

Supporting Information

for

[2.2.2]Paracyclophane-trienes – Attractive Monomers for ROMP

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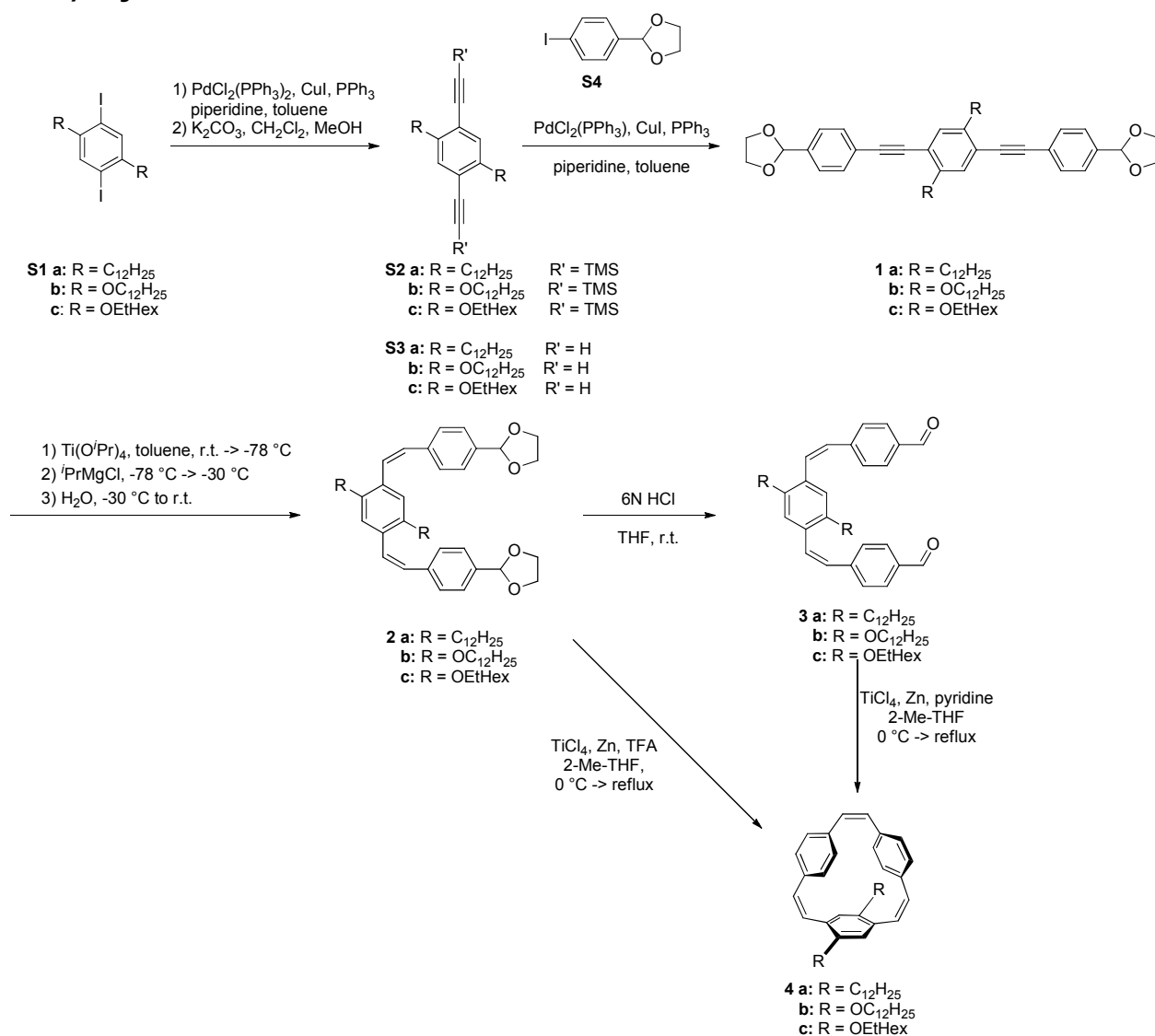
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1) Synthesis



General Remarks:

All reactions requiring exclusion of oxygen and moisture were carried out in heat-gun dried glassware under a dry and oxygen free nitrogen atmosphere. All chemicals were purchased from Sigma-Aldrich Laborchemikalien GmbH, Seelze (Germany) and were used as received. Dry solvents were taken from a *MBraun MB SPS-800* solvent purification system, except of 2-methyltetrahydrofuran, which was dried with sodium and distilled before use. Deuterated solvents were purchased from Deutero GmbH, Kastellaun.

For spectroscopic and analytic characterizations the following methods and devices were used:

NMR-Spectroscopy: All NMR spectra were recorded in the listed solvents at room temperature on a *Bruker Avance III 300* (300 MHz), *Bruker DRX 300* (300 MHz), *Bruker Avance 500*

(500 MHz) or Bruker III (600 MHz, 5 mm $^1\text{H}\{^{13}\text{C}, ^{15}\text{N}, ^{31}\text{P}\}$ QCI CryoProbe) spectrometer. Chemical shifts were reported in ppm and were referenced to the residual solvent signal. The following abbreviations were used for the multiplicity of the signals: s (singlet), d (doublet), t (triplet), qu (quartet), quint (quintet), sex (sextet), m (multiplet), br (broad signal).

CHCl_3 -GPC: The molecular weights (M_n) and polydispersity indices ($\text{PDI} = M_w/M_n$) of polymers were assessed by CHCl_3 GPC PU-2080 from Jasco. For GPC set up 3 PSS SDV columns (100 Å, 1,000 Å, 100,000 Å, particle size: 5 µm) were used with a flow rate of 1 mL/min. As solvent CHCl_3 stabilized by ethanol was used. As detectors a RI-2031 refractometer and a UV2075 detector from Jasco were used. Calibration was achieved using twelve near-monodisperse polystyrene standards purchased from PSS. Data were processed by using PSS WinGPC Unity software.

Optical Spectroscopy: Absorption spectra were recorded on a Jasco V-660 Spectrophotometer; emission spectra on a Jasco FP-6500 Spectrofluorometer.

Quantum Yields: Quantum yields were obtained using the comparative method with fluorescein ($\Phi_{\text{ref}} = 93\%$) in 0.1 M NaOH as the photoluminescent standard. Absorption and emission spectra were measured at four different concentrations for each compound. The intensity of absorption λ_{max} and the area under the emission curve were plotted, which afforded a linear fit. The gradients of the reference and the sample were compared using the following equation:

$$\phi = \Phi_{\text{ref}} \frac{\left(\frac{\text{grad}_x}{\text{grad}_{\text{ref}}}\right)}{\eta_{\text{ref}}^2} \eta_x^2$$

grad_x = gradient of the sample, η_x = refraction index of sample solvent

grad_{ref} = gradient of the reference, η_{ref} = refraction index of reference solvent.

Compounds **S1a,b,c** were synthesized according to literature. ^1H -NMR were in compliance with literature.¹

General Procedure for Sonogashira Coupling of S1: The diiodocompound **S1** was placed in a Schlenk-flask in a nitrogen atmosphere. 1 mol% palladium catalyst, 0.2 equiv. CuI and 0.1 equiv. PPh_3 were added and it was suspended in dry and degased toluene. The mixture was frozen in a liquid nitrogen bath and degased piperidine was added (toluene : piperidine 2 : 1). It was allowed to warm to room temperature and 2.5 equiv. TMS-acetylene were added. The reaction-mixture was stirred at 40 °C over night, quenched by addition of NH_4Cl -solution and extracted with Et_2O . The combined organic phases were washed with water and brine, dried over MgSO_4 and evaporated. The crude product was purified by column chromatography.

S2a: Column chromatography: petrol ether, yield: 98 %, colorless solid, $^1\text{H-NMR}$, CDCl_3 (δ , 300 MHz): 0.25 (s, 18H, TMS), 0.88 (m, 6H, CH_3), 1.26-1.31 (m, 36H, CH_2), 1.53-1.62 (m, 4H, CH_2), 2.68 (t, 4H, CH_2), 7.24 (s, 2H, Ar H).

S2b: Column chromatography: petrol ether / ethyl acetate 15 : 1, yield: 98 %, yellow solid, $^1\text{H-NMR}$, CDCl_3 (δ , 300 MHz): 0.20 (s, 18H, TMS), 0.81 – 0.85 (m, 4H, CH_3), 1.15 – 1.34 (m, 32H, CH_2), 1.37 – 1.50 (m, 4H, CH_2), 1.68 – 1.78 (m, 4H, CH_2), 3.89 (t, $J_{\text{H,H}} = 6.3$ Hz, 4H, OCH_2), 6.83 (s, 2H, Ar H).

S2c: Column chromatography: petrol ether / ethyl acetate 50 : 1, yield: 98 %, yellow oil, $^1\text{H-NMR}$, CDCl_3 (δ , 300 MHz): 0.24 (s, 18H, TMS), 0.87 – 0.98 (m, 12H, CH_3), 1.24 – 1.65 (m, 18H, CH_2), 1.66 – 1.79 (m, 2H, CH), 3.77 – 3.09 (m, 4H, OCH_2), 6.88 (s, 2H, H^{ar}).

General Procedure for deprotection of S2: Compound S2 was dissolved in a minimum amount of a solvent mixture of CH_2Cl_2 : MeOH (2 : 1) and nitrogen is bubbled through the solution for 30 min while stirring. 10 equiv. of freshly powdered potassium carbonate was added and the reaction was stirred vigorously overnight. The reaction quenched by the addition of water, extracted with CH_2Cl_2 , dried over MgSO_4 and evaporated. The crude product was purified by column chromatography.

S3a: Column chromatography: petrol ether, yield: 98 %, bluish solid, $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 0.86-0.91 (m, 6H, CH_3), 1.26-1.32 (m, 36H, CH_2), 1.59-1.63 (m, 4H, CH_2), 2.71 (t, $J_{\text{H,H}} = 7.8$ Hz, 4H, CH_2), 3.28 (s, 2H, $\text{C}\equiv\text{CH}$), 7.29 (s, 2H, Ar H).

S3b: Column chromatography: petrol ether / ethyl acetate 10 : 1, yield: 98 %, yellow solid, $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 0.81 (t, $J_{\text{H,H}} = 6.6$ Hz, 6H, CH_3), 1.13 – 1.45 (m, 36H, CH_2), 1.68 – 1.77 (m, 4H, CH_2), 3.25 (s, 2H, $\text{C}\equiv\text{CH}$), 3.90 (t, $J_{\text{H,H}} = 6.6$ Hz, 4H, OCH_2), 6.88 (s, 2H, Ar H).

S3c: Column chromatography: petrol ether / ethyl acetate 50 : 1, yield: 94 %, brown oil, $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ): 0.86 – 0.97 (m, 12H, CH_3), 1.00 – 1.08 (m, 4H, CH_2), 1.24 – 1.59 (m, 12H, CH_2), 1.68 – 1.82 (m, 2H, CH), 3.30 (s, 2H, $\text{C}\equiv\text{CH}$), 3.85 (d, 4H, $J_{\text{H,H}} = 5.8$ Hz, OCH_2), 6.95 (s, 2H, H^{ar}).

Compound **S4** was synthesized according to literature.¹ $^1\text{H-NMR}$ were in compliance with literature.²

1a: 1.70 g 1,4-Didodecyl-2,5-diethynylbenzene (3.67 mmol), 2.13 g 2-(4-iodophenyl)-1,3-dioxolane (7.72 mmol), 96.4 mg triphenylphosphine (367 μmol), 140 mg copper(I) iodide (36.7 μmol) and 25.8 mg $\text{PdCl}_2(\text{PPh}_3)_2$ (36.7 μmol , 1 mol%) were placed in a schlenk flask, dried in vacuum and dissolved in 18 mL dry and degassed toluene. The mixture was frozen in a liquid nitrogen bath and 9 mL dry and degassed piperidine were added. The solution was allowed to warm to room temperature and stirred for 2 d at 60 °C. The mixture was quenched with aqueous

NH₄Cl solution and extracted with Et₂O. The combined organic layers were washed with water, brine and dried over MgSO₄. The solvent was evaporated and the residue was purified by column chromatography (silica gel, petrol ether / ethyl acetate 15 : 1) to yield 2.23 g (80 %, 2.93 mmol) of a light beige colored solid.

¹H-NMR, C₆D₆ (δ, 600 MHz): 0.91 - 0.93 (m, 6H, CH₃), 1.27 - 1.458 (m, 36H, CH₂), 1.74 - 1.79 (m, 6H, CH₂), 2.91 (t, 4H, *J*_{H,H} = 7.6 Hz, CH₂), 3.42 - 3.48 (m, 4H, OCH₂CH₂O), 3.53 - 3.59 (m, 4H, OCH₂CH₂O), 5.71 (s, 2H, CH^{acetal}), 7.48 (d, 4H, *J*_{H,H} = 7.6 Hz, CH^{ar}), 7.56 (s, 2H, CH^{ar}), 7.61 (d, 4H, *J*_{H,H} = 7.7 Hz, CH^{ar}), **¹³C-NMR, C₆D₆ (δ, 150 MHz):** 14.0 (CH₃), 22.8, 29.5, 29.6, 29.6, 29.7, 29.8, 30.8, 32.0, 34.2 (CH₂), 64.8 (OCH₂CH₂O), 89.3, 94.3 (C≡C), 103.1 (C^{acetal}), 123.0, 123.2, 126.8, 128.0, 131.4, 132.7, 139.0, 132.6 (C^{ar}). **EA:** C: 82.24 %, H: 9.20 % (calc.: C: 82.27 %, H: 9.29 %). **HR-MS: (FAB+)** 758.5256 (calc.: 758.5274). **Mp (°C):** 53.

1b: 2.60 g 1,4-Didodecyloxy-2,5-diethynylbenzene (5.25 mmol), 3.05 g 2-(4-Iodophenyl)-1,3-dioxolane (11.0 mmol), 36.9 mg PdCl₂(PPh₃)₂ (52.6 μmol, 1 mol%), 137.8 mg PPh₃ (525.5 μmol) and 100.1 mg CuI (525.5 μmol) were placed in a Schlenk tube, dried in vacuum and put under a nitrogen atmosphere. 30 mL dry and degased toluene were added and it was frozen in a liquid nitrogen bath. 15 mL dry and degased piperidine were added and it was allowed to warm to room temperature. The reaction was stirred for 3 d at 70 °C. It was quenched by the addition of NH₄Cl-solution, extracted with Et₂O washed with water and brine, dried over MgSO₄ and purified by column chromatography (petrol ether / ethyl acetate 15 : 1) to yield 3.51 g (4.43 mmol, 84 %) of a light yellow solid.

¹H-NMR, CDCl₃ (δ, 300 MHz): 0.89 – 0.98 (m, 6H, CH₃), 1.23 – 1.40 (m, 32H, CH₂), 1.41 - 1.54 (m, 4H, CH₂), 1.62 – 1.75 (m, 4H, CH₂), 3.39 – 3.60 (m, 8H, CH₂), 3.67 (t, *J*_{H,H} = 6.3 Hz, 4H, OCH₂), 5.70 (s, 2H, CH^{acetal}), 7.14 (s, 2H, H^{ar}), 7.47 (d, *J*_{H,H} = 8.1 Hz, 4H, CH^{ar}), 7.70 (d, *J*_{H,H} = 8.1 Hz, 4H, CH^{ar}), **¹³C-NMR, CDCl₃ (δ, 75 MHz):** 14.4 (CH₃), 23.2, 26.5, 29.7, 29.9, 29.9, 30.1, 30.2, 30.2, 32.4 (CH₂), 65.1 (OCH₂CH₂O), 69.4 (OCH₃), 87.7, 95.4 (C≡C), 103.5 (CH^{acetal}), 114.7, 117.3, 124.9, 127.1, 127.9, 131.8, 139.3, 154.4 (C^{ar}). **EA:** C: 78.86 %, H: 8.96 % (calc.: C: 78.95 %, H: 8.92 %). **HR-MS: (FAB+)** 790.5194 (calc.: 790.5172). **Mp (°C):** 83.

1c: 4.00 g 1,4-diethynyl-2,5-di(2-ethylhexyloxy)benzene (10.5 mmol), 6.06 g 2-(4-iodophenyl)-1,3-dioxolane (22.0 mmol), 146.8 mg PdCl₂(PPh₃)₂ (209 μmol, 2 mol%), 274 mg PPh₃ (1.05 mmol) and 398 mg CuI (2.09 mmol) were placed in a Schlenk tube, dried in vacuum and put under a nitrogen atmosphere. 40 mL dry and degased toluene were added and it was frozen in a liquid nitrogen bath. 20 mL degased piperidine were added, it was allowed to warm to room

temperature and stirred for 2 d at 70 °C. The reaction was quenched by the addition of NH₄Cl-solution, extracted with Et₂O washed with water and brine, dried over MgSO₄ and purified by column chromatography (silica gel, petrol ether / ethyl acetate 10 : 1 to 7 : 1) to yield 6.36 g of a yellow solid (90 %, 9.37 mmol).

