Workup as with **3** gave a brown oil, which crystallized after being subjected to high vacuum for 12 h. The material was washed with Et_2O, EtOAc, CH_2Cl_2, $CHCl_3$, and H_2O to yield **13** (0.65 g, 57% yield) as white crystals: mp 162 °C; ^1H NMR (CD_3SOCD_3) major tautomer (keto form) δ 3.78, 3.80, 7.00 (br), 7.24–7.98; ^{13}C NMR (CD_3SOCD_3) tautomeric mixture δ 48.8, 56.0, 92.1, 126.9, 127.8, 129.5, 131.5, 131.6, 132.5, 133.2, 134.9, 135.3, 137.0, 168.2, 172.1, 174.1, 197.5; IR (KBr) 3450, 3200, 1720, 1700, 1670, 1640, 1600, 1565, 1385, 1280, 1250, 1170, 1000, 980, 740, 670 cm^{-1}; MS, *m/e* (relative intensity) 221 (M^+, not observed), 203 (51), 186 (19), 160 (34), 149 (16), 135 (20), 119 (24), 118 (100), 90 (69), 77 (33). Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.71; H, 5.01; N, 6.13. Found: C, 59.52; H, 5.20; N, 6.13.

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Registry No. **2**, 89462-29-3; **3**, 79-05-0; **4**, 628-02-4; **5**, 102-93-2; **6**, 705-59-9; **7**, 52042-99-6; **8**, 3446-58-0; **9**, 87318-70-5; **10**, 89462-30-6; **11**, 89462-31-7; **12**, 89462-32-8; **13**, 89462-33-9; $CH_3CONHSiMe_3$, 13435-12-6; CH_3I, 74-88-4; *n*-BuBr, 109-65-9; $C_6H_5CH_2Cl$, 100-44-7; C_6H_5CHO, 100-52-7; $C_6H_5COC_6H_5$, 119-61-9; $C_6H_5COOCH_3$, 93-58-3; *N*-methoxy-*N*-methylbenzamide, 6919-61-5; ethyl 3-hydroxy-3-phenyl-2-propenoate sodium salt, 39113-53-6; ethyl benzoylacetate, 94-02-0; methyl 2-(methoxycarbonyl)phenylacetate, 716-43-8; 2-(methoxycarbonyl)phenylacetic acid, 14736-49-3.

Ring-Opening Reactions. 20. Synthesis of Polyunsaturated Vinyl Sulfides

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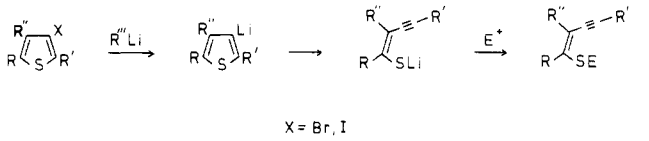
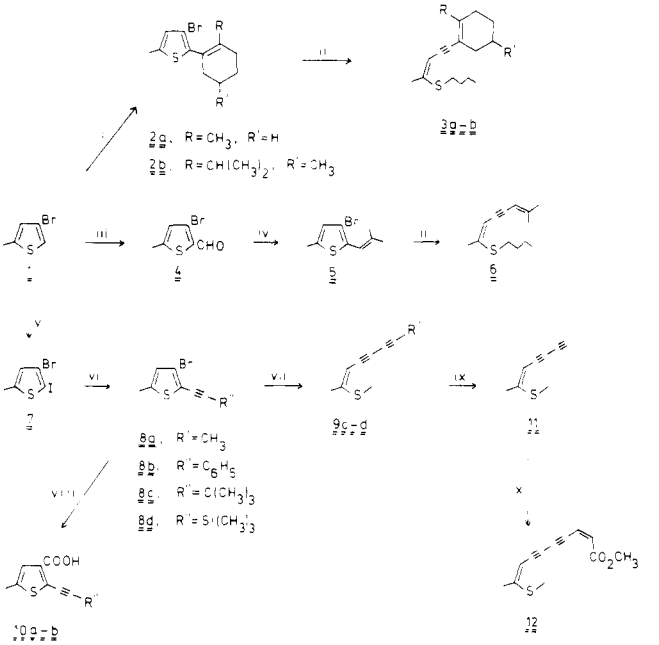
The ring-opening reaction of 3-thienyllithium derivatives constitutes a regio- and stereospecific synthesis of acetylenic vinyl sulfides (Scheme I). This kind of substance has attracted increased attention due to the possibilities presented to replace an alkyl- or arylthio group with carbon–carbon bonds.[1,2] Furthermore, the facile oxidation of sulfur to the corresponding sulfoxides and sulfones with *m*-chloroperbenzoic acid[3] presents an additional possibility of replacing the sulfur with carbon substituents.[4] This ring-opening reaction has recently been used for the total synthesis of naturally occurring substances from the plant genus *Anthemis*.[5] The scope and limitations of the reaction have been investigated rather extensively in our laboratories and have been reviewed.[6–10] It has been found that different substituents in the 2-position of the thiophene ring have more important effects on the rate of

