Tetrahedron 64 (2008) 11086–11095

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Investigation of oxacycle formation by base-promoted *endo*-mode ring-closing reaction of allenes

Shinji Kitagaki, Takamasa Kawamura, Daisuke Shibata, Chisato Mukai *

Division of Pharmaceutical Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

ARTICLE INFO

Article history:
Received 1 September 2008
Received in revised form
24 September 2008
Accepted 24 September 2008
Available online 1 October 2008

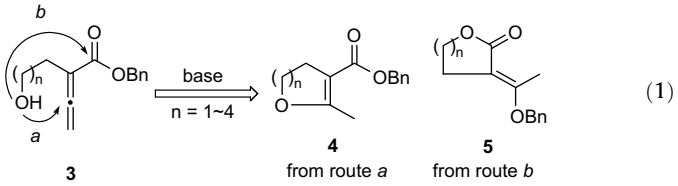
Keywords:
Allenes
Oxacycles
endo-Mode ring closure
Tandem reaction

ABSTRACT

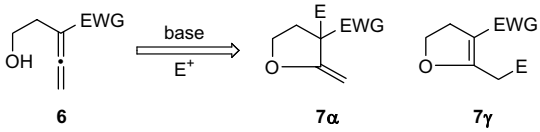
The base-promoted *endo*-mode ring closure of electron-withdrawing group-substituted allenes provided the following interesting results: (1) the *endo*-mode ring-closing reaction of 1-(benzyloxycarbonyl)-1-(ω-hydroxyalkyl)allenes smoothly proceeded during the formation of five-, seven-, and eight-membered rings; (2) base treatment of benzyloxycarbonylallene and sulfonylallene, having a 2-hydroxyethyl group at the C-1 position, in the presence of an aldehyde led to the ring closure and condensation with the aldehyde in one-pot; and (3) *endo*-mode ring closure of the sulfonylallenes by internal attack of the carboxylate anion afforded the six-membered lactone.

1. Introduction

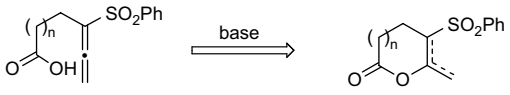
The ring-closing reaction based on the base-promoted internal nucleophilic attack is one of the most straightforward methods for the synthesis of cyclized products. This type of reaction is generally only applicable for the preparation of normal-sized rings and is regarded to be unsuitable for the construction of medium-sized ring systems, due to entropic and enthalpic problems.[1] We have found that the base-promoted *endo*-mode ring closure of 1,1-di-substituted allenes with an electron-withdrawing (SO_2Ph, SOPh, $PO(OEt)_2$, or $POPh_2$) group and an ω-hydroxyalkyl appendage at the C-1 position afforded five- to medium-sized oxacycles (Scheme 1).[2,3] The *exo*-mode ring-closing reaction of the 1-(ω-hydroxyalkyl)-3-sulfonylallenes leading to medium-sized oxacycles did not proceed.[2a,4] This methodology was successfully applied to the construction of carbocycles and azacycles using active methine nucleophiles[5] and amide nucleophiles,[6] respectively. In addition, our recent efforts[7] disclosed that the alkoxycarbonyl groups serve as a suitable electron-withdrawing group on the allene moiety during the five-membered oxacycle formation.[7–9] This paper focuses on the following topics to further understand the synthetic utility of our ring-closing method; (1) the influence of the ring size on the ring-closing mode of the 1-(alkoxycarbonyl)-1-(ω-hydroxyalkyl)allenes **3** (Eq. 1), (2) capture of the carbanion species, which should have resulted from the oxacycle formation via the *endo*-mode ring-closing reaction, with electrophiles (Eq. 2), and (3) lactonization of the sulfonylallenes **8** by internal attack of the carboxylate anion (Eq. 3).



3 **4** from route *a* **5** from route *b* (1)



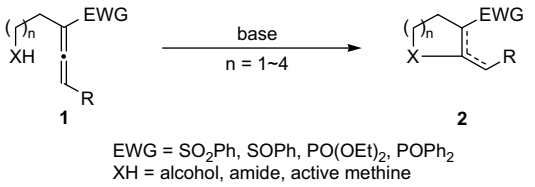
6 **7α** **7γ** (2)



8 **9** (3)

* Corresponding author. Tel.: +81 76 234 4411; fax: +81 76 234 4410.
E-mail address: cmukai@kenroku.kanazawa-u.ac.jp (C. Mukai).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.09.069

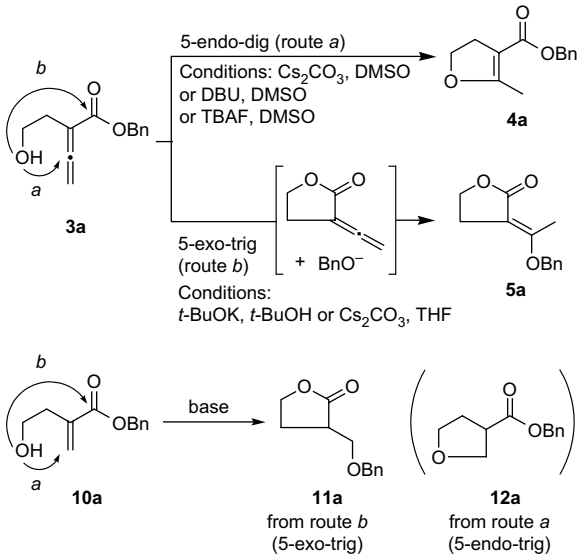


Scheme 1. Ring-closing reaction of electron-withdrawing group-substituted allenes **1**.

2. Results and discussion

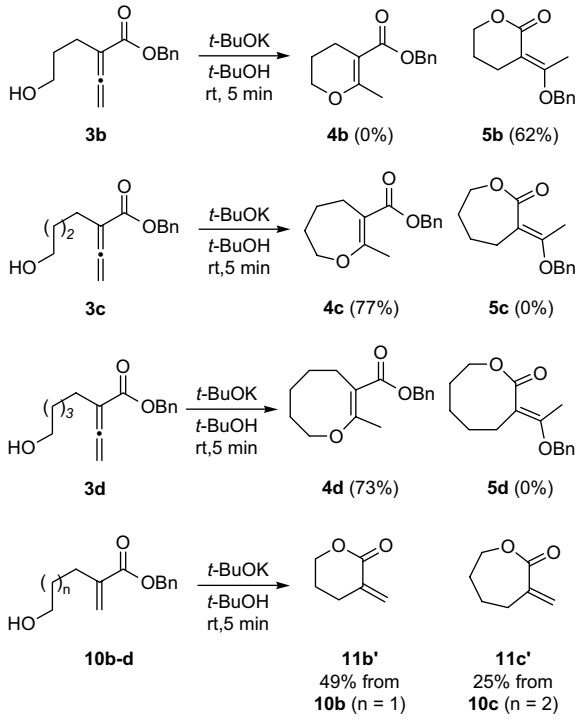
2.1. Ring-closing reaction of 1-(alkoxycarbonyl)-1-(ω-hydroxyalkyl)allenes

Alkoxycarbonylallenes **3** have two reaction sites leading to *endo*-mode and *exo*-mode ring closures. We recently found that the ring-closing mode of 1-(benzyloxycarbonyl)-1-(2-hydroxyethyl)allene **3a** could precisely be controlled in a highly selective manner by the proper choice of conditions (Scheme 2).[7] Thus, the 5-*endo*-*dig*-mode ring-closing reaction of **3a** (route a) was found to be promoted by DBU, TBAF, or Cs_2CO_3 in DMSO while the 5-*exo*-*trig*-mode ring-closing reaction (lactonization, route b) proceeded by the treatment with *t*-BuOK in *t*-BuOH or Cs_2CO_3 in THF or CH_2Cl_2.[†] The difference in the ring-closing mode of **3a** might be attributed to the electronic and/or steric property of the resulting alkoxide moiety. In particular, it was found that the dielectric constant of the solvent must play an important role in the preferential formation of **4a** or **5a** when Cs_2CO_3 was used as the base. Solvents with a higher dielectric constant tended to predominantly produce **4a**. This was not the case for the results of the reaction of the corresponding α,β-unsaturated ester **10a**, which exclusively gave the 5-*exo*-*trig*-mode product **11a**, and the formation of **12a** could never be observed.[7,11] We now investigated the ring-closing mode for the construction of the six- and larger-membered oxacycles. The treatment of 1-(benzyloxycarbonyl)-1-(3-hydroxypropyl)allene **3b** with *t*-BuOK in *t*-BuOH at room temperature exclusively furnished the 6-*exo*-*trig*-mode product **5b**[‡] in 62% yield,[§] and no 6-*endo*-*dig*-mode product **4b** could be detected (Scheme 3). The other conditions using DBU, TBAF, or Cs_2CO_3 as a base, which worked well for the ring-closing reaction of **3a**, unexpectedly gave only an intractable mixture. In sharp contrast to the results of the allene **3b**, the one-carbon homologated substrate **3c** provided the 7-*endo*-*dig* mode product **4c** in 77% yield as the sole product.[¶] The eight-membered oxacycle **4d** was also prepared from **3d** in 73% yield via the 8-*endo*-*dig* ring-closing mode.[¶] The *t*-BuOK/*t*-BuOH condition could only affect the ring-closing reaction of the allenes **3c** and **3d**. The other basic conditions were found to unsuccessful for construction of the seven- and eight-membered oxacycles.



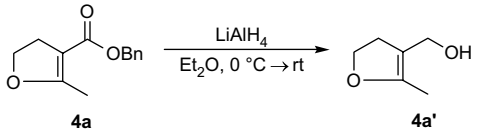
Scheme 2. Ring-closing reaction of benzyloxycarbonylallene **3a** and α,β-unsaturated ester **10a**.

The preferential formation of the *exo*-*trig*-mode product **5b** over the *endo*-mode product **4b** in the presence of *t*-BuOK in *t*-BuOH is in good agreement with the prediction based on the results of the 1-(benzyloxycarbonyl)-1-(2-hydroxyethyl)allene **3a**. Difficulty encountered in the 7- and 8-*exo*-*trig* mode ring closure might be predicted from the results of the reactions of the corresponding α,β-unsaturated esters **10c** and **10d**, wherein the seven-membered lactone **11c**′ was obtained from **10c** in 25% yield and no eight-membered one **11d**′ could be detected in the reaction of **10d**. On the other hand, the results of the reactions of allenes **3c** and **3d** indicated that the central carbon atom of the allene must have



Scheme 3. Formation of 6- and larger-membered ring oxacycles.

