A New 3-(Phenylseleno)allylic Cation: Its Regioselective C−C Bond Formation Reaction with Nucleophiles

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Highly useful C−C bond formation using 2-ethoxy-3-(phenylseleno)prop-2-enal acetal **2** was examined with various Lewis acids. The reaction of **2** with the silyl enol ether in the presence of BF_3·Et_2O, $ZnBr_2$, or $SnBr_4$ regioselectively provided *(Z)*-3,4-diethoxy-5-(phenylseleno)pent-4-enophenone **5a** in high yields. On the other hand, the reaction with other Lewis acids such as $EtAlCl_2$ or $SnCl_4$ gave 5-(phenylseleno)- **6** or non-selenopentane-1,4-dione **7**, respectively. Novel prop-2-enal acetals **2**−**4** and **13**−**15** reacted with various nucleophiles to give pent-4-enophenones **5a,b**, **10a**, **12**, and **16**−**18**, *S*-ethyl pent-4-enoate **5b**, alkylated vinylic sulfide **10b**, 3-pentenenitrile **5d**, and **10c**. A versatile pent-4-enophenone **5a** could be converted to tetrahydrofuran **20** and penta-2,4-dienophenone **19**, the Diels−Alder reactions of which with dienophiles gave the adducts **24** and **25**.

Introduction

Sulfur-stabilized allylic cations have attracted much attention as good electrophiles for C−C bond formation with soft nucleophiles and are utilized to construct cyclopentenones, which are versatile intermediates for the synthesis of biologically active compounds, by [3 + 2] cycloaddition.[1] In the cationic species, the sulfur atom plays an important role in controlling the regio- and stereoselectivities of the products.[2] On the other hand, the selenium-substituted allylic cations have not been much investigated because their precursors are difficult to prepare. A few methods exist for the generation of the 1-alkylseleno-[3] and 2-selenoallylic cations[4] from 1,3-bis-(methylseleno)prop-2-ene, 3-(methylseleno)prop-2-en-1-ol, or 1-bromo-2-(phenylseleno)prop-2-ene and their electrophilic reactions with the pyrrole and the silyl enol ethers. However, their allylic cations are quite limited because of the low regioselectivities of the products and the formation of dialkylated products. Recently, we have reported that the 2-(phenylseleno)prop-2-enal diethyl acetals are good precursors for the 2-phenylselenenyl allylic cations and the reactions with the nucleophiles are found to be regioselective, giving high yields of the products, and can be applied to the penta-2,4-dienylation or hepta-2,4,6-trienylation of the nucleophiles.[5] Continuing studies in this field prompted us to investigate this type of 3-(phenylseleno)allylic cation to find more useful electrophiles. We preliminarily performed the addition reaction of nucleophiles to the 3-(phenylseleno)prop-2-ynal acetal to introduce a chalcogene functional group at the 2-position.[6] Thus, the 3-(phenylseleno)prop-2-enal acetals bearing a 2-ethoxy, 2-(phenylthio), or 2-(phenylseleno) group would easily react with Lewis acid to afford the 3-(phenylseleno)allylic cations, α-oxy carbenium ion **Ia** stabilized by the alkylidene cation **Ib**, and α-seleno carbenium ions **Ic** stabilized by a bridged cation **Id**. Here we report a new highly regioselective alkylation of 3-seleno-allylating electrophiles functionalized by the other heteroatom at the 2-position of prop-2-enal acetals.

Results and Discussion

The 3-(phenylseleno)-2-chalcogenoprop-2-enal diethyl acetals **2**−**4** (Y = OEt, SPh, SePh) were prepared by our original methods. The reaction of 3-selenoprop-2-ynal diethyl acetal (**1**) with NaOEt in EtOH under reflux condition provided 2-ethoxyprop-2-enal acetal **2** in 75% yield (Scheme 1).[6] The *β*-(phenylthio)- or *β*-(phenylseleno)prop-2-enal acetals **3** and **4** were also obtained by the almost same method in high yields. First, we performed the reaction of *β*-ethoxyprop-2-enal acetal **2** with the silyl enol ether in the presence of BF_3·Et_2O to give *(Z)*-3,4-diethoxy-5-(phenylseleno)pent-4-enonophenone ((*Z*)-**5a**) in 71% yield. The structure of **5a** was determined by the following data. The ^1H NMR spectrum shows a singlet at δ 5.98 ppm due to the characteristic olefinic proton and a dd at δ 4.52 (*J* 4 and 7 Hz) due to the α-proton of the ethoxy group. The ^{13}C NMR spectrum shows a doublet at δ 101.02 due to the α-olefinic carbon of the phenylseleno group. The mass and elemental analysis exhibits the molecular formula ($C_{21}H_{24}O_3Se$). Other Lewis acids were examined, and the results are shown in Table 1. Yb(OTf)$_3$ afforded the alkylated products *(E)*- and *(Z)*-

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(2) Hunter, R.; Simon, C. D. *Tetrahedron Lett.* **1986**, *27*, 1385. Hunter, R.; Michael, J. P.; Walter, D. S. *Tetrahedron Lett.* **1992**, *33*, 5413. Hunter, R.; Michael, J. P.; Walter, D. S. *Tetrahedron Lett.* **1994**, *35*, 5481.

