

A Novel 3,4-Bis(sulfenyl)- or 4-Selenenyl-3-sulfenylpenta-2,4-dienylation of Aldehydes Using 4-Ethoxy-1,2-bis(sulfenyl)- or 1-Selenenyl-2-sulfenylbuta-1,3-dienyl Lithiums

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3,4-Dichalcogenopenta-2,4-dienylation of aldehydes proceeded in good to high yields using 4-ethoxy-1-(benzenesulfenyl)-2-(methanesulfenyl)- (5), 4-ethoxy-1,2-bis(benzenesulfenyl)buta-1,3-diene (6), and 1-selenenyl derivatives 7 and 8. This novel four-carbon homologation could be applied to a synthesis of 3,4,7,8-tetrakis(benzenesulfenyl)-10,10-dimethylundeca-2,4,6,8-tetraenal (20).

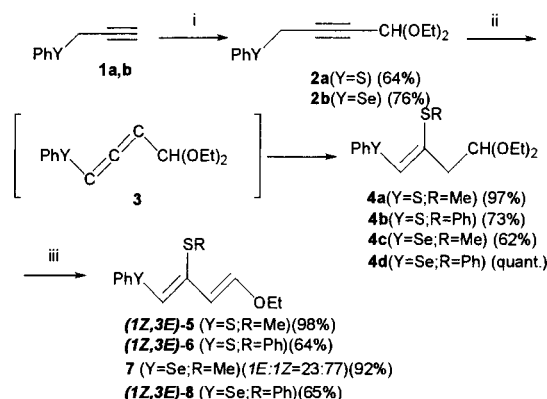
Key words 4-ethoxy-1,3-butadienyl lithium; penta-2,4-dienal; sulfur; selenium

Four-carbon homologation is one of the important processes in the syntheses of the polyene antibiotics and pheromones and other bioactive compounds.^{1–3} The most useful reagents are the triethyl phosphonoesters (Horner–Wadsworth–Emmons reagents) or the Wittig type reagents, which directly react with the aldehydes and ketones to give the penta-2,4-dienals.^{4–7} 4-Alkoxybuta-1,3-dienyl lithiums as the other useful reagents have been reported by Wollenberg or Duhamel to easily utilize the four-carbon homologation using 4-alkoxybuta-1,3-dienyl tributyltin,^{8–10} chloride and bromides;¹¹ however, more functionalized 4-alkoxybuta-1,3-dienyl lithiums have been hitherto unknown.¹² Recently, we reported the two-carbon homologations such as the α -sulfenyl^{13,14} or α -selenenyl¹⁵ formylation of aldehydes and ketones using β -alkoxyalkenyl lithiums. Next our attention has been focused on the four-carbon homologation of the carbonyl compounds. If a new 4-alkoxybuta-1,3-dienyl lithiums bearing an α - and β -sulfenyl or selenenyl functional groups would be generated, they will easily react with carbonyl compounds and the following hydrolysis to succeed a new type of four-carbon homologation of the carbonyl compounds. Now we here report a novel four-carbon homologation of aldehydes using 4-ethoxybuta-1,3-dienyl lithiums stabilized by the 1- and 2-chalcogene groups and its application to the synthesis of 2,4,6,8-nonatetraenal.

First, we show the preparations of the dienes **5**–**8** in Chart 1. Phenyl propargyl sulfide **1a** was treated with EtMgBr/CH(OEt)₃ to give the acetal **2a**, which easily isomerized to the allenyl sulfide **3** with NaOEt, the successive addition of thiophenol or 15% NaSMe in water to give (*E*)- and (*Z*)-but-3-enal acetals **4a** and (*E*)- and (*Z*)-**4b**. Treatment of (*E*)- and (*Z*)-3,4-bis(sulfenyl)but-3-enal acetals with *t*-BuOK provided the titled 4-ethoxy-1,2-bis(sulfenyl)dienes **5** and **6** in good yields. The methanesulfenyl diene **5** is so labile at room temperature that it must be immediately used at the next step. Selenium derivatives **7** and **8** were also obtained by the same methods.

Next, we examined the lithiation and the reaction of the 4-ethoxybuta-1,3-diene **5** with pivalaldehyde (Table 1). We found that **5** easily undergo lithiation with *n*-BuLi/DABCO at -50°C and react with pivalaldehyde afforded the pentadienyl alcohol **9a**. The structure of **9a** was determined by spectral and analytical data. The stereochemistry was elucidated by the ¹H-NMR coupling constants of the olefinic protons

and the NOE experiments as 4*E*,6*E*. The reaction of the dienyl lithium with aldehydes was found to stereoselectively occur by the stabilizing effect of β -heteroatom substituents of the alkenyl lithiums.^{16,17} The large excess of *n*-BuLi provided the deethoxylated penta-2,4-dienyl alcohol **10** (Entry 7).



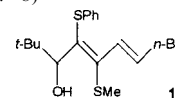
Reagents: i, EtMgBr/CH(OEt)₃/reflux; ii, NaOEt/EtOH/rt then MeSNa/reflux/2 h or PhSH/reflux/2 h; iii, *t*-BuOK/*t*-BuOH/1 h.

Chart 1

Table 1. A Lithiation and Reaction of Diene **5** with Pivalaldehyde

Entry	Condition	Products (% yield)
1	<i>n</i> -BuLi (1.5 eq)/THF/ -50°C	Recover
2	<i>t</i> -BuLi (1.5 eq)/THF/ -70°C	Recover
3	<i>t</i> -BuOK (3 eq)/ <i>n</i> -BuLi (3 eq)/THF/ -70°C	9a (34)
4	TMEDA/ <i>n</i> -BuLi (3 eq)/THF/ -50°C	Recover
5	DBU (3 eq)/ <i>n</i> -BuLi (3 eq)/THF/ -50°C	9a (30) ^{a)} 5 (14)
6	DABCO (3 eq)/ <i>n</i> -BuLi (3 eq)/THF/ -50°C	9a (60)
7	DABCO (5 eq)/ <i>n</i> -BuLi (5 eq)/THF/ -20°C	9a (53) 10 (10) ^{b)}
8	LTMP (3 eq)/THF/ -50°C	9a (40)

a) *n*-BuCH(OH)*t*-Bu was accompanied by the product **9a**. b)



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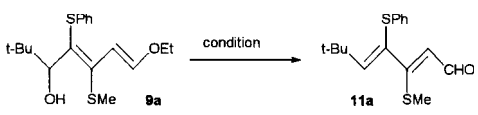
Next, we performed the conversion of the alcohol **9a** to the penta-2,4-dienals (Table 2). The desirable penta-2,4-dienal **11a** was obtained by SOCl_2 /pyridine without producing the intramolecularly cyclized products such as **12**, which could not characterize because of the existence of a lot of regio- or stereoisomers. The structure of **11a** was determined by the spectral data, which shows the characteristic pair of doublets due to the formyl proton and 2-H ($J=7$ Hz).

The penta-2,4-dienylations of other aldehydes using **5–8** were examined and the results are shown in Table 3. The reactions of **5** with aromatic and aliphatic aldehydes provided the penta-2,4-dienylated products **11b–c** in moderate yields (entries 1–2); however, the reaction with ketones such as acetophenone or acetone did not give the alcohols. The product of the reaction with propionaldehyde first provided (2*Z*,4*Z*)-**11d** as a single stereoisomer (Entry 3); however, the CDCl_3 solution of (2*Z*,4*Z*)-**11d** was stirred for overnight and

we observed it by the ^1H -NMR spectrum, exhibiting two kinds of the other doublets due to (2*E*,4*Z*)- and (2*E*,4*E*)-**11d** at 9.54 (d, $J=7$ Hz), 9.29 (d, $J=7$ Hz), 6.31 (d, $J=7$ Hz), and 5.73 (d, $J=7$ Hz). Next, we examined the lithiation and alkylation of 2-phenylsulfenylbuta-1,3-diene **6**; however, the method A was found to be not effective. 2-Phenylsulfenylbuta-1,3-diene **6** gave the alcohols by the modified Method B, then the successive treatment with SOCl_2 /pyridine afforded the penta-2,4-dienals **14a–c** (entries 4–6). The selenium analogs gave satisfactory results by the Method C and the successive reactions with SOCl_2 /pyridine (entries 7–10). The alkylation of **7** and **8** by the Methods A or B gave rise to the formation of diphenyl diselenide, which decomposed in the reaction conditions, and the yields of the products were low. We could not find the reasons; however, it is very important for the selection of the base for the α -deprotonation of the organoselenium compounds. If the formed carbanions are not utilized immediately, phenylselenenyl anion forms by the α -elimination.¹⁸⁾ When the base for the α -deprotonation of the organoselenium compounds is not suitable, the formation of the diphenyl diselenides are also observed. Potassium diisopropylamine-lithium *tert*-butoxide (KDA) has been known to act as a nonnucleophilic and strong base for the α -deprotonation of the organoselenium compounds such as the vinylic selenides and the selenoacetals.¹⁸⁾ The stereochemistries of the 2,4-pentadienylated products showing in Fig. 1 were determined by the NOE experiments. The NOE analysis indicates that the δ values for the formyl group and 2-H of 2*E*-isomers appear higher upfield than that of the 2*Z*-isomers. The stereochemistries for the other products could not be determined by the NOE experiments; however, we would speculate the stereochemistries of the other products as shown in Table 4 by supporting the chemical shifts values observed in Fig. 1.

We further investigated the penta-2,4-dienylation of aldehyde **14a** in order to clarify the scope and limitation of this methodology. 6,6-Dimethyl-3,4-bis(phenylsulfenyl)hepta-2,4-dienal **14a** reacted with the lithiated diene **6** to stereoselectively afford the alcohol **19** in 49% yield (Chart 2). Reac-

Table 2. Conversion of Penta-2,4-dien-1-ol **9a** to the Penta-2,4-dienal **11a**

		
Entry	Condition	Products (% yields)
1	TsOH(1 eq)/THF–H ₂ O(10 : 1)/reflux	11a (38)
2	TMSOTf(1 eq)/CH ₂ Cl ₂ /–78 °C	a complex mixture
3	CF ₃ SO ₃ H(1 eq)/THF–H ₂ O/0 °C	11a (32) ^{a)}
4	PPTS(1 eq)/THF–H ₂ O/reflux	Recover
5	SOCl_2 (1 eq)/pyridine(2 eq)/CH ₂ Cl ₂ /–20 °C	11a (55)
6	(CH ₃ SO ₂) ₂ O(1 eq)/ <i>i</i> -Pr ₂ NEt(2 eq)/CH ₂ Cl ₂ /–78 °C	a complex mixture
7	Polyphosphoric acid trimethylsilyl ester/ $\text{ClCH}_2\text{CH}_2\text{Cl}$ /0 °C	a complex mixture

a) Some cyclizations occurred and one type of the cyclized product **12** was shown as follows; however, they were not characterized because the products were obtained as mixtures of the stereoisomers.

