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Rhodium(II)/Chiral Phosphoric Acid Co-Catalyzed Enantioselective O–H Bond Insertion of α-Diazoesters

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Abstract. A rhodium(II)/chiral phosphoric acid system has been developed for the asymmetric catalytic insertion of α-diazoesters into the O–H bond of carboxylic acids to generate an array of synthetically useful α-hydroxy ester derivatives in good ee (up to 95% ee). Furthermore, the substrate scope could be successfully extended to a range of phenols and alcohols with high yield (up to 92%) and excellent enantioselectivity (up to 97%) under mild reaction conditions. Additionally, a density functional theory (DFT) study was performed to elucidate the reaction mechanism.

Keywords: α-diazoester; chiral phosphoric acid; rhodium; asymmetric catalysis; reaction mechanism

Construction of carbon-heteroatom bonds in a controlled and selective manner is an important task in synthetic organic chemistry.[1] In particular, one of the most direct and effective methods for the enantioselective formation of C–X bonds is the transition metal catalyzed insertion of carbenes into heteroatom–hydrogen bonds. Remarkable progress[2] has been made in this area. For example, high enantioselectivities have been achieved in the process of carbene insertion into N–H,[3] S–H,[4] B–H[5] and Si–H bonds[6] etc. Over the past few decades, many works have specifically concentrated on catalytic asymmetric O–H insertion reactions. The corresponding product, chiral α-hydroxy ester is a key substructure of many naturally occurring compounds and active pharmaceutical ingredients[7] (Figure.1). It was demonstrated that through the combination of metal catalysts and chiral ligands (cinchona alkaloid,[8] bisoxazoline,[9] bisazaferrocene[10] and imidazoindolephosphine[11] etc.), highly enantioselective insertion of α-diazo compounds into the O–H bonds of alcohols, phenols, and water have been realized.

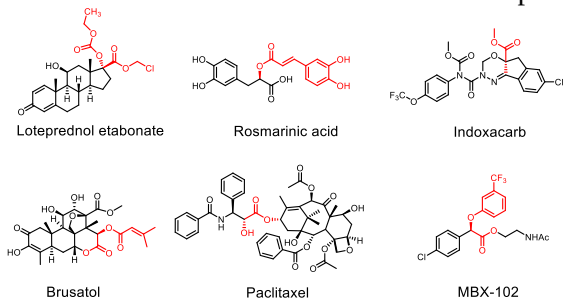

Figure 1. Selected important α-hydroxy ester-containing compounds.

Although these examples show a tremendous advance toward the synthesis of optically active α-hydroxy carbonyl containing compounds, additional studies on various metal complexes to achieve highly enantioselective carbenoid insertion into O–H bond are still needed. On the other hand, the catalytic enantioselective version of O–H insertion of carboxylic acids has not been fully addressed, probably due to the superior acidity of carboxylic acids which compromise the stability of chiral metal complex.

So far, there are only a few asymmetric examples. In 2001, Wang and co-workers[12] investigated diastereoselective insertion into carboxylic O–H bonds using camphorsultam as a chiral auxiliary, in which moderate to good selectivity was achieved (24%-90%). Feng[13] reported an efficient enantioselective (85%-95%) insertion of α-diazo carbonyl compounds into carboxylic acid using $Rh_2(OAc)_4$ and chiral guandine catalysts, in which most of the successful examples were obtained with aromatic carboxylic acids. Very recently, Ryu[14] successfully developed a method of the highly enantioselective protonation/ nucleophilic addition of substituted benzyl diazoesters with aromatic carboxy-

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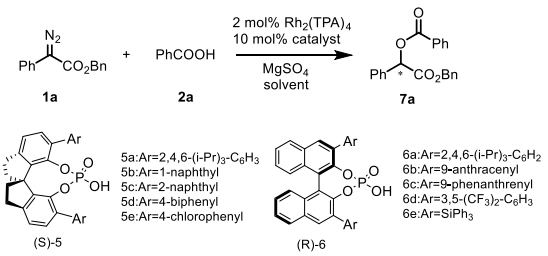
Table 1. Optimization of the reaction conditions.[a)]



