Electronic Supplementary Information

Semifluorinated, kinked polyarylenes via direct arylation polycondensation

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1. Materials and methods

All chemicals were obtained from Sigma Aldrich and used without further treatment unless specified.

DSC measurements were acquired on a DSC 2500 (TA Instruments) under a nitrogen atmosphere at a heating and cooling rate of 10 K / min.

NMR measurements were carried out on an Advance III 500 NMR spectrometer (Bruker) at 500.13 MHz (^{1}H), 125.76 MHz (^{13}C) and 470.59 MHz (^{19}F). The spectra were recorded in $CDCl_3$ and DMSO-d_6 at 30 °C or in $C_2D_2Cl_4$ at 120 °C. The spectra were referenced to the solvent signal ($CDCl_3$: δ(^{1}H) = 7.26 ppm, δ(^{13}C) = 77.0 ppm; DMSO-d_6: δ(^{1}H) = 2.50 ppm, δ(^{13}C) = 39.6 ppm; $C_2D_2Cl_4$: δ(^{1}H) = 5.98 ppm). The ^{19}F NMR spectra were referenced to external C_6F_6 (δ(^{19}F) = -163 ppm). Signal assignments were confirmed by ^{1}H - ^{1}H and ^{1}H - ^{13}C correlated spectra.

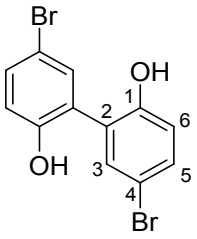
TGA measurements were done on a TGA/DSC3+ (Mettler-Toledo) under nitrogen at a heating rate of 10 K / min.

SEC measurements in $CHCl_3$ were carried out on three MZ-Gel SD plus 5 µm columns and a pre-column, with pore sizes of 10^3, 10^4 and 10^5 Å (MZ-Analysentechnik GmbH) connected in series with a SPD20AV UV detector (Shimadzu) and calibrated with polystyrene standards. $CHCl_3$ (HPLC grade) was used as eluent at 30 °C at a flow rate of 1.0 mL / min.

2. Preparation of monomers

The preparation of the linear side chain monomer 6*n* was reported previously.[1] The procedure was modified for the syntheses of the following monomers.

2.1. 5,5'-Dibromobiphenyl-2,2'-diol

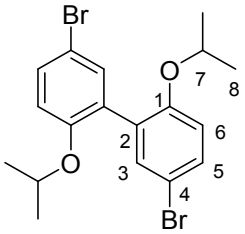


2,2'-Biphenol (10.001 g, 53.703 mmol, 1.0 eq.) and *p*-toluenesulfonic acid (12.211 g, 70.911 mmol, 1.3 eq.) were dissolved in acetonitrile (100 mL). Subsequently N-bromosuccinimide (19.168 g, 107.68 mmol, 2.00 eq.) was added and the mixture agitated for 1 h. The suspension was filtered and remaining solids recrystallized from ethanol. The product was a colorless solid (6.0 g, 17.5 mmol, 33 %).

Melting point: 176-178 °C

^{1}H NMR (500 MHz, DMSO-d_6, ppm): 9.63 (br s, 2H; OH), 7.30 (dd, 8.6 Hz, 2.6 Hz, 2H; H_5), 7.26 (d, 2.6 Hz, 2H; H_3), 6.86 (d, 8.6 Hz, 2H; H_6).
^{13}C NMR (125 MHz, $CDCl_3$, ppm): 154.1 (C_1), 133.5 (C_3), 131.1 (C_5), 126.6 (C_2), 117.8 (C_6), 109.6 (C_4).

2.2. 5,5'-Dibromo-2,2'-bis(isopropoxy)biphenyl

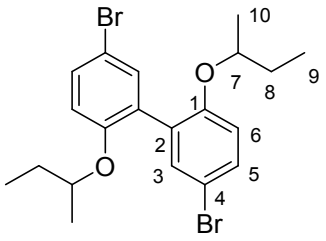


5,5'-Dibromobiphenyl-2,2'-diol (10.029 g, 29.125 mmol, 1.0 eq.), 2-bromopropane (16.4 mL, 21.5 g, 175 mmol, 6.0 eq.) and K_2CO_3 (12.059 g, 87.258 mmol, 3.0 eq.) were stirred in

acetonitrile (dry, 100 mL) and stirred at 90 °C for 24 h. Volatiles were removed under reduced pressure. Solid residue were extracted with *iso*-hexanes (60 mL) and washed with water (60 mL) and brine (25 mL). Aqueous phases were extracted with Et_2O (3 x 60 mL) and all combined organic phases dried over Na_2SO_4. Solvents were removed under reduced pressure and the product recrystallized from 2-propanol. The title compound (7.13 g, 16.66 mmol, 57 %) was a colorless solid. Melting point: 66-69 °C

^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.36 (4H; H_3, H_5), 6.82 (m, 2H; H_6), 4.34 (sept, 6.1 Hz, 2H; H_7), 1.19 (d, 6.1 Hz, 12H; H_8).
^{13}C NMR (125 MHz, $CDCl_3$, ppm): 154.5 (C_1), 134.3 (C_3), 131.1 (C_5), 130.2 (C_2), 116.3 (C_6), 112.2 (C_4), 71.3 (C_7), 21.9 (C_8).

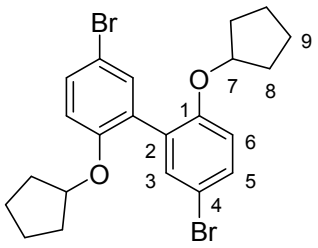
2.3. 5,5'-Dibromo-2,2'-bis(sec-butoxy)biphenyl



5,5'-Dibromobiphenyl-2,2'-diol (10.008 g, 28.594 mmol, 1.0 eq.), 2-bromobutane (19.0 mL, 23.9 g, 174 mmol, 6.0 eq.) and K_2CO_3 (12.051 g, 87.200 mmol, 3.0 eq) were stirred in acetonitrile (dry, 100 mL) at 90 °C for 24 h. Volatiles were removed under reduced pressure. Solid residues were dissolved in *iso*-hexanes (60 mL), washed with H_2O (25 mL) and brine (25 mL) and dried over Na_2SO_4. Solvents were removed under reduced pressure and the product recrystallized from 2-propanol. The title compound (7.77 g, 17.0 mmol, 58 %) was a colorless solid. Melting point: 64-67 °C

^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.35 (4H; H_3, H_5), 6.80 (d, 8.3 Hz, 2H; H_6), 4.13 (2H; H_7), 1.57 and 1.48 (2 x m, 4H; H_8), 1.15 and 1.14 (2 x d, 6.0 Hz, 6H; H_{10}), 0.83 and 0.82 (2 x t, 7.4 Hz, 6H; H_9). Note: The reaction product is the mixture of the two diastereomers.
^{13}C NMR (125 MHz, $CDCl_3$, ppm): 154.6 (C_1), 134.4 (C_3), 131.1 (C_5), 130.1 (C_2), 116.1 (C_6), 112.0 (C_4), 76.1 (C_7), 29.0 (C_8), 18.9 (C_{10}), 9.4 (C_9).

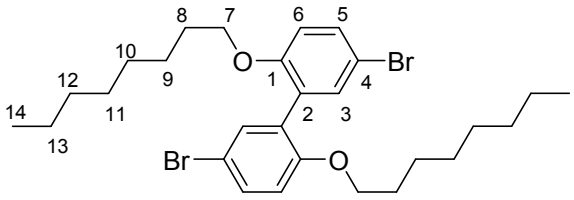
2.4. 5,5'-Dibromo-2,2'-bis(cyclopentoxy)biphenyl



5,5'-Dibromobiphenyl-2,2'-diol (6.006 g, 17.44 mmol, 1.0 eq.), DMF (1 mL), bromocyclopentane (23.0 mL, 33.9 g, 227 mmol, 13 eq.) and K_2CO_3 (7.271 g, 52.61 mmol, 3.1 eq.) were stirred at 95 °C for 18 h. The mixture was quenched with H_2O (25 mL) and washed with brine (25 mL). Aqueous phases were extracted with Et_2O (3 × 25 mL) and the organic phase dried with $MgSO_4$. Volatiles were removed under reduced pressure. Solid residues were purified in a Kugelrohr apparatus under high vaccum (0.6 bar, 280 °C). The product was recrystallized from 2-propanol. The title compound (3.78 g, 7.87 mmol, 45 %) was a colorless solid. Melting point: 133-136 °C.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.34 (4H; H_3, H_5), 6.79 (m, 2H; H_6), 4.65 (m, 2H; H_7), 1.85-1.70 (8H; H_8), 1.70-1.50 (8H; H_{10}).
^{13}C NMR (125 MHz, $CDCl_3$, ppm): 154.5 (C_1), 134.1 (C_3), 131.0 (C_5), 129.5 (C_2), 115.3 (C_6), 111.8 (C_4), 80.2 (C_7), 32.7 (C_8), 23.8 (C_9).

2.5. 5,5'-Dibromo-2,2'-bis(octyloxy)biphenyl

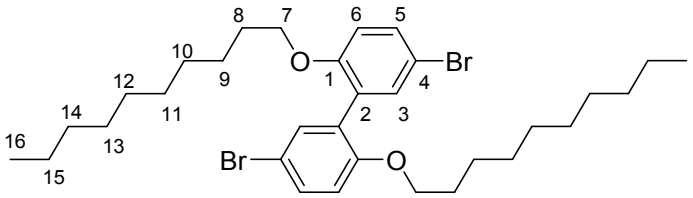


2,2'-Biphenol (10.016 g, 53.789 mmol, 1 eq.) and K_2CO_3 (15.601 g, 112.88 mmol, 2.1 eq.) were stirred in acetonitrile (dry, 150 mL) under N_2. After addition of 1-bromooctane (28.0 mL, 25.0 g, 129.66 mmol, 2.4 eq.) the reaction was heated under reflux for 18 h. The crude mixture was freed from precipitates by filtration under air (flushed with an additional 20 mL of ACN). Addition of N-bromosuccinimide (19.1 g, 107 mmol, 2.0 eq.) and continuous purging with N_2 resulted in precipitation within 30 min. After an additional 30 min of mild agitation the crude

product was isolated by filtration under air. Recrystallization from ethanol afforded the monomer as colorless crystals (17.90 g, 31.49 mmol, 59 %). Melting point: 66-67 °C.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.37 (d, 8.5 Hz, 2H; H_5), 7.36 (s, 2H; H_3), 6.79 (d, 8.5 Hz, 2H; H_6), 3.87 (t, 6.4 Hz, 4H; H_7), 1.62 (m, 4H; H_8), 1.35-1.15 (20H; H_9-H_{13}), 0.88 (t, 7.4 Hz, 6H; H_{14}). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): 155.6 (C_1), 134.0 (C_3), 131.3 (C_5), 128.7 (C_2), 113.7 (C_6), 112.1 (C_4), 68.7 (C_7), 31.8 (C_{12}), 29.2 (C_8,C_{10},C_{11}), 26.0 (C_9), 22.7 (C_{13}), 14.1 (C_{14}).

