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Ruthenium-catalysed synthesis of chiral exocyclic allylic alcohols *via* chemoselective transfer hydrogenation of 2-arylidene cycloalkanones†

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An exclusive asymmetric reduction of C═O bonds of 2-arylidene four-, five-, six-, and seven-membered cycloalkanones has been studied systematically. The asymmetric transfer hydrogenation was performed using a robust and commercially available chiral diamine-derived ruthenium complex as a catalyst and HCOOH/Et_3N as a hydrogen source under mild conditions, giving 51 examples of chiral exocyclic allylic alcohols in up to 96% yield and 99% ee. This method was also applicable to the gram-scale synthesis of the active intermediates of the anti-inflammatory loxoprofen and natural product (−)-goniomitine.

Introduction

Chiral allylic alcohols, particularly cyclic allylic alcohols, are important and versatile intermediates which can be readily converted into a variety of pharmaceuticals, agrochemicals and other biologically active molecules (Fig. 1).[1] As a result, much attention has been paid to developing efficient methods to access these compounds.[2] Although the asymmetric reduction of enones is one of the most straightforward methods for the preparation of chiral allylic alcohols, the competition between 1,2- and 1,4-reduction makes it challenging.[3] In 1995, the [$RuCl_2$(diphosphine)(diamine)] complex catalysed asymmetric hydrogenation of enones was pioneered by Noyori, which represents the most reliable approach to prepare chiral allylic alcohols.[4] Over the past two decades, a variety of acyclic and endocyclic enones have been hydrogenated with this type of catalyst, giving the corresponding chiral allylic alcohols with good chemoselectivities and enantioselectivities.[5] However, the asymmetric synthesis of chiral exocyclic allylic alcohols is still a challenging problem due to the twisting force of the ring. In 2010, Zhou developed an efficient asymmetric hydrogenation of 2-arylidene cycloalkanones to prepare chiral exocyclic allylic alcohols using an iridium/chiral spiro amino phosphine complex as a catalyst.[6] Since then, three analogues have been reported. One is catalysed by an iridium complex of the ferrocene-based chiral phosphine/oxazoline ligand.[7] The other two are catalysed by ruthenium complexes of chiral diphosphine/diamine[8] and diphosphine/oxazoline (Scheme 1a).[9] However, asymmetric hydrogenation requires air-sensitive phosphine ligands and high-pressure vessels. Thus, the development of mild and green methods for the asymmetric synthesis of chiral exocyclic allylic alcohols is yet to be explored.

Asymmetric transfer hydrogenation, featuring convenient operation and avoidance of dangerous hydrogen gas, is regarded as a green alternative to hydrogenation.[10] Since the distinguished chiral monosulfonyl diamine ruthenium complexes were developed by Noyori for the asymmetric transfer hydrogenation of ketones,[11] various analogous ruthenium, rhodium, and iridium complexes have been developed for the asymmetric transfer hydrogenation of ketones.[12] Very interestingly, this type of catalyst is exclusive for the reduction of C═O bonds and is tolerant to C═C bonds.[13] In recent years, our group has made some progress in the synthesis of various functionalized chiral alcohols through asymmetric transfer hydrogenation.[14] For example, a variety of 1-cycloalkyl chiral

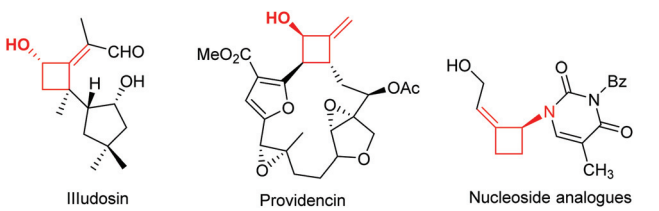

Fig. 1 Representative bioactive compounds bearing chiral cyclic allylic alcohols and their derivatives.

