Supporting Information

Transition from nematic to gyroid-type cubic soft self-assembly by side-chain engineering of π-conjugated sticky rods

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1. Additional data

1.1 DSC traces

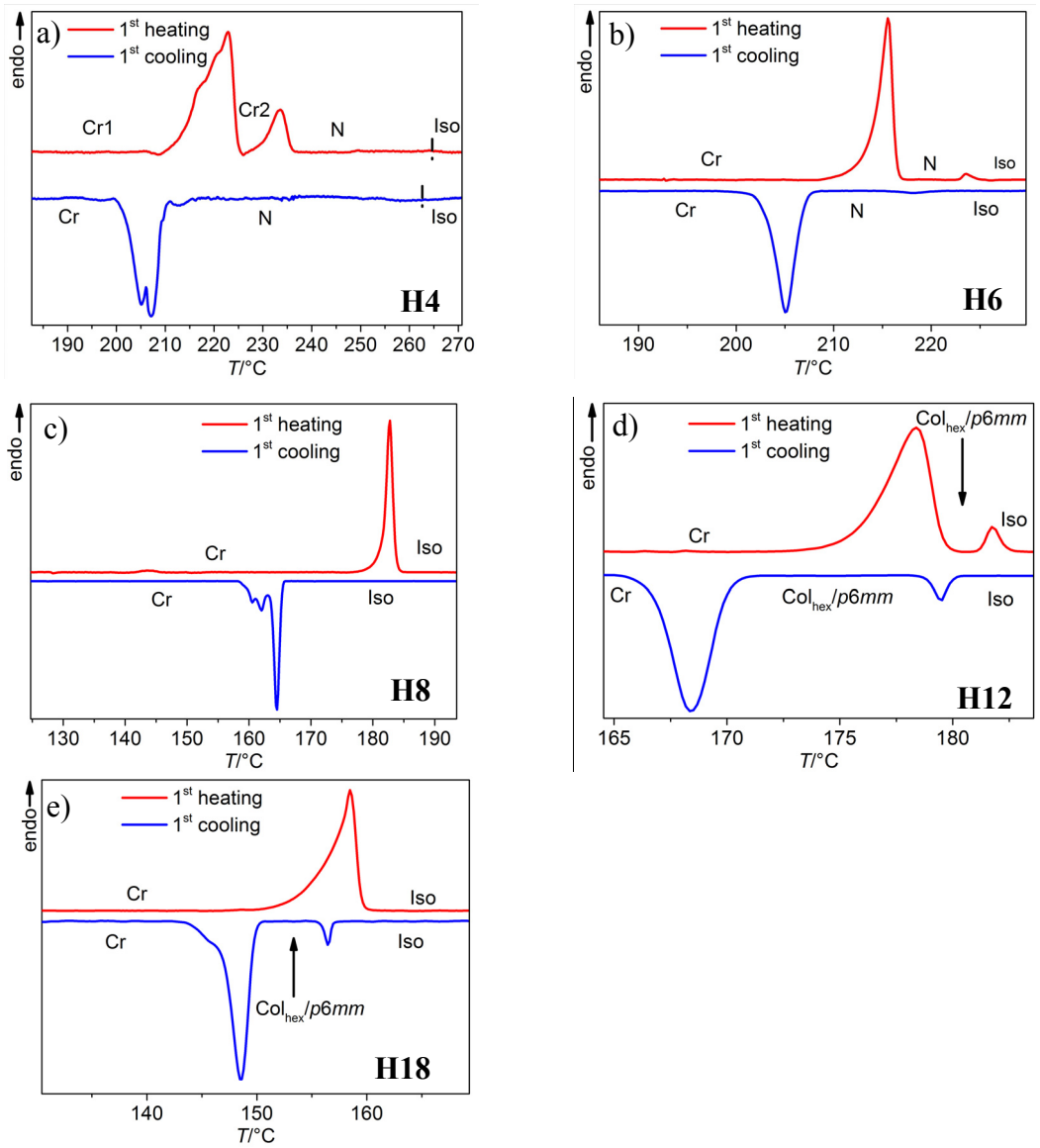


Figure S1. DSC heating and cooling traces of compounds: a) **H4**, b) **H6**, c) **H8**, d) **H12** and e) **H18**, recorded at 10 K·min^{-1}.

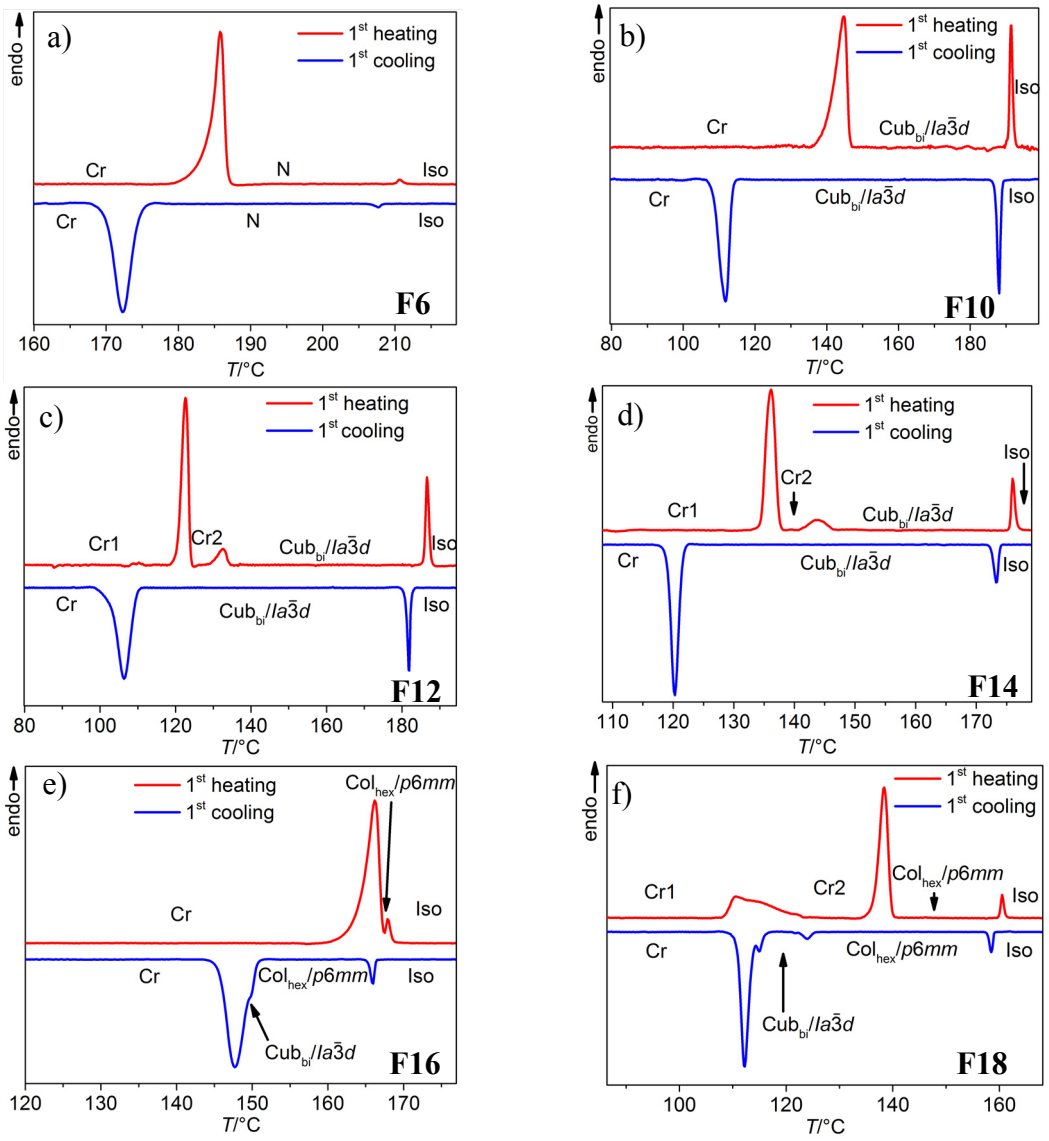


Figure S2. DSC heating and cooling traces of compounds: a) **F6**, b) **F10**, c) **F12**, d) **F14,** e) **F16** and f) **F18**, recorded at 10 K·min^{-1}.

1.2 Additional textures

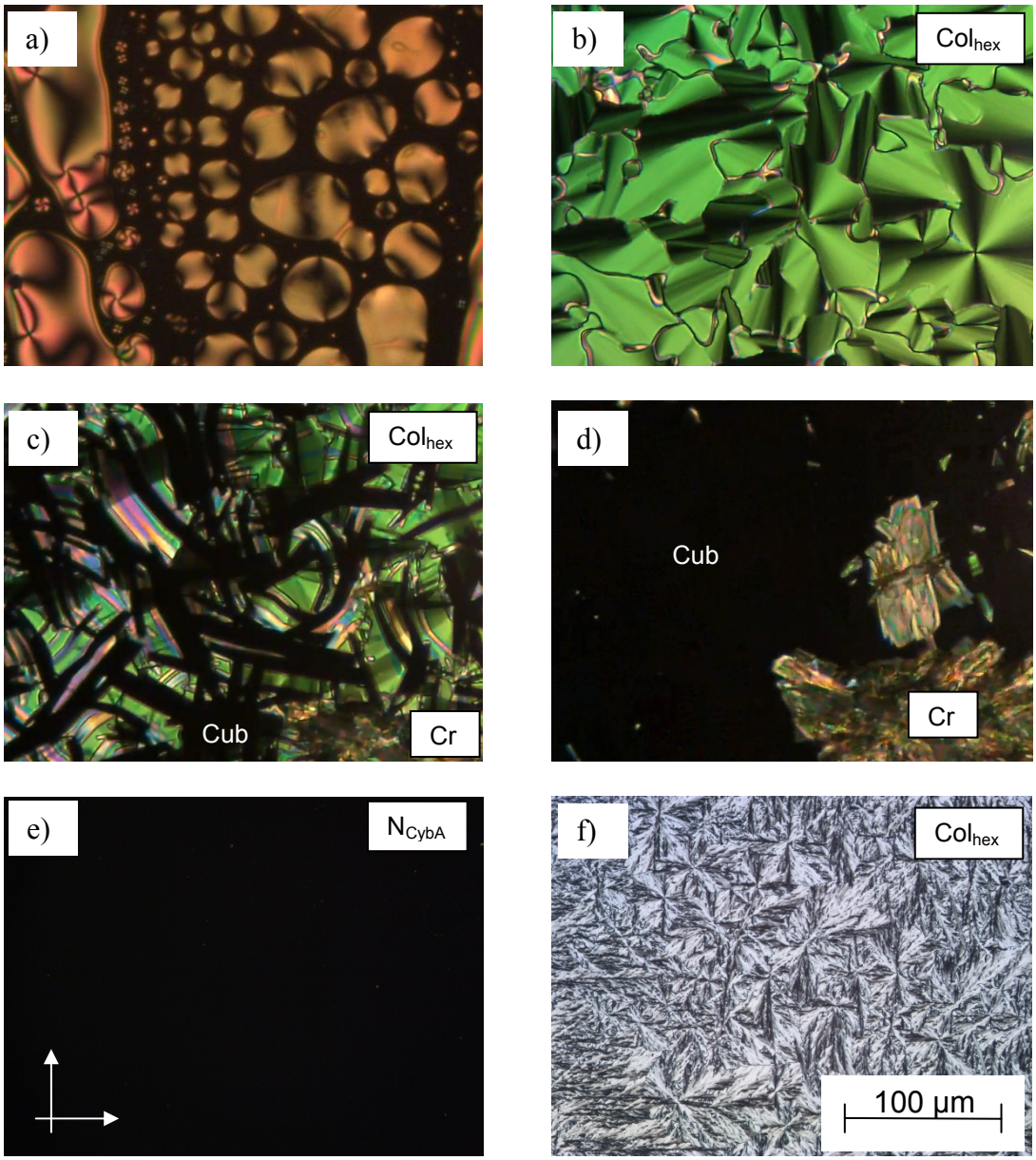


Figure S3: Selected textures of compounds **H*n*** as observed between crossed polarizers between non-treated microscopy slides: a) Iso-to-N_{CybA} transition of **H4** at 262 °C, b-c) LC phases observed for **H8** on rapid cooling; b) Col_{hex} phase at T ~ 150 °C; c) transition Col_{hex}-Cub_{bi} at T ~ 140°C and d) Cub_{bi} phase with crystallization at T ~ 138 °C, e) homeotropic N_{CybA} phase of **H6** at 200 °C and f) Col_{hex} phase of **H12** at 170 °C; arrows in e) indicate the orientation of polarizer and analyzer and the scale bar is given in f).

