Electronic Supplementary Material (ESI) for Chemical Communications

Chiral nematic organo-siloxane oligopodes based on an axially chiral binaphthalene core

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Supplementary Information

Experimental Details

Liquid Crystal Analysis

Electronic Supplementary Material (ESI) for Chemical Communications

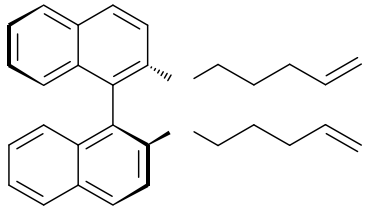
General Procedures

All reactions were performed under inert conditions, using dry solvents where stated. Tetrahydrofuran and dimethoxyethane were freshly distilled from sodium and benzophenone. Toluene and dichloromethane were freshly distilled from calcium hydride. Other solvents were SLR-grade and used without further purification. Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. ^{1}H NMR 400 MHz, ^{13}C NMR 101 MHz and were recorded on a JEOL Eclipse 400 FT NMR spectrometer at ambient temperatures. All NMR spectra were carried out using deuterated chloroform unless otherwise stated. EI, CI, MALDI and HRMS mass spectra were obtained *via* the EPSRC National Mass Spectrometry Service Centre at Swansea University, Wales.

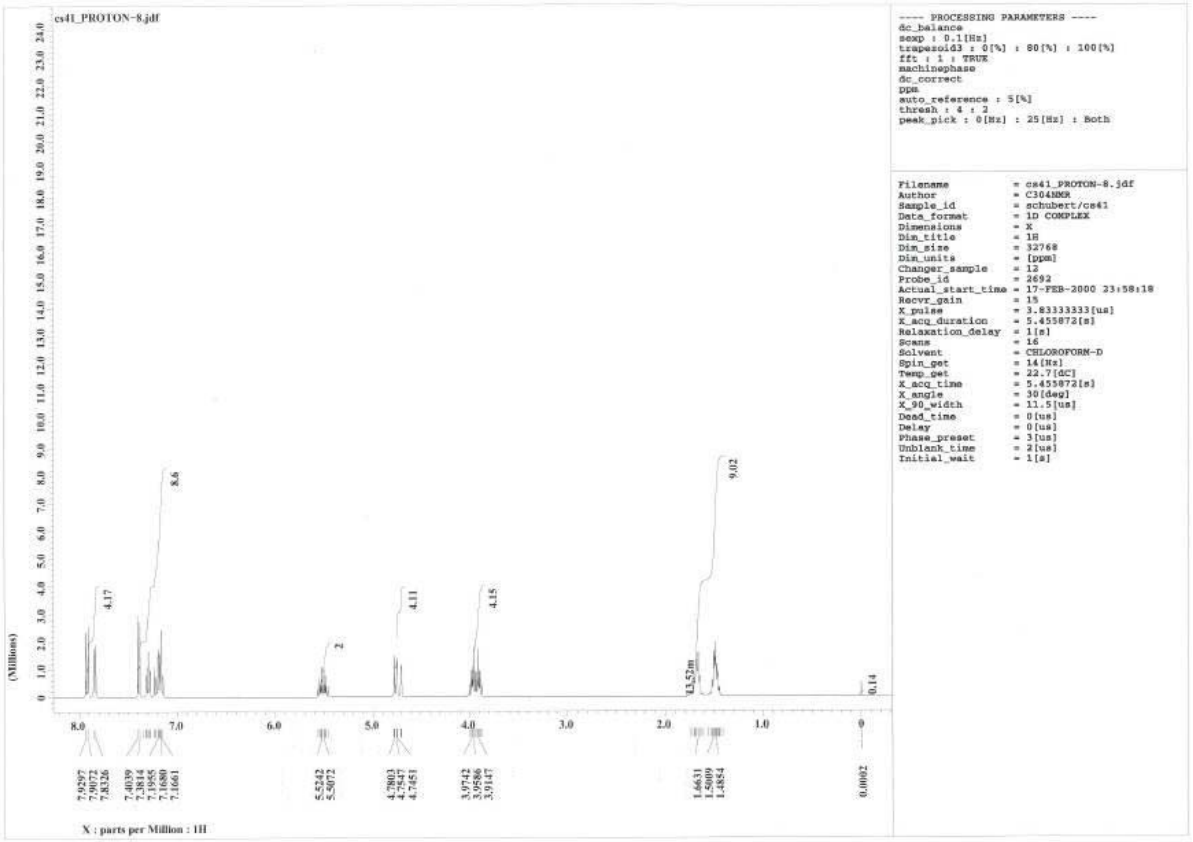
DSC data was collected on a Mettler-Toledo DSC822e. Optical rotations were recorded on a Polaar 3001 polarimeter in the solvents stated, with concentrations quoted in grams per mL. X-ray diffraction experiments were performed on a MAR345 diffractometer with a 2D image plate detector (CuKα radiation, graphite monochromator, λ = 1.54 Å). The samples were heated in the presence of a magnetic field using a home-built capillary furnace. Mesophase behaviour of the samples carried out using an Olympus BX51 polarising microscope. The microscope was equipped with a Mettler-Toledo FP900 heating stage