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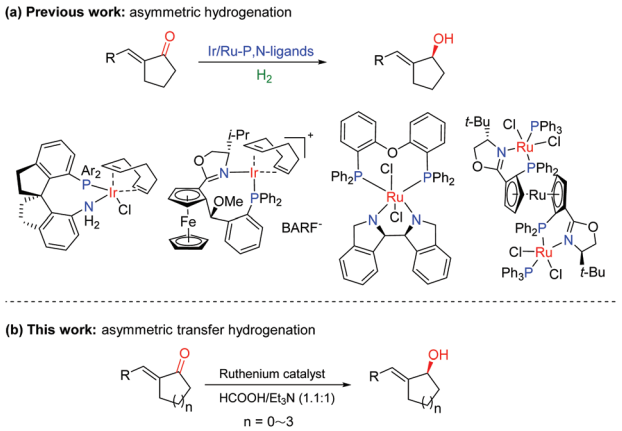


Scheme 1 Asymmetric synthesis of exocyclic allylic alcohols *via* hydrogenation and transfer hydrogenation.

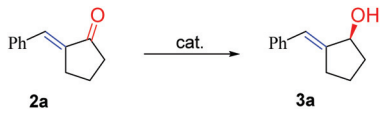
allylic alcohols were prepared by a selective asymmetric transfer hydrogenation of cycloalkyl vinyl ketones.[15] In order to study the chemoselective asymmetric transfer hydrogenation of C═O and C═C bonds deeply, we report an exclusive asymmetric transfer hydrogenation of C═O bonds of 2-arylidene four-, five-, six-, and seven-membered cycloalkanones to prepare chiral exocyclic allylic alcohols systematically, using an air- and moisture-stable and commercially available catalyst under very mild conditions (Scheme 1b).

Results and discussion

Initially, the asymmetric transfer hydrogenation of (*E*)-2-benzylidenecyclopentanone (**2a**) was conducted with an oxo-tethered chiral diamine ruthenium complex (*S*,*S*)-**1a** as a catalyst and HCOOH–NEt_3 (molar ratio = 1.1/1) as a hydrogen source at 35 °C for 6 hours in dichloromethane. To our delight, it was found that the C═O bond was reduced exclusively, affording exocyclic allylic alcohol **3a** in 69% yield and 98% ee (Table 1, entry 1). Under the identical reaction conditions, a survey of different chiral monosulfonyl diamine ruthenium complexes **1b–1f**, rhodium complex **1j**, and iridium complex **1k** indicated that (*S*,*S*)-**1f** was the best one with respect to yields and enantioselectivities (Table 1, entries 2–6, 10, and 11). It was reported that the counter anion effect plays an important role in the reactivities and enantioselectivities.[16] Therefore, the anion effect of ruthenium complexes was also evaluated with (*S*,*S*)-**1g**, (*S*,*S*)-**1h** and (*S*,*S*)-**1i**, but no positive effect was observed (Table 1, entries 7–9). Next, other hydrogen sources like HCOOH–NEt_3 (molar ratio = 5/2) and HCOONa were attempted, providing comparable or inferior results (Table 1, entries 12 and 13). The screening of solvents showed that chloroform ($CHCl_3$) was the best one among dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), toluene, water, methanol, ethanol, trifluoroethanol, and *N*,*N*-dimethylformamide (DMF) (Table 1, entries 6 and 13–19). A lower yield was obtained when the catalyst loading was decreased to 1 mol% (Table 1, entry 20). The yield decreased to 65% at 25 °C (Table 1, entry 21). When the reaction temperature was increased to 60 °C, a slightly increased yield of 89% was obtained with a lower ee value of 93% (Table 1, entry 22). Finally, the optimized reaction conditions were determined as follows: 2 mol% of (*S*,*S*)-**1f** as a catalyst, HCOOH–NEt_3 (molar ratio = 1.1/1) as a hydrogen source, 1 mL of $CHCl_3$ as a solvent, 35 °C, 6 h (Table 1, entry 19).

