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Zirconocene Catalysis in Organoaluminum Synthesis of 1-Alkenyl Sulfones and Sulfides

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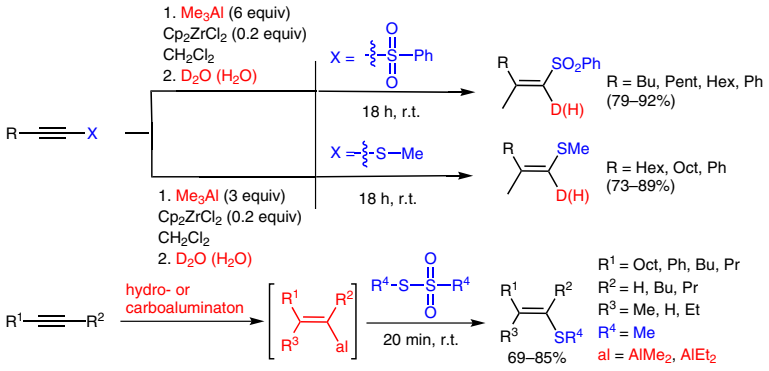

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Abstract The Cp_2ZrCl_2-catalyzed methylalumination of 1-alkynyl sulfones and 1-alkynyl sulfides with Me_3Al, followed by deuterolysis or hydrolysis, affords the corresponding β,β-disubstituted 1-alkenyl sulfones and 1-alkenyl sulfides in high yields. *S*-Methyl methanethiosulfonate is shown to be a convenient and efficient sulfanylating agent for 1-alkenylaluminum derivatives.

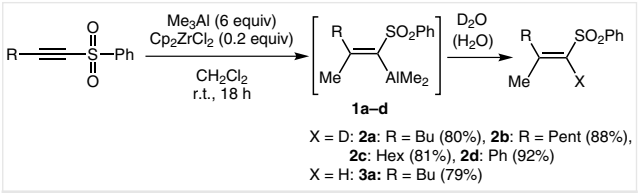
Key words alkynyl sulfones, alkynyl sulfides, alkenylaluminums, methylalumination, zirconocene catalysis

The controlled carbometalation of alkynes provides a powerful tool for the construction of new organometallic unsaturated species and various ring structures.[1] Previously, we developed methods for the preparation of 1-alkenyl phosphines and phosphine oxides based on Zr-catalyzed carboalumination of 1-alkynyl phosphines and phosphine oxides.[2,3] It has been found that the pathway of the reaction of 1-alkynyl phosphine derivatives with organoaluminum compounds strongly depends on the nature of the substrate and the solvent. The ethylalumination takes place under the action of Et_3Al in the case of 1-alkynyl phosphines and phosphine oxides in hexane as the solvent. However, our efforts to carry out Zr-catalyzed methylalumination of 1-alkynyl phosphines and phosphine oxides by Me_3Al were unsuccessful. We hypothesized that the acetylene group is deactivated due to the formation of positive-charged complexes with cationic organoaluminum and/or organozirconium intermediates. It is noteworthy that the Negishi methylalumination[4,5] holds an important place in alkyne chemistry owing to a wide variety of compounds that can be prepared in this way. The reaction was successfully carried out with terminal acetylenes,[4] heterosubstituted arylethynes containing O, S, Cl, and Si,[6] and homopropargyl alcohols.[7] Therefore, the exception that we found raised the question of the scope of applicability of the methylalumination reaction. Our attention was attracted by acetylenic sulfur derivatives. Sulfur has an electronegativity close to that of phosphorus and, like phosphorus, it is a vital element of life. Similar to phosphorus, sulfur forms diverse stable organic compounds in various oxidation states. The known examples of copper-catalyzed carbomagnesiation[8,9] and carbozincation[10,11] of alkynyl sulfones as well as carbozincation[12,13] of alkynyl sulfoxides gave hope that carboalumination of alkynyl sulfur derivatives would also proceed successfully.

The zirconium-catalyzed carbometalation of acetylenes is widely used to prepare substituted olefins that present practical values for synthetic organic chemistry.[14–16] In this paper, we report for the first time a Cp_2ZrCl_2-catalyzed methylalumination of substituted 1-alkynyl sulfones, sulfides, and sulfoxides on treatment with Me_3Al. Methylalumination of organosulfur acetylenes would open up the way for a one-pot method transforming acetylenes into substituted 1-alkenyl sulfones, sulfides, and sulfoxides. Furthermore, we report the development of a new method suitable for the conversion of a broad range of alkenylaluminum derivatives to alkenyl sulfides in one-pot processes.

We found that substituted 1-alkynyl sulfones obtained from terminal acetylenes (1-hexyne, 1-heptyne, 1-octyne, and phenylacetylene) react with 6 equivalents of Me_3Al in the presence of 1 equivalent of Cp_2ZrCl_2 in dichloromethane over a period of 18 hours to give, after deuterolysis or hydrolysis, β,β-disubstituted 1-alkenyl sulfones in high yields (Scheme 1). The reaction was stereoselective and gave *Z*-isomers of substituted 1-alkenyl sulfones. The structures of the compounds formed in the reaction were determined by means of 1D and 2D NMR spectroscopy using the products of their deuterolysis **2a–d** and hydrolysis **3a**. The NOESY spectrum of compound **3a** clearly showed coupling be-

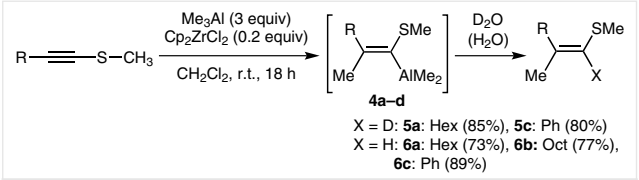
tween the signals of hydrogen at the double bond and methyl group-hydrogen at the double bond, indicating the *Z*-configuration of the 1-alkenyl sulfide formed.



Scheme 1 *syn*-Zr-catalyzed methylalumination of substituted 1-alkynyl sulfones

When (hex-1-yn-1-ylsulfonyl)benzene was reacted with 4 equivalents of Me_3Al in dichloromethane in the presence of 1 equivalent of Cp_2ZrCl_2, the conversion of the starting 1-alkynyl sulfone within 24 hours was 54%. A decrease in the amount of Cp_2ZrCl_2 down to a catalytic amount (20 mol%) also favored the reaction to afford substituted 1-alkenyl sulfones of *Z*-configuration in high yields. The use of hexane as the solvent did not hamper the reaction either.