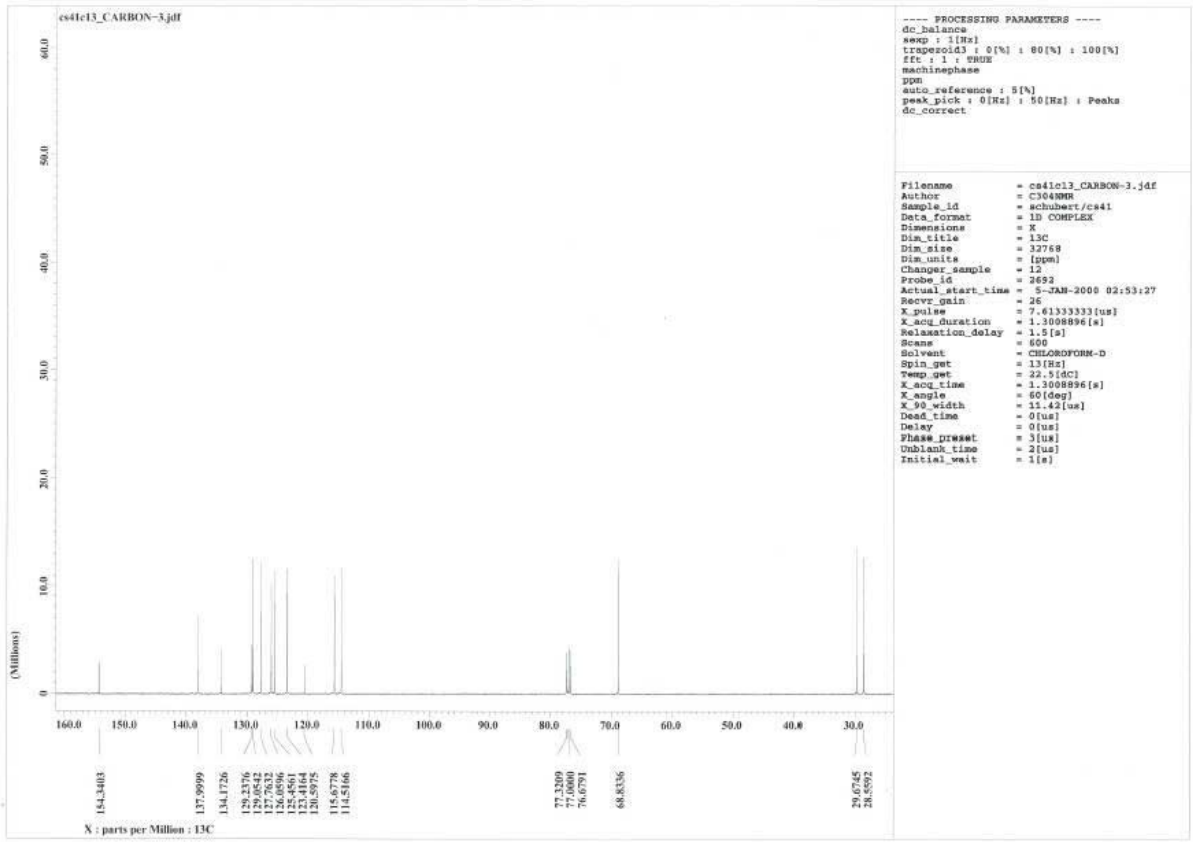
Experimental Procedures

(*S*)-(-)-2,2-Di(pent-4-enyl)oxy-1,1'-binaphthalene (4)

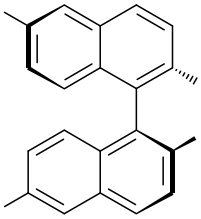


To a solution of (*S*)-1,1-bi(2-naphthol) (2.27 g, 7.93 mmol) in acetonitrile (35 mL) was added potassium carbonate (5.48 g, 39.65 mmol) and 5-bromopentene (4.73 g, 31.71 mmol, 3.8 mL) and the mixture was heated to reflux for 48 hours. The mixture was cooled, filtered and the solvent removed under reduced pressure. The crude product was dissolved in dichloromethane (25 mL), washed with 1M HCl (25 mL), water (25 mL), brine (25 mL), dried (Na_2SO_4) and the solvent removed under reduced pressure. Purification by silica gel column chromatography (Hexane/DCM 2:1) afforded the title compound as a pale yellow oil (3.23 g, 96%); δ_H (400 MHz, $CDCl_3$) 7.94 (2H, d, *J* 8.9), 7.87 (2H, d, *J* 8.1), 7.42 (2H, d, *J* 8.9), 7.32 (2H, m), 7.20 (4H, m), 5.54 (2H, ddt, *J* 16.9, 10.2, 6.6), 4.77 (4H, m), 3.96 (4H, m), 1.69 (4H, m), 1.51 (4H, m);); δ_C (101 MHz, $CDCl_3$) 154.34, 137.99, 134.17, 129.23, 129.05, 127.76, 126.05, 125.45, 123.41, 120.59, 115.67, 114.51, 68.83, 29.67, 28.55;

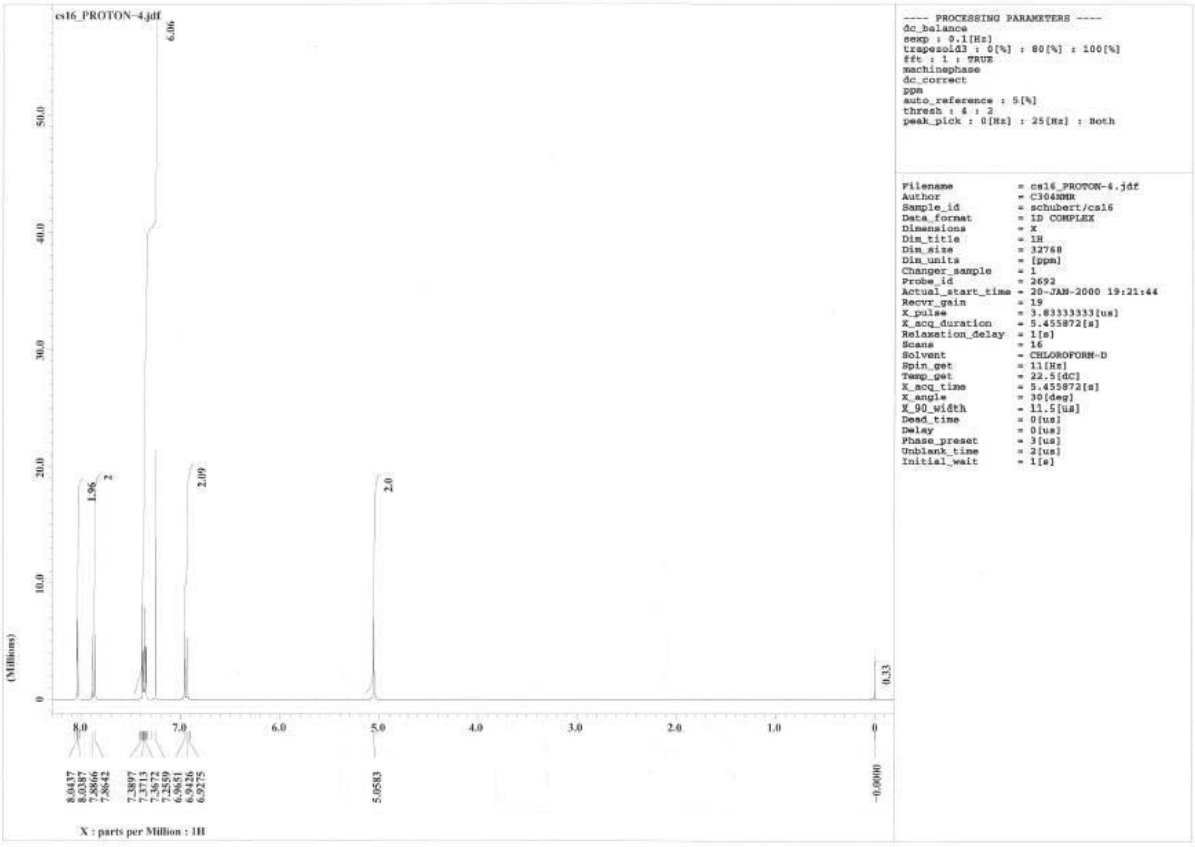




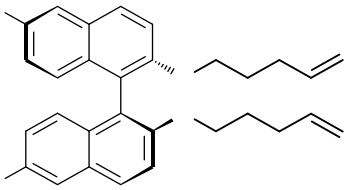
(*S*)-(-)-6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthalene (5)