[†] The structure of **4a** was unambiguously elucidated by transformation to the known alcohol **4a**′ using $LiAlH_4$.[10] The stereochemistry of **5a** was determined to be (*E*) by an NOE analysis. The exclusive formation of the (*E*)-isomer might be rationalized in terms of the thermodynamically controlled protonation of carbanion species, generated by the initial attack of alkoxide to the allene moiety. In other words, dipolar repulsion between an ester carbonyl group and the adjacent C–O bond would govern the stereochemistry of the product.

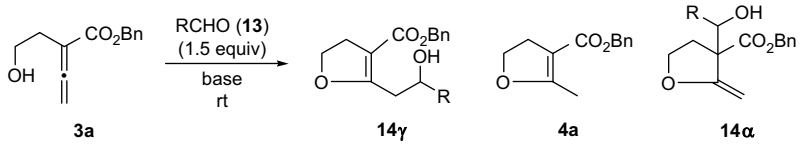


[‡] The structure of **5b** was determined by comparison of the ^1H NMR and IR data to those of the similar compounds.[12,13]

[§] A 0.025 M solution was used. Reaction in a 0.1 M solution afforded **5b** in only 5% yield.

[¶] A 0.025 M solution was used, but reaction in a 0.1 M solution gave similar results.

Table 1
Sequential reaction of allene **3a** with aldehyde **13**



3a **14γ** **4a** **14α**

Entry	Aldehyde		Base (equiv)	Solvent	Time	Product (% yield)[a]	
	13	R					
1	**13a**	Ph	DBU (1.5)	DMSO	30 min	**14γa** (51)	**4a** (16)
2	**13a**	Ph	TBAF (1.0)	DMSO	5 min	**14γa** (64)	**4a** (9)
3	**13a**	Ph	Cs_2CO_3 (1.0)	DMSO	3 h	**14γa** (49)	**4a** (23)
4	**13a**	Ph	*t*-BuOK (1.0)	*t*-BuOH	5 min	**14γa** (—)	**4a** (—)[b]
5	**13b**	3-$NO_2C_6H_4$	TBAF (1.0)	DMSO	5 min	**14γb** (71)	**4a** (—)[c]
6	**13c**	4-ClC_6H_4	TBAF (1.0)	DMSO	5 min	**14γc** (67)	**4a** (5)
7	**13d**	4-$MeOC_6H_4$	TBAF (1.0)	DMSO	5 min	**14γd** (—)	**4a** (62)
8	**13e**	PhCH=CH	TBAF (1.0)	DMSO	5 min	**14γe** (30)	**4a** (39)
9	**13f**	*n*-Bu	TBAF (1.0)	THF	5 min	**14γf** (60)	**4a** (8)
10	**13g**	*i*-Bu	TBAF (1.0)	THF	5 min	**14γg** (53)	**4a** (16)
11	**13h**	*t*-Bu	TBAF (1.0)	THF	5 min	**14γh** (27)	**4a** (40)

[a] Isolated yields.
[b] *exo-trig* Mode product **5a** was obtained in 55% yield.
[c] A trace amount of **4a** was detected by TLC.

a significantly high electrophilicity. Thus, we demonstrated that the ring-closing mode of the 1-(alkoxycarbonyl)-1-(ω-hydroxyalkyl)allenes **3** was significantly affected by the size of ring being formed.

2.2. Sequential ring closure/C–C bond forming reaction

In order to enhance the utility of our method for the synthesis of substituted oxacycles, we next investigated the trapping reaction of the allylic anion produced during the ring-closing process. By using the optimized conditions (DBU, DMSO),[7] the 5-*endo*-*dig*-mode ring closure of benzyloxycarbonylallene **3a** was performed, and after completion of the reaction (monitored by TLC), benzaldehyde (**13a**) was added to the mixture. However, neither the desired α-adduct **14αa** nor γ-adduct **14γa** could be detected. On the other hand, the addition of DBU to a mixture of an allene **3a** and aldehyde **13a** in DMSO afforded the γ-adduct **14γa** in 51% yield along with a cyclized product **4a** (16%) (Table 1, entry 1). For this sequential reaction, TBAF in DMSO was shown to afford a high yield of **14γa**, and the use of *t*-BuOK in *t*-BuOH gave *exo*-mode product **5a** as the sole isolatable product (entries 2 and 4). By using TBAF as a base, the sequential reaction of **3a** with various aldehydes was investigated. This reaction was sensitive to the electronic property of the substituent on the benzene ring of aromatic aldehydes. Thus, the electron-donating group-substituted benzaldehyde **13d** gave no adduct, while the electron-withdrawing group-substituted ones **13b** and **13c** gave the corresponding adducts **14γb** and **14γc** in good yields (entry 7 vs entries 5 and 6). The cinnamaldehyde (**13e**) afforded the 1,2-adduct **14γe** in low yield (entry 8). For the reaction of saturated aliphatic aldehydes, THF gave better results compared to DMSO, and the corresponding adducts were obtained in moderate to low yields according to the bulkiness of the alkyl group (entries 9–11). Sulfonylallene **15** is an excellent substrate for this sequential reaction (Table 2). For example, **15** reacted with the electron-donating group-substituted benzaldehyde **13d** and cinnamaldehyde **13e** to afford the γ-adducts **16γd** and **16γe** in 88% and 82% yields, respectively, using TBAF/THF or DBU/DMSO (Table 2, entries 4 and 5 vs Table 1, entries 7 and 8). The reaction of **15** with a saturated aldehyde **13f** also gave higher yields of **16γf** relative to the case of the allene **3a** (Table 2, entry 7 vs Table 1, entry 9). In all the reactions examined in this study, no α-adduct **16α** could be detected. Both of the allenes **3a** and **15** neither reacted with cyclohexanone nor iodomethane.

Scheme 4 illustrates the plausible mechanism for this sequential reaction. The fact that the aldehyde did not react with the carbanionic intermediate, formed via the *endo*-mode ring-closing reaction of the allene, suggested that the allene might condense with the aldehyde prior to the ring-closing reaction. Indeed, we have already found that the treatment of the sulfonylallene having no terminal substituents with DBU or TBAF easily produced the corresponding allenic/propargylic anion.[14–17] Furthermore, the allene **18**[‖] gave the cyclized product **16γa** in a reasonable yield under basic conditions (Scheme 5). Based on these results, it might be tentatively concluded that the condensation between the allene **6** and an aldehyde would first occur and the resulting intermediate like the alkoxide species of **18** should collapse into the oxacycle such as **16γa** (Scheme 4, **D**→**E**→**F**→**G**), although the possibility that the *endo*-mode ring closure precedes the condensation with the aldehyde (**A**→**B**→**C**) still cannot be excluded.

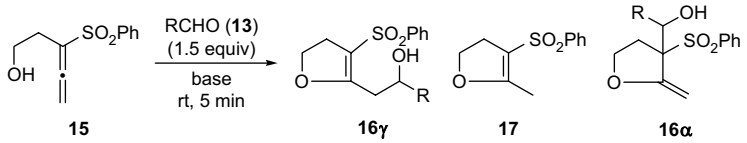
2.3. Lactonization of sulfonylallenes by internal carboxylate attack

To further increase the scope of our *endo*-mode ring-closing reaction of the allenes, we investigated the potential of a carboxyl group to serve as an internal nucleophile in the reaction of sulfonylallenes. The substrates **8** were prepared by the Jones oxidation of the 1-(ω-hydroxyalkyl)-1-sulfonylallenes. The initial attempt to cyclize **8a** to produce the six-membered lactone was conducted with *t*-BuOK in *t*-BuOH. While reaction did not proceed at room temperature, the reflux temperature led to the production of the six-membered exocyclic enol lactone *exo*-**9a** (75%)[††] along with a trace amount of the endocyclic one *endo*-**9a** (Table 3, entry 1). On the other hand, the reaction with K_2CO_3 as a base at room temperature furnished a mixture of the *exo*-**9a**[††] and *endo*-**9a**, *exo*-**9a**

[‖] Allene **18** was prepared by the condensation of the *O*-silylated **15** with the benzaldehyde, followed by desilylation.

[††] During chromatography and storage in a refrigerator, the *exo*-**9a** was contaminated with **21**, generated by the [1,3]-shift of the sulfonyl group.[18] The structure was confirmed by the alternative synthesis from the 5-oxo-6-(phenylsulfonyl)hexanoic acid.

Table 2
Sequential reaction of allene **15** with aldehyde **13**



15 **16γ** **17** **16α**

Entry	Aldehyde		Base (equiv)	Solvent	Product (% yield)[a]	
	13	R				
1	**13a**	Ph	TBAF (1.0)	THF	**16γa** (65)	**17** (5)
2	**13a**	Ph	DBU (1.5)	DMSO	**16γa** (70)	**17** (—)[b]
3	**13d**	4-$MeOC_6H_4$	TBAF (1.0)	THF	**16γd** (65)	**17** (11)
4	**13d**	4-$MeOC_6H_4$	DBU (1.5)	DMSO	**16γd** (88)	**17** (—)[b]
5	**13e**	PhCH=CH	TBAF (1.0)	THF	**16γe** (82)	**17** (—)[b]
6	**13e**	PhCH=CH	DBU (1.5)	DMSO	**16γe**(77)	**17** (6)
7	**13f**	*n*-Bu	TBAF (1.0)	THF	**16γf** (86)	**17** (—)[b]
8	**13f**	*n*-Bu	DBU (1.5)	DMSO	**16γf** (69)	**17** (10)

[a] Isolated yields.
[b] A trace amount of **17** was detected by TLC.

being predominantly formed (entries 2 and 3). The use of DMSO as a solvent showed a much faster consumption of the starting material **8a** (entry 3). We were surprised to find that the one-carbon homologation of the carboxylic acid substrate led to poor results. Indeed, the treatment of **8b** with *t*-BuOK in *t*-BuOH at refluxing temperature exclusively produced the 2-sulfonylcyclopentanone **19b**.[19] The use of K_2CO_3 at room temperature gave the desired seven-membered lactone *exo*-**9b**, cyclopentanone **19b**, and its acetylated congener **20b**. No eight-membered lactone products were obtained from **8c** under any conditions. In all the reactions using **8b** and **8c**, the formation of some amounts of carboxylic acid **22** was sometimes observed. The plausible mechanism for the formation of the undesired carbocycles **19** and **20** includes the expected nucleophilic attack of the carboxylate anion on the sp hybridized carbon center of the allene and subsequent transannular reaction of the resulting allylic anion stabilized by a sulfonyl group to the ester carbonyl group (Scheme 6). The carboxylic acid **22** would be formed by the hydrolysis of the lactone **9** or diketone **20**. Thus, the *endo*-mode ring closure of sulfonylallenes by internal attack of the carboxylate anion could be applicable to only the formation of the six-membered lactone.

