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Chemistry of allenic/propargylic anions generated by base treatment of sulfonylallenes: synthesis of 1-alkynyl-1-sulfonylcycloalkanes and cycloalkanols

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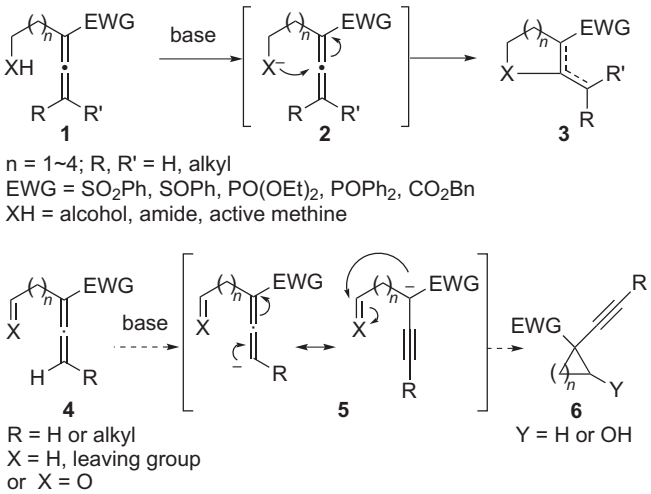
ABSTRACT

The intramolecular trapping of allenyl/propargyl anions, generated from sulfonylallenes with the proper base, by a haloalkyl group or an aldehyde functionality was investigated. The treatment of 1-(ω-iodoalkyl)-1-(phenylsulfonyl)allenes with TBAF or NaH in DMF efficiently produced the 1-alkynyl-1-(phenylsulfonyl)-substituted three- to seven-membered carbocycles. The allenyl/propargyl anions could also be intramolecularly trapped using a terminal aldehyde to stereoselectively afford the 2-alkynyl-2-(phenylsulfonyl)-substituted five- and six-membered cycloalkanols. The latter reaction could be performed using a catalytic amount of TBAF or DBU.

1. Introduction

Activated allenes with an electron-withdrawing group (EWG), like the sulfonyl, sulfinyl, phosphono, phosphoryl, or alkoxycarbonyl group, have significantly higher electrophilicities compared to the corresponding alkenes. As a result, the base-promoted *endo*-mode ring-closing reaction of the 1-alkyl-1-EWG-allenes **1** having a nucleophilic moiety at the alkyl chain terminus smoothly proceeds to produce five- to medium-sized heterocycles or carbocycles **3** (Scheme 1).[1–3] On the other hand, allenes with the EWG would also be anticipated to easily produce allenic/propargylic anions upon exposure to a weak base due to the high acidity of the proton at the C-3 position of the 1-EWG-substituted allene species[4–7] in contrast to the non-activated allenes, the anion formation of which requires a strong base exemplified by the butyl lithium.[8] We have now investigated the generation of the allenyl/propargyl anion species **5** from the 1,1-disubstituted and 1,1,3-trisubstituted allenes **4** having an EWG at the C-1 position and their intramolecular trapping by the proper electrophilic functionality, such as an alkyl halide or aldehyde, resulting in the formation of the 1-alkynyl-1-EWG-substituted carbocycles **6**.[9] The phenylsulfonyl group-substituted allene was mainly selected as the substrate because of its intrinsic strong electron-withdrawing ability as well as its ease for the preparation and further elaboration to various functional groups.[10]



Scheme 1. Base-promoted ring-closing reactions of 1-alkyl-1-EWG-allenes.

2. Results and discussion

2.1. Intramolecular trapping by alkyl halides

At the departure of this investigation, we synthesized the 1-(ω-haloalkyl)-1-(phenylsulfonyl)allenes **9** with or without

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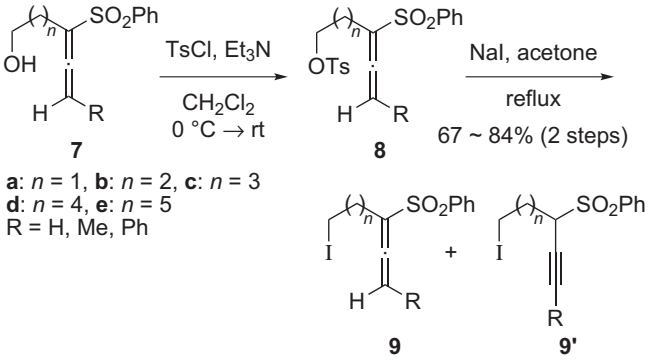
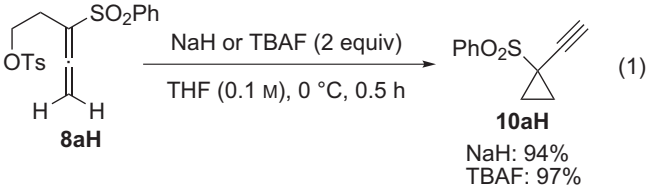
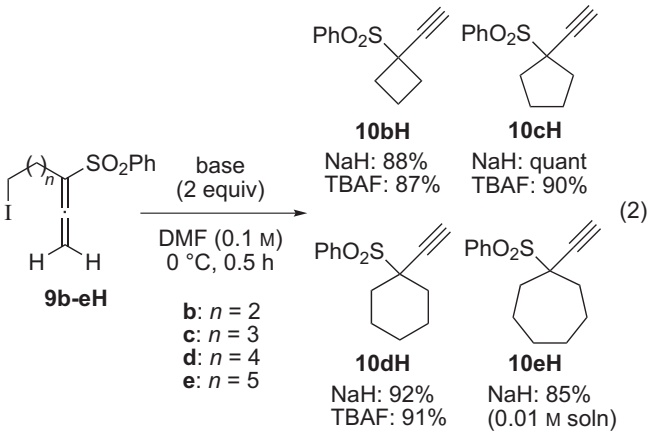
a substituent (Me or Ph) at the allenic terminus for the allenyl/propargyl anion generation and its intramolecular trapping leading to the formation of carbocycles. The tosylate **8** was prepared from the hydroxyallenes **7**[1a] under the conventional conditions (Scheme 2). The conversion of the 1,1-disubstituted allenes **8H** into **9H** occurred without contamination of **9′H**. However, iodination of the tosylates **8Me** and **8Ph** having a substituent at the allenic terminus was partly accompanied by isomerization of the allene moiety to acetylene (10–20%). We first screened various bases using the tosylate **8aH** (n=1, R=H in Scheme 2). No reaction occurred when **8aH** was treated with triethylamine. The three-membered ring product **10aH** was obtained in 71% yield upon exposure to two equivalents of K_2CO_3 in THF, although a fairly prolonged reaction time was needed (46 h, 17% recovery of starting material). Treatment with NaH or TBAF at 0 °C resulted in the full consumption of the starting material and the production of **10aH** in excellent yield (Eq. 1). Four- and larger-membered ring constructions were performed using a 0.1 M DMF solution of iodide **9b–eH** (Eq. 2). NaH or TBAF in DMF at 0 °C was effective for the conversion of **9b–eH** into the four- to seven-membered ring products **10b–eH**,[†] although a diluted condition (0.01 M) was required for the seven-membered ring formation. The eight-membered carbocycles were not obtained under any conditions.



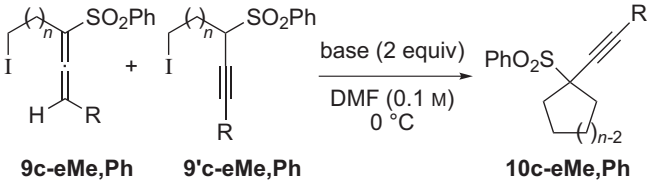
Scheme 2. Preparation of iodoallenes **9**.





The effect of the C-3 substituents on the 1-alkyl-1-sulfonylallene was studied. Upon exposure to the standard conditions (2 equiv of NaH or TBAF in DMF at 0 °C), a mixture of **9cMe** and **9′cMe** (4:1) having a methyl group at the allenic terminus produced the cyclopentane **10cMe** in high yield, which was comparable to that of **10cH** (Table 1, entries 1 and 3). Decreasing the amount of NaH to 1 equiv obviously delayed the completion of the reaction (entry 2). The phenyl-substituted allene **9cPh** and its one- or two-carbon homologated iodoallenes (**9d** or **9e**) also gave excellent results as shown in Table 1.