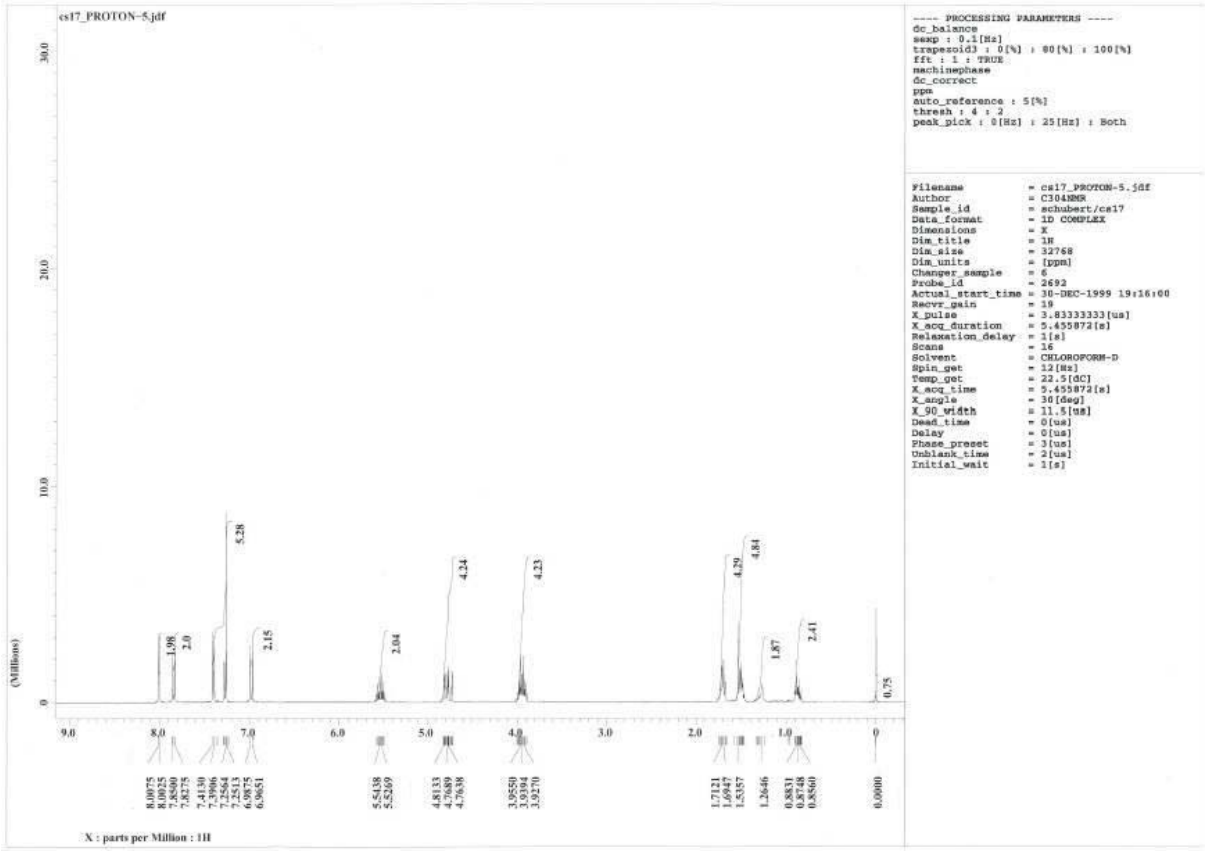
(*S*)-1,1'-Bi(2-naphthol) (10.10 g, 35.27 mmol) was dissolved in dichloromethane (150 mL) and cooled to -78 °C. A solution of bromine (14.09 g, 88.18 mmol, 4.5 mL) in dichloromethane (10 mL) was added dropwise to over 30 minutes with vigorous stirring. The solution was allowed to warm to ambient temperature over 2.5 hours and stirred for a further 12 hours. Aqueous sodium sulphite solution (10%, 100 mL) was added and the mixture stirred for a further 30 minutes. The layers were separated and the organic layer was washed with water (100 mL), brine (100 mL), dried (Na_2SO_4) and filtered. The solvent was removed under reduced pressure to afford the title compound as a brown solid (15.57 g, 99%), m.p. 197-199 °C, (lit 197-198 °C). δ_H (400 MHz, $CDCl_3$) 8.04 (2H, d, *J* 2.0), 7.89 (2H, d, *J* 8.9), 7.38 (2H, d, *J* 8.9), 7.36 (2H, dd, *J* 8.9, 2.0), 6.96 (2H, d, *J* 8.9), 2.14 (2H, s).

