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Stereoselective Hydrothiolation of Alkynes Catalyzed by Cesium Base: Facile Access to (*Z*)-1-Alkenyl Sulfides

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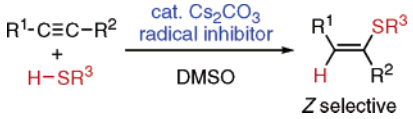
Received May 10, 2005



Treatment of alkyne with alkanethiol in the presence of a catalytic amount of cesium carbonate and a radical inhibitor in DMSO provides the corresponding adduct, (*Z*)-1-alkenyl alkyl sulfide, in good yield with high selectivity.

Introduction

Addition of thiols to alkynes (hydrothiolation) is an important reaction that produces 1-alkenyl sulfides of significant synthetic use. In light of their expected utility, stereo- and regioselective synthesis of 1-alkenyl sulfides has merited exploitation. Radical addition of thiols gave anti-Markovnikov products as mixtures of *E* and *Z* isomers.[1] Transition-metal-catalyzed hydrothiolation mostly proceed in a syn fashion to afford anti-Markovnikov (*E*)-1-alkenyl sulfide or Markovnikov adducts, sometimes suffering from low regioselectivity.[2] Base-mediated hydrothiolations are well-known and proceed mostly in an anti manner. However, stoichiometric amounts of a base were used,[3] and catalytic hydrothiolation reactions are quite rare. Here we report a cesium-catalyzed hydrothiolation of alkynes.

Results and Discussion

As the first attempt, a mixture of phenylacetylene (0.50 mmol) and dodecanethiol[4] (0.60 mmol) was treated with 10 mol % of cesium carbonate[5,6] in DMSO (dimethyl sulfoxide) at 25 °C for 4 h under argon. The reaction proceeded smoothly to provide the corresponding anti-Markovnikov adduct **1a** in good yield with high stereoselectivity (Table 1, entry 1). DMSO was the solvent choice. Use of other solvents such as NMP (1-methyl-2-pyrrolidinone) and dioxane resulted in poorer conversions and/or lower selectivities (entries 2−7). During the optimization of reaction conditions, we found that, even without cesium carbonate, the addition took place to afford **1a** in moderate yield (entry 8). Under the base-free conditions, the stereoselectivity was much lower than that of the base-promoted reaction. It was likely that the concurrence of the base-free addition with the base-promoted addition diminished the stereoselectivity and that suppression of the base-free addition would improve the stereoselectivity. We found that a radical inhibitor, TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl), completely inhibited the base-free reaction (entry 9). The base-free addition is thus a radical reaction. In the presence of TEMPO, cesium-catalyzed addition proceeded with higher stereoselectivity (entry 10 vs entry 1). Even at higher temperatures, the reactions furnished **1a** in excellent yield with high stereoselectivity (entries 11 and 12). A longer reaction time allowed us to achieve both high yield and high selectivity at 25 °C (entry 13). Cesium fluoride also worked with a slightly lower catalytic activity (entries 14 and 15). Cesium acetate was inferior to cesium carbonate and cesium fluoride (entry 16).

(1) (a) Griesbaum, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 273−287. (b) Ichinose, Y.; Wakamatsu, K.; Nozaki, K.; Birbaum, J.-L.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1987**, 1647−1650. (c) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1035−1038.

(2) (a) Ogawa, A. *J. Organomet. Chem.* **2000**, *611*, 463−474. (b) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205−3220. (c) Kuniyasu, H. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Chapter 7. (d) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368−3398. (e) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079−3159.

(3) (a) Truce, W. E.; Simms, J. A.; Boudakian, M. M. *J. Am. Chem. Soc.* **1956**, *78*, 695−696. (b) Truce, W. E.; Simms, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 2756−2759. (c) Truce, W. E.; Tichenor, G. J. W. *J. Org. Chem.* **1972**, *37*, 2391−2396.

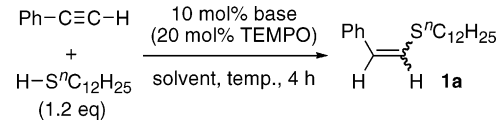
(4) (a) Nishide, K.; Node, M. *J. Synth. Org. Chem., Jpn.* **2004**, *62*, 895−910. (b) Node, M.; Kumar, K.; Nishide, K.; Ohsugi, S.; Miyamoto, T. *Tetrahedron Lett.* **2001**, *42*, 9207−9210.

(5) (a) Matsubara, S. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, Germany, 2004, Chapter 2. (b) Flessner, T.; Doye, S. *J. Prakt. Chem.* **1999**, *341*, 186−190. (c) Lehmann, F. *Synlett* **2004**, 2447−2448. (d) Nakamura, T.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2001**, *57*, 9827−9836.

(6) Knochel et al. reported addition of alcohols and amines to alkynes, although the stereoselectivity was low: Tzalis, D.; Koradin, C.; Knochel, P. *Tetrahedron Lett.* **1999**, *40*, 6193−6195.