¹H-NMR, CDCl₃ (δ, 300 MHz): 0.88 (t, *J*_{H,H} = 7.0 Hz, 6H, CH₃), 0.96 (t, *J*_{H,H} = 7.4 Hz, 6H, CH₃), 1.24 – 1.68 (m, 20H, CH₂), 1.72 – 1.86 (m, 2H, CH), 3.86 – 3.97 (m, 4H, OCH₂), 4.00 – 4.17 (m, 8H, OCH₂CH₂O), 5.83 (s, 2H, CH^{acetal}), 7.01 (s, 2H, H^{ar}), 7.46 (d, *J*_{H,H} = 8.2 Hz, 4H, H^{ar}), 7.54 (d, *J*_{H,H} = 8.2 Hz, 4H, H^{ar}), **¹³C-NMR, CDCl₃ (δ, 100 MHz):** 11.4, 14.2 (CH₃), 23.2, 24.1, 29.2, 30.7 (CH₂), 39.7 (CH), 65.4 (OCH₂CH₂O), 72.0 (OCH₂), 88.6, 94.6 (C≡C), 103.4 (C^{acetal}), 113.9, 116.5, 124.5, 126.5, 131.6, 137.8, 153.9 (C^{ar}). **EA:** C: 77.57 %, H: 8.07 % (calc.: C: 77.84 % H: 8.02 %). **HRMS:** (FAB+) 679.39883 (M+ +H; calc.: 679.39986). **Mp (°C):** 82.

2a: To a solution of 2.00 g of 2,2'-[(2,5-didodecylbenzene-1,4-diyl)bis(ethyne-2,1-diyl)benzene-4,1-diyl]bis(1,3-dioxolane) (2.63 mmol) in 150 mL dry toluene under a nitrogen atmosphere were added 5.47 g Ti(O^{*i*}Pr)₄ (19.2 mmol, 5.6 mL) and it was cooled to -78 °C. 3.52 g ^{*i*}PrMgCl (34.3 mmol, 2 M in THF) were slowly added and it was stirred for 30 min at -78 °C. The reaction was allowed to warm to -30 °C, stirred for 5 h and quenched with 10 mL H₂O. It was allowed to warm to room temperature and diluted with Et₂O. The organic layer was washed with water, brine and dried over MgSO₄. The crude product was purified by column chromatography (petrol ether / ethyl acetate 20 : 1) to yield 1.02 g (2.66 mmol, 51 %) of a yellow solid.

¹H-NMR, C₆D₆ (δ, 600 MHz): 0.91 - 0.93 (m, 6H, CH₃), 1.23 - 1.29 (m, 36H, CH₂), 1.50 (br, 4H, CH₂), 2.48 (t, *J*_{H,H} = 7.6 Hz, 4H, CH₂), 3.44 - 3.49 (m, 4H, OCH₂CH₂O), 3.57 - 3.63 (m, 4H, OCH₂CH₂O), 5.72 (s, 2H, CH^{acetal}), 6.52 (d, *J*_{H,H} = 12.1 Hz, 2H, CH^{vinyl}), 6.74 (d, *J*_{H,H} = 12.1 Hz, 2H, CH^{vinyl}), 7.26 (s, 2H, CH^{ar}), 7.30 (d, *J*_{H,H} = 7.8 Hz, 4H, CH^{ar}), 7.44 (d, *J*_{H,H} = 7.9 Hz, 4H, CH^{ar}), **¹³C-NMR, C₆D₆ (δ, 150 MHz):** 14.0 (CH₃), 22.8, 29.5, 29.6, 29.7, 29.8, 30.8, 32.0, 33.1 (CH₂), 64.7 (OCH₂CH₂O), 103.5 (C^{acetal}), 126.5, 128.0, 129.1 (C^{ar}), 130.0, 130.2 (C^{vinyl}), 130.6, 135.9, 137.7, 137.9, 138.5 (C^{ar}). **EA:** C: 82.08 %, H: 9.82 % (calc.: C: 81.84 %, H: 9.77 %). **HR-MS:** (FAB+) 762.5621 (calc.: 762.5587). **Mp (°C):** 56.

2b: To a solution of 3.00 g of 2,2'-[(2,5-didodecyloxybenzene-1,4-diyl)bis(ethyne-2,1-diyl)benzene-4,1-diyl]bis(1,3-dioxolane) (3.79 mmol) in 300 mL dry toluene under a nitrogen atmosphere were added 8.87 g Ti(O^{*i*}Pr)₄ (27.7 mmol, 8.1 mL) and it was cooled to -78 °C. 5.07 g ^{*i*}PrMgCl (49.3 mmol, 2 M in THF) were slowly added and it was stirred for 30 min at -78 °C. The reaction was allowed to warm to -30 °C, stirred for 5 h and quenched with 10 mL H₂O. It was

allowed to warm to room temperature and diluted with Et₂O. The organic layer was washed with water, brine and dried over MgSO₄. The crude product was purified by column chromatography (petrol ether / ethyl acetate 20 : 1) to yield 2.14 g (2.69 mmol, 71 %) of a yellow solid.

¹H-NMR, CDCl₃ (δ, 600 MHz): 0.91 – 0.93 (m, 6H, CH₃), 1.21 – 1.36 (m, 36H, CH₂), 1.50 – 1.54 (m, 4H, CH₂), 3.46 – 3.50 (m, 8H, OCH₂CH₂O), 3.60 – 3.62 (m, 4H, CH₂), 5.69 (s, 2H, CH^{acetal}), 6.62 (d, J_{H,H} = 12.3 Hz, 2H, CH^{vinyl}), 7.02 (s, 2H, CH^{ar}), 7.09 (d, J_{H,H} = 12.3 Hz, 2H, CH^{vinyl}), 7.36 – 7.41 (m, 8H, CH^{ar}). **¹³C-NMR, CDCl₃ (δ, 150 MHz):** 14.4 (CH₃), 23.2, 26.5, 29.7, 29.8, 29.9, 30.1, 30.1, 30.2, 30.2, 32.4 (CH₂), 65.2 (OCH₂), 65.3, 68.8 (OCH₂CH₂O), 104.0 (CH^{acetal}), 114.5, 126.7 (C^{ar}), 126.8 (C^{vinyl}), 127.0, 129.3 (C^{ar}), 129.9 (C^{vinyl}), 137.8, 139.1, 151 (C^{ar}). **IR (neat, ν, cm⁻¹):** 2920 (s), 2850 (s), 1739 (w), 1497 (m), 1472 (s), 1420 (s), 1210 (s), 1077 (s), 839 (s), 720 (m). **EA:** C: 78.44 %, H: 9.27 % (calc.: C: 78.55 %; H: 9.38 %). **HR-MS:** (FAB+) 794.5521 (calc.: 794.5485). **Mp (°C):** 65.

2c: To a solution of 3.00 g 2,2'-[(2,5-di(2-ethylhexyloxy)benzene-1,4-diyl)bis(ethyne-2,1-diyl)benzene-4,1-diyl]bis(1,3-dioxolane) (4.42 mmol) in 150 mL dry toluene under a nitrogen atmosphere were added 9.17 g Ti(OⁱPr)₄ (32.3 mmol, 9.5 mL) and it was cooled to -78 °C. 5.91 g ⁱPrMgCl (57.5 mmol, 2 M in THF) were added all at ones and it was stirred for 30 min at -78 °C. The reaction was allowed to -30 °C, stirred for 5 h and quenched with 15 mL H₂O. It was allowed to warm to room temperature and diluted with Et₂O. The organic layer was washed with water and brine, dried over MgSO₄. The crude product was purified by column chromatography (petrol ether / ethyl acetate 15 : 1) to yield 2.54 g (3.72 mmol, 84 %) of a yellow solid.

¹H-NMR, CDCl₃ (δ, 500 MHz): 0.79 (t, J_{H,H} = 7.5 Hz, 6H, CH₃), 0.87 (t, J_{H,H} = 7.1 Hz, 6H, CH₃), 1.14 – 1.39 (m, 20H, CH₂), 1.46 – 1.54 (m, 2H, CH), 3.38 (d, J_{H,H} = 5.7 Hz, 4H, OCH₂), 3.99 – 4.12 (m, 8H, OCH₂CH₂O), 5.76 (s, 2H, CH^{acetal}), 6.58 (d, J_{H,H} = 12.3 Hz, 2H, CH^{vinyl}), 6.69 (s, 2H, H^{ar}), 6.70 (d, J_{H,H} = 12.3 Hz, 2H, H^{vinyl}), 7.33 (2d, J_{H,H} = 8.3 Hz, 4H, H^{ar}). **¹³C-NMR, CDCl₃ (δ, MHz):** 11.2, 14.2 (CH₃), 23.2, 23.9, 29.1, 30.6 (CH₂), 39.3 (CH), 65.4 (OCH₂CH₂O), 71.3 (OCH₂), 103.7 (C^{acetal}), 114.0 (C^{ar}), 126.1 (C^{vinyl}), 126.2, 126.4, 129.4 (C^{ar}), 129.5 (C^{vinyl}), 136.7, 138.7, 150.5 (C^{ar}). **EA:** C: 8.53 %, H: 77.39 % (calc.: C: 8.56 %, H: 77.38 %). **HRMS:** (FAB+) 683.4272 (M⁺ +H; calc.: 683.4312). **Mp (°C):** 53-55.

3a: The reaction was carried out under exclusion of light as good as possible. 500 mg 2,2'-((2,5-didodecylbenzene-1,4-diyl)bis((Z)-ethene-2,1-diyl)benzene-4,1-diyl)bis(1,3-dioxolane) (629 μmol) were dissolved in 10 mL of a mixture of THF and H₂O (3 : 1). 0.5 mL 6 N HCl was added and nitrogen was bubbled through for 30 min. It was stirred vigorously over night. Phases were separated, the aqueous phase extracted with CH₂Cl₂ and the crude mixture was filtered

through a plug of silica. The filtrate was evaporated under exclusion of light to yield quantitatively a yellow solide.

¹H-NMR, CDCl₃ (δ, 600 MHz): 0.91 – 0.93 (m, 6H, CH₃), 1.20 – 1.42 (m, 36H, CH₂), 1.43 – 1.44 (m, 4H, CH₂), 2.44 (t, $J_{H,H}$ = 7.6 Hz, 4H, CH₂), 6.40 (d, $J_{H,H}$ = 12.1 Hz, CH^{vinyl}), 6.75 (d, $J_{H,H}$ = 12.1 Hz, CH^{vinyl}), 7.10 (s, 2H, CH^{ar}), 7.26 (overlapped by solvent, 4H, CH^{ar}), 7.48 (d, $J_{H,H}$ = 7.9 Hz, CH^{ar}), 9.66 (s, 2H, CHO).

3b: The reaction was carried out under exclusion of light as good as possible. 500 mg 2,2'-((2,5-didodecyloxybenzene-1,4-diyl)bis((Z)-ethene-2,1-diyl)benzene-4,1-diyl))bis(1,3-dioxolane) (629 μmol) were dissolved in 10 mL of a mixture of THF and H₂O (3 : 1). 0.5 mL 6 N HCl was added and nitrogen was bubbled through for 30 min. It was stirred vigorously over night. Phases were separated, the aqueous phase extracted with CH₂Cl₂ and the crude mixture was filtered through a plug of silica. The filtrate was evaporated under exclusion of light to yield quantitatively a yellow-green solid.

¹H-NMR, CDCl₃ (δ, 300 MHz): 0.88 (t, $J_{H,H}$ = 6.7 Hz, 6H, CH₃), 1.16 – 1.36 (m, 36H, CH₂), 1.43 - 1.58 (m, 4H, CH₂), 3.49 (t, $J_{H,H}$ = 6.5 Hz, 4H, OCH₂), 6.60 – 6.67 (m, 4H, CH^{ar} + CH^{vinyl}), 6.82 (d, $J_{H,H}$ = 12.3 Hz, 2H, CH^{vinyl}), 7.45 (d, $J_{H,H}$ = 8.2 Hz, 4H, CH^{ar}), 7.76 (d, $J_{H,H}$ = 8.2 Hz, 4H, CH^{ar}), 9.96 (s, 2H, CHO).

3c: The reaction was carried out under exclusion of light as good as possible. 2,2'-((2,5-Di(2-ethylhexyloxy)benzene-1,4-diyl)bis((Z)-ethene-2,1-diyl)benzene-4,1-diyl))bis(1,3-dioxolane) was dissolved in 15 mL of a mixture of THF and H₂O (3 : 1). 0.5 mL 6N HCl was added and the mixture was stirred for 2 h vigorously while bubbling nitrogen through, then without bubbling nitrogen through over night. Phases were separated, the aqueous phase extracted with CH₂Cl₂ and the crude mixture was filtered through a plug of silica. The filtrate was evaporated under exclusion of light.

¹H-NMR, CDCl₃ (δ, 300 MHz): 0.76 (t, $J_{H,H}$ = 7.4 Hz, 6H, CH₃), 0.86 (t, $J_{H,H}$ = 7.0 Hz, 6H, CH₃), 1.09 – 1.35 (m, 18H, CH₂), 1.41 - 1.51 (m, 2H, CH), 3.35 (d, $J_{H,H}$ = 5.7 Hz, 4H, OCH₂), 6.60 – 6.66 (m, 4H, CH^{ar} + CH^{vinyl}), 6.84 (d, $J_{H,H}$ = 12.2 Hz, 2H, CH^{vinyl}), 7.46 (d, $J_{H,H}$ = 8.2 Hz, 4H, CH^{ar}), 7.76 (d, $J_{H,H}$ = 8.2 Hz, 4H, CH^{ar}), 9.95 (s, 2H, CHO).

McMurry reactions starting from 2a-c:

4a: A three necked flask equipped with reflux condenser and dropping funnel was cooled to 0 °C and 100 mL dry 2-Me-THF was added. 1.24 g TiCl_4 (6.55 mmol) was added while stirring and after the addition was completed 857 mg Zn-powder (13.1 mmol) were added carefully. The resulting mixture was refluxed for 2 h and 0.1 mL dry TFA were added. 500 mg 2,2'-((2,5-Didodecylbenzene-1,4-diyl)bis[(Z)-ethene-2,1-diylbenzene-4,1-diyl])bis(1,3-dioxolane) (655 μmol) dissolved in 50 mL dry 2-Me-THF were added drop wise with a syringe pump over a period of 20 h (2.5 mL/h) and the reaction was refluxed for further 3 h. It was cooled to room temperature and quenched by the addition of NaHCO_3 solution. The precipitate was filtered off and both – filter and filter-cake - were extracted with DCM. The combined organic layers were washed with brine, dried over MgSO_4 , evaporated and purified by column chromatography (silica gel, petrol ether) to yield 139 mg (216 μmol , 33 %) of a colorless, viscous liquid.

$^1\text{H-NMR}$, CDCl_3 (δ , 300 MHz): 0.88 - 0.92 (m, 6H, CH_3), 1.29 - 1.44 (m, 40H, CH_2), 2.31 - 2.38 (m, 4H, CH_2), 6.56 (br, 4H, CH^{vinyl}), 6.76 (s, 4H, CH^{ar} + CH^{vinyl}), 6.79 (s, 2H, CH^{ar} + CH^{vinyl}), 6.83 (s, 2H, CH^{ar} + CH^{vinyl}), 6.86 (s, 2H, CH^{ar} + CH^{vinyl}), 6.88 (s, 1H, CH^{ar} + CH^{vinyl}), 6.89 (s, 1H, CH^{ar} + CH^{vinyl}), **$^{13}\text{C-NMR}$, CDCl_3 (δ , 75 MHz):** 14.2 (CH_3), 22.7, 29.4, 29.6, 29.7, 29.7, 29.8, 29.8, 30.6, 32.0, 33.0 (CH_2), 128.3 (C^{vinyl}), 131.7, 132.1, 132.6, 132.6, 134.8, 135.8, 136.1, 136.6 (C^{vinyl} + C^{ar}). **EA:** C: 89.86 %, H: 10.50 % (calc.: C: 89.65 %, H: 10.35 %). **HR-MS:** (FAB+) 642.5186 (calc.:642.5165).

4b: A three necked flask equipped with reflux condenser and dropping funnel was cooled to 0 °C and 100 mL dry 2-Me-THF were added. 1.19 g TiCl_4 (689 μL , 6.29 mmol) were added while stirring and after the addition was completed 822 mg Zn-powder (12.6 mmol) were added carefully. The resulting mixture was refluxed for 2 h and 0.1 mL dry TFA were added. 500 mg 2,2'-((2,5-didodecyloxybenzene-1,4-diyl)bis((Z)-ethene-2,1-diylbenzene-4,1-diyl))bis(1,3-dioxolane) (629 μL) dissolved in 50 mL dry 2-Me-THF were added drop wise with a syringe pump over a period of 25 h (2 mL/h) and the reaction was refluxed for further 3 h. After cooling to room temperature it was quenched by the addition of NaHCO_3 solution. It was filtered through a pad of silica gel and the pad was extracted with CH_2Cl_2 . The organic layers were washed with brine and the combined layers dried over MgSO_4 , evaporated and purified by column chromatography (silica gel, petrol ether / ethyl acetate 250 : 1) to yield 144 mg (34 %; 213 μmol) of a blue shimmering , viscous liquid.

$^1\text{H-NMR}$, CDCl_3 (δ , 300 MHz): 0.81 (t, $J_{\text{H,H}} = 6.7$ Hz, 6H, CH_3), 1.23 - 1.34 (m, 36H, CH_2), 1.54 - 1.66 (m, 4H, CH_2), 3.49 - 3.57 (m, 2H, OCH_2), 3.69 - 3.77 (m, 2H, OCH_2), 6.27 (s, 2H, CH^{ar}),

6.46 - 6.63 (m, 6H, CH^{ar} + CH^{vinyl}), 6.71 - 6.76 (m, 8H, CH^{ar} + CH^{vinyl}), **¹³C-NMR, CDCl₃ (δ, 75 MHz):** 13.1 (CH₃), 21.7, 25.0, 28.3, 28.4, 28.6, 28.6, 28.6, 28.7, 29.3, 30.9 (CH₂), 68.1 (OCH₂), 113.9 (C^{ar}), 126.2 (C^{ar} + C^{vinyl}), 126.7 (C^{ar} + C^{vinyl}), 127.6, 127.9 (C^{vinyl}), 131.7 (C^{ar} + C^{vinyl}), 132.0 (C^{ar} + C^{vinyl}), 135.0, 135.6, 149.8 (C^{ar}). **EA:** C:85.48 %, H: 9.60 % (calc.: C: 85.40 %, H: 9.85 %). **HR-MS:** (FAB+) 674.5060 (calc.:674.5063).

