

7 Experimental Section

7.1 General

All commercially available substances were purchased from Aldrich, Merck, Acros, Fluka, or Lancaster and used without further purification. Solvents were purified and dried – if necessary – according to standard methods.¹³¹ The catalysts Pd(PPh₃)₄, Pd[P(p-tol)]₃ and Pd[P(o-tol)]₃₂ were synthesized according to literature¹³² and stored in the dry-box. The nitrogen was purchased from Messer-Griesheim as nitrogen 4.0 or 5.0. For most of the Suzuki polycondensations the catalyst was prepared freshly.

7.2 Chromatography

TLC:

All reactions were monitored on silica gel alumina sheets (Merck, "Kieselgel 60", F254). For detection UV-light of the wavelengths $\lambda = 254$ nm or $\lambda = 366$ nm was used. Some of the compounds were spotted by putting the TLC plate either into a solution of 0.5 ml anisaldehyde (*p*-methoxy benzaldehyde), 50 ml glacial acetic acid, and 1 ml conc. sulfuric acid and heating it up to ~100 °C (for boranes, alcohols and ethers), or into an aqueous solution of potassium permanganate (0.5 %; for olefins), or into an iodine chamber (for oligoethylene glycols).

Column chromatography:

For column chromatography variable amounts of silica gel ("Kieselgel 60", 230-500 mesh ASTM, Merck) was used. Usually the raw product was preabsorbed onto small amounts of silica gel prior to put it into the column. For all chromatographed compounds the r_f value is given with respect of the eluent in the TLC. In some cases flash chromatography was used.

¹³¹ a) D. D. Perrin, W. L. F. Armarego *Purification of Laboratory Chemicals*, **1988**, 3rd Edition, Pergamon Press, Oxford, New York, Seoul, Tokyo; b) *Organikum, Organisch-chemisches Grundpraktikum* **1996**, 20. Auflage, Johann Ambrosius Barth Verlag, Heidelberg.

HPLC:

Reversed-Layer: *Analytical*: Knauer Eurosphere® 7µm C₁₈, 4·120 mm, UV-detection at 335 nm or 254 nm.

Preparative: Machery-Nagel, Nucleosil® 5µm C₁₈, 32·250 mm, UV-detection at 335 nm or 254 nm.

Silica gel: *Analytical*: Knauer Eurosphere® 7µm C₁₈, 4·120 mm, UV-detection at 335 nm or 254 nm.

Preparative: Knauer Eurosphere® 5µm C₁₈, 32·250 mm, UV-detection at 335 nm or 254 nm.

GPC (SEC):

Analytical: Waters Styragel HR 1 or HR 3 columns, Waters 2487 UV/VIS detector at 254 nm.

High temperature (135 °C): Styragel HT 6 L, eluent: 1,2,4-Trichlorobenzene; detector: UV S-3702 Soma.

Preparative: Polymer Laboratories Gel, Waters 484 and Knauer UV photometer detector at 254 nm. Tetrahydrofuran served as the mobile layer, the UV detection was performed vs. polystyrene (calibration) and toluene as the standard.

Dialysis

Spectra/Por CE (Cellulose Ester); Wet in 0.1 % sodium azide; MWCO: 1000; Flat Width: 16 mm; Length: 1 m.

7.3 Analysis**Melting point:**

Büchi SMP 510, uncorrected values.

NMR spectroscopy:

Bruker WH 270, Bruker AB 250, Bruker AC 500. The signal of the not-deuterated solvent served as internal standard (¹H: CDCl₃: 7.24 ppm, [D₆]-DMSO: 2.49 ppm, [D₃]-acetonitrile: 1.93 ppm; ¹³C: CDCl₃: 77.00, [D₆]-DMSO: 39.70 ppm, [D₃]-acetonitrile: 117.70 ppm). The

¹³² D. R. Coulson *Inorg. Synth.* **1972**, *13*, 121-124.

deuterated solvents were purchased from Merck and Deutero GmbH. All spectra were recorded at 20 °C.

Solid State NMR spectroscopy

The solid state NMR experiment was performed on a Varian InfinityPlus NMR spectrometer operating at a field of 14.09 T (151 MHz for ^{13}C) using an Oxford wide bore (89 mm) superconducting magnet.

Mass spectrometry

Perkin-Elmer Varian Type MAT 771 and CH6 (EI), Type CH5DF (FAB), or Bruker Reflex (MALDI-TOF) respectively. Given are the kind of ionization (EI, FAB, MALDI-TOF), the potential of ionization (70 or 80 eV) and the temperature of the ion source (EI) or the matrix material (FAB and MALDI-TOF). MALDI-TOF: UV-Laser (337 nm), delayed extraction source, reflector mode. The high resolution mass spectra were obtained according to the peak match method (MAT 771).

Infrared spectroscopy:

Nicolet 5SXC (FT-IR Interferometer). All solids were investigated in potassium bromide and the oils as films between potassium bromide plates. Only characteristic bands of important functional groups are given.

Elemental analysis:

Perkin-Elmer EA 240. In most cases a deviation of up to 0.4 % from the calculated carbon value was accepted.

Thermal Gravimetric Analysis:

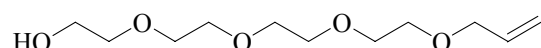
Netsch TGA 209, 20 to 600 °C, 10 K/min heating rate. N_2 as protective atmosphere.

7.4 Syntheses

Compounds **9**,⁶⁷ **11**,⁶⁹ **13**,⁷⁰ **15**,⁷⁰ **20**,⁷² **25**,⁷³ **28 a-b**,⁷⁵ **31 a-d**,⁷⁵ **33**,⁷⁹ **34**,⁷⁹ **42 a-c**,¹³³ **45**,¹³⁹ **47**,⁸⁴ **50 a**,⁸⁶ **75**,⁹³ **89**,⁹⁸ **90**,⁹⁸ **95**, **118**,¹⁰⁸ **133**,¹¹² **134**¹¹³ and **139**¹¹⁸ were prepared according to literature procedures.

7.4.1 Compounds of Chapter 4.2

2-{2-[2-(2-Allyloxy-ethoxy)-ethoxy]-ethoxy}-ethanol **8**



16.8 g (300 mmol) KOH were dissolved in 52.0 ml (300 mmol) tetraethylenglycol. The solution was cooled to 0 °C. 25.4 ml (300 mmol) allyl bromide were added dropwise. After complete addition the mixture was heated for 3 h at 60 °C. The mixture was cooled to rt and 400 ml ether were added. KBr was filtered off. The filtrate was concentrated and dissolved in 10 % hydrochloric acid. The aqueous solution was extracted three times with 100 ml ether to remove the twofold protected side product. Afterwards the aqueous layer was extracted two times with 100 ml CH₂Cl₂ to extract the desired product. The combined CH₂Cl₂ layers were dried over MgSO₄, filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; CH₂Cl₂/MeOH 19:1).

Yield: 25.0 g (36 %) colorless oil.

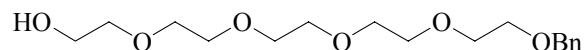
$r_f = 0.27$ (silica gel; MeCl₂/MeOH 19:1).

¹H NMR (CDCl₃, 250 MHz): $\delta = 2.98$ (s, 1 H, -OH), 3.57 (m, 16 H, -CH₂O-), 3.94 (d, ³J=7.6 Hz, 2 H, -CH₂-), 5.14 (m, 2 H, =CH₂), 5.83 (m, 1 H, -CH=) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 61.45, 69.20, 70.13, 70.40, 72.00, 72.36, 116.87, 134.54$ ppm.

MS (EI, 80 eV, 50°C): m/z (%) = 235 (1) [M+H]⁺, 191 (1) [M-C₂H₄O]⁺, 177 (1) [M-C₃H₆O]⁺, 163 (2) [M-C₄H₈O]⁺, 147 (3) [M-C₄H₈O₂]⁺, 45 (100) [C₃H₅O]⁺.

HRMS [¹²C₁₁¹H₂₂¹⁶O₅+H-C₂H₄O]⁺ calc.: 191.12833 found: 191.12632,
 [¹²C₁₁¹H₂₂¹⁶O₅+H-C₄H₈O]⁺ calc.: 163.09703 found: 163.09477.

2-(2-{2-[2-(2-Benzyloxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethanol 10

30.0 g (119.6 mmol) pentaethylene glycol were added to a solution of 6.94 g (60.0 mmol) KO^tBu in 100 ml ^tBuOH. After stirring for 20 h the solvent was evaporated and the residue was taken up in 30 ml dry dioxane. 6.95 ml (59.8 mmol) benzylchloride in 10 ml dry dioxane were added dropwise. The mixture was filtrated and the solvent evaporated. The crude product was mixed with 100 ml hydrochloric acid (pH 2) and three times extracted with each 50 ml ether. Afterwards the aqueous layer was extracted three times with 60 ml methylene chloride. The combined methylene chloride layers were dried over MgSO₄, filtrated and the solvent removed. The crude product was purified by column chromatography (silica gel; MeCl₂/MeOH 19:1).

Yield 10.16 g (52 %) of a colorless oil.

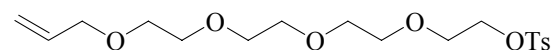
$r_f = 0.32$ (silica gel; MeCl₂/MeOH 19:1).

¹H NMR (CDCl₃, 250 MHz): $\delta = 2.95$ (s, 1 H, -OH), 3.59 (m, 20 H, -CH₂O-), 4.50 (s, 2 H, Hz, -CH₂Ph), 7.33 (m, 5 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 61.48, 69.26, 70.14, 70.39, 70.43, 72.38, 73.02, 127.38, 127.54, 128.15, 138.11$ ppm.

MS (pos. FAB, 3 kV): m/z (%) = 330 (1), 329 (8) [M+H]⁺, 285 (1), [M-C₂H₄O]⁺, 91 (100) [C₇H₇]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₁₇ H ₂₈ O ₆ | calc. | C 62.18 | H 8.59 |
| | (328.406) | found | 61.12 | 8.47 |

Toluene-4-sulfonic acid 2-{2-[2-(2-allyloxy-ethoxy)-ethoxy]-ethoxy}-ethyl ester 12

11.02 g (275.5 mmol) NaOH were dissolved in 60 ml water and added to a solution of 30.36 g (196.8 mmol) alcohol **8** in 50 ml THF. The mixture was cooled to 0 °C and a solution of 37.90 g (194.5 mmol) tosylchloride in 50 ml THF were added dropwise. After stirring for 2 h

¹³³ K.-T. Wong, Y.-Y. Chien, Y.-L. Liao, C.-C. Lin, M.-Y. Chou, M.-K. Leung *J. Org. Chem.* **2002**, *67*, 1041-1044.

the layers were separated and the aqueous layer was extracted three times with 70 ml ether. The product was purified by column chromatography (silica gel; hexane/ ethyl acetate 1:1).

Yield 33.12 g (44 %) of a colorless oil.

$r_f = 0.44$ (silica gel; hexane/ethyl acetate 1:1).

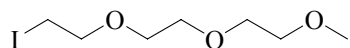
$^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 2.36$ (s, 3 H), 3.50-3.60 (m, 12 H), 3.93 (m, 2 H), 4.07 (m, 2 H), 5.08 (d, $^3J = 10.6$ Hz, 1 H), 5.19 (d, $^3J = 17.6$ Hz, 1 H), 5.82 (m, 1 H), 7.26 (d, $^3J = 8.1$ Hz, 2H), 7.71 (d, $^3J = 8.1$ Hz, 2H) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): $\delta = 21.38, 68.42, 69.06, 69.21, 70.29, 70.38, 70.48, 71.94, 116.76, 127.73, 129.61, 132.84, 134.58, 144.57$ ppm.

MS (EI, 80 eV, 30°C): m/z (%) = 388 (1) $[\text{M}]^+$, 331 (2) $[\text{M}-\text{C}_3\text{H}_5\text{O}]^+$, 287 (1), 286 (1) $[\text{M}-\text{C}_5\text{H}_9\text{O}_2]^+$, 244 (1), 243 (6) $[\text{M}-\text{C}_7\text{H}_{13}\text{O}_3]^+$, 199 (100) $[\text{M}-\text{C}_9\text{H}_{17}\text{O}_4]^+$.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | $\text{C}_{18}\text{H}_{28}\text{SO}_7$ | calc. | C 55.65 | H 7.26 |
| | (388.482) | found | 55.94 | 7.31 |

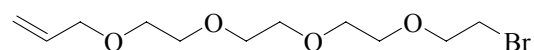
1-Iodo-2-[2-(2-methoxy-ethoxy)-ethoxy]-ethane 16



1.95 g (6.1 mmol) of tosylate **15** and 4.60 g (30.7 mmol) sodium iodide in 50 ml acetone were stirred under reflux for 3 d. The solution was filtered and the solvent evaporated. Compound **16** was used directly without further purification.

Yield: 1.21 g (75 %) of a colorless oil.

3-(2-{2-[2-(2-Bromo-ethoxy)-ethoxy]-ethoxy}-ethoxy)-propene 17



2.37 g (9.0 mmol) triphenylphosphine were dissolved in 70 ml dry methylene chloride and cooled to 0 °C. 0.46 ml (9.0 mmol) bromine were added and the mixture was stirred for 0.5 h. A solution of 1.14 ml (8.2 mmol) triethylamine and 1.91 g (8.2 mmol) allyl ether **8** in 30 ml dry MeCl_2 was added. The reaction mixture was allowed to come to rt and was stirred over night. 100 ml water were added and the layers were separated. The aqueous layer was extracted four times with 50 ml methylene chloride. The combined organic layers were dried

over MgSO₄, filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; MeCl₂/MeOH 1%).

Yield 1.30 g (53 %) of a colorless oil.

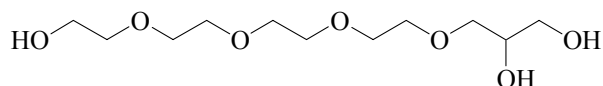
$r_f = 0.29$ (silica gel; MeCl₂/ MeOH 1 %).

¹H NMR (CDCl₃, 250 MHz): $\delta = 3.44$ (t, ³J = 7.6 Hz, 2 H, -CH₂Br), 3.56 (m, 12 H, -CH₂O-), 3.76 (t, ³J=7.6 Hz, 2 H, -CH₂CH₂Br), 3.94 (d, ³J = 7.6 Hz, 2 H, -CH₂-), 5.18 (m, 2 H, =CH₂) , 5.86 (m, 1 H, -CH=) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 30.18, 69.31, 70.40, 70.50, 70.54, 71.08, 72.07, 116.92, 134.65$ ppm.

MS (EI, 80 eV, 50°C): m/z (%) = 299 (12), 298 (2), 297 (17), 296 (2), 295 (5) [M+H]⁺, 241 (5), 239 (5) [M-C₂H₄O]⁺, 217 (1) [M-Br]⁺, 197 (4), 195 (5) [M-C₅H₉O₂]⁺, 109 (51), 107 (49) [C₂H₄Br]⁺, 41 (100) [C₃H₅]⁺.

3-(2-{2-[2-(2-Hydroxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-propane-1,2-diol 18



499 mg (2.1 mmol) Allylether **8** were dissolved in a mixture of 13 ml ethyl acetate and 13 ml acetonitril and cooled to 0 °C. A solution of 34 mg (0.2 mmol) RuCl₃·H₂O and 684 mg (3.2 mmol) NaIO₄ in 6 ml dest. water were added rapidly. After stirring for 3 minutes, 20 ml of a saturated aqueous Na₂S₂O₃ solution were added and it was stirred for 0.5 h. The solvent was evaporated and the solid residue was extracted with acetone.

Yield: 506 mg (89 %) of a colorless oil.

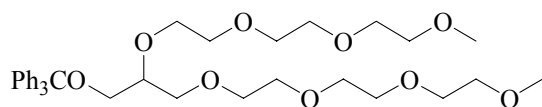
$r_f = 0.67$ (silica gel; EtOH/acetone 10:1).

¹H NMR (CDCl₃, 250 MHz): $\delta = 2.39$ (s, 3 H, -OH), 3.75 (m, 18 H, -CH₂O-), 4.00 (m, 1 H, -CH-) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 33.38, 63.31, 65.55, 72.48, 72.80, 73.24, 74.61$ ppm.

MS (pos. FAB, 3 kV, Xenon, Glycerin): m/z (%) = 307 (6) [M+K]⁺, 291 (100) [M+Na]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₁₁ H ₂₄ O ₇ | calc. | C 49.24 | H 9.02 |
| | (268.307) | found | 49.34 | 7.33 |

2,3-Bis-[2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy]-propan-1-trityl ether 21

10.00 g (29.9 mmol) of diol **20** were dissolved in 400 ml dry THF. 2.99 g (74.8 mmol) NaH were added and the mixture was stirred under reflux for 2.5 h. After cooling to rt 28.56 g (89.7 mmol) of the tosylate **15** were added and the mixture was refluxed for another 3 d. The precipitate was filtered off and the solvent was evaporated. The crude product was purified by flash column chromatography (silica gel; hexane/ethyl acetate 1:1 → 1:2).

Yield: 17.30 g (92 %) of a colorless oil.

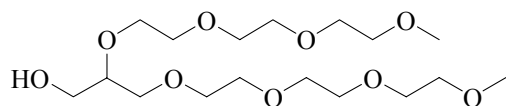
$r_f = 0.38$ (silica gel; MeCl₂/MeOH 19:1).

¹H NMR (CDCl₃, 250 MHz): $\delta = 3.15$ (d, ³J = 5.6 Hz, 2 H, -CH₂O-), 3.21 (s, 6 H, -CH₃), 3.55 (m, 25 H, -CH₂O-), 3.71 (m, 2 H, -CH₂O-), 7.25 (m, 9 H, arom.), 7.42 (d, ³J = 8.3 Hz, 6 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 58.93, 63.51, 69.88, 70.46, 70.57, 70.79, 71.74, 71.90, 78.86, 86.55, 126.86, 127.68, 127.92, 128.69, 144.03$ ppm.

MS (pos. FAB, 3 kV, Xenon, MNBA/CH₂Cl₂): m/z (%) = 665 (1) [M+K]⁺, 649 (1) [M+Na]⁺, 627 (1) [M+H]⁺, 243 (100) [C(Ph)₃]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₃₆ H ₅₀ O ₉ | calc. | C 68.99 | H 8.04 |
| | (626.788) | found | 68.66 | 7.40 |

2,3-Bis-[2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy]-propan-1-ol 22

2.41 g (3.8 mmol) of compound **21** were dissolved in a mixture of 20 ml THF and 20 ml methanol. 33 mg (0.2 mmol) p-TsOH were added and the solution was stirred for 7 d at rt. The solvent was evaporated and the crude product was purified by flash column chromatography (silica gel; MeCl₂/MeOH 1 % → 5 %).

Yield: 940 mg (64 %) colorless oil.

$r_f = 0.49$ (silica gel; MeCl₂/MeOH 10 %).

$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 3.03$ (s, 1 H, -OH), 3.32 (s, 6 H, - CH_3), 3.57 (m, 27 H, - CH_2O -), 3.78 (m, 2 H, - CH_2O -) ppm.

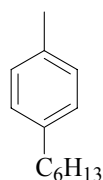
$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 58.87, 62.46, 69.43, 70.39, 70.48, 70.69, 71.15, 71.80, 79.58$ ppm.

MS (EI, 80 eV, 150°C): m/z (%) = 384 (1) $[\text{M}]^+$, 353 (2) $[\text{M}-\text{OCH}_3]^+$, 59 (100) $[\text{C}_3\text{H}_7\text{OH}]^+$.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | $\text{C}_{17}\text{H}_{36}\text{O}_9$ | calc. | C 53.11 | H 9.44 |
| | (384.467) | found | 51.27 | 9.17 |

7.4.2 Compounds of Chapter 4.3.1

1-Hexyl-4-methylbenzene 28 c



via Kumada Reaction

The procedure was analogous to that described for the dodecyl derivative **28 d**. 24.30 g (1.00 mol) Mg, 600 ml dry ether, 165.0 g (1.00 mol) 1-bromohexane, 2.17 g (4.0 mmol) $\text{Ni}(\text{dppp})\text{Cl}_2$, 63.30 g (499 mmol) 4-chlorotoluene in 400 ml dry ether.

Yield: 34.3 g (39 %) of a colorless oil.

via Suzuki Reaction

12.0 g (143 mmol) 1-hexene were dissolved in 200 ml dry toluene. 18.3 g (150 mmol) 9-BBN were added and the solution was stirred for 24 h under nitrogen. 16.8 g (420 mmol) sodium hydroxide dissolved in 250 ml water and 24.5 g (143 mmol) 4-bromo toluene **29** were added and the resulting two-layer mixture was degassed three times. 2.43 g (2.1 mmol) $\text{Pd}(\text{PPh}_3)_4$ were added, the mixture was degassed again for three times and cooked under reflux for 2 d. After cooling to rt the layers were separated and the aqueous layer was extracted twice with 50 ml ether. The combined organic layers were dried (MgSO_4), filtered and the solvent evaporated. The crude product was purified by distillation (190 °C, 1013 mbar).

Yield: 14.4 g (57 %) of a colorless oil.

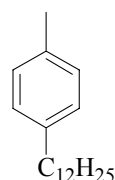
^1H NMR (CDCl_3 , 250 MHz): δ = 1.03 (t, 3J = 8.0 Hz, 3 H, $-\text{CH}_3$), 1.43 (m, 6 H, $-\text{CH}_2-$), 1.72 (quint, 3J = 8.0 Hz, 2 H, $\beta\text{-CH}_2-$), 2.44 (s, 3 H, $\alpha\text{-CH}_3$), 2.70 (t, 3J = 8.0 Hz, 2 H, $\alpha\text{-CH}_2-$), 7.20 (s, 4 H, arom.) ppm.

^{13}C NMR (CDCl_3 , 63 MHz): δ = 10.81, 14.07, 20.93, 22.64, 29.04, 31.63, 31.78, 35.55, 128.24, 128.88, 134.84, 139.81 ppm.

MS (EI, 80 eV, 30°C): m/z (%) = 177 (6), 176 (39) $[\text{M}]^+$, 147 (2) $[\text{C}_{11}\text{H}_{15}]^+$, 119 (5) $[\text{C}_9\text{H}_{11}]^+$, 105 (100) $[\text{C}_8\text{H}_9]^+$.

| | | | | |
|-----------|------------------------------|-------|---------|---------|
| EA | $\text{C}_{13}\text{H}_{20}$ | calc. | C 88.57 | H 11.43 |
| | (176.302) | found | 88.36 | 11.37 |

1-Dodecyl-4-methylbenzene 28 d



Kumada reaction

The Grignard compound was prepared from 31.6 g (1.30 mol) Mg and 319 ml (1.30 mol) 1-bromododecane in 400 ml dry ether. The dark solution was refluxed for 1 h. The reaction mixture was cooled to 5 °C and 120 ml (1.00 mol) 4-chloro toluene **30** in 400 ml dry ether and 3.79 g (0.7 mol %) were added. The mixture was cooked for 20 h under reflux. The flask was cooled to rt and 200 ml 15 % HCl were added very carefully and slowly. The layers were separated and the aqueous layer was extracted twice with 100 ml ether. The combined organic layers were dried over MgSO_4 , filtered and the solvent evaporated. The crude product was distilled under vacuum (139 °C, 0.5 mbar).

