# Reaction of γ,γ-Dialkoxyallylic Zirconium Species with Aldehyde as Protected Acryloyl Anion

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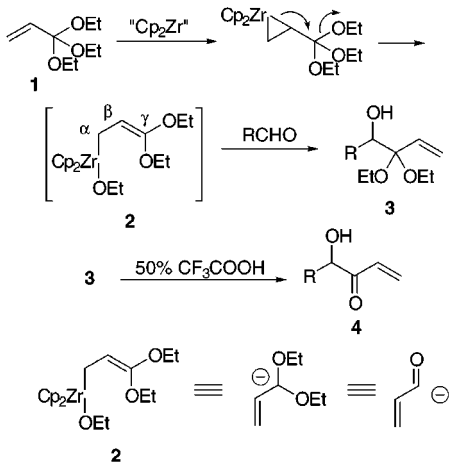
Introduction of the α,β-unsaturated carbonyl unit into an organic molecule should be an important process due to the synthetic usefulness of this functional group. One efficient method for the introduction of such functional group involves the carbon−carbon bond forming reaction of heteroatom-containing allylic or allenic organometallics as an α,β-unsaturated acyl anion equivalent.[1−4] In particular, as an acryloyl anion equivalent, 1-alkoxyallenyllithium has been widely employed due to its high reactivity with a variety of electrophiles and the further utilization of the allenyl unit in the products including the acidic hydrolysis to the vinyl ketone structure.[5,6] Recently, we reported that the reaction of γ,γ-dialkoxyallylic zirconium species **2**, generated in situ by the reaction of orthoacrylic acid triethyl ester **1**[7] with zirconocene−butene complex ("$Cp_2Zr$"),[8] with aromatic or α,β-unsaturated aldehyde provides 1-substituted-2,2-dialkoxy-3-buten-1-ol derivative **3**, which is easily converted to the vinyl ketone form **4** by treating with 50% trifluoroacetic acid in $CHCl_3$.[9] Thus, in this reaction, γ,γ-dialkoxyallylic zirconium species **2** acts as an acryloyl anion equivalent (Scheme 1). Under the similar conditions, however, the reaction of **2** with aliphatic aldehyde in toluene gave only a complex mixture. Therefore, further examination has been focused on the improvement of reaction conditions for the reaction with aliphatic aldehyde to reveal that the desired γ-adduct **3** can be obtained in a good yield when the reaction is carried out in the presence of 0.2−0.3 equiv of boron trifluoride diethyl ether complex ($BF_3$·$Et_2O$) and THF as a cosolvent. We report herein the detail of these reactions.

**Scheme 1**




The zirconium species **2** could be easily obtained in situ by the reaction of orthoacrylic acid triethyl ester **1**[7] with zirconocene−butene complex ("$Cp_2Zr$")[8] in toluene at room temperature, possibly through the formation of zirconacyclopropanes and the following β-elimination of alkoxyl group (Scheme 1).[10] The zirconium species **2** was found to be thermally stable (at ca. 40 °C) under inert atmosphere, and its γ,γ-dialkoxyallylic structure was confirmed by the NMR experiments ($^1H$, $^{13}C$, and NOE experiment, in benzene-$d_6$). As shown in Figure 1, an olefinic and methylene protons were observed at 4.50 ppm (t, $J$ = 8.7 Hz) and 1.97 ppm (d, $J$ = 8.7 Hz), respectively, and three nonequivalent methylene peaks of ethoxy groups were at 4.04, 3.91, and 3.80 ppm. In the $^{13}C$ NMR spectrum, α, β, and γ carbons of allylic part appeared at 34.3, 93.9, and 152.6 ppm, respectively.[11]

Results of the reaction of γ,γ-dialkoxyallylic zirconium species **2** with aldehydes are summarized in Table 1. The zirconium species **2**, generated in situ by the reaction of "$Cp_2Zr$" with orthoacrylic acid triethyl ester **1** in toluene, smoothly reacted with aromatic and α,β-unsaturated aldehydes in the same solvent at room temperature to give hydroxy acetal derivatives **3** in good yields (entries 1−6).[9] With aliphatic aldehyde under the similar conditions, however, the desired γ-adduct **3** was not obtained and the detectable side-reaction was self-aldolization of the aldehyde in the case of 3-phenylpropanal. We assumed that the diethoxy substituents at the γ-position would cause the decrease in the reactivity of the allylic zirconium species **2**. We reported that in the reaction of γ-alkoxyallylic zirconium species with aldehyde improve-

