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Diastereoselective Ring-Closing Metathesis as a Means to Construct Medium-Sized Cyclic Ethers: Application to the Synthesis of a Photoactivatable Gambierol Derivative

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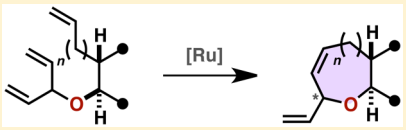
Supporting Information

ABSTRACT: This paper describes a concise synthesis of six- to eight-membered α,α'-substituted cyclic ethers by exploiting diastereoselective ring-closing metathesis (RCM) of 1,4-pentadien-3-yl ether derivatives. The RCM precursors could be efficiently prepared via a vinylation of the corresponding α-acetoxy ether derivatives using divinylzinc. Diastereoselective RCM of 1,4-pentadien-3-yl ether derivatives afforded a series of six- to eight-membered α,α'-substituted cyclic ethers with moderate to good diastereoselectivity. The stereochemical consequence of the diastereoselective RCM appeared to be dependent on the structure of the ring being forged. The diastereoselectivity of six- and seven-membered cyclic ethers appeared to be largely under kinetic control irrespective of the catalyst reactivity, whereas that of an eight-membered cyclic ether could be controlled by the catalyst reactivity. Finally, the diastereoselective RCM chemistry was applied to the synthesis of a biotin-tagged photoactivatable derivative of gambierol.

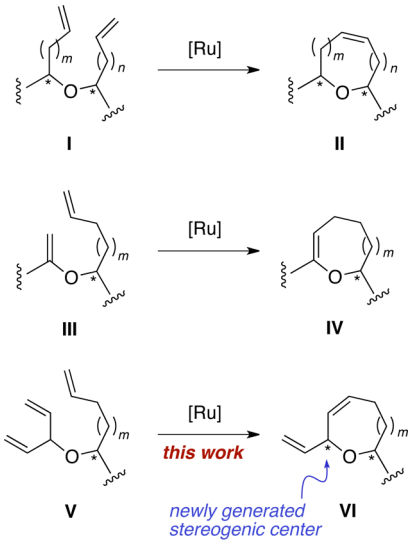


INTRODUCTION

Marine polycyclic ethers are intriguing secondary metabolites of toxic dinoflagellates because of their extraordinary complex structures and potent and diverse biological activities.[1] The low natural abundance of marine polycyclic ethers has been a serious problem for their detailed biological evaluation. Over the past two decades, significant efforts have been devoted to total synthesis of this class of natural products.[2]

Ring-closing metathesis (RCM)[3] has been extensively exploited in the synthesis of complex marine polycyclic ethers (Scheme 1).[4] Clark and Hirama have independently shown that RCM of *O*-linked dienes provides an efficient synthetic access to various medium-sized cyclic ethers (**I** to **II**).[5,6] RCM of *O*-linked dienes has been successfully implemented in total syntheses of brevetoxins, ciguatoxins, and gambieric acid A.[7] However, stereoselective synthesis of *O*-linked dienes is not always easy because of the need to establish two stereogenic centers flanking the oxygen atom. Meanwhile, RCM of acyclic enol ethers to deliver endocyclic enol ethers (**III** to **IV**) also represents a versatile strategy for the synthesis of medium-sized cyclic ethers. The product endocyclic enol ethers are amenable to further functionalization including stereoselective hydroboration or epoxidation. Grubbs and co-workers have described the prototype of this chemistry.[8] So far, several variants have been developed and applied to the synthesis of complex polycyclic ethers.[9,10] Oguri, Hirama, and co-workers have reported yet another RCM-based strategy for stereoselective synthesis of a ciguatoxin AB-ring model compound, which involved a diastereoselective RCM of a 1,4-pentadien-3-yl ether derivative.[11] Diastereoselective RCM is an attractive means to forge ring systems with simultaneous generation of a stereogenic center and has been successfully applied to the synthesis of various carbo- and heterocycles with moderate to excellent diastereoselectivity.[12] Unfortunately, the scope of diastereoselective RCM of 1,4-pentadien-3-yl ethers (**V** to **VI**) remains largely elusive,[13] presumably because of the lack of an efficient method for preparing these derivatives.

Scheme 1. Ring-Closing Metathesis as a Means To Construct Medium-Sized Cyclic Ethers



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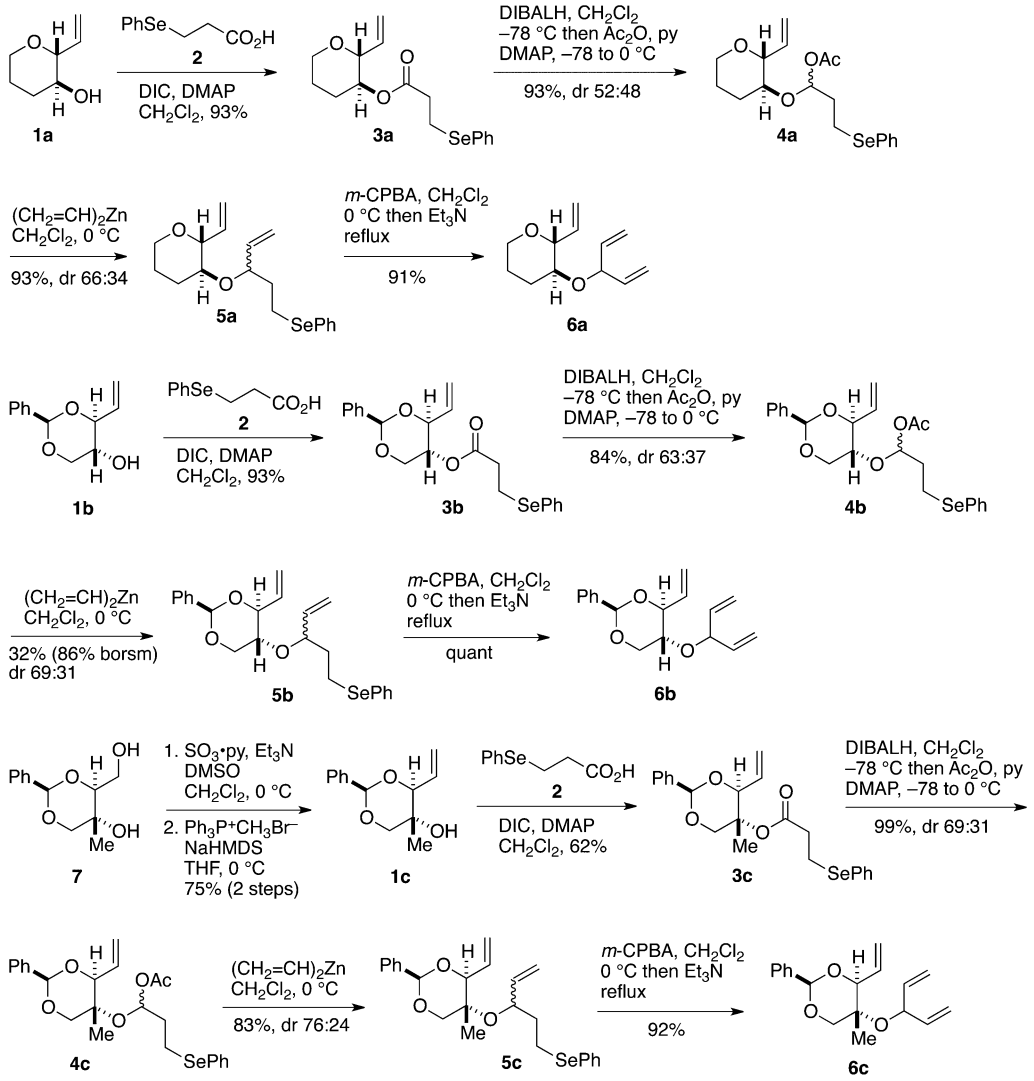
Scheme 2. Synthesis of RCM Precursors 6a−c



We describe herein concise synthesis of medium-sized cyclic ethers by means of a diastereoselective RCM of 1,4-pentadien-3-yl ether derivatives and its application to the synthesis of a biotin-tagged photoactivatable gambierol derivative.

RESULTS AND DISCUSSION

Synthesis of RCM Precursors. Our study began with the development of an efficient method for preparing 1,4-pentadien-3-yl ethers, as shown in Scheme 2.

Esterification of the alcohol **1a**[14] with known carboxylic acid **2**[15] using *N*,*N*′-diisopropylcarbodiimide (DIC)/DMAP afforded the ester **3a**. DIBALH reduction/acetylation[16] of **3a** delivered the α-acetoxy ether **4a**. Vinylation of **4a** was best achieved by using divinylzinc, prepared in situ from vinylmagnesium bromide and zinc bromide,[17] in CH_2Cl_2 at 0 °C. The use of non-Lewis basic solvent was important for the success of the present vinylation, suggesting that in situ formed magnesium bromide might act as a mild Lewis acid to generate oxocarbenium ion species from **4a**. The vinylated derivative **5a** was oxidized with *m*-CPBA, and in situ elimination of the resultant selenoxide afforded the 1,4-pentadien-3-yl ether **6a**. Compounds **6b−f** were synthesized in a similar manner from **1b**,[18] **7**,[19] **8**,[20] **1e**,[21] and **1f**,[22] respectively, as summarized in Schemes 2 and 3. Thus, a series of 1,4-pentadien-3-yl ether derivatives were prepared in only four steps from the corresponding alcohols in high overall yields.

The synthesis of 1,4-pentadien-3-yl ethers from the corresponding acryloyl esters, instead of 3-(phenylseleno)-propanoyl esters, was also examined. However, our attempts at vinylation of the α-acetoxy ether **11**, for example, were unproductive and gave the corresponding γ-adduct **12** as the major product in 57% yield, along with cyclopropane derivative **13** in 16% yield and the desired **6e** in 9% yield (Scheme 4).

Diastereoselective RCM To Construct Medium-Sized Cyclic Ethers. Next, RCM of the 1,4-pentadien-3-yl ethers **6a−f** was investigated using the first-generation Grubbs catalyst (**Ru-I**),[23] the second-generation Grubbs catalyst (**Ru-II**),[24] or the **Ru-II** variants (**Ru-III**[25] or **Ru-IV**[26]). The results are summarized in Table 1.

The RCM of **6a−c** using **Ru-I** or **Ru-II** in CH_2Cl_2 (10 mM) at room temperature for 1−2 h gave the six-membered cyclic ethers **14a−c** in good yields, albeit with only moderate diastereoselectivity. Exposure of **6a** to **Ru-II** for a prolonged reaction time (22 h) did not have a significant influence on the diastereoselectivity but instead resulted in partial degradation of the material (47%, *cis*/*trans* 42:58). Running the reaction at 40

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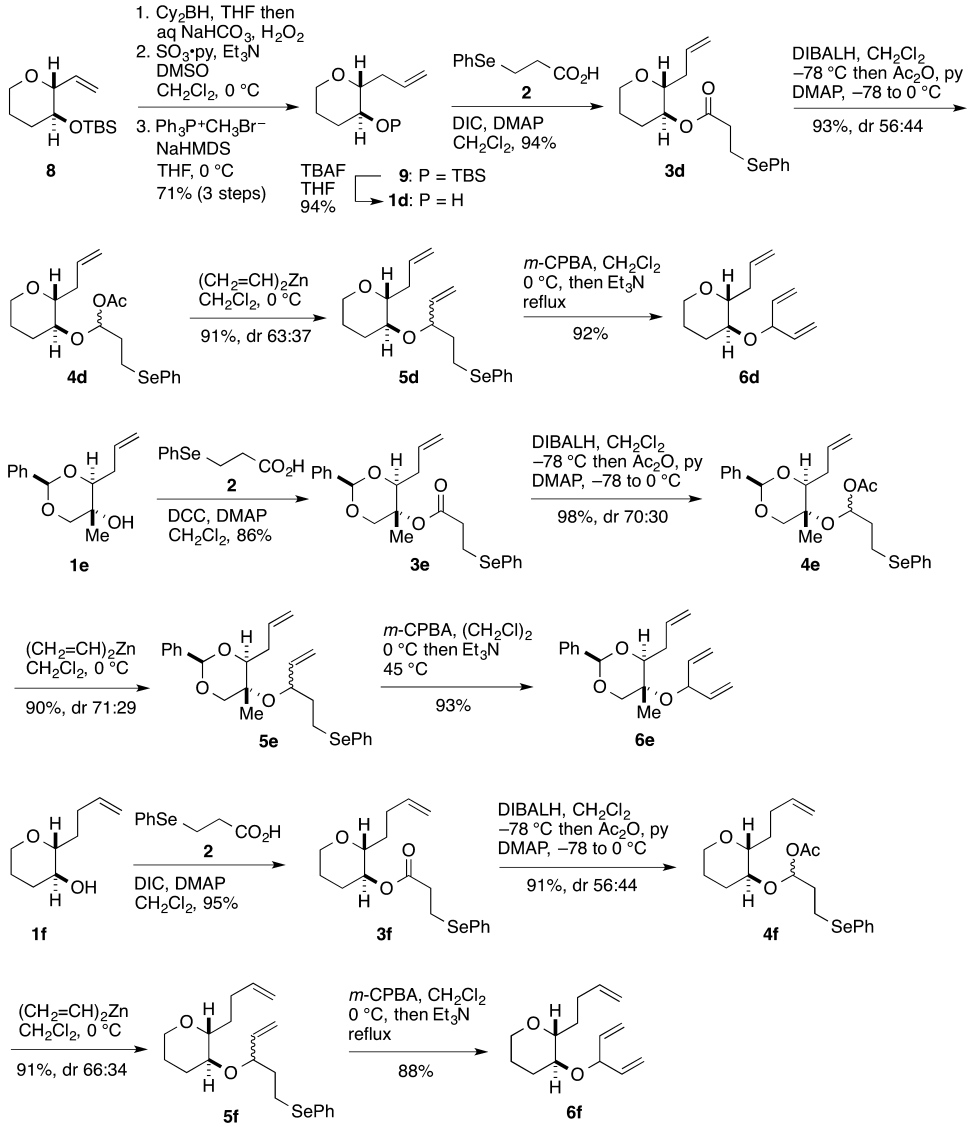
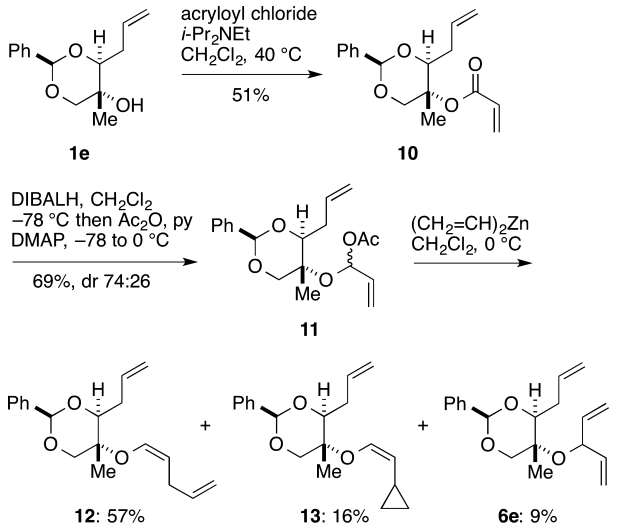
Scheme 3. Synthesis of RCM Precursors 6d−f



Scheme 4. Vinylation of α-Acetoxy Ether 11



°C for 22 h resulted in further decrease of the product yield (25%, *cis*/*trans* 42:58) without any change in the diastereoselectivity. Moreover, it was counterintuitive that essentially no diastereoselectivity was observed for the RCM of **6c** having an axially disposed methyl group.

The RCM of **6d** delivered the seven-membered cyclic ether **14d** in 77−93% yield with excellent *cis*-selectivity (*cis*/*trans* ca. 85:15), irrespective of catalyst used. Similarly, the RCM of **6e** using **Ru-I** or **Ru-II** led to the seven-membered cyclic ether *cis*-**14e** in a stereoselective manner (**Ru-I**: 93%, *cis*/*trans* 93:7; **Ru-II**: 77%, *cis*/*trans* 86:14). When the RCM of **6d** was run in the presence of **Ru-II** for 22 h, **14d** was isolated in a moderate yield with essentially no improvement of diastereoselectivity (56%, *cis*/*trans* 83:17), as was the case for **6a**. It appears that the RCM products are somewhat unstable in the presence of highly reactive **Ru-II** because of the retro-RCM and subsequent degradation of the generated ruthenium alkylidene species. Thus, the RCM of **6a−e** by the action of **Ru-II** was best performed when the reaction was carried out in CH_2Cl_2 (10 mM) at room temperature for 1−2 h. In the RCM of **6a** and **6d**, **Ru-II**, **Ru-III**, and **Ru-IV** performed almost equally.

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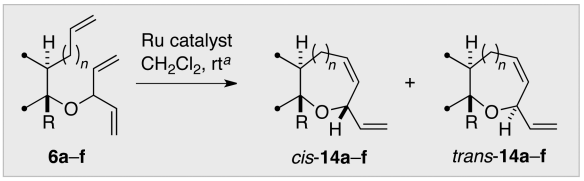
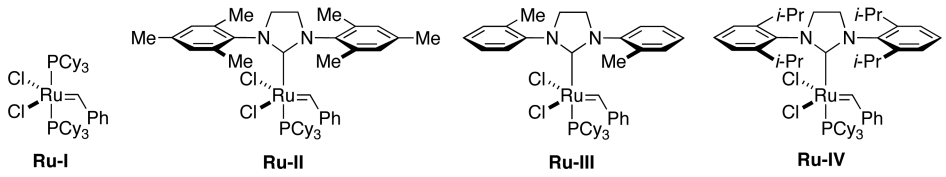
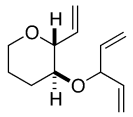
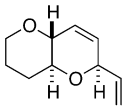
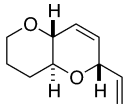
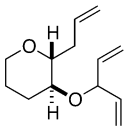
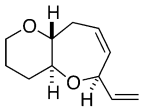
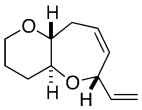
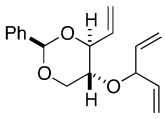
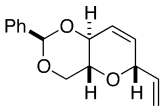
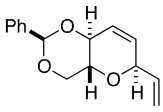
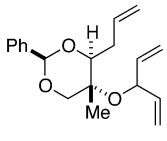
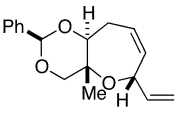
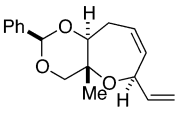
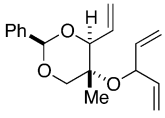
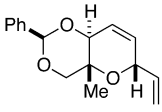
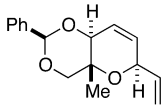
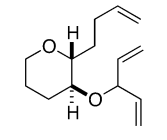
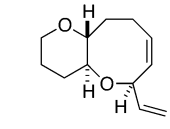
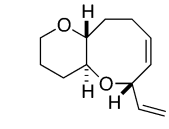
Table 1. Diastereoselective RCM of 6a–f[a]





					
6a	*cis*-**14a**	*trans*-**14a**	**6d**	*cis*-**14d**	*trans*-**14d**
Ru-I: 82% (*cis*/*trans* 32:68) **Ru-II**: 80% (*cis*/*trans* 45:55) **Ru-III**: 70% (*cis*/*trans* 60:40) **Ru-IV**: 74% (*cis*/*trans* 54:46)				**Ru-I**: 80% (*cis*/*trans* 83:17) **Ru-II**: 77% (*cis*/*trans* 86:14) **Ru-III**: 91% (*cis*/*trans* 85:15) **Ru-IV**: 93% (*cis*/*trans* 84:16)	
					
6b	*cis*-**14b**	*trans*-**14b**	**6e**	*cis*-**14e**	*trans*-**14e**
Ru-I: 85% (*cis*/*trans* 38:62) **Ru-II**: 68% (*cis*/*trans* 40:60)				**Ru-I**: 93% (*cis*/*trans* 93:7) **Ru-II**: 77% (*cis*/*trans* 86:14)	
					
6c	*cis*-**14c**	*trans*-**14c**	**6f**	*cis*-**14f**	*trans*-**14f**
Ru-I: 81% (*cis*/*trans* 55:45) **Ru-II**: 72% (*cis*/*trans* 56:44)				**Ru-I**: 45% (*cis*/*trans* 33:67)[b,c] **Ru-II**: 78% (*cis*/*trans* 79:21)[b] **Ru-III**: 70% (*cis*/*trans* 82:18)[b,c] **Ru-IV**: 41% (*cis*/*trans* 50:50)[b,c]	

[a]All reactions were performed using 10 mol % of ruthenium catalyst in degassed CH_2Cl_2 (10 mM) at room temperature for 1–2 h, unless otherwise noted. The diastereoselectivity was estimated on the basis of ^1H NMR analysis (600 MHz). The configuration of **14a–f** was assigned on the basis of NOE experiments. [b]The reactions were performed at a concentration of 3 mM for 22 h. [c]The reactions were performed using 30 mol % of catalyst.

The RCM of **6f** had to be run under more diluted conditions (3 mM) to avoid the formation of dimers and higher oligomers. Consequently, prolonged reaction time (22 h) and higher catalyst loading (30 mol %)[27] were required for consumption of the starting material. It was found that the stereochemical course of the RCM of **6f** was dependent on the reactivity of the catalyst used. Exposure of **6f** to **Ru-I** gave rise to *trans*-**14f** as the major product (*cis*/*trans* 33:67). In contrast, treatment of **6f** with **Ru-II** or **Ru-III** afforded *cis*-**14f** with good diastereoselectivity (**Ru-II**: *cis*/*trans* 79:21; **Ru-III**: *cis*/*trans* 82:18). Interestingly, the RCM of **6f** with **Ru-IV** provided **14f** in only 41% yield with no diastereoselectivity, and several unidentified byproducts were also observed.

