Supplementary Information

Controlling spontaneous chirality in achiral materials: liquid crystal oligomers and the heliconical twist-bend nematic phase

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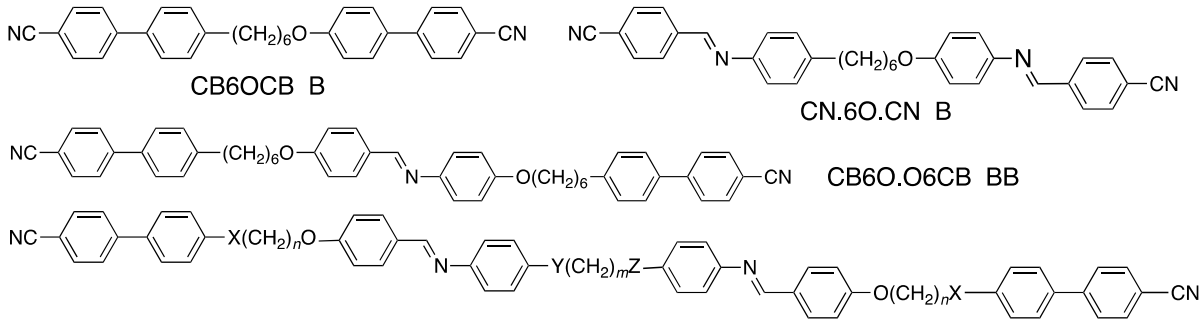
Section 1: Physiochemical characterization

1.1 Chemical Structures



X	Y	Z	*n*	*m*	Acronym	Linkage sequence
CH_2	CH_2	O	5	5	CB6O.6O.O6CB	BBB
CH_2	CH_2	CH_2	5	5	CB6O.7.O6CB	BBB
CH_2	O	O	5	5	CB6O.O5O.O6CB	BBB
CH_2	O	O	6	6	CB6O.O6O.O6CB	BLB
CH_2	CH_2	CH_2	5	6	CB6O.8.O6CB	BLB
CH_2	CH_2	CH_2	6	5	CB7O.7.O7CB	LBL
O	CH_2	CH_2	6	5	CBO6O.7.O6OCB	LBL

Figure S1: The structures and acronyms of the oligomers, and their descriptions in terms of the sequence of linear (L) and bent linkages (B). The table lists the tetramer linking groups X, Y and Z in the general molecular structure. In acronyms CB stands for cyanobiphenyl unit, dot stands for benzylideneaniline unit, and the number of carbon atoms in alkyl/alkoxyl linkages are denoted by number.

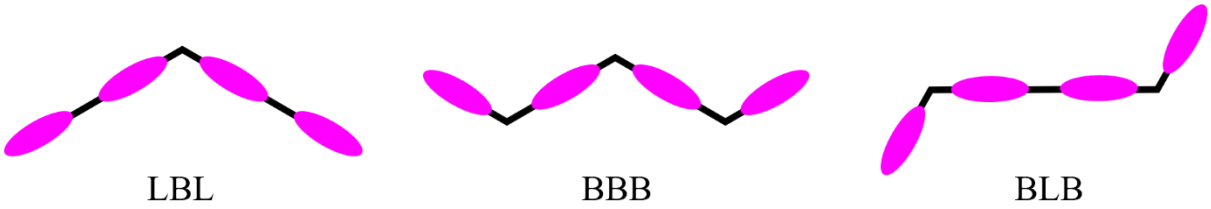


Figure S2: Graphical illustration of the oligomers structure in terms of sequence of their fragments, linear (L) or bent (B).

1.2 Thermal Analysis

The thermal phase behaviour of the oligomers, displayed in Table 1, were studied by differential scanning calorimetry (DSC) using a Mettler Toledo DSC3 calorimeter equipped with a TSO 801RO sample robot, STARe software and calibrated using indium and zinc standards.

Table 1: DSC data: melting points (m.p.) recorded on heating and the transition temperatures obtained on cooling (10 K min-1 rate); in parentheses scaled entropy changes are given. Grey shading marks monotropic phase transition.

	m.p. / ˚C (ΔS/R)	**$T_{N_{TB}N}$** / ˚C (ΔS/R)	**T_{NI}** / ˚C (ΔS/R)	**Linkage sequence**
CB6OCB [1]	99 (6.88)	109 (0.01)	155 (0.48)	B
CB6O.O6CB	153 (14.31)	142 (0.15)	185 (0.69)	BB
CB6O.7.O6CB	140 (8.32)	159 (0.84)	180 (0.81)	BBB
CB6O.6O.O6CB	151 (8.62)	158 (0.36)	195 (1.01)	BBB
CB6O.O5O.O6CB	156 (11.44)	162 (0.21)	215 (1.09)	BBB
CB6O.O6O.O6CB	166	166	235	BLB
CB6O.8.O6CB	131 (13.01)	152 (0.02)	212 (2.81)	BLB
CB7O.7.O7CB	145	132	225	LBL
CBO6O.7.O6OCB	131 (17.66)	143 (0.034)	242 (3.15)	LBL

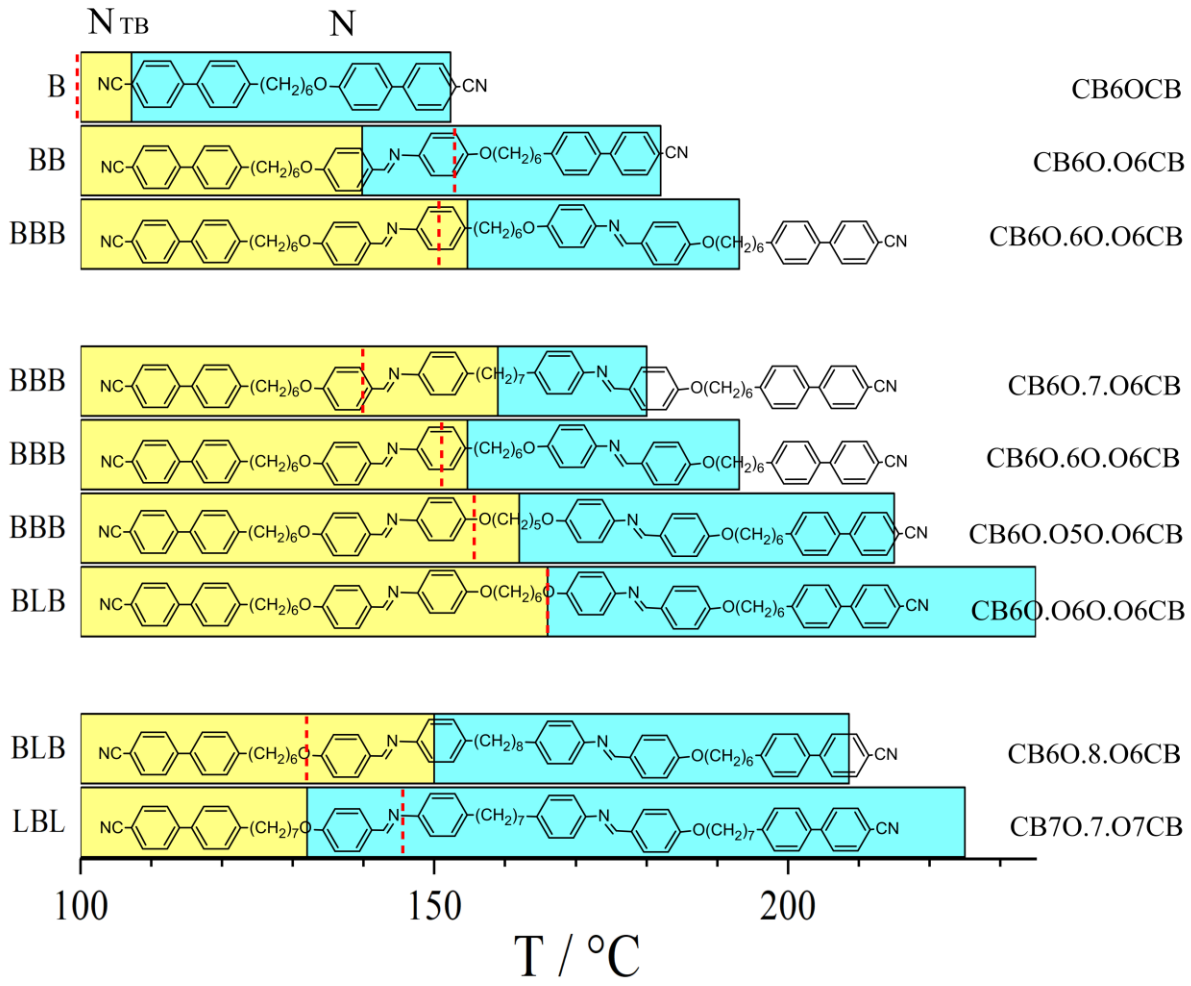


Figure S3. Temperature range for NTB phase (yellow) and N phase (blue): for a dimer, trimer and tetramer with hexyloxy (OC6) linkages (upper part), for tetramers with different central linkages C7, OC6, OC5O, OC6O and hence different molecular bend angles (middle part), and for two tetramers having differing sequences of B (bent) and L (linear) linkages (lowest part). Red dotted lines mark melting temperature.

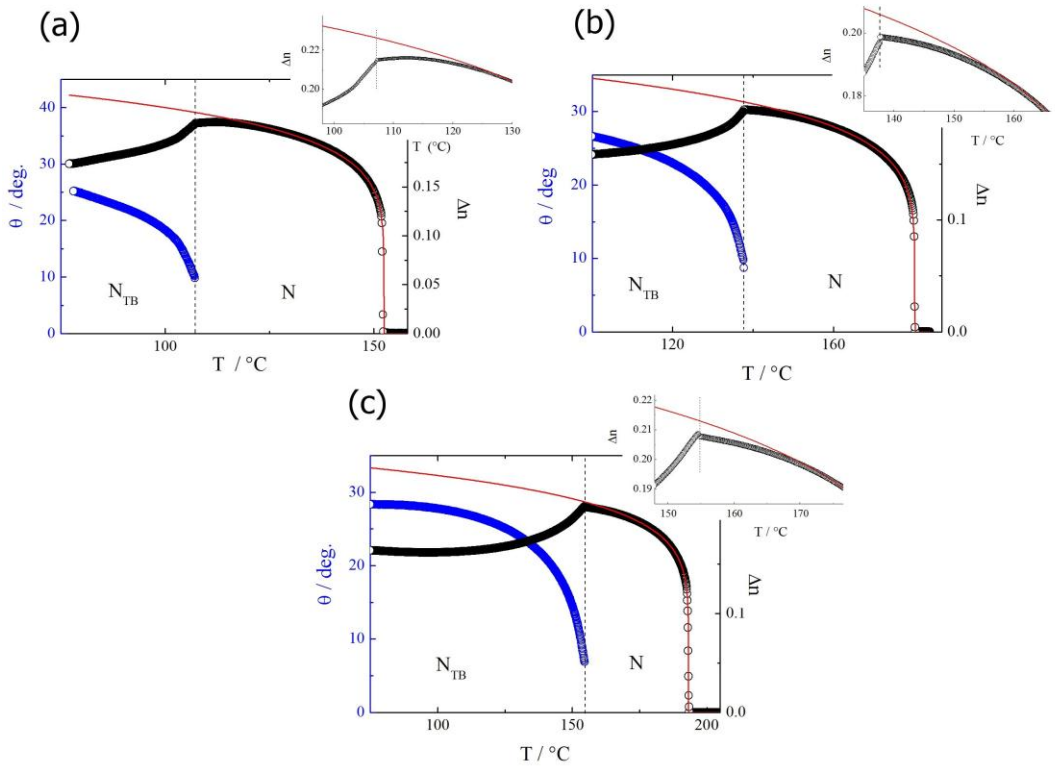


Figure S4. Optical birefringence vs. temperature for (a) the dimer CB6OCB (Δn_{max}=0.310), (b) the trimer CB6O.O6CB (Δn_{max} =0.296), and (c) the tetramer CB6O.6O.O6CB (Δn_{max}=0.298), measured for the wavelength 633 nm. The red line is the fit to the critical dependence $\Delta n = \Delta n_{max}\left(\frac{T-T_{NI}}{T_{NI}}\right)^{\beta}$, in the insets are magnified sections in the temperature range near the N-NTB transition.

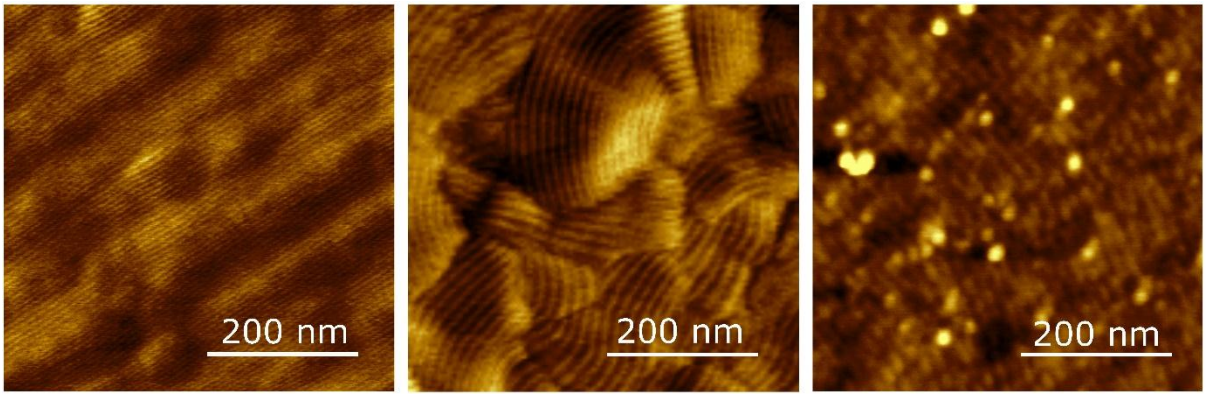


Figure S5. AFM pictures of stripes in N_{TB} phase, which correspond to helical pitch, d. Tetramer compounds from the left: BBB-type CB6O.7.O6CB, d=7 nm, BLB-type CB6O.8.O6CB, d=12 nm, and LBL-type CBO6O.7.O6OCB, d=17 nm.

1.3 Optical Characterisation

The optical studies of the phases were conducted using a Zeiss Axio Imager A2m polarised light microscope with a Linkam heating stage. The samples were placed either between two untreated thin glass slides or in glass cells with planar anchoring induced by a thin inner layer of polymer. The cells were filled by capillary action with the material in the isotropic phase.

1.4 Birefringence

Birefringence was measured using a setup based on a photoelastic modulator (PEM-90, Hinds) working at a modulation $f = 50$ kHz frequency; as a light source a halogen lamp (Hamamatsu LC8) was used, equipped with a narrow band pass filter (532 nm). The transmitted light intensity was measured with a photodiode (FLC Electronics PIN-20) and deconvoluted with a lock-in amplifier (EG&G 7265) into $1f$ and $2f$ components to yield a retardation induced by the sample.