3. Conclusions

We demonstrated the synthetic utility of our ring-closing method using electron-withdrawing group-substituted allenes, that is, (1) the *endo*-mode ring-closing reaction of the 1-(benzyloxycarbonyl)-1-(ω-hydroxyalkyl)allenes smoothly proceeded during the formation of five-, seven-, and eight-membered rings; (2) base treatment of the benzyloxycarbonylallene and sulfonylallene, having a 2-hydroxyethyl group at the C-1 position, in the presence of an aldehyde led to the ring closure and condensation with the aldehyde in one-pot; and (3) *endo*-mode ring closure of the sulfonylallene derivative by the nucleophilic attack of the internal carboxylate anion afforded the six-membered lactone.

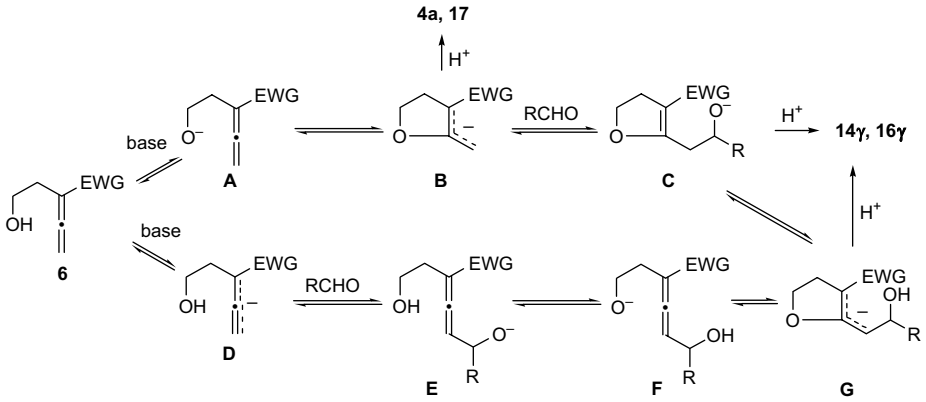
4. Experimental

4.1. General

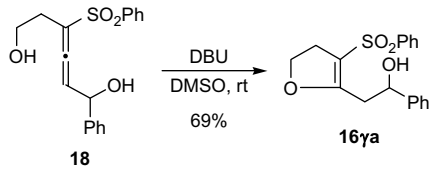
Melting points are uncorrected. IR spectra were measured in $CHCl_3$. ^1H NMR spectra were taken in $CDCl_3$. $CHCl_3$ (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group were used as internal standards. ^{13}C NMR spectra were recorded in $CDCl_3$ with $CDCl_3$ (77.00 ppm) as an internal standard. All reactions were carried out under a nitrogen atmosphere. Silica gel (silica gel 60, 230–400 mesh) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

4.2. Typical procedure for preparation of benzyloxycarbonylallenes 3

To a solution of 5-(*tert*-butyldimethylsiloxy)-2-pentyn-1-ol[2a] (400 mg, 1.86 mmol) and pyridine (0.45 mL, 5.6 mmol) in CH_2Cl_2 (10 mL) was added benzyl chloroformate (0.32 mL, 2.2 mmol) at



Scheme 4. Plausible mechanism for sequential reaction of the allene **6** and aldehyde.



Scheme 5. Reaction of **18** under basic conditions.

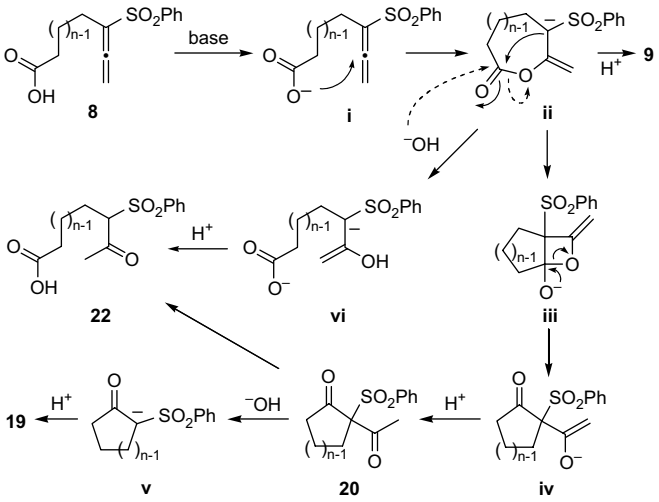
0 °C, and the mixture was stirred at that temperature for 1 h. The reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (10:1) to afford the crude carbonate (633 mg) as a colorless oil.

According to Tsuji's procedure,[20] the carbonate was converted into the allene. To a solution of the crude carbonate (500 mg, 1.44 mmol) in benzyl alcohol (2.8 mL) were added $Pd(OAc)_2$ (16.1 mg, 7.19×10^{-2} mmol) and PPh_3 (75.5 mg, 0.288 mmol), and the mixture was stirred at 40 °C under 10 atm of CO for 12 h. The reaction mixture was filtered, and the filtrate was concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (40:1) to afford the crude allene (220 mg) as a colorless oil.

To a solution of the crude allene (210 mg, 0.633 mmol) in MeOH (6.3 mL) was added $TsOH\cdot H_2O$ (21.8 mg, 0.127 mmol) at room temperature, and the mixture was stirred at that temperature for 1 h. The reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:1) afforded **3a** (125 mg, 42% for three steps) as a colorless oil.

*4.2.1. Benzyl 4-hydroxy-2-vinylidenebutanoate (**3a**)*

IR 3608, 3479, 1967, 1934, 1707 cm^{-1}; ^1H NMR δ 7.35–7.25 (m, 5H), 5.20 (s, 2H), 5.19 (t, 2H, J=2.6 Hz), 3.77 (t, 2H, J=6.2 Hz), 2.53 (tt, 2H, J=6.2, 2.6 Hz); ^{13}C NMR δ 214.3, 167.2, 135.9, 128.5, 128.1, 127.8, 97.1, 79.2, 66.7, 61.3, 31.8; MS m/z 218 (M^+, 18.6); HRMS calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0942.



Scheme 6. Plausible mechanism for reaction of **8**.

*4.2.2. Benzyl 5-hydroxy-2-vinylidenepentanoate (**3b**)*

A colorless oil: IR 3620, 3481, 1967, 1936, 1704 cm^{-1}; ^1H NMR δ 7.34–7.28 (m, 5H), 5.17 (s, 2H), 5.14 (t, 2H, J=2.9 Hz), 3.63 (t, 2H, J=6.4 Hz), 2.33 (tt, 2H, J=7.5, 2.9 Hz), 1.75–1.66 (m, 2H); ^{13}C NMR δ 214.0, 167.3, 135.9, 128.4, 128.0, 127.8, 99.5, 79.3, 66.6, 61.6, 31.1, 24.2; MS m/z 232 (M^+, 2.3); HRMS calcd for $C_{14}H_{16}O_3$ 232.1100, found 232.1102.

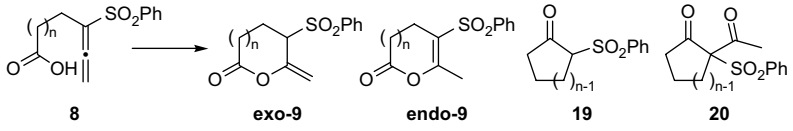
*4.2.3. Benzyl 6-hydroxy-2-vinylidenehexanoate (**3c**)*

A colorless oil: IR 3620, 3465, 1967, 1936, 1704 cm^{-1}; ^1H NMR δ 7.33–7.30 (m, 5H), 5.17 (s, 2H), 5.12 (t, 2H, J=3.1 Hz), 3.62 (t, 2H, J=6.3 Hz), 2.29–2.22 (m, 2H), 1.61–1.50 (m, 4H); ^{13}C NMR δ 213.9, 167.1, 136.1, 128.4, 128.0, 127.8, 99.9, 79.2, 66.4, 62.5, 32.0, 27.6, 24.1; MS m/z 246 (M^+, 2.7); HRMS calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1259.

*4.2.4. Benzyl 7-hydroxy-2-vinylideneheptanoate (**3d**)*

A colorless oil: IR 3620, 3469, 1967, 1936, 1701 cm^{-1}; ^1H NMR δ 7.33–7.30 (m, 5H), 5.17 (s, 2H), 5.11 (t, 2H, J=2.9 Hz), 3.58 (t, 2H,

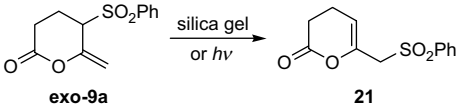
Table 3
Ring-closing reaction of allene **8**



a: n = 1; **b**: n = 2; **c**: n = 3

Entry	*n*	Base	Solvent	Temp	Time	Yield (%)[a]			
						exo-**9**	*endo*-**9**	**19**	**20**
1[b]	1	*t*-BuOK	*t*-BuOH	Reflux	9 h	75[c]	Trace	—	—
2[b]	1	K_2CO_3	CH_3CN	rt	1 h	53[c]	8	—	—
3[b]	1	K_2CO_3	DMSO	rt	5 min	58[c]	20	—	—
4[b]	2	*t*-BuOK	*t*-BuOH	Reflux	4 h	—	—	67	—
5[b]	2	K_2CO_3	CH_3CN	rt	12 h	20	—	6	20
6[b]	2	K_2CO_3	DMSO	rt	30 min	17	—	18	25
7[b]	3	K_2CO_3	DMSO	rt	24 h	—	—	12	—

[a] Isolated yields.
[b] The formation of carboxylic acid **22** was observed by TLC and crude ^1H NMR analyses.
[c] During chromatography and storage in a refrigerator, *exo*-**9a** was contaminated with **21**, generated by the [1,3]-shift of the sulfonyl group.