Yield: 131.4 g (50 %) of a colorless oil.

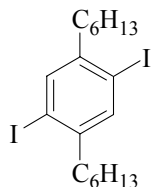
^1H NMR (CDCl_3 , 250 MHz): δ = 0.91 (t, 3J = 8 Hz, 3H, $-\text{CH}_3$), 1.32 (m, 18 H, $-\text{CH}_2-$), 1.59 (quint, 3J = 8 Hz, 2 H, $\beta\text{-CH}_2-$), 2.34 (s, 3 H, $\alpha\text{-CH}_3$), 2.59 (t, 3J = 8 Hz, $\alpha\text{-CH}_2-$), 7.10 (s, 4 H, arom.) ppm.

^{13}C NMR (CDCl_3 , 63 MHz): δ = 14.11, 20.95, 22.72, 29.39, 29.58, 29.65, 29.72, 31.67, 31.97, 35.56, 128.26, 128.90, 134.86, 139.85 ppm.

MS (EI, 80 eV, 30°C): m/z (%) = 262 (1), 261 (11), 260 (51) $[\text{M}]^+$, 147 (2) $[\text{C}_{11}\text{H}_{15}]^+$, 119 (3) $[\text{C}_9\text{H}_{11}]^+$, 105 (100) $[\text{M}-\text{C}_{11}\text{H}_{23}]^+$.

| | | | | |
|-----------|---------------------------------|-------|---------|---------|
| EA | C ₁₉ H ₃₂ | calc. | C 87.62 | H 12.38 |
| | (260.463) | found | 87.41 | 12.69 |

1,4-Dihexyl-2,5-diiodo-benzene **32 a**



The procedure was analogous to that described for compound **32 d**. 10.00 g (40.6 mmol) 1,4-Dihexylbenzene **28 a**, 8.50 g (33.5 mmol) iodine, 4.24 g (18.4 mmol) periodic acid, 50 ml acetic acid, 6 ml water and 2 ml sulfuric acid; recrystallization from ethanol.

mp.: 41.1 °C

Yield: 18.78 g (93 %) of a colorless solid

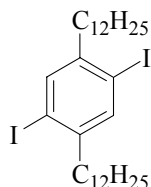
¹H NMR (CDCl₃, 250 MHz): δ = 0.89 (t, ³J = 8.0 Hz, 6 H, -CH₃), 1.31 (m, 12 H, -CH₂-), 1.56 (quint, ³J = 8.0 Hz, 4 H, β-CH₂-), 2.62 (t, ³J = 8.0 Hz, 4 H, α-CH₂-), 7.35 (s, 2 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.07, 22.58, 28.98, 30.15, 31.58, 39.82, 100.33, 119.20, 139.27, 144.81 ppm.

MS (EI, 80 eV, 100°C): m/z (%) = 500 (3), 499 (27), 498 (100) [M]⁺, 428 (5), 427 (25) [M-C₅H₁₁]⁺, 357 (4), 356 (2) [M-C₁₀H₂₂]⁺, 343 (8) [M-I-C₂H₄]⁺, 301 (7), [M-I-C₅H₁₀]⁺, 231 (3), 230 (3) [C₈H₈I]⁺, 215 (14) [M-2I-C₂H₅]⁺, 201 (12) [M-2I-C₃H₇]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₁₈ H ₂₈ I ₂ | calc. | C 43.39 | H 5.66 |
| | (498.229) | found | 43.16 | 5.35 |

1,4-Didodecyl-2,5-diiodo-benzene **32 b**



The procedure was analogous to that described for compound **32 d**. 2.00 g (4.8 mmol) 1,4-didodecylbenzene **28 b**; 1.00 g (3.9 mmol) iodine; 0.60 g (2.6 mmol) periodic acid; 17 ml acetic acid; 2 ml water and 0.6 ml sulfuric acid; recrystallization from ethanol.

Yield: 3.07 (96 %) of a colorless solid.

mp.: 62.7 °C

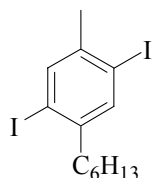
¹H NMR (CDCl₃, 250 MHz): δ = 0.87 (t, ³J = 8.0 Hz, 6 H, -CH₃), 1.28 (m, 36 H, -CH₂-), 1.54 (quint, ³J = 8.0 Hz, 4 H, β-CH₂-), 2.57 (t, ³J = 8.0 Hz, 4 H, α-CH₂-), 7.58 (s, 2 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.13, 22.70, 29.32, 29.36, 29.41, 29.57, 29.67, 30.20, 31.94, 39.85, 100.34, 139.30, 144.85 ppm.

MS (EI, 80 eV, 170°C): m/z (%) = 668 (5), 667 (34), 666 (100) [M]⁺, 356 (11) [M-C₂₂H₄₆]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₃₀ H ₅₂ I ₂ | calc. | C 54.06 | H 7.86 |
| | (666.552) | found | 53.78 | 7.51 |

2-Hexyl-5-methyl-1,4-diiodobenzene **32 c**



The procedure was analogous to that described for the dodecyl derivative **32 d**. 20.00 g (113.0 mmol) **28 c**, 11.80 g (51.8 mmol) periodic acid, 23.60 g (93.0 mmol) iodine, 142 ml acetic acid, 5.6 ml sulfuric acid, 17.4 ml water, 50 ml carbon tetrachloride; recrystallization from ethanol.

mp.: 39.3 °C

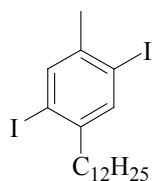
Yield: 24.10 g (50 %) of colorless crystals.

¹H NMR (CDCl₃, 250 MHz): δ = 0.88 (t, ³J = 8 Hz, 3 H, -CH₃), 1.30 (m, 6 H, -CH₂-), 1.53 (quint, ³J = 8 Hz, 2 H, β-CH₂-), 2.31 (s, 3 H, α-CH₃), 2.56 (t, ³J = 8 Hz, 2 H, α-CH₂-), 7.57 (s, 1 H, arom.), 7.63 (s, 1 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.08, 22.58, 26.86, 28.95, 30.19, 31.60, 39.80, 100.08, 100.86, 138.84, 139.72, 140.70, 144.79 ppm.

MS (EI, 80 eV, 50°C): m/z (%) = 430 (7), 429 (25), 428 (100), 427 (10), 426 (7), 425 (4) [M]⁺, 358 (11), 357 (37), 356 (4) [M-C₅H₁₁]⁺, 232 (5), 231 (42), 230 (4) [C₈H₈I]⁺, 174 (3) [C₁₉H₂₉]⁺, 145 (22) [C₁₁H₁₃]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₁₃ H ₁₈ I ₂ | calc. | C 36.47 | H 4.24 |
| | (428.095) | found | 36.28 | 3.83 |

2-Dodecyl-5-methyl-1,4-diiodobenzene 32 d

9.72 g (37.3 mmol) 1-Dodecyl-4-methylbenzene **28 d**, 3.83 g (16.8 mmol) periodic acid and 7.76 g (30.6 mmol) iodine were dissolved in a mixture of 26 ml acetic acid, 4.6 ml water, 0.9 ml conc. sulfuric acid and 7 ml carbon tetrachloride. The reaction mixture was refluxed for 5 h and then poured into 500 g ice. The excess of iodine was reduced with sodium bisulfite. After addition of 100 ml dichloromethane and layer separation, the aqueous layer was extracted two times with 50 ml dichloromethane. The combined organic layers were dried over MgSO_4 , filtered and the solvent evaporated. The solid crude product was purified by recrystallization from ethanol affording a white solid.

mp.: 46.9 °C

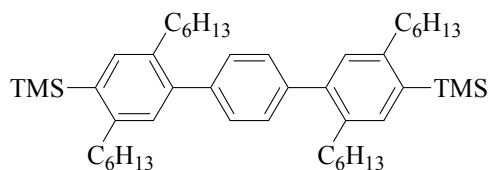
Yield: 10.2 g (53.4 %)

$^1\text{H NMR}$ (CDCl_3 , 250 MHz): δ = 0.90 (t, 3J = 8 Hz, 3 H, $-\text{CH}_3$), 1.29 (m, 18 H, $-\text{CH}_2-$), 1.53 (quint, 3J = 8 Hz, 2 H, $\beta\text{-CH}_2-$), 2.33 (s, 3 H, $\alpha\text{-CH}_3$), 2.60 (t, 3J = 8 Hz, 2 H, $\alpha\text{-CH}_2-$), 7.58 (s, 1 H, arom.), 7.66 (s, 1 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): δ = 14.36, 22.94, 27.10, 29.53, 29.60, 29.64, 29.80, 29.90, 30.46, 32.17, 40.05, 100.33, 101.09, 139.10, 139.96, 140.93, 145.05 ppm.

MS (EI, 80 eV, 30°C): m/z (%) = 512 (100) $[\text{M}]^+$, 357 (32) $[\text{M}-\text{C}_{11}\text{H}_{23}]^+$, 271 (3), 257 (2) $[\text{C}_{19}\text{H}_{29}]^+$, 231 (33) $[\text{C}_8\text{H}_8\text{I}]^+$, 159 (2), 145 (22) $[\text{C}_{11}\text{H}_{13}]^+$.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | $\text{C}_{19}\text{H}_{30}\text{I}_2$ | calc. | C 44.55 | H 5.90 |
| | (512.256) | found | 44.28 | 5.64 |

2,5,2'',5''-Tetrahexyl-4,4''-bis-trimethylsilanyl-[1,1';4',1'']terphenyl 36

6.05 g (16.7 mmol) boronic acid **34**, 2.78 g (8.3 mmol) 1,4-diiodobenzene **35**, 4.18 g (49.8 mmol) NaHCO₃ were dissolved in a mixture of 40 ml toluene and 60 ml water. The mixture was degassed three times and 67 mg (0.7 mol %) Pd(PPh₃)₄ were added under nitrogen. After degassing another three times, the two layer system was refluxed for 20 h. After standard workup the crude product was purified by flash column chromatography (silica gel; hexane).

Yield: 2.62 g (44 %) of a colorless solid.

mp.: 81.5 °C

¹H NMR (CDCl₃, 500 MHz): δ = 0.38 (s, 18 H, -TMS), 0.83 (t, ³J = 8.0 Hz, 6 H, -CH₃), 0.90 (t, ³J = 8.0 Hz, 6 H, -CH₃), 1.21-1.63 (m, 32 H, -CH₂-), 2.60 (t, ³J = 8.0 Hz, 4 H, α-CH₂-), 2.72 (t, ³J = 8.0 Hz, 4 H, α-CH₂-), 7.12 (s, 2 H, arom.), 7.34 (s, 4 H, arom.), 7.38 (s, 2 H, arom.) ppm.

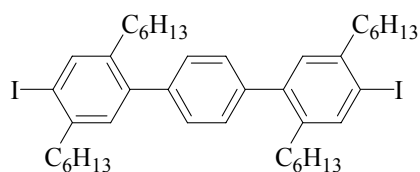
¹³C NMR (CDCl₃, 126 MHz): δ = 0.60, 14.05, 14.07, 22.54, 22.63, 29.25, 29.74, 31.51, 31.82, 32.62, 32.79, 36.02, 128.73, 128.82, 130.21, 135.69, 136.63, 140.44, 142.32, 145.97 ppm.

MS (EI, 80 eV, 180°C): m/z (%) = 714 (2), 713 (8), 712 (27), 711 (63), 710 (100), 709 (1) [M]⁺, 697 (2), 696 (5), 695 (8) [M-CH₃]⁺, 641 (3), 640 (5), 639 (5), 638 (4), 637 (3) [M-SiC₃H₉]⁺.

| | | | | |
|-----------|---|-------|---------|---------|
| EA | C ₄₈ H ₇₈ Si ₂ | calc. | C 81.04 | H 11.05 |
| | (428.095) | found | 80.74 | 10.70 |

2,5,2'',5''-Tetrahexyl-4,4''-diiodo-[1,1';4',1'']terphenyl

37



2.42 g (3.4 mmol) of compound **36** were dissolved in dry methylene chloride under nitrogen and cooled down to -78 °C. A solution of 1.16 g (7.1 mmol) iodochloride in 16 ml dry MeCl₂ was added dropwise. After stirring for 1 h at -78 °C., the reaction mixture was quenched with 20 ml saturated Na₂S₂O₃ solution. The layers were separated and the aqueous layer was extracted three times with 40 ml MeCl₂. The combined organic layers were washed with saturated NaHCO₃ solution and brine. The organic layer was dried over MgSO₄, filtered and the solvent evaporated.

Yield: 2.74 g (98 %) of a colorless solid.

$r_f = 0.84$ (silica gel; hexane/ethyl acetate 100:1).

mp.: 85.7 °C

$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 0.82$ (t, $^3J = 8$ Hz, 6 H, $-\text{CH}_3$), 0.88 (t, $^3J = 8$ Hz, 6 H, $-\text{CH}_3$), 1.06-1.70 (m, 32 H, $-\text{CH}_2-$), 2.51 (t, $^3J = 8$ Hz, 4 H, $\alpha\text{-CH}_2-$), 2.67 (t, $^3J = 8$ Hz, 4 H, $\alpha\text{-CH}_2-$), 7.07 (s, 2 H, arom.), 7.27 (s, 4 H, arom.), 7.72 (s, 2 H, arom.) ppm.

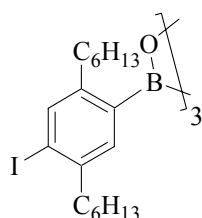
$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 14.06, 22.47, 22.60, 29.06, 29.11, 30.38, 31.17, 31.44, 31.65, 32.25, 40.36, 99.44, 128.76, 130.64, 139.81, 139.87, 140.00, 141.63, 142.62$ ppm.

MS (EI, 80 eV, 180°C): m/z (%) = 821 (2), 820 (11), 819 (44), 818 (100) $[\text{M}]^+$, 748 (1), 747 (1) $[\text{M}-\text{C}_5\text{H}_{11}]^+$, 694 (2), 693 (6), 692 (14), 690 (1) $[\text{M}-\text{I}]^+$.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | $\text{C}_{42}\text{H}_{60}\text{I}_2$ | calc. | C 61.61 | H 7.39 |
| | (818.747) | found | 61.87 | 7.35 |

7.4.3 Compounds of Chapter 4.3.2

2,4,6-Tris-(2,5-dihexyl-4-iodo-phenyl)-cyclotriboroxane **39**



3.78 g (10.4 mmol) compound **34** were dissolved in 80 ml dry methylene chloride and cooled to -78 °C under nitrogen. A solution of 2.20 g (13.6 mmol) iodochloride in 10 ml methylene chloride were added slowly. The cooling bath was removed and the mixture was stirred for 3 h. 30 ml of saturated sodium disulfite were added. The layers were separated and the aqueous layer was extracted three times with 30 ml CH_2Cl_2 . The combined organic layers were washed with aqueous NaHCO_3 and brine. The solution was dried over MgSO_4 , filtered and the solvent was evaporated. Compound **39** was purified by column chromatography (silica gel; hexane/ethyl acetate 3:1) and dried under high vacuum.

Yield: 3.95 g (95 %) colorless solid.

$r_f = 0.48$ (silica gel; hexane/ethyl acetate 2:1)

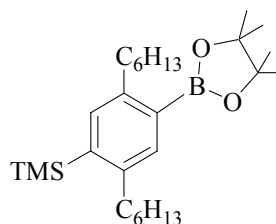
¹H NMR (CDCl₃, 250 MHz): δ = 0.88 (t, ³J = 8.0 Hz, 9 H, -CH₃), 0.92 (t, ³J = 8.0 Hz, 9 H, -CH₃), 1.12-1.50 (m, 24 H, -CH₂-), 1.62 (m, 12 H, β -CH₂-), 2.74 (t, ³J = 8.0 Hz, 6 H, α -CH₂-), 3.06 (t, ³J = 8.0 Hz, 6 H, α -CH₂-), 7.77 (s, 3 H, arom.), 7.91 (s, 3 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.02, 14.08, 22.57, 22.64, 29.17, 30.53, 31.72, 31.87, 32.92, 34.52, 40.39, 106.66, 128.63, 137.44, 140.76, 142.27, 149.98 ppm.

MS (EI, 80 eV, 300 °C): m/z (%) = 1195 (51), 1194 (100), 1193 (60), 1192 (14) [M]⁺, 1149 (12), 1148 (23), 1147 (23), 1146 (23), 1145 (15) [M-BO₂H₃]⁺, 1105 (14), 1104 (16), 1103 (27), 1102 (26), 1101 (14) [M-B₂O₄H₅]⁺, 1070 (21), 1069 (40), 1068 (33), 1067 (20), 1066 (13) [M-I+H]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₅₄ H ₈₄ B ₃ O ₃ I ₃ | calc. | C 54.30 | H 7.09 |
| | (1194.406) | found | 54.14 | 7.12 |

2-(2,5-Dihexyl-4-trimethylsilyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 40



3.59 g (9.9 mmol) **34** and 1.17 g (9.9 mmol) pinacol were dissolved in 100 ml dry methylene chloride and refluxed for 2 d in a Dean-Stark-apparatus. The solvent was removed and the crude product was purified by flash column chromatography (silica gel; hexane/ethyl acetate 10:1).

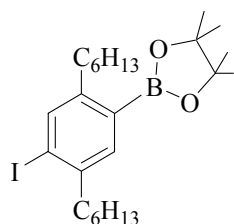
Yield: 4.20 g (95 %) colorless solid.

¹H NMR (CDCl₃, 250 MHz): δ = 0.28 (s, 9 H, -Si(CH₃)₃), 0.88 (t, J = 8.0 Hz, 6 H, -CH₃), 1.40 (m, 12 H, -CH₂-), 1.55 (m, 4 H, β -CH₂-), 2.64 (t, ³J = 8.0 Hz, 2 H, α -CH₂-), 2.81 (t, ³J = 8.0 Hz, 2 H, α -CH₂-), 7.21 (s, 1 H, arom.), 7.56 (s, 1 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 0.71, 14.32, 14.37, 22.94, 25.08, 29.80, 30.08, 32.08, 33.22, 33.22, 33.95, 35.99, 36.32, 83.48, 135.65, 136.15, 141.10, 145.19, 146.36, 154.49 ppm.

MS (EI, 80 eV, 180°C): m/z (%) = 446 (10), 445 (23), 444 (50), 443 (22), 442 (7) [M]⁺, 430 (9), 429 (18), 428 (9) [M-CH₃]⁺, 346 (9), 345 (25), 344 (67), 343 (29), 342 (11), 341 (7) [M-C₆H₁₂O]⁺, 276 (9), 275 (29), 274 (100), 273 (33), 272 (9) [M-C₆H₉O-SiC₃H₉]⁺.

| | | | | |
|-----------|--|-------|---------|---------|
| EA | C ₂₇ H ₄₉ BO ₂ Si | calc. | C 72.94 | H 11.11 |
| | (444.581) | found | 72.47 | 11.03 |

2-(2,5-Dihexyl-4-iodo-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 41

3.21 g (6.8 mmol) **40** were dissolved in 50 ml dry methylene chloride and cooled to $-78\text{ }^{\circ}\text{C}$ under nitrogen. A solution of 1.35 g (8.2 mmol) iodochloride in 10 ml CH_2Cl_2 was added slowly and the mixture was stirred for 1.25 h at $-78\text{ }^{\circ}\text{C}$. 20 ml of saturated sodium disulfite were added. The layers were separated and the organic layer was washed with aqueous NaHCO_3 and brine. The solution was dried over MgSO_4 , filtered and the solvent was evaporated. Compound **41** was purified by column chromatography (silica gel; hexane/ethyl acetate 10:1).

Yield: 3.09 g (91 %) of a colorless oil.

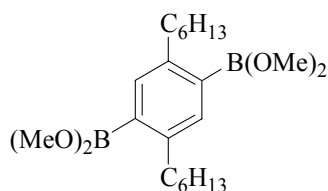
$r_f = 0.57$ (silica gel; hexane/ethyl acetate 20:1).

$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 0.87$ (m, 6 H, $-\text{CH}_3$), 1.29 (m, 12 H, $-\text{CH}_2-$), 1.50 (m, 4 H, β - CH_2-), 2.64 (t, $^3J = 8.0$ Hz, 2 H, α - CH_2-), 2.74 (t, $^3J = 8.0$ Hz, 2 H, α - CH_2-), 7.53 (s, 1 H, arom.), 7.62 (s, 1 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 14.09, 22.63, 24.83, 29.19, 29.35, 30.54, 31.65, 31.74, 33.31, 34.87, 40.22, 83.47, 104.59, 136.37, 139.99, 141.83, 149.29, 153.62$ ppm.

MS (EI, 80 eV, $180\text{ }^{\circ}\text{C}$): m/z (%) = 499 (27), 498 (88), 497 (26) $[\text{M}]^+$, 442 (18), 441 (74), 440 (33) $[\text{M}-\text{C}_4\text{H}_9]^+$, 427 (22) $[\text{M}-\text{C}_5\text{H}_{11}]^+$, 327 (10) $[\text{M}-\text{I}]^+$, 301 (27), 300 (8) $[\text{M}-\text{I}-\text{C}_5\text{H}_{11}+\text{H}]^+$, 102 (7), 101 (100) $[\text{C}_6\text{H}_{12}\text{O}]^+$.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | $\text{C}_{24}\text{H}_{40}\text{BO}_2\text{I}$ | calc. | C 57.85 | H 8.09 |
| | (498.296) | found | 58.02 | 8.30 |

Tetrakis(methyl)-1,4-Dihexylbenzene-2,5-bisboronic ester 48

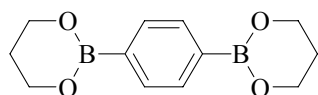
15.0 g (44.9 mmol) **45** were dissolved in 50 ml dry methanol and 50 ml dry chloroform. The solvents were evaporated and the whole procedure was repeated twice. The colorless oil was purified by high vacuum distillation and the product was stored under dry argon at -20 °C.

Yield: 17.2 g (98 %) of a colorless oil.

¹H NMR (CDCl₃, 250 MHz): δ = 0.86 (t, ³J = 8.0 Hz, 6 H), 1.24 (m, 12 H, -CH₂-), 1.49 (quint, ³J = 8.0 Hz, 4 H, β-CH₂-), 2.48 (t, ³J = 8.0 Hz, 4 H, α-CH₂-), 3.52 (s, 12 H, -OCH₃), 7.02 (s, 2 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 13.99, 22.53, 29.20, 31.64, 31.74, 35.94, 52.34, 129.84, 131.18, 132.77, 133.80, 137.59, 141.50 ppm.

Benzene-bisboronic ester **50 b**



The Grignard compound was prepared from 25.0 g (1.03 mol) Mg and 118.0 g (495 mmol) **46** in 750 ml dry THF and refluxed for 10 h. The solution was cooled to -78 °C and 120 ml (1.05 mol) trimethylborate were added dropwise. The mixture was allowed to warm to rt over night. 75 ml (1.04 mol) 1,3-propanediol and 300 ml toluene were added and the mixture was refluxed for 12 h. The suspension was filtered and the residue was extracted with toluene. The solvent was evaporated under reduced pressure and the crude product was purified by recrystallization from ether.

