Stereoselective Synthesis of (*Z*)-1,2-Dithio-1-alkenes via Copper-Catalyzed Thiolation of (*Z*)-2-Bromovinyl Sulfides

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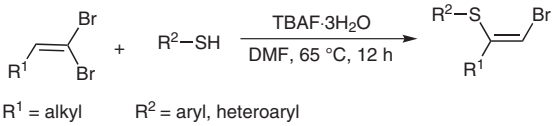
Abstract: We describe a new method for the stereoselective synthesis of (*Z*)-1,2-dithio-1-alkenes via copper-catalyzed cross-coupling of (*Z*)-2-bromovinyl sulfides and thiols. The desired products are obtained in good to excellent yields. The double bond geometry of the starting (*Z*)-2-bromovinyl sulfides is retained under these reaction conditions.

Key words: copper catalyst, cross-coupling, thiolation, (Z)-2-bromovinyl sulfide, (Z)-1,2-dithio-1-alkene

1,2-Dithio-1-alkenes are important intermediates in organic synthesis, useful precursors for optoelectronic materials, and chelate ligands in coordination chemistry.[1–4] Thus, the development of regio- and stereoselective syntheses of 1,2-dithio-1-alkenes is of practical interest. Various synthetic methods have been reported for these compounds.[5–18] Metal-catalyzed addition of a disulfide to a terminal alkyne is so far the most efficient method for the synthesis of 1,2-dithio-1-alkenes. The first example of the reaction involving terminal alkynes and a diaryl disulfide (Ar_2S_2) was reported by Sonoda in 1991.[14] The reaction was catalyzed by tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] giving the expected (*Z*)-1,2-bis(arylthio)-1-alkenes in good yields and stereoselectivity. Metal catalysts such as palladium,[6–8,11] rhodium,[9] and nickel[5] have been widely studied in the disulfidation of various alkynes normally leading to *Z*-configured products. Both aromatic disulfides and aliphatic disulfides can be used as the starting thio compounds. Gallium(III) chloride ($GaCl_3$) also promotes the disulfidation of alkynes, but leads to *E*-configured products selectively when a stoichiometric amount of the catalyst was used.[16] All these known methods are restricted to the synthesis of symmetric 1,2-dithio-1-alkenes having two identical thio groups.

Copper-catalyzed C–S coupling reactions have been demonstrated to be powerful tools for the formation of aryl C–S bonds[19–24] and vinyl C–S bonds.[25–32] Compared to vinyl iodides, vinyl bromides are less reactive. Examples of the coupling reactions of vinyl bromides with thiols in the literature are limited to 1-(2-bromovinyl)benzene derivatives.[29–31] The copper-catalyzed coupling of thiols with alkyl vinyl bromides has not been well-documented.[32] Recently, we reported the regio- and stereoselective synthesis of *N*-fused heterocycles and 1,2-hetero-disubstituted alkenes from 1,1-dibromo-1-alkenes using a copper catalyst.[33,34] (*Z*)-2-Bromovinyl sulfides were readily available by the reactions of 1,1-dibromo-1-alkenes with thiols mediated by tetrabutylammonium fluoride (Scheme 1).[33] These bromovinyl sulfides bearing a bromine atom at the double bond offer opportunities for the introduction of another sulfide group through metal-catalyzed C(sp^2)–S coupling reactions. Herein, we describe a stereoselective synthesis of (*Z*)-1,2-dithio-1-alkenes via the copper-catalyzed cross-coupling of thiols with bromovinyl sulfides.



R^1 = alkyl R^2 = aryl, heteroaryl

Scheme 1 Tetrabutylammonium fluoride mediated reactions of 1,1-dibromo-1-alkenes with thiols

As shown in Table 1, the thiolation of (*Z*)-2-bromovinyl sulfide **1a** and 4-toluenethiol (**2a**) could be carried out by using copper(I) oxide (Cu_2O) (10 mol%), *N*,*N*′-dimethylethylenediamine (DMEDA) (15 mol%) and two equivalents of cesium carbonate in *N*,*N*-dimethylformamide. (*Z*)-1,2-Dithio-1-alkene **3a** was obtained in 82% yield and the *Z*-configuration of the double bond was confirmed by NOESY measurements. To explore the scope of the reaction, we examined the cross-coupling of a number of substituted (*Z*)-2-bromovinyl sulfides with various aromatic thiols under the same catalytic conditions. The results are listed in Table 1.

In general, we were able to obtain (*Z*)-1,2-diarylthio-1-alkenes bearing two identical or two different arylthio groups in up to 91% yield at 120 °C. The carbon–sulfur coupling of **1a** with various substituted thiophenols gave high conversions and 75–85% isolated yields of products (Table 1, entries 1–4). Naphthalene-2-thiol (**2e**) coupled with **1a** smoothly giving the desired (*Z*)-1,2-dithio-1-alkene **3e** in 81% isolated yield (Table 1, entry 5). Sulfur-containing heterocycles occur in many compounds of biological interest, thus we attempted to broaden the scope of our methodology to heterocyclic thiols. 2-Mercaptopyri-

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dine (**2f**) and 2-mercaptothiophene (**2g**) were coupled with **1a** affording the desired products in 70% and 88% isolated yields, respectively (Table 1, entries 6 and 7). Unfortunately, no product was obtained when the coupling of **1a** was attempted with 4-nitrobenzenethiol (**2h**) even at higher temperatures, probably due to the low nucleophilicity of 4-nitrobenzenethiolate (Table 1, entry 8). The thiolation of vinyl bromides bearing different aryl and heteroaryl sulfide substituents with 4-toluenethiol (**2a**) was also evaluated (Table 1, entries 9–14). All the reactions proceeded smoothly, affording the corresponding products **3i**–**n** in 77–89% isolated yields. Compounds **3i**–**n** are structural isomers of **3b**–**g**. Thus both isomeric (*Z*)-1,2-dithio-1-alkenes could be easily prepared by appropriate choice of the bromovinyl sulfides and thiols. In contrast, unsymmetric (*Z*)-1,2-dithio-1-alkenes could not be prepared via disulfidation of alkynes since disulfidation of unsymmetric diaryl disulfides (Ar^1SSAr^2) would afford product mixtures without any selectivity. When vinyl bromides possessing different alkyl substituents such as 1-hexyl, isopropyl, isobutyl, *tert*-butyl, and cyclohexyl were reacted with 4-toluenethiol (**2a**), good to excellent yields of the corresponding products were obtained (Table 1, entries 15–19). It would appear that the bulkiness of the alkyl group had no effect on the reactions. Aromatic bromovinyl sulfides could not be generated according to our reported methodology,[33] thus we did not extend the reaction to these substrates. Although symmetric (*Z*)-1,2-dithio-1-alkenes such as **3a** and **3o**–**s** could also be synthesized by metal-catalyzed disulfidation of alkynes, these reactions usually require expensive palladium or rhodium as catalysts in combination with environmentally unfriendly phosphines as ligands.[5–9,11]

