Stereospecific Syntheses of 5-Alkyl-3-ethoxy-2-((phenylchalcogeno)methylene)tetrahydrofurans

Mitsuhiro Yoshimatsu,*,† Motoyo Naito,‡ Hiroshi Shimizu,‡ Osamu Muraoka,§ Genzoh Tanabe,§ and Tadashi Kataoka‡

Gifu University, Faculty of Education, Yanagido, Gifu 501-11, Japan, Gifu Pharmaceutical University, 6-1 Mitahora-higashi 5-chome, Gifu 502, Japan, and Kinki University, Faculty of Pharmaceutical Sciences, 3-4-1, Kowakae, Higashi-osaka, Osaka 577, Japan

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2-Ethoxy-4-(phenylchalcogeno)but-3-ynyl ketones **1**−**10** were reduced with $LiBH_4$ in Et_2O diastereoselectively to give 5-(phenylchalcogeno)pent-4-yn-1-ols **11**−**20**. Treatment of the phenylchalcogen-substituted alkynyl alcohols **11**−**20** with *t*-BuOK in *t*-BuOH provided useful (*Z*)-2-((phenylchalcogeno)methylene)tetrahydrofurans **21**−**31** stereoselectively.

Alkynyl sulfides and selenides are synthetic intermediates of great potential.[1] Comasseto *et al.* reported that the *m*-CPBA-oxidation of alkynyl selenides gave the symmetrical 1,4-disubstituted buta-1,3-diynes in good yields.[2] Recently, it was reported that the Lewis acid-promoted [2 + 2] cycloaddition reactions of the alkynyl chalcogenides with electron-deficient olefins proceeded smoothly and gave cyclobutene derivatives, which could be further transformed to bicyclo[3.2.1]octenones.[3] Alkynyl chalcogenides can lead to vinyl chalcogenides, which are useful synthetic intermediates,[4] by reduction[5] or hydrostannation.[6]

Previously, we prepared versatile 3-butynyl ketones[7] by α-site-selective reactions of γ-chalcogen-substituted prop-2-ynyl cations with silyl enol ethers.[8] When we reduced the 3-butynyl ketone **1** with $NaBH_4$ in EtOH at room temperature, (*Z*)-2-((phenylseleno)methylenetetrahydrofuran **21a** was obtained in 21% yield together with alcohol **11a** (68%) (Scheme 1). (*Z*)-2-Alkenyltetrahydrofurans are key intermediates in the synthesis of prostacyclin PGI_2 and have been prepared by mercury(II)- or palladium(II)-induced cyclization of *cis*-2-prop-2-ynyl cyclopentanol.[9] Generally, reactions with palladium(II), mercury(II), or Ag(I) salt have been used for the intramolecular cyclization reactions of alkynyl alcohols,[10] and reactions without a metal catalyst have been reported to give mixtures of endo- and exo-mode cyclized products.[11] Cyclization of 2,4,6-octatriynol with sodium hydroxide in methanol has been reported, but the yields and stereochemistry of the products have not been described.[12] If (*Z*)-2-alkenyltetrahydrofurans can be constructed regio- and stereoselectively without a metal salt catalyst, this novel method will be both practical and convenient for the syntheses of PGI_2 analogues and other tetrahydrofuran derivatives. Therefore, we undertook a precise investigation of the synthesis of 2-alkenyltetrahydrofurans starting from 4-(phenylchalcogeno)-3-butynyl ketones. This paper describes the regio- and stereoselective intramolecular cycloaddition of γ-ynols promoted by a strong base.

Scheme 1

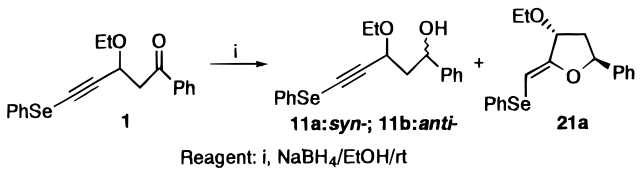

Table 1. Reductions of 3-Ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-one (1)

entry	conditions	% yield (**11a**:**11b**)
1	$NaBH_4$/EtOH/0 °C	100 (1.2:1)
2	$NaBH_4/Et_3B/CH_2Cl_2$/−78 °C	recover
3	DIBAL/Et_2O/−78 °C	100 (3:1)
4	DIBAL/$ZnCl_2/Et_2O$/−78 °C	recover
5	DIBAL/LiBr/Et_2O/−78 °C	100 (3:1)
6	$LiAlH_4/Et_2O$/−80 °C	100 (2.5:1)
7	$LiAlH_4$/LiI/Et_2O/−80 °C	100 (2.5:1)
8	$Zn(BH_4)_2/Et_2O$/−78 °C	100 (2:1)
9	$LiBH_4/Et_2O$/−80 °C	100 (9:1)

We first examined the diastereoselective reduction of β-ethoxy ketone **1**[8] by reference to the literature,[13] and the results are shown in Table 1. The combination of LiI−$LiAlH_4$ has been reported to bring about the *syn*-reduction of β-alkoxy ketones;[14] however, this method was

† Gifu University.
‡ Gifu Pharmacetuical University.
§ Kinki University.
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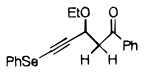
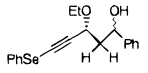
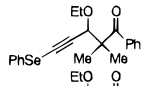
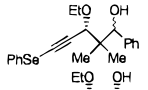
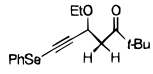
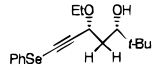
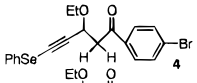
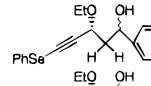
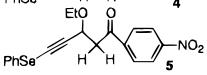
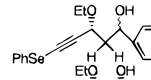
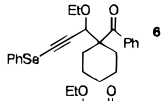
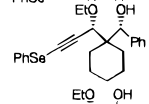
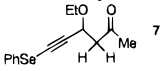
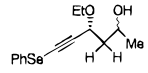
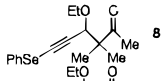
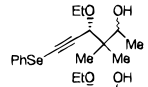
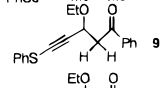
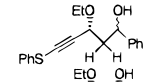
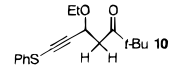
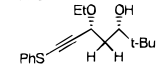
Table 2. Reductions of Various β-Alkoxy Ketones by $LiBH_4$ or $NaBH_4$

Entry	Alkynyl ketone	Conditions[b]	Products (%yields/*syn*:*anti*)[a]
1	 1	A	 **11a,b**(100/9:1)
2	 2	A	 **12a,b**(100/5.2:1)
3	 3	A	 **13a**(57/100:0)
4	**3**	B	**13a,b**(83/45:37)
5	 **4**	A	 **14a,b**(94/8:1)
6	 **5**	A	 **15a,b**(100/15:1)
7	 6	A/-30 °C	 **16a**(100/100:0)
8	 7	A	 **17a,b**(83/7:1)
9	 8	A	 **18a**(100/100:0)
10	 9	A	 **19a,b**(82/6:1)
11	 10	A	 **20a**(84/100:0)

[a] (a) *syn*- and (b) *anti*-isomer.

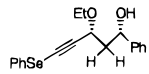
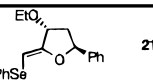
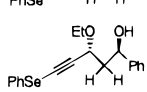
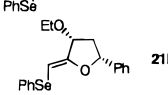
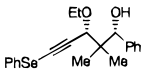
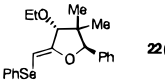
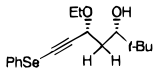
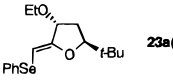
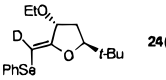
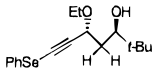
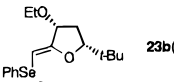
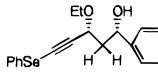
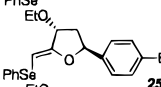
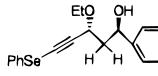
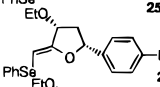
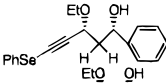
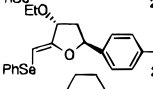
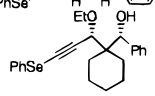
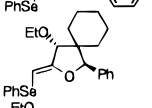
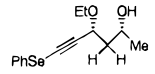
Table 3. Cyclization Reactions of Alkynyl Alcohol 13a with Some Bases

entry	conditions	% yield (**23a**:**23b**)
1	NaH (2 equiv)/THF/15-crown-5/ 0 °C/30 min	88 (29:1)
2	LiH (2 equiv)/THF/15-crown-5/ rt/12 h	recovery
3	*t*-BuOK (2 equiv)/t-BuOH/ 18-crown-6/rt/20 min	100 (100:0)
4	*t*-BuOK (2 equiv)/THF/18-crown-6/0 °C/30 s	96 (100:0)

not effective with compound **1** (Table 1, entry 7). $LiBH_4$ reduction of the β-ethoxy ketone **1** in Et_2O afforded β-ethoxy alcohols **11a** and **11b** with good diastereoselectivity (*syn*:*anti* = 9:1, Table 1, entry 9). Therefore, this reducing agent was used for the reduction of other β-alkoxy ketones **2**−**10**, and the results are shown in Table 2. *tert*-Butyl ketones **3** and **10** were exclusively reduced to the *syn*-alcohols **13a** and **20a**, respectively (Table 2, entries 3 and 11). *p*-Nitrophenyl ketone **5** also gave the *syn*-alcohol **15a** with high stereoselectivity. The alcohol **16a**, obtained from cyclohexane derivative **6**, was converted to *p*-nitrobenzoate derivative **16′**, and its stereostructure was determined by single-crystal X-ray analysis.

