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Stereoselective Construction of a *β*-Isopropenyl Alcohol Moiety at the C(2) and (3) of Kallolide A and Pinnatin A Using a [2,3] Wittig Rearrangement of Cyclic Furfuryl Ethers

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Abstract: A stereocontrolled synthesis of *anti*- and *syn*-*β*-isopropenyl alcohol moieties at the C(2)−C(3) positions of kallolide A and pinnatin A was accomplished employing the [2,3] Wittig rearrangement of (*E*)-and (Z)-cyclic furfuryl ethers **8**. Enantioselective Wittig rearrangement of (*E*)- and (*Z*)-furfuryl ethers **8** using butyllithium and a chiral bis-(oxazoline) was also examined to provide (2*R*,3*R*)-homoallylic alcohol *anti*-**9** in up to 61% ee and (2*R*,3*S*)-*syn*-**9** in up to 93% ee, respectively.

Investigation of Caribbean gorgonian octocorals of the genus *Pseudopterogorgia* has led to the isolation and structure determination of several classes of metabolites, such as pseudopterane, cembrane, and gersolane diterpenoids, many of which are of great interest because of their structural complexity and their potential pharmacological activity.[1] Kallolide A is a member of the pseudopterane class and shows anti-inflammatory activity[2] (Figure 1). Bipinnatin J is an example of the highly functionalized furanocembrane family.[3] Recently, the structure of pinnatin A, a member of the gersolane class diterpenoids, has been elucidated and exhibits significant differential antitumor activity.[4] Their common structural features are a 12- to 14-membered α,α′-disubstituted *β*-methylfuran carbocyclic skeleton possessing a butenolide and a *β*-isopropenyl alcohol moiety at the C(2) and C(3) positions. The total synthesis of kallolide A has been accomplished by Marshall et al.[5] using a diastereoselective [2,3] Wittig ring contraction; however, no total synthesis of bipinnatin J and pinnatin A has been reported to date.

We recently described the Wittig rearrangement of allyl furfuryl ethers leading to 2-furylmethanol derivatives.[6] A major advantage of this Wittig rearrangement is that the α-oxycarbanion, deprotonated preferentially by BuLi, proceeds via 2,3-sigmatropic rearrangement to give stereoselectively homoallylic alcohols. Marshall et al. have reported a [2,3] Wittig rearrangement of a macrocyclic furan diether, in which the allylic furfuryl ether moiety did not react via Wittig rearrangement, probably due to conformational constraints in the macrocyclic furanoether ring system.[7] Thus, we intended to investigate the Wittig rearrangement of cyclic allylic furfuryl ether for the synthesis of 2,5-bridged furanocycles containing a *β*-isopropenyl alcohol moiety at the C(2) and C(3) positions (Scheme 1). We report here the stereoselective construction of both *anti*- and *syn*-*β*-isopropenyl alcohol moieties in 12-membered 2,5-furanocycles.

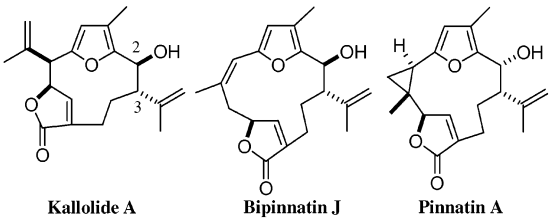
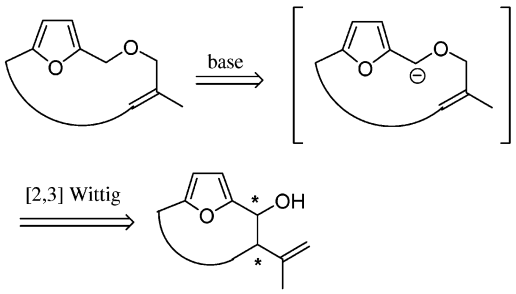


FIGURE 1. Structure of furanocyclic diterpenes.

