Supporting Information to

Adjustment of the Bioresistivity by Electron Irradiation: Self-Assembled Monolayers of Oligo(ethyleneglycol)-Terminated Alkanethiols with Imbedded Cleavable Group

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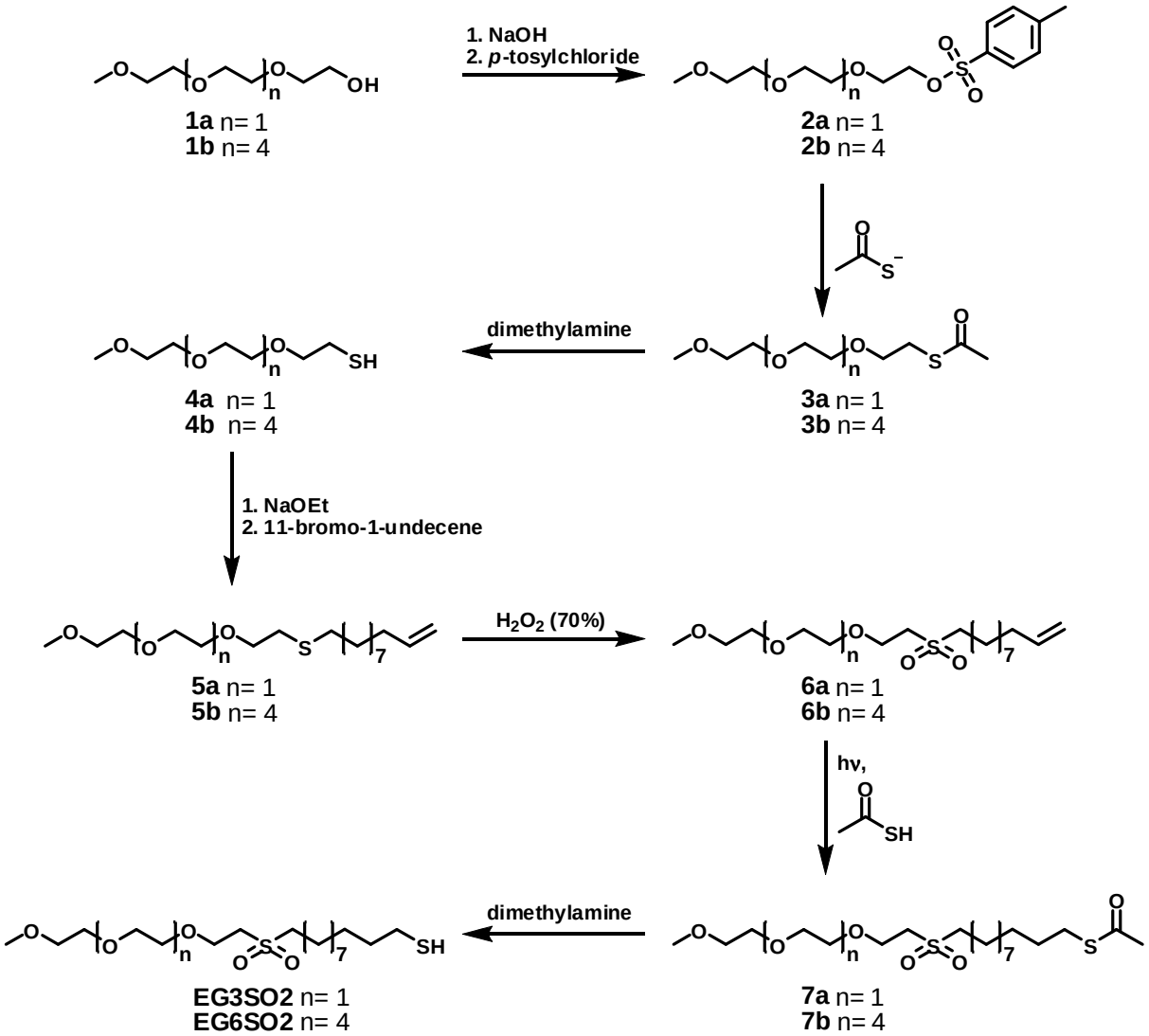
Preparation of the OEG-sulfonethiols EG3SO2 and EG6SO2

With the exception of the final products, for which the same acronyms as in the manuscript are used, the compounds are distinguished in the following, using a shortened nomenclature. Me stands for a CH_3 group, EG for an OCH_2CH_2 unit and Un signifies a linear C_{11} chain.

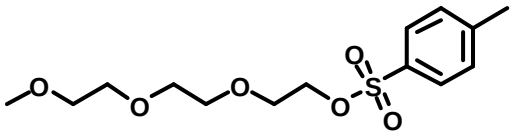
All reactions were carried out under nitrogen, if not otherwise stated.



Preparation of $MeEG_nOTos$ 2a (n = 3), 2b (n = 6)

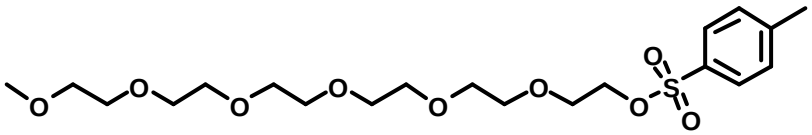
The compounds **2a** and **2b** were synthesized by conversion of the alcohol function of triethylene glycol monomethyl ether **1a** and hexaethylene glycol monomethyl ether **1b** into the better leaving group tosylate according to Refs 1-3.

