Supporting Information

Modified ε-Caprolactone Monomers: An Efficient and Very Straightforward Approach *via* Thia-Michael Addition and Baeyer-Villiger Oxidation

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Keywords: Functionalized caprolactones, thia-Michael addition, catalytic Baeyer-Villiger oxidation

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1. Materials

Cyclohex-2-enone (≥98 %, Sigma Aldrich), cyclohexanethiol (97 %,Sigma Aldrich), benzyl mercaptan (99 %,Sigma Aldrich), 1-butanethiol (99 %,Sigma Aldrich), *meta*-chloroperoxybenzoic acid (≤77 %,Sigma Aldrich), Novozyme 435 (Lipase acrylic resin from Candida Antarctica, Sigma Aldrich), 1-octanethiol (≥98.5 %,Sigma Aldrich), oxone® (potassium peroxymonosulfate, Sigma Aldrich), triethylamine (99 %, Acros), trifluoroacetic anhydride (≥99 %, Sigma Aldrich) were used as received. Urea hydrogen peroxide was synthesized according to a known literature procedure.[1] All solvents (technical grade) were used without further purification.

2. Characterization

^{1}H-NMR measurements were performed on a Bruker Avance spectrometer operating at 300 MHz for ^{1}H-NMR and 75 MHz for ^{13}C-NMR spectra. All samples were dissolved in $CDCl_3$ and the chemical shifts δ are reported in ppm relative to TMS.)

Molecular weights of the prepared polyester were determined on a Shimadzu SEC System LC-20 A equipped with a SIL-20A auto sampler, GPC pre-column PSS SDV analytical (5µm, 8x50mm), main-column PSS SDV analytical 10000 Å (5 µm, 8×300mm) and a RID-10A refractive index detector in THF (flow rate 1 mL×min^{-1}) at 50 °C. The molecular weight distributions were determined relative to PMMA standards (Polymer Standards Service, M_p 1100–981000 Da).

High resolution Fast-Atom-Bombardement-mass spectra (HRMS- FAB) were measured on a Finnigan MAT 95.

Differential scanning calorimetry (DSC) experiments were carried out on a DSC821e (Mettler Toledo) calorimeter, under nitrogen atmosphere, at a heating rate of 10 °C per min^{-1} up to a temperature of 150 °C, and using a sample mass of approximately 5 mg. Data from second heating scans are reported. The glass transition temperature, T_g, is recorded as the minimum (endothermic transitions are represented downwards) of the endothermic peak.

3. Experimental procedures

a. General procedure for Thia-Michael Additions

2.5 g cyclohex-2-enone (26.0 mmol), the respective thiol (26.5 mmol), and triethylamine (10 mol%) were weighed into a round bottom flask and vigorously stirred for 16 hours at 30 °C. After evaporation under reduced pressure (10^{-2} - 10^{-3} mbar), the products were used without further purification.

Note:

For the synthesis of 3-(cyclohexylthio)cyclohexanone **3** an excess of the thiol (1.15 equivalents) was used.

Alternatively, to improve the reaction rate, a higher excess of thiol (1.2 equivalents) at a reaction temperature of 40 °C can be used. In this case, the reaction was completed after 6 hours, but in this case the products were purified via column chromatography (hexane . ethyl acetate = 7 : 1).

3-(*n*-octylthio)cyclohexanone (1)

Pure **1** was obtained as light yellow oil (yield 97 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 3.10 – 2.97 (m, 1H, -S-C*H*-), 2.69 (dd, *J* = 14.2, 4.4 Hz, 1H, -CH-C*H*$_2$-C(O)-), 2.51 (t, *J* = 7.5 Hz, 2H, -S-C*H*$_2$-), 2.42 – 2.24 (m, 3H, -C*H*$_2$-(CO)-C*H*$_2$-), 2.21 – 2.04 (m, 2H, -CH-C*H*$_2$-CH$_2$-), 1.80 – 1.62 (m, 2H, -CH$_2$-C*H*$_2$-CO-), 1.61 – 1.47 (m, 2H, -S-CH$_2$-C*H*$_2$-), 1.44 – 1.15 (m, 10H, -C*H*$_2$-), 0.86 (t, *J* = 6.7 Hz, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 209.0, 48.4, 42.9, 41.1, 31.9, 31.8, 30.6, 29.8, 29.2, 29.0, 24.4, 22.7, 14.2.

HRMS (EI):

$C_{14}H_{26}OS$ calc. 242.1699 found 2421698

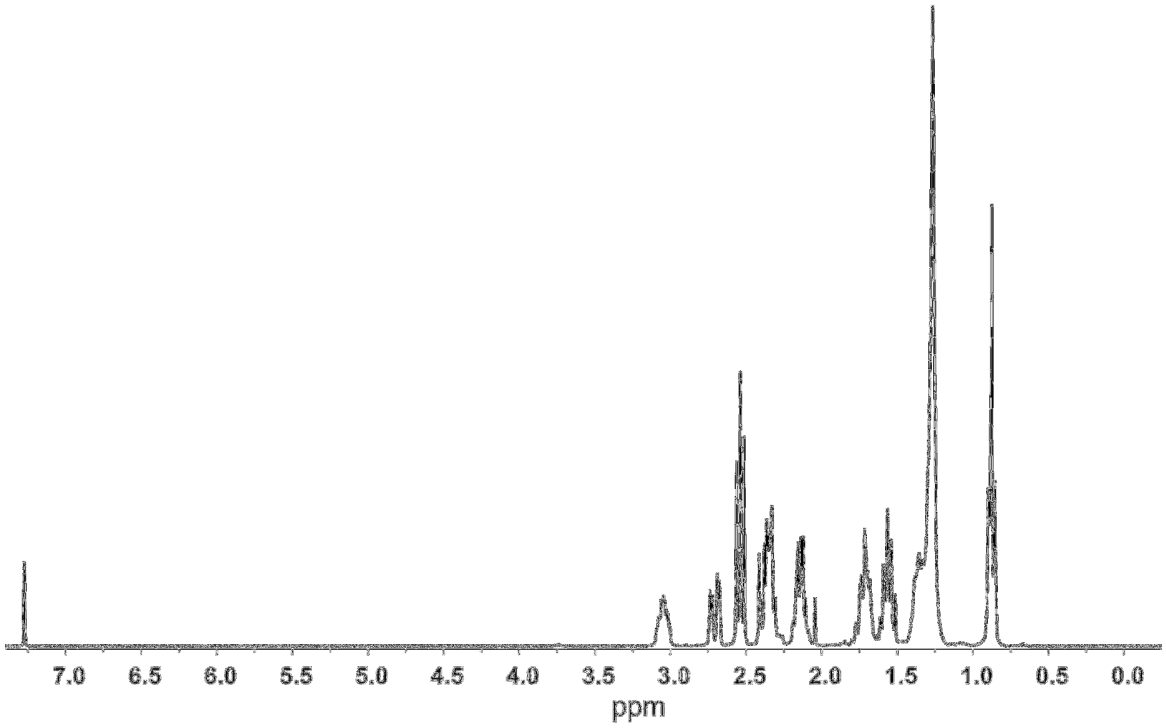

Figure S 1: ^{1}H-NMR (300 MHz/$CDCl_3$) of 3-(*n*-octylthio)cyclohexanone (**1**).

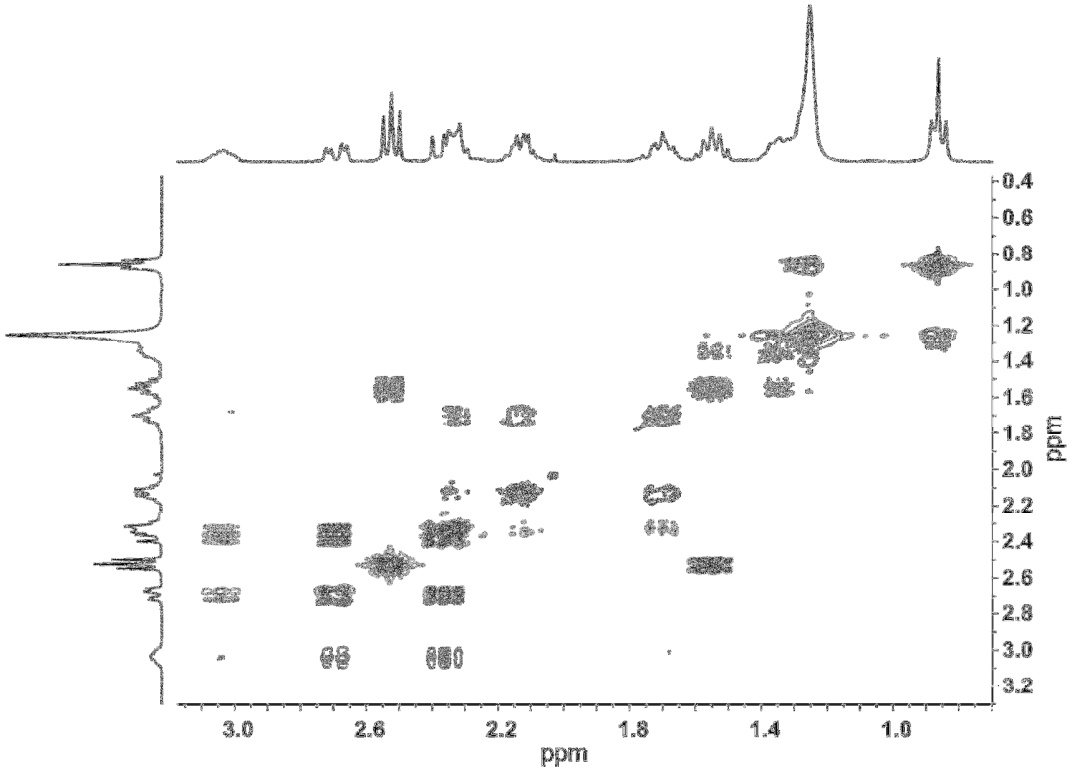

Figure S 2: ^{1}H-COSY-NMR (300 MHz/$CDCl_3$) of 3-(*n*-octylthio)cyclohexanone (**1**).

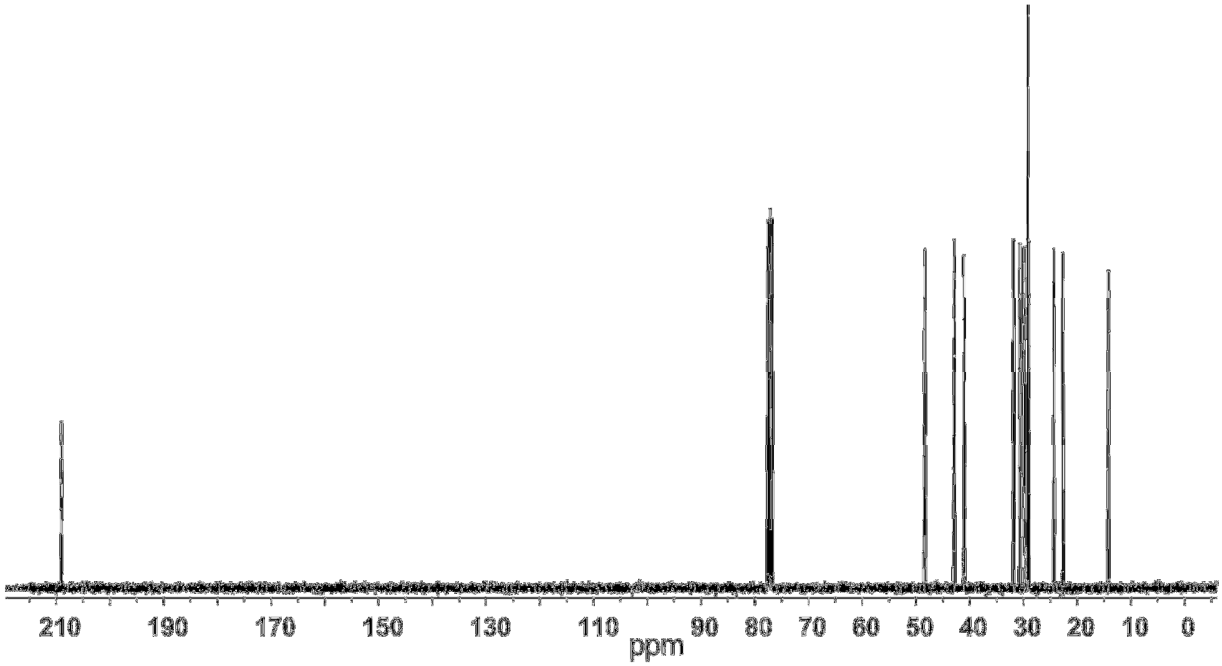

Figure S 3: ^{13}C-NMR (75 MHz/$CDCl_3$) of 3-(*n*-octylthio)cyclohexanone **(1)**.

3-(*n*-butylthio)cyclohexanone (2)

Pure **2** was obtained as light yellow oil (yield 96 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 3.09 – 2.95 (m, 1H, -S-C*H*-), 2.68 (dd, *J* = 14.2, 3.0 Hz, 1H, -CH-C*H*$_2$-C(O)-), 2.52 (td, *J* = 7.5, 1.5 Hz, 2H, -S-C*H*$_2$-), 2.41 – 2.22 (m, 3H, -C*H*$_2$-(CO)-C*H*$_2$-), 2.19 – 2.03 (m, 2H, -CH-C*H*$_2$-CH$_2$-), 1.77 – 1.60 (m, 2H, -CH$_2$-C*H*$_2$-CO-), 1.59 – 1.45 (m, 2H, -S-CH$_2$-C*H*$_2$-), 1.44 – 1.29 (m, 2H, -C*H*$_2$-), 0.88 (td, *J* = 7.3, 1.4 Hz, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 209.0, 48.3, 42.8, 41.0, 31.8, 31.7, 30.3, 24.3, 22.1, 13.7.

