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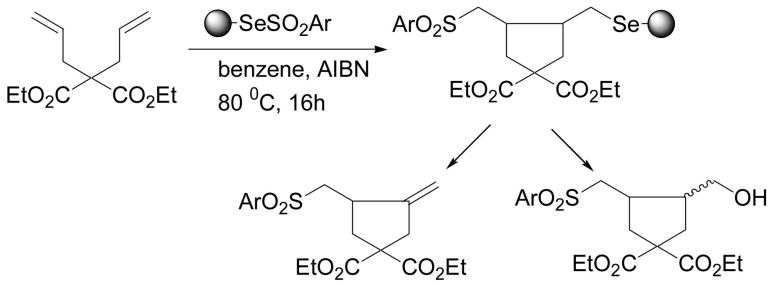

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Radical Cyclization of 1,6-Diene Using Polystyrene-Supported Selenosulfones

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Novel polystyrene supported selenosulfones from 1% cross-linked polystyrene resin were prepared and applied to free radical cyclization reactions of 1,6-dienes followed by the subsequent "traceless" resin release by oxidation−elimination, providing a convenient method for the synthesis of methylenecyclopentanes. Apart from getting the methylenecyclopentanes, we found that cyclopentanylmethyl alcohols were formed by the oxidation−elimination of the resin, which has not been observed in solution-phase synthesis under the same conditions.

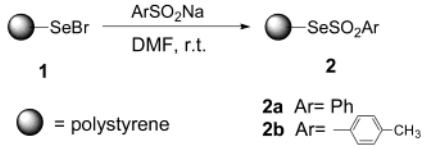
Introduction

Fueled by a rapidly growing interest in combinatorial chemistry, solid-phase organic synthesis (SPOS) is of current interest.[1] SPOS enjoys several advantages over solution-phase synthesis. For example, reactions can be driven to completion by the use of excess reagents, and the products can be isolated and purified by simple filtration. In addition, solid-supported reactions can be readily automated. These advantages offer the opportunity for rapid synthesis of compound libraries with diversity for pharmaceutical and agrochemical discovery.[2]

On the other hand, over the past 30 years, organoselenium reagents have been increasingly utilized in highly selective organic reactions, which are especially useful for the construction of complex molecules.[3] However, organic selenium reagents always have a foul smell and are quite toxic,[3d] which is often problematic in organic synthesis. Although polymers with selenium functionalities have been known for a long time,[4] there remains high interest in this kind of solid-phase organic chemistry. Recently, selenium-based approaches for solid-phase chemistry have been reported by different research groups.[5] Our research group also reported the preparation of polystyrene-supported selenosufonates from styrene/1% divinylbenzene copolymer beads **2** and their applications for regio- and stereocontrolled synthesis of vinyl sulfones and acetylenic sulfones [6] (Scheme 1). The advantages of the novel polymer reagents are their convenience of handling and their odorless nature when compared with nonpolymer-supported reagents, and resin **2** can be regenerated and reused.[6]

Free radical reactions are of paramount importance in organic synthesis. In particular, free-radical cyclization has been developed as a potential method for preparing various types of cyclic compounds via intramolecular carbon−carbon bond-forming processes.[7] Radical cyclization of dienes using selenosulfones as radical transfer agents provides a powerful method for constructing carbocycles or heterocycles with introduction of one or two functionalities.[8] In this paper, we disclose our recent results on the radical cyclization of dienes using polymer-supported radical transfer reagents.

Scheme 1



Results and Discussion

Preparation of the Polystyrene-Supported Selenosufonates. Following our published protocol[6] and others',[5] polystyrene-supported selenenyl bromide **1** was prepared with a loading of 1.71 mmol/g (Br), as determined by elemental analysis. Preparation of polystyrene-supported selenosufonates **2** was accomplished by treating a DMF-swollen suspension of resin **1** with sodium benzenesulfinate or sodium toluenesulfinate at room temperature for 6 h. This transformation could be monitored by FT-IR. There were two strong peaks at 1320 cm^{-1} and 1134 cm^{-1}, typical for $-SO_2-$ of polystyrene-supported selenosufonates **2**, with a loading of 1.33 mmol/g (**2a**, Ar = Ph) and a loading of 1.31 mmol/g (**2b**, Ar = $-C_6H_4-CH_3$-*p*), as determined by elemental analysis.

Radical Addition of the Polystyrene-Supported Selenosulfones to 1,6-Dienes. We investigated the radical addition of resin **2** with diethyl 2,2-diallylmalonate **3** (Scheme 2). Under a nitrogen atmosphere, AIBN (5% mol) and the malonate **3** were added to the benzene suspension of resin **2**, and the mixture was stirred at 80 °C for 16 h. The reaction process could be monitored by an FT-IR study.

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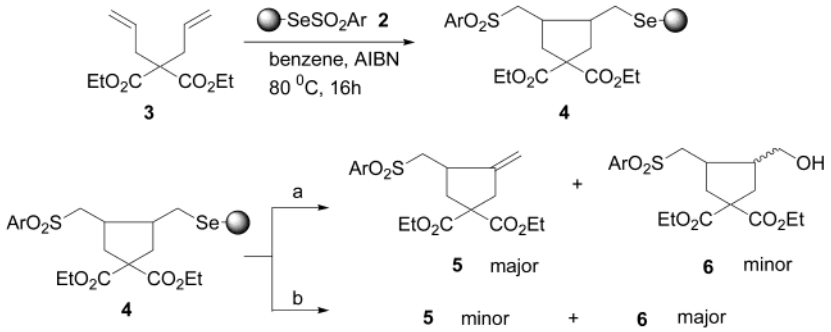
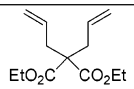
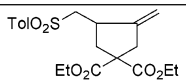
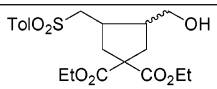
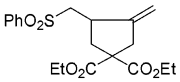
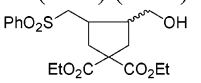
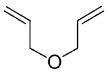
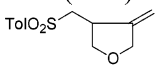
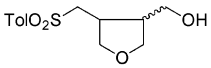
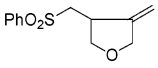
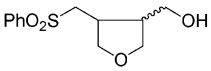
Scheme 2



(a) 20 equiv of 30% H_2O_2, 25 °C, 2 h (method A). (b) 20 equiv of 30% H_2O_2, 55-60 °C, 4 h (method B).

