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Pd(0)-Catalyzed Hydrogenolysis of Allylic and Dienylic Cyclic Carbonates: Synthesis of Optically Active Homoallylic Alcohols and Allylic Alcohols

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Pd(0)-CATALYZED HYDROGENOLYSIS OF ALLYLIC AND DIENYLIC CYCLIC CARBONATES: SYNTHESIS OF OPTICALLY ACTIVE HOMOALLYLIC ALCOHOLS AND ALLYLIC ALCOHOLS

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Abstract: Treatment of chiral allylic cyclic carbonates with ammonium formate in the presence of Pd(0) catalyst afforded optically active homoallylic alcohols with excellent regioselectivity. However, hydrogenolysis of dienylic cyclic carbonates in the presence of Pd(0) catalyst afforded conjugated or nonconjugated (*E*)-dienylic alcohols depending on Pd complexes used. Using homoallylic alcohol **3c** as a chiral synthon, (*R*)-(+)-eldanolide, the sex pheromone of the African sugarcane stem borer, *Eldana saccharina*, was synthesized.

Optically active homoallylic alcohols and allylic alcohols are versatile chiral synthons in organic synthesis. Much effort has aimed at preparing enantio-enriched homoallylic alcohols by enantioselective allylation of aldehydes[1] and some optically active (*E*)-allylic alcohols could be prepared by Sharpless kinetic resolutions.[2] As our program to utilize cyclic carbonates in preparing useful chiral synthons,[3] we have found that optically active homoallylic alcohols and allylic alcohols can be prepared from chiral allylic and dienylic cyclic carbonates by utilizing highly

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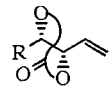
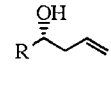
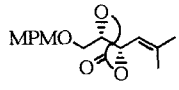
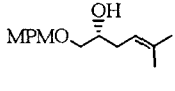
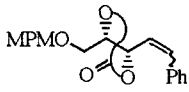
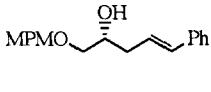
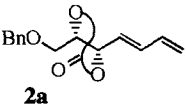
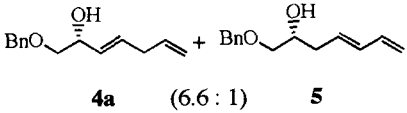
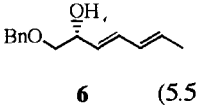
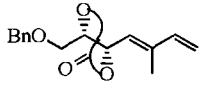
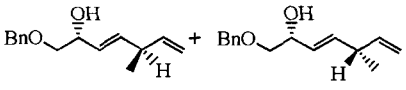
selective palladium-catalyzed hydrogenolysis.[4] The results of the palladium-catalyzed hydrogenolysis of allylic and dienyl cyclic carbonates are summarized in Table 1. The optically active allylic cyclic carbonates **1a**[3e] and **1b** were reacted with ammonium formate in the presence of $(Ph_3P)_4Pd$ (5 mol%) in refluxing THF for 10 min to afford the homoallylic alcohols **3a** and **3b** as the sole products with excellent regioselectivites (entries 1 and 2). For the substituted allylic carbonate **1c**, treatment with ammonium formate in the presence of $[Pd(acac)_2]$-nBu$_3$P(cat.) provided the homoallylic alcohol **3c** (entry 3). With $(Ph_3P)_4Pd$ as a catalyst, on treatment of the cyclic carbonate **1d** (*cis : trans* = 6 : 1), the (*E*)-homoallylic alcohol **3d** was obtained as the only isolated prduct, which was confirmed by ^{1}H NMR coupling constant (entry 4). For the (*E*)-dienylic cyclic carbonate **2a**, hydrogenolysis with ammonium formate in the presence of $(Ph_3P)_4Pd$ afforded the allylic alcohol **4a** and the homodienyl alcohol **5** in the ratio of 6.6 : 1 (entry 5). The favored regioselectivity associated with γ-hydride shift in the palladium complex of **2a** is presumed to be electronic effect of allyl unit. However, by using $Pd(acac)_2$ and *n*-tributyl phosphine as catalysts, hydrogenolysis of **2a** afforded the (*E,E*)-dienylic alcohol **6** as a major product (entry 6). Finally, the substituted (*E,E*)-dienylic cyclic carbonate **2b** with ammonium formate in the presence of a catalytic amount of $Pd_2(dba)_3$·$CHCl_3$ and nBu$_3$P afforded the homoallylic alcohols, (2*R*,5*R*)-**4b**[5] and (2*R*,5*S*)-**4b**, in the ratio of 1.2 : 1 (entry 7). To correlate the absolute configuration of the stereogenic centers of **4b**, the compounds, (2*R*,5*R*)-**4b** and (2*R*,5*S*)-**4b,** were prepared separately from the reactions of *cis* and *trans*-substituted allylic cyclic carbonates **7** and **8** with organocuprates (Scheme 1). The chemical shift for the methyl group of (*2R,5R*)-**4b** thus prepared showed a doublet at δ 1.10, whereas (*2R,5S*)-**4b** showed at δ 1.09 in 500 MHz ^{1}H NMR.