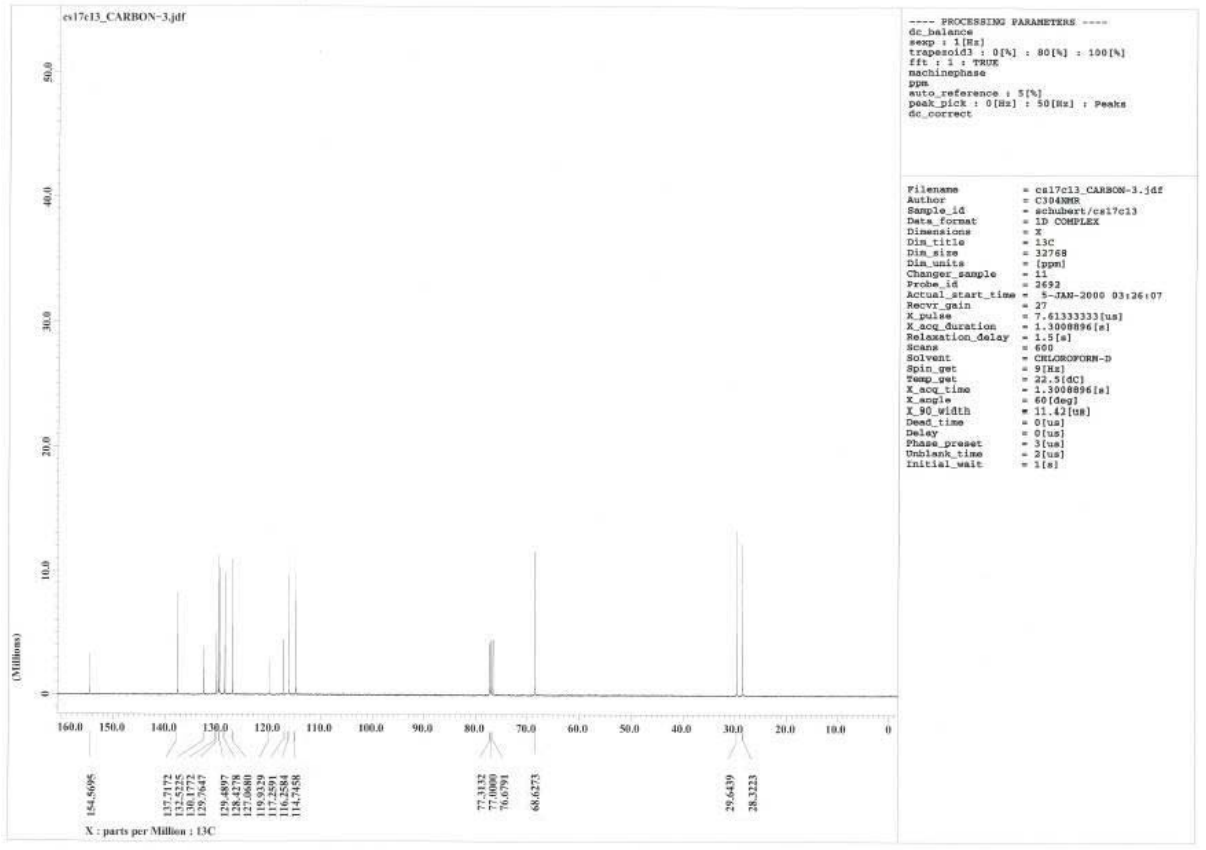


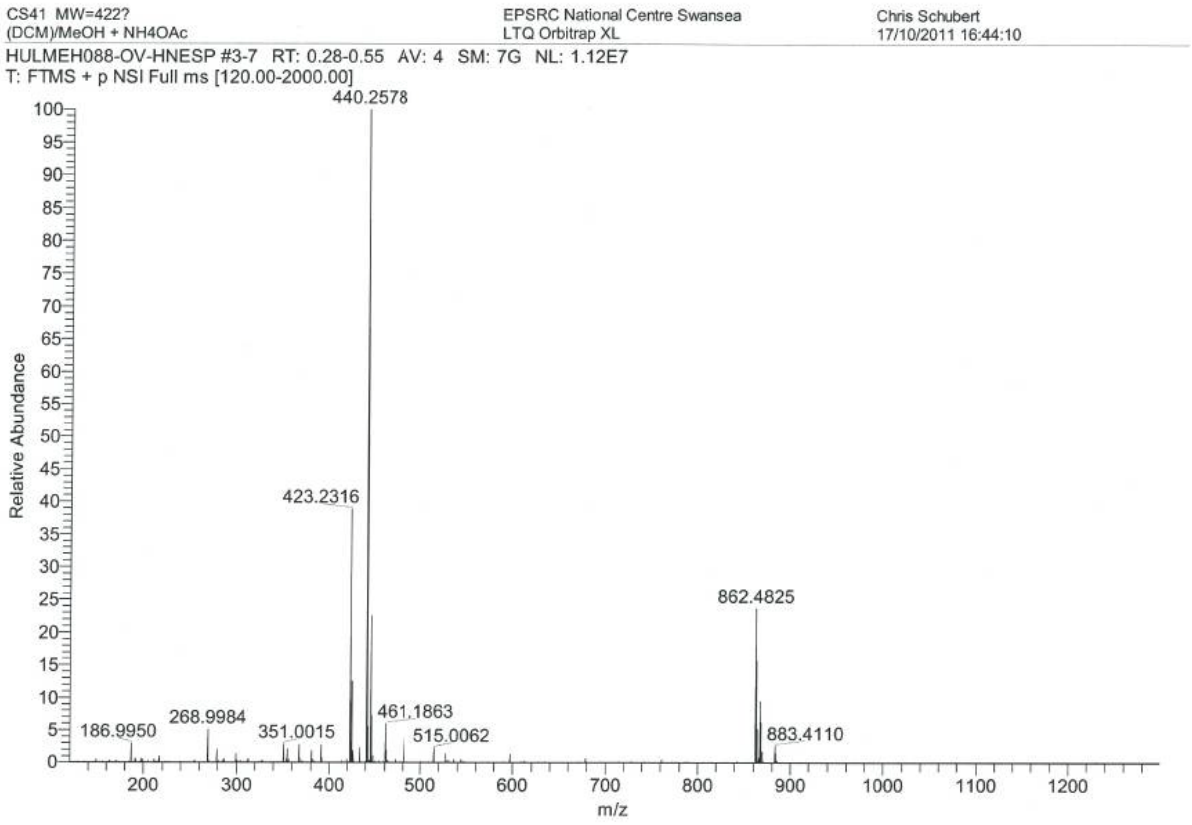
(*S*)-(-)-6,6'-Dibromo-2,2'-di(pent-4-enyl)oxy-1,1'-binaphthalene (6)



To a solution of (*S*)-6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene **5** (3.02 g, 6.80 mmol) in acetonitrile (40 mL) was added potassium carbonate (4.69 g, 34.00 mmol) and 5-bromopentene (4.05 g, 27.19 mmol, 3.2 mL) and the mixture was heated to reflux for 48 hours. The mixture was cooled, filtered and the solvent removed under reduced pressure. The product was dissolved in dichloromethane (25 mL) and washed with 1M HCl (25 mL), water (25 mL), brine (25 mL), dried (Na_2SO_4) and the solvent removed under reduced pressure. Purification by silica gel column chromatography (Hexane/DCM 2:1) afforded the *title compound* as a yellow oil (3.58 g, 91%); δ_H (400 MHz, $CDCl_3$) 8.00 (2H, d, *J* 2.0), 7.84 (2H, d, *J* 9.0), 7.40 (2H, d, *J* 9.0), 7.27 (2H, d, *J* 9.0, 2.0), 6.98 (2H, d, *J* 9.0), 5.37 (2H, m), 4.78 (4H, m), 3.94 (4H, m), 1.705 (4H, m);); δ_C (101 MHz, $CDCl_3$) 154.56, 137.71, 132.52, 130.17, 129.76, 129.48, 128.42, 127.06, 119.93, 117.25, 116.25, 114.74, 68.62, 29.64, 28.42; *m/z* (CI) 598.0 ($M+NH_4^+$, 100%); HRMS Found: 598.0775 $C_{30}H_{32}Br_2NO_2$ ($M+NH_4^+$) Requires 598.0776.



