Synthesis I. R. Ramazanov et al. Paper

One-Pot Synthesis of 1-Alkenyl Sulfides from Alkynes and Organic Disulfides with the Use of Organoaluminums

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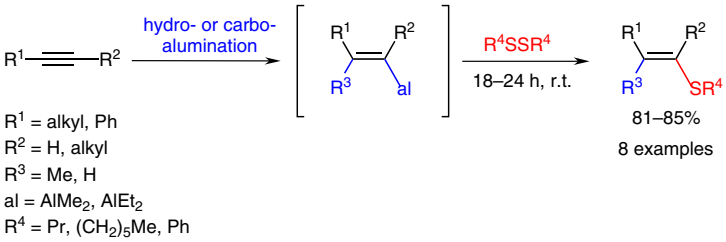

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Abstract Organic disulfides (dipropyl, dihexyl, or diphenyl disulfide) are convenient and efficient agents for the sulfanylation of 1-alkenylaluminum derivatives.

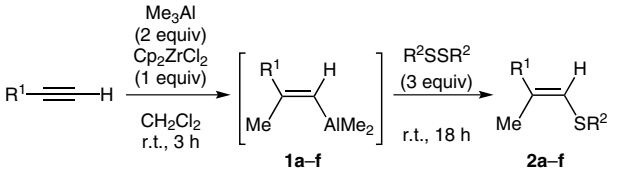
Key words disulfides, alkenes, sulfanylation, organometallic reagents

1-Alkenyl sulfides play important roles in syntheses of many naturally occurring and biologically active compounds. Because of their ease of transformation, 1-alkenyl sulfides also serve as versatile building blocks for many functional molecules. Although there are many approaches to the preparation of 1-alkenyl sulfides,[1,2] the stereoselective synthesis of *E*- and *Z*-isomers remains an important problem.[3,4] 1-Alkenyl sulfides are generally prepared by hydrosulfurization of alkynes by the action of radical initiators, bases, or metal-complex catalysts. Radical hydrosulfurization usually leads to mixtures of *anti*-Markovnikov *E*- and *Z*-isomers. Catalytic hydrosulfurization is usually complicated by the formation of byproducts of the Markovnikov addition of thiols to alkynes; however, the stereoselectivity toward the formation of the thermodynamically more stable *E*-isomer is greater than in that observed in radical hydrosulfurization. Good stereoselectivity has been achieved by using chloro(triphenylphosphine)rhodium[5,6] or gold complexes[7] as catalysts. Markovnikov adducts have been regioselectively prepared by the use of complexes of nickel, rhodium, zirconium, lanthanides, or actinides.[8–11] In general, however, only a few stereo- and regioselective methods give the *E*- or *Z*-isomer with more than 95% purity. Another approach to the selective synthesis of 1-alkenyl sulfides is cross-coupling of organic halides with thiols catalyzed by complexes of copper[12] or iron,[13] or by lanthanum(III) oxide[14] or copper(II) oxide.[15] Reactions of organic disulfides with 1-alkenyl bromides[16] and alkynes[17] have also been reported; although this reaction permits the preparation of 1-alkenyl sulfides directly from alkynes, it cannot, unfortunately, be extended to aliphatic terminal or disubstituted alkynes. Although the reaction of organic disulfides with organolithium[18] or organomagnesium compounds is the conventional approach to the synthesis of 1-alkenyl and aryl sulfides, to the best of our knowledge there is no example of the preparation of an 1-alkenyl sulfide from an organoaluminum compound. New and efficient methods are available for the hydro-, carbo-, or cycloalumination of alkynes to give organoaluminum compounds of various structures. Here, we describe the development of a one-pot method for converting a wide range of 1-alkenyl derivatives of aluminum into the corresponding 1-alkenyl sulfides.

The lack of published reports on the transformation of 1-alkenylaluminum derivatives into 1-alkenyl sulfides suggested that there might be serious obstacles to such transformations. The reaction of diisobutyl[(*E*)-oct-1-en-1-yl]aluminum with dipropyl disulfide in hexane solution at 50 °C for 18 hours did not result in the formation of the expected 1-alkenyl sulfide, and only dipropyl disulfide and oct-1-ene were detected in the reaction mixture after hydrolysis. The inactivity of 1-alkenylaluminum derivatives is probably due to the low ionicity of the metal–carbon bond in the organoaluminum compound in comparison with organic derivatives of magnesium or lithium. However, steric factors might also play a central role in the reaction. We surmised that 1-alkenylaluminum compounds containing methyl or ethyl substituents on the aluminum atom might be more reactive toward organic disulfides. Negishi methylalumination permits the preparation of 1-alkenyl(dimethyl)aluminum compounds from terminal alkynes with high yields and high stereoselectivities.[19–21] We found that the reaction of 1-alkenyl(dimethyl)aluminums **1a**–**f** with dipropyl, dihexyl, or diphenyl disulfide at room tempera-

ture for 18 hours led to the stereoselective formation of the corresponding 1-alkenyl alkyl sulfides **2a**–**f** in high yields (Table 1).

