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Nucleophile-mediated oxa-Michael addition reactions of divinyl sulfone - a thiol-free option for step-growth polymerisations

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ELECTRONIC SUPPLEMENTARY INFORMATION

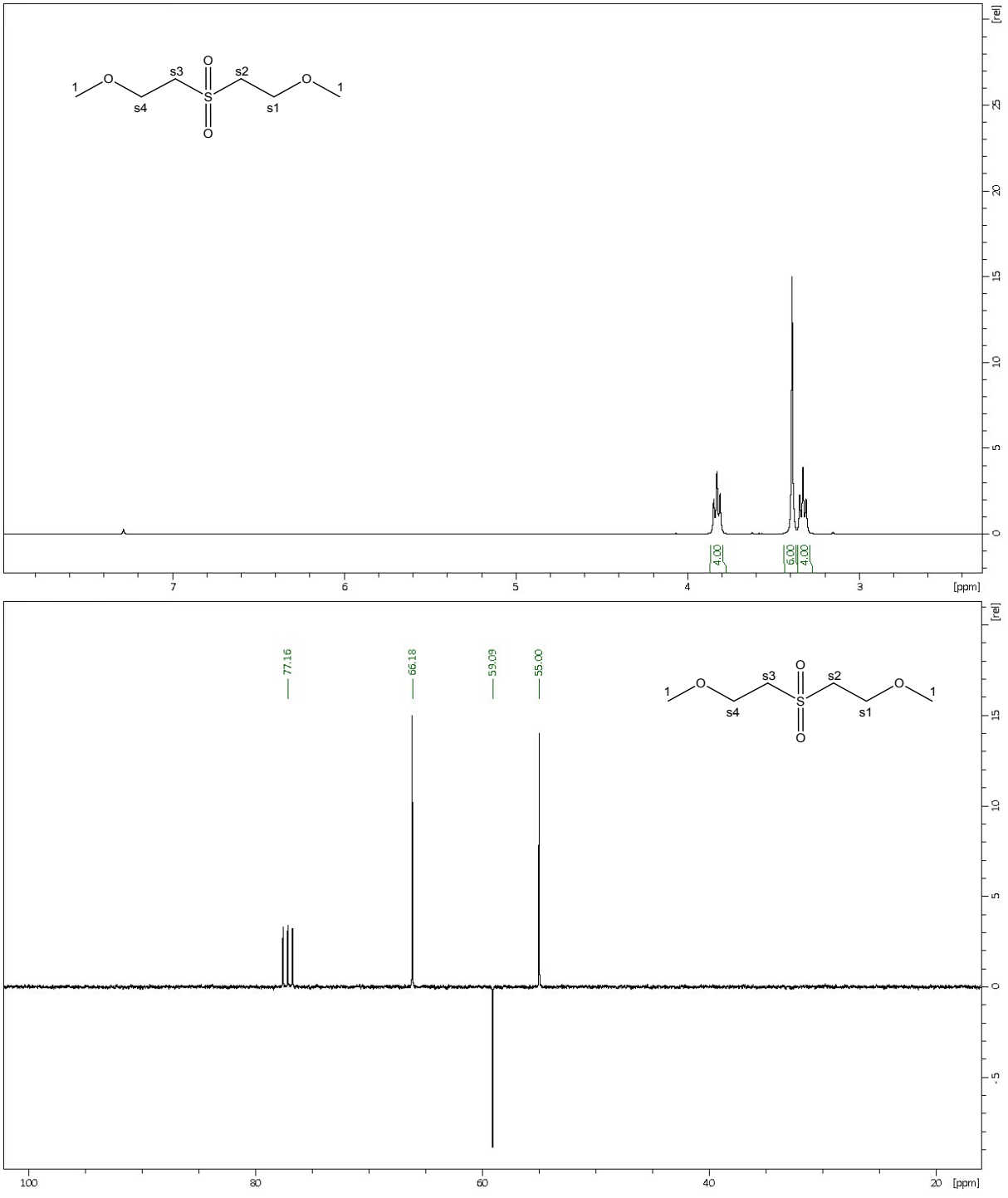
Materials & instruments:

All chemicals and substances for the syntheses in this contribution were purchased from commercial sources (Sigma Aldrich, Fluka, Alfa Aesar, ABCR) and used without further purification if not stated otherwise. Reactions were carried out either under atmospheric conditions or applying Schlenk technique under inert atmosphere of N_2 gas. Unless specified otherwise, solvents and auxiliary materials were used as purchased. Column chromatography was done using silica gel (60, 0.03-0.2 mm, product no. P090.5) purchased from Lactan, Austria or aluminum oxide (0.05-0.15 mm, type 5016 A basic, pH9-9.5, product no. 06290) purchased from Fluka. Cyclohexane (CH) and ethyl acetate (EA) were purchased in analytical reagent grade from Fisher Scientific, UK. Aluminum sheets with silica gel (60 F_{254}) for thin layer chromatography (TLC) were purchased from Merck KGaA, Germany.
^{1}H NMR measurements were performed on a Bruker Avanze 300 MHz spectrometer (^{1}H 300.36 MHz, ^{13}C 75.53 MHz) at 25 °C. Chemical shifts are given in ppm relative to a tetramethylsilan (TMS) standard. Deuterated solvents were obtained from Cambridge Isotope laboratories Inc. and spectra were referenced against the residual proton signals according to literature.[1]
^{31}P NMR measurements were performed on a Varian Unity INOVA 500 MHz (^{1}H 499.894 MHz, ^{31}P 202.32 MHz) FT NMR instrument with a ^{1}H-^{19}F / ^{15}N-^{31}P 5 mm Switchable Probe, using at least 256 scans with a delay time of 10 s to accumulate spectra. TopSpin 3.1 software was used for processing and interpretation of NMR spectra.
GPC measurements in chloroform were performed on an LC-20 AD system from Shimadzu equipped with two MZ-Gel SDplus Linear 5 µm separation columns from MZ Analysentechnik in line and a refractive index (RD-20A) as well as a UV/VIS detector (SPD-20A). Polystyrene Standards purchased from Polymer Standard Service were used for calibration and data was evaluated applying LabSolutions GPC software.
Dynamic mechanical analyses (DMA) were measured on a DMA Q 800 from TA Instruments Waters GmbH in the 3-point bending mode with a frequency of 1 Hz and amplitude of 25 µm in a temperature range from -4 to 31.2°C (3°C/min).
Differential scanning calorimetry (DSC) analyses were measured on a DSC 8500 instrument from Perkin Elmer in a temperature range from -20 to 100°C with a heating rate of 20°C/min for the first run and with 40°C/min in the second run (T_g values were retrieved from the second heating run).

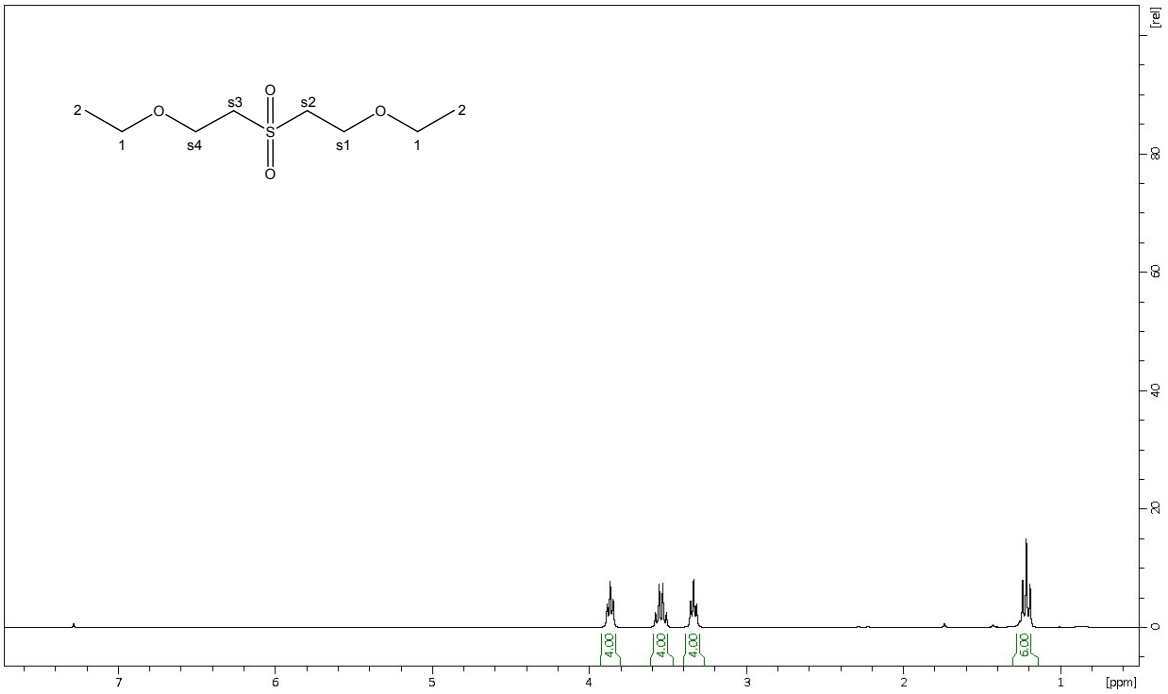
[1] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffman, K. W. Zilm, *Pure Appl. Chem.* **2008**, *80*, 59–84.

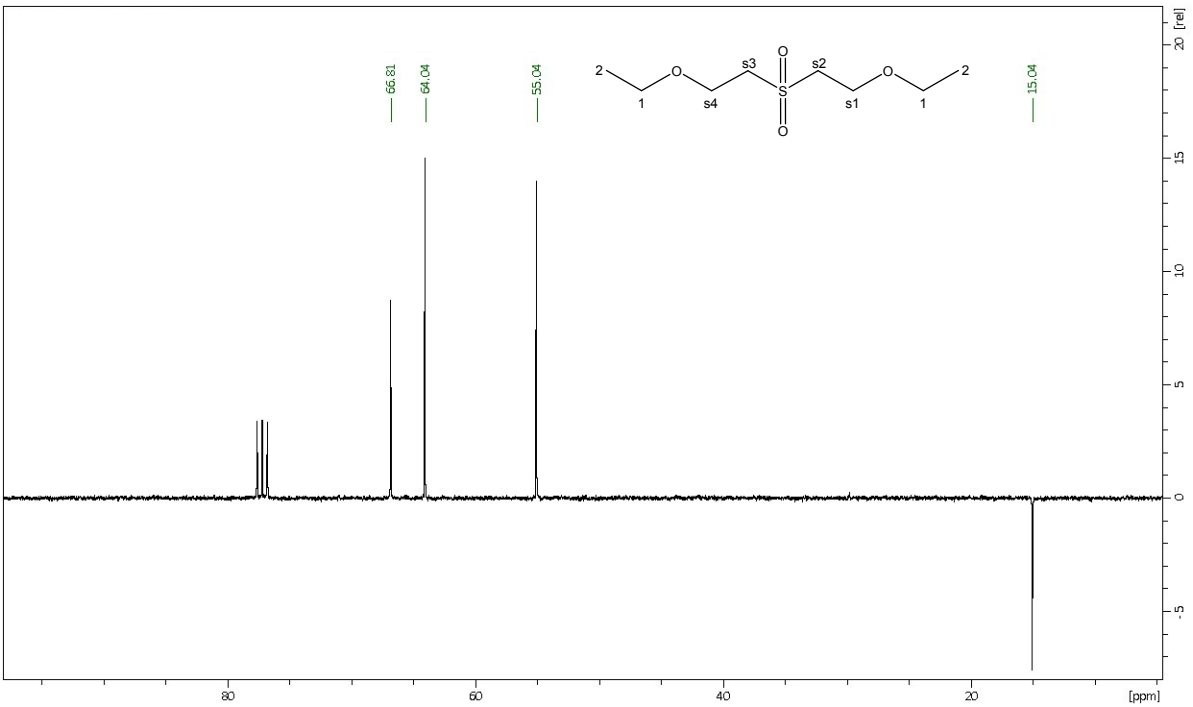
1 R=Me (1,1-sulfonylbis[2-methoxy-ethane]); $C_6H_{14}O_4S$ [182.24]
PPh_3 (13.1 mg, 0.0498 mmol, 0.1 eq) was dissolved in MeOH (505.0 µL, 12.45 mmol, 25 eq) and DVS (50 µL, 0.498 mmol, 1 eq) was added. The mixture was stirred at 23°C until complete conversion was monitored via ^{1}H NMR (2h). Excess methanol was removed under N_2 stream and the product was isolated via column chromatography (silica gel, CH/EA 20:1 (v:v)) by sampling the spot with R_f = 0.07 (CH/EA 3:1 (v:v)). Yield: 76.8 mg (0.464 mmol, 84.6 %) colorless oil.

Elemental Analysis: calculated: C, 39.55; H, 7.74; found: C, 39.37; H, 7.79. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 3.83 (t, 4H, $^3J_{HH}$ = 5.51, C$H_2^{s1,s4}$), 3.89 (s, 6H, CH_3^1), 3.33 (t, 4H, $^3J_{HH}$ = 5.51, C$H_2^{s2,s3}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 66.18 (2C, $C^{s1,s4}$), 59.09 (2C, C^1), 55.00 (2C, $C^{s2,s3}$).

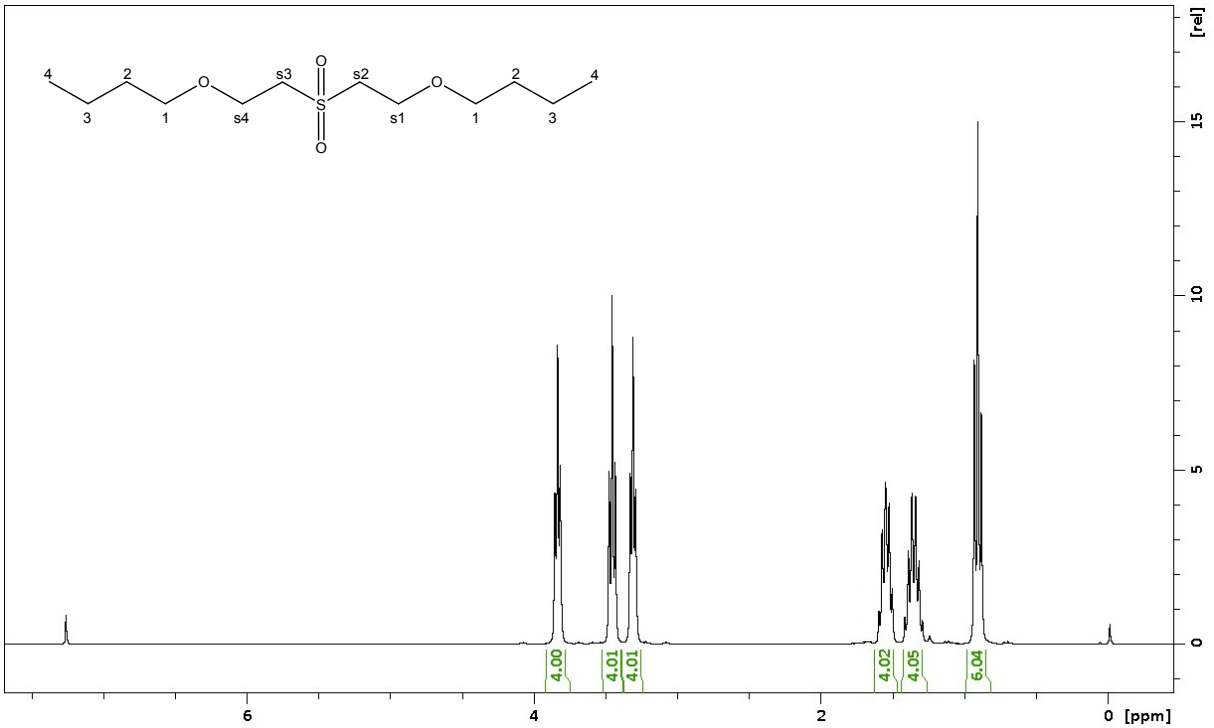


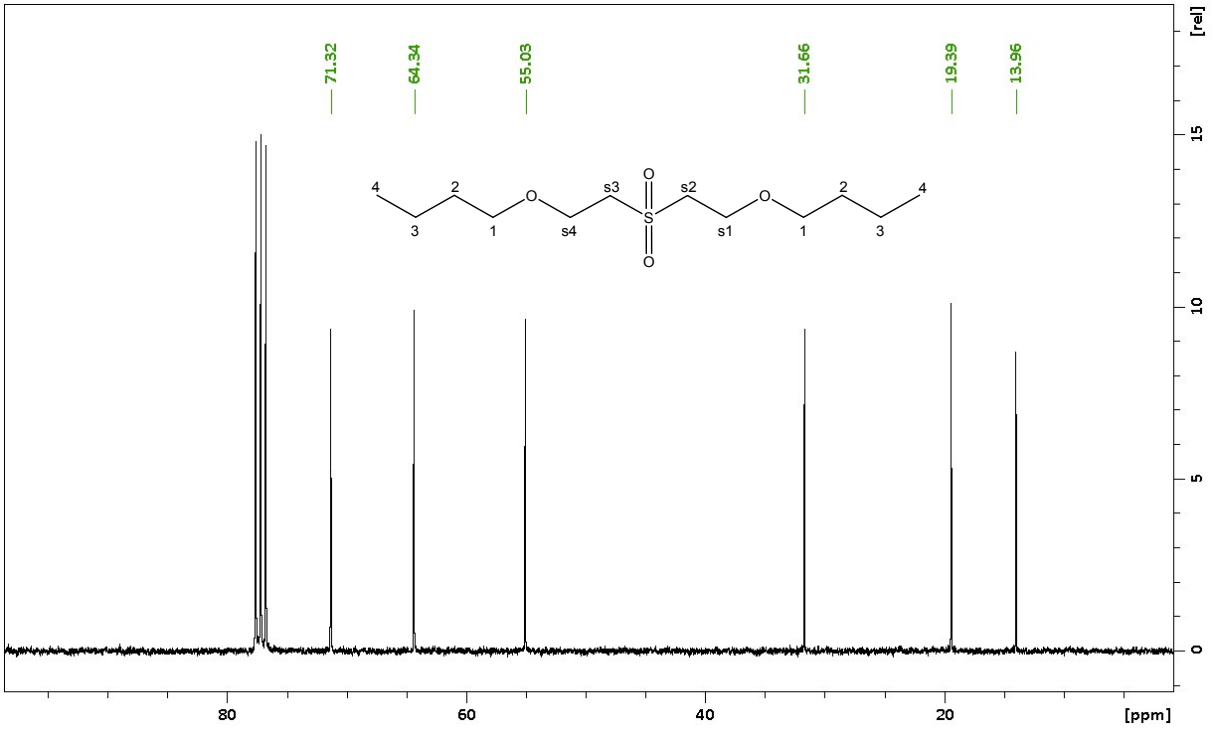
2 R= Et (1,1-sulfonylbis[2-ethoxy-ethane]) $C_8H_{18}O_4S$ [210.29]
Synthesized in the same manner as the methanol diadduct: PPh_3 (13.1 mg, 0.0498 mmol, 0.1 eq), EtOH (726.2 µL, 12.45 mmol, 25 eq) and DVS (50 µL, 0.498 mmol, 1 eq) were stirred at 23°C. Column chromatography (CH/EA 20:1 (v:v)) yielded 86.7 mg (0.412 mmol, 82.8 %) colorless oil by sampling the spot with R_f = 0.12 (CH/EA 3:1 (v:v)).
Elemental Analysis: calculated: C, 45.69; H, 8.63; found: C, 45.81; H, 8.83. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 3.87 (t, 4H, $^3J_{HH}$ = 5.71, C$H_2^{s1,s4}$), 3.54 (q, 4H, $^3J_{HH}$ = 6.80, CH_2^{1}), 3.33 (t, 4H, $^3J_{HH}$ = 5.71, C$H_2^{s2,s3}$), 1.21 (t, 6H, $^3J_{HH}$ = 7.02, CH_3^{2}). ^{13}C APT NMR (75 MHz, $CDCl_3$, 25°C): δ 66.81 (2C, C^1), 64.04 (2C, C^{s1,s4}), 55.04 (2C, C^{s2,s3}), 15.04 (2C, C^2).



