DOI: 10.1002/cjoc.201300063

Chiral Sulfinamide-Olefin Ligands: Switchable Selectivity in Rhodium-Catalyzed Asymmetric 1,2-Addition of Arylboronic Acids to Aliphatic *α*-Ketoesters†

Ting-Shun Zhu and Ming-Hua Xu*

Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China

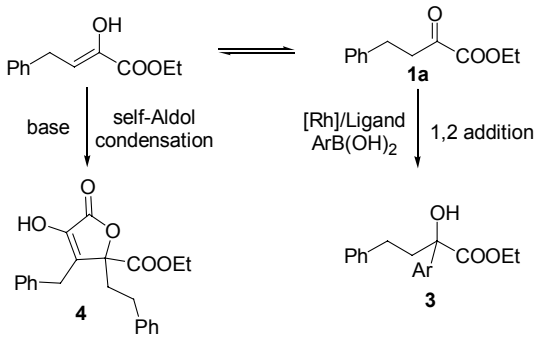
Simple and readily available chiral *N*-(sulfinyl)allylamines have been developed as efficient novel ligands for the rhodium-catalyzed enantioselective 1,2-addition of arylboronic acids to challenging aliphatic *α*-ketoesters. By employing the linear or branched sulfinamide-olefin ligands, interesting enantioselectivity as well as regioselectivity reversal in the related asymmetric additions were observed.

Keywords asymmetric catalysis, rhodium, sulfur-olefin ligand, 1,2-addition, stereoselectivity reversal

Introduction

Chiral *α*-hydroxy esters have attracted much attention owing to their presence in numerous biologically interesting compounds and their use as important building blocks or intermediates for fine chemicals and pharmaceuticals.[1] Over the past decades, various methods have been developed for the synthesis of these valuable chiral compounds.[2] Among these, transition-metal-catalyzed asymmetric 1,2-nucleophilic addition of stable, commercially available arylboronic acids to *α*-ketoesters is a particularly practical and direct approach.[3,4] However, despite some remarkable progress achieved in the rhodium or ruthenium-catalyzed asymmetric addition employing chiral phosphite,[3a] phosphoramidite[3b] or phosphine[3c] ligands, most of the substrates involved in the reactions are aromatic *α*-ketoesters, to the best of our knowledge, catalytic enantioselective addition of aliphatic *α*-ketoesters remains a challenging topic.

Scheme 1



Unlike *α*-aryl-*α*-ketoesters, aliphatic *α*-ketoesters with the existence of *α*-H can form enolate esters upon deprotonation under basic reaction conditions (see Scheme 1 for an example of **1a**). Accordingly, self-Aldol condensation of the enolate intermediate with non-enolized aliphatic *α*-ketoester followed by lactonization would lead to the formation of an unexpected heterocyclic side-product. Moreover, the enantioselectivity of the desired 1,2-addition may be affected by the coordination equilibrium between Rh-ketone oxygen and Rh-enolate oxygen.

Recently, chiral sulfur-based olefins, including sulfoxide-olefins and sulfinamide-olefins, have emerged as a novel class of promising ligands for asymmetric catalysis. As demonstrated in our previous work, they have shown unique catalytic activity and enantioselectivity in a series of transition-metal-catalyzed asymmetric transformations.[5,6] In comparison to pnictogen-containing ligands, sulfur-olefins are exceptional because of the advantages of their easy synthesis, high stability, good metal-coordination ability and special S-stereogenic control. In this context, we have been interested in the possible use of chiral sulfur-olefins as novel ligands for Rh-catalyzed asymmetric 1,2-addition of aliphatic *α*-ketoesters. Here, we report that simple sulfinamide-based branched olefin ligands can be successfully employed in Rh-catalyzed enantioselective addition of arylboronic acids to aliphatic *α*-ketoesters.

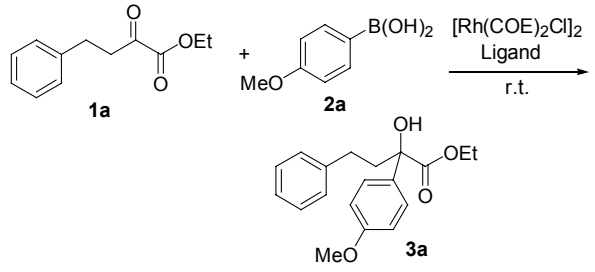
Results and Discussion

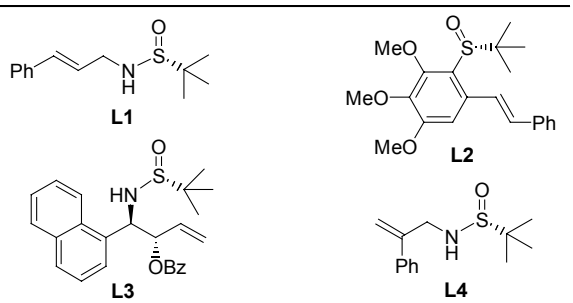
We began our study by examining the reaction of

* E-mail: xumh@simm.ac.cn; Tel.: 0086-021-50807388
Received January 24, 2013; accepted February 24, 2013; published online March 14, 2013.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201300063 or from the author.
† Dedicated to Professor Guoqiang Lin on the occasion of his 70th birthday.

ethyl 2-oxo-4-phenylbutyrate (**1a**) with 4-anisylboronic acid (**2a**) in the presence of $[Rh(COE)_2Cl]_2$ (1.5 mol%) using our recently designed chiral sulfur-olefins **L1**—**L4** as ligands. As expected, the reaction proceeded smoothly in aqueous K_3PO_4 (1.5 mol•L^{-1})/THF at room temperature, but giving the tertiary α-hydroxyester in only moderate yield and *ee* (Table 1, Entries 1—4). Not surprisingly, compound **4** was obtained as the main byproduct.[7] Interestingly, a reversal of reaction enantioselectivity[8] was observed when ligands **L3** and **L4** with terminal olefin moiety were used, as compared to the results obtained with **L1** and **L2** (Table 1, Entries 3—4 *vs.* 1—2). Solvent screening among THF, toluene, dichloromethane, methanol and ethyl acetate showed that THF is the best choice. In order to avoid side reactions, a further screening of the reaction conditions was carried out. As shown in Table 1, employing of weak base such as LiF (1.5 mol•L^{-1}, 50 mol%) or less amount of base such as KOH (0.1 mol•L^{-1}, 8 mol%) can obviously prevent the unwanted self-Aldol reaction (Entries 5, 10—11).

