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

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Supporting information

The reagents were obtained from Sigma-Aldrich or Acros. Dichloromethane and hexane were distilled over P₂O₅. S-methyl methanethiosulfonate was prepared by reduction of sulfonyl halides with zinc powder. The (methylthio)acetylenes was prepared from terminal alkynes and S-methylmethanethiosulfonate. Substituted 1-alkynyl sulfones was prepared by electrophilic substitution reaction trimethylsilyl-1-alkynes under the influence benzenesulfonyl chloride and powdered aluminum chloride. IR spectra were recorded on Bruker VE Vertex 70v spectrometer as liquid films or in Nujol and are reported in wavenumbers (cm⁻¹). Nuclear magnetic resonance spectroscopy was performed on a Bruker Avance 400. The ¹H NMR spectra were recorded at 400 MHz and ¹³C NMR spectra at 100 MHz in CDCl₃. The chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal standard. The numbering of atoms in the ¹³C and ¹H NMR spectra of the compounds 2a-d, 3a, 5a-c, 6a-c, 7b, 9a,b, 11, 13a,b and 15a,b is shown in Figures 1,2,3,4. Elemental analysis was performed using a Carlo-Erba CHN 1106 elemental analyser. Mass spectra were obtained on a Finnigan 4021 instrument. The yields were calculated from the isolated amount of 1-alkenyl sulfides, 1-alkenyl sulfones obtained from starting alkynes.

Preparation of 1-alkenyl sulfones 2a,b,c,d and 3a via Zr-catalyzed methylalumination of 1-alkynyl sulfones
Figure 1 The numbering of atoms in the 13C- 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, was added Cp₂ZrCl₂ (117 mg, 0.40 mmol) suspended in CH₂Cl₂ (5 mL) and Me₃Al (1.14 mL, 12 mmol) (caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer) at room temperature. To the solution was added 1-(phenylsulfanyl)-1-hexyne (444 mg, 2 mmol) of at room temperature and stirred for 18 h. Then, the reaction mixture was diluted with hexane (5 mL) and D₂O (3 mL) was added dropwise while cooling the reactor flask in an ice bath. The precipitate was filtered on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous CaCl₂. Evaporation of solvent and purification of the residue by column chromatography (petroleum ether : ethyl acetate, 9 : 1 to 4:1) gave a colourless oil; yield: 380 mg (80%); Rf = 0.81 (petroleum ether : ethyl acetate, 4:1).

IR (liquid film): 2958, 2933, 2872, 1612, 1447, 1304, 1290, 1151, 1085, 751, 723, 690 cm⁻¹.

¹H NMR (400MHz, CDCl₃): δ = 0.90 (t, J= 7.1, 3Н, С(6)Н₃), 1.25-1.40 (m, 4Н, С(4,5)Н₂), 1.88 (s, 3Н, С(7)Н₃), 2.59 (t, J= 7.5, 2Н, С(3)Н₂), 7.50-7.95 (m, 5Н, Ph).

¹³C NMR (100MHz, CDCl₃): δ = 13.9 (C(6)), 22.8 (C(5)), 24.5 (C(7)), 29.1 (C(4)), 32.3 (C(3)), 127.1 (2C, C(9)), 129.1 (2C, 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).


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

Using the procedure described above 1-(phenylsulfanyl)-1-heptyne (472 mg, 2 mmol) gave crude product that was purified by flash chromatography (silica gel, petroleum ether : ethyl
acetate, 9 : 1 to 4:1) to afford a colourless oil; yield: 445 mg (88%); \( R_f = 0.80 \) (petroleum ether : ethyl acetate, 4:1).

IR (liquid film): 2957, 2931, 2861, 1617, 1513, 1305, 1086, 753, 723, 690 cm\(^{-1}\).

\(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 0.89 \) (t, J= 6.7, 3H, C(7)H\(_3\)), 1.20-1.35 (m, 4H, C(4,6)H\(_2\)), 1.35-1.50 (m, 2H, C(5)H\(_2\)), 1.89 (s, 3H, C(8)H\(_3\)), 2.59 (t, J= 7.5, 2H, C(3)H\(_2\)), 7.50-7.95 (m, 5H, Ph).

