

## Supplementary Information

### **Understanding the remarkable difference in liquid crystal behaviour between secondary and tertiary amides: the synthesis and characterisation of new benzanilide-based liquid crystal dimers.**

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## Materials and Methods

Unless otherwise stated, all materials were obtained from commercial sources and used without further purification.

Where dry solvents were used, these were dried over 3 or 4 Å molecular sieves for at least 48 hours before use. Glassware used in anhydrous reactions was pre-dried in an oven set at 110 °C for at least 12 hours.

Reactions were monitored using thin layer chromatography (TLC) using aluminium-backed plates with a coating of Merck Kieselgel 60 F254 silica and an appropriate solvent system. Spots were visualised using UV light (254 nm)

Solvents were evaporated at approximately 20 mm Hg using a water aspirator pump connected to a rotary evaporator.

Flash column chromatography was carried out using silica grade 60 Å 40-63 micron.

## Instrumentation

Melting points and phase transition temperatures were measured by differential scanning calorimetry with a heating rate of 10 °C min<sup>-1</sup> unless otherwise specified. DSC traces were measured using a Mettler Toledo DSC 1 instrument.

FTIR spectra were obtained using a Perkin Elmer spectrum 2 FTIR with an ATR diamond cell.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 300 MHz Bruker Ultrashield NMR spectrometer (300 MHz for <sup>1</sup>H NMR and 75 MHz for <sup>13</sup>C NMR) or a 400 MHz Bruker Ascend NMR spectrometer (400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR) using either CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as solvent and using residual non-deuterated trace solvents as reference. Chemical shifts (δ) are given in ppm relative to TMS (δ = 0.00 ppm). Coupling constants (J) are given in Hz, and are vicinal (3J). Ar refers to an aromatic ring. Variable temperature <sup>1</sup>H NMR spectroscopy was carried out using a Bruker Ascend 600 MHz spectrometer with a cryoprobe and VT unit.

Optical textures were observed using an Olympus BH2 polarized light microscope with a Linkam TMS 92 heating stage.

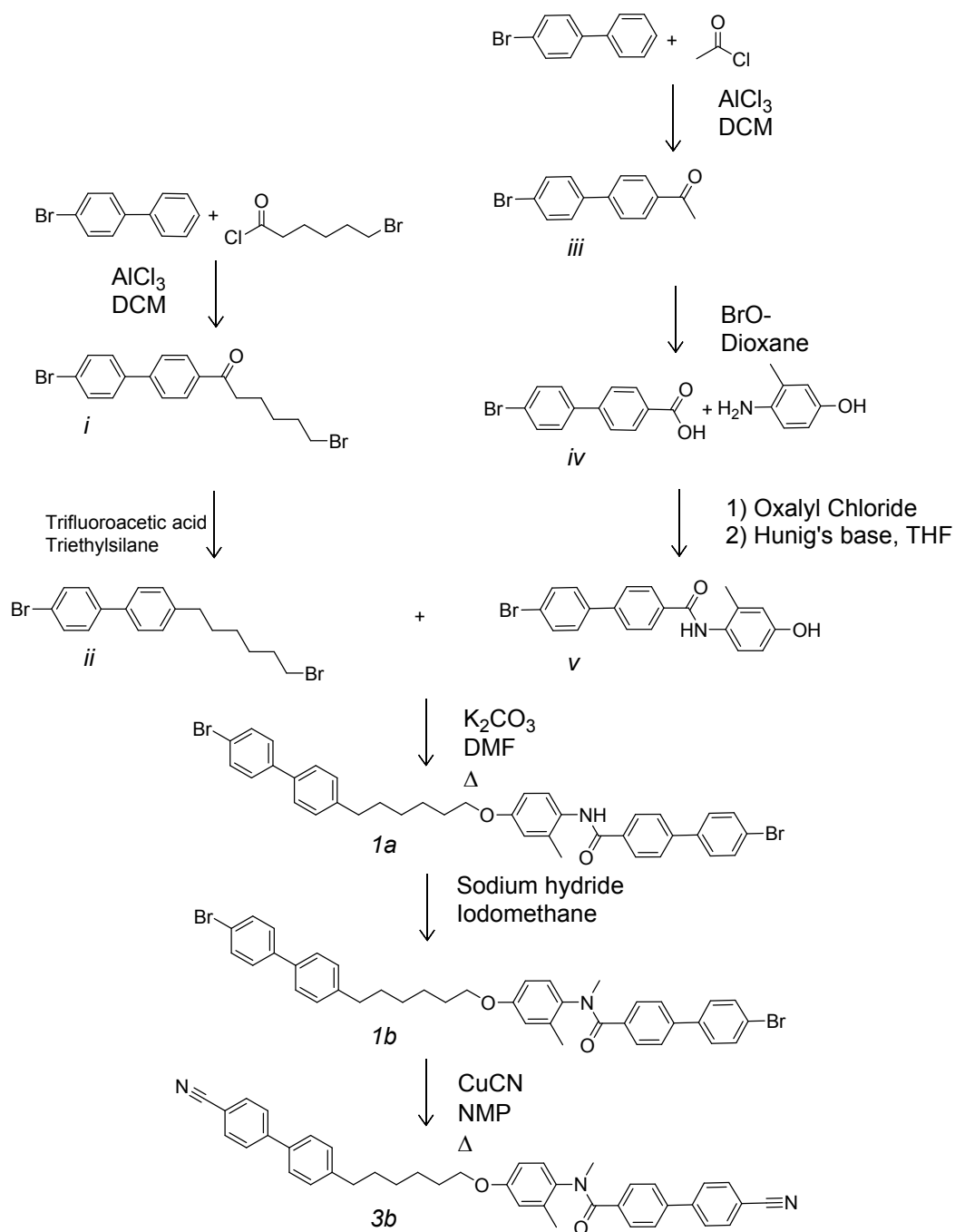
C, H, N microanalysis performed by either the elemental analysis service in the School of Chemistry at the University of Sheffield or the Elemental Microanalysis Service at OEA labs and was used to confirm the purity of the final compounds.

Q-TOF mass spectrometry was performed at the University of Aberdeen on a Waters XEVO G2 Q-ToF, S/N YCA247K. Calibration: Sodium formate. Lock mass: leucine enkephalin,  $C_{28}H_{37}N_5O_7$   $[M+H]^+$ : 556.2771

DFT geometry optimisations were carried out using the Gaussian09 software<sup>1</sup> at the B3LYP 6-31G(d) level of theory with the alkyl chains in the all-*trans* conformation, and this is in line with previous studies.<sup>2</sup> Visualisation of the optimised geometries were carried out using the Qutemol package.<sup>3</sup>

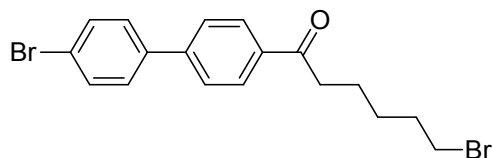
## Synthesis

Synthesis of 4-Bromo-[1,1'-biphenyl]-4'-yl-N-(4-bromo-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-[1,1'-biphenyl]-4-carboxamide (**1a**), 4-Cyano-[1,1'-biphenyl]-4'-yl-N-(4-cyano-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-N-methyl-[1,1'-biphenyl]-4-carboxamide (**1b**), and 4-Bromo-[1,1'-biphenyl]-4'-yl-N-(4-bromo-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-N-methyl-[1,1'-biphenyl]-4-carboxamide (**3b**)



Scheme S1: Synthesis of compounds 1a, 1b, and 3b.

1-Bromo-6-(4'-bromobiphenyl-4-yl)hexane-6-one (i)



To 4-bromobiphenyl (5.130 g, 22 mmol) in DCM (20 ml) was added  $\text{AlCl}_3$  (3.227 g, 24 mmol) while stirring under argon, in an ice bath and wrapped in tinfoil. 6-Bromohexanoyl chloride (4.698 g, 22 mmol) was added dropwise over half an hour and after addition was complete the ice bath was removed, and the reaction allowed to warm to room temperature. The reaction was followed by TLC (50:50 DCM: PE  $R_f$  0.23) and appeared complete after 4 hours.

When the reaction was complete the mixture was added to HCl (1M, 50 ml) with 10 g of crushed ice. The layers were separated, and the organic layer was washed with brine (3 x 15ml). The organics were dried with  $\text{MgSO}_4$  and the solvent removed *in vacuo*. The crude product was recrystallised from ethanol (370 ml). Yield 5.485 g (60%).

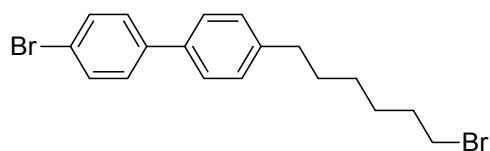
MP 74 °C (Lit<sup>4</sup> 77 °C);

$\nu_{\text{max}}/\text{cm}^{-1}$ : 2946 (C-H), 1679 (CO), 1603 (Ar), 1259 ( $\text{CH}_2\text{Br}$ ), 1185, 1000 (Ar), 970, 807 (Ar).

$\delta_{\text{H}}$  (400 MHz, Chloroform-*d*) 8.03 (2 H, d,  $J$  8.2, Ar-H), 7.64 (2 H, d,  $J$  8.2, Ar-H), 7.60 (2 H, d,  $J$  8.3, Ar-H), 7.49 (2 H, d,  $J$  8.3, Ar-H), 3.44 (2 H, t,  $J$  6.7,  $\text{CH}_2\text{-O}$ ), 3.02 (2 H, t,  $J$  7.3,  $\text{CH}_2\text{-C(O)}$ ), 1.93 (2 H, p,  $J$  6.9,  $\text{CH}_2\text{-CH}_2\text{-O}$ ), 1.80 (2 H, p,  $J$  7.4,  $\text{CH}_2\text{-CH}_2\text{-C(O)}$ ), 1.57 (2 H, m,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ )

$\delta_{\text{C}}$  (100 MHz, Chloroform-*d*) 199.46, 144.40, 138.79, 135.95, 132.11 (2C), 128.82 (2C), 128.73 (2C), 127.07 (2C), 122.65, 38.37, 33.64, 32.64, 27.90, 23.38.

1-Bromo-6-(4'-bromobiphenyl-4-yl)hexane (ii)



A solution of 1-bromo-6-(4'-bromobiphenyl-4-yl)hexane-6-one *i* (3.015 g, 7.4 mmol) in trifluoroacetic acid (14 ml) was stirred in an ice bath under argon. Triethylsilane (1.46 g, 2 ml, 12.5 mmol) was added dropwise. After addition the ice bath was removed and the reaction followed by TLC (50:50 DCM: PE  $R_f$  0.79). The reaction appeared complete after 1 hour.

The reaction mixture was added to DCM (20 ml) and H<sub>2</sub>O (50 ml). The layers were separated and the aqueous layer was washed with DCM (3 x 20 ml). The organics were combined, dried with MgSO<sub>4</sub>, and the solvent removed *in vacuo*. The crude product was recrystallised from ethanol (130 ml) to give a white solid. Yield 2.728 g (93%).

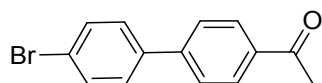
Mp 77 °C (Lit<sup>4</sup> 77 °C);

$\nu_{max}/\text{cm}^{-1}$ : 2931 (C-H), 2855 (C-H), 1464 (Ar), 1076, 999 (Ar), 804 (Ar).

$\delta_{\text{H}}$  (300 MHz, Chloroform-*d*) 7.54 (2 H, d, *J* 8.5, Ar-H), 7.45 (4 H, dd, *J* 8.5, Ar-H), 7.24 (2 H, d, *J* 8.2, Ar-H), 3.40 (2 H, t, *J* 6.8, CH<sub>2</sub>-O), 2.64 (2 H, t, *J* 7.8, CH<sub>2</sub>-Ar), 1.94 – 1.78 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-O), 1.74 – 1.60 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-Ar), 1.77 – 1.29 (4 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>).

$\delta_{\text{C}}$  (75 MHz, Chloroform-*d*) 142.17, 140.02, 137.41, 131.79 (2C), 128.94 (2C), 128.55 (2C), 126.81 (2C), 121.19, 35.42, 33.92, 32.72, 31.18, 28.38, 28.01.

#### 4-Bromo-4'-acetylbiphenyl (iii)



To 4-bromobiphenyl (3.504 g, 15 mmol) in DCM (30 ml) was added AlCl<sub>3</sub> (2.292 g, 17 mmol), while stirring under argon, in an icebath and wrapped in tinfoil. Acetyl chloride (1.3 ml, 1.44 g, 18.75 mmol) in DCM (20 ml) was added dropwise. After addition was complete, the ice bath was removed, and the reaction allowed to warm to room temperature. The reaction was followed by TLC. (Eluent 50:50 DCM / PE 40 – 60 R<sub>f</sub> 0.14).