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EPSRC National Centre Swansea
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Chris Schubert
17/10/2011 16:44:10
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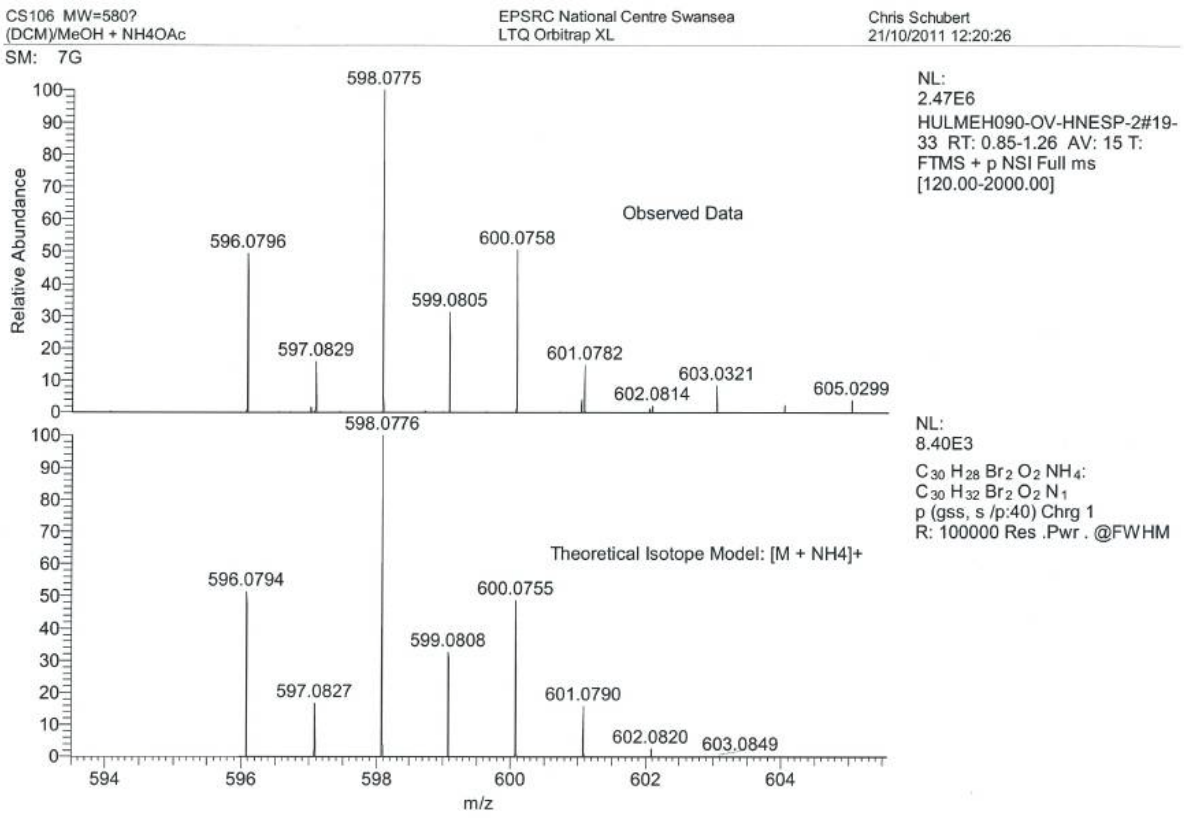
515.0062
883.4110
Relative Abundance
m/z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EPSRC National Centre Swansea
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Chris Schubert
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SM: 7G
NL:
2.47E6
HULMEH090-OV-HNESP-2#19-33 RT: 0.85-1.26 AV: 15 T: FTMS + p NSI Full ms [120.00-2000.00]
Observed Data
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596.0796
600.0758
599.0805
597.0829
601.0782
603.0321
602.0814
605.0299
NL:
8.40E3
C30 H28 Br2 O2 NH4:
C30 H32 Br2 O2 N1
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM
Theoretical Isotope Model: [M + NH4]+
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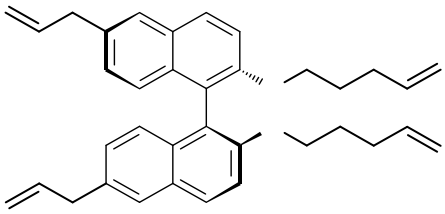
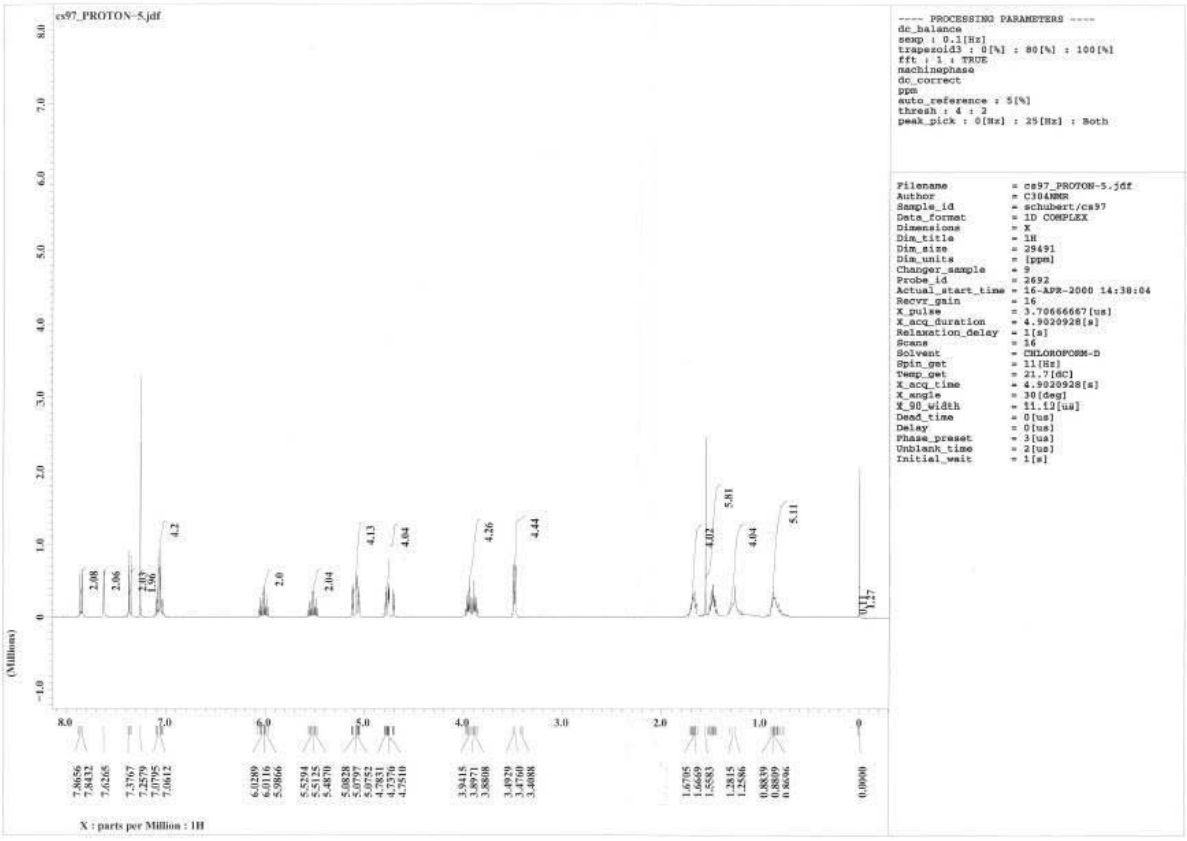
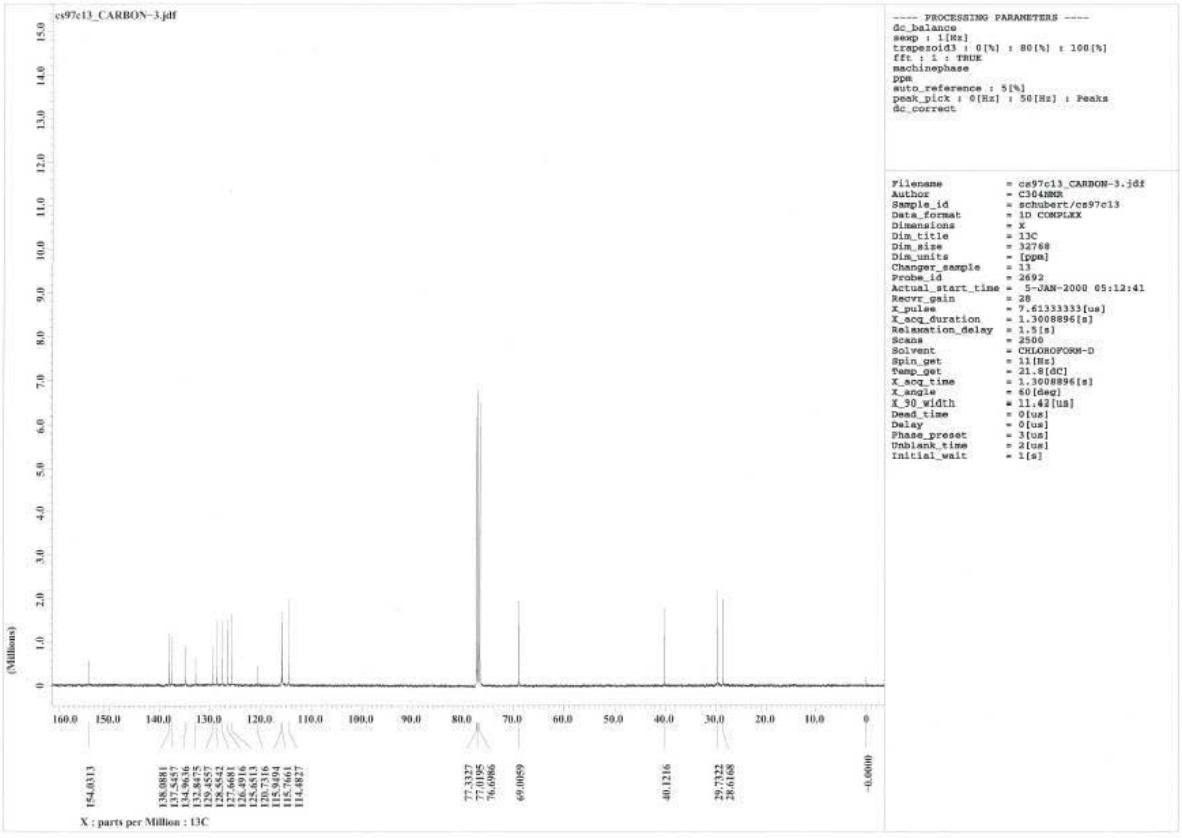
596.0794
600.0755
599.0808
597.0827
601.0790
602.0820
603.0849
Relative Abundance
m/z

