Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Selective alkoxy side chain arrangements in anthracene-containing poly(arylene ethynylene)-*alt*-poly(phenylene vinylene)s – Probing structure-property relationships

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LABELING SPECIFICATIONS

The label indices **a**, indicating octyloxy, and **b**, indicating 2-ethylhexyloxy, which follow the numerical label of the respective species (**1**, **2**, etc.), are organized in specific order. Without additional dissymmetric functionalization of the phenylene unit, **a** and **b** are noted down in alphabetical order. After formylation, the side chain closest to the introduced formyl group is accounted first and the others follow according to their succession – e.g. **8baab**, **8abba** and **8abab**.

The short labels for the polymers (**Aa**, **Ab**, **Ac**, **Ba**, etc.) are conceived in following way: Basically, the capital letter indicates the dialdehyde and the small letter the bisphosphonate, which were used in the preparation of the respective polymer. "**A**" and "**B**" were selected to account for the pure dialdehyde isomers **8baab** and **8abba**, respectively, also as a reference for the side chains in the direct proximity to the anthracene center. "**C**" refers to the dialdehyde mixture **8a/ba/b** (**8abab**, **8abba** and **8baab**). Also the small letters basically reference the involved side chains – "**a**" refers to the bisphosphonate bearing two octyloxy side chains (**3aa**); "**b**" denotes the two 2-ethylhexyloxy groups in **3bb**; and "**c**" refers to **3ab**, bearing a linear as well as a branched side chain.

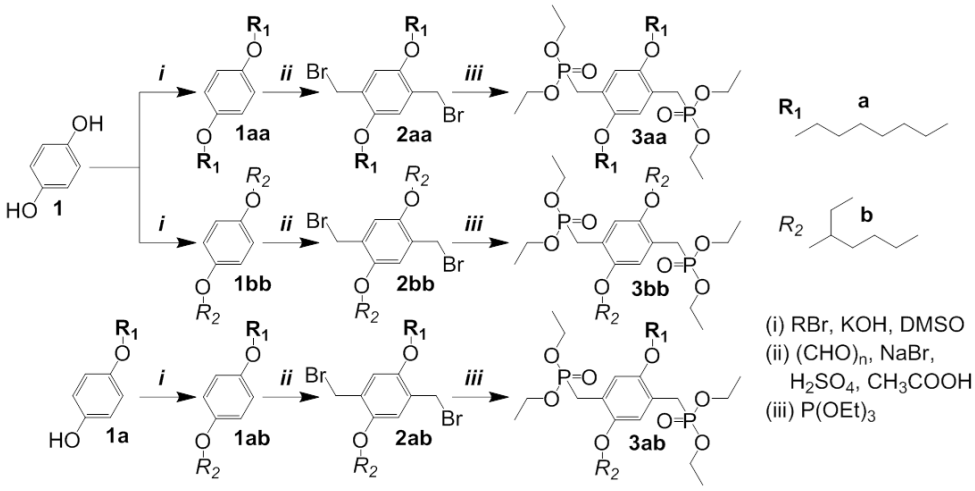
UV-Vis absorption, photoluminescence and size exclusion chromatography data of the polymers are plotted with specific color/symbol labeling. The polymer data plots are color coded to indicate the dialdehyde used in their preparation – "shades of red" for **8baab**, "shades of blue" for **8abba** and "shades of green" for **8a/ba/b**. The bisphosphonate, **3aa**, **3bb** or **3ab**, used in the preparation of the respective polymer is indicated by a square, triangular and circular symbol, respectively.

long polymer labels /	***short*** polymer labels /	***colored symbol*** coding in graphs
AnE-PVbaab-aa	**Aa**	■
AnE-PVbaab-bb	**Ab**	▲
AnE-PVbaab-a/b	**Ac**	●
AnE-PVabba-aa	**Ba**	■
AnE-PVabba-bb	**Bb**	▲
AnE-PVabba-a/b	**Bc**	●
AnE-PVa/ba/b-aa	**Ca**	■
AnE-PVa/ba/b-bb	**Cb**	▲
AnE-PVa/ba/b-a/b	**Cc**	●

SYNTHESIS AND STRUCTURAL CONSIDERATIONS

Hydroquinone (**1**, Scheme S1) is the common starting point for the preparation of phenylene building blocks with two opposing identical alkoxy substituents. For the implementation of two different alkoxy side chains a step-wise protocol initiated by a selective monoetherification[1] among others[2] can be used. Another option is to start directly from one of the numerous commercially available *p*-alkoxyphenols.

Scheme S1 displays the well-established synthesis pathway for the preparation of bisphosphonates **3**. Further synthesis information and characterization data on the new derivative **3ab** and its precursors, **1ab** and **2ab**, can be found in the "Synthesis Descriptions" later on and in the display of "NMR Spectra" at the end of the Supporting Information.



Scheme S1: Synthesis of bisphosphonates with identical side chains (**3aa**, **3bb**) and mixed side chains (**3ab**).

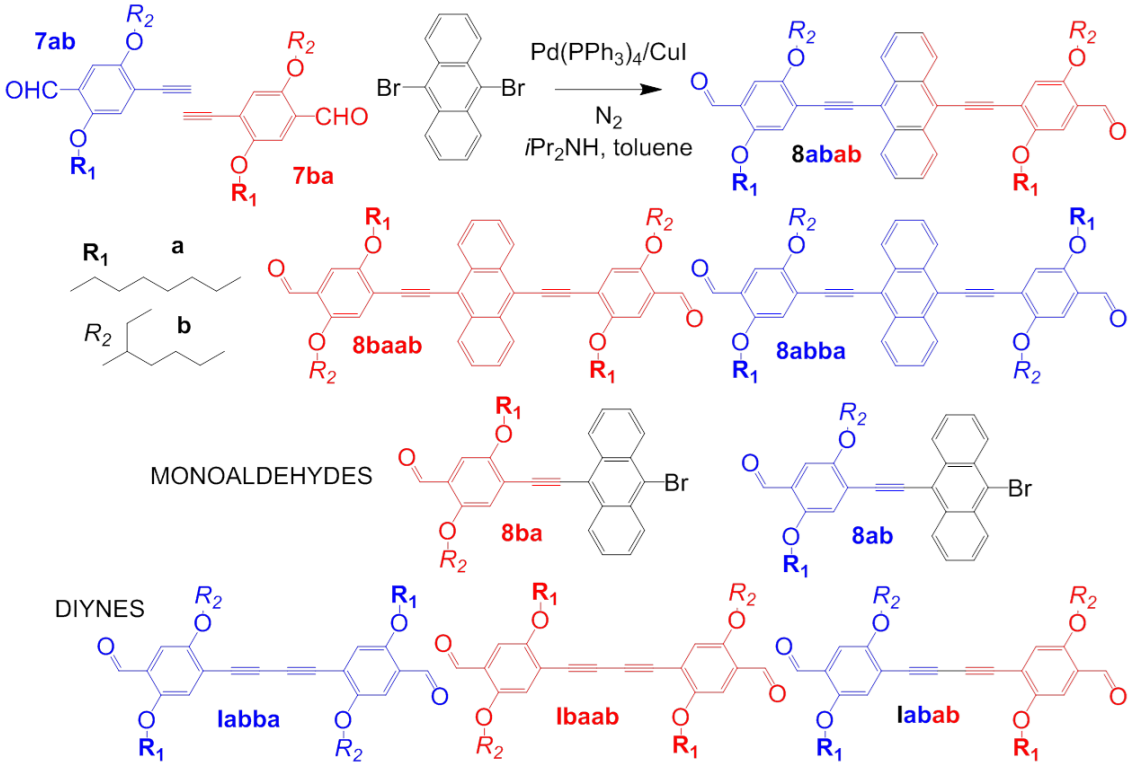
Following the "classical" approach for the dialdehyde synthesis (Scheme 2), the formylation reaction showed only limited selectivity. Also the introduction of bromo instead of iodo substituents did not lead to significant changes. Apparently the different alkoxy side chains (octyloxy and 2-ethylhexyloxy) do not lead to a sufficient differentiation of the neighboring halo-substituents.

Even in the presence of a slight excess of the acetylene compound, a complete substitution of all halo-groups during Sonogashira cross-coupling is not guaranteed, providing "intermediate stage products". Furthermore, the oxidative Glaser coupling of terminal acetylene groups, yielding

[1] Gambarotti, C.; Melone, L.; Punta, C.; Shisodia, S. U. Selective Monoetherification of 1,4-Hydroquinone Promoted by $NaNo_2$ *Curr. Org. Chem.* **2013**, *17*, 1108-1113.

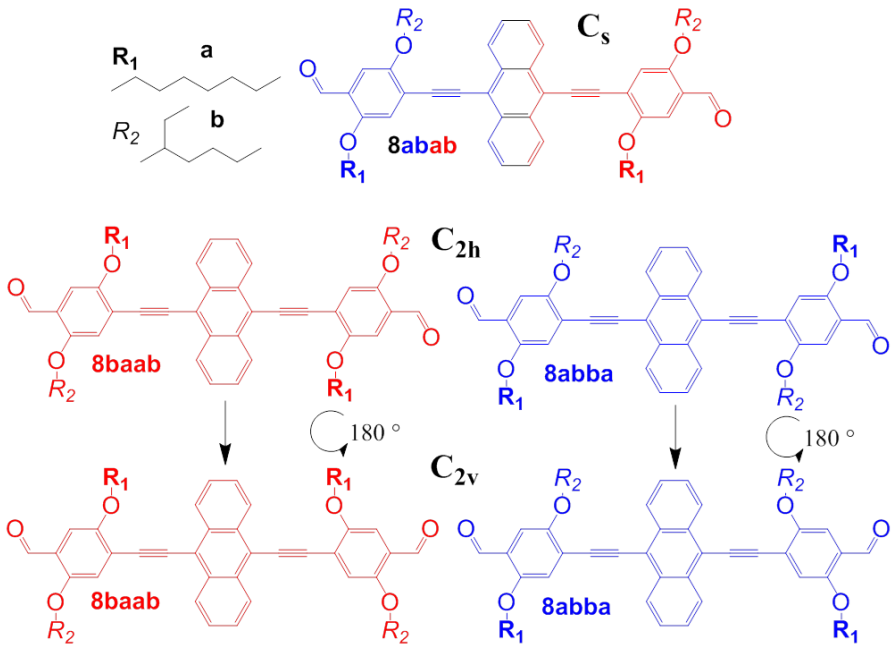
[2] Motyka, R.; Stecko, S.; Suwiński, J. W. Simple Synthesis of Non-Symmetric 1,4-Dialkoxybenzenes via 4-Alkoxyphenols. *Org. Commun*. **2016**, *9*, 23-31.

diyne derivatives, is a highly common side reaction during Sonogashira reactions. Often respective byproducts are formed, and can be isolated during chromatographic purification. Scheme S2 depicts the structures of the potential products (**8abba**, **8baab** and **8abab**) and byproducts ("reaction intermediates" **8ab** and **8ba**, as well as diynes **Iabba**, **Ibaab** and **Iabab**) of the Sonogashira cross-coupling reaction between 9,10-dibromoanthracene and the phenylacetylene derivative mixture **7a/b** (**7ab** and **7ba**).



Scheme S2: Synthesis of the dialdehyde batch **8a/ba/b** (**8abba**, **8baab** and **8abab**) via Sonogashira cross-coupling reaction between 9,10-dibromoanthracene and the regioisomer mixture **7a/b** (**7ba** and **7ab**), together with potential byproducts. The monoaldehydes **8ba** and **8ab** result from incomplete transformation, and the diynes **Iabba**, **Ibaab** and **Iabab** display the possible products from Glaser coupling.

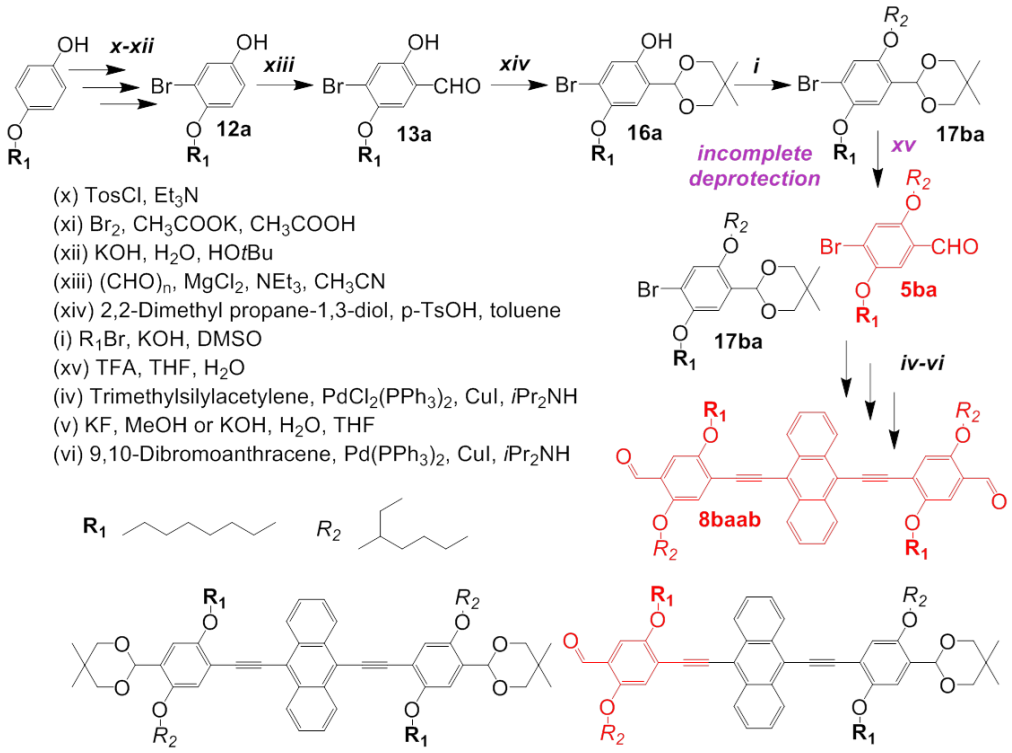
All three potential dialdehyde derivatives, **8abba**, **8baab** and **8abab**, obtained by the "classical" approach exhibit a symmetry plane along the planar conjugated backbone. In addition, the dialdehydes **8abba** and **8baab**, show another symmetry element, an inversion center or a mirror plane depending on their orientation. While the symmetry group of **8abab** is determined to C_s, **8abba** and **8baab** can be assigned either to C_{2h} or to C_{2v}, in dependence on their structural alignment (Scheme S3).



Scheme S3: Dialdehydes **8abab**, **8abba** and **8baab** with group symmetry assignments.

While for the most parts the protocol of X. Zhu *et al.*[3] proved to be very useful in the selective preparation of the double dissymmetric phenylene intermediate **5ba**, the protection of the aldehyde function through the formation of an acetal with neopentyl glycol prior the etherification step turned out problematic. Despite numerous attempts using different conditions (various solvents, acids, etc.) a hydrolysis of all acetal functionalities, after the etherification step, could not be accomplished (Scheme S4). Significant amounts of the acetal derivative remained with the desired aldehyde compound **5ba**. Moreover, also a separation of the two species by standard chromatographic methods appeared rather inefficient. Even so the entire dialdehyde synthesis sequence has been conducted, a complete deprotection and/or a sufficient separation of the species at any stage was not successful. The final product mixture (**8baab**, etc.; Scheme S4) might be still useful in the preparation of small molecules or oligomers as ill-defined reactant ratios are often not crucial, and as purification by column chromatography might become feasible at some point. For the production of polymers *via* the Honor-Wadsworth-Emmons polyolefination reaction, however, the usage of such a mixture is problematic. In polycondensation reactions, the ratio of the comonomers needs to be rather precise to obtain polymers with at least reasonable molecular masses. While the fully protected dialdehyde might simply not take part in the reaction, the monoacetal aldehyde species is likely to act as endcapper.

[3] Zhu, X.; Plunkett, K. N. Controlled Regioregularity in Oligo(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylenes. *J. Org. Chem.* **2014**, *79*, 7093-7102. *(Ref. 32 in the main text)*

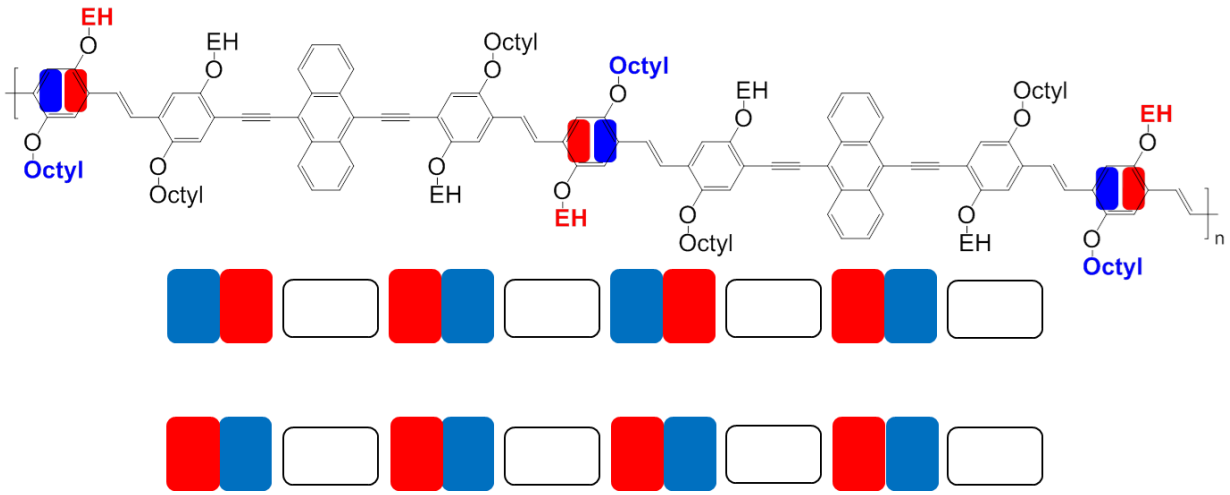


Scheme S4: Synthesis of the dialdehyde isomer **8baab** including the intermediate protection (***xiv***) and *only partial* deprotection (***xv***) of the formyl group following the protocol of X. Zhu *et al*.[3]

The high stability of the acetal functionality formed with neopentyl glycol can be attributed largely to the marginal ring-tension within the six-membered acetal ring. More labile acetals prepared, among others, with ethanol, methanol or ethylene glycol could prevent the encountered dilemma. Avoiding formyl protection and deprotection all at once by using adapted etherification conditions, however, provides an even more appealing approach (Scheme 3). It improves and simplifies the isomer selective synthesis significantly, saving time, efforts and expenses.

For the HWE polycondensation reactions stoichiometric mixtures of dialdehyde and bisphosphonate were dispersed at high concentration in toluene. In inert atmosphere potassium *tert*-butoxide was added to the heated solution to initiate the reaction. One to two hours reaction time and thorough purification led to yields between 60 and 90%. While the polycondensation of two comonomers with an overall symmetric side chain configuration, **8abba** or **8baab** with **3aa** or **3bb**, provides polymers with highly defined side chain successions, the usage of a comonomer with dissymmetric side chain configuration (**8abab** or **3ab**) introduces irregularities in the side chain sequence due to the two distinguishable orientations in which they can add on during polycondensation (Scheme S5).

Irregularities in the side chain sequence further increase, if two dissymmetric comonomers or mixtures of bisphosphonates and/or of dialdehydes are employed in the polycondensation.



Scheme S5: (*top*) Depiction of a possible structural section within polymer **AnE-PVabba-a/b** (**Bc**), synthesized from dialdehyde **8abba** (C_{2h}) and bisphosphonate **3ab** (C_s) *via* HWE reaction. (*bottom*) Simplified representation of two polymer segment options with diverse side chain sequences as a result of the two possible orientations in which the bisphosphonate comonomer **3ab** can add on to the growing polymer.

EXPERIMENTAL DESCRIPTIONS

Materials and Methods

Unless specified otherwise, reagents and solvents were purchased from commercial suppliers (Sigma-Aldrich, Fluka, VWR, etc.) and were used as received. For reactions sensitive to air and/or moisture solvents were deoxygenated by bubbling with nitrogen for one hour prior use, and a continuous gentle flow of nitrogen was applied throughout the reaction. Silica gel 60 from Merck was used in column chromatography.

Thin layer chromatography (TLC, aluminum/silica gel with binder and fluorescent indicator, Merck) was used to monitor the progress of reactions as well as the purity of isolated products. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at room temperature using a Gemini 300 MHz spectrometer. The ^{1}H and ^{13}C NMR data are listed as "residual internal $CHCl_3$ (δ 7.26 and 77.02 ppm, respectively)". Signals, which appear in defined patterns, despite distinctions in the nuclei involved, are labeled "*p*" for pseudo (e.g.: *p*s = pseudo singlet). For size exclusion chromatography (SEC) measurements a high-temperature gel permeation chromatograph (Polymer Char HT-GPC-IR), equipped with a column set from Agilent Technologies (PLgel Olexis 300 × 7.5 mm) and an infrared detector (Polymer Char IR 5), was used. The experiments were performed with 1,2,4-trichlorobenzene (TCB) as eluent at 160 °C and a flow rate of 1 mL min^{-1}. Polystyrene standards (Agilent) were used for calibration. UV-Vis and photoluminescence (PL) spectra were recorded with an UV/VIS/NIR Spectrometer Lambda 1050 (Perkin Elmer) and a Quanta Master 40 (Photon Technology International, PTI), respectively. Solvents of spectroscopic grade were used. The measurements in solution were carried out with quartz cuvettes (1 × 1 cm). The solid-state analyses were performed at polymer thin films deposited on cleaned glass substrates.

Synthesis of comonomers

The multistep reactions used in the synthesis of the bisphosphonate and dialdehydes with various side chain configurations are illustrated in Schemes 2, 3, S1 and S2.

1-(2-Ethylhexyloxy)-4-(octyloxy)benzene (**1ab**) Potassium hydroxide (KOH powder, 74.2 g, 1.32 mol) in dry DMSO (450 mL) was stirred and deaerated for one hour. 4-(Octyloxy)phenol (60 g, 269.9 mmol) and 2-ethylhexyl bromide (67.76 g, 63 mL, 350.8 mmol) were added. The reaction mixture was stirred for 3 hours at room temperature and finally poured into ice water (600 mL). The mixture was extracted with hexane (3 × 200 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated (rotary evaporator) providing a yellow oily material. Residual DMSO and 2-ethylhexyl bromide were distilled off under reduced pressure to yield **1ab** (68.73 g, 205.4 mmol, 76 % yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.90 (m, 9H, -C$\underline{H}_3$), 1.28-1.77 (m, 21H, -C$\underline{H}$-,-C$\underline{H}_2$-), 3.79 (d, 2H, ^3J = 5.8 Hz, -O-C$\underline{H}_2$-CH-), 3.89 (t, 2H, ^3J = 6.5 Hz, -O-C$\underline{H}_2$-CH_2-), 6.82 (*p*s, 4H, C_{phen}-$\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 11.1 (-CH-CH_2-$\underline{C}H_3$), 14.1 (-$\underline{C}H_3$), 22.7, 23.1, 23.8, 26.1, 29.1, 29.2, 29.38, 29.39, 30.5, 31.8 (-$\underline{C}H_2$-), 39.4 (-$\underline{C}$H-), 68.7, 71.2 (-O-$\underline{C}H_2$-), 115.4 ($\underline{C}_{phen}$-H), 153.1, 153.5 ($\underline{C}_{phen}$-O-CH_2-).

1,4-Bis(bromomethyl)-2-(2-ethylhexyloxy)-5-(octyloxy)benzene (**2ab**) A suspension of 1-(2-ethylhexyloxy)-4-(octyloxy)benzene (**1ab**, 4.1 g, 13.18 mmol), paraformaldehyde (5.4 g, 179.5 mmol), and NaBr (0.78 g, 66 mmol) in glacial acetic acid (60 mL) was heated to 70 °C. A mixture of concentrated sulfuric acid (10 g) and glacial acetic acid (10 g) was added dropwise, and the reaction mixture was kept stirring for 4 hours at 70 °C. After cooling to room temperature the mixture was poured on ice. The viscous precipitate was filtered off, washed with aqueous $NaHCO_3$ solution and with water, and dried yielding **2ab** (4.2 g, 8.07 mmol, 61 % yield) as a bright viscous material. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.86-0.97 (m, 9H, -C$\underline{H}_3$), 1.27-1.83 (m, 21H, -C$\underline{H}$-, -C$\underline{H}_2$-), 3.86 (d, 2H, ^3J = 5.4 Hz, -O-C$\underline{H}_2$-CH-), 3.98 (t, 2H, ^3J = 6.4 Hz, -O-C$\underline{H}_2$-CH_2-), 4.51, 4.53 (s, s, 2H, 2H, -C$\underline{H}_2$-Br), 6.85 (*p*s, 2H, C_{phen}-$\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 11.2 (-CH-CH_2-$\underline{C}H_3$), 14.1 (-$\underline{C}H_3$), 22.7, 23.1, 24.0, 26.1, 28.8, 28.9, 29.1, 29.3, 29.4, 30.7, 31.6, 31.9 (-$\underline{C}H_2$-, -$\underline{C}H_2$Br), 39.6 (-$\underline{C}$H-), 69.1, 70.9 (-O-$\underline{C}H_2$-), 114.2, 114.7 ($\underline{C}_{phen}$-H), 127.4, 127.5 ($\underline{C}_{phen}$-CH_2-Br), 150.6, 150.8 ($\underline{C}_{phen}$-O-CH_2-).

2-(2-Ethylhexyloxy)-5-(octyloxy)-p-xylylene-bis(diethylphosphonate) (**3ab**) A mixture of 1,4-*bis*(bromomethyl)-2-(2-ethylhexyloxy)-5-(octyloxy)benzene (**2ab**, 4.1 g, 7.88 mmol) and an excess of triethylphosphite (3.9 g, 23.6 mmol) was heated to 150-160 °C while distilling off the evolving ethylbromide simultaneously. After 4 hours, vacuum was applied and the temperature was increased to 180 °C for 30 minutes to strip off the excess of triethylphosphite yielding the bisphosphonate **3ab** (4.2 g, 6.62 mmol, 84 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.88-0.94 (m, 9H, -C$\underline{H}_3$), 1.19 (m, 12H, P-O-CH_2-C$\underline{H}_3$), 1.21-1.78 (m, 21H, -C$\underline{H}$-, -C$\underline{H}_2$-), 3.18-3.25 (m, 4H, P-C$\underline{H}_2$-), 3.80 (d, 2H, ^3J = 5.3 Hz, -O-C$\underline{H}_2$-CH-), 3.92 (t, 2H, ^3J = 6.5 Hz, -O-C$\underline{H}_2$-CH_2-), 4.05 (m, 8H, -P-O-C$\underline{H}_2$-), 6.90, 6.93 (s, s, 1H, 1H, C_{phen}-$\underline{H}$).

1,4-Diiodo-2-(2-ethylhexyloxy)-5-(octyloxy)benzene (**4ab**) 1-(2-Ethylhexyloxy)-4-(octyloxy)-benzene (**1ab**, 40.0 g, 119.5 mmol), $NaIO_3$ (9.7 g, 49 mmol), and I_2 (34.3 g, 135.1 mmol) were added to a stirred solution of glacial acetic acid (400 mL), H_2SO_4 (96 wt.%, 13 mL), H_2O (58 mL), and CCl_4 (36 mL). The reaction mixture was heated at reflux to 105 °C, and stirred overnight. After cooling to room temperature aqueous $Na_2S_2O_3$ (20 wt.%) was added until the brown color of iodine vanished. The mixture was poured into ice water. The mixture was

extracted with hexane. The combined organic layers were washed with water, aqueous K_2CO_3 solution (20 wt.%), dried over $MgSO_4$, and filtered. After removal of the solvent under reduced pressure using a rotary evaporator, the raw product was purified by column chromatography (silica, dichloromethane/cyclohexane 1:1) yielding **4ab** (57 g, 97.2 mmol, 81 % yield, Rf = 0.85) as a slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.90 (m, 9H, -C<u>H</u>$_3$), 1.29-1.81 (m, 21H, -C<u>H</u>-, -C<u>H</u>$_2$-), 3.8 (d, 2H, ^3J = 5.5 Hz, -O-C<u>H</u>$_2$-CH-), 3.89 (t, 2H, ^3J = 6.4 Hz, -O-C<u>H</u>$_2$-CH$_2$-), 7.15, 7.17 (s, s, 1H, 1H, C_{phen}-<u>H</u>).^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 11.2 (-CH-CH$_2$-<u>C</u>H$_3$), 14.1 (-<u>C</u>H$_3$), 23.1, 23.9, 26.0, 29.0, 29.1, 29.2, 30.5, 30.9, 31.8 (-<u>C</u>H$_2$-), 39.4 (-<u>C</u>H-), 70.4, 72.3 (-O-<u>C</u>H$_2$-), 86.0, 86.1 (<u>C</u>$_{phen}$-I), 122.2, 122.3 (<u>C</u>$_{phen}$-H), 152.7, 152.9 (<u>C</u>$_{phen}$-O-CH$_2$-).

2-(2-Ethylhexyloxy)-4-iodo-5-(octyloxy)benzaldehyde (**5ba**) / *5-(2-ethylhexyloxy)-4-iodo-2-(octyloxy)benzaldehyde* (**5ab**) – *mixture of regioisomers* (**5a/b**). 1,4-Diiodo-2-(2-ethylhexyloxy)-5-(octyloxy)benzene (**4ab**, 15 g, 25.6 mmol) was dissolved in dry diethyl ether (300 mL) and deaerated for 1 hour. The mixture was cooled to -40 °C and kept under nitrogen. A solution of *n*-butyllithium (*n*-BuLi, 2.5 M in hexane, 10.3 mL, 25.8 mmol) was added dropwise under stirring over a period of 1 hour. After additional 10 minutes N,N-dimethylformamide (DMF, 2.6 mL, 34 mmol) was added slowly. The cooling bath was removed and the stirring continued for 3 hours. The reaction mixture was quenched by the addition of hydrochloric acid (aqueous HCl, 10 wt.%, 160 mL). The organic layer was washed with saturated $NaHCO_3$ solution and water, dried over $Na_2S_2O_4$, and concentrated using a rotary evaporator. The crude product was further purified by column chromatography (silica gel, dichloromethane/cyclohexane 1:1) to yield the regioisomer mixture **5ab**/**5ba** (**5a/b**, 4.2 g, 8.6 mmol, 34 % yield, Rf = 0.68) as a brown oil. A separation of the isomers **5ab** and **5ba** was not successful with standard column chromatography techniques. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.86-0.95 (m, 9H, -C<u>H</u>$_3$), 1.29-1.84 (m, 21H, -C<u>H</u>-, -C<u>H</u>$_2$-), 3.87 (*p*d, 2H, ^3J = 5.5 Hz, -O-C<u>H</u>$_2$-CH-, mixture of isomers), 3.99 (*p*t, 2H, ^3J = 6.4 Hz, -O-C<u>H</u>$_2$-CH$_2$-, mixture of isomers), 7.17, 7.18 ,7.45, 7.46 (s, s, s, s, 2H, C_{phen}-<u>H</u>, mixture of isomers), 10.42 (-C<u>H</u>O).

2-(2-Ethylhexyloxy)-5-octyloxy-4-((trimethylsilyl)ethynyl)benzaldehyde (**6ba**) / *5-(2-ethylhexyloxy)-2-octyloxy-4-((trimethylsilyl)ethynyl)benzaldehyde* (**6ab**) – *mixture of regioisomers* (**6a/b**). The regioisomer mixture **5ab/5ba** (**5a/b**, 3.5 g, 7.16 mmol), $Pd(PPh_3)_2Cl_2$ (226 mg, 0.32 mmol), and CuI (41 mg, 0.22 mmol) were added to deaerated diisopropylamine (80 mL). After 15 minutes, trimethylsilylacetylene (1.1 mL, 67.22 mmol) was added dropwise under vigorously stirring. The temperature was raised (45-50 °C) and the mixture was kept stirring overnight. Toluene (45 mL) was added and the white diisopropylammonium iodide precipitate was filtered off. The filtrate was washed with water, dried over $Na_2S_2O_4$, and concentrated with a rotary evaporator. The remaining material was purified by column chromatography (silica gel, dichloromethane/cyclohexane 1:1). The isomer mixture **6ab**/**6ba** (3.17 g, 6.9 mmol, 97 % yield, Rf = 0.6) was obtained as a brown oil. A separation of the regioisomers **6ab** and **6ba** with the applied standard column chromatography methods was not possible. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.26 (m, 9H, Si-(C<u>H</u>$_3$)$_3$), 0.88-0.93 (m, 9H, -C<u>H</u>$_3$), 1.28-1.83 (m, 21H, -C<u>H</u>-, -C<u>H</u>$_2$-), 3.82-4.03 (m, 4H, -O-C<u>H</u>$_2$-), 7.03, 7.04 (*p*s, *p*s, 2H, C_{phen}-<u>H</u>, mixture of isomers). ^{13}CNMR (75 Hz, $CDCl_3$) δ/ppm: -0.2 (-Si-(<u>C</u>H$_3$)$_3$), 11.3 (-CH-CH$_2$-<u>C</u>H$_3$), 14.1 (-(CH$_2$)$_3$-<u>C</u>H$_3$), 22.6, 23.1, 23.9, 26.0, 29.07, 29.12, 29.2, 29.3, 30.5, 31.8 (-<u>C</u>H$_2$-), 39.5 (-<u>C</u>H-), 69.2, 71.5 (-O-<u>C</u>H$_2$-), 100.4, 102.8 (-C≡<u>C</u>-Si, -<u>C</u>≡C-Si), 109.5, 117.8, 120.0 (<u>C</u>$_{phen}$-H, <u>C</u>$_{phen}$-C≡C-Si-), 125.0 (<u>C</u>$_{phen}$-CHO), 154.4, 155.3 (<u>C</u>$_{phen}$-O-CH$_2$-), 189.3 (-<u>C</u>HO).