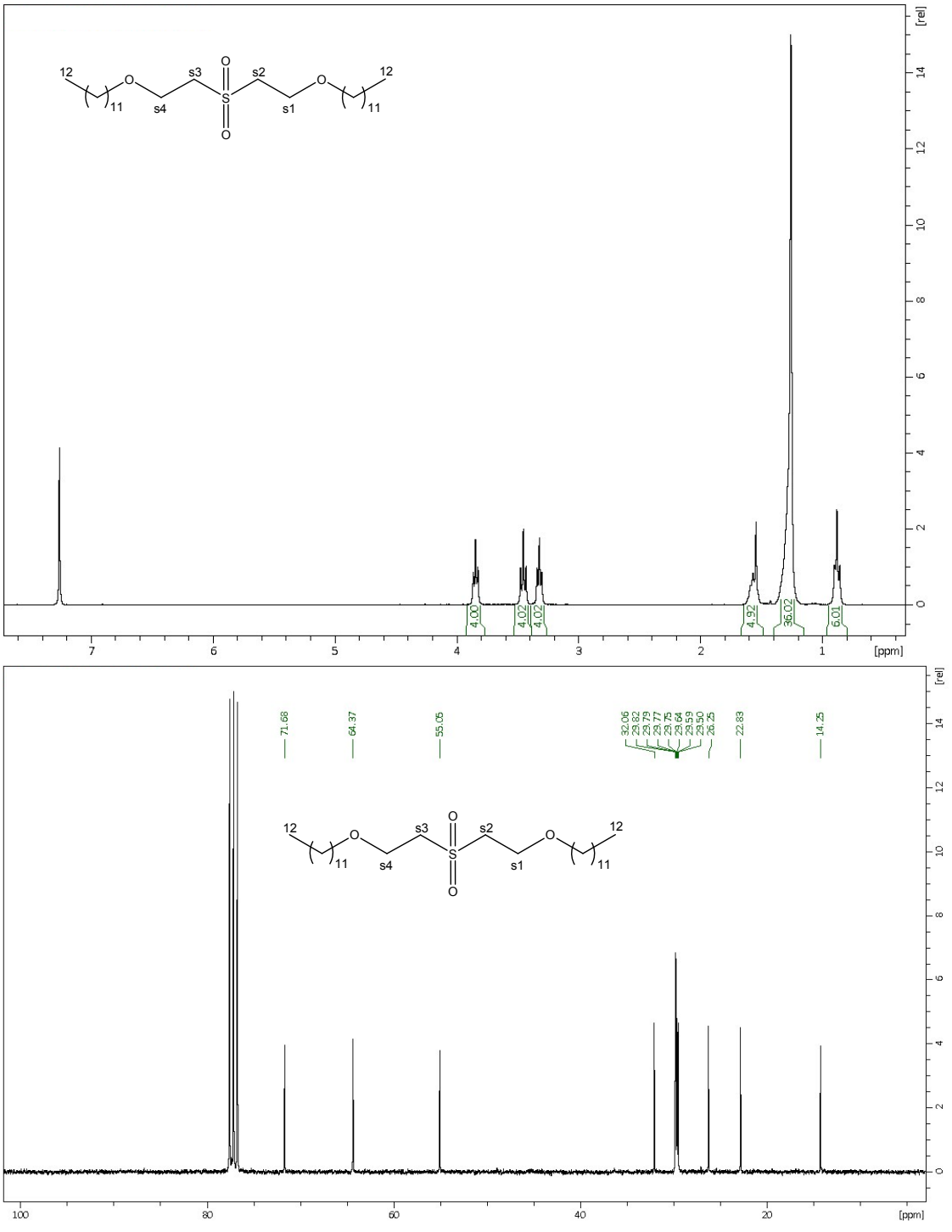


3 R=*n*-Bu (1,1-sulfonylbis[2-butoxy-ethane]) $C_{12}H_{26}O_4S$ [266.40]
Synthesized in the same manner as the methanol diadduct: PPh_3 (13.1 mg, 0.498 mmol, 0.1 eq), BuOH (1139.5 µL, 12.45 mmol, 25 eq) and DVS (50 µL, 0.498 mmol, 1 eq) were stirred 24 h at 23°C. Column chromatography (CH/EA 20:1 (v:v)) yielded 110.3 mg (0.414 mmol, 83.1 %) colorless oil by sampling the spot with R_f = 0.46 (CH/EA 3:1 (v:v)).
Elemental Analysis: calculated: C, 54.10; H, 9.84; found: C, 53.94; H, 9.99. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 3.83 (t, 4H, $^3J_{HH}$ = 5.67, C$H_2^{s1,s4}$), 3.45 (t, 4H, $^3J_{HH}$ = 6.57, CH_2^{1}), 3.31 (t, 4H, $^3J_{HH}$ = 5.71, C$H_2^{s2,s3}$), 1.55 (quintet, 4H, $^3J_{HH}$ = 7.05, CH_2^{2}), 1.35 (sextet, 4H, $^3J_{HH}$ = 7.39, CH_2^{3}), 0.91 (t, 6H, $^3J_{HH}$ = 7.26, CH_3^{4}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 71.3 (2C, C^1), 64.3 (2C, C^{s1,s4}), 55.0 (2C, C^{s2,s3}), 31.7 (2C, C^2), 19.4 (2C, C^3), 14.0 (2C, C^4).

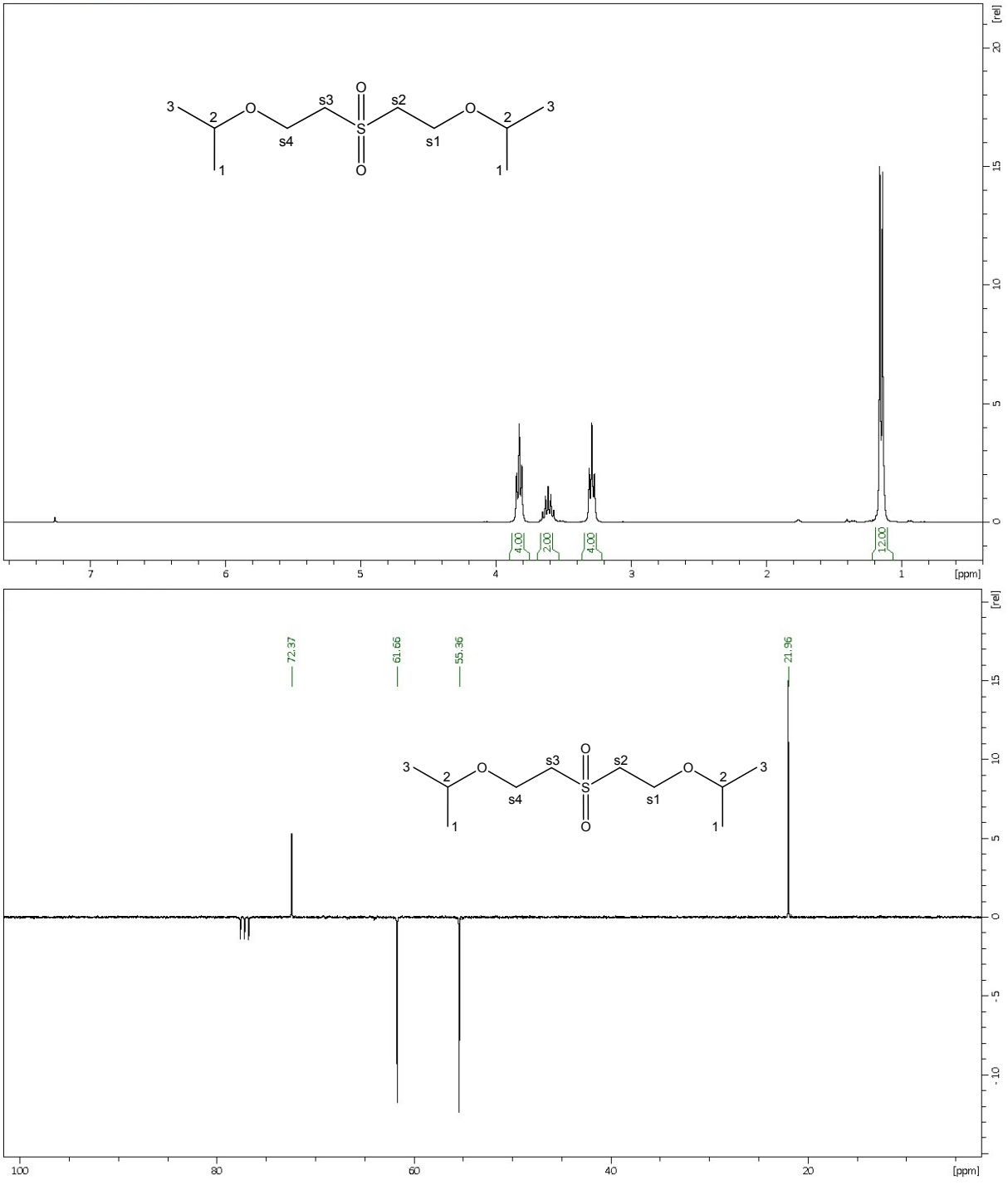




4 R=*n*-Dodecyl 1-(2-((2-(dodecyloxy)ethyl)sulfonyl)ethoxy)dodecane); ($C_{12}H_{58}O_4S$ [490.82]
PPh_3 (522.6 mg, 1.99 mmol, 0.1 eq) and dodecyl alcohol (11.138 g, 59.8 mmol, 3.0 eq) were dissolved in dry DCM (40 mL) and DVS (2.0 mL, 19.92 mmol, 1 eq) was added. The mixture was stirred 24 h at 23°C, whereas 65% di- and 35% monoadduct were formed. The solution was concentrated under reduced pressure and subjected to column chromatography (silica gel, CH/EA 20:1 (v:v), TLC: R_f = 0.75 (CH/EA 1:1 (v:v)). Yield: 4.762 g (9.70 mmol, 48.7 %) white crystals.
Elemental Analysis: calculated: C, 68.52; H, 11.91; found: C, 68.44; H, 12.17. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ3.84 (t, 4H, $^3J_{HH}$ = 5.62, C$H_2^{s1,s4}$), 3.45 (t, 4H, $^3J_{HH}$ = 6.48, CH_2^{1}), 3.32 (t, 4H, $^3J_{HH}$ = 5.62, C$H_2^{s2,s3}$), 1.65-1.50 (m, 4H, CH_2^{2}), 1.26 (bs, 36H, CH_2^{3-11}), 0.88 (t, 6H, $^3J_{HH}$ = 6.70 Hz, CH_3^{12}).
^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ71.68 (2C, C^{1}), 64.37 (2C, C^{s1,s4}), 55.05 (2C, C^{s2,s3}), 32.06, 29.82, 29.79, 29.77, 29.75, 29.64, 29.59, 29.50, 26.25, 22.83 (20C, C$^{2-11}$), 14.25 (2C, C^{12}).

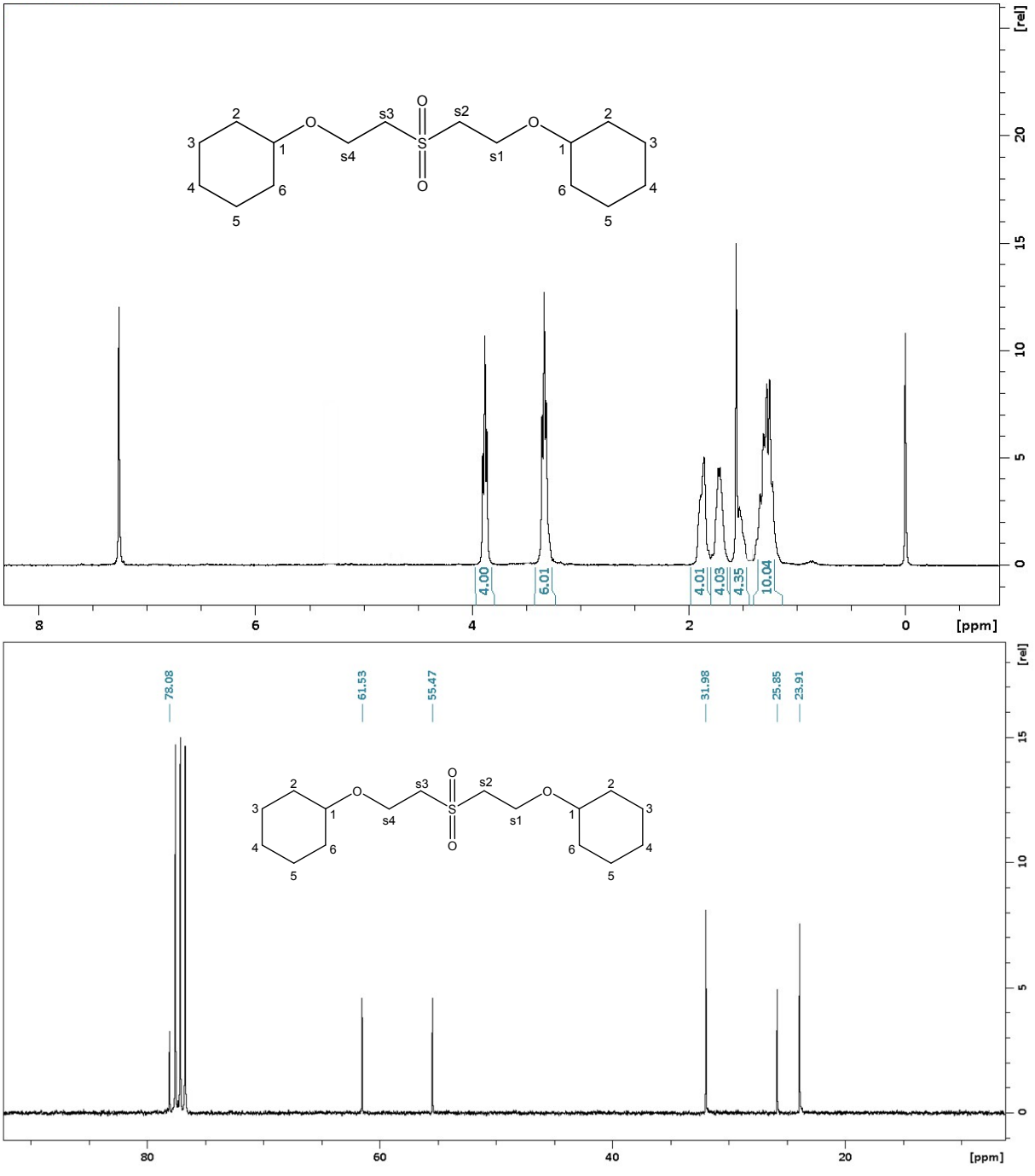


5 R=*i*-Pr (2,2'-{sulfonylbis(2,1-ethanediyloxy)]bispropane) $C_{10}H_{22}O_4S$ [238.34]
Was synthesized in the same manner as the methanol diadduct: PPh_3 (13.1 mg, 0.0498 mmol, 0.1 eq), *i*-PrOH (1.0 mL, 12.98 mmol, 26.1 eq) and DVS (50 µL, 0.498 mmol, 1 eq) were stirred at 23°C. Column chromatography (TLC: R_f = 0.58 (CH/EA 1:1 (v:v)) yielded 89.3 mg (0.375 mmol, 75.2 %) colorless oil.
Elemental Analysis: calculated: C, 50.39; H, 9.30; found: C, 50.21; H, 9.29. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 3.83 (t, 4H, $^3J_{HH}$ = 5.76, C$H_2^{s1,s4}$), 3.61 (sep, 2H, $^3J_{HH}$ = 6.15, CH^2), 3.29 (t, 4H, $^3J_{HH}$ = 5.76, C$H_2^{s2,s3}$), 1.15 (d, 12H, $^3J_{HH}$ = 6.04, C$H_3^{1,3}$). ^{13}C APT NMR (75 MHz, $CDCl_3$, 25°C): δ 72.37 (2C, C^2), 61.66 (2C, C^{s1,s4}), 55.36 (2C, C^{s2,s3}), 21.96 (4C, C^{1,3}).



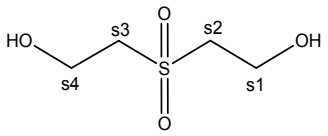
6 R=*c*-Hex (((sulfonylbis(ethane-2,1-diyl))bis(oxy))dicyclohexane) $C_{16}H_{30}O_4S$ [318.47]
DVS (588.5 mg, 4.981 mmol, 1.0 eq) was added to a solution of cyclohexanol (1.0976 g, 10.96 mmol, 2.2 eq) and PPh_3 (130.7 mg, 0.498 mmol, 0.1 eq) in DCM (500 µL) and stirred at 23°C. After complete conversion of DVS was detected via ^{1}H NMR (> 96 % diadduct after 168 h), the mixture was purified by flash chromatography (silica gel, C/EA 20:1 (v:v)). Sampling the spot with R_f = 0.45 (CH/EA 3:1 (v/v)) yielded 769.3 mg (2.416 mmol, 48.5 %) yellowish oil.

Elemental Analysis: calculated: C, 60.34; H, 9.50; found: C, 60.16; H, 9.72. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 3.88 (t, 4H, $^3J_{HH}$ = 5.72, C$H_2^{s1,s4}$), 3.33 (t, 4H, $^3J_{HH}$ = 5.63, C$H_2^{s2,s3}$), 3.36-3.25 (m, 2H, CH^1), 1.95-1.80 (m, 4H, C$H_2^{2,6}$), 1.77-1.64 (m, 4H, C$H_2^{3,5}$), 1.58-1.45 (m, 2H, CH_2^4), 1.39-1.14 (m, 10H, C$H_2^{2,3,4,5,6}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 78.08 (2C, C^1), 61.53 (2C, C^{s1,s4}), 55.47 (2C, C^{s2,s3}), 31.98 (4C, C^{2,6}), 25.85 (2C, C^4), 23.91 (4C, C^{3,5}).



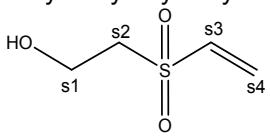
7 R=*t*-Bu (2-(2-((2-(tert-butoxy)ethyl)sulfonyl)ethoxy)-2-methylpropane); $C_{12}H_{26}O_4S$ [266.40]
The reaction mixture was prepared according to the methanol diadduct. A solution of PPh_3 (261.3 mg, 0.996 mmol, 0.1 eq), *t*-BuOH (1.624 g, 21.9 mmol, 2.2 eq) and DVS (1.0 mL, 9.96 mmol, 1 eq) in DCM (0.5 mL) was stirred 5 days at 23°C. No conversion was detected via ^{1}H NMR.

8 R=water (bis(2-hydroxyethyl)sulfone); $C_4H_{10}O_4S$ [154.18]
A Schlenk tube was equipped with DVS (118 µL, 0.996 mmol, 1 eq), H_2O *deion.* (54 µL, 2.99 mmol, eq), DCM and PPh_3 (26.12 mg, 0.0996 mmol, 0.1 eq) and stirred at 23°C. Mono- and diadduct of H_2O and 1,4-oxathiane-4,4-dioxide were found in the reaction mixture already after 2 h. The different reaction products of DVS with H_2O were not isolated separately, but the detected peaks were in good accordance with known data.[2]



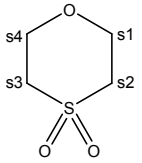
^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 3.99-3.87 (m, 4H, C$H_2^{s1,s4}$), 3.38 (m, 4H, C$H_2^{s2,s3}$).

