Meyer–Schuster Rearrangement of γ-Sulfur-Substituted Propargyl Alcohols: A Convenient Synthesis of α,β-Unsaturated Thioesters

Mitsuhiro Yoshimatsu,*,† Motoyo Naito, Masataka Kawahigashi, Hiroshi Shimizu, and Tadashi Kataoka*

Gifu Pharmaceutical University, 6-1 Mitahora-higashi 5-chome, Gifu 502, Japan

Received January 3, 1995®

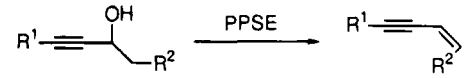
γ-Sulfur-substituted propargyl alcohols **1a–e** and **1i,j** reacted with polyphosphoric acid trimethylsilyl ester (PPSE) to give the α,β-unsaturated thioesters **3a–e** and **3i,j** in good yields. However, the reactions of 3,3-dibutyl-1-(phenylthio)propargyl alcohol (**1k**) and 1-(phenylthio)ethynyl-1-cycloalkanols **1l–n** with PPSE gave the enyne sulfides **2k–n** exclusively.

Some unsaturated thioesters have interesting insecticidal activities.[1] Thioesters have attracted much attention as active esters for syntheses of macrocyclic lactones,[2] and consequently, α,β-unsaturated thioesters have been used for the synthesis of macrocyclic α,β-unsaturated lactones.[3] However, there are only a few reports on the preparation of α,β-unsaturated thioesters: reactions of α-carbanions of ethanethioate with carbonyl compounds such as Wittig reaction,[4] Wittig–Horner reaction,[5] and Peterson reaction.[6] *S*-Alkyl or *S*-phenyl 2-(dialkoxyphosphoryl)alkanethioates are unstable and their Wittig–Horner reactions did not give satisfactory results[5] excepting, however, the reactions of *S*-propyl 2-(diethoxyphosphoryl)propanethioate with aldehydes which gave α,β-unsaturated thioesters in moderate yields. The same difficulty arises in the synthesis of α,β-unsaturated thioesters by base-induced condensation, because the bases nucleophilically attack at the carbonyl group of α,β-unsaturated thioesters and cause thioester destruction. If the synthesis of α,β-unsaturated thioesters can be achieved under neutral conditions, development of a new chemistry of the thioesters becomes feasible.

Recently, we reported a novel synthesis of (*Z*)-enynes and (*Z*)-enediynes by dehydration of propargyl alcohols with polyphosphoric acid trimethylsilyl ester (PPSE).[7] In contrast, treatment of γ-chalcogen-substituted propargyl alcohols with PPSE gave α,β-unsaturated thioesters *via* the Meyer–Schuster type rearrangement[8] instead of γ-chalcogen-substituted enynes. This paper describes a simple and novel synthesis of α,β-unsaturated thioesters from γ-sulfur-substituted propargyl alcohols.

A propargyl alcohol **1a** was treated with PPSE to give (*E*)-*S*-phenyl 2-pentenethioate (**3a**) (54%) accompanied with (*Z*)-enyne sulfide **2a** (6%). The structure of the thioester **3a** was determined by the analytical and

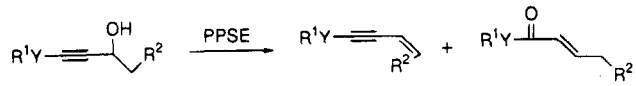
Scheme 1



R^1=*n*-Bu, Ph, $PhCH_2OCH_2$
R^2=Alkyl, Alkynyl

PPSE: Polyphosphoric acid trimethylsilyl ester

Scheme 2



1 (Y=S, Se) 2 (β-Elimination product) 3 (Meyer-Schuster Rearrangement product)

spectral data. IR spectrum showed an absorption of the thioester at ν 1680 cm^{-1}. ^1H NMR spectrum exhibited a signal due to 2-H at δ 6.17 (dt, J = 15 and 2 Hz). The enyne sulfide **2a** showed the molecular formula $C_{11}H_{10}S$ by the high-resolution mass spectra. ^1H NMR spectrum showed a *Z*-olefinic proton at δ 5.70 (dq, J = 10 and 2 Hz). Various *S*-phenyl unsaturated thioesters **3b–e** were obtained in good yields (entries 2–5). When the propargyl acetate **1f** was treated with PPSE (entry 6), the unsaturated thioester **3b** decreased and the enyne sulfide **2b** slightly increased in comparison with the treatment of the corresponding alcohol **1b** (entry 2). Other propargyl esters **1g** and **1h** similarly gave the thioester **3b** as the main product. *S*-*tert*-Butyl **1i** and *S*-mesityl derivative **1j** provided the corresponding thioesters **3i** and **3j**, respectively, in good yields.

In sharp contrast, the reactions of a tertiary propargyl alcohol **1k** and [(phenylthio)ethynyl]cycloalkanols **1l–n** with PPSE afforded the enyne sulfides **2k–n** in high yields, accompanied with trace amounts of α,β-unsaturated thioesters **3l–n**. Propargyl alcohol **1o** gave a dieneyne sulfide **2o** and an enyne ether **4o**. When the alcohol **1o** was slowly added to a PPSE solution, the dieneyne sulfide **2o** (*(3E,5E)*:*(3E,5Z)* = 1.8:1) was obtained exclusively. The isomer ratio was determined by the intensity of 3-H in ^1H NMR spectrum. The structural assignment of the dieneyne sulfide **2o** was performed by IR, ^1H, and ^{13}C NMR, and mass spectral data. Its MS showed a molecular ion peak at m/z 216 ($C_{14}H_{16}S$). IR spectrum showed the presence of acetylene at ν 2150 cm^{-1}. The ^1H NMR spectrum exhibited two pairs of doublet at δ 5.69 (J = 16 Hz, *(3E,5E)*-3-H) and 5.77 (J =