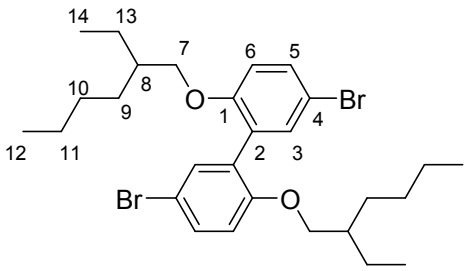
2.6. 5,5'-Dibromo-2,2'-bis(decyloxy)biphenyl



2,2'-Biphenol (10.027 g, 53.847 mmol, 1 eq.) and K_2CO_3 (15.614 g, 112.97 mmol, 2.1 eq.) were stirred in DMF (dry, 120 mL) under N_2. After addition of 1-bromodecane (33.5 mL, 35.7 g, 162 mmol, 3.0 eq.) the reaction was heated under reflux for 20 h. The crude mixture was freed from precipitates by filtration under air (flushed with an additional 100 mL of isohexanes). Volatiles ware removed under reduced pressure by Kugelrohr distillation (0.2 mbar, 160 °C). Addition of ACN (dry, 120 mL) and N-bromosuccinimide (17.3 g, 97.4 mmol, 2.0 eq.) and continuous purging with N_2 resulted in precipitation within 20 h. Recrystallization from isopropanol afforded the monomer as colorless crystals (14.97 g, 23.97 mmol, 45 %). Melting point: 73-76 °C.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.37 (d, 8.4 Hz, 2H; H_5), 7.36 (s, 2H; H_3), 6.79 (d, 8.4 Hz, 2H; H_6), 3.87 (t, 6.5 Hz, 4H; H_7), 1.62 (m, 4H; H_8), 1.35-1.15 (28H; H_9-H_{15}), 0.88 (t, 7.4 Hz, 6H; H_{16}). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): 155.6 (C_1), 134.0 (C_3), 131.3 (C_5), 128.7 (C_2), 113.7 (C_6), 112.1 (C_4), 68.7 (C_7), 31.9 (C_{14}), 29.6 - 29.1 (C_8,C_{10}-C_{13}), 26.0 (C_9), 22.7 (C_{15}), 14.1 (C_{16}).

2.7. 5,5'-Dibromo-2,2'-bis(2-ethylhexyloxy)biphenol



5,5'-Dibromobiphenyl-2,2'-diol (10.025 g, 29.143 mmol, 1.0 eq.), 2-ethylhexylbromide (31.0 mL, 33.7 g, 174 mmol, 6.0 eq.) and K_2CO_3 (12.044 g, 87.143 mmol, 3.0 eq.) were stirred in acetonitrile (dried over 3 Å mol sieve / 4 d, p.a., 100 mL) and heated under reflux for 18 h. The solvent was removed under reduced pressure. Residues were dissolved in *iso*-hexanes (50 mL) and washed with H_2O (2 x 25 mL). Aqueous phases were extracted with Et_2O (2 × 30 mL) and combined organic phases dried over $MgSO_4$. Volatiles were removed under reduced pressure. The viscous residue was purified twice with a Kugelrohr apparatus under high vacuum (0.6 bar, 260-280 °C). The title compound (6.104 g, 10.74 mmol, 37 %) was a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.37 (4H; H_3, H_5), 6.80 (m, 2H; H_6), 3.75 (d, 5.6 Hz, 4H; H_7), 1.55 (m, 4H; H_8), 1.28 (m, 4H; H_{13}), 1.25-1.10 (12H; H_9-H_{11}), 0.84 (t, 7.2 Hz, 6H; H_{12}), 0.81 (t, 7.4 Hz, 6H; H_{14}).
^{13}C NMR (125 MHz, $CDCl_3$, ppm): 155.8 (C_1), 134.0 (C_3), 131.2 (C_5), 128.6 (C_2), 113.6 (C_6), 111.9 (C_4), 71.1 (C_7), 39.4 (C_8), 30.6 (C_9), 29.0 (C_{10}), 23.8 (C_{13}), 23.0 (C_{11}), 14.1 (C_{12}), 11.1 (C_{14}).

2.8. 2,2'-Bis(hexyloxy)biphenyl

To a two-neck round bottom flask equipped with a stirring bar and condenser 2,2-dihydroxy-1,1-biphenyl (5.5 g, 29.55 mmol) was added. Then the reaction flask was placed under argon and 100 ml anhydrous acetonitrile was added, followed by the addition of potassium carbonate (24.0g, 175 mmol) and 1-bromohexane (10.0 g, 60.58 mmol). Finally, a catalytic amount (88.54 mg, 0.59 mmol) of sodium iodide was added. It was then refluxed for 72 hours. After cooling to room temperature, it was filtered and the solvent removed under vacuum evaporation. The remained liquid product was purified with column chromatography (hexane: DCM = 8:2). The product as colorless oil was obtained in 86 % yield.

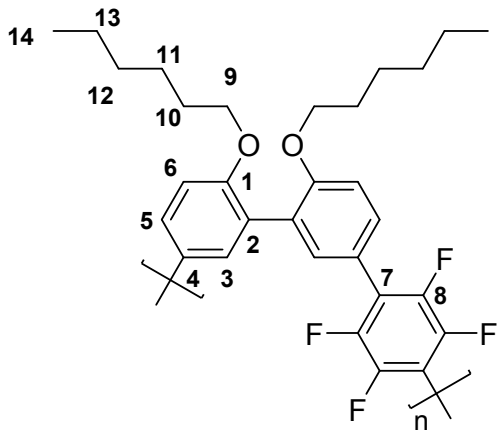
^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.27 (m, 2H; H_5), 7.25 (m, 2H; H_3), 6.96 (t, 7.5 Hz, 2H; H_4), 6.93 (d, 8.2 Hz, 2H; H_6), 3.90 (t, 6.5 Hz, 4H; H_7), 1.61 (m, 4H; H_8), 1.35-1.15 (12H; H_9-H_{11}), 0.85 (t, 7.4 Hz, 6H; H_{12}).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): 156.6 (C_1), 131.6 (C_3), 128.4 (C_2), 128.2 (C_5), 120.0 (C_4), 112.2 (C_6), 68.4 (C_7), 31.5 (C_{11}), 29.2 (C_8), 25.6 (C_9), 22.6 (C_{10}), 14.0 (C_{12}).

3. Preparation of polymers and SEC curves

Polymerization was carried out in a head-space vial with an elliptical rare earth magnetic stirrer bar. Into a screw-cap vial Pd_2dba_3 (0.5 mol-%), tris(*o*-methoxyphenyl)phosphine (2 mol-%), cesium carbonate (3.0 eq.), pivalic acid (1.0 eq.) and 2,2-bromo-4,4-dihexylbiphenol was added, and the mixture purged with nitrogen. The solvent and tetrafluorobenzene were separately purged with nitrogen and added via syringe to the vial. The mixture was stirred for one day at the indicated temperature or until gelation occurred. Precipitation into methanol and Soxhlet extraction with methanol gave the polycondensates as white powders.

NMR data of P*mmp*F4 are reported for 6*n* as an example:



^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.53 (s; H_3), 7.46 (d, 8.5 Hz; H_5), 7.07 (d, 8.5 Hz; H_6), 4.00 (t, 6.5 Hz; H_9), 1.69 (m; H_{10}), 1.31 (m; H_{11}), 1.22 (H_{12}, H_{13}), 0.82 (H_{14}).

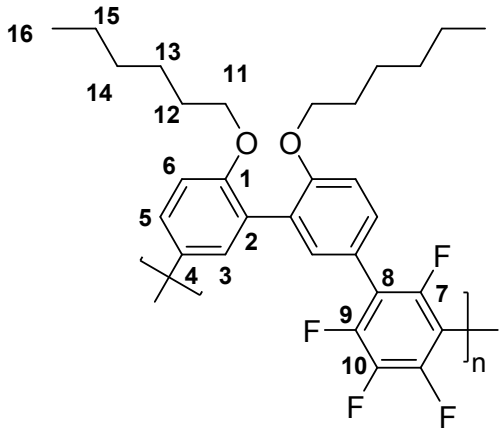
^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C, ppm): 7.55 (s; H_3), 7.49 (d, 8.7 Hz; H_5), 7.11 (d, 8.7 Hz; H_6), 4.04 (t, 6.5 Hz; H_9), 1.71 (m; H_{10}), 1.36 (m; H_{11}), 1.29 (H_{12}, H_{13}), 0.88 (H_{14}).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): 157.1 (C_1), 144.2 (m, $^1J_{CF}$ = 250 Hz, C_8), 133.7 (C_3), 130.5 (C_5), 127.4 (C_2), 119.0 (C_4), 118.8 (m, C_7), 112.0 (C_6), 68.6 (C_9), 31.4 (C_{12}), 29.0 (C_{10}), 25.7 (C_{11}), 22.5 (C_{13}), 13.9 (C_{14}); - *para* C_6H_4Ph end group observed for nOct: 127.7 (Ph_i), 130.2 (Ph_o), 128.6 (Ph_m), 129.0 (Ph_p).

^{19}F NMR (470 MHz, $CDCl_3$, ppm): -146.0 (s, F_8); -C_6F_4H end group: -140.9 (m; F *ortho* to H), -145.1 (m; F *meta* to H); -*para* C_6F_4Ph end group observed for nOct: -145.5 (m; F *ortho* to Ph), -146.05 (m; F *meta* to Ph)

^{19}F NMR (470 MHz, $C_2D_2Cl_4$, 120 °C, ppm): -144.7 (s, F_8); -C_6F_4H end group: -140.0 (m; F *ortho* to H), -143.7 (m; F *meta* to H).

NMR data of P*mmm*F4 (6*n*)



^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.41 (s; H_3), 7.36 (d, 8.7 Hz; H_5), 7.00 (d, 8.7 Hz; H_6), 3.94 (t, 6.4 Hz; H_{11}), 1.63 (m; H_{12}), 1.26 (m; H_{13}), 1.16 (H_{14}, H_{15}), 0.77 (H_{16}).

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C, ppm): 7.45 (s; H_3), 7.39 (d, 8.6 Hz; H_5), 7.05 (d, 8.6 Hz; H_6), 3.98 (t, 6.5 Hz; H_{11}), 1.66 (m; H_{12}), 1.31 (m; H_{13}), 1.24 (H_{14}, H_{15}), 0.84 (H_{16}).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): 156.8 (C_1), 151.7 (m, $^{1}J_{CF}$ = 245 Hz, C_7), 147.2 (m, $^{1}J_{CF}$ = 249 Hz, C_9), 137.7 (m, $^{1}J_{CF}$ = 248 Hz, C_{10}), 133.6 (C_3), 130.5 (C_5), 127.5 (C_2), 119.1 (C_4), 115.6 (m, C_8), 111.9 (C_6), 68.5 (C_{11}), 31.4 (C_{14}), 29.0 (C_{12}), 25.7 (C_{11}), 22.5 (C_{15}), 13.9 (C_{16}).

^{19}F NMR (470 MHz, $CDCl_3$, ppm): -123.3 (d, 10.0 Hz; F_7), -139.6 (d, 22.9 Hz; F_9), -166.6 (m; F_{10}); -*meta* C_6F_4H end group: -119.2 (d, 11.3 Hz; F *ortho* to H and to backbone), -136.9 (d, 21 Hz; F *ortho* to H and *para* to backbone), -136.6 (d, 22 Hz; F *para* to H), -166.5 (m; F *meta* to H).

