HETEROCYCLES, Vol. 62, 2004, pp. 263 - 277
Received, 7th April, 2003, Accepted, 23rd May, 2003, Published online, 27th May, 2003

GEOMETRICALLY SELECTIVE SYNTHESIS OF SULFUR-CONTAINING HETEROCYCLES BY INTRAMOLECULAR Pd-CATALYZED SULFINYLZINCATION

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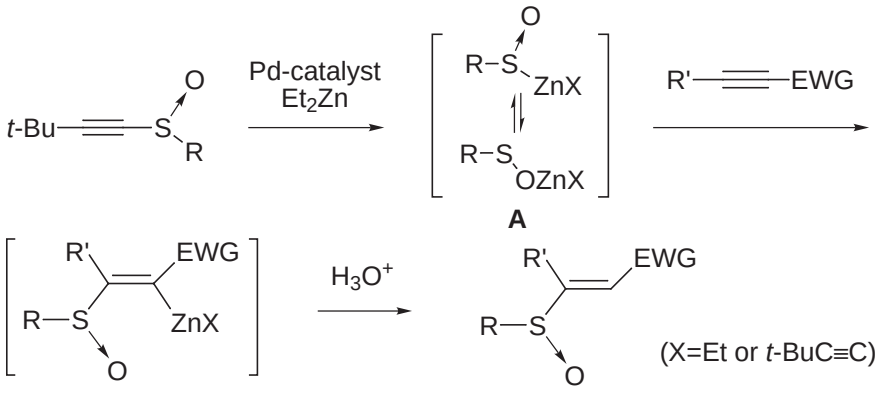
Abstract – A new method to synthesize cyclic sulfoxide derivatives was developed utilizing Pd-catalyzed sulfinylzincation, which proceeds with high *syn*-selectivity under mild conditions. The resulting vinylzinc species reacted with electrophiles such as proton, allyl bromide, and benzoyl chloride to afford a single geometric isomer.

Introduction

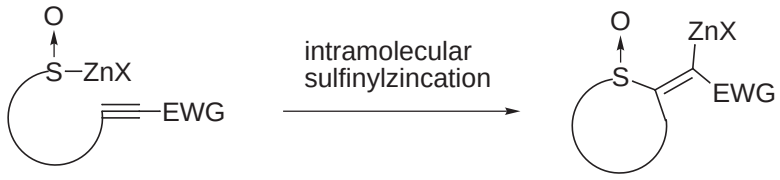
Although sulfenic acid is a biologically and chemically attractive species and has been extensively studied,[1,2] there are few reports in terms of its conjugate base, sulfinyl anion (sulfenate anion) due to its instability for oxidation and self-condensation.[3] We have recently developed a novel Pd-catalyzed sulfinylzincation of activated alkynes using 1-alkynyl sulfoxides and Et_2Zn, wherein the sulfinyl group was transferred into alkynoate, and the sulfinyl anion (sulfenate anion) intermediate (**A**) was suggested to be involved (Scheme 1).[4] The addition proceeded with high *syn*-selectivity to give (*E*)-β-sulfinyl α,β-unsaturated esters exclusively.



Scheme 1

This paper is dedicated to Professor Leo A. Paquette on the occasion of his 70th birthday.

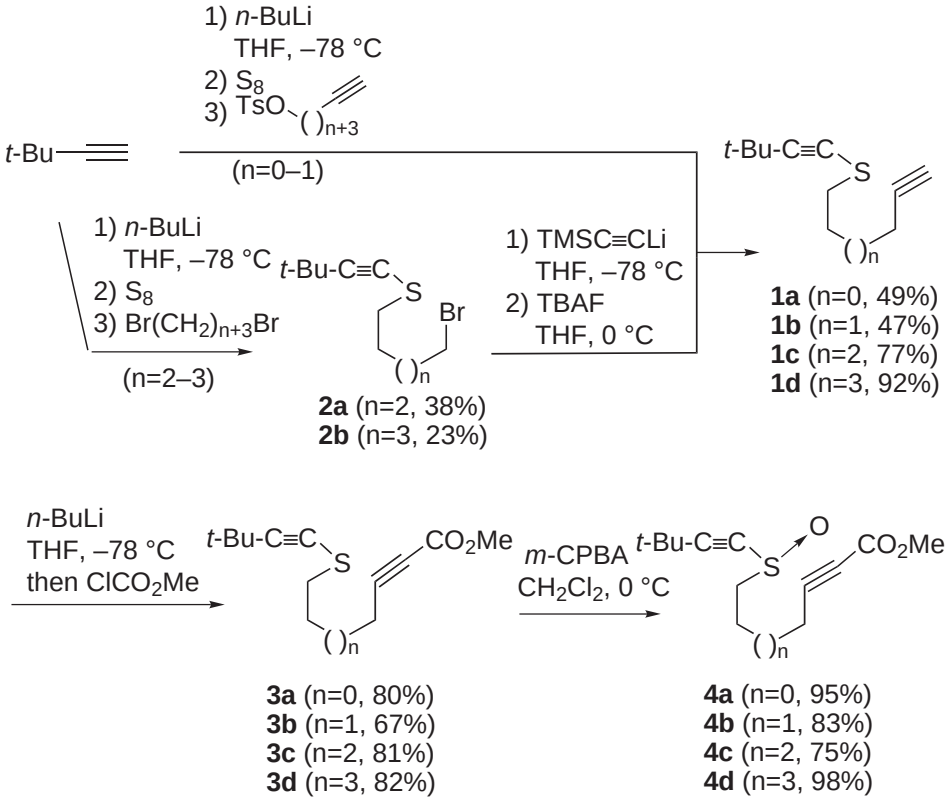
During the course of this study, we aimed to synthesize sulfur-containing heterocyclic compounds by applying the method intramolecularly (Scheme 2). The resulting cyclic sulfoxides are of interest, since many cyclic sulfoxide derivatives are known to possess interesting biological activities.[5] In this paper, we will describe the intramolecular sulfinyzincation to give cyclic sulfoxides.



Scheme 2

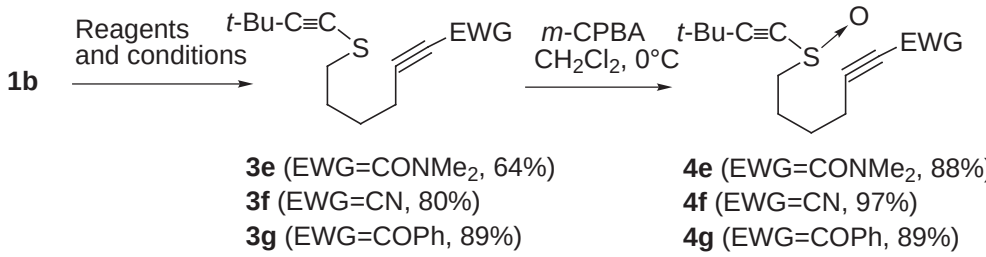
RESULTS AND DISCUSSION

Substrates (**4a**–**d**) bearing both a sulfinyl donor and acceptor were synthesized as shown in Scheme 3. Lithium acetylide generated from 3,3-dimethyl-1-butyne with *n*-BuLi reacted with sulfur[6] to give alkynethiolate (*t*-BuC≡CSLi), alkylation of which with tosylates[7,8] gave alkynes (**1a**) and (**1b**) in 49 and 47% yields, respectively. Alkynes (**1c**) and (**1d**) bearing a longer carbon chain were synthesized *via* bromides (**2a**) and (**2b**), which were derived to **1c** and **1d** by coupling with TMSC≡CLi and subsequent desilylation with tetrabutylammonium fluoride (TBAF). Then, the acetylide generated from the alkynes (**1a**–**d**) was trapped with $ClCO_2Me$ to give **3a**–**d** in 67–82% yields. Oxidation of the sulfides (**3a**–**d**) with *m*-CPBA afforded the sulfoxides (**4a**–**d**) in 75–98% yields.



