Asymmetric Dehydrative C-, N-, and O-Allylation Using Naph-diPIM-dioxo-*i*-Pr–CpRu/*p*-TsOH Combined Catalyst

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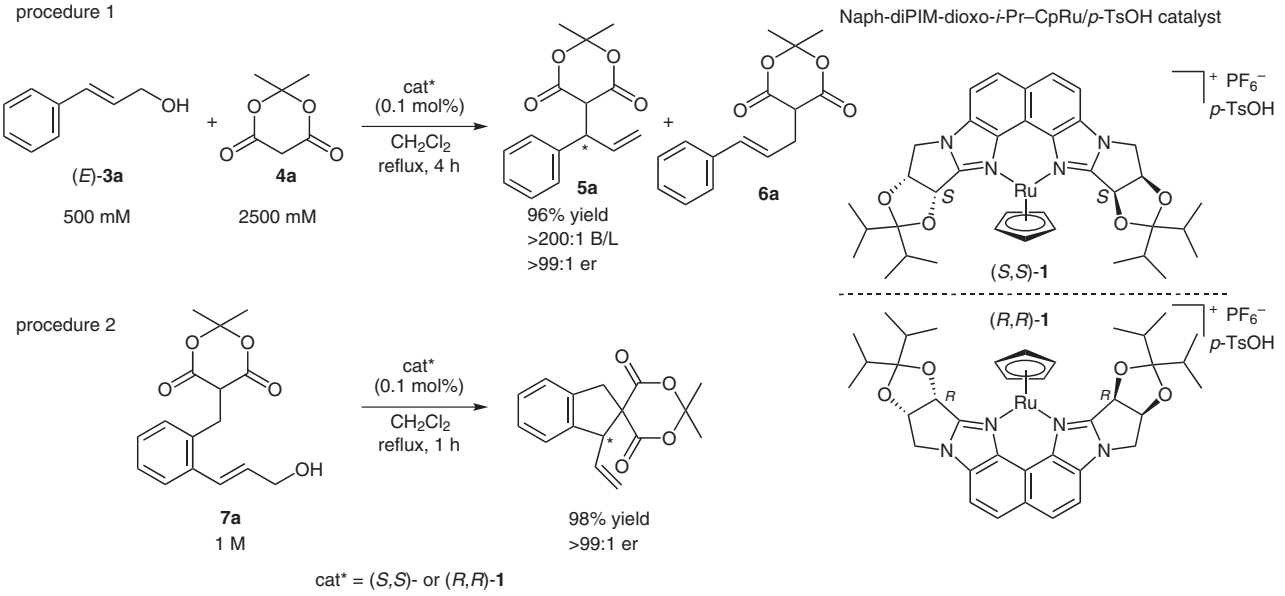
Abstract: (*S*,*S*)- or (*R*,*R*)-Naph-diPIM-dioxo-*i*-Pr–CpRu(II) complex with a Brønsted acid catalyzes dehydrative intermolecular C-allylation with high enantio- and regioselectivity. The new soft Ru/hard H^+ combined catalyst can also be used for intramolecular C-, N-, and O-allylations, giving nearly enantiomerically pure α-alkenyl-substituted cyclic compounds. As water is only the co-product, the synthetic process can be readily scaled up.

Key words: dehydrative allylation, asymmetric catalysis, cyclopentadienyl ruthenium, chiral bidentate sp^2N ligand



Scheme 1

Introduction

Geuther–Wislicenus alkylation of 1,3-dicarbonyl compounds has been one of the most frequently utilized C–C bond formations in organic synthesis since its discovery in 1863.[1] Tsuji revolutionized this chemistry by using palladium-catalyzed allylation in 1965,[2] and then Trost reported the first asymmetric version in 1977.[3] The reports have spurred subsequent research on related chemistry, which mainly utilizes various chiral phosphine–Pd complexes and others, including Mo, Ru, Rh, W, and Ir complexes.[4] Coupled with the high synthetic utility of the allyl group, the asymmetric Tsuji–Trost reaction has realized the synthesis of various natural products and is now a core reaction in organic synthesis.[5] The only disadvantage is that enolate formation using a base is required for the reaction with activated allylic alcohols, such as allyl halides and esters. An ideal reaction would be direct C–C bond formation from 1,3-dicarbonyl compounds and allylic alcohols by the liberation of water (Scheme 1, procedure 1). This can be realized using a monocationic CpRu(II) complex of a new type of chiral bisamidine ligand with a naphtho[1,2-*b*:7,8-*b*′]dipyrroloimidazole (Naph-diPIM) skeleton in combination with a Brønsted acid (Naph-diPIM-dioxo-*i*-Pr–CpRu(II)/*p*-TsOH [(*S*,*S*)- and (*R*,*R*)-**1**]. The new system, which has been designed on the basis of the 'redox-mediated donor-acceptor bifunctional catalyst (RDACat)' concept, shows high efficiency in asymmetric

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dehydrative allylation. Particularly, intramolecular C-, N-, and O-allylations have opened new practical routes to near enantiomerically pure cycloalkanes and N- and O-heterocycles (Scheme 1, procedure 2).[6,7]

Scope and Limitations

Under the conditions (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr (5 mM), $[CpRu(MeCN)_3]PF_6$ (**2**) (5 mM), *p*-TsOH (5 mM), cinnamyl alcohol [(*E*)-**3a**] (500 mM), and Meldrum's acid (**4a**) (2500 mM), in dichloromethane at reflux for one hour, the branched monoallyl product (*S*)-**5a** with >99:1 *S*/*R* er was obtained in 96% isolated yield (Table 1 entry 1). The ratio of **5a** and linear isomer **6a** [branch/linear (B/L)] is >200:1. A decrease in the catalyst concentration to 0.5 mM [substrate/catalyst (S/C) ratio = 1000] exerted little negative effect on the *S*/*R* and B/L ratios, although four hours were required for full conversion. By changing the chirality of catalyst from (*S*,*S*)-**1** to (*R*,*R*)-**1**, enantiomeric (*R*)-**5a** was also produced (entry 2). Electron-donating substituents as well as the electron-withdrawing nitro group could be introduced at the *para*-position of the phenyl group of (*E*)-**3b**–**e** (entries 3–6). An alkenyl **3f** or alkynyl group at C3 **3g** instead of a phenyl group was tolerated, giving the corresponding branched products **5f**,**g**, respecitively, with 96:4–99:1 er (entries 7 and 8). Both (*E*)-**3a** and (*Z*)-**3a** and racemic 1-phenylprop-2-en-1-ol (**3h**) were converted into (*S*)-**5a**, implying that π–σ–π interconversion should be faster than the intermolecular nucleophilic attack on a possible intermediary π-allyl–Ru(IV) complex. 5-Methyl-Meldrum's acid (**4b**), tetronic acid (**4c**), and 3-methyltetronic acid (**4d**) can be also used as C-nucleophiles. 3-Methyltetronic acid (**4d**) gave a near 1:1 diastereomer mixture with high enantiocontrol at the allylic carbon. No reaction occurred with dimethyl malonate **4e** under the present reaction conditions (entry 16). Introduction of a methyl substituent at C3 (*E*)-**3j** led to no detectable reaction (entry 15), and saturation of the phenyl group of (*E*)-**3i** caused β-elimination to give a diene product (entry 14).

