mmol), KOH (1.5 mmol), [RhCl((*R,R*)-Fc-tfb)<sub>2</sub>] (5 mol % of Rh), dioxane/H<sub>2</sub>O (1.0/0.1 mL) at 60 °C for 16 h. <sup>b</sup>Isolated yield. <sup>c</sup>The % ee was determined by HPLC on a chiral stationary phase. Absolute configuration of 4k was determined to be (*R*) by X-ray crystal analysis, and other products 4 are assumed to have the same (*R*) configuration. <sup>d</sup>The side products, analogous to 5, were also formed. <sup>e</sup>With KOH (0.75 mmol). <sup>f</sup>In dioxane/H<sub>2</sub>O (1.0/0.2 mL). <sup>g</sup>(*S,S*)-Fc-tfb was used.

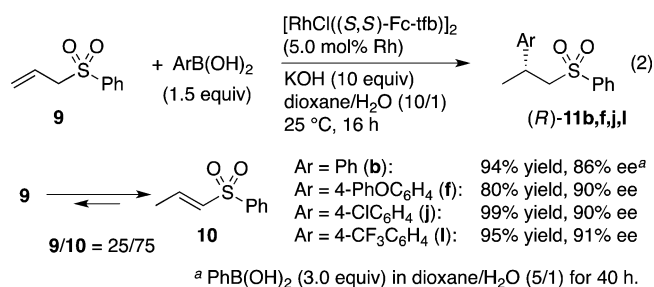
**Scheme 3. Proposed stereochemical pathway for the asymmetric arylation catalyzed by Rh/(*R,R*)-Fc-tfb**

at 60 °C for 16 h) used for the reactions in Table 2, the allylic sulfone 6<sup>28</sup> gave 25% yield of the arylation product 8a with 97% ee (eq 1). The reaction with more amount of the boronic acid 3a at a higher temperature for a longer time improved the yield of 8a to 41%.<sup>29</sup>

Lautens has reported<sup>10</sup> that the reaction of 2-propenyl phenyl sulfone (9) with arylboronic acids in the presence of rhodium catalyst [Rh(OH)(binap)]<sub>2</sub> under a neutral condition



took place with high linear selectivity to give high yields of linear products, 3-arylpropyl sulfones (Scheme 1d). Under the present basic conditions with Rh/Fc-tfb as a catalyst, the isomerization–conjugate arylation sequence proceeded efficiently to completely change the regiochemistry of the carbon–carbon bond formation. Now 2-arylpropyl sulfones 11<sup>28</sup> were obtained with perfect selectivity (eq 2). The equilibration of isomerization between 2-propenyl sulfone 9 and 1-propenyl sulfone 10 is on the side of 10,<sup>20,30</sup> and thus the yields of 11 are generally high. The enantioselectivities are also high, around 90% ee, irrespective of the electron-donating or -withdrawing substitution on the phenylboronic acid.



<sup>a</sup> PhB(OH)<sub>2</sub> (3.0 equiv) in dioxane/H<sub>2</sub>O (5/1) for 40 h.

In summary, we have developed a new type of rhodium-catalyzed asymmetric arylation, where 3-sulfolene is in equilibration with 2-sulfolene by a base-catalyzed isomerization under the conditions of rhodium-catalyzed arylation. The rhodium complex coordinated with Fc-tfb ligand efficiently catalyzed the arylation of 2-sulfolene under the isomerization condition to finally consume all the sulfolene isomers, and it gave a high yield of the conjugate arylation product with high enantioselectivity. This isomerization–asymmetric arylation sequence has been extended to 6-membered ring and linear allylic sulfones.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, compound characterization data, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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- (28) A mixture with a small amount (ca. 10%) of **7**.
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