2-(2-Ethylhexyloxy)-4-ethynyl-5-(oxtyloxy)benzaldehyde (**7ba**) and *5-(2-ethylhexyloxy)-4-ethynyl-2-(oxtyloxy)benzaldehyde* (**7ab**) – *mixture of regioisomers* (**7a/b**). The regioisomer mixture **6ab/6ba** (**6a/b**, 2.7 g, 6.28 mmol) and KF (1.14 g, 86.21 mmol) were added to a deaerated solution of methanol (20 mL) and tetrahydrofuran (THF, 25 mL). The mixture was protected from light and stirred at room temperature for 3 hours. The solvent was removed under reduced pressure (rotary evaporator); the residue was dissolved in toluene and washed with water. The organic layer was dried over $Na_2S_2O_4$ and stripped of solvent. The remaining material was purified by flash chromatography (silica gel, dichloromethane/cyclohexane 1:1) to yield the regioisomer mixture **7ab**/**7ba** (**7a/b**, 1.87 g, 4.84 mmol, 77% yield, Rf = 0.6) as a brown oil. A separation of the regioisomers **7ab**/**7ba** was not achieved. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.86-0.95 (m, 9H, -C$\underline{H}_3$), 1.28-1.84 (m, 21H, -C$\underline{H}$-, -C$\underline{H}_2$-), 3.43, 3.45 (s, s, 1H, -C≡C-$\underline{H}$, mixture of isomers), 3.90 (*p*d, 2H, "^3J = 6.4 Hz", -O-C$\underline{H}_2$-CH-, mixture of isomers), 4.04 (*p*t, 2H, "^3J = 6.6 Hz", -O-C$\underline{H}_2$-CH$_2$-, mixture of isomers), 7.07, 7.09, 7.29 (s, s, s, 2H, C_{phen}-$\underline{H}$, mixture of isomers), 10.44 (*p*s, 1H, -C$\underline{H}$O). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 11.1 (-CH-CH$_2$-$\underline{C}$H$_3$), 14.1 (-$\underline{C}$H$_3$), 22.6, 23.0, 23.9, 26.0, 29.0, 29.1, 29.2, 29.3, 30.5, 31.8 (-$\underline{C}$H$_2$-), 39.3 (-$\underline{C}$H-), 69.3, 71.9 (-O-$\underline{C}$H$_2$-), 79.4, 84.5 (-C≡$\underline{C}$-H, -$\underline{C}$≡C-H), 109.8, 118.3, 119.0 ($\underline{C}_{phen}$-H, mixture of isomers), 125.3 ($\underline{C}_{phen}$-CHO), 153.2, 153.5 ($\underline{C}_{phen}$-O-CH$_2$-), 189.22 (-$\underline{C}$HO).

9,10-Bis[(5-(2-ethylhexyloxy)-4-formyl-2-(octyloxy)phenylethynyl]anthracene (**8baab**); *9,10-bis[(2-(2-ethylhexyloxy)-4-formyl-5-(octyloxy)phenylethynyl]anthracene* (**8abba**); *9-[(5-(2-ethylhexyloxy)-4-formyl-2-(octyloxy)phenylethynyl]-10-[(2-(2-ethylhexyloxy)-4-formyl-5-(octyloxy)phenylethynyl]anthracene* (**8abab**) *1.4-bis[(5-(2-ethylhexyloxy)-4-formyl-2-(octyloxy)phenyl]-but-1,3-diyne* (**Ibaab**); *1.4-bis[(2-(2-ethylhexyloxy)-4-formyl-5-(octyloxy)phenyl]-but-1,3-diyne* (**Iabba**); *1-[(5-(2-ethylhexyl-oxy)-4-formyl-2-(octyloxy)phenyl]-4-[(2-(2-ethylhexyloxy)-4-formyl-5-(octyloxy)phenyl]-but-1,3-diyne* (**Iabab**); *mixtures of regioisomers (Scheme S1).* 9,10-Dibromoanthracene (425.8 mg, 1.27 mmol), $Pd(PPh_3)_4$ (119.5 mg, 0.10 mmol, 4 mol%), and CuI (19.7 mg, 0.10 mmol, 4 mol%) were added to a deaerated solution of diisopropylamine (18 mL) and toluene (60 mL), and the mixture was heated at 50-60 °C. The isomer mixture **7a/b** (1 g, 2.59 mmol) was added over a period of 30 minutes. The stirring under nitrogen was continued for 48 hours while keeping the temperature at 60 °C. After cooling to room temperature, the precipitated diisopropylammonium bromide was filtered off, and the solvent was distilled off under reduced pressure (rotary evaporator). Column chromatography (silica gel, toluene/cyclohexane 1:1) was used for purification, and various fractions were collected. The anthracene dialdehyde isomer mixture **8a/ba/b** was obtained as orange material (Rf = 0.64). Its purification was finalized by reprecipitation from methanol yielding an orange powder (**8a/ba/b**, 556 mg, 0.59 mmol, 46 % yield). In addition, the diyne isomer mixture **Ia/ba/b** (**Iabba**, **Ibaab** and **Iabab**, 90 mg, 0.12 mmol, 5 % yield) was isolated during column chromatography. A separation of the respective isomer mixtures did not appear possible with the applied standard column chromatography techniques. **$\underline{\text{8a/ba/b}}$**: ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.83 (m, 6H, -CH-CH$_2$-C$\underline{H}_3$), 0.87-1.02 (m, 12H, -C$\underline{H}_3$), 1.24-2.05 (m, 42H, -C$\underline{H}$-, -C$\underline{H}_2$-), 4.08 (*p*d, 4H, "^3J = 7.0 Hz", -O-C$\underline{H}_2$-CH-, mixture of isomers), 4.17 (*p*t, 4H, "^3J = 6.3 Hz", -O-C$\underline{H}_2$-CH$_2$-), 7.32, 7.43 (*p*s, *p*s, 2H, C_{phen}-$\underline{H}$), 7.64-7.67, 8.78-8.85. (m, m, 4H, 4H, C_{anth}-$\underline{H}$), 10.51 (*p*s, 2H, -C$\underline{H}$O). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 11.0 (-CH-CH$_2$-$\underline{C}$H$_3$), 14.0, 14.1 (-$\underline{C}$H$_3$), 22.2, 23.0, 23.7, 26.05, 26.11, 29.0, 29.16, 29.23, 29.3, 30.3, 31.8 (-$\underline{C}$H$_2$-), 39.5 (-$\underline{C}$H-), 69.5, 71.6 (-O-$\underline{C}$H$_2$-), 90.9, 91.1, 94.3, 99.0, 100.0 (-C≡$\underline{C}$-C_{phen}, -$\underline{C}$≡C-C_{phen}, mixture of isomers), 109.4, 117.4 ($\underline{C}_{phen}$-H), 118.4, 120.2 ($\underline{C}_{phen}$-C≡C-, -C≡C-$\underline{C}_{anth}$), 125.2 ($\underline{C}_{phen}$-CHO) 127.0, 127.5 ($\underline{C}_{anth}$-H), 132.2 ($\underline{C}_{anth}$-), 154.1, 155.5 ($\underline{C}_{phen}$-O-CH$_2$-), 189.2 (-$\underline{C}$HO).

Ia/ba/b: ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.83 (m, 6H, -CH-CH_2-C$\underline{H}_3$), 0.86-0.97 (m, 12H, -C$\underline{H}_3$), 1.29-1.87 (m, 42H, -C$\underline{H}_2$-), 3.92 (*p*d, 4H, "^{3}J = 6.1 Hz", -O-C$\underline{H}_2$-CH-, mixture of isomers), 4.04 (*p*t, 4H, "^{3}J = 6.5 Hz", -O-C$\underline{H}_2$-CH_2-, mixture of isomers), 7.08, 7.30 (*p*s, *p*s 4H, C_{phen}-$\underline{H}$), 10.44 (*p*s, 2H, -C$\underline{H}$O).

4-(Octyloxy)phenyl p-toluenesulfonate (**10a**) Triethylamine (Et_3N, 50 mL, 337.3 mmol) was added in small portions to a stirred mixture of 4-(octyloxy)phenol (50 g, 224.9 mmol), tosyl chloride (TsCl, 42.8 g, 224.9 mmol) and tetrahydrofuran (THF, 300 mL). After stirring at room temperature for 12 hours, methylene chloride (CH_2Cl_2, 200 mL) was added. The organic phase was washed with water (2 × 50 mL) and brine (50 mL), and dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, toluene/cyclohexane in a gradient from 1:1 to 1:0). The desired product **10a** was obtained as a yellowish oil, which crystallized upon standing to yield white needles (74.5 g, 197.8 mmol, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.84-0.92 (m, 3H, -CH_2-C$\underline{H}_3$), 1.19-1.50 (m, 10H, -C$\underline{H}_2$-), 1.68-1.81 (m, 2H, -O-CH_2-C$\underline{H}_2$-), 2,44 (s, 3H, C_{aryl}-C$\underline{H}_3$); 3.88 (t, 2H, ^{3}J = 6.6 Hz, -O-C$\underline{H}_2$-), 6.71-6.79 (m, 2H, C_{phen}-$\underline{H}$), 6.82-6.90 (m, 2H, C_{phen}-$\underline{H}$), 7.27-7.33 (m, 2H, C_{tos}-$\underline{H}$), 7.65-7.72 (m, 2H, C_{tos}-$\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.1 (-CH_2-$\underline{C}H_3$), 21.7 (C_{tos}-$\underline{C}H_3$), 22.7, 26.0, 29.19, 29.21, 29.3, 31.8 (-$\underline{C}H_2$-), 68.4 (-O-$\underline{C}H_2$-), 115.0, 123.3 ($\underline{C}_{phen}$-H), 128.6, 129.7 ($\underline{C}_{tos}$-H), 132.4 ($\underline{C}_{tos}$-SO_3), 142.9 ($\underline{C}_{tos}$-CH_3), 145.2 ($\underline{C}_{phen}$-OSO_2), 157.8 ($\underline{C}_{phen}$-O-CH_2-).

3-Bromo-4-(octyloxy)phenyl p-toluenesulfonate (**11a**) Bromine (Br_2, 20.38 g, 6.57 mL, 127.5 mmol) was added to a stirred mixture of **10a** (40 g, 106.3 mmol), potassium acetate (KOAc, 27.3 g, 278.3 mmol) and acetic acid (300 mL). The stirring was continued at 50 °C overnight. More bromine (2.1 g, 677 µL, 13.1 mmol, ca. 1.2 equivalents) was added and allowed to react for another 12 hours. After cooling to room temperature, $Na_2S_2O_3$, dissolved in water, was added until the red-brownish coloration from residual bromine vanished. Methylene chloride (300 mL) was added, and the mixture was washed with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The raw product **11a** was pure enough to be used in the next reaction step. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.83-0.93 (m, 3H, -CH_2-C$\underline{H}_3$), 1.20-1.53 (m, 10H, -C$\underline{H}_2$-), 1.74-1.87 (m, 2H, -O-CH_2-C$\underline{H}_2$-), 2.46 (s, 3H, C_{tos}-C$\underline{H}_3$); 3.96 (t, 2H, ^{3}J = 6.5 Hz, -O-C$\underline{H}_2$-), 6.74 (d, 1H, ^{3}J = 9.0 Hz, C_{phen}-$\underline{H}$), 6.89 (dd, 1H, ^{3}J = 9.0 Hz, ^{4}J = 2.7 Hz, C_{phen}-$\underline{H}$), 7.13 (d, 1H, ^{4}J = 2.7 Hz, C_{phen}-$\underline{H}$), 7.29-7.36 (m, 2H, C_{tos}-$\underline{H}$), 7.66-7.73 (m, 2H, C_{tos}-$\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.1 (-CH_2-$\underline{C}H_3$), 21.7 (C_{tos}-$\underline{C}H_3$), 22.6, 25.9, 29.0, 29.18, 29.24, 31.8 (-$\underline{C}H_2$-), 69.6 (-O-$\underline{C}H_2$-), 111.9 ($\underline{C}_{phen}$-Br), 112.7, 122.2, 127.3 ($\underline{C}_{phen}$-H), 128.6, 129.8 ($\underline{C}_{tos}$-H), 132.0 ($\underline{C}_{tos}$-SO_3), 142.6 ($\underline{C}_{tos}$-CH_3), 145.5 ($\underline{C}_{phen}$-OSO_2), 154.5 ($\underline{C}_{phen}$-O-CH_2-).

3-Bromo-4-(octyloxy)phenol (**12a**) An aqueous solution of NaOH (20 wt.%, 60 mL) was added to a stirred mixture of **11a** (20 g, 43.82 mmol) and *tert*-butanol (*t*BuOH, 60 mL). The reaction was heated at reflux, overnight. Cooled down to room temperature, the mixture was neutralized with hydrochloric acid (aqueous HCl, 1 M). After the addition of CH_2Cl_2 (200 mL), the organic phase was washed repeatedly with water and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2/hexane in a gradient from 1:1 to 1:0) to yield **12a** as a yellowish oil (11.5 g, 38.2 mmol, 87% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.81-0.95 (m, 3H, -CH_2-C$\underline{H}_3$), 1.19-1.54 (m, 10H, -C$\underline{H}_2$-), 1.72-1.86 (m, 2H, -O-CH_2-C$\underline{H}_2$-) 3.94 (t, 2H, ^{3}J = 6,5 Hz, -O-C$\underline{H}_2$-), 4.89 (s, 1H, -O$\underline{H}$), 6.72 (dd, 1H, ^{3}J = 8.7 Hz, ^{4}J = 2.9 Hz, C_{phen}-$\underline{H}$), 6.79 (d, 1H, ^{3}J = 8.7 Hz, C_{phen}-$\underline{H}$), 7.06 (d, 1H, ^{4}J = 2.7 Hz, C_{phen}-$\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.1 (-CH_2-$\underline{C}H_3$), 22.7,

26.0, 29.23, 29.24, 29.3, 31.8 (-$\underline{C}H_2$-), 70.4 (-O-$\underline{C}H_2$-), 112.9 ($\underline{C}_{phen}$-Br), 115.0, 120.4 ($\underline{C}_{phen}$-H), 149.8, 150.0 ($\underline{C}_{phen}$-O-CH_2-, $\underline{C}_{phen}$-OH).

4-Bromo-2-hydroxy-5-(octyloxy)benzaldehyde (**13a**) Magnesium chloride ($MgCl_2$, 3.6 g, 37.8 mmol), dry triethylamine (Et_3N, 8.5 mL, 60.9 mmol) and subsequently paraformaldehyde (5.34 g, 184 mmol) were added to a solution of **12a** (7.5 g, 24.9 mmol) in dry acetonitrile (CH_3CN, 75 mL). The reaction mixture was heated at reflux overnight. After cooling to room temperature, the mixture was poured into hydrochloric acid (aqueous HCl, 1 M) to neutralize the organic base. Methylene chloride (200 mL) was added, and the mixture was washed with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2/cyclohexane in a gradient from 1:1 to 1:0) to yield **13a** as a bright yellow solid (7.2 g, 21.9 mmol, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.83-0.95 (m, 3H, -CH_2-C$\underline{H}_3$), 1.21-1.57 (m, 10H, -C$\underline{H}_2$-), 1.77-1.91 (m, 2H, -O-CH_2-C$\underline{H}_2$-) 4.00 (t, 2H, ^3J = 6.3 Hz, -O-C$\underline{H}_2$-), 6.97, 7.26 (s, s, 1H, 1H, C_{phen}-$\underline{H}$), 9.82 (s, -C$\underline{H}$O), 10.71 (s, C-O$\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.1 (-$\underline{C}H_3$), 22.7, 26.0, 29.1, 29.2, 29.3, 31.8 (-$\underline{C}H_2$-), 70.2 (-O-$\underline{C}H_2$-), 115.4 ($\underline{C}_{phen}$-H), 119.4 ($\underline{C}_{phen}$-Br), 122.8 ($\underline{C}_{phen}$-H), 123.8 ($\underline{C}_{phen}$-CHO), 149.2, 155.8 ($\underline{C}_{phen}$-O-CH_2-, $\underline{C}_{phen}$-OH), 195.4 (-$\underline{C}$HO).

4-Bromo-2-(2-ethylhexyloxy)-5-(octyloxy)benzaldehyde (**5ba**) In analogy to reported protocols,[41,45,46] potassium carbonate (K_2CO_3 dried in vacuum at 200 °C, 15.56 g, 112.59 mmol) and 2-ethylhexyl bromide (5.99 g, 31.02 mmol) were added to a solution of 4-bromo-2-hydroxy-5-(octyloxy)benzaldehyde (**13a**, 9.1 g, 27.64 mmol) in dimethylformamide (DMF, anhydrous, 110 mL). The reaction mixture was placed in an oil bath at 80 °C and stirred for four hours. After cooling to room temperature, water (50 mL), brine (50 mL) and toluene (200 mL) were added. The organic layer was washed with water (2 × 50 mL) and brine (50 mL), and dried over Na_2SO_4. Solvents were stripped off at reduced pressure. Gel filtration yielded a clear brown oil with sufficient purity to proceed. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.82-0.99 (m, 9H, -C$\underline{H}_3$), 1.21-1.56 (m, 18H, -C$\underline{H}_2$-), 1.69-1.88 (m, 3H, -O-CH_2-C$\underline{H}_x$-), 3.91 (d, 2H, ^3J = 5.7 Hz, -O-C$\underline{H}_2$-CH-), 4.00 (t, 2H, ^3J = 6.5 Hz, -O-C$\underline{H}_2$-CH_2-), 7.23, 7.31 (s, s, 1H, 1H, C_{phen}-$\underline{H}$), 10.41 (s,1H, -C$\underline{H}$O).

2-(2-Ethylhexyloxy)-5-octyloxy-4-((trimethylsilyl)ethynyl)-benzaldehyde (**6ba**) 2-(2-Ethylhexyloxy)-4-bromo-5-octyloxy-benzaldehyde (**5ba**, 4 g, 9.1 mmol), $Pd(PPh_3)_2Cl_2$ (317.2 mg, 0.53 mmol), and CuI (52 mg, 0.27 mmol) were added to a deaerated solution of diisopropylamine (100 mL). After 15 minutes, trimethylsilylacetylene (1.95 mL, 1.38 g, 14.1 mmol) was added dropwise to the vigorously stirred mixture. The reaction was kept at 45 to 50 °C, overnight. Toluene (50 mL) was added and the white diisopropylammonium bromide precipitate was filtered off. The majority of trimethylamine was distilled off under reduced pressure, and the residual solution was washed with water, and dried over $Na_2S_2O_4$. After solvent evaporation (reduced pressure), the remaining material was purified by column chromatography (silica gel, dichloromethane/cyclohexane mixture) to yield **6ba** (3.8 g, 8.3 mmol, 91%, Rf ≈ 0.55) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.27 (s, 9H, Si-(C$\underline{H}_3$)$_3$), 0.81-0.99 (m, 9H, -C$\underline{H}_3$), 1.19-1.58 (m, 18H, -C$\underline{H}_2$-), 1.68-186 (m, 3H, -O-CH_2-C$\underline{H}_x$-), 3.91 (d, 2H, ^3J = 5.5 Hz, -O-C$\underline{H}_2$-CH-), 3.99 (t, 2H, ^3J = 6.3 Hz, -O-C$\underline{H}_2$-CH_2-), 7.04, 7.26 (s, s, 1H, 1H, C_{phen}-$\underline{H}$), 10.42 (s, 1H, -C$\underline{H}$O). ^{13}C NMR (75 Hz, $CDCl_3$) δ/ppm: -0.2 (Si-$\underline{C}H_3$), 11.1 (-CH-CH_2-$\underline{C}H_3$), 14.0, 14.1 (-$\underline{C}H_3$), 22.7, 23.0, 24.0, 26.0, 29.1, 29.2, 29.3, 29.4, 30.6, 31.8 (-$\underline{C}H_2$-), 39.5 (-$\underline{C}$H-), 69.2, 71.4 (-O-$\underline{C}H_2$-), 100.5, 103.0 (-C≡$\underline{C}$-Si-, -$\underline{C}$≡C–Si-), 109.9, 117.6 ($\underline{C}_{phen}$-H), 120.3 ($\underline{C}_{phen}$-C≡C-), 125.0 ($\underline{C}_{phen}$-CHO), 154.2, 155.5 ($\underline{C}_{phen}$-O-CH_2-), 189.1 (-$\underline{C}$HO).

2-(2-Ethylhexyloxy)-4-ethynyl-5-octyloxy benzaldehyde (**7ba**) A mixture of methanol (46 mL) and aqueous KOH (10 wt.%, 7 mL) was added to a stirred solution of **6ba** (4.10 g, 8.94 mmol) in tetrahydrofuran (THF, 90 mL). After 4 hours of stirring at room temperature and under exclusion of light, toluene (200 mL) was added. The organic phase was washed with water (3 × 50 mL) and brine (1 × 50 mL), and was dried with Na_2SO_4. All solvents were stripped off using a rotary evaporator and the remaining material was purified by silica gel filtration (toluene/cyclohexane 1:1) to yield **7ba** as a brownish oil (3.4 g, 8.80 mmol, 98 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.81-0.98 (m, 9H, -C$\underline{H}_3$), 1.19-1.56 (m, 18H, -C$\underline{H}_2$-), 1.67-187 (m, 3H, -O-CH$_2$-C$\underline{H}_x$-), 3.45 (s, 1H, -C≡C-$\underline{H}$), 3.91 (d, 2H, ^3J = 5.4 Hz, -O-C$\underline{H}_2$-CH-), 4.01 (t, 2H, ^3J = 6.8 Hz, -O-C$\underline{H}_2$-CH$_2$-), 7.08, 7.29 (s, s, 1H, 1H, C$_{aphen}$-$\underline{H}$), 10.43 (s, 1H, -C$\underline{H}$O). ^{13}C NMR (75 Hz, $CDCl_3$) δ/ppm: 11.1 (-CH-CH$_2$-$\underline{C}$H$_3$), 14.0, 14.1 (-$\underline{C}$H$_3$), 22.6, 23.0, 23.9, 25.9, 28.98, 29.03, 29.19, 29.24 30.6, 31.8 (-$\underline{C}$H$_2$-), 39.44 (-$\underline{C}$H-), 69.4, 71.4 (-O-$\underline{C}$H$_2$-), 79.4, 84.6 (-$\underline{C}$≡C-H, -C≡$\underline{C}$-H), 110.0, 118.2 ($\underline{C}_{phen}$-H), 119.0 ($\underline{C}_{phen}$-C≡C-), 125.3 ($\underline{C}_{phen}$-CHO), 154.1, 155.4 ($\underline{C}_{phen}$-O-CH$_2$-), 189.0 (-$\underline{C}$HO).

9,10-Bis((4-formyl-5-(2-ethylhexyloxy)-2-octyloxy)phenyl-ethynylene)anthracene (**8baab**); *9-(4-formyl-5-(2-ethyl-hexyloxy)-2-octyloxy)phenylethynylene)-10-bromoanthracene* (**8ba**) 2-(2-Ethylhexyloxy)-4-ethynyl-5-octyloxy-benzalde-hyde (**7ba**, 3.39 g, 8.77 mmol), tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$, 210 mg, 0.18 mmol, 0.02 equivalents) and CuI (21 mg, 0.11 mmol, 0.015 equivalents) were added to a deaerated mixture of toluene (100 mL), diisopropylamine (55 mL) and 9,10-dibromoanthracene (1.208 g, 3.59 mmol). The reaction temperature was increased in steps from room temperature (for 1 hour) to 45 °C (for 3 hours) and eventually to 50 °C (for 13 hours). Afterwards toluene (150 mL) was added, diisopropylammonium bromide was filtered off, and the filtrate was washed with dilute hydrochloric acid (aqueous HCl, 10 wt.%, 3 × 50 mL), water (3 × 50 mL) and brine (1 × 50 mL). The organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure using a rotary evaporator. The residual mixture was separated and coarsely purified by column chromatography (silica, toluene/cyclohexane 3:1) yielding fractions with the desired product **8baab** (2.94 g) and the side product **8ba** (318 mg, 0.475 mmol, 13 % yield), respectively. Repetitive precipitation in methanol eventually yielded **8baab** (1.7 g, 1.794 mmol, 50 % yield) as a bright orange crystalline powder. **<u>8baab</u>**: ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.78-1.05 (m, 18H, -C$\underline{H}_3$), 1.15-1.65 (m, 36H, -C$\underline{H}_2$-), 1.84 (*p*septet, 2H, -O-CH$_2$-C$\underline{H}$-), 2.04 (*p*quintet, 4H, -O-CH$_2$-C$\underline{H}_2$-), 4.06 (d, 4H, ^3J = 5.4 Hz, -O-C$\underline{H}_2$-CH-), 4.15 (t, 4H, ^3J = 6.7 Hz, -O-C$\underline{H}_2$-CH$_2$-), 7.29, 7.39 (s, s, 1H, 1H, C$_{phen}$-$\underline{H}$), 7.61-7.70 (m, 4H, C$_{anthr}$-$\underline{H}$), 8.77-8.87 (m, 4H, C$_{anthr}$-$\underline{H}$), 10.50 (s, 1H, -C$\underline{H}$O). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 11.3 (-CH-CH$_2$-$\underline{C}$H$_3$), 14.06, 14.10 (-$\underline{C}$H$_3$), 22.6, 23.0, 24.1, 26.1, 29.2, 29.3, 29.5, 29.6, 30.7, 31.8 (-$\underline{C}$H$_2$-), 39.6 (-$\underline{C}$H-), 69.3, 71.6 (-O-$\underline{C}$H$_2$-), 94.7, 99.1 (-C≡$\underline{C}$-C$_{phen}$, -$\underline{C}$≡C-C$_{phen}$), 109.3, 116.8 ($\underline{C}_{phen}$-H), 118.9, 120.2 ($\underline{C}_{phen}$-C≡C-, -C≡C-$\underline{C}_{anth}$-), 125.3 ($\underline{C}_{phen}$-CHO), 126.9, 127.5 ($\underline{C}_{anth}$-H), 132.3 (-$\underline{C}_{anth}$-), 153.9, 155.8 ($\underline{C}_{phen}$-O-CH$_2$-), 189.1 (-$\underline{C}$HO). **<u>8ba</u>**: ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.87 (t, 3H, ^3J = 6.8 Hz, -C$\underline{H}_3$), 0.92-1.06 (m, 6H, -C$\underline{H}_3$) 1.13-1.62 (m, 18H, -C$\underline{H}_2$-), 1.70-1.89 (m, 3H, -O-CH$_2$-C$\underline{H}_x$-), 3.82 (t, 2H, ^3J = 7.1 Hz, -O-C$\underline{H}_2$-CH$_2$-), 3.89 (d, 2H, ^3J = 5.7 Hz, -O-C$\underline{H}_2$-CH-), 6.93, 7.10 (s, s, 1H, 1H, C$_{phen}$-$\underline{H}$), 7.39-7.54 (m, 4H, C$_{anthr}$-$\underline{H}$), 8.41 (d, 2H, ^3J = 8.7 Hz, C$_{anthr}$-$\underline{H}$), 8.59 (d, 2H, ^3J = 8.4 Hz, C$_{anthr}$-$\underline{H}$), 10.42 (s, 1H, -C$\underline{H}$O).

1-Bromo-5-(2-ethylhexyloxy)-2-(octyloxy)benzene (**14ab**) A mixture of 3-bromo-4-(octyloxy)phenol (12 g, 39.84 mmol) and dried DMSO (75 mL) was stirred, and deaerated by purging with nitrogen. After 1 hour, KOH (5 g, 89.11 mmol, ~2 equiv.) and 2-ethylhexyl bromide (9 g, 46.60 mmol, ~1.2 equiv.) were added. The reaction mixture was stirred for 4 hours under nitrogen atmosphere at room temperature, and finally poured into cold water (200 mL). The

mixture was extracted with cyclohexane (3 × 70 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated using a rotary evaporator. Residual DMSO and alkyl bromide were distilled off under reduced pressure to yield **14ab** (15.14 g, 36.62 mmol, 92 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.82-0.98 (m, 9H, -C<u>H</u>$_3$), 1.22-1.58 (m, 18H, -C<u>H</u>$_2$-), 1.69 (*p*septet, 1H, -O-CH$_2$-C<u>H</u>-), 1.80 (*p*quintet, 2H, -O-CH$_2$-C<u>H</u>$_2$-), 3.77 (d, 2H, ^3J = 5.7 Hz, -O-C<u>H</u>$_2$-CH-), 3.95 (t, 2H, ^3J = 6.5 Hz, -O-C<u>H</u>$_2$-CH$_2$-), 6.78 (dd, 1H, ^3J = 8.9 Hz, ^4J = 2.6 Hz, C_{phen}-<u>H</u>), 6.83 (d, 1H, ^3J = 8.7 Hz, C_{phen}-<u>H</u>), 7.11 (d, 1H, ^4J = 2.4 Hz, C_{phen}-<u>H</u>).

5-(2-Ethylhexyloxy)-2-(octyloxy)benzaldehyde (**15ab**) 1-Bromo-5-(2-ethylhexyloxy)-2-(octyloxy) benzene (**14ab**, 10 g, 24.19 mmol) was dissolved in dry diethyl ether (260 mL). The mixture was cooled to -78 °C and deaerated for one hour. A solution of *n*-BuLi (2.5 M in hexane, 10.66 mL, 26.65 mmol, 1.1 equiv.) was added dropwise over a period of one hour. The mixture was stirred for additional 10 minutes. Afterwards dimethylformamide (DMF, 2.5 mL, 2.37 g, 32.42 mmol, 1.34 equiv.) was added. The cooling bath was removed after 15 minutes, and the solution was stirred for additional 3 hours. The reaction was quenched by the addition of hydrochloric acid (aqueous HCl, 10 wt.%, 150 mL). The organic layer was washed with saturated $NaHCO_3$ solution (70 mL), water (2 × 70 mL), dried over $MgSO_4$, and concentrated using a rotary evaporator. The crude product was further purified by column chromatography to yield **15ab** (7.28 g, 20.08 mmol, 83 % yield).). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.82-0.96 (m, 9H, -C<u>H</u>$_3$), 1.19-1.57 (m, 18H, -C<u>H</u>$_2$-), 1.70 (*p*septet, 1H, -O-CH$_2$-C<u>H</u>-), 1.81 (*p*quintet, 2H, -O-CH$_2$-C<u>H</u>$_2$-), 3.82 (d, 2H, ^3J = 6.0 Hz, -O-C<u>H</u>$_2$-CH-), 4.03 (t, 2H, ^3J = 6.5 Hz, -O-C<u>H</u>$_2$-CH$_2$-), 6.92 (d, 1H, ^3J = 9.0 Hz, C_{phen}-<u>H</u>), 7.11 (d, 1H, ^3J = 9.0 Hz, ^4J = 3.3 Hz, C_{phen}-<u>H</u>), 7.31 (d, 1H, ^4J = 3.3 Hz, C_{phen}-<u>H</u>).

4-Bromo-5-(2-ethylhexyloxy)-2-(octyloxy)benzaldehyde (**5ab**) Bromine (Br_2, 2.25 mL, 7.02 g, 43.93 mmol, 1.02 equiv.) was added to a stirred mixture of 5-(2-ethylhexyloxy)-2-(octyloxy)benzaldehyde (15.6 g, 43.03 mmol) and acetic acid (25 mL). The mixture was stirred overnight at room temperature. A saturated $NaHSO_3$ solution was added until the color of residual Br_2 vanished. After addition of methylene chloride (CH_2Cl_2, 80 mL), the mixture was washed with water (2 × 40 mL) and brine (40 mL). The organic layer was dried over $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography to yield **5ab** (14.82 g, 33.56 mmol, 78 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.80-0.98 (m, 9H, -C<u>H</u>$_3$), 1.20-1.59 (m, 18H, -C<u>H</u>$_2$-), 1.67-1.89 (m, 3H, -O-CH$_2$-C<u>H</u>$_x$-), 3.89 (d, 2H, ^3J = 5.4 Hz, -O-C<u>H</u>$_2$-CH-), 4.01 (t, 2H, ^3J = 6.5 Hz, -O-C<u>H</u>$_2$-CH$_2$-), 7.21, 7.30 (s, s, 1H, 1H, C_{phen}-<u>H</u>), 10.41 (s, 1H, -C<u>H</u>O).

5-(2-ethylhexyloxy)-2-(octyloxy)-4-((trimethylsilyl)ethynyl)-benzaldehyde (**6ab**) In analogy to the preparation of **6a/b** and **6ba**, the regioisomer **5ab** was reacted with trimethylsilylacetylene by Sonogashira cross-coupling. The desired product **6ab** was isolated by column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.26 (s, 9H, Si-(C<u>H</u>$_3$)$_3$), 0.80-1.01 (m, 9H, -C<u>H</u>$_3$), 1.19-1.65 (m, 18H, -C<u>H</u>$_2$-), 1.67-189 (m, 3H, -O-CH$_2$-C<u>H</u>$_x$-), 3.80-3.96 (m, 2H, -O-C<u>H</u>$_2$-CH-), 4.02 (t, 2H, ^3J = 6.5 Hz, -O-C<u>H</u>$_2$-CH$_2$-), 7.04, 7.26 (s, s, 1H, 1H, C_{phen}-<u>H</u>), 10.43 (s, 1H, -C<u>H</u>O). ^{13}C NMR (75 Hz, $CDCl_3$) δ/ppm: -0.2 (Si-<u>C</u>H$_3$), 11.2 (-CH-CH$_2$-<u>C</u>H$_3$), 14.1 (-<u>C</u>H$_3$), 22.6, 23.1, 23.9, 26.0, 29.09, 29.14, 29.2, 29.3, 30.5, 31.8 (-<u>C</u>H$_2$-), 39.6 (-<u>C</u>H-), 69.3, 71.5 (-O-<u>C</u>H$_2$-), 100.5, 102.8 (-C≡<u>C</u>-Si-, -<u>C</u>≡C–Si-), 109.5, 117.8 (<u>C</u>$_{phen}$-H), 120.1 (<u>C</u>$_{phen}$-C≡C-), 125.0 (<u>C</u>$_{phen}$-CHO), 154.5, 155.3 (<u>C</u>$_{phen}$-O-CH$_2$-), 189.2 (-<u>C</u>HO).

5-(2-Ethylhexyloxy)-4-ethynyl-2-(octyloxy)benzaldehyde (**7ab**) 5-(2-Ethylhexyloxy)-2-octyloxy-4-((trimethylsilyl)ethynyl)-benzaldehyde (**6ab**, 1.2 g, 2.62 mmol) and KF (0.47 g, 8.09 mmol) were added to a degassed solution of methanol (7 mL) and tetrahydrofuran (THF, 12 mL). The mixture was protected from light, and stirred at room temperature for 3 hours. The solvent was removed under reduced pressure (rotary evaporator), and the remaining material was dissolved in toluene, and washed with water. The organic layer was dried over $MgSO_4$, and the solvent was stripped off utilizing a rotary evaporator. The residue was purified by flash chromatography (silica, dichloromethane/cyclohexane 4:1) yielding **7ab** (810 mg, 2.10 mmol, 80 %) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.81-0.97 (m, 9H, -C$\underline{H}_3$), 1.19-1.58 (m, 18H, -C$\underline{H}_2$-), 1.68-1.86 (m, 3H, -O-CH$_2$-C$\underline{H}_x$-), 3.43 (s, 1H, C≡C-H), 3.88 (d, 2H, ^3J = 6.2 Hz, -O-C$\underline{H}_2$-CH-), 4.00 (t, 2H, ^3J = 6.4 Hz, -O-C$\underline{H}_2$-CH$_2$-), 7.06, 7.28 (s, s, 1H, 1H, C_{phen}-$\underline{H}$), 10.43 (s, 1H, -CHO).

