Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201800774

Link to VoR: http://dx.doi.org/10.1002/adsc.201800774

10.1002/adsc.201800774

UPDATE

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

An *Atropos* Biphenyl Bisphosphine Ligand with 2,2'-*tert*-Butylmethylphosphino Groups for the Rhodium-Catalyzed Asymmetric Hydrogenation of Enol Esters

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. This is an update of our previous work concerning the development of *Atropos* biphenyl bisphosphine ligands. An unexpected *Atropos* structural property was confirmed by Single crystal X-ray diffraction and this result is consistent with the computational calculations described in our previous work. This P-stereogenic bisphosphine ligand possessing a biphenyl backbone and 2,2'-*tert*-butylmethylphosphino groups has been applied to the Rh-catalyzed asymmetric hydrogenation of enol esters, which has not been widely studied and can be used for the synthesis of several important bioactive compounds. Although there is room for further improvement in enantioselectivity, the results reported herein provide a further understanding of such types of ligands.

Keywords: *Atropos*; Asymmetric hydrogenation; Biphenyl bisphosphine ligand; P-Stereogenic; Rhodium

The development of chiral ligands with diverse structures holds a prominent position in the field of asymmetric catalysis.[1] As the earliest that were developed, chiral bisphosphine ligands have received great attention.[2] Several types of ligands possessing different backbones and P-containing groups have been designed, synthesized and applied in numerous enantioselective transformations. In the last 20 years, the development of P-stereogenic ligands has been reignited, especially since the pioneering work of Imamoto et al.[3-6] Taking ligands bearing *tert*-butylmethylphosphino groups as typical examples, BisP*, MiniPhos, QuinoxP*, BenzP*, etc, possessing ethane, methane, quinoxaline, and benzene backbones have been reported successively (Figure 1).[4] Despite these successes, the development of new ligands bearing *tert*-butylmethylphosphino groups on other types of backbone are still greatly desired.

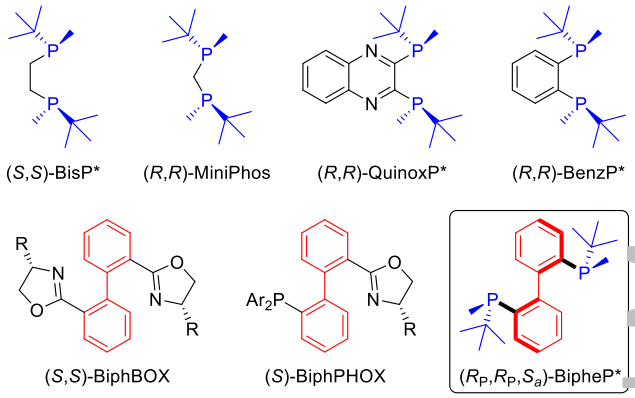

Figure 1. Ligands bearing *tert*-butylmethylphosphino groups with different backbones and ligands bearing different 2,2'-substituents with biphenyl backbone.

Our group has long focused on the development of bidentate ligands with only two chiral 2,2'-substituents on a biphenyl backbone. The *tropos* bis(oxazoline) biphenyl ligand BiphBOX and phosphine-oxazoline ligand BiphPHOX were successively developed and successfully applied in Cu-catalyzed asymmetric cyclopropanation, Pd-catalyzed asymmetric allylation, and Ir-catalyzed asymmetric hydrogenation.[7,8] Recently, we also reported the biphenyl bisphosphine ligand BipheP* bearing only 2,2'-*tert*-butylmethylphosphino groups. (Figure 1).[9] From the NMR and computational results, it can be speculated that the biphenyl axis has a single configuration due to the large rotational energy barrier and the significant free energy difference between the two diastereoisomers caused by the bulky chiral phosphino groups. Its unique structure encouraged us to investigate its application in the Rh-catalyzed asymmetric hydrogenation of enamides. Soon after our publication, the Tang's

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group and Boehringer Ingelheim Pharmaceuticals also reported a series of biphenyl dihydrobenzooxaphosphole ligands, BABIBOP or BABIPhos, and disclosed the X-ray structures of their Pd-, Rh-, and Cu-complexes.[10] The complexes bearing these structurally novel ligands possess axial chirality and showed high efficiency and excellent enantioselectivities in asymmetric hydrogenations. In order to further confirm the unique structure of such ligands and extend their utilization, herein we report the Single crystal X-ray diffraction of the free ligand BipheP* and its performance in the Rh-catalyzed asymmetric hydrogenation of enol esters. Such reactions have not been widely studied and could be useful for the synthesis of several important bioactive compounds bearing a chiral α-hydroxy acid skeleton.