Table 1
Reaction of 1-(ω-haloalkyl)-1-(phenylsulfonyl)allenes **9** with a substituent (Me or Ph) at the allenic terminus



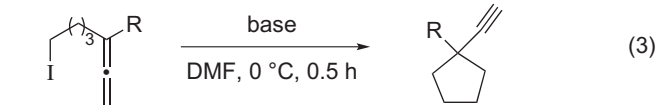
Entry	Substrate				Base	Time (h)	Yield (%)
		n	R	**9**:**9′**			
1	**9cMe**	3	Me	4:1	NaH	1	quant
2	**9cMe**	3	Me	4:1	NaH[a]	24	quant
3	**9cMe**	3	Me	4:1	TBAF	0.5	87
4	**9cPh**	3	Ph	8:1	NaH	0.25	79
5	**9cPh**	3	Ph	8:1	TBAF	0.25	91
6	**9dMe**	4	Me	4:1	NaH	1	93
7	**9dPh**	4	Ph	8:1	NaH	0.5	87
8[b]	**9eMe**	5	Me	10:1	NaH	0.5	90
9[b]	**9ePh**	5	Ph	9:1	TBAF	0.5	93

[a] One equiv of base was used.
[b] Reaction was performed in 0.01 M solution.

The phenylsulfonyl group served as a favorable functionality. Thus, some other substituents at the allenic position were examined to see if they met our requirements. While the behavior of the benzoylallene **11a** was in good accordance with those of the sulfonylallene **9cH**, the methoxycarbonylallene **11b** was found to provide a rather low yield of the cyclopentane derivative **12b** presumably due to the insufficient electron-withdrawing ability (Eq. 3). The elimination of hydrogen iodide mainly occurred when the benzylallene **11c** was treated with NaH. The use of TBAF instead of NaH resulted in the formation of the olefin **13** and fluorinated allene **14** (Eq. 4). In either event, no ring-closing product was obtained from **11c** at all. These results strongly suggest that the

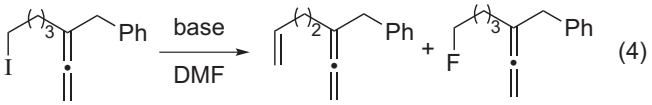
[†] Treatment of the tosyloxyallene **8dH** with NaH in THF afforded the desired product **10dH** in low yield (21%). After extensive examination on six-membered ring formation, we found that changing the leaving group from the tosyloxy group to iodo group and the reaction solvent from THF to DMF brought about a drastic improvement. Therefore, the four- to seven-membered ring formations were performed using the iodoallenes **9** as the substrates and DMF as the solvent. We have not tried any reactions using the iodoallene **9aH** because the readily available **8aH** gave the satisfactory result.

electron-withdrawing ability of the substituent at the allenic position must govern the reaction process, in particular, generation of the allenyl/propargyl anion.



(3)

11a: R = COPh **12a**: 93% (TBAF); 97% (NaH)
11b: R = COOMe **12b**: 47% (TBAF); trace (NaH)



(4)

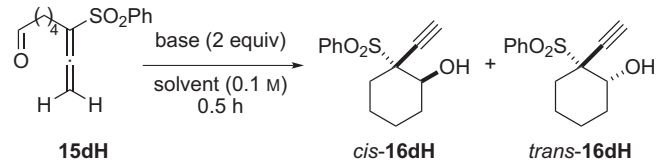
11c **13** **14**

conditions		
NaH, 0 °C → 50 °C	38%	
TBAF, 0 °C → rt	43%	45%

2.2. Intramolecular trapping by aldehydes

Our next efforts focused on the application of the aforementioned method to the construction of cycloalkanol derivatives starting from the sulfonylallenes having an aldehyde moiety as an electrophilic counterpart. The aldehyde **15dH**, prepared from **7dH** by oxidation with Dess–Martin periodinane or IBX (*o*-iodoxybenzoic acid) (Eq. 5), was exposed to NaH (2 equiv) in DMF at 0 °C expecting the production of the cyclohexanol derivative **16dH**. However, no ring-closing product could be detected in the reaction mixture. Similar conditions at a lower temperature (−78 °C) for 30 min led to the favorable result, which involved an 81% yield of **16dH** in a 56:44 ratio of cis and trans isomers (Table 2, entries 1 and 2). The reaction carried out in the range of −60 to 0 °C in the presence of TBAF produced the **16dH** in good to high yields. The higher reaction temperature, the better the yield and the higher cis selectivity were achieved (entries 3–5). Interestingly, the lower temperature (−60 °C) gave rise to a reverse stereoselectivity (entry 3). This temperature dependent stereoselectivity with TBAF in DMF indicates that *cis*-**16dH** must be the thermodynamic product under this condition. In fact, the mixture of products [Table 2, entry 3 (*cis*-**16dH**/*trans*-**16dH**=37:63)] was exposed to TBAF in DMF at 0 °C that produced a mixture of *cis*-**16dH** and *trans*-**16dH** in the ratio of 84:16, which is similar to the product ratio observed in entry 5 (Eq. 6). Less polar solvents (THF, CH_2Cl_2, toluene) provided rather low selectivities (entries 6–8). Unexpectedly, the use of *t*-BuOK as the base in THF at −78 °C predominantly afforded the *cis*-**16dH** (entry 9).[‡] Treatment with other bases, K_2CO_3 or DBU, for 30 min provided a modest selectivity (entries 10 and 11).

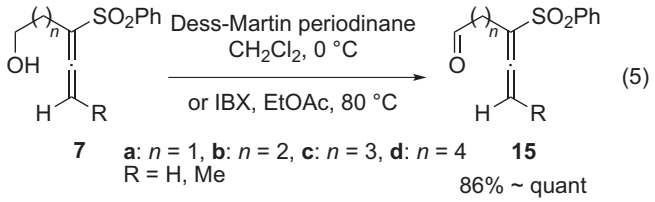
Table 2
Reaction of allenyl aldehyde **15dH** with various bases



15dH *cis*-**16dH** *trans*-**16dH**

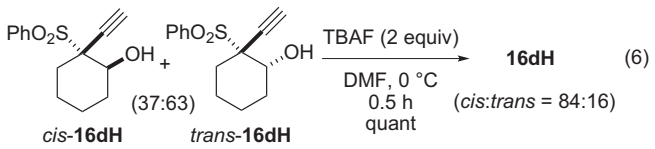
Entry	Base	Solvent	Temp (°C)	% Yield (*cis*:*trans*)[a]
1	NaH	DMF	0	—
2	NaH	DMF	−78	81 (56:44)
3	TBAF	DMF	−60	73 (37:63)
4	TBAF	DMF	−40	85 (84:16)
5	TBAF	DMF	0	92 (84:16)
6	TBAF	THF	0	90 (80:20)
7	TBAF	CH_2Cl_2	0	90 (74:26)
8	TBAF	Toluene	0	92 (67:33)
9	*t*-BuOK	THF	−78	80 (86:14)
10	K_2CO_3	DMF	0	85 (73:27)
11	DBU	DMF	0	85 (67:33)

[a] The ratio was determined by ^{1}H NMR analysis of the crude product.