Our considerations on the stereochemical consequence of the RCM of representative compounds **6a**, **6d**, and **6f** are shown in Figure 1. It is known that the moderate reactivity of **Ru-I** typically results in kinetic metathesis products, whereas the high reactivity of **Ru-II** leads to thermodynamically favored metathesis products via a sequence of ring-opening metathesis/ring-closing metathesis, provided kinetic products sufficiently reactive toward the catalyst.[28] The ruthenacyclobutane formation is considered to play a significant role in determining the stereochemical course of olefin metathesis reactions under kinetic control,[29] where parallel alignment of two π-bonds is required for achieving maximal orbital interaction.[30] Meanwhile, the energy difference between the *cis* and *trans* isomers of **14a**, **14d**, and **14f** was calculated at the RB3LYP/6-31G* level to be 3.4, 3.8, and 6.9 kJ/mol, respectively, indicating that in all cases *cis* isomers should be thermodynamically preferred over *trans* isomers.[31]

The RCM of **6a** under kinetic conditions likely proceeds via **A-1** to provide *trans*-**14a** as the major product; **A-1** should be

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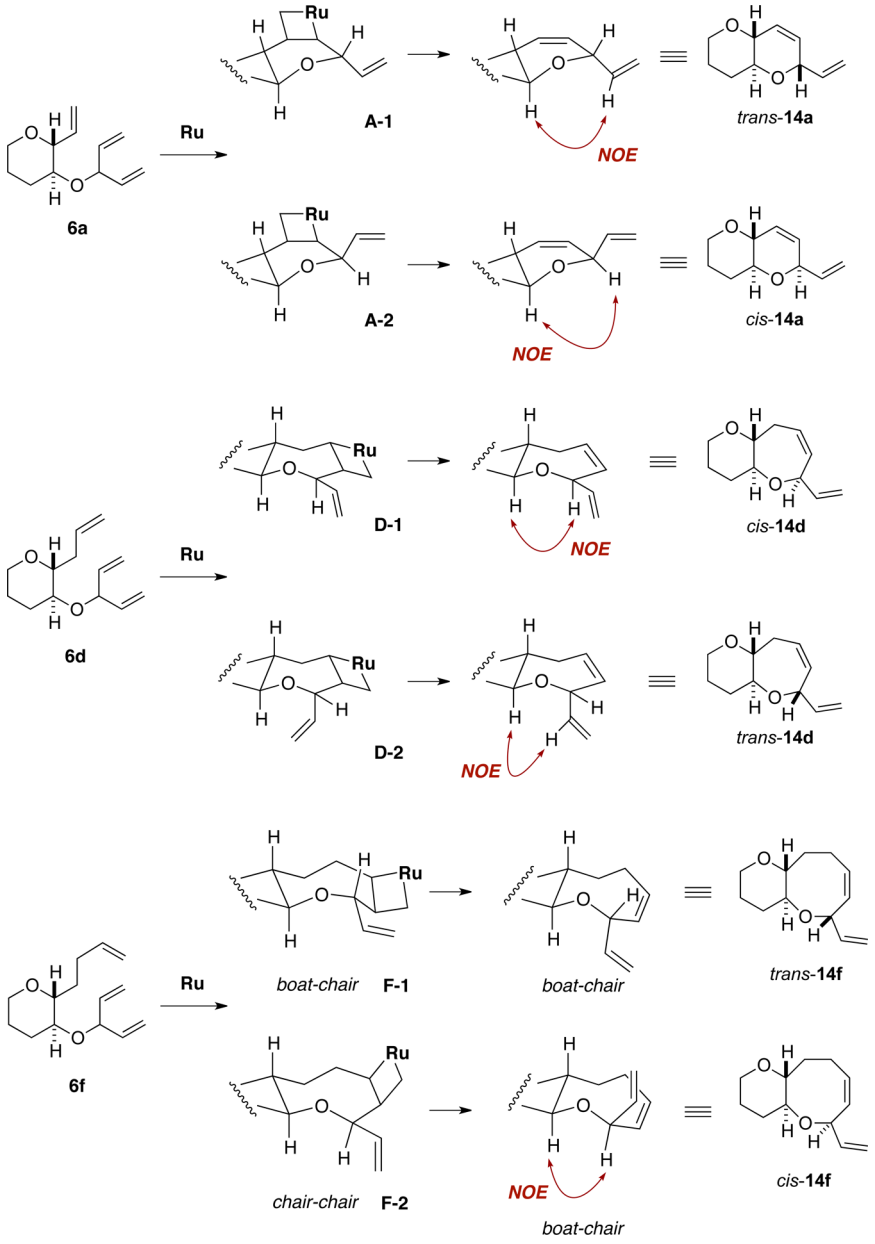

Figure 1. Plausible explanation for the stereochemical outcome of the RCM of **6a**, **6d**, and **6f**.

more energetically favored than **A-2** because in the latter the vinyl group is pseudoequatorially disposed and may have a steric interaction with the ruthenacyclobutane being formed. However, once the ruthenacyclobutane moiety collapses, *cis*-**14a** should be energetically more favored than *trans*-**14a** because the latter involves a 1,3-diaxial interaction between the vinyl group and the axial hydrogen atom. Nevertheless, the RCM of **6a** under the influence of **Ru-II** showed only moderate *cis* selectivity, being lower than that expected from the energy calculation. Furthermore, treatment of a 32:68 mixture of *cis*/*trans* isomers of **14a** to **Ru-II** in CH_2Cl_2 at room temperature for 1 h did not change the diastereomer ratio significantly (*cis*/*trans* 38:62 by ^1H NMR analysis). We considered that the reaction conditions were not effective for promoting thermodynamic equilibration between *cis*-**14a** and *trans*-**14a** and that the diastereoselective RCM of **6a** was mainly under kinetic control even if highly reactive **Ru-II** was used. The RCM of **6b** and **6c** should also be considered similarly, where **Ru-I** and **Ru-II** showed essentially the same diastereoselectivity.

The RCM of **6d** under kinetic conditions would go through **D-1**, rather than **D-2**, to avoid a 1,3-pseudodiaxial steric repulsion between the vinyl group and the proximal axial hydrogen atom, leading to *cis*-**14d** as the major product. Furthermore, *cis*-**14d** should be thermodynamically more stable than *trans*-**14d**. However, exposure of *trans*-**14d** to the RCM conditions (**Ru-II**, CH_2Cl_2, room temperature, 1 h) gave a 25:75 mixture of *cis*/*trans*-**14d**, as estimated by ^1H NMR analysis, and the ratio of *cis*/*trans* isomers differed significantly from that observed in the RCM of **6d** using **Ru-II**. Thus, it appeared that *trans*-**14d** was insufficiently reactive to reach thermodynamic equilibrium under the RCM conditions and that the diastereoselectivity of the RCM of **6d** would be largely dependent on kinetic control, regardless of the catalyst used.

The diastereoselectivity of the RCM of **6f** strikingly depended on the reaction conditions. It was considered that

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the RCM of **6f** under kinetic conditions (**Ru-I**) would favor **F-1** (boat−chair) over **F-2** (chair−chair), giving *trans*-**14f** as the major product.[32] In contrast, the RCM of **6f** under thermodynamic conditions (**Ru-II** and **Ru-III**) provided *cis*-**14f** as the major product, which should be energetically more favored than *trans*-**14f**. Indeed, resubjecting *trans*-**14f** to the RCM conditions (**Ru-II**, CH_2Cl_2, room temperature, 22 h) provided a 64:36 mixture of *cis*/*trans*-**14f** based on ^{1}H NMR analysis, which indicated thermodynamic equilibration between *cis* and *trans* isomers was achievable under these conditions.

Taking the above considerations together, the stereochemical consequence of the diastereoselective RCM of **6a−e** appeared to be mainly kinetically controlled irrespective of the catalyst reactivity. In contrast, the diastereoselectivity of the RCM of **6f** was dependent on the catalyst used. The kinetically favored *trans*-**14f** prevailed in the presence of **Ru-I**, whereas the thermodynamically favored *cis*-**14f** predominated under the influence of **Ru-II** and **Ru-III**.

Application of Diastereoselective RCM to the Synthesis of Clickable Gambierol Analogue. Gambierol (**15**, Figure 2) is a polycyclic ether neurotoxin isolated from the

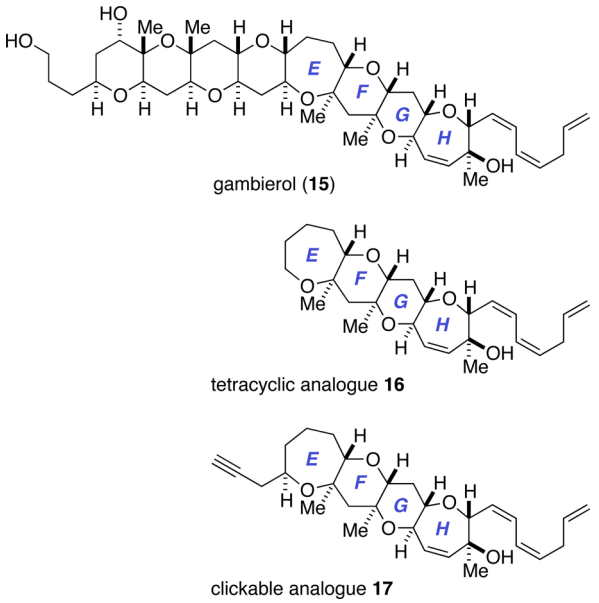

Figure 2. Structures of gambierol (**15**), tetracyclic analogue **16**, and clickable analogue **17**.

cultured cells of the ciguatera causative dinoflagellate *Gambierdiscus toxicus*.[33] Our group reported the first total synthesis of **15** and realized sufficient material supply of this naturally scarce substance.[34,35] In a collaborative study with the Bigiani group, we discovered that **15** inhibits voltage-gated potassium ion channels (K_v channels) of mice taste cells in low nanomolar concentrations.[36] Following our study, Snyders et al. reported that **15** is a subtype-selective inhibitor of K_v1 and K_v3 channels and that **15** binds to previously undescribed binding site located between the S5 and S6 segments of $K_v3.1$ channels.[37] However, the precise binding mode of **15** to K_v channels has not been characterized in detail. Photoaffinity labeling[38] of K_v channels with an appropriately designed photoactivatable probe would be a powerful means to elucidate the exact binding site of **15** at the atomic level.

Meanwhile, our group also investigated the structure−activity relationships of **15** to identify that the right half of the molecule, i.e., the EFGH-ring domain, is responsible for potent K_v channel inhibitory activity[39] and found that the tetracyclic analogue **16** inhibits human $K_v1.2$ channels with nanomolar potency. Because compound **16** does not have any appropriate handle amenable to further functionalization, the alkyne **17**, a clickable analogue, was designed as a precursor for photoactivatable probe synthesis.

We exploited the diastereoselective RCM chemistry in the synthesis of **17** (Scheme 5). The synthesis began with desilylation of known olefin **18**[39b] to give the alcohol **19**, which was esterified with **2** to afford the ester **20**. The esterification of sterically encumbered alcohol **19** was best carried out using DIC/DMAP. Nonetheless, the reaction stalled at approximately 50% conversion. However, the starting material could be cleanly recovered in 36% yield. The conversion of the esterification could not be improved by increasing the molar amounts of the reagents and/or **2** because of competitive decomposition of **2** under these conditions. It appeared that, for the same reason, Yamaguchi[40] and Shiina[41] esterifications were ineffective for the present case. DIBALH reduction/acetylation of **20** delivered the α-acetoxy ether **21** in 94% yield as a mixture of diastereomers. This was vinylated with divinylzinc (CH_2Cl_2, 0 °C) to afford the diene **22** in 86% yield. Oxidative elimination of the phenylseleno group then provided the triene **23** in 96% yield. Exposure of **23** to **Ru-II** (10 mol %) in CH_2Cl_2 (10 mM) at room temperature for 1.5 h furnished the oxepene **24** in 86% yield with 91:9 diastereoselectivity. The stereochemical consequence of the RCM was confirmed by an NOE experiment, as shown. Selective hydroboration of the terminal olefin of **24** using 9-BBN-H followed by hydrogenation delivered the oxepane **25**. During these transformations, the minor C-16 diastereomer was removed by flash column chromatography using silica gel. Silylation of the hydroxy group of **25** and ensuing acetonide cleavage gave the diol **26** in 70% yield for the two steps. Further functionalization of the right terminus of **26** was carried out according to our previously optimized sequence of transformations.[39b] Selective silylation of the primary alcohol of **26** with TBSCl/imidazole (95% yield) and oxidation of the remaining alcohol under Ley's conditions[42] provided the ketone **27** in 96% yield. Enolization of **27** with LHMDS in the presence of $TMSCl/Et_3N$, oxidation under Ito−Saegusa conditions (97% yield, two steps),[43] and stereoselective methylation[44] afforded the alcohol **28** in 97% yield as a single stereoisomer (dr >95:5). The configuration of the newly generated C-30 stereogenic center was confirmed by an NOE experiment as shown. Selective removal of the TBS group of **28** delivered the diol **29** (98% yield), which was oxidized and then dibromoolefinated to give the alcohol **30** (93% yield, two steps). Silylation of **30** with TMSOTf/2,6-lutidine delivered the silyl ether **31** in 88% yield. The dibromoolefin moiety of **31** was reduced in a stereoselective manner with n-$Bu_3SnH/Pd(PPh_3)_4$[45] in 93% yield, and subsequent cleavage of the silyl ethers afforded the diol **32** in 95% yield. The protection of the C-30 tertiary alcohol was necessary to secure the high stereoselectivity of the dibromoolefin reduction. Stille reaction[46] of **32** with the vinyl stannane **33**[47] under Corey's conditions[48] furnished the cross-coupled product **34** in 89% yield. Finally, **34** was oxidized and then alkynylated using Ohira−Bestmann reagent[49] to furnish the clickable gambierol analogue **17**.

Synthesis of a Photoactivatable Derivative of Gambierol. Compound **17** was amenable to copper-catalyzed

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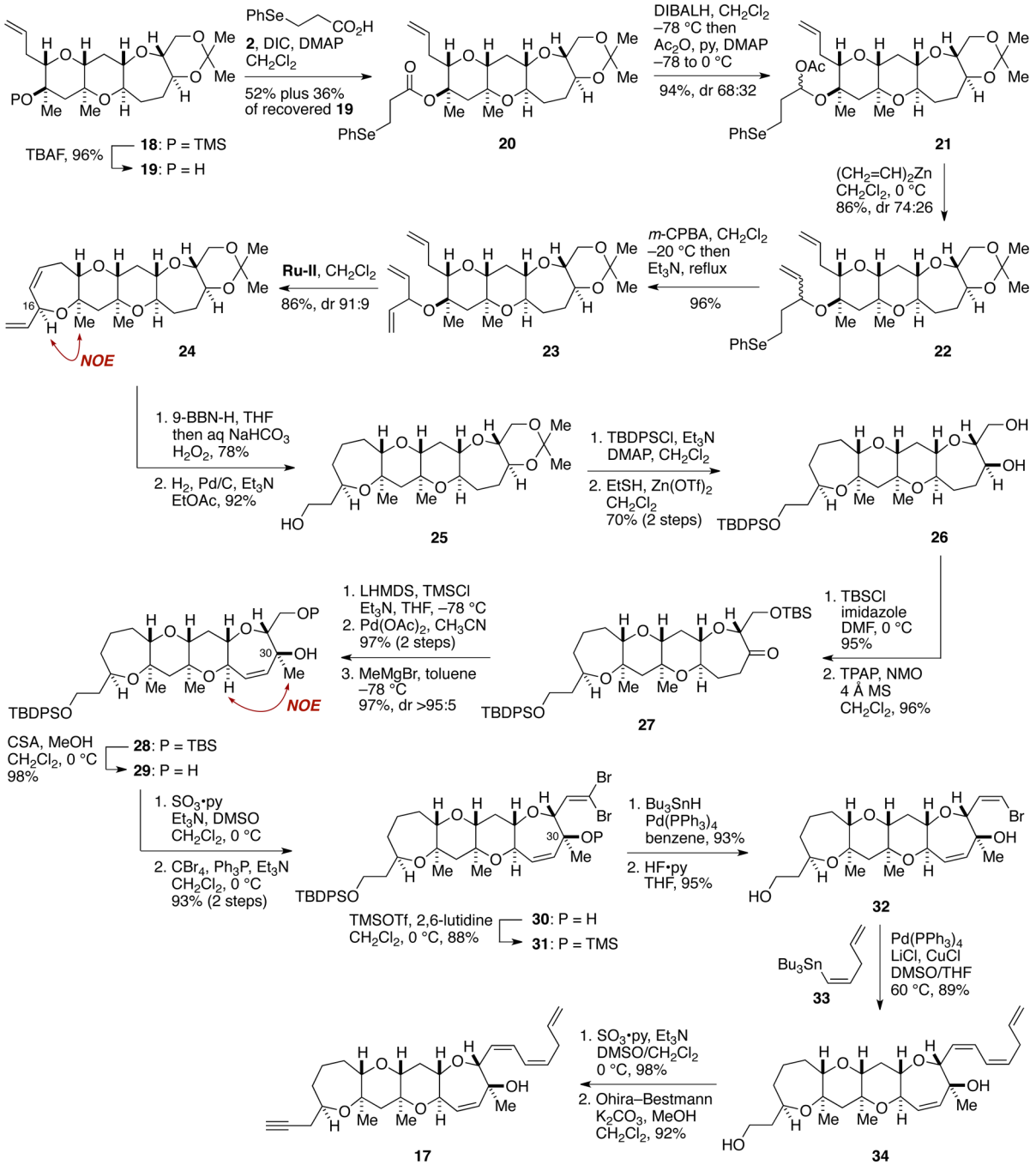
Scheme 5. Synthesis of Clickable Gambierol Analogue 17



alkyne/azide cycloaddition,[50] as exemplified by the reaction with the azide **35**[51] to afford the photoactivatable derivative **36** (Scheme 6). The reaction proceeded cleanly in the presence of tris(3-hydroxypropyltriazolylmethyl)amine (THPTA)[52] in DMSO/H_2O at room temperature. Preliminary evaluation of the biological activity of **36** against human $K_v1.2$ channels stably expressed in CHO cells showed that 100 nM of **36** was sufficient to achieve approximately 50% inhibition of the potassium ion current evoked by a 200 ms step pulse from −80 mV to +40 mV (Figure 3).[53] This result demonstrated that the clickable analogue **17** is a useful precursor for functional probes and suggested that biotin-tagged photoactivatable derivative **36** may be useful for labeling K_v channels.

■ CONCLUSION

In this study, we have investigated diastereoselective RCM of 1,4-pentadien-3-yl ether derivatives for concise synthesis of *α,α′*-substituted cyclic ethers. The stereochemical consequence of the RCM of **6a−e** to construct the six- and seven-membered cyclic ethers **14a−e** would be largely ascribed to kinetic control and likely dependent on the conformational bias of ruthenacyclobutane intermediates, regardless of the catalyst reactivity. In contrast, the diastereoselectivity of the RCM of **6f** to forge the eight-membered cyclic ether **14f** was dependent on the reactivity of the catalyst used; less reactive **Ru-I** led to kinetically favored *trans*-**14f** as the major product, whereas more reactive **Ru-II** and **Ru-III** reversed the diastereoselectivity and delivered thermodynamically favored *cis*-**14f** as the major

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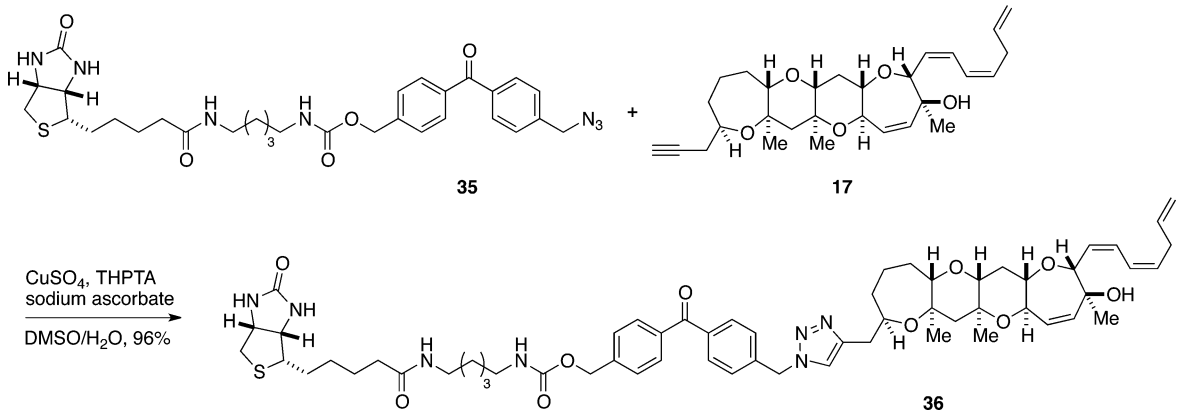
Scheme 6. Synthesis of Biotin-Tagged Photoactivatable Derivative 36



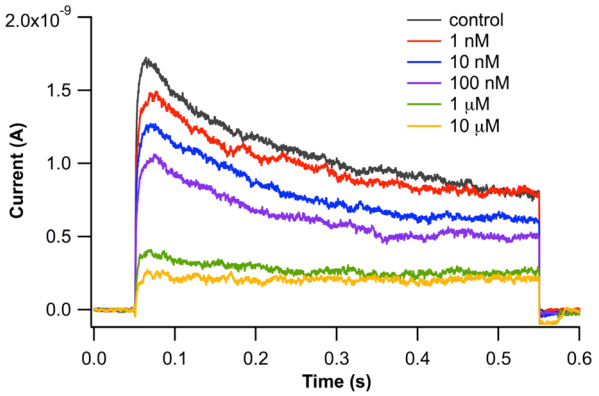


Figure 3. Patch-clamp recording of potassium ion current of CHO cells, stably expressing human $K_v1.2$ channels, treated with different concentrations of **36**.

product. Diastereoselective RCM was successfully applied to the synthesis of a clickable gambierol analogue, where Cu(I)-catalyzed alkyne/azide cycloaddition provided an easy access to a photoactivatable derivative with sufficient K_v channel inhibitory activity. Taking advantage of diastereoselective RCM, we have established the basis for photoaffinity labeling studies toward the elucidation of the gambierol binding site on human K_v channels.