9,10-Bis((4-formyl-2-(2-ethylhexyloxy)-5-octyloxy)phenyl-ethynylene)anthracene (**8abba**); The synthesis settings of the dialdehyde **8abba** are analogous with **8a/ba/b** and **8baab**. 9,10-Dibromoanthracene (340.6 mg, 1.014 mmol), $Pd(PPh_3)_4$ (95.6 mg, 0.083 mmol, 0.04 equiv.), and CuI (15.8 mg, 0.083 mmol, 0.04 equiv.) were added to a deaerated solution of diisopropylamine (15 mL) and toluene (50 mL), and heated to 50-60 °C. 5-(2-Ethylhexyloxy)-4-ethynyl-2-octyloxybenzal-dehyde (**7ab**, 800 mg, 2.069 mmol) was added over a period of 30 minutes. The mixture was stirred at 60 °C for 48 hours under nitrogen atmosphere. The raw material was isolated, and purified by column chromatography to obtain the desired product **8abba** (230 mg, 0.243 mmol, 24 % yield), which was further purified by reprecitation from methanol to yield an orange powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.81 (t, 6H, ^3J = 7.2 Hz, -C$\underline{H}_3$), 0.86-0.98 (m, 12H, -C$\underline{H}_3$), 1.17-1.72 (m, 36H, -C$\underline{H}_2$-), 1.83-2.03 (m, 6H, -O-CH$_2$-C$\underline{H}_2$-, -O-CH$_2$-C$\underline{H}$-), 4.06 (d, 4H, ^3J = 5.6 Hz, -O-C$\underline{H}_2$-CH-), 4.18 (t, 4H, ^3J = 6.4 Hz, -O-C$\underline{H}_2$-CH$_2$-), 7.33, 7.43 (s, s, 1H, 1H, C_{phen}-$\underline{H}$), 7.63-7.70 (m, 4H, C_{anthr}-$\underline{H}$), 8.76-8.84 (m, 4H, C_{anthr}-$\underline{H}$), 10.52 (s, 1H, -C$\underline{H}$O).

Synthesis of polymers – *general procedure*

Equimolar amounts of comonomers, dialdehyde **8** and bisphosphonate **3**, were dissolved in dry toluene. Heating was applied via an oil bath in the range between 100 and 120 °C. The stirred solution was kept in inert atmosphere (slight nitrogen flow). Excess of potassium *tert*-butoxide was added in portions to initiate the polyolefination reaction. Strong increases in viscosity were counterbalanced by the addition of small amounts of toluene. After 1 to 2 hours the polycondensation reaction was quenched by the addition of benzaldehyde. Heating was stopped, toluene, water and hydrochloric acid (aqueous HCl, 10 wt.%) were added in excess. The organic phase was separated, washed neutral with deionized water, and dried in a Dean-Stark apparatus. After hot filtration, the solution was concentrated using a rotary evaporator, and the polymer was precipitated in cold methanol. The precipitate was filtered off with a Soxhlet thimble. After at least 24 hours extraction with methanol, using a Soxhlet extractor, the polymer was redissolved in toluene, precipitated in cold methanol, filtered off, and dried in vacuum to provide the dark purple **AnE-PV** polymer in commonly high yields (60-90 %).

Poly[1,4-(2-(2-ethylhexyloxy)-5-octyloxy-phenylene)ethynylene-9,10-anthracenylene-ethynylene-1,4-(5-(2-ethylhexyloxy)-2-octyloxy-phenylene)-ethene-1,2-diyl-1,4-(2,5-di(octyloxy)-phenylene)-ethene-1,2-diyl] (**AnE-PVbaab-aa**, **Aa**) Dialdehyde **8baab** (400 mg, 0.422 mmol) and bisphosphonate **3aa** (268 mg, 0.422 mmol) were dissolved in dry toluene (20 mL), and heated to 100 °C under stirring and slight nitrogen flow. Potassium *tert*-butoxide (270 mg, 2.406 mmol, ~5.7 equiv.) was added to initiate the HWE olefination reaction. After 1.5 hours the polycondensation reaction was quenched with benzaldehyde (100 µL). The heating was stopped, toluene (20 mL), water (10 mL), and hydrochloric acid (aqueous HCl, 10 wt.%, 10 mL) were added. The organic layer was washed with deionized water until the aqueous phase was tested neutral. Drying in a Dean-Stark apparatus was followed by hot filtration, concentration (rotary evaporator), and precipitation in cold methanol. The polymer was filtered off and extracted with methanol (Soxhlet extractor), redissolved in toluene, precipitated in cold methanol, filtered off and dried under vacuum to yield a purple fibrous material (**Aa**, 430 mg, "0.338 mmol" (repeating unit), 80 % yield). SEC (TBC, 160 °C): M_w = 31 900 g/mol, Đ = 4.46, DP = 6. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.58-1.08 (m, 24H, -C$\underline{H}_3$), 1.09-2.22 (m, 66H, -C$\underline{H}_2$-, -C$\underline{H}$-), 3.41-4.39 (m, 12H, -O-C$\underline{H}_2$-), 6.69-7.01, 7.05-7.41, 7.43-7.87 (m, m, m, 14H, C_{vinyl}-$\underline{H}$, C_{aryl}-$\underline{H}$), 8.73-9.00 (m, 4H, -C_{anth}-$\underline{H}$).

Poly[1,4-(2-(2-ethylhexyloxy)-5-octyloxy-phenylene)ethynylene-9,10-anthracenylene-ethynylene-1,4-(5-(2-ethylhexyloxy)-2-octyloxy-phenylene)-ethene-1,2-diyl-1,4-(2,5-di(2-ethylhexyloxy)-phenylene)-ethene-1,2-diyl] (**AnE-PVbaab-bb**, **Ab**) Dialdehyde **8baab** (200 mg, 0.211 mmol) and bisphosphonate **3bb** (134 mg, 0.211 mmol) were dissolved in dry toluene (ca. 15 mL). The solution was heated using an oil bath (100-110 °C) under constant stirring and nitrogen flow. The polycondensation was initiated upon addition of potassium *tert*-butoxide in large excess. After 75 minutes benzaldehyde (100 µL) was injected. The oil bath was removed, toluene (20 mL), water (10 mL) and hydrochloric acid (aqueous HCl, 10 wt.%, 13 mL) were added. After purification the polymer **Ab** (170 mg, "0.133 mmol" (repeating unit), 63 % yield) was obtained as dark purple slightly fibrous material. SEC (TCB, 160 °C): M_w = 17 700 g/mol, Đ = 2.64, DP = 6. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.58-2.22 (m, 90H, -C$\underline{H}_3$, -C$\underline{H}_2$-, -C$\underline{H}$-), 3.41-4.36 (m, 12H, -O-C$\underline{H}_2$-), 6.66-7.01, 7.06-7.41, 7.43-7.86 (m, m, m, 14H, C_{vinyl}-$\underline{H}$, C_{aryl}-$\underline{H}$), 8.71-8.99 (m, 4H, -C_{anth}-$\underline{H}$).

Poly[1,4-(2-(2-ethylhexyloxy)-5-octyloxy-phenylene)ethynylene-9,10-anthracenylene-ethynylene-1,4-(5-(2-ethylhexyloxy)-2-octyloxy-phenylene)-ethene-1,2-diyl-1,4-(2,5-(2-ethylhexyloxy)/oxtyloxy)-phenylene)-ethene-1,2-diyl] (**AnE-PVbaab-a/b**, **Ac**) Dialdehyde **8baab** (200.5 mg, 0.212 mmol) and bisphosphonate **3ab** (134.5 mg, 0.212 mmol) were reacted, and the resulting material was purified to yield the dark purple polymer **Ac** (165 mg, "0.130 mmol" (repeating unit), 61 % yield). SEC (TCB, 160 °C): M_w = 21 800 g/mol, Đ = 2.6, DP = 7. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.59-1.10 (m, 27H, -C$\underline{H}_3$), 1.11-2.22 (m, 63H, -C$\underline{H}_2$-, -C$\underline{H}$-), 3.40-4.42 (m, 12H, -O-C$\underline{H}_2$-), 6.70-7.01, 7.08-7.41, 7.43-7.86 (m, m, m, 14H, C_{vinyl}-$\underline{H}$, C_{aryl}-$\underline{H}$), 8.72-9.00 (m, 4H, -C_{anth}-$\underline{H}$).

Poly[1,4-(5-(2-ethylhexyloxy)-2-octyloxy-phenylene)ethynylene-9,10-anthracenylene-ethynylene-1,4-(2-(2-ethylhexyloxy)-5-octyloxy-phenylene)-ethene-1,2-diyl-1,4-(2,5-di(oxtyloxy)-phenylene)-ethene-1,2-diyl] (**AnE-PVabba-aa**, **Ba**) As described for the previous HWE polycondensations, equimolar amounts of dialdehyde **8abba** (450 mg, 0.475 mmol) and bisphosphonate **3aa** (301.5 mg, 0.475 mmol), dissolved in dry toluene (25 mL), were reacted in the presence of an excessive amount of potassium *tert*-butoxide (215 mg, 1.916 mmol, ~4 equiv.) to yield, after

purification, the desired purple polymer **Ba** (520 mg, "0.408 mmol" (repeating unit), 86 % yield). SEC (TCB, 160 °C): M_w = 27 000 g/mol, Đ = 2.31, DP = 9. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.60-1.09 (m, 24H, -C<u>H</u>$_3$), 1.11-2.09 (m, 66H, -C<u>H</u>$_2$-, -C<u>H</u>-), 3.47-4.27 (m, 12H, -O-C<u>H</u>$_2$-), 6.74-6.99, 7.11-7.36, 7.45-7.79 (m, m, m, 14H, C_{vinyl}-<u>H</u>, C_{aryl}-<u>H</u>), 8.74-8.92 (m, 4H, -C_{anth}-<u>H</u>).

Poly[1,4-(5-(2-ethylhexyloxy)-2-octyloxy-phenylene)ethynylene-9,10-anthracenylene-ethynylene-1,4-(2-(2-ethylhexyloxy)-5-octyloxy-phenylene)-ethene-1,2-diyl-1,4-(2,5-di(2-ethylhexyloxy)-phenylene)-ethene-1,2-diyl] (**AnE-PVabba-bb**, **Bb**) Equimolar amounts of dialdehyde **8abba** (450 mg, 0.475 mmol) and bisphosphonate **3bb** (301.5 mg, 0.475 mmol), dissolved in dry toluene (25 mL), were reacted in the presence of potassium *tert*-butoxide (215 mg, 1.916 mmol, ~4 equiv.) to yield, after purification, the desired purple polymer **Bb** (470 mg, "0.369 mmol" (repeating unit), 78 % yield). SEC (TCB, 160 °C): M_w = 17 400 g/mol, Đ = 2.27, DP = 6. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.59-1.08 (m, 30H, -C<u>H</u>$_3$), 1.09-2.19 (m, 60H, -C<u>H</u>$_2$-, -C<u>H</u>-), 3.40-4.24 (m, 12H, -O-C<u>H</u>$_2$-), 6.69-6.98, 7.11-7.38, 7.44-7.80 (m, m, m, 14H, C_{vinyl}-<u>H</u>, C_{aryl}-<u>H</u>), 8.70-8.93 (m, 4H, -C_{anth}-<u>H</u>).

Poly[1,4-(5-(2-ethylhexyloxy)-2-octyloxy-phenylene)ethynylene-9,10-anthracenylene-ethynylene-1,4-(2-(2-ethylehxyloxy)-5-octyloxy-phenylene)-ethene-1,2-diyl-1,4-(2,5-(2-ethylhexyloxy/octyloxy)-phenylene)-ethene-1,2-diyl] **AnE-PVabba-a/b** (**Bc**) Dialdehyde **8abba** (450 mg, 0.475 mmol) and bisphosphonate **3ab** (301.5 mg, 0.475 mmol) were dissolved in dry toluene (25 mL). Potassium *tert*-butoxide (215 mg, 1.916 mmol, ~4 equiv.) was added to initiate the HWE olefination reaction. After the quenching of the reaction, extensive purification yielded the purple polymer **Bc** (540 mg, "0.424 mmol" (repeating unit), 89 % yield). SEC (TBC, 160 °C): M_w = 27 900 g/mol, Đ = 2.48, DP = 8. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.56-1.09 (m, 27H, -C<u>H</u>$_3$), 1.10-2.15 (m, 63H, -C<u>H</u>$_2$-, -C<u>H</u>-), 3.39-4.29 (m, 12H, -O-C<u>H</u>$_2$-), 6.67-7.02, 7.09-7.38, 7.43-7.82 (m, m, m, 14H, C_{vinyl}-<u>H</u>, C_{aryl}-<u>H</u>), 8.71-8.94 (m, 4H, -C_{anth}-<u>H</u>).

Poly[1,4-(2,5-(2-ethylhexyloxy/octyloxy-phenylene)ethynylene-9,10-anthracenylene-ethynylene-1,4-(2,5-(2-ethylhexyloxy/octyloxy-phenylene)-ethene-1,2-diyl-1,4-(2,5-di(octyloxy)-phenylene)-ethene-1,2-diyl] (**AnE-PVa/ba/b-aa**, **Ca**) Equimolar amounts of dialdehyde **8a/ba/b** (500 mg, 0.528 mmol) and bisphosphonate **3aa** (335 mg, 0.528 mmol) were dissolved in dry toluene (25 mL). Under nitrogen flow and heating to reflux (oil bath, 115-120 °C) potassium *tert*-butoxide (236 mg, 2.103 mmol, ~4 equiv.) was added to the stirred solution. Additional toluene (10 mL) was added in small portions to avoid too high viscosity. After 75 minutes toluene (45 mL) was added and the polycondensation reaction was quenched with an injection of benzaldehyde (1.5 mL). After another 10 minutes the oil bath was removed and hydrochloric acid (aqueous HCl, 10 wt.%, 10 mL) was added to the mixture. The organic phase was separated and washed with deionized water until reaching pH neutrality (pH = 6-7). The organic solution was dried in a Dean-Stark apparatus, concentrated with a rotary evaporator, and injected in cold methanol. The precipitated polymeric material was filtered off, extracted for 24 hours with methanol (Soxhlet extractor), redissolved in toluene, precipitated once more in methanol, filtered off and dried under vacuum to yield the purple red polymer **Ca** (525 mg, "0.412 mmol" (repeating unit), 78 % yield). SEC (TCB, 160 °C): M_w = 27 700 g/mol, Đ = 2.33, DP = 9. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.58-1.08 (m, 24H, -C<u>H</u>$_3$), 1.09-2.18 (m, 66H, -C<u>H</u>$_2$-, -C<u>H</u>-), 3.48-4.31 (m, 12H, -O-C<u>H</u>$_2$-), 6.69-6.99, 7.06-7.35, 7.41-7.76 (m, m, m, 14H, C_{vinyl}-<u>H</u>, C_{aryl}-<u>H</u>), 8.71-8.93 (m, 4H, -C_{anth}-<u>H</u>).

Poly[1,4-(2,5-(2-ethylhexyloxy/octyloxy-phenylene)ethynylene-9,10-anthracenylene-ethynylene-1,4-(2,5-(2-ethylhexyloxy/octyloxy-phenylene)-ethene-1,2-diyl-1,4-(2,5-di(2-ethylhexyloxy)-phenylene)-ethene-1,2-diyl] (**AnE-PVa/ba/b-bb**, **Cb**) A solution of dialdehyde **8a/ba/b** (490 mg, 0.517 mmol) and bisphosphonate **3bb** (328.3 mg, 0.517 mmol) in dry toluene (25 mL) was heated to reflux (oil bath, 115-120 °C). Potassium *tert*-butoxide (232 mg, 2.067 mmol, ~4 equiv.) was added. Small portions of toluene were added to keep the viscosity of the mixture reasonable low. After 75 minutes toluene (40ml), benzaldehyde (1.5 ml) and hydrochloric acid (aqueous HCl, 10 wt.%, 10 mL) were added in the before described sequence. The organic phase was separated, washed with water, dried in a Dean-Stark apparatus, concentrated, and injected into cold methanol. The precipitate was filtered off, extracted with methanol (Soxhlet extractor, 24 hours), redissolved in toluene, precipitated in methanol, filtered off and dried to yield the purple-red polymer **Cb** (492 mg, "0.386 mmol" (repeating unit), 75 % yield). SEC (TCB, 160 °C): M_w = 34 700 g/mol, Đ = 2.58, DP = 11. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.60-1.09 (m, 30H, -C$\underline{H}_3$), 1.09-2.18 (m, 60H, -C$\underline{H}_2$-, -C$\underline{H}$-), 3.40-4.42 (m, 12H, -O-C$\underline{H}_2$-), 6.64-7.03, 7.06-7.37, 7.42-7.79 (m, m, m, 14H, C_{vinyl}-$\underline{H}$, C_{aryl}-$\underline{H}$), 8.70-8.93 (m, 4H, -C_{anth}-$\underline{H}$).

Poly[1,4-(2,5-(2-ethylhexyloxy/octyloxy-phenylene)ethynylene-9,10-anthracenylene-ethynylene-1,4-(2,5-(2-ethylhexyloxy/octyloxy-phenylene)-ethene-1,2-diyl-1,4-(2,5-(2-ethylhexyloxy/octyloxy)-phenylene)-ethene-1,2-diyl] (**AnE-PVa/ba/b-a/b**, **Cc**) Dialdehyde batch **8a/ba/b** (400 mg, 0.422 mmol) and bisphosphonate (**3ab**, 268 mg, 0.422 mmol) were dissolved in dry toluene (20 mL). Providing a slight nitrogen flow and continuous stirring, the solution was heated to reflux (oil bath, 110-120 °C). The HWE reaction was initiated with potassium *tert*-butoxide (189.4 mg, 1.688 mmol). After 1.5 hours the polycondensation reaction was quenched with benzaldehyde (ca. 500 µl). The heating was stopped, toluene (50 mL), water (10 mL) and hydrochloric acid (aqueous HCl, 10 wt.%, 20 mL) were added. The organic layer was separated and washed neutral with deionized water. Drying in a Dean-Stark apparatus was followed by hot filtration, concentration (rotary evaporator), and precipitation in cold methanol. The polymer was filtered off and extracted for 24 hours with methanol (Soxhlet extractor), redissolved in toluene, precipitated in cold methanol, filtered off and dried under vacuum to yield the purple polymer **Cc** (485 mg, "0.381 mmol" (repeating unit), 90 % yield). SEC (TCB, 160 °C): M_w = 33 700 g/mol, Đ = 2.64, DP = 10. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.56-1.09 (m, 27H, -C$\underline{H}_3$), 1.09-2.22 (m, 63H, -C$\underline{H}_2$-, -C$\underline{H}$-), 3.36-4.33 (m, 12H, -O-C$\underline{H}_2$-), 6.67-7.02, 7.06-7.38, 7.42-7.81 (m, m, m, 14H, C_{vinyl}-$\underline{H}$, C_{aryl}-$\underline{H}$), 8.71-8.96 m, 4H, C_{anth}-$\underline{H}$).

Formyl protection, etherification and attempted deprotection (Scheme S5)

5-Bromo-2-(5,5-dimethyl-1,3-dioxan-2-yl)-4-octyloxy-phenol (**16a**) – following the protocol of X. Zhu et al.[3] A mixture of **13a** (5.50 g, 16.71 mmol), 2,2-dimethylpropane-1,3-diol (6.90 g, 66.25 mmol, 4 equiv.), toluene (80 mL) and catalytic amounts of *p*-toluenesulfonic acid (*p*-TsOH, 28.7 mg, 0.167 mmol, 0.01 equiv.) was heated to reflux in a Dean-Stark trap overnight. Cooled to room temperature, dichloromethane (CH_2Cl_2, 100 mL) was added, and the mixture was washed with water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, CH_2Cl_2/hexane – gradient, 3:2 >> 1:0) to yield **16a** (5.10 g, 12.28 mmol, 73 % yield) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.83 (s, 3H, -C-C$\underline{H}_3$), 0.85-0.94 (m, 3H, -C$\underline{H}_3$), 1.22-1.54 (m, 13H, -C$\underline{H}_3$, -C$\underline{H}_2$-), 1.72-1.85 (m, 2H, -O-CH$_2$-C$\underline{H}_2$-), 3.62-3.70, 3.78-3.85 (m, m, 2H, 2H, -CH-(O-C$\underline{H}_2$)$_2$-), 3.93 (t, 2H, ^3J = 6.6 Hz, O-CH$_2$), 5.49 (s, 1H, -C$\underline{H}$-(O-CH$_2$)$_2$-), 6.76, 7.11 (s, s, 1H, 1H, C_{phen}-H), 7.11 (s, 1H, C_{phen}-$\underline{H}$), 7.63 (s, 1H, C_{phen}-O$\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.1

(-C-$\underline{C}H_3$), 22.5 (-$\underline{C}H_3$), 22.6, 26.2, 29.0, 29.35, 29.37, 30.4, 31.8 (-$\underline{C}H_2$-, -$\underline{C}$-CH_2-), 70.1 (-O-$\underline{C}H_2$-CH_2-), 77.1 (CH-O-$\underline{C}H_2$-), 102.1 (C_{phen}-$\underline{C}$H-), 111.5, 112.4, 113.7 ($\underline{C}_{phen}$-Br, $\underline{C}_{phen}$-H), 130.7 ($\underline{C}_{phen}$-CH-), 149.4 ($\underline{C}_{phen}$-O-CH_2-), 157.7 ($\underline{C}_{phen}$-OH).

2-(4-Bromo-2-(2-ethylhexyloxy)-5-octyloxy-phenyl)-5,5-dimethyl-1,3-dioxan (**17ba**) – *following the protocol of X. Zhu et al. (Scheme S5)*[3] A mixture of **16a** (6.00 g, 14.44 mmol) and dimethyl sulfoxide (DMSO, 65 mL) was deaerated under a steady stream of nitrogen. After the addition of potassium hydroxide (KOH powder, 2.00 g, 35.64 mmol), 2-ethylhexyl bromide (5.70 g, 29.51 mmol) was added slowly. The mixture was stirred at 50 °C overnight. Hydrochloric acid (aqueous HCl, 1 M) was used for neutralization. Diethyl ether (200 mL) was added. The organic layer was extracted with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (silica gel, CH_2Cl_2/hexane – gradient, 1:1 >> 1:0) to yield **17ba** (7.20 g, 13.65 mmol, 94 % yield) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 0.78 (s, 3H, -C-C$\underline{H}_3$), 0.82-0.98 (m, 9H, -C$\underline{H}_3$), 1.19-1.57 (m, 21H, -C-C$\underline{H}_3$, -C$\underline{H}_2$-), 1.63-1.86 (m, 3H, -O-CH_2-C$\underline{H}$-, -O-CH_2-C$\underline{H}_2$-) 3.61, 3.73 (d, d, 2H, 2H, *J* = 10.8 Hz, *J* = 11.1 Hz, -O-C$\underline{H}_2$-C-), 3.80 (d, 2H, ^3J = 5.4 Hz, -O-C$\underline{H}_2$-CH-), 4.00 (t, 2H, ^3J = 6.5 Hz, -O-C$\underline{H}_2$-CH_2-), 5.66 (s, 1H, -C$\underline{H}$-$(O\text{-}CH_2)_2$-), 7.05, 7.20 (s, s, 1H, 1H, C_{phen}-$\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 11.2 (-CH-CH_2-$\underline{C}H_3$), 14.09, 14.11 (-$\underline{C}H_3$), 21.9, 22.7, 23.1, 23.20, 24.1, 26.0, 29.1, 29.22, 29.24, 29.28, 29.3, 30.3, 30.7, 31.8 (-C-C$\underline{H}_3$, -$\underline{C}H_2$-), 39.5 (-O-CH_2-$\underline{C}$H-), 70.2, 71.7 (-O-$\underline{C}H_2$-), 77.9 (-O-$\underline{C}H_2$-C-), 96.8, (C_{phen}-$\underline{C}$H-),112.5, 113.1, 117.4 ($\underline{C}_{phen}$-Br, $\underline{C}_{phen}$-H), 127.0 ($\underline{C}_{phen}$-CH-), 149.8, 150.7 ($\underline{C}_{phen}$-O-CH_2-).

4-Bromo-2-(2-ethylhexyloxy)-5-octyloxy-benzaldehyde (**5ba**) – *following the protocol of X. Zhu et al. (Scheme S5)*[3] 2-(4-Bromo-2-(2-ethylhexyloxy)-5-octyloxy-phenyl)-5,5-dimethyl-1,3-dioxan (**17ba**, 5.5 g, 10.42 mmol) was dissolved in a solution of trifluoro acetic acid (9.5 mL), THF (50 mL) and H_2O (9.5 mL) and stirred at 50 °C overnight. CH_2Cl_2 (100 mL) was added, and the mixture was extracted several times with water and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Thin layer chromatography indicated the presence of only a single material. The ^{1}H-NMR spectrum, however, provided evidence for a mixture of desired product (**5ba**) and starting material (**17ba**). Despite various attempts neither an efficient hydrolysis protocol for the acetal functionality, nor a sufficient isolation procedure for the product (**5ba**) could be developed.

ANALYSIS

NMR

Figure S1 depicts the ^{1}H NMR spectra stack of two regioisomer sets – **7ab**, **7ba** and **8abba**, **8baab**.

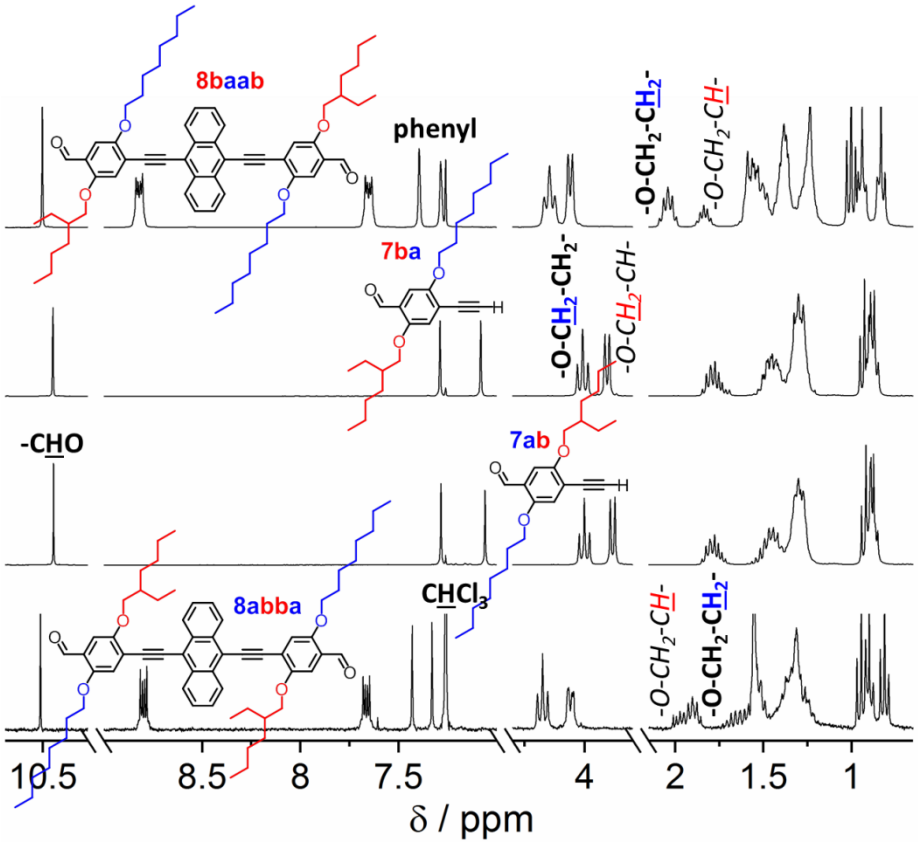


Figure S1: ^{1}H NMR (300 MHz, $CDCl_3$) spectra stack details of the double dissymmetric regioisomeric intermediates **7ab** and **7ba**, and the corresponding final dialdehyde comoners **8abba** and **8baab**.

While Figure 1 as well as S1 display selected spectral details, the complete ^{1}H NMR spectra of all three dialdehyde batches are depicted in Figure S2. The most high field signals of the dialdehyde regioisomers **8abba** and **8baab** spread out between 0.7 and 1.1 ppm and can be assigned to the various methyl protons of the side chains (-C$\underline{H}_3$). Also the following set of signals, which account for the majority of the methylene protons (-C$\underline{H}_2$-) of the alkoxy side chains, covers a rather broad range, from about 1.1 to 1.75 ppm. In the spectra of the precursor materials **7ba** and **7ab** the analogous side chain signal sets occupy significantly narrower spaces (Figure S1). In case of **8abba**, in which the two 2-ethylhexyl-oxy side chains face towards the anthracene center, these signals appear lumped into two main segments. In contrast, **8baab**, in which both octyloxy side chains point towards the anthracene unit, displays a spectrum with three major signal clusters in the same region. Closing in to the position of the deshielding oxygen the protons at the second carbon of the alkoxy chains (-O-CH_2-CH_x) appear at slightly lower field. In the spectra of the regioisomeric intermediates **7ba** and **7ab** the signals from the analogous protons strongly overlap. In the spectra of the final dialdehydes **8baab** and **8abba**, however, these signals appear rather detached from each other. Most likely the aromatic anthracene center

"deshields" the side chain protons in its proximity. In the spectrum of **8baab**, the octyloxy (-O-CH_2-C$\underline{H}_2$-) and the following 2-ethylhexyloxy (-O-CH_2-C$\underline{H}$-) multiplet appear completely separated. In contrast, the overlap of the corresponding signals in the **8abba** spectrum is significant – 2-ethylhexyloxy (-O-CH_2-C$\underline{H}$-) ca. 1.91 ppm; octyloxy (-O-CH_2-C$\underline{H}_2$-) ca. 1.90 ppm The following signals at about 4.06 (doublet) and 4.16 ppm (triplet) originate from the protons of the oxygen-linked methylene group in the 2-ethylhexyloxy (-O-C$\underline{H}_2$-CH-) and the octyloxy side chain (-O-C$\underline{H}_2$-CH_2-), respectively. It is apparent, that the switch of the side chain positions within the regioisomers **8baab** and **8abba** does not affect the chemical shifts of these protons (-O-C$\underline{H}_2$-) significantly. Also the remaining signals of the regioisomers **8baab** and **8abba**, emerging downfield in the aromatic region and beyond, show a similar alignment. The two singlets of the phenylene protons arise at about 7.3 and 7.4 ppm, respectively, and two narrow multiplets at about 7.66 and 8.81 ppm account for the proton sets of the anthracene center. The singlet of the formyl group proton, emerging almost exactly at 10.5 ppm, finalizes the spectra of **8abba** and **8baab**. The ^{1}H NMR spectrum of the dialdehyde batch **8a/ba/b** exhibits slightly more widened and complex peak sets as it can be expected for a mixture of regioisomers (Figure 1 and S2).

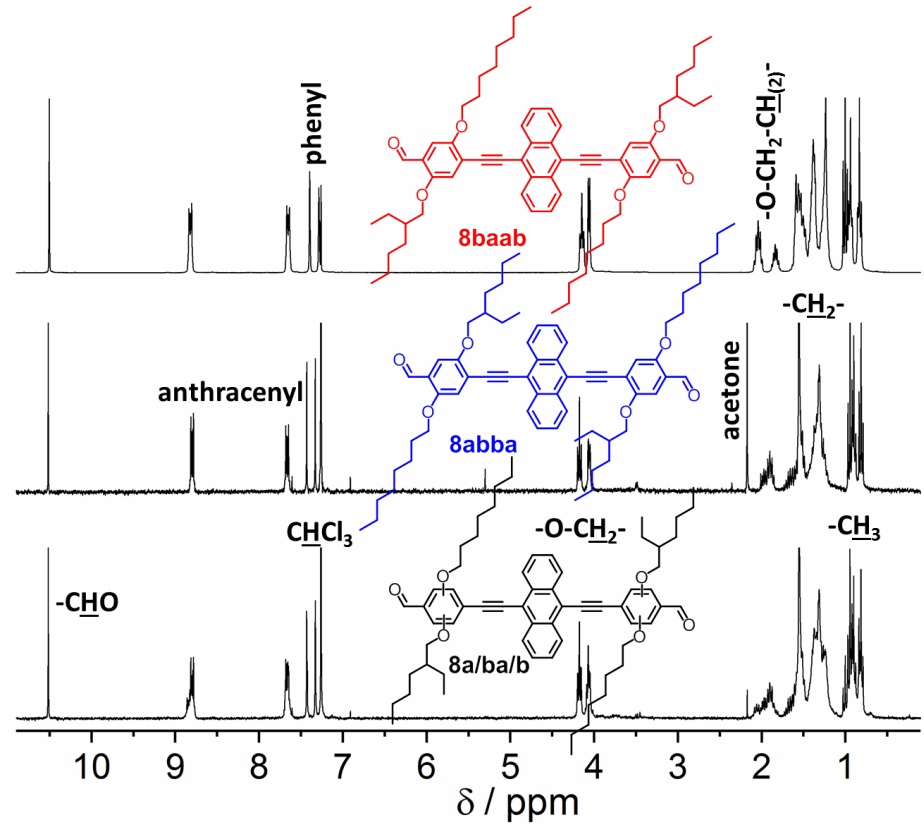


Figure S2: ^{1}H NMR (300 MHz, $CDCl_3$) spectra stack of the synthesized dialdehydes **8a/ba/b**, **8abba** and **8baab**.

The spectra of the bisphosphonate comonomers **3aa** and **3bb** are in good agreement with previous reports. The NMR spectrum of the new comonomer **3ab** shows the expected features of

a bisphosphonate derivative with mixed octyloxy/2-ethylhexyloxy side chain configuration (Figure S3).

The ^{1}H NMR spectra stack in Figure S3 (**8baab**, **3ab** and **AnE-PVbaab-a/b**) visualizes exemplarily the spectral pattern changes emerging with the successful transformation of dialdehyde and bisphosphonate comonomers into **AnE-PV** polymers. In contrast to the polymer spectra, the spectral patterns of the comonomers show narrow and well-resolved features, and exhibit comonomer-characteristic peaks – formyl (-C<u>H</u>O, ~10.5 ppm); phosphonate (e.g. -C<u>H$_2$</u>-P-, ~3.2 ppm). The strong signal broadening and loss in resolution in the polymer spectra can be attributed to polymer-immanent dispersity and increased sample viscosity.

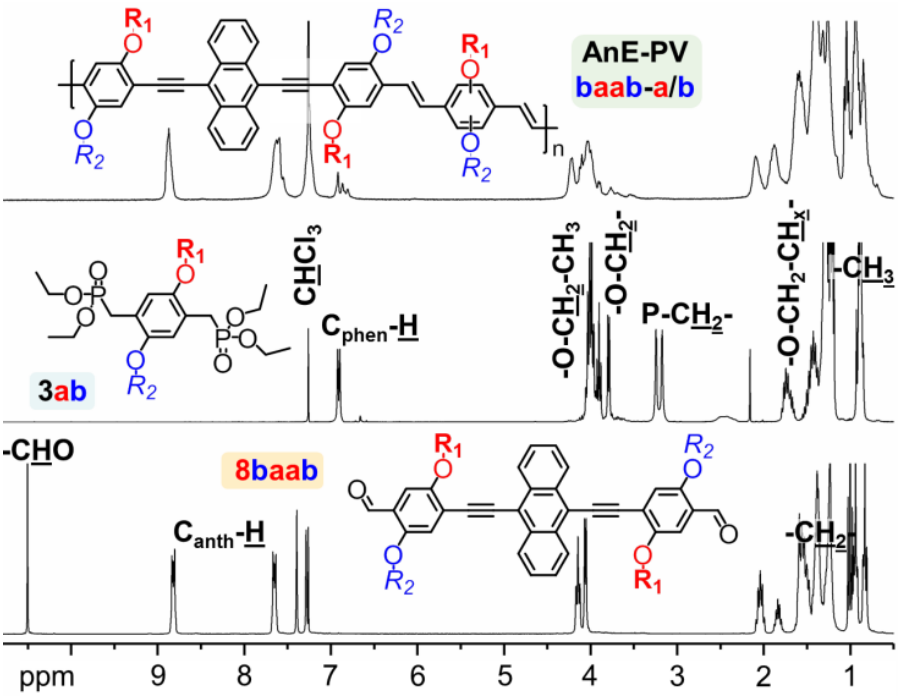


Figure S3: ^{1}H NMR spectra (300 MHz, $CDCl_3$) of the comonomers **8baab** and **3ab**, as well as their polymer product **AnE-PVbaab-a/b**.