2-Hydroxyethyl vinyl sulfone; $C_4H_8O_3S$ [136.17]



^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 6.77 (dd, 1H, $^3J_{HH(Z)}$ = 9.9, $^3J_{HH(E)}$ = 16.9, CH^{s3}), 6.44 (d, 1H, $^3J_{HH(E)}$ = 16.8, C$H^{s4(Z)}$), 6.14 (d, 1H, $^3J_{HH(E)}$ = 9.8, C$H^{s4(E)}$), 3.99-3.87 (m, 4H, C$H_2^{s1,s4}$), 3.27 (m, 4H, C$H_2^{s2,s3}$).

1,4-Oxathiane-4,4-dioxide[3]; $C_4H_8O_3S$ [136.17]



^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 4.14 (t, 4H, $^3J_{HH}$ = 5.0, C$H_2^{s1,s4}$), 3.12 (m, 4H, $^3J_{HH}$ = 5.1, C$H_2^{s2,s3}$).

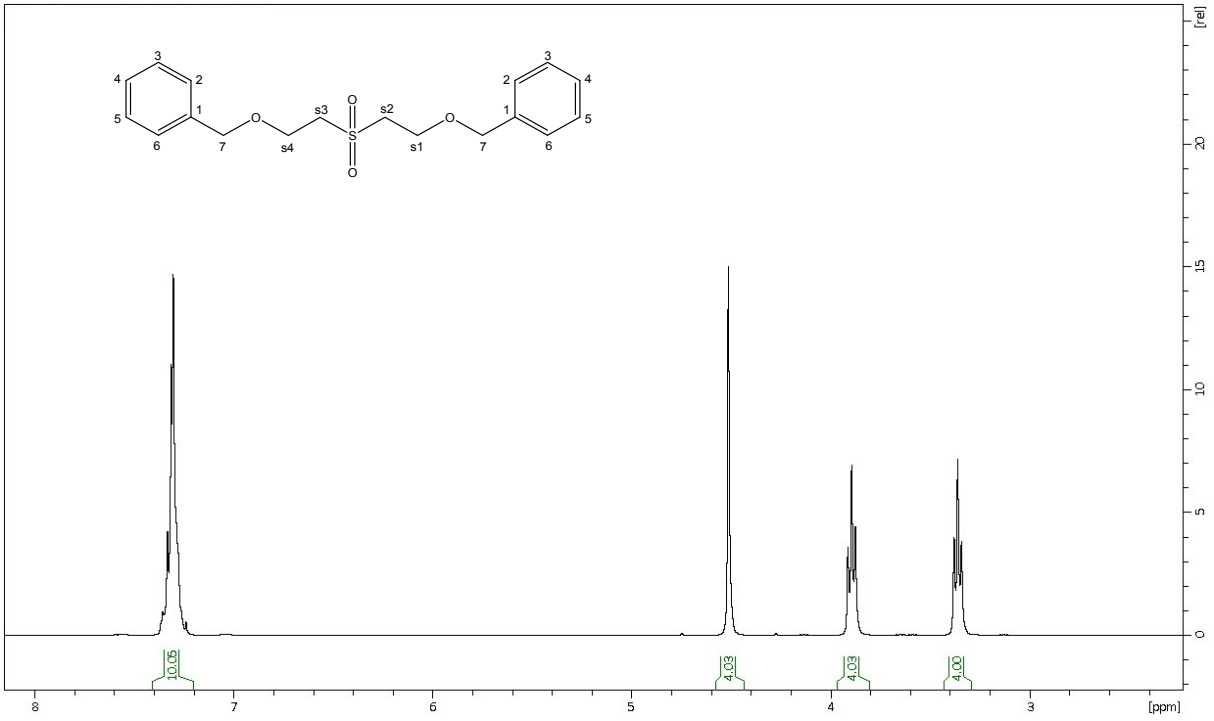
[2] N. A. Chernysheva, N. K. Gusarova, A. A. Tatarinova, M. L. Al'pert, B. A. Trofimov, *Zhurnal Organicheskoi Khimii* **1996**, *32(6)*, 832-835

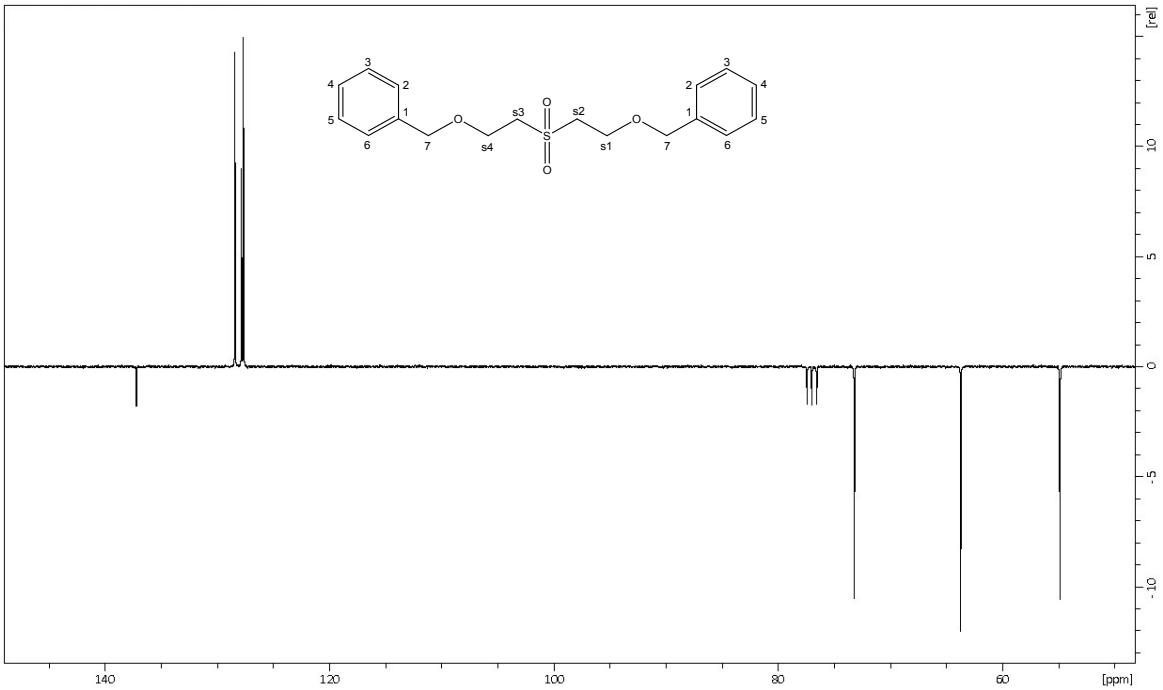
[3] M. V. Roux, M. Temprado, P. Jiménez, R. Notario, R. Guzmán-Mejía, E. Juaristi, *J. Org. Chem.* **2007**, *72(4)*, 1143-1147

9 R=benzyl (bis(2-benzyloxyethanyl)sulfone); $C_{18}H_{22}O_4S$ [334.43]

To a solution of benzyl alcohol (6.22 mL, 59.8 mmol, 3.0 eq) and DVS (2.00 mL, 19.9 mmol, 1 eq) in dry DCM (40 mL), PPh_3 (522.6 mg, 1.99 mmol, 10 mol%) was added and the mixture was stirred at 23°C for 24 h (full consumption of DVS detected via ^{1}H NMR). The solution was concentrated under reduced pressure and the remaining yellowish oil was purified via column chromatography (CH/EE, 10:1, (v:v)). Sampling the spot with R_f = 0.65 (CH/EE, 1:1, (v:v)) yielded 5.437 g (16.26 mmol, 81.6 %) colorless oil.

Elemental Analysis: calculated: C, 64.65; H, 6.63; found: C, 64.58; H, 6.60. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 7.38-7.25 (m, 10H, C*H*$^{2\text{-}6}$), 4.51 (s, 4H, CH_2^7), 3.89 (t, 4H, $^3J_{HH}$ = 5.6, C$H_2^{s1,s4}$), 3.36 (t, 4H, $^3J_{HH}$ = 5.6, C$H_2^{s2,s3}$). ^{13}C APT NMR (75 MHz, $CDCl_3$, 25°C): δ 137.2 (2C, C^1), 128.4 (4C, C^{3,5}), 127.8 (2C, C^4), 127.7 (4C, C^{2,6}), 73.2 (2C, C^7), 63.7 (2C, C^{s1,s4}), 54.9 (2C, C^{s2,s3}) ppm.

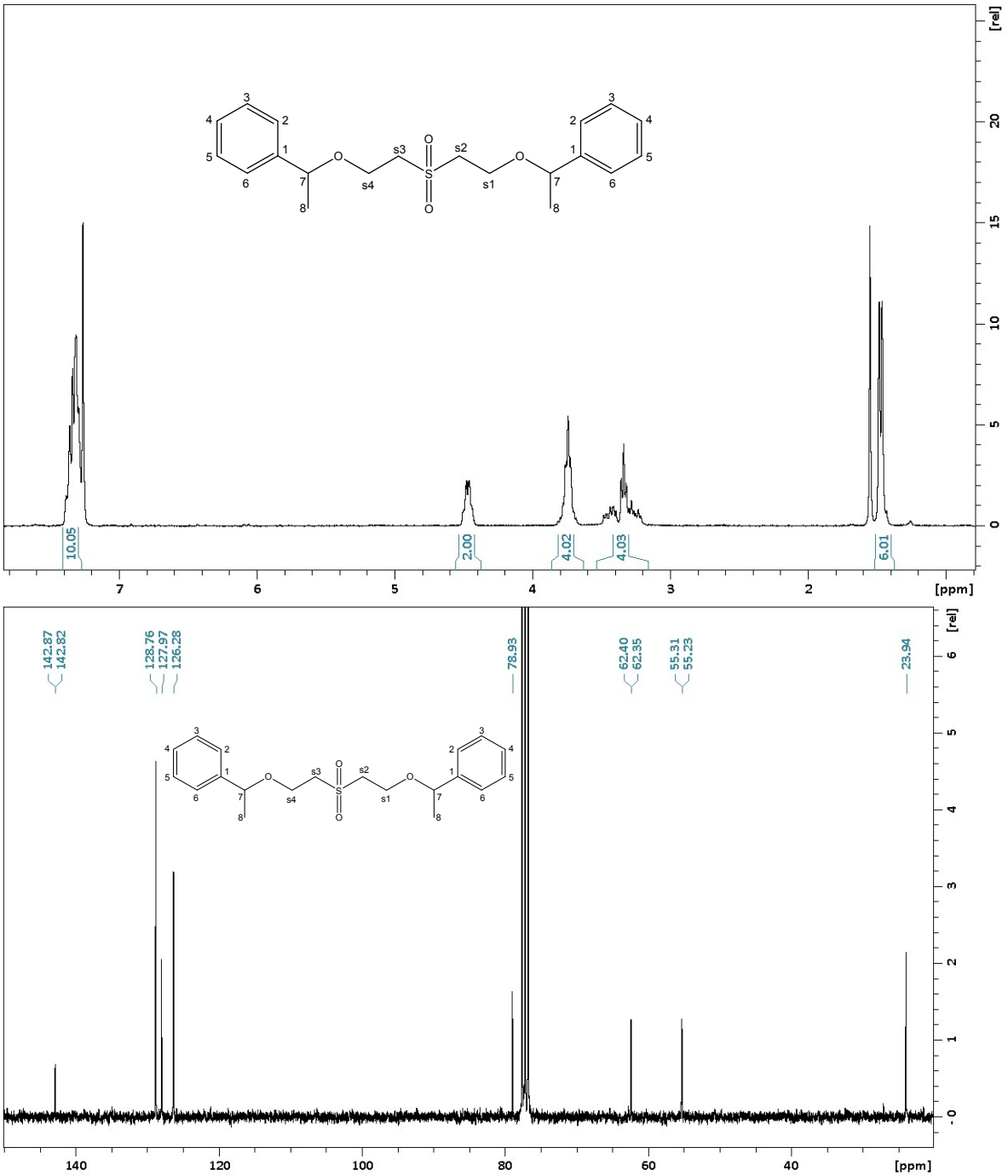




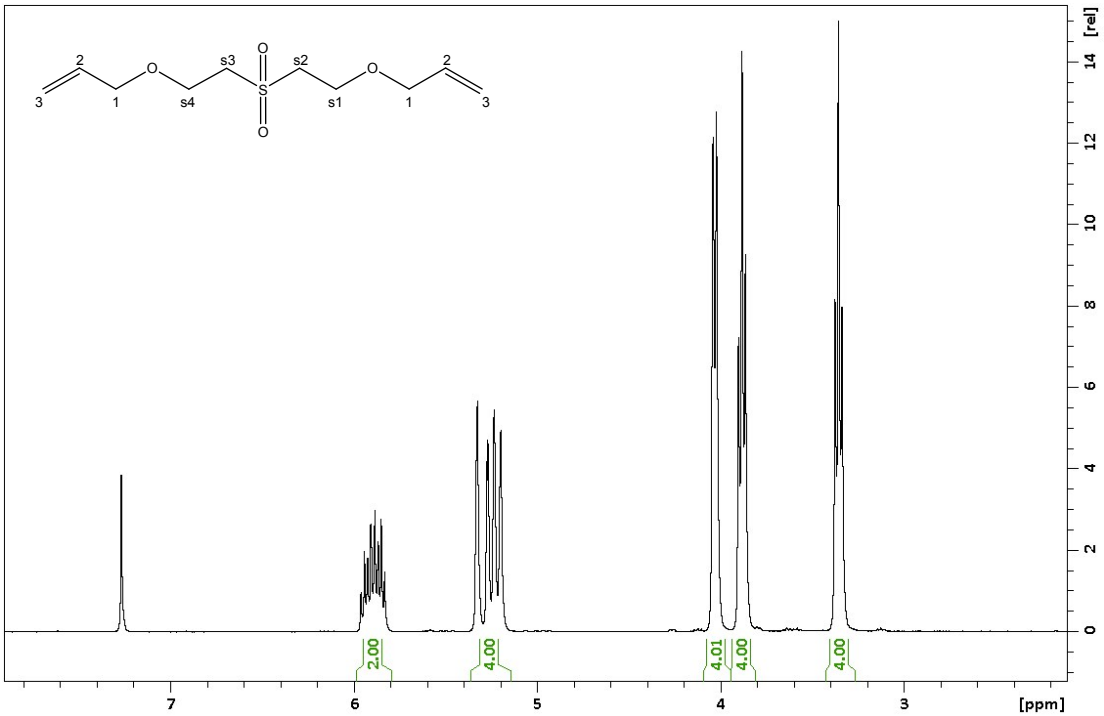
10 R= α-methyl benzyl ((((sulfonylbis(ethane-2,1-diyl))bis(oxy))bis(ethane-1,1-diyl))dibenzene); $C_{20}H_{26}O_4S$ [362.48]

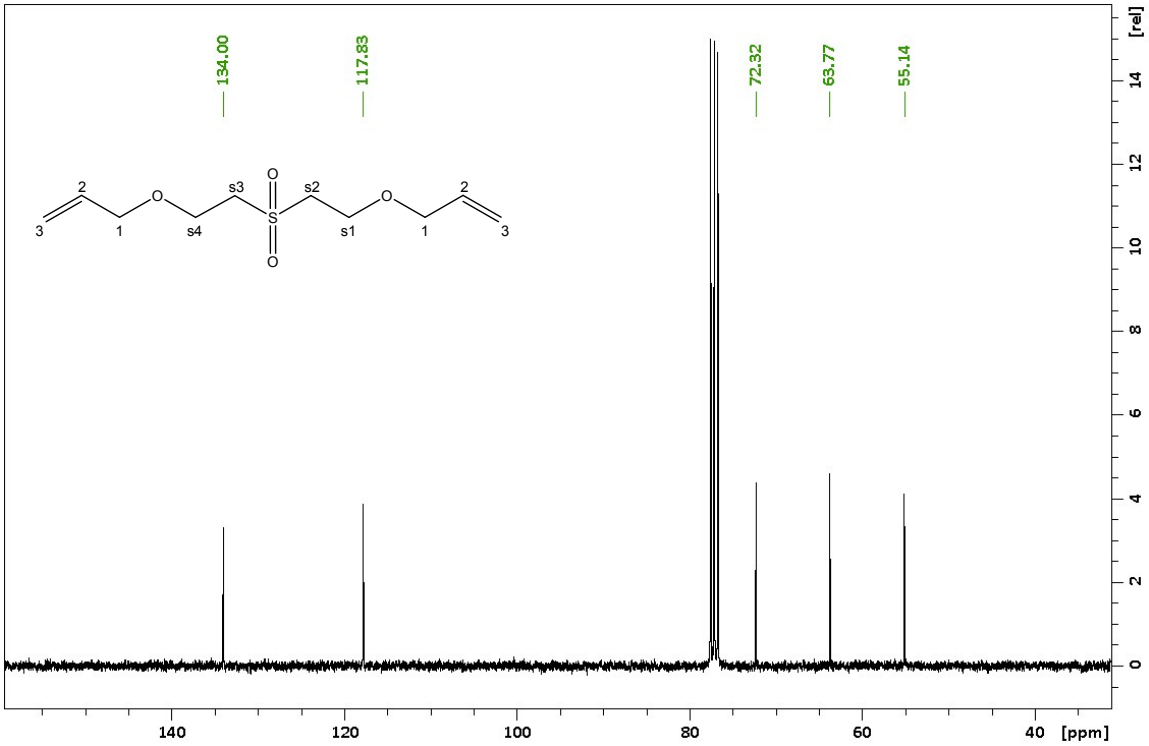
To a solution of α-methyl benzyl alcohol (1.3387 g, 10.96 mmol, 2.2 eq) and PPh_3 (130.7 mg, 0.498 mmol, 0.1 eq) in DCM (500 µL) DVS (588.5 mg, 4.981 mmol, 1.0 eq) was added and stirred at 23°C. After complete conversion of DVS (^{1}H NMR: 99% diadduct after 48 h), the mixture was purified by flash chromatography (silica gel, C/EA 20:1 (v:v). Sampling the spot with R_f = 0.42 yielded 1.123 g (3.097 mmol, 62.2 %) colorless oil (stereoisomers).

Elemental Analysis: calculated: C, 66.27; H, 7.23; found: C, 65.95; H, 7.42. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 7.41-7.26 (m, 10H, C*H*$^{2-6}$), 4.43-4.51 (m, 2H, C*H*^{7}), 3.83-3.65 (m, 4H, C$H_2^{s4,s1}$), 3.51-3.17 (m, 4H, C$H_2^{s2,s3}$), 1.47 (dd, 6H, $^3J_{HH}$ = 6.48, $^3J_{HH}$ = 1.03, CH_3^8). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 142.87, 142.82 (2C, C$^{1(R,S)}$), 128.76 (4C, C^{3,5}), 127.97 (2C, C^4), 126.28 (4C, C^{2,6}), 78.93 (2C, C^7), 62.40, 62.35 (4C, C$^{s1,s4(R,S)}$), 55.31, 55.23 (4C, C$^{s2,s3(R,S)}$), 23.94 (2C, C^8).



11 R=allyl (3-(2-((2-(allyloxy)ethyl)sulfonyl)ethoxy)prop-1-ene); $C_{10}H_{18}O_4S$ [234.31]
PPh_3 (261.3 mg, 0.996 mmol, 0.1 eq), allyl alcohol (1.736 g, 29.9 mmol, 3 eq) and DVS (1.0 mL, 9.96 mmol, 1 eq) were stirred 3 days at 23°C. Column chromatography (CH/EA 10:1 (v:v)) of the reaction mixture yielded 1.804 g (7.70 mmol, 77.3 %) yellowish oil by sampling the spot with R_f = 0.28 (C/EA 3:1 (v:v)).
Elemental Analysis: calculated: C, 51.26; H, 7.74; found: C, 51.31; H, 7.71. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 5.98-5.79 (m, 2H, C*H*^{2}), 5.29 (dd, 4H, $^3J_{HH}$ = 17.2, $^2J_{HH}$ = 1.5, C$H_2^{3(E)}$), 5.21 (dd, 4H, $^3J_{HH}$ = 10.4, $^2J_{HH}$ = 1.3, C$H_2^{3(Z)}$), 4.03 (dt, 4H, $^4J_{HH}$ = 1.3, $^3J_{HH}$ = 5.7, CH_2^1), 3.88 (t, 4H, $^3J_{HH}$ = 5.6, C$H_2^{s1,s4}$), 3.35 (t, 4H, $^3J_{HH}$ = 5.7, C$H_2^{s2,s3}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 134.0 (2C, C^2), 117.8 (2C, C^3), 72.3 (2C, C^1), 63.8 (2C, C^{s1,s4}), 55.1 (2C, C^{s2,s3}) ppm.

