Electronic Supplementary Material (ESI) for Soft Matter.

1. Methods

1.1. General Techniques

Miscellaneous solvents were purchased from Fisher Scientific dried by sequential percolation through columns of activated alumina and copper Q5 catalyst prior to use. Chemical intermediates were obtained from commercial suppliers and used without further purification, with the exceptions of 8-(4-Bromophenyl)oct-7-yn-1-ol – ***i-1*** – which was prepared as described previously in 84 % yield. [1] Compound **1** (CB8OCB) was prepared as described previously. [1]Reactions were monitored by thin layer chromatography (TLC) using an appropriate solvent system. Silica coated aluminium TLC plates used were purchased from Merck (Kieselgel 60 F-254) and visualised using UV light at wavelengths of both 254 nm and 365 nm. Column chromatography was performed using flash grade silica from Fluorochem (40 - 63μm particle size). Yields refer to chromatographically (HPLC) and spectroscopically (^{1}H NMR, ^{13}C {^{1}H} NMR and – where appropriate - ^{19}F NMR) homogenous material.

1.2. Nuclear Magnetic Resonance

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (^{1}H), 100.5 MHz (^{13}C{^{1}H}) and 376.4 MHz (^{19}F NMR) as solutions in deuterated chloroform. Spectra were referenced to the residual protic solvent for ^{1}H (7.26 ppm), ^{13}C{^{1}H} to the resonance of $CDCl_3$ (77.16 ppm) and ^{19}F were unreferenced.

1.3. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectroscopy was performed using a Shimadzu IR Prestige-21 with temperature controlled Specac Golden Gate diamond ATR IR stage and a resolution of 4 cm^{-1}.

1.4. Mass Spectrometry

Mass spectra were recorded on a Bruker compact time of flight mass spectrometer with both ESI and APCI sources, and we extend our gratitude to Mr. Karl Heaton of the University of York for obtaining MS data.

1.5. High Performance Liquid Chromatography

High-performance liquid chromatography was performed on a Shimadzu Prominence modular HPLC system comprising a LC-20A quaternary solvent pump, a DGU-20A_5 degasser, a SIL-20A autosampler, a CBM-20A communication bus, a CTO-20A column oven, and a SPO-20A dual wavelength UV-vis detector operating at 220/250 nm. The column used was an Alltech C18 bonded reverse-phase silica column with a 5 μm pore size, an internal diameter of 10 mm and a length of 250 mm. In all cases the mobile phase used was neat acetonitrile, purchased from Fisher Scientific UK.

1.6. Polarised Optical Microscopy

Polarised optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hotstage controlled by a Mettler FP90 central processor. Photomicrographs were captured *via* an InfinityX-21 MP digital camera mounted atop the microscope. Glass slides treated with octadecyltrichlorosilane were prepared according to Wong and Yu. [2]

1.7. Differential Scanning Calorimetry.

Differential scanning calorimetry was performed on a Mettler DSC822^e fitted with an autosampler operating with Mettler Star^e software and calibrated before use against an indium standard (onset = 156.55 ± 0.2 °C, ΔH = 28.45 ± 0.40 Jg^{-1}) under an atmosphere of dry nitrogen.

1.8. Small Angle X-ray Scattering

Small angle X-ray scattering was performed using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. The radiation used was copper Kα (λ = 0.154056 nm) from a 1 μS microfocus source. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample. Samples were filled into 1mm capillary tubes and aligned with a pair of 1T magnets, with the field strength at the sample position being approximately 0.6T Diffraction patterns were collected as a function of temperature and the data processed using Matlab as follows. Two-dimensional scattering patterns were collected on cooling from the isotropic liquid until crystallisation in ~ 1.2 °C intervals with a temperature accuracy of +/- 0.1 °C. 2D SAXS patterns were radially averaged (0.05 ° step

size) to give scattered intensity as a function of 2θ for each frame. Fitting of this integrated data with a either a Lorentzian, Gaussian or Voigt function as appropriate allowed the peak position and FWHM to be determined for both the small- and wide- angle peaks; the FWHM was then used to determine correlation lengths parallel and perpendicular to the director following correction for instrumental broadening.

1.9. Computational Chemistry

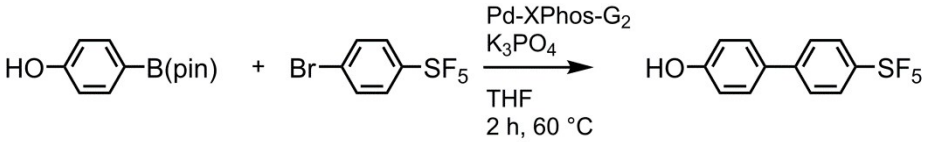
Quantum chemical calculations were performed using the Gaussian 09 revision e.01 suite of programmes. [3]

2. Synthesis

2.1. General Mitsunobu Etherification Procedure

DIAD (1.2 mmol, 242 mg, ~ 236 µl) was added dropwise to a stirred solution of the phenol (1 mmol), ***i-3*** (1 mmol) and PPh_3 (1.2 mmol, 314 mg) in anhydrous THF (3 ml). The reaction was monitored by TLC until complete consumption of either the phenol, alcohol or both (typically 4 h). The reaction solution was loaded onto celite, dried *in vacuo,* and purified by flash chromatography with a gradient of DCM/hexanes as the eluent. The target compounds were recrystalised from an appropriate solvent system.

2.2. Synthesis of Intermediates



4'-(pentafluoro-l6-sulfanyl)-[1,1'-biphenyl]-4-ol

A solution of 4-bromo(pentafluorothio)benzene (28.3 g, 0.1 mol) and K_3PO_4 (40 g, 0.188 mol) in THF (200 ml) was degassed by sparging with argon whilst agitating in an ultrasonic bath. After 15 minutes of degassing, 4-hydroxyphenyl boronic acid pinacol ester (22.0 g, 0.1 mol) was added in one portion and the degassing process continued for a further 15 minutes. The reaction suspension was heated under reflux under an atmosphere of dry nitrogen gas before the addition of Pd-XPhos-G2 (0.15 g, 0.2 mmol) in one portion. The reaction was stirred for 2 h, cooled to ambient temperature and filtered through a plug of silica gel before concentrating *in vacuo*. The crude material was recrystalised twice from ethanol to afford the

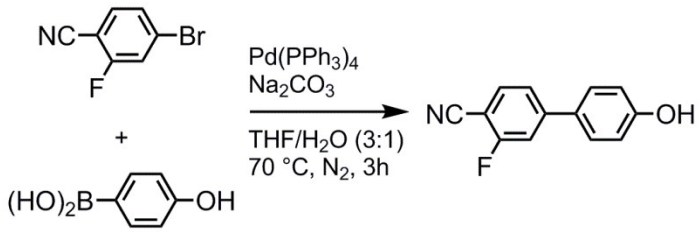
title compound as an off white crystalline solid. Spectral data was in keeping with that reported by Lakobson *et al.* [4]

Yield: 23.0 g (78 %)

Rf: 0.31 (DCM)

^{1}H NMR: 5.08 (1H, S, Ar-O<u>H</u>), 6.94 (2H, ddd, *J* = 2.4 Hz, *J* = 2.8 Hz, *J* = 8.4 Hz, Ar<u>H</u>), 7.48 (2H, ddd, *J* = 2.1 Hz, *J* = 3.1 Hz, *J* = 8.8 Hz, Ar<u>H</u>), 7.60 (2H, broad d, *J* = 8.8 Hz, Ar<u>H</u>), 7.79 (2H, ddd, *J* = 2.4 Hz, *J* = 2.8 Hz, *J* = 8.4 Hz, Ar<u>H</u>)

^{19}F NMR: 63.32 (4F, dd, J_{CF} = 17.2 Hz, J_{FF} = 150.0 Hz, S<u>F</u>$_5$ equatorial), 85.09 (1F, dd, J_{CF} = 22.2 Hz, J_{FF} = 150.0 Hz, S<u>F</u>$_5$ axial),



3-fluoro-4-cyano-4′-hydroxybiphenyl

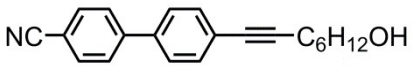
A biphasic solution of 4-bromo-2-fluorobenzonitrile (200 g, 1 mol) in THF (1.6 L) and water (500 ml) was degassed by vigorously stirring whilst sparging with nitrogen gas for 30 minutes. Separately, a solution of 4-hydroxyphenylboronic acid (151.8 g, 1.1 mol) in THF (400 ml, warmed to 40 °C to aid solubility) was degassed by sparging with nitrogen whilst agitating in an ultrasonic bath for 30 minutes. The two solutions were combined and brought to reflux (external temperature 70 °C) under an atmosphere of dry nitrogen gas. $Pd(PPh_3)_4$ (1.2 g, 1.038 mmol, ~ 0.1 mol%) was added in one portion and the reaction stirred vigorously under reflux at 70 °C (external temperature) for 3 hours; TLC analysis showed the complete consumption of the starting halide at this time. The stirring was stopped, the solution allowed to cool to ambient temperature and the aqueous layer separated and discarded. Ethanol (1 L) was added to the organic layer which was cooled to -20 °C to induce precipitation. The title compound was collected as an off-white crystalline solid. Spectral data was in keeping with literature values. [5]