Table 1 Initial screening of reaction conditions[a]



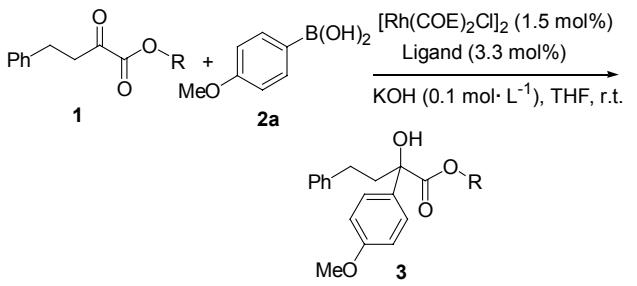


Entry	Ligand	Solvent	Base	Yield[b]/%	*ee*[c]/%
1	**L1**	THF	K_3PO_4 (1.5 mol•L^{-1})	54	30
2	**L2**	THF	K_3PO_4 (1.5 mol•L^{-1})	40	28
3	**L3**	THF	K_3PO_4 (1.5 mol•L^{-1})	12	–19
4	**L4**	THF	K_3PO_4 (1.5 mol•L^{-1})	38	–63
5	**L1**	THF	LiF (1.5 mol•L^{-1})	71	30
6	**L1**	toluene	LiF (1.5 mol•L^{-1})	36	33
7	**L1**	CH_2Cl_2	LiF (1.5 mol•L^{-1})	30	4
8	**L1**	CH_3OH	LiF (1.5 mol•L^{-1})	48	11
9	**L1**	EtOAc	LiF (1.5 mol•L^{-1})	40	24
10	**L1**	THF	KOH (0.1 mol•L^{-1})[d]	67	33
11	**L4**	THF	KOH (0.1 mol•L^{-1})[d]	46	–65

[a] Reaction conditions: 0.25 mmol of **1a**, 2.0 equiv. of **2a**, 1.5 mol% of $[Rh(COE)_2Cl]_2$, 3.3 mol% of ligand, 0.5 equiv. of base in 1 mL of solvent at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis. [d] 8 mol% of KOH was used.

Following up on the encouraging results obtained with **L1** and **L4**, the effect of ester groups in 2-oxo-4-phenylbutanoate was investigated (Table 2). Changing the ester substituent from ethyl to methyl group did not result in much difference of the enantioselectivity (Entries 1—4). Similar with the results of addition to phenylglyoxylate esters reported in our previous work,[5d] when phenyl ester was employed, an increase of the enantioselectivity from 33% to 64% *ee* was observed using linear *N*-(sulfinyl)allylamine **L1** as the ligand (Entry 5), but further altering phenyl to 2-naphtyl or (2,6-dimethyl)phenyl did not improve the enantioselectivity of the reaction (64% *ee* and 61% *ee*, respectively; not shown in Table 2). On the contrary, the result with branched *N*-(sulfinyl)allylamine **L4** showed an opposite trend. In the case of phenyl ester **1c**, a sharp decline in enantioselectivity was found (Entries 2 and 4 vs. 6). Thus, by simply tuning the ligand structure and substrate ester moiety, an interesting reversal of enantiofacial selectivity can be achieved to afford the desired addition product with the same level of enantioselectivity (64% and 65% *ee*, Entries 2 and 5). The absolute configuration of **3a** was determined by comparison of its HPLC chromatogram with the known one (see SI for details), and others were assigned by analogy. In consideration of the availability, ethyl 2-oxo-4-phenylbutyrate **1a** was selected as substrate for further investigation.

Table 2 Optimization of reaction conditions for different esters[a]



Entry	R, **1**	Ligand	**3**	Yield[b]/%	*ee*[c]/%
1	Et, **1a**	**L1**	**3a**	67	33 (*S*)
2	Et, **1a**	**L4**	**3a**	46	65 (*R*)
3	Me, **1b**	**L1**	**3b**	63	35 (*S*)
4	Me, **1b**	**L4**	**3b**	53	61 (*R*)
5	Ph, **1c**	**L1**	**3c**	55	64 (*S*)
6	Ph, **1c**	**L4**	**3c**	25	41 (*R*)

[a] Reaction conditions: 0.25 mmol of **1**, 2.0 equiv. of **2a**, 1.5 mol% of $[Rh(COE)_2Cl]_2$, 3.3 mol% of ligand, 8 mol% of KOH (0.1 mol•L^{-1}) in 1 mL of THF at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis.

Having noticed the catalytic property differences between linear and branched *N*-(sulfinyl)allylamines, we decided to further examine the influence of the substituents on the olefin moiety. As a result, linear ligands **L5**—**L8** and branched ligands **L9**—**L16** with different R^1 and R^2 substituents were designed (Table 3),

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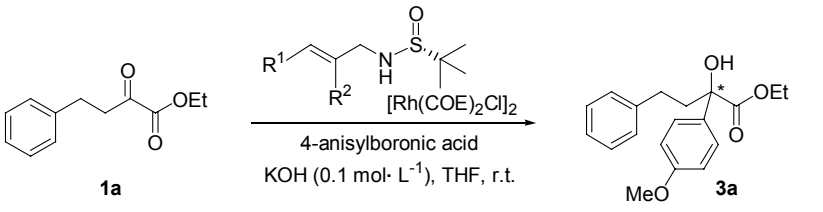
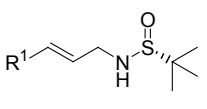
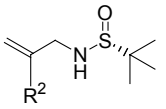
Table 3 Further screening of chiral sulfinamide-olefins for asymmetric 1,2-addtion of ethyl 2-oxo-4-phenylbutyrate[a,b,c]