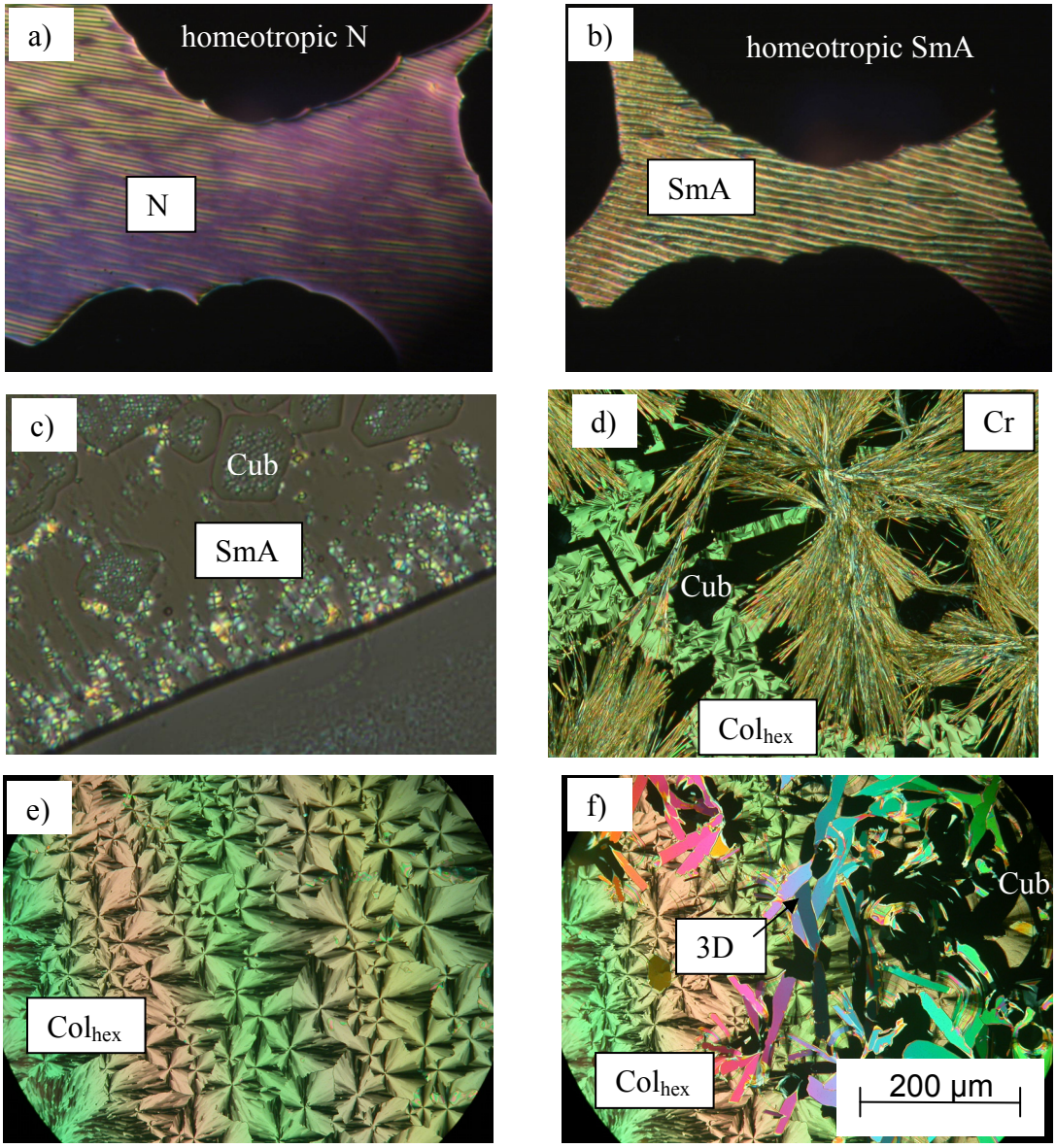


Figure S4: Selected textures of compounds **F*n*** as observed between crossed polarizers between non-treated microscopy slides: a) texture at the N_{CybA}-SmA transition of compound **F8** at 181 °C; b) SmA-phase of compound **F8** at 180.5 °C; c) oily streaks texture of the SmA phase of **F8** coexisting with the $Cub_{bi}/Ia\bar{3}d$ phase at 179 °C; d) growth of the $Cub_{bi}/Ia\bar{3}d$ (black regions) and crystalline phase into the Col_{hex} (green spherulitic region) of compound **F16** at 149 °C; e) Col_{hex} phase of compound **F18** at 140 °C and f) development of the cubic phase (black areas) and, accompanied by a non-cubic birefringent 3D phase (uniformly colored mosaics) on cooling the Col_{hex} phase of **F18** at 124 °C; the 3D phase occurs only at the Col_{hex}-Cub_{bi} phase transition and disappears on further cooling.

1.3 Additional XRD data

Table S1: Experimental and calculated *d*-spacings, relative integrated intensities, and phases used in the reconstruction of electron densities for the $Cub_{bi}/Ia\bar{3}d$ phase for **H10** at 160 ºC. All Intensities values are Lorentz and multiplicity corrected.

(*hkl*)	$d_{obs.}$- spacings (nm)	$d_{cal.}$- spacings (nm)	Intensity	Phase
(211)	3.74	3.74	100.0	π
(220)	3.24	3.24	5.7	π
(321)	2.45	2.45	0.7	π
(400)	2.29	2.29	13.0	π
(420)	2.05	2.05	37.3	π
(332)	1.95	1.95	87.2	0
(422)	1.87	1.87	44.1	0
(431)	1.80	1.80	21.0	0
(521)	1.67	1.67	0.8	0
(440)	1.62	1.62	0.4	0
(532)	1.49	1.49	0.5	/
(611)			1.0	/
(541)	1.41	1.41	0.4	/
(631)	1.35	1.41	0.04	/
a_{cub} = 9.17 nm				

Table S2: Experimental and calculated *d*-spacings, relative integrated intensities, and phases used in the reconstruction of electron densities for the $Col_{hex}/p6mm$ phase for **H10** at 176 ºC. All intensities values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$- spacings (nm)	$d_{cal.}$- spacings (nm)	Intensity	Phase
(10)	3.73	3.73	100.0	0
(11)	2.15	2.15	0.2	π
(20)	1.86	1.87	28.7	0
(21)	1.41	1.41	0.3	π
a_{hex} = 4.31 nm				

Table S3. Experimental and calculated *d*-spacings, relative integrated intensities, and phases used in the reconstruction of electron densities for the $Cub_{bi}/Ia\bar{3}d$ phase for **F18** at 120 ºC. All Intensities values are Lorentz and multiplicity corrected.

(*hkl*)	$d_{obs.}$- spacings (nm)	$d_{cal.}$- spacings (nm)	Intensity	Phase
(211)	3.69	3.69	100.0	π
(220)	3.19	3.19	3.7	π
(321)	2.41	2.41	0.5	π
(420)	2.02	2.02	2.3	π
(332)	1.92	1.93	4.2	0
(422)	1.84	1.84	1.8	0
(521)	1.65	1.65	0.1	0
(532)	1.46	1.46	0.2	/
(611)			0.4	/
(541)	1.39	1.39	0.2	/
(631)	1.33	1.33	0.3	/
(444)	1.30	1.30	3.3	/
(543)	1.27	1.28	3.2	/
(640)	1.25	1.25	0.9	/
(552)	1.23	1.23	0.7	/
(633)			0.7	/
(721)			0.3	/
(642)	1.20	1.21	0.4	/
a_{cub} = 9.03 nm				

Table S4. Experimental and calculated *d*-spacings, relative integrated intensities, and phases used in the reconstruction of electron densities for the Col_{hex}/*p6mm* phase for **F18** at 145 ºC. All intensities values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$- spacings (nm)	$d_{cal.}$- spacings (nm)	Intensity	Phase
(10)	3.72	3.72	100.0	0
(11)	2.15	2.15	0.9	π
(20)	1.86	1.86	7.9	0
(21)	1.40	1.41	1.2	π
(30)	1.24	1.24	0.1	0
a_{hex} = 4.30 nm				

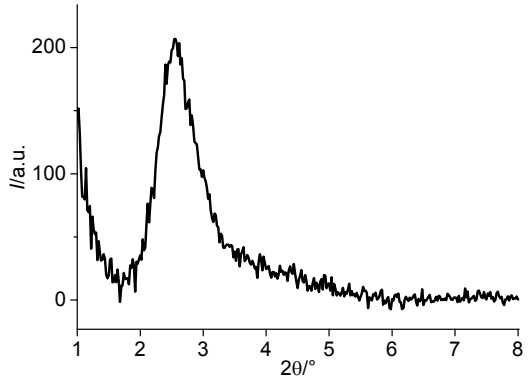


Figure S5: SAXS pattern of the N_{CybA} phase of **F8** at 186 °C.

Table S5: Experimental and calculated *d*-spacings of the Cub_{bi}/$Ia\bar{3}d$ phases.[a]

Comp.	*T*/°C	2 θ/°	θ/°	d_{obs}/nm	*hkl*	d_{calc}/nm	d_{obs}- d_{calc}/nm	a_{cub}/*nm*
F8	160	2.375	1.188	3.720	211	3.720	0.00	9.11
		2.747	1.374	3.216	220	3.221	-0.01	
F10	170	2,403	1,202	3,676	211	3,676	0,00	9.00
		2,749	1,375	3,214	220	3.184	0.03	
F14	160	2.428	1.214	3.639	211	3.637	0.00	8.91
		2.782	1.391	3.176	220	3.150	0.03	

[a] **F12** was reported in ref. [S1]; **F16** could not be investigated due to rapid crystallization during exposure time; the /$Ia\bar{3}d$ lattice was additionally supported by the absence of chiral domains.

Table S6: Experimental and calculated *d*-spacings of the $Col_{hex}/p6mm$ phase of compounds **H18** and **F16**.

Comp.	*T*/°C	2 θ/°	θ/°	d_{obs}/nm	*hk*	d_{calc}/nm	d_{obs}-d_{calc}/nm	a_{hex}/*nm*
H18	155	2.384	1.192	3.706	(10)	3.706	0.00	4.28
		4.626	2.313	1.91	(20)	1.853	0.06	
		4.879	2.439	1.811	(20)	1.821	0.01	
F16	160	2.383	1.192	3.707	(10)	3,707	0.00	4.28
		4.047	2.024	2.183	(11)	2.140	0.04	
		4.791	2.396	1.844	(20)	1.854	0.01	

[a] **H12** was reported in ref. [S2].

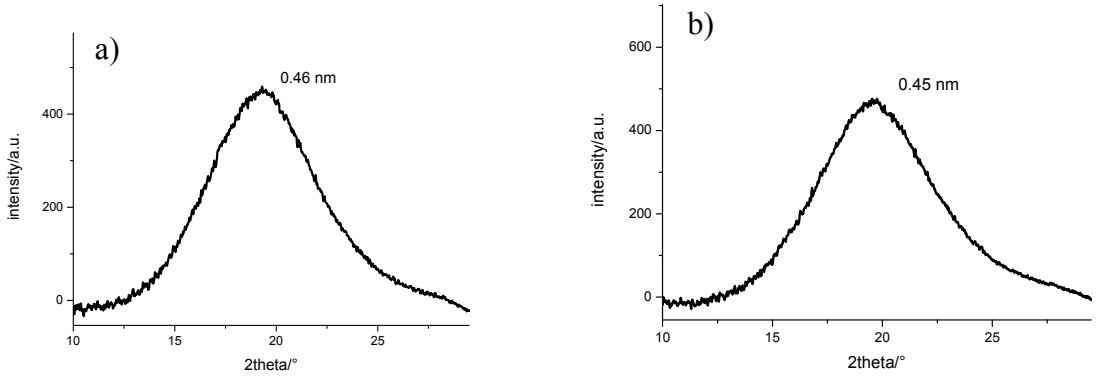


Figure S6: WAXS pattern of compound **H10** at a) 177 °C ($Col_{hex}/p6mm$) and b) 160 °C (Cub/$Ia\bar{3}d$).

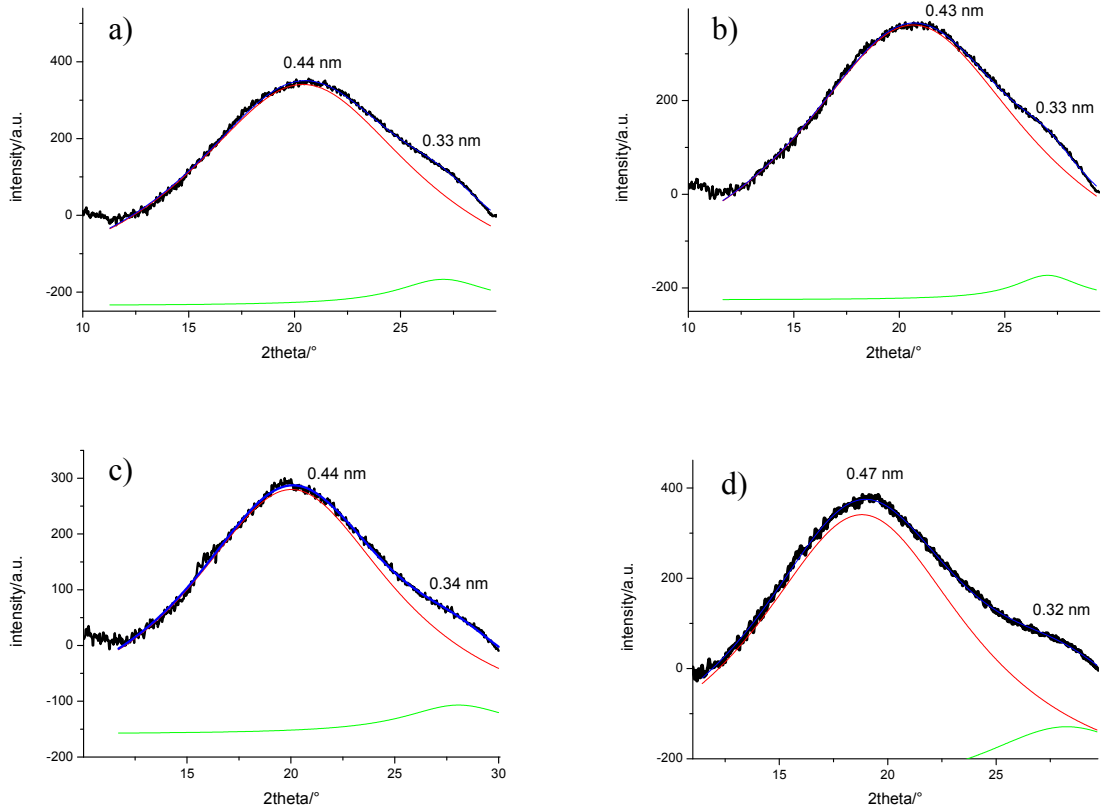


Figure S7: WAXS patterns of a) **F8** at 185 °C (nematic), b) **F8** at 160 °C (Cub/$Ia\bar{3}d$), c) **F10** at 170 °C (Cub/$Ia\bar{3}d$) and d) **F16** at 160 °C (Col_{hex}/$p6mm$).