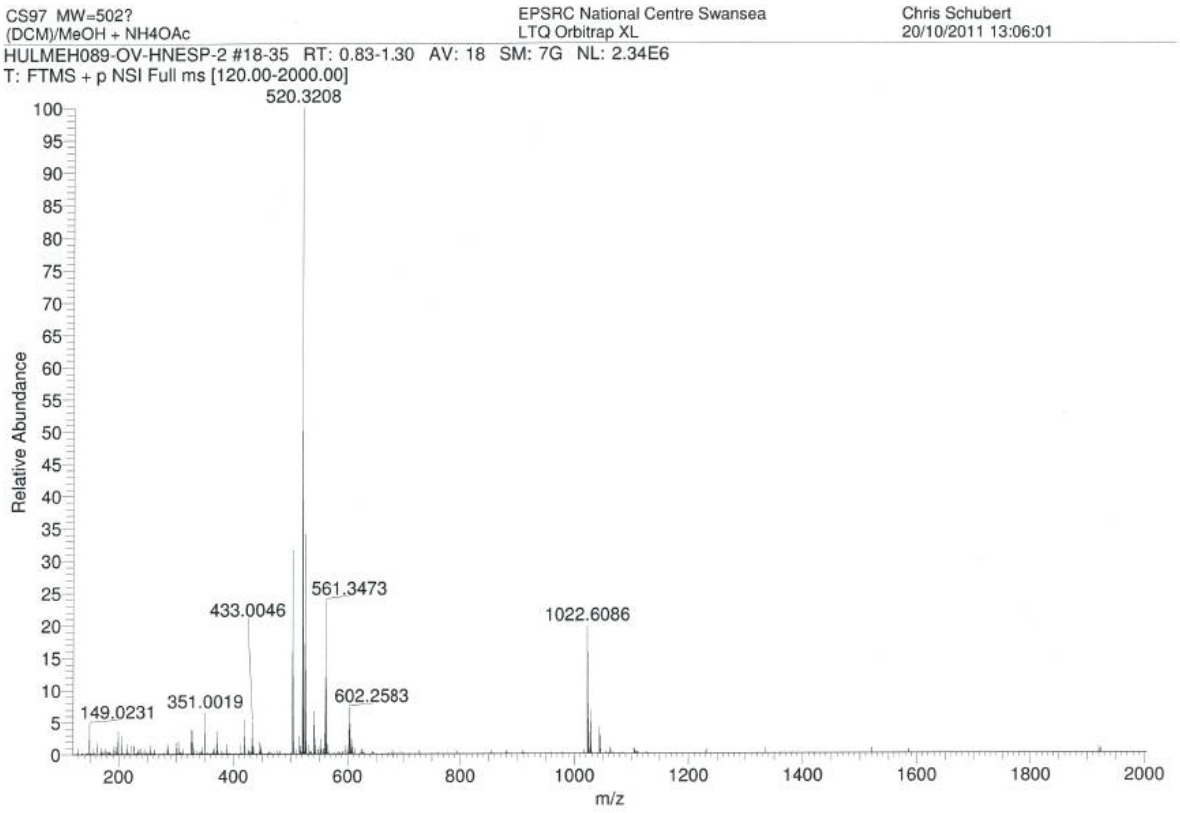
(*S*)-(-)-6,6'-Di(prop-2-enyl)-2,2'-di(pent-4-enyl)oxy-1,1'-binaphthalene (7)



(*S*)-6,6'-Dibromo-2-2'-di(pent-4-enyl)oxy-1,1'-binaphthalene **6** (0.24 g, 0.41 mmol), caesium fluoride (0.19 g, 1.24 mmol) and 2mol% $PdCl_2$(dppf) (6.69 mg, 8.20 μmol) were dissolved in degassed dimethoxymethane (5 mL) under an inert atmosphere. Allylboronic acid pinacol ester (0.21 g, 1.24 mmol) was added and the reaction mixture heated to 60 °C for 16 hours. The crude product was diluted with dichloromethane (15 mL), filtered through celite and the solvent removed under reduced pressure. Purification by silica gel column chromatography (Hexane/DCM 4:1) afforded the *title compound* as a colourless oil (0.20 g, 95%); δ_H (400 MHz, $CDCl_3$) 8.17 (2H, d, *J* 9.9), 7.91 (2H, s), 7.62 (2H, d, *J* 9.9), 7.29 (4H, m), 6.13 (2H, ddt, *J* 18.6, 11.1, 7.4), 5.58 (2H, ddt, *J* 18.8, 11.3, 7.3), 5.09 (4H, m), 4.71 (4H, m), 3.80 (4H, m), 3.31 (4H, m), 1.30 (4H, m), 1.09 (4H, m);); δ_C (101 MHz, $CDCl_3$) 154.03, 138.08, 137.54, 134.96, 132.84, 129.45, 128.55, 127.66, 126.49, 125.65, 120.73, 115.94, 115.76, 114.48, 69.00, 40.12, 29.73, 28.61; *m/z* (CI) 520.3 ($M+NH_4^+$, 100%), 503.2 ($M+H^+$, 31); HRMS Found: 520.3208 $C_{36}H_{42}NO_2$ ($M+NH_4^+$) Requires 520.3210.



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LTQ Orbitrap XL
Chris Schubert
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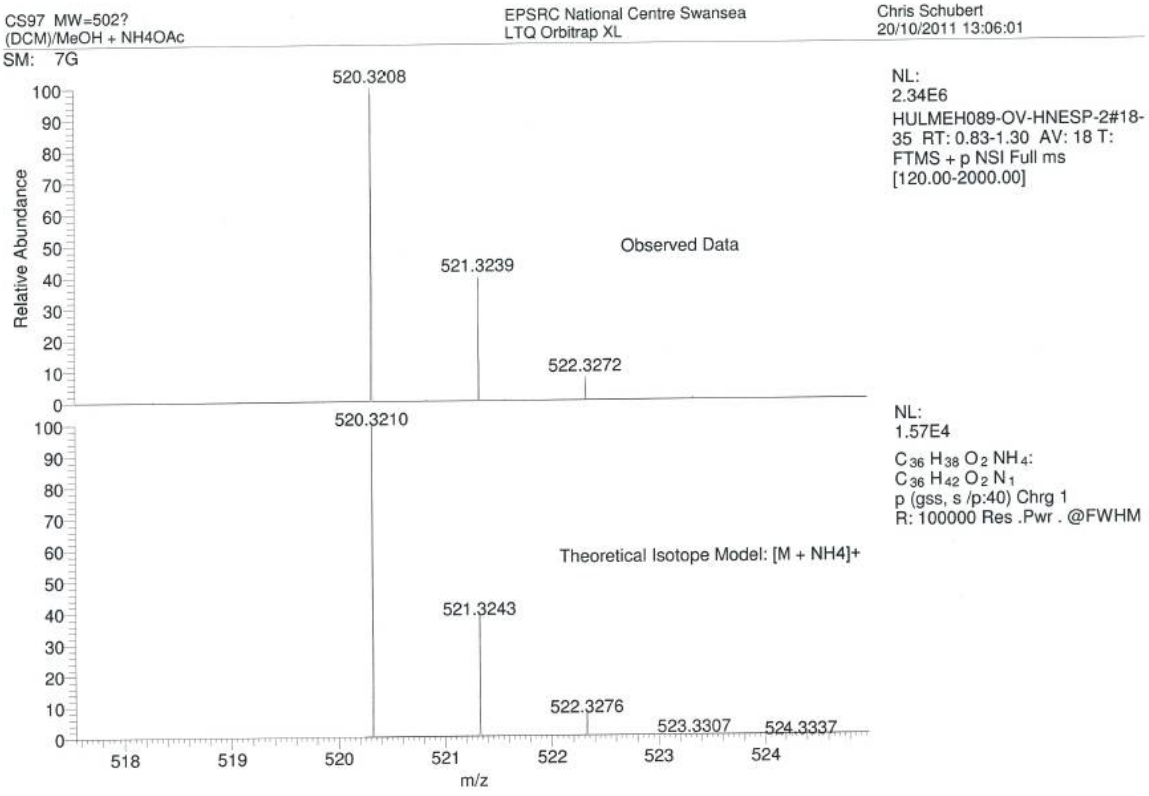
602.2583
351.0019
149.0231
Relative Abundance
m/z