HRMS (EI):
$C_{10}H_{18}OS$ calc. 186.1073 found 186.1075

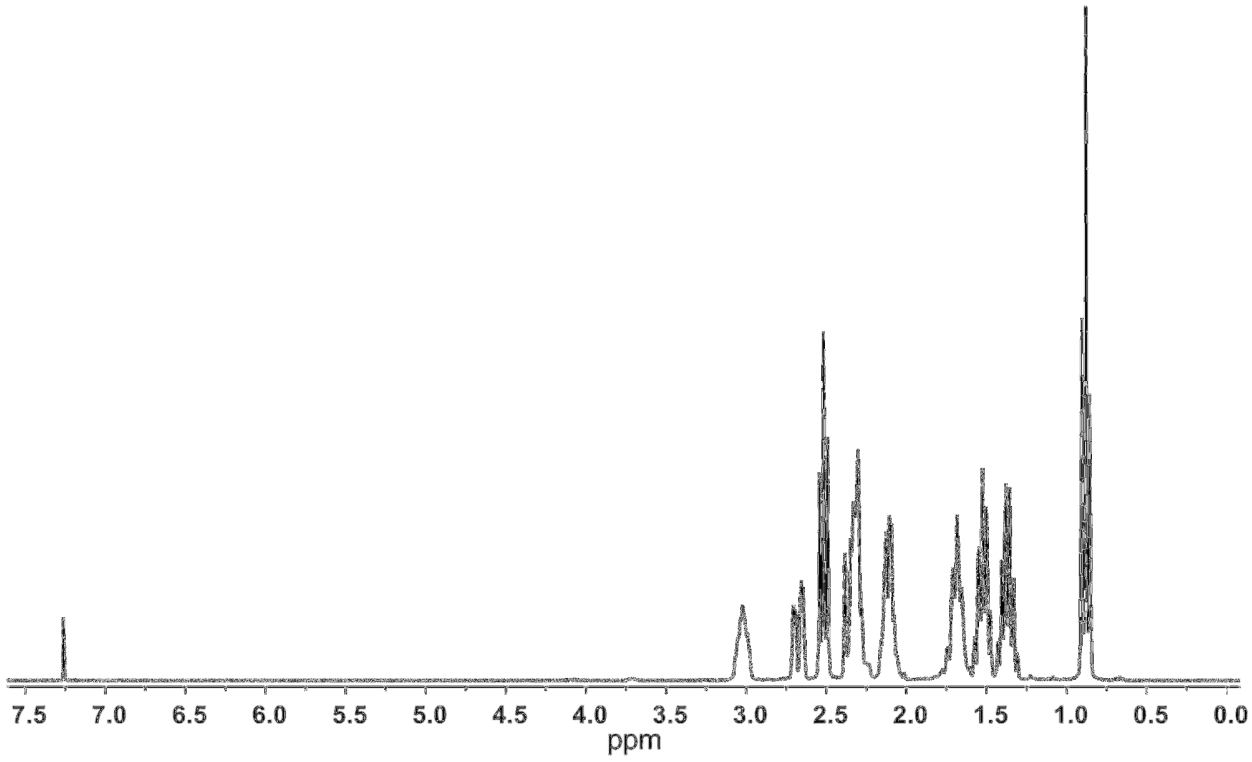

Figure S 4: ^{1}H-NMR (300 MHz/$CDCl_3$) of 3-(*n*-butylthio)cyclohexanone **(2)**.

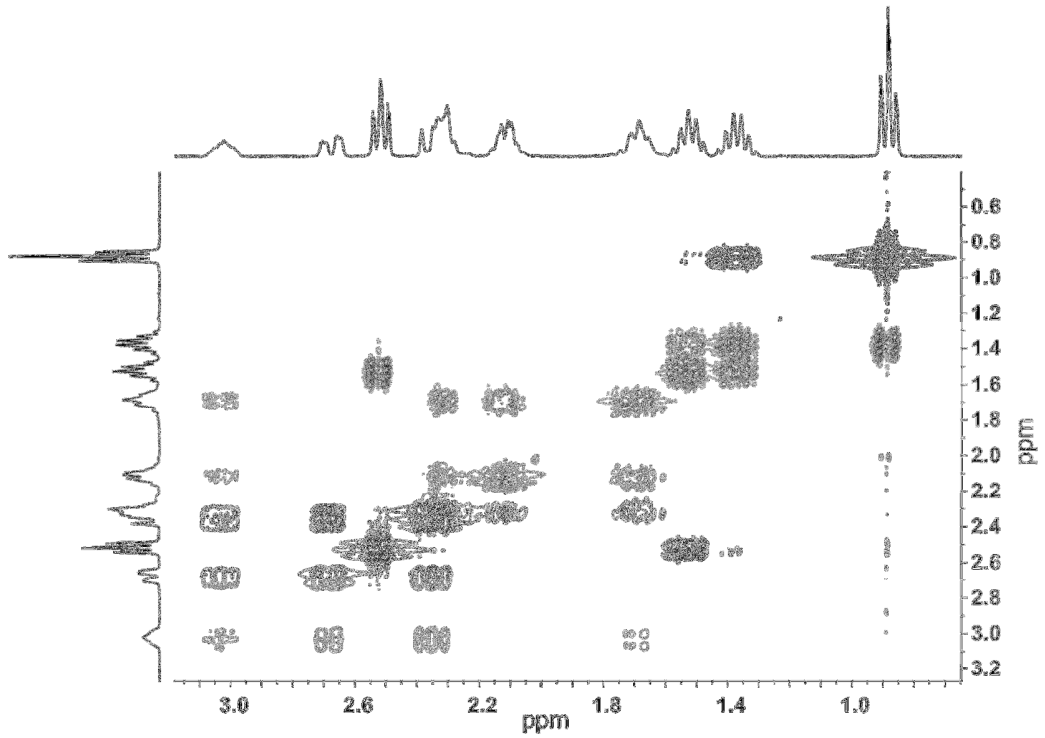

Figure S 5: ^{1}H-COSY-NMR (300 MHz/$CDCl_3$) of 3-(*n*-butylthio)cyclohexanone **(2)**.

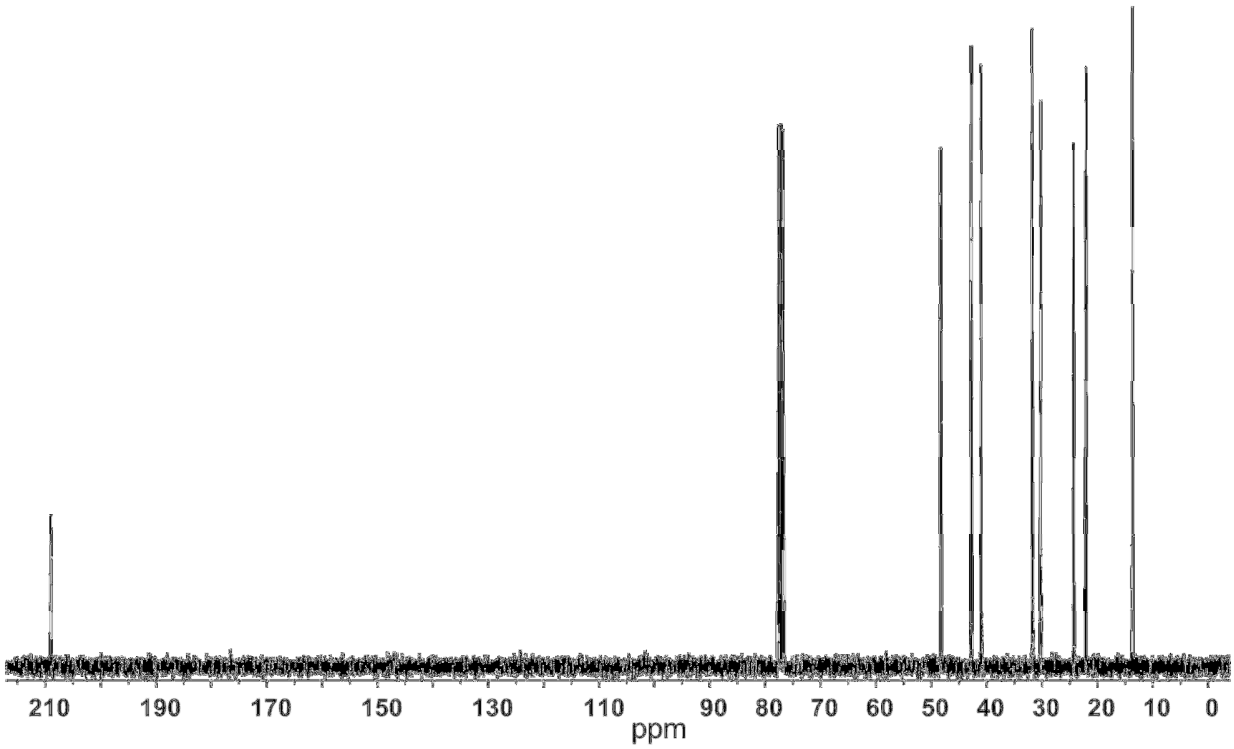

Figure S 6: ^{13}C-NMR (75 MHz/$CDCl_3$) of 3-(*n*-butylthio)cyclohexanone **(2)**.

3-(cyclohexylthio)cyclohexanone (3)

Pure **3** was obtained as light yellow oil (yield 91 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 3.19 – 3.03 (m, 1H, -S-C*H*-), 2.78 – 2.59 (m, 2H, -CH-CH_2-C(O)-, -S-C*H*-), 2.42 – 2.20 (m, 3H, -CH_2-(CO)-CH_2-), 2.19 – 2.02 (m, 2H, -CH-CH_2-CH_2-), 1.98 – 1.81 (m, 2H, -CH_2-), 1.80 – 1.50 (m, 5H, -CH_2-), 1.38 – 1.11 (m, 5H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 209.2, 48.9, 42.4, 41.2, 41.0, 34.1, 34.0, 32.2, 26.1, 26.1, 25.8, 24.5.

HRMS (EI):
$C_{12}H_{20}OS$ calc. 212.1229 found 212.1230

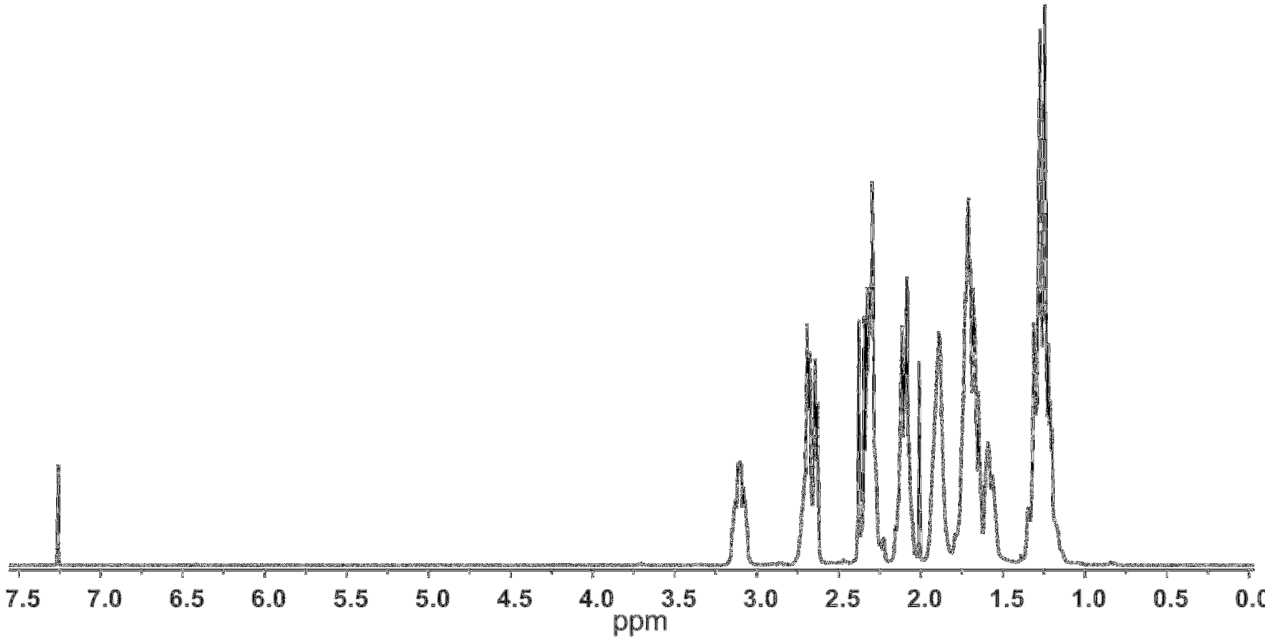

Figure S 7: ^{1}H-NMR (300 MHz/$CDCl_3$) of 3-(cyclohexylthio)cyclohexanone **(3)**.

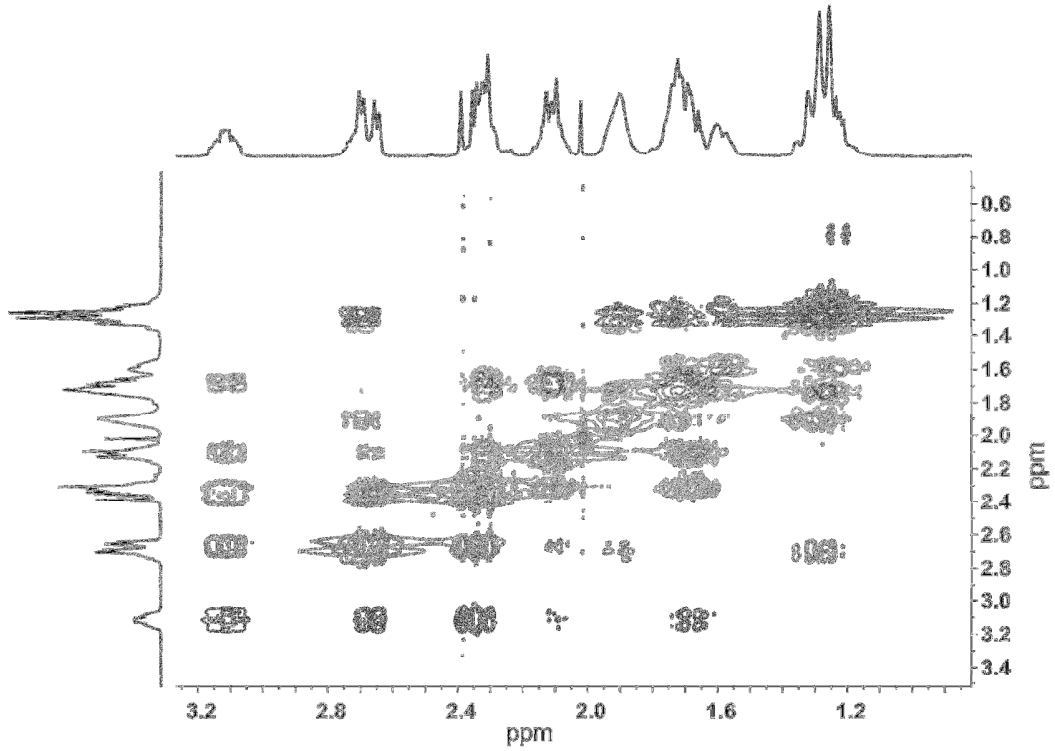

Figure S 8: ^{1}H-COSY-NMR (300 MHz/$CDCl_3$) of 3-(cyclohexylthio)cyclohexanone **(3)**.