\(^13\)C NMR (100MHz, CDCl\(_3\)): \( \delta = 13.9 \) (C(7)), 22.4 (C(6)), 24.5 (C(8)), 27.5 (C(5)), 31.8 (C(4)), 32.3 (C(3)) 127.1 (2C, C(9)), 129.1 (2C, 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\(_{19}\)DOS: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 crude product that was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate, 9 : 1 to 4:1) to afford a colourless oil; yield: 433 mg (81%); \( R_f = 0.79 \) (petroleum ether : ethyl acetate, 4:1).

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

\(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 0.89 \) (t, J= 6.7, 3H, C(7)H\(_3\)), 1.22-1.35 (m, 6H, C(5,6,7)H\(_2\)), 1.35-1.48 (m, 2H, C(4)H\(_2\)), 1.89 (s, 3H, C(9)H\(_3\)), 2.59 (t, J= 10.0, 2H, C(3)H\(_2\)), 7.50-8.05 (m, 5H, Ph).

\(^13\)C NMR (100MHz, CDCl\(_3\)): \( \delta = 14.1 \) (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 (2C, C(11)), 129.1 (2C, 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).


(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 crude product that was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate, 9 : 1 to 4:1) to afford a colorless crystals; yield: 456 mg (88%); \( R_f = 0.63 \) (petroleum ether : ethyl acetate, 4:1).

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

\(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 2.56 \) (s, 3H, C(7)H\(_3\)), 7.20-8.00 (m, 10H, Ph).
\[^{13}C\] NMR (100MHz, CDCl\(_3\)): \(\delta = 17.2\) (C(7)), 126.3 (2C, C(5)), 127.3 (2C, C(9)), 128.8 (2C, C(10)), 129.3 (2C, 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, % = 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)MS (m/z, %): 259 (24) [M]+, 224 (11), 116 (100), 106 (65), 92 (3), 77 (37), 51 (33).

Anal. calcd for C\(_{15}\)H\(_{13}\)DOS: C, 74.04. Found: C, 74.07.

\((Z)-((2\text{-Methylhex}-1\text{-en}-1\text{-yl})\text{sulfonyl})\text{benzene (3a)}\)

Using the procedure described above, reaction of 1-(phenylsulfanyl)-1-heptyne (444 mg, 2 mmol) and H\(_2\)O (instead of D\(_2\)O) gave a crude product that was purified by column chromatography on silica gel (petroleum ether : ethyl acetate, 9 : 1 to 4:1) to afford a colorless oil; yield: 376 mg (79%); \(R_f = 0.83\) (petroleum ether : ethyl acetate, 4:1).

\(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 0.91\) (t, J= 6.7, 3H, C(6)\(_3\)), 1.25-1.45 (m, 4H, C(4,5)\(_2\)), 1.88 (s, 3H, C(7)\(_3\)), 2.60 (t, J= 7.5, 2H, C(3)\(_2\)), 6.18 (s, C(1)\(_3\)), 7.50-7.95 (m, 5H, Ph).

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

\[^{13}C\] NMR (100MHz, CDCl\(_3\)): \(\delta = 13.9\) (C(6)), 22.8 (C(5)), 24.5 (C(7)), 30.1 (C(4)), 32.3 (C(3)), 126.2 (C(1)), 127.1 (2C, C(9)), 129.1 (2C, 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).


The preparation of 1-alkenyl sulfides 5a,c and 6a-c via Zr-catalyzed methylalumination of 1-alkynyl sulfides

![Figure 2](image_url)

**Figure 2** The numbering of atoms in the \(^{13}C\)- and \(^1\)H-NMR spectra of the compounds 5a,c and 6a-c
(Z)-Methyl(2-methyloct-1-en-1-yl-1-d)sulfane (5a)

To a 25-mL, argon-swept flask, equipped with a magnetic stirrer and rubber septa, was added Cp₂ZrCl₂ (117 mg, 0.40 mmol) suspended in CH₂Cl₂ (5 mL) and Me₃Al (0.57 mL, 6 mmol) (caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer) at room temperature. To the solution was added methyl(oct-1-yn-1-yl)sulfane (312 mg, 2 mmol) at room temperature and stirred for 18 h. Then, the reaction mixture was diluted with with hexane (5 mL) and D₂O (3 mL) was added dropwise while cooling the reactor flask in an ice bath. The precipitate was filtered on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous CaCl₂. Evaporation of solvent and purification of the residue by column chromatography (silica gel, n-hexane) gave a colourless oil; yield: 294 mg (85%); \( R_f = 0.43 \) (n-hexane).