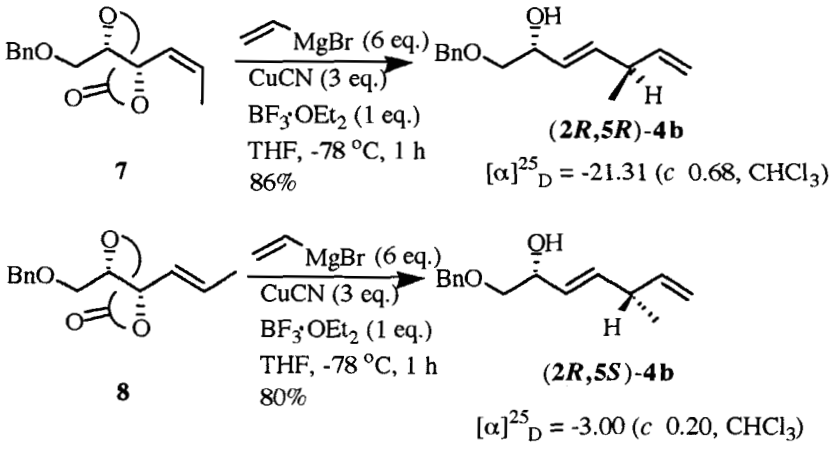
Using homoallylic alcohol **3c** as a chiral synthon, the sex pheromone of the African sugarcane stem borer, *Eldana saccharina* , was synthesized (Scheme 2).[6]

Table 1. Pd(0)-Catalyzed Hydrogenolysis of Allylic and Dienylic Cyclic Carbonates

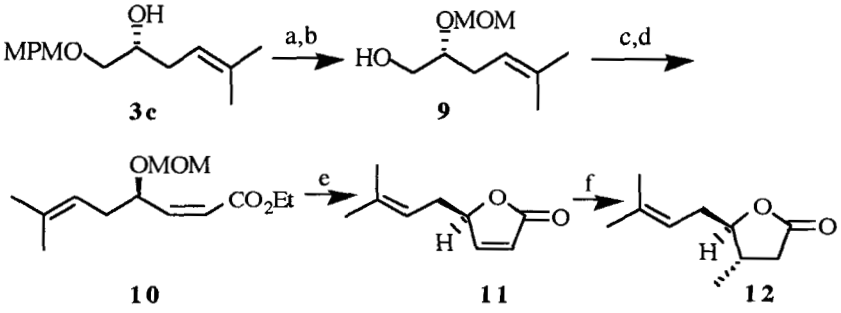
Entry	Substrate	Reaction Condition[a]	Product[b]	Yield(%)
1	 **1a** R = $BnOCH_2$-	**A**	 **3a** R = $BnOCH_2$-	95
2	**1b** R = *n*-C_3H_7-	**A**	**3b** R = *n*-C_3H_7-	83
3	 **1c**[c]	**B**	 **3c**	99
4	 **1d** (*cis* : *trans* = 6 : 1)	**A**	 **3d**	97
5	 **2a**	**A**	 **4a** (6.6 : 1) **5**	93
6	**2a**	**C**	 **6** (5.5 : 1)	98
7	 **2b**	**D**	 (2*R*, 5*R*)-**4b** (1.2 : 1)[d] (2*R*, 5*S*)-**4b**	97