Table S7: Structural data of the Col_{hex}/$p6mm$ LC-phases of compounds **H*n*** and **F*n***[a]

Comp	a /nm	V_{mol}/nm³	V_{cell}/nm³	$n_{cell,cryst}$	$n_{cell,liq}$	$n_{cell,LC}$	n_{Wall}
H10	4.31	1.358	7.40	5.45	4.28	4.87	1.6
H12[S2]	4.30	1.457	7.21	4.94	3.88	4.41	1.5
H18	4.28	1.755	7.14	4.07	3.19	3.63	1.2
F16	4.28	1.703	7.14	4.19	3.29	3.74	1.2
F18	4.30	1.802	7.37	4.09	3.21	3.65	1.2

[a] V_{cell} = volume of the unit cell defined by ($3^{½}$ a_{hex}^2/2) x h with h = 0.46 nm corresponding to the maximum of the diffuse wide angle scattering; V_{mol} = volume for a single molecule as calculated using the crystal volume increments;[S3] $n_{cell,cryst}$ = V_{cell}/V_{mol} (average packing coefficient in the crystal is k = 0.7);[S4] $n_{cell,\ liq}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient k = 0.55, calculated according to $n_{cell,\ liq}$ = 0.55/0.7 × $n_{cell,\ cryst}$; $n_{cell,LC}$ = number of molecules in the unit cell in the LC phase estimated as the average of $n_{cell,cryst}$ and $n_{cell,liq}$. n_{wall} = number of molecules in the lateral cross section of the cylinder walls, calculated for the triangular honeycombs as $n_{cell,LC}$/number of wall per unit cell = $n_{cell,LC}$/3. n_{wall} = 1.2-1.5 means that on average 1.2-1.5 molecules are laterally arranged in each hypothetical segment with h = 0.46 nm, i.e. there is a lateral staggering of the molecules in the cylinder walls or the packing of the aromatic cores is a bit closer than the assumed distance of 0.46 nm.

Table S8: Structural data of the cubic phases of compounds **H*n*** and **F*n***.[a]

Comp.	**H10**	**F8**	**F10**	**F12**[S1]	**F14**	**F18**
a (nm)	9.16	9.11	9.00	9.12	8.91	9.03
V_{cell} (nm^3)	768	756	729	758	707	736
V_{mol} (nm^3)	1.36	1.31	1.41	1.50	1.60	1.80
$n_{cell,cryst}$ = V_{cell} / V_{mol}	565	577	517	505	442	409
$n_{cell,\ liq}$	444	453	406	397	347	321
$n_{cell,LC}$	505	515	462	451	395	365
Minimal Surface S (nm^2)	206	204	199	204	195	200
n_{cell} / S (molecules/nm^{-2})	2.5	2.5	2.3	2.2	2.0	1.8
A_{mol} (nm^2)	0.41	0.40	0.43	0.45	0.49	0.55
d_{net} (nm)	3.97	3.94	3.89	3.95	3.85	3.93

[a] $V_{cell} = a_{cub}^3$; V_{mol} = volume for a single molecule as calculated using the crystal volume increments;[S3] for the calculations of $n_{cell,\ cryst}$, $n_{cell,\ liq}$ and $n_{cell,LC}$, see Table S7. S = area of the minimal surface in the unit cell of the $Ia\bar{3}d$ phase[S5] is $S = 2.4533 \times a_{cub}^2$; S_{mol} = molecular area on the minimal surface ($S_{mol} = S/n_{cell}$).[S6] d_{net} = lateral distance between the two infinite networks of the cubic mesophase as determined by $3^{1/2}a_{cub}/4$.[S5]

2. Synthesis and analytical data

2.2.1 General synthetic procedures

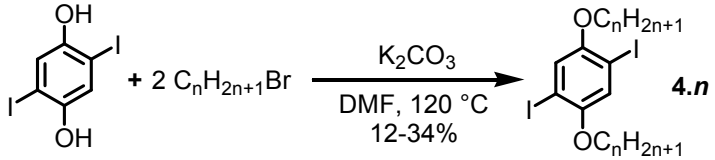
P1: Cross-coupling reaction according to *Sonogashira*[S7]: A mixture of 1,4-dialkoxy-2,5-diiodobenzene **4.*n*** (1 equ.) and the appropriate acetylene (2.1 equ.) was dissolved in purified Et_3N (50 mL/≤1 mmol). After degassing with argon for 30 min [$Pd(PPh_3)_4$] (3 mol%) and CuI (2 mol%) were added and the mixture was refluxed for 6 h. After removing the solvent the obtained residue was purified by column chromatography. In a similar way the syntheses of **2FSi** and **3FSi** were conducted by Sonogashira cross coupling of monovalent aryliodides using the molar ratios and catalyst given in the procedures in 2.2.3.

P2: Desilylation[S2]: The appropriate silyl protected acetylene (1 equ.) and K_2CO_3 (5 equ) were dissolved in DCM/MeOH (2:1; 15 mL/mmol) and stirred at 20 °C. The progress of the reaction was recorded by TLC. The reaction was quenched with H_2O (50 mL) and the different phases were separated. The aqueous phase was extracted with DCM (3 x 50 mL). The combined organic phases were washed with water and brine. After drying over Na_2SO_4

the solvent was removed under reduced pressure. The residue was purified by column chromatography.

P3: Deprotection of the glycerol group with PPTS[S8]: A mixture of the appropriate compound **5H*n*** or **5F**n (1 equ.) and PPTS (tip of a spatula) was dissolved in THF/MeOH (1:1) and stirred at 50 °C for 12 h. After finishing the reaction the solvent was removed and the residue was solved in DCM. The organic layer was washed with $NaHCO_3$ solution (3 x 50 mL), water and brine. After drying over Na_2SO_4 the solvent was removed and the residue purified with column chromatography.

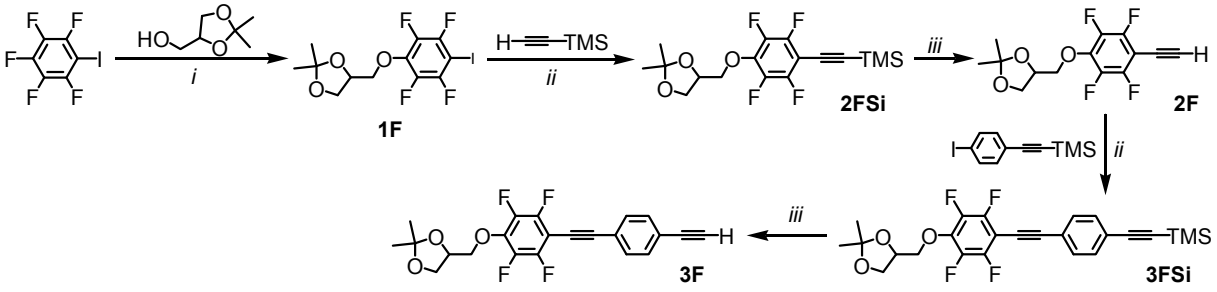
2.2.2 Synthesis of the 1,4-dialkoxy-2,5-diiodobenzenes



Scheme S1: Synthesis of the 1,4-dialkoxy-2,5-diiodobenzenes **4.*n***.

1,4-Dioctadecyloxy-2,5-diiodobenzene (4.18): A mixture of 1,4-dihydroxy-2,5-diiodobenzene (1.00 g, 2.8 mmol), *n*-bromooctadecane (2.30 g, 7.0 mmol), K_2CO_3 (1.90 g, 14.0 mmol) and Bu_4NI (tip of a spatula) in anhydrous DMF (50 mL) was stirred at 120 °C for 12 h. After cooling to room temperature, the reaction was poured into water (50 mL) and the aqueous layer was extracted with Et_2O (3x50 mL). The combined organic layers were washed with saturated aqu. LiCl, water and brine. After drying over anhydrous Na_2SO_4, filtration and evaporation of the solvent, the crude product was purified by column chromatography (eluent: *n*-hexane). Colorless solid, $C_{42}H_{76}I_2O_2$, M = 866.39 g/mol, mp 82 °C, yield: 0.76 g (32%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 2H, Ar–*H*), 3.92 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–), 1.87 – 1.66 (m, 4H, –CH_2–), 1.57 – 1.19 (m, 56H, –CH_2–), 0.87 (d, ^3J(H,H) = 7.0 Hz, 6H, –CH_3) ppm.

2.2.3 Synthesis of 3-[4-(4-ethynylphenylethynyl)-2,3,5,6-tetrafluorophenyl]-1,2-isopropylidene-*rac*-glycerol (3F)



Scheme S2: Synthesis of **3F**. *Reagents and conditions*: *i*) K_2CO_3, DMF, 40 °C, 3d, 59%, *ii*) NEt_3, [$Pd(PPh_3)_4$], CuI, 40 °C, 12h, 94%, *iii*) K_2CO_3, DCM/MeOH (2:1), 2h, 60-90%.

1,2-Isopropylidene-3-(2,3,5,6-tetrafluoro-4-iodophenyl)-*rac*-glycerol (1F): According to the procedure described by Wen et al.[S9] a mixture of pentafluoroiodobenzene (5.00 g, 17.0 mmol) and D,L-1,2-isopropylideneglycerole (2.91 g, 22.1 mmol) was solved in DMF (50 mL) and stirred for 10 min at 20 °C. After the stepwise addition of K_2CO_3 (3.04 g, 22.1 mmol) the reaction was stirred at 40 °C for 48 h. The reaction was quenched with water und the phases were separated. The aqueous phase was extracted with Et_2O (3 x 50 mL). The combined organic phases were washed with water and brine. After drying over Na_2SO_4 the solvent was removed and the residue purified by column chromatography (eluent: $CHCl_3$). Colourless liquid; $C_{12}H_{11}F_4IO_3$; *M* = 405.97 g/mol; yield: 4.86 g (70%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.53 – 4.38 (m, 1H, –OC*H*–), 4.36 – 4.26 (m, 1H, –OCH_2–), 4.24 – 4.09 (m, 2H, –OCH_2–), 4.01 – 3.89 (m, 1H, –OCH_2–), 1.42 (s, 3H, –CH_3), 1.38 (s, 3H, –CH_3) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$) δ -121.09 (td, ^3J(F,F) = 10.2 Hz, ^4J(F,F) = 5.0 Hz, Ar–*F*), -154.13 (td, ^3J(F,F) = 10.1 Hz, ^4J(F,F) = 4.9 Hz, Ar–*F*) ppm.

1,2-Isopropylidene-3-[2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)phenyl]-*rac*-glycerol (2FSi): Synthesized according to P1 from **2** (4.86 g, 11.9 mmol), ethynyltrimethylsilane (1.50 g, 15.6 mmol), [$Pd(PPh_3)_4$] (0.42 g, 0.36 mmol) and CuI (0.05 g, 0.24 mmol). Purification by column chromatography (eluent: $CHCl_3$/*n*-hexane = 1:1). Colourless liquid; $C_{17}H_{20}F_4O_3Si$; *M* = 376.11 g/mol; yield: 4.23 g (95%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.49 – 4.40 (m, 1H, –OC*H*–), 4.36 – 4.29 (m, 1H, –OCH_2–), 4.27 – 4.11 (m, 2H, –OCH_2–), 3.98 – 3.90 (m, 1H, –OCH_2–), 1.42 (s, 3H, –CH_3), 1.38 (s, 3H, –CH_3), 0.32 (s, 9H, Si–(CH_3)$_3$) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$) δ -137.42 (td, ^3J(F,F) = 10.7 Hz, ^4J(F,F) = 4.0 Hz, Ar–*F*), -156.92 (td, ^3J(F,F) = 10.6 Hz, ^4J(F,F) = 3.9 Hz, Ar–*F*) ppm.

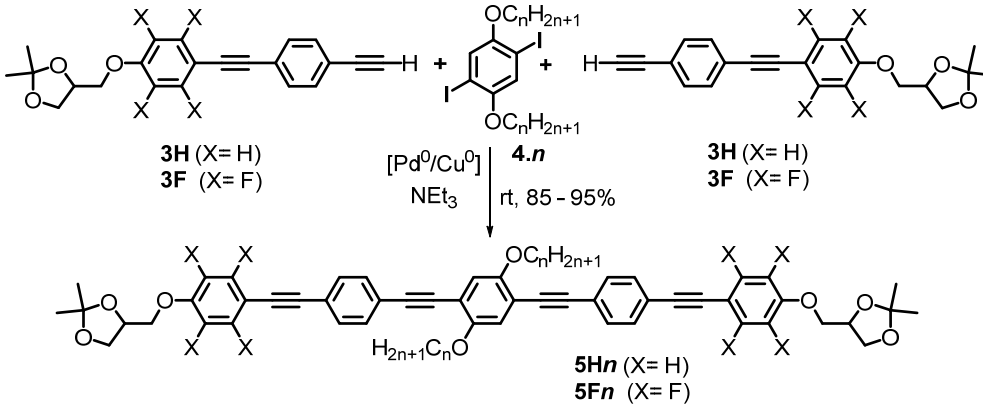
3-(4-Ethynyl-2,3,5,6-tetrafluorophenyl)-1,2-isopropylidene-*rac*-glycerol (2F): Synthesized according to P2 from **3** (4.23 g, 11.3 mmol) and K_2CO_3 (7.76 g, 56.3 mmol). Purification by column chromatography (eluent: $CHCl_3$/*n*-hexane = 1:1). Colourless liquid; $C_{14}H_{12}F_4O_3$; *M* = 334.12 g/mol; yield: 3.36 g (98%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.49 – 4.40 (m, 1H, –OC*H*–), 4.36 – 4.29 (m, 1H, –OCH_2–), 4.27 – 4.11 (m, 2H, –OCH_2–), 3.98 – 3.90 (m, 1H, –OCH_2–), 3.55 (s, 1H, –C*H*), 1.42 (s, 3H, –CH_3), 1.38 (s, 3H, –CH_3) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$) δ -137.47 (td, ^3J(F,F) = 10.7 Hz, ^4J(F,F) = 4.0 Hz, Ar–*F*), -156.70 (td, (F,F) = 10.6 Hz, ^4J(F,F) = 3.9 Hz, Ar–*F*) ppm.