Table 1. Radical Addition of Polystyrene-Supported Selenosulfones with 1,6-Diene, Followed by Oxidation-Elimination with 30% H_2O_2 at 55−60 °C (Method B)

Entry	Substrate	Resin	Products(Yield %)[a]	
			Ene	Alcohol(*cis*/*trans*)[b]
1	 **3a**	**2b**	 **5a** (20%)	 **6a** (63%) (7.2:1)
2	**3a**	**2a**	 **5b** (18%)	 **6b** (60%) (7.2:1)
3	 **3b**	**2b**	 **5c** (19%)	 **6c** (67%) (3.8:1)
4	**3b**	**2a**	 **5d** (18%)	 **6d** (69%) (3.6:1)

[a] The yields are based on the loading of resin **2**. [b] Based on ^{13}C NMR and HPLC analysis.

The cyclized resin **4** that bound the cyclized adduct shows a strong band at 1730 cm^{-1} (−COOEt). The resin **4** was collected by filtration, washed, and treated with 30% H_2O_2 in THF at room temperature for 2 h (method A) to afford the expected product **5** (54%) together with an unexpected minor product, alcohol **6** (10%). The FT-IR study of the residue resin, however, also shows the band at 1730 cm^{-1} (−COOEt), indicating an incomplete conversion. When the washed resin **4** was treated with 30% H_2O_2 in THF at room temperature with stirring at 55−60 °C for 4 h (method B), the reaction afforded the alcohol **6** as the major product (Table 1).

The alcohol products **6** were obtained as a mixture of cis and trans stereoisomers. The relative stereochemistry of the isomeric products was determined by ^{13}C NMR spectroscopy. The γ gauche interaction[9] in the cis configuration contributes to a significant shielding effect on the two methylene carbons bearing sulfonyl and hydroxy groups. On the basis of the ^{13}C NMR chemical shifts data listed in Table 2, we believed that the major isomer should be the cis isomer.

With these results in hand, next we investigated the possibility of getting the oxidation−elimination product **5** or **6** selectively by changing the reaction conditions (Table 3).

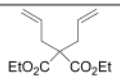
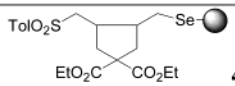
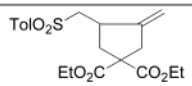
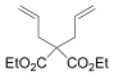
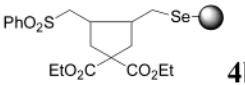
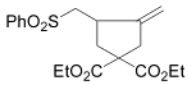
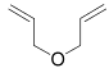
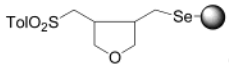
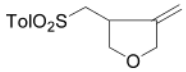
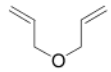
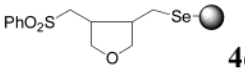
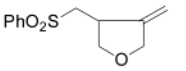
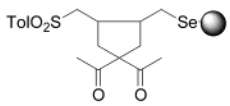
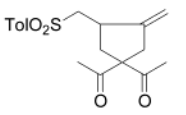
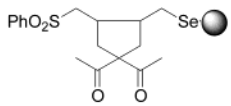
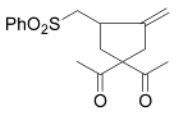
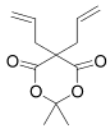
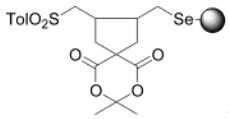
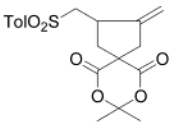
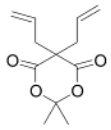
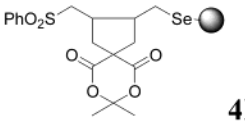
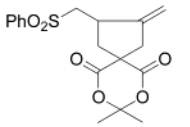
Table 2. ^{13}C NMR Chemical Shifts of cis- and trans-Isomers [10]

product **6**	$-SO_2CH_2-$	$-CH_2OH$
cis-**6a**	56.7	62.5
cis-**6b**	56.6	62.5
cis-**6c**	55.2	61.2
trans-**6c**	59.6	63.6
cis-**6d**	55.1	61.3
trans-**6d**	59.6	63.6

The results in Table 3 show that the influence of solvents and types of oxidants are not obvious. However, when resin **4** was treated with 30% H_2O_2 (20 equiv) or MCPBA (4 equiv) in THF at 0 °C for 0.5 h, followed by the subsequent removal of the oxidant by filtration/washing and stirring in CCl_4 at 90 °C for 0.5 h (method C), the reaction afforded the methylene−cyclopentane **5** as the sole product (entries 5, 10, 11, 12, Table 3). This new procedure led us to employ various 1,6-dienes in the radical cyclization reaction with resin **2**, followed by oxidation−elimination to afford the methylene-cyclopentane **5** as the sole product in moderate yields (Table 4).

9-Borabicyclo[3.3.1]nonane (9-BBN) exhibits remarkable regioselectivity in the hydroboration of olefins. Essentially, alcohols are obtained in quantitative yields after the usual

Table 3. Oxidation-Elimination Reaction of Resin **4** at Different Conditions[a]

Entry	Substrate	Resin **4**	Product **5**	Yield (%) [a]
1		 **4a**	 **5a**	54
2		 **4b**	 **5b**	52
3		 **4c**	 **5c**	58
4		 **4d**	 **5d**	57
5		 **4e**	 **5e**	47
6		 **4f**	 **5f**	44
7		 **4g**	 **5g**	51
8		 **4h**	 **5h**	52