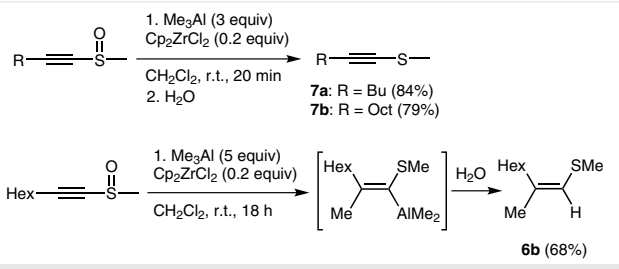
As a continuation of our studies on the carbometalation of sulfur-containing acetylenes in which the sulfur functional group is directly attached to the triple bond, we have now studied the methylalumination of 1-alkynyl sulfides. Substituted 1-alkynyl sulfides reacted with 3 equivalents of Me_3Al in the presence of 20 mol% Cp_2ZrCl_2 in dichloromethane to give, after deuterolysis or hydrolysis, β,β-disubstituted 1-alkenyl sulfides **5a**,**c** and **6a–c** in high yields (Scheme 2). The cross peak between the signals of the hydrogen atom at the double bond and the methyl group in the NOESY spectrum indicated a *Z*-configuration of **6b** after hydrolysis of a product resulting from the methylalumination reaction of dec-1-yn-1-yl(methyl)sulfane.



Scheme 2 Zr-catalyzed methylalumination of substituted 1-alkynyl sulfides

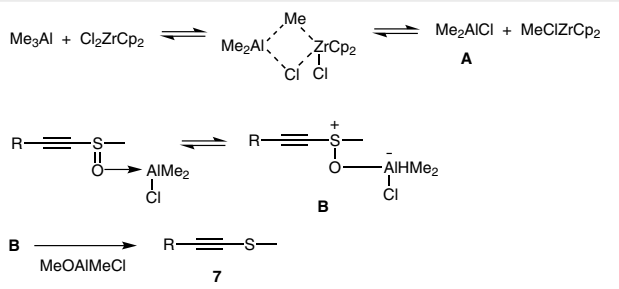
In addition, we measured the NMR spectra for organoaluminum intermediate **4b** in deuterobenzene solution. Although the ^{13}C NMR spectra of the reaction mixture of organoaluminum compounds are rather complicated for reliable assignment of signals, we succeeded in identifying some of the characteristic signals. Thus, the sole ^{27}Al NMR signal is a broadened peak at δ_{Al} =168.76. The ^{13}C NMR signal for the double bond carbon atom attached to aluminum appeared at 156.78 ppm, while the signal for the sp^2-hybridized carbon atom located in the β-position relative to aluminum appeared at 169.32 ppm. The chemical shifts found for the double bond carbon atoms are close to published data for linear alkenylalanes.[17,18] Besides, the HMBC spectrum of intermediate **4b** exhibited cross-peaks between signals of the double bond carbon atoms and the hydrogen atom of the *S*-methyl group.

The Zr-catalyzed methylalumination of 1-alkynyl sulfoxides upon treatment with 3 equivalents of Me_3Al failed. After the addition of 3 equivalents of Me_3Al to 1-(methylsulfinyl)dec-1-yne in the presence of 20 mol% Cp_2ZrCl_2 in dichloromethane followed by hydrolysis, dec-1-yn-1-yl methyl sulfide (**7b**) was isolated from the reaction mixture in 79% yield (Scheme 3). Thus, under methylalumination conditions, 1-alkynyl sulfoxides are reduced to sulfides.



Scheme 3 Reaction of 1-alkynyl sulfoxides with Cp_2ZrCl_2 and Me_3Al

We have previously described a similar reduction of sulfoxides to sulfides in the transformation of cyclic organoaluminum compounds into 3-alkyltetrahydrothiophenes under the action of thionyl chloride.[19] The reaction of dichloroborane with aliphatic sulfoxides also gives the corresponding sulfides.[20] Thus, we propose that the conversion of 1-alkynyl sulfoxides into 1-alkynyl sulfides **7** under the reaction conditions of an alkyne methylalumination, proceeds as follows. According to the Negishi methylalumination reaction of alkynes[21] under the reaction conditions, Cl_2ZrCp_2 and Me_3Al undergo a Me–Cl exchange to produce Me_2AlCl (**A**) (Scheme 4). Further, the reaction of Me_2AlCl with 1-alkynyl sulfoxides can produce intermediate **B**, which generates 1-alkynyl sulfides because of cleavage of MeOAlMeCl.

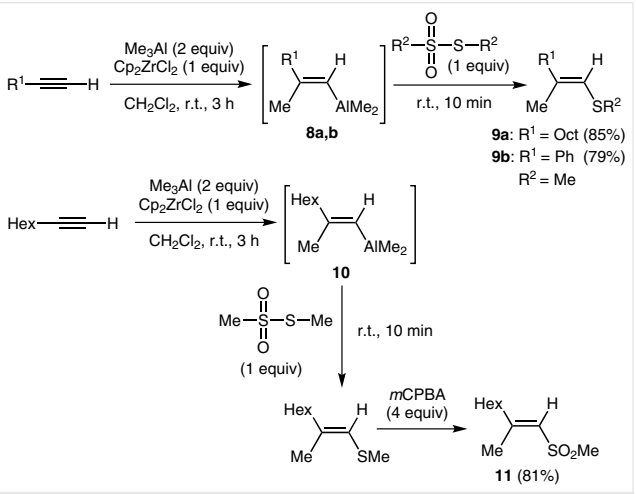


Scheme 4 A plausible mechanism for the reduction of sulfoxides to sulfides in the reaction of 1-alkynyl sulfoxides with Cp_2ZrCl_2 and Me_3Al

Note that an increasing amount of Me_3Al (5 equiv) led to alkenyl sulfides as the methylalumination products. After the addition of Me_3Al (5 equiv) to 1-(methylsulfinyl)dec-1-yne in the presence of 20 mol% Cp_2ZrCl_2 in dichloromethane followed by hydrolysis, dec-1-yn-1-yl(methyl)sulfane (**6b**) was isolated from the reaction mixture in 68% yield within 18 hours (Scheme 3).

In order to develop a new method for the synthesis of alkenyl sulfides of various structures via organoaluminum synthesis, we undertook a study aimed at the development of an efficient sulfanylation reagent for alkenylalanes. Development of such a sulfanylation reagent would enable the conversion of a wide range of organoaluminum compounds, in one preparative step, to alkenyl sulfides, which can be easily oxidized either to sulfoxides or to sulfones.

