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# Intramolecular Tsuji–Trost-type Allylation of Carboxylic Acids: Asymmetric Synthesis of Highly π-Allyl Donative Lactones

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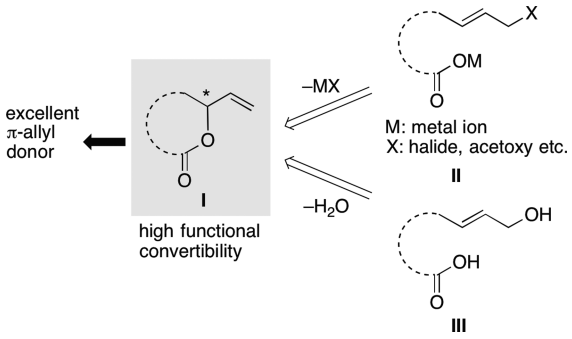
Supporting Information

**ABSTRACT:** Tsuji–Trost-type asymmetric allylation of carboxylic acids has been realized by using a cationic CpRu complex with an axially chiral picolinic acid-type ligand (Cl-Naph-PyCOOH: naph = naphthyl, py = pyridine). The carboxylic acid and allylic alcohol intramolecularly condense by the liberation of water without stoichiometric activation of either nucleophile or electrophile part, thereby attaining high atom- and step-economy, and low *E* factor. This success can be ascribed to the higher reactivity of allylic alcohols as compared with the allyl ester products in soft Ru/hard Brønstead acid combined catalysis, which can function under slightly acidic conditions unlike the traditional Pd-catalyzed system. Detailed analysis of the stereochemical outcome of the reaction using an enantiomerically enriched D-labeled substrate provides an intriguing view of enantioselection.

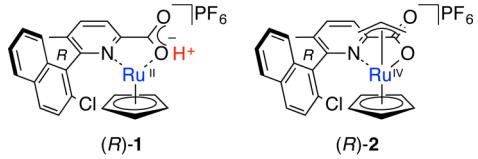
Optically active lactones represent a ubiquitous motif found in natural products and pharmaceuticals[1] and are also valuable chiral starting materials for asymmetric syntheses.[2] In particular, as shown in Scheme 1, simple lactones **I** with an allyloxycarbonyl moiety attract much attention from organic synthetic chemists because of their high functional convertibility. Among many excellent catalytic enantioselective approaches to asymmetric lactone synthesis including intramolecular hydrocarboxylation of allenes,[3] Wacker-type oxidative cyclization of alkenylalkanoic acids,[4] dearomative oxidative spirolactonization,[5] ring closure of *o*-iodobenzoates with aldehydes,[6] and [2 + 2] cycloaddition of ketenes and aldehydes,[7] intramolecular Tsuji–Trost-type allylation of carboxylate **II** seem to be the most tangible, but it is limited to only a specific case.[8] This may be ascribed mainly to the fact that the alkenyl lactone **I** is an excellent π-allyl donor, as Trost demonstrated the utility of **I** in the Pd-catalyzed synthesis of the α-tocopherol side chain in 1979 at a very early stage of Tsuji–Trost chemistry.[9]

**Scheme 1. Synthetic Processes to Alkenyl Lactones by Catalytic Asymmetric Intramolecular Tsuji–Trost-Type Allylation**




The aim of the present study was to realize the more direct process of "**III** to **I**" in which the carboxylic acid and allylic alcohol dehydratively condense without stoichiometric activation of either nucleophile or electrophile, thereby satisfying the criteria of high atom-economy and step-economy, and low *E* factor. As part of an ongoing project of "catalytic dehydrative C-,[10] N-,[11] O-,[12] and S-allylation[13] under slightly acidic conditions,"[14] the CpRu(II)/Cl-Naph-PyCOOH[15] combined catalyst **1** and its π-allyl complex **2**,[16] which were designed on the basis of the intramolecular redox-mediated donor–acceptor bifunctional catalyst (intramol-RDACat),[14a,17] were applied to the process **III** to **I**.