J=6.6 Hz), 2.27–2.19 (m, 2H), 1.57–1.36 (m, 6H); ^{13}C NMR δ 213.9, 167.1, 136.1, 128.4, 127.9, 127.7, 99.9, 79.1, 66.4, 62.6, 32.3, 27.8, 27.6, 25.1; MS m/z 260 (M^+, 3.6); HRMS calcd for $C_{16}H_{20}O_3$ 260.1413, found 260.1413.

4.3. General procedure for the ring-closing reaction of 1-(benzyloxycarbonyl)-1-(ω-hydroxyalkyl)allenes in the presence of *t*-BuOK in *t*-BuOH

t-BuOK (0.1 mmol) was added to a solution of allene **3a** (0.1 mmol) in *t*-BuOH (1 mL) at room temperature. After 5 min, the reaction was quenched by addition of 1% aqueous HCl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed on silica gel.

*4.3.1. Benzyl 2-methyl-4,5-dihydrofuran-3-carboxylate (**4a**)*

A pale yellow oil: IR 1687, 1647 cm^{-1}; ^{1}H NMR δ 7.37–7.25 (m, 5H), 5.18 (s, 2H), 4.40 (t, 2H, J=9.4 Hz), 2.91 (tq, 2H, J=9.4, 1.5 Hz), 2.18 (t, 3H, J=1.5 Hz); ^{13}C NMR δ 169.2, 165.9, 136.7, 128.4, 127.8, 127.8, 101.9, 65.2, 65.1, 29.6, 14.1; MS m/z 218 (M^+, 89.9); HRMS calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0940.

*4.3.2. (E)-2-[1-(Benzyloxy)ethylidene]-4-butanolide (**5a**)*

A colorless oil: IR 1730, 1658 cm^{-1}; ^{1}H NMR δ 7.37–7.25 (m, 5H), 5.10 (s, 2H), 4.25 (t, 2H, J=7.5 Hz), 2.93 (tq, 2H, J=7.5, 1.9 Hz), 2.48 (t, 3H, J=1.9 Hz); ^{13}C NMR δ 172.6, 164.9, 140.8, 128.4, 127.5, 126.9, 101.1, 68.8, 65.1, 25.7, 12.9; MS m/z 218 (M^+, 69.7); HRMS calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0941.

*4.3.3. (E)-2-[1-(Benzyloxy)ethylidene]-5-pentanolide (**5b**)*

A pale yellow oil: IR 1685, 1598 cm^{-1}; ^{1}H NMR δ 7.39–7.27 (m, 5H), 5.08 (s, 2H), 4.18 (t, 2H, J=5.1 Hz), 2.55 (t, 2H, J=6.7 Hz), 2.52 (s, 3H), 1.85–1.80 (m, 2H); ^{13}C NMR δ 168.2, 167.3, 140.8, 128.6, 128.4, 126.9, 103.9, 69.1, 67.9, 29.6, 22.6, 15.5; MS m/z 232 (M^+, 2.9); HRMS calcd for $C_{14}H_{16}O_3$ 232.1100, found 232.1098.

*4.3.4. Benzyl 2-methyl-4,5,6,7-tetrahydrooxepin-3-carboxylate (**4c**)*

A colorless oil: IR 1695, 1608 cm^{-1}; ^{1}H NMR δ 7.37–7.30 (m, 5H), 5.15 (s, 2H), 4.11 (t, 2H, J=5.9 Hz), 2.59–2.54 (m, 2H), 2.13 (t, 3H, J=1.1 Hz), 1.89–1.69 (m, 4H); ^{13}C NMR δ 170.5, 169.6, 136.5, 128.5, 128.0, 127.9, 111.6, 71.7, 65.9, 29.3, 26.6, 24.0, 21.7; MS m/z 246 (M^+, 74.5); HRMS calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1253.

*4.3.5. Benzyl 8-methyl-3,4,5,6-tetrahydro-2H-oxocin-7-carboxylate (**4d**)*

A colorless oil: IR 1701, 1633 cm^{-1}; ^{1}H NMR δ 7.36–7.30 (m, 5H), 5.18 (s, 2H), 3.96 (t, 2H, J=5.4 Hz), 2.51–2.49 (m, 2H), 2.18 (t, 3H, J=1.2 Hz), 1.63–1.59 (m, 6H); ^{13}C NMR δ 168.5, 164.2, 136.4, 128.4, 127.8, 127.7, 120.7, 71.7, 65.7, 29.5, 28.4, 27.2, 25.5, 17.3; MS m/z 260 (M^+, 10.5). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.58; H, 7.91.

4.4. Typical procedure for preparation of benzyl ω-hydroxy-2-methylenealkanoates

To a solution of 5-hexen-1-ol (1.50 g, 15.0 mmol) in CH_2Cl_2 (30 mL) were added 3,4-dihydro-2*H*-pyran (2.04 mL, 22.4 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (377 mg, 1.50 mmol) at room temperature. After the mixture was stirred for 2 h at that temperature, the reaction was quenched by addition of water, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (10:1) to afford the crude THP ether (2.73 g) as a colorless oil.

According to Hon's procedure,[21] the THP ether was converted into the enal. A solution of the crude THP ether (200 mg, 1.09 mmol) in CH_2Cl_2 (5.5 mL) was cooled to −78 °C, and ozone was bubbled through the solution until the solution turned blue. Nitrogen was then bubbled through the solution until the reaction mixture turned colorless. To a solution of the ozonide in CH_2Cl_2 at −78 °C were added the mixture of Et_2NH (1.68 mL, 16.3 mmol) and CH_2Br_2 (0.38 mL, 5.5 mmol) preheated at 55 °C for 1.5 h. After the mixture was stirred for 1.5 h at room temperature, the reaction mixture was concentrated. Et_2O was added and the resulting suspension was filtered. The filtrate was concentrated and passed through a short pad of silica gel with hexane–AcOEt (25:1) to afford 5-(tetrahydropyranyloxy)-2-methylenepentanal (112 mg, 56% for two steps) as a colorless oil. IR 1689 cm^{-1}; ^{1}H NMR δ 9.50 (s, 1H), 6.24 (s, 1H), 5.98 (s, 1H), 4.52 (t, 1H, J=3.6 Hz), 3.82–3.67 (m, 2H), 3.49–3.30 (m, 2H), 2.30 (t, 2H, J=7.8 Hz), 1.82–1.47 (m, 8H); ^{13}C NMR δ 194.5, 149.7, 134.1, 98.8, 66.6, 62.2, 30.6, 27.6, 25.3, 24.5, 19.5; MS m/z 198 (M^+, 1.7); HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1250.

To a solution of the aldehyde (400 mg, 2.01 mmol) in *t*-BuOH (10 mL) was added 2-methyl-2-butene (0.64 mL, 6.0 mmol) at room temperature. After the mixture was stirred at that temperature for 5 min, $NaClO_2$ (417 mg, 4.62 mmol) and $NaH_2PO_4\cdot 2H_2O$ (627 mg, 4.02 mmol) in water (3.5 mL) were added at room temperature. After the mixture was stirred for 3 h at that temperature, the reaction mixture was concentrated. After the residue was extracted with hexane, the aqueous layer was acidified to pH 3 with 2 N HCl, and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (1:1) to afford the crude carboxylic acid (465 mg) as a pale yellow oil.

To a solution of the carboxylic acid (200 mg, 0.929 mmol) in CH_2Cl_2 (3 mL) were added Et_3N (0.14 mL, 1.0 mmol) and benzyl chloroformate (0.13 mL, 0.93 mmol) at room temperature. After the mixture was stirred at that temperature for 5 min, DMAP (12.2 mg, 0.100 mmol) was added at 0 °C. After the mixture was stirred for 1.5 h at that temperature, the reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (8:1) to afford the crude ester (142 mg) as a colorless oil.

To a solution of the ester (170 mg, 0.550 mmol) in MeOH (5.5 mL) was added PPTS (28.0 mg, 0.110 mmol) at room temperature. After the mixture was stirred at that temperature for 24 h, the reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (2:1) afforded **10b** (103 mg, 40%, for three steps) as a colorless oil.

*4.4.1. Benzyl 5-hydroxy-2-methylenepentanoate (**10b**)*

IR 3625, 3490, 1712, 1629 cm^{-1}; ^{1}H NMR δ 7.37–7.32 (m, 5H), 6.23 (d, 1H, J=1.2 Hz), 5.62 (d, 1H, J=1.2 Hz), 5.20 (s, 2H), 3.64 (t, 2H, J=6.3 Hz), 2.43 (t, 2H, J=7.6 Hz), 1.78–1.72 (m, 2H); ^{13}C NMR δ 167.1, 139.9, 135.9, 128.5, 128.1, 128.0, 125.7, 66.5, 61.7, 31.6, 27.9; MS m/z 220 (M^+, 1.7); HRMS calcd for $C_{13}H_{16}O_3$ 220.1100, found 220.1100.

*4.4.2. Benzyl 4-hydroxy-2-methylenebutanoate (**10a**)*

A colorless oil: IR 3608, 3461, 1712, 1629 cm^{-1}; ^{1}H NMR δ 7.34–7.29 (m, 5H), 6.27 (d, 1H, J=1.3 Hz), 5.67 (d, 1H, J=1.3 Hz), 5.18 (s, 2H), 3.73 (t, 2H, J=6.0 Hz), 2.57 (t, 2H, J=6.0 Hz); ^{13}C NMR δ 167.0, 137.2, 135.7, 128.5, 128.1, 128.0, 127.5, 66.6, 61.4, 35.4; MS m/z 206 (M^+, 13.7); HRMS calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0942.

