Supporting Information

Incompatibility-driven Self-organization in Polycatenar Liquid Crystals bearing both Hydrocarbon and Fluorocarbon Chains

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Methods

Nuclear Magnetic Resonance (NMR)

^{1}H NMR spectra were obtained on Jeol ECS400 and ECX400 with a field strength 400 MHz, equipped with an sample changer.

Polarised Optical Microscopy (POM)

Liquid crystal textures were observed using an Olympus BX50 Optical Microscope equipped with a Linkam Scientific LTS350 heating stage, Linkam LNP2 cooling pump and a Linkam TMS92 controller.

Differential Scanning Calorimetry (DSC)

Calorimetry scans were run on a Mettler Toledo DSC822^{e}, (running on a Star^{e} software) equipped with a TSO801R0 Sample Robot and calibrated using pure indium. Samples were run at heating/cooling rates of 5 °C min^{-1}. DSC data mentioned in the article are onset temperatures.

Elemental Analysis

Analysis was carried out on an Exeter Analytical Inc CE 440 Elemental Analyzer and a Sartorius SE2 analytical balance by Dr Graeme McAllister at the University of York.

Small-Angle X-ray Scattering (SAXS)

The powdered sample was filled in Lindemann capillaries of 1 mm diameter and 10 µm wall thickness. The SAXS patterns were recorded by transmission diffraction. A linear monochromatic Cu K_α beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (600 W) equipped with a bent quartz monochromator (both generator and monochromator were manufactured by Inel). The first set of diffraction patterns was recorded on Image Plate (scanned by STORM 820 from Molecular Dynamics with 50 µm resolution). Periodicities up to 90 Å can be measured, and the sample temperature is controlled within ±0.3°C from 20 to

350°C. The second set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer, for which the sample temperature is controlled within ±0.05°C from 20 to 200°C; periodicities up to 60 Å can be measured.

Decription of the Synthetic Chemistry

NB: A simpler labelling for the final compounds is adopted in the manuscript. The correspondence key is as follows:

Supporting Information	Manuscript
11	HH/H
12a	HH/F
12b	HH/F-b
13a	HH/HH
13b	HH/HH-b
14	FF/FF
15	HH/FF
16	HF/HF
17	HH/HF

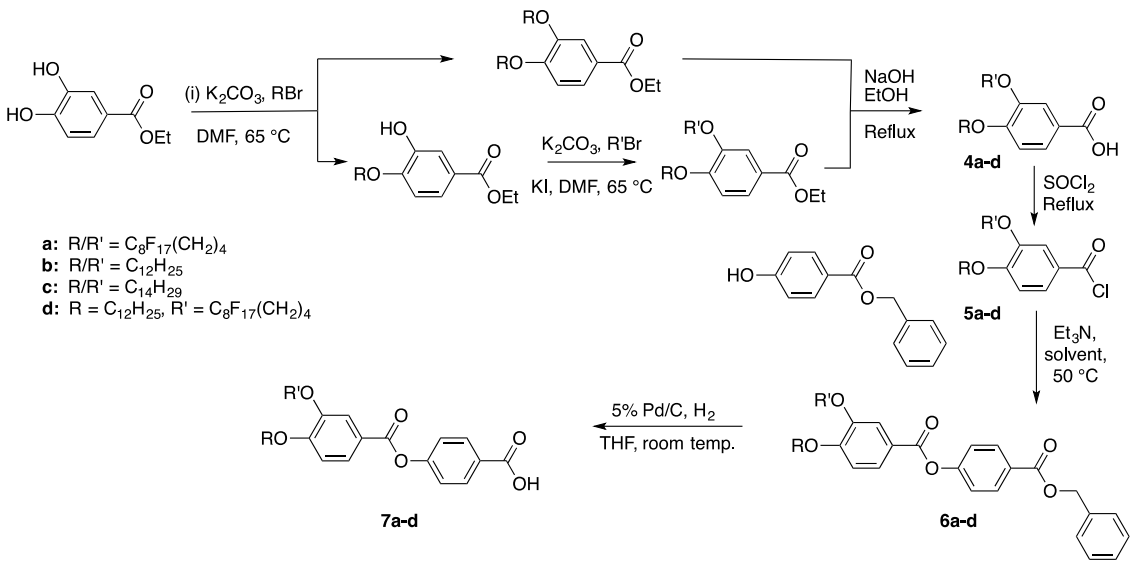
The unsymmetric nature of many of the target compounds led to a modular approach to the synthetic chemistry, which is shown in Schemes S1 and 2 (main manuscript). Note that the compound labelling in the Supporting Information is self-consistent and the correlation between the labels of the final compounds here and in the main text is given below when the synthesis of the final product is described. Thus, symmetric and unsymmetric dialkoxybenzoic acids (**4**) were converted to dialkoxybenzoyloxybenzoic acids (**7**), which could then be used to make the symmetric targets **13**, **14** and **16**. Unsymmetric targets (**11**, **12**, **15** and **17**) required 1,4-hydroquinone to be monoesterified with **7** prior to attaining the final compound, which was also helpful synthetically as the more heavily fluorinated compounds were appreciably less soluble.

Building Blocks

The semiperfluorinated alkyl chain was introduced using a tetramethylene spacer following an approach shown below[1-3] (Scheme S2); overall yield for the sequence was 60-62%. 1-Bromoperfluorooctane and 1-bromoperfluorodecane were used in these reactions, giving chains with an overall carbon length of 12 (compound **3a**) and 14 (compound **3b**), respectively: the perfluorooctyl chain was the shortest used as this is often held to be the minimum chain length required for 'fluorous' behavior to be seen.[4]

Aromatic Building Blocks

3,4-Dialkoxybenzoic acids (**4a-d**) and 3,4-dialkoxybenzoyloxybenzoic acids (**7a-d**) were prepared according to standard procedures of esterification as shown in Scheme 1 and described in the Supporting Information. Where semiperfluorinated chains were used, the solubility of any compounds in conventional solvents was reduced and so, according to methods reported by Percec,[5] trifluoromethylbenzene was used as the solvent. The unsymmetric material **4d** was obtained by taking advantage of the more acidic hydrogen of the 4-hydroxy group. Thus, reaction of ethyl 3,4-dihydroxybenzoate with one molar equivalent of 1-bromododecane gave ethyl 3-hydroxy-4-dodecyloxybenzoate (56% yield), which was then reacted with the bromo semiperfluoroalkane under more forcing conditions to give product **4d** (95% yield for this step). Primary characterization relied on ^{1}H NMR spectroscopy, which showed an AMX splitting pattern for the dialkoxy-substituted ring and an AA'XX' pattern for the 1,4-disubstituted ring.



Scheme S1. The synthetic approach to immediate precursors of the target tetracatenar mesogens.*

Synthesis of the Target Compounds

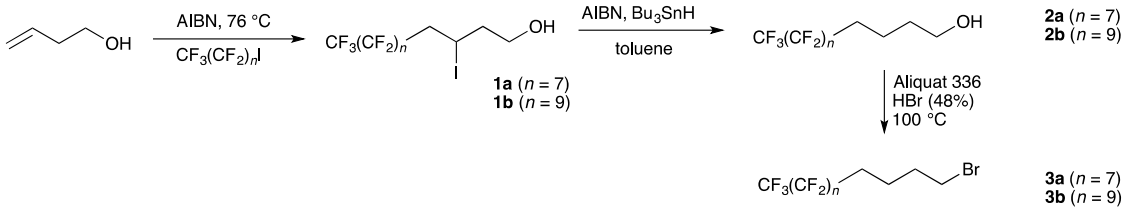
With the different starting materials in hand, preparation of the three families of target materials required simple esterification (Scheme 2 – main manuscript). That said, all reactions at this stage where the reagent/product carried a semiperfluoroalkyl chain required care owing to their low solubility, even when using trifluoromethylbenzene as solvent. Indeed, the solubility of the acids **7a** and **7d** was particularly low so that they were converted into the corresponding acid chlorides prior to esterification.[6,7]

The 3,4-substituted benzoyloxybenzoic acids (**7**) so obtained could then be used for the preparation of symmetric, tetracatenar compounds (**13**, **14**, **16**) by carrying out an esterification using two molar equivalents of the acid and one of 1,4-hydroquinone, carried out under nitrogen (Scheme 2). However, for the synthesis of the unsymmetric materials, namely tricatenar compounds **11** and **12** and tetracatenar compounds **15** and **17**, it was

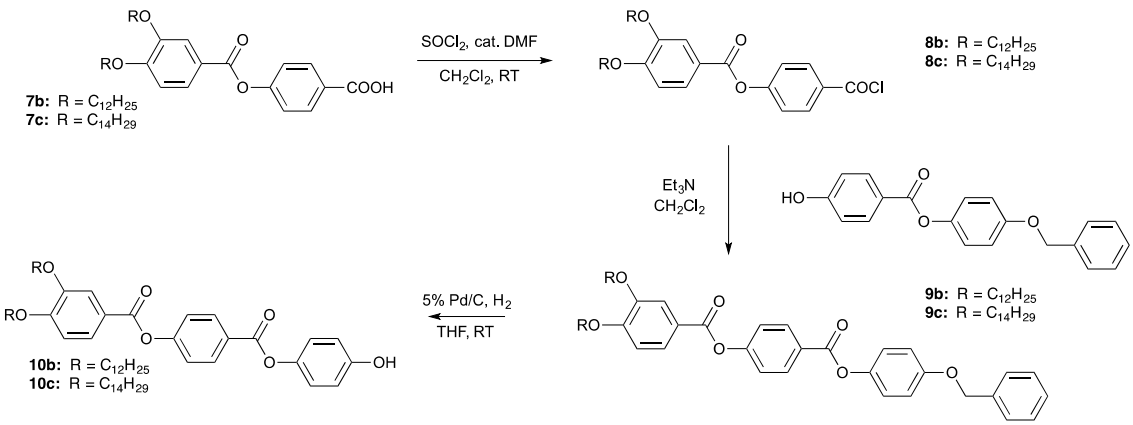
* 4-Monosubstituted benzoic acids and benzoyloxybenzoic acids were made using the same chemistry: $C_8F_{17}(CH_2)_4OC_6H_4COOH$ (**18a**); $C_{10}F_{21}(CH_2)_4OC_6H_4COOH$ (**18b**); $C_8F_{17}(CH_2)_4OC_6H_4COOC_6H_4COOH$ (**19a**); $C_{10}F_{21}(CH_2)_4OC_6H_4COOC_6H_4COOH$ (**19b**); $C_{12}H_{25}OC_6H_4COOC_6H_4COOH$ (**19c**).

necessary first to prepare 3,4-dialkoxybenzoyloxybenzoyloxyphenols (*O*-monosubstituted hydroquinones, **10b** and **10c** – Scheme S3 in the Supporting Information). This could then be coupled with a 4-alkoxybenzoyloxybenzoic acid or a 4-semiperfluoroalkoxybenzoyloxybenzoic acid (prepared in a manner analogous to **7**) to give **11** or **12**, respectively, or with **7a** or 3-(semiperfluoroalkoxy)-4-alkoxybenzoyloxybenzoic acid **7d** to give the target compounds **15** or **17**, respectively (Scheme 2).