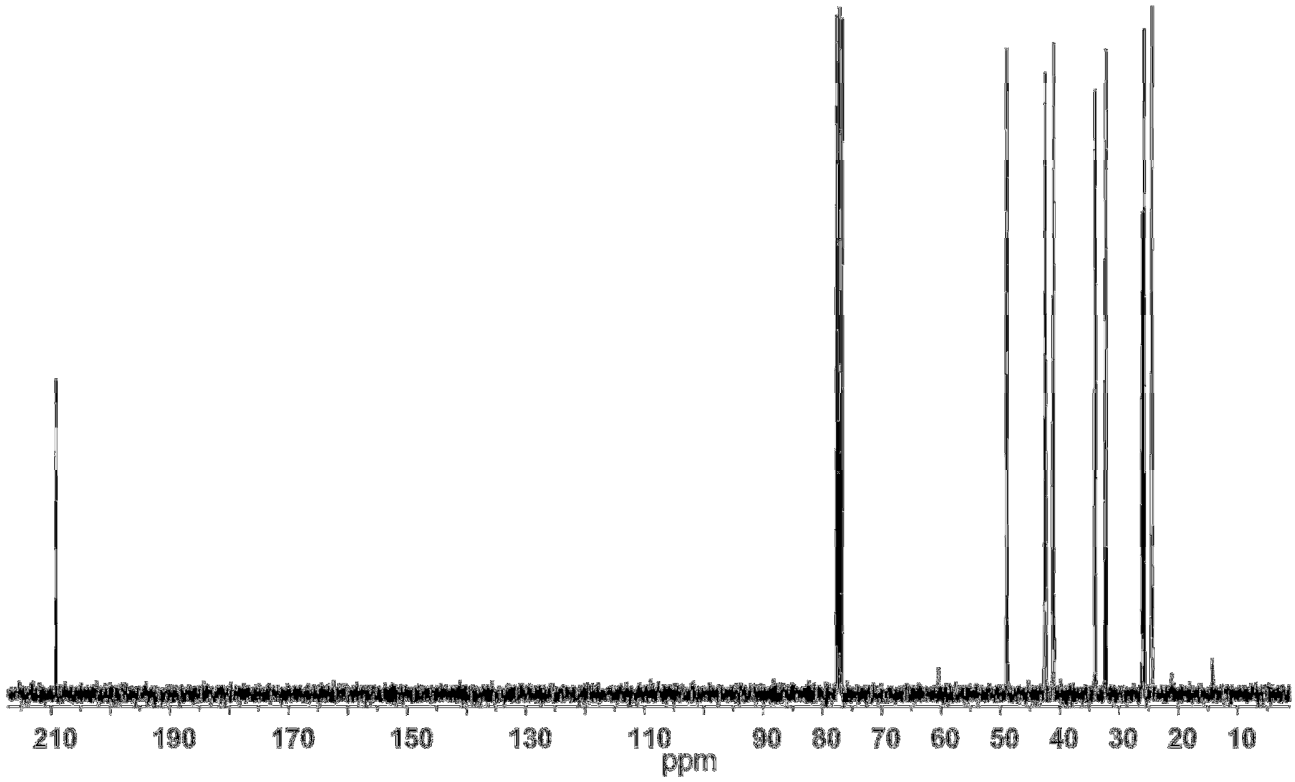

Figure S 9: ^{13}C-NMR (75 MHz/$CDCl_3$) of 3-(cyclohexylthio)cyclohexanone **(3)**.

3-(benzylthio)cyclohexanone (4)

Pure **4** was obtained as light yellow oil (yield 95 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.36 – 7.19 (m, 5H, Ph), 3.75 (s, 2H, -C*H*$_2$-Ph), 3.01 – 2.86 (m, 1H, -S-C*H*-), 2.66 (dd, *J* = 14.2, 4.5 Hz, 1H, -CH-C*H*$_2$-C(O)-), 2.45 – 2.23 (m, 3H, -C*H*$_2$-(CO)-C*H*$_2$-), 2.18 – 2.00 (m, 2H, -CH-C*H*$_2$-CH_2-), 1.81 – 1.56 (m, 2H, -CH_2-C*H*$_2$-CO-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 208.7, 138.0, 128.8, 128.7, 127.2, 47.8, 42.0, 41.0, 35.0, 31.3, 24.1.

HRMS (EI):
$C_{13}H_{16}OS$ calc. 220.0916 found 220.0917

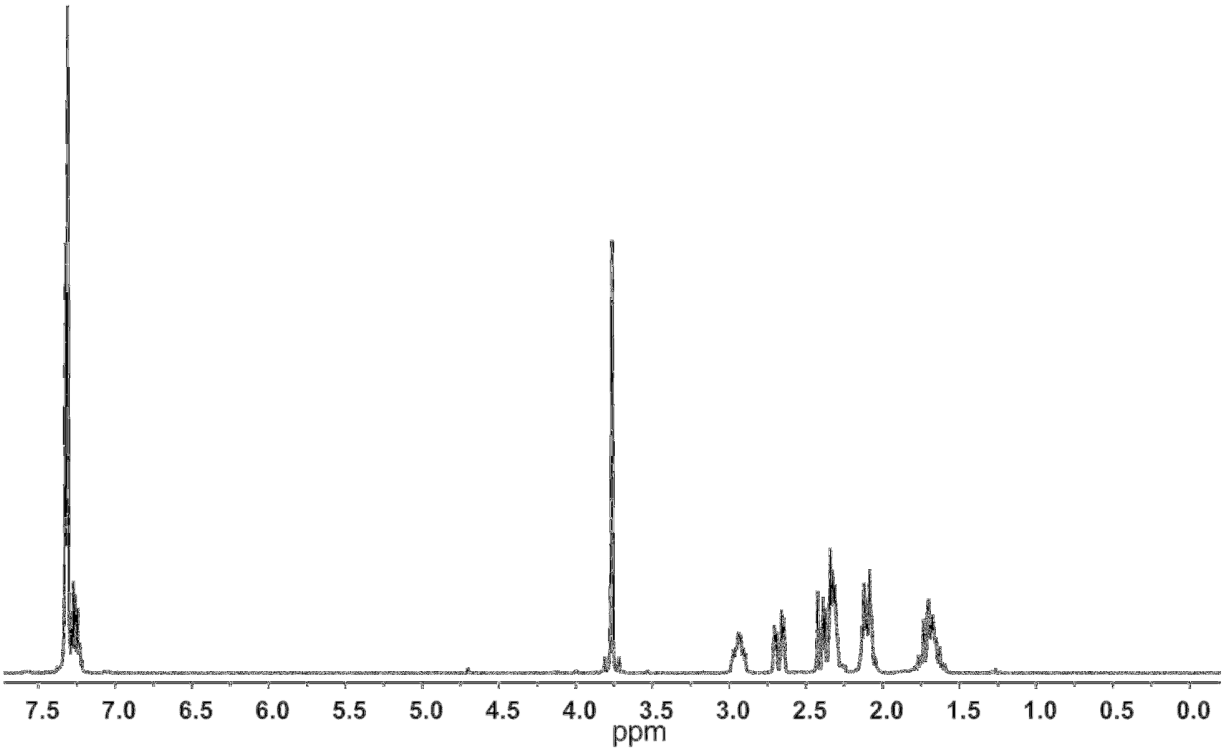

Figure S 10: ^{1}H-NMR (300 MHz/$CDCl_3$) of 3-(benzylthio)cyclohexanone **(4)**.

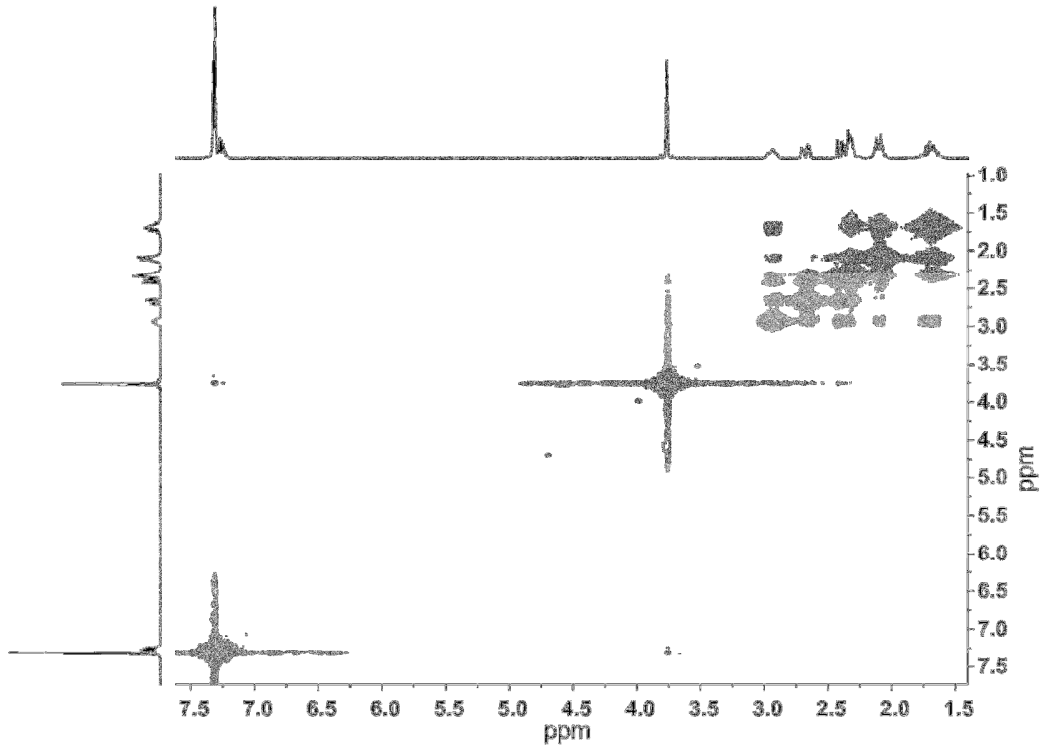

Figure S 11: ^{1}H-COSY-NMR (300 MHz/$CDCl_3$) of 3-(benzylthio)cyclohexanone **(4)**.

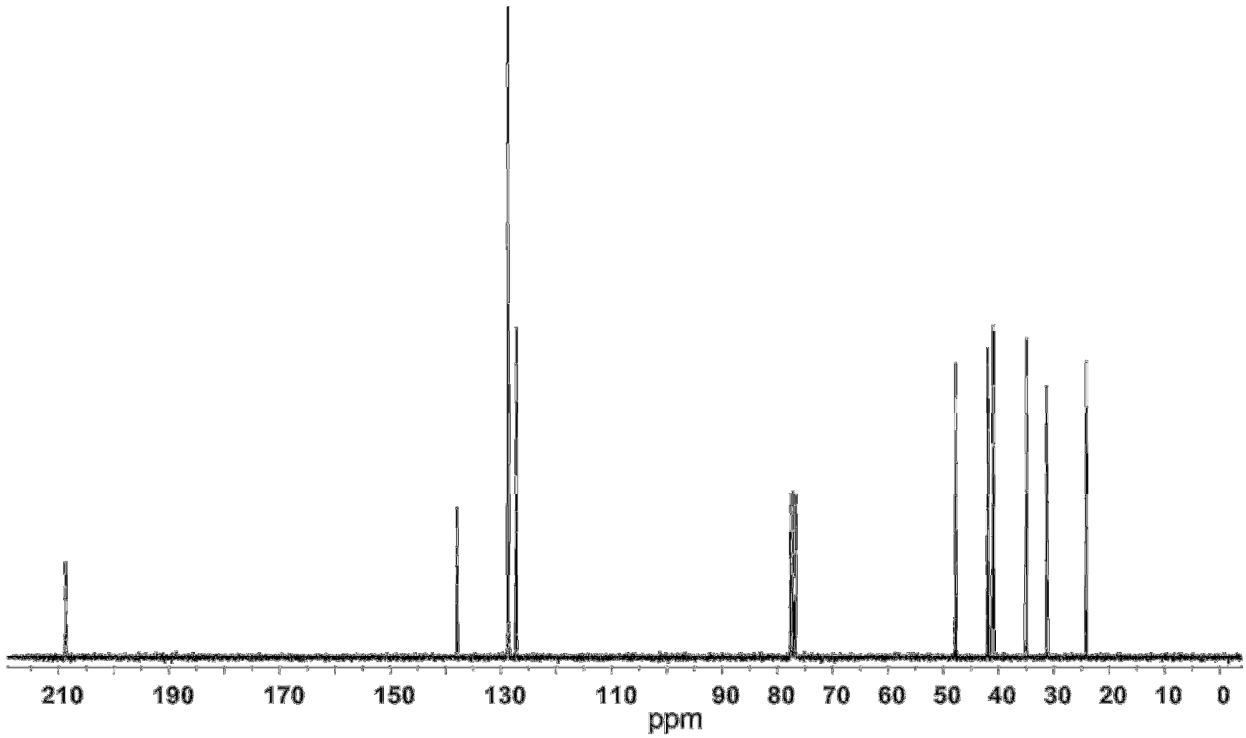

Figure S 12: ^{13}C-NMR (75 MHz/$CDCl_3$) of 3-(benzylthio)cyclohexanone **(4)**.

b. 1. General procedure for conventional Baeyer-Villiger oxidations:

The cyclohexanone substrate **1** - **4** (16.1 mmol) was dissolved in 75 mL dichloromethane and cooled with an ice bath. Subsequently, *m*CPBA 3.5 eq. was added in small portions and the reaction mixture was stirred overnight. To the crude product 75 mL dichloromethane was added and the reaction mixture was filtered. The solvent was evaporated and the crude product was dissolved in acetone and purified via column chromatography using hexane : acetone = 2 : 1 as eluent. If the product was still contaminated with *m*CPBA residues a second short column was performed using hexane : acetone = 1 : 1 as eluent.

