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Iridium-catalyzed asymmetric cyclization of alkenoic acids leading to γ-lactones†

Midori Nagamoto and Takahiro Nishimura*

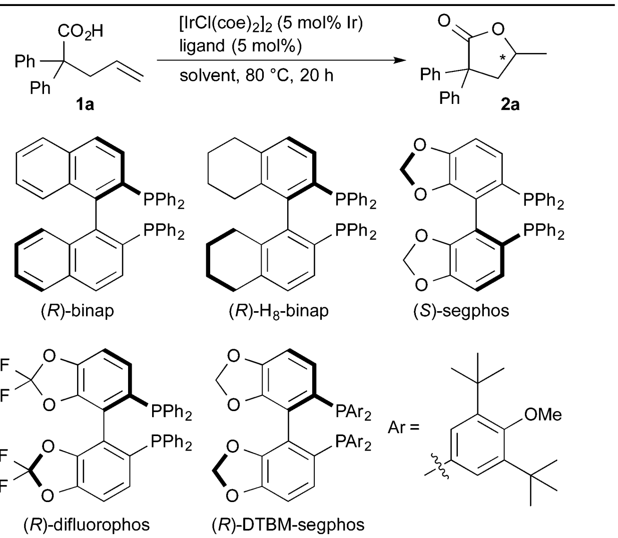
Asymmetric cyclization of alkenoic acids was realized by the use of an iridium/chiral bisphosphine catalyst, giving high yields of the corresponding γ-lactones with good enantioselectivity.

Carboxylic acid esters are one of the most ubiquitous and important compounds, and are also of great value as synthetic intermediates leading to the formation of alcohols *via* saponification or reduction. Among a variety of approaches to the esters, the catalytic addition of carboxylic acids to C–C unsaturated bonds provides highly atom-efficient and straightforward methodologies.[1] Transition metal-catalyzed addition of carboxylic acids was pioneered by Shvo and Rotem, who reported the Ru-catalyzed addition of carboxylic acids to alkynes,[2a,b] and there have been many successful examples of the addition to alkynes[2] and allenes.[3,4] Recently, the addition of carboxylic acids to unactivated alkenes has also been achieved by the use of Ru,[5] Fe,[6] Au,[7] and other metal catalysts.[8]

Asymmetric addition of oxygen nucleophiles to unsaturated bonds is still a challenging objective in organic chemistry. The successful examples of asymmetric addition have been limited to reactive unsaturated bonds such as allenes.[9–11] The research groups of Toste[9] and Widenfoefer[10] reported Au-catalyzed asymmetric intramolecular hydroalkoxylation of allenes independently. In this context, Breit and co-workers recently reported that a Rh/chiral bisphophine complex can efficiently catalyze the asymmetric intermolecular addition of carboxylic acids to allenes to give allylic esters with high enantioselectivity.[12] Meanwhile, there have been few reports on the asymmetric addition of oxygen-nucleophiles to simple alkenes. Hartwig and co-workers reported Ir-catalyzed intermolecular hydroalkoxylation of alkenes with a modest ee.[13] Hintermann and co-workers recently reported an asymmetric intramolecular hydroalkoxylation of allylphenols catalyzed by a Ti complex.[14]

An inherent problem in the asymmetric addition of carboxylic acids to alkenes is a non-asymmetric background reaction catalyzed by a strong Brønsted acid, which has been reported to be sometimes formed by use of metal triflates or cationic metal catalysts.[15] We found that a neutral Ir complex can

Table 1 Ir-catalyzed asymmetric cyclization of alkenoic acid **1a**[a]



Entry	Ligand	Solvent	Yield[b] (%)	ee[c] (%)
1	(*R*)-Binap	1,4-Dioxane	8	13
2	(*R*)-H_8-binap	1,4-Dioxane	14	10
3	(*S*)-Segphos	1,4-Dioxane	12	23
4	(*R*)-Difluorophos	1,4-Dioxane	11	25
5	(*R*)-DTBM-segphos	1,4-Dioxane	13	58
6	(*R*)-DTBM-segphos	Toluene	5	29
7	(*R*)-DTBM-segphos	NMP	39	80
8[d]	(*R*)-DTBM-segphos	NMP	95	81
9	None	NMP	4	—
10[e]	(*R*)-Binap	NMP	0	—

[a] Reaction conditions: carboxylic acid **1a** (0.10 mmol), $[IrCl(coe)_2]_2$ (5 mol% of Ir) and ligand (5 mol%) in solvent (0.40 mL) at 80 °C for 20 h. [b] Determined by ^1H NMR analysis. [c] Determined by chiral HPLC analysis. [d] At 100 °C. [e] $[RhCl(cod)]_2$ was used instead of $[IrCl(coe)_2]_2$. NMP = *N*-methyl-2-pyrrolidone.