Entry	catalyst	Solvent	T (°C)	Yield (%)[b)]	ee(%)[c)]
1	(R)-6a	$CHCl_3$	40	62	35
2	**(R)-6b**	**$CHCl_3$**	**40**	**85**	**93**
3	(R)-6c	$CHCl_3$	40	81	82
4	(R)-6d	$CHCl_3$	40	78	23
5	(R)-6e	$CHCl_3$	40	73	5
6	(S)-5a	$CHCl_3$	40	60	21
7	(S)-5b	$CHCl_3$	40	62	65
8	(S)-5c	$CHCl_3$	40	70	60
9	(S)-5d	$CHCl_3$	40	39	44
10	(S)-5e	$CHCl_3$	40	53	48
11[d)]	(R)-6b	$CHCl_3$	40	73	81
12	(R)-6b	$CHCl_3$	0	78	87
13	(R)-6b	c-hexane	40	65	88
14	(R)-6b	DCE	40	80	90
15	(R)-6b	toluene	40	46	93
16	(R)-6b	NMP	40	N.R	-
17	(R)-6b	DMF	40	10	17

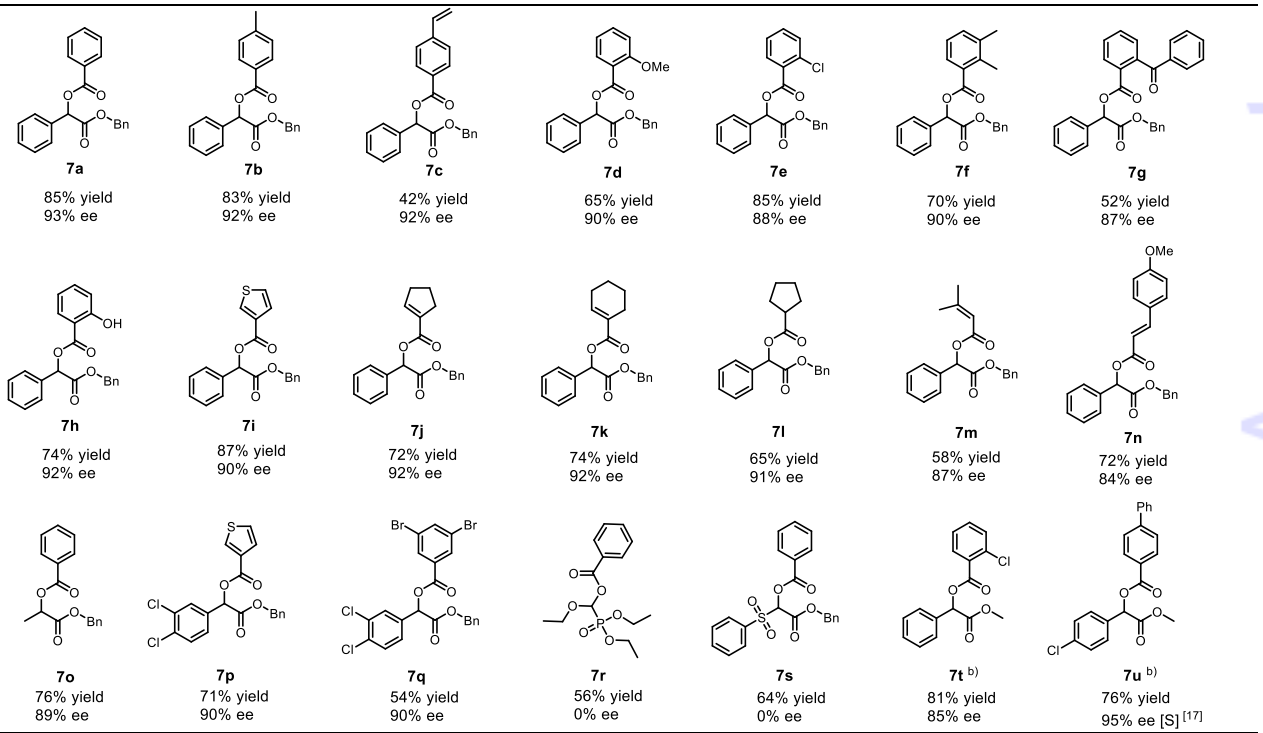
[a)] Reaction condition: **1a** (0.1 mmol), **2a** (1.3 equiv), $Rh_2(TPA)_4$ (2 mol %), catalyst (10 mol %), $MgSO_4$ (100 mg) in 1 ml solvent. [b)] Yield of isolated product after column chromatography. [c)] Determined by HPLC analysis. [d)] Using $Rh_2(OAc)_4$.