^{19}F NMR (470 MHz, $C_2D_2Cl_4$, 120 °C, ppm): -122.6 (d, 10.8 Hz; F_7), -139.5 (d, 22.0 Hz; F_9), -167.1 (m; F_{10}); -*meta* C_6F_4H end group: -118.8 (d, 11.0 Hz; F *ortho* to H and to backbone), -136.2 (d, 21 Hz; F *ortho* to H and *para* to backbone), -136.4 (d, 22 Hz; F *para* to H), -166.9 (m; F *meta* to H).

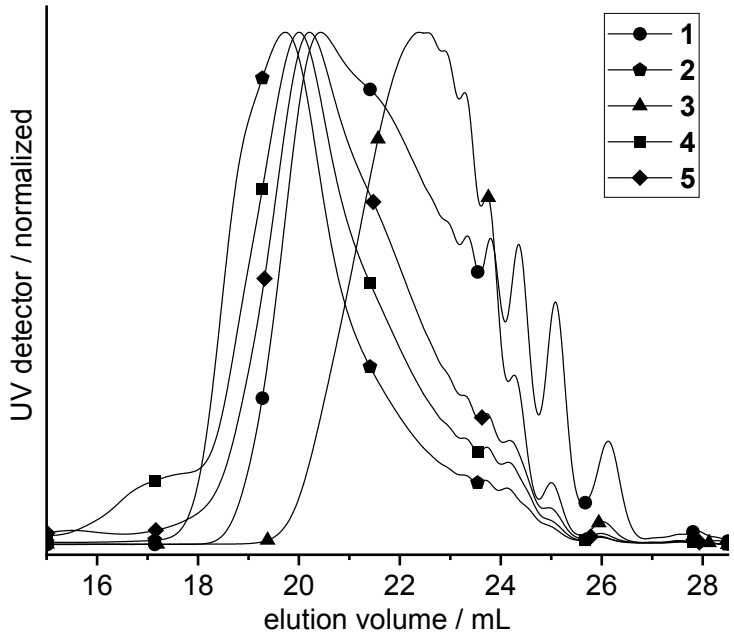


Figure S1. SEC eluograms of entries **1** – **5**.

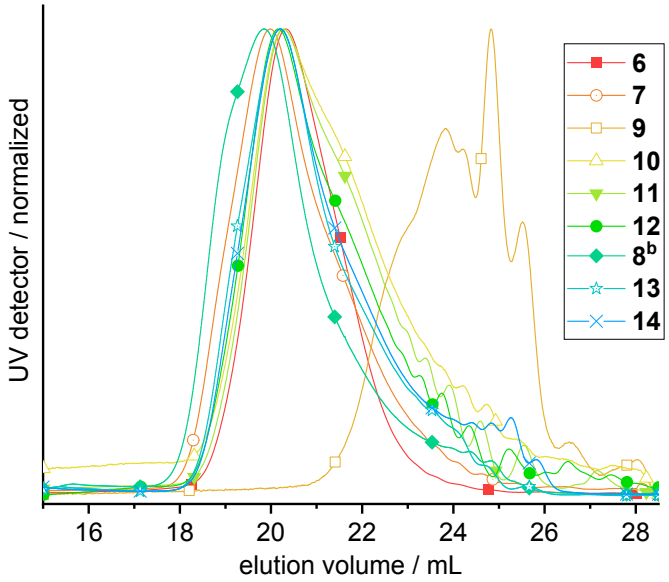


Figure S2. SEC eluograms of entries **6** – **14**.

4. NMR spectra of monomers and model compounds

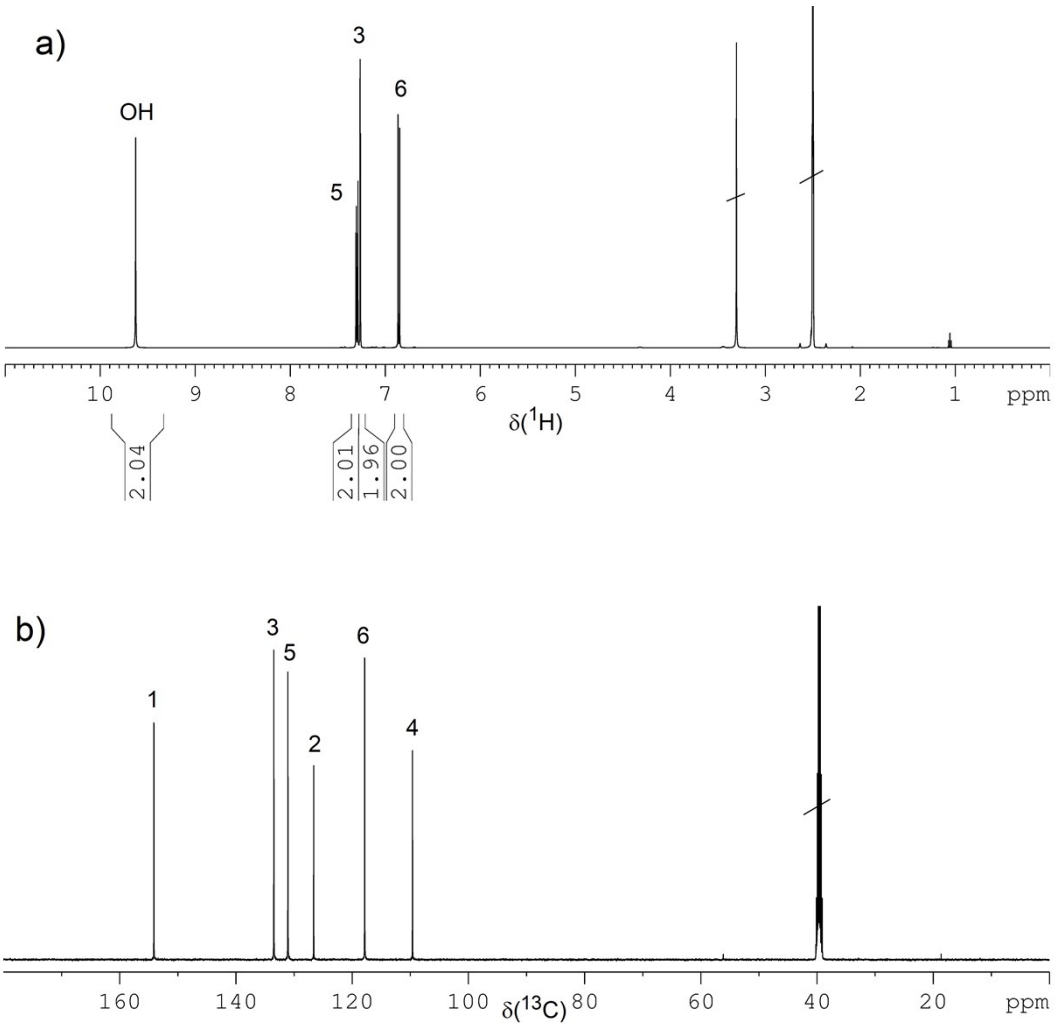


Figure S3. ^{1}H (a) and ^{13}C NMR spectrum (b) of 5,5'-dibromobiphenyl-2,2'-diol in DMSO-d_6.

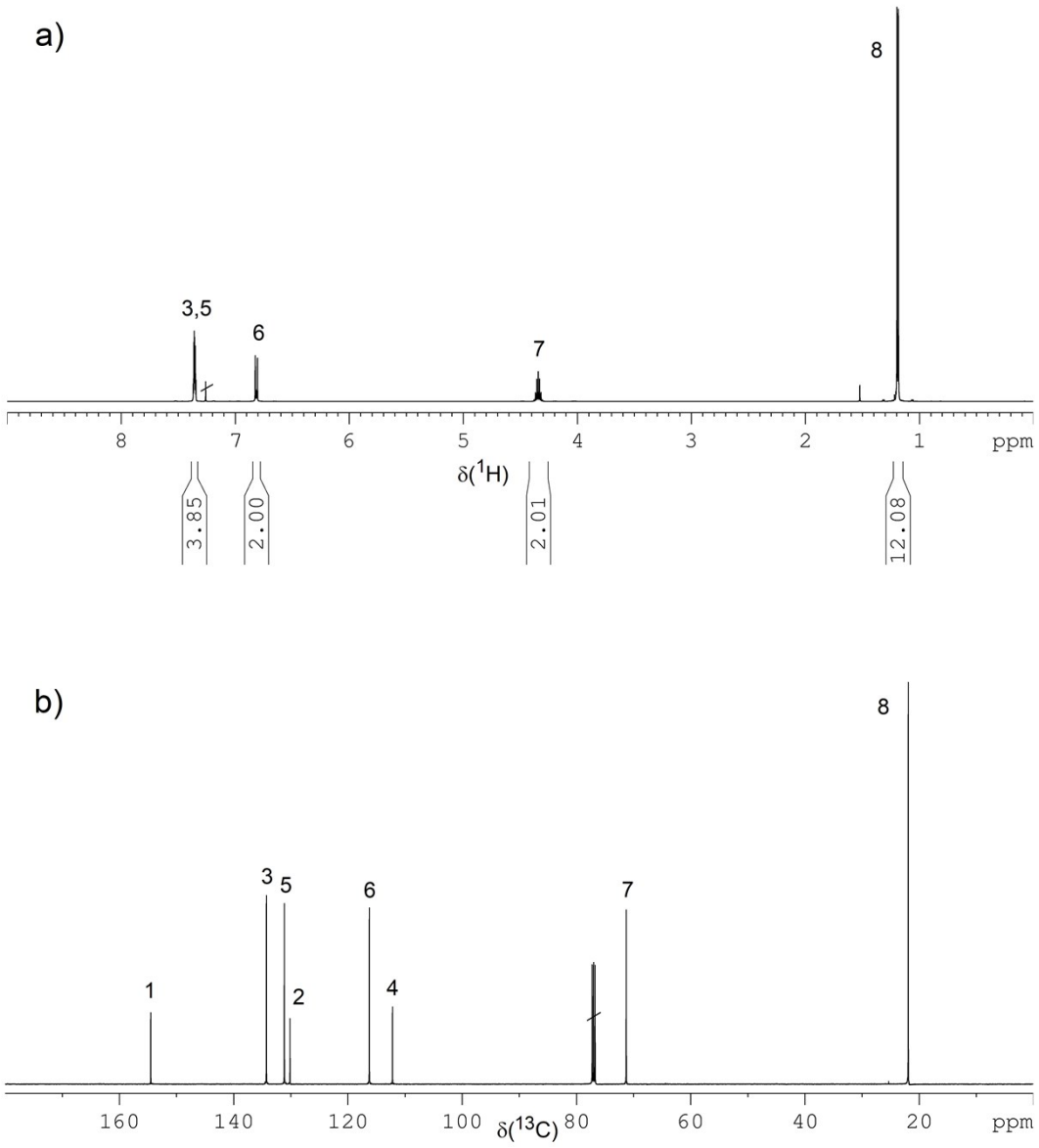


Figure S4. ^{1}H (a) and ^{13}C NMR spectrum (b) of 5,5'-dibromo-2,2'-bis(isopropoxy)biphenyl in $CDCl_3$.

