A highly selective synthesis of dialkenyl sulfones via cross-metathesis based desymmetrization of divinyl sulfone

Supplementary Information

Michał Bieniek,^a Dariusz Kołoda,^{a,b} and Karol Grela^{a,*}

^a Institute of Organic Chemistry, Polish Academy of Sciences
Kasprzaka 44/52, 01-224 Warsaw, Poland

^b Faculty of Chemistry, Warsaw University of Technology (Politechnika), Noakowskiego 3, 00-664 Warsaw, Poland

grela@icho.edu.pl

1. General

Unless otherwise noted, all reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the following drying agents and were transferred under argon: THF (K/benzophenone), toluene (Na), *n*-pentane, *n*-hexane, CH₂Cl₂ (CaH₂), Et₂O (LiAlH₄). Flash column chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker AVANCE 500, Varian Gemini 200 and 400 spectrometers in CDCl₃; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. IR: Perkin-Elmer Spectrum 2000 FT-IR, wavenumbers in cm⁻¹. MS (EI, LSIMS): AMD 604 Intectra GmbH. MS (ESI): Mariner Perseptive Biosystems, Inc. HPLC-MS (API): HP 1100 series with PE SCIEX API 365 turbo-ion spray and Nucleosil 1000-C18 column. Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw. All commercially available substrates were used as received.

2. Experimental part

2.1. Representative procedure for CM of divinyl sulfone

To a mixture of alkene (2.0 mmol) and divinylsulfone (6.0 mmol) in CH₂Cl₂ (100 mL, *c* = 0.02M) was added a Ru-catalyst **1** or **4** as a solid (5 mol%). The resulted mixture was stirred at reflux for 16–24 h under Ar. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography using *c*-hexan/ethyl acetate as eluent (Merck silica gel 60, 230–400 mesh).

(1*E*)-3-phenylprop-1-en-1-yl vinyl sulfone (**7b**)

Yellow oil (84 %). IR (film): ν 3104, 3057, 3030, 2921, 2256, 1957, 1734, 1630, 1604, 1496, 1454, 1384, 1314, 1127, 1029, 976, 851, 792, 700, 645, 585, 486 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 3.60 (dd, *J* = 6.4, 1.8 Hz, 2H), 6.05 (d, *J* = 9.9 Hz, 1H), 6.16 (dt, *J* = 15.1, 1.8 Hz, 1H), 6.37 (d, *J* = 16.5 Hz, 1H), 6.56 (dd, *J* = 16.5, 9.9 Hz, 1H), 7.11 (dt, *J* = 15.1, 6.4 Hz, 1H), 7.14–7.18 (m, 2H), 7.24–7.30 (m, 1H), 7.31–7.36 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 37.7, 127.1, 128.7, 128.8, 128.9, 129.7, 136.0, 137.4, 147.6. MS (EI) *m/z* (rel intensity) 208 (18, M⁺), 163 (5), 142 (8), 118 (10), 117 (100), 116 (41), 115 (71), 91 (34), 65 (13), 51 (5), 39 (8). HRMS (EI) calcd for M⁺ (C₁₁H₁₂O₂S): 208.05580; found: 208.05669. Anal. calcd for C₁₁H₁₂O₂S (208.28): C 63.43, H 5.81, S 15.39; found C 63.28, H 6.03, S 15.21.

(1*E*)-1-(Vinylsulfonyl)hept-1-ene (**7c**)

Yellow oil (51 %). IR (film): ν 3055, 3020, 2961, 2928, 2859, 1627, 1462, 1416, 1381, 1316, 1261, 1129, 1016, 818, 720, 647, 555, 499 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.27–1.35 (m, 4H), 1.44–1.54 (m, 2H), 2.23–2.32 (m, 2H), 6.05 (d, *J* = 9.8 Hz, 1H), 6.23 (dt, *J* = 15.1, 1.6 Hz, 1H), 6.39 (d, *J* = 16.6 Hz, 1H), 6.59 (dd, *J* = 16.6, 9.8 Hz, 1H), 6.95 (dt, *J* =

15.1, 6.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.3, 27.2, 31.1, 31.6, 128.3, 128.5, 137.7, 149.5. MS (EI) m/z (rel intensity) 145 (4), 133 (6), 119 (32), 96 (17), 93 (14), 81 (70), 75 (13), 69 (12), 67 (54), 57 (10), 55 (100), 53 (15), 43 (21), 41 (79), 39 (31). HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_9\text{H}_{16}\text{O}_2\text{SNa}$): 211.0763; found: 211.0774.