7 **a**: *n* = 1, **b**: *n* = 2, **c**: *n* = 3, **d**: *n* = 4 **15**
R = H, Me
86% ~ quant

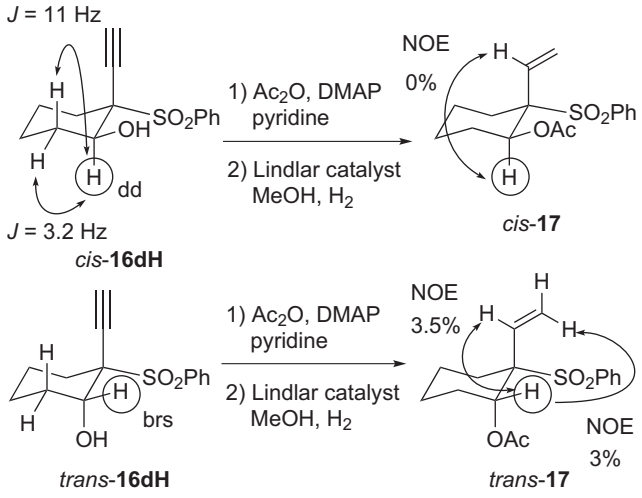
(5)



cis-**16dH** *trans*-**16dH**

(6)

The stereochemical assignments were based on a ^{1}H NMR evaluation, which involves the analysis of the coupling constants between H-6 and H-1 of the cyclohexane ring of **16dH** as described in Scheme 3. Furthermore, an NOE experiment with 2-vinylcyclohexyl acetate possessing a *trans*-relationship between the ethynyl group and hydroxy functionality (*trans*-**17**), derived from the *trans*-**16dH** by acetylation and Lindlar reduction, recorded an enhancement between the vinyl protons and H-1 of the cyclohexane ring, while no enhancement could be detected when these protons of the corresponding vinyl derivative *cis*-**17** were irradiated.



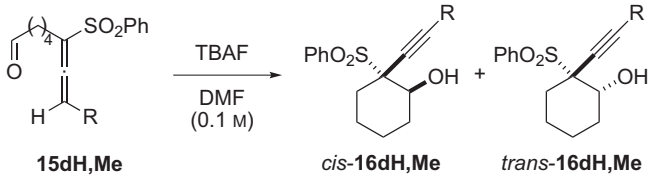
Scheme 3. Stereochemical assignments of **16dH**.

Our interest then turned to the catalytic version of this reaction using allenyl aldehydes with or without a substituent at the allenic terminus. A catalytic amount of TBAF (0.1 equiv) was found to be

[‡] Reaction of **15dH** with *t*-BuOK at 0 °C gave a complex mixture of products.

effective for the conversion of **15dH** into **16dH** at 0 °C for 30 min in both its yield and selectivity comparable to those for 2 equiv of TBAF (Table 3, entry 1 vs 2). The reaction at room temperature afforded a similar result (entry 3). In the case of the methyl-substituted allene **15dMe**, however, 0.1 equiv of TBAF at 0 °C for a prolonged reaction time (5 h) nonselectively afforded the cyclized products as a mixture of two diastereoisomers in the ratio of 48:52 (entry 6). A stereoselectivity similar to that of the stoichiometric reaction (TBAF, 1 equiv, 0 °C, 0.5 h) was observed when treated at room temperature for one day (entry 8 vs entry 4). The stereochemistry of **16dMe** was assigned by analogy to **16dH** based on the ^{1}H NMR analysis.

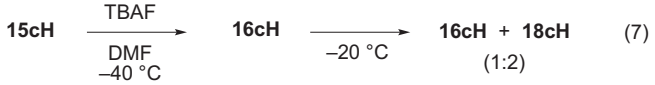
Table 3
TBAF-catalyzed reaction of **15d**



Entry	R	TBAF (equiv)	Temp	Time (h)	% Yield (*cis*:*trans*)
1	H	2	0 °C	0.5	92 (84:16)[a]
2	H	0.1	0 °C	0.5	88 (84:16)[a]
3	H	0.1	rt	0.5	84 (84:16)[a]
4	Me	1	0 °C	0.5	79 (82:18)[b]
5	Me	0.1	0 °C	0.5	71 (45:55)[b]
6	Me	0.1	0 °C	5	69 (48:52)[b]
7	Me	0.1	rt	5	73 (78:22)[b]
8	Me	0.1	rt	24	74 (84:16)[b]

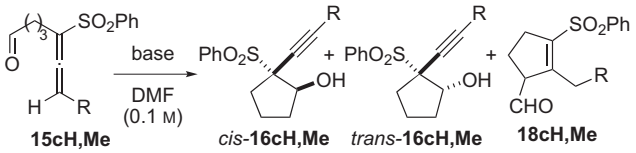
[a] The ratio was determined by ^{1}H NMR analysis of the crude product.
[b] The ratio was calculated from isolated yields of both isomers.

The one-carbon shorter aldehyde **15c** was found to show a different behavior from **15d**. Upon exposure to a catalytic amount of TBAF at room temperature, **15cH** produced an intractable mixture from which the expected cyclopentanol **16cH** was not detected (Table 4, entry 1). Lowering the reaction temperature to −40 °C resulted in the production of **16cH** in good yield with a high cis selectivity (entry 2). Raising the temperature from −40 °C to −20 °C caused the partial transformation of **16cH** into cyclopentenecarbaldehyde **18cH** (by ^{1}H NMR analysis of the crude product) (Eq. 7). The formation of the aldehyde **18cH** from **16cH** might be rationalized by the addition of an aldehyde enolate, generated from **16cH**, to the allene in an *endo*-mode ring-closing manner. A good yield of **16cH** was also recorded for the reaction with DBU (0.5 equiv) in DMF at −40 °C, although a prolonged reaction time was required to attain a high selectivity (entry 4). Interestingly, in the case of the methyl-substituted allene **15cMe**, the use of TBAF (0.1 equiv) at room temperature highly stereoselectively afforded **16cMe** in 67% yield in a 94:6 ratio of the cis and trans isomer, along with **18cMe** in 4% yield (entry 5).[§] The higher product yield was obtained using DBU as the base (entries 6 and 7).



[§] While the reasonable yield (62%, cis only) of **16cH** was obtained in the reaction of **15cH** with 2 equiv of TBAF at −40 °C for 0.5 h, the reactions of **15cMe** with TBAF at that temperature afforded the desired product **16cMe** in low yields (TBAF 2 equiv, 0.5 h: 24%; TBAF 0.5 equiv, 1 h: 35%) with high cis selectivities (>97:3).

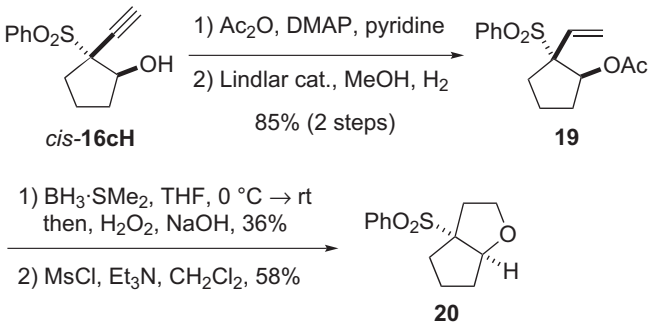
Table 4
TBAF-catalyzed reaction of **15c**



Entry	R	Base (equiv)	Temp	Time (h)	% Yield (*cis*:*trans*)[a]	
					16c	**18c**
1	H	TBAF (0.1)	rt	1	—	—
2	H	TBAF (0.2)	−40 °C	8	74 (97:3)	—
3	H	DBU (0.5)	−40 °C	1	75 (85:15)	—
4	H	DBU (0.5)	−40 °C	24	73 (96:4)	—
5	Me	TBAF (0.1)	rt	0.5	67 (94:6)	4
6	Me	DBU (0.1)	rt	0.5	80 (90:10)	1
7	Me	DBU (0.1)	rt	5	72 (94:6)	1

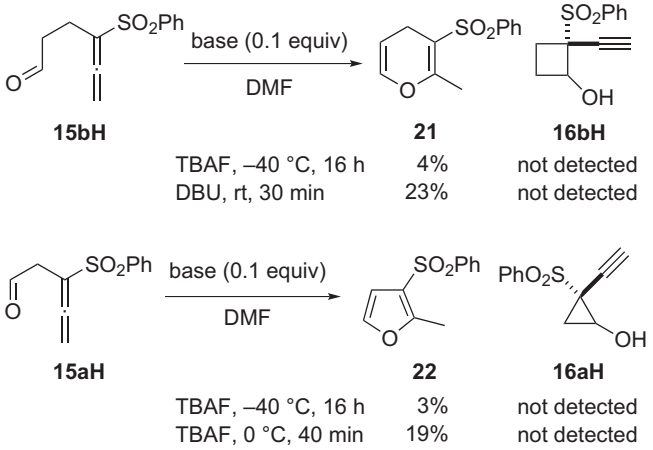
[a] The ratio was determined by ^{1}H NMR analysis of the crude product.