Table 1 Intermolecular Enantioselective Dehydrative Allylation Using (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr/$[CpRu(MeCN)_3]PF_6$/*p*-TsOH Combined Catalyst[a]

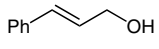
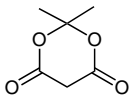
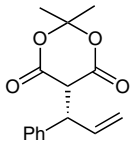
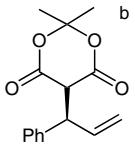
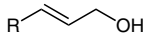
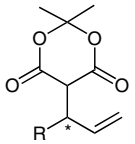
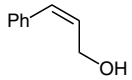
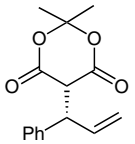
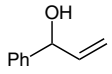
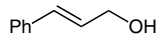
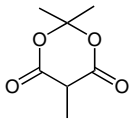
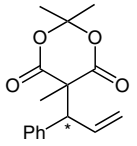
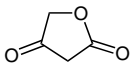
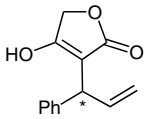
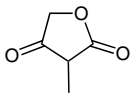
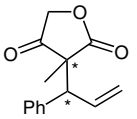
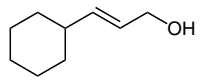
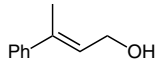
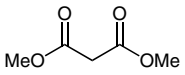
Entry	Allylic alcohol	1,3-Dione	Product	Isolated yield (%) (er)
1	 (*E*)-**3a**	 **4a**	 (*S*)-**5a**	96 (>99:1)
2	(*E*)-**3a**	**4a**	 (*R*)-**5a**	96 (1:>99)
				
3	R = 4-$MeOC_6H_4$ (*E*)-**3b**	**4a**	**5b**	95 (98:2)
4	R = 4-MeC_6H_4 (*E*)-**3c**	**4a**	**5c**	96 (99:1)
5	R = 4-ClC_6H_4 (*E*)-**3d**	**4a**	**5d**	94 (99:1)
6	R = 4-$O_2NC_6H_4$ (*E*)-**3e**	**4a**	**5e**	–[c] (99:1)
7	R = $CH{=}CMe_2$ **3f**	**4a**	**5f**	73 (96:4)
8	R = C≡CPh **3g**	**4a**	**5g**	89 (99:1)
9	 (*Z*)-**3a**	**4a**	 (*S*)-**5a**	93 (97:3)[d]

Table 1 Intermolecular Enantioselective Dehydrative Allylation Using (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr/[CpRu(MeCN)$_3$]PF$_6$/*p*-TsOH Combined Catalyst[a] (continued)

Entry	Allylic alcohol	1,3-Dione	Product	Isolated yield (%) (er)
10	 **3h**	**4a**	(*S*)-**5a**	96 (96:4)[d]
11	 (*E*)-**3a**	 **4b**	 **5h**	87 (99:1)
12	(*E*)-**3a**	 **4c**	 **5i**	89 (>99:1)[e]
13	(*E*)-**3a**	 **4d**	 **5j**	88 (95:5, 95:5)[f]
14	 (*E*)-**3i**	**4a**	–	–[g]
15	 (*E*)-**3j**	**4a**	–	no reaction
16	(*E*)-**3e**	 **4e**	–	–[h]

[a] Reaction conditions: 1.0 mmol scale; allyl alcohol **3** (500 mM), **4** (2500 mM), **2** (5 mM), (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr (5 mM), *p*-TsOH (5 mM), CH_2Cl_2, reflux, 1 h. The absolute configurations were not determined unless otherwise specified.

[b] (*R*,*R*)-**1** was used.

[c] Quantitative by ^{1}H NMR analysis, but difficult in separation from **4a**. Isolated as ethyl 3-(4-nitrophenyl)pent-4-enoate in 72% yield.

[d] Five times more diluted than the standard.

[e] HPLC analysis after acetylation.

[f] Diastereomeric ratio: ca. 1:1. 96:4 and 94:6 ers are also possible.

[g] Major product: allylidenecyclohexane.

[h] Major product: dicinnamyl ether.

Table 2 shows some examples of the intramolecular version. Intramolecular C-allylation using **7a**–**c** quantitatively afforded the 2,3-dihydro-1*H*-indene **8a**,**b** and 1,2,3,4-tetrahydronaphthalene derivatives **8c** with >99:1 er in all cases (entries 1–3). Not only C-nucleophiles, but also N- and O-nucleophiles, can be used in the intramolecular cyclization of **7d**–**i** to give isoindoline **8d**, 1,2,3,4-tetrahydroisoquinoline **8e**,**f**, phthalan **8g**, and isochromane derivatives **8h**,**i** quantitatively with high enantioselectivity (entries 4–12). In most intramolecular cyclizations the reaction proceeds with an S/C ratio of 1000–10000. Not only *N*-tosyl but also *N*-Boc can be utilized, enhancing the synthetic utility. The C3 aliphatic **7j**–**l**, having no cinnamyl alcohol unit, are poor substrates (entries 13–15) for the Naph-diPIM-dioxo-*i*-Pr–CpRu/*p*-TsOH catalyst system. Efficient dehydrative cyclization of aliphatic allylic alcohols can be attained by use of another CpRu(II) complex with Cl-Naph-PyCO$_2$H [6-(2-chloronaphthalen-1-yl)-5-methylpyridine-2-carboxylic acid] or its allyl ester.[8]

Table 2 Intramolecular Enantioselective Dehydrative Allylation Using (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr/[CpRu(MeCN)$_3$]PF$_6$/*p*-TsOH Combined Catalyst[a]