EXPERIMENTAL SECTION

General Remarks. All reactions sensitive to moisture and/or air were carried out under an atmosphere of argon in dry, freshly distilled solvents under anhydrous conditions using oven-dried glassware unless otherwise noted. Degassed solvents were obtained by repeating the freeze−thaw cycle three times immediately prior to use. All other chemicals were purchased at the highest commercial grade and used directly. ^{1}H and ^{13}C NMR chemical shift values are reported in ppm (δ) downfield from tetramethylsilane with reference to internal residual solvent [^{1}H NMR, $CHCl_3$ (7.24), C_6HD_5 (7.15), C_5HD_4N (8.74), CHD_2OD (3.31); ^{13}C NMR, $CDCl_3$ (77.0), C_6D_6 (128.0), C_5D_5N (123.9), CD_3OD (49.0)]. Coupling constants (J) are reported in hertz (Hz). The following abbreviations were used to designate the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. Diastereomer ratio (dr) was estimated by ^{1}H NMR spectroscopic analysis (600 MHz), unless otherwise noted. High-resolution mass spectra (HRMS) were measured on a mass spectrometer equipped with a TOF system and an electrospray ionization (ESI) ion source or a mass spectrometer equipped with an electron impact ionization (EI) ion source.

Alcohol ***1c.*** To a solution of diol **7** (44.1 mg, 0.197 mmol) and Et_3N (0.14 mL, 1.0 mmol) in CH_2Cl_2/DMSO (1:1, v/v, 2 mL) at 0 °C was added SO_3·pyridine (94.5 mg, 0.594 mmol), and the resultant solution was stirred at 0 °C for 40 min. The reaction mixture was diluted with *t*-BuOMe and washed successively with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give crude aldehyde, which was used in the next reaction without further purification.

To a suspension of $Ph_3P^+CH_3Br^-$ (176.5 mg, 0.4941 mmol) in THF (1.2 mL) at 0 °C was added NaHMDS (1.0 M solution in THF, 0.47 mL, 0.47 mmol), followed by a solution of the above aldehyde in THF (0.8 mL + 0.8 mL rinse), and the resultant suspension was stirred at 0 °C for 30 min. The reaction was quenched with saturated aqueous NH_4Cl solution at 0 °C. The resultant mixture was diluted with EtOAc and washed with H_2O and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 15% EtOAc/hexanes) gave alcohol **1c** (32.6 mg, 75% for the two steps) as a colorless oil: $[\alpha]_D^{27}$ −43.1 (*c* 1.00, $CHCl_3$); IR (neat) 3443, 2973, 2855, 2360, 2341, 1389, 1092 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.37−7.32 (m, 3H), 5.93 (ddd, J = 17.0, 10.6, 5.9 Hz, 1H), 5.55 (s, 1H), 5.43 (dd, J = 17.0, 1.9 Hz, 1H), 5.33 (dd, J = 10.6, 1.9 Hz, 1H), 4.14 (d, J = 5.9 Hz, 1H), 3.93 (d, J = 11.0 Hz, 1H), 3.71 (d, J = 11.0 Hz, 1H), 1.51 (s, 1H), 1.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.8, 132.7, 129.0, 128.3 (2C), 126.2 (2C), 118.5, 101.6, 84.9, 76.7, 66.5, 20.4; HRMS (ESI) calcd for $C_{13}H_{16}O_3Na$ [$(M + Na)^+$] 243.0992, found 243.0984.

Alcohol ***1d.*** To a solution of cyclohexene (0.37 mL, 3.7 mmol) in THF (11 mL) at 0 °C was added BH_3·THF (0.9 M solution in THF, 2.00 mL, 1.80 mmol), and the resultant mixture was stirred at 0 °C for 1 h. To this mixture was added a solution of olefin **8** (296.4 mg, 1.223 mmol) in THF (1.0 mL + 1.0 mL rinse), and the resultant mixture was stirred at room temperature for 19 h. The reaction was quenched with EtOH at 0 °C. To the resultant mixture were added saturated aqueous $NaHCO_3$ solution (10 mL) and 30% aqueous H_2O_2 solution (6 mL), and the resultant mixture was stirred at room temperature for 4 h. The resultant mixture was diluted with EtOAc and washed with H_2O and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 8−10% EtOAc/hexanes) gave alcohol (417.1 mg), which was contaminated with some impurities. This material was used in the next reaction without further purification.

To a solution of the above alcohol (417.1 mg) in CH_2Cl_2/DMSO (1:1, v/v, 12 mL) at 0 °C were added Et_3N (0.85 mL, 6.1 mmol) and SO_3·pyridine (584.5 mg, 3.672 mmol), and the resultant mixture was stirred at 0 °C for 1 h. To the reaction mixture was added SO_3·pyridine (97.3 mg, 0.611 mmol), and the resultant mixture was stirred at 0 °C for 0.5 h. The reaction mixture was diluted with *t*-BuOMe and washed successively with 1 M aqueous HCl solution, saturated

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aqueous $NaHCO_3$ solution, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give crude aldehyde, which was used in the next reaction without further purification.

To a suspension of $Ph_3P^+CH_3Br^-$ (1.094 g, 3.063 mmol) in THF (7.6 mL) at 0 °C were added NaHMDS (1.0 M solution in THF, 2.9 mL, 2.9 mmol) and a solution of the above aldehyde in THF (3 mL + 3 mL rinse), and the resultant mixture was stirred at 0 °C for 2 h. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was diluted with EtOAc and washed with H_2O and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 2% EtOAc/hexanes) gave olefin **9** (224.2 mg, 71% for the three steps) as a colorless oil: $[\alpha]_D^{22}$ +46.1 (*c* 0.50, $CHCl_3$); IR (neat) 2955, 2931, 2856, 2359, 2341, 1098, 837 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.86 (dddd, *J* = 17.4, 10.6, 7.8, 6.4 Hz, 1H), 5.08 (dd, *J* = 17.4, 1.9 Hz, 1H), 5.04 (dd, *J* = 10.6, 1.9 Hz, 1H), 3.87 (m, 1H), 3.31−3.27 (m, 2H), 3.07 (ddd, *J* = 8.7, 8.7, 2.8 Hz, 1H), 2.58 (m, 1H), 2.10 (m, 1H), 1.98 (m, 1H), 1.68−1.56 (m, 2H), 1.40 (m, 1H), 0.86 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.6, 116.4, 82.3, 70.9, 67.9, 36.7, 33.6, 25.8 (3C), 25.7, 18.0, −3.9, −4.7; HRMS (ESI) calcd for $C_{14}H_{28}O_2SiNa$ $[(M + Na)^+]$ 279.1751, found 279.1770.

To a solution of olefin **9** (1.66 g, 6.47 mmol) in THF (65 mL) at 0 °C was added TBAF (1.0 M solution in THF, 13.0 mL, 13.0 mmol), and the resultant solution was stirred at room temperature for 1.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was diluted with EtOAc and washed with H_2O and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 15−25% EtOAc/hexanes) gave alcohol **1d** (0.86 g, 94%) as a colorless oil: $[\alpha]_D^{22}$ +27.0 (*c* 1.00, $CHCl_3$); IR (neat) 3388, 2938, 2854, 1435, 1094, 1025, 912 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.91 (dddd, *J* = 17.4, 10.2, 7.2, 7.2 Hz, 1H), 5.14 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.07 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.89 (m, 1H), 3.38−3.29 (m, 2H), 3.09 (ddd, *J* = 10.8, 7.2, 3.6 Hz, 1H), 2.56 (m, 1H), 2.28 (m, 1H), 2.08 (m, 1H), 1.71−1.62 (m, 2H), 1.52 (br d, *J* = 4.8 Hz, 1H), 1.39 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.1, 116.8, 81.6, 70.1, 67.6, 36.8, 32.7, 25.5; HRMS (EI) calcd for $C_8H_{14}O_2$ $[M^+]$ 142.0988, found 142.0996.

Ester ***3a***. To a solution of alcohol **1a** (134.2 mg, 1.047 mmol) in CH_2Cl_2 (5 mL) were added carboxylic acid **2** (479.6 mg, 2.092 mmol), DMAP (256.0 mg, 2.095 mmol), and DIC (0.32 mL, 2.1 mmol), and the resultant solution was stirred at room temperature for 3.5 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, 3% EtOAc/hexanes) to give ester **3a** (329.1 mg, 93%) as a pale yellow oil: $[\alpha]_D^{25}$ +12.1 (*c* 1.00, $CHCl_3$); IR (neat) 2943, 2849, 2360, 2341, 1737, 1204, 1085 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.49−7.47 (m, 2H), 7.27−7.22 (m, 3H), 5.76 (ddd, *J* = 17.4, 10.5, 6.8 Hz, 1H), 5.27 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.18 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.61 (ddd, *J* = 13.7, 9.2, 4.6 Hz, 1H), 3.93 (m, 1H), 3.65 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.39 (ddd, *J* = 11.5, 11.5, 3.2 Hz, 1H), 3.08−2.99 (m, 2H), 2.69−2.61 (m, 2H), 2.13 (m, 1H), 1.77−1.66 (m, 2H), 1.48 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 135.3, 133.2 (2C), 129.2, 129.1 (2C), 127.3, 118.2, 80.6, 71.5, 67.3, 35.4, 29.1, 24.9, 21.7; HRMS (ESI) calcd for $C_{16}H_{20}O_3SeNa$ $[(M + Na)^+]$ 363.0470, found 363.0486.

Ester ***3b***. Prepared from alcohol **1b** (566.8 mg, 2.748 mmol) in the same manner as **3a**: yield 1.064 g, 93%; pale yellow oil; $[\alpha]_D^{25}$ −35.8 (*c* 1.00, $CHCl_3$); IR (neat) 3066, 2965, 2857, 1739, 1376, 1108 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.52−7.47 (m, 4H), 7.37−7.31 (m, 3H), 7.29−7.26 (m, 3H), 5.88 (ddd, *J* = 17.5, 10.6, 6.4, Hz, 1H), 5.54 (s, 1H), 5.39 (d, *J* = 17.5 Hz, 1H), 5.27 (d, *J* = 10.6 Hz, 1H), 4.87 (ddd, *J* = 10.1, 10.1, 5.5 Hz, 1H), 4.37 (dd, *J* = 10.1, 5.5 Hz, 1H), 4.18 (dd, *J* = 10.1, 6.4 Hz, 1H), 3.65 (dd, *J* = 10.1, 10.1 Hz, 1H), 3.08−3.03 (m, 2H), 2.72−2.69 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 137.3, 134.0, 133.4 (2C), 129.3 (2C), 129.2 (2C), 128.4 (2C), 127.5, 126.3 (2C), 119.1, 101.3, 80.4, 68.2, 66.5, 35.3, 21.6; HRMS (ESI) calcd for $C_{21}H_{22}O_4SeNa$ $[(M + Na)^+]$ 441.0576, found 441.0578.

Ester ***3c***. Prepared from alcohol **1c** (283.9 mg, 1.289 mmol) in the same manner as **3a**: yield 342.9 mg, 62%; pale yellow oil; $[\alpha]_D^{28}$ −45.8 (*c* 1.00, $CHCl_3$); IR (neat) 3583, 3064, 2988, 2938, 2854, 1735, 1092 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.53−7.49 (m, 4H), 7.38−7.33 (m, 3H), 7.30−7.26 (m, 3H), 5.90 (ddd, *J* = 17.4, 11.0, 5.0 Hz, 1H), 5.57 (s, 1H), 5.42 (dd, *J* = 17.7, 1.8 Hz, 1H), 5.30 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.78 (d, *J* = 11.0 Hz, 1H), 4.37 (d, *J* = 5.0 Hz, 1H), 3.90 (d, *J* = 11.0 Hz, 1H), 3.07−3.02 (m, 2H), 2.72−2.64 (m, 2H), 1.63 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 137.6, 133.4 (2C), 132.2, 129.3 (3C), 129.2, 128.4 (2C), 127.5, 126.3 (2C), 118.1, 101.8, 81.5, 76.5, 73.9, 36.0, 21.9, 16.8; HRMS (ESI) calcd for $C_{22}H_{24}O_4SeNa$ $[(M + Na)^+]$ 455.0732, found 455.0741.

Ester ***3d***. Prepared from alcohol **1d** (592.3 mg, 4.167 mmol) in the same manner as **3a**: yield 1.377 g, 94%; pale yellow oil; $[\alpha]_D^{24}$ +34.7 (*c* 1.00, $CHCl_3$); IR (neat) 3073, 2943, 2849, 2357, 1731, 1219, 734 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.51−7.48 (m, 2H), 7.28−7.24 (m, 3H), 5.82 (dddd, *J* = 17.0, 10.1, 6.9, 6.9 Hz, 1H), 5.07−5.02 (m, 2H), 4.57 (ddd, *J* = 11.0, 9.6, 4.6 Hz, 1H), 3.91 (m, 1H), 3.33 (ddd, *J* = 11.5, 11.5, 2.8 Hz, 1H), 3.29 (ddd, *J* = 11.0, 7.8, 3.2 Hz, 1H), 3.09−3.05 (m, 2H), 2.72−2.65 (m, 2H), 2.36 (m, 1H), 2.20−2.21 (m, 2H), 1.75−1.63 (m, 2H), 1.42 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 134.4, 133.3 (2C), 129.2 (3C), 127.3, 117.0, 78.8, 72.0, 67.7, 36.6, 35.4, 29.3, 25.1, 21.7; HRMS (ESI) calcd for $C_{17}H_{22}O_3SeNa$ $[(M + Na)^+]$ 377.0626, found 377.0608.

Ester ***3e***. Prepared from alcohol **1e** (178.0 mg, 0.7597 mmol) in the same manner as **3a** except that DCC was used instead of DIC: yield 291.3 mg, 86%; pale yellow oil; $[\alpha]_D^{24}$ −45.3 (*c* 1.00, $CHCl_3$); IR (neat) 3583, 3072, 2924, 2856, 2359, 1732, 1022 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.53−7.51 (m, 2H), 7.47−7.45 (m, 2H), 7.37−7.31 (m, 3H), 7.29−7.23 (m, 3H), 5.90 (dddd, *J* = 17.4, 10.6, 7.3, 7.3 Hz, 1H), 5.50 (s, 1H), 5.13 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.07 (dd, *J* = 10.6, 1.8 Hz, 1H), 4.78 (d, *J* = 11.0 Hz, 1H), 3.84−3.81 (m, 2H), 3.09−3.02 (m, 2H), 2.71−2.66 (m, 2H), 2.40 (m, 1H), 2.29 (m, 1H), 1.68 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 137.6, 134.7, 133.3 (2C), 129.2 (3C), 129.0, 128.2 (2C), 127.4, 126.1 (2C), 116.9, 101.7, 81.6, 76.4, 74.1, 35.8, 33.3, 21.9, 16.2; HRMS (ESI) calcd for $C_{23}H_{26}O_4SeNa$ $[(M + Na)^+]$ 469.0889, found 469.0895.

Ester ***3f***. Prepared from alcohol **1f** (807.3 mg, 5.168 mmol) in the same manner as **3a**: yield 1.794 g, 95%; colorless oil; $[\alpha]_D^{23}$ +35.2 (*c* 1.00, $CHCl_3$); IR (neat) 3073, 2946, 2849, 2359, 1735, 1221, 737 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.28−7.25 (m, 3H), 5.78 (dddd, *J* = 16.9, 10.6, 6.8, 6.8 Hz, 1H), 5.00 (dd, *J* = 16.9, 1.8 Hz, 1H), 4.93 (dd, *J* = 10.6, 1.8 Hz, 1H), 4.53 (ddd, *J* = 10.6, 9.2, 4.6 Hz, 1H), 3.98 (m, 1H), 3.31 (ddd, *J* = 11.5, 11.5, 2.8 Hz, 1H), 3.20 (ddd, *J* = 9.2, 9.2, 2.3 Hz, 1H), 3.09−3.04 (m, 2H), 2.71−2.64 (m, 2H), 2.23 (m, 1H), 2.13 (m, 1H), 2.07 (m, 1H), 1.75−1.62 (m, 3H), 1.48−1.38 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 138.3, 133.3 (2C), 129.2 (3C), 127.3, 114.7, 78.6, 72.4, 67.5, 35.4, 31.2, 29.3 (2C), 25.2, 21.8; HRMS (ESI) calcd for $C_{18}H_{24}O_3SeNa$ $[(M + Na)^+]$ 391.0783, found 391.0777.

α-Acetoxy Ether ***4a***. To a solution of ester **3a** (309.6 mg, 0.9125 mmol) in CH_2Cl_2 (9.1 mL) at −78 °C was added DIBALH (1.02 M solution in *n*-hexane, 1.05 mL, 1.07 mmol), and the resultant solution was stirred at −78 °C for 5 min. To the solution were sequentially added pyridine (0.29 mL, 3.6 mmol), a solution of DMAP (134.1 mg, 1.098 mmol) in CH_2Cl_2 (2 mL), and Ac_2O (0.34 mL, 3.6 mmol), and the resultant solution was stirred at −78 °C for 14 h and then allowed to warm to 0 °C over a period of 4.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was diluted with EtOAc and saturated aqueous potassium sodium tartrate solution and stirred vigorously at room temperature for 50 min. The organic layer was separated, washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 5% EtOAc/hexanes) gave α-acetoxy ether **4a** (325.8 mg, 93%, dr 52:48) as a colorless oil. A small portion of material was further purified by flash column chromatography to separate the diastereomers for compound characterization. Less polar isomer: $[\alpha]_D^{26}$ +64.5 (*c* 1.00, $CHCl_3$); IR (neat) 2938, 2851, 1738, 1437, 1373, 1237, 1086 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.49−

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7.47 (m, 2H), 7.27−7.21 (m, 3H), 6.02 (dd, J = 5.9, 4.1 Hz, 1H), 5.96 (ddd, J = 17.4, 10.6, 5.0 Hz, 1H), 5.31 (dd, J = 17.4, 1.8 Hz, 1H), 5.17 (dd, J = 10.6, 1.8 Hz, 1H), 3.92 (m, 1H), 3.55 (dd, J = 10.6, 5.0 Hz, 1H), 3.36 (ddd, J = 11.5, 11.5, 3.2 Hz, 1H), 3.30 (ddd, J = 13.8, 10.6, 4.6 Hz, 1H), 2.94−2.83 (m, 2H), 2.21 (m, 1H), 2.08−1.95 (m, 5H), 1.69−1.60 (m, 2H), 1.37 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 136.1, 132.8 (2C), 129.7, 129.1 (2C), 127.0, 116.1, 94.5, 80.0, 75.7, 67.3, 35.1, 29.5, 24.9, 21.6, 21.2; HRMS (ESI) calcd for $C_{18}H_{24}O_4SeNa$ [(M + Na)$^+$] 407.0732, found 407.0750. More polar isomer: $[\alpha]_D^{26}$ −3.9 (c 1.00, $CHCl_3$); IR (neat) 3074, 2941, 2850, 2359, 1736, 1238, 1086 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48−7.46 (m, 2H), 7.23−7.21 (m, 3H), 5.92 (dd, J = 5.0, 5.0 Hz, 1H), 5.85 (ddd, J = 17.4, 10.6, 6.9 Hz, 1H), 5.31 (dd, J = 17.4, 1.4 Hz, 1H), 5.17 (dd, J = 10.6, 1.4 Hz, 1H), 3.89 (m, 1H), 3.53 (dd, J = 8.7, 6.9 Hz, 1H), 3.38−3.31 (m, 2H), 2.88−2.84 (m, 2H), 2.06−1.96 (m, 6H), 1.67−1.63 (m, 2H), 1.49 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 136.0, 132.7 (2C), 129.7, 129.1 (2C), 127.0, 118.5, 98.6, 81.6, 78.5, 67.2, 35.2, 31.1, 25.2, 21.4 (2C); HRMS (ESI) calcd for $C_{18}H_{24}O_4SeNa$ [(M + Na)$^+$] 407.0732, found 407.0727.

α-Acetoxy ether ***4b***. Prepared from ester **3b** (535.1 mg, 1.282 mmol) in the same manner as **4a**: yield 496.9 mg, 84% (dr 63:37); colorless oil; $[\alpha]_D^{26}$ −28.0 (c 1.00, $CHCl_3$); IR (neat) 3068, 2993, 2855, 1741, 1235, 1125, 1011 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50−7.45 (m, 4H), 7.37−7.30 (m, 3H), 7.28−7.23 (m, 3H), 6.01−5.90 (m, 2H), 5.49 (s, 1H), 5.43 (dd, J = 17.4, 1.4 Hz, 2/5H), 5.42 (dd, J = 17.4, 1.0 Hz, 3/5H), 5.29 (dd, J = 10.6, 1.0 Hz, 3/5H), 5.24 (dd, J = 10.6, 1.4 Hz, 2/5H), 3.96−3.57 (m, 2H), 2.92−2.83 (m, 2H), 2.08−1.98 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5 (2/5C), 170.3 (3/5C), 137.6 (2/5C), 137.5 (3/5C), 134.4, 133.1 (4/5C), 133.0 (6/5C), 129.7 (3/5C), 129.5 (2/5C), 129.3 (4/5C), 129.2 (6/5C), 129.1, 128.4 (10/5C), 127.3 (2/5C), 127.2 (3/5C), 126.3 (4/5C), 126.2 (6/5C), 119.5 (3/5C), 117.4 (2/5C), 101.0 (3/5C), 100.9 (2/5C), 98.7 (3/5C), 95.5 (2/5C), 81.5 (3/5C), 80.0 (2/5C), 73.0 (3/5C), 71.2 (2/5C), 70.0 (3/5C), 69.2 (2/5C), 35.2 (3/5C), 35.0 (2/5C), 21.6 (2/5C), 21.4 (3/5C), 21.3 (3/5C), 21.2 (2/5C); HRMS (ESI) calcd for $C_{23}H_{26}O_5SeNa$ [(M + Na)$^+$] 485.0838, found 485.0819.