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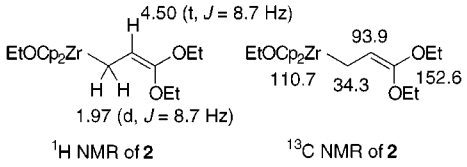



**Figure 1.**

**Table 1. Reaction of Zirconium Species 2 with Aldehyde**

| entry | R | method[a] | 3 | yield (%)[b] |
|---|---|---|---|---|
| 1 | Ph | A | **3a** | 91 |
| 2 | 2-naphthyl | A | **3b** | 96 |
| 3 | 2-furyl | A | **3c** | 90 |
| 4 | (*E*)-PhCH=CH | A | **3d** | 90 |
| 5 | $CH_2$=C($CH_3$) | A | **3e** | 58 |
| 6 | (*E*)-*n*-$C_3H_7$CH=CH | A | **3f** | 66 |
| 7 | (*E*)-*n*-$C_3H_7$CH=CH | B | **3f** | 76 |
| 8 | $PhCH_2CH_2$ | B | **3g** | 70 |
| 9 | *n*-$C_7H_{15}$ | B | **3h** | 74 |
| 10 | *c*-$C_6H_{11}$ | B | **3i** | 48 |
| 11 | $PhCH_2OCH_2$ | B | **3j** | 78 |

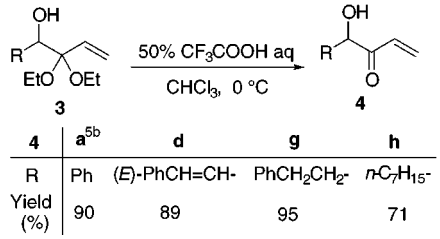
[a] Method A: in toluene. Method B: in toluene−THF (2:1), 0.3 equiv of $BF_3$·$Et_2O$. [b] Isolated yield.

ment of the yield of the product was achieved by the addition of Lewis acid such as $BF_3$·$OEt_2$ presumably through the activation of carbonyl group by coordination.[10] After the survey of Lewis acid and solvent in the reaction of **2** with aliphatic aldehyde, we found that addition of 0.2−0.3 equiv of $BF_3$·$OEt_2$ and THF as a cosolvent works nicely giving rise to the desired product **3** (entries 7−11), although in the presence of more than 1 equiv of Lewis acid ($BF_3$·$OEt_2$, TMSOTf or $TiCl_4$) the reaction of **2** with aldehyde in toluene resulted in the different reaction pathway to give *gem*-dialkoxycyclopropane derivatives.[12] It should be noted that without the addition of THF in the case of 0.2−0.3 equiv of $BF_3$·$OEt_2$ or the use of TMSOTf (0.2−0.4 equiv) either in toluene or in toluene−THF both reactions occurred competitively to give a mixture of the γ-adducts **3** and the *gem*-dialkoxycyclopropane derivative. As shown in Table 1, aliphatic aldehyde without α-alkyl branching and α-oxygenated aldehyde gave the γ-adduct **3** in a reasonable yield (entries 8−11, see also the result with glyceraldehyde acetonide). With α,β-unsaturated aldehyde, a slight improvement in the yield was observed (entry 6 vs entry 7). The γ-adducts **3** were stable enough to be purified by neutral silica gel column chromatography.

Deprotection of diethyl acetal group in **3** derived from both aromatic and aliphatic aldehydes could be achieved by simply treating with 50% trifluoroacetic acid (TFA) in chloroform at 0 °C within 10 min to give the vinyl ketone **4** in a good yield (Scheme 2).