Scheme I



Scheme II[a]



[a] (i) LDA, then 2-methylcyclohexanone or (–)-menthone, then *p*-TsOH, toluene, reflux; (ii) BuLi, 25 °C; BuBr; (iii) ref 13; (iv) $(CH_3)_2C{=}PPh_3$, THF; (v) I_2, HIO_3; (vi) RC≡CZnCl, $Pd(OAc)_2$, PPh_3; (vii) BuLi, 25 °C, MeI; (viii) BuLi, 0 °C, CO_2(s); (ix) KF·$2H_2O$, DMF; (x) (*Z*)-$BrCH{=}CHCO_2CH_3$, $Pd(OAc)_2$, PPh_3.

ring opening than 5-substituents. The rate is decreased by –I substituents in the 2-position or the reaction can be completely inhibited, whereas +I substituents have the opposite effect.

The effects of vinylic and acetylenic substituents have been investigated only very briefly. 2,5-Dimethyl-4-cyclohexenyl-3-thienyllithium derivatives with different cyclohexenyl substituents in the 4-position[11] ring-opened smoothly to give cross-conjugated polyunsaturated vinyl sulfides. Likewise, 5-(1-propynyl)-2-(trimethylsilyl)-3-thienyllithium underwent ring-opening to produce an enediynic sulfide.[5]

As pointed out earlier a more profound effect could be envisaged by introducing vinylic and acetylenic substituents in the 2-position. This would give a further possibility of making highly conjugated vinyl sulfides. A ring-opening would be expected to occur in view of the only very weak –I effect of these substituents. We now report our results on this matter.

Results and Discussion

The syntheses of the vinyl- and ethynylthiophenes are shown in Scheme II. 4-Bromo-2-methylthiophene (**1**)[12] was used as a common starting material.

The 2-cyclohexenylthiophenes **2** were obtained after metalation of **1** and reaction with 2-methylcyclohexanone and (–)-menthone, followed by dehydration. The iso-

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Table I. Results of the Ring-Opening Reactions

starting material	product	yield, %
2a	3a	49
2b	3b	66
5	6	66
8a	9a	
8b	9b	
8c	9c	56
8d	9d	52

butenylthiophene **5** was made via a Wittig reaction, starting from the aldehyde **4**,[13] and the ethynylthiophenes **8** were obtained by palladium-catalyzed coupling reactions between the iodothiophene **7** and the appropriate ethynylzinc chlorides.[14] In the case of the trimethylsilyl derivative **8d** an alternative method was tested, i.e., the palladium-catalyzed coupling of (trimethylsilyl)acetylene itself with **7**.[15] However, this method required a greater excess of (trimethylsilyl)acetylene to go to completion.

The synthesis of the vinyl sulfides **3**, **6**, and **9** involved the treatment of **2**, **5**, and **8**, respectively, with butyllithium to give a halogen–metal exchange. The initially formed 3-thienyllithium derivatives then spontaneously opened, and the resulting thiolates were trapped by an excess of either butyl bromide or methyl iodide. The yields were good and are shown in Table I. The menthenyl derivative is interesting in view of the possibility of introducing optical activity into these compounds. However, the propynyl and phenylethynyl derivatives **8a** and **8b** gave no traces of ring-opened substances. In contrast, the *tert*-butyl- and (trimethylsilyl)ethynyl derivatives **8c** and **8d** led to good yields of the thioendiynes **9c** and **9d**.