After 15 hours the reaction mixture was added to a mixture of ice (6 g) and HCl (37%, 15 ml). The layers were separated, and the organic layer was washed with H<sub>2</sub>O (2 x 20 ml) and once with NaOH (0.1 M, 20 ml). The organics were combined, dried over MgSO<sub>4</sub>, and the solvent was removed *in vacuo*. The crude product was recrystallised from ethanol (80 ml). Yield 2.79 g (70%).

MP 130 °C (Lit<sup>5</sup>. 129 – 130 °C).

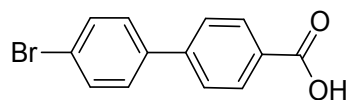
$\nu_{max}/\text{cm}^{-1}$ : 2923 (CH<sub>3</sub>), 1671 (CO), 999 (Ar), 810 (Ar).

$\delta_{\text{H}}$  (300 MHz, Chloroform-*d*) 8.05 (2 H, d, *J* 8.9, Ar-H), 7.66 (2 H, d, *J* 8.9, Ar-H), 7.61 (2 H, d, *J* 8.6, Ar-H), 7.50 (2 H, d, *J* 8.6, Ar-H), 2.66 (3 H, s, CH<sub>3</sub>-O).

$\delta_c$  (75 MHz, Chloroform-*d*) 197.60, 144.47, 138.76, 136.14, 132.10 (2C), 129.02 (2C), 128.82 (2C), 127.03 (2C), 122.66, 26.68.

This data is in agreement with published values.<sup>6</sup>

*4-Bromobiphenyl-4'-carboxylic acid (iv)*



Bromine (0.98 ml, 3.04 g, 19 mmol) was added to a solution of NaOH (5.1 M, 10 ml) at 0 °C in an ice bath. This was added in small portions to a stirred solution of *iii* (1.01 g, 3.67 mmol) in dioxane (12 ml). The temperature was maintained between 30 and 40 °C throughout addition and for a further 20 minutes. A precipitate formed, which was removed by vacuum filtration. The crude white material was suspended in water (25 ml) and acidified with HCl (conc.). The suspension was stirred for 10 min and then collected by vacuum filtration. The crude product was recrystallised from a mix of ethanol and propan-2-ol (50:50) (30 ml). Yield: 385 mg (40%).

MP 302 °C (Lit<sup>5</sup>. 301.5-302.5 °C).

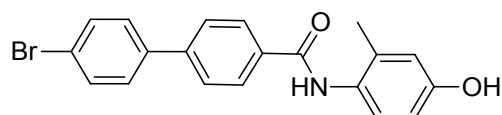
$\nu_{max}/\text{cm}^{-1}$ : 2545 (OH stretch), 1675 (CO dimer), 1607 (Ar stretch), 1424 (OH bend), 1297 (CO stretch), 1002 (Ar), 931 (OH out-of-plane bend), 821 (Ar).

$\delta_H$  (300 MHz, Chloroform-*d*) 8.10 (2 H, d, *J* 8.7, Ar-H), 7.60 (2 H, d, *J* 8.2, Ar-H), 7.56 (2 H, d, *J* 8.7, Ar-H), 7.48 (2 H, d, *J* 8.2, Ar-H), 4.69 (br, OH).

$\delta_c$  (75 MHz, DMSO-*d*<sub>6</sub>) 167.00, 142.93, 138.14, 131.93 (2C), 129.97 (2C), 129.91, 129.02 (2C), 126.72 (2C), 121.84.

This data is in agreement with that reported in the literature.<sup>6</sup>

*4'-Bromo-N-(4''-hydroxy-2-methylphenyl)[1,1'-biphenyl]-4-carboxamide (v)*



4-Bromobiphenyl-4'-carboxylic *iv* (1.499 g, 5.4 mmol) was dried by azeotropic distillation with toluene (3 x 15 ml). A solution of *iv* and oxalyl chloride (0.7 ml, 8.1 mmol) in toluene (5 ml) was stirred under argon at 40 °C with a catalytic amount of DMF. When the bubbling stopped, the

reaction was considered to be complete. The excess oxalyl chloride and toluene was then removed under vacuum (3 mmHg) to leave the acid chloride.

3-Methyl-4-aminophenol (0.675 g, 5.4 mmol) was dried by azeotropic distillation with toluene (3 x 10 ml), then dissolved in THF (80 ml) at 0 °C. Hunig's base (0.93 ml, 5.4 mmol) was added, and then the acid chloride in THF (20 ml) was added dropwise. After addition was complete the ice bath was removed and the reaction stirred for 24 hours at room temperature.

The reaction mixture was added to HCl (50 ml, 1M) and left for 10 minutes. The crude brown precipitate was collected by vacuum filtration then washed with DCM (20 ml) and the cream coloured solid was filtered off. The solid was then washed with THF (20 ml) and the white solid collected by vacuum filtration.

Yield 1.355 g (65%).

Mp 310 °C

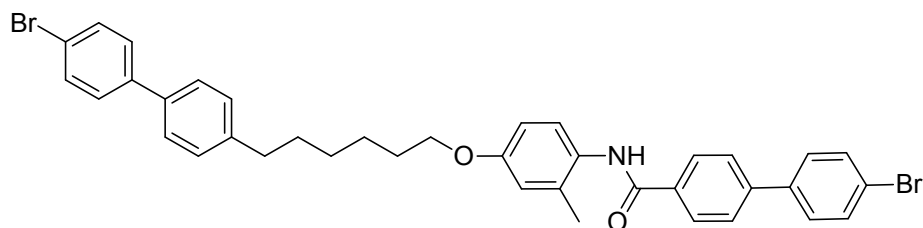
Elemental analysis Calculated for: C<sub>20</sub>H<sub>16</sub>BrNO<sub>2</sub> C 62.84 %, H 4.22 %, N 3.66 %. Found: C 62.79 %, H 4.36 %, N 3.54 %

$\nu_{max}/\text{cm}^{-1}$ : 3400 (OH), 3318 (N-H), 1651 (CO), 1604 (N-H), 1474 (Ar), 1385 (OH), 1002 (Ar), 670 (NH).

$\delta_{\text{H}}$  (400 MHz, DMSO-*d*<sub>6</sub>) 9.74 (1 H, s, NH), 9.30 (1 H, s, OH), 8.05 (2 H, d, *J* 7.9, Ar-H), 7.82 (2 H, d, *J* 7.9, Ar-H), 7.72 (4 H, dd, *J* 6.4, 6.4, Ar-H), 7.08 (1 H, d, *J* 8.5, Ar-H), 6.71 – 6.65 (1 H, m, Ar-H), 6.61 (1 H, d, *J* 8.5, Ar-H), 2.14 (3 H, s, Ar-CH<sub>3</sub>).

$\delta_{\text{C}}$  (100 MHz, DMSO)-*d*<sub>6</sub> 165.35, 156.00, 142.01, 138.83, 135.87, 134.28, 132.41 (2C), 129.47 (2C), 128.75 (2C), 128.61, 128.10, 126.98 (2C), 122.10, 117.08, 113.15, 18.48.

*4-Bromo-[1,1'-biphenyl]-4'-yl-N-(4-bromo-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-[1,1'-biphenyl]-4-carboxamide (1a)*



A mixture of 4'-bromo-N-(4''-hydroxy-2-methylphenyl)[1,1'-biphenyl]-4-carboxamide **v** ( 708 mg, 1.8 mmol), 1-bromo-6-(4'-bromobiphenyl-4-yl)hexane **2.0.2** (745 mg, 1.9 mmol), and



potassium carbonate (498 mg, 3.6 mmol) in DMF (30 ml) was heated to 90 °C for 20 hours. The reaction was followed by TLC (3:1 DCM / PE  $R_f$  0.2). The reaction mixture was then added to water (30 ml) and HCl (20 ml, 1 M). The precipitate was collected by vacuum filtration. The crude product was purified by stirring in hot ethyl acetate (100 ml) and the suspension was allowed to settle. The product was collected by vacuum filtration.

Yield 813 mg (68%).

Cr 160 °C N 212 °C I

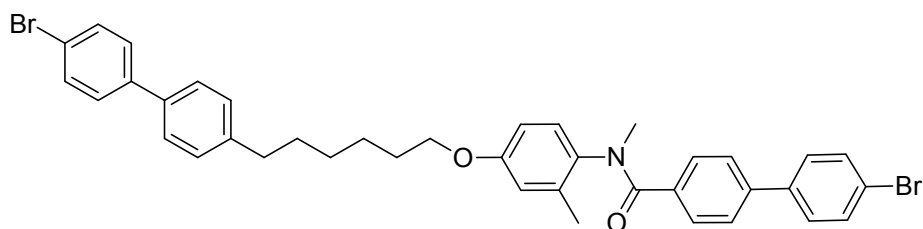
Elemental analysis: Calculated for:  $C_{38}H_{35}Br_2NO_2$  C 65.44 %, H 5.06 %, N 2.01 %. Found: C 65.35 %, H 5.00 %, N 1.93 %

$\nu_{max}/cm^{-1}$ : 3267 (NH), 2934 ( $CH_2$ ), 2864 ( $CH_2$ ), 1639 (CO), 1002 (Ar), 804 (Ar).

$\delta_H$  (400 MHz, DMSO- $d_6$ ) 9.81 (1 H, s, NH), 8.07 (2 H, d,  $J$  8.1, Ar-H), 7.83 (2 H, d,  $J$  8.1, Ar-H), 7.73 (2 H, d,  $J$  8.74, Ar-H), 7.70 (2 H, d,  $J$  8.74, Ar-H), 7.62 (4 H, overlapping doublets, Ar-H), 7.59 (2 H, d,  $J$  8.0, Ar-H), 7.30 (2 H, d,  $J$  8.0, Ar-H), 7.19 (1 H, d,  $J$  8.6, Ar-H), 6.85 (1 H, d,  $J$  2.8, Ar-H), 6.77 (1 H, dd,  $J$  8.6, 2.8, Ar-H), 3.96 (2 H, t,  $J$  6.4, 6.4,  $\underline{CH_2}$ -O), 2.64 (2 H, t,  $J$  7.6, 7.6, 13), 2.19 (3 H, s, 40), 1.72 (2 H, t,  $J$  7.2, 7.2, 17), 1.64 (2 H, p,  $J$  7.6, 7.6, 7.5, 7.5, 14), 1.54 – 1.43 (2 H, m, 15), 1.41 (2 H, dd,  $J$  14.8, 7.4, 16).

$\delta_C$  (101 MHz, Chloroform- $d$ ) 157.00, 143.31, 142.34, 140.06, 138.85, 137.36, 133.96, 132.44, 132.12 (2C), 131.79 (2C), 128.98 (2C), 128.79 (2C), 128.57 (2C), 128.40, 127.73 (2C), 127.24 (2C), 126.80 (2C), 125.56, 122.50, 121.17, 116.75, 112.33, 68.07, 35.49, 31.34, 29.21, 28.99, 25.92, 18.20.

*4-Bromo-[1,1'-biphenyl]-4'-yl-N-(4-bromo-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-N-methyl-[1,1'-biphenyl]-4-carboxamide (1b)*



The ether *1a* (1.054 g, 1.5 mmol) was dried by azeotropic distillation with toluene (3 x 5 ml). NaH (560 mg, 60% dispersion) was washed with dry petroleum ether (3 x 2 ml). Then the ether *1a* was dissolved in dry THF (50 ml) and added to the NaH. After the fizzing stopped, the

mixture was left for a further 20 minutes. Then CH<sub>3</sub>I (0.22 ml, 3.5 mmol) was added and the reaction was left overnight. The reaction was followed by TLC (1.5:1 PE/ EtOAc R<sub>f</sub> 0.61). A few drops of water were added to ensure complete reaction of NaH, followed by the removal of THF under vacuum (3 mmHg) to yield a yellow solid. This was dissolved in ethyl acetate (50 ml) and washed with water (3 x 20 ml). The organic layer was dried with MgSO<sub>4</sub> and the solvent removed *in vacuo*. Yield 0.730 g. (68 %).

MP 126 °C

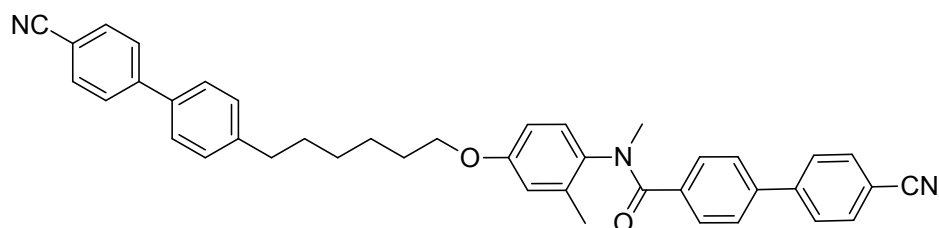
Elemental analysis: Calculated for: C<sub>39</sub>H<sub>37</sub>Br<sub>2</sub>NO<sub>2</sub> C 65.83 %, H 5.24 %, N 1.97 %. Found: C 66.20 %, H 5.48 %, N 1.90 %

$\nu_{max}/\text{cm}^{-1}$ : 2925 (CH<sub>2</sub>), 2855 (CH<sub>2</sub>), 1627 (CO), 1003 (Ar), 818 (Ar).