The results are summarized in Table 1. In the presence of 1 mol % of (*R*)-**1** or its π-allyl complex (*R*)-**2**,[16] the reaction of (*E*)-**3** successfully proceeded in *N*,*N*-dimethylacetamide (DMA) at 100 °C to give, after 20 min, the γ-ethenyl-substituted γ-lactone **4** in a quantitative yield with an *S*/*R* enantiomer ratio (er) of 99:1 (entries 1 and 2). With a substrate/catalyst (S/C) ratio of 500, the enantioselectivity decreased to 97:3, and the reaction required 5 h to realize 98% yield (entry 3). At 50 °C, the reaction also gave an er of 99:1, but it took 15 h to reach completion (entry 4). The solvents DMA, DMF, *t*-BuOH, and THF attained er ratios of 94:6–99:1 (entries 5, 6, and 9), whereas acetone, $CH_2Cl_2$, toluene, and *i*-PrOH led to decreased reactivity and/or selectivity (entries 7, 8, and 10). No reaction occurred in $CH_3CN$.[18]




(*R*)-Cl-Naph-PyCOOH/CpRu complexes
Naph: naphthalene, Py: pyridine

The scope and limitations of the reaction are shown in Table 2. First, the validity of the present reaction was confirmed in a 10 g scale reaction with S/C = 500 (entry 1).[18] When the C=C

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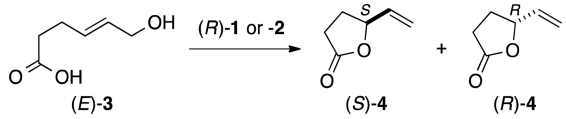
**Table 1. Asymmetric Dehydrative Lactonization of (*E*)-3 Catalyzed by (*R*)-1 or (*R*)-2[a]**



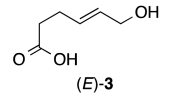
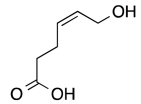
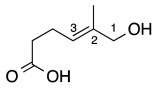
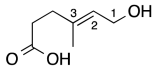
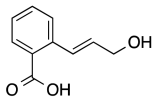
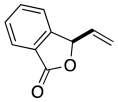
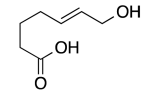
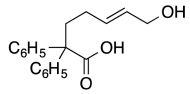
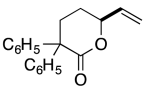
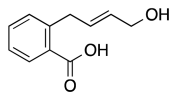
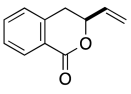
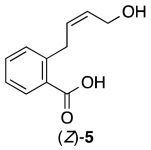
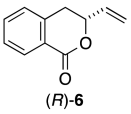
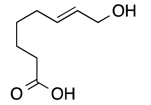

| | solvent | time (h) | yield (%)[b] | er (*S*/*R*)[c] |
|---|---|---|---|---|
| 1 | DMA | 0.3 | > 99 | 99:1 |
| 2 | DMA | 0.3 | > 99 | 99:1 |
| 3[d] | DMA | 5 | 98 | 97:3 |
| 4[e] | DMA | 15 | > 99 | 99:1 |
| 5 | DMF | 1 | > 99 | 98:2 |
| 6 | *t*-BuOH | 1 | > 99 | 97:3 |
| 7 | acetone | 15 | 70 | 85:15 |
| 8 | $CH_2Cl_2$ | 3 | > 99 | 54:46 |
| 9 | THF | 2 | > 99 | 94:6 |
| 10 | toluene | 15 | 75 | 75:25 |

[a]Catalysts (*R*)-**1** and (*R*)-**2** were prepared in situ by mixing $[RuCp(CH_3CN)_3]PF_6$ with (*R*)-Cl-Naph-PyCOOH and (*R*)-Cl-Naph-PyCOOCH$_2$CH=CH$_2$, respectively. Reactions were carried out in a 1 mmol scale under the conditions of [(*E*)-**3**] = 100 mM and [(*R*)-**1**] or [(*R*)-**2**] = 1 mM (1 mol %) in a 100 °C oil bath unless otherwise specified. Except for entry 1, (*R*)-**2** catalyst was used. [b]$^1$H-NMR yield. [c]Determined by GC analysis.[18] [d][(*E*)-**3**] = 500 mM and [(*R*)-**2**] = 1 mM (0.2 mol %). [e]50 °C.