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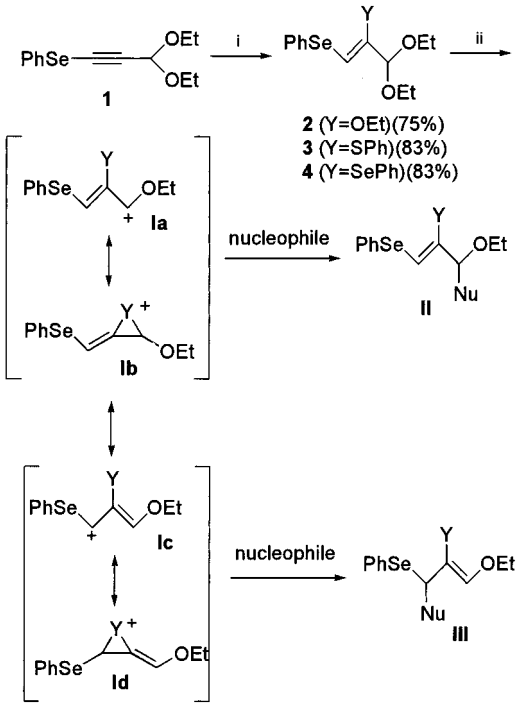
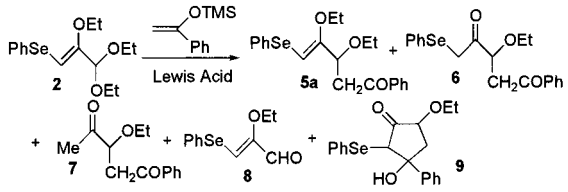
Scheme 1[a]



[a] Reagents: i, NaOEt/EtOH/reflux or PhSH/NaOEt/EtOH/reflux or $(PhSe)_2$/NaH/THF−EtOH/reflux; ii, Lewis Acid.

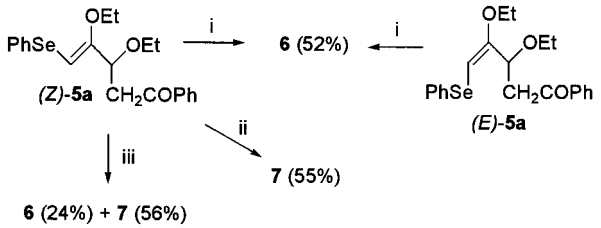
Table 1. Reaction of 2-Ethoxy-3-(phenylseleno)prop-2-enal Acetal 2 with Silyl Enol Ether



entry	Lewis acid	product (% yield)
1	BF_3•Et_2O/−78 °C	(*Z*)-**5a** (71)
2	$ZnBr_2$/−78 °C	(*Z*)-**5a** (82)
3	$Al(OBu^t)_3$/−78 °C	(*Z*)-**5a** (66)
4	$TiCl_4$/−78 °C	**6** (33), **7** (8)
5	$SnCl_4$/−78 °C	**7** (36), (*Z*)-**5a** (20), **9** (4)
6	$SnBr_4$	(*Z*)-**5a** (83)
7	$EtAlCl_2$/−78 °C	(*Z*)-**5a** (28), **6** (52)
8	$Yb(OTf)_3$/0 °C	(*Z*)-**5a** (40), (*E*)-**5a** (34)
9	$Yb(OTf)_3$/−10 °C	(*Z*)-**5a** (6), (*E*)-**5a** (52)
10	$La(OTf)_3$/0 °C	(*Z*)-**5a** (34), **8** (47)
11	$HfCl_4$	**6** (46), **7** (5)
12	$TaCl_5$	(*Z*)-**5a** (18), **6** (17), **7** (4)
13	WCl_6	**6** (21), **7** (9)

5a. The stereostructures of the products were determined by the NOE experiments. Irradiation of the olefinic proton of *(Z)*-**5a** at δ 5.98 ppm increased the intensity of the α-proton of the ethoxy group (4%). On the other hand, irradiation of the olefinic proton of *(E)*-**5a** at δ 5.57 ppm increased the intensities of both the methylene protons of the 4-ethoxy group (5%) and the methylene protons of the 3-ethoxy group (5%) and not the α-proton of the phenylseleno group. We also examined other Lewis acids such as those in entries 5−7. $EtAlCl_2$ gave the 1,4-diketone **6** in 52% yield, accompanied with the normal adduct **5a**. The reaction with $La(OTf)_3$ was very slow and afforded the α-ethoxy aldehyde **8** (entry 10). Interestingly, the cyclized product **9** was obtained in low yield (entry 5).

Scheme 2[a]



[a] Reagent: i, HCl/EtOH−H_2O; ii, $SnCl_4/CH_2Cl_2$/0 °C; iii, $TiCl_4/CH_2Cl_2$/0 °C.

In some cases tried with commonly used Lewis acids such as BF_3•Et_2O and $ZnBr_2$, the nearly exclusive formation of the 4-pentenone **5a** was observed, whereas strong Lewis acids promote successive side reactions. The use of $TiCl_4$ and $SnCl_4$ led to the formation of byproducts such as 1,4-diketones **6** and **7**, which were considered to be obtained from the acid-promoted hydrolysis of the adduct **5a**. The mechanism of the hydrolysis of vinylic selenides has been thoroughly investigated by Hevesi et al.;[7] however, that of the β-alkoxy vinylic selenides has not been reported, to our knowledge. The results, the formation of the 1,4-diketones **6** and **7**, shown in Table 1 (entries 4, 5, 7, and 11−13), are rationalized as follows. We speculated that the diketones would be obtained from the hydrolysis of **5a** with HCl, formed from the reaction mixture. Therefore, we conducted the hydrolysis of *(Z)*- and *(E)*-**5a** with HCl/EtOH/H_2O and obtained the 5-(phenylseleno)pentan-1,4-dione **6** (Scheme 2). As seen for entry 5 in Table 1, the use of $SnCl_4$ led to a high yield of the deselenylated 1,4-diketone **7**, which would be due to the strong affinity between $SnCl_4$ and the selenenyl functional groups. The activated C−Se bond was easily cleaved with Lewis acids to form the Lewis acid−SeR complex.[8] To confirm the mechanism for formation of **7**, we performed the reaction of **5a** with $SnCl_4$ or $TiCl_4$ as shown in Scheme 2. The hydrolysis of **5a** easily proceeded to give the deselenylated ketone **7**, accompanied with the β-keto selenide **6**. This result shows that the C−Se bond of the 1,4-diketone **6** is cleaved in the reaction media by the effect of $SnCl_4$ or $TiCl_4$. On the other hand, most reactions proceeded with retention of their stereochemistries; however, the use of $Yb(OTf)_3$ led to the isomerization of *(E)*-**5a** as shown in Table 1, entries 8 and 9. We consider that this isomerization results from the slow rate of the reaction with $Yb(OTf)_3$.