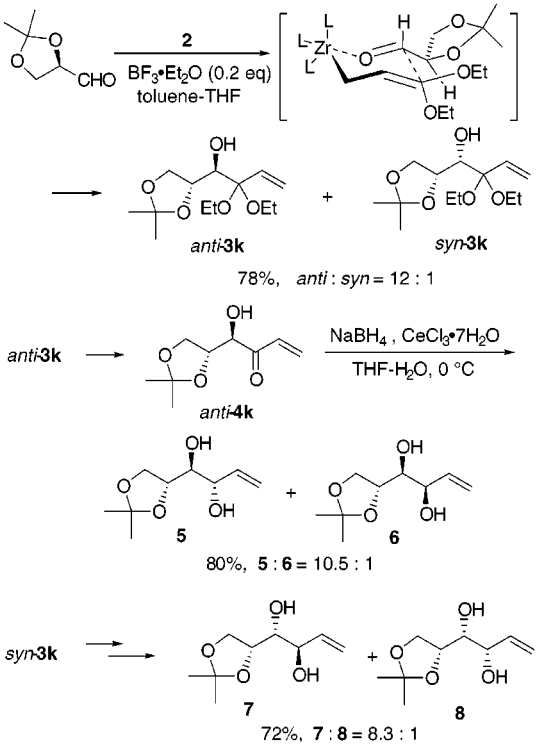
Since we could find out improved reaction conditions for the coupling reaction of **2** with aliphatic aldehyde, we examined the diastereoselectivity in the reaction of **2** with glyceraldehyde acetonide. Reaction of **2** with (*R*)-glyceraldehyde acetonide[13] in the presence of 0.2 equiv of $BF_3$·$OEt_2$ in THF−toluene at 0 °C gave the adduct **3k** (78% yield) as a mixture of diastereomers *anti*-**3k** and *syn*-**3k**

**Scheme 2**




| 4 | a[5b] | d | g | h |
|---|---|---|---|---|
| R | Ph | (*E*)-PhCH=CH- | $PhCH_2CH_2$- | *n*-$C_7H_{15}$- |
| Yield (%) | 90 | 89 | 95 | 71 |

**Scheme 3**




in a ratio of 12:1, which are separable by column chromatography. To determine the stereochemistry, the adducts **3k** were converted to the tetraol derivatives as shown in Scheme 3, since Roush reported the spectra data of these compounds obtained by his allylic borane chemistry.[14] Thus, treatment of *anti*-**3k** with aqueous TFA gave the relatively unstable vinyl ketone *anti*-**4k**, which was reduced with $NaBH_4$−$CeCl_3$·$7H_2O$[15] to give a mixture of tetraol derivatives **5** and **6** in 80% yield (two steps) in a ratio of 10.5:1. Likewise, *syn*-**3k** provided a mixture of tetraol derivatives **7** and **8** in a ratio of 8.3:1. $^1$H and $^{13}$C NMR spectra of each tetraol derivative thus obtained were clearly different from each other, and by comparing the spectra data and specific rotation values of **5** and **7** with those reported by Roush,[14] stereochemical assignment can be deduced as shown in Scheme 3. That is, addition of the zirconium species **2** to glyceraldehyde acetonide under the above conditions proceeds in *anti*-selective manner and the $NaBH_4$−$CeCl_3$ reduction of the hydroxy ketone **4** gave the *anti*-diol **5** or **7** as a major product. On the basis of these results, the observed highly *anti*-selective addition of the zirconium species **2** to glyceraldehyde acetonide is possibly explained by considering the chairlike six-membered transition state as

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in the cases of other allylic metals such as allylic boranes.[10b,16] It should be noted that such a high diastereoselection in the addition reaction of **2** with glyceraldehyde acetonide, and the functionality of the product **3** would provide an efficient procedure for the carbohydrate chemistry from acyclic precursors.

In conclusion, $\gamma,\gamma$-dialkoxyallylic zirconium species **2** reacts with a variety of aldehydes at $\gamma$-position of the zirconium metal as normal allylic organometallics to give 1-substituted-2,2-dialkoxy-3-buten-1-ol derivatives **3**, which is easily converted to the vinyl ketone form **4** by simply treating with trifluoroacetic acid. Thus, in this reaction, the zirconium species **2** acts as a synthetically useful acryloyl anion equivalent.