(1E)-1-(Vinylsulfonyl)nonadec-1-ene (7d)

Colourless powder (70 %). IR (KBr): ν 3066, 3052, 2955, 2918, 2849, 1629, 1472, 1463, 1384, 1305, 1124, 967, 847, 824, 805, 777, 759, 730, 720, 645, 554, 504, 492 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.87 (t, J = 7.0 Hz, 3H), 1.20–1.34 (m, 28H), 1.42–1.52 (m, 2H), 2.22–2.30 (m, 2H), 6.04 (d, J = 9.8 Hz, 1H), 6.22 (dt, J = 15.2, 1.5 Hz, 1H), 6.38 (d, J = 16.6 Hz, 1H), 6.57 (dd, J = 16.6, 9.8 Hz, 1H), 6.94 (dt, J = 15.2, 6.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 22.7, 27.5, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.7, 31.9, 128.3, 128.5, 137.7, 149.6. MS (EI) m/z (rel intensity) 339 (14), 321 (5), 151 (6), 145 (13), 123 (30), 109 (55), 95 (85), 81 (100), 69 (76), 57 (73), 55 (79), 53 (15), 43 (79), 41 (61). HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{40}\text{O}_2\text{SNa}$): 379.2641; found: 379.2650. Anal. calcd for $\text{C}_{21}\text{H}_{40}\text{O}_2\text{S}$ (356.62): C 70.73, H 11.31, S 8.99; found C 70.65, H 11.15, S 8.82.

Tert-butyl(dimethyl)[(5E)-6-(vinylsulfonyl)hex-5-en-1-yl]oxysilane (7e)

Yellow oil (69 %). IR (film): ν 3055, 2953, 2930, 2886, 2858, 1628, 1472, 1463, 1386, 1361, 1320, 1255, 1133, 1099, 1006, 974, 835, 776, 719, 646, 497 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 0.00 (s, 6H), 0.83 (s, 9H), 1.45–1.54 (m, 4H), 2.21–2.29 (m, 2H), 5.99 (d, J = 9.9 Hz, 1H), 6.20 (d, J = 15.2 Hz, 1H), 6.31 (d, J = 16.6 Hz, 1H), 6.53 (dd, J = 16.6, 9.9 Hz, 1H), 6.88 (dt, J = 15.2, 6.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ -5.5, 18.1, 23.9, 25.8, 31.2, 31.8, 62.3, 128.1, 128.7, 137.7, 149.0. MS (EI) m/z (rel intensity) 289 (3), 249 (10), 248 (17), 247 (100), 149 (22), 85 (42), 81 (8), 81 (100), 75 (21), 57 (8), 41 (6). HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{14}\text{H}_{28}\text{O}_3\text{SSiNa}$): 327.1421; found: 327.1440. Anal. calcd for $\text{C}_{14}\text{H}_{28}\text{O}_3\text{SSi}$ (304.53): C 55.22, H 9.27, S 10.53; found C 54.96, H 9.33, S 10.47.

(10E)-11-(Vinylsulfonyl)undec-10-en-1-ol (7f)

Yellow oil (71 %). IR (film): ν 3518, 3411, 3104, 3055, 2928, 2856, 1627, 1464, 1384, 1316, 1252, 1130, 1056, 977, 825, 722, 647, 557, 500, 433 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.25–1.38 (m, 10H), 1.41–1.51 (m, 2H), 1.52–1.60 (m, 2H), 2.27 (qd, J = 6.8, 1.4 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 6.05 (d, J = 9.9 Hz, 1H), 6.23 (dt, J = 15.1, 1.4 Hz, 1H), 6.38 (d, J = 16.6 Hz, 1H), 6.58 (dd, J = 16.6, 9.9 Hz, 1H), 6.94 (dt, J = 15.1, 6.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 25.6, 27.5, 28.9, 29.1, 29.2, 29.3, 31.6, 32.7, 62.9, 128.2, 128.6, 137.8, 149.4. MS (EI) m/z (rel intensity) 243 (1), 213 (3), 150 (8), 145 (35), 135 (12), 132 (11), 121 (26), 119 (20), 115 (16), 109 (36), 95 (88), 81 (100), 75 (19), 69 (50), 67 (82), 55 (58), 41 (38). HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{13}\text{H}_{24}\text{O}_3\text{SNa}$): 283.1338; found: 283.1325. Anal. calcd for $\text{C}_{13}\text{H}_{24}\text{O}_3\text{S}$ (260.40): C 59.96, H 9.29, S 12.31; found C 60.02, H 9.48, S 11.98.