lic acids using a chiral oxazaborolidinium ion as an activator.

Inspired by previous works, and also in conjunction with our ongoing interest in asymmetric catalysis, [15] we present herein a rhodium/chiral phosphoric acid[16] co-catalyzed enantioselective O–H insertion of α-diazoesters into O–H bonds of a diverse set of phenols, alcohols and carboxylic acids, which provides direct access to highly useful carboxylates **7**, 2-aryloxy-2-aryl esters **8** and 2-alkoxy-2-aryl esters **9** with good yields and excellent enantioselectivities under mild and neutral reaction conditions.

We began our research with asymmetric insertion reaction of benzoic acid **2a** with methyl 2-diazo-2-phenylacetate **1b**. The reaction was performed in $CHCl_3$ at 40°C with catalytic amount of $Rh_2(TPA)_4$ (2 mol %), SPA (S)-**5c** (10 mol %) and $MgSO_4$ (100 mg). It was completed in 5 min. Unfortunately, the desired product 2-methoxy-2-oxo-1-phenylethyl benzoate **4n** was observed in only 52% yield and 6% ee. However,

Table 2. Asymmetric O–H insertion of α-diazoesters into carboxylic acids. [a)]



[a)] Unless otherwise noted, the reaction was carried out on a 0.1 mmol scale under nitrogen in $CHCl_3$ at 40 °C for 30 min, the ratio of **1:2** was 1:1.3.Yields referred to isolated yields, ees were determined by HPLC; [b)] Using $Rh_2(TFA)_4$.

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when we use benzyl 2-diazo-2-phenylacetate **1a** as the substrate, the expected 2-(benzyloxy)-2-oxo-1-phenylethyl benzoate **7a** could be provided in 70% yield and 60% ee (Table 1, entry 8). Therefore, we decided to use **1a** as model substrate in the further reaction optimization. Then, we evaluated CPAs with various substituents (entries 1–10). 9-Anthracenyl substituted BINOL-derived phosphoric acid catalyst (R)-**6b** performed exceptionally in the model reaction, providing the highest enantioselectivity (93% ee, entry 2). Variation of dirhodium(II) carboxylates to $Rh_2(OAc)_4$ slightly decreased enantioselectivity (entry 11). Thus $Rh_2(TPA)_4$ still led to the best result. Having identified $Rh_2(TPA)_4$/BPA (R)-**6b** as our optimal co-catalyst system, an extensive screen of solvent was undertaken (Table 1, entries 13–17). Notably, it was observed that enantioselectivity of reaction sometimes depended on the solvent polarity, and high enantioselectivity was also achieved in toluene with an obvious lower yield (46%, entry 15). When the reaction was cooled to 0°C, the corresponding yield and enantioselectivity slightly decreased to 78% and 87% (entry 12), respectively.