1.5 Dielectric Permittivity and dielectric constant

The splay elastic constant K_{11} was determined from the threshold voltage V_{th} at which the director reorientation starts, and thus the effective permittivity (ε) starts to grow as: $K_{11} = \Delta\varepsilon\, \varepsilon_0 \left(\frac{V_{th}^2}{\pi^2}\right)$. The bend elastic constant, K_{33} was estimated by fitting the $\varepsilon(V)$ dependence far above the threshold voltage using [34]:

$$\frac{\varepsilon(V)-\varepsilon_\perp}{\varepsilon_{II}-\varepsilon_\perp} = 1 - \frac{2}{\pi}\sqrt{1+\xi}\,\frac{V_{th}}{V}\int_0^1 \sqrt{\frac{1+\kappa x^2}{1+\xi x^2}}\,\mathrm{d}x$$

$$\text{where } \xi = \frac{\varepsilon_{II}-\varepsilon_\perp}{\varepsilon_\perp} \text{ and } \kappa = \frac{K_{33}-K_{11}}{K_{11}}.$$

The dielectric permittivity was measured using a Wayne Kerr Precision Component Analyzer 6425, at the frequency 12 kHz, and with the applied voltage amplitude (V) ranging from 0.1 to 5.0 V.

1.6 Resonant X-ray

The resonant X-ray experiments were performed on the soft X-ray scattering beamline (11.0.1.2) at the Advanced Light Source of Lawrence Berkeley National Laboratory. The X-ray beam was tuned to the K-edge of carbon absorption energy ~280 eV. The X-ray beam with a cross-section of 300 × 200 μm was linearly polarized, with the polarization direction that can be continuously changed from the horizontal to vertical. Samples with thickness lower than 1 μm were placed between two 100-nm-thick Si_3N_4 slides. The scattering intensity was recorded using the Princeton PI-MTE CCD detector, cooled to −45 °C, having a pixel size of 27 μm, with an adjustable distance from the sample. The detector was translated off-axis to enable recording of the diffracted X-ray intensity. The adjustable position of the detector allowed to cover a broad range of q vectors, corresponding to periodicities from approximately 5.0 to 500 nm.

1.7 Atomic Force Microscopy

For AFM measurements, a Bruker Dimension Icon Microscope was used in tapping or scan assist mode. The cantilevers with elastic constant of 0.4 N/cm^2 were applied.

Section 2: Reagents, Separation Techniques, and Instrumentation

2.1 Reagents

All of the reagents and solvents used were commercially available at time of purchase and obtained from various suppliers and used without further purification unless otherwise stated.

Suppliers: ACROS Organics, Alfa Aesar, Fluorochem, Sigma Aldrich, TCI Chemicals.

2.2 Separation Techniques

Reactions were monitored by thin layer chromatography (TLC), unless otherwise stated, using aluminium-backed sheets with a coating of Merck Kieselgel 60 F254 silica, and were purchased from Merck KGaA.

Compound separation by column chromatography was carried out using silica gel grade 60 Å 40-63 μm particle size, purchased from Fluorochem. The column length and diameter were chosen based on crude mass and previous column chromatography separations where possible. Purification by column chromatography is denoted by '(SiO_2, Solvent system)' along with the solvent system used.

2.3 Structure Analysis

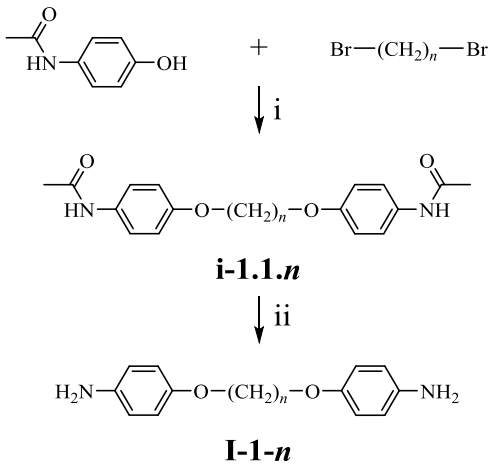
^{1}H and ^{13}C NMR spectra were recorded on either a Bruker Avance III HD 400 NMR, or a 300 MHz Bruker Ultrashield NMR spectrometer. Infrared spectra were recorded on a Thermo Scientific Nicolet IR100 FTIR spectrometer with an ATR diamond cell.

2.4 Purity Analysis

The purities of the final products where possible were verified using either C, H, N microanalysis. C, H, N microanalysis was performed at either; Sheffield Analytical and Scientific Services Elemental Microanalysis Service at the University of Sheffield; the Analysis Services Elemental Microanalysis Service at OEA labs; Centre for Chemical and Material Analysis at the University of Birmingham.

Section 3: Synthetic Procedures

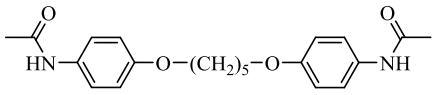
3.1 1,5-Bis(4-acetamidophenyl-4’-oxy)pentane (**I-1-5**) and 1,6-Bis(4-acetamidophenyl-4’-oxy)hexane (**I-1-6**)



i) K_2CO_3, acetone, 56 ^oC
ii) NaOH (aq), EtOH, 78 ^oC

Scheme 1: Synthetic route to form α,ω-Bis(4-aminophenyl-4’-oxy)alkanes (**I-1-*n***)

i-1.1.5 1,5-bis(4-acetamidophenyl-4'-oxy)pentane



To a stirring solution of acetaminophen (10.000 g, 0.066 mol) and 1,5-dibromopentane (6.760 g, 4.0 mL, 0.029 mol) in acetone (200 mL) was added potassium carbonate (12.024 g, 0.087 mol). The reaction mixture was stirred at 56 °C until TLC indicated near complete consumption of acetaminophen R_f 0.43 (EtOAc) after 24 hours. The reaction was cooled to room temperature, poured into H_2O (500 mL) and the resultant precipitate was collected by filtration. The crude product was purified by recrystallisation from EtOH (400 mL) to give the title compound as a white powder.

Yield: 6.408 g, 59 %

m.p. = 210–212 ˚C

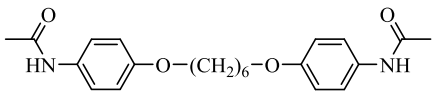
R_f (EtOAc) 0.17

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.80 (s, 2H, 2 × Ac-NH), 7.45 (d, J = 9.0 Hz, 4H, 4 × Ar-H), 6.84 (d, J = 9.0 Hz, 4H, 4 × Ar-H), 3.93 (t, J = 6.4 Hz, 4H, 2 × CH_2-O), 1.99 (s, 6H, 2 × CH_3-CO), 1.75 (quin, J = 6.8 Hz, 4H, 2 × O-CH_2-CH_2), 1.63 – 1.48 (m, 2H, O-CH_2-CH_2-CH_2).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.64 (2 × CO-NH), 154.37 (2 × Ar-O), 132.45 (2 × Ar-NHAc), 120.46 (4 × Ar-H), 114.34 (4 × Ar-H), 67.46 (2 × CH_2-O), 28.47 (2 × O-CH_2-CH_2), 23.76 (2 × CH_3-CO), 22.24 (O-CH_2-CH_2-CH_2).

IR ν (cm^{-1}): 3292 (CONH); 2949, 2867 (CH_2); 1657 (CO); 1596, 1511 (Ar); 824 (*p*-disub. Ar).

i-1.1.6 1,6-bis(4-acetamidophenyl-4'-oxy)hexane



Synthesis procedure follows that described for **i-1.1.5** 1,5-bis(4-acetamidophenyl-4'-oxy)pentane.

Quantities used: acetaminophen (6.652 g, 0.044 mol); 1,5-dibromohexane (5.000 g, 0.75 mL, 0.020 mol); acetone (150 mL), potassium carbonate (8.293 g, 0.060 mmol).

Reaction time: 21 hrs

The crude product was purified by recrystallisation from EtOH to give the title compound as an off-white powder.

Yield: 2.401 g, 31 %

m.p. = 205–209 ˚C

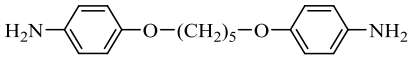
R_f (EtOAc) 0.24

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 (s, 2H, 2 × Ac-NH), 7.45 (d, J = 9.0 Hz, 4H, 4 × Ar-H), 6.84 (d, J = 9.0 Hz, 4H, 4 × Ar-H), 3.91 (t, J = 6.4 Hz, 4H, 2 × CH_2-O), 1.99 (s, 6H, 2 × CH_3-CO), 1.71 (quin, J = 6.7 Hz, 4H, 2 × O-CH_2-CH_2), 1.51 – 1.38 (m, 4H, 2 × O-CH_2-CH_2-CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.65 (2 × CO-NH), 154.40 (2 × Ar-O), 132.42 (2 × Ar-NHAc), 120.47 (4 × Ar-H), 114.34 (4 × Ar-H), 67.45 (2 × CH_2-O), 28.71 (2 × O-CH_2-CH_2), 25.34 (2 × O-CH_2-CH_2-CH_2), 23.79 (2 × CH_3-CO).

IR ν (cm^{-1}): 3300 (CONH); 2943, 2868 (CH_2); 1656 (CO); 1597, 1511 (Ar); 825 (*p*-disub. Ar).

I-1-5 1,5-Bis(4-aminophenyl-4'-oxy)pentane



To a stirring solution of **i-1.1** (3.000 g, 8.098 mmol) in EtOH (100 mL) at 78 °C was added in one portion an aqueous solution of NaOH (16.197 g, 0.405 mol) in H_2O (25 mL). The reaction was monitored by TLC until the complete consumption of **4.7** after 1 hour and the consumption of the mono-hydrolysed product (not isolated, R_f (EtOAc) 0.50) after 3 hours. The reaction mixture was cooled, the solvent was removed *in vacuo* to half volume then poured into H_2O (300 mL). The resultant solid was collected by filteration to give the title compound as a tan solid. The product was used without further purification.

Yield: 1.229 g, 53 %

m.p. = 82–84 ˚C

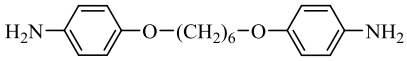
R_f (EtOAc) 0.45

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.63 (d, J = 8.7 Hz, 4H, 4 × Ar-H), 6.49 (d, J = 8.8 Hz, 4H, 4 × Ar-H), 4.56 (s, 4H, 2 × NH_2), 3.81 (t, J = 6.4 Hz, 4H, 2 × $\underline{CH_2}$-O), 1.68 (quin, J = 6.8 Hz, 4H, O-CH_2-$\underline{CH_2}$), 1.57 – 1.43 (m, 2H O- CH_2-CH_2-$\underline{CH_2}$).

^{13}C NMR (101 MHz, DMSO-d_6) δ 150.01 (2 × $\underline{Ar}$-O), 142.30 (2 × $\underline{Ar}$-NH_2), 115.38 (4 × Ar-H), 114.96 (4 × Ar-H), 67.90 (2 × $\underline{CH_2}$-O), 28.74 (2 × O-CH_2-$\underline{CH_2}$), 22.38 (CH_2).

IR ν (cm^{-1}): 3433, 3353 (Ar. NH_2); 2950, 2868 (CH_2); 1225 (Ar. C-N); 824 (*p*-disub. Ar)

i-1-6 1,6-Bis(4-aminophenyl-4'-oxy)hexane



Synthesis procedure follows that described for **I-1-5** 1,5-bis(4-aminophenyl-4'-oxy)pentane.

Quantities used: NaOH (2.250 g, 5.850 mmol); 1,6-dibromohexane (11.704 g, 0.296 mol); H_2O (25 mL), EtOH (90 mL).

Reaction time: 4.5 hrs

Yield: 1.690 g, 96 %

m.p. = 147–148 ˚C

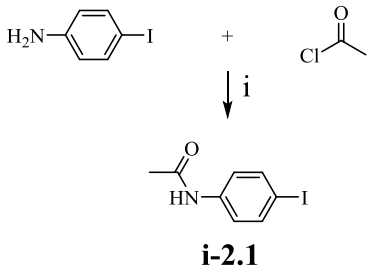
R_f (EtOAc) 0.52

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.63 (d, J = 8.8 Hz, 4H, 4 × Ar-H), 6.49 (d, J = 8.8 Hz, 4H, 4 × Ar-H), 4.56 (s, 4H, 2 × NH_2), 3.80 (t, J = 6.5 Hz, 4H, 2 × $\underline{CH_2}$-O), 1.65 (quin, J = 6.7 Hz, 4H, O-CH_2-$\underline{CH_2}$), 1.42 (m, 4H, 2 × CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 149.97 (2 × $\underline{Ar}$-O), 142.27 (2 × $\underline{Ar}$-NH_2), 115.33 (4 × Ar-H), 114.91 (4 × Ar-H), 67.84 (2 × $\underline{CH_2}$-O), 28.91 (2 × O-CH_2-$\underline{CH_2}$), 25.41 (2 x CH_2).

IR ν (cm^{-1}): 3394, 3315 (Ar. NH_2); 2936, 2865 (CH_2); 1229 (Ar. C-N); 823 (*p*-disub. Ar).

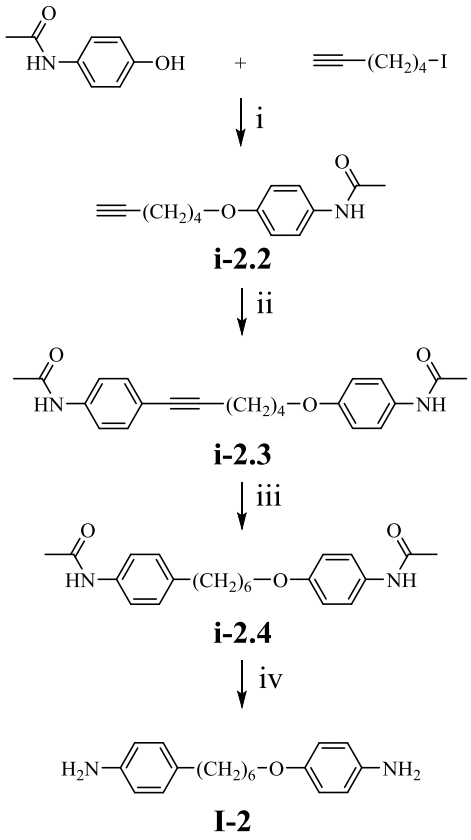
3.2 1-(4-Aminophenoxy)-6-(4-aminophenyl)hexane (**I-2**)



i-2.1

i) Et_3N, EtOAc

Scheme 2: Synthetic route to form 4-iodoacetanilide (**i-2.1**)



i-2.2

ii

i-2.3

iii

i-2.4

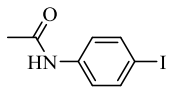
iv

I-2

i) K_2CO_3, acetone, 56 ^oC
ii) **i-2.1**, $[Pd(PPh_3)_2Cl_2]$, CuI, iPr_2NH, THF
iii) PtO_2, H_2 (g), EtOH:EtOAc (1:2) (V/V)
iv) NaOH $_{(aq)}$, EtOH, 78 ^oC

Scheme 3: Synthetic route to form 1-(4-aminophenoxy)-6-(4-aminophenyl)hexane (**I-2**)

i-2.1 4-Iodoacetanilide



To a cooled stirring solution of 4-iodoaniline (25.000 g, 0.114 mol) in EtOAc (150 mL) was added triethylamine (14.520 g, 20 mL, 0.143 mol) in one portion followed by the dropwise addition of a solution of acetyl chloride (16.500 g, 15 mL, 0.210 mol) in EtOAc (50 mL) over 30 minutes. After the complete addition of acetyl chloride the reaction was heated to room temperature and monitored by TLC until the complete consumption of 4-iodoaniline R_f 0.72 (EtOAc-light petroleum 40/60, 1:1) and the formation of product after 23 hours. Distilled water (200 mL) and EtOAc (50 mL) was added to the reaction mixture and stirred for 15 minutes. The aqueous and organic phases were then separated. The aqueous phase was extracted with EtOAc (100 mL × 2). The organic fractions were combined, washed sequentially with distilled water (50 mL × 2) and brine (50 mL × 2), then dried ($MgSO_4$). The solvent was removed *in vacuo* to give a grey solid. The crude product was purified by the addition of EtOAc (20 mL) and filtered to give the title compound as white crystals.