The ^{13}C NMR spectra of **9c** and **9d** exhibited the expected pattern,[9] with four acetylenic signals in the region 64–94 ppm, the monosubstituted vinylic carbons (3-C) at 101–102 ppm, and the sulfur-substituted ones (2-C) at 151–154 ppm.

The reaction mixtures were poured onto solid carbon dioxide soon after the addition of butyllithium at 0 °C to make certain that the halogen–metal exchange occurred in the cases of **8a** and **8b**. The formation of the corresponding thiophene carboxylic acids **10** in 60% yield verified the existence of the intermediate lithium derivatives. Similar experiments after stirring the reaction mixture at room temperature for 1.5 h gave only traces of acids. Obviously, the thienyllithium derivatives, once formed, decompose. It is plausible that they ring-open to give thiolates, which react further.

Comparison of **8a** and **8b** with **8c** and **8d** makes it probable that substance **9d** is of particular interst, since it allows further functionalization. Desilylation was achieved with potassium fluoride in DMF,[16] giving an unstable terminal acetylene **11**. A palladium-catalyzed coupling of **11** with (*Z*)-methyl-3-bromoacrylate according to Heck et al.[17] was attempted in order to obtain **12**. This compound was prepared by Bohlmann et al.[18] as cis–trans isomers of naturally occurring compounds from the genus *Anthemis*. The result of our syntheses was a low yield (ca. 5%) of **12**, as determined by its ^1H NMR spectrum. Nevertheless, **9d** should be an interesting intermediate, lending itself to further useful elaborations.

In conclusion, the work presented here clearly shows the potential of the ring-opening reaction of suitably substituted 3-thienyllithium derivatives for the construction of highly unsaturated thioenynic structures in a regio- and stereospecific manner.

Experimental Section

GLC analyses were performed on a Varian 3700 gas chromatograph. ^1H NMR spectra were recorded with JEOL FX 60 and MH 100 NMR spectrometers, IR spectra with a Perkin-Elmer 298 infrared spectrometer, and mass spectra with a Finnigan mass spectrometer.

All reactions with organometallic reagents were performed in ether freshly distilled over sodium wire under a nitrogen atmosphere. Melting points are uncorrected.

3-Bromo-5-methyl-2-(2-methyl-1-cyclohexenyl)thiophene (2a). Butyllithium (16 mL, 1.5 M, 24 mmol) in hexane was added to a solution of diisopropylamine (2.4 g, 24 mmol) in 50 mL of ether. After 10 min, 3.5 g (20 mmol) of 4-bromo-2-methylthiophene[12] dissolved in 100 mL of ether was added. The mixture was stirred for 45 min at room temperature, and 2-methylcyclohexanone (2.2 g, 20 mmol) dissolved in 20 mL of ether was then added. The solution was stirred for 3 h and then hydrolyzed with 5 M hydrochloric acid. The organic phase was separated, washed with water, dried ($MgSO_4$), and evaporated. The remaining liquid was refluxed for 1.5 h with 0.5 g of *p*-toluenesulfonic acid in toluene in a flask provided with a water separator. The mixture was diluted with water. The organic phase was washed with water, aqueous sodium bicarbonate, and water. After drying ($MgSO_4$) and evaporation, the liquid was chromatographed (silica, hexane): yield 3.6 g (67%); ^1H NMR ($CDCl_3$) δ 1.6 (s, 3 H, 2-CH_3, cyclohexene), 2.1 (m, 8 H, aliphatic), 2.4 (d, J = 1.1 Hz, 3 H, 2-CH_3), 6.6 (q, J = 1.1 Hz, 1 H, 3-H). Anal. Calcd for $C_{12}H_{15}BrS$: C, 53.1; H, 5.6. Found: C, 53.1; H, 5.6.