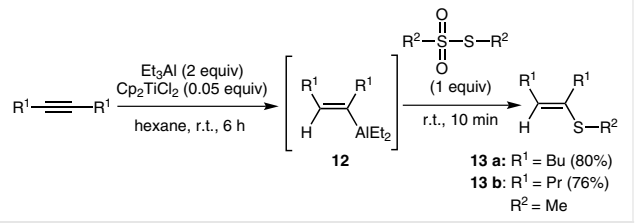
Earlier, we reported that sulfonic acid derivatives are efficient for a functionalization of various alkenylalanes. Efficient one-pot methods for alkenylalane halogenation with sulfonyl halides have been developed,[22] as well as silylation methods using trialkylsilyl sulfonates.[23] Meanwhile, recently we have developed a new method for sulfanylation of organoaluminum compounds on treatment with organic disulfides, which is suitable for the selective preparation of alkenyl sulfides in high yields in one step under mild conditions.[24] Thus, heteroatomic sulfonic acid derivatives demonstrated high performance in functionalization of organoaluminum compounds, providing introduction of a heteroatomic function into an acetylene molecule in one preparative step. In this connection, we assumed that *S*-methyl methanethiosulfonate would also be reactive toward organoaluminum compounds. The Negishi methylalumination results in the formation of 1-alkenyl(dimethyl)alanes from terminal acetylenes in high yield and with high stereoselectivity.[4,21] Our assumption was confirmed, as we found for the first time that 1-alkenyl(dimethyl)alanes **8a**,**b** reacted with *S*-methyl methanethiosulfonate at room temperature over a period of 10 minutes to give 1-alkenyl alkyl sulfides **9a**,**b** in high yields with high regio- and stereoselectivity (Scheme 5). Upon sulfide group addition, the stereochemical configuration of the double bond was retained. This was confirmed by the NOESY spectrum of compound **9a**, exhibiting coupling between hydrogen at the double bond and the α-hydrogen atoms of n-C_8H_{17} group. It is worth noting that one mole equivalent of the *S*-methyl methanesulfonothioate is sufficient for complete conversion of alkenylalane. This indicates that the transformation involves only the Al–C(sp^2) bond in alkenylalane. Apparently, this is attributable to a higher reactivity of the Al–C(sp^2) bond compared with the Al–C(sp^3) bond due to higher nucleophilicity of the carbon center at the double bond. Thus, 1-alkenyl(dimethyl)alanes reacted with *S*-methyl methanethiosulfonate to give 1-alkenyl alkyl sulfides with high regio- and stereoselectivity, that allowed the further oxidation of the sulfides to sulfones. For example, sequential treatment of 1-alkenyl(dimethyl)alane **10** with *S*-methyl methanethiosulfonate and 3-chloroperbenzoic acid yielded (*E*)-2-methyl-1-(methylsulfonyl)oct-1-ene (**11**) in 81% yield.



Scheme 5 Reaction of β,β-disubstituted 1-alkenylaluminums with *S*-methyl methanethiosulfonate

The discovered reaction is a continuation of our studies dealing with the development of efficient one-pot methods for the synthesis of alkenyl sulfides from alkenylalanes.[24] The reactions of trialkylalane with S, S_2Cl_2, or SCl_2 reported in the literature are nonselective and often produce mixtures of organic sulfides, disulfides, and trisulfides.[25]

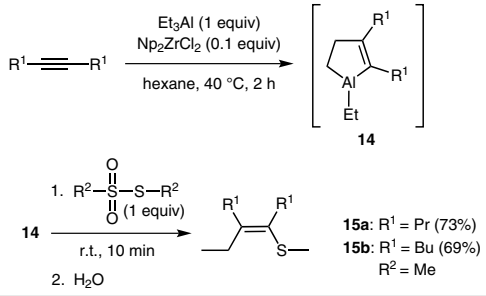
Owing to the simplicity of the procedure described above and to the high efficiency of *S*-methyl methanethiosulfonate for the preparation of alkenyl sulfides, an attempt was made to apply this strategy for the functionalization of alkenylalanes of various structures containing an ethyl group at aluminum. Previously, we reported the Ti-catalyzed hydroalumination of disubstituted acetylenes with Et_3Al.[26] The reaction of α,β-disubstituted vinylalane **12** obtained in this reaction with 1 equivalent of *S*-methyl methanethiosulfonate furnished alkenyl sulfide **13** in high yield (Scheme 6).



Scheme 6 Reaction of α,β-disubstituted 1-alkenylaluminums with *S*-methyl methanethiosulfonate

Aluminacyclopent-2-enes represent an interesting example of cyclic α,β,β-trisubstituted vinylalanes obtained by the Zr-catalyzed reaction of disubstituted acetylenes with Et_3Al.[17] The reaction of aluminacyclopentene **14** with

S-methyl methanethiosulfonate involves only the Al–C(sp^2) bond of the metallacycle and gives sulfides **15a**,**b** in a high yield (Scheme 7). An increase in the amount of the disulfide does not favor the formation of a disulfide product. Meanwhile, the sulfanylation of aluminacyclopent-2-enes with organic disulfides, which we proposed previously, furnished sulfanylation products only at the Al–C(sp^3) bond of the metallacycle.[23] The silylation of 2,3-dialkyl-substituted aluminacyclopent-2-enes on treatment with organosilicon esters of sulfonic acids also involves the Al–C(sp^3) bond of the ring.[22] Thus, methyl thiosulfonate provided a chemoselective functionalization of the Al–C(sp^2) bond of cyclic α,β,β-trisubstituted vinylalanes.



Scheme 7 Reaction of aluminacyclopent-2-enes with *S*-methyl methanethiosulfonate

In summary, we have accomplished for the first time the selective Cp_2ZrCl_2-catalyzed methylalumination of substituted 1-alkynyl sulfones and 1-alkynyl sulfides by reactions with Me_3Al providing 1-alkenyl sulfones and 1-alkenyl sulfides, respectively, in high yields. Also, we have developed a new sulfanylation method for 1-alkenylalanes with *S*-methyl methanethiosulfonate, which gives substituted 1-alkenyl sulfides in high yields and with high selectivity in one step under mild conditions.

All reagents were obtained from Sigma-Aldrich or Acros. The use of *n*-hexane as solvent is represented by – hexane – consistently throughout. CH_2Cl_2 and hexane were distilled over P_2O_5. *S*-Methyl methanethiosulfonate was prepared by reduction of sulfonyl halides with Zn powder.[27] (Methylthio)acetylenes were prepared from terminal alkynes and *S*-methyl methanethiosulfonate.[28] Substituted 1-alkynyl sulfones were prepared by electrophilic substitution reaction trimethylsilyl-1-alkynes under the influence benzenesulfonyl chloride and powdered aluminum chloride.[29] IR spectra were recorded on Bruker VE Vertex 70v spectrometer as liquid films or in Nujol and are reported in wavenumbers (cm^{-1}). NMR spectra were recorded on a Bruker Avance 400 spectrometer. The ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$. The chemical shifts are reported in ppm relative to TMS as the internal standard. The numbering of atoms for ^{13}C and ^1H NMR assignments of the compounds **2a–d**, **3a**, **5a**,**c**, **6a–c**, **7b**, **9a**,**b**, **11**, **13a**,**b**, and **15a**,**b** is shown in Figures 1–4. Elemental analysis was performed using a Carlo-Erba CHN 1106 elemental analyzer. Mass spectra were obtained on a Finnigan 4021 instrument. The yields were calculated from the isolated amounts of 1-alkenyl sulfides and 1-alkenyl sulfones obtained from starting alkynes.

