Electronic Supplementary Information

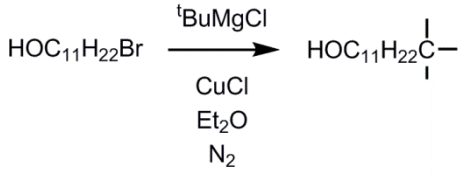
Experimental

All reagents and materials were used as received without purification, with the exception of solvents, which were dried via percolation through activated alumina. Low sulphur toluene was prepared by stirring toluene with neat sulphuric acid, removing the sulphuric acid and repeating until the acid was returned colourless. [ES1] The toluene was then dried over calcium hydride, distilled and stored over activated 3Å molecular sieves prior to use. 4-Hydroxy-[2,2]-paracyclophane was prepared in house according to an established literature procedure [ES2].

NMR spectra were recorded using a JEOL ECX spectrometer operating at 400 MHz (^{1}H), 100.5 MHz (^{13}C), 376.5 Hz (^{19}F), with the exception of silicon NMR which were recorded using a JEOL ECS spectrometer operating at 76.4 Hz. Mass spectra were recorded on either a Bruker micrOTOF MS-Agilent series 1200LC spectrometer for ESI or on a Waters GCT Premier MS-Agilent 7890A GC spectrometer (CGT) for EI. FT-IR spectroscopy was performed using a Shimadzu IR Prestige-21 with Specac Golden Gate diamond ATR IR insert. High-performance liquid chromatography was performed using 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 on a Shimadzu Prominence modular HPLC system comprising a LC-20A liquid chromatograph, a DGU-20A5 and DGU-20B 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 230/255 nm. Acetonitrile was used as the mobile phase.

Small angle X-ray diffraction was performed using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. Samples were filled into 1mm capillary tubes and aligned magnetically with a 1T magnet. Diffraction patterns were collected as a function of temperature and the data processed using Bruker DIFFRAC.SUITE EVA software. Computational studies were performed using Gaussian 09. [3] Electrooptic studies were performed by flow filling a mixture of the target compound and tetrabutylammonium bromide (TBAB, 0.09 wt%) into ITO glass cells supplied by Halation. The cell was placed in a temperature controlled furnace and an electric field of variable voltage (20 – 110 V) and frequency (1 Hz or 1 KHz) was applied *via* a custom built amplifier supplied by Halation.

Synthesis



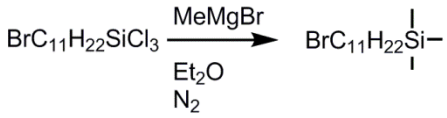
12,12-Dimethyltridecan-1-ol i1 (RM1156)

A solution of *tert*-butyl magnesium chloride in diethyl ether (2M, 200 ml, 0.4 mol) was added slowly (CAUTION, exothermic reaction) a stirred solution of 11-bromoundecanol (50 g, 199 mmol) and copper chloride (200 mg) in dry diethyl ether (400 ml) under an atmosphere of dry nitrogen. The resulting solution was stirred for 6h, before quenching with saturated aqueous ammonium chloride. The organic layer was separated and retained; the aqueous layer was washed with diethyl ether (4 x 50 ml) and discarded. The combined organic extracts were dried over $MgSO_4$, concentrated *in vacuo* and purified *via* column chromatography with 5/1 hexane/ethyl acetate as the eluent. The title compound was obtained as a colourless oil.

Yield: 42 g (93%)

^{1}H NMR: 0.81 (9H, s, C(C*H*$_3$)$_3$), 1.05 – 1.39 (20H, m, CH$_2$-(C*H*$_2$)$_{10}$-C(CH$_3$)$_3$), 1.48 (2H, Quintet, *J* = 6.1 Hz, HO-C*H*$_2$-(CH$_2$)$_{10}$-C(CH$_3$)$_3$), 3.33 (1H, t, *J* = 6.9 Hz, *H*O-CH$_2$-)

^{13}C NMR: 24.51, 25.70, 29.37, 29.40, 29.50, 29.57, 29.63, 29.68, 30.21, 30.59, 32.72, 33.89, 62.90



11-(Trimethylsilyl)undecan-1-ol i2 (RM1380)

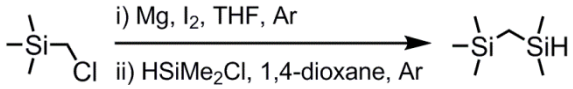
A solution of methyl magnesium chloride in diethyl ether (3 M, 108 mmol, 36.1 ml) was added dropwise to a solution of 11-bromoundecyltrichlorosilane (10 g, 27.06 mmol) in dry diethyl ether (150 ml). The resulting solution was stirred for 2h, before quenching with saturated aqueous ammonium chloride. The organic layer was separated and retained; the aqueous layer was washed with diethyl ether (4 x 25 ml) and discarded. The combined organic extracts were dried over $MgSO_4$, concentrated *in vacuo* and purified *via* flash chromatography with 1:1 DCM/hexane as the eluent. The title compound was obtained as a colourless oil

Yield: 8.2 g (98%)

^{1}H NMR: 0.00 (9H, s, Si(C*H*$_3$)$_3$), 1.25 – 1.39 (16H, m, -CH$_2$-(C*H*$_2$)$_8$-Si(CH$_3$)$_3$), 1.45 (2H, quintet, *J* = 7.0 Hz, Br-CH$_2$-CH$_2$-C*H*$_2$-CH$_2$), 1.87 45 (2H, quintet, *J* = 7.0 Hz, Br-CH$_2$-C*H*$_2$-CH$_2$), 3.43 (2H, t, *J* = 7.0 Hz, Br-C*H*$_2$-CH$_2$-).