Table 1 Thiolation of (*Z*)-2-Bromovinyl Sulfides with Aromatic Thiols[a]

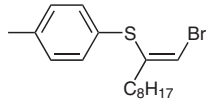
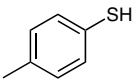
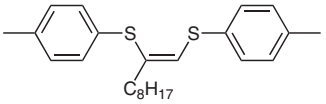
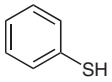
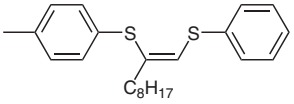
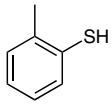
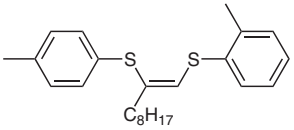
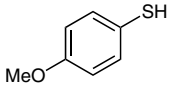
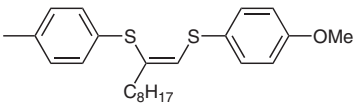
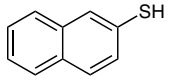
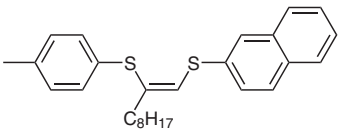
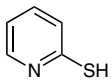
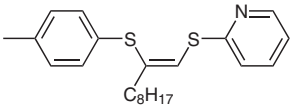
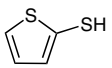
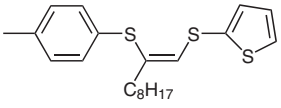
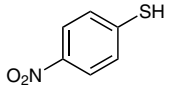
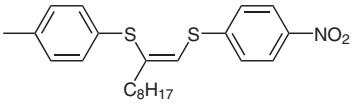
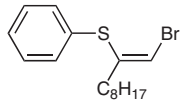
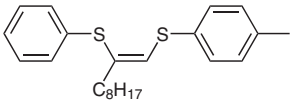
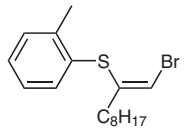
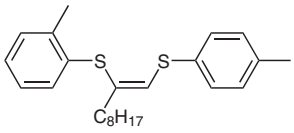
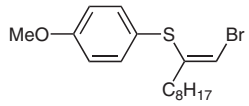
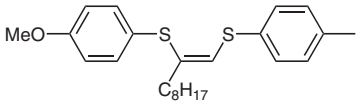
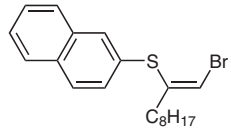
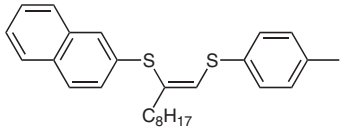
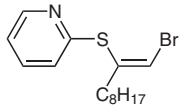
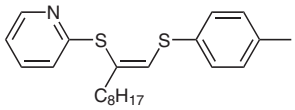
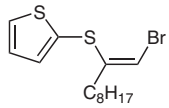
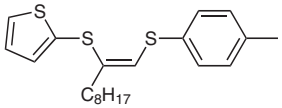
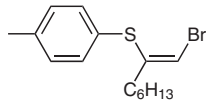
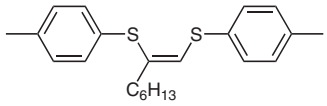
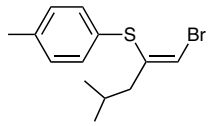
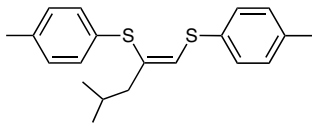
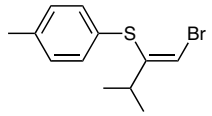
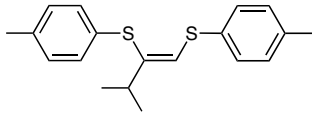
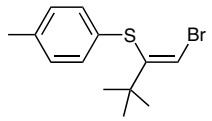
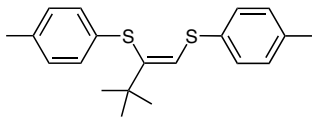
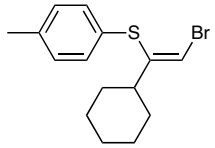
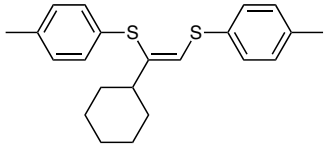
Entry	(*Z*)-2-Bromovinyl sulfide	Aromatic thiol	Product	Yield (%)
1	**1a** 	**2a** 	**3a** 	82
2	**1a**	**2b** 	**3b** 	85
3	**1a**	**2c** 	**3c** 	84
4	**1a**	**2d** 	**3d** 	75[b]
5	**1a**	**2e** 	**3e** 	81
6	**1a**	**2f** 	**3f** 	70
7	**1a**	**2g** 	**3g** 	88
8	**1a**	**2h** 	**3h** 	–
9	**1b** 	**2a**	**3i** 	84

Table 1 Thiolation of (*Z*)-2-Bromovinyl Sulfides with Aromatic Thiols[a] (continued)

Entry	(*Z*)-2-Bromovinyl sulfide	Aromatic thiol	Product	Yield (%)
10	**1c** 	**2a**	**3j** 	87
11	**1d** 	**2a**	**3k** 	77[b]
12	**1e** 	**2a**	**3l** 	89
13	**1f** 	**2a**	**3m** 	89
14	**1g** 	**2a**	**3n** 	77
15	**1h** 	**2a**	**3o** 	84
16	**1i** 	**2a**	**3p** 	87
17	**1j** 	**2a**	**3q** 	91
18	**1k** 	**2a**	**3r** 	88
19	**1l** 	**2a**	**3s** 	86

[a] Reaction conditions: (*Z*)-2-bromovinyl sulfide (0.5 mmol), aromatic thiol (0.75 mmol), Cu_2O (10 mol%), DMEDA (15 mol%), Cs_2CO_3 (2 equiv), DMF (1.5 mL), 120 °C, 24 h.
[b] Reaction at 80 °C, 36 h.