Figure S4 and S5 depict all nine polymer ^{1}H NMR spectra in full range and in selected sections, respectively.

For poly(p-phenylene vinylene) derivatives, partially equipped with hexyloxy side chains, the NMR spectroscopic distinction of *trans*(*E*) and *cis*(*Z*)-olefinic elements is documented.[4,5]

[4] Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Umeda, K.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H.; Ozawa, F. Stereocontrolled Synthesis and Optical Properties of All-cis Poly(phenylene vinylenes) (PPVs): A Method for Direct Patterning of PPVs. *J. Am. Chem. Soc.* **2005**, *127*, 4350-4353. *(Ref. 36 in the main text)*

[5] Wang, F.; He, F.; Xie, Z. O.; Li, Y. P.; Hanif, M.; Li, M.; Ma, Y. Poly(*p*-phenylene vinylene) Derivatives with Different Contents of *cis*-Olefins and their Effect on the Optical Properties. *Macromol. Chem. Phys.* **2008**, *209*, 1381-1388. *(Ref. 37 in the main text)*

The presence of olefinic segments with *cis*-configuration is revealed by two sets of peaks arising between 6.4 and 6.9, and between 3.49 and 3.83 ppm, respectively.[5] The signals at low field (6.4-6.9 ppm) can be directly assigned to the protons of *cis*-vinylene units. Furthermore, the presence of *cis*-olefinic groups apparently induces an increased shielding at adjoining alkoxy methylene groups (-O-C$\underline{H_2}$-) causing a signal shift to higher field (3.83-3.49 ppm). Differences in the cis/trans ratio can affect the characteristics, such as solubility and optical properties, significantly.[4,5]

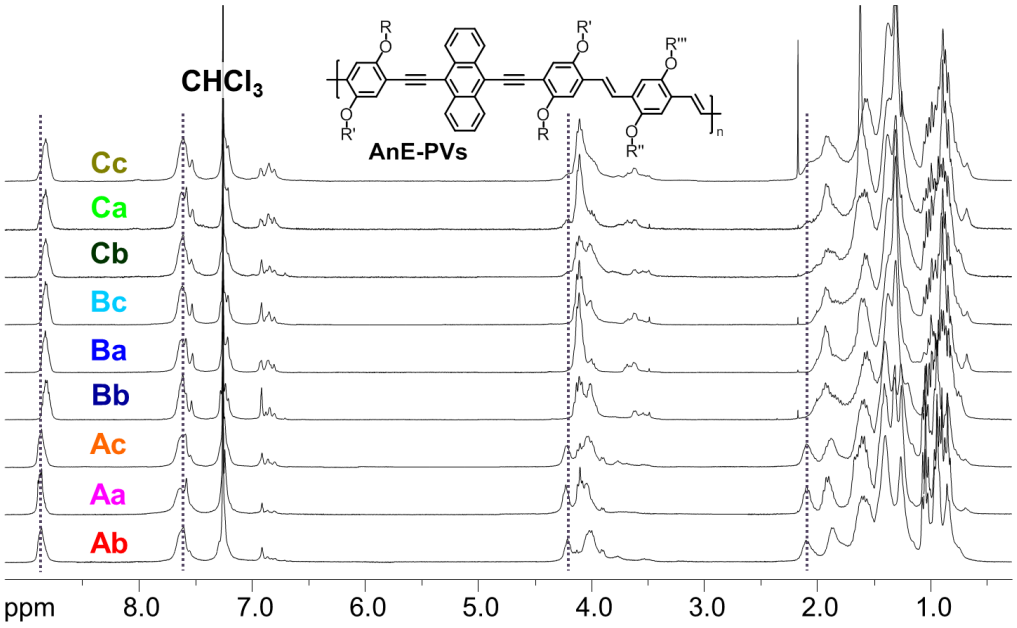


Figure S4: ^{1}H NMR (300 MHz, $CDCl_3$) spectra stack of the polymer series – **AnE-PVbaab-aa** (**Aa**), **AnE-PVbaab-bb** (**Ab**), **AnE-PVbaab-a/b** (**Ac**), **AnE-PVabba-aa** (**Ba**), **AnE-PVabba-bb** (**Bb**), **AnE-PVabba-a/b** (**Bc**), **AnE-PVa/ba/b-aa** (**Ca**), **AnE-PVa/ba/b-bb** (**Cb**) and **AnE-PVa/ba/b-a/b** (**Cc**). The dotted lines are drawn to guide the eye.

Even so all nine polymers are based on the same alternating conjugated backbone segments the different distributions of the isomeric octyloxy and 2-ethylhexyloxy side chains, attached at position 2 and 5 of the phenylene units, appear to affect the NMR signal patterns specifically (Figure S5).

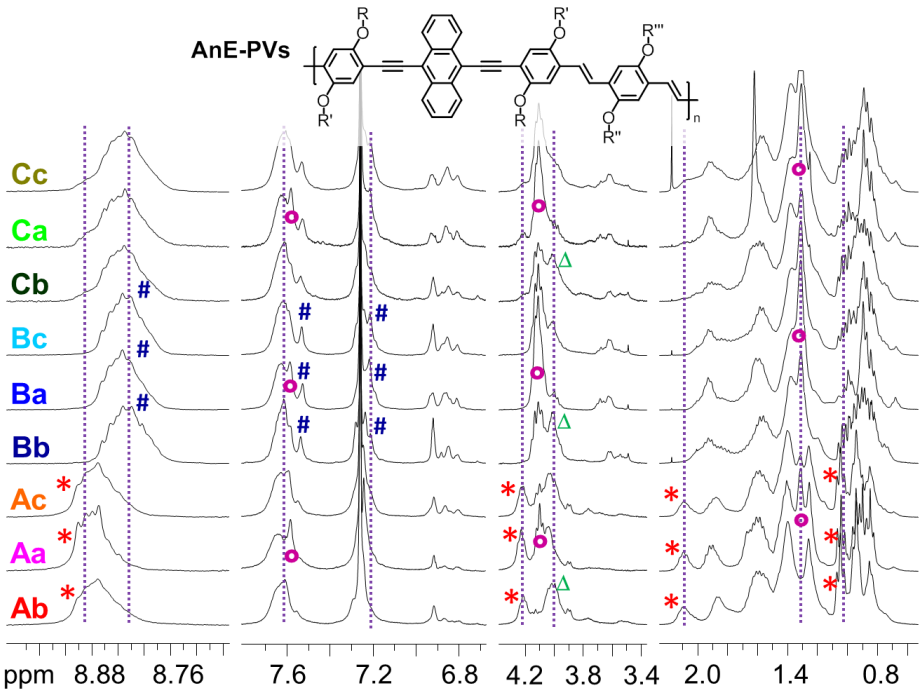


Figure S5: ^{1}H NMR (300 MHz, $CDCl_3$) spectra stack of magnified sections, polymer series – **AnE-PVbaab-aa** (**Aa**), **AnE-PVbaab-bb** (**Ab**), **AnE-PVbaab-a/b** (**Ac**), **AnE-PVabba-aa** (**Ba**), **AnE-PVabba-bb** (**Bb**), **AnE-PVabba-a/b** (**Bc**), **AnE-PVa/ba/b-aa** (**Ca**), **AnE-PVa/ba/b-bb** (**Cb**) and **AnE-PVa/ba/b-a/b** (**Cc**). The dotted lines are drawn to guide the eye. The different tags – asterisk (*), circle (°), hash tag (#) and triangle (Δ) – mark characteristics, which appear to correlate with the specific side chain arrangement at the alternating backbone segments.

The NMR features with a red asterisk (*) appear most intense in the spectra of **Aa**, **Ab** and **Ac**. Their occurrence seems to be linked to the octyloxy side chains occupying the positions in close proximity of the anthracene units. The signal segments marked with the blue hash tag (#) on the other hand are most pronounced for **Ba**, **Bb** and **Bc**, and are apparently induced by the side chain switch-over from octyloxy to 2-ethylhexyloxy at the anthracene-adjacent positions. Moreover, it seems evident that not only the side chain configuration of the dialdehyde (**8**) but also of the bisphosphonate comonomer (**3**), employed in the respective HWE polycondensation reaction, seemingly left imprints in the ^{1}H NMR spectra of the polymers. In particular phenylene-vinylene segments with two octyloxy or two 2-ethylhexyloxy chains seem to slightly boost specific features – tagged with dark magenta circles (°) and green triangles (Δ), respectively (Figure S5). The mixed side chain arrangements in the polymers **Ca**, **Cb** and **Cc**, which were prepared from the isomeric dialdehyde mixture **8a/ba/b**, appear well reflected in the ^{1}H NMR spectra as more or less a blend of the beforehand described features can be observed.

It is apparent that this comprehensive polymer series allows for in-depth insights on the detailed effects of side chain sequence fine tuning on the ^{1}H NMR output as they present themselves in fine but specific peculiarities in the signal pattern.

SIZE EXCLUSION CHROMATOGRAPHY (SEC)

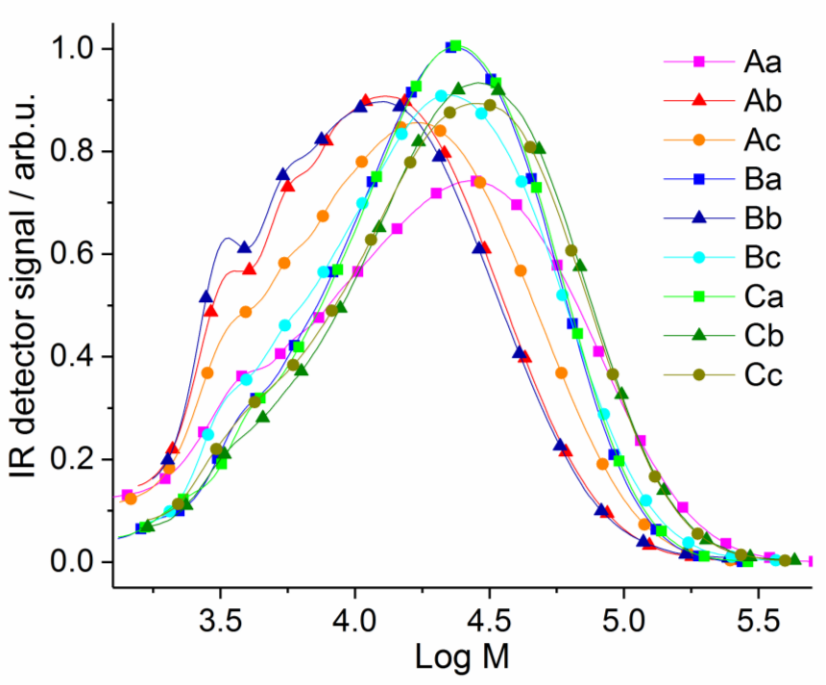


Figure S6: SEC-trace signals of all nine polymers, **AnE-PVbaab-aa**, **bb**, **a/b** (**Aa**, **Ab**, **Ac**), **AnE-PVabba-aa**, **bb**, **a/b** (**Ba**, **Bb**, **Bc**) and **AnE-PVa/ba/b-aa**, **bb**, **a/b** (**Ca**, **Cb**, **Cc**), used in the determination of polymer characteristics M_n, M_w and Đ.

Table S1: Polymer characteristics determined by HT-SEC and synthesis yield.

Polymer	M_w (g/mol)	M_n (g/mol)	Đ	DP	Yield (%)
AnE-PVbaab-aa (**Aa**)	31 900	7 200	4.46	6	80
AnE-PVbaab-bb (**Ab**)	17 700	7 700	2.30	6	63
AnE-PVbaab-a/b (**Ac**)	21 800	8 400	2.6	7	61
AnE-PVabba-aa (**Ba**)	27 000	11 700	2.31	9	86
AnE-PVabba-bb (**Bb**)	17 400	7 700	2.27	6	78
AnE-PVabba-a/b (**Bc**)	27 900	11 200	2.48	8	89
AnE-PVa/ba/b-aa (**Ca**)	27 700	11 900	2.33	9	78
AnE-PVa/ba/b-bb (**Cb**)	34 700	13 500	2.58	11	75
AnE-PVa/ba/b-a/b (**Cc**)	33 700	12 700	2.64	10	90

M_w – mass average molar mass; M_n – number average molar mass; Đ – dispersity; and DP – degree of polymerization.

Due to the strong structural deviation between the conjugated polymers and the polystyrene standards the obtained numbers are probably merely estimations at best. However, the SEC results provide a first overview and allow for a comparison within the set of analogous conjugated polymers.

UV-VIS/PL SPECTROSCOPY

Table S2: Photophysical data of the synthesized AnE-PVs.

Polymer		$\lambda_{abs,max}$ (nm)	$\lambda_{PL,max}$ [a] (nm)	$\Delta\lambda_{max}$ (cm^{-1})	E_g^{opt} [b] (eV)
	s_1	[524] 550	580 [629]	940	2.11
AnE-PVbaab-aa	s_2	[530] 557 [602]	587 [634]	920	2.05
Aa	f_1	(550) 588	622 (672)	930	1.90
	f_2 [c]	[554] 589	622 (672)	900	1.93
	s_1	[522] 544	584 [630]	1260	2.12
AnE-PVbaab-bb	s_2	[529] 552	589 [634]	1140	2.09
Ab	f_1	(543) 578	618 (664)	1120	1.92
	f_2	(547) 578	616 (660)	1070	1.97
	s_1	[526] 546	580 [628]	1070	2.12
AnE-PVbaab-a/b	s_2	[530] 553	588 [633]	1080	2.05
Ac	f_1	(547) 582	620 (668)	1050	1.91
	f_2 [c]	[554] 585	618 (668)	910	1.97
	s_1	[518] 541	579 [628]	1210	2.14
AnE-PVabba-aa	s_2	[521] 539	584 [630]	1430	2.12
Ba	f_1	[548] 577	620 (662)	1200	1.92
	f_2	544 [569]	614 (656)	2100	1.99
	s_1	520	579 [631]	1960	2.15
AnE-PVabba-bb	s_2	522	584 [635]	2030	2.13
Bb	f_1	533 [553]	610 [656]	2370	1.97
	f_2	526	606 [655]	2510	2.04
	s_1	528	578 [630]	1640	2.15
AnE-PVabba-a/b	s_2	526	584 [632]	1890	2.13
Bc	f_1	536 [558]	612 (658)	2320	1.96
	f_2	536	610 [656]	2260	2.02
	s_1	535	579 [630]	1420	2.14
AnE-PVa/ba/b-aa	s_2	537	584 [633]	1500	2.12
Ca	f_1	[548] 583	622 (667)	1080	1.92
	f_2	541 [573]	616 (660)	2250	1.99
	s_1	534	580 [627]	1490	2.14
AnE-PVa/ba/b-bb	s_2	533	585 [633]	1670	2.12
Cb	f_1	[538] 565	612 (660)	1360	1.96
	f_2	536	608 [658]	2210	2.01
	s_1	509	578 [626]	2350	2.16
AnE-PVa/ba/b-a/b	s_2	511	580 [630]	2330	2.15
Cc	f_1	525	608 [654]	2600	1.99
	f_2	520	604 [654]	2670	2.06

[a] Excitation at 500 nm. [b] Optical band gap energy (E_g^{opt}) calculated using $1240/\lambda_{10\%abs,max}$ [eV], $\lambda_{10\%abs,max}$ – wavelength at 10% of the absorption maximum intensity at the low energy side of the spectrum. [c] Film casted with doctor blade. Keys: s_1 and s_2 – measurement in dilute chloroform and chlorobenzene solution, respectively; f_1 and f_2 – measurement at thin film, casted from chloroform and chlorobenzene solution, respectively; $\lambda_{abs,max}$ – wavelength of the absorption maximum; $\lambda_{PL,max}$ – wavelength of the photoluminescence maximum; $\Delta\lambda_{max}$ – difference between absorption and PL maximum. Values in curved ( ) and square brackets [ ] represent a second local maximum and a shoulder, respectively.

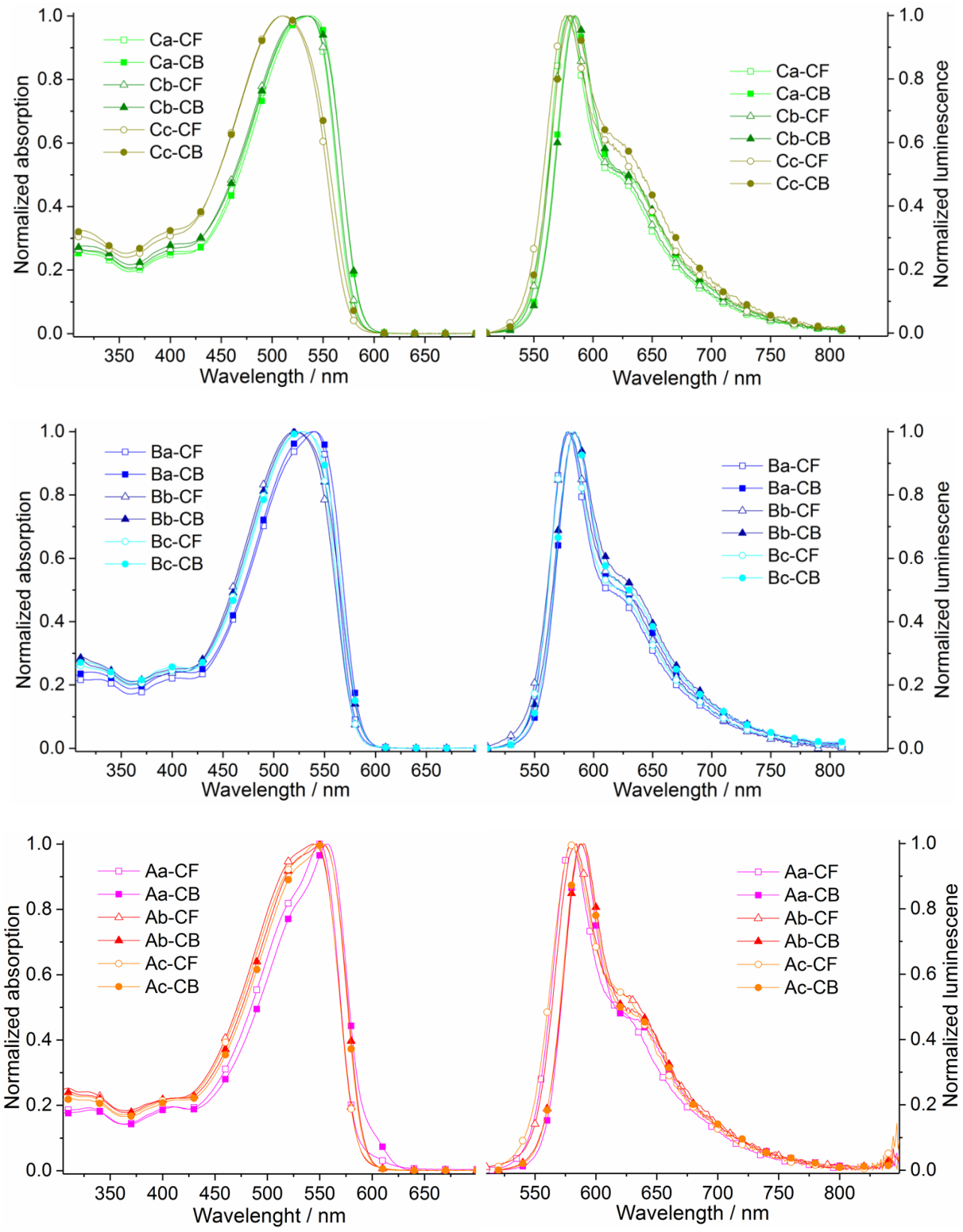


Figure S7: Normalized UV-Vis and PL spectra of polymers **AnE-PVbaab-aa**, **bb**, **a/b** (**Aa**, **Ab**, **Ac**, *bottom*), **AnE-PVabba-aa**, **bb**, **a/b** (**Ba**, **Bb**, **Bc**, *middle*) and **AnE-PVa/ba/b-aa**, **bb**, **a/b** (**Ca**, **Cb**, **Cc**, *top*) in solution – chloroform (CF), chlorobenzene (CB).

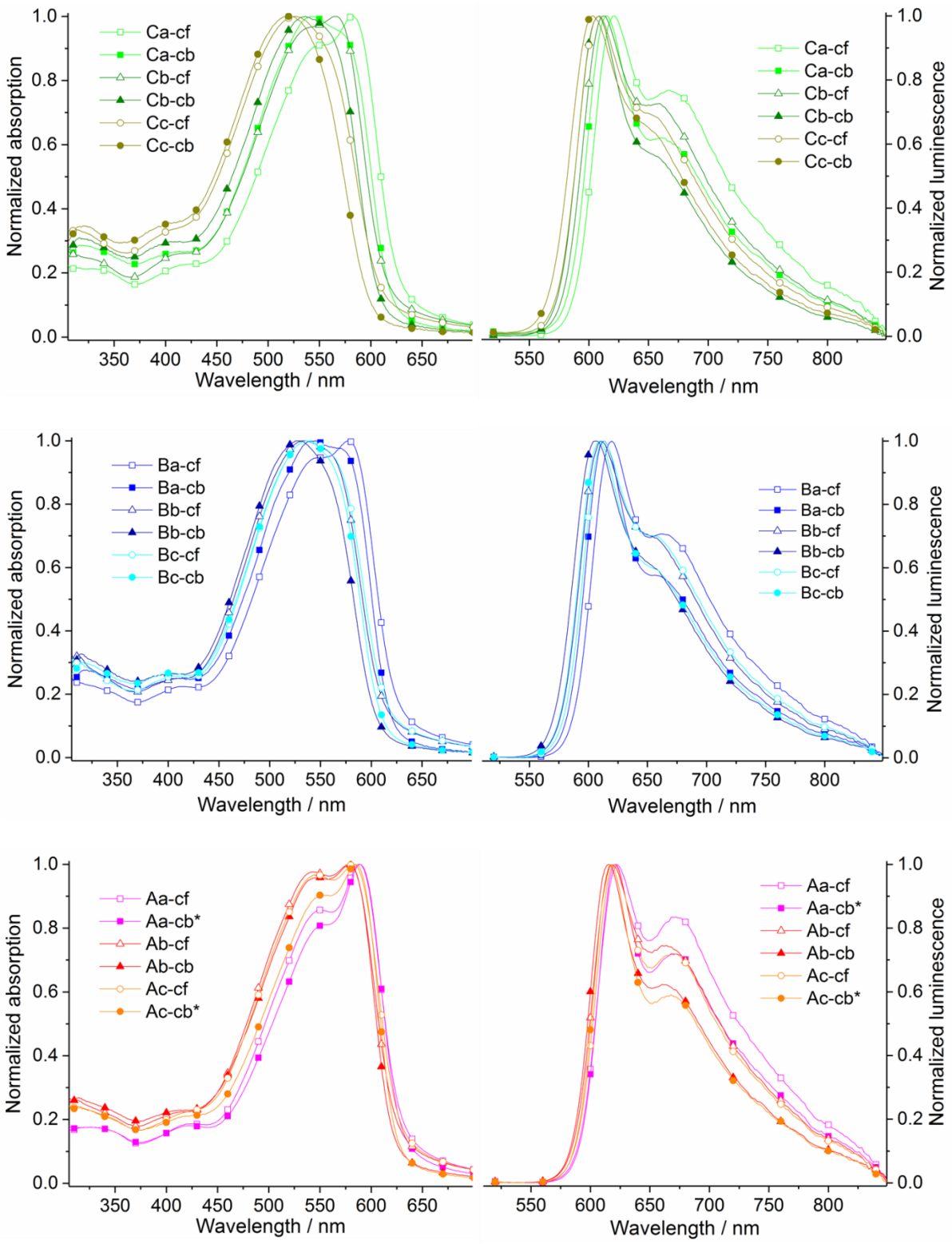


Figure S8: Normalized UV-Vis and PL spectra of polymers **AnE-PVbaab-aa**, **bb**, **a/b** (**Aa**, **Ab**, **Ac**, *bottom*), **AnE-PVabba-aa**, **bb**, **a/b** (**Ba**, **Bb**, **Bc**, *middle*) and **AnE-PVa/ba/b-aa**, **bb**, **a/b** (**Ca**, **Cb**, **Cc**, *top*) in thin film casted from chloroform (cf) and chlorobenzene (cb) solutions, respectively. The asterisks mark the films, which were obtained by blade coating instead of spin coating.

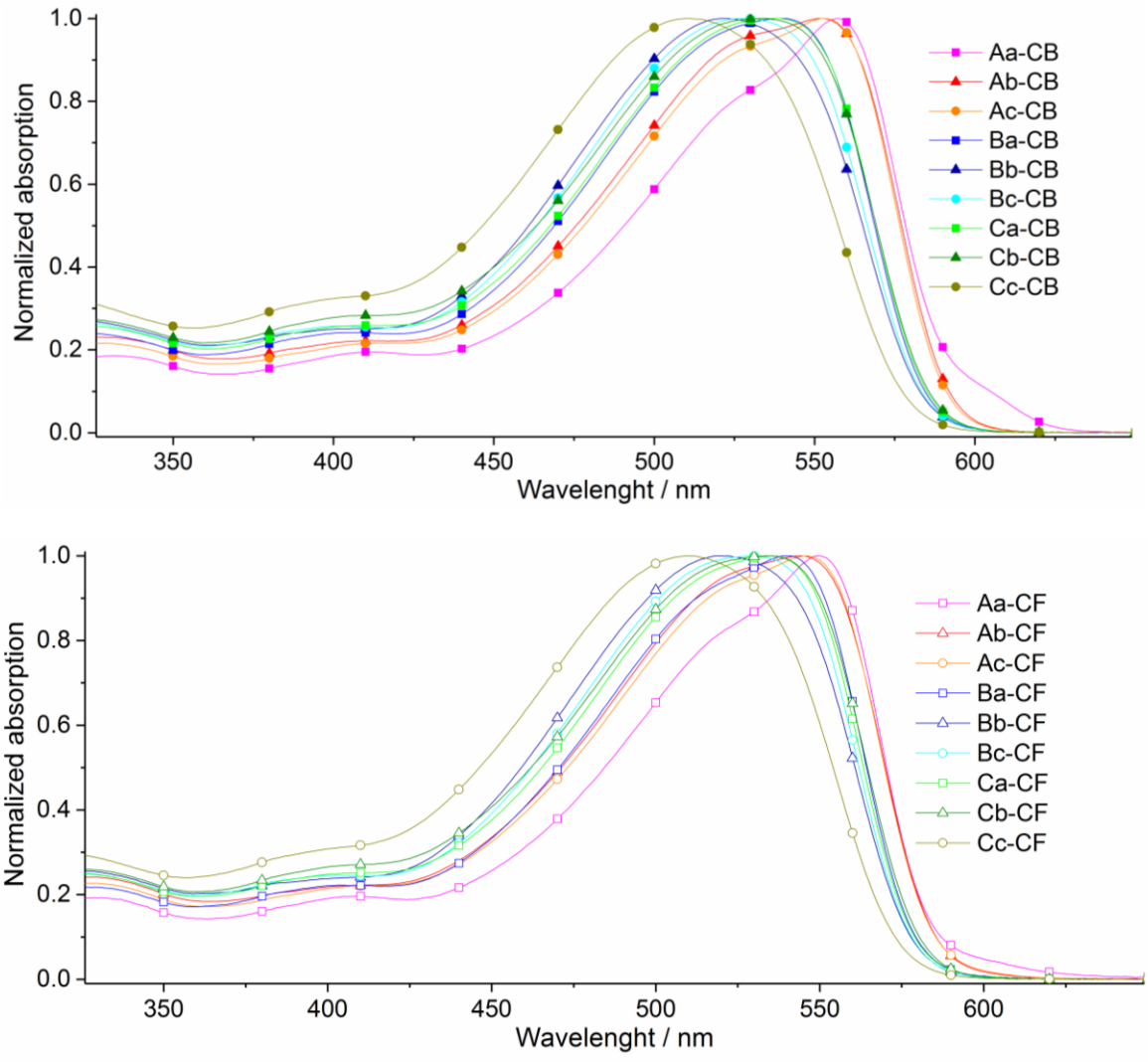


Figure S9: Normalized UV-Vis spectra of polymers **AnE-PVbaab-aa**, **bb**, **a/b** (**Aa**, **Ab**, **Ac**), **AnE-PVabba-aa**, **bb**, **a/b** (**Ba**, **Bb**, **Bc**) and **AnE-PVa/ba/b-aa**, **bb**, **a/b** (**Ca**, **Cb**, **Cc**) in solution – chloroform (CF, *bottom*), chlorobenzene (CB, *top*).

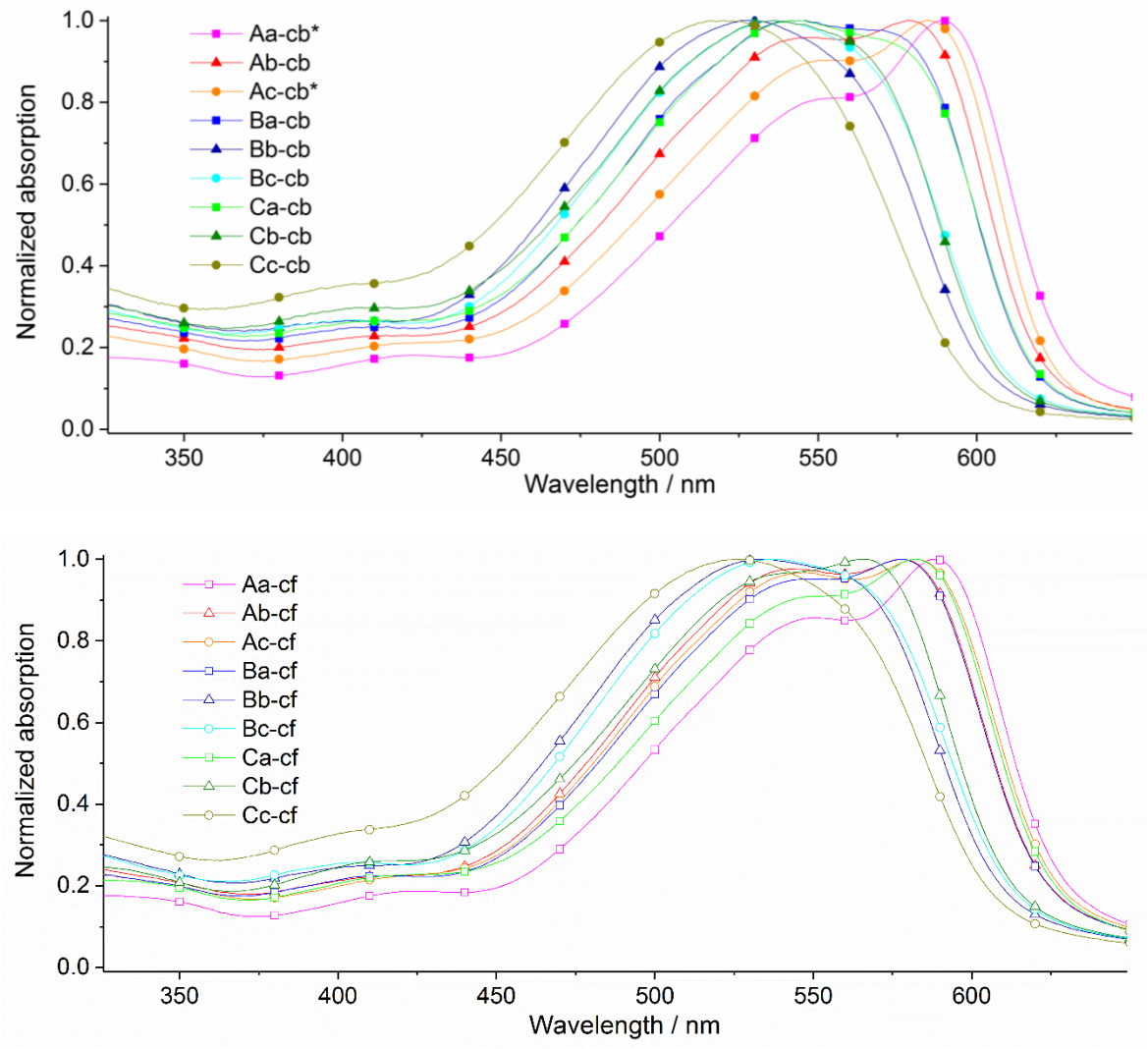


Figure S10: Normalized UV-Vis spectra of polymers **AnE-PVbaab-aa**, **bb**, **a/b** (**Aa**, **Ab**, **Ac**), **AnE-PVabba-aa**, **bb**, **a/b** (**Ba**, **Bb**, **Bc**) and **AnE-PVa/ba/b-aa**, **bb**, **a/b** (**Ca**, **Cb**, **Cc**) in thin film casted from chloroform (cf, *bottom*) and chlorobenzene (cb, *top*) solutions, respectively. The asterisks mark the films, which were obtained by blade coating instead of spin coating.