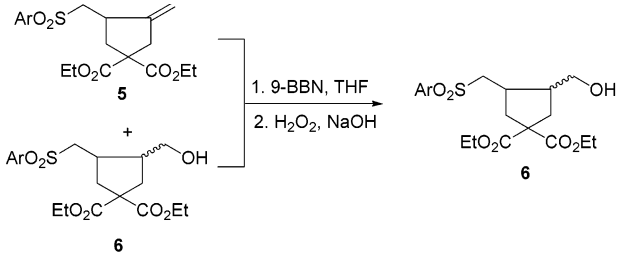
				yield *(%)*[a]	
entry	oxidant (equiv)	solvent	conditions	ene	ol
1	30% H_2O_2 (20)	THF	0 °C, 0.5 h; 25 °C, 2 h	54	10
2	30% H_2O_2 (20)	CH_2Cl_2	0 °C, 0.5 h; 25 °C, 2 h	53	10
3	30% H_2O_2 (20)	THF	0 °C, 0.5 h; 55−60 °C, 2 h	19.8	59.3
4	30% H_2O_2 (20)	THF	0 °C, 0.5 h; 55−60 °C, 4 h	19.8	63.2
5	30% H_2O_2 (20)	THF	0 °C, 1 h; remove oxidant; CCl_4, 90 °C 0.5 h	54	
6	MCPBA (4)	THF	0 °C, 0.5 h; 25 °C, 2 h	56.5	11.5
7	MCPBA (4)	THF	0 °C, 0.5 h; 55−60 °C, 2 h	25.3	60.7
8	MCPBA (4)	$CHCl_3$	0 °C, 0.5 h; 25 °C, 2 h	52.7	12.3
9	MCPBA (4)	CH_3OH	0 °C, 0.5 h; 25 °C, 2 h	52.9	17.1
10	MCPBA (4)	THF	0 °C, 0.5 h; remove oxidant; CCl_4 90 °C, 0.5 h	55	
11	MCPBA (4)	THF	0 °C, 2 h; remove oxidant; DMF/H_2O, 80 °C, 2 h	50	
12	MCPBA (4)	THF	0 °C, 2 h; remove oxidant; DMF/H_2O, 80 °C, 16 h	52	

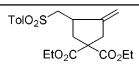
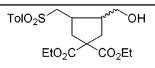
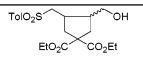
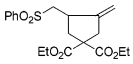
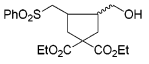
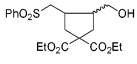
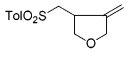
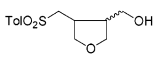
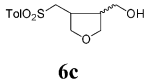
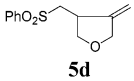
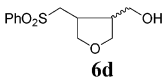
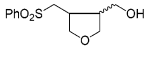
[a] The yields are based on the loading of resin **2**.

oxidation of the hydroboration products.[11] To achieve the selective formation of alcohols **6**, we succeeded in converting the methylenecyclopentane **5** in the mixture of **5** and **6** by 9-BBN. In this way, alcohol **6** was obtained highly selectively. Because the hydroboration of allyl-substituted exocyclic olefins with 9-BBN produces the thermodynamically stable products, the cis/trans ratio of **6** that is derived from hydroboration/oxidation of the mixture of intermediates **5** and **6** compared to the cis/trans ratio of **6** that is obtained from the resin bound selenide **4** is lower (Table 5).

The reaction mechanism for producing alcohols is unclear. Krief [12] reported that alkyl phenyl selenones readily undergo substitution reaction to give alcohol. Uemura[13] also reported that oxidation of alkyl phenyl selenides with excess MCPBA in methanol affords the corresponding alkyl methyl ethers almost quantitatively by substitution reaction. However, we did not get the alcohol product (entries 11, 12, Table 3) or the ether (entry 9, Table 3) by oxidation of the cyclized resin **4** under similar conditions. As a control experiment, we noted that the oxidation−elimination reaction of **7** in solution phase

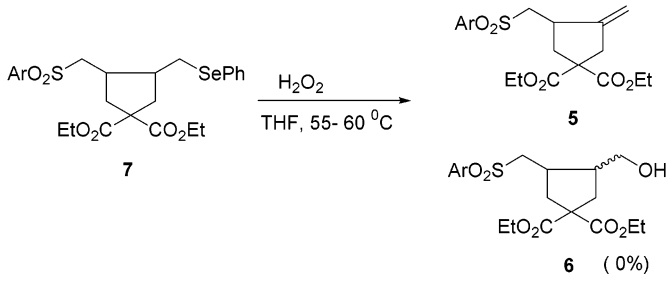
Table 4. Oxidation−Elimination of Resin **4** by H_2O_2 (Method C)[a]

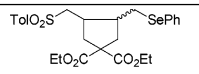
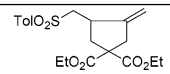
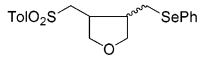
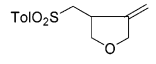
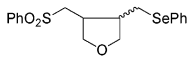
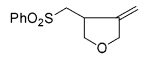


Entry	Substrate	Products	Yield[a](*cis*/*trans*)[b]
1	 **5a**	 **6a**	 **6a**	80% (4.5: 1)
2	 **5b**	 **6b**	 **6b**	72% (4.6: 1)
3	 **5c**	 **6c**	 **6c**	83% (2.7: 1)
4	 **5d**	 **6d**	 **6d**	84% (2.4: 1)

[a] The yields are based on the loading of resin **2**.

Table 5. Transformation of Mixtures of 5 and 6 to Products **6**



Entry	Substrate	Product	Yield (%)
1	 **7a**	 **5a**	84
2	 **7b**	 **5c**	89
3	 **7c**	 **5d**	86

[a] The yields are based on the loading of the resin **2**. [b] Based on HPLC analysis.

under the same conditions led to methylenecyclopentane **5** as the only product (Table 6). This result suggests that the alcohol product can only be formed by the polymer-supported oxidation−elimination reaction in this reaction.

