Asymmetric Catalysis

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Asymmetric Dehydrative Cyclization of ω-Hydroxy Allyl Alcohols Catalyzed by Ruthenium Complexes**

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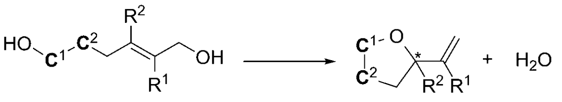
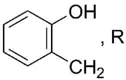
Chiral cyclic ethers constitute one of the most important structural units in biologically active compounds such as polycyclic ethers, polyether antibiotics, acetogenins, as well as coumaran- and chromane-related natural products.[1] Among many key building blocks reported so far, α-alkenyl-substituted cyclic ethers are widely recognized as the most useful because the alkenyl moiety can be transformed into a wide range of functionalities, thereby facilitating further elongation. The development of an efficient strategy for the construction of these cyclic ethers has attracted a great deal of attention over the last two decades. In particular, the focal point is the creation of catalytic enantioselective protocols, which have been categorized into three types: 1) Wacker-type oxidative cyclization of *ortho*-allyl- or homoallylphenol derivatives,[2] 2) Tsuji–Trost-type intramolecular allylation using ω-hydroxy allyl esters,[1c,f,3] and 3) hydroalkoxylation of alkynes[4] and allenes.[5] Herein, we report a new type of protocol, in which non-activated or non-protected diols **1** dehydratively cyclize into the corresponding cyclic ethers **2** with high regio- and enantioselectivity.

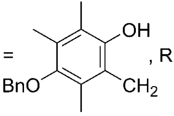
We have developed a new chiral ligand—R-naph-pyCOOH **4** [naph = naphthyl, py = pyridine, R = substituent (see structures)]—based on the knowledge that a catalytic system combining [CpRu(CH$_3$CN)$_3$]PF$_6$ (**3**; Cp = cyclopentadienyl)[6] with a pyridine-2-carboxylic acid derivative or the corresponding cationic CpRu^{IV}–π-allyl carboxylato complex can convert a 1:1 mixture of alcohols or allyl alcohols into allyl ethers with the liberation of water.[7] The ligand is characterized by the sterically flexible axial chirality through the C6–C1′ bond[8] and the adjustability of electronic and steric properties of the naphthalene ring by changing the R substituent at C2′. The allyl esters R-naph-pyCOOallyl (allyl = CH$_2$CH=CH$_2$) **5** were also target ligands because of the convenient formation of the CpRu^{IV}–π-allyl complex directly from **3**. A series of compounds **5a–c** were prepared in 44–64% yield from 2-bromo-3-methylpyridine through a Suzuki–Miyaura coupling between pyridine and naphthalene moieties, modified Reissert–Henze reaction, hydrolysis, and an allyl esterification sequence in combination with Murai–Chatani silylation of aromatic C–H bonds and chlorination or phenylation at C2′.[9] The enantiomers were separated by HPLC on a chiral stationary phase, and the absolute configurations were determined by single-crystal X-ray analysis of the ester of (1*R*,2*S*,5*R*)-menthol or the amide of (*R*)-1-phenylethylamine.[9]