Yield: 21.716 g, 73%

m.p. = 181–183 ˚C

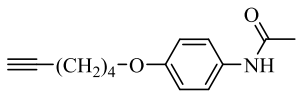
R_f (EtOAc-light petroleum 40/60, 1:1) 0.59

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 1H, Ac-NH), 7.61 (d, J = 8.8 Hz, 2H, 2 × Ar-H), 7.41 (d, J = 8.8 Hz, 2H 2 × Ar-H), 2.03 (s, 3H, CH_3-CO).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.45 (CO-NH), 139.13 (Ar-NHAc), 137.28 (2 × Ar-H), 121.13 (2 × Ar-H), 86.29 (Ar-I), 24.05 (CH_3-CO).

IR ν (cm^{-1}): 3288 (CONH); 1666 (CO); 815 (*p*-disub. Ar).

i-2.2 4-(5-Hexyn-1-yloxy)acetanilide



To a stirring solution of acetaminophen (6.557 g, 0.043 mol) and 6-iodohex-1-yne (9.500 g, 6.2 mL, 0.046 mol) in acetone (100 mL), was added potassium carbonate (12.715 g, 0.092 mol). The reaction mixture was stirred at 56 °C until TLC indicated the complete consumption of acetaminophen R_f 0.43 (EtOAc) after 48 hours. The reaction mixture was cooled to room temperature, filtered and the precipitate was washed with EtOAc (200 mL). The solvent was removed from the combined organic phases *in vacuo* to give a crude solid product. The crude product was purified (SiO_2, EtOAc) to give the title compound as a light-brown powder.

Yield: 2.841 g, 27 %

m.p. = 103–105 ˚C

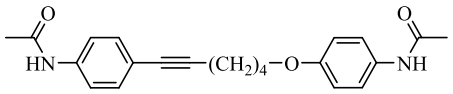
R_f (EtOAc) 0.71

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.75 (s, 1H, Ac-NH), 7.45 (d, J = 9.0 Hz, 2H, 2 × Ar-H), 6.85 (d, J = 9.0 Hz, 2H, 2 × Ar-H), 3.92 (t, J = 6.4 Hz, 2H, O-CH_2), 2.78 (t, J = 2.7 Hz, 1H, C≡CH), 2.22 (td, J = 7.1, 2.6 Hz, 2H, HC≡C-CH_2-CH_2), 1.99 (s, 3H, CH_3-CO), 1.77 (quin, J = 6.6 Hz, 2H, CH_2-CH_2-CH_2), 1.58 (quin, J = 7.1 Hz, 2H, CH_2-CH_2-CH_2).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.67 (CO-NH), 154.33 (Ar-O), 132.48 (Ar-NHAc), 120.46 (2 × Ar-H), 114.36 (2 × Ar-H), 84.31 (C≡C-H), 71.41 (C≡C-H), 66.99 (CH_2-O), 27.84 (CH_2), 24.66 (CH_2), 23.81 (CH_3-CO), 17.45 (CH_2).

IR ν (cm^{-1}): 3247 (COHN); 2936, 2870 (CH_2); 1653 (CO); 1604, 1509 (Ar), 836 (*p*-disub. Ar).

i-2.3 1-(4-Acetamidophenoxy)-6-(4-acetamidophenyl)hex-5-yne



To a solution of **i-2.1** (3.352 g, 0.013 mol) and **i-2.2** (2.700 g, 0.012 mol) in anhydrous THF (50 mL) was added diisopropylamine (20 mL). The reaction mixture was stirred and sparged with argon (g) for 2 hours. To the reaction mixture was added bis(triphenylphosphine)palladium(II) dichloride (0.082 g, 0.117 mmol) followed by copper (I) iodide (0.022 g, 0.117 mmol). The reaction headspace was evacuated and replaced with argon (g) (repeat × 2), The reaction was monitored by TLC until the complete consumption of **i-2.2** after 24 hours. The reaction mixture was filtered through a pad of celite, which was washed with THF (100 mL), followed by EtOAc (100 mL). The organic solvent mixture was removed *in vacuo* and the resultant solid was dissolved in EtOAc (400 mL) which was washed with H_2O (4 × 50 mL) and dried ($MgSO_4$). The solvent was removed *in vacuo*, and the crude product was purified (SiO2, EtOAc) to give the title compound as an off-white powder.

Yield: 3.297 g, 78 %

m.p. = 160–164 ˚C

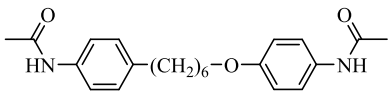
R_f (EtOAc) 0.30

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.04 (s, 1H, Ac-NH, O side), 9.76 (s, 1H, Ac-NH, C≡C side), 7.54 (d, J = 8.7 Hz, 2H, 2 × Ar-H, C≡C side), 7.45 (d, J = 9.1 Hz, 2H, 2 × Ar-H, O side), 7.29 (d, J = 8.6 Hz, 2H, 2 × Ar-H, C≡C side), 6.86 (d, J = 9.0 Hz, 2H, 2 × Ar-H, O side), 3.96 (t, J = 6.3 Hz, 2H, CH_2-O), 2.45 (t, J = 6.9 Hz, 2H, CH_2-C≡C), 2.04 (s, 3H, CH_3-CO, C≡C side), 1.99 (s, 3H, CH_3-CO, O side), 1.90 – 1.75 (m, 2H, CH_2), 1.75 – 1.58 (m, 2H, CH_2).

^{13}C NMR (75 MHz, DMSO-d_6) δ 168.40 (CO-NH), 167.68 (CO-NH), 154.33 (Ar-O), 138.96 (Ar-NHAc, C≡C side), 132.50 (Ar-NHAc, O side), 131.76 (2 × Ar-H), 120.46 (2 × Ar-H), 118.73 (2 × Ar-H), 117.43 (Ar-C≡C), 114.39 (2 × Ar-H), 89.23 (C≡C-H), 80.77 (C≡C-H), 67.05 (CH_2-O), 28.00 (CH_2), 24.95(CH_2), 24.06 (CH_3-CO), 23.82 (CH_3-CO), 18.42 (CH_2).

IR ν (cm^{-1}): 3292 (COHN); 2934, 2868 (CH_2); 1659 (CO); 1585, 1509 (Ar), 819 (*p*-disub. Ar).

i-2.4 1-(4-Acetamidophenoxy)-6-(4-acetamidophenyl)hexane



To a stirring solution of **i-2.3** (3.197 g, 8.772 mmol) in EtOH/EtOAc (300 mL, 1:2 EtOH:EtOAc V/V) was added platinum dioxide (0.050 g, 0.220 mmol). The reaction mixture was sparged with H_2 (g) (approx. 5 L) with constant stirring. The reaction headspace was evacuated and replaced with H_2 (g) (repeat × 2) and the reaction progress was monitored by NMR until the consumption of **i-2.3** after 24 hours. The reaction mixture was filtered through a pad of celite, which was washed with EtOAc (200 mL), and then solvent removed *in vacuo*. The crude product was purified (SiO_2, EtOAc) to give the title compound as an off-white powder.

Yield: 1.908g, 59 %

m.p. = 174–180 ˚C

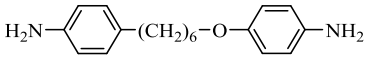
R_f (EtOAc) 0.26

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.82 (s, 1H, Ac-NH, O side), 9.75 (s, 1H, Ac-NH, C≡C side), 7.45 (2 × d overlapping (observed as dd), J = 8.8, 2.4 Hz, 4H, 4 × Ar-H), 7.09 (d, J = 8.4 Hz, 2H, 2 × Ar-H), 6.83 (d, J = 9.0 Hz, 2H, 2 × Ar-H), 3.88 (t, J = 6.4 Hz, 2H, CH_2-O), 2.53 (t (overlapping with DMSO-d_6), 2H, CH_2-Ar), 2.01 (s, 3H CH_3-CO, CH_2 side), 1.99 (s, 3H, CH_3-CO, O side), 1.66 (quin, J = 6.6 Hz, 2H, CH_2), 1.55 (quin, J = 7.5 Hz, 2H, CH_2), 1.49 – 1.23 (m, 4H, 2 × CH_2).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.97 (CO-NH), 167.65 (CO-NH), 154.39 (Ar-O), 137.01 (Ar), 136.81 (Ar), 132.40 (Ar-NHAc, O side), 128.35 (2 × Ar-H), 120.47 (2 × Ar-H), 118.99 (2 × Ar-H), 114.33 (2 × Ar-H), 67.46 (CH_2-O), 34.47 (CH_2), 30.98 (CH_2), 28.67 (CH_2), 28.34 (CH_2), 25.35 (CH_2), 23.92 (CH_3-CO), 23.79 (CH_3-CO).

IR ν (cm^{-1}): 3294 (COHN); 2926, 2858 (CH_2); 1656 (CO); 1595, 1509 (Ar), 819 (*p*-disub. Ar).

I-2 1-(4-Aminophenoxy)-6-(4-aminophenyl)hexane



Synthesis procedure follows that described for **I-1** 1,5-bis(4-aminophenyl-4'-oxy)pentane

Quantities used: **i-2.4** (1.800 g, 4.885 mmol); EtOH (150 mL); NaOH (5.862 g, 0.147 mol) in H_2O (35 mL).

TLC indicated the complete consumption of **i-2.4** after 3 hours and the mono-hydrolysed product (not isolated, R_f (EtOAc) 0.42) after 20 hours.

The crude product was purified (SiO_2, EtOAc-light petroleum 40/60, 7:3), followed by recrystallisation from EtOH/H_2O (1:1 (V/V), 60 mL) to give to give the title compound as an off-white powder.

Yield: 1.009 g, 73 %

m.p. = 39–41 ˚C

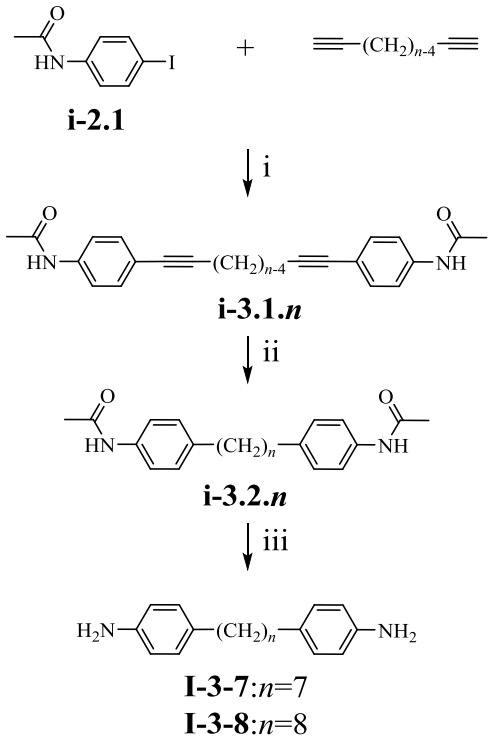
R_f (EtOAc-light petroleum 40/60, 7:3) 0.30

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.82 (d, J = 8.0 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 6.51 – 6.44 (m, 3H), 4.77 (s, 2H, Ar-$\underline{NH_2}$ methylene side), 4.56 (s, 2H, Ar-$\underline{NH_2}$ ether side), 3.78 (t, J = 6.5 Hz, 2H, O-$\underline{CH_2}$), 2.38 (t, J = 7.6 Hz, 2H, Ar-$\underline{CH_2}$), 1.61 (quin, J = 6.8 Hz, 2H, CH_2), 1.49 (quin, J = 7.5 Hz, 2H, CH_2), 1.38 (quin, J = 7.2 Hz, 2H, CH_2), 1.34 – 1.23 (m, 2H, CH_2).

^{13}C NMR (75 MHz, DMSO-d_6) δ 149.97 ($\underline{Ar}$-O), 146.33 ($\underline{Ar}$-NH_2 methylene side), 142.30 ($\underline{Ar}$-NH_2 ether side), 129.25 ($\underline{Ar}$-CH_2), 128.62 (2 × Ar-H), 115.31 (2 × Ar-H), 114.93 (2 × Ar-H), 113.96 (2 × Ar-H), 67.83 ($\underline{CH_2}$-O), 34.36 (CH_2), 31.48 (CH_2), 28.95 (CH_2), 28.45 (CH_2), 25.49 (CH_2).

IR ν (cm^{-1}): 3368, 3289 (Ar. NH_2); 2928, 2850 (CH_2); 1614, 1508 (Ar) 1238 (Ar. C-N); 805 (*p*-disub. Ar).

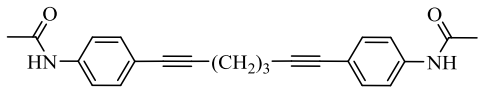
3.3 1,7- Bis(4- phenylacetamide- 4'-)heptane (**I- 3- 7**) and 1,8- bis(4- phenylacetamide- 4'-)octane (**I- 3- 8**).



i) $[Pd(PPh_3)_2Cl_2]$, CuI, iPr_2NH, THF
ii) PtO_2, H_2 (g), EtOH:EtOAc (1:2) (V/V)
iii) NaOH $_{(aq)}$, EtOH, 78 ^oC

Scheme 4: Synthetic route to form the *a,ω*-bis(4-aminophenyl-4'-)alkanes (**I-3-7** and **I-3-8**).

i-3.1.7 1,7-Bis(4-phenylacetamide-4'-)hepta-1,6-diyn



Synthesis procedure follows that described for **i-2.3** 1-(4-acetamidophenoxy)-6-(4-acetamidophenyl)hex-5-yne.

Quantities used: **i-2.1** (10.000 g, 0.038 mol); 1,6-heptadiyne (1.771 g, 2.2 mL, 0.019 mol); THF (80 mL), diisopropylamine (20 mL); bis(triphenylphosphine)palladium(II) dichloride (0.133 g, 0.190 mmol); copper (I) iodide (0.724 g, 0.38 mmol, 2 mol%).

TLC indicated the complete consumption of **i-2.1** after 48 hours.

The crude product was purified (SiO_2, EtOAc) to give the title compound as an off-white powder.