*4.4.3. Benzyl 6-hydroxy-2-methylenehexanoate (**10c**)*

A colorless oil: IR 3620, 3473, 1712, 1629 cm^{-1}; ^{1}H NMR δ 7.36–7.28 (m, 5H), 6.18 (d, 1H, J=1.3 Hz), 5.55 (d, 1H, J=1.3 Hz), 5.17 (s, 2H), 3.62 (t, 2H, J=5.9 Hz), 2.33 (t, 2H, J=6.6 Hz), 1.56–1.45 (m, 4H);

^{13}C NMR δ 167.0, 140.3, 136.0, 128.4, 128.1, 127.9, 125.1, 66.3, 62.5, 32.1, 31.4, 24.5; MS *m*/*z* 234 (M^+, 2.0); HRMS calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1259.

*4.4.4. Benzyl 7-hydroxy-2-methyleneheptanoate (**10d**)*

A colorless oil: IR 3620, 3446, 1712, 1629 cm^{-1}; ^{1}H NMR δ 7.35–7.29 (m, 5H), 6.17 (d, 1H, *J*=1.5 Hz), 5.53 (d, 1H, *J*=1.5 Hz), 5.17 (s, 2H), 3.59 (t, 2H, *J*=6.6 Hz), 2.31 (t, 2H, *J*=7.3 Hz), 1.61–1.32 (m, 6H); ^{13}C NMR δ 167.0, 140.4, 136.0, 128.4, 128.0, 127.9, 125.0, 66.3, 62.6, 32.4, 31.7, 28.1, 25.2; MS *m*/*z* 248 (M^+, 2.4); HRMS calcd for $C_{15}H_{20}O_3$ 248.1413, found 248.1410.

4.5. Ring-closing reaction of benzyl ω-hydroxy-2-methylenealkanoates

According to the procedure described for ring-closing reaction of 1-(benzyloxycarbonyl)-1-(ω-hydroxyalkyl)allenes, benzyl ω-hydroxy-2-methylenealkanoates were exposed to the standard ring-closing conditions (0.025 M solution was used).

*4.5.1. 2-(Benzyloxymethyl)-4-butanolide (**11a**)*[22]

A colorless oil: ^{1}H NMR δ 7.25–7.13 (m, 5H), 4.56 (s, 2H), 4.23 (t, 2H, *J*=7.3 Hz), 3.56–3.52 (m, 2H), 2.74–2.71 (m, 1H), 2.36 (t, 2H, *J*=7.3 Hz); ^{13}C NMR δ 177.7, 137.3, 129.2, 128.5, 127.7, 74.6, 71.7, 69.1, 45.1, 24.3.

*4.5.2. 2-Methylene-5-pentanolide (**12b′**)*[23]

A colorless oil: ^{1}H NMR δ 6.42 (d, 1H, *J*=1.6 Hz), 5.56 (d, 1H, *J*=1.6 Hz), 4.37 (t, 2H, *J*=5.3 Hz), 2.68 (tt, 2H, *J*=6.3, 1.6 Hz), 1.99–1.90 (m, 2H); ^{13}C NMR δ 167.2, 131.9, 127.1, 63.6, 25.4, 22.5.

*4.5.3. 2-Methylene-6-hexanolide (**12c′**)*[23]

A colorless oil: ^{1}H NMR δ 5.78 (s, 1H), 5.39 (s, 1H), 4.15 (t, 2H, *J*=4.3 Hz), 2.36 (t, 2H, *J*=7.4 Hz), 1.92–1.78 (m, 4H); ^{13}C NMR δ 170.7, 142.1, 122.0, 66.7, 29.4, 26.9, 26.7.

4.6. General procedure for the ring-closing reaction in the presence of aldehyde

To a solution of allene (0.1 mmol) and aldehyde (0.15 mmol) in solvent (1 mL) was added base (0.1 or 0.15 mmol) at room temperature. The reaction mixture was stirred at that temperature until the complete disappearance of the starting material as indicated by TLC. The reaction was quenched by addition of 1% aqueous HCl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed on silica gel.

*4.6.1. Benzyl 2-(2-hydroxy-2-phenylethyl)-4,5-dihydrofuran-3-carboxylate (**14γa**)*

A colorless oil: IR 3597, 3423, 1686, 1637 cm^{-1}; ^{1}H NMR δ 7.37–7.28 (m, 10H), 5.18 (s, 2H), 4.98 (dd, 1H, *J*=9.3, 3.4 Hz), 4.44 (t, 2H, *J*=9.8 Hz), 3.23 (br s, 1H), 3.13 (dd, 1H, *J*=14.1, 9.3 Hz), 2.99 (dd, 1H, *J*=14.1, 3.4 Hz), 2.94 (t, 2H, *J*=9.8 Hz); ^{13}C NMR δ 169.2, 166.4, 143.7, 136.3, 128.6, 128.4, 128.1, 128.1, 127.5, 125.5, 104.0, 72.5, 70.9, 65.8, 38.1, 29.6; MS *m*/*z* 324 (M^+, 1.5); HRMS calcd for $C_{20}H_{20}O_4$ 324.1362, found 324.1363.

*4.6.2. Benzyl 2-[2-hydroxy-2-(3-nitrophenyl)ethyl]-4,5-dihydrofuran-3-carboxylate (**14γb**)*

A colorless oil: IR 3549, 3387, 1691, 1637 cm^{-1}; ^{1}H NMR δ 8.26 (s, 1H), 8.12–8.11 (m, 1H), 7.65 (d, 1H, *J*=7.9 Hz), 7.47 (t, 1H *J*=7.9 Hz), 7.36–7.33 (m, 5H), 5.19 (s, 2H), 5.09 (t, 1H, *J*=6.1 Hz), 4.45–4.40 (m, 2H), 3.09 (d, 2H, *J*=6.1 Hz), 2.95 (t, 2H, *J*=9.2 Hz); ^{13}C NMR δ 168.3, 166.7, 148.4, 145.8, 136.1, 131.7, 129.3, 128.6, 128.3, 128.1, 122.5, 120.7, 104.7, 71.6, 71.1, 66.0, 37.8, 29.5; MS *m*/*z* 369 (M^+, 7.3); HRMS calcd for $C_{20}H_{19}O_6N$ 369.1212, found 369.1207.

*4.6.3. Benzyl 2-[2-hydroxy-2-(4-chlorophenyl)ethyl]-4,5-dihydrofuran-3-carboxylate (**14γc**)*

A pale yellow oil: IR 3599, 3408, 1690, 1637 cm^{-1}; ^{1}H NMR δ 7.37–7.25 (m, 9H), 5.18 (s, 2H), 4.95 (dd, 1H, *J*=9.2, 3.1 Hz), 4.43 (t, 2H, *J*=9.8 Hz), 3.06 (dd, 1H, *J*=14.1, 9.2 Hz), 2.98 (dd, 1H, *J*=14.1, 3.1 Hz), 2.94 (t, 2H, *J*=9.8 Hz); ^{13}C NMR δ 168.9, 166.5, 142.2, 136.2, 133.1, 128.6, 128.5, 127.6, 127.0, 126.9, 104.2, 71.8, 70.9, 65.9, 37.9, 29.5; MS *m*/*z* 358 (M^+, 2.4); HRMS calcd for $C_{20}H_{19}O_4Cl$ 358.0972, found 358.0962.

*4.6.4. Benzyl 2-(2-hydroxy-4-phenylbut-3-enyl)-4,5-dihydrofuran-3-carboxylate (**14γe**)*

A pale yellow oil: IR 3605, 3433, 1726, 1688, 1637 cm^{-1}; ^{1}H NMR δ 7.39–7.22 (m, 10H), 6.61 (d, 1H, *J*=15.9 Hz), 6.21 (dd, 1H, *J*=15.9, 6.1 Hz), 5.18 (s, 2H), 4.59–4.58 (m, 1H), 4.45 (t, 2H, *J*=9.8 Hz), 3.02 (dd, 1H, *J*=13.4, 7.9 Hz), 2.96 (dd, 1H, *J*=13.4, 4.8 Hz), 2.94 (t, 2H, *J*=9.8 Hz); ^{13}C NMR δ 169.2, 166.5, 140.9, 136.7, 131.3, 130.1, 128.6, 128.5, 127.7, 127.0, 126.5, 104.1, 70.9, 70.9, 65.4, 36.0, 29.6; MS *m*/*z* 350 (M^+, 24.1); HRMS calcd for $C_{22}H_{22}O_4$ 350.1518, found 350.1512.

*4.6.5. Benzyl 2-(2-hydroxyhexyl)-4,5-dihydrofuran-3-carboxylate (**14γf**)*

A pale yellow oil: IR 3600, 3439, 1686, 1637 cm^{-1}; ^{1}H NMR δ 7.37–7.29 (m, 5H), 5.17 (s, 2H), 4.45 (t, 2H, *J*=9.7 Hz), 3.88–3.83 (m, 1H), 2.94 (t, 2H, *J*=9.7 Hz), 2.84 (dd, 1H, *J*=14.1, 3.9 Hz), 2.79 (dd, 1H, *J*=14.1, 7.8 Hz), 1.47–1.25 (m, 6H), 0.94–0.88 (m, 3H); ^{13}C NMR δ 170.2, 166.4, 136.4, 128.5, 128.0, 127.0, 103.5, 70.8, 70.3, 65.4, 37.2, 35.6, 29.5, 27.6, 22.6, 14.0; MS *m*/*z* 304 (M^+, 3.7); HRMS calcd for $C_{18}H_{24}O_4$ 304.1675, found 304.1677.

*4.6.6. Benzyl 2-(2-hydroxy-4-methylpentyl)-4,5-dihydrofuran-3-carboxylate (**14γg**)*

A colorless oil: IR 3593, 3445, 1682, 1636 cm^{-1}; ^{1}H NMR δ 7.35–7.25 (m, 5H), 5.15 (s, 2H), 4.43 (t, 2H, *J*=9.7 Hz), 3.95–3.90 (m, 1H), 2.92 (t, 2H, *J*=9.7 Hz), 2.81 (dd, 1H, *J*=14.1, 3.6 Hz), 2.75 (dd, 1H, *J*=14.1, 7.8 Hz), 1.79–1.72 (m, 1H), 1.24–1.18 (m, 2H), 0.89 (d, 3H, *J*=6.6 Hz), 0.87 (d, 3H, *J*=6.6 Hz); ^{13}C NMR δ 170.1, 166.4, 136.4, 128.5, 128.0, 127.0, 103.6, 70.8, 68.4, 65.4, 46.6, 36.0, 29.5, 24.5, 23.2, 22.1; MS *m*/*z* 304 (M^+, 13.3); HRMS calcd for $C_{18}H_{24}O_4$ 304.1675, found 304.1668.