2. Baeyer-Villiger oxidations using oxone®:

The cyclohexanone substrate **1** - **4** (4.54 mmol) was dissolved in 20 mL DMF, set under an argon atmosphere and cooled with an ice bath. Subsequently, 7.68 g oxone® (25.0 mmol) was added in small portions and the reaction mixture was stirred for 24 hours slowly warming to room temperature. Another portion of oxone® (4.5 mmol) was added and the reaction mixture was stirred for further 24 hours. Afterwards, reaction mixture was filtered, 100 mL dichloromethane was added and the reaction mixture was washed with saturated NaCl solution (1×80 mL). The aqueous phase was again extracted with dichloromethane and the combined organic layers were dried over Na_2SO_4. The crude product was further purified by column chromatography using hexane : acetone = 2 : 1 as eluent.

3. Baeyer-Villiger oxidations using urea hydrogen peroxide / TFAA:

5.0 g Urea hydrogen peroxide (52.8 mmol), 4.5 g Na_2HPO_4 (31.8 mmol) were weighted in a round bottom flask and set under an argon atmosphere. The cyclohexanone substrate **1** - **4** (4.54 mmol) dissolved in 70 mL dry dichloromethane was added. The mixture was cooled with an ice bath and 6.68 g trifluoroacetic anhydride (31.8mmol) was slowly added. The reaction mixture was stirred for 48 hours slowly warming to room temperature. The crude reaction mixture was washed with $NaHCO_3$ (1×25 ml), saturated NaCl solution (1×25 mL) and dried over Na_2SO_4. After evaporation of the solvent the crude product was analyzed via GC-MS and NMR analysis.

4. Baeyer-Villiger oxidations using hydrogen peroxide and Novozyme 435:

Method a)

The cyclohexanone substrate **1** - **4** (1.6 mmol) was dissolved in 2 mL toluene, 0.69 g octanoic acid (4.81 mmol) and 50 mg Novozyme 435 were added. To the reaction mixture, 2×1 mL H_2O_2 (30%) was added at 0 hours and 72 hours. The reaction mixture was stirred at 50 °C for 7 days. The crude reaction mixture was diluted with 25 mL dichloromethane and washed with $NaHCO_3$ (1x10 ml), saturated NaCl solution (1x10 mL) and dried over Na_2SO_4. After evaporation of the solvent the crude product was analyzed via GC-MS and NMR analysis.

Method b)

The cyclohexanone substrate **1** - **4** (1.5 mmol) was dissolved in 5 mL ethyl acetate, 50 mg Novozyme 435 and urea-hydrogen peroxide (8.0 mmol) were added. The reaction mixture was stirred for 7 days. Subsequently, the crude reaction mixture was diluted with 25 mL ethyl acetate and washed with $NaHCO_3$ (1×10 ml), saturated NaCl solution (1×10 mL) and dried over Na_2SO_4. After evaporation of the solvent the crude product was analyzed via GC-MS and NMR analysis.

Note: The yields given for the compounds **5** – **8** are related to the oxidation procedure making use of *m*CPBA.

6-(*n*-octylsulfonyl)oxepan-2-one (5)

Pure **5** was obtained as colorless solid (yield 82 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 4.42 – 4.34 (m, 1H, -C*H*$_2$-O-(CO)-), 4.29 – 4.20 (m, 1H, -C*H*$_2$-O-(CO)-), 3.21 – 2.87 (m, 5H, -C*H*$_2$-SO_2-, -(CO)-C*H*$_2$-, -SO_2-C*H*-), 2.51 – 2.39 (m, 1H, -C*H*$_2$-), 2.30 – 2.17 (m, 1H, -C*H*$_2$-), 2.08 – 1.74 (m, 4H, -C*H*$_2$-), 1.50 – 1.38 (m, 2H, -C*H*$_2$-), 1.37 – 1.21 (m, 8H, -C*H*$_2$-), 0.88 (t, *J* = 6.7 Hz, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 171.2, 68.7, 55.9, 50.6, 34.1, 31.8, 29.1, 29.0, 28.7, 27.3, 26.8, 22.7, 21.7, 14.2.

HRMS (FAB):
$C_{14}H_{26}O_4S$ $[M+H]^+$ calc. 291.1625 found 291.1626

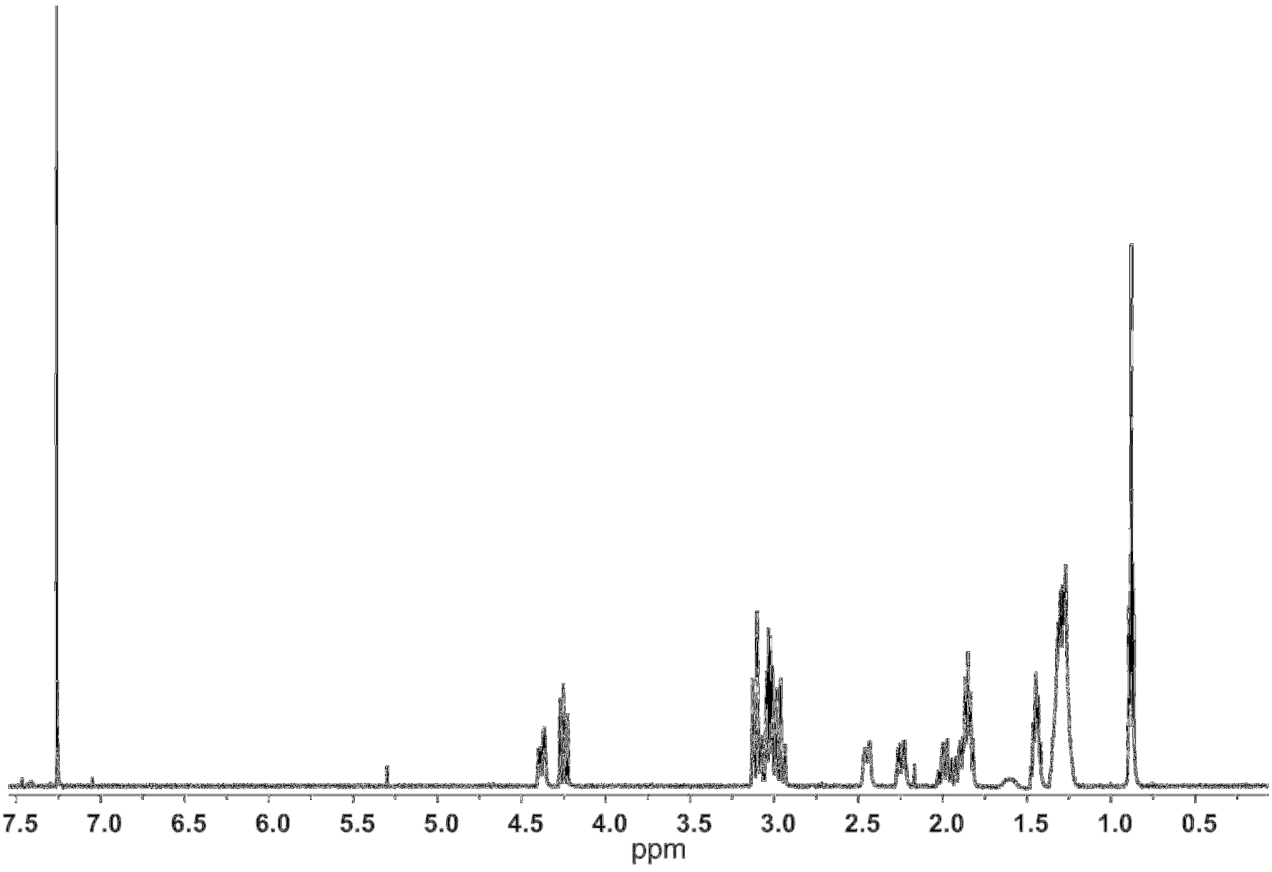

Figure S 13: ^{1}H-NMR (500 MHz/$CDCl_3$) of 6-(*n*-octylsulfonyl)oxepan-2-one **(5)**.

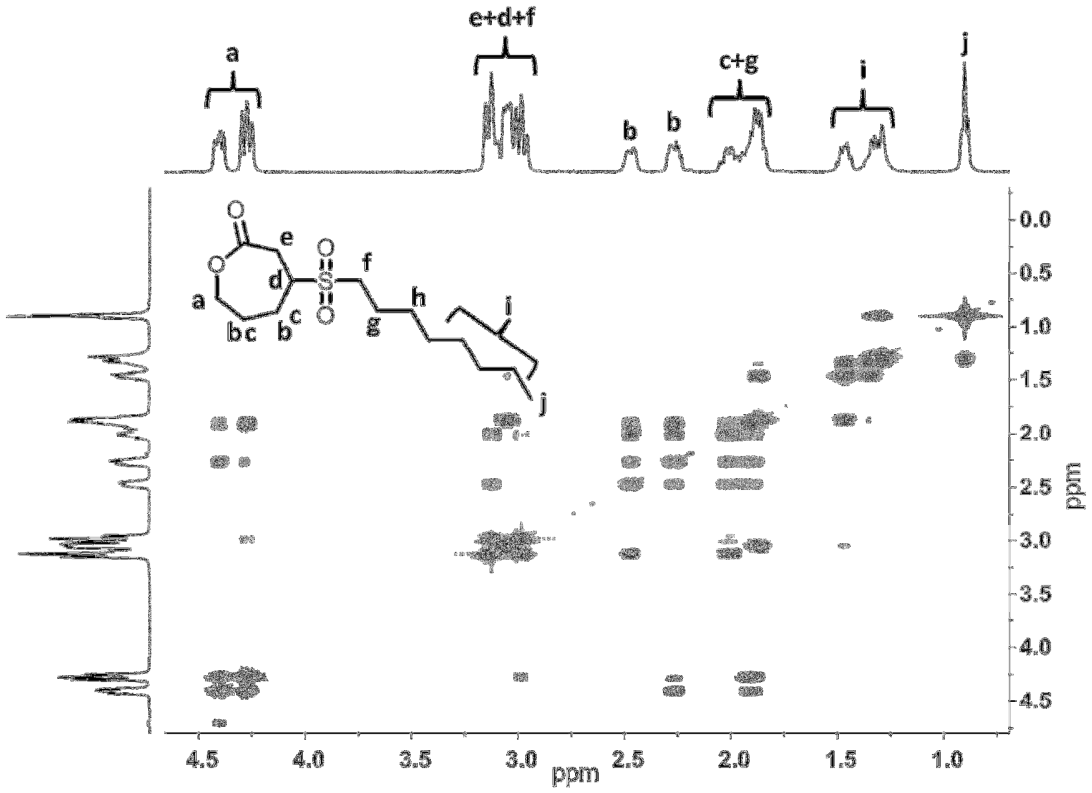

Figure S 14: ^{1}H-COSY-NMR (500 MHz/$CDCl_3$) of 6-(*n*-octylsulfonyl)oxepan-2-one **(5)**.

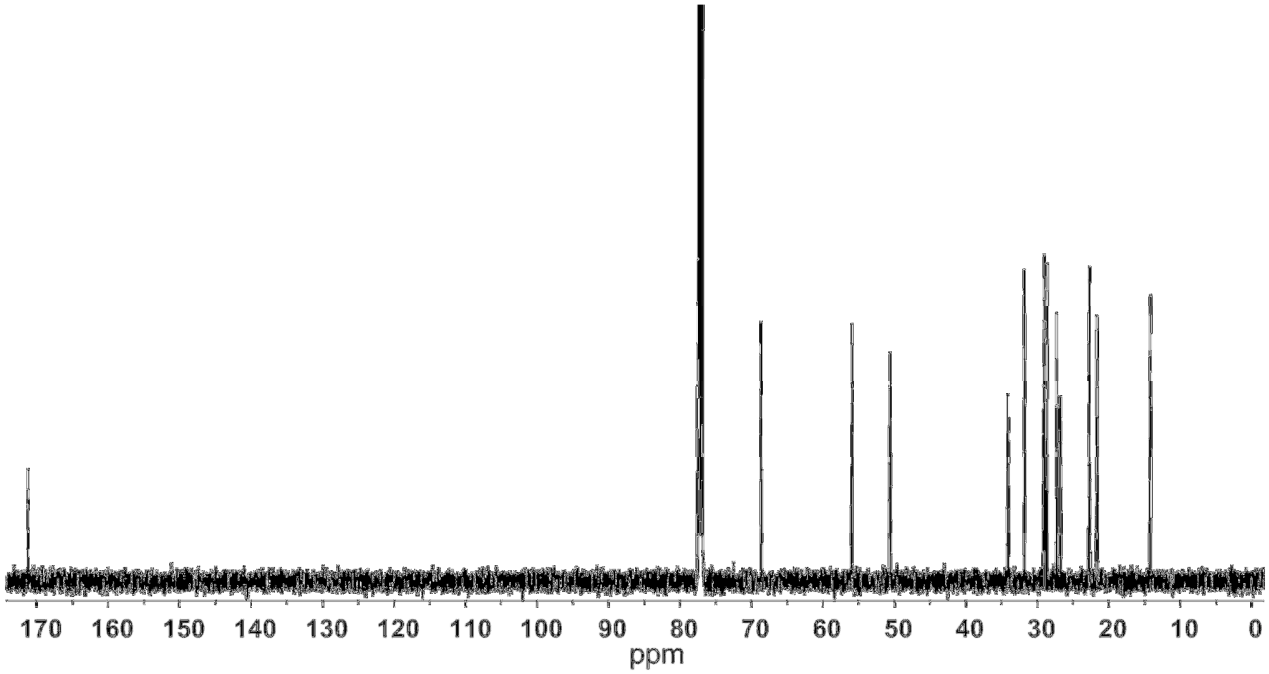

Figure S 15: ^{13}C-NMR (75 MHz/$CDCl_3$) of 6-(*n*-octylsulfonyl)oxepan-2-one (**5**).