Yield: 4.568 g, 67%

m.p. = 195–200 ˚C

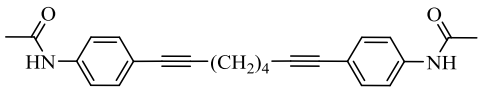
R_f (EtOAc) 0.29

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.03 (s, 2H, 2 × Ac-NH), 7.55 (d, J = 8.8 Hz, 4H, 4 × Ar-H), 7.32 (d, J = 8.7 Hz, 4H, 4 × Ar-H), 2.54 (t, J = 7.1 Hz, 4H, 2 × C≡C-CH_2), 2.04 (s, 6H, 2 × CH_3-CO), 1.79 (quin, J = 7.1 Hz, 2H, CH_2-CH_2-CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.41 (2 × CO-NH), 139.03 (2 × Ar-NHAc), 131.82 (4 × Ar-H), 118.72 (4 × Ar-H), 117.30 (2 × Ar-C≡C), 88.57 (2 × Ar-C≡C), 81.03 (2 × Ar-C≡C), 27.68 (CH_2-CH_2-CH_2), 24.06 (2 × CH_3-CO), 17.99 (2 × C≡C-CH_2).

IR ν (cm^{-1}): 3301 (COHN); 1667 (CO); 1599, 1508 (Ar), 836 (*p*-disub. Ar).

i-3.1.8 1,8-Bis(4-phenylacetamide-4'-)octa-1,7-diyn



Synthesis procedure follows that described for **i-2.3** 1-(4-acetamidophenoxy)-6-(4-acetamidophenyl)hex-5-yne.

Quantities used: **i-2.1** (4.908 g, 0.019 mol); 1,8-nonadiyne (1.000 g, 0.75 mL, 0.009 mol); THF (75 mL), diisopropylamine (25 mL); bis(triphenylphosphine)palladium(II) dichloride (0.100 g, 0.143 mmol); copper (I) iodide (0.019 g, 0.009 mmol).

TLC indicated the complete consumption of **i-2.1** after 48 hours.

The crude product was purified (SiO_2, EtOAc) to give the title compound as an off-white powder.

Yield: 0.812 g, 22 %

m.p. = 213–217 ˚C

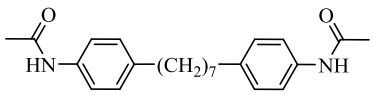
R_f (EtOAc) 0.27

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 2H, 2 × Ac-NH), 7.54 (d, J = 8.6 Hz, 4H, 4 × Ar-H), 7.30 (d, J = 8.6 Hz, 4H, 4 × Ar-H), 2.51 – 2.40 (t (observed as m), 4H, 2 × C≡C-CH_2), 2.04 (s, 6H, 2 × CH_3-CO), 1.67 (m, 4H, 2 × CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.37 (2 × CO-NH), 138.90 (2 × Ar-NHAc), 131.70 (4 × Ar-H), 118.74 (4 × Ar-H), 117.51 (2 × Ar-C≡C), 89.40 (2 × Ar-C≡C), 80.62 (2 × Ar-C≡C), 27.77 (2 × C≡C-CH_2-CH_2), 24.04 (2 × CH_3-CO), 18.58 (2 × C≡C-CH_2).

IR ν (cm^{-1}): 3310 (COHN); 1667 (CO); 1595, 1523 (Ar), 838 (*p*-disub. Ar).

i-3.2.7 1,7-bis(4-phenylacetamide-4'-)heptane



Synthesis procedure follows that described for **i-2.4** 1-(4-acetamidophenoxy)-6-(4-acetamidophenyl)hexane

Quantities used: **i-3.1.7** (4.400 g, 0.012 mol); platinum dioxide (0.100 g, 0.044 mmol); EtOAc/EtOH (400 mL, 2:1 EtOAc:EtOH V/V);. H_2 (g) (approx. 10 L).

Reaction was monitored by NMR until the complete consumption of **i-3.1.7** after 48 hours.

The crude product was purified by recrystallisation from toluene (150 mL) to give the title compound as a white powder.

Yield: 2.763 g, 61 %

m.p. = 185–189 ˚C

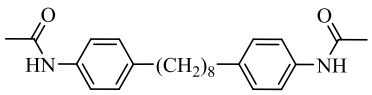
R_f (EtOAc) 0.30

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.81 (s, 2H, 2 × Ac-NH), 7.45 (d, J = 8.4 Hz, 4H, 4 × Ar-H), 7.07 (d, J = 8.4 Hz, 4H, 4 × Ar-H), 2.47 (t, J = 7.9 Hz, 4H, 2 × Ar-CH_2), 2.01 (s, 6H, 2 × CH_3-CO), 1.50 (quin, J = 7.4 Hz, 4H, 2 × Ar-CH_2-CH_2), 1.34 – 1.17 (m, 6H, 3 × CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.96 (2 × CO-NH), 136.99 (2 × Ar-X), 136.84 (2 × Ar-X), 128.33 (4 × Ar-H, CH_2 side), 118.98 (4 × Ar-H, NHAc side), 34.50 (2 × CH_2), 30.98 (2 × CH_2), 28.63 (CH_2), 28.52 (2 × CH_2), 23.92 (2 × CH_3-CO).

IR ν (cm^{-1}): 3293 (COHN); 2918, 2849 (CH_2); 1660 (CO); 1596, 1532 (Ar), 837 (*p*-disub. Ar).

i-3.2.8 1,8-Bis(4-phenylacetamide-4'-)octane



Synthesis procedure follows that described for **i-2.4** 1-(4-acetamidophenoxy)-6-(4-acetamidophenyl)hexane

Quantities used: **i-3.1.8** (0.800 g, 2.148 mmol); platinum dioxide (0.050 g, 0.220 mmol); EtOAc/EtOH (150 mL, 2:1 EtOAc:EtOH V/V);. H_2 (g) (approx. 10 L).

Reaction was monitored by NMR until the complete consumption of **i-3.1.8** after 48 hours.

The crude product was purified (SiO_2, EtOAc) to give the title compound as a white powder.

m.p. = 197–210 ˚C

Yield: 0.721 g, 88 %

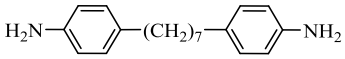
R_f (EtOAc) 0.41

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (s, 2H, 2 × Ac-NH), 7.45 (d, J = 8.5 Hz, 4H, 4 × Ar-H), 7.07 (d, J = 8.4 Hz, 4H, 4 × Ar-H), 2.50 – 2.42 (2 × t (overlapping with DMSO-d_6, observed as m), 4H, 2 × Ar-CH_2), 2.01 (s, 6H, 2 × CH_3-CO), 1.51 (quin, J = 7.2 Hz, 4H, 2 × Ar-CH_2-CH_2), 1.34 – 1.13 (m, 8H, 4 × CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.97 (2 × CO-NH), 136.98 (2 × Ar-X), 136.86 (2 × Ar-X), 128.33 (4 × Ar-H, CH_2 side), 118.99 (4 × Ar-H, NHAc side), 34.53 (2 × CH_2), 31.01 (2 × CH_2), 28.81 (2 × CH_2), 28.57 (2 × CH_2), 23.92 (2 × CH_3-CO).

IR ν (cm^{-1}): 3297 (COHN); 2918, 2849 (CH_2); 1660 (CO); 1597, 1525 (Ar), 837 (*p*-disub. Ar).

I-3-7 1,7-Bis(4-phenylamine-4'-)heptane



Synthesis procedure follows that described for **I-1-5** 1,5-bis(4-aminophenyl-4'-oxy)pentane

Quantities used: **i-3.2.7** (2.550 g, 6.958 mmol); EtOH (50 mL); NaOH (8.350 g, 0.209 mol) in H_2O (20 mL).

TLC indicated the complete consumption of **i-3.2** after 3 hours and the mono-hydrolysed product (not isolated) after 5 hours.

The crude product was used without further purification.

Yield: 1.836 g, 93%

m.p. = 82–84 ˚C

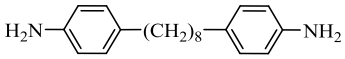
R_f (EtOAc) 0.58

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.80 (d, J = 8.2 Hz, 4H, 4 × Ar-H), 6.46 (d, J = 8.3 Hz, 4H, 4 × Ar-H), 4.77 (s, 4H, 2 × NH_2), 2.36 (t, J = 7.6 Hz, 4H, 2 × Ar-$\underline{CH_2}$), 1.45 (quin, J =7.3 Hz, 4H, 2 × Ar-CH_2-$\underline{CH_2}$), 1.24 (m, 6H, 3 × CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.25 (2 × $\underline{Ar}$-NH_2), 129.28 (4 × Ar-H, CH_2 side), 128.55 (2 × $\underline{Ar}$-CH_2), 113.94 (4 × Ar-H, NH_2 side), 34.35 (2 × CH_2), 31.41 (2 × CH_2), 28.75 (CH_2), 28.60 (2 × CH_2).

IR ν (cm^{-1}): 3314, 3217 (Ar. NH_2); 2917, 2849 (CH_2); 1609, 1515 (Ar); 1267 (Ar. C-N); 826 (*p*-disub. Ar)

I-3-9 1,8-Bis(4-phenylamine-4’-)octane



Synthesis procedure follows that described for **I-1-5** 1,5-bis(4-aminophenyl-4’-oxy)pentane

Quantities used: **i-3.2.8** (0.600 g, 1.577 mmol); EtOH (15 mL); NaOH (1.892 g, 0.047 mol) in H_2O (5 mL).

TLC indicated the complete consumption of **i-3.2.8** and the mono-hydrolysed product (not isolated) after 3 hours.

The crude product was used without further purification.

Yield: 0.348 g, 74%

m.p. = 80–85 ˚C

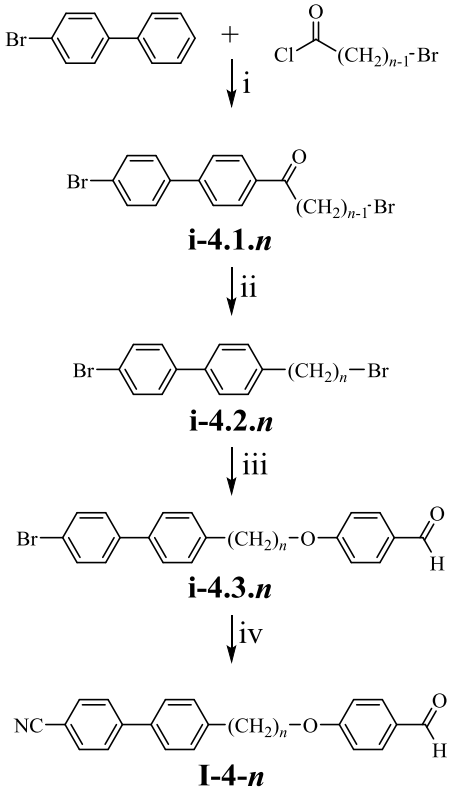
R_f (EtOAc) 0.68

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.80 (d, J = 8.3 Hz, 4H, 4 × Ar-H), 6.46 (d, J = 8.3 Hz, 4H, 4 × Ar-H), 4.77 (s, 4H, 2 × NH_2), 2.36 (t, J = 7.5 Hz, 4H, 2 × Ar-$\underline{CH_2}$), 1.60 – 1.35 (m, 4H, 2 × Ar-CH_2-$\underline{CH_2}$), 1.35 – 1.14 (m, 8H, 4 × CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.24 (2 × $\underline{Ar}$-NH_2), 129.28 (4 × Ar-H, CH_2 side), 128.54 (2 × $\underline{Ar}$-CH_2), 113.94 (4 × Ar-H, NH_2 side), 34.36 (2 × CH_2), 31.42 (2 × CH_2), 28.90 (2 × CH_2), 28.60 (2 × CH_2).

IR ν (cm^{-1}): 3327, 3210 (Ar. NH_2); 2916, 2848 (CH_2); 1611, 1515 (Ar); 1255 (Ar. C-N); 837 (*p*-disub. Ar)

3.4 1-(4-Formylphenoxy)-6-(4-cyanobiphenyl-4'-yl)hexane (**I-4-6**) and 1-(4-formylphenoxy)-7-(4-cyanobiphenyl-4'-yl)heptane (**I-4-7**)



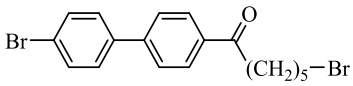
i) $AlCl_3$, DCM; ii) Et_3SiH, TFA, DCM

iii) 4-Hydroxybenzaldehyde, K_2CO_3, DMF, 90 ^oC

iv) 1) CuCN, NMP, 200 ^oC, 2) NH_4OH

Scheme 5: Synthetic route to form 1-(4-formylphenoxy)-6-(4-cyanobiphenyl-4'-yl)hexane (**I-4-6**) and 1-(4-formylphenoxy)-7-(4-cyanobiphenyl-4'-yl)heptane (**I-4-7**).

6-Bromo-1-[4-(4-bromophenyl)phenyl]hexan-1-one (**i-4.1.6**)



A solution of 4-bromobiphenyl (27.295 g, 0.117 mol) in DCM (200 mL) was added dropwise to a suspension of aluminium (III) chloride (15.614 g, 0.117 mol) in DCM (100 mL) at 0 ˚C, under argon. 6-Bromohexanoyl chloride (25.000 g, 17.9 mL, 0.117 mol) was added dropwise at 0 ˚C, in the dark, under argon. The reaction mixture was slowly warmed to room temperature and allowed to react for 23 hours. The reaction mixture was quenched by the addition of HCl (500 mL, 0.5 M) and ice (100 g) and then extracted with DCM (3 × 50 mL). The organics were combined and washed with HCl (2 × 50 mL, 1 M), sat. aq. NaCl solution (2 × 50 mL) and H_2O (2 × 50 mL), then dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to yield a yellow oil that solidified on cooling. The crude product was purified by recrystallisation from EtOH (400 mL) to give the title compound as an off-white powder.

Yield: 39.644 g, 83%

m.p. = 87–89 ˚C

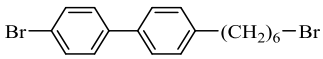
R_f (DCM-light petroleum 40/60, 1:1) 0.48

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.7 Hz, 2H, 2 × Ar-H), 7.65 (d, *J* = 8.7 Hz, 2H, 2 × Ar-H), 7.61 (d, *J* = 8.7 Hz, 2H, 2 × Ar-H), 7.50 (d, *J* = 8.7 Hz, 2H, 2 × Ar-H), 3.46 (t, *J* = 6.4 Hz, 2H, $\underline{CH_2}$-Br), 3.03 (t, *J* = 7.6 Hz, 2H, $\underline{CH_2}$-CO), 1.94 (quin, *J* = 7.2 Hz, 2H, CH_2), 1.81 (quin, *J* = 7.6 Hz, 2H, CH_2-$\underline{CH_2}$-CH_2), 1.57 (m, 2H, CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 199.45 (C=O), 144.34 (Ar), 138.73 (Ar), 135.89 (Ar), 132.11 (2 × Ar-H), 128.82 (2 × Ar-H), 128.74 (2 × Ar-H), 127.05 (2 × Ar-H), 122.65 (Ar), 38.38 (CH_2) 33.74 (CH_2), 32.65 (CH_2), 27.89 (CH_2), 23.35 (CH_2).

IR ν (cm^{-1}): 2937, 2862 (CH_2); 1677 (C=O); 1604 (Ar); 822 (*p*-disub. Ar).

