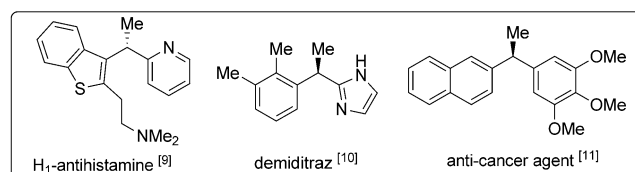
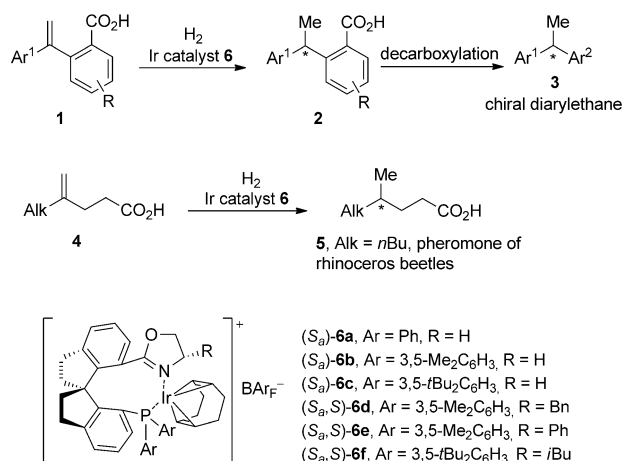


Carboxy-Directed Asymmetric Hydrogenation of 1,1-Diarylethenes and 1,1-Dialkylethenes**

Song Song, Shou-Fei Zhu, Yan-Bo Yu, and Qi-Lin Zhou*

Owing to high atom economy, chemoselectivity, and stereo-selectivity, the transition-metal-catalyzed asymmetric hydrogenation of C=C bonds has become one of the most reliable methods for the preparation of optically active compounds both in academia and in industry.^[1] In the asymmetric hydrogenation of a double bond, chiral induction arises from catalyst differentiation of the prochiral faces of the bond. The *Re* and *Si* faces are much easier to differentiate if the substituents are very different in size, as is the case for 1-aryl-1-alkyl ethenes, and high enantioselectivities can be achieved.^[2] In sharp contrast, differentiation of the *Re*- and *Si*-faces is difficult if the substituents are very similar in size, as is the case for 1,1-diarylethenes and 1,1-dialkylethenes, and enantioselectivities with such substrates are low. In the hydrogenation of 1,1-diarylethenes, high enantioselectivities have been achieved only when one of the aryl groups has an *ortho*-substituent.^[2,f,g,3] In the asymmetric hydrogenation of 1,1-dialkylethenes, the highest enantioselectivity reported to date is only 41% *ee*.^[4] Therefore, it is highly desirable to develop a new strategy to realize the asymmetric hydrogenation of 1,1-diarylethenes and 1,1-dialkylethenes, because the products of this reaction, diaryl and dialkylethanes, are very useful in the synthesis of biologically active compounds.

Recently, we developed highly efficient chiral iridium catalysts bearing spiro phosphine–oxazoline ligands for the asymmetric hydrogenation of α,β -unsaturated^[5] and β,γ -unsaturated carboxylic acids.^[6] The carboxy group of the unsaturated acids anchors the catalyst and directs the hydrogenation of the double bond.^[5a] This finding encouraged us to study the carboxy group as a directing group^[7] for the asymmetric hydrogenation of 1,1-diarylethenes and 1,1-dialkylethenes. Herein, we report the highly enantioselective iridium-catalyzed hydrogenation of 1,1-diarylethenes **1**^[8] and 1,1-dialkylethenes **4** directed by a carboxy group. When used in combination with a convenient decarboxylation, the hydrogenation of **1** provides an effective method for the construction of chiral diarylethanes **3**, which are core structures for many biologically active compounds, such as sleep-inducing H₁-antihistamines,^[9] the antiparasitic agent demiditraz,^[10] and anticancer agents.^[11] The hydrogenation of



Scheme 1. Carboxy-directed asymmetric hydrogenation of 1,1-diarylethenes and 1,1-dialkylethenes catalyzed by chiral iridium phosphine–oxazoline complexes. BARF[−] = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

4 provides an efficient method for preparing chiral γ -methyl fatty acids **5**, which are important intermediates for natural products such as the pheromone of rhinoceros beetles (Scheme 1).^[12]

