Supporting Information

Influence of Position Isomerism on the Chiral Properties in Sequence-Defined Conjugated Macromolecules

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Content

1 General methods

1.1 Materials

All reagents were purchased either from Acros Organics, BLDpharm, Fluorochem, Sigma-Aldrich, TCI or Thermo Scientific and used without further purification. Dry solvents were bought from Sigma-Aldrich. Solvents for reactions and purifications were bought from Fisher Scientific or Chem-Lab.

1.2 Instrumentation

NMR

High-field nuclear magnetic resonance (NMR) spectra are recorded on a Bruker Avance III HD 400 spectrometer with a Bruker AscendTM 400 magnet system (^{1}H basic frequency of 400.17 MHz) and a 5 mm PABBO BB/19F-1H/D probe with z-gradients and on a Bruker Avance II+ 600 spectrometer with a Bruker 600 UltraShieldTM magnet system (^{1}H basic frequency of 600.13 MHz) and a 5 mm PABBO BB-1H/D probe with z-gradients. ^{13}C-detected experiments are ^{1}H-decoupled using power-gated decoupling. All samples are dissolved in deuterated chloroform ($CDCl_3$), deuterated dichloromethane (CD_2Cl_2). Data are recorded at room temperature using Bruker TopSpin 3.6.x (Bruker Avance III HD 400 and Bruker Avance II+ 600 spectrometers) and processed and analyzed using Bruker TopSpin 4.2.x. ^{1}H data are calibrated using tetramethylsilane (TMS) as an internal calibration reference while ^{13}C data are calibrated using the deuterated solvents as internal calibration reference (for $CDCl_3$ a 1:1:1 triplet at 77.16 ppm and for CD_2Cl_2 a 1:2:3:2:1 quintet at 53.42 ppm). The δ-values are expressed in parts per million (ppm). The following acronyms are used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), brd (broadened). The prefix app. can denote the apparent multiplicity of a signal or the theoretically expected multiplicity based on the molecular structure of the compound.

Size Exclusion Chromatography

Size exclusion chromatography (SEC) measurements for determining the purity of the developed oligomer and the molar mass properties of the structures is carried out on a Shimadzu LC20 apparatus (PLgel 3 µm MIXED-E column, LC-20AT pump, CBM-20A controller, SPD-20A and RID-20A detectors) using tetrahydrofuran (THF) as the eluent. The SEC apparatus is calibrated towards a series of polystyrene standards (Polymer Laboratories) in THF. Before the measurements, all samples are fully dissolved/diluted in THF (concentration ≈ 1 mg/mL) and filtered (pore size 0.2 µm).

The preparative SEC is performed on a Shimadzu LC20 apparatus, equipped with two PLgel 10 µm 50Å (300 x 25 mm) columns placed in series. The same pump, controller and detectors are used as in the regular SEC measurements. Samples are dissolved in 1 mL of eluent (THF) and filtered (pore size 0.2 µm). The preparative SEC does not require any calibration.

UV-vis spectrometer

The absorbance of the synthesized oligomers are determined using a Agilent Cary 60 UV-Vis spectrometer. The spectra are recorded within the wavelength range of 250 nm to 800 nm, with a resolution of 0.5 nm and a scanning speed of 600 nm/min, a data interval of 1 nm and an ave. time of 0.1 second. To compensate for the signal originating from the cuvette and solvent, a blank measurement is conducted. The samples For UV-vis and fluorescence spectroscopy are conducted in quartz cuvettes 10x10 mm, while the measurements prior to CD analysis are performed with 2x10 mm quartz cuvettes. The concentrations of the oligomers in 10x10 mm quartz cuvettes were in the order of 10^{-6} M and 10^{-5} M in the 2x10 mm quartz cuvettes prior the CD measurements.

Fluoresce spectrometer

The fluorescence of the synthesized oligomers is measured using an Edinburgh FLS980 spectrofluorometer. The spectrum is recorded within the wavelength range of 350 nm to 800 nm, with a specified interval of 1 nm and a dwell time of 0.2. The excitation wavelength for the nonamers is set at 380 nm with slit openings as of 1.8. The excitation wavelength for the **SM$_{//}$OM$_{//}$(*S*)** tetramer is set at 370 nm with slit openings as of 1.8.

Circular Dichroism spectrometer

CD spectra are acquired at room temperature using a JASCO J-1500 Spectrometer to measure the ellipticity of the dissolved and aggregation induced oligomer samples. The apparatus is configured with settings spanning a wavelength range of 250 nm to 600 nm, utilizing an interval of 0.1 nm and a scanning speed of 100 nm/min. To account for the signals originating from the solvent and the cuvette, a blank measurement is taken prior to each scan. Measurements are conducted in 2x10 mm quartz cuvettes and in 10x10 quartz cuvettes in the concentration tests.

Aggregation is induced by the addition of a nonsolvent to a solution of the oligomer in a good solvent. The addition of the nonsolvent is been done at a rate of 100 µL/min for the 2x10mm cuvettes and at a rate of 0.5 mL/min for the 10x10 cuvettes with a automated syringe pump and the solution is stirred at 400 RPM. After the addition, the sample is transferred to a quartz vial and measured on the UV-vis spectrometer and CD spectrometer as soon as possible.

Chromatography

Thin layer chromatography (TLC) plates used to monitor reactions consisted of 0.2 mm thick pre-coated silica gel 60 with fluorescent indicator UV_{254} on aluminium bought from Machery-Nagel. The UV lamp used to analyze the TLC is a CAMAG UV Lamp 4 able to illuminate UV 254 nm and UV 366 nm, each with 8W. Silica used for column chromatography or filtrations through a plug of silica were 0.060-0.200 mm in size with 60 Å pores, purchased from Thermo Scientific.

2 Synthesis

2.1 Monomer synthesis[1]

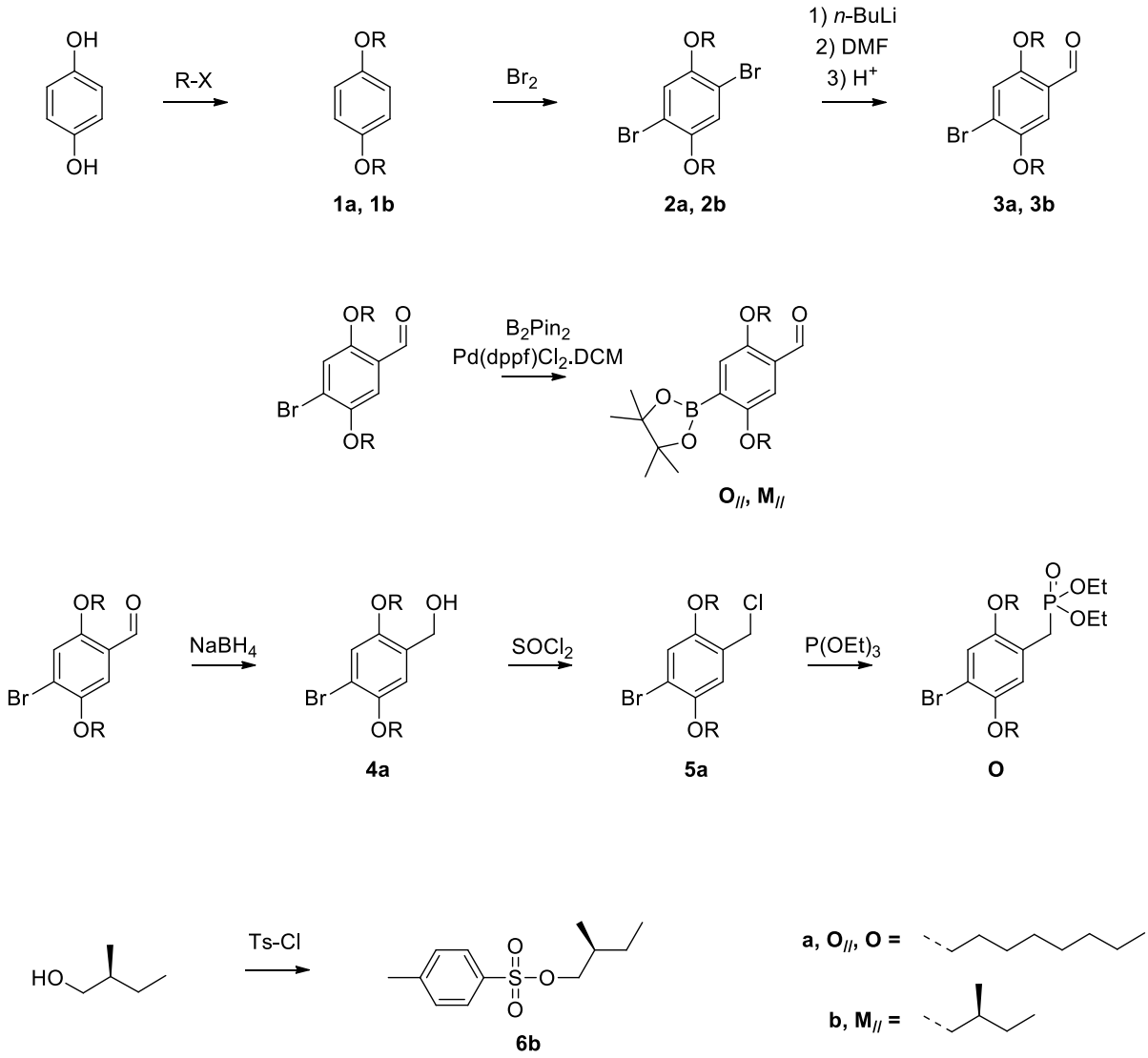
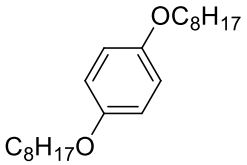


Figure S1. Overview of the monomer synthesis

1,4-di(octyloxy)benzene (1a)



Synthesis is performed as described in literature. In a multi-neck flask, hydroquinone (150 mmol, 16.5 g) is dissolved in degassed ethanol (500 ml) under an inert atmosphere. Next, K_2CO_3 (600 mmol, 82.9 g) and KI (4.50 mmol, 744 mg) are added and the mixture is refluxed for 30 minutes. 1-Bromooctane (330 mmol, 63.7 g) is added dropwise to the mixture via an addition funnel and the reaction is stirred overnight at reflux temperature. The warm reaction mixture is filtered and the remaining salts are washed with ethyl acetate (EA). The filtrate is cooled to recrystallize the product and filtered with a Büchner filter to obtain the pure product as white flakes. NMR data matches with literature.

Quantity: 39.3 g

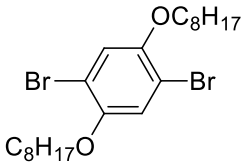
Yield: 79%

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ6.81 (s, 4H), 3.89 (t, J = 6.61 Hz, 4H), 1.74 (m, 4H), 1.44 (m, 4H), 1.29 (m, 16H), 0.88 (t, J = 6.86 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ153.20, 115.40, 68.68, 31.83, 29.41, 29.39, 29.26, 26.07, 22.67, 14.11

1,4-dibromo-2,5-di(octyloxy)benzene (2a)



Synthesis is performed as described in literature. In a multi-neck flask, 1,4-di(octyloxy)benzene (**1a**) (118 mmol, 39.3 g) is dissolved in DCM (200 mL) under an inert atmosphere and cooled to 0 °C. Bromine (235 mmol, 37.6 g) is added dropwise to the solution via an addition funnel and stirred for two hours. The reaction mixture is quenched with a saturated $NaHSO_3$ solution and extracted with DCM. The organic phase is consecutively washed with a saturated $NaHSO_3$ solution, a

saturated $NaHCO_3$ solution, and a saturated NaCl solution and dried over $MgSO_4$. After filtration, the solvent is removed under reduced pressure to obtain the crude product which is purified by recrystallization from cold ethanol. The product is filtered using a Büchner filter to obtain the pure product as white crystals with a faint yellow shade.

Quantity: 50.2 g

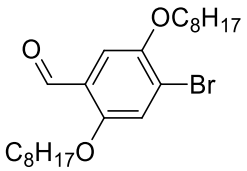
Yield: 87 %

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.08 (s, 2H), 3.94 (t, J = 6.58 Hz, 4H), 1.79 (m, 4H), 1.48 (m, 4H), 1.23-1.40 (m, 16H), 0.88 (t, J = 6.87 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ150.09, 118.49, 111.14, 70.33, 31.80, 29.26, 29.21, 29.12, 25.94, 22.66, 14.11

4-bromo-2,5-di(octyloxy)benzaldehyde (3a)



Synthesis is performed as described in literature. In an oven dried multi-neck flask, 1,4-dibromo-2,5-di(octyloxy)benzene (**2a**) (102 mmol, 50.1 g) is dissolved in dry diethyl ether (Et_2O) (500 ml) under an inert atmosphere and cooled to 0 °C. *n*-BuLi (2.5 M in hexane) (103 mmol, 41.3 mL) is added dropwise the solution via a syringe and stirred for one hour. Next, dry DMF (135 mmol, 10.5 mL) is added at room temperature and stirred for one additional hour. The reaction is quenched by the addition of a 1 M solution of HCl and extracted with Et_2O. The combined organic phase is consecutively washed with a saturated $NaHCO_3$ solution, and a saturated NaCl solution and dried over $MgSO_4$. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified by column chromatography (SiO_2, *n*-heptane (Hep)/DCM 5.5/2.5). The pure product is obtained as a yellow solid.

Quantity: 32.4 g

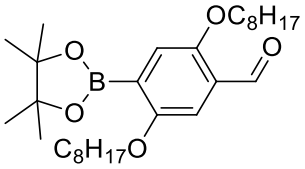
Yield: 72 %

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ10.41 (s, 1H), 7.31 (s, 1H), 7.22 (s, 1H), 4.02 (t, J = 6.51 Hz, 2H), 4.00 (t, J = 6.51 Hz, 2H), 1.81 (m, 4H), 1.46 (m, 4H), 1.31 (m, 16H), 0.86 (m, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ188.99, 155.80, 149.88, 124.30, 120.99, 118.50, 110.66, 77.33, 77.02, 76.70, 69.88, 69.50, 31.80, 31.78, 29.27, 29.22, 29.20, 29.08, 29.03, 26.01, 25.95, 22.66, 22.65, 14.11, 14.09

2,5-di(octyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde ($O_{//}$)



Synthesis is performed as described in literature. In an oven dried flask, 4-bromo-2,5-di(octyloxy)benzaldehyde (**3a**) (11.7 mmol, 5.18 g), potassium acetate (35.2 mmol, 3.46 g), Pd(dppf)Cl_2.DCM (0.23 mmol, 192 mg) and bis(pinacolato)diboron (B_2Pin_2) (12.9 mmol, 3.28 g) are dissolved in dry 1,4-dioxane (50 ml) under an inert atmosphere. The reaction mixture is stirred overnight at reflux temperature. Next, Et_2O is added and the organic phase is washed with brine and dried over $MgSO_4$. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified by crystallization from cold MeOH. The pure product is obtained as a brown solid with a yellow shade.

Quantity: 5.62g

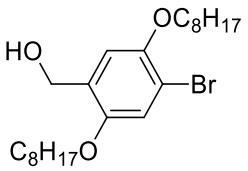
Yield: 98 %

NMR data obtained are consistent with literature values.