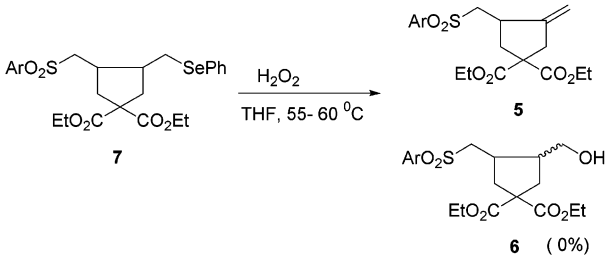
Conclusion

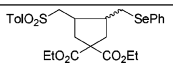
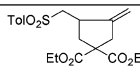
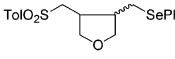
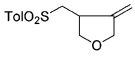
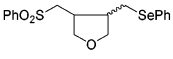
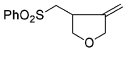
In summary, we have developed a method for the preparation of polystyrene-supported selenosulfones from 1% cross-linked polystyrene resin. The polystyrene-supported selenosulfones were applied to the free radical cyclization reactions of 1,6-dienes and subsequent "traceless" resin release by oxidation−elimination, providing a convenient method for the synthesis of cyclopentane derivates in good yield and purity. We also found that the alcohol product can be formed in the polymer-supported oxidation−elimination reaction, which was not observed in solution phase synthesis under the same conditions. By applying a different oxidation−elimination procedure, methylenecyclopentanes can be formed as the only products, while cyclopentanylmethyl alcohols were obtained as the only product employing an oxidation−hydroboration−oxidation sequence.

Experimental Section

Melting points were uncorrected. ^{1}H NMR(400 MHz) and ^{13}C NMR(100 MHz) spectra were recorded using $CDCl_3$ as the solvent and TMS as the internal standard. Mass spectra were obtained by EI methods. Infrared spectra were measured as thin film or in KBr. High performance liquid chroma-

Table 6. Solution-Phase Oxidation-Elimination of the Cyclization Adducts from Selenosulfones and 1,6-Diene by H_2O_2



Entry	Substrate	Product	Yield (%)
1	 **7a**	 **5a**	84
2	 **7b**	 **5c**	89
3	 **7c**	 **5d**	86

tography (HPLC) was conducted with a UV spectrophotometric detector using a Symmetry C18 column (4.6 × 250 mm). Diethyl-2,2-diallyl-malonate,[14] diallyl ether,[15] 3,3-diallylpentane-2,4-dione,[16] 5,5-diallyl-2,2-dimethyl-[1,3]dioxane-4,6-dione,[17] and compounds **7**[8c] were prepared according to the literature method.

Typical Procedure for the Preparation of Polystyrene-Supported Phenyl Selenosulfonate.[5] Under a nitrogen atmosphere, resin **1** (2 g) was swelled in DMF (20 mL) overnight. To the mixture was added sodium benzenethiosulfonate (12 mmol), and the mixture was stirred at room temperature for 6 h. Resin **2** was collected by filtration and washed with DMF (15 mL), H_2O (20 mL × 4), EtOH (15 mL × 2), MeOH (15 mL), THF (15 mL × 2), and CH_2Cl_2 (15 mL × 2) and dried in a vacuum. **2a.** (S, 1.33 mmol/g), IR ν (KBr): 3024, 2921, 1600, 1492, 1446, 1320, 1134, 1073, 823, 753, 697, 579, 527 cm^{-1}. **2b**. (S, 1.30 mmol/g), IR ν (KBr): 3024, 2921, 1600, 1492, 1457, 1452, 1320, 1134, 1075, 811, 757, 698, 645, 572, 512 cm^{-1}.

General Procedure for the Cyclization Reaction of 1,6-Diene Using Polystyrene-Supported Phenyl Selenosulfonate. Under a nitrogen atmosphere, to a suspension of the swelled resin **2b** (0.5 g) in dry benzene (20 mL) was added 1,6-diene (3 mmol) and AIBN (0.15 mmol, 24 mg). The mixture was stirred at 80 °C for 16 h. Resin **4** was collected by filtration and washed with benzene (15 mL × 2), MeOH (15 mL × 2), THF (15 mL × 2), and CH_2Cl_2 (15 mL × 2).

General Procedure for Oxidation−Elimination of the Resins. Method A. The washed resin **4** was suspended in THF (15 mL) and treated with 30% H_2O_2 (2 mL) at 0 °C for 0.5 h and at 25 °C for 2 h. The mixture was filtered, and the resin was washed with CH_2Cl_2 (15 mL × 3). The filtrate was washed with H_2O (30 mL × 2) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by preparative TLC on silica gel (hexane/ethyl acetate = 4:2).

Method B. The washed resin **4** was suspended in THF (15 mL) and treated with 30% H_2O_2 (2 mL) at room temperature and at 60 °C for 4 h. The mixture was filtered, and the resin was washed with CH_2Cl_2 (15 mL × 3). The filtrate was washed with H_2O (30 mL × 2) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by preparative TLC on silica gel (hexane/ethyl acetate = 4:2).

Method C. The washed resin **4** was suspended in THF (15 mL) and treated with 30% H_2O_2 (2 mL) at 0 °C for 0.5 h, followed by removal the oxidant by filtration and washing. The washed resin was stirred in CCl_4 at 90 °C for 0.5 h, filtered, and washed with CH_2Cl_2 (15 mL × 3). The filtrate was washed with H_2O (30 mL × 2) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by preparative TLC on silica gel (hexane/ethyl acetate = 4:2).

Diethyl-3-methylene-4-(toluene-4-sulfonylmethyl)cyclopentane-1,1-dicarboxylate (5a). The reaction of resin **2b** (0.5 g), diethyl-2,2-diallyl-malonate (720 mg, 3 mmol) and AIBN (24 mg, 0.15 mol), followed by workup using method C, afforded 141 mg (54%) of **5a**: oil, IR 3064, 2982, 1729, 1658, 1597, 1447, 1302, 1254, 1149, 1087, 564 cm^{-1}; ^1H NMR δ 1.24 (t, 3H, J = 7.14 Hz), 1.25 (t, 3H, J = 7.11 Hz), 2.13−2.07 (m, 1H), 2.46 (s, 3H), 2.84−2.78 (m, 1H), 3.00−2.97 (m, 3H), 3.12 (d, d, J = 14.0 Hz, J = 10.7 Hz, 1H) (−SO_2CH_2−), 3.36 (d, d, J = 14.0 Hz, J = 2.82 Hz, 1H) (−SO_2CH_2−), 4.17 (q, J = 7.14 Hz, 2H), 4.18 (q, J = 6.91 Hz, 2H), 4.77 (d, J = 2.09 Hz, 1H), 5.00 (d, J = 2.07 Hz, 1H), 7.38 (d, J = 7.96 Hz, 2H), 7.82 (d, J = 8.21 Hz, 2H); ^{13}C NMR δ 171.23, 171.18, 149.4, 144.8, 136.4, 130.0, 128.0, 101.9 (=CH_2), 61.7, 61.6, 60.7, 58.5, 40.2, 39.5, 36.8, 21.6, 14.0; MS (*m*/*z*) 395 (M^+ + 1), 349, 239, 193, 165, 137, 119, 105, 91, 77. Anal. Calcd for $C_{20}H_{26}O_6S$: C, 60.89; H, 6.64. Found: C, 60.78; H, 6.64.