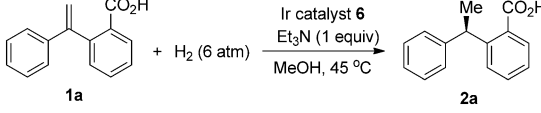
Substrates **1** and **4** were easily prepared by Wittig olefination of the corresponding ketones (for details, see the Supporting Information). First, we chose 2-(1-phenylvinyl)-benzoic acid (**1a**) as a model substrate to evaluate various chiral iridium/spiro phosphine–oxazoline catalysts **6**^[13] for the carboxy-directed asymmetric hydrogenation (Scheme 1). Catalyst (S_a) -**6a**, which has phenyl groups on the phosphorous atom and no substituent on the oxazoline ring, showed 100% conversion and afforded **2a** with 99% *ee* within 5 h (Table 1, entry 1). The substituents on the aryl groups of the phosphorous atom affected the reaction rate and enantioselectivity only slightly (entries 2 and 3 vs. entry 1). The use of catalyst (S_a) -**6b**, which has 3,5-dimethylphenyl groups on the phosphorous atom, decreased the reaction time from 5 to 4 h, but the enantioselectivity remained high (99% *ee*; entry 2). However, catalyst (S_a) -**6c**, which has bulkier 3,5-di-*tert*-butylphenyl groups on the phosphorous atom, required

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[**] We thank the National Natural Science Foundation of China, the National Basic Research Program of China (2011CB808600), and the Ministry of Education of China (B06005) for financial support.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201208606>.

Table 1: Comparison of catalysts for the carboxy-directed asymmetric hydrogenation of 1,1-diarylethenes.^[a]



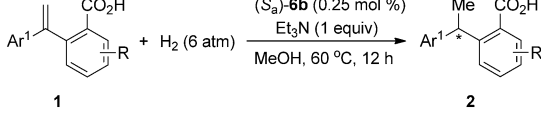
Entry	Catalyst	<i>t</i> [h]	Conv. [%] ^[b]	<i>ee</i> [%] ^[c]
1	(<i>S_a</i>)- 6a	5	100	99
2	(<i>S_a</i>)- 6b	4	100	99
3	(<i>S_a</i>)- 6c	10	100	97
4	(<i>S_a</i> , <i>S</i>)- 6d	4	100	95
5	(<i>S_a</i> , <i>R</i>)- 6d	20	71	91
6	(<i>S_a</i> , <i>S</i>)- 6e	20	55	51
7 ^[d]	(<i>S_a</i>)- 6b	20	28	–
8 ^[e]	(<i>S_a</i>)- 6b	4	100	98
9 ^[f]	(<i>S_a</i>)- 6b	6	100	96
10 ^[g]	(<i>S_a</i>)- 6b	20	< 5	–
11 ^[h]	(<i>S_a</i>)- 6b	6	100	98
12 ^[i]	(<i>S_a</i>)- 6b	20	100	98

[a] Reaction conditions: 0.5 mmol scale, [substrate] = 0.25 mol L^{−1}, substrate/catalyst = 200:1, H₂ (6 atm), Et₃N (1.0 equiv) as an additive. [b] Determined by ¹H NMR spectroscopy. [c] Determined by HPLC analysis on a chiral stationary phase. [d] At ambient hydrogen pressure. [e] H₂ (50 atm). [f] Na₂CO₃ (1.0 equiv) was used as base. [g] Without base. [h] substrate/catalyst = 400:1, 60 °C. [i] Substrate/catalyst = 1000:1, 70 °C.

a longer reaction time (10 h) and gave slightly lower enantioselectivity (97% *ee*; entry 3). We also studied the effect of the substituent on the oxazoline ring of the catalyst on the enantioselectivity of the reaction. Introduction of a benzyl group at the 4-position, (*S_a*,*S*)-**6d**, resulted in slightly lower enantioselectivity (95% *ee*; entry 4). When catalyst (*S_a*,*R*)-**6d**, a diastereoisomer of (*S_a*,*S*)-**6d**, was used, both the conversion and the enantioselectivity were reduced (to 71% and 91% *ee*, respectively; entry 5). This result demonstrates that the chirality in catalyst (*S_a*,*S*)-**6d** was matched for achieving high enantioselectivity in the hydrogenation of 1,1-diarylethenes. However, replacement of the benzyl group on the oxazoline ring with a phenyl group, (*S_a*,*S*)-**6e**, dramatically diminished the rate, conversion, and enantioselectivity of the reaction (entry 6). Experiments on hydrogen pressure showed that the reaction gave significantly lower conversion under ambient hydrogen pressure (entry 7). The catalyst has the same activity and slightly lower enantioselectivity under 50 atm of hydrogen (entry 8). The choice of the base also played an important role in the reaction. Et₃N provided the best results. An inorganic base, Na₂CO₃, gave a slightly reduced reaction rate and enantioselectivity (entry 9), whereas the conversion was less than 5% in the absence of base (entry 10). Catalyst (*S_a*)-**6b** was active enough that the reaction could be performed at a catalyst loading of 0.25 mol% at 60 °C (entry 11) or 0.1 mol% at 70 °C without any reduction in the enantioselectivity (entry 12).