Yield: 185.3 g (87%)

^{1}H NMR: 6.63 – 6.68 (2H, m, ArH), 7.08 – 7.13 (1H, m, ArH), 7.15 – 7.21 (3H, m, ArH), 7.33 – 7.39 (1H, m, ArH)

^{19}F NMR: -107.32 (ddd *J* = 1.6 Hz, *J* = 7.0 Hz, *J* = 10.5 Hz, ArF)

MS (ESI): 214.0639 (calcd. For $C_{13}H_9FNO$: 214.0663, M + H)



i-2: **4'-(8-Hydroxyoct-1-yn-1-yl)-[1,1'-biphenyl]-4-carbonitrile**

i-1 (7.7 g, 27.2 mmol), THF (75 ml) and 2M aqueous sodium carbonate (25 ml) were degassed by sparging with argon whilst agitating in an ultrasonic bath. 4-Cyanophenyl boronic acid (6.0 g, 40.9 mmol) was then added and the biphasic mixture brought to reflux under an atmosphere of dry nitrogen. In a separate vial palladium acetate (10 mg) and SPHOS (20 mg) were dissolved into THF (1 ml) and the suspension degassed by sparging with argon. The Pd/SPHOS solution was added in one portion to the reaction mixture, which was stirred whilst heating under reflux for 1 h before cooling to ambient temperature. The aqueous layer was separated, washed with DCM (3 x 25 ml) and discarded. The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash chromatography with DCM as the eluent followed by recrystalisation from 8:1 ethanol/hexane affording the title compound as a white solid.

Yield: 7.9 (96%)

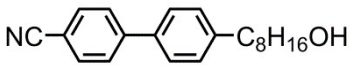
Rf: 0.15 (DCM)

^{1}H NMR: 1.35 – 1.52 (4H, m, Ar-CC-CH_2-CH_2-($C\underline{H}_2$)$_2$-CH_2-CH_2-OH), 1.55 – 1.68 (4H, m, Ar-CC-CH_2-$C\underline{H}_2$-(CH_2)$_2$-$C\underline{H}_2$-CH_2-OH), 2.43 (2H, t, *J* = 7.0 Hz, Ar-CC-$C\underline{H}_2$-CH_2-(CH_2)$_2$-CH_2-CH_2-OH), 3.65 (2H, t, *J* = 7.0 Hz, Ar-CC-CH_2-CH_2-(CH_2)$_2$-CH_2-$C\underline{H}_2$-OH), 7.44 – 7.52 (4H, m, Ar$\underline{H}$), 7.65 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.4 Hz, Ar$\underline{H}$), 7.70 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.4 Hz, Ar$\underline{H}$).

^{13}C{^{1}H} NMR: 19.16, 25.11, 28.354, 28.51, 32.33, 62.33, 79.49, 91.39, 110.65, 119.22, 127.21, 127.53, 127.72, 129.32, 132.58, 132.81, 136.57, 143.90, 145.77.

FT-IR (cm^{-1}): 717, 819, 860, 1004, 1024, 1039, 1055, 1180, 1313, 1394, 1463, 1477, 1492, 1604, 2229, 2860, 2935

MS: 304.1699 (calcd. for $C_{21}H_{22}NO$: 304.1696, M + H)



i-3: 4'-(8-Hydroxyocyl)-[1,1'-biphenyl]-4-carbonitrile

i-2 (5.8 g, 18.2 mmol) was added to a suspension of Pd/C (5wt %, 25 mg) poisoned with diaminoethane in THF (50 ml) and vigorously stirred. The flask was evacuated with a vacuum and the internal atmosphere replaced with hydrogen gas delivered *via* a balloon. This degassing process was repeated 3 times before allowing the suspension to stir under an atmosphere of hydrogen for 20 minutes. TLC analysis showed consumption of the starting material and the formation of a new material ($\Delta Rf_{DCM} \approx +0.03$). The reaction was filtered through a packed bed of celite, concentrated to a white solid *in vacuo* and recrystalised from ethanol to afford the title compound as a low density white powder.

Yield: 5.4 g (92%)

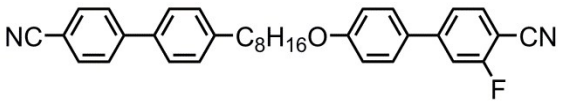
Rf: 0.18 (DCM)

^{1}H NMR: 1.20 – 1.40 (8H, m, -CH_2-($C\underline{H}_2$)$_4$-CH_2-), 1.50 – 1.70 (4H, m, HO-CH_2-$C\underline{H}_2$-(CH_2)$_4$-$C\underline{H}_2$-CH_2-Ar), 2.66 (2H, t, *J* = 6.6 Hz, Ar-$C\underline{H}_2$-CH_2-), 3.64 (2H, t, *J* = 6.6 Hz, HO-$C\underline{H}_2$-CH_2-), 7.29 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.8 Hz, Ar$\underline{H}$), 7.51 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.8 Hz, Ar$\underline{H}$), 7.67 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, Ar$\underline{H}$), 7.71 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, Ar$\underline{H}$)

^{13}C{^{1}H} NMR: 25.86, 29.36, 29.48, 29.58, 31.51, 32.89, 35.75, 63.19, 110.63, 119.20, 127.22, 127.50, 127.70, 129.31, 132.58, 132.80, 136.59, 143.87, 145.75.

MS: 308.2014 (calcd. for $C_{21}H_{26}NO$: 308.2009, M + H)
330.1833 (calcd. for $C_{21}H_{25}NNaO$: 330.1828, M + Na)

2.3. Characterisation of Dimeric Liquid Crystals



2: 4'-((8-(4'-cyano-[1,1'-biphenyl]-4-yl)octyl)oxy)-3-fluoro-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (100 mg, 0.270 mmol), PPh_3 (1 mmol, 262 mg), DIAD (1 mmol, 202 mg), 4′-cyano-3′-fluoro-4-hydroxybiphenyl (63.4 mg, 0.297 mmol). The general mitsunobu protocol was followed. The crude reaction mixture was purified by flash chromatography with 3:2 DCM/hexanes as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as fine white powder

Yield: 110 mg (81%)

Rf: 0.62 (DCM)

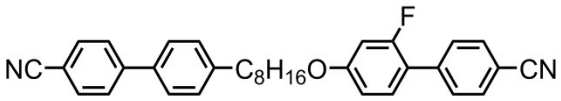
^{1}H NMR: 1.34 – 1.42 (6H, m, -CH_2-($C\underline{H}_2$)$_3$-CH_2-), 1.42 – 1.52 (2H, m, -CH_2-$C\underline{H}_2$-CH_2-), 1.62 – 1.71 (2H, m, Ar-CH_2-$C\underline{H}_2$-CH_2-), 1.76 – 1.84 (2H, m, ArO-CH_2-$C\underline{H}_2$-CH_2-), 2.67 (2H, t, *J* = 7.0 Hz, Ar-$C\underline{H}_2$-CH_2), 4.00 (2H, t, *J* = 7.0 Hz, ArO-$C\underline{H}_2$-CH_2-), 6.99 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.7 Hz, Ar$\underline{H}$), 7.29 (2H, d, *J* = 8.1 Hz, Ar$\underline{H}$), 7.37 (1H, dd, *J* = 1.5 Hz, *J* = 10.0 Hz, Ar$\underline{H}$), 7.43 Hz (1H, dd, *J* = 1.5 Hz, *J* = 8.1 Hz, Ar$\underline{H}$), 7.52 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.7 Hz, Ar$\underline{H}$), 7.61 – 7.75 (5H, m, Ar$\underline{H}$)

^{13}C{^{1}H} NMR: 26.13, 29.29, 29.35, 29.42, 29.53, 31.50, 35.73, 68.29, 98.95 (d, *J* = 15.7 Hz), 110.64, 114.09 (d, *J* = 20.1 Hz), 114.42, 115.28, 119.17, 122.78 (d, *J* = 3.0 Hz), 127.20, 127.59, 128.47, 129.30, 130.16 (d, *J* = 2.7 Hz), 132.69, 133.74, 136.59, 143.82, 145.70, 148.29 (d, *J* = 8.0 Hz), 160.37, 163.64 (d, *J* = 246.6 Hz)

^{19}F NMR: -106.32 (dd, *J* = 8.1 Hz, *J* = 10.0 Hz, Ar$\underline{F}$)

MS: 503.249160 (calcd. for $C_{34}H_{32}FN_2O$: 503.249318, M + H)

HPLC: >99.5%



3: 4'-((8-(4'-cyano-[1,1'-biphenyl]-4-yl)octyl)oxy)-2'-fluoro-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (100 mg, 0.270 mmol), PPh_3 (1 mmol, 262 mg), DIAD (1 mmol, 202 mg), 4′-cyano-2-fluoro-4-hydroxybiphenyl (63.4 mg, 0.297 mmol). The general mitsunobu protocol was followed. The crude reaction mixture was purified by flash chromatography with 5:3 DCM/hexanes as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as fine white powder

