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 $Pd(PPh_3)_4$, $Pd[P(p\text{-}tol)_3]_3$ and $Pd[P(o\text{-}tol)_3]_2$ were synthesized according to literature[132] 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”, F_{254}). 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.

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[131] a) D. D. Perrin, W. L. F. Armarego *Purificationof 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*: Knaur Eurosphere® 7µm C_{18}, 4·120 mm, UV-detection at 335 nm or 254 nm.

Preparative: Machery-Nagel, Nucleosil® 5µm C_{18}, 32·250 mm, UV-detection at 335 nm or 254 nm.

Silica gel: *Analytical*: Knaur Eurosphere® 7µm C_{18}, 4·120 mm, UV-detection at 335 nm or 254 nm.

Preparative: Knaur Eurosphere® 5µm C_{18}, 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 Knaur 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; Lenght: 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 (^{1}H: $CDCl_3$: 7.24 ppm , [D_6]-DMSO: 2.49 ppm, [D_3]-acetonitrile: 1.93 ppm; ^{13}C: $CDCl_3$: 77.00, [D_6]-DMSO: 39.70 ppm, [D_3]-acetonitrile: 117.70 ppm). The

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[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:

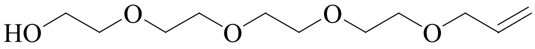
Netsch TGA 209, 20 to 600 °C, 10 K/min heating rate. N_2 as protective atmosphere.

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

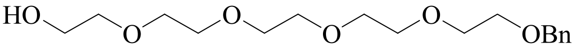


16.8 g (300 mmol) KOH were dissolved in 52.0 ml (300 mmol) tetraethylenglycol. The solution was cooled to 0 °C. 25.4 ml (300 mmol) allyl bromide were added dropwise. After complete addition the mixture was heated for 3 h at 60 °C. The mixture was cooled to rt and 400 ml ether were added. KBr was filtered 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 CH_2Cl_2 to extract the desired product. The combined CH_2Cl_2 layers were dried over $MgSO_4$, filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; CH_2Cl_2/MeOH 19:1).

Yield: 25.0 g (36 %) colorless oil.

$r_f = 0.27$ (silica gel; $MeCl_2$/MeOH 19:1).
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.98 (s, 1 H, -OH), 3.57 (m, 16 H, $-CH_2O-$), 3.94 (d, $^3J=7.6$ Hz, 2 H, $-CH_2-$), 5.14 (m, 2 H, $=CH_2$) , 5.83 (m, 1 H, -CH=) ppm.
^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M+H]^{+\cdot}$, 191 (1) $[M-C_2H_4O]^{+\cdot}$, 177 (1) $[M-C_3H_6O]^{+\cdot}$, 163 (2) $[M-C_4H_8O]^{+\cdot}$, 147 (3) $[M-C_4H_8O_2]^{+\cdot}$, 45 (100) $[C_3H_5O]^{+\cdot}$.
HRMS $[^{12}C_{11}{}^{1}H_{22}{}^{16}O_5+H-C_2H_4O]^{+\cdot}$ calc.: 191.12833 found: 191.12632,
$[^{12}C_{11}{}^{1}H_{22}{}^{16}O_5+H-C_4H_8O]^{+\cdot}$ 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^{t}Bu in 100 ml ^{t}BuOH. 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 $MgSO_4$, filtrated and the solvent removed. The crude product was purified by column chromatography (silica gel; $MeCl_2$/MeOH 19:1).

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

$r_f = 0.32$ (silica gel; $MeCl_2$/MeOH 19:1).

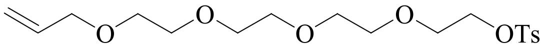
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.95 (s, 1 H, -OH), 3.59 (m, 20 H, -CH_2O-), 4.50 (s, 2 H, Hz, -C$\underline{H}_2$Ph), 7.33 (m, 5 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M+H]^{+\cdot}$, 285 (1), $[M-C_2H_4O]^{+\cdot}$, 91 (100) $[C_7H_7]^{+\cdot}$.

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

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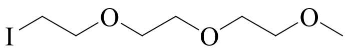
[133] K.-T. Wong, Y.-Y. Chien, Y.-L. Liao, C.-C. Lin, M.-Y. Chou, M.-K. Leung *J. Org. Chem.* **2002**, *67*, 1041-1044.

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}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}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) $[M]^{+\cdot}$, 331 (2) $[M-C_3H_5O]^{+\cdot}$, 287 (1), 286 (1) $[M-C_5H_9O_2]^{+\cdot}$, 244 (1), 243 (6) $[M- C_7H_{13}O_3]^{+\cdot}$, 199 (100) $[M-C_9H_{17}O_4]^{+\cdot}$.

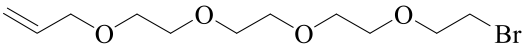
EA	$C_{18}H_{28}SO_7$	calc.	C 55.65	H 7.26
	(388.482)	found	55.94	7.31

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 mml (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 $MgSO_4$, filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; $MeCl_2$/MeOH 1%).

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

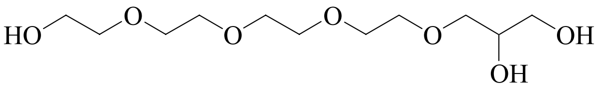
$r_f = 0.29$ (silica gel; $MeCl_2$/ MeOH 1 %).

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.44 (t, ^3J = 7.6 Hz, 2 H, $-CH_2Br$), 3.56 (m, 12 H, $-CH_2O-$), 3.76 (t, ^3J=7.6 Hz, 2 H, $-C\underline{H_2}CH_2Br$), 3.94 (d, ^3J = 7.6 Hz, 2 H, $-CH_2-$), 5.18 (m, 2 H, $=CH_2$) , 5.86 (m, 1 H, -CH=) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M+H]^{+\cdot}$, 241 (5), 239 (5) $[M-C_2H_4O]^{+\cdot}$, 217 (1) $[M-Br]^{+\cdot}$, 197 (4), 195 (5) $[M-C_5H_9O_2]^{+\cdot}$, 109 (51), 107 (49) $[C_2H_4Br]^{+\cdot}$, 41 (100) $[C_3H_5]^{+\cdot}$.

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) $RuCl_3 \cdot H_2O$ and 684 mg (3.2 mmol) $NaIO_4$ in 6 ml dest. water were added rapidly. After stirring for 3 minutes, 20 ml of a saturated aqueous $Na_2S_2O_3$ solution were added and it was stirred for 0.5 h. The solvent was evaporated and the solid residue was extracted with aceton.

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

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

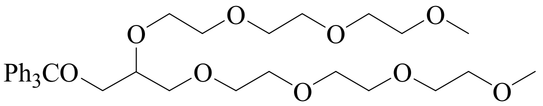
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.39 (s, 3 H, -OH), 3.75 (m, 18 H, $-CH_2O-$), 4.00 (m, 1 H, -CH-) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M+K]^{+\cdot}$, 291 (100) $[M+Na]^{+\cdot}$.

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; $MeCl_2$/MeOH 19:1).

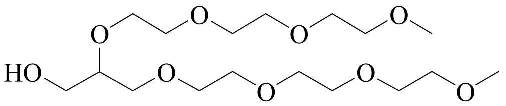
^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 3.15$ (d, $^3J = 5.6$ Hz, 2 H, $-CH_2O-$), 3.21 (s, 6 H, $-CH_3$), 3.55 (m, 25 H, $-CH_2O-$), 3.71 (m, 2 H, $-CH_2O-$), 7.25 (m, 9 H, arom.), 7.42 (d, $^3J = 8.3$ Hz, 6 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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/CH_2Cl_2): m/z (%) = 665 (1) $[M+K]^{+\cdot}$, 649 (1) $[M+Na]^{+\cdot}$, 627 (1) $[M+H]^{+\cdot}$, 243 (100) $[C(Ph)_3]^{+\cdot}$.

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; $MeCl_2$/MeOH 1 % → 5 %).

Yield: 940 mg (64 %) colorless oil.

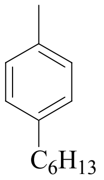
$r_f = 0.49$ (silica gel; $MeCl_2$/MeOH 10 %).

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 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}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 353 (2) $[M-OCH_3]^{+\cdot}$, 59 (100) $[C_3H_7OH]^{+\cdot}$.

EA	$C_{17}H_{36}O_9$	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 discribed 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) Ni(dppp)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) $Pd(PPh_3)_4$ were added, the mixture was degassed again for three times and cooked under relux for 2 d. After cooling to rt the layers were separeted 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 destillation (190 °C, 1013 mbar).
Yield: 14.4 g (57 %) of a colorless oil.

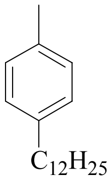
^{1}H NMR (CDCl$_3$, 250 MHz): δ = 1.03 (t, ^{3}J = 8.0 Hz, 3 H, -CH$_3$), 1.43 (m, 6 H, -CH$_2$-), 1.72 (quint, ^{3}J = 8.0 Hz, 2 H, β-CH$_2$-), 2.44 (s, 3 H, α-CH$_3$), 2.70 (t, ^{3}J = 8.0 Hz, 2 H, α-CH$_2$-), 7.20 (s, 4 H, arom.) ppm.

^{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) [M]$^{+\cdot}$, 147 (2) [$C_{11}H_{15}$]$^{+\cdot}$, 119 (5) [C_9H_{11}]$^{+\cdot}$, 105 (100) [C_8H_9]$^{+\cdot}$.

EA	$C_{13}H_{20}$	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 destillated under vacuum (139 °C, 0.5 mbar).

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

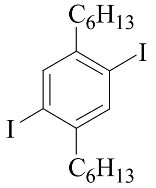
^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.91 (t, ^{3}J = 8 Hz, 3H, -CH$_3$), 1.32 (m, 18 H, -CH$_2$-), 1.59 (quint, ^{3}J = 8 Hz, 2 H, β-CH$_2$-), 2.34 (s, 3 H, α-CH$_3$), 2.59 (t, ^{3}J = 8 Hz, α-CH$_2$-), 7.10 (s, 4 H, arom.) ppm.

^{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) [M]$^{+\cdot}$, 147 (2) [$C_{11}H_{15}$]$^{+\cdot}$, 119 (3) [C_9H_{11}]$^{+\cdot}$, 105 (100) [M-$C_{11}H_{23}$]$^{+\cdot}$.

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

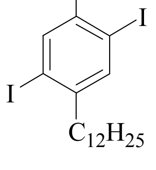
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, ^3J = 8.0 Hz, 6 H, -CH_3), 1.31 (m, 12 H, -CH_2-), 1.56 (quint, ^3J = 8.0 Hz, 4 H, β-CH_2-), 2.62 (t, ^3J = 8.0 Hz, 4 H, α-CH_2-), 7.35 (s, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 428 (5), 427 (25) $[M\text{-}C_5H_{11}]^{+\cdot}$, 357 (4), 356 (2) $[M\text{-}C_{10}H_{22}]^{+\cdot}$, 343 (8) $[M\text{-}I\text{-}C_2H_4]^{+\cdot}$, 301 (7), $[M\text{-}I\text{-}C_5H_{10}]^{+\cdot}$, 231 (3), 230 (3) $[C_8H_8I]^{+\cdot}$, 215 (14) $[M\text{-}2I\text{-}C_2H_5]^{+\cdot}$, 201 (12) $[M\text{-}2I\text{-}C_3H_7]^{+\cdot}$.

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

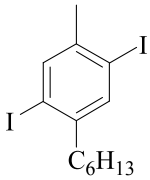
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.87 (t, ^3J = 8.0 Hz, 6 H, $-CH_3$), 1.28 (m, 36 H, $-CH_2-$), 1.54 (quint, ^3J = 8.0 Hz, 4 H, β-CH_2-), 2.57 (t, ^3J = 8.0 Hz, 4 H, α-CH_2-), 7.58 (s, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 356 (11) $[M-C_{22}H_{46}]^{+\cdot}$.