Using the reaction conditions described above, we were also able to prepare (*Z*)-1,2-alkylthio/arylthio-1-alkenes in excellent yields from (*Z*)-2-bromovinyl sulfides and alkyl thiols. The results are summarized in Table 2. (*Z*)-2-Bromovinyl sulfide (**1a**) reacted with benzyl thiol (**2i**), cyclohexane thiol (**2j**), and linear aliphatic chain thiols **2k**,**l** at 120 °C in the presence of two equivalents of cesium carbonate to afford the corresponding (*Z*)-1,2-dithio-1-alkenes **3t**–**w** in excellent yields (Table 2, entries 1–4). In the case of cyclohexane thiol, a 94% yield of the desired product **3u** was obtained. The thiolation with aliphatic thiols also showed excellent stereoselectivity, and as with aromatic thiols, we did not observe the formation of (*E*)-1,2-dithio-1-alkenes.

To examine the substituent compatibility of (*Z*)-2-bromovinyl sulfides in the thiolation reaction, a number of (*Z*)-2-bromovinyl sulfides **1b**–**l** were reacted with octane-1-thiol (**2k**) in the presence of copper(II) oxide (10 mol%)

and *N*,*N*′-dimethylethylenediamine (15 mol%) at 120 °C. In general, the alkyl thiols were more reactive than aryl thiols as was demonstrated by the higher isolated yields obtained. This was to be expected since alkyl thiolates are more nucleophilic than aryl thiolates. The reactions of **1b–l** and **2k** proceeded with complete conversion into the desired disulfides in excellent yields. Both electron-rich and electron-poor substituents on the aryl and heteroaryl groups were well tolerated. In addition, steric hindrance had little influence on the thiolation reaction (Table 2, entries 12–14). The *Z*-configuration of the products was confirmed by NOESY experiments. In the NOESY spectra of **3t** and **3y**, the alkene protons exhibited cross peaks with the adjacent methylene protons of the octyl groups (see Supporting Information).[9,35] The reaction of a 1,2-dibromoalkene with aliphatic thiols often gave a mixture of an alkynyl sulfide and a bromovinyl sulfide which could not be separated by column chromatography.[33] Therefore, we did not study the synthesis of 1,2-dialkylthioalkenes.

Table 2 Thiolation of (*Z*)-2-Bromovinyl Sulfides with Alkyl Thiols[a]

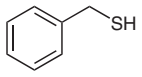
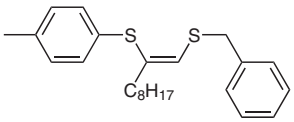
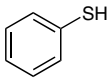
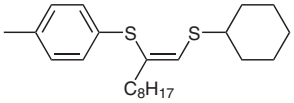
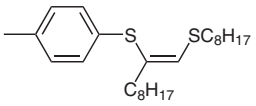
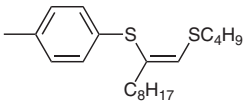
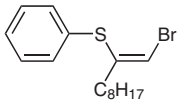
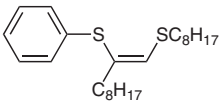
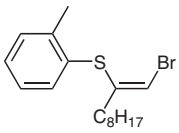
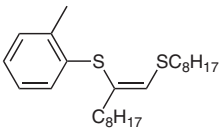
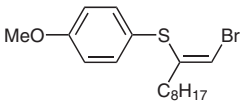
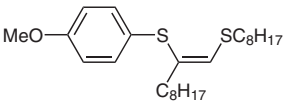
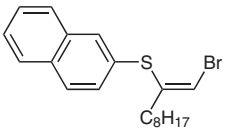
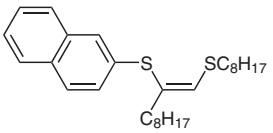
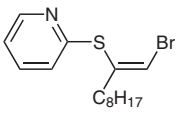
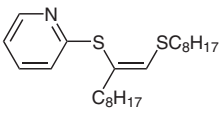
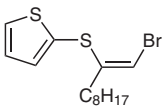
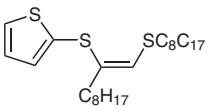
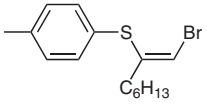
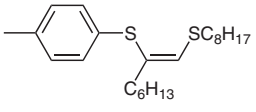
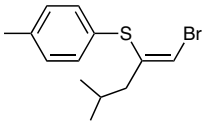
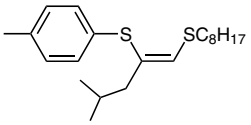
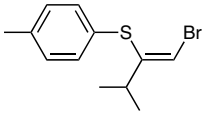
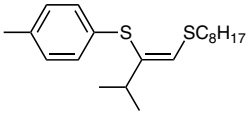
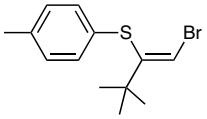
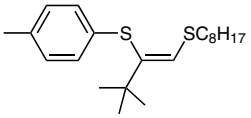
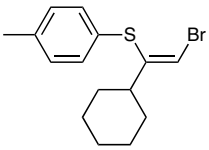
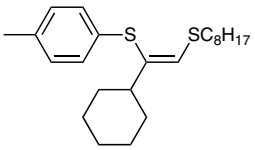
Entry	(*Z*)-2-Bromovinyl sulfide	Alkyl thiol	Product	Yield (%)
1	**1a**	**2i** 	**3t** 	83
2	**1a**	**2j** 	**3u** 	94
3	**1a**	**2k** $H_{17}C_8SH$	**3v** 	91
4	**1a**	**2l** H_9C_4SH	**3w** 	89
5	**1b** 	**2k**	**3x** 	92
6	**1c** 	**2k**	**3y** 	89
7	**1d** 	**2k**	**3z** 	87[b]
8	**1e** 	**2k**	**3aa** 	90
9	**1f** 	**2k**	**3bb** 	92
10	**1g** 	**2k**	**3cc** 	93
11	**1h** 	**2k**	**3dd** 	90

Table 2 Thiolation of (*Z*)-2-Bromovinyl Sulfides with Alkyl Thiols[a] (continued)

Entry	(*Z*)-2-Bromovinyl sulfide	Alkyl thiol	Product	Yield (%)
12	**1i** 	**2k**	**3ee** 	97
13	**1j** 	**2k**	**3ff** 	95
14	**1k** 	**2k**	**3gg** 	95
15	**1l** 	**2k**	**3hh** 	93

[a] Reaction conditions: (*Z*)-2-bromovinyl sulfide (0.5 mmol), alkyl thiol (0.75 mmol), Cu_2O (10 mol%), DMEDA (15 mol%), Cs_2CO_3 (2 equiv), DMF (1.5 mL), 120 °C, 24 h.
[b] Reaction at 80 °C, 36 h.