double bond stereochemistry of **3** was switched from *E* to *Z*, the stereochemical outcome was altered, and the enantioselectivity was decreased to 12:88 (entry 2) (vide infra). Introduction of a methyl substituent at either C(2) or C(3) of the allylic alcohol moiety in (*E*)-**3** was acceptable, giving nearly optically pure hop lactone[19] and lavender lactone[20] (entries 3 and 4). The high enantiocontrol of the oxygen-containing tetra-substituted carbon center is noteworthy. An isobenzofuranone derivative was also prepared from cinnamyl alcohol-type substrate, although the enantioselectivity was lower at 86:14 (entry 5). The er at the 16% conversion stage was 92:8, indicating this particular product racemizes, probably via a carbocation intermediate, under acidic conditions. Elongation of the tether of (*E*)-**3** by one methylene led to oligomerization of the initially formed $\delta$-ethenyl-$\delta$-valerolactone and diene formation,[21] giving the desired $\delta$-lactone with a 98:2 er in 32% yield (entry 6). Introduction of two phenyl groups at the $\alpha$ position resulted in quantitative formation of the desired $\delta$-lactone (entry 7). The benzene-condensed substrate (*E*)-**5** gave the dihydroisocoumarin derivative (*S*)-**6** with a 98:2 er together with the diene product **7** in 5% yield (entry 8). Formation of the diene could be suppressed in *t*-BuOH, although the enantioselectivity decreased to 90:10 (entry 9). For (*Z*)-**5**, the stereochemical outcome was inverted with less deterioration in er than observed for (*Z*)-**3** (entry 10). A further increase in the methylene chain ($(CH_2)_4$) did not produce $\varepsilon$-lactone but resulted mainly in the formation of diene compounds (entry 11).[18] Intermolecular reaction of (*E*)-hept-2-en-1-ol with benzoic acid gave the linear allyl ester product under the standard conditions.

*E* substrates are converted by (*R*)-**1** or (*R*)-**2** to the corresponding product with the alkenyl group up when the structures are drawn as in Table 2. In order to gain information on the reaction pathway that would explain the stereochemical outcome, the products of the reaction using C(1)D-labeled (*E*)-**5**[22] were analyzed. As shown in Figure 1, a 81.0:19.0 mixture of (*S*)-(*E*)-**5**-*d* and (*R*)-(*E*)-**5**-*d* was converted in DMA, under the

**Table 2. Scope and Limitation of (*R*)-2-Catalyzed Asymmetric Lactone Synthesis[a]**

| | Substrate | Product | time (h) | Yield (%)[b] | er (*S*/*R*)[c] |
|---|---|---|---|---|---|
| 1[d] |  (*E*)-**3** |  (*S*)-**4** | 10 | 97 | 97:3 |
| 2 |  (*Z*)-**3** |  (*R*)-**4** | 1.5 | 93 | 12:88 |
| 3 |  |  | 1 | 90 | 99:1 |
| 4 |  |  | 24 | 91 | 96:4 |
| 5 |  |  | 4 | 92 | 14:86 |
| 6[e] |  |  | 10 | 32[f] | 98:2[g] |
| 7[e] |  |  | 10 | 90 | 99:1[g] |
| 8 |  |  | 0.5 | 88[h] | 98:2 |
| 9[i] | (*E*)-**5** | (*S*)-**6** | 1 | 95 | 90:10 |
| 10 |  (*Z*)-**5** |  (*R*)-**6** | 6 | 77[j] | 6:94 |
| 11 |  | — | 1 | —[k] | — |

[a]Conditions: 0.7−1 mmol scale; [substrate] = 100 mM; [(*R*)-**2**] = 1 mM (1 mol %); DMA; 100 °C unless otherwise specified. In all cases, the conversions were >99%. [b]Isolated yield. [c]Determined by GC or HPLC analysis except for entries 6 and 7.[18] [d]10 g scale; [substrate] = 500 mM; [(*R*)-**2**] = 1 mM (0.2 mol %). [e]70 °C. [f]Undetermined compounds formed.[18] [g]The er was determined, after converting to the hydroxy ester, by the $^1$H NMR analysis of the MTPA ester.[18] [h]2-(Buta-1,3-dien-1-yl)benzoic acid was obtained in ca. 5% yield.[18] [i]In *t*-BuOH. [j]2-(Buta-1,3-dien-1-yl)benzoic acid was obtained in ca. 15% yield.[18] [k]A 2:1 *E*/*Z* mixture of octa-5,7-dienoic acid was mainly obtained.[18]