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.

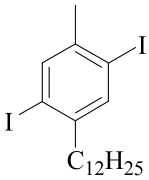
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, ^3J = 8 Hz, 3 H, $-CH_3$), 1.30 (m, 6 H, $-CH_2-$), 1.53 (quint, ^3J = 8 Hz, 2 H, β-CH_2-), 2.31 (s, 3 H, α-CH_3), 2.56 (t, ^3J = 8 Hz, 2 H, α-CH_2-), 7.57 (s, 1 H, arom.), 7.63 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 358 (11), 357 (37), 356 (4) $[M-C_5H_{11}]^{+\cdot}$, 232 (5), 231 (42), 230 (4) $[C_8H_8I]^{+\cdot}$, 174 (3) $[C_{19}H_{29}]^{+\cdot}$, 145 (22) $[C_{11}H_{13}]^{+\cdot}$.

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 than 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 %)

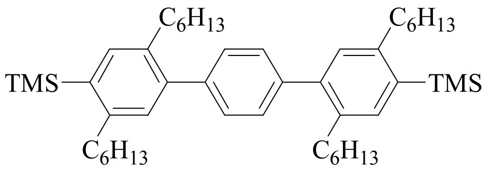
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.90 (t, ^3J = 8 Hz, 3 H, $-CH_3$), 1.29 (m, 18 H, $-CH_2-$), 1.53 (quint, ^3J = 8 Hz, 2 H, β-CH_2-), 2.33 (s, 3 H, α-CH_3), 2.60 (t, ^3J = 8 Hz, 2 H, α-CH_2-), 7.58 (s, 1 H, arom.), 7.66 (s, 1 H, arom.) ppm.

^{13}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) $[M]^{+\cdot}$, 357 (32) $[M-C_{11}H_{23}]^{+\cdot}$, 271 (3), 257 (2) $[C_{19}H_{29}]^{+\cdot}$, 231 (33) $[C_8H_8I]^{+\cdot}$, 159 (2), 145 (22) $[C_{11}H_{13}]^{+\cdot}$.

EA	$C_{19}H_{30}I_2$	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) $NaHCO_3$ 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 %) $Pd(PPh_3)_4$ 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

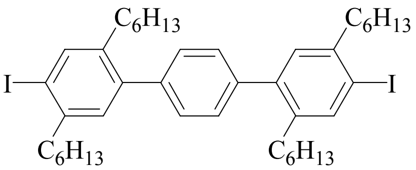
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.38 (s, 18 H, -TMS), 0.83 (t, ^3J = 8.0 Hz, 6 H, $-CH_3$), 0.90 (t, ^3J = 8.0 Hz, 6 H, $-CH_3$), 1.21-1.63 (m, 32 H, $-CH_2-$), 2.60 (t, ^3J = 8.0 Hz, 4 H, α-CH_2-), 2.72 (t, ^3J = 8.0 Hz, 4 H, α-CH_2-), 7.12 (s, 2 H, arom.), 7.34 (s, 4 H, arom.), 7.38 (s, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 697 (2), 696 (5), 695 (8) $[M-CH_3]^{+\cdot}$, 641 (3), 640 (5), 639 (5), 638 (4), 637 (3) $[M-SiC_3H_9]^{+\cdot}$.

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 $MeCl_2$ was added dropwise. Ater stirring for 1 h at – 78 °C., the reaction mixture was quenched with 20 ml saturated $Na_2S_2O_3$ solution. The layers were separated and the aqueous layer was extracted three times with 40 ml $MeCl_2$. The combined organic layers were washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over $MgSO_4$, 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}H NMR ($CDCl_3$, 250 MHz): δ = 0.82 (t, ^3J = 8 Hz, 6 H, -CH_3), 0.88 (t, ^3J = 8 Hz, 6 H, -CH_3), 1.06-1.70 (m, 32 H, -CH_2-), 2.51 (t, ^3J = 8 Hz, 4 H, α-CH_2-), 2.67 (t, ^3J = 8 Hz, 4 H, α-CH_2-), 7.07 (s, 2 H, arom.), 7.27 (s, 4 H, arom.), 7.72 (s, 2 H, arom.) ppm.

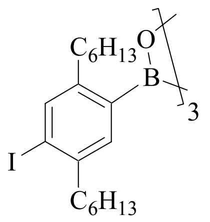
^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.06, 22.47, 22.60, 29.06, 29.11, 30.38, 31.17, 31.44, 31.65, 32.25, 40.36, 99.44, 128.76, 130.64, 139.81, 139.87, 140.00, 141.63, 142.62 ppm.

MS (EI, 80 eV, 180°C): m/z (%) = 821 (2), 820 (11), 819 (44), 818 (100) $[M]^{+\cdot}$, 748 (1), 747 (1) $[M-C_5H_{11}]^{+\cdot}$, 694 (2), 693 (6), 692 (14), 690 (1) $[M-I]^{+\cdot}$.

EA	$C_{42}H_{60}I_2$	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)

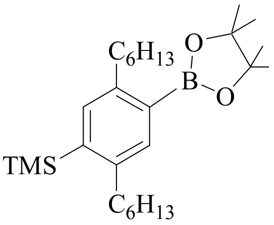
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, ^3J = 8.0 Hz, 9 H, -CH_3), 0.92 (t, ^3J = 8.0 Hz, 9 H, -CH_3), 1.12-1.50 (m, 24 H, -CH_2-), 1.62 (m, 12 H, β-CH_2-), 2.74 (t, ^3J = 8.0 Hz, 6 H, α-CH_2-), 3.06 (t, ^3J = 8.0 Hz, 6 H, α-CH_2-), 7.77 (s, 3 H, arom.), 7.91 (s, 3 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 1149 (12), 1148 (23), 1147 (23), 1146 (23), 1145 (15) $[M-BO_2H_3]^{+\cdot}$, 1105 (14), 1104 (16), 1103 (27), 1102 (26), 1101 (14) $[M-B_2O_4H_5]^{+\cdot}$, 1070 (21), 1069 (40), 1068 (33), 1067 (20), 1066 (13) $[M-I+H]^{+\cdot}$.

EA	$C_{54}H_{84}B_3O_3I_3$	calc.	C 54.30	H 7.09
	(1194.406)	found	54.14	7.12

2-(2,5-Dihexyl-4-trimethylsilanyl-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.

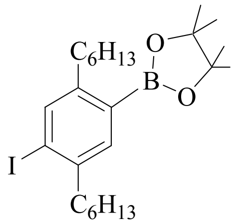
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.28 (s, 9 H, -$Si(CH_3)_3$), 0.88 (t, J = 8.0 Hz, 6 H, -CH_3), 1.40 (m, 12 H, -CH_2-), 1.55 (m, 4 H, β-CH_2-), 2.64 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 2.81 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 7.21 (s, 1 H, arom.), 7.56 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 430 (9), 429 (18), 428 (9) $[M-CH_3]^{+\cdot}$, 346 (9), 345 (25), 344 (67), 343 (29), 342 (11), 341 (7) $[M-C_6H_{12}O]^{+\cdot}$, 276 (9), 275 (29), 274 (100), 273 (33), 272 (9) $[M-C_6H_9O-SiC_3H_9]^{+\cdot}$.

EA	$C_{27}H_{49}BO_2Si$	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 °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 °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).

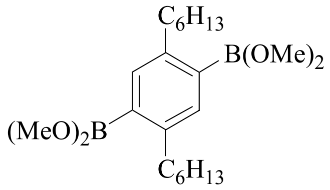
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.87 (m, 6 H, $-CH_3$), 1.29 (m, 12 H, $-CH_2-$), 1.50 (m, 4 H, β-CH_2-), 2.64 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 2.74 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 7.53 (s, 1 H, arom.), 7.62 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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°C): m/z (%) = 499 (27), 498 (88), 497 (26) $[M]^{+\cdot}$, 442 (18), 441 (74), 440 (33) $[M-C_4H_9]^{+\cdot}$, 427 (22) $[M-C_5H_{11}]^{+\cdot}$, 327 (10) $[M-I]^{+\cdot}$, 301 (27), 300 (8) $[M-I-C_5H_{11}+H]^{+\cdot}$, 102 (7), 101 (100) $[C_6H_{12}O]^{+\cdot}$.

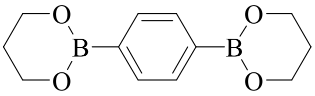
EA	$C_{24}H_{40}BO_2I$	calc.	C 57.85	H 8.09
	(498.296)	found	58.02	8.30

Tetrakismethyl-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 destillation and the product was stored under dry argon at -20 °C.
Yield: 17.2 g (98 %) of a colorless oil.
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, ^3J = 8.0 Hz, 6 H), 1.24 (m, 12 H, $-CH_2-$), 1.49 (quint, ^3J = 8.0 Hz, 4 H, β-CH_2-), 2.48 (t, ^3J = 8.0 Hz, 4 H, α-CH_2-), 3.52 (s, 12 H, $-OCH_3$), 7.02 (s, 2 H, arom.) ppm.
^{13}C NMR ($CDCl_3$, 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

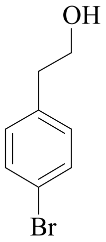


The Grignard compound was prepared from 25.0 g (1.03 mol) Mg and 118.0 g (495 mmol) **46** in 750 ml dry THF and refluxed for 10 h. The solution was cooled to -78 °C and 120 ml (1.05 mol) trimethylborate were added dropwise. The mixture was allowed to warm to rt over night. 75 ml (1.04 mol) 1,3-propandiol 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).
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.03 (quint, ^3J = 6.0 Hz, 4 H, $-CH_2-$), 4.14 (t, ^3J = 6.0 Hz, 8 H, $-OCH_2-$), 7.72 (s, 4 H, arom.) ppm.
^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 189 (10), 188 (39), 187 (19) $[M-C_3H_6O]^{+\cdot}$.

EA	$C_{12}H_{16}B_2O_4$	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 $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The crude product was purified by vacuum destillation (90 °C, $1.6 \cdot 10^{-2}$ mbar).

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

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

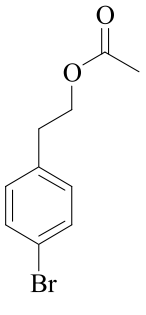
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.28 (s, 1 H, -OH), 2.76 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 3.77 (t, ^3J = 8.0 Hz, 2 H, -CH_2OH), 7.05 (d, ^3J = 11.0 Hz, 2 H, arom.), 7.39 (d, ^3J = 11.0 Hz, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 172 (32), 171 (98), 170 (33), 169 (100) $[M-CH_3O]^{+\cdot}$, 121 (9) $[C_8H_9O]^{+\cdot}$, 92 (5), 91 (46), 90 (30), 89 (19) $[C_7H_7]^{+\cdot}$.

EA	C_8H_9OBr	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 $MgSO_4$, filterered 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.

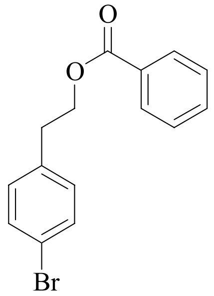
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.01 (s, 1 H, -CH_3), 2.86 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 4.22 (t, ^3J = 8.0 Hz, 2 H, -CH_2OAc), 7.06 (d, ^3J = 10.0 Hz, 2 H, arom.), 7.40 (d, ^3J = 10.0 Hz, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 185 (9), 184 (87), 183 (9), 182 (89) $[C_8H_7{}^{79}Br]^{+\cdot}$, 172 (1), 171 (9), 170 (1), 169 (10) $[C_7H_6{}^{79}Br]^{+\cdot}$, 104 (6),103 (9), 102 (2) $[C_8H_7]^{+\cdot}$, 43 (100) $[C_2H_3O]^{+\cdot}$.

EA	$C_{10}H_{11}O_2Br$	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 form 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 %).