A brief study on the diastereoselective cyclization of alkynyl alcohol **13a** was conducted employing a few bases, and the results are shown in Table 3. *t*-BuOK was found to be a very suitable base for this cyclization reaction. The reaction of alkynyl alcohol **13a** with *t*-BuOK/*t*-BuOH/18-crown-6 gave (*Z*)-2-((phenylseleno)-methylene)tetrahydrofuran derivative **23a** diastereoselectively (Table 3, entry 3). These reaction conditions were applied to alkynyl alcohols **11**−**20**, and the results obtained are shown in Table 4. *syn*-Alkynyl alcohol **11a**

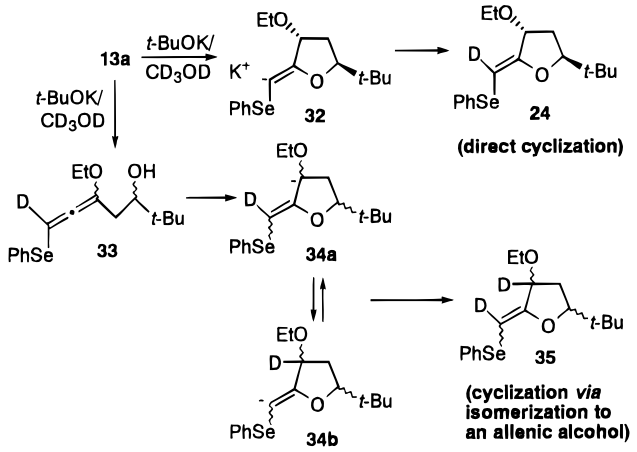
Table 4. Cyclization Reactions of Alkynyl Alcohols with *t*-BuOK

Entry	Alkynyl Alcohol	Conditions[a]	Product (%yield)
1	 **11a**	*t*-BuOH/rt/1h	 **21a**(93)
2	 **11b**	*t*-BuOH/rt/1h	 **21b**(88)
3	 **12a**	*t*-BuOH/rt/1h	 **22**(93)
4	 **13a**	*t*-BuOH/83°C/1h	 **23a**(90)
5	**13a**	CD_3OD/rt/12h	 **24**(69)
6	 **13b**	*t*-BuOH/83°C/1h	 **23b**(64)
7	 **14a**	*t*-BuOH/rt/1h	 **25a**(100)
8	 **14b**	*t*-BuOH/rt/1h	 **25b**(88)
9	 **15a**	*t*-BuOH/rt/10min	 **26**(40)
10	 **16a**	*t*-BuOH/rt/30min	 **27**(83)
11	 **17a**	*t*-BuOH/rt/1h	**28**(quant.)
12	**18a**	*t*-BuOH/rt/1h	**29**(73)
13	**19a**	*t*-BuOH/rt/20min	**30**(83)
14	**20a**	*t*-BuOH/rt/1h	**31**(74)

gave rise to *trans*-(*Z*)-2-((phenylseleno)methylene)-substituted tetrahydrofuran derivative **21a** in 93% yield, while *anti*-isomer **11b** provided *cis*-tetrahydrofuran derivative **21b** exclusively. Structure assignment of the product **21a** was performed using analytical and NMR spectral data. The analytical data indicated the molecular formula: $C_{19}H_{20}O_2Se$. The ^1H NMR spectrum exhibited a broad singlet at δ 5.48 due to the characteristic vinyl proton and two pairs of doublets at δ 2.53 (J = 5, 13 Hz) and 5.60 (J = 5, 10 Hz) due to one 4-H and 5-H, respectively. The *trans*-configuration between the phenyl group and the ethoxy group of the isomer **21a** was determined by reference to Williams' report on the chemical shift method of 3,5-disubstituted tetrahydrofuran derivatives.[15] The diastereotopic hydrogens of the 4-position methylene show the largest shift difference at 0.26 ppm for **21b**, which has a 3,5-*syn* relationship in contrast to that for **21a**, which has a 3,5-*anti* stereochemistry. Moreover, the stereochemical assignment of the products was supported by a single X-ray analysis of product **27**. β,β-Dimethyl alcohol **12a** afforded 4,4-dimethyltetrahydrofuran derivative **22** (Table 4, entry 3).

(15) 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.

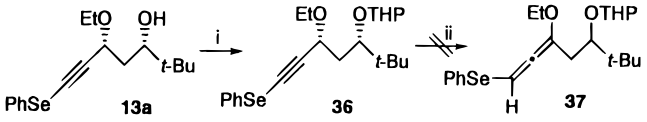
Scheme 2



Cyclohexane derivative **16a** gave 4-spirocyclohexane derivative **27** in 83% yield (Table 4, entry 10). Hexynols **17a** and **18a** furnished 5-methyl-substituted tetrahydrofurans **28** and **29** in quantitative yields, respectively (Table 4, entries 11 and 12). (Phenylthio)alkynyl derivatives **19a** and **20a** also gave 2-((phenylthio)methylene)-tetrahydrofurans **30** and **31** in good yields, respectively (Table 4, entries 13 and 14).

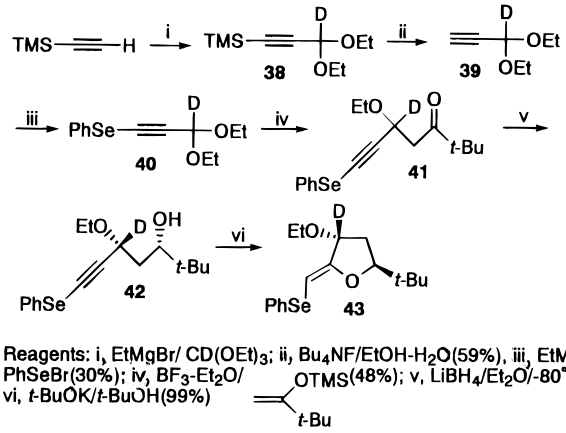
In order to determine the reaction intermediate, the cyclization of **13a** was conducted in CD_3OD to give (deuteriomethylene)tetrahydrofuran **24** in 69% yield (Table 4, entry 5). It has been reported that alkynyl alcohols isomerize to the corresponding allenic alcohols under basic conditions to afford oxygen heterocycles upon cyclization.[11,12] Thus, cyclization of β-allenic alcohols with silver nitrate proceeds in the 6-endo manner to afford 5,6-dihydro-2*H*-pyrans,[16] while the reaction with sodium hydroxide in methanol gave 2-alkylidenetetrahydrofurans *via* the 5-exo-mode cyclization.[12] If the reaction described herein proceeded *via* the allenic intermediate **33** (Scheme 2), the reaction of **13a** in CD_3OD should have yielded 3-deuterio-2-(deuteriomethylene)tetrahydrofuran derivative **35** through the deuteration of the anions **34a** or **34b**. The fact that the reaction gave 2-(1-deuteriomethylene)tetrahydrofuran derivative **24** shows that the intermediate is the *exo*-vinyl anion **32**. Luo *et al.* reported that the intramolecular oxypalladation of acetylenic alkoxides[17] followed by a cross-coupling reaction leads to the stereoselective construction of 2-(methylene)-tetrahydrofurans; however, if our cyclization proceeds *via* the direct attack of the alkoxide on the alkynes, the progression of the reaction without a transition metal shows that the phenylchalcogeno group of the alkynyl alcohol would effectively stabilize the transient vinyl anion intermediate **32**. The reaction mechanism was further examined as described in Schemes 3 and 4. In order to investigate the potential cyclization reaction of allenyl alcohol, the alkynyl alcohol **13a** was protected as the THP derivative **36**. However, subsequent isomerization of **36** to allene **37** by *t*-BuOK/*t*-BuOH was attempted with no success whatsoever. To determine unequivocally whether this cyclization reaction proceeds *via* an allenyl ether intermediate or by the direct addition of alkoxide to the alkynyl moiety, the 3-deuterated alkynyl alcohol **42** was specifically prepared (Scheme 4).

Scheme 3[a]



[a] Reagents: (i) 3,4-Dihydro-2*H*-pyran/PPTS; (ii) *t*-BuOK/*t*-BuOH/ reflux.