CS97 MW=502?
(DCM)/MeOH + NH4OAc
SM: 7G
EPSRC National Centre Swansea
LTQ Orbitrap XL
Chris Schubert
20/10/2011 13:06:01
520.3208
521.3239
522.3272
Observed Data
NL:
2.34E6
HULMEH089-OV-HNESP-2#18-35 RT: 0.83-1.30 AV: 18 T: FTMS + p NSI Full ms [120.00-2000.00]
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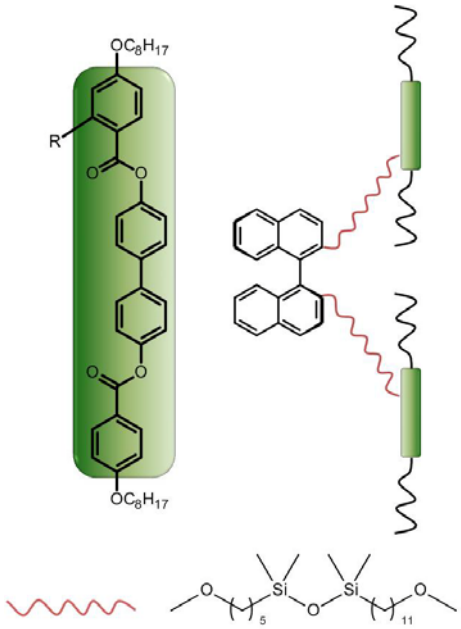
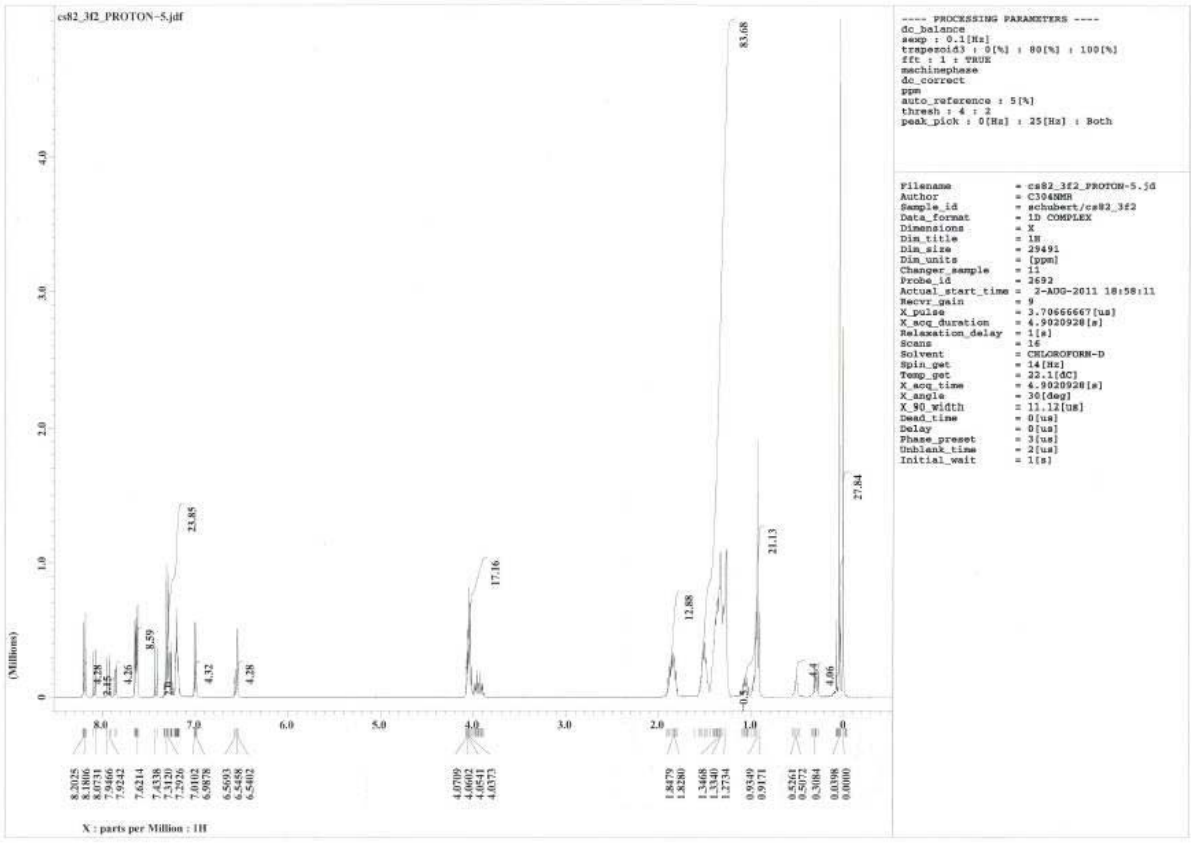
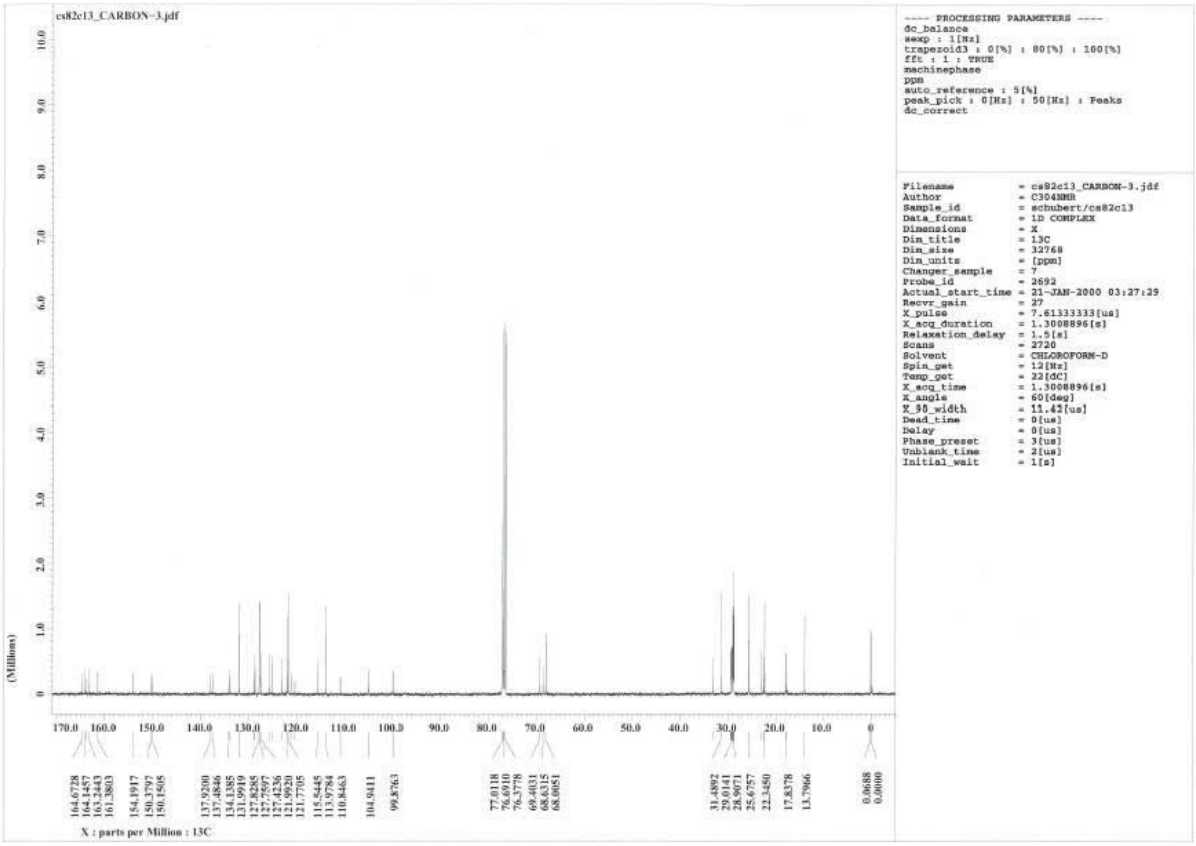
521.3243
522.3276
523.3307
524.3337
Theoretical Isotope Model: [M + NH4]+
NL:
1.57E4
C36 H38 O2 NH4:
C36 H42 O2 N1
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM
Relative Abundance
m/z