$\delta$  H (400 MHz, Chloroform-d) 7.54 – 7.43 (3 H, m, Ar-H), 7.47 – 7.38 (2 H, m, Ar-H), 7.42 – 7.22 (8 H, m, Ar-H), 7.24 – 7.13 (3 H, m, Ar-H), 6.90 (1 H, d, J 8.4, Ar-H), 6.58 (1 H, d, J 2.7, Ar-H), 6.55 (1 H, dd, J 8.6, 2.9, Ar-H), 3.80 (2 H, t, J 6.5, CH<sub>2</sub>-O), 3.29 (3 H, s, CH<sub>3</sub>-N), 2.57 (2 H, t, J 7.7, CH<sub>2</sub>-Ar), 2.11 (3 H, s, CH<sub>3</sub>-Ar), 1.68 (2 H, p, J 7.0, CH<sub>2</sub>-CH<sub>2</sub>-O), 1.58 (2 H, p, J 6.1, CH<sub>2</sub>-CH<sub>2</sub>-Ar), 1.38 (4 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>).

$\delta$  C (101 MHz, Chloroform-d) 170.42, 158.18, 142.25, 140.78, 139.99, 139.06, 137.40, 136.34, 136.01, 135.25, 131.87, 131.81, 129.42, 129.00, 128.94, 128.60, 128.54, 126.80, 126.00, 121.99, 121.22, 116.71, 112.78, 67.99, 37.90, 35.48, 31.32, 29.17, 29.01, 25.91, 18.08.

4-Cyano-[1,1'-biphenyl]-4'-yl-N-(4-cyano-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-N-methyl-[1,1'-biphenyl]-4-carboxamide (3b)



N-methylpyrrolidone (30 ml) was stirred rapidly under argon, and then compound **1b** (589 mg, 0.83 mmol) and CuCN (288 mg, 3.2 mmol) was added, and the mixture heated to 200 °C. The reaction was followed by TLC (eluent 50:50 DCM: PE, R<sub>f</sub> 0.45). After 7 hours the reaction mixture was cooled to RT, quenched with conc. ammonia solution (20 ml) and then added to a mix of DCM (100 ml) and H<sub>2</sub>O (50 ml). The layers were separated and the aqueous layer was washed once with DCM (25 ml). The organics were combined, washed with water (3 x 15 ml),

dried with  $\text{MgSO}_4$  and the solvent was removed *in vacuo*. The crude product was purified by sequential column chromatography (eluent a) 50:50 DCM: PE  $R_f$  0.45 b) 2:1 PE: EtOAc  $R_f$  0.28) The product was then recrystallised from toluene (2 ml). Yield 0.145 g. (30 %).

MP 123 °C

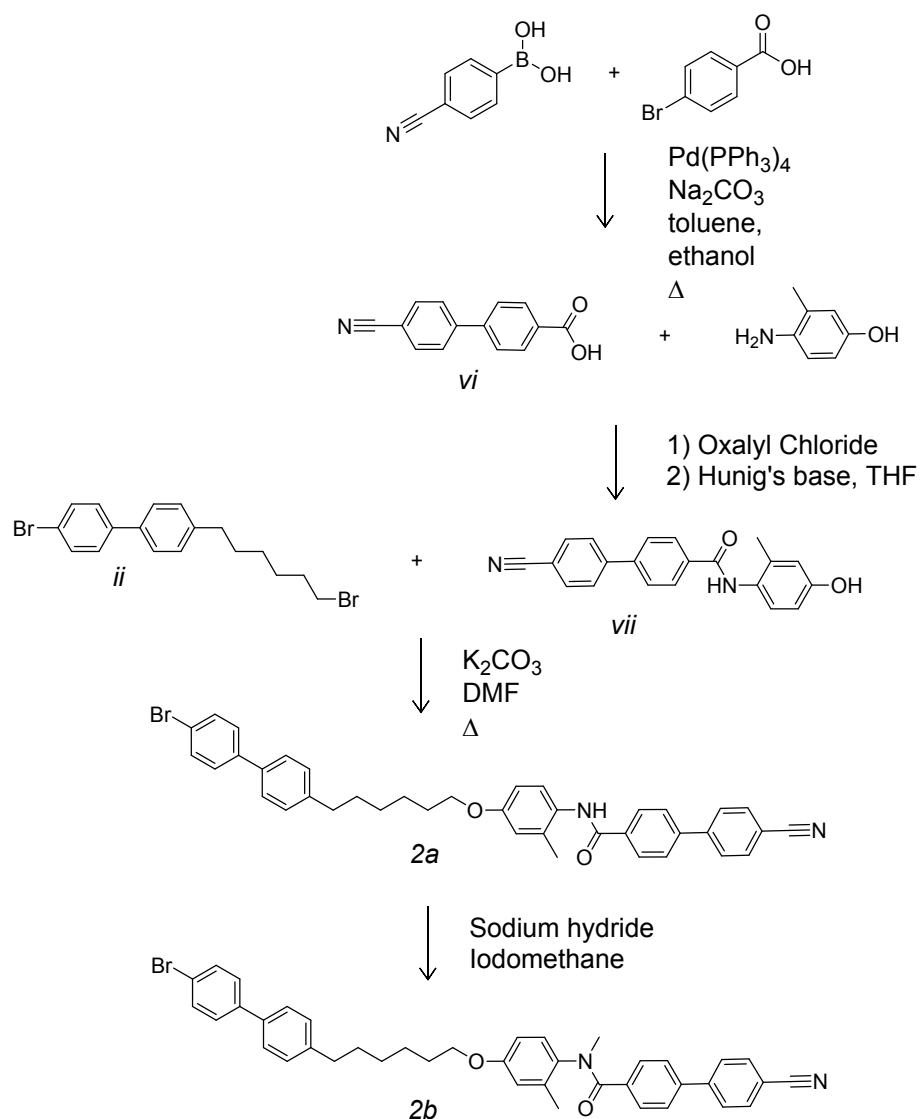
Elemental analysis: Calculated for:  $\text{C}_{41}\text{H}_{37}\text{N}_3\text{O}_2$  C 81.56 %, H 6.18 %, N 6.96 %. Found: C 81.33 %, H 6.03 %, N 7.00 %

$\nu_{max}/\text{cm}^{-1}$ : 2925 ( $\text{CH}_2$ ), 2854 ( $\text{CH}_2$ ), 2225 (CN), 1635 (CO), 1006 (Ar), 827 (Ar).

$\delta$  H (400 MHz, Chloroform-d) 7.77 – 7.65 (6 H, m, Ar-H), 7.62 (2 H, d, J 8.1, Ar-H), 7.53 (3 H, d, J 7.8, Ar-H), 7.46 – 7.36 (1 H, m, Ar-H), 7.41 (2 H, m, Ar-H), 7.29 (2 H, d, J 9.3, Ar-H), 7.00 (1 H, d, J 8.4, Ar-H), 6.67 (1 H, s, Ar-H), 6.64 (1 H, dd, J 8.4, 2.8, Ar-H), 3.89 (2 H, t, J 6.4,  $\underline{\text{CH}_2\text{-O}}$ ), 3.39 (3 H, s,  $\underline{\text{CH}_3\text{-N}}$ ), 2.68 (2 H, t, J 7.7,  $\underline{\text{CH}_2\text{-Ar}}$ ), 2.21 (3 H, s,  $\underline{\text{CH}_3\text{-Ar}}$ ), 1.81 – 1.73 (2 H, m,  $\underline{\text{CH}_2\text{-CH}_2\text{-O}}$ ), 1.68 (2 H, q, J 7.6,  $\underline{\text{CH}_2\text{-CH}_2\text{-Ar}}$ ), 1.53 – 1.41 (4 H, m,  $\underline{\text{CH}_2\text{-CH}_2\text{-CH}_2}$ ).

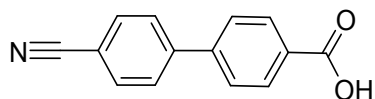
$\delta$  C (101 MHz, DMSO- $d_6$ ) 169.65, 158.06, 145.03, 143.80, 143.62, 137.09, 136.30, 136.20, 136.05, 133.27, 130.25, 129.57, 129.04, 127.98, 127.73, 127.38, 126.66, 119.38, 116.77, 113.29, 110.84, 110.13, 67.86, 37.65, 35.12, 31.17, 29.00, 28.78, 25.74, 18.01.

Synthesis of 4-Cyano-[1,1'-biphenyl]-4'-yl-N-(4-bromo-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-[1,1'-biphenyl]-4-carboxamide **2a** and 4-Cyano-[1,1'-biphenyl]-4'-yl-N-(4-bromo-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-N-methyl-[1,1'-biphenyl]-4-carboxamide **2b**.



Scheme S2: Synthesis of compounds 2a and 2b

#### 4-Cyanobiphenyl-4'-carboxylic acid **vi**



To a 100 ml round bottom flask was added 4-bromobenzoic acid (2.646 g, 13 mmol), 4-cyanophenylboronic acid (2.133 g, 14.5 mmol) and tetrakis(triphenylphosphine) palladium (0) (0.136 g, 0.01 mmol) in a mixture of toluene (20 ml), ethanol (10 ml), and aqueous sodium

carbonate (2M, 10 ml) and heated to 80 °C under an argon atmosphere. The reaction was followed by TLC (50:50 DCM: PE  $R_f$  0.31). After 22 h the reaction was allowed to cool to RT and HCl (1M, 450 ml) was added slowly. The grey precipitate was collected by vacuum filtration and washed with water (50 ml). The crude product was recrystallized from ethanol (280 ml) Yield 1.540 g. (53 %).

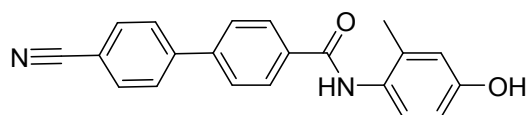
Cr 275 °C N 318 °C I (Lit<sup>7</sup> melt 273-275 °C)

$\nu_{max}/\text{cm}^{-1}$ : 2830 (OH), 2226 (CN), 1680 (CO), 1007 (Ar), 829 (Ar).

$\delta_H$  (400 MHz, DMSO- $d_6$ ) 13.11 (1 H, s, OH), 8.06 (2 H, d,  $J$  8.0, Ar-H), 8.01 – 7.92 (4 H, m, Ar-H), 7.89 (2 H, d,  $J$  8.0, Ar-H).

$\delta_C$  (101 MHz, DMSO- $d_6$ ) 167.41, 143.94, 142.71, 133.41, 131.33, 130.50, 128.36, 127.78, 119.18, 111.29.

4'-Cyano-N-(4''-hydroxy-2-methylphenyl)[1,1'-biphenyl]-4-carboxamide vii



Compound vi (2.977 g, 12.8 mmol) was dried by azeotropic distillation with toluene (3 x 10 ml). This was then dissolved in toluene (20 ml) and oxalyl chloride (1.8 ml, 20 mmol) was added, along with a catalytic amount of DMF and stirred under an argon atmosphere at 40 °C for 2 hours. The reaction was allowed to cool to room temperature and the excess toluene and oxalyl chloride was removed under vacuum (3 mmHg).

4-Amino-3-methylphenol (1.689 g, 13.7 mmol) was dried by azeotropic distillation with toluene (3 x 10 ml), then dissolved in dry THF (100 ml), cooled to 0 °C in an ice bath and Hunig's base (2.4 ml, 13.5 mmol) was added. The acid chloride was dissolved in THF (40 ml) and added dropwise to the reaction mixture. After addition was complete, the ice bath was removed and the reaction continues at room temperature. After 48 hours the THF was removed *in vacuo*, then DCM (50 ml) was added and the precipitate was collected by vacuum filtration. Yield 2.950 g (67 %).

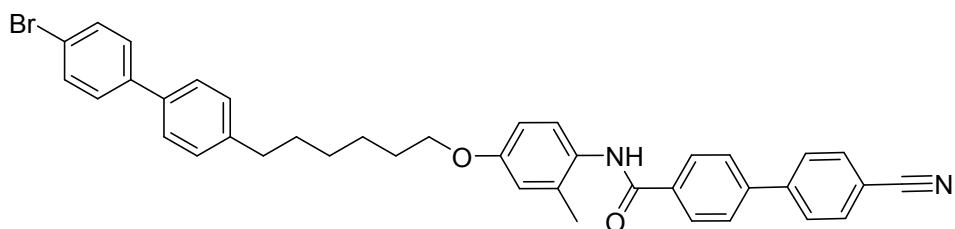
MP Cr 243 °C N 274 °C I

$\nu_{max}/\text{cm}^{-1}$ : 3261 (OH), 2223 (CN), 1641 (CO), 1003 (Ar), 817 (Ar).