3-{4-[4-(Trimethylsilylethynyl)phenylethynyl]-2,3,5,6-tetrafluorophenyl}-1,2-isopropylidene-*rac*-glycerol (3FSi): Synthesized according to P1 from **4** (3.37 g, 11.1 mmol), (4-iodophenylethynyl)trimethylsilane (3.66 g, 12.2 mmol), [$Pd(PPh_3)_2Cl_2$] (0.24 g, 0.3 mmol) and CuI (0.06 g, 0.31 mmol). Purification by column chromatography (eluent: $CHCl_2$/*n*-hexane = 4:1). Colorless solid; $C_{25}H_{24}F_4O_3Si$; *M* = 476.14 g/mol; yield: 3.23 g (61%); mp = 95 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.42 (m, 4H, Ar–*H*), 4.51 – 4.40 (m, 1H, –OC*H*–), 4.33 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.1 Hz, 1H, –OCH_2–), 4.23 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.6 Hz, 1H, –OCH_2–), 4.20 – 4.11 (m, 1H, –OCH_2–), 3.99 – 3.92 (m, 1H, –OCH_2–), 1.43 (s, 3H, –CH_3), 1.38 (s, 3H, –CH_3), 0.26 (s, 9H, –Si–(CH_3)$_3$) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$) δ -137.53 (td, ^3J(F,F) = 10.2 Hz, ^4J(F,F) = 3.4 Hz, Ar–*F*), -156.90 (td, ^3J(F,F) = 9.8 Hz, ^4J(F,F) = 2.9 Hz, Ar–*F*) ppm.

3-[4-(4-Ethynylphenylethynyl)-2,3,5,6-tetrafluorophenyl]-1,2-isopropylidene-*rac*-glycerol (3F): Synthesized according to P2 from **5** (3.23 g, 6.8 mmol) and K_2CO_3 (4.70 g, 33.9 mmol). Purification by column chromatography (eluent: $CHCl_2$/*n*-hexane = 4:1). Yellow solid; $C_{22}H_{16}F_4O_3$; *M* = 434.15 g/mol; yield: 1.22 g (44%); mp = 42 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.45 (m, 4H, Ar – *H*), 4.53 – 4.39 (m, 1H, –OC*H*–), 4.33 (dd, ^2J(H,H) = 10.1

Hz, ^{3}J(H,H) = 5.1 Hz, 1H, –OCH_2–), 4.24 (dd, ^{2}J(H,H) = 10.1 Hz, ^{3}J(H,H) = 5.6 Hz, 1H, –OCH_2–), 4.16 (dd, ^{2}J(H,H) = 8.5 Hz, ^{3}J(H,H) = 6.5 Hz, 1H, –OCH_2–), 3.96 (dd, ^{2}J(H,H) = 8.6 Hz, ^{3}J(H,H) = 5.6 Hz, 1H, –OCH_2–), 3.20 (s, 1H, –C*H*), 1.43 (s, 3H, –CH_3), 1.38 (s, 3H, –CH_3) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$) δ -137.48 (td, ^{3}J(F,F) = 10.2 Hz, ^{4}J(F,F) = 3.4 Hz, Ar–*F*), -156.87 (td, (F,F) = 9.8 Hz, ^{4}J(F,F) = 2.8 Hz, Ar–*F*) ppm.

2.2.4 Synthesis of the fluorinated and non fluorinated acetonides



Scheme S3: Synthesis of the fluorinated and non fluorinated acentonides **5H*n*** and **5F*n***.

1,4-Dibutyloxy-2,5-bis{4-[4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenylethynyl}benzene (5H4): Synthesized according to P1 from **4.4** (133 mg, 0.28 mmol), **3H** (195 mg, 0.59 mmol), [$Pd(PPh_3)_4$] (9.7 mg, 0.008 mmol), CuI (1.1 mg, 0.006 mmol) in NEt_3 (50 mL). Purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{58}H_{58}O_8$, *M* = 882.41 g/mol, mp 210 °C, yield: 250 mg (95%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 12H, Ar–*H*), 7.01 (s, 2H, Ar–*H*), 6.94 – 6.86 (m, 4H, Ar–*H*), 4.53 – 4.43 (m, 2H, –C*H*–), 4.18 (dd, ^{2}J(H,H) = 8.5 Hz, ^{3}J(H,H) = 6.4 Hz, 2H, –OCH_2–), 4.11 – 4.02 (m, 4H, –OCH_2–), 3.97 (dd, ^{2}J(H,H) = 9.5 Hz, ^{3}J(H,H) = 5.8 Hz, 2H, –OCH_2–), 3.91 (dd, ^{2}J(H,H) = 8.5 Hz, ^{3}J(H,H) = 5.8 Hz, 2H, –OCH_2–), 1.93 – 1.79 (m, 4H, –CH_2–), 1.66 – 1.50 (m, 4H, –CH_2–), 1.47 (s, 3H, –CH_3), 1.41 (s, 3H, –CH_3), 1.01 (t, ^{3}J(H,H) = 7.4 Hz, 3H, –CH_3) ppm.

1,4-Dihexyloxy-2,5-bis{4-[4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenylethynyl}benzene (5H6): Synthesized according to P1 from **4.6** (328 mg, 0.75 mmol), **3H** (600 mg, 1.81 mmol), [$Pd(PPh_3)_4$] (26.2 mg, 0.027 mmol), CuI (2.9 mg, 0.015 mmol) in NEt_3 (50 mL). Purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{62}H_{66}O_8$, M = 939.20 g/mol, yield: 371 mg (53%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.36 (m, 12H, Ar–*H*), 6.99 (s, 2H, Ar–*H*), 6.91 – 6.84 (m, 4H, Ar–*H*), 4.51 – 4.42 (m, 2H, –OC*H*–), 4.16 (dd, ^{2}J(H,H) = 8.5 Hz, ^{3}J(H,H) 6.4 Hz, 2H, –OCH_2–), 4.11 – 3.99 (m, 6H, –OCH_2–), 3.95 (dd, ^{2}J(H,H) = 9.6 Hz, ^{3}J(H,H) = 5.9 Hz, 2H, –OCH_2–), 3.89 (dd, ^{2}J(H,H) = 8.5 Hz, ^{3}J(H,H) = 5.8 Hz, 2H, –OCH_2–), 1.88 –1.78 (m, 4H, –CH_2–), 1.59 – 1.48 (m, 4H, –CH_2–), 1.45 (s, 6H, –CH_3), 1.39 (s, 6H, –CH_3), 1.38 – 1.27 (m, 8H, –CH_2–), 0.89 (t, ^{3}J(H,H) = 7.1 Hz, 6H, –CH_3) ppm.

1,4-Dioctyloxy-2,5-bis{4-[4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenyl-ethynyl}benzene (5H8): Synthesized according to P1 from **4.8** (147 mg, 0.25 mmol), **3H** (175 mg, 0.52 mmol), $[Pd(PPh_3)_4]$ (8.7 mg, 0.008 mmol), CuI (1.0 mg, 0.005 mmol) in NEt_3 (50 mL). Purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{66}H_{74}O_8$, *M* = 994.54 g/mol, mp, 157 °C, yield: 250 mg (95%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 12H, Ar–*H*), 7.01 (s, 2H, Ar–*H*), 6.94 – 6.87 (m, 4H, Ar–*H*), 4.54 – 4.44 (m, 2H), 4.18 (dd, ^2J(H,H) = 8.5 Hz, ^3J(H,H) = 6.4 Hz, 2H, –OC*H*–), 4.13 – 4.01 (m, 4H, –OCH_2–), 3.97 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 5.9 Hz, 2H, –OCH_2–), 3.91 (dd, ^2J(H,H) = 8.5 Hz, ^3J(H,H) = 5.8 Hz, 2H, –OCH_2–), 1.92 – 1.78 (m, 4H, –CH_2–), 1.61 – 1.20 (m, 34H, –CH_2–, –OCH_3–), 0.88 (t, ^3J(H,H) = 6.9 Hz, 6H, –CH_3) ppm.

1,4-Didecyloxy-2,5-bis{4-[4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenyl-ethynyl}benzene (5H10): Synthesized according to P1 from **4.10** (122 mg, 0.20 mmol), **3H** (139 mg, 0.42 mmol), $[Pd(PPh_3)_4]$ (6.9 mg, 0.006 mmol), CuI (0.7 mg, 0.004 mmol) in NEt_3 (50 mL). Purification by column chromatography (eluent: $CHCl_3$).Yellow solid, $C_{70}H_{82}O_8$, *M* = 1050.60 g/mol, mp 142 °C, yield: 200 mg (95%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 12H, Ar–*H*), 7.01 (s, 2H, Ar–*H*), 6.94 – 6.86 (m, 4H, Ar–*H*), 4.53 – 4.45 (m, 2H, –OC*H*–), 4.18 (dd, ^2J(H,H) = 8.5 Hz, ^3J(H,H) = 6.4 Hz, 2H, –OCH_2–), 4.08 (dd, ^2J(H,H) = 9.5 Hz, ^3J(H,H) = 5.4 Hz, 2H, –OCH_2–), 4.04 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–CH_2–), 3.97 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 5.9 Hz, 2H, –OCH_2–), 3.91 (dd, ^2J(H,H) = 8.5 Hz, ^3J(H,H) = 5.8 Hz, 2H, –OCH_2–), 1.92 – 1.79 (m, 4H, –CH_2–), 1.62 – 1.16 (m, 40H, –CH_2–, –CH_3), 0.88 (t, ^3J(H,H) = 6.9 Hz, 6H, –CH_3) ppm.

1,4-Dioctadecyloxy-2,5-bis{4-[4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenyl-ethynyl}benzene (5H18): Synthesized according to P1 from **4.18** (310 mg, 0.40 mmol), **3H** (315 mg, 0.95 mmol), $[Pd(PPh_3)_4]$ (14.0 mg, 0.012 mmol), CuI (2.0 mg, 0.008 mmol) in NEt_3 (50 mL). Purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{86}H_{114}O_8$, M = 1275.84 g/mol, yield: 93 mg (18%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.39 (m, 12H, Ar–*H*), 6.99 (s, 2H, Ar–*H*), 6.91 – 6.85 (m, 4H, Ar–*H*), 4.52 – 4.42 (m, 2H, –C*H*–), 4.16 (dd, ^2J(H,H) = 8.5 Hz, ^{3}J(H,H) = 6.5 Hz, 2H, –OCH_2–), 4.06 (dd, ^2J(H,H) = 9.5 Hz, ^3J(H,H) = 5.4 Hz, 2H, –OCH_2–), 4.02 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–), 3.95 (dd, ^2J(H,H) = 9.5 Hz, ^3J(H,H) = 5.9 Hz, 2H, –OCH_2–), 3.89 (dd, ^2J(H,H) = 8.5 Hz, ^3J(H,H) = 5.8 Hz, 2H, –OCH_2–), 1.89 – 1.77 (m, 4H, –CH_2–), 1.60 – 1.47 (m, 4H, –CH_2–), 1.45 (s, 6H, –CH_3), 1.42 – 1.15 (m, 62H, –CH_2–), 0.85 (t, ^3J(H,H) = 6.8 Hz, 6H, –CH_3) ppm.

1,4-Dihexyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(1,2-isopropylidene-*rac*-glycero-3)phenyl-ethynyl]phenylethynyl}benzene (5F6): Synthesized according to P1 from **4.6** (122 mg, 0.23 mmol), **3F** (196 mg, 0.48 mmol), $[Pd(PPh_3)_4]$ (7.9 mg, 0.007 mmol), CuI (0.9 mg, 0.005 mmol) in NEt_3 (50 mL). Purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{62}H_{58}F_8O_8$, *M* = 1082.40 g/mol, mp 146 °C, yield: 240 mg (96%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.51 – 4.41 (m, 2H, –OC*H*–), 4.34 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.1 Hz, 2H, –OCH_2–), 4.24 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 4.16 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 6.4 Hz, 2H, –OCH_2–), 4.04 (t, ^3J(H,H) = 6.5 Hz, 4H, –OCH_2–), 3.96 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 1.91 – 1.81 (m, 4H, –CH_2–), 1.61 – 1.29 (m, 24H, –CH_2–, –CH_3), 0.91 (t, ^3J(H,H) =

7.1 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$) δ -137.48 – -137.59 (m, Ar–*F*), -156.82 – -156.97 (m, Ar–*F*) ppm.

1,4-Dioctyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenylethynyl}benzene (5F8): Synthesized according to P1 from **4.8** (129 mg, 0.22 mmol), **3F** (185 mg, 0.46 mmol), [$Pd(PPh_3)_4$] (5.2 mg, 0.007 mmol), CuI (0.8 mg, 0.004 mmol) in NEt_3 (50 mL). Purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{66}H_{66}F_8O_8$, *M* = 1138.46 g/mol, mp 135 °C, yield: 240 mg (95%), ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 8H, Ar–*H*), 7.03 (s, 2H, Ar–*H*), 4.53 – 4.42 (m, 2H, –OC*H*–), 4.35 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.2 Hz, 2H, –OCH_2–), 4.25 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 4.18 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 6.4 Hz, 2H, –OCH_2–), 4.05 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–), 3.98 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 1.97 – 1.80 (m, 4H, –CH_2–), 1.65 – 1.19 (m, 32H, –CH_2–, –CH_3), 0.89 (t, ^3J(H,H) = 6.8 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (470 MHz, $CDCl_3$) δ -137.53 (td, ^3J(F,F) = 9.9 Hz, ^4J(F,F) = 3.0 Hz, Ar–*F*), -156.89 (td, ^3J(F,F) = 9.7 Hz, ^4J(F,F) = 2.6 Hz, Ar–*F*) ppm.