1-Bromo-4-[4-(6-bromohexyl)phenyl]benzene (**i-4.2.6**)



To a solution of **i-4.1.6** (38.000 g, 0.093 mol) in DCM (150 mL), trifluoroacetic acid (85.840 g, 58 mL, 0.741 mol) was added in one portion at 0 °C, under argon. A solution of triethylsilane (42.301 g, 58 mL, 0.371 mol) was added dropwise to the stirring solution over 1 hour. The solution was slowly warmed to room temperature and allowed to react until TLC indicated complete consumption of **i-4.1.6** after 24 hours. The reaction was quenched by addition of the reaction to H_2O (400 mL). The organic and aqueous phases were separated, and the aqueous phase extracted with DCM (3 × 30mL). The organic phases were combined, washed with H_2O (3 × 50 mL) and then dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to yield a white solid. The resultant solid was recrystallised from EtOH (400 mL) to give the product as a white powder.

Yield: 26.911 g, 73%

m.p. = 78–79 ˚C

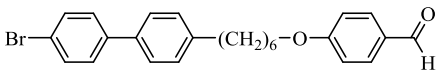
R_f (DCM-light petroleum 40/60, 1:1) 0.76

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.7 Hz, 2H, 2 × Ar-H), 7.46 (d, *J* = 8.7 Hz, 4H, 2 × Ar-H), 7.24 (d, *J* = 8.2 Hz, 2H, 2 × Ar-H), 3.41 (t, *J* = 6.4 Hz, 2H, $\underline{CH_2}$-Br), 2.65 (t, *J* = 6.8 Hz, 2H, $\underline{CH_2}$-Ar), 1.86 (quin, *J* = 6.7 Hz, 2H, CH_2), 1.67 (quin, *J* = 7.5 Hz, 2H,CH_2), 1.53-1.32 (m, 4H, 2 × CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.19 (Ar), 140.01 (Ar), 137.41 (Ar), 131.81 (2 × Ar-H), 128.96 (2 × Ar-H), 128.57 (2 × Ar-H), 126.82 (2 × Ar-H), 121.21 (Ar), 35.44 (CH_2), 34.02 (CH_2), 32.73 (CH_2), 31.23 (CH_2), 28.41 (CH_2), 28.04 (CH_2).

IR ν (cm^{-1}): 2931, 2855 (CH_2); 1604 (Ar); 804 (*p*-disub. Ar).

1-(4-Formylphenoxy)-6-(4-bromobiphenyl-4'-yl)hexane (**i-4.3.6**)



i-4.2.6 (8.000 g, 0.020 mol) and 4-hydroxybenzaldehyde (2.711 g, 0.022 mol) were dissolved in DMF (40 mL) before the addition of potassium carbonate (4.127 g, 0.030 mol). The reaction mixture was stirred at 90 °C until TLC indicated complete consumption of **i-4.2.6** after 20 hours, then cooled to room temperature before addition to H_2O (300 mL). The resultant precipitate was filtered, dissolved in DCM (150 mL) and washed with sat. aq. NaCl (2 × 50 mL) and H_2O (2 × 50 mL), then dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to give a brown solid. The crude product was purified by recrystallisation from EtOH (250 mL) to give the product as a light brown powder.

Yield: 6.830 g, 77%

m.p. = 93–95 ˚C (lit. 87.7-89.3 °C [3])

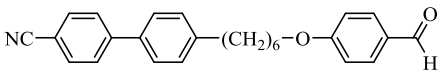
R_f (DCM) 0.60

^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.90 (s, 1H, CHO), 7.85 (d, *J* = 8.8 Hz, 2H, 2 × Ar-H), 7.55 (d, *J* = 8.6 Hz, 2H, 2 × Ar-H), 7.47 (2 × d overlapping, *J* = 8.4 Hz, 4H, 4 × Ar-H), 7.26 (d, *J* = 8.74 Hz, 2H, 2 × Ar-H), 6.98 (d, *J* = 8.8 Hz, 2H, 2 × Ar-H), 4.04 (t, *J* = 6.4 Hz, 2H, CH_2-O), 2.67 (t, *J* = 7.8 Hz, 2H, CH_2-Ar), 1.83 (quin, *J* = 6.6 Hz, 2H, CH_2), 1.69 (quin, *J* = 7.4 Hz, 2H, CH_2), 1.60-1.38 (m, 4H, 2 × CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.87 (CHO), 164.21 (CHO-Ar), 142.24 (Ar), 139.98 (Ar), 137.37 (Ar), 132.03 (2 × Ar-H), 131.83 (2 × Ar-H), 129.75 (Ar), 128.99 (2 × Ar-H), 128.56 (2 × Ar-H), 126.82 (2 × Ar-H), 121.23 (Ar), 114.75 (2 × Ar-H), 68.31 (CH_2-O), 35.49 (CH_2), 31.34 (CH_2), 29.00 (CH_2), 28.96 (CH_2), 25.88 (CH_2).

IR ν (cm^{-1}): 2862, 2732 (CH_2); 1680 (C=O); 1601, 1574 (Ar); 803 (*p*-disub. Ar).

1-(4-Formylphenoxy)-6-(4-cyanobiphenyl-4'-yl)hexane (**I-4-6**)



A solution of **i-4.3.6** (5.000 g, 0.014 mol) and copper (I) cyanide (2.046 g, 0.028 mol) in NMP (50 mL) was heated to 200 °C, under argon. The reaction was monitored until TLC indicated complete consumption of **i-4.3.6** after 6 hours and the reaction was cooled to room temperature. The reaction was quenched by the slow addition of aq. ammonium hydroxide (50 mL, 10%). The evolved gas, which was passed through aq. sodium hypochlorite, was monitored until its termination. The reaction mixture was added to H_2O (200 mL) and DCM (200 mL). The organic and aqueous phases were separated, and the aqueous phase extracted with DCM (3 × 30 mL). The organic fractions were combined, washed with HCl (2 × 50 mL), sat. aq. NaCl (2 × 50 mL), H_2O (2 × 50 mL) and then dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a brown oil. The oil was added to H_2O (400 mL) and the resultant precipitate was filtered, dissolved in DCM (150 mL) and then dried ($MgSO_4$). The solvent was removed *in vacuo* to give a brown solid. The crude product was purified (SiO_2, DCM) followed by recrystallisation from EtOH (50 mL) to give the product as yellow needles.

Yield: 2.510 g, 47%

m.p. = 85–88 ˚C (lit. 80.6-81.8 ˚C [3])

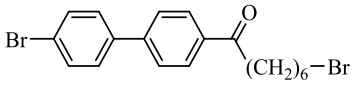
R_f (DCM) 0.38

^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.90 (s, 1H, CHO), 7.85 (d, *J* = 8.8 Hz, 2H, 2 × Ar-H), 7.74 (d, *J* = 8.6 Hz, 2H, 2 × Ar-H), 7.69 (d, *J* = 8.8 Hz, 2H, 2 × Ar-H), 7.53 (d, *J* = 8.20 Hz, 2H, 2 × Ar-H), 7.31 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 7.01 (d, *J* = 8.7 Hz,2H, 2 × Ar-H), 4.06 (t, *J* = 6.4 Hz, 2H, CH_2-O), 2.71 (t, *J* = 7.7 Hz, 2H, CH_2-Ar), 1.85 (quin, *J* = 6.7 Hz, 2H, CH_2), 1.72 (quin, *J* = 7.5 Hz, 2H, CH_2), 1.60-1.40 (m, 4H, 2 × CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.89 (CHO), 164.18 (Ar), 145.53 (Ar), 143.45 (Ar), 136.56 (Ar), 132.60 (2 × Ar-H), 132.03 (2 × Ar-H), 129.74 (Ar), 129.19 (2 × Ar-H), 127.48 (2 × Ar-H), 127.13 (2 × Ar-H), 119.09 (C≡N), 114.72 (2 × Ar-H), 110.55 (Ar), 68.28 (CH_2-O), 35.52 (CH_2), 31.31 (CH_2), 28.99 (CH_2), 28.95 (CH_2), 25.87 (CH_2).

IR ν (cm^{-1}): 2222 (CN), 1689 (CHO), 1598 (Ar C=C), 1574 (Ar C=C), 1160 (C-O-Ar).

7-Bromo-1-[4-(4-bromophenyl)phenyl]heptan-1-one (**i-4.1.7**)



To a solution of 7-bromoheptanoic acid (25.000 g, 0.120 mol) in toluene (10 mL) was added oxalyl chloride (19.240 g, 13 mL, 0.152 mol), followed by a catalytic quantity of DMF (5 drops) and the reaction was stirred for 30 minutes at room temperature, under argon. The reaction was then heated to 40 °C and stirred for 6 hours before the toluene and excess oxalyl chloride was removed via distillation (20 °C, 5 mmHg). The crude product was purified via distillation (150–160 °C, 5 mmHg) to give the intermediate 7-bromoheptanoyl chloride as a clear oil, which was used without further analysis (15.017 g, 0.066 mol, 55%).

The second stage of the reaction was carried out in the dark. A solution of 4-bromobiphenyl (15.369 g, 0.066 mol) in DCM (100 mL) was added dropwise to a suspension of aluminium (III) chloride (9.666 g, 0.073 mol) in DCM (100 mL) at 0 ˚C, under argon. The previously prepared 7-bromoheptanoyl chloride (15.000 g, 0.066 mol) was added dropwise at 0 ˚C, under argon. The reaction mixture was slowly warmed to room temperature and allowed to react until TLC indicated the complete consumption of 4-bromobiphenyl R_f 0.80 (DCM-light petroleum 40/60, 1:1) after 7 hours. The reaction mixture was quenched by the addition of HCl (300 mL, 0.5 M) and ice (100g) and then extracted with DCM (3 × 50 mL). The organic fractions were combined and washed with HCl (2 × 50 mL, 1 M), sat. aq. NaCl solution (2 × 50 mL) and H_2O (2 × 50 mL), then dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave a yellow oil that solidified on cooling. The crude product was purified by recrystallisation from EtOH (400 mL) to give the title compound as a white powder.

Yield: 9.653 g, 35%

m.p. = 107–114 ˚C

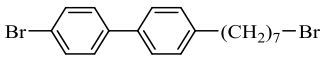
R_f (DCM-light petroleum 40/60, 1:1) 0.22

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H, Ar), 7.64 (d, *J* = 8.2 Hz, 2H, Ar), 7.60 (d, *J* = 8.0 Hz, 2H, Ar), 7.49 (d, *J* = 7.2 Hz, 2H, Ar), 3.42 (t, *J* = 6.8 Hz, 2H, $\underline{CH_2}$-Br), 3.00 (t, *J* = 7.5 Hz, 2H, $\underline{CH_2}$-CO), 1.89 (quin, *J* = 7.1 Hz, 2H, CH_2-$\underline{CH_2}$-CH_2), 1.78 (quin, *J* = 7.5 Hz, 2H), 1.54 – 1.39 (m, 4H, 2 × CH_2-$\underline{CH_2}$-CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.86 (CHO), 144.49 (Ar), 138.96 (Ar), 136.16 (Ar), 132.25 (2 × Ar-H), 128.96 (2 × Ar-H), 128.89 (2 × Ar-H), 127.20 (2 × Ar-H), 122.78 (Ar), 38.59 (CH_2), 33.99 (CH_2), 32.73 (CH_2), 28.60 (CH_2), 28.15 (CH_2), 24.24 (CH_2).

IR ν (cm^{-1}): 2935, 2861 (CH_2); 1675 (CO); 1605 (Ar); 812 (*p*-disub. Ar)

1-Bromo-4-[4-(6-bromoheptyl)phenyl]benzene (**i-4.2.7**)



To a solution of **i-4.1.7** (9.500 g, 0.022 mol) in DCM (50 mL), trifluoroacetic acid (20.720 g, 14 mL, 0.182 mol) was added in one portion at 0 °C, under argon. A solution of triethylsilane (10.410 g, 14 mL, 0.090 mol) was added dropwise to the stirring solution over 2 hours. The solution was slowly warmed to room temperature and allowed to react until TLC indicated complete consumption of **i-4.1.7** after 28 hours. The reaction was quenched by addition of the reaction to H_2O (300 mL). The organic and aqueous phases were separated, and the aqueous phase extracted with DCM (3 × 30mL). The organic phases were combined, washed with sat. aq. NaCl solution (2 × 50 mL), H_2O (4 × 100 mL) and then dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to yield a white solid. The resultant solid was recrystallised from EtOH (400 mL) to give the product as a white powder.

Yield: 5.466 g, 59%

m.p. = 65–67 ˚C

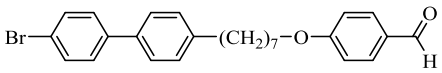
R_f (DCM-light petroleum 40/60, 1:1) 0.78

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.7 Hz, 2H, Ar), 7.50 – 7.41 (2 × d overlpping (observed as m), 4H, Ar), 7.25 (d, *J* = 8.2 Hz, 2H, Ar), 3.41 (t, *J* = 6.8 Hz, 2H, $\underline{CH_2}$-Br), 2.64 (t, *J* = 7.7 Hz 2H, $\underline{CH_2}$-Ar), 1.86 (quin, *J* = 6.9 Hz, 2H, CH_2), 1.73 – 1.58 (m, 2H, CH_2), 1.51 – 1.31 (m, 8H, 4 × CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.49 (Ar), 140.19 (Ar), 137.51 (Ar), 131.94 (2 × Ar-H), 129.09 (2 × Ar-H), 128.70 (2 × Ar-H), 126.94 (2 × Ar-H), 121.32 (Ar), 35.68 (CH_2), 34.14 (CH_2), 32.93 (CH_2), 31.46 (CH_2), 29.24 (CH_2), 28.78 (CH_2), 28.23 (CH_2).

IR ν (cm^{-1}): 2928, 2853 (CH_2); 805 (*p*-disub. Ar).

1-(4-Formylphenoxy)-6-(4-bromobiphenyl-4'-yl)heptane (**i-4.3.7**)



i-4.2.7 (5.334 g, 0.013 mol) and 4-hydroxybenzaldehyde (1.954 g, 0.016 mol) were dissolved in DMF (20 mL) before the addition of potassium carbonate (2.695g, 0.020 mol). The reaction mixture was stirred at 90 °C until TLC indicated complete consumption of **i-4.2.7** after 21 hours, then cooled to room temperature before addition to H_2O (300 mL). The resultant precipitate was filtered, dissolved in DCM (150 mL) and washed with sat. aq. NaCl (2 × 50 mL) and H_2O (2 × 50 mL), then dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to give a brown solid. The crude product was purified by recrystallisation from EtOH (200 mL) to give the product as off-white powder.