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

\(^1\)H NMR (400MHz, CDCl₃): \( \delta = 0.91 \) (t, J= 7.5, 3H, C(8)H₃), 1.24-1.36 (m, 6H, C(5-7)H₂), 1.36-1.46 (m, 2H, C(4)H₂), 1.76 (s, 3H, C(9)H₃), 2.15 (t, J= 7.5, 2H, C(3)H₂), 2.24 (s, 3H, C(10)H₃).

\(^{13}\)C NMR (100MHz, CDCl₃): \( \delta = 14.1 \) (C(8)), 17.3 (C(10)), 22.6 (C(7)), 22.8 (C(9)), 27.3 (C(4)), 29.1 and 31.8 (2C, C(5,6)), 33.6 (C(3)), 119.70 (t, \( ^{1}J_{CD}=21.0 \), 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).


(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 crude product that was purified by flash chromatography (silica gel, n-hexane) to afford a colorless oil; yield: 261 mg (79%); \( R_f = 0.50 \) (n-hexane).

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

\(^1\)H NMR (400MHz, CDCl₃): \( \delta = 2.19 \) (d, J= 3.4, 3H, C(8)H₃), 2.29 (d, J= 3.4, 3H, C(7)H₃), 7.10-7.65 (m, 5H, Ph).

\(^{13}\)C NMR (100MHz, CDCl₃): \( \delta = 18.1 \) (C(7)), 24.8 (C(8)), 123.6 (t, \( ^{1}J_{CD}=21.0 \), C(1)), 127.1 (C(6)), 127.5 (C(5)), 128.1 (C(4)) 133.6 (C(3)), 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).


(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 H₂O (instead of D₂O) gave a crude product that was purified by column chromatography (silica gel, n-hexane) to afford a colorless oil; yield: 294 mg (85%); \( R_f = 0.43 \) (n-hexane).

IR (liquid film): 2958, 2933, 2859, 2200, 1730, 1698, 1467, 1457, 1377, 1307, 1099, 1041, 1009, 804, 780, 750, 698 cm⁻¹.
chromatography on silica gel (n-hexane) to afford a colorless oil; yield: 292 mg (85%); $R_f = 0.45$ (n-hexane).

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

$^1$H NMR (400MHz, CDCl$_3$): $\delta = 0.91$ (t, J= 6.3, 3H, C(8)H$_3$), 1.26-1.36 (m, 6H, C(5-7)H$_2$), 1.36-1.48 (m, 2H, C(4)H$_2$), 1.76 (s, 3H, C(9)H$_3$), 2.16 (t, J= 8.0, 2H, C(3)H$_2$), 2.24 (s, 3H, C(10)H$_3$), 5.60 (s, C(1)H).

$^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 14.1$ (C(8)), 17.3 (C(10)), 22.6 (C(7)), 22.9 (C(9)), 27.3 (C(4)), 29.1 and 31.8 (2C, 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).


(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, was added Cp$_2$ZrCl$_2$ (117 mg, 0.40 mmol) suspended in CH$_2$Cl$_2$ (5 mL) and Me$_3$Al (0.57 mL, 6 mmol) (caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer) at room temperature. To the solution was added dec-1-yn-1-yl(methyl)sulfane (424 mg, 2 mmol) of at room temperature and stirred for 18 h. Then, the reaction mixture was diluted with hexane (5 mL) and H$_2$O (3 mL) was added dropwise while cooling the reactor flask in an ice bath. The precipitate was filtered on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous CaCl$_2$. Evaporation of solvent and purification of the residue by column chromatography (silica gel, n-hexane) gave a colourless oil; yield: 308 mg (77%); $R_f = 0.47$ (n-hexane).

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

$^1$H NMR (400MHz, CDCl$_3$): $\delta = 0.90$ (t, J= 6.8, 3H, C(10)H$_3$), 1.15-1.35 (m, 8H, C(5-8)H$_2$), 1.35-1.50 (m, 2H, C(4)H$_2$), 1.76 (s, 3H, C(11)H$_3$), 2.16 (t, J= 7.5, 2H, C(3)H$_2$), 2.24 (s, 3H, C(12)H$_3$), 5.60 (s, C(1)H).