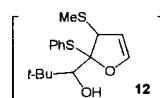


Table 3. β,γ -Bis(chalcogeno)penta-2,4-dienylation of Aldehydes

Reaction scheme showing the synthesis of aldehydes **11,14,16,18** from dienes **5-8** and aldehydes **R²CHO**. The reaction proceeds via an intermediate alcohol **9,13,15,17**. The first step uses Method A-C at 50 °C. The second step uses SOCl₂ and pyridine.

Entry	Diene 5—8		Aldehyde		Products (% yields)	
	R ¹	Y	R ²	Alcohol	Method ^{a)}	Aldehyde

1	5	Me	S	2,4,6-Trimethylphenyl	9b (57)	A	(2 <i>Z</i> ,4 <i>Z</i>)- 11b (37) (2 <i>Z</i> ,4 <i>E</i>)- 11b (10)
2	5	Me		Ph	9c (50)	A	(2 <i>Z</i> ,4 <i>Z</i>)- 11c (59)
3	5	Me		CH ₃ CH ₂	9d (47)	A	(2 <i>Z</i> ,4 <i>Z</i>)- 11d (37) 2 <i>E</i> - 11d (4 <i>Z</i> :4 <i>E</i> =41 : 59) (15)
4	6	Ph	S	<i>t</i> -Bu	13a (56)	B	(2 <i>Z</i> ,4 <i>Z</i>)- 14a (70)
5	6	Ph		Ph	13b (68)	B	(2 <i>Z</i> ,4 <i>Z</i>)- 14b (67) ^{b)}
6	6	Ph		(<i>E</i>)-PhCH=CH	13c (63)	B	(2 <i>Z</i> ,4 <i>E</i>)- 14c (75)
7	7	Me	Se	Ph	15a (54)	C	(2 <i>Z</i> ,4 <i>E</i>)- 16a (67) (2 <i>E</i>)- 16a (4 <i>Z</i> :4 <i>E</i> =65 : 35) (24)
8	7	Me		(<i>E</i>)-PhCH=CH	15b (68)	C	16b (4 <i>Z</i> :4 <i>E</i> =83 : 17) (53)
9	8	Ph	Se	Ph	17a (67)	C	(2 <i>Z</i> ,4 <i>Z</i>)- 18a (73) ^{c)}
10	8	Ph		(<i>E</i>)-PhCH=CH	17b (76)	C	(2 <i>Z</i> ,4 <i>Z</i> ,6 <i>E</i>)- 18b (39) ^{d)} (2 <i>E</i> ,4 <i>Z</i> ,6 <i>E</i>)- 18b (4 <i>Z</i> :4 <i>E</i> =72 : 28) (26)

a) Method A: DABCO(3 eq)/*n*-BuLi(3 eq)/–50 °C/THF (4 ml/1 mmol of **5**)/10 min; method B: lithium 2,2,6,6-tetramethylpiperide (LTMP)(3 eq)/–50 °C/THF (3.6 ml/1 mmol of **6**)/10 min; method C: *t*-BuOK(3 eq)/LTMP(3 eq)/–78 °C/THF (5 ml/1 mmol of **7** or **8**)/10 min. b) The diethyl acetal of **14b** was obtained in 17% yield. c) The diethyl acetal of **18a** was obtained in 12% yield. d) The diethyl acetal of **18b** was obtained in 22% yield.

Table 4. Chemical Shifts of the 2,4-Pentadienals

Compound	Chemical shifts (ppm)		Compound	Chemical shifts (ppm)	
	CHO	2-H		CHO	2-H
(2Z,4Z)-11a	9.85	6.26	(2Z,4Z)-16a	9.83	6.10
(2Z,4Z)-11b	9.95	6.36	(2E,4Z)-16a	9.32	5.66
(2Z,4E)-11b	9.91	5.63	(2E,4E)-16a	9.66	5.49
(2Z,4Z)-11c	9.95	6.31	(2E,4Z,6E)-16b	9.35	5.80
(2Z,4Z)-11d	9.96	6.24	(2E,4E,6E)-16b	9.45	5.65
(2E,4Z)-11d	9.54	6.06	(2Z,4Z)-18a	10.11	6.57
(2E,4E)-11d	9.29	5.73	(2Z,4Z,6E)-18b	10.25	6.87
(2Z,4Z)-14a	10.09	6.42	(2E,4Z,6E)-18b	9.35	5.48
(2Z,4Z)-14b	10.02	6.80	(2E,4E,6E)-18b	9.49	5.33
(2Z,4Z,6E)-14c	10.26	7.05			

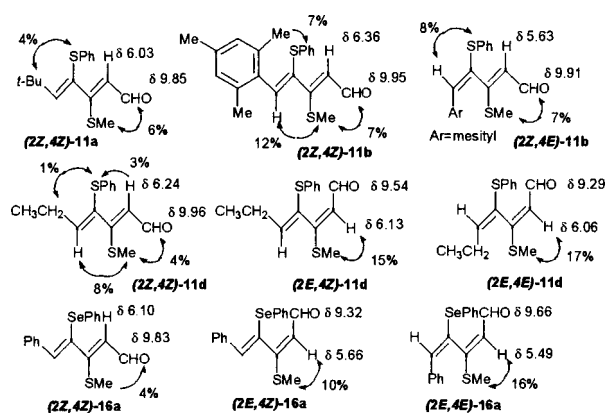
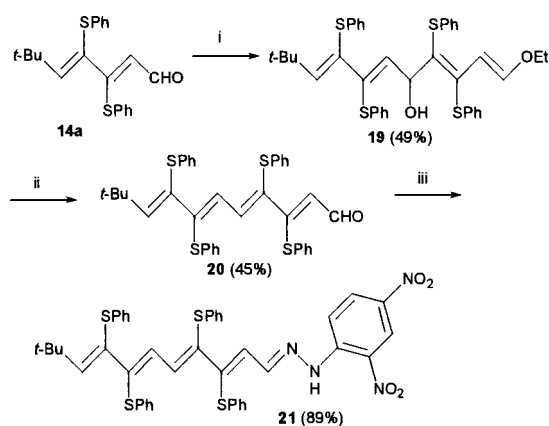


Fig. 1. NOE Enhancements of the Penta-2,4-dienals

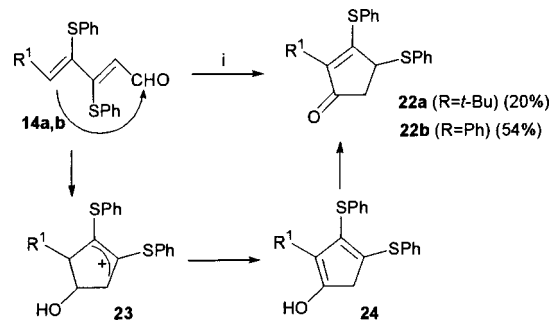


Reagents: i, $\text{PhSCH}=\text{C}(\text{SPh})\text{CH}=\text{CHOEt}/\text{LTMP}/-50^\circ\text{C}$; ii, $\text{SOCl}_2/\text{pyridine}/-20^\circ\text{C}$; iii, 2,4-dinitrophenylhydrazine/*p*-toluenesulfonic acid/benzene/reflux/10 min.

Chart 2

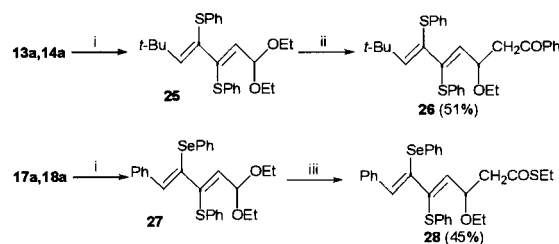
tion of **19** with $\text{SOCl}_2/\text{pyridine}$ gave 3,4,7,8-tetrakis(phenylsulfenyl)-10,10-dimethylundeca-2,4,6,8-tetraenal **20** as a single stereoisomer. The structure of **20** was determined by the IR, the ^1H - and the ^{13}C -NMR, the high-resolution mass spectrum. The aldehyde **20** is a red oil, of which converted to the corresponding hydrazone **21** and could be isolated as red needles.

These 2,3-bis(sulfenyl)penta-2,4-dienals were found to be highly reactive. The CH_2Cl_2 solution of **14a** was stirred for 30 min in the presence of a catalytic amount of *p*-toluenesul-



Reagents: i, 0.1 eq *p*-TsOH/ $\text{CH}_2\text{Cl}_2/\text{rt}$.

Chart 3



Reagents: i, $\text{CH}(\text{OEt})_3(5 \text{ eq})/\text{EtOH}/p\text{-TsOH}(0.1 \text{ eq})$; ii, 1-phenyl-1-trimethylsilyloxyethene/ $\text{BF}_3 \cdot \text{Et}_2\text{O}/-70^\circ\text{C}$; iii, 1-ethylthio-1-trimethylsilyloxyethylene/ $\text{BF}_3 \cdot \text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2/-78^\circ\text{C}$.

Chart 4

fonic acid at room temperature. The intramolecular cyclization occurred to give a cyclopentenone **22a** in 20% yield, accompanied by the other complex mixtures. The plausible mechanism for this cyclization is shown in Chart 3. The formyl group of the diene would be activated by the protic acid. The nucleophilic double bond attacks to the carbonyl carbon to give the allylic cation **23**. It would undergo isomerization to the cyclopentenone via the dienol **24**. 5-Phenyl substituted pentadienal **14b** also underwent acid-promoted cyclization to afford the cyclopentenone **22b**.

Both the pentadienyl alcohol **13a**, **17a**, and the penta-2,4-dienals **14a**, **18a** easily converted to the corresponding acetals **25** and **27**, respectively. Although the sulfur and selenium functional groups could stabilize the carbenium ions,^{19–22} we investigated Lewis-acid promoted nucleophilic substitution reaction of these acetals with some nucleophiles. Reaction of **25** with the 1-phenyl-1-trimethylsilyloxyethene gave the alkylated dienone **26** in 51% yield (Chart 4). The reaction of **27** with 1-ethylthio-1-trimethylsilyloxyethylene gave the thio ester **28**.