Yield: 3.948 g, 67%

m.p. = 227–230 ˚C

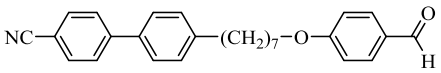
R_f (DCM) 0.53

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H, CHO), 7.82 (d, *J* = 7.3 Hz, 2H, Ar), 7.54 (d, *J* = 7.2 Hz, 2H, Ar), 7.51 – 7.41 (2 × overlapping d, (observed as m), 4H, Ar), 7.25 (d, *J* = 8.4 Hz, 2H, Ar), 6.98 (d, *J* = 8.1 Hz, 2H, Ar), 4.04 (t, *J* = 6.6 Hz, 2H, CH_2-O), 2.65 (t, *J* = 7.8 Hz, 2H, CH_2-Ar), 1.82 (quin, *J* = 5.8 Hz, 2H, CH_2-CH_2-CH_2), 1.67 (quin, *J* = 7.3 Hz, 2H, CH_2-CH_2-CH_2), 1.54 – 1.35 (m, 6H, 3 × CH_2-CH_2-CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.94 (CHO), 164.36 (Ar), 142.50 (Ar), 140.16 (Ar), 137.51 (Ar), 132.13 (2 × Ar-H), 131.95 (2 × Ar-H), 129.92 (Ar), 129.09 (2 × Ar-H), 128.69 (2 × Ar-H), 126.94 (2 × Ar-H), 121.34 (Ar), 114.88 (2 × Ar-H), 68.50 (CH_2-O), 35.71 (CH_2), 31.49 (CH_2), 29.35 (2 × CH_2), 29.19 (CH_2), 26.06 (CH_2).

IR ν (cm^{-1}): 2925, 2855 (CH_2); 1683 (CHO); 1597 1507 (Ar); 801 (*p*-disub. Ar).

1-(4-Formylphenoxy)-6-(4-cyanobiphenyl-4'-yl)heptane (**I-4-7**)



A solution of **i-4.3.7** (3.700 g, 8.197 mmol) and copper (I) cyanide (1.470 g, 16.425 mmol) in NMP (20 mL) was heated to 200 °C, under argon. The reaction was monitored until TLC indicated complete consumption of **i-4.3.7** after 4 hours and the reaction was cooled to room temperature. The reaction was quenched by the slow addition of aq. ammonium hydroxide (60 mL, 10%). The evolved gas, which was passed through aq. sodium hypochlorite, was monitored until its termination. The reaction mixture was added to H_2O (100 mL) and DCM (200 mL). The organic and aqueous phases were separated, and the aqueous phase extracted with DCM (3 × 30 mL). The organic fractions were combined, washed with HCl (2 × 50 mL), sat. aq. NaCl (2 × 50 mL), H_2O (4 × 50 mL) and then dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a brown solid. The crude product was purified (SiO_2, DCM) to give the product as a white solid.

Yield: 1.295g, 40%

m.p. = 80 ˚C (Cr-N) , T_{Cl} = 99 ˚C (N-I)

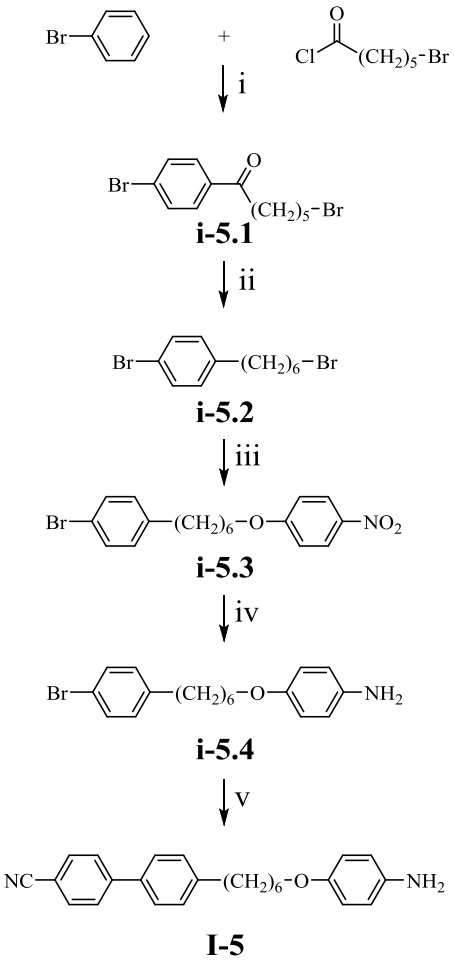
R_f (DCM) 0.38

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H, CHO), 7.82 (d, *J* = 6.8 Hz, 2H), 7.71 (d, *J* = 7.1 Hz, 2H, Ar), 7.67 (d, *J* = 9.0 Hz, 2H, Ar), 7.51 (d, *J* = 6.2 Hz, 2H, Ar), 7.29 (d, *J* = 6.8 Hz, 2H, Ar), 6.98 (d, *J* = 6.8 Hz, 2H, Ar), 4.03 (d, *J* = 5.9 Hz, 2H, CH_2-O), 2.67 (t, *J* = 7.9 Hz, 2H, CH_2-Ar), 1.82 (quin, *J* = 6.9 Hz, 2H, CH_2-CH_2-CH_2), 1.67 (quin, *J* = 7.4 Hz, 2H, CH_2-CH_2-CH_2), 1.53 – 1.35 (m, 6H, 3 × CH_2-CH_2-CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.93 (CHO), 164.35 (Ar), 145.71 (Ar), 143.72 (Ar), 136.67 (Ar), 132.71 (2 × Ar-H), 132.13 (2 × Ar-H), 129.93 (Ar), 129.31 (2 × Ar-H), 127.61 (2 × Ar-H), 127.24 (2 × Ar-H), 119.17 (C≡N), 114.87 (2 × Ar-H), 110.72 (Ar), 68.49 (CH_2-O), 35.74 (CH_2), 31.43 (CH_2), 29.34 (2 × CH_2), 29.18 (CH_2), 26.06 (CH_2).

IR ν (cm^{-1}): 2924, 2851 (CH_2); 2221 (CN) 1683 (CHO); 1595 1508 (Ar); 814 (*p*-disub. Ar)

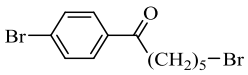
3.5 1-(4-Aminophenoxy)-6-(4-cyanobiphenyl-4'-yl)hexane (**1-5**)



i) $AlCl_3$, DCM; ii) Et_3SiH, TFA, DCM; iii) 4-Nitrophenol, KI, K_2CO_3, acetone, 56 ^oC
iv) Zinc dust, $NH_4Cl_{(aq)}$, MeOH : THF (3:1) (V/V)
v) 1) 4-Cyanophenylboronic acid, $[Pd(PPh_3)_4]$, $Na_2CO_{3\ (aq)}$, toluene:EtOH (4:1) (V/V)

Scheme 6: Synthetic route to form 1-(4-aminophenoxy)-6-(4-cyanobiphenyl-4'-yl) hexane (**I-5**).

4-Bromo-1-(6-bromohexan-1-oyl)benzene (**i-5.1**)



A solution of bromobenzene (15.330 g, 10.3 mL, 0.098 mol) and 6-bromohexanoyl chloride (25.000 g, 17.9 mL, 0.117 mol) in DCM (150 mL) was added dropwise to a suspension of aluminium (III) chloride (15.600 g, 0.117 mol) in DCM (200 mL) at 0 ˚C, in the dark, under argon. The reaction mixture was slowly warmed to room temperature and allowed to react for 20 hours. The reaction mixture was quenched with HCl (250 mL, 1 M) and ice (100 g), the organic phase was separated, the solvent was removed *in vacuo* and the oil was solubilised in EtOAc (200 mL). The organic fraction was washed with HCl (2 × 50 mL, 1 M), sat. aq. NaCl solution (2 × 50 mL), NaOH (6 × 50 mL, 1 M) and H_2O (2 × 50 mL), then dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to leave a yellow oil. Excess bromobenzene was removed via distillation (38.4 °C, 9 mmHg). The crude product was purified (SiO_2, DCM) to give the title compound as a brown powder.

Yield: 6.411 g, 20%

m.p. = 47–49 ˚C

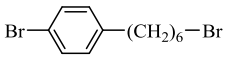
R_f (DCM-petroleum ether 40/60, 3:2) 0.47

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 7.60 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 3.42 (t, *J* = 6.7 Hz, 2H, $\underline{CH_2}$-Br), 2.95 (t, *J* = 7.2 Hz, 2H, $\underline{CH_2}$-CO), 1.91 (quin, *J* = 6.9 Hz, 2H, CH_2), 1.76 (quin, *J* = 7.4 Hz, 2H, CH_2), 1.61 – 1.46 (m, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.99 (C=O), 135.76 (Ar), 132.03 (2 × Ar-H), 129.67 (2 × Ar-H), 128.28 (Ar), 38.37 (CH_2), 33.71 (CH_2), 32.71 (CH_2), 27.94 (CH_2), 23.32 (CH_2).

IR ν (cm^{-1}): 2934 (CH_2); 1673 (C=O); 1601, 1512 (Ar); 817 (*p*-disub. Ar).

4-Bromo-1-(6-bromohexane)benzene (**i-5.2**)



To a solution of **i-5.1** (4.500 g, 0.013 mol) in DCM (50 mL), trifluoroacetic acid (12.290 g, 8.3 mL, 0.108 mol) was added in one portion at 0 °C, under argon. A solution of triethylsilane (6.280 g, 8.6 mL, 0.054 mol) in DCM (50 mL) was added dropwise to the stirring solution over 1 hour. The solution was slowly warmed to room temperature and allowed to react until TLC indicated the complete consumption of **i-5.1** after 72 hours. The reaction was quenched by the addition of the reaction to H_2O (300 mL), The organic and aqueous phases were separated, and the aqueous phase was extracted with DCM (3 × 50mL). The organic fractions were combined, washed with H_2O (2 × 50 mL), sat. aq. NaCl (2 × 50 mL) and then dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to yield a colourless oil. The excess triethylsilane was removed via distillation (20 °C, 9 mmHg). The crude product was purified (SiO_2, DCM-petroleum ether 40/60, 0.5:9.5) to give the title compound as a colourless oil.

Yield: 3.107 g, 72%

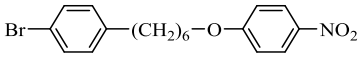
R_f (DCM-petroleum ether 40/60, 0.5:9.5) 0.45

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H, 2 × Ar-H), 7.04 (d, *J* = 8.3 Hz, 2H, 2 × Ar-H), 3.40 (t, *J* = 6.9 Hz, 2H, $\underline{CH_2}$-Br), 2.56 (t, *J* = 7.7 Hz, 2H, $\underline{CH_2}$-Ar), 1.85 (quin, *J* = 7.0 Hz, 2H, CH_2), 1.61 (quin, *J* = 7.5 Hz, 2H, CH_2), 1.46 (quin, *J* = 7.3 Hz, 2H, CH_2), 1.40 – 1.29 (m, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.59 (Ar), 131.45(2 × Ar-H), 130.29(2 × Ar-H), 119.51 (Ar), 35.32 (CH_2), 34.04 (CH_2), 32.81 (CH_2), 31.20 (CH_2), 28.38 (CH_2), 28.10 (CH_2).

IR ν (cm^{-1}): 2930, 2855 (CH_2); 1487 (Ar); 1072, 1010; 798 (*p*-disub. Ar).

1-(4-Oxynitrobenzene)-6-(4-bromobenzene)hexane (**i-5.3**)



i-5.2 (3.000 g, 9.373 mmol) and 4-nitrophenol (1.564 g, 11.243 mmol) were dissolved in acetone (75 mL) before the addition of potassium carbonate (1.765 g, 12.70 mmol) and potassium iodide (0.778 g, 4.687 mmol). The reaction mixture was stirred at reflux until TLC indicated the complete consumption of **i-5.2** after 40 hours, then cooled to room temperature. The insoluble salts were filtered off and washed with acetone (200 mL). The organic fractions were combined, and the solvent was removed *in vacuo* to give a white solid. The crude product was purified by recrystallisation from EtOH (50 mL) to give the title compound as a brown powder.

Yield: 2.451 g, 69 %

m.p. unknown.

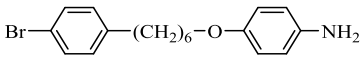
R_f (DCM-petroleum ether 40/60, 2:3) 0.37

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.2 Hz, 2H, 2 × Ar-H), 7.31 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 6.97 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 6.85 (d, *J* = 9.1 Hz, 2H, 2 × Ar-H), 3.96 (t, *J* = 6.4 Hz, 2H, $\underline{CH_2}$-O), 2.51 (t, *J* = 7.6 Hz, 2H, $\underline{CH_2}$-Ar), 1.74 (quin, *J* = 6.7 Hz, 2H, CH_2), 1.56 (quin, *J* = 7.6 Hz, 2H, CH_2), 1.42 (quin, *J* = 7.1 Hz, 2H, CH_2), 1.37 – 1.27 (m, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.17 (Ar), 141.45 (Ar), 141.36 (Ar), 131.32 (2 × Ar-H), 130.15 (2 × Ar-H), 125.93 (2 × Ar-H), 119.39 (Ar), 114.38 (2 × Ar-H), 68.74 ($\underline{CH_2}$-O), 35.22 (CH_2), 31.13 (CH_2), 28.88 (CH_2), 28.76 (CH_2), 25.79 (CH_2).

Infrared ν (cm^{-1}): 2938, 2858 (CH_2), 1903 (C-H Ar overtone), 1593, 1505 (N-O).

1-(4-Oxyphenylamine)-6-(4-bromobenzene)hexane (**i-5.4**)



To a stirring solution of **i-5.3** (2.400 g, 6.345 mmol) in MeOH/THF (250 mL, 3:1 MeOH:THF V/V) was added in one portion sat. aq. ammonium chloride (25 mL) followed by zinc dust (4.148 g, 63.447 mmol). The reaction was heated to 30 °C and monitored until TLC indicated complete consumption of **i-5.3** after 5 hours, then cooled to room temperature. The formed salts were filtered and washed with EtOAc (100 mL). The organic fractions were combined, and the volume was reduced to half *in vacuo*. H_2O (100 mL) was added and the organic and aqueous phases were separated. The aqueous phase was extracted with EtOAc (3 × 50 ml). The organic fractions were combined and washed with water (1 × 100 ml) and sat. aq. NaCl solution (1 × 100 ml). The organic fraction was dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to yield a brown solid. The crude product was purified (SiO_2, DCM) to give the title compound as a brown powder.

Yield: 1.790 g, 81 %

m.p. = 33–36 ˚C

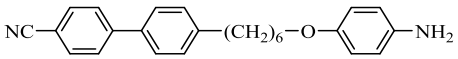
R_f (DCM) 0.30

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 (d, J = 8.3 Hz, 2H, 2 × Ar-H), 7.15 (d, J = 8.4 Hz, 2H, 2 × Ar-H), 6.61 (d, J = 8.8 Hz, 2H, 2 × Ar-H), 6.49 (d, J = 8.8 Hz, 2H, 2 × Ar-H), 4.56 (s, 2H, NH_2), 3.78 (t, J = 6.4 Hz, 2H, $\underline{CH_2}$-O), 2.54 (t, J = 7.6 Hz, 2H, $\underline{CH_2}$-Ar), 1.68 – 1.49 (m, 4H, 2 × CH_2), 1.45 – 1.25 (m, 4H, 2 × CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 149.94 (Ar), 142.27 (Ar), 141.71 (Ar), 131.02 (2 ×Ar-H), 130.57 (2 × Ar-H), 118.57 (Ar), 115.31 (2 × Ar-H), 114.90 (2 × Ar-H), 67.80 ($\underline{CH_2}$-O), 34.34 (CH_2), 30.68 (CH_2), 28.81 (CH_2), 28.27 (CH_2), 25.35 (CH_2).