Synthesis

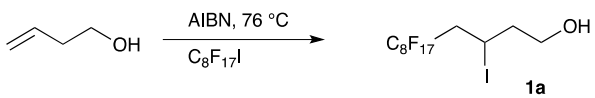


Scheme S2. Synthetic route to the semiperfluoroalkyl bromides.



Scheme S3. Synthesis of *O*-monosubstituted hydroquinones **10b** and **10c**.

Compound 1a:

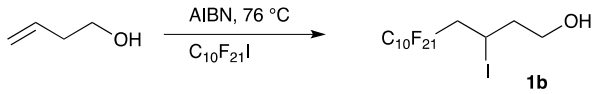


A mixture of 3-buten-1-ol (0.845 g, 11.73 mmol) and perfluorooctyliodide $C_8F_{17}I$ (5.285 g, 9.68 mmol) was placed in a Schlenk flask, and degassed successively three times using the freeze-

pump-thaw method. AIBN (0.079 g, 0.48 mmol, 5 mol-%) was added to the reaction mixture under a flow of nitrogen. The tube was then sealed and the mixture heated at 76 °C for 2h. More AIBN (0.079 g, 0.48 mmol, 5 mol-%) was added under a flow of nitrogen afterwards. The reaction was heated once more at 76 °C for 3h. The flask was then cooled to room temperature and a yellow solid was obtained. The crude compound was crystallised from hexane, and the pale yellow solid collected and dried under high vacuum.[1,3]

Yield: 95.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.57-4.50 (m, 1H; C*H*I), 3.93-3.76 (m, 2H; C*H*$_2$OH), 3.06-2.80 (m, 2H; C*H*$_2$CF$_2$), 2.11-1.97 (m, 2H; CH$_2$C*H*$_2$CHI), 1.43 (br s, 1H; O*H*).

Compound 1b:

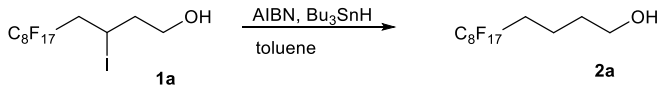


1b

This procedure is analogous to the one above; 3-buten-1-ol (0.845 g, 11.73 mmol), and perfluorodecyliodide $C_{10}F_{21}I$ (6.252 g, 9.68 mmol), AIBN (0.079 g, 0.48 mmol, 5 mol-%) for the first addition, and AIBN (0.079 g, 0.48 mmol, 5 mol-%) for the second addition.

Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.57-4.50 (m, 1H; C*H*I), 3.93-3.76 (m, 2H; C*H*$_2$OH), 3.06-2.80 (m, 2H; C*H*$_2$CF$_2$), 2.11-1.96 (m, 2H; CH$_2$C*H*$_2$CHI), 1.43 (br s, 1H; O*H*).

Compound 2a:

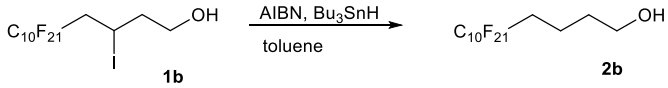


1a **2a**

Compound **1a** (5.246 g, 8.49 mmol) was dissolved in anhydrous toluene (50 cm^3, purged with nitrogen for 15 min) in a two-necked round-bottom flask. Bu_3SnH (4.60 cm^3, 17.06 mmol) and AIBN (0.139 g, 0.85 mmol, 10 mol-%) were then added under nitrogen flow at room temperature. The reaction mixture was stirred at 70 °C for 4h and then allowed to cool down. The solvent was then evaporated at the rotary evaporator and the solid filtered off. The mixture was washed with cold petroleum ether (5 cm^3) to remove the Bu_3SnH/Bu_3SnI residue and dried under high vacuum.[1,3]

Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73-3.68 (m, 2H; C*H*$_2$OH), 2.18-2.05 (m, 2H; C*H*$_2$CF$_2$), 1.76-1.62 (m, 4H; overlapped C*H*$_2$C*H*$_2$CH$_2$CF$_2$), 1.32 (t, *J* = 5.1 Hz, 1H; O*H*).

Compound 2b:

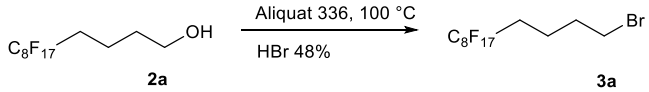


1b **2b**

This procedure is analogous to the one above; prepared from **1b** (6.095 g, 8.49 mmol), tributyltin hydride (4.60 cm^3, 17.06 mmol) and AIBN (0.139 g, 0.85 mmol, 10 mol-%).

Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73-3.68 (m, 2H; C*H*$_2$OH), 2.18-2.05 (m, 2H; C*H*$_2$CF$_2$), 1.76-1.62 (m, 4H; overlapped C*H*$_2$C*H*$_2$CH$_2$CF$_2$), 1.32 (t, *J* = 5.1 Hz, 1H; O*H*).

Compound 3a:

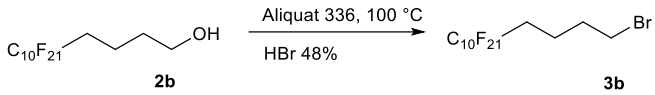


2a **3a**

A mixture of the alcohol **2a** (0.836 g, 1.70 mmol), Aliquat 336 (0.028 g, 0.07 mmol, 4 mol-%) and hydrobromic acid (48% aqueous solution, 0.55 cm^3, 4.70 mmol) was heated at 100 °C while stirring for 12h. The mixture was cooled to room temperature, diluted with diethyl ether (15 cm^3) and water (10 cm^3) and the upper (organic) layer was then collected. The diethyl ether was removed at the rotary evaporator and the solid residue subjected to a pad of silica (using hexane : ethyl acetate = 5 : 1 as eluent). The hexane-ethyl acetate mixture was then evaporated from the solution at the rotary evaporator, leading to a white solid. Crystallisation from methanol yielded the bromo compound **3a** as white needle-like crystals.[2,5]

Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.42 (t, *J* = 6.5 Hz, 2H; C*H*$_2$Br), 2.16-1.74 (m, 6H; overlapped CF$_2$C*H*$_2$C*H*$_2$C*H*$_2$).

Compound 3b:

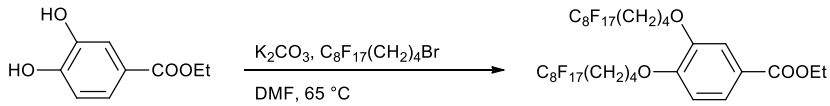


2b 3b

This procedure is analogous to the one above; prepared from **2b** (1.006 g, 1.70 mmol), Aliquat 336 (0.028 g, 0.07 mmol, 4 mol-%) and hydrobromic acid (48% aqueous solution, 0.55 cm^3, 4.70 mmol).

Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.42 (t, *J* = 6.5 Hz, 2H; C*H*$_2$Br), 2.16-1.74 (overlapped peaks, 6H; $CF_2CH_2CH_2CH_2$).

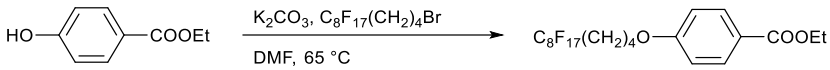
Precursor compound for 4a:



Ethyl 3, 4-dihydroxybenzoate (0.446 g, 2.45 mmol) was dissolved in dry DMF (25 cm^3), and K_2CO_3 (1.382 g, 10 mmol) was added and stirred for 15 min. The bromo compound **3a** (2.919 g, 5.27 mmol) was then added. The mixture was heated at 65 ^{o}C for 12h and cooled to room temperature. Cold water (25 cm^3) was then poured in the solution and the resulting white precipitate was collected after filtration, washed with water (10 cm^3), acetone (5 cm^3) and dried under high vacuum.

Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 1.9 and 8.4 Hz, 1H; arom. H-6), 7.54 (d, *J* = 2.0 Hz, 1H; arom. H-2), 6.87 (d, *J* = 8.5 Hz, 1H; arom. H-5), 4.30 (q, *J* = 7.2 Hz, 2H; $COOCH_2CH_3$), 4.11 (t, *J* = 5.6 Hz, 4H; 2 OCH_2CH_2), 2.24-2.11 (m, 4H; overlapped 2 CH_2CF_2), 1.95-1.82 (m, 8H; overlapped 2 $CH_2CH_2CH_2CH_2CF_2$), 1.38 (t, *J* = 7.2 Hz, 3H; $COOCH_2CH_3$).

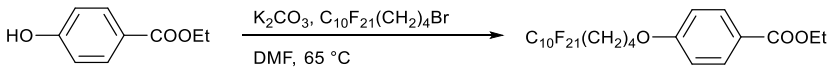
Precursor compound for 18a:



The procedure above was repeated starting from ethyl 4-hydroxybenzoate (0.830 g, 5 mmol), K_2CO_3 (1.382 g, 10 mmol) and bromo compound **3a** (2.825 g, 5.10 mmol).

Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (AA'XX', *J* = 8.9 Hz, 2H; arom. H-3 and arom. H-5), 6.90 (AA'XX', *J* = 8.9 Hz, 2H; arom. H-2 and H-6), 4.34 (q, *J* = 7.2 Hz, 2H; $COOCH_2CH_3$), 4.05 (t, *J* = 5.9 Hz, 2H; OCH_2CH_2), 2.23-2.10 (m, 2H; CH_2CF_2), 1.94-1.79 (m, 4H; overlapped $OCH_2CH_2CH_2CH_2CF_2$), 1.38 (t, *J* = 7.1 Hz, 3H; $COOCH_2CH_3$).

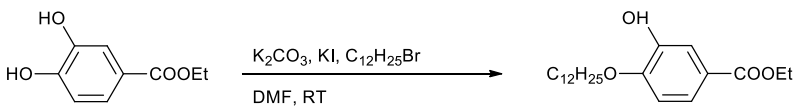
Precursor compound for 18b:



The procedure above was repeated starting from ethyl 4-hydroxybenzoate (0.830 g, 5 mmol), K_2CO_3 (1.382 g, 10 mmol) and bromo compound **3b** (3.335 g, 5.10 mmol).

Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (AA'XX', *J* = 8.9 Hz, 2H; arom. H-3 and arom. H-5), 6.90 (AA'XX', *J* = 8.9 Hz, 2H; arom. H-2 and H-6), 4.34 (q, *J* = 7.2 Hz, 2H; $COOCH_2CH_3$), 4.05 (t, *J* = 5.9 Hz, 2H; OCH_2CH_2), 2.23-2.10 (m, 2H; CH_2CF_2), 1.94-1.79 (m, 4H; overlapped $OCH_2CH_2CH_2CH_2CF_2$), 1.38 (t, *J* = 7.1 Hz, 3H; $COOCH_2CH_3$).

Precursor compound for 4d (step 1):

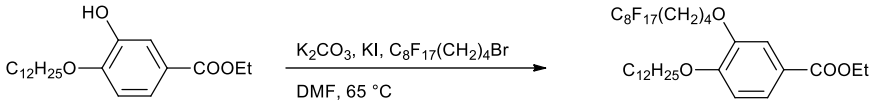


Ethyl 3, 4-dihydroxybenzoate (0.446 g, 2.45 mmol) was dissolved in dry DMF (25 cm^3), and K_2CO_3 (1.379 g, 10 mmol) and KI (1.659 g, 10 mmol) were added and stirred for 15 min. The dodecyl bromide (0.670 g, 2.70 mmol) was then added. The mixture was stirred at room temperature for 12h. Cold water (25 cm^3) was then poured in the solution, and the mixture

cooled on a water-ice bath. The resulting precipitate was collected after filtration, washed with water (10 cm^3), acetone (5 cm^3) and dried under high vacuum.

Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.58 (m, 2H; overlapped arom. H-6 and arom. H-2), 6.85 (d, *J* = 8.8 Hz, 1H; arom. H-5), 5.64 (s, 1H; O*H*), 4.33 (q, *J* = 7.2 Hz, 2H; $COOCH_2CH_3$), 4.09 (t, *J* = 6.8 Hz, 2H; OCH_2CH_2), 1.87-1.80 (m, 2H; OCH_2CH_2), 1.50-1.20 (m, 21H; overlapped $OCH_2CH_2(CH_2)_9CH_3$ and $COOCH_2CH_3$), 0.88 (t, *J* = 6.8 Hz, 3H; $O(CH_2)_{11}CH_3$).

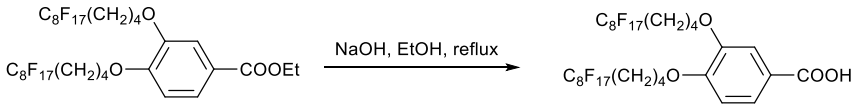
Precursor compound for 4d (step 2):



Ethyl ester (0.858 g, 2.45 mmol) was dissolved in dry DMF (25 cm^3), and K_2CO_3 (1.379 g, 10 mmol) and KI (1.659 g, 10 mmol) were added and stirred for 15 min. The bromo compound **3a** (1.496 g, 2.70 mmol) was then added. The mixture was heated at 65 °C for 12h and cooled to room temperature. Cold water (25 cm^3) was then poured in the solution and the resulting precipitate was collected after filtration, washed with water (10 cm^3), acetone (5 cm^3) and dried under high vacuum.

Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 1.6 and 8.5 Hz, 1H; arom. H-6), 7.53 (d, *J* = 2.0 Hz, 1H; arom. H-2), 6.87 (d, *J* = 8.8 Hz, 1H; arom. H-5), 4.34 (q, *J* = 7.2 Hz, 2H; $COOCH_2CH_3$), 4.09 (t, *J* = 6.0 Hz, 2H; $OCH_2(CH_2)_3(CF_2)_7CF_3$), 4.03 (t, *J* = 6.8 Hz, 2H; $OCH_2(CH_2)_{10}CH_3$), 2.26-2.00 (m, 2H; CH_2CF_2), 1.97-1.77 (m, 6H; overlapped $OCH_2(CH_2)_2CH_2CF_2$ and $OCH_2CH_2(CH_2)_9CH_3$), 1.50-1.20 (m, 21H; overlapped $OCH_2CH_2(CH_2)_9CH_3$ and $COOCH_2CH_3$), 0.87 (t, *J* = 7.2 Hz, 3H; $O(CH_2)_{11}CH_3$).

Compound 4a:

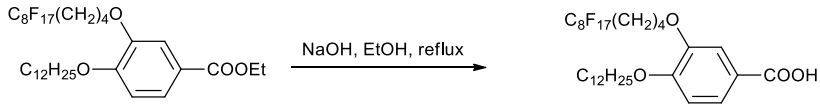


4a

The ethyl ester (2.712 g, 2.40 mmol) was added to a mixture of EtOH (50 cm^3) and NaOH 10 N aqueous solution (3 cm^3). The suspension was refluxed for 12h for the hydrolysis to be complete, and then allowed to cool to room temperature. The reaction mixture was kept on an ice bath and brought to pH 4 by dropwise addition of concentrated HCl solution. The resulting white precipitate was collected by suction filtration, sequentially washed with water (2 × 5 cm^3) and dried under high vacuum.

Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOH$): δ 7.85 (dd, *J* = 2.0 and 8.6 Hz, 1H; arom. H-6), 7.68 (d, *J* = 2.0 Hz, 1H; arom. H-2), 7.02 (d, *J* = 8.8 Hz, 1H; arom. H-5), 4.22 (q, *J* = 6.0 Hz, 4H; 2 OCH_2CH_2), 2.22-2.09 (m, 4H; overlapped 2 CH_2CF_2), 1.99-1.79 (m, 8H; overlapped 2 $OCH_2(CH_2)_2CH_2CF_2$).

Compound 4d:

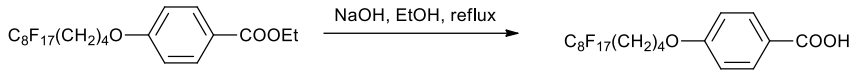


4d

The procedure above was repeated, starting from the ethyl ester (1.978 g, 2.40 mmol) which was hydrolysed with 3 cm^3 of 10 N NaOH aqueous solution in 50 cm^3 of EtOH.

Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOH$): δ 7.81 (dd, *J* = 2.0 and 8.5 Hz, 1H; arom. H-6), 7.61 (d, *J* = 2.0 Hz, 1H; arom. H-2), 6.99 (d, *J* = 8.4 Hz, 1H; arom. H-5), 4.19-4.13 (m, 4H; overlapped $OCH_2(CH_2)_{10}CH_3$ and $OCH_2(CH_2)_3(CF_2)_7CF_3$), 2.22-2.09 (m, 2H; CH_2CF_2), 1.96-1.77 (m, 6H; overlapped $OCH_2(CH_2)_2CH_2CF_2$ and $OCH_2CH_2(CH_2)_9CH_3$), 1.47-1.19 (m, 18H; overlapped $OCH_2CH_2(CH_2)_9CH_3$), 0.87 (t, *J* = 7.2 Hz, 3H; $O(CH_2)_{11}CH_3$).

Compound 18a:

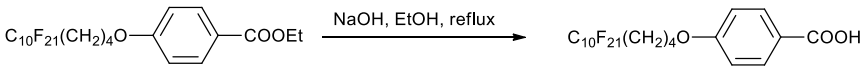


18a

The procedure above was repeated, starting from the ethyl ester (1.536 g, 2.4 mmol) which was hydrolysed with 3 cm^3 of 10 N NaOH aqueous solution in 50 cm^3 of EtOH.

Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOH$): δ 8.03 (AA'XX', *J* = 8.8 Hz, 2H; arom. H-2 and arom. H-6), 6.93 (AA'XX', *J* = 8.8 Hz, 2H; arom. H-3 and H-5), 4.06 (t, *J* = 5.8 Hz, 2H; OCH_2CH_2), 2.24-2.11 (m, 2H; CH_2CF_2), 1.97-1.80 (m, 4H; overlapped $CH_2CH_2CF_2$).

Compound 18b:

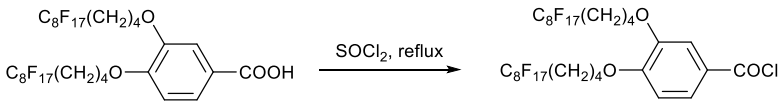


18b

The procedure above was repeated, starting from the ethyl ester (1.78 g, 2.4 mmol) which was hydrolysed with 3 cm^3 of 10 N NaOH aqueous solution in 50 cm^3 of EtOH.

Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOH$): δ 8.03 (AA'XX', *J* = 8.8 Hz, 2H; arom. H-2 and arom. H-6), 6.93 (AA'XX', *J* = 8.8 Hz, 2H; arom. H-3 and H-5), 4.10 (t, *J* = 5.9 Hz, 2H; OCH_2CH_2), 2.24-2.11 (m, 2H; CH_2CF_2), 1.97-1.80 (m, 4H; overlapped $CH_2CH_2CF_2$).

Compound 5a:

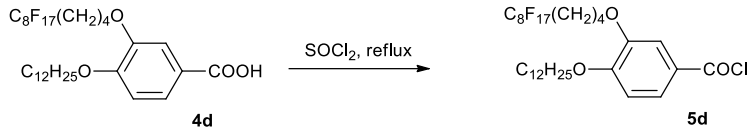


4a **5a**

Thionyl chloride (5 cm^3) was added in excess to a flask containing the benzoic acid **4a** (2.204 g, 2 mmol). The mixture was stirred at 40 °C under nitrogen for 1h and refluxed for 3h at 80 °C. The unreacted thionyl chloride was evaporated at the rotary evaporator and the solid obtained was dried under high vacuum for several hours without further purification.[6,7]

Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 2.2 and 8.6 Hz, 1H; arom. H-6), 7.53 (d, *J* = 1.7 Hz, 1H; arom. H-2), 6.91 (d, *J* = 8.6 Hz, 1H; arom. H-5), 4.13 (t, *J* = 5.7 Hz, 4H; 2 OC*H*$_2$CH$_2$), 2.25-2.11 (m, 4H; overlapped 2 C*H*$_2$CF$_2$), 1.98-1.82 (m, 8H; overlapped 2 OCH$_2$(C*H*$_2$)$_2$CH$_2$CF$_2$).

Compound 5d:

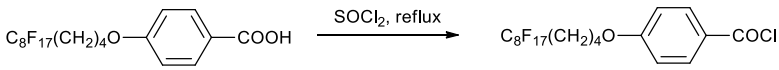


4d **5d**

Repeating the procedure above, the acid **4d** (1.592 g, 2 mmol) was mixed with thionyl chloride (5 cm^3).

Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 1.6 and 8.2 Hz, 1H; arom. H-6), 7.62 (d, *J* = 2.0 Hz, 1H; arom. H-2), 6.97 (d, *J* = 8.4 Hz, 1H; arom. H-5), 4.21-4.14 (m, 4H; overlapped OC*H*$_2$(CH$_2$)$_{10}$CH$_3$ and OC*H*$_2$(CH$_2$)$_3$(CF$_2$)$_7$CF$_3$), 2.23-2.12 (m, 2H; C*H*$_2$CF$_2$), 1.97-1.76 (m, 6H; overlapped OCH$_2$(C*H*$_2$)$_2$CH$_2$CF$_2$ and OCH$_2$C*H*$_2$(CH$_2$)$_9$CH$_3$), 1.49-1.20 (m, 18H; overlapped OCH$_2$CH$_2$(C*H*$_2$)$_9$CH$_3$), 0.87 (t, *J* = 7.0 Hz, 3H; O(CH$_2$)$_{11}$C*H*$_3$).

Acid chloride of compound 18a:

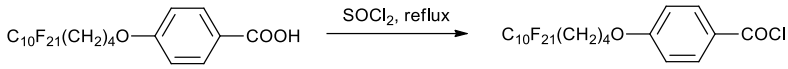


18a

Repeating the procedure above, the acid **18a** (1.224 g, 2 mmol) was mixed with thionyl chloride (5 cm^3).

Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$/CF_3COOH): δ 8.05 (AA'XX', *J* = 9.0 Hz, 2H; arom. H-2 and arom. H-6), 6.95 (AA'XX', *J* = 9.0 Hz, 2H; arom. H-3 and H-5), 4.10 (t, *J* = 5.9 Hz, 2H; OC*H*$_2$CH$_2$), 2.22-2.11 (m, 2H; C*H*$_2$CF$_2$), 1.97-1.76 (m, 4H; overlapped C*H*$_2$C*H*$_2$CF$_2$).