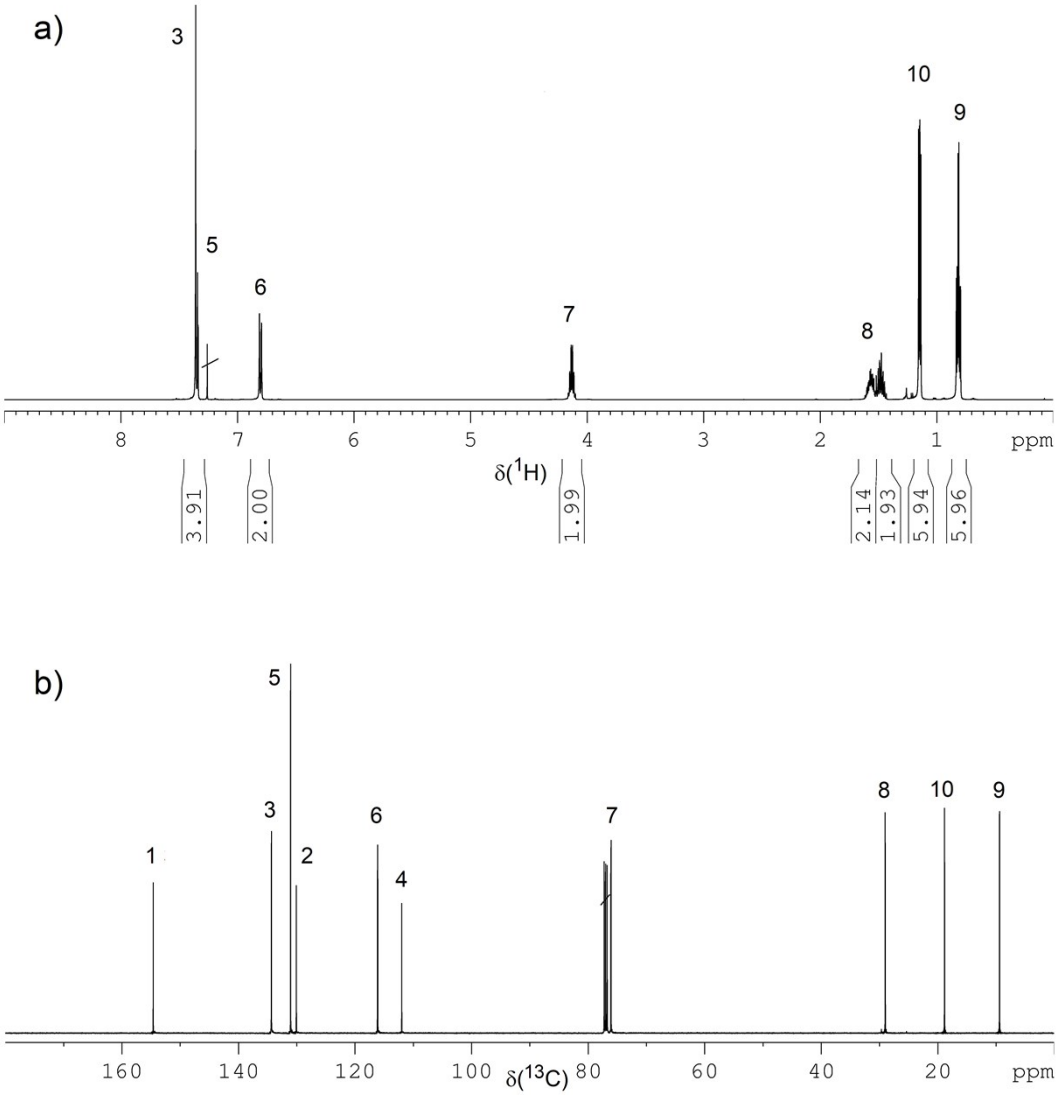


Figure S5. ^{1}H (a) and ^{13}C NMR spectrum (b) of 5,5'-dibromo-2,2'-bis(sec-butoxy)biphenyl in $CDCl_3$.

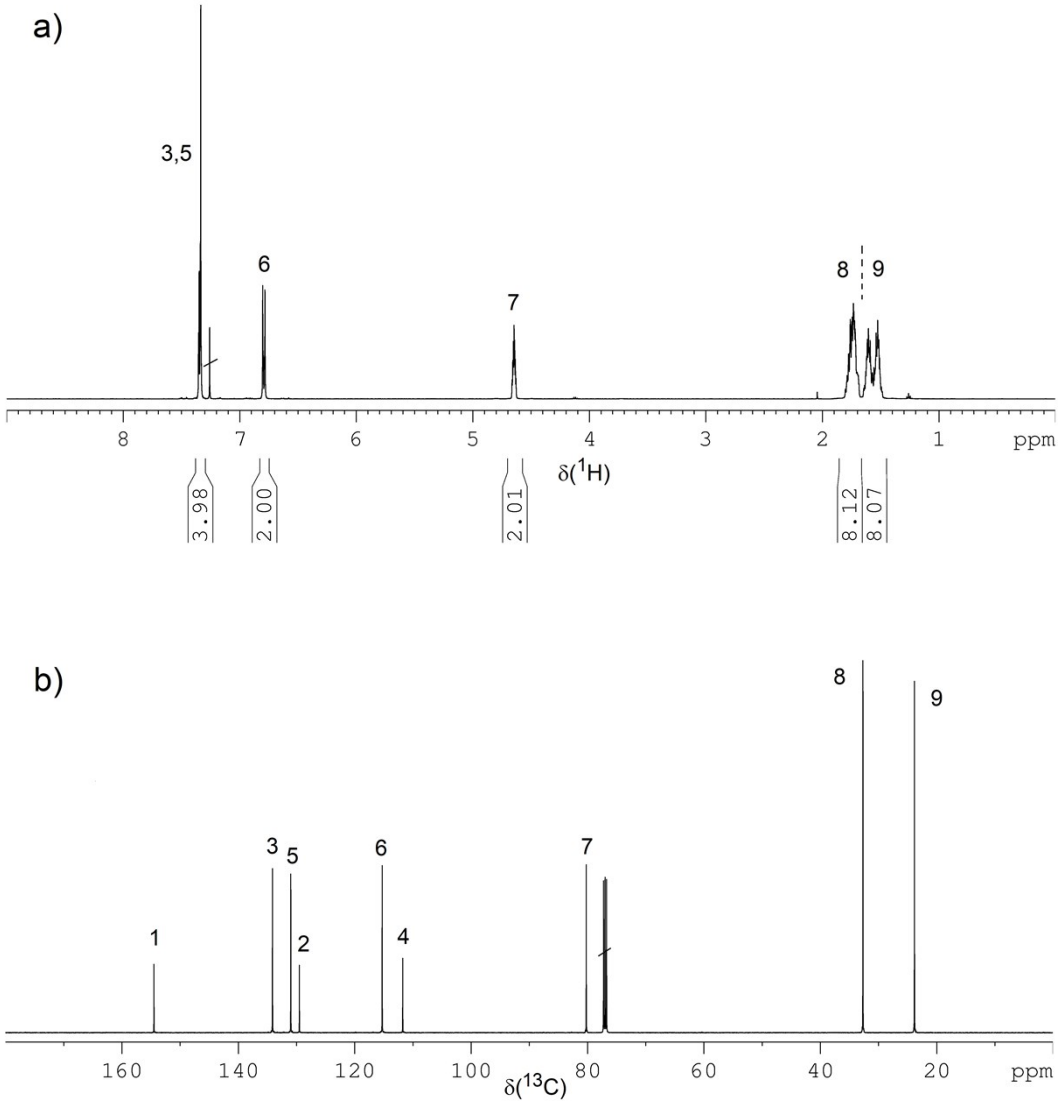


Figure S6. ^{1}H (a) and ^{13}C NMR spectrum (b) of 5,5'-dibromo-2,2'-bis(cyclopentoxy)biphenyl in $CDCl_3$.

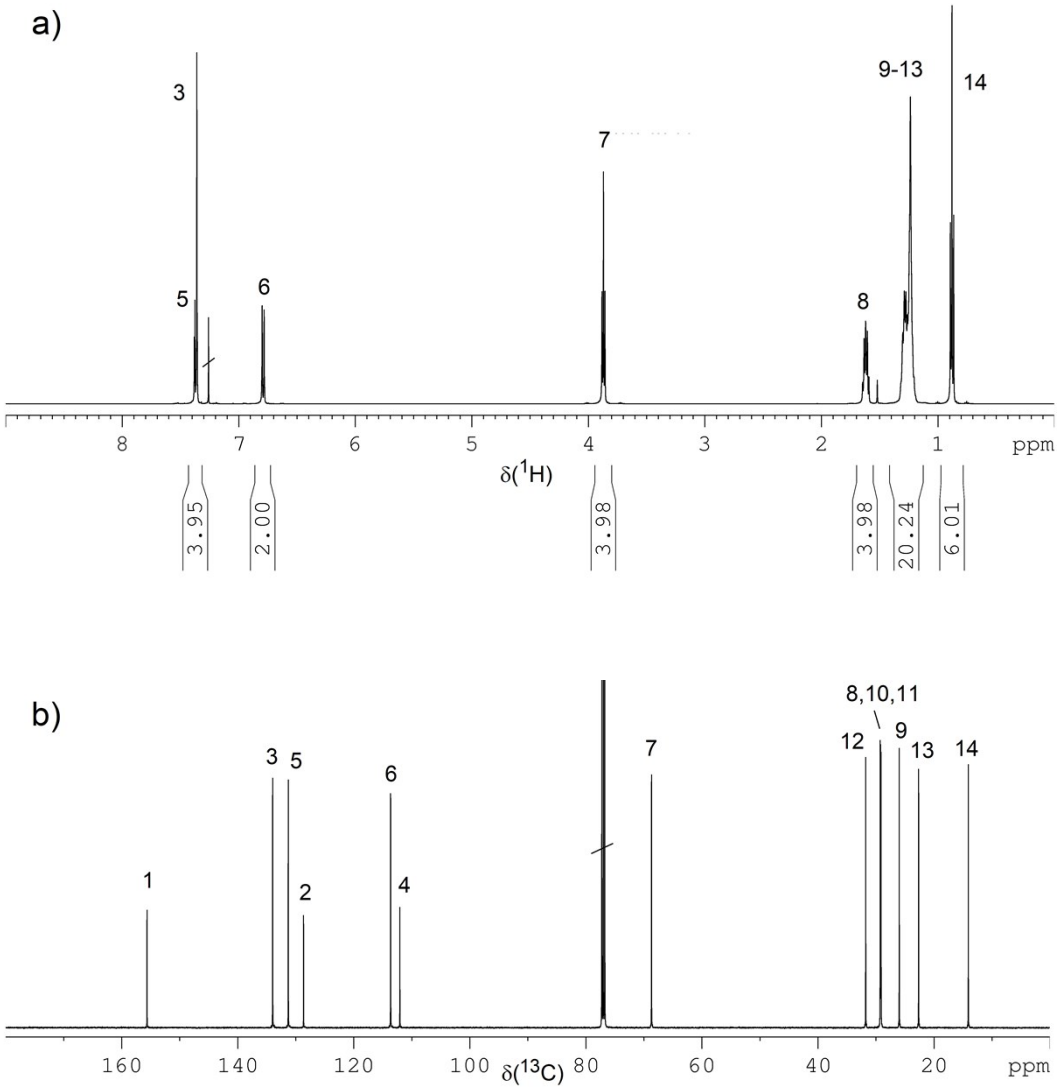


Figure S7. ^{1}H (a) and ^{13}C NMR spectrum (b) of 5,5'-dibromo-2,2'-bis(octyloxy)biphenyl in $CDCl_3$.

