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Asymmetric Catalytic Insertion of α-Diazo Carbonyl Compounds into O−H Bonds of Carboxylic Acids

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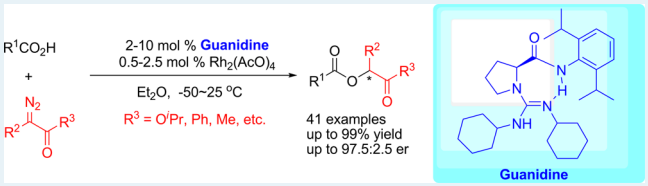
Supporting Information

ABSTRACT: An efficient enantioselective insertion of α-diazoesters and α-diazoketones into O−H bonds of carboxylic acids was realized by the use of $Rh_2(OAc)_4$ and a chiral guanidine. Optically active α-acyloxy carbonyl compounds were generated under mild reaction conditions in high yields (up to 99%) and good enantioselectivities (up to 97.5:2.5 er).



KEYWORDS: *asymmetric catalysis, rhodium, chiral guanidine, insertion, carboxylic acids*

Transition-metal-catalyzed asymmetric insertion of α-diazo compounds into O−H bond donors, such as alcohols, phenols, H_2O, and carboxylic acids is highly selective and synthetically useful for the synthesis of α-alkoxy, α-aryloxy, α-hydroxyl, or α-acyloxy carbonyl derivatives, respectively.[1] Chiral α-acyloxy carbonyl compounds were usually synthesized from chiral α-hydroxy carbonyl compounds, which, for example, can be obtained from copper- or iron-catalyzed O−H insertion of H_2O with α-diazocarbonyl compounds in excellent enantioselectivities.[1i,j] Additionally, asymmetric Passerini reaction[2] and carboxylation reaction[3] could provide access to α-acyloxy carbonyl compounds. The O−H insertion of carboxylic acids with α-diazocarbonyl compounds provides a direct and convenient alternative for the α-acyloxy carbonyl compounds synthesis. The racemic synthesis of α-acyloxy carbonyl compounds via O−H insertion of carboxylic acids with α-diazo compounds have been reported by several groups after the pioneering work of Wolfrom and co-workers in 1945.[4a] Metal salts, including cupric chloride,[4b] $Cu(acac)_2$,[4c] $Cu(OAc)_2$,[4g] $Rh_2(OAc)_4$,[4e] $Rh_2(esp)_2$,[4h] and $Pd(OAc)_2$,[4f] have been used. However, the asymmetric catalytic version of O−H insertion of carboxylic acids has not been addressed, which is quite different from the other O−H bond donors. The only asymmetric example of $Cu(acac)_2$-mediated carbenoid insertion into acetic acid and pivalic acid was exploited with the aid of a chiral auxiliary by Wang.[4d] The catalytic enantioselective O−H insertion of carboxylic acids is difficult, and one explanation could be that the acidity of carboxylic acids may compromise the stability of chiral metal complex and lead to dissociation, resulting in poor enantiocontrol.

A computational study from the Yu group suggests that a free-ylide pathway is favored in the neutral dirhodium(II) complex-catalyzed system in O−H insertion reaction, and water can act as an efficient proton-transport catalyst for the [1,2]-H shift.[5] These useful inferences have been demonstrated by cooperative catalysis in asymmetric N−H, C−H, and S−H insertions,[6] using chiral phosphoric acids or cinchona alkaloids as the chiral proton shutters. Taking inspiration from our recently developed asymmetric catalysis using chiral guanidines as organocatalysts and ligands,[7] we sought to extend the utility of chiral guanidine to the O−H insertion of carboxylic acids. We hypothesized that carboxylic acids could take precedence to react with basic guanidine over transition metal salt, forming chiral guanidinium salt, which can participate in an insertion reaction of Rh carbenoids, acting as a chiral proton-transport catalyst for the [1,2]-H shift. Herein, the first example of the catalytic enantioselective O−H insertion of α-diazoesters and α-diazoketones to carboxylic acids was reported. A catalytic system containing a simple chiral guanidine-amide and dirhodium(II) carboxylate was proven to be efficient, and various α-acyloxy carbonyl compounds were obtained with good enantioselectivities and yields under mild reaction conditions.