Figure 2. ORTEP drawing of **BipheP*** (dotted lines represent the C-H···π interactions).

The compound BipheP* was synthesized from (*S*)-*tert*-butylmethylphosphane-borane and 1,2-dibromobenzene via a simple route. Finally, a white solid was obtained after crystallization from methanol.[9] Recently, we have succeeded in obtaining its absolute configuration by single crystal X-ray diffraction (Figure 2).[11] This experimental data is exactly the same as the previously calculated result. The axial chirality of the ligand is exclusively *S*-configuration. The dihedral angle of the two benzene rings is 65°, which is the same as that in the simulated structure following minimum energy optimization. The four C-H···π interactions exist with a $H_{tBu}\cdots C_{Ar}$ distance less than 3 Å, which lowers the molecular energy and stabilizes the conformation.

Asymmetric hydrogenation is regarded as a practical methodology due to its high efficiency and environmental friendliness, and so has attracted much attention from academia and industry.[12] In our initial report, we found that the rhodium complex of BipheP* is a highly active and enantioselective catalyst for the asymmetric hydrogenation of β-aryl enamides under mild conditions.[9] Considering the same catalytic mechanism and similar stereocontrol model, we believed that it could also be a potential catalyst for the asymmetric hydrogenation of β-aryl enol esters. This transformation has been demonstrated to be one of the most feasible methods for the preparation of chiral β-aryl α-hydroxy acids, which comprise versatile building blocks in organic synthesis for the preparation of optically active pharmaceutical and agrochemical compounds (Figure 3).[13] However, due to the lower reactivity caused by the weaker coordinating ability of the ester group, the hydrogenation of such substrates has not been thoroughly studied.

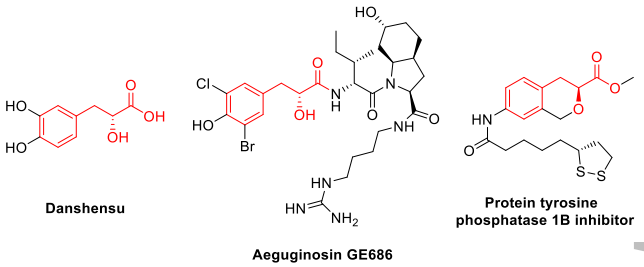
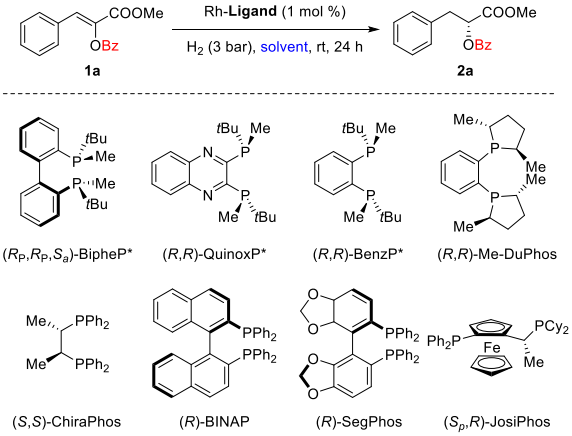


Figure 3. Selective examples of bioactive molecules synthesized from chiral β-aryl α-hydroxy acids.

Table 1. Condition Optimization.



Entry[a)]	Solvent	Ligand	Conv (%)[b)]	Ee (%)[c)]
1	THF	BipheP*	60	72
2	EtOAc	BipheP*	62	73
3	DCM	BipheP*	64	74
4	toluene	BipheP*	7	75
5	H_2O	BipheP*	28	84
6	MeOH	BipheP*	99	94
7[d)]	MeOH	BipheP*	99	82
8	MeOH	QuinoxP*	92	54
9	MeOH	BenzP*	94	59
10	MeOH	Me-DuPhos	98	92
11	MeOH	ChiraPhos	trace	-
12	MeOH	BINAP	trace	-
13	MeOH	SegPhos	trace	-
14	MeOH	JosiPhos	trace	-

[a)] Substrate **1a** (0.05 M), [Rh(BipheP*)(cod)]SbF_6 or [Rh(cod)$_2$]SbF_6/ligand (1 mol %), H_2 (3 bar), solvent (2 mL), rt, 24 h, unless otherwise noted. [b)] Conversions were calculated from ^{1}H NMR spectra. [c)] The ee values were determined by HPLC using chiral columns (Daicel IC-3). [d)] Acetyl-substituted substrate **1a'** was used instead of **1a**.

