Supplementary Information

Liquid crystal trimers containing tertiary benzanilide groups.

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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^{-1} unless otherwise specified. FT-IR spectra were obtained using a Perkin Elmer spectrum 2 FTIR with an ATR diamond cell. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz Bruker Ultrashield NMR spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) or a 400 MHz Bruker Ascend NMR spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) using either $CDCl_3$ or DMSO-d_6 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 (^{3}J). Ar refers to an aromatic ring. 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

The phase behaviour of the materials was studied using differential scanning calorimetry (DSC) with a Mettler Toledo DSC3 differential scanning calorimeter equipped with a TSO 801RO sample robot and calibrated with indium and zinc standards. The heating and cooling rates were 10 K min^{-1} and the transition temperatures and their associated enthalpy changes were extracted from heating traces unless otherwise noted.

Optical textures were used to identify the liquid crystal phases, and these were observed using an Olympus BH2 polarising optical microscope equipped with a Linkam TMS 92 heating stage. Optical birefringence was measured with a setup based on a photoelastic modulator (PEM-90, Hinds) working at a modulation frequency f = 50 kHz; a halogen lamp (Hamamatsu LC8) equipped with narrow bandpass filters was used as a light source. The signal from a photodiode (FLC Electronics PIN-20) was deconvoluted with a lock-in amplifier (EG&G 7265) into 1 f and 2 f components to yield a retardation induced by the sample. Knowing the sample thickness, the retardation was recalculated into optical birefringence. Samples were prepared in 3-micron-thick cells with planar anchoring. The alignment quality was checked prior to measurement by inspection under the polarised optical microscope.

AFM measurements were performed using a Bruker Dimension Icon Microscope working in tapping or scan assist mode and cantilevers with elastic constant of 0.4 N/m were applied.

X-ray diffraction measurements were carried out using a Bruker D8 GADDS system with CuKα radiation, Goebel mirror monochromator, point beam collimator, and VANTEC2000 area detector. SAXS measurements were performed on a Bruker Nanostar system using CuKα radiation and patterns were collected with an area detector VANTEC2000.

Synthetic procedures

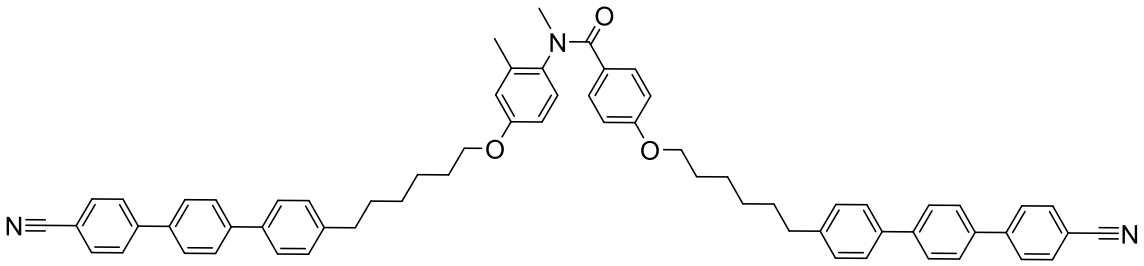
The tertiary amides reported here were prepared by alkylation of the corresponding secondary benzanilide, the synthesis of which is reported elsewhere.[1]

General method: N-alkylation

The amide was dried by azeotropic distillation with toluene (3 x 2ml). Sodium hydride (60% dispersion, 2.5 eq) was washed with petroleum ether (3 x 1 ml). The amide was dissolved in dry THF 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 the appropriate alkyl iodide or benzyl bromide (2.5 eq) was added and the reaction was followed by TLC. When the reaction was deemed complete 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 chloroform (30 ml) and washed with water (3 x 25 ml). The organic layer is dried and removed *in vacuo*. The crude solid was dissolved in the minimum amount of chloroform (2-

10 ml) and methanol added dropwise until a precipitate begins to form. This was collected by vacuum filtration.

4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-*N*-(4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-2-methylphenyl)-*N*-methylbenzamide 1



amide	0.415 g	0.4 mmol
NaH	0.045 g	1.1 mmol
CH_3I	0.08 mL	1.1 mmol
THF	15 mL	

12 h at RT

Yield 0.318 g (85%).

Cr 102 °C Sm 132 °C N 182 °C I

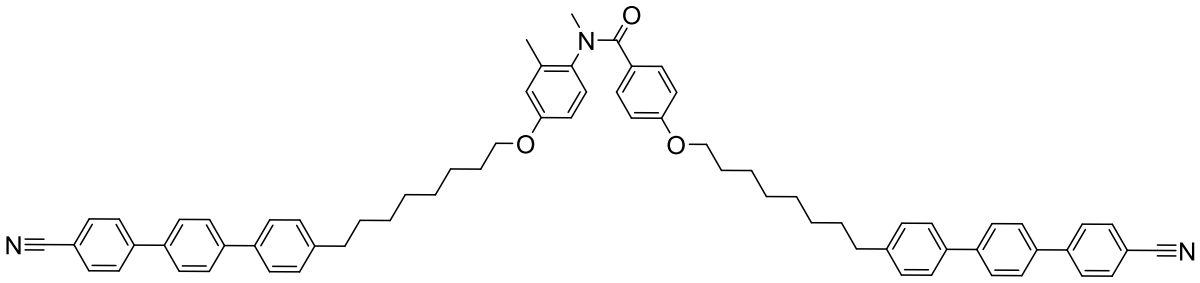
M/Z Calculated mass [M+H]: 932.4791 ($C_{65}H_{62}N_3O_3$) Found 932.4828 Difference 4.0 ppm.

ν_{max}/cm^{-1}: 2926 (CH_2), 2854 (CH_2), 2226 (CN), 1635 (C=O), 1604 (Ar), 1004 (Ar), 812 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (overlapping doublets, 8H, Ar-H), 7.72 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.68 (d, *J* = 8.5 Hz, 4H, Ar-H), 7.57 (overlapping doublets, 4H, Ar-H), 7.29 (overlapping doublets, 6H, Ar-H), 6.96 (6.97 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.66 (overlapping doublets and singlet, 4H, Ar-H), 3.90 (overlapping triplets, 4H, O-$\underline{CH_2}$), 3.35 (s, 3H, N-CH_3), 2.69 (overlapping triplets, 4H, Ar-$\underline{CH_2}$), 2.16 (s, 3H, Ar-CH_3), 1.81 – 1.64 (m, 8H, CH_2-$\underline{CH_2}$), 1.59 – 1.41 (m, 8H, CH_2-CH_2-$\underline{CH_2}$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.45, 159.99, 157.98, 145.18, 145.16, 142.40 (2C), 141.44, 141.43, 137.65, 137.62, 137.55, 137.53, 136.89, 135.96, 132.64 (4C), 130.40 (2C), 129.29, 128.98 (4C), 127.94, 127.58 (4C), 127.56 (4C), 127.52 (4C), 126.92 (4C), 118.97 (2C), 116.66, 113.29 (2C), 112.76, 110.84, 110.82, 67.97, 67.78, 38.02, 35.50, 35.49, 31.34, 31.31, 29.18, 29.08, 29.02, 28.99, 25.92, 25.87, 18.03.