^{13}C NMR: -1.53, 16.78, 24.01, 28.30, 28.90, 29.49, 29.55, 29.67, 29.70, 32.96, 33.74, 33.88

^{29}Si NMR: 1.63



((Trimethylsilyl)methyl)dimethylsilane i3 (RM1381)

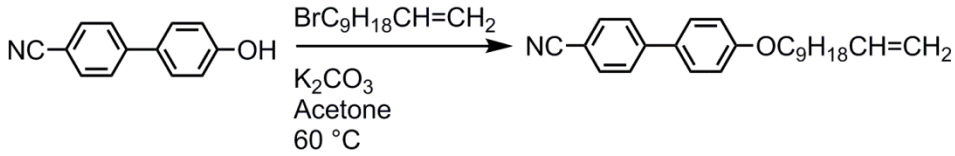
Magnesium metal (4.4 g) was ground under an argon atmosphere, suspended in dry THF (100 ml) and a crystal of iodine added. Dibromoethane (250 µl) was added and the reaction solution stirred until the Gringard reaction initiated. Once the reaction had initiated, chloro(trimethylsilyl)methane (20 g, 23 ml, 0.164 mol) was added dropwise over a period of 1 h. Once the formation of the Gringard reagent was complete dimethylchlorosilane (16.9 g, 20 ml, 180 mmol) in 1,4-dioxane (80 ml) was added dropwise and the resulting solution stirred for 3 h. The reaction was quenched with saturated aqueous ammonium chloride. The organic layer was separated and retained; the aqueous layer was washed with diethyl ether (3 x 50 ml) and discarded. The combined organic extracts were dried over $MgSO_4$, concentrated *in vacuo* and purified *via* distillation (114-116 °C, 760 Torr) to yield the title compound as a colourless, oil.

Yield: 22 g (91%)

^{1}H NMR: -0.27 (2H, d, *J* = 3.7 Hz, Si-C*H*$_2$-Si), 0.00 (9H, s, -CH$_2$-Si(C*H*$_3$)$_3$), 0.06 (6H, d, *J* = 3.7 Hz, -CH$_2$-Si(C*H*$_3$)$_2$H)

^{13}C NMR: -1.49, 0.81, 1.49

^{29}Si NMR: -16.09 (-CH$_2$-*Si*(CH$_3$)$_2$-H), 1.06 (-CH$_2$-*Si*(CH$_3$)$_3$)



4'-(11-Hydroxyundecyloxy)-4-cyanobiphenyl i4

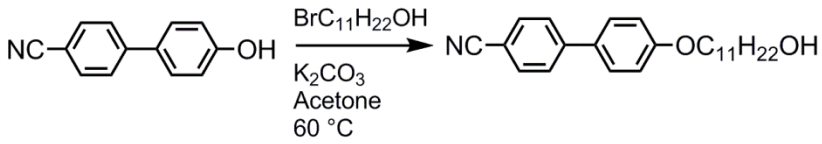
A stirred suspension of 4'-hydroxy-4-cyanobiphenyl (10 g, 51 mmol), 1-bromoundec-11-ene (11.9 g, 51 mmol) and potassium carbonate (14 g, 102 mmol) in acetone (150 ml) was heated under reflux for 20 h, until complete consumption of 4'-hydroxy-4-cyanobiphenyl as evidenced by TLC. The suspension was cooled to ambient temperature, diluted with DCM (200 ml) and the insoluble matter removed by filtration. The filtrate was evaporated to dryness and recrystalised from ethanol, giving the title compound as white needles.

Yield: 16.4 g (95%)

^{1}H NMR: 1.26 – 1.53 (12 H, m, -CH_2-(CH_2)$_6$-CH_2-), 1.84 (2H, quintet, *J* = 6.4 Hz, -CH_2-(CH_2)$_6$-CH_2-CH_2-), 2.01 – 2.08 (2H, m, -CH_2-(CH_2)$_6$-CH_2-CH_2-), 4.01 (2H, t, *J* = 6.4 Hz, ArOCH_2-CH_2-), 4.94 (1H, dtt, *J* = 1.2 Hz, *J* = 2.1 Hz, *J* = 10.1 Hz, -CH_2-CH=C*H*H), 5.00 (1H, dtt, *J* = 1.2 Hz, *J* = 2.1 Hz, *J* = 17.1 Hz, -CH_2-CH=CH*H*), 7.00 (2H, ddd, *J* = 2.1 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*), 7.52 (2H, ddd, *J* = 2.1 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*), 7.63 (2H, ddd, *J* = 1.5 Hz, *J* = 2.1 Hz, *J* = 8.5 Hz, Ar*H*), 7.68 (2H, ddd, *J* = 1.5 Hz, *J* = 2.1 Hz, *J* = 8.5 Hz, Ar*H*).

^{13}C NMR: 25.95, 28.84, 29.04, 29.14, 29.29, 29.34, 29.44, 33.72, 68.07, 109.92, 114.08, 114.99, 119.03, 126.96, 128.22, 131.11, 132.46, 139.10, 145,17, 159.73

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.7%



4'-(11-Hydroxyundecyloxy)-4-cyanobiphenyl (RM1416) (1)

Quantities used: 4'-hydroxy-4-cyanobiphenyl (5 g, 25.5 mmol), 11-bromoundecan-1-ol (6.4 g, 25.5 mmol), potassium carbonate (5 g), acetone (100 ml). The experimental procedure was as described for the synthesis of compound **i4**, recrystallisation of the crude material from ethanol gave the title compound as fine colourless needles.

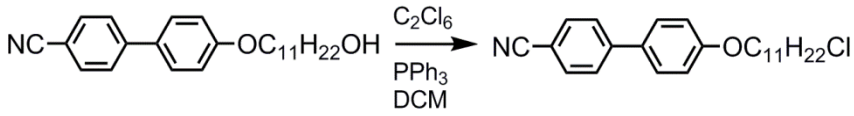
Yield: 8.7 g (93%)

^{1}H NMR: 1.20 – 1.45 (14 H, m, -CH_2-(CH_2)$_7$-CH_2-), 1.49 (2H, Quintet, *J* = 6.7 Hz, -CH_2-CH_2-(CH_2)$_7$-) 1.73 (2H, Quintet, *J* = 6.7 Hz, -(CH_2)$_7$-CH_2-CH_2-), 3.56 (2H, t, *J* = 6.7 Hz, -CH_2-OH), 3.92 (2H, t, *J* = 6.7 Hz, ArOCH_2-CH_2-), 6.91 (2H, ddd, *J* = 2.1 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*), 7.51 (2H, ddd, *J* = 2.1 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*), 7.63 (2H, ddd, *J* = 1.8 Hz, *J* = 2.8 Hz, *J* = 8.5 Hz, Ar*H*).), 7.68 (2H, ddd, *J* = 1.8 Hz, *J* = 2.8 Hz, *J* = 8.5 Hz, Ar*H*).