(1E)-10-Bromo-1-(vinylsulfonyl)dec-1-ene (7g)

Pale brown oil (72 %). IR (film): ν 3103, 3054, 3017, 2930, 2856, 1628, 1463, 1438, 1383, 1317, 1252, 1131, 971, 825, 721, 645, 559, 500, 431 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.28–1.36 (m, 6H), 1.38–1.53 (m, 4H), 1.81–1.88 (m, 2H), 2.27 (qd, J = 6.8, 1.6 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 6.05 (d, J = 9.9 Hz, 1H), 6.24 (dt, J = 15.1, 1.6 Hz, 1H), 6.40 (d, J = 16.6 Hz, 1H), 6.58 (dd, J = 16.6, 9.9 Hz, 1H), 6.94 (dt, J = 15.1, 6.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 27.5, 28.0, 28.5, 28.5, 29.0, 31.6, 32.7, 33.9, 128.2, 128.7, 137.8, 149.3. HRMS (LSIM(+)) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{12}\text{H}_{21}\text{O}_2\text{S}^{79}\text{Br}$): 309.05239; found: 309.05091.

(1E)-6-Bromo-1-(vinylsulfonyl)hex-1-ene (7h)

Yellow oil (36 %). IR (film): ν 3103, 3054, 2939, 2865, 1628, 1455, 1435, 1383, 1316, 1250, 1130, 971, 827, 720, 645, 559, 502 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.67 (quint, J = 7.7 Hz, 2H), 1.86–1.94 (m, 2H), 2.32 (qd, J = 6.8, 1.5 Hz, 2H), 3.41 (t, J = 6.6 Hz, 2H), 6.07 (d, J = 9.8 Hz, 1H), 6.27 (dt, J = 15.2, 1.6 Hz, 1H), 6.40 (d, J = 16.6 Hz, 1H), 6.58 (dd, J = 16.6, 9.8 Hz, 1H), 6.94 (dt, J = 15.2, 6.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 26.0, 30.7, 31.8, 32.8, 128.6, 129.3, 137.6, 148.1. MS (EI) m/z (rel intensity) 252 (3, M^+), 237 (44), 235 (44), 209 (10), 187 (10), 173 (25), 145 (84), 119 (21), 107 (18), 93 (15), 81 (100), 79 (28), 75 (13), 67 (12), 55 (12), 53

(13), 41 (32), 39 (18). HRMS (EI) calcd for M^{+} ($C_8H_{13}O_2S^{79}Br$): 251.98196; found: 251.98109.

trimethyl[(2E)-3-(vinylsulfonyl)prop-2-en-1-yl]silane (7i)

Pale brown oil (66 %). IR (film): ν 3053, 2961, 2926, 2855, 1740, 1614, 1412, 1317, 1294, 1261, 1098, 1028, 801, 724, 699, 640, 500 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.83 (dd, $J = 9.1, 1.3$ Hz, 2H), 6.00 (d, $J = 9.7$ Hz, 1H), 6.05 (dt, $J = 14.8, 1.3$ Hz, 1H), 6.34 (d, $J = 16.6$ Hz, 1H), 6.57 (dd, $J = 16.6, 9.7$ Hz, 1H), 6.99 (dt, $J = 14.8, 9.1$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.9, 24.7, 125.4, 127.2, 138.3, 148.7. MS (EI) m/z (rel intensity) 188 (3), 187 (17), 122 (12), 113 (5), 97 (32), 75 (11), 73 (100), 67 (15), 59 (8), 45 (7). HRMS (ESI) calcd for $[M+Na]^+$ ($C_8H_{16}O_2SSiNa$): 227.0533; found: 227.0521.

1,1'-[Sulfonyldi(1E)prop-1-ene-1,3-diyl]dibenzene (8b)

Brown oil (9 %). IR (KBr): ν 3063, 3044, 3028, 2923, 1727, 1634, 1599, 1495, 1453, 1437, 1307, 1273, 1122, 983, 929, 856, 800, 750, 724, 699, 612, 570, 523, 493, 477 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$) δ 3.55 (dd, $J = 6.5, 1.7$ Hz, 4H), 6.15 (dt, $J = 15.1, 1.7$ Hz, 2H), 7.03 (dt, $J = 15.1, 6.5$ Hz, 2H), 7.12–7.16 (m, 4H), 7.24–7.28 (m, 2H), 7.30–7.34 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.7, 127.1, 128.8, 128.9, 130.5, 136.2, 146.4. MS (EI) m/z (rel intensity) 298 (40, M^{+}), 281 (5), 232 (8), 147 (4), 118 (10), 117 (100), 116 (25), 115 (38), 91 (16), 65 (4). HRMS (EI) calcd for M^{+} ($C_{18}H_{18}O_2S$): 298.10275; found: 298.10367.