4-{[8-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)octyl]oxy}-*N*-(4-{[8-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)octyl]oxy}-2-methylphenyl)-N-methylbenzamide 2



Amide	0.360	0.37 mmol
NaH	0.037 g	0.93 mmol
CH_3I	0.05 mL	0.89 mmol
THF	20 mL	
17 h at RT		
Yield 0.079 g (22%)		

Cr 106 °C Sm 148 °C N 178 °C I

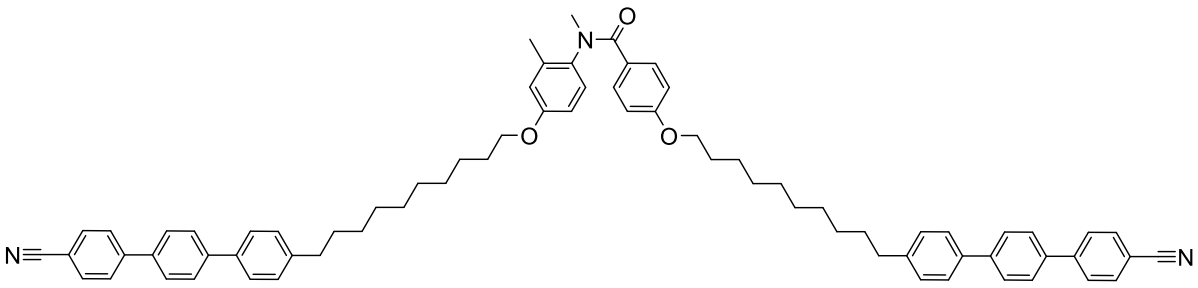
M/Z Calculated mass [M+Na]: 1010.5237 ($C_{69}H_{69}N_3O_3Na$) Found 1010.5252. Difference 1.5 ppm.

ν_{max} /cm^{-1}: 2926 (CH_2), 2854 (CH_2), 2226 (CN), 1636 (C=O), 1604 (Ar), 1004 (Ar), 812 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (overlapping doublets, 8H, Ar-H), 7.72 (d, *J* = 9.0 Hz, 4H, Ar-H), 7.68 (d, *J* = 9.0 Hz, 4H, Ar-H), 7.58 (overlapping doublets, 4H, Ar-H), 7.31 (d, *J* = 2.7 Hz, 4H, Ar-H), 7.26 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.96 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.64 (overlapping doublets and singlet, 4H, Ar-H), 3.89 (overlapping triplets, 4H, O-$\underline{CH_2}$), 3.34 (s, 3H, N-CH_3), 2.68 (overlapping triplets, 4H, Ar-$\underline{CH_2}$), 2.15 (s, 3H, Ar-CH_3), 1.79 – 1.74 (m, 4H, O-CH_2-$\underline{CH_2}$), 1.77 – 1.64 (m, 4H, Ar-CH_2-$\underline{CH_2}$), 1.45 – 1.34 (m, 16H, CH_2-CH_2-$\underline{CH_2}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.42, 160.02, 158.00, 145.20, 145.18, 142.60 (2C), 141.50, 141.48, 137.65, 137.62, 137.52, 137.49, 136.91, 135.97, 132.64 (4C), 130.41 (2C), 129.29, 128.98 (4C), 127.95, 127.60 (4C), 127.56 (4C), 127.52 (4C), 126.91 (4C), 118.97 (2C), 116.66, 113.29 (2C), 112.75, 110.87, 110.85, 68.06, 67.86, 38.02, 35.63, 35.61, 31.46, 31.43, 29.44, 29.40, 29.33, 29.29 (2C), 29.25 (2C), 29.15, 26.05, 25.99, 18.04.

4-{[10-(3⁴-cyano[1¹,2¹:2⁴,3¹-terphenyl]-1⁴-yl)decyl]oxy}-*N*-(4-{[10-(3⁴-cyano[1¹,2¹:2⁴,3¹-terphenyl]-1⁴-yl)decyl]oxy}-2-methylphenyl)-N-methylbenzamide 3



Amide	0.400	0.4 mmol
NaH	0.050 g	1.3 mmol
CH_3I	0.06 mL	1.0 mmol
THF	50 mL	

15 h at RT

Recrystalised 25 ml EtOH

Yield 0.236 g (57%)

Cr 100 °C Sm 148 °C N 178 °C I

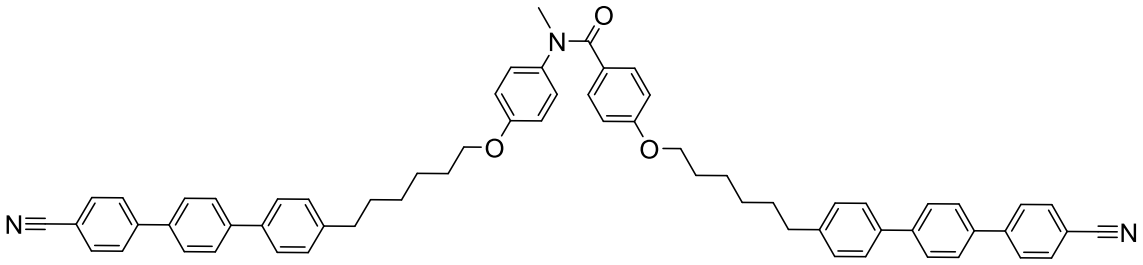
M/Z Calculated mass [M+H]: 1044.6043 ($C_{73}H_{78}N_3O_3$) Found 1044.6084. Difference 3.9 ppm.