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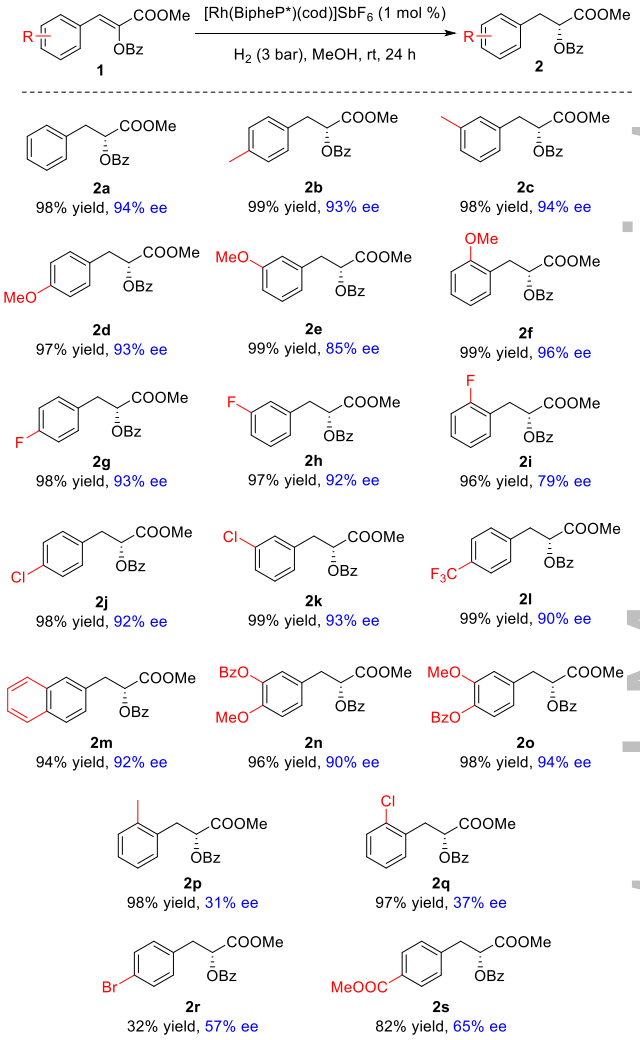
Primarily, the hydrogenation of a model substrate **1a** was tested in different solvents (Table 1, entries 1-6). In tetrahydrofuran (THF), ethyl acetate (EtOAc) and dichloromethane (DCM), the reaction showed similar results giving the desired product in approximately 60% conversion and 70% ee after 24 hours (entries 1-3). When the transformation was conducted in toluene or water, the conversion was dramatically reduced because of the poor solubility for the substrate (entries 4 and 5). However, the ee value increased siginificantly in water to 84%. Much to our delight, in the protic solvent methanol, the reaction proceeded much more effectively, and the ee of the hydrogenated product **2a** reached 94%, significantly better than other solvents (entry 6). We then changed the benzoyl group to acetyl, but the ee of the obtained product **2a'** dropped down to 82% (entry 7). Other important bisphosphine ligands, such as (*R*,*R*)-QuinoxP*, (*R*,*R*)-BenzP*, (*R*,*R*)-Me-DuPhos, (*S*,*S*)-ChiraPhos, (*R*)-BINAP, (*R*)-SegPhos and (*S*$_p$,*R*)-JosiPhos, were also evaluated for the asymmetric hydrogenation of **1a** under the same conditions (entries 8-14). Other electron-rich bisphosphine ligands bearing *tert*-butylmethylphosphino groups gave lower enantioselectivities (entries 8 and 9). (*S*,*S*)-Me-DuPhos provided good results with 98% conversion and 92% ee (entry 10). Using the ligands bearing diphenylphosphine groups, very little of the reduced product was obtained under the standard conditions (entries 11-14).