[a] **A:** $(Ph_3P)_4Pd$ (5 mol%), HCO_2NH_4 (2 eq.), THF, reflux, 10 min. **B:** $Pd(acac)_2$ (5 mol%), nBu_3P (5 mol%), HCO_2NH_4 (2 eq.), PhH, reflux, 30 min. **C:** $Pd(acac)_2$ (5 mol%), nBu_3P (5 mol%), HCO_2NH_4 (2 eq.), PhH, rt, 30 min. **D:** $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%), nBu_3P (5 mol%), HCO_2NH_4 (2 eq.), PhH, reflux, 10 min. [b] $[\alpha]^{25}_D$ values in $CHCl_3$, **3a**: -6.60 (*c* 0.42), **3b**: -12.67 (*c* 0.54), **3c**: -10.01 (*c* 0.12), **3d**: -8.41 (*c* 0.16). [c] MPM = *p*-methoxyphenylmethyl. [d] The ratio was determined by comparison of the chemical shift for the methyl group in 500 MHz ^1H NMR.

Synthesis of (2*R*,5*R*)-4b and (2*R*,5*S*)-4b



Scheme 1



Reagents and conditions: (a) MOMCl,*i*Pr$_2$NEt, CH_2Cl_2, rt, 2 h (91%) (b) DDQ, CH_2Cl_2/H_2O (18 : 1), rt, 10 min (82%) (c) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78 °C→rt, 1.5 h (d) $(CF_3CH_2O)_2POCH_2CO_2Et$, $KN(TMS)_2$, 18-crown-6, THF, -78 °C, 1 h (76% overall) (e) TFA, CH_2Cl_2/H_2O (10 : 1), rt, 1 h (73%) (f) Me_2CuLi, Et_2O, -20 °C, 30 min

Scheme 2

The homoallylic alcohol **3c** was protected as methoxymethylether (MOM) and then *p*-methoxyphenylmethyl (MPM) protecting group was removed[7] to provide the alcohol **9**. The alcohol **9** was oxidized and then *cis*-Wittig olefination[8] gave (*Z*)-α,β-unsaturated ester **10** (*Z* : *E* = 20 : 1). The (*Z*)-α,β-unsaturated ester was subjected to deprotection, followed by lactonization to afford the penultimate product **11**, $[\alpha]^{25}_{D}$ -127 (*c* 0.16, MeOH) [lit[6d] $[\alpha]^{25}_{D}$ -130 (*c* 0.80, MeOH)]. The unsaturated lactone **11** was converted to the final product **12** by the reported procedure[6d] (Scheme 2).

EXPERIMENTAL

(2*R*)-1-*O*-Benzyl-4-penten-2-ol (3a)

General Procedures. Method A: To a stirred solution of the carbonate **1a** (258 mg, 1.10 mmol) in dry THF (4 ml) under N_2 was added ammonium formate (139 mg, 2.20 mmol) and $Pd(PPh_3)_4$ (38 mg, 5 mol%). After stirring at reflux for 10 min, the reaction mixture was cooled and THF was evaporated. The residue was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 3 R_f = 0.29) to afford **3a** (183 mg, 95%). TLC; SiO_2, EtOAc/hexanes 1 : 3, R_f = 0.29. $[\alpha]^{25}_{D}$ = -6.60 (*c* 0.42, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 2.27 (m, 2H), 3.38 (dd, 1H, *J* = 9.4, 7.4 Hz), 3.52 (dd, *J* = 9.5, 3.4 Hz), 3.89 (m, 1H), 4.56 (s, 2H), 5.12 (m, 2H), 5.38 (m, 1H), 7.33 (s, 5H). IR(neat) 3400, 1620 cm^{-1}. MS(m/e): 192(M^+), 174, 107, 91(base peak), 71, 65, 43.

(4*S*)-1-Hepten-4-ol (3b)

TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.71. $[\alpha]^{25}_{D}$ = -12.7 (*c* 0.54, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 6.7 Hz), 1.42 (m, 4H), 2.20 (m, 2H),

3.65 (m, 1H), 5.12 (m, 2H), 5.83 (m, 1H). IR(neat) 3400, 1620 cm^{-1}. MS(m/e): 114(M^+), 96.