ν_{max}/cm^{-1}: 2926 (CH_2), 2854 (CH_2), 2225 (CN), 1634(C=O), 1604 (Ar), 1004 (Ar), 812 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (overlapping doublets, 8H, Ar-H), 7.63 (d, *J* = 8.3 Hz, 4H, Ar-H), 7.59 (d, *J* = 8.3 Hz, 4H, Ar-H), 7.48 (d, *J* = 7.8 Hz, 4H, Ar-H), 7.21 (overlapping doublets, 6H, Ar-H), 6.87 (d, *J* = 8.9 Hz, 1H, Ar-H), 6.55 (overlapping doublet and singlet, 4H, Ar-H), 3.79 (overlapping triplets, 4H, O-$\underline{CH_2}$), 3.25 (s, 3H, N-CH_3), 2.58 (t, *J* = 8.0 Hz, 4H, Ar-$\underline{CH_2}$), 2.05 (s, 3H, Ar-CH_3), 1.81 – 1.52 (m, 12H, CH_2-$\underline{CH_2}$), 1.42 – 1.16 (m, 20H, CH_2-CH_2-$\underline{CH_2}$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.54 (HMBC), 160.02, 158.01, 145.21, 145.19, 142.68 (2C), 141.52 (2C), 137.64, 137.62, 137.49, 137.47, 136.90, 135.96, 132.64 (4C), 130.41 (4C), 129.29, 128.98 (4C), 127.60 (4C), 127.56 (4C), 127.52 (4C), 126.94 , 126.90 (4C), 118.97 (2C), 116.66, 113.29 (2C), 112.75, 110.85, 68.09, 67.89, 38.02, 35.64, 31.50, 31.48, 29.56, 29.53, 29.53 (2C), 29.49, 29.49, 29.39, 29.38, 29.36, 29.34, 29.26, 29.16, 26.04, 26.00, 18.04.

4-{[6-(3⁴-cyano[1¹,2¹:2⁴,3¹-terphenyl]-1⁴-yl)hexyl]oxy}-*N*-(4-{[6-(3⁴-cyano[1¹,2¹:2⁴,3¹-terphenyl]-1⁴-yl)hexyl]oxy}phenyl)-*N*-methylbenzamide 4



Amide	0.250	0.29 mmol
NaH	0.029 g	0.75 mmol
CH_3I	0.06 mL	1.0 mmol
THF	50 mL	

62 h at RT

Yield 0.075 g (28 %).

M/Z Calculated mass [M+H]: 918.4635 ($C_{64}H_{60}N_3O_3$) Found 918.4636. Difference 0.1 ppm.

M/Z Calculated mass [M+Na]: 940.4454 ($C_{64}H_{59}N_3O_3Na$) Found 940.4420. Difference -3.6 ppm.

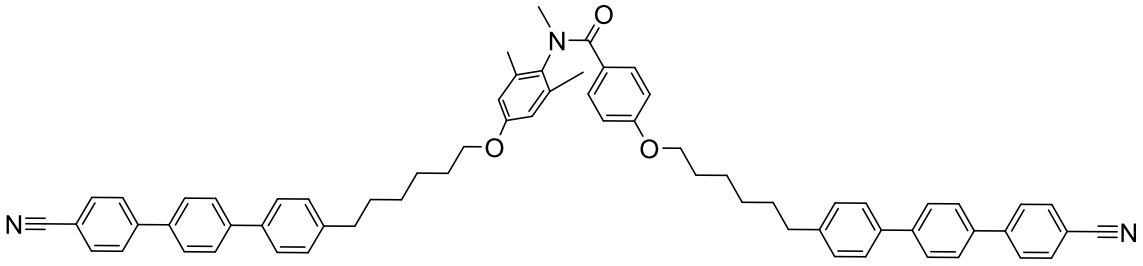
Cr 92 °C N 201 °C I

ν_{max}/cm^{-1}: 2926 (CH_2), 2854 (CH_2), 2226 (CN), 1636 (C=O), 1604 (Ar), 1004 (Ar), 813 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (overlapping doublets, 8H, Ar-H), 7.72 (d, *J* = 8.5 Hz, 4H, Ar-H), 7.68 (d, *J* = 8.5 Hz, 4H, Ar-H), 7.57 (overlapping doublets, 4H, Ar-H), 7.29 (overlapping doublets, 6H, Ar-H), 6.97 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.76 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.68 (d, *J* = 8.8 Hz, 2H, Ar-H), 3.91 (t, *J* = 6.4 Hz, 4H, O-$\underline{CH_2}$), 3. 3.45 (s, 3H, N-CH_3), 45 (s, 3H), 2.69 (overlapping triplets, 4H, Ar-$\underline{CH_2}$), 1.85 – 1.62 (m, 8H, CH_2-$\underline{CH_2}$), 1.58 – 1.35 (m, 8H, CH_2-CH_2-$\underline{CH_2}$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.34, 160.02, 157.30, 145.21, 145.19, 142.40, 141.46, 141.44, 137.68, 137.65, 137.57, 137.55, 132.71, 132.64 (4C), 132.31, 130.83 (2C), 128.98 (4C), 127.94, 127.87, 127.80, 127.59 (4C), 127.57 (4C), 127.53 (4C), 126.93 (4C), 118.96 (2C), 114.91, 114.21, 113.44 (2C), 110.86 (2C), 68.10, 67.82, 38.91, 35.50, 35.43, 31.32, 31.27, 29.15, 29.09, 29.02, 28.99, 25.92, 25.88.

4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-*N*-(4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-2,6-dimethylphenyl)-*N*-methylbenzamide 5



Amide	0.470	0.5 mmol
NaH	0.058 g	1.5 mmol
CH_3I	0.08 mL	1.3 mmol
THF	50 mL	
14 h at RT		

Yield 0.144 g (30 %).

Cr 98 °C Sm 130 °C N 175 °C I

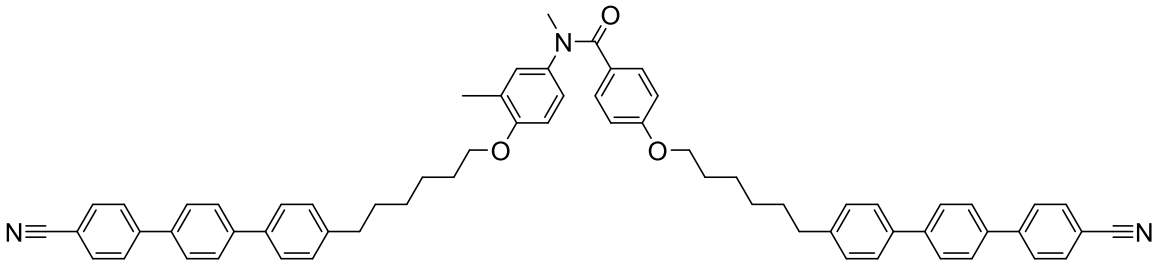
M/Z Calculated mass [M+Na]: 968.4767 ($C_{66}H_{63}N_3O_3Na$) Found 968.4747. Difference -2.1 ppm.