Table 1 Preparation of 1-Alkenyl Alkyl Sulfides **2** from Terminal Alkynes **1**



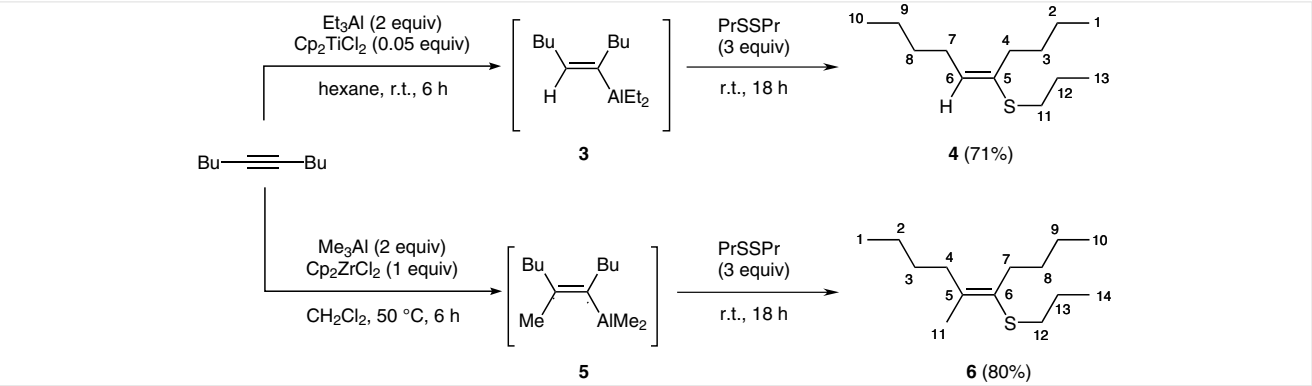
Entry	2	R^1	R^2	Yield (%)
1	**2a**	$(CH_2)_5Me$	$(CH_2)_5Me$	71
2	**2b**	$(CH_2)_5Me$	Pr	76
3	**2c**	$(CH_2)_5Me$	Ph	85
4	**2d**	Ph	$(CH_2)_5Me$	79
5	**2e**	Ph	Pr	84
6	**2f**	Ph	Ph	77

Although all the Al–C bonds might be involved in the reaction, three molar equivalents of the organic disulfide were sufficient to ensure the complete conversion of the 1-alkenylaluminum into the corresponding 1-alkenyl sulfide. This appears to be due to the higher reactivity of the Al–C(sp^2) bond in comparison with that of the Al–C(sp^3) bonds. The free energies of activation for the reactions of dimethyl(2-methylprop-1-en-1-yl)aluminum and trimethylaluminum with dimethyl disulfide at 298 K were estimated to be 46.1 and 60.2 kcal/mol, respectively by the B3LYP/6-31G(d) method. However, the use of one equivalent of dihexyl disulfide in the reaction with 1-alkenylaluminum **1a** resulted in the formation of a mixture of alkenyl sulfides and hexyl methyl sulfide in a 2:1 ratio. Because one Al–C(sp^2) bond and five Al–C(sp^3) bonds take part in the reaction, the difference in the free energies of activation at 298 K can be approximately estimated as $\Delta G^{\neq} = RT^{*}\ln(10) = 0.593 \times 2.303 = 1.37$ kcal/mol. The discrepancy between the calculated and experimental values can be explained by an underestimation of the steric factor in the calculation model.

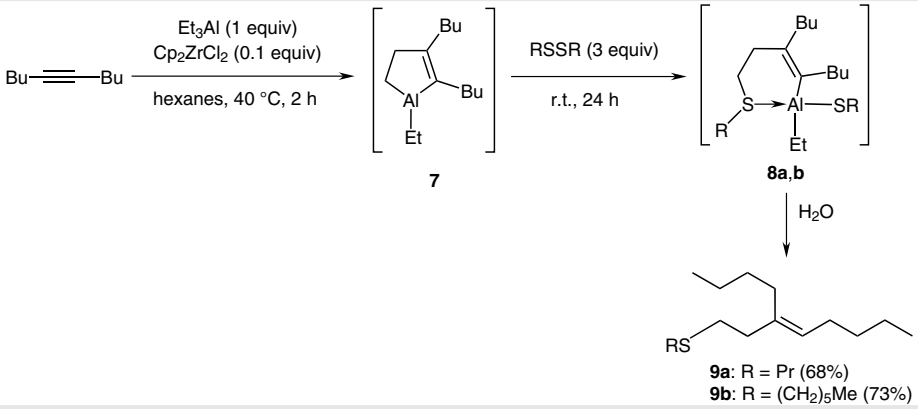
The observed reaction is a rare example of the selective conversion of organoaluminum compounds into organic sulfides. It is known that trialkylaluminums react nonselectively with sulfur, disulfur dichloride, or sulfur dichloride to give mixtures of organic sulfides, disulfides, and trisulfides.[22] Because of the simplicity and the high efficiency of our new procedure, we examined the possibility of applying this method to the functionalization of 1-alkenylaluminums of various structures.