10.1021/jo050931z CCC: $30.25
Published on Web 07/14/2005

TABLE 1. Optimization of Reaction Conditions



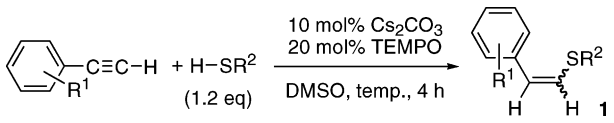
entry	base	TEMPO	solvent	temp, °C	yield, %	*E*/*Z*[a]
1	Cs_2CO_3	no	DMSO	25	87	10:90
2	Cs_2CO_3	no	NMP	25	69	13:87
3	Cs_2CO_3	no	dioxane	25	10	0:100
4	Cs_2CO_3	no	dioxane	85	46	21:79
5	Cs_2CO_3	no	THF	25	47	27:73
6	Cs_2CO_3	no	THF	66	59	32:68
7	Cs_2CO_3	no	ethanol	25	30	34:66
8	none	no	DMSO	25	40	26:74
9	none	20 mol %	DMSO	25	0	
10	Cs_2CO_3	20 mol %	DMSO	25	86	7:93
11	Cs_2CO_3	20 mol %	DMSO	55	92	10:90
12	Cs_2CO_3	20 mol %	DMSO	85	99	10:90
13[b]	Cs_2CO_3	20 mol %	DMSO	25	93	7:93
14	CsF	20 mol %	DMSO	25	54	12:88
15	CsF	20 mol %	DMSO	85	95	13:87
16	CsOAc	20 mol %	DMSO	25	16	25:75
17	K_2CO_3	20 mol %	DMSO	25	63	5:95
18	K_2CO_3	20 mol %	DMSO	55	89	10:90
19	K_2CO_3	20 mol %	DMSO	85	99	12:88
20[b]	K_2CO_3	20 mol %	DMSO	25	85	6:94
21	Na_2CO_3	20 mol %	DMSO	25	3	
22	Na_2CO_3	20 mol %	DMSO	85	98%	17:83
23	Et_3N	20 mol %	DMSO	25	0	
24	Et_3N	20 mol %	DMSO	85	34	29:71

[a] Determined by NMR. [b] Performed for 8 h.

Potassium carbonate, a cheaper base than cesium carbonate, was examined (entries 17−20). The use of potassium carbonate attained quite satisfactory results, although the reactivity is slightly lower than that with cesium carbonate. In a large-scale synthesis, potassium carbonate is the choice owing to its low cost. Sodium carbonate and triethylamine suffered from low yields at 25 °C (entries 21 and 23). Higher temperature enhanced the reaction, yet with lower stereoselectivity (entries 22 and 24).

A variety of 1-aryl-1-alkynes underwent the hydrothiolation (Table 2). Alkynes with electron-donating substituents were converted into the corresponding alkenyl sulfides with complete stereoselectivity even at 85 °C (entries 1, 4, 6, and 8). Reactions at 25 °C resulted in lower conversion (entries 3, 5, 7, and 9). Fortunately, an amino group did not retard the reaction (entry 8). Potassium carbonate also served to furnish **1b** in 78% yield (entry 2). Electron-withdrawing substituents led to lower stereoselectivity even at a low reaction temperature (entries 11, 13, 15, and 17). The reaction of 4-ethynylbenzonitrile gave an *E* isomer mainly (entry 17). At a higher temperature, the *E*/*Z* ratios increased (entries 10, 12, 14, and 16). On the other hand, the reaction with 3-ethynylbenzoate resulted in the formation of the corresponding *Z* isomer predominantly irrespective of reaction temperature (entries 18 and 19). Other thiols participated in this addition reaction (entries 20−29). Addition of 3-phenyl-2-propene-1-thiol at 85 °C gave 3-phenyl-2-propenyl styryl sulfide (**1l**) in excellent yield with high stereoselectivity (entry 22). Introduction of arylmethylthio groups led to lower stereoselectivity

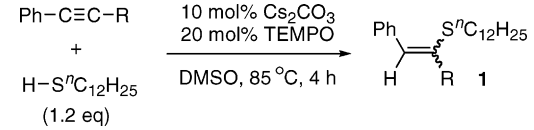
TABLE 2. Addition of Thiols to Arylacetylenes under Cs_2CO_3 Catalysis



entry	R^1	R^2	temp, °C	**1**	yield, %	*E*/*Z*[a]
1	4-MeO	$^nC_{12}H_{25}$	85	**1b**	90	0:100
2[b]	4-MeO	$^nC_{12}H_{25}$	85	**1b**	78	0:100
3	4-MeO	$^nC_{12}H_{25}$	25	**1b**	16	0:100
4	2-MeO	$^nC_{12}H_{25}$	85	**1c**	85	0:100
5	2-MeO	$^nC_{12}H_{25}$	25	**1c**	26	0:100
6	4-^{n}Bu	$^nC_{12}H_{25}$	85	**1d**	96	0:100
7	4-^{n}Bu	$^nC_{12}H_{25}$	25	**1d**	43	0:100
8	4-H_2N	$^nC_{12}H_{25}$	85	**1e**	70	0:100
9	4-H_2N	$^nC_{12}H_{25}$	25	**1e**	<1	N.D.[c]
10	4-CF_3	$^nC_{12}H_{25}$	85	**1f**	87	86:14
11	4-CF_3	$^nC_{12}H_{25}$	25	**1f**	83	16:84
12	4-$Et_2NC(=O)$	$^nC_{12}H_{25}$	85	**1g**	60	28:72
13	4-$Et_2NC(=O)$	$^nC_{12}H_{25}$	25	**1g**	64	17:83
14	4-MeOC(=O)	$^nC_{12}H_{25}$	85	**1h**	82	52:48
15	4-MeOC(=O)	$^nC_{12}H_{25}$	25	**1h**	81	33:67
16	4-CN	$^nC_{12}H_{25}$	85	**1i**	81	90:10
17	4-CN	$^nC_{12}H_{25}$	25	**1i**	85	70:30
18	3-MeOC(=O)	$^nC_{12}H_{25}$	85	**1j**	86	13:87
19	3-MeOC(=O)	$^nC_{12}H_{25}$	25	**1j**	89	13:87
20	H	$^nC_4H_9$	85	**1k**	99	9:91
21	H	$^nC_4H_9$	25	**1k**	95	5:95
22	H	$PhCH=CHCH_2$	85	***1l***	92	8:92
23	H	$PhCH=CHCH_2$	25	***1l***	37	N.D.[c]
24	H	$PhCH_2$	85	**1m**	99	19:81
25	H	$PhCH_2$	25	**1m**	66	10:90
26	H	2-furylmethyl	85	**1n**	99	22:78
27	H	2-furylmethyl	25	**1n**	42	6:94
28	H	Ph	85	**1o**	14	12:88
29	H	Ph	25	**1o**	trace	N.D.[c]

[a] Determined by NMR. [b] Potassium carbonate was used instead of cesium carbonate. [c] Not determined.