Yield: 110 mg (81%)

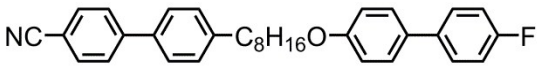
Rf: 0.61 (DCM)

^{1}H NMR: 1.33 – 1.50 (8H, m, -CH_2-($C\underline{H}_2$)$_4$-CH_2-), 1.60 – 1.73 (2H, m, Ar-CH_2-$C\underline{H}_2$-(CH_2)$_4$-CH_2-CH_2OAr), 1.76 – 1.87 (2H, m, ArOCH_2-$C\underline{H}_2$-(CH_2)$_6$-Ar), 2.67 (2H, t, *J* = 6.5 Hz, Ar$C\underline{H}_2$-CH_2-), 3.98 (2H, t, *J* = 6.5 Hz, ArO-$C\underline{H}_2$-CH_2), 6.71 (1H, dd, *J* = 2.4 Hz, *J* = 12.8 Hz, Ar$\underline{H}$), 6.78 (1H, dd, *J* = 2.4 Hz, *J* = 8.6 Hz, Ar$\underline{H}$), 7.28 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.4 Hz, Ar$\underline{H}$), 7.33 (1H, t, *J* = 8.9 Hz, Ar$\underline{H}$), 7.51 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.4 Hz, Ar$\underline{H}$), 7.58 – 7.74 (8H, m, Ar$\underline{H}$)^{13}C{^{1}H} NMR: 26.07, 29.14, 29.32, 29.37, 29.50, 31.47, 35.71, 68.61, 102.61, 110.64 (d, *J* = 5.1 Hz), 111.36 (d, *J* = 2.8 Hz), 119.07, 119.15, 119.20 (d, *J* = 12.3 Hz), 127.18, 127.56, 129.28, 129.36 (d, *J* = 3.6 Hz), 130.88 (d, *J* = 4.8 Hz), 136.56, 140.61, 143.79, 145.66, 145.66, 159.21, 160.45 (d, *J* = 249.9 Hz), 160.91, 161.02

^{19}F NMR: -115.08 - -114.90 (m, Ar$\underline{F}$)

MS: 503.2514 (calcd. for $C_{34}H_{32}FN_2O$: 503.2493, M + H)
525.2324 (calcd. for $C_{34}H_{31}FN_2NaO$: 525.2313, M + Na)

HPLC: >99.5%



4: 4'-(8-((4'-fluoro-[1,1'-biphenyl]-4-yl)oxy)octyl)-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (250 mg, 0.813 mmol), PPh_3 (1.626 mmol, 426 mg), DIAD (1.626 mmol, 320 µl), 4-hydroxy-4′-fluorobiphenyl (153 mg, 0.813 mmol). The general mitsunobu protocol was followed. The crude reaction mixture was purified by flash chromatography with 3:2 DCM/hexanes as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as fine colourless needles.

Yield: 200 mg (52%)

Rf: 0.67 (DCM)

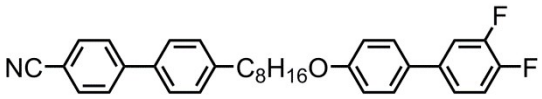
^{1}H NMR: 1.25 – 1.50 (8H, m, -CH_2-($C\underline{H}_2$)$_4$-CH_2-), 1.57 – 1.71 (2H, m, Ar-CH_2-$C\underline{H}_2$-CH_2-), 1.72 – 1.86 (2H, m, ArO-CH_2-$C\underline{H}_2$-CH_2-), 2.64 (2H, t, *J* = 6.5 Hz, Ar-$C\underline{H}_2$-CH_2), 3.99 (2H, t, *J* = 6.5 Hz, ArO-$C\underline{H}_2$-CH_2-), 6.95 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.7 Hz, Ar$\underline{H}$), (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.7 Hz, *J* = 8.7 Hz, Ar$\underline{H}$), 7.29 (2H, d, *J* = 8.9 Hz, Ar$\underline{H}$), 7.42 – 7.52 (6H, m, Ar$\underline{H}$), 7.67 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 9.2 Hz, Ar$\underline{H}$), 7.72 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 9.2 Hz, Ar$\underline{H}$)

^{13}C{^{1}H} NMR: 26.16, 29.33, 29.38, 29.41, 29.52, 31.49, 35.73, 68.16, 110.63, 114.91, 115.64 (d, *J* = 21.2 Hz), 119.18, 127.20, 127.59, 128.10, 128.28 (d, *J* = 7.8 Hz), 129.31, 132.68, 136.57, 137.10 (d, *J* = 3.0 Hz), 143.84, 145.71, 158.77, 160.95, 163.40

^{19}F NMR: -116.68 (tt, *J* = 5.8 Hz, *J* = 8.7 Hz, Ar$\underline{F}$)

MS (APCI): 478.253980 (calcd. for $C_{33}H_{33}FNO$: 478.254069, M + H)

HPLC: >99.5%



5: 4'-(8-((3',4'-difluoro-[1,1'-biphenyl]-4-yl)oxy)octyl)-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (100 mg, 0.270 mmol), PPh_3 (1 mmol, 262 mg), DIAD (1 mmol, 202 mg), 3′,4′-difluoro-4-hydroxybiphenyl (61 mg, 0.297 mmol). The general mitsunobu protocol was followed. The crude reaction mixture was purified by flash chromatography with 3:2 DCM/hexanes as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as fine colourless needles.

Yield: 95 mg (73%)

Rf: 0.71 (DCM)

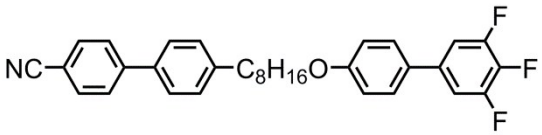
^{1}H NMR: 1.35 – 1.50 (8H, m, -CH_2-($C\underline{H}_2$)$_4$-CH_2-), 1.60 – 1.69 (2H, m, Ar-CH_2-$C\underline{H}_2$-CH_2-), 1.75 – 1.84 (2H, m, ArO-CH_2-$C\underline{H}_2$-CH_2-), 2.66 (2H, t, *J* = 7.0 Hz, Ar-$C\underline{H}_2$-CH_2), 3.99 (2H, t, *J* = 7.0 Hz, ArO-$C\underline{H}_2$-CH_2-), 6.85 – 6.97 (3H, m [ddd + m], Ar$\underline{H}$), 7.20 – 7.44 (6H, m, Ar$\underline{H}$), 7.53 (2H, ddd, *J* = 2.1 Hz ,*J* = 2.4 Hz, *J* = 8.8 Hz, Ar$\underline{H}$), 7.67 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, Ar$\underline{H}$), 7.71 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, Ar$\underline{H}$)

^{13}C{^{1}H} NMR: 26.17, 29.34, 29.36, 29.42, 29.53, 31.51, 35.75, 68.13, 104.42 (t, *J* = 26.7 Hz), 110.64, 111.57 (dd, *J* = 3.7 Hz, *J* = 20.8 Hz), 114.65, 119.21, 127.22, 129.61, 129.33, 130.11 (d, *J* = 2.7 Hz), 131.23 (dd, *J* = 5.2 Hz, *J* = 9.2 Hz), 132.70, 136.60, 143.86, 145.74, 158.93, 162.12 (dd, *J* = 11.6 Hz, *J* = 225.2 Hz)

^{19}F NMR: -113.90 - -113.70 (1F, m, Ar$\underline{F}$), -112.40 - -112.35 (1F, m, Ar$\underline{F}$)

MS (APCI): 496.244547 (calcd. for $C_{33}H_{32}F_2NO$: 496.244648, M + H)

HPLC: 99.1%



6: 4'-(8-((3',4',5'-trifluoro-[1,1'-biphenyl]-4-yl)oxy)octyl)-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (100 mg, 0.270 mmol), PPh_3 (1 mmol, 262 mg), DIAD (1 mmol, 202 mg), 3′,4′,5′-trifluoro-4-hydroxybiphenyl (66.6 mg, 0.297 mmol). The general mitsunobu protocol was followed. The crude reaction mixture was purified by flash chromatography with 2:1 DCM/hexanes as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as fine colourless needles.