SCHEME 1. Synthetic Strategy for a *β*-Isopropenyl Alcohol Moiety of the Furanocyclic Diterpenes



Isomers **8** were chosen to study their [2,3] Wittig rearrangement, and this constituted a model study for the natural furanocyclic compounds. Preparation of (*E*)-**8** is shown in Scheme 2. The Pd-catalyzed cross-coupling reaction[8] of 6-cyanohexylzinc bromide with known bromofuran **1**[9] gave cyano ester **2**, whose partial reduction with DIBAL afforded hydroxy aldehyde **3**. The Wittig reaction of ethyl 2-(triphenylphosphoranylidene)propionate with aldehyde **3** gave the unstable methacrylate, which was directly protected as silyl ether (*E*)-**4**. Reduction of ester (*E*)-**4** with DIBAL afforded allylic alcohol (*E*)-**5**, which was chlorinated using the Meyers' procedure[10]

(1) (a) Fenical, W. *J. Nat. Prod.* **1987**, *50*, 1001−1008. (b) Rodríguez, A. D. *Tetrahedron* **1995**, *51*, 4571−4618 and references therein.
(2) Look, S. A.; Burch, M. T.; Fenical, W.; Zhen, Q.-t.; Clardy, J. *J. Org. Chem.* **1985**, *50*, 5741−5746.
(3) Rodríguez, A. D.; Shi, J.-G.; Huang, S. D. *J. Nat. Prod.* **1999**, *62*, 1228−1237.
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(5) Marshall, J. A.; Liao, J. *J. Org. Chem.* **1998**, *63*, 5962−5970.
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(7) Marshall, J. A.; Nelson, D. J. *Tetrahedron Lett.* **1988**, *29*, 741−744.
(8) (a) Zhu, L.; Wehmeyer, R. M.; Rieke, R. D. *J. Org. Chem.* **1991**, *56*, 1445−1453. (b) Biller, S. A.; Abt, J. W.; Pudzianowski, A. T.; Rich, L. C.; Slusarchyk, D. A.; Ciosek, C. P., Jr. *Bioorg. Med. Chem. Lett.* **1993**, *3*, 595−600. (c) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1157−1158. (d) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340−348.
(9) (a) Knight, D. W.; Rustidge, D. C. *J. Chem. Soc., Perkin Trans. 1* **1981**, 679−683. (b) Grigg, R.; Knight, J. A.; Sargent, M. V. *J. Chem. Soc.* **1966**, 976−981.
(10) Collington, E. W.; Meyers, A. I. *J. Org. Chem.* **1971**, *36*, 3044−3045.

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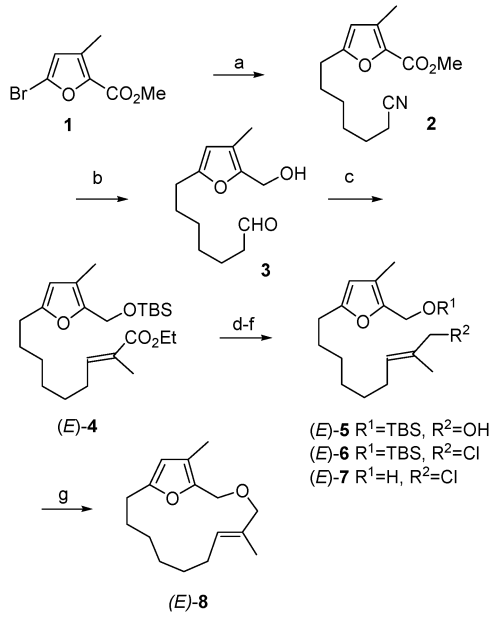
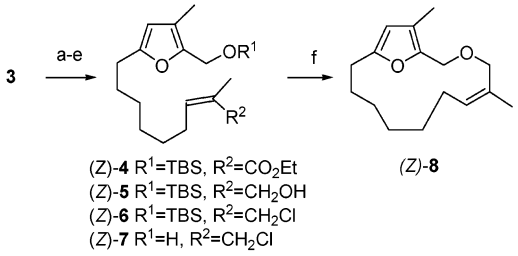
SCHEME 2. Preparation of (*E*)-Cyclic Furfuryl Ether (*E*)-8[a]