$\delta$  H (400 MHz, DMSO-d<sub>6</sub>) 9.78 (1 H, s, NH), 9.31 (1 H, s, OH), 8.10 (2 H, d, J 8.0, Ar-H), 7.98 (4 H, s, Ar-H), 7.91 (2 H, d, J 8.0, Ar-H), 7.08 (1 H, d, J 8.4, Ar-H), 6.68 (1 H, d, J 2.8, Ar-H), 6.62 (1 H, dd, J 8.4, 2.8, Ar-H), 2.15 (3 H, s, CH<sub>3</sub>).

$\delta$  C (101 MHz, DMSO-d<sub>6</sub>) 165.34, 156.00, 144.09, 141.35, 135.90, 135.04, 133.40, 128.81 (2C), 128.60 (2C), 128.27, 128.00 (2C), 127.54 (2C), 119.25, 117.09, 113.17, 111.05, 18.45.

*4-Cyano-[1,1'-biphenyl]-4'-yl-N-(4-bromo-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-[1,1'-biphenyl]-4-carboxamide 2a.*



A mixture of *vii* (0.86 g, 2.2 mmol) and *ii* (1.037 g, 2.6 mmol) was dried by azeotropic distillation with toluene (3 x 15 ml). To this was added K<sub>2</sub>CO<sub>3</sub> (0.719 g, 5.2 mmol), and dry DMF (50 ml). The reaction was heated to 80 °C and followed by TLC (DCM as eluent, R<sub>f</sub> 0.24). When reaction was deemed to be complete (24 h), the mixture was allowed to cool to RT and added to a mix of water (50 ml) and HCl (1 M, 50 ml). The precipitate was collected by vacuum filtration and recrystallised from toluene (30 ml). Yield 0.930 g (55 %).

Cr 188 °C N 199 °C I

Elemental analysis: Calculated for: C<sub>39</sub>H<sub>35</sub>BrN<sub>2</sub>O<sub>2</sub> C 72.78 %, H 5.48 %, N 4.35 %. Found: C 72.81 %, H 5.57 %, N 4.18 %

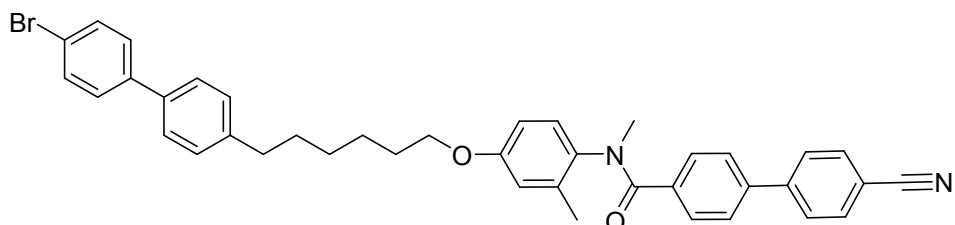
$\nu_{max}$ /cm<sup>-1</sup>: 3279 (NH<sub>2</sub>), 2925 (CH<sub>2</sub>), 2850 (CH<sub>2</sub>), 2227 (CN), 1641 (CO), 1002 (Ar), 805 (Ar).

$\delta$  H (400 MHz, Chloroform-*d*) 8.03 (2 H, d, J 7.6, Ar-H), 7.80 (2 H, d, J 8.1, Ar-H), 7.77 (2 H, s, Ar-H), 7.74 (2 H, d, J 7.3, Ar-H), 7.69 (2 H, d, J 8.3, Ar-H), 7.57 (2 H, d, J 7.6, Ar-H), 7.48 (3 H, m, Ar-H), 7.28 (2 H, d, J 5.3, Ar-H), 6.82 (2 H, m, Ar-H), 3.98 (2 H, t, J 6.3 CH<sub>2</sub>-O), 2.69 (2 H, t, J 7.7, CH<sub>2</sub>-Ar), 2.34 (3 H, s, CH<sub>3</sub>-Ar), 1.82 (2 H, t, J 7.1, CH<sub>2</sub>-CH<sub>2</sub>-O), 1.72 (2 H, t, J 7.6, CH<sub>2</sub>-CH<sub>2</sub>-O), 1.57 – 1.44 (4 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>).

$\delta$  C (101 MHz, Chloroform-*d*) 157.11, 144.37, 142.34, 140.05, 137.88, 137.35, 134.91, 132.77 (2C), 132.62, 131.80 (2C), 129.05, 128.99 (2C), 128.57 (2C), 128.27, 128.24 (2C), 127.92,

127.88 (2C), 127.61, 126.80 (2C), 125.31, 121.18, 118.69, 116.76, 112.35, 111.77, 68.08, 35.49, 31.34, 29.20, 28.98, 25.92, 18.21.

4-Cyano-[1,1'-biphenyl]-4'-yl-N-(4-bromo-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-N-methyl-[1,1'-biphenyl]-4-carboxamide 2b



Compound 2a (0.800 g, 1.24 mmol) was dried by azeotropic distillation with toluene (3 x 5 ml). Sodium hydride (60% dispersion, 0.160 g, 4.0 mmol) was washed with petroleum ether (3 x 2 ml). Compound 2a was dissolved in dry THF (50 ml) and added to the NaH under an argon atmosphere. When reaction was complete (fizzing stops) the reaction was left for a further 30 minutes and then methyl iodide (0.2 ml, 3.2 mmol) was added and the reaction was followed by TLC (eluent 50: 50 EtOAc: PE  $R_f$  0.69). When the reaction was deemed complete (19 h) the excess NaH was quenched with a few drops of propanol, and the THF was removed under vacuum (3 mmHg). The crude solid was dissolved in ethyl acetate (40 ml) and washed with water (3 x 20 ml). The ethyl acetate was removed *in vacuo* to give the pure product. Yield 0.60 g, (74 %).

MP 138 °C

Elemental analysis: Calculated for:  $C_{40}H_{37}BrN_2O_2$  C 73.05 %, H 5.67 %, N 4.26 %. Found: C 72.80 %, H 6.11 %, N 3.95 %

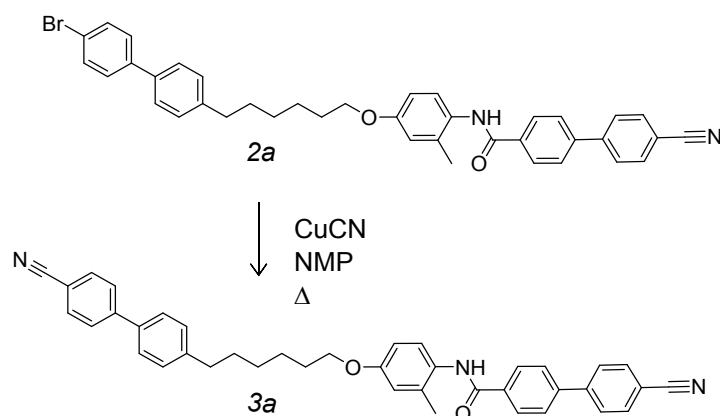
$\nu_{max}/cm^{-1}$ : 2925 ( $CH_2$ ), 2853 ( $CH_2$ ), 2222 (CN), 1631 (CO), 1001 (Ar), 809 (Ar).

$\delta_H$  (400 MHz, Chloroform-*d*) 7.69 (2 H, d,  $J$  8.2, Ar-H), 7.60 (2 H, d,  $J$  8.2, Ar-H), 7.55 (2 H, d,  $J$  8.2, Ar-H), 7.50 – 7.34 (8 H, m, Ar-H), 7.24 (2 H, d,  $J$  7.7, Ar-H), 6.98 (1 H, d,  $J$  8.5, Ar-H), 6.65 (1 H, s, Ar-H), 6.62 (1 H, d,  $J$  8.5, Ar-H), 3.87 (2 H, t,  $J$  6.5  $CH_3$ -O), 3.38 (3 H, s,  $CH_3$ -N), 2.65 (2 H, t,  $J$  7.7,  $CH_2$ -Ar), 2.19 (3 H, s,  $CH_3$ -Ar), 1.74 (2 H, q,  $J$  7.9, 7.5,  $CH_2$ - $CH_2$ -O), 1.67 (2 H, t,  $J$  7.5,  $CH_2$ - $CH_2$ -Ar), 1.44 (4 H, m,  $CH_2$ - $CH_2$ - $CH_2$ ).

$\delta_C$  (101 MHz, Chloroform-*d*) 170.16, 158.25, 144.58, 142.22, 139.96, 139.88, 137.41, 136.32, 136.16, 136.01, 132.56 (2C), 131.82 (2C), 129.44, 129.11 (2C), 128.93 (2C), 128.53 (2C), 127.65

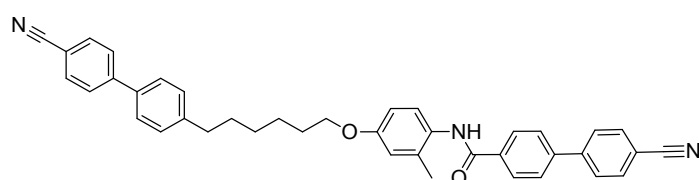
(2C), 126.80 (2C), 126.39 (2C), 121.24, 118.77, 116.72, 112.81, 111.29, 68.01, 37.88, 35.47, 31.31, 29.17, 29.00, 25.91, 18.06.

**Synthesis of 4-Cyano-[1,1'-biphenyl]-4'-yl-N-(4-cyano-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-[1,1'-biphenyl]-4-carboxamide *3a***



Scheme S3: Synthesis of compound **3a**

**4-Cyano-[1,1'-biphenyl]-4'-yl-N-(4-cyano-[1,1'-biphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-[1,1'-biphenyl]-4-carboxamide *3a***



N-methylpyrrolidone (30 ml) was stirred rapidly under argon, and then **2a** (736 mg, 1.1 mmol) and CuCN (850 mg, 9.4 mmol) were added, and the mixture heated to 200 °C. After 9 h the reaction mixture was cooled to RT, quenched with conc. ammonia solution (5 ml) and then added to a mix of DCM (50 ml) and H<sub>2</sub>O (10 ml). The layers were separated and the aqueous layer was washed once with DCM (25 ml). The solvent was removed *in vacuo* and the residual liquid poured into water (5 ml). The precipitate was collected by vacuum filtration and purified by column chromatography (eluent 50: 50 DCM EtOAc R<sub>f</sub> 0.4) to yield the pure product. Yield 0.250 g. (38 %).

Cr 186 °C N 224 °C I



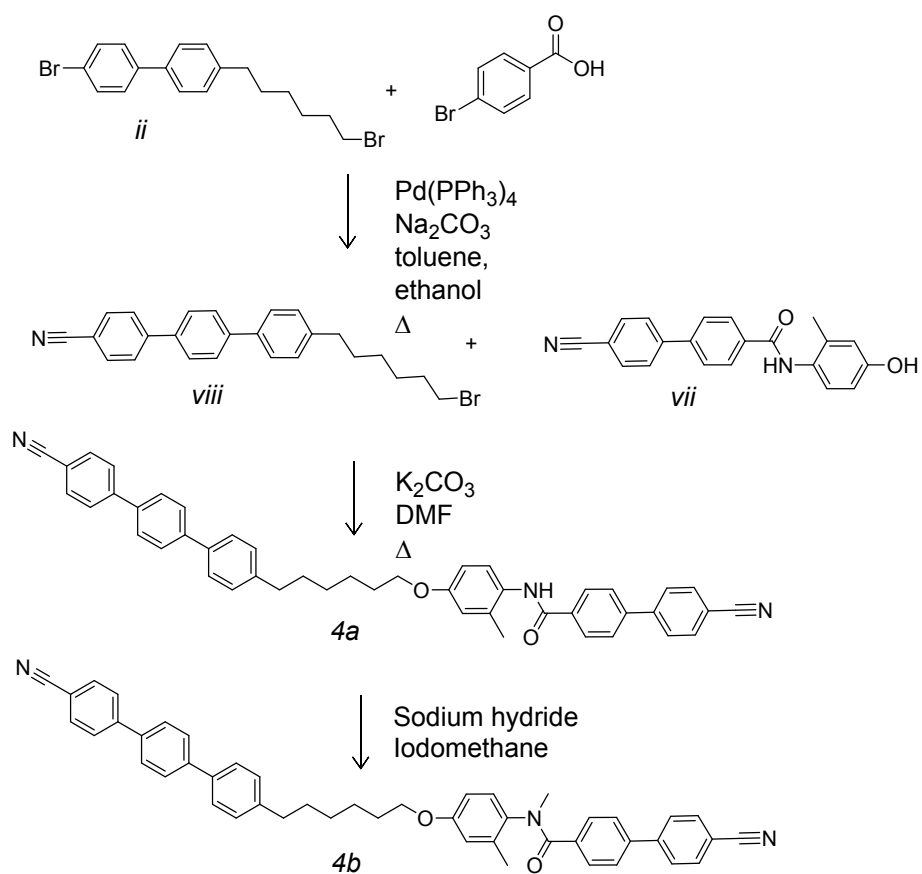
M/Z: Calculated mass 612.2627 (C<sub>40</sub>H<sub>35</sub>N<sub>3</sub>O<sub>2</sub>Na) Found 612.2615. Difference -2.0 ppm.