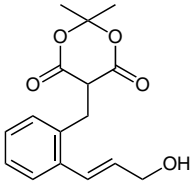
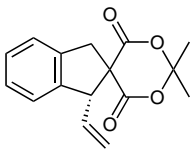
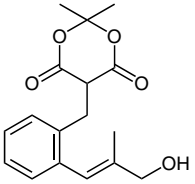
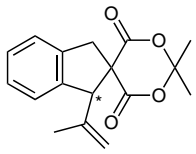
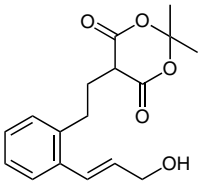
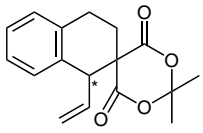
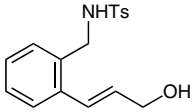
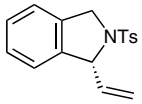
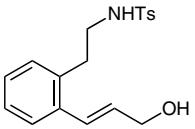
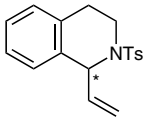
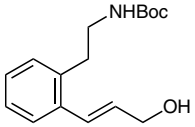
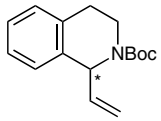
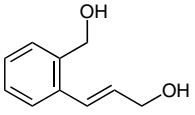
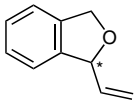
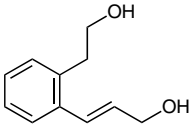
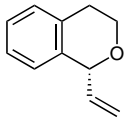
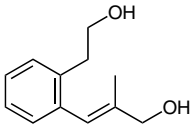
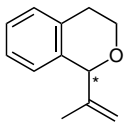
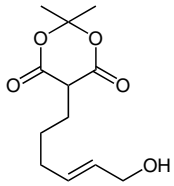
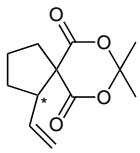
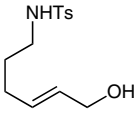
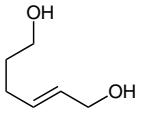
Entry	Reactant	Product	Isolated yield (%) (er)
1	 **7a**	 (*R*)-**8a**	98 (>99:1)
2	 **7b**	 **8b**	98 (>99:1)[b]
3	 **7c**	 **8c**	97 (>99:1)
4	 **7d**	 (*R*)-**8d**	99 (>99:1)
5 6 7	 **7e**	 **8e**	99 (99:1) 95 (99:1)[c] 83 (95:5)[d]
8	 **7f**	 **8f**	96 (>99:1)[b]
9	 **7g**	 **8g**	89 (99:1)
10 11	 **7h**	 (*R*)-**8h**	98 (>99:1) 93 (94:6)[c]

Table 2 Intramolecular Enantioselective Dehydrative Allylation Using (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr/[CpRu(MeCN)$_3$]PF$_6$/*p*-TsOH Combined Catalyst[a] (continued)

Entry	Reactant	Product	Isolated yield (%) (er)
12	 **7i**	 **8i**	94 (99:1)[b]
13	 **7j**	 **8j**	57 (88:12)[b,e]
14	 **7k**	 **8k**	97 (82:18)[b]
15	 **7l**	 **8l**	–[b,f] (60:40)

[a] Reaction conditions: 1.0 mmol scale; substrate **7** (1 M), **2** (1.0 mM), (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr (1.0 mM), *p*-TsOH (1.0 mM), CH_2Cl_2, reflux, 1 h. The absolute configurations were not determined unless otherwise specified.
[b] S/C = 100; (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr (10 mM), *p*-TsOH (10 mM).
[c] S/C = 5000; **7** (1 M), **2** (0.2 mM), (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr (0.2 mM), *p*-TsOH (0.4 mM), 6 h.
[d] S/C = 10000; **7** (1 M), **2** (0.1 mM), (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr (0.1 mM), *p*-TsOH (0.4 mM), 12 h.
[e] A 61:39 mixture of (*Z*)- and (*E*)-5-(hexa-3,5-dienyl)-2,2-dimethyl-1,3-dioxane-4,6-dione was isolated in 13% yield.
[f] Not isolated. Quantitative by GC analysis.

Experimental Procedures

All reactions were carried out an under argon atmosphere using general Schlenk techniques unless otherwise specified. A Schlenk tube with Teflon J. Young valve was specified by 'Young-type Schlenk'. Schlenk tubes were dried at ca. 250 °C using a heat gun under a reduced pressure. A Teflon-coated magnetic bar was used for stirring the reaction mixture. Liquid reagents were introduced by use of a syringe via a septum rubber. After introduction, the septum was replaced with a Young valve. Heating in a closed system was carried out after raising the temperature followed by closing the system. Cannulation was performed by use of a Teflon tube or a stainless tube through a septum rubber under a slightly positive pressure of argon. Solvents after general workup process were removed using a rotary evaporator. The concentration of a reaction mixture in a Schlenk tube was performed by connecting to a vacuum–argon line via a cold trap.

(*S*)-2,2-Dimethyl-5-[1-phenylallyl]-1,3-dioxane-4,6-dione [(*S*)-5a]; Typical Procedure for Intermolecular Allylation (Table 1)

S/C 1000: Chiral ligand (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr (5.45 mg, 10.0 μmol) and acetone-d_6 (0.50 mL) were added to a 5-mm Young-type NMR tube. To another 5-mm Young-type NMR tube were added [CpRu(MeCN)$_3$]PF$_6$ (**2**) (4.34 mg, 10.0 μmol) and acetone-d_6 (0.50 mL). The soln of **2** was transferred to the soln of (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr. After shaking for 10 min, the formation of (*S*,*S*)-**1** was confirmed by ^{1}H NMR analysis. The 10 mM (*S*,*S*)-**1** soln was used for the reaction. A soln of *p*-TsOH·H_2O (10 mM in MeOH, 0.10 mL, 1.0 μmol) was added to a 20-mL Young-type Schlenk, and the soln was concentrated in vacuo. To this was added the (*S*,*S*)-**1** soln (10 mM in acetone-d_6, 0.10 mL, 1.0 μmol). After concentration of the mixture in vacuo, cinnamyl alcohol (*E*-**3a**, 500 mM in CH_2Cl_2, 2.0 mL, 134.2 mg, 1.00 mmol) and Meldrum's acid (**4a**, 720.6 mg, 5.00 mmol) were introduced. After freezing the mixture followed by evacuation, the whole system was closed. The yellow soln was stirred for 4 h in a 60 °C oil bath, and then cooled to r.t. After removal of all of volatiles in vacuo, the residue was purified by column chromatography (silica gel, 50 g, EtOAc–hexane, 1:5) to give (*S*)-**5a** as a white solid; yield: 249.9 mg (96%); er *S*/*R* 99.5:0.5 [HPLC analysis (5 mm φ × 250 mm Chiralpak AD-H; hexane–*i*-PrOH, 1.0 mL/min flow rate; 220-nm detection, 27 °C): t_R = 26.5 (*R*), 32.5 min (*S*)]. $[\alpha]_D^{21}$ –50.7 (*c* 1.0, $CHCl_3$) {$[\alpha]_D^{20}$ 51.5 (*c* 1.0, $CHCl_3$) for (*R*)-**5a** obtained with (*R*,*R*)-**1**}.

S/C 100: *E*-**3a** (500 mM in CH_2Cl_2, 2.0 mL, 134.2 mg, 1.00 mmol), **4a** (720.6 mg, 5.00 mmol), the solns of 40 mM (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr (0.250 mL, 10.0 μmol), 40 mM **2** (0.250 mL, 10.0 μmol), and 40 mM *p*-TsOH·H_2O (0.250 mL, 10.0 μmol) were used.