Yield: 70 mg (50 %)

Rf: 0.71 (DCM)

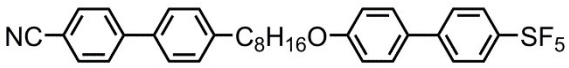
^{1}H NMR: 1.33 – 1.50 (8H, m, -CH_2-($C\underline{H}_2$)$_4$-CH_2-), 1.62 – 1.70 (2H, m, Ar-CH_2-$C\underline{H}_2$-CH_2-), 1.76 – 1.84 (2H, m, ArO-CH_2-$C\underline{H}_2$-CH_2-), 2.65 (2H, t, *J* = 7.0 Hz, Ar-$C\underline{H}_2$-CH_2), 3.99 (2H, t, *J* = 6.5 Hz, ArO-$C\underline{H}_2$-CH_2-), 6.95 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.4 Hz, Ar$\underline{H}$), 7.12 (2H, dd, *J* = 6.5 Hz, *J* = 9.0 Hz, Ar$\underline{H}$), 7.28 (2H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 8.9 Hz, Ar$\underline{H}$), 7.42 (2H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 8.9 Hz, Ar$\underline{H}$), 7.53 (2H, ddd, *J* = 2.1 Hz ,*J* = 2.8 Hz, *J* = 8.4 Hz, Ar$\underline{H}$), 7.67 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, Ar$\underline{H}$), 7.71 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, Ar$\underline{H}$)

^{13}C{^{1}H} NMR: 26.16, 29.33, 29.37, 29.43, 29.54, 31.51, 35.75, 68.24, 110.43, 110.54 (d, *J* = 9.9 Hz), 110.66, 115.12, 119.19, 127.22, 127.61, 128.03, 130.57, 132.71, 136.62, 137.0 – 137.50 (m) 143.84, 145.72, 150.20 – 150.40 (m) 152.65 – 152. 72 (m), 159.59

^{19}F NMR: -163.73 (1F, tt, *J* = 6.1 Hz, *J* = 20.4 Hz, Ar$\underline{F}$), -134.40 (2F, dd, *J* = 8.7 Hz, *J* = 20.4 Hz, Ar$\underline{F}$)

MS (APCI): 514.234880 (calcd. for $C_{33}H_{31}F_3NO$: 514.235226, M + H)

HPLC: 99.2%



7: 4'-(8-((4'-(pentafluoro-l6-sulfanyl)-[1,1'-biphenyl]-4-yl)oxy)octyl)-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (250 mg, 0.813 mmol), PPh_3 (1.63 mmol, 426 mg), DIAD (1.63 mmol, 320 µl), 4-pentafluorosulphanyl-4′-hydroxybiphenyl (241 mg, 0.813 mmol). The general mitsunobu protocol was followed. The crude reaction mixture was purified by flash chromatography with 3:2 DCM/hexanes as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as fine colourless crystals

Yield: 250 mg (53 %)

Rf: 0.74 (DCM)

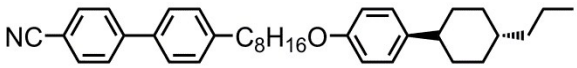
^{1}H NMR: 1.34 – 1.50 (8H, m, -CH_2-($C\underline{H}_2$)$_4$-CH_2-), 1.62 – 1.72 (2H, m, Ar-CH_2-$C\underline{H}_2$-CH_2-), 1.77 – 1.86 (2H, m, ArO-CH_2-$C\underline{H}_2$-CH_2-), 2.67 (2H, t, *J* = 6.7 Hz, Ar-$C\underline{H}_2$-CH_2), 4.00 (2H, t, *J* = 6.7 Hz, ArO-$C\underline{H}_2$-CH_2-), 6.98 (2H, ddd, *J* = 2.2 Hz, *J* = 2.7 Hz, *J* = 9.1 Hz, Ar$\underline{H}$), 7.29 (2H, d, *J* = 8.2 Hz, Ar$\underline{H}$), 7.48 – 7.52 (4H, m, Ar$\underline{H}$), 7.61 (2H, d, *J* = 8.7 Hz, Ar$\underline{H}$), 7.65 – 7.72 (4H, m, Ar$\underline{H}$), 7.78 (2H, ddd, *J* = 1.8 Hz, *J* = 2.5 Hz, *J* = 9.2 Hz, Ar$\underline{H}$)

^{13}C{^{1}H} NMR: 26.16, 29.36, 29.43, 29.54, 31.51, 35.75, 38.23, 110.66, 115.14, 119.14, 126.40 – 126.60 (m, $\underline{C}$-SF_5), 126.72, 127.22, 127.61, 128.49, 129.32, 131.35, 132.71, 136.61, 143.84, 144.23, 145.73, 159.72

^{19}F NMR: 63.33 (4F, dd, J_{CF} = 17.0 Hz, J_{FF} = 149.8 Hz, $ArSF_5$ equatorial), 85.16 (1F, quintet, J_{FF}= 149.8 Hz, SF_5 axial)

MS: 586. 2201 (calcd. for $C_{33}H_{32}F_5NOS$: 586.2198, M + H)

HPLC: >99.5%



8: 4'-(8-(4-((*trans*)-4-propylcyclohexyl)phenoxy)octyl)-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (154 mg, 0.5 mmol), *trans* 4-propylcyclohexylphenol (1 mmol, 218 mg), triphenyl phosphine (262 mg, 1 mmol), DIAD (1 mmol, 202 mg, ~197 µl), THF (4 ml). The experimental procedure was as described in the general Mitsunobu method. The crude reaction mixture was purified by flash chromatography with DCM as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as a white powder.

Yield: 240 mg (91 %)

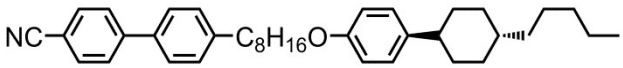
Rf: 0.82 (DCM)

^{1}H NMR: 0.90 (3H, t, *J* = 7.2 Hz, Cy-CH_2-CH_2-$C\underline{H}_3$), 0.94 – 1.09 (2H, m, Cy$\underline{H}$), 1.30 – 1.50 (13H, m, Cy$\underline{H}$ + -$C\underline{H}_2$-), 1.60 – 1.71 (2H, m, Cy$\underline{H}$), 1.70 – 1.80 (2H, m, -CH_2-$C\underline{H}_2$-CH_2), 1.81 – 1.89 (4H, m, Cy$\underline{H}$), 2.40 (1H, tt, *J* = 3.1 Hz, *J* = 12.3 Hz, Cy$\underline{H}$-Ar), 2.66 (2H, t, *J* = 7.2 Hz, Ar-$C\underline{H}_2$-CH_2-), 3.92 (2H, t, *J* = 7.2 Hz, ArO-$C\underline{H}_2$-CH_2), 6.81 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.8 Hz, Ar$\underline{H}$), 7.11 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.4 Hz, Ar$\underline{H}$), 7.29 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.4 Hz, Ar$\underline{H}$), 7.51 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.8 Hz, Ar$\underline{H}$), 7.67 (2H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 9.2 Hz, Ar$\underline{H}$), 7.71 (2H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 9.2 Hz, Ar$\underline{H}$)

^{13}C{^{1}H} NMR: 14.57, 20.19, 26.18, 29.34, 29.42, 29.45, 29.53, 29.54, 34.56, 34.75, 35.74, 37.12, 37.16, 39.88, 68.03, 110.63, 114.37, 115.36, 119.22, 127.23, 127.72, 129.32, 132.80, 136.59, 140.12, 143.88, 145.77, 157.32.

MS: 508.357320 (cald. for $C_{36}H_{46}NO$: 508.357392, M + H)

HPLC: 99.4%



9: 4'-(8-(4-((*trans*)-4-pentlcyclohexyl)phenoxy)octyl)-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (154 mg, 0.5 mmol), *trans* 4-pentylcyclohexylphenol (1 mmol, 246 mg), triphenyl phosphine (262 mg, 1 mmol), DIAD (1 mmol, 202 mg, ~197 µl), THF (4 ml). The experimental procedure was as described in the general Mitsunobu method. The crude reaction mixture was purified by flash chromatography with DCM as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as a white powder.

Yield: 210 mg (78 %)

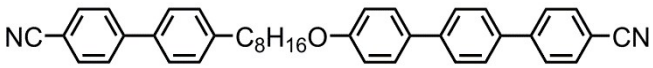
Rf: 0.80 (DCM)

^{1}H NMR: 0.89 (3H, t, *J* = 7.0 Hz, Cy-CH_2-CH_2-CH_3), 0.94 – 1.09 (2H, m, Cy<u>H</u>), 1.12 – 1.50 (17H, m, Cy<u>H</u> + -CH_2-), 1.61 – 1.70 (2H, m, Cy<u>H</u>), 1.72 – 1.80 (2H, m, -CH_2-CH_2-CH_2), 1.82 – 1.90 (4H, m, Cy<u>H</u>), 2.40 (1H, tt, *J* = 3.1 Hz, *J* = 12.3 Hz, Cy<u>H</u>-Ar), 2.67 (2H, t, *J* = 7.0 Hz, Ar-CH_2-CH_2-), 3.94 (2H, t, *J* = 7.0 Hz, ArO-CH_2-CH_2), 6.82 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.8 Hz, Ar<u>H</u>), 7.11 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.4 Hz, Ar<u>H</u>), 7.29 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.4 Hz, Ar<u>H</u>), 7.51 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.8 Hz, Ar<u>H</u>), 7.67 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, Ar<u>H</u>), 7.71 (2H, ddd, *J* = 2.1Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, Ar<u>H</u>)

^{13}C{^{1}H} NMR: 14.28, 22.87, 26.81, 26.99, 29.34, 29.43, 29.45, 29.47, 29.53, 29.56, 31.51, 32.36, 35.74, 37.46, 37.55, 43.82, 68.02, 110.63, 114.32, 119.21, 127.19, 127.22, 127.71, 127.76, 129.32, 136.59, 140.11, 143.88, 145.76, 157.31.