L1, R^1 = Ph, 67%, 33% *ee* (*S*)
L5, R^1 = 4-$MeOC_6H_4$, 57%, 33% *ee* (*S*)
L6, R^1 = 4-$CF_3C_6H_4$, 64%, 33% *ee* (*S*)
L7, R^1 = 4-$NO_2C_6H_4$, 31%, 32% *ee* (*S*)
L8, R^1 = CH_3, 83%, 3% *ee* (*S*)

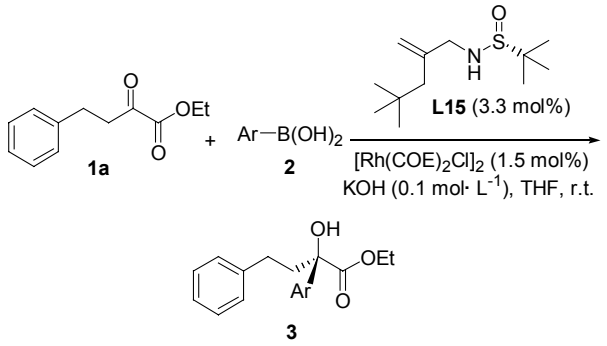
L4, R^2 = Ph, 46%, 65% *ee* (*R*)
L9, R^2 = 4-$CF_3C_6H_4$, 13%, 41% *ee* (*R*)
L10, R^2 = 2-$MeOC_6H_4$, 67%, 41% *ee* (*R*)
L11, R^2 = CH_3, 61%, 47% *ee* (*R*)
L12, R^2 = ^{i}Pr, 10%, 19% *ee* (*R*)
L13, R^2 = CH_2Ph, 85%, 40% *ee* (*R*)
L14, R^2 = CH_2(1-naphthyl), 68%, 39% *ee* (*R*)
L15, R^2 = $CH_2C(CH_3)_3$, 87%, 63% *ee* (*R*)
L16, R^2 = CH_2(9-anthryl), 18%, 28% *ee* (*R*)

[a] Reaction conditions: 0.25 mmol of **1a**, 2.0 equiv. of **2a**, 1.5 mol% of $[Rh(COE)_2Cl]_2$, 3.3 mol% of ligand, 8 mol% of KOH (0.1 mol•L^{-1}) in 1 mL of THF at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis.

synthesized and employed in the rhodium-catalyzed 1,2-additon of 4-anisylboronic acid to ethyl 2-oxo-4-phenylbutyrate (**1a**). With all linear *N*-(sulfinyl)allylamines (**L5**—**L8**), unfortunately, no better results in enantioselectivity was obtained. In the cases of branched *N*-(sulfinyl)allylamines, it was also disappointing that analogues **L9**—**L16** containing substituents with different steric and electronic natures were generally less effective and gave no higher *ee*. On the other hand, it was found that incorporation of an appropriate electron-rich R^2 substituent would be helpful for enhancing the catalytic activity (**L10, L11, L13**—**L15**). With **L15** (R^2 = neopentyl), significantly improved yield (87%) together with equally good enantioselectivity (63%) were achieved.

With **L15** as optimal ligand, we decided to examine the reaction generality. A wide range of arylboronic acids were reacted with ethyl 2-oxo-4-phenylbutyrate (**1a**) in KOH (0.1 mol•L^{-1}, 8 mol%)/THF at room temperature. As summarized in Table 4, arylboronic acids bearing electron-donating group at *meta*- or *para*-position of the phenyl ring can all be employed successfully to afford the desired products in moderate to good yields and enantioselectivities (Entries 1—3, 7—9), but arylboronic acids with electron-withdrawing groups are less reactive, giving low yield of the addition reaction (Entries 4—6). Among all examples, the highest enantioselectivity of 70% was attained when 4-*tert*-butylphenylboronic acid was employed. Notably, in the cases of sterically hindered 2-naphthalenyl- and 1-naphthalenylboronic acids, the reaction proceeded smoothly to give the adducts **3j** and **3k** in moderate yields and with similarly good level of enantioselectivities (Entries 10 and 11).

Table 4 Substrate scope of asymmetric 1,2-addtion to ethyl 2-oxo-4-phenylbutyrate[a]

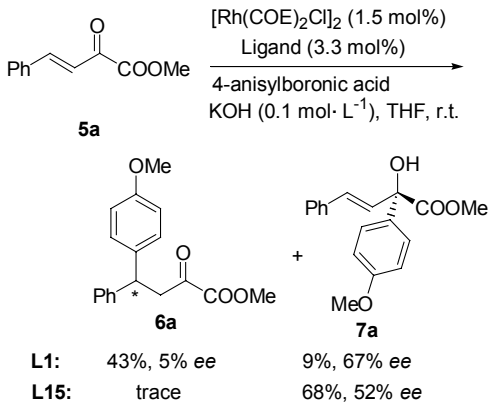


Entry	Ar	Product	Yield[b]/%	*ee*[c]/%
1	4-$MeOC_6H_4$	**3a**	87	63
2	Ph	**3b**	61	64
3	4-MeC_6H_4	**3c**	82	61
4	4-ClC_6H_4	**3d**	14	57
5	4-FC_6H_4	**3e**	21	61
6	4-PhC_6H_4	**3f**	34	61
7	4-^{t}BuC_6H_4	**3g**	72	70
8	3-$MeOC_6H_4$	**3h**	68	65
9	3-MeC_6H_4	**3i**	67	51
10	2-nathphyl	**3j**	62	67
11	1-nathphyl	**3k**	57	65

[a] Reaction conditions: 0.25 mmol of **1a**, 2.0 equiv. of arylboronic acid, 1.5 mol% of $[Rh(COE)_2Cl]_2$, 3.3 mol% of **L15**, 8 mol% of KOH (0.1 mol•L^{-1}) in 1 mL of THF at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis.