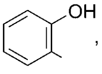


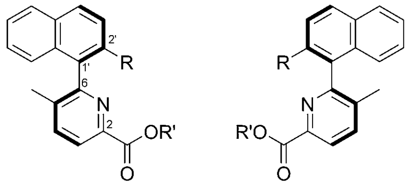
1 **2**

a: **C**^{1}–**C**^{2} = CH$_2$CH$_2$CH$_2$, R^1 = R^2 = H
b: **C**^{1}–**C**^{2} = CH$_2$CH$_2$, R^1 = R^2 = H
c: **C**^{1}–**C**^{2} = CH$_2$CH$_2$CH$_2$CH$_2$, R^1 = R^2 = H
d: **C**^{1}–**C**^{2} = CH$_2$CH$_2$CH$_2$, R^1 = CH$_3$, R^2 = H
e: **C**^{1}–**C**^{2} = CH$_2$CH$_2$, R^1 = CH$_3$, R^2 = H
f: **C**^{1}–**C**^{2} = CH$_2$CH$_2$CH$_2$, R^1 = C$_2$H$_5$, R^2 = H
g: **C**^{1}–**C**^{2} = CH$_2$CH$_2$CH$_2$, R^1 = *n*C$_5$H$_{11}$, R^2 = H
h: **C**^{1}–**C**^{2} = CH$_2$CH$_2$CH$_2$, R^1 = CH$_2$(*i*C$_3$H$_7$), R^2 = H
i: **C**^{1}–**C**^{2} = CH$_2$CH$_2$CH$_2$, R^1 = H, R^2 = CH$_3$
j: **C**^{1}–**C**^{2} = C(CH$_3$)$_2$CH$_2$CH$_2$, R^1 = R^2 = H

k: HO-**C**^{1}–**C**^{2} =  , R^1 = CH$_3$, R^2 = H

l: HO-**C**^{1}–**C**^{2} =  , R^1 = H, R^2 = CH$_3$

m: HO-**C**^{1}–**C**^{2} =  , R^1 = CH$_3$, R^2 = H



4: R′ = H
5: R′ = CH$_2$CH=CH$_2$

a: R = Cl
b: R = CH$_3$
c: R = C$_6$H$_5$

The effectiveness of R-naph-pyCOOH **4** and the allyl ester **5** in combination with **3** in the asymmetric dehydrative cyclization was investigated by use of **1a** (**C**^{1}–**C**^{2} = (CH$_2$)$_3$; R^1 = R^2 = H) under a standard set of reaction conditions ([**1a**] = 100 mM; [(*R*)-**4** or (*R*)-**5**] = [[CpRu(CH$_3$CN)$_3$]PF$_6$ (**3**)] = 1 mM; DMA; 100 °C; 1 h). The results are listed in

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Table 1. The ligand (*R*)-Cl-naph-pyCOOH (*R*)-**4a** quantitatively afforded 2-vinyltetrahydro-2*H*-pyran (**2a**) with an *S*/*R* enantiomeric ratio (e.r.) of 97:3 with 6-*exo*-trig selectivity (Table 1, entry 1). The reaction was completed within 10 minutes. The enantiomeric ligand (*S*)-**4a** gave a mixture (*S*/*R* = 3:97; Table 1, entry 2). (*R*)-Cl-naph-pyCOOallyl (*R*)-**5a** gave the same result as (*R*)-**4a** (Table 1, entry 3). Increasing the substrate concentration to 1 M had no effect on either the enantioselectivity or the reactivity (Table 1, entry 4). The substrate/catalyst (S/C) ratio was increased to 1000 without any adverse effects on the reaction outcome (Table 1, entries 5 and 6). The reaction proceeded even with an S/C ratio of 10000 or at lower temperatures, although more slowly (Table 1, entries 7–9). Aprotic solvents, such as DMF, THF, and CPME, were also tested and had no significant effect on the reaction outcome (Table 1, entries 10, 13, and 14). However, enantioselectivity decreased to some extent in acetone, dioxane, or dichloromethane (Table 1, entries 12, 15, and 16). The reactivity was appreciably decreased in toluene (Table 1, entry 17), and acetonitrile almost stopped the reaction (Table 1, entry 11). *tert*-Butyl alcohol or isopropyl alcohol were found to be the solvents of choice, although the e.r. was marginally decreased (Table 1, entries 18–20). In other protic solvents, such as ethanol, methanol, water, and acetic acid, the reaction proceeded but not with as high efficiency as *tert*-butyl alcohol (Table 1, entries 21–24). Replacement of the chloro group with a methyl group at C2′ of the ligand, however, resulted in a decrease in reactivity by two orders of magnitude (compare Table 1, entries 5 and 26). Moreover, there was also a reversal in the enantiofacial selectivity of the reaction when using (*R*)-Cl-naph-pyCOOallyl (**5a**; compare Table 1, entries 3 and 25).[10] Introduction of a phenyl group at C2′ (**5c**) further decreased the reactivity compared to **5b** (compare Table 1, entries 25 and 27). Use of a catalyst consisting of (*R*)-**5a** and [Cp*Ru(CH_3CN)$_3$]PF_6 (Cp* = pentamethylcyclopentadienyl) instead of **3** afforded little product **2a** under the standard reaction condition (0.1% after 10 min; 0.5% after 60 min).