Scheme 4[a]



Deuterated orthoformate[18] was treated with trimethylsilyl acetylide to provide (trimethylsilyl)propynal acetal **38**, which after desilylation using $Bu_4NF/EtOH-H_2O$ was transformed to **39** in satisfactory yield. In turn, the alkynyl alcohol **42** was obtained according to the procedure described above (Scheme 4). The cyclization of alcohol **42** afforded the 3-deuterated tetrahydrofuran derivative **43** quantitatively. These results support our conclusion that the novel cyclization described in this paper proceeds *via* intramolecular oxymetalation of the acetylenic moiety of the alkynyl alcohol substrates.

The 2-((phenylseleno)alkenyl) group can in principle be converted to alkyl- and aryl-substituted vinyl derivatives[19] and allylsilanes[20] by a Ni-catalyzed cross-coupling reaction. Furthermore, allylic ether derivatives are also converted to allylic zirconium reagents by Cp_2ZrCl_2, which react with aldehydes in a highly diastereoselective manner to give homoallylic alcohols.[21] Hence, the ((phenylseleno)methylene)tetrahydrofurans described herein can be functionalized at both the vinyl carbon and the 3-position and used as versatile synthetic intermediates.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. ^1H and ^{13}C NMR spectra were determined with a JEOL GX-270 (270 MHz) or a JEOL EX-400 (400 MHz) spectrometer at Gifu Pharmaceutical University and at the Center of Instrumentation of 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

(16) Chilot, J.-T.; Doutheau, A.; Gore, J. *Tetrahedron Lett.* **1982**, *23*, 4693; *Bull. Soc. Chim. Fr.* **1984**, 307.

(17) Luo, F.-T.; Schreuder, I.; Wang, R.-T. *J. Org. Chem.* **1992**, *57*, 2213.

(18) Sako, M.; Hayashi, T.; Hirota, K.; Maki, Y. *Chem. Pharm. Bull.* **1992**, *40*, 1656.

(19) Okamura, H.; Miura, M.; Kosugi, K.; Takei, H. *Tetrahedron Lett.* **1980**, *21*, 87.

(20) Hevesi, L.; Hermans, B.; Allard, C. *Tetrahedron Lett.* **1994**, *35*, 6729.

(21) Ito, H.; Taguchi, T.; Hanzawa, Y. *Tetrahedron Lett.* **1992**, *33*, 1295.

on a JASCO IRA-100 infrared spectrometer and are expressed in reciprocal centimeters. EI mass spectra (MS) were obtained using a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. All exact mass determinations were obtained on the JMA 2000 on-line system.

Preparation of Acetylenic Ketones 1−10. Typical Procedure. $BF_3{\cdot}Et_2O$ (2.47 g, 17.4 mmol) was added dropwise to a dry CH_2Cl_2 (20 mL) solution of 3,3-diethoxy-1-(phenylseleno)-1-propyne (2.08 g, 7.34 mmol) and 1-((trimethylsilyl)oxy)styrene (2.52 g, 13.1 mmol) under an Ar atmosphere at −78 °C. The reaction mixture was stirred for 30 min and poured into a saturated $NaHCO_3$ solution (200 mL). The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The organic layer and the extracts were combined and 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-Ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-one (**1**) (1.95 g, 63%) was obtained as a yellow oil.

3-Ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-one (1): a yellow oil; IR (film, cm^{-1}) 2170 (acetylene), 1680 (CO); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.20 (3H, t, J = 7 Hz), 3.32 (1H, dd, J = 5, 16 Hz), 3.51−3.60 (1H, m), 3.55 (1H, dd, J = 5, 16 Hz), 3.83−3.90 (1H, m), 4.94 (1H, dd, J = 5, 8 Hz), 7.21−7.29 (2H, m), 7.43−7.57 (6H, m), 7.95−7.97 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.03 (q), 44.79 (t), 64.89 (t), 65.73 (s), 66.28 (d), 102.52 (s), 128.24 (d), 128.38 (s), 128.60 (d), 129.00 (d), 129.50 (d), 133.28 (d), 136.83 (s), 196.23 (s). Anal. Calcd for $C_{19}H_{18}O_2Se$: C, 63.87; H, 5.08. Found: C, 63.66; H, 5.08.

2,2-Dimethyl-3-ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-one (2): a yellow oil; IR (film, cm^{-1}) 2170 (acetylene), 1680 (CO); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.12 (3H, t, J = 7 Hz), 1.40 (3H, s), 1.42 (3H, s), 3.23−3.28 (1H, m), 3.75−3.81 (1H, m), 4.66 (1H, s), 7.24−7.55 (10H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 14.85 (q), 20.65 (q), 23.50 (q), 52.38 (s), 65.18 (t), 66.84 (s), 76.46 (d), 100.86 (s), 126.90 (d), 128.51 (s), 129.06 (d), 129.53 (d), 130.30 (d), 139.89 (s), 208.83 (s); MS m/z 386 (small M^+). Anal. Calcd for $C_{21}H_{22}O_2Se$: C, 65.45; H, 5.75. Found: C, 65.19; H, 5.70.

2,2-Dimethyl-5-ethoxy-7-(phenylseleno)hept-6-yn-3-one (3): a yellow oil; IR (film, cm^{-1}) 2125 (acetylene), 1700 (CO); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.13 (9H, s), 1.18 (3H, t, J = 7 Hz), 2.81 (1H, dd, J = 5, 17 Hz), 3.12 (1H, dd, J = 8 and 17 Hz), 3.42−3.49 (1H, m), 3.78−3.84 (1H, m), 4.78 (1H, dd, J = 5, 8 Hz), 7.25−7.38 (3H, m), 7.49−7.57 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.05 (q), 25.93 (q), 43.03 (t), 44.17 (s), 64.92 (t), 65.22 (s), 66.40 (d), 102.71 (s), 127.12 (d), 128.58 (s), 129.02 (d), 129.50 (d), 130.38 (d), 211.74 (s); MS m/z 337 (M^+-1). Anal. Calcd for $C_{17}H_{22}O_2Se$: C, 60.53; H, 6.57. Found: C, 60.24; H, 6.46.

1-(*p*-Bromophenyl)-3-ethoxy-5-(phenylseleno)pent-4-yn-1-one (4): a yellow oil; IR (film, cm^{-1}) 2170 (acetylene), 1690 (CO); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.19 (3H, t, J = 7 Hz), 3.27 (1H, dd, J = 5, 17 Hz), 3.49−3.55 (2H, m), 3.82−3.88 (1H, m), 4.90 (1H, dd, J = 5, 8 Hz), 7.25−7.30 (3H, m), 7.48 (2H, brd, J = 6 Hz), 7.58 (2H, d, J = 9 Hz), 7.81 (2H, d, J = 9 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 14.97 (q), 44.65 (t), 64.88 (t), 66.01 (s), 66.19 (d), 102.15 (s), 127.13 (d), 128.23 (s), 128.48 (s), 129.03 (d), 129.49 (d), 129.76 (d), 131.87 (d), 135.54 (s), 195.29 (s); MS m/z 436 (M^+ − 1). Anal. Calcd for $C_{19}H_{17}BrO_2Se$: C, 52.32; H, 3.93. Found: C, 52.10; H, 3.96.

3-Ethoxy-1-(*p*-nitrophenyl)-5-(phenylseleno)pent-4-yn-1-one (5): yellow needles; mp 55−56 °C; IR (KBr, cm^{-1}) 2170 (acetylene), 1700 (CO), 1540, 1340 (NO_2); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.19 (3H, t, J = 7 Hz), 3.34 (1H, dd, J = 5, 16 Hz), 3.49−3.55 (1H, m), 3.60 (1H, dd, J = 8, 16 Hz), 3.84−3.91 (1H, m), 4.90 (1H, dd, J = 5, 8 Hz), 7.26−7.32 (3H, m), 7.48 (2H, d, J = 8 Hz), 8.12 (2H, d, J = 8 Hz), 8.28 (2H, d, J = 8 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 14.98 (q), 45.19 (t), 65.01 (t), 66.17 (d), 66.59 (s), 101.70 (s), 123.81 (d), 127.28 (d), 128.11 (s), 129.13 (d), 129.33 (d), 129.57 (d), 141.28 (s), 150.35 (s), 195.12 (s). Anal. Calcd for $C_{19}H_{17}NO_4Se$: C, 56.72; H, 4.26; N, 3.48. Found: C, 56.94; H, 4.33; N, 3.56.