Having established the optimized reaction conditions, we then investigated the substrate scope for the asymmetric hydrogenation (Scheme 1). For most of the substrates, the reaction went to completion in 24 hours and with more than 90% ee. The *para*-methyl- and *meta*-methyl-substituted substrates **1b** and **1c** were hydrogenated to give the corresponding products with similar results compared with that of the model substrate **1a**. The methoxy group, as a more electron-donating substituent, exhibited a more obvious position effect (**1d-f**). A methoxy group at the *meta* position had a negative influence on the reaction, while an *ortho*-methoxy group gave the highest enantioselectivity for this reaction. An opposite position effect was observed for the fluoro group (**1g-i**). The *meta*-fluoro-substituted substrate gave a similar result to that of the *para*-substituted compound, while the *ortho*-fluoro-substituted substrate gave its corresponding product with an obviously lower enantioselectivity. Again, the outcomes of *para*- and *meta*-chloro-substituted substrates were almost identical (**1j** and **1k**). Another substrate **1l** bearing a *para*-trifluoromethyl, and the 2-naphthyl-substituted substrate **1m**, also gave the corresponding products with good enantioselectivities of 90% and 92% ee's, respectively. We also tested two disubstituted substrates **1n** and **1o** to give the corresponding products with 90% and 94% ee, respectively. Their products can be further converted to Danshensu (Figure 4), which is a very important bioactive compound.[13e] Surprisingly, for other *ortho*-substituted substrates possessing an *ortho*-methyl or *ortho*-chloro substituent, the ee values dropped drastically to 31% and 37%, although the reactivity is still high enough for complete conversion (**1p** and **1q**). For other electron-withdrawing substituents, such as a *para*-bromo group and *para*-methoxycarbonyl group, lower reactivities were observed under the same conditions and lower enantioselectivities of 57% and 65% ee's were obtained, respectively (**1r** and **1s**).

Scheme 1. Substrate Scope.



We then studied the hydrogenation with a low catalyst loading. The hydrogenation of substrate **1a** and **1o** under 400/1 S/C gave complete conversion to the desired product in 48 hours without loss of enantiomeric excess. The applicability for this reaction was also evaluated (Scheme 2). The hydrogenated product **2a** was easily hydrolyzed to *β*-phenyl *α*-hydroxy acid **3a** and smoothly cyclized to **4a**, which can be further derivatized to the enantiomer of a protein tyrosine phosphatase 1B (PTP1B) inhibitor.[13b] The chiral product **2a** can also be directly reduced to chiral diol **5a** and further converted to a monoamine oxidase-B (MAO-B) inhibitor named (*R*)-selegiline.[14]

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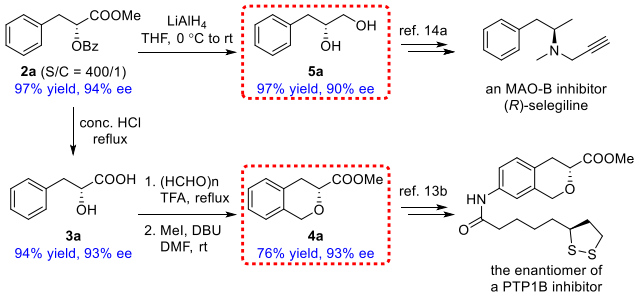
Scheme 2. Further applications.



In summary, we have confirmed the *atropos* property of BipheP* by single crystal X-ray diffraction. The biphenyl axis possesses chirality which is induced by the two chiral *ortho*-substituents. This result is consistent with the previously reported computational data. The application scope of this ligand has been extended to the Rh-catalyzed asymmetric hydrogenation of enol esters with high reactivities and good enantioselectivities. We are continuing our efforts to develop more ligands using this protocol and to broaden the usage of these types of ligands.

Experimental Section

General procedure for asymmetric hydrogenation: the enol ester (0.1 mmol), rhodium catalyst (0.001 mmol), and a magnetic stirrer bar were charged in a hydrogenation bottle and put in the autoclave. The system was evacuated and filled with hydrogen. After repeating this operation several times, degassed methanol (2 mL) was added and the hydrogen pressure was adjusted to 3 bar. After vigorous stirring for 24 hours, the volatile solvent was evaporated under reduced pressure and the residue was passed through a short column of silica gel. The solvent was removed by evaporation and the product was dried in vacuum. The enantiomeric excess of the product was determined by HPLC using chiral columns.

(*R*)-1-methoxy-1-oxo-3-phenylpropan-2-yl benzoate (2a):[15a] Colorless oil, 28.1 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.35-7.20 (m, 5H), 5.45 (dd, J = 8.0, 5.2 Hz, 1H), 3.75 (s, 3H), 3.37-3.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.07, 165.84, 135.89, 133.31, 129.80, 129.30, 129.25, 128.50, 128.38, 127.06, 73.43, 52.36, 37.52. 94% ee (Daicel Chiralcel IC-3 column, hexane/*i*PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_S = 13.8 min, t_R = 14.6 min.).