MS (APCI): 536.390904 (calcd. for $C_{38}H_{50}NO$: 536.388692, M + H)

HPLC: >99.5%



10: 4''-((8-(4'-cyano-[1,1'-biphenyl]-4-yl)octyl)oxy)-[1,1':4',1''-terphenyl]-4-carbonitrile

Quantities used: ***i-3*** (100 mg, 0.27 mmol), PPh_3 (1 mmol, 262 mg), DIAD (1 mmol, 199 µl), 4-hydroxy-4″-cyanoterphenyl (80.6 mg, 0.297 mmol). The general mitsunobu protocol was followed. The crude reaction mixture was purified by flash chromatography with 1:1 DCM/hexanes as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as a white powder.

Yield: 120 mg (79%)

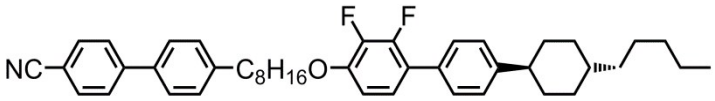
Rf: 0.50 (DCM)

^{1}H NMR: 1.33 – 1.43 (6H, m, -CH_2-($C\underline{H}_2$)$_3$-CH_2-), 1.43 – 1.53 (2H, m, -CH_2-$C\underline{H}_2$-CH_2-), 1.62 – 1.71 (2H, m, Ar-CH_2-$C\underline{H}_2$-CH_2-), 1.76 – 1.84 (2H, m, ArO-CH_2-$C\underline{H}_2$-CH_2-), 2.67 (2H, t, *J* = 6.5 Hz, Ar-$C\underline{H}_2$-CH_2), 4.01 (2H, t, *J* = 6.5 Hz, ArO-$C\underline{H}_2$-CH_2-), 6.99 (2H, ddd, *J* = 2.2 Hz, *J* = 2.7 Hz, *J* = 9.1 Hz, Ar$\underline{H}$), 7.29 (2H, ddd, *J* = 1.9 Hz, *J* = 2.2 Hz, *J* = 8.2 Hz, Ar$\underline{H}$), 7.51 (2H, ddd, *J* = 1.9 Hz, *J* = 2.2 Hz, *J* = 8.2 Hz, Ar$\underline{H}$), 7.56 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.7 Hz, Ar$\underline{H}$), 7.63 – 7.74 (12H, m, Ar$\underline{H}$).

^{13}C{^{1}H} NMR: 26.14, 29.31, 29.36, 29.39, 29.51, 31.46, 35.71, 68.18, 110.61, 110.86, 115.01, 119.12, 119.17, 127.19, 127.37, 127.58, 127.67, 128.17, 129.30, 132.50, 132.67, 132.75, 136.56, 137.32, 141.29, 143.82, 145.30, 145.69, 159.19

MS: 561.290186 (calcd. for $C_{40}H_{37}N_2O$: 561.290040, M + H)

HPLC: 99.2%



11: 4'-(8-((2,3-difluoro-4'-((*trans* (4-pentylcyclohexyl)-[1,1'-biphenyl]-4-yl)oxy)octyl)-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (250 mg, 0.813 mmol), PPh_3 (1.63 mmol, 426 mg), DIAD (1.63 mmol, 320 µl), *trans* 4-pentylcyclohexyl-4′-(4-hydroxy-2,3-difluorobiphenyl) (291.5 mg, 0.813 mmol). The general mitsunobu protocol was followed. The crude reaction mixture was purified by flash chromatography with 3:2 DCM/hexanes as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as fine colourless crystals

Yield: 350 mg (67%)

Rf: 0.76 (DCM)

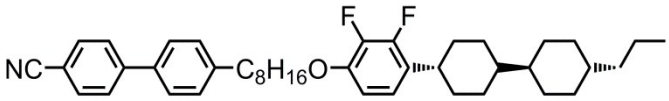
^{1}H NMR: 0.90 (3H, t, *J* = 7.0 Hz, -CH_2-C$\underline{H}_3$), 1.00 – 1.15 (2H, m, Cy$\underline{H}$), 1.20 – 1.34 (10H, m, Cy$\underline{H}$ + -C$\underline{H}_2$-C$\underline{H}_2$-CH_3), 1.42 – 1.54 (4H, m, Cy$\underline{H}$ + -C$\underline{H}_2$-), 1.62 – 1.70 (2H, m, -C$\underline{H}_2$-), 1.78 – 1.96 (7H, m, Cy$\underline{H}$), 2.51 (1H, tt, *J* = 3.5 Hz, *J* = 12.9 Hz, Cy$\underline{H}$-Ar), 2.66 (2H, t, *J* = 6.7 Hz, Ar-C$\underline{H}_2$-CH_2-), 4.00 (2H, t, *J* = 6.7 Hz, ArO-C$\underline{H}_2$-CH_2), 6.77 (1H, td, *J* = 5.4 Hz, *J* = 8.1 Hz, Ar$\underline{H}$), 7.07 (1H, td,*J* = 5.4 Hz, *J* = 11.5 Hz, Ar$\underline{H}$), 7.26 – 7.31 (4H, m, Ar$\underline{H}$), 7.42 (2H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz,*J* = 8.4 Hz, Ar$\underline{H}$), 7.53 (2H, ddd, *J* = 2.1 Hz, *J* = 2.9 Hz, *J* = 8.9 Hz, Ar$\underline{H}$), 7.67 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.9 Hz, Ar$\underline{H}$), 7.71 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 8.9 Hz, Ar$\underline{H}$)

^{13}C{^{1}H} NMR: 14.27, 22.87, 25.99, 26.80, 29.26, 29.31, 29.34, 29.49, 31.48, 32.36, 33.71, 34.43, 35.73, 37.43, 37.52, 44.47, 69.93, 109.61 (d, *J* = 3.0 Hz), 110.62, 119.20, 123.14 (d, *J* = 11.0 Hz), 123.60 (d, *J* = 4.1 Hz), 123.66, 127.19, 128.72 (d, *J* = 2.6 Hz), 129.32, 132.46, 132.68, 136.58, 141.92 (dd, *J* = 15.1 Hz, *J* = 246.7 Hz), 143.84, 145.74, 147.57, 147.60 – 147.80 (m), 148.98 (dd, *J* = 9.2 Hz, *J* = 246.8 Hz)

^{19}F NMR: -158.85 (1F, dd, *J* = 7.0 Hz, *J* = 19.4 Hz, Ar$\underline{F}$), -141.80 (1F, dd, *J* = 7.8 Hz, *J* = 19.4 Hz, Ar$\underline{F}$)

MS (APCI): 648.400856 (calcd. for $C_{44}H_{52}F_2NO$: 648.401148, M + H)

HPLC: >99.5%



12: 4'-(8-(2,3-difluoro-4-((*trans trans 4'*-propyl-[1,1'-bi(cyclohexan)]-4-yl)phenoxy)octyl)-[1,1'-biphenyl]-4-carbonitrile

Quantities used: ***i-3*** (250 mg, 0.813 mmol), PPh_3 (1.63 mmol, 426 mg), DIAD (1.63 mmol, 320 µl), *trans trans* 2,3-difluoro-4-(4'-propyl-[1,1'-bi(cyclohexan)]-4-yl)phenol (336 mg, 0.831 mmol). The general mitsunobu protocol was followed. The crude reaction mixture was purified by flash chromatography with 2:1 DCM/hexanes as the eluent. Recrystalisation of the chromatographed material from ethanol afforded the title compound as fine colourless crystals

Yield: 310 mg (61%)

Rf: 0.81 (DCM)

^{1}H NMR: 1.15 – 1.25 (5H, m, CyH + -CH_2-CH_3), 1.28 – 1.55 (1 H, m, CyH + -CH_2-), 1.55 – 1.85 (12 H, m, CyH + -CH_2-), 1.95 – 2.30 (12 H, m, CyH + -CH_2-), 2.94 – 3.16 (3H, m, Ar-CH_2-CH_2 + Ar-CyH-), 4.35 (2H, t, *J* = 7.0 Hz, ArOCH_2-CH_2-), 7.01 (1H, td, *J* = 1.8 Hz, *J* = 8.3 Hz, ArH), 7.18 (1H, td, *J* = 2.3 Hz, *J* = 8.3 Hz, ArH), 7.63 (2H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 8.9 Hz, ArH), 7.88 (2H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 8.9 Hz, ArH), 8.02 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, ArH), 8.07 (2H, ddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, ArH)

^{13}C {^{1}H} NMR: 14.58, 20.19, 26.00, 29.31, 29.35, 29.49, 30.21, 30.34, 31.48, 33.42, 33.72, 35.73, 37.08, 37.75, 39.96, 43.02, 43.51, 69.95, 109.48 (d, *J* = 2.7 Hz), 110.63, 120.52 (t, *J* = 10.3 Hz), 127.22, 127.62, 128.38 (d, *J* = 12.4 Hz), 129.32, 132.70, 136.59, 141.59 (dd, *J* = 15.5 Hz, *J* = 246.3 Hz), 143.86, 145.76, 146.90 – 147.05 (m), 147.33 (dd, *J* = 10.2 Hz, *J* = 192.6 Hz)