1-Benzoyl-1-(1-ethoxy-3-(phenylseleno)prop-2-ynyl)cyclohexane (6): a yellow oil; IR (film, cm^{-1}) 2170 (acetylene), 1680 (CO); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.05−1.19 (1H, m), 1.17 (3H, t, J = 7 Hz), 1.46−1.60 (6H, m), 1.74−1.79 (1H, m), 2.31 (1H, brd, J = 12 Hz), 2.53 (1H, brd, J = 14 Hz), 3.31−3.35 (1H, m), 3.84−3.88 (1H, m), 4.44 (1H, s), 7.22−7.41 (6H, m), 7.53 (2H, brd, J = 8 Hz), 7.67 (2H, brd, J = 8 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 14.69 (q), 22.28 (t), 22.96 (t), 25.67 (t), 28.87 (t), 32.60 (t), 56.88 (s), 65.22 (t), 67.77 (s), 78.17 (d), 100.99 (d), 129.41 (d), 129.98 (d), 141.37 (s), 209.42 (s); high-resolution mass calcd for $C_{24}H_{26}O_2Se$ m/z 426.1098, found m/z 426.1113.

4-Ethoxy-6-(phenylseleno)hex-5-yn-2-one (7): a yellow oil; IR (film, cm^{-1}) 2170 (acetylene), 1720 (CO); ^1H NMR (270 MHz) ($CDCl_3$) δ 1.20 (3H, t, J = 7 Hz), 2.20 (3H, s), 2.78 (1H, dd, J = 5, 16 Hz), 2.98 (1H, dd, J = 8, 16 Hz), 3.43−3.54 (1H, m), 3.77−3.89 (1H, m), 4.71 (1H, dd, J = 5, 8 Hz), 7.23−7.35 (3H, m), 7.48−7.52 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 14.97 (q), 30.81 (q), 49.35 (t), 64.79 (t), 66.02 (d), 68.58 (s), 102.05 (s), 127.19 (d), 128.33 (s), 129.07 (d), 129.53 (d), 204.90 (s). A small M^+ was observed at m/z 296 but was too small for the high-resolution mass spectrum to be measured.

3,3-Dimethyl-4-ethoxy-6-(phenylseleno)hex-5-yn-2-one (8): a yellow oil; IR (film, cm^{-1}) 2160 (acetylene), 1710 (CO); ^1H NMR (270 MHz) ($CDCl_3$) δ 1.17 (3H, t, J = 7 Hz), 1.18 (3H, s), 1.25 (3H, s), 2.18 (3H, s), 3.36−3.47 (1H, m), 3.76−3.88 (1H, m), 4.47 (1H, s), 7.17−7.40 (3H, m), 7.49−7.60 (2H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 14.84 (q), 19.44 (q), 22.19 (q), 26.49 (q), 65.19 (t), 75.73 (s), 76.18 (d), 100.81 (s), 127.15 (d), 129.14 (d), 129.51 (s), 129.55 (d), 211.58 (s). A small M^+ was observed at m/z 324 but was too small for the high-resolution mass spectrum to be measured.

3-Ethoxy-1-phenyl-5-(phenylthio)pent-4-yn-1-one (9): a yellow oil; IR (film, cm^{-1}) 2170 (acetylene), 1680 (CO); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.20 (3H, t, J = 7 Hz), 3.33 (1H, dd, J = 5, 16 Hz), 3.51−3.62 (2H, m), 3.83−3.90 (1H, m), 4.96 (1H, dd, J = 5, 7 Hz), 7.18−7.22 (1H, m), 7.24−7.32 (2H, m), 7.37−7.40 (2H, m), 7.42−7.46 (2H, m), 7.53−7.57 (1H, m), 7.95−7.97 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 14.95 (q), 44.63 (t), 64.80 (t), 66.10 (d), 72.36 (s), 97.67 (s), 126.14 (d), 126.49 (d), 128.15 (d), 128.54 (d), 129.14 (d), 132.40 (s), 133.24 (d), 136.73 (s), 196.07 (s); MS m/z 309 (M^+ − 1). Anal. Calcd for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84. Found: C, 73.29; H, 5.82.

2,2-Dimethyl-5-ethoxy-6-(phenylthio)hept-7-yn-3-one (10): a yellow oil; IR (film, cm^{-1}) 2170 (acetylene), 1710 (CO); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.14 (9H, s), 1.20 (3H, t, J = 7 Hz), 2.83 (1H, dd, J = 5, 17 Hz), 3.11 (1H, dd, J = 8, 17 Hz), 3.46−3.50 (1H, m), 3.80−3.84 (1H, m), 4.78 (1H, dd, J = 5, 8 Hz), 7.31−7.40 (5H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.00 (q), 25.90 (q), 42.93 (t), 44.14 (s), 64.89 (t), 66.25 (d), 71.90 (s), 97.90 (s), 126.16 (d), 126.52 (d), 129.18 (d), 132.45 (s), 211.66 (s); MS m/z 289 (M^+ − 1). Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.64. Found: C, 70.00; H, 7.45.

Preparation of Alkynyl Alcohols 11a,b−20a, Typical Procedure. An Et_2O (3 mL) solution of 3-ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-one (**1**) (0.10 g, 0.28 mmol) was added dropwise to an Et_2O suspension of $LiBH_4$ (0.01 g, 0.60 mmol) under an Ar atmosphere at −80 °C. The reaction mixture 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 organic layer and the extracts were combined and 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 (1:10) and afforded (*1S*,3R**)- (**11a**) and (*1R*,3R**)-3-ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-ol (**11b**) (0.1 g, 100%) as a pale yellow oil.

***(1S*,3R*)*-3-Ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-ol (11a)**: a colorless oil; IR (film, cm^{-1}) 3700−3200 (OH), 2170 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.24 (3H, t, J = 7 Hz), 2.04−2.09 (1H, m), 2.25−2.33 (1H, m), 3.43−3.50 (2H, m), 3.84−3.90 (1H, m), 4.44 (1H, dd, J = 5, 9 Hz), 4.92 (1H, dd, J = 4, 9 Hz), 7.22−7.34 (8H, m), 7.47−7.51 (2H, m). ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.10 (q), 45.00 (t), 64.70 (t), 66.25 (s), 69.82 (d), 72.89 (d), 102.13 (s), 125.72 (d), 127.13 (d), 127.49 (d), 128.23 (s), 128.37 (d), 128.96 (d), 129.49 (d), 143.75 (s). Anal. Calcd for $C_{19}H_{20}O_2Se$: C, 63.56; H, 5.61. Found: C, 63.82; H, 5.68.

***(1R*,3R*)*-3-Ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-ol (11b)**: a colorless oil; IR (film, cm^{-1}) 3600−3200 (OH), 2170 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.27 (3H, J = 7 Hz), 2.20−2.24 (2H, m), 3.42−3.50 (2H, m), 3.86−3.93 (1H, m), 4.47 (1H, dd, J = 4, 6 Hz), 5.13 (1H, brs), 7.25−7.38 (8H, m), 7.52−7.54 (2H, m); high-resolution mass calcd for $C_{19}H_{20}O_2Se$ m/z 360.0628, found m/z 360.0636.

***(1R*,3R*)*- and *(1S*,3R*)*-2,2-Dimethyl-3-ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-ol (12a,b)**: **12a**:**12b** = 5.2:1; a colorless oil; IR (film, cm^{-1}) 3600−3200 (OH), 2170 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 0.80 (s), 0.98 (s), 1.27 (t, J = 7 Hz), 3.43−3.51 (m), 3.78 (brs), 3.88−3.96 (m), 4.16 (s), 4.18 (s), 4.73 (s), 4.84 (s), 7.20−7.32 (m), 7.49−7.51 (m); ^{13}C NMR of **12a** (100 MHz) ($CDCl_3$) δ 15.06 (q), 15.64 (q), 21.92 (q), 43.13 (s), 66.74 (t and s), 79.94 (d), 80.58 (d), 101.03 (s), 127.15 (d), 127.42 (d), 127.55 (d), 128.01 (d), 128.55 (s), 129.07 (d), 129.51 (d), 141.10 (s). Anal. Calcd for $C_{21}H_{24}O_2Se$: C, 65.11; H, 6.30. Found: C, 64.99; H, 6.30.

***(3S*,5R*)*-2,2-Dimethyl-5-ethoxy-7-(phenylseleno)hept-6-yn-3-ol (13a)**: a colorless oil; IR (film, cm^{-1}) 3650−3200 (OH), 2170 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 0.91 (9H, s), 1.25 (3H, t, J = 7 Hz), 1.87−1.97 (2H, m), 3.09 (1H, brs), 3.47−3.53 (2H, m), 3.89−3.90 (1H, m), 4.46 (1H, dd, J = 5, 9 Hz), 7.26−7.34 (3H, m), 7.51 (2H, d, J = 7 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.10 (q), 25.57 (q), 34.70 (s), 37.75 (t), 64.88 (t), 65.97 (s), 71.11 (d), 78.68 (d), 102.44 (s), 127.16 (d), 128.30 (s), 128.99 (d), 129.52 (d); high-resolution mass calcd for $C_{17}H_{24}O_2Se$ m/z 340.0941, found m/z 340.0957.