$\nu_{max}/\text{cm}^{-1}$ : 3275 (NH), 2929 (CH<sub>2</sub>), 2853 (CH<sub>2</sub>), 2222 (CN), 1644 (CO), 1005 (Ar), 806 (Ar).

$\delta_{\text{H}}$  (400 MHz, Chloroform-*d*) 8.02 (2 H, d, *J* 8.0, Ar-H), 7.76 (10 H, m, Ar-H), 7.58 (1 H, s, Ar-H), 7.54 (2 H, d, *J* 7.8, Ar-H), 7.32 (2 H, d, *J* 7.8, Ar-H), 6.81 (2 H, d, *J* 7.5, Ar-H), 3.98 (2 H, t, *J* 6.4, CH<sub>2</sub>-O), 2.72 (2 H, t, *J* 7.7, CH<sub>2</sub>-Ar), 2.33 (3 H, s, Ar-CH<sub>3</sub>), 1.82 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-O), 1.73 (2 H, t, *J* 7.7, CH<sub>2</sub>-CH<sub>2</sub>-Ar), 1.61 – 1.44 (4 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>).

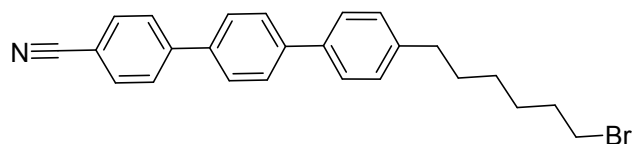
$\delta_{\text{C}}$  (101 MHz, Chloroform-*d*) 157.08, 145.60, 144.36, 143.54 (2C), 142.39, 136.52, 134.90, 132.77 (2C), 132.57 (2C), 129.21 (2C), 128.28, 127.88 (4C), 127.63, 127.49 (4C), 127.11 (2C), 125.63, 119.06, 118.67, 116.76, 112.34, 111.80, 110.54, 68.04, 35.51, 31.27, 29.19, 28.94, 25.90, 18.20.

*Synthesis of 4-Cyano-[1,1'-biphenyl]-4'-yl-N-(1<sup>4</sup>-cyano-[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-Terphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-[1,1'-biphenyl]-4-carboxamide **4a** and 4-Cyano-[1,1'-biphenyl]-4'-yl-N-(1<sup>4</sup>-cyano-[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-Terphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-N-methyl-[1,1'-biphenyl]-4-carboxamide **4b***



Scheme S4: Synthesis of compounds *4a* and *4b*

*1-Bromo-6-(4'-cyanoterphenyl-4-yl)hexane iii*



A mixture of *ii*, (1.119 g, 3 mmol), 4-cyanophenyl boronic acid (0.496 g, 3 mmol), and tetrakis(triphenylphosphine) palladium (0) (0.035 g, 0.03 mmol) was heated at 85 °C in a mixture of toluene (12 ml), ethanol (3 ml) and sodium carbonate (2 M, aq, 6 ml) under argon. The reaction was followed by TLC (3:1 DCM: PE,  $R_f$  0.39) and appeared complete after approximately 24 h.

The solvent was removed in vacuo, then the solid was dissolved in DCM (20 ml) and washed twice with water (10 ml). The organic layer was dried with MgSO<sub>4</sub> and the solvent removed in vacuo. The crude solid was purified by column chromatography using 3:1 DCM: PE as eluent. (Rf 0.39). The white solid thus obtained was recrystallised from toluene (20 ml), yielding 0.643 mg as white needles (55%).

Cr 120 °C N 209 °C |

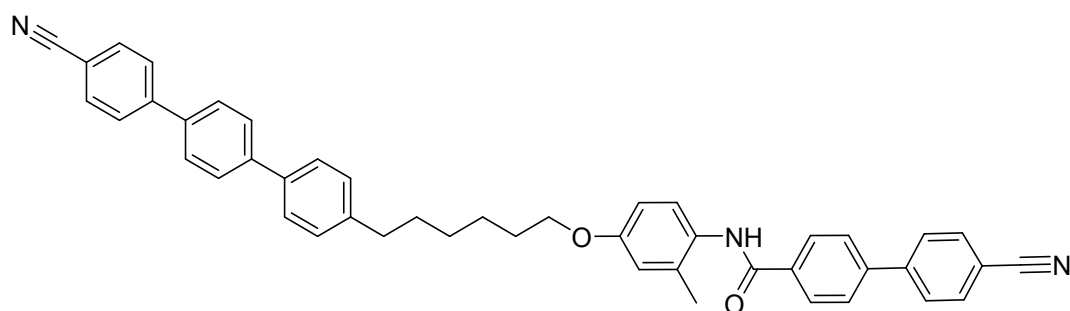
Elemental analysis: Calculated for: C<sub>25</sub>H<sub>24</sub>BrN C 71.77 %, H 5.78 %, N 3.35 %. Found: C 72.02 %, H 5.90 %, N 3.19 %

$\nu_{\max}$  /cm<sup>-1</sup>: 2926 (C-H), 2854 (C-H), 2224 (CN), 1599 (Ar), 1487 (Ar), 1467 (Ar), 1236 (CH<sub>2</sub>Br), 807 (Ar).

$\delta$  H (400 MHz, Chloroform-d) 7.75 (4 H, d, J 1.2, Ar-H), 7.72 (2 H, d, J 8.3, Ar-H), 7.68 (2 H, d, J 8.3, Ar-H), 7.58 (2 H, d, J 8.0, Ar-H), 7.29 (2 H, d, J 8.0, Ar-H), 3.43 (2 H, t, J 6.8, Br-CH<sub>2</sub>), 2.69 (2 H, t, J 7.7, Ar-CH<sub>2</sub>), 1.89 (2 H, p, J 7.0, Br-CH<sub>2</sub>CH<sub>2</sub>), 1.70 (2 H, p, J 7.5, Ar-CH<sub>2</sub>CH<sub>2</sub>), 1.59 – 1.35 (4 H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

$\delta$  C (100 MHz, Chloroform-d) 145.21, 142.32, 141.48, 137.66, 137.60, 132.64 (2C), 128.99 (2C), 127.61 (2C), 127.57 (2C), 127.53 (2C), 126.96 (2C), 118.98, 110.86, 35.47, 33.96, 32.73, 31.22, 28.42, 28.04.

*4-Cyano-[1,1'-biphenyl]-4'-yl-N-(1<sup>4</sup>-cyano-[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-Terphenyl]-4'-hexyl-6-oxy-{2-methylphenyl}-[1,1'-biphenyl]-4-carboxamide 4a*



A mixture of *viii* (0.483 g, 1.2 mmol) and *vii* (0.387 g, 1.2 mmol) was dried by azeotropic distillation with toluene (3 x 15 ml). To this was added  $K_2CO_3$  (0.329 g, 2.4 mmol), KI (0.122 g 0.7 mmol), and dry DMF (50 ml). The reaction was heated to 80 °C and followed by TLC (50: 50 DCM: PE as eluent,  $R_f$  0.28). When reaction was deemed to be complete (24 h), the mixture was allowed to cool to RT and added to a mix of water (50 ml) and HCl (1 M, 50 ml). The precipitate was collected by vacuum filtration and recrystallised from toluene (10 ml). Yield 0.504 g (64%)

Cr 208 °C N 318 °C I

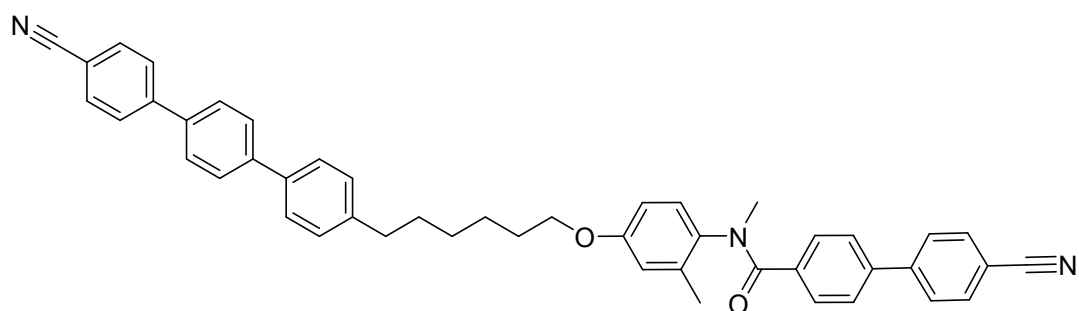
Elemental analysis: Calculated for:  $C_{46}H_{39}N_3O_2$  C 82.98 %, H 5.90 %, N 6.31 %. Found: C 82.96 %, H 5.82 %, N 6.26 %.

$\nu_{max}/cm^{-1}$ : 3300 (NH), 2927 ( $CH_2$ ), 2855 ( $CH_2$ ), 2227 (CN), 1646 (CO), 1004 (Ar), 811 (Ar).

$\delta_H$  (400 MHz, Chloroform-*d*) 7.92 (2 H, d,  $J$  7.9 Ar-H), 7.70 (2 H, d,  $J$  8.2, Ar-H), 7.68 – 7.54 (12 H, m, Ar-H), 7.53 – 7.45 (3 H, m, Ar-H), 7.22 (2 H, d,  $J$  7.8, Ar-H), 6.71 (2 H, d,  $J$  8.1, Ar-H), 3.88 (2 H, t,  $J$  6.5, Ar-H), 2.62 (2 H, t,  $J$  7.7,  $CH_2$ -O), 2.23 (3 H, s, Ar- $CH_3$ ), 1.73 (2 H, p,  $J$  6.7,  $CH_2$ -Ar), 1.64 (2 H, p,  $J$  7.6  $CH_2$ - $CH_2$ -O), 1.44 (2 H, q,  $J$  7.8, 7.3,  $CH_2$ - $CH_2$ -Ar), 1.38 (2H, m  $CH_2$ - $CH_2$ - $CH_2$ ).

$\delta_C$  (101 MHz, Chloroform-*d*) 165.18, 157.15, 145.22, 144.35, 142.46, 141.51, 137.88, 137.62, 137.55, 134.90, 132.77 (2C), 132.64 (2C), 129.04 (2C), 129.01 (2C), 128.23 (2C), 127.92 (2C), 127.87 (2C), 127.61 (2C), 127.56 (2C), 127.53 (2C), 126.94 (2C), 125.30, 118.98, 118.67, 116.78, 112.36, 111.80, 110.83, 68.10, 35.53, 31.35, 29.22, 29.01, 25.93, 18.20.

4-Cyano-[1,1'-biphenyl]-4'-yl-N-(1<sup>4</sup>-cyano-[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-Terphenyl]-4'-hexyl-6-oxy-{2-methylphenyl})-N-methyl-4-carboxamide **4b**



Compound **4a** (0.250 g, 0.4 mmol) was dried by azeotropic distillation with toluene (3 x 5 ml). Sodium hydride (60% dispersion, 0.038 g, 0.9 mmol) was washed with petroleum ether (3 x 2 ml). Compound **4a** was dissolved in dry THF (30 ml) and added to the NaH under an argon atmosphere. When reaction was complete (fizzing stops) the reaction was left for a further 30 min and then methyl iodide (0.06 ml, 0.4 mmol) was added and the reaction was followed by TLC (eluent 50: 50 EtOAc: PE  $R_f$  0.56). When the reaction was deemed complete (16 h) the excess NaH was quenched with a few drops of propanol, and the THF was removed under vacuum (3 mmHg). The crude solid was dissolved in ethyl acetate (25 ml) and washed with water (3 x 10 ml). The ethyl acetate was removed *in vacuo* and the crude product was purified by column chromatography (50:50 DCM EtOAc as eluent,  $R_f$  0.56). Yield 0.235 g, (86%).

MP 145 °C

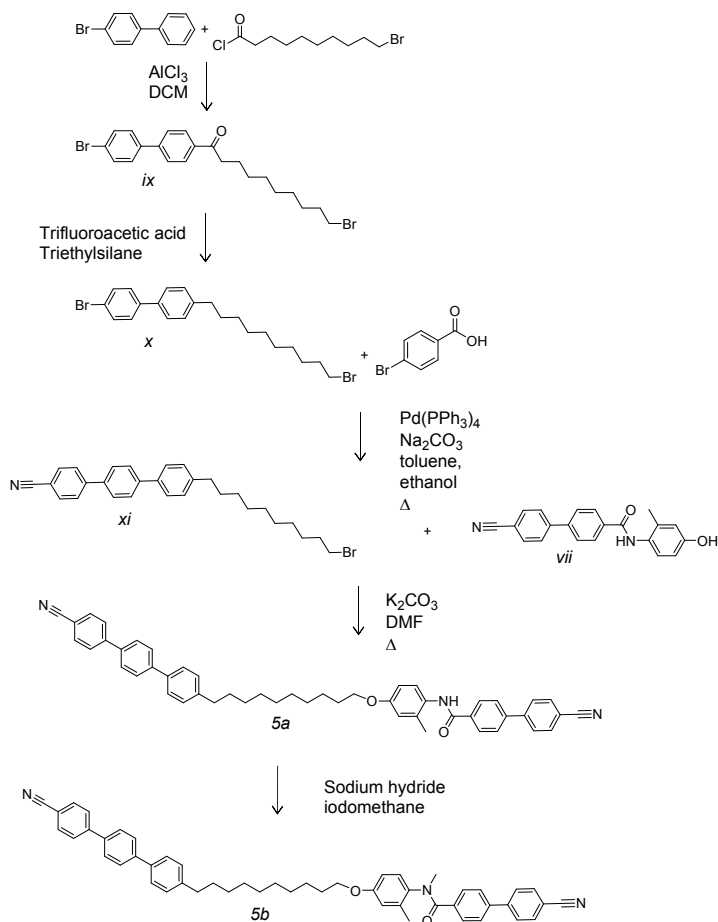
M/Z: Calculated mass: 702.3096 ( $C_{47}H_{41}N_3O_2Na$ ). Found 702.3094. (-0.3 ppm).