α-Acetoxy Ether ***4c***. Prepared from ester **3c** (337.7 mg, 0.7828 mmol) in the same manner as **4a**: yield 366.7 mg, 99% (dr 69:31); colorless oil; $[\alpha]_D^{27}$ −17.2 (c 1.00, $CHCl_3$); IR (neat) 3068, 2993, 2855, 1741, 1235, 1125, 1011 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51−7.46 (m, 4H), 7.38−7.32 (m, 3H), 7.29−7.23 (m, 3H), 6.15 (dd, J = 5.9, 3.7 Hz, 5/7H), 6.12 (dd, J = 6.4, 4.1 Hz, 2/7H), 5.97 (ddd, J = 17.4, 10.6, 5.0 Hz, 2/7H), 5.87 (ddd, J = 17.4, 10.6, 5.0 Hz, 5/7H), 5.54 (s, 5/7H), 5.52 (s, 2/7H), 5.42 (dd, J = 17.4, 1.9 Hz, 2/7H), 5.40 (dd, J = 17.4, 1.9 Hz, 5/7H), 5.27 (m, 1H), 4.22 (m, 1H), 4.10 (d, J = 11.0 Hz, 2/7H), 3.97 (d, J = 11.0 Hz, 5/7H), 3.82 (d, J = 11.0 Hz, 5/7H), 3.70 (d, J = 11.0 Hz, 2/7H), 2.94−2.81 (m, 2H), 2.09−1.98 (m, 5H), 1.41 (s, 15/7H), 1.35 (s, 6/7H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8 (2/7C), 169.7 (5/7C), 137.6, 132.9 (2C), 132.4 (5/7C), 132.3 (2/7C), 129.6, 129.2 (4/7C), 129.1 (10/7C), 129.0, 128.3 (2C), 127.2 (2/7C), 127.1 (5/7C), 126.2 (4/7C), 126.1 (10/7C), 117.9 (5/7C), 117.2 (2/7C), 101.5 (2/7C), 101.4 (5/7C), 93.1 (5/7C), 92.5 (2/7C), 82.5 (5/7C), 81.9 (2/7C), 75.9 (5/7C), 75.1 (2/7C), 73.0 (5/7C), 72.6 (2/7C), 35.9 (2/7C), 35.6 (5/7C), 21.6 (5/7C), 21.5 (4/7C), 21.4 (5/7C), 16.5 (2/7C), 15.6 (5/7C); HRMS (ESI) calcd for $C_{24}H_{28}O_5SeNa$ [(M + Na)$^+$] 499.0994, found 499.0987.

α-Acetoxy Ether ***4d***. Prepared from ester **3d** (1.004 g, 2.842 mmol) in the same manner as **4a**: yield 1.056 g, 93% (dr 56:44); colorless oil; $[\alpha]_D^{24}$ +35.3 (c 1.00, $CHCl_3$); IR (neat) 3073, 2940, 2849, 2359, 1737, 1239, 1097 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50−7.46 (m, 2H), 7.27−7.21 (m, 3H), 6.02 (dd, J = 6.4, 4.6 Hz, 3/7H), 5.96 (dd, J = 5.0, 5.0 Hz, 4/7H), 5.84 (m, 1H), 5.11−5.03 (m, 2H), 3.86 (m, 1H), 3.34−3.24 (m, 2H), 3.14 (m, 1H), 2.93−2.83 (m, 2H), 2.57 (m, 3/7H), 2.47 (m, 4/7H), 2.23−2.11 (m, 11/7H), 2.09−1.96 (m, 38/7H), 1.64−1.58 (m, 2H), 1.45 (m, 4/7H), 1.30 (m, 3/7H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7 (4/7C), 170.3 (3/7C), 135.0 (3/7C), 134.7 (4/7C), 132.9 (2C), 129.7 (3/7C), 129.6 (4/7C), 129.1 (2C), 127.1 (4/7C), 127.0 (3/7C), 117.0 (4/7C), 116.7 (3/7C), 98.5 (4/7C), 94.3 (3/7C), 79.9 (4/7C), 79.6 (3/7C), 78.5 (4/7C), 74.6 (3/7C), 67.6 (4/7C), 67.7 (3/7C), 36.5 (4/7C), 36.2 (3/7C), 35.5 (4/7C), 35.1 (3/7C), 31.0 (4/7C), 29.2 (3/7C), 25.4 (4/7C), 25.1 (3/7C), 21.5 (4/7C), 21.4 (3/7C), 21.3 (4/7C), 21.2 (3/7C); HRMS (ESI) calcd for $C_{19}H_{26}O_4SeNa$ [(M + Na)$^+$] 421.0889, found 421.0883.

α-Acetoxy Ether ***4e***. Prepared from ester **3e** (493.0 mg, 1.107 mmol) in the same manner as **4a**: yield 481.5 mg, 98% (dr 70:30); pale yellow oil; $[\alpha]_D^{24}$ −18.8 (c 1.00, $CHCl_3$); IR (neat) 3071, 2979, 2934, 2859, 1734, 1241, 1118 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.45−7.43 (m, 2H), 7.35−7.29 (m, 3H), 7.27−7.22 (m, 3H), 6.15 (dd, J = 5.9, 4.1 Hz, 7/10H), 6.11 (dd, J = 6.4, 4.1 Hz, 3/10H), 5.89 (m, 1H), 5.47 (s, 7/10H), 5.45 (s, 3/10H), 5.15−5.03 (m, 2H), 4.10 (d, J = 11.0 Hz, 3/10H), 3.95 (d, J = 11.0 Hz, 7/10H), 3.79 (d, J = 11.0 Hz, 7/10H), 3.72 (dd, J = 10.1, 2.8 Hz, 7/10H), 3.68 (dd, J = 10.1, 2.8 Hz, 3/10H), 3.64 (d, J = 11.0 Hz, 3/10H), 2.93−2.82 (m, 2H), 2.49 (m, 1H), 2.37 (m, 1H), 2.21 (m, 1H), 2.09−1.97 (m, 5H), 1.44 (s, 21/10H), 1.39 (s, 9/10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8 (3/10C), 169.7 (7/10C), 137.7, 135.1 (3/10C), 135.0 (7/10C), 133.0 (6/10C), 132.9 (14/10C), 129.6, 129.1 (23/10C), 128.9 (7/10C), 128.2 (2C), 127.2, 126.1 (6/10C), 126.0 (14/10C), 116.7, 101.6 (3/10C), 101.5 (7/10C), 93.0 (7/10C), 92.5 (3/10C), 82.5 (3/10C), 82.4 (7/10C), 76.1 (7/10C), 75.4 (3/10C), 72.9 (7/10C), 72.3 (3/10C), 35.9 (3/10C), 35.7 (7/10C), 33.2 (7/10C), 32.9 (3/10C), 21.6, 21.5, 16.1 (3/10C), 15.3 (7/10C); HRMS (ESI) calcd for $C_{25}H_{30}O_5SeNa$ [(M + Na)$^+$] 513.1151, found 513.1177.

α-Acetoxy Ether ***4f***. Prepared from ester **3f** (786.4 mg, 2.141 mmol) in the same manner as **4a**: yield 802.5 mg, 91% (dr 56:44); colorless oil; $[\alpha]_D^{24}$ +38.2 (c 1.00, $CHCl_3$); IR (neat) 3073, 2940, 2849, 2359, 1736, 1239, 1098 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48−7.46 (m, 2H), 7.26−7.21 (m, 3H), 6.01 (dd, J = 6.4, 4.6 Hz, 3/7H), 5.97 (dd, J = 5.0, 5.0 Hz, 4/7H), 5.80 (m, 1H), 5.00 (m, 1H), 4.93 (m, 1H) 3.84 (m, 1H), 3.29−3.21 (m, 2H), 3.04 (m, 1H), 2.93−2.82 (m, 2H), 2.25−2.17 (m, 11/7H), 2.09−1.96 (m, 45/7H), 1.91 (m, 3/7H), 1.77 (m, 4/7H), 1.65−1.55 (m, 2H), 1.45 (m, 1H), 1.38 (m, 4/7H), 1.30 (m, 3/7H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7 (3/7C), 170.3 (4/7C), 138.7 (3/7C), 138.4 (4/7C), 132.8 (2C), 129.7 (4/7C), 129.6 (3/7C), 129.1 (2C), 127.1 (4/7C), 127.0 (3/7C), 114.7 (4/7C), 114.4 (3/7C), 98.6 (4/7C), 94.6 (3/7C), 79.6 (4/7C), 79.4 (3/7C), 79.1 (4/7C), 75.5 (3/7C), 67.5 (3/7C), 67.4 (4/7C), 35.4 (4/7C), 35.1 (3/7C), 31.3 (4/7C), 31.2 (3/7), 31.1 (4/7C), 29.4 (10/7C), 25.4 (4/7C), 25.2 (3/7C), 21.6 (3/7C), 21.4 (8/7C) 21.2 (3/7C); HRMS (ESI) calcd for $C_{20}H_{28}O_4SeNa$ [(M + Na)$^+$] 435.1045, found 435.1031.

Olefin ***5a***. To a suspension of $ZnBr_2$ (391.5 mg, 1.739 mmol) in CH_2Cl_2 (8.7 mL) at 0 °C was added vinylmagnesium bromide (1.0 M solution in THF, 3.2 mL, 3.2 mmol), and the resultant mixture was stirred at room temperature for 30 min. To the resultant mixture at 0 °C was added a solution of α-acetoxy ether **4a** (302.3 mg, 0.7886 mmol) in CH_2Cl_2 (5.0 mL + 5.2 mL rinse), and the resultant mixture was stirred at 0 °C for 13 h. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was extracted with EtOAc, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 2% EtOAc/hexanes) gave olefin **5a** (258.4 mg, 93%, dr 66:34) as a colorless oil: $[\alpha]_D^{26}$ +26.9 (c 1.00, $CHCl_3$); IR (neat) 3074, 2937, 2850, 2359, 1478, 1437, 1088 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47−7.44 (m, 2H), 7.25−7.19 (m, 3H), 5.91 (m, 1H), 5.65 (ddd, J = 17.5, 10.6, 8.3 Hz, 2/3H), 5.58 (m, 1/3H), 5.33 (dd, J = 17.5, 1.8 Hz, 2/3H), 5.29 (dd, J = 17.5, 1.8 Hz, 1/3H), 5.20−5.11 (m, 3H), 3.95−3.84 (m, 2H), 3.55 (m, 1H), 3.34 (m, 1H), 3.11 (ddd, J = 10.5, 9.2, 4.7 Hz, 1/3H), 3.04 (ddd, J = 10.5, 9.2, 4.7 Hz, 2/3H), 2.96−2.84 (m, 2H), 2.15 (m, 1/3H), 2.03 (m, 2/3H), 1.92 (m, 1H), 1.76 (m, 1H), 1.67−1.56 (m, 2H), 1.35 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.3 (2/3C), 138.6 (1/3C), 136.7, 132.5 (2C), 130.2, 129.0 (2C), 126.8, 117.4 (3/7C), 117.3 (4/7C), 117.0 (4/7C), 116.3 (3/7C), 82.1 (2/3C), 81.0 (1/3C), 80.9 (2/3C), 77.3 (1/3C), 76.5 (2/3C), 74.1 (1/3C), 67.4, 36.0 (2/3C), 35.9 (1/3C), 31.5 (2/3C), 29.3 (1/3C), 25.4 (2/3C), 25.1 (1/3C), 23.5

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(1/3C), 23.3 (2/3C); HRMS (ESI) calcd for $C_{18}H_{24}O_2SeNa$ [(M + Na)$^+$] 375.0834, found 375.0834.

Olefin ***5b***. Prepared from α-acetoxy ether **4b** (440.4 mg, 0.9544 mmol) in the same manner as **5a**: yield 276.4 mg, 32% (dr 69:31), 86% based on recovered starting material; colorless oil; $[\alpha]_D^{26}$ −28.4 (*c* 1.00, $CHCl_3$); IR (neat) 2925, 2854, 2359, 1386, 1092, 1023 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50−7.45 (m, 4H), 7.36−7.30 (m, 3H), 7.27−7.21 (m, 3H), 5.97 (m, 1H), 5.59 (m, 1H), 5.50 (s, 1/3H), 5.48 (s, 2/3H), 5.46 (dd, *J* = 17.0, 1.4 Hz, 2/3H), 5.42 (dd, *J* = 17.0, 1.4 Hz, 1/3H), 5.28 (dd, *J* = 10.6, 1.4 Hz, 2/3H), 5.24 (dd, *J* = 10.6, 1.4 Hz, 1/3H), 5.22−5.16 (m, 2H), 4.35 (dd, *J* = 10.6, 4.6 Hz, 1/3H), 4.22 (dd, *J* = 11.0, 5.5 Hz, 2/3H), 4.06 (m, 1H), 3.91 (m, 1H), 3.56 (m, 1H), 3.45 (ddd, *J* = 9.2, 9.2, 4.6 Hz, 1/3H), 3.37 (ddd, *J* = 9.7, 9.7, 5.5 Hz, 2/3H), 2.94−2.87 (m, 2H), 1.94 (m, 1H), 1.79 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5 (2/3C), 137.8 (1/3C), 137.7, 135.0 (2/3C), 134.8 (1/3C), 132.7 (2/3C), 132.6 (4/3C), 130.0 (1/3C), 129.0 (2/3C), 129.0 (4/3C), 128.9 (2/3C), 128.2 (3C), 126.9, 126.1 (2C), 118.5 (2/3C), 118.4 (1/3C), 118.3 (2/3C), 117.5 (1/3C), 100.8 (1/3C), 100.6 (2/3C), 82.0 (2/3C), 81.8 (2/3C), 80.8 (1/3C), 79.1 (1/3C), 71.8 (2/3C), 70.3 (2/3C), 69.5 (1/3C), 69.4 (1/3C), 35.9 (2/3C), 35.7 (1/3C), 23.3 (1/3C), 23.2 (2/3C); HRMS (ESI) calcd for $C_{23}H_{26}O_3SeNa$ [(M + Na)$^+$] 453.0939, found 453.0944.

Olefin ***5c***. Prepared from α-acetoxy ether **4c** (352.4 mg, 0.7412 mmol) in the same manner as **5a**: yield 271.7 mg, 83% (dr 76:24); colorless oil; $[\alpha]_D^{28}$ −22.5 (*c* 1.00, $CHCl_3$); IR (neat) 2980, 2935, 2855, 1126, 1096, 1023, 735 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51−7.46 (m, 4H), 7.38−7.31 (m, 3H), 7.28−7.21 (m, 3H), 5.96 (m, 1H), 5.74 (m, 1H), 5.52 (s, 1/4H), 5.51 (s, 3/4H), 5.39 (m, 1H), 5.23 (m, 1H), 5.16 (m, 1H), 5.08 (m, 1H), 4.21−4.16 (m, 2H), 4.09 (d, *J* = 10.5 Hz, 3/4H), 4.08 (d, *J* = 10.1 Hz, 1/4H), 3.68 (m, 1H), 2.96−2.87 (m, 2H), 1.91 (m, 1H), 1.77 (m, 1H), 1.37 (s, 9/4H), 1.31 (s, 3/4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.2 (3/4C) 140.6 (1/4C), 138.0 (3/4C), 137.9 (1/4C), 133.1, 132.6 (2/4C), 132.5 (6/4C), 130.0, 129.1 (2/4C), 129.0 (6/4C), 128.9, 128.2 (2C), 126.9 (1/4C), 126.8 (3/4C), 126.2 (2C), 117.0 (3/4C), 116.8 (1/4C), 115.9 (3/4C), 115.1 (1/4C), 101.4 (1/4C), 101.3 (3/4C), 83.0 (3/4C), 82.7 (1/4C), 76.7 (3/4C), 75.7 (1/4C), 73.5 (3/4C), 72.6 (1/4C), 72.1 (3/4C), 71.7 (1/4C), 37.4 (1/4C), 37.1 (3/4C), 23.4 (3/4C), 23.3 (1/4C), 17.0 (1/4C), 16.0 (3/4C); HRMS (ESI) calcd for $C_{24}H_{28}O_3SeNa$ [(M + Na)$^+$] 467.1096, found 467.1108.

Olefin ***5d***. Prepared from α-acetoxy ether **4d** (1.039 g, 2.614 mmol) in the same manner as **5a**: yield 870.7 mg, 91% (dr 63:37); colorless oil; $[\alpha]_D^{24}$ +57.2 (*c* 1.00, $CHCl_3$); IR (neat) 3073, 2937, 2847, 2359, 1437, 1097, 735 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47−7.45 (m, 2H), 7.25−7.20 (m, 3H), 5.86 (m, 1H), 5.68 (ddd, *J* = 17.4, 10.5, 8.2 Hz, 5/8H), 5.60 (ddd, *J* = 17.4, 10.6, 8.2 Hz, 5/8H), 5.18−5.02 (m, 4H), 3.93 (ddd, *J* = 7.8, 7.8, 5.0 Hz, 5/8H), 3.86 (m, 11/8H), 3.28 (m, 1H), 3.14 (m, 1H), 3.09 (ddd, *J* = 10.6, 10.6, 4.1 Hz, 5/8H), 3.02 (ddd, *J* = 10.5, 9.2, 4.6 Hz, 3/8H), 2.97−2.86 (m, 2H), 2.57 (m, 1H), 2.20−2.08 (m, 13/8H), 2.04 (m, 3/8H), 1.94 (m, 1H), 1.79 (m, 1H), 1.65−1.52 (m, 2H), 1.32 (m, 3/8H), 1.24 (m, 5/8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.5 (3/8C), 138.6 (5/8C), 135.5 (5/8C), 135.3 (3/8C), 132.7 (6/8C), 132.5 (10/8C), 130.2 (5/8C), 130.0 (3/8C), 129.0 (2C), 126.9 (3/8C), 126.8 (5/8C), 117.8 (5/8C), 116.9 (3/8C), 116.6 (3/8C), 116.4 (5/8C), 80.8 (3/8C), 80.7 (3/8C), 80.4 (5/8C), 77.0 (3/8C), 76.2 (5/8C), 73.4 (5/8C), 67.8 (5/8C), 67.7 (3/8C), 36.6, 36.0 (5/8C), 35.9 (3/8C), 31.3 (3/8C), 29.0 (5/8C), 25.5 (3/8C), 25.3 (5/8C), 23.6 (5/8C), 23.3 (3/8C); HRMS (ESI) calcd for $C_{19}H_{26}O_2SeNa$ [(M + Na)$^+$] 389.0990, found 389.0976.

Olefin ***5e***. Prepared from α-acetoxy ether **4e** (157.5 mg, 0.3422 mmol) in the same manner as **5a**: yield 141.5 mg, 90% (dr 71:29); yellow oil; $[\alpha]_D^{24}$ −18.8 (*c* 1.00, $CHCl_3$); IR (neat) 3071, 2979, 2934, 2859, 1734, 1241, 1118 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50−7.44 (m, 2H), 7.36−7.30 (m, 2H), 7.28−7.21 (m, 3H), 7.28−7.21 (m, 3H), 5.90 (m, 1H), 5.74 (m, 1H), 5.44 (s, 5/7H), 5.43 (s, 2/7H), 5.17−5.02 (m, 4H), 4.17 (m, 1H), 4.07 (d, *J* = 10.5 Hz, 1H), 3.66−3.63 (m, 2H), 2.95−2.87 (m, 2H), 2.51 (m, 2/7H), 2.44 (m, 5/7H), 2.18 (m, 1H), 1.90 (m, 1H), 1.77 (m, 1H), 1.40 (s, 15/7H), 1.35 (s, 6/7H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.2 (5/7C), 140.8 (2/7C), 138.1 (5/7C), 138.0 (2/7C), 135.6 (2/7C), 135.5 (5/7C), 132.6 (2C), 130.3 (2/7C), 130.0 (5/7C), 129.1 (2C), 128.8 (2/7C), 128.7 (5/7C), 128.2 (2C), 126.9, 126.1 (4/7C), 126.0 (10/7C), 116.4, 115.9 (5/7C), 115.1 (2/7C), 101.5 (2/7C), 101.4 (5/7C), 83.2, 76.8 (5/7C), 76.0 (2/7C), 73.4 (5/7C), 72.7 (2/7C), 71.9 (5/7C), 71.4 (2/7C), 37.4 (2/7C), 37.2 (5/7C), 33.1, 23.6 (5/7C), 23.3 (2/7C), 16.9 (2/7C), 15.8 (5/7C); HRMS (ESI) calcd for $C_{25}H_{30}O_5SeNa$ [(M + Na)$^+$] 513.1151, found 513.1177.

Olefin ***5f***. Prepared from α-acetoxy ether **4f** (745.2 mg, 1.811 mmol) in the same manner as **5a**: yield 628.5 mg, 91% (dr 66:34); pale yellow oil; $[\alpha]_D^{24}$ +56.8 (*c* 1.00, $CHCl_3$); IR (neat) 3073, 2936, 2848, 1477, 1437, 1098, 735 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47−7.45 (m, 2H), 7.25−7.20 (m, 3H), 5.81 (m, 1H), 5.68 (ddd, *J* = 17.9, 10.5, 7.8 Hz, 1/3H), 5.60 (ddd, *J* = 17.0, 10.1, 8.3 Hz, 2/3H), 5.17−5.11 (m, 2H), 5.01 (dd, *J* = 17.9, 1.9 Hz, 1/3H), 5.00 (dd, *J* = 17.0, 1.4 Hz, 2/3H), 4.92 (m, 1H), 3.92 (ddd, *J* = 8.2, 8.2, 5.5 Hz, 2/3H), 3.85 (m, 4/3H), 3.27 (m, 1H), 3.07−3.02 (m, 2H), 3.00−2.87 (m, 2H), 2.22 (m, 1H), 2.14 (m, 2/3H), 2.05 (m, 4/3H), 1.98−1.86 (m, 2H), 1.78 (m, 1H), 1.64−1.52 (m, 2H), 1.46−1.20 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.6 (1/3C), 139.0 (2/3C), 138.7, 132.7 (2/3C), 132.5 (4/3C), 130.2 (2/3C), 130.0 (1/3C), 129.0 (2C), 126.8 (1/3C), 126.7 (2/3C), 117.7 (2/3C), 116.8 (1/3C), 114.5 (1/3C), 114.2 (2/3C), 80.8 (1/3C), 80.6 (1/3C), 80.3 (2/3C), 77.1 (2/3C), 76.9 (1/3C), 73.9 (2/3C), 67.6 (2/3C), 67.5 (1/3C), 36.0 (2/3C), 36.0 (1/3C), 31.6 (1/3C), 31.4 (2/3C), 31.4 (1/3C), 29.7, 29.1 (2/3C), 25.6 (1/3C), 25.4 (2/3C), 23.6 (2/3C), 23.4 (1/3C); HRMS (ESI) calcd for $C_{20}H_{28}O_2SeNa$ [(M + Na)$^+$] 403.1147, found 403.1139.