Table 1: Enantioselective intramolecular dehydrative cyclization of (*E*)-hept-2-ene-1,7-diol ((*E*)-**1a**) to 2-vinyltetrahydro-2*H*-pyran (**2a**) using a catalytic system consisting of R-naph-pyCOOH **4** or its allyl ester **5** and [CpRu(CH_3CN)$_3$]PF_6 (**3**).[a]

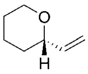
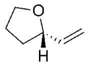
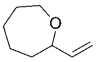
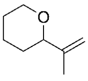
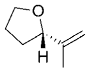
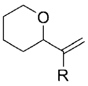
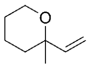
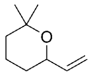
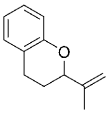
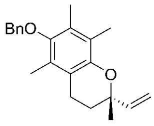
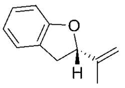
Entry	Conc. of substr. [mM]	Ligand (mM)	Solvent	Conv. [%][b]	e.r. (*S*/*R*)[c]
1	100	(*R*)-**4a** (1)	DMA	>99[d]	97:3
2	100	(*S*)-**4a** (1)	DMA	>99[d]	3:97
3	100	(*R*)-**5a** (1)	DMA	>99[d]	97:3
4	1000	(*R*)-**5a** (10)	DMA	>99	97:3
5	100	(*R*)-**5a** (0.1)	DMA	>99	97:3
6	1000	(*S*)-**5a** (1)	DMA	>99	3:97
7[e]	1000	(*R*)-**5a** (0.1)	DMA	30	97:3
8[f]	100	(*R*)-**5a** (1)	DMA	74[g]	97:3
9[h]	100	(*R*)-**5a** (1)	DMA	5[i]	96:4
10	100	(*R*)-**5a** (1)	DMF[j]	>99	97:3
11	100	(*R*)-**5a** (1)	CH_3CN	7	73:27
12	100	(*R*)-**5a** (1)	acetone	>99	80:20
13	100	(*R*)-**5a** (1)	THF	>99	95:5
14	100	(*R*)-**5a** (1)	CPME	>99	95:5
15	100	(*R*)-**5a** (1)	dioxane	>99	72:28
16	100	(*R*)-**5a** (1)	CH_2Cl_2	>99	81:19
17	100	(*R*)-**5a** (1)	toluene	78	87:13
18	100	(*R*)-**5a** (1)	*t*BuOH	>99	92:8
19	1000	(*R*)-**5a** (1)	*t*BuOH	>99	92:8
20	100	(*R*)-**5a** (1)	*i*PrOH	98	91:9
21	100	(*R*)-**5a** (1)	C_2H_5OH	92	85:15
22	100	(*R*)-**5a** (1)	CH_3OH	95	76:24
23	100	(*R*)-**5a** (1)	H_2O	>99	77:23
24	100	(*R*)-**5a** (1)	CH_3COOH	>99	65:35
25	100	(*S*)-**5b** (1)	DMA	70	9:91
26	100	(*S*)-**5b** (0.1)	DMA	3	–
27	100	(*S*)-**5c** (1)	DMA	3	–