TABLE 3. Addition of Dodecanethiol to Internal Alkynes under Cs_2CO_3 Catalysis



entry	R	**1**	yield, %	*E*/*Z*[a]
1	Ph	**1p**	94	15:85
2	Me	**1q**	56	22:78
3	CH_2OMe	**1r**	95	17:83
4	CH_2OH	**1s**	99	0:100

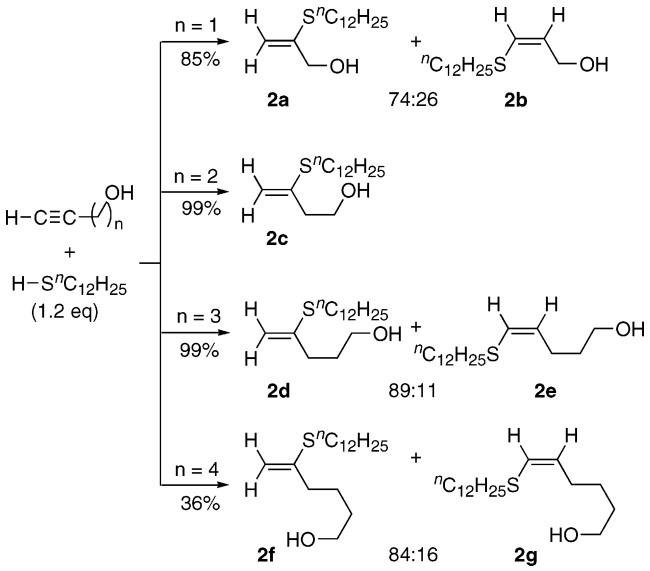
[a] Determined by NMR.

(entries 24−27). Attempted addition of aromatic thiols resulted in failure (entries 28 and 29).

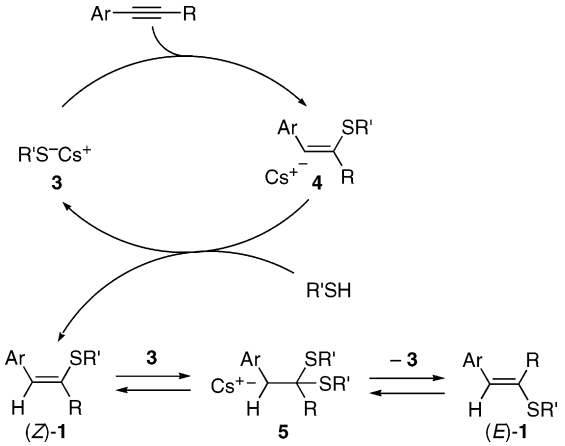
Next we examined addition to internal alkynes (Table 3). The reaction of diphenylacetylene with dodecanethiol at 85 °C afforded the (*Z*)-adduct predominantly in excellent yield (entry 1). However, 1-phenyl-1-propyne was converted to the corresponding adduct in fair yield (entry 2). Coordinating functional groups such as methoxy and hydroxy groups in close proximity to the triple bonds facilitated the hydrothiolation (entries 3 and 4).[7]

Although aliphatic alkynes such as 1-octyne and 4-octyne resisted the hydrothiolation, 3-butyn-1-ol readily underwent Markovnikov addition at 85 °C to yield

SCHEME 1



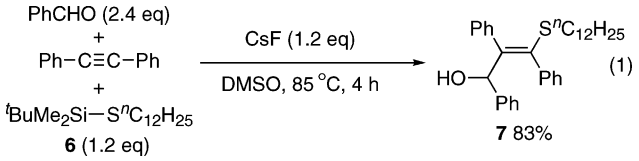
SCHEME 2



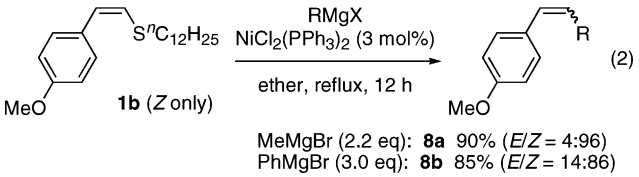
3-dodecylthio-3-buten-1-ol (**2c**) exclusively (Scheme 1, $n = 2$). The reactions of propargyl alcohol and 4-pentyn-1-ol furnished mixtures of regioisomers. A longer tether ($n = 4$) diminished the yield significantly.

The catalytic reaction would consist of the following reactions (Scheme 2): (1) Nucleophilic addition of a thiolate anion **3** to an alkyne occurs in an anti fashion to yield the corresponding alkenyl anion **4**. (2) Hydrogen abstraction from a thiol produces the product with concomitant regeneration of **3**. Poor or inverse stereoselectivities observed in the reactions of arylacetylenes having electron-withdrawing groups (Table 1) would stem from reversible addition of thiolate **3** to the products **1f**–**i**. The electron-withdrawing groups stabilize the benzylic anions **5** and enhance the addition of **3** to (*Z*)-**1**.

Alkenyl anion intermediate **4** seemed a potent intermediate that can undergo further carbon–carbon bond formation upon reaction with electrophiles. Use of alkyl silyl sulfide, instead of alkanethiol, was expected to enable such a bond formation. This was indeed the case, and treatment of diphenylacetylene with *tert*-butyldimethylsilyl dodecyl sulfide (**6**) in the presence of benzaldehyde and a stoichiometric amount of cesium fluoride provided the anticipated three-component coupling product **7** in 83% yield (eq 1). No stereoisomer of **7** was detected.



Cross-coupling reactions of (*Z*)-1-alkenyl sulfides with organometallic reagents were reported.[8,9] However, little attention has been paid to the reaction probably because there are few methods for stereoselective synthesis of (*Z*)-1-alkenyl sulfides. Moreover, volatile organosulfur compounds of unpleasant odor are liberated as unavoidable byproducts. Combined with the cross-coupling reaction, the present sulfidation would allow easy and odorless access to (*Z*)-alkenes.[10] To our delight, the dodecylthio group proved to be comparable to other shorter alkylthio groups such as the methylthio group.[8] Treatment of **1b** with methylmagnesium bromide afforded (*Z*)-**8a** in 90% yield with retention of configuration (eq 2). Phenylation also proceeded smoothly, albeit partial inversion of configuration was observed. Attempted butylation resulted in low yield, producing 4-methoxystyrene mainly. Further optimization of reaction conditions is necessary.