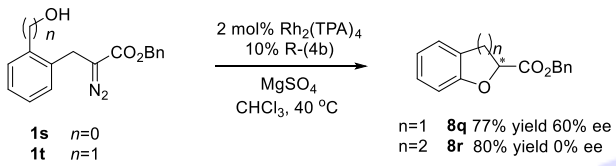
With the optimized reaction conditions established (Table 1, entry 2), we first investigated the substrate scope by carrying out reactions of various carboxylic acids with benzyl 2-diazo-2-phenylacetate **1a** (Table 2). Both aromatic and aliphatic carboxylic acids could undergo the O−H insertion reaction with good yields and high ee values. Substituents on the aromatic ring of benzoic acid seem to have a negligible effect on enantioselectivity (**7b**–**7g)**. Cinnamic type acid **1n** and thiophene-2-carboxylic acid **1i** were proved to be suitable substrates for this reaction. Interestingly enough here, when using salicylic acid as reactant, the desired product **7h** was obtained in 74% isolated yield. It could be an indirect proof that the O–H bond of acid occured much faster than the O–H bond of phenol under our reaction condition. A preliminary study showed that the reaction exhibited a significant first order kinetic isotope effect (see in SI). Notably, this reaction proceeded with aliphatic carboxylic acid smoothly to generate the related insertion products **7j**–**7m** with satisfactory enantioselectivities and moderate to good yields. Then we continued to explore the substrate scope of α-diazoesters. To our delight, a good result was obtained when using benzyl 2-diazo-4-phenylbut-3-enoate **1o** (76% yield, 89% ee) as reactant. Nevertheless, when diazo phosphonates or diazo (phenylsulfonyl)acetate was used in the reaction, the corresponding product **7r** or **7s** was obtained as a racemic compound, probably due to the larger steric hindrance of the substrates. These substrates could possibly coordinate differently from the successful examples, and that would lower the enantioselectivity significantly.

Considering the similar chemical process of O–H insertion using ROHs or carboxylic acids, asymmetric O–H insertion of α-diazoesters **1** into phenols or alcohols was subsequently explored. Under the standard condition, the desired product benzyl 2-phenoxy-2-phenylacetate **8a** or benzyl 2-butoxy-2-phenylacetate **9a** was formed in low or moderate enantioselectivity (12% or 81% ee). Aiming to get better reaction results, we restarted the optimization of the reaction conditions and then found that SPINOL-derived acid (S)-**5b** and BINOL-derived acid (R)-**6c** could be applied to these two transformations with both good yields (82% and 75%) and enantioselectivities (94% and 90%), separately. Moreover, when $Mg(OTf)_2$ (2 mol %) was added to the phenol type O–H insertion reaction with $Rh_2(TPA)_4$ (2 mol %) and S-(**5b**) (2 mol %), the enantioselectivity slightly improved to 96%.

Under the optimal reaction condition, various phenols and α-diazoesters were evaluated as substrates (Table 3, **8a**–**8p**). Impressively, all reactions exhibited good to high yields (75–96%) and excellent enantioselectivities (83–96%). The electronic properties of substituents on phenyl ring of the α-diazoesters affected yields and enantioselectivities slightly, whereas the ortho-methyl substituent phenol **2d** remarkably increased the enantioselectivity. Then we studied the substituent effect of α-diazoesters. Better enantioselectivity was obtained when changing the methyl ester to either ethyl or benzyl ester, suggesting that a larger ester group may lead to a higher ee. The substrates with fused rings such as 2-naphthyl, thienyl, and indolyl were proved to be tolerated in the reaction with a little loss of ee value.

In addition to phenols, we also evaluated alcohols **4** with a new condition (Table 3, **9a**–**9f**). The reactions of alcohols and α-diazoesters proceeded smoothly to afford the corresponding O–H insertion products with moderate to good yields (62–76%) and high enantioselectivities (81–90%).

We next turned our attention to asymmetric intramolecular O–H insertion, and the results were presented in Scheme 1. Unfortunately, the corresponding products benzyl 2,3-dihydrobenzofuran-2-carboxylate **8q** and benzyl chromane-2-carboxylate **8r** were obtained in low enantioselectivities.[9e]



Scheme 1. Asymmetric intramolecular O–H insertion.

On the basis of aforementioned results and previous reports,[18, 4a] a possible mechanism of the asymmetric O–H insertion process is proposed (Scheme 2). First step is rhodium-catalyzed nitrogen extrusion from diazoacetate to form rhodium carbenoid. Subsequently, nucleophilic attacked by free O–H either from alcohol, phenol or carboxylic acid gives metal-associated ylide intermediates.