[a] Key: (a) $NC(CH_2)_6ZnBr$, $Pd(PPh_3)_4$, THF (84%); (b) DIBAL,-CH_2Cl_2, −78 °C (80%); (c) (i) $Ph_3P{=}C(CH_3)CO_2Et$, CH_3CN, (ii) TBSOTf, γ-collidine,CH_2Cl_2, −78 °C (82%, two steps); (d) DIBAL, CH_2Cl_2, −78 °C (89%); (e) MsCl, LiCl, 2,6-lutidine, DMF, −5 °C (93%); (f) TBAF, THF (98%); (g) NaH, 18-crown-6, benzene, reflux (92%).

SCHEME 3. Preparation of (*Z*)-Cyclic Furfuryl Ether (*Z*)-8[a]



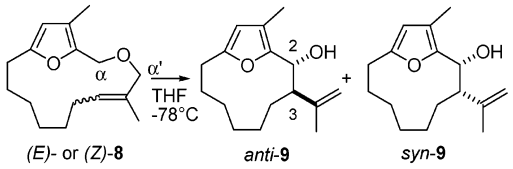
[a] Key: (a) $(PhO)_2P(O)CH(CH_3)CO_2Et$, NaH, THF, −78 °C (69%); (b) TBSOTf, γ-collidine, CH_2Cl_2, −78 °C (87%); (c) DIBAL,CH_2Cl_2, −78 °C (88%); (d) MsCl, LiCl, 2,6-lutidine, DMF, −5 °C (94%); (e) TBAF, THF (93%); (g) NaH, 18-crown-6, benzene, reflux (81%).

to yield allylic chloride (*E*)-**6**. Deprotection of the silyl moiety in (*E*)-**6** produced furfuryl alcohol (*E*)-**7**, which was cyclized using Marshall's condition[5] to furnish the desired cyclic ether (*E*)-**8**.

(*Z*)-Cyclic furfuryl ether (*Z*)-**8** was also prepared from aldehyde **3** as shown in Scheme 3. Methacrylate (*Z*)-**4** was obtained by reaction of the anion of ethyl 2-(diphenylphosphono)propionate with **3** using Ando's protocol.[11] In this Horner−Wadsworth−Emmons reaction, (*Z*)-methacrylate was formed as a predominant stereoisomer (ca. 10:1). Conversion of ester (*Z*)-**4** into cyclic ether (*Z*)-**8** was carried out by the same reactions used for the preparation of (*E*)-alkenes.[12]

We were pleased to observe that selective deprotonation at the α position followed by 2,3 rearrangement occurred in the Wittig rearrangement of both cyclic furfuryl ethers (*E*)- and (*Z*)-**8**, although the deprotonation site was affected by the base employed in the acyclic system.[6] The results of the diastereoselective Wittig rearrangement of cyclic furfuryl ethers **8** are shown in Table 1. Treatment of (*E*)-**8** with excess alkyllithium or LDA in THF afforded isopropenyl alcohol *anti*-**9** as a predominant stereoisomer in moderate to good selectivity (56−90%de) (entries 1−3 and 7). Decreasing the amount of *t*-BuLi used resulted in low conversion (entry 4). Interestingly, when the reaction of (*E*)-**8** using 6.6 equiv of *t*-BuLi in the case of entry 3 was quenched with deuterium oxide, deuteriolysis occurred at the isopropenyl methyl moiety to provide the deuterated *anti*-**9** in 80% *d*-content, indicating that at least 1 equiv of *t*-BuLi was consumed in deprotonation at the isopropenyl methyl moiety. Excess *t*-BuLi was required for the rearrangement regardless of the use of HMPA as an additive[13] (entry 6). A solvent effect was observed when the reaction did not proceed in Et_2O[14] (entry 5). The rearrangement of (*Z*)-**8** proceeded with relatively high diastereoselectivity (84−92%de) compared with that of (*E*)-**8** (entries 8−10). Assignment of the relative stereochemistry of both *anti*- and *syn*-**9** was based on 2D-NOE experiments[15] and comparison of the ^1H NMR chemical shifts and coupling constants with those of kallolide A and pinnatin A.