[a] All reactions were carried out at 100 °C for 1 h using 1 mol of **3** for ligand **4** or **5**, unless otherwise specified.[9] [b] Determined by GC analysis (J&W Scientific DB-5).[9] The conversions are nearly identical to the yield of **2a**. [c] Determined by GC analysis on a chiral stationary phase (CHIRALDEX G-BP).[9] [d] The reaction was completed within 10 min. [e] 100 °C, 24 h. [f] 50 °C. [g] >99% conversion after 5 h. [h] 30 °C. [i] 83% conversion after 80 h. [j] Contamination by dimethylamine dramatically decreased the reactivity. Careful purification is essential. CPME = cyclopentyl methyl ether, DMA = *N*,*N*-dimethylacetamide, DMF = *N*,*N*-dimethylformamide, THF = tetrahydrofuran.

Table 2 shows the generality of the present asymmetric catalysis using a variety of *E*-configured ω-hydroxy allyl alcohols **1a**–**m**. Removal of one methylene unit from **1a** ($\mathbf{C^1}$–$\mathbf{C^2}$ = $(CH_2)_3$) to **1b** ($\mathbf{C^1}$–$\mathbf{C^2}$ = $(CH_2)_2$) gave 2-vinyltetrahydrofuran (**2b**) with an e.r. of *S*/*R* = 94:6, while an extra methylene unit **1c** ($\mathbf{C^1}$–$\mathbf{C^2}$ = $(CH_2)_4$) resulted in no production of oxepane derivative **2c** (Table 2, entries 1–3). Introduction of a methyl group at the β position of the allylic moiety of **1a** and **1b** exerted no negative influence on the reactivity or enantioselectivity (Table 2, entries 4 and 5). The β-methyl group of **1d** can be replaced with an ethyl, *n*-pentyl, or isobutyl group (Table 2, entries 6–8). γ-Disubstituted allyl alcohol **1i** can be also used as a substrate, thus constructing α-disubstituted cyclic ether **2i** with high stereocontrol at the *tert*-alkyl stereogenic carbon center having no proton (Table 2, entry 9). *tert*-Alkyl alcohol **1j** at the ω-hydroxy end of the molecule can be applied to this intramolecular cyclization and gave **2j** with an e.r. = 96:4 (Table 2, entry 10). A phenolic hydroxy group also quantitatively reacted and gave 2-propenyl substituted chromane **2k** (Table 2, entry 11). Cyclization of **1l** gave a key synthetic intermediate for vitamin E (Table 2, entry 12).[1c,3b] A coumaran derivative **2m** was quantitatively obtained with nearly perfect enantioselection when **1m** was used (Table 2, entry 13). This framework will be of interest in the synthesis of tremetone, fomannoxin, rotenone, and deoxypsorospermin.[1f]

The preliminary investigation on the ligand structure/reactivity/enantioselectivity relationship has clearly indicated that the existence of electron-withdrawing chloro group on the naphthalene ring of the ligand, and the sterically less congested Cp ring (rather than Cp*) on Ru are important for attaining high reactivity and selectivity. We speculate that a redox-mediated donor–acceptor bifunctional mechanism is operating[7,11] and that the chloro group is playing a key role in stabilizing a favorable transition state probably through a decrease in the LUMO level—thus facilitating a possible rate-determining Ru^{IV}/Ru^{II} step[11a]—and also through a CpH/Cl hydrogen bond.[12] Elucidation of the detailed mechanism is now an on-going project in our research group.