We have here showed that the penta-2,4-dienylations with aldehydes using 4-ethoxy-1,2-bis(sulfenyl)- or 1-sulfenyl-2-selenenylbuta-1,3-dienes proceeded in moderate to good yields. The penta-2,4-dienals and the acetals are highly reactive and converted to the more useful compounds. The aldehyde **20**, obtained by the second pentadienylation reaction, has a unique alkattetraenal structure. Now we are studying the photo-reactions of the 3,4,7,8-tetrakis(sulfenyl)-2,4,6,8-alkattetraenals. These results will be reported elsewhere.

Experimental

Melting points were determined on Yanagimoto micro-melting point apparatus and are uncorrected. Elemental analyses were performed at the Center of Instrumentation of Gifu University. ^1H - and ^{13}C -NMR spectra were

determined with a JEOL ECA (500 MHz) spectrometer at the Center of Instrumentation of Gifu University. Chemical shifts are expressed in ppm with respect to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s=singlet, d=doublet, t=triplet and q=quartet. *J* values are given in Hz. IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IR A-100 infrared spectrometer. Electron impact mass spectra (EI-MS) were obtained using a JEOL GCmate spectrometer with a direct insertion probe at an ionization voltage of 70 eV.

Preparations of 4-Benzenesulfonyl- (2a) or 4-Benzeneselenenyl-but-2-ynal Diethyl Acetals (2b) Thiophenol (11.0 g, 0.10 mol) was added dropwise to an ether (100 ml) solution of propargyl bromide (11.9 g, 0.10 mol) and triethylamine (20.2 g, 0.20 mol) at 0 °C. The mixture was stirred for 2 h at room temperature. The precipitates were filtered off and washed with ether. The combined ether solution was poured into water (200 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over MgSO_4 . The solvent was removed under reduced pressure. The residue was almost pure propargyl phenyl sulfide (**1a**) (quant.) and used to the next step without any purification. An ether (20.0 ml) solution of phenyl propargyl sulfide (6.08 g, 41.0 mmol) was added dropwise to an ether (100 ml) solution of ethyl magnesium bromide (prepared from EtBr (6.70 g, 61.5 mmol) and Mg (1.50 g, 61.5 mmol)) at room temperature. The reaction mixture was refluxed for 30 min. Triethyl orthoformate (36.5 g, 246 mmol) was added to the mixture. After the further reflux for 2 h, the whole was poured into water (300 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over MgSO_4 . The solvent and triethyl orthoformate were removed under reduced pressure. The residue was purified by the column chromatography on silica gel eluting with AcOEt-*n*-hexane (1:10) to give 4-benzenesulfonylbut-2-ynal diethyl acetal (**2a**) (6.57 g, 64%) as a yellow oil. IR (film, cm^{-1}) ν 2200 (acetylene); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.18 (6H, t, $J=7$ Hz, $\text{Me}\times 2$), 3.48–3.54 (2H, m, CH_2), 3.59–3.65 (2H, m, CH_2), 3.67 (2H, d, $J=2$ Hz, SCH_2), 5.23 (1H, t, $J=2$ Hz, CH), 7.23–7.29 (1H, m, ArH), 7.30–7.33 (2H, m, ArH), 7.42–7.45 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 15.22 (q $\times 2$), 22.94 (t), 60.93 (t $\times 2$), 78.94 (s), 81.72 (s), 91.46 (d), 127.13 (d), 129.11 (d $\times 2$), 130.48 (d $\times 2$), 135.03 (s); EI-MS m/z 250 (M^+). *Anal.* Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S}$: C, 67.17; H, 7.25. Found: C, 67.02; H, 7.23.

4-Benzeneselenenylbut-2-ynal Diethyl Acetal (2b) 76%, pale yellow oil, IR (film, cm^{-1}) ν 2200 (acetylene); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.19 (6H, t, $J=7$ Hz, $\text{Me}\times 2$), 3.47–3.53 (2H, m, CH_2), 3.55 (2H, d, $J=2$ Hz, SeCH_2), 3.60–3.67 (2H, m, CH_2), 5.24 (1H, t, $J=2$ Hz, CH), 7.26–7.30 (3H, m, ArH), 7.57–7.60 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 12.64 (q $\times 2$), 15.25 (t $\times 2$), 60.90 (t), 79.15 (s), 82.75 (s), 91.53 (d), 127.90 (d), 129.27 (d $\times 2$), 129.58 (s), 133.66 (d $\times 2$); EI-MS m/z 298 (M^+). *Anal.* Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Se}$: C, 56.57; H, 6.10. Found: C, 56.18; H, 6.14.

Preparations of 3,4-Diorganylchalcogenobut-3-enal Acetals 4a—d (Typical Procedure) 4-Benzenesulfonylbut-2-ynal diethyl acetal (**2a**) (4.30 g, 17.1 mmol) was added dropwise to an EtOH (100 ml) solution of EtONa (prepared from Na (3.90 g, 0.17 mol) and EtOH (100 ml)). The reaction mixture was stirred for 30 min. Then the 15% NaSeMe water solution (20.0 ml) was added to the mixture. The whole was refluxed for 4 h and then poured into water (300 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over MgSO_4 . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-*n*-hexane (1:20). 3*Z*- and 3*E*-4-benzenesulfonyl-3-(methanesulfonyl)but-3-enal diethyl acetal (**4a**) (4.95 g, 97%) was obtained as a pale yellow oil. The stereochemistries of 3*Z* and 3*E*-isomers were determined by NOE experiments irradiating the olefinic H of *E*-isomer at δ 5.89 ppm. The intensity of the methylsulfonyl group was increased; however, that of *Z*-isomer could not be observed. IR (film, cm^{-1}) ν 1120, 1060 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.21 (t, $J=7$ Hz, *Z*- and *E*-Me), 2.33 (s, *Z*-SMe), 2.34 (s, *E*-SMe), 2.67 (dd, $J=1$, 6 Hz, *Z*- CH_2), 2.87 (d, $J=6$ Hz, *E*- CH_2), 3.50–3.57 (m, OCH_2), 3.65–3.73 (m, OCH_2), 4.73 (t, *Z*-CHO), 4.75 (t, $J=6$ Hz, CHO), 5.89 (s, *E*-olefinic H), 6.41 (d, $J=6$ Hz, *Z*-olefinic H), 7.19–7.40 (m, ArH); EI-MS m/z 298 (M^+). *Anal.* Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{S}_2$: C, 60.37; H, 7.43. Found: C, 60.16; H, 7.28.

3*Z*- and 3*E*-3,4-Bis(benzenesulfonyl)but-3-enal Diethyl Acetal (4b) 73%, yellow oil, IR (film, cm^{-1}) ν 1120, 1060 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.15 (t, $J=7$ Hz, *Z*-Me), 1.20 (t, $J=7$ Hz, *E*-Me), 2.57 (d, $J=5$ Hz, *Z*- CH_2), 2.79 (d, $J=6$ Hz, *E*- CH_2), 3.38–3.45 (m, OCH_2), 3.58–3.62 (m, OCH_2), 4.66 (t, $J=5$ Hz, *Z*-CHO), 4.80 (t, $J=6$ Hz, *E*-CHO), 6.54 (s, *E*-olefinic H), 6.77 (s, *Z*-olefinic H), 7.20–7.42 (m, ArH); EI-MS m/z 360 (M^+). *Anal.* Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{S}_2$: C, 66.63; H, 6.71. Found: C, 66.66; H,

6.90.

3*Z*- and 3*E*-4-(Benzeneselenenyl)-3-(methanesulfonyl)but-3-enal Diethyl Acetal (4c) 62%, yellow oil, IR (film, cm^{-1}) ν 1120, 1060 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.20 (t, $J=7$ Hz, *Z*-Me), 1.22 (t, $J=7$ Hz, *E*-Me $\times 2$), 2.04 (s, *Z*-Me), 2.31 (s, *E*-SMe), 2.65 (d, $J=6$ Hz, *Z*- CH_2), 2.84 (d, $J=6$ Hz, *E*- CH_2), 3.50–3.57 (m, OCH_2), 3.67–3.74 (m, OCH_2), 4.70 (t, $J=5$ Hz, *E*-CHO), 4.73 (t, $J=6$ Hz, *Z*-CHO), 6.13 (s, *E*-olefinic H), 6.66 (s, *Z*-olefinic H), 7.20–7.29 (m, ArH), 7.42–7.45 (m, ArH); EI-MS m/z 346 (M^+). *Anal.* Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{SSe}$: C, 52.17; H, 6.42. Found: C, 52.10; H, 6.37.

3*Z*- and 3*E*-4-(Benzeneselenenyl)-3-(benzenesulfonyl)but-3-enal Diethyl Acetal (4d) Quant., yellow oil, IR (film, cm^{-1}) ν 1120, 1060 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.15 (t, $J=7$ Hz, *Z*-Me), 1.21 (t, $J=7$ Hz, *E*-Me), 2.55 (d, $J=6$ Hz, *Z*-olefinic H), 2.76 (d, $J=6$ Hz, *E*-olefinic H), 3.48–3.53 (m, OCH_2), 3.65–3.69 (m, OCH_2), 4.67 (t, $J=6$ Hz, *Z*-olefinic H), 4.74 (t, $J=6$ Hz, *E*-olefinic H), 6.83 (s, *E*-olefinic H), 7.23–7.44 (m, ArH); EI-MS m/z 408 (M^+). *Anal.* Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{SSe}$: C, 58.96; H, 5.94. Found: C, 58.77; H, 5.89.

Preparation of (1*Z*,3*E*)-1-Benzenesulfonyl-2-ethoxy-3-(methanesulfonyl)buta-1,3-diene (5) (Typical Procedure) *t*-BuOK (3.76 g, 33.5 mmol) was added to a solution of 3*Z*- and 3*E*-4-(benzenesulfonyl)-3-(methanesulfonyl)but-3-enal diethyl acetal (**4a**) (1.0 g, 3.35 mmol) in *t*-BuOH (30 ml). The reaction mixture was refluxed for 1 h and then poured into water (150 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over MgSO_4 . The solvent was removed under reduced pressure. The residue was purified with column chromatography on silica gel eluting with AcOEt-*n*-hexane (1:100). (1*Z*,3*E*)- and (1*E*,3*E*)-1-benzenesulfonyl-4-ethoxy-2-(methanesulfonyl)buta-1,3-diene (**5**) (0.85 g, 97%) (1*Z*: 1*E*=85:15) was obtained as a pale yellow oil. The diene should be used immediately. IR (film, cm^{-1}) ν 1200–900 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.30 (t, $J=7$ Hz, *E*-Me), 1.31 (t, $J=7$ Hz, *Z*-Me), 2.04 (s, *E*-Me), 2.29 (s, *Z*-Me), 3.83 (q, $J=7$ Hz, OCH_2), 3.89 (q, $J=7$ Hz, OCH_2), 5.59 (d, $J=12$ Hz, *E*-olefinic H), 5.97 (s, *Z*-olefinic H), 6.07 (d, $J=12$ Hz, *Z*-olefinic H), 6.39 (s, *E*-olefinic H), 6.91 (d, $J=12$ Hz, *E*-olefinic H), 7.08 (d, $J=12$ Hz, *Z*-olefinic H), 7.16–7.23 (m, ArH), 7.24–7.33 (m, ArH); $^{13}\text{C-NMR}$ of *Z*-5 δ : 14.92 (q), 16.45 (q), 66.12 (t), 102.38 (d), 114.25 (d), 126.28 (d), 128.36 (d $\times 2$), 128.36 (d $\times 2$), 136.18 (s), 137.09 (s), 152.45 (d); high-resolution mass calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{S}_2$: 252.0643, found m/z 252.0629.