***(3R*,5R*)*-2,2-Dimethyl-5-ethoxy-7-(phenylseleno)hept-6-yn-3-ol (13b)**: a colorless oil; IR (film, cm^{-1}) 3700−3100 (OH), 2170 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 0.91 (9H, s), 1.23 (3H, t, J = 7 Hz), 1.79−1.86 (1H, m), 1.92−1.96 (1H, m), 2.85 (1H, brs), 3.43−3.50 (1H, m), 3.73−3.75 (1H, m), 3.84−3.90 (1H, m), 4.59−4.61 (1H, m), 7.26−7.33 (3H, m), 7.52−7.54 (2H, m); high-resolution mass calcd for $C_{17}H_{24}O_2Se$ m/z 340.0941, found m/z 340.0958.

***(1S*,3R*)*-1-(*p*-Bromophenyl)-3-ethoxy-5-(phenylseleno)pent-4-yn-1-ol (14a)**: a colorless oil; IR (film, cm^{-1}) 3600−3200 (OH), 2170 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.26 (3H, t, J = 7 Hz), 2.01−2.20 (1H, m), 2.23−2.28 (1H, m), 3.46−3.53 (1H, m), 3.61 (1H, brs), 3.86−3.94 (1H, m), 4.47 (1H, dd, J = 5, 9 Hz), 4.83−4.90 (1H, m), 7.20−7.31 (5H, m), 7.44 (2H, d, J = 8 Hz), 7.48 (2H, dd, J = 1, 8 Hz). ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.06 (q), 44.85 (t), 64.75 (t), 66.58 (s), 69.78 (d), 72.34 (d), 101.74 (s), 121.18 (s), 127.44 (d), 128.10 (s), 128.99 (d), 129.51 (d), 131.39 (d), 142.76 (s); high-resolution mass calcd for $C_{19}H_{19}BrO_2Se$ m/z 437.9733, found m/z 437.9712.

***(1R*,3R*)*-1-(*p*-Bromophenyl)-3-ethoxy-5-(phenylseleno)pent-4-yn-1-ol (14b)**: a colorless oil; IR (film, cm^{-1}) 3650−3100 (OH), 2170 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.26 (3H, t, J = 7 Hz), 2.13−2.18 (2H, m), 3.43−3.48 (1H, m), 3.61 (1H, brs), 3.85−3.91 (1H, m), 4.44−4.47 (1H, m), 5.02−5.08 (1H, m), 7.21−7.40 (5H, m), 7.45 (2H, d, J = 8 Hz), 7.51 (2H, d, J = 8 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.08 (q), 43.97 (t), 64.97 (t), 66.92 (s), 68.64 (d), 70.73 (d), 101.63 (s), 120.96 (s), 127.27 (d), 127.37 (d), 128.19 (s), 129.14 (d), 129.54 (d), 131.39 (d), 142.93 (s); high-resolution mass calcd for $C_{19}H_{19}BrO_2Se$ m/z 437.9734, found m/z 437.9714.

***(1S*,3R*)*- and *(1R*,3R*)*-3-ethoxy-1-(*p*-nitrophenyl)-5-(phenylseleno)-pent-4-yn-1-ol (15a,b)**: **15a**:**15b** = 15:1; a yellow oil; IR (film, cm^{-1}) 3700−3200 (OH), 2170 (acetylene), 1520, 1350 (NO_2); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.26 (t, J = 7 Hz), 2.07−2.14 (m), 2.15−2.27 (m), 3.44−3.56 (m), 3.88−3.95 (m), 3.40 (brs), 4.50−4.53 (m), 4.54 (dd, J = 5, 9 Hz), 5.04 (brd, J = 9 Hz), 5.21−5.23 (m), 7.23−7.31 (m), 7.47−7.52 (m), 8.14 (d, J = 8 Hz); ^{13}C NMR of **15a** (100 MHz) ($CDCl_3$) δ 14.93 (q), 44.59 (t), 64.71 (t), 66.96 (s), 69.56 (d), 71.93 (d), 101.31 (s), 123.43 (d), 126.36 (d), 127.18 (d), 128.94 (d), 129.43 (d), 146.97 (s), 151.09 (s); high-resolution mass calcd for $C_{19}H_{19}NO_4Se$ m/z 405.0479, found m/z 405.0460.

***(1R*,3R*)*-3-Ethoxy-2,2-pentamethylene-1-phenyl-5-(phenylseleno)pent-4-yn-1-ol (16a)**: a yellow oil; IR (film, cm^{-1}) 3620−3200 (OH), 2170 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.25 (3H, t, J = 7 Hz), 1.32−1.59 (8H, m), 1.82−2.01 (2H, m), 3.37−3.41 (1H, m), 3.83 (1H, d, J = 7 Hz), 3.90−3.95 (1H, m), 4.44 (1H, s), 4.80 (1H, d, J = 7 Hz), 7.19−7.28 (6H, m), 7.35−7.39 (4H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 14.93 (q), 21.42 (t), 21.50 (t), 25.65 (t), 29.84 (t), 30.82 (t), 44.69 (s), 65.28 (t), 68.73 (s), 74.48 (d), 78.46 (d), 100.70 (s), 126.80 (d), 126.96 (d), 127.04 (d), 128.08 (d), 128.79 (d), 129.27 (d), 141.41 (s). Anal. Calcd for $C_{24}H_{28}O_2Se$: C, 67.44; H, 6.60. Found: C, 67.27; H, 6.75.

***(2R*,4R*)*- and *(2S*,4R*)*-4-ethoxy-6-(phenylseleno)-hex-5-yn-2-ol (17a,b)**: **17a**:**17b** = 7:1; a yellow oil; IR (film, cm^{-1}) 3650−3200 (OH), 2150 (acetylene); ^1H NMR (270 MHz) ($CDCl_3$) δ 1.19 (d, J = 6 Hz), 1.21 (t, J = 7 Hz), 1.22 (t, J = 7 Hz), 1.24 (t, J = 7 Hz), 1.82−2.04 (m), 3.19 (brs), 3.43−3.54 (m), 3.81−3.89 (m), 3.98−4.11 (m), 4.19−4.21 (m), 4.45 (dd, J = 5, 8 Hz), 4.53 (dd, J = 5, 6 Hz), 7.20−7.33 (m), 7.46−7.51 (m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 14.92 (q), 23.28 (q), 44.31 (t), 64.42 (t), 65.80 (s), 66.42 (d), 69.81 (d), 102.27 (s), 126.97 (d), 128.16 (s), 128.78 (d), 129.35 (d); high-resolution mass calcd for $C_{14}H_{18}O_2Se$ m/z 298.0472, found m/z 298.0465.

***(2R*,4R*)*-3,3-Dimethyl-4-ethoxy-6-(phenylseleno)hex-5-yn-2-ol (18a)**: a yellow oil; IR (film, cm^{-1}) 3650−3200 (OH), 2170 (acetylene); ^1H NMR (270 MHz) ($CDCl_3$) δ 0.93 (3H, s), 1.06 (3H, s), 1.12 (3H, d, J = 6 Hz), 1.24 (3H, t, J = 7 Hz), 3.38−3.53 (1H, m), 3.77−3.98 (2H, m), 4.16 (1H, s), 7.19−7.34 (3H, m), 7.49−7.53 (2H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 15.39 (q), 15.50 (q), 18.34 (q), 22.41 (q), 42.77 (s), 65.72 (t), 66.92 (s), 74.51 (d), 80.70 (d), 101.59 (s), 127.55 (d), 129.20 (s), 129.50 (d), 129.92 (d). A small M^+ was observed at m/z 326 but was too small for the high-resolution mass spectrum to be measured.

***(1S*,3R*)*- and *(1R*,3R*)*-3-ethoxy-1-phenyl-5-(phenylthio)pent-4-yn-1-ol (19a,b)**: **19a**:**19b** = 6:1; a yellow oil; IR (film, cm^{-1}) 3650−3100 (OH), 2170 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.26 (t, J = 7 Hz), 1.27 (t, J = 7 Hz), 2.08−2.13 (m), 2.20−2.23 (m), 3.42 (s), 3.45−3.54 (m), 3.84−3.93 (m), 4.45−4.50 (m), 4.93 (dd, J = 3, 9 Hz), 5.11−5.12 (m), 7.07−7.45 (m); ^{13}C NMR of **19a** (100 MHz) ($CDCl_3$) δ 15.12 (q), 44.97 (t), 64.76 (t), 68.45 (s), 69.77 (d), 72.93 (d), 97.42 (s), 125.79 (d), 126.17 (d), 126.64 (d), 128.44 (d), 129.28 (d), 132.30 (s), 143.78 (s). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 63.51; H, 5.61. Found: C, 63.39; H, 5.64.