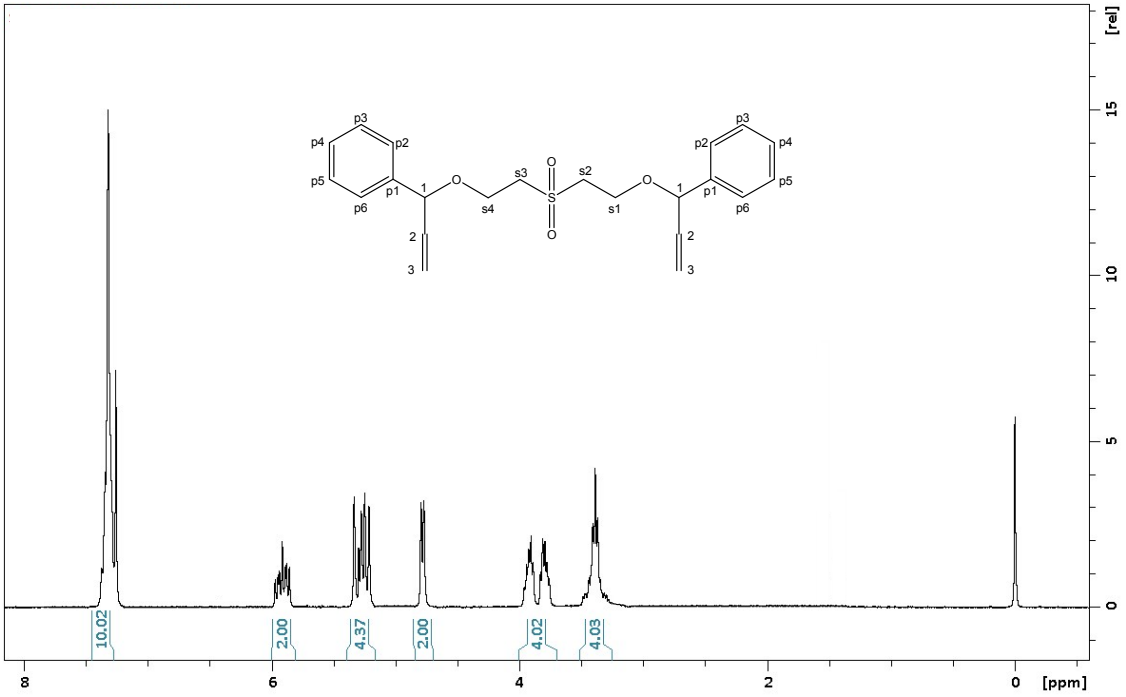


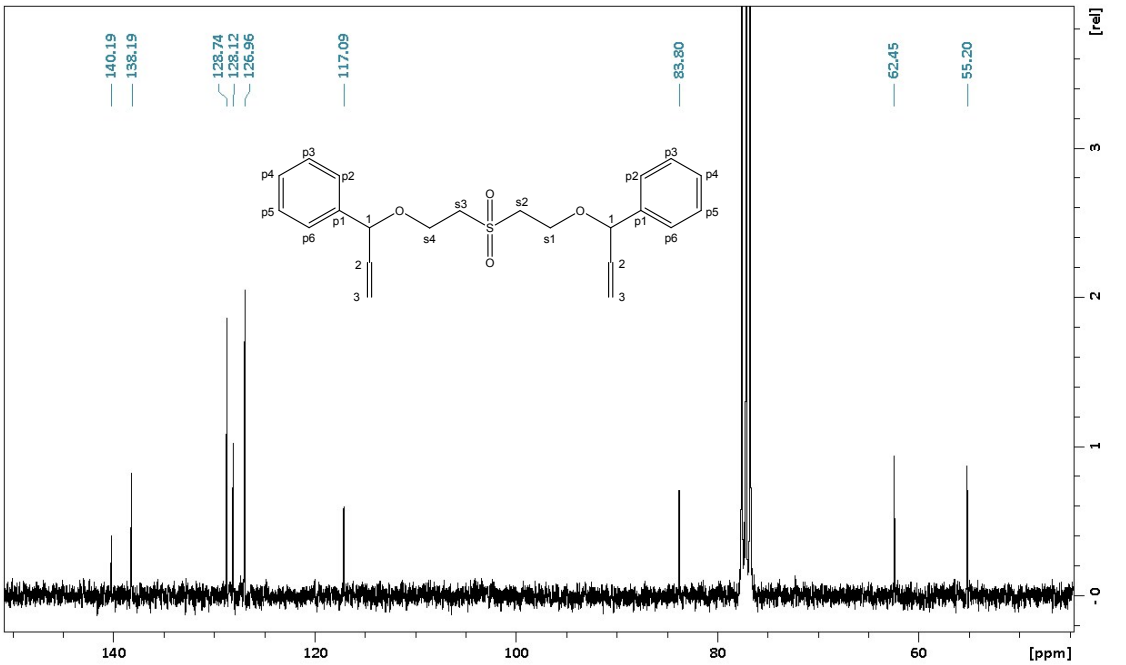


12 R=phenyl allyl ((((sulfonylbis(ethane-2,1-diyl))bis(oxy))bis(prop-2-ene-1,1-diyl))dibenzene) $C_{22}H_{26}O_4S$ [386.50]

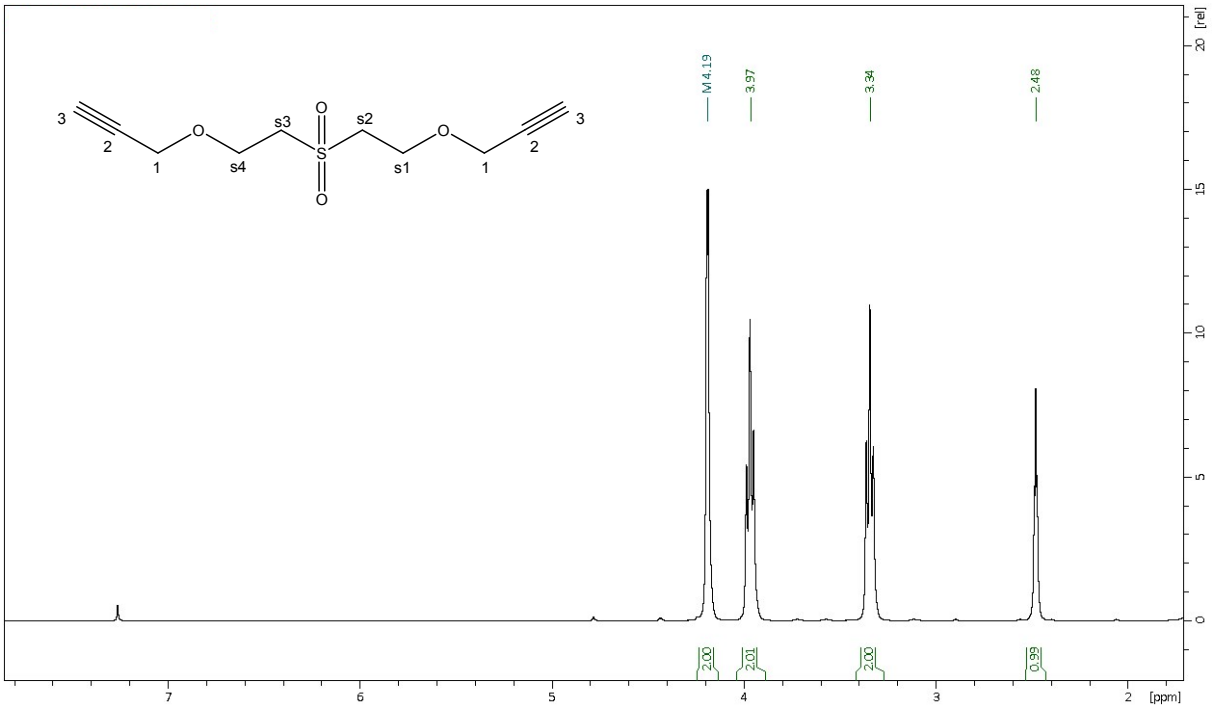
To a solution of phenyl allyl alcohol (294.1 mg, 2.192 mmol, 2.2 eq) and PPh_3 (26.13 mg, 0.0996 mmol, 0.1 eq) in DCM (200 µL) DVS (117.7 mg, 0.996 mmol, 1.0 eq) was added and stirred at 23°C. After 168 h, 55.6 % (214.1 mg, 0.554 mmol) diadduct were detected by ^{1}H NMR, which was isolated by flash chromatography (silica gel, C/EA 20:1 (v:v)). Sampling the spot with R_f = 0.44 yielded 172.7 mg (0.447 mmol, 44.9 %) colorless oil.

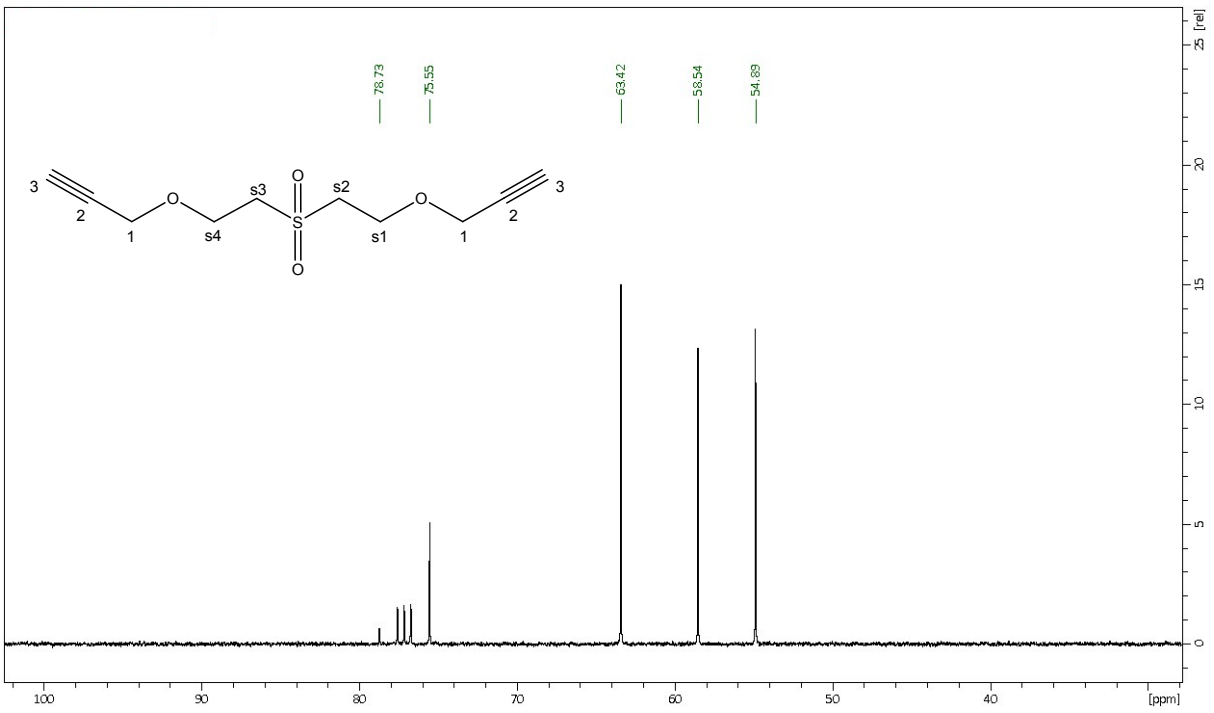
Elemental Analysis: calculated: C, 68.37; H, 6.78; found: C, 68.27; H, 6.61. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 7.43-7.26 (m, 10H, C*H*$^{p2\text{-}p6}$), 5.99-5.83 (m, 2H, C*H*^{2}), 5.36-5.18 (m, 4H, CH_2^3), 4.78 (d, 2H, $^3J_{HH}$ = 6.67, C*H*^{1}), 3.98-3.73 (m, 4H, C$H_2^{s1,s4}$), 3.50-3.27 (m, 4H, C$H_2^{s2,s3}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 140.19 (2C, C^{p1}), 138.19 (2C, C^2), 128.74, 126.96 (8C, C^{p2,p3,p5,p6}), 128.12 (2C, C^{p4}), 117.09 (2C, C^3), 83.80 (2C, C^1), 62.45 (2C, C^{s1,s4}), 55.20 (2C, C^{s2,s3}).





13 R=propargyl (3-(2-((2-(prop-2-yn-1-yloxy)ethyl)sulfonyl)ethoxy)prop-1-yne); $C_{10}H_{14}O_4S$ [230.28]
Propargyl alcohol (3.45 mL, 59.8 mmol, 3.0 eq) and DVS (2.00 mL, 19.9 mmol, 1 eq) were dissolved in dry DCM (40 mL) under inert conditions. PPh_3 (522.6 mg, 1.99 mmol, 0.1 eq) was added and the reaction solution was stirred at 23°C until complete conversion of DVS was detected via ^{1}H NMR. The solution was concentrated under reduced pressure and the remaining yellowish oil was purified via column chromatography (CH/EE, 10:1 and 3:1, (v:v)) by sampling the spot with R_f = 0.41 (CH/EE, 1:1, (v:v)). Yield: 4.095 g (17.8 mmol, 89.3 %) colorless oil.
Elemental Analysis: calculated: C, 52.16; H, 6.13; found: C, 52.11; H, 6.24. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 4.19 (d, 4H, $^2J_{HH}$ = 1.91, CH_2^1), 3.97 (t, 4H, $^3J_{HH}$ = 5.56, C$H^{s4,s1}$), 3.34 (t, 4H, $^3J_{HH}$ = 5.56, C$H^{s2,s3}$), 2.48 (t, 2H, $^4J_{HH}$ = 2.19, CH^3). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 78.7 (2C, C^2), 75.6 (2C, C^3), 63.4 (2C, $C^{s1,s4}$), 58.5 (2C, C^1), 54.9 (2C, $C^{s2,s3}$).

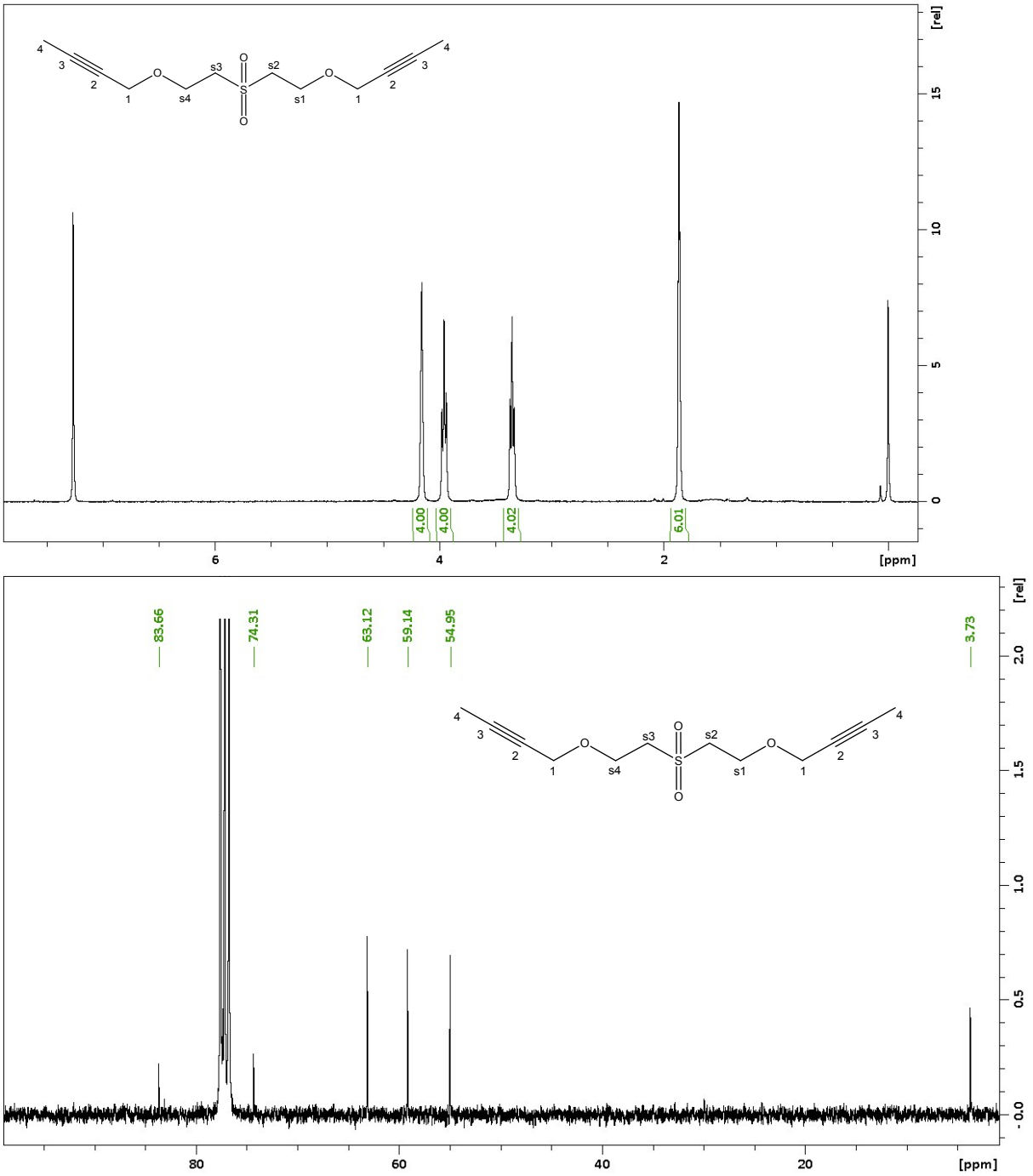




14 R=3-methyl propargyl (1-(2-((2-(but-2-yn-1-yloxy)ethyl)sulfonyl)ethoxy)but-2-yne); $C_{12}H_{18}O_4S$ [258.33]

To a solution of 2-butyn-1-ol (768.1 mg, 10.96 mmol, 2.2 eq) and PPh_3 (130.6 mg, 0.498 mmol, 0.1 eq) in dry DCM (1.5 mL), DVS (588.5 mg, 4.981 mmol, 1.0 eq) was added (exothermic!) and stirred 22 h (complete conversion of DVS detected by ^{1}H NMR) under inert atmosphere of N_2. Flash chromatography (CH/EA 20:1 (v:v), gradient to pure EA) of the reaction mixture yielded 689.3 mg (2.668 mmol, 53.8 %) white solid by sampling the spot with R_f = 0.23 (C/EA 3:1 (v:v)).