In the initial study, we conducted the reaction of ethyl α-diazo-α-phenylacetate (**2a**) with benzoic acid (**1a**) in chloroform at 0 °C, and a selection of chiral guanidine **G1** and Rh(II) salts were evaluated as the catalysts (Table 1, entries 1−4). In the presence of 2.5 mol % of $Rh_2(OAc)_4$, the O−H insertion product **3a** was formed in 51% yield and 87:13 er (entry 1). When $Rh_2(oct)_4$ and $Rh_2(TPA)_4$ were used, the reaction results were comparable (entries 3 and 4). $Rh_2(TFA)_4$, which has electron-deficient carboxylate ligands, slowed the reaction and lowered the enantioselectivity (entry 2). In an attempt to improve the enantioselectivity, the structures of chiral guanidines were varied (entries 5−12). Guanidine-amides **G2**−**G4**, which carried different amino acid backbones, were unfavorable in terms of er value (entries 5−7). The use of guanidine **G1** derived from L-proline and ether as the reaction solvent led to a slight improvement in the enantioselectivity (entry 8). The 2,6-diisopropylphenyl-substituted **G8** was nearly

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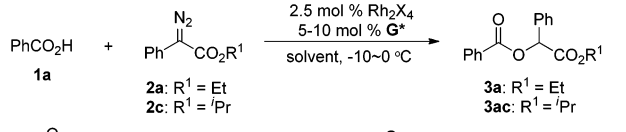
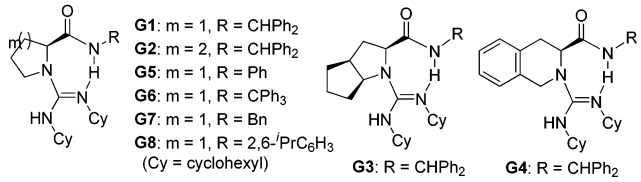
Table 1. Optimization of the Reaction Conditions[a]

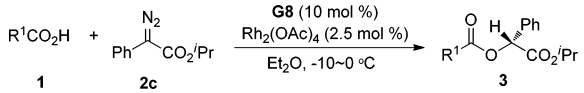




entry	Rh(II)	G*	solvent	yield (%)[b]	er[c]
1	$Rh_2(OAc)_4$	**G1**	$CHCl_3$	51	87:13
2[d]	$Rh_2(TFA)_4$	**G1**	$CHCl_3$	51	75.5:24.5
3	$Rh_2(oct)_4$	**G1**	$CHCl_3$	56	85:15
4	$Rh_2(TPA)_4$	**G1**	$CHCl_3$	51	86.5:13.5
5	$Rh_2(OAc)_4$	**G2**	$CHCl_3$	53	71:29
6	$Rh_2(OAc)_4$	**G3**	$CHCl_3$	35	62.5:37.5
7	$Rh_2(OAc)_4$	**G4**	$CHCl_3$	50	72.5:27.5
8	$Rh_2(OAc)_4$	**G1**	Et_2O	54	91:9
9	$Rh_2(OAc)_4$	**G5**	Et_2O	48	73:27
10	$Rh_2(OAc)_4$	**G6**	Et_2O	61	80:20
11	$Rh_2(OAc)_4$	**G7**	Et_2O	55	78:22
12	$Rh_2(OAc)_4$	**G8**	Et_2O	54	91.5:8.5
13[e]	$Rh_2(OAc)_4$	**G8**	Et_2O	66	92:8
14[e,f]	$Rh_2(OAc)_4$	**G8**	Et_2O	79	92.5:7.5
15[e,f,g]	$Rh_2(OAc)_4$	**G8**	Et_2O	72	94:6
16[e,f,h]	$Rh_2(OAc)_4$	**G8**	Et_2O	89	94:6