Next, we examined the reactions of **2** with other soft nucleophiles, and the results are shown in Table 2 (entries 1−6). Almost the same products were obtained in good yields except for entries 3 and 6. Furthermore, the nucleophilic addition of **3** (Y = SPh) with silyl enol ether, Et_3Al, and (TMS)CN gave the products in good yields (entries 7−11). The 3-(phenylsulfenyl)propenal acetal **3** exclusively and stereoselectively formed the alkylated products, without the formation of byproducts (entries 7−9), for two main reasons. One is that the 2-(phenylsulfenyl)prop-2-enylated products are more stable

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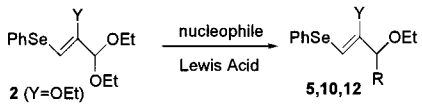
(8) Hermans, B.; Colard, N.; Hevesi, L. *Tetrahedron Lett.* **1992**, *33*, 4629. Yoshimatsu, M.; Asahi, T.; Shimizu, H.; Kataoka, T. *Heteroat. Chem.* **1995**, *6*, 259.

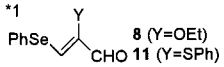
Table 2. Reaction of 2-Ethoxy-3-(phenylseleno)prop-2-enal Acetals 2−4 with Soft Nucleophiles



2 (Y=OEt)
3 (Y=SPh); **4** (Y=SePh)

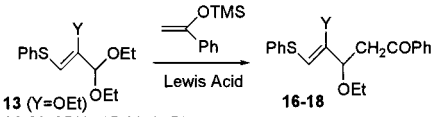
5,10,12

Entry	Acetal (Y)	Nucleophile	Lewis Acid	R	Product (%yield)	
1	**2**(OEt)		BF_3-Et_2O	CH_2COSEt	*(Z)*-**5b** (80)	
2	**2**		$Yb(OTf)_3$	CH_2COSEt	*(E)*-**5b** (35)	
3	**2**	Me_3Al	BF_3-Et_2O	Me	*(Z)*-**5c** (4)	
4	**2**	TMSCN	BF_3-Et_2O	CN	*(Z)*-**5d** (64)	
5	**2**	TMSCN	$Yb(OTf)_3$		**8** (69)	
6	**2**	allyltrimethylsilane	BF_3-Et_2O		Complex mixture	
7	**3**(SPh)		BF_3-Et_2O	CH_2COPh	*(Z)*-**10a** (84)	
8	**3**		$Yb(OTf)_3$	CH_2COPh	*(Z)*-**10a** (71)	
9	**3**	Et_3Al	BF_3-Et_2O	Et	*(Z)*-**10b** (72)	
10	**3**	TMSCN	BF_3-Et_2O	CN	*(Z)*-**10c** (74)	**11** (6)[*1]
11	**3**	TMSCN	$SnCl_4$	CN	*(Z)*-**10c** (81)	**11** (15)[*1]
12	**4**(SePh)		BF_3-Et_2O	CH_2COPh	*(Z)*-**12** (60)	
13	**4**		$Yb(OTf)_3$	CH_2COPh	*(Z)*-**12** (60)	

*1 

8 (Y=OEt)
11 (Y=SPh)

Table 3. Reaction of 2-Ethoxy-3-(phenylthio)prop-2-enal Acetals with Soft Nucleophiles



13 (Y=OEt)
14 (Y=SPh); **15** (Y=SePh)

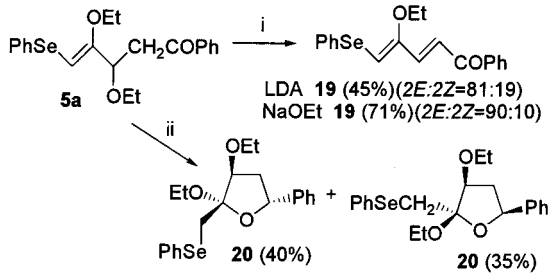
16-18

entry	acetal (Y)	Lewis acid	product (% yield)
1	**13** (OEt)	BF_3·Et_2O	**16** (74)
2	**13**	$Yb(OTf)_3$	**16** (70)
3	**14** (SPh)	BF_3·Et_2O	**17** (80)
4	**15** (SePh)	BF_3·Et_2O	**18** (80)

than the 2-ethoxyprop-2-enylated products, which contain the structure of the enol ether. The other is the stabilizing effect of the 2-phenylsulfenyl group of the propenyl cation. The 2-phenylsulfenyl group would more effectively stabilize the transient allylic cation **Ia,b** (Y = SPh) than the 2-alkoxyallylic cation **Ia,b** (Y = OEt). The 2-selenium-substituted prop-2-enal acetal **4** with the silyl enol ether afforded the adduct **12** (entries 12 and 13). Furthermore, the reaction of 3-(phenylthio)-substituted derivatives **13**−**15** gave satisfactory results (Table 3).

The method reported here appears to be one choice for the efficient preparation of the 4-pentenones. We next tried to apply the conversion of the new types of 4-pentenones to other useful compounds. First, we examined the transformation of the 4-ethoxy-4-pentenone **5a**, and the results are shown in Scheme 3. The treatment of **5a** with LDA gave the 2,4-pentadienophenone **19** in 45% yield. A better result was obtained from the reaction using NaOEt in THF−EtOH (*E:Z* = 90:10). Previously, we reported the transformation of the 4-pentenones to furanosides.[6] The reduction of **5a** and the successive treatment with *t*-BuOK/*t*-BuOH afforded the intermediate alkoxide **21** (Figure 1). We thought that the 5-exo-mode cyclization gives the carbanion stabilized by the selenium functional group. The procedure provided two

Scheme 3[a]



[a] Reagents: i, LDA/THF/−78 °C or NaOEt/THF−EtOH; ii, $LiAlH_4$/Et_2O/*t*-BuOK/*t*-BuOH (75%).