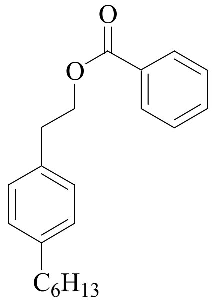
^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 3.01$ (t, $^3J = 8.0$ Hz, 2 H, α-CH_2-), 4.53 (t, $^3J = 8.0$ Hz, 2 H, -CH_2OBz), 7.14 (d, $^3J = 10.0$ Hz, 2 H, arom.), 7.42 (m, 4 H, arom.), 7.56 (t, $^3J = 10.0$ Hz, 1 H, arom.), 8.01 (d, $^3J = 10.0$ Hz, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 186 (1), 185 (13), 184 (99), 183 (14), 182 (100) $[C_8H_7{}^{79}Br]^{+\cdot}$, 171 (4), 169 (4) $[C_7H_6Br]^{+\cdot}$, 105 (93) $[C_7H_5O]^{+\cdot}$.

EA	$C_{15}H_{13}O_2Br$	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) $Pd(PPh_3)_4$ 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 separeted 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.

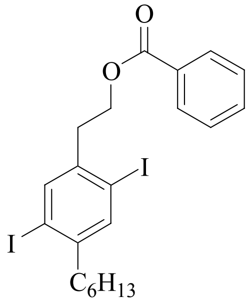
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, ^3J = 7.0 Hz, 3 H, $-CH_3$), 1.29 (m, 6 H, $-CH_2-$), 1.61 (quint, ^3J = 7.0 Hz, 2 H, *β*-CH_2-), 2.60 (t, ^3J = 7.0 Hz, 2 H, *α*-CH_2-), 3.08 (t, ^3J = 6 Hz, 2 H, *α*-CH_2-), 4.52 (t, ^3J = 6 Hz, 2 H, *β*-CH_2OBz), 7.20 (AA′BB′, ^3J = 10.0 Hz, 4 H), 7.46 (t, ^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.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 191 (2), 190 (17), 189 (100), 188 (37), 187 (11) $[C_{14}H_{21}]^{+\cdot}$, 175 (5) $[C_{13}H_{19}]^{+\cdot}$, 131 (9) $[C_{10}H_{21}]^{+\cdot}$. (MS-EI does not work).

EA	$C_{15}H_{13}O_2Br$	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 CH_2Cl_2 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.

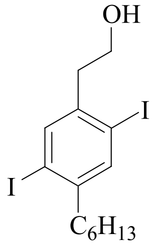
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, ^3J = 7.0 Hz, 3 H, $-CH_3$), 1.32 (m, 6 H, $-CH_2-$), 1.53 (quint, ^3J = 7.0 Hz, 2 H, *β*-CH_2-), 2.59 (t, ^3J = 7.0 Hz, 2 H, *α*-CH_2-), 3.11 (t, ^3J = 7.0 Hz, 2 H, *α*-CH_2-), 4.46 (t, ^3J = 10.0 Hz, 1 H, $-OCH_2-$), 7.44 (t, ^3J = 10.0 Hz, 2 H, arom.), 7.53 (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.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 441 (16), 440 (100) $[M\text{-}C_7H_6O_2]^{+\cdot}$, 371 (1), 370 (5), 369 (22) $[M\text{-}C_7H_6O_2\text{-}C_5H_{11}]^{+\cdot}$, 244 (2), 243 (19), 242 (2) $[M\text{-}C_7H_5O_2\text{-}C_5H_{11}\text{-}I]^{+\cdot}$.

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

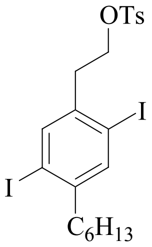
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, ^3J = 7.0 Hz, 3 H, $-CH_3$), 1.32 (m, 6 H, $-CH_2-$), 1.54 (quint, ^3J = 7.0 Hz, 3 H, β-CH_2- and -OH), 2.56 (t, ^3J = 7.0 Hz, 2 H, α-CH_2-), 2.88 (t, ^3J = 7.0 Hz, 2 H, α-CH_2-), 3.80 (t, ^3J = 7.0 Hz, 2 H, $-OCH_2-$), 7.60 (s, 1 H, arom.), 7.65 (s, 1 H, arom.) 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) $[M]^{+\cdot}$, 428 (7), 427 (33) $[M\text{-}CH_3O]^{+\cdot}$, 388 (1), 387 (8) $[M\text{-}C_5H_{11}]^{+\cdot}$, 332 (8), 331 (51) $[M\text{-}I]^{+\cdot}$.

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.

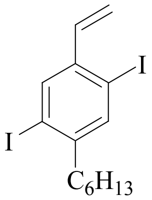
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, ^3J = 7.0 Hz, 3 H, $-CH_3$), 1.28 (m, 6 H, $-CH_2-$), 1.47 (quint, ^3J = 7.0 Hz, 3 H, β-CH_2-), 2.40 (s, 3 H, $-CH_3$), 2.56 (t, ^3J = 7.0 Hz, 2 H, α-CH_2-), 2.96 (t, ^3J = 7.0 Hz, 2 H, α-CH_2-), 4.16 (t, ^3J = 7.0 Hz, 2 H, $-OCH_2-$), 7.24 (d, ^3J = 11.0 Hz, 2 H, arom.), 7.51 (s, 2 H, arom.), 7.66 (d, ^3J = 11.0 Hz, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 442 (2), 441 (27), 440 (100) $[M-C_7H_8SO_3]^{+\cdot}$, 428 (2), 427 (13) $[M-C_8H_9SO_3]^{+\cdot}$, 370 (9), 369 (33) $[M-C_7H_8SO_3-C_5H_{11}]^{+\cdot}$.

EA	$C_{21}H_{26}OI_2O_3S$	calc.	C 41.19	H 4.28
	(612.311)	found	41.11	4.28

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

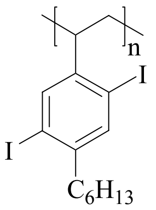


^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.88 (t, ^{3}J = 7.0 Hz, 3 H, -CH$_3$), 1.28 (m, 6 H, -CH$_2$-), 1.49 (quint, ^{3}J = 7.0 Hz, 3 H, *β*-CH$_2$-), 2.56 (t, ^{3}J = 7.0 Hz, 2 H, *α*-CH$_2$-), 5.22 (d, ^{3}J = 11.0 Hz, 2 H, =CH$_2$), 5.52 (d, ^{3}J = 17.0 Hz, 2 H, =CH$_2$), 6.68 (dd, ^{3}J = 17.0 Hz, ^{3}J = 11.0 Hz, 1 H, =CH-), 7.56 (s, 1 H, arom.), 7.87 (s, 1 H, arom.) ppm.

^{13}C NMR (CDCl$_3$, 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



^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.87 (m, 3 H, -CH$_3$), 1.29 (m, 6 H, -CH$_2$-), 1.49 (m, 4 H, *β*-CH$_2$-), 2.50 (m, 3 H, *α*-CH$_2$-, *α*-CH), 7.45 (m, 2 H, arom.) ppm.

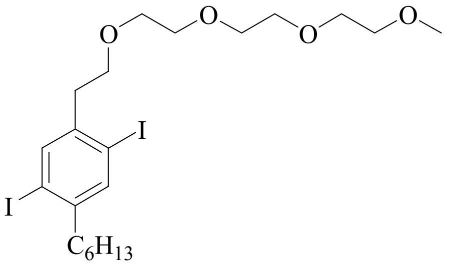
^{13}C NMR (CDCl$_3$, 63 MHz): δ = 14.08, 22.65, 28.95, 29.07, 29.63, 31.51, 39.97, 99.13, 100.44, 117.06, 136.50, 138.39, 138.87, 139.17, 144.91 ppm.

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.

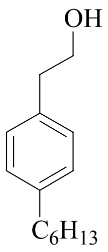
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.85 (t, ^3J = 7.0 Hz, 3 H, -CH_3), 1.32 (m, 6 H, -CH_2-), 1.51 (quint, ^3J = 7.0 Hz, 3 H, β-CH_2-), 2.55 (t, ^3J = 7.0 Hz, 2 H, α-CH_2-), 2.89 (t, ^3J = 7.0 Hz, 2 H, α-$C\underline{H}_2CH_2O$-), 3.36 (s, 3 H, -CH_3), 3.50 (m, 2 H, -OCH_2-), 3.60 (m, 12 H, -OCH_2-), 7.56 (s, 1 H, arom.), 7.64 (s, 1 H, arom.) ppm.

^{13}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) $[M]^{+\cdot}$, 500 (1) $[M-C_5H_{12}O_2]^{+\cdot}$, 442 (3), 441 (27), 440 (100) $[M-C_7H_{16}O_4]^{+\cdot}$, 317 (2), 316 (1), 315 (7), 314 (25) $[M-C_7H_{15}O_4-I]^{+\cdot}$.

EA	$C_{21}H_{34}O_4I_2$	calc.	C	41.74	H	5.67
	(604.308)	found		41.11		4.28

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



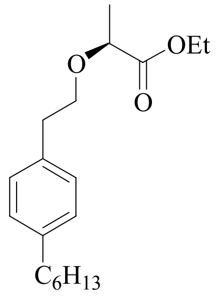
1.00 g (3.2 mmol) benzoic acid 2-(4-hexylphenyl)-ethyl ester **58**, 3.0 g (53.5 mmol) KOH were dissolved in 40 ml methanol and 40 ml THF and cooked under reflux for 20 h. After addition of 100 ml ether the layers were separated and the organic layer was washed with aqueous saturated Na_2CO_3 solution.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

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

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, ^3J = 7.0 Hz, 3 H, -CH_3), 1.29 (m, 6 H, -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, -OCH_2-), 3.90 (s, 1 H, -OH), 7.14 (s, 4 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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 addionally 3 h. The crude mixture was dried under vacuum and the residue was purified by column chromatography (silica gel; hexane/ethyl acetate 20:1).

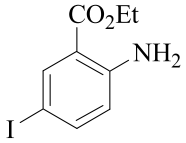
Yield: 0.70 g (76 %) of a colorless oil.

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

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, ^3J = 7.0 Hz, 3 H, -CH_3), 1.30 (m, 12 H, -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, -OCH_2-), 3.80 (dt, ^3J = 9.0 Hz, 1 H, -OCH_2-), 3.96 (q, ^3J = 9.0 Hz, 1 H, -$OCH(CH_3)$-), 4.20 (q, ^3J = 9.0 Hz, 2 H, -$OCOCH_2$-), 7.10 (dd, ^3J = 11.0 Hz, 4 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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 Na_2CO_3 and the precepitate 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

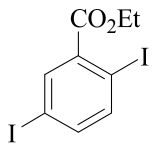
^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.36 (t, ^3J = 8.0 Hz, 3 H, $-CH_3$), 4.30 (q, ^3J = 8.0 Hz, 2 H, $-CH_2-$), 5.66 (s, 2 H, $-NH_2$), 6.58 (d, ^3J = 9.8 Hz, 1 H, arom.), 7.45 (d, ^3J = 9.8 Hz, 1 H, arom.), 8.12 (s, 1 H, arom.) ppm.

^{13}C NMR (63 MHz, $CDCl_3$): δ = 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) $[M]^{+\cdot}$, 263 (4) $[M-C_2H_4]^{+\cdot}$, 247 (1), 246 (15), 245 (56) $[M-C_2H_4-OH]^{+\cdot}$, 219 (1), 218 (6) $[M-EtOH-HCN]^{+\cdot}$.

HRMS $[^{12}C_9{}^1H_{10}{}^{14}N_1{}^{16}O_2{}^{127}I_1]^+$ 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 $Na_2S_2O_3$ solution were added to reduce the excess of iodine. The mixture was extracted twice with CH_2Cl_2 and the combined organic layers were washed with saturated $NaHCO_3$ and brine. The solution was dried over $MgSO_4$, 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

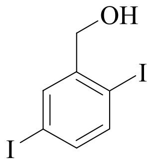
^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (t, J= 7.5 Hz, 3 H), 4.38 (q, ^3J = 7.5 Hz, 2 H), 7.42 (d, ^3J = 9.7 Hz, 1 H, arom.), 7.66 (d, ^3J = 9.7 Hz, 1 H, arom.), 8.06 (s, 1 H, arom.) ppm.