(2*R*)-1-*O*-(4-Methoxybenzyl)-5-methyl-4-hexen-2-ol (3c)

Method B: $Pd(acac)_2$ (13 mg, 5 mol%) and nBu_3P (8.6 mg, 5 mol%) were mixed in a 1 : 1 ratio in dry benzene (4 ml) to form a pale yellow solution. Then the carbonate **1c** (250 mg, 0.85 mmol) in dry benzene (4 ml) was added followed by ammonium formate (107 mg, 1.70 mmol) and the mixture was stirred for 30 min at reflux. THF was evaporated and then the residue was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 2, R_f = 0.48) to afford **3c** (248 mg, 99%). TLC; SiO_2, EtOAc/hexanes 1 : 2, R_f = 0.48. $[\alpha]^{25}_D$ = -10.0 (*c* 0.12, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 1.62 (s, 3H), 1.70 (s, 3H), 2.18 (m, 2H), 3.30 (dd, 1H, *J* = 9.5, 7.4 Hz), 3.47 (dd, 1H, *J* = 9.5, 3.3 Hz), 3.80 (s, 3H), 3.80 (m, 1H), 4.49 (s, 2H), 5.14 (m, 1H), 6.85 (m, 2H), 7.25 (m, 2H). IR(neat) 3400, 2850, 1620 cm^{-1}. MS(m/e): 250(M^+), 193, 179, 163, 152, 137, 121(base peak), 99, 91, 77.

(2*R*,4*E*)-1-*O*-Benzyl-5-phenyl-4-penten-2-ol (3d)

TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.51. $[\alpha]^{25}_D$ = -8.4 (*c* 0.16, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 2.38 (m, 2H), 3.41 (dd, 1H, *J* = 9.5, 7.4 Hz), 3.57 (dd, 1H, *J* = 9.5, 3.5 Hz), 3.95 (m, 1H), 4.56 (s, 2H), 6.21 (dt, 1H, *J* = 15.9, 7.2 Hz), 6.45 (d, 1H, *J* = 15.9 Hz), 7.27 (m, 10H). IR(neat) 3400 cm^{-1}. MS(m/e): 268(M^+), 250, 193, 144, 117, 91(base peak), 77, 65, 51.

(2*S*,4*E*)-1-*O*-Benzyl-3-heptadien-2-ol (4a) and (2*R*,4*E*)-1-*O*-Benzyl-4,6-heptadien-2-ol (5)

4a (major): TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.70. ^1H NMR (200 MHz,

$CDCl_3$) δ 2.82 (m, 2H), 3.38 (m, 1H), 3.52 (m, 1H), 4.34 (m, 1H), 4.56 (s, 2H), 5.04 (m, 2H), 5.48 (dd, 1H, J = 15.5, 6.4 Hz), 5.78 (m, 2H), 7.35 (s, 5H). IR(neat) 3400, 1620 cm^{-1}. MS(m/e): 218(M^+), 189, 176, 150, 127, 105, 91(base peak), 79, 41. **5** (minor): TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.70. ^1H NMR (200 MHz, $CDCl_3$) δ 2.31 (t, 2H, J = 6.8 Hz), 3.38 (m, 1H), 3.52 (m, 1H), 3.89 (m, 1H), 4.56 (s, 2H), 5.04 (m, 2H), 5.62 (m, 1H), 6.05 (m, 1H), 6.30 (m, 1H), 7.35 (s, 5H).

(2*S*,3*E*,5*E*)-1-*O*-benzyl-3,5-heptadien-2-ol (6) and (2*R*,4*E*)-1-*O*-benzyl-4,6-heptadien-2-ol (5)

Method C: $Pd(acac)_2$ (11 mg, 5 mol%) and nBu_3P (7.1 mg, 5 mol%) were mixed in a 1 : 1 ratio in dry benzene (4 ml) to form a pale yellow solution. Then carbonate **1c** (200 mg, 0.70 mmol) in dry benzene (4 ml) was added followed by ammonium formate (88 mg, 1.40 mmol) and the mixture was stirred for 30 min. The benzene was evaporated and then the residue was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 1, R_f = 0.70) to afford **6** and **5** (196 mg, 98%). **6**: TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.70. ^1H NMR (200 MHz, $CDCl_3$) δ 1.75 (d, 3H, J = 14.7 Hz), 3.38 (dd, 1H, J = 9.3, 8.2 Hz), 3.52 (dd, 1H, J = 9.6, 3.4 Hz), 4.38 (m, 1H), 4.56 (s, 2H), 5.51 (dd, 1H, J = 15.4, 6.4 Hz), 5.76 (m, 1H), 6.07 (dd, 1H, J = 15.4, 10.6 Hz), 6.29 (dd, 1H, J = 15.4, 10.6 Hz), 7.35 (m, 5H). IR(neat) 3400, 1620 cm^{-1}. MS(m/e): 218(M^+), 189, 176, 150, 127, 105, 91(base peak), 79, 41.