(*R*)-1-methoxy-1-oxo-3-(*p*-tolyl)propan-2-yl benzoate (2b):[15a] Colorless oil, 29.5 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 5.38 (dd, J = 8.0, 5.2 Hz, 1H), 3.71 (s, 3H), 3.27-3.16 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.25, 165.99, 136.63, 133.35, 132.70, 129.78, 129.22, 129.19, 129.15, 128.38, 73.62, 52.35, 37.08, 20.99. 93% ee (Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 10.7 min, t_S = 35.0 min.).

(*R*)-1-methoxy-1-oxo-3-(*m*-tolyl)propan-2-yl benzoate (2c):[15a] Colorless oil, 29.2 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.15-7.02 (m, 3H), 5.46-5.39 (m, 1H), 3.75 (s, 3H), 3.31-3.18 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.15, 165.86, 138.06, 135.80, 133.30, 133.10, 130.13, 129.80, 129.31, 128.36, 127.78, 126.32, 73.52, 52.34, 37.47, 21.33. 94% ee (Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 10.3 min, t_S = 19.5 min.).

(*R*)-1-methoxy-3-(4-methoxyphenyl)-1-oxopropan-2-yl benzoate (2d):[15a] Colorless oil, 30.5 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 5.41 (t, J = 6.4 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.30-3.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.12, 165.86, 158.61, 133.30, 130.33, 129.80, 129.30, 128.38, 127.85, 113.90, 73.62, 55.18, 52.32, 36.69. 93% ee (Daicel Chiralcel IC-3 column, hexane/*i*PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_S = 22.0 min, t_R = 24.5 min.).

(*R*)-1-methoxy-3-(3-methoxyphenyl)-1-oxopropan-2-yl benzoate (2e):[15a] Colorless oil, 31.1 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.43 (d, J = 7.6 Hz, 2H), 7.28-7.20 (m, 2H), 6.93-6.82 (m, 2H), 5.49 (t, J = 6.8 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 3.42 (dd, J = 14.0, 8.8 Hz, 1H), 3.22 (dd, J = 14.0, 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.60, 165.94, 157.58, 133.16, 131.22, 129.78, 129.45, 128.46, 128.28, 124.06, 120.29, 110.17, 72.30, 55.21, 52.21, 32.51. 85% ee (Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 21.5 min, t_S = 23.5 min.).

(*R*)-1-methoxy-3-(2-methoxyphenyl)-1-oxopropan-2-yl benzoate (2f):[15a] Colorless oil, 31.2 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.83 (s, 1H), 6.77 (d, J = 8.4 Hz, 1H), 5.43 (t, J = 6.8 Hz, 1H), 3.74 (d, J = 7.2 Hz, 6H), 3.31-3.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.05, 165.81, 159.63, 137.42, 133.32, 129.80, 129.48, 129.27, 128.38, 121.63, 114.90, 112.59, 73.37, 55.10, 52.37, 37.55. 96% ee (Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 18.4 min, t_S = 28.3 min.).

(*R*)-3-(4-fluorophenyl)-1-methoxy-1-oxopropan-2-yl benzoate (2g):[15a] Colorless oil, 29.7 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.27-7.19 (m, 2H), 6.98 (t, J = 8.8 Hz, 2H), 5.45-5.38 (m, 1H), 3.72 (s, 3H), 3.32-3.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.87, 165.76, 163.19 (160.74, d, J = 245 Hz), 133.40, 131.57 (131.53, d, J = 4 Hz), 130.86 (130.78, d, J = 8 Hz), 129.76, 129.16, 128.43, 115.49 (115.28, d, J = 21 Hz), 73.25, 52.39, 36.70. 93% ee (Daicel Chiralcel IC-3 column, hexane/*i*PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_S = 12.5 min, t_R = 13.6 min.).

(*R*)-3-(3-fluorophenyl)-1-methoxy-1-oxopropan-2-yl benzoate (2h): Colorless oil, 29.3 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.30-7.20 (m, 2H),

7.05 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 9.6 Hz, 1H), 6.92 (t, *J* = 8.8 Hz, 1H), 5.51-5.40 (m, 1H), 3.73 (s, 3H), 3.35-3.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.76, 165.74, 163.97 (161.52, d, *J* = 245 Hz), 138.36 (138.28, d, *J* = 8 Hz), 133.42, 130.03 (129.94, d, *J* = 9 Hz), 129.78, 129.11, 128.44, 124.97 (124.94, d, *J* = 3 Hz), 116.40 (116.18, d, *J* = 22 Hz), 114.17 (113.96, d, *J* = 21 Hz), 73.00, 52.44, 37.17. HRMS (ESI) calculated for $C_{17}H_{16}FO_4^+$ $[M+H]^+$ 303.1027, found 303.1042. 92% ee (Daicel Chiralcel IC-3 column, hexane/*i*PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_S = 11.5 min, t_R = 13.1 min.). $[\alpha]_D^{23}$ = +45 (*c* = 0.21, MeOH).