^{13}C NMR (63 MHz, $CDCl_3$): 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) $[M]^{+\cdot}$, 375 (1), 374 (5), 373 (6) $[M-C_2H_5]^{+\cdot}$, 358 (5), 357 (51) $[M-OC_2H_5]^{+\cdot}$, 330 (1), 329 (10), 328 (2) $[M-CO_2C_2H_5]^{+\cdot}$, 203 (1), 202 (7), 201 (1) $[M-CO_2C_2H_5-I]^{+\cdot}$.

HRMS $[^{12}C_9{}^1H_8{}^{16}O_2{}^{127}I_2]^+$ 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 $MgSO_4$, 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).

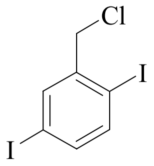
^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.07 (s, 1 H, -OH), 4.24 (s, 2 H, $-CH_2-$), 7.02 (d, ^3J = 9.0 Hz, 1 H, arom.), 7.23 (d, ^3J = 9.0 Hz, 1 H, arom.), 7.54 (s, 1 H, arom.) ppm.

^{13}C NMR (63 MHz, $CDCl_3$): 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) $[M]^{+\cdot}$, 343 (1) $[M-OH]^{+\cdot}$, 329 (2) $[M-CH_2OH]^{+\cdot}$, 233 (10), 232 (4), 231 (12), $[M-HI-H]^{+\cdot}$, 216 (2), 215(5) $[M-I-H_2O]^{+\cdot}$, 204 (7), 203 (5), 202 (3) $[M-I-C_2H_5]^{+\cdot}$.

HRMS $[^{12}C_7{}^1H_6{}^{16}O_1{}^{127}I_2]^+$ 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 $MgSO_4$, filtered and a small amount of silica gel was added before the solvent was evaporated. The purification was done by flash column chomatography (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).

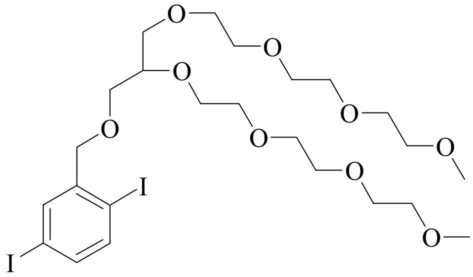
^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.56 (s, 2 H, $-CH_2Cl$), 7.30 (d, ^3J = 9.0 Hz, 1 H, arom.), 7.53 (d, ^3J = 9.0 Hz, 1 H, arom.), 7.78 (s, 1 H, arom.) ppm.

^{13}C NMR (63 MHz, $CDCl_3$): 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) $[M]^{+\cdot}$, 344 (6), 343 (75) $[M\text{-}Cl]^{+\cdot}$, 251 (3) $[M\text{-}HI]^{+\cdot}$, 217 (1), 216 (15), 215 (1) $[M\text{-}I\text{-}Cl]^{+\cdot}$.

HRMS	$[^{12}C_7{}^1H_6{}^{35}Cl_1{}^{127}I_2]^{+\cdot}$	calc.:	377.81693	found:	377.81555.
	$[M\text{-}^{35}Cl_1]^{+\cdot}$	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; $MeCl_2$/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; $MeCl_2$/MeOH 2 %).

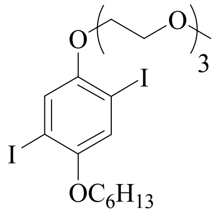
^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.35 (s, 6 H, $-CH_3$), 3.52 (dt, ^3J = 7 Hz, 4 H), 3.57-3.72 (m, 22 H, $-CH_2O-$), 3.72 (m, 1 H), 3.78 (t, ^3J = 7.0 Hz, 2 H), 4.43 (s, 2 H), 7.28 (d, ^3J = 9.0 Hz, 1 H, arom.), 7.48 (d, ^3J = 9.0 Hz, 1 H, arom.), 7.73 (s, 1 H, arom.).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 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) $[M]^{+\cdot}$, 599 (1) $[M-I]^{+\cdot}$, 399 (1), 398 (1) $[M-C_{14}H_{32}O_8]^{+\cdot}$, 353 (3) $[C_{12}H_{18}O_4I]^{+\cdot}$, 344 (2), 343 (25) $[C_7H_5I_2]^{+\cdot}$, 59 (100) $[C_3H_7O]^{+\cdot}$.

HRMS $[^{12}C_{24}{}^1H_{40}{}^{16}O_9{}^{127}I_2]^{+\cdot}$ 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-(trifuoroacetoxy)-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 than quenched with 20 ml of a saturated aqueous $Na_2S_2O_3$ solution. The organic layer was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, 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).

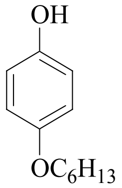
^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 0.87 (t, 3 H, ^3J = 7.0 Hz, $-CH_3$), 1.33 (m, 4 H, $-CH_2-$), 1.47 (m, 2 H, γ-CH_2-), 1.77 (quint, 2 H, ^3J = 7.5 Hz, β-CH_2-), 3.35 (s, 3 H, $-OCH_3$), 3.50 (m, 2 H), 3.62 (m, 4 H), 3.73 (t, 2 H, ^3J = 5.5 Hz, $-OCH_2-$), 3.86 (m, 4 H, $-OCH_2-$), 3.86 (m, 4 H, α-CH_2-; $-CH_2O-$), 4.05 (t, 2 H, ^3J = 5.5 Hz, α-OCH_2-), 7.11 (s, 1 H, arom.), 7.20 (s, 1 H, arom.) ppm.

^{13}C-NMR (63 MHz, $CDCl_3$, 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/$CDCl_3$): m/z (%) = 593 (5), 592 (19) $[M]^{+\cdot}$, 466 (26) $[M-I+H]^{+\cdot}$, 390 (2) $[M-I-C_3H_7O_2]^{+\cdot}$, 262 (14) $[C_8H_7O_2I]^{+\cdot}$, 147 (12) $[C_7H_{15}O_3]^{+\cdot}$, 59 (100) $[C_3H_7O]^{+\cdot}$.

EA	$[C_{19}H_{30}O_5I_2]$	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) K_2CO_3 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 $MgSO_4$, 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

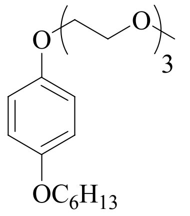
^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 0.89 (t, 3 H, ^3J = 7.5 Hz, $-CH_3$), 1.33 (m, 6 H, $-CH_2-$), 1.72 (quint, 2 H, ^3J = 7.5 Hz, β-CH_2-), 3.87 (t, 2 H, ^3J = 7.5 Hz, α-CH_2-), 5.36 (s, 1 H, -OH), 6.77 (s, 4 H, arom.) ppm.

^{13}C-NMR (63 MHz, $CDCl_3$, 20 °C): δ = 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) $[M]^{+\cdot}$, 123 (18) $[M-C_5H_9]^{+\cdot}$, 110 (100) $[M-C_6H_{12}]^{+\cdot}$, 43 (49) $[C_3H_7]^{+\cdot}$.

EA	$[C_{12}H_{18}O_2]$	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 precepitate 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).

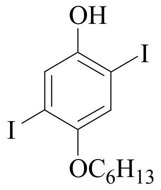
^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 0.88 (t, 3 H, ^3J = 7.0 Hz, $-CH_3$), 1.29 (m, 4 H, $-CH_2-$), 1.42 (m, 2 H, γ-CH_2-), 1.71 (quint, 2 H, ^3J = 7.5 Hz, β-CH_2-), 3.30 (s, 3 H, $-OCH_3$), 3.52 (m, 2 H), 3.64 (m, 6 H), 3.80 (t, 2 H, ^3J = 5.5 Hz, $-OCH_2-$), 3.86 (t, 2 H, ^3J = 7.5 Hz, α-CH_2-), 4.04 (t, 2 H, ^3J = 5.5 Hz, α-OCH_2-), 6.80 (s, 4 H, arom.) ppm.

^{13}C-NMR (63 MHz, $CDCl_3$, 20 °C): δ = 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) $[M]^{+\cdot}$, 194 (7) $[M-C_7H_{14}O_3]^{+\cdot}$, 147 (12) $[C_7H_{15}O_3]^{+\cdot}$, 59 (100) $[C_3H_7O]^{+\cdot}$.

HRMS $[^{12}C_{19}{}^{1}H_{32}{}^{16}O_5]^+$ 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 precepitate 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

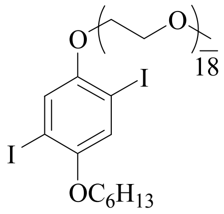
^{1}H-NMR (250 MHz, CDCl$_3$, 20 °C): δ = 0.86 (t, 3 H, ^3J = 7.0 Hz, -CH$_3$), 1.29 (m, 4 H, -CH$_2$-), 1.45 (quint, 2 H, ^3J = 7.0 Hz, γ-CH$_2$-), 1.77 (quint, 2 H, ^3J = 7.0 Hz, β-CH$_2$-), 3.89 (t, 2 H, ^3J = 7.0 Hz, α-CH$_2$-), 4.92 (bs, 1 H, -OH), 6.99 (s, 1 H, arom.), 7.39 (s, 1 H, arom.) ppm.

^{13}C-NMR (63 MHz, CDCl$_3$, 20 °C): δ = 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) $[M]^{+\cdot}$, 362 (100) $[M-C_6H_{12}]^{+\cdot}$, 235 (5) $[C_6H_4O_2I]^{+\cdot}$.

HRMS $[^{12}C_{12}{}^{1}H_{16}{}^{16}O_{2}{}^{127}I_{2}]^+$ 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) diiosopropyl 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.

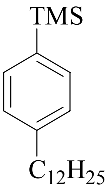
Yield: 1.38 g (40 %) of a yellow waxy solid.

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

^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 0.87 (t, 3 H, ^3J = 7.0 Hz, $-CH_3$), 1.33 (m, 4 H, $-CH_2-$), 1.47 (m, 2 H, γ-CH_2-), 1.77 (quint, 2 H, ^3J = 7.5 Hz, β-CH_2-), 3.30 (s, 3 H, $-OCH_3$), 3.50 (m, 2 H, $-CH_2O-$), 3.62 (m, 60 H, $-CH_2O-$), 3.73 (t, 2 H, ^3J = 5.5 Hz, α-OCH_2-), 3.86 (m, 4 H, α-CH_2-; $-CH_2O-$), 4.05 (t, 2 H, ^3J = 5.5 Hz, α-OCH_2-), 7.11 (s, 1 H, arom.), 7.18 (s, 1 H, arom.) ppm.

^{13}C-NMR (63 MHz, $CDCl_3$, 20 °C): δ = 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) $Pd(PPh_3)_4$ 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 separeted 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.

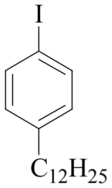
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.30 (s, 9 H, -TMS), 0.89 (t, ^3J = 8.0 Hz, 3 H, $-CH_3$), 1.29 (m, 18 H, $-CH_2-$), 1.63 (quint, ^3J = 8.0 Hz, 2 H, *β*-CH_2-), 2.63 (t, ^3J = 8.0 Hz, 2 H, *α*-CH_2-), 7.17 (d, ^3J = 9.0 Hz, 2 H, arom.), 7.44 (d, ^3J = 9.0 Hz, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 303 (100) $[M-CH_3]^{+\cdot}$.