Diethyl-3-benzenesulfonylmethyl-4-methylenecyclopentane-1,1-dicarboxylate (5b). The reaction of resin **2a** (0.5 g), diethyl-2,2-diallyl-malonate (720 mg, 3 mmol), and AIBN (24 mg, 0.15 mol), followed by workup using method C, afforded 128 mg (52%) of **5b**: oil; IR 3062, 2983, 2930, 1729, 1653, 1558, 1506, 1447, 1367, 1306, 1151, 1086, 747, 689 cm^{-1}; ^1H NMR δ 1.24 (t, 3H, J = 7.12 Hz), 1.25 (t, 3H, J = 7.12 Hz), 2.10 (m, 1H), 2.81 (m, 1H), 3.01−2.92 (m, 3H), 3.15 (d, d, J = 10.63 Hz, J = 13.97 Hz, 1H), 3.38 (d, d, J = 2.93 Hz, J = 13.98 Hz, 1H), 4.17 (q, J = 7.12 Hz, 2H), 4.184 (q, J = 7.12 Hz, 2H), 4.78 (d, J = 2.22 Hz, 1H), 5.00 (d, J = 2.24 Hz, 1H), 7.59 (t, J = 7.54 Hz, 2H), 7.68 (t, J = 7.42 Hz, 1H), 7.94 (d, J = 7.18 Hz, 2H); ^{13}C NMR δ 171.25, 171.16, 149.4, 139.4, 133.8, 129.4, 128.0, 108.0, 61.7, 60.7, 58.6, 40.2, 39.5, 36.7, 14.0; MS (*m*/*z*) 381 (M^+ + 1), 335, 239, 193, 165, 137, 119, 91, 77. Anal. Calcd for $C_{19}H_{24}O_6S$: C, 59.98; H, 6.36. Found: C, 59.87; H, 6.33.

3-Methylene-4-(toluene-4-sulfonylmethyl)tetrahydrofuran (5c). The reaction of resin **2b** (0.5 g), diallyl ether (294 mg, 3 mmol), and AIBN (24 mg, 0.15 mol), followed by workup using method C, afforded 97 mg (58%) of **5c**: white solid; mp 74−76 °C ($CHCl_3$), IR 3067, 2923, 2863, 1670, 1596, 1412, 1300, 1288, 1178, 1138, 1088, 910, 771, 562, 523 cm^{-1}; ^1H NMR δ 2.47 (s, 3H), 3.17 (t, J = 10.76 Hz, 2H), 3.30 (d, J = 11.08 Hz, 1H), 3.73 (d, d, J = 9.39 Hz, J = 6.16 Hz, 1H), 4.14 (d, d, J = 9.36 Hz, J = 6.35 Hz, 1H), 4.27 (m, 2H), 4.93 (d, J = 2.04 Hz, 1H), 5.03 (d, J = 1.81

Hz, 1H), 7.38 (d, $J = 7.97$ Hz, 2H), 7.81 (d, $J = 8.28$ Hz, 2H); ^{13}C NMR δ 149.3, 145.1, 136.3, 130.1, 128.0, 105.6, 73.1, 70.7, 59.2, 38.3, 21.7; MS (*m*/*z*) 253 ($M^+ + 1$), 251 ($M^+ - 1$), 155, 139, 129, 96, 91, 77, 65, 41. Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 61.76; H, 6.37.

3-Benzenesulfonylmethyl-4-methylenetetrahydrofuran (5d). The reaction of resin **2a** (0.5 g), diallyl ether (294 mg, 3 mmol), and AIBN (24 mg, 0.15 mol), followed by workup using method C, afforded 88 mg (57%) of **5d**: oil; IR 3065, 2923, 2852, 1670, 1585, 1447, 1305, 1146, 1086, 1064, 659 cm^{-1}; ^{1}H NMR δ 3.19 (t, $J = 10.22$ Hz, 2H), 3.31 (m, 2H), 3.75 (d, d, $J = 9.44$ Hz, $J = 6.00$ Hz, 1H), 4.15 (d, d, $J = 9.28$ Hz, $J = 6.31$ Hz, 1H), 4.27 (m, 2H), 4.94 (d, $J = 1.97$ Hz, 1H), 5.03 (d, $J = 1$H), 7.60 (t, $J = 7.56$ Hz, 2H), 7.69 (t, $J = 7.44$ Hz, 1H), 7.94 (d, $J = 7.14$ Hz, 2H); ^{13}C NMR δ 149.1, 139.2, 134.0, 129.5, 128.0, 105.6, 73.0, 70.6, 59.0, 38.2; MS (*m*/*z*) 239 ($M^+ + 1$), 237 ($M^+ - 1$), 195, 182, 165, 141, 125, 117, 97, 77, 51. Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.32; H, 5.93.