Conclusion

Base-catalyzed hydrothiolation of alkynes proved to be a highly efficient method for the synthesis of alkenyl sulfides. Cesium carbonate shows the highest reactivity, although potassium carbonate is also useful with respect to its cost. DMSO is the choice of solvent. The products, alkenyl sulfides, recently attracted increasing attention as precursors for carbon–carbon bond formation reactions, the circumstance which emphasizes the utility of the present hydrothiolation reactions.

Experimental Section

Cesium-Mediated Addition of Thiol to Alkyne: A Typical Procedure. The reaction of dodecanethiol with phenylacetylene is representative (Table 1, entry 10). Cesium carbonate (0.016 g, 0.050 mmol) was placed in a 20-mL reaction flask under argon. Dimethyl sulfoxide (3.0 mL) and dodecanethiol (0.12 g, 0.60 mmol) were added at room tem-

(7) A stoichiometric amount of sodium hydroxide promoted a similar transformation: Water, M. S.; Cowen, J. A.; McWilliams, J. C.; Maligres, P. E.; Askin, D. *Tetrahedron Lett.* **2000**, *41*, 141–144.

(8) Okamura, H.; Miura, M.; Takei, H. *Tetrahedron Lett.* **1979**, *1*, 43–46.

(9) For review of sulfides in cross-coupling reactions: (a) Luh, T.-Y.; Ni, Z.-J. *Synthesis* **1990**, 89–103. (b) Liebeskind, L. S.; Srogl, J.; Savarin, C.; Polanco, C. *Pure Appl. Chem.* **2002**, *74*, 115–122. (c) Yu, Y.; Liebeskind, L. S. *J. Org. Chem.* **2004**, *69*, 3554–3557 and references cited therein.

(10) The ability of the long chain alkylthio group as a leaving group in cross-coupling reactions has scarcely been investigated: Miyazaki, T.; Han-ya, Y.; Tokuyama, H.; Fukuyama, T. *Synlett* **2004**, 477–480.

perature. After the mixture was stirred for 15 min, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (0.016 g, 0.10 mmol) was added. The whole mixture was stirred for 15 min. Finally, phenylacetylene (0.051 g, 0.50 mmol) was added and the resulting mixture was stirred for 4 h. Water (10 mL) was added, and the product was extracted with hexane/ethyl acetate (40:1, 3 × 10 mL). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Silica gel column purification of the crude oil provided 0.13 g of dodecyl styryl sulfide (**1a**, 0.43 mmol, *E*/*Z* = 7:93) in 86% yield.

Three-Component Coupling Reaction (Eq 1). Cesium fluoride (0.91 g, 6.0 mmol) and DMSO (10 mL) were placed in a 50-mL reaction flask under argon atmosphere. After CsF was completely dissolved, *tert*-butyldimethylsilyl dodecyl sulfide (**6**, 1.90 g, 6.0 mmol), benzaldehyde (1.27 g, 12 mmol), and diphenylacetylene (0.89 g, 5.0 mmol) were sequentially added. The resulting mixture was heated in an oil bath (85 °C). After being stirred for 4 h, the mixture was cooled to room temperature. Water (30 mL) was added, and the product was extracted with hexane/ethyl acetate (5:1, 3 × 30 mL). Concentration followed by purification on silica gel afforded **7** (2.02 g, 4.15 mmol, 83%) as a white solid.

Cross-Coupling Reaction of (*Z*)-1-Alkenyl Sulfide with a Grignard Reagent (Eq 2). $NiCl_2(PPh_3)_2$ (0.0098 g, 0.015 mmol) was placed in a 30-mL reaction flask under argon. Ether (3 mL) and **1b** (0.17 g, 0.50 mmol) were added. Methylmagnesium bromide (3.0 M in ether, 0.37 mL, 1.1 mmol) was then added at ambient temperature, and the resulting mixture was heated at reflux for 12 h. The reaction was quenched with water and the products were extracted with hexane/ethyl acetate (10:1, 3 × 3 mL). After evaporation, chromatographic purification on silica gel yielded *p*-(1-propenyl)anisole (**8a**, 0.067 g, 0.45 mmol, 90%, *E*/*Z* = 4:96).

Characterization Data. Spectral data for some products (**1k**,[11] **1m**,[12] **1n**,[13] **1o**[14]) were found in the literature.

Dodecyl styryl sulfide (1a, *E*/*Z* = 7:93): IR (neat) 3022, 2926, 2853, 1593, 1491, 1466, 1445, 1364, 849, 773, 725, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20−1.45 (m, 18H), 1.69 (tt, J = 7.5, 7.0 Hz, 2H), 2.78 (t, J = 7.5 Hz, 0.93 × 2H), 2.80 (t, J = 7.5 Hz, 0.07 × 2H), 6.25 (d, J = 10.5 Hz, 0.93 × 1H), 6.43 (d, J = 10.5 Hz, 0.93 × 1H), 6.46 (d, J = 16.0 Hz, 0.07 × 1H), 6.73 (d, J = 16.0 Hz, 0.07 × 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.35 (dd, J = 7.5, 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) for major isomer δ 14.1, 22.7, 28.6, 29.2, 29.3, 29.5, 29.57, 29.61, 29.63, 30.2, 31.9, 35.9, 125.2, 126.5, 127.7, 128.2, 128.6, 137.0. Found: C, 78.82; H, 10.82. Calcd for $C_{20}H_{32}S$: C, 78.88; H, 10.59.