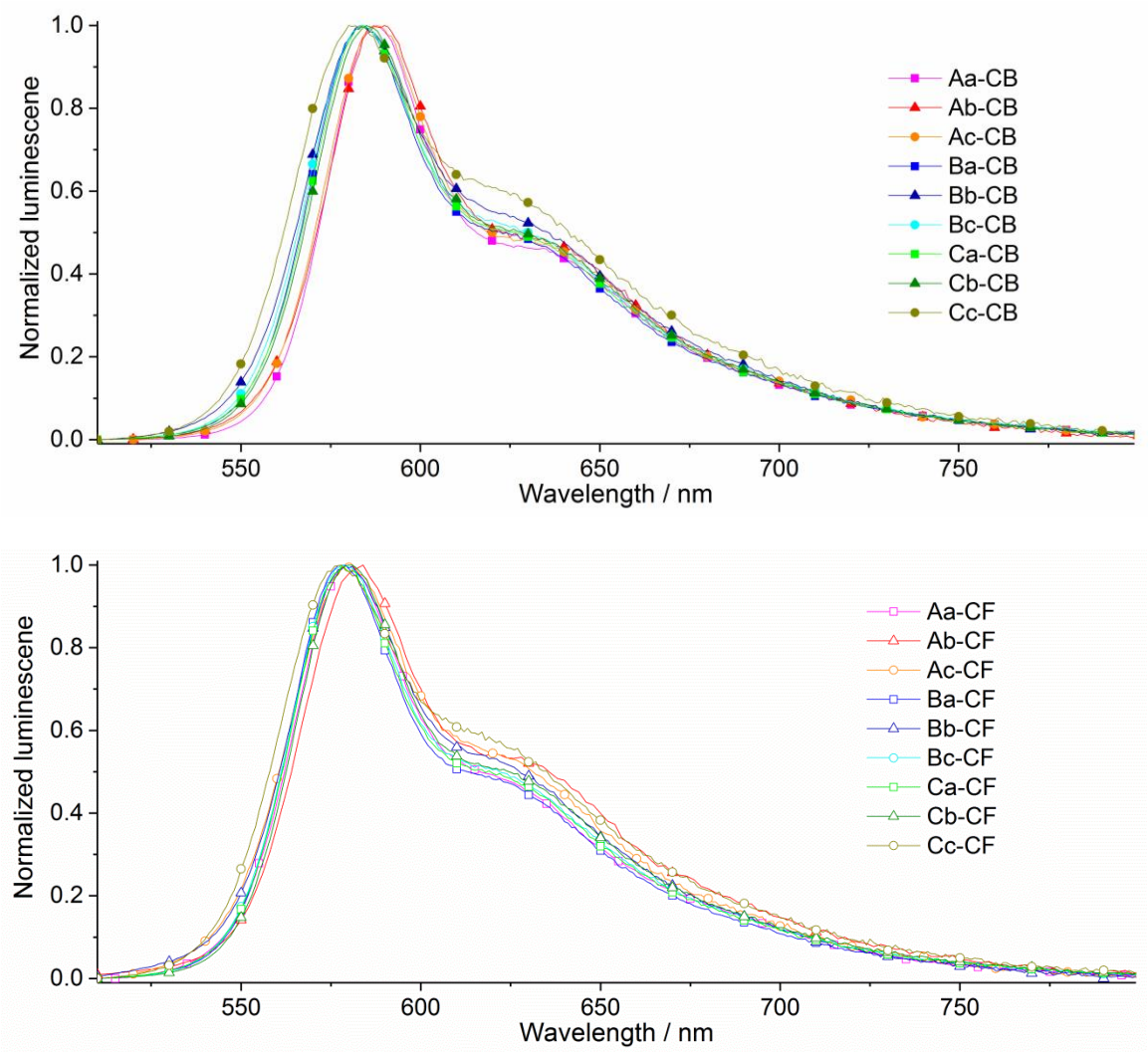


Figure S11: Normalized PL spectra of polymers **AnE-PVbaab-aa**, **bb**, **a/b** (**Aa**, **Ab**, **Ac**), **AnE-PVabba-aa**, **bb**, **a/b** (**Ba**, **Bb**, **Bc**) and **AnE-PVa/ba/b-aa**, **bb**, **a/b** (**Ca**, **Cb**, **Cc**) in solution – chloroform (CF, *bottom*), chlorobenzene (CB, *top*).

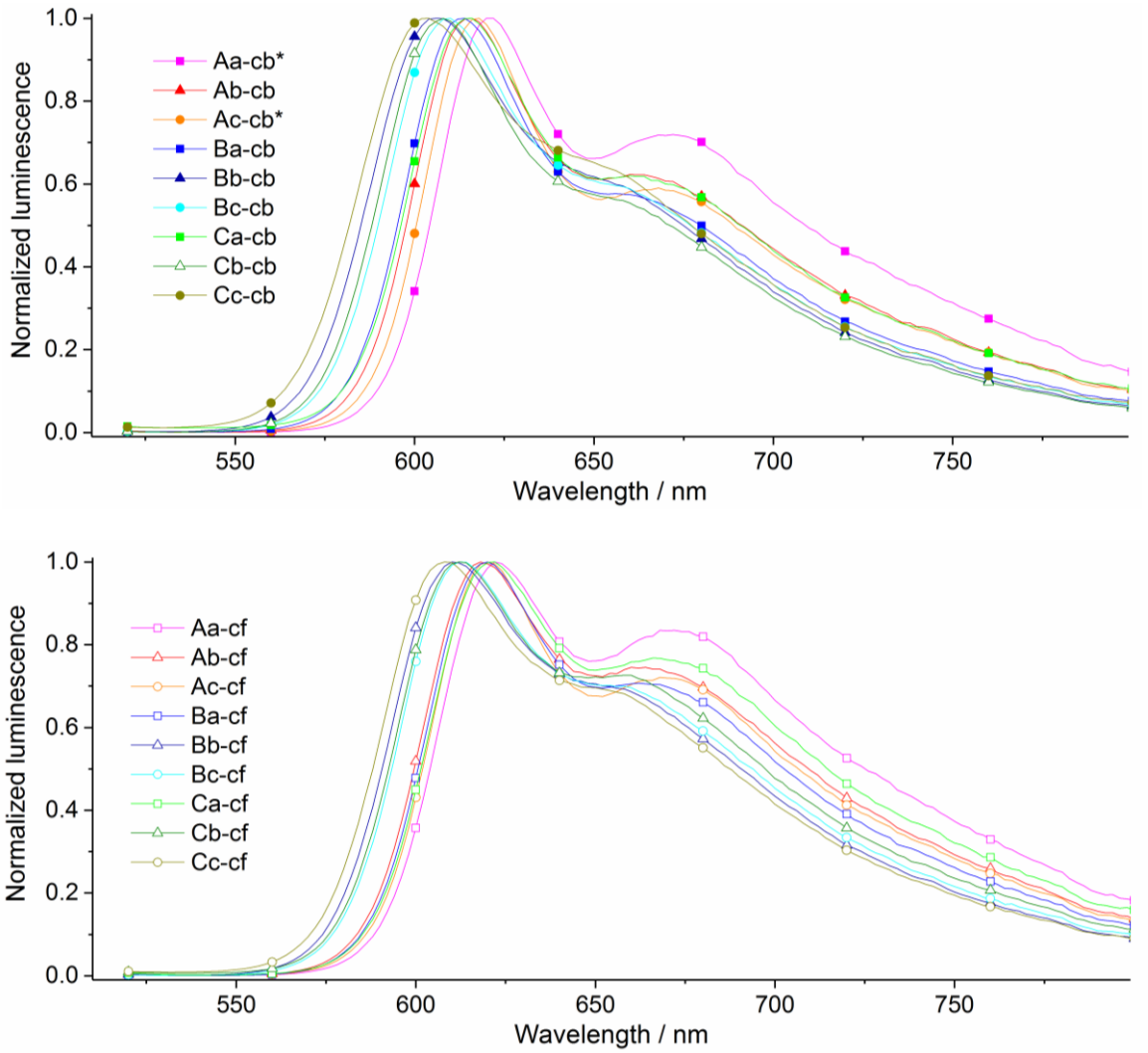
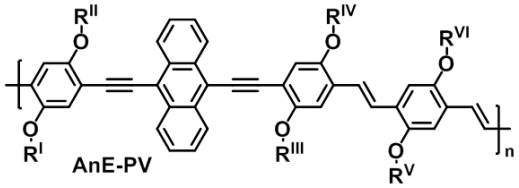


Figure S12: Normalized PL spectra of polymers **AnE-PVbaab-aa**, **bb**, **a/b** (**Aa**, **Ab**, **Ac**), **AnE-PVabba-aa**, **bb**, **a/b** (**Ba**, **Bb**, **Bc**) and **AnE-PVa/ba/b-aa**, **bb**, **a/b** (**Ca**, **Cb**, **Cc**) in thin film casted from chloroform (cf, *bottom*) and chlorobenzene (cb, *top*) solutions, respectively. The asterisks mark the films, which were obtained by blade coating instead of spin coating.

Table S3: Photophysical data of **AnE-PV** polymers from the current and previous studies with various side chain configurations (see structural scheme below).

	AnE-PV	I	II	III	IV	V	VI	solvents / films	$\lambda_{abs,max}$ (nm)	$\lambda_{PL,max}$ (1) (nm)	$\Delta\lambda_{max}$ (cm^{-1})	E_g^{opt} (2) (eV)	Ref.
Aa	baab-aa	EH	octyl	octyl	EH	octyl	octyl	s_1	**550**	**580**	940	2.11	
								s_2	**557**, 602	**587**	920	2.05	
								f_1	550, **588**	**622**, 672	930	1.90	
								f_2 (3)	**589**	**622**, 672	900	1.93	
	“ad”	octyl	octyl	octyl	octyl	decyl	decyl	s_1	**545**, ~600	**578**	1050	2.03	1
								f_1	544, **583**	**623**, 673	1100	1.98	1
								f_2	552, **590**	**621**	850	1.91	1
	“ae”	octyl	octyl	octyl	octyl	dodecyl	dodecyl	s_1	**540**, ~600	**577**	1190	2.05	1
								f_1	**550**, 580	**623**	2130	1.94	1
								f_2	**539**, 577	**605**	2020	1.98	1
Ab	baab-bb	EH	octyl	octyl	EH	EH	EH	s_1	**544**	**584**	1260	2.12	
								s_2	**552**	**589**	1140	2.09	
								f_1	543, **578**	**618**, 664	1120	1.92	
								f_2	547, **578**	**616**, 660	1070	1.97	
	“ab”	octyl	octyl	octyl	octyl	EH	EH	s_1	**546**	**579**	1050	2.12	1
								s_2	**553**	**585**	990	2.10	2
								f_1	**541**, 570	**622**	2400	1.99	1
								f_2	508, **583**	**624**	1100	1.80	1
Ac	baab-a/b	EH	octyl	octyl	EH	EH / octyl		s_1	**546**	**580**	1070	2.12	
								s_2	**553**	**588**	1080	2.05	
								f_1	547, **582**	**620**, 668	1050	1.91	
								f_2 (3)	**585**	**618**, 668	910	1.97	
	“cc”	EH	meth	meth	EH	EH / meth		s_1	**544**	**578**	1080	2.13	1
								f_1	**540**, 578	**617**	2300	1.97	1
								f_2	**532**, 580	**617**	2590	1.84	1
Ba	abba-aa	octyl	EH	EH	octyl	octyl	octyl	s_1	**541**	**579**	1210	2.14	
								s_2	**539**	**584**	1430	2.12	
								f_1	**577**	**620**, 662	1200	1.92	
								f_2	**544**	**614**, 656	2100	1.99	

	“ba”	EH	EH	EH	EH	octyl	octyl	s_1	**510**	**575**	2250	2.15	1
								s_2	**510**	**583**	2500	2.15	2
								f_1	**507**	**602**	3100	2.08	1
								f_2	**504**	**605**	3300	1.95	1
Bb	abba-bb	octyl	EH	EH	octyl	EH	EH	s_1	**520**	**579**	1960	2.15	
								s_2	**522**	**584**	2030	2.13	
								f_1	**533**	**610**	2370	1.97	
								f_2	**526**	**606**	2510	2.04	
	“bb”	EH	EH	EH	EH	EH	EH	s_1	**519**	**580**	2030	2.14	1
								s_2	**522**	**583**	3200	2.13	2
								f_1	**521**	**598**	2470	2.03	1
								f_2	**527**	**600**	2300	2.02	1
Bc	abba-a/b	octyl	EH	EH	octyl	EH / octyl		s_1	**528**	**578**	1640	2.15	
								s_2	**526**	**584**	1890	2.13	
								f_1	**536**	**612**, 658	2320	1.96	
								f_2	**536**	**610**	2260	2.02	
Ca	a/ba/b-aa	octyl / EH		EH / octyl		octyl	octyl	s_1	**535**	**579**	1420	2.14	
								s_2	**537**	**584**	1500	2.12	
								f_1	**583**	**622**, 667	1080	1.92	
								f_2	**541**	**616**, 660	2250	1.99	
Cb	a/ba/b-bb	octyl / EH		EH / octyl		EH	EH	s_1	**534**	**580**	1490	2.14	
								s_2	**533**	**585**	1670	2.12	
								f_1	**565**	**612**, 660	1360	1.96	
								f_2	**536**	**608**	2210	2.01	
Cc	a/ba/b-a/b	octyl / EH		EH / octyl		EH / octyl		s_1	**509**	**578**	2350	2.16	
								s_2	**511**	**580**	2330	2.15	
								f_1	**525**	**608**	2600	1.99	
								f_2	**520**	**604**	2670	2.06	



(1) Excitation at 500 nm. (2) Optical band gap energy (E_g^{opt}) calculated using: $1240/\lambda_{10\%abs,max}$ [eV], $\lambda_{10\%abs,max}$ – wavelength at 10% of the absorption maximum intensity at the low energy side of the spectrum. (3) Film casted with doctor blade. Keys: EH – 2-ethylhexyl; s_1 and s_2 – measurement in dilute chloroform and chlorobenzene solution, respectively; f_1 and f_2 – measurement at thin film, casted from chloroform and chlorobenzene, respectively; $\lambda_{abs,max}$ – wavelength of the absorption maximum; $\lambda_{PL,max}$ – wavelength of the PL maximum; $\Delta\lambda_{max}$ – difference between maxima. Additional numbers (non-bold) for a local maximum. Underlined values indicate a low energy shoulder attributed to aggregation in solution. Ref.1 D. A. M. Egbe et al. *Macromolecules* **2010**, *43*, 1261; Ref.2 D. A. M. Egbe et al. *J. Mater. Chem.* **2010**, *20*, 9726.

NMR SPECTRA

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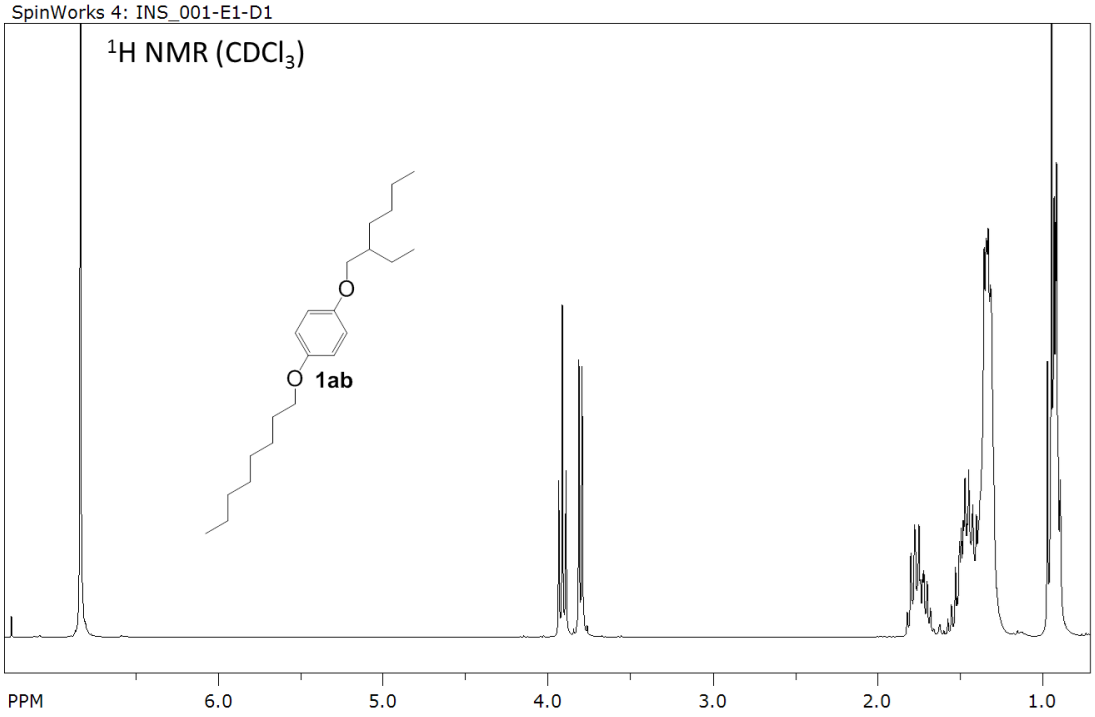

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processed size: 65536 complex points
LB: 0.300 GF: 0.0000

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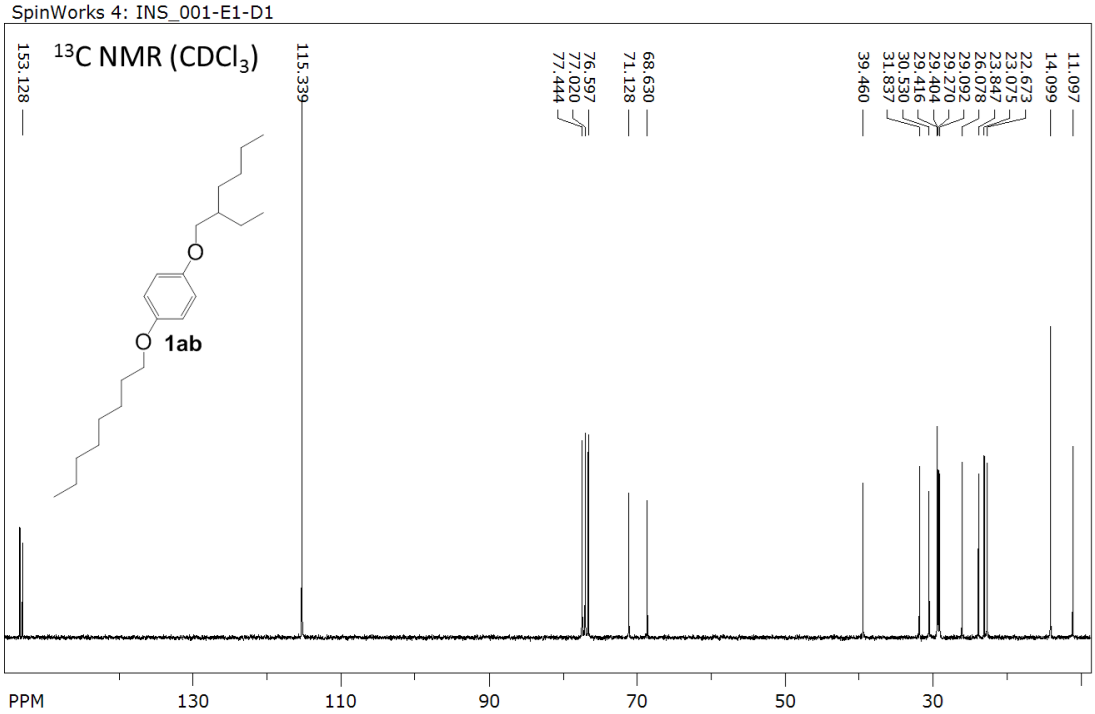

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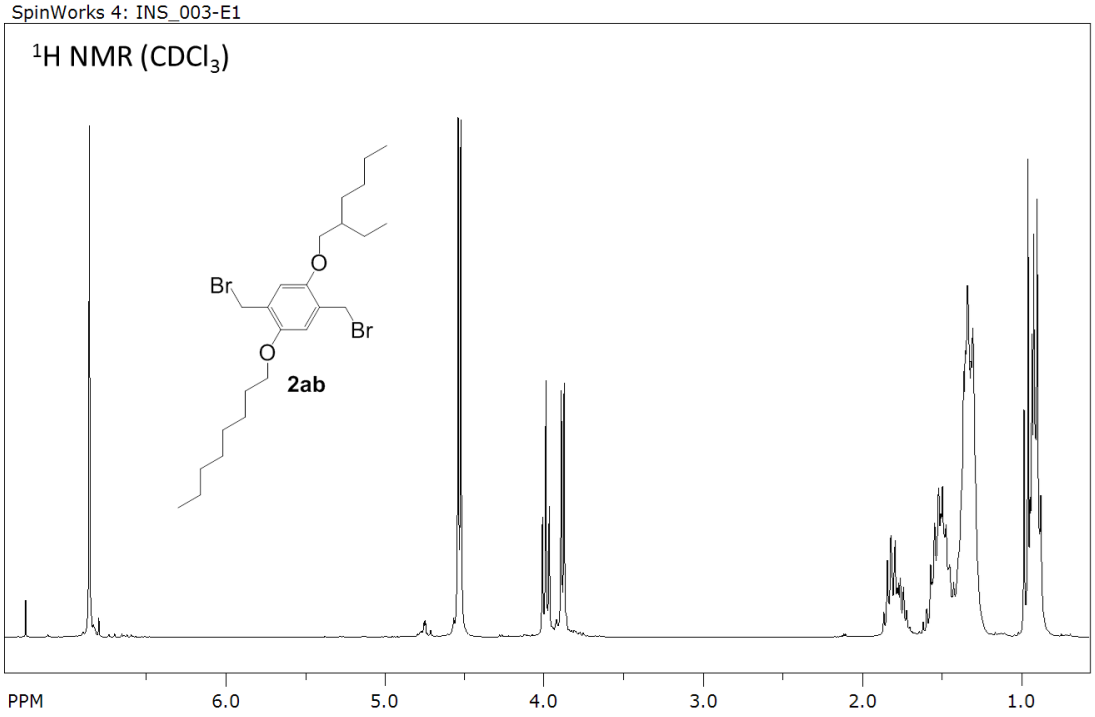

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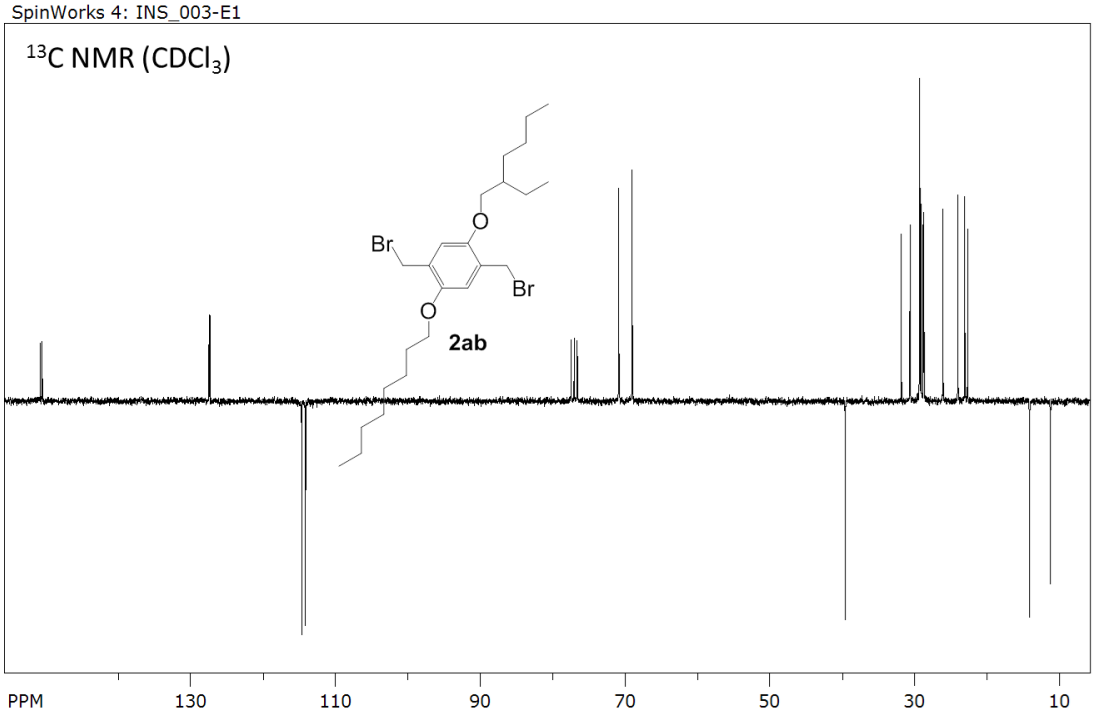
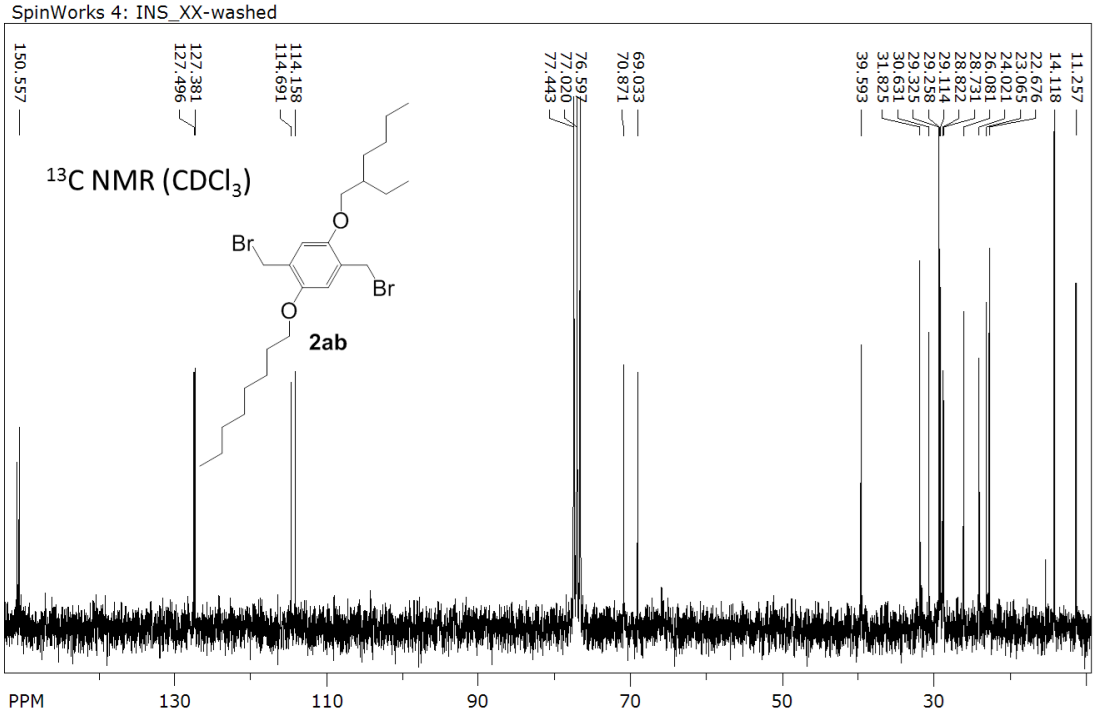
SpinWorks 4: INS_003-E1



file: ...INZ-D\NMR-(LIOS)\INS_003-E1\11\fid expt: <jmod>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 256

freq. of 0 ppm: 75.467751 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

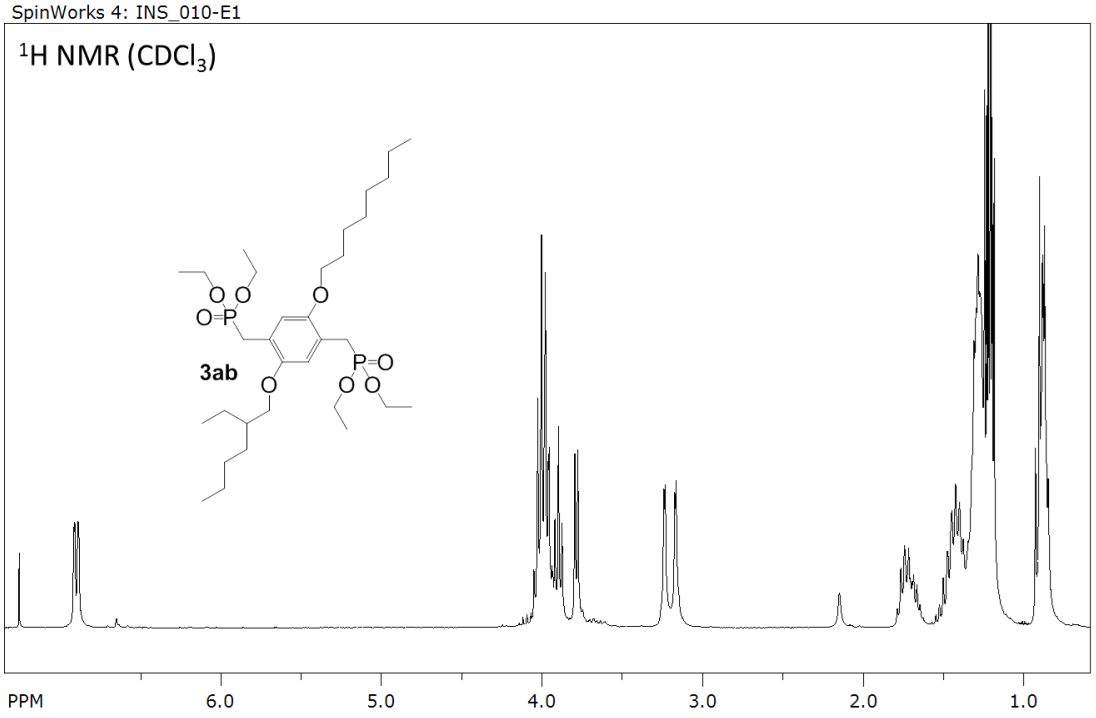
SpinWorks 4: INS_XX-washed



file: ...-D\NMR-(LIOS)\INS_XX-washed\11\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 256

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

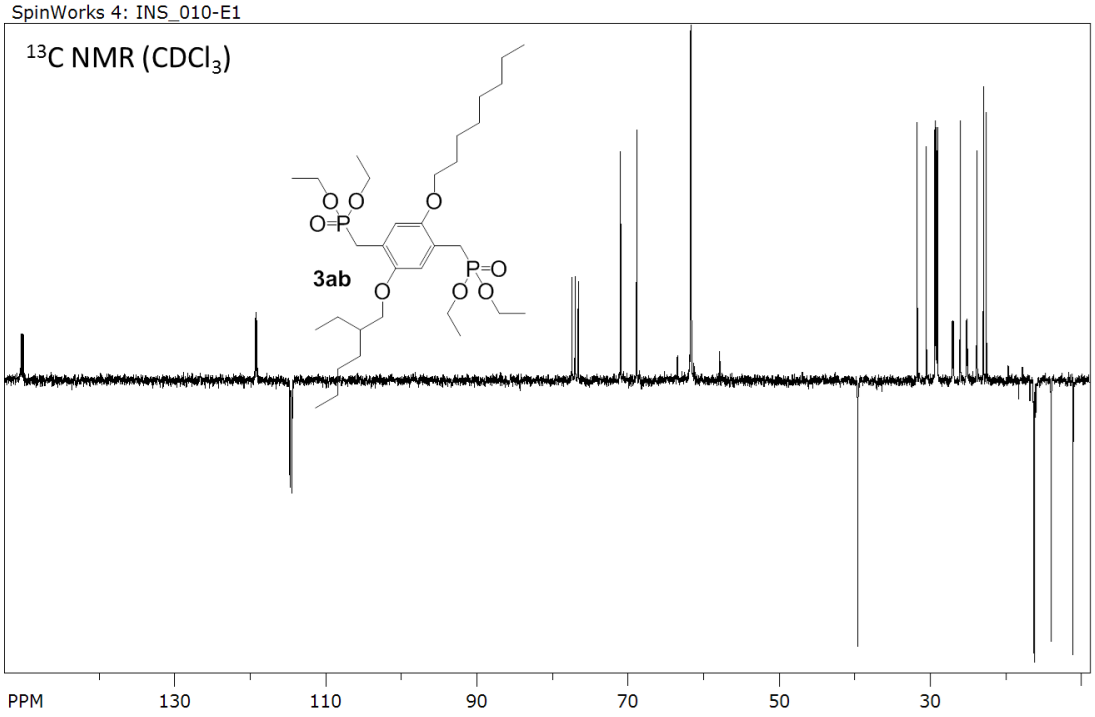
SpinWorks 4: INS_010-E1



file: ...INZ-D\NMR-(LIOS)\INS_010-E1\20\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

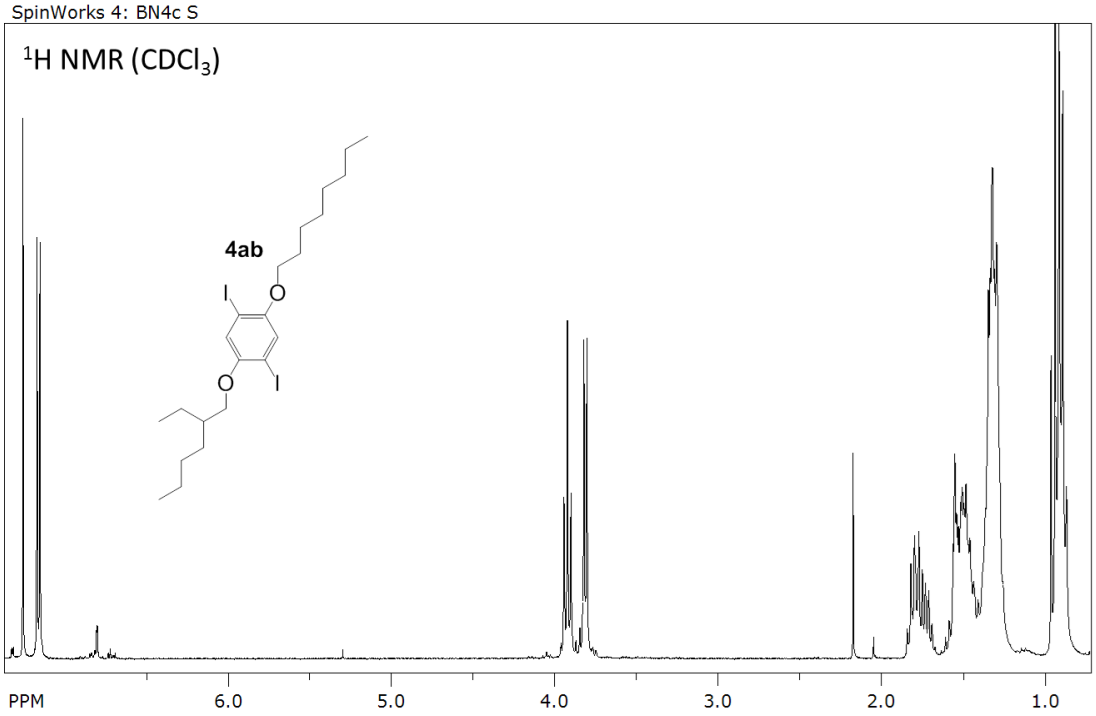
SpinWorks 4: INS_010-E1



file: ...INZ-D\NMR-(LIOS)\INS_010-E1\31\fid expt: <jmod>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 256

freq. of 0 ppm: 75.467754 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

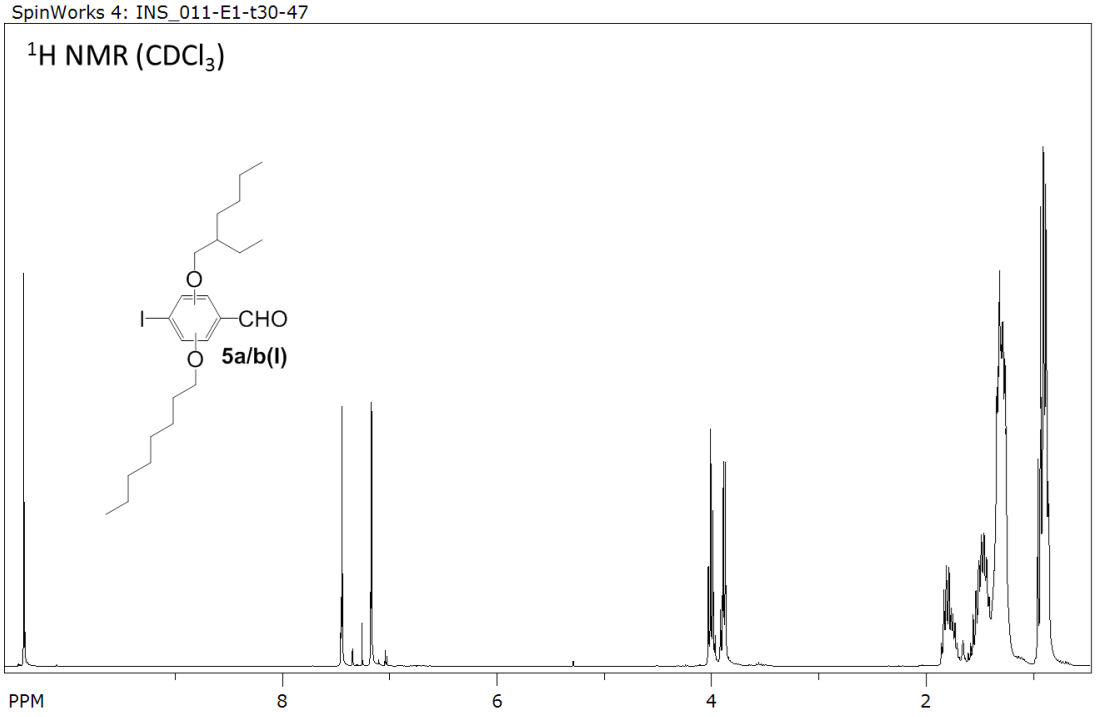
SpinWorks 4: BN4c S



file: ...S)\BN4c S_(Phen(X2)-O,EH_H)\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