The stereochemical relationship between the alkynyl group and hydroxy functionality of the major isomers of **16c** was determined to be cis as described in Scheme 4 based on the following facts. (1) The major isomer of **16cH** could successfully be transformed into 1-oxabicyclo[3.3.0]octane **20**. (2) The ^{1}H NMR spectrum of a diastereomeric mixture of **16cMe** was very similar to that of **16cH**, except for the peak due to the acetylenic terminus.

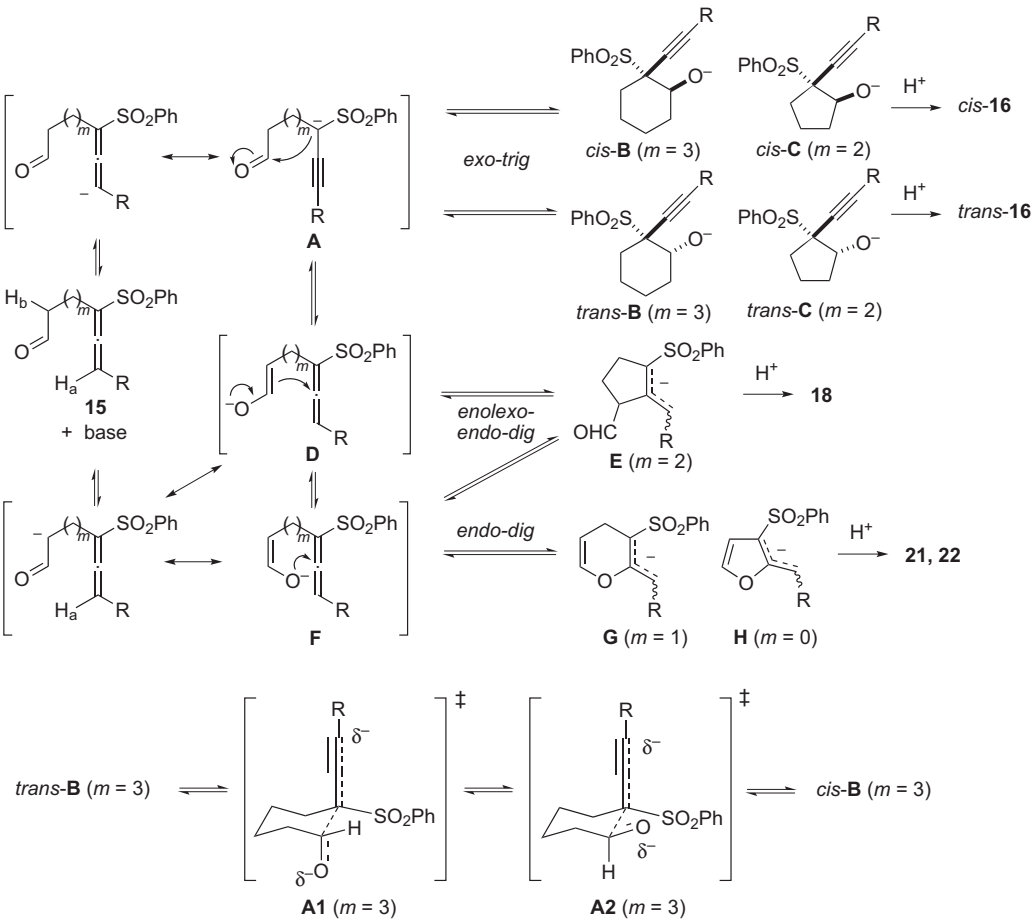


Scheme 4. Stereochemical consideration of cyclopentanol **16c**.

The smaller ring formation via the allenyl/propargyl anion was next examined. The treatment of **15bH** and **15aH** with a base at −40 °C or room temperature produced neither the corresponding cycloalkanol **16bH** nor **16aH**, and the pyran **21** and furan **22** were obtained as the only isolable products, respectively (Scheme 5).



Scheme 5. Reaction of allenyl aldehydes **15bH** and **15aH** with TBAF or DBU.



Scheme 6. Reaction pathway for treatment of **15** with TBAF.

The results so far obtained strongly indicate that there exists an equilibrium under the stated reaction conditions (TBAF in DMF) as depicted in Scheme 6. In the case of **15dH** and **15dMe** (m=3), the allenyl/propargyl anions **A**, generated by kinetic abstraction of H_a, would attack the aldehyde carbonyl carbon to produce the *cis*- and *trans*-cyclohexanols **B**. The nonchelation transition state **A1** collapsing to the *trans*-**B** might minimize the dipolar repulsion between the allene and aldehyde functionalities in comparison to that of another nonchelation transition state **A2** leading to *cis*-**B**. The once preferentially formed *trans*-**B** would subsequently isomerize again to the thermodynamically more stable *cis*-**B** via the allenyl/propargyl anions **A** finally reaching equilibrium. In contrast, the one-carbon shorter aldehyde **15cH** (m=2) might kinetically and/or thermodynamically produce the anion intermediate *cis*-**C** in the presence of TBAF at low temperature presumably due to the five-membered framework. At higher temperature, the intermediate **C** should isomerize to **E** via the successive formation of anion **A** and abstraction of H_b leading to the enolate anion (**D** and/or **F**). On the other hand, the methyl-substituted allene **15cMe** hardly produces **E** because the methyl group inhibits the attack of the enolate anion on the central carbon of the allene; therefore, cyclopentanol **16cMe** is produced in good yield at room temperature. Neither cyclobutanol **16b** nor cyclopropanol **16a** are obtained because of their high strain energies, and the lower energy intermediates **G** and **H**, leading to the pyran **21** and furan **22**, respectively, are formed based on attack of the (*Z*)-enolate oxygens on the allene moieties.

3. Conclusions

We demonstrated that the 1,1-disubstituted or 1,1,3-trisubstituted allenes possessing a sulfonyl group at the C-1 position generated the corresponding allenyl/propargyl anions by treatment with NaH or TBAF, and the anions were intramolecularly captured by the haloalkyl group to produce the 1-alkynyl-1-sulfonyl-substituted three- to seven-membered carbocycles in high yields. The intramolecular reaction of the anions, generated by TBAF or DBU treatment, with the aldehyde functionality afforded the 2-alkynyl-2-sulfonylcyclopentanols or cyclohexanols in good to high yields with moderate to high diastereoselectivities. This aldol-type reaction smoothly proceeded even by the catalytic use of the base. Application of these newly developed cyclization methods for the synthesis of natural products is now in progress.

4. Experimental

4.1. General

Melting points are uncorrected. IR spectra were measured in $CHCl_3$. ^1H NMR spectra were taken in $CDCl_3$ unless otherwise indicated. $CHCl_3$ (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 iodo(phenylsulfonyl)alkadienes

5-(Phenylsulfonyl)octa-5,6-dien-1-ol (**7cMe**) was prepared according to literature procedures.[1a] To a solution of **7cMe** (195 mg, 0.732 mmol) in CH_2Cl_2 (7 mL) were added Et_3N (0.4 mL, 2.9 mmol) and TsCl (282 mg, 1.47 mmol) at 0 °C. After stirring for 22 h at room temperature, the reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ and extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane/EtOAc (2:1) afforded the tosylate **8cMe** (290 mg, 93%) as a yellow oil. To a solution of **8cMe** (280 mg, 0.666 mmol) in acetone (6.7 mL) was added NaI (465 mg, 3.10 mmol). After being refluxed for 5.5 h, the mixture was allowed to cool to room temperature, diluted with water, and extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane/EtOAc (4:1) afforded a mixture of **9cMe** and **9′cMe** in the ratio of 4:1 (225 mg, 90%) as a yellow oil.