^{13}C NMR: 25.69, 25.98, 29.16, 29.32, 29.37, 29.46, 29.49, 29.53, 32.74, 63.00, 68.12, 109.95, 115.03, 119.08, 127.01, 128.26, 131.18, 132.51, 145.24, 159.75

MS: 388.2238 (100%, $C_{24}H_{31}NNaO_2$ M + Na)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.2%



4'-(11-Chloroundecyloxy)-4-cyanobiphenyl (RM1437) (2)

Hexachloroethane (647 mg, 2.73 mmol) was added to a stirred solution of **1** (1 g, 2.73 mmol) and PPh_3 (717 mg, 2.74 mmol) in DCM (20 ml) and the resulting solution stirred for 3 h, at which time TLC analysis showed complete consumption of compound **1**. The solvent was then removed *in vacuo* and the crude residue purified by chromatography with DCM as the eluent, followed by recrystalisation from ethanol, giving the title compound as colourless plates.

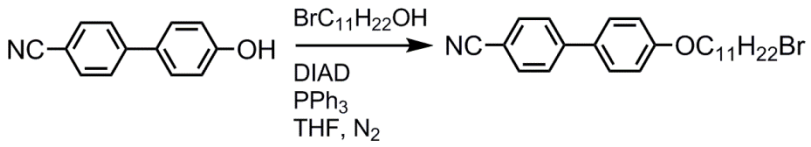
Yield: 950 mg (90%)

^{1}H NMR: 1.27 – 1.51 (14 H, m, -CH_2-(CH_2)$_7$-CH_2-), 1.72 – 1.84 (4H, m, -CH_2-CH_2-(CH_2)$_7$-CH_2-CH_2-), 3.52 (2H, t, *J* = 6.7 Hz, -CH_2-Cl), 3.99 (2H, t, *J* = 6.7 Hz, ArOCH_2-CH_2-), 6.98 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.51 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.63 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.68 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*).

^{13}C NMR: 25.98, 26.83, 28.83, 29.17, 29.31, 29.39, 29.41, 29.47, 32.59, 41.15, 68.10, 109.97, 115.03, 119.09, 127.01, 128.26, 131.19, 132.51, 145.23, 159.75

MS: 401.2356 (100%, $C_{24}H_{30}ClNNaO$, M + Na)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.5%



4'-(11-Bromoundecyloxy)-4-cyanobiphenyl (RM1370) (3)

Quantities used: 4'-cyano-4-hydroxybiphenyl (5 g, 25.64 mmol), 11-bromoundecan-1-ol (6.5 g, 25.64 mmol), PPh_3 (6.7 g, 25.64 mmol), DIAD (5.2 g, 5.04 ml, 25.74 mmol), THF (100 ml). The experimental procedure was as described in the synthesis of compound **1**. The crude material was purified by flash chromatography with 3/2 DCM/hexane as the eluent followed by recrystalisation from 5/1 toluene/hexane, giving the title compound as colourless plates.

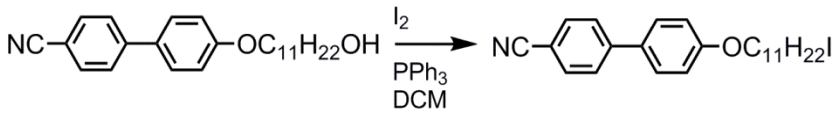
Yield: 7.8 g (71%)

^{1}H NMR: 1.24 – 1.48 (14 H, m, -CH_2-(CH_2)$_7$-CH_2-), 1.75 – 1.86 (4H, m, -CH_2-CH_2-(CH_2)$_7$-CH_2-CH_2-), 3.38 (2H, t, *J* = 7.0 Hz, -CH_2-Br), 3.98 (2H, t, *J* =7.0 Hz, ArOCH_2-CH_2-), 6.97 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.50 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.61 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.66 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*).

^{13}C NMR: 25.96, 28.09, 28.69, 29.15, 29.29, 29.34, 29.38, 29.44, 32.76, 34.01, 68.08, 109.94, 115.02, 119.05, 126.99, 128.24, 131.15, 132.49, 145.20, 159.74

MS: 450.1412 (100%, $C_{24}H_{30}BrNNaO$, M + Na)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.8%



4'-(11-Iodoundecyloxy)-4-cyanobiphenyl (**RM1438) (4)**

Iodine (695 mg, 2.74 mmol) was added to a stirred solution of **1** (1 g, 2.74 mmol) and PPh_3 (717 mg, 2.74 mmol) in DCM (20 ml), and the resulting solution stirred for 3 h with the exclusion of light. The solvent was then removed *in vacuo* and the crude residue purified by chromatography with DCM as the eluent, giving the title compound as an orange solid. This solid was recrystalised three times from ethanol to give the title compound as a colourless solid.

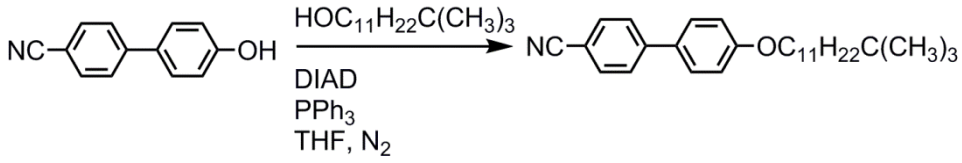
Yield: 850 mg (65%)

^{1}H NMR: 1.24 – 1.48 (14 H, m, -CH_2-(CH_2)$_7$-CH_2-), 1.75 – 1.83 (4H, m, -CH_2-CH_2-(CH_2)$_7$-CH_2-CH_2-), 3.16 (2H, t, *J* = 7.0 Hz, -CH_2-I), 3.98 (2H, t, *J* =7.0 Hz, ArOCH_2-CH_2-), 6.98 (2H, ddd, *J* = 1.8 Hz, *J* = 3.0 Hz, *J* = 8.5 Hz, Ar*H*), 7.51 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.61 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.67 (2H, ddd, *J* = 1.8 Hz, *J* = 3.0 Hz, *J* = 8.5 Hz, Ar*H*).

