Umpolung of Carbon−Sulfur Bonds. Novel Synthesis of Substituted Allenes from Propargylic Dithioacetals

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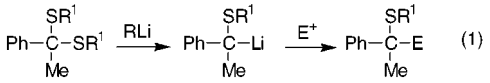
Received June 28, 1999

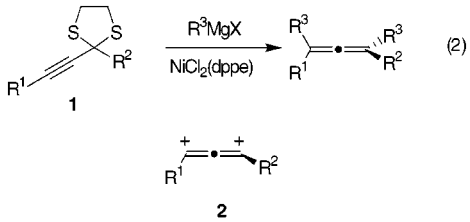
Umpolung of the carbon−sulfur bonds can be achieved by treatment of propargylic dithioacetals **1** with organocuprates. The organocopper intermediates **3** gave the corresponding allenyl thioethers **4** upon protonolysis. When alkyl halides were used, propargylic thioethers **5** were obtained exclusively. Transmetalation of organocopper intermediates **3** with $ZnBr_2$ followed by $Pd(PPh_3)_4$-catalyzed coupling with vinylic or aryl halides afforded the corresponding allenyl thioethers **4**. Either **4** or **5** reacted with Grignard reagents in the presence of $NiCl_2$(dppf) to yield the corresponding allenes **9** or **10**, respectively. The overall reaction can be considered to use **1** as allene-1,3-zwitterion synthons. The relative reactivities of a propargylic ether versus a propargylic dithioacetal toward an organocopper reagent were compared. The sulfur moiety apparently has higher reactivity toward the copper reagent.

Carbon and sulfur have similar electronegativities; therefore, the carbon−sulfur bond is ambiphilic. Accordingly, the carbon end of a thioether linkage can serve either as an electrophilic center or as a carbanionic leaving group (Scheme 1). Numerous reactions are known to employ the sulfide leaving group in organic synthesis. For example, the conversion of a carbon−sulfur bond to a carbon−carbon bond can be achieved by the nickel-catalyzed cross coupling reactions of organosulfur compounds with Grignard reagents.[1−3] Umpolung of a carbon−sulfur bond to generate a carbanionic leaving group from the corresponding thioether is rare.[4] In general, a stabilized anionic species is essential for such heterolytic cleavage reaction. Desulfurization of an α-thioalkoxycarbonyl compound can be achieved upon treatment with a thioalkoxide anion.[4a] Benzylic dithioacetals react chemoselectively with organolithium reagents leading to the formation of the corresponding sulfur-stabilized carbanions (eq 1).[4b]



(1)

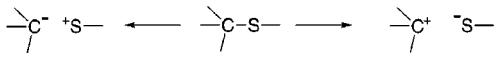
We recently disclosed that propargylic dithioacetal **1** can serve as an allene-1,3-dication synthon **2**. Thus, treatment of **1** with the Grignard reagent in the presence of a nickel catalyst (eq 2) results in replacing the two carbon−sulfur bonds by two carbon−carbon bonds.[2,5] The



(2)

reaction would be more versatile if the two carbon−sulfur bonds in **1** could be sequentially substituted by different moieties. It is well-documented that propargylic acetals

Scheme 1



react readily with organocopper reagents to give the corresponding allenyl ethers.[6] The extension of this reaction to sulfur analogues, however, has not been explored.[7] Copper is thiophilic, so the complexation of the organocopper reagent with the sulfur moiety might occur readily. As such, the transfer of an alkyl nucleophile from the organocopper reagent to the sulfur atom of the dithioacetal group might generate intermediate **3** (eq 3). Similar to that described in eq 1, this organometallic anionic species **3** is stabilized by the remaining thioether moiety and by the triple bond. As part of our continuing interest in the synthetic applications of the dithioacetal functionality, we herewith report an unprecedented organocopper-induced C−S bond cleavage reaction of propargylic dithioacetals followed by treatment with an electrophile leading to the corresponding thioethers **4** or **5**.[7]

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(3) For reviews, see: (a) Luh, T.-Y. *Acc. Chem. Res.* **1991**, *24*, 257. (b) Luh, T.-Y.; Leung, M.-K. In *Advances in the Use of Synthons in Organic Chemistry*; Dondoni, A., Ed.; JAI: London, **1995**; Vol 2, p 129. (c) Luh, T.-Y. *Pure Appl. Chem.* **1996**, *68*, 105.

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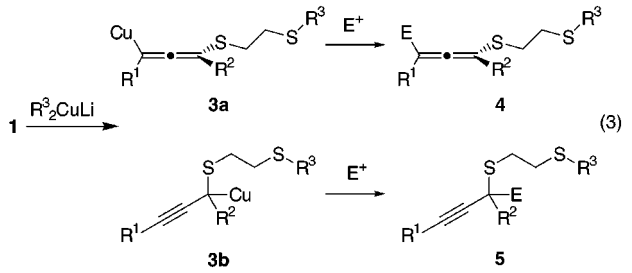
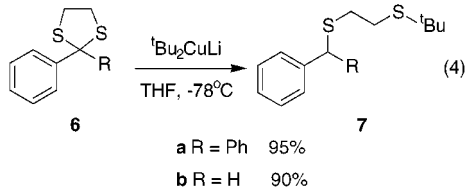
(7) Preliminary communication: Tseng, H.-R.; Luh, T.-Y. *J. Org. Chem.* **1997**, *62*, 4568.

10.1021/jo991032b CCC: $18.00
Published on Web 10/21/1999



Results and Discussion

In the beginning of this investigation, benzylic dithioacetals **6** were employed to test the reactivity toward organocopper reagents. Thus, each of **6a** and **6b** were allowed to react with 0.6 equiv of $^{t}Bu_2CuLi$ at −78 °C followed by quenching with methanol to give **7a** and **7b** in 95 and 90% yields, respectively (eq 4).



An extension of this procedure to the reaction of **1a** under the same conditions gave the corresponding allenyl thioether **4a** (entry 1, Table 1). Deuterium incorporation at allenyl carbon (C_3) was observed when the organocopper intermediate was quenched with D_2O (entry 2). As can be seen from Table 1, a variety of electrophiles ranging from proton (entries 1−4, 7−9), organosilyl (entry 5) and tin (entry 6) reagents can be used to furnish the reaction in good to excellent yields. Substituents in the starting **1** can vary from hydrogen, alkyl, to aryl groups.

The reaction may proceed via intermediate **3a**. It is well documented that there is an equilibrium between an allenyl organometallic intermediate **3a** and a propargylic species **3b**. The corresponding **5**, however, was not obtained when these electrophiles were used.