1,4-Didecyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenylethynyl}benzene (5F10): Synthesized according to P1 from **4.10** (135 mg, 0.21 mmol), **3F** (178 mg, 0.44 mmol), [$Pd(PPh_3)_4$] (7.3 mg, 0.006 mmol), CuI (0.8 mg, 0.004 mmol) in NEt_3 (50 mL). Purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{70}H_{74}F_8O_8$, *M* = 1194.53 g/mol, mp 141 °C, yield: 230 mg (92%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.50 – 4.42 (m, 2H, –OC*H*–), 4.34 (dd, ^2J(H,H) = 10.2 Hz, ^3J(H,H) = 5.1 Hz, 2H, –OCH_2–), 4.24 (dd, ^2J(H,H) = 10.2 Hz, ^3J(H,H) = 5.5 Hz, 2H, –OCH_2–), 4.16 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 6.4 Hz, 2H, –OCH_2–), 4.04 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–), 3.96 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 1.92 – 1.78 (m, 4H, –CH_2–), 1.61 – 1.18 (m, 40H, –CH_2–, –CH_3), 0.87 (t, ^3J(H,H) = 7.0 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$) δ -137.49 – -137.60 (m, Ar–*F*), -156.85 – -156.97 (m, Ar–*F*) ppm.

1,4-Didodecyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenylethynyl}benzene (5F12): Synthesized according to P1 from **4.12** (119 mg, 0.17 mmol), **3F** (144 mg, 0.36 mmol), [$Pd(PPh_3)_4$] (3.6 mg, 0.005 mmol), CuI (0.6 mg, 0.003 mmol) in NEt_3 (50 mL). Purification by column chromatography (eluent: $CHCl_3$). Yellow solid, $C_{74}H_{82}F_8O_8$, *M* = 1250.59 g/mol, mp 126 °C, yield: 210 mg (95%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.50 – 4.41 (m, 2H, –OC*H*), 4.33 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.1 Hz, 2H, –OCH_2), 4.24 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2), 4.16 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 6.5 Hz, 2H, –OCH_2), 4.04 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2), 3.96 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2), 1.92 – 1.79 (m, 4H, –CH_2), 1.60 – 1.48 (m, 8H, –CH_2), 1.47 – 1.17 (m, 48H, –CH_2, –CH_3), 0.86 (t, ^3J(H,H) = 6.7 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$) δ -137.46 – -137.64 (m, Ar–*F*), -156.85 – -156.99 (m, Ar–*F*) ppm.

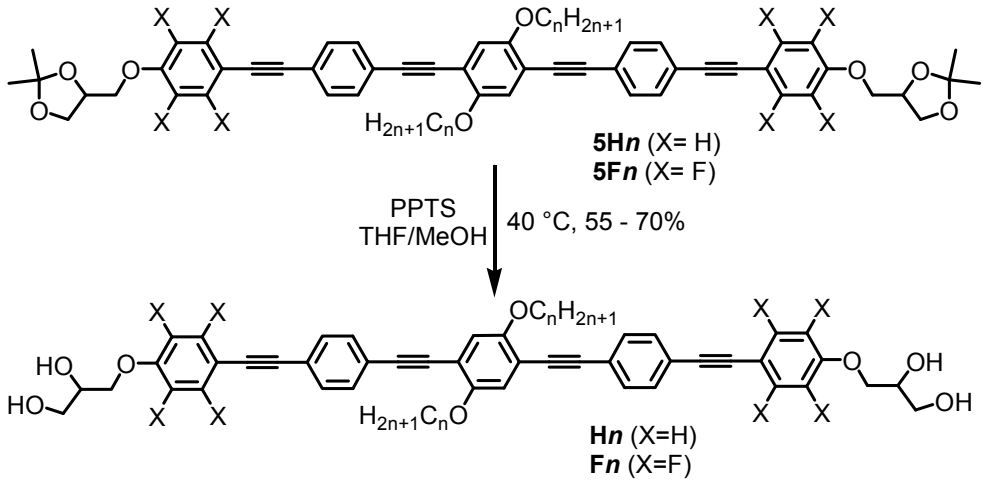
1,4-Ditetradecyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenylethynyl}benzene (5F14): Synthesized according to P1 from **4.14**

(144 mg, 0.19 mmol), **3F** (161 mg, 0.40 mmol), [Pd(PPh$_3$)$_4$] (6.6 mg, 0.006 mmol), CuI (0.7 mg, 0.004 mmol) in NEt$_3$ (50 mL). Purification by column chromatography (eluent: CHCl$_3$). Yellow solid, $C_{78}H_{90}F_8O_8$, *M* = 1306.65 g/mol, mp 135 °C, yield: 220 mg (88%), ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.58 – 7.50 (m, 8H, Ar–*H*), 7.02 (s, 2H, Ar–*H*), 4.51 – 4.41 (m, 2H, –OC*H*–), 4.34 (dd, ^2J(H,H) = 10.0 Hz, ^3J(H,H) = 5.1 Hz, 2H, –OCH_2–), 4.24 (dd, ^2J(H,H) = 10.0 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 4.16 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 6.4 Hz, 2H, –OCH_2–), 4.04 (t, ^3J(H,H) = 6.5 Hz, 4H, –OCH_2–), 3.96 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 1.91 – 1.80 (m, 4H, –CH_2–), 1.61 – 1.17 (m, 56H, –CH_2–, –CH_3), 0.86 (t, ^3J(H,H) = 6.8 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (376 MHz, CDCl$_3$) δ -137.53 (td, ^3J(F,F) = 10.2 Hz, ^4J(F,F) = 3.3 Hz, Ar–*F*), -156.92 (td, ^3J(F,F) = 9.8 Hz, ^4J(F,F) = 2.8 Hz, Ar–*F*) ppm.

1,4-Dihexadecyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenylethynyl}benzene (5F16): Synthesized according to P1 from **4.16** (148 mg, 0.18 mmol), **3F** (155 mg, 0.38 mmol), [Pd(PPh$_3$)$_4$] (6.2 mg, 0.005 mmol), CuI (0.7 mg, 0.004 mmol) in NEt$_3$ (50 mL). Purification by column chromatography (eluent: CHCl$_3$). Yellow solid, $C_{82}H_{98}F_8O_8$, *M* = 1362.71 g/mol, mp 89 °C, yield: 240 mg (95%), ^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.59 – 7.52 (m, 8H, Ar–*H*), 7.03 (s, 2H, Ar–*H*), 4.50 – 4.43 (m, 2H, –OC*H*–), 4.35 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.0 Hz, 2H´, –OCH_2–), 4.25 (dd, ^2J(H,H) = 10.2 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 4.18 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 6.4 Hz, 2H, –OCH_2–), 4.05 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–), 3.98 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 1.93 – 1.81 (m, 4H, –CH_2–), 1.68 – 1.12 (m, 64H, –CH_2–, –CH_3), 0.88 (t, ^3J(H,H) = 7.1 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (470 MHz, CDCl$_3$) δ -137.46 – -137.56 (m, Ar–*F*), -156.85 – -156.95 (m, Ar–*F*) ppm.

1,4-Dioctadecyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(1,2-isopropylidene-*rac*-glycero-3)phenylethynyl]phenylethynyl}benzene (5F18): Synthesized according to P1 from **4.18** (152 mg, 0.17 mmol), **3F** (144 mg, 0.36 mmol), [Pd(PPh$_3$)$_4$] (3.5 mg, 0.005 mmol), CuI (0.6 mg, 0.003 mmol) in NEt$_3$ (50 mL). Purification by column chromatography (eluent: CHCl$_3$). Yellow solid, $C_{86}H_{106}F_8O_8$, *M* = 1418.78 g/mol, mp 128 °C, yield: 240 mg (95%), ^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.60 – 7.52 (m, 8H, Ar–*H*), 7.03 (s, 2H, Ar–*H*), 4.52 – 4.42 (m, 2H, –OC*H*–), 4.35 (dd, ^2J(H,H) = 10.2 Hz, ^3J(H,H) = 5.0 Hz, 2H, –OCH_2–), 4.25 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 4.18 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 6.4 Hz, 2H, –OCH_2–), 4.05 (t, ^3J(H,H) = 6.5 Hz, 4H, –OCH_2–), 3.98 (dd, ^2J(H,H) = 8.6 Hz, ^3J(H,H) = 5.6 Hz, 2H, –OCH_2–), 1.92 – 1.81 (m, 4H, –CH_2–), 1.61 – 1.17 (m, 72H, –CH_2–, –CH_3), 0.89 (t, ^3J(H,H) = 7.0 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (470 MHz, CDCl$_3$) δ -137.51 (td, ^3J(F,F) = 9.9 Hz, ^4J(F,F) = 3.0 Hz, Ar–*F*), -156.90 (td, ^3J(F,F) = 9.6 Hz, ^4J(F,F) = 2.5 Hz, Ar–*F*) ppm.

2.2.5 Synthesis of compounds H*n* and F*n*



Scheme S4: Synthesis of compounds **H*n*** and **F*n***.

1,4-Dibutyloxy-2,5-bis{4-[4-(*rac*-glycero-1)phenylethynyl]phenylethynyl}benzene (H4): Synthesized according to P3 from **5H4** (250 mg, 0.28 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{52}H_{50}O_8$, *M* = 802.35 g/mol, yield: 183 mg (81%), ^{1}H-NMR (400 MHz, pyridine-d_5) δ 7.78 – 7.72 (m, 4H, Ar–*H*), 7.71 – 7.66 (m, 4H, Ar–*H*), 7.66 – 7.62 (m, 4H, Ar–*H*), 7.45 (s, 2H, Ar–*H*), 7.13 – 7.08 (m, 4H, Ar–*H*), 6.94 (br, 2H, –O*H*), 6.54 (br, 2H, –O*H*), 4.61 – 4.54 (m, 2H, –OC*H*–), 4.52 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 4.3 Hz, 2H, –OCH_2–), 4.43 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H)= 6.3 Hz, 2H, –OCH_2–), 4.28 – 4.18 (m, 4H, –OCH_2–), 4.09 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–), 1.87 – 1.76 (m, 4H, –CH_2–), 1.66 – 1.51 (m, 4H, –CH_2–), 0.95 (t, ^3J(H,H) = 7.4 Hz, 6H, –CH_3) ppm. ^{13}C-NMR (126 MHz, pyridine-d_5) δ 160.06 (–O*C*H$_2$–), 154.07 (–O*C*H$_2$–), 133.38 (*C*$_{Ar}$–H), 131.80 (*C*$_{Ar}$–H), 131.77, 123.94, 117.25, 115.19, 114.96, 114.31, 95.19 (—C≡C—), 92.46 (—C≡C—), 88.89 (—C≡C—), 88.33 (—C≡C—), 71.12 (HO*C*H$_2$–), 70.86, 69.21, 64.04, 31.36 (–*C*H$_2$–), 19.34, 13.76 (–*C*H$_3$) ppm. HRMS (m/z): [M]+Li$^+$-calcd. for $C_{52}H_{50}O_8Li$, 809.366; found 809.367. Anal. Calcd. for $C_{52}H_{50}O_8 \cdot H_2O$: C, 76.08; H, 6.38. Found: C, 76.21; H, 6.25.

1,4-Dihexyloxy-2,5-bis{4-[4-(*rac*-glycero-1)phenylethynyl]phenylethynyl}benzene (H6): Synthesized according to P3 from **5H6** (371 mg, 0.40 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{56}H_{58}O_8$, M = 859.07 g/mol, yield: 100 mg (29%), ^{1}H-NMR (500 MHz, pyridine-d_5) δ 7.73 – 7.67 (m, 4H, Ar–*H*), 7.64 – 7.60 (m, 4H, Ar–*H*), 7.60 – 7.56 (m, 4H, Ar–*H*), 7.41 (s, 2H, Ar–*H*), 7.07 – 7.02 (m, 4H, Ar–*H*), 4.56 – 4.48 (m, 2H, –OC*H*–), 4.45 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 4.3 Hz, 2H, –OCH_2–), 4.37 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 6.3 Hz, 2H, –OCH_2–), 4.21 – 4.13 (m, 4H, –OCH_2–), 4.04 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–), 1.84 – 1.74 (m, 4H, –CH_2–), 1.57 – 1.45 (m, 4H, –CH_2–), 1.30 – 1.18 (m, 8H, –CH_2–), 0.81 (t, ^3J(H,H) = 7.0 Hz, 6H, –CH_3) ppm. ^{13}C-NMR (126 MHz, pyridine-d_5) δ 160.02 (–O*C*H$_2$–), 154.05 (–O*C*H$_2$–), 133.33 (*C*$_{Ar}$–H), 131.77 (*C*$_{Ar}$–H), 131.70, 117.21, 115.15, 114.91, 114.27, 95.16 (—C≡C—), 92.42 (—C≡C—), 88.86 (—C≡C—), 88.28

(—C≡C—), 71.08 (HO*C*H$_2$–), 70.82, 69.48, 63.99, 31.48 (–*C*H$_2$–), 29.31, 25.77, 22.62, 13.89 (–*C*H$_3$) ppm. HRMS (m/z): [M]+Cl-calcd. for $C_{56}H_{58}O_8Cl$, 893.381; found 893.384.