^{13}C NMR: 7.33, 25.98, 28.46, 29.17, 29.31, 29.34, 29.41, 29.46, 30.45, 33.50, 68.12, 109.98, 115.04, 119.08, 127.03, 128.28, 131.20, 132.52, 145.24, 159.73

MS: 498.1223 (100%, $C_{24}H_{30}INNaO$, M + Na)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.4%



4'-((12,12-dimethyltridecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (RM1179) (5)

DIAD (1.03 g, 1ml, 5.1 mmol) was added dropwise to a stirred solution of 4'-cyano-4-hydroxybiphenyl (1 g, 5.1 mmol), **i2** (1 g, 4.39 mmol), PPh_3 (1.4 g, 5.1 mmol) in THF (10 ml). The reaction was stirred until complete consumption of 4'-cyano-4-hydroxybiphenyl, as evidenced by TLC analysis. The crude material was purified by flash chromatography with DCM as the eluent followed by recrystalisation from 3/1 toluene/hexane, giving the title compound as colourless plates.

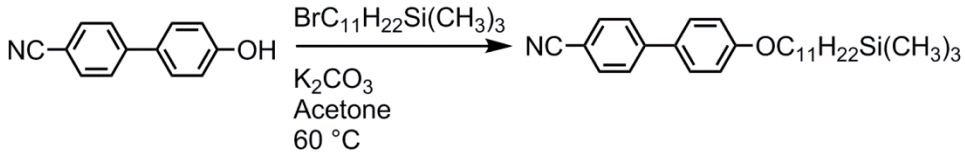
Yield: 1.1 g (59%)

^{1}H NMR: 0.78 (9H, s, -C(C*H*$_3$)$_3$), 1.04 – 1.43 (16 H, m, -CH$_2$-(C*H*$_2$)$_8$-C(CH$_3$)$_3$), 1.73 (2H, Quintet, *J* = 6.4 Hz, -CH$_2$-C*H*$_2$-(CH$_2$)$_8$C(CH$_3$)$_3$), 3.93 (2H, t, *J* = 6.4 Hz, ArOC*H*$_2$-CH$_2$-), 6.91 (2H, ddd, *J* = 2.1 Hz, *J* = 3.0 Hz, *J* = 8.9 Hz, Ar*H*), 7.45 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.56 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.62 (2H, ddd, *J* = 2.1 Hz, *J* = 3.0 Hz, *J* = 8.9 Hz, Ar*H*).

^{13}C NMR: 24.55, 26.01, 29.20, 29.37, 29.41, 29.55, 29.60, 29.66, 29.72, 30.26, 30.62, 68.17, 110.00, 115.06, 119.11, 127.05, 128.29, 131.22, 132.54, 145.28, 159.79

MS: 428.2949 (100%, $C_{28}H_{39}NNaO$, M + Na)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.5%



4'-((11-(trimethylsilyl)undecyloxy)-[1,1'-biphenyl]-4-carbonitrile (RM1383) (6)

Quantities used: 4'-cyano-4-hydroxybiphenyl (800 mg, 4.1 mmol), **i2** (1.3 g, 4.1 mmol), potassium carbonate (1.4 g, 10 mmol), acetone (40 ml). The experimental procedure was as described in the synthesis of compound **i4**. The crude material was purified by flash chromatography with DCM as the eluent followed by recrystalisation from ethanol, giving the title compound as colourless plates.

Yield: 1.2 g (69%)

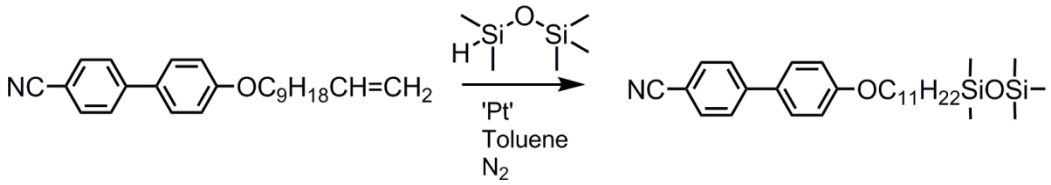
^{1}H NMR: 0.00 (9H, s, -CH_2-Si(CH_3)$_3$), 0.47 – 0.54 (2H, m, -CH_2-CH_2-Si(CH_3)$_3$), 1.26 – 1.55 (16H, m, -CH_2-(CH_2)$_8$-CH_2-Si(CH_3)$_3$), 1.84 (2H, Quintet, *J* = 6.9 Hz, ArO-CH_2-CH_2-(CH_2)$_9$-), 4.03 (2H, t, *J* = 6.9 Hz, ArO-CH_2-(CH_2)$_{10}$-), 7.02 (2H, ddd, *J* = 1.8 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*), 7.55 (2H, ddd, *J* = 1.8 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*), 7.67 (2H, ddd, *J* = 1.8 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*), 7.72 (2H, ddd, *J* = 1.8 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*)

^{13}C NMR: -1.53, 16.78, 24.00, 26.12, 29.31, 29.48, 29.66, 29.68, 29.73, 30.60, 33.72, 68.26, 110.09, 115.16, 119.22, 127.15, 128.40, 131.32, 132.64, 145.38, 159.89

^{29}Si NMR: 0.00

MS: 444.2698 (100%, $C_{27}H_{39}NNaOSi$, M + Na),

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.4%



4'-((11-(Dimethyl((trimethylsilyloxy)silyl)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (RM1342) (**7**)

Karstedts catalyst (10 µl) was added in one portion to a stirred solution of **i4** (500 mg, 1.45 mmol) and pentamethyldisiloxane (1 g) in low sulphur toluene (5 ml) in a Schlenk tube, under an atmosphere of dry nitrogen. Once the reaction was complete, as evidenced by TLC analysis, the title compound was obtained by dry vacuum flash chromatography over silica gel with 5:2 hexanes/DCM as the eluent, giving the title compound as a colourless, viscous smectic liquid crystal that solidified upon standing.