6-(*n*-butylsulfonyl)oxepan-2-one (6)

Pure **6** was obtained as light yellow and highly viscous oil (yield 77 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 4.45 – 4.33 (m, 1H, -C*H*$_2$-O-(CO)-), 4.31 – 4.18 (m, 1H, -C*H*$_2$-O-(CO)-), 3.18 – 2.89 (m, 5H, -C*H*$_2$-SO_2-, -(CO)-C*H*$_2$-, -SO_2-C*H*-), 2.53 – 2.38 (m, 1H, -C*H*$_2$-), 2.33 – 2.19 (m, 1H, -C*H*$_2$-), 2.08 – 1.76 (m, 4H, -C*H*$_2$-), 1.57 – 1.39 (m, 2H, -C*H*$_2$-), 0.98 (t, *J* = 7.3 Hz, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 171.5, 68.6, 55.9, 50.1, 33.7, 30.9, 29.2, 27.1, 26.9, 23.5, 23.3, 21.8, 13.6.

HRMS (FAB):

$C_{10}H_{18}O_4S$ $[M+H]^+$ calc. 235.0999 found 235.0996

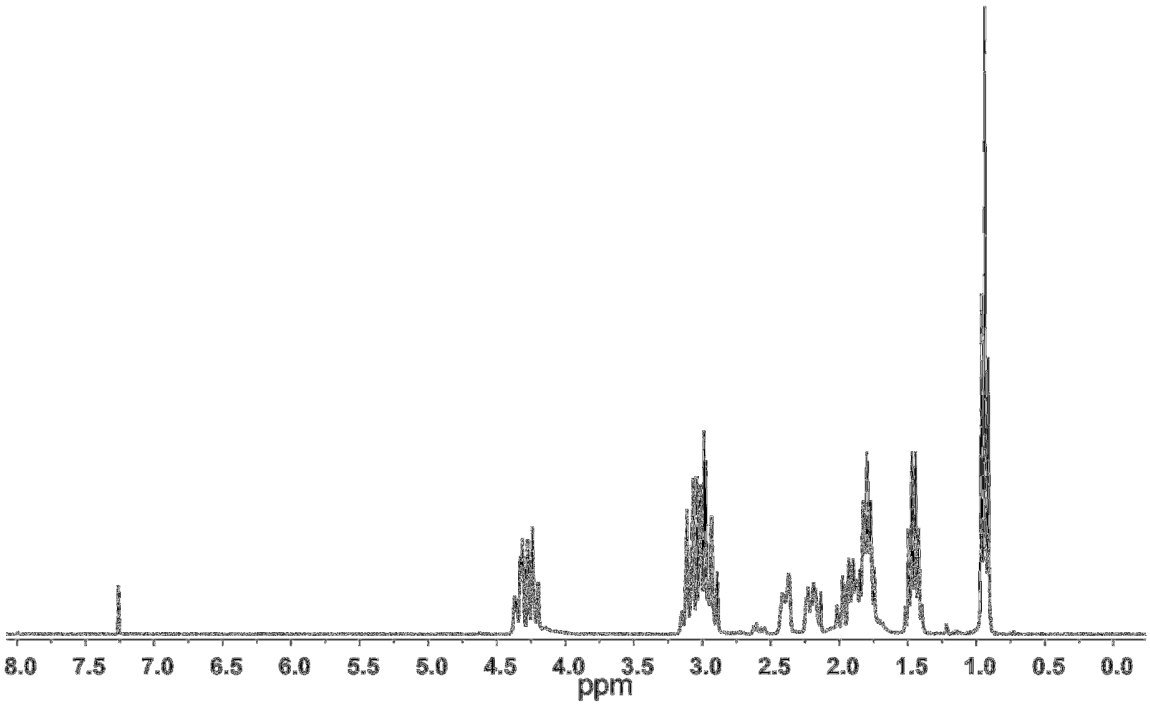

Figure S 16: ^{1}H-NMR (300 MHz/$CDCl_3$) of 6-(*n*-butylsulfonyl)oxepan-2-one **(6)**.

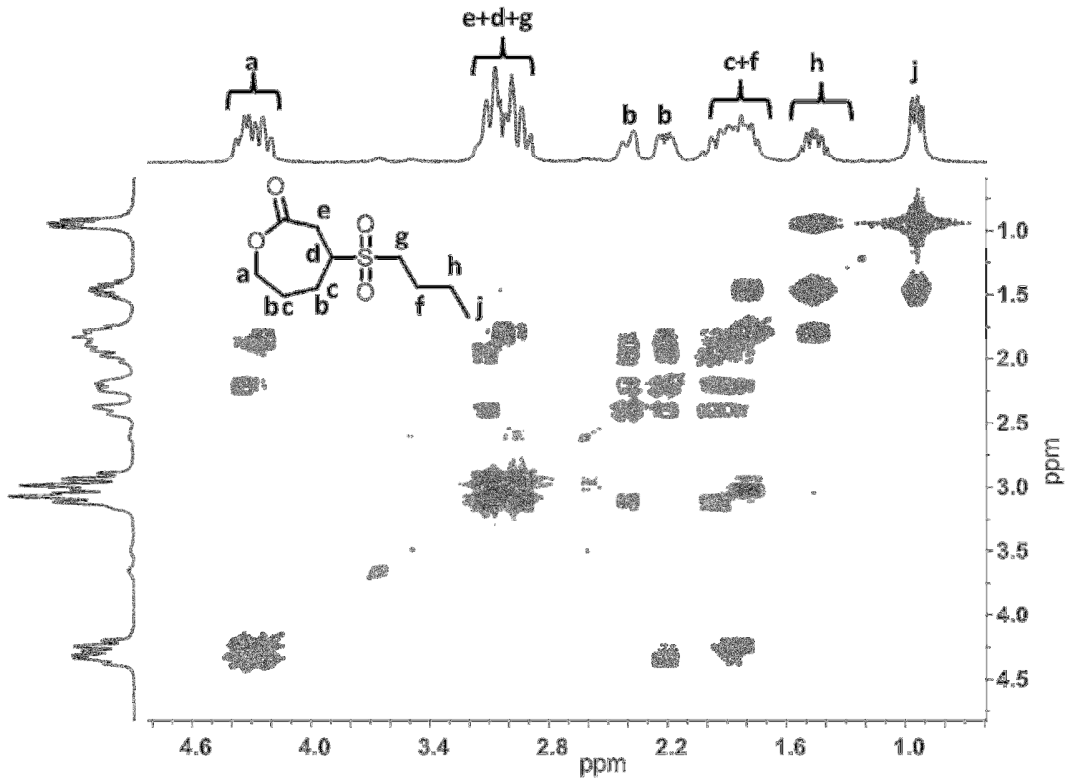

Figure S 17: ^{1}H-COSY-NMR (300 MHz/$CDCl_3$) of 6-(*n*-butylsulfonyl)oxepan-2-one **(6)**.

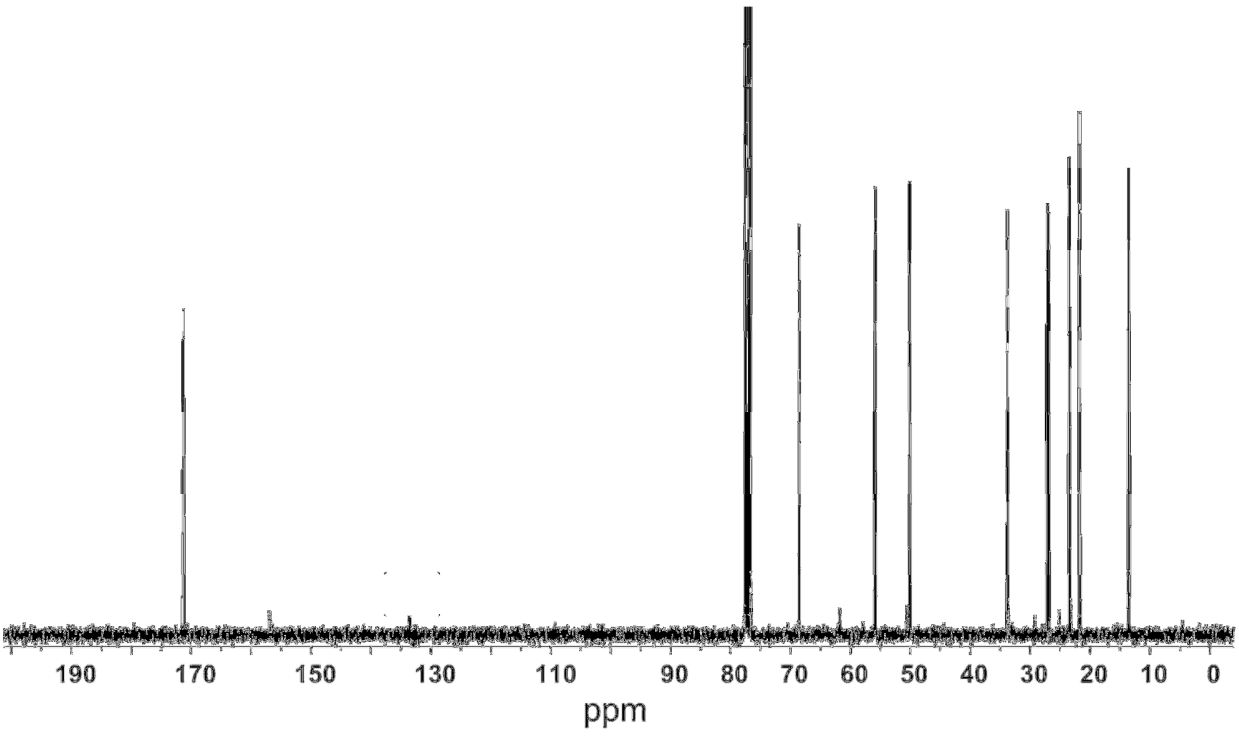

Figure S 18: ^{13}C-NMR (75 MHz/$CDCl_3$) of 6-(*n*-butylsulfonyl)oxepan-2-one **(6)**.

6-(cyclohexylsulfonyl)oxepan-2-one (7)

Pure **7** was obtained as colorless solid (yield 79 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 4.46 – 4.18 (m, 2H, -C*H*$_2$-O(CO)-), 3.30 – 2.87 (m, 4H, -C*H*-SO_2-C*H*-, -(CO)-C*H*$_2$), 2.48 – 2.35 (m, 1H, -CH_2-C*H*-), 2.31 – 2.18 (m, 1H, -C*H*$_2$-CH-), 2.16 – 1.82 (m, 5H, -C*H*$_2$), 1.79 – 1.45 (m, 4H, -C*H*$_2$), 1.43 – 1.16 (m, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 171.5, 68.7, 58.5, 52.5, 33.9, 27.3, 26.7, 25.3, 25.1, 25.1, 24.4.

HRMS (FAB):

$C_{12}H_{20}O_4S$ $[M+H]^+$ calc. 261.1155 found 261.1152

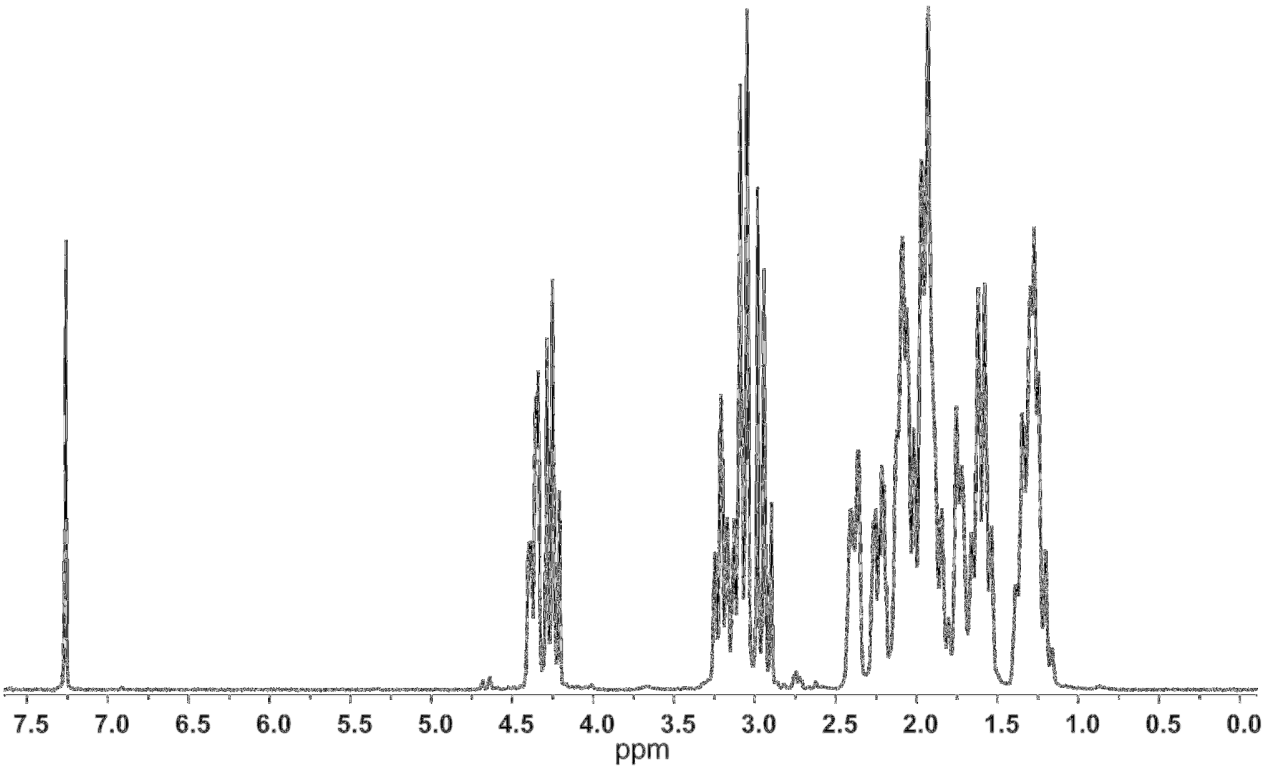

Figure S 19: ^{1}H-NMR (300 MHz/$CDCl_3$) of 6-(cyclohexylsulfonyl)oxepan-2-one **(7)**.