4c: A three necked flask equipped with reflux condenser and dropping funnel was cooled to 0 °C and 100 mL dry 2-Me-THF was added. 1.25 g TiCl₄ (4.39 mmol) were added while stirring and after the addition was completed 574 mg Zn-powder (8.79 mmol) were added carefully. The resulting mixture was refluxed for 2 h and 0.5 mL dry TFA were added. 300 mg 2,2'-((2,5-Di(2-ethylhexyloxy)benzene-1,4-diyl)bis((Z)-ethene-2,1-diyl)benzene-4,1-diyl))bis(1,3-dioxolane) (146 μmol) dissolved in 50 mL dry 2-Me-THF was added drop wise with a syringe pump over a period of 25 h (2.5 mL/h) and the reaction was refluxed for further 3 h. After cooling to room temperature it was quenched by the addition of 10 mL NaHCO₃-solution. It was filtered through a pad of silica gel and the pad was extracted with CH₂Cl₂. The organic layers were washed with brine and the combined layers dried over MgSO₄, evaporated and purified by column chromatography (silica gel, petrol ether / ethyl acetate 400 : 1) to yield 48.6 mg (20 %, 86.4 μmol) of a light yellow, viscous liquid.

¹H-NMR, CDCl₃ (δ, 300 MHz): 0.86 – 0.98 (m, 12H, CH₃), 1.23 – 1.56 (m, 16H, CH₂), 1.61 – 1.73 (m, 2H, CH), 3.57 – 3.66 (m, 2H, OCH₂), 3.67 – 3.77 (m, 2H, OCH₂), 6.38 (s, 2H, CH^{ar}), 6.62 (br, 4H, CH^{vinyl} + CH^{ar}), 6.72 (d, J_{H,H} = 11.3 Hz, 2H, CH^{vinyl}), 6.77 – 6.91 (m, 8H, CH^{ar}). **¹³C-NMR, CDCl₃ (δ, 125 MHz):** 11.2, 11.3, 14.2 (CH₃), 23.18, 23.20, 24.0, 24.1, 29.22, 29.24, 30.65, 30.67 (CH₂), 39.38, 39.71 (CH), 71.49, 71.50 (OCH₂), 114.66, 114.67, 114.73, 114, 75 (C^{vinyl}), 124.35, 124.37, 129.2, 132.9, 133.0, 136.04, 136.05, 136.79, 136.80, 151.26, 151.27 (C^{ar}). **EA:** for compound **4c** no adequate elemental analysis could be achieved. **HR-MS:** (FAB+) 563.3864 (calc.: 563.3889 [M+H]⁺).

McMurry reactions starting from 3a-c:

(for analytics see previous section)

4a: A three necked flask equipped with reflux condenser and dropping funnel was cooled to 0 °C and 140 mL dry 2-Me-THF were added. A TiCl_4 -solution in 10 mL dry 2-Me-THF prepared in a GloveBox was added while stirring and after the addition was completed Zn-powder was added carefully. 1 mL dry pyridine was added and the resulting mixture was refluxed for 2 h. 350 mg of the crude dialdehyde (519 μmol) dissolved in 50 mL dry THF was added drop wise (syringe pump, 8 mL/h) and the reaction was refluxed for further 4 h. It was allowed to cool to room temperature and quenched by the addition of NaHCO_3 solution. It was filtered through a plug of silica and the filter plug extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over MgSO_4 , evaporated and purified by column chromatography (silica gel, petrol ether) to yield 185 mg (55 %; 288 μmol) of a colorless, viscous liquid.

4b: A three necked flask equipped with reflux condenser and dropping funnel was cooled to 0 °C and 100 mL dry 2-Me-THF were added. A TiCl_4 -solution in 10 mL dry 2-Me-THF prepared in a GloveBox was added while stirring and after the addition was completed Zn-powder was added carefully. 1 mL dry pyridine was added and the resulting mixture was refluxed for 2 h. 300 mg of the crude dialdehyde (424 μmol) dissolved in 40 mL dry THF was added drop wise (syringe pump, 8 mL/h) and the reaction was refluxed for further 4 h. It was allowed to cool to room temperature and quenched by the addition of NaHCO_3 solution. It was filtered through a plug of silica and the filter plug extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over MgSO_4 , evaporated and purified by column chromatography (silica gel, petrol ether / ethyl acetate 250 : 1) to yield 167 mg (58 %; 247 μmol) of a slide blue, viscous liquid.

4c: A three necked flask equipped with reflux condenser and dropping funnel was cooled to 0 °C and 100 mL dry 2-Me-THF were added. A TiCl_4 -solution in 10 mL dry 2-Me-THF prepared in a GloveBox was added while stirring and after the addition was completed Zn-powder was added carefully. 1 mL dry pyridine was added and the resulting mixture was refluxed for 2 h. 384 mg of the crude dialdehyde (645 μmol) dissolved in 50 mL dry THF was added drop wise (syringe pump, 8 mL/h) and the reaction was refluxed for further 5 h. It was allowed to cool to room temperature and quenched by the addition of NaHCO_3 solution. It was filtered through a plug of silica and the filter plug extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over MgSO_4 , evaporated and purified by column chromatography (silica gel, petrol ether / ethyl acetate 300 : 1) to yield 230 mg (64 %, 409 μmol) of a pale yellow, viscous liquid.

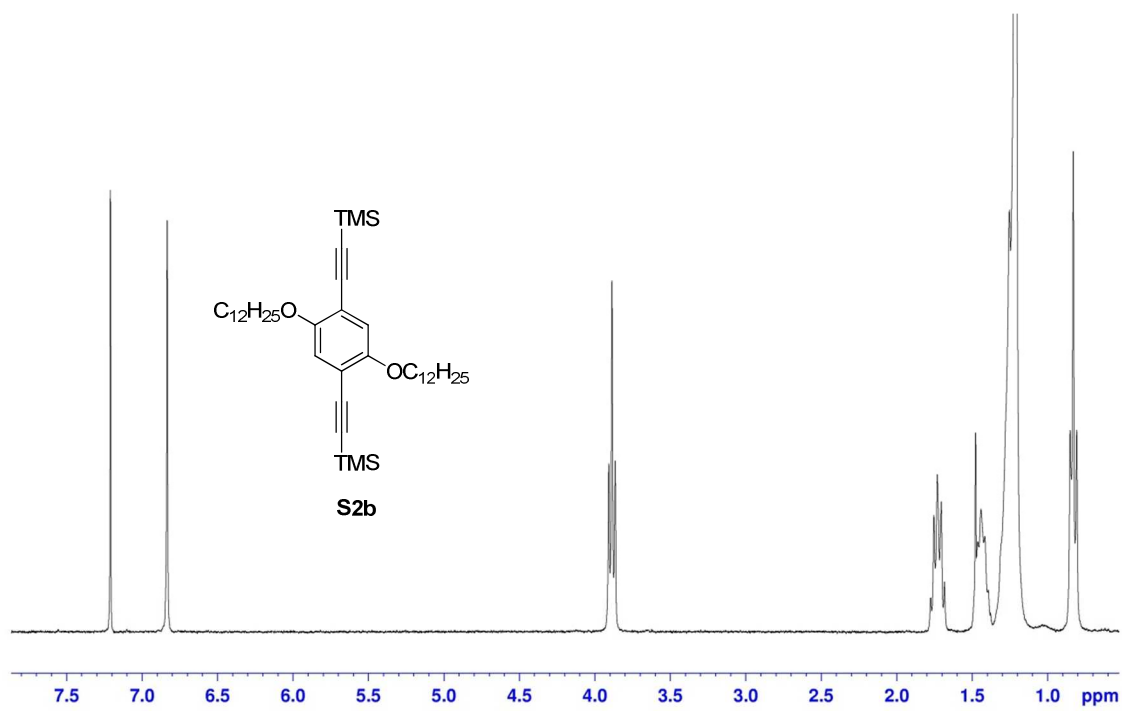
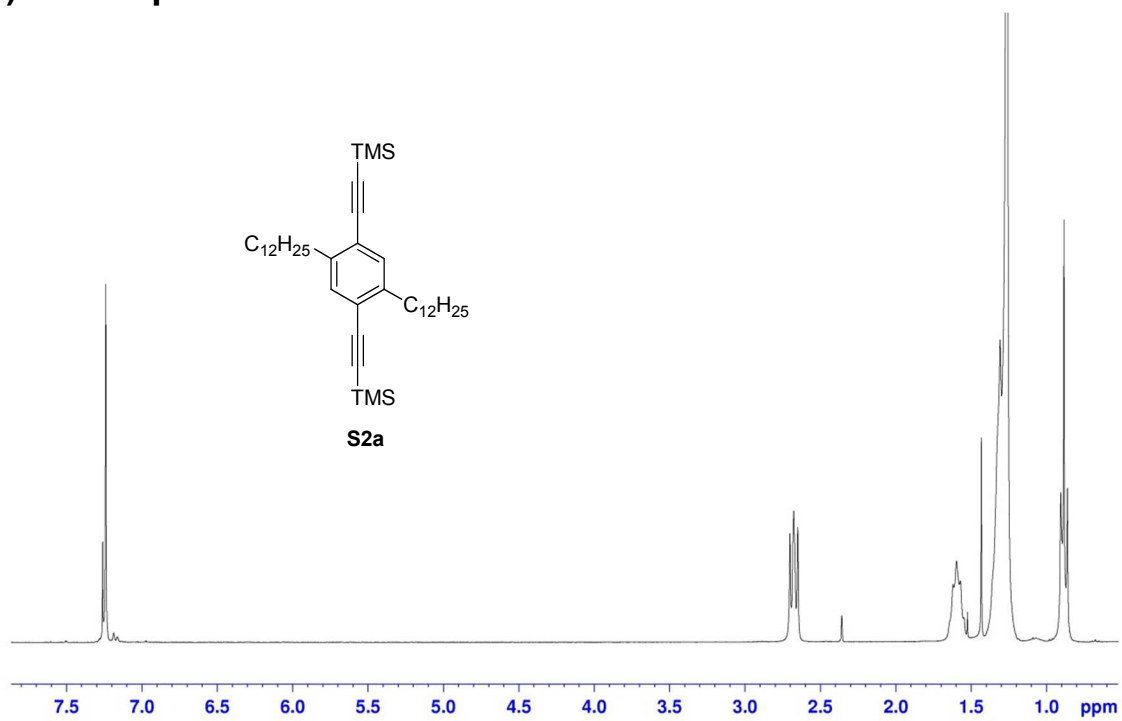
2) Polymerization

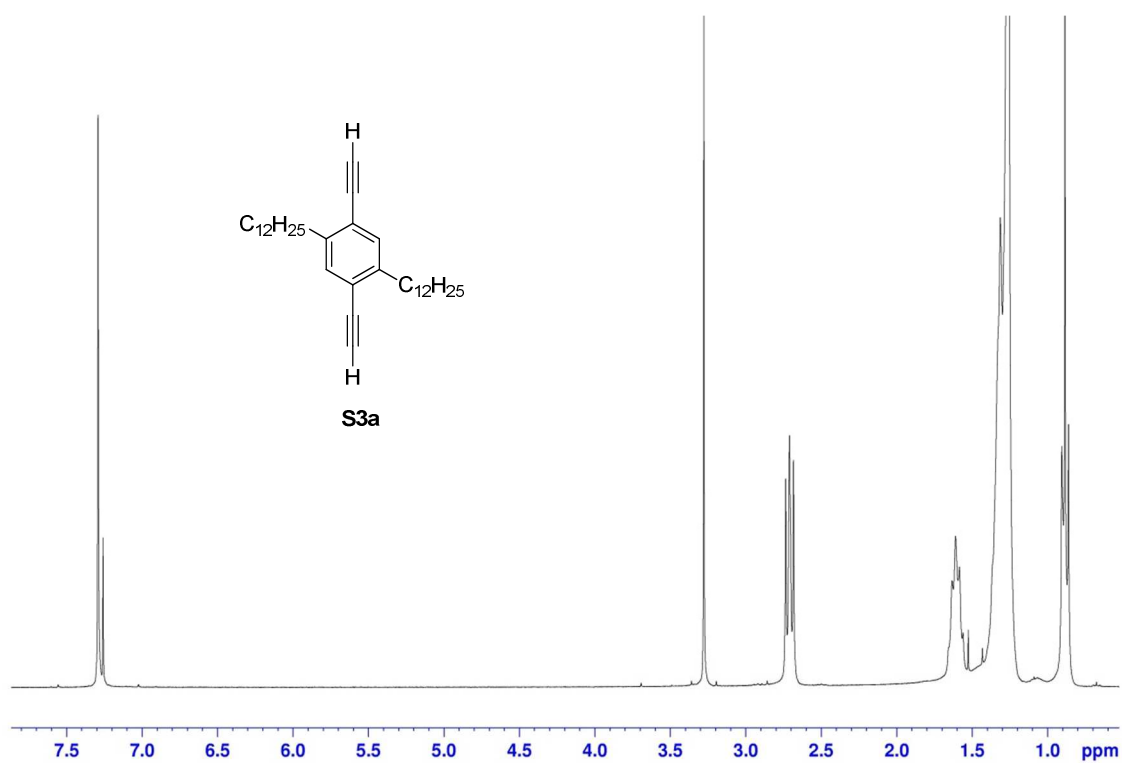
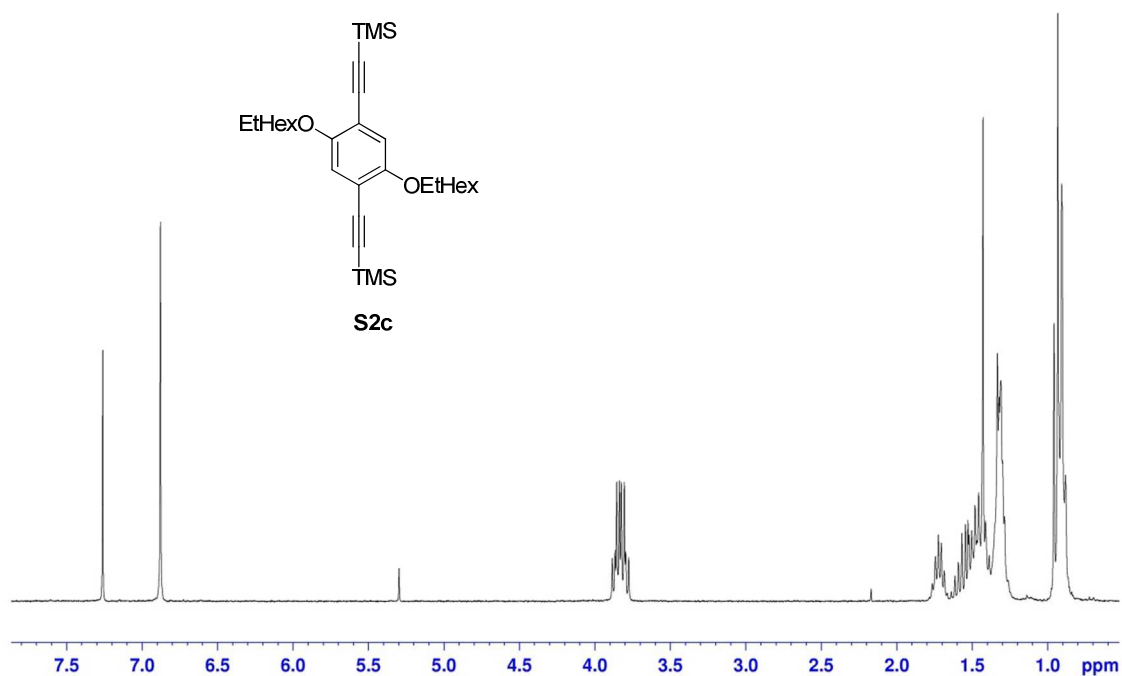
5a: In a Finger-Schlenk under a nitrogen atmosphere 59.6 mg 4,7-didodecyl[2.2.2]paracyclophane-1,9,17-triene (92.7 μmol) were dissolved in 3 ml dry THF. To the monomer solution 0.1 mL of a freshly prepared solution of 2nd generation Hoveyda-Grubbs catalyst in dry THF (9.88 mg in 0.1 mL) was added and it was refluxed for 48 h. The reaction was quenched by the addition of 0.1 mL ethyl vinyl ether and it was stirred additional for 30 min at room temperature. The crude product was precipitated into MeOH, centrifuged and decanted. It was dissolved again in CHCl_3 , precipitated into MeOH, centrifuged and decanted. The residue was dried under reduced pressure to yield 53.6 mg (90 %, 83.4 μmol) of a bright yellow solid.