Acid chloride of compound 18b:

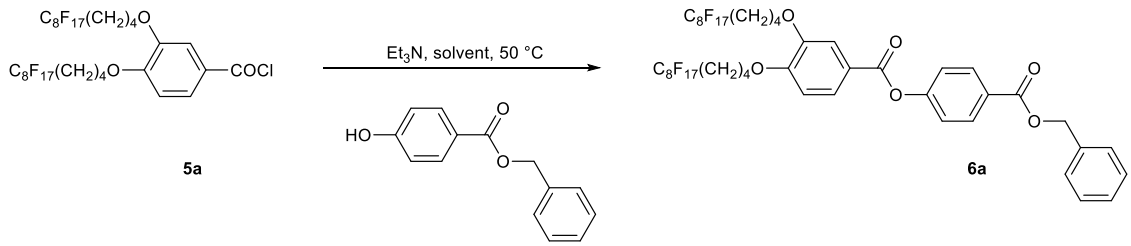


18b

This procedure is analogous to the one above; the acid **18b** (1.424 g, 2 mmol) was mixed with thionyl chloride (5 cm^3).

Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOH$): δ 8.05 (AA'XX', *J* = 9.0 Hz, 2H; arom. H-2 and arom. H-6), 6.96 (AA'XX', *J* = 9.0 Hz, 2H; arom. H-3 and H-5), 4.10 (t, *J* = 5.9 Hz, 2H; OCH_2CH_2), 2.22-2.11 (m, 2H; CH_2CF_2), 1.95-1.82 (m, 4H; overlapped $CH_2CH_2CF_2$).

Compound 6a:

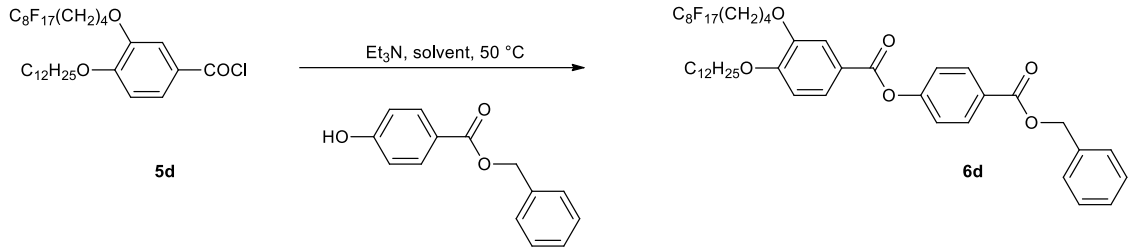


5a **6a**

Acid chloride **5a** (2.240 g, 2.0 mmol) and benzyl 4-hydroxybenzoate (0.490 g, 2.15 mmol) were dissolved in anhydrous α,α,α-trifluorotoluene (25 cm^3). Anhydrous Et_3N (0.5 cm^3, 3.58 mmol), was added afterwards. The mixture was then heated at 50 °C for 12h, and then cooled to room temperature. The solvent was evaporated at the rotary evaporator and the crude solid washed with methanol to remove the excess of benzyl 4-hydroxybenzoate, leading to a white solid.

Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (AA'XX', *J* = 8.7 Hz, 2H), 7.84 (dd, *J* = 2.0 and 8.4 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.47-7.33 (m, 5H; overlapped arom. H), 7.29 (AA'XX', *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 1H), 5.38 (s, 2H; $COOCH_2C_6H_5$), 4.12 (t, *J* = 5.6 Hz, 4H; 2 OCH_2CH_2), 2.25-2.12 (m, 4H; overlapped 2 CH_2CF_2), 1.98-1.83 (m, 8H; overlapped 2 $OCH_2CH_2CH_2CH_2CF_2$).

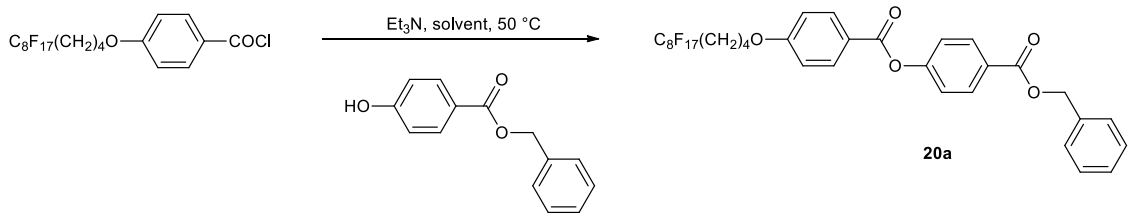
Compound 6d:



This procedure is analogous to the one above; acid chloride **5d** (1.628 g, 2 mmol), benzyl 4-hydroxybenzoate (0.490 g, 2.15 mmol), and anhydrous Et_3N (0.5 cm^3, 3.58 mmol) in anhydrous α,α,α-trifluorotoluene (25 cm^3).

Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (AA'XX', *J* = 8.8 Hz, 2H), 7.81 (dd, *J* = 2.0 and 8.4 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1 H), 7.47-7.33 (m, 5H; overlapped arom. H), 7.29 (AA'XX', *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.38 (s, 2H; $COOCH_2C_6H_5$), 4.13 (t, *J* = 5.6 Hz, 2H; $OCH_2(CH_2)_3CF_2$), 4.06 (t, *J* = 6.0 Hz, 2H; $OCH_2(CH_2)_{10}CH_3$), 2.31-2.11 (m, 2H; CH_2CF_2), 2.02-1.79 (m, 6H; overlapped $OCH_2CH_2CH_2CH_2CF_2$ and $OCH_2CH_2(CH_2)_9CH_3$), 1.50-1.19 (m, 18H; overlapped $OCH_2CH_2(CH_2)_9CH_3$), 0.87 (t, *J* = 7.2 Hz, $O(CH_2)_{11}CH_3$).

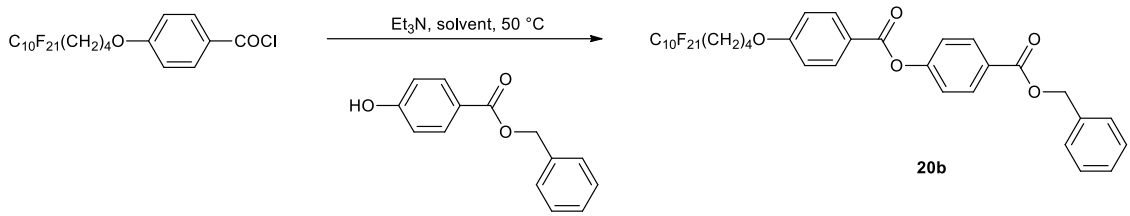
Compound 20a:



This procedure is analogous to the one above; acid chloride (1.260 g, 2 mmol), benzyl 4-hydroxybenzoate (0.490 g, 2.15 mmol), and anhydrous Et_3N (0.5 cm^3, 3.58 mmol) in anhydrous α,α,α-trifluorotoluene (25 cm^3).

Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (AA'XX', *J* = 8.7 Hz, 2H), 8.13 (AA'XX', *J* = 8.7 Hz, 2H), 7.47-7.33 (m, 5H; overlapped arom. H), 7.28 (AA'XX', *J* = 8.7 Hz, 2H), 6.97 (AA'XX', *J* = 8.7 Hz, 2H), 5.37 (s, 2H; $OCH_2C_6H_5$), 4.09 (t, *J* = 6.0 Hz, 2H; OCH_2CH_2), 2.24-2.11 (m, 2H; CH_2CF_2), 1.97-1.81 (m, 4H; overlapped $OCH_2CH_2CH_2CH_2CF_2$).

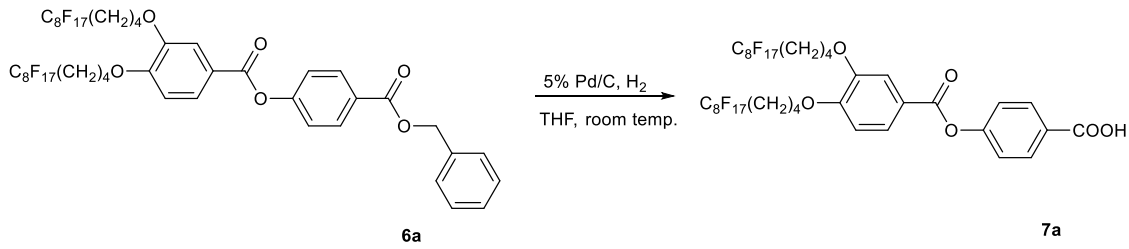
Compound 20b:



This procedure is analogous to the one above; acid chloride (1.460 g, 2 mmol), benzyl 4-hydroxybenzoate (0.490 g, 2.15 mmol) and anhydrous Et_3N (0.5 cm^3, 3.58 mmol) in anhydrous α,α,α-trifluorotoluene (25 cm^3).

Yield: 81%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.16 (AA'XX', *J* = 8.7 Hz, 2H), 8.14 (AA'XX', *J* = 8.7 Hz, 2H), 7.47-7.33 (m, 5H; overlapped arom. H), 7.28 (AA'XX', *J* = 8.7 Hz, 2H), 6.95 (AA'XX', *J* = 8.7 Hz, 2H), 5.37 (s, 2H; $OCH_2C_6H_5$), 4.09 (t, *J* = 6.0 Hz, 2H; OCH_2CH_2), 2.25-2.11 (m, 2H; CH_2CF_2), 1.96-1.81 (m, 4H; overlapped $OCH_2CH_2CH_2CH_2CF_2$).

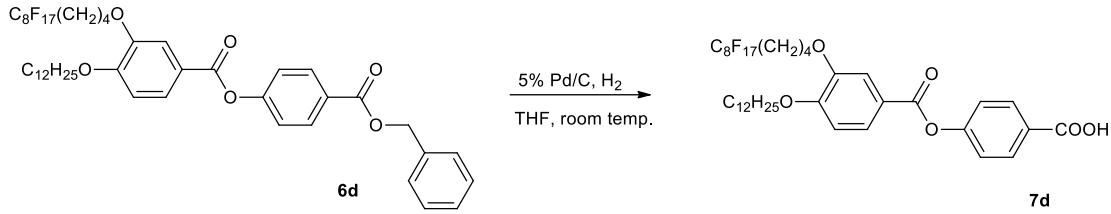
Compound 7a:



A flask equipped with compound **6a** (2.624 g, 2 mmol) suspended in anhydrous THF (100 cm^3) and 5% Pd/C catalyst (0.100 g) was connected to a balloon filled with hydrogen at normal atmospheric pressure and room temperature. The reaction was stirred until no hydrogen was taken up (thin layer chromatography shows the completion of the reaction). The solvent was evaporated at the rotary evaporator, and the resulting solid was treated with a large amount of hot CF_3COOH to dissolve the two-ring benzoic acid product **7a**, and the Pd/C was filtered off on a sintered funnel. The CF_3COOH was subsequently removed at the rotary evaporator, and the solid was washed with methanol, yielding to a white compound.

Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOH$): δ 8.21 (AA'XX', *J* = 8.8 Hz, 2H), 7.92 (dd, *J* = 2.0 and 8.6 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.34 (AA'XX', *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 1H), 4.19 (t, *J* = 6.9 Hz, 4H; 2 OCH_2CH_2), 2.25-2.10 (m, 4H; overlapped 2 CH_2CF_2), 2.00-1.80 (m, 8H; overlapped 2 $OCH_2CH_2CH_2CH_2CF_2$).

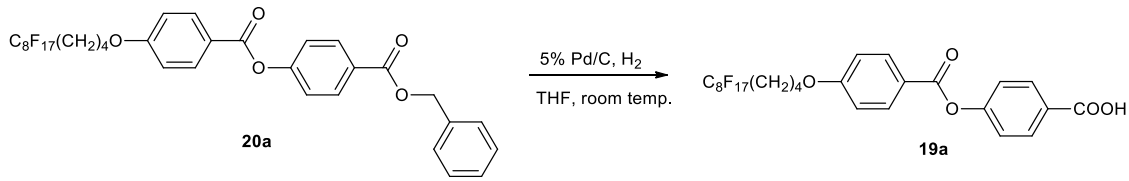
Compound 7d:



This procedure is analogous to the one above; the benzyl compound **6d** (2.013 g, 2 mmol) was suspended in anhydrous THF (100 cm^3) and 5% Pd/C (0.100 g) was added as catalyst.

Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOH$): δ 8.21 (AA'XX', *J* = 8.8 Hz, 2H), 7.93 (dd, *J* = 2.1 and 8.5 Hz, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.33 (AA'XX', *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 1H), 4.22-4.17 (m, 4H; overlapped $OCH_2(CH_2)_3CF_2$ and $OCH_2(CH_2)_{10}CH_3$), 2.28-2.09 (m, 2H; CH_2CF_2), 1.98-1.79 (m, 6H; overlapped $OCH_2CH_2CH_2CH_2CF_2$ and $OCH_2CH_2(CH_2)_9CH_3$), 1.49-1.20 (m, 18H; overlapped $OCH_2CH_2(CH_2)_9CH_3$), 0.87 (t, *J* = 7.0 Hz, $O(CH_2)_{11}CH_3$).

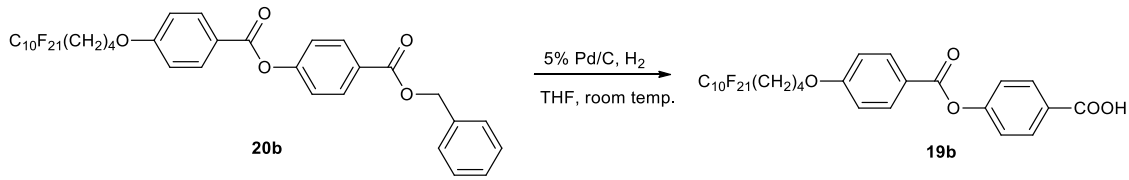
Compound 19a:



This procedure is analogous to the one above; the benzyl compound **20a** (1.644 g, 2 mmol) was suspended in anhydrous THF (100 cm^3) and 5% Pd/C (0.100 g) was added as catalyst.

Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOH$): δ 8.21 (AA'XX', *J* = 8.8 Hz, 2H), 8.17 (AA'XX', *J* = 8.9 Hz, 2H), 7.35 (AA'XX', *J* = 8.8 Hz, 2H), 7.03 (AA'XX', *J* = 8.9 Hz, 2H), 4.14 (t, *J* = 5.9 Hz, 2H; OCH_2CH_2), 2.25-2.12 (m, 2H; CH_2CF_2), 1.99-1.82 (m, 4H; overlapped $OCH_2CH_2CH_2CH_2CF_2$).

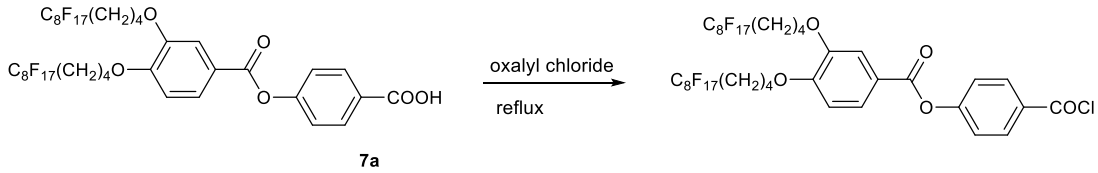
Compound 19b:



This procedure is analogous to the one above; the benzyl compound **19b** (1.844 g, 2 mmol) was suspended in anhydrous THF (100 cm^3) and 5% Pd/C (0.100 g) was added as catalyst.

Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOH$): δ 8.20 (AA'XX', *J* = 8.8 Hz, 2H), 8.17 (AA'XX', *J* = 8.9 Hz, 2H), 7.35 (AA'XX', *J* = 8.8 Hz, 2H), 7.03 (AA'XX', *J* = 8.9 Hz, 2H), 4.13 (t, *J* = 5.9 Hz, 2H; $OC\mathit{H}_2CH_2$), 2.25-2.12 (m, 2H; $C\mathit{H}_2CF_2$), 1.99-1.82 (m, 4H; overlapped $OCH_2C\mathit{H}_2C\mathit{H}_2CH_2CF_2$).

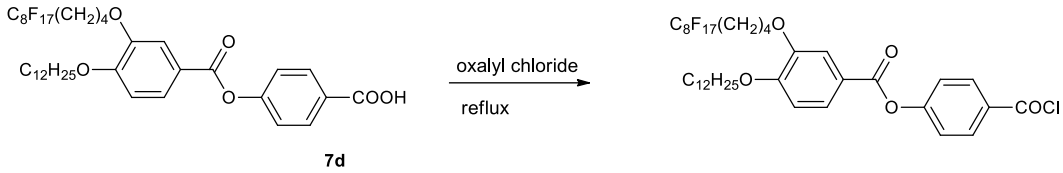
Acid chloride of compound 7a:



The carboxylic acid **7a** (2.444 g, 2 mmol) was suspended in excess of oxalyl chloride (5 cm^3) and the mixture was refluxed for 12h. The solvent was removed at the rotary evaporator, and the solid obtained did not require further purification.

Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (AA'XX', *J* = 8.9 Hz, 2H), 7.85 (dd, *J* = 2.0 and 8.5 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.38 (AA'XX', *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 1H), 4.19 (t, *J* = 6.9 Hz, 2H; 2 $OC\mathit{H}_2CH_2$), 2.26-2.12 (m, 4H; overlapped 2 $C\mathit{H}_2CF_2$), 1.99-1.83 (m, 8H; overlapped 2 $OCH_2C\mathit{H}_2C\mathit{H}_2CH_2CF_2$).

Acid chloride of compound 7d:

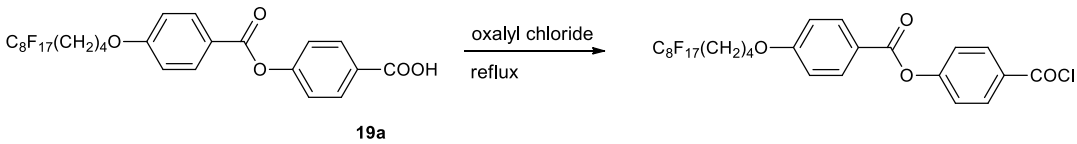


7d

This procedure is analogous to the one above; compound **7d** (1.833 g, 2 mmol) was suspended in oxalyl chloride (5 cm^3).

Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (AA'XX', *J* = 8.9 Hz, 2H), 7.85 (dd, *J* = 2.0 and 8.5 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.38 (AA'XX', *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 1H), 4.22-4.17 (m, 4H; overlapped $OCH_2(CH_2)_3CF_2$ and $OCH_2(CH_2)_{10}CH_3$), 2.28-2.09 (m, 2H; CH_2CF_2), 1.98-1.79 (m, 6H; overlapped $OCH_2CH_2CH_2CH_2CF_2$ and $OCH_2CH_2(CH_2)_9CH_3$), 1.49-1.20 (m, 18H; overlapped $OCH_2CH_2(CH_2)_9CH_3$), 0.87 (t, *J* = 7.0 Hz, $O(CH_2)_{11}CH_3$).

Acid chloride of compound 19a:

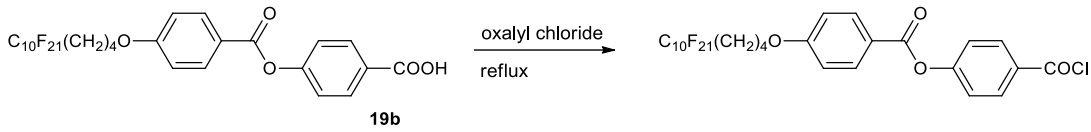


19a

This procedure is analogous to the one above; compound **19a** (1.464 g, 2 mmol) was suspended in oxalyl chloride (5 cm^3).

Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (AA'XX', *J* = 8.9 Hz, 2H), 8.17 (AA'XX', *J* = 9.0 Hz, 2H), 7.39 (AA'XX', *J* = 8.9 Hz, 2H), 6.99 (AA'XX', *J* = 9.0 Hz, 2H), 4.11 (t, *J* = 5.9 Hz, 2H; OCH_2CH_2), 2.26-2.12 (m, 2H; CH_2CF_2), 1.98-1.81 (m, 4H; overlapped $OCH_2CH_2CH_2CH_2CF_2$).

Acid chloride of compound 19b:

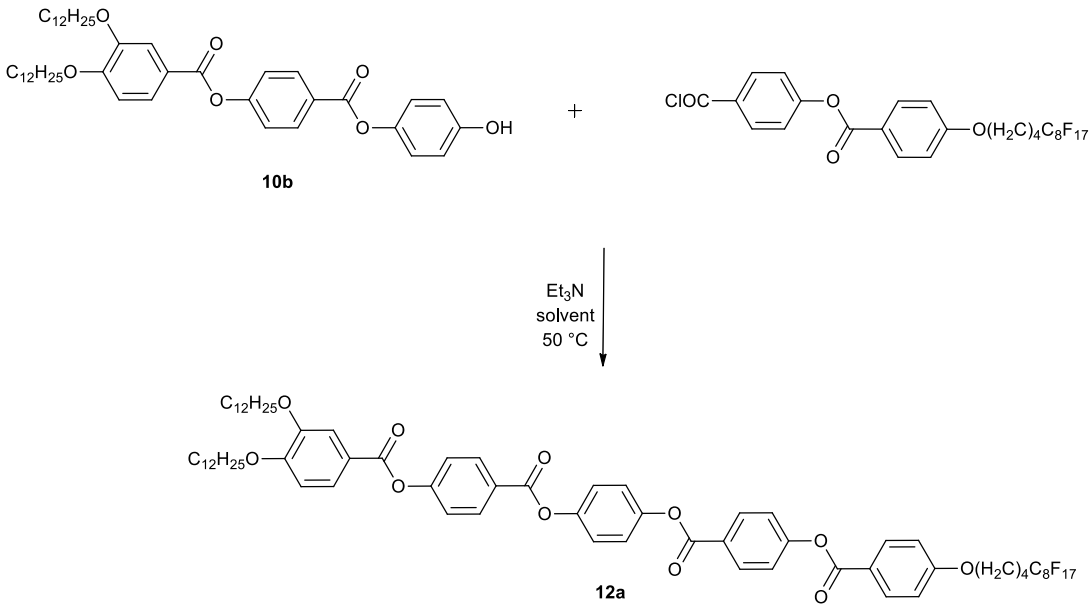


19b

This procedure is analogous to the one above; compound **19b** (1.664 g, 2 mmol) was suspended in oxalyl chloride (5 cm^3).