***(3S*,5R*)*-2,2-Dimethyl-5-ethoxy-7-(phenylthio)hept-6-yn-3-ol (20a)**: a yellow oil; IR (film, cm^{-1}) 3700−3200 (OH), 2180 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 0.91 (9H, s), 1.24 (3H, t, J = 7 Hz), 1.88−1.93 (1H, m), 1.96−2.00 (1H, m), 3.15 (1H, brs), 3.48−3.52 (2H, m), 3.88−3.91 (1H, m), 4.47 (1H, dd, J = 6, 8 Hz), 7.19−7.22 (1H, m), 7.30−7.33 (2H, m), 7.38−7.41 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 14.99 (q), 25.74 (q), 34.57 (s), 37.61 (t), 64.67 (t), 70.78 (d), 72.52 (s), 78.34 (d), 97.63 (s), 125.99 (d), 126.47 (d), 129.10 (d), 132.25 (s); high-resolution mass calcd for $C_{17}H_{24}O_2S$ m/z 292.1597, found m/z 292.1501.

Cyclization Reactions of Alkynyl Alcohols 11a−20a. Typical Procedure. *t*-BuOK (47 mg, 0.42 mmol) was added to a *t*-BuOH (1 mL) solution of (*1S*,3R**)-3-ethoxy-1-phenyl-5-(phenylseleno)pent-4-yn-1-ol (**11a**) (76 mg, 0.21 mmol). The mixture was stirred for 30 min. The solvent was removed under reduced pressure. The residue was poured into water (70 mL) and extracted with ether. The extracts were 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). (*Z*)-(*3R*,5S**)-3-Ethoxy-5-phenyl-2-((phenylseleno)methylene)tetrahydrofuran (**21a**) (71 mg, 93%) was obtained as a yellow oil: IR (film, cm^{-1}) 1650, 1240, 1090 (COC); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.25 (3H, t, J = 7 Hz), 2.04−2.11 (1H, m), 2.53 (1H, dd, J = 5, 13 Hz), 3.42−3.48 (1H, m), 3.71−3.77 (1H, m), 4.37 (1H, brd, J = 4 Hz), 5.48 (1H, s), 5.60 (1H, dd, J = 5, 10 Hz), 7.19−7.34 (8H, m), 7.51−7.53 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.13 (q), 42.24 (t), 63.94 (t), 78.94 (d), 82.83 (d), 86.38 (d), 125.54 (d), 126.40 (d), 127.88 (d), 128.46 (d), 129.03 (d), 131.08 (d), 131.83 (s), 140.48 (s), 158.29 (s). Anal. Calcd for $C_{19}H_{20}O_2Se$: C, 63.51; H, 5.61. Found: C, 63.62; H, 5.59.

***(Z)*-(*3R*,5R**)-3-Ethoxy-5-phenyl-2-((phenylseleno)-methylene)tetrahydrofuran (21b)**: a yellow oil; IR (film, cm^{-1}) 1650, 1240, 1090 (COC); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.21 (3H, t, J = 7 Hz), 2.01−2.09 (1H, m), 2.73−2.79 (1H, m),

3.52−3.66 (2H, m), 4.61 (1H, brt, J = 6 Hz), 5.30 (1H, dd, J = 6, 9 Hz), 5.48 (1H, d, J = 2 Hz), 7.17−7.32 (8H, m), 7.49−7.52 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.29 (q), 40.41 (t), 65.08 (t), 78.66 (d), 81.37 (d), 83.44 (d), 125.79 (d), 126.18 (d), 127.90 (d), 128.37 (d), 128.96 (d), 130.77 (d), 132.14 (s), 140.55 (s), 159.26 (s); high-resolution mass calcd for $C_{19}H_{20}O_2Se$ m/z 360.0628, found m/z 360.0647.

(*Z*)-(*3R*,5S)-4,4-Dimethyl-3-ethoxy-5-phenyl-2-((phenylseleno)methylene)tetrahydrofuran (22)**: a yellow oil; IR (film, cm^{-1}) 1640, 1260, 1090 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 0.59 (3H, s), 1.14 (3H, s), 1.24 (3H, t, J = 7 Hz), 3.36−3.44 (1H, m), 3.76 (1H, s), 3.77−3.85 (1H, m), 5.29 (1H, s), 5.47 (1H, s), 7.18−7.31 (8H, m), 7.52−7.54 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.06 (q), 18.41 (q), 20.49 (q), 46.22 (s), 64.16 (t), 86.18 (d), 86.84 (d), 89.13 (d), 126.12 (d), 126.55 (d), 127.80 (d), 129.03 (d), 130.84 (d), 132.33 (s), 136.60 (s), 158.66 (s); high-resolution mass calcd for $C_{21}H_{24}O_2Se$ m/z 388.0942, found m/z 388.0930.

(*Z*)-(*3R*,5S)-5-*tert*-Butyl-3-ethoxy-2-((phenylseleno)methylene)tetrahydrofuran (23a)**: a yellow oil; IR (film, cm^{-1}) 1640, 1240, 1090 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 0.90 (9H, s), 1.21 (3H, t, J = 7 Hz), 1.87−1.94 (1H, m), 2.00−2.05 (1H, m), 3.35−3.42 (1H, m), 3.67−3.74 (1H, m), 4.24 (1H, brd, J = 5 Hz), 4.34 (1H, dd, J = 5, 10 Hz), 5.31 (1H, s), 7.17−7.25 (3H, m), 7.47−7.49 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.40 (q), 25.51 (q), 33.80 (s), 34.24 (t), 64.01 (t), 79.57 (d), 85.52 (d), 89.70 (d), 126.54 (d), 129.23 (d), 131.29 (d), 132.33 (s), 158.80 (s); high-resolution mass calcd for $C_{17}H_{24}O_2Se$ m/z 340.0941, found m/z 340.0925.

(*Z*)-(*3R*,5R)-5-*tert*-Butyl-3-ethoxy-2-((phenylseleno)methylene)tetrahydrofuran (23b)**: a yellow oil; IR (film, cm^{-1}) 1640, 1120, 980 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 0.91 (9H, s), 1.25 (3H, t, J = 7 Hz), 1.74−1.76 (1H, m), 2.29−2.35 (1H, m), 3.60−3.65 (2H, m), 3.97 (1H, dd, J = 5, 10 Hz), 4.54 (1H, brt, J = 7 Hz), 5.31 (1H, s), 7.16−7.26 (3H, m), 7.46−7.48 (2H, brd, J = 7 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.42 (q), 25.21 (q), 32.69 (s), 33.75 (t), 65.53 (s), 78.85 (d), 81.08 (d), 87.17 (d), 125.96 (d), 128.87 (d), 130.62 (d), 159.82 (s); high-resolution mass calcd for $C_{17}H_{24}O_2Se$ m/z 340.0942, m/z 340.0916.

(*Z*)-(*3R*,5S)-5-*tert*-Butyl-3-ethoxy-2-(deuterio(phenylseleno)methylene)tetrahydrofuran (24)**: a yellow oil; IR (film, cm^{-1}) 2300, 1640, 1220 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 0.90 (9H, s), 1.21 (3H, t, J = 7 Hz), 1.87−1.94 (1H, m), 2.03 (1H, dd, J = 5, 13 Hz), 3.36−3.40 (1H, m), 3.69−3.73 (1H, m), 4.24 (1H, brd, J = 5 Hz), 4.34 (1H, dd, J = 6, 10 Hz), 7.19−7.25 (3H, m), 7.47 (2H, brd, J = 7 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.14 (q), 25.24 (q), 33.52 (s), 33.96 (t), 63.73 (t), 76.26 (d), 89.43 (d), 126.26 (d), 128.97 (d), 131.00 (d), 132.04 (s), 158.50 (s); high-resolution mass calcd for $C_{17}H_{23}DO_2Se$ m/z 341.1004, found m/z 341.0987.

(*Z*)-(*3R*,5S)-5-(*p*-Bromophenyl)-3-ethoxy-2-((phenylseleno)methylene)tetrahydrofuran (25a)**: a yellow oil; IR (film, cm^{-1}) 1640, 1480, 1220, 1080 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 1.23 (3H, t, J = 7 Hz), 1.96−2.03 (1H, m), 2.52 (1H, dd, J = 5, 13 Hz), 3.39−3.46 (1H, m), 3.69−3.75 (1H, m), 4.35 (1H, d, J = 5 Hz), 5.49 (1H, s), 5.54 (1H, dd, J = 5, 10 Hz), 7.15 (2H, d, J = 8 Hz), 7.21−7.27 (3H, m), 7.43 (2H, d, J = 8 Hz), 7.50 (2H, d, J = 8 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.08 (q), 42.16 (t), 63.89 (t), 78.74 (d), 82.07 (d), 86.84 (d), 121.62 (s), 126.45 (d), 127.18 (d), 129.03 (d), 131.02 (d), 131.52 (d), 139.47 (s), 157.83 (s); high-resolution mass calcd for $C_{19}H_{19}BrO_2Se$ m/z 437.9734, found m/z 437.9714.