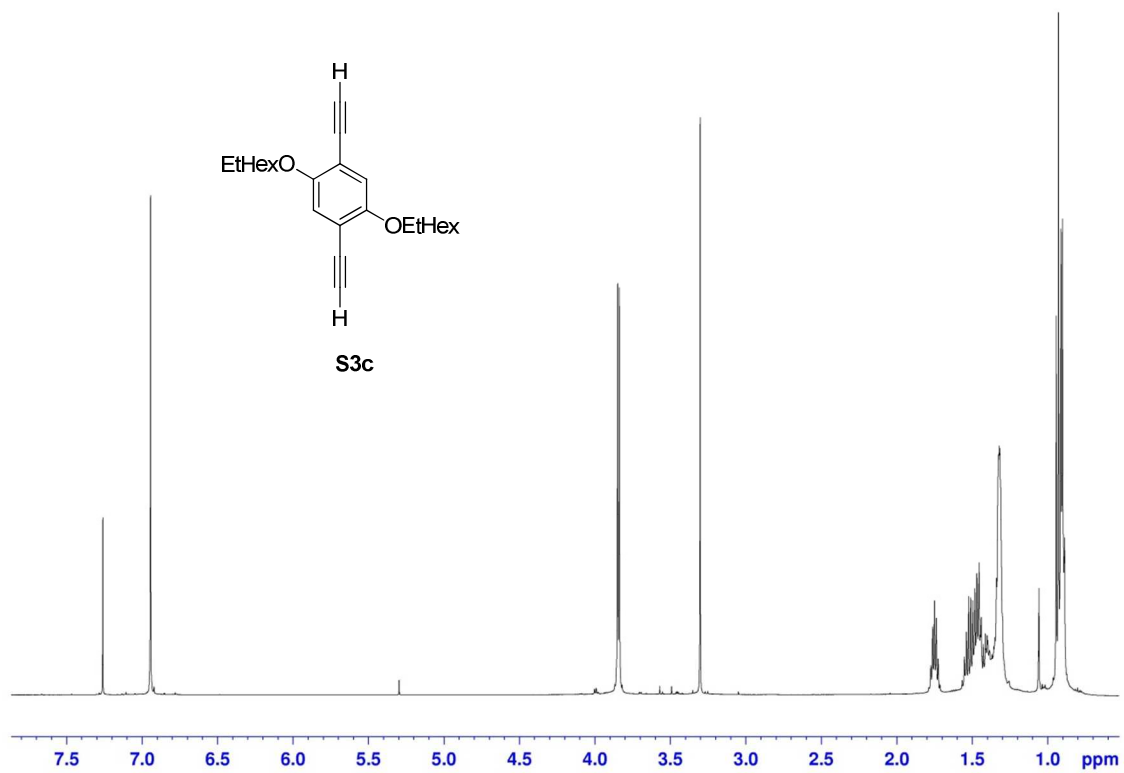
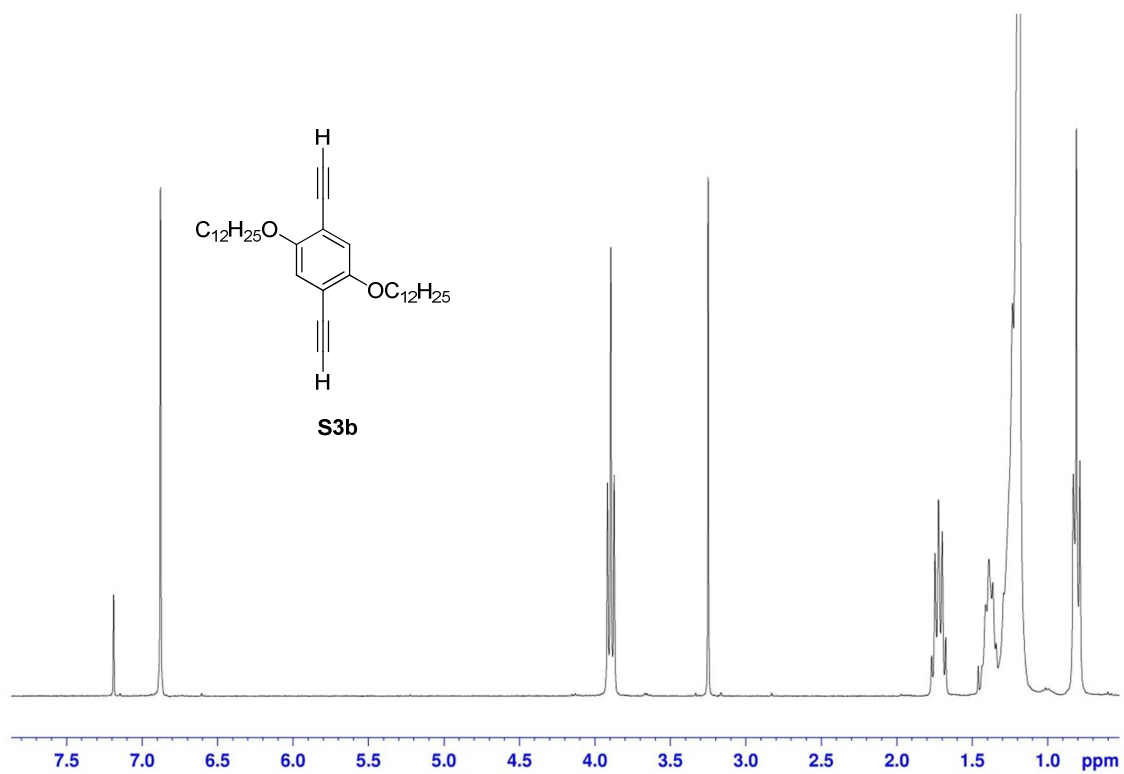
5b: In a Finger-Schlenk under nitrogen atmosphere 53.2 mg 4,7-didodecyloxy [2.2.2]paracyclophane-1,9,17-triene (78.8 μmol) were dissolved in 3 ml dry toluene. To the monomer solution 0.1 mL of a freshly prepared solution of 2nd generation Hoveyda-Grubbs catalyst in dry toluene (9.87 mg in 1 mL) was added and it was refluxed for 48 h. The reaction was quenched by the addition of 0.1 mL ethyl vinyl ether and it was stirred additional for 30 min at room temperature. The crude product was precipitated into MeOH, centrifuged and decanted. It was dissolved again in CHCl_3 , precipitated into MeOH, centrifuged and decanted. The residue was dried under reduced pressure to yield 48.6 mg (91 %, 72.0 μmol) of a bright orange solid.

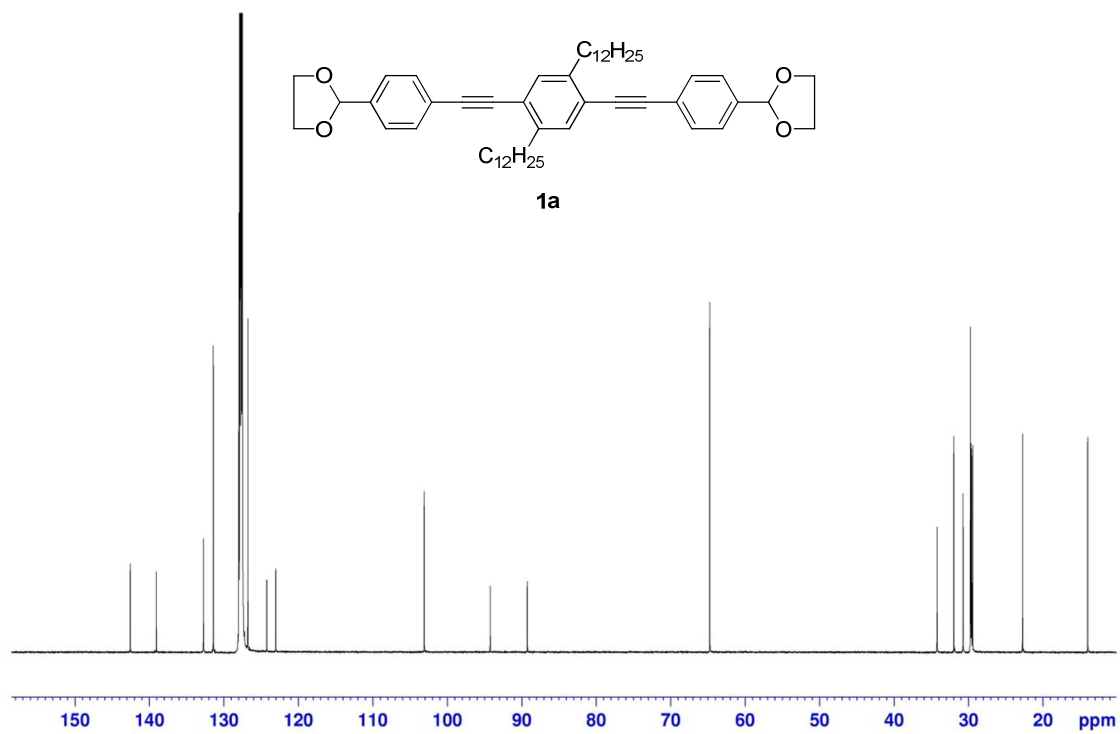
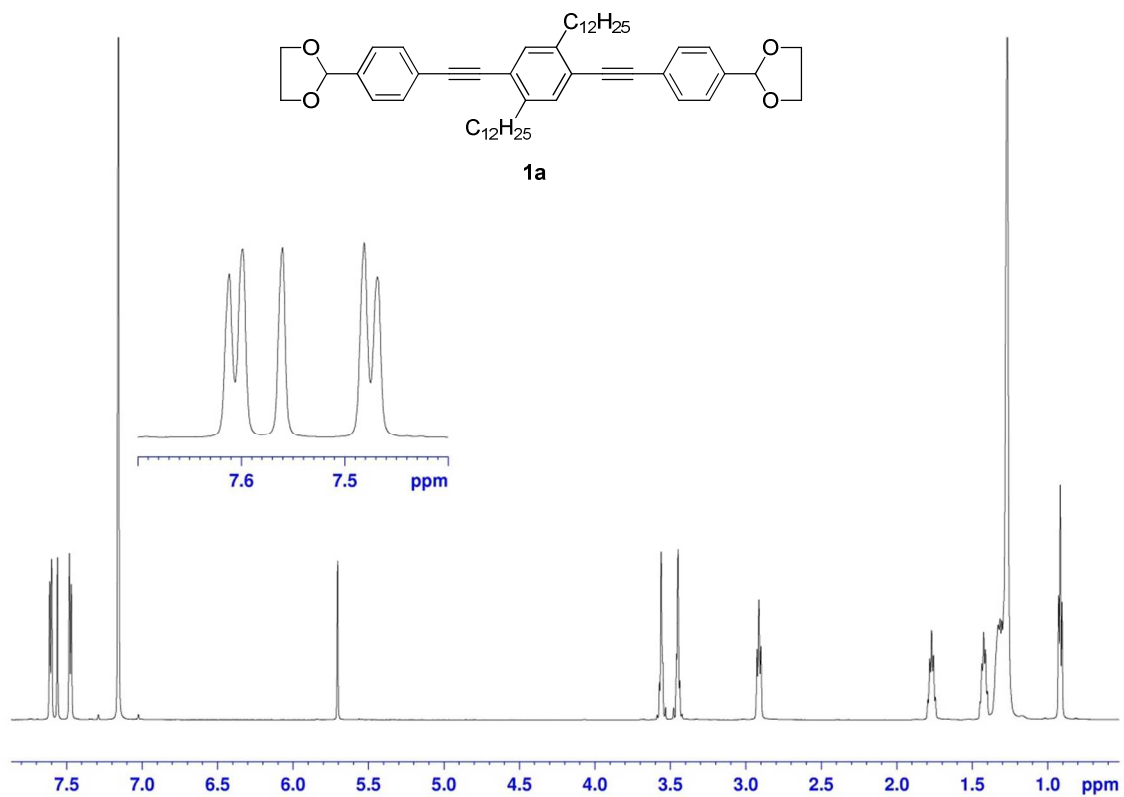
5c: In a Schlenk tube under a nitrogen atmosphere 49.1 mg 4,7-(2-ethylhexyloxy)[2.2.2] paracyclophane-1,9,17-triene (87.4 μmol) were dissolved in 3 mL dry toluene. 0.1 mL of a 2nd generation Hoveyda-Grubbs catalyst solution (5.5 mg in 0.5 mL dry toluene) was added and it was refluxed for 48 h. The reaction was quenched by the addition of 0.5 mL ethyl vinyl ether. The crude product was precipitated into MeOH, centrifuged and decanted. It was dissolved again in CHCl_3 , precipitated into MeOH, centrifuged and decanted. The residue was dried under reduced pressure to yield 45.7 mg (93 %, 81.2 μmol) of a bright orange solid.

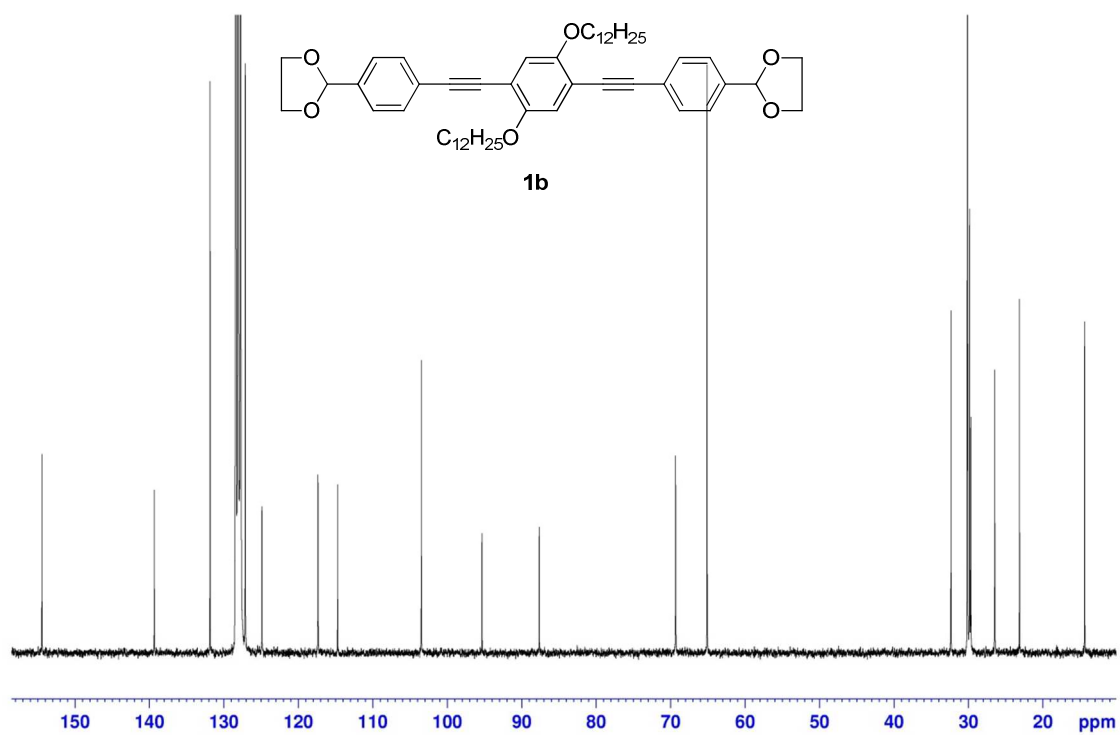
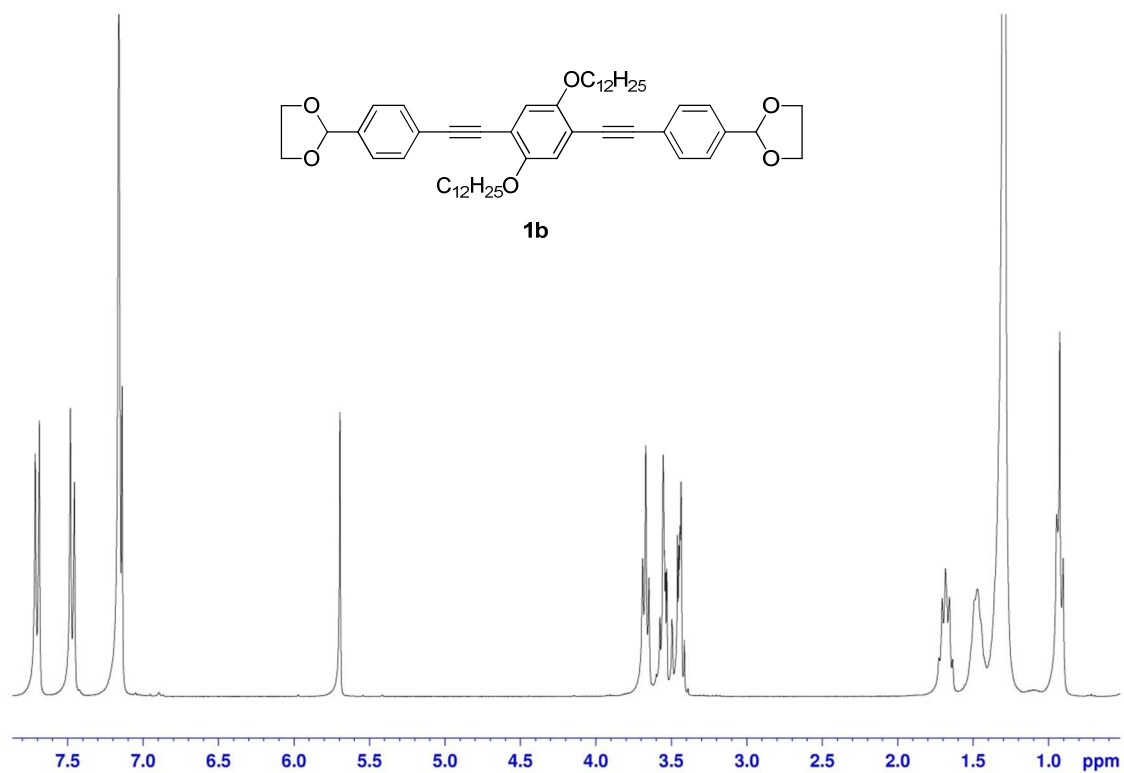
3) NMR-spectra