The ^{1}H and ^{13}C NMR spectra were consistent with the reported data.[9]

5-[1-(4-Methoxyphenyl)allyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (5b)
Yellow solid; yield 275.6 mg (95%); er 97.7:2.3 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99:1, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 48.8, 56.8 min].

$[\alpha]_D^{22}$ –51.5 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.46 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 3.78 (s, 3 H, $ArOCH_3$), 3.83 [d, $J_{H,H}$ = 2.75 Hz, 1 H, COC*H*(CH)CO], 4.51 (dd, $J_{H,H}$ = 2.75, 8.26 Hz, 1 H, ArCH), 5.24 (d, $J_{H,H}$ = 10.33 Hz, 1 H, CH=CH*H*), 5.25 (d, $J_{H,H}$ = 17.21 Hz, 1 H, CH=C*H*H), 6.51 (ddd, $J_{H,H}$ = 8.26, 10.33, 17.21 Hz, 1 H, CHC*H*=CH_2), 6.84 (d, $J_{H,H}$ = 8.94 Hz, 2 H, ArH), 7.28 (d, $J_{H,H}$ = 8.94 Hz, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.00, 28.43, 47.92, 52.62, 55.41, 105.39, 114.16, 117.91, 130.00, 131.49, 137.38, 159.01, 164.64, 164.87.

HRMS (FAB): *m*/*z* [M^+] calcd for $C_{16}H_{18}O_5$: 290.1154; found: 290.1142.

5-[1-(4-Methylphenyl)allyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (5c)
White solid; yield: 262.3 mg (96%); er 99.0:1.0 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99:1, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 31.0, 38.5 min].

$[\alpha]_D^{22}$ –53.4 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.47 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 2.31 (s, 3 H, $ArCH_3$), 3.85 [d, $J_{H,H}$ = 2.75 Hz, 1 H, COC*H*(CH)CO], 4.52 (dd, $J_{H,H}$ = 2.75, 8.26 Hz, 1 H, ArCH), 5.25 (d, $J_{H,H}$ = 8.95 Hz, 1 H, CH=CH*H*), 5.27 (d, $J_{H,H}$ = 17.21 Hz, 1 H, CH=C*H*H), 6.50 (ddd, $J_{H,H}$ = 8.26, 8.95, 17.21 Hz, 1 H, CHC*H*=CH_2), 7.12 (d, $J_{H,H}$ = 8.26 Hz, 2 H, ArH), 7.24 (d, $J_{H,H}$ = 8.26 Hz, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 21.16, 27.96, 28.41, 48.16, 52.51, 105.38, 118.20, 128.64, 129.48, 136.54, 137.11, 137.25, 164.64, 164.72.

HRMS (FAB): *m*/*z* [M^+] calcd for $C_{16}H_{18}O_4$: 274.1205; found: 274.1216.

5-[1-(4-Chlorophenyl)allyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (5d)
Pale yellow solid; yield: 275.9 mg (94%); er 98.8:1.2 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99:1, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 39.5, 48.1 min].

$[\alpha]_D^{22}$ –51.3 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.57 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 3.85 [d, $J_{H,H}$ = 2.75 Hz, 1 H, COC*H*(CH)CO], 4.52 (dd, $J_{H,H}$ = 2.75, 8.26 Hz, 1 H, ArCH), 5.275 (d, $J_{H,H}$ = 11.02 Hz, 1 H, CH=CH*H*), 5.28 (d, $J_{H,H}$ = 15.84 Hz, 1 H, CH=C*H*H), 6.46 (ddd, $J_{H,H}$ = 8.26, 11.02, 15.84 Hz, 1 H, CHC*H*=CH_2), 7.28 (d, $J_{H,H}$ = 8.26 Hz, 2 H, ArH), 7.31 (d, $J_{H,H}$ = 8.26 Hz, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 27.78, 28.41, 47.49, 52.31, 105.41, 118.87, 128.87, 130.31, 133.46, 136.43, 138.07, 164.31, 164.42.

HRMS (FAB): *m*/*z* [M^+] calcd for $C_{15}H_{15}ClO_4$: 294.0659; found: 294.0652.

2,2-Dimethyl-5-[1-(4-nitrophenyl)allyl]-1,3-dioxane-4,6-dione (5e)
The er was determined after converting into ethyl 3-(4-nitrophenyl)pent-4-enoate.

^{1}H NMR ($CDCl_3$): δ = 1.67 (s, 3 H, CH_3), 1.77 (s, 3 H, CH_3), 3.93 [d, $J_{H,H}$ = 2.75 Hz, 1 H, COC*H*(CH)CO], 4.67 (dd, $J_{H,H}$ = 2.75, 8.95 Hz, 1 H, ArCH), 5.347 (d, $J_{H,H}$ = 17.90 Hz, 1 H, CH=CH*H*), 5.354 (d, $J_{H,H}$ = 10.33 Hz, 1 H, CH=C*H*H), 6.45 (ddd, $J_{H,H}$ = 8.95, 10.33, 17.90 Hz, 1 H, CHC*H*=CH_2), 7.58 (d, $J_{H,H}$ = 8.26 Hz, 2 H, ArH), 8.17 (d, $J_{H,H}$ = 8.26 Hz, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 27.51, 28.38, 47.31, 51.99, 105.55, 120.19, 123.77, 129.87, 135.19, 147.19, 147.24, 163.93, 163.97.

HRMS (FAB): *m*/*z* [M^+] calcd for $C_{15}H_{15}NO_6$: 305.0899; found: 305.0898.

2,2-Dimethyl-5-(5-methylhexa-1,4-dien-3-yl)-1,3-dioxane-4,6-dione (5f)
Pale yellow oil; yield: 133.9 mg (73%); er 95.7:4.3 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99.5:0.5, 0.5 mL/min flow rate, 220-nm detection, 27 °C): t_R = 48.8, 54.6 min].

$[\alpha]_D^{22}$ –39.1 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.69 (s, 3 H, C=CCH_3), 1.73 [s, 6 H, $C(CH_3)_2$], 1.74 (s, 3 H, C=CCH_3), 3.55 [d, $J_{H,H}$ = 2.07 Hz, 1 H, COC*H*(CH)CO], 4.09–4.12 [m, 1 H, C=CHC*H*(CH)CH=CH_2], 5.09 (d, $J_{H,H}$ = 10.33 Hz, 1 H, CH=CH*H*), 5.18 (d, $J_{H,H}$ = 17.21 Hz, 1 H, CH=C*H*H), 5.42 [d, $J_{H,H}$ = 9.64 Hz, 1 H, $(CH_3)_2$C=C*H*CH], 6.00 (ddd, $J_{H,H}$ = 7.23, 10.33, 17.21 Hz, 1 H, CHC*H*=CH_2).