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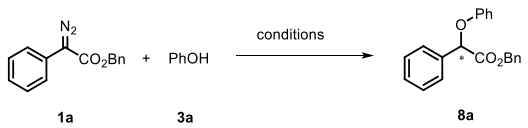
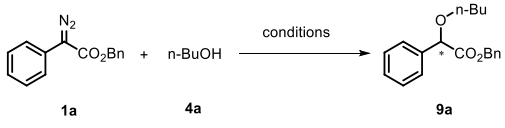
Table 3. Asymmetric O–H insertion of α-diazoesters into ROHs.



1a **3a** **8a**

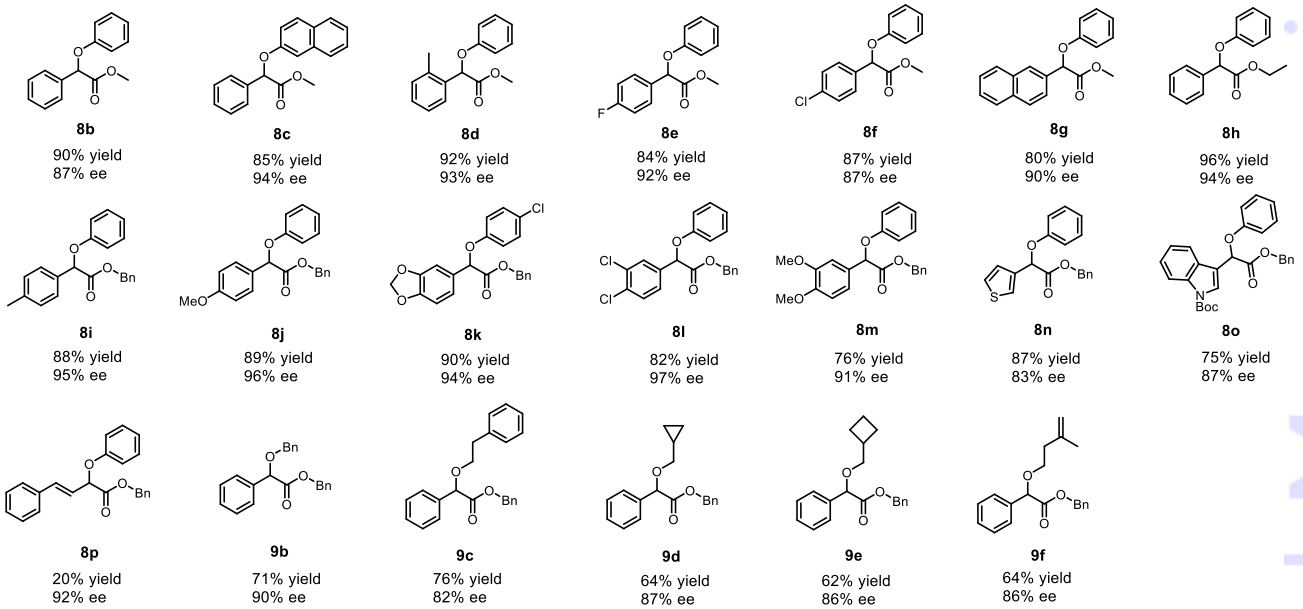
coditions	results
2 mol% $Rh_2(TPA)_4$ 10 mol% R-(6b) $MgSO_4$,$CHCl_3$, 40 °C	74% yield, 12% ee
2 mol% $Rh_2(TPA)_4$ 2 mol% $Mg(OTf)_2$ 2 mol% S-(5b) $MgSO_4$,$CHCl_3$, 40 °C	82% yield, 96% ee