Table 2: Catalytic asymmetric cyclization of ω-hydroxy allyl alcohols **1** to give α-alkenyl cyclic ethers **2** using (*R*)-Cl-naph-pyCOOallyl [(*R*)-**5a**] and [CpRu($CH_3CN)_3]PF_6$ (**3**).[a]

Entry		Product	Yield [%][b]	e.r.[c]
1	**2a**		90[d]	97:3 (*S*/*R*)
2	**2b**		–[e]	94:6 (*S*/*R*)
3[f]	**2c**		–	–
4	**2d**		87	98:2
5	**2e**		–[e]	97:3 (*S*/*R*)
				
6	**2f**	R = C_2H_5	93[g]	98:2
7	**2g**	R = C_5H_{11}	98	98:2
8[h]	**2h**	R = *i*Bu	94	98:2
9[i]	**2i**		92[g]	96:4
10	**2j**		92[g]	96:4
11[j,k]	**2k**		98	97:3
12[j,l]	**2l**		97	97:3 (*S*/*R*)
13[j,k]	**2m**		98	>99:1 (*S*/*R*)

[a] All reactions were carried out under the standard reaction conditions (1 mmol scale, [**1**] = 100 mM; [**3**] = [(*R*)-**5a**] = 1 mM; DMA; 100 °C; 1 h) unless otherwise specified. In all cases, the conversions were >99 %. The absolute configurations were determined for **2a**, **2b**, **2e**, **2l**, and **2m**.[9] [b] Yield of isolated product. Extraction carried out using pentane/diethyl ether. [c] Determined by GC analysis using a chiral stationary phase.[9] [d] 10 g reaction scale (73.8 mmol, [**1a**] = 1000 mM; [**3**] = [(*R*)-**5a**] = 1 mM; DMA). Yield of isolated product after distillation. [e] ^{1}H NMR experiment in [D$_7$]DMF. The conversion was >99 %. [f] Undetermined products such as oligomers were formed, but not **2c**. [g] Yield after taking into consideration of the amount of the contaminated pentane/diethyl ether. [h] 3 h. [i] 70 °C, 10 h. The diene-like products were produced at 100 °C for 1 h. [j] A 10:1 tC_4H_9OH/DMA mixture was used as the solvent. [k] The diene-like products were produced only in DMA. [l] 24 h. Bn = benzyl.

In summary, we have developed a novel axially chiral ligand R-naph-pyCOOH **4** and its corresponding allyl esters (**5**), and have shown that the combination of Cl-naph-pyCOOH or Cl-naph-pyCOOallyl with a Trost-type CpRu complex achieves dehydrative intramolecular cyclization of ω-hydroxy allyl alcohols with excellent reactivity and selectivity.[13] Both aliphatic and aromatic alcohols can be used as nucleophiles at the ω-hydroxy end of the substrate. The present results will help facilitate the synthesis of a variety of chiral α-alkenyl cyclic ethers, which are potentially important intermediates for natural product synthesis, as well as assisting in the development of higher-performance ligands.

Experimental Section

[CpRu($CH_3CN)_3]PF_6$ (**3**; 32.0 mg, 73.8 μmol) and (*R*)-**5a** (10.0 mM in CH_2Cl_2, 7.38 mL, 73.8 μmol) were added to a 500 mL Schlenk tube. The resulting pale yellow solution was carefully concentrated in vacuo and to this residue was added (*E*)-**1a** (1000 mM in DMA, 73.8 mL, 73.8 mmol) at RT. After stirring for 1 h at 100 °C the mixture was cooled to RT and the mixture was partitioned between pentane/diethyl ether (3:1, 30 mL) and water (20 mL). The aqueous layer was extracted with pentane/diethyl ether (3:1, 30 mL × 5), and the combined organic extracts were passed through a pad of silica gel (2 cm × 2 cm). The filtrate was concentrated to a volume of about 10 mL, which was distilled at 150 °C and 760 mmHg by using a Kugelrohr apparatus to give (*S*)-**2a** (7.41 g, 90 % yield).

Details of the synthetic methods used for the preparation of chiral ligands, general procedure for asymmetric cyclization, and the NMR spectroscopic data of the substrates and products are available in the Supporting Information.

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Keywords: asymmetric catalysis · chiral cyclic ethers · cyclization · homogeneous catalysis · ruthenium

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