3-Bromo-5-methyl-2-(1-menthenyl)thiophene (2b) was prepared in the same way as **2a** from 1.1 g (40 mmol) of 2-methyl-4-bromothiophene[12] in 50 mL of dry ether, 32 mL (48 mmol) of 1.5 M butyllithium, 4.8 g (48 mmol) of diisopropylamine in 10 mL of dry ether, and 6.2 g (40 mmol) of (−)-menthone in 15 mL of dry ether: yield 5.5 g (44%); ^1H NMR ($CDCl_3$) δ 0.91 (m, 9 H, isopropyl + methyl), 1.6–2.0 (m, 8 H, aliphatic), 2.4 (d, J = 1.1 Hz, 3 H, 2-CH_3), 6.6 (q, J = 1.1 Hz, 1 H, 3-H). Anal. Calcd for $C_{15}H_{21}BrS$: C, 57.5; H, 6.76. Found: C, 57.1; H, 6.81.

3-Bromo-5-methyl-2-(2-methyl-1-propenyl)thiophene (5). Butyllithium in hexane (7.0 mL, 1.5 M, 10 mmol) was added to 4.3 g (10 mmol) of isopropyltriphenylphosphonium iodide dissolved in 100 mL of THF. After 15 min, 2.1 g (10 mmol) of 3-bromo-2-formyl-5-methylthiophene (**4**)[13] dissolved in 50 mL of THF was added. The solution was stirred for 1 h and then poured onto ice water and acidified with 5 N hydrochloric acid. The mixture was extracted with ether and the organic phase was washed with aqueous sodium bicarbonate and water. After drying ($MgSO_4$) and evaporation, the remaining liquid was chromatographed (silica, hexane), yielding 1.4 g (61 %) of the title compound: ^1H NMR ($CDCl_3$) δ 1.95 (2 br s, 6 H, $=C(CH_3)_2$, 2.45 (d, J = 1.1 Hz, 3 H, 5-CH_3), 6.35 (br s, 1 H, CH=C), 6.66 (q, J = 1.1 Hz, 1 H, 4-H). Anal. Calcd for $C_9H_{11}BrS$: C, 46.8; H, 4.80. Found; C, 47.3; H, 4.81.

(*Z*)-2-(Butylthio)-5-(2-methyl-1-cyclohexenyl)-2-penten-4-yne (3a). Butyllithium (2.6 mL, 1.5 M, 3.9 mmol) in hexane was added to 1.0 g (3.7 mmol) of **2a** in 20 mL of anhydrous ether at room temperature. After 1 h, excess butyl bromide (14 mmol) was added and the stirring was continued overnight. The reaction mixture was poured into water and the aqueous phase was extracted several times with ether. The combined organic phases were wased with water, dried ($MgSO_4$), and evaporated to give an oil. Chromatography (silica, hexane) was used for isolation of the title compound: yield, 0.45 g (49%); IR 2175 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.0–1.5 (m, 8 H, aliphatic), 1.59 (s, 3 H, cyclohexene CH_3), 1.92 (m, 4 H, allylic), 2.08 (d, J = 1.4 Hz, 3 H, 1-CH_3), 2.82 (t, J = 7 Hz, 2 H, SCH_2), 5.59 (q, J = 1.4 Hz, 1 H, 3-H). Anal. Calcd for $C_{16}H_{24}S$: C, 77.3; H, 9.7; S, 12.9. Found: C, 77.2; H, 9.8; S, 12.7.

(*Z*)-2-(Butylthio)-5-(1-menthenyl)-2-penten-4-yne (3b) was prepared in the same way as **3a** from 1.56 g (5.0 mmol) of **2b** in

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10 mL of dry ether, 3.7 mL (5.5 mmol) of 1.5 M butyllithium, and 3.0 g (22 mmol) of butyl bromide: yield 0.95 g (66%); IR 2175 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.0 (m, 9 H, isopropyl + methyl), 1.3-1.8 (m, 12 H, aliphatic), 2.10 (d, J = 1.4 Hz, 3 H, 1-CH_3), 2.82 (t, J = 7 Hz, 2 H, SCH_2), 5.60 (d, J = 1.4 Hz, 1 H, 3-H). Anal. Calcd for $C_{19}H_{30}S$: C, 78.6; H, 10.4; S, 11.0. Found: C, 78.4; H, 10.2; S, 11.0.