^{19}F NMR: -159.65 (1F, dd, *J* = 7.1 Hz, *J* = 19.6 Hz, ArF), -143.27 (1F, dd, *J* = 7.3 Hz, *J* = 19.6 Hz, ArF)

MS (APCI): 626.415254 (calcd. for $C_{42}H_{54}F_2NO$: 626.416798, M + H)

HPLC: >99.5%

4. Supplementary Data

4.1. Supplementary POM photomicrographs

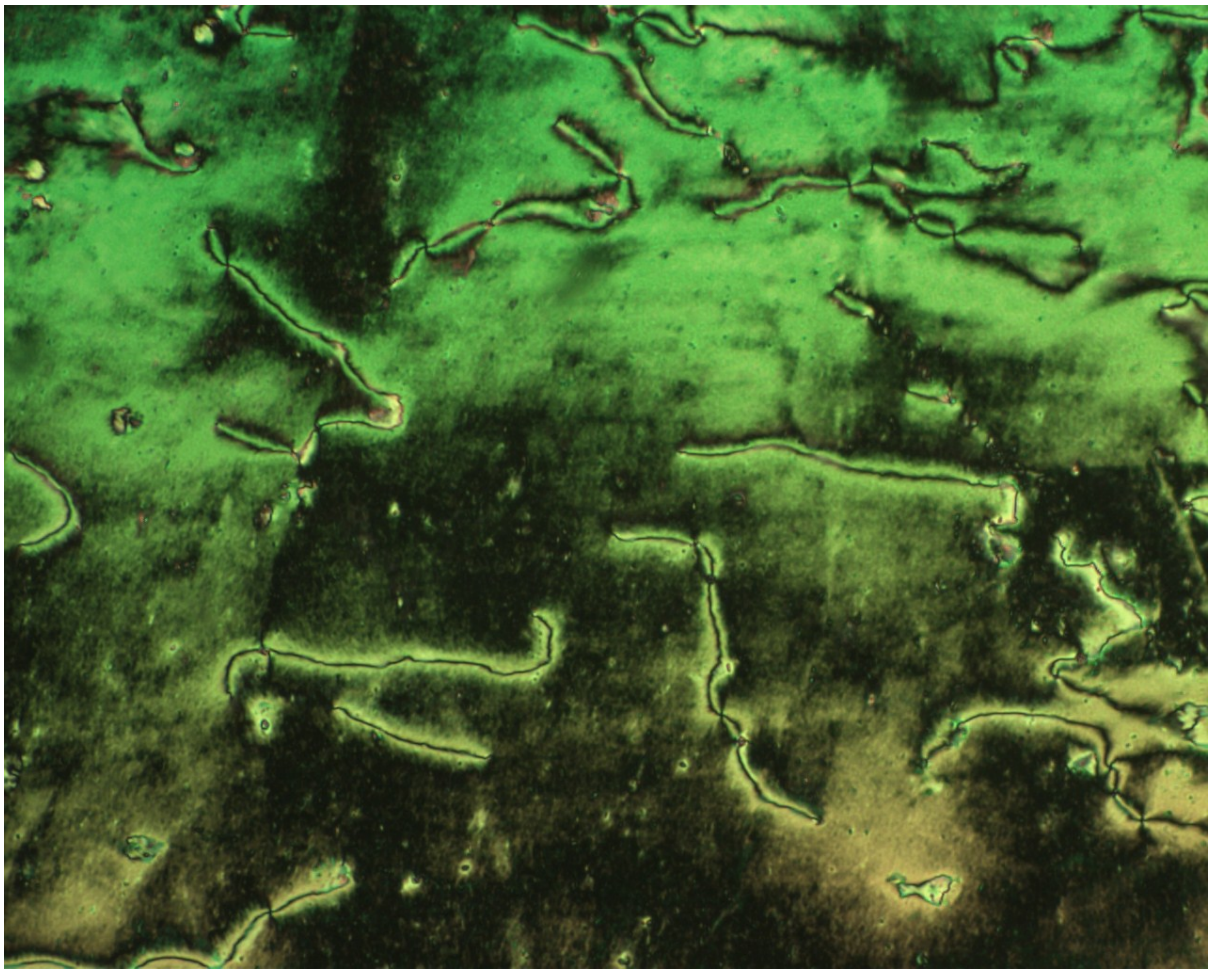


Figure SI1: Photomicrograph (x100, crossed polarisers) of the nematic phase of compound **3** at 105 °C

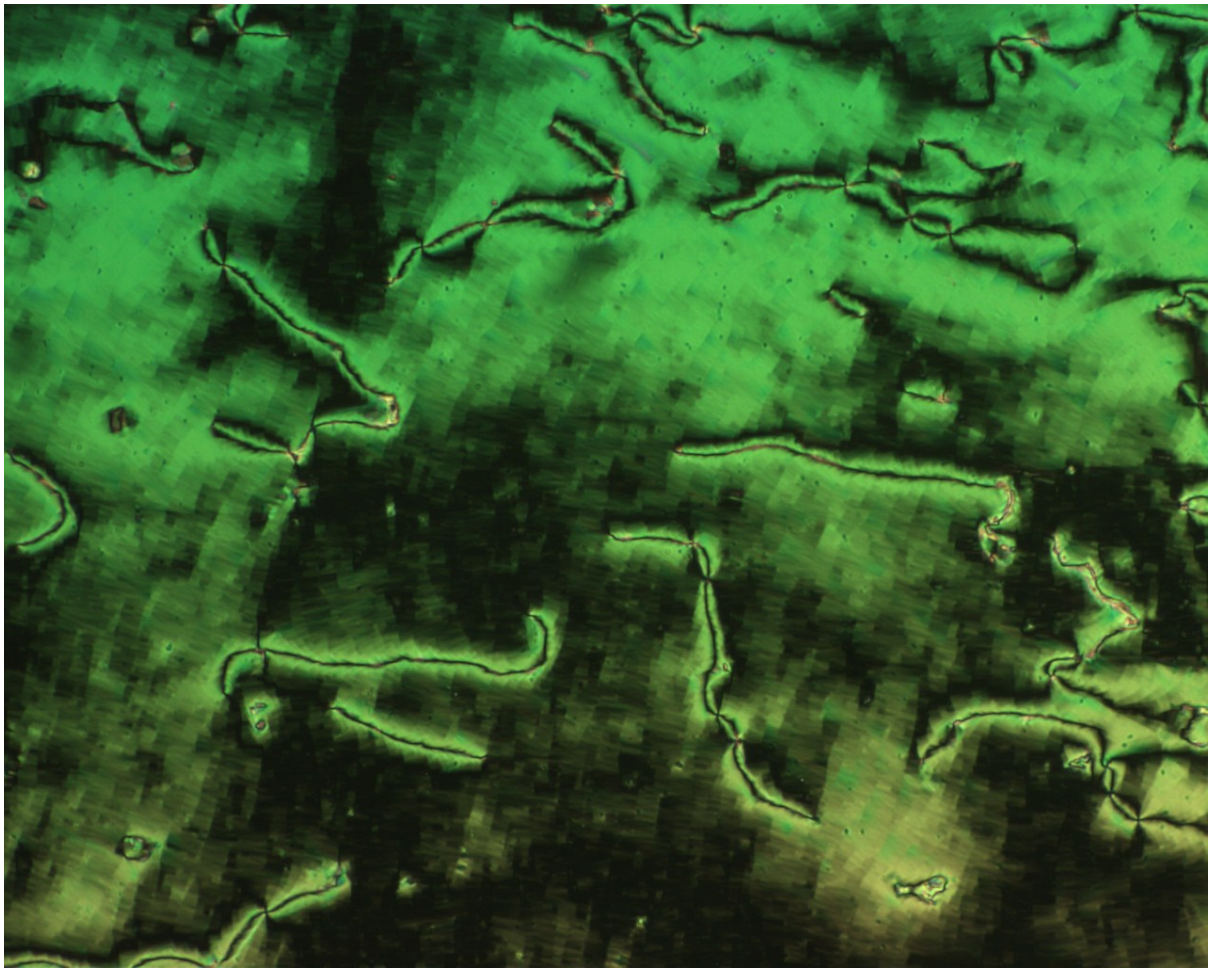


Figure SI2: Photomicrograph (x100, crossed polarisers) of the blocky texture of the twist-bend phase of compound **3** at 94 °C