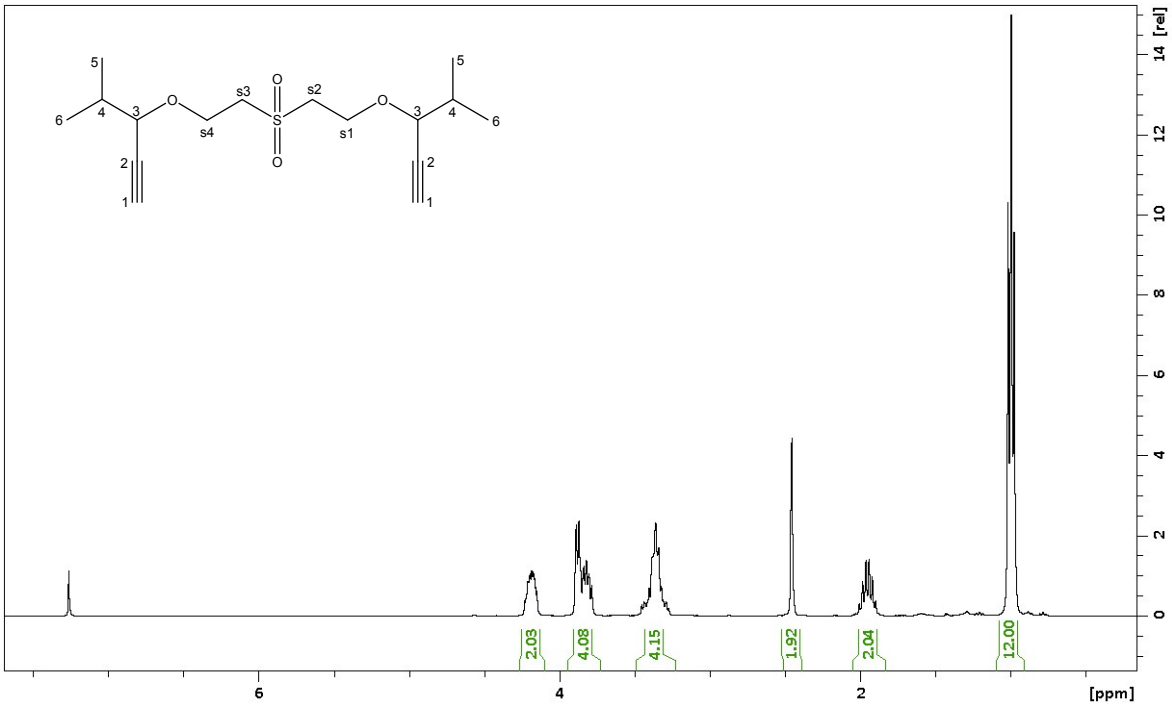
Elemental Analysis: calculated: C, 55.79; H, 7.02; found: C, 55.64; H, 6.88. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 4.15 (q, 4H, $^5J_{HH}$ = 2.18, CH_2^1), 3.95 (t, 4H, $^3J_{HH}$ = 5.80, C$H_2^{s1,s4}$), 3.35 (t, 4H, $^3J_{HH}$ = 5.58, C$H_2^{s2,s3}$), 1.86 (t, 6H, $^5J_{HH}$ = 2.13, CH_3^4). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 83.66 (2C, C^2), 74.31 (2C, C^3), 63.12 (2C, C^{s1,s4}), 59.14 (2C, C^1), 54.95 (2C, C^{s2,s3}), 3.73 (2C, C^4).

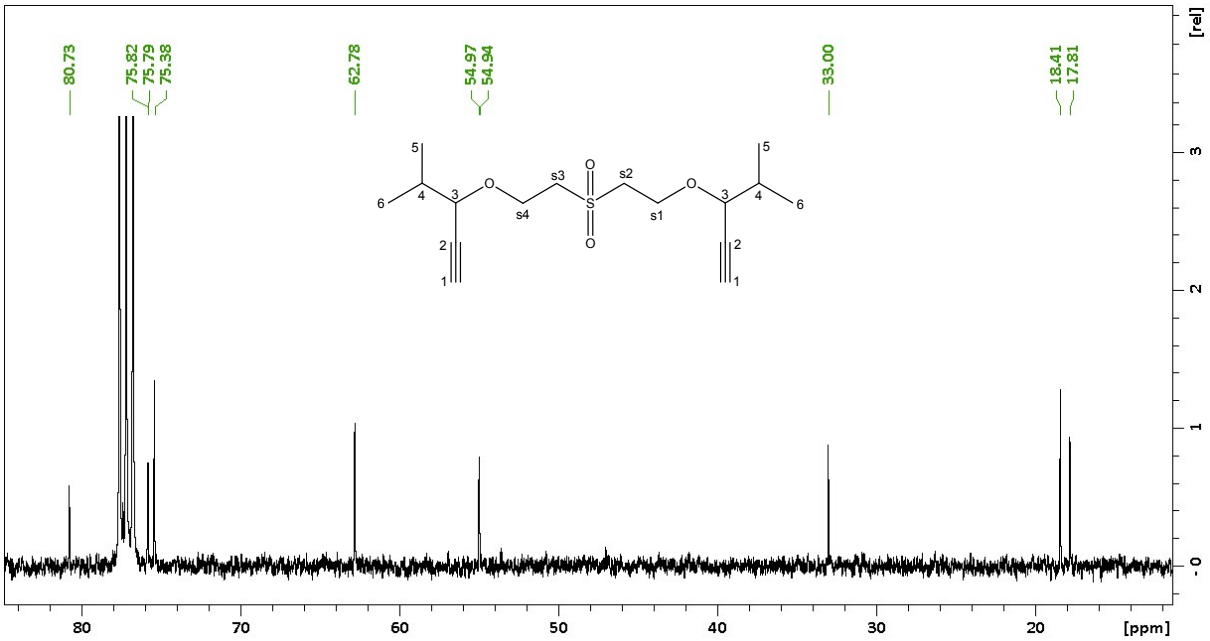


15 R=1-*i*-Pr propargyl (4-methyl-3-(2-((2-((4-methylpent-1-yn-3-yl)oxy)ethyl)sulfonyl)ethoxy)pent-1-yne); $C_{16}H_{26}O_4S$ [314.44]

DVS (1.177 g, 9.962 mmol, 1.0 eq) was added (exothermic!) to a solution of 4-methyl-1-pentyn-3-ol (2.1509 g, 21.92 mmol, 2.2 eq) and PPh_3 (261.28 mg, 0.996 mmol, 0.1 eq) in dry DCM (2 mL). The mixture was stirred 24 h (complete conversion of DVS detected by ^{1}H NMR) at 23°C. Flash chromatography (silica gel, CH/EA 20:1 (v:v)) yielded 1.331 g (4.233 mmol, 42.5 %) pure product by sampling the spot with R_f = 0.42 (CH/EA 3:1 (v:v)).

Elemental Analysis: calculated: C, 63.12; H, 8.83; found: C, 62.97; H, 8.69. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 4.26-4.11 (m, 2H, C*H*^{3}), 3.95-3.74 (m, 4H, C$H_2^{s1,s4}$), 3.46-3.24 (m, 4H, C$H_2^{s2,s3}$), 2.45 (d, 2H, $^4J_{HH}$ = 1.98 Hz, C*H*^{1}), 1.95 (oct, 2H, $^3J_{HH}$ = 6.38, C*H*^{4}), 0.99 (t, 12H, $^3J_{HH}$ = 6.08, C$H_3^{5,6}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 80.73 (2C, C^2), 75.82 and 75.79 (4C, C$^{3(R,S)}$), 75.38 (2C, C^1), 62.78 (2C, C^{s1,s4}), 54.97 and 54.94 (4C, C$^{s2,s3(R,S)}$), 33.00 (2C, C^4), 18.41 and 17.81 (4C, C^{5,6}).

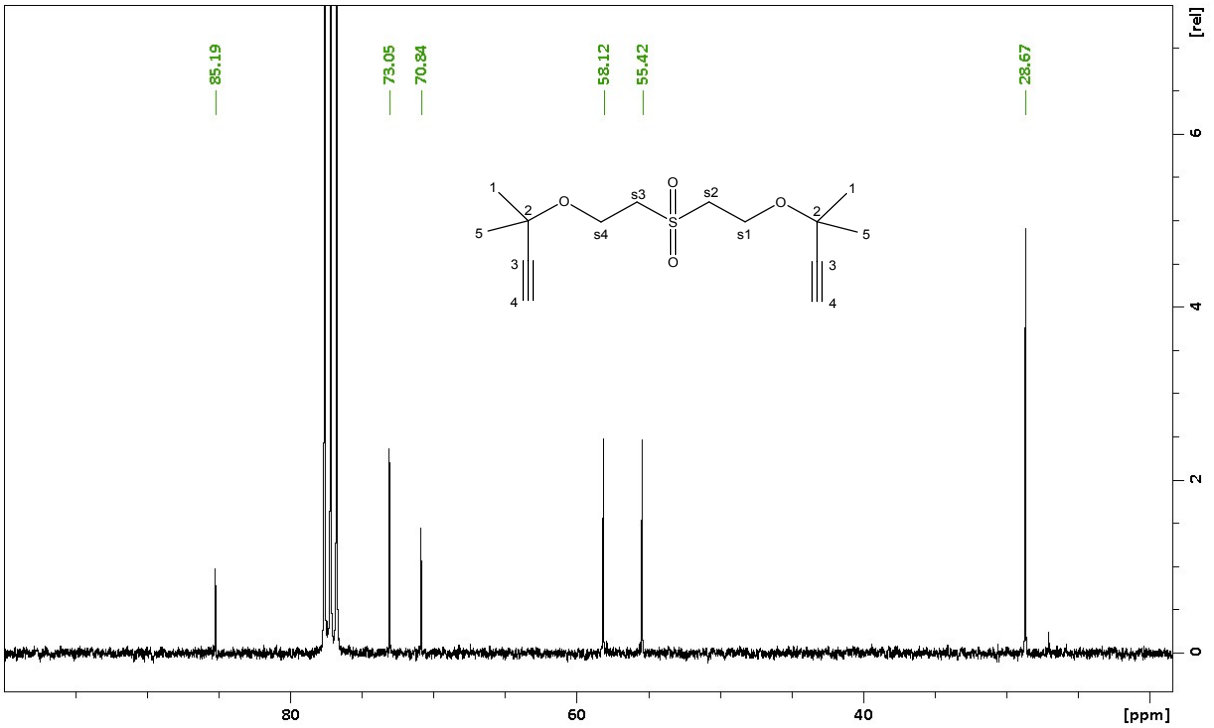




16 R=1,1-dimethyl propargyl (3-methyl-3-(2-((2-((2-methylbut-3-yn-2-yl)oxy)ethyl)sulfonyl) ethoxy)but-1-yne) $C_{14}H_{22}O_4S$ [286.39]

DVS (1.177 g, 9.96 mmol, 1.0 eq) was added (exothermic!) to a solution of 2-methyl-3-butyn-2-ol (2.124 mL, 21.92 mmol, 2.2 eq) and PPh_3 (261.3 mg; 0.996 mmol. 0.1 eq) in dry DCM (1 mL). The mixture was stirred 48 h at 23°C (>95% conversion of DVS detected via ^{1}H NMR). Column chromatography (silica gel, CH/EA 20:1 (v:v)) yielded 1.0986 g (3.836 mmol, 38.5 %) yellow liquid by sampling the spot with R_f = 0.79 (TLC, C/EA 1:1 (v:v)).

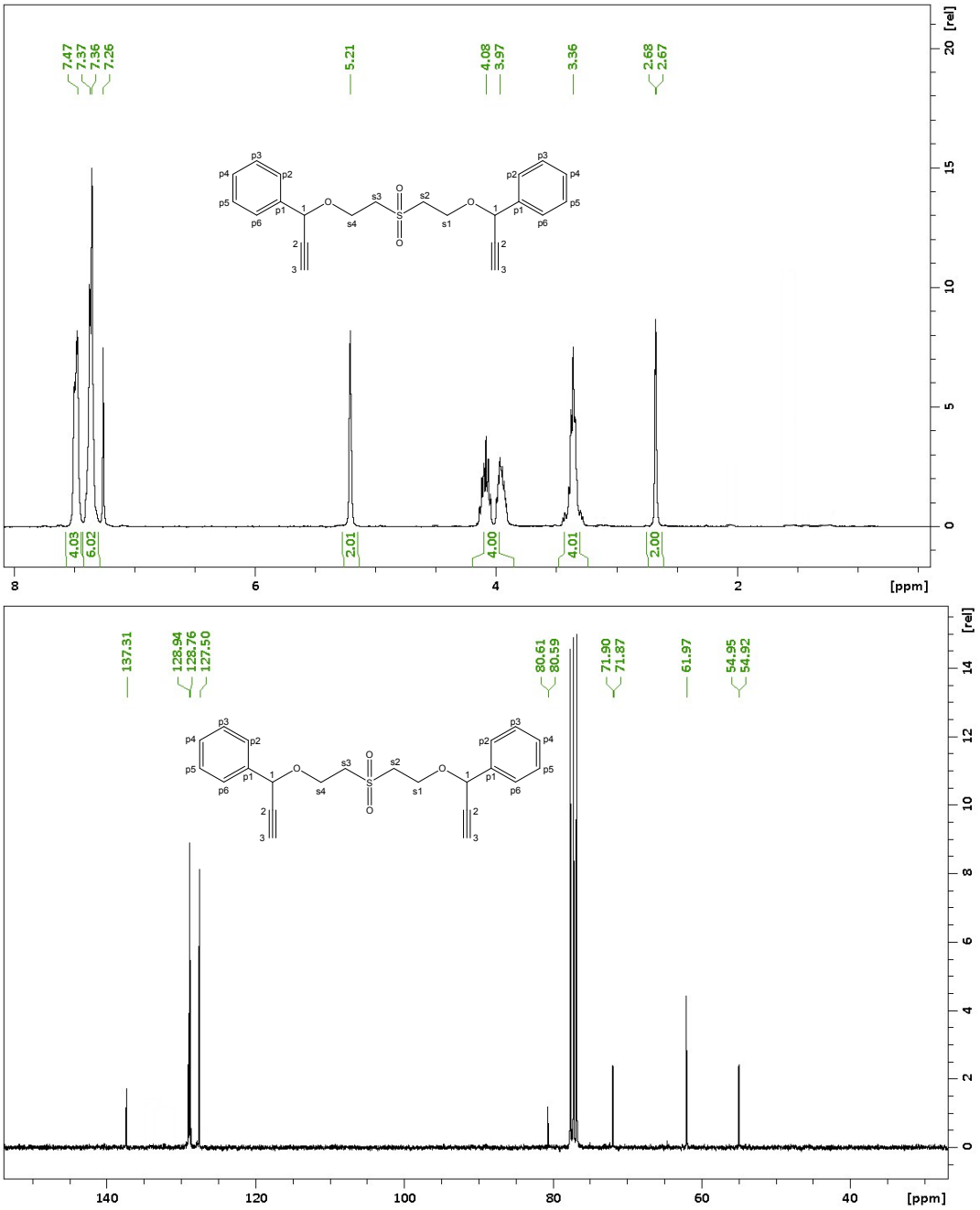
Elemental Analysis: calculated: C, 61.12; H, 8.33; found: C, 60.88; H, 8.21. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 4.00 (t, 4H, $^3J_{HH}$ = 5.84, C$H_2^{s1,s4}$), 3.33 (t, 4H, $^3J_{HH}$ = 5.84, C$H_2^{s2,s3}$), 2.47 (s, 2H, CH^4), 1.48 (2, 12H, C$H^{1,5}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 85.19 (2C, C^3), 73.05 (2C, C^4), 70.84 (2C, C^2), 58.12 (2C, $C^{s1,s4}$), 55.42 (2C, $C^{s2,s3}$), 28.67 (4C, $C^{1,5}$).



17 R=1-phenyl propargyl ((((sulfonylbis(ethane-2,1-diyl))bis(oxy))bis(prop-2-yne-1,1-diyl))dibenzene) $C_{22}H_{22}O_4S$ [382.47]

To a solution of 1-phenyl propargyl alcohol (1.817 mL, 14.94 mmol, 3 eq) and PPh_3 (130.6 mg, 0.498 mmol, 0.1 eq) in dry DCM (5 mL) DVS (588.5 mg, 4.981 mmol, 1.0 eq) was added and stirred at 23°C. After complete conversion of DVS (1 h), flash chromatography (silica gel, CH/EA 20:1) yielded 1.727 g (4.516 mmol, 90.7 %) yellowish oil by sampling the spot with R_f = 0.67 (CH/EA 1:1 (v:v)).

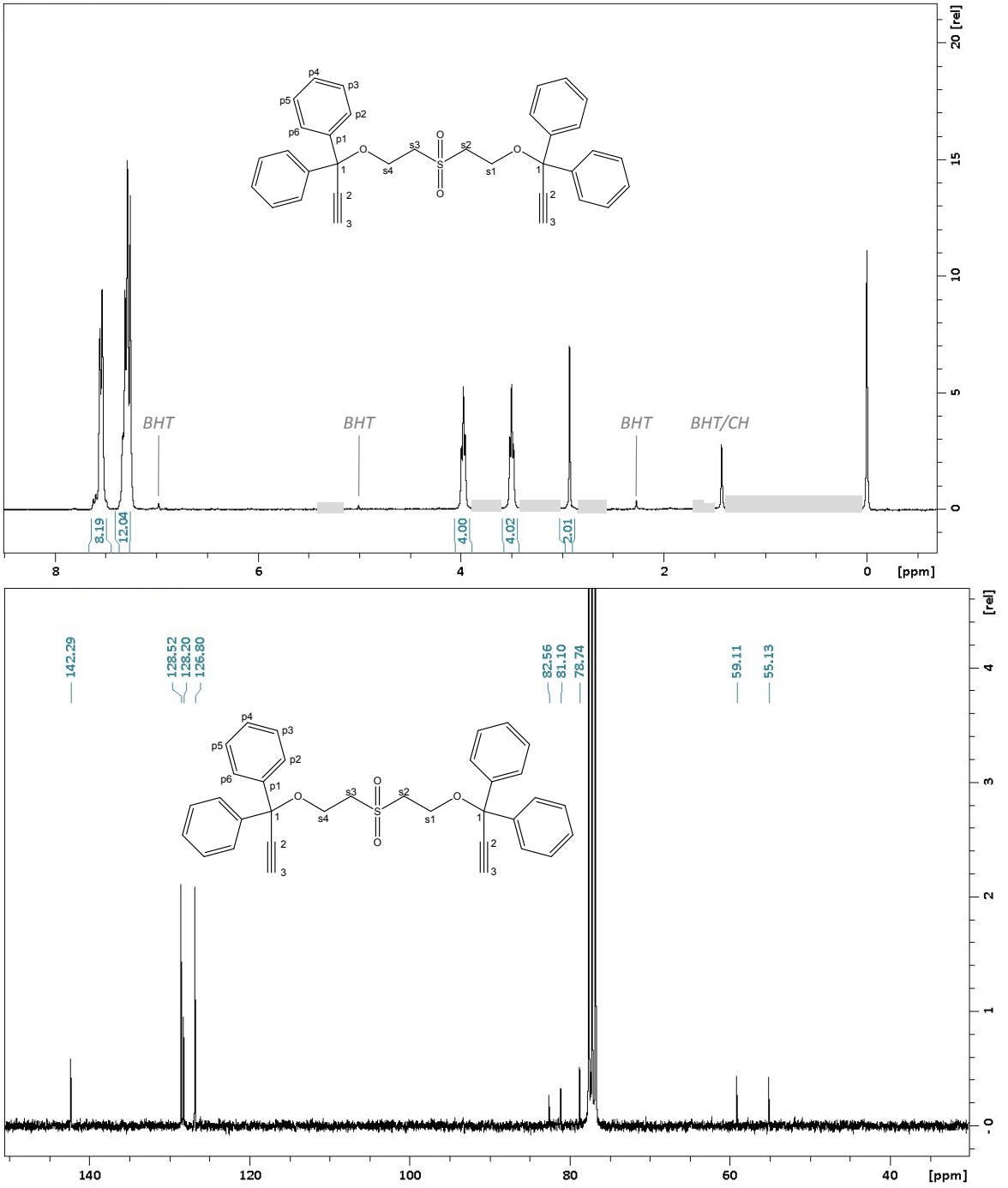
Elemental Analysis: calculated: C, 70.22; H, 6.38; found: C, 69.98; H, 6.48. ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 7.55-7.43 and 7.42-7.29 (m, 10H, C*H*$^{p2\text{-}p6}$), 5.21 (s, 2H, C*H*^{1}), 4.17-4.02 and 4.01-3.88 (m, 4H, C*H*$_2^{s1,s4}$), 3.47-3.25 (m, 4H, C*H*$_2^{s2,s3}$), 2.70-2.64 (m, 2H, C*H*^{3}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 137.31 (2C, C^{p1}), 128.94 (2C, C^{p4}), 128.76, 127.50 (8C, C$^{p2,6\text{ and }p5,3}$), 80.61 and 80.59 (4C, C$^{2(R,S)}$), 76.79 (2C, C^3), 71.90 and 71.87 (4C, C$^{1(R,S)}$), 61.97 (2C, C^{s1,s4}), 54.95 and 54.92 (4C, C$^{s2,s3(R,S)}$). NMR measurements after a few days storage under atmospheric conditions of the product indicated the decomposition of the compound.