When a soft alkyl halide electrophile was employed to react with the organocopper intermediate **3**, selective carbon−carbon bond formation leading to a propargylic thioether **5** was observed. Typical examples are outlined in Table 2. It is noteworthy that neither **4** nor **5** reacted further with the organocopper reagent under these conditions. Interestingly, the protonolysis of the organocopper intermediate arisen from the reaction of **1f** with $^{t}Bu_2CuLi$ gave **5d**. The steric bulkiness of the trimethylsilyl substituent presumably determines the chemoselectivity of the reaction.

As can be seen in Table 2, the reaction proceeds successfully with carbon electrophiles having $C_{sp}3$ hybridization. The reaction would be more versatile if other carbon electrophiles could also be employed. Transmetalation of the organocopper intermediate with $ZnBr_2$ followed by the palladium-catalyzed coupling reaction gave the corresponding allenes **4** in good yield (eq 5). Typical examples are tabulated in Table 3. Attempts to synthesize the allyl-substituted allene by using allyl bromide as an electrophile yielded the rearranged triene (eq 6). Presumably, the allenyl double bond may migrate under the reaction conditions.

Table 1. Reaction of 1 with R^3_2CuLi Followed by Treatment with Selected Electrophile

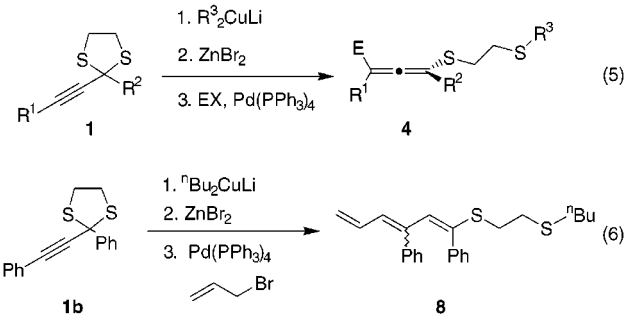
entry	substrate	R^1	R^2	R^3	E	X	product (%yield)
1	**1a**	Ph	Me	^{t}Bu	H	MeO	**4a** (88)
2				^{t}Bu	D	DO	**4b** (81)
3	**1b**	Ph	Ph	^{t}Bu	H	MeO	**4c** (95)
4				^{n}Bu	H	MeO	**4d** (93)
5				^{n}Bu	TMS	Cl	**4e** (94)
6				^{n}Bu	$^{n}Bu_3Sn$	Cl	**4f** (81)[a]
7	**1c**	^{n}Bu	Me	^{t}Bu	H	MeO	**4g** (82)
8	**1d**	H	Ph	^{n}Bu	H	MeO	**4h** (82)
9	**1e**	^{n}Bu	^{i}Pr	^{n}Bu	H	MeO	**4i** (73)

[a] Compound **4f** decomposes gradually upon standing and in $CDCl_3$ solution.

Table 2. Reaction of 1 with R^3_2CuLi Followed by Treatment with Alkyl Halide

entry	substrate	R^1	R^2	R^3	E	X	product (%yield)
10	**1a**	Ph	Me	^{t}Bu	Me	I	**5a** (81)
11				^{t}Bu	CH_2=$CHCH_2$	Br	**5b** (80)[a]
12	**1b**	Ph	Ph	^{n}Bu	^{n}Bu	Br	**5c** (89)
13	**1f**	TMS	Me	^{t}Bu	H	MeO	**5d** (94)

[a] Crude yield. The product was used for the next reaction.



As can be seen from Tables 1−3, a number of allenyl/propargylic thioethers **4**/**5** can be easily obtained from the reactions of **1** with organocopper reagents. Sequential treatment of these thioethers with the Grignard reagent in the presence of 5 mol % of $NiCl_2$(dppf) resulted in a convenient synthesis of substituted allenes **9** or **10** (eqs 7 and 8). Table 4 summarizes representative examples. As expected,[8] reduction of the C−S bond in **3c** was observed when *i*-PrMgBr was employed (entry 20). These results demonstrate the first examples of using propargylic dithioacetals as allene zwitterion synthons **12**.

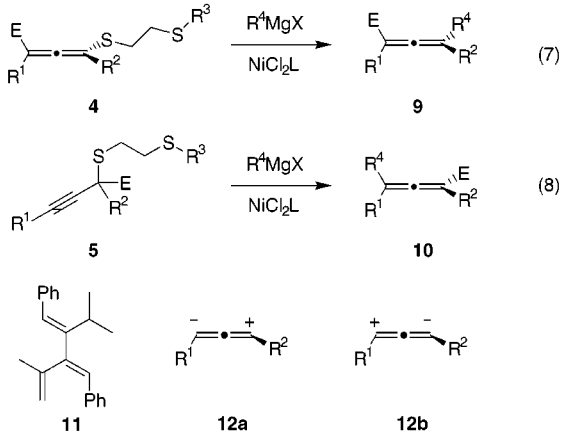


Table 3. Reaction of 1 with R^3_2CuLi Followed by Treatment with $ZnBr_2$ and Then Coupling with Electrophile under Pd Catalyst

entry	substrate	R^1	R^2	R^3	E	X	product (%yield)
14	**1b**	Ph	Ph	^{n}Bu	4-MeC_6H_4	I	**4j** (69)
15				^{n}Bu	^{t}BuCO	Cl	**4k** (65)[a]
16				^{n}Bu	PhC≡C	Br	**4l** (30)
17	**1c**	^{n}Bu	Me	^{n}Bu	4-MeC_6H_4	I	**4m** (78)[a]

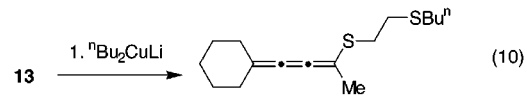
[a] Crude yield. The product was used directly for the next reaction.

When $NiCl_2$(dppe) was employed as the catalyst in the coupling reaction of **4a**, the corresponding dimeric product **11** was obtained in 52% yield (entry 25). The stereochemistry of **11** was determined by the NOE experiments. Dimerization of **9a** was also achieved in 59% yield upon treatment with MeMgI in the presence of $NiCl_2$(dppe).

It is known that propargylic ether can readily undergo an S_N2' reaction to give the corresponding allene.[6] It is highly intriguing to compare the reactivities of a propargylic ether versus a propargylic dithioacetal upon treatment with an organocopper reagent. Thus, **13** was synthesized (eq 9) and allowed to react with ^{n}Bu_2CuLi followed by the usual workup to give **15** in 91% yield (eq 10). Attempts to synthesize the higher cumulenes from **16** or **17** were unsuccessful and a mixture of unidentified products was obtained.