$^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 14.1$ (C(10)), 17.4 (C(12)), 22.7 (C(9)), 22.9 (C(11)), 27.4 (C(4)), 29.3 and 29.5 and 30.1 and 31.9 (4C, C(5-8)), 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 crude product that was purified by flash chromatography (silica gel, silica gel, n-hexane) to afford a colorless oil; yield: 292 mg (89%); $R_f = 0.41$ (n-hexane).
IR (liquid film): 3019, 2980, 2962, 2919, 1599, 1490, 1437, 1316, 1027, 1013, 803, 762, 725, 697 cm\(^{-1}\).

\(^{1}\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 2.20\) (s, 3H, C(8)H\(_3\)), 2.30 (s, 3H, C(7)H\(_3\)), 6.03 (s, C(1)H), 7.15-7.65 (m, 5H, Ph).

\(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 18.2\) (C(7)), 24.9 (C(8)), 124.1 (C(1)), 127.2 (C(6)), 127.6 (2C, C(5)), 128.1 (2C, 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-alkynylsulfoxides with Cp\(_2\)ZrCl\(_2\) and Me\(_3\)Al**

**Dec-1-yn-1-yl(methyl)sulfane (7b)**

To a 25-mL, argon-swept flask, equipped with a magnetic stirrer and rubber septa, was added Cp\(_2\)ZrCl\(_2\) (117 mg, 0.40 mmol) suspended in CH\(_2\)Cl\(_2\) (5 mL) and Me\(_3\)Al (0.57 mL, 6 mmol) (caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer) at 0 \(^\circ\)C. To the solution was added 1-(methylsulfinyl)dec-1-yne (400 mg, 2 mmol) of at room temperature and stirred for 20 min. Then, the reaction mixture was diluted with hexane (5 mL) and H\(_2\)O (3 mL) was added dropwise while cooling the reactor flask in an ice bath. The precipitate was filtered on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL) and dried over anhydrous CaCl\(_2\). Evaporation of solvent and purification of the residue by column chromatography (hexane as eluant) gave a colorless oil; yield: 291 g (79%); \(R_f = 0.48\) (n-hexane).

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

\(^{1}\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 0.90\) (t, J= 6.7, 3H, C(10)H\(_3\)), 1.20-1.45 (m, 10H, C(5-9)H\(_2\)), 1.45-1.58 (m, 2H, C(4)H\(_2\)), 2.29 (t, J= 8.0, 2H, C(3)H\(_2\)), 2.37 (s, 3H, C(11)H\(_3\)).

\(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 14.1\) (C(10)), 19.3 (C(11)), 20.1 and 28.8 and 28.9 and 29.1 and 29.2 (C(5-9)), 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.

Preparation of 1-alkenyl sulfides 9a,b via Zr-catalyzed methylalumination of alkynes followed by treatment with S-methyl methanethiosulfonate

![Chemical structures](image)

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

(E)-Methyl(2-methyldec-1-en-1-yl)sulfane (9a)

To a 25-mL, argon-swept flask, equipped with a magnetic stirrer and rubber septa, was added Cp$_2$ZrCl$_2$ (580 mg, 2 mmol) suspended in CH$_2$Cl$_2$ (5 mL) and Me$_3$Al (0.38 mL, 4 mmol) (caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer) at 0 °C. To the solution was added 1-octyne (220 mg, 2 mmol) of at room temperature and stirred for 3 h. S-methyl methanethiosulfonate (252 mg, 2 mmol) was added to the reaction mixture at 0 °C and stirred at room temperature for 10 minutes. Then, the reaction mixture was diluted with hexane (5 mL) and H$_2$O (3 mL) was added dropwise while cooling the reactor flask in an ice bath. The precipitate was filtered on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL) and dried over anhydrous CaCl$_2$. Evaporation of solvent and purification of the residue by column chromatography (hexane as eluant) gave a colorless oil; yield: 284 mg (71%); $R_f = 0.49$ (n-hexane).
IR (liquid film): 2958, 2923, 2871, 2858, 2845, 1730, 1696, 1465, 1377, 1310, 1099, 1041, 1008, 801, 777, 750, 722, 698 cm\(^{-1}\).