MeEG$_3$OTos **2a**; 2-[2-(2-methoxyethoxy)ethoxy]ethyl 4-methylbenzenesulfonate



Yield: 17.62 g (55 mmol, 91 %), colourless oil.
IR ν $_{max}$ (KBr)/cm^{-1} 2868 ($\nu_{(-CH2)}$), 1598 ($\nu_{(C\text{-}C\ ar)}$), 1453 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1356 ($\nu_{(-RSO2R-)}$), 1292 ($\nu_{(-C\text{-}O\text{-}C-)}$), 1250 ($\nu_{(-C\text{-}O\text{-}C-)}$), 1189 ($\nu_{(-C\text{-}O\text{-}C-)}$), 1177 ($\nu_{(-C\text{-}O\text{-}C-)}$), 1098 ($\nu_{(-C\text{-}O\text{-}C-)}$), 1018 ($\delta_{(-C\text{-}H)ar}$), 923 ($\delta_{(-C\text{-}H)ar}$).
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm]: 7.76 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_2), 7.32 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H_3), 4.14 (t, $^3J_{HH}$ = 4.8 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2C\mathit{H}_2OTos$), 3.67 (t, $^3J_{HH}$ = 4.9 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OC\mathit{H}_2CH_2OTos$),
3.63-3.53 (m, 6H, $CH_3OCH_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OCH_2CH_2OTos$),
3.53-3.48 (m, 2H, $CH_3OC\mathit{H}_2CH_2OCH_2CH_2OCH_2CH_2OTos$),
3.35 (s, 3H, $C\mathit{H}_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OTos$),
2.43 (s, 3H, Tos$C\mathit{H}_3$).
^{13}C-NMR (125 MHz, $CDCl_3$), δ [ppm]: 144.72 (C_4), 132.98 (C_1), 129.74 (C_3), 127.88 (C_2),
71.82 ($CH_3OC\mathit{H}_2CH_2OCH_2CH_2OCH_2CH_2OTos$),
70.65 ($CH_3OCH_2CH_2OC\mathit{H}_2C\mathit{H}_2OCH_2CH_2OTos$),
70.45 ($CH_3OCH_2C\mathit{H}_2OCH_2CH_2OCH_2CH_2OTos$),
69.16 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2C\mathit{H}_2OTos$),
68.59 ($CH_3OCH_2CH_2OCH_2CH_2OC\mathit{H}_2CH_2OTos$),
58.91 ($C\mathit{H}_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OTos$),
21.53 (Tos$C\mathit{H}_3$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{14}H_{22}NaO_6S$, 341.1035; found, 341.1029.
Anal. calcd for $C_{14}H_{22}O_6S$: C 52.81, H 6.96, S 10.07; found: C 52.45, H 7.05, S 9.90.

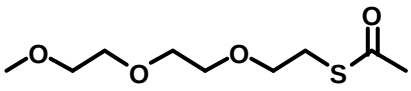
MeEG$_6$OTos **2b**



Yield: 10.7 g (24 mmol, 85 %), colourless liquid.
^{1}H-NMR (300 MHz, $CDCl_3$), δ [ppm]: 7.79 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_2), 7.34 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H_3), 4.20-4.10 (m, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2C\mathit{H}_2OTos$), 3.90-3.42 (m, 22H, $CH_3OC\mathit{H}_2C\mathit{H}_2(OC\mathit{H}_2C\mathit{H}_2)_4OC\mathit{H}_2CH_2OTos$), 3.37 (s, 3H, $C\mathit{H}_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2OTos$), 2.44 (s, 3H, Tos$C\mathit{H}_3$).

Preparation of thioacetates MeEG$_n$SAc 3a (n = 3), 3b (n = 6)[4,5]

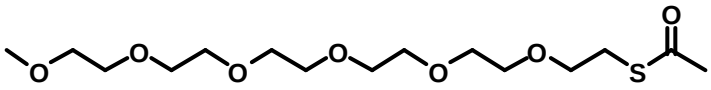
MeEG$_3$SAc **3a**; Typical Procedure



To a solution of potassium *tert*-butoxide (12.4 g, 110 mmol) in dry DMF (50 mL) thioacetic acid (16.9 g, 220 mmol) was added. The mixture was cooled with an ice bath. Then $MeEG_3OTos$ **2a** (17.6 g, 55 mmol) dissolved in dry DMF (30 mL) was added. The mixture was stirred at room temperature for 24 h. DMF and thioacetic acid were removed *in vacuo*. The residue dissolved in water and extracted with dichloromethane. The organic phase was evaporated *in vacuo*. For purification the residue was titurated twice with water for 15 minutes followed by decantation. The residue was further purified by chromatography on silica gel using dichloromethane/ ethanol (1%->2%->5%) as eluent to yield $MeEG_3SAc$ **3a** as a brown-red oil (7.8 g, 35 mmol, 64 % yield).

Yield: 7.8 g (35 mmol, 64 %), brown-red oil.
IR ν $_{max}$ (KBr)/cm^{-1} 2874 ($\nu_{(-CH2)}$), 1692 ($\nu_{(C=O)}$), 1455 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1354 ($\delta_{(-CH3)}$), 1292 ($\nu_{(-C-O-C-)}$), 1246 ($\nu_{(-C-O-C-)}$), 1199 ($\nu_{(-C-O-C-)}$), 1109 ($\nu_{(-C-O-C-)}$).
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm]: 3.67-3.61 (m, 6H, $CH_3OCH_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OCH_2CH_2SCOCH_3$),
3.59 (t, $^3J_{HH}$ = 6.5 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OC\mathit{H}_2CH_2SCOCH_3$),
3.56-3.51 (m, 2H, $CH_3OC\mathit{H}_2CH_2OCH_2CH_2OCH_2CH_2SCOCH_3$),
3.37 (s, 3H, $C\mathit{H}_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCOCH_3$),
3.08 (t, $^3J_{HH}$ = 6.5 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2C\mathit{H}_2SCOCH_3$),
2.32 (s, 3H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCOC\mathit{H}_3$).
^{13}C-NMR (125 MHz, $CDCl_3$), δ [ppm]: 195.44 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCOCH_3$),
71.90 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCOCH_3$),
70.53, 70.28 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCOCH_3$),
69.72 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCOCH_3$),
58.98 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCOCH_3$),
30.49 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCOCH_3$),
28.80 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCOCH_3$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_9H_{18}NaO_4S$, 245.0823; found, 245.0818.

$MeEG_6SAc$ **3b**



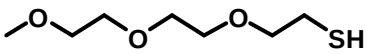
Similar to **2a**, $MeEG_6OTos$ **2b** (9.4 g, 20 mmol) was converted to $MeEG_6SAc$ **3b.** After purification by chromatography on silica gel using dichloromethane/ ethanol (1%->2%->5%) as eluent, a brown-red oil (6.3 g, 18 mmol, 88 % yield) was obtained.