14 **13**

a ^{i}PrMgBr, then cyclohexanone; *b* MeLi, then MeI, DMSO.



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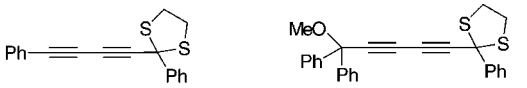

16 **17**

Conclusions

In summary, we have demonstrated for the first time the use of propargylic dithioacetals as allene-1,3-zwitterion synthons **12**. By employing this procedure, di-, and tri- as well as tetrasubstituted allenes are synthesized conveniently.

Experimental Section

Preparation of Cuprate Reagents. Under argon atmosphere, to a slurry of CuI (114 mg, 0.60 mmol) in THF (5 mL) at −78 °C was added a pentane solution of ^{t}BuLi (0.7 mL of 1.7 M solution, 1.2 mmol). The mixture was stirred at −78 °C for 15 min to give a THF/pentane solution of ^{t}Bu_2CuLi which was used directly for the next reaction. A THF/hexane solution of ^{n}Bu_2CuLi (5.7 mL, 0.6 mmol) was prepared similarly.

6,6-Dimethyl-1,1-diphenyl-2,5-dithiaheptane (7a). Under argon atmosphere, to a THF/pentane solution of ^{t}Bu_2CuLi (5.7 mL, 0.6 mmol) at −78 °C was added dropwise **6a** (258 mg, 1.0 mmol) in THF (5 mL) over a period of 10 min. The mixture was stirred at −78 °C for 30 min, quenched with methanol (0.3 mL), and passed through a short-path of neutral alumina. The solvent was removed in vacuo to give the residue which was chromatographed on silica gel (1% EtOAc in hexane) to afford **6a** as a colorless oil (301 mg, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 9 H), 2.56−2.69 (m, 4 H), 5.22 (s, 1 H), 7.21 (t, J = 7.2 Hz, 2 H), 7.30 (t, J = 7.2 Hz, 4 H), 7.43 (d, J = 7.2 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3, 30.9, 32.8, 42.5, 54.3, 127.2, 128.3, 128.5, 141.1; HRMS calcd for $C_{19}H_{24}S_2$: 316.1319, found: 316.1322.

6,6-Dimethyl-1-phenyl-2,5-dithiaheptane (7b). In a manner similar to that described for the reaction of **6a**, **6b** (182 mg, 1.00 mmol) was allowed to react with ^{t}Bu_2CuLi (5 mL, 0.6 mmol in THF/pentane) at −78 °C for 30 min to yield a colorless oil **7b** (163 mg, 90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 9 H), 2.55−2.68 (m, 4 H), 3.73 (s, 2 H), 7.20−7.32 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.4, 31.0, 31.7, 36.4, 42.5, 127.0, 128.5, 128.8, 138.2; HRMS calcd for $C_{13}H_{20}S_2$: 240.1006, found: 240.1017.

3,8,8-Trimethyl-1-phenyl-4,7-dithia-1,2-nonadiene (4a). In a manner similar to that described for the reaction of **6a**, ^{t}Bu_2CuLi (5.7 mL, 0.6 mmol in THF/pentane) was allowed to react with **1a** (220 mg, 1.0 mmol) in THF (5 mL) to give **4a** as a colorless oil (243 mg, 88%): bp 90 °C (0.05 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 9 H), 2.04 (d, J = 3.0 Hz, 3 H), 2.67−2.79 (m, 4 H), 6.36 (q, J = 3.0 Hz, 1 H), 7.15−7.30 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6, 28.4, 30.9, 32.8, 42.6, 99.7, 101.9, 127.0, 127.3, 128.6, 134.6, 198.4; IR (NaCl, neat) 1919 cm^{-1}; HRMS calcd for $C_{16}H_{22}S_2$: 278.1162, found: 278.1172.

A similar reaction of **1a** (220 mg, 1.00 mmol) with ^{t}Bu_2CuLi (5.0 mL, 0.6 mmol in THF/pentane) followed by quenching with D_2O (0.3 mL) to give **4b** as a colorless oil (226 mg, 81%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 9 H), 2.03 (s, 3 H), 2.67−2.79 (m, 4 H), 7.15−7.26 (m, 3 H), 7.28 (d, J = 4.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6, 28.4, 30.9, 32.8, 42.5, 99.5 (t, J = 24.3 Hz), 102.1, 127.0, 127.3, 128.6, 134.6, 198.3; HRMS calcd for $C_{16}H_{21}DS_2$: 279.1225, found: 279.1227.

8,8-Dimethyl-1,3-diphenyl-4,7-dithia-1,2-nonadiene (4c). In a manner similar to that described for the reaction of **6a**, ^{t}Bu_2CuLi (5.7 mL, 0.6 mmol in THF/pentane) at −78 °C was allowed to react with **1b** (282 mg, 1.00 mmol) in THF (5 mL) to give **4c** as a colorless oil (323 mg, 95%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.19 (s, 9 H), 2.70−2.95 (m, 4 H), 6.73 (s, 1 H), 7.21−7.39 (m, 8 H), 7.54−7.60 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.4, 30.9, 33.0, 42.6, 101.5, 108.2, 126.6, 127.3, 127.8, 128.1, 128.5, 128.9, 133.6, 134.2, 202.8; IR (NaCl, neat) 1948 cm^{-1}; HRMS calcd for $C_{16}H_{22}S_2$: 340.1319, found: 340.1320.

1,3-Diphenyl-4,7-dithia-1,2-undecadiene (4d). In a manner similar to that described for the reaction of **6a**, the reaction of **1b** (220 mg, 1.00 mmol) with ^{n}Bu_2CuLi (5.7 mL, 0.6 mmol in THF/hexane) gave **4d** as a colorless oil (316 mg, 93%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (t, J = 7.2 Hz, 3 H), 1.27 (sextet, J = 7.2 Hz, 2 H), 1.42 (quin, J = 7.2 Hz, 2 H), 2.27−2.43 (m, 2 H), 2.63−2.80 (m, 2 H), 2.91 (t, J = 7.2 Hz, 2 H), 6.73 (s, 1 H), 7.22−7.36 (m, 8 H), 7.54−7.57 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 21.0, 25.6, 31.7, 31.9, 32.8, 101.8, 108.3, 126.6, 127.2, 127.9, 128.2, 128.5, 128.9, 133.6, 134.2, 202.5; IR (NaCl, neat) 1949 cm^{-1}; HRMS calcd for $C_{16}H_{22}S_2$: 340.1319, found: 340.1319.