^{1}H NMR (600 MHz, $CDCl_3$): δ10.48 (s, 1H), 7.24 (s, 1H), 7.20 (s, 1H), 4.08 (t, J = 6.45 Hz, 2H), 3.95 (t, J = 6.31 Hz, 2H), 1.78 (m, 4H), 1.48 (m, 4H), 1.36 (s, 12H), 1.24-1.38 (m, 16H), 0.89 (t, J = 6.87 Hz, 3H), 0.88 (t, J = 6.76Hz, 3H)

^{13}C NMR (150 MHz, $CDCl_3$): δ190.14, 157.27, 155.61, 126.80, 120.33, 109.25, 84.01, 69.24, 69.02, 31.87, 31.80, 29.44, 29.36, 29.33, 29.30, 29.23, 26.09, 26.03, 24.86, 22.69, 22.66, 14.10

4-bromo-2,5-di(octyloxy)benzyl alcohol (4a)



Synthesis is performed as described in literature. In an oven dried multi-neck flask, $NaBH_4$ (60.0 mmol, 2.26 g) is dissolved in a mixture of dry ethanol (5 ml) and diethyl ether (10 ml) under inert an atmosphere and cooled to 0 °C. Next, 4-bromo-2,5- di(octyloxy)benzaldehyde (**3a**) (30.0 mmol, 13.2 g) is dissolved in diethyl ether (200 ml) and added dropwise to the mixture via an addition funnel. The reaction is monitored by TLC and quenched with HCl (1 M) after which it is extracted with DCM. The combined organic phase is consecutively washed with a saturated $NaHCO_3$ solution, and a saturated NaCl solution and dried over $MgSO_4$. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified by column chromatography (SiO_2, Hep/EA: 7/1). The pure product is obtained as a white solid.

Quantity: 9.62 g

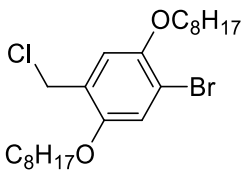
Yield: 72 %

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.05 (s, 1H), 6.90 (s, 1H), 4.63 (d, J = 6.34 Hz, 2H), 3.97 (t, J = 6.50Hz, 2H), 3.94 (t, J = 6.46 Hz, 2H), 2.24 (t, J = 6.42 Hz, 1H), 1.79 (m, 4H), 1.46 (m, 4H), 1.31 (m, 16H), 0.88 (m, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ151.04, 149.60, 129.30, 116.52, 114.56, 111.25, 70.33, 68.89, 61.82, 31.82, 31.80, 29.30, 29.25, 29.22, 26.11, 25.99, 22.66, 14.10

4-bromo-2,5-di(octyloxy)benzyl chloride (5a)



Synthesis is performed as described in literature. In a multi-neck flask, 4-bromo-2,5-di(octyloxy)benzyl alcohol (**4a**) (21.7 mmol, 9.62 g) and a catalytic amount of DMF are dissolved in toluene (150 ml) and cooled to 0 °C closed by a $CaCl_2$ tube. Next, thionyl chloride ($SOCl_2$) (65.1

mmol, 4.72 ml) is added dropwise to the solution via an addition funnel and the reaction is monitored by TLC. After the reactions, toluene and $SOCl_2$ are evaporated under reduced pressure to obtain the crude product which is purified by column chromatography (SiO_2, Hep). The pure product is obtained as white crystals.

Quantity: 7.19 g

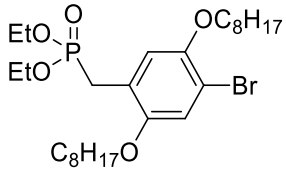
Yield: 72 %

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.06 (s, 1H), 6.93 (s, 1H), 4.59 (s, 2H), 3.97 (t, J = 6.66 Hz, 2H), 3.94 (t, J = 6.48 Hz, 2H), 1.79 (m, 4H), 1.48 (m, 4H), 1.31 (m, 16H), 0.88 (m, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ151.08, 149.54, 125.86, 117.30, 115.86, 112.91, 70.27, 69.27, 41.19, 31.81, 29.31, 29.28, 29.24, 29.22, 26.01, 25.99, 22.67, 14.11

Diethyl (4-bromo-2,5-di(octyloxy))benzyl phosphonate (O)



Synthesis is performed as described in literature. 4-Bromo-2,5-di(octyloxy)benzyl chloride (**5a**) (15.6 mmol, 7.19 g) is dissolved in triethyl phosphite (77.8 mmol, 13.3 ml) and refluxed for five hours. The crude product is purified by short path vacuum distillation to obtain the pure product as faint yellow oil.

Quantity: 7.45 g

Yield: 85 %

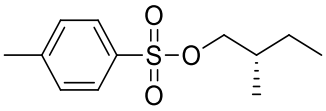
NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.03 (d, J = 0.83 Hz, 1H), 6.97 (d, J = 2.78 Hz, 1H), 4.03 (m, 4H), 3.96 (t, J = 6.56 Hz, 2H), 3.89 (t, J = 6.55 Hz, 2H), 3.19 (d, J = 21.79 Hz, 2H), 1.78 (m, 4H), 1.46 (m, 4H, 1.30 (m, 16H), 1.25 (t, J = Hz, 6H), 0.88 (m, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ151.13, 151.05, 149.35, 149.32, 120.43, 120.33, 116.94, 116.91, 116.74, 116.69, 110.71, 110.66, 70.10, 69.28, 62.00, 61.93, 31.81, 29.34, 29.33, 29.24, 27.03, 26.08, 25.99, 25.64, 22.66, 16.41, 16.35, 14.11, 14.10

^{31}P-NMR (162 MHz, $CDCl_3$): δ26.42 (s, 1P)

(*S*)-2-methylbutyl-*p*-toluenesulfonate (6b)



Synthesis is performed as described in literature. In a multi-neck flask, (*S*)-2-methylbutanol (200 mmol, 17.6 g) and triethylamine (250 mmol, 25.3 g) are dissolved in DCM (200 mL) under an inert atmosphere and cooled to a temperature of 0 °C. Next, 4-toluenesulfonyl chloride (TsCl) (300 mmol, 57.1 g) diluted in DCM (150 mL) is added dropwise to the reaction mixture via an addition funnel and the reaction is monitored by TLC. The reaction is quenched with HCl (1 M) and the mixture is extracted with DCM afterwards. The combined organic phase is consecutively washed with a saturated $NaHCO_3$ solution, and a saturated NaCl solution and dried over $MgSO_4$. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified by column chromatography (SiO_2, Hep/EA: 7.8/0.2). The pure product is obtained as clear oil.

Quantity: 34.6 g

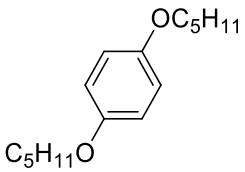
Yield: 72%

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.79 (d, J = 8.42Hz, 2H), 7.34 (d, J=8.42 Hz, 2H), 3.85 (m, 2H), 2.45 (s, 3H), 1.70 (m, 1H), 1.39 (m, 1H), 1.14 (m, 1H), 0.88 (d, J = 6.80 Hz, 3H), 0.83 (t, J = 7.52 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ144.61, 133.18, 129.79, 127.90, 74.83, 34.35, 25.43, 21.65, 15.96, 10.96

1,4-di((*S*)-2-methylbutyloxy)benzene (1b)



Synthesis is performed as described in literature. In a multi-neck flask, Potassium hydroxide (KOH) (149 mmol, 10.8 g) is dissolved in degassed ethanol (200 ml), and hydroquinone (64.9 mmol, 7.15 g) is subsequently added. The mixture is flushed with nitrogen and heated to reflux temperature. (*S*)-2-Methylbutyl-*p*-toluenesulfonate (**6b**) (143 mmol, 34.6 g) is added dropwise via an addition funnel and the mixture is refluxed overnight. The solvent is removed via rotary evaporation and the product is dissolved in ethyl acetate. The organic phase is washed with brine and dried over $MgSO_4$. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified by column chromatography (SiO_2, Hep/EA: 7.5/0.5). The pure product is obtained as light yellow oil.

Quantity: 13.5 g

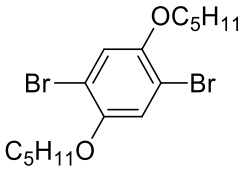
Yield: 83 %

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ6.81 (s, 4H), 3.72 (m, 4H), 1.83 (m, 2H), 1.53 (m, 2H), 1.25 (m, 2H), 1.01 (d, J = 6.83 Hz, 2H), 0.93 (t, J = 7.46 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ153.39, 115.41, 73.65, 34.80, 26.17, 16.55, 11.32

1,4-dibromo-2,5-di((*S*)-2-methylbutyloxy)benzene (2b)



The synthesis is performed analogously to the synthesis of 1,4-dibromo-2,5-di(octyloxy)benzene (**2a**) with 1,4-di((*S*)-2-methylbutyl)benzene (**1b**) (53.9 mmol, 13.5 g) in DCM (150 mL) and bromine (108 mmol, 17.2 g). The product did not require any purification and is obtained as white crystals.

Quantity: 18.5 g

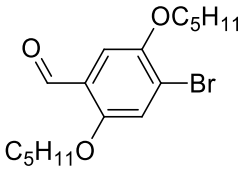
Yield: 85 %

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.07 (s, 2H), 3.77 (m, 4H), 1.89 (m, 2H), 1.59 (m, 2H), 1.30 (m, 2H), 1.05 (d, J = 6.74 Hz, 6H), 0.95 (t, J = 7.45 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ150.14, 118.28, 111.08, 74.95, 34.79, 26.05, 16.55, 11.34

4-bromo-2,5-di((*S*)-2-methylbutyloxy)benzaldehyde (3b)



The synthesis is performed analogously to the synthesis of 4-bromo-2,5-di(octyloxy)benzaldehyde (**3a**) with 1,4-dibromo-2,5-di((*S*)-2-methylbutyloxy)benzene (**2b**) (40.9 mmol, 16.7 g) in Et_2O (250 mL), *n*-BuLi (2.5 M in hexanes) (41.3 mmol, 16.5 mL) and, DMF (54.4 mmol, 4.25 mL). The pure product is obtained as viscous yellow oil.

Quantity: 10.5 g

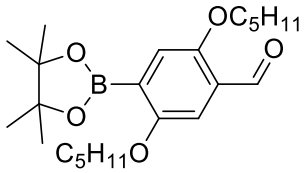
Yield: 98 %

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ10.43 (s, 1H), 7.30 (s, 1H), 7.22 (s, 1H), 3.76-3.91 (m, 4H), 1.92 (m, 2H), 1.51-1.65 (m, 2H), 1.25-1.38 (m, 2H), 1.05 (d, J = 6.76 Hz, 3H), 1.04 (d, J = 6.76 Hz, 2H), 0.96 (t, J = 7.46 Hz, 3H), 0.95 (t, J = 7.46 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ188.91, 155.90, 149.99, 124.29, 121.05, 118.42, 110.45, 74.51, 74.12, 34.77, 34.72, 26.10, 26.08, 16.57, 16.55, 11.33, 11.31

2,5-di((*S*)-2-methylbutyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (M$_{//}$)



The synthesis is performed analogously to the synthesis of 2,5-di(octyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (**O$_{//}$**) with 4-bromo-2,5-di((*S*)-2-methylbutoxy)benzaldehyde (**3b**) (31.3 mmol, 11.2 g), B_2Pin_2 (47.0 mmol, 11.9 g), KOAc (93.9 mmol, 9.22 g) and Pd(dppf)Cl_2.DCM (626 µmol, 511 mg) in 1,4-dioxane (100 mL). The purified product is obtained as brown solid with yellow shade.

Quantity: 9.50 g

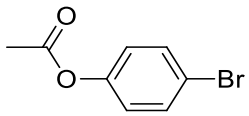
Yield: 87 %

NMR data obtained are consistent with literature values.

^{1}H NMR (600 MHz, $CDCl_3$): δ10.50 (s, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 3.85-3.96 (m, 2H), 3.72-3.84 (m, 2H), 1.82-1.94 (m, 2H), 1.53-1.67 (m, 2H), 1.36 (s, 12H), 1.30 (m, 2H), 1.04 (d, J = 6.83 Hz, 3H), 1.03 (d, J = 6.61 Hz, 3H), 0.96 (t, J = 7.51 Hz, 3H), 0.94 (t, J = 7.51 Hz, 3H)

^{13}C NMR (150 MHz, $CDCl_3$): δ190.10, 157.42, 155.66, 126.82, 120.34, 108.89, 83.97, 73.81, 73.63, 34.97, 29.71, 26.17, 25.99, 24.91, 24.87, 16.68, 16.42, 11.38

4-Bromophenyl acetate (S)



The synthesis is performed as described in literature. An oven dried flask is loaded with 4-bromophenol (5.00 mmol, 865 mg) dissolved in DCM (6.5 mL, 1.3 M) and cooled to 0 °C. Pyridine (6.50 mmol, 542 µL) was added to the solution immediately followed by acetyl chloride (6.00 mmol, 424 µL). The reaction mixture was allowed to warm to room temperature and monitored by TLC. The reaction mixture was washed with water, HCl solution (1 M), a saturated $NaHCO_3$ solution, and a saturated NaCl solution and dried over $MgSO_4$. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified by column chromatography (SiO_2, Hep/EA: 6/2).

Quantity: 1.00 g

Yield: 93 %

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.49 (d, J = 8.96 Hz, 2H), 6.98 (d, J = 8.96 Hz, 2H), 2.29 (s, 3H)

2.2 Oligomer synthesis[1]

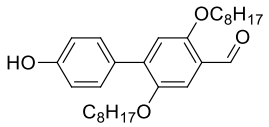
General procedure A (Suzuki-Miyaura cross coupling)

An oven dried multi-neck flask is loaded with the growing macromolecule (1 eq.), the monomer (1.2 eq.), palladium(II)acetate (0.05 eq), RuPhos (0.25 eq.) and K_3PO_4 (3 eq.) and purged with N2. Anhydrous degassed THF is added to establish a concentration of 0.2 M and water is added to a ratio of 50/1 relative to THF. Next, the reaction mixture is placed in a preheated oil bath of 65 °C and stirred for 30 minutes. Afterwards, the reaction is quenched with a saturated NH_4Cl solution and extracted with Et_2O. The combined organic phase is consecutively washed with a saturated NH_4Cl solution, a saturated $NaHCO_3$ solution, and a saturated NaCl solution and dried over Na_2SO_4. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified as explained in the relevant section.

General procedure B (Horner-Wadsworth-Emmons coupling)

An oven dried flask is loaded with the growing macromolecule (1 eq.), and the monomer (1.1 eq.) under N_2 atmosphere and dissolved in anhydrous THF. Another dried flask is loaded with KO*t*Bu (3 eq.) under N_2 atmosphere and suspended in anhydrous THF as well. The solution with both components is dropwise added to the base suspension through a canula and the reaction is stirred for 20 minutes and protected from light with Al-foil. A saturated solution of NH_4Cl is added to quench the reaction and extracted with Et_2O. The combined organic phase is consecutively washed with a saturated NH_4Cl solution, a saturated $NaHCO_3$ solution, and a saturated NaCl solution and dried over Na_2SO_4. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified as explained in the relevant section.

SO//



The synthesis is performed analogously as described in literature according to **general procedure A** with 4-bromophenyl acetate (**S**) (2.00 mmol, 430 mg), 2,5-di(octyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (**O//**) (2.40 mmol, 1.17 g), $Pd(OAc)_2$ (100 µmol, 22.5 mg), RuPhos (500 µmol, 233 mg) and K_3PO_4 (6.00 mmol, 1.27 g) dissolved in a mixture of THF (10 mL) and water (0.2 mL). After quenching and work-up of the reaction, the crude product is dissolved in THF and a few mL of NaOH solution (1 M) is added to deprotect the hydroxyl group. The reaction is neutralized with HCl (1 M) and extracted with Et_2O. The combined organic phase is consecutively washed with a saturated $NaHCO_3$ solution, and a saturated NaCl solution and dried over Na_2SO_4. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified by a filtration through a plug of silica (SiO_2, hep/EA 7.8/0.2). The pure product is obtained as a yellow solid.