Yield: 45.03 g (47 %) of colorless crystals (subliming at 197 °C).

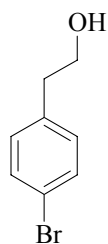
¹H NMR (CDCl₃, 250 MHz): δ = 2.03 (quint, ³J = 6.0 Hz, 4 H, -CH₂-), 4.14 (t, ³J = 6.0 Hz, 8 H, -OCH₂-), 7.72 (s, 4 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 27.34, 61.88, 132.65 ppm.

MS (EI, 80 eV, 90°C): m/z (%) = 247 (13), 246 (100), 245 (48), 244 (6) [M]⁺, 189 (10), 188 (39), 187 (19) [M-C₃H₆O]⁺.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | C ₁₂ H ₁₆ B ₂ O ₄ | calc. | C 58.62 | H 6.56 |
| | (245.879) | found | 58.34 | 6.40 |

7.4.4 Compounds of Chapter 4.4.1

2-(4-Bromophenyl)-ethan-1-ol **56**

A suspension of 50.02 g 4-bromophenyl acetic acid **55** in 500 ml dry ether were added slowly to a suspension of 6.76 g (172.7 mmol) lithium aluminium hydride in 200 ml dry ether. After complete addition the reaction mixture was cooked under reflux over night. 100 ml water were added carefully, followed by 200 ml HCl (10%). The layers were separated and the aqueous layer was extracted three times with 100 ml ether. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated under reduced pressure. The crude product was purified by vacuum distillation (90 °C, 1.6·10⁻² mbar).

Yield: 40.61 g (88 %) of a colorless oil.

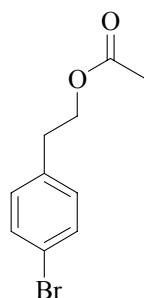
$r_f = 0.09$ (silica gel; hexane/ethyl acetate 4:1).

¹H NMR (CDCl₃, 250 MHz): $\delta = 2.28$ (s, 1 H, -OH), 2.76 (t, ³J = 8.0 Hz, 2 H, α -CH₂-), 3.77 (t, ³J = 8.0 Hz, 2 H, -CH₂OH), 7.05 (d, ³J = 11.0 Hz, 2 H, arom.), 7.39 (d, ³J = 11.0 Hz, 2 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 38.36, 63.14, 120.45, 130.66, 131.46, 137.52$ ppm.

MS (EI, 80 eV, 30°C): m/z (%) = 203 (4), 202 (40), 201 (4), 200 (41) [M]⁺, 172 (32), 171 (98), 170 (33), 169 (100) [M-CH₃O]⁺, 121 (9) [C₈H₉O]⁺, 92 (5), 91 (46), 90 (30), 89 (19) [C₇H₇]⁺.

| | | | | |
|-----------|-----------------------------------|-------|---------|--------|
| EA | C ₈ H ₉ OBr | calc. | C 47.79 | H 4.51 |
| | (201.063) | found | 47.56 | 4.73 |

Acetic acid 2-(4-bromophenyl)-ethyl ester **57**

32.59 g (162.1 mmol) 2-(4-bromophenyl)ethan-1-ol **56**, 77.0 ml (993 mmol) pyridine and 30 mg (0.2 mmol) DMAP were dissolved in 40 ml of dry dichloromethane and cooled to 0 °C. 50 ml (444 mmol) acetic acid anhydride were added dropwise. The reaction mixture was allowed to warm to rt and 300 ml of water were added. The product was extracted 3 times with 100 ml dichloromethane. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The product was dried under high vacuum.

$r_f = 0.49$ (silica gel; hexane/ethyl acetate 4:1).

Yield: 37.1 g (94 %) of a colorless oil.

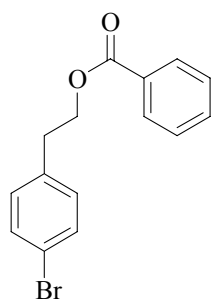
¹H NMR (CDCl₃, 250 MHz): $\delta = 2.01$ (s, 1 H, -CH₃), 2.86 (t, ³J = 8.0 Hz, 2 H, α -CH₂-), 4.22 (t, ³J = 8.0 Hz, 2 H, -CH₂OAc), 7.06 (d, ³J = 10.0 Hz, 2 H, arom.), 7.40 (d, ³J = 10.0 Hz, 2 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 20.75, 34.31, 64.31, 120.27, 130.47, 131.40, 136.71, 170.71$ ppm.

MS (EI, 80 eV, 30°C): m/z (%) = 244 (1), 242 (1) [M]⁺, 185 (9), 184 (87), 183 (9), 182 (89) [C₈H₇⁷⁹Br]⁺, 172 (1), 171 (9), 170 (1), 169 (10) [C₇H₆⁷⁹Br]⁺, 104 (6), 103 (9), 102 (2) [C₈H₇]⁺, 43 (100) [C₂H₃O]⁺.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | C ₁₀ H ₁₁ O ₂ Br | calc. | C 49.41 | H 4.56 |
| | (201.063) | found | 49.38 | 4.52 |

Benzoic acid 2-(4-bromophenyl)-ethyl ester **58**



22.72 g (113.0 mmol) 2-(4-bromophenyl)ethan-1-ol **56**, 28.2 ml (203.5 mmol) triethylamine were dissolved in 50 ml dry methylene chloride and cooled to 0 °C. 19.9 ml (169.5 mmol) benzoyl chloride in 50 ml dry methylene chloride were added slowly. The mixture was stirred over night and allowed to warm up to rt. 100 ml of water were added and the layers were separated. The organic layer was washed three times with 10 % aqueous citric acid. After

drying over MgSO_4 , filtering and evaporating the solvent the brown oil was recrystallized from ethanol to obtain a white solid.

$r_f = 0.45$ (silica gel; hexane/ethyl acetate 4:1).

mp.: 77.6 °C

Yield: 33.53 g (97 %).

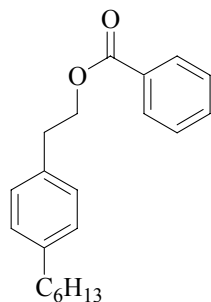
$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 3.01$ (t, $^3J = 8.0$ Hz, 2 H, $\alpha\text{-CH}_2\text{-}$), 4.53 (t, $^3J = 8.0$ Hz, 2 H, $\text{-CH}_2\text{OBz}$), 7.14 (d, $^3J = 10.0$ Hz, 2 H, arom.), 7.42 (m, 4 H, arom.), 7.56 (t, $^3J = 10.0$ Hz, 1 H, arom.), 8.01 (d, $^3J = 10.0$ Hz, 2 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 34.61, 64.95, 112.31, 118.84, 120.44, 128.34, 129.49, 130.63, 131.58, 132.95, 136.90, 166.36$ ppm.

MS (EI, 80 eV, 100°C): m/z (%) = 304 (1) $[\text{M}]^+$, 186 (1), 185 (13), 184 (99), 183 (14), 182 (100) $[\text{C}_8\text{H}_7^{79}\text{Br}]^+$, 171 (4), 169 (4) $[\text{C}_7\text{H}_6\text{Br}]^+$, 105 (93) $[\text{C}_7\text{H}_5\text{O}]^+$.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | $\text{C}_{15}\text{H}_{13}\text{O}_2\text{Br}$ | calc. | C 59.04 | H 4.29 |
| | (305.171) | found | 59.46 | 4.31 |

Benzoic acid 2-(4-hexylphenyl)-ethyl ester **59**



3.52 g (28.3 mmol) 9-BBN and 3.8 ml (29.7 mmol) 1-hexene were dissolved in 100 ml dry toluene and stirred over night at rt. 3.90 g (84.9 mmol) NaOH in 85 ml water and 8.49 g (27.7 mmol) benzoic acid 2-(4-bromophenyl)-ethyl ester **58** were added and the solution was degassed three times by evacuation and N_2 ventilating for 10 minutes per operation. 500 mg (0.42 mmol) $\text{Pd}(\text{PPh}_3)_4$ was added immediately followed by again three times degassing. The reaction mixture was refluxed under nitrogen for 2 d. The two-layer-system was cooled to rt, the layers were separated and the aqueous layer was extracted three times with 50 ml toluene. The combined organic layers were dried over MgSO_4 , filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate 7:1; $r_f = 0.63$).

Yield: 8.15 g (92.5 %) of a colorless oil.

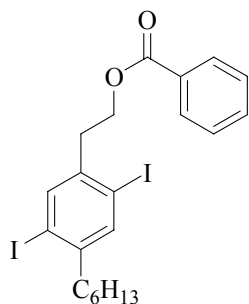
¹H NMR (CDCl₃, 250 MHz): δ = 0.86 (t, ³J = 7.0 Hz, 3 H, -CH₃), 1.29 (m, 6 H, -CH₂-), 1.61 (quint, ³J = 7.0 Hz, 2 H, β -CH₂-), 2.60 (t, ³J = 7.0 Hz, 2 H, α -CH₂-), 3.08 (t, ³J = 6 Hz, 2 H, α -CH₂-), 4.52 (t, ³J = 6 Hz, 2 H, β -CH₂OBz), 7.20 (AA'BB', ³J = 10.0 Hz, 4 H), 7.46 (t, ³J = 10.0 Hz, 1 H, *p*-benzoate), 7.58 (t, ³J = 10.0 Hz, 1 H, arom.), 8.04 (d, ³J = 10.0 Hz, 2 H, *o*-benzoate) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.08, 22.58, 28.98, 31.46, 31.70, 34.79, 35.54, 65.60, 128.29, 128.53, 128.78, 129.53, 130.30, 132.83, 134.92, 141.19, 166.50 ppm.

MS (pos. FAB): *m/z* (%) = 311 (4), 309 (3) [M]⁺, 191 (2), 190 (17), 189 (100), 188 (37), 187 (11) [C₁₄H₂₁]⁺, 175 (5) [C₁₃H₁₉]⁺, 131 (9) [C₁₀H₂₁]⁺. (MS-EI does not work).

| | | | | |
|-----------|---|-------|---------|--------|
| EA | C ₁₅ H ₁₃ O ₂ Br | calc. | C 81.25 | H 8.44 |
| | (310.436) | found | 81.03 | 8.68 |

Benzoic acid 2-(4-hexyl-2,5-diiodophenyl)-ethyl ester **60**



10.00 g (32.1 mmol) Benzoic acid 2-(4-hexylphenyl)-ethyl ester **59**, 16.36 g (36.9 mmol) bis(trifluoroacetoxy)phenyl iodine and 8.96 g (35.3 mmol) iodine were dissolved in 30 ml dry CH₂Cl₂ under nitrogen. The solution was stirred for 2 h at rt. The solvent was evaporated and the crude product was purified by column chromatography (silica gel; hexane/ethyl acetate 10:1; *r_f* = 0.49).

Yield: 18.02 g (100 %) of a colorless solid.

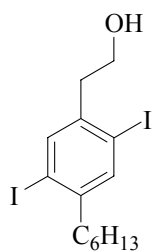
¹H NMR (CDCl₃, 250 MHz): δ = 0.88 (t, ³J = 7.0 Hz, 3 H, -CH₃), 1.32 (m, 6 H, -CH₂-), 1.53 (quint, ³J = 7.0 Hz, 2 H, β -CH₂-), 2.59 (t, ³J = 7.0 Hz, 2 H, α -CH₂-), 3.11 (t, ³J = 7.0 Hz, 2 H, α -CH₂-), 4.46 (t, ³J = 10.0 Hz, 1 H, -OCH₂-), 7.44 (t, ³J = 10.0 Hz, 2 H, arom.), 7.53 (t, ³J = 10.0 Hz, 1 H, arom.), 7.63 (s, 1 H, arom.), 7.75 (s, 1 H, arom.), 8.04 (d, ³J = 10.0 Hz, 2 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.04, 22.52, 28.91, 30.00, 31.51, 38.74, 39.83, 63.63, 100.20, 128.31, 129.58, 130.02, 132.88, 139.38, 139.90, 140.47, 145.94, 166.26 ppm.

MS (EI, 80 eV, 155 °C): m/z (%) = 563 (1), 562 (6) $[M]^+$, 441 (16), 440 (100) $[M-C_7H_6O_2]^+$, 371 (1), 370 (5), 369 (22) $[M-C_7H_6O_2-C_5H_{11}]^+$, 244 (2), 243 (19), 242 (2) $[M-C_7H_5O_2-C_5H_{11}-I]^+$.

| | | | | |
|-----------|----------------------|-------|---------|--------|
| EA | $C_{21}H_{24}O_2I_2$ | calc. | C 44.86 | H 4.30 |
| | (562.229) | found | 44.55 | 4.31 |

2-(4-Hexyl-2,5-diiodophenyl)-ethanol 67



18.42 g (32.8 mmol) Benzoic acid 2-(4-hexyl-2,5-diiodophenyl)-ethyl ester **60**, 9.00 g (160 mmol) KOH and 0.50 g (1.9 mmol) 18-crown-6 were dissolved in a mixture of 80 ml THF, 80 ml methanol and 40 ml water. The solution was stirred at rt for 20 h. 200 ml brine and 200 ml ether were added. The layers were separated and the aqueous layer was extracted three times with 70 ml ether. The combined organic layers were dried over $MgSO_4$, filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate 10:1; $r_f = 0.06$).

Yield: 14.50 g (97 %) of a colorless solid.

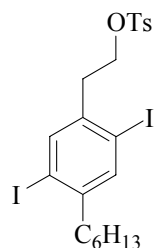
mp.: 78.9 °C

1H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, $^3J = 7.0$ Hz, 3 H, - CH_3), 1.32 (m, 6 H, - CH_2 -), 1.54 (quint, $^3J = 7.0$ Hz, 3 H, β - CH_2 - and -OH), 2.56 (t, $^3J = 7.0$ Hz, 2 H, α - CH_2 -), 2.88 (t, $^3J = 7.0$ Hz, 2 H, α - CH_2 -), 3.80 (t, $^3J = 7.0$ Hz, 2 H, - OCH_2 -), 7.60 (s, 1 H, arom.), 7.65 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.06, 22.54, 28.95, 30.06, 31.53, 39.85, 42.52, 62.02, 100.37, 100.48, 139.44, 140.22, 140.43, 145.75 ppm.

MS (EI, 80 eV, 155 °C): m/z (%) = 460 (1), 459 (16), 458 (100) $[M]^+$, 428 (7), 427 (33) $[M-CH_3O]^+$, 388 (1), 387 (8) $[M-C_5H_{11}]^+$, 332 (8), 331 (51) $[M-I]^+$.

| | | | | |
|-----------|--------------------|-------|---------|--------|
| EA | $C_{14}H_{20}OI_2$ | calc. | C 36.71 | H 4.40 |
| | (458.121) | found | 36.42 | 4.35 |

Toluene-4-sulfonic acid 2-(4-hexyl-2,5-diiodophenyl)-ethyl ester 68

2.26 g (4.9 mmol) **67** and 2.73 ml (19.7 mmol) triethylamine were dissolved in 40 ml dry CH_2Cl_2 . A solution of 2.86 g (14.7 mmol) tosyl chloride in 10 ml dry CH_2Cl_2 was added dropwise at rt under stirring. The mixture was stirred for 12 h at rt. 20 ml hydrochloric acid (6 %) were added. The layers were separated and the aqueous layer was extracted twice with 50 ml CH_2Cl_2 . The combined organic layers were washed with saturated aqueous NaHCO_3 solution and water. The organic layer was dried over MgSO_4 , filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate 10:1; $r_f = 0.40$).

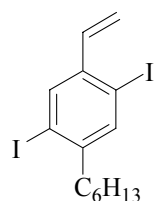
Yield: 2.30 g (77 %) of a colorless oil.

$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 0.88$ (t, $^3J = 7.0$ Hz, 3 H, $-\text{CH}_3$), 1.28 (m, 6 H, $-\text{CH}_2-$), 1.47 (quint, $^3J = 7.0$ Hz, 3 H, $\beta\text{-CH}_2-$), 2.40 (s, 3 H, $-\text{CH}_3$), 2.56 (t, $^3J = 7.0$ Hz, 2 H, $\alpha\text{-CH}_2-$), 2.96 (t, $^3J = 7.0$ Hz, 2 H, $\alpha\text{-CH}_2-$), 4.16 (t, $^3J = 7.0$ Hz, 2 H, $-\text{OCH}_2-$), 7.24 (d, $^3J = 11.0$ Hz, 2 H, arom.), 7.51 (s, 2 H, arom.), 7.66 (d, $^3J = 11.0$ Hz, 2 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 14.06$, 21.67, 22.55, 28.95, 30.04, 31.53, 38.75, 39.89, 68.57, 99.91, 100.27, 110.36, 113.54, 127.82, 129.79, 138.11, 139.36, 140.40, 146.31 ppm.

MS (EI, 80 eV, 155 °C): m/z (%) = 614 (2), 613 (6), 612 (22) $[\text{M}]^+$, 442 (2), 441 (27), 440 (100) $[\text{M}-\text{C}_7\text{H}_8\text{SO}_3]^+$, 428 (2), 427 (13) $[\text{M}-\text{C}_8\text{H}_9\text{SO}_3]^+$, 370 (9), 369 (33) $[\text{M}-\text{C}_7\text{H}_8\text{SO}_3-\text{C}_5\text{H}_{11}]^+$.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | $\text{C}_{21}\text{H}_{26}\text{OI}_2\text{O}_3\text{S}$ | calc. | C 41.19 | H 4.28 |
| | (612.311) | found | 41.11 | 4.28 |

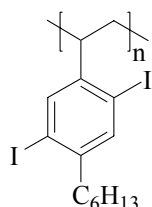
1-Hexyl-2,5-diiodo-4-vinyl-benzene 69

¹H NMR (CDCl₃, 250 MHz): δ = 0.88 (t, ³J = 7.0 Hz, 3 H, -CH₃), 1.28 (m, 6 H, -CH₂-), 1.49 (quint, ³J = 7.0 Hz, 3 H, β -CH₂-), 2.56 (t, ³J = 7.0 Hz, 2 H, α -CH₂-), 5.22 (d, ³J = 11.0 Hz, 2 H, =CH₂), 5.52 (d, ³J = 17.0 Hz, 2 H, =CH₂), 6.68 (dd, ³J = 17.0 Hz, ³J = 11.0 Hz, 1 H, =CH-), 7.56 (s, 1 H, arom.), 7.87 (s, 1 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.08, 22.58, 28.95, 30.05, 31.57, 40.03, 42.82, 99.23, 100.53, 117.14, 136.52, 138.90, 139.21, 140.08, 146.70 ppm.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₁₄ H ₁₈ I ₂ | calc. | C 38.21 | H 4.12 |
| | (440.106) | found | 37.67 | 3.94 |

Poly-(2,5-diiodo-4-hexylstyrene) 70



¹H NMR (CDCl₃, 250 MHz): δ = 0.87 (m, 3 H, -CH₃), 1.29 (m, 6 H, -CH₂-), 1.49 (m, 4 H, β -CH₂-), 2.50 (m, 3 H, α -CH₂-, α -CH), 7.45 (m, 2 H, arom.) ppm.

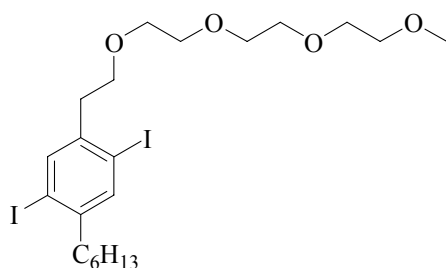
¹³C NMR (CDCl₃, 63 MHz): δ = 14.08, 22.65, 28.95, 29.07, 29.63, 31.51, 39.97, 99.13, 100.44, 117.06, 136.50, 138.39, 138.87, 139.17, 144.91 ppm.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₁₄ H ₁₈ I ₂ | calc. | C 38.21 | H 4.12 |
| | (440.106) | found | 37.20 | 3.62 |

GPC (THF; *versus* PS standards)

M_n = 530000 M_p = 860000 M_w = 860000 D = 1.62.

1-Hexyl-2,5-diiodo-4-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethyl)-benzene 71



366 mg (0.8 mmol) **67**, 782 mg (2.4 mmol) Cs_2CO_3 , and 1.00 g (3.8 mmol) **16** were dissolved in 15 ml dry DMF. The solution was stirred for 3 d under nitrogen at rt. The solvent was removed and the crude product was purified by column chromatography (aluminium oxide; hexane/ethyl acetate 10:1).

Yield: 242 mg (50 %) of a colorless waxy solid.

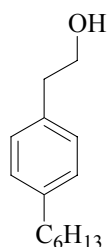
$^1\text{H NMR}$ (CDCl_3 , 250 MHz): δ = 0.85 (t, ^3J = 7.0 Hz, 3 H, $-\text{CH}_3$), 1.32 (m, 6 H, $-\text{CH}_2-$), 1.51 (quint, ^3J = 7.0 Hz, 3 H, β - CH_2-), 2.55 (t, ^3J = 7.0 Hz, 2 H, α - CH_2-), 2.89 (t, ^3J = 7.0 Hz, 2 H, α - $\text{CH}_2\text{CH}_2\text{O}$ -), 3.36 (s, 3 H, $-\text{CH}_3$), 3.50 (m, 2 H, $-\text{OCH}_2-$), 3.60 (m, 12 H, $-\text{OCH}_2-$), 7.56 (s, 1 H, arom.), 7.64 (s, 1 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): δ = 14.00, 22.51, 28.91, 30.05, 31.51, 39.74, 39.81, 58.97, 70.24, 70.32, 70.48, 70.53, 70.63, 71.91, 100.22, 100.40, 139.22, 140.13, 140.87, 145.45 ppm.

MS (EI, 80 eV, 140 °C): m/z (%) = 605 (1), 604 (4) $[\text{M}]^+$, 500 (1) $[\text{M}-\text{C}_5\text{H}_{12}\text{O}_2]^+$, 442 (3), 441 (27), 440 (100) $[\text{M}-\text{C}_7\text{H}_{16}\text{O}_4]^+$, 317 (2), 316 (1), 315 (7), 314 (25) $[\text{M}-\text{C}_7\text{H}_{15}\text{O}_4-\text{I}]^+$.

| | | | | | | |
|-----------|--|-------|---|-------|---|------|
| EA | $\text{C}_{21}\text{H}_{34}\text{O}_4\text{I}_2$ | calc. | C | 41.74 | H | 5.67 |
| | (604.308) | found | | 41.11 | | 4.28 |

2-(4-Hexylphenyl)-ethanol **72**



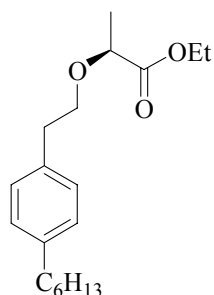
1.00 g (3.2 mmol) benzoic acid 2-(4-hexylphenyl)-ethyl ester **58**, 3.0 g (53.5 mmol) KOH were dissolved in 40 ml methanol and 40 ml THF and cooked under reflux for 20 h. After addition of 100 ml ether the layers were separated and the organic layer was washed with aqueous saturated Na_2CO_3 solution. The organic layer was dried over MgSO_4 , filtered and the solvent evaporated.