Yield: 720 mg (95%)

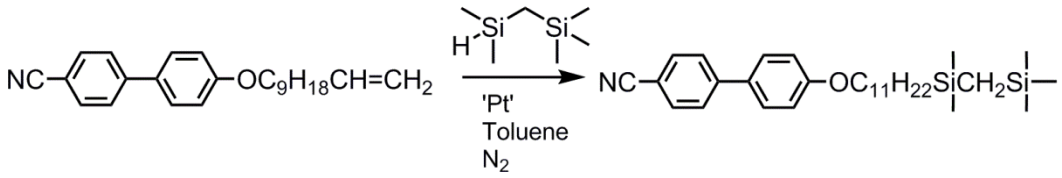
^{1}H NMR: -0.03 (6H, s, -CH_2-Si(C*H*$_3$)$_2$-O-Si(CH_3)$_3$)), 0.00 (9H, s, -CH_2-Si(CH_3)$_2$-O-Si(C*H*$_3$)$_3$)), 0.41 – 0.49 (2H, m, -CH_2-C*H*$_2$-Si(CH_3)$_2$-), 1.18 – 1.46 (16 H, m, -CH_2-(C*H*$_2$)$_8$-CH_2-Si(CH_3)2), 1.74 (2H, Quintet, *J* = 7.0 Hz, -CH_2-C*H*$_2$-(CH_2)$_9$Si(CH_3)$_2$), 3.93 (2H, t, *J* = 7.0 Hz, ArOC*H*$_2$-CH_2-), 6.92 (2H, ddd, *J* = 2.1 Hz, *J* = 3.0 Hz, *J* = 8.7 Hz, Ar*H*), 7.46 (2H, ddd, *J* = 1.8 Hz, *J* = 3.2 Hz, *J* = 8.5 Hz, Ar*H*), 7.57 (2H, ddd, *J* = 1.8 Hz, *J* = 3.2 Hz, *J* = 8.5 Hz, Ar*H*), 7.62 (2H, ddd, *J* = 2.1 Hz, *J* = 3.0 Hz, *J* = 8.9 Hz, Ar*H*)

^{13}C NMR: 0.44, 2.07, 18.46, 23.37, 26.13, 29.32, 29.48, 29.50, 29.68, 29.73, 33.51, 68.26, 110.10, 115.16, 119.21, 127.14, 128.39, 131.31, 132.64, 145.37, 159.90

^{29}Si NMR: 7.50, 8.13

MS: 518.2890 (100%, $C_{29}H_{45}NNaO_2Si_2$, M + Na),

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.2%



4'-((11-(Dimethyl((trimethylsilyl)methyl)silyl)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (DL14) (**8**)

Quantities used: **i4** (1 g), **i3** (500 mg), Karstedts catalyst (10 µl), low sulphur toluene (5 ml). The experimental procedure was as described in the synthesis of compound **7**. Dry vacuum flash chromatography over silica gel with 4:1 hexanes/DCM as the eluent gave the title compound as a colourless, viscous smectic liquid crystal.

Yield: 342 mg (48%)

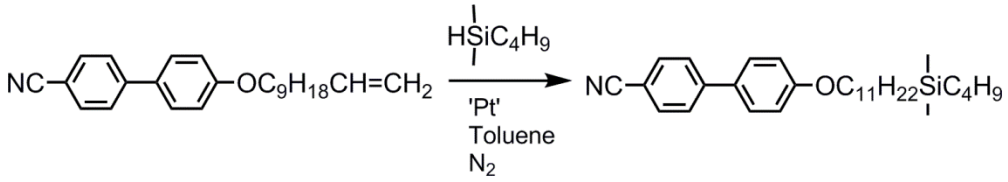
^{1}H NMR: -0.37 (2H, s, -CH_2-Si(CH_3)$_2$-CH_2-Si(CH_3)$_3$)), -0.02 (6H, s, -CH_2-Si(CH_3)$_2$-CH_2-Si(CH_3)$_3$)), 0.00 (9H, s, -C-H_2-Si(CH_3)$_2$-CH_2-Si(CH_3)$_3$)), 0.41 – 0.51 (2H, m, -CH_2-CH_2-Si(CH_3)$_2$-),1.18 – 1.50 (16 H, m, -CH_2-(CH_2)$_8$-CH_2-Si(CH_3)2), 1.79 (2H, Quintet, *J* = 6.9 Hz, -CH_2-CH_2-(CH_2)$_9$Si(CH_3)$_2$), 3.98 (2H, t, *J* = 6.9 Hz, ArOCH_2-CH_2-), 6.97 (2H, ddd, *J* = 2.3 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*), 7.51 (2H, ddd, *J* = 2.3 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*), 7.62 (2H, ddd, *J* = 2.3 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*), 7.67 (2H, ddd, *J* = 2.3 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*)

^{13}C NMR: -0.46, 1.50, 2.66, 18.05, 24.06, 26.13, 29.32, 29.49, 29.67, 29.70, 29.73, 33.82, 68.26, 110.10, 115.16, 119.21, 127.15, 128.40, 131.31, 132.64, 143.37, 159.89

^{29}Si NMR: 0.00, 1.98

MS: 516.3079 (100%, $C_{30}H_{47}NNaOSi_2$, M + Na),

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.3%



4'-((11-(Butyldimethylsilyl)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (CV7) (9)

Quantities used: **i4** (1 g, 2.9 mmol), butyldimethylsilane (670 mg, 5.8 mmol), Karstedts catalyst (10 µl), low sulphur toluene (5 ml). The experimental procedure was as described in the synthesis of compound **7**. Dry vacuum flash chromatography over silica gel with 4:1 hexanes/DCM as the eluent gave the title compound as a colourless, viscous smectic liquid crystal.

Yield: 1.2 g (89%)

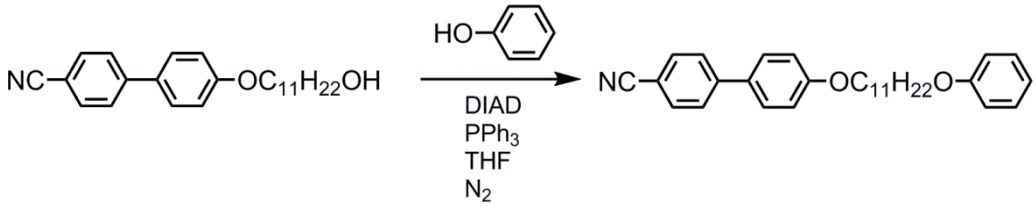
^{1}H NMR: 0.00 (6H, S, CH_2-Si(C*H*$_3$)$_2$-CH_2-), 0.47-0.58 (4H, m, -CH_2-C*H*$_2$-Si(CH_3)$_2$-C*H*$_2$-CH_2-), 0.94 (3H, t, *J* = 6.9 Hz, CH_2-C*H*$_3$), 1.27-1.46 (18H, m, -CH_2-(C*H*$_2$)$_9$-CH_2-), 1.48-1.58 (2H, m, -CH_2-C*H*$_2$-CH_2-), 1.86 (2H, Quintet, *J* = 6.9 Hz, ArO-CH_2-C*H*$_2$-CH_2-), 4.06 (2H, t, *J* = 6.9 Hz, ArO-C*H*$_2$-CH_2-), 7.04 (2H, ddd, *J* = 2.3 Hz, *J* = 2.8 Hz, *J* = 8.7 Hz, Ar*H*), 7.58 (2H, ddd, *J* = 1.8 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*), 7.69 (2H, ddd, *J* = 1.8 Hz, *J* = 3.2 Hz, *J* = 8.7 Hz, Ar*H*), 7.75 (2H, ddd, *J* = 2.3 Hz, *J* = 2.8 Hz, *J* = 8.7 Hz, Ar*H*).