In conclusion, we have described a concise synthetic methodology for the stereoselective synthesis of (*Z*)-1,2-dithio-1-alkenes. Both symmetric and unsymmetric (*Z*)-1,2-dithio-1-alkenes have been obtained via copper-catalyzed thiolation of (*Z*)-2-bromovinyl sulfides in very good to excellent yields. The copper-catalyzed C–S coupling offers a novel route to (*Z*)-1,2-dithio-1-alkenes using an inexpensive catalyst and readily available starting materials. Further investigation of the utility of this method and of the obtained products is currently in progress.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ using a Bruker Avance 400 spectrometer. Chemical shifts (δ) are expressed in ppm downfield relative to TMS (0 ppm) and coupling constants (*J*) are given in Hz. The following abbreviations are used to describe the signal patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, td = triplet of doublets, m = multiplet. HRMS were obtained using a Waters GCT Premier TOF mass spectrometer with EI source. Column chromatography was performed using high purity silica gel (60 Å, 200–300 mesh). Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. (*Z*)-2-Bromovinyl sulfides were prepared according to our previously reported method.[33]

(*Z*)-(1-Bromodec-1-en-2-yl)(*o*-tolyl)sulfane (1c)

Light yellow oil; yield: 155 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.2 Hz, 1 H), 7.24–7.23 (m, 2 H), 7.17–7.13 (m, 1 H), 6.29 (s, 1 H), 2.40 (s, 3 H), 2.00 (t, *J* = 7.4 Hz, 2 H), 1.40–1.33 (m, 2 H), 1.27–1.12 (m, 10 H), 0.87 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.3, 141.3, 134.3, 130.9, 130.4, 128.5, 126.3, 103.3, 35.8, 31.7, 29.1, 29.0, 28.6, 28.0, 22.5, 20.6, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{17}H_{25}BrS$: 340.0860; found: 340.0858.

(*Z*)-(1-Bromodec-1-en-2-yl)(4-methoxyphenyl)sulfane (1d)

Light yellow oil; yield: 157 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.0 Hz, 2 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 6.13 (s, 1 H), 3.83 (s, 3 H), 2.04 (t, *J* = 7.6 Hz, 2 H), 1.38–1.35 (m, 2 H), 1.28–1.13 (m, 10 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 143.5, 136.1, 121.8, 114.5, 100.5, 55.2, 35.5, 31.7, 29.0, 28.9, 28.6, 28.1, 22.5, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{17}H_{25}BrOS$: 356.0809; found: 356.0808.

(*Z*)-(1-Bromodec-1-en-2-yl)(naphthalen-2-yl)sulfane (1e)

Light yellow oil; yield: 170 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (s, 1 H), 7.87–7.81 (m, 3 H), 7.55–7.49 (m, 3 H), 6.40 (s, 1 H), 2.20 (t, *J* = 7.4 Hz, 2 H), 1.48–1.45 (m, 2 H), 1.29–1.14 (m, 10 H), 0.89 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 133.5, 132.5, 132.0, 129.9, 129.4, 128.6, 127.7, 127.5, 126.6, 126.5, 104.4, 36.3, 31.7, 29.1, 29.0, 28.6, 28.1, 22.5, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{20}H_{25}BrS$: 376.0860; found: 376.0864.

(*Z*)-2-[(1-Bromodec-1-en-2-yl)thio]thiophene (1g)

Light yellow oil; yield: 148 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 5.2 Hz, 1 H), 7.25 (d, *J* = 3.6 Hz, 1 H), 7.04 (t, *J* = 4.4 Hz, 1 H), 6.11 (s, 1 H), 2.09 (t, *J* = 7.4 Hz, 2 H), 1.48–1.41 (m, 2 H), 1.32–1.18 (m, 10 H), 0.89 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 136.9, 131.5, 128.8, 127.6, 100.0, 35.1, 31.7, 29.1, 29.0, 28.7, 28.3, 22.6, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{14}H_{21}BrS_2$: 332.0268; found: 332.0265.

(*Z*)-(1-Bromo-3,3-dimethylbut-1-en-2-yl)(*p*-tolyl)sulfane (1k)

Light yellow oil; yield: 133 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.06 (s, 1 H), 2.37 (s, 3 H), 1.32 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 135.0, 132.2, 129.6, 126.9, 115.7, 41.3, 29.2, 21.0.

HRMS (TOF): *m*/*z* calcd for $C_{13}H_{17}BrS$: 284.0234; found: 284.0239.

(*Z*)-Dec-1-ene-1,2-diylbis(*p*-tolylsulfane) (3a);[33] Typical Procedure

(*Z*)-(1-Bromodec-1-en-2-yl)(*p*-tolyl)sulfane (**1a**) (171 mg, 0.5 mmol) was added to a stirred solution of 4-toluenethiol (**2a**) (70 mg, 0.75 mmol), Cu_2O (7 mg, 0.05 mmol), DMEDA (8 μL, 0.075 mmol), Cs_2CO_3 (326 mg, 1 mmol) in DMF (2 mL) under N_2. The resulting mixture was stirred at 120 °C for 24 h. After being cooled to r.t., the mixture was diluted with H_2O (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The crude residue was purified by flash column chromatography (eluent: PE–EtOAc, 50:1).

Light yellow oil; yield: 157 mg (82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.27 (m, 4 H), 7.13–7.08 (m, 4 H), 6.45 (s, 1 H), 2.32 (s, 3 H), 2.31 (s, 3 H), 2.20 (t, *J* = 7.2 Hz, 2 H), 1.49–1.46 (m, 2 H), 1.29–1.20 (m, 10 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.12, 137.11, 134.7, 132.8, 131.5, 130.4, 130.3, 130.1, 130.0, 128.8, 37.2, 32.1, 29.6, 29.5, 29.1, 28.8, 22.9, 21.4, 21.3, 14.4.

(*Z*)-Phenyl[2-(*p*-tolylthio)dec-1-en-1-yl]sulfane (3b)

Light yellow oil; yield: 157 mg (85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.2 Hz, 2 H), 7.33–7.28 (m, 4 H), 7.22 (t, *J* = 7.2 Hz, 1 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 6.48 (s, 1 H), 2.32 (s, 3 H), 2.21 (t, *J* = 7.2 Hz, 2 H), 1.50–1.46 (m, 2 H), 1.30–1.20 (m, 10 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0, 136.1, 135.7, 131.3, 129.9, 129.7, 129.5, 129.0, 126.9, 126.6, 36.8, 31.8, 29.2, 29.1, 28.8, 28.5, 22.6, 21.1, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{23}H_{30}S_2$: 370.1789; found: 370.1799.