We found that zirconium-catalyzed hydroalumination[23] or methylalumination of dec-5-yne followed by treatment with three equivalents of dipropyl disulfide gave the alkenyl sulfides **4** and **6**, respectively, in high yields (Scheme 1).

The zirconium-catalyzed reaction of disubstituted alkynes with triethylaluminum gives aluminacyclopent-2-enes, a particular type of 1-alkenylaluminum compound.[24] The reaction of aluminacyclopent-2-ene **7** with organic disulfides (dipropyl or dihexyl disulfide) gave sulfides **9a** and **9b** in high yield (Scheme 2). Increasing the amount of organic disulfide did not result in the formation of the expected products of disulfanylation. We assume that the reaction stopped at the stage of the formation of the stable intramolecular six-membered cyclic complex **8**, in which the sulfur atom is coordinated to the aluminum atom, thereby reducing the the reactivity of the Al–C bonds. The free energies of activation for the reactions of 1,2,3-trimethylaluminacyclopent-2-ene with dimethyl disulfide, as estimated by the B3LYP/6-31G(d) method, are 45.8, 53.8, and 62.7 kcal/mol for the reactions with the Al–C(sp^2) bond, the Al–CH_2 bond, and the Al–Me bond, respectively. The greater activity of the Al–CH_2 bond can be explained by taking into account the steric factors and the calculated activation energy for the reaction with dimethyl(2-methylprop-1-en-1-yl)aluminum.



Scheme 1 Preparation of alkenyl sulfides **4** and **6** from dec-4-yne

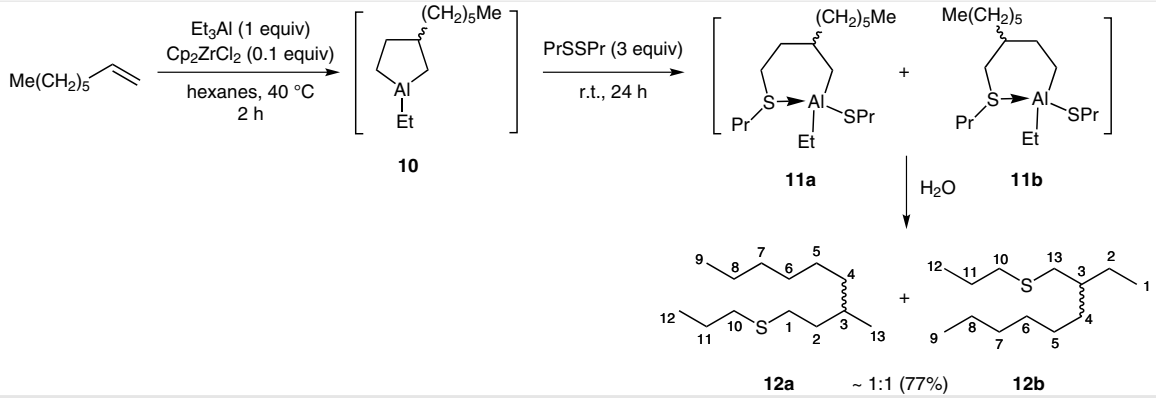


Scheme 2 Preparation of alkenyl sulfides **9a** and **9b** from dec-5-yne

Because the functionalization of aluminacyclopent-2-enes involved only the Al–C(sp^3) bond of the metallacycle, we were interested in examining the reactions of aluminacyclopentanes with disulfides. Zirconium-catalyzed cycloalumination of oct-1-ene,[25] followed by treatment with dipropyl disulfide, gave a mixture of the two monosulfanylation products **12a** and **12b** (Scheme 3). The use of ten molar equivalents of the disulfide did not lead to the formation of the product of double sulfanylation. The reaction appears to stop at the stage of formation of the stable intramolecular six-membered cyclic complex **11**. Quantum chemical calculations showed that the Al–C bond of the aluminacycle **10** has a higher activity than the Al–Et bond.

We have therefore developed an efficient method for the preparation of 1-alkenyl sulfides from 1-alkenylaluminums by the action of organic disulfides. This is a useful extension of existing approaches to the formation of C–S bonds, and is an analogue of the alkyne carbosulfurization reaction. The advantages of our new method are its one-pot character and the elimination of the need to isolate the intermediate 1-alkenylaluminums. For example, the 1-alkenyl sulfide **2a** can be prepared in two steps by a zirconium-catalyzed methylalumation of oct-1-yne followed by iodinolysis of the reaction mixture. In the next step, the isolated 1-iodoalkene is converted into sulfide **2a** by treatment with hexane-1-thiol in the presence of bis(triphenyl)(phenanthroline)copper(I) nitrate.[12] Our method is therefore convenient for the synthesis of β,β- and α,β,β-substituted vinyl sulfides. The high regio- and stereoselectivity of the reaction arises from the well-proven method of zirconium-catalyzed carboalumination of alkynes.