(*Z*)-2-(Butylthio)-7-methyl-2,6-octadien-4-yne (6). Butyllithium in hexane (3.1 mL, 1.5 M, 4.7 mmol) was added to 1.0 g (4.3 mmol) of 5 dissolved in 50 mL of ether. After 2 h, 2.0 g (14 mmol) of butyl bromide was added and the solution was stirred for 4 h. The reaction mixture was poured into water and the aqueous phase was extracted several times with ether. The combined organic phases were washed with water, dried ($MgSO_4$), and evaporated to give an oil. Chromatography (silica, hexane and then hexane–ethyl acetate (75:25)) was used for isolation of the title compound: yield 0.60 g (66%), IR 2180 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.1–1.7 (m, 4 H, aliphatic), 1.81 (br s, 3 H, CH_3), 1.94 (br s, 3 H, CH_3), 2.08 (d, J = 1.6 Hz, 3 H, 1-CH_3), 2.80 (t, J = 7 Hz, 2 H, S-CH_2), 5.62 (m, 1 H, 3-H), 5.74 (m, 1 H, 6-H). Anal. Calcd for $C_{13}H_{20}S$: C, 74.9; H, 9.68. Found: C, 75.0; H, 9.71.

3-Bromo-2-iodo-5-methylthiophene (7). A mixture of 35.4 g (0.200 mol) of 4-bromo-2-methylthiophene,[12] 23 g (0.090 mol) of iodine, 7.9 g (0.045 mol) of iodic acid, 64 mL of acetic acid, 64 mL of water, 16 mL of CCl_4, and 1.1 mL of concentrated H_2SO_4 was stirred vigorously at 40 °C for 2 h. The reaction mixture was poured into aqueous sodium thiosulfate and extracted with ether. The combined ethereal portions were washed with aqueous sodium bicarbonate and water, dried ($MgSO_4$), and evaporated. Distillation gave 45.4 g (75 %) of the title compound: bp 124–126 °C (8 mm); ^1H NMR ($CDCl_3$) δ 2.43 (d, J = 1.1 Hz, 3 H, CH_3), 6.55 (q, J = 1.1 Hz, 1 H, 4-H). Anal. Calcd for C_5H_4BrIS: C, 19.8; H, 1.33; S, 10.6. Found: C, 19.9; H, 1.29; S, 10.5.

General Procedure for the Preparation of the 3-Bromo-2-ethynyl-5-methylthiophenes 8. The method described by King and Negishi[14] was used throughout. 3-Bromo-2-iodo-5-methylthiophene (7) was coupled under palladium catalysis with the appropriate enthynylzinc chloride.

3-Bromo-5-methyl-2-(1-propynyl)thiophene (8a) was prepared from 10 g (0.029 mol) of 7 and propynylzinc chloride, prepared from 2.0 g (0.044 mol) of propynyllithium (Alfa Corp.) and 6.0 g (0.044 mol) of dry zinc chloride: reaction time 3 h; yield 9.6 g (68%); bp 120–122 °C (8 mm); IR (film) 2230 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 2.05 (s, 3 H, CH_3, propargylic), 2.35 (d, J = 1.2 Hz, 3 H, 5-CH_3), 6.55 (q, J = 1.2 Hz, 1 H, 4-H). Anal. Calcd for C_8H_7BrS: C, 44.7; H, 3.28. Found: C, 44.7; H, 3.26.

3-Bromo-5-methyl-2-(phenylethynyl)thiophene (8b) was prepared from 7.0 g (0.023 mol) of 7 and (phenylethynyl)zinc chloride, prepared from 2.9 g (0.029 mol) of phenylacetylene, 21 mL (0.032 mol) of 1.52 M BuLi in hexane, and 4.0 g (0.029 mol) of dry zinc chloride: reaction time 20 h; yield 4.5 g (70%); bp 140–144 °C (0.02 mm); IR (film) 2200 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 2.39 (d, J = 1.1 Hz, 3 H, 5-CH_3), 6.61 (q, J = 1.1 Hz, 1 H, 4-H), 7.0-7.2 (m, 5 H, Ar). Anal. Calcd for $C_{13}H_9BrS$: C, 56.3; H, 3.27. Found: C, 56.5; H, 3.35.