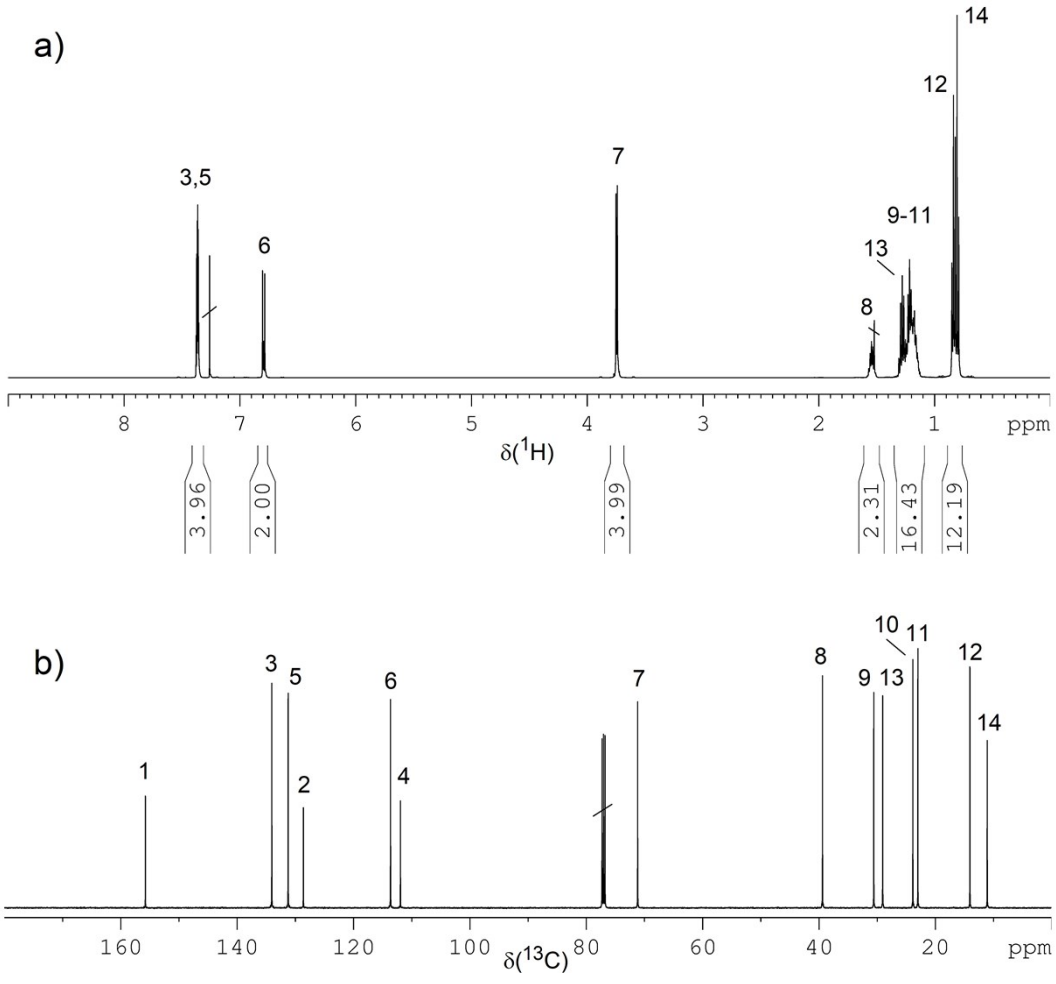


Figure S8. ^{1}H (a) and ^{13}C NMR spectrum (b) of 5,5'-dibromo-2,2'-bis(2-ethylhexyloxy)biphenyl in $CDCl_3$.

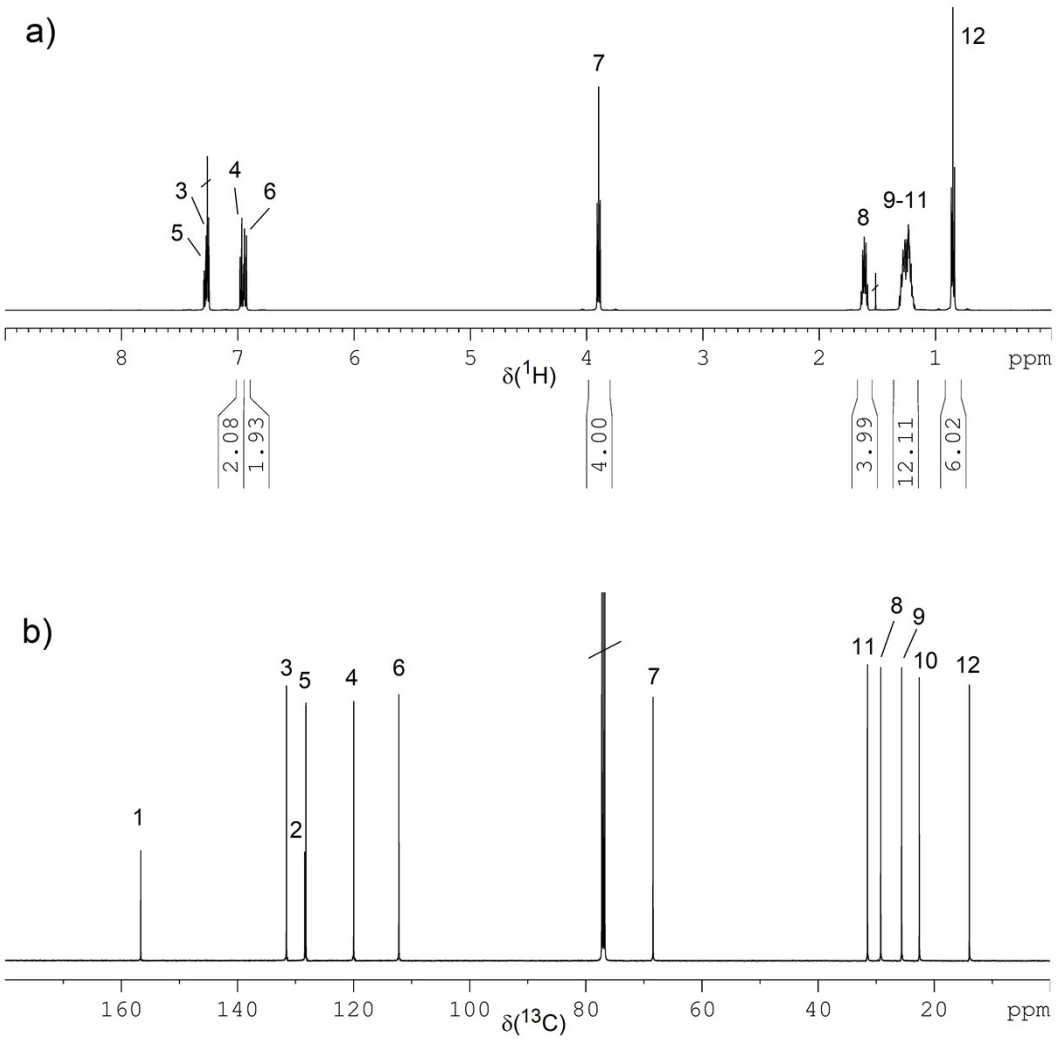


Figure S9. ^{1}H (a) and ^{13}C NMR spectrum (b) of the model compound 2,2'-(hexyloxy)biphenyl in $CDCl_3$.

5. NMR spectra of polymers

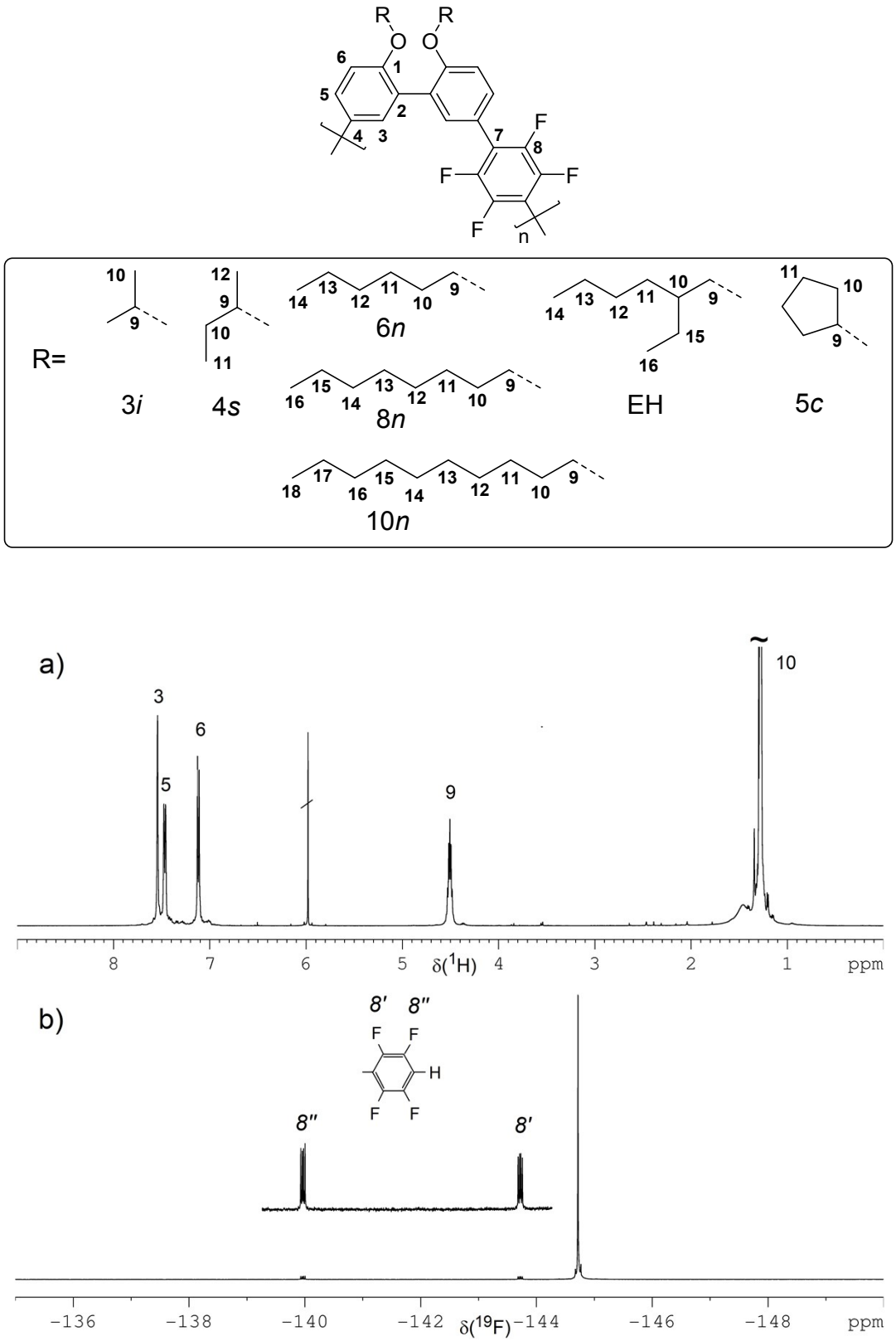


Figure S10. ^{1}H (a) and ^{19}F NMR spectrum (b) of entry 9 (3*i*) ($C_2D_2Cl_4$; 120 °C)