1a **4a** **9a**

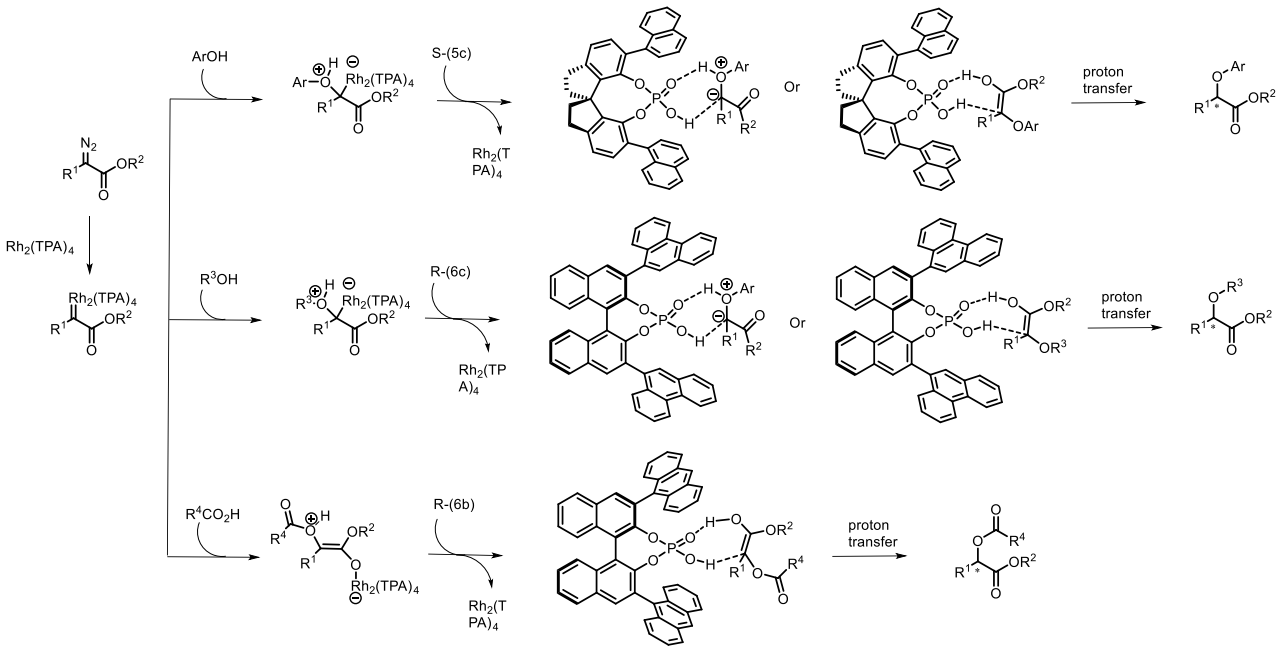
coditions	results
2 mol% $Rh_2(TPA)_4$ 10 mol% R-(6b) $MgSO_4$,$CHCl_3$, 40 °C	77% yield, 81% ee
2 mol% $Rh_2(TPA)_4$ 2 mol% R-(6c) $MgSO_4$,$CHCl_3$, 40 °C	75% yield, 89% ee

additional examples



8b 90% yield, 87% ee
8c 85% yield, 94% ee
8d 92% yield, 93% ee
8e 84% yield, 92% ee
8f 87% yield, 87% ee
8g 80% yield, 90% ee
8h 96% yield, 94% ee
8i 88% yield, 95% ee
8j 89% yield, 96% ee
8k 90% yield, 94% ee
8l 82% yield, 97% ee
8m 76% yield, 91% ee
8n 87% yield, 83% ee
8o 75% yield, 87% ee
8p 20% yield, 92% ee
9b 71% yield, 90% ee
9c 76% yield, 82% ee
9d 64% yield, 87% ee
9e 62% yield, 86% ee
9f 64% yield, 86% ee

[a]Unless otherwise noted, the reaction was carried out on a 0.1 mmol scale under nitrogen in $CHCl_3$ at 40 °C for 30 min, the ratio of **1**:**3** was 1.2:1, and the ratio of **1**:**4** was 1:1.5. Yields referred to isolated yields, ees were determined by HPLC.



Scheme 2. Proposed reaction mechanism.