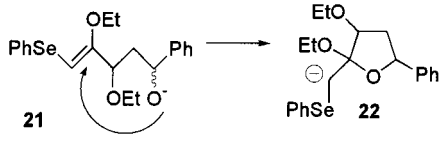
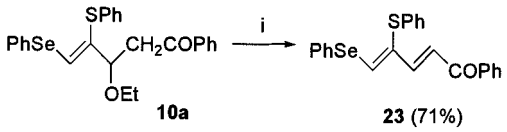


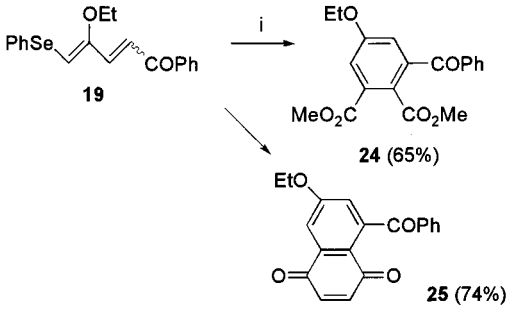
Figure 1.

Scheme 4[a]



[a] Reagent: i, $TiCl_4$/−78 °C.

Scheme 5[a]



[a] Reagents: i, dimethyl acetylenedicarboxylate/benzene/reflux/52 h; ii, benzoquinone/toluene/reflux/8 h.

kinds of the furanoside **20** in 75% yield. The two furanosides were found to be the stereoisomers by determining their structures. The stereochemistries of the isomers were assigned by the NOE experiments and Williams's chemical shift method[9] of the 3,5-disubstituted tetrahydrofurans. Furthermore, we conducted the transformation of the 4-(phenylthio)-4-pentenophenone **10a** with Lewis acid to afford the 2,4-pentadienophenone **23** in 71% yield (Scheme 4).

Dichalcogene-substituted 1,3-butadienes have been easily applied to the Diels−Alder reactions with the activated dienophiles.[10] We further performed the Diels−Alder reactions of the 4,5-bis(chalcogeno)penta-2,4-dienophenone **19** with the dienophiles. The reaction with dimethyl acetylenedicarboxylate in benzene afforded the dimethyl phthalate **24** in 65% yield (Scheme 5). The reaction with benzoquinone also underwent the desele-

(9) Williams, D. R.; Harigaya, Y.; Moore, J. L.; D'sa, A. *J. Am. Chem. Soc.* **1984**, *106*, 2641. Mihelich, E. D.; Hite, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 7318.

nylation to give the aromatic compound **25** in good yield. Now, we are investigating the Diels−Alder reactions of the 4-ethoxy-5-(phenylseleno)penta-2,4-dienophenone with other dienophiles and the Diels−Alder reactions of other chalcogene-substituted penta-2,4-dienophenones. The full details of the Diels−Alder reactions will be reported elsewhere.

Conclusion

We have shown novel allylating reactions using the new 2- and 3-chalcogene-substituted allylic cations with soft nucleophiles. The reactions of the 2-ethoxy-3-(phenylseleno)prop-2-enal acetal **2** with the soft nucleophiles afforded the adducts using BF_3·Et_2O and $ZnBr_2$. The use of a strong Lewis acid such as $SnCl_4$ or $TiCl_4$ afforded the 1,4-diketones, exclusively. The 2-(phenylsulfenyl)-3-(phenylseleno)-prop-2-enal acetal **3** underwent various C−C bond formations to give the products using BF_3·Et_2O, $Yb(OTf)_3$, and $SnCl_4$. The 4-ethoxy-5-(phenylseleno)pent-4-enophenone **5a**, formed from the reaction of the 2-ethoxy-3-(phenylseleno)prop-2-enal acetal **2** with the silyl enol ether, was found to be a versatile precursor for the synthesis of useful compounds such as 1,4-diketones, 2,4-pentadienophenones, tetrahydrofurans, and Diels−Alder adducts.

Experimental Section

Melting points were determined on a 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 Varian Inova 400 (400 MHz) spectrometer at Gifu University. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. IR spectra were determined on a JASCO IRA-100 infrared spectrometer and are expressed in reciprocal centimeters. EI mass spectra (MS) were obtained using a JEOL GCmate spectrometer with direct-insertion probe at 70 eV. All exact mass determinations were obtained on the JMA 2000 on-line system.

Preparations of (*Z*)-2-Ethoxy-3-(phenylseleno)-2-propenal Diethyl Acetals (2). A EtOH (5.0 mL) solution of **1** (1.85 g, 6.53 mmol) was added dropwise to a EtOH solution of NaOEt (prepared from Na (0.75 g, 32.7 mmol) and EtOH (20 mL)). The mixture was refluxed for 30 min. The solvent was removed under reduced pressure. The mixture was poured into water (100 mL), and the organic layer was separated. 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−hexane (1:10). *(Z)*-2-Ethoxy-3-(phenylseleno)prop-2-enal diethyl acetal (**2**) (1.60 g, 75%) was obtained as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, J = 7 Hz), 1.23 (3H, t, J = 7 Hz), 1.31 (3H, t, J = 7 Hz), 3.50−3.58 (2H, m), 3.62−3.69 (2H, m), 4.07 (2H, q, J = 7 Hz), 4.93 (1H, s), 6.09 (1H, d, J = 1 Hz), 7.21−7.36 (3H, m), 7.50−7.70 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.31 (q × 2), 15.83 (q), 61.84 (t × 2), 66.11 (t), 99.29 (d), 103.47 (d), 127.04 (d), 129.27 (d × 2), 131.08 (s), 132.14 (d × 2), 150.91 (s); MS *m*/*z* 330 (M^+). Anal. Calcd for $C_{15}H_{22}O_3Se$: C, 54.88; H, 6.73. Found: C, 54.72; H, 6.54.