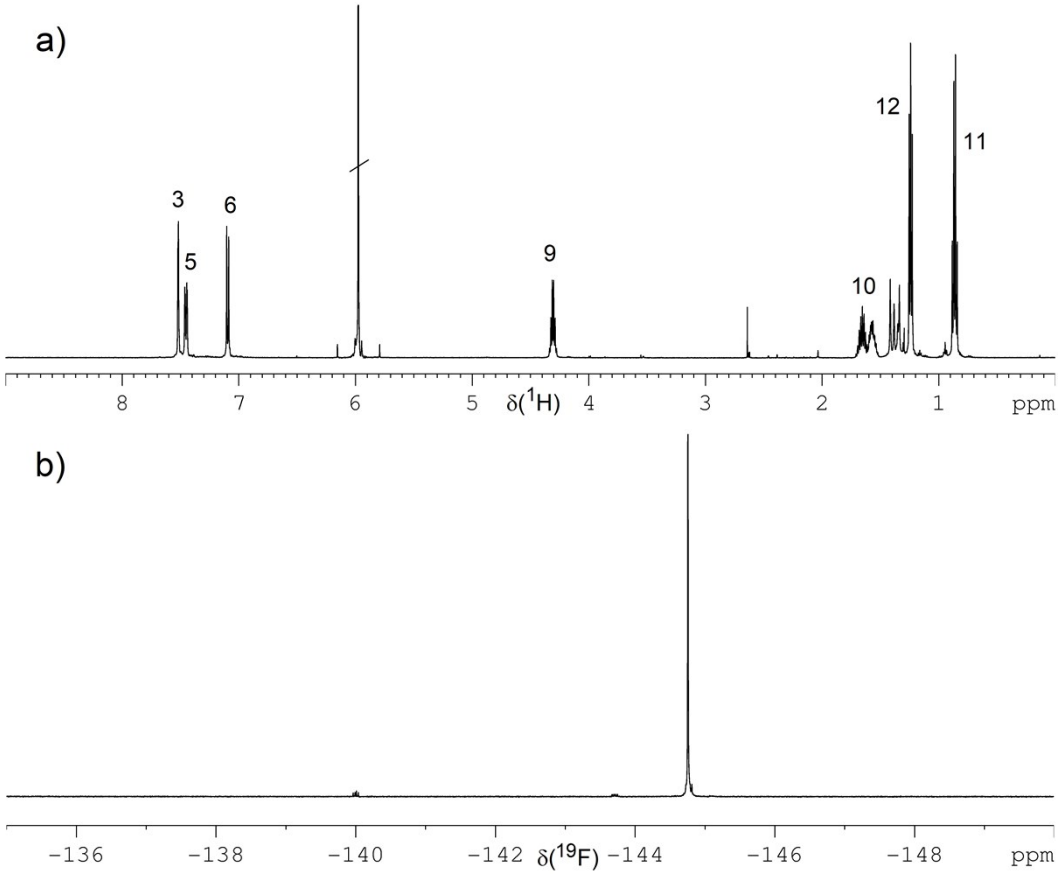


Figure S11. ^{1}H (a) and ^{19}F NMR spectrum (b) of entry 7 (4*s*) ($C_2D_2Cl_4$; 120 °C)

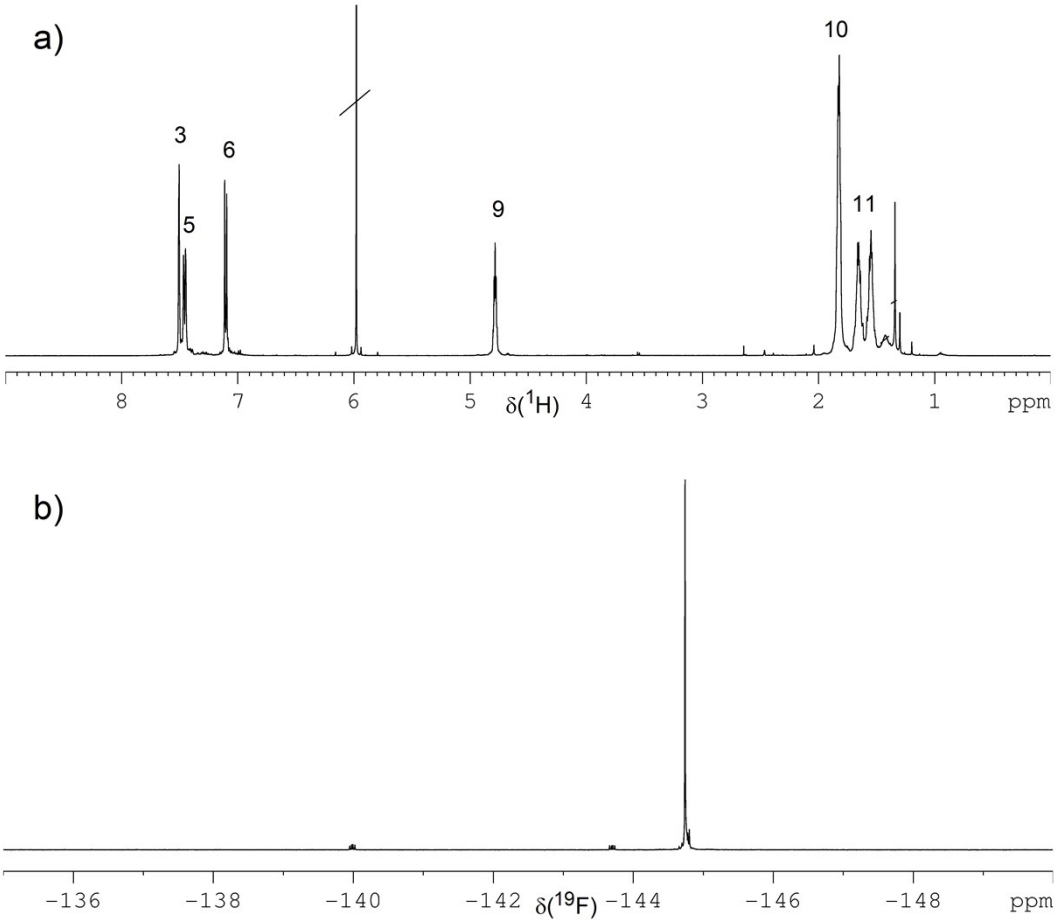


Figure S12. ^{1}H (a) and ^{19}F NMR spectrum (b) of entry 10 (5*c*) ($C_2D_2Cl_4$; 120 °C)

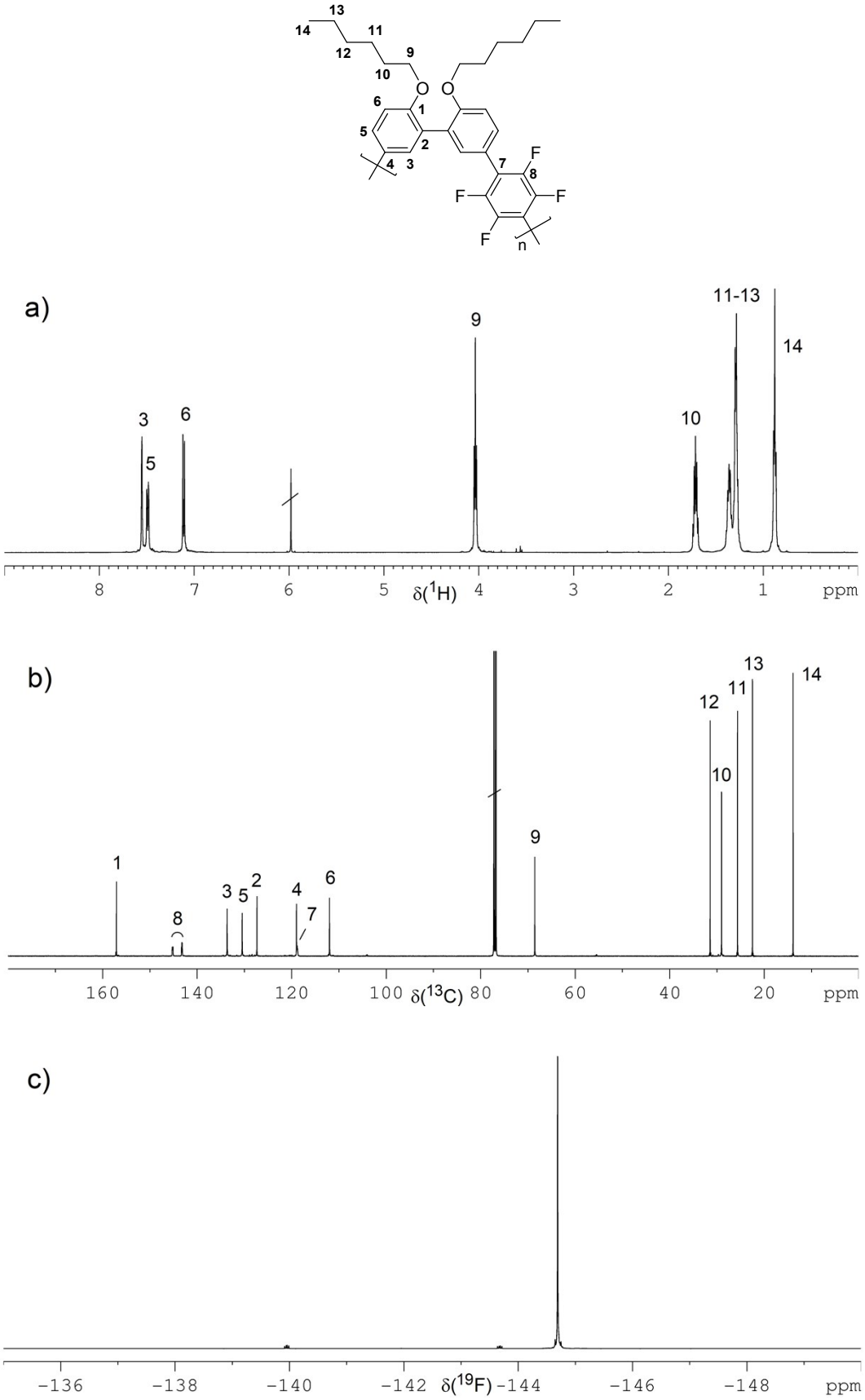


Figure S13. ^{1}H (a), ^{13}C (b) and ^{19}F NMR spectrum (c) of entry 2 (6*n*) (a,c: $C_2D_2Cl_4$; 120 °C and b: $CDCl_3$, 30°C)