1-Alkenyl Sulfones 2a–d and 3a via Zr-Catalyzed Methylalumination of 1-Alkynyl Sulfones (Figure 1)

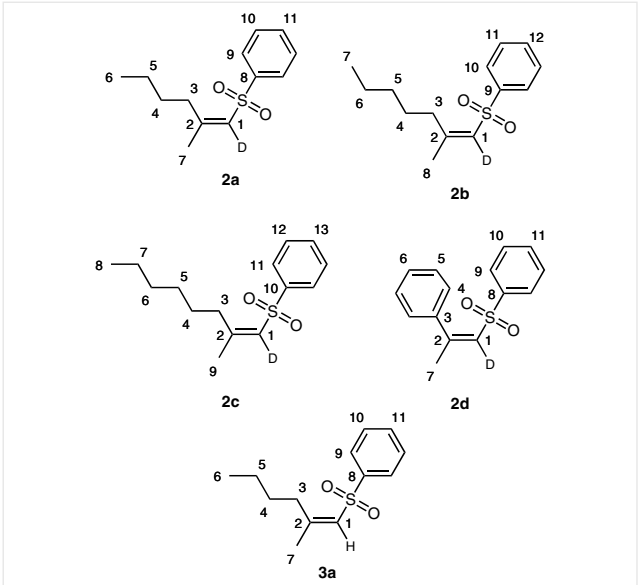


Figure 1 Numbering of atoms in the ^{13}C and ^1H NMR spectra of the compounds **2a–d** and **3a**

(*Z*)-[(2-Methylhex-1-en-1-yl-1-*d*)sulfonyl]benzene (2a); Typical Procedure

To a 25 mL, argon-swept flask, equipped with a magnetic stirrer and rubber septa, were added Cp_2ZrCl_2 (117 mg, 0.40 mmol) suspended in CH_2Cl_2 (5 mL) and Me_3Al (1.14 mL, 12 mmol) (**Caution**: organoaluminums are pyrophoric and can ignite on contact with air, H_2O, or any oxidizer) at r.t. To the solution was added 1-(phenylsulfonyl)-1-hexyne (444 mg, 2 mmol) at r.t. and stirred for 18 h. Then, the reaction mixture was diluted with hexane (5 mL) and D_2O (3 mL) was added dropwise while cooling the reaction flask in an ice bath. The precipitate was filtered on a filter paper and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried (anhyd $CaCl_2$). Evaporation of solvent and purification of the residue by column chromatography (PE/EtOAc, 9:1 to 4:1) gave a colorless oil; yield: 380 mg (80%); R_f = 0.81 (PE/EtOAc, 4:1).

IR (film): 2958, 2933, 2872, 1612, 1447, 1304, 1290, 1151, 1085, 751, 723, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.1 Hz, 3 H, 6-CH_3), 1.25–1.40 (m, 4 H, 4,5-CH_2), 1.88 (s, 3 H, 7-CH_3), 2.59 (t, *J* = 7.5 Hz, 2 H, 3-CH_2), 7.50–7.95 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (C-6), 22.8 (C-5), 24.5 (C-7), 29.1 (C-4), 32.3 (C-3), 127.1 (2 C, C-9), 129.1 (2 C, C-10), 132.1 (C-11), 142.6 (C-8), 158.3 (C-2).

MS (EI): *m*/*z* (%) = 239 (27, [M^+]), 210 (47), 204 (7), 173 (11), 144 (32), 125 (68), 97 (92), 82 (100), 56 (79), 41 (57).

Anal. Calcd for $C_{13}H_{17}DO_2S$: C, 69.91. Found: C, 69.94.

(*Z*)-[(2-Methylhept-1-en-1-yl-1-*d*)sulfonyl]benzene (2b)

Using the procedure described above, 1-(phenylsulfonyl)-1-heptyne (472 mg, 2 mmol) gave a crude product that was purified by flash chromatography (silica gel, PE/EtOAc, 9:1 to 4:1) to afford a colorless oil; yield: 445 mg (88%); R_f = 0.80 (PE/EtOAc, 4:1).

IR (film): 2957, 2931, 2861, 1612, 1447, 1313, 1305, 1151, 1086, 753, 723, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 3 H, 7-CH_3), 1.20–1.35 (m, 4 H, 4,6-CH_2), 1.35–1.50 (m, 2 H, 5-CH_2), 1.89 (s, 3 H, 8-CH_3), 2.59 (t, *J* = 7.5 Hz, 2 H, 3-CH_2), 7.50–7.95 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (C-7), 22.4 (C-6), 24.5 (C-8), 27.5 (C-5), 31.8 (C-4), 32.3 (C-3) 127.1 (2 C, C-9), 129.1 (2 C, C-10), 132.1 (C-11), 142.7 (C-8), 158.3 (C-1).

MS (EI): *m*/*z* (%) = 253 (30, [M^+]), 236 (3), 210 (52), 198 (7), 162 (10), 130 (36), 125 (88), 96 (89), 82 (54), 69 (100), 56 (81), 41 (97).

Anal. Calcd for $C_{14}H_{19}DO_2S$: C, 70.84. Found: C, 70.87.

(*Z*)-[(2-Methyloct-1-en-1-yl-1-*d*)sulfonyl]benzene (2c)

Using the procedure described above, (oct-1-yn-1-ylsulfonyl)benzene (500 mg, 2 mmol) gave a crude product that was purified by flash chromatography (silica gel, PE/EtOAc, 9:1 to 4:1) to afford a colorless oil; yield: 433 mg (81%); R_f = 0.79 (PE/EtOAc, 4:1).

IR (film): 2955, 2930, 2858, 1612, 1545, 1447, 1312, 1305, 1150, 1085, 754, 725, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 3 H, 8-CH_3), 1.22–1.35 (m, 6 H, 5,6,7-CH_2), 1.35–1.48 (m, 2 H, 4-CH_2), 1.89 (s, 3 H, 9-CH_3), 2.59 (t, *J* = 10.0, 2 H, 3-CH_2), 7.50–8.05 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (C-8), 22.5 (C-7), 24.5 (C-9), 27.9 (C-4), 29.4 and 31.6 (C-5,6), 32.5 (C-3) 127.2 (2 C, C-11), 129.1 (2 C, C-12), 132.9 (C-13), 142.7 (C-10), 158.3 (C-2).

MS (EI): *m*/*z* (%) = 267 (2, [M^+]), 257 (81), 229 (52), 217 (64), 189 (17), 187 (13), 157 (15), 133 (14), 115 (8), 73 (10), 57 (100), 41 (33).

Anal. Calcd for $C_{15}H_{21}DO_2S$: C, 67.37. Found: C, 67.39.

(*Z*)-[(2-Phenylprop-1-en-1-yl-1-*d*)sulfonyl]benzene (2d)

Using the procedure described above, [(phenylethynyl)sulfonyl]benzene (484 mg, 2 mmol) gave a crude product that was purified by flash chromatography (silica gel, PE/EtOAc, 9:1 to 4:1) to afford colorless crystals; yield: 456 mg (92%); R_f = 0.63 (PE/EtOAc, 4:1).

IR (film): 3043, 3029, 2959, 2928, 1612, 1483, 1445, 1411, 1392, 1316, 1029, 984, 750, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.56 (s, 3 H, 7-CH_3), 7.20–8.00 (m, 10 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2 (C-7), 126.3 (2 C, C-5), 127.3 (2 C, C-9), 128.8 (2 C, C-10), 129.3 (2 C, C-4), 129.9 (C-6), 133.2 (C-11), 153.4 (C-1), 140.1 (C-8), 142.2 (C-3).

MS (EI): *m*/*z* (%) = 259 (24, [M^+]), 224 (11), 116 (100), 106 (65), 92 (3), 77 (37), 51 (33).