Characterization data for compounds **8aH** and **9b–eH** have been shown in Supplementary data of Ref. 9.

*4.2.1. 8-Iodo-4-(phenylsulfonyl)octa-2,3-diene (**9cMe**) and 8-iodo-4-(phenylsulfonyl)oct-2-yne (**9′cMe**).* IR 1960 cm^{-1}; ^1H NMR (270 MHz) δ 7.92–7.86 (m, 2H), 7.65–7.53 (m, 3H), 5.74 (qt, 0.8H, J=7.4, 3.1 Hz), 3.80–3.73 (m, 0.2H), 3.16 (td, 0.2×2H, J=6.8, 1.3 Hz), 3.11 (t, 0.8×2H, J=6.8 Hz), 2.28 (td, 0.8×2H, J=7.7, 3.1 Hz), 1.74 (d, 0.8×3H, J=7.4 Hz), 1.84–1.48 (m, 5H); ^{13}C NMR (67.8 MHz) δ 204.2, 140.1, 136.8, 133.9, 133.3, 129.5, 129.0, 128.8, 128.0, 112.3, 96.6, 85.2, 71.1, 59.3, 32.7, 32.3, 28.3, 27.7, 27.5, 25.6, 13.5, 5.9, 5.8, 3.7; MS m/z 376 (M^+, 16.6); HRMS calcd for $C_{14}H_{17}O_2IS$ 375.9994, found 375.9993.

*4.2.2. 7-Iodo-1-phenyl-3-(phenylsulfonyl)hepta-1,2-diene (**9cPh**) and 7-iodo-1-phenyl-3-(phenylsulfonyl)hept-1-yne (**9′cPh**).* Title compounds (318 mg, 77%) were obtained as an inseparable mixture in the ratio of 8:1 from **7cPh** (313 mg, 0.953 mmol). A yellow oil; IR 1948 cm^{-1}; ^1H NMR (270 MHz) δ 8.02–7.90 (m, 2H), 7.72–7.46 (m, 3H), 7.35–7.15 (m, 5H), 6.69 (t, 0.89H, J=3.1 Hz), 4.06 (dd, 0.11H, J=10.7, 4.1 Hz), 3.20 (td, 0.11×2H, J=6.6, 1.6 Hz), 3.09 (t, 0.89×2H, J=6.8 Hz), 2.51–2.43 (m, 0.89×2H), 2.31–2.19 (0.11H), 1.93–1.52 (m, 4.11H); ^{13}C NMR (67.8 MHz) δ 205.2, 139.9, 136.6, 134.0, 133.5, 131.5, 130.8, 129.4, 129.0, 128.8, 128.7, 128.6, 128.2, 127.9, 127.4, 121.5, 116.8, 103.9, 95.9, 88.3, 59.6, 32.5, 32.3, 28.2, 27.6, 27.2, 26.2, 5.7; MS m/z 438 (M^+, 9.5); HRMS calcd for $C_{19}H_{19}O_2IS$ 438.0151, found 438.0151.

*4.2.3. 9-Iodo-4-(phenylsulfonyl)nona-2,3-diene (**9dMe**) and 9-iodo-4-(phenylsulfonyl)non-2-yne (**9′dMe**).* Title compounds (80.7 mg, 80%) were obtained as an inseparable mixture in the ratio of 4:1 from **7dMe** (74.5 mg, 0.266 mmol). A yellow oil; IR 1961 cm^{-1}; ^1H NMR (270 MHz) δ 7.94–7.85 (m, 2H), 7.68–7.50 (m, 3H), 5.72 (qt, 0.8H, J=7.4, 3.1 Hz), 3.80–3.75 (m, 0.2H), 3.16 (t, 0.2×2H, J=6.9 Hz), 3.11 (t, 0.8×2H, J=6.9 Hz), 2.28–2.22 (m, 0.8×2H), 1.74 (d, 0.8×3H, J=7.4 Hz), 2.10–1.31 (m, 7H); ^{13}C NMR (67.8 MHz) δ 204.3, 140.2, 136.8, 133.9, 133.2, 129.5, 128.9, 128.7, 127.9, 112.5, 96.3, 85.0, 71.2, 59.4, 33.0, 32.9, 29.8, 29.4, 28.4, 26.5, 26.4, 25.6, 13.5, 6.7, 6.6, 3.7; MS m/z 390 (M^+, 18.4); HRMS calcd for $C_{15}H_{19}O_2IS$ 390.0151, found 390.0153.

*4.2.4. 8-Iodo-1-phenyl-3-(phenylsulfonyl)octa-1,2-diene (**9dPh**) and 8-iodo-1-phenyl-3-(phenylsulfonyl)oct-1-yne (**9′dPh**).* Title compounds (124 mg, 73%) were obtained as an inseparable mixture in the ratio of 8:1 from **7dPh** (132 mg, 0.386 mmol). A yellow oil; IR 1948 cm^{-1}; ^1H NMR (270 MHz) δ 8.01–7.90 (m, 2H), 7.73–7.47 (m, 3H), 7.39–7.17 (m, 5H), 6.68 (t, 0.89H, J=3.3 Hz), 4.05 (dd, 0.11H, J=10.6, 4.1 Hz), 3.18 (t, 0.11×2H, J=6.9 Hz), 3.08 (t, 0.89×2H, J=6.9 Hz), 2.49–2.42 (m, 0.89×2H), 2.30–1.33 (m, 6.22H); ^{13}C NMR (67.8 MHz) δ 205.3, 140.2, 136.8, 134.1, 133.5, 131.7, 131.1, 129.6, 129.0, 128.9, 128.8, 128.7, 128.3, 128.1, 127.5, 117.2, 103.8, 59.9, 33.0, 32.9, 29.8, 29.7, 28.2, 27.2, 26.5, 25.8, 6.5; MS m/z 452 (M^+, 1.7); HRMS calcd for $C_{20}H_{21}O_2IS$ 452.0307, found 452.0305.

*4.2.5. 10-Iodo-4-(phenylsulfonyl)deca-2,3-diene (**9eMe**) and 10-iodo-4-(phenylsulfonyl)dec-2-yne (**9′eMe**).* Title compounds (319 mg, 84%) were obtained as an inseparable mixture in the ratio of 10:1 from **7eMe** (278 mg, 0.944 mmol). A yellow oil; IR 1960 cm^{-1}; ^1H NMR (270 MHz) δ 7.96–7.87 (m, 2H), 7.68–7.51 (m, 3H), 5.72 (qt, 0.91H, J=7.3, 3.1 Hz), 3.79–3.75 (m, 0.09H), 3.20–3.12 (m, 0.09×2H), 3.15 (t, 0.91×2H, J=7.0 Hz), 2.28–2.22 (m, 0.91×2H), 1.74 (d, 0.91×3H, J=7.3 Hz), 2.10–1.27 (m, 8.45H); ^{13}C NMR (67.8 MHz) δ 204.3, 140.3, 136.9, 133.9, 133.2, 129.5, 128.9, 128.7, 127.9, 112.7, 96.2, 84.9, 71.3, 59.5, 33.2, 30.1, 30.0, 28.4, 27.8, 27.5, 27.2, 26.6, 26.5, 13.4, 6.9, 3.7; MS m/z 404 (M^+, 54.9); HRMS calcd for $C_{16}H_{21}O_2IS$ 404.0307, found 404.0312.