(1*Z*,3*E*)-1,2-Bis(benzenesulfonyl)-4-ethoxybuta-1,3-diene (6) 64%, yellow oil, IR (film, cm^{-1}) ν 1620, 1180, 1080 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.23 (3H, t, $J=7$ Hz, Me), 3.79 (2H, q, $J=7$ Hz, OCH_2), 6.01 (1H, d, $J=12$ Hz, olefinic H), 6.50 (1H, s, olefinic H), 7.05 (1H, d, $J=12$ Hz, olefinic H), 7.20–7.40 (10H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.66 (q), 66.15 (t), 101.87 (d), 125.97 (d), 126.69 (d), 126.74 (d), 128.03 (s), 128.15 (d–2), 128.94 (d $\times 2$), 129.10 (d $\times 2$), 129.14 (d $\times 2$), 135.47 (s), 136.19 (s), 153.61 (d); EI-MS m/z 314 (small M^+). *Anal.* Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}_2$: C, 68.75; H, 5.77. Found: C, 68.32; H, 5.68.

(1*Z*,3*E*)- and (1*E*,3*E*)-1-(Benzeneselenenyl)-4-ethoxy-2-(methanesulfonyl)buta-1,3-diene (7) 92%, 1*Z*: 1*E*=77:23. The stereochemistry of each isomer was determined by the NOE experiments. Irradiation of the olefinic H of the 1*E* isomer at δ 6.63 ppm increased the intensity of the methanesulfonyl group. Yellow oil, IR (film, cm^{-1}) ν 1220–1000 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.29 (t, $J=7$ Hz, *E*-Me), 1.32 (t, $J=7$ Hz, *Z*-Me), 2.28 (s, *E*-SMe), 2.32 (s, *Z*-Me), 3.83 (q, $J=7$ Hz, *E*- OCH_2), 3.87 (2H, q, $J=7$ Hz, *Z*- OCH_2), 5.56 (q, $J=12$ Hz, *E*-olefinic H), 5.98 (d, $J=12$ Hz, *Z*-olefinic H), 6.21 (s, *Z*-olefinic H), 6.63 (s, *E*-olefinic H), 6.89 (d, $J=12$ Hz, *E*-olefinic H), 7.07 (d, $J=12$ Hz, *Z*-olefinic H), 7.21–7.36 (3H, m, ArH), 7.42–7.49 (1H, m, ArH), 7.53–7.62 (1H, m, ArH); $^{13}\text{C-NMR}$ of (1*Z*,3*E*) (125 MHz, CDCl_3) δ : 14.95 (q), 16.35 (q), 66.20 (t), 103.94 (d), 110.56 (d), 126.95 (d), 129.42 (d $\times 2$), 131.25 (d $\times 2$), 135.79 (s), 136.63 (s), 152.55 (d); EI-MS m/z 300 (M^+). *Anal.* Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{SSe}$: C, 52.17; H, 5.39. Found: C, 51.97; H, 5.26.

(1*Z*,3*E*)-1-(Benzeneselenenyl)-2-(benzenesulfonyl)-4-ethoxybuta-1,3-diene (8) 65%, yellow oil, IR (film, cm^{-1}) ν 1180, 1020 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.22 (3H, t, $J=7$ Hz, Me), 3.77 (2H, q, $J=7$ Hz, OCH_2), 5.88 (1H, d, $J=12$ Hz, olefinic H), 6.77 (1H, s, olefinic H), 7.05 (1H, d, $J=12$ Hz, olefinic H), 7.13–7.16 (1H, m, ArH), 7.23–7.30 (7H, m, ArH), 7.47–7.49 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.66 (q), 66.25 (t), 103.20 (d), 124.07 (d), 126.02 (d), 127.25 (d), 128.33 (d $\times 2$), 128.93 (d $\times 2$), 129.29 (d $\times 2$), 129.38 (s), 130.78 (s), 131.86 (d $\times 2$), 136.01 (s), 153.89 (d); EI-MS m/z 362 (M^+). *Anal.* Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2\text{SSe}$: C, 59.83; H, 5.02. Found: C, 59.35; H, 4.89.

Lithiation and Reaction of 1,3-Butadienes with Aldehydes (Typical

Procedure Under an Ar atmosphere, a *n*-BuLi was added dropwise to a THF (6 ml) solution of (1*Z*,3*E*)-4-ethoxy-2-(methanesulfonyl)-1-(phenylsulfonyl)-1,3-butadiene (**5**) (0.35 g, 1.38 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.78 g, 6.92 mmol) at -30°C . The reaction mixture was stirred for 10 min and then cooled at -50°C . A THF (2 ml) solution of the corresponding aldehydes was added to the mixture. The whole was stirred for 10 min and poured into water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over MgSO_4 . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt -*n*-hexane (1 : 20) to give (4*E*,6*E*)-4-benzenesulfonyl-7-ethoxy-5-(methanesulfonyl)-2,2-dimethylhepta-4,6-dien-3-ol (**9a**) (0.28 g, 60%) as a yellow oil. IR (film, cm^{-1}) ν 3480 (OH); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 0.97 (9H, s, Me $\times$ 3), 1.18 (3H, t, $J=7$ Hz, Me), 2.22 (3H, s, SMe), 2.73 (1H, d, $J=11$ Hz, OH), 3.56–3.59 (1H, m, OCH_2), 3.67–3.70 (1H, m, OCH_2), 5.27 (1H, d, $J=11$ Hz, OCH_2), 5.92 (1H, d, $J=13$ Hz, olefinic H), 7.10 (1H, d, $J=13$ Hz, olefinic H), 7.09–7.12 (2H, m, ArH), 7.21–7.26 (3H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.48 (q), 18.42 (q), 26.67 (q $\times$ 3), 37.56 (s), 65.57 (t), 78.27 (d), 103.95 (d), 125.33 (d), 126.78 (d $\times$ 2), 128.84 (d $\times$ 2), 132.80 (s), 137.36 (s), 141.86 (s), 155.25 (d); m/z 400 (M^+). *Anal.* Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_5\text{S}_2$: C, 63.86; H, 7.74. Found: C, 63.48; H, 7.46. The NOE enhancement of **9a** was observed 3% at the α -H of the hydroxy group by irradiating the methyl protons of the methanesulfonyl group at δ 2.22 ppm.

(4*E*,6*E*)-4-(Benzenesulfonyl)-5-(methanesulfonyl)-2,2-dimethylundeca-4,6-dien-3-ol (10) 10%, pale yellow oil, IR (film, cm^{-1}) ν 3480 cm^{-1} (OH); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 0.80 (3H, t, $J=7$ Hz, Me), 0.98 (9H, s, Me $\times$ 3), 1.07–1.32 (4H, m, CH_2), 1.94–2.11 (2H, m, CH_2), 2.17 (3H, s, SMe), 2.80 (1H, d, $J=11$ Hz, OH), 5.24 (1H, d, $J=11$ Hz, CHO), 6.19 (1H, dt, $J=7, 15$ Hz, olefinic H), 6.40 (1H, dt, $J=15, 1$ Hz, olefinic H), 7.07–7.12 (1H, m, ArH), 7.13–7.30 (3H, m, ArH), 7.38–7.41 (1H, m, ArH); EI-MS m/z 350 (M^+). *Anal.* Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_5\text{S}_2$: C, 68.52; H, 8.63. Found: C, 68.88; H, 8.47.

(2*E*,4*E*)-2-(Benzenesulfonyl)-5-ethoxy-3-(methanesulfonyl)-1-mesitylpenta-2,4-dien-1-ol (9b) 57%, pale yellow oil, IR (film, cm^{-1}) ν 3450 (OH), 1610, 1190 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.18 (3H, t, $J=7$ Hz, Me), 2.04 (3H, s, Me), 2.15 (3H, s, Me), 2.37 (6H, s, Me $\times$ 2), 3.04 (1H, brs, OH), 3.57–3.61 (1H, m, OCH_2), 3.68–3.71 (1H, m, OCH_2), 6.06 (1H, d, $J=12$ Hz, olefinic H), 6.49 (1H, d, $J=5$ Hz, CHO), 6.75 (2H, s, ArH), 7.05–7.18 (6H, m, olefinic and ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.51 (q), 18.03 (q), 20.74 (q), 21.41 (q $\times$ 2), 65.60 (t), 73.02 (d), 104.22 (d), 125.35 (d), 127.37 (d $\times$ 2), 128.68 (d $\times$ 2), 129.89 (d $\times$ 2), 134.54 (s), 135.25 (s), 136.57 (s), 136.86 (s $\times$ 2), 137.27 (s), 141.01 (s), 154.76 (d); high-resolution mass calcd for $\text{C}_{23}\text{H}_{28}\text{O}_5\text{S}_2$: 400.1531, found m/z 400.1512.

(2*E*,4*E*)-2-(Benzenesulfonyl)-5-ethoxy-3-(methanesulfonyl)-1-phenylpenta-2,4-dien-1-ol (9c) 50%, yellow oil, IR (film, cm^{-1}) ν 3460 (OH); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.18 (3H, t, $J=7$ Hz, Me), 2.30 (3H, s, SMe), 3.07 (1H, d, $J=8$ Hz, OH), 3.62–3.70 (2H, m, OCH_2), 6.02 (1H, d, $J=12$ Hz, olefinic H), 6.61 (1H, d, $J=8$ Hz, CHO), 7.04–7.33 (9H, m, olefinic and ArH), 7.41–7.42 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.48 (q), 18.59 (q), 65.70 (t), 73.58 (d), 103.62 (d), 125.47 (d), 125.83 (d $\times$ 2), 127.18 (d), 127.24 (d $\times$ 2), 128.15 (d $\times$ 2), 128.77 (d $\times$ 2), 133.89 (s), 136.35 (s), 140.71 (s), 142.48 (s), 155.56 (d); high-resolution mass calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5\text{S}_2$: 358.1061, found m/z 358.1085.