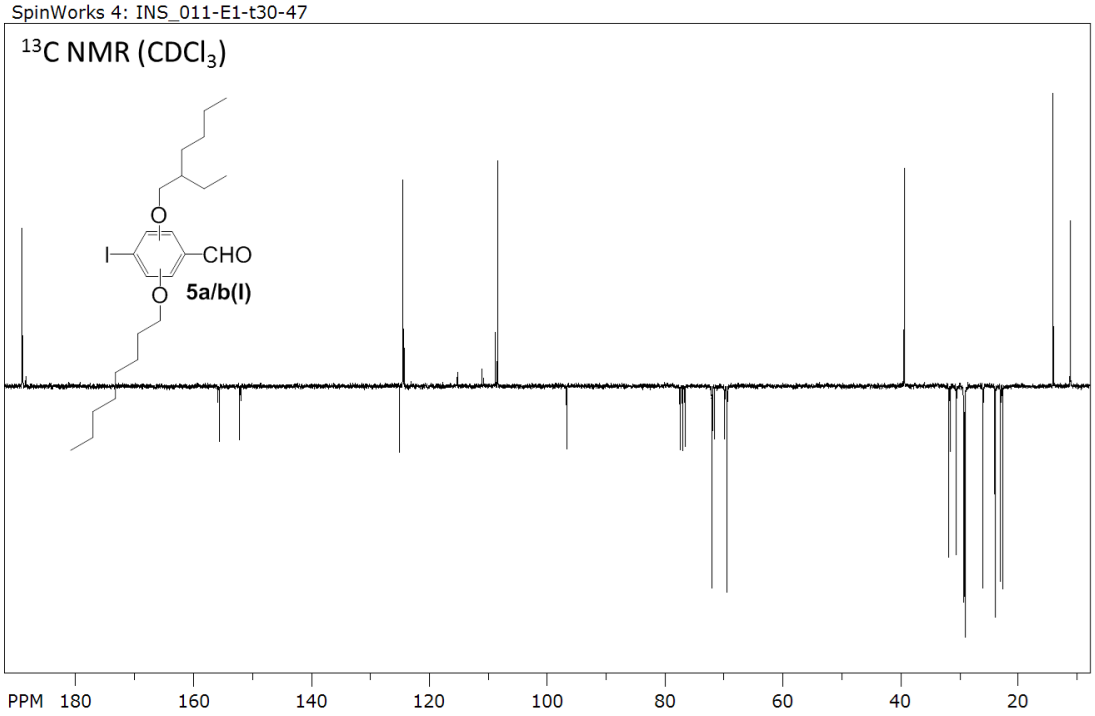
SpinWorks 4: INS_011-E1-t30-47



file: ...MR-(LIOS)\INS_011-E1-t30-47\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

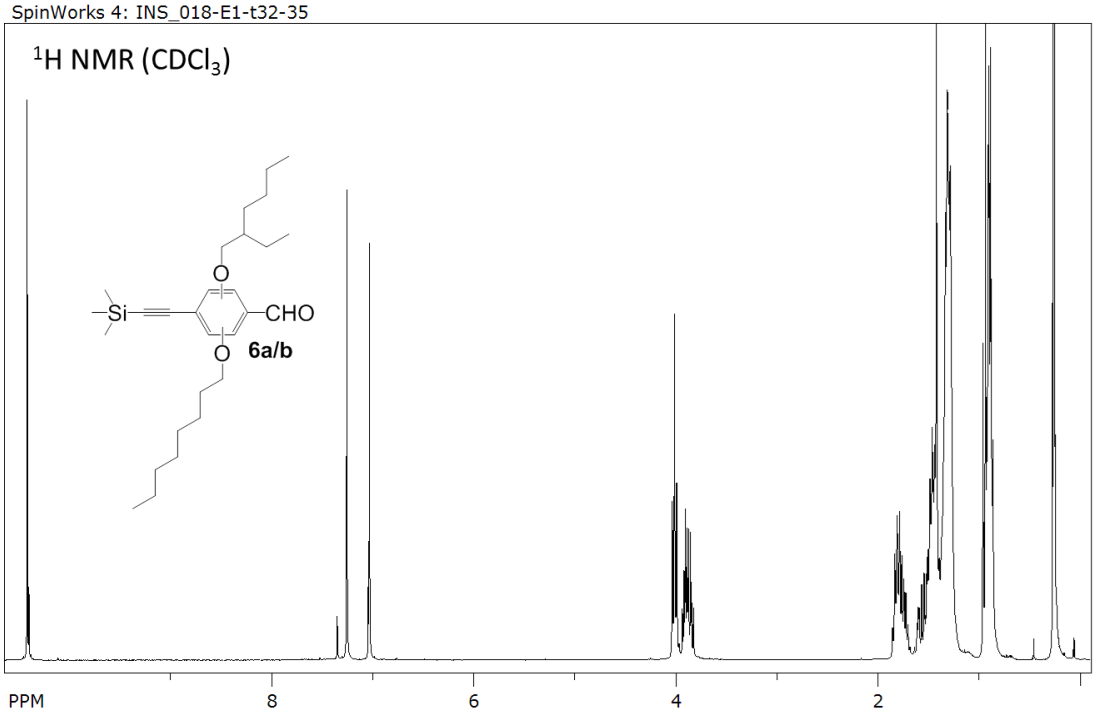
SpinWorks 4: INS_011-E1-t30-47



file: ...MR-(LIOS)\INS_011-E1-t30-47\43\fid expt: <jmod>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 512

freq. of 0 ppm: 75.467751 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

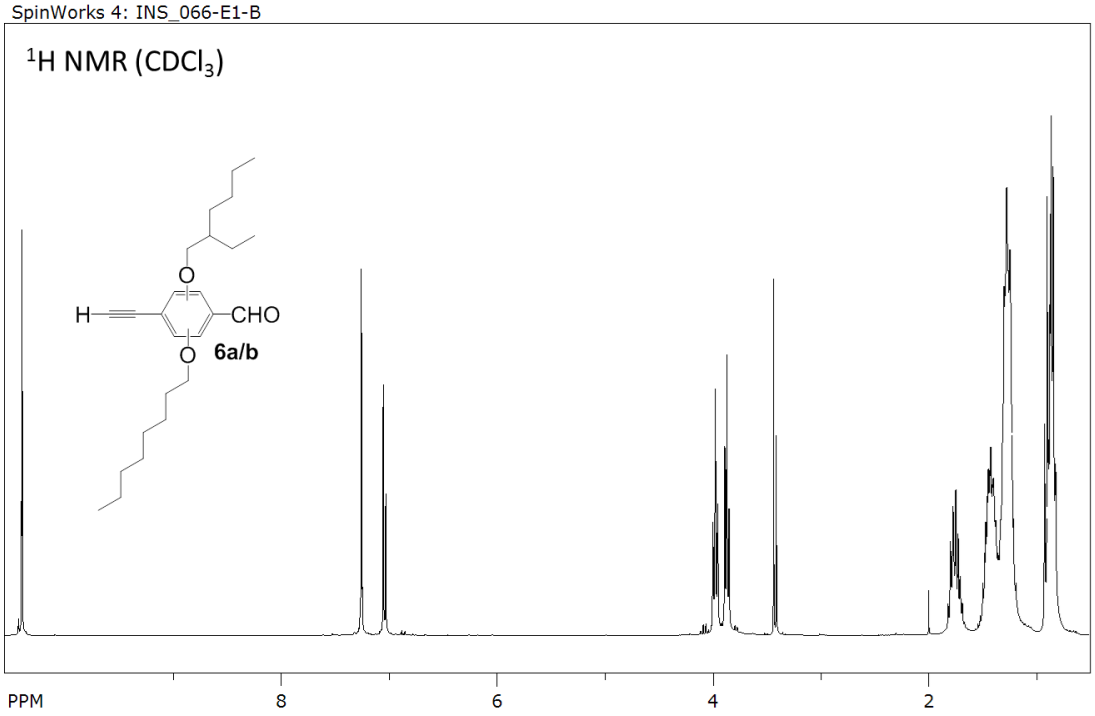
SpinWorks 4: INS_018-E1-t32-35



file: ...MR-(LIOS)\INS_018-E1-t32-35\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130006 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

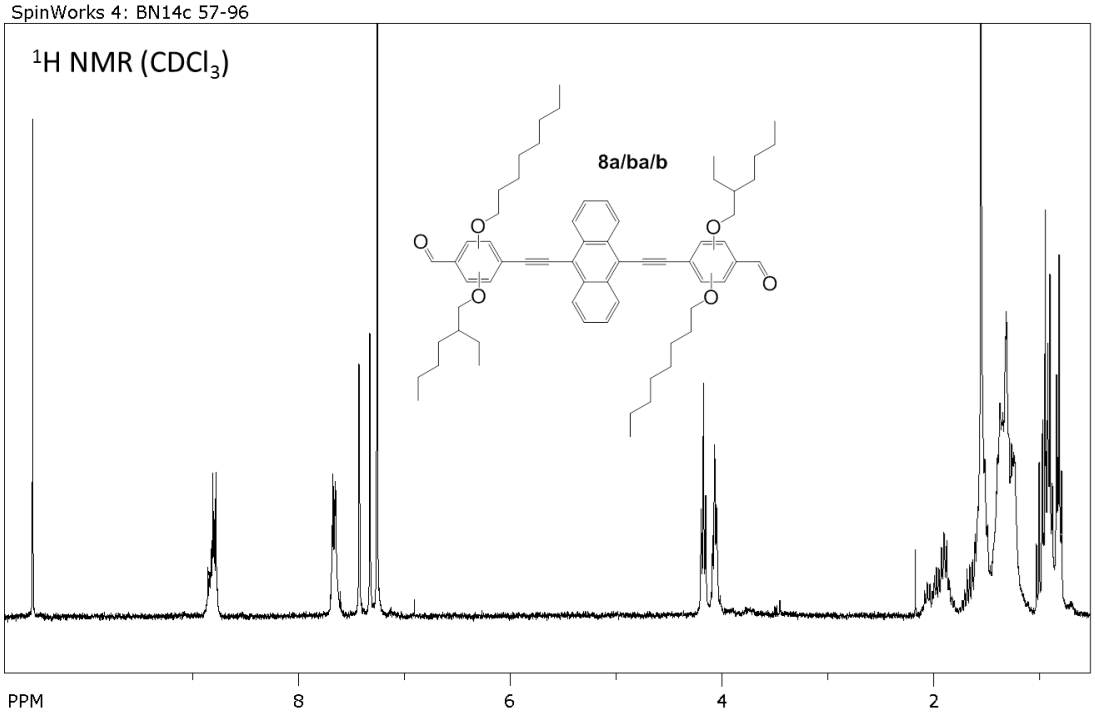
SpinWorks 4: INS_066-E1-B



file: ...Z-D\NMR-(LIOS)\INS_066-E1-B\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130009 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

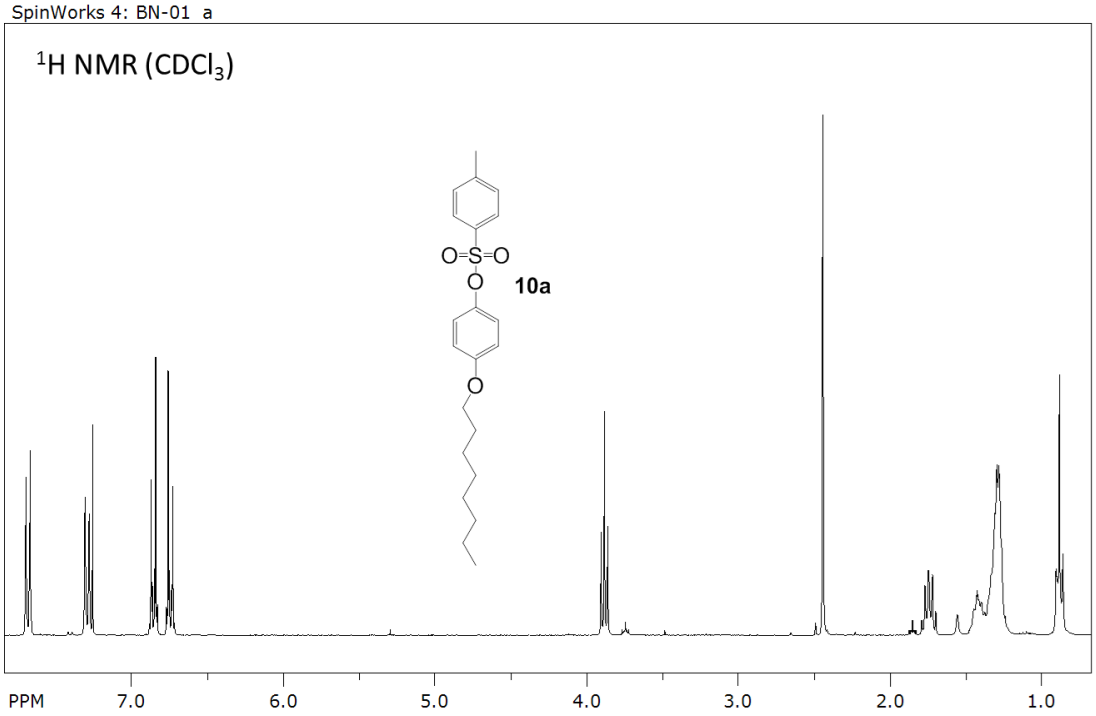
SpinWorks 4: BN14c 57-96



file: ...H)O-CHO),BN14,C\BN14c 57-96\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

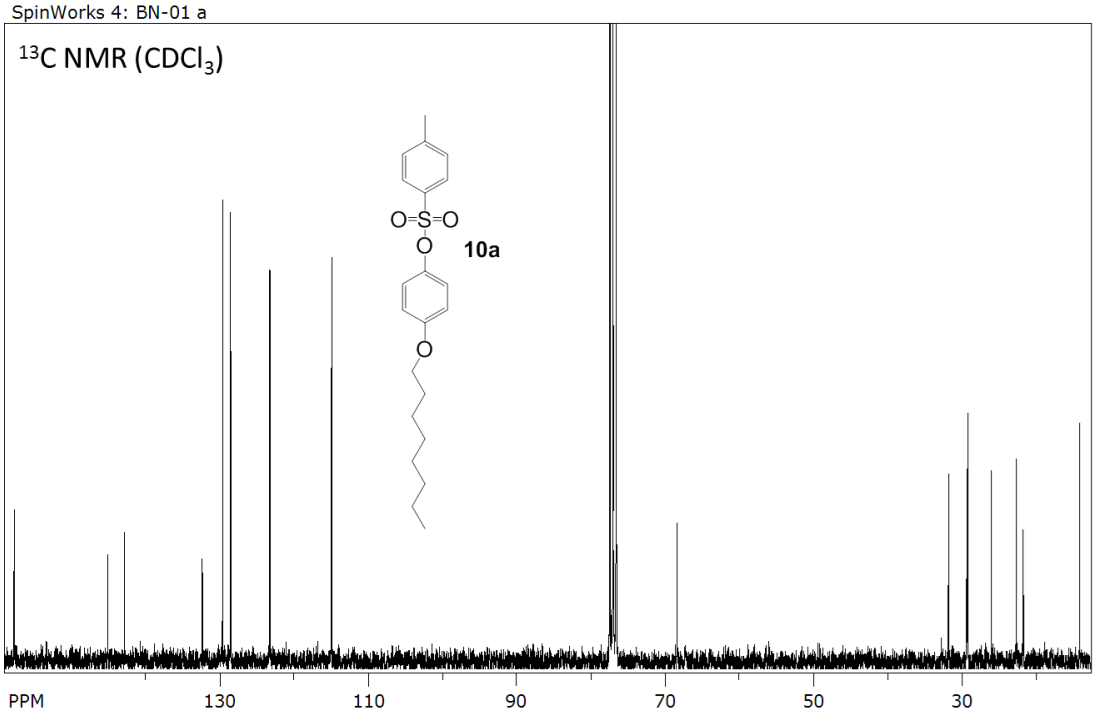
SpinWorks 4: BN-01 a



file: ..._LINZ-D\NMR-(LIOS)\BN-01 a\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

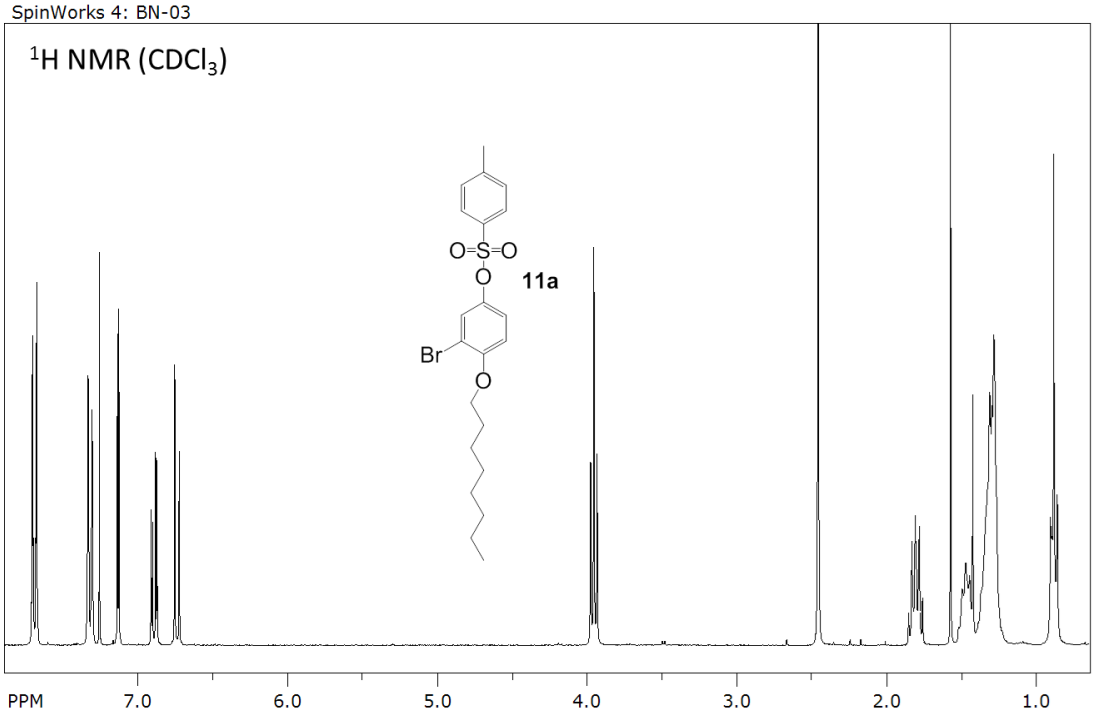
SpinWorks 4: BN-01 a



file: ...BN-01 a_10a_Phen(tosyl)-O_C\11\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 500

freq. of 0 ppm: 75.467748 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

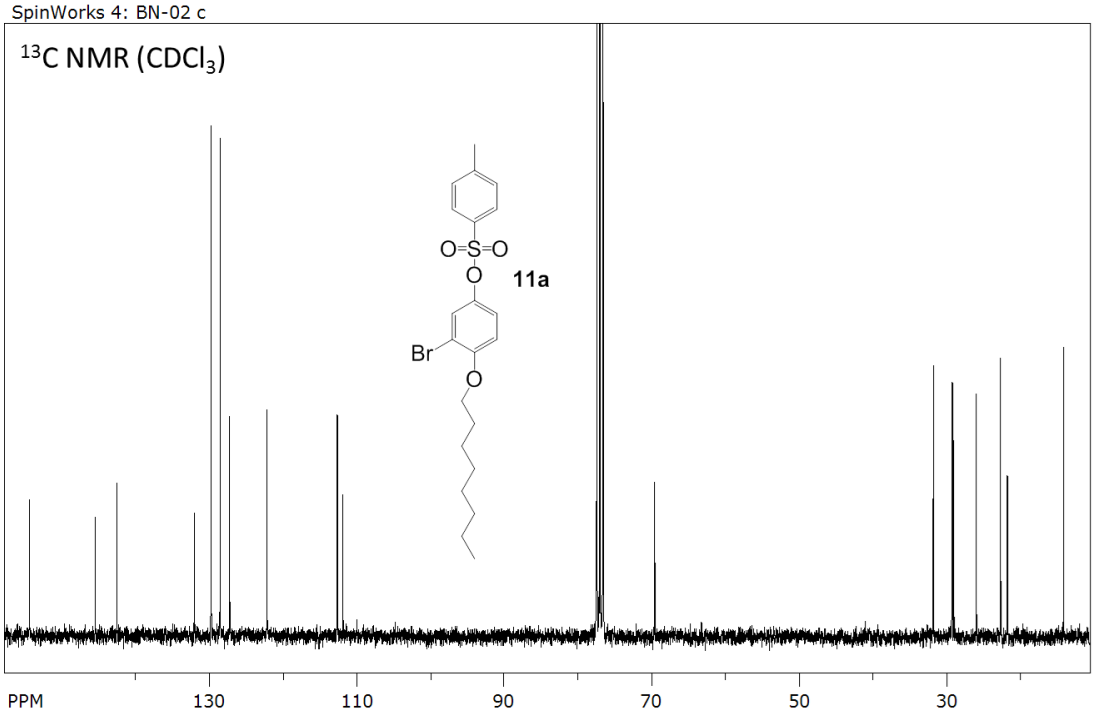
SpinWorks 4: BN-03



file: ...N-03_11a_Phen(Br,Tosyl)-O_H\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

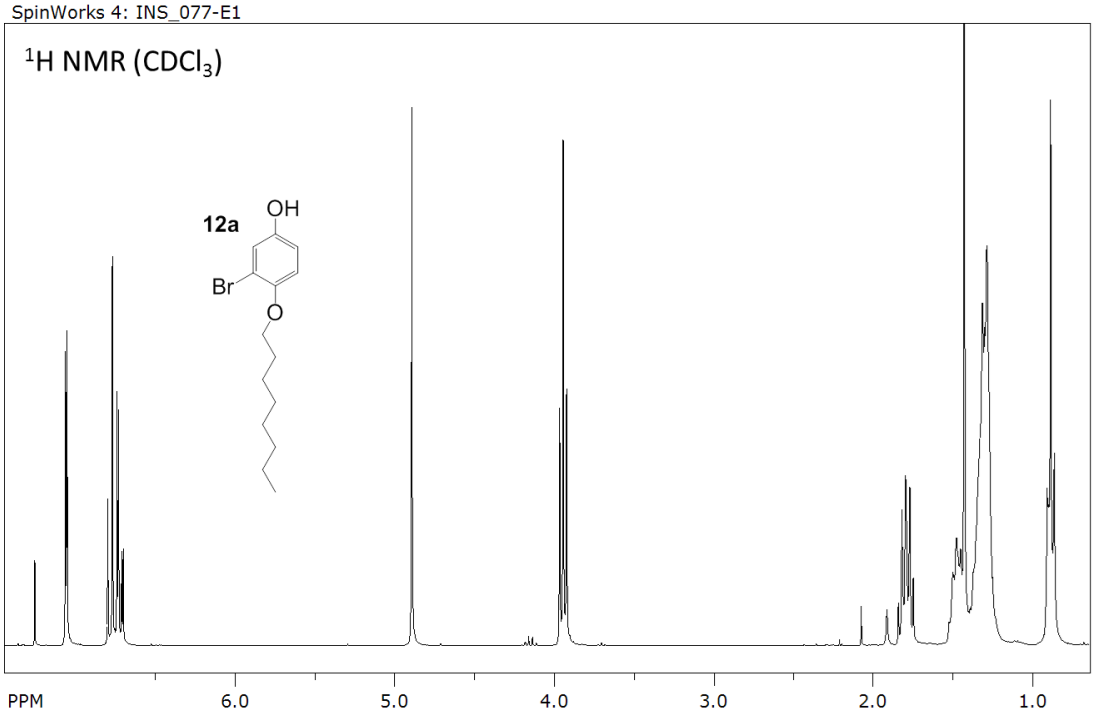
SpinWorks 4: BN-02 c



file: ...4_LINZ-D\NMR-(LIOS)\BN-02 c\11\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 600

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

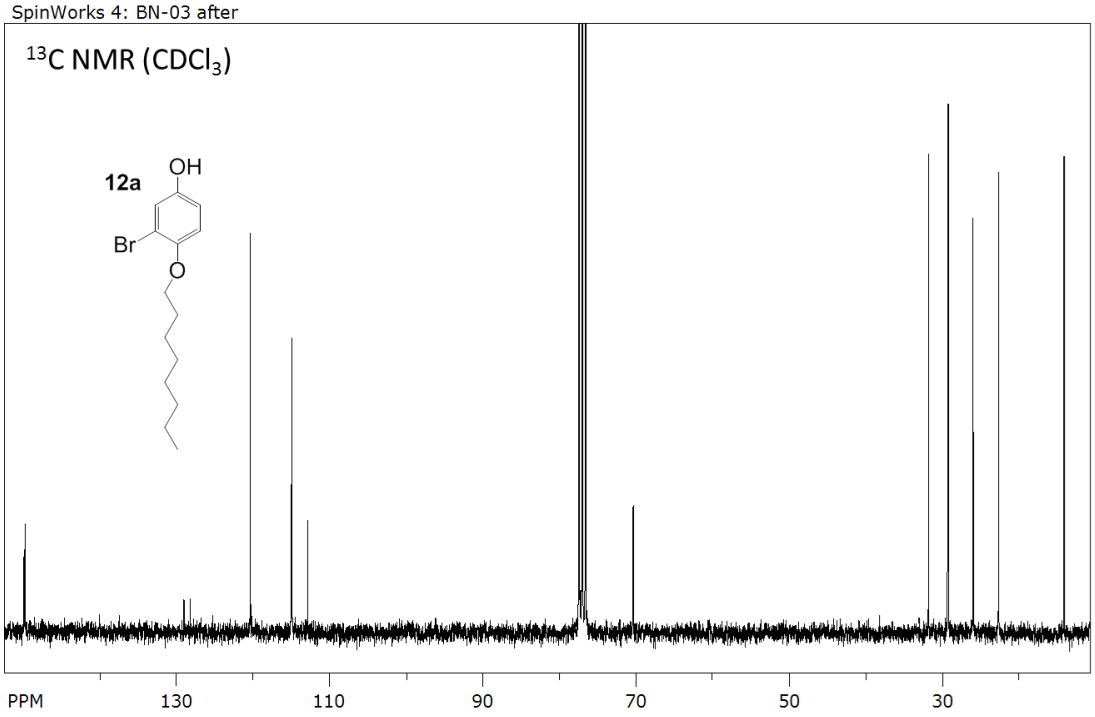
SpinWorks 4: INS_077-E1



file: ..._077-E1_12a_HO-Phen(Br)-O_H\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

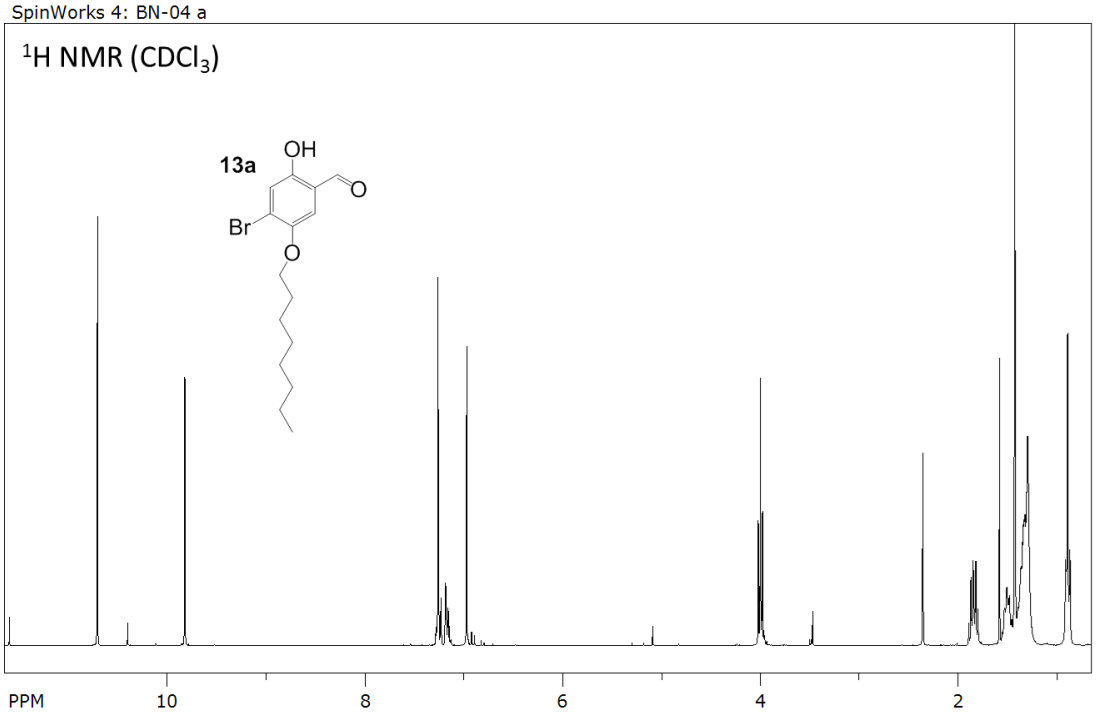
SpinWorks 4: BN-03 after



file: ...NZ-D\NMR-(LIOS)\BN-03 after\11\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 600

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

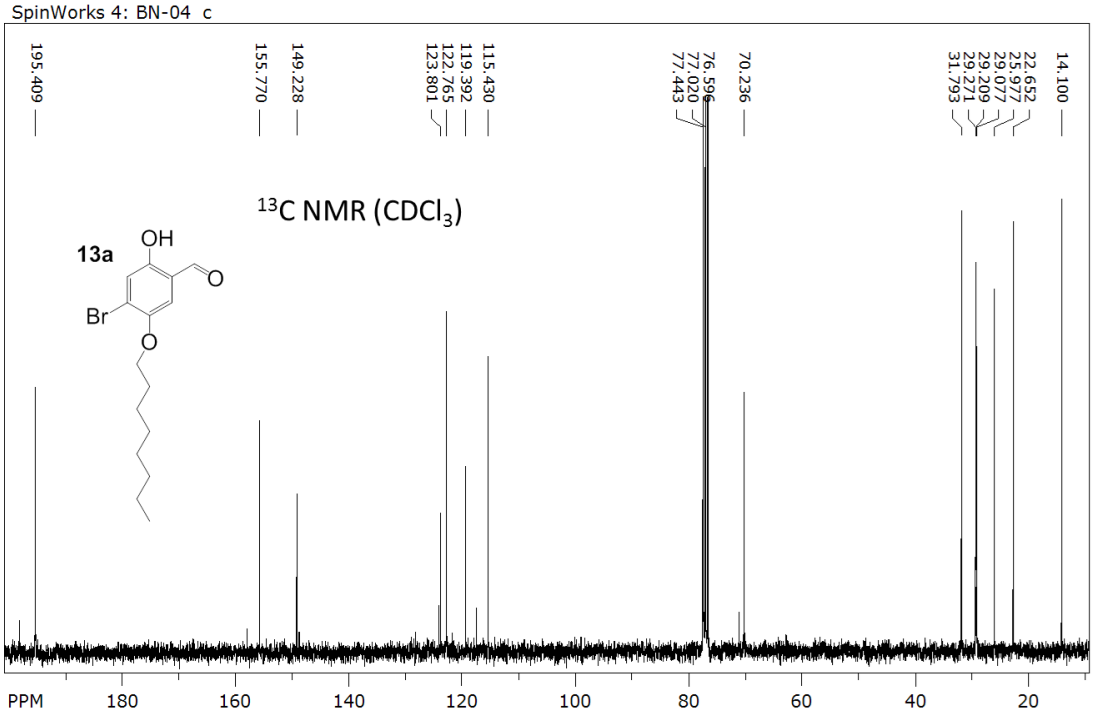
SpinWorks 4: BN-04 a



file: ...en(CHO,Br,OH)-O_(tol)_H(10)\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

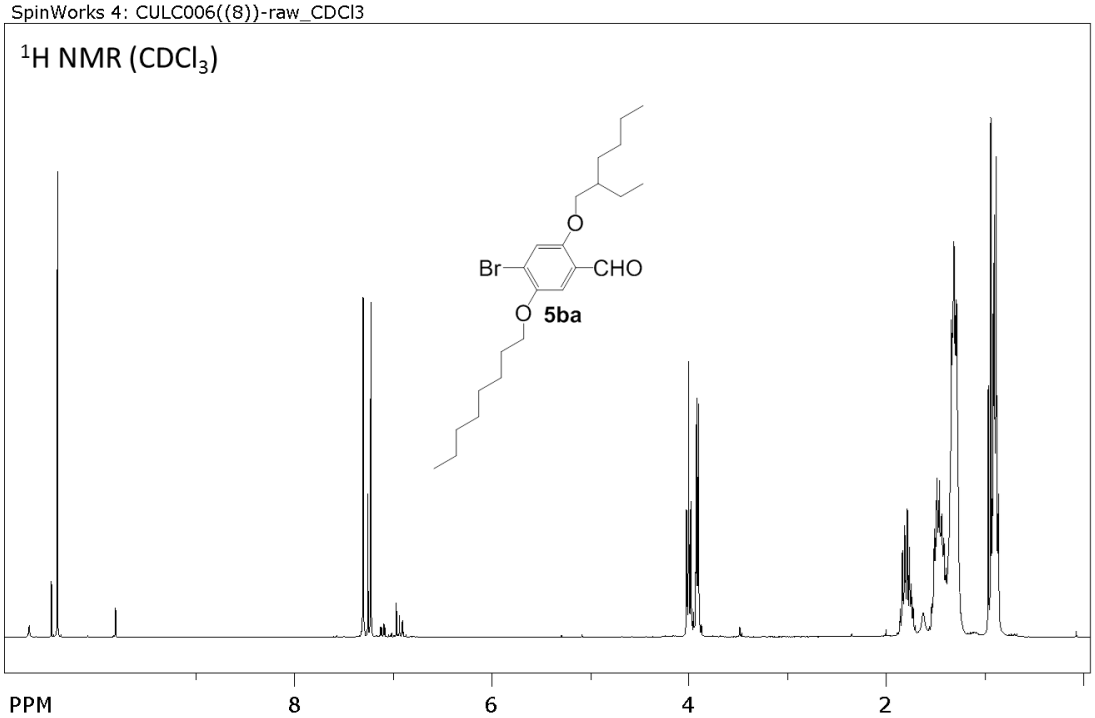
SpinWorks 4: BN-04 c



file: ..._LINZ-D\NMR-(LIOS)\BN-04 c\11\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 650