IR ν (cm^{-1}): 3421, 3346 (NH_2); 2921, 2850 (CH_2); 1607, 1511 (Ar); 822 (*p*-disub. Ar).

1-(4-Aminophenoxy)-6-(4-cyanobiphenyl-4'-yl)hexane (**I-5**)



To a stirring solution of **i-5.4** (1.700 g, 4.881 mmol) in toluene (40 mL) was added aq. sodium carbonate (7.5 mL, 2 M) followed by tetrakis(triphenylphosphine)palladium(0) (0.100 g, 0.086 mmol) and a solution of 4-cyanophenylboronic acid (1.076 g, 7.322 mmol) in EtOH (10 mL). The reaction was stirred at reflux, under argon, and monitored until TLC indicated the complete consumption of **i-5.4** after 64 hours, then cooled to room temperature. To the stirring reaction was added H_2O (200 mL) followed by DCM (100 mL), and the organic and aqueous phases separated. The aqueous phase was extracted with DCM (3 × 50 ml). The organic fractions were combined and washed with water (2 × 50 ml) and sat. aq. NaCl solution (2 × 50 ml), and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a brown oil. The crude product was purified (SiO_2, EtOAc-petroleum ether 40/60, 1:2) followed by recrystallisation from EtOH (25 mL) to give the title compound as a brown solid.

Yield: 0.748 g, 55 %

m.p. = 120–122 ˚C

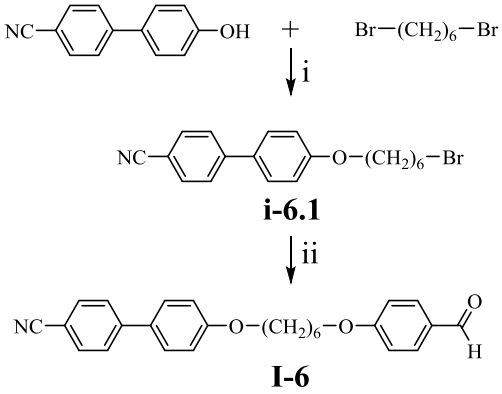
R_f (EtOAc-petroleum ether 40/60, 1:2) 0.26

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (d, J = 8.6 Hz, 2H, 2 × Ar-H), 7.85 (d, J = 8.8 Hz, 2H, 2 × Ar-H), 7.65 (d, J = 8.2 Hz, 2H, 2 × Ar-H), 7.33 (d, J = 8.2 Hz, 2H, 2 × Ar-H), 6.62 (d, J = 8.8 Hz, 2H, 2 × Ar-H), 6.49 (d, J = 8.8 Hz, 2H, 2 × Ar-H), 4.57 (s, 2H, NH_2), 3.79 (t, J = 6.4 Hz, 2H, $\underline{CH_2}$-O), 2.63 (t, J = 7.6 Hz, 2H, CH_2-Ar), 1.68 – 1.56 (m, 4H, 2 × CH_2), 1.49 – 1.29 (m, 4H, 2 × CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 149.96 (Ar), 144.59 (Ar), 143.19 (Ar), 142.28 (Ar), 135.58 (Ar), 132.81 (2 × Ar-H), 129.14 (2 × Ar-H), 127.28 (2 × Ar-H), 126.93 (2 × Ar-H), 118.94 (C≡N), 115.31 (2 × Ar-H), 114.91 (2 × Ar-H), 109.65 (Ar), 67.78 ($\underline{CH_2}$-O), 34.67 (CH_2), 30.76 (CH_2), 28.83 (CH_2), 28.36 (CH_2), 25.38 (CH_2).

IR ν (cm^{-1}): 3451, 3366 (NH_2); 2926, 2853 (CH_2); 2229 (C≡N) 1604, 1510 (Ar); 1228 (Ar-NH_2); 822 (*p*-disub. Ar).

3.6 1-(4-Formylphenoxy)-6-(4-cyanobiphenyl-4'-yloxy) hexane (**I-6**)

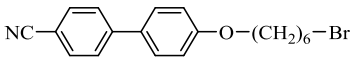


i) K_2CO_3, acetone 56 ^oC;

ii) 4-Hydroxybenzaldehyde, K_2CO_3, DMF, 90 ^oC

Scheme 7: Synthetic route to form 1-(4-formylphenoxy)-6-(4-cyanobiphenyl-4'-yloxy) hexane (**I-6**).

4'-(6-Bromohexyloxy)-4-cyanobiphenyl (**i-6.1**)



To a stirring solution of 4-hydroxy-4'cyanobiphenyl (5.000 g, 0.026 mol) and 1,6-dibromohexane (38.414 g, 24.2 mL, 0.137 mol) in acetone (100 mL) was added potassium carbonate (7.076 g, 0.051 mol). The reaction mixture was stirred at 56 °C until TLC indicated near complete consumption of 4-hydroxy-4'cyanobiphenyl R_f 0.26 (DCM) after 18 hours. The reaction was cooled to room temperature, filtered to remove excess potassium carbonate. The resultant liquid was poured into petroleum ether (250 mL) and the resultant precipitate was collected by filtration. The crude product was purified by recrystallisation from EtOH:$CHCl_3$ (150 mL, 2:1, V/V) to give the title compound as a white powder.

Yield: 5.704 g, 62 %

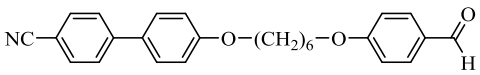
R_f (DCM) 0.78

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 7.90 (d, *J* = 8.1 Hz, 2H, 2 × Ar-H), 7.79 (d, *J* = 8.2 Hz, 2H, 2 × Ar-H), 7.25 (d, *J* = 8.2 Hz, 2H, 2 × Ar-H), 4.28 (t, *J* = 6.4 Hz, 4H, 2 × $\underline{CH_2}$-O), 3.69 (t, *J* = 6.8 Hz, 4H, 2 × $\underline{CH_2}$-Br), 2.24 – 2.04 (m, 4H, 2 × $\underline{CH_2}$), 1.88 – 1.72 (m, 4H, 2 × $\underline{CH_2}$),

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.84 ($\underline{Ar}$-O), 145.40 (Ar), 132.71 (2 × Ar-H), 131.52 (Ar), 128.49 (2 × Ar-H), 127.23 (2 × Ar-H), 119.25 (C≡N), 115.22 (2 × Ar-H), 110.22 (Ar), 68.03 (2 × $\underline{CH_2}$-O), 33.92 (CH_2), 32.80 (CH_2), 29.18 (CH_2), 28.04 (CH_2), 25.43 (CH_2).

IR ν (cm^{-1}): 2223 (CN); 1598 (Ar C=C), 1572 (Ar C=C), 1163 (C-O-Ar).824 (*p*-disub. Ar).

1-(4-Formylphenoxy)-6-(4-cyanobiphenyl-4'-yloxy)hexane (**I-6**)



i-6.1 (3.000 g, 8.373 mmol) and 4-hydroxybenzaldehyde (1.221 g, 0.010 mol) were dissolved in DMF (15 mL) before the addition of potassium carbonate (1.741 g, 0.013 mol). The reaction mixture was stirred at 90 °C until TLC indicated complete consumption of **i-6.1** R_f (DCM) 0.78 after 24 hours, then cooled to room temperature before addition to H_2O (300 mL). The resultant precipitate was filtered, dissolved in DCM (100 mL) and washed with sat. aq. NaCl (2 × 50 mL) and H_2O (2 × 50 mL), then dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to give a solid. The crude product was purified by recrystallisation from EtOH (50 mL) to give the product as a light brown powder.

Yield: 2.187 g, 65%

R_f (DCM) 0.70

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.88 (s, 1H, CHO), 7.83 (d, J = 8.3 Hz, 2H, 2 × Ar-H), 7.69 (d, J = 8.2 Hz, 2H, 2 × Ar-H), 7.64 (d, J = 8.2 Hz, 2H, 2 × Ar-H), 7.53 (d, J = 8.3 Hz, 2H, 2 × Ar-H), 6.99 (2 × d overlapping, J = 8.3 Hz, 4H, 4 × Ar-H), 4.05 (2 × t overlapping, J = 13.7, 6.4 Hz, 4H, CH_2-O-Ph-Ph-CN, CH_2-O-Ph-CHO), 1.94 – 1.79 (m, 4H, 2 × CH_2), 1.65 – 1.52 (m, 4H, 2 × CH_2).

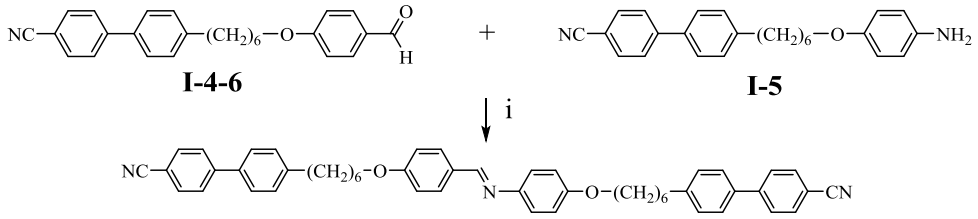
^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.94 (CHO), 164.31 (CHO-Ar), 159.85 (Ar), 145.37 (Ar), 132.72 (2 × Ar-H), 132.14 (2 × Ar-H), 131.53 (Ar), 129.97 (Ar), 128.49 (2 × Ar-H), 127.22 (2 × Ar-H), 119.24 (Ar), 115.21 (2 × Ar-H), 114.88 (2 × Ar-H), 110.24 (Ar), 68.35 (CH_2-O), 68.07 (CH_2-O), 29.29 (CH_2), 29.15 (CH_2), 25.98 (CH_2), 25.94 (CH_2).

IR ν (cm^{-1}): 2225 (CN), 1682 (CHO), 1599 (Ar C=C), 1571 (Ar C=C), 1159 (C-O-Ar).

3.7 Benzylideneaniline-Based Liquid Crystal Oligomers

The synthesis of the dimers CB6OCB and CN.6O.CN have been previously reported[1,2]. The synthesis of trimer CB6O.O6CB follows Scheme 8. The synthesis of the tetramers follows Scheme 9. The synthetic procedure for CB6O.7.O6CB is described in detail as a representative example for all tetramer syntheses, and the reaction conditions for the synthesis of the liquid crystal tetramers are given in Table 2.

CB6O.O6CB



Synthesis of trimer CB6O.O6CB

i) *p*TsOH, EtOH

Scheme 8: Synthetic route to trimer CB6O.O6CB (**BB**).

After the complete dissolution of **I-4-6** (0.261 g, 0.679 mmol) by heating in EtOH (10 mL) to reflux, **I-5** (0.252 g, 0.679 mmol) was added in one portion, followed by a crystal of *p*- toluenesulfonic acid. The reaction was stirred at reflux for 5 hours. The reaction mixture was cooled to room temperature before the precipitate was collected. The crude product was purified by recrystallisation from EtOH/chloroform (4:3 (v/v), 35 mL) to give the title compound as a light brown powder.

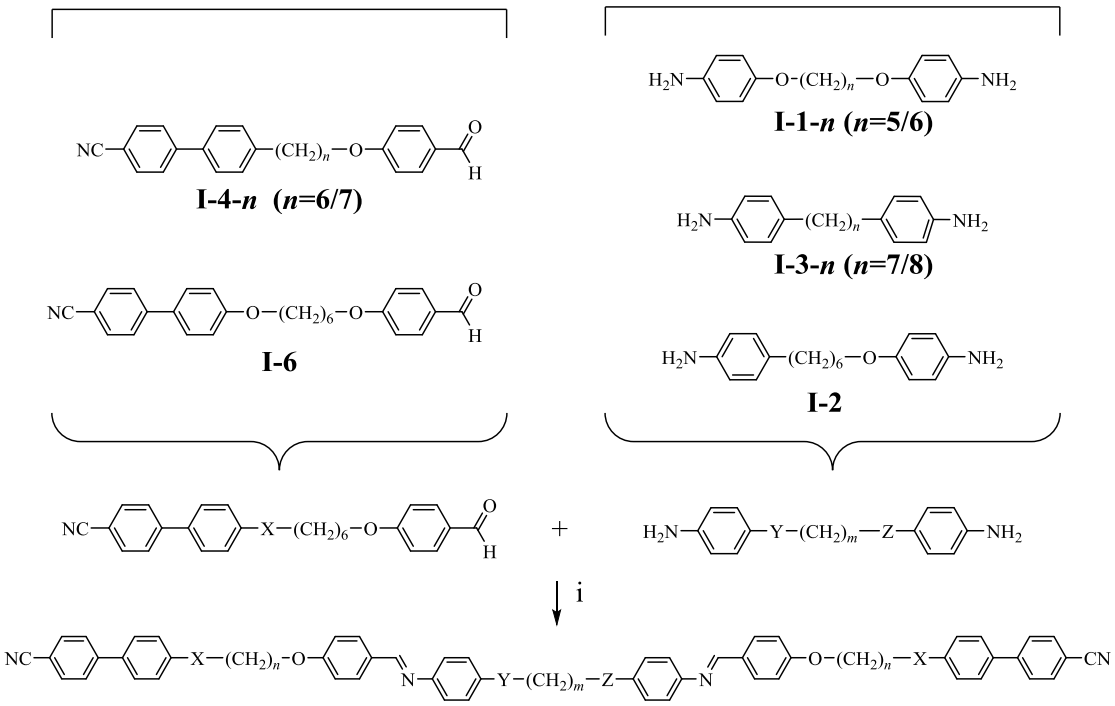
Yield: 0.354 g, 71 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, 1H, CH=N), 7.81 (d, *J* = 8.8 Hz, 2H, 2 × Ar-H), 7.71 (d, *J* = 8.7 Hz, 4H, 4 × Ar-H), 7.67 (d, *J* = 8.8 Hz, 4H, 4 × Ar-H), 7.51 (d, *J* = 8.2 Hz, 4H, 4 × Ar-H), 7.29 (d, *J* = 8.2 Hz, 4H, 4 × Ar-H), 7.19 (d, *J* = 8.9 Hz, 2H, 2 × Ar-H), 6.95 (d, *J* = 8.8 Hz, 2H, 2 × Ar-H), 6.91 (d, *J* = 8.9 Hz, 2H, 2 × Ar-H), 3.99 (2 × t (observed as dt), *J* = 6.4 Hz, 4H, 2 × CH_2-O), 2.69 (t, *J* = 7.6 Hz, 4H, 2 × CH_2-Ar), 1.90 – 1.62 (m, 8H, 4 × CH_2), 1.58 – 1.37 (m, 8H, 4 × CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.64, 157.95, 157.57, 145.70, 145.68, 145.19, 143.67, 143.62, 136.64, 136.62, 132.70, 130.33, 129.38, 129.33, 127.61, 127.23, 122.18, 119.21, 115.04, 114.75, 110.63, 68.19, 68.11, 35.62, 31.41, 29.33, 29.21, 29.07, 29.05, 26.03, 26.00.

Infrared ν (cm^{-1}): 2925, 2834 (CH_2), 2221 (C≡N), 1604, 1509 (Ar. C-C), 1241 (Ar. C-N), 815 (*p*-disub. Ar).