Under the optimized reaction conditions, various 1,1-diarylethenes **1** bearing an *ortho*-carboxy group were hydrogenated (Table 2). The carboxy-directed asymmetric hydrogenation showed a wide substrate scope and a strong tolerance for various functional groups, including heterocycles such as furans and thiophenes. The substituents on the aryl rings of

Table 2: Substrate scope of the carboxy-directed asymmetric hydrogenation of 1,1-diarylethenes.^[a]



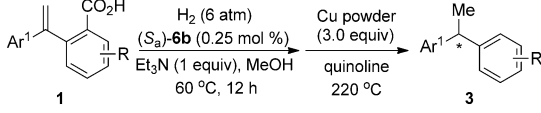
Entry	Ar ¹ ; R (1)	Product (2)	Yield [%]	<i>ee</i> [%]
1	C ₆ H ₅ ; H (1a)	2a	98	98 (R)
2	4-MeC ₆ H ₄ ; H (1b)	2b	97	98 (R)
3	4-MeOC ₆ H ₄ ; H (1c)	2c	96	98
4	4-ClC ₆ H ₄ ; H (1d)	2d	98	98 (R)
5	3,4-Me ₂ C ₆ H ₃ ; H (1e)	2e	97	97
6	3-BrC ₆ H ₄ ; H (1f)	2f	97	97
7	2,5-Me ₂ C ₆ H ₃ ; H (1g)	2g	97	99.6
8 ^[b]	2-naphthyl; H (1h)	2h	99	98 (R)
9 ^[c]	2-thiophenyl; H (1i)	2i	99	97
10 ^[c]	2-furanyl; H (1j)	2j	97	99
11	Ph; 4-Br (1k)	2k	98	96
12	Ph; 4-Me (1l)	2l	96	98
13	Ph; 5-Br (1m)	2m	99	96
14	Ph; 4,5-Cl ₂ (1n)	2n	97	97
15 ^[d]	Ph; 6-Me (1o)	2o	97	99.3
16	Ph; 4,5-(CH ₃) ₄ (1p)	2p	97	98 (R)

[a] Reaction conditions: 0.5 mmol scale, [substrate] = 0.25 mol L^{−1}, substrate/catalyst = 400:1, 60 °C, H₂ (6 atm), Et₃N (1.0 equiv) as an additive. Full conversion was obtained within 12 h. [b] (*S_a*)-**6b** (0.5 mol%) was used. [c] (*S_a*)-**6b** (1 mol%) was used. [d] (*S_a*)-**6c** (1 mol%) was used.

1,1-diarylethenes **1** had a negligible influence on the yield and enantioselectivity of the reaction: all of the tested substrates afforded essentially the same yields (96–99%) and enantioselectivities (96–99.6% *ee*; entries 1–16). The highest enantioselectivity was obtained in the hydrogenation of **1g** (99.6% *ee*; entry 7).

Because the carboxy group could be easily removed by decarboxylation, it could serve as a traceless directing group. The combination of copper-promoted decarboxylation and carboxy-directed asymmetric hydrogenation of 1,1-diarylethenes **1** allowed us to synthesize chiral diarylethanes **3** in one pot (Table 3). The methanol solvent was evaporated after the hydrogenation, and the residue was heated with copper

Table 3: One-pot preparation of chiral diarylethanes **3**.^[a]



Entry	Ar ¹ ; R (1)	Product (3)	Yield [%]	<i>ee</i> [%] ^[b]
1	4-MeC ₆ H ₄ ; H (1b)	3b	80	98 (S)
2	4-ClC ₆ H ₄ ; H (1d)	3d	81	98 (S)
3	2-naphthyl; H (1h)	3h	83	98 (S)
4	Ph; 4,5-(CH ₃) ₄ (1p)	3h	76	98 (R)
5	2-thiophenyl; H (1i)	3i	77	97 ^[c]