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

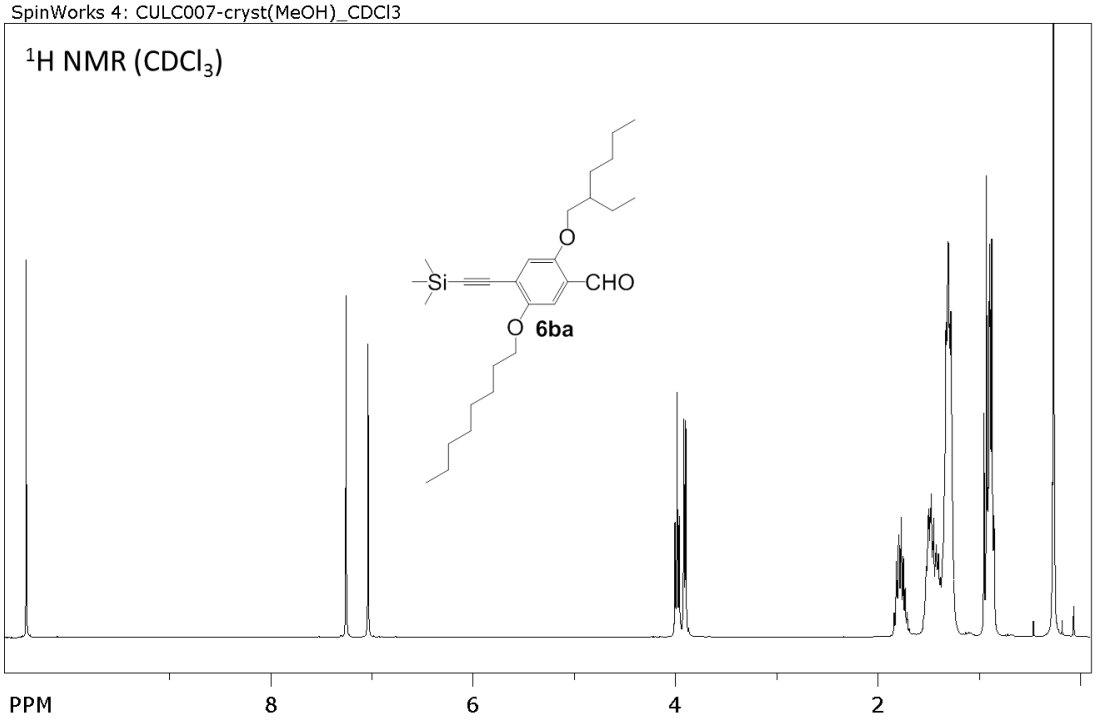
SpinWorks 4: CULC006((8))-raw_CDCl3



file: ...2017\CULC006((8))-raw_CDCl3\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6009.62 Hz = 20.0233 ppm = 0.091699 Hz/pt
number of scans: 28

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

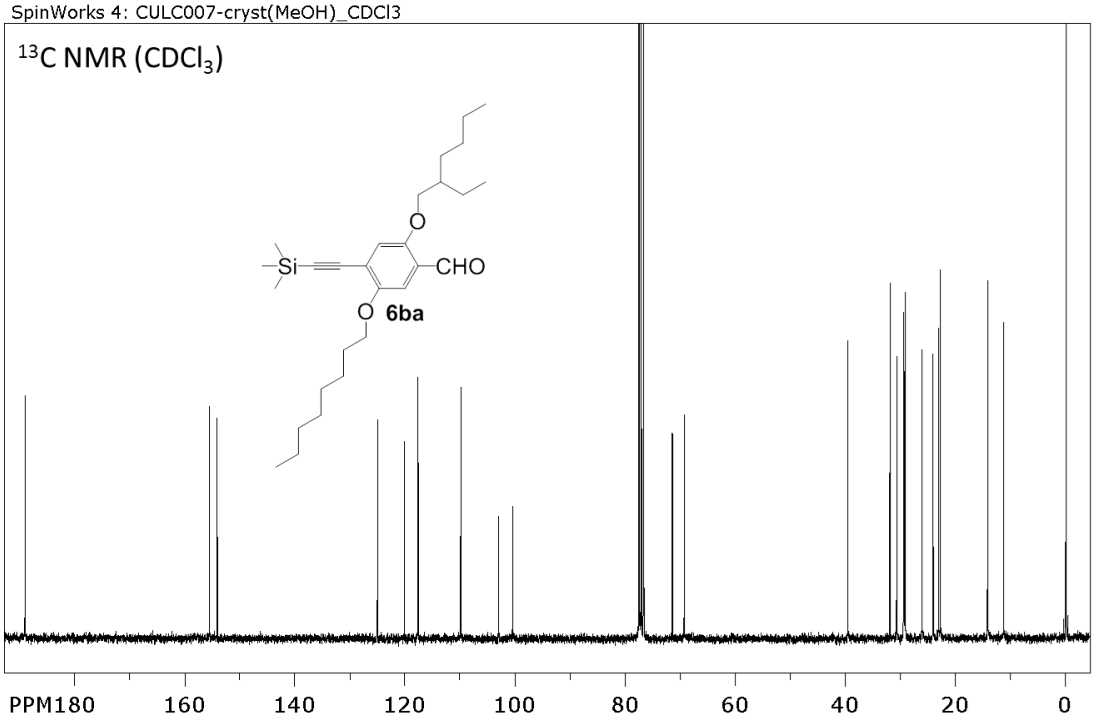
SpinWorks 4: CULC007-cryst(MeOH)_CDCl3



file: ...7\CULC007-cryst(MeOH)_CDCl3\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6009.62 Hz = 20.0233 ppm = 0.091699 Hz/pt
number of scans: 36

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

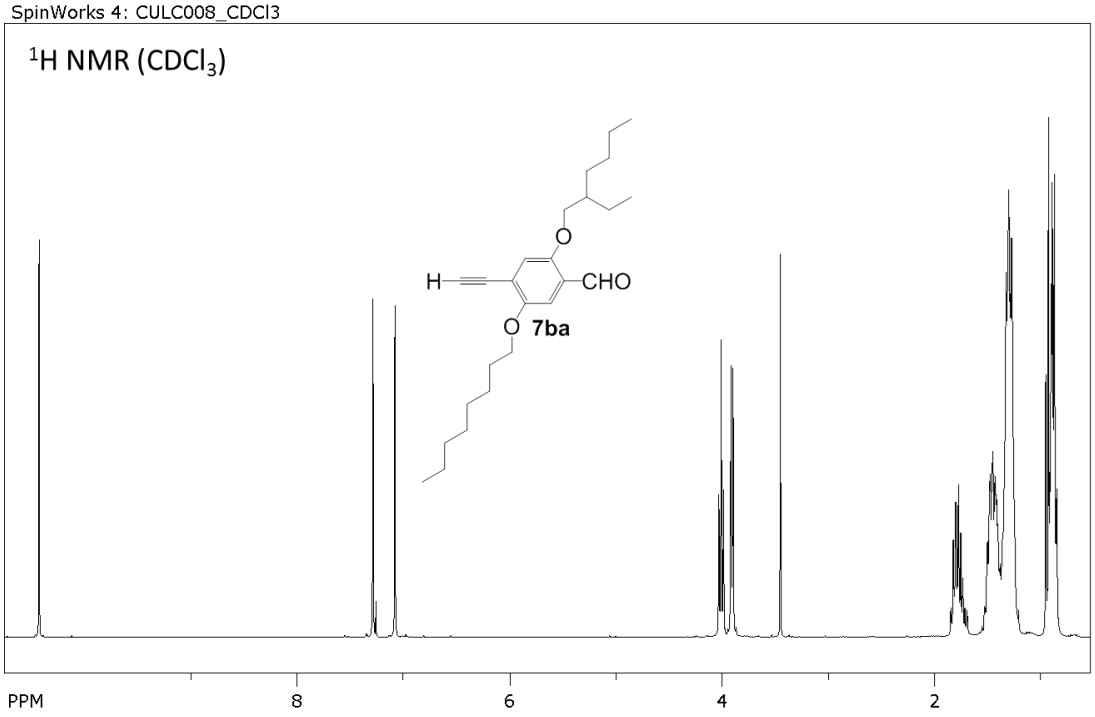
SpinWorks 4: CULC007-cryst(MeOH)_CDCl3



file: ...7\CULC007-cryst(MeOH)_CDCl3\20\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 932

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

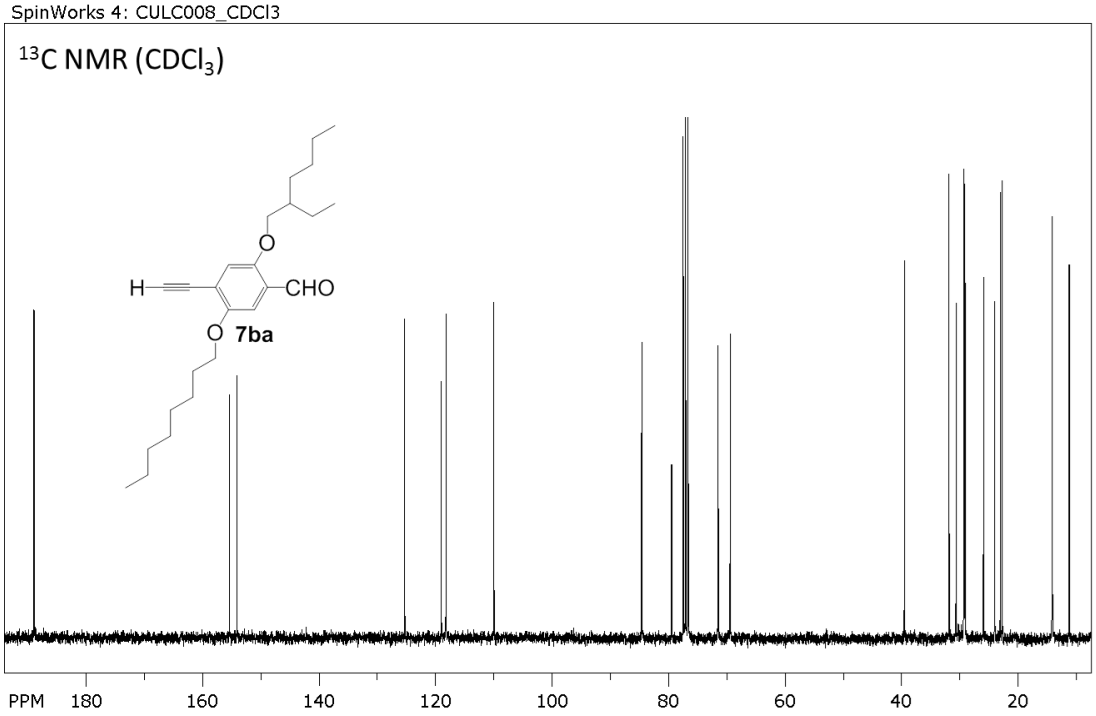
SpinWorks 4: CULC008_CDCl3



file: ...YTIC\NMR\2017\CULC008_CDCl3\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6009.62 Hz = 20.0233 ppm = 0.091699 Hz/pt
number of scans: 28

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

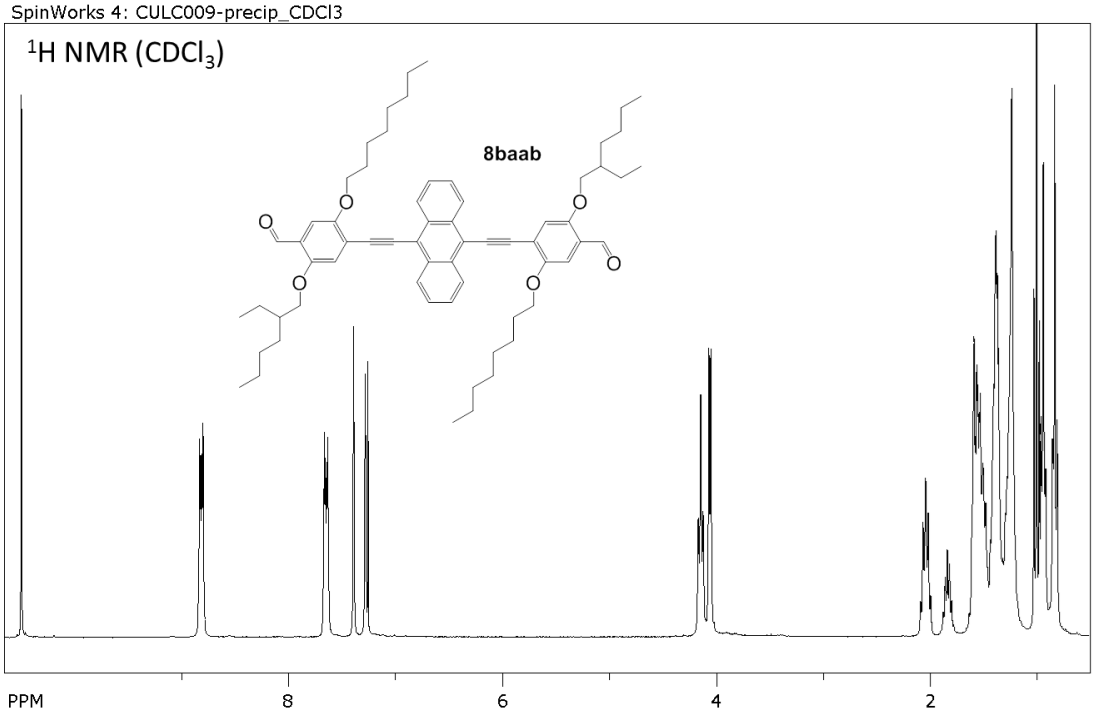
SpinWorks 4: CULC008_CDCl3



file: ...YTIC\NMR\2017\CULC008_CDCl3\20\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 360

freq. of 0 ppm: 75.467750 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

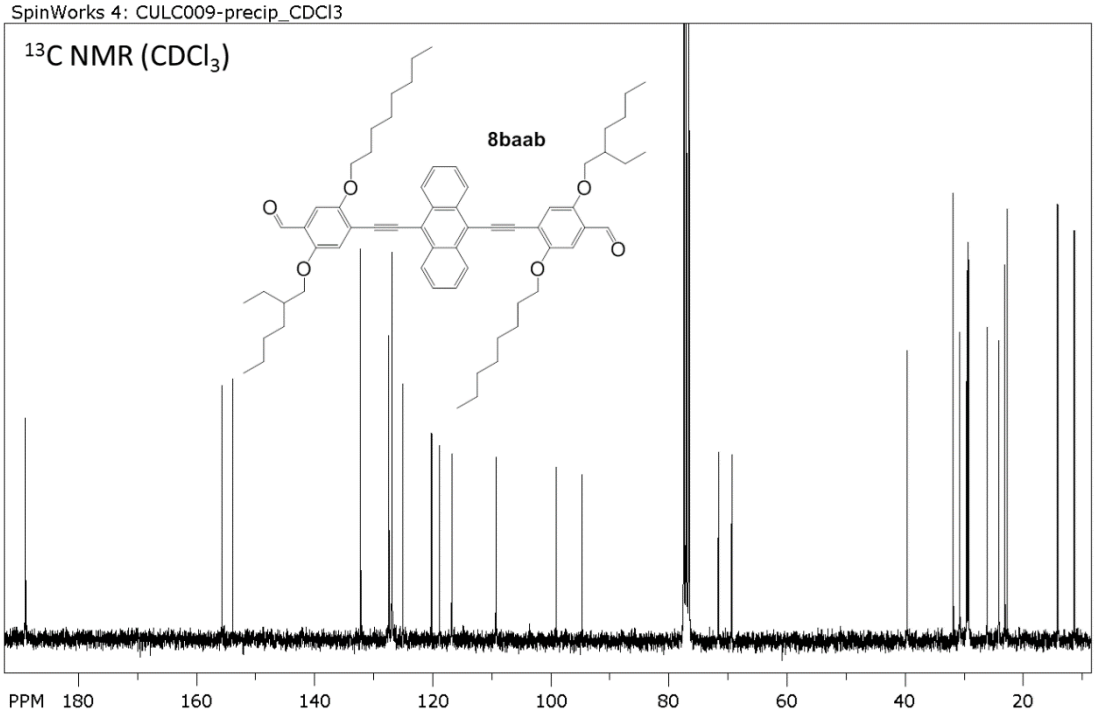
SpinWorks 4: CULC009-precip_CDCl3



file: ...R\2017\CULC009-precip_CDCl3\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6009.62 Hz = 20.0233 ppm = 0.091699 Hz/pt
number of scans: 24

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

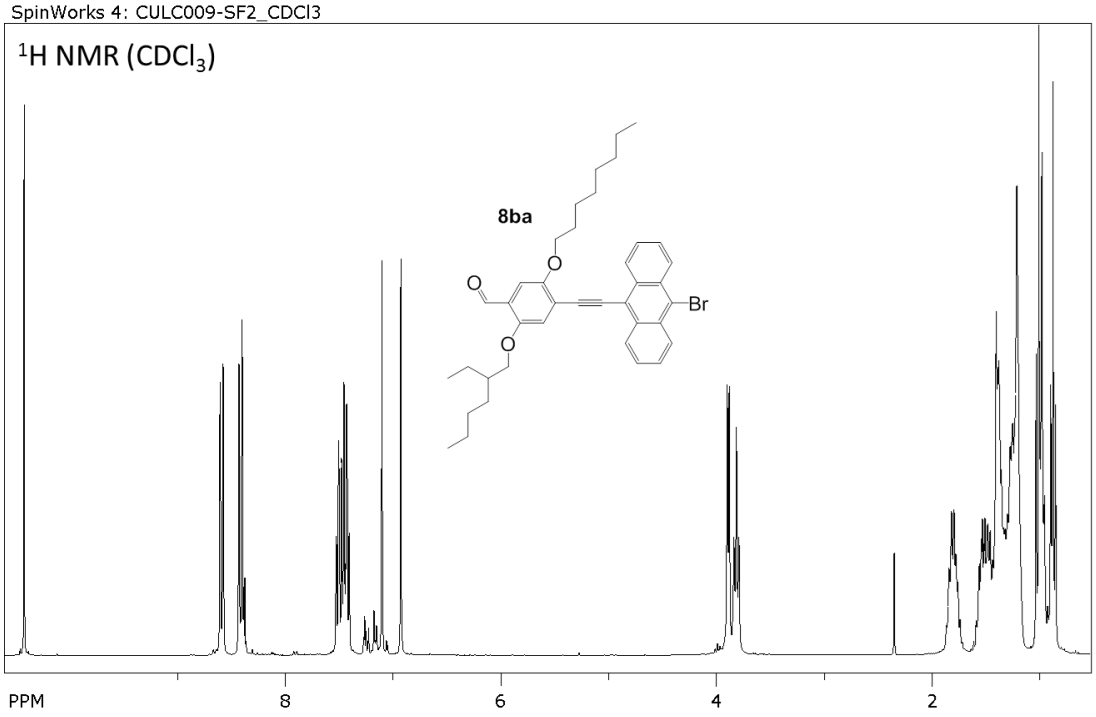
SpinWorks 4: CULC009-precip_CDCl3



file: ...R\2017\CULC009-precip_CDCl3\11\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 3600

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

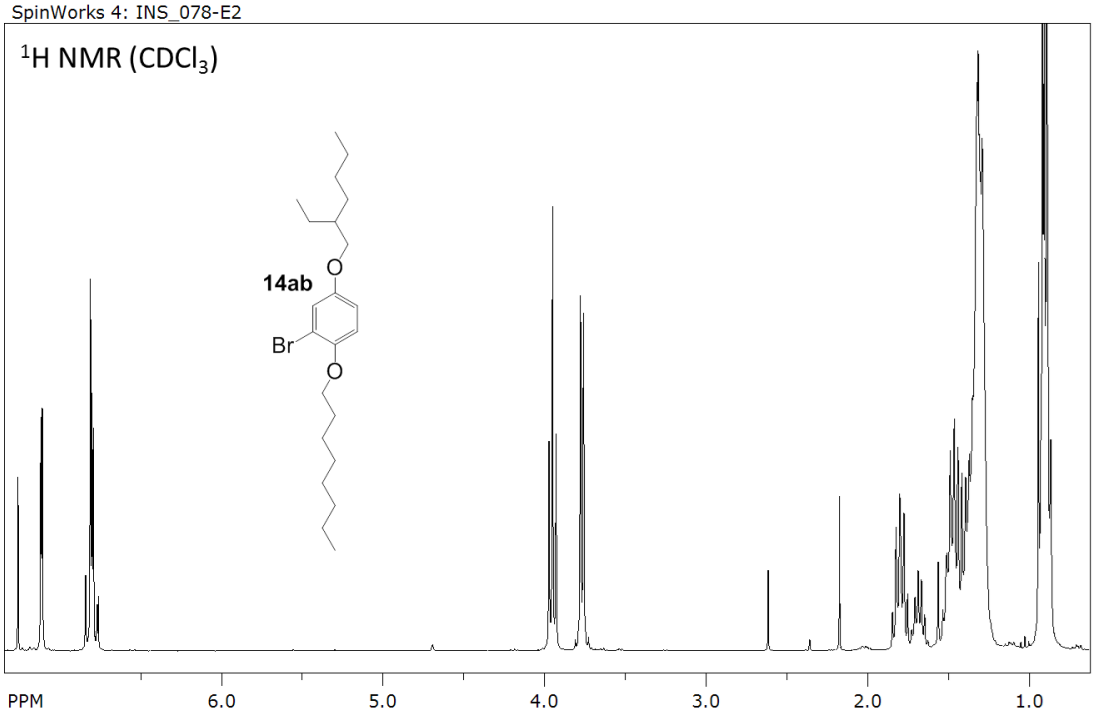
SpinWorks 4: CULC009-SF2_CDCl3



file: ...\NMR\2017\CULC009-SF2_CDCl3\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6009.62 Hz = 20.0233 ppm = 0.091699 Hz/pt
number of scans: 24

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

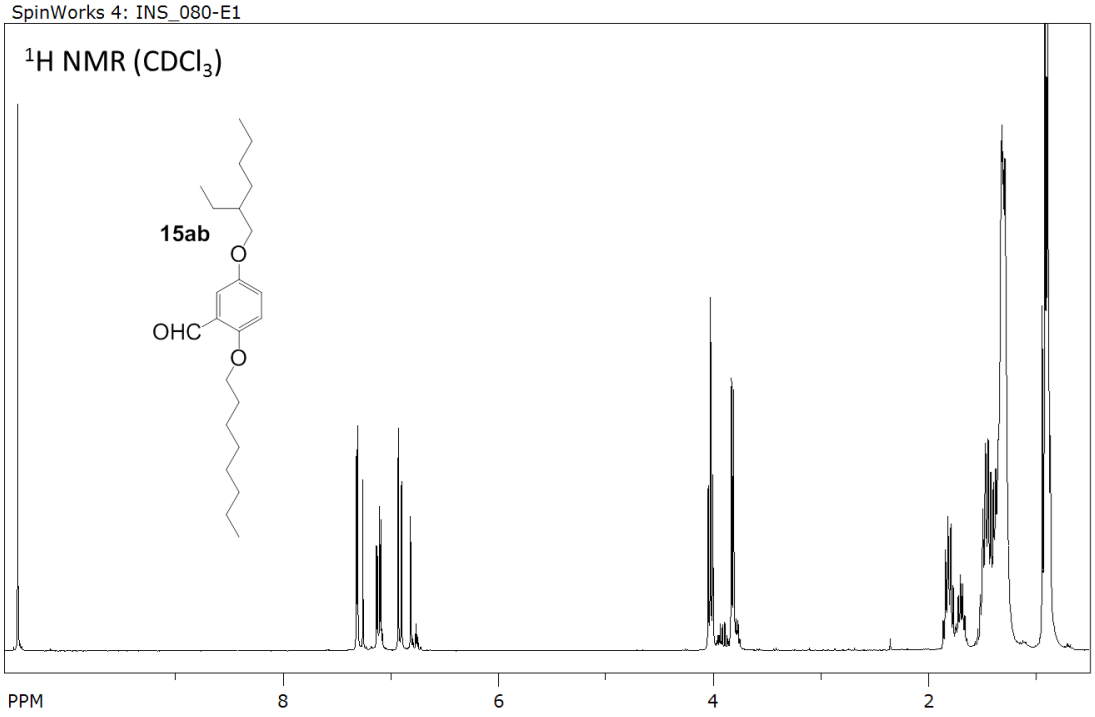
SpinWorks 4: INS_078-E2



file: ...S_078-E2_14ab_Phen(Br)-O,EH\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

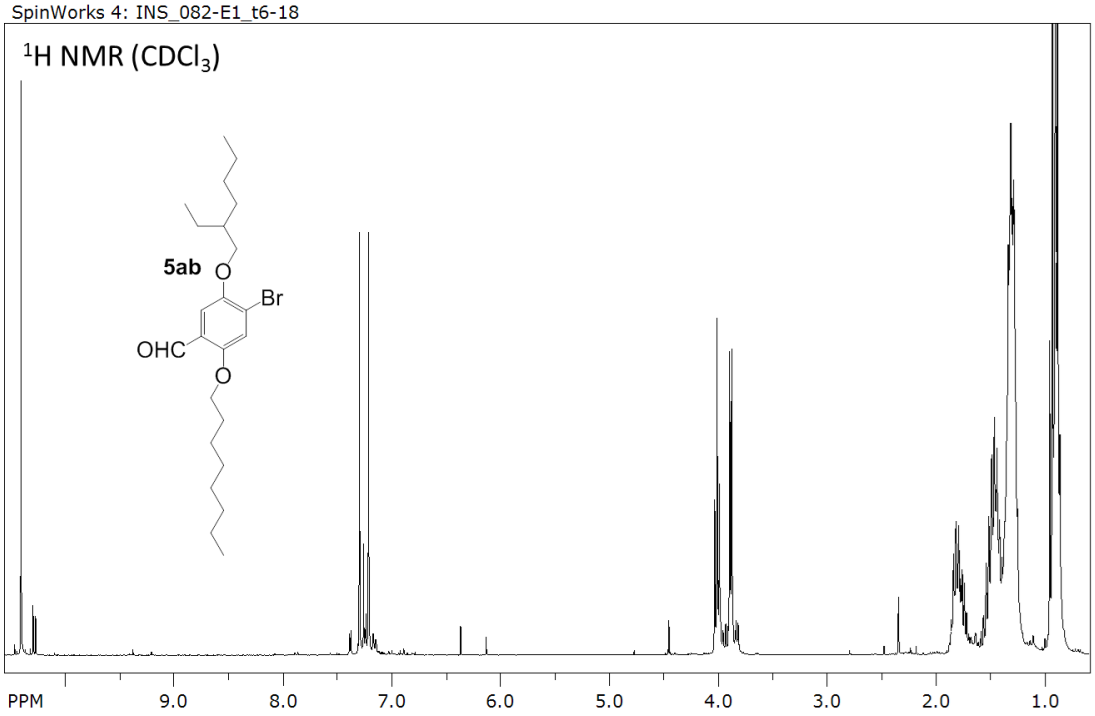
SpinWorks 4: INS_080-E1



file: ..._080-E1_15ab_Phen(CHO)-O,EH\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

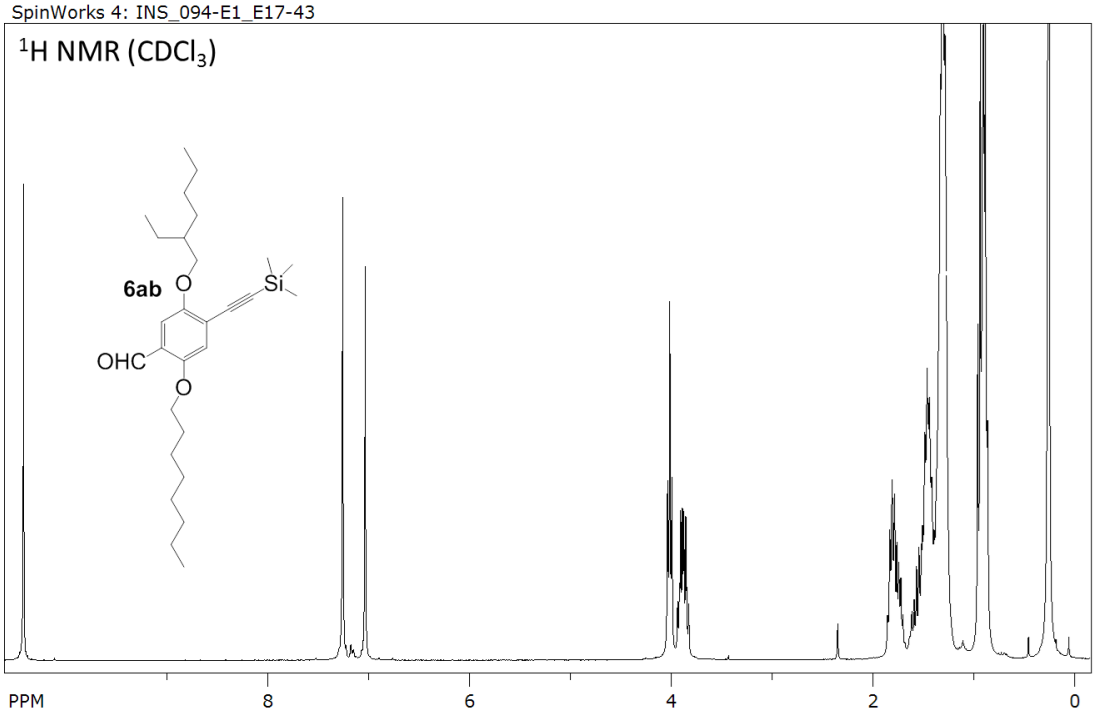
SpinWorks 4: INS_082-E1_t6-18



file: ...t6-18_5ab_Phen(Br,CHO)-O,EH\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

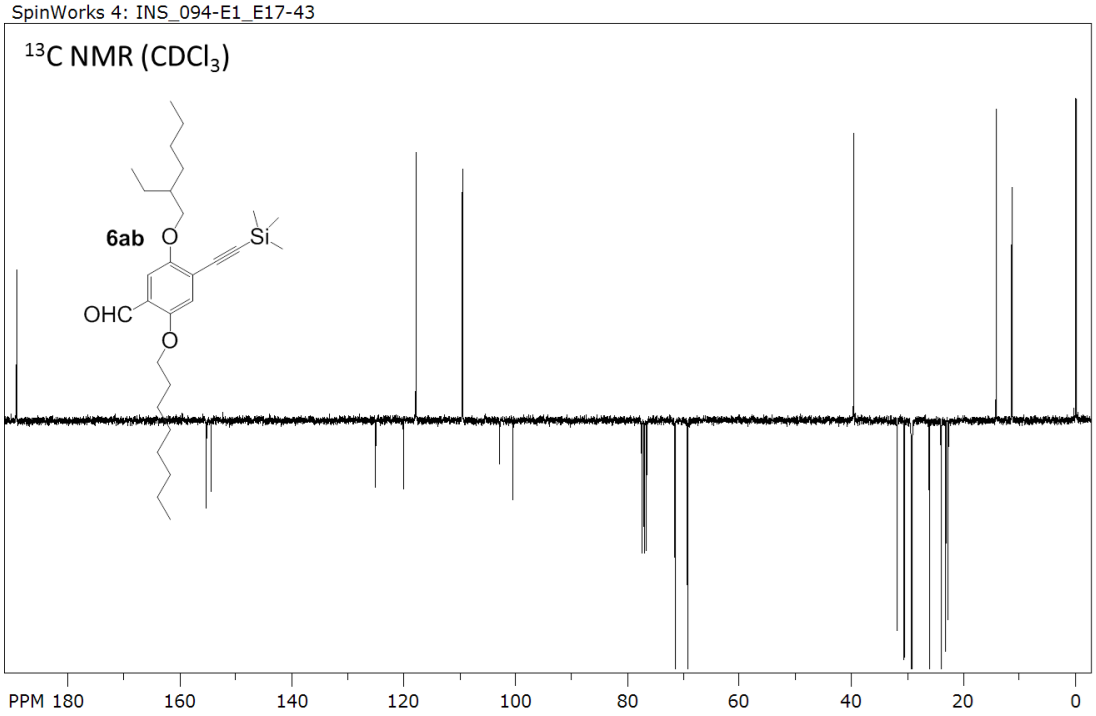
SpinWorks 4: INS_094-E1_E17-43



file: ...Phen(CHO,ethyn-Si)-O,EH_H,C\20\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130006 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

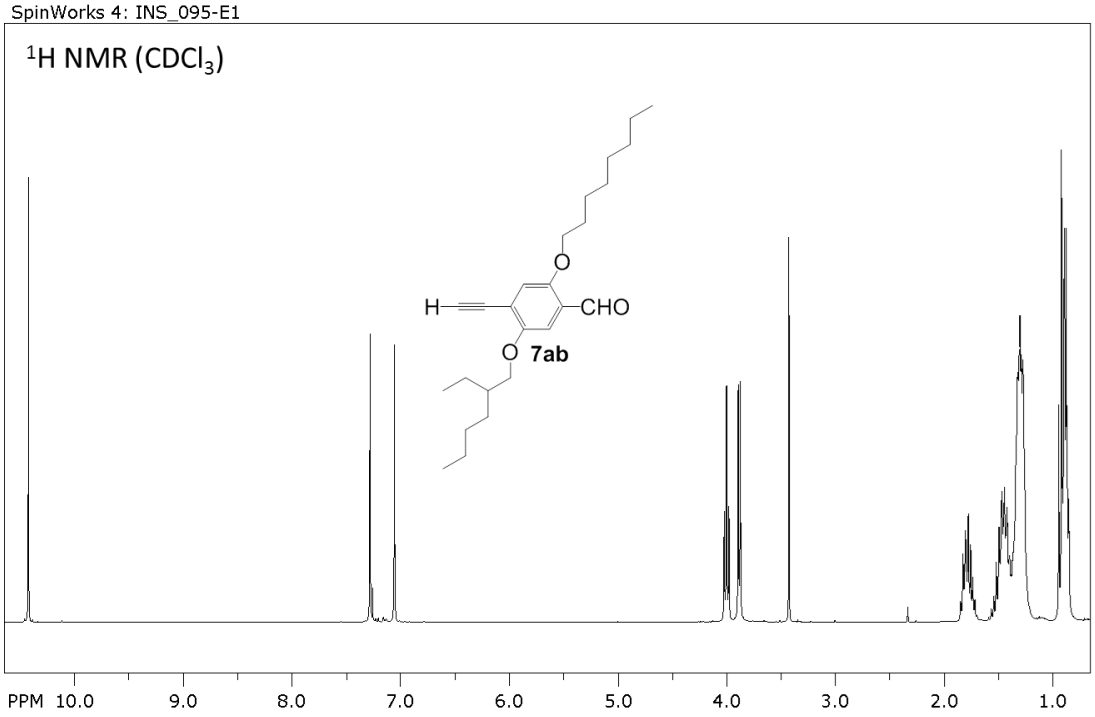
SpinWorks 4: INS_094-E1_E17-43



file: ...MR-(LIOS)\INS_094-E1_E17-43\21\fid expt: <jmod>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467748 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