(*Z*)-*p*-Tolyl[1-(*o*-tolylthio)dec-1-en-2-yl]sulfane (3c)

Light yellow oil; yield: 161 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.43 (m, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.24–7.18 (m, 3 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 6.39 (s, 1 H), 2.45 (s, 3 H), 2.36 (s, 3 H), 2.23 (t, *J* = 7.4 Hz, 2 H), 1.52–1.49 (m, 2 H), 1.33–1.23 (m, 10 H), 0.90 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 137.0, 136.1, 135.0, 131.4, 130.3, 130.0, 129.9, 129.7, 126.9, 126.6, 126.5, 36.7, 31.8, 29.2, 29.1, 28.7, 28.5, 22.6, 21.1, 20.6, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{24}H_{32}S_2$: 384.1945; found: 384.1949.

(*Z*)-(4-Methoxyphenyl)[2-(*p*-tolylthio)dec-1-en-1-yl]sulfane (3d)

Light yellow oil; yield: 150 mg (75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.8 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 6.89 (d, *J* = 9.2 Hz, 2 H), 6.43 (s, 1 H), 3.81 (s, 3 H), 2.35 (s, 3 H), 2.20 (t, *J* = 7.2 Hz, 2 H), 1.50–1.47 (m, 2 H), 1.31–1.22 (m, 10 H), 0.89 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 136.7, 133.0, 132.5, 130.9, 130.1, 130.0, 129.6, 126.3, 114.7, 55.3, 36.8, 31.8, 29.2, 29.1, 28.7, 28.5, 22.6, 21.0, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{24}H_{32}OS_2$: 400.1895; found: 400.1900.

(*Z*)-Naphthalen-2-yl[2-(*p*-tolylthio)dec-1-en-1-yl]sulfane (3e)

Light yellow oil; yield: 170 mg (81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1 H), 7.84–7.79 (m, 3 H), 7.53–7.46 (m, 3 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 6.60 (s, 1 H), 2.37 (s, 3 H), 2.27 (t, *J* = 7.4 Hz, 2 H), 1.55–1.52 (m, 2 H), 1.33–1.25 (m, 10 H), 0.90 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1, 136.4, 133.7, 133.4, 132.0, 131.4, 129.8, 129.7, 128.6, 127.7, 127.5, 127.4, 127.2, 126.6, 126.4, 125.9, 36.8, 31.8, 29.2, 29.1, 28.8, 28.5, 22.6, 21.1, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{27}H_{32}S_2$: 420.1945; found: 420.1951.

(*Z*)-2-{[2-(*p*-Tolylthio)dec-1-en-1-yl]thio}pyridine (3f)

Light yellow oil; yield: 130 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 4.0 Hz, 1 H), 7.53 (td, *J* = 8.0, 1.6 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.16–7.12 (m, 3 H), 7.05–7.02 (m, 1 H), 6.73 (s, 1 H), 2.40 (t, *J* = 7.6 Hz, 2 H), 2.36 (s, 3 H), 1.61–1.55 (m, 2 H), 1.29–1.26 (m, 10 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 149.6, 140.3, 137.7, 136.4, 132.4, 129.9, 129.7, 121.5, 120.0, 117.7, 33.1, 31.8, 29.3, 29.1, 29.0, 28.1, 22.6, 21.1, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{22}H_{29}NS_2$: 371.1741; found: 371.1747.

(*Z*)-2-{[2-(*p*-Tolylthio)dec-1-en-1-yl]thio}thiophene (3g)

Light yellow oil; yield: 165 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 5.6 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 3.2 Hz, 1 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 7.02–7.00 (m, 1 H), 6.40 (s, 1 H), 2.35 (s, 3 H), 2.17 (t, *J* = 7.6 Hz, 2 H), 1.49–1.45 (m, 2 H), 1.31–1.22 (m, 10 H), 0.89 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.9, 133.5, 132.8, 132.7, 131.1, 130.9, 129.8, 129.7, 129.2, 127.6, 36.6, 31.8, 29.2, 29.1, 28.7, 28.3, 22.6, 21.1, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{21}H_{28}S_3$: 376.1353; found: 376.1354.

(*Z*)-Phenyl[1-(*p*-tolylthio)dec-1-en-2-yl]sulfane (3i)

Light yellow oil; yield: 156 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.32 (t, *J* = 8.0 Hz, 2 H), 7.24 (t, *J* = 7.2 Hz, 1 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.57 (s, 1 H), 2.36 (s, 3 H), 2.26 (t, *J* = 7.2 Hz, 2 H), 1.53–1.50 (m, 2 H), 1.32–1.24 (m, 10 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0, 133.9, 133.0, 132.1, 130.5, 130.3, 130.2, 129.8, 128.9, 126.6, 37.1, 31.8, 29.2, 29.1, 28.8, 28.5, 22.6, 21.0, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{23}H_{30}S_2$: 370.1789; found: 370.1785.

(*Z*)-*o*-Tolyl[1-(*p*-tolylthio)dec-1-en-2-yl]sulfane (3j)

Light yellow oil; yield: 167 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.35 (m, 3 H), 7.24–7.22 (m, 1 H), 7.21–7.16 (m, 4 H), 6.55 (s, 1 H), 2.46 (s, 3 H), 2.38 (s, 3 H), 2.19 (t, *J* = 7.4 Hz, 2 H), 1.53–1.49 (m, 2 H), 1.34–1.25 (m, 10 H), 0.92 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.3, 136.8, 133.6, 132.6, 132.4, 131.2, 130.3, 130.1, 129.8, 128.8, 127.0, 126.3, 36.8, 31.8, 29.3, 29.2, 28.8, 28.5, 22.6, 21.0, 20.5, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{24}H_{32}S_2$: 384.1945; found: 384.1956.

(*Z*)-(4-Methoxyphenyl)[1-(*p*-tolylthio)dec-1-en-2-yl]sulfane (3k)

Light yellow oil; yield: 154 mg (77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.2 Hz, 2 H), 7.33 (d, *J* = 7.2 Hz, 2 H), 7.15 (d, *J* = 7.6 Hz, 2 H), 6.87 (d, *J* = 7.2 Hz, 2 H), 6.36 (s, 1 H), 3.81 (s, 3 H), 2.35 (s, 3 H), 2.16 (t, *J* = 7.2 Hz, 2 H), 1.49–1.46 (m, 2 H), 1.29–1.22 (m, 10 H), 0.89 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 136.7, 136.0, 133.9, 132.5, 129.9, 129.8, 125.8, 123.8, 114.4, 55.2, 36.4, 31.8, 29.2, 29.1, 28.7, 28.4, 22.6, 21.0, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{24}H_{32}OS_2$: 400.1895; found: 400.1898.