[a] The hydrogenation reactions were followed by copper-powder-promoted decarboxylation in a one-pot procedure (see the Supporting Information for details). [b] Determined by HPLC analysis on a chiral stationary phase, or supercritical fluid chromatography. [c] The *ee* shown is that of **2i**.

powder in quinoline at 220 °C for 3 h to produce **3** in good yields (76–83 %) with excellent enantioselectivities (97–98 % *ee*). It is remarkable that chiral diarylethanes with opposite configurations, for example, (*S*)-**3h** and (*R*)-**3h**, could be obtained from different substrates by means of this one-pot procedure (entries 3 and 4). Because chiral diarylethanes **3** are generally prepared by means of multistep transformations,^[14] the present one-pot procedure provides an efficient method for the synthesis of these bioactive compounds.

The carboxy-directing strategy can also be utilized in the asymmetric hydrogenation of 1,1-dialkylethenes **4**, which are even more difficult substrates and for which there are no highly enantioselective hydrogenation methods reported. In the hydrogenation of 1,1'-dialkylethenes, the iridium complex (*S_aS_a*)-**6f**, which bears an *iso*-butyl group on the oxazoline ring and 3,5-di-*tert*-butylphenyl groups on the phosphorous atom, was the most effective catalyst (for a comparison of catalysts, see the Supporting Information). By using catalyst (*S_aS_a*)-**6f** (1.5 mol % in MeOH under 6 atm of H₂ at 45 °C), various 1,1-dialkylethenes **4** were hydrogenated to the corresponding chiral γ -methyl fatty acids **5** in high yields (91–97 %) and high enantioselectivities (89–99 % *ee*; Table 4). This asymmetric

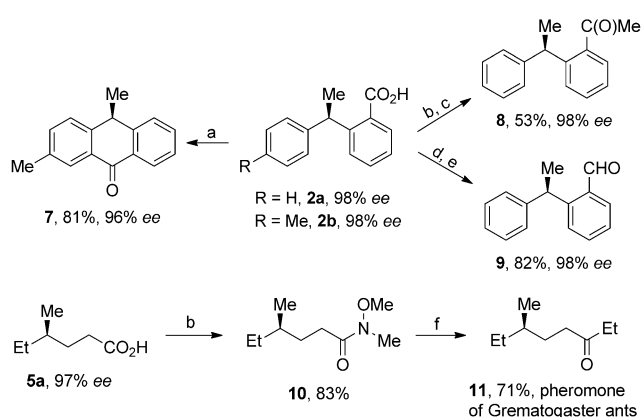
Table 4: Asymmetric hydrogenation of 1,1-dialkylethenes **4**.^[a]

$\text{R} \begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array} \text{CH}_2\text{CH}_2\text{CO}_2\text{H} \xrightarrow[\text{MeOH, 45 }^\circ\text{C, 20 h}]{\text{H}_2 \text{ (6 atm)} \atop (\text{S}_{\text{a}},\text{S}_{\text{a}})\text{-6f (1.5 mol \%)} \atop \text{Et}_3\text{N (1 equiv)}} \text{R} \begin{array}{c} \diagup \\ \text{CH}(\text{Me}) \\ \diagdown \end{array} \text{CH}_2\text{CH}_2\text{CO}_2\text{H}$				
Entry	R (4)	Product	Yield [%]	<i>ee</i> [%] ^[b]
1	Et (4a)	5a	97	97 (<i>R</i>)
2	<i>n</i> Bu (4b)	5b	96	96 (<i>R</i>)
3	<i>n</i> C ₆ H ₁₃ (4c)	5c	95	95 (<i>R</i>)
4	<i>n</i> C ₇ H ₁₅ (4d)	5d	96	96 (<i>R</i>)
5	<i>i</i> Pr (4e)	5e	95	99
6 ^[c]	<i>i</i> Bu (4f)	5f	94	89
7	PhCH ₂ CH ₂ (4g)	5g	97	94
8	MeO ₂ CCH ₂ CH ₂ (4h)	5h	91	97

[a] Reaction conditions: 0.5 mmol scale, [substrate] = 0.25 mol L⁻¹, (*S_aS_a*)-**6f** (1.5 mol %) as catalyst, H₂ (6 atm), NEt₃ (1.0 equiv) as an additive. Full conversions were obtained in all cases. [b] Determined by HPLC analysis of the corresponding anilide on a chiral stationary phase. [c] Using (*S_aS_a*)-**6f** (2 mol %) as catalyst.