4-[(*Z*)-2-Dodecylthioethenyl]anisole (1b): IR (neat) 2924, 2853, 1607, 1508, 1466, 1304, 1254, 1175, 1038, 831, 534 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.18−1.45 (m, 18H), 1.68 (t, J = 7.5, 7.5 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 3.81 (s, 3H), 6.11 (d, J = 11.0 Hz, 1H), 6.38 (d, J = 11.0 Hz, 1H), 6.89 (d, J = 9.0 Hz, 2H), 7.44 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.6, 29.2, 29.3, 29.5, 29.57, 29.61, 29.63, 30.2, 31.9, 35.8, 55.2, 113.7, 124.8, 125.1, 129.9, 129.7, 158.1. Found: C, 75.33; H, 10.27. Calcd for $C_{21}H_{34}OS$: C, 75.39; H, 10.24.

2-[(*Z*)-2-Dodecylthioethenyl]anisole (1c, mixture of two indivisible atropisomers): IR (neat) 2924, 2853, 2345, 1597, 1570, 1483, 1458, 1437, 1244, 1111, 1032, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20−1.44 (m, 18H), 1.67 (tt, J = 8.0, 8.0 Hz, 0.89 × 2H), 1.69 (tt, J = 7.5, 7.5 Hz, 0.11 × 2H), 2.75 (t, J = 8.0 Hz, 0.89 × 2H), 2.82 (t, J = 7.5 Hz, 0.11 × 2H), 3.84 (s, 0.89 × 3H), 3.84 (s, 0.11 × 3H), 6.28 (d, J = 11.0 Hz, 0.89 × 1H), 6.74 (d, J = 11.0 Hz, 0.89 × 1H), 6.77 (d, J = 7.5 Hz, 0.11 × 1H), 6.83−6.93 (m, 0.89 × 1H, 0.11 × 3H), 6.98 (dd, J = 7.5, 7.5 Hz, 0.89 × 1H), 7.17 (dd, J = 7.5, 7.5 Hz, 0.11 × 1H), 7.21 (dd, J = 7.5, 7.5 Hz, 0.89 × 1H), 7.32 (dd, J = 7.5, 7.5 Hz, 0.11 × 1H), 7.64 (dd, J = 7.5, 7.5 Hz, 0.89 × 1H); ^{13}C NMR ($CDCl_3$) for major isomer δ 14.1, 22.7, 28.6, 29.2, 29.3, 29.5, 29.57, 29.60, 29.62, 30.2, 31.9, 35.6, 55.4, 110.2, 119.8, 120.1, 125.9, 127.5, 128.0, 129.0, 156.4. Found: C, 75.62; H, 10.43. Calcd for $C_{21}H_{34}SO$: C, 75.39; H, 10.24.

(*Z*)-2-(4-Butylphenyl)ethenyl dodecyl sulfide (1d): IR (neat) 2924, 2853, 1591, 1560, 1510, 1466, 1414, 1377, 1362, 1234, 1123, 856, 833, 814, 783, 721, 683, 546 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H), 1.20−1.45 (m, 20H), 1.59 (tt, J = 7.8, 7.5 Hz, 2H), 1.68 (tt, J = 7.5, 7.5 Hz, 2H), 2.59 (t, J = 7.8 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 6.18 (d, J = 10.5 Hz, 1H), 6.41 (d, J = 10.5 Hz, 1H), 7.16 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.1, 22.3, 22.7, 28.6, 29.2, 29.3, 29.5, 29.58, 29.62, 29.64, 30.2, 31.9, 33.5, 35.4, 35.9, 125.2, 126.5, 128.3, 128.5, 134.5, 141.4. Found: C, 79.93; H, 11.41. Calcd for $C_{24}H_{40}S$: C, 79.93; H, 11.18.

4-[(*Z*)-2-Dodecylthioethenyl]aniline (1e): IR (Nujol) 3337, 2918, 2851, 1614, 1512, 1470, 1377, 1279, 1186, 1173, 1132, 827, 715, 679, 532 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.18−1.44 (m, 18H), 1.68 (tt, J = 7.5, 7.5 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H), 3.69 (s, 2H), 6.05 (d, J = 11.0 Hz, 1H), 6.34 (d, J = 11.0 Hz, 1H), 6.76 (d, J = 9.0 Hz, 2H), 7.34 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.6, 29.2, 29.3, 29.5, 29.58, 29.61, 29.63, 30.2, 31.9, 35.8, 114.8, 123.4, 125.3, 128.0, 129.9, 145.0. Found: C, 74.93; H, 10.41. Calcd for $C_{20}H_{33}NS$: C, 75.17; H, 10.41. Mp: 73.0−75.0 °C (amorphous solid).

Dodecyl 2-(4-trifluoromethylphenyl)ethenyl sulfide (1f, *E*/*Z* = 16:84): IR (neat) 2924, 2851, 1923, 1614, 1593, 1568, 1470, 1410, 1325, 1252, 1165, 1124, 1069, 1015, 930, 843, 793, 719, 756, 691, 594, 525, 507 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20−1.48 (m, 18H), 1.66−1.72 (m, 2H), 2.81 (t, J = 7.5 Hz, 0.84 × 2H), 2.83 (t, J = 7.0 Hz, 0.16 × 2H), 6.41 (d, J = 11.0 Hz, 0.84 × 1H), 6.43 (d, J = 15.5 Hz, 0.16 × 1H), 6.44 (d, J = 11.0 Hz, 0.84 × 1H), 6.88 (d, J = 15.5 Hz, 0.16 × 1H), 7.36 (d, J = 8.5 Hz, 0.84 × 2H), 7.53 (d, J = 8.5 Hz, 0.84 × 2H), 7.55−7.61 (m, 0.16 × 4 H); ^{13}C NMR ($CDCl_3$) for major isomer δ 14.1, 22.7, 28.5, 29.2, 29.3, 29.5, 29.57, 29.62, 29.63, 29.64, 30.2, 31.9, 36.0, 123.7, 125.4, 128.2, 128.6, 131.0, 140.5. Found: C, 67.87; H, 8.61. Calcd for $C_{21}H_{31}F_3S$: C, 67.71; H, 8.31. Mp: 20.0−25.0 °C (amorphous solid).