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 CH_2Cl_2 and cooled to -40 °C. A solution of 15.45 g (93.3 mmol) iodine chloride in 100 ml dry CH_2Cl_2 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 $Na_2S_2O_3$ solution were added and the layers were separated. The aqueous layer was extracted three times with 50 ml CH_2Cl_2. The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution, dried over $MgSO_4$, 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).

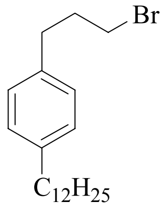
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.90 (t, ^3J = 8.0 Hz, 3 H, $-CH_3$), 1.29 (m, 18 H, $-CH_2-$), 1.59 (quint, ^3J = 8.0 Hz, 2 H, *β*-CH_2-), 2.59 (t, ^3J = 8.0 Hz, 2 H, *α*-CH_2-), 6.93 (d, ^3J = 9.0 Hz, 2 H, arom.), 7.59 (d, ^3J = 9.0 Hz, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 246 (7) $[M-I+H]^{+\cdot}$, 218 (10), 217 (54) $[M-C_{11}H_{23}]^{+\cdot}$.

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-dodecyliodobenzene **97** were dissolved in 13 ml dry THF and cooled to 0 °C. 3 ml (5.9 mmol) of a ^{i}PrMgCl 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 Li_2CuCl_4 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).

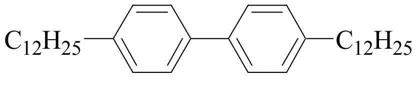
^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.90$ (t, $^3J = 8$ Hz, 3 H, -CH_3), 1.25 (m, 18 H, -CH_2-), 1.60 (quint, $^3J = 8$ Hz, 2 H, β-CH_2-), 2.15 (m, 2 H, β-CH_2-), 2.55 (t, $^3J = 8$ Hz, 2 H, α-CH_2-), 2.75 (t, $^3J = 8$ Hz, 2 H, α-CH_2-), 3.40 (t, $^3J = 8$ Hz, 2 H, -CH_2Br), 7.12 (s, 4 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): $\delta =$ 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) $[M]^{+\cdot}$, 214 (21), 213 (87), 212 (21), 211 (86) $[M-C_{11}H_{23}]^{+\cdot}$, 105 (100), 104 (78) $[C_2H_2Br]^{+\cdot}$.

HRMS $[^{12}C_{21}{}^{1}H_{31}{}^{79}Br_1]^+$ 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 N_2 ventilating for 10 minutes per operation. 350 mg (1 mol %) $Pd(PPh_3)_4$ 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 $MgSO_4$, 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).

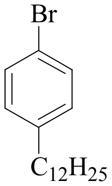
mp.: 75.9 °C

^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.87$ (t, $^3J = 8.0$ Hz, 6 H, $-CH_3$), 1.27 (m, 36 H, $-CH_2-$), 1.64 (quint, $^3J = 8.0$ Hz, 4 H, β-CH_2-), 2.62 (t, $^3J = 8.0$ Hz, 4 H, α-CH_2-), 7.22 (d, $^3J = 9.8$ Hz, 4 H, arom.), 7.48 (d, $^3J = 9.8$ Hz, 4 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 336 (3), 335 (12) $[M-C_{11}H_{23}]^{+\cdot}$, 182 (2), 181 (16), 180 (12) $[M-C_{22}H_{45}]^{+\cdot}$.

1-Bromo-4-dodecylbenzene 100



9.78 g (30.7 mmol) **96** were dissolved in 50 ml dry CH_2Cl_2 and cooled to -78 °C. 1.6 ml (30.7 mmol) bromine in 5 ml dry CH_2Cl_2 were added dropwise. The solution was warmed to rt and stirred for 1 h. 20 ml of a saturated aqueous $Na_2S_2O_3$ solution were added. The layers were separated and the aqueous layer was extracted twice with 30 ml CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered and the solvent evaporated. The crude product was purified by vacuum destillation (147 °C; $3.1 \cdot 10^{-1}$ mbar).

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

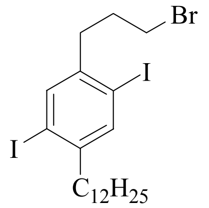
^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.90$ (t, $^3J = 8.0$ Hz, 3 H, $-CH_3$), 1.29 (m, 18 H, $-CH_2-$), 1.60 (quint, $^3J = 8.0$ Hz, 2 H, β-CH_2-), 2.59 (t, $^3J = 8.0$ Hz, 2 H, α-CH_2-), 7.09 (d, $^3J = 10.0$ Hz, 2 H, arom.), 7.42 (d, $^3J = 10.0$ Hz, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 171 (81), 169 (83) $[M\text{-}C_{11}H_{23}]^{+\cdot}$, 91 (78) $[C_7H_7]^{+\cdot}$, 43 (100) $[C_3H_7]^{+\cdot}$.

EA	$C_{18}H_{29}Br$	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 sligtly 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).

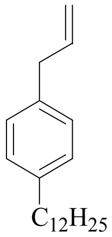
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, ^3J = 8.0 Hz, 3 H, $-CH_3$), 1.24 (m, 18 H, $-CH_2-$), 1.52 (quint, ^3J = 8.0 Hz, 2 H, β-CH_2-), 2.12 (m, 2 H, β-CH_2-), 2.56 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 2.76 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 3.42 (t, ^3J = 8.0 Hz, 2 H, $-CH_2Br$), 7.59 (s, 1 H, arom.), 7.64 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 494 (5), 492 (5) $[M\text{-}I]^{+\cdot}$, 465 (6), 464 (14), 463 (6), 462 (11) $[M\text{-}I\text{-}C_2H_5]^{+\cdot}$.

EA	$C_{21}H_{33}BrI_2$	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 °C (EtOH/liquid nitrogen bath). 52 ml (83.2 mmol) ^{t}BuLi-solution were added slowly. After complete addition the mixture was warmed to 7 °C. The solution was again cooled to -45 °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 ° C

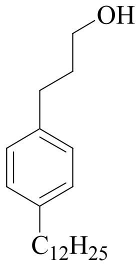
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.90 (t, ^3J = 8.0 Hz, 3 H, CH_3), 1.40 (s, 18 H, $-CH_2-$), 1.60-1.70 (m, 2 H, β-CH_2-), 2.60 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 3.45 (d, ^3J = 8.0 Hz, 2 H, allylic-γ-CH_2-), 5.10 (t, ^3J = 8.0 Hz, 2 H, allylic-α-CH_2-), 5.80-6.05 (m, 1 H, allylic-CH-), 7.15 (s, 4 H) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 248 (1), 247 (6), 246 (30) $[M-C_3H_4]^{+\cdot}$, 131 (100) $[M-C_{11}H_{23}]^{+\cdot}$, 117 (52) $[M-C_{12}H_{25}]^{+\cdot}$.

HRMS $[^{12}C_{21}{}^1H_{34}]^+$ 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 nitrogene. 30 ml 3 N aqueous NaOH and 39 ml H_2O_2 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 $MgSO_4$, 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).

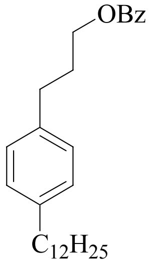
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.85 (t, ^3J = 8.0 Hz, 3 H, -CH_3), 1.30 (m, 18 H, -CH_2-), 1.55 (quint, 2 H, ^3J = 8.0 Hz, β-CH_2-), 1.95 (quint, 2 H, ^3J = 9.0 Hz, β-CH_2-), 2.50 (t, 2 H, ^3J = 9.0 Hz, α-CH_2-), 2.70 (t, ^3J = 9.0 Hz, 2 H, α-CH_2-), 3.65 (t, 2 H, ^3J = 8.0 Hz, -$C\underline{H}_2OH$), 7.05 (s, 4 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 288 (6), 287 (25) $[M-H_2O]^{+\cdot}$, 261 (8) $[M-C_2H_5O]^{+\cdot}$, 149 (25) $[M-C_{11}H_{23}]^{+\cdot}$, 131 (28) $[C_{10}H_{11}]^{+\cdot}$.

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 (22.0mmol) **105** and 5.5 ml (39.6 mmol) dry triethylamine were dissolved in 100 ml dry CH_2Cl_2 and cooled to 0 °C. 3.9 ml (33.0 mmol) benzoyl chloride in 20 ml dry CH_2Cl_2 were added dropwise. The mixture was allowed to warm to rt and stirred for 16 h und nitrogen. After addition of 50 ml aqueous 1 M $NaHCO_3$ 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 $MgSO_4$, 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).

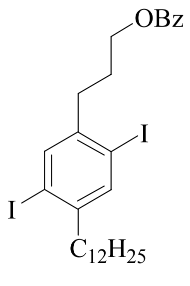
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (t, ^3J = 8.0 Hz, 3H, $-CH_3$), 1.29 (m, 18 H, $-CH_2-$), 1.62 (quint, ^3J = 8.0 Hz, 2 H, β-CH_2-), 2.12 (quint, 2H, ^3J = 8.0 Hz, β-CH_2-), 2.59 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 2.78 (t, ^3J = 8.0 Hz, 2 H, α-CH_2-), 4.36 (t, ^3J = 8 Hz, 2 H, $-C\underline{H_2}OBz$), 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.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 288 (3), 287 (23), 286 (100) $[M-C_7H_6O_2]^{+\cdot}$, 131 (56) $[C_{10}H_{11}]^{+\cdot}$.

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}H NMR ($CDCl_3$, 250 MHz): δ = 0.87 (t, ^3J = 8.0 Hz, 3 H, -CH_3), 1.27 (m, 18 H, -CH_2-), 1.57 (quint, ^3J = 8.0 Hz, 2 H, *β*-CH_2-), 2.06 (quint, 2 H, ^3J = 8.0 Hz, *β*-CH_2-), 2.56 (t, ^3J = 8.0 Hz, 2 H, *α*-CH_2-), 2.77 (t, ^3J = 8.0 Hz, 2 H *α*-CH_2-), 4.41 (t, ^3J = 8.0 Hz, 2 H, -$C\underline{H_2}OBz$), 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.

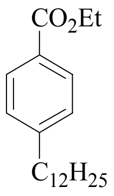
^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.08, 22.66, 29.18, 29.35, 29.53, 29.64, 30.12, 30.33, 31.52, 31.89, 35.54, 36.42, 39.84, 64.08, 64.32, 100.14, 100.42, 128.31, 128.45, 129.53, 129.60, 132.78, 132.86, 138.24, 139.45, 140.60, 143.24, 145.41, 173.51 ppm.

MS (EI, 80 eV, 120°C): m/z (%) = 661 (3), 660 (4), 659 (2) $[M]^{+\cdot}$, 540 (1), 539 (9), 538 (27) $[M\text{-}C_7H_6O_2]^{+\cdot}$, 413 (3), 412 (9), 411 (1) $[M\text{-}C_7H_5O_2\text{-}I]^{+\cdot}$, 384 (1), 383 (6), 382 (7) $[M\text{-}C_7H_7O_2\text{-}C_{11}H_{23}]^{+\cdot}$, 288 (3), 287 (29), 286 (100) $[M\text{-}2I\text{-}C_7H_5O_2\text{+}H]^{+\cdot}$, 258 (1), 257 (8) $[C_{10}H_{10}I]^{+\cdot}$, 131 (65) $[C_{10}H_{11}]^{+\cdot}$.

EA	$C_{28}H_{38}O_2I_2$	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) $Pd(PPh_3)_4$ were added rappidly and the solution was degassed and flushed with N_2 again for three times. Afterwards the mixture was cooked uder reflux for 2 d with vigorous stirring. The mixture was allowed to cool to r.t., the layers were separated, the aquous layer was washed twice with 150 ml toluene, dried over $MgSO_4$, 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).