influence of the *R* catalyst, to a 74.9:17.6:0.8:1.7:3.8:1.2 mixture of, respectively, (*S*)-(*Z*)-**6**-*d* (***SZ***), (*S*)-(*E*)-**6**-*d* (***SE***), (*R*)-(*Z*)-**6**-*d* (***RZ***), (*R*)-(*E*)-**6**-*d* (***RE***), (*Z*)-**7**-*d*, and (*E*)-**7**-*d* (*S*/*R* = 97.4:2.6, **6**/**7** = 95:5). The most tangible pathway would be one in which the 81.0 and 19.0 parts are transformed mainly to the ***SZ*** and ***RE*** lactones with a 98:2 er and the ***SE*** and ***RZ*** lactones with a 96:4 er, respectively. The ***SZ***/***RE*** and ***SE***/***RZ*** combination is also



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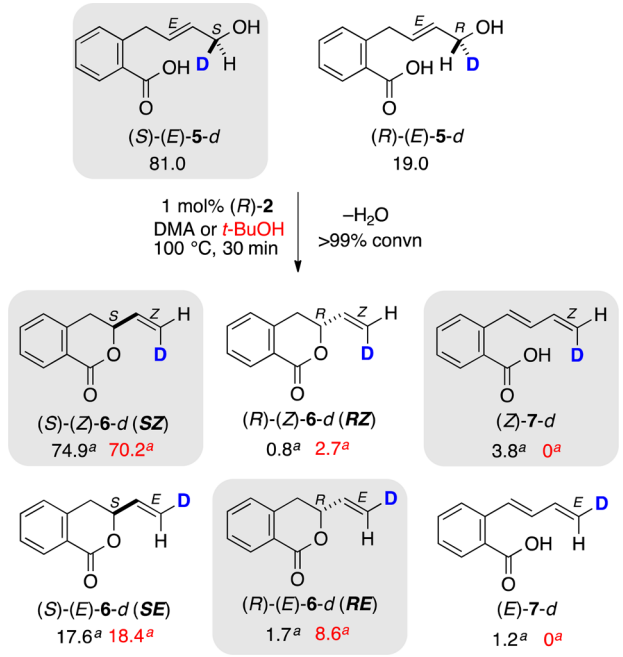


**Figure 1.** Reaction using D-labeled **5** and (*R*)-**2** in DMA or *t*-BuOH. [a]The molar ratio was determined by $^1$H NMR and/or HPLC analysis of the crude reaction mixture, (*S*)-**6**, (*R*)-**6**, and **7**.[18]

supported by the result obtained in *t*-BuOH (Figure 1, red values): the ratio of ***SZ***/***RE*** and ***SE***/***RZ*** lactone was 89.1:10.9 and 87.2:12.8, respectively. Although there is some deviation from the ideal, these values are close to the observed value. Another combination, ***SZ***/***RZ*** and ***SE***/***RE***, gave an er ratio that was inconsistent with the observed value in either DMA or *t*-BuOH.

Figure 2 shows one possible reaction pathways explaining the stereorelationship in Figure 1. The (*R*)-Cl-Naph-PyCOOH/CpRu(II) catalyst ($R$,$R_{Ru}$)-**1**[16] captures (*S*)-(*E*)-**5**-*d* via a soft/soft and hard/hard interaction. In the substrate/catalyst complex (*S*)-(*E*)-**5**-*d*/($R$,$R_{Ru}$)-**1**, intramol-RDACat mechanism[14a,17] facilitates formation of the $\pi$-allyl intermediate **INT**$_{endo\text{-}syn,anti\text{-}Re C(3)}$ in which the $\pi$-allyl ligand takes a stable endo conformation toward CpRu,[23] such that the C(3) substituent is syn to C(2)H and anti to the COO group of the *R* ligand. The sterically unfavored intermediate moves to the sterically favored **INT**$_{endo\text{-}syn,syn\text{-}Si C(3)}$ via $\pi-\sigma-\pi$ isomerization through C(1)–Ru bond rotation. Here, the nucleophilicity of COOH in the substrate is enhanced by formation of a hydrogen bond with the basic carboxylate oxygen atom of the *R* ligand, and thus, COOH attacks the $\pi$-allyl C(3) from the inside to give the ***SZ*** lactone and (*R*)-**1**. A small contribution of **INT**$_{endo\text{-}anti,syn\text{-}Re C(3)}$ generated via a C(3)–Ru bond rotation followed by the hydrogen-bond-assisted inside attack gives ***RE*** lactone. The stereochemical outcome of the reaction of diastereomeric (*Z*)-**5** as well as the lower enantioselectivity can be also understood by assuming the reaction pathways in Figure 2.