***N*,*N*-Diethyl-4-(2-dodecylthioethenyl)benzamide (1g, *E*/*Z* = 17:83):** IR (neat) 2926, 2853, 1632, 1595, 1553, 1423, 1364, 1348, 1285, 1221, 1094, 1069, 1018, 941, 845, 696, 571 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.05−1.46 (m, 24H), 1.70 (tt, J = 7.5, 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 0.83 × 2H), 2.82 (t, J = 7.5 Hz, 0.17 × 2H), 3.28 (s, 2H), 3.54 (s, 2H), 6.32 (d, J = 11.0 Hz, 0.83 × 1H), 6.42 (d, J = 11.0 Hz, 0.83 × 1H), 6.43 (d, J = 16.0 Hz, 0.17 × 1H), 6.79 (d, J = 16.0 Hz, 0.17 × 1H), 7.28−7.32 (m, 0.17 × 4H), 7.36 (d, J = 8.5 Hz, 0.83 × 2H), 7.51 (d, J = 8.5 Hz, 0.83 × 2H); ^{13}C NMR ($CDCl_3$) for major isomer δ 12.9, 14.1, 14.2, 22.6, 28.5, 29.1, 29.1, 29.50, 29.51, 29.55, 29.57, 30.2, 31.8, 36.0, 39.2, 43.2, 124.3, 126.3, 128.4, 129.0, 135.0, 137.8, 171.1. Found: C, 74.19; H, 10.38. Calcd for $C_{25}H_{41}NOS$: C, 74.39; H, 10.24.

Methyl 4-(2-dodecylthioethenyl)benzoate (1h, *E*/*Z* = 33:67): IR (Nujol) 2920, 2851, 1726, 1705, 1607, 1593, 1470, 1435, 1408, 1377, 1312, 1277, 1178, 1105, 932, 868, 781, 754, 718, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20−1.47 (m, 18H), 1.70 (tt, J = 7.5, 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 0.67 × 2H), 2.83 (t, J = 7.5 Hz, 0.33 × 2H), 3.90 (s, 0.33 × 3H), 3.91 (s, 0.67 × 3H), 6.42 (d, J = 11.0 Hz, 0.67 × 1H), 6.45 (d, J = 11.0 Hz, 0.67 × 1H), 6.43 (d, J = 15.5 Hz, 0.33 × 1H), 6.91 (t, J = 15.5 Hz, 0.33 × 1H), 7.32 (d, J = 8.0 Hz, 0.33 × 2H), 7.54 (d, J = 8.5 Hz, 0.67 × 2H), 7.95 (d, J = 8.0 Hz, 0.33 × 2H), 8.01 (d, J = 8.5 Hz, 0.67 × 2H); ^{13}C NMR ($CDCl_3$) for major isomer δ 14.1, 22.7, 28.5, 29.2, 29.3, 29.5,

(11) Hoshi, M.; Masuda, Y.; Arase, A. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 447−452.
(12) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Org. Chem*. **1994**, *59*, 2818−2823.
(13) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Org. Chem*. **1995**, *60*, 7941−7946.
(14) Silveira, C. C.; Perin, G.; Braga, A. L.; Dabdoub, M. J.; Jacob, R. G. *Tetrahedron* **1999**, *55*, 7421−7432.

29.56, 29.61, 29.62, 30.2, 31.9, 36.1, 52.0, 124.1, 127.6, 128.3, 129.5, 131.2, 141.5, 166.9. Found: C, 72.82; H, 9.64. Calcd for $C_{22}H_{34}O_2S$: C, 72.88; H, 9.45. Mp: 36.0−37.5 °C (amorphous solid).

4-(2-Dodecylthioethenyl)benzonitrile (1i, *E*/*Z* = 70:30): IR (Nujol) 2922, 2853, 2228, 1591, 1468, 1377, 1177, 937, 854, 829, 789, 721, 646, 550, 502, 488 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.20−1.47 (m, 18H), 1.70 (tt, J = 7.5, 7.5 Hz, 2H), 2.84 (t, J = 7.5 Hz, 0.70 × 2H), 2.83 (t, J = 7.5 Hz, 0.30 × 2H), 6.38 (d, J = 15.5 Hz, 0.70 × 1H), 6.40 (d, J = 11.0 Hz, 0.30 × 1H), 6.50 (d, J = 11.0 Hz, 0.30 × 1H), 6.94 (d, J = 15.5 Hz, 0.70 × 1H), 7.34 (d, J = 8.5 Hz, 0.70 × 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 0.30 × 2H); ^{13}C NMR ($CDCl_3$) for major isomer δ 14.1, 22.7, 28.8, 29.1, 29.2, 29.3, 29.5, 29.55, 29.60, 29.62, 31.9, 32.4, 109.4, 119.1, 123.5, 125.6, 130.9, 132.5, 141.5. Found: C, 76.48; H, 9.27. Calcd for $C_{21}H_{31}NS$: C, 76.54; H, 9.48. Mp: 42.5−43.5 °C (amorphous solid).

Methyl 3-(2-dodecylthioethenyl)benzoate (1j, *E*/*Z* = 13:87): IR (neat) 2924, 2853, 1724, 1578, 1421, 1277, 1177, 1109, 1086, 999, 762, 747, 673 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20−1.47 (m, 18H), 1.70 (tt, J = 7.5, 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 0.87 × 2H), 2.82 (t, J = 7.5 Hz, 0.13 × 2H), 3.92 (s, 0.13 × 3H), 3.93 (s, 0.87 × 3H), 6.35 (d, J = 11.0 Hz, 0.87 × 1H), 6.45 (d, J = 15.5 Hz, 0.13 × 1H), 6.46 (d, J = 11.0 Hz, 0.87 × 1H), 6.84 (d, J = 15.5 Hz, 0.13 × 1H), 7.36 (dd, J = 8.0, 8.0 Hz, 0.13 × 1H), 7.43 (dd, J = 8.0, 8.0 Hz, 0.87 × 1H), 7.45 (d, J = 8.0 Hz, 0.13 × 1H), 7.72 (d, J = 8.0 Hz, 0.87 × 1H), 7.84 (d, J = 8.0 Hz, 0.13 × 1H), 7.87 (d, J = 8.0 Hz, 0.87 × 1H), 7.97 (s, 0.13 × 1H), 8.12 (s, J = 0.87 × 1H); ^{13}C NMR ($CDCl_3$) for major isomer δ 14.1, 22.7, 28.5, 29.2, 29.3, 29.5, 29.55, 29.59, 29.61, 30.2, 31.9, 35.9, 52.1, 124.1, 127.4, 128.2, 129.3, 129.8, 130.1, 132.6, 137.3, 167.1. Found: C, 73.08; H, 9.25. Calcd for $C_{22}H_{34}O_2S$: C, 72.88; H, 9.45.