(2*S*,5*R*,3*E*)-1-*O*-Benzyl-5-methyl-3,6-heptadien-2-ol [(2*R*,5*R*)-4b] and (2*S*,5*S*,3*E*)-1-*O*-Benzyl-5-methyl-3,6-heptadien-2-ol [(2*R*,5*S*)-4b]

Method D: $Pd_2(dba)_3 \cdot CHCl_3$ (52 mg, 5 mol%) and nBu_3P (10 mg, 5 mol%) were

mixed in a 1 : 1 ratio in dry benzene (4 ml) to form a pale yellow solution. Then the carbonate **2b** (250 mg, 0.91 mmol) in dry benzene (4 ml) was added followed by ammonium formate (114 mg, 1.82 mmol) and the mixture was stirred for 10 min at reflux. The benzene was evaporated and then the residue was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 5, R_f = 0.27) to afford (2*R*,5*R*)-**4b** and (2*R*,5*S*)-**4b** (242 mg, 97%). (2*R*,5*R*)-**4b** : TLC; SiO_2, EtOAc/hexanes 1 : 5, R_f = 0.27. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (d, 3H, *J* = 6.9 Hz), 2.87 (m, 1H), 3.38 (dd, 1H, *J* = 9.5, 8.2 Hz), 3.52 (dd, 1H, *J* = 9.6, 3.4 Hz), 4.34 (m, 1H), 5.01 (m, 2H), 5.45 (dd, 1H, *J* = 15.6, 6.4 Hz), 5.75 (m, 2H). IR(neat) 3400, 1640 cm^{-1}. MS(m/e): 232(M^+), 214, 189, 171, 158, 111, 91(base peak), 77, 65, 55, 43. (2*R*,5*S*)-**4b**: TLC; SiO_2, EtOAc/hexanes 1 : 5, R_f = 0.27. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.09 (d, 3H, *J* = 6.9 Hz), 2.87 (m, 1H), 3.38 (dd, 1H, *J* = 9.5, 8.2 Hz), 3.52 (dd, 1H, *J* = 9.6, 3.4 Hz), 4.34 (m, 1H), 5.01 (m, 2H), 5.45 (dd, 1H, *J* = 15.6, 6.4 Hz), 5.75 (m, 2H). IR(neat) 3400, 1640 cm^{-1}. MS(m/e): 232(M^+), 214, 189, 171, 158, 111, 91(base peak), 77, 65, 55, 43.

Preparation of (2*R*,5*R*)-4b:

To a stirred solution of CuCN (53.7 mg, 0.60 mmol) in dry THF (1 ml) at -78 °C under N_2 was added vinylmagnesium bromide (1.20 ml, 1.20 mmol, 1 M in THF) followed by BF_3·OEt_2 (0.025 ml, 0.20 mmol) in dry THF (1 ml) and then **7** (50 mg, 0.20 mmol) in dry THF (0.5 ml). After stirring for 10 min at -78 °C, the reaction mixture was quenched with saturated NH_4Cl solution (1 ml). THF was evaporated and the residue was extracted with ether (20 ml). The ether layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 4, R_f = 0.43) to afforded (2*R*,5*R*)-**4b** (43 mg, 86%).

Preparation of (2*R*,5*S*)-4b:

To a stirred solution of CuCN (64.4 mg, 0.72 mmol) in the dry THF (1 ml) at -78 °C under N_2 was added vinylmagnasium bromide (1.44 ml, 1.44 mmol, 1M in THF) followed by $BF_3{\cdot}OEt_2$ (0.03 ml, 0.24 mmol) in dry THF (1 ml) and then **8** (60 mg, 0.24mmol) in dry THF (0.5 ml). After stirring for 10 min at -78 °C, the reaction mixture was quenched with saturated NH_4Cl solution (1 ml). THF was evaporated and the residue was extracted with ether (20 ml). The ether layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 4, R_f= 0.43) to afforded (2*R*,5*S*)-**4b** (48 mg, 80%).