Yield: 6.3 g (18 mmol, 88 %), brown-red liquid.
IR ν $_{max}$ (KBr)/cm^{-1} 2872 ($\nu_{(-CH2)}$), 1693 ($\nu_{(C=O)}$), 1457 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1354 ($\delta_{(-CH3)}$), 1296 ($\nu_{(-C-O-C-)}$), 1249 ($\nu_{(-C-O-C-)}$), 1199 ($\nu_{(-C-O-C-)}$), 1111 ($\nu_{(-C-O-C-)}$).
^{1}H-NMR (400 MHz, $CDCl_3$), δ [ppm]: 3.68-3.50 (m, 20H, $CH_3OCH_2C\mathit{H}_2(OC\mathit{H}_2C\mathit{H}_2)_4OC\mathit{H}_2CH_2SCOCH_3$),
3.50-3.43 (m, 2H, $CH_3OC\mathit{H}_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOCH_3$),
3.31 (s, 3H, $C\mathit{H}_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOCH_3$),
3.02 (t, $^3J_{HH}$ = 6.5 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2C\mathit{H}_2SCOCH_3$),
2.26 (s, 3H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOC\mathit{H}_3$).
^{13}C-NMR (100 MHz, $CDCl_3$), δ [ppm]:

195.19 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOCH_3$),
71.71 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOCH_3$),
70.44, 70.38, 70.31 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOCH_3$),
68.54 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOCH_3$),
58.80 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOCH_3$),
30.34 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOCH_3$),
28.63 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCOCH_3$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{15}H_{30}NaO_7S$, 377.1610; found, 377.1604.

Preparation of MeEG$_n$SH 4a (n = 3), 4b (n = 6)

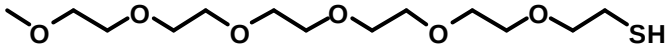
MeEG$_3$SH **4a**; Typical Procedure



To a solution of MeEG$_3$SAc **3a** (7.8 g, 35 mmol) in dry methanol (40 mL) was added neat dimethylamine (6.9 g, 154 mmol). The solution was stirred at room temperature for 24 h followed by acidification with degassed acetic acid. The solvent was removed *in vacuo* and the residue portioned between dichloromethane and water. The organic phase was evaporated to dryness and the residue was further purified by chromatography on silica gel using dichloromethane/ ethylacetate 9:1 -> 1:1 as eluent to yield MeEG$_3$SH **4a** as a slight yellow oil (5.5 g, 30 mmol, 87 % yield).

Yield: 5.5 g (30 mmol, 87 %), slight yellow oil.
IR ν $_{max}$ (KBr)/cm^{-1} 2873 ($\nu_{(-CH2)}$), 2556 ($\nu_{(S-H)}$), 1455 ($\delta_{(-CH2)}$, $\delta_{(-CH3)}$), 1351 ($\delta_{(-CH3)}$), 1294 ($\nu_{(-C-O-C-)}$), 1246 ($\nu_{(-C-O-C-)}$), 1199 ($\nu_{(-C-O-C-)}$), 1108 ($\nu_{(-C-O-C-)}$).
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm]: 3.70-3.59 (m, 8H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$),
3.59-3.50 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$),
3.37 (s, 3H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$),
2.69 (q, $^3J_{HH}$ = 7.0 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$),
1.57 (t, $^3J_{HH}$ = 8.2 Hz, 1H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$).
^{13}C-NMR (125 MHz, $CDCl_3$), δ [ppm]: 72.87 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$),
71.92 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$),
70.55, 70.21 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$),
59.00 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$),
24.23 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SH$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_7H_{16}NaO_3S$, 203.0718; found, 203.0713.

MeEG$_6$SH **4b**



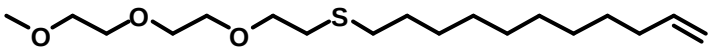
Similarly as described for **4a**, MeEG$_6$SAc **3b** (3.0 g, 8.5 mmol) was converted to yield MeEG$_6$SH **4b** (2.5 g, 8.0 mmol, 94 %). The crude product was used without chromatography.

Yield: 2.5 g (8.0 mmol, 94 %), light yellow oil.
^{1}H-NMR (300 MHz, $CDCl_3$), δ [ppm]: 3.70-3.57 (m, 20H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SH$),
3.57-3.51 (m, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SH$),
3.38 (s, 3H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SH$),
2.69 (q, $^3J_{HH}$ = 7.0 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SH$),

1.59 (t, $^{3}J_{HH}$ = 8.2 Hz, 1H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SH$).

Undecenylation of $MeEG_nSH$ 4a,b to $MeEG_nSUn$ 5a (n = 3), 5b (n = 6)

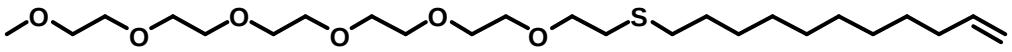
$MeEG_3SUn$ **5a**; Typical Procedure[1,6]



To a solution of sodium (0.27 g, 12 mmol) in dry ethanol (30 mL), a solution of $MeEG_3SH$ **4a** (2.1 g, 12 mmol) in dry ethanol (30 mL) was added. The mixture was stirred at room temperature for 20 min before 11-bromo-1-undecen (2.7 g, 12 mmol) was added. The stirring was continued at room temperature for 24 h before the mixture was acidified with degassed acetic acid. Then the solvent was removed *in vacuo* and the residue extracted with dichloromethane and water. The organic phase was evaporated to dryness to yield $MeEG_3SUn$ **5a** (3.8 g, 11.4 mmol, 99 %), which was used without further purification.