1-(Trimethylsilyl)-1,3-diphenyl-4,7-dithia-1,2-undecadiene (4e). In a manner similar to that described for the reaction of **6a**, the reaction of **1b** (282 mg, 1.0 mmol) with ^{n}Bu_2CuLi (5.7 mL, 0.6 mmol in THF/hexane) at −78 °C. The mixture was stirred at −78 °C for 1.5 h, chlorotrimethylsilane (0.2 mL, 1.5 mmol) was introduced, and the mixture was

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Table 4. $NiCl_2(L)$-Catalyzed Cross-Coupling Reactions of 4 or 5 with Grignard Reagents

entry	substrate	R^1	R^2	E	R^4	L	product (%yield)
18	**4a**	Ph	Me	H	Me	dppf	**9a** (81)
19	**4g**	^{n}Bu	Me	H	Ph	dppf	**9b** (67)
20	**4c**	Ph	Ph	H	^{i}Pr	dppe	**9c** (50)
21	**4m**	^{n}Bu	Me	4-MeC_6H_4	Ph	dppe	**9d** (55)
22	**5a**	Ph	Me	Me	$TMSCH_2$	dppe	**10a** (72)
23	**5b**	Ph	Me	$H_2C{=}CGCH_2$	^{n}Bu	dppe	**10b** (62)
24	**5c**	Ph	Ph	Bu	Ph	dppe	**10c** (67)
25	**4a**	Ph	Me	H	Me	dppe	**11** (52)

gradually warmed to room temperature and stirred for 1 h. The mixture was taken up in pentane (20 mL) and passed through a short basic alumina column. The solution was evaporated in vacuo, and the residue was chromatographed on basic alumina (1% EtOAc in hexane pretreated with K_2CO_3) to give **4e** (328 mg, 94%): ^{1}H NMR (200 MHz, acetone-d_6) δ 0.32 (s, 9 H), 0.83 (t, J = 7.1 Hz, 3 H), 1.20−1.50 (m, 4 H), 2.34−2.45 (m, 2 H), 2.63−2.80 (m, 2 H), 2.85−2.92 (m, 2 H), 7.20−7.42 (m, 8 H), 7.55−7.65 (m, 2 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ −0.2, 13.6, 21.9, 31.7, 31.8, 32.0, 33.2, 99.4, 106.0, 126.1, 126.9, 127.1, 127.9, 128.5, 128.7, 134.7, 136.1, 207.3; IR (NaCl, neat) 1901 cm^{-1}; HRMS calcd for $C_{24}H_{32}S_2Si$: 412.1715, found: 412.1725.

1-(Tributylstannyl)-1,3-diphenyl-4,7-dithia-1,2-undecadiene (4f). In a manner similar to that described for the reaction of **4e**, the reaction of **1b** (282 mg, 1.0 mmol) with ^{n}Bu_2CuLi (5.7 mL, 0.6 mmol in THF/hexane) at −78 °C. Bu_3SnCl (0.4 mL, 1.5 mmol) was introduced, and the mixture was gradually warmed to room temperature and stirred for an additional 6 h. Pentane (20 mL) was added, and the mixture was passed through basic alumina. The solution was evaporated in vacuo, and the residue was chromatographed on basic alumina (hexane pretreated with K_2CO_3) to give **4f** (510 mg, 81%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.73−1.10 (m, 12 H), 1.15−1.70 (m, 22 H), 2.30−2.40 (m, 2 H), 2.60−3.00 (m, 4 H), 7.10−7.50 (m, 8 H), 7.55−7.65 (m, 2 H); IR (NaCl, neat) 1897 cm^{-1}; HRMS (FAB) calcd for $C_{33}H_{50}S_2120Sn$: 630.2376, found: 630.2383. Compound **4f** decomposes gradually upon standing and in $CDCl_3$ solution. No satisfactory ^{13}C NMR was obtained. Neverthelss, it did show absorption at δ 202.9 attrbuted to the C_{sp} allenyl carbon. No signals due to alkyne carbons (δ 80−95) were observed.

2,2,7-Trimethyl-3,6-dithiatrideca-7,8-diene (4g). In a manner similar to that described for the reaction of **6a**, the reaction of **1c** (200 mg, 1.00 mmol) with ^{t}Bu_2CuLi (5.7 mL, 0.6 mmol in THF/pentane) gave **4g** as a colorless oil (211 mg, 82%): bp 75 °C (0.05 mmHg) ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (t, J = 7.2 Hz, 3 H), 1.22−1.39 (m, 13 H, embodied a singlet at 1.28 due to the ^{t}Bu group), 1.84 (d, J = 2.8 Hz, 3 H), 1,92−1.99 (m, 2 H), 2.66−2.70 (m, 4 H), 5.31 (tq, J = 7.2, 2.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 20.1, 22.2, 28.2, 29.2, 31.0, 31.2, 32.7, 42.5, 96.8, 97.0, 197.5; IR (NaCl, neat) 1932 cm^{-1}; HRMS calcd for $C_{14}H_{26}S_2$: 258.1476, found: 258.1490.

3-Phenyl-4,7-dithiaundeca-1,2-diene (4h). In a manner similar to that described for the reaction of **4a**, ^{n}Bu_2CuLi (5.7 mL, 0.6 mmol in THF/hexane) at −78 °C was allowed to react with **1d** (206 mg, 1.00 mmol) in THF (5 mL) to give **4h** as a colorless oil (216 mg, 82%): bp 65 °C (0.05 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3 H), 1.36 (tq, J = 7.3, 7.5 Hz, 2 H), 1.52 (tt, J = 7.3, 7.5 Hz, 2 H), 2.49 (t, J = 7.3 Hz, 2 H), 2.72−2.76 (m, 2 H), 2.86−2.89 (m, 2 H), 5.27 (s, 2 H), 7.23 (t, J = 7.2 Hz, 1 H), 7.29−7.37 (m, 2 H), 7.53 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 21.9, 31.5, 31.8, 31.9, 32.9, 81.0, 103.0, 126.7, 127.7, 128.5, 134.2, 206.3; IR (neat, cm^{-1}) 1935 (allene); HRMS calcd for $C_{15}H_{20}S_2$: 264.1007, found: 264.1006.