Scheme 3

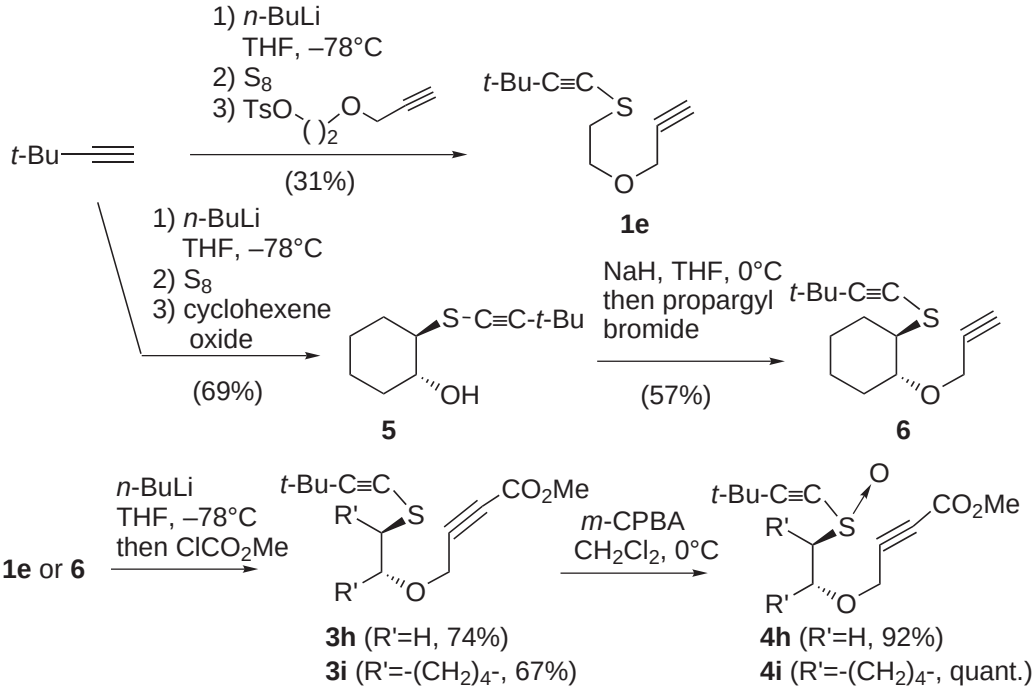
On the other hand, alkynyl sulfoxdes (**4e**) and (**4f**) bearing other electron-withdrawing groups ($CONMe_2$ and CN, respectively) were synthesized from **1b** in a similar manner as described for **4a**, but with employing $ClCONMe_2$ and PhOCN instead of $ClCO_2Me$ (Scheme 4). Phenyl alkynyl kotone (**4g**) was prepared by the procedure developed by Tohda and co-workers (BzCl, $Pd(PPh_3)_4$, CuI, Et_3N)[9] followed by *m*-CPBA oxidation.



Scheme 4. *Reagents and conditions:* For **3e**; *n*-BuLi, THF, –78 °C then $ClCONMe_2$. For **3f**; *n*-BuLi, ether, –78 °C then PhOCN. For **3g**; BzCl, $Pd(PPh_3)_4$, CuI, Et_3N, rt.

Scheme 4

Scheme 5 shows a preparation of the substrates (**4h**) and (**4i**) having ether tethers. Synthesis of alkyne (**1e**) was performed in a similar manner as described for **1a** using known tosylate.[10] Alkyne (**6**) involving a cyclohexane ring was obtained by the reaction of *t*-BuC≡CSLi with cyclohexene oxide followed by alkylation of the resulting alcohol with propargyl bromide. The alkynes (**1e**) and (**6**) were converted into alkynoates (**4h**) and (**4i**),[11] respectively, by the conventional protocol.

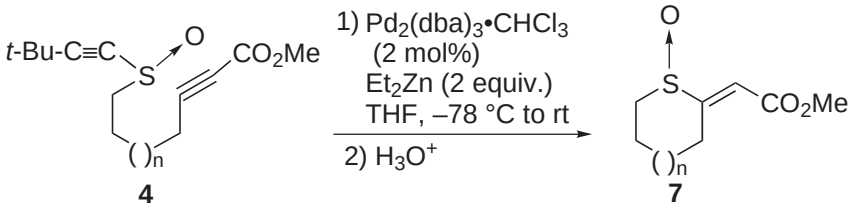


Scheme 5

With these substrates in hand, we examined intramolecular sulfinylation *via* the sulfinylzincation followed by protonation. The alkynoates (**4a**–**d**) were treated with Et_2Zn (2 equiv.) and $Pd_2(dba)_3$•$CHCl_3$ (2 mol%) in THF at room temperature (Table 1). Five- and six-membered ring formation proceeded

stereoselectively to provide the (*E*)-isomers (**7a**) and (**7b**) exclusively in 65 and 92% yields, respectively (entries 1 and 2).[12] Sulfinylzincation of **4c** also proceeded, giving the seven-membered ring in 49% yield (entry 3). However, the eight-membered ring formation using **4d** did not proceed and no cyclic product was obtained even at the low concentration to prevent the intermolecular reaction (entries 4 and 5).

Table 1. Effect of Ring Size on Intramolecular Sulfinylzincation[a]

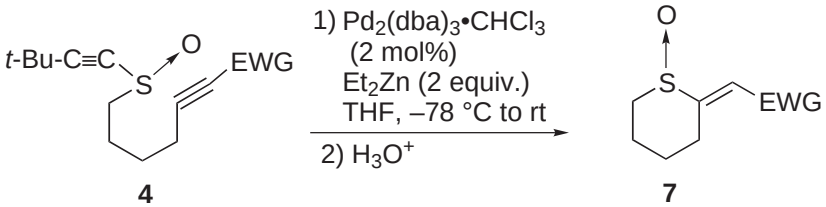


entry	substrate	n	ring size	conc. (M)	time (h)	product (yield/%)
1	**4a**	0	5	0.1	5	**7a** (65)
2	**4b**	1	6	0.1	4	**7b** (92)
3	**4c**	2	7	0.1	5	**7c** (49)
4	**4d**	3	8	0.1	5	**7d** (0)
5	**4d**	3	8	0.01	5	**7d** (0)

[a]All reactions were carried out using 2 mol% of $Pd_2(dba)_3 \cdot CHCl_3$ at the concentration of 0.1 M.

Next, we investigated the influence of an acceptor of the nucleophile for the reaction (Table 2). Ester and amide were good acceptors, giving the cyclized products (**7b**) and (**7e**) in 92 and 80% yields, respectively (entries 1 and 2). However, alkynyl nitrile and alkynyl ketone were not appropriate as an acceptor, yielding **7f** and **7g** in poor yields, respectively (entries 3 and 4).

Table 2. Effect of Acceptor on Intramolecular Sulfinylzincation[a]

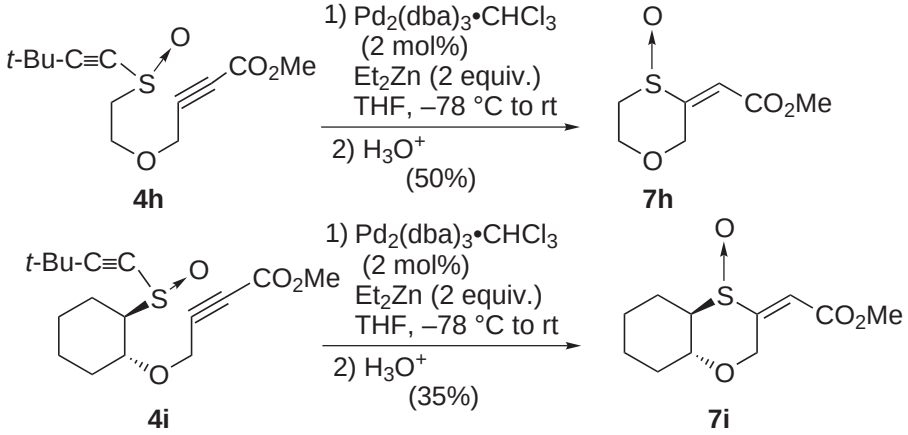


entry	substrate	EWG	time (h)	product (yield/%)
1	**4b**	CO_2Me	4	**7b** (92)
2	**4e**	$CONMe_2$	3	**7e** (80)
3	**4f**	CN	1	**7f** (31)
4	**4g**	COPh	5	**7g** (39)

[a]All reactions were carried out using 2 mol% of $Pd_2(dba)_3 \cdot CHCl_3$ at the concentration of 0.1 M.