^{13}C NMR ($CDCl_3$): δ = 18.21, 26.07, 27.69, 41.98, 51.55, 105.11, 116.73, 121.78, 136.07, 137.43, 164.67, 164.76.

HRMS (FAB): *m*/*z* [M^+] calcd for $C_{13}H_{18}O_4$: 238.1205; found: 238.1204.

2,2-Dimethyl-5-(5-phenylpent-1-en-4-yn-3-yl)-1,3-dioxane-4,6-dione (5g)
Pale yellow solid; yield: 252.0 mg (89%); er 98.6:1.4 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99:1, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 48.8, 72.9 min].

$[\alpha]_D^{23}$ –118.1 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.78 (s, 3 H, CH_3), 1.79 (s, 3 H, CH_3), 3.80 [d, $J_{H,H}$ = 2.75 Hz, 1 H, COC*H*(CH)CO], 4.42–4.44 (m, 1 H, C≡CCH), 5.31 (d, $J_{H,H}$ = 10.33 Hz, 1 H, CH=CH*H*), 5.53 (d, $J_{H,H}$ = 17.21 Hz, 1 H, CH=C*H*H), 6.12 (ddd, $J_{H,H}$ = 9.64, 10.33, 17.21 Hz, 1 H, C*H*=CH_2), 7.25–7.29 (m, 3 H, PhH), 7.41–7.43 (m, 2 H, PhH).

^{13}C NMR ($CDCl_3$): δ = 27.64, 28.59, 35.50, 51.27, 85.04, 85.87, 105.43, 119.06, 122.86, 128.33, 128.46, 131.99, 133.84, 163.33, 163.56.

HRMS (FAB): *m*/*z* [M^+] calcd for $C_{17}H_{16}O_4$: 284.1049; found: 284.1053.

2,2,5-Trimethyl-5-(1-phenylallyl)-1,3-dioxane-4,6-dione (5h)
White solid; yield: 239.2 mg (87%); er 98.9:1.1 [HPLC (5 mm φ × 250 mm Chiralcel OJ–H, hexane–*i*-PrOH, 99:1, 0.5 mL/min flow rate, 220-nm detection, 27 °C): t_R = 40.1, 47.6 min].

$[\alpha]_D^{21}$ –75.5 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 0.93 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3), 1.64 [s, 3 H, COC(CO)CH_3C], 3.93 (d, $J_{H,H}$ = 9.97 Hz, 1 H, PhCH), 5.27 (dd, $J_{H,H}$ = 1.36, 17.18 Hz, 1 H, CH=CH*H*), 5.31 (dd, $J_{H,H}$ = 1.36, 10.31 Hz, 1 H, CH=C*H*H), 6.55 (ddd, $J_{H,H}$ = 9.97, 10.31, 17.18 Hz, 1 H, CHC*H*=CH_2), 7.19 (d, $J_{H,H}$ = 6.87 Hz, 2 H, PhH), 7.24 (t, $J_{H,H}$ = 6.87 Hz, 1 H, PhH), 7.29 (t, $J_{H,H}$ = 6.87 Hz, 2 H, PhH).

^{13}C NMR ($CDCl_3$): δ = 23.76, 27.83, 30.10, 54.30, 58.51, 105.37, 119.79, 128.05, 128.89, 129.01, 134.92, 138.90, 168.82, 170.42.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{16}H_{18}NaO_4$: 297.1097; found: 297.1087.

4-Hydroxy-3-(1-phenylallyl)furan-2(5*H*)-one (5i)
White solid; yield: 192.3 mg (89%); the er was determined after acetylation.

$[\alpha]_D^{21}$ –54.5 (*c* 1.0, MeOH).

^{1}H NMR (CD_3OD): δ = 4.45 (d, $J_{H,H}$ = 8.25 Hz, 1 H, PhCH), 4.62 (s, 2 H, $COCH_2O$), 5.099 (d, $J_{H,H}$ = 10.31 Hz, 1 H, CH=CH*H*), 5.100 (d, $J_{H,H}$ = 17.18 Hz, 1 H, CH=C*H*H), 6.40 (ddd, $J_{H,H}$ = 8.25, 10.31, 17.18 Hz, 1 H, CHC*H*=CH_2), 7.15 (t, $J_{H,H}$ = 7.56 Hz, 1 H, PhH), 7.24 (t, $J_{H,H}$ = 7.56 Hz, 2 H, PhH), 7.30 (d, $J_{H,H}$ = 7.56 Hz, 2 H, PhH).

^{13}C NMR (CD_3OD): δ = 43.70, 68.04, 103.22, 115.91, 127.34, 128.76, 129.24, 139.00, 143.10, 175.30, 177.25.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{13}H_{12}NaO_3$: 239.0679; found: 239.0687.

3-Methyl-3-(1-phenylallyl)furan-2,4(3*H*,5*H*)-dione (5j)
White solid; yield: 202.7 mg (88%); er 95:5 and 95:5 (or 96:4 and 94:6) [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99:1, 1 mL/min flow rate, 220-nm detection, 27 °C): t_R = 11.8, 13.3, 15.1, 26.4 min].

^{1}H NMR ($CDCl_3$): δ = 1.32 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 3.46 (d, $J_{H,H}$ = 16.53 Hz, 1 H, OCH*H*CO), 3.54 (d, $J_{H,H}$ = 10.33 Hz, 1 H, OCH*H*CO), 3.64 (d, $J_{H,H}$ = 10.33 Hz, 1 H, OC*H*HCO), 3.78 (d, $J_{H,H}$ = 16.53 Hz, 1 H, OC*H*HCO), 4.31 (d, $J_{H,H}$ = 17.21 Hz, 1 H, PhCH), 4.35 (d, $J_{H,H}$ = 17.21 Hz, 1 H, PhCH), 5.26 (d, $J_{H,H}$ = 17.21 Hz, 2 H, 2 × CH=CH*H*), 5.31 (d, $J_{H,H}$ = 10.33 Hz, 2 H, 2 × CH=C*H*H), 6.37 (ddd, $J_{H,H}$ = 10.33, 17.21, 17.21 Hz, 1 H, CHC*H*=CH_2), 6.46 (ddd, $J_{H,H}$ = 10.33, 17.21, 17.21 Hz, 1 H, CHC*H*= CH_2), 7.18 (d, $J_{H,H}$ = 7.57 Hz, 2 H, PhH), 7.20 (d, $J_{H,H}$ = 7.57 Hz, 2 H, PhH), 7.25–7.32 (m, 6 H, PhH).

^{13}C NMR ($CDCl_3$): δ = 18.95, 19.18, 52.66, 52.74, 56.26, 56.82, 72.72, 72.82, 119.83, 120.08, 128.14, 128.18, 128.28, 128.34, 129.06, 129.22, 133.43, 133.88 137.97, 176.29, 176.86, 210.69, 210.83.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_{14}O_3$: 230.0943; found: 230.0933.