Yield: 0.59 g (89 %) of a colorless oil.

$^1\text{H NMR}$ (CDCl_3 , 250 MHz): δ = 0.89 (t, ^3J = 7.0 Hz, 3 H, $-\text{CH}_3$), 1.29 (m, 6 H, $-\text{CH}_2-$), 1.58 (quint, ^3J = 7.0 Hz, 2 H, β - CH_2-), 2.57 (t, ^3J = 7.0 Hz, 2 H, α - CH_2-), 2.83 (t, ^3J = 6 Hz, 2 H, α - CH_2-), 3.81 (t, ^3J = 6 Hz, 2 H, $-\text{OCH}_2-$), 3.90 (s, 1 H, $-\text{OH}$), 7.14 (s, 4 H, arom.) ppm.

^{13}C NMR (CDCl_3 , 63 MHz): $\delta = 14.07, 22.58, 28.99, 31.49, 35.53, 38.73, 52.07, 63.69, 118.92, 128.57, 128.84, 132.88, 135.46$ ppm.

2-[2-(4-Hexylphenyl)-ethoxy]-propionic acid ethyl ester **73**



0.5 ml (3.0 mmol) Triflate anhydride were cooled to 0 °C and a solution of 610 mg (3.0 mmol) **72** and 0.5 ml (3.0 mmol) triethylamine in 4 ml dry CH_2Cl_2 was added dropwise over 5 minutes. The cooling bath was removed and the solution was stirred for 0.5 h. 2 ml (13.5 mmol) (S)-lactic acid ethyl ester were added and stirred for additionally 3 h. The crude mixture was dried under vacuum and the residue was purified by column chromatography (silica gel; hexane/ethyl acetate 20:1).

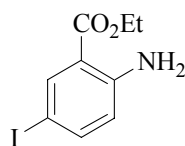
Yield: 0.70 g (76 %) of a colorless oil.

$r_f = 0.32$ (silica gel; hexane/ethyl acetate 10:1).

^1H NMR (CDCl_3 , 250 MHz): $\delta = 0.86$ (t, $^3J = 7.0$ Hz, 3 H, $-\text{CH}_3$), 1.30 (m, 12 H, $-\text{CH}_2-$; 2- CH_3), 1.76 (quint, $^3J = 7.0$ Hz, 2 H, β - CH_2-), 2.56 (t, $^3J = 7.0$ Hz, 2 H, α - CH_2-), 2.89 (t, $^3J = 6$ Hz, 2 H, α - CH_2-), 3.55 (dt, $^3J = 9.0$ Hz, 1 H, $-\text{OCH}_2-$), 3.80 (dt, $^3J = 9.0$ Hz, 1 H, $-\text{OCH}_2-$), 3.96 (q, $^3J = 9.0$ Hz, 1 H, $-\text{OCH}(\text{CH}_3)-$), 4.20 (q, $^3J = 9.0$ Hz, 2 H, $-\text{OCOCH}_2-$), 7.10 (dd, $^3J = 11.0$ Hz, 4 H, arom.) ppm.

^{13}C NMR (CDCl_3 , 63 MHz): $\delta = 14.01, 14.14, 18.54, 22.54, 28.94, 31.44, 31.66, 35.49, 35.84, 60.68, 71.23, 75.07, 128.29, 128.69, 135.54, 140.77, 173.27$ ppm.

2-Amino-5-iodobenzoic acid ethyl ester **78**



20.00 g (76.0 mmol) **75** were dissolved in a mixture of 500 ml dry ethanol and 200 ml concentrated sulfuric acid at rt. The mixture was refluxed for 3 h and poured onto 1500 g ice. The solution was neutralized with Na₂CO₃ and the preprecipitate was filtered off. The product was dried under high vacuum.

Yield: 18.9 g (85 %) of a colorless solid.

$r_f = 0.66$ (silica gel; hexane/ethyl acetate 1:1).

mp.: 69.1 °C

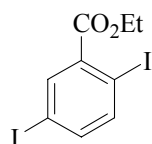
¹H NMR (250 MHz, CDCl₃): $\delta = 1.36$ (t, ³J = 8.0 Hz, 3 H, -CH₃), 4.30 (q, ³J = 8.0 Hz, 2 H, -CH₂-), 5.66 (s, 2 H, -NH₂), 6.58 (d, ³J = 9.8 Hz, 1 H, arom.), 7.45 (d, ³J = 9.8 Hz, 1 H, arom.), 8.12 (s, 1 H, arom.) ppm.

¹³C NMR (63 MHz, CDCl₃): $\delta = 14.28, 60.63, 118.73, 127.47, 128.20, 139.35, 142.02, 149.78, 164.88$ ppm.

MS (EI, 80 eV, 30 °C): m/z (%) = 293 (1), 292 (11), 291 (100) [M]⁺, 263 (4) [M-C₂H₄]⁺, 247 (1), 246 (15), 245 (56) [M-C₂H₄-OH]⁺, 219 (1), 218 (6) [M-EtOH-HCN]⁺.

HRMS [¹²C₉¹H₁₀¹⁴N₁¹⁶O₂¹²⁷I₁]⁺ calc.: 290.97563 found: 290.97455.

2,5-Diiodobenzoic acid ethyl ester **79**



10.00 g (34.4 mmol) **78** were suspended in 35 ml water and 9 ml concentrated hydrochloric acid. The mixture was cooled to 0 °C and a solution of 2.40 g (34.8 mmol) sodium nitrite in 7 ml water was added at a temperature between 0 and 5 °C. After 1 h the mixture was dropped into an ice cooled solution of 7.50 g (50 mmol) sodium iodide in 9 ml water. After 1 h 20 ml of a saturated Na₂S₂O₃ solution were added to reduce the excess of iodine. The mixture was extracted twice with CH₂Cl₂ and the combined organic layers were washed with saturated NaHCO₃ and brine. The solution was dried over MgSO₄, filtered and the solvent evaporated. The crude produkt was purified by flash column chromatography (silica gel; hexane/ethyl acetate 100:1).

Yield: 8.05 g (60 %) of a colorless solid.

$r_f = 0.39$ (silica gel; hexane/ethyl acetate 10:1).

mp : 58.8 °C

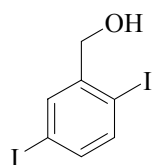
¹H NMR (250 MHz, CDCl₃): δ = 1.39 (t, J = 7.5 Hz, 3 H), 4.38 (q, ³J = 7.5 Hz, 2 H), 7.42 (d, ³J = 9.7 Hz, 1 H, arom.), 7.66 (d, ³J = 9.7 Hz, 1 H, arom.), 8.06 (s, 1 H, arom.) ppm.

¹³C NMR (63 MHz, CDCl₃): δ = 14.16, 62.06, 93.01, 93.15, 139.43, 141.33, 142.64, 154.23, 164.88 ppm.

MS (EI, 80 eV, 30-40 °C): m/z (%) = 404 (1), 403 (10), 402(100), 401 (2) [M]⁺, 375 (1), 374 (5), 373 (6) [M-C₂H₅]⁺, 358 (5), 357 (51) [M-OC₂H₅]⁺, 330 (1), 329 (10), 328 (2) [M-CO₂C₂H₅]⁺, 203 (1), 202 (7), 201 (1) [M-CO₂C₂H₅-I]⁺.

HRMS [¹²C₉¹H₈¹⁶O₂¹²⁷I₂]⁺ calc.: 401.86138 found: 401.86432.

(2,5-Diiodophenyl)-methanol 80



13.13 g (32.7 mmol) of ester **79** were dissolved in 80 ml dry THF and cooled to 0 °C. 98 ml of a 1 M solution of DIBAH in hexane were added slowly under stirring. The mixture was stirred over night and allowed to come to rt. After addition of water, hydrochloric acid and ether the layers were separated. The aqueous layer was extracted two times with 50 ml ether. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The crude product was purified by recrystallization from chloroform.

Yield: 7.73 g (66 %) of a bright yellow solid.

r_F = 0.19 (silica gel; hexane/ethyl acetate 10:1).

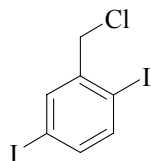
mp : 119.5 ° C (slightly subliming).

¹H NMR (250 MHz, CDCl₃): δ = 3.07 (s, 1 H, -OH), 4.24 (s, 2 H, -CH₂-), 7.02 (d, ³J = 9.0 Hz, 1 H, arom.), 7.23 (d, ³J = 9.0 Hz, 1 H, arom.), 7.54 (s, 1 H, arom.) ppm.

¹³C NMR (63 MHz, CDCl₃): δ = 67.27, 93.51, 95.07, 136.06, 137.22, 139.93, 145.00 ppm.

MS (EI, 80 eV, 50-80 °C): m/z (%) = 361 (15), 360 (100), 359 (3) [M]⁺, 343 (1) [M-OH]⁺, 329 (2) [M-CH₂OH]⁺, 233 (10), 232 (4), 231 (12), [M-HI-H]⁺, 216 (2), 215(5) [M-I-H₂O]⁺, 204 (7), 203 (5), 202 (3) [M-I-C₂H₅]⁺.

HRMS [¹²C₇¹H₆¹⁶O₁¹²⁷I₂]⁺ calc.: 359.85082 found: 359.85333.

2-Chloromethyl-1,4-diiodobenzene 81

2.00 g (5.6 mmol) of benzylic alcohol **80** and 3.9 ml (27.8 mmol) triethylamine were dissolved in 30 ml dry methylene chloride. 1.0 ml (11.2 mmol) mesylchloride were added slowly under stirring at rt. After 2 h stirring 10 ml water were added and the layers were separated. The organic layer was dried over MgSO₄, filtered and a small amount of silica gel was added before the solvent was evaporated. The purification was done by flash column chromatography (silica gel; hexane/ethyl acetate 10:1).

Yield: 1.35 g (64 %) of a colorless solid.

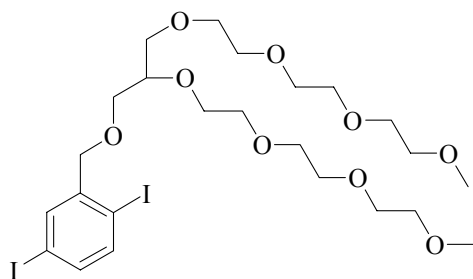
r_f = 0.50 (silica gel; hexane/ethyl acetate 10:1).

¹H NMR (250 MHz, CDCl₃): δ = 4.56 (s, 2 H, -CH₂Cl), 7.30 (d, ³J = 9.0 Hz, 1 H, arom.), 7.53 (d, ³J = 9.0 Hz, 1 H, arom.), 7.78 (s, 1 H, arom.) ppm.

¹³C NMR (63 MHz, CDCl₃): δ = 49.94, 93.96, 98.63, 138.77, 138.97, 141.15, 141.82 ppm.

MS (EI, 80 eV, 50-80 °C): m/z (%) = 381 (2), 380 (32), 379 (6), 378 (100) [M]⁺, 344 (6), 343 (75) [M-Cl]⁺, 251 (3) [M-HI]⁺, 217 (1), 216 (15), 215 (1) [M-I-Cl]⁺.

HRMS [¹²C₇¹H₆³⁵Cl₁¹²⁷I₂]⁺ calc.: 377.81693 found: 377.81555.
[M-³⁵Cl₁]⁺ calc.: 342.84808 found: 342.84567.

2-(2,3-Bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-propoxymethyl)-1,4-diiodobenzene 82

283 mg (0.7 mmol) of alcohol **22** were dissolved in 15 ml dry THF under nitrogen. 29 mg (0.7 mmol) sodium hydride were added at rt and the resulting mixture was stirred for 40

minutes. 253 mg (0.7 mmol) of benzylic chloride **81** were added and stirred for 1 h at rt. The mixture was refluxed for 2 d and was diluted with 20 ml methylene chloride. The precipitate was filtered off. The solvent was evaporated and the residue was purified by flash column chromatography (silica gel; MeCl₂/MeOH 3 %). The product was dried under high vacuum for 2 d.

Yield: 290 mg (60 %) of a colorless solid.

$r_f = 0.18$ (silica gel; MeCl₂/MeOH 2 %).

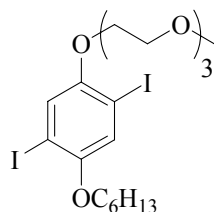
¹H NMR (500 MHz, CDCl₃): $\delta = 3.35$ (s, 6 H, -CH₃), 3.52 (dt, ³J = 7 Hz, 4 H), 3.57-3.72 (m, 22 H, -CH₂O-), 3.72 (m, 1 H), 3.78 (t, ³J = 7.0 Hz, 2 H), 4.43 (s, 2 H), 7.28 (d, ³J = 9.0 Hz, 1 H, arom.), 7.48 (d, ³J = 9.0 Hz, 1 H, arom.), 7.73 (s, 1 H, arom.).

¹³C NMR (126 MHz, CDCl₃): $\delta = 58.84, 69.74, 70.37, 70.43, 70.48, 70.49, 70.70, 70.76, 70.92, 70.94, 71.82, 76.28, 76.75, 77.01, 77.26, 78.27, 93.87, 96.18, 137.19, 137.84, 140.31, 142.76$.

MS (EI, 80 eV, 200 °C): m/z (%) = 727 (1), 726 (2) [M]⁺, 599 (1) [M-I]⁺, 399 (1), 398 (1) [M-C₁₄H₃₂O₈]⁺, 353 (3) [C₁₂H₁₈O₄I]⁺, 344 (2), 343 (25) [C₇H₅I₂]⁺, 59 (100) [C₃H₇O]⁺.

HRMS [¹²C₂₄¹H₄₀¹⁶O₉¹²⁷I₂]⁺ calc.: 726.07619 found: 726.07624.

1-Hexyloxy-2,5-diiodo-4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene **84**



508 mg (2.0 mmol) iodine and 860 mg (2.0 mmol) bis-(trifluoroacetoxy)-iodobenzene were dissolved in 10 ml methylene chloride and stirred for 10 minutes at rt. 501 mg (1.5 mmol) of compound **87** in 5 ml methylene chloride were added slowly. The resulting mixture was stirred for 3 h at r.t. and then quenched with 20 ml of a saturated aqueous Na₂S₂O₃ solution. The organic layer was washed with saturated NaHCO₃ solution, dried over MgSO₄, filtered and the solvent evaporated. The yellow oil was purified by column chromatography (silica gel; hexane/ethyl acetate 5:1).

Yield: 610 mg (61 %) of a colorless solid.

$r_f = 0.46$ (silica gel; hexane/ethyl acetate 1:2).

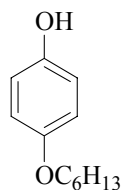
¹H-NMR (250 MHz, CDCl₃, 20 °C): δ = 0.87 (t, 3 H, ³J = 7.0 Hz, -CH₃), 1.33 (m, 4 H, -CH₂-), 1.47 (m, 2 H, γ -CH₂-), 1.77 (quint, 2 H, ³J = 7.5 Hz, β -CH₂-), 3.35 (s, 3 H, -OCH₃), 3.50 (m, 2 H), 3.62 (m, 4 H), 3.73 (t, 2 H, ³J = 5.5 Hz, -OCH₂-), 3.86 (m, 4 H, -OCH₂-), 3.86 (m, 4 H, α -CH₂-; -CH₂O-), 4.05 (t, 2 H, ³J = 5.5 Hz, α -OCH₂-), 7.11 (s, 1 H, arom.), 7.20 (s, 1 H, arom.) ppm.

¹³C-NMR (63 MHz, CDCl₃, 20 °C): δ = 13.89, 22.42, 25.55, 28.94, 31.30, 58.89, 69.49, 70.15, 70.20, 70.44, 70.60, 70.98, 71.82, 86.11, 86.38, 122.47, 123.56, 152.61, 153.08 ppm.

MS (pos. FAB, 3 kV, MNBA/CDCl₃): m/z (%) = 593 (5), 592 (19) [M]⁺, 466 (26) [M-I+H]⁺, 390 (2) [M-I-C₃H₇O₂]⁺, 262 (14) [C₈H₇O₂I]⁺, 147 (12) [C₇H₁₅O₃]⁺, 59 (100) [C₃H₇O]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | [C ₁₉ H ₃₀ O ₅ I ₂] | calc. | C 38.53 | H 5.11 |
| | (592.253) | found | 38.31 | 5.06 |

4-Hexyloxyphenol **86**



12.00 g (107.9 mmol) 1,4-dihydroquinone **85**, 100 ml (576.6 mmol) tetraethylene glycol as cosolvent, 14.2 ml (100.0 mmol) 1-bromohexane, and 13.81 g (100.0 mmol) K₂CO₃ were dissolved in 300 ml dioxane under nitrogen. The reaction mixture was cooked under reflux for 20h. The solvent was evaporated and the viscous oil was mixed with 200 ml water and extracted three times with each 100 ml ether. The organic layer was washed two times with 1 N hydrochloric acid and another two times with dest. water. The organic layer was dried over MgSO₄, filtered and the solvent evaporated. The brown oil was purified by column chromatography (silica gel; methylene chloride).

Yield: 9.89 g (51 %).

r_f = 0.24 (silica gel; methylene chloride).

mp.: 44.2 °C

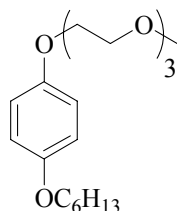
¹H-NMR (250 MHz, CDCl₃, 20 °C): δ = 0.89 (t, 3 H, ³J = 7.5 Hz, -CH₃), 1.33 (m, 6 H, -CH₂-), 1.72 (quint, 2 H, ³J = 7.5 Hz, β -CH₂-), 3.87 (t, 2 H, ³J = 7.5 Hz, α -CH₂-), 5.36 (s, 1 H, -OH), 6.77 (s, 4 H, arom.) ppm.

$^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , 20 °C): $\delta = 13.97, 22.56, 25.66, 29.27, 31.55, 68.94, 103.39, 115.76, 116.07, 149.39, 153.13$ ppm.

MS (pos. FAB, 3 kV): m/z (%) = 194 (89) $[\text{M}]^+$, 123 (18) $[\text{M}-\text{C}_5\text{H}_9]^+$, 110 (100) $[\text{M}-\text{C}_6\text{H}_{12}]^+$, 43 (49) $[\text{C}_3\text{H}_7]^+$.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | $[\text{C}_{12}\text{H}_{18}\text{O}_2]$ | calc. | C 74.19 | H 9.34 |
| | (194.274) | found | 73.75 | 9.05 |

1-Hexyloxy-4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene **87**



9.70 g (49.9 mmol) phenol **86**, 13.80 g (99.8 mmol) K_2CO_3 and 19.9 g (62.4 g) tosylate **15** were dissolved under nitrogen in 250 ml dioxane p. a. and cooked under reflux for 2 d. The preprecipitate was filtered off and the solvent was evaporated. The orange oil was purified by column chromatography (silica gel; hexane/ethyl acetate 4:1).

Yield: 9.48 g (56 %) of a colorless oil.

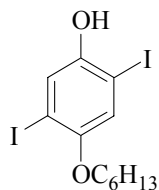
$r_f = 0.35$ (silica gel; hexane/ethyl acetate 1:1).

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , 20 °C): $\delta = 0.88$ (t, 3 H, $^3J = 7.0$ Hz, $-\text{CH}_3$), 1.29 (m, 4 H, $-\text{CH}_2-$), 1.42 (m, 2 H, $\gamma\text{-CH}_2-$), 1.71 (quint, 2 H, $^3J = 7.5$ Hz, $\beta\text{-CH}_2-$), 3.30 (s, 3 H, $-\text{OCH}_3$), 3.52 (m, 2 H), 3.64 (m, 6 H), 3.80 (t, 2 H, $^3J = 5.5$ Hz, $-\text{OCH}_2-$), 3.86 (t, 2 H, $^3J = 7.5$ Hz, $\alpha\text{-CH}_2-$), 4.04 (t, 2 H, $^3J = 5.5$ Hz, $\alpha\text{-OCH}_2-$), 6.80 (s, 4 H, arom.) ppm.

$^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , 20 °C): $\delta = 13.88, 22.46, 25.61, 29.24, 31.47, 58.85, 68.03, 68.49, 69.76, 70.44, 70.54, 70.68, 71.83, 115.25, 115.52, 152.75, 153.39$ ppm.

MS (EI, 80 eV, 3 kV): m/z (%) = 341 (10), 340 (43) $[\text{M}]^+$, 194 (7) $[\text{M}-\text{C}_7\text{H}_{14}\text{O}_3]^+$, 147 (12) $[\text{C}_7\text{H}_{15}\text{O}_3]^+$, 59 (100) $[\text{C}_3\text{H}_7\text{O}]^+$.

HRMS $[\text{C}_{19}\text{H}_{32}\text{O}_5]^+$ calc.: 340.22498 found: 340.22517.

4-Hexyloxy-2,5-diiodophenol 91

8.05 g (22.2 mmol) 2,5-Diiodohydroquinone **90** and 3.74 g (66.7 mmol) powdered KOH were dissolved in 60 ml DMSO under nitrogen. An emulsion of 3.12 ml (22.2 mmol) 1-bromohexane in 10 ml DMSO were added rapidly under stirring at rt. The reaction mixture was stirred for 24 h at rt. The mixture was poured into water and the side product was filtered off. The aqueous solution was acidified (pH 3) and the preprecipitate was collected and washed with water to remove residue DMSO. The crude product was purified by recrystallization from chloroform.

Yield: 5.12 g (52 %).

$r_f = 0.70$ (silica gel; hexane/ethyl acetate 1:1).

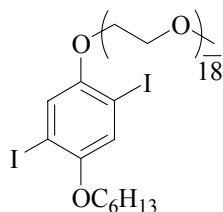
mp.: 55.1 °C

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , 20 °C): $\delta = 0.86$ (t, 3 H, $^3J = 7.0$ Hz, $-\text{CH}_3$), 1.29 (m, 4 H, $-\text{CH}_2-$), 1.45 (quint, 2 H, $^3J = 7.0$ Hz, $\gamma\text{-CH}_2-$), 1.77 (quint, 2 H, $^3J = 7.0$ Hz, $\beta\text{-CH}_2-$), 3.89 (t, 2 H, $^3J = 7.0$ Hz, $\alpha\text{-CH}_2-$), 4.92 (bs, 1 H, $-\text{OH}$), 6.99 (s, 1 H, arom.), 7.39 (s, 1 H, arom.) ppm.

$^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , 20 °C): $\delta = 14.01, 22.54, 25.66, 29.04, 31.41, 70.38, 84.38, 87.59, 120.97, 124.79, 149.78, 152.60$ ppm.

MS (EI, 80 eV, 3 kV): m/z (%) = 447 (5), 446 (30) $[\text{M}]^+$, 362 (100) $[\text{M}-\text{C}_6\text{H}_{12}]^+$, 235 (5) $[\text{C}_6\text{H}_4\text{O}_2\text{I}]^+$.

HRMS $[\text{C}_{12}\text{H}_{16}\text{O}_2\text{I}_2]^+$ calc.: 445.92398 found: 445.92654.