(9E,12E)-2,2,3,3,19,19,20,20-Octamethyl-4,18-dioxa-11-thia-3,19-disilahenicososa-9,12-diene 11,11-dioxide (8e)

Yellow oil (13 %). IR (film): ν 2952, 2930, 2886, 2858, 1633, 1472, 1463, 1388, 1321, 1255, 1130, 1101, 1005, 976, 836, 775, 661, 607 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$) δ 0.04 (s, 12H), 0.88 (s, 18H), 1.51–1.56 (m, 8H), 2.23–2.31 (m, 4H), 3.58–3.63 (m, 4H), 6.22 (dt, $J = 15.1, 1.4$ Hz, 2H), 6.88 (dt, $J = 15.1, 6.8$ Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ -5.3, 18.3, 24.1, 25.9, 31.3, 32.0, 62.5, 129.6, 147.6. MS (EI) m/z (rel intensity) 476 (4), 435 (17), 434 (33), 433 (100), 221 (3), 149 (5), 115 (3), 81 (26), 75 (20), 73 (20), 57 (5), 55 (5), 41 (6). HRMS (ESI) calcd for $[M+Na]^+$ ($C_{24}H_{50}O_4Si_2S$): 513.2861; found: 513.2883. Anal. calcd for $C_{24}H_{50}O_4Si_2S$ (490.90): C 58.72, H 10.27, S 6.53; found C 58.77, H 10.37, S 6.54.

(10E,10'E)-11,11'-Sulfonylbisundec-10-en-1-ol (8f)

Yellow solid (12 %). IR (KBr): ν 3410, 3344, 2926, 2850, 1638, 1465, 1371, 1317, 1306, 1281, 1265, 1120, 1063, 1003, 972, 843, 810, 728, 627, 535, 492 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$) δ 1.25–1.36 (m, 22H), 1.43–1.50 (m, 4H), 1.51–1.59 (m, 4H), 2.24 (qd, $J = 6.8, 1.5$ Hz, 4H), 3.62 (t, $J = 6.6$ Hz, 4H), 6.20 (dt, $J = 15.1, 1.5$ Hz, 4H), 6.86 (dt, $J = 15.1, 6.8$ Hz, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.6, 27.6, 28.9, 29.1, 29.2, 29.3, 31.5, 32.7, 62.9, 129.5, 147.8. HRMS (ESI) calcd for $[M+Na]^+$ ($C_{22}H_{42}O_4SNa$): 425.2696; found: 425.2715.

(1E,1'E)-1,1'-Sulfonylbis(10-bromodec-1-ene) (8g)

Pale brown oil (19 %). IR (film): ν 2929, 2856, 1629, 1582, 1516, 1463, 1339, 1318, 1271, 1129, 968, 834, 756, 609, 558 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$) δ 1.25–1.35 (m, 12H), 1.38–1.51 (m, 8H), 1.81–1.88 (m, 4H), 2.24 (qd, $J = 6.8, 1.4$ Hz, 4H), 3.40 (t, $J = 6.8$ Hz, 4H), 6.21 (dt, $J = 15.1, 1.4$ Hz, 2H), 6.87 (dt, $J = 15.1, 6.8$ Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 28.0, 28.5, 28.9, 29.1, 31.5, 32.7, 33.9, 129.6, 147.7. MS (EI) m/z (rel intensity) 500 (2, M^{+}), 483 (2), 481 (1), 324 (7), 285 (26), 283 (25), 137 (100), 136 (27), 109 (18), 95 (80), 82 (21), 81 (94), 69 (37), 67 (53), 55 (50), 41 (35). HRMS (EI) calcd for M^{+} ($C_{20}H_{36}O_2S^{79}Br^{81}Br$): 500.07823; found: 500.08063.

[Sulfonyldi(1E)prop-1-ene-1,3-diyl]bis(trimethylsilane) (8i)

Colourless oil (31 %). 1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 18H), 1.77 (dd, $J = 9.0, 1.3$ Hz, 4H), 6.02 (dt, $J = 14.9, 1.3$ Hz, 2H), 6.89 (dt, $J = 14.9, 9.0$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.9, 24.2, 127.3, 145.8. MS (EI) m/z (rel intensity) 290 (1, M^{+}), 210 (7), 161 (4), 147 (8), 133 (3), 111 (20), 79 (6), 75 (6), 73 (100), 45 (11). HRMS (EI) calcd for M^{+} ($C_{12}H_{26}O_2Si_2S$): 290.11997; found: 290.11921.