(*R*)-2,2-Dimethyl-1′-vinyl-1′,3′-dihydrospiro[[1,3]dioxane-5,2′-indene]-4,6-dione [(*R*)-8a]; Typical Procedure for Intramolecular Allylation (Table 2)
The 10 mM (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr–CpRu soln and 10 mM *p*-TsOH·H_2O solns were prepared in the same way as that of intermolecular case. The 10 mM ligand/CpRu soln (0.10 mL, 1.0 μmol) was introduced to a 20-mL Young-type Schlenk containing to *p*-TsOH·H_2O (1.0 μmol), and the soln was concentrated. To this was added (*E*)-5-[2-(3-hydroxyprop-1-enyl)benzyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (**7a**) (1000 mM in CH_2Cl_2, 1.0 mL, 290.3 mg, 1.0 mmol). After freezing the mixture followed by evacuation, the whole system was closed. The yellow soln was stirred for 1 h in a 60 °C oil bath, and then cooled to r.t. After concentration of the mixture, the residue was subjected to chromatography (silica gel, 5 g, EtOAc–hexane, 1:4) to give (*R*)-**8a** as a white solid; yield: 266.5 mg (98%); er *S*/*R* 0.3:99.7.

$[\alpha]_D^{21}$ –104.9 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.76 (s, 3 H, CH_3), 1.77 (s, 3 H, CH_3), 3.64 (d, $J_{H,H}$ = 15.84 Hz, 1 H, ArCH*H*C), 3.74 (d, $J_{H,H}$ = 15.84 Hz, 1 H, ArC*H*HC), 4.61 (d, $J_{H,H}$ = 8.94 Hz, 1 H, ArCHC), 5.37 (d, $J_{H,H}$ = 9.64 Hz, 1 H, CH=CH*H*), 5.38 (d, $J_{H,H}$ = 17.21 Hz, 1 H, CH=C*H*H), 5.90 (ddd, $J_{H,H}$ = 8.94, 9.64, 17.21 Hz, 1 H, CHC*H*=CH_2), 7.06 (d, $J_{H,H}$ = 5.51 Hz, 1 H, ArH), 7.21–7.27 (m, 3 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 29.13, 29.83, 43.66, 59.60, 61.80, 105.45, 121.25, 123.96, 124.06, 127.63, 128.13, 134.76, 139.33, 141.27, 167.78, 170.96.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{16}H_{16}NaO_4$: 295.0941; found: 295.0936.

2,2-Dimethyl-1′-(prop-1-en-2-yl)-1′,3′-dihydrospiro[[1,3]dioxane-5,2′-indene]-4,6-dione (8b)
White solid; yield: 280.9 mg (98% yield); er 99.5:0.5 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99:1, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 29.6, 44.1 min].

$[\alpha]_D^{22}$ –3.2 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.72 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 1.81 [s, 3 H, (CH_3)C=CH_2], 3.67 (s, 2 H, ArCH_2C), 4.67 (s, 1 H, ArCHC), 5.05 (d, $J_{H,H}$ = 1.38 Hz, 1 H, C=CH*H*), 5.16 (d, $J_{H,H}$ = 1.38 Hz, 1 H, C=C*H*H), 7.08 (d, $J_{H,H}$ = 6.89 Hz, 1 H, ArH), 7.22–7.28 (m, 3 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 21.45, 28.31, 30.41, 42.06, 60.57, 66.26, 105.17, 118.23, 124.11, 125.01, 127.32, 128.04, 140.02, 140.73, 141.50, 167.82, 171.16.

HRMS (FAB): *m*/*z* [M^+] calcd for $C_{17}H_{18}O_4$: 286.1205; found: 286.1191.

2,2-Dimethyl-1′-vinyl-3′,4′-dihydro-1′*H*-spiro[[1,3]dioxane-5,2′-naphthalene]-4,6-dione (8c)
White solid; yield: 278.6 mg (97%); er 99.9:0.1 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99:1, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 17.7, 19.4 min].

$[\alpha]_D^{22}$ –169.4 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.73 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3), 2.31 (ddd, $J_{H,H}$ = 4.12, 4.81, 13.75 Hz, 1 H, ArCH_2CH*H*C), 2.47–2.53 (m, 1 H, ArCH_2C*H*HC), 2.93 (ddd, $J_{H,H}$ = 4.67, 4.81, 16.70 Hz, 1 H, ArCH*H*CH_2C), 3.01–3.08 (m, 1 H, ArC*H*HCH_2C), 4.32 (d, $J_{H,H}$ = 9.62 Hz, 1 H, ArCHC), 5.39 (d, $J_{H,H}$ = 17.18 Hz, 1 H, CH=CH*H*), 5.40 (d, $J_{H,H}$ = 10.31 Hz, 1 H, CH=C*H*H), 5.83 (ddd, $J_{H,H}$ = 9.62, 10.31, 17.18 Hz, 1 H, CH=C*H*CH_2), 7.13–7.19 (m, 3 H, ArH), 7.25–7.27 (m, 1 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 26.14, 29.28, 29.69, 32.33, 49.39, 54.30, 105.36, 122.08, 126.46, 126.48, 127.30, 128.16, 134.58, 135.32, 135.72, 166.32, 170.51.

HRMS (FAB): *m*/*z* [M^+] calcd for $C_{17}H_{18}O_4$: 286.1205; found: 286.1192.

(*R*)-2-Tosyl-1-vinylisoindoline [(*R*)-8d]
White solid; yield: 295.8 mg (99%); er 99.5:0.5 [HPLC [5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 95:5, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 25.0 (*R*), 34.7 min (*S*)].

$[\alpha]_D^{21}$ –127.6 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H, $SO_2C_6H_4CH_3$), 4.64 (d, $J_{H,H}$ = 13.06 Hz, 1 H, ArCH*H*N), 4.73 (d, $J_{H,H}$ = 13.06 Hz, 1 H, ArC*H*HN), 5.24 (d, $J_{H,H}$ = 10.31 Hz, 1 H, CH=CH*H*), 5.41 (d, $J_{H,H}$ = 17.18 Hz, 1 H, CH=C*H*H), 5.55 (d, $J_{H,H}$ = 5.73 Hz, 1 H, ArCHN), 5.89 (ddd, $J_{H,H}$ = 5.73, 10.31, 17.18 Hz, 1 H, CHC*H*=CH_2), 7.05–7.08 (m, 1 H, ArH), 7.15–7.18 (m, 1 H, ArH), 7.24 (t, $J_{H,H}$ = 4.12 Hz, 2 H, ArH), 7.28 (d, $J_{H,H}$ = 8.25 Hz, 2 H, tosyl-ArH), 7.76 (d, $J_{H,H}$ = 8.25 Hz, 2 H, tosyl-ArH).