3-Bromo-2-(*tert*-butylethynyl)-5-methylthiophene (8c) was prepared from 7.0 g (0.023 mol) of 7 and (*tert*-butylethynyl)zinc chloride, prepared from 2.4 g (0.029 mol) of *tert*-butylacetylene, 22 mL (0.032 mol) of 1.45 M BuLi in hexane, and 4.0 g (0.029 mol) of dry zinc chloride: reaction time 24 h; yield 4.3 g (72%); bp 119–121 °C (8 mm); IR (film) 2205 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 1.30 (s, 9 H, *tert*-butyl), 2.40 (d, J = 1.1 Hz, 3 H, 5-CH_3), 6.58 (q, J = 1.1 Hz, 1 H, 4-H). Anal. Calcd for $C_{11}H_{13}BrS$: C, 51.4; H, 5.09. Found: C, 51.3; H, 5.14.

3-Bromo-5-methyl-2-[(trimethylsilyl)ethynyl]thiophene (8d) was prepared from 18.2 g (0.060 mol) of 7 and [(trimethylsilyl)ethynyl]zinc chloride, prepared from 7.4 g (0.075 mol) of (trimethylsilyl)acetylene, 58 mL (0.083 mol) of 1.41 M BuLi in hexane, and 10.2 g (0.075 mol) of dry zinc chloride; reaction time 24 h. Careful distillation to remove some remaining 7 yielded 9.3 g (57%) of the title compound; bp 135–139 °C (10 mm); IR 2140 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 0.25 (s, 9 H, $Si(CH_3)_3$), 2.40 (d, J = 1.1 Hz, 3 H, 5-CH_3), 6.50 (q, J = 1.1 Hz, 1 H, 4-H). Anal. Calcd for $C_{10}H_{13}BrSSi$: C, 43.9; H, 4.79; S, 11.7. Found: C, 43.8; H, 4.87; S, 11.6.

(*Z*)-8,8-Dimethyl-2-(methylthio)-2-nonene-4,6-diyne (9c). To a solution of 1.0 g (3.9 mmol) of **8c** in 40 mL of dry ether under a nitrogen atmosphere was added 30 mL (4.3 mmol) of 1.45 M BuLi in hexane. After 2 h, 2.8 g (20 mmol) of methyl iodide was added, and the reaction mixture was allowed to stand for 2 h. An aqueous workup yielded a crude product, which was purified by column chromatography (silica, hexane–ethyl acetate (95:5)) to give an oil: yield 0.42 g (56%); IR (film) 2130, 2220 cm^{-1} (C≡CC≡C); ^1H NMR ($CDCl_3$) δ 1.22 (s, 9 H, $C(CH_3)_3$), 2.08 (d, J = 1.5 Hz, 3 H, 1-CH_3), 2.37 (s, 3 H, SCH_3), 5.41 (q, J = 1.5 Hz, 3-H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.4, 28.3, 30.5, 64.0, 73.0, 80.4, 93.4, 102.0, 151.4. Anal. Calcd for $C_{12}H_{16}S$: C, 74.9; H, 8.39. Found: C, 74.8; H, 8.37.

(*Z*)-2-(Methylthio)-7-(trimethylsilyl)hept-2-ene-4,6-diyne (9d) was prepared in the same way as the previous compound from 2.0 g (7.3 mmol) of **8d**, 5.7 mL (8.1 mmol) of 1.41 M BuLi in hexane, and 4.5 g (32 mmol) of methyl iodide in 50 mL of dry ether. Column chromatography (silica, hexane) yielded 0.80 g (52 %) of an oil; IR (film) 2080, 2180 cm^{-1} (C≡CC≡C); ^1H NMR ($CDCl_3$) δ 0.32 (s, 9 H, $Si(CH_3)_3$), 2.19 (d, J = 1.4 Hz, 3 H, 1-CH_3), 2.48 (s, 3 H, SCH_3), 5.48 (q, J = 1.4 Hz, 1 H, 3-H); ^{13}C NMR ($CDCl_3$) δ −0.3, 14.2, 22.6, 73.9, 80.4, 88.1, 91.9, 101.2, 153.8. Anal. Calcd for $C_{11}H_{16}SSi$: C, 63.4; H, 7.74. Found: C, 63.4; H, 7.69.