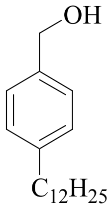
^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.85 (t, ^3J = 8.0 Hz, 3 H, ω-CH_3), 1.28 (m, 18 H, -CH_2-), 1.45 (t, ^3J = 8.0 Hz, 3 H, -$OCH_2C\underline{H}_3$), 1.60 (m, 2 H, *β*-CH_2-), 2.66 (t, ^3J = 8.0 Hz, 2 H, *α*-CH_2), 4.35 (q, ^3J = 8.0 Hz, 2 H, -$OC\underline{H}_2CH_3$), 7.25 (AA´BB´, ^3J = 9.8 Hz, 2 H, arom.), 7.95 ppm (d, ^3J = 9.8 Hz, AA´BB´, 2 H, arom.).

^{13}C NMR ($CDCl_3$, 68 Hz): δ = 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) $[M]^{+\cdot}$, 290 (7), 289(2) $[M-C_2H_4]^{+\cdot}$, 274 (6), 273 (27) $[M-OEt]^{+\cdot}$.

HRMS $[^{12}C_{21}{}^1H_{34}{}^{16}O_2]^{+\cdot}$ calc.: 318.25588 found: 318.25559.

(4-Dodecylphenyl)-methanol 51



To a suspension of 2.5 g (67 mmol) $LiAlH_4$ 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 seperated and the aqueous layer was extracted with ether (3 x 100 ml). The combined organic layers were dried over $MgSO_4$, 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).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.89 (t, ^3J = 7.0 Hz, 3 H, ω-CH_3), 1.28 (m, 18 H, -CH_2-), 1.63 (q, ^3J = 7.8 Hz, 2 H, β-CH_2-), 1.84 (s, 1 H, -OH), 2.61 (t, ^3J = 7.8 Hz, 2 H, α-CH_2-), 4.66 (s, 2 H, -CH_2OH), 7.14 (AA´BB´, 2 H, arom.), 7.25 ppm (AA´BB´, 2 H, arom.).

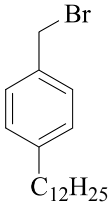
^{13}C NMR ($CDCl_3$, 126 Hz): δ = 14.11, 22.67, 29.29, 29.34, 29.49, 29.58, 29.62, 29.65, 31.54, 31.89, 35.62, 65.17, 127.07, 128.34, 138.01, 142.45 ppm.

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

EA	$C_{19}H_{32}O$	calc.	C 82.55	H 11.67
	(276.46)	found	82.32	11.58

HRMS $[^{12}C_{19}{}^{1}H_{32}{}^{16}O_1]^{+\cdot}$ 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 seperated 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

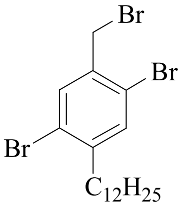
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.92 (t, ^3J = 7.1 Hz , 3 H, -CH_3), 1.27 (m, 18 H, -CH_2-), 1.63 (quint, ^3J = 7.6 Hz, 2 H, β-CH_2-), 2.61 (t, ^3J = 7.6 Hz, 2 H, α-CH_2-), 4.50 (s, 2 H, benzylic-CH_2-), 7.16 (d, ^3J = 8.0 Hz, 2 H, arom.), 7.31 (d, ^3J = 8.0 Hz, 2 H, arom.) ppm.

^{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) $[M]^{+\cdot}$, 261 (2), 260 (14), 259 (37) $[M-Br]^{+\cdot}$, 183 (3) $[M-C_{11}H_{23}]^{+\cdot}$, 105 (100) $[C_8H_9]^{+\cdot}$.

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 CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, 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

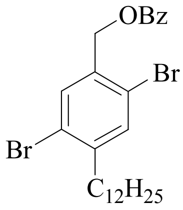
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.87 (t, ^{3}J = 7.1 Hz , 3 H, -CH_3), 1.27 (m, 18 H, -CH_2-), 1.58 (quint, ^{3}J = 7.6 Hz, 2 H, β-CH_2-), 2.66 (t, ^{3}J = 7.6 Hz, 2 H, α-CH_2-), 4.50 (s, 2 H, -CH_2Br), 7.40 (s, 1 H, arom.), 7.59 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 419 (5), 418 (4), 417 (9), 415 (5) $[M-Br]^{+\cdot}$, 266 (5), 265 (50), 264 (19), 263 (100), 262 (24), 261 (52), 260 (10) $[M-Br-C_{11}H_{23}]^{+\cdot}$.

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 CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, 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).

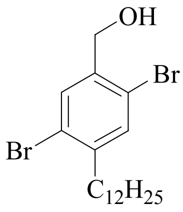
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, ^3J = 7.1 Hz , 3 H, -CH_3), 1.29 (m, 18 H, -CH_2-), 1.61 (quint, ^3J = 7.6 Hz, 2 H, β-CH_2-), 2.73 (t, ^3J = 7.6 Hz, 2 H, α-CH_2-), 5.33 (s, 2 H, -CH_2Br), 7.42 (m, 3 H, arom.), 7.59 (m, 2 H, arom.), 8.06 (d, ^3J = 9.0 Hz, 2 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 459 (73), 458 (19), 457 (67) $[M-Br]^{+\cdot}$, 265 (4), 264 (2), 263 (7), 262 (4) $[C_8H_9Br_2]^{+\cdot}$, 105 (100) $[C_8H_9]^{+\cdot}$.

HRMS $[^{12}C_{26}{}^{1}H_{34}{}^{16}O_2{}^{79}Br_2]^{+\cdot}$ 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).

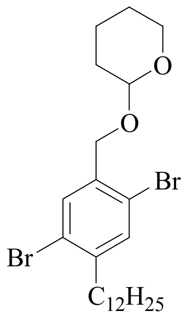
^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.82$ (t, $^3J = 7.1$ Hz , 3 H, $-CH_3$), 1.22 (m, 18 H, $-CH_2-$), 1.50 (quint, $^3J = 7.6$ Hz, 2 H, β-CH_2-), 1.91 (s, 1 H, -OH), 2.62 (t, $^3J = 7.6$ Hz, 2 H, α-CH_2-), 4.62 (s, 2 H, $-CH_2OH$), 7.32 (s, 1 H, arom.), 7.58 (s, 1 H, arom.) ppm.

^{13}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) $[M]^{+\cdot}$, 355 (6), 353 (6) $[M\text{-}Br]^{+\cdot}$, 282 (4), 281 (7), 280 (9), 279 (13), 278 (6), 277 (8) $[M\text{-}C_{11}H_{23}]^{+\cdot}$.

HRMS $[^{12}C_{19}{}^{1}H_{30}{}^{16}O_{1}{}^{79}Br_{2}]^{+\cdot}$ 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-TsOH·H_2O 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.

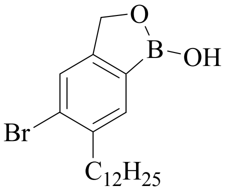
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.87 (t, ^{3}J = 7.6 Hz, 3 H, $-CH_3$), 1.29 (m, 18 H, $-CH_2-$), 1.56 (m, 5 H, $-CH_2-$), 1.74 (m, 1 H), 1.87 (m, 1 H), 2.65 (t, ^{3}J = 7.6 Hz, 2 H, α-CH_2-), 3.56 (m, 1 H), 3.89 (m, 1 H), 4.44 (m, 2 H), 4.75 (m, 2 H), 7.40 (d, ^{3}J = 8.0 Hz, 1 H, arom.), 7.59 (d, ^{3}J = 8.0 Hz, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 474 (6), 473 (5), 472 (10), 470 (5) $[M-C_2H_6O]^{+\cdot}$, 420 (7), 419 (7), 418 (14), 417 (9), 416 (8), 415 (4) $[M-C_5H_8O_2]^{+\cdot}$, 85 (100) $[C_5H_9O]^{+\cdot}$.

EA	$C_{24}H_{38}O_2Br_2$	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 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 over night 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 $MgSO_4$, filtered and the solvent evaporated. The crude product was recrystallized from ether.

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

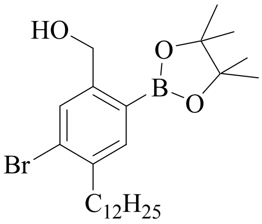
^{1}H NMR (D_6-DMSO, 250 MHz): δ = 0.84 (t, ^{3}J = 7.6 Hz , 3 H, $-CH_3$), 1.23 (m, 18 H, $-CH_2-$), 1.55 (m, 2 H, β-CH_2-), 2.71 (t, ^{3}J = 7.6 Hz, 2 H, α-CH_2-), 4.92 (s, 2 H, $-CH_2O-$), 7.62 (s, 1 H, arom.), 7.65 (s, 1 H, arom.), 9.22 (s, 1 H, -OH) ppm.

^{13}C NMR (D_6-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) $[M]^{+\cdot}$, 357 (1), 356 (1), 355 (1), 354 (3), 353 (1), 352 (1) $[M\text{-}BOH]^{+\cdot}$, 340 (5), 338 (5) $[M\text{-}CH_2BOH]^{+\cdot}$, 85 (100) $[C_5H_9O]^{+\cdot}$.

HRMS $[^{12}C_{19}{}^{1}H_{30}{}^{16}O_{1}{}^{11}B_{1}{}^{79}Br_{1}]^{+\cdot}$ 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 chlorofom and refluxed for 2d in a Dean-Stark apparatus. The solvent was evaporated.

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

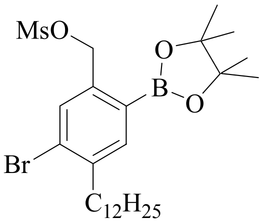
^{1}H NMR (D_6-DMSO, 250 MHz): δ = 0.85 (t, ^3J = 7.6 Hz , 3 H, $-CH_3$), 1.27 (m, 30 H, $-CH_2-$; $-CH_3$), 1.55 (m, 2 H, β-CH_2-), 2.67 (t, ^3J = 7.6 Hz, 2 H, α-CH_2-), 4.60 (s, 2 H, $-CH_2O-$), 7.47 (s, 1 H, arom.), 7.65 (s, 1 H, arom.) ppm.

^{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) $[M]^{+\cdot}$, 465 (9) $[M\text{-}OH]^{+\cdot}$, 425 (12), 424 (15), 423 (16), 422 (15) $[M\text{-}C_3H_6O]^{+\cdot}$, 84 (100) $[C_5H_8O]^{+\cdot}$.

HRMS $[^{12}C_{25}{}^{1}H_{42}{}^{16}O_{3}{}^{11}B_{1}{}^{79}Br_{1}]^{+\cdot}$ 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 5ml (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 $MgSO_4$, 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).

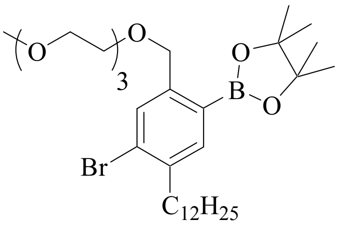
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.85 (t, ^3J = 7.6 Hz , 3 H, -CH_3), 1.27 (m, 30 H, -CH_2-; -CH_3), 1.55 (m, 2 H, β-CH_2-), 2.69 (t, ^3J = 7.6 Hz, 2 H, α-CH_2-), 2.92 (s, 3 H, S-CH_3) 5.43 (s, 2 H, -CH_2O-), 7.56 (s, 1 H, arom.), 7.61 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 503 (18), 502 (68), 501 (31), 500 (61), 499 (15) $[M-C_3H_6O]^{+\cdot}$, 382 (20), 381 (99), 380 (44), 379 (100), 378 (26) $[M-SO_3CH_3-C_6H_{12}]^{+\cdot}$.

HRMS $[^{12}C_{26}{}^{1}H_{44}{}^{16}O_{5}{}^{11}B_{1}{}^{79}Br_{1}{}^{32}S_{1}]^{+\cdot}$ 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 $MgSO_4$, filtered and the solvent evaporated. The orange oil was purified by flash column chromatography (silica gel; $MeCl_2$/MeOH 3 %).