Preparation of (*Z*)-2-(Phenylthio)-3-(phenylseleno)-prop-2-enal Diethyl Acetal (3). A THF (3.00 mL) solution of **1** (0.28 g, 1.00 mmol) was added dropwise to a EtOH solution of PhSNa (prepared from PhSH (1.10 mmol) and NaOEt (5.5 mmol)). The mixture was refluxed for 30 min and poured into water (50 mL), and the organic layer was separated. The aqueous layer was extracted with ether. The workup procedure afforded a titled compound **3** (0.33 g, 84%) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.15 (6H, t, J = 7 Hz), 3.41−3.49 (2H, m), 3.53−3.61 (2H, m), 4.78 (1H, d, J = 1 Hz), 7.18−7.32 (5H, m), 7.41−7.44 (2H, m), 7.55−7.59 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.24 (q × 2), 62.01 (t × 2), 101.67 (d), 126.78 (d), 127.95 (d), 129.11 (dx2), 129.49 (dx2), 129.75 (s), 129.81 (dx2), 130.49 (s), 133.29 (d × 2), 133.95 (s), 138.21 (d); high-resolution mass calcd for $C_{19}H_{22}O_2SSe$ 394.0505, found *m*/*z* 394.0502.

Preparation of (*Z*)-2,3-Bis(phenylseleno)prop-2-enal Diethyl Acetal (4). A mixture of diphenyl diselenide (0.33 g, 1.06 mmol) and NaH (0.14 g, 3.54 mmol) was refluxed for 1 h under an Ar atmosphere. To the cooling mixture of PhSeNa, a EtOH (5.00 mL) solution of **1** (0.50 g, 1.77 mmol) was added dropwise. The whole was refluxed for 30 min and poured into water (50.0 mL). The workup procedure afforded the titled **4** (0.65 g, 83%) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (3H, t, J = 7 Hz), 3.40−3.48 (2H, m), 3.53−3.61 (2H, m), 4.81 (1H, d, J = 1 Hz), 7.23−7.35 (6H, m), 7.54−7.59 (4H, m), 7.70 (1H, d, J = 1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.19 (q × 2), 62.13 (t × 2), 103.19 (d), 127.23 (d), 128.89 (d), 128.87 (s), 129.22 (d × 2), 129.44 (d × 2), 129.64 (s), 130.68 (s), 132.40 (d × 2), 133.24 (d × 2), 138.38 (d); MS *m*/*z* 442 (M^+). Anal. Calcd for $C_{19}H_{22}O_2Se_2$: C, 51.83; H, 5.04. Found: C, 51.57; H, 4.97.

Preparation of (*Z*)-2-Ethoxy-3-(phenylthio)prop-2-enal Diethyl Acetal (13). An EtOH (3.00 mL) solution of 3-(phenylthio)prop-2-enal diethyl acetal (0.47 g, 2.00 mmol) was added dropwise to a EtONa (prepared from EtOH (10.0 mL) and Na (0.23 g, 10.0 mmol)). The mixture was refluxed for 30 min. The workup procedure gave the titled compound **13** (0.23 g, 42%) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (6H, t, J = 7 Hz), 1.32 (3H, t, J = 7 Hz), 3.51−3.60 (2H, m), 3.62−3.71 (2H, m), 4.09−4.17 (2H, m), 4.92 (1H, s), 5.94 (1H, d, J = 1 Hz), 7.16−7.21 (1H, m), 7.26−7.33 (2H, m), 7.33−7.43 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.33 (q × 2), 15.81 (q), 61.95 (t × 2), 66.58 (t), 99.46 (d), 106.14 (d), 126.29 (d), 128.63 (d × 2), 128.93 (d × 2), 136.59 (s), 151.08 (s); MS *m*/*z* 282 (M^+). Anal. Calcd for $C_{15}H_{22}O_3S$: C, 63.80; H, 7.85. Found: C, 63.65; H, 7.73.

Reaction of 2-Ethoxy-3-(phenylseleno)prop-2-enal Diethyl Acetal 2 with Nucleophiles: Typical Procedure. BF_3·Et_2O (0.14 g, 1.00 mmol) was added dropwise to a CH_2Cl_2 (1.00 mL) solution of **2** (0.16 g, 0.50 mmol) and 1-phenyl *O*-(trimethylsilyl)enol ether (0.28 g, 1.50 mmol) at −78 °C under an Ar atmosphere. The mixture was stirred for 10 min and poured into a $NaHCO_3$ (50 mL) solution. 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−hexane (1:20) to give *(Z)*-3,4-diethoxy-5-(phenylseleno)pent-4-enophenone (**5a**) (0.14 g, 71%) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (3H, t, J = 7 Hz), 1.33 (3H, t, J = 7 Hz), 3.18 (1H, dd, J = 4 and 16 Hz), 3.39−3.53 (1H, m), 3.50 (1H, dd, J = 7 and 16 Hz), 3.64−3.71 (1H, m), 4.06−4.17 (2H, m), 4.52 (1H, dd, J = 4 and 7 Hz), 5.98 (1H, s), 7.21−7.32 (3H, m), 7.43−7.50 (4H, m), 7.53−7.61 (1H, m), 7.95−7.99 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.40 (q), 15.93 (q), 43.19 (t), 65.24 (t), 67.09 (t), 101.02 (d), 127.03 (d), 128.40 (d × 2), 128.63 (d × 2), 129.39 (d × 2), 131.41 (s), 131.64 (d × 2), 133.31 (d), 137.35 (s), 155.39 (s), 197.87 (s); MS *m*/*z* 404 (M^+). Anal. Calcd for $C_{21}H_{24}O_3Se$: C, 62.53; H, 6.00. Found: C, 62.37; H, 5.89.

***(E)*-3,4-Diethoxy-5-(phenylseleno)pent-4-enophenone (5a):** a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.15 (3H, t, J = 7 Hz), 1.33 (3H, t, J = 7 Hz), 3.27 (1H, dd, J = 6 and 16 Hz), 3.52 (1H, dd, J = 7 and 16 Hz), 3.43−3.60 (2H, m), 3.81−

(10) 1-Phenylthio-1,3-butadiene: Maddaluno, J.; Gaonac'h, O.; Marcual, A.; Toupet, L.; Giessner-Prettre, C. *J. Org. Chem*. **1996**, *61*, 5290. 4-Alkoxy-1-(phenylseleno)-1,3- butadiene: Fryzuk, M. D.; Bates, G. S.; Stone, C. *J. Org. Chem*. **1987**, *52*, 2234. 2-Thio- or 2-Seleno-1,3-butadiene: Liotta, C. L.; Verbicky, J. W. *Tetrahedron Lett*. **1985**, *26*, 1395.