Anal. Calcd for $C_{15}H_{13}DO_2S$: C, 74.04. Found: C, 74.07.

(*Z*)-[(2-Methylhex-1-en-1-yl)sulfonyl]benzene (3a)

Using the procedure described above, reaction of 1-(phenylsulfonyl)-1-heptyne (444 mg, 2 mmol) and H_2O (instead of D_2O) gave a crude product that was purified by column chromatography on silica gel (PE/EtOAc, 9:1 to 4:1) to afford a colorless oil; yield: 376 mg (79%); R_f = 0.83 (PE/EtOAc, 4:1).

IR (film): 2958, 2933, 2872, 1611, 1446, 1323, 1290, 1151, 1085, 751, 723, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.7 Hz, 3 H, 6-CH_3), 1.25–1.45 (m, 4 H, 4,5-CH_2), 1.88 (s, 3 H, 7-CH_3), 2.60 (t, *J* = 7.5 Hz, 2 H, 3-CH_2), 6.18 (s, 1-CH), 7.50–7.95 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (C-6), 22.8 (C-5), 24.5 (C-7), 30.1 (C-4), 32.3 (C-3), 126.2 (C-1), 127.1 (2 C, C-9), 129.1 (2 C, C-10), 132.1 (C-11), 142.6 (C-8), 158.3 (C-2).

MS (EI): *m*/*z* (%) = 238 (23, [M^+]), 209 (39), 143 (36), 125 (52), 96 (67), 81 (100), 55 (92), 41 (73).

Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.54; H, 7.67.

1-Alkenyl Sulfides 5a,c and 6a–c via Zr-Catalyzed Methylalumination of 1-Alkynyl Sulfides (Figure 2)

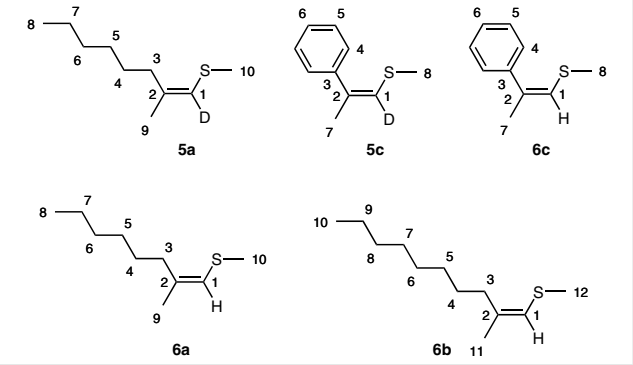


Figure 2 Numbering of atoms in the ^{13}C and ^1H NMR spectra of the compounds **5a**,**c** and **6a–c**

(*Z*)-Methyl(2-methyloct-1-en-1-yl-1-*d*)sulfane (5a); Typical Procedure

To a 25 mL, argon-swept flask, equipped with a magnetic stirrer and rubber septa, were added Cp_2ZrCl_2 (117 mg, 0.40 mmol) suspended in CH_2Cl_2 (5 mL) and Me_3Al (0.57 mL, 6 mmol) (**Caution**: organoaluminums are pyrophoric and can ignite on contact with air, H_2O, or any oxidizer) at r.t. To the solution was added methyl(oct-1-yn-1-yl)sulfane (312 mg, 2 mmol) of at r.t. and stirred for 18 h. Then, the reaction mixture was diluted with hexane (5 mL), and D_2O (3 mL) was added dropwise while cooling the reaction flask in an ice bath. The precipitate was filtered on a filter paper and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried (anhyd $CaCl_2$). Evaporation of solvent and purification of the residue by column chromatography (silica gel, hexane) gave a colorless oil; yield: 294 mg (85%); R_f = 0.43 (hexane).

IR (film): 2958, 2933, 2859, 2200, 1730, 1698, 1467, 1457, 1377, 1307, 1099, 1041, 1009, 804, 780, 750, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.5 Hz, 3 H, 8-CH_3), 1.24–1.36 (m, 6 H, 5,6,7-CH_2), 1.36–1.46 (m, 2 H, 4-CH_2), 1.76 (s, 3 H, 9-CH_3), 2.15 (t, *J* = 7.5 Hz, 2 H, 3-CH_2), 2.24 (s, 3 H, 10- CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (C-8), 17.3 (C-10), 22.6 (C-7), 22.8 (C-9), 27.3 (C-4), 29.1 and 31.8 (2 C, C-5,6), 33.6 (C-3), 119.70 (t, $^1J_{C,D}$ = 21.0, C-1), 137.4 (C-2).

MS (EI): *m*/*z* (%) = 173 (2, [M^+]), 157 (3), 124 (2), 115 (4), 101 (100), 67 (21), 59 (23), 41 (21).

Anal. Calcd for $C_{10}H_{19}DS$: C, 69.29. Found: C, 69.32.

(*Z*)-Methyl(2-phenylprop-1-en-1-yl-1-*d*)sulfane (5c)

Using the procedure described above, methyl(phenylethynyl)sulfane (296 mg, 2 mmol) gave a crude product that was purified by flash chromatography (silica gel, hexane) to afford a colorless oil; yield: 261 mg (80%); R_f = 0.50 (hexane).

IR (film): 3019, 2986, 2962, 2923, 2200, 1600, 1495, 1437, 1316, 1300, 1027, 1013, 803, 762, 750, 725, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.19 (d, *J* = 3.4 Hz, 3 H, 8-CH_3), 2.29 (d, *J* = 3.4 Hz, 3 H, 7-CH_3), 7.10–7.65 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1 (C-7), 24.8 (C-8), 123.6 (t, $^1J_{C,D}$ = 21.0 Hz, C-1), 127.1 (C-6), 127.5 (C-5), 128.1 (C-4) 133.6 (C-2), 140.5 (C-3).

MS (EI): *m*/*z* (%) = 165 (100, [M^+]), 150 (68), 135 (82), 116 (67), 106 (18), 91 (15), 77 (20), 63 (11), 51 (22), 40 (8).

Anal. Calcd for $C_{10}H_{11}DS$: C, 72.67. Found: C, 72.61.

(*Z*)-Methyl(2-methyloct-1-en-1-yl)sulfane (6a)

Using the procedure described above, reaction of methyl(oct-1-yn-1-yl)sulfane (368 mg, 2 mmol) and H_2O (instead of D_2O) gave a crude product that was purified by column chromatography on silica gel (hexane) to afford a colorless oil; yield: 292 mg (73%); R_f = 0.45 (hexane).

IR (film): 2955, 2930, 2858, 1612, 1545, 1447, 1377, 1307, 1099, 1041, 1009, 804, 780, 750, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.3 Hz, 3 H, 8-CH_3), 1.26–1.36 (m, 6 H, 5,6,7-CH_2), 1.36–1.48 (m, 2 H, 4-CH_2), 1.76 (s, 3 H, 9-CH_3), 2.16 (t, *J* = 8.0 Hz, 2 H, 3-CH_2), 2.24 (s, 3 H, 10-CH_3), 5.60 (s, 1 H, 1-CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (C-8), 17.3 (C-10), 22.6 (C-7), 22.9 (C-9), 27.3 (C-4), 29.1 and 31.8 (2 C, C-5,6), 33.7 (C-3), 120.1 (C-1), 137.5 (C-2).