(*Z*)-(*3R*,5R)-5-(*p*-Bromophenyl)-3-ethoxy-2-((phenylseleno)methylene)tetrahydrofuran (25b)**: a yellow oil; IR (film, cm^{-1}) 1650, 1480, 1230, 1105, 1005 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 1.20 (3H, t, J = 7 Hz), 1.98−2.05 (1H, m), 2.73−2.80 (1H, m), 3.51−3.57 (1H, m), 3.58−3.64 (1H, m), 4.57 (1H, brt, J = 7 Hz), 5.29 (1H, brt, J = 7 Hz), 5.50 (1H, s), 7.18−7.28 (5H, m), 7.44 (2H, d, J = 8 Hz), 7.50 (2H, d, J = 8 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.26 (q), 40.28 (t), 65.04 (t), 78.46 (d), 80.86 (d), 84.35 (d), 121.70 (s), 126.34 (d), 127.49 (d), 129.03 (d), 130.86 (d), 131.46 (d), 131.90 (s), 139.86 (s), 158.80 (s); high-resolution mass calcd for $C_{19}H_{19}BrO_2Se$ m/z 437.9734, found m/z 437.9750.

(*Z*)-(*3R*,5S)-3-Ethoxy-5-(*p*-nitrophenyl)-2-((phenylseleno)methylene)tetrahydrofuran (26)**: a yellow oil; IR (film, cm^{-1}) 1640, 1520, 1340 (NO_2), 1220, 1080 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 1.26 (3H, t, J = 7 Hz), 1.98−2.04 (1H, m), 2.63 (1H, dd, J = 5, 13 Hz), 3.44−3.48 (1H, m), 3.74−3.78 (1H, m), 4.39 (1H, brd, J = 5 Hz), 5.56 (1H, s), 5.69 (1H, dd, J = 5, 10 Hz), 7.44−7.47 (3H, m), 7.45 (2H, d, J = 8 Hz), 7.53 (2H, d, J = 7 Hz), 8.20 (2H, d, J = 8 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.10 (q), 42.27 (t), 64.02 (t), 78.54 (d), 81.59 (d), 87.96 (d), 123.84 (d), 126.12 (d), 126.71 (d), 129.16 (d), 131.35 (d), 147.48 (s), 147.98 (s), 157.27 (s); high-resolution mass calcd for $C_{19}H_{19}NO_4Se$ m/z 405.0475, found m/z 405.0454.

(*Z*)-(*3R*,5S)-3-Ethoxy-5-phenyl-2-((phenylseleno)-methylene)tetrahydrofuran-4-spiro-1′-cyclohexane (27)**: colorless prisms; mp 73−78 °C; IR (KBr, cm^{-1}) 1640, 1100, 1000 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 0.57 (1H, dt, J = 4, 14 Hz), 0.92−0.95 (1H, m), 1.03−1.10 (1H, m), 1.23−1.50 (3H, m), 1.25 (3H, t, J = 7 Hz), 1.54−1.64 (3H, m), 2.13 (1H, brd, J = 13 Hz), 3.37−3.45 (1H, m), 3.82−3.89 (1H, m), 4.13 (1H, s), 5.22 (1H, s), 5.47 (1H, s), 7.16−7.20 (2H, m), 7.21−7.29 (6H, m), 7.52 (2H, d, J = 8 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.09 (q), 22.44 (t), 23.12 (t), 25.64 (t), 27.10 (t), 27.98 (t), 49.82 (s), 64.12 (t), 81.84 (d), 86.25 (d), 90.05 (d), 126.30 (d), 126.75 (d), 127.78 (d), 129.06 (d), 130.91 (d), 132.24 (s), 136.52 (s), 158.65 (s); Anal. Calcd for $C_{24}H_{28}O_2Se$: C, 67.44; H, 6.60. Found: C, 67.36; H, 6.61.

(*Z*)-(*3R*,5R)-3-Ethoxy-5-methyl-2-((phenylseleno)-methylene)tetrahydrofuran (28)**: a yellow oil; IR (film, cm^{-1}) 1650, 1250, 1100 (COC); ^{1}H NMR (270 MHz) ($CDCl_3$) δ 1.20 (3H, t, J = 7 Hz), 1.35 (3H, d, J = 6 Hz), 1.70−1.80 (1H, m), 2.23 (1H, ddd, J = 1, 5, 13 Hz), 3.35−3.46 (1H, m), 3.60−3.75 (1H, m), 4.28 (1H, brd, J = 4 Hz), 4.67−4.75 (1H, m), 5.33 (1H, s), 7.15−7.27 (3H, m), 7.44−7.49 (2H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 15.08 (q), 20.49 (q), 40.73 (t), 63.80 (t), 78.38 (d), 79.26 (d), 84.76 (d), 126.18 (d), 128.89 (d), 130.71 (d), 131.95 (s), 159.02 (s). Anal. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10. Found: C, 56.42; H, 6.06.

(*Z*)-(*3R*,5R)-3-Ethoxy-4,4,5-trimethyl-2-((phenylseleno)methylene)tetrahydrofuran (29)**: a yellow oil; IR (film, cm^{-1}) 1640, 1270, 1090 (COC); ^{1}H NMR (270 MHz) ($CDCl_3$) δ 0.85 (3H, s), 0.87 (3H, s), 1.18 (3H, d, J = 7 Hz), 1.19 (3H, t, J = 7 Hz), 3.31−3.42 (1H, m), 3.63 (1H, s), 3.69−3.78 (1H, m), 4.34 (1H, q, J = 6 Hz), 5.29 (1H, s), 7.14−7.27 (3H, m), 7.43−7.48 (2H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 13.50 (q), 15.03 (q), 18.01 (q), 19.48 (q), 44.31 (s), 64.24 (t), 84.24 (d), 84.32 (d), 86.87 (d), 126.07 (d), 128.89 (d), 130.56 (d), 132.34 (s), 159.46 (s); high-resolution mass calcd for $C_{16}H_{22}O_2Se$ m/z 326.0785, found m/z 326.0772.

(*Z*)-(*3R*,5S)-3-Ethoxy-5-phenyl-2-((phenylthio)methylene)tetrahydrofuran (30)**: a yellow oil; IR (film, cm^{-1}) 1650, 1480, 1090 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 1.26 (3H, t, J = 7 Hz), 2.06−2.13 (1H, m), 2.53 (1H, ddd, J = 1, 5, 13 Hz), 3.43−3.50 (1H, m), 3.73−3.80 (1H, m), 4.40 (1H, d, J = 5 Hz), 5.32 (1H, s), 5.61 (1H, dd, J = 5, 10 Hz), 7.41−7.18 (1H, m), 7.23−7.38 (9H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.15 (q), 41.91 (t), 64.00 (t), 78.96 (d), 83.13 (d), 90.63 (d), 125.52 (d), 125.61 (d), 127.73 (d), 127.93 (d), 128.48 (d), 137.22 (s), 140.30 (s), 158.78 (s); high-resolution mass calcd for $C_{19}H_{20}O_2S$ m/z 312.1184, found m/z 312.1170.

(*Z*)-(*3R*,5S)-5-*tert*-Butyl-3-ethoxy-2-((phenylthio)-methylene)tetrahydrofuran (31)**: a yellow oil; IR (film, cm^{-1}) 1640, 1480, 1090 (COC); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 0.90 (9H, s), 1.22 (3H, t, J = 7 Hz), 1.90−1.99 (1H, m), 2.01−2.04 (1H, m), 3.36−3.42 (1H, m), 3.67−3.73 (1H, m), 4.25 (1H, brd, J = 5 Hz), 4.33−4.37 (1H, m), 5.15 (1H, s), 7.13 (1H, brt, J = 7 Hz), 7.25 (2H, brt, J = 7 Hz), 7.32 (2H, brd, J = 7 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.11 (q), 25.19 (q), 33.48 (s), 33.60 (t), 63.71 (t), 79.27 (d), 89.31 (d), 89.67 (d), 125.30 (d), 127.62 (d), 128.68 (d), 137.57 (s), 159.21 (s). Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27. Found: C, 69.58; H, 8.31.