The reagents were obtained from Sigma-Aldrich or Acros. CH_2Cl_2 and hexane were distilled over P_2O_5. The diphenyl and dialkyl disulfides were prepared by oxidation of the corresponding thiols with a $KMnO_4$–$CuSO_4$·5 H_2O system.[26] NMR spectra were recorded on Bruker Avance 400 and 500 spectrometers. Chemical shifts are referenced to TMS as the internal standard. The numbering of the atoms in the ^{13}C and ^1H NMR spectra of the compounds **2a**–**f** and **5a**,**b** is shown in Figure 1. Elemental analysis was performed by using a Carlo-Erba CHN 1106 elemental analyzer. Mass spectra were recorded on a Finnigan 4021 instrument. The yields were calculated from the isolated amounts of the 1-alkenyl sulfides obtained from the starting alkynes. All quantum chemical calculations were performed by using *Gaussian 09* software.[27]



Scheme 3 Preparation of dialkyl sulfides **12** from oct-1-ene

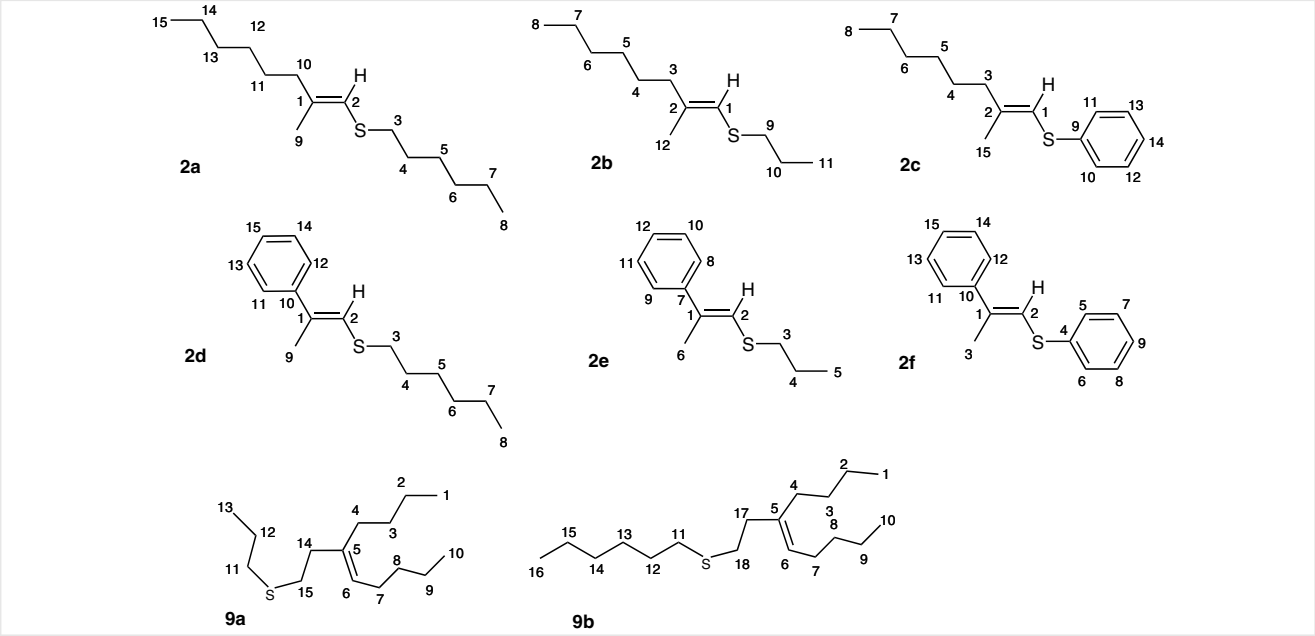


Figure 1 Numbering of atoms in the ^{13}C NMR and ^{1}H NMR spectra of the compounds **2a–f** and **5a**,**b**

(1*E*)-1-(Hexylsulfanyl)-2-methyloct-1-ene (2a); Typical Procedure

A 25-mL argon-swept flask, equipped with a magnetic stirrer and a rubber septum, was charged with a suspension of Cp_2ZrCl_2 (0.58 g, 2 mmol) in CH_2Cl_2 (5 mL) and with Me_3Al (0.38 mL, 4 mmol) at room temperature. (**CAUTION:** *Organoaluminum compounds are pyrophoric and can ignite on contact with air, water, or any oxidizer*). Oct-1-yne (0.30 mL, 2 mmol) was added, and the mixture was stirred at r.t. for 3 h. The mixture was cooled to 0 °C, dihexyl disulfide (1.41 g, 6 mmol) was added, and the resulting mixture was stirred at r.t. for 18 h. The mixture was then diluted with hexane (5 mL), and H_2O (3 mL) was added dropwise while the flask was cooled in an ice bath. The precipitate that formed was removed by filtration on a filter paper, and the aqueous layer was extracted with Et_2O (3 × 5 mL). The organic layers were combined, washed with brine (10 mL), dried ($CaCl_2$), and concentrated. The residue was purified by column chromatography (silica gel, hexane) to give a colorless oil; yield: 0.34 g (71%); R_f = 0.79 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85–0.95 [m, 6 H, C(8,15)H_3], 1.20–1.36 [m, 10 H, C(6,7,12,13,14)H_2], 1.36–1.50 [m, 4 H, C(5,11)H_2], 1.55–1.68 [m, 2 H, C(4)H_2], 1.73 [s, 3 H, C(9)H_3], 2.04 [t, *J* = 10.0 Hz, 2 H, C(10)H_2], 2.64 [t, *J* = 7.5, 2 H, C(3)H_2], 5.63 [s, 1 H, C(2)H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.17 and 14.23 [C(8,15)], 17.96 [C(9)], 22.70 and 22.77 [C(7,14)], 27.79 [C(11)], 28.36 [C(5)], 28.87 [C(12)], 30.26 [C(4)], 31.43 [C(6)], 31.72 [C(13)], 34.03 [C(3)], 39.30 [C(10)], 118.22 [C(2)], 137.63 [C(1)].