Elemental analysis: Calculated %: C 83.23, H 6.71, N 5.71. Found %: C 83.11, H 6.59, N 5.72.



General Structure of Liquid Crystal Tetramer
X/Y/Z = CH_2, O

i) *p*TsOH, EtOH

Scheme 9: Synthetic route to form the target liquid crystal tetramers.

After the complete dissolution of **I-4-6** (0.350 g, 0.913 mmol) by heating in EtOH (20 mL) to 78 °C, **I-3-7** (0.129 g, 0.456 mmol) was added in one portion, followed by a crystal of *p*- toluenesulfonic acid. The reaction was stirred at 78 °C for 3 hours, cooled to room temperature before the resultant precipitate was collected. The crude product was purified by recrystallisation from EtOH/acetonitrile (1:5 (V/V), 60 mL) to give the title compound as a white powder.

Table 2: Reaction conditions for the synthesis of liquid crystal tetramers.

Compound	Aldehyde moiety **I-** mass / g (moles / mmol)	Amine moiety **I-** mass / g (moles / mmol)	Reaction time / hr	Recrystallisation solvent volume / mL
CB6O.7.O6CB **BBB**	**I-4-6** 0.350 (0.913)	**I-3-7** 0.129 (0.456)	3.0	EtOH:MeCN (1:5 (V/V)) 60 mL
CB6O.8.O6CB **BLB**	**I-4-6** 0.129 (0.337)	**I-3-8** 0.050 (0.158)	5.0	EtOH:$CHCl_3$ (1:1 (V/V)) 20 mL
CB6O.O5O.O6CB **BBB**	**I-4-6** 0.150 (0.391)	**I-1-5** 0.056 (0.196)	3.0	EtOH:$CHCl_3$ (1:1 (V/V)) 30 mL
CB6O.O6O.O6CB **BLB**	**I-4-6** 0.150 (0.391)	**I-1-6** 0.059 (0.196)	3.0	EtOH:$CHCl_3$ (1:2.5 (V/V)) 30 mL
CB6O.6O.O6CB **BBB**	**I-4-6** 0.100 (0.261)	**I-2** 0.037 (0.130)	4.0	EtOH:$CHCl_3$ (1:2 (V/V)) 25 mL
CBO6O.7.O6OCB **LBL**	**I-6** 0.150 (0.375)	**I-3-7** 0.053 (0.188)	3.5	EtOH:$CHCl_3$ (1:3 (V/V)) 40 mL
CB7O.7.O7CB **LLL**	**I-4-7** 0.100 (0.252)	**I-3-7** 0.036 (0.126)	4.0	EtOH:$CHCl_3$ (1:1 (V/V)) 11 mL

CB6O.7.O6CB (**BBB**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 2H, 2 × CH=N), 7.84 (d, *J* = 8.4 Hz, 4H), 7.73 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.69 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.53 (d, *J* = 7.9 Hz, 4H, 4 × Ar-H), 7.32 (d, *J* = 7.9 Hz, 4H, 4 × Ar-H), 7.21 (d, *J* = 8.1 Hz, 4H, 4 × Ar-H), 7.15 (d, *J* = 8.1 Hz, 4H, 4 × Ar-H), 6.98 (d, *J* = 8.4 Hz, 4H, 4 × Ar-H), 4.04 (t, *J* = 6.5 Hz, 4H, 2 × CH_2-O), 2.71 (t, *J* = 7.7 Hz, 4H, 2 × CH_2-Ar), 2.64 (t, *J* = 7.7 Hz, 4H, 2 × CH_2-Ar), 1.85 (quin, *J* = 6.8 Hz, 4H, 2 × CH_2), 1.73 (quin, *J* = 7.8 Hz, 4H, 2 × CH_2), 1.69 – 1.42 (m, 12H, 6 × CH_2), 1.39 (m, 6H, 3 × CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.78, 159.06, 150.06, 145.71, 143.63, 140.56, 136.69, 132.71, 130.51, 129.42, 129.33, 129.21, 127.62, 127.25, 120.90, 119.17, 114.78, 110.71, 68.16, 35.64, 35.61, 31.65, 31.39, 29.49, 29.33, 29.23, 29.07, 26.01.

IR ν (cm^{-1}): 2924, 2852 (CH_2); 2225 (CN); 1604, 1509 (CH_2); 1245 (Ar. C-N); 814 (*p*-disub. Ar)

Elemental analysis: Calculated %: C 84.15, H 7.16, N 5.53. Found %: C 84.10, H 6.88, N 5.47.

CB6O.8.O6CB (**BLB**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 2H, 2 × CH=N), 7.82 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.71 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.67 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.51 (d, *J* = 7.8 Hz, 4H, 4 × Ar-H), 7.29 (d, *J* = 8.1 Hz, 4H, 4 × Ar-H), 7.19 (d, *J* = 7.9 Hz, 4H, 4 × Ar-H), 7.13 (d, *J* = 8.0 Hz, 4H, 4 × Ar-H), 6.95 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 4.02 (t, *J* = 6.6 Hz, 4H, 2 × CH_2-O), 2.69 (t, *J* = 7.8 Hz, 4H, 2 × CH_2-Ar), 2.61 (t, *J* = 7.8 Hz, 4H, 2 × CH_2-Ar), 1.82 (quin, *J* = 6.8, 6.1 Hz, 4H, 2 × CH_2), 1.75 – 1.39 (m, 16H, 8 × CH_2), 1.38 – 1.29 (m, 8H, 4 × CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.78, 159.07, 150.05, 145.71, 143.64, 140.60, 136.69, 132.71, 130.51, 129.42, 129.33, 129.21, 127.62, 127.25, 120.90, 119.18, 114.79, 110.71, 68.16, 35.63, 31.69, 31.39, 29.59, 29.42, 29.23, 29.07, 26.01.

IR ν (cm^{-1}): 2921, 2851 (CH_2); 2225 (CN); 1605, 1509 (CH_2); 1246 (Ar. C-N); 811 (*p*-disub. Ar)

Elemental analysis: Calculated %: C 84.17, H 7.26, N 5.45. Found %: C 84.22, H 7.28, N 5.41.

CB6O.O5O.O6CB (**BBB**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 2H, 2 × CH=N), 7.81 (d, *J* = 8.2 Hz, 4H, 4 × Ar-H), 7.71 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.67 (d, *J* = 8.2 Hz, 4H, 4 × Ar-H), 7.51 (d, *J* = 7.7 Hz, 4H, 4 × Ar-H), 7.29 (d, *J* = 8.0 Hz, 4H, 4 × Ar-H), 7.19 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 6.93 (2 × d overlapping (observed as dd,) *J* = 12.1, 8.4 Hz, 8H , 8 × Ar-H), 4.02 (t, *J* = 6.4 Hz, 8H, 4 × CH_2-O), 2.69 (t, *J* = 7.6 Hz, 4H, 2 × CH_2-Ar), 1.85 (2 × quin overlapping (observed as dquin), *J* = 27.1, 6.8 Hz, 8H, 4 × CH_2), 1.70 (quin, *J* = 7.6 Hz, 6H, 3 × CH_2), 1.45 (m, 8H, 4 × CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.66, 157.94, 157.59, 145.71, 145.32, 143.63, 136.68, 132.71, 130.35, 129.50, 129.33, 127.62, 127.25, 122.19, 119.18, 115.13, 114.78, 110.70, 68.18, 68.15, 35.63, 31.39, 29.24, 29.07, 26.01, 22.91.

IR ν (cm^{-1}): 2933, 2860 (CH_2); 2228 (CN); 1605, 1510 (CH_2); 1240 (Ar. C-N); 828 (*p*-disub. Ar).

Elemental analysis: Calculated %: C 81.46, H 6.74, N 5.51. Found %: C 81.31, H 6.84, N 5.35.

CB6O.O6O.O6CB (**BLB**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 2H, 2 × CH=N), 7.81 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.71 (d, *J* = 8.2 Hz, 4H, 4 × Ar-H), 7.67 (d, *J* = 8.2 Hz, 4H, 4 × Ar-H), 7.51 (d, *J* = 7.8 Hz, 4H, 4 × Ar-H), 7.29 (d, *J* = 8.0 Hz, 4H, 4 × Ar-H), 7.19 (d, *J* = 8.4 Hz, 4H, 4 × Ar-H), 6.95 (d, *J* = 8.6 Hz, 4H, 4 × Ar-H), 6.92 (d, *J* = 8.6 Hz, 4H, 4 × Ar-H), 4.01 (2 × t overlapping (observed as q), *J* = 6.9 Hz, 8H, 4 × CH_2-O), 2.69 (t, *J* = 7.7 Hz, 4H, 2 × CH_2-Ar), 1.82 (quin, *J* = 6.9 Hz, 8H, 4 × CH_2), 1.70 (quin, *J* = 7.6 Hz, 4H, 2 × CH_2), 1.62 – 1.49 (m, 8H, 4 × CH_2), 1.44 (quin, *J* = 7.3 Hz, 4H, 2 × CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) Product crystallised during ^{13}C NMR experiment.

IR ν (cm^{-1}): 2933, 2855 (CH_2); 2224 (CN); 1606, 1509 (CH_2); 1241 (Ar. C-N); 807 (*p*-disub. Ar).

Elemental analysis: Calculated %: C 81.52, H 6.84, N 5.43. Found %: C 81.30, H 6.91, N 5.31.

CB6O.6O.O6CB (**BBB**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 2H, 2 × CH=N), 7.81 (2x d overlapping (observed as dd), *J* = 8.3, 5.2 Hz, 4H, 4 × Ar-H), 7.71 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.67 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.51 (d, *J* = 7.8 Hz, 4H, 4 × Ar-H), 7.29 (d, *J* = 7.9 Hz, 4H, 4 × Ar-H), 7.19 (d, *J* = 8.0 Hz, 4H, 4 × Ar-H), 7.13 (d, *J* = 8.0 Hz, 2H, 2 × Ar-H), 6.95 (d, *J* = 8.4 Hz, 4H, 4 × Ar-H), 6.91 (d, *J* = 8.5 Hz, 2H, 2 × Ar-H), 4.02 (t, *J* = 6.5 Hz, 4H, 2 × CH_2-O-Ar-C=N), 3.97 (t, *J* = 6.5 Hz, 2H, CH_2-O-Ar-N=C), 2.67 (2 × t overlapping (observed as dt), *J* = 17.3, 7.8 Hz, 6H 3 × CH_2-Ar), 1.87 – 1.75 (m, 6H, 3 × CH_2), 1.75 – 1.62 (m, 6H, 3 × CH_2), 1.59 – 1.37 (m, 12H, 6 × CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.78, 161.64, 159.10, 157.87, 157.66, 150.12, 145.71, 145.23, 143.63, 140.36, 136.68, 132.71, 130.51, 130.34, 129.51, 129.40, 129.33, 129.23, 127.62, 127.25, 122.18, 120.93, 119.17, 115.11, 114.78, 110.70, 68.32, 68.15, 35.63, 35.52, 31.57, 31.39, 29.39, 29.23, 29.10, 29.07, 26.07, 26.01.

IR ν (cm^{-1}): 2927, 2853 (CH_2); 2224 (CN); 1606, 1510 (CH_2); 1244 (Ar. C-N); 813 (*p*-disub. Ar).

Elemental analysis: Calculated %: C 82.81, H 6.95, N 5.52. Found %: C 82.81, H 7.02, N 5.41.

CBO6O.7.O6OCB (**LBL** - AMF)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 2H, 2 × CH=N), 7.82 (d, *J* = 8.6 Hz, 4H, 4 × Ar-H), 7.69 (d, *J* = 8.6 Hz, 4H, 4 × Ar-H), 7.64 (d, *J* = 8.4 Hz, 4H, 4 × Ar-H), 7.52 (d, *J* = 8.7 Hz, 4H, 4 × Ar-H), 7.18 (d, *J* = 8.1 Hz, 4H, 4 × Ar-H), 7.13 (d, *J* = 8.1 Hz, 4H, 4 × Ar-H), 6.98 (2 × d (observed as dd), *J* = 12.4, 8.5 Hz, 8H, 8 × Ar-H, 4.04 (2 × t (observed as td, *J* = 6.4, 4.3 Hz, 8H, 2× CH_2-O), 2.61 (t, *J* = 7.7 Hz, 4H, 2 × CH_2-Ar), 1.93 – 1.79 (m, 8H, 4 × CH_2), 1.70 – 1.51 (m, 12H, 6 × CH_2), 1.52 – 1.30 (m, 6H, 3 × CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.78, 159.06, 150.06, 145.71, 143.63, 140.56, 136.69, 132.71, 130.51, 129.42, 129.33, 129.21, 127.62, 127.25, 120.90, 119.17, 114.78, 110.71, 68.16, 35.64, 35.61, 31.65, 31.39, 29.49, 29.33, 29.23, 29.07, 26.01.

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.77, 159.88, 159.09, 150.05, 145.41, 132.72, 132.15, 131.50, 130.53, 129.21, 128.49, 127.23, 120.91, 119.26, 115.23, 114.89, 114.79, 110.22, 68.35, 68.10, 35.61, 31.65, 29.32, 29.29, 29.26, 29.15, 25.99, 25.95.

IR ν (cm^{-1}): 2939, 2860 (CH_2); 2236 (CN); 1604, 1510 (CH_2); 1247 (Ar. C-N); 825 (p-disub. Ar)

Elemental analysis: Calculated %: C 81.58, H 6.94, N 5.36. Found %: C 81.51, H 7.05, N 5.41.

CB7O.7.O7CB (**LBL**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 2H, 2 × CH=N), 7.82 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.71 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.67 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 7.51 (d, *J* = 7.7 Hz, 4H, 4 × Ar-H), 7.29 (d, *J* = 8.8 Hz, 4H, 4 × Ar-H), 7.18 (d, *J* = 8.0 Hz, 4H, 4 × Ar-H), 7.12 (d,

J = 8.0 Hz, 4H, 4 × Ar-H), 6.95 (d, *J* = 8.3 Hz, 4H, 4 × Ar-H), 4.01 (t, *J* = 6.6 Hz, 4H, 2 × $\underline{CH_2}$-O), 2.67 (t, *J* = 7.7 Hz, 4H, 2 × $\underline{CH_2}$-Ar), 2.61 (t, *J* = 7.8 Hz, 4H, 2 × $\underline{CH_2}$-Ar), 1.87 – 1.75 (m, 4H, 2 × CH_2), 1.74 – 1.57 (m, 8H, 4 × CH_2), 1.52 – 1.30 (m, 18H, 9 × CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.81, 159.09, 150.06, 145.73, 143.77, 140.55, 136.65, 132.71, 130.51, 129.39, 129.32, 129.21, 127.62, 127.24, 120.90, 119.18, 114.78, 110.70, 68.23, 35.74, 35.61, 31.65, 31.44, 29.49, 29.36, 29.33, 29.30, 26.10.

IR ν (cm^{-1}): 2927, 2853 (CH_2); 2228 (CN); 1607, 1509 (CH_2); 1246 (Ar. C-N); 810 (*p*-disub. Ar).

Elemental analysis: Calculated %: C 84.19, H 7.36, N 5.38. Found %: C 83.80, H 7.85, N 5.37.

Section 4: References

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