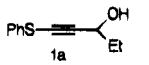
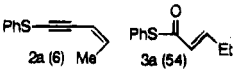
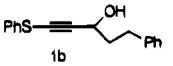
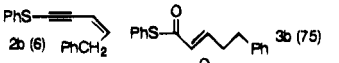
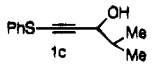
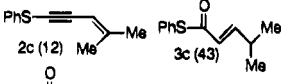
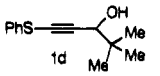
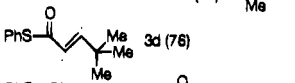
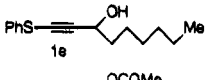
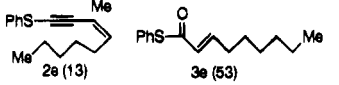
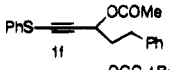
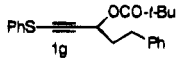
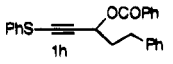
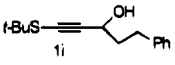
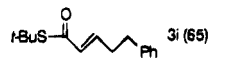
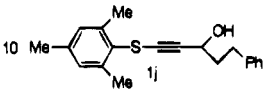
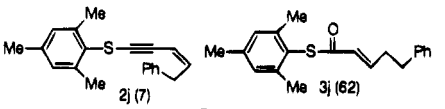
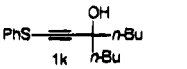
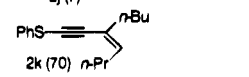
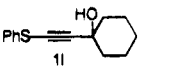
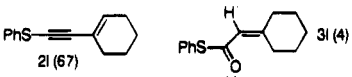
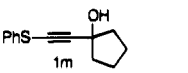
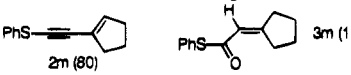
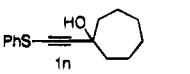
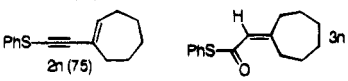
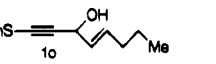
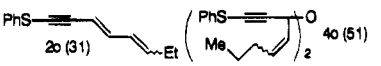
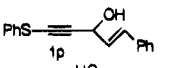
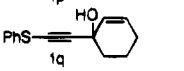
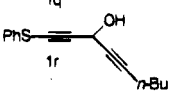
† Present address: Dr. Mitsuhiro Yoshimatsu, Department of Chemistry, Faculty of Education, Gifu University, Yanagido, Gifu 501-11, Japan.

® Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) Karrer, F.; Farooq, S. *German Patent* 2452721, 1975, Ciba-Geigy Corp.; *Chem. Abstr.* **1975**, *83*, 147310.
(2) Nicolaou, K. C. *Tetrahedron*, **1977**, *33*, 683. Masamune, S. *Aldrichim. Acta* **1978**, *11*, 23.
(3) Masamune, S.; Hayase, Y.; Schilling, W.; Chan, W. K.; Bates, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 6756.
(4) Keck, G. E.; Boden, E. P.; Mabury, S. A. *J. Org. Chem.* **1985**, *50*, 709.
(5) Coutrot, Ph.; Charbonnier, C.; Grison, C. *Synthesis* **1991**, 23.
(6) Lucast, D. H.; Wemple, J. *Tetrahedron Lett.* **1977**, 1103.
(7) Yoshimatsu, M.; Yamada, H.; Shimizu, H.; Kataoka, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2107.
(8) Theron, F.; Verny, M.; Vessiere, R. *In The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; John-Wiley & Sons: Chichester, 1978; Part 1, Chapter 10.

0022-3263/95/1960-4798$09.00/0

Table 1. Reaction of Propargyl Alcohols and Polyphosphoric Acid Trimethylsilyl Ester (PPSE)

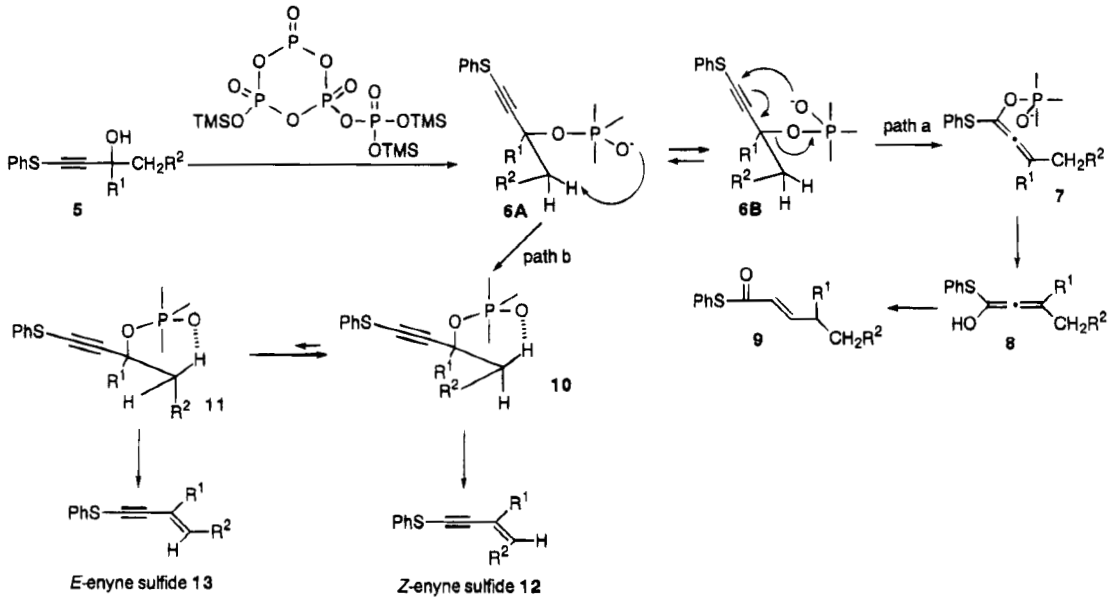
Entry	Propargyl alcohol	Conditions	Products (% yields)
1	 1a	83 °C, 30 min	 2a (6) 3a (54)
2	 1b	83 °C, 30 min	 2b (6) 3b (75)
3	 1c	83 °C, 30 min	 2c (12) 3c (43)
4	 1d	83 °C, 30 min	 3d (76)
5	 1e	83 °C, 30 min	 2e (13) 3e (53)
6	 1f	83 °C, 2h	2b (24) 3b (65)
7	 1g	83 °C, 2h	2b (13) 3b (53)
8	 1h	83 °C, 2h	2b (18) 3b (55)
9	 1i	83 °C, 2h	 3i (65)
10	 1j	83 °C, 2h	 2j (7) 3j (62)
11	 1k	83 °C, 30 min	 2k (70)
12	 1l	rt, 30 min	 2l (67) 3l (4)
13	 1m	rt, 30 min	 2m (80) 3m (13)
14	 1n	rt, 30 min	 2n (75) 3n (1)
15	 1o	0 °C, 10 min	 2o (31) 4o (51)
16	1o	0 °C, 10 min*1	2o (70)*1
17	 1p	0 °C, 10 min	complex mixture
18	 1q	0 °C, 10 min	complex mixture
19	 1r	0 °C, 10 min	complex mixture

*1) A $ClCH_2CH_2Cl$ solution of propargyl alcohol 1o was added dropwise to the PPSE solution at 0 °C.