[a]Unless otherwise noted, all reactions were performed with Rh_2X_4 (2.5 mol %), **G*** (5 mol %), **1a** (0.1 mmol), and **2a** (1.0 equiv) in solvent (0.6 mL) at 0 °C for 3 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]The reaction time was 8 h. [e]$Rh_2(OAc)_4$ (2.5 mol %), **G8** (5 mol %) and **1a** (0.1 mmol) were stirred in THF (0.2 mL) at 30 °C for 0.5 h, then evaporated in vacuo and reacted with **2a** (1.0 equiv) in Et_2O (0.6 mL) at −10 °C for 2 h. [f]**G8** (10 mol %). [g]**2c** was used. [h]**2c** (1.4 equiv) was used.

Table 2. Scope of Carboxylic Acids[a]



entry	R^1	t (h)	yield (%)[b]	er[c]
1	C_6H_5	2	89 (**3ac**)	94:6
2	2-MeC_6H_4	2	99 (**3bc**)	93.5:6.5
3	2-FC_6H_4	2	78 (**3cc**)	95.5:4.5
4	2-ClC_6H_4	2	86 (**3dc**)	95:5
5	2-IC_6H_4	2	80 (**3ec**)	94.5:5.5
6[d]	3-MeC_6H_4	7	61 (**3fc**)	92.5:7.5
7	4-MeC_6H_4	2	95 (**3gc**)	94.5:5.5
8	4-$^tBuC_6H_4$	2	99 (**3hc**)	92.5:7.5
9	4-PhC_6H_4	2	75 (**3ic**)	94:6
10	1-naphthyl	2	96 (**3jc**)	93.5:6.5
11	2-thienyl	2	82 (**3kc**)	95.5:4.5
12		2	92 (**3lc**)	96:4
13		2	75 (**3mc**)	96.5:3.5
14		2	78 (**3nc**)	97:3 (*R*)
15		7	73 (**3oc**)	86.5:13.5
16	1-adamantyl	2	94 (**3pc**)	79:21

[a]Unless otherwise noted, all reactions were performed with $Rh_2(OAc)_4$ (2.5 mol %), **G8** (10 mol %), and **1** (0.1 mmol) stirred in THF (0.2 mL) at 30 °C for 0.5 h, then evaporated in vacuo and reacted with **2c** (1.4 equiv) in Et_2O (0.6 mL) at −10 °C. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]At 0 °C.

as effective as the chiral guanidine **G1** (entries 8 and 12). Changing the preparation procedure of the catalyst and lowering the reaction temperature, an improvement in yield and enantioselectivity was obtained (entry 13). Moreover, the best results for the product **3a** (79% yield, and 92.5:7.5 er) could be achieved by the use of 2.5 mol % of $Rh_2(OAc)_4$ and 10 mol % of **G8** (entry 14). The ester group of α-diazoesters influenced the reaction minimally (SI, Table S8), and the use of **2c** gave the product **3ac** in 89% yield and 94:6 er when its amount increased to 1.4 equiv (entries 15 and 16). Additionally, **G8**−$Rh_2(esp)_2$ exhibited high reactivity but with negative results for the desired product **3a** (49% yield, 85.5:14.5 er), and a certain amount of byproduct α-ketoester (ethyl 2-oxo-2-phenylacetate) was generated (see SI for details). In the absence of chiral guanidines, chiral dirhodium catalyst (Rh_2(5*S*-MEPY)$_4$) alone showed low activity with the generation of trace amount of the racemic product, and α-ketoester was detected as the main product (see SI for details).