***p*-Nitrobenzoylation of Alkynyl Alcohol 16.** 4-(Dimethylamino)pyridine (10 mg, 0.08 mmol) was added to a CH_2Cl_2 (3 mL) solution of (*1R*,3R**)-3-ethoxy-2,2-pentamethylene-1-phenyl-5-(phenylseleno)pent-4-yn-1-ol (**16a**) (0.10 g, 0.23 mmol) and Et_3N (47 mg, 0.47 mmol). The mixture was stirred for 2 h. The mixture was poured into water (100 mL). The organic

layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and 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 (1:10). (*1R*,3R**)-3-Ethoxy-1-((*p*-nitrobenzoyl)oxy)-2,2-pentamethylene-1-phenyl-5-(phenylseleno)pent-4-yne (**16′**) (0.13 g, quant) was obtained as colorless prisms: mp 119−120 °C; IR (KBr, cm^{-1}) 2150 (acetylene), 1730 (CO), 1530, 1280 (NO_2); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.20 (3H, t, J = 7 Hz), 1.22−1.27 (1H, m), 1.52−1.54 (6H, m), 1.72 (1H, brs), 1.82 (1H, brs), 2.29 (1H, brs), 3.38−3.42 (1H, m), 3.86−3.90 (1H, m), 4.52 (1H, brs), 6.40 (1H, brs), 7.20−7.32 (8H, m), 7.39 (2H, brd, J = 7 Hz), 8.11 (2H, d, J = 9 Hz), 8.24 (2H, brd, J = 9 Hz); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.05 (q), 21.34 (t), 25.49 (t), 28.02 (t), 28.53 (t), 44.82 (s), 60.39 (t), 65.01 (t), 66.13 (s), 71.51 (d), 78.57 (d), 102.49 (s), 123.37 (d), 126.92 (d), 127.83 (d), 127.91 (d), 128.18 (d), 128.40 (d), 128.73 (s), 129.50 (d), 131.02 (d), 135.88 (s), 137.69 (s), 150.22 (s), 163.50 (s). Anal. Calcd for $C_{31}H_{31}NO_5Se$: C, 64.58; H, 5.42; N, 2.43. Found: C, 64.45; H, 5.46; N, 2.44.

(*3S*,5R)-2,2-Dimethyl-5-ethoxy-7-(phenylseleno)hept-6-yn-3-yl Tetrahydropyranyl Ether (36).** The THP ether **36** was prepared from the corresponding alcohol **13a** by the general procedure[22] using pyridinium *p*-toluenesulfonate (PPTS) quantitatively. The ether **36** was obtained as a diastereoisomeric mixture. The isomer ratio (1:1) was determined by the intensities of the *t*-Bu groups in the ^1H NMR spectrum; IR (film, cm^{-1}) 2200 (acetylene); ^1H NMR (270 MHz) ($CDCl_3$) δ 0.88 (s), 0.93 (s), 1.23 (t, J = 7 Hz), 1.25 (t, J = 7 Hz), 1.43−1.48 (m), 1.90−1.97 (m), 3.33−3.44 (m), 3.51 (q, J = 7 Hz), 3.82−3.92 (m), 4.27 (dd, J = 10, 6 Hz), 4.40 (brs), 4.64 (brs), 4.73 (dd, J = 10, 5 Hz), 7.23−7.32 (m), 7.51−7.55 (m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 15.06 (q), 15.15 (q), 20.56 (t), 21.15 (t), 25.25 (t), 25.35 (t), 25.99 (q), 26.38 (q), 31.03 (t), 31.49 (t), 34.88 (s), 35.65 (s), 38.06 (t), 38.29 (t), 60.19 (s), 63.69 (t), 64.20 (t), 64.53 (t), 66.29 (s), 69.23 (d), 69.57 (d), 81.79 (d), 85.25 (d), 99.15 (d), 102.71 (d), 102.95 (s), 104.41 (s), 126.76 (d), 127.04 (d), 128.67 (d), 129.02 (d), 129.13 (d), 129.26 (d), 129.37 (d). Anal. Calcd for $C_{22}H_{32}O_3Se$: C, 61.93; H, 7.62. Found: C, 61.96; H, 7.50.

A Preparation of 3-Deuterio-3,3-diethoxy-1-(phenylseleno)-1-propyne (40). An Et_2O (18 mL) solution of (trimethylsilyl)acetylene (2.80 g, 28.1 mmol) was added dropwise to EtMgBr (prepared from Mg (0.680 g, 28.1 mmol) and EtBr (3.06 g, 28.1 mmol) in Et_2O (20 mL)) at room temperature. The mixture was refluxed for 30 min. An Et_2O solution (10 mL) of $CD(OEt)_3$[18] (2.80 g, 18.8 mmol) was added dropwise to the mixture at room temperature. The 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 Et_2O. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure. The mixture was not purified at this point, and the next desilylation was performed. Bu_4NF (7.30 g, 28.1 mmol) was added to an EtOH (20 mL)−H_2O (10 mL) solution of the mixture at 0 °C. The reaction mixture was stirred for 1 h and poured into water (150 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by distillation. 3-Deuterio-3,3-diethoxy-1-propyne (**39**) (1.43 g, 59.0%) (bp 75−80 °C/100 mmHg) was obtained as a colorless oil: IR (film, cm^{-1}) 3260, 2120 (acetylene); ^1H NMR (270 MHz) ($CDCl_3$) δ 1.18 (6H, t, J = 8 Hz), 2.50 (1H, s), 3.41−3.75 (4H, m). An Et_2O (5 mL) solution of propyne **39** (0.65 g, 5.0 mmol) was added dropwise to the EtMgBr (10 mmol) prepared as described above. The reaction mixture was refluxed for 30 min. A THF (10 mL) solution of PhSeBr (prepared from $(PhSe)_2$ (0.78 g, 2.5 mmol) and Br_2 (0.40 g, 2.5 mmol)) was added dropwise to the mixture over 30 min at 0 °C. 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). 3-Deuterio-3,3-diethoxy-1-(phenylseleno)-1-propyne (**40**) (0.43 g, 30%) was obtained as a pale yellow oil: IR (film, cm^{-1}) 2150 (acetylene); ^1H NMR (270 MHz) ($CDCl_3$) δ 1.25 (6H, dt, J = 2, 7 Hz), 3.54−3.83 (4H, m), 7.23−7.35 (3H, m), 7.50−7.55 (2H, m); high-resolution mass calcd for $C_{13}H_{15}DO_2Se$ m/z 285.0378, found m/z 285.0377. The following experiments were performed by the same procedures as described above.

5-Deuterio-2,2-dimethyl-5-ethoxy-7-(phenylseleno)hept-6-yn-3-one (41): a yellow oil; IR (film, cm^{-1}) 2150 (acetylene), 1720 (CO); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.13 (9H, s), 1.19 (3H, t, J = 7 Hz), 2.79 (1H, d, J = 17 Hz), 3.08 (1H, d, J = 17 Hz), 3.44−3.50 (1H, m), 3.76−3.84 (1H, m), 7.24−7.37 (3H, m), 7.48−7.56 (2H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 14.95 (q), 25.84 (q), 42.86 (t), 44.05 (s), 64.75 (t), 65.12 (s), 102.62 (s), 127.02 (d), 128.47 (s), 128.95 (d), 129.40 (d), 211.55 (s); high-resolution mass calcd for $C_{17}H_{21}DO_2Se$ m/z 339.0845, found m/z 339.0844.

(*3S*,5R)-5-Deuterio-2,2-dimethyl-5-ethoxy-7-(phenylseleno)hept-6-yn-3-ol (42)**: a colorless oil; IR (film, cm^{-1}) 3650−3200 (OH), 2180 (acetylene); ^1H NMR (270 MHz) ($CDCl_3$) δ 0.91 (9H, s), 1.25 (3H, t, J = 7 Hz), 1.82−2.00 (2H, m), 3.10 (1H, brs), 3.48−3.54 (2H, m), 3.87−3.93 (1H, m), 7.25−7.34 (3H, m), 7.49−7.53 (2H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 15.06 (q), 25.55 (q), 34.66 (s), 37.65 (t), 64.75 (t), 65.93 (s), 70.66 (sx3), 78.52 (d), 102.41 (s), 127.13 (d), 128.30 (s), 128.98 (d), 129.48 (d); high-resolution mass calcd for $C_{17}H_{23}DO_2Se$ m/z 341.1004, found m/z 341.1009.

(*Z*)-(*3R*,5S)-5-*tert*-Butyl-3-deuterio-3-ethoxy-2-((phenylseleno)methylene)tetrahydrofuran (43)**: a yellow oil; IR (film, cm^{-1}) 1640, 1240, 1070 (COC); ^1H NMR (400 MHz) ($CDCl_3$) δ 0.90 (9H, s), 1.21 (3H, t, J = 7 Hz), 1.90 (1H, dd, J = 10, 13 Hz), 2.02 (1H, dd, J = 6, 13 Hz), 3.33−3.44 (1H, m), 3.65−3.76 (1H, m), 4.34 (1H, dd, J = 6, 10 Hz), 5.31 (1H, s), 7.15−7.27 (3H, m), 7.46−7.49 (2H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 15.10 (q), 25.20 (q), 33.49 (s), 33.82 (t), 63.65 (t), 79.22 (sx3), 85.16 (d), 89.40 (d), 126.21 (d), 128.93 (d), 130.98 (d), 132.04 (s), 158.54 (s); high-resolution mass calcd for $C_{17}H_{23}DO_2Se$ m/z 341.1004, found m/z 341.1008.

Supporting Information Available: NMR characterization data of all compounds complete with peak assignments (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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