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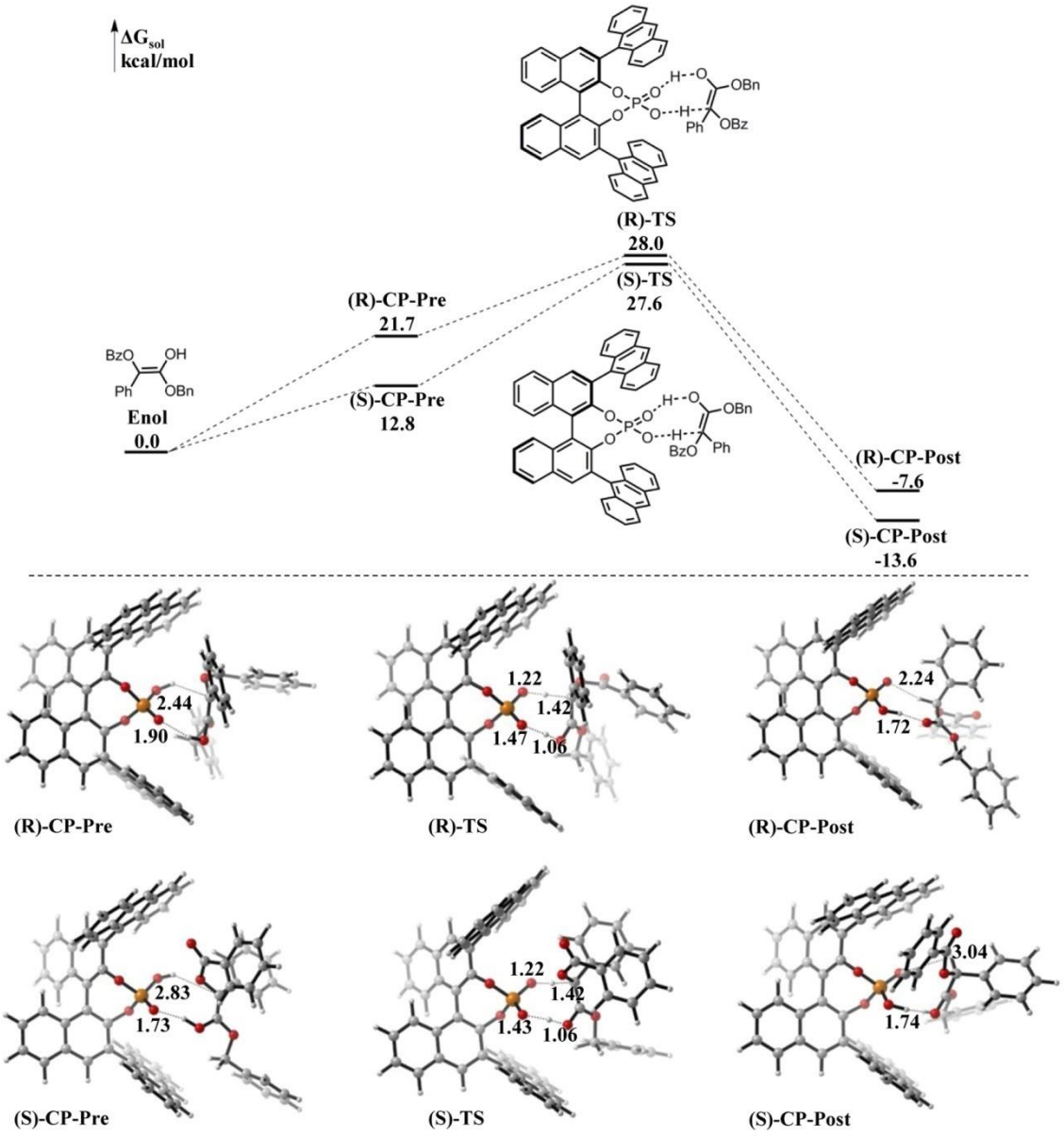

Figure 2. The computed energy surfaces for the phosphoric acid-catalyzed proton shift.