^{13}C NMR: -3.25, 13.94, 15.09, 15.39, 23.99, 26.13, 26.25, 26.75, 29.32, 29.47, 29.50, 29.67, 29.69, 29.73, 33.82, 68.26, 110.10, 115.16, 119.21, 127.14, 128.39, 131.31, 132.64, 145.37, 159.90

^{29}Si NMR: 2.71

MS: 486.3170 (100%, $C_{30}H_{45}NNaOSi$, M + Na)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.8%



4'-((11-(phenoxy)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (RM1510-1) (10)

Quantities used: Compound **1** (400 mg, 1.14 mmol), phenol (113 mg, 1.2 mmol), PPh_3 (299 mg, 1.14 mmol), DIAD (230 mg, 224 µl, 1.14 mmol), anhydrous THF (2 ml). The experimental procedure was as described in the synthesis of compound **5**, with the title compound purified by flash chromatography over silica gel with 3:1 DCM/hexane as the eluent followed by recrystalisation from ethanol, to yield the title compound as fine colourless needles.

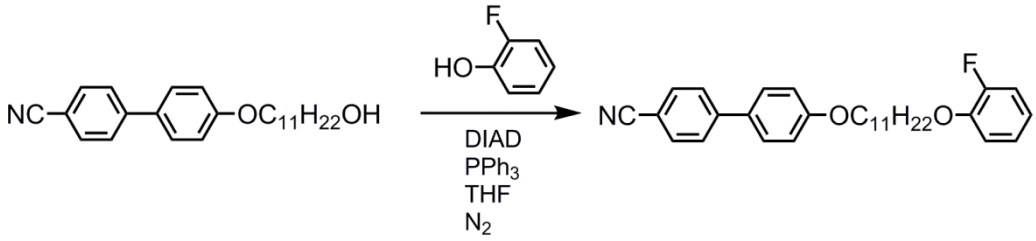
Yield: 380mg (76%)

^{1}H NMR: 1.28 – 1.52 (14H, m, -CH_2-(C*H*$_2$)$_7$-CH_2-), 1.74 – 1.86 (4H, m, ArO-CH_2-C*H*$_2$-(CH$_2$)$_7$-C*H*$_2$-CH_2-OAr), 3.94 (2H, t, *J* = 6.7 Hz, ArO-C*H*$_2$-CH_2-), 3.99 (2H, t, *J* = 6.7 Hz, ArO-C*H*$_2$-CH_2-), 6.90 (2H, d, *J* = 7.6 Hz, Ar*H*), 6.93 (1H, t, *J* = 8.4 Hz, Ar*H*), 6.99 (2H ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.27 (2H, dddd, *J* = 2.1 Hz, *J* = 2.4 Hz, *J* = 7.6 Hz, *J* = 8.4 Hz, Ar*H*), 7.52 (2H, ddd, *J* = 1.8 Hz, *J* = 3.0 Hz, *J* = 8.5 Hz, Ar*H*), 7.62 (2H, ddd, *J* = 1.8 Hz, *J* = 3.0 Hz, *J* = 8.5 Hz, Ar*H*), 7.67 (2H ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*)

^{13}C NMR: 25.93, 25.96, 28.04, 29.12, 29.21, 29.27, 29.30, 29.41, 29.44, 67.27, 109.88, 114.36, 114.97, 119.01, 120.34, 126.92, 128.19, 129.29, 131.06, 132.43, 145.12, 159.00, 159.71

MS: 464.2557 (100%, $C_{30}H_{35}NNaO_2$, M + Na)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.4%



4'-((11-(2-fluorophenoxy)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (RM1510-2) (11)

Quantities used: Compound **1** (400 mg, 1.14 mmol), 2-fluorophenol (134 mg, 1.2 mmol), PPh_3 (299 mg, 1.14 mmol), DIAD (230 mg, 224 µl, 1.14 mmol), anhydrous THF (2 ml). The experimental procedure was as described in the synthesis of compound **5**, with the title compound purified by flash chromatography over silica gel with 3:1 DCM/hexane as the eluent followed by recrystalisation from ethanol, to yield the title compound as fine colourless crystals.

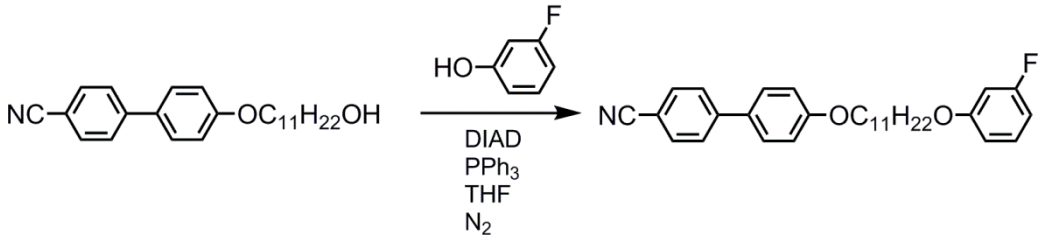
Yield: 470 mg (89%)

^{1}H NMR: 1.16 – 1.43 (14H, m, -CH_2-(CH_2)$_7$-CH_2-), 1.71 (4H, Quintet, *J* = 7.0 Hz, -CH_2-CH_2-(CH_2)$_7$-CH_2-CH_2-), 3.90 (2H, t, *J* = 6.4 Hz, ArO-CH_2-CH_2), 3.91 (2H, t, *J* = 6.4 Hz, ArO-CH_2-CH_2), 6.77 (1H, dddd, *J* = 1.5 Hz, *J* = 4.6 Hz, *J* = 7.6 Hz, *J* = 8.2 Hz, Ar*H*), 6.86 (1H, ddd, *J* =1.8 Hz, *J* =8.2 Hz, *J* = 16.8 Hz, Ar*H*), 6.89 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*), 6.92 – 7.00 (2H, m, Ar*H*), 7.42 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.52 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.57 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*).