1,4-Pentadien-3-yl Ether ***6a***. To a solution of olefin **5a** (112.6 mg, 0.3205 mmol) in CH_2Cl_2 (3.2 mL) at 0 °C was added *m*-CPBA (78.0 mg, 0.452 mmol), and the resultant mixture was stirred at 0 °C for 30 min. To the reaction mixture was added Et_3N (0.22 mL, 1.6 mmol), and the resultant mixture was heated to reflux for 6 h. The reaction mixture was concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 2% Et_2O/*n*-pentane then 40% CH_2Cl_2/*n*-pentane) gave 1,4-pentadien-3-yl ether **6a** (56.6 mg, 91%) as a yellow oil: $[\alpha]_D^{24}$ +45.7 (*c* 1.00, $CHCl_3$); IR (neat) 3081, 2925, 2852, 1272, 1091, 989, 924 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.95 (ddd, *J* = 17.0, 11.0, 5.9 Hz, 1H), 5.76 (ddd, *J* = 17.0, 10.1, 6.4 Hz, 1H), 5.70 (ddd, *J* = 17.0, 10.1, 6.4 Hz, 1H), 5.33 (dd, *J* = 17.0, 1.9 Hz, 1H), 5.22−5.13 (m, 5H), 4.28 (t, *J* = 6.4 Hz, 1H), 3.91 (m, 1H), 3.60 (dd, *J* = 9.2, 5.9 Hz, 1H), 3.36 (ddd, *J* = 11.5, 11.5, 3.2 Hz, 1H), 3.13 (ddd, *J* = 10.5, 9.2, 4.1 Hz, 1H), 2.11 (m, 1H), 1.66−1.58 (m, 2H), 1.41 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 137.6, 136.6, 116.6, 116.5, 116.4, 81.6, 80.7, 75.2, 67.4, 30.4, 25.4; HRMS (ESI) calcd for $C_{12}H_{18}O_2Na$ [(M + Na)$^+$] 217.1199, found 217.1178.

1,4-Pentadien-3-yl Ether ***6b***. Prepared from olefin **5b** (93.7 mg, 0.218 mmol) in the same manner as **6a**: yield 59.2 mg, quantitative; colorless oil; $[\alpha]_D^{26}$ −45.6 (*c* 1.00, $CHCl_3$); IR (neat) 2981, 2925, 2853, 2361, 1091, 927, 752 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49−7.47 (m, 3H), 7.36−7.30 (m, 2H), 6.01 (ddd, *J* = 17.4, 11.0, 5.9 Hz, 1H), 5.77−5.70 (m, 2H), 5.51 (s, 1H), 5.46 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.28−5.17 (m, 5H), 4.30−4.27 (m, 2H), 4.12 (m, 1H), 3.62 (t, *J* = 10.1 Hz, 1H), 3.47 (ddd, *J* = 10.1, 9.2, 5.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.7, 137.4, 137.0, 134.8, 128.9, 128.2 (2C), 126.1 (2C), 117.7, 117.6, 117.1, 100.7, 82.2, 81.4, 70.7, 69.9; HRMS (ESI) calcd for $C_{17}H_{20}O_3Na$ [(M + Na)$^+$] 295.1305, found 295.1311.

1,4-Pentadien-3-yl Ether ***6c***. Prepared from olefin **5c** (104.3 mg, 0.2352 mmol) in the same manner as **6a**: yield 61.9 mg, 92%; colorless oil; $[\alpha]_D^{28}$ −32.5 (*c* 1.00, $CHCl_3$); IR (neat) 2982, 2856, 1382, 1127, 1095, 1028, 925 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.37−7.32 (m, 3H), 6.02 (ddd, *J* = 17.4, 11.0, 4.6 Hz, 1H), 5.82−5.75 (m, 2H), 5.54 (s, 1H), 5.42 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.26 (dd, *J* = 11.0, 1.8 Hz, 1H), 5.24−5.20 (m, 2H), 5.13 (dd, *J* = 10.1, 1.4 Hz, 1H), 5.10 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.57 (m, 1H), 4.25 (m, 1H), 4.10 (d, *J* = 10.1 Hz, 1H), 3.76 (d, *J* = 10.1 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.7, 139.0, 138.0, 133.1, 128.9, 128.2 (2C), 126.2 (2C), 116.8, 115.5, 114.7, 101.4, 82.8, 76.2, 74.2, 72.3, 16.2; HRMS (ESI) calcd for $C_{18}H_{22}O_3Na$ [(M + Na)$^+$] 309.1461, found 309.1483.

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1,4-Pentadien-3-yl Ether ***6d***. Prepared from olefin **5d** (380.9 mg, 1.042 mmol) in the same manner as **6a**: yield 200.5 mg, 92%; yellow oil; $[\alpha]_D^{26}$ +58.6 (*c* 1.00, $CHCl_3$); IR (neat) 3076, 2937, 2849, 2359, 1098, 1080, 924 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.87 (dddd, *J* = 17.5, 10.1, 7.8, 6.4 Hz, 1H), 5.79 (ddd, *J* = 17.0, 10.1, 6.4 Hz, 1H), 5.71 (ddd, *J* = 17.4, 10.6, 7.3 Hz, 1H), 5.22 (dd, *J* = 10.6, 1.4 Hz, 1H), 5.21−5.17 (m, 2H), 5.13 (dd, *J* = 10.1, 1.4 Hz, 1H), 5.08 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.04 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.29 (dd, *J* = 7.3, 6.4 Hz, 1H), 3.87 (m, 1H), 3.30 (ddd, *J* = 11.0, 11.0, 3.7 Hz, 1H), 3.20 (ddd, *J* = 9.2, 9.2, 3.2 Hz, 1H), 3.14 (ddd, *J* = 9.2, 9.2, 4.6 Hz, 1H), 2.60 (m, 1H), 2.20−2.12 (m, 2H), 1.64−1.54 (m, 2H), 1.34 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 137.7, 135.5, 117.0, 116.5, 116.1, 80.6, 80.3, 74.6, 67.8, 36.6, 29.9, 25.5; HRMS (ESI) calcd for $C_{13}H_{20}O_2Na$ $[(M + Na)^+]$ 231.1356 found 231.1353.

1,4-Pentadien-3-yl Ether ***6e***. Prepared from olefin **5e** (13.1 mg, 0.0286 mmol) in the same manner as **6a**, except that $(CH_2Cl)_2$ was used as the solvent and the selenoxide elimination step was performed at 45 °C: yield 8.0 mg, 93%; colorless oil; $[\alpha]_D^{23}$ −38.3 (*c* 1.00, $CHCl_3$); IR (neat) 3075, 2979, 2924, 2858, 1397, 1113, 1029 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.47−7.45 (m, 2H), 7.36−7.30 (m, 3H), 5.92 (dddd, *J* = 17.5, 10.1, 7.4, 7.4 Hz 1H), 5.83−5.74 (m, 2H), 5.47 (s, 1H), 5.21 (dd, *J* = 17.5, 1.4 Hz, 2H), 5.14−5.10 (m, 3H), 5.04 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.55 (m, 1H), 4.09 (d, *J* = 10.1 Hz, 1H), 3.74−3.71 (m, 2H), 2.54 (m, 1H), 2.22 (m, 1H), 1.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.6, 139.1, 138.1, 135.5, 128.8, 128.2 (2C), 126.1 (2C), 116.5, 115.5, 114.7, 101.5, 83.1, 76.4, 74.2, 72.0, 33.1, 16.1; HRMS (ESI) calcd for $C_{19}H_{24}O_3Na$ $[(M + Na)^+]$ 323.1618 found 323.1605.

1,4-Pentadien-3-yl Ether ***6f***. Prepared from olefin **5f** (139.1 mg, 0.3666 mmol) in the same manner as **6a**: yield 72.1 mg, 88%; yellow oil; $[\alpha]_D^{26}$ +71.9 (*c* 1.00, $CHCl_3$); IR (neat) 3078, 2936, 2849, 2359, 1640, 1099, 923 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.85−5.76 (m, 2H), 5.71 (ddd, *J* = 17.5, 10.6, 6.9 Hz, 1H), 5.22 (dd, *J* = 10.6, 1.4 Hz, 1H), 5.20−5.17 (m, 2H), 5.13 (dd, *J* = 10.5, 1.4 Hz, 1H), 5.00 (dd, *J* = 17.0, 1.8 Hz, 1H), 4.92 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.27 (t, *J* = 6.9 Hz, 1H), 3.85 (m, 1H), 3.28 (ddd, *J* = 11.5, 11.5, 2.7 Hz, 1H), 3.12−3.07 (m, 2H), 2.23 (m, 1H), 2.13−2.04 (m, 2H), 1.93 (m, 1H), 1.65−1.55 (m, 2H), 1.41 (m, 1H), 1.33 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.9, 138.4, 137.8, 117.0, 116.0, 114.3, 80.5, 80.3, 75.1, 67.6, 31.5, 30.0, 30.7, 25.6; HRMS (ESI) calcd for $C_{14}H_{22}O_2Na$ $[(M + Na)^+]$ 245.1512, found 245.1526.

Acrylate ***10***. To a solution of alcohol **1e** (282.0 mg, 1.204 mmol) in CH_2Cl_2 (12 mL) were added *i*-Pr_2NEt (4.2 mL, 24 mmol) and acryloyl chloride (0.975 mL, 12.1 mmol), and the resultant mixture was stirred at 40 °C for 7 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution. The resultant mixture was stirred at room temperature for 1 h and then extracted with EtOAc. The organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 2% EtOAc/hexanes) gave acrylate **10** (178.7 mg, 51%) as a colorless oil: $[\alpha]_D^{25}$ −88.9 (*c* 1.00, $CHCl_3$); IR (neat) 2925, 2858, 1726, 1400, 1273, 1194, 1030 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.48−7.46 (m, 2H), 7.37−7.31 (m, 3H), 6.34 (dd, *J* = 17.0, 1.4 Hz, 1H), 6.05 (dd, *J* = 17.0, 10.1 Hz, 1H), 5.92 (dddd, *J* = 17.5, 10.1, 6.4, 6.4 Hz, 1H), 5.82 (dd, *J* = 10.1, 1.4 Hz, 1H), 5.52 (s, 1H), 5.14 (dd, *J* = 17.5, 1.8 Hz, 1H), 5.08 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.84 (d, *J* = 10.6 Hz, 1H), 3.90 (dd, *J* = 10.1, 3.2 Hz, 1H), 3.86 (d, *J* = 10.6 Hz, 1H), 2.46 (m, 1H), 2.32 (m, 1H), 1.71 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7, 137.6, 134.8, 131.1, 129.0, 128.9, 128.3 (2C), 126.1 (2C), 116.9, 101.7, 81.7, 76.0, 74.2, 33.4, 16.1; HRMS (ESI) calcd for $C_{17}H_{20}O_4Na$ $[(M + Na)^+]$ 311.1254, found 311.1263.

α-Acetoxy Ether ***11***. To a solution of acrylate **10** (26.2 mg, 0.0909 mmol) in CH_2Cl_2 (0.91 mL) at −78 °C was added DIBALH (1.02 M solution in *n*-hexane, 0.11 mL, 0.11 mmol), and the resultant solution was stirred at −78 °C for 5 min. To this solution were added pyridine (0.030 mL, 0.37 mmol), DMAP (13.3 mg, 0.109 mmol), and Ac_2O (0.034 mL, 0.36 mmol), and the resultant mixture was stirred at −78 °C for 15 h and then allowed to warm to 0 °C over 3.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was diluted with EtOAc and saturated aqueous potassium sodium tartrate solution and stirred vigorously at room temperature for 1 h. The reaction mixture was extracted with EtOAc, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 2% EtOAc/hexanes containing 1% Et_3N) gave α-acetoxy ether **11** (20.1 mg, 69%, dr 74:26) as a colorless oil: $[\alpha]_D^{24}$ −38.1 (*c* 1.00, $CHCl_3$); IR (neat) 2979, 2862, 1736, 1371, 1238, 1117, 1026 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.48−7.45 (m, 2H), 7.37−7.30 (m, 3H), 6.42 (d, *J* = 5.0 Hz, 3/4H), 6.35 (d, *J* = 5.5 Hz, 1/4H), 5.90 (m, 1H), 5.83 (m, 1H), 5.52−5.41 (m, 2H), 5.28 (m, 1H), 5.13 (dd, *J* = 17.0, 1.4 Hz, 1/4H), 5.11 (dd, *J* = 17.0, 1.4 Hz, 3/4H), 5.05 (m, 1H), 4.09 (d, *J* = 10.6 Hz, 1/4H), 4.01 (d, *J* = 10.6 Hz, 3/4H), 3.82 (d, *J* = 10.6 Hz, 3/4H), 3.75 (m, 1H), 3.71 (d, *J* = 10.6 Hz, 1/4H), 2.51 (m, 1/4H), 2.43 (m, 3/4H), 2.22 (m, 1H), 2.07 (s, 9/4H), 2.07 (s, 3/4H), 1.48 (s, 9/4H), 1.45 (s, 3/4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7 (1/4C), 169.6 (3/4C), 137.8 (3/4C), 137.7 (1/4C), 135.1 (1/4C), 135.0 (3/4C), 134.2 (1/4C), 133.8 (3/4C), 128.9, 128.2 (2C), 126.1 (2/4C), 126.0 (6/4C), 118.4 (3/4C), 118.3 (1/4C), 116.8 (1/4C), 116.7 (3/4C), 101.6 (1/4C), 101.5 (3/4C), 92.2 (3/4C), 91.8 (1/4C), 82.4, 76.1 (3/4C), 75.3 (1/4C), 73.1 (3/4C), 72.7 (1/4C), 33.1 (3/4C), 32.9 (1/4C), 21.6 (3/4C), 21.5 (1/4C), 15.2 (1/4C), 15.3 (3/4C); HRMS (ESI) calcd for $C_{19}H_{24}O_5Na$ $[(M + Na)^+]$ 355.1516, found 355.1533.

Enol Ether ***12***. To a suspension of $ZnBr_2$ (27.9 mg, 0.124 mmol) in CH_2Cl_2 (0.62 mL) at 0 °C was added vinylmagnesium bromide (1.0 M solution in THF, 0.23 mL, 0.23 mmol), and the resultant mixture was stirred at room temperature for 30 min. To this mixture at 0 °C was added a solution of α-acetoxy ether **11** (18.3 mg, 0.0568 mmol) in CH_2Cl_2 (0.53 mL + 0.53 mL rinse), and the resultant mixture was stirred at 0 °C for 13 h. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was extracted with EtOAc, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 40% CH_2Cl_2/hexanes) gave a mixture of enol ether **12**, cyclopropane **13**, and 1,4-pentadien-3-yl ether **6e** (13.9 mg, 82% combined yield). The yields of **12**, **13**, and **6e** reported in Scheme 4 were calculated on the basis of ^1H NMR analysis of this mixture. A small amount of this mixture was further purified by preparative HPLC to characterize each product. Data for **12**: $[\alpha]_D^{25}$ −59.1 (*c* 0.100, $CHCl_3$); IR (neat) 2978, 2860, 1666, 1386, 1151, 1117, 914 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.47−7.45 (m, 2H), 7.36−7.30 (m, 3H), 6.20 (dd, *J* = 11.9, 1.4 Hz, 1H), 5.91 (dddd, *J* = 17.5, 10.6, 7.4, 6.4 Hz, 1H), 5.79 (dddd, *J* = 16.0, 10.1, 6.4, 6.4 Hz, 1H), 5.47 (s, 1H), 5.13 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.10−5.01 (m, 3H), 4.97 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.05 (d, *J* = 10.5 Hz, 1H), 3.77−3.73 (m, 2H), 2.67−2.64 (m, 2H), 2.47 (m, 1H), 2.22 (m, 1H), 1.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.6, 137.8, 137.4, 135.0, 128.9, 128.2 (2C), 126.1 (2C), 116.8, 114.9, 108.8, 101.6, 82.5, 75.5, 72.2, 33.0, 31.5, 16.2; HRMS (ESI) calcd for $C_{19}H_{24}O_3Na$ $[(M + Na)^+]$ 323.1618, found 323.1617. Data for **13**: $[\alpha]_D^{25}$ −39.9 (*c* 0.05, $CHCl_3$); IR (neat) 2925, 2856, 2360, 1664, 1144, 1119, 1028 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.46−7.44 (m, 2H), 7.36−7.30 (m, 3H), 6.29 (d, *J* = 11.9 Hz, 1H), 5.90 (dddd, *J* = 17.5, 10.1, 7.4, 6.4 Hz, 1H), 5.46 (s, 1H), 5.12 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.04 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.75 (dd, *J* = 11.9, 8.2 Hz, 1H), 4.06 (d, *J* = 10.6 Hz, 1H), 3.75 (d, *J* = 10.6 Hz, 1H), 3.73 (dd, *J* = 10.1, 2.3 Hz, 1H), 2.46 (m, 1H), 2.21 (m, 1H), 1.44 (s, 3H), 1.23 (m, 1H), 0.65−0.60 (m, 2H), 0.27−0.23 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.8, 137.7, 135.1, 128.2 (3C), 126.1 (2C), 116.7, 115.3, 101.6, 82.6, 75.5, 72.1, 33.0, 16.2, 9.1, 6.0 (2C); HRMS (ESI) calcd for $C_{19}H_{24}O_3Na$ $[(M + Na)^+]$ 323.1618, found 323.1602.

Six-Membered Cyclic Ether ***14a***. To a solution of the first-generation Grubbs catalyst (**Ru-I**) (9.9 mg, 0.012 mmol) in CH_2Cl_2 (10 mL) was added a solution of 1,4-pentadien-3-yl ether **6a** (23.3 mg, 0.120 mmol) in CH_2Cl_2 (1 mL + 1 mL rinse), and the resultant solution was stirred at room temperature for 1 h. The reaction mixture was then treated with Et_3N (excess) and exposed to air to quench the

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catalyst. The reaction mixture was concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 2 to 3% Et_2O/*n*-pentane) gave six-membered cyclic ether **14a** (16.4 mg, 82%, *cis*/*trans* 32:68) as a pale yellow oil: $[\alpha]_D^{24}$ +30.8 (*c* 1.00, $CHCl_3$); IR (neat) 2953, 2924, 2853, 2358, 1733, 1462, 1378 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 5.97 (br d, *J* = 10.1 Hz, 2/3H), 5.91 (br d, *J* = 10.1 Hz, 1/3H), 5.78 (m, 1H), 5.39 (m, 1H), 5.15 (dd, *J* = 17.0, 1.4 Hz, 1/3H), 5.15 (dd, *J* = 17.4, 1.4 Hz, 2/3H), 5.02 (dd, *J* = 10.1, 1.4 Hz, 2/3H), 4.98 (dd, *J* = 10.1, 1.4 Hz, 1/3H), 4.57 (m, 2/3H), 4.57 (m, 1/3H), 3.68 (m, 1H), 3.59 (m, 1H), 3.35 (ddd, *J* = 11.0, 8.1, 4.1 Hz, 2/3H), 3.23 (ddd, *J* = 11.5, 8.3, 4.1 Hz, 1H), 3.09 (m, 1H), 1.87 (m, 1H), 1.49−1.23 (m, 2H), 1.16 (m, 1H); ^{13}C NMR (150 MHz, C_6D_6) δ 137.8 (1/3C), 136.8 (2/3C), 129.8 (1/3C), 129.1 (2/3C), 128.3 (1/3C), 128.6 (2/3C), 115.7 (2/3C), 115.5 (1/3C), 77.0 (1/3C), 76.1 (2/3C), 75.9 (1/3C), 75.6 (1/3C), 74.1 (2/3C), 70.1 (2/3C), 68.0, 29.8 (1/3C), 29.7 (2/3C), 26.1; HRMS (EI) calcd for $C_{10}H_{14}O_2$ [M^+] 166.0998, found 166.0996.

Six-Membered Cyclic Ether ***14b***. Prepared from 1,4-pentadien-3-yl ether **6b** (26.2 mg, 0.0962 mmol) in the same manner as **14a** by using **Ru-I**: yield 20.0 mg, 85% (*cis*/*trans* 38:62); colorless crystals; mp 71−74 °C; $[\alpha]_D^{26}$ +47.1 (*c* 1.00, $CHCl_3$); IR (neat) 2976, 2857, 2360, 2341, 1384, 1094, 998 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.52−5.48 (m, 2H), 5.38−5.32 (m, 2H), 6.04 (br d, *J* = 10.6 Hz, 2/3H), 5.98 (br d, *J* = 10.6 Hz, 1/3H), 5.93 (ddd, *J* = 17.0, 10.1, 5.0 Hz, 2/3H), 5.81−5.74 (m, 1H), 5.68 (ddd, *J* = 10.6, 2.3, 2.3 Hz, 1/3H), 5.60 (s, 1/3H), 5.59 (s, 2/3H), 5.34 (dd, *J* = 17.0, 1.0 Hz, 1/3H), 5.30−5.24 (m, 4/3H), 5.21 (dd, *J* = 10.6, 1.0 Hz, 1/3H), 4.78 (m, 1/3H), 4.72 (m, 1/3H), 4.33 (dd, *J* = 9.7, 4.1 Hz, 1/3H), 4.29 (dd, *J* = 11.0, 5.0 Hz, 2/3H), 4.21 (m, 1/3H), 4.17 (m, 2/3H), 3.82 (dd, *J* = 10.6, 10.6 Hz, 1/3H), 3.77 (dd, *J* = 10.6, 10.6 Hz, 2/3H), 3.63 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.5, 136.2 (1/3C), 135.2 (2/3C), 129.8 (1/3C), 129.1 (2/3C), 128.8 (2/3C), 128.3 (4/3C), 127.3 (2/3C), 126.6 (1/3C), 126.2 (3C), 117.4 (1/3C), 117.1 (2/3C), 101.9, 77.3 (1/3C), 75.2 (2/3C), 75.0 (1/3C), 74.4 (2/3C), 70.7 (1/3C), 69.6 (2/3C), 69.5 (1/3C), 65.5 (2/3C); HRMS (ESI) calcd for $C_{15}H_{16}O_3Na$ [(M + Na)$^+$] 267.0992, found 267.0996.