(4*E*,6*E*)-4-(Benzenesulfonyl)-7-ethoxy-5-(methanesulfonyl)hepta-4,6-dien-3-ol (9d) 47%, yellow oil, IR (film, cm^{-1}) ν 3450 (OH), 1620, 1190 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 0.93 (3H, t, $J=7$ Hz, Me), 1.20 (3H, t, $J=7$ Hz, Me), 1.55–1.69 (4H, m, CH_2), 2.27 (3H, s, SMe), 2.45 (1H, d, $J=9$ Hz, OH), 3.68 (2H, q, $J=7$ Hz, OCH_2), 5.24 (1H, d, $J=9$ Hz, CHO), 6.05 (1H, d, $J=12$ Hz, olefinic H), 7.08–7.11 (1H, m, ArH), 7.16–7.23 (6H, m, olefinic and ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 10.27 (q), 14.47 (q), 18.50 (q), 30.25 (t), 65.65 (t), 74.31 (d), 103.76 (d), 125.31 (d), 126.96 (d $\times$ 2), 128.78 (d $\times$ 2), 134.45 (s), 136.68 (s), 140.49 (s), 155.07 (d); high-resolution mass calcd for $\text{C}_{16}\text{H}_{22}\text{O}_5\text{S}_2$: 310.1061, found m/z 310.1073.

(4*E*,6*E*)-4,5-Bis(benzenesulfonyl)-7-ethoxy-2,2-dimethylhepta-4,6-dien-3-ol (13a) 56%, pale yellow oil, IR (film, cm^{-1}) ν 3500 (OH), 1610, 1190 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.00 (9H, s, Me $\times$ 3), 1.02 (3H, t, $J=7$ Hz, Me), 2.78 (1H, d, $J=11$ Hz, OH), 3.42–3.46 (1H, m, OCH_2), 3.53–3.56 (1H, m, OCH_2), 5.30 (1H, d, $J=11$ Hz, CHO), 6.11 (1H, d, $J=12$ Hz, olefinic H), 7.01 (1H, d, $J=11$ Hz, olefinic H), 7.08–7.25 (8H, m, ArH), 7.36–7.37 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.33 (q), 26.78 (q $\times$ 3), 37.61 (s), 65.66 (t), 78.48 (d), 104.90 (d), 125.86 (d), 125.87 (d), 127.93 (d $\times$ 2), 128.22 (d $\times$ 2), 128.80 (d $\times$ 2), 128.84 (d $\times$ 2), 136.28 (s), 136.82 (s), 137.40 (s), 137.55 (s), 156.06 (d); high-resolution mass calcd for

$\text{C}_{25}\text{H}_{28}\text{O}_5\text{S}_2$: 400.1531, found m/z 400.1535.

(2*E*,4*E*)-2,3-Bis(benzenesulfonyl)-5-ethoxy-1-phenylpenta-2,4-dien-1-ol (13b) 68%, yellow oil, IR (film, cm^{-1}) 3460 (OH), 1620, 1190 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.03 (3H, t, $J=7$ Hz, Me), 2.95 (1H, d, $J=9$ Hz, OH), 3.45–3.55 (2H, m, OCH_2), 6.18 (1H, d, $J=12$ Hz, olefinic H), 6.67 (1H, d, $J=9$ Hz, CHO), 7.12–7.26 (9H, m, olefinic and ArH), 7.38–7.40 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.30 (q), 65.77 (t), 73.69 (d), 104.65 (d), 125.76 (d), 125.92 (d $\times$ 2), 126.02 (d), 127.23 (d), 127.89 (d $\times$ 2), 128.03 (d $\times$ 2), 128.06 (d $\times$ 2), 128.75 (d $\times$ 2), 129.01 (d $\times$ 2), 135.89 (s), 136.25 (s), 136.33 (s), 137.59 (s), 141.98 (s), 156.42 (d); high-resolution mass calcd for $\text{C}_{25}\text{H}_{24}\text{O}_5\text{S}_2$: 420.1218, found m/z 420.1211.

(1*E*,4*E*,6*E*)-4,5-Bis(benzenesulfonyl)-7-ethoxy-1-phenylhepta-1,4,6-trien-3-ol (13c) 63%, yellow oil, IR (film, cm^{-1}) ν 3250 (OH), 1610, 1200 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.10 (3H, t, $J=7$ Hz, Me), 2.72 (1H, d, $J=9$ Hz, OH), 3.60 (2H, q, $J=7$ Hz, OCH_2), 6.07–6.12 (2H, m, CHO and olefinic H), 6.30 (1H, d, $J=12$ Hz, olefinic H), 6.49 (1H, d, $J=14$ Hz, olefinic H), 7.11–7.38 (16H, m, olefinic and ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.42 (q), 66.06 (t), 73.52 (d), 105.10 (d), 125.92 (d), 126.07 (d), 126.48 (d $\times$ 2), 127.50 (d), 127.94 (d $\times$ 2), 127.97 (d $\times$ 2), 128.33 (d $\times$ 2), 128.97 (d $\times$ 2), 129.11 (d $\times$ 2), 129.64 (d), 130.61 (d), 136.01 (s), 136.38 (s), 136.52 (s), 136.61 (s), 136.73 (s), 156.51 (d); high-resolution mass calcd for $\text{C}_{27}\text{H}_{26}\text{O}_5\text{S}_2$: 446.1374, found m/z 446.1440.

Preparation of 2-(Benzeneselenenyl)-5-ethoxy-3-(methanesulfonyl)-1-phenylpenta-2,4-dien-1-ol (15a) (Method B) (Typical Procedure) *n*-BuLi (1.70 ml, 2.51 mmol) was added to a THF (3.0 ml) solution of 2,2,6,6-tetramethylpiperidine (0.35 g, 2.51 mmol) and *t*-BuOK (0.28 g, 2.51 mmol) at -78°C under an Ar atmosphere. The mixture was stirred for 10 min, and then a THF (2 ml) solution of 1-benzeneselenenyl-4-ethoxy-2-methanesulfonylbuta-1,3-diene (**7**) (0.25 g, 0.84 mmol) was added dropwise to the mixture. A THF (1.0 ml) solution of benzaldehyde (0.27 g, 2.51 mmol) was added to the reaction mixture. The whole was stirred for 10 min and poured into water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over MgSO_4 . The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt -*n*-hexane (1 : 20). The title compound (0.17 g, 54%) was obtained as a yellow oil.

15a: IR (film, cm^{-1}) ν 3450 (OH), 1610, 1180 (C–O); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.17 (3H, t, $J=7$ Hz, Me), 2.29 (3H, s, Me), 2.96 (1H, d, $J=9$ Hz, OH), 3.57–3.65 (2H, m, OCH_2), 5.98 (1H, d, $J=12$ Hz, olefinic H), 6.65 (1H, d, $J=9$ Hz, CHO), 7.10–7.30 (11H, m, olefinic and ArH), 7.41–7.43 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.47 (q), 18.67 (q), 65.53 (t), 73.67 (d), 105.43 (d), 125.79 (d $\times$ 2), 126.16 (d), 127.14 (d), 128.12 (d $\times$ 2), 128.94 (d $\times$ 2), 130.03 (d $\times$ 2), 131.74 (s), 135.79 (s), 138.75 (s), 142.61 (s), 155.36 (d); MS m/z 406 (small M^+).

(1*E*,4*E*,6*E*)-4-(Benzeneselenenyl)-7-ethoxy-5-(methanesulfonyl)-1-phenylhepta-1,4,6-trien-3-ol (15b) 68%, IR (film, cm^{-1}) ν 3430 (OH); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.18 (3H, t, $J=7$ Hz, Me), 2.27 (3H, s, Me), 2.91 (1H, brs, OH), 3.61–3.67 (2H, m, OCH_2), 6.05 (1H, d, $J=12$ Hz, olefinic H), 6.11 (1H, dd, $J=6, 1$ Hz, 3-H), 6.20 (1H, dd, $J=6, 16$ Hz, 2-H), 6.63 (1H, dd, $J=16, 1$ Hz, 1-H), 7.10–7.26 (9H, m, olefinic and ArH), 7.40–7.53 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.33 (q), 18.46 (q), 65.45 (t), 73.31 (d), 105.43 (d), 126.05 (d), 126.31 (d $\times$ 2), 127.32 (d), 128.20 (d $\times$ 2), 128.91 (d $\times$ 2), 129.88 (d $\times$ 2), 130.24 (d), 130.29 (d), 131.76 (s), 134.54 (s), 136.52 (s), 138.77 (s), 155.07 (d); EI-MS m/z 432 (small M^+).

(2*E*,4*E*)-2-(Benzeneselenenyl)-3-(benzenesulfonyl)-5-ethoxypenta-2,4-dien-1-ol (17a) 67%, yellow oil, IR (film, cm^{-1}) ν 3450 (OH); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.05 (3H, t, $J=7$ Hz, Me), 2.83 (1H, d, $J=8$ Hz, OH), 3.46–3.54 (2H, m, OCH_2), 6.17 (1H, dd, $J=12, 1$ Hz, olefinic H), 6.67 (1H, d, $J=8$ Hz, CHO), 7.10–7.14 (5H, m, ArH), 7.19–7.26 (9H, m, olefinic and ArH), 7.31–7.40 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.35 (q), 65.64 (t), 73.88 (d), 106.55 (d), 125.88 (d $\times$ 3), 126.48 (d), 127.24 (d), 127.87 (d $\times$ 3), 128.09 (d $\times$ 2), 128.97 (d $\times$ 3), 130.71 (d $\times$ 2), 131.72 (s), 134.41 (s), 136.16 (s), 139.60 (s), 142.15 (s), 156.21 (s); high-resolution mass calcd for $\text{C}_{23}\text{H}_{24}\text{O}_5\text{SSe}$: 468.0662, found m/z 468.0714.