*4.2.6. 9-Iodo-1-phenyl-3-(phenylsulfonyl)nona-1,2-diene (**9ePh**) and 9-iodo-1-phenyl-3-(phenylsulfonyl)non-1-yne (**9′ePh**).* Title compounds (223 mg, 67%) were obtained as an inseparable mixture in the ratio of 9:1 from **7ePh** (257 mg, 0.721 mmol). A yellow oil; IR 1948 cm^{-1}; ^1H NMR (270 MHz) δ 8.02–7.90 (m, 2H), 7.72–7.47 (m, 3H), 7.35–7.17 (m, 5H), 6.67 (t, 0.9H, J=3.3 Hz), 4.05 (dd, 0.1H, J=10.9, 4.1 Hz), 3.18 (t, 0.1×2H, J=6.9 Hz), 3.09 (t, 0.9×2H, J=6.9 Hz), 2.47–2.40 (m, 0.9×2H), 2.30–1.29 (m, 8.2H); ^{13}C NMR (67.8 MHz) δ 205.4, 140.2, 134.0, 133.5, 131.7, 131.1, 129.6, 129.0, 128.9, 128.7, 128.3, 128.1, 127.5, 117.4, 103.7, 88.2, 81.5, 60.0, 33.2, 30.1, 30.0, 28.3, 27.9, 27.7, 27.3, 27.2, 26.6, 6.9; MS m/z 466 (M^+, 1.3); HRMS calcd for $C_{21}H_{23}O_2IS$ 466.0464, found 466.0458.

Procedure for the preparation of iodoalkadienes **11a–c** and their characterization data have been shown in Supplementary data of Ref. 9.

4.3. Typical procedure for preparation of (phenylsulfonyl)alkadienals

To a solution of **7cMe** (42.3 mg, 0.160 mmol) in CH_2Cl_2 (1.6 mL) was added Dess–Martin periodinane (210 mg, 0.495 mmol) at 0 °C. After stirring for 1.5 h at that temperature, saturated aqueous $NaHCO_3$ and aqueous $Na_2S_2O_3$ were added to the reaction mixture, which was stirred for 30 min at room temperature. The mixture was extracted with EtOAc, and the extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane/Et_2O (1:2) afforded **15cMe** (39.2 mg, 93%) as a colorless oil.

Characterization data for compounds **15dH** and **15cH** have been shown in Supplementary data of Ref. 9.

*4.3.1. 5-(Phenylsulfonyl)octa-5,6-dien-1-al (**15cMe**).* IR 1961, 1724 cm^{-1}; ^1H NMR (270 MHz) δ 9.72 (t, 1H, J=1.3 Hz), 7.90–7.86 (m, 2H), 7.66–7.50 (m, 3H), 5.75 (qt, 1H, J=7.4, 3.1 Hz), 2.45 (td, 2H, J=7.4, 1.3 Hz), 2.33–2.28 (m, 2H), 1.78 (quin, 2H, J=7.4 Hz), 1.74 (d, 3H, J=7.4 Hz); ^{13}C NMR (100 MHz) δ 204.3, 201.4, 140.0, 133.4, 129.0, 128.0, 112.1, 96.7, 42.7, 26.1, 20.0, 13.4; MS m/z 264 (M^+, 2.0); HRMS calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0814.

*4.3.2. 6-(Phenylsulfonyl)nona-6,7-dien-1-al (**15dMe**).* Title compound (201 mg, 93%) was obtained as a colorless oil from **7dMe** (219 mg, 0.781 mmol). IR 1960, 1722 cm^{-1}; ^1H NMR (270 MHz) δ 9.68 (t, 1H, J=1.5 Hz), 7.86–7.83 (m, 2H), 7.62–7.47 (m, 3H), 5.70

(qt, 1H, *J*=7.4, 3.1 Hz), 2.45 (td, 2H, *J*=7.3, 1.3 Hz), 2.24 (td, 2H, *J*=7.4, 3.1 Hz), 1.69 (d, 3H, *J*=7.4 Hz), 1.63–1.37 (m, 4H); ^{13}C NMR (67.8 MHz) δ 204.2, 202.0, 140.1, 133.3, 128.9, 127.9, 112.3, 96.4, 43.3, 26.9, 26.4, 21.0, 13.4.

*4.3.3. 4-(Phenylsulfonyl)hexa-4,5-dien-1-al (**15bH**).* Title compound (31.6 mg, quant.) was obtained as a colorless oil from **7bH** (31.4 mg, 0.132 mmol). IR 1971, 1728 cm^{-1}; ^{1}H NMR (400 MHz) δ 9.71 (s, 1H), 7.95–7.89 (m, 2H), 7.70–7.55 (m, 3H), 5.43 (t, 2H, *J*=3.7 Hz), 2.68 (t, 2H, *J*=7.3 Hz), 2.57 (tt, 2H, *J*=7.3, 3.7 Hz); ^{13}C NMR (100 MHz) δ 207.4, 199.8, 139.6, 133.7, 129.1, 128.0, 111.9, 85.2, 41.2, 19.6; MS *m*/*z* 236 (M$^+$, 6.2); HRMS calcd for $C_{12}H_{12}O_3S$ 236.0507, found 236.0511.

*4.3.4. 3-(Phenylsulfonyl)penta-3,4-dien-1-al (**15aH**).* To a solution of **7aH** (35.2 mg, 0.157 mmol) in EtOAc (1.6 mL) was added IBX (132 mg, 0.471 mmol) at room temperature, and the mixture was stirred for 2 h at 80 °C. The reaction mixture was allowed to cool to room temperature and filtered. The filtrate was concentrated to dryness and the residue was chromatographed with hexane/EtOAc (3:2) to afford **15aH** (30.1 mg, 86%) as a colorless oil. IR 1969, 1734 cm^{-1}; ^{1}H NMR (400 MHz) δ 9.60 (t, 1H, *J*=1.8 Hz), 7.91–7.89 (m, 2H), 7.69–7.65 (m, 1H), 7.59–7.55 (m, 2H), 5.50 (t, 2H, *J*=2.3 Hz), 3.33 (td, 2H, *J*=2.3, 1.8 Hz); ^{13}C NMR (100 MHz) δ 209.3, 195.5, 139.3, 134.0, 129.3, 128.2, 105.5, 84.9, 41.0; MS *m*/*z* 222 (M$^+$, 43.3); HRMS calcd for $C_{11}H_{10}O_3S$ 222.0351, found 222.0351.

4.4. General procedure for ring-closing reaction

To a solution of allene (0.1 mmol) in solvent (1 mL) was added base (0.01–0.2 mmol) at the temperature shown in Eqs. 1–4, Tables 1–4 and Scheme 5, and the reaction mixture was stirred at that temperature until the complete disappearance of the starting material (monitored by TLC). The mixture was quenched by addition of water and extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane/EtOAc afforded the ring-closing products in pure form. Characterization data for compounds **10a**–**eH**, **12a**,**b**, *cis*-**16cH**, *cis*- and *trans*-**16dH**, and **18cH** have been shown in Supplementary data of Ref. 9.

*4.4.1. 1-(Phenylsulfonyl)-1-(1-propynyl)cyclopentane (**10cMe**).* A yellow oil; IR 2253 cm^{-1}; ^{1}H NMR (500 MHz) δ 7.98 (d, 2H, *J*=8.1 Hz), 7.66 (dd, 1H, *J*=7.6, 7.3 Hz), 7.55 (dd, 2H, *J*=7.8, 7.6 Hz), 2.49–2.44 (m, 2H), 1.95–1.78 (m, 6H), 1.78 (s, 3H); ^{13}C NMR (67.8 MHz) δ 136.8, 133.6, 130.2, 128.4, 83.1, 78.1, 68.3, 36.2, 25.1, 3.7; FABMS *m*/*z* 249 (M$^+$+1, 14.4); FABHRMS calcd for $C_{14}H_{17}O_2S$ 249.0949, found 249.0956.

*4.4.2. 1-(Phenylethynyl)-1-(phenylsulfonyl)cyclopentane (**10cPh**).* A white solid; ^{1}H NMR (270 MHz) δ 8.05–8.02 (m, 2H), 7.69–7.63 (m, 1H), 7.57–7.51 (m, 2H), 7.35–7.27 (m, 5H), 2.65–2.54 (m, 2H), 2.13–2.04 (m, 2H), 1.98–1.87 (m, 4H); ^{13}C NMR (67.8 MHz) δ 136.7, 133.8, 131.5, 130.3, 128.6, 128.5, 128.3, 122.1, 88.2, 86.4, 68.7, 36.3, 25.3; MS *m*/*z* 310 (M$^+$, 1.3); HRMS calcd for $C_{19}H_{18}O_2S$ 310.1028, found 310.1022.