^{13}C NMR ($CDCl_3$): δ = 21.62, 53.89, 68.65, 116.70, 122.61, 123.58, 127.78, 127.89, 128.26, 129.82, 135.20, 135.45, 138.31, 138.96, 143.66.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{17}NO_2S$: 299.0980; found: 299.0978.

2-Tosyl-1-vinyl-1,2,3,4-tetrahydroisoquinoline (8e)
White solid; yield: 368.6 mg (99%); er 99.4:0.6 [HPLC (5 mm φ × 250 mm Chiralpak AD-H; hexane–*i*-PrOH, 98:2, 0.8 mL/min flow rate, 220-nm detection, 27 °C): t_R = 33.8, 46.9 min].

$[\alpha]_D^{22}$ –97.0 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 3 H, $SO_2C_6H_4CH_3$), 2.62 (ddd, $J_{H,H}$ = 5.51, 6.20, 16.04 Hz, 1 H, ArCH*H*CH_2N), 2.72–2.81 (m, 1 H, ArC*H*HCH_2N), 3.32–3.39 (m, 1 H, ArCH_2CH*H*N), 3.82–3.87 (m, 1 H, ArCH_2C*H*HN), 5.04 (dd, $J_{H,H}$ = 1.15, 17.18 Hz, 1 H, CH=CH*H*), 5.16 (dd, $J_{H,H}$ = 1.15, 10.31 Hz, 1 H, CH=C*H*H), 5.55 (d, $J_{H,H}$ = 5.73 Hz, 1 H, ArCHN), 5.90 (ddd, $J_{H,H}$ = 5.73, 10.31, 17.18 Hz, 1 H, C*H*=CH_2), 7.00 (d, $J_{H,H}$ = 7.45 Hz, 1 H, ArH), 7.06 (d, $J_{H,H}$ = 7.45 Hz, 1 H, ArH), 7.14 (d, $J_{H,H}$ = 6.30, 6.87 Hz, 2 H, ArH), 7.18 (d, $J_{H,H}$ = 8.02 Hz, 2 H, tosyl-ArH), 7.66 (d, $J_{H,H}$ = 8.02 Hz, 2 H, tosyl-ArH).

^{13}C NMR ($CDCl_3$): δ = 21.60, 27.82, 39.47, 58.30, 117.75, 126.23, 127.12, 127.32, 1238.06, 129.12, 129.57, 133.69, 133.85, 137.54, 137.92, 143.23.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{19}NO_2S$: 313.1137; found: 313.1136.

2-(*tert*-Butoxycarbonyl)-1-vinyl-1,2,3,4-tetrahydroisoquinoline (8f)

Colorless oil; yield: 249.9 mg (96%); 99.8:0.2 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 98:2, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 6.6, 8.8 min].

$[\alpha]_D^{20}$ –118.7 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.48 [s, 9 H, $C(CH_3)_3$], 2.71 (dt, $J_{H,H}$ = 4.12, 16.50 Hz, 1 H, ArCH*H*CH_2N), 2.87–2.92 (m, 1 H, ArC*H*HCH_2N), 3.23 (br, 1 H, $ArCH_2CH$*H*N), 4.06 (br, 1 H, $ArCH_2C$*H*HN), 5.04 (dd, $J_{H,H}$ = 1.37, 17.18 Hz, 1 H, CH=CH*H*), 5.13 (dd, $J_{H,H}$ = 1.37, 9.62 Hz, 1 H, CH=C*H*H), 5.58 (br, 1 H, ArCHN), 5.95 (ddd, $J_{H,H}$ = 5.50, 9.62, 17.18 Hz, 1 H, C*H*=CH_2), 7.10–7.18 (m, 4 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.63, 28.90, 38.46, 56.99, 79.90, 115.64, 126.15, 126.82, 128.00, 128.94, 135.02, 135.29, 138.09, 154.84.

HRMS (EI): *m*/*z* [M + Na$^+$] calcd for $C_{16}H_{21}NNaO_2$: 282.1465; found: 282.1464.

1-Vinyl-1,3-dihydroisobenzofuran (8g)

Colorless oil; yield: 129.6 mg (89%); er 99.4:0.6 [HPLC (5 mm φ × 250 mm Chiralpak AD-H hexane–*i*-PrOH, 99.7:0.3, 0.8 mL/min flow rate, 220-nm detection, 27 °C): t_R = 13.8, 16.2 min].

$[\alpha]_D^{20}$ –67.7 (*c* 1.09, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 5.10 (d, $J_{H,H}$ = 12.39 Hz, 1 H, ArCH*H*O), 5.18 (dd, $J_{H,H}$ = 1.38, 11.71 Hz, 1 H, CH=CH*H*), 5.25 (d, $J_{H,H}$ = 12.39 Hz, 1 H, ArC*H*HO), 5.43 (dd, $J_{H,H}$ = 1.38, 17.21 Hz, 1 H, CH=C*H*H), 5.59 (d, $J_{H,H}$ = 7.57 Hz, 1 H, ArCHO), 5.94 (ddd, $J_{H,H}$ = 7.57, 11.71, 17.21 Hz, 1 H, CHC*H*=CH_2), 7.14–7.16 (m, 1 H, ArH), 7.23–7.30 (m, 3 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 73.67, 73.92, 127.02, 127.52, 127.97, 128.81, 130.73, 132.82, 136.14, 139.39.

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{10}H_{10}NaO$: 169.0624; found: 169.0625.

(*R*)-1-Vinylisochromane [(*R*)-8h]

Colorless oil; yield: 156.5 mg (98%); er 99.7:0.3 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99.5:0.5, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 8.1 (*S*), 9.4 min (*R*)].

$[\alpha]_D^{22}$ –10.9 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.76 (ddd, $J_{H,H}$ = 0.69, 4.13, 15.84 Hz, 1 H, ArCH*H*CH_2O), 2.94–3.00 (m, 1 H, ArC*H*HCH_2O), 3.86 (ddd, $J_{H,H}$ = 4.13, 8.95, 11.02 Hz, 1 H, $ArCH_2CH$*H*O), 4.16 (ddd, $J_{H,H}$ = 0.69, 4.82, 11.02 Hz, 1 H, $ArCH_2C$*H*HO), 5.16 (d, $J_{H,H}$ = 6.89 Hz, 1 H, ArCHO), 5.34 (d, $J_{H,H}$ = 10.33 Hz, 1 H, CH=CH*H*), 5.38 (d, $J_{H,H}$ = 17.21 Hz, 1 H, CH=C*H*H), 5.97 (ddd, $J_{H,H}$ = 6.89, 10.33, 17.21 Hz, 1 H, CHC*H*=CH_2), 7.04–7.06 (m, 1 H, ArH), 7.11–7.13 (m, 1 H, ArH), 7.15–7.19 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 28.87, 63.29, 78.26, 118.61, 126.10, 126.22, 126.78, 129.04, 133.71, 136.24, 138.18.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{11}H_{12}O$: 160.0888; found: 160.0889.