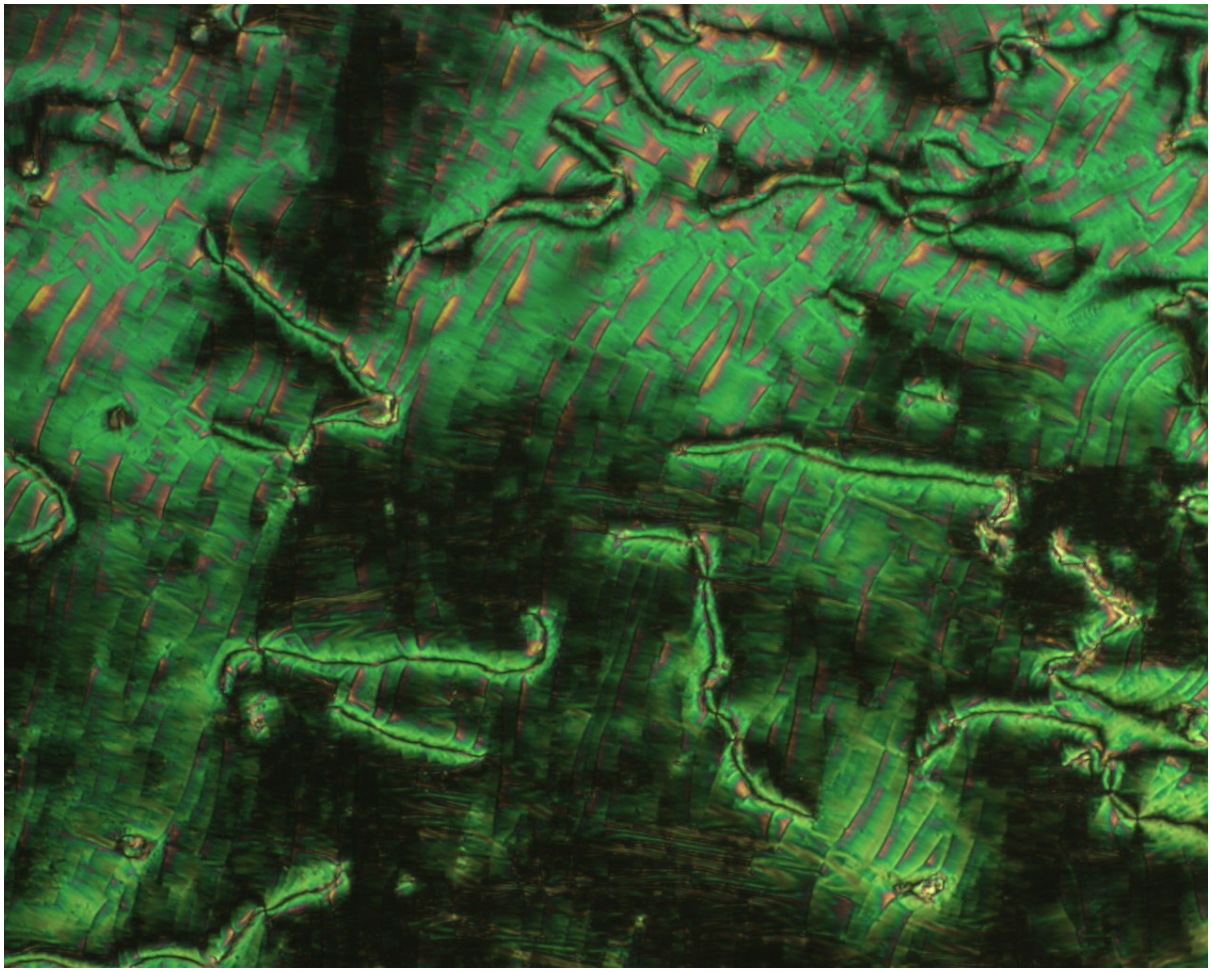


Figure SI3: Photomicrograph (x100, crossed polarisers) of the evolution of the blocky texture of the twist-bend phase of compound **3** at 92 °C

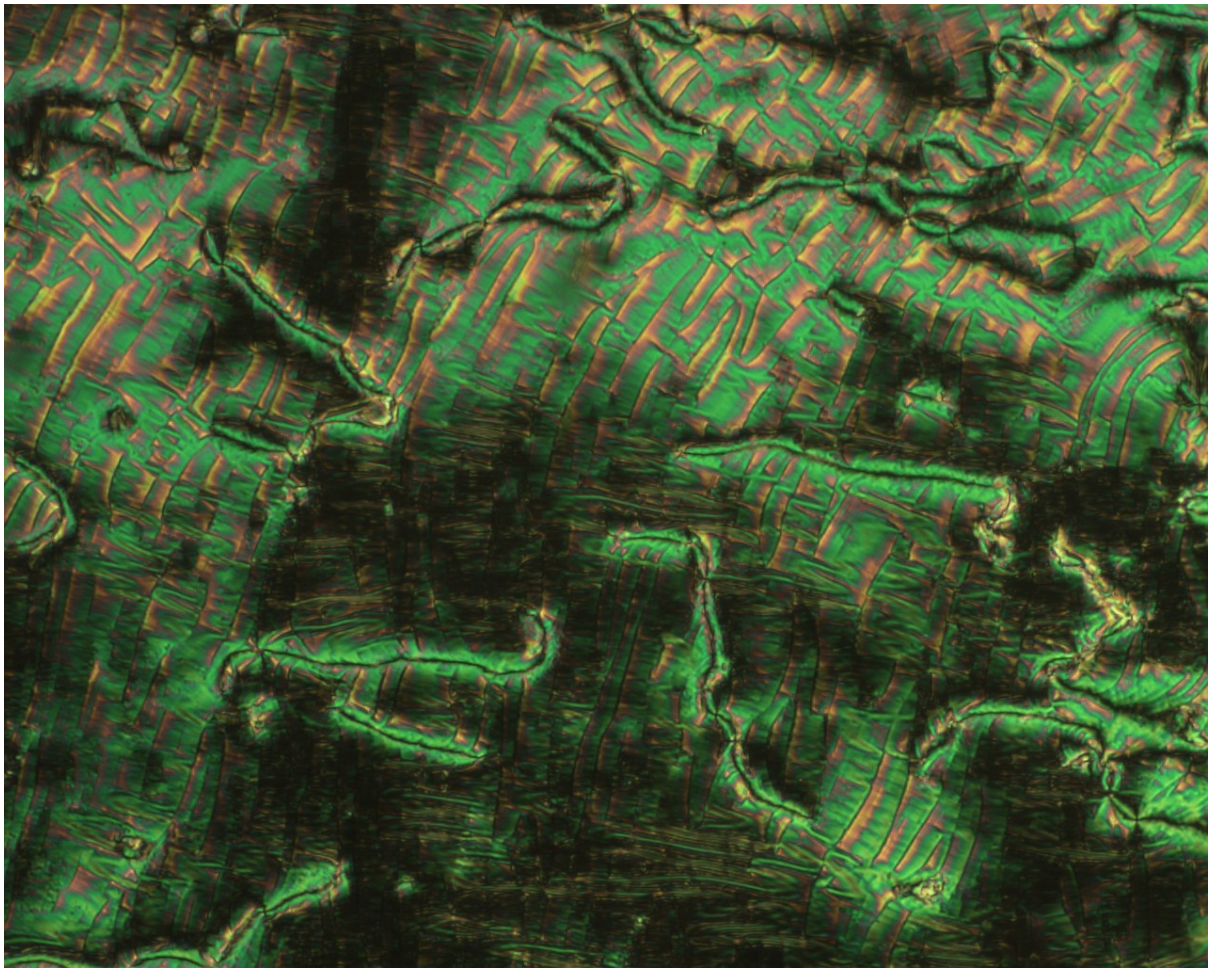


Figure SI4: Photomicrograph (x100, crossed polarisers) of the evolution of the blocky texture of the twist-bend phase of compound **3** at 90 °C