MS (EI): *m*/*z* (%) = 172 (21, [M^+]), 157 (3), 115 (4), 101 (100), 81 (12), 67 (22), 59 (23), 41 (21).

Anal. Calcd for $C_{10}H_{20}S$: C, 69.70; H, 11.70. Found: C, 69.68; H, 11.66.

(*Z*)-Methyl(2-methyldec-1-en-1-yl)sulfane (6b)

To a 25 mL, argon-swept flask, equipped with a magnetic stirrer and rubber septa, were added Cp_2ZrCl_2 (117 mg, 0.40 mmol) suspended in CH_2Cl_2 (5 mL) and Me_3Al (0.57 mL, 6 mmol) (**Caution**: organoaluminums are pyrophoric and can ignite on contact with air, H_2O, or any oxidizer) at r.t. To the solution was added dec-1-yn-1-yl(methyl)sulfane (424 mg, 2 mmol) of at r.t. and stirred for 18 h. Then, the reaction mixture was diluted with hexane (5 mL), and H_2O (3 mL) was added dropwise while cooling the reaction flask in an ice bath. The precipitate was filtered on a filter paper and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried (anhyd $CaCl_2$). Evaporation of solvent and purification of the residue by column chromatography (silica gel, hexane) gave a colorless oil; yield: 308 mg (77%); R_f = 0.47 (hexane).

IR (film): 2957, 2923, 2871, 2855, 1730, 1696, 1465, 1457, 1377, 1307, 1099, 1041, 1005, 801, 777, 722, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.8 Hz, 3 H, 10-CH_3), 1.15–1.35 (m, 8 H, 5,6,7,8-CH_2), 1.35–1.50 (m, 2 H, 4-CH_2), 1.76 (s, 3 H, 11-CH_3), 2.16 (t, *J* = 7.5 Hz, 2 H, 3-CH_2), 2.24 (s, 3 H, 12-CH_3), 5.60 (s, 1 H, 1-CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (C-10), 17.4 (C-12), 22.7 (C-9), 22.9 (C-11), 27.4 (C-4), 29.3 and 29.5, 30.1 and 31.9 (4 C, C-5,6,7,8), 33.6 (C-3), 120.1 (C-1), 137.5 (C-2).

MS (EI): *m*/*z* (%) = 200 (21, [M^+]), 185 (3), 101 (100), 81 (12), 67 (17), 41 (27).

Anal. Calcd for $C_{12}H_{24}S$: C, 71.93; H, 12.07. Found: C, 71.97; H, 12.11.

(*Z*)-Methyl(2-phenylprop-1-en-1-yl)sulfane (6c)

Using the procedure described above, methyl(phenylethynyl)sulfane (296 mg, 2 mmol) gave a crude product that was purified by flash chromatography (silica gel, hexane) to afford a colorless oil; yield: 292 mg (89%); R_f = 0.41 (hexane).

IR (film): 3019, 2980, 2962, 2919, 1599, 1490, 1437, 1316, 1027, 1013, 803, 762, 725, 697 cm^{-1}.

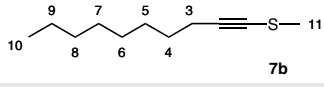
^1H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, 8-CH_3), 2.30 (s, 3 H, 7-CH_3), 6.03 (s, 1-CH), 7.15–7.65 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2 (C-7), 24.9 (C-8), 124.1 (C-1), 127.2 (C-6), 127.6 (2 C, C-5), 128.1 (2 C, C-4) 131.5 (C-2), 140.7 (C-3).

MS (EI): *m*/*z* (%) = 164 (100, [M^+]), 149 (73), 134 (85), 115 (74), 105 (20), 91 (20), 77 (21), 51 (21).

Anal. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36. Found: C, 73.15; H, 7.40.

Reaction of 1-Alkynyl Sulfoxides with Cp_2ZrCl_2 and Me_3Al (Figure 3)



7b

Figure 3 Numbering of atoms in the ^1H and ^{13}C NMR spectra of **7b**

Dec-1-yn-1-yl(methyl)sulfane (7b); Typical Procedure

To a 25 mL, argon-swept flask, equipped with a magnetic stirrer and rubber septa, were added Cp_2ZrCl_2 (117 mg, 0.40 mmol) suspended in CH_2Cl_2 (5 mL) and Me_3Al (0.57 mL, 6 mmol) (**Caution**: organoaluminums are pyrophoric and can ignite on contact with air, H_2O, or any oxidizer) at 0 °C. To the solution was added 1-(methylsulfinyl)dec-1-yne (400 mg, 2 mmol) of at r.t. and stirred for 20 min. Then, the reaction mixture was diluted with hexane (5 mL), and H_2O (3 mL) was added dropwise while cooling the reaction flask in an ice bath. The precipitate was filtered on a filter paper and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried (anhyd $CaCl_2$). Evaporation of solvent and purification of the residue by column chromatography (eluent: hexane) gave a colorless oil; yield: 291 mg (79%); R_f = 0.48 (hexane).

IR (film): 3260, 3323, 2957, 2923, 2871, 2855, 2260, 2200, 1698, 1468, 1457, 1377, 1096, 1041, 1009, 806, 720, 695, 680 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.7 Hz, 3 H, 10-CH_3), 1.20–1.45 (m, 10 H, 5,6,7,8,9-CH_2), 1.45–1.58 (m, 2 H, 4-CH_2), 2.29 (t, *J* = 8.0 Hz, 2 H, 3-CH_2), 2.37 (s, 3 H, 11-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (C-10), 19.3 (C-11), 20.1, 28.8, 28.9, 29.1, and 29.2 (C-5,6,7,8,9), 22.7 (C-4), 31.8 (C-3), 69.8 (C-1), 93.3 (C-2).

MS (EI): *m*/*z* (%) = 184 (2, [M^+]), 183 (14), 155 (7), 141 (26), 127 (33), 93 (53), 79 (67), 55 (57), 41 (100).

Anal. Calcd for $C_{11}H_{20}S$: C, 71.67; H, 10.94. Found: C, 71.69; H, 10.91.