*4.4.3. 1-(Phenylsulfonyl)-1-(1-propynyl)cyclohexane (**10dMe**).* A white solid; IR 2243 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.96–7.92 (m, 2H), 7.68–7.62 (m, 1H), 7.57–7.51 (m, 2H), 1.83 (s, 3H), 1.90–1.10 (m, 10H); ^{13}C NMR (67.8 MHz) δ 135.2, 133.6, 130.8, 128.2, 85.3, 75.2, 64.9, 30.6, 24.9, 22.3, 3.8; MS *m*/*z* 262 (M$^+$, 1.0); HRMS calcd for $C_{15}H_{18}O_2S$ 262.1028, found 262.1033.

*4.4.4. 1-(Phenylethynyl)-1-(phenylsulfonyl)cyclohexane (**10dPh**).* A white solid; IR 2228 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.02–7.99 (m, 2H), 7.69–7.63 (m, 1H), 7.56–7.51 (m, 2H), 7.38–7.27 (m, 5H), 2.04–1.99 (m, 4H), 1.84–1.19 (m, 6H); ^{13}C NMR (67.8 MHz) δ 135.2, 133.8, 131.6, 130.9, 128.7, 128.3, 128.3, 122.1, 88.9, 85.4, 65.3, 30.6, 24.9, 22.5; MS *m*/*z* 324 (M$^+$, 0.5); HRMS calcd for $C_{20}H_{20}O_2S$ 324.1184, found 324.1186.

*4.4.5. 1-(Phenylsulfonyl)-1-(1-propynyl)cycloheptane (**10eMe**).* A yellow oil; ^{1}H NMR (270 MHz) δ 7.97–7.94 (m, 2H), 7.68–7.61 (m, 1H), 7.55–7.50 (m, 2H), 2.14–1.98 (m, 4H), 1.83 (s, 3H), 1.78–1.53 (m, 8H); ^{13}C NMR (67.8 MHz) δ 135.6, 133.6, 131.0, 128.2, 84.7, 76.6, 67.6, 33.8, 27.6, 23.1, 3.8; MS *m*/*z* 276 (M$^+$, 3.4); HRMS calcd for $C_{16}H_{20}O_2S$ 276.1184, found 276.1180.

*4.4.6. 1-(Phenylethynyl)-1-(phenylsulfonyl)cycloheptane (**10ePh**).* A colorless oil; ^{1}H NMR (270 MHz) δ 8.02 (d, 2H, *J*=7.4 Hz), 7.66 (t, 1H, *J*=7.4 Hz), 7.53 (t, 2H, *J*=7.4 Hz), 7.38–7.28 (m, 5H), 2.27–2.14 (m, 4H), 1.90–1.55 (m, 8H); ^{13}C NMR (67.8 MHz) δ 135.5, 133.8, 131.6, 131.1, 128.7, 128.4, 128.3, 122.2, 88.3, 86.7, 67.9, 33.8, 27.6, 23.3; MS *m*/*z* 338 (M$^+$, 1.0); HRMS calcd for $C_{21}H_{22}O_2S$ 338.1341, found 338.1334.

*4.4.7. 3-Benzylhepta-1,2,6-triene (**13**).* A colorless oil; IR 1958 cm^{-1}; ^{1}H NMR (600 MHz) δ 7.30–7.20 (m, 5H), 5.80 (ddt, 1H, *J*=17.2, 10.3, 6.9 Hz), 4.99 (d, 1H, *J*=17.2 Hz), 4.93 (d, 1H, *J*=10.3 Hz), 4.69 (t, 2H, *J*=3.4 Hz), 3.31 (s, 2H), 2.17 (td, 2H, *J*=7.2, 6.9 Hz), 1.97 (tt, 2H, *J*=7.2, 3.4 Hz); ^{13}C NMR (151 MHz) δ 206.7, 139.5, 138.3, 128.9, 128.2, 126.2, 114.6, 102.2, 75.7, 39.7, 31.6, 30.4; FABMS *m*/*z* 185 (M$^+$+1, 12.8); FABHRMS calcd for $C_{14}H_{17}$ 185.1330, found 185.1337.

*4.4.8. 7-Fluoro-3-benzylhepta-1,2-diene (**14**).* A colorless oil; IR 1958 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.30–7.20 (m, 5H), 4.69 (quin, 2H, *J*=2.7 Hz), 4.40 (dt, 2H, *J*=47.2, 6.0 Hz), 3.30 (t, 2H, *J*=2.3 Hz), 1.92 (tt, 2H, *J*=7.3, 3.7 Hz), 1.74–1.49 (m, 4H); ^{13}C NMR (151 MHz) δ 206.6, 139.5, 128.9, 128.2, 126.2, 102.2, 84.0 (d, *J*=163.9 Hz), 75.6, 39.6, 30.5, 29.9 (d, *J*=19.2 Hz), 23.0 (d, *J*=5.8 Hz); FABMS *m*/*z* 205 (M$^+$+1, 1.2); FABHRMS calcd for $C_{14}H_{18}F$ 205.1393, found 205.1396.

4.4.9. (1R,2S*)-2-(Phenylsulfonyl)-2-(1-propynyl)cyclohexanol (cis-**16dMe**).* A colorless oil; IR 3533 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.96–7.93 (m, 2H), 7.70–7.64 (m, 1H), 7.58–7.52 (m, 2H), 4.20 (dd, 1H, *J*=10.9, 4.5 Hz), 3.04 (br s, 1H), 1.87 (s, 3H), 1.99–1.21 (m, 8H); ^{13}C NMR (67.8 MHz) δ 135.3, 134.1, 130.8, 128.4, 87.6, 71.9, 70.3, 70.2, 31.9, 31.6, 23.6, 21.8, 3.9; FABMS *m*/*z* 279 (M$^+$+1, 30.9); FABHRMS calcd for $C_{15}H_{19}O_3S$ 279.1055, found 279.1055.

4.4.10. (1R,2R*)-2-(Phenylsulfonyl)-2-(1-propynyl)cyclohexanol (trans-**16dMe**).* A white solid; IR 3499, 2249 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.96–7.93 (m, 2H), 7.72–7.66 (m, 1H), 7.60–7.54 (m, 2H), 4.13 (br s, 1H), 2.37 (td, 1H, *J*=12.0, 3.5 Hz), 1.78 (s, 3H), 1.86–1.25 (m, 7H); ^{13}C NMR (67.8 MHz) δ 134.8, 134.1, 130.6, 128.5, 87.5, 74.4, 68.4, 67.4, 29.6, 24.5, 22.0, 18.1, 3.8; MS *m*/*z* 278 (M$^+$, 5.3); HRMS calcd for $C_{15}H_{18}O_3S$ 278.0977, found 278.0977.

4.4.11. (1R,2R*)-2-Ethynyl-2-(phenylsulfonyl)cyclopentanol (trans-**16cH**).* A white solid; IR 3495, 3304 cm^{-1}; ^{1}H NMR (600 MHz) δ 8.01 (d, 2H, *J*=8.2 Hz), 7.70 (t, 1H, *J*=7.6 Hz), 7.59 (t, 2H, *J*=7.6 Hz), 4.42 (br s, 1H), 2.75 (dt, 1H, *J*=11.7, 8.2 Hz), 2.48 (d, 1H, *J*=1.4 Hz), 2.17–2.03 (m, 3H), 1.96–1.86 (m, 2H); ^{13}C NMR (151 MHz) δ 136.6, 134.3, 130.0, 128.7, 80.0, 79.1, 77.8, 70.5, 33.3, 31.5, 20.6; MS *m*/*z* 250 (M$^+$, 4.9); HRMS calcd for $C_{13}H_{14}O_3S$ 250.0664, found 250.0665.