ν_{max}/cm^{-1}: 2922 (CH_2), 2851 (CH_2), 2227 (CN), 1650 (C=O), 1604 (Ar), 1003 (Ar), 810 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (overlapping doublets, 8H, Ar-H), 7.72 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.68 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.57 (overlapping doublets, 4H, Ar-H), 7.28 (overlapping doublets, 6H, Ar-H), 6.65 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.54 (s, 2H, Ar-H), 3.89 (overlapping triplets, 4H, O-$\underline{CH_2}$), 3.28 (s, 3H, N-CH_3), 2.69 (overlapping triplets, 4H, Ar-$\underline{CH_2}$), 2.17 (s, 6H, Ar-CH_3), 1.80 – 1.65 (m, 8H, CH_2-$\underline{CH_2}$), 1.52 – 1.43 (m, 8H, CH_2-CH_2-$\underline{CH_2}$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.18, 160.18, 157.85, 145.19, 145.17, 142.40 (2C), 141.47, 141.44, 137.68, 137.65, 137.58, 137.56, 136.48 (2C), 135.78, 132.64 (4C), 129.95 (2C), 128.98 (4C), 127.84, 127.60 (4C), 127.56 (4C), 127.52 (4C), 126.93 (4C), 118.97 (2C), 114.32 (2C), 113.24 (2C), 110.88, 110.86, 67.84, 67.78, 36.74, 35.52, 35.50, 31.36, 31.32, 29.23, 29.09, 29.05, 29.01, 25.94, 25.89, 18.36 (2C).

4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-*N*-(4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-3-methylphenyl)-*N*-methylbenzamide 6



Amide	0.461	0.5 mmol
NaH	0.054 g	1.4 mmol
CH_3I	0.08 mL	1.3 mmol
THF	20 mL	
13 h at RT		

Yield 0.045g (10 %).

Cr 97 °C Sm 123 °C N 180 °C I

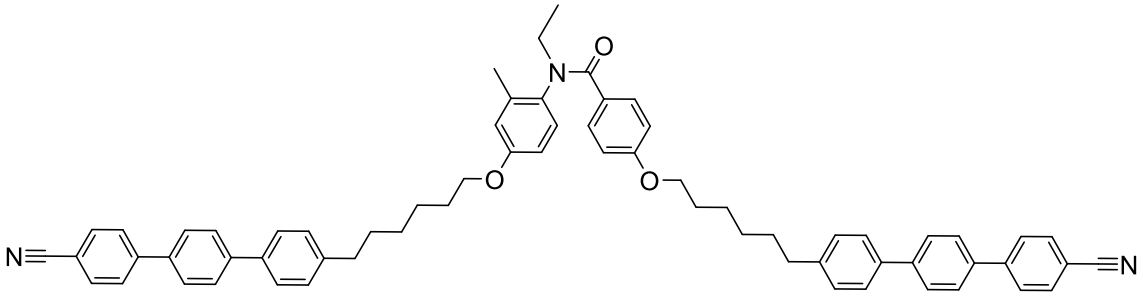
M/Z Calculated mass [M+H]: 932.4791 ($C_{65}H_{62}N_3O_3$) Found 932.4767. Difference -2.6 ppm.

ν_{max}/cm^{-1}: 2924(CH_2), 2853 (CH_2), 2227 (CN), 1639 (C=O), 1604 (Ar), 1004 (Ar), 811 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (overlapping doublets, 8H, Ar-H), 7.72 (d, *J* = 8.7 Hz, 4H, Ar-H), 7.68 (d, *J* = 8.7 Hz, 4H, Ar-H), 7.57 (overlapping doublets, 4H, Ar-H), 7.30 (d, *J* = 5.0 Hz, 4H, Ar-H), (7.29 HSQC, 2H, Ar-H), 6.90 (d, *J* = 2.6 Hz, 1H, Ar-H), 6.77 (dd, *J* = 8.6, 2.7 Hz, 1H, Ar-H), 6.67 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.63 (d, *J* = 8.6 Hz, 1H, Ar-H), 3.91 (t, *J* = 6.4 Hz, 4H, O-$\underline{CH_2}$), 3.44 (s, 3H, N-CH_3), 2.69 (q, *J* = 7.2 Hz, 4H, Ar-$\underline{CH_2}$), 2.16 (s, 3H, Ar-CH_3), 1.87 – 1.64 (m, 8H, CH_2-$\underline{CH_2}$), 1.62 – 1.39 (m, 8H, CH_2-CH_2-$\underline{CH_2}$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.24, 159.93, 155.47, 145.19, 145.17, 143.94, 142.40 (2C), 141.47, 141.44, 137.68, 137.65, 137.58, 137.56, 132.65 (4C), 130.81 (2C), 128.98 (4C), 128.81, 128.08, 127.73, 127.59 (4C), 127.57 (4C), 127.52 (4C), 126.93 (4C), 125.26, 118.97 (2C), 113.39 (2C), 110.94, 110.88, 110.86, 68.04, 67.82, 39.00, 35.53, 35.50, 31.38, 31.32, 29.24, 29.10, 29.03, 29.00, 26.03, 25.88, 16.27.

4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-*N*-(4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-2-methylphenyl)-*N*-ethylbenzamide 7



Amide	0.099g	0.11 mmol
NaH	0.022 g	0.55 mmol
C_2H_5I	0.02 mL	0.25 mmol
THF	15 mL	

88 h at RT, then 52 h at 35 °C

Column chromatography 7 % EtOAc / toluene, R_f 0.18

Yield 0.02 g (20 %).

Cr 100 °C Sm 123 °C N 154 °C I

M/Z Calculated mass [M+H]: 946.4948 ($C_{66}H_{64}N_3O_3$) Found 946.4916. Difference -3.4 ppm.

M/Z Calculated mass [M+Na]: 968.4767 ($C_{66}H_{63}N_3O_3Na$) Found 968.4720. Difference -4.9 ppm.