Yield: 3.8 g (11.4 mmol, 99 %), light brown-yellow oil.
IR ν_{max} (KBr)/cm^{-1} 3075 ($\nu_{(=CH2)}$), 2925 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2854 ($\nu_{(-CH2)}$), 1640 ($\nu_{(C=C)}$), 1462 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1351 ($\delta_{(-CH3)}$), 1291 ($\nu_{(-C-O-C-)}$), 1246 ($\nu_{(-C-O-C-)}$), 1200 ($\nu_{(-C-O-C-)}$), 1111 ($\nu_{(-C-O-C-)}$), 910 ($\delta_{(=CH)}$).
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm]: 5.87-5.73 (m, 1H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 5.04-4.86 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 3.69-3.58 (m, 8H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 3.57-3.51 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 3.37 (s, 3H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 2.69 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 2.52 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 2.02 (q, $^{3}J_{HH}$ = 7.1 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 1.61-1.51 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 1.42-1.31 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$), 1.31-1.20 (m, 10H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$).
^{13}C-NMR (125 MHz, $CDCl_3$), δ [ppm]:
139.15 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
114.06 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
71.92 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
71.01, 70.60, 70.54, 70.27
($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
58.98 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
33.74 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
32.55 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
31.35 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
29.77 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
29.41, 29.37, 29.18, 29.05, 28.87
($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$),
28.81 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH{=}CH_2$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{18}H_{36}NaO_3S$, 355.2283; found 355.2277.

MeEG$_6$SUn **5b**

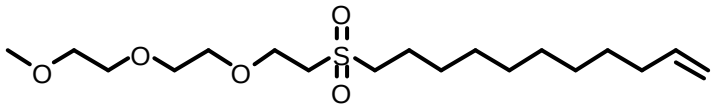


MeEG$_6$SH **4b** (2.5 g, 8.0 mmol) was converted to MeEG$_6$SUn **5b** (3.7 g, 7.9 mmol, 99 %) following the procedure given for **5a**. The crude product was used without further purification.

Yield: 3.7 g (7.9 mmol, 99 %), light brown-yellow oil.
IR ν $_{max}$ (KBr)/cm^{-1} 3075 ($\nu_{(=CH2)}$), 2925 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2854 ($\nu_{(-CH2)}$), 1640 ($\nu_{(C=C)}$), 1461 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1350 ($\delta_{(-CH3)}$), 1293 ($\nu_{(-C-O-C-)}$), 1249 ($\nu_{(-C-O-C-)}$), 1199 ($\nu_{(-C-O-C-)}$), 1112 ($\nu_{(-C-O-C-)}$), 911 ($\delta_{(=CH)}$).
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm]: 5.86-5.73 (m, 1H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2C\mathit{H}=CH_2$), 5.04-4.87 (m, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=C\mathit{H_2}$), 3.68-3.58 (m, 20H, $CH_3OCH_2C\mathit{H_2}(OC\mathit{H_2}C\mathit{H_2})_4OC\mathit{H_2}CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.56-3.50 (m, 2H, $CH_3OC\mathit{H_2}CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.36 (s, 3H, $C\mathit{H_3}OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 2.68 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2C\mathit{H_2}SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 2.52 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SC\mathit{H_2}CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 2.02 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2C\mathit{H_2}CH=CH_2$), 1.62-1.50 (m, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2C\mathit{H_2}CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 1.42-1.30 (m, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2C\mathit{H_2}(CH_2)_4CH_2CH_2CH=CH_2$), 1.30-1.20 (m, 10H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(C\mathit{H_2})_4C\mathit{H_2}CH_2CH=CH_2$).
^{13}C-NMR (125 MHz, $CDCl_3$), δ [ppm]:
139.13 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2\mathit{C}H=CH_2$),
114.06 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=\mathit{CH_2}$),
71.90 ($CH_3O\mathit{C}H_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
70.98, 70.54, 70.47, 70.26
($CH_3OCH_2\mathit{C}H_2(O\mathit{C}H_2\mathit{C}H_2)_4O\mathit{C}H_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
58.96 ($\mathit{C}H_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
33.72 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(CH_2)_4CH_2\mathit{C}H_2CH=CH_2$),
32.53 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2S\mathit{C}H_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
31.33 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2\mathit{C}H_2SCH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
29.75 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2\mathit{C}H_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
29.39, 29.35, 29.16, 29.03, 28.85
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2CH_2(\mathit{C}H_2)_4\mathit{C}H_2CH_2CH=CH_2$),
28.79 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SCH_2CH_2\mathit{C}H_2(CH_2)_4CH_2CH_2CH=CH_2$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{24}H_{48}NaO_6S$, 487.3069; found, 487.3064.

Oxidation of the sulfide function to generate the sulfones MeEG$_n$SO$_2$Un 6a (n = 3), 6b (n = 6)

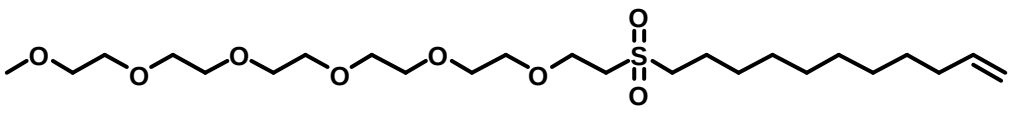
MeEG$_3$SO$_2$Un **6a**



A solution of $MeEG_3SUn$ **5a** (3.3 g, 9.9 mmol) in THF (15 mL) was cooled to 0 °C before H_2O_2 (70%, 0.78 mL) was slowly added. The mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to yield 3.8 g. The residue was purified by chromatography on Al_2O_3 using dichloromethane/ethyl acetate (4:1->3:1->1:1) as eluent to yield $MeEG_3SO_2Un$ **6a** as a colourless oil (1.4 g, 3.8 mmol, 39 % yield).