7-(2-Propyl)-8,11-dithia-5,6-pentadecadiene (4i). In a manner similar to that described for the reaction of **6a**, the reaction of **1e** (228 mg, 1.0 mmol) with ^{n}Bu_2CuLi (5.7 mL, 0.6 mmol in THF/hexane) followed by quenching with methanol gave **4i** as a colorless oil (210 mg, 73%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 3 H), 0.90 (t, J = 7.3 Hz, 3 H), 1.07 (d, J = 6.7 Hz, 3 H), 1.08 (d, 6.7 Hz, 3 H), 1.28−1.44 (m, 6 H), 1.49−1.60 (m, 2 H), 1.96−2.05 (m, 2 H), 2.16−2.27 (m, 1 H), 2.51 (t, J = 7.6 Hz, 2 H), 2.61−2.80 (m, 4 H), 5.43 (dt, J = 2.1 Hz, J = 6.6 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.6, 13.9, 21.9, 22.0, 22.2, 22.3, 29.4, 31.4, 31.7, 31.9, 32.4, 32.8, 98.8, 109.2, 195.7; IR (NaCl, neat) 1951 cm^{-1}; HRMS calcd for $C_{16}H_{30}S_2$ 286.1789, found 286.1797.

3,3,8,8-Tetramethyl-1-phenyl-4,7-dithia-1-nonyne (5a). To a THF/pentane solution of ^{t}Bu_2CuLi (11.4 mL, 1.2 mmol in THF/pentane) at −78 °C was added dropwise **1a** (440 mg, 2.00 mmol) in THF (10 mL) over a period of 15 min. The mixture was stirred at −78 °C for 5 min. HMPA (0.33 mL, 2.0 mmol) and MeI (0.19 mL, 3.0 mmol) were then added, and the mixture was stirred at −78 °C for 30 min and then passed through a short neutral alumina. The solvent was removed in vacuo to give the residue which was distilled to give **5a** as a colorless oil (472 mg, 81%): bp 120 °C (0.05 mmHg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (s, 9 H), 1.63 (s, 6 H), 2.78−3.03 (m, 4 H), 7.24−7.27 (m, 3 H), 7.34−7.41 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6, 28.6, 30.9, 31.2, 39.2, 42.5, 82.4, 93.3, 126.5, 127.9, 128.1, 131.6; IR (NaCl, neat) 2201 cm^{-1}; HRMS calcd for $C_{16}H_{22}S_2$: 292.1319, found: 292.1312.

3-Butyl-1,3-diphenyl-4,7-dithia-1-undecyne (5c). Under argon atmosphere, a THF solution (5 mL) of ^{n}Bu_2CuLi (prepared from 1.2 mmol of ^{n}BuLi and CuI (114 mg 0.6 mmol)) was added dropwise to a solution of **1b** (282 mg, 1.0 mmol) in THF (5 mL) at −78 °C and the mixture was stirred at −78 °C for 0.5 h. HMPA (0.26 mL, 1.5 mmol) was introduced, and the mixture was stirred for an additional 1 h. After 1-bromobutane (0.16 mL, 1.5 mmol) was added, the mixture was allowed to warm to room temperature and stirred overnight, taken up in pentane (20 mL), and passed through basic alumina. The solution was evaporated in vacuo, and the residue was chromatographed on basic alumina (hexane pretreated with K_2CO_3) to give **5c** (353 mg, 89%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.82 (t, J = 7.2 Hz, 3 H), 0.84 (t, J = 7.0 Hz, 3 H), 1.10−1.65 (m, 8 H), 2.0−2.2 (m, 2 H), 2.35 (t, J = 7.3, 2 H), 2.4−2.85 (m, 2 H) 7.2−7.45 (m, 6 H) 7.42−7.6 (m, 2 H) 7.65−7.8 (m, 2 H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.60, 13.88, 14.11, 21.91, 22.61, 27.76, 31.24, 31.62, 31.71, 43.30, 51.89, 87.17, 90.44, 123.04, 127.18, 127.28, 128.19, 128.28, 128.34, 131.67, 142.02.; HRMS calcd for $C_{25}H_{32}S_2$: 396.1945, found: 396.1942.

3,8,8-Trimethyl-1-(trimethylsilyl)-4,7-dithia-1-nonyne (5d). In a manner similar to that described for the reaction of **6a**, **1f** (216 mg, 1.00 mmol) was treated with ^{t}Bu_2CuLi (5 mL, 0.6 mmol in THF/pentane) to give **5d** as a colorless oil (257 mg, 94%): bp 85 °C (0.05 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 1.30 (s, 9 H), 1.44 (d, J = 4.2 Hz, 3 H), 2.71−2.97 (m, 4 H), 3.67 (q, J = 4.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.0, 21.6, 28.6, 29.8, 31.1, 31.9, 42.6, 87.6, 106.1; IR (NaCl, neat) 2165 cm^{-1}; HRMS calcd for $C_{13}H_{26}SiS_2$: 274.1245, found: 274.1264.

1,3-Diphenyl-1-(4-methylphenyl)-4,7-dithiaundeca-1,2-diene (4j). Under argon atmosphere, to a THF/hexane solution of ^{n}Bu_2CuLi (5.7 mL, 0.6 mmol) at −78 °C was added dropwise **1b** (282 mg, 1.00 mmol) in THF (5 mL) over a period of 15 min. The mixture was stirred at −78 °C for 5 min. THF solution of $ZnCl_2$ (1.0 mL, 1.0 mmol in THF) was then added, the mixture was stirred at −78 °C for 30 min, and then a THF solution of 4-iodotoluene (244 mg, 1.2 mmol) and $Pd(PPh_3)_4$ (57.5 mg, 0.05 mmol) was added at −78 °C. The mixture was stirred at room temperature and then passed through a short-

path neutral alumina. The solvent was removed in vacuo to give a pale yellow oil, which was chromatographed on basic alumina (EtOAc/hexane = 1/50) to give **4j** as a colorless oil (296 mg, 69%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3 H), 1.22−1.51 (m, 4 H), 2.32 (t, J = 7.2 Hz, 3 H), 2.41 (s, 3 H), 2.60−2.68 (m, 2 H), 2.96−3.04 (m, 2 H), 7.22 (d, J = 7.8 Hz, 2 H), 7.30−7.51 (m, 10 H), 7.68 (dt, J = 6.6, 1.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.5, 21.1, 21.8, 31.6, 31.8, 32.0, 32.7, 107.0, 116.4, 126.5, 127.8, 128.0, 128.2, 128.3, 128.4, 128.5, 129.2, 132.8, 134.5, 136.0, 137.7, 203.3; IR (NaCl, neat) 1908 cm^{-1}; HRMS calcd for $C_{28}H_{30}S_2$: 430.1789, found: 430.1794.