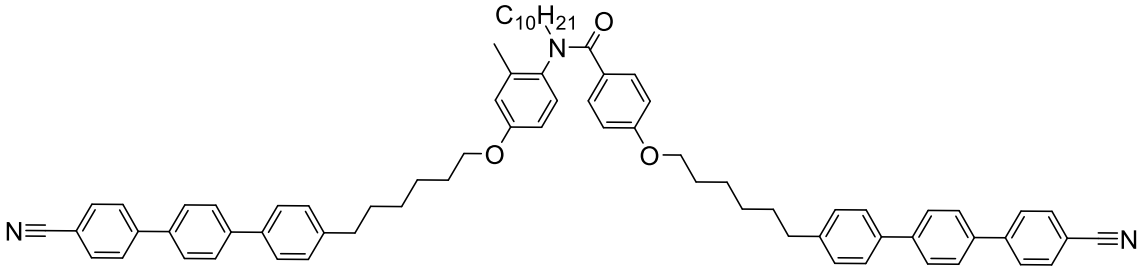
ν_{max}/cm^{-1}: 2925 (CH_2), 2854 (CH_2), 2226 (CN), 1635 (C=O), 1604 (Ar), 1004 (Ar), 812 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (overlapping doublets, 8H, Ar-H), 7.72 (d, *J* = 8.2 Hz, 4H, Ar-H), 7.68 (d, *J* = 8.2 Hz, 4H, Ar-H), 7.58 (overlapping doublets, 4H, Ar-H), 7.27 (overlapping doublets, 6H, Ar-H), 6.97 (d, *J* = 9.0 Hz, 1H, Ar-H), 6.64 (overlapping doublets, *J* = 9.7 Hz, 4H, Ar-H), 4.12 – 4.03 (m, 1H, N-C<u>H</u>), 3.90 (overlapping triplets, 4H, O-<u>CH_2</u>), 3.66 – 3.56 (m, 1H, N-C<u>H</u>), 2.69 (overlapping triplets, 4H, Ar-<u>CH_2</u>), 2.12 (s, 3H, Ar-CH_3), 1.82 – 1.67 (m, 8H, CH_2-<u>CH_2</u>), 1.55 – 1.39 (m, 8H, CH_2-CH_2-<u>CH_2</u>), 1.21 (t, *J* = 7.2 Hz, 3H, CH_2-<u>CH_3</u>).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.78, 159.85, 157.90, 145.19, 145.16, 142.41 (2C), 141.46, 141.44, 137.68, 137.64, 137.57, 137.55, 136.51, 134.99, 132.66 (4C), 130.38 (2C), 130.28, 128.99 (4C), 128.48, 127.60 (4C), 127.58 (4C), 127.53 (4C), 126.94 (4C), 119.00 (2C), 116.57, 113.23 (2C), 112.48, 110.87, 110.84, 67.94, 67.76, 44.96, 35.53, 35.51, 31.38, 31.35, 29.22, 29.10, 29.06, 29.02, 25.95, 25.89, 18.28, 12.50.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.45, 159.99, 157.98, 145.18, 145.16, 142.40 (2C), 141.44, 141.43, 137.65, 137.62, 137.55, 137.53, 136.89, 135.96, 132.64 (4C), 130.40 (2C), 129.29, 128.98 (4C), 127.94, 127.58 (4C), 127.56 (4C), 127.52 (4C), 126.92 (4C), 118.97 (2C), 116.66, 113.29 (2C), 112.76, 110.84, 110.82, 67.97, 67.78, 38.02, 35.50, 35.49, 31.34, 31.31, 29.18, 29.08, 29.02, 28.99, 25.92, 25.87, 18.03.

4-{[6-(3^{4}-cyano[1^{1},2^{1}:2^{4},3^{1}-terphenyl]-1^{4}-yl)hexyl]oxy}-*N*-(4-{[6-(3^{4}-cyano[1^{1},2^{1}:2^{4},3^{1}-terphenyl]-1^{4}-yl)hexyl]oxy}-2-methylphenyl)-*N*-decylbenzamide 8



Amide	0.571 g	0.6 mmol
NaH	0.056 g	1.4 mmol
$C_{10}H_{21}I$	0.05 mL	0.23 mmol
THF	50 mL	

12 h at RT followed by 50 h at reflux

Recrystallise from EtOAc (25 ml), then dissolve in $CHCl_3$ (2 mL) and add MeOH until a precipitate forms.

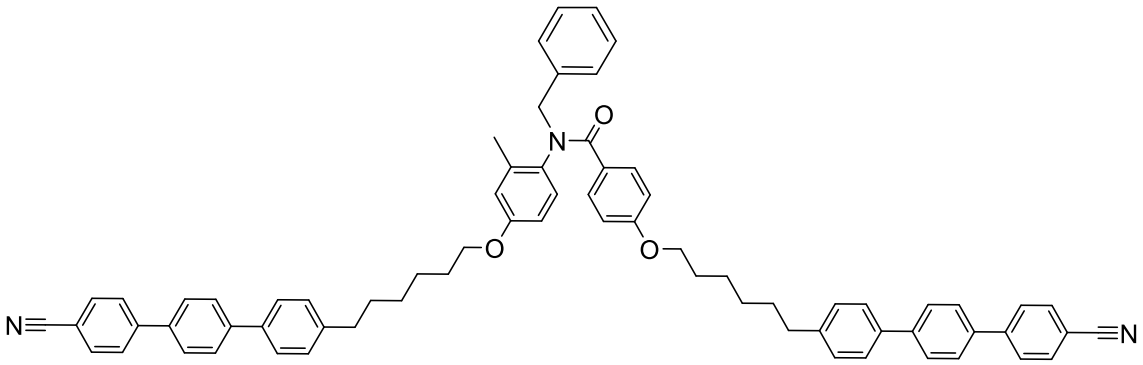
Yield 0.023 g, (4 %)

Cr 108 °C Sm 131 °C N 143 °C I

M/Z Calculated mass [M+Na]: 1080.6019 ($C_{74}H_{79}N_3O_3Na$) Found 1080.6003. Difference -1.5 ppm.

ν_{max}/cm^{-1}: 2928 (CH_2), 2855 (CH_2), 2227 (CN), 1637 (C=O), 1605 (Ar), 1004 (Ar), 812 (Ar).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (overlapping doublets, 8H, Ar-H), 7.71 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.68 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.57 (overlapping doublets, 4H, Ar-H), 7.30 (overlapping doublets, 4H, Ar-H), 7.23 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.97 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.63 (overlapping doublets and singlet, 4H, Ar-H), 4.06 – 4.01 (m, 2H, N-C<u>H</u>), 3.90 (overlapping triplets, 4H, O-<u>CH_2</u>), 3.54 – 3.40 (m, 1H, N-C<u>H</u>), 2.69 (overlapping triplets, 4H, Ar-<u>CH_2</u>), 2.10 (s, 3H, Ar-CH_3), 1.83 – 1.65 (m, 8H, CH_2-<u>CH_2</u>), 1.52 – 1.43 (m, 8H, CH_2-CH_2-<u>CH_2</u>), 1.33 – 1.19 (m, 16H CH_2-CH_2-<u>CH_2</u>), 0.90 (t, *J* = 6.8 Hz, 3H, CH_2-<u>CH_3</u>).
^{13}C NMR (101 MHz, Chloroform-*d*) not all peaks could be identified due to overlapping signals in aliphatic region δ 169.85, 159.81, 157.88, 145.19, 145.17, 142.50, 142.41 (2C), 141.51, 141.47, 141.45, 137.68, 137.64, 137.58, 137.55, 135.37, 132.64 (4C), 130.35 (2C), 130.20, 128.98 (4C), 128.58, 127.61, 127.60 (4C), 127.56 (4C), 127.52 (4C), 126.94 (4C), 118.97 (2C), 116.57, 113.22 (2C), 112.47, 110.88, 110.86, 67.96, 67.77, 50.11, 35.53, 35.50, 31.90, 31.36, 31.32, 29.73, 29.63, 29.56, 29.46, 29.30, 29.22, 29.09, 29.06, 29.00, 27.31, 27.19, 25.95, 25.88, 22.69, 18.27, 14.13.