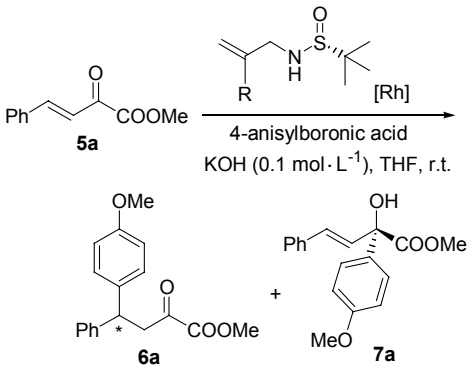
To further realize the interesting catalytic performance differences between the linear and branched sulfinamide-olefin ligands, we next turned our attention to the asymmetric addition of styrylglyoxylate. To our knowledge, there is only one example of enantioselective addition of arylboronic acids to 2-oxo-4-phenylbut-3-enoate been reported by Zhou,[3a] the development of catalytic asymmetric reactions to afford useful level of enantioselectivity still represents a challenging task. As depicted in Scheme 2, the reaction of methyl styrylglyoxylate with 4-anisylboronic acid in the presence of *N*-(sulfinyl)allylamine **L1** and **L15** was carried out under rhodium catalysis, respectively. Surprisingly, the two ligands exhibited very different regioselectivity propensities.[9] With **L1**, conjugate addition to the unsaturated double bond is favored, furnishing *β*,*β*-diaryl-*α*-ketoester **6a** in 43% yield but with only 5% *ee*. In sharp contrast, when the branched *N*-(sulfinyl)allylamine (**L15**) was used, the reaction took place preferably at the ketone carbonyl, affording the 1,2-addition product *β*,*γ*-unsatured-*α*-hydroxyester (**7a**) in 68% yield with 52% *ee*. In both cases, no further 1,2-addition of product **6a** was observed. Though the mechanism remains unknown, these results indicate that the insertion pathway of the two aryl rhodium intermediates was clearly different.

Scheme 2



To attain higher enantioselectivity of the 1,2-addition, an extensive screening of the branched sulfinamide-olefin ligands was carried out again (Table 5). Similar with the previous observations of addition to 2-oxo-4-phenylbutyrate (**1a**), electron-rich olefin substituent (R) with proper steric hinderance was crucial. Phenyl and bulkyl isopropyl substituent led to poor results in both regioselectivity and enantioselectivity (Entries 2—3). Surprisingly, with phenyl substituted **L4**, **7a** with opposite configuration was produced. An improved enantiomeric excess (65%) was observed when benzyl-substituted **L13** was used (Entry 4). Further investigation revealed that the incorporation of a large planar structure such as 1-naphthyl and 9-anthryl is a little more beneficial (Entries 5 and 6); and the best 72% *ee* and 70% yield (>20∶1 regioselectivity) was attained when ligand **L16** was employed (Entry 6).

Table 5 Screening of chiral sulfinamide-olefins for asymmetric 1,2-addtion of (*E*)-2-oxo-4-phenylbut-3-enoate[a]



Entry	R, Ligand	Yield[b]/%	**6a**/**7a**[c]	*ee* of **6a**[d]/%	*ee* of **7a**[d]/%
1	$CH_2{}^tBu$, **L15**	72	1∶20	—	52
2	Ph, **L4**	54	1∶12	5	–23
3	^{i}Pr, **L12**	56	<1∶20	—	37
4	Bn, **L13**	76	<1∶20	—	65
5	CH_2(2-Naph), **L14**	74	<1∶20	—	68
6	CH_2(9-anthryl), **L16**	70	<1∶20	—	72

[a] Reaction conditions: 0.25 mmol of **5a**, 2.0 equiv. of **2a**, 1.5 mol% of $[Rh(COE)_2Cl]_2$, 3.3 mol% of ligand, 8 mol% of KOH (0.1 mol•L^{-1}) in 1 mL of THF at room temperature. [b] Isolated yield. [c] Determined by ^{1}H NMR of the crude materials. [d] Determined by HPLC analysis.

Having identified a suitable chiral ligand, we examined the reaction scope with respect to the styrylglyoxylate derivatives under the above optimized conditions. As shown in Table 6, a range of *β*,*γ*-unsatured *α*-ketoesters **7a**—**7j** with different R^1 or R^2 substituent were evaluated with 4-anisylboronic acids. In general, all reactions proceeded smoothly to provide the desired 1,2-addition products in good to moderate yields with excellent regioselectivity (>20∶1). It appeared that varing the ester group could have a dramatic effect on reaction enantioselectivity. For instance, the isopropyl (*E*)-2-oxo-4-phenylbut-3-enoate (**5c**) gave both lower yield (65%) and enantioselectivity (64%) compared to those obtained from their methyl and ethyl esters (**5a** and **5b**, Entries 1—3). When phenyl (*E*)-2-oxo-4-phenylbut-3-enoate (**5d**) was employed, product **7d** was obtained with much improved enantioselectivity (80%, Entry 4). However, in this case, a sharp decline in the reaction yield (52%) was found mainly due to significant hydrolysis of the aromatic ester substrate. To our delight, benzyl (*E*)-2-oxo-4-phenylbut-3-enoate (**5e**) underwent clean reaction and could lead to 1,2-adduct in good yield (81%), albeit in somewhat lower *ee* (76%, Entry 5). By comparing the HPLC chromatogram with known data,[3a] the absolute configuration was determined as *S*. Subsequently, the impact of varying the R^1

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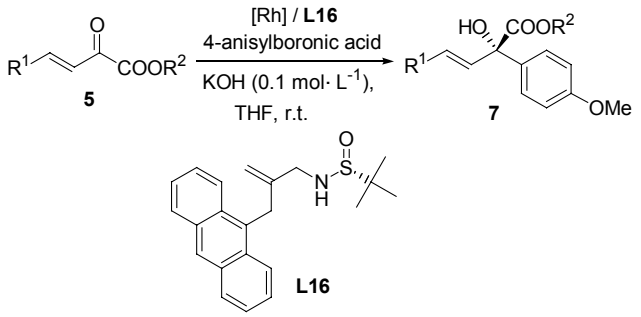
substituent on the olefin was also investigated. Electron-donating as well as electron-withdrawing groups were all likely applicable and gave the corresponding tertiary α-hydroxyesters in moderate to good yields and equally high level of enantioselectivity (80%) (Entries 6 −9). However, when a very bulky 9-anthryl group was introduced, a dramatic decrease in enantioselectivity occurred (from 76% to 14% *ee*, Entries 4 *vs.* 11). Unfortunately, this reaction is very sensitive to the reactivity of the arylboronic acid. When non-electron rich phenylboronic acid was employed, a much lower yield (＜10%) was found.