(*Z*)-Naphthalen-2-yl[1-(*p*-tolylthio)dec-1-en-2-yl]sulfane (3l)
Light yellow oil; yield: 187 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 1 H), 7.85–7.80 (m, 3 H), 7.54–7.47 (m, 3 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 6.67 (s, 1 H), 2.39 (s, 3 H), 2.33 (t, *J* = 7.6 Hz, 2 H), 1.61–1.56 (m, 2 H), 1.33–1.25 (m, 10 H), 0.92 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0, 133.7, 132.9, 132.2, 132.1, 131.5, 130.8, 130.3, 129.9, 128.7, 128.5, 128.0, 127.7, 127.3, 126.5, 125.9, 37.2, 31.8, 29.3, 29.2, 28.8, 28.5, 22.6, 21.1, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{27}H_{32}S_2$: 420.1945; found: 420.1948.

(*Z*)-2-{[1-(*p*-Tolylthio)dec-1-en-2-yl]thio}pyridine (3m)
Light yellow oil; yield: 165 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 4.4 Hz, 1 H), 7.52 (td, *J* = 8.0, 1.6 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 1 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 7.02–6.99 (m, 1 H), 6.77 (s, 1 H), 2.42 (t, *J* = 7.6 Hz, 2 H), 2.32 (s, 3 H), 1.56–1.51 (m, 2 H), 1.23 (br m, 10 H), 0.86 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 149.8, 137.2, 136.5, 135.6, 131.6, 130.5, 129.8, 129.2, 121.8, 119.9, 38.3, 31.8, 29.2, 29.1, 28.9, 28.5, 22.6, 21.0, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{22}H_{29}NS_2$: 371.1741; found: 371.1748.

(*Z*)-2-{[1-(*p*-Tolylthio)dec-1-en-2-yl]thio}thiophene (3n)
Light yellow oil; yield: 145 mg (77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 5.2 Hz, 1 H), 7.33 (d, *J* = 7.6 Hz, 2 H), 7.23 (d, *J* = 3.2 Hz, 1 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 7.03–7.01 (m, 1 H), 6.28 (s, 1 H), 2.36 (s, 3 H), 2.19 (t, *J* = 7.4 Hz, 2 H), 1.54–1.51 (m, 2 H), 1.31–1.25 (m, 10 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0, 136.8, 135.1, 132.3, 130.9, 130.2, 129.8, 129.7, 127.4, 124.3, 36.0, 31.8, 29.2, 29.1, 28.8, 28.5, 22.6, 21.0, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{21}H_{28}S_3$: 376.1353; found: 376.1357.

(*Z*)-Oct-1-ene-1,2-diylbis(*p*-tolylsulfane) (3o)[11]
Light yellow oil; yield: 150 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.48 (s, 1 H), 2.35 (s, 3 H), 2.34 (s, 3 H), 2.22 (t, *J* = 7.8 Hz, 2 H), 1.51–1.46 (m, 2 H), 1.29–1.22 (m, 6 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.8, 134.3, 132.4, 131.1, 130.1, 129.8, 129.7, 128.4, 36.8, 31.5, 28.4, 22.5, 21.0, 20.9, 14.0.

(*Z*)-(4-Methylpent-1-ene-1,2-diyl)bis(*p*-tolylsulfane) (3p)
Light yellow oil; yield: 143 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.6 Hz, 2 H), 7.32 (d, *J* = 7.6 Hz, 2 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 7.14 (d, *J* = 7.6 Hz, 2 H), 6.47 (s, 1 H), 2.36 (s, 6 H), 2.09 (d, *J* = 6.8 Hz, 2 H), 1.96–1.90 (m, 1 H), 0.87 (s, 3 H), 0.85 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.8, 133.2, 132.4, 131.2, 130.1, 130.0, 129.8, 129.7, 129.4, 46.0, 26.9, 22.0, 21.1, 21.0.

HRMS (TOF): *m*/*z* calcd for $C_{20}H_{24}S_2$: 328.1319; found: 328.1328.

(*Z*)-(3-Methylbut-1-ene-1,2-diyl)bis(*p*-tolylsulfane) (3q)
Light yellow oil; yield: 143 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 6.61 (s, 1 H), 2.51–2.44 (m, 1 H), 2.32 (s, 3 H), 2.30 (s, 3 H), 1.12 (s, 3 H), 1.10 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 137.0, 136.1, 132.3, 131.1, 130.7, 130.4, 129.8, 129.7, 129.5, 35.6, 22.2, 21.0.

HRMS (TOF): *m*/*z* calcd for $C_{19}H_{22}S_2$: 314.1163; found: 314.1160.

(*Z*)-(3,3-Dimethylbut-1-ene-1,2-diyl)bis(*p*-tolylsulfane) (3r)[36]
Light yellow oil; yield: 144 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.92 (s, 1 H), 2.30 (s, 3 H), 2.28 (s, 3 H), 1.20 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 137.2, 136.2, 134.7, 132.5, 132.2, 130.7, 129.8, 129.6, 126.7, 39.9, 29.5, 21.1, 21.0.

(*Z*)-(1-Cyclohexylethene-1,2-diyl)bis(*p*-tolylsulfane) (3s)
Light yellow oil; yield: 152 mg (86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 7.6 Hz, 2 H), 7.11 (d, *J* = 7.6 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 6.62 (s, 1 H), 2.32 (s, 3 H), 2.30 (s, 3 H), 2.09 (t, *J* = 11.2 Hz, 1 H), 1.91 (d, *J* = 12.8 Hz, 2 H), 1.71 (d, *J* = 10.8 Hz, 2 H), 1.61 (d, *J* = 8.0 Hz, 1 H), 1.29–1.08 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0, 136.8, 135.8, 132.4, 131.8, 131.3, 130.3, 129.8, 129.6, 129.0, 45.8, 32.8, 26.4, 26.1, 21.0.

HRMS (TOF): *m*/*z* calcd for $C_{22}H_{26}S_2$: 354.1476; found: 354.1478.