(1*E*,4*E*,6*E*)-4-(Benzeneselenenyl)-5-(benzenesulfonyl)-7-ethoxy-1-phenylhepta-1,4,6-trien-3-ol (17b) 76%, yellow oil, IR (film, cm^{-1}) ν 3420 (OH); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.10 (3H, t, $J=7$ Hz, Me), 2.65 (1H, brs, OH), 3.55–3.59 (2H, m, OCH_2), 6.08–6.11 (2H, m, olefinic H and CHO), 6.28 (1H, d, $J=12$ Hz, olefinic H), 6.50 (1H, d, $J=14$ Hz, olefinic H), 7.14–7.25 (14H, m, olefinic and ArH), 7.40–7.42 (2H, m, ArH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.43 (q), 65.91 (t), 73.69 (d), 107.11 (d), 125.95 (d), 126.49 (d $\times$ 2), 126.61 (d), 127.52 (d), 127.83 (d $\times$ 2), 128.34 (d $\times$ 2), 129.05 (d $\times$ 2), 129.15 (d $\times$ 2), 129.92 (d), 130.67 (d), 130.80 (d $\times$ 2),

131.80 (s), 134.71 (s), 136.31 (s), 136.63 (s), 138.47 (s), 156.23 (d); high-resolution mass calcd for $C_{27}H_{20}O_2SSe$: 494.0819, found m/z 494.0758.

Reaction of 5-Ethoxy-3-(methanesulfonyl)-2-(benzenesulfonyl)pent-2,4-dien-1-ol (9a) with $SOCl_2$ /pyridine (Typical Procedure) $SOCl_2$ (66 mg, 0.56 mmol) was added dropwise to a CH_2Cl_2 (3 ml) solution of (1*E*,3*E*)-1-ethoxy-3-(methanesulfonyl)-6,6-dimethyl-4-(benzenesulfonyl)hepta-1,3-dien-5-ol (9a) (0.19 g, 0.56 mmol) and pyridine (89 mg, 1.12 mmol) at $-20^\circ C$. The reaction mixture was stirred for 10 min and poured into a sat. $NaHCO_3$ solution (50 ml). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with $AcOEt$ -*n*-hexane (1:20) to give 3-(methanesulfonyl)-6,6-dimethyl-4-(benzenesulfonyl)hepta-2,4-dienal (11a) (0.14 g, 85%) as a pale yellow oil. IR (film, cm^{-1}) ν 1660 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.35 (9H, s, $Me \times 3$), 2.35 (3H, s, SMe), 6.03 (1H, d, $J=7$ Hz, olefinic H), 6.31 (1H, s, olefinic H), 7.21–7.26 (3H, m, ArH), 7.29–7.31 (2H, m, ArH), 9.85 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 15.60 (q), 30.36 (q $\times 3$), 34.34 (s), 127.61 (d), 128.78 (d $\times 2$), 129.47 (d), 131.85 (d $\times 2$), 132.27 (s), 132.82 (s), 151.46 (d), 163.46 (s), 190.12 (d); MS m/z 292 (M^+). Anal. Calcd for $C_{16}H_{20}OS_2$: C, 65.71; H, 6.89. Found: C, 65.65; H, 6.97.

(2*Z*,4*Z*)-4-(Benzenesulfonyl)-3-(methanesulfonyl)-5-mesitylpenta-2,4-dienal (11b) 37%, yellow oil, IR (film, cm^{-1}) ν 1670 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 2.24 (6H, s, $Me \times 2$), 2.29 (3H, s, SMe), 2.40 (3H, s, Me), 6.36 (1H, d, $J=7$ Hz, 2-H), 6.92 (2H, s, ArH), 7.02 (1H, s, olefinic H), 7.20–7.27 (5H, m, ArH), 9.95 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 16.16 (q), 20.50 (q $\times 2$), 21.06 (q), 127.92 (d), 128.29 (d $\times 2$), 128.75 (d $\times 2$), 130.32 (d), 131.70 (s), 132.01 (s), 132.31 (d $\times 2$), 135.46 (s), 136.12 (d), 137.63 (s $\times 2$), 138.43 (s), 161.86 (s), 190.12 (d); high-resolution mass calcd for $C_{21}H_{22}OS_2$: 354.1112, found m/z 354.1102.

(2*Z*,4*E*)-4-(Benzenesulfonyl)-3-(methanesulfonyl)-5-mesitylpenta-2,4-dienal (11b) Yellow oil, IR (film, cm^{-1}) ν 1670 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 2.18 (3H, s, SMe), 2.29 (3H, s, Me), 2.31 (6H, s, $Me \times 2$), 5.63 (1H, d, $J=8$ Hz, 2-H), 7.21–7.27 (3H, m, ArH), 7.38–7.39 (2H, m, ArH), 9.91 (1H, d, $J=8$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 15.68 (q), 20.42 (q $\times 2$), 21.09 (q), 123.36 (d), 128.33 (d $\times 2$), 128.73 (d $\times 2$), 128.89 (d), 130.79 (s), 131.33 (s), 133.85 (d), 134.54 (d $\times 2$), 134.57 (s), 135.74 (d $\times 2$), 137.70 (s), 166.14 (s), 188.53 (d); high-resolution mass calcd for $C_{21}H_{22}OS_2$: 354.1112, found m/z 354.1079.

(2*Z*,4*Z*)-4-(Benzenesulfonyl)-3-(methanesulfonyl)-5-phenylpenta-2,4-dienal (11c) 59%, yellow oil, IR (film, cm^{-1}) ν 1660 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 2.41 (3H, s, Me), 6.31 (1H, d, $J=7$ Hz, 2-H), 7.19–7.43 (9H, m, olefinic and ArH), 7.76–7.78 (2H, m, ArH), 9.95 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 16.07 (q), 127.95 (d), 128.41 (d $\times 2$), 128.94 (d $\times 2$), 129.03 (d), 129.99 (d $\times 2$), 130.21 (d), 132.00 (d $\times 2$), 132.35 (s), 133.37 (s), 134.91 (s), 137.42 (d), 162.57 (s), 190.28 (d); high-resolution mass calcd for $C_{18}H_{16}OS_2$: 312.0643, found m/z 312.0595.

(2*Z*,4*Z*)-4-(Benzenesulfonyl)-3-(methanesulfonyl)hepta-2,4-dienal (11d) 37%, yellow oil, IR (film, cm^{-1}) ν 1660 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.12 (3H, t, $J=7$ Hz, Me), 2.31 (3H, s, SMe), 2.52–2.59 (2H, m, CH_2), 6.24 (1H, d, $J=7$ Hz, 2-H), 6.50 (1H, t, $J=7$ Hz, 5-H), 7.18–7.28 (5H, m, ArH), 9.96 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 13.48 (q), 16.18 (q), 23.92 (t), 127.26 (d), 128.87 (d $\times 2$), 129.93 (d), 130.91 (d $\times 2$), 132.34 (s), 133.20 (s), 145.45 (d), 190.47 (d); EI-MS m/z 264 (M^+). Anal. Calcd for $C_{14}H_{16}OS_2$: C, 63.59; H, 6.10. Found: C, 63.37; H, 6.08.

(2*E*,4*Z*)- and (2*E*,4*E*)-4-(Benzenesulfonyl)-3-(methanesulfonyl)hepta-2,4-dienal (11d) 15%, yellow oil, 2*Z*:4*E*=41:59, IR (film, cm^{-1}) ν 1660 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 0.98 (t, $J=7$ Hz, 4*Z*-Me), 1.12 (t, $J=7$ Hz, 4*E*-Me), 2.09–2.12 (m, 4*E*- CH_2), 2.18 (s, 4*Z*- SMe), 2.29 (s, 4*E*- SMe), 2.49–2.55 (m, 4*Z*- CH_2), 5.66 (d, $J=7$ Hz, 4*Z*-2-H), 5.73 (d, $J=8$ Hz, 4*E*-2-H), 6.06 (t, $J=7$ Hz, 4*E*-5-H), 6.13 (t, $J=7$ Hz, 4*Z*-5-H), 7.25–7.39 (m, ArH), 7.47–7.49 (m, ArH), 9.29 (d, $J=8$ Hz, 4*E*-CHO), 9.54 (d, $J=7$ Hz, 4*Z*-CHO); high-resolution mass calcd for $C_{14}H_{16}OS_2$: 264.0643, found m/z 264.0613.

(2*Z*,4*Z*)-3,4-Bis(benzenesulfonyl)-6,6-dimethylhepta-2,4-dienal (14a) 70%, yellow oil, IR (film, cm^{-1}) ν 1660 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.10 (9H, s, $Me \times 3$), 6.42 (1H, d, $J=7$ Hz, 2-H), 6.60 (1H, s, olefinic H), 7.16–7.25 (5H, m, ArH), 7.32–7.33 (5H, m, ArH), 10.09 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 29.96 (q $\times 3$), 34.18 (s), 127.03 (d), 128.37 (d), 128.78 (d $\times 2$), 128.81 (d $\times 2$), 130.67 (d $\times 2$), 131.06 (s), 131.83 (d), 131.96 (s), 133.29 (d $\times 2$), 133.74 (s), 155.91 (d), 160.09 (s), 191.18 (d); high-resolution mass calcd for $C_{27}H_{20}OS_2$: 354.1112, found m/z 354.1128.

(2*Z*,4*Z*)-3,4-Bis(benzenesulfonyl)-5-phenylpenta-2,4-dienal (14b) 67%, yellow oil, IR (film, cm^{-1}) ν 1650 (CO); 1H -NMR (500 MHz, $CDCl_3$)

δ : 6.80 (1H, d, $J=7$ Hz, 2-H), 7.13–7.33 (13H, m, ArH), 7.51–7.53 (2H, m, ArH), 7.66 (1H, s, olefinic H), 10.20 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 127.15 (d), 128.15 (d $\times 2$), 128.18 (d), 128.94 (d $\times 2$), 129.06 (d $\times 2$), 129.11 (d), 129.95 (d $\times 2$), 130.34 (d $\times 2$), 132.01 (d $\times 2$), 132.08 (s), 132.35 (s), 133.37 (d), 134.95 (s), 142.35 (d), 158.06 (s), 191.61 (d); high-resolution mass calcd for $C_{25}H_{18}OS_2$: 374.0799, found m/z 374.0834.

(2*Z*,4*Z*)-3,4-Bis(benzenesulfonyl)-5-phenylpenta-2,4-dienal Diethyl Acetal 17%, yellow oil, IR (film, cm^{-1}) ν 1100, 1040 (C–O); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.09 (6H, t, $J=7$ Hz, $Me \times 2$), 3.26–3.31 (1H, m, OCH_2), 3.34–3.39 (1H, m, OCH_2), 5.47 (1H, d, $J=7$ Hz, 1-H), 6.55 (1H, d, $J=7$ Hz, 2-H), 7.16–7.32 (13H, m, ArH), 7.44–7.46 (3H, m, olefinic and ArH); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 15.21 (q $\times 2$), 61.06 (t $\times 2$), 99.54 (d), 126.58 (d), 126.91 (d), 127.94 (d $\times 2$), 128.06 (d), 128.67 (d $\times 3$), 129.56 (d $\times 2$), 130.63 (d $\times 2$), 130.92 (d $\times 2$), 133.09 (s), 134.16 (s), 134.51 (s), 135.92 (s), 136.98 (d), 138.37 (s), 138.94 (d); EI-MS m/z 448 (M^+). Anal. Calcd for $C_{27}H_{28}O_2S_2$: C, 72.28; H, 6.29. Found: C, 72.17; H, 6.21.