Table 6 Substrate scope of asymmetric 1,2-addtion to (*E*)-2-oxo-4-arylbut-3-enoate[a]



Entry	R^1, R^2 (**5**)	**7**	1,2/1,4[b]	Yield[c]/%	*ee*[d]/%
1	Ph, Me (**5a**)	**7a**	＞20∶1	70	72
2	Ph, Et (**5b**)	**7b**	＞20∶1	72	71
3	Ph, ^{i}Pr (**5c**)	**7c**	20∶1	65	64
4	Ph, Ph (**5d**)	**7d**	＞20∶1	52	80
5	Ph, Bn (**5e**)	**7e**	＞20∶1	81	76
6	4-MeC_6H_4, Bn (**5f**)	**7f**	＞20∶1	83	80
7	4-MeOC_6H_4, Bn (**5g**)	**7g**	＞20∶1	73	80
8	4-ClC_6H_4, Bn (**5h**)	**7h**	＞20∶1	62	80
9	4-BrC_6H_4, Bn (**5i**)	**7i**	＞20∶1	75	80
10	9-anthryl, Bn (**5j**)	**7j**	＞20∶1	82	14

[a] Reaction condition: 0.25 mmol of **5**, 1.5 equiv. of **2a**, 1.5 mol% of $[Rh(COE)_2Cl]_2$, 3.3 mol% of ligand, 8 mol% of KOH (0.1 mol•L^{-1} aq.) in 1 mL of THF at room temperature. [b] Determined by ^{1}H NMR of the crude materials. [c] Isolated yield. [d] Determined by HPLC analysis.

Conclusions

In summary, we have developed an efficient rhodium-catalyzed asymmetric 1,2-addition of aryl boronic acdis to 2-oxo-4-phenylbuturates and (*E*)-2-oxo-4-arylbut-3-enoates through the use of extremely simple chiral *N*-(sulfinyl)allylamine ligands. The method offers a potentially easy and practical access to a variety of optically active tertiary α-hydroxyesters. Of particular note is that catalytic enantioselective 1,2-addtion of arylboronic acids to α-H-containing aliphatic α-ketoesters has been an important but difficult subject. Moreover, studies have shown that the ligand catalytic performance can be dramatically altered by simply tuning the substituent on the olefin moiety. By employing the readily available linear or branched sulfinamide-olefin ligands, interesting enantioselectivity as well as regioselectivity reversal in the related asymmetric additions were observed. Efforts to investigate the insight of the stereoselectivity reversal mechanism and the further applications of sulfur-olefin ligands are currently underway in our laboratory.

Experimental

General procedure for Rh-catalyzed 1,2-addition of arylboronic acids to α-ketoesters

Under Ar atmosphere, a solution of α-ketoester (0.25 mmol), $[Rh(COE)_2Cl]_2$ (2.7 mg, 0.0075 mmol of Rh, 1.5 mol%), *N*-(sulfinyl)allylamine ligand (0.00825 mmol, 3.3 mol%), and arylboronic acid (0.5 mmol for addition to ethyl 2-oxo-4-phenylbutyrate; 0.375 mmol for addition to 2-oxo-4-arylbut-3-enoate) in 1.0 mL of THF was stirred at room temperature for 30 min. To this mixture was added aqueous KOH (0.2 mL, 0.1 mol•L^{-1}, 0.02 mmol). After being stirred at r.t. for 3 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding addition product **3** or **7**.

(*R*)-Ethyl 2-hydroxy-2-(4-methoxyphenyl)-4-phenyl-butanoate (3a) Colorless oil, 87% yield, 63% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.28 (t, *J*=7.2 Hz, 3H), 2.26−2.79 (m, 4H), 3.81 (s, 3H), 3.89 (s, 1H), 4.18−4.23 (m, 2H), 6.89 (d, *J*=9.0 Hz, 2H), 7.18−7.30 (m, 5H), 7.54 (d, *J*=8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 30.1, 41.5, 55.2, 62.4, 75.6, 113.5, 125.8, 126.7, 128.3, 128.4, 133.7, 141.7, 159.0, 175.3. HRMS (ESI) calcd for $C_{19}H_{22}O_4Na$ $[M+Na]^+$: 337.1416, found 337.1418.

(*R*)-Ethyl 2-hydroxy-2,4-diphenylbutanoate (3b) Colorless oil, 61% yield, 64% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (t, *J*=6.9 Hz, 3H), 2.30−2.80 (m, 4H), 3.93 (s, 1H), 4.17−4.29 (m, 2H), 7.20 (d, *J*=6.0 Hz, 3H), 7.29 (t, *J*=6.0 Hz, 3H), 7.38 (dd, *J*=6.9, 7.5 Hz, 2H), 7.65 (d, *J*=6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 30.2, 41.6, 62.6, 77.9, 125.4, 125.9, 127.7, 128.2, 128.36, 128.43, 141.6, 141.7, 175.1. HRMS (ESI) calcd for $C_{18}H_{20}O_3Na$ $[M+Na]^+$: 307.1310, found 307.1318.