(*Z*)-Benzyl[2-(*p*-tolylthio)dec-1-en-1-yl]sulfane (3t)
Light yellow oil; yield: 159 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 5 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 6.27 (s, 1 H), 3.97 (s, 2 H), 2.35 (s, 3 H), 2.13 (t, *J* = 7.6 Hz, 2 H), 1.46–1.39 (m, 2 H), 1.32–1.19 (m, 10 H), 0.92 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 136.5, 133.1, 130.7, 130.2, 129.5, 128.8, 128.5, 128.3, 127.1, 38.1, 36.9, 31.8, 29.2, 29.1, 28.6, 28.3, 22.6, 21.0, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{24}H_{32}S_2$: 384.1945; found: 384.1938.

(*Z*)-Cyclohexyl[2-(*p*-tolylthio)dec-1-en-1-yl]sulfane (3u)
Light yellow oil; yield: 177 mg (94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.31 (s, 1 H), 2.88–2.83 (m, 1 H), 2.27 (s, 3 H), 2.12 (t, *J* = 7.2 Hz, 2 H), 1.99 (d, *J* = 11.6 Hz, 2 H), 1.78–1.75 (m, 2 H), 1.61–1.58 (m, 1 H), 1.44–1.16 (m, 17 H), 0.84 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.3, 131.8, 130.5, 130.4, 129.5, 128.2, 45.9, 36.9, 33.7, 31.8, 29.2, 29.1, 28.7, 28.5, 25.9, 25.6, 22.6, 21.0, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{23}H_{36}S_2$: 376.2258; found: 376.2260.

(*Z*)-Octyl[2-(*p*-tolylthio)dec-1-en-1-yl]sulfane (3v)
Light yellow oil; yield: 185 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.4 Hz, 2 H), 6.24 (s, 1 H), 2.69 (t, *J* = 7.4 Hz, 2 H), 2.28 (s, 3

H), 2.13 (t, *J* = 7.6 Hz, 2 H), 1.66–1.59 (m, 2 H), 1.44–1.36 (m, 4 H), 1.25 (br m, 10 H), 1.18 (br m, 8 H), 0.88–0.83 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.3, 131.5, 130.5, 130.2, 129.5, 37.0, 34.0, 31.8, 31.7, 30.4, 29.2, 29.1, 28.7, 28.6, 28.4, 22.6, 21.0, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{25}H_{42}S_2$: 406.2728; found: 406.2731.

(*Z*)-Butyl[2-(*p*-tolylthio)dec-1-en-1-yl]sulfane (3w)
Light yellow oil; yield: 156 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 6.28 (s, 1 H), 2.74 (t, *J* = 7.6 Hz, 2 H), 2.32 (s, 3 H), 2.17 (t, *J* = 7.4 Hz, 2 H), 1.70–1.62 (m, 2 H), 1.50–1.41 (m, 4 H), 1.31–1.22 (m, 10 H), 0.95 (t, *J* = 7.2 Hz, 3 H), 0.89 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.3, 131.5, 130.5, 130.4, 130.1, 129.5, 36.9, 33.7, 32.4, 31.8, 29.2, 29.1, 28.7, 28.4, 22.6, 21.7, 21.0, 14.0, 13.6.

HRMS (TOF): *m*/*z* calcd for $C_{21}H_{34}S_2$: 350.2102; found: 350.2104.

(*Z*)-Octyl[2-(phenylthio)dec-1-en-1-yl]sulfane (3x)
Light yellow oil; yield: 175 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 7.6 Hz, 2 H), 7.26 (t, *J* = 7.6 Hz, 2 H), 7.18 (t, *J* = 7.2 Hz, 1 H), 6.37 (s, 1 H), 2.73 (t, *J* = 7.4 Hz, 2 H), 2.20 (t, *J* = 7.2 Hz, 2 H), 1.70–1.63 (m, 2 H), 1.49–1.39 (m, 4 H), 1.29 (br m, 10 H), 1.23 (br m, 8 H), 0.91–0.87 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 132.0, 130.5, 129.7, 128.7, 126.1, 37.2, 34.0, 31.8, 31.7, 30.4, 29.2, 29.1, 28.8, 28.5, 28.4, 22.6, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{24}H_{40}S_2$: 392.2571; found: 392.2584.

(*Z*)-Octyl[2-(*o*-tolylthio)dec-1-en-1-yl]sulfane (3y)
Light yellow oil; yield: 187 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.25 (m, 1 H), 7.18–7.15 (m, 1 H), 7.14–7.09 (m, 2 H), 6.33 (s, 1 H), 2.73 (t, *J* = 7.4 Hz, 2 H), 2.39 (s, 3 H), 2.12 (t, *J* = 7.6 Hz, 2 H), 1.70–1.62 (m, 2 H), 1.47–1.40 (m, 4 H), 1.30 (br m, 10 H), 1.22 (br m, 8 H), 0.92–0.87 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7, 133.0, 130.8, 130.5, 130.4, 130.2, 126.5, 126.1, 37.0, 34.1, 31.8, 31.7, 30.4, 29.2, 29.1, 28.7, 28.5, 28.4, 22.6, 20.3, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{25}H_{42}S_2$: 406.2728; found: 406.2727.

(*Z*)-(4-Methoxyphenyl)[1-(octylthio)dec-1-en-2-yl]sulfane (3z)
Light yellow oil; yield: 184 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 6.15 (s, 1 H), 3.77 (s, 3 H), 2.71 (t, *J* = 7.2 Hz, 2 H), 2.09 (t, *J* = 7.4 Hz, 2 H), 1.69–1.62 (m, 2 H), 1.44–1.39 (m, 4 H), 1.28–1.18 (m, 18 H), 0.90–0.85 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 133.4, 132.9, 127.7, 124.3, 114.3, 55.1, 36.5, 34.1, 31.8, 31.7, 30.3, 29.2, 29.1, 28.7, 28.6, 28.4, 22.6, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{25}H_{42}OS_2$: 422.2677; found: 422.2678.

(*Z*)-Naphthalen-2-yl[1-(octylthio)dec-1-en-2-yl]sulfane (3aa)
Light yellow oil; yield: 199 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.75 (m, 4 H), 7.49–7.41 (m, 3 H), 6.46 (s, 1 H), 2.78 (t, *J* = 7.2 Hz, 2 H), 2.27 (t, *J* = 7.4 Hz, 2 H), 1.74–1.67 (m, 2 H), 1.57–1.51 (m, 2 H), 1.46–1.42 (m, 2 H), 1.31–1.23 (m, 18 H), 0.94–0.87 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.7, 132.3, 131.9, 130.4, 128.3, 128.0, 127.7, 127.6, 127.1, 126.3, 125.6, 37.4, 34.1, 31.8, 30.5, 29.3, 29.2, 28.8, 28.6, 28.5, 22.7, 22.6, 14.1.