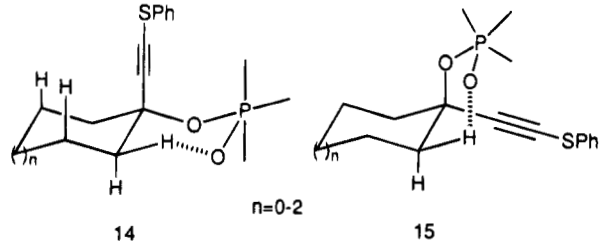
16 Hz, *(3E,5Z)*-3-H) due to 3-H, and two pairs of double of doublet at δ 6.65 (J = 11 and 16 Hz, *(3E,5E)*-4-H) and 6.96 (J = 12 and 16 Hz, *(3E,5Z)*-4-H) due to 4-H. The signals at δ 5.90 (d, J = 15 Hz) and at δ 6.13 (dd, J = 11 and 15 Hz) were assigned as 6-H and 5-H, respectively, by irradiation of 7-CH_2 in the ^{1}H-decoupling experiment of *(3E,5E)*-**2o**. These data suggested that the major isomer of **2o** has the *(3E,5E)*-configuration.

The mechanism for formation of the products **2** and **3** are shown in Scheme 3. The propargyl alcohol **5** attacks at the phosphorus atom of PPSE to give the pentavalent phosphorane intermediate **6**. The intermediate **6** (R^1 = H), formed from a secondary alcohol, undergoes a Meyer–Schuster rearrangement *via* the intermediate **6B** (path a) rather than the dehydration. The resulting phosphate **7** is hydrolyzed to give an allenol intermediate **8**. The allenol **8** easily isomerizes to α,β-unsaturated thioester **9**. On the contrary, the propargyl carbon–oxygen bond of the intermediate **6** ($R^1 \neq$ H), formed from a tertiary alcohol, is cleaved more readily than that of the intermediate **6** (R^1 = H), formed from a secondary alcohol, and consequently, the intermediate **6** ($R^1 \neq$ H) causes dehydration *via* the intermediate **6A** (path b). The dehydration of the intermediate **6** would proceed *via* a six-membered transition state (**10**), in which an alkyl and an alkynyl group lie in the side opposite to the bulky phosphorus moieties, and the intermediate **10** affords the enyne sulfide **12** *Z*-selectively. When steric hindrance between the acetylenic moiety and R^2 becomes larger, the intermediate **10** transforms into the other intermediate **11** and forms the more stable *E*-isomer **13**. The cycloalkanols **1l–n** also form the hypervalent intermediates **14** and **15** as shown in Scheme 4. These intermediates would take six-membered chair conformations by the hydrogen-bonding. The *cis*-intermediate **15** should be unfavorable because of the destabilization by the steric

Scheme 3



Scheme 4



hindrance between the bulky phosphorus moiety and the 1,3-diaxial hydrogens. The intermediate **14** possesses an axial alkynyl group, and the attack of a nucleophile at the alkynyl carbon is hindered by the bulky ligands of PPSE and the 1,3-diaxial hydrogens. Therefore, **14** preferentially undergoes dehydration and provides the enyne.

Experimental Section[9]

Preparation of Propargyl Alcohols 1a–e, i–k. General Procedure. A solution of (phenylthio)acetylene (0.67 g, 5.0 mmol) in ether (10 mL) was added to an ether (20 mL) solution of EtMgBr (7.5 mmol). The ether solution was refluxed for 30 min and then cooled at 0 °C. An ether (10 mL) solution of an aldehyde or a ketone (7.5 mmol) was added dropwise to the reaction mixture. The whole was stirred for 10 min at 0 °C and then poured into water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane–AcOEt (10:1) to give a propargyl alcohol as a pale yellow oil.

1-(Phenylthio)pent-1-yn-3-ol (1a): yield 81%; IR (film, cm^{-1}) 3600–3100 (OH), 2190 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.05 (3H, t, J = 7 Hz), 1.79–1.83 (2H, m), 2.23 (1H, brs), 4.52–4.54 (1H, m), 7.19–7.23 (1H, m), 7.30–7.34 (2H, m), 7.40–7.42 (2H, m); ^{13}C NMR (100 MHz)($CDCl_3$) δ 9.50 (q), 30.79 (t), 64.58 (d), 71.64 (s), 99.71 (s), 126.20 (d), 126.54 (d), 129.19 (d), 132.43 (s); high-resolution mass calcd for $C_{11}H_{12}OS$ m/z 192.0609, found m/z 192.0623.

5-Phenyl-1-(phenylthio)pent-1-yn-3-ol (1b): yield quant; IR (film, cm^{-1}) 3600–3200 (OH), 2190 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 2.00 (1H, d, J = 5 Hz), 2.08–2.16 (2H, m), 2.84 (2H, t, J = 8 Hz), 4.56–4.60 (1H, m), 7.18–7.43 (5H, m); ^{13}C NMR (100 MHz)($CDCl_3$) δ 31.45 (t), 39.14 (t), 62.64 (d), 72.30 (s), 99.51 (s), 126.07 (d), 126.30 (d), 126.67 (d), 128.46 (d), 129.25 (d), 132.32 (s), 141.00 (s). Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 76.13; H, 6.23.