## Experimental Section

**General.** THF was distilled from sodium benzophenone ketyl before use. Zirconocene dichloride was purchased from Tokyo Kasei Kogyo. All reactions were conducted under an argon atmosphere. $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$, and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for $^1$H NMR and $CDCl_3$ (77.01 ppm) for $^{13}$C NMR as an internal standard, respectively. Mass spectra and HRMS were recorded by electron impact ionization at 70 eV. Column chromatography was performed on neutral silica gel (75−150 $\mu$m). Medium-pressure liquid chromatography (MPLC) was performed on a 30 × 2.2 cm i.d. prepacked column (silica gel, 50 $\mu$m) with a UV or RI detector.

**$\gamma,\gamma$-Diethoxyallylic Zirconium Species (2).** A solution of triethyl orthoacrylate (174 mg, 1 mmol) in toluene (2 mL) was added to a solution of "$Cp_2Zr$" (1.2 mmol), prepared from $Cp_2ZrCl_2$ with n-BuLi[8,10] at −78 °C. After being stirred for 3 h at room temperature, the mixture was concentrated under reduced pressure. To the residue was added benzene-$d_6$, and the NMR was measured. $^1$H NMR (300 MHz, benzene-$d_6$) $\delta$ 6.00−5.92 (10H, m), 4.50 (1H, t, $J$ = 8.7 Hz), 4.04 (2H, q, $J$ = 7.2 Hz), 3.91 (2H, q, $J$ = 7.0 Hz), 3.80 (2H, q, $J$ = 6.9 Hz), 1.97 (2H, d, $J$ = 8.7 Hz), 1.33 (3H, t, $J$ = 7.2 Hz), 1.25 (3H, t, $J$ = 6.9 Hz), 1.08 (3H, t, $J$ = 7.0 Hz). $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 152.6, 110.7, 93.9, 68.8, 64.2, 64.0, 34.3, 20.1, 15.6, 15.1.

**General Procedure of Generation of 2 and Its Reaction with Aromatic or $\alpha,\beta$-Unsaturated Aldehyde.** A solution of triethyl orthoacrylate (174 mg, 1 mmol) in toluene (2 mL) was added to a solution of "$Cp_2Zr$" (1.2 mmol), prepared from $Cp_2ZrCl_2$ with n-BuLi[8,10] at −78 °C. After being stirred for 3 h at room temperature, a solution of aromatic or $\alpha,\beta$-unsaturated aldehyde (1.2 mmol) shown in Table 1 in toluene (2 mL) was added at −78 °C and then stirred at room temperature for 3 h. The reaction mixture was extracted with diethyl ether after addition of $NH_4Cl$ aq, and the extract was washed with brine and dried over $MgSO_4$. Purification of the residue, obtained by evaporation of the solvent, by neutral silica gel column chromatography (hexane−AcOEt) gave the product **3** shown in Table 1.

**2,2-Diethoxy-1-phenyl-3-buten-1-ol (3a)**: colorless oil; IR (neat) $\nu$ cm$^{-1}$; 3478, 1410, 1057. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.54−7.40 (2H, m), 7.33−7.23 (3H, m), 5.43 (1H, s), 5.42 (1H, d, $J$ = 3.1 Hz), 5.28 (1H, dd, $J$ = 5.0, 8.1 Hz), 4.88 (1H, d, $J$ = 2.0 Hz), 3.67 (2H, q, $J$ = 7.0 Hz), 3.53 (1H, qd, $J$ = 7.0, 9.8 Hz), 3.48 (1H, qd, $J$ = 7.0, 9.8 Hz), 2.66 (1H, d, $J$ = 2.0 Hz), 1.27 (3H, t, $J$ = 7.0 Hz), 1.16 (3H, $J$ = 7.0 Hz). $^{13}$C NMR (100.6 MHz, $CDCl_3$)-$\delta$ 139.2, 134.1, 127.6, 127.4, 127.2, 119.7, 101.8, 74.4, 57.6, 56.6, 15.3, 15.2. EI-MS $m/z$ 219 ($M^+$ − OH), 191 ($M^+$ − OEt). HRMS calcd for $C_{14}H_{19}O_2$: 219.1385 ($M^+$ − OH). Found: 219.1389. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.04; H, 8.52.