Yield: 79%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (AA'XX', *J* = 8.9 Hz, 2H), 8.17 (AA'XX', *J* = 9.0 Hz, 2H), 7.39 (AA'XX', *J* = 8.9 Hz, 2H), 6.99 (AA'XX', *J* = 9.0 Hz, 2H), 4.11 (t, *J* = 5.9 Hz, 2H; OCH_2CH_2), 2.26-2.12 (m, 2H; CH_2CF_2), 1.98-1.81 (m, 4H; overlapped $OCH_2CH_2CH_2CH_2CF_2$).

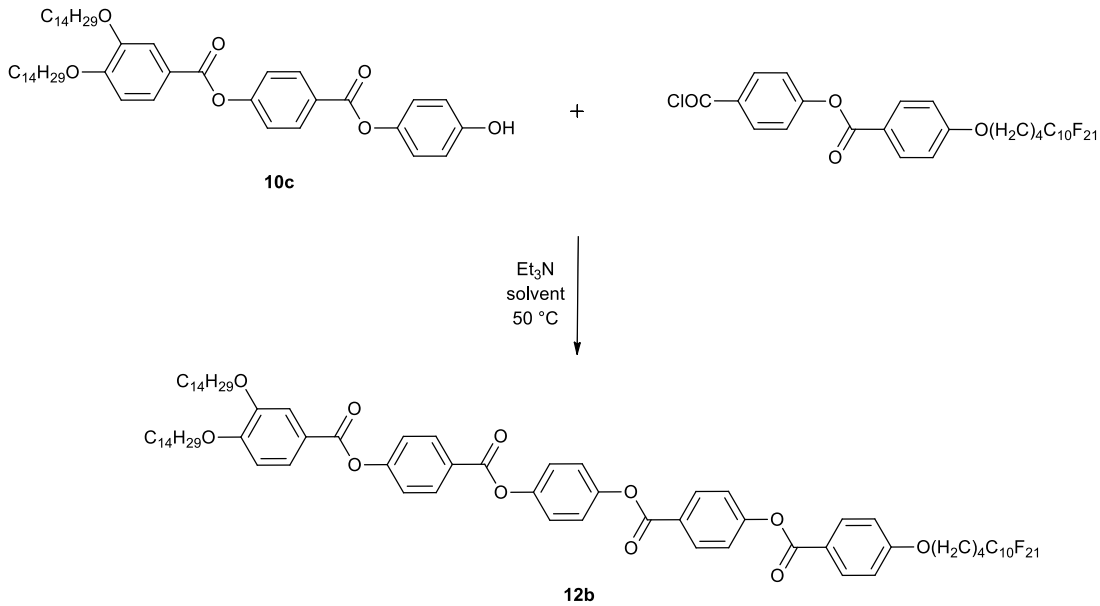
Compound 12a (HH/F):



The acid chloride (0.825 g, 1.10 mmol) was dissolved in anhydrous α,α,α-trifluorotoluene (10 cm^3), and *O*-monosubstituted hydroquinone **10b** (0.702 g, 1 mmol) was then added, followed by Et_3N (0.5 cm^3, 3.58 mmol). The mixture was heated at 50 °C for 12h and the solvent removed at the rotary evaporator. The crude solid was washed with methanol. Purification was made by precipitating the pure solid with a solvent-antisolvent mixture of CF_3COOH/CH_3CN.

Yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (AA'XX', *J* = 8.6 Hz, 4H), 8.18 (AA'XX', *J* = 8.9 Hz, 2H), 7.84 (dd, *J* = 2.0 and 8.4 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.38 (AA'XX', *J* = 8.8 Hz, 2H), 7.37 (AA'XX', *J* = 8.8 Hz, 2H), 7.31 (s, 4H), 6.99 (AA'XX', *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 1H), 4.12-4.06 (m, 6H; overlapped 3 OC*H*$_2$CH$_2$), 2.24-2.13 (m, 2H; C*H*$_2$CF$_2$), 1.97-1.82 (m, 8H; overlapped OCH$_2$C*H*$_2$C*H*$_2$CH$_2$CF$_2$ and 2 OCH$_2$C*H*$_2$(CH$_2$)$_9$CH$_3$), 1.53-1.22 (m, 18H; overlapped 2 OCH$_2$CH$_2$*(*C*H*$_2$*)*$_9$CH$_3$), 0.89-0.86 (m, 6H; 2 O(CH$_2$)$_{11}$C*H*$_3$).

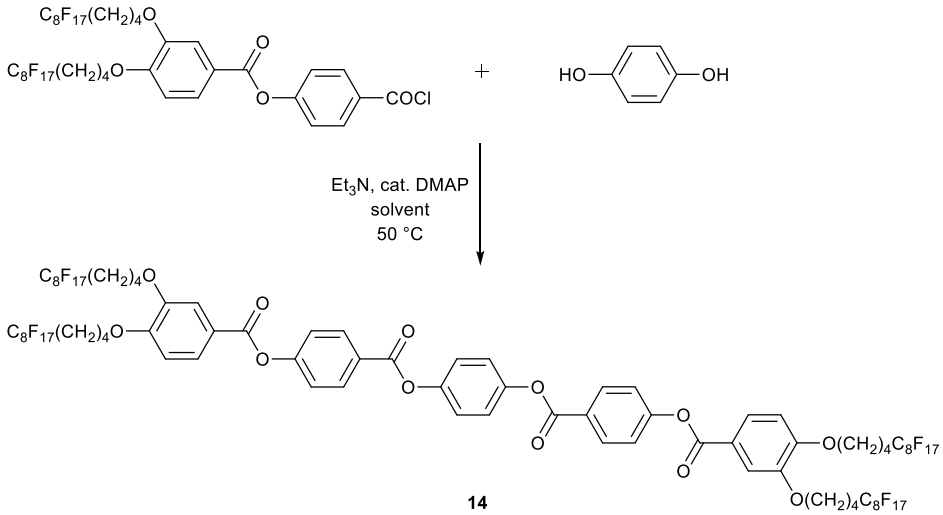
Compound 12b (HH/F-b):



This procedure is analogous to the one above; acid chloride (0.935 g, 1.10 mmol) was dissolved in anhydrous α,α,α-trifluorotoluene (10 cm^3) ,and *O*-monosubstituted hydroquinone **10c** (0.759 g, 1 mmol) was then added, followed by Et_3N (0.5 cm^3, 3.58 mmol).

Yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (AA'XX', *J* = 8.6 Hz, 4H), 8.18 (AA'XX', *J* = 8.9 Hz, 2H), 7.84 (dd, *J* = 2.0 and 8.4 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.38 (AA'XX', *J* = 8.8 Hz, 2H), 7.37 (AA'XX', *J* = 8.8 Hz, 2H), 7.31 (s, 4H), 6.99 (AA'XX', *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 1H), 4.12-4.06 (m, 6H; overlapped 3 OC*H*$_2$CH$_2$), 2.24-2.13 (m, 2H; C*H*$_2$CF$_2$), 1.97-1.82 (m, 8H; overlapped OCH$_2$C*H*$_2$C*H*$_2$CH$_2$CF$_2$ and 2 OCH$_2$C*H*$_2$(CH$_2$)$_{11}$CH$_3$), 1.53-1.22 (m, 22H; overlapped 2 OCH$_2$CH$_2$*(*C*H*$_2$*)*$_{11}$CH$_3$), 0.89-0.86 (m, 6H; 2 O(CH$_2$)$_{13}$C*H*$_3$).

Compound 14 (FF/FF):

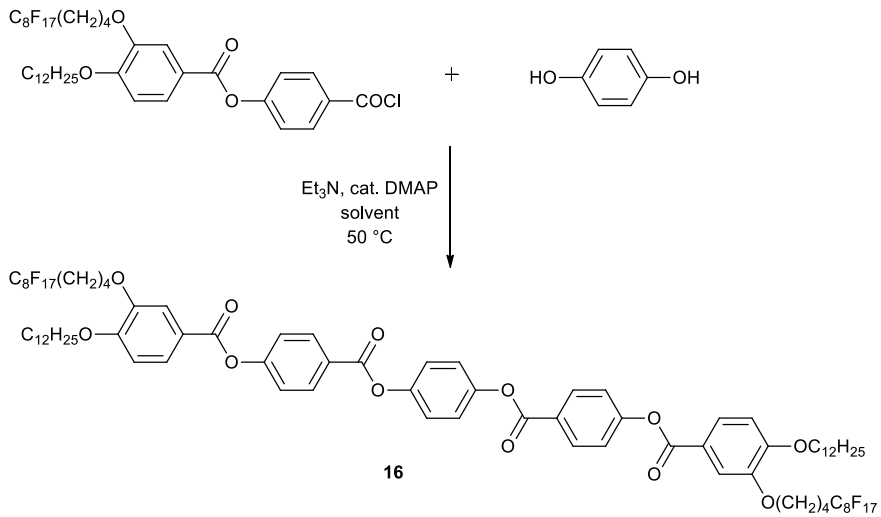


14

The acid chloride (1.364 g, 1.1 mmol) was dissolved in anhydrous α,α,α-trifluorotoluene (10 cm^3) and hydroquinone (0.110 g, 1.0 mmol) was added, followed by Et_3N (0.5 cm^3, 3.58 mmol) and catalytic DMAP (0.489 g, 0.40 mmol). The mixture was then heated at 50 °C for 12h and the solvent removed at the rotary evaporator. The crude solid was washed with methanol yielding to a white solid. Purification was made by precipitating the pure solid with a solvent-antisolvent mixture of CF_3COOH/CH_3CN.

Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (AA'XX', *J* = 8.8 Hz, 4H), 7.86 (dd, *J* = 2.1 and 8.6 Hz, 2H), 7.67 (d, *J* = 2.0 Hz, 2H), 7.38 (AA'XX', *J* = 8.8 Hz, 4H), 7.31 (s, 4H), 6.96 (d, *J* = 8.7 Hz, 2H), 4.11 (t, *J* = 6.1 Hz, 8H; overlapped 4 O*CH*$_2$CH$_2$), 2.23-2.10 (m, 8H; overlapped 4 C*H*$_2$CF$_2$), 2.00-1.81 (m, 16H; overlapped 4 OCH$_2$C*H*$_2$C*H*$_2$CH$_2$CF$_2$).