*4.6.7. Benzyl 2-(2-hydroxy-3,3-dimethylbutyl)-4,5-dihydrofuran-3-carboxylate (**14γh**)*

A colorless oil: IR 3566, 3431, 1680, 1636 cm^{-1}; ^{1}H NMR δ 7.36–7.33 (m, 5H), 5.17 (s, 2H), 4.46 (t, 2H, *J*=9.7 Hz), 3.48 (dd, 1H, *J*=10.0, 2.9 Hz), 2.95 (t, 2H, *J*=9.7 Hz), 2.81 (dd, 1H, *J*=13.9, 10.0 Hz), 2.72 (dd, 1H, *J*=13.9, 2.9 Hz), 0.90 (s, 9H); ^{13}C NMR δ 171.4, 166.7, 136.3, 128.5, 128.1, 128.1, 103.4, 78.0, 70.8, 65.7, 35.2, 30.9, 29.6, 25.4; MS *m*/*z* 304 (M^+, 3.1); HRMS calcd for $C_{18}H_{24}O_4$ 304.1675, found 304.1668.

*4.6.8. 1-Phenyl-2-(3-phenylsulfonyl-4,5-dihydrofuran-2yl)-ethanol (**16γa**)*

A pale yellow oil: IR 3597, 3504, 1632 cm^{-1}; ^{1}H NMR δ 7.82–7.79 (m, 2H), 7.61–7.27 (m, 8H), 5.06 (dd, 1H, *J*=9.0, 3.9 Hz), 4.43 (t, 2H, *J*=9.6 Hz), 3.25 (dd, 1H, *J*=14.2, 9.0 Hz), 3.06 (dd, 1H, *J*=14.2, 3.9 Hz), 2.86 (t, 2H, *J*=9.6 Hz); ^{13}C NMR δ 166.2, 143.3, 141.3, 132.9, 129.1, 128.5, 127.8, 126.9, 125.6, 110.8, 71.9, 70.3, 37.0, 30.2; MS *m*/*z* 330 (M^+, 9.2); HRMS calcd for $C_{18}H_{18}O_4S$ 330.0926, found 330.0936.

*4.6.9. 1-(4-Methoxyphenyl)-2-(3-phenylsulfonyl-4,5-dihydrofuran-2yl)ethanol (**16γd**)*

A pale yellow oil: IR 3599, 3508, 1632 cm^{-1}; ^{1}H NMR δ 7.77–7.74 (m, 2H), 7.58–7.44 (m, 3H), 7.32 (d, 2H, *J*=8.7 Hz), 6.87 (d, 2H,

J=8.7 Hz), 4.99 (dd, 1H, J=8.7, 4.3 Hz), 4.39 (t, 2H, J=9.6 Hz), 3.79 (s, 3H), 3.21 (dd, 1H, J=14.3, 8.7 Hz), 3.02 (dd, 1H, J=14.3, 4.3 Hz), 2.81 (t, 2H, J=9.6 Hz), 2.74 (br s, 1H); ^{13}C NMR δ 166.3, 159.2, 141.4, 135.5, 132.8, 129.1, 126.9, 126.9, 113.9, 110.7, 71.5, 70.2, 55.3, 37.0, 30.2; MS m/z 360 (M^+, 81.5); HRMS calcd for $C_{19}H_{20}O_5S$ 360.1031, found 360.1032.

4.6.10. 4-Phenyl-1-(3-phenylsulfonyl-4,5-dihydrofuran-2yl)but-3-en-2-ol (**16γe**)

A pale yellow oil: IR 3595, 3504, 1632 cm^{-1}; ^{1}H NMR δ 7.82–7.79 (m, 2H), 7.49–7.17 (m, 8H), 6.59 (d, 1H, J=15.8 Hz), 6.19 (dd, 1H, J=15.8, 6.1 Hz), 4.58–4.56 (m, 1H), 4.34 (t, 2H, J=9.6 Hz), 3.08 (dd, 1H, J=14.2, 7.9 Hz), 2.91 (dd, 1H, J=14.2, 4.6 Hz), 2.77 (t, 2H, J=9.6 Hz); ^{13}C NMR δ 166.0, 141.4, 136.5, 132.9, 130.8, 130.6, 129.1, 128.6, 127.8, 126.9, 126.6, 111.0, 70.3, 70.3, 35.1, 30.2; MS m/z 356 (M^+, 40.6); HRMS calcd for $C_{20}H_{20}O_4S$ 356.1082, found 356.1077.

4.6.11. 1-(3-Phenylsulfonyl-4,5-dihydrofuran-2yl)hexan-2-ol (**16γf**)

A pale yellow oil: IR 3566, 3529, 1632 cm^{-1}; ^{1}H NMR δ 7.91–7.86 (m, 2H), 7.61–7.52 (m, 3H), 4.43 (t, 2H, J=9.8 Hz), 3.91–3.88 (m, 1H), 2.93–2.82 (m, 4H), 1.59–1.26 (m, 6H), 0.92 (t, 3H, J=7.3 Hz); ^{13}C NMR δ 167.2, 141.6, 132.9, 129.2, 126.9, 110.5, 70.2, 69.7, 37.4, 35.0, 30.2, 27.7, 22.6, 14.0; MS m/z 310 (M^+, 7.4); HRMS calcd for $C_{16}H_{22}O_4S$ 310.1239, found 310.1245.

4.7. Preparation of 1-phenyl-4-(phenylsulfonyl)hexa-2,3-diene-1,6-diol (18)

To a solution of 5-(*tert*-butyldimethylsiloxy)-3-(phenylsulfonyl)penta-1,2-diene[2a] (97.4 mg, 0.28 mmol) and benzaldehyde (**13a**) (0.03 mL, 0.3 mmol) in DMSO (1.5 mL) was added DBU (0.04 mL, 0.3 mmol) at room temperature. After the mixture was stirred for 5 min at that temperature, the reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (4:1) to afford the crude alcohol. To a solution of the alcohol in MeOH (2 mL) was added $TsOH\cdot H_2O$ (4.2 mg, 0.02 mmol) at room temperature. After stirring for 12 h, the reaction was quenched by addition of saturated aqueous $NaHCO_3$, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:1) afforded **18** (14.3 mg, 15% for two steps) as a 1:1 mixture of diastereoisomers as a colorless oil. IR 3416, 1963 cm^{-1}; ^{1}H NMR δ 7.94–7.91 (m, 2H), 7.65–7.60 (m, 1H), 7.55–7.50 (m, 2H), 7.45–7.44 (m, 1H), 7.40–7.30 (m, 4H), 6.07 (dt, 50/100×1H, J=4.4, 2.4 Hz), 6.02 (dt, 50/100×1H, J=4.4, 2.7 Hz), 5.41 (d, 50/100×1H, J=4.4 Hz), 5.35 (d, 50/100×1H, J=4.4 Hz), 3.75–3.67 (m, 2H), 3.32 (br s, 50/100×1H), 3.11 (br s, 50/100×1H), 2.57–2.53 (m, 3H); ^{13}C NMR δ 202.9, 202.8, 141.4, 140.6, 139.6, 139.5, 133.7, 133.6, 129.1, 129.1, 128.8, 128.8, 128.6, 128.3, 128.2, 127.0, 126.1, 113.7, 113.3, 105.7, 105.4, 71.3, 71.0, 59.8, 59.8, 30.9, 30.8; MS m/z 330 (M^+, 1.8); HRMS calcd for $C_{18}H_{18}O_4S$ 330.0926, found 330.0929.

4.8. Reaction of 18 with DBU

To a solution of allene **18** (37.1 mg, 0.112 mmol) in DMSO (1 mL) was added DBU (0.02 mL, 0.13 mmol) at room temperature, and the mixture was stirred for 30 min. The reaction was quenched by addition of 1% aqueous HCl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (2:1) afforded **16γa** (25.6 mg, 69%).

4.9. General procedure for preparation of allenoic acids 8

To a solution of allenyl alcohol **15** in acetone (0.1 M) at 0 °C was added Jones reagent (2.5 equiv), prepared from CrO_3 (300 mg, 3.0 mmol), concd. H_2SO_4 (0.26 mL, 4.8 mmol), and water (1.2 mL, 2.5 M). After stirring for 1 h, the reaction was quenched by addition of *i*-PrOH, and the mixture was filtered and concentrated. The residue was dissolved in AcOEt and extracted with saturated aqueous $NaHCO_3$. The aqueous phase was acidified by addition of 10% aqueous HCl, and the solution was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:1) afforded allenoic acid **8**.

4.9.1. 4-(Phenylsulfonyl)hexa-4,5-dienoic acid (**8a**)

White needles: mp 107–108 °C (hexane–AcOEt); IR 3030, 1971, 1940, 1717 cm^{-1}; ^{1}H NMR δ 7.91–7.90 (m, 2H), 7.66–7.54 (m, 3H), 5.43 (t, 2H, J=3.3 Hz), 2.57–2.54 (m, 4H); ^{13}C NMR δ 207.2, 177.7, 139.5, 133.6, 129.1, 127.9, 111.7, 85.3, 31.5, 21.7; MS m/z 252 (M^+, 14.8); HRMS calcd for $C_{12}H_{12}O_4S$ 252.0456, found 252.0458.