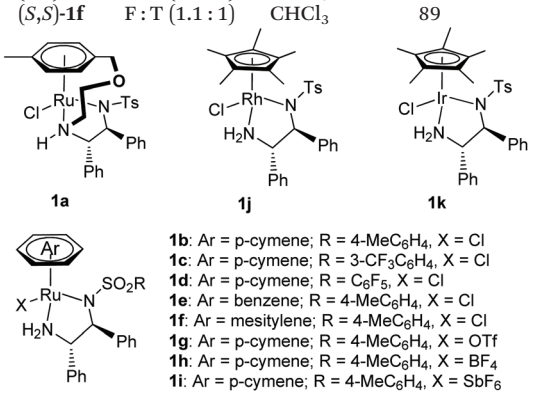
Under the optimized reaction conditions, the scope of 2-arylidene cyclopentanones was investigated (Scheme 2). In general, the electron-donating or electron-withdrawing substituent on the phenyl ring of the substrates had no effect on the enantioselectivities but a slight effect on the reactivities. For example, irrespective of the substituents like F, Cl, Br, Me,

Table 1 Optimization of the reaction conditions[a]

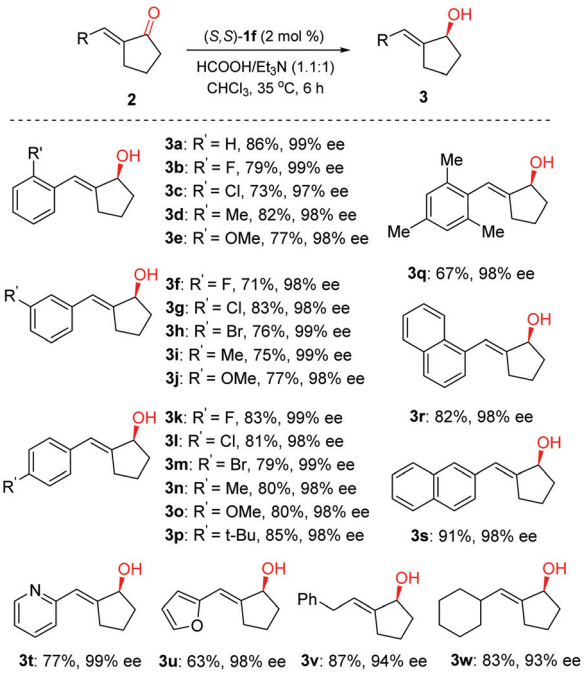


2a **3a**

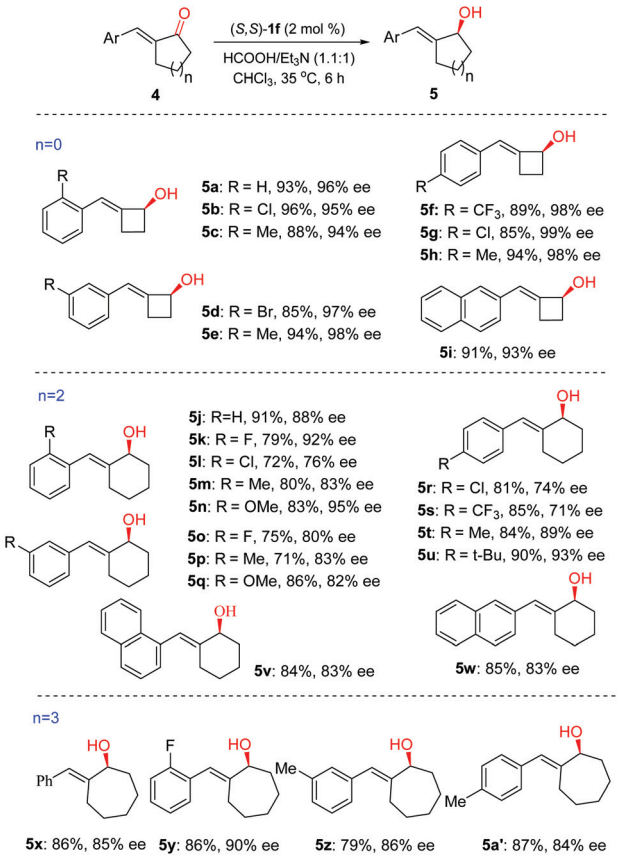
Entry	Cat.	[H] source[b]	Solvent (v/v)	Yield (%)	ee (%)
1	(*S*,*S*)-**1a**	F : T (1.1 : 1)	CH_2Cl_2	69	98
2	(*S*,*S*)-**1b**	F : T (1.1 : 1)	CH_2Cl_2	77	93
3	(*S*,*S*)-**1c**	F : T (1.1 : 1)	CH_2Cl_2	60	83
4	(*S*,*S*)-**1d**	F : T (1.1 : 1)	CH_2Cl_2	57	94
5	(*S*,*S*)-**1e**	F : T (1.1 : 1)	CH_2Cl_2	66	77
6	(*S*,*S*)-**1f**	F : T (1.1 : 1)	CH_2Cl_2	75	98
7	(*S*,*S*)-**1g**	F : T (1.1 : 1)	CH_2Cl_2	68	89
8	(*S*,*S*)-**1h**	F : T (1.1 : 1)	CH_2Cl_2	62	91
9	(*S*,*S*)-**1i**	F : T (1.1 : 1)	CH_2Cl_2	66	90
10	(*S*,*S*)-**1j**	F : T (1.1 : 1)	CH_2Cl_2	63	96
11	(*S*,*S*)-**1k**	F : T (1.1 : 1)	CH_2Cl_2	66	65
12	(*S*,*S*)-**1f**	F : T (5 : 2)	CH_2Cl_2	64	98
13	(*S*,*S*)-**1f**	HCOONa	H_2O	51	96
14	(*S*,*S*)-**1f**	F : T (1.1 : 1)	Toluene	66	93
15	(*S*,*S*)-**1f**	F : T (1.1 : 1)	MeOH	70	98
16	(*S*,*S*)-**1f**	F : T (1.1 : 1)	EtOH	61	96
17	(*S*,*S*)-**1f**	F : T (1.1 : 1)	CF_3CH_2OH	71	91
18	(*S*,*S*)-**1f**	F : T (1.1 : 1)	DMF	62	97
19	(*S*,*S*)-**1f**	F : T (1.1 : 1)	$CHCl_3$	86	99
20[c]	(*S*,*S*)-**1f**	F : T (1.1 : 1)	$CHCl_3$	71	99
21[d]	(*S*,*S*)-**1f**	F : T (1.1 : 1)	$CHCl_3$	65	99
22[e]	(*S*,*S*)-**1f**	F : T (1.1 : 1)	$CHCl_3$	89	93