3.90 (2H, m), 5.29 (1H, dd, J = 6 and 7 Hz), 5.57 (1H, s), 7.16−7.26 (3H, m), 7.41−7.56 (4H, m), 7.94−7.96 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.55 (q), 15.45 (q), 41.95 (t), 63.65 (t), 64.65 (t), 73.78 (d), 87.96 (d), 126.35 (d), 128.42 (d × 2), 128.65 (d × 2), 129.26 (d × 2), 129.97 (d × 2), 133.18 (d), 133.51 (s), 137.31 (s), 159.89 (s), 197.65 (s); high-resolution mass calcd for $C_{21}H_{24}O_3Se$ 404.0889, found m/z 404.0881.

3-Ethoxy-1-phenyl-5-(phenylseleno)-1,4-pentanedione (6): a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, t, J = 7 Hz), 3.44 (2H, dd, J = 5 and 6 Hz), 3.56−3.65 (2H, m), 3.80 (1H, d, J = 12 Hz), 4.02 (1H, d, J = 12 Hz), 4.62 (1H, dd, J = 5 and 6 Hz), 7.26−7.30 (3H, m), 7.44−7.48 (2H, m), 7.55−7.59 (3H, m), 7.92−7.94 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.59 (q), 32.43 (t), 41.79 (t), 67.20 (t), 79.50 (d), 127.98 (d), 128.25 (s), 128.38 (d × 2), 128.81 (d × 2), 129.43 (d × 2), 129.53 (s), 133.39 (d × 2), 133.55 (d), 197.00 (s), 206.98 (s); MS m/z 376 (M^+). Anal. Calcd for $C_{19}H_{20}O_3Se$: C, 60.80; H, 5.37. Found: C, 60.89; H, 5.41.

3-Ethoxy-1-phenyl-1,4-pentanedione (7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (3H, t, J = 7 Hz), 2.32 (3H, s), 3.35 (2H, d, J = 6 Hz), 3.62 (2H, q, J = 7 Hz), 4.37 (1H, t, J = 6 Hz), 7.45−7.49 (2H, m), 7.55−7.59 (1H, m), 7.94−7.96 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.58 (q), 26.62 (q), 40.98 (t), 67.12 (t), 81.36 (d), 128.43 (d × 2), 128.87 (d × 2), 133.56 (d), 136.98 (s), 197.12 (s), 206.37 (s); MS m/z 220 (M^+). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.52; H, 7.29.

(*Z*)-2-Ethoxy-3-(phenylseleno)prop-2-enal (8): a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (3H, t, J = 7 Hz), 4.22 (2H, q, J = 7 Hz), 7.27 (1H, s), 7.35−7.38 (3H, m), 7.59−7.62 (2H, m), 9.17 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.97 (q), 67.21 (t), 128.77 (d), 128.99 (s), 129.85 (d × 2), 133.48 (d × 2), 138.76 (d), 153.05 (s), 183.91 (d); MS m/z 256 (M^+). Anal. Calcd for $C_{11}H_{12}O_2Se$: C, 52.10; H, 4.74. Found: C, 52.07; H, 4.98.

5-Ethoxy-3-hydroxy-3-phenyl-2-(phenylseleno)cyclopentanone (9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (3H, t, J = 7 Hz), 3.18−3.23 (2H, m), 5.50 (1H, s), 7.16−7.27 (3H, m), 7.41−7.59 (6H, m), 7.93 (2H, dd, J = 8 and 1 Hz); MS m/z 376 (small M^+).

(*Z*)-*S*-Ethyl 3,4-Diethoxy-5-(phenylseleno)pent-4-enoate (5b): a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, t, J = 7 Hz), 1.25 (3H, t, J = 7 Hz), 1.32 (3H, t, J = 7 Hz), 2.82−2.94 (4H, m), 3.39−3.47 (1H, m), 3.60−3.68 (1H, m), 4.04−4.11 (2H, m), 4.29 (1H, dd, J = 4 and 7 Hz), 5.90 (1H, s), 7.22−7.32 (3H, m), 7.46−7.56 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.90 (q), 15.30 (q), 15.90 (q), 23.63 (t), 48.51 (t), 65.24 (t), 67.10 (t), 77.18 (d), 101.06 (d), 127.09 (d), 129.40 (d × 2), 131.38 (s), 131.70 (d × 2), 154.65 (s), 197.11 (s); MS m/z 388 (M^+). Anal. Calcd for $C_{17}H_{24}O_3SSe$: C, 52.71; H, 6.24. Found: C, 52.19; H, 5.97.

(*E*)-*S*-Ethyl 3,4-Diethoxy-5-(phenylseleno)pent-4-enoate (5b): a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, t, J = 7 Hz), 1.23 (3H, t, J = 7 Hz), 1.37 (3H, t, J = 7 Hz), 2.81 (1H, dd, J = 6 and 15 Hz), 2.86 (2H, dd, J = 1 and 7 Hz), 3.04 (1H, dd, J = 8 and 15 Hz), 3.38−3.46 (1H, m), 3.50−3.58 (1H, m), 3.85−3.93 (2H, m), 5.13 (1H, dd, J = 6 and 8 Hz), 5.57 (1H, s), 7.17−7.28 (3H, m), 7.38−7.42 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.56 (q), 14.93 (q), 15.38 (q), 23.57 (t), 47.31 (t), 63.77 (t), 64.76 (t), 73.87 (d), 87.89 (d), 126.40 (d), 129.29 (d × 2), 129.90 (d × 2), 133.35 (s), 159.60 (s), 196.55 (s); MS m/z 388 (M^+). Anal. Calcd for $C_{17}H_{24}O_3SSe$: C, 52.71; H, 6.24. Found: C, 52.47; H, 6.12.