(2*Z*,4*Z*,6*E*)-3,4-Bis(benzenesulfonyl)-7-phenylhepta-2,4,6-trienal (14c) 75%, yellow oil, IR (film, cm^{-1}) ν 1660 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 6.91 (1H, d, $J=15$ Hz, olefinic H), 7.05 (1H, d, $J=7$ Hz, olefinic H), 7.08–7.47 (15H, m, ArH), 7.52 (1H, dd, $J=11$, 15 Hz, olefinic H), 7.80 (1H, d, $J=11$ Hz, olefinic H), 10.26 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 125.98 (d), 126.77 (d), 127.38 (d $\times 2$), 127.63 (d), 128.75 (d $\times 2$), 129.03 (d $\times 2$), 129.23 (d $\times 4$), 130.44 (d $\times 2$), 131.25 (s), 133.43 (s), 134.29 (d), 136.15 (s), 141.29 (d), 145.60 (d), 154.74 (s), 192.56 (d); high-resolution mass calcd for $C_{25}H_{20}OS_2$: 400.0956, found m/z 400.1001.

(2*Z*,4*Z*)-4-(Benzeneselenenyl)-3-(methanesulfonyl)-5-phenylpenta-2,4-dienal (16a) 67%, yellow oil, IR (film, cm^{-1}) ν 1640 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 2.38 (3H, s, SMe), 6.10 (1H, d, $J=7$ Hz, 2-H), 7.16 (1H, s, olefinic H), 7.19–7.28 (3H, m, ArH), 7.33–7.40 (3H, m, ArH), 7.41–7.43 (2H, m, ArH), 7.56–7.57 (2H, m, ArH), 9.83 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 15.58 (q), 127.64 (s), 128.27 (d $\times 2$), 128.56 (d $\times 2$), 128.69 (d), 128.89 (d $\times 2$), 129.32 (d $\times 2$), 131.60 (s), 135.15 (d $\times 2$), 135.57 (s), 135.65 (d), 162.73 (s), 189.50 (d); MS m/z 360 (M^+). Anal. Calcd for $C_{18}H_{16}OSSe$: C, 60.16; H, 4.49. Found: C, 60.29; H, 4.59. The NOE enhancement of the formyl proton (4%) was observed by irradiating the methanesulfonyl group of (2*Z*,4*Z*) isomer.

(2*E*,4*Z*)- and (2*E*,4*E*)-4-(Benzeneselenenyl)-3-(methanesulfonyl)-5-phenylpenta-2,4-dienal (16a) 24%, yellow oil, 4*Z*:4*E*=65:35, IR (film, cm^{-1}) ν 1640 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 2.10 (s, 4*E*- SMe), 2.31 (s, 4*Z*- SMe), 5.49 (d, $J=8$ Hz, 4*E*-2-H), 5.66 (d, $J=8$ Hz, 4*Z*-2-H), 6.99 (s, 4*Z*-olefinic H), 7.02 (s, 4*E*-olefinic H), 7.20–7.44 (m, ArH), 7.53–7.58 (m, ArH), 7.65–7.67 (m, ArH), 9.32 (d, $J=8$ Hz, 4*Z*-CHO), 9.66 (d, $J=8$ Hz, 4*E*-CHO); MS m/z 360 (M^+). Anal. Calcd for $C_{18}H_{16}OSSe$: C, 60.16; H, 4.49. Found: C, 59.84; H, 4.64. The stereochemistries of the isomers were determined by NOE experiments. Irradiation of the methanesulfonyl group at δ 2.10 or 2.31 ppm increased the intensities of the 2-H, (10%) respectively.

(2*E*,4*Z*,6*E*)- and (2*E*,4*Z*,6*E*)-4-(Benzeneselenenyl)-3-(methanesulfonyl)-7-phenylhepta-2,4,6-trienal (16b) 53%, yellow oil, 2*Z*:2*E*=83:17, IR (film, cm^{-1}) ν 1640 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 2.16 (t, 2*Z*- SMe), 2.30 (s, 2*E*- SMe), 5.65 (d, $J=8$ Hz, 2*Z*-olefinic H), 5.80 (d, $J=8$ Hz, 2*E*-olefinic H), 6.68–6.70 (m, 2*E*-olefinic H), 6.78 (dd, $J=11$, 15 Hz, 2*Z*-olefinic H), 7.21–7.35 (m, olefinic and ArH), 7.44–7.55 (m, ArH), 9.35 (d, $J=8$ Hz, 2*E*-CHO), 9.45 (d, $J=8$ Hz, 2*Z*-CHO); MS m/z 386 (M^+). Anal. Calcd for $C_{18}H_{16}OSSe$: C, 60.16; H, 4.49. Found: C, 59.84; H, 4.64.

(2*Z*,4*Z*)-4-(Benzeneselenenyl)-3-(benzenesulfonyl)-5-phenylpenta-2,4-dienal (18a) 73%, yellow oil, IR (film, cm^{-1}) ν 1660 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 6.57 (1H, d, $J=8$ Hz, 2-H), 7.16–7.33 (15H, m, ArH), 7.50 (1H, s, olefinic H), 10.11 (1H, d, $J=8$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 127.91 (d), 127.98 (d $\times 2$), 128.31 (d), 128.59 (d), 128.71 (s), 128.93 (d $\times 2$), 128.96 (d $\times 2$), 129.28 (d $\times 2$), 131.26 (s), 131.81 (s), 132.32 (d), 132.85 (d $\times 2$), 133.75 (d $\times 2$), 135.78 (s), 140.82 (d), 159.28 (s), 190.99 (d); MS m/z 422 (M^+). Anal. Calcd for $C_{23}H_{18}OSSe$: C, 65.55; H, 4.31. Found: C, 65.04; H, 4.23.

(2*Z*,4*Z*)-4-(Benzeneselenenyl)-3-(benzenesulfonyl)-5-phenylpenta-2,4-dienal Diethyl Acetal (27) 12%, yellow oil, IR (film, cm^{-1}) ν 1120, 1050 (C–O); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.11 (6H, t, $J=7$ Hz, $Me \times 2$), 3.26–3.29 (1H, m, OCH_2), 3.35–3.38 (1H, m, OCH_2), 5.44 (1H, d, $J=7$ Hz, CHO), 6.41 (1H, d, $J=7$ Hz, olefinic H), 7.18–7.41 (16H, m, olefinic and ArH); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 15.19 (q $\times 2$), 61.01 (t $\times 2$), 99.44 (d), 126.90 (d), 127.19 (d), 127.76 (d $\times 3$), 128.55 (d $\times 2$), 128.72 (d $\times 2$), 129.10

(d×2), 129.78 (s), 131.35 (d×2), 132.66 (s), 133.60 (d×2), 133.96 (s), 136.19 (d), 136.78 (s), 138.49 (d), 139.40 (d); MS *m/z* 496 (M^+). *Anal.* Calcd for $C_{27}H_{28}O_2S_2$: C, 65.44; H, 5.70. Found: C, 65.52; H, 5.40.

(2E,4Z,6E)- and (2E,4E,6E)-4-(Benzeneselenenyl)-3-(benzenesulfonyl)-7-phenylhepta-2,4,6-trienal (18b) 26%, orange powders, mp 120–126 °C, 4Z:4E=72:28, IR (film, cm^{-1}) ν 1650 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 5.33 (d, $J=8$ Hz, 4Z-2-H), 5.48 (d, $J=7$ Hz, 4E-2-H), 6.60 (d, $J=15$ Hz, 4E-olefinic H), 6.75–6.88 (m, 4Z- and 4E-olefinic H), 7.26–7.42 (m, olefinic and ArH), 7.47–7.69 (m, ArH), 9.35 (d, $J=7$ Hz, 4E-olefinic H), 9.49 (d, $J=8$ Hz, 4Z-olefinic H); MS *m/z* 446 (M^+).

(2Z,4Z,6E)-4-(Benzeneselenenyl)-3-(benzenesulfonyl)-7-phenylhepta-2,4,6-trienal (18b) 39%, orange powders, mp 107–110 °C, IR (KBr, cm^{-1}) ν 1650 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 6.87 (1H, d, $J=15$ Hz, olefinic H), 7.04 (1H, d, $J=7$ Hz, 2-H), 7.14–7.49 (16H, m, olefinic and ArH), 7.70 (1H, d, $J=11$ Hz, olefinic H), 10.25 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 127.30 (d×2), 127.36 (d), 127.52 (d), 127.89 (d), 128.72 (d×2), 129.12 (d), 129.19 (d×2), 129.23 (d×2), 129.81 (s), 130.49 (d×2), 130.80 (s), 131.96 (d×2), 133.42 (s), 135.08 (d), 136.19 (s), 140.81 (d), 145.16 (d), 155.73 (s), 192.37 (d); high-resolution mass calcd for $C_{25}H_{20}OS_2$: 448.0400, found *m/z* 448.0397.

(2Z,4Z,6E)-4-(Benzeneselenenyl)-3-(benzenesulfonyl)-7-phenylhepta-2,4,6-trienal Diethyl Acetal 12%, yellow oil, IR (film, cm^{-1}) ν 1120, 1050 (C–O); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.10 (6H, t, $J=7$ Hz, $Me \times 2$), 3.30–3.36 (1H, m, OCH_2), 3.40–3.46 (1H, m, OCH_2), 5.52 (1H, d, $J=7$ Hz, CHO), 6.71 (1H, d, $J=14$ Hz, olefinic H), 6.82 (1H, d, $J=7$ Hz, 2-H), 7.13–7.46 (17H, m, olefinic and ArH); MS *m/z* 522 (M^+).