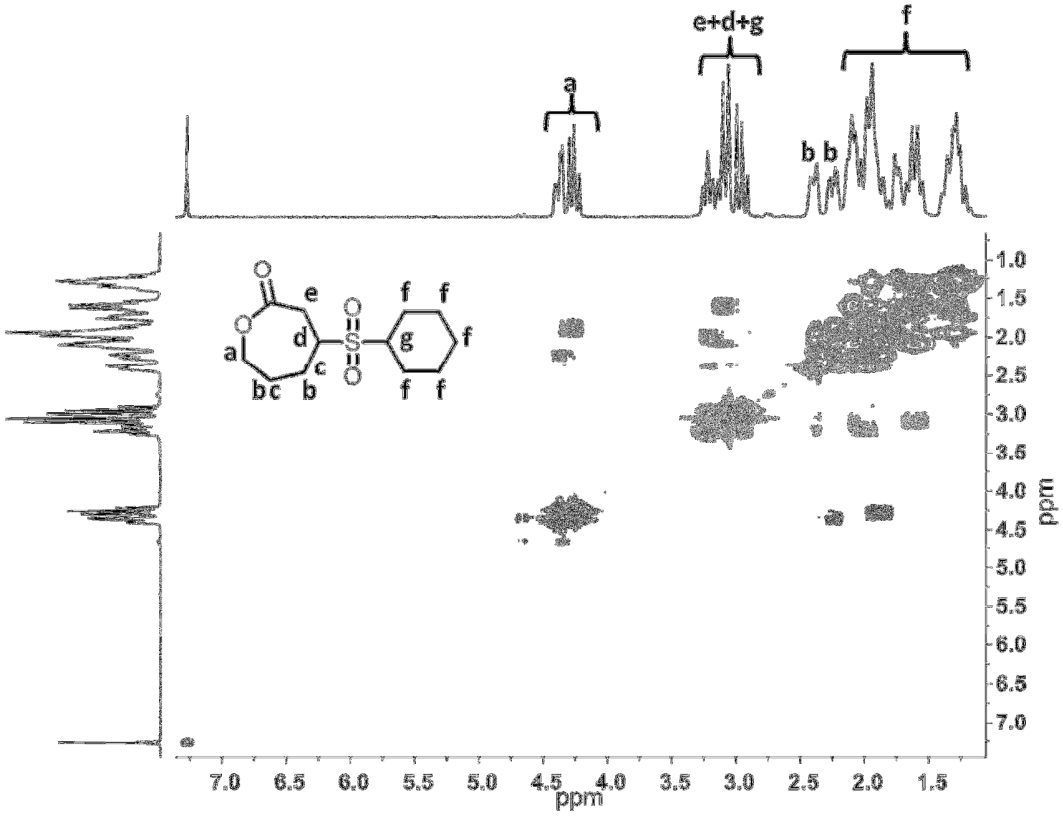

Figure S 20: ^{1}H-COSY-NMR (300 MHz/$CDCl_3$) of 6-(cyclohexylsulfonyl)oxepan-2-one **(7)**.

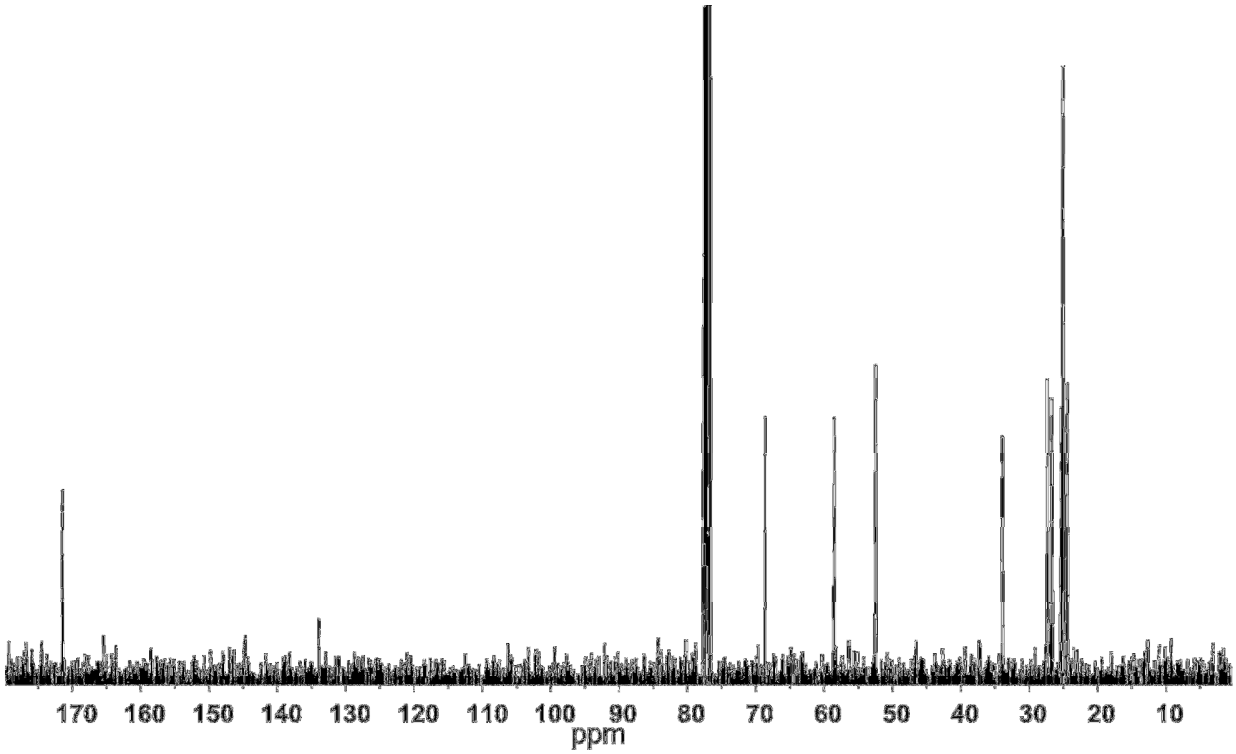

Figure S 21: ^{13}C-NMR (75 MHz/$CDCl_3$) of 6-(cyclohexylsulfonyl)oxepan-2-one **(7)**.

6-(benzylsulfonyl)oxepan-2-one (8)

Pure **8** was obtained as colorless solid (yield 85 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ /ppm: 7.53 – 7.35 (m, 5H, -Ph), 4.49 – 4.12 (m, 4H, -C*H*$_2$-O-(CO)-, -C*H*$_2$-Ph), 3.19 – 3.05 (m, 1H, -C*H*), 3.04 – 2.89 (m, 2H, -C*H*$_2$), 2.44 – 2.30 (m, 1H, -C*H*$_2$), 2.26 – 2.12 (m, 1H, -C*H*$_2$), 2.06 – 1.87 (m, 1H, -C*H*$_2$), 1.86 – 1.69 (m, 1H, -C*H*$_2$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 170.9, 130.8, 129.45, 129.4, 127.2, 68.6, 57.1, 53.5, 34.4, 27.1, 26.4.

HRMS (FAB):
$C_{13}H_{16}O_4S$ $[M+H]^+$ calc. 269.0842 found 269.0844

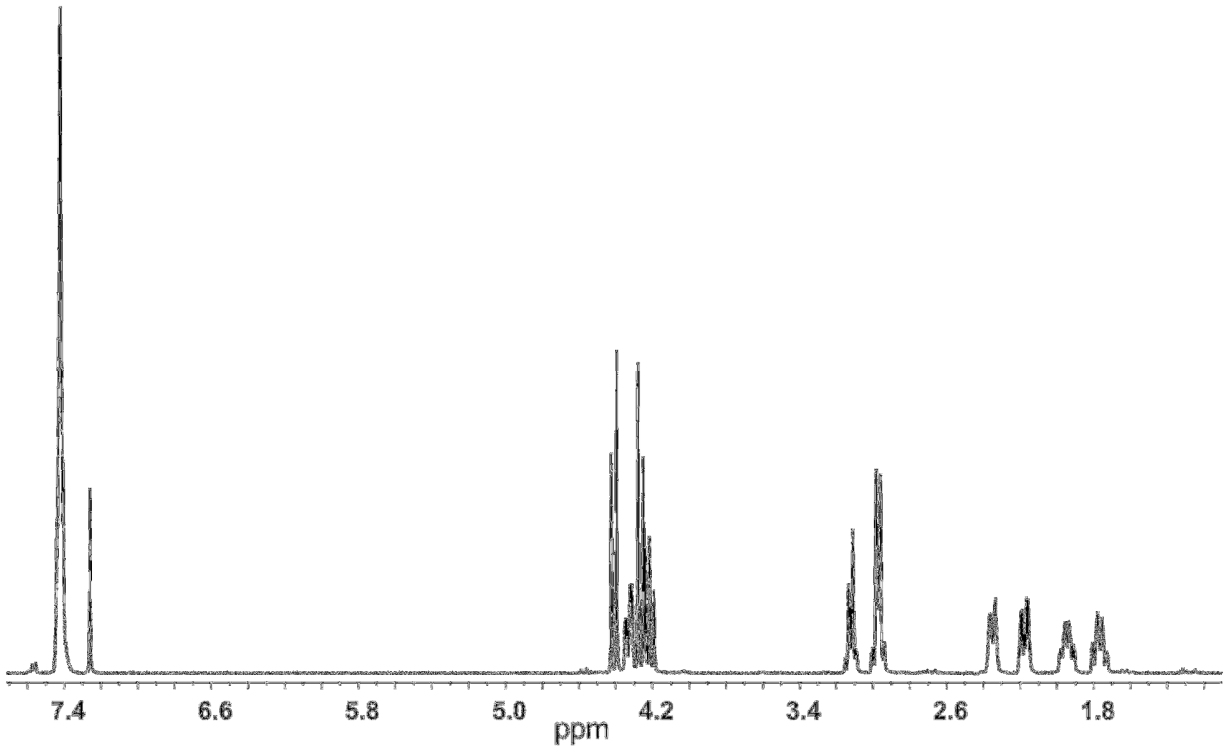

Figure S 22: ^{1}H-NMR (300 MHz/$CDCl_3$) of 6-(benzylsulfonyl)oxepan-2-one **(8)**.

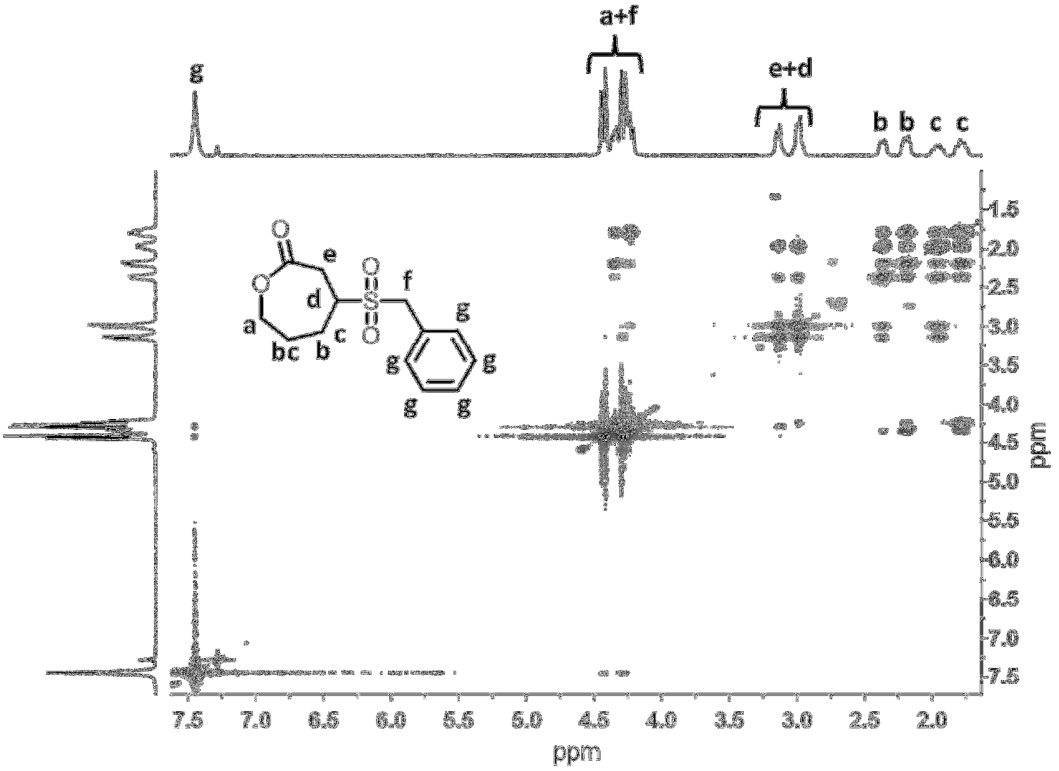

Figure S 23: ^{1}H-COSY-NMR (500 MHz/$CDCl_3$) of 6-(benzylsulfonyl)oxepan-2-one **(8)**.