1,1-Diacetyl-3-methylene-4-(toluene-4-sulfonylmethyl)-cyclopentane (5e). The reaction of resin **2b** (0.5 g), 3,3-diallyl-pentane- 2,4-dione (540 mg, 3 mmol), and AIBN (24 mg, 0.15 mol), followed by workup using method C, afforded 104 mg (47%) of **5e**: oil; IR 3069, 2924, 1718, 1699, 1597, 1429, 1359, 1315, 1198, 1147, 1018, 566 cm^{-1}; ^{1}H NMR δ 2.00 (m, 1H), 2.11 (s, 3H), 2.12 (s, 3H), 2.46 (s, 3H), 2.79−2.92 (m, 4H), 3.04 (d, d, $J = 13.96$ Hz, $J = 10.13$ Hz, 1H), 3.31 (d, d, $J = 14.14$ Hz, $J = 2.48$ Hz, 1H), 4.73 (d, $J = 1.91$ Hz, 1H), 4.98 (d, $J = 1.76$ Hz, 1H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR δ 203.77, 203.75, 148.4, 144.4, 135.9, 129.5, 127.5, 107.4, 72.6, 59.7, 36.6, 36.4, 36.1, 26.1, 25.7, 21.1; MS (*m*/*z*) 335 ($M^+ + 1$), 291, 273, 178, 135, 91, 77, 43. Anal. Calcd for $C_{18}H_{22}O_4S$: C, 64.64; H, 6.63. Found: C, 64.50; H, 6.62.

1,1-Diacetyl-3-benzenesulfonylmethyl-4-methylenecyclopentane (5f). The reaction of resin **2a** (0.5 g), 3,3-diallyl-pentane- 2,4-dione (540 mg, 3 mmol), and AIBN (24 mg, 0.15 mol), followed by workup using method C, afforded 92 mg (44%) of **5f**: oil; IR 3070, 2924, 1718, 1699, 1447, 1359, 1306, 1199, 1149, 1085, 896, 784, 749, 690, 590 cm^{-1}; ^{1}H NMR δ 1.99 (m, 1H), 2.11 (s, 3H), 2.12 (s, 3H), 2.93−2.77 (m, 4H), 3.08 (d, d, $J = 14.01$ Hz, $J = 10.34$ Hz, 1H), 3.35 (d, d, $J = 13.95$ Hz, $J = 2.67$ Hz, 1H), 4.75 (d, $J = 2.12$ Hz, 1H), 4.99 (d, $J = 2.06$ Hz, 1H), 7.61 (t, $J = 7.41$ Hz, 2H), 7.69 (t, $J = 7.48$ Hz, 1H), 7.95 (d, $J = 8.57$ Hz, 2H); ^{13}C NMR δ 203.7, 148.4, 138.8, 133.3, 128.9, 127.4, 107.5, 76.9, 76.6, 76.2, 72.5, 59.6, 36.6, 36.3, 36.0, 26.1, 25.6; MS (*m*/*z*) 321 ($M^+ + 1$), 303, 277, 261, 221, 179, 161, 136, 119, 93, 77, 43. Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.73; H, 6.29. Found: C, 63.72; H, 6.27.

8,8-Dimethyl-2-methylene-3-(toluene-4-sulfonylmethyl)-7,9-dioxaspiro[4.5]decane-6,10-dione (5g). The reaction of resin **2b** (0.5 g), 5,5-diallyl-2,2-dimethyl- [1,3]dioxane-4,6-dione (672 mg, 3 mmol), and AIBN (24 mg, 0.15mol), followed by workup using method C, afforded 128 mg (51%) of **5g**: white solid; mp 138−140 °C ($CHCl_3$); IR 3040, 2930, 1773, 1740, 1620, 1598, 1395, 1383, 1302, 1206, 1148, 1087, 1047, 1006, 766, 663, 566 cm^{-1}; ^{1}H NMR δ 1.75 (s, 3H), 1.78 (s, 3H), 2.40 (d, d, $J = 13.69$ Hz, $J = 9.34$ Hz, 1H), 2.46 (s, 3H), 2.86 (d, d, $J = 8.23$ Hz, $J = 13.68$ Hz, 1H), 3.09 (s, 2H), 3.23 (d, d, $J = 14.19$ Hz, $J = 11.18$ Hz, 1H), 3.39−3.48 (m, 2H), 4.86 (d, $J = 1.76$ Hz, 1H), 5.05 (d, $J = 68$ Hz, 1H), 7.38 (d, $J = 7.97$ Hz, 2H), 7.80 (d, $J = 8.25$ Hz, 2H); ^{13}C NMR δ 169.96, 169.41, 148.3, 144.5, 135.8, 129.5, 127.4, 107.4, 101.7, 59.6, 51.1, 43.9, 43.2, 37.0, 28.3, 28.2, 21.1; MS (*m*/*z*) 379 ($M^+ + 1$), 321, 277, 214, 165, 137, 120, 93, 77, 43. Anal. Calcd for $C_{19}H_{22}O_6S$: C, 60.30; H, 5.86. Found: C, 60.24; H, 5.85.

2-Benzenesulfonylmethyl-8,8-dimethyl-3-methylene-7,9-dioxaspiro[4.5]decane-6,10-dione (5h). The reaction of resin **2a** (0.5 g), 5,5-diallyl-2,2-dimethyl-[1,3] dioxane-4,6-dione (672 mg, 3 mmol), and AIBN (24 mg, 0.15 mol), followed by workup using method C, afforded 123 mg (52%) of **5h**: white solid; mp 108−110 °C; IR 3096, 2926, 1774, 1743, 1620, 1446, 1390, 1377, 1293, 1228, 1142, 1044, 954, 750 cm^{-1}; ^{1}H NMR δ 1.76 (s, 3H), 1.78 (s, 3H), 2.41 (d, d, $J = 13.57$ Hz, $J = 9.07$ Hz, 1H), 2.87 (d, d, $J = 13.45$ Hz, $J = 8.01$ Hz, 1H), 3.05 (s, 2H), 3.26 (d, d, $J = 14.36$ Hz, $J = 11.35$ Hz, 1H), 3.47 (d, d, $J = 14.15$ Hz, $J = 2.85$ Hz, 2H), 4.87 (d, $J = 1.94$ Hz, 1H), 5.06 (d, $J = 1.90$ Hz, 1H), 7.60 (t, $J = 7.53$ Hz, 2H), 7.69 (t, $J = 7.40$ Hz, 1H), 7.94 (d, $J = 8.63$ Hz, 2H); ^{13}C NMR δ 170.56, 169.99, 148.9, 139.4, 134.0, 129.5, 128.0, 108.1, 105.3, 60.1, 51.8, 44.5, 43.8, 37.5, 28.9, 28.8; MS (*m*/*z*) 365 ($M^+ + 1$), 307, 263, 200, 165, 137, 120, 105, 91, 77, 43. Anal. Calcd for $C_{18}H_{20}O_6S$: C, 59.33; H, 5.53. Found: C, 59.22; H, 5.54.