1,4-Dioctyloxy-2,5-bis{4-[4-(*rac*-glycero-1)phenylethynyl]phenylethynyl}benzene (H8): Synthesized according to P3 from **5H8** (250 mg, 0.25 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{60}H_{66}O_8$; *M* = 914.48 g/mol, yield: 208 mg (90%), **^{1}H-NMR** (500 MHz, pyridine-d_5) δ 7.79 – 7.74 (m, 4H, Ar–*H*), 7.71 – 7.67 (m, 4H, Ar–*H*), 7.66 – 7.62 (m, 4H, Ar–*H*), 7.49 (s, 2H, Ar–*H*), 7.12 – 7.08 (m, 4H, Ar–*H*), 4.65 – 4.53 (m, 2H, –OC*H*–), 4.51 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 4.3 Hz, 2H, –OC*H*$_2$–), 4.43 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 6.3 Hz, 2H, –OC*H*$_2$–), 4.27 – 4.19 (m, 4H, –OC*H*$_2$–), 4.13 (t, ^3J(H,H) = 6.4 Hz, 4H, –OC*H*$_2$–), 1.93 – 1.83 (m, 4H, –C*H*$_2$–), 1.62 – 1.56 (m, 4H, –C*H*$_2$–), 1.42 – 1.18 (m, 16H, –C*H*$_2$–), 0.87 (t, ^3J(H,H) = 6.9 Hz, 6H, –C*H*$_3$) ppm. **^{13}C-NMR** (126 MHz, pyridine-d_5) δ 160.06 (–O*C*H$_2$–), 154.11 (–O*C*H$_2$–), 133.37 (*C*$_{Ar}$–H), 131.83 (*C*$_{Ar}$–H), 131.75, 117.29, 115.19, 114.95, 114.35, 95.21 (—C≡C—), 92.46 (—C≡C—), 88.92 (—C≡C—), 88.32 (—C≡C—), 71.12 (HO*C*H$_2$–), 70.86, 69.55, 64.03, 31.78 (–*C*H$_2$–), 29.42, 29.38, 29.35, 26.19, 22.69, 14.03 (–*C*H$_3$) ppm. HRMS (m/z): [M]+Li$^+$-calcd. for $C_{60}H_{66}O_8$, 914.476; found 914.476. Anal. Calcd. for $C_{60}H_{66}O_8 \cdot H_2O$: C, 77.22; H, 7.34. Found: C, 77.68; H, 7.42.

1,4-Didecyloxy-2,5-bis{4-[4-(*rac*-glycero-1)phenylethynyl]phenylethynyl}benzene (H10): Synthesized according to P3 from **5H10** (200 mg, 0.20 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{64}H_{74}O_8$, *M* = 970.54 g/mol, yield: 153 mg (81%), ^{1}H-NMR (400 MHz, pyridine-d_5) δ 7.80 – 7.74 (m, 4H, Ar–*H*), 7.72 – 7.67 (m, 4H, Ar–*H*), 7.67 – 7.62 (m, 4H, Ar–*H*), 7.49 (s, 2H, Ar–*H*), 7.14 – 7.06 (m, 4H, Ar–*H*), 6.94 (br, 2H, –O*H*), 6.56 (br, 2H, –O*H*), 4.61 – 4.54 (m, 2H, –OC*H*–), 4.52 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 4.3 Hz, 2H, –OC*H*$_2$–), 4.43 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 6.3 Hz, 2H, –OC*H*$_2$–), 4.28 – 4.19 (m, 4H, –OC*H*$_2$–), 4.14 (t, ^3J(H,H) = 6.4 Hz, 4H, –OC*H*$_2$–), 1.96 – 1.84 (m, 4H, –C*H*$_2$–), 1.68 – 1.55 (m, 4H, –C*H*$_2$–), 1.45 – 1.16 (m, 24H, –C*H*$_2$–), 0.89 (t, ^3J(H,H) = 6.9 Hz, 6H, –C*H*$_3$) ppm. ^{13}C-NMR (101 MHz, pyridine-d_5) δ 161.56 (–O*C*H$_2$–), 155.62 (–O*C*H$_2$–), 134.87 (*C*$_{Ar}$–H), 133.33 (*C*$_{Ar}$–H), 133.25, 118.78, 116.68, 116.46, 115.85, 96.72 (—C≡C—), 93.95 (—C≡C—), 90.41 (—C≡C—), 89.81 (—C≡C—), 72.62 (HO*C*H$_2$–), 72.36, 71.06, 69.11, 65.53, 33.39 (–*C*H$_2$–), 31.25, 31.11, 30.97, 30.90, 27.73, 27.09, 24.23, 15.57 (–*C*H$_3$) ppm. HRMS (m/z): [M]+Li$^+$-calcd. for $C_{64}H_{74}O_8Li$, 977.554, found 977.546. Anal. Calcd. for $C_{64}H_{74}O_8 \cdot H_2O$: C, 77.70; H, 7.74. Found: C, 77.65; H, 7.83.

1,4-Dioctadecyloxy-2,5-bis{4-[4-(*rac*-glycero-1)phenylethynyl]phenylethynyl}benzene (H18): Synthesized according to P3 from **5H18** (93 mg, 0.07 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{80}H_{106}O_8$, *M* = 1195.71 g/mol, yield: 20 mg (23%), ^{1}H-NMR (500 MHz, pyridine-d_5) δ 7.74 – 7.69 (m, 4H, Ar–*H*), 7.66 – 7.62 (m, 4H, Ar–*H*), 7.62 – 7.56 (m, 4H, Ar–*H*), 7.43 (s, 2H, Ar–*H*), 7.08 – 7.03 (m, 4H, Ar–*H*), 4.54 – 4.49 (m, 2H, –OC*H*–), 4.46 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 4.4 Hz, 2H, –OC*H*$_2$–), 4.37 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 6.3 Hz, 2H, –OC*H*$_2$–), 4.21 – 4.14 (m, 4H, –OC*H*$_2$–), 4.09 (t, ^3J(H,H) = 6.3 Hz, 4H, –OC*H*$_2$–), 1.89 – 1.80 (m, 4H, –C*H*$_2$–), 1.62 – 1.53 (m, 4H, –C*H*$_2$–), 1.40 – 1.09 (m, 56H, –C*H*$_2$–), 0.82 (t, ^3J(H,H) = 7.0 Hz, 6H, –C*H*$_3$) ppm. ^{13}C-NMR (126

MHz, pyridine-d_5) δ 160.03 (–O*C*H$_2$–), 154.07 (–O*C*H$_2$–), 135.62 (*C*$_{Ar}$–H), 135.51 (*C*$_{Ar}$–H), 135.42, 135.33, 135.22, 135.13, 135.02, 134.80, 133.33, 131.79, 131.72, 123.61, 123.51, 123.42, 123.22, 123.02, 122.78, 119.42, 115.14, 114.91, 103.99, 95.91 (—C≡C—), 95.20 (—C≡C—), 89.11 (—C≡C—), 88.86 (—C≡C—), 71.39 (HO*C*H$_2$–), 71.08, 70.83, 64.00, 31.85 (–*C*H$_2$–), 29.75, 29.72, 29.66, 29.35, 26.19, 22.67, 14.01 (–*C*H$_3$) ppm. HRMS (m/z): [M]+Cl-calcd. for $C_{80}H_{106}O_8Cl$, 1229.757; found 1229.759.

1,4-Dihexyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(*rac*-glycero-1)phenylethynyl]phenylethynyl}benzene (F6): Synthesized according to P3 from **5F6** (93 mg, 0.07 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{56}H_{50}F_8O_8$, *M* = 1002.34 g/mol, yield: 175 mg (79%), ^{1}H-NMR (400 MHz, pyridine-d_5) δ 7.80 – 7.75 (m, 4H, Ar–*H*), 7.73 – 7.67 (m, 4H, Ar–*H*), 7.50 (s, 2H, Ar–*H*), 4.94 – 4.86 (m, 2H, –OC*H*$_2$–), 4.85 – 4.76 (m, 2H, –OC*H*$_2$–), 4.62 – 4.51 (m, 2H, –OC*H*–), 4.26 – 4.20 (m, 4H, –OC*H*$_2$–), 4.12 (t, ^3J(H,H) = 6.4 Hz, 4H, –OC*H*$_2$–), 1.92 – 1.80 (m, 4H, –C*H*$_2$–), 1.64 – 1.51 (m, 4H, –C*H*$_2$–), 1.39 – 1.25 (m, 8H, –C*H*$_2$–), 0.88 (t, ^3J(H,H) = 7.0 Hz, 6H, –C*H*$_3$) ppm. ^{19}F-NMR (376 MHz, pyridine-d_5) δ -139.28 – -140.26 (m, Ar–*F*), -157.71 – -158.43 (m, Ar–*F*) ppm. ^{13}C-NMR (101 MHz, pyridine-d_5) δ 154.45 (–O*C*H$_2$–), 154.45 (–O*C*H$_2$–), 142.50 (*C*$_{Ar}$–F), 132.45 (*C*$_{Ar}$–F), 132.18 (*C*$_{Ar}$–H), 125.09, 122.13, 117.56, 114.57, 100.26, 97.55 (—C≡C—), 95.24 (—C≡C—), 89.92 (—C≡C—), 77.88 (HO*C*H$_2$–), 72.05, 69.83, 63.84, 31.83 (–*C*H$_2$–), 29.64, 26.12, 22.97, 14.24 (–*C*H$_3$) ppm. HRMS (m/z): [M]+Li$^+$-calcd. for $C_{56}H_{50}F_8O_8Li$, 1009.353, found 1009.355. Anal. Calcd. for $C_{56}H_{50}F_8O_8 \cdot H_2O$: C, 65.83; H, 5.13. Found: C, 65.91; H, 5.06.

1,4-Dioctyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(*rac*-glycero-1)phenylethynyl]phenylethynyl}benzene (F8): Synthesized according to P3 from **5F8** (240 mg, 0.21 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{60}H_{58}F_8O_8$, *M* = 1058.40 g/mol, yield: 160 mg (72%), ^{1}H-NMR (400 MHz, pyridine-d_5) δ 7.84 – 7.79 (m, 4H, Ar–*H*), 7.76 – 7.71 (m, 4H, Ar–*H*), 7.54 (s, 2H, Ar–*H*), 4.97 – 4.90 (m, 2H, –OC*H*$_2$–), 4.88 – 4.80 (m, 2H, –OC*H*$_2$–), 4.64 – 4.56 (m, 2H, –OC*H*–), 4.28 – 4.22 (m, 4H, –OC*H*$_2$–), 4.18 (t, ^3J(H,H) = 6.4 Hz, 4H, –OC*H*$_2$–), 1.99 – 1.86 (m, 4H, –C*H*$_2$–), 1.70 – 1.58 (m, 4H, –C*H*$_2$–), 1.47 – 1.21 (m, 16H, –C*H*$_2$–), 0.91 (t, ^3J(H,H) = 6.9 Hz, 6H, –C*H*$_3$) ppm. ^{19}F-NMR (376 MHz, pyridine-d_5) δ -139.86 – -140.01 (m, Ar–*F*), -158.02 – -158.18 (m, Ar–*F*) ppm. ^{13}C-NMR (126 MHz, pyridine-d_5) δ 154.17 (–O*C*H$_2$–), 132.14 (*C*$_{Ar}$–F), 131.88 (*C*$_{Ar}$–H), 124.78, 121.83, 117.29, 114.30, 94.95 (—C≡C—), 89.62 (—C≡C—), 79.54 (–OH*C*H$_2$–), 77.57, 71.74, 69.56, 63.53, 31.79 (–*C*H$_2$–), 29.41, 29.39, 29.36, 26.20, 22.70, 14.01 (–*C*H$_3$) ppm. HRMS (m/z): [M]+Li$^+$-calcd. for $C_{60}H_{58}F_8O_8Li$, 1065.416; found 1065.415. analysis (calcd. for $C_{60}H_{58}F_8O_8 \cdot H_2O$): C (66.91, 66.83), H (5.61, 5.50). Anal. Calcd. for $C_{60}H_{58}F_8O_8 \cdot H_2O$: C, 66.91; H, 5.61. Found: C, 66.83; H, 5.50.

1,4-Didecyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(*rac*-glycero-1)phenylethynyl]phenylethynyl}benzene (F10): Synthesized according to P3 from **5F10** (230 mg, 0.21 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{64}H_{66}F_8O_8$, *M* = 1114.46 g/mol, yield: 181 mg (77%), ^{1}H-NMR (400 MHz, pyridine-d_5) δ 7.82 – 7.76 (m, 4H,

Ar–*H*), 7.73 – 7.68 (m, 4H, Ar–*H*), 7.51 (s, 2H, Ar–*H*), 4.95 – 4.86 (m, 2H, –OCH_2–), 4.85 – 4.75 (m, 2H, –OCH_2–), 4.62 – 4.52 (m, 2H, –OC*H*–), 4.26 – 4.20 (m, 4H, –OCH_2–), 4.15 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–), 1.97 – 1.85 (m, 4H, –CH_2–), 1.69 – 1.57 (m, 4H, –CH_2–), 1.46 – 1.19 (m, 20H, –CH_2–), 0.89 (t, ^3J(H,H) = 6.9 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (376 MHz, pyridine-d_5) δ -139.88 – -140.00 (m, Ar–*F*), -158.02 – -158.20 (m, Ar–*F*) ppm. ^{13}C-NMR (126 MHz, pyridine-d_5) δ 154.18 (–O*C*H_2–), 132.14 (C_{Ar}–F), 131.88 (C_{Ar}–H), 124.79, 121.83, 117.28, 114.30, 99.94 (—C≡C—), 94.95 (—C≡C—), 89.62 (—C≡C—), 77.60 (HO*C*H_2–), 77.57, 77.55, 76.40, 71.74, 69.56, 63.53, 31.89 (–*C*H_2–), 29.76, 29.62, 29.47, 29.43, 29.40, 26.24, 22.73, 14.04 (–*C*H_3) ppm. HRMS (m/z): [M]+Li^+-calcd. for $C_{64}H_{66}F_8O_8Li$, 1121.478, found 1121.473. Anal. Calcd. for $C_{64}H_{66}F_8O_8 \cdot H_2O$: C, 67.83; H, 6.05. Found: C, 67.54; H, 5.94.