\(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 0.90\) (t, \(J= 6.7\), 3H, C(10)H\(_3\)), 1.15-1.35 (m, 10H, C(5-9)H\(_2\)), 1.35-1.50 (m, 2H, C(4)H\(_2\)), 1.73 (s, 3H, C(11)H\(_3\)), 2.05 (t, \(J= 8.0\), 2H, C(3)H\(_2\)), 2.26 (s, 3H, C(12)H\(_3\)), 5.60 (s, C(1)H).

\(^13\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 14.1\) (C(10)), 17.2 (C(12)), 17.8 (C(11)), 22.7 and 29.3 and 29.4 and 29.5 and 31.9 (C(5-9)), 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).


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

Using the procedure described above ethynylbenzene (204 mg, 2 mmol) and S-methyl methanethiosulfonate (252 mg, 2 mmol) gave crude product that was purified by flash chromatography (silica gel, n-hexane) to afford a colourless oil; yield: 177 mg (54%; \(R_f = 0.89\) (hexane)).

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

\(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 2.15\) (s, 3H, C(8)H\(_3\)), 2.42 (s, 3H, C(7)H\(_3\)), 6.30 (s, C(1)H), 7.20-7.40 (m, 5H, Ph).

\(^13\)C NMR (100MHz, CDCl\(_3\)): \(\delta = 17.3\) (C(7)), 17.5 (C(8)), 125.1 (2C, C(5)), 125.3 (C(1)), 125.9 (C(6)), 128.3 (2C, 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.

Preparation of \((E)\)-alkenyl sulfone 11 via the oxidation of methyl(2-methyloct-1-en-1-yl)sulfane on treatment with 3-chloreperbenzoc acid

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

Using the procedure described above oct-1-yne (220 mg, 2 mmol) and S-methyl methanethiosulphonate (252 mg, 2 mmol) gave 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 dry DCM (20 mL/mmol sulfide) was added 3-chloroperoxybenzoic acid (692 mg, 4.0 equiv) in one portion at 0 \(^\circ\)C and the reaction mixture was stirred at 0 \(^\circ\)C for 2 h. The reaction was quenched with 30% aqueous Na\(_2\)SO\(_3\) and extracted with DCM. The combined organic extracts were washed with saturated aqueous NaHCO\(_3\) and brine, and dried with MgSO\(_4\). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (petroleum ether : ethyl acetate, 9 : 1) gave a colourless oil; yield: 330 mg (81%); \(R_f = 0.84\).
IR (liquid film): 2956, 2930, 2859, 1645, 1413, 1379, 1300, 1132, 963, 813, 771, 752 cm⁻¹.

1H NMR (400MHz, CDCl₃): δ = 0.90 (t, J= 5.9, 3H, С(8)Н3), 1.22-1.40 (m, 6H, С(5-7)Н2), 1.40-1.56 (m, 2H, С(4)Н2), 2.12-2.21 (s, 3H, С(9)Н3, t, 2H, С(3)Н2), 2.95 (s, 3H, С(10)Н3), 6.12 (s, С(1)Н).

13C NMR (100MHz, CDCl₃): 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).


Preparation of 1-alkenyl sulfi des 13a,b via Ti-catalyzed hydrol alumination of alkynes followed by treatment with S-methyl methanethiosulfonate

(E)-Dec-5-en-5-yl(methyl)sulfane 13a

To Cp₂TiCl₂ (250 mg, 0.10 mmol) suspended in hexane (5 mL) was added under an atmosphere of argon 5-decyne (276 mg, 2 mmol) and Et₃Al (0.30 mL, 2 mmol) at room temperature. After 6 h, to the reaction mixture was added S-methyl methanethiosulfonate (250 mg, 2 mmol) at 0 °C and stirred for 10 minutes at room temperature. Then, the reaction mixture was diluted with hexane (5 mL) and H₂O (3 mL) was added dropwise while cooling the reactor flask in an ice bath. The precipitate was filtered on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous CaCl₂. Evaporation of solvent and purification of the residue by column chromatography (hexane as eluant) gave a colourless oil; yield: 298 mg (80%); Rf = 0.53 (hexane).