[a] Reaction conditions: (*E*)-2-Benzylidenecyclopentanone (**2a**; 0.2 mmol), 2 mol% catalyst, 1 mL of solvent, 35 °C, 6 h; isolated yield. The ee values were determined by HPLC analysis. [b] F : T = HCOOH : NEt_3; the data in the parentheses are the molar ratios. [c] 1 mol% catalyst was used. [d] 25 °C. [e] 60 °C.



Scheme 2 Scope of 2-arylidene cyclopentanones. Reaction conditions: 2-Arylidene cyclopentanone **2** (0.2 mmol), (*S*,*S*)-**1f** (2 mol%), HCOOH/NEt_3 (molar ratio = 1.1 : 1, 5 equiv.), 35 °C, 6 h; isolated yield. The ee values were determined by HPLC analysis.



Scheme 3 Scope of 4-, 6-, and 7-membered cycloalkanones. Reaction conditions: 2-Arylidene cycloalkanone **4** (0.2 mmol), (*S*,*S*)-**1f** (2 mol%), HCOOH/NEt_3 (molar ratio = 1.1 : 1, 5 equiv.), 35 °C, 6 h; isolated yield. The ee values were determined by HPLC analysis.

OMe, or *t*Bu at the *ortho*-, *meta*-, or *para*-position of the benzene ring, the corresponding chiral exoallylic alcohols **3a–3p** were obtained in above 97% ee and 71–86% yields. The trimethyl substituted cyclopentanone **2q** gave 67% yield and 98% ee. Additionally, 2-naphthylidene cyclopentanones **2r** and **2s** also provided the corresponding products **3r** and **3s** in 98% ee. Pleasingly, excellent catalytic behaviours were also observed for heterocyclic substrates like 2-pyridylidene cyclopentanone (**2t**) and 2-furylidene cyclopentanone (**2u**), affording chiral 2-heteroarylidene cyclopentanols **3t** and **3u** in more than 98% ee. Furthermore, the aryl substituent can be replaced by alkyl groups, such as benzyl and cyclohexyl group, to afford the desired products 2-benzylidene cyclopentanol (**3v**) and 2-cyclohexylidene cyclopentanol (**3w**) in 94% and 93% ee, respectively.