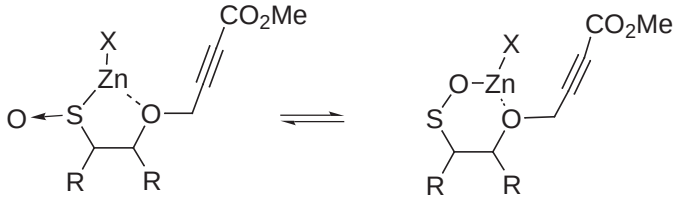
Cyclization of the oxygen-containing substrates would afford a new method to synthesize oxathiane derivatives. Thus, substrates (**4h**) and (**4i**) afforded oxathians (**7h**) and (**7i**)[13] in 50 and 35% yields,

respectively (Scheme 6). Although the expected cyclic sulfoxides were obtained, the yields were not sufficient compared with the intermolecular sulfinylzincation of β-oxyalkynoates that proceeded in very good yields.[14]



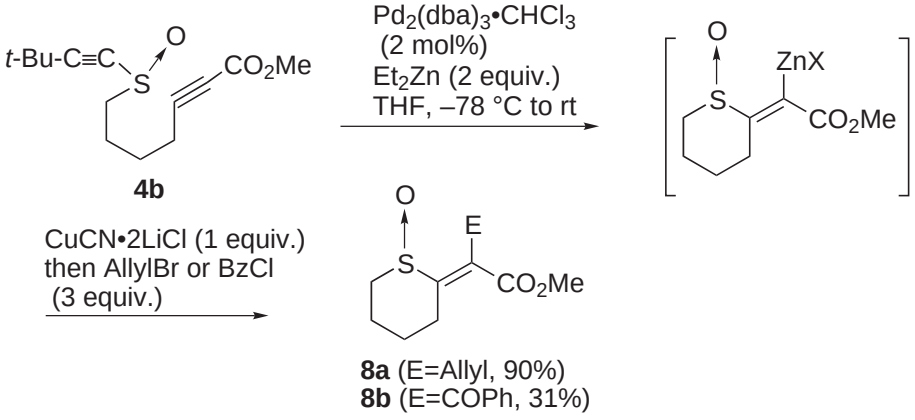
Scheme 6

The reduced yields would be rationalized by the fact that coordination of the sulfinylzinc intermediate to the oxygen was interfered with the cyclization by directing the sulfinylzinc moiety far from the reaction site as depicted in Scheme 7.



Scheme 7

Next, we examined the reaction of the β-sulfinyl vinylzinc intermediate with electrophiles besides proton. The β-sulfinyl vinylzinc intermediate generated from the alkynoate (**4b**) was transmetalated with CuCN•2LiCl,[15] and trapped with three equivalents of allyl bromide and benzoyl chloride to furnish the trisubstituted vinylic sulfoxides (**8a**) and (**8b**) in 90 and 31% yields, respectively. The reaction also proceeded with high *syn*-selectivity, and the geometric isomers of **8a** and **8b** were not detected (Scheme 8).[16]



Scheme 8

CONCLUSION

We have developed a new method to synthesize cyclic sulfoxides *via* intramolecular sulfinylzincation. Five to seven-membered rings involving a sulfinyl group were synthesized under mild conditions. The reaction proceeds with high *syn*-selectivity to give β-sulfinyl vinylzinc species, which can be trapped with allyl bromide and benzoyl chloride as well as proton.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ solution at 500 MHz with a JEOL JNM-GX500 spectrometer. ^{13}C NMR spectra were recorded in $CDCl_3$ at 75 or 125 MHz with a JEOL JMN-AL-300 or a JEOL JNM-GX500 spectrometer, respectively. Chemical shifts of ^{1}H NMR are expressed in ppm downfield from tetramethylsilane as an internal standard (δ=0). Chemical shifts of ^{13}C NMR are expressed as ppm in $CDCl_3$ as an internal standard (δ=77). IR absorption spectra (FT: diffuse reflectance spectroscopy) were recorded with KBr powder with a Horiba FT-210 IR spectrophotometer, and only noteworthy absorptions (cm^{-1}) are listed. EI-MS spectra were taken with a JMS-600H mass spectrometer. FAB-MS spectra were measured by a JEOL JMS-700. Kanto Chemical Silica Gel 60 was used as an adsorbent for column chromatography. All air- or moisture-sensitive reactions were carried out in flame-dried glassware under Ar atmosphere. All organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated with a rotary evaporator under reduced pressure.

5-(3,3-Dimethyl-1-butynylthio)-1-pentyne (1a). *n*-BuLi (1.56 M in hexane) (4.62 mL, 7.20 mmol) was added slowly to a solution of 3,3-dimethyl-1-butyne (0.81 mL, 6.60 mmol) in THF (15 mL) with stirring at –78 °C. After 30 min, sulfur (231 mg, 7.20 mmol) was added to the mixture. The stirring was continued at –78 °C for 15 min. A solution of 4-pentynyl tosylate (1.39 g, 5.50 mmol) in THF (5 mL) was added to the mixture and the whole was stirred at –78 °C for 1 h, and at 0 °C for 3 h. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (30:1) to give **1a** (530 mg, 49%) as a colorless oil. ^{1}H NMR δ: 1.23 (s, 9H, *t*-Bu), 1.95 (quint, *J*=6.7 Hz, 2H, H-4), 1.97 (t, *J*=2.4 Hz, 1H, H-1), 2.38 (td, *J*=6.7, 2.4 Hz, 2H, H-3), 2.77 (t, *J*=6.7 Hz, 2H, H-5). ^{13}C NMR (75 MHz) δ: 16.9, 27.7, 28.7, 30.9 (3C), 34.0, 66.2, 69.1, 83.2, 102.5. IR 3298 (C≡CH), 2119 (C≡C). *Anal.* Calcd for $C_{11}H_{16}S$: C, 73.27; H, 8.94. Found: C, 72.92; H, 8.87.

6-(3,3-Dimethyl-1-butynylthio)-1-hexyne (1b). In a manner similar to that described for **1a**, 5-hexynyl tosylate (5.05 g, 20.0 mmol) was converted into **1b** (1.84 g, 47%) as a colorless oil. ^{1}H NMR δ: 1.23 (s, 9H, *t*-Bu), 1.67 (quint, *J*=7.3 Hz, 2H, H-4), 1.86 (quint, *J*=7.3 Hz, 2H, H-5), 1.96 (t, *J*=2.4 Hz, 1H, H-1), 2.24 (td, *J*=7.3, 2.4 Hz, 2H, H-3), 2.68 (t, *J*=7.3 Hz, 2H, H-6). ^{13}C NMR (125 MHz) δ: 18.0, 26.8, 28.0, 28.7, 31.0 (3C), 34.8, 66.6, 68.7, 83.9, 102.5. IR 3300 (C≡CH), 2118 (C≡C).

1-Bromo-5-(3,3-dimethyl-1-butynylthio)pentane (2a). In a manner similar to that described for **1a**, 3,3-dimethyl-1-butyne (1.23 mL, 10.0 mmol) was converted into **2a** (99 mg, 38%) as a colorless oil. ^{1}H NMR δ: 1.20 (s, 9H, *t*-Bu), 1.55 (quint, *J*=7.3 Hz, 2H, H-3), 1.73 (quint, *J*=7.3 Hz, 2H, H-4), 1.87 (quint,

J=7.3 Hz, 2H, H-2), 2.63 (t, *J*=7.3 Hz, 2H, H-5), 3.39 (t, *J*=7.3 Hz, 2H, H-1). ^{13}C NMR (125 MHz) □: 26.8, 28.2, 28.7, 31.0 (3C), 32.3, 33.4, 35.1, 66.7, 102.5. IR 2164 (C≡C). MS (FAB): 262 [M^+(^{79}Br)], 264 [M^+(^{81}Br)]. HRMS (FAB) Calcd for $C_{11}H_{19}BrS$ [M^+(^{79}Br)]: 262.0391. Found: 262.0394.

1-Bromo-6-(3,3-dimethyl-1-butynylthio)hexane (2b). In a manner similar to that described for **2a**, 3,3-dimethyl-1-butyne (1.85 mL, 15.0 mmol) was converted into **2b** (936 mg, 23%) as a colorless oil. ^{1}H NMR □: 1.20 (s, 9H, *t*-Bu), 1.40-1.49 (m, 4H, H-3, H-4), 1.71 (quint, *J*=7.3 Hz, 2H, H-5), 1.86 (quint, *J*=7.3 Hz, 2H, H-2), 2.64 (t, *J*=7.3 Hz, 2H, H-6), 3.39 (t, *J*=7.3 Hz, 2H, H-1). ^{13}C NMR (125 MHz) □: 27.2, 27.6, 28.7 (2C), 31.0 (3C), 32.5, 33.7, 35.2, 66.7, 102.3. IR 2164 (C≡C). MS (FAB): 276 [M^+(^{79}Br)], 278 [M^+(^{81}Br)]. HRMS (FAB) Calcd for $C_{12}H_{21}BrS$ [M^+(^{79}Br)]: 276.0548. Found: 276.0555.

7-(3,3-Dimethyl-1-butynylthio)-1-heptyne (1c). *n*-BuLi (1.56 M in hexane) (1.67 mL, 2.60 mmol) was added slowly to a solution of trimethylsilylacetylene (0.34 mL, 2.40 mmol) in THF (2.0 mL) with stirring at –78 °C. The stirring was continued at –78 °C for 15 min and at 0 °C for 15 min. A solution of **2a** (527 mg, 2.00 mmol) in THF (2.0 mL) was added to the mixture and the whole was stirred at –78 °C for 2 h, and at rt for 10 h. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane to give the adduct, which was dissolved with THF (10 mL). TBAF (1.0 M in THF) (0.87 mL, 0.870 mmol) was added to the solution with stirring at 0 °C. The whole was stirred at rt for 2 h. Water was added to the mixture and the mixture was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane to give **1c** (319 mg, 77%) as a colorless oil. ^{1}H NMR □: 1.23 (s, 9H, *t*-Bu), 1.50–1.60 (m, 4H, H-4, H-5), 1.74 (quint, *J*=6.7 Hz, 2H, H-6), 1.95 (t, *J*=3.0 Hz, 1H, H-1), 2.21 (td, *J*=6.7, 3.0 Hz, 2H, H-3), 2.66 (t, *J*=6.7 Hz, 2H, H-7). ^{13}C NMR (125 MHz) □: 18.3, 27.3, 28.0, 28.5, 28.7, 31.0 (3C), 35.2, 66.8, 68.4, 84.5, 102.3. IR 3300 (C≡CH), 2118 (C≡C). MS (FAB): 209 (MH^+). HRMS (FAB) Calcd for $C_{13}H_{21}S$ (MH^+): 209.1364. Found: 209.1360.