2,2-Dimethyl-4,6-diphenyl-3-oxo-7,10-dithiatetradeca-4,5-diene (4k). In a manner similar to that described for preparation of **4j**, **1b** (282 mg, 1.00 mmol) was allowed to react with ^{n}Bu$_2$CuLi (5.7 mL, 0.6 mmol in THF/hexane) and then added THF solution of $ZnBr_2$ (1.0 mL, 1.0 mmol in THF) and stirred at −78 °C, followed the THF solution (5 mL) of pivaloyl chloride (0.15 mL, 1.2 mmol) and $Pd(PPh_3)_4$ (57.5 mg, 0.05 mmol). The mixture was stirred at room temperature for 12 h to give **4k** as yellow oil (274 mg, 65%): ^{1}H NMR (300 MHz, acetone-d_6) δ 0.89 (t, J = 7.2 Hz, 3 H), 1.18−1.45 (m, 13H, embodied a singlet at 1.24 due to the *tert*-butyl group), 2.30−2.44 (m, 2 H), 2.58−2.72 (m, 2 H), 2.91−3.00 (m, 2 H), 7.30−7.48 (m, 8 H), 7.62−7.65 (m, 2 H); ^{13}C NMR (75 MHz, acetone-d_6) δ 13.9, 22.4, 27.3, 32.0, 32.3, 32.5, 33.7, 46.1, 110.0, 113.5, 127.5, 128.3, 129.0, 129.5, 129.6, 129.8, 134.3, 134.4, 202.4, 206.2; IR (NaCl, neat) 1951 cm^{-1}; HRMS calcd for $C_{26}H_{32}OS_2$: 424.1895, found: 424.1901.

1,3,5-Triphenyl-6,9-dithiatrideca-3,4-dien-1-yne (4l). In a manner similar to that described for the reaction of **4j**, **1b** (282 mg, 1.00 mmol) was allowed to react with ^{n}Bu$_2$CuLi (5.7 mL, 0.6 mmol in THF/hexane), followed by the addition of a THF solution of $ZnBr_2$ (1.0 mL, 1.0 mmol in THF) and stirred at −78 °C for 30 min. A THF solution (5 mL) of 1-bromo-2-phenylacetylene (217 mg, 1.2 mmol) and $Pd(PPh_3)_4$ (57.5 mg, 0.05 mmol) was then added, the mixture was stirred at room temperature for 12 h to give **4l** as yellow oil (130 mg, 30%): ^{1}H NMR (300 MHz, acetone-d_6) δ 0.79 (t, J = 7.2 Hz, 3 H), 1.20−1.32 (m, 2 H), 1.37−1.47 (m, 2 H), 2.40−2.50 (m, 2 H), 2.76−3.06 (m, 4 H), 7.36−7.51 (m, 9 H), 7.60−7.64 (m, 4 H), 7.74−7.77 (m, 2 H); ^{13}C NMR (75 MHz, acetone-d_6) δ 13.5, 21.9, 22.6, 31.5, 33.0, 38.7, 81.7, 95.1, 100.7, 110.3, 122.9, 126.4, 126.9, 128.1, 128.3, 128.6, 128.7, 128.8, 131.6, 132.3, 133.4, 207.5; IR (NaCl, neat) 1903, 2202 cm^{-1}; HRMS calcd for $C_{29}H_{28}S_2$: 440.1632, found: 440.1644.

7-Methyl-5-(4-methylphenyl)-8,11-dithiapentadeca-5,6-diene (4m). In a manner similar to that described for the reaction of **4j**, **1c** (200 mg, 1.00 mmol) was allowed to react with ^{n}Bu$_2$CuLi (5.7 mL, 0.6 mmol in THF/hexane) and then with $ZnBr_2$ (1.0 mL, 1.0 mmol in THF), 4-iodotoluene (244 mg, 1.2 mmol), and $Pd(PPh_3)_4$ (57.5 mg, 0.05 mmol) in THF (5 mL) to give **4m** as yellow oil (269 mg, 78%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (t, J = 7.0 Hz, 3 H), 0.92 (t, J = 7.1 Hz, 3 H), 1.24−1.60 (m, 8 H), 2.01 (s, 3 H), 2.27−2.33 (m, 5H, embodied a singlet at 2.31 due to the methyl group), 2.45 (d, J = 6.8 Hz, 2 H), 2.50−2.74 (m, 4 H), 7.06−7.28 (m, 5 H). The product was used for the next reaction without further purification.

3-Methyl-1-phenyl-1,2-butadiene (9a). An ether solution of MeMgI (1.0 mL of 2.0 M solution, 2.0 mmol) was evacuated to remove the ether solvent. Under argon atmosphere, a benzene (5 mL) solution of **4a** prepared above and $NiCl_2$(dppf) (34 mg, 0.05 mmol) were added and the mixture was refluxed for 12 h, quenched with saturated NH_4Cl (10 mL), and extracted with ether (10 mL × 3). The organic layer was dried ($MgSO_4$), and the solvent was removed by distillation to give a pale yellow oil, which was chromatographed on silica gel (pentane) to give **9a** as a colorless oil (116 mg, 81%)[1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.86 (d, J = 3 Hz, 6 H), 6.02 (septet, J = 3 Hz, 1 H), 7.16−7.34 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 92.5, 99.1, 126.3, 126.6, 128.4, 136.0, 203.1; IR (NaCl, neat) 1954 cm^{-1}; HRMS calcd for $C_{11}H_{12}$: 144.0939, found: 144.0933.

2-Phenyl-2,3-octadiene (9b). In a manner similar to that described for the reaction of **4a**, crude **4g** prepared above was treated with PhMgBr (2.0 mL of 1 M solution, 2.0 mmol) in the presence of $NiCl_2$(dppf) (34 mg, 0.05 mmol) to yield **9b** (125 mg, 67%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 6.9 Hz, 3 H), 1.33−1.52 (m, 4 H), 2.07−2.17 (m, 5 H embodied a doublet at 2.10 for Me group, J = 3.0 Hz), 5.46 (tq, J = 6.0, 3.0 Hz, 1 H), 7.20 (t, J = 7.0 Hz, 1 H), 7.29−7.35 (m, 2 H), 7.41−7.45 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 17.2, 22.3, 28.7, 31.4, 93.0, 100.2, 125.6, 126.2, 128.2, 137.8, 204.1; IR (NaCl, neat) 1948 cm^{-1}; HRMS calcd for $C_{14}H_{18}$: 186.1408, found: 186.1414.