Yield: 1.4 g (3.8 mmol, 39 %), colourless oil.
IR ν $_{max}$ (KBr)/cm^{-1} 3076 ($\nu_{(=CH2)}$), 2924 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2855 ($\nu_{(-CH2)}$), 1640 ($\nu_{(C=C)}$), 1463 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1351 ($\delta_{(-CH3)}$), 1312 ($\nu_{(-RSO2R-)}$), 1287 ($\nu_{(-C-O-C-)}$), 1239 ($\nu_{(-C-O-C-)}$), 1200 ($\nu_{(-C-O-C-)}$), 1123 ($\nu_{(-C-O-C-)}$), 910 ($\delta_{(=CH)}$).
^{1}H-NMR (400 MHz, $CDCl_3$), δ [ppm]: 5.87-5.71 (m, 1H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2C\mathit{H}=CH_2$), 5.03-4.86 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=C\mathit{H_2}$), 3.89 (t, $^3J_{HH}$ = 5.4 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OC\mathit{H_2}CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.69-3.51 (m, 6H, $CH_3OCH_2C\mathit{H_2}OC\mathit{H_2}C\mathit{H_2}OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.50-3.47 (m, 2H, $CH_3OC\mathit{H_2}CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.35 (s, 3H, $C\mathit{H_3}OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.17 (t, $^3J_{HH}$ = 5.4 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2C\mathit{H_2}SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.07 (t, $^3J_{HH}$ = 8.1 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2C\mathit{H_2}CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 2.02 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2C\mathit{H_2}CH=CH_2$), 1.90-1.74 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2C\mathit{H_2}CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 1.49-1.19 (m, 12H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2C\mathit{H_2}(C\mathit{H_2})_4C\mathit{H_2}CH_2CH=CH_2$).
^{13}C-NMR (100 MHz, $CDCl_3$), δ [ppm]:
139.04 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2\mathit{C}H=CH_2$),
114.10 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=\mathit{CH_2}$),
71.85 ($CH_3O\mathit{C}H_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
70.50, 70.44, 70.25
($CH_3OCH_2\mathit{C}H_2O\mathit{C}H_2\mathit{C}H_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
64.75 ($CH_3OCH_2CH_2OCH_2CH_2O\mathit{C}H_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
58.96 ($\mathit{C}H_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
54.76 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2\mathit{C}H_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
53.19 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2\mathit{C}H_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
33.69 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2\mathit{C}H_2CH=CH_2$),
29.27, 29.16, 29.03, 28.97, 28.80, 28.43
($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2\mathit{C}H_2(\mathit{C}H_2)_4\mathit{C}H_2CH_2CH=CH_2$),
21.78 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2\mathit{C}H_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{18}H_{36}NaO_5S$, 387.2181; found 387.2176.

$MeEG_6SO_2Un$ **6b**

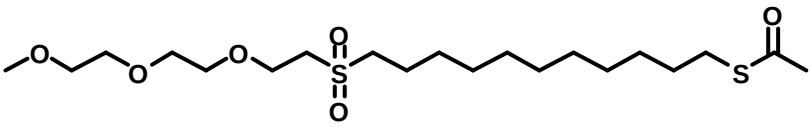


To compound $MeEG_6SUn$ **5b** (1.0 g, 2.2 mmol) was slowly added H_2O_2 (70%, 0.18 mL). The mixture was heated to 50 °C for 30 min and then was stirred at room temperature for 24 h. Dichloromethane was added and the solvent was removed under reduced pressure to yield 1.2 g. The residue was purified by chromatography on silica gel using ethylacetate/ ethanol (10->20%) as eluent to yield $MeEG_6SO_2Un$ **6b** as a colourless oil (0.5 g, 1.0 mmol, 46 % yield).

Yield: 0.5 g (1.0 mmol, 46 %), colourless oil.
IR ν_{max} (KBr)/cm^{-1} 3075 ($\nu_{(=CH2)}$), 2925 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2854 ($\nu_{(-CH2)}$), 1640 ($\nu_{(C=C)}$), 1463 ($\delta_{(-CH2)}$, $\delta_{(-CH3)}$), 1351 ($\nu_{(-RSO2R-)}$), 1317 ($\nu_{(-RSO2R-)}$), 1289 ($\nu_{(-C-O-C-)}$), 1251 ($\nu_{(-C-O-C-)}$), 1199 ($\nu_{(-C-O-C-)}$), 1125 ($\nu_{(-C-O-C-)}$).
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm]: 5.82-5.70 (m, 1H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2C\mathit{H}=CH_2$), 5.02-4.82 (m, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=C\mathit{H_2}$), 3.87 (t, $^3J_{HH}$ = 5.4 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OC\mathit{H_2}CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.66-3.56 (m, 18H, $CH_3OCH_2C\mathit{H_2}(OC\mathit{H_2}C\mathit{H_2})_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.54-3.48 (m, 2H, $CH_3OC\mathit{H_2}CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.34 (s, 3H, $C\mathit{H_3}OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.15 (t, $^3J_{HH}$ = 5.4 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2C\mathit{H_2}SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 3.05 (t, $^3J_{HH}$ = 8.0 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2C\mathit{H_2}CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 2.00 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2C\mathit{H_2}CH=CH_2$), 1.86-1.72 (m, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2C\mathit{H_2}CH_2(CH_2)_4CH_2CH_2CH=CH_2$), 1.44-1.20 (m, 12H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2C\mathit{H_2}(C\mathit{H_2})_4C\mathit{H_2}CH_2CH=CH_2$).
^{13}C-NMR (125 MHz, $CDCl_3$), δ [ppm]:
138.98 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2\mathit{C}H=CH_2$),
114.06 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=\mathit{CH_2}$),
71.82 ($CH_3O\mathit{C}H_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
70.48, 70.46, 70.39, 70.20,
($CH_3OCH_2\mathit{C}H_2(O\mathit{C}H_2\mathit{C}H_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
64.71 ($CH_3OCH_2CH_2(OCH_2CH_2)_4O\mathit{C}H_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
58.88 ($\mathit{C}H_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
54.70 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2\mathit{C}H_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
53.16 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2\mathit{C}H_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$),
33.63 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2\mathit{C}H_2CH=CH_2$),
29.22, 29.10, 28.98, 28.92, 28.75, 28.38
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2\mathit{C}H_2(\mathit{C}H_2)_4\mathit{C}H_2CH_2CH=CH_2$),
21.73 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2\mathit{C}H_2CH_2(CH_2)_4CH_2CH_2CH=CH_2$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{24}H_{48}NaO_8S$, 519.2968; 519.2962.
Anal. calcd for $C_{24}H_{48}O_8S$: C 58.03, H 9.74, S 6.46; found: C 57.40, H 9.64, S 6.57.