8-(3,3-Dimethyl-1-butynylthio)-1-octyne (1d). In a manner similar to that described for **1c**, **2b** (923 mg, 3.33 mmol) was converted into **1d** (684 mg, 92%) as a colorless oil. ^{1}H NMR □: 1.16 (s, 9H, *t*-Bu), 1.34-1.40 (m, 4H, H-5, H-6), 1.46 (quint, *J*=6.7 Hz, 2H, H-4), 1.66 (quint, *J*=6.7 Hz, 2H, H-7), 1.87 (t, *J*=2.4 Hz, 1H, H-1), 2.13 (td, *J*=6.7, 2.4 Hz, 2H, H-3), 2.59 (t, *J*=6.7 Hz, 2H, H-8). ^{13}C NMR (125 MHz) □: 18.3, 27.6, 28.19, 28.23, 28.7, 28.8, 31.0 (3C), 35.3, 66.9, 68.2, 84.5, 102.2. IR 3298 (C≡CH), 2118 (C≡C). *Anal.* Calcd for $C_{14}H_{22}S$: C, 75.61; H, 9.97. Found: C, 75.61; H, 9.92.

Methyl 6-(3,3-Dimethyl-1-butynylthio)-2-hexynoate (3a). *n*-BuLi (1.56 M in hexane) (2.40 mL, 2.40 mmol) was added slowly to a solution of **1a** (360 mg, 2.00 mmol) in THF (4.00 mL) with stirring at –78 °C. After 30 min, $ClCO_2Me$ (0.23 mL, 3.00 mmol) was added to the mixture. The stirring was continued at –78 °C for 1 h and at rt for 3 h. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (30:1) to give **3a** (379 mg, 80%) as a colorless oil. ^{1}H

NMR δ: 1.23 (s, 9H, *t*-Bu), 2.02 (quint, *J*=6.7 Hz, 2H, H-5), 2.54 (t, *J*=6.7 Hz, 2H, H-4), 2.75 (t, *J*=6.7 Hz, 2H, H-6), 3.77 (s, 3H, OCH_3). ^{13}C NMR (125 MHz) δ: 17.0, 26.8, 28.7, 30.8 (3C), 33.9, 52.6, 65.9, 73.4, 88.2, 102.8, 154.0. IR 2237 (C≡C), 1720 (C=O). MS (EI) *m/z* (%): 238 (M^+, 27.9), 113 (100). HRMS (EI) Calcd for $C_{13}H_{18}O_2S$ (M^+): 238.1027. Found: 238.1026.

Methyl 7-(3,3-Dimethyl-1-butynylthio)-2-heptynoate (3b). In a manner similar to that described for **3a**, **1b** (820 mg, 4.22 mmol) was converted into **3b** (710 mg, 67%) as a colorless oil. ^1H NMR δ: 1.23 (s, 9H, *t*-Bu), 1.74 (quint, *J*=7.3 Hz, 2H, H-5), 1.86 (quint, *J*=7.3 Hz, 2H, H-6), 2.40 (t, *J*=7.3 Hz, 2H, H-4), 2.67 (t, *J*=7.3 Hz, 2H, H-7), 3.76 (s, 3H, OCH_3). ^{13}C NMR (125 MHz) δ: 18.3, 25.9, 28.0, 30.9 (4C), 34.6, 52.5, 66.4, 73.3, 88.9, 102.6, 154.1. IR 2237 (C≡C), 1716 (C=O). MS (FAB): 253 (MH^+). HRMS (FAB) Calcd for $C_{14}H_{21}O_2S$ (MH^+): 253.1263. Found: 253.1268.

Methyl 8-(3,3-Dimethyl-1-butynylthio)-2-octynoate (3c). In a manner similar to that described for **3a**, **1c** (159 mg, 0.763 mmol) was converted into **3c** (165 mg, 81%) as a colorless oil. ^1H NMR δ: 1.23 (s, 9H, *t*-Bu), 1.51–1.58 (m, 2H, H-6), 1.63 (quint, *J*=6.7 Hz, 2H, H-5), 1.74 (quint, *J*=7.3 Hz, 2H, H-7), 2.37 (t, *J*=6.7 Hz, 2H, H-4), 2.66 (t, *J*=7.3 Hz, 2H, H-8), 3.76 (s, 3H, OCH_3). ^{13}C NMR (125 MHz) δ: 18.5, 27.1, 27.3, 28.4, 28.7, 31.0 (3C), 35.0, 52.5, 66.6, 73.0, 89.3, 102.4, 154.2. IR 2237 (C≡C), 1716 (C=O). MS (FAB): 267 (MH^+). HRMS (FAB) Calcd for $C_{15}H_{23}O_2S$ (MH^+): 267.1419. Found: 267.1422.

Methyl 9-(3,3-Dimethyl-1-butynylthio)-2-nonynoate (3d). In a manner similar to that described for **3a**, **1d** (400 mg, 1.80 mmol) was converted into **3d** (412 mg, 82%) as a colorless oil. ^1H NMR δ: 1.23 (s, 9H, *t*-Bu), 1.42–1.46 (m, 2H, H-6, H-7), 1.60 (quint, *J*=7.3 Hz, 2H, H-5), 1.73 (quint, *J*=7.3 Hz, 2H, H-8), 2.35 (t, *J*=7.3 Hz, 2H, H-4), 2.65 (t, *J*=7.3 Hz, 2H, H-9), 3.76 (s, 3H, OCH_3). ^{13}C NMR (125 MHz) δ:18.6, 27.3, 27.5, 28.3, 28.7 (2C), 31.0 (3C), 35.3, 52.5, 66.8, 73.0, 89.6, 102.3, 154.2. IR 2237 (C≡C), 1716 (C=O). MS (FAB): 281 (MH^+). HRMS (FAB) Calcd for $C_{16}H_{25}O_2S$ (MH^+): 281.1575. Found: 281.1596.

Methyl 6-(3,3-Dimethyl-1-butynylsulfinyl)-2-hexynoate (4a). *m*-CPBA (containing 30% of water) (381 mg, 1.55 mmol) was added to a solution of **3a** (335 mg, 1.41 mmol) in CH_2Cl_2 (4.00 mL) with stirring at 0 °C. After 30 min, the reaction was quenched with saturated $NaHCO_3$ aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (2:1) to give **4a** (346 mg, 95%) as a colorless oil. ^1H NMR δ: 1.31 (s, 9H, *t*-Bu), 2.11–2.26 (m, 2H, H-5), 2.57 (dt, *J*=17.7, 6.7 Hz, 1H, H-4), 2.62 (dt, *J*=17.7, 6.7 Hz, 1H, H-4), 3.12 (ddd, *J*=12.8, 8.5, 6.1 Hz, 1H, H-6), 3.15 (ddd, *J*=12.8, 8.5, 6.7 Hz, 1H, H-6), 3.77 (s, 3H, OCH_3). ^{13}C NMR (125 MHz) δ: 17.7, 20.4, 28.4, 29.9 (3C), 52.6, 54.2, 73.9, 75.1, 87.0, 113.1, 153.8. IR 2237 (C≡C), 1716 (C=O), 1045 (S=O). *Anal.* Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13; S, 12.61. Found: C, 61.92; H, 8.87; S, 12.37.

Methyl 7-(3,3-Dimethyl-1-butynylsulfinyl)-2-heptynoate (4b). In a manner similar to that described for **4a**, **3b** (658 mg, 2.16 mmol) was converted into **4b** (580 mg, 83%) as a colorless oil. ^1H NMR δ: 1.29–1.30 (m, 9H, *t*-Bu), 1.73–1.84 (m, 2H, H-5), 1.94–2.08 (m, 2H, H-6), 2.42–2.45 (m, 2H, H-4), 3.02–3.06 (m, 2H, H-7), 3.75–3.77 (m, 3H, OCH_3). ^{13}C NMR (125 MHz) δ: 18.3, 21.6, 26.3, 28.4, 29.9

(3C), 52.5, 55.4, 73.5, 75.4, 88.1, 112.7, 153.9. IR 2237 (C≡C), 1716 (C=□), 1072 (S=O). *Anal.* Calcd for $C_{14}H_{20}O_3S$: C, 62.66; H, 7.51; S, 11.95. Found: C, 61.42; H, 7.35; S, 11.69.