Next, we investigated the scope of carboxylic acids (Table 2). Methyl-substituted benzoic acid at *meta*-position reduced the yield remarkably in comparison with those at *ortho*- or *para*-positions (entries 2, 6, and 7). 2-Halo-substituted benzoic acids undergo the reaction smoothly, and the desired products were given in moderate yields with slightly improved enantioselectivities (entries 3−5). A sterically hindered group at *para*-position and a substituent at *meta*-position had a minor impact on the enantioselectivity (entries 6 and 8). 1-Naphthoic acid (**1j**) was a suitable substrate for the reaction and afforded the corresponding product **3jc** in 96% yield and 93.5:6.5 er (entry 10). Thiophene-2-carboxylic acid and its derivatives reacted smoothly to generate the related insertion products **3kc**−**3nc** with satisfactory enantioselectivities and good yields (75−92% yields and 95.5:4.5−97:3 er; entries 11−14). The absolute configuration of **3nc** was determined to be *R* by X-ray crystallographic analysis,[8] and the others showed similar stereoarrangement from the CD spectra analysis (see SI for details). Additionally, cinnamic acid (**1o**) and aliphatic carboxylic acid (**1p**) can also undergo the O−H insertion reaction to form the products with moderate er values and good yields (entries 15 and 16).

Then, we continued to explore the substrate scope of α-diazoesters by using thiophene-2-carboxylic acid **1k** as the O−H bond donor (Table 3). Either electron-donating or electron-withdrawing substituents at varied position of α-phenyl rings affected the enantioselection, and the corresponding α-acyloxy esters were formed in 92:8−96.5:3.5 er and 71−94% yields (entries 1−13). The α-diazoester **2w** bearing 1-naphthyl substituent underwent the reaction efficiently, resulting in 77% yield and 95:5 er (entry 14). (*E*)-2-diazo-4-phenylbut-3-enoate was successfully employed in the reaction, albeit a

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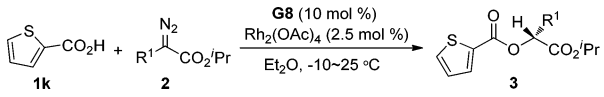
Table 3. Substrate Scope of α-Diazoesters[a]



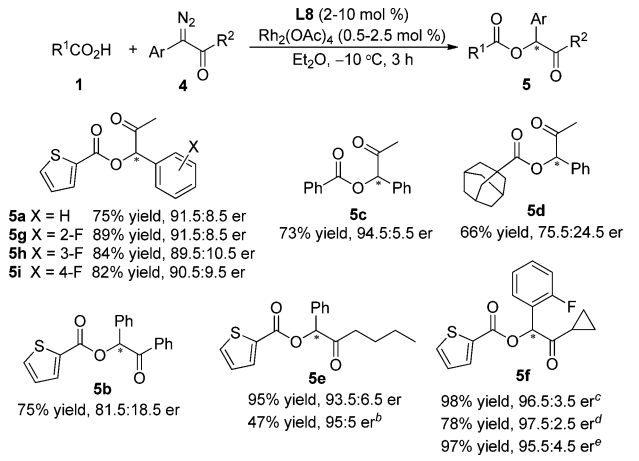
entry	R^1	T (°C)	t (h)	yield (%)[b]	er[c]
1	2-MeC_6H_4	0	3	88 (**3kk**)	94:6
2	2-$MeOC_6H_4$	−10	2	77 (**3kl**)	95:5
3	2-FC_6H_4	−10	1	94 (**3km**)	96:4
4[d]	2-FC_6H_4	−10	2	99 (**3km**)	95.5:4.5
5	2-ClC_6H_4	−10	2	84 (**3kn**)	96.5:3.5
6	2-BrC_6H_4	−10	2	86 (**3ko**)	96.5:3.5
7	2-IC_6H_4	−10	15	87 (**3kp**)	96.5:3.5
8	3-MeC_6H_4	0	3	71 (**3kq**)	94:6
9	4-MeC_6H_4	−10	2	82 (**3kr**)	96:4
10	4-PhC_6H_4	−10	2	79 (**3ks**)	94:6
11	4-FC_6H_4	−10	2	86 (**3kt**)	95:5
12	4-ClC_6H_4	−10	2	77 (**3ku**)	92:8
13	2,4-$F_2C_6H_3$	−10	2	86 (**3kv**)	96:4
14	1-naphthyl	−10	2	77 (**3kw**)	95:5
15	3-thienyl	−10	2	78 (**3kx**)	69.5:30.5
16		25	15	48 (**3ky**)	90:10
17	isobutyl	−10	2	65 (**3kz**)	67.5:32.5