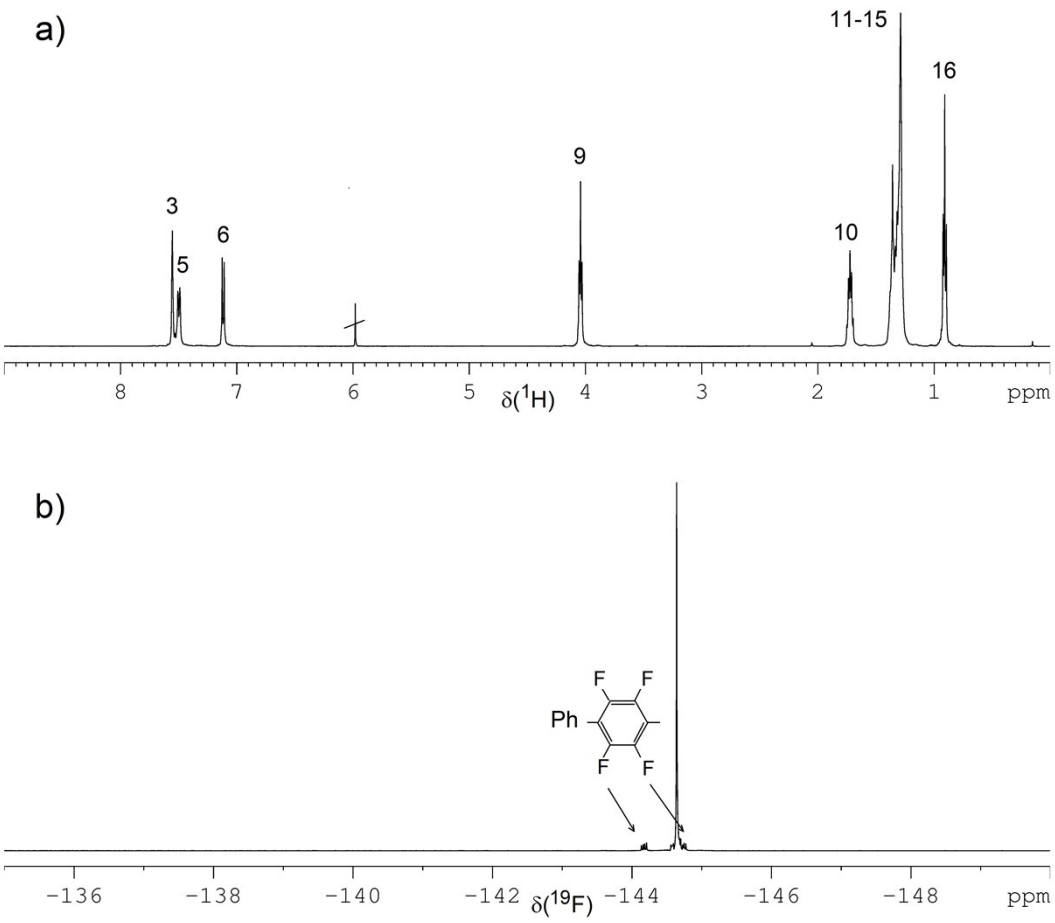


Figure S14. ^{1}H (a) and ^{19}F NMR spectrum (b) of entry 12 (8*n*) ($C_2D_2Cl_4$; 120 °C)

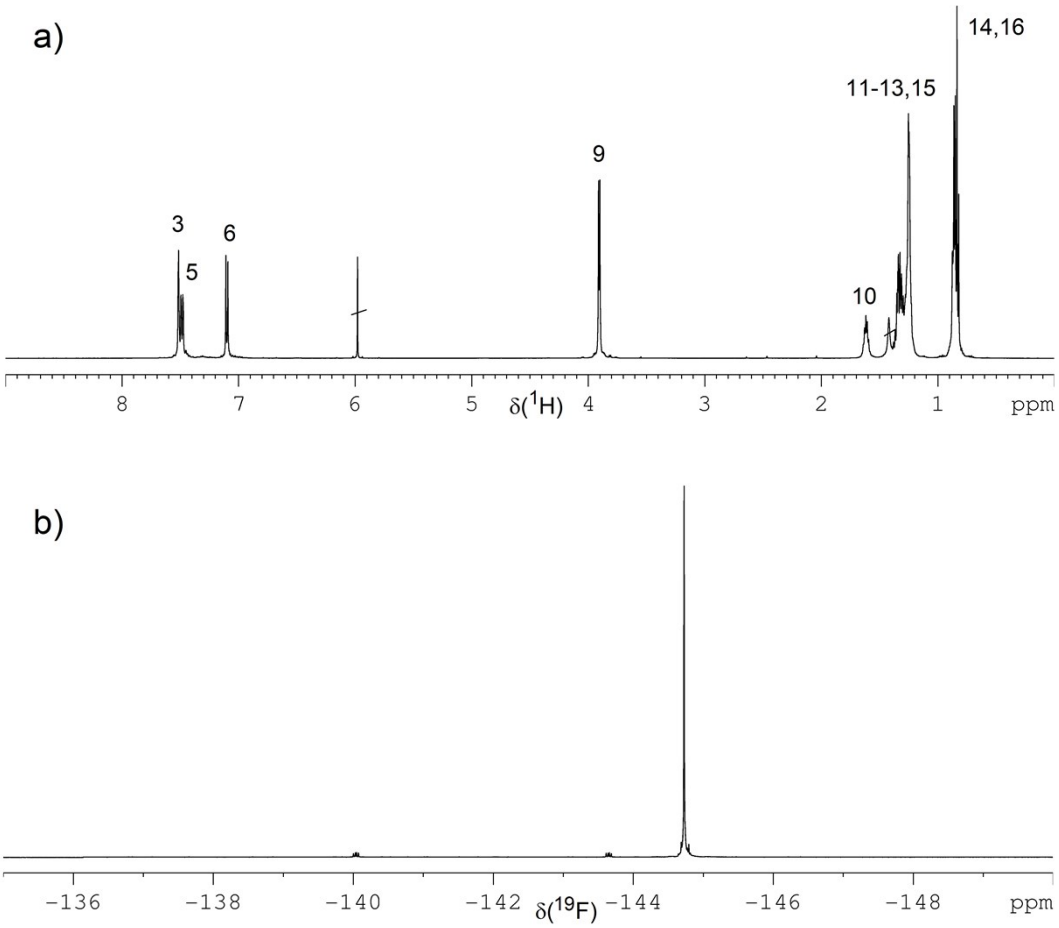


Figure S15. ^{1}H (a) and ^{19}F NMR spectrum (b) of entry 6 (EH) ($C_2D_2Cl_4$; 120 °C)

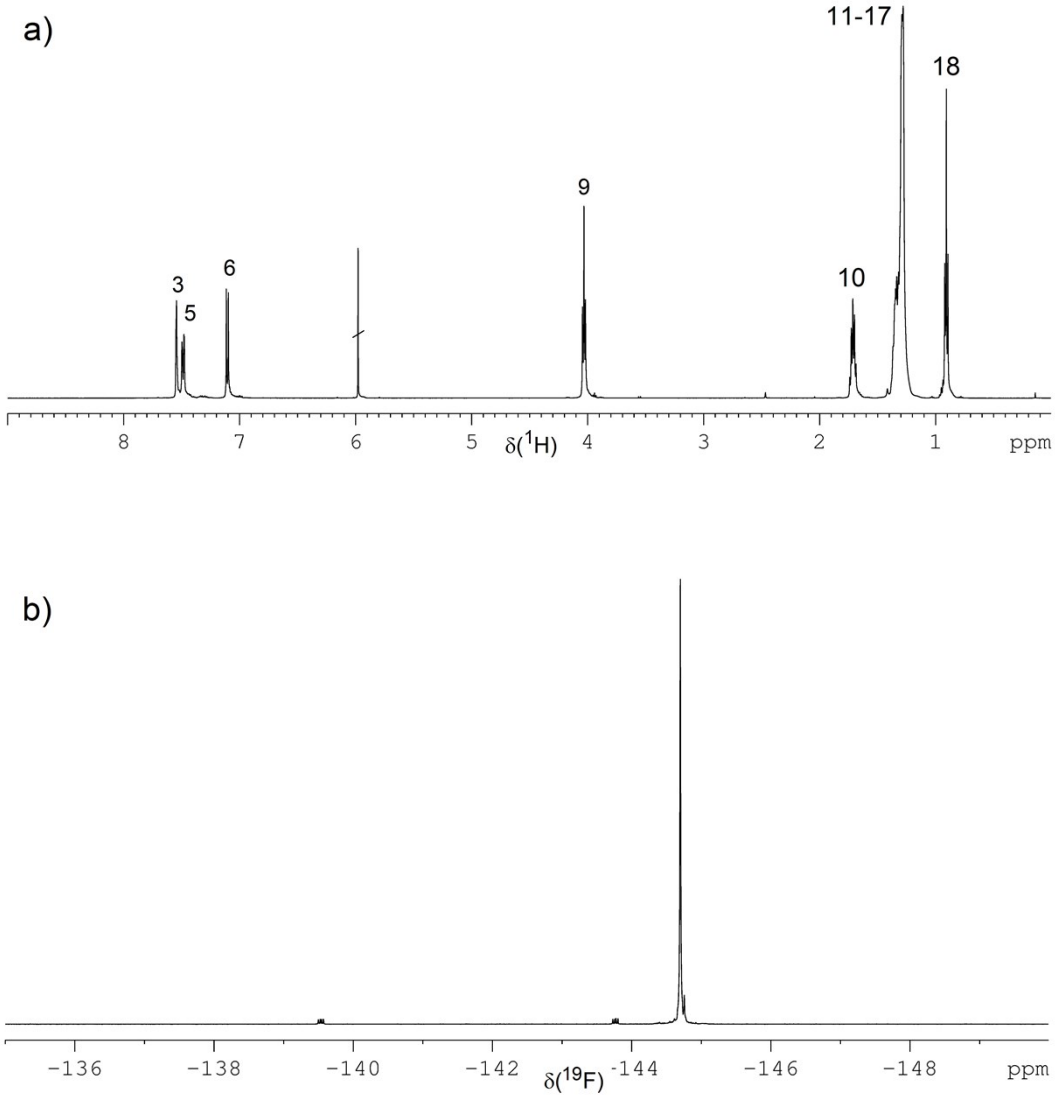


Figure S16. ^{1}H (a) and ^{19}F NMR spectrum (b) of entry 13 (10*n*) ($C_2D_2Cl_4$; 120 °C)