Methyl 8-(3,3-Dimethyl-1-butynylsulfinyl)-2-octynoate (4c). In a manner similar to that described for **4a**, **3c** (147 mg, 0.552 mmol) was converted into **4c** (116 mg, 75%) as a colorless oil. ^{1}H NMR □: 1.22–1.23 (m, 9H, *t*-Bu), 1.50–1.63 (m, 4H, H-5, H-6), 1.74–1.89 (m, 2H, H-7), 2.30–2.33 (m, 2H, H-4), 2.91–3.00 (m, 2H, H-8), 3.69–3.70 (m, 3H, OCH_3). ^{13}C NMR (125 MHz) □: 18.3, 21.8, 27.0, 27.6, 28.4, 29.9 (3C), 52.5, 55.9, 73.2, 75.5, 88.8, 112.5, 154.0. IR 2237 (C≡C), 1716 (C=□), 1704 (S=O). MS (FAB): 283 (MH^+). HRMS (FAB) Calcd for $C_{15}H_{23}O_3S$ (MH^+): 283.1368. Found: 283.1368.

Methyl 9-(3,3-Dimethyl-1-butynylsulfinyl)-2-nonynoate (4d). In a manner similar to that described for **4a**, **3d** (400 mg, 1.43 mmol) was converted into **4d** (413 mg, 98%) as a colorless oil. ^{1}H NMR □: 1.24–1.26 (m, 9H, *t*-Bu), 1.42–1.49 (m, 4H, H-6, H-7), 1.54–1.61 (m, 2H, H-5), 17.4–1.89 (m, 2H, H-8), 2.29–2.33 (m, 2H, H-4), 2.92–3.03 (m, 2H, H-9), 3.71–3.73 (m, 3H, OCH_3). ^{13}C NMR (125 MHz) □: 18.5, 22.1, 27.1, 27.9, 28.3, 28.4, 29.9 (3C), 52.5, 56.1, 73.0, 75.5, 89.3, 112.4, 154.1. IR 2237 (C≡C), 1714 (C=□), 1072 (S=O). MS (FAB): 297 (MH^+). HRMS (FAB) Calcd for $C_{16}H_{25}O_3S$ (MH^+): 297.1524. Found: 297.1531.

***N*,*N*-Dimethyl 7-(3,3-Dimethyl-1-butynylthio)-2-heptynamide (3e).** *n*-BuLi (1.56 M in hexane) (1.10 mL, 17.2 mmol) was added slowly to a solution of **1b** (304 mg, 1.56 mmol) in THF (3.12 mL) with stirring at –78 °C. After 30 min, $ClCONMe_2$ (0.22 mL, 2.40 mmol) was added to the mixture. The stirring was continued at –78 °C for 1 h and at rt overnight. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (20:1) to give **3e** (265 mg, 64%) as a colorless oil. ^{1}H NMR □: 1.15 (s, 9H, *t*-Bu), 1.67 (quint, *J*=7.3 Hz, 2H, H-5), 1.79 (quint, *J*=7.3 Hz, 2H, H-6), 2.35 (t, *J*=7.3 Hz, 2H, H-4), 2.61 (t, *J*=7.3 Hz, 2H, H-7), 2.90 (s, 3H, NCH_3), 3.13 (s, 3H, NCH_3). ^{13}C NMR (75 MHz) □: 18.5, 26.2, 28.1, 28.6, 30.9 (3C), 33.9, 34.7, 38.3, 66.4, 74.3, 92.1, 102.4, 154.5. IR 2249 (C≡C), 1639 (C=O). MS (FAB): 266 (MH^+). HRMS (FAB) Calcd for $C_{15}H_{24}NOS$ (MH^+): 266.1579. Found: 266.1579.

7-(3,3-Dimethyl-1-butynylthio)-2-heptynenitrile (3f). *n*-BuLi (1.56 M in hexane) (1.08 mL, 1.68 mmol) was added slowly to a solution of **1b** (311 mg, 1.60 mmol) in ether (3.20 mL) with stirring at –78 °C. After 30 min, PhOCN (210 mg, 1.72 mmol) was added to the mixture. The stirring was continued at –78 °C for 1 h and at rt for 4 h. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane to give **3f** (282 mg, 80%) as a colorless oil. ^{1}H NMR □: 1.17 (s, 9H, *t*-Bu), 1.66-1.74 (m, 2H, H-5), 1.75-1.83 (m, 2H, H-6), 2.36 (t, *J*=7.3 Hz, 2H, H-4), 2.60 (t, *J*=6.7 Hz, 2H, H-7). ^{13}C NMR (75 MHz) □: 18.5, 25.4, 27.8, 28.7, 31.0 (3C), 34.3, 55.7, 66.1, 86.6, 102.9, 105.1. IR 2313 (C≡N), 2260 (C≡C). MS (FAB): 220 (MH^+). HRMS (FAB) Calcd for $C_{13}H_{18}NS$ (MH^+): 220.1160. Found: 220.1168.

7-(3,3-Dimethyl-1-butynylthio)-1-phenyl-2-heptyn-1-one (3g). BzCl (0.378 mL, 3.41 mmol) was added to a solution of **1b** (221 mg, 1.14 mmol), $Pd(PPh_3)_4$ (26.3 mg, 0.0227 mmol), and CuI (43.2 mg, 0.227 mmol) in Et_3N (2.28 mL) with stirring at 0 °C. The stirring was continued at rt for 30 min. The reaction was quenched with MeOH and the solvent was evaporated. The residue was dissolved in AcOEt and the solution was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane to give **3g** (301 mg, 89%) as a colorless oil. ^{1}H NMR □: 1.20 (s, 9H, *t*-Bu), 1.84 (quint, *J*=6.7 Hz, 2H, H-5), 1.93 (quint, *J*=6.7 Hz, 2H, H-6), 2.56 (t, *J*=6.7 Hz, 2H, H-4), 2.72 (t, *J*=6.7 Hz, 2H, H-7), 7.46 (t, *J*=7.3 Hz, 2H, Ar-H), 7.58 (t, *J*=7.3 Hz, 1H, Ar-H), 8.11 (d, *J*=7.3 Hz, 2H, Ar-H). ^{13}C NMR (75 MHz) □: 18.8, 26.2, 28.2, 28.7, 30.9 (3C), 34.7, 66.4, 80.0, 95.7, 102.6, 128.5 (2C), 129.5 (2C), 133.9, 136.8, 178.1. IR 2233 (C≡C), 1643 (C=□). MS (FAB): 299 (MH^+). HRMS (FAB) Calcd for $C_{19}H_{23}OS$ (MH^+): 299.1470. Found: 299.1484.

***N*,*N*-Dimethyl 7-(3,3-Dimethyl-1-butynylsulfinyl)-2-heptynamide (4e).** In a manner similar to that described for **4a**, **3e** (216 mg, 0.814 mmol) was converted into **4e** (201 mg, 88%) as a colorless oil. ^{1}H NMR □: 1.22–1.23 (m, 9H, *t*-Bu), 1.66–1.78 (m, 2H, H-5), 1.87–2.01 (m, 2H, H-6), 2.37–2.41 (m, 2H, H-4), 2.89 (s, 3H, NCH_3), 2.93–3.00 (m, 2H, H-7), 3.12 (s, 3H, NCH_3). ^{13}C NMR (125 MHz) □: 18.5, 21.6, 26.6, 28.3, 29.8 (3C), 33.9, 38.2, 55.5, 74.6, 75.4, 91.3, 112.5, 154.3. IR 2270 (C≡C), 1635 (C=□), 1065 (S=O). MS (FAB): 282 (MH^+). HRMS (FAB) Calcd for $C_{15}H_{24}NO_2S$ (MH^+): 282.1528. Found: 282.1530.

7-(3,3-Dimethyl-1-butynylsulfinyl)-2-heptynenitrile (4f). In a manner similar to that described for **4a**, **3f** (252 mg, 1.15 mmol) was converted into **4f** (264 mg, 97%) as a colorless oil. ^{1}H NMR □: 1.24 (s, 9H, *t*-Bu), 1.68–1.81 (m, 2H, H-5), 1.87–2.03 (m, 2H, H-6), 2.40 (t, *J*=7.3 Hz, 2H, H-4), 2.95 (m, 2H, H-7). ^{13}C NMR (75 MHz) □: 18.6, 21.5, 25.9, 28.4, 29.9 (3C), 55.0, 55.9, 75.1, 86.0, 105.0, 113.0. IR 2314 (C≡N), 2260 (C≡C), 1066 (S=□). MS (FAB): 236 (MH^+). HRMS (FAB) Calcd for $C_{13}H_{18}NOS$ (MH^+): 236.1109. Found: 236.1091.