Diethyl-3-hydroxymethyl-4-(toluene-4-sulfonylmethyl)-cyclopentane-1,1-dicarboxylate (6a). The reaction of resin **2b** (0.5 g), diethyl-2,2-diallyl-malonate (720 mg, 3 mmol), and AIBN (24 mg, 0.15 mol), followed by workup using method B, afforded 173 mg (63%) of **6a** (mixture of diastereoisomers): oil; IR 3530, 2982, 2936, 1728, 1597, 1446, 1368, 1302, 1262, 1184, 1147, 1088, 1034, 861, 766, 565 cm^{-1}; ^{1}H NMR δ 1.20 (t, $J = 3.80$ Hz, 3H), 1.23 (t, $J = 3.80$ Hz, 3H), 2.14 (m, 2H), 2.34 (m, 2H), 2.44 (s, 3H), 2.59 (m, 2H), 3.13 (m, 1H), 3.44 (m, 1H), 3.59 (d, $J = 5.63$ Hz, 2H), 4.14 (q, $J = 5.53$ Hz, 2H), 4.16 (q, $J = 3.36$ Hz, 2H), 7.34 (d, $J = 8.14$ Hz, 2H), 7.78 (d, $J = 8.17$ Hz, 2H); ^{13}C NMR δ 172.7, 172.1, 144.8, 136.5, 130.0, 128.0, 62.5, 61.8, 61.7, 58.5, 56.7, 43.5, 39.3, 36.3, 35.6, 21.7, 14.02, 13.99; MS (*m*/*z*) 413 ($M^+ + 1$), 395, 367, 275, 257, 239, 211, 183, 173, 153, 137, 127, 107, 91, 79, 77, 65. Anal. Calcd for $C_{20}H_{28}O_7S$: C, 58.23; H, 6.84. Found: C, 58.20; H, 6.86.

Diethyl-3-benzenesulfonylmethyl-4-hydroxymethylcyclopentane-1,1- dicarboxylate (6b). The reaction of resin **2a** (0.5 g), diethyl-2,2-diallyl-malonate (720 mg, 3 mmol), and AIBN (24 mg, 0.15mol), followed by workup using method B, afforded 155 mg (60%) of **6b** (mixture of diastereoisomers): oil; IR 3527, 2982, 1728, 1559, 1447, 1368, 1305, 1262, 1183, 1146, 1086, 1031, 749, 670, 567 cm^{-1}; ^{1}H NMR δ 1.18 (t, $J = 3.96$ Hz, 3H), 1.21 (t, $J = 3.98$ Hz, 3H), 2.13 (m, 2H), 2.34 (m, 2H), 2.47 (s, 1H), 3.15 (d, d, $J = 7.39$ Hz, $J = 7.39$ Hz, 1H), 3.47 (d, d, $J = 5.72$ Hz, 1H), 3.56 (d, $J = 4.50$ Hz, 2H), 4.10−4.17 (m, 4H), 7.54 (t, $J = 7.35$ Hz, 2H), 7.63 (t, $J = 7.26$ Hz, 1H), 7.88 (d, $J = 7.25$, 2H); ^{13}C NMR δ 172.7, 172.0, 139.4, 133.8,

129.4, 127.9, 62.5, 61.8, 61.7, 58.5, 56.6, 43.4, 39.3, 36.2, 35.5, 14.0, 13.97; MS (*m*/*z*): 399 ($M^+ + 1$), 381, 353, 335, 307, 261, 239, 211, 183, 173, 165, 153, 137, 107, 93, 77. Anal. Calcd for $C_{19}H_{26}O_7S$: C, 57.27; H, 6.58. Found: C, 57.13; H, 6.59.

3-Hydroxymethyl-4-(toluene-4-sulfonylmethyl)tetrahydrofuran (6c). The reaction of resin **2b** (0.5 g), diallyl ether (294 mg, 3 mmol), and AIBN (24 mg, 0.15mol), followed by workup using method B, afforded 120 mg (67%) of **6c** (mixture of diastereoisomers): oil; IR 3424, 2939, 2874, 1597, 1301, 1145, 1087, 820, 768, 561 cm^{-1}; ^1H NMR δ 2.46 (s, 3H), 2.50 (m, 1H), 2.52 (s, 1H), 2.80 (m, 1H), 3.18 (m, 1H), 3.40 (m, 1H), 3.60 (m, 4H), 3.87 (m, 1H), 3.99 (m, 1H), 7.37 (d, $J = 7.98$ Hz, 2H), 7.78 (d, $J = 8.00$ Hz, 2H); ^{13}C NMR δ 145.1, 136.2, 130.1, 128.0, 72.9 (weak), 71.9, 70.5, 70.0 (weak), 63.6 (weak), 61.2, 59.6 (weak), 55.2, 47.3 (weak), 43.3, 36.8 (weak), 35.4, 21.7; MS (*m*/*z*) 272 ($M^+ + 2$), 271 ($M^+ + 1$), 253, 223, 157, 139, 113, 105, 97, 96, 91, 81, 65, 41. Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.76; H, 6.71. Found: C, 57.71; H, 6.73.

3-Benzenesulfonylmethyl-4-hydroxymethyltetrahydrofuran (6d). The reaction of resin **2a** (0.5 g), diallyl ether (294 mg, 3 mmol), and AIBN (24 mg, 0.15 mol), followed by workup using method B, afforded 115 mg (69%) of **6d** (mixture of diastereoisomers): oil; IR 3422, 3064, 2932, 2876, 1585, 1480, 1447, 1305, 1146, 1085, 1051, 749, 689, 562 cm^{-1}; ^1H NMR δ 2.30 (s, 1H), 2.52 (m, 1H), 2.83 (m, 1H), 3.20 (m, 1H), 3.56 (m, 1H), 3.65 (m, 4H), 3.88 (m, 1H), 3.99 (m, 1H), 7.59 (t, $J = 7.44$ Hz, 2H), 7.68 (t, $J = 7.60$ Hz, 1H), 7.92 (d, $J = 7.11$ Hz, 2H); ^{13}C NMR δ 139.2, 134.0, 129.5, 127.9, 72.9 (weak), 71.9, 70.5, 70.0 (weak), 63.6 (weak), 61.3, 59.6 (weak), 55.1, 47.3 (weak), 43.3, 36.7 (weak), 35.3; MS (*m*/*z*) 257 ($M^+ + 1$), 239, 196, 183, 143, 125, 114, 101, 97, 96, 83, 77, 67, 55, 41. Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.11; H, 6.31.