4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-*N*-(4-{[6-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)hexyl]oxy}-2-methylphenyl)-*N*-benzylbenzamide 9



Amide	0.189 g	0.2 mmol
NaH	0.024 g	0.6 mmol
Benzyl bromide	0.05 mL	0.42 mmol
THF	10 mL	

48 h at RT
Column chromatography (5 % EtOAc / toluene, R_f 0.18)
Yield 0.098 g (50 %).
Cr 111 °C Sm 133 °C N 147 °C I
M/Z Calculated mass [M+H]: 1008.5104 ($C_{71}H_{66}N_3O_3$) Found 1008.5074. Difference -3.0 ppm.

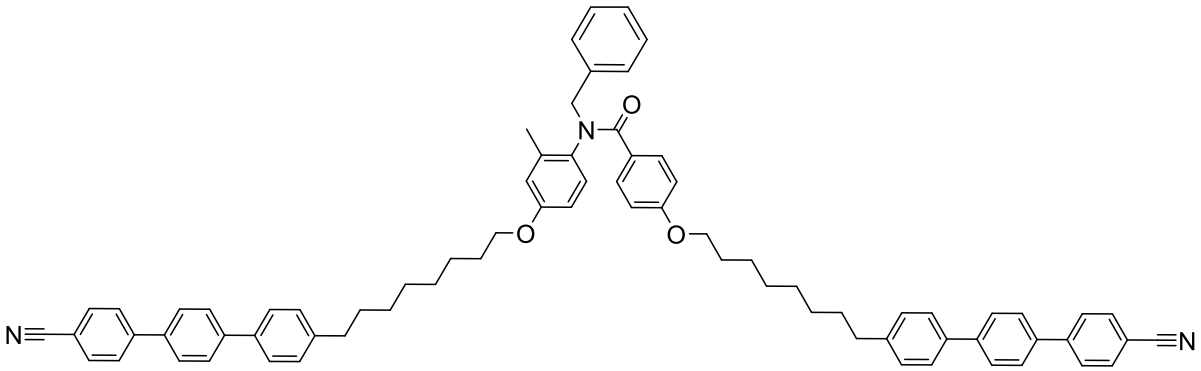
M/Z Calculated mass [M+Na]: 1030.4924 ($C_{71}H_{65}N_3O_3Na$) Found 1030.4950. Difference 2.5 ppm.

ν_{max}/cm^{-1}: 2926 (CH_2), 2855 (CH_2), 2226 (CN), 1633 (C=O), 1604 (Ar), 1004 (Ar), 811 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (overlapping doublets, 8H, Ar-H), 7.72 (d, *J* = 8.2 Hz, 4H, Ar-H), 7.68 (d, *J* = 8.2 Hz, 4H, Ar-H), 7.57 (overlapping doublets, 4H, Ar-H), 7.29 (overlapping peaks, 11H, Ar-H), 6.82 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.63 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.57 (overlapping doublet and singlet, 2H, Ar-H) 5.29 (d, *J* = 14.0 Hz, 1H, N-C<u>H</u>), 4.66 (d, *J* = 13.9 Hz, 1H, N-C<u>H</u>), 3.89 (t, *J* = 5.7 Hz, 4H, O-<u>CH_2</u>), 2.69 (overlapping triplets, 4H, Ar-<u>CH_2</u>), 1.84 (s, 3H, Ar-CH_3), 1.81 – 1.65 (m, 8H, CH_2-<u>CH_2</u>), 1.51 – 1.43 (m, 8H, CH_2-).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.95, 159.99, 157.95, 145.19, 145.16, 142.40 (2C), 141.46, 141.44, 137.68, 137.64, 137.58, 137.55, 137.37, 136.77, 134.96, 132.65 (4C), 130.55 (2C), 130.16 (2C), 129.45 (2C), 128.98 (4C), 128.26, 128.18, 127.59 (4C), 127.57 (4C), 127.52 (4C), 127.36, 126.94 (2C), 126.93 (2C), 118.97 (2C), 116.44, 113.23 (2C), 112.43, 110.88, 110.86, 67.90, 67.78, 53.70, 35.53, 35.50, 31.35, 31.32, 29.22, 29.09, 29.07, 29.00, 25.94, 25.88, 18.02.

4-{[8-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)octyl]oxy}-*N*-(4-{[8-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)octyl]oxy}-2-methylphenyl)-N-benzylbenzamide 10



Amide	0.062	0.063 mmol
NaH	0.032 g	0.80 mmol
Benzyl bromide	0.04 mL	0.71 mmol
THF	10 mL	
48 h at RT		
Yield 0.032 g (48 %)		

Cr 117 °C Sm 143 °C N 148 °C I

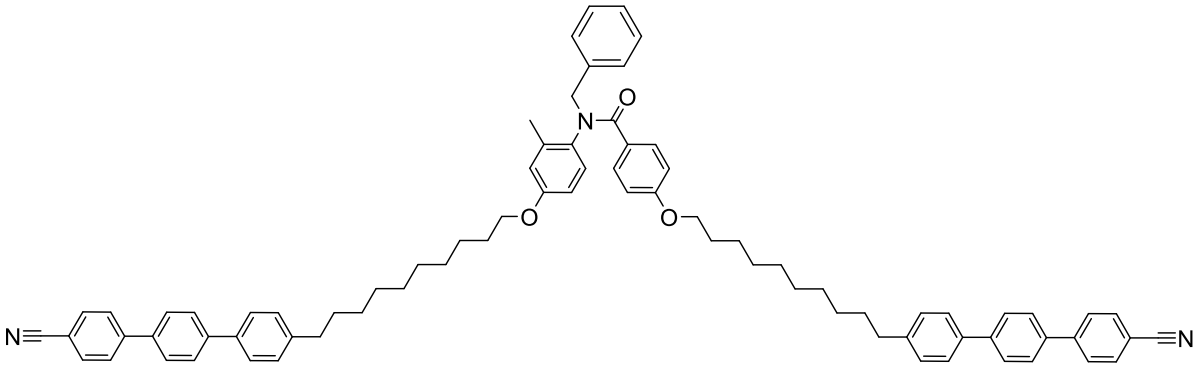
M/Z Calculated mass [M+Na]: 1086.5550 ($C_{75}H_{73}N_3O_3Na$) Found 1086.5601. Difference 4.7 ppm.