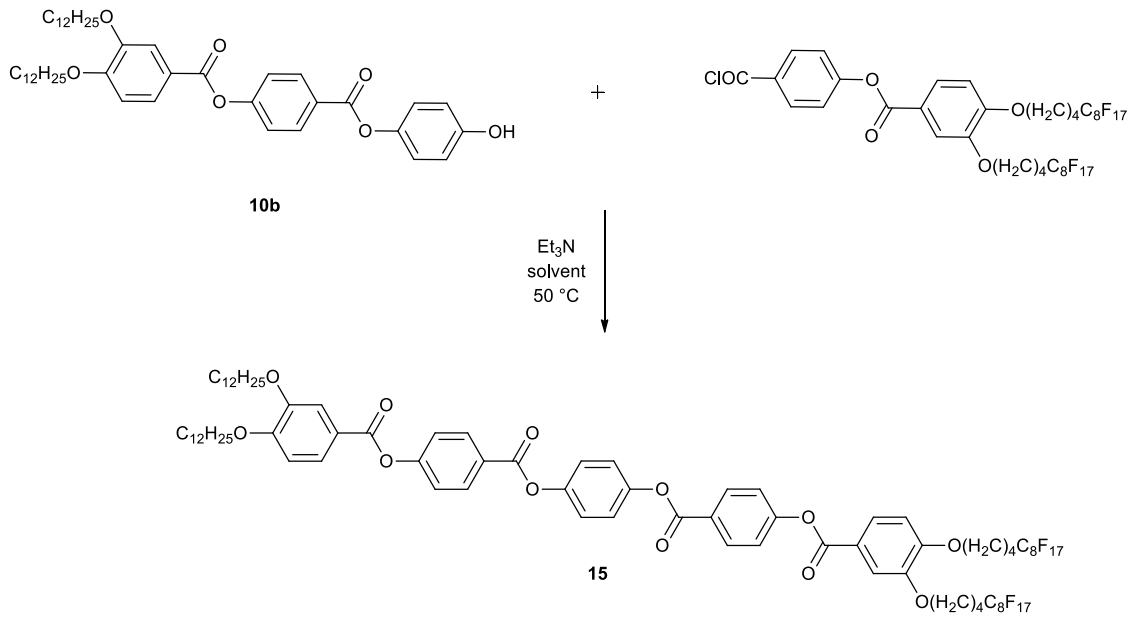
Compound 16 (HF/HF):



This procedure is analogous to the one above; the acid chloride (1.028 g, 1.1 mmol) was dissolved in anhydrous α,α,α-trifluorotoluene (10 cm^3) and hydroquinone (0.110 g, 1.0 mmol) was added, followed by Et_3N (0.5 cm^3, 3.58 mmol) and catalytic DMAP (0.489 g, 0.40 mmol). The mixture was then heated at 50 °C for 12h and the solvent removed at the rotary evaporator. The crude solid was washed with methanol yielding to a white solid. Purification was made by precipitating the pure solid with a solvent-antisolvent mixture of CF_3COOH/CH_3CN.

Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (AA'XX', *J* = 8.8 Hz, 4H), 7.87 (dd, *J* = 2.0 and 8.5 Hz, 2H), 7.67 (d, *J* = 2.0 Hz, 2H), 7.37 (AA'XX', *J* = 8.8 Hz, 4H), 7.31 (s, 4H), 6.96 (d, *J* = 8.7 Hz, 2H), 4.15-4.07 (m, 8H; overlapped 2 $OCH_2(CH_2)_3CF_2$ and 2 $OCH_2(CH_2)_{10}CH_3$), 2.28-2.11 (m, 4H; 2 CH_2CF_2), 2.00-1.81 (m, 12H; overlapped 2 $OCH_2CH_2CH_2CH_2CF_2$ and 2 $OCH_2CH_2(CH_2)_9CH_3$), 1.49-1.20 (m, 36H; overlapped 2 $OCH_2CH_2(CH_2)_9CH_3$), 0.88 (t, *J* = 7.0 Hz, 6H; 2 $O(CH_2)_{11}CH_3$).

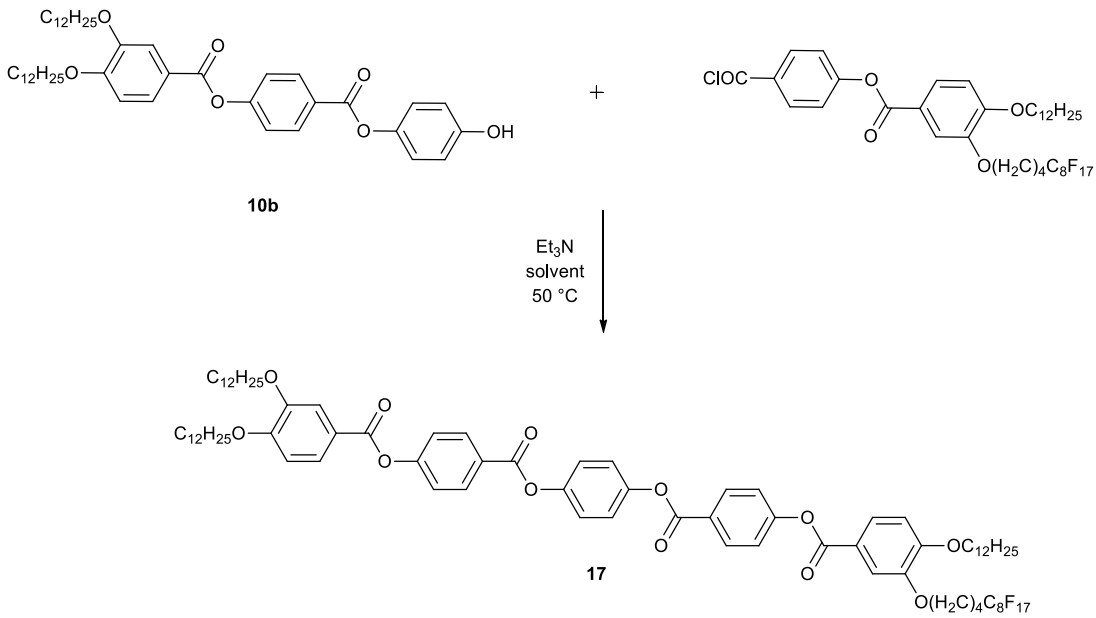
Compound 15 (HH/FF):



The acid chloride (1.364 g, 1.10 mmol) was dissolved in anhydrous α,α,α-trifluorotoluene (10 cm^3), and *O*-monosubstituted hydroquinone **10b** (0.702 g, 1 mmol) was then added, followed by Et_3N (0.5 cm^3, 3.58 mmol). The mixture was heated at 50 °C for 12h and the solvent removed at the rotary evaporator. The crude solid was washed with methanol. Purification was made by precipitating the pure solid with a solvent-antisolvent mixture of CF_3COOH/CH_3CN.

Yield: 47%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (AA'XX', *J* = 8.7 Hz, 4H), 7.87 (dd, *J* = 2.0 and 8.4 Hz, 1H), 7.84 (dd, *J* = 2.0 and 8.2 Hz, 1H), 7.68-7.65 (overlapped 2H), 7.38 (AA'XX', *J* = 8.7 Hz, 4H), 7.31 (s, 4H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 4.16-4.06 (m, 8H; overlapped 4 OCH_2CH_2), 2.27-2.13 (m, 4H; overlapped 2 CH_2CF_2), 2.01-1.82 (m, 12H; overlapped 2 $OCH_2CH_2CH_2CH_2CF_2$ and 2 $OCH_2CH_2(CH_2)_9CH_3$), 1.56-1.26 (m, 36H; overlapped 2 $OCH_2CH_2(CH_2)_9CH_3$), 0.88 (t, *J* = 7.0 Hz, 6H; 2 CH_3).

Compound 17 (HH/HF):



This procedure is analogous to the one above; acid chloride (1.027 g, 1.10 mmol) was dissolved in anhydrous α,α,α-trifluorotoluene (10 cm^3) ,and *O*-monosubstituted hydroquinone **10b** (0.702 g, 1 mmol) was then added, followed by Et_3N (0.5 cm^3, 3.58 mmol).

Yield: 68%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (AA'XX', *J* = 8.8 Hz, 4H), 7.87 (dd, *J* = 2.0 and 8.4 Hz, 1H), 7.82 (dd, *J* = 2.0 and 8.3 Hz, 1H), 7.66-7.63 (overlapped, 2H), 7.36 (AA'XX', *J* = 8.8 Hz, 4H), 7.31 (s, 4H), 6.94 (d, *J* = 8.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.14-4.03 (m, 8H; overlapped 4 OCH_2CH_2), 2.27-2.13 (m, 2H; overlapped CH_2CF_2), 2.01-1.82 (m, 10H; overlapped $OCH_2CH_2CH_2CH_2CF_2$ and 3 $OCH_2CH_2(CH_2)_9CH_3$), 1.53-1.23 (m, 54H; overlapped 3 $OCH_2CH_2(CH_2)_9CH_3$), 0.88 (t, *J* = 7.0 Hz, 9H; 3 CH_3).

Elemental Analysis

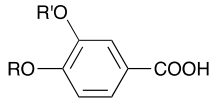
Table S1. Elemental analysis results

Compound	Experimental Analysis: Found (Required) / %			
	C		H	
18a	36.71	(37.27)	2.09	(2.14)
18b	35.15	(35.41)	1.84	(1.84)
4a	33.57	(33.77)	1.81	(1.83)
4d	46.65	(46.74)	4.57	(4.68)
19a	42.55	(42.64)	2.26	(2.34)
19b	40.00	(40.40)	2.00	(2.06)
7a	38.80	(37.33)	2.62	(1.98)
7d	49.69	(49.79)	4.47	(4.51)
20a	47.86	(48.19)	2.75	(2.82)
20b	45.31	(45.57)	2.37	(2.51)
6a	41.05	(41.17)	2.34	(2.30)
6d	53.58	(53.68)	4.72	(4.71)
9b	76.81	(77.24)	8.39	(8.64)
9c	77.42	(77.79)	8.87	(9.02)
10b	75.15	(75.18)	8.80	(8.89)
10c	75.43	(75.95)	9.21	(9.30)
11	74.90	(75.64)	8.33	(8.52)
12a	59.25	(59.32)	5.36	(5.48)
12b	58.16	(58.01)	5.44	(5.45)
14	38.95	(39.10)	2.05	(2.00)
15	51.55	(51.63)	4.37	(4.44)
17	61.96	(61.49)	6.48	(6.36)
16	51.27	(51.63)	4.35	(4.44)

Liquid Crystal Properties of the Intermediate Compounds

While many of the intermediate compounds used in the preparation of the target compounds were liquid crystalline,[9-14] the mesomorphism of a few of them has never been described previously.

One-ring Benzoic Acids



4a: R = R' = $C_8F_{17}(CH_2)_4$
4d: R = $C_{12}H_{25}$, R' = $C_8F_{17}(CH_2)_4$

Table S2. Thermal behavior of one-ring benzoic acids*

Compound	Transition	*T*/°C	Δ*H*/kJ mol^{-1}
4a	Cr–Cr_1	46.8	6.1
	Cr_1–Iso	138.2	47.7
	(Col_h–Iso)	(133.8)	(–0.8)
	(Cr_1-Col_h)	(130.7)	(–39.2)
4d	Cr–Iso	113.2	33.3
	(M^a–Iso)	(110.5)	(–34.1)

*The following footnote applies to all tables of thermal data. Cr, Cr_1, Cr_2: crystalline phases; Iso: Isotropic liquid; N: nematic phase; SmA: smectic A phase; SmC: smectic C phase; Col_h: hexagonal columnar mesophase; Col_r: rectangular columnar mesophase; dec.: decomposition
[a]M represents an unidentified high-order crystal smectic mesophase

The mesomorphism of the one-ring acids with one chain that is semiperfluorinated is already described in the literature[9-13] and they show only smectic phases, with the N phase of the all-hydrocarbon analogues[9,14] being suppressed by the perfluorinated section of the terminal chain. Two-chain acid **4a** showed a monotropic Col_h phase (identified by the characteristic optical texture) (Figure S1) and the induction of mesomorphism is attributed to the rigidity of the perfluorocarbon chains and the increased volume that they occupy. Unsymmetric compound **4d** showed a monotropic phase for which a very good texture could not be obtained prior to crystallisation, but it was clear that the phase was neither SmC nor SmA,

suggesting perhaps that a columnar phase might have been induced. Confirmation from X-ray measurements was precluded as under the conditions of the experiment, the compound crystallised before a diffraction pattern could be recorded.