Previous DFT calculation by Yu et al.[18] and Zhou et al.[4a] have confirmed that free ylide was generated in X–H insertion reaction when the neutral dirhodium(II) complex is used as the catalyst. For alcohols and phenols in the present system, we hypothesize that once the free ylide is generated, the plausible pathway could be either [1,2]-proton shift or tandem [1,4]-proton shift followed by [1,3]-proton shift processes. Lastly, the pathway that involves chiral phosphate acid assisted proton transfer to enol intermediates or oxonium ylides affords enantiomerically enriched products.

Then we ruled out enantioselective enol keto tautomerism in the products under the influence of the phosphoric acid. Reactions of racemic product **7a** and **8a** with chiral phosphoric acid (R)-**6b** or (S)-**5c** under the optional condition continued for 2 days, and there were no ees in the re-isolated products.

In order to check whether the asymmetric O–H insertion of carboxylic acid shares the mechanism mentioned above, we performed the density functional theory (DFT) calculations at B3LYP/6-311++G(2d,2p)//B3LYP/6-31G(d) level in chloroform solution using SMD model to reveal the detailed mechanism. Calculations first showed that O–H insertion of carboxylic acid catalysted by Rh catalyst generated a stable enol intermediate, not the corresponding ylide form (see in SI).

Once the enol intermediate is formed, it could generate the final insertion products catalyzed by BINOL-derived phosphoric acid catalyst (R)-**6b** through a [1,3]-proton transfer pathway as shown in

Figure 2. One can see that the enol intermediate first forms two complexes (R)-CP-Pre and (S)-CP-Pre with the catalyst. Then they can undergo the concerted BPA-assisted [1,3]-proton shift to afford (R)- and (S)-products, respectively. It should be pointed out that (S)-CP-Pre is 8.9 kcal/mol lower in energy than (R)-CP-Pre, indicating that it is much more favorable to form (S)-CP-Pre. In addition, both (S)-TS and (S)-CP-Post locate below (R)-TS and (R)-CP-Post, showing that the reaction pathway affording the product with S configuration is more favorable in both dynamics and thermodynamics. This is in consistent with our experimental result discussed above. Obviously, the reaction mechanism for O–H insertion of carboxylic acid is significantly different from Zhou's work of asymmetric S–H bond insertion.[4a]

In summary, a rhodium/chiral phosphoric acid co-catalyzed asymmetric O–H insertionreaction between α-diazoesters and O–H donors containing phenols, alcohols and carboxylic acids was developed. Rhodium/chiral phosphoric acid was found to be an efficient and highly enantioselective catalyst for the reaction. The mild and neutral reaction conditions, operational simplicity, and very short reaction time of this method make this transformation one of the most convenient and general methods for the preparation of chiral α-hydroxy esters, which are important structural units in many biologically pharmaceutical intermediates. DFT calculation showed that asymmetric O–H insertion of carboxylic acid undergoes a [1,3]-proton shift process to afford the product with S configuration.

Experimental Section

General procedure for asymmetric O–H insertion of acids:

Under N_2 atmosphere, the $Rh_2(TPA)_4$ (1 mol %), $MgSO_4$ (100 mg), acid (0.10 mmol) and catalyst **R-(6b)** (10 mol %) were added into an oven-dried Schlenk tube. After $CHCl_3$ (0.5 mL) being injected into the Schlenk tube, the solution was stirred at 40 °C for 1 min. The diazo compound (0.15 mmol) was dissolved in 0.5 mL $CHCl_3$ and introduced into the reaction mixture. The resulting mixture was stirred at 40 °C for 30 min and purified by flash chromatography.

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[17] CCDC 1547668 (**7u**) contains the supplementary crystallographic data for this paper. These data can be obtained free of chargefrom The Cambrige Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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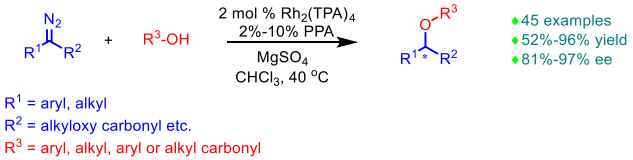

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