Diethyl-3-phenylselanylmethyl-4-(toluene-4-sulfonylmethyl)cyclopentane-1,1-dicarboxylate (7a) (Mixture of Diastereoisomers).[8c] Oil; IR 3060, 2980, 2934, 1727, 1597, 1579, 1478, 1438, 1302, 1260, 1181, 1148, 1088, 739, 562 cm^{-1}; ^1H NMR δ 1.20−1.25 (m, 6H), 2.28 (m, 1H), 2.38 (m, 2H), 2.43 (m, 3H), 2.52 (m, 3H), 2.70 (m, 1H), 2.86 (m, 1H), 3.01 (m, 1H), 3.18 (m, 1H), 4.13−4.19 (m, 4H), 7.24 (m, 3H), 7.34 (d, $J = 8.17$ Hz, 2H), 7.43 (m, 2H), 7.76 (d, $J = 8.21$ Hz, 2H); ^{13}C NMR δ 172.3, 171.9, 144.8, 136.5, 133.0, 130.0, 129.5, 129.2, 128.0, 127.2, 61.8, 61.7, 58.3 (C_4), 55.9 ($-SO_2CH_2-$), 42.2, 38.8, 37.9, 37.0, 27.9 ($-SeCH_2-$), 21.6, 14.02, 14.01; MS (*m*/*z*) 552 (M^+), 507, 395, 349, 275, 239, 193, 165, 139, 119, 91, 77, 65.

3-Phenylselanylmethyl-4-(toluene-4-sulfonylmethyl)tetrahydrofuran (7b) (Mixture of Diastereoisomers). [8c] Oil; IR 3056, 2926, 2864, 1597, 1578, 1478, 1437, 1302, 1147, 1087, 1022, 816, 740, 560 cm^{-1}; ^1H NMR δ 2.41 (s, 3H), 2.52 (m, 1H), 2.68 (m, 2H), 2.87 (m, 1H), 3.09 (m, 1H), 3.30 (m, 1H), 3.66 (m, 1H), 3.72 (m, 1H), 3.84 (m, 1H), 3.92 (m, 1H), 7.22 (m, 3H), 7.33 (d, $J = 8.02$ Hz, 2H), 7.42 (m, 2H), 7.76 (d, $J = 8.27$ Hz, 2H); ^{13}C NMR δ 145.2 (145.1), 136.3, 133.0, 132.8, 130.2 (130.1), 129.4 (129.3), 128.10 (128.05), 127.43 (127.36), 72.93 (72.91 weak), 72.5, 71.5, 59.4 (weak), 54.8, 45.4 (weak), 42.0, 40.4 (weak), 37.0, 30.3 (weak), 26.1, 21.8; MS (*m*/*z*) 410 (M^+), 253, 171, 157, 139, 105, 97, 91, 83, 77, 67, 51.

3-Benzenesulfonylmethyl-4-phenylselanylmethyltetrahydrofuran (7c) (Mixture of Diastereoisomers). [8c] Oil; IR 3059, 2928, 2863, 1578, 1478, 1447, 1306, 1147, 1086, 1022, 741, 689, 561 cm^{-1}; ^1H NMR δ 2.56 (m, 1H), 2.72 (m, 2H), 2.88 (m, 1H), 3.10 (m, 1H), 3.30 (m, 1H), 3.67 (m, 1H), 3.75 (m, 1H), 3.86 (m, 1H), 3.93 (m, 1H), 7.23 (m, 3H), 7.43 (m, 2H), 7.55 (m, 2H), 7.65 (m, 1H), 7.89 (d, $J = 7.44$ Hz, 2H); ^{13}C NMR δ 139.2, 134.1, 133.1, 133.0, 129.5, 129.2, 128.0, 127.4, 72.9 (weak), 72.4, 71.5, 59.4 (weak), 54.7, 45.4 (weak), 41.9, 36.9, 30.3 (weak), 26.1; MS (*m*/*z*) 396 (M^+), 255, 239, 209, 171, 157, 143, 125, 97, 91, 77, 67, 41.

General Procedure for Oxidation−Elimination of the Cyclization Adducts from Selenosulfones and 1,6-Diene in Solution Phase. In THF (20 mL), adducts **7** (0.5 mmol) were treated by 30% H_2O_2 (2 mL) at room temperature for 0.5 h, then the mixture was stirred for 4 h at 60 °C. The reaction was quenched with water (30 mL). The mixture was extracted with chloroform (20 mL × 3), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated, and the residue was purified by preparative TLC of silica gel (hexane/ethyl acetate = 4:2) to give the product **5**.

General Procedure for Transformation of the Mixture of 5 and 6 to the Products 6 by 9-BBN. Under N_2 ,the mixture of **5** and **6**, obtained from the treatment of resin **4** (0.5 g) with 30% H_2O_2 (20 equiv) in THF at 55−60 °C for 4 h, was treated with 9-BBN (0.7 mmol) in THF at 30 °C for 4 h, followed by the addition 6 mol of NaOH (1 mL) and 30% H_2O_2 (2 mL). The mixture was then stirred at 50 °C for 1 h. The reaction was quenched with water (30 mL) and extracted with chloroform (20 mL × 3), and the combined organic layers were washed with water (20 mL × 2), dried over $MgSO_4$, filtered, and concentrated, and the residue was purified by a TLC of silica gel (hexane/ethyl acetate = 4:2) to give the product **6**.

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Supporting Information Available. ^1H NMR spectra **5a**−**h**, **6a**−**d** and ^{13}C NMR spectra of **5a**−**h**, **6a**−**d.** This material is available free of charge via the Internet at http://pubs.acs.org.

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