1-Alkenyl Sulfides 9a,b via Zr-Catalyzed Methylalumination of Terminal Alkynes Followed by Treatment with *S*-Methyl Methanethiosulfonate (Figure 4)

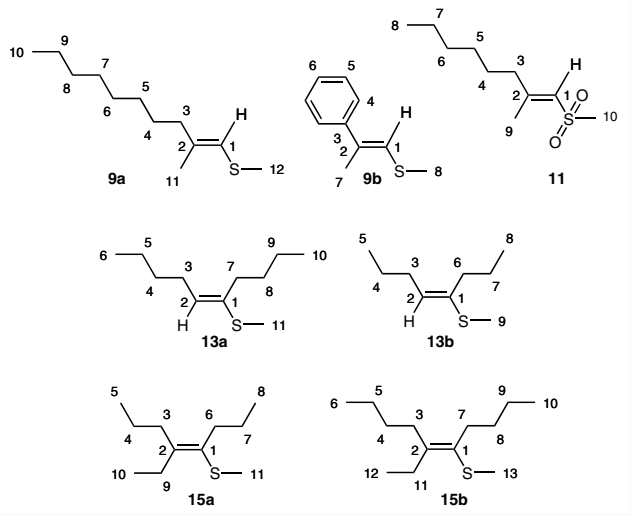


Figure 4 Numbering of atoms in the ^{1}H and ^{13}C NMR spectra of the compounds **9a**,**b**, **11**, **13a**,**b** and **15a**,**b**

(*E*)-Methyl(2-methyldec-1-en-1-yl)sulfane (9a); Typical Procedure

To a 25 mL, argon-swept flask, equipped with a magnetic stirrer and rubber septa, were added Cp_2ZrCl_2 (580 mg, 2 mmol) suspended in CH_2Cl_2 (5 mL) and Me_3Al (0.38 mL, 4 mmol) (**Caution**: organoaluminums are pyrophoric and can ignite on contact with air, H_2O, or any oxidizer) at 0 °C. To the solution was added 1-octyne (220 mg, 2 mmol) at r.t. and stirred for 3 h. *S*-Methyl methanethiosulfonate (252 mg, 2 mmol) was added to the reaction mixture at 0 °C and stirred at r.t. for 10 min. Then, the mixture was diluted with hexane (5 mL), and H_2O (3 mL) was added dropwise while cooling the reaction flask in an ice bath. The precipitate was filtered on a filter paper and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried (anhyd $CaCl_2$). Evaporation of solvent and purification of the residue by column chromatography (eluent: hexane) gave a colorless oil; yield: 284 mg (85%); R_f = 0.49 (hexane).

IR (film): 2958, 2923, 2871, 2858, 2845, 1730, 1696, 1465, 1377, 1310, 1099, 1041, 1008, 801, 777, 750, 722, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.7 Hz, 3 H, 10-CH_3), 1.15–1.35 (m, 10 H, 5,6,7,8,9-CH_2), 1.35–1.50 (m, 2 H, 4-CH_2), 1.73 (s, 3 H, 11-CH_3), 2.05 (t, *J* = 8.0 Hz, 2 H, 3-CH_2), 2.26 (s, 3 H, 12-CH_3), 5.60 (s, 1 H, 1-CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (C-10), 17.2 (C-12), 17.8 (C-11), 22.7, 29.3, 29.4, 29.5, and 31.9 (C-5,6,7,8,9), 27.8 (C-4), 39.2 (C-3), 119.7 (C-1), 136.9 (C-2).

MS (EI): *m*/*z* (%) = 200 (23, [M$^+$]), 185 (3), 115 (3), 101 (100), 67 (17), 55 (16), 41 (23).

Anal. Calcd for $C_{12}H_{24}S$: C, 71.93; H, 12.07. Found: C, 71.98; H, 12.15.

(*E*)-Methyl(2-phenylprop-1-en-1-yl)sulfane (9b)

Using the procedure described above, phenylacetylene (204 mg, 2 mmol) and *S*-methyl methanethiosulfonate (252 mg, 2 mmol) gave a crude product that was purified by flash chromatography (silica gel, hexane) to afford a colorless oil; yield: 177 mg (79%); R_f = 0.89 (hexane).

IR (film): 3056, 3027, 2956, 2922, 1730, 1685, 1595, 1493, 1443, 1377, 1313, 1028, 984, 810, 750, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3 H, 8-CH_3), 2.42 (s, 3 H, 7-CH_3), 6.30 (s, 1 H, 1-CH), 7.20–7.40 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.3 (C-7), 17.5 (C-8), 125.1 (2 C, C-5), 125.3 (C-1), 125.9 (C-6), 128.3 (2 C, C-4) 133.1 (C-2), 141.9 (C-3).

MS (EI): *m*/*z* (%) = 164 (100, [M$^+$]), 149 (74), 134 (84), 115 (73), 105 (19), 91 (19), 77 (20), 63 (12), 51 (21).

Anal. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36. Found: C, 73.09; H, 7.41.

(*E*)-2-Methyl-1-(methylsulfonyl)oct-1-ene (11)

Using the procedure described above, oct-1-yne (220 mg, 2 mmol) and *S*-methyl methanethiosulfonate (252 mg, 2 mmol) gave a crude product that was used without further purification. To a solution of methyl(2-methyloct-1-en-1-yl)sulfane (400 mg, 2 mmol) in anhyd CH_2Cl_2 (20 mL/mmol sulfide) was added 3-chloroperbenzoic acid (692 mg, 4.0 equiv) in one portion at 0 °C and the reaction mixture was stirred at 0 °C for 2 h. The reaction was quenched with 30% aq Na_2SO_3 and extracted with CH_2Cl_2. The combined organic extracts were washed with sat. aq $NaHCO_3$ and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE/EtOAc, 9:1) to give a colorless oil; yield: 330 mg (81%); R_f = 0.84.

IR (film): 2956, 2930, 2859, 1631, 1465, 1413, 1379, 1300, 1132, 963, 813, 771, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 5.9 Hz, 3 H, 8-CH_3), 1.22–1.40 (m, 6 H, 5,6,7-CH_2), 1.40–1.56 (m, 2 H, 4-CH_2), 2.12–2.21 (m, 2 H, 3-CH_2), 2.17 (s, 3 H, 9-CH_3), 2.95 (s, 3 H, 10-CH_3), 6.12 (s, 1 H, 1-CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (C-8), 17.8 (C-9), 22.5 (C-7), 27.1 (C-4), 28.7 and 31.5 (C-5,6), 40.3 (C-3), 43.8 (C-10), 125.1 (C-1), 158.9 (C-2).

MS (EI): *m*/*z* (%) = 204 (<1, [M$^+$]), 147 (14), 134 (22), 124 (15), 109 (9), 95 (40), 81 (48), 69 (60), 55 (97), 41 (100).

Anal. Calcd for $C_{12}H_{24}S$: C, 58.78; H, 9.87. Found: C, 59.98; H, 9.91.

1-Alkenyl Sulfides 13a,b via Ti-Catalyzed Hydrolalumination of Alkynes Followed by Treatment with *S*-Methyl Methanethiosulfonate

(*E*)-Dec-5-en-5-yl(methyl)sulfane (13a); Typical Procedure

To Cp_2TiCl_2 (250 mg, 0.10 mmol) suspended in hexane (5 mL) were added 5-decyne (276 mg, 2 mmol) and Et_3Al (0.30 mL, 2 mmol) at r.t. under an argon atmosphere. After 6 h, to the reaction mixture was added *S*-methyl methanethiosulfonate (250 mg, 2 mmol) at 0 °C and stirred for 10 min at r.t. Then, the mixture was diluted with hexane (5 mL), and H_2O (3 mL) was added dropwise while cooling the reaction flask in an ice bath. The precipitate was filtered on a filter paper and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried (anhyd

$CaCl_2$). Evaporation of solvent and purification of the residue by column chromatography (eluent: hexane) gave a colorless oil; yield: 298 mg (80%); R_f = 0.53 (hexane).