$\nu_{max}/cm^{-1}$ : 2926 ( $CH_2$ ), 2850 ( $CH_2$ ), 2225 (CN), 1637 (CO), 1005 (Ar), 812 (Ar).

$\delta$  H (400 MHz, Chloroform-*d*) 7.79 – 7.67 (10 H, m, Ar-H), 7.70 – 7.58 (2 H, m, Ar-H), 7.58 (2 H, d, J 7.6, Ar-H), 7.41 (4 H, d, J 2.3, Ar-H), 7.29 (2 H, d, J 7.3, Ar-H), 7.00 (1 H, d, J 8.5, Ar-H), 6.68 (1 H, s, Ar-H), 6.65 (1 H, d, J 8.5, Ar-H), 3.90 (2 H, t, J 6.4,  $\underline{CH_2}$ -O), 3.39 (3 H, s, N- $CH_3$ ), 2.69 (2 H, t, J 7.7,  $\underline{CH_2}$ -Ar), 2.21 (3 H, s, Ar- $CH_3$ ), 1.73 (4 H, dq, J 29.7, 7.0), 1.46 (4H, d, J 14.2).

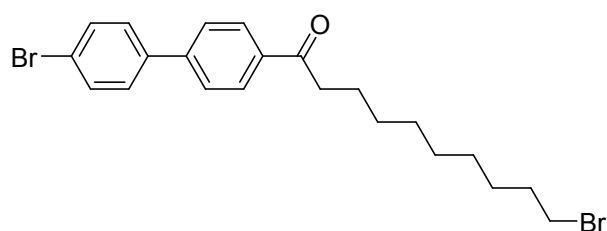
$\delta$  c (101 MHz, Chloroform-*d*) 170.17, 158.25, 145.17, 144.59, 142.34, 141.42, 139.88, 137.70, 137.61, 136.31, 136.16, 136.02, 132.65, 132.56, 129.44, 129.11, 128.96, 127.65, 127.58, 127.53, 126.94, 126.39, 118.76, 116.73, 112.81, 111.30, 110.88, 68.02, 37.88, 35.50, 31.33, 29.17, 29.03, 25.92, 18.06.

Synthesis of 4-Cyano-[1,1'-biphenyl]-4'-yl-N-(1<sup>4</sup>-cyano-[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-Terphenyl]-4'-decyl-10-oxy-{2-methylphenyl})-[1,1'-biphenyl]-4-carboxamide **5a**, and 4-cyano-[1,1'-biphenyl]-4'-yl-N-(1<sup>4</sup>-cyano-[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-Terphenyl]-4'-decyl-10-oxy-{2-methylphenyl})-N-decyl-[1,1'-biphenyl]-4-carboxamide **5b**.



Scheme S5: Synthesis of compounds **5a** and **5b**.

1-Bromo-10-(4'-bromobiphenyl-4-yl)decane-10-one **ix**.



10-Bromodecanoic acid (5.343 g, 21 mmol) was dried by azeotropic distillation with toluene (3 x 15 ml). To this was added toluene (20 ml), oxalyl chloride (2.75 ml, 32 mmol), and a catalytic

amount of DMF and the mixture was stirred under argon at 40 °C. When the bubbling stopped, the reaction was considered to be complete. The excess oxalyl chloride and toluene was then removed under vacuum (3 mmHg) to leave the acid chloride.

This was added dropwise to a solution of 4-bromobiphenyl (5.010 g, 21 mmol) and AlCl<sub>3</sub> (3.23 g, 24 mmol) in DCM (100 ml), in an ice bath, and wrapped in tinfoil to protect the reaction from light. When addition was complete the ice bath was removed and the reaction allowed to continue at RT and followed by TLC (eluent 50: 50 DCM: PE, R<sub>f</sub> 0.38). After 9 h the reaction mixture was added to water (100 ml), the layers were separated, and the organic layer was washed with water (2 x 50 ml) and sodium bicarbonate (50 ml, 1 M). The organic fraction was dried with MgSO<sub>4</sub> and the solvent removed *in vacuo*. The crude product was purified by column chromatography (50:50 DCM: PE as eluent, R<sub>f</sub> 0.38). Yield 3.513 g (33%).

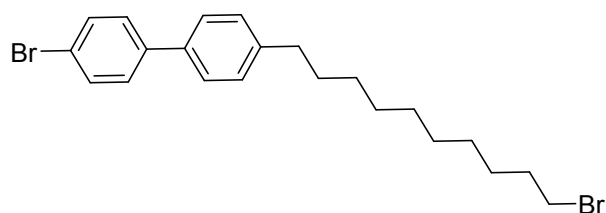
MP 93 °C (Lit<sup>4</sup> 96 °C)

$\nu_{max}/\text{cm}^{-1}$ : 2929 (CH<sub>2</sub>), 2915 (CH<sub>2</sub>), 2847 (CH<sub>2</sub>), 1674 (CO), 1000 (Ar), 810 (Ar).

$\delta$  H (400 MHz, Chloroform-d) 8.05 (2 H, d, J 8.2, Ar-H), 7.67 (2 H, d, J 8.2, Ar-H), 7.62 (2 H, t, J 8.0, Ar-H), 7.52 (2 H, d, J 7.8, Ar-H), 3.43 (2 H, t, J 6.9, CH<sub>2</sub>-Br), 3.01 (2 H, t, J 7.4, CH<sub>2</sub>-Ar), 1.89 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-Br), 1.78 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-Ar), 1.50 – 1.32 (10 H, m).

$\delta$  C (101 MHz, Chloroform-d) 199.98, 144.27, 138.85, 136.11, 132.10 (2C), 128.80 (2C), 128.76 (2C), 127.02 (2C), 122.61, 38.67, 34.00, 32.81, 29.36, 29.32, 29.27, 28.70, 28.14, 24.39.

*1-Bromo-10-(4'-bromobiphenyl-4-yl)decane x*



A solution of *ix* (3.0 g, 6.4 mmol) in trifluoroacetic acid (5.8 g, 51 mmol, 3.9 ml) and DCM (20 ml) was stirred in an ice bath under argon. Triethylsilane (2.91 g, 25 mmol, 4 ml) was added dropwise. After addition the ice bath was removed and the reaction followed by TLC (50:50 DCM: PE R<sub>f</sub> 0.81). The reaction appeared complete after 22 h.

The reaction mixture was added to DCM (50ml) and H<sub>2</sub>O (200 ml). The layers were separated, and the organic layer was washed with water (3 x 20 ml). The organic layer was dried with

MgSO<sub>4</sub> and the solvent removed *in vacuo*. The crude product was recrystallised from ethyl acetate (10 ml). Yield 1.45 g (55 %)

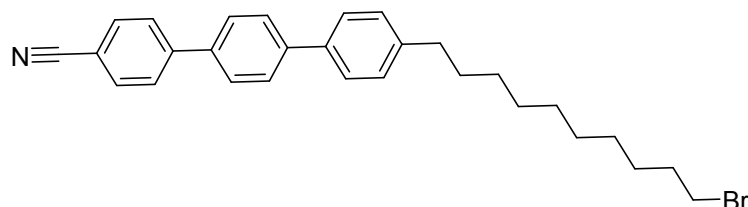
MP 58 °C

$\nu_{max}/\text{cm}^{-1}$ : 2923 (CH<sub>2</sub>), 2852 (CH<sub>2</sub>), 1001 (Ar), 808 (Ar).

$\delta$  H (400 MHz, Chloroform-d) 7.57 (2 H, d, J 8.6, Ar-H), 7.48 (4 H, t, J 8.6, 7.7, Ar-H), 7.29 (2 H, d, J 7.7, Ar-H), 3.43 (2 H, t, J 6.8, Ar-H), 2.67 (2 H, t, J 7.7, CH<sub>2</sub>-Br), 1.88 (2 H, p, J 7.0, CH<sub>2</sub>-Ar), 1.68 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-Br), 1.50 – 1.41 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-Ar), 1.49 – 1.30 (10 H, m).

$\delta$  C (101 MHz, Chloroform-d) 142.55, 140.08, 137.30, 131.80 (2C), 128.96 (2C), 128.56 (2C), 126.77 (2C), 121.17, 35.61, 34.05, 32.85, 31.45, 29.47 (2C), 29.43, 29.32, 28.77, 28.18.

*1-Bromo-10-(4''-cyanoterphenyl-4-yl)decane xi*



To a 50 ml round bottom flask was added x (1.206 g, 2.7 mmol), 4-cyanophenylboronic acid (0.478 g, 3.2 mmol) and tetrakis(triphenylphosphine) palladium (0) (0.059 g, 0.0023 mmol) in a mixture of toluene (16 ml), ethanol (4 ml), and aqueous sodium carbonate (2M, 8 ml) and heated to 80 °C under an argon atmosphere. The reaction was followed by TLC (50:50 DCM: PE R<sub>f</sub> 0.16). After 25 h the reaction was allowed to cool to RT and HCl (20 ml, conc) was added slowly. The solvents were removed *in vacuo*, dissolved in 100 ml DCM, and filtered through celite. The liquid was then dried with MgSO<sub>4</sub> and the solvent removed *in vacuo*. The crude product was recrystallized from toluene (10 ml) Yield 0.744 g (60%).

Cr 81 °C SmX 93 °C SmA 158 °C N 182 °C I

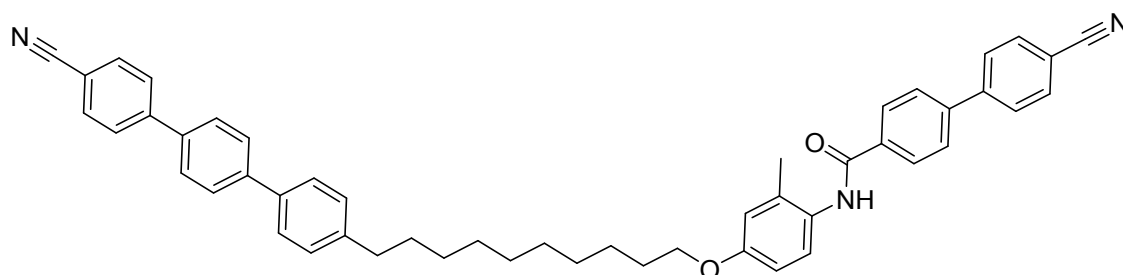
$\nu_{max}/\text{cm}^{-1}$ : 2920 (CH<sub>2</sub>), 2848 (CH<sub>2</sub>), 2220 (CN), 1004 (Ar), 808 (Ar).

$\delta$  H (400 MHz, Chloroform-d) 7.79 – 7.76 (4 H, m, Ar-H), 7.73 (2 H, d, J 8.0, Ar-H), 7.69 (2 H, d, J 8.0, Ar-H), 7.59 (2 H, d, J 7.7, Ar-H), 7.31 (2 H, d, J 7.7, Ar-H), 3.43 (2 H, t, J 6.9, CH<sub>2</sub>-Br), 2.69 (2 H, t, J 7.8, CH<sub>2</sub>-Ar), 1.88 (2 H, p, J 7.1, CH<sub>2</sub>-CH<sub>2</sub>-Br), 1.73 – 1.65 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-Ar), 1.50 – 1.43 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Br), 1.35 (10 H, d, J 16.9).



$\delta$  C (101 MHz, Chloroform-d) 145.23, 142.68, 141.54, 137.62, 137.48, 132.64 (2C), 128.99 (2C), 127.60 (2C), 127.56 (2C), 127.53 (2C), 126.90 (2C), 118.97, 110.86, 35.64, 34.05, 32.84, 31.46, 29.46 (2C), 29.42, 29.32, 28.76, 28.18.