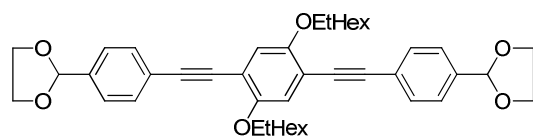




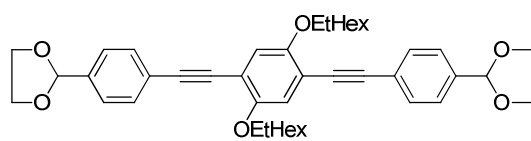
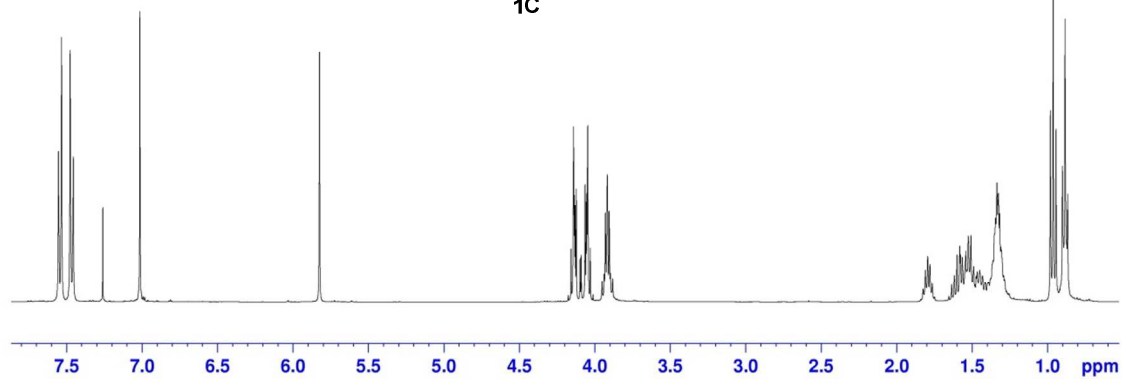




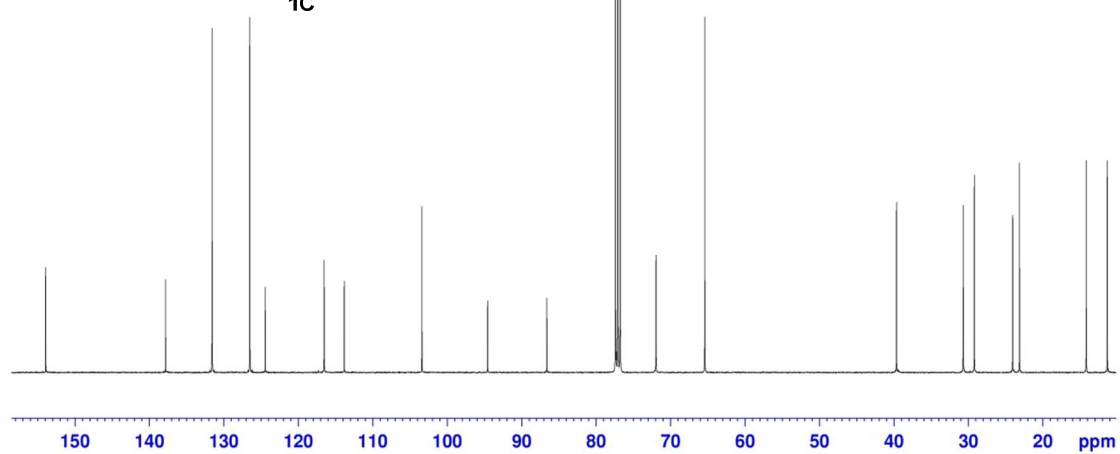


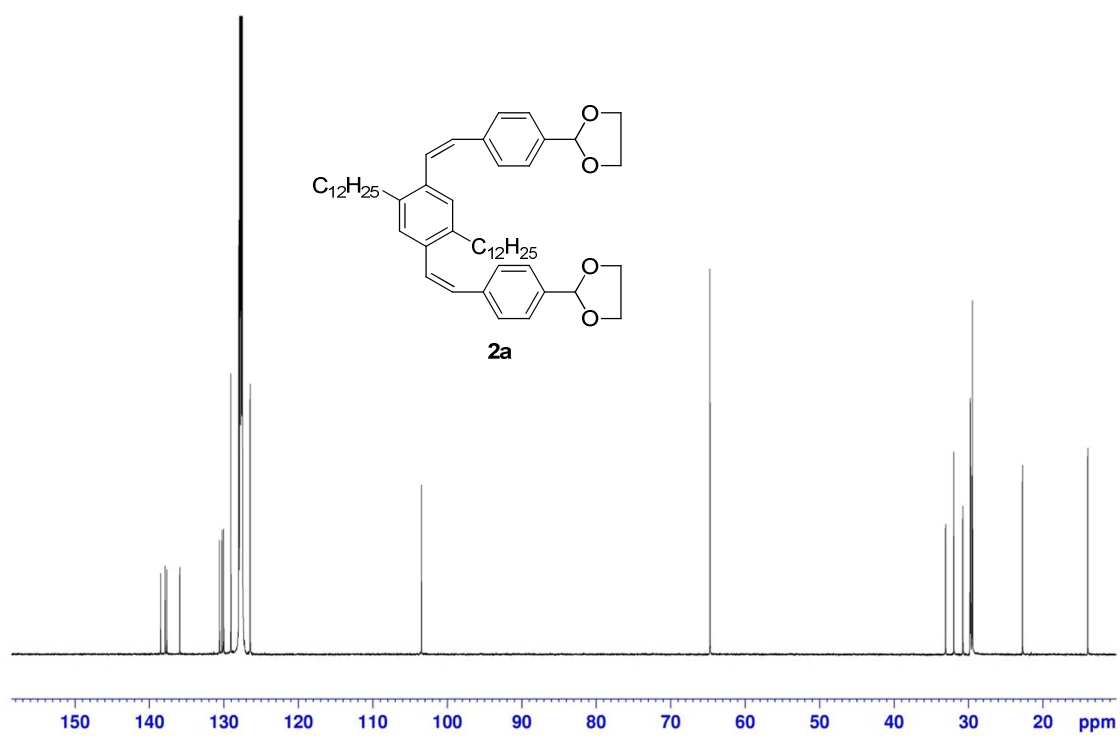
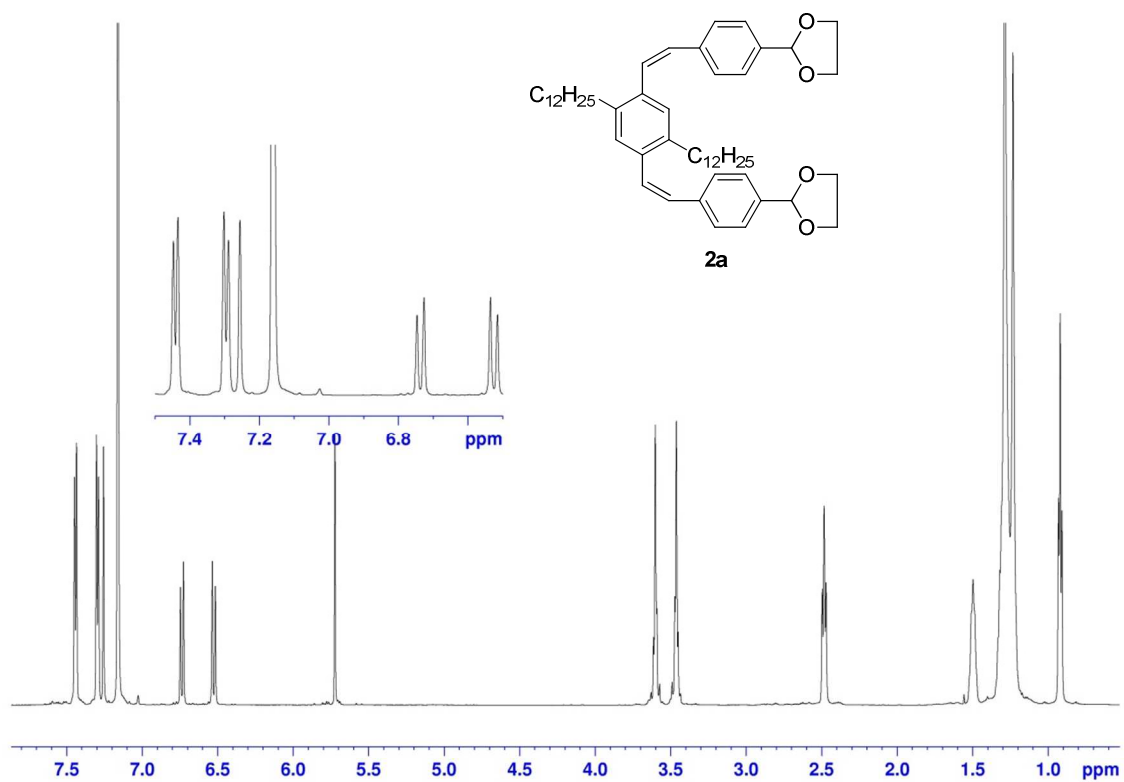


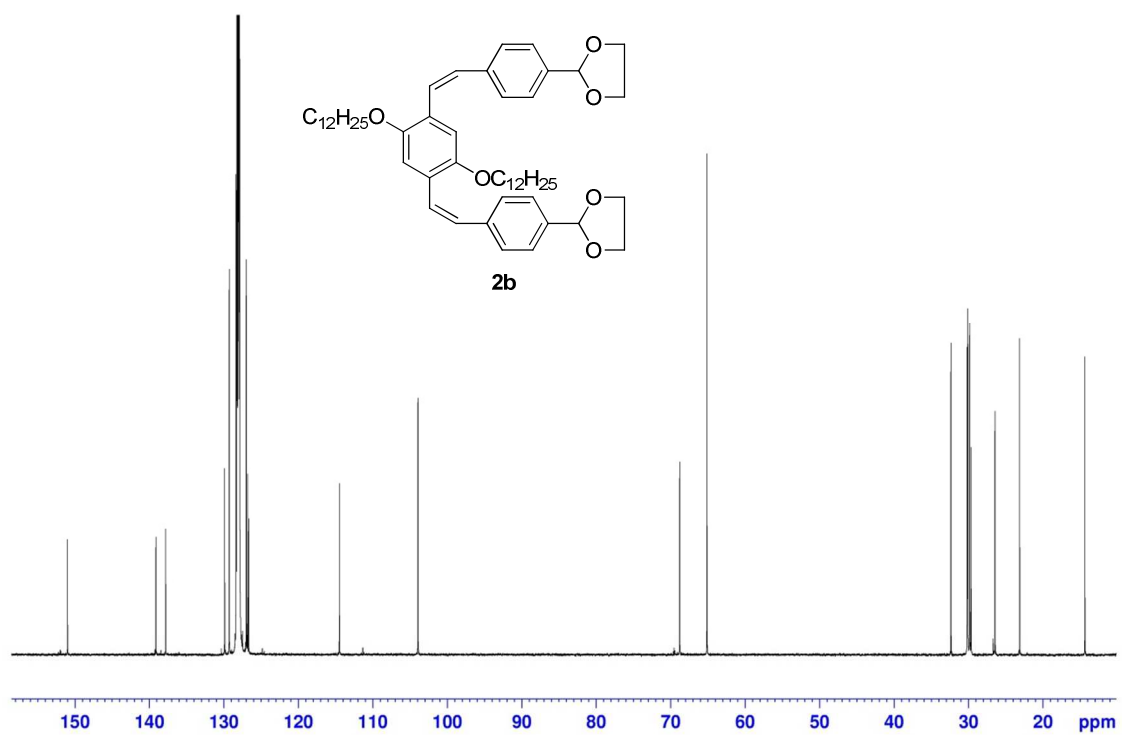
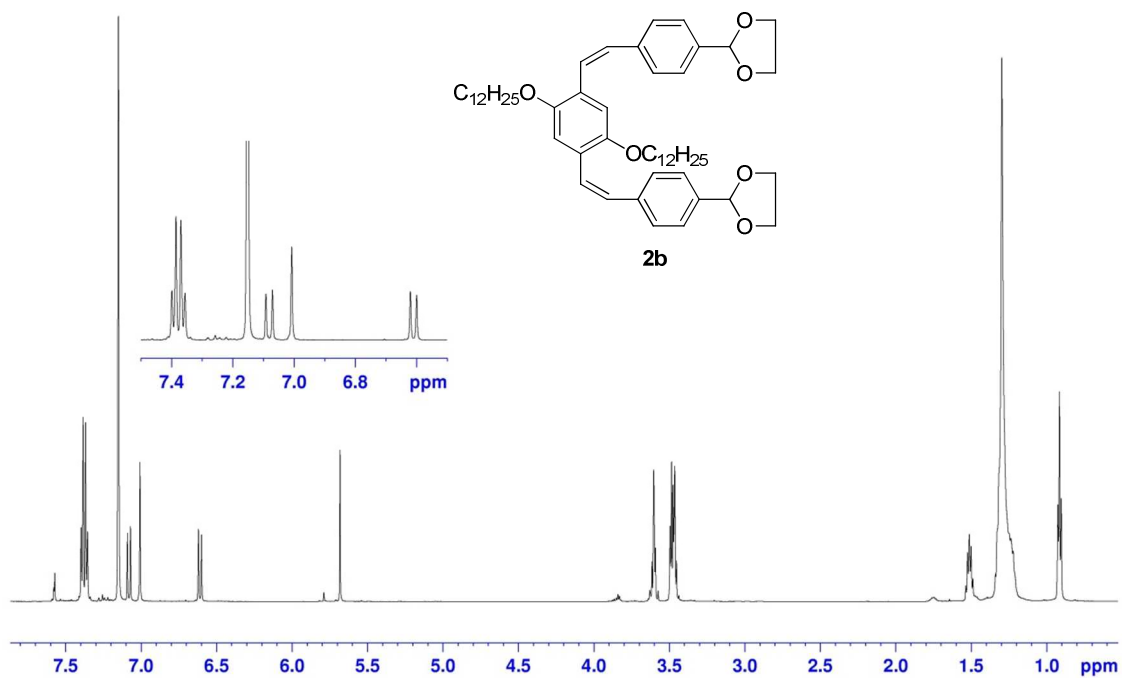
1C

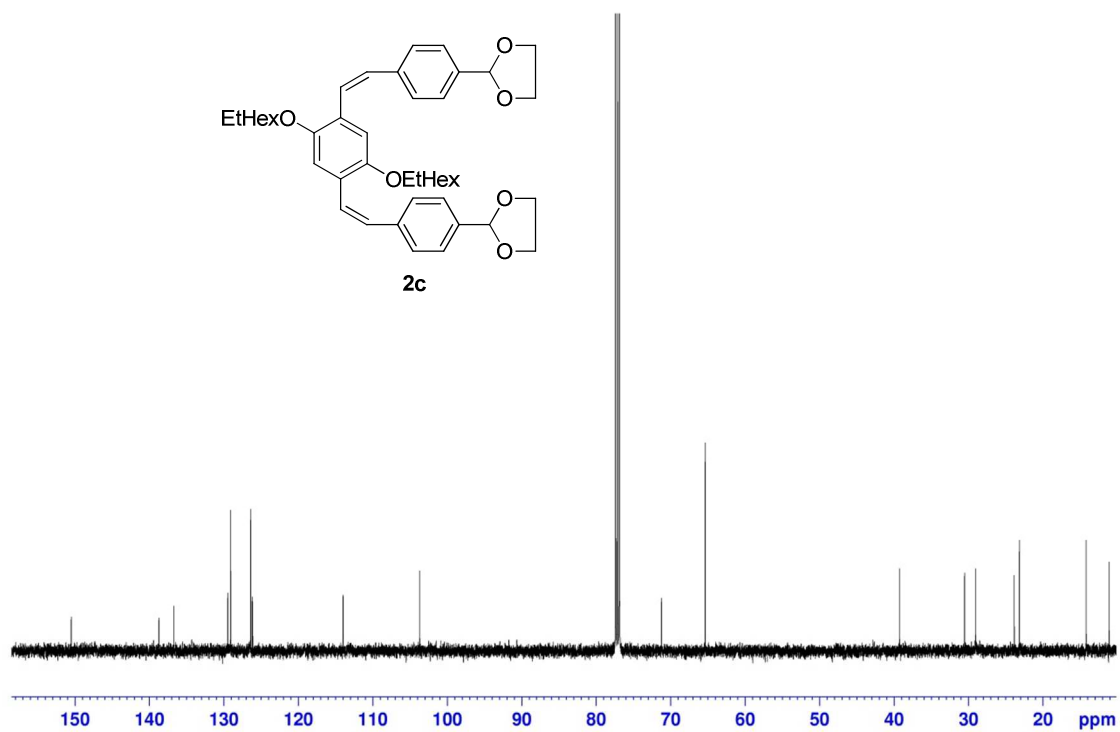
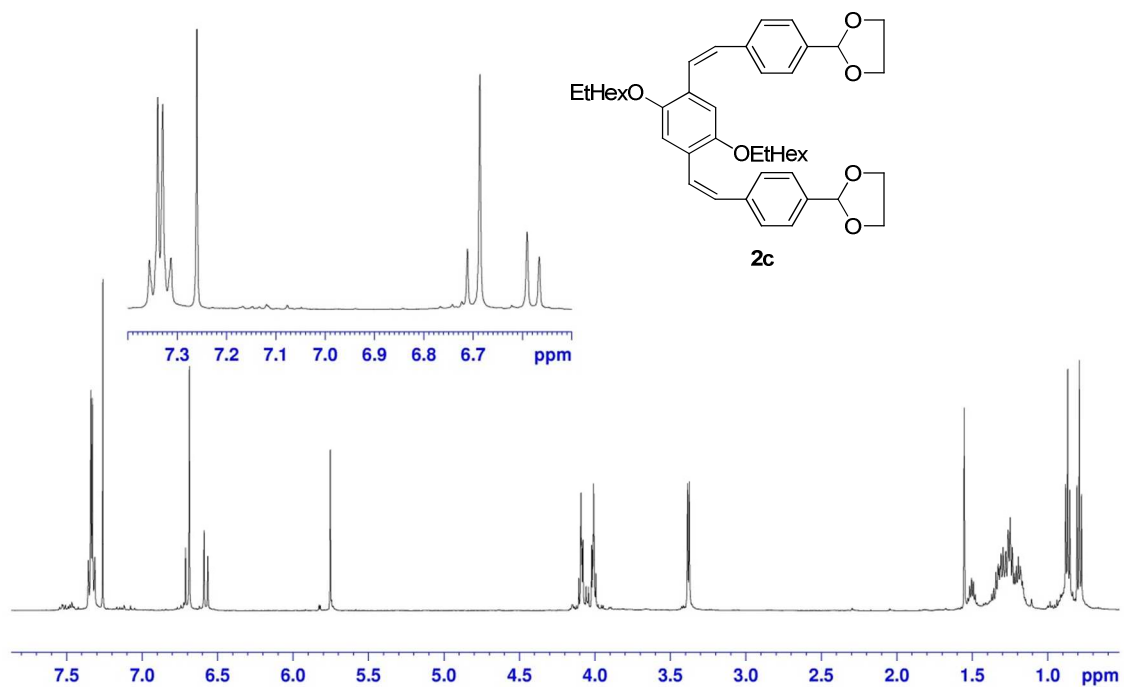