1,3-Diphenyl-1,2-propadiene (9c). In a manner similar to that described for the reaction of **4a**, crude **4c** prepared above was treated at room temperature with ^{i}PrMgBr (2.0 mL of 1.0 M solution, 2.0 mmol) in the presence of $NiCl_2$(dppe) (33 mg, 0.05 mmol) to yield **9c** (96 mg, 50%): mp: 46−48 °C (lit.[9] 49−51 °C).

2-Phenyl-4-(4-methylphenyl)-2,3-octadiene (9d). In a manner similar to that described for **5a**, crude **4m** was allowed to react with a benzene/ether (9/1, 5 mL) solution of PhMgBr (2.0 mmol) in the presence of $NiCl_2$(dppe) (26 mg, 0.05 mmol) under reflux for 12 h to yield **9d** as a colorless oil (152 mg, 55%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.0 Hz, 3 H), 1.39−1.71 (m, 4 H), 2.26 (s, 3 H), 2.38 (s, 3 H), 2.60 (t, J = 7.2 Hz, 2 H), 7.17 (d, J = 8.0 Hz, 2 H), 7.23−7.41 (m, 5 H), 7.49−7.53 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 16.9, 21.1, 22.6, 30.0, 30.1, 103.4, 107.6, 125.6, 125.9, 126.5, 128.3, 129.1, 134.0, 136.3, 137.4, 205.3; IR (NaCl, neat) 1934 cm^{-1}; HRMS calcd for $C_{21}H_{24}$: 276.1878, found: 276.1884.

4-Methyl-2-phenyl-1-(trimethylsilyl)-2,3-pentadiene (10a). In a manner similar to that described for the reaction of **4a**, crude **5a** prepared above was allowed to react with $TMSCH_2MgCl$ (2.0 mL of 1 M solution, 2.0 mmol) to yield **10a** (164 mg, 72%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 1.80 (s, 3 H), 1.82 (s, 6 H), 7.13−7.45 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.2, 19.0, 20.6, 96.7, 100.3, 125.9, 126.2, 128.0, 139.6, 202.4; IR (NaCl, neat) 1949 cm^{-1}; HRMS calcd for $C_{13}H_{18}Si$: 230.1491, found: 230.1488.

1-Phenyl-1-(trimethylsilyl)-1,2-butadiene (10c). In a manner similar to that described for the reaction of **4a**, crude **5c** prepared above was allowed to react with PhMgBr (2.0 mL of 1 M solution, 2.0 mmol) to yield **10c** (135 mg, 67%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.23 (s, 9 H), 1.73 (d, J = 7.0, 3 H), 5.11 (q, J = 7.0 Hz, 1 H), 7.12−7.33 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.3, 13.4, 81.5, 99.6, 126.0, 127.6, 128.3, 138.1, 209.3; IR (NaCl, neat) 1927 cm^{-1}; HRMS calcd for $C_{13}H_{18}Si$: 202.1179, found: 202.1177.

4-Methyl-6-phenyl-1,4,5-decatriene (10b). Under argon atmosphere, to a THF/pentane solution of ^{t}Bu$_2$CuLi (11.4 mL, 1.2 mmol in THF/pentane) at −78 °C was added dropwise propargyl dithiolane **1a** (440 mg, 2.00 mmol) in THF (10 mL) over a period of 15 min. The mixture was stirred at −78 °C for 5 min, allyl bromide (0.24 mL, 3 mmol) was added, and the mixture was stirred at −78 °C for 30 min. The mixture was passed through a short-path neutral alumina. The solvent was removed in vacuo to give a pale yellow oil **5b** (251 mg, 80%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.18 (s, 9 H), 2.04 (s, 3 H), 2.61−2.82 (m, 4 H), 3.25 (d, J = 6.3 Hz, 2 H), 5.06−5.18 (m, 2 H), 5.87−6.07 (m, 1 H), 7.14−7.45 (m, 5 H). Crude **5b** was allowed to react with ^{n}BuMgBr (4.0 mL of 1M solution, 4.0 mmol) in the presence of $NiCl_2$(dppf) (68 mg, 0.10 mmol) in benzene (10 mL) at room temperature for 6 h to yield **10b** (279 mg, 62%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.96 (t, J = 7.2 Hz, 3 H), 1.34−1.60 (m, 4 H), 1.82 (s, 3 H), 2.43 (t, J = 6.8 Hz, 2 H), 2.86 (d, J = 6.8 Hz, 2 H), 5.04−5.18 (m, 2 H), 5.90 (ddt, J = 7.0, 10.0, 16.8 Hz, 1 H), 7.14−7.45 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 18.5, 22.5, 29.9, 30.2, 39.2, 101.0, 104.8, 115.9, 125.9, 126.1, 128.2, 136.0, 138.2, 201.7; IR (NaCl, neat) 1951 cm^{-1}; HRMS calcd for $C_{13}H_{18}Si$: 226.1722, found: 226.1719.

1,4-Diphenyl-2-(2-propyl)-3-(2-propenyl)-1,3-butadiene (11). In a manner similar to that described for the reaction of **4a**, crude **4a** was allowed to react with MeMgI (1.0 mL of 2.0 M solution, 2.0 mmol) in the presence of $NiCl_2$(dppe) (26

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mg, 0.05 mmol) under reflux for 12 h to yield **11** (75 mg, 52%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (d, J = 6.8 Hz, 3 H, 6% NOE upon irradiation at δ 6.56), 1.08 (d, J = 6.8 Hz, 3 H, 5% NOE upon irradiation at δ 6.56), 2.06 (s, 3 H, 9% NOE upon irradiation at δ 6.68), 2.32 (doublet of septet, J = 1.2, 6.8 Hz, 1 H, 3% NOE upon irradiation at δ 6.56), 4.94 (s, 1 H), 5.14 (s, 1 H), 6.56 (s, 1 H), 6.68 (s, 1H, 19% NOE upon irradiation at δ 2.06), 7.11−7.25 (m, 6 H), 7.39 (d, J = 7.2 Hz, 2 H), 7.50 (d, J = 7.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 21.8, 22.1, 35.9, 116.7, 126.5, 126.6, 127.0, 128.0, 128.1, 128.7, 137.5, 137.9, 140.8, 143.5, 145.6; HRMS calcd for $C_{22}H_{24}$: 288.1878, found: 288.1870.