Thioacetylation of the double bonds to yield $MeEG_nSO_2UnSAc$ 7a (n = 3), 7b (n = 6)

$MeEG_3SO_2UnSAc$ **7a**; Typical Procedure[7]

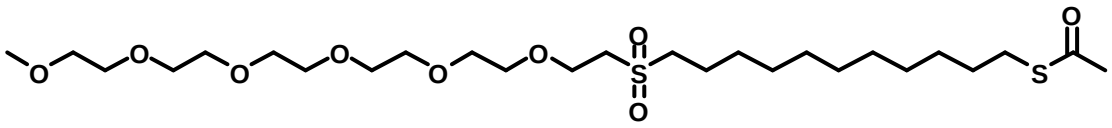


To a solution of $MeEG_3SO_2Un$ **6a** (0.6 g, 1.6 mmol) in dry THF (23 mL) was added thioacetic acid (0.6 g, 7.9 mmol). The mixture was irradiated with a 25 W mercury lamp. After 6 h the solvent and the excess of thioacetic acid were removed in vacuum. The residue was dissolved in dichloromethane and washed with water. The organic phase was removed under reduced pressure to yield 0.8 g. The residue was purified twice by chromatography on Al_2O_3 using dichloromethane/ethyl acetate (1%->3%->10%) as eluent to yield $MeEG_3SO_2UnSAc$ **7a** as a slight yellow oil (0.45 g, 1.0 mmol, 64 % yield).

Yield: 0.45 g (1.0 mmol, 64 %), slight yellow oil.
IR ν_{max} (KBr)/cm^{-1} 2925 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2855 ($\nu_{(-CH2)}$), 1690 ($\nu_{(C=O)}$), 1463 ($\delta_{(-CH2)}$, $\delta_{(-CH3)}$), 1354 ($\nu_{(-RSO2R-)}$), 1317 ($\nu_{(-RSO2R-)}$), 1288 ($\nu_{(-C-O-C-)}$), 1251 ($\nu_{(-C-O-C-)}$), 1199 ($\nu_{(-C-O-C-)}$), 1128 ($\nu_{(-C-O-C-)}$).
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm]: 3.89 (t, $^3J_{HH}$ = 5.4 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OC\mathit{H}_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.67-3.56 (m, 6H, $CH_3OCH_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.55-3.47 (m, 2H, $CH_3OC\mathit{H}_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.35 (s, 3H, $C\mathit{H}_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.17 (t, $^3J_{HH}$ = 5.4 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2C\mathit{H}_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.07 (t, $^3J_{HH}$ = 8.1 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2C\mathit{H}_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 2.84 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2C\mathit{H}_2SCOCH_3$), 2.30 (s, 3H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOC\mathit{H}_3$), 1.87-1.74 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2C\mathit{H}_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 1.59-1.47 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2C\mathit{H}_2CH_2SCOCH_3$), 1.45-1.35 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2C\mathit{H}_2CH_2CH_2SCOCH_3$), 1.35-1.16 (m, 12H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2C\mathit{H}_2(C\mathit{H}_2)_4C\mathit{H}_2CH_2CH_2CH_2SCOCH_3$).
^{13}C-NMR (125 MHz, $CDCl_3$), δ [ppm]:
195.91 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2S\mathit{C}OCH_3$), 71.86 ($CH_3O\mathit{C}H_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 70.51, 70.44, 70.26 ($CH_3OCH_2\mathit{C}H_2O\mathit{C}H_2\mathit{C}H_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 64.75 ($CH_3OCH_2CH_2OCH_2CH_2O\mathit{C}H_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 58.96 ($\mathit{C}H_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 54.76 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2\mathit{C}H_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 53.21 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2\mathit{C}H_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 30.55 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOC\mathit{H}_3$),

29.41 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 29.38, 29.31, 29.17, 29.04, 28.98 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 28.70 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 28.43 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 21.78 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{20}H_{40}NaO_6S_2$, 463.2164; found 463.2159.

MeEG$_6$SO$_2$UnSAc **7b**



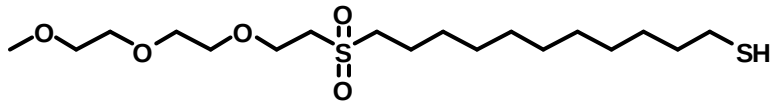
MeEG$_6$SO$_2$Un **6b** (0.7 g, 1.5 mmol) and thioacetic acid (0.5 g, 6.6 mmol) in dry THF (10 mL) were irradiated and isolated as stated above. For chromatography on silica gel ethyl acetate/ethanol (1%->5%->10%) was used as eluent to yield MeEG$_6$SO$_2$UnSAc **7b** as a slightly yellow oil (0.8 g, 1.4 mmol, 95 % yield).

Yield: 0.8 g (1.4 mmol, 95 %), slightly yellow oil.
IR ν_{max} (KBr)/cm^{-1} 2929 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2872 ($\nu_{(-CH2)}$), 1692 ($\nu_{(C=O)}$), 1464 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1354 ($\nu_{(-RSO2R-)}$), 1317 ($\nu_{(-RSO2R-)}$), 1289 ($\nu_{(-C-O-C-)}$), 1252 ($\nu_{(-C-O-C-)}$), 1200 ($\nu_{(-C-O-C-)}$), 1114 ($\nu_{(-C-O-C-)}$).
^{1}H-NMR (400 MHz, $CDCl_3$), δ [ppm]: 3.87 (t, $^3J_{HH}$ = 5.4 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OC\mathit{H}_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.66-3.56 (m, 18H, $CH_3OCH_2C\mathit{H}_2(OC\mathit{H}_2C\mathit{H}_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.54-3.47 (m, 2H, $CH_3OC\mathit{H}_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.33 (s, 3H, $C\mathit{H}_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.15 (t, $^3J_{HH}$ = 5.4 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2C\mathit{H}_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 3.04 (t, $^3J_{HH}$ = 8.0 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2C\mathit{H}_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 2.82 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2C\mathit{H}_2SCOCH_3$), 2.28 (s, 3H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOC\mathit{H}_3$), 1.85-1.72 (m, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2C\mathit{H}_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 1.58-1.45 (m, 2H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2C\mathit{H}_2CH_2SCOCH_3$), 1.45-1.15 (m, 14H, $CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2C\mathit{H}_2(C\mathit{H}_2)_4C\mathit{H}_2C\mathit{H}_2CH_2CH_2SCOCH_3$).
^{13}C-NMR (100 MHz, $CDCl_3$), δ [ppm]: 195.86 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2S\mathit{C}OCH_3$), 71.80 ($CH_3OC\mathit{H}_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$), 70.46, 70.43, 70.37, 70.18 ($CH_3OCH_2C\mathit{H}_2(OC\mathit{H}_2C\mathit{H}_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$),