7-(3,3-Dimethyl-1-butynylsulfinyl)-1-phenyl-2-heptyn-1-one (4g). In a manner similar to that described for **4a**, **3g** (261 mg, 0.875 mmol) was converted into **4g** (244 mg, 89%) as a colorless oil. ^{1}H NMR □: 1.19 (s, 9H, *t*-Bu), 1.75–1.88 (m, 2H, H-5), 1.93–2.10 (m, 2H, H-6), 2.51–2.55 (m, 2H, H-4), 2.96–3.05 (m, 2H, H-7), 7.49 (t, *J*=7.3 Hz, 2H, Ar-H), 7.61 (t, *J*=7.3 Hz, 1H, Ar-H), 8.13 (d, *J*=7.3 Hz, 2H, Ar-H). ^{13}C NMR (125 MHz) □: 19.0, 21.8, 26.8, 28.4, 29.9 (3C), 55.6, 75.4, 80.2, 94.9, 112.8, 128.6 (2C), 129.5 (2C), 134.0, 136.7, 178.0. IR 2200 (C≡C), 1643 (C=□), 1068 (S=O). MS (FAB): 315 (MH^+). HRMS (FAB) Calcd for $C_{19}H_{23}O_2S$ (MH^+): 315.1419. Found: 315.1406.

3,3-Dimethyl-1-[2-(2-propynyloxy)ethylthio]-1-butyne (1e). In a manner similar to that described for **1a**, 2-(2-propynyloxy)ethyl tosylate (1.53 g, 6.00 mmol) was converted into **1e** (362 mg, 31%) as a colorless oil. ^{1}H NMR □: 1.23 (s, 9H, *t*-Bu), 2.45 (t, *J*=2.4 Hz, 1H, C≡CH), 2.85 (t, *J*=6.7 Hz, 2H, $SC\underline{H}_2CH_2O$), 3.83 (t, *J*=6.7 Hz, 2H, $SCH_2C\underline{H}_2O$), 4.21 (s, 2H, $OCH_2C{\equiv}C$). ^{13}C NMR (125 MHz) □: 28.7, 30.9 (3C), 34.4, 58.2, 66.0, 67.8, 74.7, 79.4, 102.6. IR 3288 (C≡CH), 2118 (C≡C). MS (FAB): 197 (MH^+). HRMS (FAB) Calcd for $C_{11}H_{17}OS$ (MH^+): 197.1000. Found: 197.0999.

***trans*-2-(3,3-Dimethyl-1-butynylthio)cyclohexanol (5).** In a manner similar to that described for **1a** but with the addition of cyclohexene oxide (1.01 mL, 10.0 mmol) instead of the tosylate, 3,3-dimethyl-1-butyne (1.12 mL, 9.09 mmol) was converted into **5** (1.32 g, 69%) as a colorless oil. ^{1}H NMR δ: 1.20–1.38 (m, 3H, H-4, H-5), 1.24 (s, 9H, *t*-Bu), 1.60–1.69 (m, 1H, H-5), 1.74–1.79 (m, 2H, H-3, H-6), 2.04–2.08 (m, 1H, H-6), 2.12–2.16 (m, 1H, H-3), 2.45 (ddd, *J*=12.2, 9.2, 4.3 Hz, 1H, H-2), 2.79 (s, 1H, OH), 3.56 (ddd, *J*=9.8, 9.2, 4.3 Hz, 1H, H-1). ^{13}C NMR (75 MHz) δ: 24.4, 26.1, 28.8, 31.0 (3C), 31.4, 33.7, 54.7, 63.3, 71.6, 104.2. IR 3320 (OH), 2150 (C≡C). MS (FAB): 235 (MNa^+). HRMS (FAB) Calcd for $C_{12}H_{20}ONaS$ (MNa^+): 235.1133. Found: 235.1108.

***trans*-1-(3,3-Dimethyl-1-butynylthio)-2-(2-propynyloxy)cyclohexane (6).** A solution of **5** (1.18 g, 5.53 mmol) in THF (10 mL) was added to a suspension of NaH (60% in oil) (243 mg, 6.09 mmol) in THF (20 mL) with stirring at 0 °C. After 30 min, propargyl bromide (0.51 mL, 6.64 mmol) was added to the mixture. The stirring was continued at 0 °C for 12 h. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (25:1) to give **6** (772 mg, 57%) as a colorless oil. ^{1}H NMR δ: 1.22–1.38 (m, 3H, H-4, H-5), 1.25 (s, 9H, *t*-Bu), 1.60–1.76 (m, 3H, H-3, H-4, H-6), 2.11–2.21 (m, 2H, H-3, H-6), 2.41 (t, *J* = 2.4 Hz, 1H, C≡CH), 2.67 (ddd, *J*=11.0, 9.2, 4.3 Hz, 1H, H-1), 3.46 (ddd, *J*=9.8, 9.2, 4.3 Hz, 1H, H-2), 4.32 (d, *J*=2.4 Hz, 2H, $OCH_2C{\equiv}C$). ^{13}C NMR (125 Hz) δ: 23.8, 25.2, 28.8, 31.0 (3C), 31.5, 31.6, 51.1, 57.1, 65.0, 73.8, 78.0, 80.4, 104.3. IR 3290 (C≡CH), 2115 (C≡C). MS (FAB): 273 (MNa^+). HRMS (FAB) Calcd for $C_{15}H_{22}ONaS$ (MNa^+): 273.1289. Found: 273.1291.

Methyl 4-[2-(3,3-Dimethyl-1-butynylthio)ethoxy]-2-butynoate (3h). In a manner similar to that described for **3a**, **1e** (312 mg, 1.59 mmol) was converted into **3h** (300 mg, 74%) as a colorless oil. ^{1}H NMR δ: 1.23 (s, 9H, *t*-Bu), 2.85 (t, *J*=6.7 Hz, 2H, $SC\underline{H}_2CH_2O$), 3.79 (s, 3H, OCH_3), 3.83 (t, *J*=6.7 Hz, 2H, $SCH_2C\underline{H}_2O$), 4.35 (s, 2H, H-4). ^{13}C NMR (75 MHz) δ: 28.7, 30.9 (3C), 34.4, 52.8, 58.0, 65.8, 68.2, 78.0, 83.2, 102.8, 153.4. IR 2239 (C≡C), 1720 (C=O). MS (FAB): 255 (MH^+). HRMS (FAB) Calcd for $C_{13}H_{19}O_3S$ (MH^+): 255.1055. Found: 255.1055.

Methyl 4-[2-(3,3-Dimethyl-1-butynylsulfinyl)ethoxy]-2-butynoate (4h). In a manner similar to that described for **4a**, **3h** (216 mg, 0.848 mmol) was converted into **4h** (210 mg, 92%) as a colorless oil. ^{1}H NMR δ: 1.30 (s, 9H, *t*-Bu), 3.25 (ddd, *J*=13.4, 9.2, 5.5 Hz, 1H, $SC\underline{H}_2CH_2O$), 3.35 (dt, *J*=13.4, 5.5 Hz, 1H, $SC\underline{H}_2CH_2O$), 3.79 (s, 3H, OCH_3), 3.96-4.06 (m, 2H, $SCH_2C\underline{H}_2O$), 4.30 (d, *J*=17.1 Hz, 1H, H-4), 4.38 (d, *J* = 17.1 Hz, 1H, H-4). ^{13}C NMR (75 MHz) δ: 28.4, 29.9 (3C), 52.8, 56.6, 58.2, 63.2, 75.5, 78.3, 82.5, 113.0, 153.3. IR 2239 (C≡C), 2160 (C≡C), 1720 (C=□), 1065 (S=□). *Anal.* Calcd for $C_{13}H_{18}O_4S$: C, 57.68; H, 6.71; S, 11.86. Found: C, 57.76; H, 6.66; S, 11.88.

Methyl *trans*-4-[2-(3,3-Dimethyl-1-butynylthio)cyclohexyloxy]-2-butynoate (3i). In a manner similar to that described for **3a**, **6** (646 mg, 2.58 mmol) was converted into **3i** (831 mg, 67%) as a colorless oil. ^{1}H NMR δ: 1.21–1.41 (m, 3H, H-4', H-5'), 1.25 (s, 9H, *t*-Bu), 1.61–1.80 (m, 3H, H-3', H-4', H-6'), 2.10–2.14 (m, 1H, H-3'), 2.17 (m, 1H, H-6'), 2.64 (ddd, *J*=10.4, 9.2, 4.3 Hz, 1H, H-2'), 3.42 (ddd,

J=9.8, 9.2, 4.3 Hz, 1H, H-1'), 3.78 (s, 3H, OCH_3), 4.47 (s, 2H, $OCH_2C{\equiv}C$). ^{13}C NMR (75 MHz) *δ*: 23.9, 25.2, 28.9, 31.0 (3C), 31.6, 31.8, 51.2, 52.7, 57.2, 64.7, 77.1, 79.0, 94.5, 104.6, 153.6. IR 2234 (C≡C), 1720 (C=O). MS (FAB): 309 (MH^+). HRMS (FAB) Calcd for $C_{17}H_{25}O_3S$ (MH^+): 309.1525. Found: 309.1530.