(*Z*)-3-Cyano-2,3-diethoxy-1-(phenylseleno)-1-propene (5d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (3H, t, J = 7 Hz), 1.35 (3H, t, J = 7 Hz), 3.56−3.64 (1H, m), 3.73−3.80 (1H, m), 4.07−4.23 (2H, m), 4.74 (1H, d, J = 1 Hz), 6.26 (1H, s), 7.25−7.40 (3H, m), 7.50−7.58 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.92 (q), 15.65 (q), 65.73 (t), 67.38 (t), 69.08 (d), 107.79 (d), 116.14 (s), 127.76 (d), 129.55 (d × 2), 130.54 (s), 132.58 (d × 2), 146.40 (s); MS m/z 311 (M^+). Anal. Calcd for $C_{14}H_{17}NO_2Se$: C, 54.20; H, 5.52; N, 4.51. Found: C, 54.09; H, 5.49; N, 4.28.

(*Z*)-3,4-Diethoxy-5-(phenylthio)pent-4-enophenone (16): a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, t, J = 7 Hz), 1.32 (3H, t, J = 7 Hz), 3.21 (1H, dd, J = 4 and 16 Hz), 3.42 (1H, dd, J = 8 and 16 Hz), 3.30−3.55 (1H, m), 3.65−3.72 (1H, m), 4.10−4.23 (2H, m), 4.48 (1H, dd, J = 4 and 8 Hz), 5.78 (1H, s), 7.16−7.20 (1H, m), 7.23−7.35 (4H, m), 7.43−7.47 (2H, m), 7.51−7.57 (1H, m), 7.96−7.99 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.39 (q), 15.88 (q), 43.18 (t), 65.24 (t), 67.49 (t), 76.82 (d), 102.96 (d), 126.16 (d), 128.28 (d × 2), 128.40 (d × 2), 128.73 (d × 2), 129.18 (d × 2), 133.29 (d), 136.97 (s), 137.38 (s), 155.96 (s), 197.85 (s); MS m/z 356 (M^+). Anal. Calcd for $C_{21}H_{24}O_3S$: C, 70.76; H, 6.79. Found: C, 70.50; H, 6.65.

Hydrolysis of 5a with HCl/EtOH−H_2O. A 3% HCl solution (2.00 mL) was added to a EtOH (3.00 mL) solution of **5a** (0.12 g, 0.293 mmol). The mixture was refluxed for 10 min and then poured into a $NaHCO_3$ solution (50.0 mL). The organic layer was separated, and the aqueous layer was extracted with ether. The workup procedure afforded 3-ethoxy-1-phenyl-5-(phenylseleno)-1,4-pentanedione (**6**) (57 mg, 52%).

Reaction of 5a with $TiCl_4$. $TiCl_4$ (94 mg, 0.50 mmol) was added dropwise to a CH_2Cl_2 (1.00 mL) solution of **5a** (0.10 g, 0.25 mmol) at 0 °C under an Ar atmosphere. The mixture was stirred for 10 min and poured into a saturated $NaHCO_3$ solution (50 mL). The workup procedure afforded **7** (30.0 mg, 56%) and **6** (23.0 mg, 25%).

Reaction of 5a with $SnCl_4$. $SnCl_4$ (0.04 mL, 0.40 mmol) was added dropwise to a CH_2Cl_2 (1.00 mL) solution of **5a** (0.10 g, 0.25 mmol) at 0 °C under an Ar atmosphere. The reaction mixture was stirred for 2 h, and the workup procedure afforded **7** (30 mg, 55%).

Reaction of 4-Pentenophenone 5a with LDA. A THF (0.50 mL) solution of **5a** (0.10 g, 0.248 mmol) was added dropwise to a THF (0.50 mL) solution of LDA (prepared from diisopropylamine (0.15 g, 1.49 mmol) and *n*-BuLi (0.66 mL, 0.99 mmol)) at −45 °C. The mixture was stirred for 10 min and poured into water (50 mL). The workup procedure afforded (2*E*,4*Z*)- and (2*Z*,4*Z*)-4-ethoxy-5-(phenylseleno)penta-2,4-dienophenone (**19**) as a yellow oil: 2*E*:2*Z* = 81:19; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (t, J = 7 Hz), 1.45 (t, J = 7 Hz), 4.04 (2H, q, J = 7 Hz), 6.03 (s), 6.72 (s), 7.07 (d, J = 15 Hz), 7.21 (d, J = 15 Hz), 7.30−7.59 (m), 7.90−7.99 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.05 (q), 67.29 (t), 99.23 (s), 119.47 (d), 124.53 (d), 128.59 (d × 2), 128.82 (d × 2), 129.73 (d × 2), 132.93 (d), 132.96 (dx2), 136.28 (s), 138.40 (d), 152.77 (s), 190.67 (s); high-resolution mass calcd for $C_{19}H_{18}O_2Se$ 358.0471, found m/z 358.0477.

Reduction and Cyclization of 5a with $LiBH_4$/Successive Treatment with *t*-BuOK/t-BuOH. A THF (1.00 mL) solution of **5a** (0.10 g, 0.248 mmol) was added dropwise to a dry Et_2O (3.00 mL) suspension of $LiBH_4$ (11 mg, 0.50 mmol) at −78 °C. The mixture was stirred for 10 min and poured into water (50 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 dissolved in *t*-BuOH (2.00 mL). *t*-BuOK (0.24 g, 2.12 mmol) was added to the mixture. The whole was refluxed for 2.5 h and poured into water (50 mL). The workup procedure afforded (2*R**,3*S**,5*R**)-**20** (47 mg, 40%) and (2*S**,3*S**,5*S**)-2,3-diethoxy-5- phenyl-2-(phenylselenomethyl)tetrahydrofuran ((2*S**,3*S**,5*S**)-**20**) (40 mg, 35%) as a yellow oil.