MS (EI): *m*/*z* (%) = 242 (22) [M^+], 213 (15) [M – Et]$^+$, 157 (41), 123 (9), 115 (24), 87 (41), 81 (41), 55 (78), 41 (100).

Anal. Calcd for $C_{15}H_{30}S$: C, 74.31; H, 12.47. Found: C, 74.60; H, 12.53.

(1*E*)-2-Methyl-1-(propylsulfanyl)oct-1-ene (2b)

Prepared by the typical procedure from oct-1-yne (0.22 g, 2 mmol) and PrSSPr (0.90 g, 6 mmol) as a colorless oil; yield: 0.30 g (76%); R_f = 0.87 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 [t, *J* = 6.8 Hz, 3 H, C(8)H_3], 1.02 [t, *J* = 7.6 Hz, 3 H, C(11)H_3], 1.20–1.38 [m, 6 H, C(5–7)H_2], 1.37–1.47 [m, 2 H, C(4)H_2], 1.60–1.71 [m, 2 H, C(10)H_2], 1.74 [s, 3 H, C(12)H_3], 2.06 [t, *J* = 7.2 Hz, 2 H, C(3)H_2], 2.62 [t, *J* = 8.0 Hz, 2 H, C(9)H_2], 5.63 [s, 1 H, C(1)H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.23 [C(11)], 14.06 [C(8)], 17.78 [C(12)], 22.62 [C(7)], 23.55 [C(10)], 27.80 [C(4)], 28.87 and 31.72 [C(5,6)], 36.04 [C(9)], 39.30 [C(3)], 118.07 [C(1)], 137.47 [C(2)].

MS (EI): *m*/*z* (%) = 200 (49) [M^+], 157 (17) [M – Pr]$^+$, 129 (100) [M – Am]$^+$, 95 (34), 87 (75), 55 (29).

Anal. Calcd for $C_{12}H_{24}S$: C, 71.93; H, 12.07. Found: C, 72.14; H, 12.11.

{[(1*E*)-2-Methyloct-1-en-1-yl]sulfanyl}benzene (2c)

Prepared by the typical procedure from oct-1-yne (0.22 g, 2 mmol) and PhSSPh (1.31 g, 6 mmol) as a colorless oil; yield: 0.40 g (85%); R_f = 0.81 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0. 94 [t, *J* = 6.8 Hz, 3 H, C(8)H_3], 1.28–1.43 [m, 6 H, C(5–7)H_2], 1.48–1.58 [m, 2 H, C(4)H_2], 1.89 [s, 3 H, C(15)H_3], 2.21 [t, *J* = 8.0 Hz, 2 H, C(3)H_2], 5.97 [s, 1 H, C(1)H], 7.15–7.38 (m, 5 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.11 [C(8)], 18.02 [C(15)], 22.66 [C(7)], 27.76 [C(4)], 28.91 [C(6)], 31.71 [C(5)], 39.41 [C(3)], 115.13 [C(1)], 123.53 [C(14)], 127.85 and 128.86 [2 C and 2 C, C(10–13)], 137.52 [C(9)], 143.70 [C(2)].

MS (EI): *m*/*z* (%) = 234 (100) [M^+], 163 (75) [M – Am]$^+$, 135 (52), 110 (17), 91 (21), 69 (33), 55 (17), 41 (24).

Anal. Calcd for $C_{15}H_{22}S$: C, 76.86; H, 9.46. Found: C, 77.21; H, 9.45.