**General Procedure of the Reaction of 2 with Aliphatic Aldehyde.** A solution of triethyl orthoacrylate (174 mg, 1 mmol) in toluene (2 mL) was added to a solution of "$Cp_2Zr$" (1.2 mmol), prepared from $Cp_2ZrCl_2$ with n-BuLi[8,10] at −78 °C. After being stirred for 3 h at room temperature, the reaction mixture was cooled with dry ice/acetone bath. To the mixture were successively added THF (1 mL), $BF_3{\cdot}Et_2O$ (0.3 mmol), and aliphatic aldehyde (1.2 mmol), and the whole was stirred at 0 °C for 1−2 h (in the case of glyceraldehyde acetonide 0.2 mmol of $BF_3{\cdot}Et_2O$ was used). The reaction mixture was extracted with diethyl ether after addition of $NH_4Cl$ aq, and the extract was washed with brine and dried over $MgSO_4$. Purification of the residue, obtained by evaporation of the solvent, by neutral silica gel column chromatography (hexane−AcOEt) gave the product **3f**−**k**.

**4,4-Diethoxy-1-phenyl-5-hexen-3-ol (3g)**: colorless oil; IR (neat) $\nu$ cm$^{-1}$; 3476, 1411, 1049. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.31−7.15 (5H, m), 5.74 (1H, dd, $J$ = 10.9, 17.5 Hz), 5.52 (1H, dd, $J$ = 2.1, 17.5 Hz), 5.36 (1H, dd, $J$ = 2.1, 10.9 Hz), 3.74 (1H, ddd, $J$ = 2.1, 2.1, 10.4 Hz), 3.50 (2H, q, $J$ = 7.1 Hz), 3.47 (1H, qd, $J$ = 7.0, 9.4 Hz), 3.28 (1H, qd, $J$ = 7.0, 9.4 Hz), 2.90 (1H, ddd, $J$ = 4.8, 10.0, 14.0 Hz), 2.64 (1H, ddd, $J$ = 7.5, 9.4, 14.0 Hz), 2.28 (1H, s), 1.82 (1H, m), 1.62 (1H, ddd, $J$ = 4.8, 9.4, 19.8 Hz), 1.18 (3H, t, $J$ = 7.1 Hz), 1.12 (3H, t, $J$ = 7.0 Hz). $^{13}$C NMR (125.7 MHz, $CDCl_3$) $\delta$ 142.3, 134.5, 128.6, 128.2, 125.7, 119.4, 101.6, 72.5, 56.9, 56.5, 32.6, 32.5, 15.4, 15.3. EI-MS $m/z$: 264 ($M^+$), 219 ($M^+$ − OEt). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.52; H, 9.09.

**(1*R*)-1-[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2,2-diethoxy-3-buten-1-ol (*anti*-3k)**: colorless oil; $[\alpha]^{22}_D$ +8.8 ($c$ 1.18, $CHCl_3$). IR (neat) $\nu$ cm$^{-1}$; 3481, 1057. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.70 (1H, dd, $J$ = 10.7, 17.5 Hz), 5.54 (1H, dd, $J$ = 2.1, 17.5 Hz), 5.37 (1H, dd, $J$ = 2.1, 10.7 Hz), 4.21 (1H, dt, $J$ = 3.2, 6.8 Hz), 4.08 (1H, dd, $J$ = 2.0, 3.2 Hz), 3.98 (1H, dd, $J$ = 6.8, 8.2 Hz), 3.87 (1H, dd, $J$ = 6.8, 8.2 Hz), 3.62−3.48 (2H, m), 3.49 (2H, q, $J$ = 7.0 Hz), 2.31 (1H, d, $J$ = 2.0 Hz), 1.42 (3H, s), 1.34 (3H, s), 1.19 (3H, t, $J$ = 7.0 Hz), 1.18 (3H, t, $J$ = 7.0 Hz). $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 134.4, 119.7, 108.0, 100.2, 75.3, 73.7, 64.6, 57.1, 56.9, 26.3, 25.3, 15.4, 15.3. EI-MS $m/z$: 245 ($M^+$ − Me), 215 ($M^+$ − OEt). Anal. Calcd for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29. Found: C, 59.85; H, 9.23.