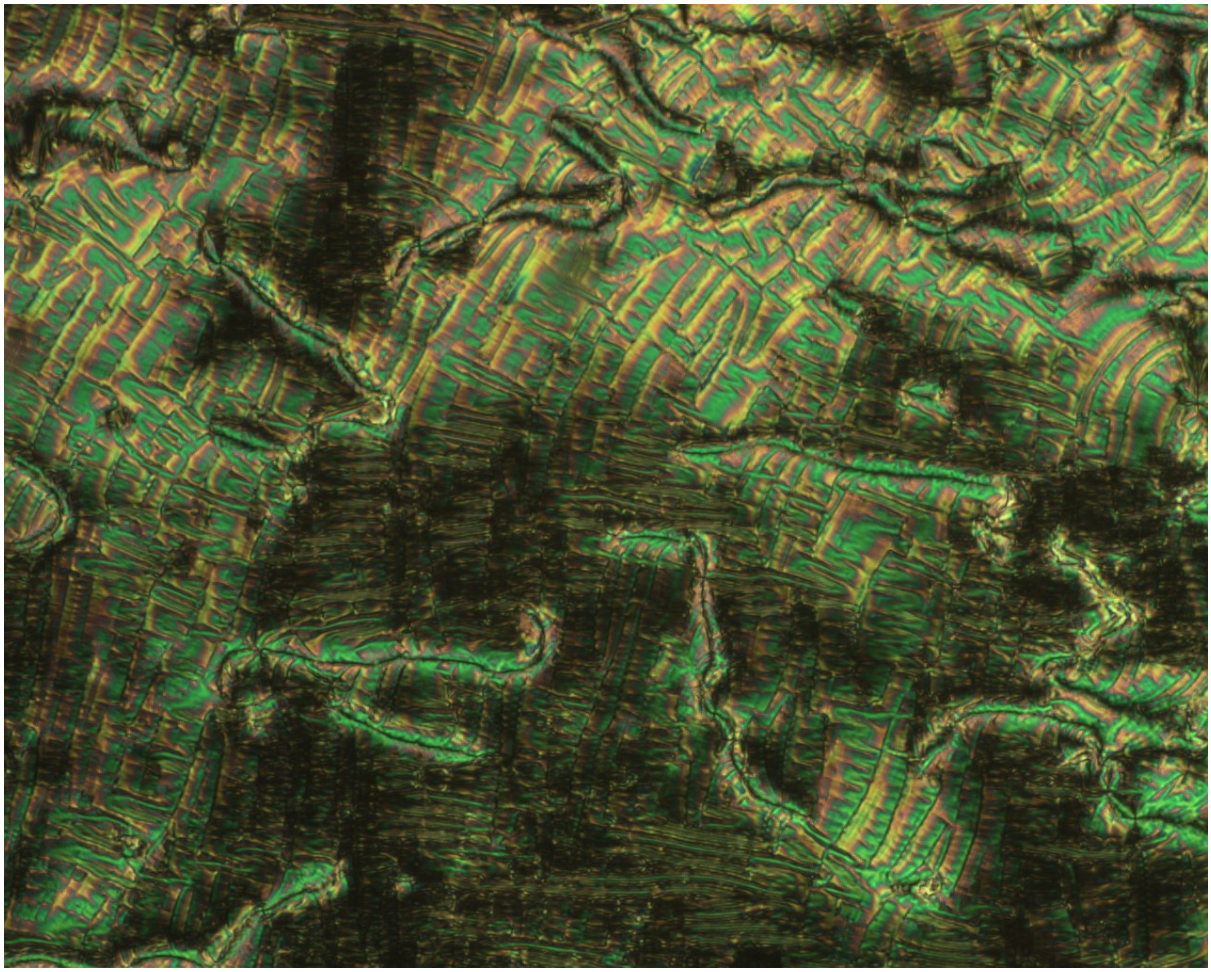


Figure SI5: Photomicrograph (x100, crossed polarisers) of the evolution of the blocky texture of the twist-bend phase of compound **3** at 88 °C

4.2. Supplementary SAXS data

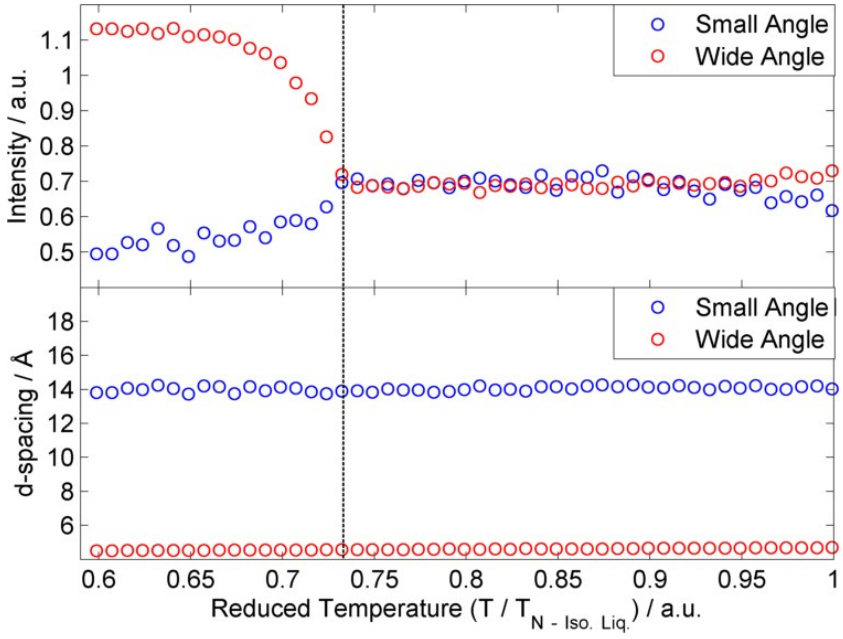


Figure SI6: Plot of the intensity of the small- and wide-angle peaks as a function of reduced temperature for compound **3** (top). Plot of the d-spacing (Å) of both the small- and wide-angle peaks as a function of reduced temperature for compound **3**. The dashed line corresponds to the location of the N-TB phase transition.

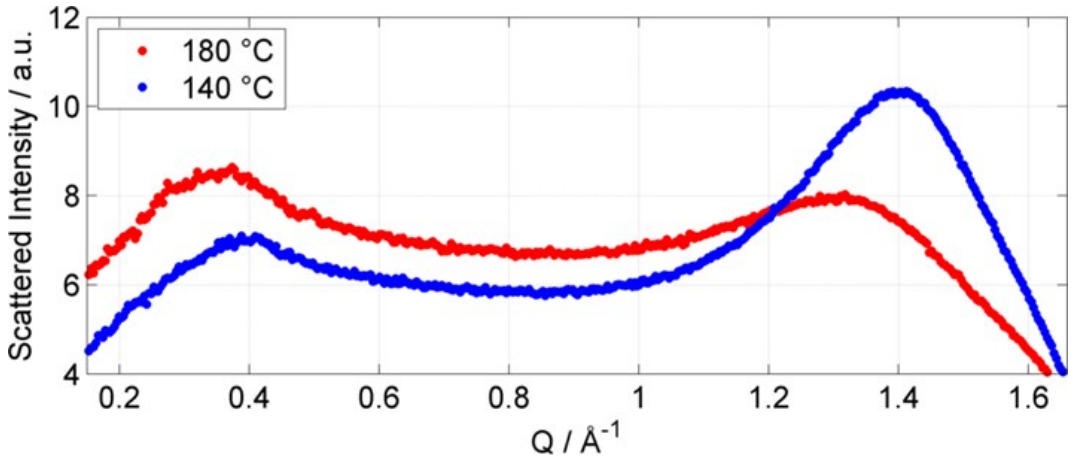


Figure SI7: plot of scattered intensity as a function of Q ($Å^{-1}$) in both phases of compound **10** (CB8OCT) at the specified temperatures.

4.3. Supplemental Conformational Analysis Data

As discussed in the text, we observed the distribution of conformers for both CB9CB (-CH_2-/-CH_2-) and CB8OCB (-CH_2/-O-) to be approximately Gaussian, albeit with different a FWHM (19 ° and 31 ° for CB9CB and CB8OCB respectively). However, as the data was presented as a histogram we wanted to ensure that the number of bins (bin size = 180 / number of bins) did not impact the FWHM. Figure SI8 shows a plot of the FWHM of a Gaussian fit to the histogram plot of probability versus bend angle for each conformer library as a function of the number of bins. We find that provided a sensible number of bins is chosen (>10) the FWHM is unaffected.

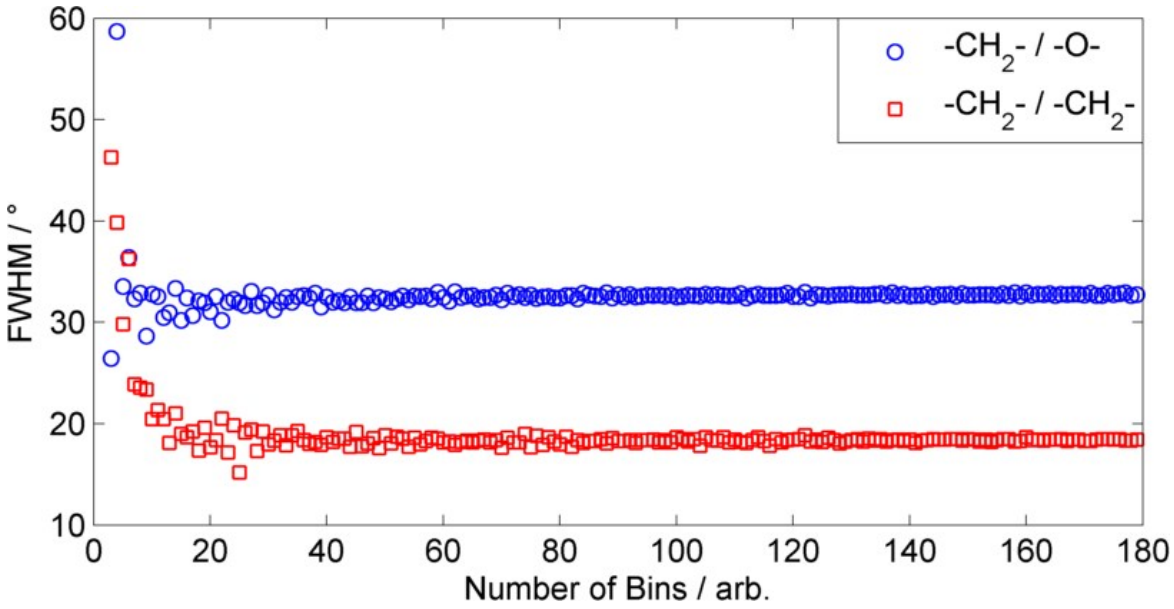


Figure SI8: Plot of the FWHM of a Gaussian fit to histogram data (probability versus bend angle) as a function of bin size for CB9CB (-CH_2-/-CH_2-) and CB8OCB (-CH_2/-O-).

5. References

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