2.2. Representative procedure for CM of sulfones 7

To a mixture of alkene (8.0 mmol) and sulfone **7** (2.0 mmol) in CH₂Cl₂ (100 mL, *c* = 0.02M) was added a Ru-catalyst **1** or **4** as a solid (20–8 mol%). The resulted mixture was stirred at reflux for 16–44 h under Ar. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography using *c*-hexan/ethyl acetate as eluent (Merck silica gel 60, 230–400 mesh).

(10E)-11-[(1E)-10-bromodec-1-en-1-yl]sulfonylundec-10-en-1-ol (10fg)

Colourless solid (74 %). IR (KBr): ν 3421, 3057, 2931, 2852, 1638, 1466, 1316, 1279, 1118, 1061, 963, 851, 832, 811, 729, 649, 625, 533, 486 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 1.26–1.36 (m, 16H), 1.38–1.50 (m, 6H), 1.52–1.59 (m, 2H), 1.81–1.88 (m, 2H), 2.24 (q, *J* = 7.3 Hz, 4H), 3.40 (t, *J* = 6.8 Hz, 2H), 3.60–3.66 (m, 2H), 6.20 (d, *J* = 15.1 Hz, 2H), 6.83–6.90 (m, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 25.7, 27.6, 28.0, 28.5, 28.9, 29.0, 29.1, 29.2, 29.3, 29.4, 31.5, 32.7, 33.9, 63.0, 129.5, 129.6, 147.6, 147.8. MS (EI) *m/z* (rel intensity) 422 (15), 420 (14), 405 (9), 403 (8), 337 (11), 335 (10), 307 (10), 305 (10), 285 (59), 283 (57), 217 (17), 215 (12), 168 (12), 151 (68), 150 (60), 137 (99), 135 (32), 121 (43), 109 (56), 107 (24), 95 (100), 81 (69), 67 (41), 55 (43), 41 (39). HRMS (ESI) calcd for [M+Na]⁺ (C₂₁H₃₉O₃S⁷⁹BrNa): 473.1695; found: 473.1699. Anal. calcd for C₂₁H₃₉O₃SBr (451.51): C 55.86, H 8.71, S 7.10; found C 56.08, H 8.91, S 7.05.

(1E)-Nonadec-1-en-1-yl (1E)-3-phenylprop-1-en-1-yl sulfone (10db)

Yellow oil (54 %). IR (KBr): ν 2957, 2921, 2848, 1640, 1462, 1321, 1278, 1119, 964, 850, 826, 803, 744, 724, 698, 624, 578, 486 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 0.91 (t, *J* = 7.1 Hz, 3H), 1.26–1.34 (m, 28H), 1.42–1.54 (m, 2H), 2.23–2.30 (m, 2H), 3.59 (dd, *J* = 6.4, 1.5 Hz, 2H), 6.18 (dt, *J* = 15.1, 1.7 Hz, 1H), 6.23 (dt, *J* = 15.1, 1.5 Hz, 1H), 6.86–6.94 (m, 1H), 7.07 (dt, *J* = 15.1, 6.4 Hz, 1H), 7.17–7.21 (m, 2H), 7.27–7.43 (m, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 14.1, 22.7, 27.6, 29.0, 29.3, 29.5, 29.6, 29.7, 31.6, 31.9, 37.7, 127.1, 128.8, 128.9, 129.2, 130.8, 136.3, 145.9, 148.3. MS (EI) *m/z* (rel intensity) 446 (1, M⁺), 355 (2), 118 (10), 117 (100), 115 (7), 91 (3), 43 (2). HRMS (EI) calcd for M⁺ (C₂₈H₄₆O₂S): 446.32185; found: 446.32201.

Tert-butyl((5E)-6-[(1E)-hept-1-en-1-ylsulfonyl]hex-5-en-1-yloxy)dimethylsilane (10ec)

Yellow oil (85 %). IR (KBr): ν 2955, 2930, 2858, 1634, 1471, 1463, 1320, 1256, 1131, 1102, 977, 836, 776, 608, 548 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 0.04 (s, 6H), 0.86–0.91 (m, 12H), 1.26–1.34 (m, 4H), 1.44–1.51 (m, 2H), 1.51–1.57 (m, 4H), 2.20–2.30 (m, 4H), 3.58–3.63 (m, 2H), 6.20 (dt, *J* = 15.1, 1.5 Hz, 1H), 6.22 (dt, *J* = 15.1, 1.5 Hz, 1H), 6.87 (dt, *J* = 15.1, 6.7 Hz, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ -5.3, 13.9, 18.3, 22.3, 24.1, 25.9, 27.3, 31.2, 31.3, 31.5, 32.1, 62.6, 129.5, 129.7, 147.5, 147.9. MS (EI) *m/z* (rel intensity) 359 (3), 319 (11), 318 (24), 317 (100), 155 (17), 95 (3), 81 (5), 75 (15), 73 (8), 41 (5). HRMS (ESI) calcd for [M+Na]⁺ (C₁₉H₃₈O₃SSiNa): 397.2203; found: 397.2224.