4-Methyl-1-(phenylthio)pent-1-yn-3-ol (1c): yield 54%; IR (film, cm^{-1}) 3600–3200 (OH), 2180 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.04 (3H, d, J = 7 Hz), 1.06 (3H, d, J = 6 Hz), 1.95–2.00 (1H, m), 2.06 (1H, brs), 4.40 (1H, brs), 7.22–7.24 (1H, m), 7.31–7.35 (2H, m), 7.42 (2H, brd, J = 8 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 17.64 (q), 18.17 (q), 34.63 (d), 68.84 (d), 72.23 (s), 98.73 (s), 126.27 (d), 126.56 (d), 129.19 (d), 132.56 (s); high-resolution mass calcd for $C_{10}H_{14}OS$ m/z 206.0766, found m/z 206.0757.

4,4-Dimethyl-1-(phenylthio)pent-1-yn-3-ol (1d): yield 89%; IR (film, cm^{-1}) 3600–3200 (OH), 2190 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.04 (9H, s), 2.18 (1H, brs), 4.23 (1H, d, J = 5 Hz), 7.18–7.22 (1H, m), 7.30–7.33 (2H, m), 7.41 (2H, brd, J = 8 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 14.09 (q × 3), 36.15 (s), 72.25 (d), 86.86 (s), 98.69 (s), 126.21 (d), 126.49 (d), 129.14 (d), 132.58 (s); high-resolution mass calcd for $C_{13}H_{16}OS$ m/z 220.0922, found m/z 220.0937.

1-(Phenylthio)oct-1-yn-3-ol (1e): yield 97%: IR (film, cm^{-1}) 3600–3100 (OH), 2170 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 0.86 (3H, t, J = 6 Hz), 1.23–1.31 (6H, m), 1.45–1.51 (2H, m), 1.75–1.82 (2H, m), 2.23 (1H, brs), 4.58 (1H, brs), 7.19–7.23 (1H, m), 7.30–7.34 (2H, m), 7.41 (2H, brd, J = 7 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 14.00 (q), 22.52 (t), 25.15 (t), 28.87 (t), 31.66 (t), 37.70 (t), 63.38 (d), 71.53 (s), 100.06 (s), 126.20 (d), 126.52 (d), 129.18 (d), 132.50 (s). Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12. Found: C, 72.33; H, 8.33.

1-*tert*-(Butylthio)-5-phenylpent-1-yn-3-ol (1i): yield 52%; IR (film, cm^{-1}) 3600–3200 (OH), 2170 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.42 (9H, s), 2.02–2.09 (2H, m), 2.79 (2H, t, J = 8 Hz), 4.51 (1H, t, J = 7 Hz), 7.19–7.30 (5H, m). Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12. Found: C, 72.48; H, 8.10.

1-(Mesitylthio)-5-phenylpent-1-yn-3-ol (1j): yield 98%; colorless needles, mp 56–57 °C; IR (KBr, cm^{-1}) 3600–3200 (OH), 2190 (acetylene); ^1H NMR (400 MHz) ($CDCl_3$) δ 1.82 (1H, brs), 1.92–2.02 (2H, m), 2.26 (3H, s), 2.53 (3H, s), 2.54 (3H, s), 2.72 (2H, t, J = 8 Hz), 6.93 (2H, brs), 7.13–7.25 (5H, m). Anal. Calcd for $C_{20}H_{22}OS$: C, 77.38; H, 7.14. Found: C, 77.26; H, 7.13.

3-*n*-Butyl-1-(phenylthio)hept-1-yn-3-ol (1k): yield 73%; IR (film, cm^{-1}) 3600–3200 (OH), 2160 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 0.93 (6H, t, J = 7 Hz), 1.26–1.44 (8H, m), 1.47–1.61 (4H, m), 1.69–1.81 (4H, m), 2.38 (1H, brs), 7.18–7.43 (5H, m). ^{13}C NMR (67.5 MHz)($CDCl_3$) δ 14.03 (q), 22.88

(9) For general experimental procedures, see: Yoshimatsu, M.; Sato, T.; Shimizu, H.; Hori, M.; Kataoka, T. *J. Org. Chem.* **1994**, *59*, 1011.

(t), 26.56 (t), 41.77 (t), 42.89 (s), 72.33 (s), 102.15 (s), 126.12 (d), 126.45 (d), 129.34 (d), 132.92 (s); high-resolution mass calcd for $C_{17}H_{24}OS$ m/z 276.1548, m/z 276.1573.

1-[(Phenylthio)ethynyl]-1-cyclohexanol (1l): yield quant; IR (film, cm^{-1}) 3600–3200 (OH), 2200 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.54–1.70 (8H, m), 1.96–1.98 (2H, m), 2.48 (1H, brs), 7.18–7.21 (1H, m), 7.30–7.33 (2H, m), 7.40 (2H, brd, J = 8 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 23.26 (t), 25.13 (t), 39.83 (t), 69.70 (s), 70.52 (s), 102.63 (s), 125.95 (d), 126.43 (d), 129.21 (d), 132.83 (s). Anal. Calcd for $C_{14}H_{17}OS$: C, 72.37; H, 6.94. Found: C, 72.09; H, 7.06.

1-[(Phenylthio)ethynyl]-1-cyclopentanol (1m): yield quant; IR (film, cm^{-1}) 3600–3200 (OH), 2180 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.75–1.89 (4H, m), 1.99–2.10 (4H, m), 2.14 (1H, brs), 7.19–7.22 (1H, m), 7.30–7.40 (2H, m), 7.41 (2H, brd, J = 3 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 23.56 (t), 42.57 (t), 69.66 (s), 75.38 (s), 102.58 (s), 125.99 (d), 126.44 (d), 129.21 (d), 132.79 (s); high-resolution mass calcd for $C_{13}H_{14}OS$ m/z 218.0765, found m/z 218.0760.

1-[(Phenylthio)ethynyl]-1-cycloheptanol (1n): yield 76%; IR (film, cm^{-1}) 3600–3200 (OH), 2190 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.58–1.64 (6H, m), 1.89–1.92 (2H, m), 2.08–2.13 (2H, m), 2.46–2.48 (2H, m), 2.72 (1H, brs), 7.17–7.21 (1H, m), 7.29–7.33 (2H, m), 7.39 (2H, brd, J = 7 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 22.08 (t), 24.15 (t), 27.92 (t), 30.24 (t), 42.84 (t), 43.70 (t), 69.37 (s), 72.52 (s), 103.74 (s), 125.76 (d), 126.21 (d), 129.03 (d), 132.80 (s); high-resolution mass calcd for $C_{15}H_{18}OS$ m/z 246.1078, found m/z 246.1069.