1,4-Didodecyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(*rac*-glycero-1)phenylethynyl]phenyl-ethynyl}benzene (F12): Synthesized according to P3 from **5F12** (210 mg, 0.18 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{68}H_{74}F_8O_8$, *M* = 1170.53 g/mol, yield: 143 mg (72%), ^{1}H-NMR (400 MHz, pyridine-d_5) δ 7.85 – 7.74 (m, 4H, Ar–*H*), 7.75 – 7.66 (m, 4H, Ar–*H*), 7.51 (s, 2H, Ar–*H*), 7.13 (d, ^3J(H,H) = 5.1 Hz, 2H, –O*H*), 6.65 (t, ^3J(H,H) = 5.4 Hz, 2H, –O*H*), 4.96 – 4.86 (m, 2H, –OCH_2–), 4.85 – 4.76 (m, 2H, –OCH_2–), 4.62 – 4.51 (m, 2H, –OC*H*–), 4.23 (t, ^3J(H,H) = 5.2 Hz, 4H, –OCH_2–), 4.16 (pt, ^3J(H,H) = 6.1 Hz, 4H, –OCH_2–), 2.01 – 1.84 (m, 4H, –CH_2–), 1.71 – 1.58 (m, 4H, –CH_2–), 1.50 – 1.18 (m, 32H, –CH_2–), 0.89 (t, ^3J(H,H) = 6.3 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (376 MHz, pyridine-d_5) δ -139.83 – -140.00 (m, Ar–*F*), -158.02 – -158.19 (m, Ar–*F*) ppm. ^{13}C-NMR (126 MHz, pyridine-d_5) δ 154.88 (–O*C*H_2–), 136.25 (C_{Ar}–F), 124.35, 117.98, 115.00 (C_{Ar}–H), 100.65 (—C≡C—), 95.64 (—C≡C—), 90.32 (—C≡C—), 78.27 (HO*C*H_2–), 77.09, 72.44, 70.26, 64.23, 32.61 (–*C*H_2–), 30.47, 30.40, 30.38, 30.17, 30.13, 30.11, 26.94, 23.41 (–*C*H_2–), 14.73 (–*C*H_3) ppm. HRMS (m/z): [M]+Li^+-calcd. for $C_{68}H_{74}F_8O_8Li$, 1177.541; found 1177.534. Anal. Calcd. for $C_{68}H_{74}F_8O_8 \cdot 2H_2O$: C, 67.65; H, 6.37. Found: C, 67.65; H, 6.51.

1,4-Ditetradecyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(*rac*-glycero-1)phenylethynyl]-phenylethynyl}benzene (F14): Synthesized according to P3 from **5F14** (220 mg, 0.17 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{72}H_{82}F_8O_8$, *M* = 1226.59 g/mol, yield: 154 mg (74%), ^{1}H-NMR (400 MHz, pyridine-d_5) δ 7.82 – 7.76 (m, 4H, Ar–*H*), 7.74 – 7.69 (m, 4H, Ar–*H*), 7.51 (s, 2H, Ar–*H*), 4.95 – 4.87 (m, 2H, –OCH_2–), 4.84 – 4.77 (m, 2H, –OCH_2–), 4.63 – 4.52 (m, 2H, –OC*H*–), 4.26 – 4.20 (m, 4H, –OCH_2–), 4.16 (t, ^3J(H,H) = 6.3 Hz, 4H, –OCH_2–), 1.98 – 1.85 (m, 4H, –CH_2–), 1.71 – 1.58 (m, 4H, –CH_2–), 1.49 – 1.20 (m, 40H, –CH_2–), 0.88 (t, ^3J(H,H) = 6.9 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (376 MHz, pyridine-d_5) δ -139.83 – -139.99 (m, Ar–*F*), -158.01 – -158.20 (m, Ar–*F*) ppm. ^{13}C-NMR (101 MHz, pyridine-d_5) δ 152.98 (–O*C*H_2–), 148.79 (C_{Ar}–F), 130.94 (C_{Ar}–H), 130.69, 123.60, 120.63, 116.08, 113.10, 98.76 (—C≡C—), 93.75 (—C≡C—), 88.43 (—C≡C—), 78.34 (HO*C*H_2–), 76.38, 75.20, 70.54, 68.36, 62.33, 30.71 (–*C*H_2–), 28.60, 28.58, 28.52, 28.50, 28.28, 28.23, 28.21, 25.04, 21.52, 12.84 (–*C*H_3). HRMS (m/z): [M]+Li^+-calcd. for $C_{72}H_{82}F_8O_8Li$, 1233.604, found 1233.605. Anal. Calcd. for $C_{72}H_{82}F_8O_8 \cdot 2H_2O$: C, 68.45; H, 6.86. Found: C, 68.65; H, 6.58.

1,4-Dihexadecylloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(*rac*-glycero-1)phenylethynyl]-phenylethynyl}benzene (F16): Synthesized according to P3 from **5F16** (240 mg, 0.17 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{76}H_{90}F_8O_8$, *M* = 1282.85 g/mol, yield: 181 mg (83%), ^{1}H-NMR (500 MHz, pyridine-d_5) δ 7.81 – 7.77 (m, 4H, Ar–*H*), 7.74 – 7.69 (m, 4H, Ar–*H*), 7.51 (s, 2H, Ar–*H*), 4.90 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 4.0 Hz, 2H, –OCH_2–), 4.80 (dd, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 6.3 Hz, 2H, –OCH_2–), 4.61 – 4.52 (m, 2H, –OC*H*–), 4.26 – 4.20 (m, 4H), 4.16 (t, ^3J(H,H) = 6.4 Hz, 4H, –OCH_2–), 1.99 – 1.87 (m, 4H, –CH_2–), 1.71 – 1.59 (m, 4H, –CH_2–), 1.48 – 1.18 (m, 48H, –CH_2–), 0.88 (t, ^3J(H,H) = 6.9 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (470 MHz, pyridine-d_5) δ -138.65 – -138.77 (m, Ar–*F*), -156.85 – -156.97 (m, Ar–*F*) ppm. ^{13}C-NMR (101 MHz, pyridine-d_5) δ 152.98 (–O*C*H$_2$–), 148.78 (–O*C*H$_2$–), 130.94 (C_{Ar}–F), 130.69 (C_{Ar}–H), 123.60, 120.63, 116.08, 113.10, 98.77 (—C≡C—), 96.05 (—C≡C—), 93.75 (—C≡C—), 88.43 (—C≡C—), 76.38 (HO*C*H$_2$–), 76.35, 75.20, 70.53, 68.36, 62.33, 30.71 (–*C*H$_2$–), 28.61, 28.59, 28.58, 28.51, 28.28, 28.23, 28.20, 25.04, 21.51, 12.84 (–*C*H$_2$–). HRMS (m/z): [M]+Li$^+$-calcd. for $C_{76}H_{90}F_8O_8Li$, 1289.666, found 1289.667. Anal. Calcd. for $C_{76}H_{90}F_8O_8 \cdot H_2O$: C, 70.13; H, 7.12. Found: C, 70.24; H, 7.25.

1,4-Dioctadecyloxy-2,5-bis{4-[2,3,5,6-tetrafluoro-4-(*rac*-glycero-1)phenylethynyl]phenyl-ethynyl}benzene (F18): Synthesized according to P3 from **5F18** (240 mg, 0.17 mmol) and PPTS (tip of a spatula) in MeOH/THF (1:1, 30 mL:30 mL). Purification by column chromatography (eluent: $CHCl_3$:MeOH = 9:1). Yellow-greenish solid, $C_{80}H_{98}F_8O_8$, *M* = 1368.76 g/mol, yield: 201 mg (88%), ^{1}H-NMR (400 MHz, pyridine-d_5) δ 7.82 – 7.77 (m, 4H, Ar–*H*), 7.75 – 7.68 (m, 4H, Ar–*H*), 7.51 (s, 2H, Ar–*H*), 4.94 – 4.86 (m, 2H, –OCH_2–), 4.85 – 4.76 (m, 2H, –OCH_2–), 4.62 – 4.52 (m, 2H, –OC*H*–), 4.26 – 4.20 (m, 4H, –OCH_2–), 4.16 (t, ^3J(H,H) = 6.3 Hz, 4H, –OCH_2–), 1.98 – 1.86 (m, 4H, –CH_2–), 1.71 – 1.59 (m, 4H, –CH_2–), 1.51 – 1.19 (m, 56H, –CH_2–), 0.88 (t, ^3J(H,H) = 6.9 Hz, 6H, –CH_3) ppm. ^{19}F-NMR (376 MHz, pyridine-d_5) δ -139.81 – -139.99 (m, Ar–*F*), -158.01 – -158.18 (m, Ar–*F*) ppm. ^{13}C-NMR (101 MHz, pyridine-d_5) δ 152.98 (–O*C*H$_2$–), 148.79 (–O*C*H$_2$–), 130.95 (C_{Ar}–F), 130.69 (C_{Ar}–H), 123.60, 120.63, 116.09, 113.11, 93.75 (—C≡C—), 88.43 (—C≡C—), 76.38 (HO*C*H$_2$–), 70.53, 68.36, 62.33, 30.70 (–*C*H$_2$–), 28.60, 28.58, 28.50, 28.27, 28.23, 28.19, 25.04, 21.51, 12.84 (–*C*H$_3$) ppm. HRMS (m/z): [M]+Li$^+$-calcd. for $C_{80}H_{98}F_8O_8Li$, 1345.729; found 1345.729. Anal. Calcd. for $C_{80}H_{98}F_8O_8 \cdot H_2O$: C, 70.77; H, 7.42. Found: C, 70.55; H, 7.11.

3. Representative NMR spectra

3.1 NMR spectra of H10

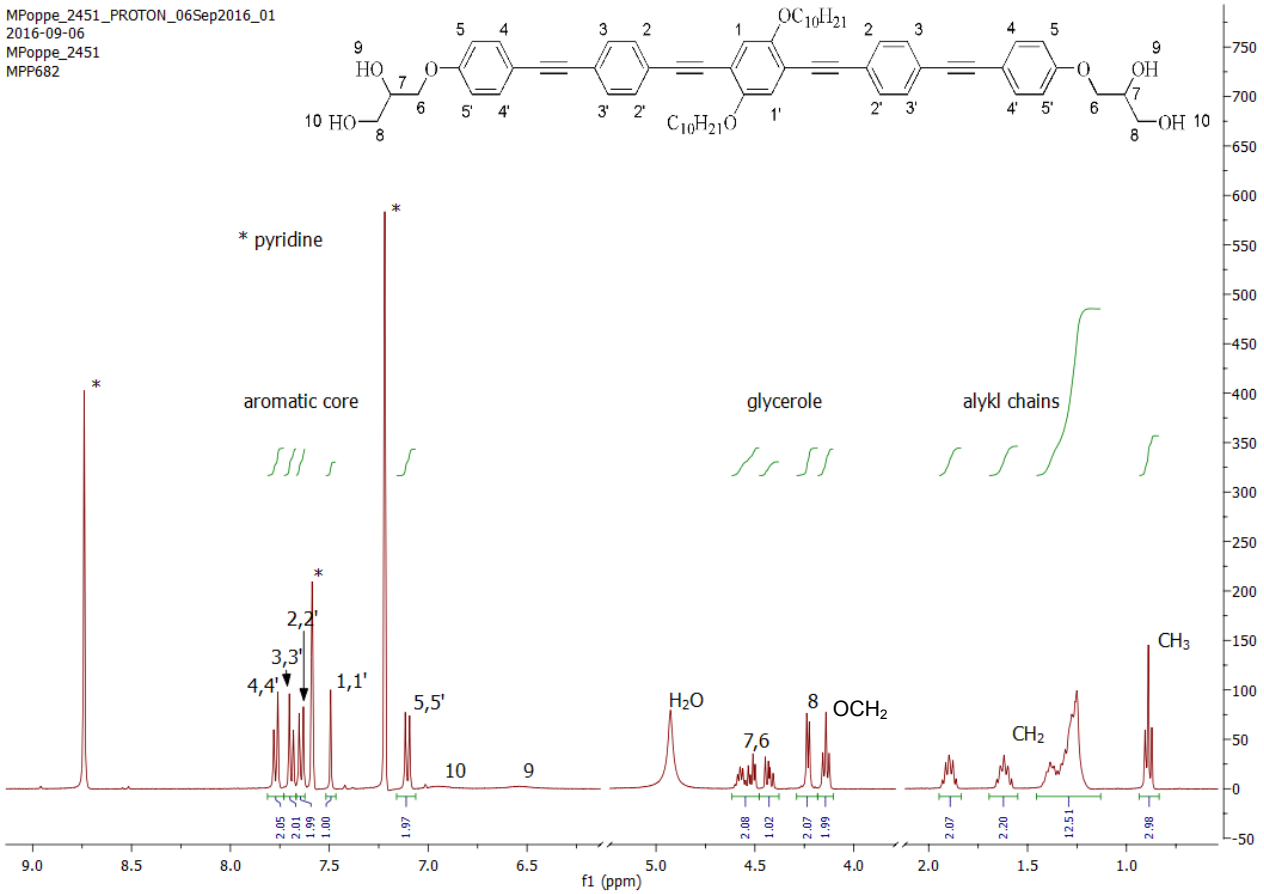


Figure S8: ^{1}H-NMR spectra of **H10** (400 MHz, pyridine-d_5).