TABLE 1. Wittig Rearrangement of Cyclic Furfuryl Ethers 8



entry	substrate	base[a]	yield (%)	ratio of *anti*-**9**/*syn*-**9**
1[b]	(*E*)-**8**	*n*-BuLi	52	89:11
2	(*E*)-**8**	*s*-BuLi	75	95:5
3	(*E*)-**8**	*t*-BuLi	73	92:8
4	(*E*)-**8**	*t*-BuLi*c*	23[d]	99:1
5[e]	(*E*)-**8**	*t*-BuLi	NR	
6[f]	(*E*)-**8**	*t*-BuLi	56	47:53
7[b]	(*E*)-**8**	LDA	70	78:22
8[b]	(*Z*)-**8**[g]	*n*-BuLi	77	4:96
9	(*Z*)-**8**[g]	*s*-BuLi	84	5:95
10	(*Z*)-**8**[g]	*t*-BuLi	80	8:92

[a] *n*-BuLi (10 equiv), s-BuLi (3 equiv), *t*-BuLi (6.6 equiv), and LDA (10 equiv) were employed except as noted. [b] *T* (°C): −78 to 0. [c] *t*-BuLi (1.2 equiv) was used. [d] (*E*)-**8** was recovered. [e] Et_2O was used as solvent. [f] HMPA (2.7 equiv) was used as additive. [g] 91% *Z*.

We next turned our attention to the enantioselective Wittig rearrangement[16] of furanocyclic ethers **8**.[17] Ini-

(11) Ando, K. *J. Org. Chem.* **1998**, *63*, 8411−8416.

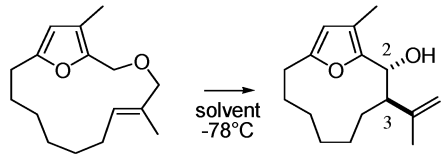
(12) As an alternative route, we examined the cyclization of 5-(7-octenyl)furfuryl methallyl ether using a ring closing metathesis reaction. Among commercially available Mo and Ru catalysts for RCM, only the use of a second-generation Grubbs' catalyst led to a 1:1 mixture of (*E*)- and (*Z*)-cyclic ethers in low yield. Chatterjee, A.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783−3784.

(13) The combined use of *t*-BuLi (6.6 equiv) and TMEDA (2.7 equiv) provided a 9:1 mixture of *anti*- and *syn*-**9** in 73% yield.

(14) None of the rearrangement occurred in hexane.

(15) NOE between the oxymethine proton H(2) and the isopropenyl methyl protons was observed in the spectrum of *anti*-**9**, whereas correlation between H(2) and H(3) was observed in the spectrum of *syn*-**9**.

TABLE 2. Enantioselective Wittig Rearrangement of (*E*)-8[a]



(E)-**8** *anti*-**9**

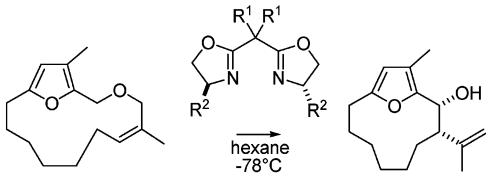
entry	base/Lc*	solvent	yield (%)	de (%)	ee[b] (%)
1	*s*-BuLi/**10**	THF	65	84	−9[c]
2	*s*-BuLi/**10**	hexane	0		
3	*t*-BuLi/**10**	THF	79	88	−6[c]
4	*t*-BuLi/**10**	hexane	0		
5	*s*-BuLi/**11**	THF	47	70	0
6	*s*-BuLi/**11**	hexane	34	98	0
7	*t*-BuLi/**11**	THF	70	74	5
8	*t*-BuLi/**11**	hexane	32	98	61