Ethyl 2-hydroxy-4-phenyl-2-*p*-tolylbutanoate (3c) Colorless oil, 82% yield, 61% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (t, *J*=6.9 Hz, 3H), 2.30−2.82 (m, 4H), 2.45 (s, 3H), 3.93 (s, 1H), 4.20−4.26 (m, 2H), 7.18−7.23 (m, 4H), 7.31 (dd, *J*=6.6, 8.1 Hz, 2H), 7.54 (d, *J*=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 21.0, 30.1, 41.5, 62.5, 77.8, 125.3, 125.8, 128.3, 128.4, 128.9, 137.4, 138.7, 141.8, 175.3. HRMS (ESI) calcd for $C_{19}H_{22}O_3Na$ $[M+Na]^+$: 321.1467, found 321.1462.

(*R*)-Ethyl 2-(4-chlorophenyl)-2-hydroxy-4-phenylbutanoate (3d) Colorless oil, 14% yield, 57% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.28 (t, *J*=5.1 Hz, 3H),

2.24−2.75 (m, 4H), 3.94 (s, 1H), 4.17−4.26 (m, 2H), 7.19 (dd, J=8.1, 7.2 Hz, 3H), 7.27−7.35 (m, 5H), 7.59 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 30.1, 41.7, 62.8, 77.6, 125.6, 126.0, 127.1, 1284, 128.5, 133.7, 140.2, 141.5, 174.8. HRMS (ESI) calcd for $C_{18}H_{19}O_3ClNa$ $[M + Na]^+$: 341.0920, found 341.0925.

(*R*)-Ethyl 2-(4-fluorophenyl)-2-hydroxy-4-phenylbutanoate (3e) Colorless oil, 21% yield, 61% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.29 (t, J=7.2 Hz, 3H), 2.30−2.36 (m, 1H), 2.46−2.68 (m, 3H), 3.95 (s, 1H), 4.22 (dt, J=7.2, 1.5 Hz, 2H), 7.05 (dd, J=9.0 Hz, J_F=8.7 Hz, 2H), 7.20 (t, J=8.1 Hz, 3H), 7.29 (dd, J=7.2, 7.8 Hz, 2H), 7.62 (dd, J=9.0 Hz, J_F=5.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 30.1, 41.8, 62.7, 77.5, 115.0 (d, J_{CF}=17 Hz), 125.9, 127.3 (d, J_{CF}=6 Hz), 128.4 (d, J_{CF}=2 Hz), 137.3, 137.4, 141.5, 162.3 (d, J=196 Hz), 175.0. HRMS (ESI) calcd for $C_{18}H_{19}O_3FNa$ $[M+ Na]^+$: 325.1216, found 325.1212.

(*R*)-Ethyl 2-(biphenyl-4-yl)-2-hydroxy-4-phenylbutanoate (3f) Colorless oil, 34% yield, 62% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.33 (t, J=6.9 Hz, 3H), 2.35−2.85 (m, 4H), 3.99 (s, 1H), 4.20−4.32 (m, 2H), 7.24 (dd, J=9.9, 9.0 Hz, 3H), 7.31 (dd, J=6.9, 7.2 Hz, 2H), 7.38 (d, J=6.9 Hz, 1H), 7.46 (dd, J=7.5, 7.2 Hz, 2H), 7.62 (d, J=6.3 Hz, 4H), 7.72 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 30.2, 41.6, 62.6, 77.9, 125.9, 126.0, 127.0, 127.1, 127.35, 127.37, 128.4, 128.8, 140.5, 140.6, 140.7, 141.7, 175.1. HRMS (ESI) calcd for $C_{24}H_{24}O_3Na$ $[M + Na]^+$: 381.1623, found 381.1611.

(*R*)-Ethyl 2-(4-*tert*-butylphenyl)-2-hydroxy-4-phenylbutanoate (3g) Colorless oil, 72% yield, 70% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.33 (t, J=6.9 Hz, 3H), 1.35 (s, 9H), 2.33 (dt, J=4.8, 12.0 Hz, 1H), 2.46−2.66 (m, 2H), 2.79 (dt, J=4.8, 12.0 Hz, 1H), 3.90 (s, 1H), 4.21−4.27 (m, 2H), 7.21 (d, J=7.5 Hz, 3H), 7.29 (dd, J=6.6, 7.2 Hz, 2H), 7.40 (d, J=8.1 Hz, 2H), 7.57 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 30.2, 31.3, 34.4, 41.6, 62.5, 77.8, 125.1, 125.2, 125.8, 128.3, 128.4, 138.7, 141.8, 150.5, 175.2; HRMS (ESI) calcd for $C_{22}H_{28}O_3Na$ $[M + Na]^+$: 363.1936, found 363.1934.

(*R*)-Ethyl 2-hydroxy-2-(3-methoxyphenyl)-4-phenylbutanoate (3h) Colorless oil, 68% yield, 65% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.31 (t, J=7.2 Hz, 3H), 2.34 (dt, J=5.1, 11.2 Hz, 1H), 2.48 (dt, J=5.1, 11.2 Hz, 1H), 2.62 (dt, J=5.1, 11.2 Hz, 1H), 2.75 (dt, J=5.1, 11.2 Hz, 1H), 3.84 (s, 3H), 3.93 (s, 3H), 4.22−4.26 (m, 2H), 6.86 (d, J=7.2 Hz, 1H), 7.22 (t, J=6.6 Hz, 4H), 7.26−7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 30.2, 41.6, 55.2, 62.6, 77.9, 111.3, 113.1, 117.8, 125.9, 128.3, 128.4, 129.2, 141.7, 143.3, 159.6, 175.0; HRMS (ESI) calcd for $C_{19}H_{22}O_4Na$ $[M + Na]^+$: 337.1416, found 337.1407.