(*R*)-3-(2-fluorophenyl)-1-methoxy-1-oxopropan-2-yl benzoate (2i): Colorless oil, 28.9 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30-7.20 (m, 2H), 7.13-6.98 (m, 2H), 5.48-5.40 (m, 1H), 3.74 (s, 3H), 3.40-3.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.88, 165.80, 162.52 (160.07, d, *J* = 245 Hz), 133.33, 131.54 (131.50, d, *J* = 4 Hz), 129.82, 129.15, 129.08 (129.00, d, *J* = 8 Hz), 128.37, 124.10 (124.07, d, *J* = 3 Hz), 122.94 (122.79, d, *J* = 15 Hz), 115.53 (115.31, d, *J* = 22 Hz), 72.39, 52.43, 30.86 (30.83, d, *J* = 3 Hz). HRMS (ESI) calculated for $C_{17}H_{16}FO_4^+$ $[M+H]^+$ 303.1027, found 303.1028. 79% ee (Daicel Chiralcel IC-3 column, hexane/*i*PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_S = 14.0 min, t_R = 15.1 min.). $[\alpha]_D^{23}$ = +10 (*c* = 0.17, MeOH).

(*R*)-3-(4-chlorophenyl)-1-methoxy-1-oxopropan-2-yl benzoate (2j): Colorless oil, 31.3 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.30-7.16 (m, 4H), 5.42 (t, *J* = 6.4 Hz, 1H), 3.73 (s, 3H), 3.30-3.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.79, 165.74, 134.34, 133.45, 133.00, 130.67, 129.77, 129.10, 128.68, 128.45, 73.05, 52.45, 36.83. HRMS (ESI) calculated for $C_{17}H_{16}ClO_4^+$ $[M+H]^+$ 319.0732, found 319.0746. 92% ee (Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 12.9 min, t_S = 19.8 min.). $[\alpha]_D^{23}$ = +26 (*c* = 0.13, MeOH).

(*R*)-3-(3-chlorophenyl)-1-methoxy-1-oxopropan-2-yl benzoate (2k): Colorless oil, 31.5 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.29 (s, 1H), 7.26-7.19 (m, 2H), 7.18-7.13 (m, 1H), 5.42 (t, *J* = 6.4 Hz, 1H), 3.74 (s, 3H), 3.33-3.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.73, 165.73, 137.84, 134.24, 133.44, 129.79, 129.77, 129.60, 129.08, 128.45, 127.45, 127.33, 72.95, 52.46, 37.11. HRMS (ESI) calculated for $C_{17}H_{15}ClNaO_4^+$ $[M+Na]^+$ 341.0551, found 341.0553. 93% ee (Daicel Chiralcel IC-3 column, hexane/*i*PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_S = 11.9 min, t_R = 13.3 min.). $[\alpha]_D^{23}$ = +33 (*c* = 0.22, MeOH).

(*R*)-1-methoxy-1-oxo-3-(4-(trifluoromethyl)phenyl)propan-2-yl benzoate (2l):[15a] Colorless oil, 34.8 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 3H), 7.46-7.36 (m, 4H), 5.48 (t, *J* = 6.4 Hz, 1H), 3.74 (s, 3H), 3.41-3.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.64, 165.68, 140.00, 133.49, 129.93 (129.61, 129.29, 128.97, q, *J* = 32 Hz), 129.76, 129.67, 129.03, 128.47, 128.13 (125.43, 122.72, 120.01, q, *J* = 271 Hz), 125.51 (125.47, 125.44, 125.40, q, *J* = 4 Hz), 72.79, 52.49, 37.21. 90% ee (Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 9.8 min, t_S = 12.2 min.).

(*R*)-1-methoxy-3-(naphthalen-2-yl)-1-oxopropan-2-yl benzoate (2m):[15a] Colorless oil, 31.2 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.84-7.72 (m, 4H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.48-7.37 (m, 5H), 5.55 (t, *J* = 6.8 Hz, 1H), 3.73 (s, 3H), 3.52-3.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.09, 165.85, 133.43, 133.40, 133.33, 132.45, 129.81, 129.23, 128.38, 128.16, 128.07, 127.63, 127.56, 127.41, 126.12, 125.73, 73.42, 52.40, 37.68. 92% ee (Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 24.5 min, t_S = 98.3 min.).