(2*R*)-2-*O*-(methoxymethyl)-5-methyl-4-hexen-1-ol (9)

To a stirred solution of **3c** (400 mg, 1.60 mmol) in dry methylene chloride (3 ml) under N_2 was added diisopropylethylamine (310 mg, 2.40 mmol) and chloromethyl methylether (193 mg, 2.40 mmol). After stirring for 2 h at room temperature, the reaction mixture was quenched with saturated NH_4Cl solution (1 ml) and then extracted with ether (40 ml). The ether layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 2, R_f = 0.76) to afford the protected compound (364 mg, 91%). This compound was added to methylene chloride and H_2O (18 : 1) and DDQ (363 mg, 1.60 mmol). After stirring at room temperature for 10 min, the reaction mixture was filtered through Celite to remove the solid and washed with ether. The ether layer was dried anhydrous magnesium sulfate and evaporated *in vacuo*. The residue was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 1, R_f = 0.49) to afford **9** (216 mg, 82%). TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.49. $[\alpha]^{25}_D$ = -54 (*c* 0.35, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 1.62 (s, 3H), 1.70 (s, 3H), 2.18 (m, 2H), 3.40 (s,

3H), 3.51 (m, 1H), 3.60 (m, 1H), 3.80 (m, 1H), 4.62 (s, 2H), 5.14 (m, 1H). IR(neat) 3400, 2850, 1620 cm^{-1}. MS(m/e): 174(M^+), 143, 129, 69, 45(base peak).

Ethyl (4*R*,2*Z*)-4-*O*-(methoxymethyl)-7-methyl-2,6-octadienoate (10)

To a stirred solution of oxalyl chloride (189 mg, 1.49 mmol) in dry methylene chloride (4 ml) at -78 °C was added dimethylsulfoxide (232 mg, 2.98 mmol) dropwise and the reaction mixture was stirred 10 min. The alcohol **9** (216 mg, 1.24 mmol) was added and the mixture was stirred for 45 min at -78 °C and then triethylamine (897 mg, 8.68 mmol) was added. The reaction mixture was allowed to warm up to room temperature and srirred for 30 min. The solution was evaporated and the residue was extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo* to afford the crude aldehyde. To a solution of $(CF_3CH_2O)_2POCH_2CO_2Et$ (592 mg, 1.86 mmol), 18-crown-6 (983 mg, 3.72 mmol) in THF (3 ml) at -78 °C was added $KN(TMS)_2$ (506 mg, 1.86 mmol). The crude aldehyde was added and the mixture was stirred for 1 h at -78 °C. After quenching with saturated NH_4Cl, the reaction mixture was extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 4, R_f = 0.54) to afford **10** (164 mg, 76%). (TLC; SiO_2, EtOAc/hexanes 1 : 4, R_f = 0.54. ^1H NMR (200 MHz, $CDCl_3$) δ 1,30 (t, 3H, J = 6.9 Hz) 1.62 (s, 3H), 1.70 (s, 3H), 2.34 (m, 2H), 3.38 (s, 3H), 4.32 (q, 2H, J = 6.9 Hz) 4.64 (s, 2H), 5.18 ~ 5.28 (m, 2H), 5.83 (d, 1H, J = 11.4 Hz), 6.19 (dd, 1H, J = 11.4, 8.6 Hz). IR(neat) 2850, 1720 cm^{-1}. MS(m/e): 242(M^+), 197, 173, 69, 45(base peak).

(5*R*)-5-(3-methyl-2-butenyl)-2(5H)-furanone (11)

To a solution of the **10** (164 mg, 0.70 mmol) in methylene chloride and H_2O (10 : 1) was added trifluoroacetic acid (159 mg, 1.40 mmol). After stirring at

room temperature for 1 h, the reaction mixture was extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The residue was separated by SiO_2 column chromatography (EtOAc/hexanes 1 : 4 R_f = 0.32) to afford **11** (116 mg, 73%). TLC; SiO_2, EtOAc/hexanes 1 : 4, R_f = 0.32. $[\alpha]^{25}_D$ = -127 (*c* 0.16, MeOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.58 (s, 3H), 1.97 (m, 2H), 5.04 ~ 5.10 (m, 2H), 6.18 (dd, 1H, *J* = 6.0, 1.0 Hz), 7.45 (dd, 1H, *J* = 6.0, 1.0 Hz). MS(m/e): 152(M^+), 97, 84, 83, 69(base peak), 55.

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