HRMS (TOF): *m*/*z* calcd for $C_{28}H_{42}S_2$: 442.2728; found: 442.2715.

(*Z*)-2-{[1-(Octylthio)dec-1-en-2-yl]thio}pyridine (3bb)
Light yellow oil; yield: 181 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 4.8 Hz, 1 H), 7.44 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 6.94–6.91 (m, 1 H), 6.55 (s, 1 H), 2.67 (t, *J* = 7.4 Hz, 2 H), 2.32 (t, *J* = 7.4 Hz, 2 H), 1.62–1.54 (m, 2 H), 1.49–1.46 (m, 2 H), 1.34–1.28 (m, 2 H), 1.21–1.19 (br m, 18 H), 0.84–0.80 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 149.6, 136.4, 136.2, 127.3, 121.5, 119.6, 38.3, 33.7, 31.7, 31.6, 30.3, 29.2, 29.1, 29.0, 28.8, 28.5, 28.4, 22.5, 14.0, 13.9.

HRMS (TOF): *m*/*z* calcd for $C_{23}H_{39}NS_2$: 393.2524; found: 393.2523.

(*Z*)-2-{[1-(Octylthio)dec-1-en-2-yl]thio}thiophene (3cc)
Light yellow oil; yield: 185 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 5.6 Hz, 1 H), 7.16 (d, *J* = 3.2 Hz, 1 H), 6.97–6.95 (m, 1 H), 6.06 (s, 1 H), 2.72 (t, *J* = 7.4 Hz, 2 H), 2.11 (t, *J* = 7.4 Hz, 2 H), 1.69–1.58 (m, 2 H), 1.50–1.40 (m, 4 H), 1.29–1.23 (m, 18 H), 0.90–0.86 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 133.9, 131.5, 129.7, 127.2, 126.1, 36.1, 34.3, 31.8, 31.7, 30.3, 29.2, 29.1, 28.7, 28.5, 28.4, 22.6, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{22}H_{38}S_3$: 398.2136; found: 398.2133.

(*Z*)-Octyl[2-(*p*-tolylthio)oct-1-en-1-yl]sulfane (3dd)
Light yellow oil; yield: 170 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 7.6 Hz, 2 H), 6.26 (s, 1 H), 2.71 (t, *J* = 7.4 Hz, 2 H), 2.30 (s, 3 H), 2.15 (t, *J* = 7.6 Hz, 2 H), 1.69–1.61 (m, 2 H), 1.46–1.38 (m, 4 H), 1.28–1.19 (m, 14 H), 0.90–0.83 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.3, 131.5, 130.5, 130.2, 129.5, 37.0, 34.1, 31.7, 31.5, 30.4, 29.1, 28.6, 28.4, 22.6, 22.5, 21.0, 14.0, 13.9.

HRMS (TOF): *m*/*z* calcd for $C_{23}H_{38}S_2$: 378.2415; found: 378.2421.

(*Z*)-[4-Methyl-1-(octylthio)pent-1-en-2-yl](*p*-tolyl)sulfane (3ee)
Light yellow oil; yield: 170 mg (97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 8.0 Hz, 2 H), 7.08 (d, *J* = 7.6 Hz, 2 H), 6.25 (s, 1 H), 2.73 (t, *J* = 7.2 Hz, 2 H), 2.31 (s, 3 H), 2.02 (d, *J* = 6.8 Hz, 2 H), 1.90–1.83 (m, 1 H), 1.70–1.63 (m, 2 H), 1.43–1.40 (m, 2 H), 1.29 (br m, 8 H), 0.89 (t, *J* = 6.6 Hz, 3 H), 0.83 (s, 3 H), 0.81 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.3, 131.2, 130.6, 130.5, 130.4, 129.5, 46.2, 34.1, 31.7, 30.4, 29.1, 28.5, 26.8, 22.6, 22.0, 21.0, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{21}H_{34}S_2$: 350.2102; found: 350.2109.

(*Z*)-[3-Methyl-1-(octylthio)but-1-en-2-yl](*p*-tolyl)sulfane (3ff)
Light yellow oil; yield: 159 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.4 Hz, 2 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 6.45 (s, 1 H), 2.74 (t, *J* = 7.2 Hz, 2 H), 2.49–2.44 (m, 1 H), 2.32 (s, 3 H), 1.70–1.63 (m, 2 H), 1.43–1.38 (m, 2 H), 1.30 (br m, 8 H), 1.13 (s, 3 H), 1.11 (s, 3 H), 0.91 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9, 135.6, 131.8, 131.5, 129.5, 128.9, 35.7, 34.0, 31.7, 30.4, 29.1, 28.6, 22.6, 22.1, 20.9, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{20}H_{32}S_2$: 336.1945; found: 336.1941.

(*Z*)-[3,3-Dimethyl-1-(octylthio)but-1-en-2-yl](*p*-tolyl)sulfane (3gg)
Light yellow oil; yield: 166 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 6.71 (s, 1 H), 2.67 (t, *J* = 7.2 Hz, 2 H), 2.27 (s, 3 H), 1.64–1.57 (m, 2 H), 1.37–1.26 (m, 10 H), 1.18 (s, 9 H), 0.88 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.8, 136.1, 134.4, 132.5, 129.4, 126.5, 39.7, 33.8, 31.7, 30.5, 29.4, 29.1, 29.0, 28.5, 22.6, 20.9, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{21}H_{34}S_2$: 350.2102; found: 350.2104.

(*Z*)-[2-Cyclohexyl-2-(*p*-tolylthio)ethenyl](octyl)sulfane (3hh)
Light yellow oil; yield: 175 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.46 (s, 1 H), 2.71 (t, *J* = 7.4 Hz, 2 H), 2.30 (s, 3 H), 2.11–2.05 (m, 1 H), 1.89 (d, *J* = 11.6 Hz, 2 H), 1.73 (d, *J* = 9.2 Hz, 2 H), 1.68–1.61 (m, 3 H), 1.41–1.36 (m, 2 H), 1.32–1.15 (m, 13 H), 0.90 (t, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.3, 134.7, 132.9, 131.7, 129.5, 128.4, 46.0, 33.9, 32.7, 31.7, 30.4, 29.1, 28.5, 26.4, 26.1, 22.6, 20.9, 14.0.

HRMS (TOF): *m*/*z* calcd for $C_{23}H_{36}S_2$: 376.2258; found: 376.2259.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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