5-Methyl-2-(1-propynyl)-3-thiophenecarboxylic Acid (10a). To a solution of 1.0 g (4.7 mmol) of **8a** in 50 mL of dry ether under a nitrogen atmosphere at 0 °C was added 3.4 mL (5.1 mmol) of 1.52 M BuLi in hexane. After 15 min, the mixture was poured onto crushed solid carbon dioxide. After workup and recrystallization from aqueous ethanol, 0.50 g (60 %) of the title compound was obtained: mp 128–129 °C; IR (KBr) typical carboxylic acid, 1675 cm^{-1} (C=O), 2220 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 2.14 (s, 3 H, CH_3, propargylic), 2.40 (d, J = 1.0 Hz, 3 H, 5-CH_3), 7.09 (q, J = 1.0 Hz, 1 H, 4-H), 9.10 (br s, 1 H, COOH). Anal. Calcd for $C_9H_8O_2S$: C, 60.0, H, 4.47. Found: C, 60.0; H, 4.50.

5-Methyl-2-(phenylethynyl)-3-thiophenecarboxylic acid (10b) was made in the same way as the previous compound, from 1.0 g (3.6 mmol) of **8b**: yield 0.52 g (60%); mp 153–155 °C; IR (KBr) typical carboxylic acid, 1670 cm^{-1} (C=O), 2200 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 2.46 (d, J = 1.0 Hz, 3 H, 5-CH_3), 7.17 (q, J = 1.0 Hz, 1 H, 4-H), 7.2–7.4 (m, 5 H, Ar). Anal. Calcd for $C_{14}H_{10}O_2S$: C, 69.4; H, 4.16. Found: C, 69.5; H, 4.20.

(*Z*)-2-(Methylthio)-2-heptene-4,6-diyne (11). A sample of 0.31 g (1.5 mmol) of **9d** was stirred overnight with 0.27 g (3.0 mmol) of potassium fluoride dihydrate in 10 mL of dimethylformamide according to ref 16. The mixture was poured onto ice–water and extracted with ether. The organic phase was washed with water, dried ($MgSO_4$ plus carbon black), and evaporated to give 0.18 g (90 %) of crude **11**: IR (film) 3280 cm^{-1} (C≡CH), 2180 and 2200 cm^{-1} (C≡CC≡C); ^1H NMR ($CDCl_3$) δ 2.07 (d, J = 1.4 Hz, 3 H, 1-CH_3), 2.39 (s, 3 H, S-CH_3), 2.57 (d, J = 1 Hz, 1 H, 7-H), 5.39 (m, 1 H, 3-H). The crude product was used without further purification due to its instability.

Methyl (1*Z*,7*Z*)-8-(Methylthio)-1,7-nonadiene-3,5-diynecarboxylate (12).[18] A solution of 0.60 g (4.4 mmol) of 11, 0.73 g (4.4 mmol) of (*Z*)-methyl-3-bromoacrylate,[17] 8 mg of palladium acetate, and 20 mg of triphenylphosphine in 5 mL of triethylamine was stirred for 24 h under an argon atmosphere. An aqueous workup and chromatography on silica–hexane/ethyl acetate (85:15) gave 50 mg (5%) of the title compound. The ^1H NMR spectrum was in good agreement with the published data.[18]

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Registry No. **2a**, 89556-02-5; **2b**, 89556-03-6; **3a**, 89556-05-8; **3b**, 89556-06-9; **4**, 36155-82-5; **5**, 89556-04-7; **6**, 89556-07-0; **7**, 89556-08-1; **8a**, 89556-10-5; **8b**, 89556-11-6; **8c**, 89556-12-7; **8d**, 89556-13-8; **9c**, 89556-14-9; **9d**, 89556-15-0; **10a**, 89556-16-1; **10b**, 89556-17-2; **11**, 89556-18-3; **12**, 2258-50-6; 4-bromo-2-methylthiophene, 29421-92-9; 2-methylcyclohexanone, 583-60-8; (−)-menthone, 14073-97-3; isopropyltriphenylphosphonium iodide, 24470-78-8; propynylzinc chloride, 64146-56-1; (phenylethynyl)zinc chloride, 13984-49-1; (*tert*-butylethynyl)zinc chloride, 89556-09-2; [(trimethylsilyl)ethynyl]zinc chloride, 78389-87-4; methyl (*Z*)-3-bromoacrylate, 6214-22-8.