^{13}C NMR: 25.83, 25.93, 29.12, 29.26, 29.39, 29.41, 29.44, 68.04, 69.23, 109.87, 114.73 (d, *J* = 1.5 Hz), 114.98, 116.00 (d, *J* = 18.0 Hz), 119.04, 120.69 (d, *J* = 6.9 Hz), 124.13 (d, *J* = 3.3 Hz), 126.94, 128.20, 131.07, 132.45, 145.14, 147.08, 152.65 (d, *J* = 244.7 Hz), 159.71

^{19}F NMR: -134.69 (1F, m, Ar*F*)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.8%



4'-((11-(3-fluorophenoxy)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (RM1510-3) (12)

Quantities used: Compound **1** (400 mg, 1.14 mmol), 3-fluorophenol (134 mg, 1.2 mmol), PPh_3 (299 mg, 1.14 mmol), DIAD (230 mg, 224 µl, 1.14 mmol), anhydrous THF (2 ml). The experimental procedure was as described in the synthesis of compound **5**, with the title compound purified by flash chromatography over silica gel with 3:1 DCM/hexane as the eluent followed by recrystalisation from ethanol, to yield the title compound as large colourless needles.

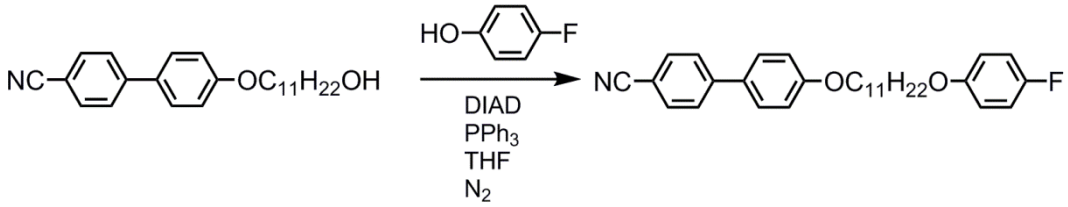
Yield: 430 mg (82%)

^{1}H NMR: 1.18 – 1.42 (14H, m, -CH_2-(CH_2)$_7$-CH_2-), 1.63 – 1.76 (4H, m, ArO-CH_2-CH_2-(CH_2)$_7$-CH_2-CH_2-OAr), 3.83 (2H, t, *J* = 6.7 Hz, ArO-CH_2-CH_2-), 3.91 (2H, t, *J* = 6.7 Hz, ArO-CH_2-CH_2-), 6.51 (2H, tt, *J* = 2.4 Hz, *J* = 11.0 Hz, Ar*H*), 6.58 (1H, dd, *J* = 2.4 Hz, *J* = 8.5 Hz, Ar*H*), 6.89 (2H, ddd, *J* = 2.1 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*), 7.11 (1H, m, Ar*H*), 7.43 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*), 7.53 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*), 7.58 (2H, ddd, *J* = 2.1 Hz, *J* = 3.1 Hz, *J* = 8.9 Hz, Ar*H*).

^{13}C NMR: 25.93, 25.96, 29.05, 29.15, 29.28, 29.30, 29.42, 29.45, 68.07, 68.17, 102.01 (d, *J* = 25.3 Hz), 107.12 (d, *J* = 20.7 Hz), 110.23 (d, *J* = 3.0 Hz), 115.00, 119.04, 126.97, 128.23, 130.03 (d, *J* = 10.0 Hz), 131.13, 132.47, 145.17, 159.74, 160.46 (d, *J* = 11.5 Hz), 164.57 (d, *J* =244.7 Hz)

^{19}F NMR: -111.71 (1F, dt, *J* = 8.0 Hz, *J* = 10.3 Hz, Ar*F*)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.7%



4'-((11-(4-fluorophenoxy)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (RM1510-4) (13)

Quantities used: Compound **1** (400 mg, 1.14 mmol), 4-fluorophenol (134 mg, 1.2 mmol), PPh_3 (299 mg, 1.14 mmol), DIAD (230 mg, 224 µl, 1.14 mmol), anhydrous THF (2 ml). The experimental procedure was as described in the synthesis of compound **5**, with the title compound purified by flash chromatography over silica gel with 3:1 DCM/hexane as the eluent followed by recrystalisation from ethanol, to yield the title compound as large colourless needles.

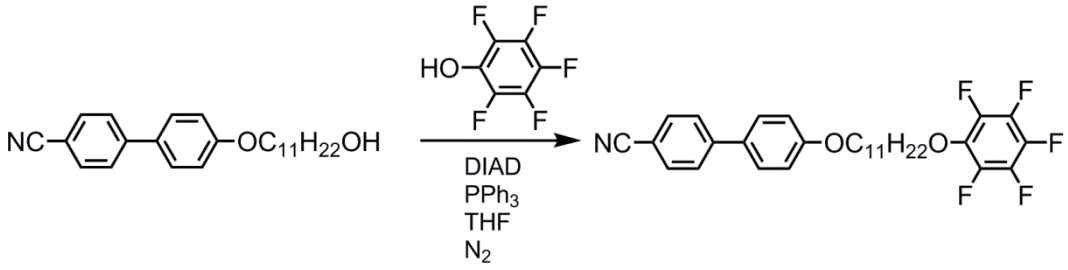
Yield: 510 mg (97%)

^{1}H NMR: 1.18 – 1.43 (14H, m, -CH_2-(C*H*$_2$)$_7$-CH_2-), 1.62 – 1.76 (4H, m, ArO-CH_2-C*H*$_2$-(CH$_2$)$_7$-C*H*$_2$-CH_2-OAr), 3.81 (2H, t, *J* = 6.4 Hz, ArO-C*H*$_2$-CH_2-), 3.89 (2H, t, *J* = 6.4 Hz, ArO-C*H*$_2$-CH_2-), 6.67 – 6.76 (2H, m, Ar*H*), 6.83 – 6.87 (2H, m, Ar*H*), 6.90 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.43 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.5 Hz, Ar*H*), 7.53 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.5 Hz, Ar*H*), 7.59 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*).