[(*E*)-2-(Hexylsulfanyl)-1-methylvinyl]benzene (2d)

Prepared by the typical procedure from PhC≡CH (0.20 g, 2 mmol) and dihexyl disulfide (1.41 g, 6 mmol) as a colorless oil; yield: 0.37 g (79%); R_f = 0.89 (hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 [t, *J* = 6.8 Hz, 3 H, C(8)H_3], 1.30–1.44 [m, 4 H, C(6,7)H_2], 1.44–1.53 [m, 2 H, C(5)H_2], 1.69–1.79 [m, 2 H, C(4)H_2], 2.18 [s, 3 H, C(9)H], 2.83 [t, *J* = 7.6 Hz, 2 H, C(3)H_2], 6.37 [s, 1 H, C(2)H], 7.23–7.50 (m, 5 H, Ph).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.09 [C(8)], 17.63 [C(9)], 22.61 [C(7)], 28.39 [C(5)], 30.55 [C(4)], 31.46 [C(6)], 34.31 [C(3)], 123.99 [C(2)], 125.12 and 128.35 [2 C and 2 C, C(11–14)], 126.59 [C(15)], 133.22 [C(10)], 142.16 [C(1)].

MS (EI): *m/z* (%) = 234 (100) $[M]^+$, 149 (62) $[M - Am]^+$, 135 (53), 115 (30), 105 (20), 77 (9), 55 (7), 43 (35).

Anal. Calcd for $C_{15}H_{22}S$: C, 76.86; H, 9.46. Found: C, 76.63; H, 9.42.

[(*E*)-1-Methyl-2-(propylsulfanyl)vinyl]benzene (2e)

Prepared by the typical procedure from PhC≡CH (0.20 g, 2 mmol) and PrSSPr (0.90 g, 6 mmol); yield: 0.32 g (84%); R_f = 0.73 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 [t, *J* = 7.6 Hz, 3 H, C(5)H_3], 1.71–1.82 [m, 2 H, C(4)H_2], 2.17 [s, 3 H, C(6)H_3], 2.80 [t, *J* = 7.2 Hz, 2 H, C(3)H_2], 6.35 [s, 1 H, C(1)H], 7.23–7.44 (m, 5 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.31 [C(5)], 17.61 [C(6)], 23.81 [C(4)], 36.28 [C(3)], 123.94 [C(2)], 125.11 and 128.33 [2 C and 2 C, C(8–11)], 126.58 [C(12)], 133.26 [C(7)], 142.15 [C(1)].

MS (EI): *m/z* (%) = 192 (100) $[M]^+$, 163 (4) $[M - Et]^+$, 149 (80) $[M - Pr]^+$, 134 (47), 115 (34), 105 (18), 77 (16), 65 (7), 51 (11).

Anal. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39. Found: C, 74.79; H, 8.31.

[(*E*)-1-Methyl-2-(phenylsulfanyl)vinyl]benzene (2f)[28]

Prepared by the typical procedure from PhC≡CH (0.20 g, 2 mmol) and PhSSPh (1.31 g, 6 mmol) as a colorless oil; yield: 0.35 g (77%); R_f = 0.65 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 [s, 3 H, C(3)H_3], 6.66 [s, 1 H, C(2)H], 7.26–7.36 [m, 2 H, C(9,15)H], 7.36–7.52 [m, 8 H, C(5–8,11–14)H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.86 [C(3)], 121.45 [C(2)], 125.50 [C(13,14)], 126.52 and 127.27 [C(9,15)], 128.49 [C(5,6)], 129.15 and 129.18 [2 C and 2 C, C(7,8,11,12)], 136.48 [C(10)], 137.29 [C(4)], 141.78 [C(1)].

(5*E*)-5-Methyl-6-(propylsulfanyl)dec-5-ene (6)

Me_3Al (0.38 mL, 4 mmol) and dec-5-yne (0.28 g, 2 mmol) were added to a suspension of Cp_2ZrCl_2 (0.58 g, 2 mmol) in CH_2Cl_2 (5 mL) under argon at r.t., and the mixture was stirred for 6 h at 60 °C. PrSSPr (0.90 g, 6 mmol) was added, and the mixture was stirred for 18 h at r.t. Workup as described above gave a crude product that was purified by flash chromatography (silica gel, hexane) to give a colorless oil; yield: 0.37 g (80%); R_f = 0.68 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86–0.95 [m, 6 H, C(1,10)H_3], 0.99 [t, *J* = 7.4 Hz, 3 H, C(14)H_3], 1.26–1.44 [m, 6 H, C(2,3,9)H_2], 1.44–1.59 [m, 4 H, C(8,13)H_2], 1.93 [s, 3 H, C(11)H_3], 2.12 [t, *J* = 7.6 Hz, 2 H, C(4)H_2], 2.25 [t, *J* = 7.8 Hz, 2 H, C(7)H_2], 2.54 [t, *J* = 7.2 Hz, 2 H, C(12)H_2].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.43 [C(14)], 14.00 [2 C, C(1,10)], 20.76 [C(11)], 22.63 and 22.76 [C(2,9)], 23.14 [C(13)], 30.71 [C(3)], 31.39 [C(8)], 31.78 [C(7)], 34.41 [C(12)], 34.56 [C(4)], 127.80 [C(6)], 139.33 [C(5)].

MS (EI): *m/z* (%) = 228 (66) $[M]^+$, 185 (100) $[M - Pr]^+$, 143 (23), 129 (18), 109 (32), 101 (35), 67 (40), 55 (43), 41 (47).