(*E*)-3-Phenyl-2-propenyl styryl sulfide (1*l*, *E*/*Z* = 8:92 with respect to the styryl moiety): IR (neat) 3024, 2918, 1597, 1491, 1443, 1418, 1362, 1225, 1074, 1028, 964, 910, 843, 773, 750, 729, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.58 (d, J = 7.5 Hz, 2H), 6.21−6.30 (m, 2H), 6.47 (d, J = 11.0 Hz, 0.92 × 1H), 6.56 (d, J = 15.5 Hz, 0.92 × 1H), 6.58 (d, J = 16.0 Hz, 0.08 × 1H), 6.74 (d, J = 16.0 Hz, 0.08 × 1H), 7.15−7.50 (m, 10H); ^{13}C NMR ($CDCl_3$) for major isomer δ 37.6, 125.2, 125.6, 126.0, 126.4, 126.7, 127.8, 128.2, 128.58, 128.59, 133.1, 136.4, 136.9. Found: C, 81.11; H, 6.50. Calcd for $C_{17}H_{16}S$: C, 80.90; H, 6.39.

Dodecyl 1,2-diphenylethenyl sulfide (1p, *E*/*Z* = 15:85): IR (neat) 3057, 3022, 2924, 2853, 1597, 1489, 1445, 1074, 1030, 939, 914, 764, 698, 669, 556, 509 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.06−1.36 (m, 18H), 1.41 (tt, J = 7.5, 7.5 Hz, 0.85 × 2H), 1.57 (tt, J = 7.5, 7.5 Hz, 0.15 × 2H), 2.39 (t, J = 7.5 Hz, 0.85 × 2H), 2.52 (t, J = 7.5 Hz, 0.15 × 2H), 6.72 (s, 0.15 × 1H), 6.79 (s, 0.85 × 1H), 6.91−7.75 (m, 10H); ^{13}C NMR ($CDCl_3$) for major isomer δ 14.1, 22.7, 28.5, 29.0, 29.3, 29.4, 29.5, 29.61, 29.63, 29.8, 31.9, 32.8, 127.1, 127.8, 128.0, 128.30, 128.31, 129.6, 131.9, 137.1, 137.9, 141.2. Found: C, 82.12; H, 9.75. Calcd for $C_{26}H_{36}S$: C, 82.04; H, 9.53.

Dodecyl 1-methyl-2-phenylethenyl sulfide (1q, *E*/*Z* = 22:78): IR (neat) 3022, 2924, 2853, 1599, 1572, 1491, 1466, 1441, 1375, 1115, 1074, 1032, 910, 829, 748, 721, 694, 525 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20−1.47 (m, 18H), 1.57 (tt, J = 7.5, 7.5 Hz, 0.78 × 2H), 1.68 (tt, J = 7.5, 7.5 Hz, 0.22 × 2H), 2.12 (s, 0.22 × 3H), 2.22 (s, 0.78 × 3H), 2.77 (t, J = 7.5 Hz, 0.78 × 2H), 2.81 (t, J = 7.5 Hz, 0.22 × 2H), 6.33 (s, 0.22 × 1H), 6.46 (s, 0.78 × 1H), 7.16−7.52 (m, 5H); ^{13}C NMR ($CDCl_3$) for major isomer δ 19.62, 19.63, 24.9, 28.9, 29.2, 29.3, 29.5, 29.56, 29.61, 29.62, 29.64, 30.0, 31.0, 126.3, 127.1, 127.9, 129.0, 132.8, 137.2. Found: C, 78.93; H, 10.63. Calcd for $C_{21}H_{34}S$: C, 79.18; H, 10.76.

2-Dodecylthio-3-phenyl-2-propenyl methyl ether (1r, *E*/*Z* = 17:83): IR (neat) 2924, 2853, 2820, 1599, 1491, 1445, 1192, 1117, 1084, 1032, 914, 847, 752, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.18−1.40 (m, 18H), 1.56 (tt, J = 7.5, 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 0.83 × 2H), 2.83 (t, J = 7.5 Hz, 0.17 × 2H), 3.39 (s, 0.17 × 3H), 3.41 (s, 0.83 × 3H), 4.17 (s, 0.17 × 2H), 4.20 (s, 0.83 × 2H), 6.49 (s, 0.17 × 1H), 6.73 (s, 0.83 × 1H), 7.15−7.38 (m, 3H), 7.60 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) for major isomer δ 14.1, 22.7, 28.8, 29.2, 29.3, 29.5, 29.55, 29.58, 29.61, 29.62, 29.9, 31.9, 57.5, 76.4, 127.1, 128.0, 129.4, 129.7, 132.9, 136.3. Found: C, 75.74; H, 10.18. Calcd for $C_{22}H_{36}OS$: C, 75.80; H, 10.41.