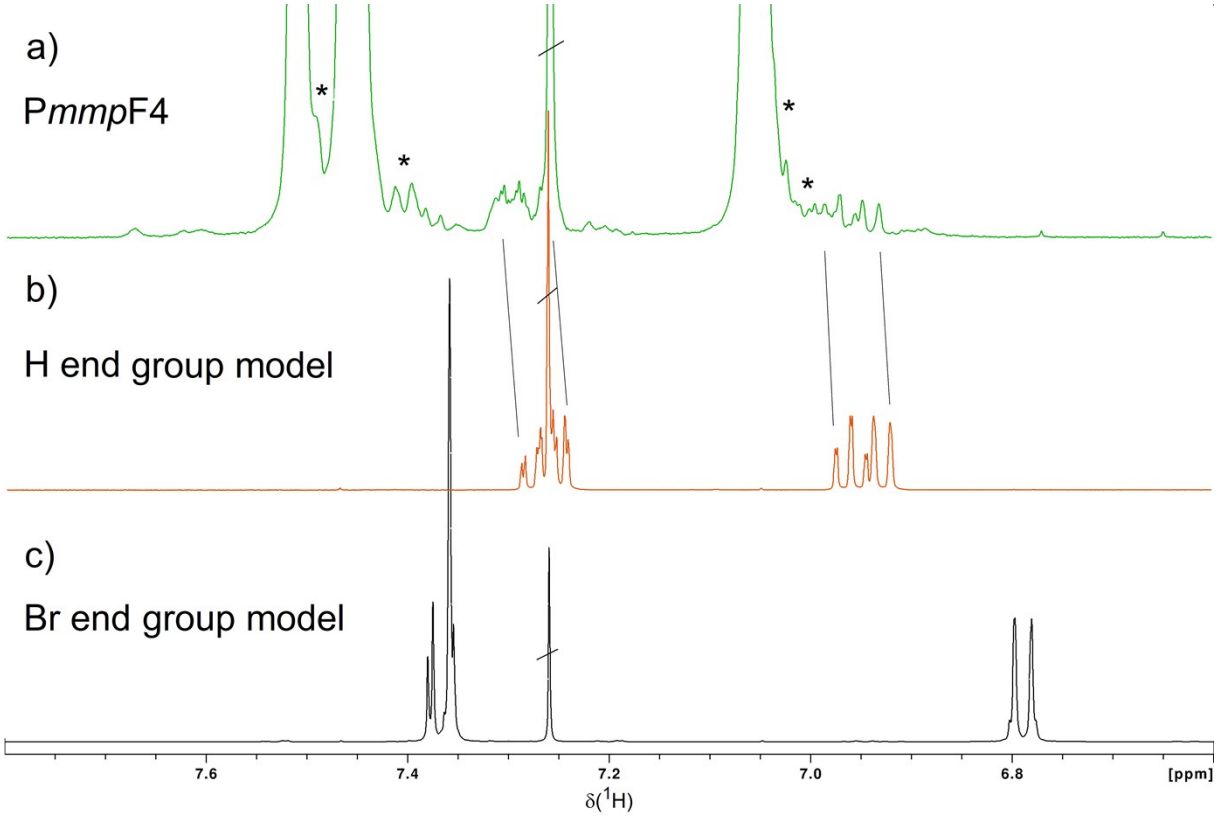


Figure S17. ^{1}H NMR spectra (aromatic region) of (a) P*mmp*F4 (entry 13, 10*n*), (b) 2,2'-(hexyloxy)biphenyl and (c) 5,5'-dibromo-2,2'-bis(decyloxy)biphenyl ($CDCl_3$). Signals marked with an asterix result from –*para* C_6F_4H end group.

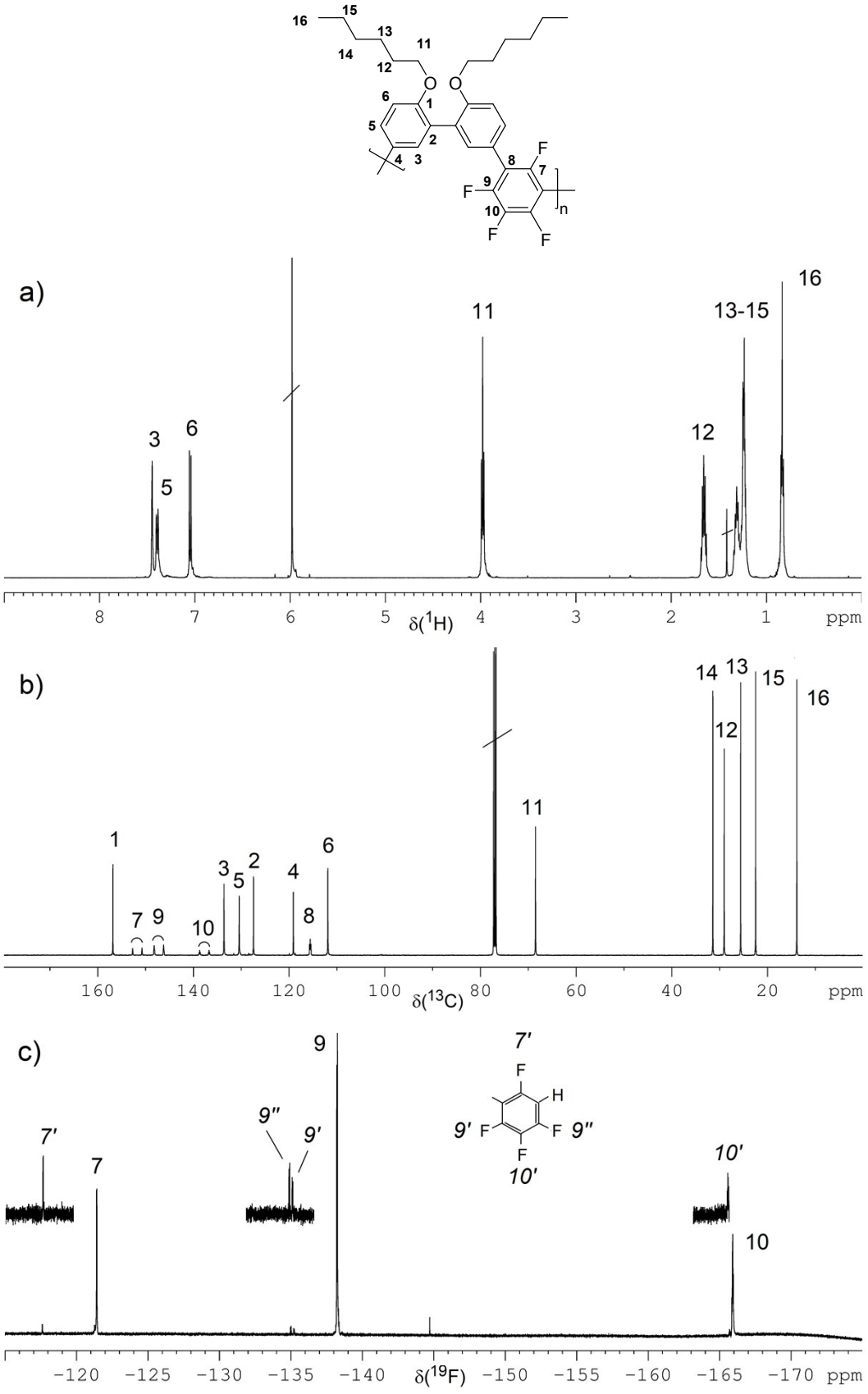


Figure S18. ^{1}H (a), ^{13}C (b) and ^{19}F NMR spectrum (c) of P*mmm*F4 (entry 14, 6*n*) (a,c: $C_2D_2Cl_4$; 120 °C and b: $CDCl_3$, 30°C)

6. Theoretical methods

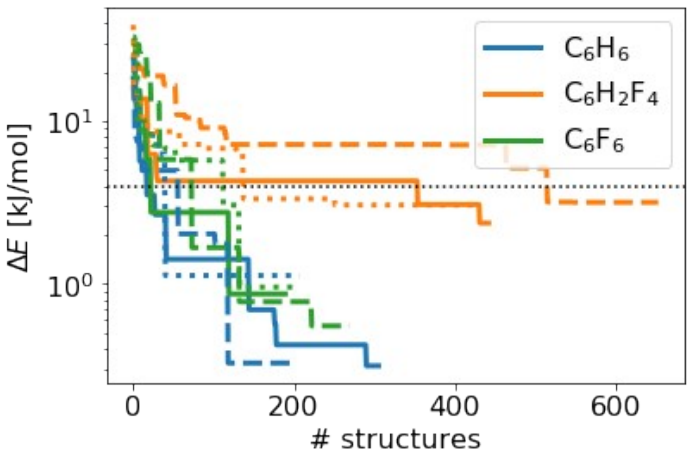


Figure S19. Development of the energetic distance ΔE between the best and the second best structure with number of structures tried for $C_{15}H_{14}$ (solid), $C_{16}H_{18}$ (dashed) and $C_{14}H_{14}O_2$ (dotted) in interaction with the color-coded smaller molecules. The dotted horizontal line indicates 4 kJ/mol. The structures involving $C_6H_2F_4$ show slower convergence than C_6H_6 or C_6F_6.

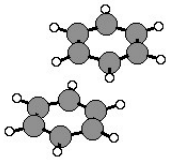
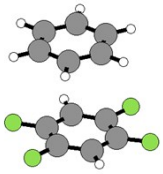
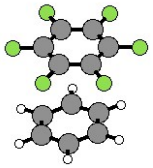
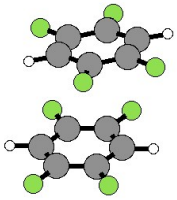
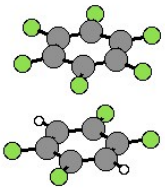
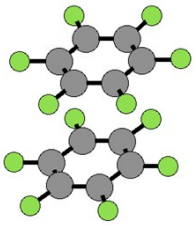
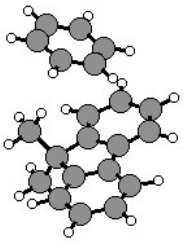
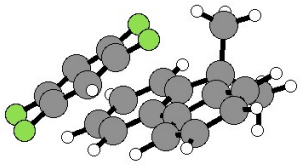
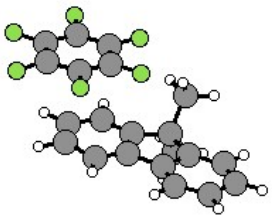
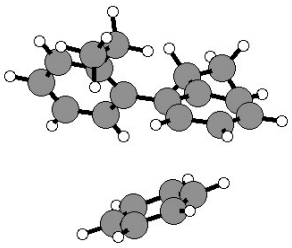
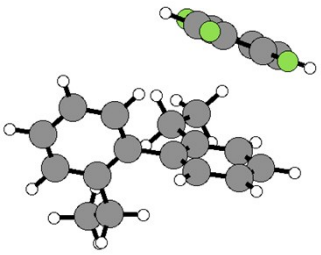
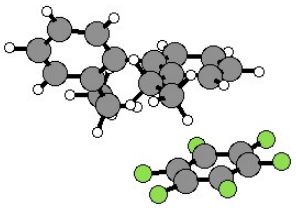
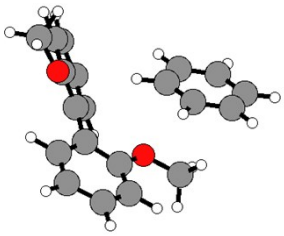
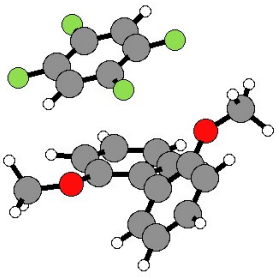
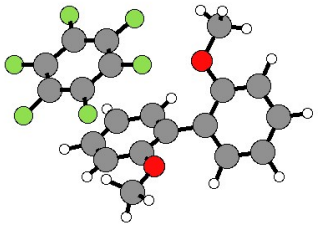
	C_6H_6	$C_6H_2F_4$	C_6F_6
C_6H_6			
$C_6H_2F_4$			
C_6F_6			
$C_{15}H_{14}$			
$C_{16}H_{18}$			
$C_{14}H_{14}O_2$			

Figure S20. Lowest energy structures found. C: grey, O: red, H: white, F: green

7. References

[1] F. Kempe, O. Brügner, H. Buchheit, S. N. Momm, F. Riehle, S. Hameury, M. Walter, M. Sommer, *Angew. Chem. Int. Ed.* **2018**, *57*, 997–1000.