ν_{max}/cm^{-1}: 2924 (CH_2), 2853 (CH_2), 2226 (CN), 1639 (C=O), 1605 (Ar), 1004 (Ar), 813 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (overlapping doublets, 8H, Ar-H), 7.72 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.68 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.57 (overlapping doublets, 4H, Ar-H), 7.29 (overlapping signals, 11H, Ar-H), 6.82 (d, *J* = 8.6 Hz, 1H, Ar-H), 6.63 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.57 (overlapping doublet and singlet, 2H, Ar-H), 5.29 (d, *J* = 13.9 Hz, 1H, N-C<u>H</u>), 4.66 (d, *J* = 13.9 Hz, 1H, N-C<u>H</u>), 3.87 (overlapping triplets, 4H, O-<u>CH_2</u>), 2.68 (overlapping triplets, 4H, Ar-<u>CH_2</u>), 1.84 (s, 3H, Ar-CH_3), 1.80 – 1.64 (m, 8H, CH_2-<u>CH_2</u>), 1.42 – 1.34 (m, 16H, CH_2-CH_2-<u>CH_2</u>).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.02 (HMBC), 160.01, 157.96, 145.20, 145.18, 142.59 (2C), 141.50, 141.48, 137.65, 137.63, 137.52, 137.49, 137.38, 136.74, 134.94, 132.64 (4C), 130.54 (2C), 130.13 (2C), 129.44 (2C), 128.97 (4C), 128.25, 128.15, 127.59 (4C), 127.56 (4C), 127.52 (4C), 127.35, 126.91 (4C), 118.97 (2C), 116.44, 113.22 (2C), 112.43, 110.87, 110.85, 67.97, 67.86, 53.69, 35.63, 35.61, 31.46, 31.43, 29.43, 29.39, 29.34, 29.32, 29.29, 29.27, 29.24, 29.14, 26.06, 25.98, 18.01.

4-{[10-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)decyl]oxy}-*N*-(4-{[10-(3^4-cyano[1^1,2^1:2^4,3^1-terphenyl]-1^4-yl)decyl]oxy}-2-methylphenyl)-N-benzylbenzamide 11



Amide	0.515	0.50 mmol
NaH	0.050 g	1.3 mmol
Benzyl bromide	0.07 mL	0.59 mmol
THF	15 mL	

18 h at RT

Column 2:1:1 toluene: EtOAc: DCM R_f 0.72

Yield 57 mg (10 %)

Cr 118 °C Sm 144 °C N 147 °C I

M/Z Calculated mass [M+H]: 1120.6356 ($C_{79}H_{82}N_3O_3$) Found 1120.6350. Difference -0.5 ppm.

M/Z Calculated mass [M+Na]: 1142.6176 ($C_{79}H_{81}N_3O_3Na$) Found 1142.6177. Difference 0.1 ppm.

ν_{max}/cm^{-1}: 2925 (CH_2), 2854 (CH_2), 2226 (CN), 1635 (C=O), 1604 (Ar), 1004 (Ar), 812 (Ar).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (overlapping doublets, 8H, Ar-H), 7.62 (d, *J* = 8.3 Hz, 4H, Ar-H), 7.58 (d, *J* = 8.2 Hz, 4H, Ar-H), 7.48 (overlapping doublets, 4H, Ar-H) 7.20 (overlapping signals, 11H, Ar-H) 6.72 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.53 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.49 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.45 (s, 1H, Ar-H), 5.19 (d, *J* = 13.9 Hz, 1H, N-C<u>H</u>), 4.56 (d, *J* = 13.9 Hz, 1H, N-C<u>H</u>), 3.77 (overlapping triplets, 4H, O-<u>CH_2</u>), 2.57 (overlapping triplets, 4H, Ar-<u>CH_2</u>), 1.74 (s, 3H, Ar-CH_3), 1.69 – 1.52 (m, 8H, CH_2-<u>CH_2</u>), 1.40 – 1.19 (m, 24H, CH_2-CH_2-<u>CH_2</u>).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.95, 160.02, 157.97, 145.21, 145.18, 142.67, 142.66, 141.52, 141.50, 137.64, 137.62, 137.49, 137.47, 137.38, 136.74, 134.93, 132.64 (4C), 130.54 (2C), 130.13 (2C), 129.45 (2C), 128.98 (4C), 128.25, 128.13, 127.60 (4C), 127.56 (4C), 127.52 (4C), 127.35, 126.90 (4C), 118.98 (2C), 116.44, 113.22 (2C), 112.43, 110.86, 110.85, 68.00, 67.89, 53.70, 35.65, 35.64, 31.50, 31.47, 29.56, 29.53 (3C), 29.49 (2C), 29.41, 29.39, 29.36, 29.34, 29.28, 29.16, 26.05, 25.99, 18.01.