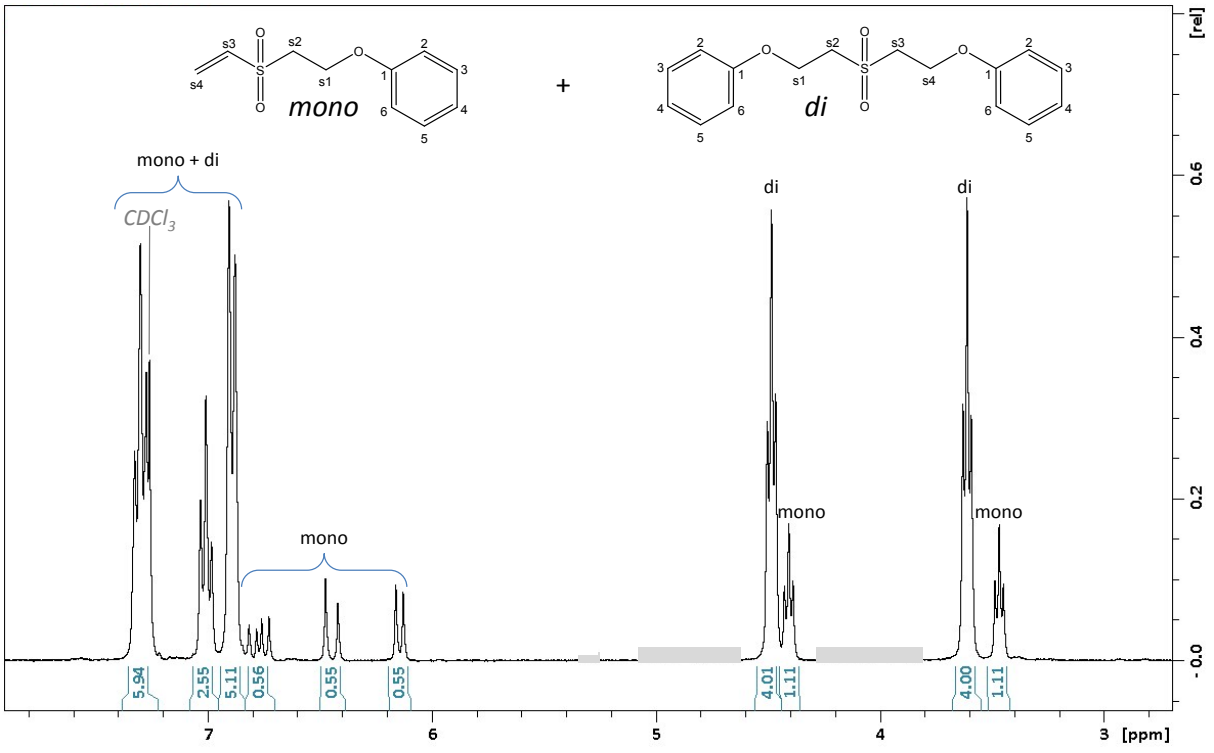
18 R=1,1-diphenyl propargyl ((((sulfonylbis(ethane-2,1-diyl))bis(oxy))bis(prop-2-yne-1,1,1-triyl))tetrabenzene) $C_{34}H_{30}O_4S$ [534.66]

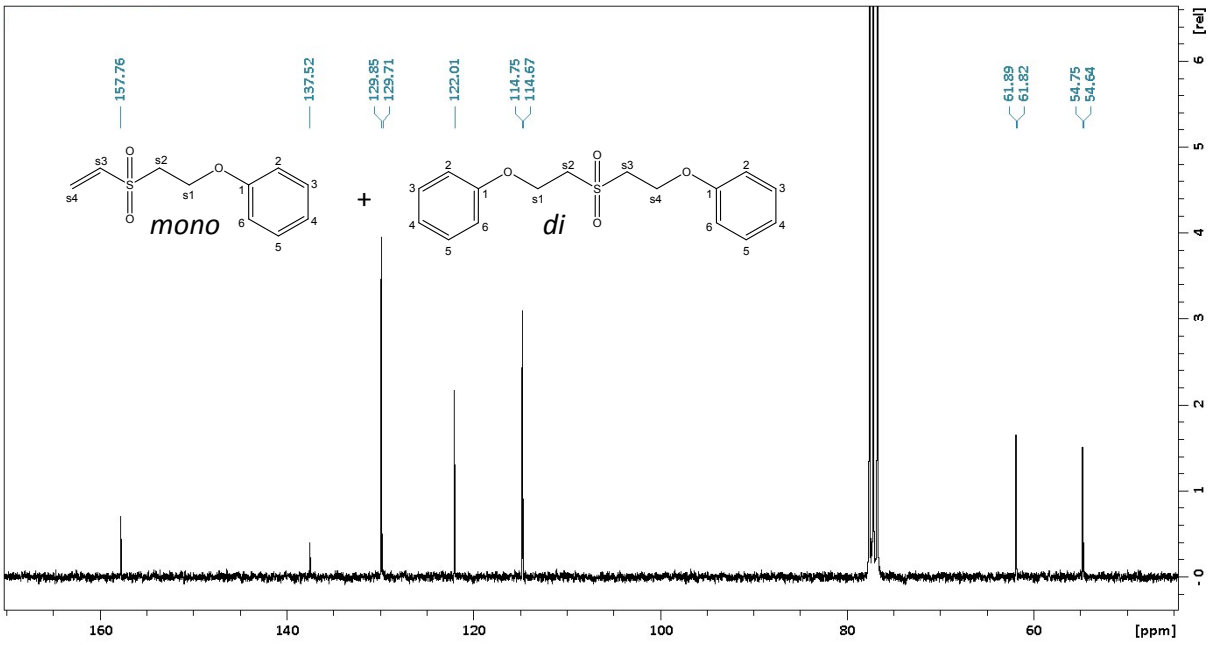
To a solution of DVS (100 µL, 0.996 mmol, 1.0 eq) and triphenyl methanol (778.0 mg, 2.989 mmol, 3.0 eq) in dry DCM (2 mL) PPh_3 (26.13 mg,0.0996 mmol, 0.1 eq) was added and stirred at 40 °C. After 168 h 52.1 % monoadduct and 47.9 % (0.477 mmol, 255.1 mg) diadduct were observed by ^{1}H NMR. The product was purified by flash chromatography (aluminium oxide, pH9-9.5, CH/EA 20:1 (v:v), with 10 ppm BHT in the eluent) and isolated by sampling the spot with R_f = (CH/EA 3:1 (v:v)). Yield: 82.5 mg (0.154 mmol, 15.5 %) white crystals.

^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 7.60-7.48 and 7.36-7.26 (m, 20H, C*H*$^{p2\text{-}p6}$), 3.98 (t, 4H, $^3J_{HH}$ = 5.50, C$H_2^{s1,s4}$), 3.50 (t, 4H, $^3J_{HH}$ = 5.50, C$H_2^{s2,s3}$), 2.93 (s, 2H, C*H*^{3}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 142.29 (4C, C^{p1}), 128.52, 126.80 (16C, C^{p2,p3,p5,p6}), 128.20 (4C, C^{p4}), 82.56, 81.10 (4C, C^{1,2}), 78.74 (2C, C^3), 59.11 (2C, C^{s1,s4}), 55.13 (2C, C^{s2,s3}).



19 R=phenol (((sulfonylbis(ethane-2,1-diyl))bis(oxy))dibenzene $C_{16}H_{18}O_4S$ [306.38]
DVS (1.177 g, 9.962 mmol, 1.0 eq) and phenol (2.3438 g, 24.91 mmol, 2.5 eq) were dissolved in dry DCM (2 mL) and PPh_3 (261.3 mg, 0.996 mmol, 0.1 eq) was added. After 7d stirring at 23°C a composition of 21.1 % DVS, 42.1 % monoadduct (0.419 mmol, 89.0 mg)and 36.8 % diadduct (0.367 mmol, 112.3 mg) was detected by ^{1}H NMR. The reaction mixture was purified by column chromatography (CH/EA 20:1 → 10:1 (v:v)), whereas 186.3 mg white solid were observed (mixture of mono- and diadduct ($R_{f(mono)}$ = 0.29 and $R_{f(di)}$ = 0.34 (C/EA 3:1 (v:v)).
diadduct: ((sulfonylbis(ethane-2,1-diyl))bis(oxy))dibenzene $C_{16}H_{18}O_4S$ [306.38]
^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 7.30 (t, 4H, $^3J_{HH}$ = 8.07, C$H^{3,5}$), 7.01 (t, 2H, $^3J_{HH}$ = 7.36, CH^4), 6.89 (d, 4H, $^3J_{HH}$ = 8.07, C$H^{2,6}$), 4.48 (t, 4H, $^3J_{HH}$ = 5.65, C$H_2^{s1,s4}$), 3.61 (t, 4H, $^3J_{HH}$ = 5.65, C$H_2^{s2,s3}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 157.76 (2C, C^1), 129.85 (4C, $C^{3,5}$), 122.01 (2C, C^4), 114.75 (4C, $C^{2,6}$), 61.89 (2C, $C^{s1,s4}$), 54.75 (2C, $C^{s2,s3}$).
monoadduct: (2-(vinylsulfonyl)ethoxy)benzene $C_{10}H_{12}O_3S$ [212.27]
^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 7.31 (t, 2H, $^3J_{HH}$ = 7.41, C$H^{3,5}$), 7.01 (t, 1H, $^3J_{HH}$ = 7.36, CH^4), 6.89 (d, 2H, $^3J_{HH}$ = 8.07,C$H^{2,6}$), 6.77 (dd, 1H, $^3J_{HH(Z)}$ = 10.0, $^3J_{HH(E)}$ = 16.8, CH^{s3}), 6.45 (d, 1H, $^3J_{HH}$ = 16.8, C$H_2^{s4(Z)}$), 6.15 (d, 1H, $^3J_{HH}$ = 9.7, C$H_2^{s4(E)}$), 4.41 (t, 2H, $^3J_{HH}$ = 5.65, CH_2^{s1}), 3.47 (t, 2H, $^3J_{HH}$ = 5.65, CH_2^{s2}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 157.71 (1C, C^1), 137.52 (C^{s3}), 129.85 (2C, $C^{3,5}$), 129.71 (1C, C^{s4}), 122.01 (2C, C^4), 114.67 (2C, $C^{2,6}$) 61.82 (1C, C^{s1}), 54.64 (1C, C^{s2}).

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137.52
129.85
129.71
122.01
114.75
114.67
61.89
61.82
54.75
54.64
mono
+
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[rel]
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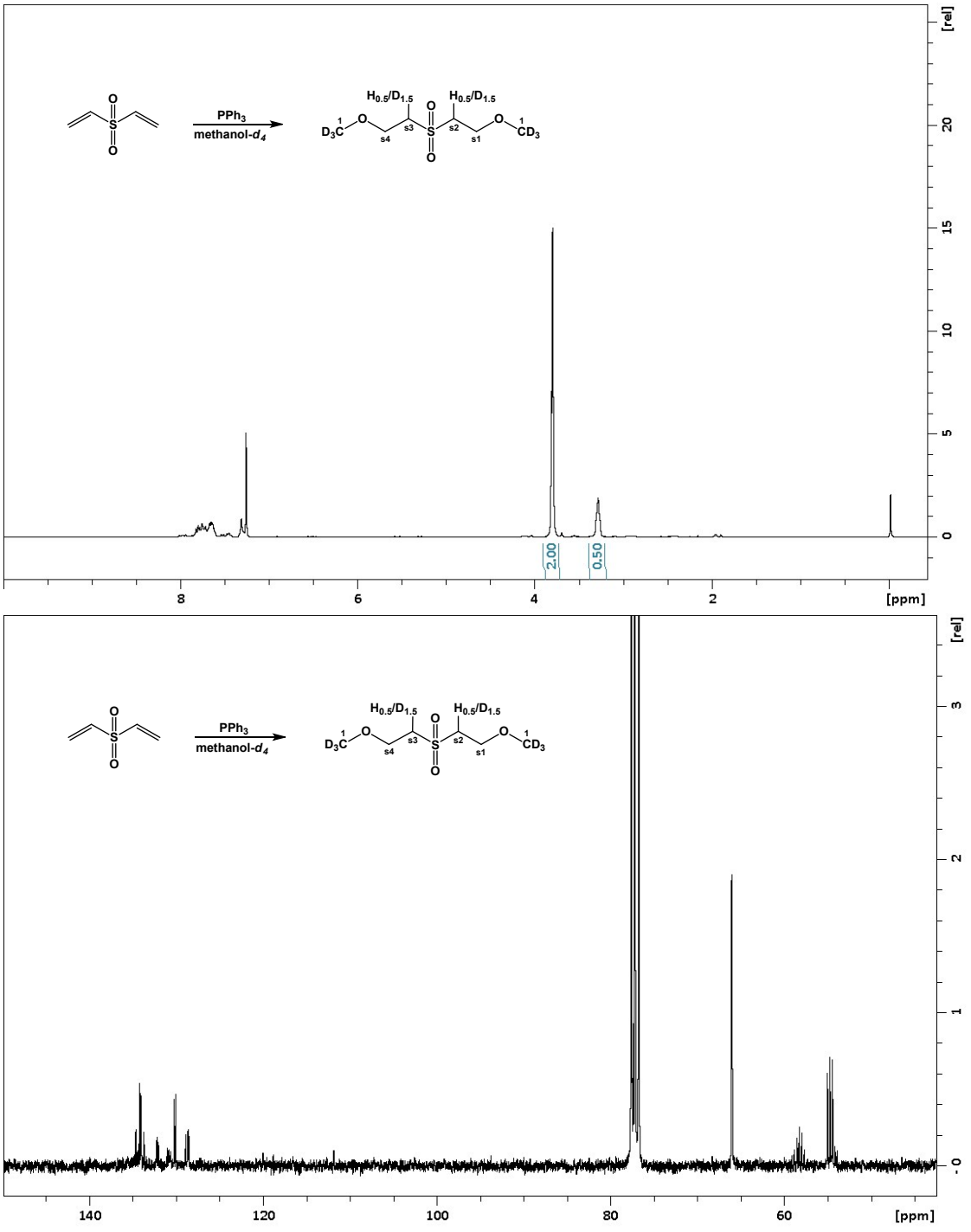
160
140
120
100
80
60

Deuterium incorporation:

1,1-sulfonylbis[2-methoxy-ethane]-*d*$_9$

PPh_3 (2.61 mg, 0.00996 mmol 0.1 eq) was added to a solution of DVS (10 µL, 0.0996 mmol, 1.0 eq) in methanol-*d*$_4$ (600 µL, 18.73 mmol, 188 eq) in a NMR tube. The reaction was performed at 25°C and monitored via ^{1}H NMR kinetic measurements. The formed product was not isolated, but characterized by ^{1}H and ^{13}C NMR.

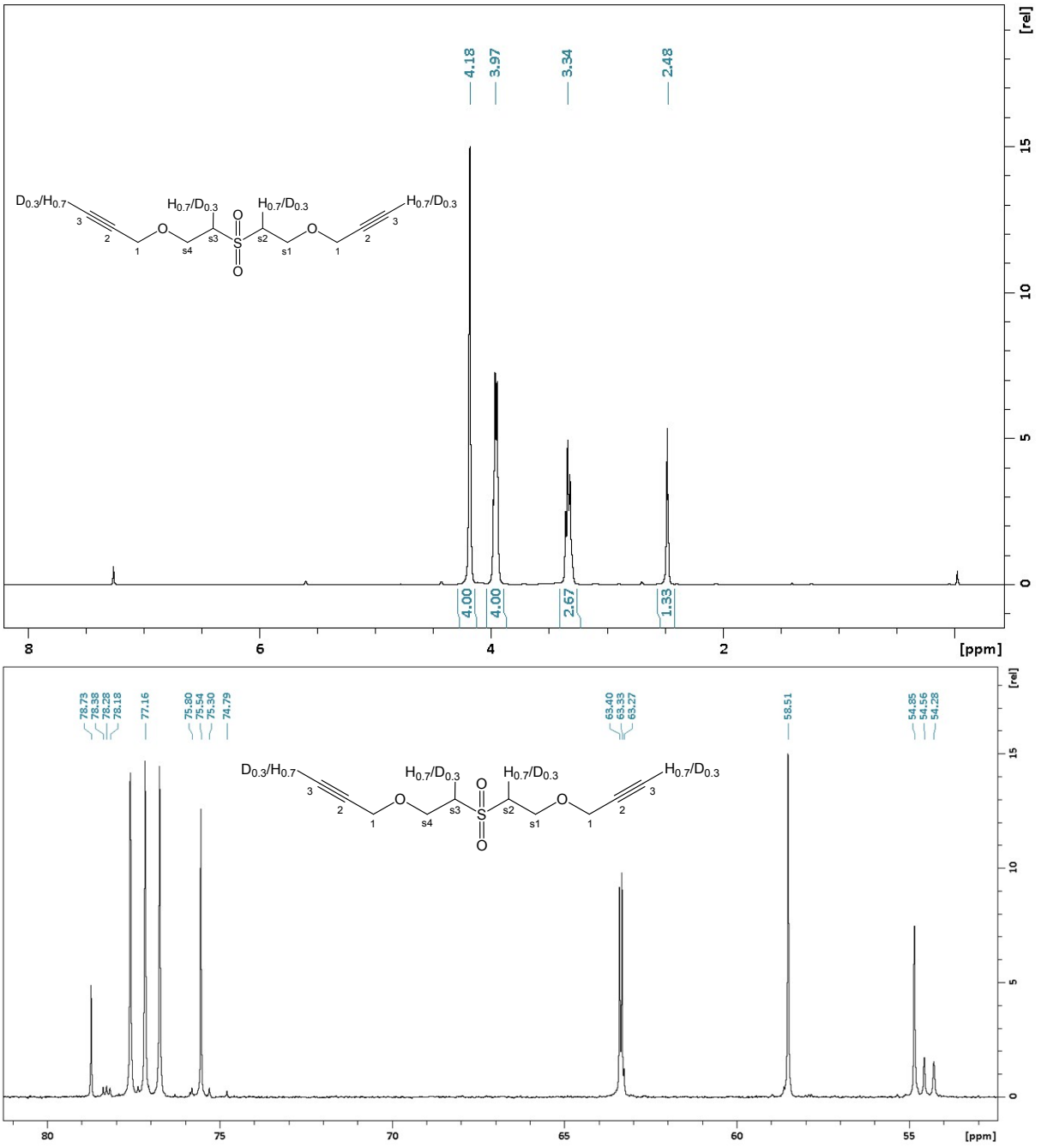
^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 3.83-3.77 (4H, C$H_2^{s4,s1}$), 3.35-3.23 (1H, C$H_2^{s2,s3}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 66.06, 65.99 (2C, C^{s1,s4}), 58.26 (septet, 2C, $^1J_{CD}$ = 21.52, C^1), 54.73 (t, 2C, $^1J_{CD}$ = 21.04, C^{s2,s3}) ppm.