(*Z*)-2-Dodecylthio-3-phenyl-2-propen-1-ol (1s): IR (Nujol) 3285, 2922, 2853, 1591, 1464, 1445, 1377, 1115, 1101, 972, 849, 752, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.18−1.37 (m, 18H), 1.55 (tt, J = 7.5, 7.5 Hz, 2H), 1.94 (s, 1H), 2.76 (t, J = 7.5 Hz, 2H), 4.36 (s, 2H), 6.82 (s, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.35 (dd, J = 7.5, 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.7, 29.1, 29.3, 29.4, 29.5, 29.56, 29.57, 29.8, 31.3, 31.9, 66.9, 127.3, 128.0, 129.3, 129.8, 135.6, 136.1. Found: C, 75.16; H, 10.11. Calcd for $C_{21}H_{34}OS$: C, 75.39; H, 10.24. Mp: 38.0−39.5 °C (amorphous solid).

2-Dodecylthio-2-propen-1-ol (2a): IR (Nujol) 3213, 2922, 2853, 2729, 2332, 1605, 1468, 1377, 1298, 1217, 1126, 1067, 989, 856, 835, 762, 733, 719, 696, 638 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20−1.45 (m, 18H), 1.61−1.71 (m, 3H), 2.74 (t, J = 7.5 Hz, 2H), 4.18 (d, J = 6.5 Hz, 2H), 4.93 (s, 1H), 5.36 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.5, 29.0, 29.2, 29.3, 29.5, 29.57, 29.61, 29.63, 31.2, 31.9, 66.1, 108.0, 145.3. Found: C, 69.49; H, 11.40. Calcd for $C_{15}H_{30}OS$: C, 69.70; H, 11.70. Mp: 43.0−44.0 °C (amorphous solid).

(*Z*)-3-Dodecylthio-2-propen-1-ol (2b): IR (Nujol) 3414, 2924, 2855, 1595, 1460, 1377, 1120, 1041, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20−1.48 (m, 19H), 1.62 (tt, J = 7.5, 7.5 Hz, 2H), 2.67 (t, J = 7.5 Hz, 2H), 4.62 (t, J = 6.5 Hz, 2H), 5.75 (dt, J = 10.0, 6.5 Hz, 1H), 6.12 (d, J = 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.5, 29.2, 29.3, 29.5, 29.57, 29.62, 29.63, 30.3, 31.9, 34.3, 60.0, 127.1, 128.4. Mp: 43.5−44.5 °C (amorphous solid).

3-Dodecylthio-3-buten-1-ol (2c): IR (neat) 3358, 2924, 2853, 2683, 1603, 1466, 1439, 1377, 1148, 1047, 845, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.14−1.46 (m, 18H), 1.56−1.70 (m, 3H), 2.49 (t, J = 6.0 Hz, 2H), 2.71 (t, J = 7.0 Hz, 2H), 3.75−3.83 (m, 2H), 4.80 (s, 1H), 5.11 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.3, 27.8, 28.75, 28.83, 29.0, 29.1, 29.2, 29.26, 29.27, 31.0, 31.5, 40.6, 60.9, 107.1, 142.0. Found: C, 70.38; H, 11.60. Calcd for $C_{16}H_{32}OS$: C, 70.53; H, 11.84.

4-Dodecylthio-4-penten-1-ol (2d): IR (neat) 3348, 3092, 2924, 2853, 1601, 1466, 1441, 1377, 1205, 1148, 1042, 945, 908, 841, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.13−1.44 (m, 19H), 1.64 (tt, J = 7.5, 7.5 Hz, 2H), 1.82 (tt, J = 7.5, 7.5 Hz, 2H), 2.33 (t, J = 7.5 Hz, 2H), 2.70 (t, J = 7.5 Hz, 2H), 3.64−3.72 (m, 2H), 4.72 (s, 1H), 5.06 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 28.1, 29.1, 29.1, 29.3, 29.4, 29.49, 29.54, 29.56, 31.2, 31.6, 31.8, 33.8, 62.0, 105.6, 145.3. Found: C, 71.53; H, 12.10. Calcd for $C_{17}H_{34}OS$: C, 71.26; H, 11.96.

5-Dodecylthio-5-hexen-1-ol (2f): IR (neat) 3350, 2924, 2855, 2685, 1601, 1466, 1439, 1377, 1142, 1063, 991, 841, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.13−1.70 (m, 25H), 2.58 (t, J = 7.5 Hz, 2H), 2.69 (t, J = 7.5 Hz, 2H), 3.62−3.72 (m, 2H), 4.69 (s, 1H), 5.02 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.01, 22.57, 24.79, 28.14, 29.04, 29.10, 29.23, 29.39, 29.47, 29.51, 29.53, 31.08, 31.79, 31.89, 37.18, 62.61, 105.22, 145.55. Found: C, 71.84; H, 12.23. Calcd for $C_{18}H_{36}OS$: C, 71.93; H, 12.07.

(*E*)-3-Dodecylthio-1,2,3-triphenyl-2-propen-1-ol (7): IR (Nujol) 3522, 2851, 1599, 1495, 1443, 1377, 1323, 1219, 1175, 1063, 1036, 926, 901, 854, 777, 752, 741, 700, 648, 600, 544 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 3H), 1.01−1.35 (m, 20H), 1.84 (d, J = 7.0 Hz, 1H), 2.03−2.14 (m, 2H), 5.62 (d, J = 7.0 Hz, 1H), 6.91−6.70 (m, 2H), 7.01−7.05 (m, 2H), 7.14−7.22 (m, 3H), 7.23−7.29 (m, 3H), 7.35−7.40 (m, 1H), 7.44−7.49 (m, 2H), 7.52−7.56 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.5, 29.0, 29.3, 29.4, 29.5, 29.6, 30.0, 31.8, 31.9, 73.7, 125.8,

126.9, 127.3, 127.77, 127.82, 127.9, 128.6, 129.7, 130.3, 137.1, 137.6, 138.3, 140.7, 142.1. Found: C, 81.30; H, 8.67. Calcd for $C_{33}H_{42}OS$: C, 81.43; H, 8.70. Mp: 89.0−90.0 °C (amorphous solid).

Acknowledgment. This work is supported by Grants-in-Aid for Scientific Research, Young Scientists, and COE Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. K.T. acknowledges JSPS for financial support.

Supporting Information Available: NMR spectra of **1k**, **1m**, **1n**, and **1o**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050931Z