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan. E-mail: tnishi@kuchem.kyoto-u.ac.jp

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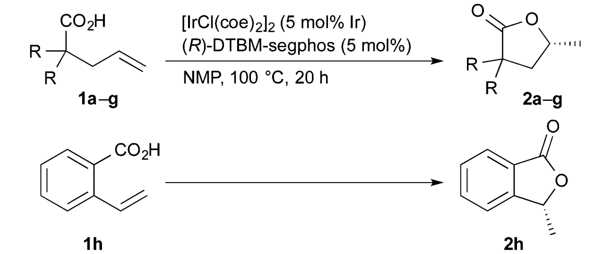
Table 2 Ir-catalyzed asymmetric cyclization of 4-pentenoic acids[a]



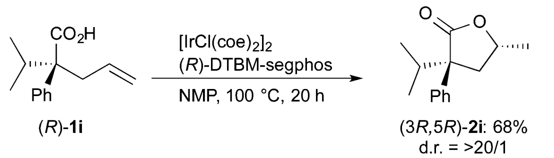
Entry	R		Yield[b] (%)	ee[c] (%)
1	Ph	**1a**	92 (**2a**)	81
2	4-MeC_6H_4	**1b**	98 (**2b**)	85
3	4-$MeOC_6H_4$	**1c**	96 (**2c**)	83
4	4-FC_6H_4	**1d**	86 (**2d**)	70
5	4-ClC_6H_4	**1e**	53 (**2e**)	61
6[d]	Benzyl	**1f**	87 (**2f**)	86
7[d]	*n*-Hexyl	**1g**	74 (**2g**)	89
8[e]	—	**1h**	57 (**2h**)	49

[a] Reaction conditions: carboxylic acid **1** (0.20 mmol), $[IrCl(coe)_2]_2$ (5 mol% Ir) and (*R*)-DTBM-segphos in NMP (0.80 mL) at 100 °C for 20 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] For 48 h. [e] At 120 °C.

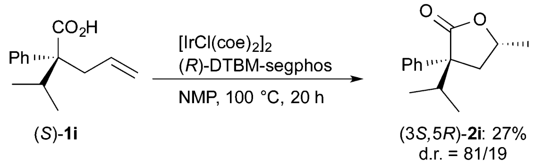
catalyze the intramolecular addition of a carboxylic acid to an alkene. Here we report the iridium-catalyzed asymmetric cyclization of alkenic acids to give the corresponding γ-lactones in high yields with good enantioselectivity.

Treatment of 2,2-diphenyl-4-pentenoic acid (**1a**) in the presence of $[IrCl(coe)_2]_2$ (5 mol% of Ir) and (*R*)-binap[16] in 1,4-dioxane at 80 °C for 20 h gave lactone **2a** in 8% yield with 13% ee (Table 1, entry 1). The use of (*R*)-H_8-binap[17] was also less effective in both the yield and the enantioselectivity (entry 2). (*S*)-Segphos,[18] (*R*)-difluorophos,[19] and (*R*)-DTBM-segphos[18] displayed better enantioselectivity than (*R*)-binap (entries 3–5), where the use of (*R*)-DTBM-segphos gave **2a** with 58% ee (entry 5). The use of a non-polar solvent such as toluene resulted in a low yield and enantioselectivity (entry 6). A significant improvement of the catalytic activity and enantioselectivity was observed by the use of *N*-methylpyrrolidone (NMP) as a solvent, giving the lactone in 39% yield with 80% ee (entry 7). The reaction at higher temperature (100 °C) in NMP gave **2a** in 95% yield without a decrease of the enantioselectivity (81% ee, entry 8). An Ir complex $[IrCl(coe)_2]_2$ without the phosphine ligand displayed a very low catalytic activity (entry 9). A rhodium catalyst did not promote the present cyclization (entry 10).