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

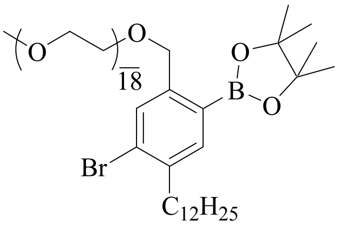
r_f = 0.11 (silica gel; hexane/ethyl acetate 4:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.87 (t, ^3J = 7.6 Hz, 3 H, $-CH_3$), 1.27 (m, 30 H, $-CH_2-$; $-CH_3$), 1.58 (quint, ^3J = 7.6 Hz, 2 H, β-CH_2-), 2.68 (t, ^3J = 7.6 Hz, 2 H, α-CH_2-), 3.33 (s, 3 H, $-CH_3$), 3.59 (m, 12 H, $-CH_2O-$), 4.71 (s, 2 H, α-CH_2O-), 7.56 (s, 1 H, arom.), 7.62 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 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	$C_{32}H_{56}O_6BBr$	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; $MeCl_2$/MeCN 5 %).

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

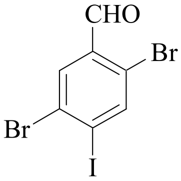
r_f = 0.15 (silica gel; ether/acetone 7:3).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.87 (t, ^3J = 7.6 Hz, 3 H, $-CH_3$), 1.27 (m, 30 H, $-CH_2-$; $-CH_3$), 1.52 (quint, ^3J = 7.6 Hz, 2 H, β-CH_2-), 2.62 (t, ^3J = 7.6 Hz, 2 H, α-CH_2-), 3.31 (s, 3 H, $-CH_3$), 3.59 (m, ~72 H, $-CH_2O-$), 4.68 (s, 2 H, α-CH_2O-), 7.52 (s, 1 H, arom.), 7.58 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 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	$C_{61}H_{114}O_{21.5}BrB$	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 °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 saparated and the aqueous layer was extractes 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 °C.

Yield: 458 mg (57 %).

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

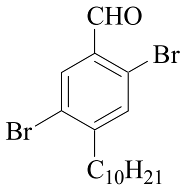
^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 8.02 (1 H, s, arom.), 8.14 (1 H, s, arom.), 10.16 (1 H, s, -CHO) ppm.

^{13}C-NMR (63 MHz, $CDCl_3$, 20 °C): δ = 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) $[M]^{+\cdot}$, 362 (6) $[M-CO]^{+\cdot}$, 310 (5) $[M-Br]^{+\cdot}$, 280 (5) $[M-Br-CH_2O]^{+\cdot}$, 263 (4) $[M-I]^{+\cdot}$, 234 (11) $[M-CHO-I]^{+\cdot}$, 155 (35) $[M-CO-I-Br]^{+\cdot}$, 127 (33) $[I]^{+\cdot}$, 74 (100) $[M-I]^{+\cdot}$.

EA	$C_7H_3O_1Br_2I_1$	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 N_2 ventilating for 10 minutes per operation. 268 mg (2 mol %) $Pd(PPh_3)_4$ 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 $MgSO_4$, filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate 4:1).

Yield: 630 mg (13 %).

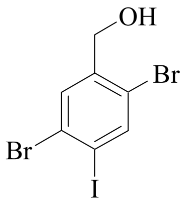
$r_f = 0.54$ (silica gel; hexane/ethyl acetate 10:1).

^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): $\delta = 0.83$ (t, 3 H, $^3J = 6$ Hz, $-CH_3$), 1.26 (m, 14 H, $-CH_2-$), 1.56 (m, 2 H, β-CH_2-), 2.70 (t, $^3J = 9$ Hz, 2 H, α-CH_2-), 7.45 (s, 2 H, arom.), 8.00 (s, 1 H, arom.), 10.81 (s, 1 H, -CHO) ppm.

^{13}C-NMR (62.9 MHz, $CDCl_3$, 20 °C): δ = 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) $[M]^{+\cdot}$), 325 (13) $[M-^{79}Br]^{+\cdot}$, 323 (13) $[M-^{81}Br]^{+\cdot}$, 249 (58) $[M-CO, -C_9H_{19}]^{+\cdot}$, 197 (37) $[M-Br, -C_9H_{19}]^{+\cdot}$, 169 (48) $[-CO, -Br, -C_9H_{19}]^{+\cdot}$, 128 (34) $[C_9H_{20}]^{+\cdot}$, 115 (44) $[M-2Br,-C_9H_{19}]^{+\cdot}$, 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 $NaBH_4$ were added. The solution was stirred over nigth 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 $MgSO_4$, 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).

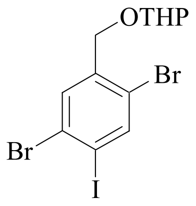
^{1}H-NMR (250 MHz, D_6-DMSO, $CDCl_3$, 20 °C): $\delta = 4.42$ (d, $^3J = 10.0$ Hz, $-CH_2-$), 5.51 (t, $^3J = 10.0$ Hz, -OH), 7.72 (s, 1 H, arom.), 7.92 (s, 1 H, arom.) ppm.

^{13}C-NMR (63 MHz, D_6-DMSO, $CDCl_3$, 20 °C): $\delta = 61.66$, 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) $[M]^{+\cdot}$, 314 (4), 313 (42), 312 (7), 311 (46) $[M-Br]^{+\cdot}$, 159 (3), 158 (43), 157 (11), 156 (53), 155 (13), 154 (8), 153 (6) $[M-Br-I-CH_2O]^{+\cdot}$.

EA	$C_7H_5O_1Br_2I_1$	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) $TsOH\cdot H_2O$ were dissolved in 50 ml CH_2Cl_2. 3.0 ml (33.0 mmol) dihydropyrane were added dropwise. The mixture was stirred for 12 h at rt and poured into an aqueous $NaHCO_3$ solution. The layers were separated and the aqueous layer was extracted twice with 50 ml CH_2Cl_2. 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/ethyl acetate 10:1).

Yield: 1.26 g (40 %).

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

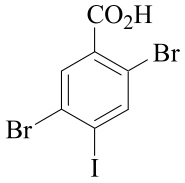
^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 1.70 (m, 6 H, $-CH_2-$), 3.56 (m, 1 H, THP), 3.87 (m, 1 H, THP), 4.43 (d, ^3J = 12.0 Hz, 1 H, α-CH_2-), 4.71 (d, ^3J = 12.0 Hz, 1 H, α-CH_2-), 4.74 (m, 1 H, THP), 7.22 (s, 1 H, arom.), 7.97 (s, 1 H, arom.) ppm.

^{13}C-NMR (63 MHz, $CDCl_3$, 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) $[M]^{+\cdot}$, 430 (13) $[M-C_2H_6O]^{+\cdot}$, 397 (10) $[M-Br]^{+\cdot}$, 378 (7), 377 (49), 376 (17), 375 (100), 374 (9), 373 (50) $[M-C_6H_{13}O]^{+\cdot}$.

EA	$C_{12}H_{13}O_2Br_2I_1$	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 ^{i}PrMgCl solution in ether were added dropwise and stirred for 5 minutes at -12 °C. CO_2 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).

^{1}H-NMR (250 MHz, CD_3OD, $CDCl_3$, 20 °C): δ = 7.98 (s, 1 H, arom.), 8.04 (s, 1 H, arom.) ppm.

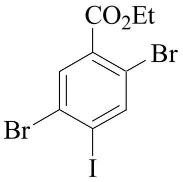
^{13}C-NMR (63 MHz, CD_3OD, 20 °C): δ = 106.57, 121.10, 129.83, 135.19, 145.94, 165.95 ppm.

MS (EI, 80 eV, 130 °C): m/z (%) = 409 (16), 408 (51), 407 (32), 406 (100), 405 (17), 404 (51) $[M]^{+\cdot}$, 391 (19), 389 (37), 387 (19) $[M-OH]^{+\cdot}$, 361 (7) $[M-CO_2H]^{+\cdot}$.

EA	$C_7H_3O_2Br_2I_1$	calc.	C 20.72	H 0.75
	(405.812)	found	20.56	0.70

HRMS	$[^{12}C_7{}^1H_3{}^{16}O_2{}^{127}J_1{}^{81}Br_1{}^{79}Br_1]^+$	calc.: 405.75241	found: 405.75460
	$[^{12}C_7{}^1H_3{}^{16}O_2{}^{127}J_1{}^{79}Br_2]^+$	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).

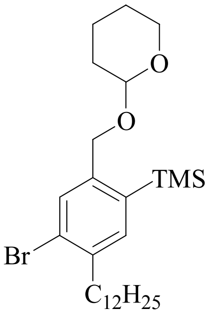
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.40 (t, $^3J = 8.0$ Hz, 3 H, $-CH_3$), 4.37 (q, $^3J = 8.0$ Hz, 2 H, $-CH_2-$), 7.92 (s, 1 H, arom.), 8.15 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 408 (18), 407 (4), 406 (37), 404 (20) $[M-C_2H_4]^{+\cdot}$, 392 (6), 391 (50), 390 (14), 389 (100), 388 (11), 387 (52) $[M-C_2H_5O]^{+\cdot}$.

HRMS $[^{12}C_9{}^1H_7{}^{16}O_2{}^{127}J_1{}^{79}Br_2]^+$ 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}BuLi solution in hexane were added dropwise. The mixture was allowed to warm up to 0 °C and freezed 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 $MgSO_4$, filtered and the solvent evaporated.

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

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.32 (s, 9 H, -Si(CH_3)$_3$), 0.89 (t, ^3J = 7.1 Hz , 3 H, -CH_3), 1.29 (m, 18 H, -CH_2-), 1.69 (m, 8 H, -CH_2-), 2.69 (t, ^3J = 7.6 Hz, 2 H, α-CH_2-), 3.55 (m, 1 H, -OC$\underline{H}_2$-), 3.92 (m, 1 H, -OC$\underline{H}_2$-), 4.51 (d, ^3J = 12.0 Hz, 1 H, α-CH_2O), 4.70 (m, 1 H, -OC$\underline{H}$O), 4.79 (d, ^3J = 12.0 Hz, 1 H, α-CH_2O), 7.29 (s, 1 H, arom.), 7.63 (s, 1 H, arom.) ppm.

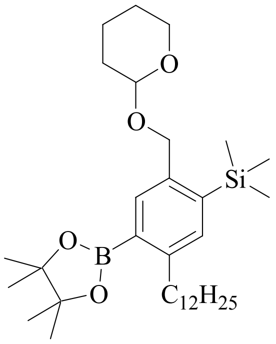
^{13}C NMR ($CDCl_3$, 63 MHz): δ = 0.32, 14.09, 19.37, 22.68, 25.47, 29.34, 29.43, 29.65, 30.06, 30.58, 31.92, 35.93, 62.15, 67.90, 97.97, 125.95, 132.43, 136.28, 137.37, 140.27, 142.96 ppm.

MS EI (80 eV, 3 kV, 150 °C): m/z (%) = 512 (0.04), 510 (0.04) $[M]^{+\cdot}$, 413 (2), 412 (6), 411 (3), 410 (6), 409 (1) $[M-C_5H_8O_2]^{+\cdot}$, 259 (3), 258 (2), 257 (8), 256 (2), 255 (6), 254 (1) $[M-Br-TMS-C_5H_9O_2]^{+\cdot}$, 85 (100) $[C_5H_9O]^{+\cdot}$.

HRMS $[^{12}C_{27}{}^{1}H_{47}{}^{16}O_2{}^{28}Si_1{}^{79}Br_1]^{+\cdot}$

$[M-CH_3]^{+\cdot}$ calc.: 495.22941 found: 495.22996.

2-[4-Dodecyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-2-trimethylsilanyl-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)·CH_2Cl_2 was added rapidly and the mixture was degassed again 3 times. The reaction mixture was heated to 80 °C fo 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}H NMR ($CDCl_3$, 250 MHz): δ = 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.