Methyl *trans*-4-[2-(3,3-Dimethyl-1-butynylsulfinyl)cyclohexyloxy]-2-butynoate (4i). In a manner similar to that described for **4a**, **3i** (354 mg, 1.15 mmol) was converted into **4i** (372 mg, quant., 6:4 diastereomeric mixture) as a colorless oil. ^1H NMR *δ*: 1.15–1.46 (m, 12H, *t*-Bu, H-4', H-5'), 1.42–1.54 (m, 0.6H, H-3'), 1.73–1.90 (m, 2.4H, H-3', H-4', H-6'), 2.18–2.44 (m, 2H, H-3', H-6'), 2.48–2.55 (m, 0.4H, H-2'), 2.97–3.03 (m, 0.6H, H-2'), 3.46–3.58 (m, 1H, H-1'), 3.67–3.73 (m, 3H, OCH_3), 4.20–4.37 (m, 2H, $OCH_2C{\equiv}C$). ^{13}C NMR (125 MHz) *δ*: 21.5 (0.4C), 22.4 (0.6C), 23.6 (0.6C), 24.3 (0.4C), 24.4, 28.3 (0.4C), 28.4 (0.6C), 29.85 (1.2C), 29.89 (1.8C), 31.1 (0.6C), 31.2 (0.4C), 52.6, 55.7 (0.6C), 56.4 (0.4C), 67.0 (0.6C), 67.9 (0.4C), 73.0 (0.6C), 74.4 (0.4C), 75.9 (0.6C), 77.2 (0.4C), 77.4 (0.4C), 77.5 (0.6C), 83.2 (0.6C), 83.4 (0.4C), 113.1 (0.4C), 114.2 (0.6C), 153.2 (0.6C), 153.3 (0.4C). IR 2238 (C≡C), 2158 (C≡C), 1716 (C=O), 1057 (S=O). MS (FAB): 325 (MH^+). HRMS (FAB) Calcd for $C_{17}H_{25}O_4S$ (MH^+): 325.1474. Found: 325.1448.

General Procedure for Intramolecular Sulfinylzincation:

Methyl (*E*)-(1-Oxothiolan-2-ylidene)acetate (7a). Et_2Zn (1.00 M in hexane) (0.45 mL, 0.45 mmol) in THF (2.22 mL) was added slowly to a mixture of **4a** (53.0 mg, 0.222 mmol) and $Pd_2(dba)_3{\bullet}CHCl_3$ (4.6 mg, 0.00445 mmol) in THF (2.22 mL) with stirring at –78 °C. The stirring was continued at rt for 5 h. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:1) to give **7a** (25.1 mg, 65%) as a pale yellow oil. ^1H NMR *δ*: 2.09–2.19 (m, 1H, H-4), 2.47–2.57 (m, 1H, H-4), 2.91–3.00 (m, 2H, H-3, H-5), 3.02–3.08 (m, 1H, H-5), 3.37 (dddd, *J*=19.5, 8.5, 6.7, 2.4 Hz, 1H, H-3), 3.78 (s, 3H, OCH_3), 6.53 (dd, *J*=3.1, 2.4 Hz, 1H, C=CH). ^{13}C NMR (125 MHz) *δ*: 21.6, 29.1, 51.7, 51.9, 122.3, 165.0, 167.7. IR 1720 (C=O), 1645 (C=C), 1043 (S=O). MS (EI) *m/z* (%): 174. (M+, 44.4), 97 (100). HRMS (EI) Calcd for $C_7H_{10}O_3S$ (M^+): 174.0351. Found: 174.0364.

Methyl (*E*)-(1-Oxothian-2-ylidene)acetate (7b). In a manner similar to that described for **7a**, **4b** (25.5 mg, 0.095 mmol) was converted into **7b** (16.4 mg, 92%) as a pale yellow oil. ^1H NMR *δ*: 1.51–1.60 (m, 1H, H-4), 1.83–1.97 (m, 2H, H-4, H-5), 2.09–2.19 (m, 2H, H-3, H-5), 2.71–2.77 (m, 1H, H-6), 3.49–3.53 (m, 1H, H-6), 3.78 (s, 3H, OCH_3), 4.00-4.06 (m, 1H, H-3), 6.45 (s, 1H, C=CH). ^{13}C NMR (125 MHz) *δ*: 22.8, 27.2, 27.4, 51.7, 56.0, 115.8, 164.8, 165.0. IR 1716 (C=O), 1643 (C=C), 1066 (S=O). MS (FAB): 189 (MH^+). HRMS (FAB) Calcd for $C_8H_{13}O_3S$ (MH^+): 189.0586. Found: 189.0586.

Methyl (*E*)-(1-Oxothiepan-2-ylidene)acetate (7c). In a manner similar to that described for **7a**, **4c** (49.9 mg, 0.177 mmol) was converted into **7c** (17.5 mg, 49%) as a pale yellow oil. ^1H NMR *δ*: 1.44–1.98 (m, 6H, H-4, H-5, H-6), 2.41 (ddd, *J*=15.9, 9.2, 3.7 Hz, 1H, H-3), 2.77 (ddd, *J*=13.4, 10.4, 2.4 Hz, 1H, H-7), 3.21 (ddd, *J*=13.4, 7.9, 2.4 Hz, 1H, H-7), 3.32 (dddd, *J*=15.9, 7.9, 4.3, 1.8 Hz, 1H, H-3), 3.71 (s, 3H, OCH_3), 6.49 (s, 1H, C=CH). ^{13}C NMR (125 MHz) *δ*: 22.1, 24.5, 26.4, 27.8, 51.6, 56.3, 119.0, 164.9,

165.4. IR 1716 (C=O), 1632 (C=C), 1045 (S=O). MS (FAB): 203 (MH^+). HRMS (FAB) Calcd for $C_9H_{15}O_3S$ (MH^+): 203.0742. Found: 203.0746.

***N*,*N*-Dimethyl-(*E*)-(1-oxothian-2-ylidene)acetamide (7e).** In a manner similar to that described for **7a**, **4e** (68.3 mg, 0.243 mmol) was converted into **7e** (39.1 mg, 80%) as pale yellow columns. mp. 115.5–116.5 °C (hexane–AcOEt). ^{1}H NMR δ: 1.45–1.55 (m, 1H, H-4), 1.74–1.85 (m, 2H, H-4, H-5), 1.96–2.05 (m, 1H, H-3), 2.06–2.13 (m, 1H, H-5), 2.61–2.67 (m, 1H, H-6), 2.95 (s, 3H, NCH_3), 3.01 (s, 3H, NCH_3), 3.36–3.42 (m, 1H, H-6), 3.52 (ddd, *J*=14.6, 6.1, 4.3 Hz, 1H, H-3), 6.66 (s, 1H, C=CH). ^{13}C NMR (125 MHz) δ: 22.6, 27.0, 27.5, 34.9, 37.8, 55.5, 118.3, 156.7, 165.2. IR 1653 (C=O), 1605 (C=C), 1061 (S=O). MS (FAB): 202 (MH^+). HRMS (FAB) Calcd for $C_9H_{16}NO_2S$ (MH^+): 202.0902. Found: 202.0879.

(*E*)-(1-Oxothian-2-ylidene)acetonitrile (7f). In a manner similar to that described for **7a**, **4f** (45.6 mg, 0.194 mmol) was converted into **7f** (9.3 mg, 31%) as colorless columns. mp. 61.0–62.0 °C (hexane–AcOEt). ^{1}H NMR δ: 1.57 (qt, *J*=13.4, 3.7 Hz, 1H, H-4), 1.83–1.93 (m, 1H, H-5), 2.04 (m, 1H, H-4), 2.17–2.24 (m, 1H, H-5), 2.32 (ddd, *J*=14.6, 13.4, 4.9 Hz, 1H, H-3), 2.75 (ddd, *J*=13.4, 11.6, 3.1 Hz, 1H, H-6), 3.32 (ddd, *J*=14.6, 6.1, 3.7 Hz, 1H, H-3), 3.58 (ddd, *J*=11.6, 4.3, 3.1 Hz, 1H, H-6), 6.03 (s, 1H, C=CH). ^{13}C NMR (75 MHz) δ: 22.8, 27.1, 30.4, 55.9, 97.1, 114.3, 170.4. IR 2222 (C≡N), 1618 (C=C), 1070 (S=O). MS (EI) *m/z* (%): 155 (M^+, 41.5), 79 (100). HRMS (EI) Calcd for C_7H_9NOS (M^+): 155.0405. Found: 155.0402.