[a]Unless otherwise noted, all reactions were performed with $Rh_2(OAc)_4$ (2.5 mol %), **G8** (10 mol %) and **1k** (0.1 mmol) in THF (0.2 mL) at 30 °C for 0.5 h, then evaporated in vacuo and reacted with **2** (1.4 equiv) in Et_2O (0.6 mL) at indicate temperature. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]$Rh_2(OAc)_4$ (1.25 mol %), **G8** (5 mol %), **1k** (4.0 mmol) and **2m** (5.6 mmol).

higher reaction temperature was required to achieve acceptable yield and enantioselectivity (entry 16). Meanwhile, α-diazoesters with 3-thienyl or isobutyl substituent performed smoothly with moderate enantioselectivities (entries 15 and 17). The reaction between carboxylic acid **1k** and α-diazoester **2m** was run on a gram scale in the presence of 1.25 mol % of $Rh_2(OAc)_4$ and 5 mol % of **G8**, and it performed well with 99% yield and 95.5:4.5 er (entry 4).

The chiral catalyst for the asymmetric O−H insertion of α-diazoesters can be applied without modification to the reaction of α-diazoketones. Compared with α-diazoesters, the use of α-diazoketones as carbene precursors for the X−H (X = O, B, N, etc.) insertion reaction is far less studied.[6d,9] As summarized in Scheme 1, O−H insertion of thiophene-2-carboxylic acid with α-diazoketone containing an acetyl substituent showed higher enantioselectivity than benzoyl-substituted one (**5a** vs **5b**). Fluoro-substituted 1-diazo-1-phenylpropan-2-ones afforded the desired products **5g**−**5i** in slightly higher yields and similar enantioselectivities. The O−H insertion of benzoic acid gave better results than adamantane-1-carboxylic acid (**5c** vs **5d**). Moreover, *n*-butyl and cyclopropyl-substituted α-diazoketones could perform the products **5e** and **5f** in good yields and excellent enantioselectivities, and up to 95:5 er (**5e**) and 97.5:2.5 er (**5f**) could be given when the reaction temperature dropped. Notably, the O−H insertion of cyclopropyl-substituted α-diazoketone could proceed efficiently even at

Scheme 1. Substrate Scope of Asymmetric O−H Insertion of α-Diazoketones with Carboxylic Acids[a]

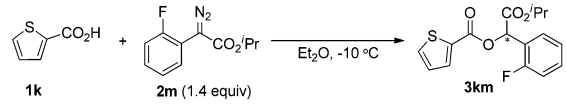


[a]Unless otherwise noted, all reactions were performed with $Rh_2(OAc)_4$ (2.5 mol %), **G8** (10 mol %) and **1** (0.1 mmol) in THF (0.2 mL) at 30 °C for 0.5 h, then evaporated in vacuo and reacted with **4** (1.4 equiv) in Et_2O (0.6 mL) at −10 °C for 3 h. [b]At −30 °C for 23 h. [c]At −30 °C for 3 h. [d]At −50 °C for 27 h. [e]$Rh_2(OAc)_4$ (0.5 mol %) and **G8** (2 mol %) at −10 °C for 9 h.

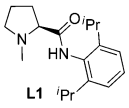
0.5 mol % of $Rh_2(OAc)_4$ and 2.0 mol % of guanidine **G8**, affording **5f** in 97% yield and 95.5:4.5 er.