1-Hexyloxy-2,5-diiodo-4-[PEG mono methyl ether 750]-benzene 92

1.50 g (2.8 mmol) phenol **91**, 1.12 g (4.2 mmol) triphenylphosphine and 2.32 g (2.80 mmol) PEG 750 mono methyl ether **26** were dissolved in 30 ml dry THF. 909 mg (4.3 mmol) diisopropyl azodicarboxylate (DIAD) in 10 ml dry THF were added dropwise under nitrogen and light exclusion. The mixture was stirred for 1 d at rt. The solvent was evaporated and the crude product was purified by dialysis in water. Traces of TPPO could not be removed.

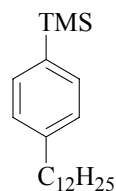
Yield: 1.38 g (40 %) of a yellow waxy solid.

$r_f = 0.18$ (acetone/ ether 7:3).

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , 20 °C): $\delta = 0.87$ (t, 3 H, $^3J = 7.0$ Hz, $-\text{CH}_3$), 1.33 (m, 4 H, $-\text{CH}_2-$), 1.47 (m, 2 H, $\gamma\text{-CH}_2-$), 1.77 (quint, 2 H, $^3J = 7.5$ Hz, $\beta\text{-CH}_2-$), 3.30 (s, 3 H, $-\text{OCH}_3$), 3.50 (m, 2 H, $-\text{CH}_2\text{O}-$), 3.62 (m, 60 H, $-\text{CH}_2\text{O}-$), 3.73 (t, 2 H, $^3J = 5.5$ Hz, $\alpha\text{-OCH}_2-$), 3.86 (m, 4 H, $\alpha\text{-CH}_2-$; $-\text{CH}_2\text{O}-$), 4.05 (t, 2 H, $^3J = 5.5$ Hz, $\alpha\text{-OCH}_2-$), 7.11 (s, 1 H, arom.), 7.18 (s, 1 H, arom.) ppm.

$^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , 20 °C): $\delta = 13.91, 22.45, 25.58, 28.97, 31.33, 58.89, 69.51, 70.21, 70.28, 70.46, 70.61, 71.02, 71.83, 86.14, 86.41, 122.54, 123.62, 152.86, 153.25$ ppm.

1-Dodecyl-4-trimethylsilylbenzene **96**



12.04 g (96.7 mmol) 9-BBN and 22.6 ml (96.7 mmol) 1-dodecene were dissolved in 340 ml dry toluene and stirred for 10 h. 11.60 g (290.1 mmol) NaOH, 21.12 g (92.1 mmol) **95** and 290 ml water were added and the solution was degassed three times by evacuation and N_2 ventilating for 10 minutes per operation. 1.38 g (1.2 mmol) $\text{Pd}(\text{PPh}_3)_4$ was added immediately followed by again three times degassing. The reaction mixture was refluxed under nitrogen for 2 d. The two-layer-system was cooled to rt, the layers were separated and the aqueous layer was extracted three times with 50 ml toluene. The combined organic layers were dried over MgSO_4 , filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate 10/1; $r_f = 0.81$).

Yield: 28.42 g (97 %) of a colorless solid.

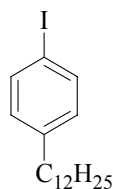
¹H NMR (CDCl₃, 250 MHz): δ = 0.30 (s, 9 H, -TMS), 0.89 (t, ³J = 8.0 Hz, 3 H, -CH₃), 1.29 (m, 18 H, -CH₂-), 1.63 (quint, ³J = 8.0 Hz, 2 H, β -CH₂-), 2.63 (t, ³J = 8.0 Hz, 2 H, α -CH₂-), 7.17 (d, ³J = 9.0 Hz, 2 H, arom.), 7.44 (d, ³J = 9.0 Hz, 2 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 0.95, 14.11, 22.70, 29.38, 29.46, 29.55, 29.70, 31.43, 31.95, 36.01, 127.90, 133.32, 137.03, 143.63 ppm.

MS (EI, 80 eV, 90 °C): m/z (%) = 318 (10) [M]⁺, 303 (100) [M-CH₃]⁺.

| | | | | |
|-----------|------------------------------------|-------|---------|---------|
| EA | C ₂₁ H ₃₈ Si | calc. | C 79.16 | H 12.02 |
| | (318.616) | found | 78.61 | 11.81 |

1-Dodecyl-4-iodobenzene 97



28.30 g (88.8 mmol) **96** were dissolved in 150 ml dry CH₂Cl₂ and cooled to -40 °C. A solution of 15.45 g (93.3 mmol) iodine chloride in 100 ml dry CH₂Cl₂ was added dropwise under stirring. After complete addition the mixture was allowed to come to rt and stirred for 1 h. 30 ml saturated aqueous Na₂S₂O₃ solution were added and the layers were separated. The aqueous layer was extracted three times with 50 ml CH₂Cl₂. The combined organic layers were washed with saturated aqueous NaHCO₃ solution, dried over MgSO₄, filtered and the solvent evaporated.

Yield: 31.50 g (95 %) of a colorless oil.

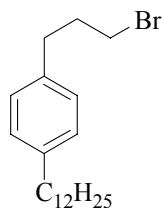
r_f = 0.73 (silica gel, hexane/ethyl acetate 10:1).

¹H NMR (CDCl₃, 250 MHz): δ = 0.90 (t, ³J = 8.0 Hz, 3 H, -CH₃), 1.29 (m, 18 H, -CH₂-), 1.59 (quint, ³J = 8.0 Hz, 2 H, β -CH₂-), 2.59 (t, ³J = 8.0 Hz, 2 H, α -CH₂-), 6.93 (d, ³J = 9.0 Hz, 2 H, arom.), 7.59 (d, ³J = 9.0 Hz, 2 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.12, 22.70, 29.21, 29.37, 29.47, 29.58, 29.66, 31.26, 31.93, 35.45, 90.51, 130.50, 137.21, 142.45 ppm.

MS (EI, 80 eV, 90 °C): m/z (%) = 374 (2), 373 (20), 372 (100) [M]⁺, 246 (7) [M-I+H]⁺, 218 (10), 217 (54) [M-C₁₁H₂₃]⁺.

| | | | | |
|-----------|-----------------------------------|-------|---------|--------|
| EA | C ₁₈ H ₂₉ I | calc. | C 58.07 | H 7.85 |
| | (372.333) | found | 58.45 | 7.71 |

1-(3-Bromopropyl)-4-dodecylbenzene 98

2.00 g (5.4 mmol) 4-dodecyl iodobenzene **97** were dissolved in 13 ml dry THF and cooled to 0 °C. 3 ml (5.9 mmol) of a ¹PrMgCl solution (2M) in ether were added slowly. After 0.5 h stirring the solution was taken up in a syringe and 2.7 ml (26.9 mmol) 1,3-dibromopropane and 0.7 ml lithium chlorocuprate (0.1 M in THF) were added to the empty flask and cooled to 0 °C. The Grignard compound was added during 1 h and the resulting mixture was stirred for 2 d at rt. 0.7 ml, 0.7 ml and 0.4 ml Li₂CuCl₄ solution were added after 3 h, 6 h and after 20 h, respectively. The reaction mixture was quenched with water and extracted three times with ether. After drying the crude product under high vacuum to remove 1,3-dibromopropane, it was purified by flash column chromatography (silica gel; hexane).

Yield: 1.63 g (83 %) of a colorless oil.

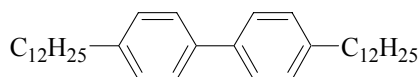
*r*_F = 0.39 (silica gel; hexane).

¹H NMR (CDCl₃, 250 MHz): δ = 0.90 (t, ³J = 8 Hz, 3 H, -CH₃), 1.25 (m, 18 H, -CH₂-), 1.60 (quint, ³J = 8 Hz, 2 H, β-CH₂-), 2.15 (m, 2 H, β-CH₂-), 2.55 (t, ³J = 8 Hz, 2 H, α-CH₂-), 2.75 (t, ³J = 8 Hz, 2 H, α-CH₂-), 3.40 (t, ³J = 8 Hz, 2 H, -CH₂Br), 7.12 (s, 4 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.08, 22.67, 29.35, 29.51, 29.59, 29.66, 31.52, 31.91, 33.08, 33.58, 34.25, 35.56, 128.37, 128.48, 137.60, 140.76 ppm.

MS (EI, 80 eV, 120 °C): *m/z* (%) = 369 (16), 368 (67), 367 (17), 366 (65) [M]⁺, 214 (21), 213 (87), 212 (21), 211 (86) [M-C₁₁H₂₃]⁺, 105 (100), 104 (78) [C₂H₂Br]⁺.

HRMS [¹²C₂₁¹H₃₁⁷⁹Br₁]⁺ calc.: 366.19221 found: 366.19455.

4,4'-Didodecylbiphenyl 99

1.10 g (3.0 mmol) **97** were dissolved in 30 ml toluene p. a. and 25 ml 1 M aqueous NaOH solution were added. The mixture was degassed three times by evacuation and N₂ ventilating

for 10 minutes per operation. 350 mg (1 mol %) Pd(PPh₃)₄ was added immediately followed by again three times degassing. The reaction mixture was refluxed under nitrogen for 4 d. The layers were separated and the aqueous layer was extracted twice with 20 ml toluene. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The yield was determined by HPLC analysis. The crude product was purified by recrystallization from methylene chloride.

Yield: 390 mg (53 %) of a colorless oil.

$r_f = 0.74$ (silica gel; hexane/ethyl acetate 10:1).

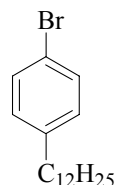
mp.: 75.9 °C

¹H NMR (CDCl₃, 250 MHz): $\delta = 0.87$ (t, ³J = 8.0 Hz, 6 H, -CH₃), 1.27 (m, 36 H, -CH₂-), 1.64 (quint, ³J = 8.0 Hz, 4 H, β -CH₂-), 2.62 (t, ³J = 8.0 Hz, 4 H, α -CH₂-), 7.22 (d, ³J = 9.8 Hz, 4 H, arom.), 7.48 (d, ³J = 9.8 Hz, 4 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 14.10, 22.68, 29.36, 29.53, 29.61, 29.66, 31.48, 31.92, 35.60, 126.77, 128.78, 138.49, 141.73$ ppm.

MS (EI, 80 eV, 120°C): m/z (%) = 493 (6), 492 (28), 491 (58), 490 (100) [M]⁺, 336 (3), 335 (12) [M-C₁₁H₂₃]⁺, 182 (2), 181 (16), 180 (12) [M-C₂₂H₄₅]⁺.

1-Bromo-4-dodecylbenzene 100



9.78 g (30.7 mmol) **96** were dissolved in 50 ml dry CH₂Cl₂ and cooled to -78 °C. 1.6 ml (30.7 mmol) bromine in 5 ml dry CH₂Cl₂ were added dropwise. The solution was warmed to rt and stirred for 1 h. 20 ml of a saturated aqueous Na₂S₂O₃ solution were added. The layers were separated and the aqueous layer was extracted twice with 30 ml CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The crude product was purified by vacuum distillation (147 °C; 3.1·10⁻¹ mbar).

Yield: 8.79 g (88 %) of a colorless oil.

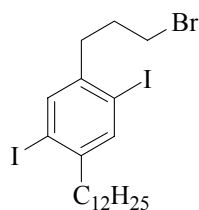
¹H NMR (CDCl₃, 250 MHz): $\delta = 0.90$ (t, ³J = 8.0 Hz, 3 H, -CH₃), 1.29 (m, 18 H, -CH₂-), 1.60 (quint, ³J = 8.0 Hz, 2 H, β -CH₂-), 2.59 (t, ³J = 8.0 Hz, 2 H, α -CH₂-), 7.09 (d, ³J = 10.0 Hz, 2 H, arom.), 7.42 (d, ³J = 10.0 Hz, 2 H, arom.) ppm.

^{13}C NMR (CDCl_3 , 63 MHz): $\delta = 14.12, 22.70, 29.21, 29.37, 29.47, 29.58, 29.66, 31.26, 31.93, 35.45, 119.27, 130.10, 131.23, 141.75$ ppm.

MS (EI, 80 eV, 90 °C): m/z (%) = 326 (65), 324 (67) $[\text{M}]^+$, 171 (81), 169 (83) $[\text{M}-\text{C}_{11}\text{H}_{23}]^+$, 91 (78) $[\text{C}_7\text{H}_7]^+$, 43 (100) $[\text{C}_3\text{H}_7]^+$.

| | | | | |
|----|---------------------------------------|-------|---------|--------|
| EA | $\text{C}_{18}\text{H}_{29}\text{Br}$ | calc. | C 66.45 | H 8.98 |
| | (325.332) | found | 67.79 | 9.01 |

1-(3-Bromopropyl)-4-dodecyl-2,5-diiodobenzene **101**



1.08 g (4.2 mmol) Iodine and 2.04 g (4.6 mmol) bis-(trifluoroacetoxy)phenyl iodine were dissolved in 40 ml dry methylene chloride. 1.30 g (3.5 mmol) of compound **100** in 10 ml dry CH_2Cl_2 were added dropwise under slightly cooling at rt. The solution was stirred for 2 h at rt and quenched with 30 ml saturated NaHCO_3 solution. The layers were separated and the organic layer was washed with brine. After drying over MgSO_4 and filtering, the solvent was evaporated and the crude product was purified by flash column chromatography (silica gel; hexane).

Yield: 1.29 g (60 %) of a colorless solid.

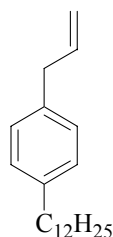
$r_f = 0.38$ (silica gel; hexane).

^1H NMR (CDCl_3 , 250 MHz): $\delta = 0.86$ (t, $^3J = 8.0$ Hz, 3 H, $-\text{CH}_3$), 1.24 (m, 18 H, $-\text{CH}_2-$), 1.52 (quint, $^3J = 8.0$ Hz, 2 H, $\beta\text{-CH}_2-$), 2.12 (m, 2 H, $\beta\text{-CH}_2-$), 2.56 (t, $^3J = 8.0$ Hz, 2 H, $\alpha\text{-CH}_2-$), 2.76 (t, $^3J = 8.0$ Hz, 2 H, $\alpha\text{-CH}_2-$), 3.42 (t, $^3J = 8.0$ Hz, 2 H, $-\text{CH}_2\text{Br}$), 7.59 (s, 1 H, arom.), 7.64 (s, 1 H, arom.) ppm.

^{13}C NMR (CDCl_3 , 63 MHz): $\delta = 14.14, 22.68, 29.37, 29.54, 29.64, 30.13, 31.91, 32.68, 38.03, 39.85, 100.14, 100.43, 139.48, 139.58, 142.56, 145.55$ ppm.

MS (EI, 80 eV, 120 °C): m/z (%) = 622 (7), 621 (39), 620 (100), 619 (52), 618 (99) $[\text{M}]^+$, 494 (5), 492 (5) $[\text{M}-\text{I}]^+$, 465 (6), 464 (14), 463 (6), 462 (11) $[\text{M}-\text{I}-\text{C}_2\text{H}_5]^+$.

| | | | | |
|----|--|-------|---------|--------|
| EA | $\text{C}_{21}\text{H}_{33}\text{BrI}_2$ | calc. | C 40.73 | H 5.37 |
| | (619.206) | found | 40.75 | 5.14 |

1-Allyl-4-dodecylbenzene**104**

12.56 g (38.6 mmol) of 4-dodecylbromobenzene **100** were dissolved in 125 ml dry ether under nitrogen and cooled to $-45\text{ }^{\circ}\text{C}$ (EtOH/liquid nitrogen bath). 52 ml (83.2 mmol) $^t\text{BuLi}$ -solution were added slowly. After complete addition the mixture was warmed to $7\text{ }^{\circ}\text{C}$. The solution was again cooled to $-45\text{ }^{\circ}\text{C}$ and 23.35 g (193.0 mmol) 1-bromopropene were added dropwise. The solution was stirred over night and allowed to warm up to rt. The mixture was quenched with 60 ml water, the layers were separated and the aqueous layer was extracted twice with 50 ml ether. The combined organic layers were dried over MgSO_4 , filtered and the solvent evaporated. The crude product was purified by flash column chromatography (silica gel; hexane).

Yield: 8,48 g (76 %) of a colorless solid.

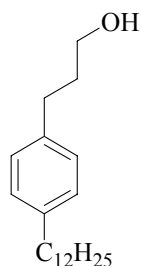
mp.: $42.3\text{ }^{\circ}\text{C}$

^1H NMR (CDCl_3 , 250 MHz): $\delta = 0.90$ (t, $^3\text{J} = 8.0\text{ Hz}$, 3 H, CH_3), 1.40 (s, 18 H, $-\text{CH}_2-$), 1.60-1.70 (m, 2 H, $\beta\text{-CH}_2-$), 2.60 (t, $^3\text{J} = 8.0\text{ Hz}$, 2 H, $\alpha\text{-CH}_2-$), 3.45 (d, $^3\text{J} = 8.0\text{ Hz}$, 2 H, allylic- $\gamma\text{-CH}_2-$), 5.10 (t, $^3\text{J} = 8.0\text{ Hz}$, 2 H, allylic- $\alpha\text{-CH}_2-$), 5.80-6.05 (m, 1 H, allylic- CH-), 7.15 (s, 4 H) ppm.

^{13}C NMR (CDCl_3 , 63 MHz): $\delta = 14.10, 22.70, 29.37; 29.55, 29.63; 29.69, 31.32, 31.59, 31.94, 35.366, 35.58, 36.01, 39.87, 128.20, 137.16, 137.70, 140.64$ ppm.

MS (EI, 80 eV, 120°C): m/z (%) = 288 (2), 287 (19), 286 (84), 285 (1) $[\text{M}]^+$, 248 (1), 247 (6), 246 (30) $[\text{M}-\text{C}_3\text{H}_4]^+$, 131 (100) $[\text{M}-\text{C}_{11}\text{H}_{23}]^+$, 117 (52) $[\text{M}-\text{C}_{12}\text{H}_{25}]^+$.

HRMS $[\text{C}_{21}\text{H}_{34}]^+$ calc.: 286.26605 found: 286.26532.

3-(4-Dodecylphenyl)-propan-1-ol **105**

4.47 g (35.9 mmol) 9-BBN were dissolved in 100 ml dry THF and 9.35 g (32.6 mmol) **104** were added. The mixture was stirred for 20 h at rt under nitrogen. 30 ml 3 N aqueous NaOH and 39 ml H₂O₂ were added and refluxed for 1 h. The two layers were separated and the aqueous layer was extracted three times with 50 ml ether. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The crude product was purified by flash column chromatography (silica gel; hexane/ethyl acetate 10:1).

Yield: 7.33 g (74 %) of a colorless solid.

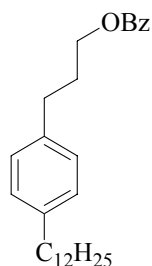
$r_f = 0.17$ (silica gel; hexane/ethyl acetate 10:1).

¹H NMR (CDCl₃, 250 MHz): $\delta = 0.85$ (t, ³J = 8.0 Hz, 3 H, -CH₃), 1.30 (m, 18 H, -CH₂-), 1.55 (quint, 2 H, ³J = 8.0 Hz, β -CH₂-), 1.95 (quint, 2 H, ³J = 9.0 Hz, β -CH₂-), 2.50 (t, 2 H, ³J = 9.0 Hz, α -CH₂-), 2.70 (t, ³J = 9.0 Hz, 2 H, α -CH₂-), 3.65 (t, 2 H, ³J = 8.0 Hz, -CH₂OH), 7.05 (s, 4 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 14.11, 22.68, 29.37, 29.53, 29.66, 31.57, 31.64, 31.92, 34.28, 35.55, 62.38, 128.25, 128.41$ ppm.

MS (EI, 80 eV, 120°C): m/z (%) = 306 (23), 305 (100) [M]⁺, 288 (6), 287 (25) [M-H₂O]⁺, 261 (8) [M-C₂H₅O]⁺, 149 (25) [M-C₁₁H₂₃]⁺, 131 (28) [C₁₀H₁₁]⁺.

| | | | | |
|-----------|-----------------------------------|-------|---------|---------|
| EA | C ₂₁ H ₃₆ O | calc. | C 82.83 | H 11.92 |
| | (304.516) | found | 82.81 | 11.43 |

Benzoic acid 3-(4-dodecylphenyl)-propyl ester **106**

6.70 g (22.0 mmol) **105** and 5.5 ml (39.6 mmol) dry triethylamine were dissolved in 100 ml dry CH₂Cl₂ and cooled to 0 °C. 3.9 ml (33.0 mmol) benzoyl chloride in 20 ml dry CH₂Cl₂ were added dropwise. The mixture was allowed to warm to rt and stirred for 16 h under nitrogen. After addition of 50 ml aqueous 1 M NaHCO₃ solution the two layers were separated and the aqueous layer was extracted three times with 50 ml methylene chloride. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The crude product was dried under high vacuum and purified by flash column chromatography (silica gel; hexane/ethyl acetate 10:1).

Yield: 8.45 g (94 %) of a colorless solid.

r_f = 0.48 (silica gel; hexane/ethyl acetate 10:1).

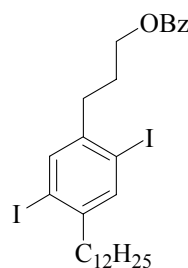
¹H NMR (CDCl₃, 250 MHz): δ = 0.91 (t, ³J = 8.0 Hz, 3H, -CH₃), 1.29 (m, 18 H, -CH₂-), 1.62 (quint, ³J = 8.0 Hz, 2 H, β -CH₂-), 2.12 (quint, 2H, ³J = 8.0 Hz, β -CH₂-), 2.59 (t, ³J = 8.0 Hz, 2 H, α -CH₂-), 2.78 (t, ³J = 8.0 Hz, 2 H, α -CH₂-), 4.36 (t, ³J = 8 Hz, 2 H, -CH₂OBz), 7.15 (s, 4H, arom.), 7.45 (dd, 2H, ³J = 8.0 Hz, *m*-benzoyl), 7.57 (t, ³J = 8.0 Hz, 1 H, *p*-benzoyl), 8.08 (d, 2 H, ³J = 8.0 Hz, *o*-benzoyl) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.07, 22.65, 29.33, 29.49, 29.63, 30.30, 31.51, 31.83, 31.88, 35.52, 64.27, 128.23, 128.25, 128.42, 129.50, 130.40, 132.76, 138.21, 140.56, 166.50 ppm.

MS (EI, 80 eV, 3 kV, 140°C): m/z (%) = 408 (2) [M]⁺, 288 (3), 287 (23), 286 (100) [M-C₇H₆O₂]⁺, 131 (56) [C₁₀H₁₁]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₂₈ H ₄₀ O ₂ | calc. | C 82.30 | H 9.87 |
| | (408.624) | found | 82.16 | 9.61 |

Benzoic acid 3-(4-dodecyl-2,5-diiodophenyl)-propyl ester **107**



5.51 g (21.7 mmol) Iodine and 10.10 g (22.7 mmol) bis-(trifluoroacetoxy)iodobenzene were dissolved in 10 ml dry methylene chloride and stirred for 10 minutes at rt under nitrogen. A

solution of 8.45 g (20.7 mmol) **106** in 60 ml dry CH_2Cl_2 was added slowly and stirred for 1 h. 50 ml of a 1 M NaHSO_3 solution were added to remove remaining iodine. The layers were separated and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with aqueous NaHCO_3 and brine. After drying over MgSO_4 and filtering the solvent was removed. The crude product was purified by flash column chromatography (silica gel; hexane/ethyl acetate 50:1).