Six-Membered Cyclic Ether ***14c***. Prepared from 1,4-pentadien-3-yl ether **6c** (26.5 mg, 0.0925 mmol) in the same manner as **14a** by using **Ru-I**: yield 19.3 mg, 81% (*cis*/*trans* 55:45); pale yellow oil; $[\alpha]_D^{28}$ + 77.6 (*c* 1.00, $CHCl_3$); IR (neat) 2980, 2934, 2861, 1378, 1113, 1005, 920 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.52−7.48 (m, 2H), 7.40−7.33 (m, 3H), 5.99−5.93 (m, 1H), 5.88 (br d, *J* = 10.6 Hz, 1H), 5.81−5.74 (m, 1H), 5.65−5.60 (m, 5/2H), 5.33 (dd, *J* = 17.5, 1.4 Hz, 1/2H), 5.26 (dd, *J* = 17.0, 1.4 Hz, 1/2H), 5.19 (dd, *J* = 10.1, 1.4 Hz, 1/2H), 5.16 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.72 (m, 1/2H), 4.69 (m, 1/2H), 4.32 (m, 1/2H), 4.26 (m, 1/2H), 4.02 (d, *J* = 10.1 Hz, 1/2H), 4.00 (d, *J* = 10.1 Hz, 1/2H), 3.76 (d, *J* = 10.1 Hz, 1/2H), 3.71 (d, *J* = 10.1 Hz, 1/2H), 1.49 (s, 3/2H), 1.39 (s, 3/2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2 (1/2C), 137.6, 136.2 (1/2C), 129.1, 128.5 (1/2C), 128.4 (2C), 127.6 (1/2C), 126.3 (2C), 126.1 (1/2C), 125.3 (1/2C), 117.0 (1/2C), 116.2 (1/2C), 102.9, 78.2 (1/2C), 77.8 (1/2C), 76.1 (1/2C), 75.8 (1/2C), 73.7 (1/2C), 73.1 (1/2C), 68.9 (1/2C), 67.2 (1/2C), 18.7 (1/2C), 15.5 (1/2C); HRMS (ESI) calcd for $C_{16}H_{18}O_3Na$ [(M + Na)$^+$] 281.1148, found 281.1132.

Seven-Membered Cyclic Ether ***14d***. Prepared from 1,4-pentadien-3-yl ether **6d** (16.6 mg, 0.0797 mmol) in the same manner as **14a** by using **Ru-I**: yield 11.5 mg, 80% (*cis*/*trans* 83:17); pale yellow oil. A small portion of this material was further purified by preparative TLC to separate *cis*-**14d** and *trans*-**14d**. Data for *cis*-**14d**: $[\alpha]_D^{26}$ −7.6 (*c* 0.50, $CHCl_3$); IR (neat) 3026, 2939, 2850, 1439, 1144, 1094, 923 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.96−5.85 (m, 2H), 5.81 (ddd, *J* = 10.5, 3.7, 2.3 Hz, 1H), 5.29 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.13 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.52 (m, 1H), 3.85 (m, 1H), 3.37 (ddd, *J* = 10.1, 8.7, 4.6 Hz, 1H), 3.30 (ddd, *J* = 11.0, 11.0, 3.2 Hz, 1H), 3.02 (ddd, *J* = 10.1, 8.7, 3.7 Hz, 1H), 2.49 (ddd, *J* = 15.1, 7.8, 3.7 Hz, 1H), 2.41 (m, 1H), 2.10 (m, 1H), 1.74−1.64 (m, 2H), 1.51 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 135.8, 128.8, 115.0, 83.0, 78.0, 77.7, 67.6, 34.7, 31.3, 26.0; HRMS (ESI) calcd for $C_{11}H_{17}O_2$ [(M + H)$^+$] 181.1223, found 181.1215. Data for *trans*-**14d**: $[\alpha]_D^{26}$ +79.5 (*c* 0.10, $CHCl_3$); IR (neat) 3026, 2938, 2851, 1439, 1094, 1033, 923 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 17.4, 10.1, 4.6 Hz, 1H), 5.76 (m, 1H), 5.67 (ddd, *J* = 11.9, 4.6, 3.2 Hz, 1H), 5.26−5.23 (m, 2H), 4.81 (m, 1H), 3.83 (m, 1H), 3.50 (ddd, *J* = 11.0, 8.8, 4.6 Hz, 1H), 3.28 (ddd, *J* = 11.0, 9.6, 6.8 Hz, 1H), 3.20 (ddd, *J* = 10.1, 10.1, 4.6 Hz, 1H), 2.50 (ddd, *J* = 17.2, 7.8, 4.6 Hz, 1H), 2.26 (m, 1H), 2.00 (m, 1H), 1.67−1.62 (m, 2H), 1.28 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.9, 131.3, 126.3, 118.2, 79.1, 75.4, 73.4, 67.3, 35.0, 31.1, 25.6; HRMS (ESI) calcd for $C_{11}H_{17}O_2$ [(M + H)$^+$] 181.1223, found 181.1223.

Seven-Membered Cyclic Ether ***14e***. Prepared from 1,4-pentadien-3-yl ether **6e** (12.6 mg, 0.0420 mmol) in the same manner as **14a** by using **Ru-I**: yield 10.6 mg, 93% (*cis*/*trans* 93:7); pale yellow oil; $[\alpha]_D^{24}$ +25.4 (*c* 1.00, $CHCl_3$); IR (neat) 2978, 2925, 2859, 1384, 1135, 1103, 1028 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major diastereomer) δ 7.49−7.47 (m, 2H), 7.37−7.31 (m, 3H), 5.87 (ddd, *J* = 17.0, 10.8, 5.9 Hz, 1H), 5.61−5.53 (m, 2H), 5.48 (s, 1H), 5.27 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.13 (dd, *J* = 10.8, 1.4 Hz, 1H), 4.76 (m, 1H), 3.92 (d, *J* = 11.0 Hz, 1H), 3.83 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.70 (d, *J* = 11.0 Hz, 1H), 2.57 (m, 1H), 2.38 (m, 1H), 1.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, major diastereomer) δ 138.6, 137.9, 132.9, 129.0, 128.3 (2C), 126.2 (2C), 124.1, 115.1, 101.3, 81.9, 76.5, 73.3, 70.8, 32.3, 13.8; HRMS (ESI) calcd for $C_{17}H_{20}O_3Na$ [(M + Na)$^+$] 295.1305, found 295.1311.

Eight-Membered Cyclic Ether ***14f***. Prepared from 1,4-pentadien-3-yl ether **6f** (122.0 mg, 0.5488 mmol) in the same manner as **14a** by using **Ru-II** instead of **Ru-I**: yield 83.3 mg, 78% (*cis*/*trans* 79:21); pale yellow oil. A small portion of this material was further purified by preparative TLC to separate *cis*-**14f** and *trans*-**14f**. Data for *cis*-**14f**: $[\alpha]_D^{26}$ −179.5 (*c* 0.50, $CHCl_3$); IR (neat) 3013, 2931, 2849, 1449, 1098, 1078, 927 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 17.0, 10.5, 6.4 Hz, 1H), 5.79 (ddd, *J* = 11.5, 8.7, 8.7 Hz, 1H), 5.28 (dd, *J* = 11.5, 3.7 Hz, 1H), 5.23 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.10 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.52 (m, 1H), 3.82 (m, 1H), 3.37 (ddd, *J* = 10.5, 10.5, 5.0 Hz, 1H), 3.29 (ddd, *J* = 11.5, 11.5, 2.3 Hz, 1H), 3.23 (ddd, *J* = 10.5, 10.1, 5.5 Hz, 1H), 2.73 (m, 1H), 2.10 (m, 1H), 2.03 (dddd, *J* = 8.7, 8.7, 5.5, 5.5 Hz, 1H), 1.94 (m, 1H), 1.65−1.52 (m, 2H), 1.47−1.39 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.3, 131.7, 128.8, 115.6, 80.5, 79.9, 76.6, 67.4, 33.6, 31.0, 25.6, 22.4; HRMS (ESI) calcd for $C_{12}H_{19}O_2$ [(M + H)$^+$] 195.1380, found 195.1377. Data for *trans*-**14f**: $[\alpha]_D^{26}$ +2.8 (*c* 0.10, $CHCl_3$); IR (neat) 3013, 2932, 2848, 1449, 1098, 1078, 986 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.91 (ddd, *J* = 17.4, 10.6, 6.4 Hz, 1H), 5.82 (ddd, *J* = 10.6, 10.6, 8.3 Hz, 1H), 5.37 (dd, *J* = 10.6, 2.3 Hz, 1H), 5.25 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.16 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.92 (m, 1H), 3.81 (m, 1H), 3.56 (ddd, *J* = 9.6, 9.6, 5.1 Hz, 1H), 3.31 (ddd, *J* = 9.6, 9.6, 5.5 Hz, 1H), 3.26 (m, 1H), 2.46−2.38 (m, 2H), 2.05 (m, 1H), 1.92 (m, 1H), 1.62−1.47 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.5, 133.7, 131.5, 117.6, 78.2, 78.1, 77.5, 68.0, 31.4, 29.7, 29.6, 25.8; HRMS (ESI) calcd for $C_{12}H_{19}O_2$ [(M + H)$^+$] 195.1380, found 195.1366.

Alcohol ***19***. To a solution of olefin **18** (1.1861 g, 2.6086 mmol) in THF (26 mL) at 0 °C was added TBAF (1.0 M solution in THF, 5.2 mL, 5.2 mmol), and the resultant solution was stirred at room temperature for 15 min. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was extracted with EtOAc, and the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 20 to 30% EtOAc/hexanes) gave alcohol **19** (0.9581 g, 96%) as colorless crystals: mp 169−171 °C; $[\alpha]_D^{25}$ −14.6 (*c* 1.00, $CHCl_3$); IR (neat) 3457, 2991, 2943, 2878, 1381, 1095, 1065 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.90 (dddd, *J* = 17.4, 10.6, 7.8, 6.0 Hz, 1H), 5.11 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.04 (dd, *J* = 10.6, 1.8 Hz, 1H), 3.84 (dd, *J* = 11.5, 5.9 Hz, 1H), 3.71 (ddd, *J* = 9.1, 7.8, 7.8 Hz, 1H), 3.56 (dd, *J* = 11.5, 9.2 Hz, 1H), 3.46 (ddd, *J* = 9.1, 9.1, 4.1 Hz, 1H), 3.32 (ddd, *J* = 9.2, 9.2, 5.9 Hz, 1H), 3.26−3.21 (m, 2H), 3.05 (dd, *J* = 12.8, 3.7 Hz, 1H), 2.38 (m, 1H), 2.17 (m, 1H), 2.10 (m, 1H), 2.06−1.97 (m, 2H), 1.92 (m, 1H), 1.79 (m, 1H), 1.73 (m, 1H), 1.64−1.55 (m, 2H), 1.42 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.20 (s, 3H), one proton missing due to H/D exchange; ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.8, 116.6, 98.5, 87.0, 80.9, 80.2, 75.7, 72.9, 72.7, 71.9, 71.1, 63.2, 54.2, 33.4, 31.7, 29.7, 29.3, 28.4, 24.1, 19.5, 15.6; HRMS (ESI) calcd for $C_{21}H_{34}O_6Na$ [(M + Na)$^+$] 405.2248, found 405.2254.

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Ester ***20***. To a solution of alcohol **19** (3.53 g, 9.24 mmol) in CH_2Cl_2 (18.5 mL) were added carboxylic acid **2** (4.66 g, 20.3 mmol), DMAP (2.26 g, 18.5 mmol), and DIC (2.85 mL, 18.4 mmol), and the resultant mixture was stirred at room temperature for 20.5 h. The reaction mixture was directly loaded onto a silica gel column. Elution with 0 to 15 to 35% EtOAc/hexanes gave ester **20** (2.86 g, 52%) as a yellow oil, along with recovered **19** (1.29 g, 36%). Data for **20**: $[\alpha]_D^{25}$ −17.7 (*c* 1.00, $CHCl_3$); IR (neat) 2989, 2944, 2877, 1734, 1200, 1100, 1063 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.49−7.46 (m, 2H), 7.27−7.21 (m, 3H), 5.84 (dddd, *J* = 17.5, 10.6, 7.8, 6.0 Hz, 1H), 5.08 (dd, *J* = 17.5, 1.9 Hz, 1H), 5.02 (dd, *J* = 10.6, 1.9 Hz, 1H), 3.83 (dd, *J* = 11.5, 5.5 Hz, 1H), 3.71 (ddd, *J* = 9.2, 7.3, 7.3 Hz, 1H), 3.56 (dd, *J* = 11.5, 9.2 Hz, 1H), 3.47−3.42 (m, 2H), 3.32 (ddd, *J* = 9.2, 9.2, 6.0 Hz, 1H), 3.21 (ddd, *J* = 11.0, 9.2, 5.0 Hz, 1H), 3.10 (dd, *J* = 12.8, 3.7 Hz, 1H), 3.03−2.98 (m, 2H), 2.85 (d, *J* = 12.4 Hz, 1H), 2.63−2.55 (m, 2H), 2.27 (m, 1H), 2.15 (m, 1H), 2.09 (ddd, *J* = 11.9, 4.1, 4.1 Hz, 1H), 2.02 (m, 1H), 1.91 (m, 1H), 1.79−1.68 (m, 3H), 1.62−1.54 (m, 4H), 1.41 (s, 3H), 1.34 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 135.4, 133.1 (2C), 129.3, 129.2 (2C), 127.3, 116.5, 98.5, 84.7, 81.1, 80.9, 80.4, 75.7, 72.9, 72.6, 71.4, 63.2, 49.5, 36.1, 33.3, 31.7, 29.7, 29.3, 28.4, 21.9, 21.6, 19.5, 15.7; HRMS (ESI) calcd for $C_{30}H_{42}O_7SeNa$ [(M + Na)$^+$] 617.1988, found 617.1995.

α-Acetoxy Ether ***21***. To a solution of ester **20** (28.9 mg, 0.0487 mmol) in CH_2Cl_2 (0.5 mL) at −78 °C was added DIBALH (1.02 M solution in *n*-hexane, 0.053 mL, 0.054 mmol), and the resultant solution was stirred at −78 °C for 5 min. To this solution were added pyridine (0.016 mL, 0.20 mmol), a solution of DMAP (7.3 mg, 0.060 mmol) in CH_2Cl_2 (0.1 mL), and Ac_2O (0.018 mL, 0.19 mmol), and the resultant solution was stirred at −78 °C for 14.5 h and then allowed to warm to 0 °C over a period of 3.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was diluted with EtOAc and saturated aqueous potassium sodium tartrate solution and stirred vigorously at room temperature for 1 h. The resultant mixture was extracted with EtOAc, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 8−10% EtOAc/hexanes) gave α-acetoxy ether **21** (29.3 mg, 94%, dr 68:32) as a colorless oil: $[\alpha]_D^{26}$ −12.8 (*c* 1.00, $CHCl_3$); IR (neat) 2946, 2876, 1732, 1242, 1097, 1064, 930 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 7.48−7.46 (m, 2H), 7.00−6.93 (m, 3H), 6.37 (dd, *J* = 6.4, 4.1 Hz, 2/3H), 6.32 (dd, *J* = 6.0, 4.1 Hz, 1/3H), 6.07 (m, 1H), 5.19−5.08 (m, 2H), 3.92 (m, 1H), 3.72−3.60 (m, 2H), 3.49 (dd, *J* = 10.1, 1.9 Hz, 2/3H), 3.44−3.39 (m, 4/3H), 3.25 (ddd, *J* = 9.2, 9.2, 5.5 Hz, 1/3H), 3.21 (ddd, *J* = 9.2, 9.2, 5.5 Hz, 2/3H), 2.93−2.86 (m, 4/3H), 2.83−2.75 (m, 5/3H), 2.70 (m, 1H), 2.55 (m, 1/3H), 2.35 (m, 2/3H), 2.27 (d, *J* = 11.9 Hz, 1/3H), 2.21−1.87 (m, 23/3H), 1.80−1.68 (m, 2H), 1.64−1.58 (m, 4H), 1.46 (s, 1H), 1.45 (s, 3H), 1.29 (s, 1H), 1.28 (s, 3H), 1.22 (s, 1H), 1.17 (s, 3H), 1.06 (s, 1H), 1.05 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 169.6 (2/3C), 169.3 (1/3C), 136.4, 133.2 (4/3C), 133.1 (2/3C), 130.5 (1/3C), 130.4 (2/3C), 129.4 (4/3C), 129.3 (2/3C), 127.2 (2/3C), 127.1 (1/3C), 116.5 (1/3C), 116.4 (2/3C), 98.5 (1/3C), 98.4 (2/3C), 92.5 (2/3C), 92.4 (1/3C), 86.1 (1/3C), 85.5 (2/3C), 80.9 (1/3C), 80.8 (2/3C), 80.4 (1/3C), 80.3 (2/3C), 77.6 (2/3C), 77.1 (1/3C), 76.0 (1/3C), 75.9 (2/3C), 73.3, 73.1, 71.8 (1/3C), 71.6 (2/3C), 63.4, 51.7 (2/3C), 51.1 (1/3C), 36.8 (1/3C), 36.6 (2/3C), 33.9 (2/3C), 33.7 (1/3C), 32.2, 30.1, 29.8, 28.9, 21.8 (2/3C), 21.6 (2/3C), 21.2 (2/3C), 21.1 (2/3C), 21.0 (1/3C), 19.4, 16.0 (2/3C), 15.9 (1/3C); HRMS (ESI) calcd for $C_{32}H_{46}O_8SeNa$ [(M + Na)$^+$] 661.2250, found 661.2267.

Olefin ***22***. To a suspension of $ZnBr_2$ (66.2 mg, 0.294 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C was added vinylmagnesium bromide (1.0 M solution in THF, 0.53 mL, 0.53 mmol), and the resultant mixture was stirred at room temperature for 30 min. To this mixture at 0 °C was added a solution of α-acetoxy ether **21** (84.6 mg, 0.133 mmol) in CH_2Cl_2 (0.84 mL + 0.84 mL rinse), and the resultant mixture was stirred at 0 °C for 14 h. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was extracted with EtOAc, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 6% EtOAc/hexanes) gave olefin **22** (69.2 mg, 86%, dr 74:26) as a colorless oil: $[\alpha]_D^{22}$ −16.5 (*c* 1.00, $CHCl_3$); IR (neat) 2989, 2944, 2876, 1380, 1097, 1065, 1034 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.46−7.44 (m, 2H), 7.24−7.19 (m, 3H), 5.85 (m, 1H), 5.73 (m, 1H), 5.11−4.98 (m, 4H), 4.12 (m, 1H), 3.83 (m, 1H), 3.71 (m, 1H), 3.56 (m, 1H), 3.45 (m, 1H), 3.35−3.26 (m, 2H), 3.22 (m, 1H), 3.03 (m, 1H), 2.90−2.82 (m, 2H), 2.39 (m, 1/4H), 2.31 (m, 3/4H), 2.11−1.98 (m, 4H), 1.96−1.82 (m, 2H), 1.81−1.52 (m, 5H), 1.42 (s, 3/4H), 1.41 (s, 9/4H), 1.35 (s, 3/4H), 1.34 (s, 9/4H), 1.24 (s, 9/4H), 1.21 (s, 3/4H), 1.17 (s, 3/4), 1.16 (s, 9/4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.3, 136.3 (1/4C), 136.1 (3/4C), 132.5 (6/4C), 132.3 (2/4C), 130.3 (1/4C), 130.1 (3/4C), 129.0 (2C), 126.8 (3/4C), 126.7 (1/4C), 116.0, 115.4 (3/4C), 114.9 (1/4C), 98.5, 86.1 (1/4C), 85.8 (3/4C), 80.9, 79.9, 76.0 (3/4C), 75.8 (1/4C), 75.7 (1/4C), 75.6 (3/4C), 72.9 (2C), 72.7 (3/4C), 72.5 (1/4C), 72.0, 63.2, 52.0 (3/4C), 50.7 (1/4C), 37.5 (1/4C), 37.4 (3/4C), 33.2, 31.8, 29.8, 29.4, 28.4, 23.5 (3/4C), 23.2 (1/4C), 22.6 (1.4C), 21.4 (3/4C), 19.4, 16.0; HRMS (ESI) calcd for $C_{32}H_{46}O_6SeNa$ [(M + Na)$^+$] 629.2352, found 629.2334.