[a] *s*-BuLi (3 equiv) and *t*-BuLi (6.6 equiv). (1.5 equiv) of chiral ligand, (−)-sparteine **10** and (*S*)-2,2′-(2-pentylidene)bis(4-isoproyl-2-oxazoline) **11**, were used. [b] Values are for the anti isomer. Determined by HPLC analysis using a Daicel Chiralcel AD. [c] A negative sign indicates the absolute stereochemistry to be opposite to that depicted in *anti*-**9**.

tially, the rearrangement of (*E*)-**8** was studied, and the results are shown in Table 2. The reactions were carried out by treatment of (*E*)-**8** with excess amount of base (*s*- or *t*-BuLi) in the presence of chiral ligand ((−)-sparteine **10**[18] or (*S*,*S*)-bis(oxazoline) **11**[19]) at −78 °C. The use of BuLi and **10** in THF resulted in poor enantioselectivity (entries 1 and 3), while in hexane the reactions gave none of the [2,3] Wittig rearrangement products (entries 2 and 4). Interestingly, the combination of *t*-BuLi and **11** in hexane was found to provide higher enantioselectivity than those performed with the other alkyllithium and **10** in THF to furnish *anti*-**9** in 61%ee with 98%de (entry 8). In contrast, the use of *s*-BuLi and **11** in THF or hexane provided only racemic anti-**9** (entries 5 and 6). A similar result was reported in the enantioselective [2,3] Wittig rearrangement of crotyl propargyl ethers by Nakai et al.[20]

We further examined the enantioselective Wittig rearrangement of (*Z*)-**8** using bis(oxazoline) as a chiral ligand (Table 3). Surprisingly, the rearrangement of (*Z*)-**8** using *t*-BuLi and **11** resulted in poor enantioselectivity compared with that of (*E*)-**8** (entry 1). Thus, the effect of substituents on the bis(oxazoline) rings was studied. To our delight, changing the isopropyl group for a *tert*-butyl moiety at the C(4) position of oxazoline provided a significant improvement in enantioselectivity, and *syn*-**9**

TABLE 3. Enantioselective Wittig Rearrangement of (*Z*)-8[a]



(Z)-**8** *syn*-**9**

entry	ligand	yield (%)	de (%)	ee[b] (%)
1	**11**: R^1 = Et, R^2 = *i*-Pr	13	98	18
2	**12**: R^1 = Me, R^2 = *t*-Bu	16	98	91
3	**13**: R^1 = Et, R^2 = *t*-Bu	19	98	93
4	**14**: R^1 = Me, R^2 = Ph	0		

[a] *t*-BuLi (6.6 equiv) and bis(oxazoline) **11**−**14** (1.5 equiv) were used. The geometric purity was 91%. [b] Values are for the syn isomer. Determined by HPLC analysis using a Daicel Chiralcel AD.

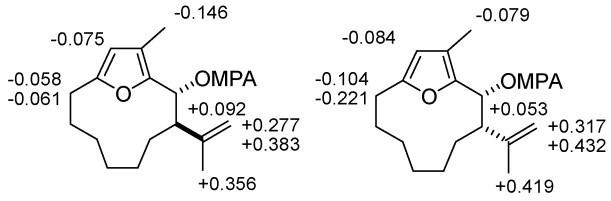


FIGURE 2. $\Delta\delta_{R-S}$ values obtained for the MPA esters of chiral *anti*- and *syn*-**9**.

was isolated in 91−93% ee (entries 2 and 3). The use of bis(4-phenyl-2-oxazoline) **14** did not give any desired product (entry 4).

The absolute configuration of *anti*-**9** (Table 2, entry 8) and *syn*-**9** (Table 3, entry 3) was determined by the MPA (methoxyphenylacetic acid) ester method[21] and is shown in Figure 2. Thus, both diastereomers have the same (*R*) configuration at C(2), indicating that the stereogenic centers of *anti*- and *syn*-**9** should be (2*R*,3*R*) and (2*R*,3*S*), respectively.