(2*R,3*S**,5*R**)-20**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (3H, t, J = 7 Hz), 1.16 (3H, t, J = 7 Hz), 2.24−2.37 (2H, m), 3.43 (1H, d, J = 12 Hz), 3.36−3.52 (2H, m), 3.56 (1H, d, J = 12 Hz), 3.63−3.70 (2H, m), 4.09 (1H, d, J = 4 Hz), 5.30 (1H, dd, J = 6 and 10 Hz), 7.22−7.30 (4H, m), 7.34−7.35 (4H, m), 7.56−7.59 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.24 (q), 15.68 (q), 28.70 (t), 37.96 (t), 56.63 (t), 65.73 (t), 82.61 (d), 110.98 (s), 126.83 (d × 2), 126.93 (d), 127.88 (d), 128.63 (d × 2), 129.13 (d × 2), 131.29 (s), 132.92 (s), 142.22 (s); high-resolution mass calcd for $C_{21}H_{26}O_3Se$ 406.1046, found m/z 406.1055.

(2*S,3*S**,5*S**)-20**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, t, J = 7 Hz), 1.27 (3H, t, J = 7 Hz), 2.12−2.27 (1H, m), 2.44−2.61 (1H, m), 3.33 (1H, d, J = 13 Hz), 3.46 (1H, d, J = 13 Hz), 3.42−3.55 (1H, m), 3.56−3.67 (1H, m), 3.67−3.85 (2H, m), 4.33 (1H, t, J = 8 Hz), 5.17 (1H, dd, J = 5 and 8 Hz), 7.20−7.30 (4H, m), 7.32−7.38 (4H, m), 7.55−7.57 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.65 (q), 16.22 (q), 32.68 (t), 38.87 (t), 57.00 (t), 66.58 (t), 78.24 (d), 80.91 (d), 105.94 (d), 126.03 (d × 2), 126.92 (d), 127.68 (d), 127.91 (s), 128.64 (d × 2), 129.30 (d ×

2), 131.54 (s), 132.13 (d × 2), 142.95 (s); high-resolution mass calcd for $C_{21}H_{26}O_3Se$ 406.1046, found *m*/*z* 406.1033.

Reaction of 4-Pentenophenone 10a with $TiCl_4$. $TiCl_4$ (0.05 mL, 0.40 mmol) was added dropwise to a CH_2Cl_2 (3.00 mL) solution of **10a** (mg, mmol) at −78 °C. The reaction mixture was poured into a saturated $NaHCO_3$ (100 mL). The organic layer was separated the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$. The workup procedure afforded (2*E*,4*Z*)-5-(phenylseleno)-4-(phenylthio)pent-2,4-dienophenone (**23**) (64 mg, 71%) as a yellow oil. **23**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (1H, d, J = 14 Hz), 7.37 (1H, d, J = 14 Hz), 7.15−7.61 (12H, m), 7.77−7.80 (3H, m), 8.05 (1H, d, J = 1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.4 (d), 126.6 (d), 128.1 (d × 2), 128.4 (s), 128.6 (d × 2), 128.7 (d × 2), 128.8 (d), 129.5 (d × 2), 129.9 (d × 2), 132.9 (d), 133.5 (d × 2), 133.9 (s), 138.4 (s), 142.8 (d), 153.9 (d), 190.6 (s); MS *m*/*z* 265 (M^+ − PhSe). Anal. Calcd for $C_{23}H_{18}OSSe$: C, 65.55; H, 4.31. Found: C, 65.18; H, 4.41.

Diels−Alder Reaction of 4-Ethoxy-5-(phenylseleno)-penta-2,4-dienophenone (19). Reaction of 19 with Dimethyl Acetylenedicarboxylate. A toluene (1.00 mL) solution of **19** (0.10 g, 0.28 mmol) and dimethyl acetylenedicarboxylate (0.40 g, 2.80 mmol) was heated under the reflux condition for 52 h. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt−hexane (1:10) to give dimethyl 3-benzoyl-5-ethoxyphthalate (**24**) (62 mg, 65%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (3H, t, J = 7 Hz), 3.60 (3H, s), 3.90 (3H, s), 4.10 (2H, q, J = 7 Hz), 7.07 (1H, d, J = 2 Hz), 7.41 (1H, d, J = 2 Hz), 7.44−7.48 (2H, m), 7.57−7.61 (1H, m), 7.76−7.78 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.77 (q), 52.66 (q), 53.10 (q), 64.64 (t), 116.92 (d), 117.96 (d), 125.07 (s), 128.74 (s), 128.98 (s), 130.06 (d × 2), 133.64 (d), 136.69 (s), 141.40 (s), 159.88 (s), 167.12 (s), 167.42 (s), 195.63 (s); MS *m*/*z* 342 (M^+). Anal. Calcd for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.48; H, 5.23.

Reaction of 19 with Benzoquinone. A toluene (2.0 mL) solution of **19** (0.10 g, 0.28 mmol) and benzoquinone (0.30 g, 2.80 mmol) was refluxed for 8 h. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt−hexane (1:10) to give 5-benzoyl-7-ethoxynaphthoquinone (**25**) (63 mg, 74%) as purple prisms.

25: mp 145−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (3H, t, J = 7 Hz), 4.21 (2H, q, J = 7 Hz), 6.80 (1H, d, J = 9 Hz), 6.93 (1H, d, J = 9 Hz), 7.07 (1H, d, J = 2 Hz), 7.41−7.47 (3H, m), 7.53−7.58 (1H, m), 7.63 (1H, dd, J = 1 and 2 Hz), 7.76−7.79 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.72 (q), 65.02 (t), 111.86 (d), 119.22 (d), 128.82 (d × 2), 129.24 (d × 2), 133.59 (d), 134.72 (s), 136.56 (s), 138.15 (d), 139.24 (d), 139.51 (s), 143.92 (s), 163.46 (s), 183.31 (s), 184.73 (s), 196.39 (s); MS *m*/*z* 306 (M^+). Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.41; H, 4.58.

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Supporting Information Available: Characterization data for the products **5c**, **10a**−**c**, **11**, **12**, **14**, **15**, **17**, and **18,** ^{1}H and ^{19}F NMR spectra complete peak assignments of other products, and full lists of IR spectral data. This material data is available free of charge via the Internet at http://pubs.acs.org.

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