1,4-Pentadien-3-yl Ether ***23***. To a solution of olefin **22** (53.3 mg, 0.0879 mmol) in CH_2Cl_2 (0.9 mL) at −20 °C was added *m*-CPBA (16.8 mg, 0.0973 mmol), and the resultant mixture was stirred at −20 °C for 30 min. To this mixture was added Et_3N (0.06 mL, 0.4 mmol), and the resultant mixture was stirred at 0 °C for 5 min and then heated at reflux (45 °C) for 8 h. The resultant mixture was cooled to room temperature and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 15% Et_2O/hexanes) gave 1,4-pentadien-3-yl ether **23** (37.8 mg, 96%) as a colorless oil: $[\alpha]_D^{22}$ −23.1 (*c* 1.00, $CHCl_3$); IR (neat) 2990, 2947, 2876, 2362, 1098, 1064, 1032 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 6.14 (dddd, *J* = 17.4, 10.1, 7.3, 5.9 Hz, 1H), 5.78−5.70 (m, 2H), 5.20 (dd, *J* = 17.4, 1.9 Hz, 1H), 5.14−5.10 (m, 2H), 5.07 (dd, *J* = 17.4, 1.4 Hz, 1H), 4.95 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.90 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.34 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.93 (dd, *J* = 11.5, 5.9 Hz, 1H), 3.70 (ddd, *J* = 9.2, 7.4, 6.0 Hz, 1H), 3.63 (dd, *J* = 11.5, 9.2 Hz, 1H), 3.54 (dd, *J* = 10.6, 3.5 Hz, 1H), 3.46 (ddd, *J* = 8.7, 8.7, 4.1 Hz, 1H), 3.24 (ddd, *J* = 9.2, 9.2, 5.9 Hz, 1H), 2.95 (dd, *J* = 11.9, 3.7 Hz, 1H), 2.89 (ddd, *J* = 11.0, 8.7, 5.0 Hz, 1H), 2.60 (m, 1H), 2.21 (m, 1H), 2.09 (d, *J* = 11.9 Hz, 1H), 2.03 (m, 1H), 1.98−1.89 (m, 3H), 1.80−1.72 (m, 2H), 1.67 (ddd, *J* = 11.9, 11.9, 8.7 Hz 1H), 1.46 (s, 3H), 1.28 (s, 3H), 1.16 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 140.5, 140.3, 136.8, 116.3, 114.6, 114.2, 98.4, 86.4, 81.0, 80.3, 76.4, 75.9, 73.8, 73.3, 73.1, 72.0, 63.5, 51.7, 34.0, 32.3, 30.2, 29.8, 28.9, 21.9, 19.4, 16.1; HRMS (ESI) calcd for $C_{26}H_{40}O_6Na$ [(M + Na)$^+$] 471.2717, found 471.2705.

Oxepene ***24***. To a solution of the second-generation Grubbs catalyst (**Ru-II**) (24.5 mg, 0.0289 mmol) in degassed CH_2Cl_2 (29 mL) at room temperature was added a solution of 1,4-pentadien-3-yl ether **23** (0.1280 g, 0.2853 mmol) in degassed CH_2Cl_2 (3 mL + 2 mL rinse), and the resultant solution was stirred at room temperature for 1.5 h. The resultant solution was then treated with Et_3N (five drops) and exposed to air with stirring for 15 h. The resultant solution was concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 15% Et_2O/hexanes) gave oxepene **24** (0.1033 g, 86%, dr 91:9) as colorless crystals: mp 162−165 °C; $[\alpha]_D^{22}$ +24.2 (*c* 1.00, $CHCl_3$); IR (neat) 2993, 2942, 2875, 1372, 1110, 1077, 1038 cm^{-1}; ^1H NMR (600 MHz, C_6D_6, major diastereomer) δ 5.90 (ddd, *J* = 17.4, 10.5, 5.9 Hz, 1H), 5.36−5.26 (m, 3H), 5.01 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.57 (m, 1H), 3.89 (dd, *J* = 11.5, 6.0 Hz, 1H), 3.70 (ddd, *J* = 9.2, 7.8, 6.0 Hz, 1H), 3.64−3.59 (m, 2H), 3.47 (ddd, *J* = 9.1, 9.1, 4.1 Hz, 1H), 3.22 (ddd, *J* = 9.2, 9.2, 6.0 Hz, 1H), 3.03 (dd, *J* = 12.8, 3.7 Hz, 1H), 2.94 (ddd, *J* = 11.0, 9.1, 5.0 Hz, 1H), 2.52 (m, 1H), 2.18−2.06 (m, 4H), 1.99−1.90 (m, 2H), 1.80−1.67 (m, 3H), 1.44 (s, 3H), 1.27 (s, 3H), 1.16 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6, major diastereomer) δ 139.5, 132.9, 123.2, 114.0, 98.4, 85.4, 81.0, 79.8, 75.9, 75.4, 73.2, 73.1 (2C), 71.9, 63.4, 54.0, 32.7, 32.4, 30.1, 29.8, 28.8, 19.4, 16.8, 16.2; HRMS (ESI) calcd for $C_{24}H_{36}O_6Na$ [(M + Na)$^+$] 443.2404, found 443.2396.

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Alcohol ***25***. To a solution of oxepene **24** (85.7 mg, 0.204 mmol) in THF (2 mL) was added 9-BBN-H (0.30 M solution in THF, 2.40 mL, 0.720 mmol), and the resultant solution was stirred at room temperature for 1.5 h. The reaction was quenched with EtOH (1 mL) at 0 °C, and the resultant solution was treated with saturated aqueous $NaHCO_3$ solution (1.6 mL) and 30% aqueous H_2O_2 solution (1 mL). The resultant mixture was stirred at room temperature for 12.5 h. The resultant mixture was diluted with EtOAc and washed with saturated aqueous Na_2SO_3 solution, H_2O, and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 25% EtOAc/benzene) gave alcohol **S1** (70.1 mg, 78%) as a colorless foam. At this stage, the minor diastereomer originated from the diastereoselective RCM was removed. Data for **S1**: $[\alpha]_D^{24}$ +14.9 (*c* 1.00, $CHCl_3$); IR (neat) 3436, 2991, 2943, 2876, 1108, 1075, 1031 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 5.27 (dddd, *J* = 12.8, 5.0, 2.8, 2.8 Hz, 1H), 5.12 (br d, *J* = 12.8 Hz, 1H), 4.17 (m, 1H), 3.91 (dd, *J* = 11.5, 5.5 Hz, 1H), 3.77 (ddd, *J* = 11.0, 7.3, 4.1 Hz, 1H), 3.73−3.61 (m, 3H), 3.49−3.43 (m, 2H), 3.24 (ddd, *J* = 9.2, 9.2, 5.5 Hz, 1H), 2.97−2.93 (m, 2H), 2.48 (ddd, *J* = 17.9, 5.0, 5.0 Hz, 1H), 2.38 (br s, 1H), 2.14−2.08 (m, 2H), 2.01−1.91 (m, 4H), 1.81−1.73 (m, 2H), 1.72−1.66 (m, 2H), 1.60 (m, 1H), 1.45 (s, 3H), 1.28 (s, 3H), 1.14 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 133.4, 123.4, 98.2, 85.0, 80.6, 79.5, 75.7, 75.4, 72.9 (2C), 71.6, 71.4, 63.2, 60.6, 53.7, 38.9, 32.3, 32.1, 29.8, 29.6, 28.5, 19.2, 16.3, 15.9; HRMS (ESI) calcd for $C_{24}H_{38}O_7Na$ [(M + Na)$^+$] 461.2510, found 461.2510.

To a solution of alcohol **S1** (64.3 mg, 0.147 mmol) in EtOAc (3 mL) were added Et_3N (0.03 mL, 0.2 mmol) and 10% Pd/C (12.9 mg), and the resultant mixture was stirred at room temperature under an atmosphere of H_2 (balloon) for 2.5 h. The resultant mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure to give alcohol **25** (59.5 mg, 92%) as colorless crystals: mp 173−175 °C; $[\alpha]_D^{22}$ −8.6 (*c* 1.00, $CHCl_3$); IR (neat) 3443, 2991, 2942, 2873, 2359, 1094, 1065 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.90 (ddd, *J* = 9.7, 6.9, 3.2 Hz, 1H), 3.85 (dd, *J* = 11.5, 5.5 Hz, 1H), 3.73−3.69 (m, 3H), 3.56 (dd, *J* = 11.5, 8.8 Hz, 1H), 3.46 (ddd, *J* = 8.8, 8.8, 4.1 Hz, 1H), 3.40 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.32 (ddd, *J* = 8.8, 8.8, 5.5 Hz, 1H), 3.21 (ddd, *J* = 11.0, 8.8, 5.0 Hz, 1H), 3.04 (dd, *J* = 12.8, 3.2 Hz, 1H), 2.96 (br s, 1H), 2.08−1.99 (m, 2H), 1.96−1.88 (m, 3H), 1.80−1.68 (m, 5H), 1.64−1.52 (m, 6H), 1.41 (s, 3H), 1.34 (s, 6H), 1.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 98.5, 85.7, 81.0, 80.0, 76.3, 75.7, 74.8, 72.7, 72.6, 71.9, 63.2, 62.0, 54.1, 39.1, 34.6, 31.8, 29.7, 29.3, 28.5, 28.3, 20.5, 19.5, 18.7, 16.1; HRMS (ESI) calcd for $C_{24}H_{40}O_7Na$ [(M + Na)$^+$] 463.2666, found 463.2658.

Diol ***26***. To a solution of alcohol **25** (193 mg, 0.438 mmol) in CH_2Cl_2 (4 mL) were added Et_3N (0.46 mL, 4.4 mmol), TBDPSCl (0.34 mL, 0.88 mmol), and DMAP (5.0 mg, 0.041 mmol), and the resultant solution was stirred at room temperature for 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution. The resultant mixture was diluted with EtOAc, washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was roughly purified by flash column chromatography (10% EtOAc/hexanes) to remove baseline impurities, giving crude TBDPS ether (530 mg), which was used in the next reaction without further purification.

To a solution of the above TBDPS ether (530 mg) in CH_2Cl_2 (4 mL) were added EtSH (0.65 mL, 8.8 mmol) and $Zn(OTf)_2$ (5.6 mg, 0.088 mmol), and the resultant mixture was stirred at room temperature for 20 min. The reaction was quenched with Et_3N. The resultant mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 30% EtOAc/hexanes) gave diol **26** (195 mg, 70% for the two steps) as a colorless oil: $[\alpha]_D^{25}$ −16.7 (*c* 1.00, $CHCl_3$); IR (neat) 3398, 2931, 2870, 1110, 1052, 702 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.66−7.61 (m, 4H), 7.42−7.31 (m, 6H), 3.87−3.84 (m, 2H), 3.76 (ddd, *J* = 10.0, 8.2, 5.5 Hz, 1H), 3.67−3.62 (m, 2H), 3.54−3.49 (m, 2H), 3.42−3.36 (m, 2H), 3.26 (ddd, *J* = 11.0, 10.0, 4.5 Hz, 1H), 3.04 (dd, *J* = 12.8, 3.7 Hz, 1H), 2.07 (m, 1H), 1.92−1.53 (m, 14H), 1.44 (m, 1H), 1.28 (s, 3H), 1.24 (s, 3H), 1.02 (s, 9H), two protons missing due to H/D exchange; ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.5 (4C), 134.0 (2C), 129.5 (2C), 127.6 (4C), 86.3, 86.2, 82.3, 80.1, 75.2, 73.7, 72.2, 69.3, 64.6, 60.7, 54.0, 40.5, 34.6, 32.2, 29.8, 28.5, 26.9, 26.8 (4C), 20.8, 19.2, 18.7, 16.3; HRMS (ESI) calcd for $C_{37}H_{54}O_7SiNa$ [(M + Na)$^+$] 661.3531, found 661.3535.

Ketone ***27***. To a solution of diol **26** (594.5 mg, 0.9305 mmol) in DMF (9.3 mL) at 0 °C were added imidazole (190.3 mg, 2.795 mmol) and TBSCl (210.9 mg, 1.399 mmol), and the resultant solution was stirred at 0 °C for 90 min. The resultant mixture was diluted with EtOAc, washed with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 10 to 20% EtOAc/hexanes) gave silyl ether **S2** (667.1 mg, 95%) as a colorless oil: $[\alpha]_D^{25}$ −11.4 (*c* 1.00, $CHCl_3$); IR (neat) 3408, 2927, 2856, 1111, 1054 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.65−7.62 (m, 4H), 7.41−7.34 (m, 6H), 3.90 (m, 1H), 3.85 (m, 1H), 3.79−3.75 (m, 2H), 3.64 (ddd, *J* = 10.6, 6.0, 6.0 Hz, 1H), 3.50 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.43 (ddd, *J* = 11.9, 7.8, 6.0 Hz, 1H), 3.39−3.36 (m, 2H), 3.22 (ddd, *J* = 11.0, 10.1, 4.6 Hz, 1H), 3.04 (dd, *J* = 12.4, 3.7 Hz, 1H), 2.50 (br s, 1H), 2.05 (m, 1H), 1.92−1.53 (m, 14H), 1.44 (m, 1H), 1.28 (s, 3H), 1.23 (s, 3H), 1.02 (s, 9H), 0.88 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.5 (4C), 134.1, 134.0, 129.5 (2C), 127.6 (4C), 86.3, 85.0, 83.3, 80.4, 75.2, 74.3, 73.0, 72.2, 69.3, 65.9, 60.7, 54.1, 40.5, 34.6, 32.4, 29.6, 28.6, 27.3, 26.9 (3C), 25.8 (3C), 20.9, 19.2, 18.7, 18.2, 16.3, −5.4, −5.6; HRMS (ESI) calcd for $C_{43}H_{68}O_7Si_2Na$ [(M + Na)$^+$] 775.4396, found 775.4384.

To a solution of silyl ether **S2** (217.6 mg, 0.2889 mmol) in CH_2Cl_2 (3 mL) were added 4 Å molecular sieves (220 mg), NMO (68.3 mg, 0.583 mmol), and TPAP (5.2 mg, 0.015 mmol), and the resultant mixture was stirred at room temperature for 30 min. The resultant mixture was directly loaded onto a silica gel column and eluted with 5−10% EtOAc/hexanes to give ketone **27** (207.7 mg, 96%) as a colorless foam: $[\alpha]_D^{25}$ +22.1 (*c* 0.50, $CHCl_3$); IR (neat) 2929, 2856, 1717, 1386, 1111, 1045, 703 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.65−7.61 (m, 4H), 7.42−7.33 (m, 6H), 3.87−3.81 (m, 4H), 3.77 (ddd, *J* = 10.1, 8.2, 5.5 Hz, 1H), 3.68 (ddd, *J* = 10.5, 5.5, 5.5 Hz, 1H), 3.64 (ddd, *J* = 10.0, 10.0, 5.0 Hz, 1H), 3.36 (dd, *J* = 11.0, 4.1 Hz, 1H), 3.01−2.95 (m, 2H), 2.87 (ddd, *J* = 14.2, 11.9, 2.3 Hz, 1H), 2.38 (ddd, *J* = 11.0, 7.4, 5.5 Hz, 1H), 2.10 (ddd, *J* = 11.9, 3.7, 3.7 Hz, 1H), 2.04 (m, 1H), 1.92 (m, 1H), 1.85 (d, *J* = 12.8 Hz, 1H), 1.77−1.52 (m, 8H), 1.48−1.40 (m, 2H), 1.28 (s, 6H), 1.02 (s, 9H), 0.85 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.3, 135.5 (4C), 134.1, 134.0, 129.5 (2C), 127.6 (4C), 88.3, 86.2, 82.4, 79.8, 75.2, 72.7, 72.3, 69.3, 65.2, 60.7, 53.9, 40.5, 38.8, 34.6, 32.0, 30.1, 28.6, 26.9 (3C), 25.8 (3C), 20.8, 19.2, 18.6, 18.3, 16.2, −5.3, −5.4; HRMS (ESI) calcd for $C_{43}H_{66}O_7Si_2Na$ [(M + Na)$^+$] 773.4239, found 773.4261.

Allylic Alcohol ***28***. To a solution of ketone **27** (207.9 mg, 0.2768 mmol) in THF (9.2 mL) at −78 °C were added Et_3N (0.39 mL, 2.8 mmol), TMSCl (0.35 mL, 2.8 mmol), and LHMDS (1.0 M solution in THF, 0.83 mL, 0.83 mmol), and the resultant solution was stirred at −78 °C for 30 min. The reaction was quenched with pH 7 buffer. The resultant mixture was extracted with EtOAc, and the organic layer was washed with pH 7 buffer and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give crude enol silyl ether, which was immediately used in the next reaction without purification.

To a solution of the above enol silyl ether in CH_3CN (10 mL) was added $Pd(OAc)_2$ (232.0 mg, 1.033 mmol), and the resultant mixture was stirred at room temperature for 1 h. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 20% EtOAc/hexanes) gave enone **S3** (202.1 mg, 97% for the two steps) as colorless crystals: mp 120−122 °C; $[\alpha]_D^{25}$ −50.2 (*c* 0.40, $CHCl_3$); IR (neat) 3409, 2928, 2856, 1732, 1667, 1112, 1061 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.66−7.62 (m, 4H), 7.42−7.34 (m, 6H), 6.42 (dd, *J* = 12.8, 2.3 Hz, 1H), 5.98 (dd, *J* = 12.8, 2.8 Hz, 1H), 4.26 (ddd, *J* = 8.3, 2.8, 2.3 Hz, 1H), 4.20 (dd, *J* = 4.6, 2.3 Hz, 1H), 3.91−3.85 (m, 3H), 3.77 (ddd, *J* = 10.1, 8.3, 5.0 Hz, 1H), 3.64 (ddd, *J* = 10.1, 5.5, 5.5 Hz, 1H), 3.41−3.35 (m, 2H), 3.05 (dd, *J* = 12.8, 3.7 Hz, 1H), 2.19 (ddd, *J* = 11.9, 4.1, 4.1 Hz, 1H), 1.92

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(m, 1H), 1.87 (d, J = 12.8 Hz, 1H), 1.77 (ddd, J = 11.5, 11.5, 11.5 Hz, 1H), 1.73−1.55 (m, 7H), 1.44 (m, 1H), 1.30 (s, 3H), 1.29 (s, 3H), 1.02 (s, 9H), 0.83 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.4, 145.6, 135.5 (4C), 134.1 (2C), 129.5 (2C), 128.6, 127.6 (4C), 88.1, 86.4, 79.6, 79.1, 75.2, 73.0, 72.5, 69.3, 65.2, 60.7, 53.7, 40.4, 34.6, 31.5, 28.6, 26.9 (3C), 25.8 (3C), 20.7, 19.2, 18.6, 18.2, 15.8, −5.3 (2C); HRMS (ESI) calcd for $C_{43}H_{64}O_7Si_2Na$ [(M + Na)$^+$] 771.4083, found 771.4082.

To a solution of enone **S3** (186.3 mg, 0.2487 mmol) in toluene (5.0 mL) at −78 °C was added MeMgBr (3.0 M solution in Et_2O, 0.25 mL, 0.75 mmol), and the resultant solution was stirred at −78 °C for 40 min. The reaction was quenched with saturated aqueous NH_4Cl solution. The resultant mixture was extracted with EtOAc, and the organic layer was washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 9% EtOAc/hexanes) gave allylic alcohol **28** (184.5 mg, 97%, dr >95:5) as a colorless foam: $[\alpha]_D^{24}$ +9.4 (c 1.00, $CHCl_3$); IR (neat) 3466, 2928, 2855, 1112, 1094, 1071 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65−7.62 (m, 4H), 7.39−7.33 (m, 6H), 5.60 (dd, J = 12.8, 2.8 Hz, 1H), 5.44 (dd, J = 12.8, 1.9 Hz, 1H), 4.24 (br s, 1H), 4.11 (ddd, J = 9.7, 2.8, 1.9 Hz, 1H), 3.86 (m, 1H), 3.78−3.70 (m, 3H), 3.66−3.60 (m, 2H), 3.36 (dd, J = 11.0, 4.1 Hz, 1H), 3.31 (ddd, J = 11.0, 9.7, 5.0 Hz, 1H), 3.03 (dd, J = 12.4, 3.2 Hz, 1H), 2.01 (ddd, J = 11.5, 3.7, 3.7 Hz, 1H), 1.90 (m, 1H), 1.85 (d, J = 12.8 Hz, 1H), 1.70−1.53 (m, 8H), 1.44 (m, 1H), 1.28 (s, 3H), 1.27 (s, 3H), 1.22 (s, 3H), 1.02 (s, 9H), 0.88 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 135.5 (4C), 134.1, 134.0, 129.6, 129.5 (2C), 127.6 (4C), 86.2, 82.1, 81.6, 79.7, 76.4, 75.2, 72.0, 71.5, 69.2, 63.9, 60.7, 53.9, 40.5, 34.6, 32.1, 28.6, 26.9 (3C), 25.7 (3C), 21.3, 20.8, 19.2, 18.6, 18.0, 15.8, −5.6, −5.8; HRMS (ESI) calcd for $C_{44}H_{68}O_7Si_2Na$ [(M + Na)$^+$] 787.4396, found 787.4377.

Diol ***29***. To a solution of allylic alcohol **28** (171.2 mg, 0.2237 mmol) in MeOH/CH_2Cl_2 (1:1, v/v, 5 mL) at 0 °C was added CSA (5.2 mg, 0.022 mmol), and the resultant solution was stirred at 0 °C for 2 h. The reaction mixture was neutralized with Et_3N and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 40 to 50 to 60% EtOAc/hexanes) gave diol **29** (143.2 mg, 98%) as a colorless foam: $[\alpha]_D^{24}$ −27.6 (c 0.30, $CHCl_3$); IR (neat) 3388, 2929, 2856, 1383, 1095, 1069, 703 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66−7.62 (m, 4H), 7.42−7.34 (m, 6H), 5.64 (dd, J = 12.8, 2.7 Hz, 1H), 5.48 (dd, J = 12.8, 1.9 Hz, 1H), 4.18 (ddd, J = 9.2, 2.7, 1.9 Hz, 1H), 3.86 (m, 1H), 3.82 (dd, J = 11.0, 4.6 Hz, 1H), 3.77 (ddd, J = 10.1, 8.3, 5.5 Hz, 1H), 3.66−3.60 (m, 2H), 3.55 (dd, J = 7.8, 5.0 Hz, 1H), 3.38−3.31 (m, 2H), 3.04 (dd, J = 12.8, 3.7 Hz, 1H), 2.07 (ddd, J = 11.9, 4.1, 4.1 Hz, 1H), 1.91 (m, 1H), 1.85 (d, J = 12.8 Hz, 1H), 1.74−1.53 (m, 8H), 1.44 (m, 1H), 1.27 (s, 6H), 1.24 (s, 3H), 1.02 (s, 9H), two protons missing due to H/D exchange; ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.9, 135.5 (4C), 134.1, 134.0, 130.8, 129.5 (2C), 127.6 (4C), 86.3, 85.8, 81.7, 79.6, 75.8, 75.2, 72.2, 71.6, 69.3, 62.1, 60.7, 53.8, 40.5, 34.6, 31.9, 28.6, 26.9 (3C), 21.0, 20.8, 19.2, 18.7, 15.8; HRMS (ESI) calcd for $C_{38}H_{54}O_7SiNa$ [(M + Na)$^+$] 673.3531, found 673.3516.