1-(Phenylthio)oct-4-en-1-yn-3-ol (1o): yield 57%; IR (film, cm^{-1}) 3600–3200 (OH), 2120 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 0.91 (3H, t, J = 7 Hz), 1.38–1.47 (2H, m), 1.99–2.08 (2H, m), 2.42 (1H, brs), 5.05 (1H, brs), 5.65 (1H, dd, J = 6 and 15 Hz), 5.87–5.93 (1H, m), 7.19–7.23 (1H, m), 7.30–7.34 (2H, m), 7.41 (2H, brd, J = 8 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 13.60 (q), 21.97 (t), 33.95 (t), 63.72 (d), 72.56 (s), 98.27 (s), 126.27 (d), 126.56 (d), 128.59 (d), 129.16 (d), 132.56 (s), 134.06 (d). Anal. Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.03; H, 6.88.

5-Phenyl-1-(phenylthio)pent-4-en-1-yn-3-ol (1p): yield 57%; mp 65–68 °C; IR (KBr, cm^{-1}) 3600–3200 (OH), 2180 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 2.19 (1H, brs), 5.29 (1H, brs), 6.34 (1H, dd, J = 6 and 16 Hz), 6.81 (1H, brd, J = 16 Hz), 7.21–7.46 (10H, m). Anal. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.66; H, 5.29.

1-[(Phenylthio)ethynyl]cyclohex-2-en-1-ol (1q): yield 61%; IR (film, cm^{-1}) 3600–3200 (OH), 2170 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.79–1.83 (2H, m), 1.95–2.15 (4H, m), 2.27 (1H, brs), 5.79–5.89 (2H, m), 7.19–7.43 (5H, m). Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13. Found: C, 73.01; H, 5.91.

1-(Phenylthio)non-1,4-diyn-3-ol (1r): yield 42%; IR (film, cm^{-1}) 3600–3200 (OH), 2230, 2180 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 0.91 (3H, t, J = 7 Hz), 1.36–1.55 (4H, m), 2.24 (2H, dt, J = 2 and 7 Hz), 5.32 (1H, brs), 7.19–7.21 (1H, m), 7.23–7.33 (2H, m), 7.43 (2H, dd, J = 1 and 8 Hz); high-resolution mass calcd for $C_{15}H_{16}OS$ m/z 244.0938, found m/z 244.0930.

Preparation of Propargyl Esters 1f–h. General Procedure. The compounds **1f–h** were prepared from **1b** and the corresponding acid anhydride or acyl chlorides. 4-(Dimethylamino)pyridine (0.03 g, 0.24 mmol) was added to a mixture of propargyl alcohol **1b** (3.0 mmol) and acid anhydride or acid chloride (4.5 mmol) at room temperature. The solution was stirred for 1 h and poured into water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane–AcOEt (20:1).

3-Acetyl-5-phenyl-1-(phenylthio)pent-1-yne (1f): yield 99%; IR (film, cm^{-1}) 2180 (acetylene), 1740 (CO), 1230 (OCO); ^1H NMR (270 MHz)($CDCl_3$) δ 2.08 (3H, s), 2.13–2.22 (2H, m), 2.82 (2H, t, J = 8 Hz), 5.55 (1H, t, J = 7 Hz), 7.15–7.44 (10H, m). Anal. Calcd for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84. Found: C, 73.64; H, 5.95.

3-(Pivaloyloxy)-5-phenyl-1-(phenylthio)pent-1-yne (1g): yield 72%; IR (film, cm^{-1}) 2180 (acetylene), 1720 (CO), 1150 (OCO); ^1H NMR (400 MHz)($CDCl_3$) δ 1.24 (9H, s), 2.16–2.20 (2H, m), 2.81 (2H, t, J = 8 Hz), 5.54 (1H, brs), 7.18–7.42 (10H, m). Anal. Calcd for $C_{22}H_{24}O_2S$: C, 74.96; H, 6.86. Found: C, 75.04; H, 6.89.

3-(Benzoyloxy)-5-phenyl-1-(phenylthio)pent-1-yne (1h): yield 77%, IR (film, cm^{-1}) 2180 (acetylene), 1720 (CO), 1260 (OCO); ^1H NMR (400 MHz)($CDCl_3$) δ 2.27–2.35 (2H, m), 2.89 (2H, t, J = 8 Hz), 5.80 (1H, t, J = 7 Hz), 7.15–7.53 (13H, m), 8.03 (2H, d, J = 8 Hz). Anal. Calcd for $C_{24}H_{20}O_2S$: C, 77.39; H, 5.41. Found: C, 77.38; H, 5.52.

Reactions of Propargyl Alcohols 1a–e, 1i–r and α-Acyloxy Propargyl Esters 1f-h with PPSE. General Procedure. A solution of propargyl alcohol **1** (1.0 mmol) in $ClCH_2CH_2Cl$ (1 mL) was added to a $ClCH_2CH_2Cl$ (5 mL) solution of PPSE[10] (prepared from hexamethyldisiloxane (1.5 mL) and P_2O_5 (0.5 g)) under an Ar atmosphere. The reaction mixture was refluxed for 30 min, cooled to 0 °C, and then poured into a saturated $NaHCO_3$ solution (150 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The organic layer and the extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with hexane. The enyne sulfides **2** and thioesters **3** were obtained as pale yellow oils. The results are shown in Table 1.

***(Z)*-1-(Phenylthio)pent-3-en-1-yne (2a):** a pale yellow oil, IR (film, cm^{-1}) 2150 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.94 (3H, dt, J = 5 and 2 Hz), 5.70 (1H, dq, J = 10 and 2 Hz), 6.05 (1H, brs), 7.21–7.27 (1H, m), 7.32–7.35 (2H, m), 7.44–7.46 (2H, m); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 16.23 (q), 79.16 (s), 95.03 (s), 109.90 (d), 126.01 (d), 126.38 (d), 129.16 (d), 133.31 (s), 139.22 (d); high-resolution mass calcd for $C_{11}H_{10}S$ m/z 174.0504, found m/z 174.0501.