64.69
($CH_3OCH_2CH_2(OCH_2CH_2)_4O\mathit{C}H_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$),
58.88
($\mathit{C}H_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$),
54.68
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2\mathit{C}H_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$),
53.12
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2\mathit{C}H_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$),
30.50
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCO\mathit{C}H_3$),
29.34
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2\mathit{C}H_2CH_2SCOCH_3$),
29.28, 29.25, 29.10, 28.97, 28.92
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2\mathit{C}H_2(\mathit{C}H_2)_4\mathit{C}H_2CH_2CH_2CH_2CH_2SCOCH_3$),
28.64
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2\mathit{C}H_2SCOCH_3$),
28.36
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2\mathit{C}H_2CH_2CH_2CH_2SCOCH_3$),
21.71
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2\mathit{C}H_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SCOCH_3$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{26}H_{52}NaO_9S_2$, 595.2950; found 595.2945.

Deprotection of the thiol groups to yield EGnSO2 (n = 3, 6)

EG3SO2; Typical Procedure

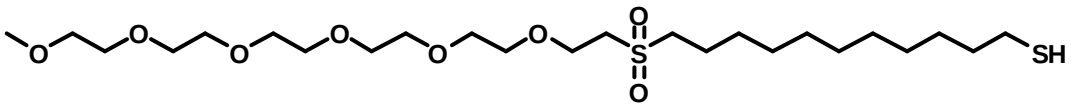


To a solution of $MeEG_3SO_2UnSAc$ **7a** (0.35 g, 0.8 mmol) in dry methanol (40 mL) was added dimethylamine (0.2 g, 4.4 mmol). The solution was stirred at room temperature for 24 h followed by acidification with degassed acetic acid. Before the solvent was removed *in vacuo* and the residue extracted with dichloromethane and water. The organic phase was evaporated to dryness to yield **EG3SO2** (0.37 g, 0.75 mmol, 95 % yield). The resulting product was spectroscopically pure.

Yield: 0.37 g (0.75 mmol, 95 %), colourless solid like compound.
IR ν_{max} (KBr)/cm^{-1} 2919 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2847 ($\nu_{(-CH2)}$), 1460 ($\delta_{(-CH2)}$, $\delta_{(-CH3)}$), 1403 ($\nu_{(-RSO2R-)}$), 1383 ($\nu_{(-RSO2R-)}$), 1321 ($\nu_{(-RSO2R-)}$), 1285 ($\nu_{(-C-O-C-)}$), 1267 ($\nu_{(-C-O-C-)}$), 1237 ($\nu_{(-C-O-C-)}$), 1194 ($\nu_{(-C-O-C-)}$), 1127 ($\nu_{(-C-O-C-)}$).
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm]: 3.88 (t, $^3J_{HH}$ = 5.4 Hz, 2H,
$CH_3OCH_2CH_2OCH_2CH_2O\mathit{C}H_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
3.68-3.56 (m, 6H,
$CH_3OCH_2\mathit{C}H_2O\mathit{C}H_2\mathit{C}H_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
3.55-3.44 (m, 2H,
$CH_3O\mathit{C}H_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
3.35 (s, 3H, $C\mathit{H}_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
3.16 (t, $^3J_{HH}$ = 5.4 Hz, 2H,
$CH_3OCH_2CH_2OCH_2CH_2OCH_2C\mathit{H}_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
3.06 (t, $^3J_{HH}$ = 8.0 Hz, 2H,
$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2C\mathit{H}_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),

2.49 (q, $^{3}J_{HH}$ = 7.4 Hz, 2H,
$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
1.87-1.72 (m, 2H,
$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
1.72-1.61 (m, 2H,
$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
1.61-1.49 (m, 2H,
$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
1.47-1.15 (m, 13H,
$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$).
Traces of the respective disulfide could be detected at 2.65 ppm (t, $^{3}J_{HH}$ = 7.3 Hz, 2H,
$CH_2CH_2S_2$).
^{13}C-NMR (125 MHz, $CDCl_3$), δ [ppm]:
71.85 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
70.50, 70.44, 70.25
($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
64.75 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
58.95 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
54.75 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
53.22 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
33.93 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
29.34, 29.16, 29.12, 29.03, 28.94
($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
28.42 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
28.25 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
24.53 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
21.77 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$).
[39.07 ($CH_2CH_2CH_2S_2$)].
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{18}H_{38}NaO_5S_2$, 421.2058; found 421.2053.