**(1*S*)-1-[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2,2-diethoxy-3-buten-1-ol (*syn*-3k)**: colorless oil; $[\alpha]^{26}_D$ −8.0 ($c$ 1.78, $CHCl_3$). IR (neat) $\nu$ cm$^{-1}$; 3445, 1065. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.74 (1H, dd, $J$ = 10.7, 17.3 Hz), 5.56 (1H, dd, $J$ = 1.9, 17.3 Hz), 5.41 (1H, dd, $J$ = 1.9, 10.7 Hz), 4.14 (1H, dt, $J$ = 6.2, 8.0 Hz), 4.02 (1H, dd, $J$ = 6.2, 8.4 Hz), 3.79 (1H, dd, $J$ = 8.0, 8.4 Hz), 3.73 (1H, dd, $J$ = 5.0, 6.2 Hz), 3.60−3.37 (4H, m), 2.42 (1H, d, $J$ = 5.0 Hz), 1.41 (3H, s), 1.38 (3H, s), 1.23 (3H, t, $J$ = 7.0 Hz), 1.15 (3H, t, $J$ = 7.0 Hz). $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 134.5, 119.9, 108.9, 100.6, 75.9, 72.4, 67.0, 57.2, 56.3, 26.6, 25.9, 15.3, 15.2. EI-MS $m/z$: 245 ($M^+$ − Me), 215 ($M^+$ − OEt). Anal. Calcd for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29. Found: C, 60.01; H, 9.11.

**4-Hydroxy-6-phenyl-1-hexen-3-one (4g)**. To a solution of **3g** (42 mg, 0.17 mmol) in chloroform (1 mL) cooled with an ice-bath was added 50% trifluoroacetic acid (0.2 mL), and the mixture was stirred for 10 min. The reaction mixture was neutralized by addition of $NaHCO_3$ aq and extracted with chloroform. The organic layer was washed with brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was purified by neutral silica gel column chromatography (hexane−AcOEt = 3:1) to give **4g** (30 mg, 95%) as a colorless oil. IR (neat) $\nu$ cm$^{-1}$; 3465, 1695. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.32−7.17 (5H, m), 6.47 (1H, dd, $J$ = 10.4, 17.4 Hz), 6.33 (1H, dd, $J$ = 1.2, 17.4 Hz), 5.87 (1H, dd, $J$ = 1.2, 10.4 Hz), 4.41 (1H, ddd, $J$ = 3.5, 5.2, 8.4 Hz), 3.55 (1H, d, $J$ = 5.2 Hz), 2.85−2.69 (2H, m), 2.19−2.08 (1H, m), 1.81 (1H, dddd, $J$ = 5.0, 8.4, 8.4, 13.9 Hz). $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 201.0, 141.1, 131.2, 130.5, 128.6, 128.5, 126.1, 74.3, 36.1, 31.1. EI-MS $m/z$ 190 ($M^+$). HRMS Calcd for $C_{12}H_{14}O_2$: 190.0994 ($M^+$). Found: 190.0994.

**(1*S*,2*S*)- and (1*S*,2*R*)-1-[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-3-butene-1,2-diol (5 and 6).** After a solution of *anti*-**3k** (31 mg, 0.12 mmol) in 50% trifluoroacetic acid (0.3 mL) and chloroform (1.5 mL) was stirred for 10 min at 0 °C, the reaction mixture was neutralized by addition of $NaHCO_3$ aq and extracted with chloroform. The organic layer was washed with brine, dried over $MgSO_4$, and then concentrated under reduced pressure to give the crude hydroxy ketone *anti*-**4k** (20.6 mg) after