Anal. Calcd for $C_{14}H_{28}S$: C, 73.61; H, 12.36. Found: C, 73.73; H, 12.44.

(5*E*)-5-(Propylsulfanyl)dec-5-ene (4)

Dec-5-yne (0.28 g, 2 mmol) and Et_3Al (0.3 mL, 2 mmol) were added to a suspension of Cp_2TiCl_2 (0.025 g, 0.1 mmol) in hexane (5 mL) under argon at r.t. After 6 h, PrSSPr (0.90 g, 6 mmol) was added at 0 °C, and the mixture was stirred for 18 h at r.t. The mixture was diluted with hexane (5 mL), and H_2O (3 mL) was added dropwise while the flask was cooled in an ice bath. The precipitate was removed by filtration on a filter paper and the aqueous layer was extracted with Et_2O (3 × 5 mL). The organic layers were combined, washed with brine (10 mL), dried ($CaCl_2$), and concentrated. The residue was purified by column chromatography (hexane) to give a colorless oil; yield: 0.36 g (83%); R_f = 0.71 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85–0.97 [m, 6 H, C(1,10)H_3], 1.00 [t, *J* = 7.2 Hz, 3 H, C(13)H_3], 1.25–1.44 [m, 6 H, C(2,3,9)H_2], 1.44–1.55 [m, 2 H, C(8)H_2], 1.65–1.77 [m, 2 H, C(12)H_2], 2.05–2.20 [m, 2 H, C(4)H_2], 2.37 [t, *J* = 7.6 Hz, 2 H, C(7)H_2], 2.64 [t, *J* = 7.0 Hz, 2 H, C(11)H_2], 5.84 [t, *J* = 7.5 Hz, 1 H, C(6)H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.29 [C(13)], 14.07 and 14.11 [C(1,10)], 22.27 [C(11)], 22.47 and 22.57 [C(2,9)], 28.78 [C(4)], 29.50 [C(7)], 30.78 [C(8)], 31.87 [C(3)], 40.48 [C(11)], 130.82 [C(6)], 134.87 [C(5)].

MS (EI): *m/z* (%) = 214 (56) $[M]^+$, 192 (5), 185 (4) $[M - Et]^+$, 171 (100) $[M - Pr]^+$, 129 (69), 116 (40), 95 (58), 74 (49), 67 (79), 55 (83).

Anal. Calcd for $C_{13}H_{26}S$: C, 72.82; H, 12.22. Found: C, 72.93; H, 12.20.

(5*E*)-5-[2-(Propylsulfanyl)ethyl]dec-5-ene (9a)

Dec-5-yne (0.28 g, 2 mmol) and Et_3Al (0.3 mL, 2 mmol) were added to a suspension of Cp_2TiCl_2 (0.025 g, 0.1 mmol) in hexane (5 mL) under argon at 40 °C. After 2 h, PrSSPr (0.90 g, 6 mmol) was added at 0 °C, and the mixture was stirred for 24 h at r.t. The mixture was then diluted with hexane (5 mL), and H_2O (3 mL) was added dropwise while the flask was cooled in an ice bath. The precipitate was removed by filtration on a filter paper. The aqueous layer was extracted with Et_2O (3 × 5 mL). The organic layers were combined, washed with brine (10 mL), dried ($CaCl_2$), and concentrated. The residue was purified by column chromatography (silica gel, hexane) to give a colorless oil; yield: 0.33 g (68%); R_f = 0.49 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86–0.97 [m, 6 H, C(1,10)H_3], 1.01 [t, *J* = 7.4 Hz, 3 H, C(13)H_3], 1.25–1.40 [m, 8 H, C(2,3,8,9)H_2], 1.58–1.69 [m, 2 H, C(12)H_2], 1.95–2.06 [m, 4 H, C(4,7)H_2], 2.26 [t, *J* = 8.2 Hz, 2 H, C(14)H_2], 2.53 [t, *J* = 7.2 Hz, 2 H, C(11)H_2], 2.58 [t, *J* = 8.2 Hz, 2 H, C(15)H_2], 5.18 [t, *J* = 7.6 Hz, 1 H, C(6)H].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.53 [C(13)], 14.02 [2C, C(1,10)], 22.79 and 27.41 [C(2,9)], 23.02 [C(12)], 27.41 [C(7)], 29.70 [C(4)], 30.73 [C(3)], 31.16 and 34.27 [C(11,15)], 32.22 [C(8)], 37.26 [C(14)], 126.33 [C(6)], 137.86 [C(5)].

MS (EI): *m/z* (%) = 242 (3) $[M]^+$, 213 (4) $[M - Et]^+$, 200 (35), 199 (100) $[M - Pr]^+$, 185 (15) $[M - Bu]^+$, 157 (12), 143 (16), 123 (78), 109 (45), 89 (78), 81 (61), 55 (76).

Anal. Calcd for $C_{15}H_{30}S$: C, 74.31; H, 12.47. Found: C, 74.12; H, 12.40.