4-Cyano-[1,1'-biphenyl]-4'-yl-N-(1<sup>4</sup>-cyano-[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-Terphenyl]-4'-decyl-10-oxy-{2-methylphenyl}-[1,1'-biphenyl]-4-carboxamide 5a



A mixture of xi (0.599 g, 1.3 mmol) and 2.0.7 (0.535 g, 1.6 mmol) was dried by azeotropic distillation with toluene (3 x 10 ml). To this was added  $K_2CO_3$  (0.370 g, 2.5 mmol), KI (0.108 g 0.7 mmol), and dry DMF (50 ml). The reaction was heated to 80 °C and followed by TLC (50: 50 DCM: PE as eluent,  $R_f$  0.72). When reaction was deemed to be complete (26 h), the mixture was allowed to cool to RT and added to a mix of water (25 ml) and HCl (1 M, 50 ml). The precipitate was collected by vacuum filtration and washed with hot ethyl acetate (15 ml). Yield 0.737 g (80%)

Cr 176 °C N 261 °C I

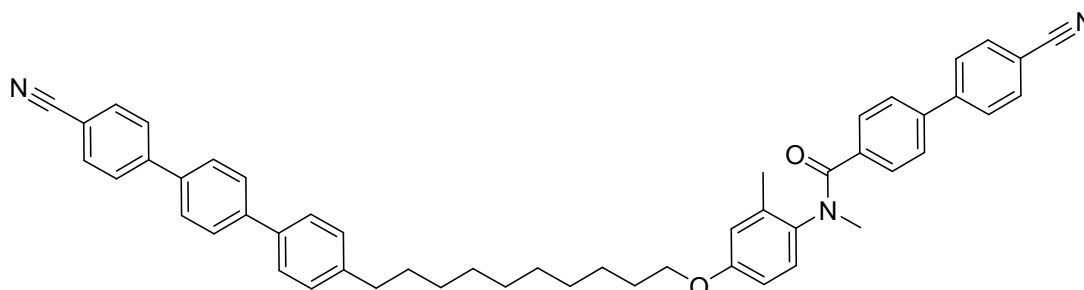
Elemental analysis: Calculated for:  $C_{50}H_{47}N_3O_2$  C 83.19 %, H 6.56 %, N 5.82 %. Found: C 83.03 %, H 6.65 %, N 5.78 %

$\nu_{max}/cm^{-1}$ : 3298 (NH), 2920 ( $CH_2$ ), 2851 ( $CH_2$ ), 2228 (CN), 1644 (CO), 1005 (Ar), 812 (Ar).

$\delta$  H (400 MHz, Chloroform-d) 9.52 (1 H, s, N-H), 8.01 (2 H, d,  $J$  7.9 Ar-H), 7.78 (2 H, d,  $J$  8.1, Ar-H), 7.77 – 7.63 (13 H, m, Ar-H), 7.57 (2 H, d,  $J$  7.7, Ar-H), 7.29 (2 H, d,  $J$  15.7, Ar-H), 6.81 (2 H, s, Ar-H), 3.96 (2 H, t,  $J$  6.5,  $CH_2$ -O), 2.67 (2 H, t,  $J$  7.8,  $CH_2$ -Ar), 2.32 (3 H, s, Ar- $CH_3$ ), 1.83 – 1.74 (2 H, m,  $CH_2$ - $CH_2$ -O), 1.67 (2 H, m,  $CH_2$ - $CH_2$ -Ar), 1.47 (2 H, m,  $CH_2$ - $CH_2$ - $CH_2$ -O), 1.35 (10 H, d,  $J$  12.1).

$\delta$  C (101 MHz, Chloroform-d) 165.47, 157.21, 144.90, 144.36, 142.44, 141.14, 137.28, 137.10, 134.93, 134.69, 132.51 (2C), 132.43 (2C), 128.83 (2C), 128.53, 128.31(2C), 127.69 (2C), 127.38 (2C), 127.34 (3C), 127.30 (2C), 127.03 (2C), 126.61 (2C), 118.76, 118.56, 116.24, 111.92, 111.18, 110.45, 67.91, 35.36, 31.23, 29.29, 29.23, 29.21, 29.13, 29.06, 29.04, 25.80, 18.24.

4-Cyano-[1,1'-biphenyl]-4'-yl-N-(1<sup>4</sup>-cyano-[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-Terphenyl]-4'-decyl-10-oxy-{2-methylphenyl}-N-methyl-[1,1'-biphenyl]-4-carboxamide 5b.



Compound 5a (0.664 g, 0.83 mmol) was dried by azeotropic distillation with toluene (3 x 5 ml). Sodium hydride (60% dispersion, 0.066 g, 1.7 mmol) was washed with petroleum ether (3 x 1 ml). Compound 2.5.1 was dissolved in dry THF (20 ml) and added to the NaH under an argon atmosphere. When reaction was complete (fizzing stops) the reaction was left for a further 30 min and then methyl iodide (0.1 ml, 1.6 mmol) was added and the reaction was followed by TLC (eluent 50: 50 EtOAc: PE  $R_f$  0.63). When the reaction was deemed complete (15 h) the excess NaH was quenched with a few drops of propanol, and the THF was removed under vacuum (3 mmHg). The crude solid was dissolved in ethyl acetate (50 ml) and washed with water (3 x 20 ml). The ethyl acetate was removed *in vacuo* and the crude solid recrystallised from a 1:1 mix of ethanol and toluene (10 ml). This was further purified by column chromatography (50:50 EtOAc: PE as eluent,  $R_f$  0.63)

Yield 150 mg (25%).

Cr 86 °C N 88 °C I

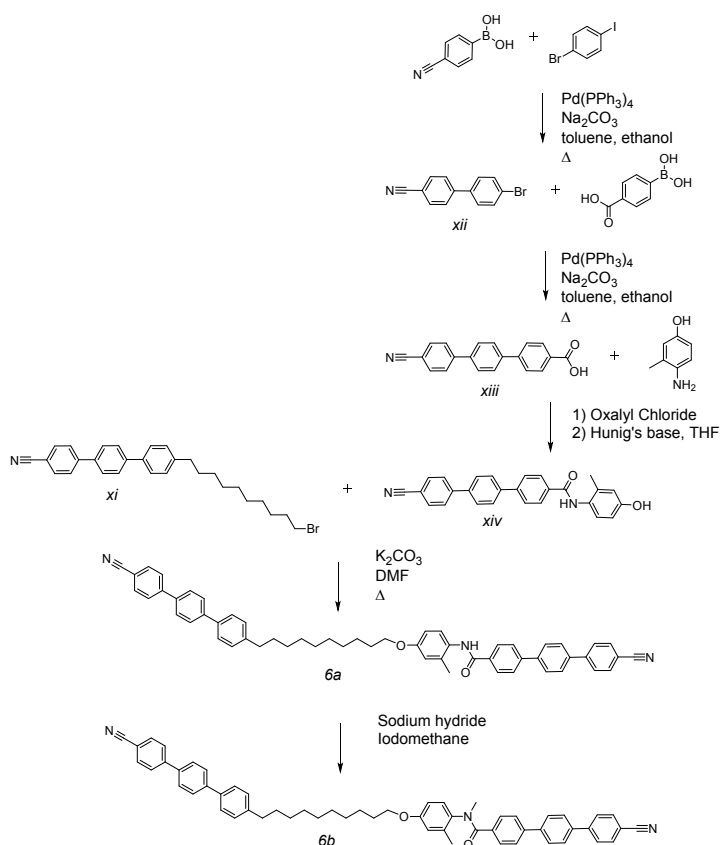
Elemental analysis: Calculated for: C<sub>51</sub>H<sub>49</sub>N<sub>3</sub>O<sub>2</sub> C 83.23 %, H 6.71 %, N 5.71 %. Found: C 81.95 %, H 6.08 %, N 5.33 %

$\nu_{max}/\text{cm}^{-1}$ : 2922 (CH<sub>2</sub>), 2852 (CH<sub>2</sub>), 2224 (CN), 1639 (CO), 1005 (Ar), 811 (Ar).

$\delta_H$  (400 MHz, Chloroform-*d*) 7.81 – 7.65 (10 H, m, Ar-H), 7.60 (4 H, dd,  $J$  14.3, 7.9. Ar-H), 7.41 (4 H, d,  $J$  2.1, Ar-H), 7.30 (2 H, d,  $J$  9.1, Ar-H), 6.99 (1 H, d,  $J$  8.5, Ar-H), 6.67 (1 H, d,  $J$  2.4, Ar-H), 6.64 (1 H, m, Ar-H), 3.89 (2 H, t,  $J$  6.6, CH<sub>2</sub>-O), 3.39 (3 H, d,  $J$  1.9, N-CH<sub>3</sub>), 2.68 (2 H, t,  $J$  7.8, CH<sub>2</sub>-Ar), 2.21 (3 H, s, Ar-CH<sub>3</sub>), 1.76 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-O), 1.68 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-Ar), 1.48 – 1.39 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O), 1.34 (10 H, d,  $J$  15.4).

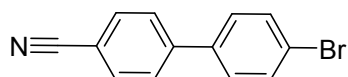
$\delta$  C (101 MHz, Chloroform-d) 170.16, 158.28, 145.20, 144.60, 142.65, 141.50, 139.87, 137.64, 137.50, 136.32, 136.12, 136.00, 132.65 (2C), 132.56 (2C), 129.42, 129.11 (2C), 128.98 (2C), 127.66 (2C), 127.60 (2C), 127.57 (2C), 127.53 (2C), 126.91 (2C), 126.38 (2C), 118.97, 118.77, 116.73, 112.82, 111.29, 110.86, 68.12, 37.87, 35.65, 31.49, 29.55, 29.52 (3C), 29.38, 29.23, 26.03, 18.06.

Synthesis of 3<sup>4</sup>-Cyano-N-(4-[[10-(3<sup>4</sup>-cyano[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-yl)decyl]oxy}-2-methylphenyl)[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-carboxamide **6a**, and 3<sup>4</sup>-Cyano-N-(4-[[10-(3<sup>4</sup>-cyano[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-yl)decyl]oxy}-2-methylphenyl)-N-methyl[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-carboxamide, **6b**



Scheme S6: Synthesis of compounds **6a** and **6b**

4-Bromo-4'-cyanobiphenyl **xii**



To a 100 ml round bottom flask was added 4-bromoiodobenzene (2.83 g, 10 mmol), 4-cyanophenylboronic acid (1.47 g, 10 mmol) in a mixture of toluene (40 ml), ethanol (10 ml), and aqueous sodium carbonate (2M, 20 ml) and sparged with argon for one hour. To this was added tetrakis(triphenylphosphine) palladium (0) (0.116 g, 1 mol %) and the mixture heated to 85 °C under an argon atmosphere. The reaction was followed by TLC (50:50 DCM: PE R<sub>f</sub> 0.42). After 26 h the reaction was allowed to cool to RT and the solvents were removed *in vacuo*, and the crude product was purified by column chromatography (50:50 DCM: PE R<sub>f</sub> 0.42). Yield 1.8 g, (70 %).

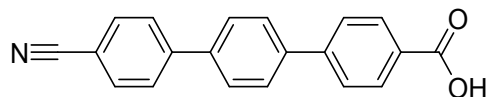
MP 158 °C

$\nu_{max}/\text{cm}^{-1}$ : 2226 (CN), 1003 (Ar), 814 (Ar).

$\delta$  H (400 MHz, Chloroform-d) 7.76 (2 H, d, J 8.5, Ar-H), 7.68 (2 H, d, J 8.5 Ar-H), 7.64 (2 H, d, J 8.5 Ar-H), 7.48 (2 H, d, J 8.5 Ar-H).

$\delta$  C (101 MHz, Chloroform-d) 144.44, 138.07, 132.73 (2C), 132.30 (2C), 128.78 (2C), 127.55 (2C), 123.19, 118.75, 111.36.

*3<sup>4</sup>-Cyanof[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-carboxylic acid xiii*



To a 250 ml round bottom flask was added *xii* (1.747 g, 6.8 mmol), 4-carboxybenzeneboronic acid (1.273 g, 7.6 mmol) and tetrakis(triphenylphosphine) palladium (0) (200 mg, 2.5 mol %) in a mixture of toluene (40 ml), ethanol (40 ml), and aqueous sodium carbonate (2M, 20 ml) and heated to 85 °C under an argon atmosphere. The reaction was stopped after 53 h and was cooled to RT and HCl (8ml) was added slowly. The grey precipitate was collected by vacuum filtration and added to water (50 ml). This was neutralised with a few drops of 1M NaOH and the product collected by vacuum filtration. Yield 1.8 g, (89 %).

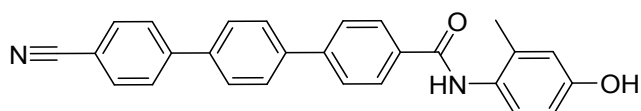
MP 301 °C

$\nu_{max}/\text{cm}^{-1}$ : 3332 (OH), 2247 (CN), 1683 (C=O), 1003 (Ar), 815 (Ar).

$\delta$  H (400 MHz, DMSO-d<sub>6</sub>) 13.02 (1 H, br, OH), 8.05 (2 H, d, J 8.2 Ar-H), 7.97 (4 H, d, J 1.5 Ar-H), 7.89 (5 H, d, J 11.1 Ar-H).