Yield: 11.51 g (84 %) of a colorless solid.

$r_f = 0.30$ (silica gel; hexane/ethyl acetate 50:1).

$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 0.87$ (t, $^3J = 8.0$ Hz, 3 H, $-\text{CH}_3$), 1.27 (m, 18 H, $-\text{CH}_2-$), 1.57 (quint, $^3J = 8.0$ Hz, 2 H, $\beta\text{-CH}_2-$), 2.06 (quint, 2 H, $^3J = 8.0$ Hz, $\beta\text{-CH}_2-$), 2.56 (t, $^3J = 8.0$ Hz, 2 H, $\alpha\text{-CH}_2-$), 2.77 (t, $^3J = 8.0$ Hz, 2 H $\alpha\text{-CH}_2-$), 4.41 (t, $^3J = 8.0$ Hz, 2 H, $-\text{CH}_2\text{OBz}$), 7.14 (s, 4 H, arom.), 7.44 (t, 2 H, $^3J = 8.0$ Hz, *m*-benzoyl), 7.57 (t, 1 H, $^3J = 8.0$ Hz, *p*-benzoyl), 8.06 (d, 2 H, $^3J = 8.0$ Hz, *o*-benzoyl) ppm.

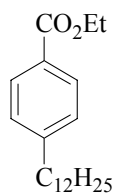
$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 14.08, 22.66, 29.18, 29.35, 29.53, 29.64, 30.12, 30.33, 31.52, 31.89, 35.54, 36.42, 39.84, 64.08, 64.32, 100.14, 100.42, 128.31, 128.45, 129.53, 129.60, 132.78, 132.86, 138.24, 139.45, 140.60, 143.24, 145.41, 173.51$ ppm.

MS (EI, 80 eV, 120°C): m/z (%) = 661 (3), 660 (4), 659 (2) $[\text{M}]^+$, 540 (1), 539 (9), 538 (27) $[\text{M}-\text{C}_7\text{H}_6\text{O}_2]^+$, 413 (3), 412 (9), 411 (1) $[\text{M}-\text{C}_7\text{H}_5\text{O}_2\text{-I}]^+$, 384 (1), 383 (6), 382 (7) $[\text{M}-\text{C}_7\text{H}_7\text{O}_2\text{-C}_{11}\text{H}_{23}]^+$, 288 (3), 287 (29), 286 (100) $[\text{M}-2\text{I}-\text{C}_7\text{H}_5\text{O}_2+\text{H}]^+$, 258 (1), 257 (8) $[\text{C}_{10}\text{H}_{10}\text{I}]^+$, 131 (65) $[\text{C}_{10}\text{H}_{11}]^+$.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | $\text{C}_{28}\text{H}_{38}\text{O}_2\text{I}_2$ | calc. | C 50.92 | H 5.80 |
| | (660.417) | found | 51.47 | 5.96 |

7.4.5 Compounds of Chapter 4.4.2

4-Dodecylbenzoic acid ethyl ester 109



49.80 g (400 mmol) 9-BBN were dissolved in 300 ml dry toluene and 93.4 ml (400 mmol) 1-dodecene were slowly added at rt. After complete addition the mixture was stirred for 1 d. 700

ml 1 M aqueous NaOH and 64.1 ml (396 mmol) 4-bromoethyl benzoate **108** were added. The solution was degassed and flushed with nitrogen three times. 2.50 g (2.2 mmol) Pd(PPh₃)₄ were added rapidly and the solution was degassed and flushed with N₂ again for three times. Afterwards the mixture was cooked under reflux for 2 d with vigorous stirring. The mixture was allowed to cool to r.t., the layers were separated, the aqueous layer was washed twice with 150 ml toluene, dried over MgSO₄, filtered and the solvent removed. Chromatographic separation on silica gel with hexane/ethylacetate (10:1) gave **109** as a colorless oil.

Yield: 110.10 g (87 %).

$r_f = 0.52$ (silica gel; hexane/ethyl acetate 10:1).

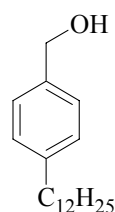
¹H NMR (CDCl₃, 270 MHz): $\delta = 0.85$ (t, ³J = 8.0 Hz, 3 H, ω -CH₃), 1.28 (m, 18 H, -CH₂-), 1.45 (t, ³J = 8.0 Hz, 3 H, -OCH₂CH₃), 1.60 (m, 2 H, β -CH₂-), 2.66 (t, ³J = 8.0 Hz, 2 H, α -CH₂), 4.35 (q, ³J = 8.0 Hz, 2 H, -OCH₂CH₃), 7.25 (AA'BB', ³J = 9.8 Hz, 2 H, arom.), 7.95 ppm (d, ³J = 9.8 Hz, AA'BB', 2 H, arom.).

¹³C NMR (CDCl₃, 68 Hz): $\delta = 14.04, 14.30, 22.64, 29.21, 29.32, 29.43, 29.53, 29.61, 31.10, 31.89, 35.97, 60.62, 127.98, 128.31, 129.54, 148.29, 166.63$ ppm.

MS (EI, 70 eV): m/z (%) = 320 (3), 319 (24), 318 (100) [M]⁺, 290 (7), 289(2) [M-C₂H₄]⁺, 274 (6), 273 (27) [M-OEt]⁺.

HRMS [¹²C₂₁¹H₃₄¹⁶O₂]⁺ calc.: 318.25588 found: 318.25559.

(4-Dodecylphenyl)-methanol **51**



To a suspension of 2.5 g (67 mmol) LiAlH₄ in 300 ml anhydrous ether was added slowly a solution of 61.0g (191.0 mmol) **109** in 200 ml ether. The mixture was refluxed for 3 h, cooled to 0 °C and then aq. 12.5 % HCl (200 ml) was added. The layers were separated and the aqueous layer was extracted with ether (3 x 100 ml). The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. Chromatographic separation on silica gel in hexane/ethyl acetate (6:1) afforded **51** as an oil that crystallized at rt.

Yield: 40.93 g (100 %).

$r_f = 0.13$ (silica gel; hexane/ethyl acetate 7:1).

^1H NMR (CDCl_3 , 500 MHz): δ = 0.89 (t, 3J = 7.0 Hz, 3 H, ω - CH_3), 1.28 (m, 18 H, $-\text{CH}_2-$), 1.63 (q, 3J = 7.8 Hz, 2 H, β - CH_2-), 1.84 (s, 1 H, $-\text{OH}$), 2.61 (t, 3J = 7.8 Hz, 2 H, α - CH_2-), 4.66 (s, 2 H, $-\text{CH}_2\text{OH}$), 7.14 (AA'BB', 2 H, arom.), 7.25 ppm (AA'BB', 2 H, arom.).

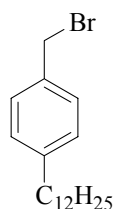
^{13}C NMR (CDCl_3 , 126 Hz): δ = 14.11, 22.67, 29.29, 29.34, 29.49, 29.58, 29.62, 29.65, 31.54, 31.89, 35.62, 65.17, 127.07, 128.34, 138.01, 142.45 ppm.

MS (EI, 80 eV, 150 °C): m/z (%) = 277 (19), 276 (93) $[\text{M}]^+$, 122 (17), 121 (100) $[\text{M}-\text{C}_{11}\text{H}_{23}]^+$, 108 (9), 107 (94) $[\text{M}-\text{C}_{12}\text{H}_{25}]^+$.

| | | | | |
|-----------|--------------------------------------|-------|---------|---------|
| EA | $\text{C}_{19}\text{H}_{32}\text{O}$ | calc. | C 82.55 | H 11.67 |
| | (276.46) | found | 82.32 | 11.58 |

HRMS $[\text{C}_{19}\text{H}_{32}\text{O}]^+$ calc.: 276.24532 found: 276.24734.

1-Bromomethyl-4-dodecylbenzene 52



To a solution of 82.15 g (297.1 mmol) 4-dodecylbenzylic alcohol **51** in 500 ml dry ether, 14.2 ml of PBr_3 in 50 ml dry ether were added. After 1 h stirring at rt the reaction mixture was quenched carefully with water. The layers were separated and the aqueous layer was extracted with ether (3 x 100 ml). The combined organic extracts were dried over MgSO_4 , filtered and the solvent evaporated. Chromatographic separation on silica gel in hexane afforded **51** as a colorless solid.

Yield: 96.70 g (96 %).

r_f = 0.66 (silica gel; hexane/ethyl acetate 7:1).

mp.: 43.0 °C

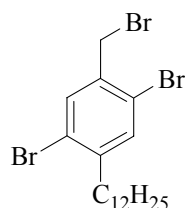
^1H NMR (CDCl_3 , 500 MHz): δ = 0.92 (t, 3J = 7.1 Hz, 3 H, $-\text{CH}_3$), 1.27 (m, 18 H, $-\text{CH}_2-$), 1.63 (quint, 3J = 7.6 Hz, 2 H, β - CH_2-), 2.61 (t, 3J = 7.6 Hz, 2 H, α - CH_2-), 4.50 (s, 2 H, benzylic- CH_2-), 7.16 (d, 3J = 8.0 Hz, 2 H, arom.), 7.31 (d, 3J = 8.0 Hz, 2 H, arom.) ppm.

^{13}C NMR (CDCl_3 , 126 MHz): δ = 14.10, 22.68, 29.30, 29.34, 29.49, 29.57, 29.66, 31.32, 31.91, 33.68, 35.67, 128.78, 128.92, 134.96, 143.36 ppm.

MS EI (80 eV, 3 kV, 90 °C): m/z (%) = 340 (4), 339 (1), 338 (4) $[\text{M}]^+$, 261 (2), 260 (14), 259 (37) $[\text{M}-\text{Br}]^+$, 183 (3) $[\text{M}-\text{C}_{11}\text{H}_{23}]^+$, 105 (100) $[\text{C}_8\text{H}_9]^+$.

| | | | | |
|-----------|------------------------------------|--------|---------|--------|
| EA | C ₁₉ H ₃₁ Br | calc.: | C 67.25 | H 9.21 |
| | (339.359) | found: | C 67.19 | H 9.04 |

1,4-Dibromo-2-bromomethyl-5-dodecylbenzene **110**



24.07 g (70.9 mmol) **52** were mixed with 522 mg (2.1 mmol) powdered iodine. The waxy mixture was cooled to 0 °C and 22 ml (26 mmol) bromine were added dropwise under exclusion of light. The mixture was stirred with a stirring bar for 6 d at rt. 200 ml methylene chloride were added and the dark solution was poured into an ice cold excess of aqueous NaOH to reduce residue bromine. The yellow layers were separated quickly and the aqueous layer was extracted twice with 200 ml CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. Chromatographic separation on silica gel in hexane afforded **110** as a colorless solid.

Yield: 34.52 g (98 %).

r_f = 0.77 (silica gel; hexane/ethyl acetate 10:1).

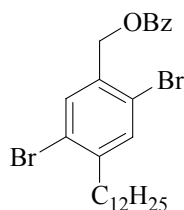
mp.: 46.8 °C

¹H NMR (CDCl₃, 250 MHz): δ = 0.87 (t, ³J = 7.1 Hz, 3 H, -CH₃), 1.27 (m, 18 H, -CH₂-), 1.58 (quint, ³J = 7.6 Hz, 2 H, β -CH₂-), 2.66 (t, ³J = 7.6 Hz, 2 H, α -CH₂-), 4.50 (s, 2 H, -CH₂Br), 7.40 (s, 1 H, arom.), 7.59 (s, 1 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.10, 22.68, 29.35, 29.51, 29.60, 29.63, 31.92, 32.07, 35.74, 122.99, 123.39, 134.33, 134.79, 136.04, 144.64 ppm.

MS EI (80 eV, 3 kV, 120 °C): m/z (%) = 500 (6), 499 (6), 498 (17), 497 (6), 496 (17), 494 (6) [M]⁺, 419 (5), 418 (4), 417 (9), 415 (5) [M-Br]⁺, 266 (5), 265 (50), 264 (19), 263 (100), 262 (24), 261 (52), 260 (10) [M-Br-C₁₁H₂₃]⁺.

| | | | | |
|-----------|---|--------|---------|--------|
| EA | C ₁₉ H ₂₉ Br ₃ | calc.: | C 45.90 | H 5.88 |
| | (497.151) | found: | C 46.37 | H 5.78 |

Benzoic acid 2,5-dibromo-4-dodecylbenzyl ester 111

44.27 g (89.0 mmol) **110**, 14.50 g (100.6 mmol) sodium benzoate, 1.40 g (9.3 mmol) sodium iodide and 2 ml (4.4 mmol) Aliquat 336 were dissolved in 170 ml water and refluxed for 6 h. The aqueous solution was extracted three times with 80 ml CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The product was purified by recrystallization from ethanol.

Yield: 47.45 g (99 %) of a colorless solid.

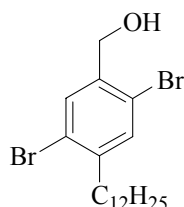
$r_f = 0.54$ (silica gel; hexane/ethyl acetate 10:1).

¹H NMR (CDCl₃, 250 MHz): $\delta = 0.89$ (t, ³J = 7.1 Hz, 3 H, -CH₃), 1.29 (m, 18 H, -CH₂-), 1.61 (quint, ³J = 7.6 Hz, 2 H, β -CH₂-), 2.73 (t, ³J = 7.6 Hz, 2 H, α -CH₂-), 5.33 (s, 2 H, -CH₂Br), 7.42 (m, 3 H, arom.), 7.59 (m, 2 H, arom.), 8.06 (d, ³J = 9.0 Hz, 2 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 14.08, 22.65, 29.33, 29.40, 29.54, 29.61, 29.82, 31.87, 35.90, 65.37, 122.06, 123.29, 128.45, 129.76, 133.21, 133.70, 134.00, 134.45, 144.15, 166.05$ ppm.

MS EI (80 eV, 3 kV, 160 °C): m/z (%) = 539 (1), 538 (1), 537 (1), 536 (1) [M]⁺, 459 (73), 458 (19), 457 (67) [M-Br]⁺, 265 (4), 264 (2), 263 (7), 262 (4) [C₈H₉Br₂]⁺, 105 (100) [C₈H₉]⁺.

HRMS [¹²C₂₆¹H₃₄¹⁶O₂⁷⁹Br₂]⁺ calc.: 536.09255 found: 536.09442.

(2,5-Dibromo-4-dodecylphenyl)-methanol 112

49.67 g (92.3 mmol) **111** and 8.43 g (210.8 mmol) NaOH were dissolved in a mixture of 330 ml THF and 65 ml water. The mixture was refluxed for 12 h. 400 ml ether were added. The

layers were separated and the organic layer was dried over MgSO_4 , filtered and the solvent evaporated. The crude product was recrystallized from chloroform.

Yield: 35.82 % (83 %) of a colorless solid.

$r_f = 0.16$ (silica gel; hexane/ethyl acetate 10:1).

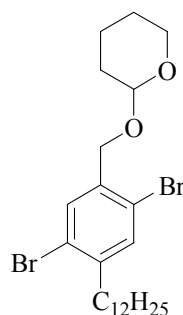
$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 0.82$ (t, $^3J = 7.1$ Hz, 3 H, $-\text{CH}_3$), 1.22 (m, 18 H, $-\text{CH}_2-$), 1.50 (quint, $^3J = 7.6$ Hz, 2 H, $\beta\text{-CH}_2-$), 1.91 (s, 1 H, $-\text{OH}$), 2.62 (t, $^3J = 7.6$ Hz, 2 H, $\alpha\text{-CH}_2-$), 4.62 (s, 2 H, $-\text{CH}_2\text{OH}$), 7.32 (s, 1 H, arom.), 7.58 (s, 1 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 14.08, 22.68, 29.30, 29.33, 29.37, 29.53, 29.63, 29.72, 31.91, 35.68, 64.25, 120.88, 123.54, 132.64, 133.69, 138.85, 143.30$ ppm.

MS EI (80 eV, 3 kV, 160 °C): m/z (%) = 438 (3), 437 (16), 436 (51), 435 (30), 434 (100) $[\text{M}]^+$, 355 (6), 353 (6) $[\text{M}-\text{Br}]^+$, 282 (4), 281 (7), 280 (9), 279 (13), 278 (6), 277 (8) $[\text{M}-\text{C}_{11}\text{H}_{23}]^+$.

HRMS $[\text{C}_{19}\text{H}_{30}\text{O}_1\text{Br}_2]^+$ calc.: 432.06634 found: 432.06888.

2-(2,5-Dibromo-4-dodecylbenzyloxy)-tetrahydropyran 113



25.28 g (58.2 mmol) **112**, 0.13 g (0.7 mmol) $p\text{-TsOH}\cdot\text{H}_2\text{O}$ was suspended in 320 ml dry carbon tetrachloride and cooled to 0 °C. 6.4 ml (70.9 mmol) DHP was added slowly. The mixture was allowed to rise to r.t. over night. The clear colorless solution was quenched with 50 ml saturated aqueous NaHCO_3 solution and stirred for 30 minutes. The layers were separated and the aqueous layer was extracted three times with 50 ml ether. The combined organic layers were washed twice with dest. water and brine. The organic layer was dried over MgSO_4 , filtrated and the solvent evaporated under reduced pressure. The slightly yellow oil was purified by flash column chromatography ($r_f = 0.56$; silica gel; hexane/ethyl acetate 10:1).

Yield: 29.84 g (99 %) of a colorless oil.

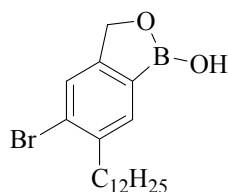
¹H NMR (CDCl₃, 250 MHz): δ = 0.87 (t, ³J = 7.6 Hz, 3 H, -CH₃), 1.29 (m, 18 H, -CH₂-), 1.56 (m, 5 H, -CH₂-), 1.74 (m, 1 H), 1.87 (m, 1 H), 2.65 (t, ³J = 7.6 Hz, 2 H, α -CH₂-), 3.56 (m, 1 H), 3.89 (m, 1 H), 4.44 (m, 2 H), 4.75 (m, 2 H), 7.40 (d, ³J = 8.0 Hz, 1 H, arom.), 7.59 (d, ³J = 8.0 Hz, 1 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 14.03, 19.13, 22.60, 25.33, 29.23, 29.27, 29.31, 29.47, 29.56, 29.64, 30.32, 31.83, 35.59, 61.85, 67.61, 98.21, 120.93, 123.22, 132.54, 133.36, 136.90, 142.65 ppm.

MS EI (80 eV, 3 kV, 160 °C): m/z (%) = 520 (4), 519 (5), 518 (8) [M]⁺, 474 (6), 473 (5), 472 (10), 470 (5) [M-C₂H₆O]⁺, 420 (7), 419 (7), 418 (14), 417 (9), 416 (8), 415 (4) [M-C₅H₈O₂]⁺, 85 (100) [C₅H₉O]⁺.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | C ₂₄ H ₃₈ O ₂ Br ₂ | calc. | C 55.61 | H 7.39 |
| | (518.373) | found | 55.74 | 7.17 |

5-Bromo-6-dodecyl-3H-benzo[c][1,2]oxaborol-1-ol 114



28.63 g (55.2 mmol) **113** were dissolved in 500 ml dry ether and cooled to -78 °C under nitrogen. 41.1 ml (65.8 mmol) of a 1.6 M n-butyl lithium solution in hexane were added dropwise. The mixture was warmed to -20 °C and cooled again to -78 °C. 39.0 ml (165.6 mmol) triisopropyl borate were added dropwise. The solution was allowed to rise to rt overnight under stirring. 200 ml hydrochloric acid (10 %) were added and stirred for 6 h. The layers were separated and the aqueous layer was extracted twice with 100 ml ether. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The crude product was recrystallized from ether.

Yield: 12.56 g (60 %) of a colorless solid.

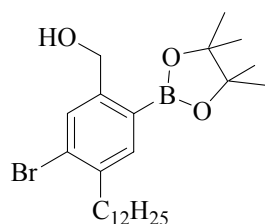
¹H NMR (D₆-DMSO, 250 MHz): δ = 0.84 (t, ³J = 7.6 Hz, 3 H, -CH₃), 1.23 (m, 18 H, -CH₂-), 1.55 (m, 2 H, β -CH₂-), 2.71 (t, ³J = 7.6 Hz, 2 H, α -CH₂-), 4.92 (s, 2 H, -CH₂O-), 7.62 (s, 1 H, arom.), 7.65 (s, 1 H, arom.), 9.22 (s, 1 H, -OH) ppm.

¹³C NMR (D₆-DMSO, 63 MHz): δ = 13.86, 22.01, 28.58, 28.71, 28.93, 29.55, 31.22, 35.26, 69.13, 125.56, 126.82, 130.30, 131.99, 139.45, 153.43 ppm.

MS EI (80 eV, 3 kV, 100 °C): m/z (%) = 383 (1), 382 (2), 381 (2), 380 (2), 379 (1) $[M]^+$, 357 (1), 356 (1), 355 (1), 354 (3), 353 (1), 352 (1) $[M-BOH]^+$, 340 (5), 338 (5) $[M-CH_2BOH]^+$, 85 (100) $[C_5H_9O]^+$.

HRMS $[^{12}C_{19}^{1}H_{30}^{16}O_1^{11}B_1^{79}Br_1]^+$ calc.: 380.15222 found: 380.15423.

[5-Bromo-4-dodecyl-2-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-methanol
115



20.81 g (54.6 mmol) **114** and 6.58 g (54.6 mmol) pinacol were dissolved in 200 ml chloroform and refluxed for 2d in a Dean-Stark apparatus. The solvent was evaporated.

Yield: 26.20 g (99 %) of a colorless oil.

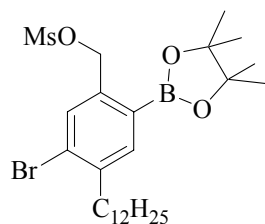
1H NMR (D_6 -DMSO, 250 MHz): δ = 0.85 (t, 3J = 7.6 Hz, 3 H, -CH₃), 1.27 (m, 30 H, -CH₂-; -CH₃), 1.55 (m, 2 H, β -CH₂-), 2.67 (t, 3J = 7.6 Hz, 2 H, α -CH₂-), 4.60 (s, 2 H, -CH₂O-), 7.47 (s, 1 H, arom.), 7.65 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.07, 22.66, 24.81, 29.33, 29.42, 29.51, 29.64, 30.11, 31.90, 35.18, 65.10, 84.40, 125.44, 128.06, 132.92, 138.38, 140.91, 146.56 ppm.

MS EI (80 eV, 3 kV, 140 °C): m/z (%) = 483 (12), 482 (20), 481 (13), 480 (19) $[M]^+$, 465 (9) $[M-OH]^+$, 425 (12), 424 (15), 423 (16), 422 (15) $[M-C_3H_6O]^+$, 84 (100) $[C_5H_8O]^+$.