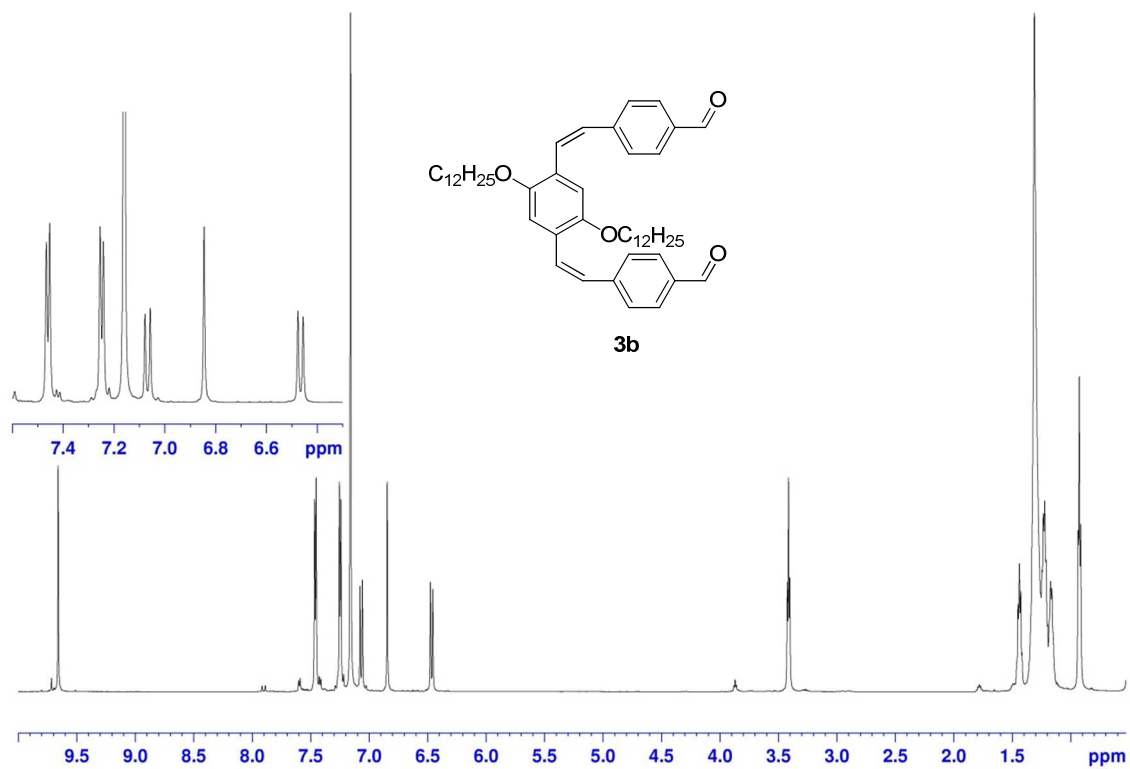
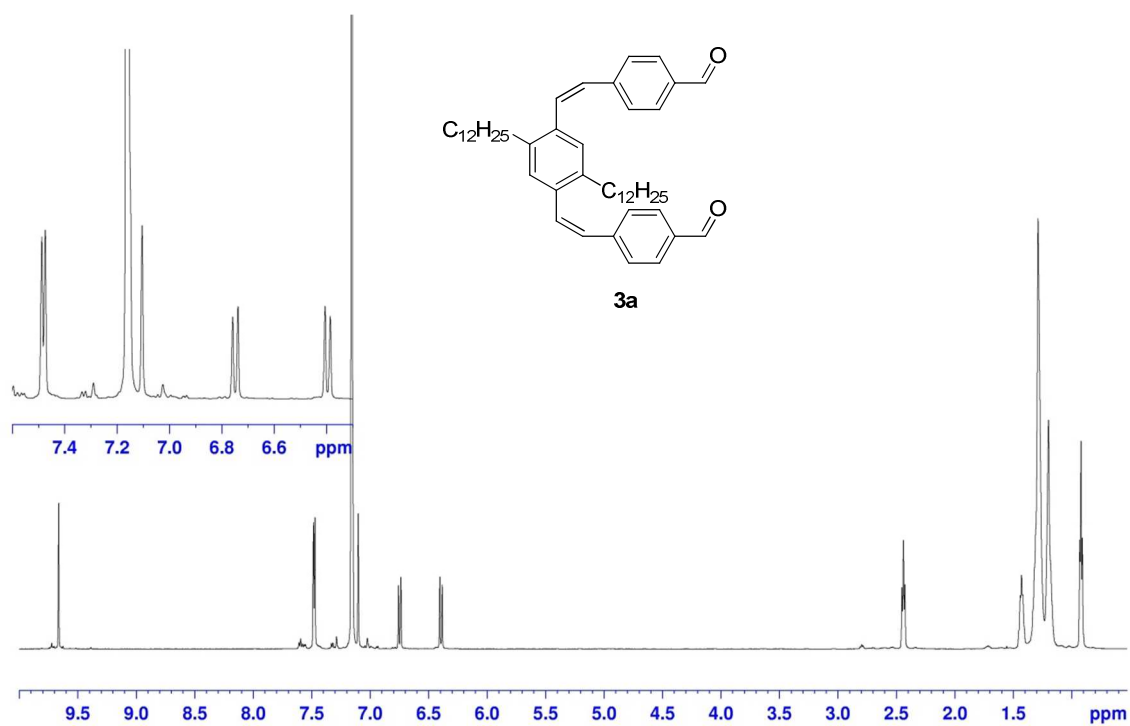
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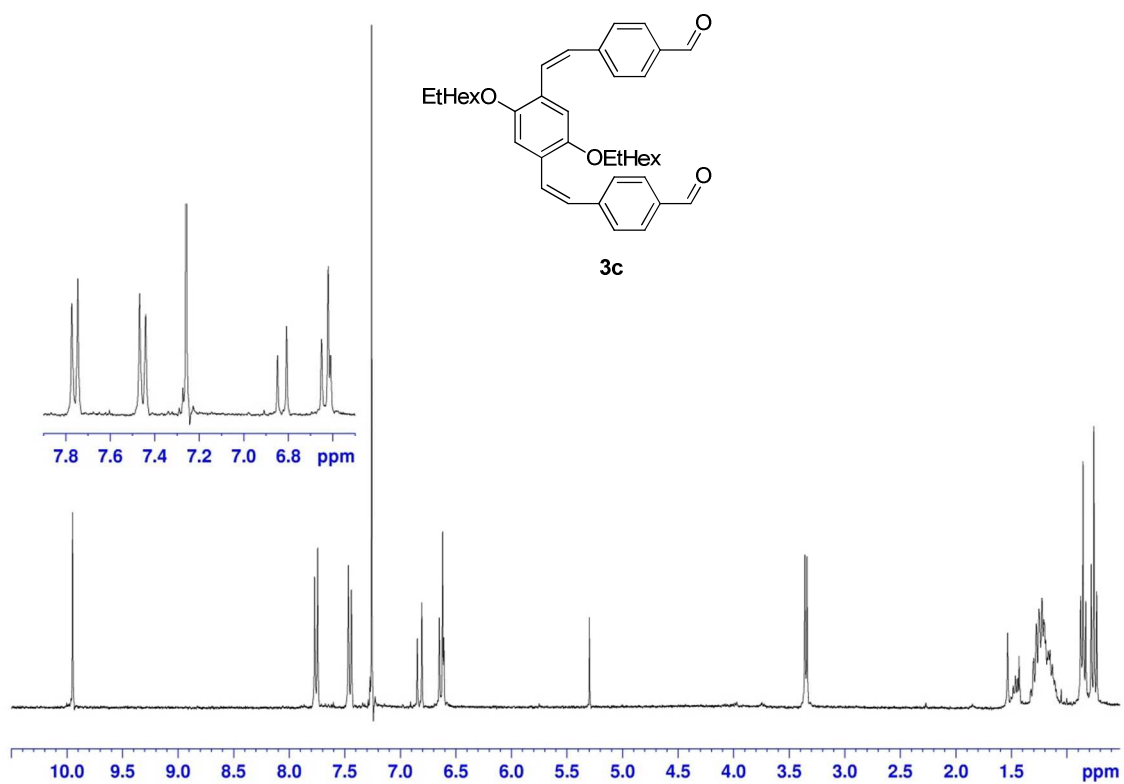


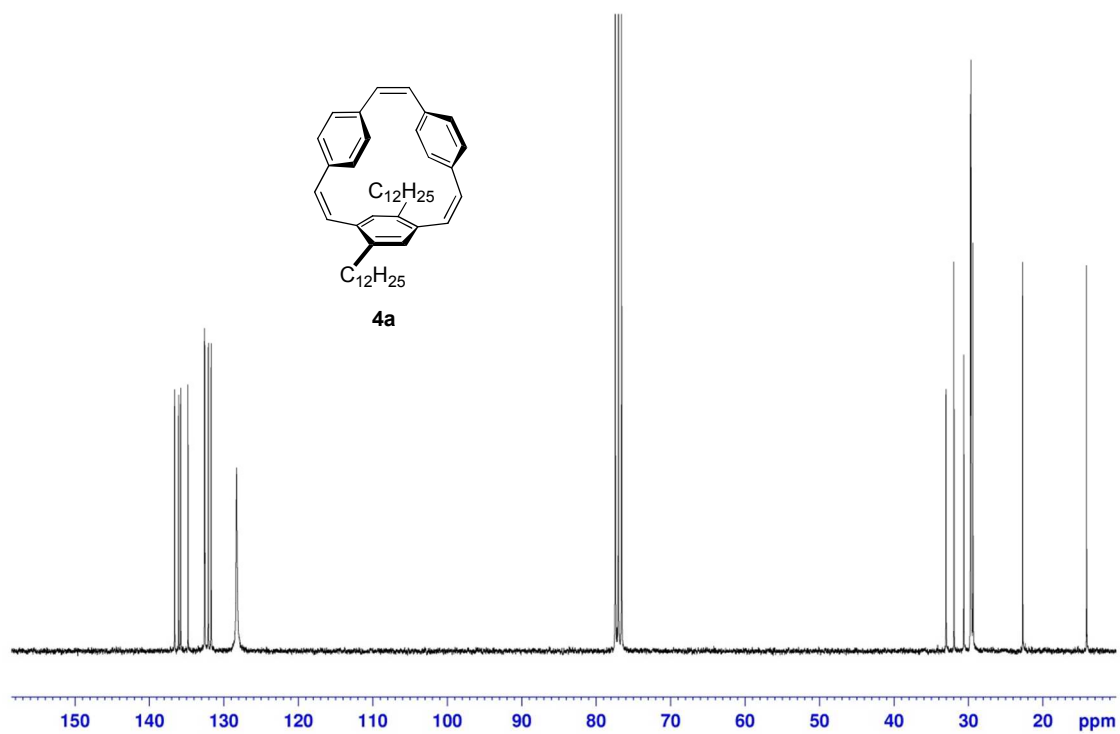
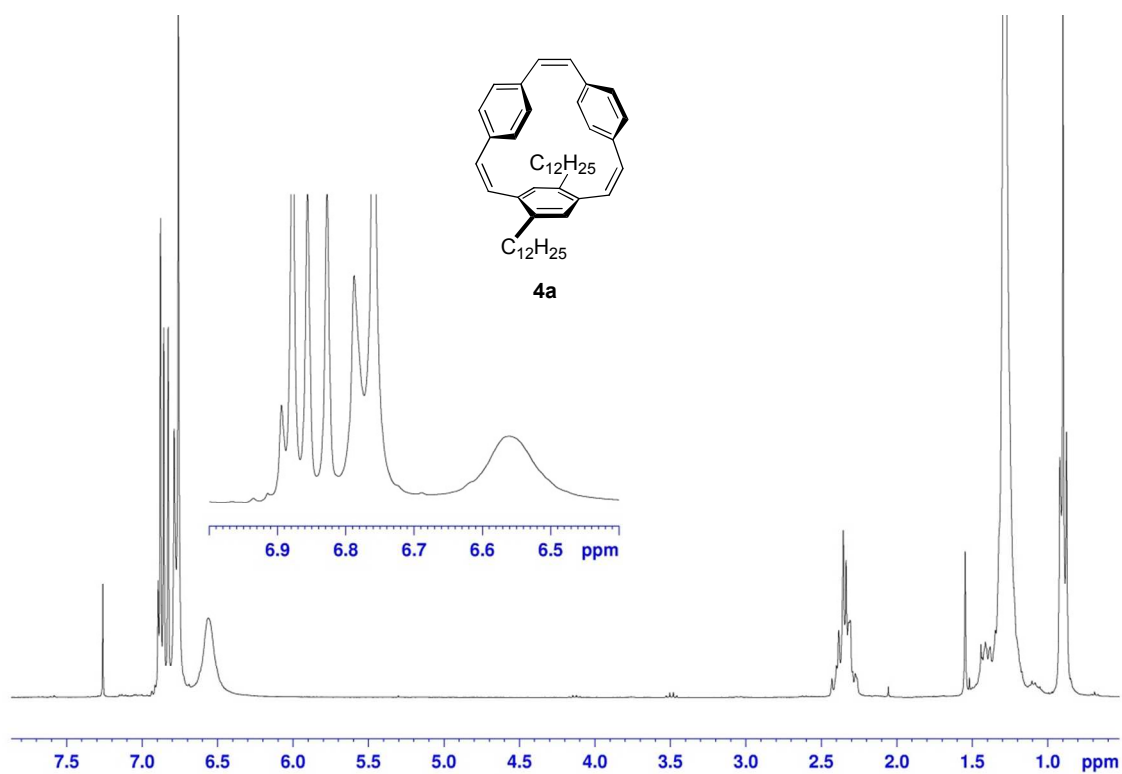