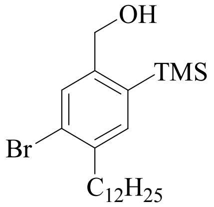
^{13}C NMR ($CDCl_3$, 63 MHz): δ = 0.21, 14.00, 19.46, 22.58, 24.74, 25.49, 26.29, 28.50, 29.27, 29.51, 29.57, 29.62, 29.74, 30.61, 31.84, 33.58, 35.76, 62.11, 69.09, 83.13, 97.88, 129.34, 135.52, 136.67, 139.46, 141.92, 148.28 ppm.

MS EI(80 eV, 3 kV, 130 °C): m/z (%) = 558 (1) $[M]^{+\cdot}$, 543 (1) $[M\text{-}CH_3]^{+\cdot}$, 473 (1) $[M\text{-}C_6H_{13}]^{+\cdot}$, 458 (20) $[M\text{-}C_5H_8O_2]^{+\cdot}$, 85 (100) $[C_6H_{13}]$.

HRMS $[C_{32}H_{56}O_4{}^{11}B\,{}^{28}Si]^+$

$[M\text{-}CH_3]^+$ calc.: 543.40409 found: 543.40467.

(5-Bromo-4-dodecyl-2-trimethylsilanylphenyl)-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.

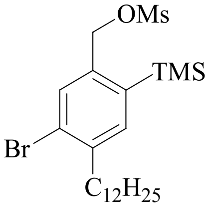
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.30 (s, 9 H, -$Si(CH_3)_3$), 0.83 (t, ^3J = 7.1 Hz , 3 H, -CH_3), 1.27 (m, 18 H, -CH_2-), 1.58 (quint, ^3J = 7.6 Hz, 2 H, *β*-CH_2-), 1.86 (s, 1 H, -OH), 2.68 (t, ^3J = 7.6 Hz, 2 H, *α*-CH_2-), 4.68 (s, 2 H, -$C\underline{H_2}OH$), 7.27 (s, 1 H, arom.), 7.61 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 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) $[M]^{+\cdot}$, 411 (1) $[M\text{-}OH]^{+\cdot}$, 337 (3), 336 (1), 335 (3) $[M\text{-}OH\text{-}TMS]^{+\cdot}$, 260 (2), 259 (15), 258 (3), 257 (15) $[M\text{-}C_{12}H_{25}]^{+\cdot}$, 75 (100) $[C_2H_7OSi]^{+\cdot}$,

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 $MgSO_4$, 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.

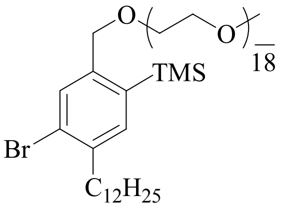
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.43 (s, 9 H, -TMS), 0.87 (t, ^3J = 7.1 Hz , 3 H, -CH_3), 1.27 (m, 18 H, -CH_2-), 1.58 (quint, ^3J = 7.6 Hz, 2 H, β-CH_2-), 2.70 (t, ^3J = 7.6 Hz, 2 H, α-CH_2-), 2.97 (s, 3 H, -OMs), 5.23 (s, 2 H, -C$\underline{H_2}$OMs), 7.36 (s, 1 H, arom.), 7.58 (s, 1 H, arom.) ppm.

^{13}C NMR ($CDCl_3$, 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) $[M]^{+\cdot}$, 491 (1) $[M-CH_3]^{+\cdot}$, 255 (2) $[C_{11}H_{15}BrSi]^{+\cdot}$, 153 (100) $[C_{11}H_{21}]^{+\cdot}$.

HRMS $[^{12}C_{23}{}^{1}H_{41}{}^{16}O_3{}^{79}Br^{28}Si^{32}S]^{+\cdot}$ 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; $MeCl_2$/MeOH 3 %).

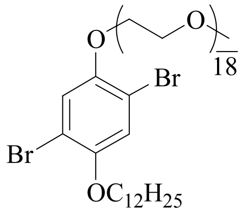
Yield: 9.60 g (83 %) of a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.23 (s, 9 H, -TMS), 0.87 (t, ^3J =7.1 Hz ,3 H, $-CH_3$), 1.27 (m, 18 H, $-CH_2-$), 1.59 (quint, ^3J = 7.6 Hz, 2 H, β-CH_2-), 2.66 (t, ^3J = 7.6 Hz, 2 H, α-CH_2-), 3.31 (s, 3 H, $-OCH_3$), 3.48 (t, ^3J = 8.0 Hz, 2 H, $-C\underline{H}_2OCH_3$), 3.58 (m, 64 H, $-CH_2O-$), 4.49 (s, 2 H, α-CH_2O-), 7.26 (s, 1 H, arom.), 7.53 (s, 1 H, arom.) ppm.

^{13}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) diiosopropyl 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; CH_2Cl_2/CH_3OH 2 %).

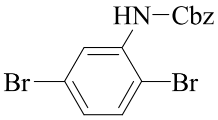
Yield: 15.17 g (60 %) of a colorless waxy solid.

r_f = 0.25 (silica gel; CH_2Cl_2/CH_3OH 2 %).

^{1}H-NMR (500 MHz, $CDCl_3$, 20 °C): δ = 0.87 (t, 3 H, ^3J = 7.0 Hz, $-CH_3$), 1.33 (m, 4 H, $-CH_2-$), 1.47 (m, 2 H, γ-CH_2-), 1.77 (quint, 2 H, ^3J = 7.5 Hz, β-CH_2-), 3.30 (s, 3 H, $-OCH_3$), 3.50 (m, 2 H, $-CH_2O-$), 3.62 (m, 60 H, $-CH_2O-$), 3.73 (t, 2 H, ^3J = 5.5 Hz, α-OCH_2-), 3.87 (m, 4 H, α-CH_2-; $-CH_2O-$), 4.07 (t, 2 H, ^3J = 5.5 Hz, α-OCH_2-), 7.01 (s, 1 H, arom.), 7.11 (s, 1 H, arom.) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$, 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 $MgSO_4$, 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).

^{1}H-NMR (500 MHz, $CDCl_3$, 20 °C): δ = 5.23 (2 H, s, benz.-CH_2-), 7.05 (d, 1 H, ^3J = 9.0 Hz, $-CH_2-$), 7.20 (s, 1 H, arom.), 7.51 (m, 6 H), 8.40 (s, 1 H, arom.), ppm.

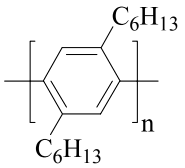
^{13}C-NMR (126 MHz, $CDCl_3$, 20 °C): δ = 67.58, 110.75, 122.11, 122.77, 127.16, 133.17, 135.50, 136.86, 152.69 ppm.

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

EA	$[C_{14}H_{11}Br_2NO_2]$	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 Na_2CO_3 solution were added. The mixture was freeze degassed three times and 9.0 mg (0.7 mol %) $Pd(PPh_3)_4$ 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 $MgSO_4$, filtered and the solvent evaporated. 60 w. t. % of PPP **142** were not soluble in refluxing toluene.

Yield: 123 mg (97 %).

^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 0.75 (m, 6 H, $-CH_3$), 1.19 (m, 12 H, $-CH_2-$), 1.46 (m, 2 H, β-CH_2-), 2.39 (m, 2 H, α-CH_2-), 7.19 (m, 2 H, arom.) ppm.

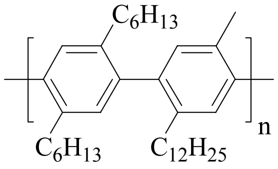
^{13}C-NMR (63 MHz, $CDCl_3$, 20 °C): δ = 14.03, 22.56, 28.70, 29.28, 31.15, 31.72, 32.87, 33.92, 127.92, 128.42, 129.43, 130.27, 132.02, 132.18, 133.58, 133.89, 137.43 ppm.

[$C_{18}H_{28}$]	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 Na_2CO_3 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 %) $Pd(PPh_3)_4$ 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 $MgSO_4$, filtered and the solvent evaporated. The product was purified by a twofold precipitation from acetone.

Yield: 423 mg of a colorless solid.

^{1}H-NMR (500 MHz, $CDCl_3$, 20 °C): δ = 0.82 (m, 9 H, $-CH_3$), 1.21 (m, 30 H, $-CH_2-$), 1.47 (m, 6 H, β-CH_2-), 2.12 (m, 3 H, α-CH_3), 2.41 (m, 6 H, α-CH_2-), 7.13 (m, 4 H, arom.) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$, 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

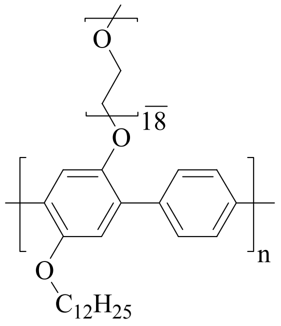
GPC

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 $NaHCO_3$ solution were added. The two layer system was degassed three times by evacuating and ventilating with argon each 10 minutes. The apparatus was oppened 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 $MgSO_4$, 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: 8.24 g light violet solid.

^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 0.85 (m, 3 H, $-CH_3$), 1.23 (m, 4 H, $-CH_2-$), 1.40 (m, 2 H, γ-CH_2-), 1.74 (m, 2 H, β-CH_2-), 3.35 (m, 3 H, $-OCH_3$), 3.52 (m, 2 H, $-CH_2O-$), 3.62 (m, 60 H, $-CH_2O-$), 3.79 (m, 2 H, α-OCH_2-), 3.98 (m, 4 H, α-CH_2-; $-CH_2O-$), 4.14 (m, 2 H, α-OCH_2-), 7.07 (m, 1 H, arom.), 7.11 (m, 1 H, arom.), 7.18 (m, 1 H, arom.) ppm.

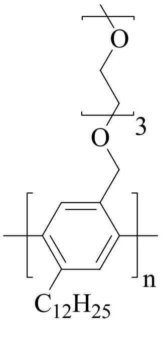
^{13}C-NMR (63 MHz, $CDCl_3$, 20 °C): δ = 14.04, 22.63, 29.35, 29.67, 31.88, 32.98, 58.92, 69.79, 70.48, 71.86, 128.99, 129.19, 130.58, 131.95, 138.90, 139.68 ppm.

[$C_{60}H_{104}O_{19.5}$]	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 $NaHCO_3$ solution were added. The mixture was freeze degassed three times and 5 mg (1.4 mol %) $Pd(PPh_3)_4$ were added. The freeze-degassing was repeated and the mixture was refluxed for 2 d. The crude mixture was extracted with CH_2Cl_2 three times. The combined organic layers were dried over $MgSO_4$, filtered and the solvent evaporated.

Yield: 123 mg (97 %).

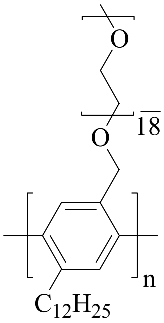
^{1}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 0.77 (m, 3 H, $-CH_3$), 1.12 (m, 18 H, $-CH_2-$), 1.40 (m, 2 H, β-CH_2-), 2.34 (m, 2 H, α-CH_2-), 3.27 (s, 3 H, $-OCH_3$), 3.50 (m, 12 H, $-OCH_2-$), 4.25 (s, 2 H, α-CH_2O-), 7.09 (s, 1 H, arom.), 7.30 (s, 1 H, arom.) ppm.

^{13}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 oppened under an argon stream and 25 mg (0.8 mol %) $Pd[P(p\text{-}tol)_3]_3$ 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 $MgSO_4$, filtert 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}H-NMR (250 MHz, $CDCl_3$, 20 °C): δ = 0.83 (m, 3 H, $-CH_3$), 1.20 (m, 18 H, $-CH_2-$), 1.42 (m, 2 H, β-CH_2-), 2.40 (m, 2 H, α-CH_2-), 3.33 (s, 3 H, $-OCH_3$), 3.59 (m, 72 H, $-OCH_2-$), 4.33 (s, 2 H, α-CH_2O-), 7.12 (s, 1 H, arom.), 7.37 (s, 1 H, arom.) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$, 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).