HRMS $[^{12}C_{25}^{1}H_{42}^{16}O_3^{11}B_1^{79}Br_1]^+$ calc.: 480.24105 found: 480.24138.

Methanesulfonic acid 5-bromo-4-dodecyl-2-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzyl ester **116**



3.39 g (7.0 mmol) **115** and 5 ml (35.2 mmol) triethylamine were dissolved in 50 ml dry toluene and cooled to 0 °C. 0.9 ml (10.6 mmol) methanesulfonyl chloride were added dropwise and stirred for 2h. 50 ml water were added and the layers were separated. The aqueous layer was extracted twice with 20 ml toluene. The combined organic layers were washed with brine and water, dried over MgSO₄, filtered over celite and the solvent evaporated.

Yield: 3.93 g (100 %) of a yellow oil.

$r_f = 0.30$ (silica gel; hexane/ethyl acetate 4:1).

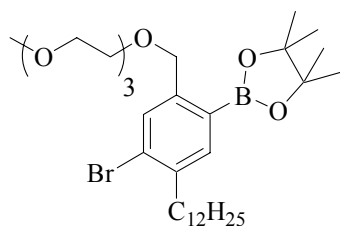
¹H NMR (CDCl₃, 250 MHz): $\delta = 0.85$ (t, ³J = 7.6 Hz, 3 H, -CH₃), 1.27 (m, 30 H, -CH₂-; -CH₃), 1.55 (m, 2 H, β -CH₂-), 2.69 (t, ³J = 7.6 Hz, 2 H, α -CH₂-), 2.92 (s, 3 H, S-CH₃) 5.43 (s, 2 H, -CH₂O-), 7.56 (s, 1 H, arom.), 7.61 (s, 1 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): $\delta = 14.06, 22.64, 24.80, 29.30, 29.37, 29.48, 29.55, 29.61, 29.98, 31.88, 35.83, 37.85, 70.23, 84.22, 127.96, 133.54, 138.02, 138.32, 142.59, 153.18$ ppm.

MS EI (80 eV, 3 kV, 140 °C): m/z (%) = 561 (8), 560 (24), 559 (11), 558 (22) [M]⁺, 503 (18), 502 (68), 501 (31), 500 (61), 499 (15) [M-C₃H₆O]⁺, 382 (20), 381 (99), 380 (44), 379 (100), 378 (26) [M-SO₃CH₃-C₆H₁₂]⁺.

HRMS [¹²C₂₆¹H₄₄¹⁶O₅¹¹B₁⁷⁹Br₁³²S₁]⁺ calc.: 558.21860 found: 558.21889.

2-[4-Bromo-5-dodecyl-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxymethyl}-phenyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 1



6.40 g (41.0 mmol) triethylene glycol monomethyl ether were dissolved in 30 ml dry THF under nitrogen. 630 mg (27.4 mmol) sodium dust were added and cooked under reflux for 1 d. 6.61 g (11.8 mmol) of compound **116** in 30 ml dry THF were added dropwise at rt and the mixture was stirred for 5d at rt. 100 ml of water and 100 ml methylene chloride were added. The layers were separated and the aqueous layer was extracted three times with 50 ml methylene chloride. The organic layer was washed with brine, dried over MgSO₄, filtered and the solvent evaporated. The orange oil was purified by flash column chromatography (silica gel; MeCl₂/MeOH 3 %).

Yield: 3.95 g (53 %) of a yellow oil.

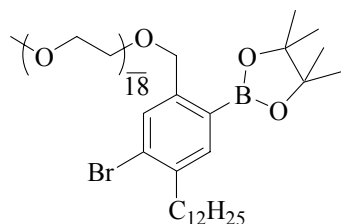
$r_f = 0.11$ (silica gel; hexane/ethyl acetate 4:1).

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.87$ (t, $^3J = 7.6$ Hz, 3 H, $-\text{CH}_3$), 1.27 (m, 30 H, $-\text{CH}_2-$; $-\text{CH}_3$), 1.58 (quint, $^3J = 7.6$ Hz, 2 H, $\beta\text{-CH}_2-$), 2.68 (t, $^3J = 7.6$ Hz, 2 H, $\alpha\text{-CH}_2-$), 3.33 (s, 3 H, $-\text{CH}_3$), 3.59 (m, 12 H, $-\text{CH}_2\text{O}-$), 4.71 (s, 2 H, $\alpha\text{-CH}_2\text{O}-$), 7.56 (s, 1 H, arom.), 7.62 (s, 1 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): $\delta = 14.07, 22.64, 24.81, 29.30, 29.40, 29.51, 29.56, 29.60, 29.63, 30.15, 31.88, 35.76, 36.08, 58.97, 68.98, 69.66, 70.00, 70.44, 70.50, 70.56, 70.62, 71.39, 71.91, 83.67, 127.84, 131.67, 137.44, 137.89, 140.31, 144.07$ ppm.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | $\text{C}_{32}\text{H}_{56}\text{O}_6\text{BBr}$ | calc. | C 61.25 | H 9.00 |
| | (627.508) | found | 60.87 | 8.94 |

2-[4-Bromo-5-dodecyl-2-(2-methoxy-PEG-750-methyl)-phenyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 117



6.72 g (8.4 mmol) PEG 750 monomethyl ether **26** were dissolved in 30 ml dry THF under nitrogen. 168 mg (7.3 mmol) sodium dust were added and cooked under reflux for 1 d. 3.90 g (7.0 mmol) of compound **116** in 100 ml dry THF were added slowly at 0 °C. The mixture was stirred for 5 d at rt. 100 ml of water and 100 ml methylene chloride were added. The layers were separated and the aqueous layer was extracted three times with 50 ml methylene chloride. The organic layer was washed with brine, dried over MgSO_4 , filtered and the solvent evaporated. The orange oil was purified by flash column chromatography (silica gel; $\text{MeCl}_2/\text{MeCN}$ 5 %).

Yield: 5.96 g (66 %) of a yellow oil.

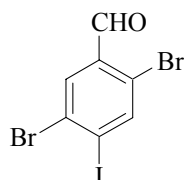
$r_f = 0.15$ (silica gel; ether/acetone 7:3).

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.87$ (t, $^3J = 7.6$ Hz, 3 H, $-\text{CH}_3$), 1.27 (m, 30 H, $-\text{CH}_2-$; $-\text{CH}_3$), 1.52 (quint, $^3J = 7.6$ Hz, 2 H, $\beta\text{-CH}_2-$), 2.62 (t, $^3J = 7.6$ Hz, 2 H, $\alpha\text{-CH}_2-$), 3.31 (s, 3 H, $-\text{CH}_3$), 3.59 (m, ~ 72 H, $-\text{CH}_2\text{O}-$), 4.68 (s, 2 H, $\alpha\text{-CH}_2\text{O}-$), 7.52 (s, 1 H, arom.), 7.58 (s, 1 H, arom.) ppm.

^{13}C NMR (CDCl_3 , 126 MHz): $\delta = 13.97, 22.52, 24.72, 29.18, 29.39, 29.44, 29.47, 29.50, 31.75, 58.85, 70.35, 70.42, 71.78, 83.56, 127.70, 131.53, 137.32, 140.17, 143.95$ ppm.

| | | | | |
|-----------|--|-------|---------|--------|
| EA | $\text{C}_{61}\text{H}_{114}\text{O}_{21.5}\text{BrB}$ | calc. | C 57.09 | H 8.95 |
| | (1282.278) | found | 56.63 | 8.66 |

2,5-Dibromo-4-iodobenzaldehyde **119**



1.00 g (2.05 mmol) 2,5-Dibromo-1,4-diiodobenzene **118** were dissolved in 80 ml dry THF and cooled to $-10\text{ }^\circ\text{C}$. 1.1 ml (2.2 mmol) Isopropylmagnesium chloride were added rapidly. After 4 minutes 0.24 ml (2.1 mmol) N-formylpiperidine were added dropwise. After 4 h stirring 10 ml HCl (10 %) were added. The layers were separated and the aqueous layer was extracted three times with 40 ml ether. The combined organic layers were washed with saturated NaHCO_3 -solution and brine, dried over MgSO_4 , filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate 10:1). If necessary the product can be recrystallized from hexane.

mp: sublimed at $113\text{ }^\circ\text{C}$.

Yield: 458 mg (57 %).

$r_f = 0.49$ (silica gel; hexane/ethyl acetate 10:1).

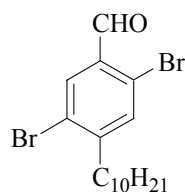
$^1\text{H-NMR}$ (250 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$): $\delta = 8.02$ (1 H, s, arom.), 8.14 (1 H, s, arom.), 10.16 (1 H, s, -CHO) ppm.

$^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , $20\text{ }^\circ\text{C}$): $\delta = 110.04$ (C-I), 124.59 (C-Br), 130.12 (C-Br), $132.59, 133.98, 144.34$ (arom.), 189.76 (-CHO) ppm.

MS (EI, 80 eV): m/z (%) = 390 (60) $[\text{M}]^+$, 362 (6) $[\text{M-CO}]^+$, 310 (5) $[\text{M-Br}]^+$, 280 (5) $[\text{M-Br-CH}_2\text{O}]^+$, 263 (4) $[\text{M-I}]^+$, 234 (11) $[\text{M-CHO-I}]^+$, 155 (35) $[\text{M-CO-I-Br}]^+$, 127 (33) $[\text{I}]^+$, 74 (100) $[\text{M-I}]^+$.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | $\text{C}_7\text{H}_3\text{O}_1\text{Br}_2\text{I}_1$ | calc. | C 21.57 | H 0.78 |
| | (389.813) | found | 21.74 | 0.79 |

2,5-Dibromo-4-decylbenzaldehyde **120**



1.52 g (12.2 mmol) 9-BBN and 2.5 ml (12.8 mmol) 1-decene were dissolved in 100 ml dry THF and stirred over night at rt. The solvent was evaporated and 60 ml toluene p. a. were added. 1.46 g (3 equi) NaOH in 80 ml water and 4.53 g (11.6 mmol) 2,5-dibromo-4-iodobenzaldehyde **119** were added and the solution was degassed three times by evacuation and N₂ ventilating for 10 minutes per operation. 268 mg (2 mol %) Pd(PPh₃)₄ was added immediately followed by again three times degassing. The reaction mixture was refluxed under nitrogen for 2 d. The mixture was cooled to rt, the layers were separated and the aqueous layer was extracted three times with 50 ml toluene. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate 4:1).

Yield: 630 mg (13 %).

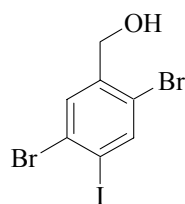
$r_f = 0.54$ (silica gel; hexane/ethyl acetate 10:1).

¹H-NMR (250 MHz, CDCl₃, 20 °C): $\delta = 0.83$ (t, 3 H, ³J = 6 Hz, -CH₃), 1.26 (m, 14 H, -CH₂-), 1.56 (m, 2 H, β -CH₂-), 2.70 (t, ³J = 9 Hz, 2 H, α -CH₂-), 7.45 (s, 2 H, arom.), 8.00 (s, 1 H, arom.), 10.81 (s, 1 H, -CHO) ppm.

¹³C-NMR (62.9 MHz, CDCl₃, 20 °C): $\delta = 14.10, 22.66, 28.17, 29.30, 29.47, 29.55, 31.86, 36.32$ (α -C), 124.20, 125.35, 132.33, 133.64, 134.81, 150.51 (arom.), 190.18 (-CHO) ppm.

MS (EI, 80 eV): m/z (%) = 404 (44) [M]⁺, 325 (13) [M-⁷⁹Br]⁺, 323 (13) [M-⁸¹Br]⁺, 249 (58) [M-CO, -C₉H₁₉]⁺, 197 (37) [M-Br, -C₉H₁₉]⁺, 169 (48) [-CO, -Br, -C₉H₁₉]⁺, 128 (34) [C₉H₂₀]⁺, 115 (44) [M-2Br, -C₉H₁₉]⁺, 102 (29), 89 (35), 43 (100).

(2,5-Dibromo-4-iodophenyl)-methanol **121**



4.00 g (10.3 mmol) **119** were dissolved in 100 ml dry THF and 203 mg NaBH₄ were added. The solution was stirred overnight at rt. 20 ml hydrochloric acid and 100 ml ether were added. The layers were separated and the aqueous layer was extracted twice with 50 ml ether. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The crude product was purified by flash column chromatography (silica gel; hexane/ethyl acetate 10:1).

Yield: 2.77 g (69 %).

r_f = 0.08 (silica gel; hexane/ethyl acetate 10:1).

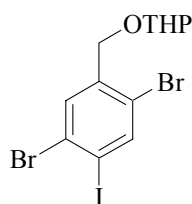
¹H-NMR (250 MHz, D₆-DMSO, CDCl₃, 20 °C): δ = 4.42 (d, ³J = 10.0 Hz, -CH₂-), 5.51 (t, ³J = 10.0 Hz, -OH), 7.72 (s, 1 H, arom.), 7.92 (s, 1 H, arom.) ppm.

¹³C-NMR (63 MHz, D₆-DMSO, CDCl₃, 20 °C): δ = 61.66, 99.03, 119.50, 128.04, 130.78, 141.26, 142.92 ppm.

MS (EI, 80 eV, 120 °C): m/z (%) = 395 (1), 394 (48), 393 (10), 392 (100), 391 (9), 390 (53), 389 (4) [M]⁺, 314 (4), 313 (42), 312 (7), 311 (46) [M-Br]⁺, 159 (3), 158 (43), 157 (11), 156 (53), 155 (13), 154 (8), 153 (6) [M-Br-I-CH₂O]⁺.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | C ₇ H ₅ O ₁ Br ₂ I ₁ | calc. | C 21.46 | H 1.29 |
| | (391.829) | found | 21.55 | 1.13 |

2-(2,5-Dibromo-4-iodobenzyloxy)-tetrahydropyran **122**



2.60 g (6.6 mmol) **121** and 25.2 mg (0.1 mmol) TsOH·H₂O were dissolved in 50 ml CH₂Cl₂. 3.0 ml (33.0 mmol) dihydropyran were added dropwise. The mixture was stirred for 12 h at rt and poured into an aqueous NaHCO₃ solution. The layers were separated and the aqueous layer was extracted twice with 50 ml CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The crude product was purified by flash column chromatography (silica gel; hexane/ethyl acetate 10:1).

Yield: 1.26 g (40 %).

r_f = 0.40 (silica gel; hexane/ethyl acetate 7:1).

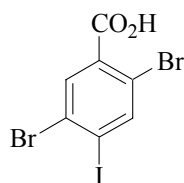
¹H-NMR (250 MHz, CDCl₃, 20 °C): δ = 1.70 (m, 6 H, -CH₂-), 3.56 (m, 1 H, THP), 3.87 (m, 1 H, THP), 4.43 (d, ³J = 12.0 Hz, 1 H, α-CH₂-), 4.71 (d, ³J = 12.0 Hz, 1 H, α-CH₂-), 4.74 (m, 1 H, THP), 7.22 (s, 1 H, arom.), 7.97 (s, 1 H, arom.) ppm.

¹³C-NMR (63 MHz, CDCl₃, 20 °C): δ = 19.24, 25.32, 30.38, 62.21, 67.48, 98.53, 99.67, 120.98, 128.92, 132.08, 139.92, 142.50 ppm.

MS (EI, 80 eV, 80 °C): m/z (%) = 478 (4), 476 (8), 474 (4) [M]⁺, 430 (13) [M-C₂H₆O]⁺, 397 (10) [M-Br]⁺, 378 (7), 377 (49), 376 (17), 375 (100), 374 (9), 373 (50) [M-C₆H₁₃O]⁺.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | C ₁₂ H ₁₃ O ₂ Br ₂ I ₁ | calc. | C 30.28 | H 2.75 |
| | (475.946) | found | 30.34 | 2.43 |

2,5-Dibromo-4-iodobenzoic acid **123**



4.00 g (8.2 mmol) **118** were dissolved in 60 ml dry THF and cooled to -20 °C. 4.2 ml (8.4 mmol) of a 2 M ¹PrMgCl solution in ether were added dropwise and stirred for 5 minutes at -12 °C. CO₂ was bubbled through the solution for 1 h. The solvent was evaporated and the crude mixture was purified by flash column chromatography (silica gel; hexane/ethyl acetate 1:1).

Yield: 1.33 g (40 %).

r_f = 0.06 (silica gel; hexane/ethyl acetate 1:1).

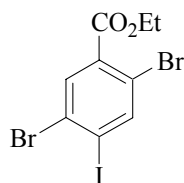
¹H-NMR (250 MHz, CD₃OD, CDCl₃, 20 °C): δ = 7.98 (s, 1 H, arom.), 8.04 (s, 1 H, arom.) ppm.

¹³C-NMR (63 MHz, CD₃OD, 20 °C): δ = 106.57, 121.10, 129.83, 135.19, 145.94, 165.95 ppm.

MS (EI, 80 eV, 130 °C): m/z (%) = 409 (16), 408 (51), 407 (32), 406 (100), 405 (17), 404 (51) [M]⁺, 391 (19), 389 (37), 387 (19) [M-OH]⁺, 361 (7) [M-CO₂H]⁺.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | C ₇ H ₃ O ₂ Br ₂ I ₁ | calc. | C 20.72 | H 0.75 |
| | (405.812) | found | 20.56 | 0.70 |

HRMS [¹²C₇¹H₃¹⁶O₂¹²⁷J₁⁸¹Br₁⁷⁹Br₁]⁺ calc.: 405.75241 found: 405.75460
 [¹²C₇¹H₃¹⁶O₂¹²⁷J₁⁷⁹Br₂]⁺ calc.: 403.75445 found: 403.75674.

2,5-Dibromo-4-iodobenzoic acid ethyl ester 125

1.00 g (2.5 mmol) **123** were dissolved in 200 ml dry ethanol and 5 ml concentrated sulfuric acid. The mixture was refluxed for 15 h under nitrogen and neutralized carefully with aqueous Na_2CO_3 solution. The solvent was evaporated and the crude mixture was purified by flash column chromatography (silica gel; hexane/ethyl acetate 20:1).

Yield: 748 mg (70 %) of a colorless solid.

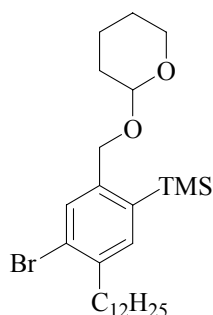
$r_f = 0.38$ (silica gel; hexane/ethyl acetate 10:1).

$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 1.40$ (t, $^3J = 8.0$ Hz, 3 H, $-\text{CH}_3$), 4.37 (q, $^3J = 8.0$ Hz, 2 H, $-\text{CH}_2-$), 7.92 (s, 1 H, arom.), 8.15 (s, 1 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 14.12$, 62.10, 105.97, 120.42, 128.74, 133.14, 134.24, 144.73, 164.20 ppm.

MS (EI, 80 eV, 180°C): m/z (%) = 437 (6), 436 (45), 435 (12), 434 (91), 433 (7), 432 (47) $[\text{M}]^+$, 408 (18), 407 (4), 406 (37), 404 (20) $[\text{M}-\text{C}_2\text{H}_4]^+$, 392 (6), 391 (50), 390 (14), 389 (100), 388 (11), 387 (52) $[\text{M}-\text{C}_2\text{H}_5\text{O}]^+$.

HRMS $[\text{C}_9\text{H}_7\text{O}_2\text{I}^{127}\text{J}_1^{79}\text{Br}_2]^+$ calc.: 431.78575 found: 431.78332.

[4-Bromo-5-dodecyl-2-(tetrahydropyran-2-yloxymethyl)-phenyl]-trimethylsilane 127

6.20 g (12.0 mmol) **113** were dissolved in 100 ml dry ether under nitrogen and cooled to -78 °C. 8.2 ml (13.1 mmol) of a 1.6 M $^n\text{BuLi}$ solution in hexane were added dropwise. The mixture was allowed to warm up to 0 °C and frozen again to -78 °C. 4.7 ml (36.0 mmol)

TMSCl were added dropwise and the mixture was allowed to rise to rt. 80 ml water were added and stirred for 1 h. The layers were separated and the aqueous layer was extracted twice with 100 ml ether. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated.

Yield: 5.60 g (91 %) of a colorless oil.

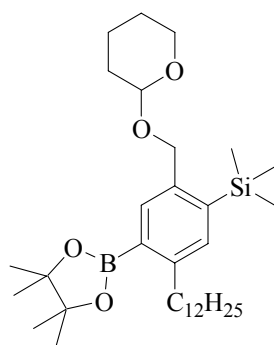
¹H NMR (CDCl₃, 250 MHz): δ = 0.32 (s, 9 H, -Si(CH₃)₃), 0.89 (t, ³J = 7.1 Hz, 3 H, -CH₃), 1.29 (m, 18 H, -CH₂-), 1.69 (m, 8 H, -CH₂-), 2.69 (t, ³J = 7.6 Hz, 2 H, α-CH₂-), 3.55 (m, 1 H, -OCH₂-), 3.92 (m, 1 H, -OCH₂-), 4.51 (d, ³J = 12.0 Hz, 1 H, α-CH₂O), 4.70 (m, 1 H, -OCHO), 4.79 (d, ³J = 12.0 Hz, 1 H, α-CH₂O), 7.29 (s, 1 H, arom.), 7.63 (s, 1 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 0.32, 14.09, 19.37, 22.68, 25.47, 29.34, 29.43, 29.65, 30.06, 30.58, 31.92, 35.93, 62.15, 67.90, 97.97, 125.95, 132.43, 136.28, 137.37, 140.27, 142.96 ppm.

MS EI (80 eV, 3 kV, 150 °C): m/z (%) = 512 (0.04), 510 (0.04) [M]⁺, 413 (2), 412 (6), 411 (3), 410 (6), 409 (1) [M-C₅H₈O₂]⁺, 259 (3), 258 (2), 257 (8), 256 (2), 255 (6), 254 (1) [M-Br-TMS-C₅H₉O₂]⁺, 85 (100) [C₅H₉O]⁺.

HRMS [¹²C₂₇¹H₄₇¹⁶O₂²⁸Si₁⁷⁹Br₁]⁺
[M-CH₃]⁺ calc.: 495.22941 found: 495.22996.

2-[4-Dodecyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-2-trimethylsilyl-benzyloxy]-tetrahydropyran 128 a



A mixture of 1.24 g (2.4 mmol) reactant, 716 mg (7.3 mmol) potassium acetate, 678 mg (2.7 mmol, 1.1 equi) bis(pinacolato)-diboron in 15 ml DMSO was degassed 3 times. 60 mg (3 mol %) 1,1'-Bis(diphenylphosphino)ferrocenedichloro palladium(II)·CH₂Cl₂ was added rapidly and the mixture was degassed again 3 times. The reaction mixture was heated to 80 °C for 6 h. The solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate 20:1 → 10:1).

Yield: 617 mg (46 %)

$r_f = 0.57$ (silica gel; hexane/ethyl acetate 7:1).