In a separate experiment treatment of **5a** (144 mg, 1.00 mmol) in benzene (5 mL) with MeMgI (0.1 mL of 1.0 M solution, 0.1 mmol) in the presence of $NiCl_2$(dppe) (26 mg, 0.05 mmol) under reflux for 12 h yielded **11** (85 mg, 59%).

4,6-Diphenyl-7,10-dithiatetradeca-1,3,5-triene (8). In a manner similar to that described for the preparation of **4j**, **1b** (282 mg, 1.00 mmol) was allowed to react with ^{n}Bu$_2$CuLi (5.7 mL, 0.6 mmol in THF/hexane). A THF solution of $ZnBr_2$ (1.0 mL, 1.0 mmol in THF) and stirred at −78 °C, followed by treatment with allyl bromide (0.11 mL, 1.2 mmol) and Pd(PPh$_3$)$_4$ (57.5 mg, 0.05 mmol) in THF (5 mL). The mixture was stirred at room temperature for 12 h to give **8** as a mixture of stereoisomers (312 mg, 82%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 6 H), 1.29−1.46 (m, 8 H), 2.25−2.34 (m, 4 H), 2.56−2.58 (m, 4 H), 2.67−2.71 (m, 4 H), 5.00 (d, J = 9.8 Hz, 1 H), 5.07 (d, J = 10.1 Hz, 1 H), 5.16 (d, J = 16.1 Hz, 1 H), 5.18 (d, J = 16.8 Hz, 1 H), 6.21−6.37 (m, 2 H, embodied a doublet at 6.27 due to the olefinic proton), 6.57−6.77 (m, 2 H, embodied a doublet at 6.75 due to the olefinic proton), 6.95−7.32 (m, 22 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 21.8, 31.55, 31.62, 31.69, 31.72, 31.8, 31.9, 32.0, 118.5, 118.6, 125.9, 126.6, 126.8, 127.1, 127.4, 127.5, 127.6, 127.8, 128.0, 129.0, 129.5, 129.6, 131.1, 133.8, 134.2, 137.1, 137.2, 137.9, 138.0, 139.7, 140.5; HRMS calcd for $C_{24}H_{28}S_2$: 380.1632, found: 380.1635.

2-Methyl-2-[2-(1-methoxycyclohexyl)ethynyl]-1,3-dithiolane (13). Under argon atmosphere, to a THF solution (8 mL) of **14** (1.44 g, 10 mmol) at −78 °C was treated with ^{n}BuLi (6.32 mL, 11.0 mmol in hexane). The mixture was stirred at −78 °C for 30 min to which cyclohexanone (1.30 mL, 10.0 mmol) was added. After stirring at room temperature for 30 min, the mixture was quenched with saturated NH_4Cl (10 mL) and extracted with ether (30 mL × 3). The organic layer was dried ($MgSO_4$), and the solvent was removed in vacuo to give a pale yellow oil, which was chromatographed on silica gel (EtOAc/hexane = 1/5) to give 2-methyl-2-[2-(1-hydroxycyclohexyl)ethynyl]-1,3-dithiolane as a white solid (2.01 g, 83%): mp 72−75 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10−1.13 (m, 1 H), 1.35−1.75 (m, 7 H), 1.80−1.90 (m, 2 H), 1.97 (s, 3 H), 2.29 (s, 1 H), 3.40−3.57 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.3, 25.1, 31.2, 39.9, 40.5, 54.2, 68.6, 86.3, 88.3; HRMS calcd for $C_{12}H_{18}OS_2$: 242.0799, found: 242.0799.

Under argon atmosphere, to a THF solution (80 mL) of the alcohol prepared above (1.21 g, 5.0 mmol) at −78 °C was added MeLi (3.5 mL, 5.5 mmol in ether). The mixture was stirred for 30 min to which MeI (0.44 mL, 7.0 mmol) in DMSO (5 mL) was added at −78 °C. The mixture was stirred at room temperature for 6 h, quenched with saturated NH_4Cl (10 mL), and extracted with ether (20 mL × 3). The organic layer was dried ($MgSO_4$), and the solvent was removed in vacuo to give the residue which was chromatographed on silica gel (EtOAc/hexane = 1/10) to give **13** as a white solid (1.16 g, 91%): mp: 51−53 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12−1.19 (m, 1 H), 1.36−1.68 (m, 7 H), 1.76−1.88 (m, 2 H), 1.98 (s, 3 H), 3.29 (s, 3 H), 3.37−3.53 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.9, 25.4, 31.2, 36.7, 40.4, 50.7, 54.3, 74.0, 83.7, 90.3; IR (KBr) 2222 cm^{-1}; HRMS calcd for $C_{13}H_{20}OS_2$: 256.0955, found: 256.0959.

4-Methyl-1,1-pentamethylene-5,8-dithia-1,2,3-dodecatriene (15). Under argon atmosphere, to a THF/hexane solution of ^{n}Bu$_2$CuLi (5.7 mL, 0.6 mmol in THF/pentane) at −78 °C was added dropwise **13** (256 mg, 1.0 mmol) in THF (5 mL) over a period of 15 min. The mixture was stirred at −78 °C for 15 min, quenched with methanol (0.3 mL, 11.4 mmol) and then passed through a short-path neutral alumina column. The solvent was removed in vacuo to give **15** as colorless oil (257 mg, 91%): ^{1}H NMR (200 MHz, benzene-d_6) δ 0.75 (t, J = 7.4 Hz, 3 H), 1.15−1.65 (m, 10 H), 2.00 (s, 3 H), 2.22−2.35 (m, 6 H), 2.68−2.76 (m, 2 H), 2.92−3.00 (m, 2 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 13.9, 22.2, 22.8, 26.4, 28.0, 28.2, 32.1, 32.2, 33.4, 34.8, 35.3, 107.7, 115.1, 146.7, 154.5; IR (NaCl, neat) 2050 cm^{-1}; HRMS calcd for $C_{13}H_{20}OS_2$: 282.1476, found: 282.1479.

Acknowledgment. This work was supported by the National Science Council of the Republic of China.

Supporting Information Available: ^{1}H NMR spectra of **4a**−**l**, **5a**, **5c**, **5d**, **7a**, **7b**, **8**, **9a**, **9b**, **9d**, **10a**−**c**, **11**, **13**, and **15** and ^{13}C NMR spectra of **4a**−**d**, **4g**−**l**, **5a**, **5c**, **5d**, **7a**, **7b**, **8**, **9a**, **9b**, **9d**, **10a**−**c**, **11**, **13**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991032B