$\delta_c$  (101 MHz, DMSO- $d_6$ ) 167.54, 144.32, 143.83, 139.67, 138.42, 133.38 (2C), 130.48 (2C), 130.37, 128.22 (2C), 128.16 (2C), 127.98 (2C), 127.28 (2C), 119.32, 110.69.

3<sup>4</sup>-Cyano-N-(4-hydroxy-2-methylphenyl)[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-carboxamide *xiv*



Compound *xiii* (1.104 g, 3.7 mmol) was dried by azeotropic distillation with toluene (3 x 5 ml). This was then dissolved in toluene (13 ml) and oxalyl chloride (0.5 ml, 5.6 mmol) was added, along with a catalytic amount of DMF and stirred under an argon atmosphere at 40 °C for 2 hours. The reaction was allowed to cool to room temperature and the excess toluene and oxalyl chloride was removed under vacuum (3 mmHg).

4-Amino-3-methylphenol (0.49g, 4.0 mmol) was dried by azeotropic distillation with toluene (3 x 5 ml), then dissolved in dry THF (40 ml), cooled to 0 °C in an ice bath and Hunig's base (0.6 ml, 3.4 mmol) was added. The acid chloride was dissolved in THF (40 ml) and added dropwise to the reaction mixture. After addition was complete, the ice bath was removed and the reaction continues at room temperature. After 48 hours the THF was removed *in vacuo*, then DCM (100 ml) and water (50 ml) was added and the precipitate was collected by vacuum filtration. Yield 1.34 g (90%).

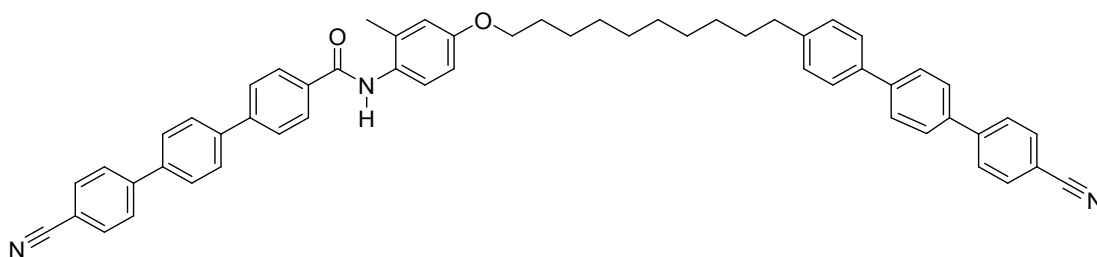
Cr 284 N (decomp.)

$\nu_{max}/\text{cm}^{-1}$ : 3346 (NH), 3273 (OH), 2227 (CN), 1635 (C=O), 1605 (NH/ amide II), 1005 (Ar), 819 (Ar).

$\delta_H$  (400 MHz, DMSO- $d_6$ ) 9.76 (1 H, br, OH), 9.31 (1 H, br, NH), 8.09 (2 H, d, *J* 8.1, Ar-H), 7.97 (4 H, d, *J* 1.3, Ar-H), 7.91 (6 H, m, Ar-H), 7.08 (1 H, d, *J* 8.3, Ar-H), 6.68 (1 H, d, *J* 2.6, Ar-H), 6.62 (1 H, dd, *J* 8.3, 2.6, Ar-H), 2.15 (3 H, s, Ar-CH<sub>3</sub>).

$\delta_c$  (101 MHz, DMSO- $d_6$ ) 165.38, 155.98, 144.40, 139.85, 138.23, 135.86, 134.23, 133.39 (2C), 128.74 (2C), 128.60, 128.21 (2C), 128.07 (2C), 127.97 (2C), 127.03 (2C), 119.34, 117.08, 113.14, 110.64, 18.49.

*3<sup>4</sup>-Cyano-N-(4-{{10-(3<sup>4</sup>-cyano[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-yl)decyl}oxy)-2-methylphenyl)[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-carboxamide 6a*



A mixture of *xi* (0.352 g, 0.74 mmol) and *xiv* (0.298 g, 0.74 mmol) was dried by azeotropic distillation with toluene (3 x 5 ml). To this was added  $K_2CO_3$  (0.283 g, 2.1 mmol), KI (0.105 g 0.7 mmol), and dry DMF (25 ml). The reaction was heated to 90 °C and followed by TLC (50: 50 DCM: PE as eluent,  $R_f$  0.08). When reaction was deemed to be complete (27 h), the mixture was allowed to cool to RT and added to a mix of water (20 ml) and HCl (1 M, 40 ml). The precipitate was collected by vacuum filtration and purified by sequential column chromatography (eluent a) DCM, b) chloroform, c) ethanol). Yield 250 mg, (42 %).

Cr 186 °C N 386 °C I

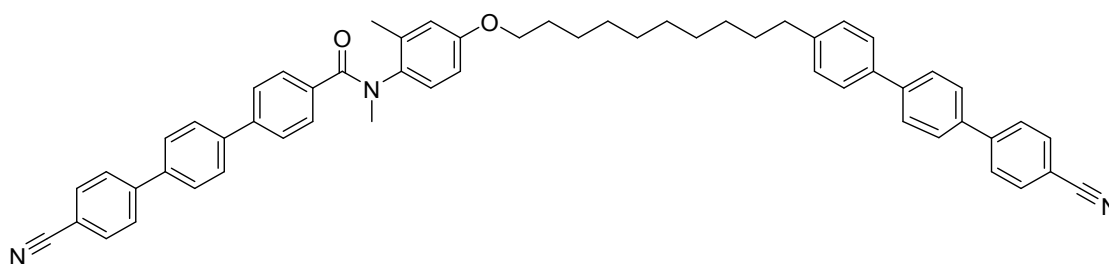
Calculated for  $C_{56}H_{51}N_3O_2$ : C 84.28% H 6.44 % N 5.27 % found C 83.87 % H 6.56 % N 4.96 %.

$\nu_{max}/cm^{-1}$ : 3301 (NH), 2920 ( $CH_2$ ), 2850 ( $CH_2$ ), 2226 (CN), 1644 (C=O), 1605 (NH/amide II), 1003 (Ar), 819 (Ar).

$\delta_{\text{H}}$  (400 MHz, Chloroform-*d*) 8.00 (2 H, d, *J* 7.9, Ar-H), 7.75 (18 H, d, *J* 9.2 Ar-H), 7.67 (2 H, d, *J* 8.5 Ar-H), 7.57 (3 H, d, *J* 7.9 Ar-H), 7.30 (2 H, d, *J* 7.7 Ar-H), 6.81 (2 H, d, *J* 7.4 Ar-H), 3.96 (2 H, t, *J* 6.7, O-CH<sub>2</sub>), 2.68 (2 H, t, *J* 7.9, Ar-CH<sub>2</sub>), 2.33 (3 H, s, Ar-CH<sub>3</sub>), 1.79 (2 H, t, *J* 7.3, O-CH<sub>2</sub>-CH<sub>2</sub>), 1.68 (2 H, p, *J* 7.5), 1.47 (2 H, p, *J* 7.5, Ar-CH<sub>2</sub>-CH<sub>2</sub>), 1.43 – 1.31 (10 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>).

$\delta_{\text{C}}$  (101 MHz, CDCl<sub>3</sub>) 165.38, 157.06, 145.22, 144.88, 143.50, 142.71, 141.54, 140.21, 138.82, 137.60, 137.46, 134.03, 132.72 (2C), 132.64 (2C), 132.40, 129.00 (2C), 128.38, 127.91 (2C), 127.81 (2C), 127.74 (2C), 127.63 (2C), 127.61 (2C), 127.55 (2C), 127.53 (2C), 127.36 (2C), 126.90 (2C), 125.54, 118.99, 118.87, 116.76, 112.34, 111.20, 110.83, 68.20, 35.64, 31.48, 29.54, 29.48 (2C), 29.37, 29.33, 29.30, 26.04, 18.21.

*3*<sup>4</sup>-Cyano-*N*-(4-[[10-(*3*<sup>4</sup>-cyano[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-yl)decyl]oxy]-2-methylphenyl)-*N*-methyl[1<sup>1</sup>,2<sup>1</sup>:2<sup>4</sup>,3<sup>1</sup>-terphenyl]-1<sup>4</sup>-carboxamide **6b**



Compound **6a** (0.240 g, 0.3 mmol) was dried by azeotropic distillation with toluene (3 x 5 ml). Sodium hydride (60% dispersion, 0.079 g, 2.0 mmol) was washed with petroleum ether (3 x 1 ml). Compound **6a** was dissolved in dry THF (10 ml) and added to the NaH under an argon atmosphere. When reaction was complete (fizzing stops) the reaction was left for a further 30 min and then methyl iodide (0.1 ml, 1.6 mmol) was added and the reaction was allowed to continue for 15 h. The excess NaH was quenched with a few drops of propanol, and the THF was removed under vacuum (3 mmHg). The crude solid was dissolved in ethyl acetate (50 ml) and washed with water (3 x 20 ml). The ethyl acetate was removed *in vacuo* and the crude solid purified by column chromatography (50:50 EtOAc: PE as eluent, *R<sub>f</sub>* 0.63). Yield 130 mg, (43 %).

Calculated for C<sub>57</sub>H<sub>53</sub>N<sub>3</sub>O<sub>2</sub> C 84.31% H 6.58 % N 5.17 %. Found: C 84.08% H 6.61 % N 4.92 %.

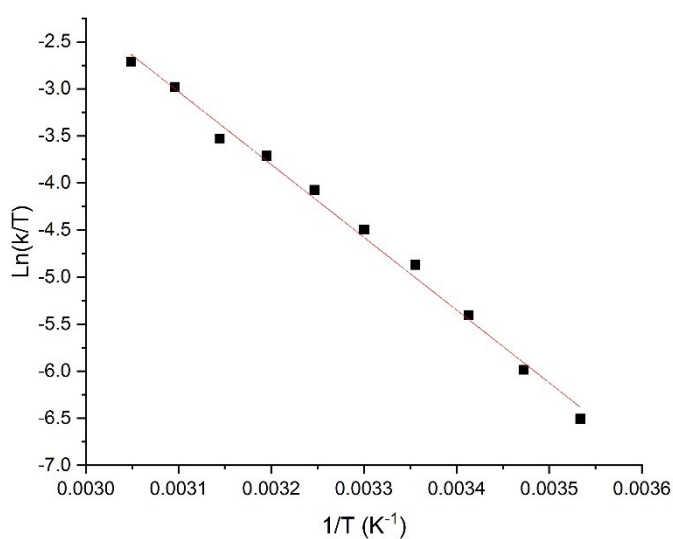
Cr 177 °C | (N 142 °C).

$\nu_{max}/cm^{-1}$ : 2923 (CH<sub>2</sub>), 2854 (CH<sub>2</sub>), 2224 (CN), 1633 (C=O), 1604 (NH/amide II), 1003 (Ar), 814 (Ar).

$\delta_H$  (400 MHz, Chloroform-*d*) 7.81 – 7.62 (18 H, m, Ar-H), 7.58 (2 H, d, *J* 7.9 Ar-H), 7.45 (2 H, d, *J* 8.2, Ar-H), 7.41 (2 H, d, *J* 8.2, Ar-H), 7.30 (2 H, d, *J* 7.1, Ar-H), 7.01 (1 H, d, *J* 8.5, Ar-H), 6.68 (1 H, s, Ar-H), 6.65 (1 H, d, *J* 8.6, Ar-H), 3.89 (2 H, t, *J* 6.6, O-CH<sub>2</sub>), 3.40 (3 H, d, *J* 1.9, N-CH<sub>3</sub>), 2.67 (2 H, t, *J* 7.8, Ar-CH<sub>2</sub>), 2.22 (3 H, s, Ar-CH<sub>3</sub>), 1.77 (2 H, p, *J* 7.2, O-CH<sub>2</sub>-CH<sub>2</sub>), 1.66 (2 H, p, *J* 9.3 Ar-CH<sub>2</sub>-CH<sub>2</sub>), 1.38 (12 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>)

$\delta_C$  (101 MHz, Chloroform-*d*) 170.45, 158.20, 145.18, 144.95, 142.64, 141.47, 140.94, 140.45, 138.31, 137.64, 137.49, 136.31, 136.01, 135.31, 132.65 (4C), 129.43, 129.02 (2C), 128.97 (2C), 127.70 (2C), 127.59 (2C), 127.57 (2C), 127.56 (2C), 127.53 (2C), 126.90 (2C), 126.12 (2C), 118.99, 118.91, 116.69, 112.78, 111.00, 110.84, 68.09, 37.91, 35.64, 31.50, 29.55, 29.51 (2C), 29.38 (2C), 29.23, 26.03, 18.09.

### VT NMR of **5b** in deuterated DMF



Slope  $-7730 \pm 216$  K

Intercept  $20.9 \pm 0.710$

R<sup>2</sup> 0.994

Figure S. 1: The Eyring plot of compound **5b** in DMF.



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