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

1H NMR (400MHz, CDCl₃): δ = 0.80-1.05 (m, 6H, C(6,10)Н3), 1.25-1.45 (m, 6H, C(4,5,9)Н3), 1.45-1.55 (m, 2H, C(8)Н2), 2.11 (q, J= 7.1, 2H, C(3)Н2), 2.15-2.30 (m, 2H, C(7)Н2, 3Н, C(11)Н3), 5.12 (t, J= 7.3, C(2)Н).

13C NMR (100MHz, CDCl₃): 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).


(E)-Methyl(oct-4-en-4-yl)sulfane (13b)
Using the procedure described above oct-4-yne (220 mg, 2 mmol) and S-methyl methanethiosulfonate (250 mg, 2 mmol) gave crude product that was purified by flash chromatography (silica gel, n-hexane) to afford a colourless oil; yield: 250 mg (79%); \( R_f = 0.46 \) (hexane).

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

\(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 0.85-1.06 \) (m, 6H, C(5,8)H\(_3\)), 1.35-1.47 (m, 2H, C(4)H\(_2\)), 1.47-1.60 (m, 2H, C(7)H\(_2\)), 2.09 (q, \( J = 7.6 \), 2H, C(3)H\(_2\)), 2.16-2.26 (m, 2H, C(6)H\(_2\), 3H, C(9)H\(_3\)), 5.14 (t, \( J = 7.2 \), C(2)H).

\(^{13}\)C NMR (100MHz, CDCl\(_3\)): \( \delta = 13.8 \) (2C, 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).


The preparation of 1-alkenyl sulfides 15a,b via Zr-catalyzed cyclic carboalumination of alkynes followed by treatment with S-methyl methanethiosulfonate

\((E)-(6\text{-Ethyldec-5-en-5-yl})(methyl)sulfane (15a)\)

To Cp\(_2\)ZrCl\(_2\) (580 mg, 0.20 mmol) suspended in hexane (5 mL) was added under an atmosphere of argon 5-decyne (276 mg, 2 mmol) and Et\(_3\)Al (0.30 mL, 2 mmol) at 40 \(^\circ\)C. After 2 h, to the reaction mixture was added S-methyl methanethiosulfonate (250 mg, 2 mmol) at 0 \(^\circ\)C and stirred for 24 hours at room temperature. Then, the reaction mixture was diluted with hexane (5 mL) and H\(_2\)O (3 mL) was added dropwise while cooling the reactor flask in an ice bath. The precipitate was filtered on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous CaCl\(_2\). Evaporation of solvent and purification of the residue by column chromatography (hexane as eluant) gave a colorless oil; yield: 272 mg (73%); \( R_f = 0.48 \) (hexane).

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

\(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 0.80-0.95 \) (m, 6H, C(6,10)H\(_3\)), 0.99 (t, \( J = 6.0 \), 3H, C(12)H\(_3\)), 1.15-1.45 (m, 6H, C(4,5,9)H\(_2\)), 1.45-1.60 (m, 2H, C(8)H\(_2\)), 2.09 (t, \( J = 8.0 \), 2H, C(3)H\(_2\)), 2.15 (s, 3H, C(13)H\(_3\)), 2.26 (t, \( J = 8.0 \), 2H, C(7)H\(_2\)), 2.35 (q, \( J = 8.0 \), 2H, C(11)H\(_2\)).

\(^{13}\)C NMR (100MHz, CDCl\(_3\)): \( \delta = 13.3 \) (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).

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

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

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

$^1$H NMR (400MHz, CDCl$_3$): $\delta = 0.80-0.95$ (m, 6H, C(5,8)H$_3$), 1.00 (t, J= 6.0, 3H, C(10)H),
1.25-1.45 (m, 2H, C(4)H$_2$), 1.45-1.60 (m, 2H, C(7)H$_2$), 2.09 (t, J= 6.0, 2H, C(6)H$_2$), 2.16 (s, 3H, C(11)H$_3$), 2.26 (t, J= 8.0, 2H, C(3)H$_2$), 2.37 (q, J= 8.0, 2H, C(9)H$_2$).

$^{13}$C NMR (100MHz, CDCl$_3$): $\delta = 13.4$ (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.

References.