Encouraged by the good results of the chemoselective asymmetric transfer hydrogenation of 2-arylidene cyclopentanones, we explored the reaction of four-, six- and seven-membered cycloalkanone substrates, as shown in Scheme 3. It was found that the size of the cycloalkyl group had an effect on the enantioselectivities of the products. First, the four-membered 2-arylidene cyclobutanones **4a–4h** with different substituents (Me, Cl, Br, and CF_3) at the *ortho*-, *meta*-, or *para*-position of the phenyl rings were examined. Electronic properties had no apparent effect on the reaction, and 85–96% yields and 94–99% ee were observed. When the phenyl ring was replaced by naphthalene, 91% yield and 93% ee were also obtained for **5i**. Next, the six-membered 2-arylidene cyclohexanones **4j–4u** were investigated. The substrates with electron-donating groups provided higher enantioselectivities than those with electron-withdrawing ones. For example, the electron-rich **5n** (OMe) was obtained in 95% ee. In contrast, the electron-deficient **5s** (CF_3) was obtained in 71% ee. The substituents at different positions of the phenyl ring had no apparent effect on the reactivities and enantioselectivities. For example, the *ortho*-substituted **4m** and the *meta*-substituted **4p** provided the same ee value of 83%. 2-Naphthylidene cyclohexanones **4v** and **4w** also gave the desired products **5v** and **5w** with 83% ee. Moreover, this asymmetric transfer hydrogenation was also amenable for seven-membered 2-arylidene cycloheptanones **4x–4a′**. The desired chiral exoallylic alcohols **5x–5a′** were obtained in 79–87% yields and 84–90% ee.

To examine the utility of this asymmetric transfer hydrogenation, a gram-scale reaction of **2m** (1.25 g) was carried out with 1 mol% of (*S*,*S*)-**1f** at 35 °C for 24 h. To our delight, product **3m**, a key intermediate in the preparation of the active form of the anti-inflammatory loxoprofen, was isolated in 81% yield (1.1 g) and 90% ee. After recrystallization, the ee value was increased to 99% (Fig. 2). Additionally, a gram-scale asymmetric transfer hydrogenation of compound **6** (1.61 g) was conducted with 1 mol% of (*S*,*S*)-**1f** at 40 °C for 24 h. The *cis*

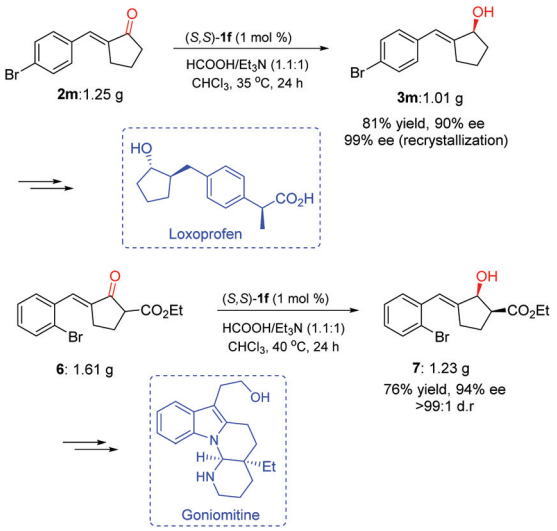


Fig. 2 Gram scale synthesis.