^{13}C NMR: 25.96, 29.15, 29.22, 29.31, 29.44, 29.47, 68.08, 68.53, 109.94, 115.01, 115.31 (d, *J* = 8.4 Hz), 115.63 (d, *J* = 23.0 Hz), 119.05, 126.97, 128.24, 131.14, 132.48, 145.18, 155.18 (d, *J* = 3.0 Hz), 157.01 (d, *J* = 237.8 Hz), 159.74

^{19}F NMR: -124.28 (1F, tt, *J* = 3.5 Hz, *J* = 8.1 Hz, Ar*F*)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.6%



4'-((11-(2,3,4,5,6-pentafluorophenoxy)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (RM1510-5) (14)

Quantities used: Compound **1** (400 mg, 1.14 mmol), 2,3,4,5,6-pentafluorophenol (220 mg, 1.2 mmol), PPh_3 (299 mg, 1.14 mmol), DIAD (230 mg, 224 µl, 1.14 mmol), anhydrous THF (2 ml). The experimental procedure was as described in the synthesis of compound **5**, with the title compound purified by flash chromatography over silica gel with 3:1 DCM/hexane as the eluent followed by recrystalisation from ethanol, to yield the title compound as an amorphous white solid.

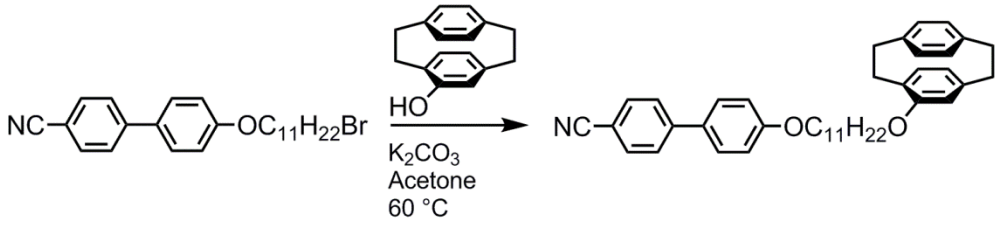
Yield: 490 mg (81%)

^{1}H NMR: 1.19 – 1.44 (14H, m, -CH_2-(C*H*$_2$)$_7$-CH_2-), 1.63 – 1.76 (4H, m, ArO-CH_2-C*H*$_2$-(CH$_2$)$_7$-C*H*$_2$-CH_2-OAr), 3.92 (2H, t, *J* = 6.7 Hz, ArO-C*H*$_2$-CH_2-), 4.06 (2H, t, *J* = 6.7 Hz, F_5PhO-C*H*$_2$-CH_2), 6.90 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*), 7.43 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.5 Hz, Ar*H*), 7.54 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.5 Hz, Ar*H*), 7.59 (2H, ddd, *J* = 2.1 Hz, *J* = 2.8 Hz, *J* = 8.9 Hz, Ar*H*).

^{13}C NMR: 25.44, 25.98, 29.15, 29.17, 29.31, 29.41, 29.47, 29.76, 68.10, 75.78, 109.98, 115.02, 119.04, 126.98, 128.23, 131.17, 133.49, 133.77 (m), 136.22 (m), 138.67 (m), 141.68 (m), 145.21, 159.77

^{19}F NMR: -163.85 (1F, t, *J* = 21.0 Hz, Ar*F*), -163.48 (2F, t, *J* = 21.0 Hz, Ar*F*), -156.82 (2F, m, Ar*F*)

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.1%



4'-((11-([2,2]-paracyclophanyloxy)undecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (RM1460) (15)

Quantities used: Compound **3** (500 mg, 1.158 mmol), 4-hydroxy-[2,2]-paracyclophane (261 mg, 1.168 mmol), potassium carbonate (322 mg, 2.336 mmol), acetone (30 ml). The experimental procedure was as described in the synthesis of compound **6**. Dry vacuum flash chromatography over silica gel with DCM as the eluent gave the title compound, followed by recrystalisation from ethanol gave the title compound as a colourless white solid.

Yield: 480 mg (69%)

^{1}H NMR: 1.25 - 1.70 (14H, m, -CH_2-(CH_2)$_7$-CH_2), 1.76 – 1.87 (4H, m, ArO-CH_2-CH_2-$(CH_2)_7$-CH_2-CH_2-OAr), 2.53 – 2.63 (1H, m, ArC*H*H-CH_2-Ar), 2.91 – 3.10 (4H, m, Ar-CH_2-CH_2Ar), 3.45 (1H, m, ArCH*H*-CH_2-Ar), 3.62 – 3.76 (2H, m, ArCH*H*-CH_2-Ar), 3.86 (1H, m, (1H, m, ArC*H*H-CH_2-Ar), 3.99 (4H, m, ArOCH_2-$(CH_2)_9$-CH_2OAr), 6.23 (1H, dd, *J* = 1.5 Hz, *J* = 7.6 Hz, Ar*H*), 6.36 (1H, dd, *J* = 1.8 Hz, *J* = 7.6 Hz, Ar*H*), 6.39 (1H, d, *J* = 7.6 Hz, Ar*H*), 6.42 (1H, dd, *J* = 1.8 Hz, *J* = 7.6 Hz, Ar*H*), 6.50 (1H, dd *J* = 1.8 Hz, *J* = 7.6 Hz, Ar*H*), 6.73 (1H, dd, *J* = 1.8 Hz, *J* = 7.6 Hz, Ar*H*), 6.98 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.5 Hz, Ar*H*), 7.51 (2H, ddd, *J* = 2.1 Hz, *J* = 2.9 Hz, *J* = 8.9 Hz, Ar*H*), 7.61 (2H, ddd, *J* = 2.1 Hz, *J* = 2.9 Hz, *J* = 8.9 Hz, Ar*H*), 7.67 (2H, ddd, *J* = 1.8 Hz, *J* = 3.1 Hz, *J* = 8.5 Hz, Ar*H*),

^{13}C NMR: 25.91, 25.93, 28.41, 29.10, 29.28, 29.39, 29.44, 30.37, 31.50, 33.42, 33.93, 35.12, 35.20, 66.44, 68.03, 109.85, 114.95, 117.16, 119.00, 123.88, 126.91, 127.24, 128.18, 131.02, 131.05, 131.22, 132.42, 132.82, 133.33, 134.61, 138.50, 139.92, 141.66, 145.10, 156.97, 159.67

Assay (HPLC, 230/255 nm, 100% H_3CCN): 99.2 %

ESI References

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