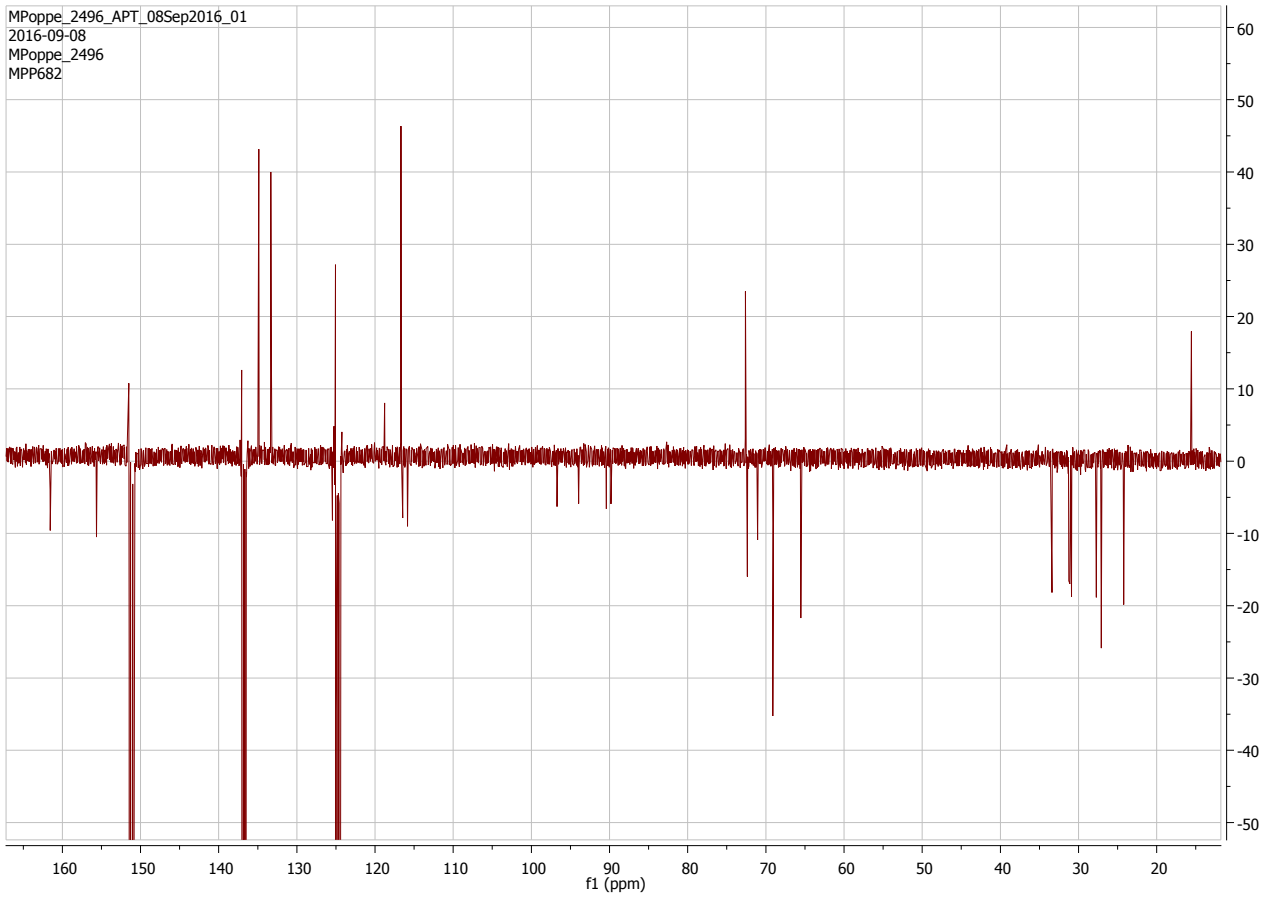


Figure S9: ^{13}C-NMR (APT) spectra of **H10** (101 MHz, pyridine-d_5).

3.2 NMR spectra of F10

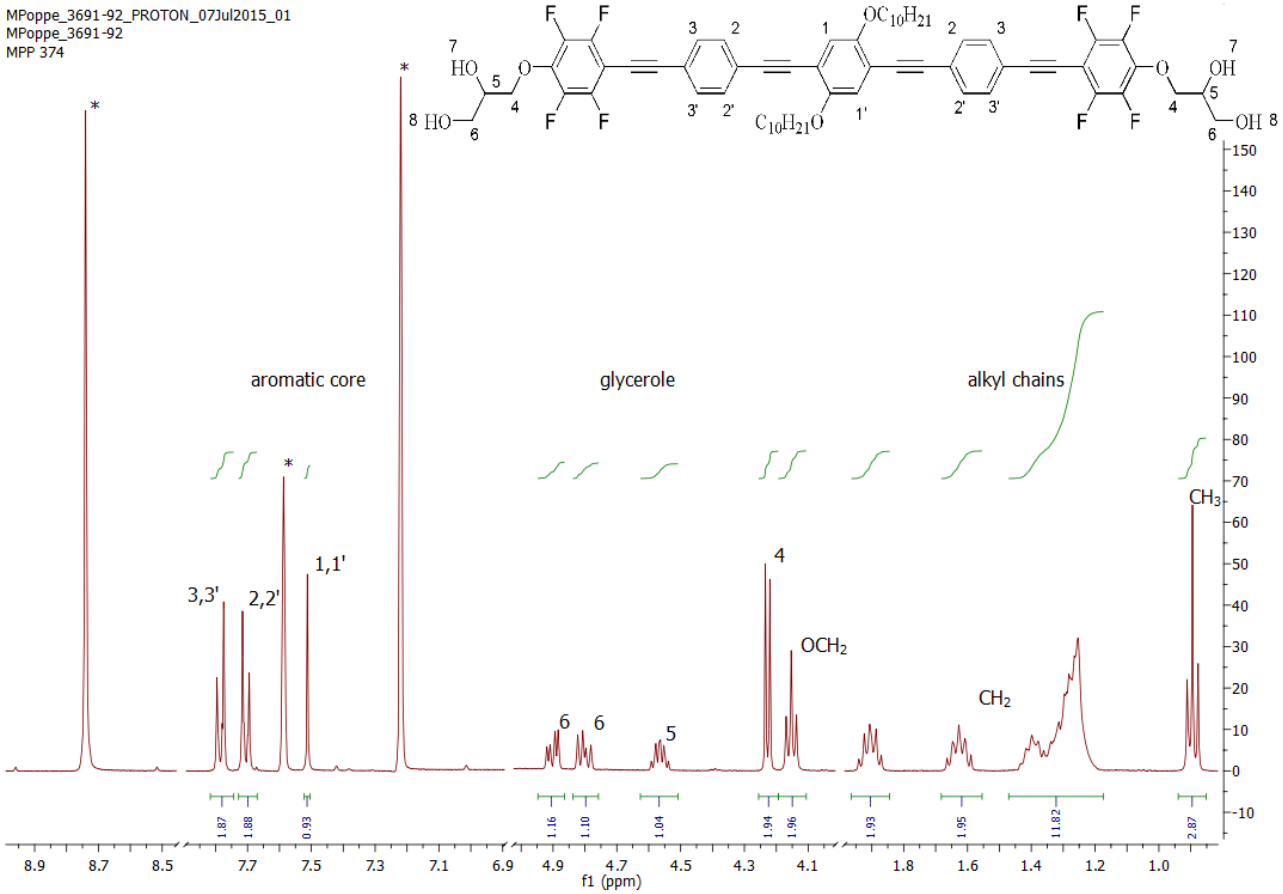


Figure S10: ^{1}H-NMR spectra of **F10** (400 MHz, pyridine-d_5).

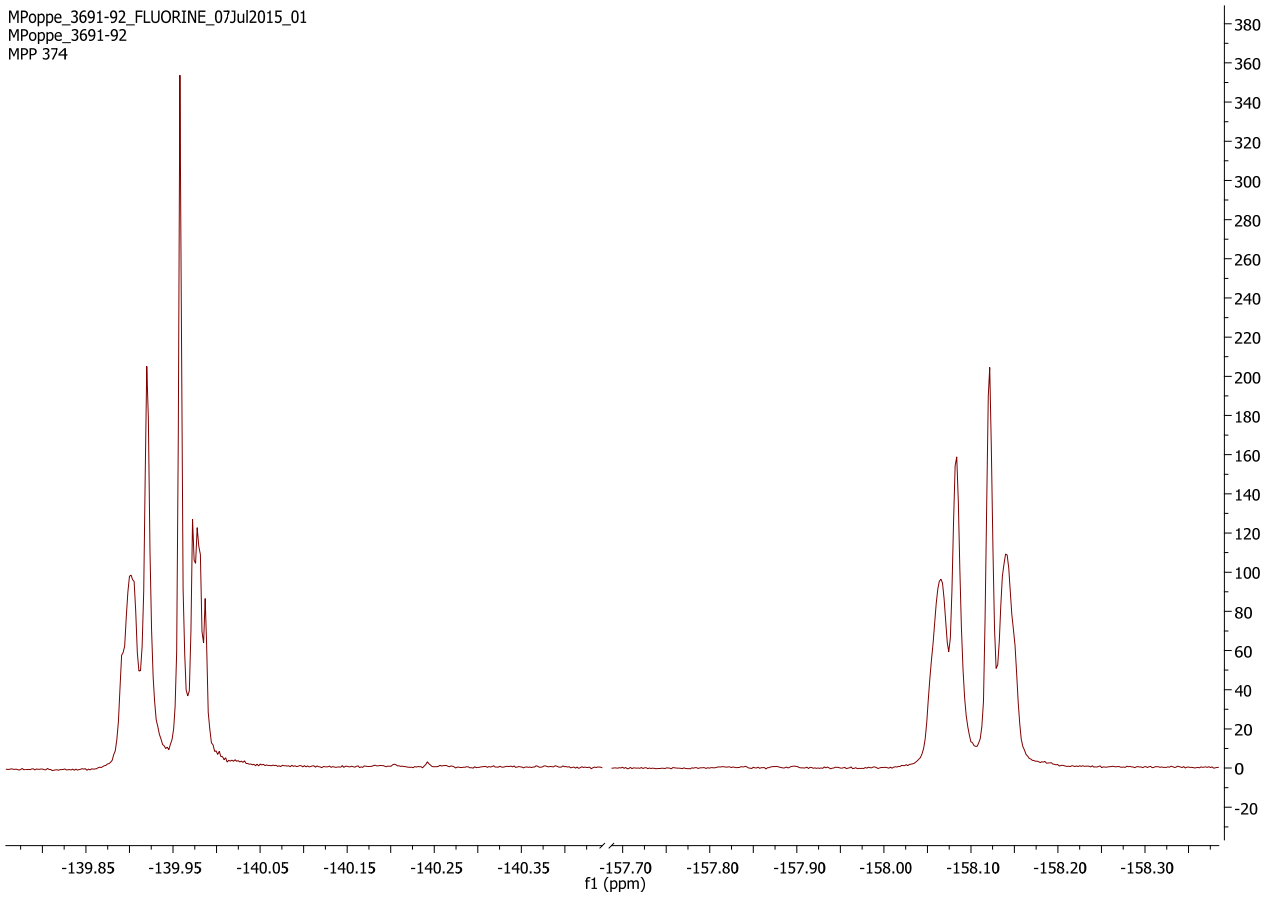


Figure S11: ^{19}F-NMR spectra of **F10** (176 MHz, pyridine-d_5).

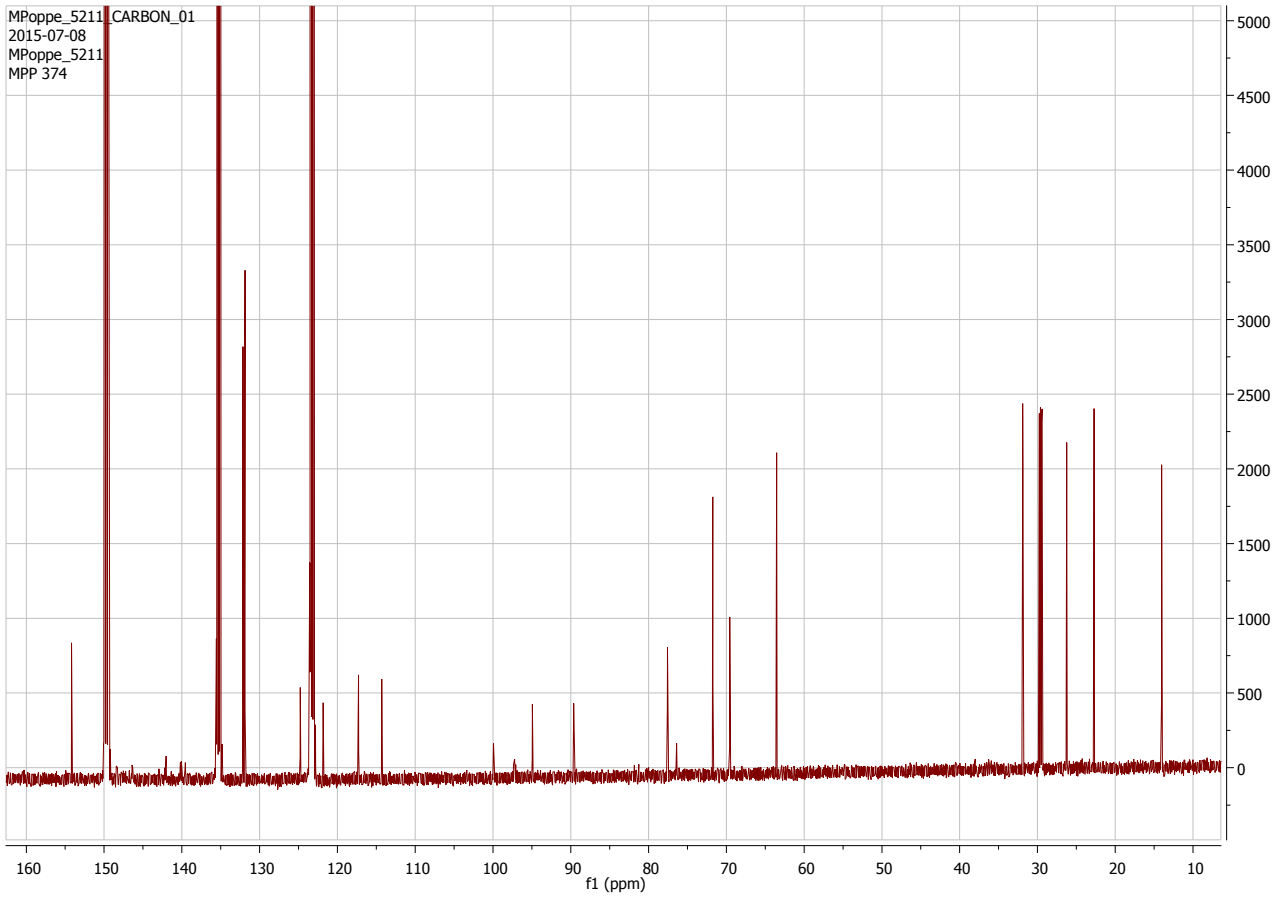


Figure S12: ^{13}C-NMR spectra of **F10** (101 MHz, pyridine-d_5).

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