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briefly purified by passing neutral silica gel column chromatography (hexane−AcOEt = 5:1). To a solution of *anti*-**4k** (20.6 mg) in THF (1.5 mL) cooled with ice-bath were added $CeCl_3 \cdot 7H_2O$ (41.2 mg) in $H_2O$ (0.5 mL) and $NaBH_4$ (38 mg) in $H_2O$ (0.5 mL), and the mixture was stirred for 15 min. Extractive workup (AcOEt for extraction) and purification by silica gel column chromatography (hexane−AcOEt = 1:2) gave a mixture of the dihydroxy compounds **5** and **6** (17.9 mg, 80%) in a ratio of 10.5:1 as determined by $^1$H NMR. Further purification by MPLC ($CHCl_3$−*i*-PrOH = 7:1) gave pure **5** and **6**, respectively. **5**: colorless oil; $[\alpha]^{28}_D$ +4.44 (c 1.71, $CHCl_3$), [lit.[14] $[\alpha]^{23}_D$ +7.0 (*c* 0.95, $CHCl_3$)]. $^1$H NMR (400 MHz, $CDCl_3$)[14] $\delta$ 5.92 (1H, ddd, *J* = 6.3, 10.6, 17.3 Hz), 5.39 (1H, ddd, *J* = 1.4, 2.9, 17.3 Hz), 5.29 (1H, ddd, *J* = 1.4, 2.9, 10.6 Hz), 4.30 (1H, dd, *J* = 5.0, 6.3 Hz), 4.09−4.02 (2H, m), 3.99−3.93 (1H, m), 3.72 (1H, dd, *J* = 5.0, 5.0 Hz), 2.75 (1H, brs), 2.50 (1H, brs), 1.42 (3H, s), 1.34 (3H, s). $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 135.8, 118.0, 109.0, 76.3, 74.1, 73.5, 66.2, 26.6, 25.3. **6**: colorless oil; $[\alpha]^{27}_D$ +35.3 (c 0.16, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.95 (1H, ddd, *J* = 5.8, 10.5, 17.3 Hz), 5.39 (1H, ddd, *J* = 1.4, 1.4, 17.3 Hz), 5.28 (1H, ddd, *J* = 1.4, 1.4, 10.5 Hz), 4.28−4.23 (1H, m), 4.16 (1H, ddd, *J* = 6.2, 6.2, 6.2 Hz), 4.08 (1H, dd, *J* = 6.2, 8.4 Hz), 3.97 (1H, dd, *J* = 6.2, 8.4 Hz), 3.62 (1H, ddd, *J* = 3.4, 5.7, 6.2 Hz), 2.32 (1H, d, *J* = 5.1 Hz), 2.25 (1H, *J* = 5.7 Hz), 1.43 (3H, s), 1.37 (3H, s). $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 137.1, 117.1, 109.2, 75.9, 73.7, 72.1, 66.0, 26.7, 25.2.

**(1*R*,2*R*)-1-[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-3-butene-1,2-diol (7).** In a similar manner as above, *syn*-**3** (10.4 mg) gave *syn*-**4** (6.8 mg), which was reduced to a mixture of the alcohol **7** and **8** (5.4 mg, 72%) in a ratio of 8.3:1. MPLC purification ($CHCl_3$−AcOEt = 1:2) gave pure **7** and a mixture of **7** and **8**. **7**: colorless oil; $[\alpha]^{26}_D$ +13.4 (*c* 1.00, $CHCl_3$), [lit.[14] $[\alpha]^{23}_D$ +13.9 (*c* 0.72, $CHCl_3$)]. $^1$H NMR (400 MHz, $CDCl_3$)[14] $\delta$ 5.95 (1H, ddd, *J* = 5.6, 10.6, 17.2 Hz), 5.38 (1H, ddd, *J* = 1.5, 1.5, 17.2 Hz), 5.28 (1H, ddd, *J* = 1.5, 1.5, 10.6 Hz), 4.30−4.22 (2H, m), 4.03 (2H, dd, *J* = 6.5, 8.2 Hz), 3.88 (1H, dd, *J* = 7.2, 8.2 Hz), 3.53 (1H, ddd, *J* = 4.5, 4.5, 7.1 Hz), 2.62 (1H, m), 2.15 (1H, m), 1.44 (3H, s), 1.37 (3H, s). $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 136.7, 116.8, 109.4, 75.4, 74.4, 72.9, 66.3, 26.3, 25.3.

**Supporting Information Available:** Characterization data ($^1$H and $^{13}$C NMR, IR, MS, and elemental analyses data) of **3b**−**f**,**h**−**j** and **4d**,**h**; $^1$H and $^{13}$C NMR spectra of **3e** and **4d**,**g**,**h**; $^1$H, $^1$H−$^1$H COSY, and $^{13}$C NMR spectra of **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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