Quantity: 884 mg

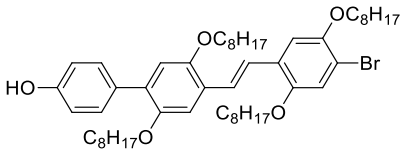
Yield: 97 %

NMR data obtained are consistent with literature values.

^{1}H NMR (600 MHz, $CDCl_3$): δ10.47 (s, 1H), 7.47 (d, J = 8.39 Hz, 2H), 7.38 (s, 1H), 6.93 (s, 1H), 6.89 (d, J = 8.58Hz, 2H), 5.08 (s, 1H), 4.06 (t, J = 6.55 Hz, 2H), 3.94 (t, J = 6.55 Hz, 2H), 1.83 (m, 2H), 1.69 (m, 2H), 1.47 (m, 2H), 1.20-1.39 (m, 18H), 0.88 (m, 6H)

^{13}C NMR (150 MHz, $CDCl_3$): δ189.49, 156.33, 155.48, 150.12, 138.60, 130.92, 130.09, 123.70, 115.39, 114.94, 110.53, 69.27, 69.09, 31.80, 31.78, 29.31, 29.25, 29.23, 29.21, 29.11, 26.08, 26.05, 22.66, 14.12, 14.10

SO$_{//}$O



The synthesis is performed analogously as described in literature according to **general procedure B** with **SO$_{//}$** (4.00 mmol, 1.82 g) and diethyl (4-bromo-2,5-di(octyloxy))benzyl phosphonate (**O**) (4.40 mmol, 2.45 g) dissolved in THF (20 mL) and KO*t*Bu (12.0 mmol, 1.35 g) suspended in THF (10 mL). The crude product is dissolved in a minimal amount of DCM and added to EtOH at room temperature to precipitate the product. The purified product is obtained as fluffy light yellow solid.

Quantity: 2.83 g

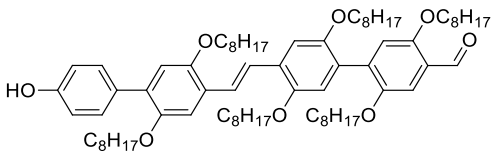
Yield: 82 %

NMR data obtained are consistent with literature values.

^{1}H NMR (600 MHz, $CDCl_3$): δ7.47 (d, J = 8.94 Hz, 2H), 7.45 (d, J = 16.60 Hz, 1H), 7.39 (d, J = 16.60 Hz, 1H), 7.18 (s, 1H), 7.15 (s,1H), 7.08 (s, 1H), 6.87 (d, J = 8.80 Hz, 2H), 6.86 (s, 1H), 4.71 (s, 1H), 4.03 (t, J = 6.35 Hz, 2H), 4.00 (t, J = 6.35 Hz, 2H), 3.96 (t, J = 6.35 Hz, 2H), 3.92 (t, J = 6.35 Hz, 2H), 1.83, (m, 6H), 1.69 (m, 2H), 1.50 (m, 6H), 1.21-1.40 (m, 34H), 0.88 (m, 12H)

^{13}C NMR (150 MHz, $CDCl_3$): δ154.63, 151.05, 150.24, 149.84, 131.08, 130.91, 130.76, 127.40, 124.18, 123.06, 117.87, 115.44, 114.81, 111.73, 111.55, 111.50, 70.27, 69.63, 69.59, 69.53, 31.87, 31.85, 31.81, 29.51, 29.42, 29.36, 29.34, 29.32, 29.30, 29.27, 26.22, 26.17, 26.15, 26.08, 22.67, 14.12, 14.09

SO$_{//}$OO$_{//}$



The synthesis is performed analogously as described in literature according to **general procedure A** with (**SO$_{//}$O**) (500 µmol, 432 mg), 2,5- di(octyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (**O$_{//}$**) (600 µmol, 293 mg), Pd(OAc)2 (25.0 µmol, 5.60 mg), RuPhos (150 µmol, 70.0 mg) and K_3PO_4 (1.50 mmol, 318 mg) dissolved in a mixture of THF (2.50 mL) and water (50.0 µL).

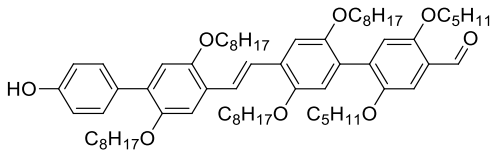
The crude product is purified by recrystallization from MeOH. The purified product is obtained as yellow solid.

NMR data obtained are consistent with literature values.

^{1}H NMR (600 MHz, $CDCl_3$): δ10.50 (s, 1H), 7.53 (d, J = 16.90 Hz, 1H), 7.50 (d, J = 16.90 Hz, 1H), 7.48 (d, 8.60 Hz, 2H), 7.38 (s, 1H), 7.23 (s, 1H), 7.03 (s, 1H), 6.90 (s, 1H), 6.88 (s, 1H), 6.88 (d, J = 8.53 Hz, 2H), 4.88 (s, 1H), 4.03 (t, J = 6.37 Hz, 2H), 4.02 (t, J = 6.47 Hz, 2H), 3.97 (t, J = 6.58 Hz, 2H), 3.90-3.95 (m, 6H), 1.83 (m, 6H), 1.1 7(m, 2H), 1.64 (m, 4H), 1.49 (m, 6H), 1.17-1.42 (m, 54H), 084-0.91 (m, 18H)

^{13}C NMR (150 MHz, $CDCl_3$): δ 189.59, 155.69, 154.66, 151.08, 150.65, 150.45, 150.35, 150.26, 136.18, 131.09, 130.77, 127.82, 126.89, 126.63, 123.98, 123.83, 123.48, 117.02, 116.30, 115.48, 114.82, 111.49, 111.09, 110.17, 69.62, 69.54, 69.18, 31.89, 31.82, 29.55, 29.51, 29.47, 29.44, 29.40, 29.36, 29.34, 29.30, 29.28, 29.26, 26.27, 26.22, 26.17, 26.13, 26.06, 22.67, 14.13, 14.10

SO$_{//}$OM$_{//}$



The synthesis is performed analogously as described in literature according to **general procedure A** with (**SO$_{//}$O**) (1.08 mmol, 1.05 g), 2,5- di((*S*)-2-methylbutyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (**M$_{//}$**) (1.45 mmol, 586 mg), Pd(OAc)2 (60.0 µmol, 13.4 mg), RuPhos (300 µmol, 140 mg) and K3PO4 (3.63 mmol, 771 mg) dissolved in a mixture of THF (5.4 mL) and water (108 µL). The crude product is purified by filtration through a plug of silica (SiO_2, Hep/EA: 7.8/0.2) followed by a recrystallization from MeOH. The purified product is obtained as yellow solid.

Quantity: 1.08 g

Yield: 94 %

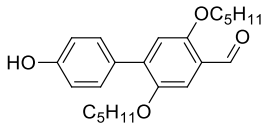
NMR data obtained are consistent with literature values.

^{1}H NMR (600 MHz, $CDCl_3$): δ10.52 (s, 1H), 7.52 (s, 2H), 7.49 (d, 8.59 Hz, 2H), 7.38 (s, 1H), 7.23 (2s, 2H), 7.02 (s, 1H), 6.89 (s, 1H), 6.88 (s, 1H), 6.87 (d, J = 8.60 Hz, 2H), 4.82 (s, 1H), 4.02 (t, J = 6.39 Hz, 2H), 3.97 (t, J = 6.39 Hz, 2H), 3.94 (t, J = 6.39 Hz, 2H), 3.90 (m, 3H), 3.83 (m, 1H), 3.80 (m, 1H),

3.70 (m, 1H), 1.92 (m, 2H), 1.84 (m, 4H), 1.71 (m, 3H), 1.62 (m, 2H), 1.50 (m, 4H), 1.17-1.43 (m, 40H), 1.04 (d, J = 6.82 Hz, 3H), 0.96 (t, J = 7.44 Hz, 3H), 0.86 (m, 18H)

^{13}C NMR (150 MHz, $CDCl_3$): δ 189.52, 155.80, 154.64, 151.07, 150.76, 150.45, 150.35, 150.27, 136.22, 131.12, 130.78, 127.79, 127.03, 126.62, 123.98, 123.78, 123.49, 116.94, 116.37, 115.47, 114.81, 111.46, 111.12, 109.93, 73.85, 69.65, 69.62, 69.59, 69.54, 34.87, 34.72, 31.88, 31.81, 29.54, 29.47, 29.44, 29.42, 29.37, 29.34, 29.31, 29.28, 29.27, 26.23, 26.18, 26.17, 26.13, 26.07, 22.69, 22.67, 22.65, 16.62, 14.13, 14.09, 11.34, 11.23

SM$_{//}$



The synthesis is performed analogously as described in literature according to **general procedure A** with 4-bromophenyl acetate (**S**) (500 µmol, 108 mg), 2,5-di((*S*)-2-methylbutyloxy)-4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl)benzaldehyde (**M$_{//}$**) (600 µmol, 222 mg), Pd(OAc)2 (25.0 µmol, 5.60 mg), RuPhos (125 µmol, 58.3 mg) and K_3PO_4 (1.50 mmol, 318 mg) dissolved in a mixture of THF (2.5 mL) and water (0.05 mL). After quenching and work-up of the reaction, the crude product is dissolved in THF and a few mL of NaOH solution (1 M) is added to deprotect the hydroxyl group. The reaction is neutralized with HCl (1 M) and extracted with Et_2O. The combined organic phase is consecutively washed with a saturated $NaHCO_3$ solution, and a saturated NaCl solution and dried over Na_2SO_4. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product which is purified by column chromatography (SiO_2, Hep/EA: 7.8/0.2). The pure product is obtained as a yellow solid.

Quantity: 141 mg

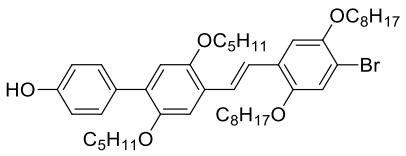
Yield: 76 %

NMR data obtained are consistent with literature values.

^{1}H NMR (600 MHz, $CDCl_3$): δ10.49 (s, 1H), 7.47 (d, J = 8.58 Hz, 2H), 7.37 (s, 1H), 6.93 (s, 1H), 6.89 (d, J = 8.58 Hz, 2H), 4.87 (s, 1H), 3.89 (m, 2H), 3.77 (m, 2H), 1.93 (m, 1H), 1.78 (m, 1H), 1.58 (m, 1H), 1.44(m, 1H), 1.32 (m, 1H), 1.20 (m, 1H), 1.05 (d, J = 6.94 Hz, 3H), 0.96 (t, J = 7.36 Hz, 3H), 0.92 (d, J = 6.74 Hz, 3H), 0.87 (t, J = 7.36 Hz, 3H)

^{13}C NMR (150 MHz, $CDCl_3$): δ189.37, 156.42, 155.40, 150.25, 138.66, 130.94, 130.14, 123.71, 115.29, 114.87, 110.29, 73.91, 73.87, 34.89, 34.73, 26.16, 26.10, 16.69, 16.64, 11.34, 11.26

SM$_{//}$O



The synthesis is performed analogously as described in literature according to **general procedure B** with **SM$_{//}$** (380 µmol, 14.1 mg) and diethyl (4-bromo-2,5-di(octyloxy))benzyl phosphonate **(O)** (418 µmol, 236 mg) dissolved in THF (1.5 mL) and KO*t*Bu (1.14 mmol, 128 mg) suspended in THF (1 mL). The crude product is purified by filtration through a plug of silica (SiO_2, Hep/EA: 7/1) followed by precipitation in MeOH at 0 °C. The pure product is obtained as yellow solid.

Quantity: 207 mg

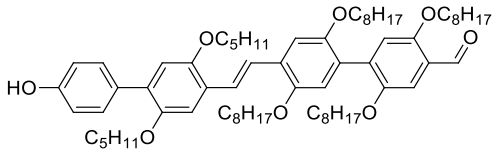
Yield: 70 %

NMR data obtained are consistent with literature values.

^{1}H NMR (600 MHz, $CDCl_3$): δ7.48 (d, J = 16.67 Hz, 1H), 7.47 (d, J = 8.39 Hz, 2H), 7.40 (d, J = 16.67 Hz, 1H), 7.18 (s, 1H), 7.17 (s,1H), 7.08 (s, 1H), 6.87 (d, J = 8.39 Hz, 2H), 6.86 (s, 1H), 4.76 (brd, s, 1H), 4.03 (t, J = 6.54 Hz, 2H), 3.96 (t, J = 6.56 Hz, 2H), 3.87 (m, 1H), 3.80 (m, 2H), 3.71 (m, 1H), 1.93, (m, 1H), 1.87-1.75 (m, 5H), 1.62 (m, 1H), 1.42-1.54 (m, 5H), 1.42-1.16 (m, 18H), 1.07 (d, J = 6.86 Hz, 3H), 0.97 (t, J = 7.57 Hz, 3H), 0.94 (d, J = 6.62 Hz, 3H), 0.88 (m, 9H)

^{13}C NMR (150 MHz, $CDCl_3$): δ154.58, 151.09, 150.95, 150.39, 149.83, 131.11, 130.98, 130.82, 127.44, 126.25, 124.00, 122.67, 117.96, 115.39, 114.74, 111.41, 111.34, 111.07, 74.40, 74.29, 70.14, 69.66, 35.06, 34.92, 31.86, 31.84, 29.38, 29.35, 29.32, 29.30, 29.27, 26.35, 26.15, 26.13, 26.04, 22.69, 22.66, 16.84, 16.73, 14.12, 14.09, 11.45, 11.32

SM//OO//



The synthesis is performed analogously as described in literature according to **general procedure A** with (**SM//O** (510 µmol, 402 mg), 2,5-di(oxtyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (**O//**) (560 µmol, 274 mg), $Pd(OAc)_2$ (26.0 µmol, 5.80 mg), RuPhos (128 µmol, 59.5 mg) and K_3PO_4 (1.53 mmol, 325 mg) dissolved in a mixture of THF (2.55 mL) and water (0.051 mL). The crude product is purified by filtration through a plug of silica (SiO_2, Hep/EA: 7.8/0.2) followed by a recrystallization from MeOH. The purified product is obtained as yellow solid.

Quantity: 469 mg

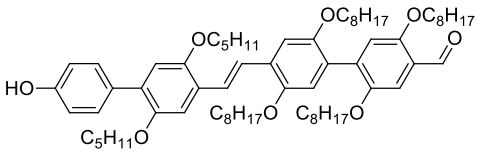
Yield 87 %

NMR data obtained are consistent with literature values.