In summary, we have realized, for the first time, the direct Tsuji–Trost-type synthesis of various $\gamma$- and $\delta$-alkenyl substituted lactones by using $\omega$-carboxyl-substituted allylic alcohols as the substrate. Furthermore, the deuterium labeling experiment has provided insight into our understanding of the mechanism. The electrophilicity of allyl carboxylates is higher than that of allylic alcohols, but the use of intramol-RDACat,[14a,17] which works in a slightly acidic condition, can alter this situation. The hydroxy oxygen atom in allylic alcohol

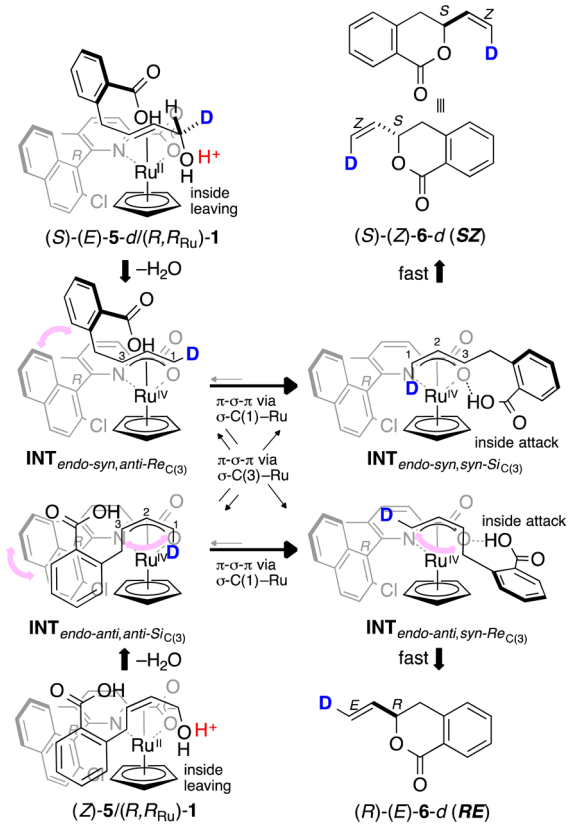


**Figure 2.** Supposed reaction pathways of (*R*)-**1**-catalyzed intramolecular dehydrative allylation. $PF_6$ was omitted for clarity. Blue D indicates H in (*Z*)-**5**.

substrate **I** is more efficiently activated by a hard Brønstead acid as compared with the less basic acyloxy group in alkenyl lactone product **III**, thereby lowering the degree of product inhibition to move the reaction to the entropically favored product side by liberation of "$H_2O$". This new method should further enhance the utility of Tsuji–Trost-type asymmetric allylation,[24] widening the scope of retrosynthetic analyses of natural and unnatural important chiral compounds.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05786.

Details of the general procedure for asymmetric lactonization and the NMR spectral data of the substrates and products (PDF)

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### Notes

The authors declare no competing financial interest.

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Carbon Utilization (ACT-C) from Japan Science and Technology Agency (JST).

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(16) The catalysts (*R*)-**1** and -**2** were prepared in situ by mixing $[RuCp(CH_3CN)_3]PF_6$ with (*R*)-Cl-Naph-PyCOOH and (*R*)-Cl-Naph-PyCOOCH$_2$CH=CH$_2$, respectively. Due to the easier manipulation of the allyl ester, (*R*)-**2** was used in most cases. The $^1$H NMR spectrum of (*R*)-**1** in $CD_2Cl_2$ gave broad and complex signals, while that of (*R*)-**2** gave two sets of sharp signals in a 3:2 ratio. The same spectrum was obtained by mixing $[RuCp(CH_3CN)_3]PF_6$, (*R*)-Cl-Naph-PyCOOH, and allyl alcohol. $^1$H NMR behavior indicates that two diastereomers, ($R$,$R_{Ru}$)-**1** and ($R$,$S_{Ru}$)-**1**, are generated in the reaction system. We believe that ($R$,$R_{Ru}$)-**1** in which a Cl···HCp hydrogen bond is possible would have higher reactivity to catalyze the present reaction more smoothly. Elucidation of the detailed mechanism is an ongoing project.

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