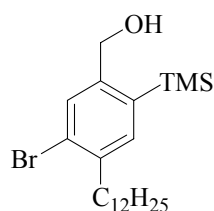
$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 0.40$ (s, 9 H, Si- CH_3), 0.93 (t, 3 H, CH_3), 1.35 (m, 18 H, - CH_2 -), 2.64 (t, $^3J = 8.0$ Hz, 3 H, α - CH_2), 3.55, 3.95, 4.53 (d, $^3J = 8.0$ Hz, 1 H, benzylic- CH_2), 4.73 (m, 1 H,), 4.79 (d, 1 H, benzylic- CH_2), 7.31 (s, 1 H, arom.), 7.65 (s, 1 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 0.21$, 14.00, 19.46, 22.58, 24.74, 25.49, 26.29, 28.50, 29.27, 29.51, 29.57, 29.62, 29.74, 30.61, 31.84, 33.58, 35.76, 62.11, 69.09, 83.13, 97.88, 129.34, 135.52, 136.67, 139.46, 141.92, 148.28 ppm.

MS EI (80 eV, 3 kV, 130 °C): m/z (%) = 558 (1) $[\text{M}]^+$, 543 (1) $[\text{M}-\text{CH}_3]^+$, 473 (1) $[\text{M}-\text{C}_6\text{H}_{13}]^+$, 458 (20) $[\text{M}-\text{C}_5\text{H}_8\text{O}_2]^+$, 85 (100) $[\text{C}_6\text{H}_{13}]$.

HRMS $[\text{C}_{32}\text{H}_{56}\text{O}_4^{11}\text{B}^{28}\text{Si}]^+$
 $[\text{M}-\text{CH}_3]^+$ calc.: 543.40409 found: 543.40467.

(5-Bromo-4-dodecyl-2-trimethylsilylphenyl)-methanol 129



5.60 g (10.9 mmol) **127** were dissolved in a mixture of 40 ml methanol, 100 ml chloroform and 120 mg p-TsOH were added and stirred for 9 h at rt. The layers were separated, the aqueous layer was extracted three times with ether. The combined organic layers were dried over MgSO_4 , filtrated and the solvent evaporated. The crude product was purified by flash column chromatography (silica gel; hexane/ethyl acetate 10:1).

Yield: 4.32 g (93 %) of a colorless oil.

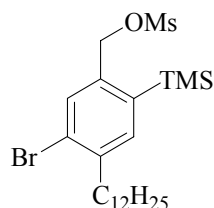
$^1\text{H NMR}$ (CDCl_3 , 250 MHz): $\delta = 0.30$ (s, 9 H, - $\text{Si}(\text{CH}_3)_3$), 0.83 (t, $^3J = 7.1$ Hz, 3 H, - CH_3), 1.27 (m, 18 H, - CH_2 -), 1.58 (quint, $^3J = 7.6$ Hz, 2 H, β - CH_2 -), 1.86 (s, 1 H, -OH), 2.68 (t, $^3J = 7.6$ Hz, 2 H, α - CH_2 -), 4.68 (s, 2 H, - CH_2OH), 7.27 (s, 1 H, arom.), 7.61 (s, 1 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 63 MHz): $\delta = 0.19$, 14.06, 22.66, 29.32, 29.40, 29.63, 30.03, 31.90, 35.87, 64.38, 126.05, 131.79, 132.51, 136.51, 137.01, 140.48, 145.41 ppm.

MS EI (80 eV, 3 kV, 150 °C): m/z (%) = 428 (2), 426 (2) $[\text{M}]^+$, 411 (1) $[\text{M}-\text{OH}]^+$, 337 (3), 336 (1), 335 (3) $[\text{M}-\text{OH}-\text{TMS}]^+$, 260 (2), 259 (15), 258 (3), 257 (15) $[\text{M}-\text{C}_{12}\text{H}_{25}]^+$, 75 (100) $[\text{C}_2\text{H}_7\text{OSi}]^+$,

| | | | | |
|-----------|---------------------------------------|-------|---------|--------|
| EA | C ₂₂ H ₃₉ OBrSi | calc. | C 61.80 | H 9.19 |
| | (427.541) | found | 61.50 | 9.03 |

Methanesulfonic acid 5-bromo-4-dodecyl-2-trimethylsilanylbenzyl ester 130



4.30 g (9.4 mmol) of compound **129**, 6.5 ml (46.8 mmol) triethylamine was dissolved in 50 ml dry toluene and cooled to 0 °C. 1.1 ml (14 mmol) of methanesulfonyl chloride were added slowly and stirred for 2 h at 0 °C. The solution was quenched with 50 ml dest. water. The layers were separated and the organic layer was washed with brine and water. The combined organic layers were dried over MgSO₄, filtrated over celite and the solvent evaporated. The crude product is a yellow oil which crystallize in the refridgerator.

Yield: 4.76 g (100 %) of a colorless solid.

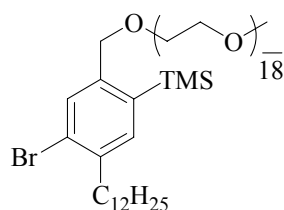
¹H NMR (CDCl₃, 250 MHz): δ = 0.43 (s, 9 H, -TMS), 0.87 (t, ³J = 7.1 Hz, 3 H, -CH₃), 1.27 (m, 18 H, -CH₂-), 1.58 (quint, ³J = 7.6 Hz, 2 H, β-CH₂-), 2.70 (t, ³J = 7.6 Hz, 2 H, α-CH₂-), 2.97 (s, 3 H, -OMs), 5.23 (s, 2 H, -CH₂OMs), 7.36 (s, 1 H, arom.), 7.58 (s, 1 H, arom.) ppm.

¹³C NMR (CDCl₃, 63 MHz): δ = 0.18, 14.07, 22.66, 29.32, 29.37, 29.62, 29.88, 31.90, 35.96, 38.34, 69.79, 125.91, 134.04, 136.80, 137.46, 139.03, 142.47 ppm.

MS EI (80 eV, 3 kV, 180 °C): m/z (%) = 506 (1) [M]⁺, 491 (1) [M-CH₃]⁺, 255 (2) [C₁₁H₁₅BrSi]⁺, 153 (100) [C₁₁H₂₁]⁺.

HRMS [¹²C₂₃¹H₄₁¹⁶O₃⁷⁹Br²⁸Si³²S]⁺ calc.: 504.17292 found: 504.17243.

(4-Bromo-5-dodecyl-2-{2-methoxy-PEG 750-methyl}-phenyl)-trimethylsilane 131



9.06 g (11.3 mmol) PEG 750 mono methyl ether **26** were dissolved in 30 ml dry THF under nitrogen. 227 (9.9 mmol) sodium dust were added and cooked under reflux for 1 d. 4.76 g (9.4 mmol) of compound **130** were added at rt and the mixture was stirred for 5 d at rt. 100 ml of water and 100 ml methylene chloride were added. The layers were separated and the aqueous layer was extracted three times with 50 ml methylene chloride. The organic layer was washed with brine, dried over MgSO_4 , filtered and the solvent evaporated. The orange oil was purified by flash column chromatography (silica gel; $\text{MeCl}_2/\text{MeOH}$ 3 %).

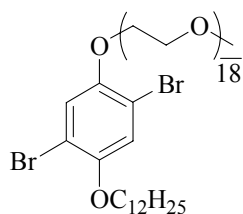
Yield: 9.60 g (83 %) of a colorless oil.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 0.23 (s, 9 H, -TMS), 0.87 (t, $^3J = 7.1$ Hz, 3 H, $-\text{CH}_3$), 1.27 (m, 18 H, $-\text{CH}_2-$), 1.59 (quint, $^3J = 7.6$ Hz, 2 H, $\beta\text{-CH}_2-$), 2.66 (t, $^3J = 7.6$ Hz, 2 H, $\alpha\text{-CH}_2-$), 3.31 (s, 3 H, $-\text{OCH}_3$), 3.48 (t, $^3J = 8.0$ Hz, 2 H, $-\text{CH}_2\text{OCH}_3$), 3.58 (m, 64 H, $-\text{CH}_2\text{O}-$), 4.49 (s, 2 H, $\alpha\text{-CH}_2\text{O}-$), 7.26 (s, 1 H, arom.), 7.53 (s, 1 H, arom.) ppm.

$^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ = 0.10, 14.05, 22.61, 29.35, 29.56, 29.58, 29.60, 31.84, 58.95, 69.51, 70.45, 70.50, 70.54, 72.03, 72.84, 125.81, 132.28, 136.34, 137.27, 140.30, 142.81 ppm.

7.4.6 Compounds of Chapter 4.4.3

1-Dodecyloxy-2,5-dibromo-4-[PEG mono methyl ether 750]-benzene 135



8.98 g (20.6 mmol) phenol **134**, 6.24 g (30.9 mmol) triphenylphosphine and 6.24 g (30.9 mmol) PEG 750 mono methyl ether **26** were dissolved in 40 ml dry THF. 6.58 g (32.5 mmol) diisopropyl azodicarboxylate (DIAD) in 10 ml dry THF were added dropwise under nitrogen and light exclusion. The mixture was stirred for 1 d at rt. The solvent was evaporated and the crude product was purified by flash column chromatography (silica gel; $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ 2 %).

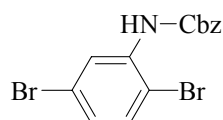
Yield: 15.17 g (60 %) of a colorless waxy solid.

r_f = 0.25 (silica gel; $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ 2 %).

¹H-NMR (500 MHz, CDCl₃, 20 °C): δ = 0.87 (t, 3 H, ³J = 7.0 Hz, -CH₃), 1.33 (m, 4 H, -CH₂-), 1.47 (m, 2 H, γ -CH₂-), 1.77 (quint, 2 H, ³J = 7.5 Hz, β -CH₂-), 3.30 (s, 3 H, -OCH₃), 3.50 (m, 2 H, -CH₂O-), 3.62 (m, 6 H, -CH₂O-), 3.73 (t, 2 H, ³J = 5.5 Hz, α -OCH₂-), 3.87 (m, 4 H, α -CH₂-; -CH₂O-), 4.07 (t, 2 H, ³J = 5.5 Hz, α -OCH₂-), 7.01 (s, 1 H, arom.), 7.11 (s, 1 H, arom.) ppm.

¹³C-NMR (126 MHz, CDCl₃, 20 °C): δ = 14.06, 22.64, 25.90, 29.08, 29.26, 29.29, 29.52, 29.60, 30.24, 31.86, 69.59, 70.31, 70.57, 71.06, 71.22, 111.16, 111.45, 118.38, 119.47, 149.93, 150.58 ppm.

(2,5-Dibromophenyl)-carbamic acid benzyl ester **140**



5.00 g (19.9 mmol) 2,5-Dibromophenylamine **139** were dissolved in a mixture of 30 ml ethyl acetate and 30 ml 1 M aqueous NaOH. 3.2 ml (21.9 mmol) Cbz-chloride were added dropwise at 0 °C. After 1 h stirring at rt the layers were separated and the aqueous layer was extracted two times with 30 ml ethyl acetate. The organic layer was dried over MgSO₄, filtered and the solvent evaporated. The crude product was purified by recrystallization from hexane.

Yield: 7.51 (98 %) g colorless solid.

r_f = 0.40 (silica gel; hexane/ethyl acetate 4:1).

¹H-NMR (500 MHz, CDCl₃, 20 °C): δ = 5.23 (2 H, s, benz.-CH₂-), 7.05 (d, 1 H, ³J = 9.0 Hz, -CH₂-), 7.20 (s, 1 H, arom.), 7.51 (m, 6 H), 8.40 (s, 1 H, arom.), ppm.

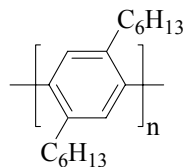
¹³C-NMR (126 MHz, CDCl₃, 20 °C): δ = 67.58, 110.75, 122.11, 122.77, 127.16, 133.17, 135.50, 136.86, 152.69 ppm.

MS (EI, 80 eV): m/z (%) = 388 (1), 387 (5), 386 (2), 385 (11), 384 (1), 383 (6) [M]⁺, 341 (5), 304 (2) [M-Br]⁺, 277 (2), 91 (100).

| | | | | | |
|-----------|--|-------|---------|--------|--------|
| EA | [C ₁₄ H ₁₁ Br ₂ NO ₂] | calc. | C 43.67 | N 3.64 | H 2.88 |
| | (385.055) | found | 43.48 | 3.47 | 2.77 |

7.4.7 Compounds of Chapter 4.5

Poly(2,5,-dihexylphenyl-4,4'-diyl) 142



519.6 mg (1.04 mmol) **32 a** and 339.7 mg (1.04 mmol) **45** were dissolved in 100 ml toluene and 150 ml of a 1 M aqueous Na₂CO₃ solution were added. The mixture was freeze degassed three times and 9.0 mg (0.7 mol %) Pd(PPh₃)₄ were added. The freeze degassing was repeated and the mixture was refluxed for 2 d. The crude mixture was extracted with hot toluene three times. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. 60 w. t. % of PPP **142** were not soluble in refluxing toluene.

Yield: 123 mg (97 %).

¹H-NMR (250 MHz, CDCl₃, 20 °C): δ = 0.75 (m, 6 H, -CH₃), 1.19 (m, 12 H, -CH₂-), 1.46 (m, 2 H, β-CH₂-), 2.39 (m, 2 H, α-CH₂-), 7.19 (m, 2 H, arom.) ppm.

¹³C-NMR (63 MHz, CDCl₃, 20 °C): δ = 14.03, 22.56, 28.70, 29.28, 31.15, 31.72, 32.87, 33.92, 127.92, 128.42, 129.43, 130.27, 132.02, 132.18, 133.58, 133.89, 137.43 ppm.

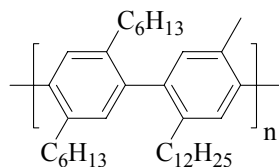
| | | | |
|------------------------------------|-------|---------|---------|
| [C ₁₈ H ₂₈] | calc. | C 88.45 | H 11.55 |
| (244.420) | found | 87.74 | 10.67 |

GPC

M_n = 7600 M_w = 8500 D = 1.11 (vs. PS in THF; not complete soluble).

M_n = 1400 M_w = 9800 D = 7.06 (vs. PS in 1,3,4-Trichlorobenzene at 135°C).

Poly(2-methyl-5-dodecyl-2',5'-dihexylbiphenyl-4,4'-diyl) 143



506.5 mg (1.4782 mol) **45** and 757.2 mg (1.4782 mmol) **32 d** were dissolved in 60 ml xylene p. a. (o-, m-, p-mixture) and 100 ml of a 1 M aqueous Na₂CO₃ solution were added. The

mixture was degassed three times by evacuating and ventilating with argon each 10 minutes. The apparatus was opened under an argon stream and 15.7 mg (0.9 mol %) Pd(PPh₃)₄ were added quickly. The apparatus was closed and the degassing was repeated as described above. The reaction mixture was cooked under reflux for 3 d. The crude mixture was extracted with xylene three times. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated. The product was purified by a twofold precipitation from acetone.

Yield: 423 mg of a colorless solid.

¹H-NMR (500 MHz, CDCl₃, 20 °C): δ = 0.82 (m, 9 H, -CH₃), 1.21 (m, 30 H, -CH₂-), 1.47 (m, 6 H, β-CH₂-), 2.12 (m, 3 H, α-CH₃), 2.41 (m, 6 H, α-CH₂-), 7.13 (m, 4 H, arom.) ppm.

¹³C-NMR (126 MHz, CDCl₃, 20 °C): δ = 14.06, 14.11, 19.56, 19.76, 22.54, 22.61, 22.71, 29.38, 29.41, 29.71, 30.86, 31.07, 31.64, 31.70, 31.94, 32.91, 130.26, 130.39, 131.15, 131.33, 132.60, 137.35, 137.56, 137.63, 139.71, 139.87, 140.20 ppm.

| | | | |
|------------------------------------|-------|---------|---------|
| [C ₃₇ H ₅₈] | calc. | C 88.37 | H 11.63 |
| (502.868) | found | 83.65 | 10.87 |

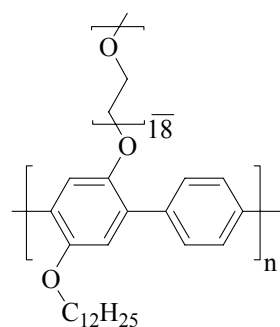
GPC

M_n = 9600 M_w = 14800 D = 1.46 (vs. PS in THF).

M_n = 7100 M_w = 9900 D = 1.55 (vs. PPP in THF).

M_n = 3500 M_w = 43700 D = 1.26 (vs. PS in 1,3,4-Trichlorobenzene at 135°C).

Amphiphilic AA-BB-type polymer 145



10.000 g (9.38 mmol) monomer **135** and 2.306 g (9.38 mmol) bisboronic ester **50 b** were dissolved in 30 ml dioxane. 30 ml of a 2 M aqueous NaHCO₃ solution were added. The two layer system was degassed three times by evacuating and ventilating with argon each 10 minutes. The apparatus was opened under an argon stream and 86 mg (0.9 mol %) tris-(tri-p-tolylphosphine)-palladium were added quickly. The apparatus was closed and the degassing

was repeated like before. The reaction mixture was cooked under reflux for 3 d. After cooling to r.t. 115 mg (0.47 mmol) bisboronic ester **50 b** were added. The mixture was refluxed for additional 3 h. The two layers were separated and the aqueous was extracted four times with chloroform. The combined organic layers were dried over MgSO₄, filtered and the solvent was evaporated to a concentrate solution. This solution was added dropwise to 400 ml hexane under vigorous stirring. The precipitate was centrifuged, dried and freeze-dried from dioxane. Yield: 8.24 g light violet solid.

¹H-NMR (250 MHz, CDCl₃, 20 °C): δ = 0.85 (m, 3 H, -CH₃), 1.23 (m, 4 H, -CH₂-), 1.40 (m, 2 H, γ-CH₂-), 1.74 (m, 2 H, β-CH₂-), 3.35 (m, 3 H, -OCH₃), 3.52 (m, 2 H, -CH₂O-), 3.62 (m, 60 H, -CH₂O-), 3.79 (m, 2 H, α-OCH₂-), 3.98 (m, 4 H, α-CH₂-; -CH₂O-), 4.14 (m, 2 H, α-OCH₂-), 7.07 (m, 1 H, arom.), 7.11 (m, 1 H, arom.), 7.18 (m, 1 H, arom.) ppm.

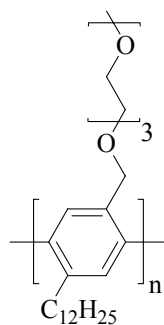
¹³C-NMR (63 MHz, CDCl₃, 20 °C): δ = 14.04, 22.63, 29.35, 29.67, 31.88, 32.98, 58.92, 69.79, 70.48, 71.86, 128.99, 129.19, 130.58, 131.95, 138.90, 139.68 ppm.

| | | | |
|---|-------|---------|--------|
| [C ₆₀ H ₁₀₄ O _{19.5}] | calc. | C 63.35 | H 9.22 |
| (1137.474) | found | 63.67 | 9.03 |

GPC

M_n = 50100 M_w = 66600 D = 1.33 (in THF *versus* PS standards).

Amphiphilic AB-type polymer 2



188 mg (0.3 mmol) **1** were dissolved in 1 ml THF and 3 ml 1 M aqueous NaHCO₃ solution were added. The mixture was freeze degassed three times and 5 mg (1.4 mol %) Pd(PPh₃)₄ were added. The freeze-degassing was repeated and the mixture was refluxed for 2 d. The crude mixture was extracted with CH₂Cl₂ three times. The combined organic layers were dried over MgSO₄, filtered and the solvent evaporated.

Yield: 123 mg (97 %).

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , 20 °C): δ = 0.77 (m, 3 H, $-\text{CH}_3$), 1.12 (m, 18 H, $-\text{CH}_2-$), 1.40 (m, 2 H, $\beta\text{-CH}_2-$), 2.34 (m, 2 H, $\alpha\text{-CH}_2-$), 3.27 (s, 3 H, $-\text{OCH}_3$), 3.50 (m, 12 H, $-\text{OCH}_2-$), 4.25 (s, 2 H, $\alpha\text{-CH}_2\text{O-}$), 7.09 (s, 1 H, arom.), 7.30 (s, 1 H, arom.) ppm.

$^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , 20 °C): δ = 14.04, 22.63, 29.35, 29.67, 31.88, 32.98, 58.92, 69.79, 70.48, 71.86, 128.99, 129.19, 130.58, 131.95, 138.90, 139.68 ppm.

GPC (*versus* PS standards)

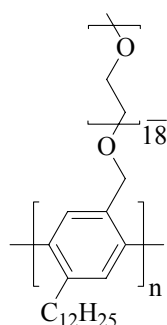
$M_n = 6600$

$M_p = 8400$

$M_w = 9400$

$D = 1.43$

Amphiphilic AB-type polymer 146



3.91 g (3.1 mmol) monomer **117** were dissolved in 20 ml dioxane. 30 ml of an aqueous 2 M NaHCO_3 solution were added. The two layer system was degassed by three times evacuating and ventilating with argon each 10 minutes. The apparatus was opened under an argon stream and 25 mg (0.8 mol %) $\text{Pd}[\text{P}(\text{p-tol})_3]_3$ were added quickly. The apparatus was closed and the degassing was repeated like before. The reaction mixture was cooked under reflux for 3 d. 13 ml solvent were evaporated after 3 d and the residue was refluxed for 3 h. The two layers were separated and the aqueous was extracted four times with chloroform. The combined organic layers were dried over MgSO_4 , filtered and the solvent was evaporated to a concentrate solution. This solution was added dropwise to 400 ml hexane under vigorous stirring. The precipitate was centrifuged, dried and freeze-dried from dioxane.

Yield: 2.48 g of a light yellow solid.

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , 20 °C): δ = 0.83 (m, 3 H, $-\text{CH}_3$), 1.20 (m, 18 H, $-\text{CH}_2-$), 1.42 (m, 2 H, $\beta\text{-CH}_2-$), 2.40 (m, 2 H, $\alpha\text{-CH}_2-$), 3.33 (s, 3 H, $-\text{OCH}_3$), 3.59 (m, 12 H, $-\text{OCH}_2-$), 4.33 (s, 2 H, $\alpha\text{-CH}_2\text{O-}$), 7.12 (s, 1 H, arom.), 7.37 (s, 1 H, arom.) ppm.

¹³C-NMR (126 MHz, CDCl₃, 20 °C): δ = 14.17, 22.73, 29.42, 29.44, 29.53, 29.72, 29.77, 29.82, 31.06, 31.23, 31.96, 32.97, 59.06, 69.74, 69.86, 70.24, 70.48, 70.55, 70.60, 70.64, 70.80, 70.85, 70.95, 71.03, 71.96, 71.98, 71.99, 76.91, 129.17, 130.69, 139.45, 139.55 ppm.

| | | | | |
|-----------|---|-------|---------|--------|
| EA | [C ₅₅ H ₁₀₂ O _{18.5}] | calc. | C 62.03 | H 9.38 |
| | (1059.404) | found | 62.36 | 9.70 |

GPC

M_n = 10500 M_w = 14300 D = 1.36 (in THF *versus* PS standards).