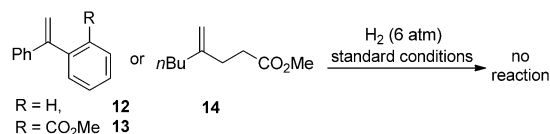
hydrogenation of 1,1-dialkylethenes **4** provides a new and short route to optically active γ -methyl chiral fatty acids.^[12] Product **5b**, (*R*)-4-methyloctanoic acid, is a pheromone for rhinoceros beetles.^[12a]

The carboxy group could also be conveniently converted to other functional groups (Scheme 2). For example, hydrogenation product **2b** was transformed into chiral anthrone **7** in 81 % yield with 96 % *ee* by means of a Friedel–Crafts acylation. Furthermore, chiral diarylethanes bearing an *ortho*-acetyl group (**8**) or an *ortho*-formyl group (**9**) were obtained from **2a** by means of simple transformations, with the complete preservation of enantiomeric purity. (*R*)-6-Methyl-3-octanone (**11**), a component of the alarm pheromone of *Grematogaster* ants,^[15] was synthesized in 59 % overall yield starting from acid **5a**.



Scheme 2. Transformations of hydrogenation products. a) Trifluoroacetic anhydride, CH₂Cl₂, 0 °C. b) *N,O*-dimethylhydroxylamine hydrochloride, (3-dimethylaminopropyl)ethyl-carbodiimide hydrochloride, 1-hydroxybenzotriazole, *i*Pr₂NEt, CH₂Cl₂, 0 °C. c) MeMgBr, THF, 0 °C. d) LiAlH₄, THF, 0 °C. e) Dess–Martin periodinane, CH₂Cl₂, 0 °C; f) EtMgBr, THF, 0 °C.

We performed additional experiments to investigate the role of the carboxy group in the reactions. When 1,1-diphenylethene **12** and esters **13** and **14** were subjected to the standard hydrogenation conditions, no reaction was observed (Scheme 3), thus showing that the carboxy group



Scheme 3. Substrate studies.

is indispensable. Moreover, the presence of a base was necessary for the hydrogenation of **1a** (Table 1, entry 10). The substrates *meta*-carboxy diphenylethene and *para*-carboxy diphenylethene could not be hydrogenated under the standard hydrogenation conditions. These experiments indicate that, upon interaction with a base, the carboxy group of the substrates acts as an anchor, coordinating with the iridium of the catalyst and endowing the catalyst with the ability to discriminate between the prochiral faces of the substrates and to catalyze their hydrogenation with high enantioselectivity.

In conclusion, we have developed a new strategy to realize the asymmetric hydrogenation of 1,1-diarylethenes and 1,1-dialkylethenes by using carboxy as a directing group. Under mild reaction conditions, a wide range of 1,1-diarylethenes and 1,1-dialkylethenes were hydrogenated to chiral 1,1-diarylethanes and chiral γ -methyl fatty acids with high enantioselectivities by chiral iridium/spiro phosphine–oxazoline catalysts. This carboxy-directing strategy should be applicable for the asymmetric hydrogenation of other substrate types.

Experimental Section

General hydrogenation procedure: A hydrogenation tube was charged with a stir bar, 1,1-diarylethene **1** (0.5 mmol), and catalyst (*S_a*)-**6b** (2.2 mg, 0.00125 mmol) in an argon-filled glove box. MeOH (2 mL) and Et₃N (51 mg, 0.5 mmol) were injected into the hydrogenation tube with a syringe while stirring. The hydrogenation tube was placed in an autoclave, which was purged five times with hydrogen gas. The autoclave was then charged with hydrogen gas to 6 atm, and the reaction mixture was stirred at 60 °C for 12 h before releasing the hydrogen. The reaction mixture was treated with 5 % aq. NaOH (10 mL). The aqueous layer was separated and washed with Et₂O (10 mL), acidified with HCl (3 M, pH 1), and extracted with Et₂O (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl, dried over MgSO₄, and evaporated in vacuo to give the hydrogenation product. The *ee* values of the products were determined by means of supercritical fluid chromatography or HPLC analysis on a chiral stationary phase.

Received: October 26, 2012

Published online: December 17, 2012

Keywords: asymmetric hydrogenation · chiral spiro ligands · diarylethanes · directing groups · iridium

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