3-(2-((2-(prop-2-yn-1-yloxy)ethyl)sulfonyl)ethoxy)prop-1-yne-*d*$_{1.2}$

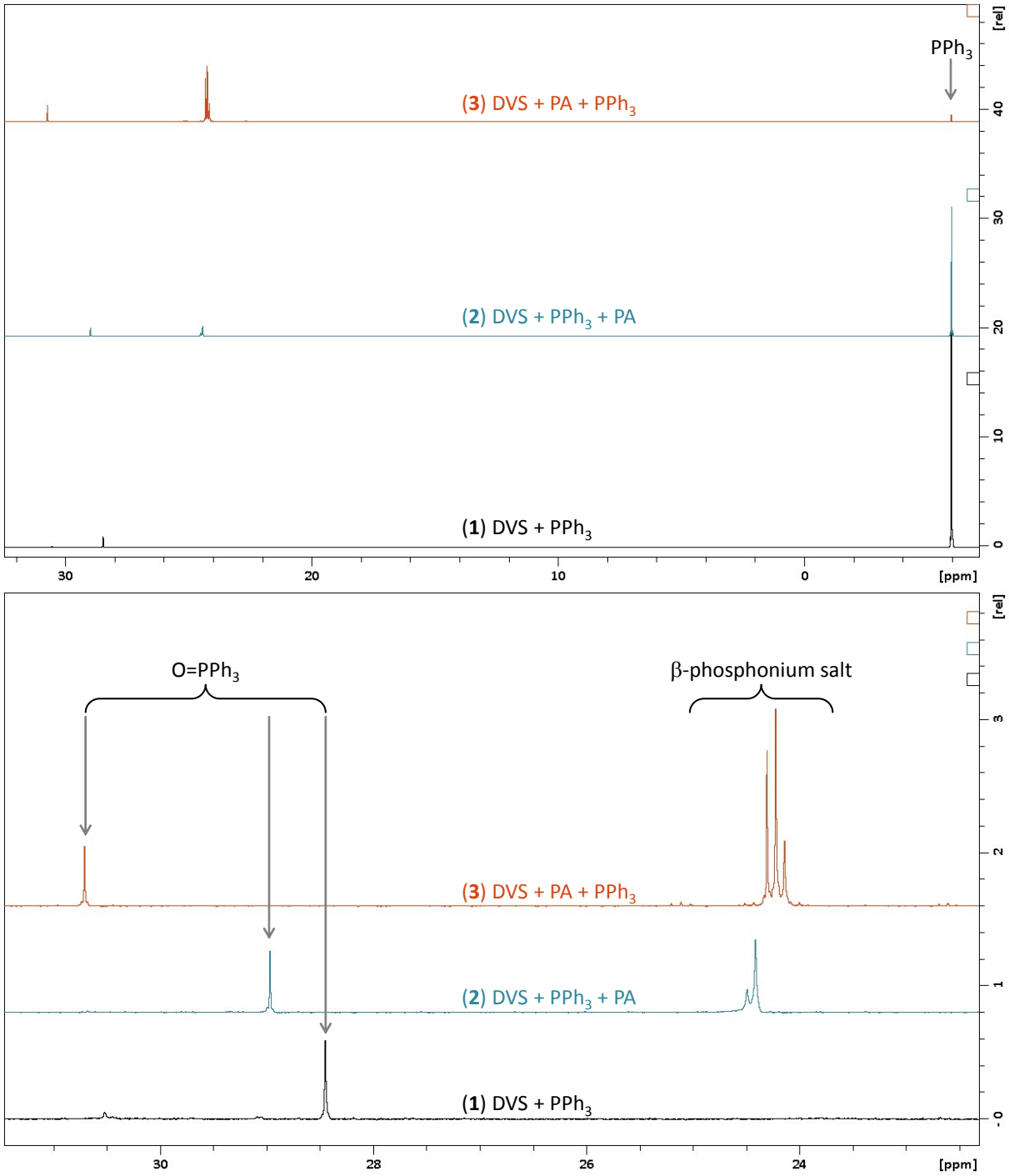
To a solution of DVS (50 µL, 0.498 mmol, 1.0 eq) and PA (86.2 µL, 1.494 mmol, 3.0 eq) in $CDCl_3$ (3.49 mL), PPh_3 (13.1 mh, 0.0498 mmol, 0.1 eq) was added and the mixture was stirred at 23°C. After 24 h more than 99 % diadduct were formed and the product was isolated via column chromatography (silica gel, CH/EA 20:1 → 10:1 (v:v)). Sampling the spot with R_f = 0.53 (CH/EA 1:1 (v:v)) yielded 67.0 mg (0.286 mmol, 57.4 %) colorless oil. H/D exchange was observed at positions s2 and s3 in approximately one third of the formed product and can be clearly evidenced by ^{13}C NMR spectroscopy via ^{13}C-^{2}D couplings.

^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 4.22-4.15 (m, 4H, CH_2^{1}), 4.01-3.96 (m, 4H, C$H_2^{s1,s4}$), 3.39-3.27 (m, 2.67H, C$H_2^{s2,s3}$), 2.48 (t, 1.33H, $^{4}J_{HH}$ =2.31, CH^{3}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 78.7 (2C, C^{2}), 78.3 (t, 2C, $^{2}J_{CD}$ = 7.46, C^{2}), 75.5 (1.4C, C^{3}), 75.3 (t, 0.6C, $^{1}J_{CD}$ = 38.41, C^{3}), 63.4, 63.33 (2C, $C^{s1,s4}$), 58.5 (2C, C^{1}), 54.8 (1.4C, $CH^{s2,s3}$), 54.6 (t, 0.6C, $^{1}J_{CD}$ = 21.14, $CD^{s2,s3}$) ppm.



^{31}P NMR experiments:

DVS (20 µL, 0.199 mmol, 1.0 eq, c = 0.31 M) and PPh_3 (52.3 mg, 0.199 mmol, 1.0 eq) were dissolved in $CDCl_3$ (650 µL) and subjected to ^{31}P NMR measurements (**1**). Then PA (20 µL, 0.347 mmol, 1.7 eq) was added and the mixture was measured again (**2**). The spectra were compared with the ^{31}P NMR spectrum of the following reaction solution after complete conversion (**3**): PA (1.817 mL, 29.89 mmol, 3.0 eq), DVS (1.00 mL, 9.96 mmol, 1.0 eq, c = 1.99 M) and PPh_3 (261.3 mg, 0.996 mmol, 0.1 eq) in $CDCl_3$ (5.00 mL).
^{31}P {^{1}H} NMR (200 MHz; $CDCl_3$, 25°C): δ (**1**) 28.47 ($O=PPh_3$), -6.00 (PPh_3). (**2**) 28.98 ($O=PPh_3$), 24.49, 24.42 (β-phosphonium salts). (**3**) 30.74 ($O=PPh_3$), 24.30, 24.22, 24.14 (β-phosphonium salts).



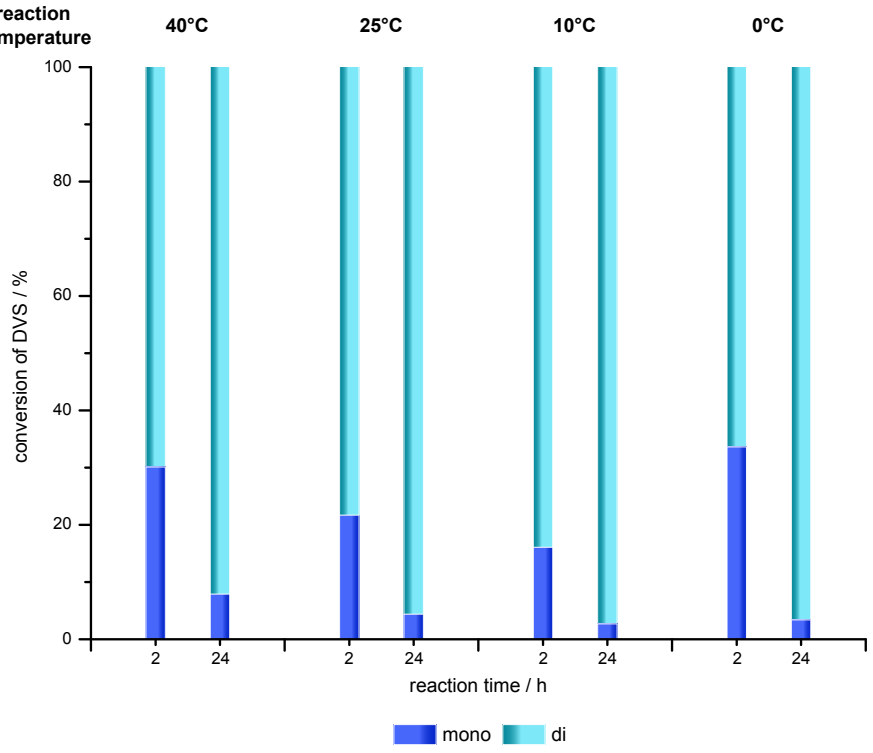
variable reaction temperature:

DVS (100 µL, 0.996 mmol, 1.0 eq, c = 0.55 M) and benzyl alcohol (BA) (310.8 µL, 2.989 mmol, 3.0 eq) were dissolved in dry DCM and then PPh_3 (13.1 mg, 0.0498 mmol, 0.05 eq) was added.

Optimization of the reaction temperature for the oxa-Michael addition of DVS (0.55 M) and BA.

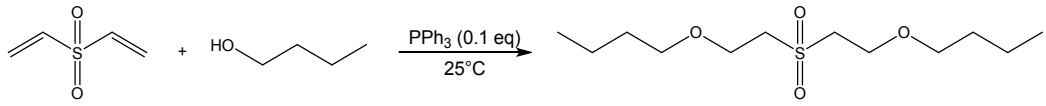
entry	reaction temperature / °C	PPh_3 loading / mol%	reaction time / h	distribution / %		
				DVS	mono	di
1	40	5	2	0	30.1	69.9
			24	0	7.9	92.1
			168	0	2.4	97.6
2	25	5	2	0	21.7	78.3
			24	0	4.4	95.6
			168	0	0	>99.9
3	10	5	2	0	16.1	83.9
			24	0	2.7	97.3
			168	0	0	>99.9
4	0	5	2	0	33.6	66.4
			24	0	3.4	96.6
			168	0	0	>99.9

The conversions carried out in DCM at different reaction temperatures are depicted in **Fehler! Verweisquelle konnte nicht gefunden werden.**. 10°C were found to be the optimal reaction temperature for the oxa-Michael addition of divinyl sulfone as the most diadduct was formed after 2 h. Interestingly, room temperature is similarly good, but 0°C are even less appropriate than 40°C.



Influence of the reaction temperature on the conversion of DVS and BA (dry DCM, [DVS] = 0.55 M).

variable concentration:

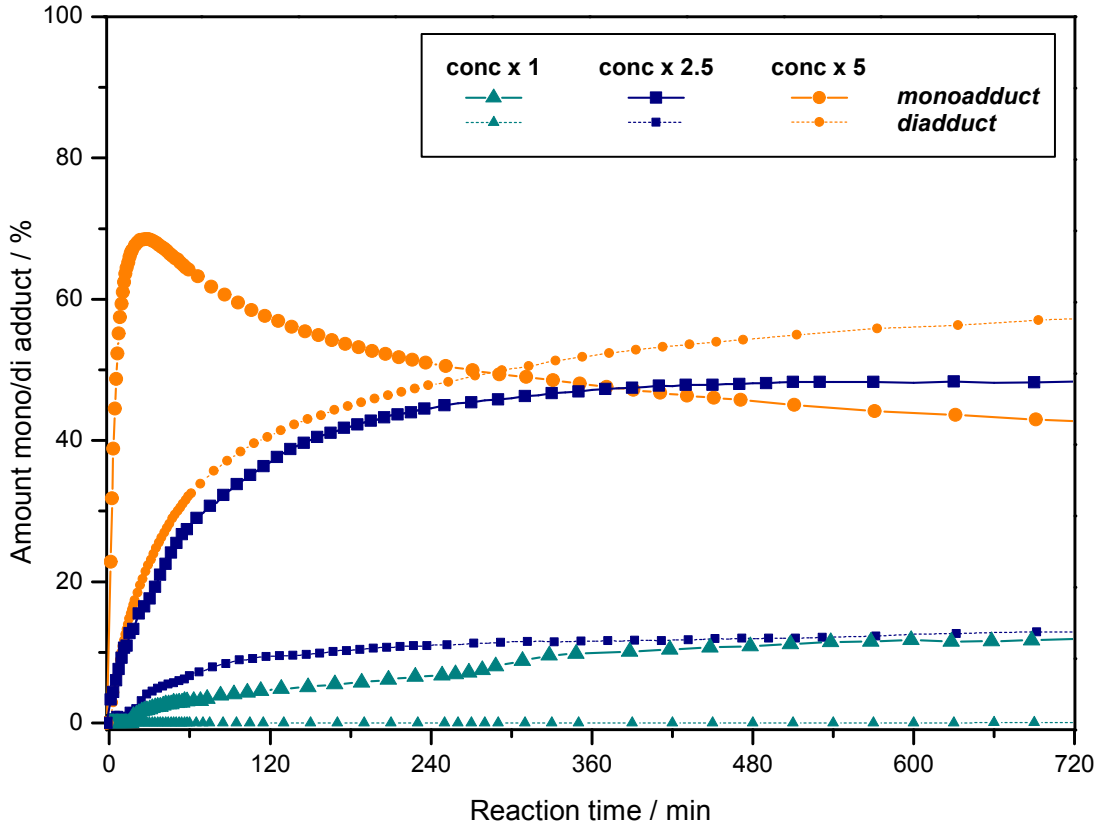


n-Butanol and DVS were reacted in presence of PPh_3 in $CDCl_3$ in different concentrations (entries 1-3, **Fehler! Verweisquelle konnte nicht gefunden werden.**) or in bulk (entry 4, **Fehler! Verweisquelle konnte nicht gefunden werden.**) at room temperature: (**1**) DVS (10.0 µL, 0.0996 mmol, 1.0 eq), *n*-BuOH (27.35 µL, 0.299 mmol, 3.0 eq), PPh_3 (2.61 mg, 0.00996 mmol, 0.1 eq) in 612 µL $CDCl_3$; (**2**) DVS (25.0 µL, 0.249 mmol, 1.0 eq), *n*-BuOH (63.37 µL, 0.747 mmol, 3.0 eq), PPh_3 (6.53 mg, 0.0249 mmol, 0.1 eq) in 614 µL $CDCl_3$; (**3**) DVS (50.0 µL, 0.489 mmol, 1.0 eq), *n*-BuOH (136.74 µL, 1.494 mmol, 3.0 eq), PPh_3 (13.1 mg, 0.0498 mmol, 0.1 eq) in 526 µL $CDCl_3$; (**4**) DVS (50.0 µL, 0.498 mmol, 1.0 eq), *n*-BuOH (547.0 µL, 5.977 mmol, 12.0 eq) and PPh_3 (13.1 mg, 0.0498 mmol, 0.1 eq).

Formation of *n*-BuOH mono- and diadduct with increasing concentration of reactants.

entry	concentration of DVS mol·L^{-1}	*n*-BuOH eq	reaction mixture after 24 h	
			monoadduct / %	diadduct / %
1	0.15*	3	13	< 1
2	0.38*	3	48	14
3	0.75*	3	40	60
4	bulk (0.91)	12	0	100

**in $CDCl_3$*



Reaction progress with increasing concentration of DVS and BuOH (25°C, $CDCl_3$, 500 MHz).
(conc x 1 = 0.15 M; conc x 2.5 = 0.38 M; conc x 5 = 0.75 M)

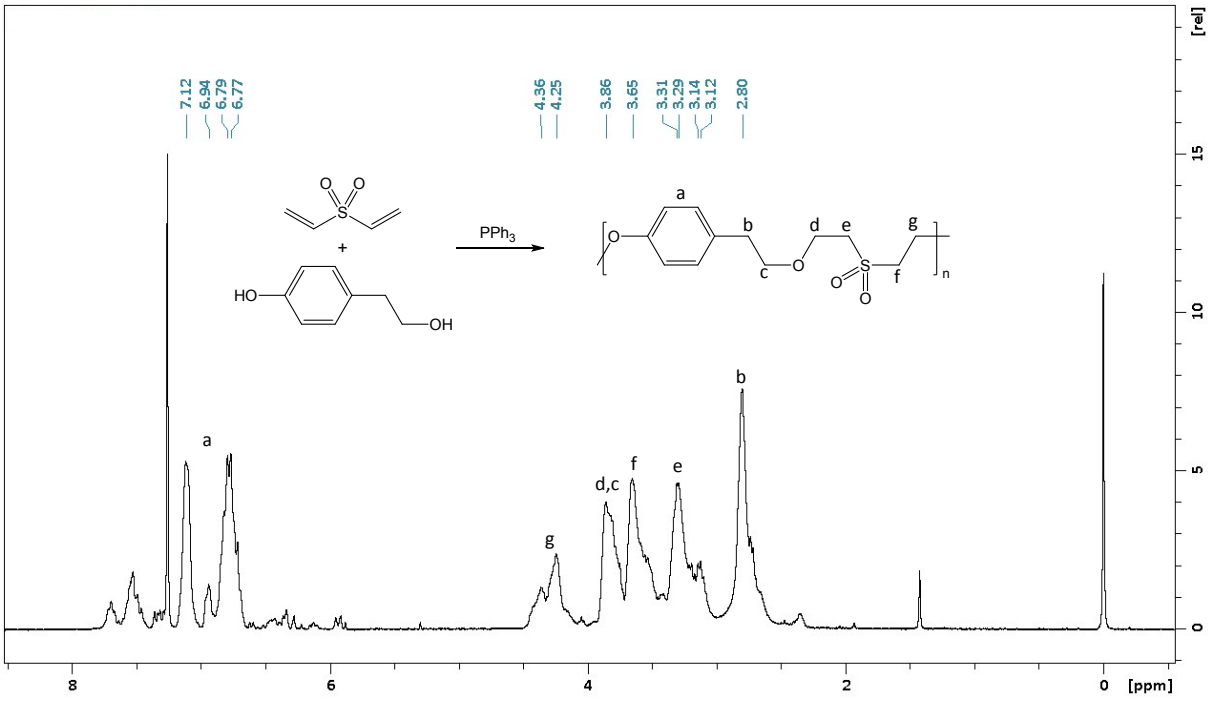
Preparation of polymers:

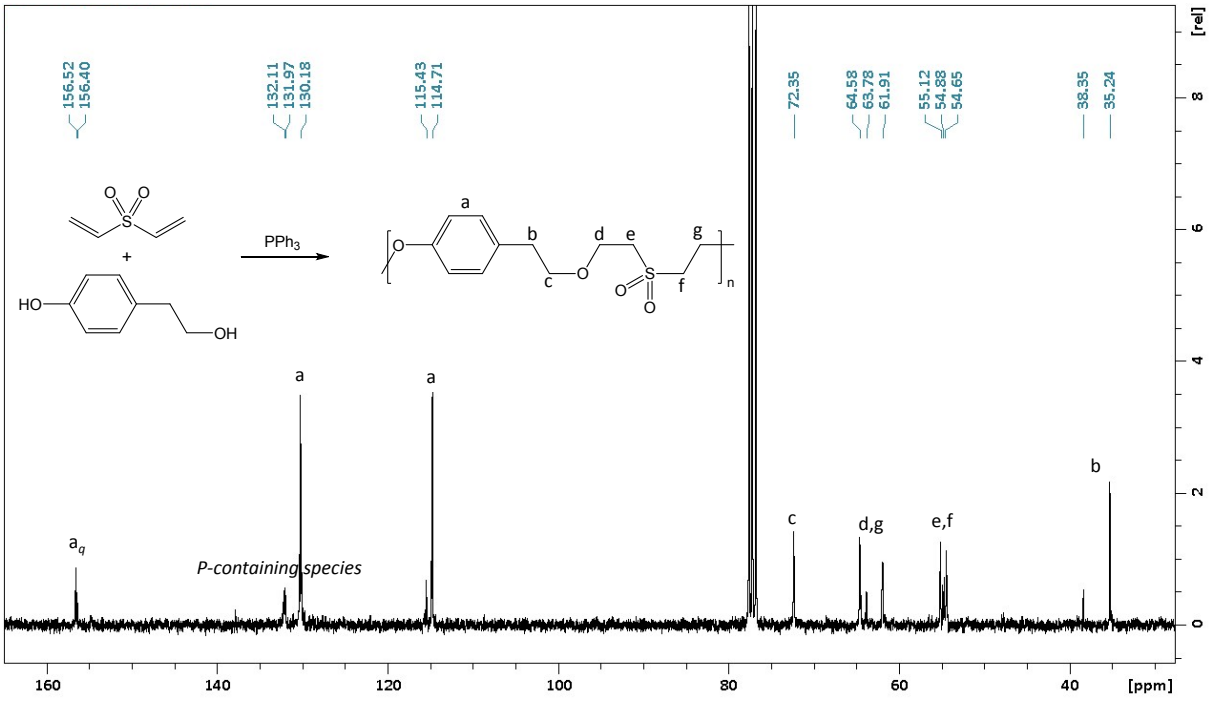
4-(2-Hydroxyethyl)phenol + DVS

4-(2-Hydroxyethyl)phenol (275.28 mg, 1.992 mmol, 1.0 eq) and H_2O (119.5 µL, 9.962 mmol, 5.0 eq) were mixed and heated until the alcohol melted. PPh_3 (52.26 mg, 0.199 mmol, 0.1 eq, dissolved in 52.3 µL DCM) was added and the mixture was stirred shortly. The Michael addition polymerisation was started upon addition of DVS (200.0 µL, 1.992 mmol, 1.0 eq). The mixture was stirred vigorously for a few seconds and was then dropped onto a vitreous object carrier and cured 24 h at 23°C and 4 h at 80°C. SEC ($CHCl_3$ relative to PS): M_n = 630 g/mol , M_w = 1130 g/mol, PDI = 1.8 (cured at 23°C) and M_n = 780 g/mol, M_w = 1270 g/mol, PDI = 1.6 (cured at 80°C).