Dibromoolefin ***30***. To a solution of diol **29** (135.0 mg, 0.2074 mmol) in CH_2Cl_2/DMSO (1:1, v/v, 4 mL) at 0 °C were added Et_3N (0.29 mL, 2.1 mmol) and SO_3·pyridine (198.5 mg, 1.247 mmol), and the resultant mixture was stirred at 0 °C for 40 min. The reaction mixture was diluted with t-BuOMe and washed with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give crude aldehyde, which was used in the next reaction without further purification.

To a solution of CBr_4 (210.1 mg, 0.6335 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added Ph_3P (334.1 mg, 1.274 mmol), and the resultant solution was stirred at 0 °C for 20 min. To this solution were added Et_3N (0.35 mL, 2.5 mmol) and a solution of the above aldehyde in CH_2Cl_2 (1 mL + 1 mL rinse), and the resultant solution was stirred at 0 °C for 20 min. The reaction was quenched with saturated aqueous $NaHCO_3$ solution. The resultant mixture was extracted with EtOAc, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 10% EtOAc/hexanes) gave dibromoolefin **30** (154.7 mg, 93% for the two steps) as a colorless foam: $[\alpha]_D^{24}$ −8.0 (c 0.85, $CHCl_3$); IR (neat) 3435, 2931, 2857, 1104, 1065, 758, 702 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66−7.62 (m, 4H), 7.41−7.34 (m, 6H), 6.53 (d, J = 8.3 Hz, 1H), 5.72 (dd, J = 12.8, 2.8 Hz, 1H), 5.52 (dd, J = 12.8, 2.3 Hz, 1H), 4.20 (ddd, J = 9.1, 2.8, 2.3 Hz, 1H), 4.10 (d, J = 8.3 Hz, 1H), 3.86 (m, 1H), 3.77 (ddd, J = 10.1, 8.2, 5.5 Hz, 1H), 3.64 (ddd, J = 10.1, 5.5, 5.5 Hz, 1H), 3.42−3.35 (m, 2H), 3.04 (dd, J = 12.8, 3.2 Hz, 1H), 2.14 (ddd, J = 11.5, 3.7, 3.7 Hz, 1H), 1.91 (m, 1H), 1.85 (d, J = 12.4 Hz, 1H), 1.74−1.55 (m, 8H), 1.44 (m, 1H), 1.33 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H), 1.02 (s, 9H), one proton missing due to H/D exchange; ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 135.5 (4C), 135.2, 134.1, 134.0, 131.6, 129.5 (2C), 127.6 (4C), 95.1, 86.3, 86.1, 82.0, 79.7, 75.9, 75.2, 72.2, 71.6, 69.2, 60.7, 53.8, 40.5, 34.6, 31.8, 28.6, 26.9 (3C), 21.4, 20.8, 19.2, 18.6, 15.7; HRMS (ESI) calcd for $C_{39}H_{52}Br_2O_6SiNa$ [(M + Na)$^+$] 825.1792, found 825.1784.

Silyl Ether ***31***. To a solution of dibromoolefin **30** (150.0 mg, 0.1864 mmol) in CH_2Cl_2 (2 mL) at 0 °C were added 2,6-lutidine (0.130 mL, 1.12 mmol) and TMSOTf (0.100 mL, 0.553 mmol), and the resultant solution was stirred at 0 °C for 30 min. The reaction was quenched with H_2O. The resultant mixture was extracted with EtOAc, and the organic layer was washed with 1 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 5% Et_2O/hexanes) gave silyl ether **31** (143.9 mg, 88%) as a colorless foam: $[\alpha]_D^{24}$ −9.6 (c 0.29, $CHCl_3$); IR (neat) 2952, 2857, 1129, 1099, 1067, 841, 702 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66−7.59 (m, 4H), 7.42−7.34 (m, 6H), 6.50 (d, J = 7.8 Hz, 1H), 5.77 (dd, J = 12.8, 2.8 Hz, 1H), 5.44 (dd, J = 12.8, 1.9 Hz, 1H), 4.17 (ddd, J = 9.7, 2.8, 1.9 Hz, 1H), 4.05 (d, J = 7.8 Hz, 1H), 3.85 (m, 1H), 3.77 (ddd, J = 10.1, 8.3, 5.0 Hz, 1H), 3.64 (ddd, J = 10.6, 5.5, 5.5 Hz, 1H), 3.40−3.35 (m, 2H), 3.04 (dd, J = 12.8, 3.7 Hz, 1H), 2.15 (ddd, J = 11.9, 4.1, 4.1 Hz, 1H), 1.91 (m, 1H), 1.85 (d, J = 12.4 Hz, 1H), 1.72−1.54 (m, 8H), 1.44 (m, 1H), 1.34 (s, 3H), 1.27 (s, 3H), 1.22 (s, 3H), 1.02 (s, 9H), 0.13 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1, 136.1, 135.5 (4C), 134.1 (2C), 130.3, 129.5 (2C), 127.6 (4C), 94.7, 86.3, 86.1, 82.1, 79.8, 78.5, 75.2, 72.2, 71.7, 69.2, 60.7, 53.9, 40.5, 34.6, 31.7, 28.6, 26.9 (3C), 21.9, 20.8, 19.2, 18.6, 15.8, 2.4 (3H); HRMS (ESI) calcd for $C_{42}H_{60}Br_2O_6Si_2Na$ [(M + Na)$^+$] 897.2187, found 897.2195.

Diol ***32***. To a solution of silyl ether **31** (138.9 mg, 0.1584 mmol) in benzene (3 mL) were added Bu_3SnH (0.085 mL, 0.32 mmol) and $Pd(PPh_3)_4$ (36.6 mg, 0.0317 mmol), and the resultant mixture was stirred at room temperature for 1.5 h. The reaction mixture was directly loaded onto a silica gel column and eluted with 5% Et_2O/hexanes to give vinyl bromide **S4** (117.5 mg, 93%) as a colorless foam: $[\alpha]_D^{24}$ +6.0 (c 1.00, $CHCl_3$); IR (neat) 2951, 2857, 1110, 1068, 841, 702 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66−7.62 (m, 4H), 7.42−7.34 (m, 6H), 6.43 (dd, J = 7.3, 2.3 Hz, 1H), 6.26 (dd, J = 7.3, 7.3 Hz, 1H), 5.81 (dd, J = 12.8, 2.7 Hz, 1H), 5.46 (dd, J = 12.8, 1.8 Hz, 1H), 4.28 (dd, J = 7.3, 2.3 Hz, 1H), 4.18 (ddd, J = 9.2, 2.7, 1.8 Hz, 1H), 3.86 (m, 1H), 3.78 (ddd, J = 10.1, 8.2, 5.0 Hz, 1H), 3.44 (ddd, J = 11.0, 9.2, 4.1 Hz, 1H), 3.37 (dd, J = 11.0, 4.1 Hz, 1H), 3.07 (dd, J = 12.8, 3.7 Hz, 1H), 2.18 (ddd, J = 11.5, 4.1, 4.1 Hz, 1H), 1.91 (m, 1H), 1.86 (d, J = 12.8 Hz, 1H), 1.72−1.53 (m, 9H), 1.45 (m, 1H), 1.35 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H), 1.02 (s, 9H), 0.11 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1, 135.5 (4C), 134.1 (2C), 132.3, 130.1, 129.5 (2C), 127.6 (4C), 112.7, 86.2, 83.8, 82.0, 79.8, 78.5, 75.2, 72.2, 71.9, 69.2, 60.7, 53.9, 40.5, 34.6, 31.8, 28.6, 26.9 (3C), 22.1, 20.8, 19.2, 18.6, 15.8, 2.4 (3C); HRMS (ESI) calcd for $C_{42}H_{61}BrO_6Si_2Na$ [(M + Na)$^+$] 819.3082, found 819.3077.

To a solution of vinyl bromide **S4** (102.9 mg, 0.1289 mmol) in THF (10 mL) at 0 °C was added HF·pyridine (1.0 mL), and the resultant solution was stirred at room temperature for 6 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution at 0 °C. The resultant mixture was extracted with EtOAc, and the organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by

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flash column chromatography (silica gel, 60% EtOAc/hexanes) gave diol **32** (59.4 mg, 95%) as colorless crystals: mp 162−165 °C; $[\alpha]_D^{24}$ +53.0 (*c* 1.50, $CHCl_3$); IR (neat) 3419, 2941, 2871, 1126, 1069, 1049, 756 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 6.47 (dd, *J* = 7.4, 0.9 Hz, 1H), 6.23 (dd, *J* = 7.4, 7.4 Hz, 1H), 5.75 (dd, *J* = 12.8, 2.8 Hz, 1H), 5.51 (d, *J* = 12.8 Hz, 1H), 4.35 (d, *J* = 7.4 Hz, 1H), 4.21 (ddd, *J* = 9.7, 2.8, 1.9 Hz, 1H), 3.91 (m, 1H), 3.72−3.68 (m, 2H), 3.46−3.39 (m, 2H), 3.09−3.06 (m, 2H), 2.13 (ddd, *J* = 11.5, 3.7, 3.7 Hz, 1H), 1.96−1.91 (m, 2H), 1.80−1.71 (m, 3H), 1.64−1.53 (m, 5H), 1.35 (s, 3H), 1.31 (s, 3H), 1.24 (s, 3H), two proton missing due to H/D exchange; ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 131.7, 131.0, 112.7, 85.8, 83.8, 81.6, 79.8, 76.4, 75.9, 74.9, 72.0, 71.8, 62.0, 54.0, 39.0, 34.6, 31.8, 28.5, 21.2, 20.5, 18.7, 15.7; HRMS (ESI) calcd for $C_{23}H_{35}BrO_6Na$ $[(M + Na)^+]$ 509.1509, found 509.1501.

Tetraene ***34***. To a suspension of LiCl (95.1 mg, 2.24 mmol), CuCl (220.3 mg, 2.230 mmol), and $Pd(PPh_3)_4$ (51.4 mg, 0.0445 mmol) in degassed DMSO (3.1 mL) was added a solution of diol **32** (54.4 mg, 0.112 mmol) and vinylstannane **33** (221.6 mg, 0.6204 mmol) in degassed THF (2.0 mL + 1.1 mL rinse), and the resultant mixture was stirred at 60 °C for 21 h. The reaction was quenched with 3% NH_4OH solution at room temperature. The resultant mixture was extracted with EtOAc, and the organic layer was washed with 3% NH_4OH solution and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 40% EtOAc/hexanes) gave tetraene **34** (47.5 mg, 89%) as colorless crystals: mp 164−167 °C; $[\alpha]_D^{24}$ +53.0 (*c* 1.00, benzene); IR (neat) 3419, 2941, 2871, 1126, 1069, 1049, 756 cm^{-1}; ^1H NMR (600 MHz, pyridine-d_5) δ 6.84 (dd, *J* = 11.6, 11.5 Hz, 1H), 6.63 (dd, *J* = 11.5, 11.5 Hz, 1H), 6.43 (br s, 1H), 6.29 (dd, *J* = 12.8, 2.8 Hz, 1H), 6.00 (dd, *J* = 11.6, 7.8 Hz, 1H), 5.88 (dd, *J* = 12.8, 1.9 Hz, 1H), 5.82 (dddd, *J* = 16.9, 10.1, 6.4, 6.4 Hz, 1H), 5.59 (ddd, *J* = 11.5, 9.2, 7.3 Hz, 1H), 5.13 (br s, 1H), 5.09 (dd, *J* = 16.9, 1.8 Hz, 1H), 5.01 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.86 (d, *J* = 7.8 Hz, 1H), 4.59 (ddd, *J* = 9.1, 2.8, 1.9 Hz, 1H), 4.05−3.98 (m, 3H), 3.76 (ddd, *J* = 11.0, 9.7, 5.0 Hz, 1H), 3.54 (dd, *J* = 11.5, 4.1 Hz, 1H), 3.24 (dd, *J* = 12.8, 3.7 Hz, 1H), 2.98−2.90 (m, 2H), 2.30 (ddd, *J* = 11.5, 4.1, 4.1 Hz, 1H), 2.13 (d, *J* = 12.4 Hz, 1H), 2.04 (d, *J* = 12.4 Hz, 1H), 2.02−1.96 (m, 2H), 1.93 (ddd, *J* = 11.5, 11.5, 11.5 Hz, 1H), 1.82 (m, 1H), 1.71−1.43 (m, 8H), 1.34 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, pyridine-d_5) δ 141.9, 137.1, 131.1, 130.5, 130.3, 127.0, 126.7, 115.7, 86.8, 84.1, 82.3, 80.7, 76.2, 76.1, 73.0, 72.7, 71.3, 59.9, 55.1, 41.9, 35.2, 33.2, 32.3, 29.3, 22.0, 21.4, 19.2, 16.4; HRMS (ESI) calcd for $C_{28}H_{42}O_6Na$ $[(M + Na)^+]$ 497.2874, found 497.2875.

Clickable Gambierol Analogue ***17***. To a solution of tetraene **34** (4.1 mg, 0.0087 mmol) in $(CH_2Cl)_2$/DMSO (1:1, v/v, 0.5 mL) at 0 °C were added Et_3N (0.024 mL, 0.17 mmol) and SO_3·pyridine (13.8 mg, 0.0867 mmol), and the resultant mixture was stirred at 0 °C for 30 min. The resultant mixture was diluted with *t*-BuOMe, washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 20% EtOAc/hexanes) gave aldehyde **S5** (4.0 mg, 98%) as colorless crystals: mp 145−147 °C; $[\alpha]_D^{24}$ +103.4 (*c* 0.50, benzene); IR (neat) 3448, 2942, 2871, 1723, 1127, 1065, 1033 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 9.45 (dd, *J* = 2.8, 1.4 Hz, 1H), 6.50 (dd, *J* = 11.9, 11.5 Hz, 1H), 6.30 (dd, *J* = 11.5, 11.5 Hz, 1H), 5.95 (dd, *J* = 12.8, 2.8 Hz, 1H), 5.80 (dd, *J* = 12.8, 1.8 Hz, 1H), 5.67 (dddd, *J* = 16.5, 10.1, 6.4, 6.4 Hz, 1H), 5.49−5.45 (m, 2H), 5.00 (dd, *J* = 16.5, 1.8 Hz, 1H), 4.95 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.50 (d, *J* = 8.3 Hz, 1H), 4.39 (ddd, *J* = 9.2, 2.8, 1.8 Hz, 1H), 3.71 (m, 1H), 3.36 (ddd, *J* = 11.0, 9.2, 4.6 Hz, 1H), 3.27 (dd, *J* = 11.5, 4.6 Hz, 1H), 2.95 (dd, *J* = 12.8, 3.7 Hz, 1H), 2.74−2.72 (m, 2H), 2.21 (ddd, *J* = 15.5, 8.2, 2.8 Hz, 1H), 2.09 (ddd, *J* = 11.9, 4.6, 4.6 Hz, 1H), 1.98−1.93 (m, 2H), 1.88−1.75 (m, 3H), 1.47 (m, 1H), 1.38−1.30 (m, 4H), 1.26−1.09 (m, 7H), 1.05 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 199.9, 138.8, 136.2, 131.4 (2C), 128.3, 127.0, 125.3, 115.4, 86.0, 83.1, 81.8, 80.2, 76.3, 76.1, 72.4, 72.1, 69.1, 54.3, 50.8, 34.3, 32.6, 31.8, 28.7, 21.9, 20.7, 18.5, 15.8; HRMS (ESI) calcd for $C_{28}H_{40}O_6Na$ $[(M + Na)^+]$ 495.2717, found 495.2714.

To a solution of aldehyde **S5** (4.0 mg, 0.0085 mmol) in MeOH (0.2 mL) at 0 °C were added a solution of Ohira−Bestmann reagent (14.9 mg, 0.0776 mmol) in CH_2Cl_2 (0.1 mL + 0.1 mL rinse) and K_2CO_3 (21.6 mg, 0.156 mmol), and the resultant mixture was stirred at room temperature for 1 h. The resultant mixture was diluted with EtOAc, washed with H_2O and brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel, 8−10% EtOAc/hexanes) gave clickable gambierol analogue **17** (3.6 mg, 92%) as a colorless oil: $[\alpha]_D^{24}$ +114.2 (*c* 0.40, benzene); IR (neat) 3467, 3294, 2939, 2871, 1381, 1127, 1065 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 6.50 (dd, *J* = 11.5, 11.5 Hz, 1H), 6.30 (dd, *J* = 11.5, 11.5 Hz, 1H), 5.94 (dd, *J* = 12.8, 2.8 Hz, 1H), 5.80 (dd, *J* = 12.8, 2.3 Hz, 1H), 5.67 (dddd, *J* = 16.5, 10.1, 6.4, 6.4 Hz, 1H), 5.49−5.45 (m, 2H), 5.00 (dd, *J* = 16.5, 1.9 Hz, 1H), 4.94 (dd, *J* = 10.1, 1.9 Hz, 1H), 4.49 (d, *J* = 8.2 Hz, 1H), 4.38 (ddd, *J* = 9.6, 2.8, 2.3 Hz, 1H), 3.59 (m, 1H), 3.37−3.32 (m, 2H), 2.95 (dd, *J* = 12.8, 3.7 Hz, 1H), 2.74−2.72 (m, 2H), 2.33 (ddd, *J* = 16.5, 4.6, 2.8 Hz, 1H), 2.19 (ddd, *J* = 16.5, 7.8, 2.8 Hz, 1H), 2.09−2.03 (m, 3H), 1.87 (m, 1H), 1.80−1.74 (m, 2H), 1.63 (m, 1H), 1.51−1.41 (m, 3H), 1.29 (s, 3H), 1.25−1.13 (m, 5H), 1.08 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 138.7, 136.2, 131.5, 131.4, 128.5, 127.0, 125.3, 115.4, 86.1, 83.1, 81.9, 81.8, 80.2, 76.3, 76.0, 72.4, 72.2 (2C), 70.1, 54.5, 33.3, 32.6, 31.8, 29.0, 27.6, 21.9, 20.6, 18.6, 15.8; HRMS (ESI) calcd for $C_{29}H_{40}O_5Na$ $[(M + Na)^+]$ 491.2768, found 491.2781.

Biotin-Tagged Photoaffinity Labeling Probe ***36***. To a solution of clickable gambierol analogue **17** (3.6 mg, 0.0078 mmol) and azide **35** (5.3 mg, 0.0085 mmol) in DMSO (0.39 mL) were added THPTA (0.1 M solution in DMSO, 0.078 mL, 0.0078 mmol), sodium ascorbate (0.2 M solution in H_2O, 0.078 mL, 0.016 mmol), and $CuSO_4·5H_2O$ (0.2 M solution in H_2O, 0.039 mL, 0.0078 mmol), and the resultant mixture was stirred at room temperature for 1 h. The reaction mixture was directly loaded onto a silica gel column. Purification by flash column chromatography (EtOAc then $CHCl_3$ then 10% MeOH/$CHCl_3$) gave biotin-tagged photoaffinity labeling probe **36** (8.2 mg, 96%) as a colorless amorphous solid: $[\alpha]_D^{25}$ +17.5 (*c* 1.00, MeOH); IR (neat) 3295, 2928, 2864, 1697, 1653, 1273, 1064 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.81−7.75 (m, 5H), 7.54−7.43 (m, 4H), 6.50−6.41 (m, 2H), 5.82 (dddd, *J* = 16.9, 10.1, 6.4, 6.4 Hz, 1H), 5.75−5.68 (m, 3H), 5.56−5.48 (m, 2H), 5.33 (d, *J* = 13.3 Hz, 1H), 5.22−5.15 (m, 2H), 5.05 (d, *J* = 16.9 Hz, 1H), 4.98 (d, *J* = 10.1 Hz, 1H), 4.47 (dd, *J* = 7.8, 5.0 Hz, 1H), 4.36 (d, *J* = 7.8 Hz, 1H), 4.29 (dd, *J* = 7.3, 4.6 Hz, 1H), 4.15 (br d, *J* = 9.6 Hz, 1H), 3.90 (m, 1H), 3.68−3.64 (m, 2H), 3.41 (ddd, *J* = 10.6, 10.6, 4.6 Hz, 1H), 3.20−3.12 (m, 4H), 3.01 (dd, *J* = 12.8, 3.2 Hz, 1H), 2.97−2.94 (m, 2H), 2.91 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.80 (m, 1H), 2.69 (d, *J* = 12.4 Hz, 1H), 2.20−2.18 (m, 2H), 1.96 (m, 1H), 1.88 (m, 1H), 1.76−1.51 (m, 17H), 1.45−1.39 (m, 2H), 1.38−1.33 (m, 2H), 1.27 (s, 3H), 1.19 (s, 3H), 1.14 (s, 3H), five protons missing due to H/D exchange; ^{13}C NMR (150 MHz, CD_3OD) δ 197.2, 176.0, 166.1, 158.6, 147.1, 143.8, 142.0, 140.7, 138.7, 138.0, 137.5, 131.7 (2C), 131.4 (2C), 131.3 (2C), 129.1, 128.9 (2C), 128.4 (2C), 127.8, 126.4, 125.1, 87.4, 83.7, 82.6, 81.2, 76.8, 76.7, 73.3, 73.2 (2C), 71.5, 66.5, 63.4, 61.6, 57.0, 55.1, 54.2, 41.7, 41.0, 40.2, 36.8, 35.0, 34.7, 33.1, 32.6, 30.5, 30.1, 29.8, 29.6, 29.5, 26.9, 25.1, 21.6, 20.9, 19.1, 16.2; HRMS (ESI) calcd for $C_{60}H_{80}O_{10}N_7S$ $[(M + H)^+]$ 1090.5682, found 1090.5687.

■ ASSOCIATED CONTENT

Supporting Information

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^1H and ^{13}C NMR spectra for all new compounds (PDF)

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Notes

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