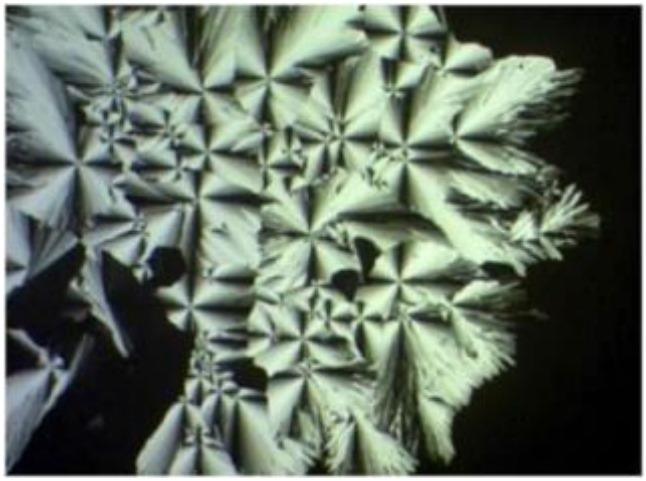
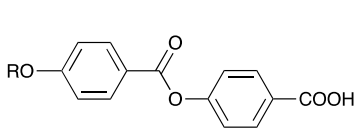
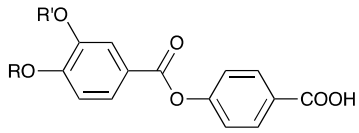


Figure S1. Optical photomicrograph representing the Col_h mesophase of compound **4a** at 131 °C on cooling.

Two-ring Benzoic Acids



19a: R = $C_8F_{17}(CH_2)_4$
19b: R = $C_{10}F_{21}(CH_2)_4$



7a: R/R' = $C_8F_{17}(CH_2)_4$
7d: R = $C_{12}H_{25}$, R' = $C_8F_{17}(CH_2)_4$

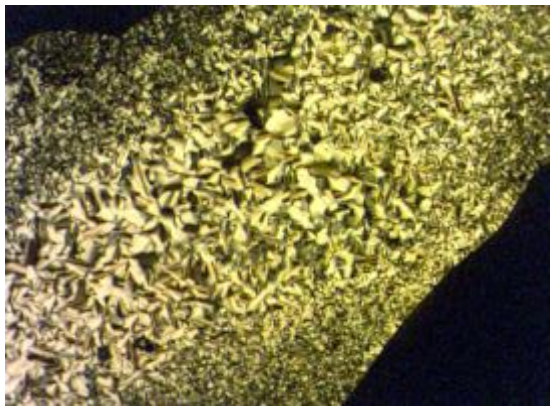
Table S3. Thermal behavior of two-ring benzoic acids

Compound	Transition	*T*/°C	Δ*H*/kJ mol^{-1}
19a[a]	Cr–SmC	189.9	17.7
	SmC–dec.	>275	–
19b[a]	Cr–SmC	198.8	20.9
	SmC–dec.	>275	–
7a[a]	Cr–Col_h	180.4	36.7
	Col_h–Iso	197.9	4.1
7d	Cr–Col_h	136.9	29.9
	Col_h–Iso	174.2	4.8

[a] Compounds **19a**, **19b** and **7a** show transitions between what are presumed to be different crystal polymorphs at: 93.3 and 115.2 °C, 106.4 and 122.3 °C, and 46.9 and 58.9 °C, respectively. Note that all-hydrocarbon 3,4-dialkoxybenzoyloxybenzoic acids most typically show SmC phases).[15]

The simplest of these compounds, **19a** and **19b**, showed only a SmC phase and at somewhat elevated temperatures so that above 275 °C, the darkening of the sample was clearly due to decomposition and not clearing. Interestingly and in common with the one-ring benzoic acids, a tilted phase is seen whereas in many cases mesogens with perfluorocarbon chains tend to show orthogonal phases such as SmA and SmB. Thus, it seems that formation of the tilted phase is facilitated by the tetramethylene spacer. Compounds **7a** and **7d** both showed a single, columnar phase as identified by the characteristic optical texture (Figure S2), which demonstrates the fact that, as postulated for **4d**, a single semiperfluorocarbon chain adds sufficient terminal volume to tip the mesomorphism over from lamellar to columnar. X-ray diffraction studies in the mesophases of **7a** and **7d** each showed a single reflection corresponding to *d* = 41.8 and 37.8 Å, respectively, and supported by optical textures,

correspond to hexagonal columnar phases, with lattice parameters *a* = 48.3 and 43.6 Å, respectively.



(a)

(b)

Figure S2. Columnar phase of (a) compound **7a** on cooling at 185 °C and (b) compound **7d** on cooling at 174 °C.

Benzyl Esters

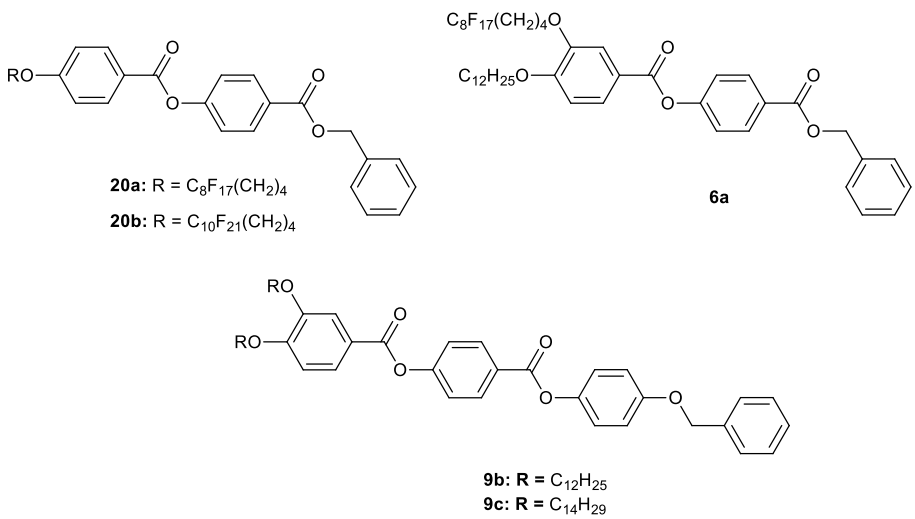
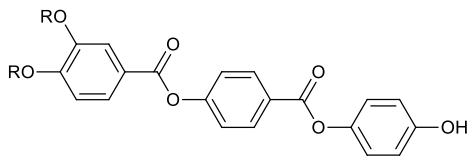


Table S4. Thermal behavior of benzyl compounds

Compound[a]	Transition	*T*/°C	Δ*H*/kJ mol^{-1}
20a	Cr–Cr_1	88.6	0.4
	Cr_1–SmA	103.3	32.2
	SmA–Iso	128.3	3.9
	(SmA–Iso)	(130.3)	(–4.2)
	(Cr–SmA)	(85.2)	(–33.2)
20b	Cr–SmA	110.4	15.2
	SmA–Iso	135.3	7.4
6a	Cr–Cr_1	67.6	–1.0
	Cr_1–Iso	99.6	42.8
	(SmA–Iso)	(104.1)	(–0.4)
	(Cr_1–SmA)	(96.9)	(–1.0)
	(Cr–Cr_1)	(76.9)	(–30.9)
9b	Cr–Cr_1	93.5	1.0
	Cr_1–Cr_2	103.5	0.5
	Cr_2–Iso	111.4	66.5
	(N–Iso)	(109.0)	(–1.7)
	(SmC–N)	(104.0)	(–4.1)
	(Cr–SmC)	(91.4)	(–54.1)
9c	Cr–Cr_1	102.1	3.8[b]
	Cr_1–Cr_2	108.3	
	Cr_2–Iso	111.7	71.0
	(N–Iso)	(106.9)	(–7.9[b])
	(SmC–N)	(104.1)	
	(Cr–SmC)	(94.9)	(–65.9)

[a] Compound **6d** does not possess liquid crystal properties; [b] Sum of enthalpies

O-Monosubstituted Hydroquinones



10b: R = $C_{12}H_{25}$
10c: R = $C_{14}H_{29}$

Table S5. Thermal behavior of *O*-monosubstituted hydroquinones

Compound	Transition	*T*/°C	Δ*H*/kJ mol^{-1}
10b	Cr–Iso	120.0	52.0
	(SmC–Iso)	(117.7)	(–8.1)
	(Cr–SmC)	(110.2)	(–39.4)
10c	Cr–Cr_1	113.6	48.4[a]
	Cr_1–Iso	120.7	
	(SmC–Iso)	(116.8)	(–6.5)
	(Cr–SmC)	(107.4)	(–34.4)

[a] Sum of enthalpies

Typical Textures of Final Compounds

Representative textures, obtained on cooling, of the final compounds are given below (Figure S3).

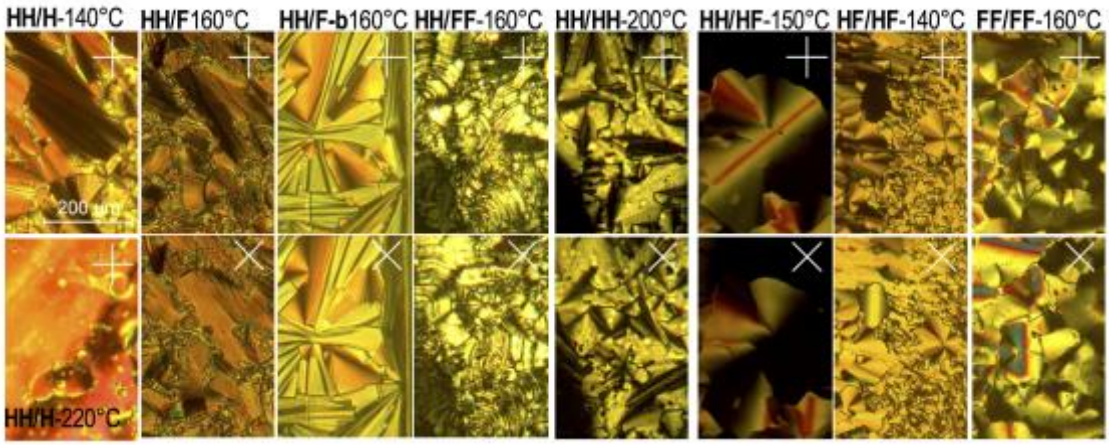


Figure S3. Optical textures of the final compounds.

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