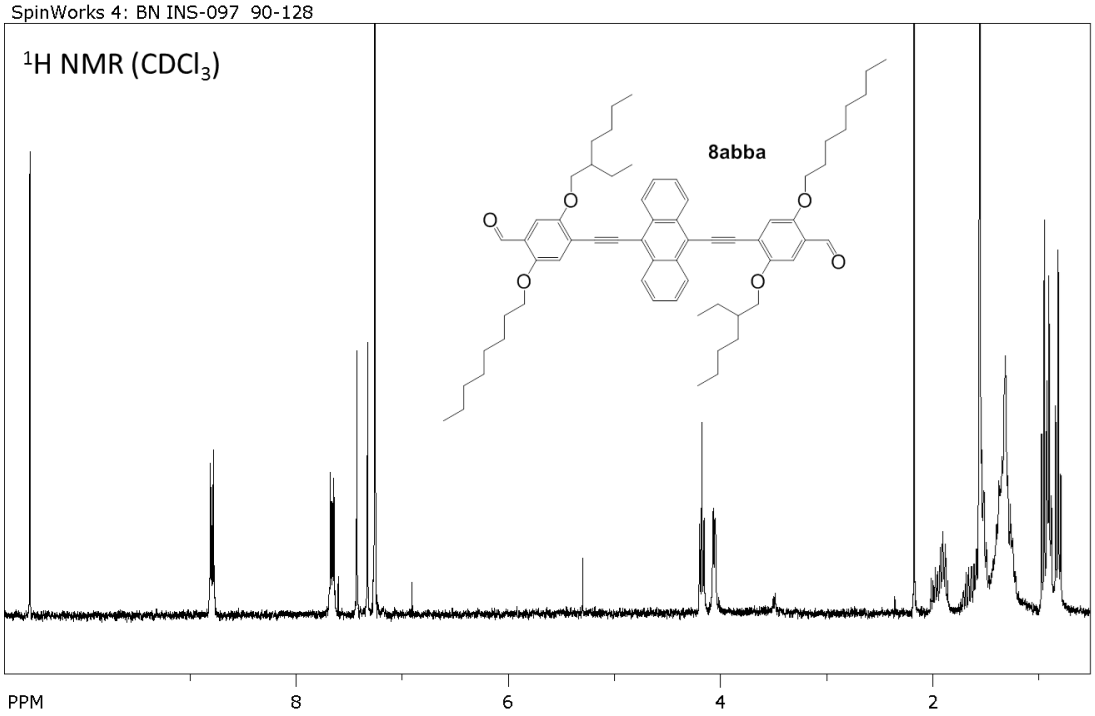
SpinWorks 4: INS_095-E1



file: ...zzz_JACS\NMR\7ab,INS_095-E1\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

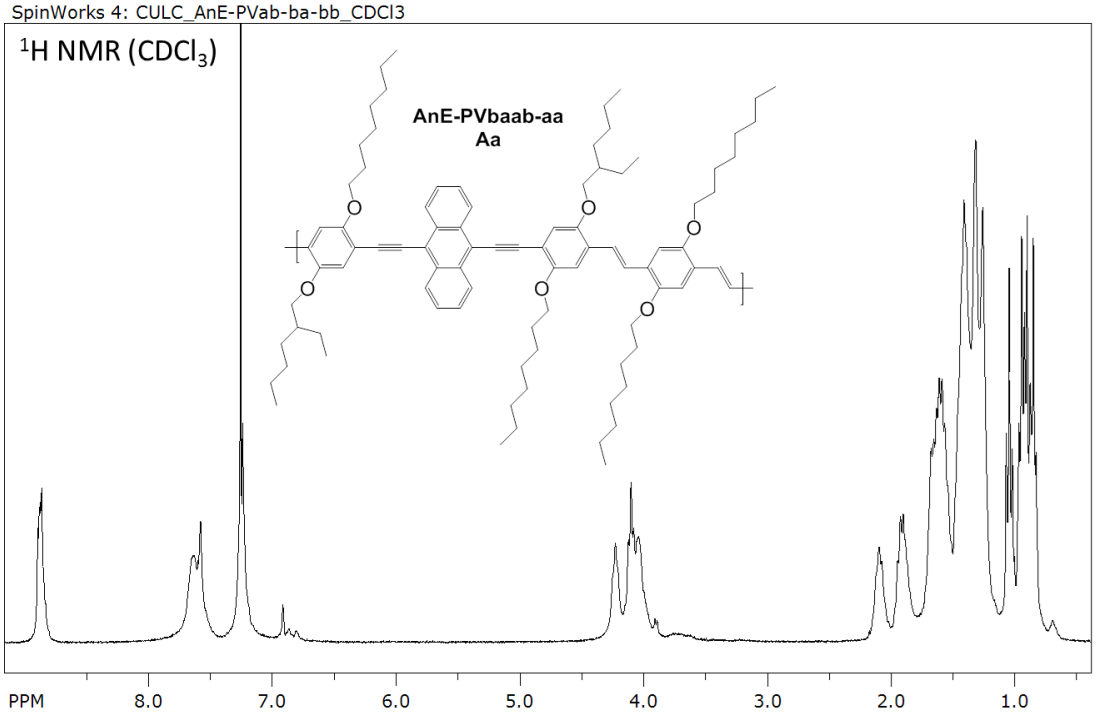
SpinWorks 4: BN INS-097 90-128



file: ...0-128),B\BN INS-097 90-128\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

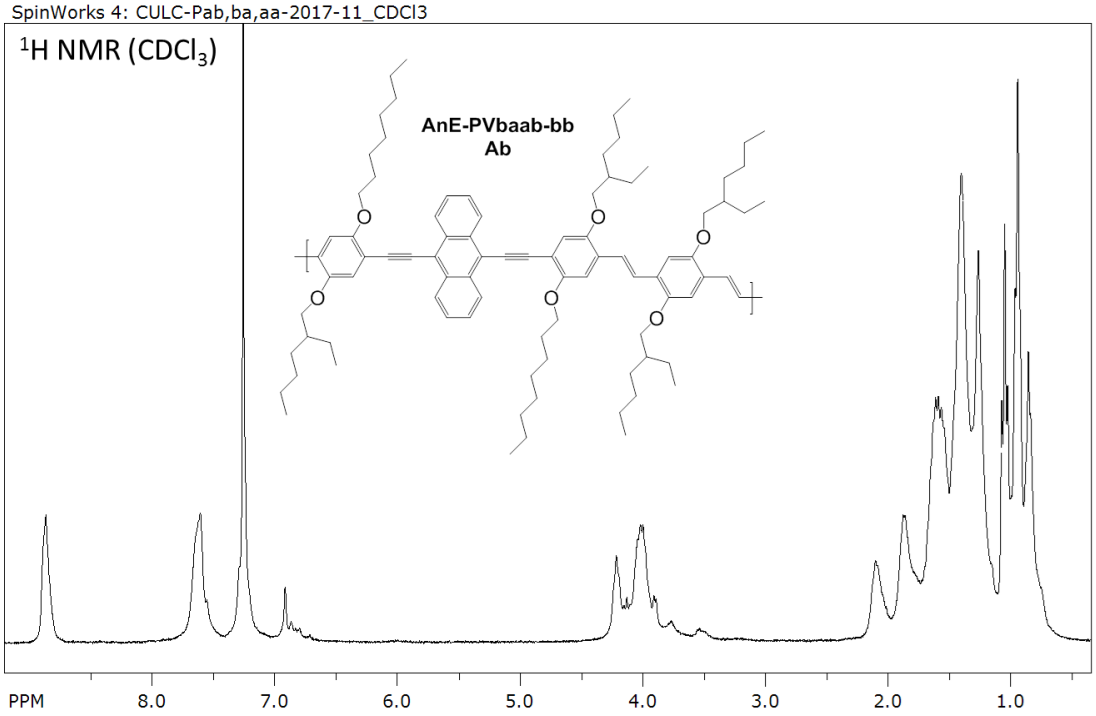
SpinWorks 4: CULC_AnE-PVab-ba-bb_CDCl3



file: ...),CULC_AnE-PVab-ba-bb_CDCl3\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6009.62 Hz = 20.0233 ppm = 0.091699 Hz/pt
number of scans: 80

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

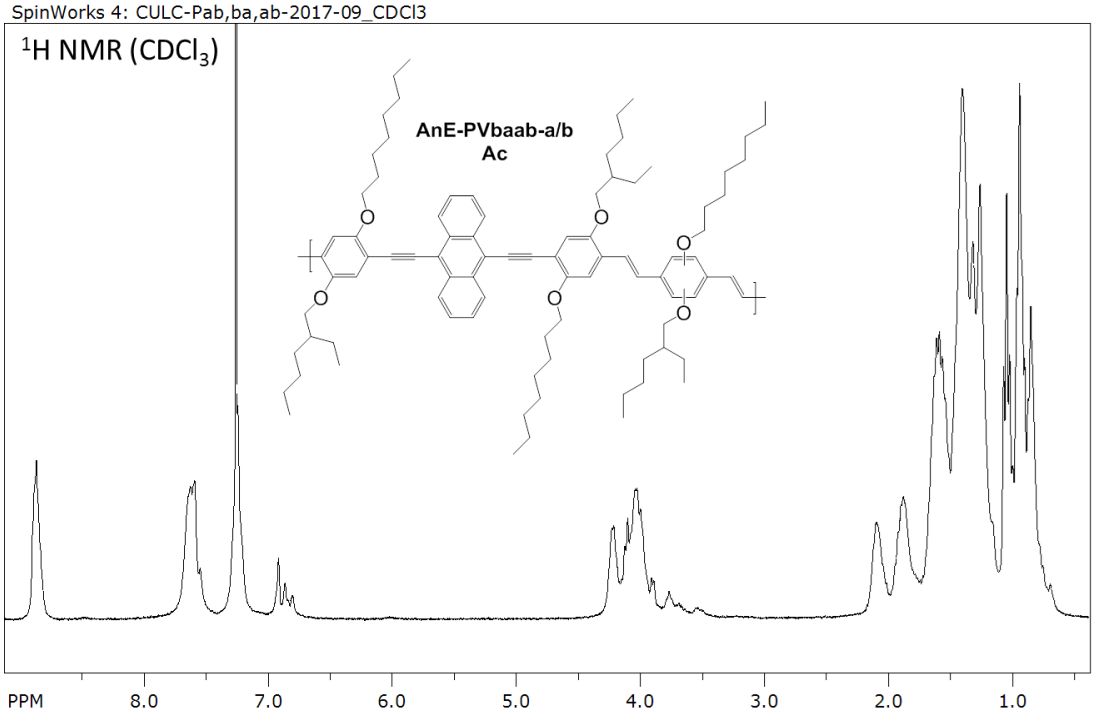
SpinWorks 4: CULC-Pab,ba,aa-2017-11_CDCl3



file: ...ULC-Pab,ba,aa-2017-11_CDCl3\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6009.62 Hz = 20.0233 ppm = 0.091699 Hz/pt
number of scans: 64

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

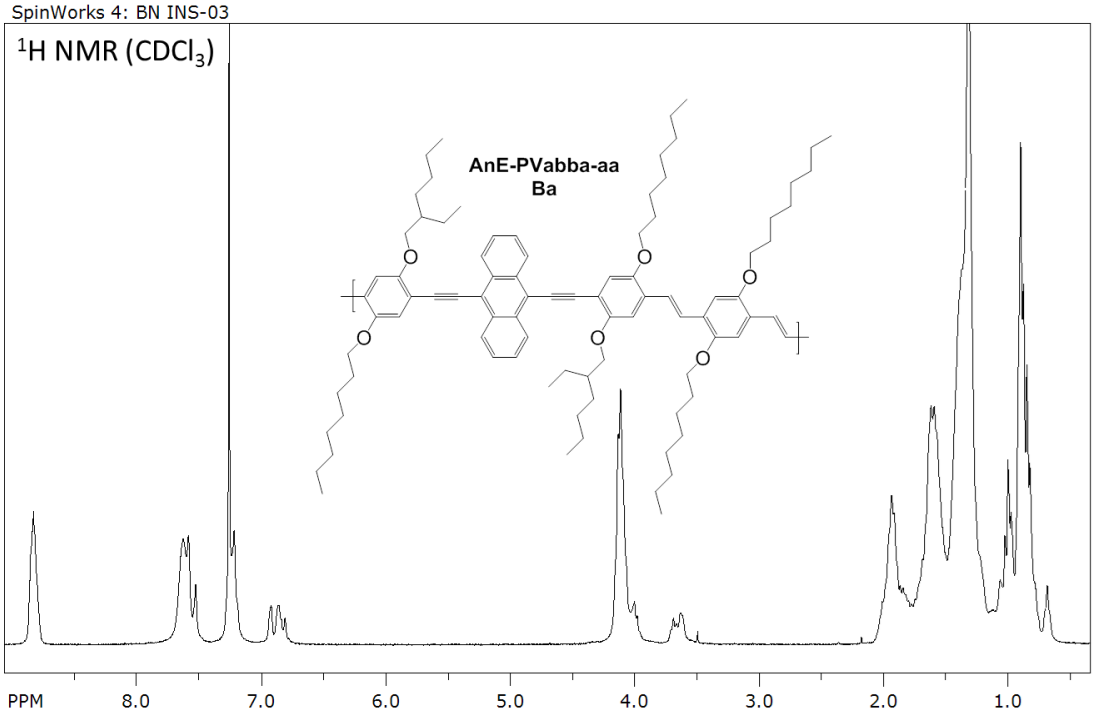
SpinWorks 4: CULC-Pab,ba,ab-2017-09_CDCl3



file: ...ULC-Pab,ba,ab-2017-09_CDCl3\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6009.62 Hz = 20.0233 ppm = 0.091699 Hz/pt
number of scans: 64

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

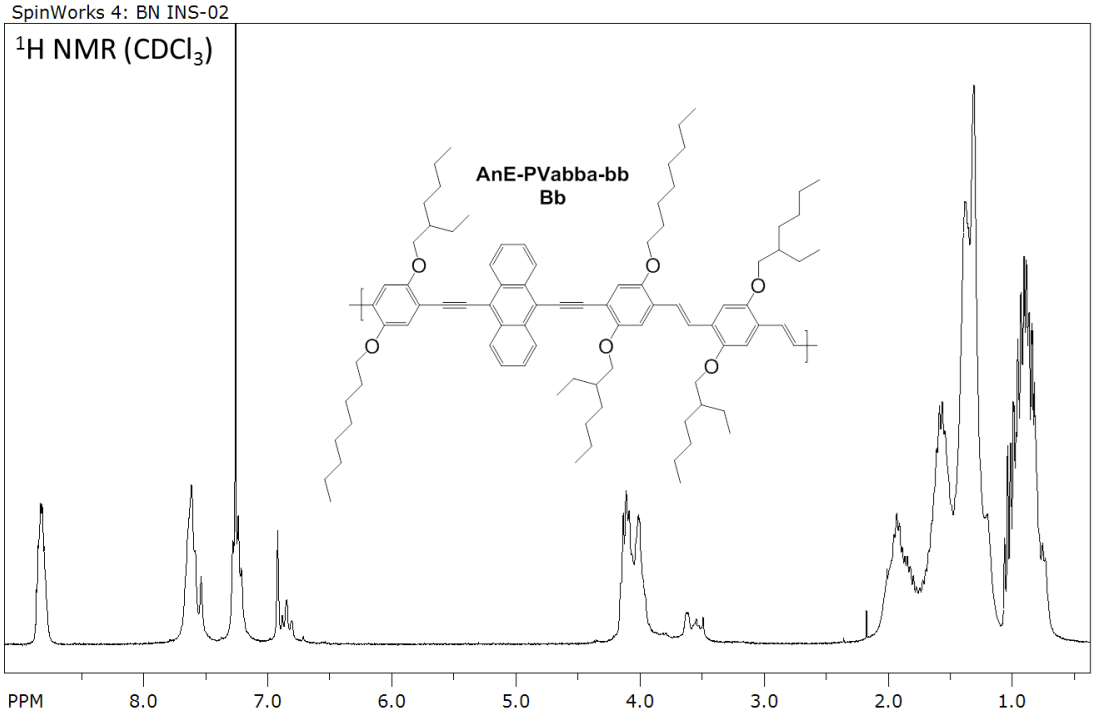
SpinWorks 4: BN INS-03



file: ...(P_O,EH,EH,O-O,O),BN INS-03\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 32

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

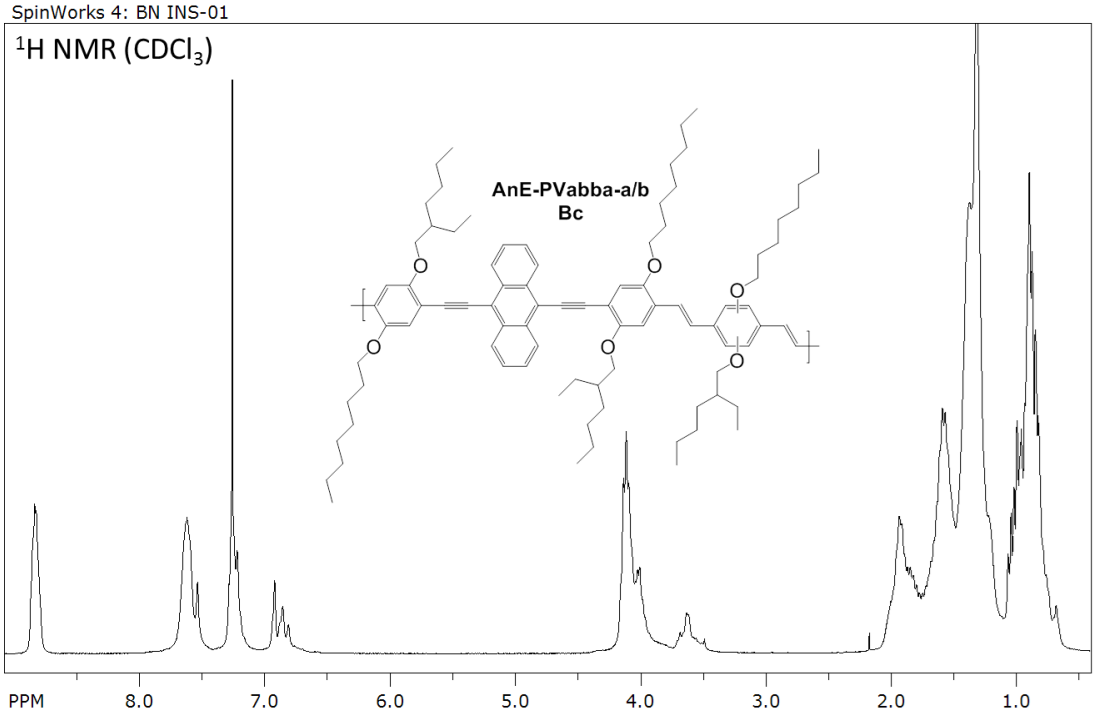
SpinWorks 4: BN INS-02



file: ..._O,EH,EH,O-EH,EH),BN INS-02\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 32

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

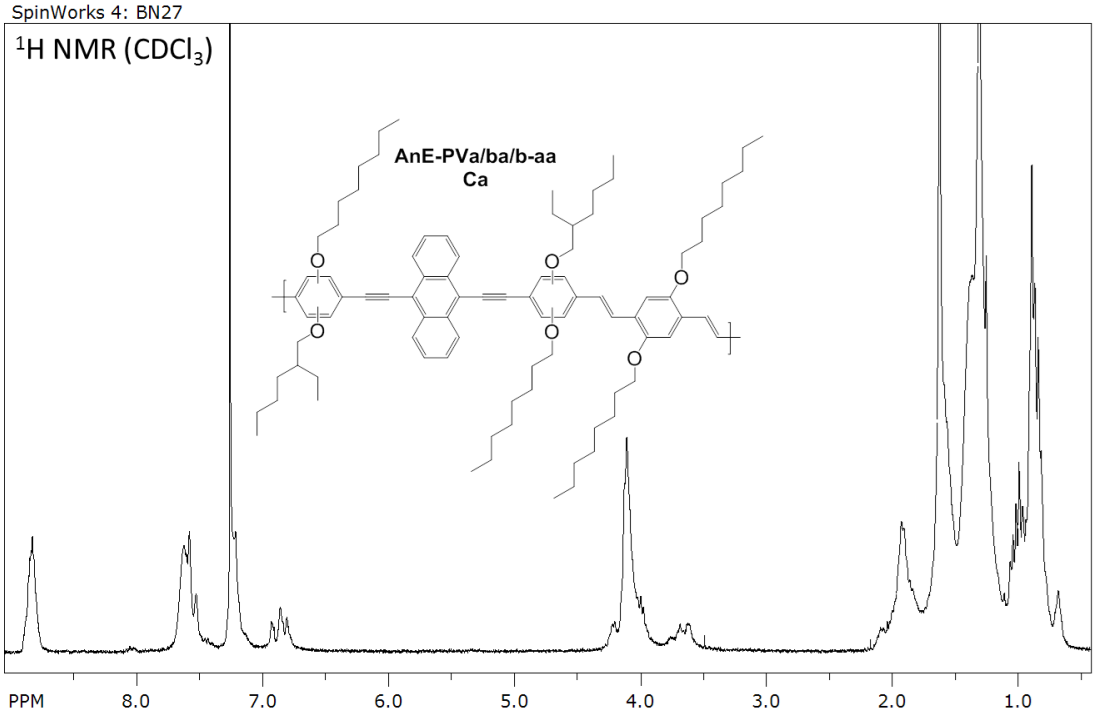
SpinWorks 4: BN INS-01



file: ..._O,EH,EH,O-EH(O)),BN INS-01\20\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 32

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

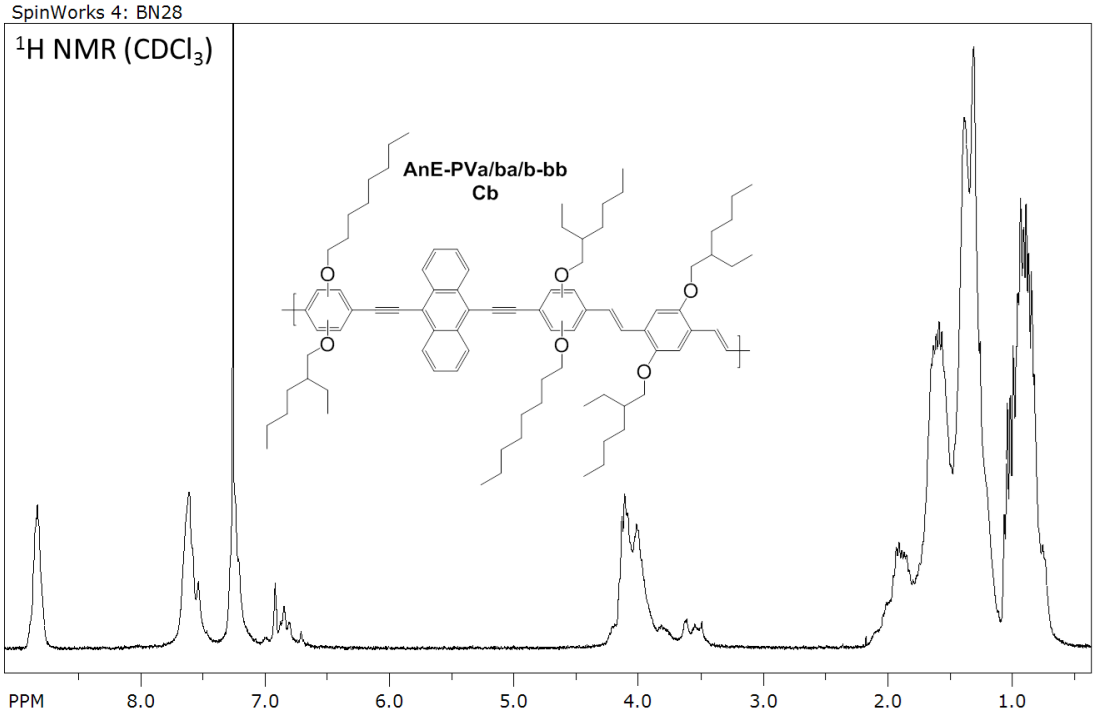
SpinWorks 4: BN27



file: ...Ca,(P_O(EH),O(EH)-O,O),BN27\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

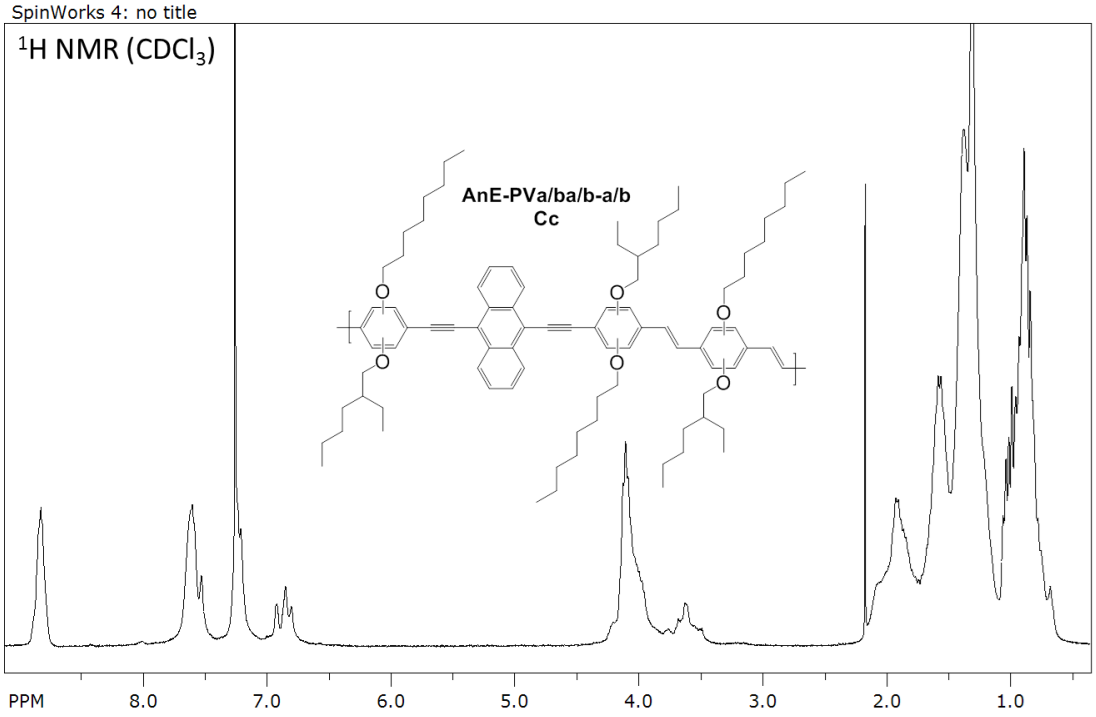
SpinWorks 4: BN28



file: ...,(P_O(EH),O(EH)-EH,EH),BN28\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

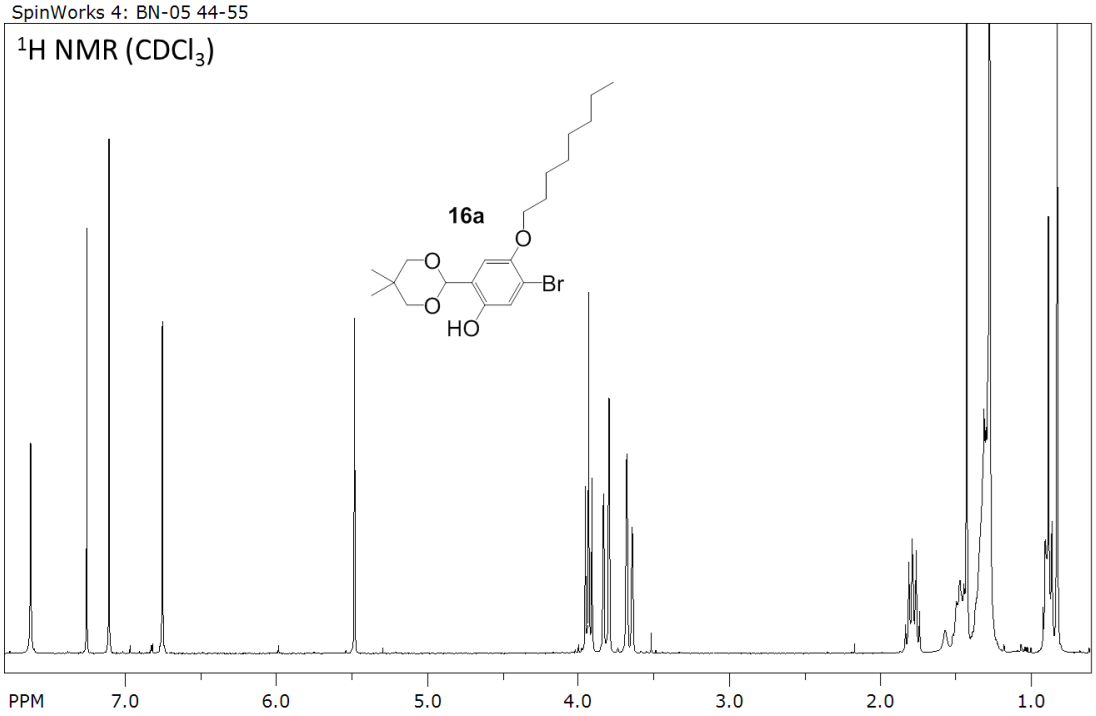
SpinWorks 4: no title



file: ...EH),O(EH)-EH(O)),BN15-CDCl3\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 160

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

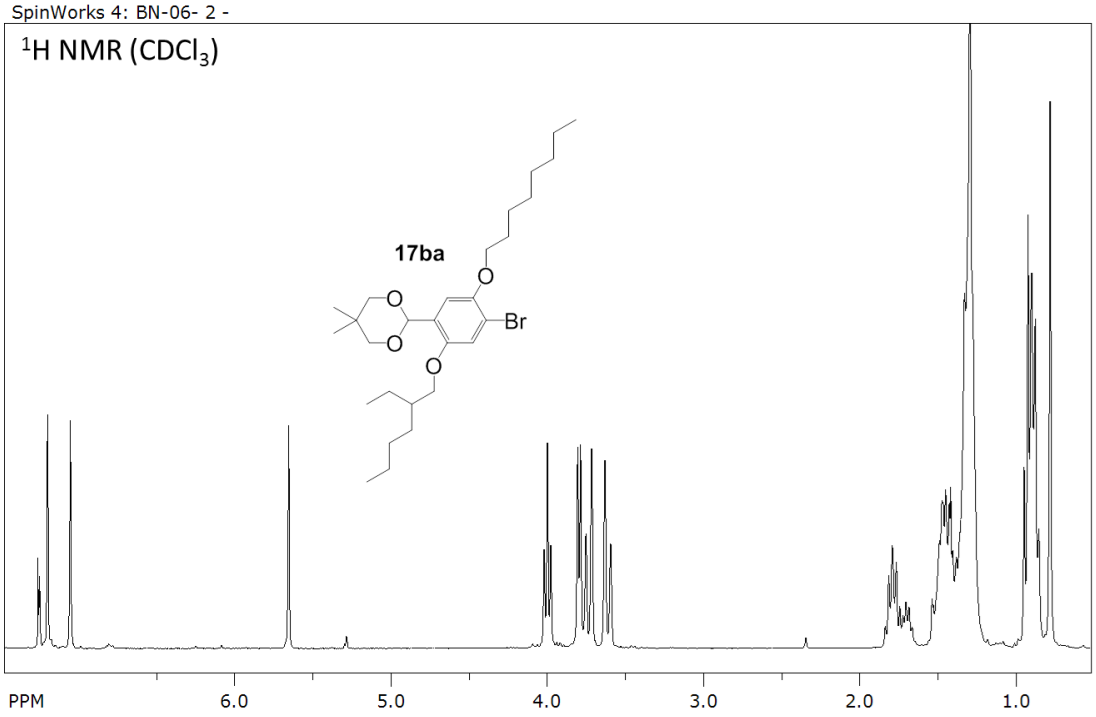
SpinWorks 4: BN-05 44-55



file: ..._Phen(CHO-acetal,Br)-OH,O_H\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

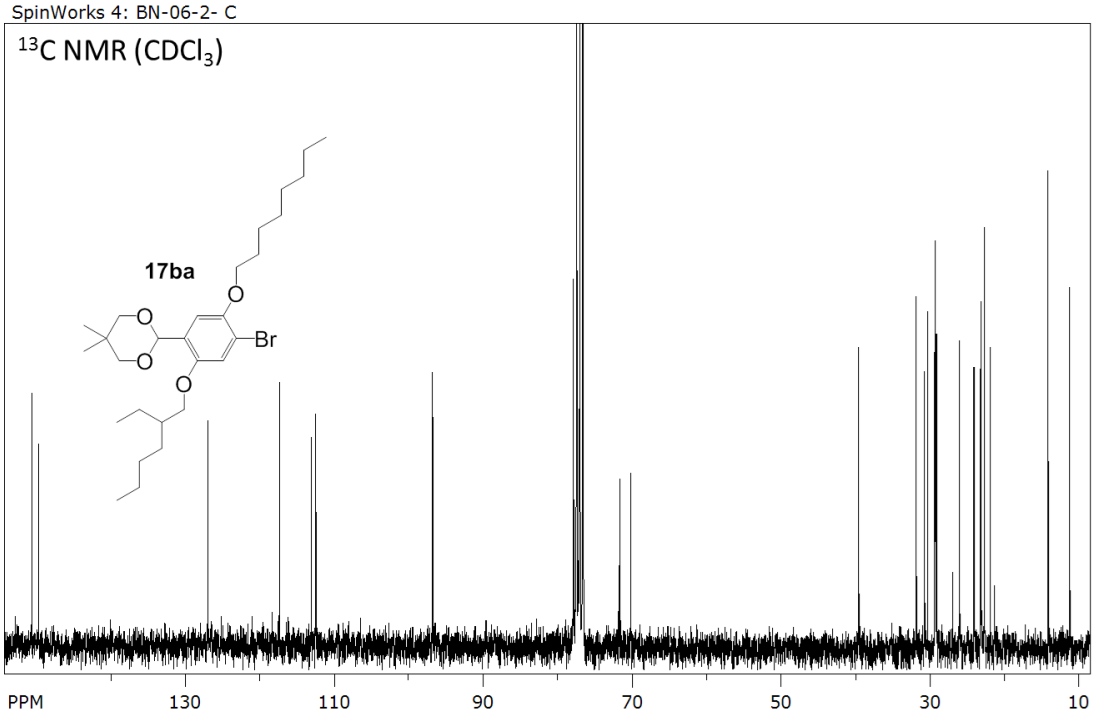
SpinWorks 4: BN-06- 2 -



file: ..._Phen(CHO-acetal,Br)-EH,O_H\10\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6188.12 Hz = 20.6180 ppm = 0.094423 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130010 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

SpinWorks 4: BN-06-2- C



file: ..._Phen(CHO-acetal,Br)-EH,O_C\11\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 18028.85 Hz = 238.8708 ppm = 0.275098 Hz/pt
number of scans: 650

freq. of 0 ppm: 75.467748 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000