(1E)-3-(4-Bromophenyl)prop-1-en-1-yl (1E)-3-phenylprop-1-en-1-yl sulfone (10bj)

Yellow solid (74 %). IR (film): ν 3047, 3028, 2904, 1630, 1488, 1422, 1316, 1282, 1127, 1072, 1012, 976, 858, 818, 794, 751, 700, 629, 603, 513 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 3.50 (dd, *J* = 6.4, 1.5 Hz, 2H), 3.56 (dd, *J* = 6.4, 1.5 Hz, 2H), 6.10–6.16 (m, 2H), 6.95–7.08 (m, 4H), 7.14 (d, *J* = 7.0 Hz, 2H), 7.24–7.35 (m, 3H), 7.45 (d, *J* = 8.4 Hz, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 37.0, 37.7, 121.1, 127.1, 128.8, 128.9, 130.3, 130.5, 131.0, 132.0, 135.2, 136.2, 145.5, 146.7. MS (EI) *m/z* (rel intensity) 378 (100, M⁺), 376 (95), 312 (16), 310 (17), 197 (65), 195 (70), 171 (21), 169 (21), 117 (81), 116 (89), 115 (66) 91 (21), 89 (10), 65 (8). HRMS (EI) calcd for M⁺ (C₁₈H₁₇O₂S⁷⁹Br): 376.01326; found: 376.01312. Anal. calcd for C₁₈H₁₇O₂SBr (377.30): C 57.30, H 4.54, S 8.50; found C 57.19, H 4.60, S 8.40.

2.3. Preparation of thiomorpholine 1,1-dioxides

Neat benzylamine or hydrazine hydrate (0.1 mmol) was added to the solution of sulfone **7**, **8** or **10** (0.1 mmol) in a mixture of propan-2-ol (10 mL) and H₂O (5 mL) and the reaction was refluxed for 24 h. After cooling the reaction mixture to room temperature the solvents were removed under reduced pressure. The crude product was purified by flash chromatography using *c*-hexan/ethyl

acetate as eluent (Merck silica gel 60, 230–400 mesh).¹

4-Benzyl-3-heptadecylthiomorpholine 1,1-dioxide (11a)

Yellow solid (80 %). IR (KBr): ν 2955, 2919, 2850, 1474, 1467, 1340, 1295, 1129, 985, 741, 704, 681, 519 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.88 (t, J = 6.8 Hz, 3H), 1.20–1.34 (m, 28H), 1.36–1.46 (m, 2H), 1.60–1.82 (m, 2H), 2.78–2.86 (m, 1H), 2.92–3.09 (m, 4H), 3.20–3.26 (m, 1H), 3.27–3.35 (m, 1H), 3.66 (d, J = 13.5 Hz, 1H), 3.72 (d, J = 13.5 Hz, 1H), 7.27–7.37 (m, 5H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 14.1, 22.7, 25.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.4, 31.9, 46.5, 47.4, 51.4, 52.4, 59.2, 127.6, 128.4, 128.6, 137.9. MS (EI) m/z (rel intensity) 252 (2), 226 (6), 225 (13), 224 (100), 133 (4), 92 (7), 91 (87), 69 (3), 57 (6) 55 (6), 43 (13), 41 (9). HRMS (EI) calcd for M^+ ($\text{C}_{28}\text{H}_{49}\text{O}_2\text{NS}$): 463.34840; found: 463.34754.

4-Benzyl-3-(4-[tert-butyl(dimethyl)silyl]oxybutyl)thiomorpholine 1,1-dioxide (11b)