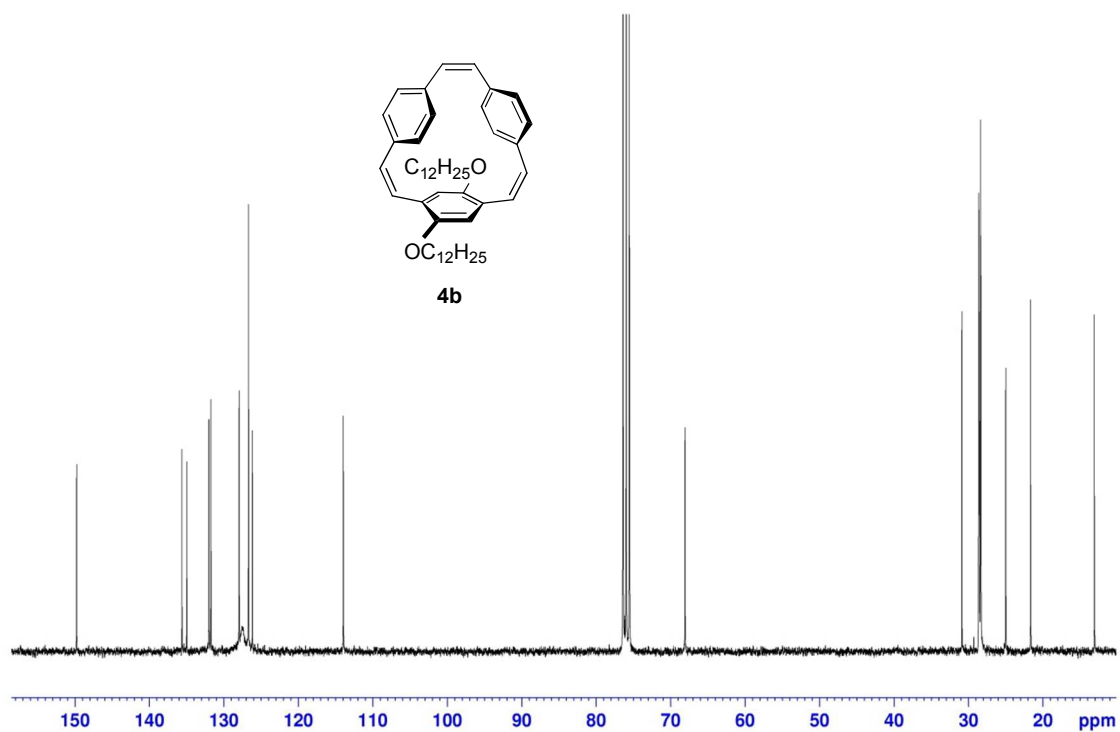
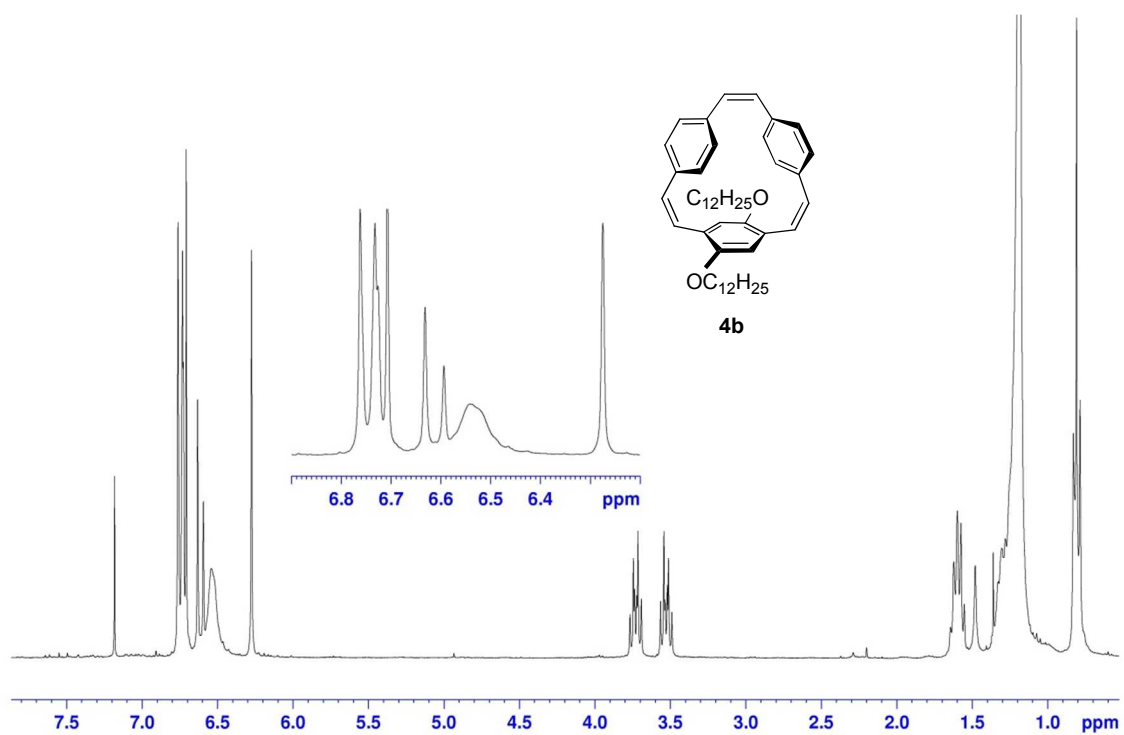


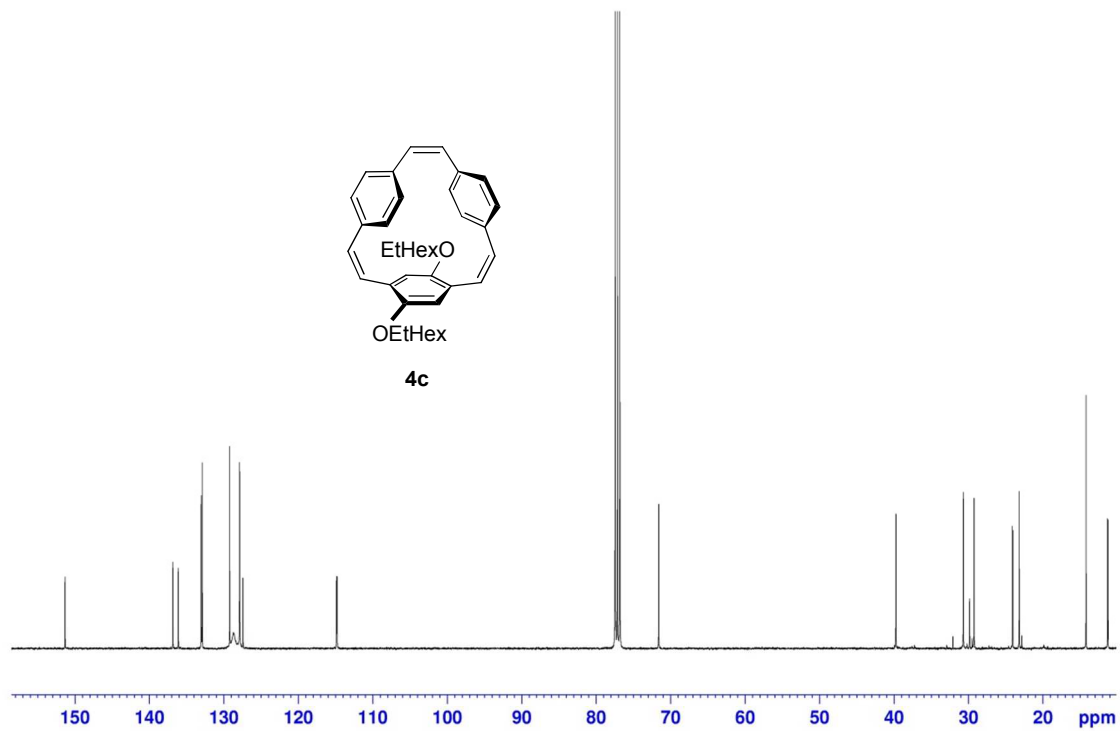
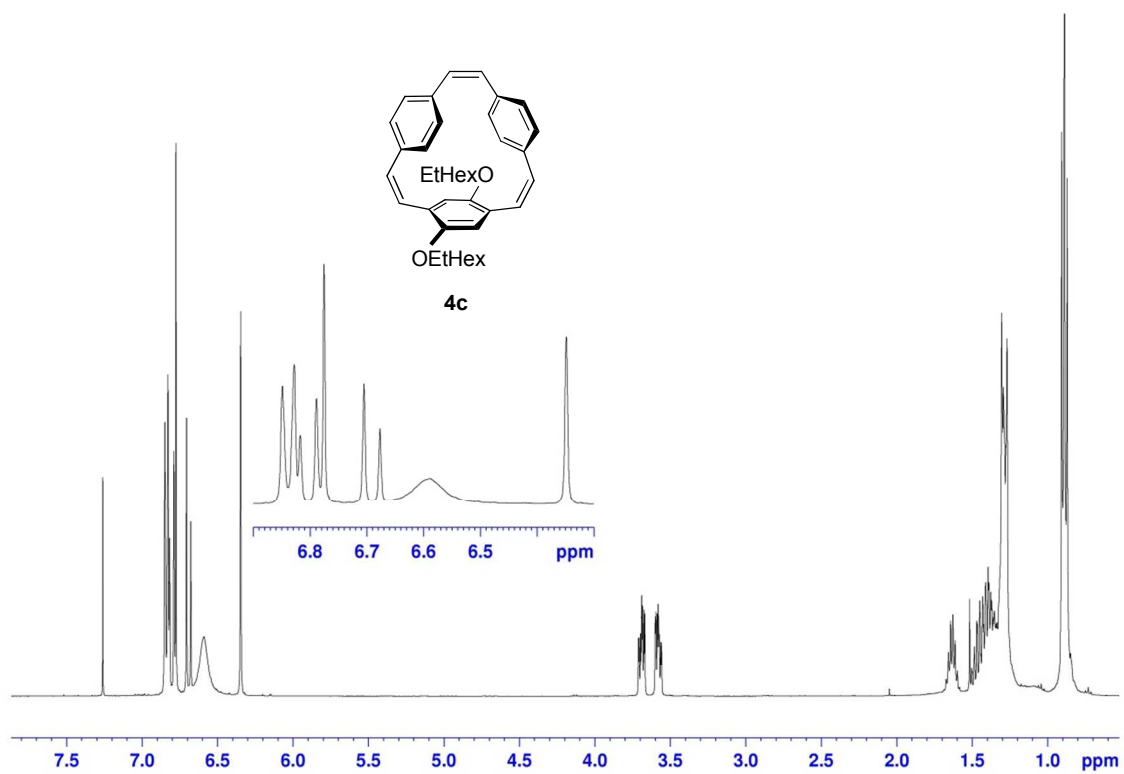


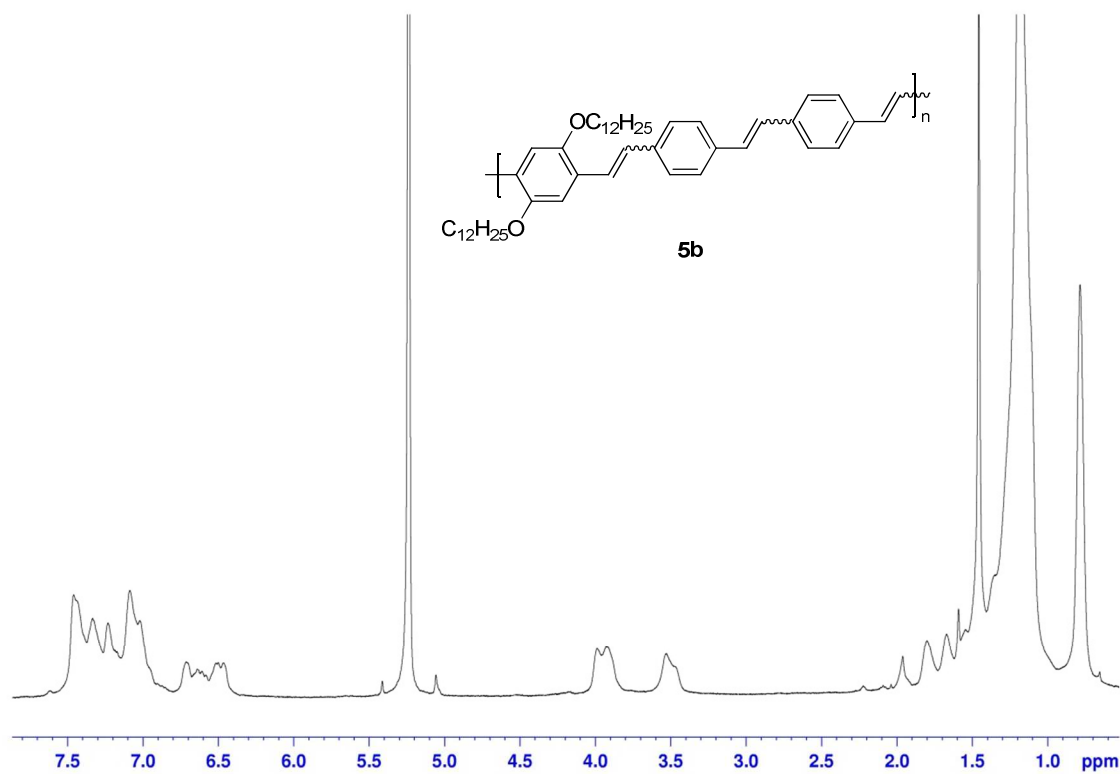
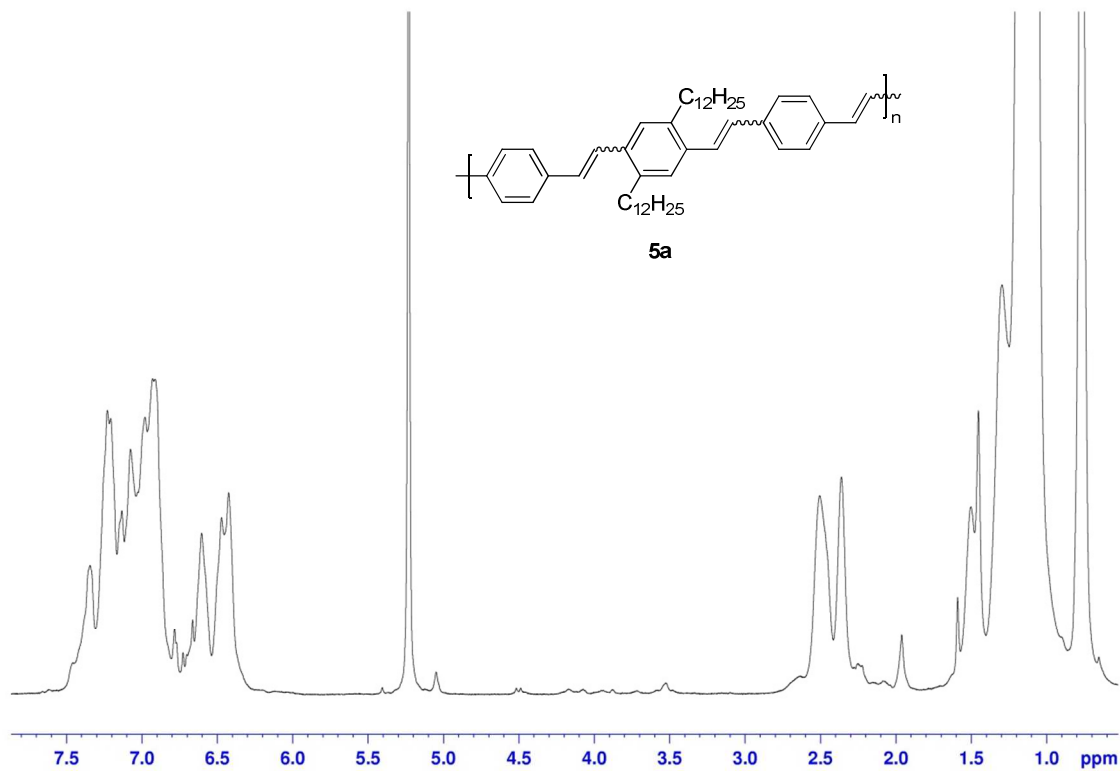


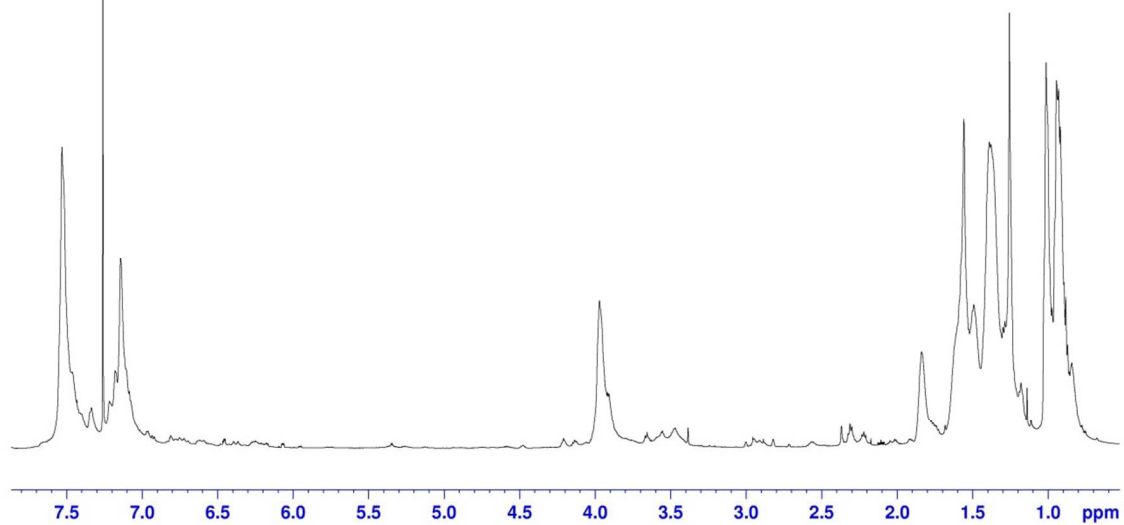
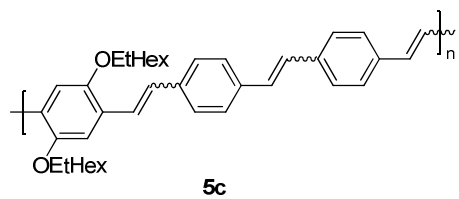