***(E)*-*S*-Phenyl pent-2-enethioate (3a):** a yellow oil, IR (film, cm^{-1}) 1680 (COS); ^1H NMR (400 MHz)($CDCl_3$) δ 1.09 (3H, t, J = 7 Hz), 2.22–2.28 (2H, m), 6.17 (1H, dt, J = 15 and 2 Hz), 7.03 (1H, dt, J = 15 and 6 Hz), 7.24–7.44 (5H, m); ^{13}C NMR (100 MHz)($CDCl_3$) δ 11.97 (q), 25.32 (t), 126.91 (d), 127.66 (s), 129.03 (d), 129.22 (d), 134.57 (d), 148.03 (d), 187.97 (s). Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.51; H, 6.31.

***(Z)*-1-(Phenylthio)-5-phenylpent-3-en-1-yne (2b):** a pale yellow oil, IR (film, cm^{-1}) 2150 (acetylene); ^1H NMR (400 MHz)-($CDCl_3$) δ 3.70 (2H, d, J = 7 Hz), 5.79 (1H, dt, J = 10 and 2 Hz), 6.12 (1H, dt, J = 10 and 7 Hz), 7.17–7.45 (10H, m); ^{13}C NMR (100 MHz)($CDCl_3$) δ 36.77 (t), 79.47 (s), 95.01 (s), 109.75 (d), 126.16 (d), 126.30 (d), 126.51 (d), 128.48 (d), 128.57 (d), 129.21 (d), 133.02 (s), 133.05 (s), 139.34 (s), 142.14 (d); high-resolution mass calcd for $C_{17}H_{14}S$ m/z 250.0816, found m/z 250.0810.

***(E)*-*S*-Phenyl 5-phenylpent-2-enethioate (3b):** a yellow oil, IR (film, cm^{-1}) 1690 (COS); ^1H NMR (400 MHz)($CDCl_3$) δ 2.51–2.57 (2H, m), 2.79 (2H, t, J = 7 Hz), 6.19 (1H, dt, J = 16 and 2 Hz), 7.01 (1H, dt, J = 16 and 7 Hz), 7.17–7.23 (2H, m), 7.28–7.32 (2H, m), 7.39–7.45 (6H, m); ^{13}C NMR (100 MHz)-($CDCl_3$) δ 34.00 (t), 34.25 (t), 126.26 (d), 127.60 (s), 128.27 (d), 128.33 (d), 128.53 (d), 129.13 (d), 129.33 (d), 134.62 (d), 140.53 (s), 145.46 (d), 187.93 (s). Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 75.92; H, 5.97.

***(Z)*-4-Methyl-1-(phenylthio)pent-3-en-1-yne (2c):** a pale yellow oil, IR (film, cm^{-1}) 2140 (acetylene); ^1H NMR (400 MHz)-($CDCl_3$) δ 1.55 (3H, s), 1.86 (3H, s), 5.48 (1H, brs), 7.18–7.21 (1H, m), 7.25–7.34 (2H, m), 7.43 (2H, dd, J = 7 and 1 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 21.31 (q), 24.86 (q), 75.99 (s), 96.31 (s), 105.27 (d), 125.85 (d), 126.18 (d), 129.10 (d), 133.84 (s), 150.81 (s). Anal. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42. Found: C, 76.57; H, 6.63.

***(E)*-*S*-Phenyl 4-methylpent-2-enethioate (3c):** a yellow oil, IR (film, cm^{-1}) 1680 (COS); ^1H NMR (400 MHz)($CDCl_3$) δ 1.09 (6H, dd, J = 4 and 2 Hz), 2.44–2.50 (1H, m), 6.13 (1H, dd, J = 14 and 1 Hz), 6.95 (1H, dd, J = 14 and 7 Hz), 7.23–7.45 (5H, m); ^{13}C NMR (100 MHz)($CDCl_3$) δ 21.08 (q), 31.02 (d), 125.17 (d), 127.69 (s), 129.05 (d), 129.23 (d), 134.59 (d),

(10) Hori, M; Kataoka, T.; Shimizu, H.; Tsutsumi, K.; Yoshimatsu, M. *J. Org. Chem.* **1990**, *55*, 2458.

152.68 (d), 188.21 (s). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 69.84; H, 7.05.

***(E)*-*S*-Phenyl 4,4-dimethylpent-2-enethioate (3d):** a pale yellow oil, IR (film, cm^{-1}) 1680 (COS); ^1H NMR (400 MHz)-($CDCl_3$) δ 1.10 (9H, s), 6.08 (1H, d, J = 15 Hz), 6.97 (1H, d, J = 15 Hz), 7.38−7.44 (5H, m); ^{13}C NMR (100 MHz)($CDCl_3$) δ 28.48 (q), 33.88 (s), 123.27 (d), 127.71 (s), 129.01 (d), 129.18 (d), 134.55 (d), 156.11 (d), 188.34 (s). Anal. Calcd for $C_{13}H_{16}$-OS: C, 70.87; H, 7.32. Found: C, 70.87; H, 7.31.

***(Z)*-1-(Phenylthio)non-3-en-1-yne (2e):** a pale yellow oil, IR (film, cm^{-1}) 2140 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 0.89 (3H, t, J = 7 Hz), 1.25−1.34 (4H, m), 1.43−1.54 (2H, m), 2.35 (2H, dq, J = 7 and 1 Hz), 5.65 (1H, brd, J = 9 Hz), 5.98 (1H, dq, J = 9 and 7 Hz), 7.19−7.25 (1H, m), 7.31−7.35 (2H, m), 7.43 (2H, dd, J = 7 and 2 Hz); ^{13}C NMR (100 MHz)-($CDCl_3$) δ 14.00 (q), 22.48 (t), 28.56 (t), 30.57 (t), 31.41 (t), 78.63 (s), 95.36 (s), 108.77 (d), 126.01 (d), 126.34 (d), 129.14 (d), 133.38 (s), 144.87 (d); high-resolution mass calcd for $C_{15}H_{18}S$ m/z 230.1130, m/z 230.1137.