1-(Prop-1-en-2-yl)isochromane (8i)

Colorless oil; yield: 164.5 mg (94%); er 99.1:0.9 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 99.5:0.5, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 5.4, 6.8 min].

$[\alpha]_D^{22}$ –22.9 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.62 (s, 3 H, CH_2=CCH_3), 2.69 (ddd, $J_{H,H}$ = 2.75, 3.44, 15.84 Hz, 1 H, ArCH*H*CH_2O), 3.00–3.08 (m, 1 H, ArC*H*HCH_2O), 3.82 (ddd, $J_{H,H}$ = 2.75, 4.13, 11.02 Hz, 1 H, $ArCH_2CH$*H*O), 4.18 (ddd, $J_{H,H}$ = 3.44, 5.51, 11.02 Hz, 1 H, $ArCH_2C$*H*HO), 5.06 (s, 1 H, CH*H*=C), 5.09 (s, 1 H, C*H*H=C), 5.16 (s, 1 H, ArCHO), 7.04 (d, $J_{H,H}$ = 7.57 Hz, 1 H, ArH), 7.11 (d, $J_{H,H}$ = 7.57 Hz 1 H, ArH), 7.14–7.19 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 17.54, 28.92, 63.72, 81.77, 116.04, 125.79, 126.10, 126.65, 128.83, 134.23, 135.84, 145.41.

HRMS (FAB): *m*/*z* [M$^+$] calcd for $C_{12}H_{14}O$: 174.1045; found: 174.1051.

8,8-Dimethyl-1-vinyl-7,9-dioxaspiro[4.5]decane-6,10-dione (8j)

White solid; yield: 127.8 mg (57%); er 87.5:12.5 [GC (0.25 mm × 0.12 μm × 30 m Chiraldex B-PM; temp, 100 °C, 140 kPa, split ratio 100:1): t_R = 94.2, 95.7 min]. In this reaction, a 61:39 mixture of (*Z*)- and (*E*)-5-(hexa-3,5-dienyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (30.1 mg, 13% yield) was also isolated.

^{1}H NMR ($CDCl_3$): δ = 1.698 (s, 3 H, CH_3), 1.704 (s, 3 H, CH_3), 1.98–2.12 (m, 4 H, CH_2=CHCH_2CH_2CH_2), 2.31–2.42 (m, 2 H, CH_2=CHCH_2CH_2CH_2), 3.33 (dt, $J_{H,H}$ = 7.57, 8.26 Hz, 1 H, C*H*CH=CH_2), 5.13 (dd, $J_{H,H}$ = 1.38, 9.64 Hz, 1 H, CH=CH*H*), 5.18 (dd, $J_{H,H}$ = 1.38, 17.21 Hz, 1 H, CH=C*H*H), 5.73 (ddd, $J_{H,H}$ = 8.26, 9.64, 17.21 Hz, 1 H, CHC*H*=CH_2).

^{13}C NMR ($CDCl_3$): δ = 25.65, 28.75, 29.81, 32.81, 39.05, 58.43, 100.06, 104.96, 119.08, 135.61, 169.36, 172.21.

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{12}H_{16}NaO_4$: 247.0941; found: 247.0940.

1-Tosyl-2-vinylpyrrolidine (8k)

White solid; yield: 242.6 mg (97%); er 82.4:17.6 [HPLC (5 mm φ × 250 mm Chiralpak AD-H, hexane–*i*-PrOH, 98:2, 1.0 mL/min flow rate, 220-nm detection, 27 °C): t_R = 28.4, 31.7 min].

^{1}H NMR ($CDCl_3$): δ = 1.59–1.85 (m, 4 H, NCH_2C*H*$_2$C*H*$_2$), 2.43 (s, 3 H, $SO_2C_6H_4CH_3$), 3.24 (m, 1 H, NCH*H*), 3.44 (ddd, $J_{H,H}$ = 4.82, 7.57, 10.16 Hz, 1 H, NC*H*H), 4.14 (m, 1 H, C*H*CH=CH_2), 5.11 (dd, $J_{H,H}$ = 1.38, 10.33 Hz, 1 H, CH=CH*H*), 5.27 (dd, $J_{H,H}$ = 1.38, 17.21 Hz, 1 H, CH=C*H*H), 5.81 (ddd, $J_{H,H}$ = 6.20, 10.33, 17.21 Hz, 1 H, CHC*H*=CH_2), 7.30 (d, $J_{H,H}$ = 8.26 Hz, 2 H, tosyl-ArH), 7.72 (d, $J_{H,H}$ = 8.26 Hz, 2 H, tosyl-ArH).

^{13}C NMR ($CDCl_3$): δ = 21.65, 23.88, 32.44, 48.91, 62.04, 115.43, 127.68, 129.70, 135.36, 138.84, 143.36.

HRMS (FAB): *m*/*z* [M$^+$] calcd for $C_{19}H_{21}NO_2S$: 327.1293; found: 327.1289.

2-Vinyltetrahydrofuran (8l)

According to the reported method,[8] the conversion and er were determined by the GC analysis of the reaction mixture; conversion >99% [GC (J&W Scientific DB-5, 0.25 mm × 0.25 μm × 30 m, temp, 50 °C for 10 min at >10 °C increase/min to > 200 °C, 140 kPa; splitless)]; er 60:40 [GC (Chiraldex B-DM, 0.25 mm × 0.25 μm × 30 m, temp 40 °C, 140 kPa; splitless)].

2,2-Dimethyl-1′-vinyl-1′,3′-dihydrospiro[[1,3]dioxane-5,2′-indene]-4,6-dione [(*R*)-8a); Intramolecular Allylation on a 10-Gram Scale

A 150-mL Young-type Schlenk tube was charged with [Cp-Ru(MeCN)$_3$]PF_6 (14.9 mg, 34.4 μmol), (*S*,*S*)-Naph-diPIM-dioxo-*i*-Pr (18.8 mg, 34.4 μmol), and acetone (2.0 mL). The mixture was stirred at r.t. for 30 min and then the resulting pale yellow soln was concentrated in vacuo. To this was added CH_2Cl_2 (35.0 mL), *p*-TsOH·H_2O (6.5 mg, 34.4 μmol) and **7a** (10.0 g, 34.4 mmol). After stirring at reflux temperature for 3 h followed by cooling to r.t., the mixture was concentrated and the residue passed through a pad of silica gel (15 g, 3.5 cm φ × 3.7 cm). The filtrate was concentrated to give the 5-*endo*-*trig*-cyclized product (9.18 g, 98%); er *R*/*S* 99.7:0.3. The white solid was recrystallized [EtOAc (20 mL) and hexane (60 mL)] to give enantiomerically pure (*R*)-**8a** (8.00 g, 85%) as prismatic crystals; mp 84 °C.

$[\alpha]_D^{20}$ –108.5 (*c* 1.0, $CHCl_3$).

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