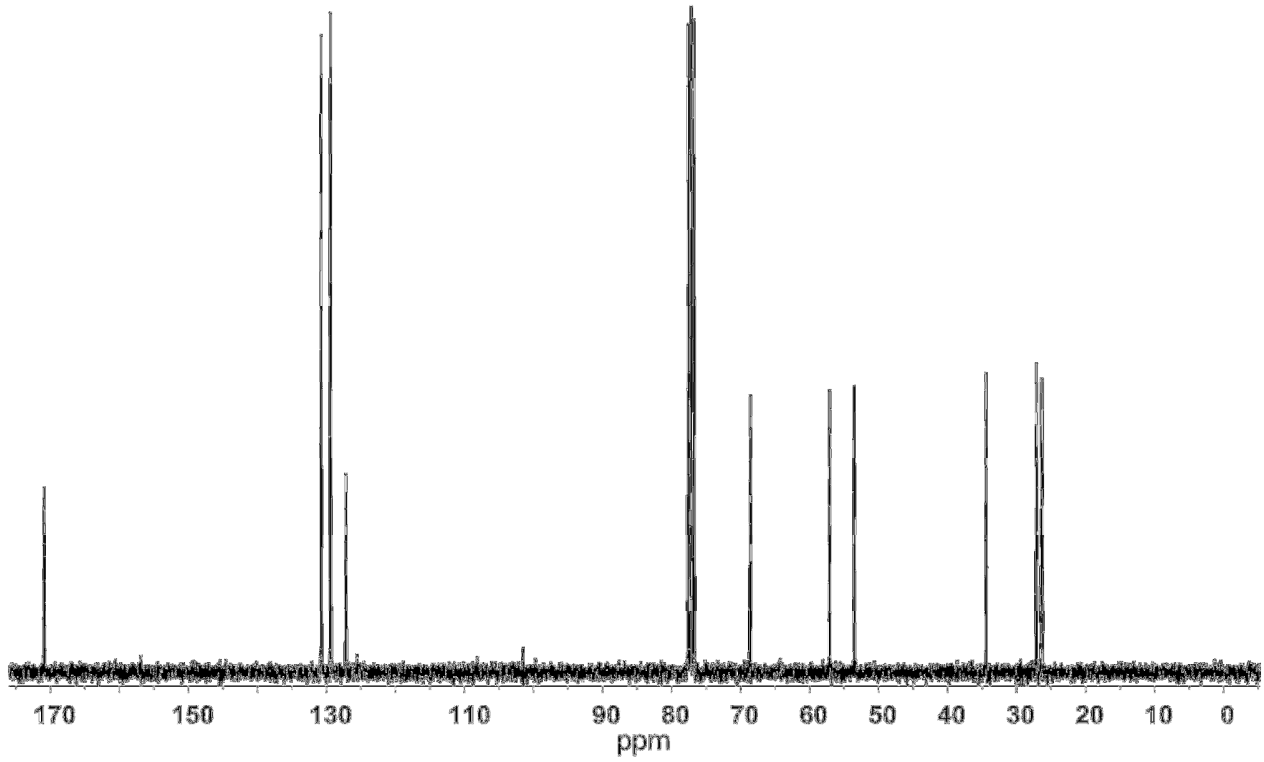

Figure S 24: ^{13}C-NMR (75 MHz/$CDCl_3$) of 6-(benzylsulfonyl)oxepan-2-one **(8)**.

c. General procedure for the synthesis of polyesters:

Monomer **5** – **8** (0.40 g) was weighed in a 5 mL round bottom flask, heated to 150 °C and degased with argon for 15 min. Subsequently, the corresponding amount of 1-octanol (1/20, 1/30, 1/40 or 1/50 mol) and tin(II) octanoate (1/20 mol to 1-octanol) was added. Depending on the monomer to initiator ratio the polymerization was quenched after 2 – 4 hours by cooling the reaction mixture in an ice bath. The polymer was dissolved in THF and precipitated in a mixture of cold hexane : acetone = 10 : 1.

Note: Octanol and tin (II) octanoate were added as solution in dry toluene 0.627 mol/L and $3.1 \cdot 10^{-3}$ mol/L, respectively.

Polyester P9 octyl

^{1}H-NMR ($CDCl_3$, 300 MHz) δ /ppm: 4.32 – 4.02 (m, 2H, -C*H*$_2$-O-), 3.82 – 3.68 (m, 1H, -(CO)-C*H*$_2$-), 3.59 – 3.41 (m, 1H, -C*H*-), 3.08 – 2.88 (m, 3H, -SO_2-C*H*$_2$, -CH-C*H*$_2$-), 2.68 – 2.51 (m, 1H, (CO)-C*H*$_2$-), 2.16 – 1.97 (m, 1H, -C*H*$_2$-), 1.96 – 1.65 (m, 5H, -C*H*$_2$-), 1.52 – 1.15 (m, 9H, -C*H*$_2$-), 0.88 (t, *J* = 6.6 Hz, 3H, -C*H*$_3$).

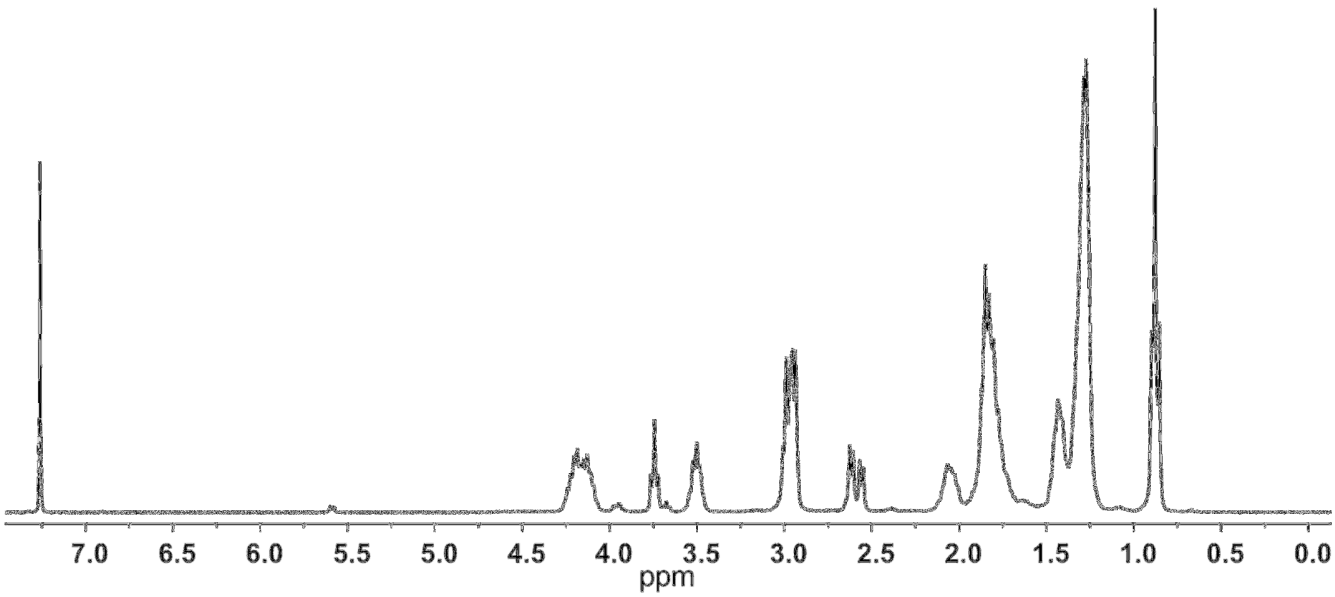

Figure S 25: ^{1}H-NMR (300 MHz/$CDCl_3$) of Polyester **P9**.

Polyester P3 butyl

^{1}H-NMR ($CDCl_3$, 300 MHz) δ /ppm: 4.31 – 4.03 (m, 2H, -C*H*$_2$-O-), 3.80 – 3.68 (m, 1H, -(CO)-C*H*$_2$-), 3.59 – 3.44 (m, 1H, -C*H*-), 3.07 – 2.87 (m, 3H, -SO_2-C*H*$_2$, -CH-C*H*$_2$-), 2.68 – 2.52 (m, 1H, (CO)-C*H*$_2$-), 2.17 – 1.97 (m, 1H, -C*H*$_2$-), 1.94 – 1.68 (m, 3H, -C*H*$_2$-), 1.57 – 1.39 (m, 2H, -C*H*$_2$-), 1.36 – 1.21 (m, 1H, -C*H*$_2$-), 0.97 (t, *J* = 7.3 Hz, 3H, -C*H*$_3$).

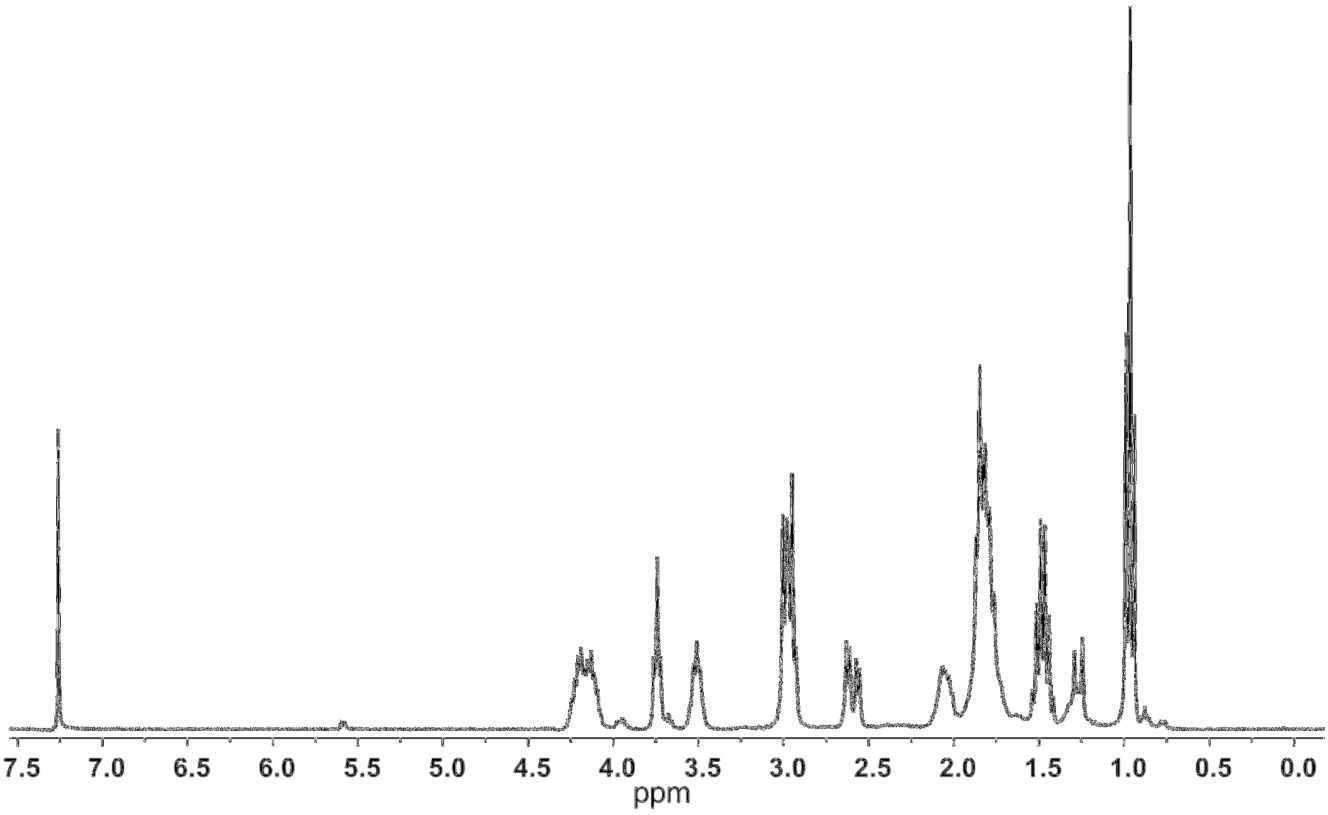

Figure S 26: ^{1}H-NMR (300 MHz/$CDCl_3$) of Polyester **P3**.

Polyester P8 cyclohexyl

^{1}H-NMR ($CDCl_3$, 300 MHz) δ /ppm: 4.31 – 4.04 (m, 2H, -C*H*$_2$-O-), 3.82 – 3.71 (m, 1H, -(CO)-C*H*$_2$-), 3.72 – 3.56 (m, 1H, -C*H*-), 3.09 – 2.88 (m, 2H, -C*H*-, -C*H*$_2$-), 2.68 – 2.51 (m, 1H, -(CO)-C*H*$_2$-), 2.24 – 1.67 (m, 7H, -C*H*$_2$-), 1.67 – 1.47 (m, 2H, -C*H*$_2$-), 1.44 – 1.15 (m, 4H, -C*H*$_2$-).

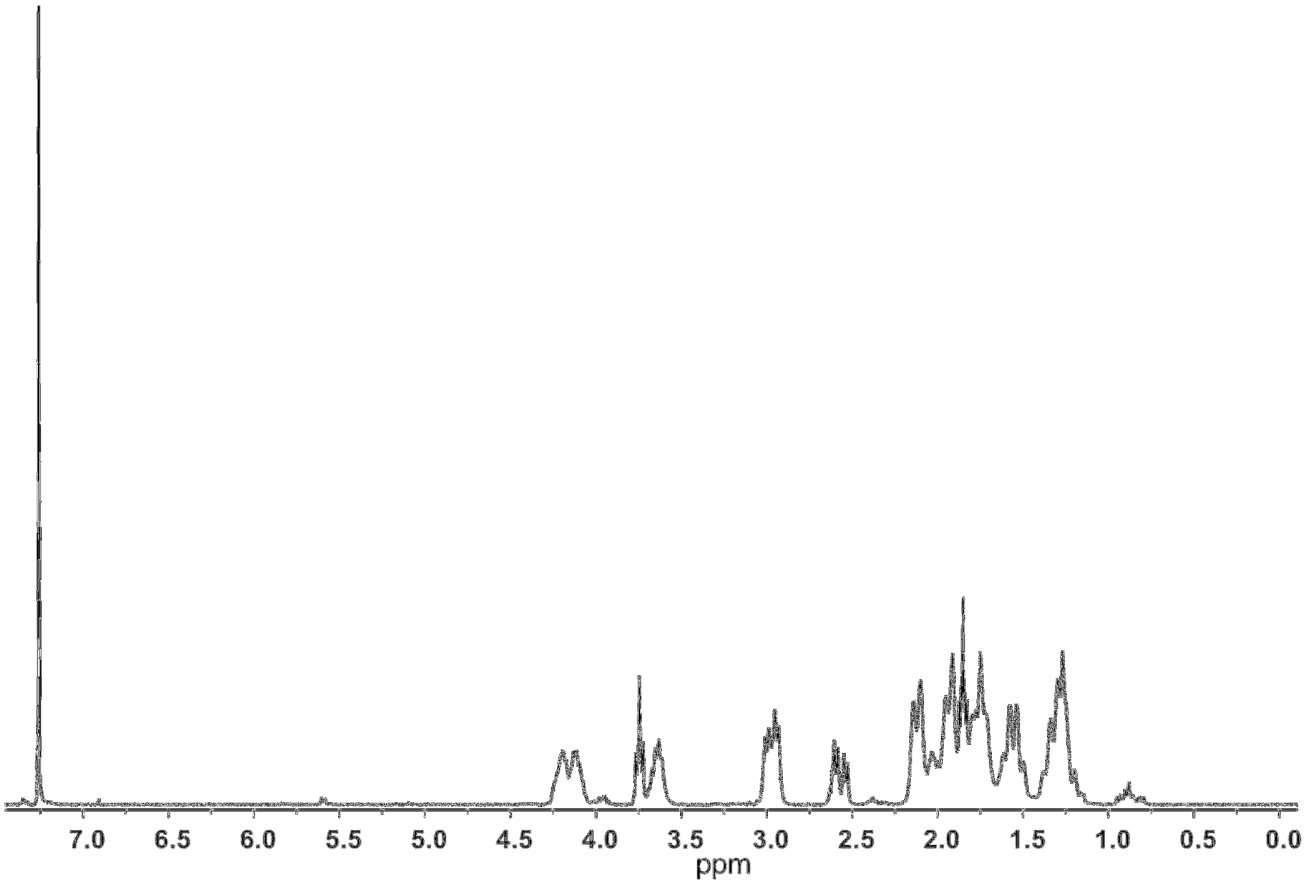

Figure S 27: ^{1}H-NMR (300 MHz/$CDCl_3$) of Polyester **P8**.