Yellow solid (83 %). IR (film): ν 3029, 2949, 2929, 2858, 1471, 1386, 1361, 1286, 1254, 1125, 1101, 1003, 835, 774, 731, 699, 679, 511, 440, 432 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.45–1.60 (m, 4H), 1.64–1.74 (m, 1H), 1.75–1.90 (m, 1H), 2.77–2.85 (m, 1H), 2.93–3.07 (m, 4H), 3.20–3.28 (m, 1H), 3.28–3.35 (m, 1H), 3.62 (t, J = 6.1 Hz, 2H), 3.67 (d, J = 13.5 Hz, 1H), 3.72 (d, J = 13.5 Hz, 1H), 7.25–7.35 (m, 5H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ -5.3, 18.3, 22.1, 25.9, 31.2, 32.5, 46.5, 47.4, 51.5, 52.4, 59.2, 62.8, 127.6, 128.4, 128.6, 137.9. MS (EI) m/z (rel intensity) 411 (1, M^+), 396 (3), 355 (14), 354 (53), 339 (5), 224 (53), 174 (5), 133 (5), 91 (100), 73 (5). Anal. calcd for $\text{C}_{21}\text{H}_{37}\text{NO}_3\text{SSi}$ (411.68): C 61.27, H 9.06, N 3.40, S 7.79; found C 61.48, H 8.98, N 3.31, S 7.58.

4-Benzyl-3-(4-[tert-butyl(dimethyl)silyl]oxybutyl)-5-pentylthiomorpholine 1,1-dioxide (11c)

Colourless oil (71 %). IR (film): ν 3031, 2954, 2930, 2858, 2949, 2929, 2858, 1603, 1494, 1462, 1360, 1300, 1255, 1133, 1099, 1027, 836, 776, 726, 697, 523 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 0.04 (s, 6H), 0.82 (t, J = 6.8 Hz, 3H), 0.87 (s, 9H), 1.15–1.38 (m, 8H), 1.45–1.65 (m, 4H), 1.70–1.77 (m, 1H), 1.85–1.98 (m, 1H), 2.78–2.86 (m, 2H), 2.92–3.01 (m, 2H), 3.37–3.44 (m, 2H), 3.59 (t, J = 6.2 Hz, 2H), 3.65 (s, 2H), 7.19–7.23 (m, 1H), 7.27–7.33 (m, 2H), 7.34–7.38 (m, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ -5.3, 13.9, 18.3, 22.4, 23.0, 25.9, 26.2, 31.4, 32.3, 33.7, 33.9, 44.8, 50.3, 50.4, 61.7, 62.7, 126.7, 127.2, 128.2, 141.0. MS (EI) m/z (rel intensity) 466 (2), 424 (19), 411 (5), 410 (18), 295 (11), 294 (62), 92 (7), 91 (100), 75 (4). Anal. calcd for $\text{C}_{26}\text{H}_{47}\text{NO}_3\text{SSi}$ (481.82): C 64.81, H 9.83, N 2.91, S 6.65; found C 64.82, H 9.97, N 2.95, S 6.54.

3-Heptadecylthiomorpholin-4-amine 1,1-dioxide (11d)

Colourless solid (66 %). IR (KBr): ν 2849, 1472, 1291, 1127, 868, 717, 684, 520, 449 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.88 (t, J = 6.6 Hz, 3H), 1.18–1.40 (m, 30H), 1.40–1.52 (m, 1H), 1.70–1.80 (m, 1H), 2.80–2.90 (m, 3H), 2.96–3.10 (m, 3H), 3.27–3.34 (m, 2H), 3.44–3.52 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 22.7, 25.1, 29.5, 29.6, 29.7, 47.6, 51.8, 55.3, 62.4. MS (EI) m/z (rel intensity) 388 (19, M^+), 177 (2), 151 (5), 150 (6), 149 (100), 134 (13), 83 (3), 69 (5) 58 (6), 57 (9), 55 (9) 43 (16), 41 (13). Anal. calcd for $\text{C}_{21}\text{H}_{44}\text{N}_2\text{O}_2\text{S}$ (388.6610): C 64.90, H 11.41, N 7.21, S 8.25; found C 64.69, H 11.65, N 7.14, S 8.17.

3,5-Dibenzylthiomorpholin-4-amine 1,1-dioxide (11e)

Colourless solid (48 %). IR (KBr): ν 3477, 3346, 3060, 3026, 2968, 2952, 2922, 2853, 1681, 1603, 1495, 1454, 1310, 1278, 1239, 1140, 1119, 1012, 994, 972, 873, 745, 698, 596, 512, 464, 433 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 2.64–2.76 (m, 4H), 2.82 (s, 2H), 2.94–3.60 (m, 2H), 3.17 (dd, J = 13.9, 6.7 Hz, 2H), 3.52–3.62 (m, 2H), 7.10–7.16 (m, 4H), 7.20–7.30 (m, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 39.2, 48.0, 63.4, 126.8, 128.7, 129.0, 137.1. MS (EI) m/z (rel intensity) 330 (4, M^+), 241 (6), 240 (14), 239 (100), 183 (10), 158 (3), 119 (5), 117 (36) 115 (6), 91 (21), 65 (4), 57 (31). HRMS (EI) calcd for M^+ ($\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_2\text{S}$): 330.14020; found: 330.13973.