^{1}H NMR (600 MHz, $CDCl_3$): δ10.49 (s, 1H), 7.55 (d, J = 16.36 Hz, 1H), 7.51 (d, J = 16.36 Hz, 1H), 7.48 (d, 8.68 Hz, 2H), 7.38 (s, 1H), 7.24 (s, 1H), 7.23 (s, 1H), 7.03 (s, 1H), 6.90 (s, 1H), 6.88 (s, 1H), 6.88 (d, J = 8.68 Hz, 2H), 4.77 (s, 1H), 4.03 (t, J = 6.44 Hz, 2H), 3.98 (t, J = 6.47 Hz, 2H), 3.94 (t, J = 6.39 Hz, 2H), 3.92 (2t, J = 6.46, 6.53 Hz, 4H), 3.89 (m, 1H), 3.81 (m, 2H), 3.73 (m, 1H), 1.95 (m, 1H), 1.81 (m, 5H), 1.64 (m, 5H), 1.43-1.53 (m, 5H), 1.17-1.39 (m, 38H), 1.08 (d, J = 6.80Hz, 3H), 0.98 (t, J = 7.56 Hz, 3H), 0.95 (d, J = 6.66 Hz, 3H), 0.84-0.91 (m, 15H)

^{13}C NMR (150 MHz, $CDCl_3$): δ189.57, 155.69, 154.59, 151.09, 150.65, 150.45, 150.41, 150.24, 136.14, 131.15, 130.83, 127.84, 126.80, 126.54, 123.99, 123.63, 123.07, 117.02, 116.39, 115.42, 114.75, 111.00, 110.63, 110.18, 74.43, 74.29, 69.57, 69.45, 69.18, 35.10, 34.94, 31.88, 31.82, 29.53, 29.47, 29.45, 29.34, 29.30, 29.26, 26.37, 26.23, 26.17, 26.13, 26.07, 22.67, 16.85, 16.74, 14.10, 11.47, 11.33

SM//OM//



The synthesis is performed as described in **general procedure A** with (**SM//O** (843 µmol, 659 mg), 2,5-di(oxtyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (**O//**) (1.01 mmol, 410 mg), $Pd(OAc)_2$ (43.5 µmol, 9.60 mg), RuPhos (211 µmol, 98.0 mg) and K_3PO_4 (2.53 mmol, 538 mg) dissolved in a mixture of THF (4.22 mL) and water (0.084 mL). The crude product is purified by filtration through a plug of silica (SiO_2, Hep/EA: 7.8/0.2) followed by a recrystallization from EtOH. The purified product is obtained as yellow solid

Quantity: 478 mg

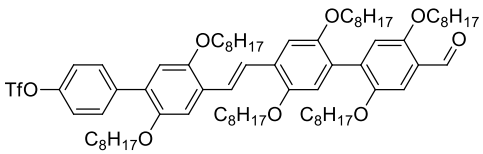
Yield 58 %

^{1}H NMR (600 MHz, $CDCl_3$): δ10.52 (s, 1H), 7.56 (d, J = 16.68 Hz, 1H), 7.52 (d, J = 16.68 Hz, 1H), 7.48 (d, J = 8.58 Hz, 2H), 7.38 (s, 1H), 7.25 (s, 1H), 7.24 (s, 1H), 7.03 (s, 1H), 6.90 (s, 1H), 6.88 (s, 1H), 6.88 (d, J = 8.58 Hz, 2H), 4.92 (s, 1H), 3.98 (t, J = 6.51 Hz, 2H), 3.90 (m, 4H), 3.81 (m, 4H), 3.72 (m, 2H), 1.94 (m, 2H), 1.04-1.87 (m, 34H), 1.09 (d, J = 6.78 Hz, 3H), 1.05 (d, J = 6.78 Hz, 3H), 0.98 (t, J = 7.53, 3H), 0.96 (t, J = 7.41 Hz, 3H), 0.95 (d, J = 6.60 Hz, 3H), 0.89 (t, J = 7.43 Hz, 3H), 0.88 (m, 12H)

^{13}C NMR (150 MHz, $CDCl_3$): δ189.57, 155.83, 154.64, 151.09, 150.77, 150.46, 150.43,150.24, 136.24, 131.10, 130.86, 130.83, 127.84, 126.93, 126.52, 123.97, 123.61, 123.07, 116.93, 116.48, 115.46, 114.75, 110.97, 110.64, 109.95, 74.46, 74.30, 73.86, 69.64, 69.49, 35.11, 34.94, 34.88, 34.73, 31.87, 31.81, 29.51, 29.43, 29.40, 29.34, 29.32, 29.27, 26.37, 26.20, 26.18, 26.17, 26.09, 26.08, 22.66, 16.85, 16.75, 16.63, 16.61, 14.09, 11.47, 11.33, 11.24

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 976.6792; found 976.6797

TfSO//OO//



The synthesis is performed analogously as described in literature. An oven dried flask was loaded with **SO//OO//** (100 µmol, 115 mg), $PhNTf_2$ (150 µmol, 53.6 mg), DMAP (10.0 µmol, 1.22 mg) and

flushed with N_2. Next, DCM (1 mL) and Et_3N (200 µmol, 27.9 µL) were added to the mixture and the reaction was monitored by TLC. The reaction was terminated by the addition of HCl (1 M) and extracted with Et_2O. The combined organic phase is consecutively washed with a saturated $NaHCO_3$ solution, and a saturated NaCl and dried over Na_2SO_4. After filtration, the solvent is evaporated under reduced pressure to obtain the crude product with is purified by filtration through a plug of silica (SiO_2, Hep/EA: 7.5/0.5) and followed by recrystallization from EtOH. The pure product is obtained as lime green solid.

Quantity: 93.3 mg

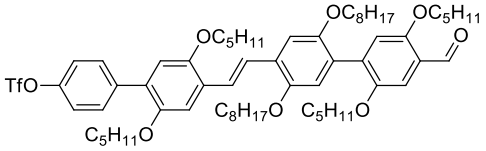
Yield: 74 %

NMR data obtained are consistent with literature values.

^{1}H NMR (400 MHz, $CDCl_3$): δ10.50 (s, 1H), 7.66 (d, J = 8.80 Hz, 2H), 7.55 (d, J = 16.65 Hz, 1H), 7.51 (d, J = 16.65 Hz, 1H), 7.39 (s, 1H), 7.30 (d, J = 8.80 Hz, 2H), 7.24 (s, 1H), 7.23 (s, 1H), 7.02 (s, 1H), 6.90 (s, 1H), 6.87 (s, 1H), 4.03 (t, J = 6.72 Hz, 2H), 4.02 (t, J = 6.72 Hz, 2H), 3.98 (t, J = 6.60 Hz, 2H), 3.96 (t, J = 6.36 Hz, 2H), 3.93 (t, J = 6.60 Hz, 2H), 3.92 (t, J = 6.42 Hz, 2H), 1.84 (m, 6H), 1.58-1.75 (m, 6H), 1.50 (m, 6H), 1.17-1.41 (m, 54H), 0.87 (m, 18H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.52, 151.04, 150.63, 150.43, 150.15, 148.44, 138.95, 136.04, 131.25, 128.76, 127.99, 127.50, 124.29, 124.05, 123.52, 120.71, 116.99, 116.25, 115.40, 111.21, 110.17, 69.66, 69.49, 69.17, 31.88, 31.82, 29.51, 29.47, 29.42, 29.40, 29.36, 29.30, 29.27, 29.26, 26.27, 26.21, 26.15, 26.13, 26.06, 22.67,14.09

TfSM//OM//



The synthesis is performed analogously to the synthesis of **TfSO//OO//** with **SM//OM//** (105 µmol, 102 mg), $PhNTf_2$ (157 µmol, 53.6 mg), DMAP (10.5 µmol, 1.28 mg) dissolved in DCM (1 mL) and Et_3N (209 µmol, 30.0 µL). The crude product is filtered through a plug of silica (SiO2, Hep/EA: 7.5/0.5) and followed by a recrystallization from EtOH. The pure product is obtained as a bright yellow solid.

Quantity: 112 mg

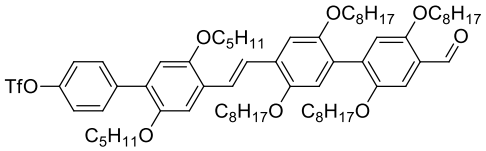
Yield: 97 %

^{1}H NMR (600 MHz, CD_2Cl_2): δ10.54 (s, 1H), 7.72 (d, J = 8.82 Hz, 2H), 7.61 (s 1H), 7.40 (s, 1H), 7.36 (d, J = 8.82 Hz, 2H), 7.32 (s, 1H), 7.29 (s, 1H), 7.08 (s, 1H), 6.96 (s, 1H), 6.95 (s, 1H), 4.03 (t, J = 6.42 Hz, 2H), 3.80-3.99 (m, 9H), 3.76 (m, 1H), 1.15-2.04 (m, 36H), 1.13 (d, J = 6.78 Hz, 3H), 1.08 (d, J = 6.60 Hz, 3H), 1.02 (t, J = 7.41 Hz, 3H), 0.99 (t, J = 7.44 Hz, 3H), 0.97 (d, J = 6.78 Hz, 3H), 0.87 (m, 15H)

^{13}C NMR (150 MHz, CD_2Cl_2): δ 188.96, 155.73, 151.08, 150.73, 150.45, 150.29, 150.24, 148.47, 139.06, 135.89, 131.34, 128.79, 127.64, 127.28, 127.12, 124.11, 123.77, 123.26, 120.64, 119.88, 116.95, 116.32, 115.28, 110.62, 110.14, 109.62, 74.42, 74.16, 73.91, 73.82, 69.52, 69.25, 35.10, 34.92, 34.90, 34.80, 31.86, 31.80, 29.46, 29.41, 29.37, 29.32, 29.25, 26.33, 26.18, 26.13, 26.06, 22.64, 16.56, 16.41, 16.34, 16.33, 13.83, 11.22, 11.09, 11.03, 11.00

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 1108.6285; found 1108.6281

TfSM$_{//}$OO$_{//}$



The synthesis is performed analogously to the synthesis of **TfSO$_{//}$OO$_{//}$** with **SM$_{//}$OO$_{//}$** (53.1 µmol, 56.4 mg), $PhNTf_2$ (79.7 µmol, 28.5 mg), DMAP (5.31 µmol, 649 µg) dissolved in DCM (0.5 mL) and Et_3N (106 µmol, 14.8 µL). The crude product is filtered through a plug of silica (SiO_2, Hep/EA: 7.5/0.5) and followed by a recrystallization from EtOH. The pure product is obtained as a bright yellow solid.

Quantity: 50.2 mg

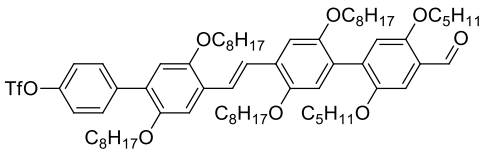
Yield: 79 %

^{1}H NMR (600 MHz, CD_2Cl_2): δ10.48 (s, 1H), 7.69 (d, J = 8.64 Hz, 2H), 7.57 (s 1H), 7.36 (s, 1H), 7.34 (d, J = 8.64 Hz, 2H), 7.28 (s, 1H), 7.25 (s, 1H), 7.05 (s, 1H), 6.92 (s, 1H), 6.92 (s, 1H), 4.06 (t, J = 6.42 Hz, 2H), 4.00 (t, J = 6.51 Hz, 2H), 3.95 (t, J = 6.60 Hz, 2H), 3.94 (t, J = 6.51 Hz, 2H), 3.91 (m, 1H), 3.85 (m, 2H), 3.79 (m, 1H), 1.97 (m, 1H), 1.75-1.88 (m, 5H), 1.65 (m, 5H), 1.17-1.56 (m, 43H), 1.10 (d, J = 6.60 Hz, 3H), 0.99 (t, J = 7.50 Hz, 3H), 0.94 (d, J = 6.84Hz, 3H), 0.88 (m, 15H)

^{13}C NMR (150 MHz, CD_2Cl_2): δ189.02, 155.63, 151.08, 150.63, 150.44, 150.28, 150.25, 148.47, 139.07, 135.82, 131.34, 128.80, 127.62, 127.31, 127.02, 124.12, 123.74, 123.31, 120.64, 119.88, 117.05, 116.24, 115.25, 110.65, 110.15, 109.73, 74.40, 74.16, 69.50, 69.30, 69.24, 69.14, 35.10, 34.92, 31.87, 31.82, 29.48, 29.45, 29.42, 29.35, 29.33, 29.27, 29.25, 26.33, 26.21, 26.13, 26.10, 26.09, 26.06, 22.66, 16.57, 16.41, 13.86, 13.85, 11.23, 11.03

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 1192.7224; found 1192.7252

TfSO//OM//



The synthesis is performed analogously to the synthesis of **TfSO//OO//** with **SO//OM//** (167 µmol, 177 mg), $PhNTf_2$ (250 µmol, 89.3 mg), DMAP (16.7 µmol, 2.04 mg) dissolved in DCM (1 mL) and Et_3N (333 µmol, 46.2 µL). The crude product is filtered through a plug of silica (SiO_2, Hep/EA: 7.5/0.5) and followed by a recrystallization from EtOH. The pure product is obtained as a bright yellow solid.

Quantity: 191mg

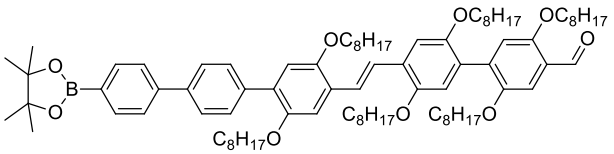
Yield: 96 %

^{1}H NMR (600 MHz, CD_2Cl_2): δ10.52 (s, 1H), 7.70 (d, J = 8.64 Hz, 2H), 7.57 (d, J = 16.86 Hz, 1H), 7.54 (d, J = 16.86 Hz, 1H), 7.36 (s, 1H), 7.33 (d, J = 8.64 Hz, 2H), 7.27 (s, 1H), 7.24 (s, 1H), 7.04 (s, 1H), 6.92 (s, 1H), 6.91 (s, 1H), 4.04 (t, J = 6.42 Hz, 2H), 4.00 (t, J = 6.42 Hz, 2H), 3.99 (t, J = 6.51 Hz, 2H), 3.93 (m, 3H), 3.84 (m, 2H), 3.72 (m, 1H), 1.93 (m, 1H), 1.85 (m, 4H), 1.72 (m, 3H),1.47-1.67 (m, 6H), 1.11-1.46 (m, 40H), 1.05 (d, J = 6.78 Hz, 3H), 0.96 (t, J = 7.44, 3H), 0.87 (m, 18H)

^{13}C NMR (150 MHz, CD_2Cl_2): δ155.73, 151.01, 150.73, 150.45, 150.35, 150.13, 148.45, 139.07, 135.91, 131.30, 128.61, 127.70, 127.24, 124.17, 124.11, 123.46, 120.69, 116.97,116.25, 115.30, 110.89, 110.56, 109.61, 73.91, 73.82, 69.59, 69.50, 69.39, 69.33, 34.89, 34.80, 31.87, 31.80, 29.49, 29.45, 29.41, 29.39, 29.35, 29.34, 29.33, 29.26, 29.23, 26.22, 26.21, 26.14, 26.10, 26.06, 22.66, 22.64, 16.34,13.83, 11.09, 11.00

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 1192.7224; found 1192.7218

CSO//OO//



The synthesis is performed as described in **general procedure A** with 1,4-benzenediboronic acid bis(pinacol) ester (**C**) (1.00 mmol, 330 mg), $Pd(OAc)_2$ (5.00 µmol, 1.12 mg), RuPhos (25 µmol, 11.7 mg) and K_3PO_4 (300 µmol, 63.7 mg) dissolved in a mixture of THF (0.5 mL) and water (0.010 mL). **TfSO//OO//** (100 µmol, 128 mg) is dissolved in THF (0.5 mL) and added dropwise to the mixture over a timespan of 10 minutes. The crude product is purified by column chromatography (SiO_2, Hep -> Hep/EA: 7.8/0.2) followed by a precipitation in MeOH. The purified product is obtained as yellow solid.