EG6SO2

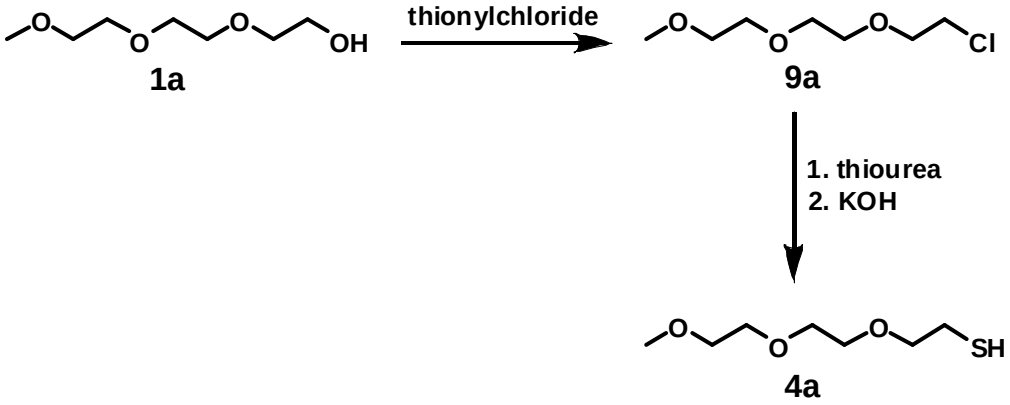


$MeEG_6SO_2UnSAc$ **7b** (0.5 g, 0.9 mmol) was converted to the thiol analogous to **7a** using dimethylamine (0.2 g, 4.4 mmol). The crude product was purified by chromatography on silica gel using ethylacetate/ ethanol (1% to 20%) as eluent to yield EG6SO2 as a colourless oil (0.37 g, 0.7 mmol, 78 % yield).

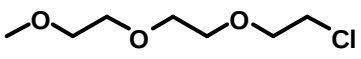
Yield: 0.37 g (0.7 mmol, 78 %), colourless oil.
IR ν $_{max}$ (KBr)/cm^{-1} 2925 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2856 ($\nu_{(-CH2)}$), 1463 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1351 ($\nu_{(-RSO2R-)}$), 1317 ($\nu_{(-RSO2R-)}$), 1288 ($\nu_{(-C-O-C-)}$), 1251 ($\nu_{(-C-O-C-)}$), 1199 ($\nu_{(-C-O-C-)}$), 1118 ($\nu_{(-C-O-C-)}$).
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm]: 3.90 (t, $^{3}J_{HH}$ = 5.5 Hz, 2H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
3.68-3.58 (m, 18H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
3.57-3.51 (m, 2H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
3.37 (s, 3H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),

3.18 (t, $^{3}J_{HH}$ = 5.4 Hz, 2H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2C\mathit{H}_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
3.08 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2C\mathit{H}_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
2.51 (q, $^{3}J_{HH}$ = 7.4 Hz, 2H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2C\mathit{H}_2SH$),
1.88-1.78 (m, 2H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2C\mathit{H}_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
1.65-1.53 (m, 2H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2C\mathit{H}_2CH_2SH$),
1.46-1.18 (m, 15H,
$CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2C\mathit{H}_2(C\mathit{H}_2)_4C\mathit{H}_2C\mathit{H}_2CH_2CH_2S\mathit{H}$).
^{13}C-NMR (125 MHz, $CDCl_3$), δ [ppm]:
71.94 ($CH_3O\mathit{C}H_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
70.61, 70.57, 70.52, 70.31
($CH_3OCH_2\mathit{C}H_2(O\mathit{C}H_2\mathit{C}H_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
64.82 ($CH_3OCH_2CH_2(OCH_2CH_2)_4O\mathit{C}H_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
59.01 ($\mathit{C}H_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
54.82 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2\mathit{C}H_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
53.29 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2\mathit{C}H_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$),
34.00 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2\mathit{C}H_2CH_2SH$),
29.43, 29.24, 29.10, 29.02, 28.50
($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2\mathit{C}H_2(\mathit{C}H_2)_4\mathit{C}H_2CH_2CH_2CH_2SH$),
28.33 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2\mathit{C}H_2CH_2CH_2SH$),
24.61 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2CH_2CH_2(CH_2)_4CH_2CH_2CH_2\mathit{C}H_2SH$),
21.83 ($CH_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2SO_2CH_2\mathit{C}H_2CH_2(CH_2)_4CH_2CH_2CH_2CH_2SH$).
HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{24}H_{50}NaO_8S_2$, 553.2845; found 553.2839.

Alternative synthesis of MeEG$_3$SH 4a via MeEG$_3$Cl 9a



MeEG$_3$Cl **9a**[1,8-11]

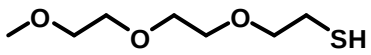


MeEG$_3$OH **1a** (20.08 g, 122 mmol) was added to thionylchloride (14.95 g, 126 mmol) over a period of 2 h while maintaining a temperature of 0 °C. The mixture was stirred at RT for 24 h and then transferred dropwise into a preheated flask (110 °C) within 2 h resulting a vivid gas

evolution (mainly SO_2). Heating was continued at 120 °C until the gas production was over and the product was purified by distillation to yield 11.6 g (64 mmol, 52 %).

Yield: 11.6 g (64 mmol, 52 %), colourless liquid.
^{1}H-NMR (300 MHz, $CDCl_3$), δ [ppm]: 3.82-3.72 (m, 2H, $CH_3OCH_2CH_2OCH_2CH_2OCH_2C\mathit{H}_2Cl$), 3.72-3.60 (m, 8H, $CH_3OCH_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OC\mathit{H}_2CH_2Cl$), 3.60-3.50 (m, 2H, $CH_3OC\mathit{H}_2CH_2OCH_2CH_2OCH_2CH_2Cl$), 3.38 (s, 3H, $C\mathit{H}_3OCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2Cl$).

MeEG$_3$SH **4a**[12-15]



A solution of MeEG$_3$Cl **9a** (11.6 g, 64 mmol) and thiourea (5.9 g, 77.5 mmol) in dimethylformamide (100 mL) was heated to 90 °C for 3 days. The solvent was removed *in vacuo* and the residue was taken up in dry ethanol (120 mL). Then a solution of KOH (18.7 g, 333 mmol) in dry ethanol (80 mL) was added and the mixture was heated to 100 °C for 3 days. The mixture was acidified by the addition of degassed hydrochloric acid (25 %, 40 mL). The solvent was removed *in vacuo* and the residue portioned between dichloromethane and water. The organic phase was concentrated under reduced pressure to yield a residue of 7.3 g that was purified by distillation to yield MeEG$_3$SH **4a** (2.2 g, 12.2 mmol, 19 %).

Yield: 2.2 g (12.2 mmol, 19%), colourless liquid.
Analytical data are identical to the ones mentioned above.

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