The results obtained for the iridium-catalyzed asymmetric cyclization of alkenoic acids are summarized in Table 2. Several 2,2-disubstituted 4-pentenoic acids **1** underwent the cyclization to give the corresponding lactones **2** (entries 1–7). The reaction of 2,2-diaryl-4-pentenoic acids **1b** and **1c**, having electron-donating substituents on the aromatic rings, proceeded to give **2b** and **2c** in high yields with 85 and 83% ee, respectively (entries 2 and 3). The reaction of **1d** and **1e**, having electron-withdrawing fluoro and chloro groups, gave **2d** and **2e** with modest enantioselectivity, 70 and 61% ee, respectively (entries 4 and 5). The modest yield (53%) of **2e** is due to the loss of **1e** by decarboxylation, which was proven to proceed without the iridium catalyst under the reaction conditions: heating of **1e** in NMP at 100 °C for 20 h gave 4,4-di(4-chlorophenyl)-1-butene in 56% yield (66% conversion of **1e**). 2,2-Dialkyl-4-pentenoic acids **1f** and **1g** are also good substrates to give corresponding lactones **2f** and **2g** in good yields with 86 and 89% ee, respectively (entries 6 and 7). The substituents at the 2-position of carboxylic acids **1** are essential for the present reaction: 2-pentenioc acid did not undergo the cyclization.[20] On the other hand, the reaction of 2-vinylbenzoic acid **1h** proceeded at 120 °C to give **2h** with a moderate enantioselectivity (entry 8).[21]

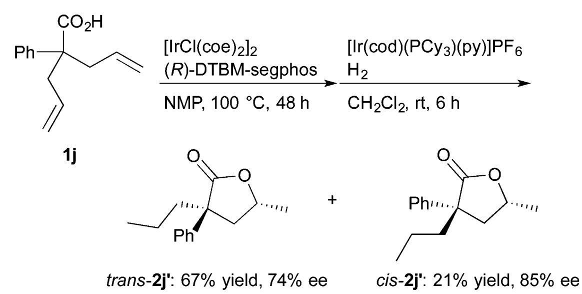


(1)



(2)

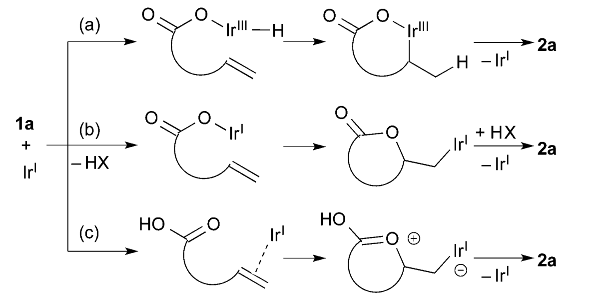
The stereochemistry of the lactone formed in the present catalytic conditions was estimated by the reaction of enantiomerically pure carboxylic acids **1i.** The reaction of (*R*)-**1i** in the presence of the Ir/(*R*)-DTBM-segphos catalyst gave lactone **2i** in 68% yield with very high diastereoselectivity (eqn (1)). The absolute configuration of the lactone **2i** was determined to be 3*R*,5*R*, which was assigned by comparison of the optical rotation ($[\alpha]_D = -27$, *c* 0.74 in $CHCl_3$) with the reported one ($[\alpha]_D = -45.3$, *c* 1.17 in $CHCl_3$ for (3*R*,5*R*)-**2i**).[22] On the other hand, a lower diastereoselectivity 81 : 19 was observed in the reaction of (*S*)-**1i** (eqn (2)), indicating that the face-selectivity of the cyclization is influenced by the substituents at the α-position of the carboxylic acids **1**.



(3)

The reaction of 2,2-diallylphenylacetic acid (**1j**) proceeded well to give the corresponding lactones in good yields, where the lactones contained double bond isomers and they were hydrogenated in the presence of $[Ir(cod)(PCy_3)(py)]PF_6$[23] (Cy = cyclohexyl, py = pyridine, eqn (3)). The saturated lactones *trans*-**2j**′ and *cis*-**2j**′ were formed in moderate diastereoselectivity and good enantioselectivity.

Scheme 1 shows three possible reaction pathways for the Ir-catalyzed cyclization. One involves the oxidative addition of the carboxylic acid **1a** to the Ir(I) giving a hydridoiridium(III) species, and a sequential alkene insertion into the Ir(III) leads to the formation of lactone **2a** *via* reductive elimination

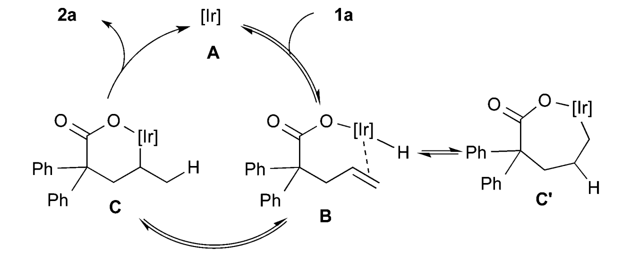


Scheme 1 Possible reaction pathways.