Polyester P10 benzyl

^{1}H-NMR ($CDCl_3$, 300 MHz) δ /ppm: 7.45 – 7.31 (m, 5H, -Ph), 4.37 – 3.89 (m, 4H, -C*H*$_2$-O-, -C*H*$_2$-Ph), 3.62 – 3.41 (m, 1H, -C*H*-), 2.99 – 2.79 (m, 1H, -(CO)-C*H*$_2$-), 2.62 – 2.44 (m, 1H, -(CO)-C*H*$_2$-), 2.06 – 1.81 (m, 1H, -C*H*$_2$-), 1.79 – 1.46 (m, 3H, -C*H*$_2$-).

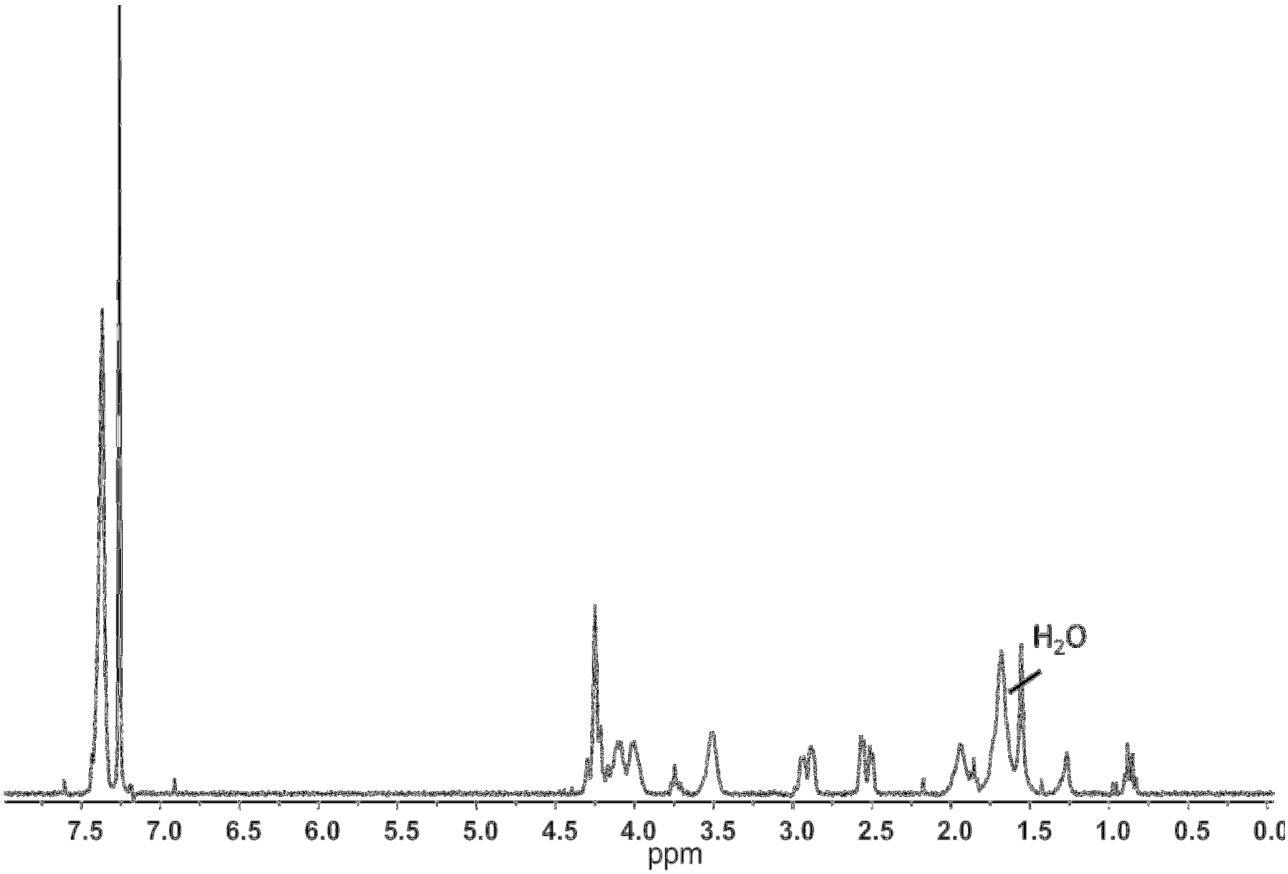

Figure S 28: ^{1}H-NMR (300 MHz/$CDCl_3$) of Polyester **P10**.

Table S 1: Results of the SEC and DSC analysis of the prepared polyesters **P5** – **P7** using monomer **7** and different monomer to initiator ([M] : [I]) ratios.

Polymer	[M] : [I]	$M_{n,\,theo.}$ [Da]	$M_{n,\,SEC}$ [Da]	Đ
P6	20 : 1	5333	3760	1.16
P7	30 : 1	7935	6340	1.11
P8	40 : 1	10536	7680	1.17

Synthesis and stability test of (*n*-butylsulfonyl)cyclohexane

1.0 g cyclohexene (12.2 mmol) and 5.5 g *n*-butanethiol (61.0 mmol) were added in a quartz glass vial. 2,2-dimethoxy-2-phenylacetophenone (DMPA) (2 mol%) was added and the reaction was stirred for 16 hours under uv light (251 nm) irradiation. Afterwards, ethyl acetate (20 mL) was added and the crude reaction mixture was washed with 1M HCl (2 x 20 mL), 1M NaOH (2 x 20 mL), H_20 (1 x 20 mL) and brine (1 x 20 mL), dried over Na_2SO_4 and evaporated to dryness. 0.5 g of the obtained yellow oil was diluted with dichloromethane (20 mL) and mCPBA (3.5 equivalents) was carefully added under ice cooling. The reaction mixture was stirred for 16 hours at room temperature. Subsequently, 20 mL dichloromethane was added and the crude product was washed with a saturated solution of $Na_2S_2O_3$ (20 mL), Na_2SO_3 (20 mL) and NaCl (20 mL), dried over Na_2SO_4 and evaporated to dryness. Pure (n-butylsulfonyl)cyclohexane was obtained by column chromatography (hexane : ethyl acetate = 5:1 → 3:1).

To 0.1 g (*n*-butylsulfonyl)cyclohexane (0.49 mmol) , tin(II)octanoate (1/20 mol to *n*-octanol) and *n*-octanol (0.0245 mmol) was added. The reaction mixture was stirred for 4 hours at 150 °C and then analyzed by ^{1}H-NMR analysis.

Note: Octanol and tin (II) octanoate were added as solution in dry toluene.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ /ppm: 2.97 – 2.74 (m, 3H, -C*H*$_2$-SO$_2$-C*H*-), 2.21 – 2.06 (m, 2H, -C*H*$_2$-), 2.00 – 1.86 (m, 2H, -C*H*$_2$-), 1.86 – 1.64 (m, 3H, -C*H*$_2$-), 1.62 – 1.38 (m, 4H, -C*H*$_2$-), 1.37 – 1.11 (m, 3H, -C*H*$_2$-), 0.95 (t, *J* = 7.3 Hz, 3H, --C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 60.9, 49.2, 25.2, 25.1, 23.4, 22.0, 13.7.

HRMS (FAB):

$C_{10}H_{20}O_2S$ $[M+H]^+$ calc. 205.1257 found 205.1262

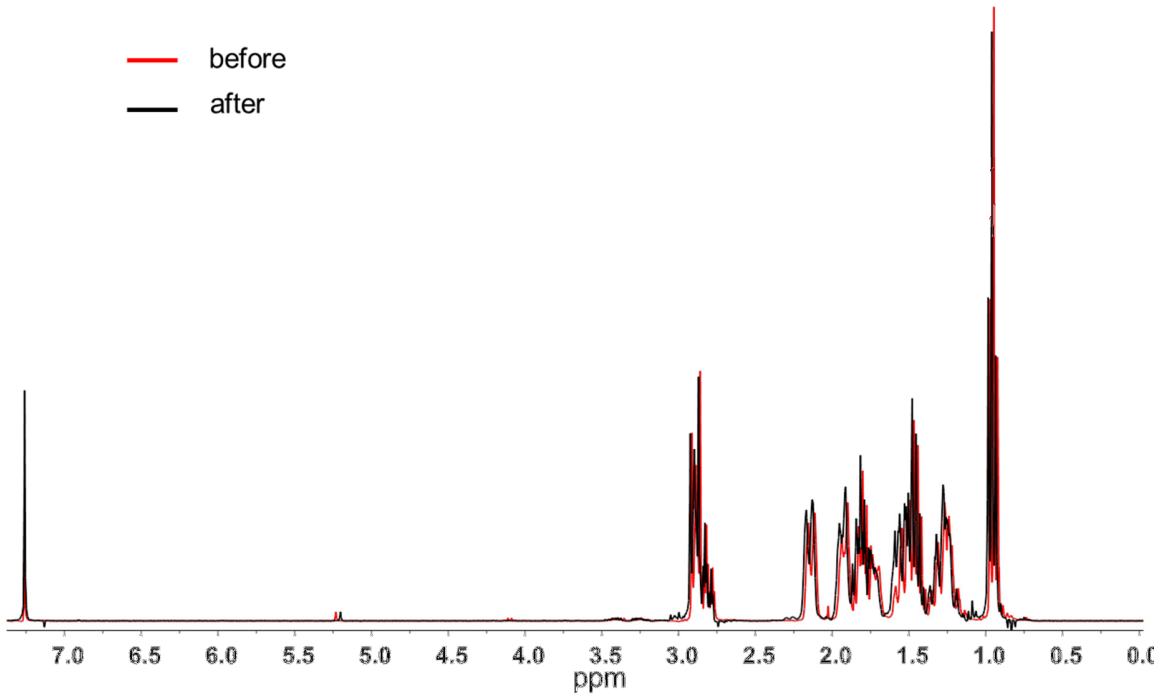

Figure S 29: ^{1}H-NMR (300 MHz/$CDCl_3$) of (*n*-butylsulfonyl)cyclohexane before and after the stability test.

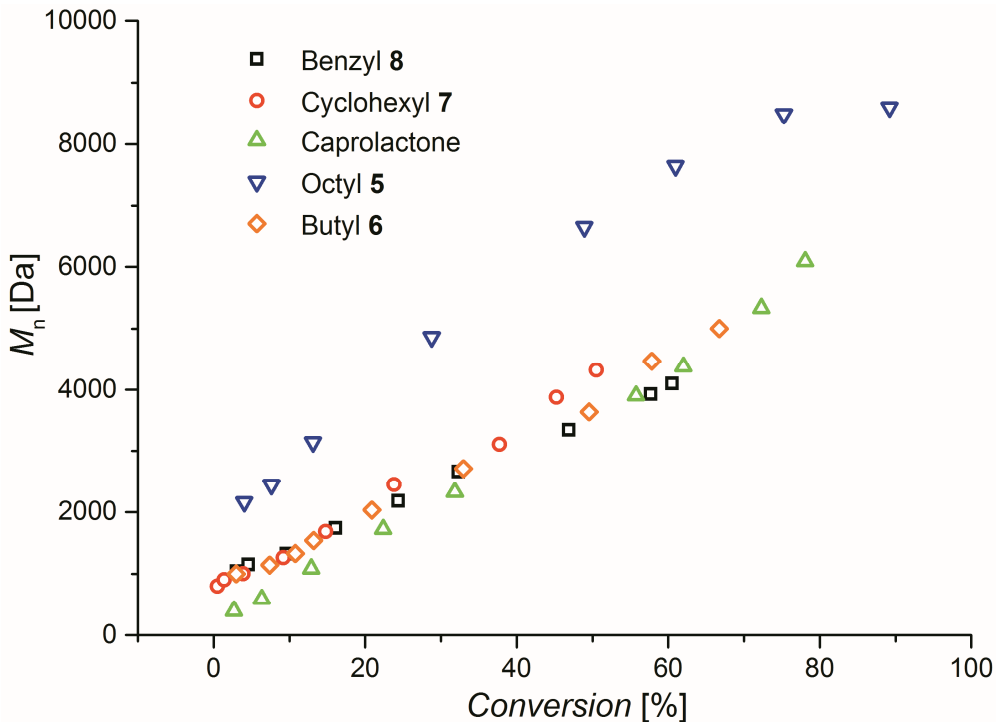

Figure S 30: Kinetic plot of the polymerization of the different modified CL monomers with a monomer to initiator ratio of [40] : [1].

References:

1. C.-S. Lu, E. W. Hughes and P. A. Giguère, *J. Am. Chem. Soc.*, 1941, **63**, 1507-1513.