In conclusion, we have achieved a diastereoselective construction of *anti*- and *syn*-isopropenyl alcohol moieties at the C(2) and C(3) positions of 2,5-bridged furanocycles based on the [2,3] Wittig rearrangement of cyclic furfuryl ethers as a key step. This is a first example of a synthetic approach toward natural furanocycles based on the [2,3] Wittig rearrangement of cyclic furfuryl ethers. In addition, enantioselective Wittig rearrangement of cyclic furfuryl ethers using *t*-BuLi and bis(oxazoline) resulted in moderate to high enantioselectivity, although the chemical yields were low. Studies on the synthesis of kallolide A, bippinatin J, and pinnatin A are now in progress.

Experimental Section

The detailed procedures in the synthesis of cyclic furfuryl ethers **8** are described in the Supporting Information.

General Procedure for Wittig Rearrangement of Cyclic Furfuryl Ethers (Table 1). To a solution of cyclic furfuryl ether

(16) For recent reviews, see: (a) Marshall, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds; Pergamon Press: New York, 1991; Vol. 3, 975−1014. (b) Nakai, T.; Mikami, K. *Org. React*. **1994**, *46*, 105−209. (c) Nakai, T.; Tomooka, K. *Pure Appl. Chem*. **1997**, *69*, 595−600.

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(20) Tomooka, K.; Komine, N.; Nakai, T. *Tetrahedron Lett*. **1998**, *39*, 5513−5516.

(21) (a) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem*. **1986**, *51*, 2370−2374. (b) Seco, J. M.; Latypov, S. K.; Quinoa, E.; Riguera, R. *Tetrahedron* **1997**, *53*, 8541−8564.

8 (49.6 mg, 0.2 mmol) in THF (1 mL) was added dropwise a base (*n*-BuLi 1.6 M in hexane, 1.33 mL, 2.0 mmol; *s*-BuLi 1 M in cyclohexane, 0.6 mL, 0.6 mmol; *t*-BuLi 1.5 M in pentane, 0.8 mL, 1.2 mmol; or LDA 0.3 M in THF, 0.7 mL, 1.2 mmol) at −78 °C under Ar. After being stirred for 1 h (the reaction mixture was allowed to warm to 0 °C in the cases of *n*-BuLi or LDA used as the base), the reaction mixture was quenched with saturated aqueous NH_4Cl solution, and the solvent was removed under vacuum. The residue was extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil which was purified by silica gel chromatography using hexanes−Et_2O (95:5, v/v) as the eluent to give *syn*- and *anti*-homoallylic alcohols, respectively. Yields and the ratio of *anti*- and *syn*-**9** are shown in Table 1.

(2*R,3*R**)-3-Isopropenyl-12-methyl-13-oxabicyclo[8.2.1]-trideca-1(12),10-dien-2-ol *anti*-9:** colorless oil; IR ν max 3440 cm^{-1}; ^1H NMR ($CDCl_3$; 500 MHz) δ 0.70−1.25 (6H, m, $CH_2 \times 3$), 1.58−1.80 (4H, m, $2 \times CH_2$), 1.80 (3H, s, C=CCH_3), 1.97 (1H, br s, OH), 2.05 (1H, s, 12-CH_3), 2.55−2.78 (3H, m, 3-CH and 9-CH_2), 4.48 (1H, d, J = 10.4 Hz, 2-CH), 4.96 (2H, d, J = 12.8 Hz, =CH_2), 5.83 (1H, s, 11-CH); ^{13}C NMR ($CDCl_3$; 125 MHz) δ 9.7, 18.0, 23.5, 23.8, 25.5, 25.6, 25.7, 27.6, 52.4, 66.1, 109.2, 114.6, 119.9, 146.4, 146.7, 154.8; MS (EI) 248 (M^+); HRMS (EI) calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1792.