39-[4-Amino-5-(8-bromooctyl)-1,1-dioxidothiomorpholin-3-yl]nonan-1-ol (11f)

Yellow solid (17 %). IR (KBr): ν 3369, 2929, 2850, 1740, 1468, 1333, 1291, 1151, 1132, 1059, 1011, 906, 890, 721, 649, 543, 452 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.22–1.48 (m, 24H),

¹ Teyssot, M.-L.; Fayolle, M.; Philouze, C.; Dupuy, C. *Eur. J. Org. Chem.* **2003**, 54–62.

1.50–1.60 (m, 2H), 1.68–1.80 (m, 2H), 1.80–1.90 (m, 2H), 2.64–2.72 (m, 2H), 2.92–3.20 (m, 2H), 3.22–3.32 (m, 2H), 3.40 (t, $J = 6.9$ Hz, 2H), 3.64 (t, $J = 6.6$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 25.8, 25.9, 26.0, 28.2, 28.8, 29.3, 29.4, 29.5, 29.6, 29.7, 32.9, 34.2, 49.0, 61.6, 63.0. MS (EI) m/z (rel intensity) 484 (36, M^+), 241 (6), 240 (14), 239 (100), 183 (10), 158 (3), 119 (5), 117 (36), 115 (6), 91 (21), 65 (4), 57 (31). HRMS (EI) calcd for M^+ ($\text{C}_{21}\text{H}_{43}\text{O}_3\text{N}_2\text{S}^{79}\text{Br}$): 482.21778; found: 482.21810.

2.4. Isomerisation of 8b

1,1'-[Sulfonyldi(1E)prop-1-ene-3,1-diyl]dibenzene (8b'): sulfone **8b** (0.1 mmol) and tetrabutylammonium hydroxide (40 % water solution, 0.1 mmol) were added to the solution of propan-2-ol (10 mL) and H_2O (5 mL) and reaction was refluxed for 24 h. After cooling down the reaction mixture white crystals precipitated and were filtered off on Buchner funnel to give 17.3 mg (55 %) of the product as a colourless solid (55 %). IR (KBr): ν 3050, 3030, 2976, 2926, 1596, 1576, 1497, 1449, 1414, 1320, 1290, 1277, 1147, 1115, 996, 978, 912, 759, 732, 714, 691, 596, 586, 484 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 3.90 (d, $J = 7.5$ Hz, 4H), 6.27 (dt, $J = 15.8, 7.5$ Hz, 2H), 6.68 (d, $J = 15.8$ Hz, 2H), 7.30–7.38 (m, 6H), 7.39–7.43 (m, 4H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 56.1, 115.2, 126.7, 128.8, 135.4, 139.2. MS (EI) m/z (rel intensity) 298 (1, M^+), 234 (1), 232 (1), 118 (10), 117 (100), 116 (7), 115 (23), 91 (10), 65 (2), 39 (3). HRMS (EI) calcd for M^+ ($\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}$): 298.10275; found: 298.10223.

3. Copies of ^1H and ^{13}C -NMR spectra

L. Rupnicki
 GRK 8_306/02
 ZESPOL_S/grkb30802h
 Pulse Sequence: szpul
 Date: Nov 30 2005
 Solvent: CDCl3
 Ambient temperature
 Mercury-400BB "SchliffSUN"
 Relax. delay 1.000 sec
 Pulse 33.3 degrees
 Acq. time 5.746 sec
 Width 3472.2 Hz
 80 Repetitions
 OBSERVE H1 400.0418219 MHz
 DATA PROCESSING
 FT size 65536

O. Koloda
GRK B 11401
ZESPOL_3/grkb11401
Pulse Sequence: s2pu1
Solvent: CDC13
Ambient temperature
Mercury-40006 "SchiffSUN"
Relax. delay 1.000 sec
Pulse 33.3 degrees
Acq. time 4.756 sec
Width 4504.5 Hz
68 repetitions
OBSERVE H1, 400.0418333 MHz
DATA PROCESSING
FT size 65536

N. Bieniek
GRK 840291
ZESPOL_S/grkb40201
Pulse Sequence: szpul
Date: Apr 18 2006
Solvent: CDCl3
Ambient temperature
Mercury-400BB "Schiffsun"
Relax. delay 1.000 sec
Pulse 33.3 degrees
Acq. time 5.355 sec
Width 6009.6 Hz
32 repetitions
OBSERVE H1: 400.0418291 MHz
DATA PROCESSING
F1 size 65536