The Michael addition polymerization of 4-(2-hydroxyethyl)phenol (275.74 mg, 1.992 mmol, 1.0 eq) and DVS (200.0 µL, 1.992 mmol, 1.0 eq) in solution (DCM/THF 1:1 (v:v), 0.5 mL) at 23°C promoted by PPh_3 (52.26 mg, 0.199 mmol, 0.1 eq) yielded 363.9 mg (71.3 %) yellowish soft solid after precipitation in cold MeOH. SEC ($CHCl_3$ relative to PS): M_n = 760 g/mol, M_w = 1400 g/mol, PDI = 1.8.

NMR spectra of the obtained polymers appear equally: ^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 7.82-7.27 (m, P-containing species), 7.20-6.64 (m, CH^a) 6.64-5.86 (m, C$H^{\text{vinyl end group}}$), 4.50-4.00 (m, C$H_2^g$), 3.99-3.72 (C$H_2^{d,c}$), 3.71-3.45 (m, C$H_2^f$), 3.38-3.00 (m, C$H_2^e$), 2.99-2.51 (m, C$H_2^b$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 156.5, 156.4 (2C, C$^{a(\text{quarternary})}$), 132.1, 132.0 (P-containing species), 130.2 (2C, C^a), 115.4 (2C, C^a), 114.7 (2C, C^a), 72.4 (1C, C^c), 70.4 (2C, C^{b,c}), 64.6, 61.9 (2C, C^{d,g}), 63.8 (C), 55.1, 54.7 (2C, C^{e,f}), 54.9 (C), 38.4, 35.2 (2C, C^b).

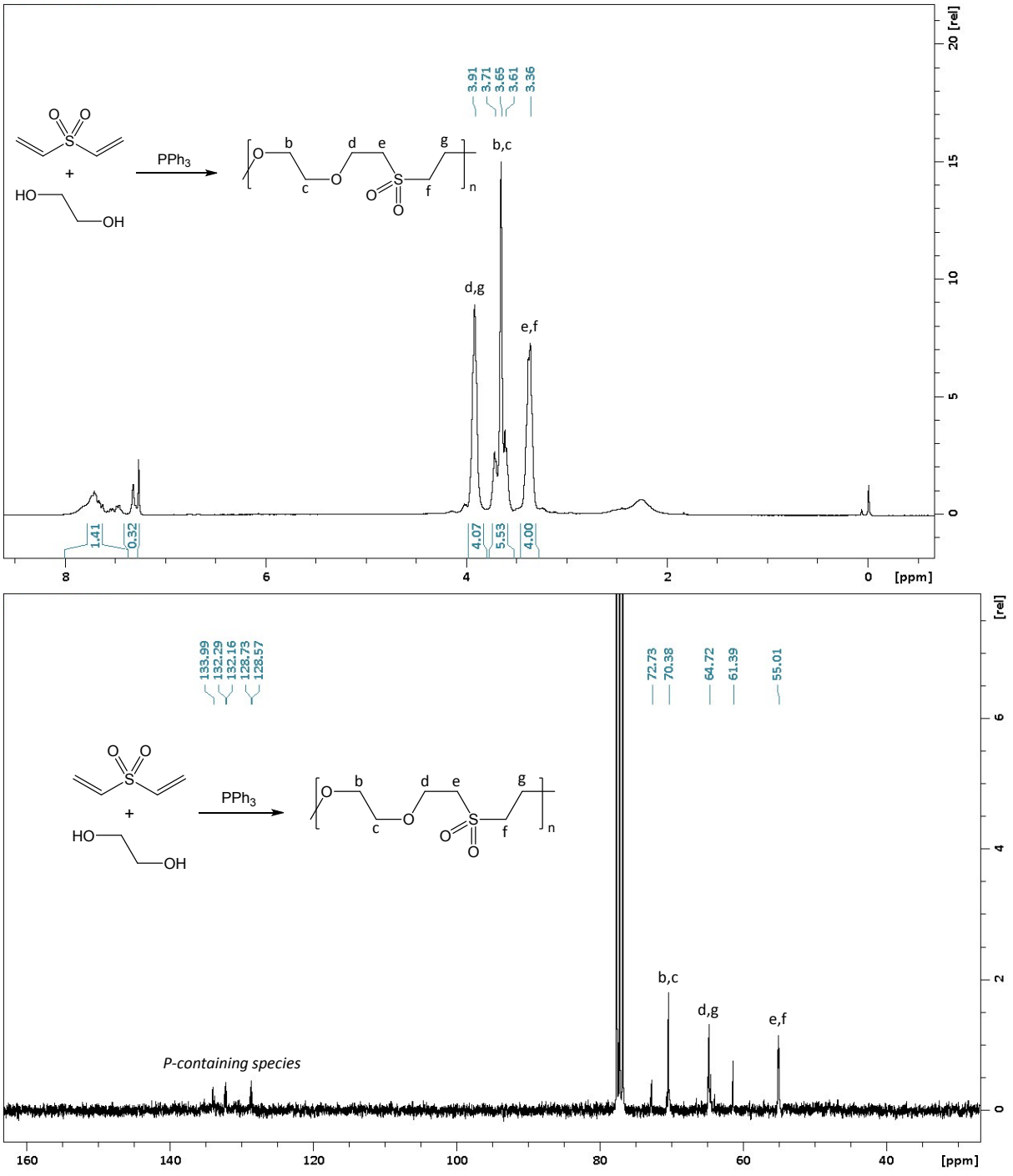



156.52
156.40
132.11
131.97
130.18
115.43
114.71
72.35
64.58
63.78
61.91
55.12
54.88
54.65
38.35
35.24
PPh3
HO
OH
a
b
c
d
e
f
g
n
a
a
b
c
d,g
e,f
aq
P-containing species
160
140
120
100
80
60
40
[ppm]
[rel]

Ethane-1,2-diol + DVS

Ethane-1,2-diol (123.67 mg, 1.992 mmol, 1.0 eq), H_2O (119.5 µL, 9.962 mmol, 5.0 eq) and PPh_3 (52.26 mg, 0.199 mmol, 0.1 eq, dissolved in 52.3 µL DCM) were mixed and stirred shortly. The Michael addition polymerisation was started upon addition of DVS (200.0 µL, 1.992 mmol, 1.0 eq). The mixture was dropped onto a vitreous object carrier and cured 8 h at 23°C and 4 h at 80°C. SEC ($CHCl_3$ relative to PS): M_n = 830 g/mol, M_w = 1170 g/mol, PDI = 1.4 (cured at 23°C) and M_n = 790 g/mol, M_w = 1140 g/mol, PDI = 1.5 (cured at 80°C).

^{1}H-NMR (300 MHz; $CDCl_3$, 25°C): δ 8.00-7.27 (m, 1.7H, P-containing species), 3.91 (m, 4.1H, C$H_2^{d,g}$), 3.78-3.52 (m, 5.5H, C$H_2^{b,c}$), 3.46-3.28 (m, 4H, C$H_2^{e,f}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25°C): δ 134.0, 132.3, 132.2, 128.7, 128.6 (P-containing species), 72.7 (1C), 70.4 (2C, C^{b,c}), 64.7 (2C, C^{d,g}), 61.4 (1C), 55.0 (2C, C^{e,f}).

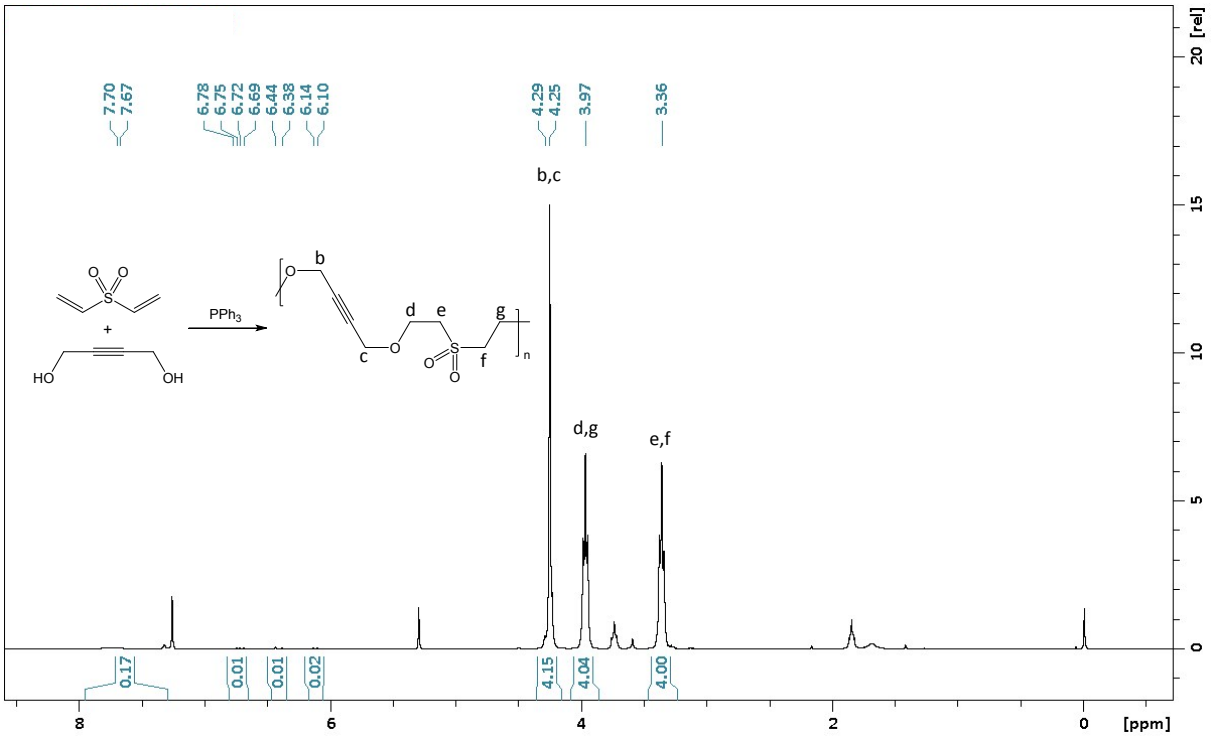


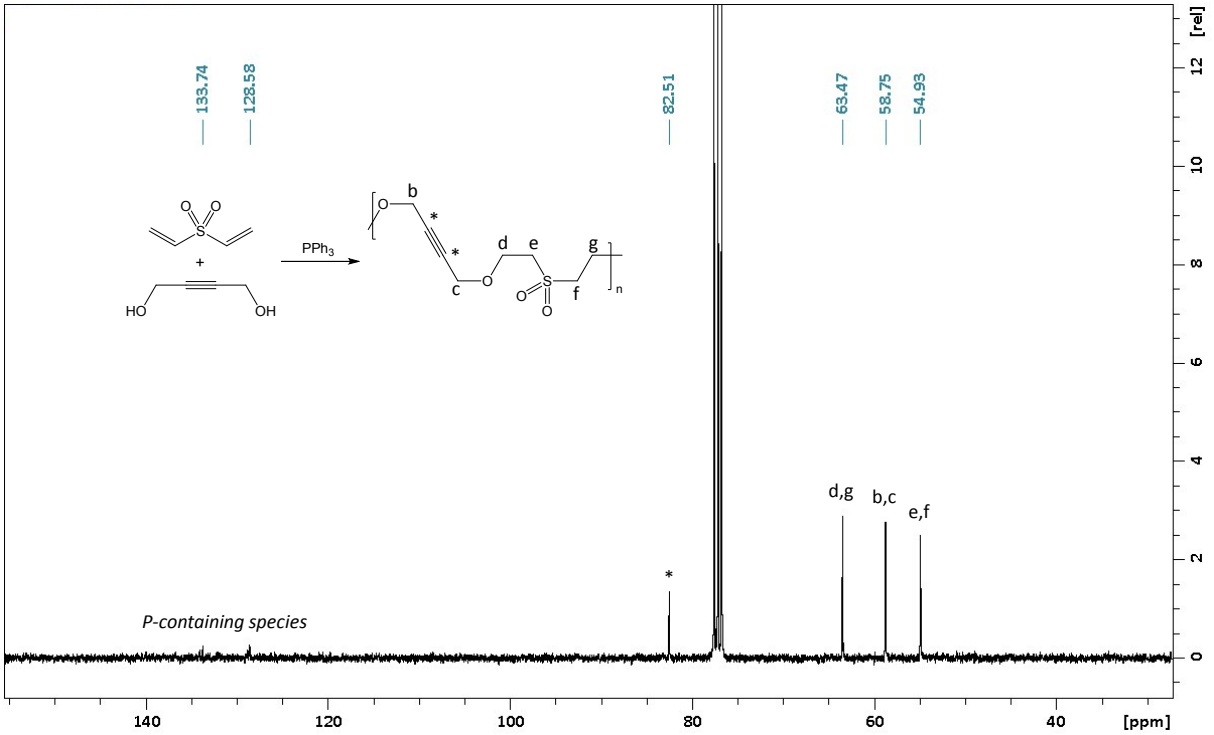
But-2-yne-1,4-diol + DVS

But-2-yne-1,4-diol (174.1 mg, 2.022 mmol, 1.015 eq) were dissolved in H_2O (119.5 µL, 9.962 mmmol, 5.0 eq) and PPh_3 (52.26 mg, 0.199 mmol, 0.1 eq, dissolved in 52.3 µL DCM) was added. DVS (200.0 µL, 1.992 mmol, 1.0 eq) was added and the mixture was transferred onto glass object carriers to cure 8 h at 23°C (M_n = 3190, M_w = 6020, PDI = 1.9) and at 80°C (M_n = 2420, M_w = 4480, PDI = 1.9).

To a solution of but-2-yne-1,4-diol (85.29 mg, 0.991 mmol) and DVS (100.20 µL, 0.998 mmol) in THF/CH_2Cl_2 = 1:1 (2 mL) PPh_3 (26.24 mg, 0.100 mmol) was added and the reaction mixture was stirred at 23°C for 16 h. The reaction mixture turned yellow and a yellow precipitate formed, which was collected on a glass frit and washed with THF (2 times, 0.5 mL each) and dried in vacuum. Yield: 142.26 mg (70 %). SEC ($CHCl_3$ relative to PS): M_n = 6400 g/mol, M_w = 11090 g/mol, PDI = 1.7. A T_g of 6.0°C was detected via DSC measurements.

^{1}H NMR (300 MHz; $CDCl_3$, 25°C): δ 6.73 (dd, $^3J_{HH}$ = 16.9, $^3J_{HH}$ = 10.7, 0.01H, SO_2-C*H*=CH_2), 6.41 (d, $^3J_{HH}$ = 16.9, 0.01H, SO_2-CH=$CH_{cis}H_{trans}$), 6.12 (d, $^3J_{HH}$ = 10.7, 0.01H, SO_2-CH=CH_{cis}H$_{trans}$), 4.29 (s, 0.1H, C≡C-CH_2-OH), 4.25 (s, 4H, C$H_2^{b,c}$), 3.97 (t, 4H, C$H_2^{d,g}$), 3.36 (t, 4H, C$H_2^{e,f}$). ^{13}C {^{1}H} NMR (75 MHz; $CDCl_3$, 25°C): δ 133.7, 128.6 (P-containing species), 82.5 (2C, C*), 63.5 (2C, C^{d,g}), 58.8 (2C, C^{b,c}), 54.9 (2C, C^{e,f}).





After combining the reaction solution from the filtration described above with the corresponding washing-solutions volatiles were removed in vacuum yielding 87 mg of an oily residue consisting of species with lower molecular mass and phosphorous containing species. ^{1}H NMR (300 MHz; $CDCl_3$, 25°C): δ 7.95-7.27 (bm, 3.9H, aromatic protons), 6.73 (dd, $^{3}J_{HH}$ = 16.9, $^{3}J_{HH}$ = 10.7, 0.12H, SO_2-C*H*=CH_2), 6.42 (d, $^{3}J_{HH}$ = 16.9, 0.12H, SO_2-CH=$CH_{cis}H_{trans}$), 6.13 (d, $^{3}J_{HH}$ = 10.7, 0.12H, SO_2-CH=C$H_{cis}H_{trans}$), 4.29 (s, 0.37H, C≡C-CH_2-OH), 4.25 (s, 4H, C≡C-CH_2-O-), 3.97 (t, 4H, SO_2-CH_2-CH_2-O-), 3.36 (t, 3.75H, SO_2-CH_2-CH_2-O-), 3.29 (t, 0.25H, H_2C=CH-SO_2-CH_2-CH_2-O-).

Propane-1,2,3-triol +DVS

DMAP (40.55 mg, 0.498 mmol, 0.05 eq) was dissolved in propane-1,2,3-triol (611.60 mg, 6.641 mmol, 2.0 eq). DVS (1.0 mL, 9.962 mmol, 3.0 eq) was added and the mixture was placed in rectangular teflon molds (5 x 2 x 22 mm) to cure 4 h at 80°C. DMA measurements of the sample failed due to sample rupture shortly after the start at -30°C. A T_g of 64.8°C was determined by DSC measurements.

2-Ethyl-2-(hydroxymethyl)propane-1,3-diol + DVS

DMAP (40.55 mg, 0.498 mmol, 0.05 eq) was dissolved in 2-ethyl-2-(hydroxymethyl)propane-1,3-diol (891.13 mg, 6.641 mmol, 2.0 eq). DVS (1.0 mL, 9.962 mmol, 3.0 eq) was added and the mixture was placed in rectangular teflon molds (5 x 3 x 22 mm) to cure 4 h at 80°C. A T_g of 28°C was determined by DMA measurements and evaluation of the loss modulus maximum. The T_g of 29.7°C determined by DSC measurements is in good accordance with the DMA results (see below).