(2*R,3*S**)-3-Isopropenyl-12-methyl-13-oxabicyclo[8.2.1]-trideca-1(12),10-dien-2-ol *syn*-9:** colorless oil; IR ν max 3450 cm^{-1}; ^1H NMR ($CDCl_3$; 500 MHz) δ 0.48−0.78 (2H, m, CH_2), 1.04−1.38 (4H, m, $2 \times CH_2$), 1.50−1.75 (2H, m, CH_2), 1.88 (3H, s, C=CCH_3), 1.97 (3H, s, 12-CCH_3), 1.97−2.06 (2H, m, CH_2), 2.11 (1H, s, OH), 2.27 (1H, sextet, J = 5.8 Hz, 3-CH), 2.44−2.66 (2H, m, CH_2), 4.79 (1H, d, J = 1.2 Hz, 2-CH), 4.91 (2H, d, J = 11.9 Hz, =CH_2), 5.78 (1H, s, 11-CH); ^{13}C NMR ($CDCl_3$; 125 MHz) δ 9.6, 22.7, 24.0, 24.4, 27.2, 27.9, 28.0, 30.1, 54.3, 65.5, 107.8, 111.4, 115.9, 148.2, 149.1, 156.1; MS (EI) 248 (M^+); HRMS (EI) calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1765.

General Procedure for Enantioselective Wittig Rearrangement of (*E*)-Cyclic Furfuryl Ether (Table 2). To a solution of (*E*)-**8** (49.6 mg, 0.2 mmol) and a chiral ligand ((−)-sparteine **10** 70.2 mmg, 0.3 mmol; bis(oxazoline) **11** 88.2 mg, 0.3 mmol) in hexane or THF (10 mL) was added dropwise BuLi (*s*-BuLi 1 M in cyclohexane, 0.6 mL, 0.6 mmol; or *t*-BuLi 1.5 M in pentane, 0.88 mL, 1.32 mmol) at −78 °C under Ar. After being stirred for 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, and the solvent was removed under vacuum. The residue was extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified with silica gel chromatography using hexanes−Et_2O (95:5, v/v) as the eluent to give *syn*- and *anti*-homoallylic alcohols **9**, respectively. The enantiomeric excess (ee) of the major *anti*-isomer was determined by HPLC analysis using a Daicel Chiralcel AD column-[hexane/^{i}PrOH = 95:5, flow rate 1.0 mL/min, t_R(2*S*,3*S*) 8.8 min and t_R(2*R*,3*R*) 11.2 min], and the results are shown in Table 2.

(2*R*,3*R*)-3-Isopropenyl-12-methyl-13-oxabicyclo[8.2.1]-trideca-1(12),10-dien-2-ol (Table 2, entry 8): 15.8 mg (32%) as a colorless oil; $[\alpha]^{26}_D$ +44.3 (*c* 0.34, $CHCl_3$). HPLC analysis showed the product to be 61% ee. The ^1H and ^{13}C NMR spectra were identical with those above.

General Procedure for Enantioselective Wittig Rearrangement of (*Z*)-Cyclic Furfuryl Ether (Table 3). To a solution of (*Z*)-**8** (49.6 mg, 0.2 mmol) and bis(oxazoline) **11**−**14** (0.30 mmol) in hexane (1 mL) was added dropwise *t*-BuLi (1.5 M in pentane, 0.88 mL, 1.32 mmol) at −78 °C under Ar. After being stirred for 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, and the solvent was removed under vacuum. The residue was extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave an oil which was purified with silica gel chromatography using hexanes−Et_2O (95:5, v/v) as the eluent to give *syn*- and *anti*-homoallylic alcohols **9**. The enantiomeric excess (ee) of the major *syn*-isomer was determined by HPLC analysis using a Daicel Chiralcel AD column [hexane/^{i}PrOH = 95:5, flow rate 1.0 mL/min, t_R(2*S*,3*R*) 6.7 min and t_R(2*R*,3*S*) 7.8 min], and the results are shown in Table 3.

(2*R*,3*S*)-3-Isopropenyl-12-methyl-13-oxabicyclo[8.2.1]-trideca-1(12),10-dien-2-ol (Table 3, entry 3): 9.4 mg (19%) as a colorless oil; $[\alpha]^{26}_D$ +28.4 (*c* 0.03, $CHCl_3$). HPLC analysis showed it to be 93% ee. The ^1H and ^{13}C NMR spectra were identical with those above.

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Supporting Information Available: Experimental procedures and product characterization for new compounds and selected ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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