In order to gain insight into the mechanism, some additional experiments were carried out. First, we investigated the effect of guanidine on the reactions between α-diazoester **2m** and acid **1k** (Scheme 2). With 2.5 mol % of $Rh_2(OAc)_4$, a 99% yield of

Scheme 2. Control Experiments for Mechanism Study



Conditions	yield	er
$Rh_2(OAc)_4$ (2.5 mol %), 1 h	99%	50:50
$Rh_2(OAc)_4$ (2.5 mol %), **L1** (10 mol %), 15.5 h	91%	47:53
$Rh_2(OAc)_4$ (2.5 mol %), cinchonine (10 mol %), 12 h, rt	18%	79:21
$Rh_2(OAc)_4$ (0.5 mol %), **G8** (2 mol %), 3 h	99%	95:5
$Rh_2(OAc)_4$ (0.5 mol %), **G8** (10 mol %), 3 h	84%	96:4
$Rh_2(OAc)_4$ (0.5 mol %), **G8** (20 mol %), 3 h	72%	96:4



the racemic product **3km** was found within 1 h. Using amino amide **L1** as the chiral source instead of guanidine **G8** resulted in a 91% yield but with dramatically decreased enantioselectivity after a longer reaction time. It indicates the chiral guanidine benefits the proton transfer process in an enantioselective manner. Using cinchonine as the chiral proton-transfer shuttle instead resulted in a dramatically reduced yield (18%) with moderate er (79:21 er) even at improved reaction temperature. Moreover, by using 0.5 mol % of $Rh_2(OAc)_4$ and 2.0 mol % of guanidine **G8**, a complete conversion to the O−H insertion product was given, whereas the yields dropped gradually, and the enantioselectivity was maintained if the amount of guanidine **G8** increased. It is consistent with our hypothesis that carboxylic acid will tightly interact with guanidine to generate guanidinium salt, and it could not easily disassociate to participate in the O−H insertion reaction. The interaction among guanidine, carboxylic acid, and $Rh_2(OAc)_4$ was further detected by CD and NMR

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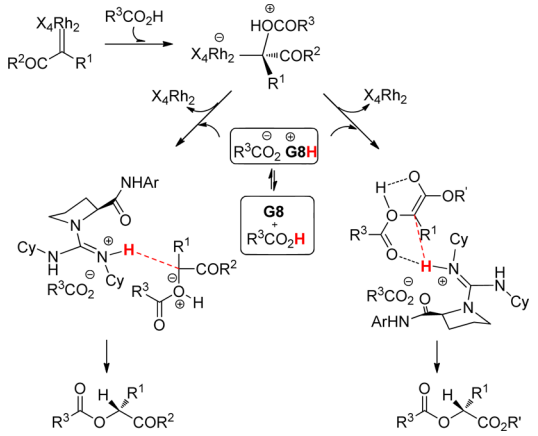
studies (see SI for details). The phenomena indicate negligible interaction between $Rh_2(OAc)_4$ and guanidine but strong interaction between guanidine and carboxylic acid.

On the basis of the aforementioned results and previous reports,[5,6,10] a plausible cooperative catalysis mechanism of the asymmetric O−H insertion of carboxylic acid is proposed (Scheme 3). Dinitrogen is extruded from α-diazo carbonyl compounds, generating a metallo-carbene intermediate. Subsequent nucleophilic attack by free carboxylic acid gives free oxonium ylide intermediates. On the other hand, the chiral guanidinium carboxylate generates in situ from guanidine **G8** and the acid. Lastly, the pathway that involves chiral guanidinium salt assisted proton transfer to an enol intermediate or oxonium ylide affords enantiomerically enriched α-acyloxy ester or ketone, respectively.

Scheme 3. Proposed Reaction Mechanism



In summary, the first catalytic asymmetric O−H insertion of carboxylic acids with α-diazo carbonyl compounds was achieved under mild conditions. Dirhodium(II) complex with chiral guanidine-amide was proved to be efficient cooperative catalysts. Various α-acyloxy esters and ketones were obtained in good enantioselectivities and yields. Additional studies directed at expanding the application of chiral guanidine and mechanism are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02184.

Experimental details, analytic data (NMR, HPLC, CD, and ESI-HRMS) (PDF)

X-ray data (CIF)

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Notes

The authors declare no competing financial interest.

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(8) CCDC 1403604 (**3nc**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge

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