(*R*)-Ethyl 2-hydroxy-4-phenyl-2-*m*-tolylbutanoate (3i) Colorless oil, 67% yield, 57% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (t, J=7.5 Hz, 3H), 2.28−2.38 (m, 1H), 2.38 (s, 3H), 2.45−2.66 (m, 2H), 2.75 (dt, J=4.8, 11.2 Hz, 1H), 3.90 (s, 1H), 4.18−4.28 (m, 2H), 7.12 (d, J=7.5 Hz, 1H), 7.22 (dd, J=7.2, 5.7 Hz, 3H), 7.27−7.32 (m, 3H), 7.44 (dd, J=6.3, 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 21.6, 30.2, 41.5, 62,5. 77.9, 122.5, 125.9, 126.0, 128.1, 128.3, 128.4, 137.9, 141.6, 141.8, 175.2; HRMS (ESI) calcd for $C_{19}H_{22}O_3Na$ $[M+ Na]^+$: 321.1467, found 321.1461.

(*R*)-Ethyl 2-hydroxy-2-(naphthalen-2-yl)-4-phenylbutanoate (3j) Colorless oil, 62% yield, 67% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (t, J=6.9 Hz, 3H), 2.41−2.82 (m, 4H), 4.06 (s, 1H), 4.18−4.30 (m, 2H), 7.21 (d, J=8.1 Hz, 3H), 7.29 (dd, J=6.9, 8.7 Hz, 2H), 7.49−7.52 (m, 2H), 7.74 (d, J=8.7 Hz, 1H), 7.84−7.87 (m, 3H), 8.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 30.2, 41.4, 62.7, 78.1, 123.5, 124.6, 125.9, 126.18, 126.20, 127.4, 128.0, 128.3, 128.4, 128.5, 132.8, 133.0, 138.9, 141.7, 175.1; HRMS (ESI) calcd for $C_{22}H_{22}O_3Na$ $[M+Na]^+$: 357.1467, found 357.1449.

(*R*)-Ethyl 2-hydroxy-2-(naphthalen-1-yl)-4-phenylbutanoate (3k) Colorless oil, 57% yield, 65% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.17 (t, J=6.9 Hz, 3H), 2.59−2.78 (m, 3H), 2.88−2.98 (m, 1H), 3.85 (s, 1H), 7.26 (dq, J=7.5 Hz, J_{AB}=33.6 Hz, 2H), 7.22−7.32 (m, 5H), 7.42−7.51 (m, 3H), 7.69 (d, J=8.4 Hz, 1H), 7.82−7.89 (m, 2H), 8.37 (d, J=9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 30.0, 40.5, 62.4, 78.6, 124.2, 124.7, 125.0, 125.5, 126.0, 126.2, 128.5, 129.0, 129.5, 131.2, 134.5, 136.6, 141.6, 176.0; HRMS (ESI) calcd for $C_{22}H_{22}O_3Na$ $[M+Na]^+$: 357.1467, found 357.1453.

(*S*,*E*)-Methyl 2-hydroxy-2-(4-methoxyphenyl)-4-phenylbut-3-enoate (7a) Colorless oil, 70% yield, 72% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.81 (s, 3H), 3.84 (s, 3H), 3.94 (s, 1H), 6.71 (d, J=15.9 Hz, 1H), 6.90 (d, J=9.0 Hz, 2H), 6.95 (d, J=15.9 Hz, 1H), 7.28 (d, J=6.6 Hz, 1H), 7.34 (t, J=7.5 Hz, 2H), 7.44−7.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 53.6, 55.3, 78.1, 113.8, 126.8, 127.4, 127.9, 128.6, 129.1, 130.4, 133.6, 136.3, 159.4, 174.9; HRMS (ESI) calcd for $C_{18}H_{18}O_4Na$ $[M+Na]^+$: 321.1103, found 321.1105.

(*S*,*E*)-Ethyl 2-hydroxy-2-(4-methoxyphenyl)-4-phenylbut-3-enoate (7b) Colorless oil, 72% yield, 71% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.31 (t, J=7.2 Hz, 3H), 3.82 (s, 3H), 4.04 (s, 1H), 4.31 (q, J=7.2 Hz, 2H), 6.74 (d, J=15.9 Hz, 1H), 6.92 (d, J=9.0 Hz, 2H), 6.98 (d, J=15.9 Hz, 1H), 7.29 (d, J=7.2 Hz, 1H), 7.36 (t, J=6.9 Hz, 2H), 7.49 (dd, J=7.5, 9.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 55.2, 62.8, 77.9, 113.7, 126.8, 127.4, 127.8, 128.5, 129.3, 130.2, 133.7, 136.4, 159.3, 174.3; HRMS (ESI) calcd for $C_{19}H_{20}O_4Na$ $[M+Na]^+$: 335.1259, found 335.1251.

(*S*,*E*)-Isopropyl 2-hydroxy-2-(4-methoxyphenyl)-4-phenylbut-3-enoate (7c) Colorless oil, 65% yield, 64% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.26 (d, J=6.0 Hz, 3H), 1.32 (d, J=6.0 Hz, 3H), 3.82 (s, 3H), 4.08 (s, 1H), 6.72 (d, J=15.6 Hz, 1H), 6.91 (d, J=8.7 Hz, 2H), 6.98 (d, J=15.6 Hz, 1H), 7.29 (d, J=7.2 Hz, 1H), 7.35 (t, J=7.2 Hz, 2H), 7.49 (dd, J=11.7, 8.7 Hz, 4H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ: 21.4, 21.6, 55.2, 77.8, 113.6, 126.7, 127.3, 127.8, 128.5, 129.4, 130.1, 133.8, 136.4, 159.2, 173.8; HRMS (ESI) calcd for $C_{20}H_{22}O_4Na$ [M+Na]$^+$: 349.1416, found 349.1423.

(*S*,*E*)-Benzyl 2-hydroxy-2-(4-methoxyphenyl)-4-phenylbut-3-enoate (7d)[3a] Colorless oil, 81% yield, 76% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.82 (s, 3H), 4.03 (s, 1H), 5.29 (s, 2H), 6.76 (d, J=15.3 Hz, 1H), 6.90 (d, J=8.7 Hz, 2H), 6.97 (d, J=15.3 Hz, 1H), 7.29−7.38 (m, 8H), 7.43 (d, J=7.8 Hz, 2H), 7.48 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.2, 68.2, 78.1, 113.7, 126.8, 127.5, 128.9, 128.0, 128.4, 128.52, 128.54, 129.1, 130.5, 133.4, 134.9, 136.2, 159.3, 174.1.