$^{13}$C-NMR spectrum of (Z)-((2-methylhex-1-en-1-yl-1-d)sulfonyl)benzene (2a)
$^1$H-NMR spectrum of (Z)-((2-methylhex-1-en-1-yl-1-d)sulfonyl)benzene (2a)
$^{13}$C-NMR spectrum of (Z)-((2-methylhept-1-en-1-yl-1-d)sulfonyl)benzene (2b)
$^1$H-NMR spectrum of (Z)-((2-methylhept-1-en-1-yl-1-d)sulfonyl)benzene (2b)
$^{13}$C-NMR spectrum of (Z)-((2-methyloct-1-en-1-yl-1-d)sulfonyl)benzene (2c)
$^1$H-NMR spectrum of (Z)-((2-methyl-1-en-1-yl-1-d)sulfonyl)benzene (2c)
$^{13}$C-NMR spectrum of (Z)-((2-phenylprop-1-en-1-yl-1-d)sulfonyl)benzene (2d)
\(^1\)H-NMR spectrum of (Z)-((2-phenylprop-1-en-1-yl-1-d)sulfonyl)benzene (2d)
$^{13}$C-NMR spectrum of (Z)-((2-methylhex-1-en-1-yl)sulfonyl)benzene (3a)
$^1$H-NMR spectrum of (Z)-(2-methylhex-1-en-1-yl)sulfonylbenzene (3a)
$^{13}$C-NMR spectrum of (Z)-methyl(2-methyloct-1-en-1-yl-1-d)sulfane (5a)
$^1$H-NMR spectrum of (Z)-methyl(2-methyloct-1-en-1-yl-1-d)sulfane (5a)
$^{13}$C-NMR spectrum of (Z)-methyl(2-phenylprop-1-en-1-yl-1-d)sulfane (5c)
$^1$H-NMR spectrum of (Z)-methyl(2-phenylprop-1-en-1-yl-1-d)sulfane (5c)
$^{13}$C-NMR spectrum of (Z)-methyl(2-methyloct-1-en-1-yl)sulfane (6a)
$^1$H-NMR spectrum of (Z)-methyl(2-methyloct-1-en-1-yl)sulfane (6a)
$^{13}$C-NMR spectrum of (Z)-methyl(2-methyldec-1-en-1-yl)sulfane (6b)
$^1$H-NMR spectrum of (Z)-methyl(2-methyldec-1-en-1-yl)sulfane (6b)
$^{13}$C-NMR spectrum of (Z)-methyl(2-phenylprop-1-en-1-yl)sulfane (6c)
$^1$H-NMR spectrum of (Z)-methyl(2-phenylprop-1-en-1-yl)sulfane (6c)
$^{13}$C-NMR spectrum of dec-1-yn-1-yl(methyl)sulfane (7b)
$^1$H-NMR spectrum of dec-1-yn-1-yl(methyl)sulfane (7b)
$^{13}$C-NMR spectrum of (E)-methyl(2-methyldec-1-en-1-yl)sulfane (9a)
$^{1}$H-NMR spectrum of (E)-methyl(2-methyldec-1-en-1-yl)sulfane (9a)
$^{13}$C-NMR spectrum of (E)-methyl(2-phenylprop-1-en-1-yl)sulfane (9b)
$^1$H-NMR spectrum of (E)-methyl(2-phenylprop-1-en-1-yl)sulfane (9b)
$^{13}$C-NMR spectrum of (E)-2-methyl-1-(methylsulfonyl)dec-1-ene (11)
$^{1}$H-NMR spectrum of (E)-2-methyl-1-(methylsulfonyl)dec-1-ene (11)
$^{13}$C-NMR spectrum of (E)-dec-5-en-5-yl(methyl)sulfane (11a)
$^1$H-NMR spectrum of (E)-dec-5-en-5-yl(methyl)sulfane (11a)
$^{13}$C-NMR spectrum of (E)-methyl(oct-4-en-4-yl)sulfane (11b)
$^1$H-NMR spectrum of (E)-methyl(oct-4-en-4-yl)sulfane (11b)
$^{13}$C-NMR spectrum of (E)-(6-ethyldec-5-en-5-yl)(methyl)sulfane (13a)
$^1$H-NMR spectrum of (E)-(6-ethyldec-5-en-5-yl)(methyl)sulfane (13a)
$^{13}$C-NMR spectrum of (E)-5-ethyl-4-en-4-yl)(methyl)sulfane (13b)
$^1$H-NMR spectrum of (E)-(5-ethyloct-4-en-4-yl)(methyl)sulfane (13b)