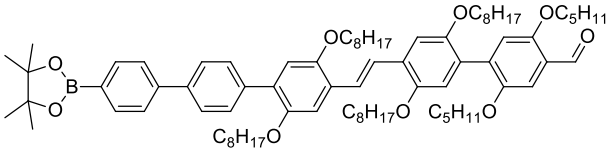
Quantity: 25.4 mg

Yield: 19 %

^{1}H NMR (600 MHz, $CDCl_3$): δ10.52 (s, 1H), 7.90 (d, J = 8.28 Hz, 2H), 7.68 (s, 4H), 7.67 (d, J = 8.28 Hz, 2H), 7.54 (s, 2H), 7.38 (s, 1H), 7.27 (s, 1H), 7.24 (s, 1H), 7.02 (s, 1H), 6.96 (s, 1H), 6.90 (s, 1H), 4.04 (t, J = 6.60 Hz, 2H), 3.98 (t, J = 6.42 Hz, 2H), 3.98 (t, J = 6.60 Hz, 2H), 3.91 (m, 3H), 3.82 (m, 2H), 3.71 (m, 1H), 1.93 (m, 1H), 1.85 (m, 4H), 1.73 (m, 3H), 1.47-1.66 (m, 7H), 1.09-1.45 (m, 39H), 1.38 (s, 12H), 1.05 (d, J = 6.78 Hz, 3H), 0.96 (t, J = 7.41 Hz, 3H), 0.86 (m, 18H)

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 1392.9923; found 1329.9946

CSO//OM//



The synthesis is performed as described in **general procedure A** with 1,4-benzenediboronic acid bis(pinacol) ester (**C**) (419 µmol, 138 mg), $Pd(OAc)_2$ (2.10 µmol, 471 µg), RuPhos (10.5 µmol, 4.89 mg) and K_3PO_4 (126 µmol, 26.7 mg) dissolved in a mixture of THF (1.51 mL) and water (0.010 mL). **TfSO//OM//** (41.9 µmol, 50.0 mg) is dissolved in THF (0.5 mL) and added dropwise to the mixture over a timespan of 10 minutes. The crude product is partly purified similar as **CSO//OO//** by

column chromatography (SiO_2, Hep -> Hep/EA: 7.8/0.2) followed by a precipitation in MeOH and partly by using preparative SEC followed by a precipitation in MeOH.

Quantity: 17.0 mg

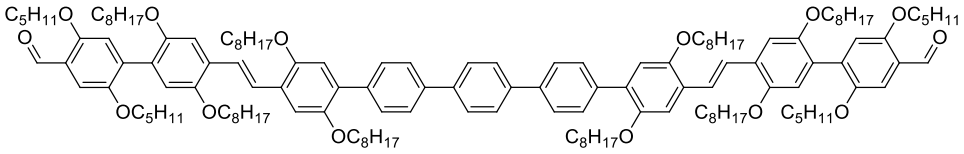
Overall yield: 33 %

Yield preparative SEC: 76 %

^{1}H NMR (600 MHz, $CDCl_3$): δ10.52 (s, 1H), 7.90 (d, J = 8.28 Hz, 2H), 7.68 (s, 4H), 7.67 (d, J = 8.28 Hz, 2H), 7.54 (s, 2H), 7.38 (s, 1H), 7.27 (s, 1H), 7.24 (s, 1H), 7.02 (s, 1H), 6.96 (s, 1H), 6.90 (s, 1H), 4.04 (t, J = 6.60 Hz, 2H), 3.98 (t, J = 6.42 Hz, 2H), 3.98 (t, J = 6.60 Hz, 2H), 3.91 (m, 3H), 3.82 (m, 2H), 3.71 (m, 1H), 1.93 (m, 1H), 1.85 (m, 4H), 1.73 (m, 3H), 1.47-1.66 (m, 7H), 1.09-1.45 (m, 39H), 1,38 (s, 12H), 1.05 (d, J = 6.78 Hz, 3H), 0.96 (t, J = 7.41 Hz, 3H), 0.86 (m, 18H)

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 1245.8983; found 1245.9009

//MO//OSCSO//OM//



The synthesis is performed as described in **general procedure A** with **TfSO//OM//** (35.4 µmol, 42.2 mg), 1,4-benzenediboronic acid bis(pinacol) ester (**C**) (16.1 µmol, 5.31 mg), $Pd(OAc)_2$ (804 nmol, 181 µg), RuPhos (4.02 µmol, 1.88 mg) and K_3PO_4 (48.3 mmol, 10.2 mg) dissolved in a mixture of THF (0.5 mL) and water (1.6 µL). The crude product is purified by recrystallization from acetone and obtained as a yellow solid.

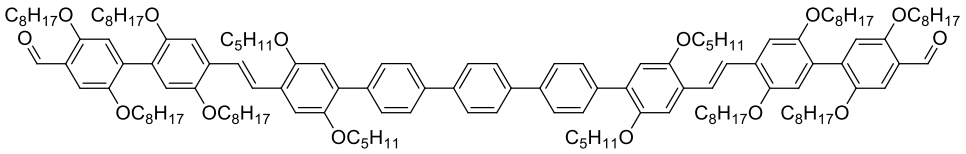
Quantity: 28.7 mg

Yield 82 %

^{1}H NMR (600 MHz, CD_2Cl_2): δ10.51 (s, 1H), 7.81 (s, 4H), 7.75 (m, 8H), 7.59 (s, 4H), 7.38 (s, 2H), 7.30 (s, 2H), 7.27 (s, 2H), 7.06 (s, 2H), 7.01 (s, 2H), 6.94 (s, 2H), 4.08 (t, J = 6.51 Hz, 4H), 4.04 (t, J = 6.39 Hz, 4H), 4.01 (t, J = 6.33 Hz, 4H), 3.96 (t, J = 6.33 Hz, 4H), 3.94 (m, 2H), 3.85 (m, 4H), 3.74 (m, 2H), 1.83-1.98 (m, 10H), 1.70-1.81 (m, 6H), 1.51-1.69 (m, 12H), 1.13-1.49 (m, 80H), 1.07 (d, J = 6.96 Hz, 6H), 0.97 (t, J = 7.53 Hz, 6H), 0.88 (m, 36H)

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 2163.5721; found 2163.5779

//OO//MSCSM//OO//



The synthesis is performed as described in **general procedure A** with **TfSM//OO//** (35.5 µmol, 42.4 mg), 1,4-benzenediboronic acid bis(pinacol) ester (**C**) (16.1 µmol, 5.33 mg), $Pd(OAc)_2$ (807 nmol, 181 µg), RuPhos (4.04 µmol, 1.88 mg) and K_3PO_4 (48.4 mmol, 10.3 mg) dissolved in a mixture of THF (0.5 mL) and water (1.6 µL). The crude product is purified by recrystallization from acetone and obtained as a yellow solid.

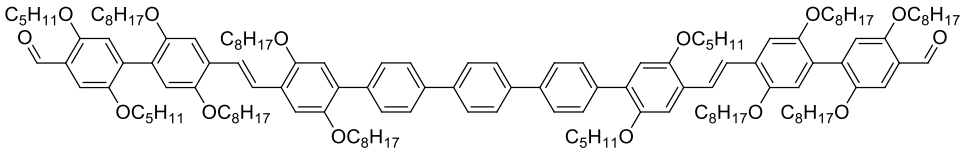
Quantity: 26.08 mg

Yield 75 %

^{1}H NMR (600 MHz, CD_2Cl_2): δ10.49 (s, 1H), 7.81 (s, 4H), 7.75 (m, 8H), 7.62 (d, J = 16.53 Hz, 2H), 7.59 (d, J = 16.53 Hz, 2H), 7.37 (s, 2H), 7.31 (s, 2H), 7.29 (s, 2H), 7.07 (s, 2H), 7.02 (s, 2H), 6.94 (s, 2H), 4.07 (t, J = 6.69 Hz, 4H), 4.02 (t, J = 6.42 Hz, 4H), 3.86-4.00 (m, 14H), 3.83 (m, 2H), 1.99 (m, 2H), 1.86 (m, 10H), 1.67 (m,10H), 1.46-1.59 (m, 12H), 1.16-1.44 (m, 74H), 1.13 (d, J = 6.78 Hz, 6H), 1.02 (d, J = 6.78 Hz, 6H), 1.01 (t, J = 7.05, 6H), 0.94 (t, J = 7.41 Hz, 6H), 0.88 (m, 24H)

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 2163.5721; found 2163.5657

//MO//OSCSM//OO//



The synthesis is performed as described in **general procedure A** with **CSO//OM//** (7.08 µmol, 8.84 mg), **TfSM//OO//** (8.50 µmol, 10.14 mg), $Pd(OAc)_2$ (354 nmol, 70.0 µg), RuPhos (1.77 µmol, 825 µg) and K_3PO_4 (21.2 µmol, 4.51 mg) dissolved in a mixture of THF (0.5 mL) and water (1.0 µL). The crude product is purified by recrystallization from acetone and obtained as a yellow solid.

Quantity: 9.98 mg

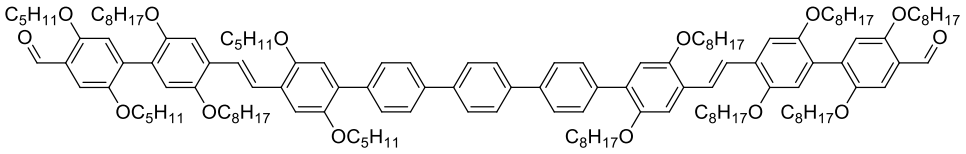
Yield 65 %

^{1}H NMR (600 MHz, CD_2Cl_2): δ10.51 (s, 1H), 10.49 (s, 1H), 7.81 (s, 4H), 7.74 (m, 8H), 7.61 (d, J = 16.68 Hz, 1H), 7.58 (d, J = 16.68 Hz, 1H), 7.58 (s, 2H), 7.37 (s, 1H), 7.37 (s, 1H), 7.30 (s, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 7.26 (s, 1H), 7.06 (s, 1H), 7.06 (s, 1H), 7.01 (s, 1H), 7.01 (s, 1H), 6.93 (s, 2H),

3.80-4.10 (m, 23H), 3.73 (m, 1H), 1.14-2.03 (m, 108H), 1.12 (d, J = 6.60 Hz, 3H), 1.06 (d, J = 6.60 Hz, 3H), 1.01 (d, J = 6.60 Hz, 3H), 1.01 (t, J = 7.32, 3H), 0.97 (t, J = 7.41 Hz, 3H), 0.94 (t, J = 7.41 Hz, 3H), 0.87 (m, 30H)

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 2163.5721; found 2163.5647

//MO//MSCSO//OO//



The synthesis is performed as described in **general procedure A** with **CSO//OO//** (11.5 µmol, 15.33 mg), **TfSM//OM//** (13.8 µmol, 15.3 mg), $Pd(OAc)_2$ (575 nmol, 129 µg), RuPhos (2.88 µmol, 1.34 mg) and K_3PO_4 (34.5 µmol, 7.32 mg) dissolved in a mixture of THF (0.5 mL) and water (1.0 µL). The crude product is purified by recrystallization from acetone and obtained as a yellow solid.

Quantity: 16.8 mg

Yield 67 %

^{1}H NMR (600 MHz, CD_2Cl_2): δ10.51 (s, 1H), 10.49 (s, 1H), 7.81 (s, 4H), 7.75 (m, 8H), 7.62 (d, J = 16.68 Hz, 1H), 7.58 (d, J = 16.68 Hz, 1H), 7.58 (s, 2H), 7.37 (s, 2H), 7.31 (s, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 7.06 (s, 1H), 7.02 (s, 1H), 7.01 (s, 1H), 6.94 (s, 1H), 6.93 (s, 1H), 3.80-4.11 (m, 23H), 3.74 (m, 1H), 1.14-2.03 (m, 108H), 1.13 (d, J = 6.78 Hz, 3H), 1.06 (d, J = 6.78 Hz, 3H), 1.01 (d, J = 6.60 Hz, 3H), 1.01 (t, J = 7.26, 3H), 0.97 (t, J = 7.53 Hz, 3H), 0.94 (t, J = 7.59 Hz, 3H), 0.88 (m, 30H)

HRMS (m/z): [M]+ calcd. For $C_{29}H_{49}B_1O_5$, 2163.5721; found 2163.5654

3 Characterization

3.1 NMR

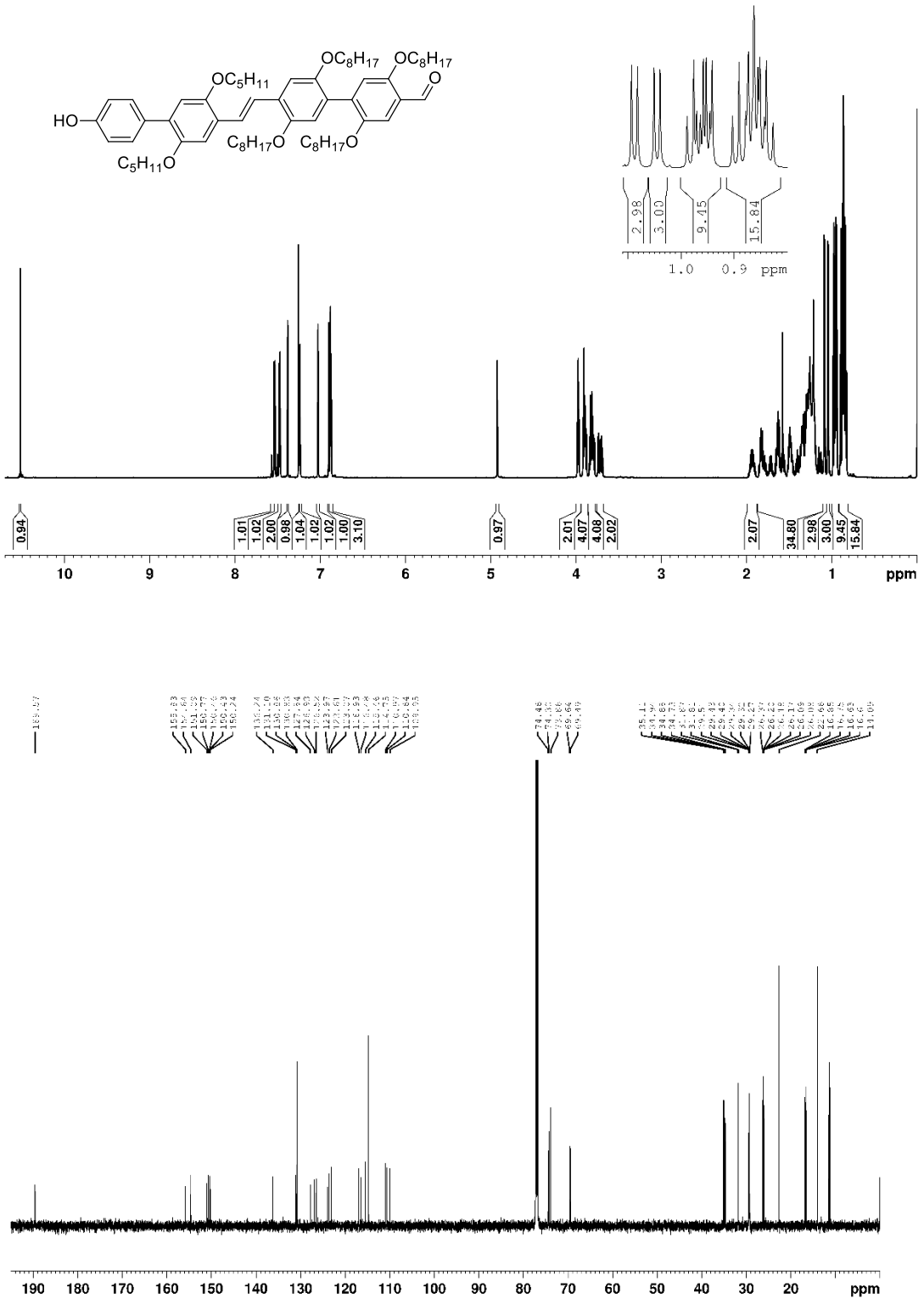


Figure S2. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectrum of $SM_{//}OM_{//}$ measured in $CDCl_3$.