(2Z,4Z,6Z,8Z)-3,4,7,8-Tetrakis(benzenesulfonyl)-10,10-dimethylundeca-2,4,6,8-tetraenal (20) 45%, yellow oil, IR (film, cm^{-1}) ν 1660 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.09 (9H, s, $Me \times 3$), 6.71 (1H, s, olefinic H), 6.91–7.28 (21H, m, olefinic and ArH), 7.60 (1H, d, $J=7$ Hz, olefinic H), 8.26 (1H, d, $J=11$ Hz, olefinic H), 10.21 (1H, d, $J=7$ Hz, CHO); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 30.19 (q×3), 34.04 (s), 126.36 (d), 126.88 (d), 127.40 (d), 127.70 (d), 128.55 (d×2), 128.63 (d×2), 128.95 (d), 129.03 (d×2), 129.79 (d×2), 130.21 (d×2), 131.38 (s), 131.44 (d×2), 131.83 (d×2), 132.79 (s), 132.83 (d), 133.45 (s), 134.01 (s), 134.07 (s), 134.20 (d), 134.59 (s), 142.33 (d), 145.81 (s), 154.97 (d), 155.22 (s), 192.38 (d); high-resolution mass calcd for $C_{37}H_{34}OS_4$: 622.1493, found *m/z* 622.1493. *Anal.* Calcd for the 2,4-dinitrophenylhydrazon: orange needles, mp 178–182 °C, C: 64.31; H: 4.77; N: 6.98. Found: C, 63.97; H, 4.81; N, 6.86. The intermediate, 11-ethoxy-2,2-dimethyl-4,5,8,9-tetrakis(phenylsulfonyl)undec-3,5,8,9-tetraen-7-ol (19) was obtained in 49% yield as the mixture with a small amount of the aldehyde 20. The spectral data is shown as follows. IR (film, cm^{-1}) ν 3550 (OH); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.02 (9H, s, $Me \times 3$), 1.05 (3H, t, $J=7$ Hz, Me), 2.44 (1H, d, $J=8$ Hz, OH), 3.54 (2H, q, $J=7$ Hz, OCH_2), 6.16–6.20 (3H, m, olefinic H), 6.35 (1H, t, $J=8$ Hz, CHO), 7.06–7.39 (22H, m, olefinic and ArH); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 14.33 (q), 30.07 (q×3), 33.42 (s), 65.84 (t), 71.47 (d), 104.64 (d), 125.66 (d), 125.82 (d), 126.28 (d), 126.85 (d), 127.64 (d×2), 128.06 (d×2), 128.16 (d×2), 128.38 (d×2), 128.78 (d×2), 128.83 (d×2), 130.67 (d×2), 131.23 (s), 132.39 (d×2), 133.89 (s), 134.80 (s), 135.93 (s), 135.98 (s), 136.33 (d), 136.63 (s), 137.16 (s), 138.50 (s), 151.27 (d), 156.24 (d); MS *m/z* 325, 297, 272.

Intramolecular Cyclization of Penta-2,4-dienals (Typical Procedure) A CH_2Cl_2 (2 ml) solution of 14a (50 mg, 0.14 mmol) and *p*-toluenesulfonic acid (2.7 mg, 0.01 mmol) was stirred for 30 min at room temperature. The reaction mixture was poured into a sat. $NaHCO_3$ (50 ml). The work-up procedure and the purification by preparative TLC on silica gel eluting with $AcOEt$ -*n*-hexane (1:20) gave 3,4-bis(benzenesulfonyl)-2-*t*-butyl-2-cyclopentenone (22a) (10 mg, 20%) as a yellow oil.

22a: IR (film, cm^{-1}) ν 1670 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.26 (9H, s, $Me \times 3$), 2.48 (1H, d, $J=19$ Hz, 5-H), 2.64 (1H, dd, $J=7, 19$ Hz, 5-H), 3.76 (1H, d, $J=7$ Hz, 4-H), 7.19–7.22 (5H, m, ArH), 7.38–7.44 (3H, m, ArH), 7.68–7.70 (2H, m, ArH); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 29.21 (q×3), 34.30 (s), 44.05 (t), 47.02 (d), 128.70 (d), 128.86 (d×2), 129.11 (d×2), 129.48 (d), 129.86 (s), 131.03 (s), 134.81 (d×2), 135.84 (d×2), 147.60 (s), 164.98 (s), 202.10 (s); MS *m/z* 354 (M^+). *Anal.* Calcd for $C_{21}H_{22}OS_2$: C, 71.15; H, 6.25. Found: C, 70.87; H, 6.22.

3,4-Bis(benzenesulfonyl)-2-phenyl-2-cyclopentenone (22b) 54%, IR (film, cm^{-1}) ν 1700 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 2.70 (1H, d, $J=18$ Hz, 5-H), 2.92 (1H, dd, $J=7, 18$ Hz, 5-H), 4.01 (1H, d, $J=7$ Hz, 4-H), 7.12–7.45 (13H, m, ArH), 7.65–7.68 (2H, m, ArH); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 43.90 (t), 47.15 (d), 128.11 (d×2), 128.38 (d), 128.92 (d×2), 129.00 (d×3), 129.16 (d×2), 129.68 (d), 130.26 (s), 130.50 (s), 132.63 (s), 134.99 (d×2), 135.59 (d×2), 139.33 (s), 168.44 (s), 200.18 (s); MS *m/z* 374

(M^+). *Anal.* Calcd for $C_{23}H_{18}OS_2$: C, 73.76; H, 4.84. Found: C, 73.68; H, 4.75.

Preparations of Penta-2,4-dienal Acetals (Typical Procedure) *p*-Toluenesulfonic acid (50 mg, 0.1 mmol) was added to a $EtOH$ (5.0 ml) solution of (4E,6E)-4,5-bis(benzenesulfonyl)-7-ethoxy-2,2-dimethylhepta-4,6-dien-3-ol (13a) (0.52 g, 1.31 mmol) and triethylorthoformate (0.97 g, 6.55 mmol) at 0 °C. The mixture was stirred for 30 min and poured into water. The organic layer was separated and the aqueous layer extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with $AcOEt$ -*n*-hexane (1:50). (2Z,4Z)-3,4-bis(benzenesulfonyl)-6,6-dimethylhepta-2,4-dienal diethyl acetal (25) (0.33 g, 59%) was obtained as a pale yellow oil. IR (film, cm^{-1}) ν 1100, 1050 (C–O); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.05 (6H, t, $J=7$ Hz, $Me \times 2$), 1.08 (9H, s, $Me \times 3$), 3.14–3.36 (2H, m, OCH_2), 5.37 (1H, d, $J=7$ Hz, 2-H), 6.07 (1H, d, $J=7$ Hz, CHO), 6.37 (1H, s, 5-H), 7.12–7.27 (3H, m, ArH), 7.30–7.32 (2H, m, ArH); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 15.17 (q×2), 30.21 (q×3), 33.59 (s), 60.66 (t×2), 99.09 (d), 126.38 (d), 127.11 (d), 128.34 (d×2), 128.52 (d×2), 130.93 (d×2), 131.33 (s), 132.47 (d×2), 133.79 (s), 133.90 (d), 134.86 (s), 140.13 (s), 152.14 (d); MS *m/z* 428 (M^+). *Anal.* Calcd for $C_{25}H_{32}O_2S_2$: C, 70.05; H, 7.52. Found: C, 70.16; H, 7.49.

Reaction of Acetal with Nucleophiles (Typical Procedure) $BF_3 \cdot Et_2O$ (33 mg, 0.23 mmol) was added dropwise to a CH_2Cl_2 (1.0 ml) solution of (2Z,4Z)-3,4-bis(benzenesulfonyl)-6,6-dimethylhepta-2,4-dienal diethyl acetal (25) (0.10 g, 0.23 mmol) and 1-phenyl-1-trimethylsilyloxyethylene (0.16 g, 0.70 mmol) at –50 °C under an Ar atmosphere. The reaction mixture was stirred for 10 min and poured into sat. $NaHCO_3$ solution (100 ml). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with $AcOEt$ -*n*-hexane (1:50). (4Z,6Z)-5,6-bis(benzenesulfonyl)-3-ethoxy-8,8-dimethylnona-4,6-dienophenone (26) (60 mg, 51%) was obtained as a yellow oil. IR (film, cm^{-1}) ν 1690 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 0.94 (3H, t, $J=7$ Hz, Me), 1.09 (9H, s, $Me \times 3$), 2.66 (1H, dd, $J=5, 15$ Hz, 2-H), 2.96–2.99 (1H, m, OCH_2), 3.08–3.13 (2H, m, 2-H and OCH_2), 4.94–5.04 (1H, m, 3-H), 6.07 (1H, d, $J=9$ Hz, 4-H), 6.31 (1H, s, 7-H), 7.08–7.30 (10H, m, ArH), 7.40–7.54 (3H, m, ArH), 7.85–7.87 (2H, m, ArH); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 15.18 (q), 30.30 (q×3), 33.58 (s), 44.26 (t), 63.98 (t), 73.33 (d), 126.48 (d), 127.11 (d), 127.67 (s), 128.25 (d×2), 128.42 (d×2), 128.45 (d×2), 128.49 (d×2), 131.18 (d×2), 131.43 (s), 132.27 (d×2), 132.87 (d), 134.10 (s), 137.19 (s), 138.28 (d), 151.32 (d), 197.06 (s); MS *m/z* 502 (M^+). *Anal.* Calcd for $C_{31}H_{34}O_2S_2$: C, 74.06; H, 6.82. Found: C, 73.82; H, 6.87.

S-Ethyl (4Z,6Z)-6-(Benzeneselenenyl)-5-(benzenesulfonyl)-3-ethoxy-7-phenylhepta-4,6-dienoate (28) 45%, IR (film, cm^{-1}) ν 1680 (CO); 1H -NMR (500 MHz, $CDCl_3$) δ : 1.03 (3H, t, $J=7$ Hz, Me), 1.23 (3H, t, $J=7$ Hz, Me), 2.31 (1H, dd, $J=4, 15$ Hz, 2-H), 2.65 (1H, dd, $J=9, 15$ Hz, 2-H), 2.86 (2H, q, $J=7$ Hz, CH_2), 3.06–3.17 (2H, m, OCH_2), 4.88–4.93 (1H, m, 3-H), 6.26 (1H, d, $J=9$ Hz, 4-H), 7.18–7.39 (16H, m, olefinic and ArH); ^{13}C -NMR (125 MHz, $CDCl_3$) δ : 14.63 (q), 15.15 (q), 23.34 (t), 49.11 (t), 64.26 (t), 73.73 (d), 127.07 (d), 127.43 (d), 127.77 (d), 127.85 (d×2), 128.66 (d×2), 128.78 (d×2), 129.15 (d×2), 129.87 (s), 131.46 (d×2), 133.09 (s), 133.96 (d×2), 136.91 (s), 137.81 (d), 138.48 (s), 139.62 (d), 196.01 (s); MS *m/z* 493 (M^+ –EtS). *Anal.* Calcd for $C_{29}H_{30}O_2S_2Se$: C, 62.91; H, 5.46. Found: C, 62.85; H, 5.48.

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