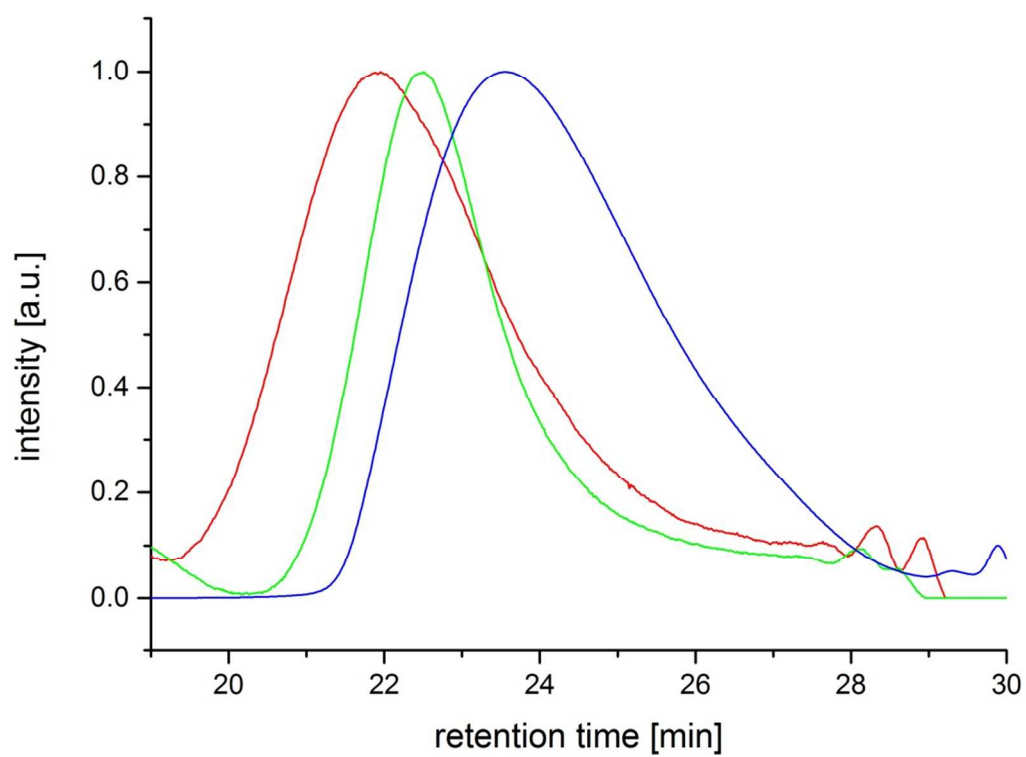








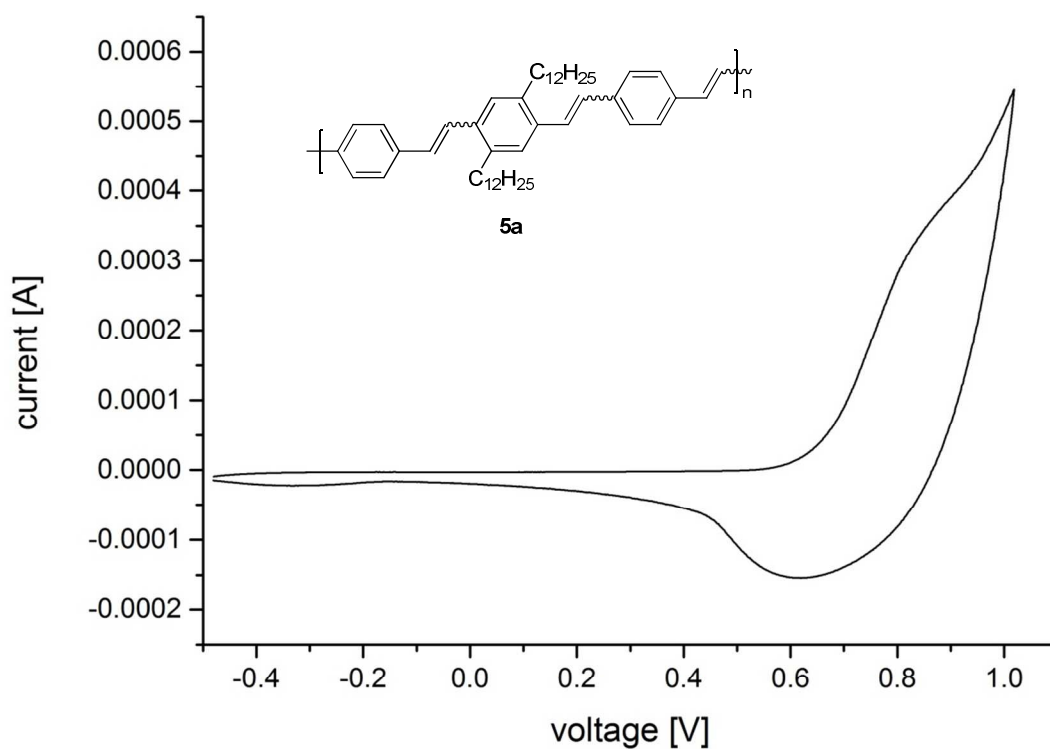
4) GPC data



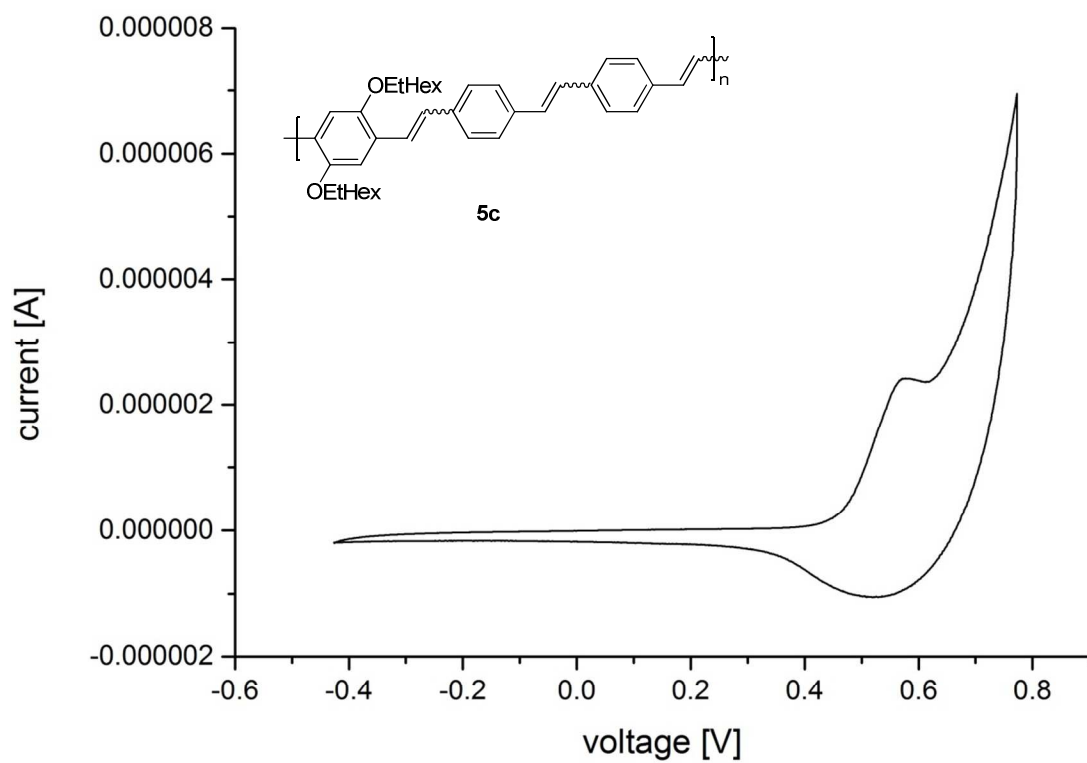
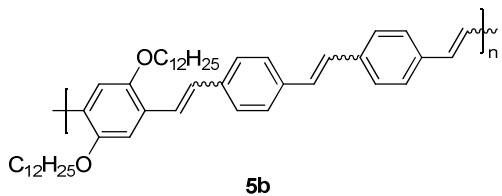
GPC-elogramm for polymer **5a** (red), **5b** (green) and **5c** (blue).

5) Cyclic voltammetry data

Cyclic voltammetry was carried out with a VERSASTAT3-200 potentiostat (Princeton Applied Research). Measurements were performed in solid state by drop casting a thin film onto a platinum working electrode. Measurements were carried out in dry and degassed acetonitrile with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as electrolyte.



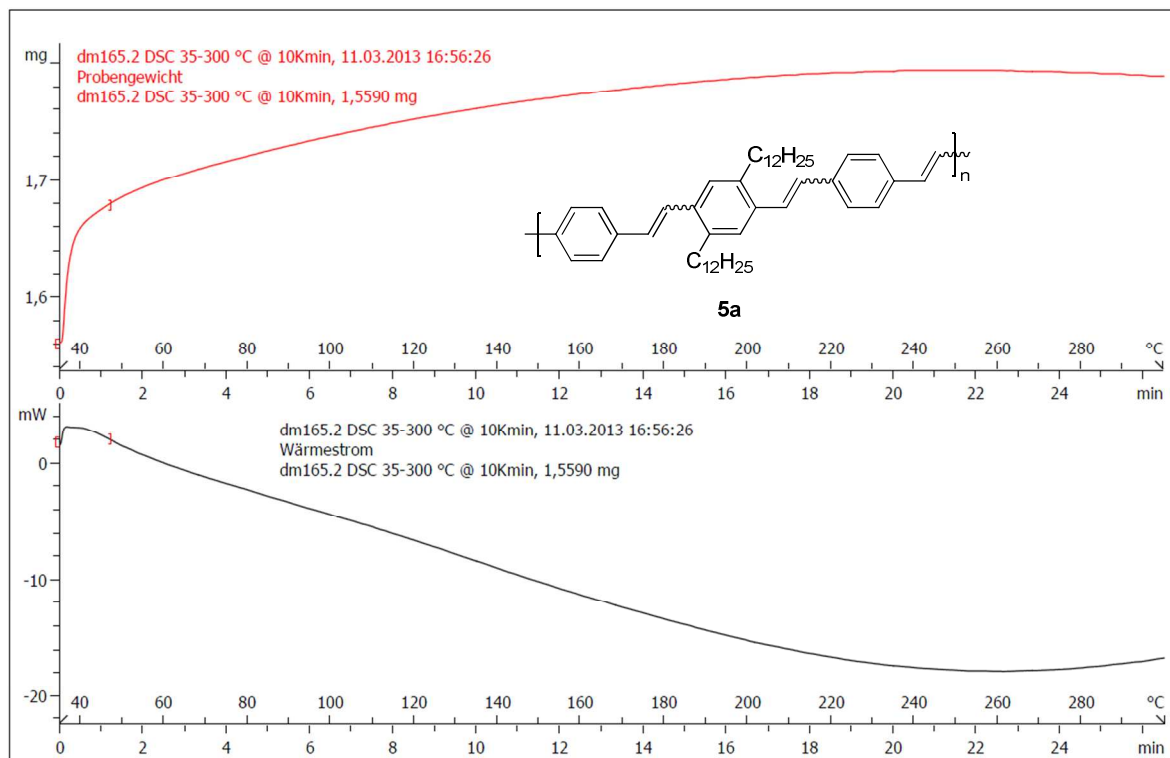
Cyclic voltammetry curve of **5a**.



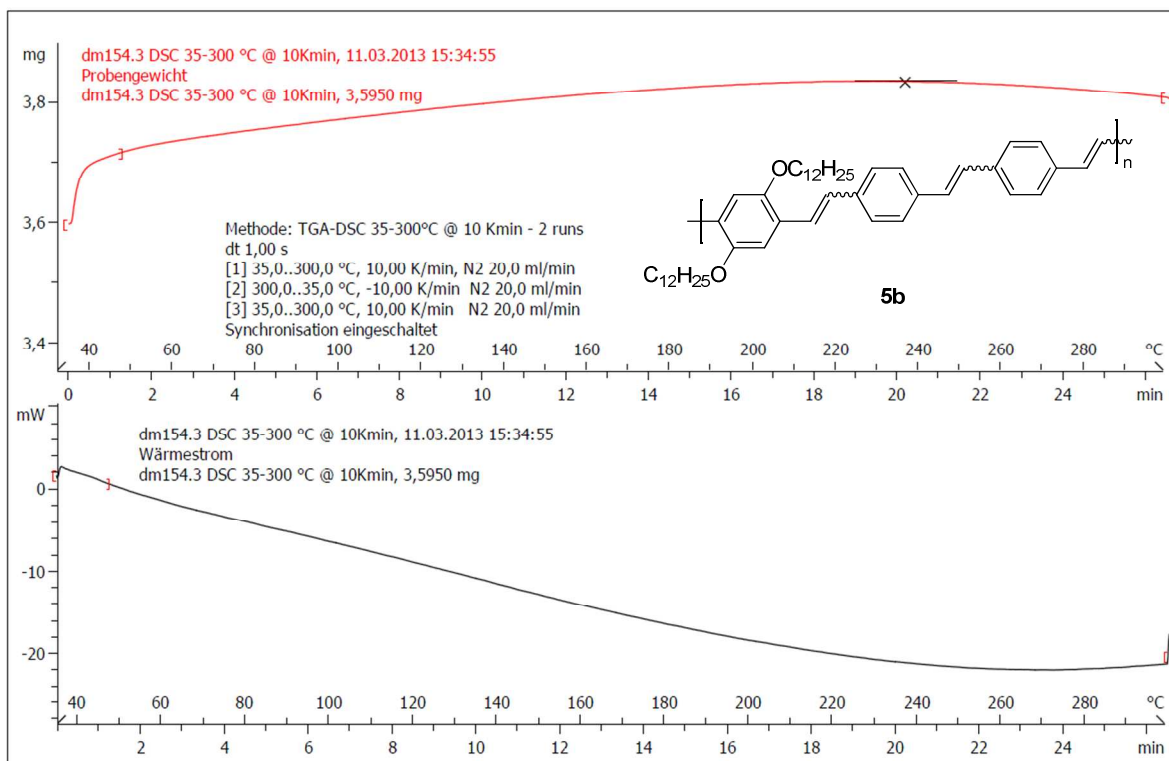
Cyclic voltammetry curve of **5c**.

6) TGA/DCS of pristine polymers

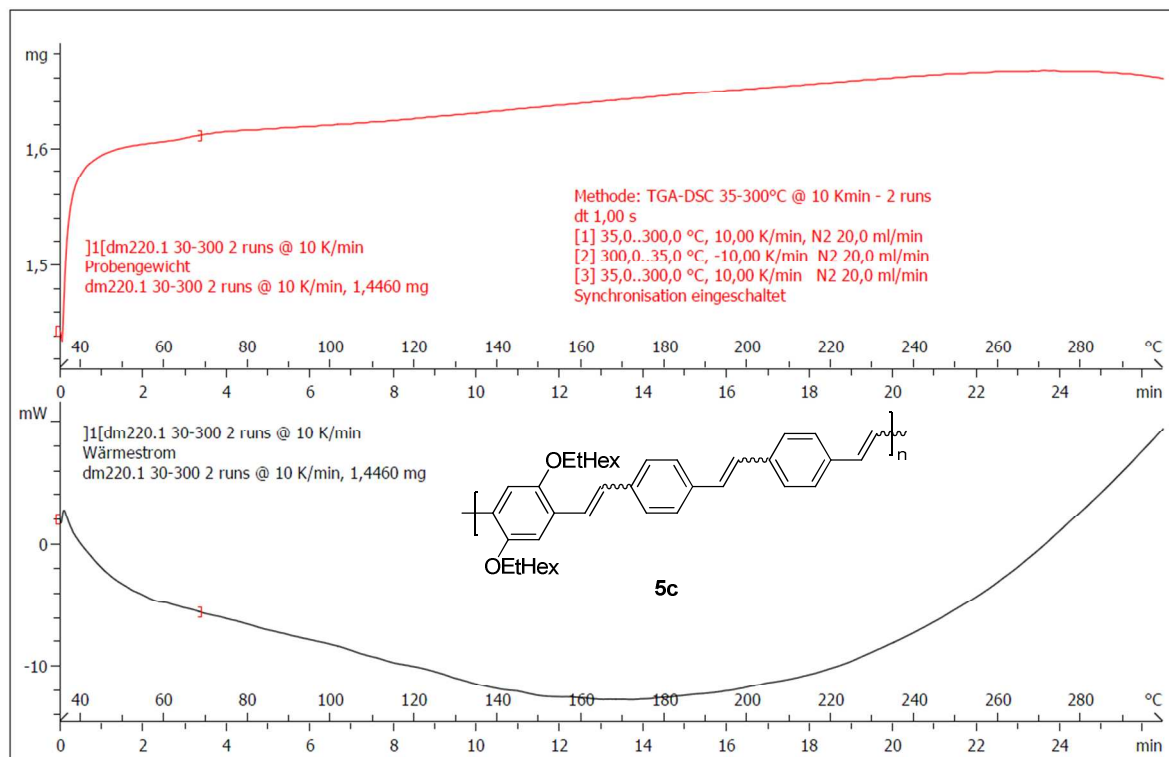
TGA/DCS measurements were carried out on a Mettler-Toledo TGA/DSC1 instrument with a TGA/DSC-Sensor 100 equipped with a MX1 balance (Mettler-Toledo) and a GC100 gas control box for nitrogen supply. TGA/DCS measurements were performed for pristine polymers.



TGA/DSC curve of **5a**.



TGA/DSC curve of **5b**.



TGA/DSC curve of **5c**.

7) References

¹ a) Llanes-Pallas, A.; Yoosaf, K.; Traboulsi, H. ; Mohanraj, J.; Seldrum, T.; Dumont, J.; Minoia, A.; Lazzaroni, R.; Armaroli, N.; Bonifazi, D. *J. Am. Chem. Soc.* **2011**, *133*, 15412. b) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374. c) Koike, R.; Katayose, Y.; Ohta, A.; Motoyoshiya, J.; Nishii, Y.; Aoyama, H. *Tetrahedron* **2005**, *61*, 11020. Iodination: I₂, H₅IO₆, KIO₄, H₂SO₄, CH₃COOH, CH₂Cl₂, H₂O, 70°C, 72h

² Colvin, M. T.; Smeigh, A. L.; Giacobbe, E. M.; Conron, S. M. M.; Ricks A. B.; Wasielewski, M. R. *J. Phys. Chem. A* **2011**, *115*, 7538. Protection to 1,3-dioxolane by refluxing with ethylene glycol and a catalytic amount of toluene sulfonic acid in toluene and purification by column chromatography.