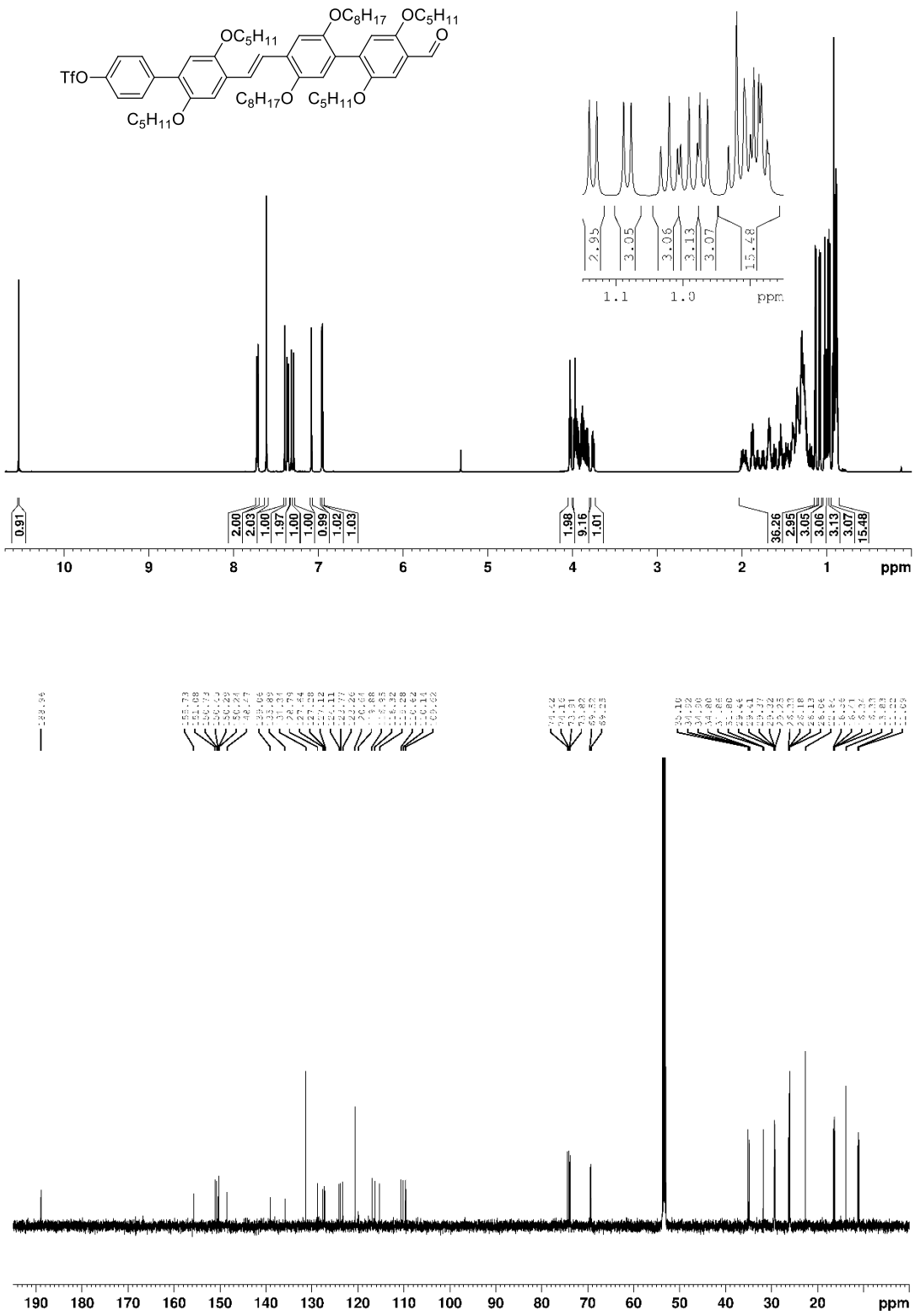


Figure S3. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectrum of $TfSM_{//}OM_{//}$ measured in CD_2Cl_2.

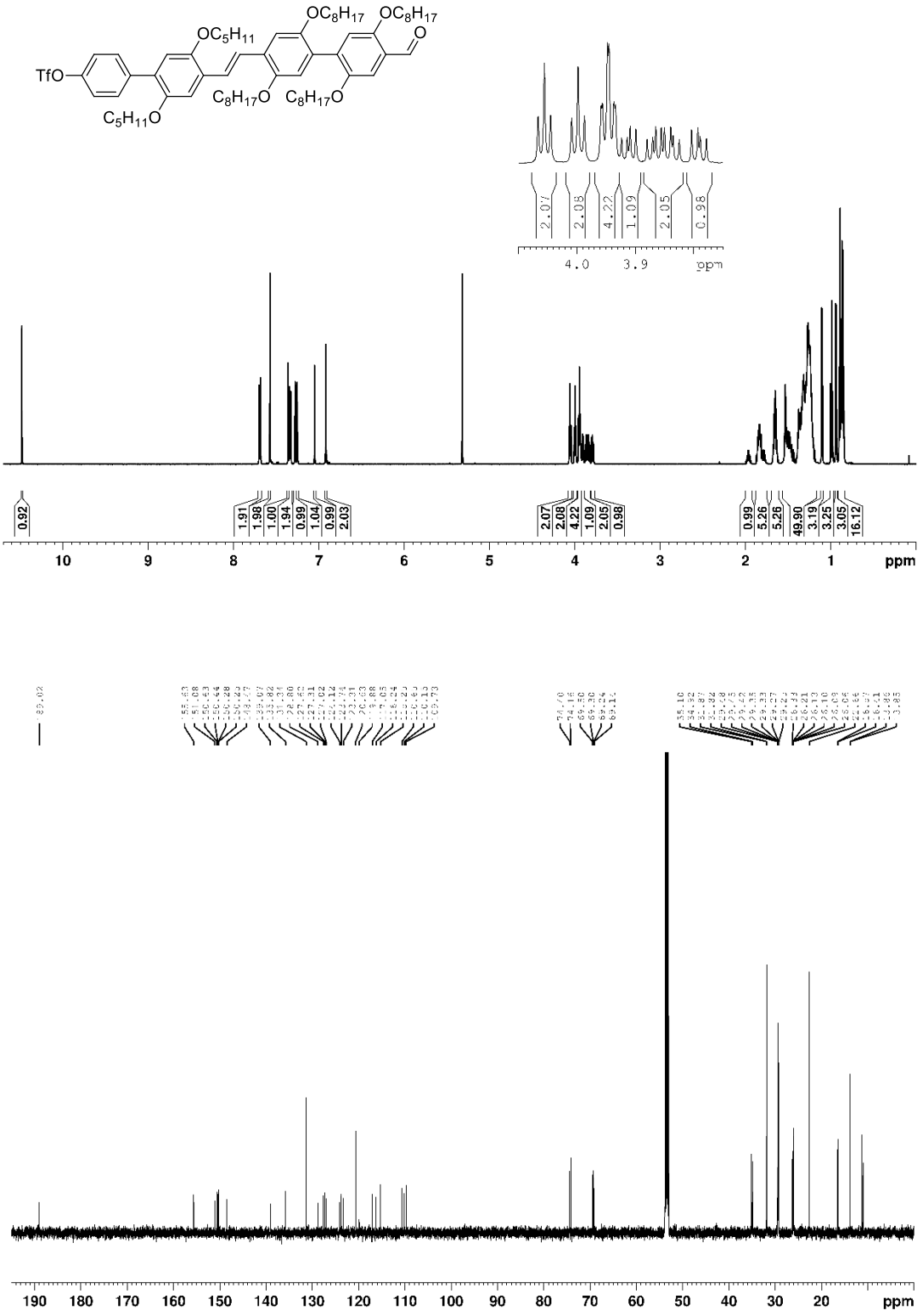


Figure S4. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectrum of TfSM//OO// measured in CD_2Cl_2.

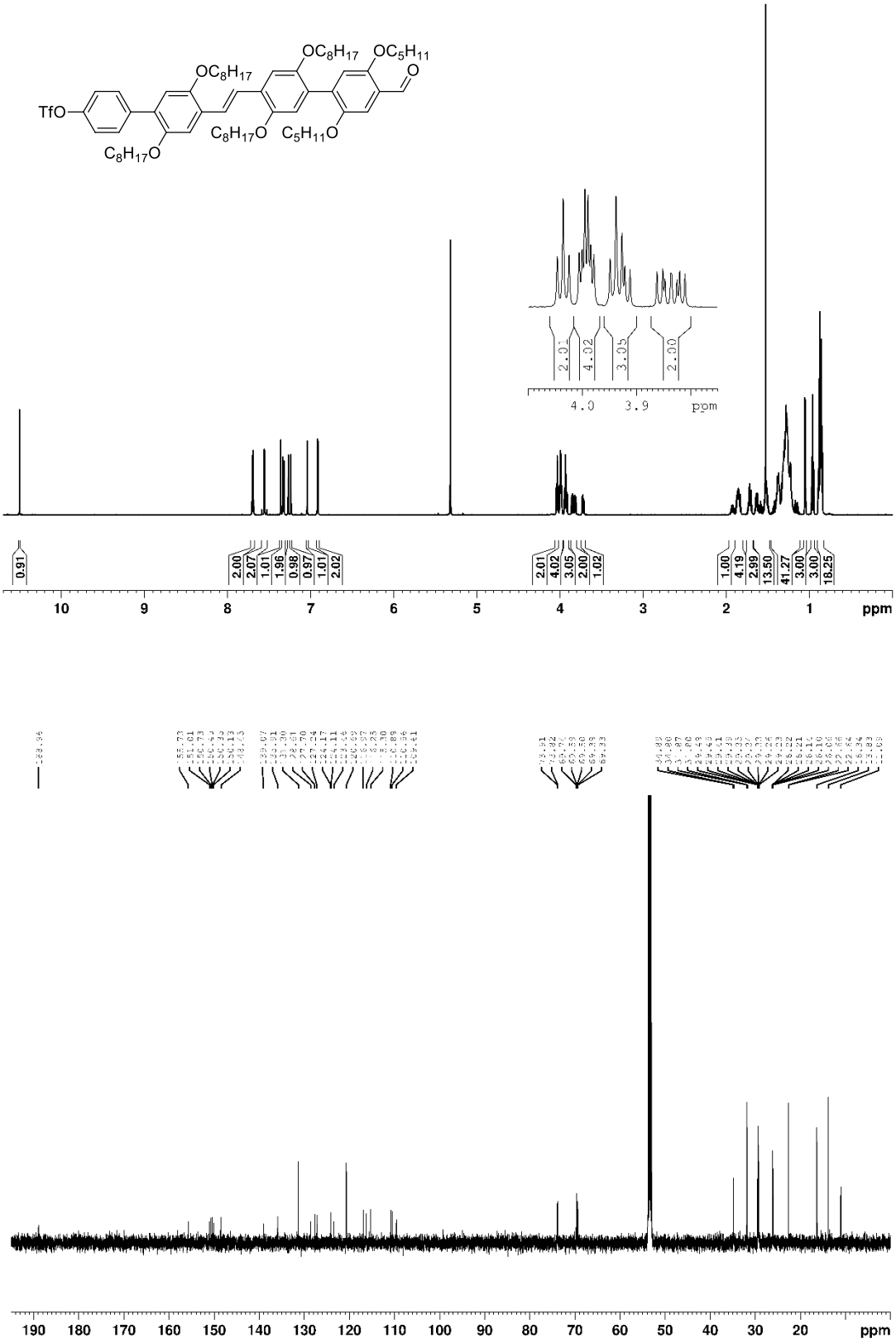


Figure S5. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectrum of $TfSO_{//}OM_{//}$ measured in CD_2Cl_2.

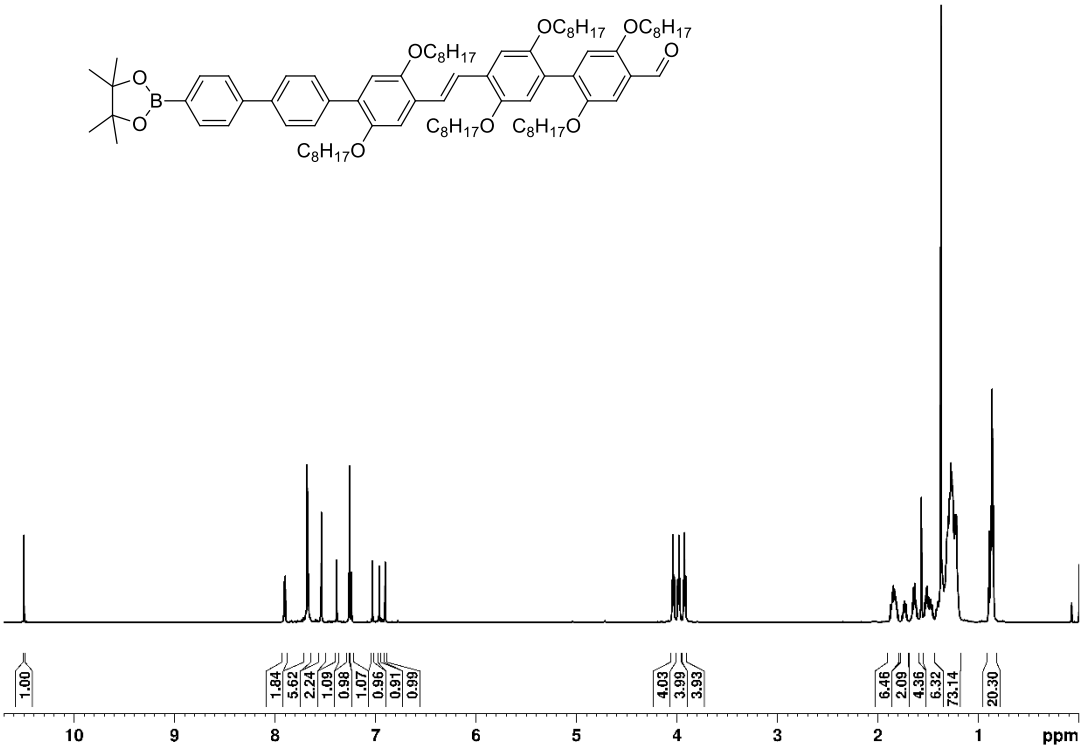


Figure S6. ^{1}H NMR spectrum of CSO//OO// measured in $CDCl_3$.