(*R*)-5-(2-(benzoyloxy)-3-methoxy-3-oxopropyl)-2-methoxyphenyl benzoate (2n): White solid, 41.9 mg, 96% yield. M.p. 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.10 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.42 (t, *J* = 6.4 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.27-3.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.98, 165.85, 164.59, 150.42, 139.78, 133.44, 133.31, 130.24, 129.87, 129.36, 129.28, 128.48, 128.40, 128.37, 127.55, 124.13, 112.51, 73.33, 55.93, 52.39, 36.60. HRMS (ESI) calculated for $C_{25}H_{23}O_7^+$ $[M+H]^+$ 435.1444, found 435.1443. 90% ee (Daicel Chiralcel IC-3 column, hexane/*i*PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_S = 59.7 min, t_R = 74.3 min.). $[\alpha]_D^{23}$ = +62 (*c* = 0.14, MeOH).

(*R*)-4-(2-(benzoyloxy)-3-methoxy-3-oxopropyl)-2-methoxyphenyl benzoate (2o): White solid, 42.5 mg, 98% yield. M.p. 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.67-7.37 (m, 6H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.99-6.85 (m, 2H), 5.47 (t, *J* = 6.8 Hz, 1H), 3.75 (s, 6H), 3.35-3.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.99, 165.77, 164.66, 151.14, 139.00, 134.87, 133.42, 130.24, 129.80, 129.33, 129.23, 128.52, 128.47, 128.42, 122.87, 121.61, 113.53, 73.28, 55.84, 52.45, 37.40. HRMS (ESI) calculated for $C_{25}H_{23}O_7^+$ $[M+H]^+$ 435.1444, found 435.1456. 94% ee (Daicel Chiralcel IC-3 column, hexane/*i*PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_S = 70.0 min, t_R = 111.9 min.). $[\alpha]_D^{23}$ = +23 (*c* = 0.17, MeOH).

(*R*)-1-methoxy-1-oxo-3-(*o*-tolyl)propan-2-yl benzoate (2p)[15a]: Colorless oil, 29.1 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.23-7.04 (m, 4H), 5.06 (q, *J* = 7.6 Hz, 1H), 3.72 (s, 3H), 3.34-3.14 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.56, 166.89, 136.77, 134.19, 133.75, 131.75, 130.63, 129.80, 128.57, 127.24, 126.96, 125.97, 52.74, 52.37, 35.73, 19.35. 31% ee (Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 50.0 min, t_S = 53.4 min.).

(*R*)-3-(2-chlorophenyl)-1-methoxy-1-oxopropan-2-yl benzoate (2q): Colorless oil, 30.9 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.47-7.29 (m, 4H), 7.22-7.13 (m, 2H), 5.53-5.47 (m, 1H), 3.75 (s, 3H), 3.55-3.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.03, 165.81, 134.38, 133.68, 133.33, 131.53, 129.83, 129.68, 129.13, 128.64, 128.36, 126.80, 72.08, 52.47, 35.09. HRMS (ESI) calculated for $C_{17}H_{16}ClO_4^+$ $[M+H]^+$ 319.0732, found 319.0729. 37% ee

(Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 13.2 min, t_S = 16.2 min.). $[\alpha]_D^{23}$ = +17 (*c* = 0.27, MeOH).

(*R*)-3-(4-bromophenyl)-1-methoxy-1-oxopropan-2-yl benzoate (2r):[15a] Colorless oil, 11.8 mg, 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.43 (t, *J* = 6.4 Hz, 1H), 3.72 (s, 3H), 3.30-3.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.77, 165.72, 134.86, 133.45, 131.63, 131.03, 129.77, 129.09, 128.45, 121.11, 72.96, 52.45, 36.89. 57% ee (Daicel Chiralcel OJ-H column, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 220 nm, t_R = 12.8 min, t_S = 14.3 min.).

methyl (*R*)-4-(2-(benzoyloxy)-3-methoxy-3-oxopropyl)benzoate (2s): Colorless oil, 28.0 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.94 (m, 4H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 5.47 (t, *J* = 6.4 Hz, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 3.39-3.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.72, 166.81, 165.70, 141.19, 133.45, 129.81, 129.76, 129.38, 129.04, 128.44, 72.84, 52.47, 52.07, 37.42. HRMS (ESI) calculated for $C_{19}H_{19}O_4^+$ $[M+H]^+$ 311.1283, found 311.1293. 65% ee (Daicel Chiralcel IC-3 column, hexane/*i*PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_S = 52.7 min, t_R = 58.2 min.). $[\alpha]_D^{23}$ = +43 (*c* = 0.44, MeOH).