(*S*,*E*)-Phenyl 2-hydroxy-2-(4-methoxyphenyl)-4-phenylbut-3-enoate (7e) Colorless oil, 52% yield, 80% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.84 (s, 3H), 3.92 (s, 1H), 6.90 (d, J=15.6 Hz, 1H), 6.96 (d, J=8.7 Hz, 2H), 7.06−7.12 (m, 3H), 7.27−7.32 (m, 2H), 7.35−7.52 (m, 4H), 7.51 (d, J=7.5 Hz, 2H), 7.61 (d, J=9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.3, 78.3, 114.0, 121.0, 126.4, 126.9, 127.6, 128.1, 128.5, 128.6, 129.6, 131.1, 133.2, 136.2, 150.5, 159.6, 173.1; HRMS (ESI) calcd for $C_{23}H_{20}O_4Na$ [M+Na]$^+$: 383.1259, found 383.1267.

(*S*,*E*)-Benzyl 2-hydroxy-2-(4-methoxyphenyl)-4-*p*-tolylbut-3-enoate (7f) Colorless oil, 83% yield, 80% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.36 (s, 3H), 3.81 (s, 3H), 3.96 (s, 1H), 5.26 (s, 2H), 6.66 (d, J=15.9 Hz, 1H), 6.86−6.93 (m, 3H), 7.14 (d, J=7.8 Hz, 2H), 7.27−7.36 (m, 6H), 7.45 (d, J=9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.2, 55.3, 68.2, 78.1, 113.7, 126.7, 127.6, 128.0, 128.1, 128.5, 128.6, 129.2, 130.4, 133.5, 133.6, 135.0, 137.8, 159.3, 174.3; HRMS (ESI) calcd for $C_{25}H_{24}O_4Na$ [M+Na]$^+$: 411.1572, found 411.1566.

(*S*,*E*)-Benzyl 2-hydroxy-2,4-bis(4-methoxy-phenyl)but-3-enoate (7g) Colorless oil, 73% yield, 80% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.81 (s, 6H), 3.98 (s, 1H), 5.27 (s, 2H), 6.59 (d, J=15.9 Hz, 1H), 6.84−6.89 (m, 5H), 7.27−7.34 (m, 2H), 7.34−7.37 (m, 5H), 7.46 (d, J=9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.2, 68.1, 78.1, 113.7, 113.9, 126.9, 127.6, 127.99, 128.02, 128.4, 128.5, 129.0, 130.0, 133.6, 135.0, 159.3, 159.4, 174.3; HRMS (ESI) calcd for $C_{25}H_{24}O_5Na$ [M+Na]$^+$: 427.1521, found 427.1532.

(*S*,*E*)-Benzyl 4-(4-chlorophenyl)-2-hydroxy-2-(4-methoxyphenyl)but-3-enoate (7h) Colorless oil, 61% yield, 80% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.81 (s, 3H), 3.98 (s, 1H), 5.26 (s, 2H), 6.68 (d, J=15.9 Hz, 1H), 6.87 (d, J=9.0 Hz, 2H), 6.88 (d, J=15.9 Hz, 1H), 7.27−7.36 (m, 9H), 7.42 (d, J=9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.2, 68.3, 78.0, 113.7, 128.3, 127.9, 128.0, 128.5, 128.6, 128.7, 129.2, 129.7, 133.2, 133.5, 134.7, 134.8, 159.4, 173.9; HRMS (ESI) calcd for $C_{24}H_{21}O_4ClNa$ [M+Na]$^+$: 431.1026, found 431.1039.

(*S*,*E*)-Benzyl 4-(4-bromophenyl)-2-hydroxy-2-(4-methoxyphenyl)but-3-enoate (7i) Colorless oil, 75% yield, 80% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.81 (s, 3H), 3.97 (s, 1H), 5.27 (s, 2H), 6.70 (d, J=15.6 Hz, 1H), 6.84−6.89 (m, 3H), 7.24−7.28 (m, 4H), 7.34−7.36 (m, 3H), 7.42−7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.3, 68.3, 78.0, 113.8, 121.7, 127.4, 128.1, 128.3, 128.57, 128.62, 129.3, 129.9, 131.7, 133.2, 134.8, 135.2, 159.4, 174.0; HRMS (ESI) calcd for $C_{24}H_{21}O_4BrNa$ [M+Na]$^+$: 475.0521, found 475.0512.

(*S*,*E*)-Benzyl 4-(anthracen-9-yl)-2-hydroxy-2-(4-methoxyphenyl)but-3-enoate (7j) Colorless oil, 82% yield, 14% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.84 (s, 3H), 4.32 (s, 1H), 5.28 (d, J=12.6 Hz, 1H), 5.44 (d, J=11.7 Hz, 1H), 6.66 (d, J=15.9 Hz, 1H), 6.96 (d, J=8.7 Hz, 2H), 7.36−7.41 (m, 8H), 7.48 (d, J=6.9 Hz, 2H), 7.63 (d, J=8.7 Hz, 2H), 7.75 (d, J=16.2 Hz, 1H), 8.01 (d, J=8.1 Hz, 2H), 8.21 (d, J=9.0 Hz, 2H), 8.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.4, 68.6, 78.5, 114.0, 125.2, 125.5, 125.8, 126.6, 127.1, 127.6, 128.3, 128.7, 128.8, 129.5, 131.4, 131.8, 133.5, 134.9, 137.5, 159.5, 174.5; HRMS (ESI) calcd for $C_{32}H_{26}O_4Na$ [M+Na]$^+$: 475.0521, found 475.0527.

Acknowledgement

Financial support from the National Natural Science Foundation of China (Nos. 20972172, 21021063).

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