4.9.2. 5-(Phenylsulfonyl)hepta-5,6-dienoic acid (**8b**)

White solids: mp 132–134 °C (hexane–AcOEt); IR 3026, 1969, 1942, 1713 cm^{-1}; ^{1}H NMR δ 7.90–7.88 (m, 2H), 7.65–7.62 (m, 1H), 7.56–7.53 (m, 2H), 5.40 (t, 2H, J=3.6 Hz), 2.35 (t, 2H, J=7.3 Hz), 2.32 (tt, 2H, J=7.3, 3.7 Hz), 1.79 (quin, 2H, J=7.3 Hz); ^{13}C NMR δ 207.6, 178.6, 139.8, 133.6, 129.1, 128.1, 112.5, 84.8, 32.7, 25.9, 22.4; MS m/z 266 (M^+, 4.1); HRMS calcd for $C_{13}H_{14}O_4S$ 266.0613, found 266.0616.

4.9.3. 6-(Phenylsulfonyl)octa-6,7-dienoic acid (**8c**)

Title compound was prepared by the following method. To a solution of methyl 8-hydroxyoct-6-ynoate[24] (146 mg, 0.86 mmol) and Et_3N (0.50 mL, 3.5 mmol) in THF (9 mL) was added PhSCl (0.38 mL, 3.4 mmol) dropwise at −78 °C, and the mixture was stirred for 2 h at the same temperature. The reaction was quenched by addition of saturated aqueous $NaHCO_3$, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (2:1) to afford the crude sulfoxide (213 mg). To a solution of the crude sulfoxide in CH_2Cl_2 (9 mL) was added *m*CPBA (160 mg, 0.9 mmol) at 0 °C, and the mixture was stirred for 1 h at the same temperature. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was exposed to Ma's hydrolysis condition.[25] The residue was dissolved in the mixed solvent (14 mL) of 10% aqueous HCl (7 mL), 1,4-dioxane (6 mL), and THF (1 mL), and the solution was stirred for 1 day. The reaction mixture was extracted with Et_2O, and the extract was washed with brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (3:2) afforded **8c** (200 mg, 83% for three steps) as white solids. Mp 83–84 °C (CH_2Cl_2–Et_2O); IR 3026, 1971, 1940, 1709 cm^{-1}; ^{1}H NMR δ 7.89–7.86 (m, 2H), 7.65–7.50 (m, 3H), 5.36 (t, 2H, J=3.4 Hz), 2.32–2.21 (m, 4H), 1.65–1.42 (m, 4H); ^{13}C NMR δ 207.5, 179.4, 139.9, 133.5, 129.0, 128.0, 112.8, 84.6, 33.4, 26.6, 26.2, 23.6; MS m/z 280 (M^+, 4.2); HRMS calcd for $C_{14}H_{16}O_4S$ 280.0769, found 280.0766.

4.10. Typical procedure for the ring-closing reaction of allenoic acid 8

To a solution of carboxylic acid **8a** (26.4 mg, 0.105 mmol) in DMSO (1 mL) was added K_2CO_3 (7.2 mg, 0.052 mmol) at room temperature, and the mixture was stirred for 5 min. The reaction

was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:1) afforded *exo*-**9a** (15.2 mg, 58%) and *endo*-**9a** (5.2 mg, 20%).

*4.10.1. 5-Methylene-4-(phenylsulfonyl)-5-pentanolide (exo-**9a**)*

A colorless oil: IR 1767, 1655 cm^{-1}; ^1H NMR δ 7.92–7.90 (m, 2H), 7.72–7.57 (m, 3H), 4.92 (d, 1H, J=2.1 Hz), 4.17 (d, 1H, J=2.1 Hz), 3.99 (dd, 1H, J=6.6, 3.9 Hz), 3.07–2.99 (m, 1H), 2.67–2.59 (m, 2H), 2.38–2.28 (m, 1H); ^{13}C NMR δ 166.1, 147.5, 135.8, 134.5, 129.4, 129.2, 102.8, 61.4, 26.8, 18.5; MS m/z 252 (M^+, 1.2); HRMS calcd for $C_{12}H_{12}O_4S$ 252.0456, found 252.0454.

*4.10.2. 5-Methyl-4-(phenylsulfonyl)-4-penten-5-olide (endo-**9a**)*

White needles: mp 89.5–91 °C (hexane); IR 1786, 1711, 1653 cm^{-1}; ^1H NMR δ 7.88–7.86 (m, 2H), 7.67–7.64 (m, 1H), 7.59–7.56 (m, 2H), 2.68–2.61 (m, 4H), 2.45 (s, 3H); ^{13}C NMR δ 165.4, 159.5, 140.9, 133.7, 129.5, 127.0, 116.9, 28.0, 21.0, 17.9; MS m/z 252 (M^+, 93.8); HRMS calcd for $C_{12}H_{12}O_4S$ 252.0456, found 252.0451.

*4.10.3. 5-Oxo-4-(phenylsulfonyl)hexanoic acid (**22a**)*

White solids: mp 145–147 °C (hexane–AcOEt); IR 3028, 2927, 1720 cm^{-1}; ^1H NMR δ 7.81–7.79 (m, 2H), 7.72–7.69 (m, 1H), 7.60–7.57 (m, 2H), 4.33 (dd, 1H, J=9.5, 4.6 Hz), 2.47–2.41 (m, 4H), 2.34–2.28 (m, 1H), 2.22–2.10 (m, 2H); ^{13}C NMR δ 199.7, 176.1, 136.1, 134.5, 129.3, 129.2, 74.1, 32.0, 30.3, 21.9; FABMS m/z 293 (M^++23, 22.0); FABHRMS calcd for $C_{12}H_{15}O_5S$ 271.0640, found 271.0641.

*4.10.4. 6-Methylene-5-(phenylsulfonyl)-6-hexanolide (exo-**9b**)*

White solids: mp 124.5–126 °C (hexane–AcOEt); IR 1767, 1651 cm^{-1}; ^1H NMR δ 7.90–7.88 (m, 2H), 7.70–7.67 (m, 1H), 7.59–7.55 (m, 2H), 5.17–5.16 (m, 2H), 3.88 (dd, 1H, J=10.3, 4.4 Hz), 2.78–2.72 (m, 1H), 2.58–2.53 (m, 1H), 2.40–2.35 (m, 1H), 2.17–2.04 (m, 2H), 1.84–1.75 (m, 1H); ^{13}C NMR δ 170.1, 148.9, 136.3, 134.3, 129.4, 129.2, 110.0, 66.8, 30.8, 25.0, 19.3; MS m/z 266 (M^+, 30.1); HRMS calcd for $C_{13}H_{14}O_4S$ 266.0613, found 266.0612.

*4.10.5. 2-(Phenylsulfonyl)cyclopentanone (**19b**)*[19]

White solids: mp 115.5–116.5 °C (hexane–AcOEt); IR 1749 cm^{-1}; ^1H NMR δ 7.90–7.88 (m, 2H), 7.70–7.67 (m, 1H), 7.60–7.57 (m, 2H), 3.75 (dd, 1H, J=8.5, 7.3 Hz), 2.72–2.65 (m, 1H), 2.46–2.37 (m, 2H), 2.33–2.17 (m, 2H), 1.94–1.86 (m, 1H); ^{13}C NMR δ 207.1, 138.1, 134.1, 129.1, 129.0, 69.4, 38.7, 24.9, 20.1.

*4.10.6. 2-Acetyl-2-(phenylsulfonyl)cyclopentanone (**20b**)*

A colorless oil: IR 1751, 1713 cm^{-1}; ^1H NMR δ 7.81–7.80 (m, 2H), 7.71–7.68 (m, 1H), 7.58–7.55 (m, 2H), 2.73–2.67 (m, 1H), 2.60–2.54 (m, 1H), 2.49 (s, 3H), 2.46–2.39 (m, 2H), 2.04–1.97 (m, 1H), 1.75–1.68 (m, 1H); ^{13}C NMR δ 204.6, 195.6, 136.3, 134.7, 130.1, 129.1, 86.8, 39.5, 30.3, 28.6, 18.9; MS m/z 266 (M^+, 5.1); HRMS calcd for $C_{13}H_{14}O_4S$ 266.0613, found 266.0610.

*4.10.7. 6-Oxo-5-(phenylsulfonyl)heptanoic acid (**22b**)*

A colorless oil: IR 3020, 2930, 1718 cm^{-1}; ^1H NMR δ 7.81–7.77 (m, 2H), 7.73–7.67 (m, 1H), 7.61–7.54 (m, 2H), 4.08 (dd, 1H, J=7.3, 6.9 Hz), 2.43 (s, 3H), 2.33 (t, 2H, J=7.3 Hz), 2.00–1.91 (m, 2H), 1.66–1.50 (m, 2H); ^{13}C NMR δ 200.0, 177.4, 136.3, 134.5, 129.2, 75.6, 33.0, 31.5, 26.1, 21.8; FABMS m/z 307 (M^++23, 17.9); FABHRMS calcd for $C_{13}H_{17}O_5S$ 285.0797, found 285.0796.

*4.10.8. 2-(Phenylsulfonyl)cyclohexanone (**19c**)*

White solids: mp 85–86 °C (hexane–AcOEt) [lit.[26a] mp 65.7–66.6 °C (hexane–AcOEt); lit.[26b] mp 87 °C (CCl_4)]; IR 1709 cm^{-1}; ^1H NMR δ 7.91–7.88 (m, 2H), 7.70–7.63 (m, 1H), 7.59–7.53 (m, 2H), 3.84 (dt, 1H, J=5.4, 1.1 Hz), 2.87–2.76 (m, 1H), 2.60–2.40 (m, 2H), 2.29–2.17 (m, 2H), 2.08–1.95 (m, 1H), 1.90–1.69 (m, 2H); ^{13}C NMR δ 202.2, 138.1, 134.0, 129.0, 128.9, 72.7, 41.6, 27.4, 26.4, 21.2.

*4.10.9. 7-Oxo-6-(phenylsulfonyl)octanoic acid (**22c**)*

A colorless oil: IR 3029, 2932, 1718 cm^{-1}; ^1H NMR δ 7.80–7.78 (m, 2H), 7.71–7.68 (m, 1H), 7.59–7.55 (m, 2H), 4.08 (dd, 1H, J=7.6, 7.1 Hz), 2.41 (s, 3H), 2.34–2.27 (m, 2H), 1.94–1.89 (m, 2H), 1.66–1.51 (m, 2H), 1.33–1.26 (m, 2H); ^{13}C NMR δ 200.1, 177.3, 136.4, 134.4, 129.2, 129.1, 75.6, 33.0, 31.7, 26.5, 26.2, 24.1; FABMS m/z 321 (M^++23, 1.1); FABHRMS calcd for $C_{14}H_{19}O_5S$ 299.0953, found 299.0959.