IR (film): 2958, 2933, 2873, 2862, 1716, 1466, 1457, 1411, 1379, 1261, 1097, 1088, 1047, 1020, 805, 731 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.80–1.05 (m, 6 H, 6,10-CH_3), 1.25–1.45 (m, 6 H, 4,5,9-CH_2), 1.45–1.55 (m, 2 H, 8-CH_2), 2.11 (q, *J* = 7.1 Hz, 2 H, 3-CH_2), 2.15–2.30 (m, 2 H, 7-CH_2), 2.21 (s, 3 H, 11-CH_3), 5.12 (t, *J* = 7.3 Hz, 2-CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 and 14.1 (C-6,10), 14.8 (C-11), 22.3 (C-4), 22.5 (C-8), 28.2 (C-7), 31.3 and 31.6 (C-5,9), 32.2 (C-3), 122.5 (C-2), 135.7 (C-1).

MS (EI): *m*/*z* (%) = 186 (2, [M^+]), 157 (<1), 131 (8), 117 (17), 97 (28), 83 (57), 69 (52), 61 (63), 55 (72), 41 (57).

Anal. Calcd for $C_{11}H_{22}S$: C, 70.89; H, 11.90. Found: C, 70.91; H, 11.88.

(*E*)-Methyl(oct-4-en-4-yl)sulfane (13b)

Using the procedure described above, 4-octyne (220 mg, 2 mmol) and *S*-methyl methanethiosulfonate (250 mg, 2 mmol) gave a crude product that was purified by flash chromatography (silica gel, hexane) to afford a colorless oi; yield: 250 mg (76%); R_f = 0.46 (hexane).

IR (film): 2958, 2933, 2873, 1730, 1715, 1465, 1457, 1437, 1378, 1140, 1119, 755, 735 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.85–1.06 (m, 6 H, 5,8-CH_3), 1.35–1.47 (m, 2 H, 4-CH_2), 1.47–1.60 (m, 2 H, 7-CH_2), 2.09 (q, *J* = 7.6 Hz, 2 H, 3-CH_2), 2.16–2.26 (m, 2 H, 6-CH_2), 2.21 (s, 3 H, 9-CH_3), 5.14 (t, *J* = 7.2 Hz, 1 H, 2-CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (2 C, C-5,8), 14.8 (C-9), 22.2 (C-4), 23.2 (C-7), 30.6 (C-3), 33.8 (C-6), 122.5 (C-2), 135.6 (C-1).

MS (EI): *m*/*z* (%) = 158 (44, [M^+]), 143 (21), 129 (100), 115 (11), 88 (18), 81 (60), 67 (27), 55 (29), 41 (49).

Anal. Calcd for $C_9H_{18}S$: C, 68.28; H, 11.46. Found: C, 68.31; H, 11.48.

1-Alkenyl Sulfides 15a,b via Zr-Catalyzed Cyclic Carboalumination of Alkynes Followed by Treatment with *S*-Methyl Methanethiosulfonate

(*E*)-(6-Ethyldec-5-en-5-yl)(methyl)sulfane (15a); Typical Procedure

To Cp_2ZrCl_2 (580 mg, 0.20 mmol) suspended in hexane (5 mL) were added 5-decyne (276 mg, 2 mmol) and Et_3Al (0.30 mL, 2 mmol) at 40 °C under an atmosphere of argon. After 2 h, to the reaction mixture was added *S*-methyl methanethiosulfonate (250 mg, 2 mmol) at 0 °C and stirred for 24 h at r.t. Then, the mixture was diluted with hexane (5 mL), and H_2O (3 mL) was added dropwise while cooling the reaction flask in an ice bath. The precipitate was filtered on a filter paper and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried (anhyd $CaCl_2$). Evaporation of solvent and purification of the residue by column chromatography (eluent: hexane) gave a colorless oil; yield: 272 mg (73%); R_f = 0.48 (hexane).

IR (film): 2959, 2931, 2872, 1465, 1457, 1378, 1261, 1095, 1036, 1019, 909, 806, 735 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.80–0.95 (m, 6 H, 6,10-CH_3), 0.99 (t, *J* = 6.0, 3 H, 12-CH_3), 1.15–1.45 (m, 6 H, 4,5,9-CH_2), 1.45–1.60 (m, 2 H, 8-CH_2), 2.09 (t, *J* = 8.0 Hz, 2 H, 3-CH_2), 2.15 (s, 3 H, 13-CH_3), 2.26 (t, *J* = 8.0 Hz, 2 H, 7-CH_2), 2.35 (q, *J* = 8.0 Hz, 2 H, 11-CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.3 (C-12), 14.1 and 14.2 (C-6,10), 15.9 (C-13), 22.5 (C-4), 23.1 (C-8), 27.1 (C-11), 30.7 (C-7), 31.1 and 31.4 (C-5,9), 32.0 (C-3), 128.7 (C-1), 143.4 (C-2).

MS (EI): *m*/*z* (%) = 214 (7, [M^+]), 200 (42), 185 (4), 172 (90), 158 (19), 124 (20), 117 (37), 95 (24), 82 (63), 55 (48).

Anal. Calcd for $C_{13}H_{26}S$: C, 72.82; H, 12.22. Found: C, 72.79; H, 12.19.

(*E*)-(5-Ethyloct-4-en-4-yl)(methyl)sulfane (15b)

Using the procedure described above, 4-octyne (220 mg, 2 mmol) and *S*-methyl methanethiosulfonate (250 mg, 2 mmol) gave a crude product that was purified by flash chromatography (silica gel, hexane) to afford a colorless oil; yield: 295 mg (69%); R_f = 0.51 (hexane).

IR (film): 2957, 2930, 2873, 2861, 1711, 1458, 1378, 1336, 1309, 1140, 956, 745 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.80–0.95 (m, 6 H, 5,8-CH_3), 1.00 (t, *J* = 6.0 Hz, 3 H, 10-CH_3), 1.25–1.45 (m, 2 H, 4-CH_2), 1.45–1.60 (m, 2 H, 7-CH_2), 2.09 (t, *J* = 6.0 Hz, 2 H, 6-CH_2), 2.16 (s, 3 H, 11-CH_3), 2.26 (t, *J* = 8.0 Hz, 2 H, 3-CH_2), 2.37 (q, *J* = 8.0 Hz, 2 H, 9-CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 (C-10), 13.8 and 14.3 (C-5,8), 15.9 (C-11), 22.1 (C-4), 22.3 (C-7), 27.1 (C-9), 32.9 (C-3), 34.4 (C-6), 128.7 (C-1), 143.5 (C-2).

MS (EI): *m*/*z* (%) = 186 (73, [M^+]), 171 (41), 144 (23), 129 (49), 1116 (11), 101 (23), 95 (46), 87 (28), 81 (63), 79 (30), 67 (100), 55 (87), 41 (99).

Anal. Calcd for $C_{11}H_{22}S$: C, 70.89; H, 11.90. Found: C, 70.87; H, 11.93.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588387.

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