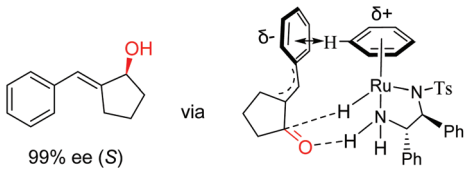


Fig. 3 A mode of ATH of 2-arylidene cyclopentanone: the CH/π interaction.

product 7 was obtained in 76% yield (1.23 g), 94% ee and >99 : 1 dr, which is a key intermediate for the synthesis of the natural product goniomitine.[17]

Based on the experimental results and reported putative outer sphere mechanism for the reduction of aryl ketones,[18] we propose that the enantioselectivity originates from the CH/π interaction between the C–H bond of the η^6-arene ligand and the π bond of the benzyl ring or the C=C bond (2v, 3w), affording the chiral exocyclic alcohol with an *S* configuration[19] (Fig. 3).

Conclusions

In summary, we have developed a chemoselective asymmetric transfer hydrogenation of 2-arylidene four-, five-, six-, and seven-membered cycloalkanones with a commercially available catalyst under mild conditions. The desired chiral exocyclic allylic alcohols were obtained in up to 99% ee and moderate to good yields. This reaction could also be performed on a gram-scale, and the resulting products can be used as intermediates for drugs and natural products. This asymmetric protocol provides an efficient and mild methodology for the synthesis of various chiral exocyclic allylic alcohols.

Experimental section

General information

Unless otherwise noted, all reagents, catalysts and solvents were purchased from commercial suppliers and used without further purification. Column chromatography was performed with silica gel. NMR spectra were recorded on a Bruker AVANCE III (400 MHz) spectrometer. $CDCl_3$ was used for NMR analysis with tetramethyl silane as the internal standard. Chemical shifts were observed up field to TMS (0.00 ppm) for ^{1}H NMR spectra and relative to $CDCl_3$ (77.0 ppm) for ^{13}C NMR spectra. HPLC analyses were conducted on a Waters 2489 Series instrument with chiral columns OJ-H and OD-H. Optical rotations were measured on an MCP-500 polarimeter. Melting points were determined using X-4 made by Peking Taike Apparatus Co., Ltd. HRMS spectra were recorded using an Agilent 6540 ESI/TOF mass spectrometer.

General procedure for the asymmetric transfer hydrogenation of 2-arylidene cycloalkanones. In a 10 mL Schlenk tube, formic acid (1.1 mmol, 42 μL), triethylamine (1.0 mmol, 139 μL), and 1.0 mL of $CHCl_3$ were added. After stirring the mixture for 1 h, (*S*,*S*)-**1f** (0.004 mmol, 2.49 mg) and 2-arylidene cycloalkanone (0.2 mmol) were added. Then, the mixture was stirred at 35 °C for 6 h. The solvent was removed under reduced pressure. Saturated sodium bicarbonate (5 mL) was added and extracted 3 times with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was further purified using a silica gel column to give the desired 2-arylidene cycloalkanol.

Gram-scale synthesis of compound 3m

In a 30 mL Schlenk tube, formic acid (5.5 mmol, 208 μL), triethylamine (5.0 mmol, 695 μL), and 10 mL of $CHCl_3$ were added. After stirring the mixture for 1 h, (*S*,*S*)-**1f** (0.025 mmol, 6.2 mg) and compound **2m** (1.25 g, 5 mmol) were added. Then, the mixture was stirred at 35 °C for 24 h. The solvent was removed under reduced pressure. Then, saturated sodium bicarbonate (5 mL) was added and extracted 3 times with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was further purified using a silica gel column to give compound **3m** (1.01 g, 81% yield, and 90% ee). The ee value was improved to 99% by recrystallization from ethyl acetate/petroleum ether.

Gram-scale synthesis of compound 7

In a 30 mL Schlenk tube, formic acid (5.5 mmol, 208 μL), triethylamine (5.0 mmol, 695 μL), and 10 mL of $CHCl_3$ were added. After stirring the mixture for 1 h, (*S*,*S*)-**1f** (0.025 mmol, 6.2 mg) and compound **6** (1.61 g, 5 mmol) were added. Then, the mixture was stirred at 40 °C for 24 h. The solvent was removed under reduced pressure. Saturated sodium bicarbonate (5 mL) was added and extracted 3 times with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was further purified using a silica gel column to give compound **7** (1.23 g, 76% yield, and 94% ee).

Conflicts of interest

There are no conflicts to declare.

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