Supplementary Figures

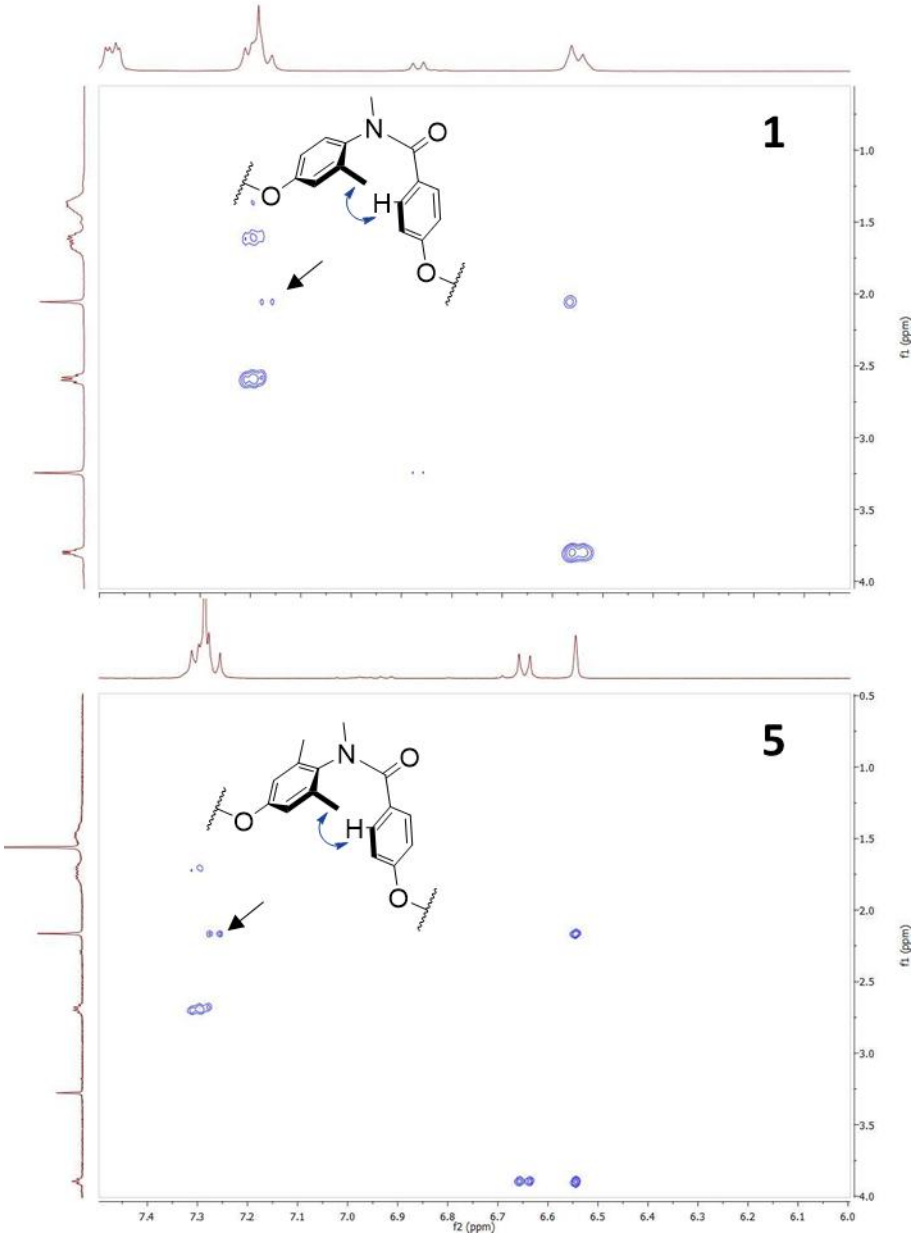


Figure S1: 2D NOESY spectra of trimer **1** (top) and **5** (below) showing cross-peaks between the aryl methyl and the protons ortho to the carbonyl.

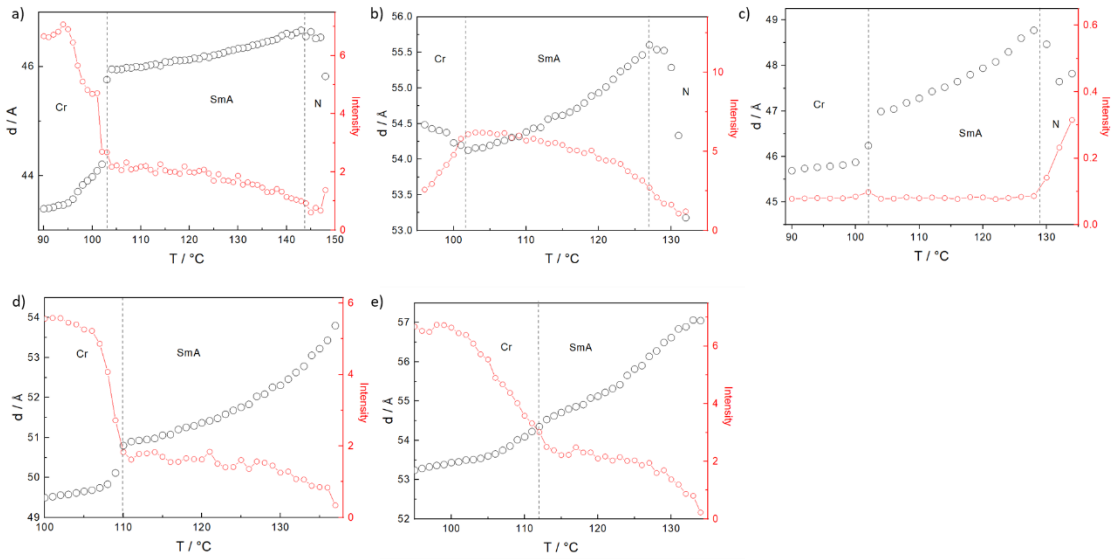


Figure S2: The temperature dependence of the layer spacing of trimer **2** (a), **8** (b), **9** (c), **10** (d), and **11** (e).

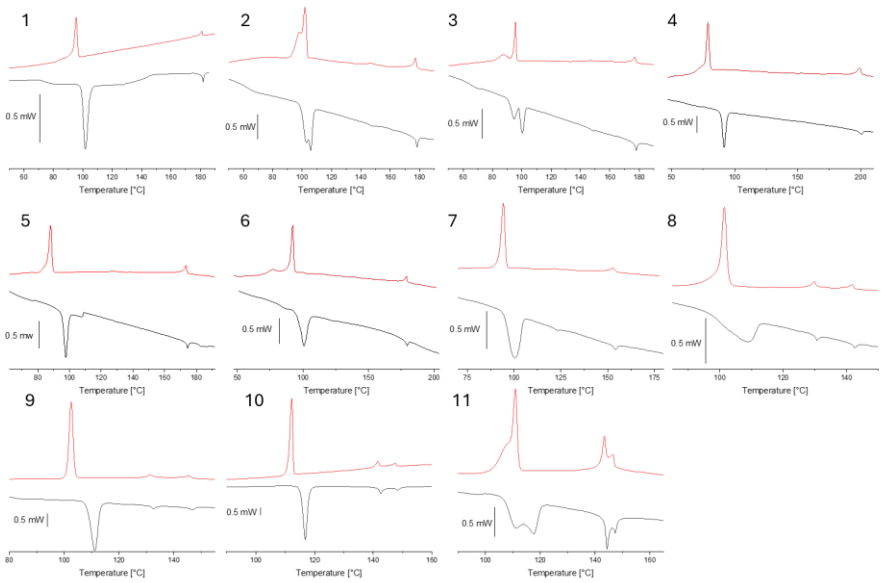


Figure S3: DSC traces for the new tertiary amide-based trimers.

References

1 Strachan, G. J., Majewska, M. M., Pociecha, D., Gorecka, E., Storey, J. M. D., & Imrie, C. T. (2024). Liquid crystal trimers containing secondary amide groups. *Liquid Crystals*. https://doi.org/10.1080/02678292.2024.2382301