***(E)*-*S*-Phenyl non-2-enethioate (3e):** a yellow oil, IR (film, cm^{-1}) 1680 (COS); ^1H NMR (400 MHz)($CDCl_3$) δ 0.89 (3H, t, J = 6 Hz), 1.29−1.32 (6H, m), 1.44−1.49 (2H, m), 2.21 (2H, dq, J = 7 and 1 Hz), 6.17 (1H, brd, J = 16 Hz), 6.98 (1H, dt, J = 16 and 7 Hz), 7.38−7.45 (5H, m); ^{13}C NMR (100 MHz)($CDCl_3$) δ 13.98 (q), 22.47 (t), 27.84 (t), 28.78 (t), 31.50 (t), 32.25 (t), 127.73 (d), 129.03 (d), 129.19 (d), 134.57 (d), 146.90 (d), 187.88 (s). Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12. Found: C, 72.79; H, 8.28.

***S*-*tert*-Butyl 5-phenylpent-2-enethioate (3i):** a pale yellow oil, IR (film, cm^{-1}) 1660 (COS); ^1H NMR (400 MHz)($CDCl_3$) δ 1.68 (9H, s), 2.62−2.67 (2H, m), 2.93 (2H, t, J = 7 Hz), 6.22 (1H, d, J = 16 Hz), 7.03 (1H, dt, J = 7 and 16 Hz), 7.34−7.40 (3H, m), 7.45−7.48 (2H, m). ^{13}C NMR (100 MHz)($CDCl_3$) δ 29.84 (q × 3), 33.66 (t), 34.26 (t), 47.76 (s), 126.09 (d), 128.21 (d), 128.39 (d), 129.67 (d), 140.64 (s), 142.69 (d), 190.51. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12. Found: C, 72.43; H, 8.07.

***(Z)*- and *(E)*-1-(Mesitylthio)-5-phenylpent-3-en-1-yne (2j):** a pale yellow oil, IR (KBr, cm^{-1}) 2150 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 2.27 (s), 2.53 (s), 2.56 (s), 3.40 (d, J = 7 Hz), 3.56 (d, J = 7 Hz), 5.54 (d, J = 16 Hz), 5.58 (d, J = 11 Hz), 5.96 (dt, J = 7 and 11 Hz), 6.17 (dt, J = 7 and 16 Hz), 6.94 (brs), 7.18−7.27 (m). ^{13}C NMR (100 MHz)($CDCl_3$) δ 20.98 (*Z*-q), 21.73 (*Z*-q × 2), 36.60 (*Z*-t), 83.16 (*Z*-s), 87.42 (*Z*-s), 110.04 (*Z*-d), 126.12 (*Z*-d), 128.46 (*Z*-d), 129.38 (*Z*-d), 139.22 (*Z*-s), 141.08 (*Z*-d), 141.78 (*Z*-s); high resolution mass calcd for $C_{20}H_{20}S$ m/z 292.1286, found m/z 292.1267.

***(E)*-*S*-Mesityl 5-phenylpent-2-enethioate (3j):** colorless needles, mp 60−62 °C; IR (KBr, cm^{-1}) 1680 (COS); ^1H NMR (400 MHz)($CDCl_3$) δ 2.28 (3H, s), 2.31 (6H, s), 2.52−2.56 (2H, m), 2.80 (2H, t, J = 7 Hz), 6.21 (1H, d, J = 15 Hz), 6.97 (2H, brs), 7.02 (1H, dt, J = 7 and 15 Hz), 7.17−7.22 (3H, m), 7.27−7.31 (2H, m). ^{13}C NMR (100 MHz)($CDCl_3$) δ 21.14 (q), 21.60 (q × 2), 34.03 (t), 34.30 (t), 123.46 (s), 126.24 (d), 128.35 (d), 128.47 (d), 128.51 (d), 129.19 (d), 139.85 (s), 140.67 (s), 142.68 (s), 144.86 (d), 187.65 (s). Anal. Calcd for $C_{20}H_{22}OS$: C, 77.38; H, 7.14. Found: C, 77.39; H, 7.18.

***(Z)*-3-*n*-Butyl-1-(phenylthio)hept-3-en-1-yne (2k):** a pale yellow oil, IR (film, cm^{-1}) 2150 (acetylene); ^1H NMR (400 MHz)-($CDCl_3$) δ 0.91 (3H, t, J = 7 Hz), 0.93 (3H, t, J = 7 Hz), 1.24−1.58 (6H, m), 2.18 (2H, brt, J = 7 Hz), 2.28 (2H, brq, J = 7 Hz), 5.72 (1H, t, J = 7 Hz), 7.16−7.22 (1H, m), 7.31−7.34 (2H, m), 7.41−7.45 (2H, m). ^{13}C NMR (100 MHz)($CDCl_3$) δ 13.77 (q), 13.91 (q), 22.04 (t), 22.52 (t), 30.83 (t), 32.79 (t), 36.70 (t), 77.62 (s), 97.56 (s), 123.17 (s), 125.88 (d), 126.23 (d), 129.12 (d), 133.76 (s), 138.15 (d); high-resolution mass calcd for $C_{17}H_{22}S$ m/z 258.1442, found m/z 258.1462.

1-[(Phenylthio)ethynyl]cyclohexene (2l): a pale yellow oil, IR (film, cm^{-1}) 2150 (acetylene); ^1H NMR (400 MHz)-($CDCl_3$) δ 1.58−1.67 (4H, m), 2.12−2.13 (2H, m), 2.20 (2H, brs), 6.21 (1H, brs), 7.16−7.18 (1H, m), 7.20−7.33 (2H, m), 7.40 (2H, dd, J = 8 and 1 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 21.39 (t), 22.23 (t), 25.72 (t), 29.09 (t), 71.84 (s), 100.06 (s), 120.67 (s), 125.79 (d), 126.14 (d), 129.07 (d), 133.57 (s), 136.09 (d); high-resolution mass calcd for $C_{14}H_{14}S$ m/z 214.0817, found m/z 214.0807.

***S*-Phenyl cyclohexylideneethanethioate (3l):** a yellow oil, IR (film, cm^{-1}) 1680 (COS); ^1H NMR (400 MHz)($CDCl_3$) δ 1.58−1.69 (6H, m), 2.20 (2H, brt, J = 6 Hz), 2.77−2.78 (2H, m), 5.99 (1H, brs), 7.26−7.44 (5H, m); high-resolution mass calcd for $C_{14}H_{16}OS$ m/z 232.0921, found m/z 232.0932.