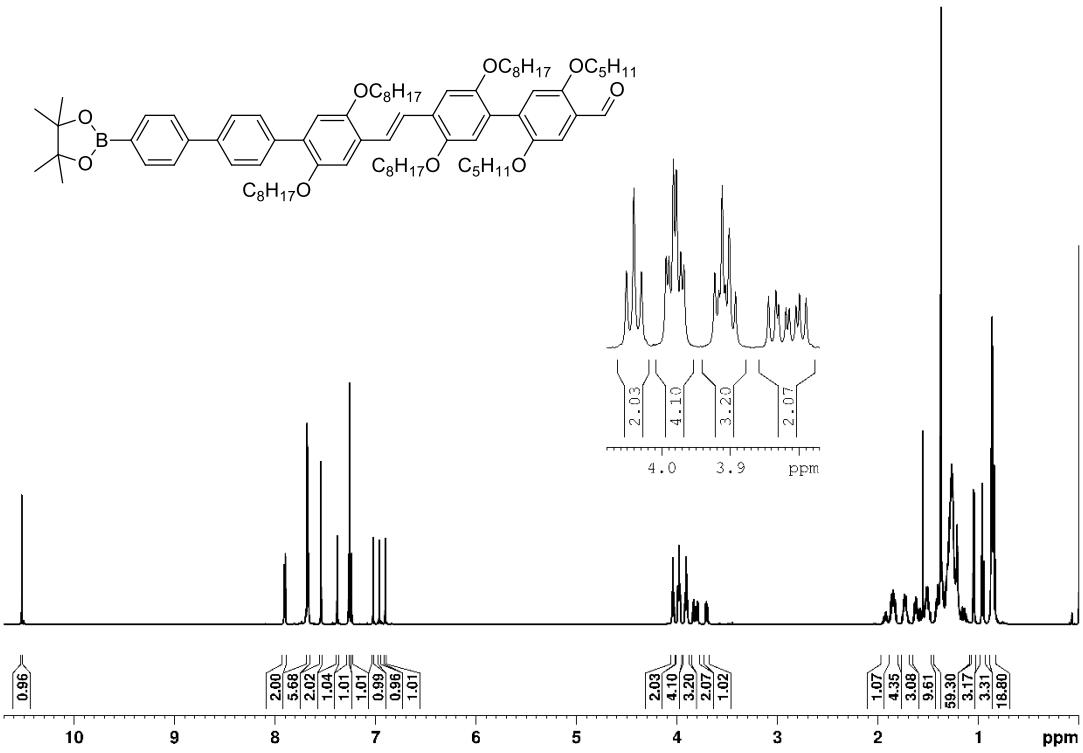


Figure S7. ^{1}H NMR spectrum of CSO//OM// measured in $CDCl_3$.

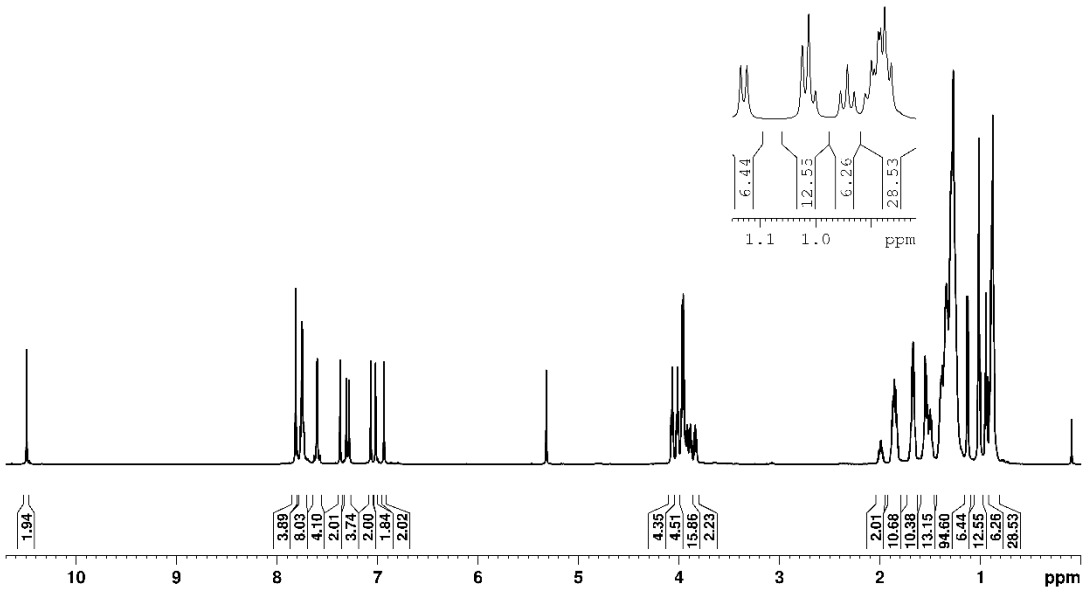


Figure S8. ^{1}H NMR spectrum of //OO//MSCSM//OO// measured in CD_2Cl_2.

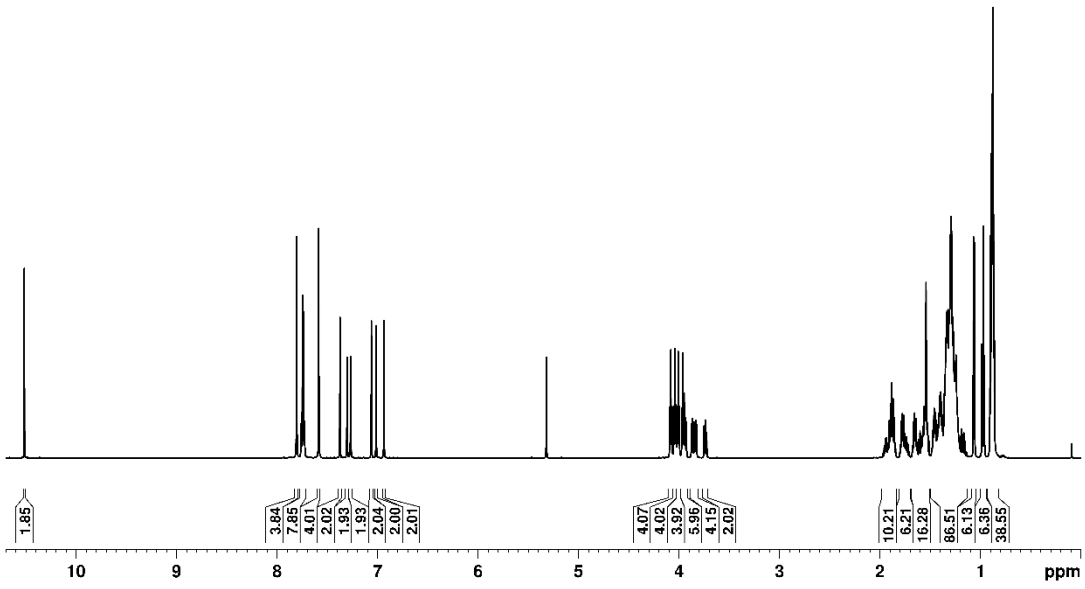


Figure S9. ^{1}H NMR spectrum of //MO//OSCSO//OM// measured in CD_2Cl_2.

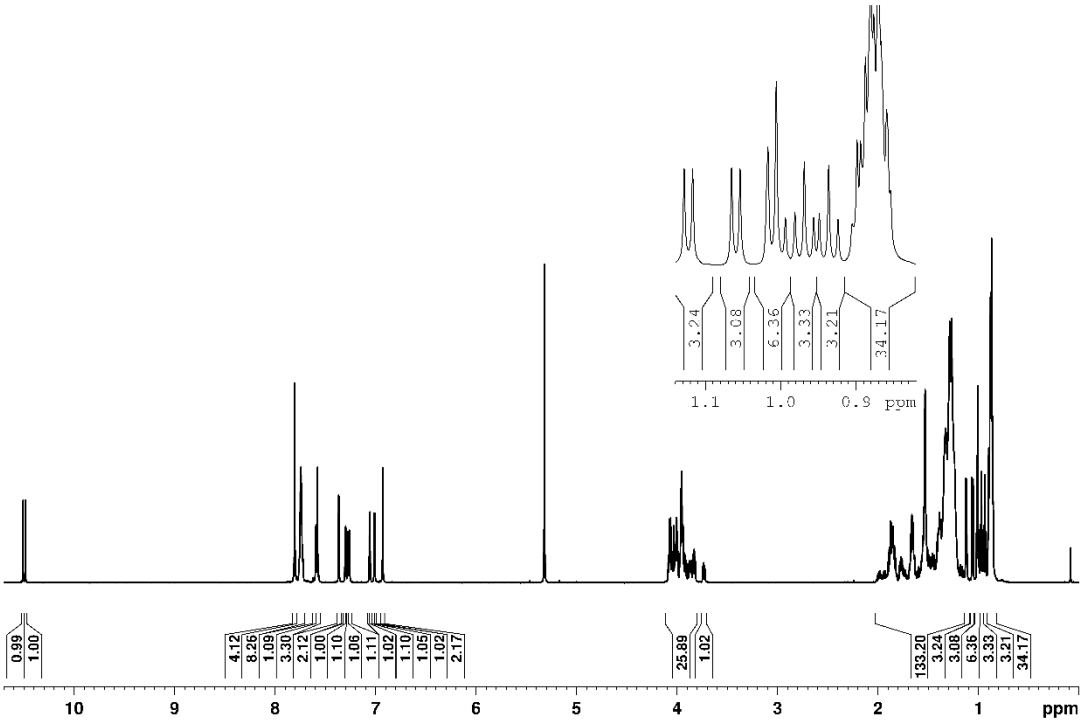


Figure S10. ^{1}H NMR spectrum of //MO//OSCSM//OO// measured in CD_2Cl_2.

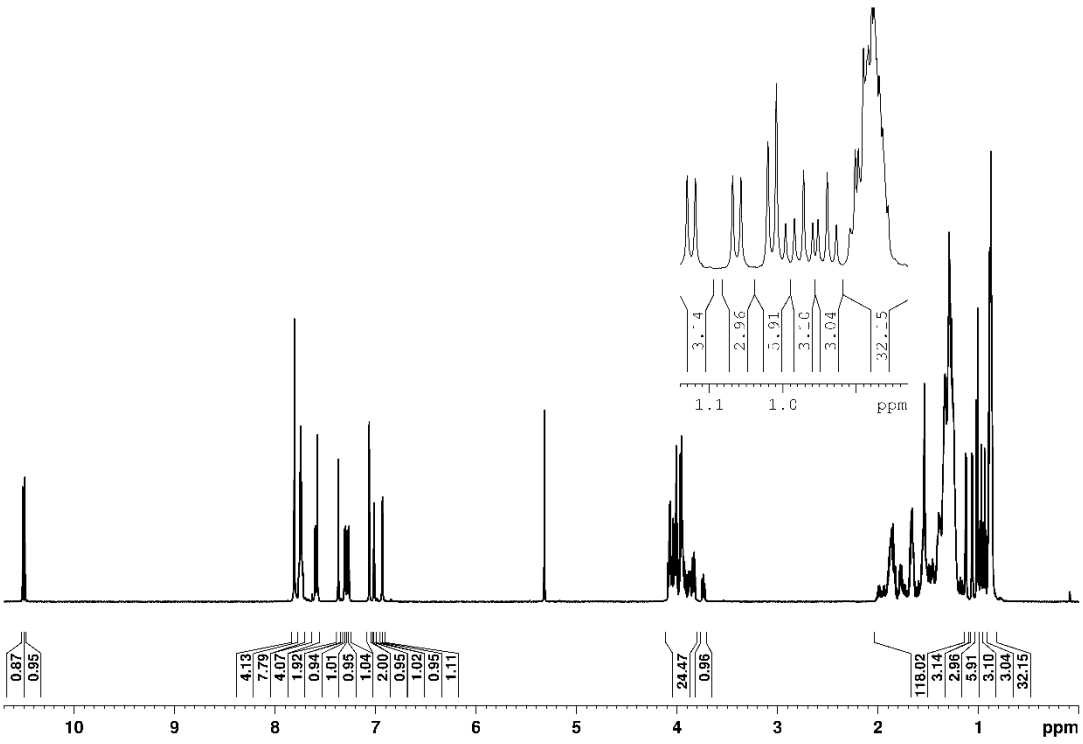


Figure S11. ^{1}H NMR spectrum of //MO//MSCSO//OO// measured in CD_2Cl_2.

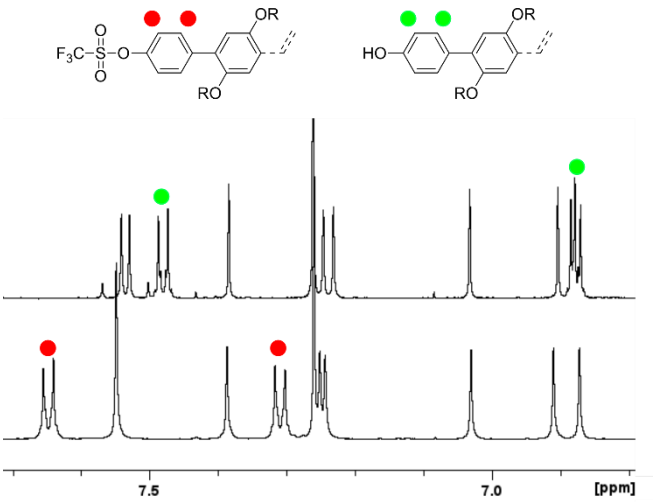


Figure S12. ^{1}H NMR spectra to monitor the triflate reaction of **TfSM//OO//**. The green dots point the doublet belonging to the protons of the starting molecule that shift to higher ppm in the product (red dots). Note that the signal at ± 7.55 ppm corresponds to the protons of the double bond and changes from two doublets with *J* = 16.65 Hz to a singlet at approximately the same ppm.

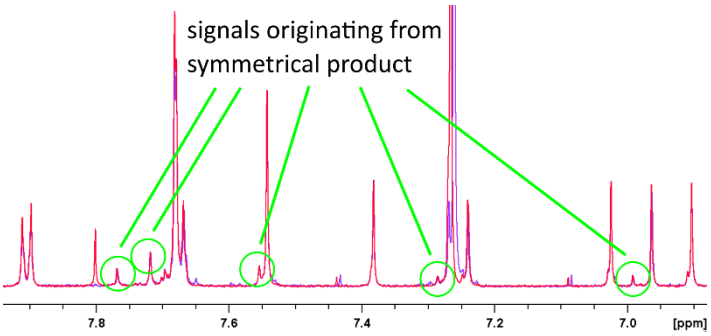


Figure S13. Overlap of the ^{1}H NMR spectra of **CSO//OM//** synthesized with different concentrations. Both crude products are precipitated in MeOH and the product signals are placed at equal intensity, showing that the symmetrical product is equally present in both synthetic procedures.