(*E*)-(1-Oxothian-2-ylidene)-1-phenylethanone (7g). In a manner similar to that described for **7a**, **4g** (63.0 mg, 0.200 mmol) was converted into **7g** (18.2 mg, 39%) as a pale yellow oil. ^{1}H NMR δ: 1.56–1.65 (m, 1H, H-4), 1.86–1.99 (m, 2H, H-4, H-5), 2.09–2.22 (m, 2H, H-3, H-5), 2.79 (ddd, *J*=12.8, 11.6, 3.1 Hz, 1H, H-6), 3.55–3.61 (m, 1H, H-6), 3.87 (ddd, *J*=14.0, 5.5, 3.7 Hz, 1H, H-3), 7.47–7.51 (m, 3H, C=CH, Ar-H), 7.60 (t, *J*=7.3 Hz, 1H, Ar-H), 8.03 (d, *J*=7.3 Hz, 2H, Ar-H). ^{13}C NMR (125 MHz) δ: 23.1, 27.6, 27.9, 56.4, 120.4, 128.7 (2C), 128.8 (2C), 133.5, 137.7, 163.1, 189.8. IR 1664 (C=O), 1610 (C=C), 1068 (S=O). MS (FAB): 235 (MH^+). HRMS (FAB) Calcd for $C_{13}H_{15}O_2S$ (MH^+): 235.0793. Found: 235.0808.

Methyl (*E*)-(4-Oxo-[1,4]oxathian-3-ylidene)acetate (7h). In a manner similar to that described for **7a**, **4h** (40.8 mg, 0.151 mmol) was converted into **7h** (14.2 mg, 50%) as a pale yellow oil. ^{1}H NMR δ: 3.11 (ddd, *J*=12.2, 11.0, 3.7 Hz, 1H, H-5), 3.53 (dt, *J*=12.2, 3.7 Hz, 1H, H-5), 3.80 (s, 3H, OCH_3), 3.86 (ddd, *J*=13.4, 11.0, 3.7 Hz, 1H, H-6), 4.14 (d, *J*=14.0 Hz, 1H, H-2), 4.27 (dt, *J*=13.4, 3.7 Hz, 1H, H-6), 5.70 (d, *J*=14.0 Hz, 1H, H-2), 6.55 (s, 1H, C=CH). ^{13}C NMR (125 MHz) δ: 52.1, 55.1, 63.3, 64.2, 119.7, 158.2, 164.0. IR 1720 (C=O), 1647 (C=C), 1090 (S=O). MS (EI) *m/z* (%): 190 (M^+, 6.0), 173 (100). HRMS (EI) Calcd for $C_7H_{10}O_4S$ (M^+): 190.0300. Found: 190.0306.

Methyl (*E*)-(*trans*-4-Oxohexahydrobenzo[1,4]oxathian-3-ylidene)acetate (7i). In a manner similar to that described for **7a**, **4i** (50.0 mg, 0.154 mmol) was converted into **7i** (13.3 mg, 35%) as a pale yellow oil. ^{1}H NMR δ: 1.23–1.42 (m, 3H, H-7, H-8), 1.50–1.59 (m, 1H, H-5), 1.82–1.91 (m, 2H, H-6), 2.10–2.15 (m, 1H, H-8), 2.50–2.55 (m, 1H, H-5), 2.77 (ddd, *J*=12.8, 10.4, 4.3 Hz, 1H, H-4a), 3.46 (td, *J*=10.4, 4.9 Hz, 1H, H-8a), 3.79 (s, 3H, OCH_3), 3.94 (d, *J*=14.0 Hz, 1H, H-2), 5.86 (d, *J*=14.0 Hz, 1H, H-2), 6.53 (s, 1H,

C=CH). ^{13}C NMR (125 MHz) □: 23.8, 24.4, 26.8, 31.9, 52.0, 63.3, 72.0, 77.1, 118.2, 158.3, 164.2. IR 1722 (C=□), 1647 (C=C), 1087 (S=O). MS (FAB): 254 (MH^+). HRMS (FAB) Calcd for $C_{11}H_{17}O_4S$ (MH^+): 245.0847. Found: 245.0824.

Methyl (*E*)-2-(1-Oxothian-2-ylidene)-4-pentenoate (8a). Et_2Zn (1.00 M in hexane) (0.26 mL, 0.26 mmol) in THF (1.30 mL) was added slowly to a mixture of **4b** (35.0 mg, 0.130 mmol) and $Pd_2(dba)_3$•$CHCl_3$ (2.7 mg, 0.00261 mmol) in THF (1.30 mL) with stirring at –78 °C. The stirring was continued at rt for 5 h. A mixture of CuCN (117 mg, 0.130 mmol) and LiCl (11.1 mg, 0.261 mmol) was dried at 140 °C for 2 h under reduced pressure, and dissolved in THF (0.13 mL). The THF solution of CuCN•2LiCl was added to the above-mentioned reaction mixture. After 10 min, allyl bromide (34 □L, 0.391 mmol) was added to the mixture. The whole was stirred at 0 °C for 30 min. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:1) to give **8a** (26.8 mg, 90%) as a colorless oil. ^{1}H NMR □: 1.64 (dtt, *J*=13.7, 12.8, 3.7 Hz, 1H, H-4'), 1.76–1.80 (m, 1H, H-5'), 1.95–2.00 (m, 1H, H-4'), 2.44–2.59 (m, 2H, H-5', H-6'), 2.78 (dt, *J*=13.7, 3.7 Hz, 1H, H-3'), 2.99 (td, *J*=13.7, 3.7 Hz, 1H, H-3'), 3.14–3.17 (m, 1H, H-6'), 3.34 (dd, *J*=15.9, 6.1 Hz, 1H, C$\underline{H}_2$CH=CH_2), 3.47 (dd, *J*=15.3, 6.7 Hz, 1H, C$\underline{H}_2$CH=CH_2), 3.79 (s, 3H, OCH_3), 5.03–5.10 (m, 2H, CH=C$\underline{H}_2$), 5.72–5.81 (m, 1H, C$\underline{H}$=CH_2). ^{13}C NMR (125 MHz) □: 16.0, 23.1, 27.8, 34.0, 50.5, 52.2, 117.0, 132.4, 134.0, 150.4, 167.2. IR 1724 (C=O), 1637 (C=C), 1088 (S=O). MS (EI) *m/z* (%): 228 (M^+, 1.3), 179 (100). HRMS (EI) Calcd for $C_{11}H_{16}O_3S$ (M^+): 228.0820. Found: 228.0820.

Methyl (*E*)-3-Oxo-2-(1-oxothian-2-ylidene)-3-penylpropionate (8b). In a manner similar to that described for **8a** but with the addition of benzoyl chloride (32 □L, 0.293 mmol), **4b** (26.2 mg, 0.0976 mmol) was converted into **8b** (6.7 mg, 31%) as a colorless oil. ^{1}H NMR □: 1.74–1.85 (m, 2H, H-4', H-5'), 2.04–2.11 (m, 1H, H-4'), 2.47–2.57 (m, 1H, H-5'), 2.74–2.81 (m, 1H, H-6'), 3.06–3.12 (m, 1H, H-3'), 3.22–3.29 (m, 1H, H-3'), 3.31–3.37 (m, 1H, H-6'), 3.71 (s, 3H, OCH_3), 7.50 (dd, *J*=7.9, 7.3 Hz, 2H, Ar-H), 7.62 (t, *J*=7.3 Hz, 1H, Ar-H), 7.92 (d, *J*=7.9 Hz, 2H, Ar-H). ^{13}C NMR (75 MHz) □: 16.7, 22.3, 28.4, 51.5, 52.7, 129.0 (2C), 129.3 (2C), 131.8, 134.3, 135.8, 162.0, 163.2, 191.5. IR 1728 (C=□), 1672 (C=C), 1063 (S=O). MS (FAB): 293 (MH^+). HRMS (FAB) Calcd for $C_{15}H_{17}O_4S$ (MH^+): 293.0847. Found: 293.0856.

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11. The sulfoxide (**4i**) was a 6:4 diastereomeric mixture on the sulfur stereogenic center.
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13. Compound (**7i**) was a single diastereomer (racemic) although the relative configuration of the sulfoxide was not determined.
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16. The geometry of the *N*,*N*-dimethylamide (**7e**) and the □-sulfinyl □,□-unsaturated methyl esters except for **7i** and **8b** was determined by NOE experiments. The NOE was registered on the methyl group, and was not observed on the vinylic proton or the allyl group for **8a** by irradiating one of the allylic proton on the ring. The geometry of other vinylic sulfoxides was deduced from the results.