1-[(Phenylthio)ethynyl]cyclopentene (2m): a pale yellow oil, IR (film, cm^{-1}) 2130 (acetylene); ^1H NMR (400 MHz)-($CDCl_3$) δ 1.88−1.95 (2H, m), 2.42−2.47 (2H, m), 2.49−2.54 (2H, m), 6.12 (1H, t, J = 2 Hz), 7.16−7.21 (1H, m), 7.28−7.32 (2H, m), 7.40 (2H, dd, J = 8 and 2 Hz); ^{13}C NMR (100 MHz)-($CDCl_3$) δ 23.27 (t), 33.31 (t), 36.31 (t), 75.88 (s), 95.64 (s), 124.27 (s), 125.90 (d), 126.23 (d), 129.10 (d), 133.22 (s), 138.74 (d); high-resolution mass calcd for $C_{13}H_{12}S$ m/z 200.0659, found m/z 200.0650.

***S*-Phenyl cyclopentylideneethanethioate (3m):** a yellow oil, IR (film, cm^{-1}) 1680 (COS); ^1H NMR (400 MHz)($CDCl_3$) δ 1.65−1.78 (4H, m), 2.37−2.46 (2H, m), 2.73−2.77 (2H, m), 6.24 (1H, t, J = 2 Hz), 7.38−7.45 (5H, m); ^{13}C NMR (100 MHz)-($CDCl_3$) δ 25.45 (t), 26.47 (t), 33.95 (t), 36.07 (t), 117.78 (d), 128.54 (s), 129.03 (d), 129.08 (d), 134.64 (d), 168.50 (s), 186.73 (s). Anal. Calcd for $C_{13}H_{14}OS$: C, 71.52; H, 6.46. Found: C, 71.52; H, 6.61.

1-[(Phenylthio)ethynyl]cycloheptene (2n): a pale yellow oil, IR (film, cm^{-1}) 2150 (acetylene); ^1H NMR (400 MHz)-($CDCl_3$) δ 1.51−1.63 (4H, m), 1.73−1.79 (2H, m), 2.20−2.25 (2H, m), 2.39−2.41 (2H, m), 6.39 (1H, t, J = 7 Hz), 7.17−7.21 (1H, m), 7.30−7.34 (2H, m), 7.41 (2H, ddd, J = 7, 2, and 1 Hz); ^{13}C NMR (100 MHz)($CDCl_3$) δ 26.45 (t), 26.54 (t), 29.23 (t), 32.05 (t), 34.12 (t), 71.79 (s), 101.63 (s), 125.83 (d), 126.16 (d), 126.77 (s), 129.10 (d), 133.73 (s), 140.94 (d). Anal. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06. Found: C, 79.00; H, 7.18.

***S*-Phenyl cycloheptylideneethanethioate (3n):** a yellow oil, IR (film, cm^{-1}) 1690 (COS); ^1H NMR (400 MHz)($CDCl_3$) δ 1.53−1.75 (8H, m), 2.37−2.40 (2H, m), 2.81−2.84 (2H, m), 6.07 (1H, brs), 7.26−7.44 (5H, m); MS m/z 246 (M^+); high-resolution mass was not measured because **3m** was contaminated with a trace amount of other complex compounds.

***(3E,5E)*- and *(3E,5Z)*-1-(Phenylthio)octa-3,5-dien-1-yne (2o):** a pale yellow oil, IR (film, cm^{-1}) 2140 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 1.02 (t, J = 8 Hz), 1.03 (t, J = 7 Hz), 2.12−2.19 (m), 2.22−2.27 (m), 5.69 (d, J = 16 Hz), 5.77 (d, J = 16 Hz), 5.86−5.93 (m), 6.01−6.15 (m), 6.65 (dd, J = 11 and 15 Hz), 6.96 (dd, J = 12 and 16 Hz), 7.19−7.23 (m), 7.31−7.35 (m), 7.41−7.47 (m); ^{13}C NMR (100 MHz)($CDCl_3$) δ 13.80 (*(3E,5E)*-q), 14.69 (*(3E,5Z)*-q), 22.05 (*(3E,5Z)*-t), 26.45 (*(3E,-5E)*-t), 77.00 (s), 77.42 (s), 98.38 (*(3E,5E)*-s), 106.90 (*(3E,5Z)*-s), 108.91 (*(3E,5E)*-d), 110.83 (*(3E,5Z)*-d), 126.65 (d), 126.71 (d), 126.76 (d), 126.98 (d), 127.07 (d), 127.69 (d), 129.19 (d), 129.76 (d), 129.80 (d), 133.77 (s), 133.93 (s), 138.23 (d), 138.32 (d), 141.05 (d), 141.43 (s), 141.70 (s), 143.57 (d); high-resolution mass calcd for $C_{14}H_{14}S$ m/z 214.0817, m/z 214.0812.

***(E)*- and *(Z)*-3,3′-Oxybis[1-(phenylthio)oct-4-en-1-yne] (4o):** a pale yellow oil, IR (film, cm^{-1}) 2150 (acetylene); ^1H NMR (400 MHz)($CDCl_3$) δ 0.91 (t, J = 7 Hz), 0.92 (t, J = 7 Hz), 1.30−1.63 (m), 3.79−3.84 (m), 3.85−3.89 (m), 5.79 (brd, J = 16 Hz), 5.85 (brd, J = 16 Hz), 6.01 (dd, J = 16 and 8 Hz), 6.10 (dd, J = 16 and 7 Hz), 7.17−7.44 (m); ^{13}C NMR (100 MHz)($CDCl_3$) δ 14.29 (q), 14.38 (q), 18.56 (t), 18.84 (t), 37.46 (t), 38.16 (t), 76.07 (s), 76.29 (s), 96.37 (s), 96.62 (s), 110.49 (d), 111.44 (d), 126.49 (d), 126.58 (d), 129.51 (d), 133,09 (s), 133.22 (s), 144.89 (d), 145.16 (d). Anal. Calcd for $C_{28}H_{30}OS_2$: C, 75.29; H, 6.77. Found: C, 75.32; H, 6.86.

Supporting Information Available: Characterization data for NMR, complete with peak assignments (6 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.

JO950023+