(Scheme 1a). Another reaction pathway is associated with the formation of an Ir(I) carboxylate species (Scheme 1b). In consideration of a weak basicity of NMP, the Ir(I) carboxylate species could be formed by deprotonation and the species undergoes the alkene insertion. Scheme 1c shows the other pathway initiated by an electrophilic activation of the alkene moiety with the Ir(I) species, where the subsequent attack of the carboxyl group to the alkene forms the C–O bond. Mashima and co-workers reported the synthesis of hydridoiridium(III) carboxylate complexes *via* oxidative addition of carboxylic acids to an Ir(I)/binap complex.[24] Krische and co-workers reported an iridium-catalyzed addition of carboxylic acids to allenes,[3c] where it is proposed that oxidative addition is the initial step of the reaction. To gain some insight into the mechanism, a stoichiometric reaction of **1a** with $[IrCl(coe)_2]_2$ and (*R*)-DTBM-segphos in benzene-d_6 was conducted. Treatment of $[IrCl(coe)_2]_2$, (*R*)-DTBM-segphos, and carboxylic acid **1a** in benzene-d_6 at room temperature for 24 h brought about the formation of hydridoiridium complexes as a mixture of two isomers (73 : 27). The major isomer showed a virtual triplet at −27.1 ppm (J_{P-H} = 22 Hz) in the ^{1}H NMR analysis, which was tentatively assigned to be a hydride at a *cis*-position to two phosphorous atoms.[25] The result indicates that the reaction pathway (a) initiated by the oxidative addition of the carboxylic acid is plausible in the present cyclization.

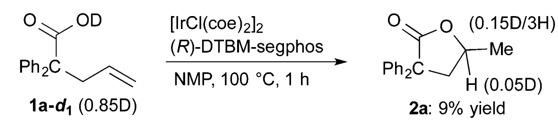
The possible intermediacy of the iridium(I) carboxylate species was also investigated by the use of a hydroxoiridium(I) complex as a catalyst precursor. The reaction of **1a** was conducted in the presence of $[Ir(OH)(cod)]_2$ and (*R*)-DTBM-segphos, which is expected to react with **1a** to form the iridium(I) carboxylate. The reaction gave the lactone in 20% yield accompanied by decarboxylation products in 62% yield as a mixture of the double bond isomers.[26] The result indicates that the iridium(I) carboxylate is not likely to be the intermediate in the present reaction, because the formation of such decarboxylation products was not observed in the reaction of **1a** catalyzed by the IrCl/(*R*)-DTBM-segphos complex.

Determining the stereochemistry of the addition using deuterated carboxylic acids would be helpful in distinguishing pathway (c) from others; pathway (c) leads to an *anti*-addition product while others lead to a *syn*-addition product. Unfortunately, however, the reactions of carboxylic acids containing internal alkenes were unsuccessful, and thus, the pathway (c) could not be excluded at this stage.[26]

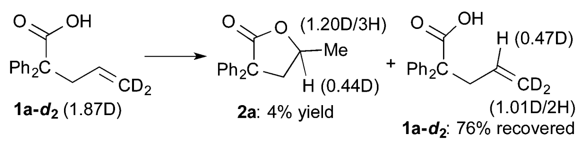


Scheme 2 Plausible catalytic cycle.

The results of deuterium-labeling experiments are shown in eqn (4) and (5). In the reaction of deuterated carboxylic acid **1a-*d*$_1$**, deuterium incorporation into a methyl group of **2a** was low (0.15D/3H, eqn (4)). The low content of the deuterium is probably due to an incorporation of hydrogen atoms from solvent NMP *via* the C–H activation of a methyl group on NMP.[27] A 5% of deuterium incorporation at the γ-position was also observed. On the other hand, in the reaction of **1a-*d*$_2$**, which is substituted at the alkene terminus with two deuterium atoms, a significant amount of a migration of deuterium into the γ-position of **2a** was observed (0.44D, eqn (5)). A migration of deuterium from the terminal position to the internal one was also detected in a recovered **1a-*d*$_2$**.



(4)



(5)

In light of the results of the stoichiometric reaction and deuterium-labeling experiments, the catalytic cycle is postulated as illustrated in Scheme 2. Oxidative addition of O–H bond to Ir(I) forms (carboxylato)iridium(III) hydride **B.** The alkene insertion into the Ir–H bond in an *exo*-fashion forms alkyliridium(III) **C** and the successive reductive elimination gives lactone **2a** and regenerates the Ir(I) species. The migration of deuterium observed as shown in eqn (5) can be explained by reversible insertion and β-hydride elimination of intermediate **C′**, which is formed *via* the alkene insertion in an *endo*-fashion.

In summary, we have developed an asymmetric cyclization of alkenoic acids using an Ir/(*R*)-DTBM-segphos catalyst that gives lactones with good enantioselectivity.

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