(*R*)-2-hydroy-3-phenylpropanoic acid (3a):[15b] The solution of hydrogenated product **2a** (70.0 mg, 0.24 mmol) in concentrated HCl (15 mL) was heated to reflux for 8 hours. After cooling down to room temperature, the reaction was extracted with DCM (15 mL × 3). After drying over $MgSO_4$, the solvent was evaporated and the pure product was isolated by column chromatography using DCM then DCM/MeOH (10/1) as eluent to obtain a white solid in 94% yield (37.6 mg) and with 93% ee (Daicel Chiralcel OJ-H, hexane/*i*PrOH/CF_3COOH = 96/4/0.1, 1.0 mL/min, λ = 210 nm, 25 °C, t_R = 23.8 min, t_S = 27.5 min.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.24 (m, 5H), 4.55 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.24 (dd, *J* = 14.0, 4.4 Hz, 1H), 3.03 (dd, *J* = 14.0, 7.2 Hz, 1H).

methyl (*R*)-isochromane-3-carboxylate (4a):[15c] To a solution of **3a** (33.4 mg, 0.20 mmol) in trifluoroacetic acid (1.0 mL) was added paraformaldehyde (0.33 eq, 6.0 mg) and the reaction mixture was heated at reflux for 36 h. Solvent was then distilled off from the reaction mixture and the residue was diluted with water (5 mL) and extracted with ethyl acetate (5 mL × 3). The organic layer was dried over $MgSO_4$, filtered and evaporated to give the corresponding crude acid product (39.7 mg). This crude product was dissolved in DMF (5 mL), and DBU (2.0 eq, 0.6 mL) and MeI (4.0 eq, 0.6 mL) were added. The reaction was stirred overnight. 10% HCl (10 mL) was added and the solution was extracted with ethyl acetate (EA) (10 mL × 3). The organic layer was dried over $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography using EA/PE(1/5) as eluent to obtain a colorless oil in 76% yield (29.3 mg) and with 93% ee (Daicel Chiralcel OD-H, hexane/*i*PrOH = 85/15, 1.0 mL/min, λ = 210 nm, 25 °C, t_R = 12.1 min, t_S = 14.9 min.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.13 (m, 3H), 7.07-7.00 (m, 1H), 5.04 (d, *J* = 14.8 Hz, 1H), 4.90 (d, *J* = 14.8 Hz, 1H), 4.42 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.85 (s, 3H), 3.18-3.04 (m, 2H).

(*R*)-3-phenylpropane-1,2-diol (5a):[15d] A solution of $LiAlH_4$ in THF (10.0 eq, 1.4 mL, 1M) was added dropwise to **2a** (39.8 mg, 0.14 mmol) at 0 °C under N_2. The mixture was allowed to warm to room temperature and stirred overnight. The resulting suspension was cooled to 0 °C and then the $LiAlH_4$ was quenched by addition of EA (2 mL) and diluted HCl (4 mL, 10%). The organic layer was dried over $MgSO_4$, filtered and evaporated. Pure product was obtained by column chromatography as a colorless oil in 97% yield (20.6 mg) and with 90% ee (Daicel Chiralcel IC-3, hexane/*i*PrOH = 90/10, 1.0 mL/min, λ = 210 nm, 25 °C, t_R = 11.1 min, t_S = 12.2 min.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.13 (m, 5H), 3.96-3.84 (m, 1H), 3.63 (dd, *J* = 11.2, 2.4 Hz, 1H), 3.46 (dd, *J* = 11.2, 7.2 Hz, 1H), 3.11 (s, 2H), 2.81-2.66 (m, 2H).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21572131 and 21620102003), Shanghai Municipal Education Commission (201701070002E00030), and Science and Technology Commission of Shanghai Municipality (15JC1402200). We also thank the Instrumental Analysis Center of SJTU for characterization.

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[11] CCDC-1846976 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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10.1002/adsc.201800774

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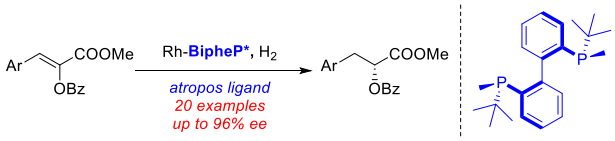

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