(5*E*)-5-[2-(Hexylsulfanyl)ethyl]dec-5-ene (9b)

Prepared by the same procedure as above from dec-5-yne (0.28 g, 2 mmol) and dihexyl disulfide (1.41 g, 6 mmol) as a colorless oil; yield: 0.42 g (73%); R_f = 0.50 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83–1.00 [m, 9 H, C(1,10,16)H_3], 1.23–1.39 [m, 10 H, C(2,8,9,14,15)H_2], 1.39–1.46 [m, 4 H, C(3,13)H_2], 1.56–1.66 [m, 2 H, C(12)H_2], 1.97–2.06 [m, 2 H, C(7)H_2], 2.26 [t, *J* = 7.6 Hz, 2 H, C(17)H_2], 2.39–2.45 [m, 2 H, C(4)H_2], 2.54 [t, *J* = 7.2 Hz, 2 H, C(11)H_2], 2.58 [t, *J* = 7.6 Hz, 2 H, C(18)H_2], 5.18 [t, *J* = 7.2 Hz, 1 H, C(6)H_2].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.03 [3 C, C(1,10,16)], 22.40 and 22.57 and 22.79 [C(2,9,15)], 27.41 [C(7)], 28.64 [2 C, C(3,13)], 29.70 [C(12)], 30.73 and 31.47 [C(8,14)], 31.25 [C(18)], 32.21 [2 C, C(4,11)], 37.25 [C(17)], 126.34 [C(6)], 137.87 [C(5)].

MS (EI): *m/z* (%) = 284 (<1) [M]$^+$, 255 (<1) [M – Et]$^+$, 241 (3) [M – Pr]$^+$, 227 (4), 199 (19), 157 (3), 137 (14), 123 (33), 95 (36), 81 (35), 55 (95), 41 (100).

Anal. Calcd for $C_{18}H_{36}S$: C, 75.98; H, 12.75. Found: C, 76.24; H, 12.71.

3-Methyl-1-(propylsulfanyl)nonane (12a) and 3-[(propylsulfanyl)methyl]nonane (12b)

Oct-1-ene (0.22 g, 2 mmol) and Et_3Al (0.3 mL, 2 mmol) were added to a suspension of Cp_2ZrCl_2 (0.058 g, 0.2 mmol) in hexane (5 mL) under argon at 40 °C. After 2 h, dihexyl disulfide (1.41 g, 6 mmol) was added at 0 °C, and the mixture was stirred for 24 h at r.t. The mixture was then diluted with hexane (5 mL), and D_2O (3 mL) was added dropwise while the flask was cooled in an ice bath. The precipitate was removed by filtration on a filter paper. The aqueous layer was extracted with Et_2O (3 × 5 mL). The organic layers were combined, washed with brine (10 mL), dried ($CaCl_2$), and concentrated. The residue was purified by column chromatography (hexane) to give a mixture of the two regioisomers **12a** and **12b** as a colorless oil; yield: 0.33 g (77%); R_f = 0.67 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85–0.95 [m, 6 H, 0.5 × C(9,13)H_3, 0.5 × C(1′,9′)H_3], 1.0 [t, *J* = 7.4 Hz, 3 H, 0.5 × C(12)H_3, 0.5 × C(12′)H_3], 1.20–1.56 [m, 13 H, 0.5 × C(2–8)H_2, 0.5 × C(2′-8′)H_2], 1.56–1.68 [m, 2 H, 0.5 × C(11)H_2, 0.5 × C(11′)H_2], 2.44–2.60 [m, 4 H, 0.5 × C(1,10)H_2, 0.5 × C(10′,13′)H_2].

Anal. Calcd for $C_{13}H_{28}S$: C, 72.15; H, 13.04.

^{13}C NMR (100 MHz, $CDCl_3$): δ (**12a**) = 13.52 [C(12)], 14.08 [C(9)], 19.37 [C(13)], 22.66 [C(8)], 23.06 [C(11)], 25.56 [C(2)], 26.89 [C(7)], 29.59 and 31.90 and 32.74 [C(4–6)], 34.21 [C(1)], 36.91 [C(10)], 39.41 [C(3)].

MS (EI): *m/z* (%) (**12a**) = 216 (40) [M]$^+$, 173 (45) [M – Pr]$^+$, 140 (9), 111 (44), 89 (47), 83 (31), 70 (100), 55 (85).

^{13}C NMR (100 MHz, $CDCl_3$): δ (**12b**) = 10.80 [C(1′)], 13.52 [C(12′)], 14.08 [C(9′)], 22.66 [C(8′)], 23.00 [C(11′)], 25.56 [C(2′)], 26.63 [C(7′)], 29.87 and 31.94 and 32.26 [C(4′-6′)], 39.94 [C(13′)], 36.76 [C(10′)], 39.41 [C(3′)].

MS (EI): *m/z* (%) (**12b**) = 216 (20) [M]$^+$, 173 (17) [M – Pr]$^+$, 111 (27), 89 (10), 83 (14), 70 (100), 56 (51), 55 (40).

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380755.

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