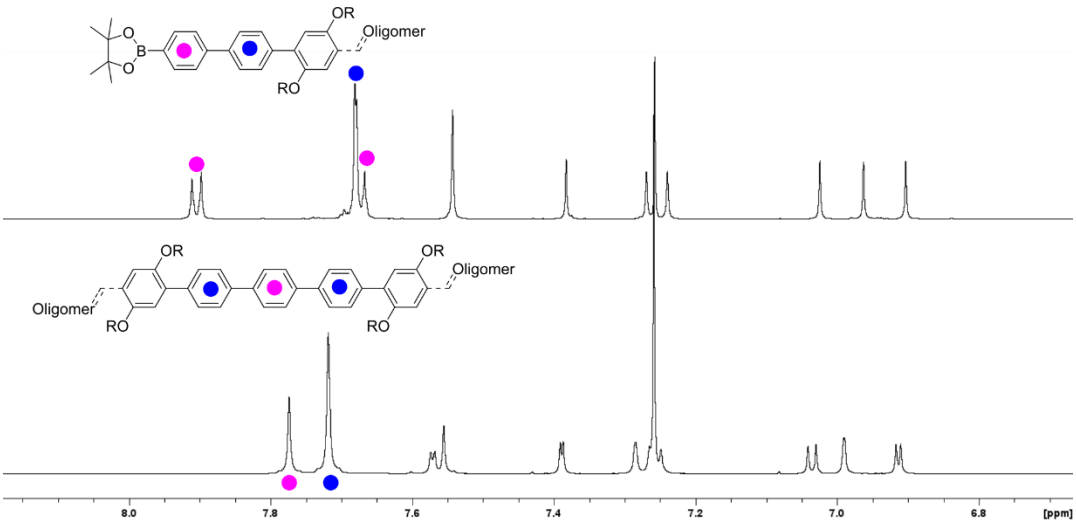


Figure S14. Overlap of the ^{1}H NMR spectra in the asymmetrical nonamer synthesis. The pink dots point the signals corresponding to the central core molecule (**C**), while the blue dots indicate the signals corresponding to the starting molecule **S**.

3.2 Size Exclusion Chromatography (SEC)

The preparative SEC consists of two columns placed in series, which can be loaded for an extra run automatically. In the first run, the product before 38.5 min is been removed and the product afterwards is recycled on the preparative SEC once again automatically. In this second run, the product is collected in different fractions over a time frame from 78.5 minutes until 86.4 minutes from which the pure product is obtained. By using preparative SEC, tedious and destructive purifications such as column chromatography were avoided and improved the yield significantly.

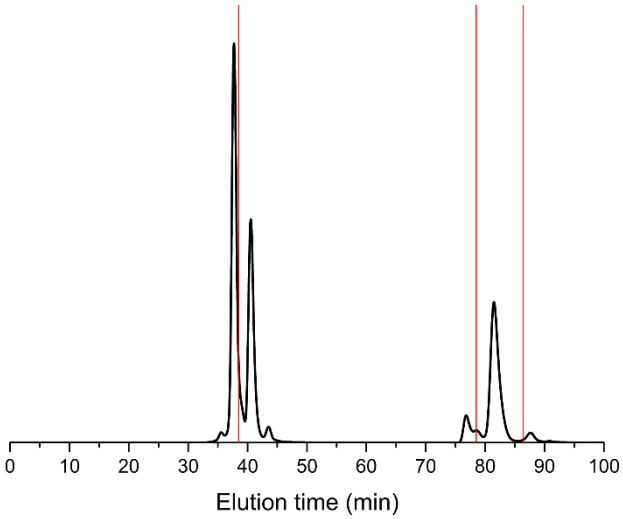


Figure S15. The preparative SEC spectrum with the red lines indicating the timeslots 38.5 min, 78.5 min and 86.4 min from left to right. The product right before the first red line corresponds to the unwanted symmetrical product.

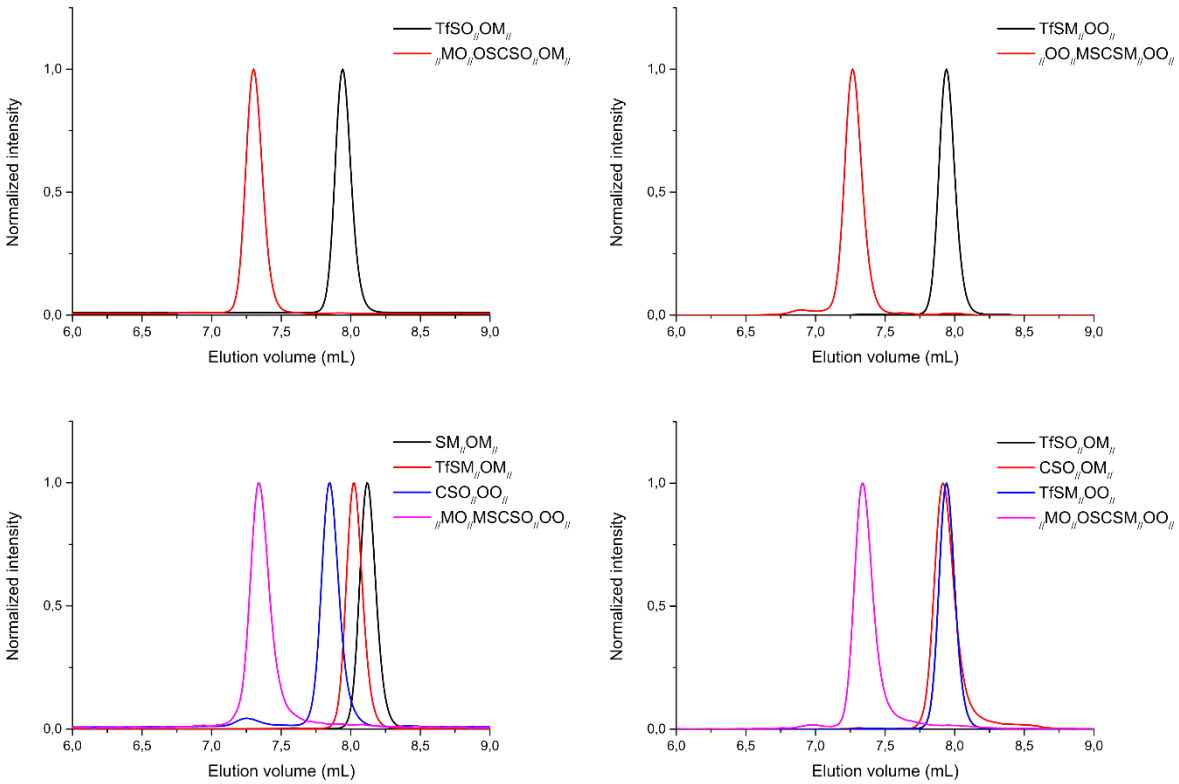


Figure S16. SEC elution graphs of the different tetramers, pentamers and nonamers.

3.3 UV-vis and fluorescence spectroscopy

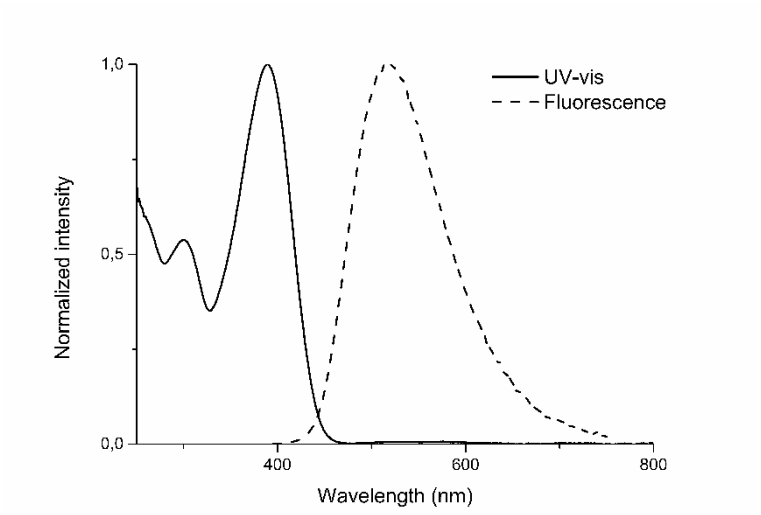


Figure S17. UV-vis (solid line) and fluorescence (dashed line) of the **SM//OM//** tetramer. The optical properties are in correspondence with literature data of equal oligomer backbones with different sidechains (fwhm, Stokes shift, λ_{max}).[1]

3.4 Circular Dichroism spectroscopy and corresponding UV-vis spectroscopy

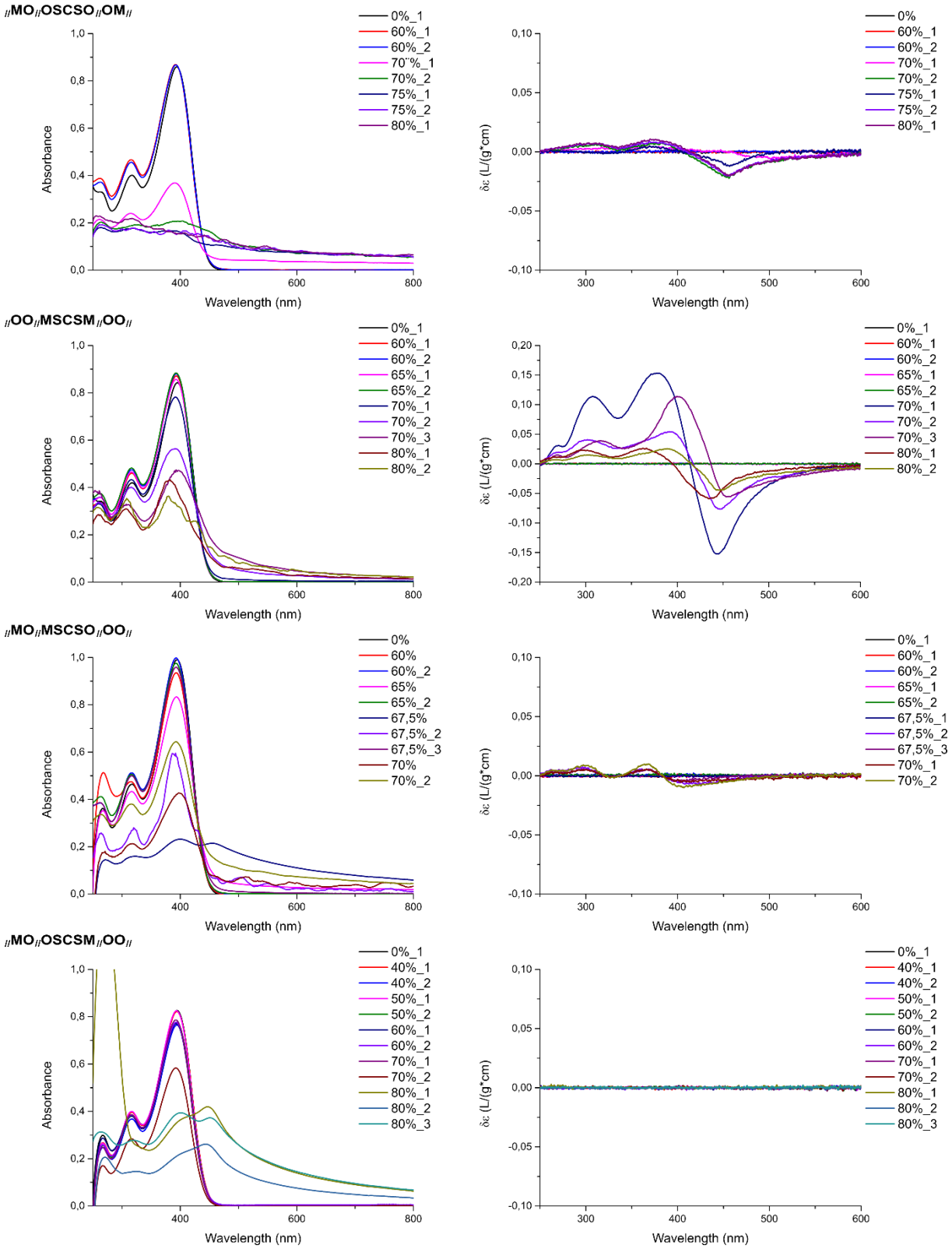


Figure S18. Overview of all the UV-vis and CD measurements. The concentration of nonsolvent (MeOH) is given in percentages followed by the iteration number of the experiment.

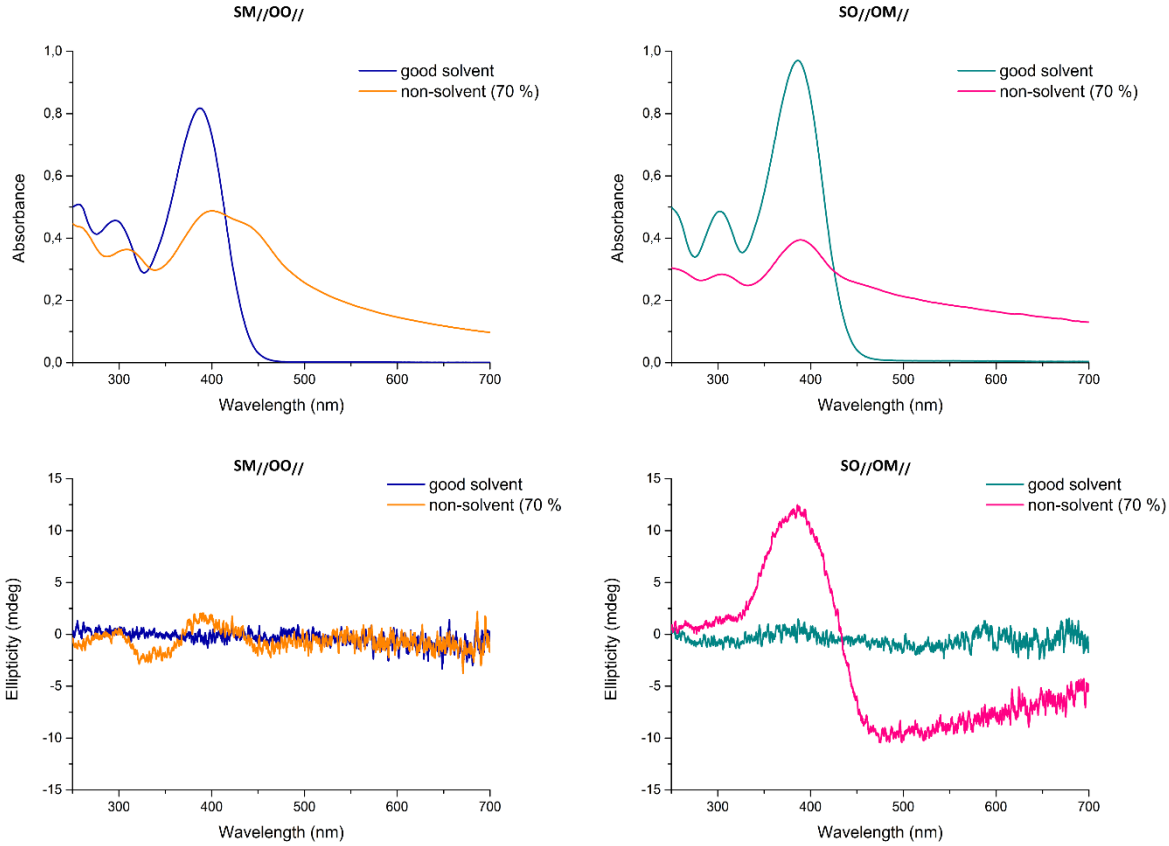


Figure S19. UV-vis (top) and CD (bottom) spectra of the **SM//OO//** (left) and **SO//OM//** (right) tetramers. The data shown are the samples measured in 2 mm quartz cuvettes with isopropanol as good solvent and a mixture of water/MeOH (3/7 ratio) as nonsolvent added to a percentage of 70 %.[1]

4 References

(1) Milis, W.; Peeters, J.; Erkens, R.; De Winter, J.; Gerbaux, P.; Koeckelberghs, G. Versatile Strategy to Develop Sequence-Defined Conjugated Macromolecules: A Powerful Tool toward Tunable Optoelectronic Properties. *ACS Macro Letters* **2024**, 1293–1303. https://doi.org/10.1021/acsmacrolett.4c00526.