*4.10.10. 5-(Phenylsulfonyl)methyl-4-penten-5-olide (**21**)*

White solids: mp 95–96.5 °C (hexane–AcOEt); IR 1771 cm^{-1}; ^1H NMR δ 7.91–7.90 (m, 2H), 7.69–7.66 (m, 1H), 7.59–7.56 (m, 2H), 5.46 (t, 1H, J=4.3 Hz), 3.92 (s, 2H), 2.50 (t, 2H, J=7.3 Hz), 2.38–2.34 (m, 2H); ^{13}C NMR δ 166.9, 142.4, 138.5, 134.2, 129.2, 128.4, 108.9, 60.0, 27.6, 19.1; MS m/z 252 (M^+, 17.2); HRMS calcd for $C_{12}H_{12}O_4S$ 252.0456, found 252.0459.

This compound was hydrogenated by $Et_3SiH/BF_3\cdot OEt_2$[27] and correlated with 5-(phenylsulfonyl)methyl-5-pentanolide, which was prepared by the following method.

To a solution of methyl phenyl sulfone (97.9 mg, 0.628 mmol) in THF (6 mL) was added *n*-BuLi in hexane (1.48 M, 0.42 mL, 0.62 mmol) at −78 °C, and the mixture was stirred at 0 °C for 0.5 h. After cooling to −78 °C, a solution of mono-methyl glutarate (29.6 mg, 0.203 mmol) in THF (2 mL) was added to the mixture, which was stirred for 1 h at −40 °C. The reaction was quenched by addition of water, and the mixture was extracted with saturated aqueous $NaHCO_3$. The aqueous phase was acidified with 10% aqueous HCl and extracted with AcOEt. The extract was washed with brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (2:3) to afford 6-(phenylsulfonyl)-5-oxohexanoic acid (46.0 mg) as white solids. To a solution of the acid (11.1 mg, 0.041 mmol) and Et_3N (0.04 mL, 0.3 mmol) in CH_2Cl_2 (1 mL) was added MsCl (0.01 mL, 0.1 mmol) at 0 °C, and the mixture was stirred for 30 min at that temperature. The reaction was quenched by addition of 1% aqueous HCl, and the mixture was extracted with CH_2Cl_2. The extract was washed with saturated aqueous $NaHCO_3$ and brine, dried, and concentrated to dryness. The residue was dissolved in CH_2Cl_2 (1 mL), and Et_3SiH (0.01 mL, 0.06 mmol) and $BF_3\cdot OEt_2$ (0.01 mL, 0.08 mmol) were added to the solution at 0 °C. After stirring for 8 h at room temperature, the reaction was quenched by addition of water, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:1) afforded 5-(phenylsulfonyl)methyl-5-pentanolide (4.0 mg, 32% for three steps) as white solids. Mp 105.5–106.5 °C (hexane–AcOEt); IR 1742 cm^{-1}; ^1H NMR δ 7.96–7.94 (m, 2H), 7.71–7.68 (m, 1H), 7.61–7.58 (m, 2H), 4.85–4.80 (m, 1H), 3.56 (dd, 1H, J=14.4, 5.6 Hz), 3.34 (dd, 1H, J=14.3, 6.6 Hz), 2.59 (dt, 1H, J=17.7, 6.5 Hz), 2.44 (ddd, 1H, J=17.7, 8.1, 7.8 Hz), 2.27–2.22 (m, 1H), 1.98–1.89 (m, 2H), 1.74–1.66 (m, 1H); ^{13}C NMR δ 169.6, 139.5, 134.2, 129.4, 128.1, 74.2, 61.0, 29.2, 27.9, 18.2; MS m/z 254 (M^+, 3.6); HRMS calcd for $C_{12}H_{14}O_4S$ 254.0613, found 254.0610.

References and notes

1. Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95–102.
2. (a) Mukai, C.; Yamashita, H.; Hanaoka, M. *Org. Lett.* **2001**, *3*, 3385–3387; (b) Mukai, C.; Ohta, M.; Yamashita, H.; Kitagaki, S. *J. Org. Chem.* **2004**, *69*, 6867–6873; (c) Miyakoshi, N.; Ohgaki, Y.; Masui, K.; Mukai, C. *Heterocycles* **2007**, *74*, 185–189.
3. For another example, see: Pravia, K.; White, R.; Fodda, R.; Maynard, D. F. *J. Org. Chem.* **1996**, *61*, 6031–6032.
4. For *exo*-mode ring-closing reaction of allenyl sulfoxide derivatives, see: (a) Pairaudeau, G.; Parsons, P. J.; Underwood, J. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1718–1720; (b) Gray, M.; Parsons, P. J.; Neary, A. P. *Synlett* **1992**, 597–598; For *exo*-mode ring-closing reaction of allenyl sulfone derivatives, see: (c) Dai,

W.-M.; Lee, M. Y. H. *Tetrahedron* **1998**, *54*, 12497–12512; For *exo*-mode ring-closing reaction of allenylphosphonate derivatives, see: (d) Brel, V. K. *Synthesis* **2001**, 1539–1545.
5. (a) Mukai, C.; Ukon, R.; Kuroda, N. *Tetrahedron Lett.* **2003**, *44*, 1583–1586; (b) Mukai, C.; Kuroda, N.; Ukon, R.; Itoh, R. *J. Org. Chem.* **2005**, *70*, 6282–6290.
6. Mukai, C.; Kobayashi, M.; Kubota, S.; Takahashi, Y.; Kitagaki, S. *J. Org. Chem.* **2004**, *69*, 2128–2136.
7. Kitagaki, S.; Shibata, D.; Mukai, C. *Tetrahedron Lett.* **2007**, *48*, 1735–1738.
8. For other examples of *endo*-mode ring-closing reaction of allenyl ester derivatives, see: (a) Nagao, Y.; Kim, K.; Sano, S.; Kakegawa, H.; Lee, W. S.; Shimizu, H.; Shiro, M.; Katunuma, N. *Tetrahedron Lett.* **1996**, *37*, 861–864; (b) Evans, C. A.; Cowen, B. J.; Miller, S. J. *Tetrahedron* **2005**, *61*, 6309–6314.
9. For our other studies on the *endo*-mode ring-closing reaction of allenic compounds, see: (a) Mukai, C.; Takahashi, Y. *Org. Lett.* **2005**, *7*, 5793–5796; (b) Kuroda, N.; Takahashi, Y.; Yoshinaga, K.; Mukai, C. *Org. Lett.* **2006**, *8*, 1843–1845.
10. Pettigrew, J. D.; Wilson, P. D. *J. Org. Chem.* **2006**, *71*, 1620–1625.
11. (a) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736; (b) Baldwin, J. E.; Cutting, J.; Dupont, W.; Kruse, L.; Silberman, L.; Thomas, R. C. *J. Chem. Soc., Chem. Commun.* **1976**, 736–738.
12. Raulins, N. R.; Berdahl, D. R.; Bury, T. G. *J. Org. Chem.* **1980**, *45*, 920–922.
13. Chan, Y.-Y.; Li, X.; Zhu, C.; Liu, X.; Zhang, Y.; Leung, H.-K. *J. Org. Chem.* **1990**, *55*, 5497–5504.
14. Kitagaki, S.; Teramoto, S.; Mukai, C. *Org. Lett.* **2007**, *9*, 2549–2552.
15. Yoshimoto and Kishida reported that the treatment of 2-butynyl phenyl sulfone and substituted benzaldehyde with NaH afforded many products derived from γ-adduct (based on the condensation of allenyl anion with aldehyde). See: (a) Yoshimoto, M.; Kishida, Y. *Chem. Pharm. Bull.* **1970**, *18*, 2518–2527; (b) Yoshimoto, M.; Kishida, Y. *Chem. Pharm. Bull.* **1970**, *18*, 2528–2534.
16. Hammond and co-worker reported that propargyl or allenyl esters reacted with aldehydes in the presence of 2 equiv of TBAF to produce γ-adduct. See: Xu, B.; Hammond, G. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 689–692.
17. For condensation of allenyl esters or allenyl ketones with aldehydes or imines based on Baylis–Hillman reaction, see: (a) Zhao, G.-L.; Huang, J.-W.; Shi, M. *Org. Lett.* **2003**, *5*, 4737–4739; (b) Zhao, G.-L.; Shi, M. *Org. Biomol. Chem.* **2005**, *3*, 3686–3694.
18. For examples, see: (a) Ogura, K.; Iihama, T.; Kiuchi, S.; Kajiki, T.; Koshikawa, O.; Takahashi, K.; Iida, H. *J. Org. Chem.* **1986**, *51*, 700–705; (b) Padwa, A.; Bullock, W. H.; Dyszlewski, A. D. *J. Org. Chem.* **1990**, *55*, 955–964; (c) Roy, S.; Das, I.; Bhanuprakash, K.; Gupta, B. D. *Tetrahedron* **1994**, *50*, 1847–1858.
19. Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 1287–1290.
20. Tsuji, J.; Sugiura, T.; Minami, I. *Tetrahedron Lett.* **1986**, *27*, 731–734.
21. Hon, Y.-S.; Chang, F.-J.; Lu, L.; Lin, W.-C. *Tetrahedron* **1998**, *54*, 5233–5246.
22. Sime, J. T.; Barnes, R. D.; Elson, S. W.; Jarvest, R. L.; O'Toole, K. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1653–1658.
23. Ogawa, A.; Kawabe, K.; Kawakami, J.; Mihara, M.; Hirao, T.; Sonoda, N. *Organometallics* **1998**, *17*, 3111–3114.
24. Cossy, J.; Pete, J. P. *Tetrahedron Lett.* **1986**, *27*, 573–574.
25. Ma, S.; Yu, F. *Tetrahedron* **2005**, *61*, 9896–9901.
26. (a) Loughlin, W. A.; McCleary, M. A. *Org. Biomol. Chem.* **2003**, *1*, 1347–1353; (b) Mussatto, M. C.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 260–263.
27. Pelter, A.; Ward, R. S.; Little, G. M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2775–2790.