4.4.12. (1R,2S*)-2-(Phenylsulfonyl)-2-(1-propynyl)cyclopentanol (cis-**16cMe**).* A colorless oil; IR 3560, 2243 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.98–7.94 (m, 2H), 7.71–7.64 (m, 1H), 7.58–7.53 (m, 2H), 4.75–4.69 (m, 1H), 2.54–2.44 (m, 1H), 2.30–2.12 (m, 2H), 2.04–1.93 (m, 1H), 1.84 (s, 3H), 1.86–1.69 (m, 3H); ^{13}C NMR (67.8 MHz)

δ 136.4, 133.9, 130.1, 128.5, 87.8, 74.8, 73.1, 72.5, 34.3, 32.8, 19.7, 3.9; MS *m*/*z* 264 (M^+, 1.1); HRMS calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0819.

4.4.13. (1R,2R*)-2-(Phenylsulfonyl)-2-(1-propynyl)cyclopentanol (trans-**16cMe**).* A colorless oil; IR 3482, 2245 cm^{-1}; ^1H NMR (600 MHz) δ 7.98 (d, 2H, *J*=8.2 Hz), 7.69 (dd, 1H, *J*=8.2, 7.6 Hz), 7.58 (t, 2H, *J*=7.6 Hz), 4.31 (d, 1H, *J*=3.4 Hz), 2.71 (dt, 1H, *J*=11.7, 8.9 Hz), 2.12–2.00 (m, 3H), 1.91–1.80 (m, 2H), 1.72 (s, 3H); ^{13}C NMR (151 MHz) δ 137.0, 134.0, 129.8, 128.6, 85.9, 79.0, 75.3, 70.9, 33.2, 31.2, 20.6, 3.8; MS *m*/*z* 264 (M^+, 6.7); HRMS calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0820.

*4.4.14. 2-Ethyl-3-(phenylsulfonyl)cyclohex-2-ene-1-carbaldehyde (**18cMe**).* A colorless oil; IR 1670 cm^{-1}; ^1H NMR (270 MHz) δ 10.0 (s, 1H), 7.89–7.85 (m, 2H), 7.70–7.64 (m, 1H), 7.58–7.52 (m, 2H), 4.48–4.43 (m, 1H), 3.10 (dq, 1H, *J*=14.5, 7.4 Hz), 2.88–2.73 (m, 1H), 2.51–2.25 (m, 2H), 2.17–1.93 (m, 2H), 1.25 (t, 3H, *J*=7.4 Hz); ^{13}C NMR (67.8 MHz) δ 187.6, 156.5, 144.0, 137.2, 134.2, 129.2, 128.9, 74.1, 28.4, 25.2, 20.6, 13.7; MS *m*/*z* 264 (M^+, 22.2); HRMS calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0817.

*4.4.15. 2-Methyl-3-(phenylsulfonyl)-4H-pyran (**21**).* A red oil; ^1H NMR (270 MHz, C_6D_6) δ 7.79–7.74 (m, 2H), 6.95–6.86 (m, 3H), 5.66 (dt, 1H, *J*=6.2, 2.0 Hz), 4.28 (dt, 1H, *J*=6.2, 3.6 Hz), 2.77–2.74 (m, 2H), 2.18 (t, 3H, *J*=1.3 Hz); ^{13}C NMR (100 MHz, C_6D_6) δ 158.3, 142.1, 139.1, 132.7, 129.0, 127.3, 111.5, 102.5, 21.5, 17.8; MS *m*/*z* 236 (M^+, 100); HRMS calcd for $C_{12}H_{12}O_3S$ 236.0507, found 236.058.

*4.4.16. 2-Methyl-3-(phenylsulfonyl)furan (**22**)[11].* A red oil; ^1H NMR (400 MHz) δ 7.94–7.92 (m, 2H), 7.61–7.51 (m, 3H), 7.26 (s, 1H), 6.59 (d, 1H, *J*=1.8 Hz), 2.59 (s, 3H); ^{13}C NMR (100 MHz) δ 156.7, 142.4, 141.2, 133.1, 129.2, 126.8, 122.7, 110.0, 12.9; MS *m*/*z* 222 (M^+, 50.2); HRMS calcd for $C_{11}H_{10}O_3S$ 222.0351, found 222.0354.

4.5. Derivatization of ring-closing products

4.5.1. (1R,2S*)-2-Ethenyl-2-(phenylsulfonyl)cyclopent-1-yl acetate (**19**).* To a solution of *cis*-**16cH** (23.8 mg, 9.51×10^{-2} mmol) in pyridine (1 mL) was added Ac_2O (45 μL, 0.48 mmol) and DMAP (12 mg, 9.8×10^{-2} mmol) at room temperature. After stirring for 19 h, the reaction mixture was quenched by addition of water and extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane/EtOAc (3:1) afforded the acetate (26.3 mg, 95%) as a colorless oil. To a solution of the acetate (22.8 mg, 7.80×10^{-2} mmol) in MeOH (1 mL) was added Lindlar catalyst (33 mg, 1.6×10^{-2} mmol) at room temperature. After stirring under H_2 atmosphere for 1 h, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated to dryness, and the residue was chromatographed with hexane/EtOAc (3:2) to afford **19** (20.5 mg, 89%) as a colorless oil. IR 1738 cm^{-1}; ^1H NMR (270 MHz) δ 7.83–7.79 (m, 2H), 7.67–7.61 (m, 1H), 7.55–7.49 (m, 2H), 6.04 (dd, 1H, *J*=17.6, 10.9 Hz), 5.73 (t, 1H, *J*=7.7 Hz), 5.51 (d, 1H, *J*=10.9 Hz), 5.38 (d, 1H, *J*=17.6 Hz), 2.48–2.27 (m, 2H), 2.17–2.05 (m, 1H), 1.87 (s, 3H), 1.84–1.44 (m, 3H); ^{13}C NMR (67.8 MHz) δ 169.6, 136.7, 133.7, 130.3, 130.2, 128.5, 121.8, 75.5, 75.0, 30.4, 28.0, 20.8, 19.3; FABMS *m*/*z* 295 (M^++1, 35.4); FABHRMS calcd for $C_{15}H_{19}O_4S$ 295.1004, found 295.1004.

4.5.2. (1R,5S*)-5-(Phenylsulfonyl)-2-oxabicyclo[3.3.0]octane (**20**).* To a solution of **19** (27.8 mg, 9.44×10^{-2} mmol) in THF (1 mL) was added dropwise $BH_3\cdot SMe_2$ (71.6 μL, 0.755 mmol) at 0 °C, and the mixture was stirred for 40 h at room temperature. A 3 M aqueous solution of NaOH (0.85 mL, 2.6 mmol) and 30% aqueous H_2O_2 were successively added to the mixture, which was stirred for three days. The mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane/EtOAc (1:1) afforded the diol (9.1 mg, 36%) as a white solid. To a solution of the diol (2.3 mg, 8.5×10^{-3} mmol) in CH_2Cl_2 (0.5 mL) were added Et_3N (0.1 mL, 0.7 mmol) and a solution of MsCl in CH_2Cl_2 (0.13 M, 0.13 mL, 1.7×10^{-2} mmol) at −78 °C. After stirring for 22 h at room temperature, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with EtOAc. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane/EtOAc (1:1) afforded **20** (2.5 mg, 58%) as a colorless oil. ^1H NMR (270 MHz) δ 7.97–7.94 (m, 2H), 7.71–7.66 (m, 1H), 7.61–7.55 (m, 2H), 4.89 (d, 1H, *J*=5.3 Hz), 3.90 (td, 1H, *J*=7.9, 2.6 Hz), 3.59 (ddd, 1H, *J*=9.4, 9.3, 5.9 Hz), 2.69 (ddd, 1H, *J*=13.5, 5.9, 2.6 Hz), 2.33–2.23 (m, 1H), 1.95–1.88 (m, 1H), 1.81–1.57 (m, 5H); ^{13}C NMR (67.8 MHz) δ 137.3, 133.9, 129.8, 129.2, 85.7, 78.8, 68.4, 37.7, 35.9, 33.7, 24.0; FABMS *m*/*z* 253 (M^++1, 13.6); FABHRMS calcd for $C_{13}H_{17}O_3S$ 253.0899, found 253.0904.

Procedure for the preparation of *cis*- and *trans*-**17** and their characterization data have been shown in Supplementary data of Ref. 9.

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