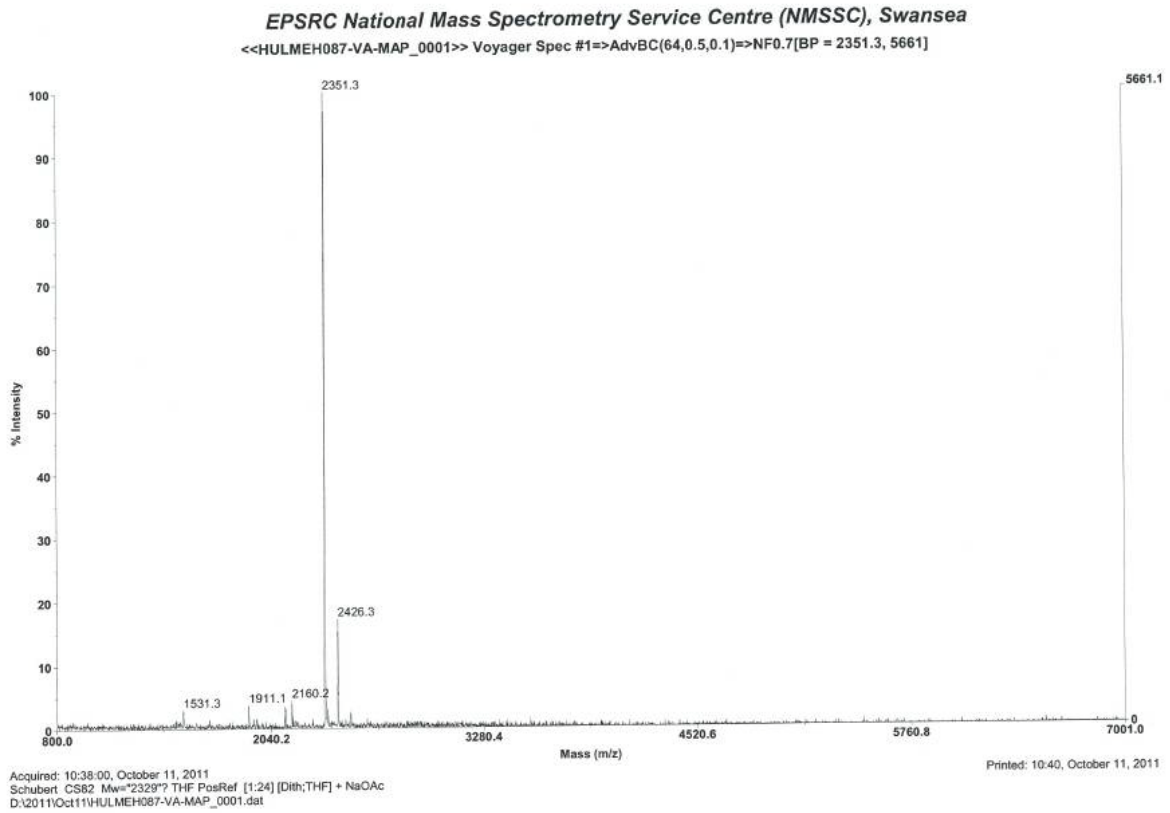
Dimer (1)



To a solution of (*S*)-2,2'-di(4-pentenyloxy)-1,1'-binaphthalene **4** (0.19 g, 0.47 mmol) in anhydrous toluene (30 mL) was added 4-octyloxy-biphenyl-4-yl 4-octyloxy-2-[11-(1,1,3,3-tetramethyldisiloxanyl)-undec-1-yloxybenzoate **8** (0.94 g, 0.99 mmol). A stream of anhydrous air was passed through the solution for 5 minutes before adding Karstedt's catalyst (30 μL, ~2% in xylenes) and stirring for 16 hours at ambient temperature. The solvent was removed under reduced pressure and the crude product purified initially by graduated silica gel column chromatography (Hexane/DCM 1:1, 3:2) and then by subsequent silica gel column chromatography (Toluene/DCM 2:1) to afford the *title compound* as white solid (0.69 g, 63%), $[\alpha]_D^{22}$ -9.82 (*c* 0.01, chloroform). δ_H (400 MHz, $CDCl_3$) 8.29 (4H, d, *J* 9.9), 8.18 (2H, d, *J* 9.4), 8.01 (2H, d, *J* 9.9), 7.93 (2H, d, *J* 9.0), 7.68 (8H, m), 7.44 (2H, d, *J* 9.9), 7.16-7.34 (14H, m), 6.97 (4H, d, *J* 9.9), 6.48 (4H, m), 3.70 (12H, m), 3.58 (4H, m), 1.25 (12H, m), 0.87 (12H, m), 0.61-0.79 (52H, m), 0.39 (4H, m), 0.24 (12H, t, *J* 7.68), -0.75 (12H, s), -0.79 (12H, s); δ_C (101 MHz, $CDCl_3$) 165.09, 164.56, 164.22, 163.66, 161.80, 154.61, 150.80, 150.57, 138.34, 137.90, 134.56, 134.29, 132.41, 129.31, 129.08, 128.24, 127.84, 126.08, 125.59, 123.45, 122.41, 122.19, 151.58, 120.78, 115.96, 114.39, 111.27, 105.36, 100.29, 69.82, 69.05, 68.42, 35.57, 31.90, 29.78, 29.74, 29.69, 29.53, 29.48, 29.43, 29.37, 29.32, 29.23, 29.20, 26.09, 23.38, 22.91, 22.76, 18.49, 18.26, 14.21, 0.48, 0.42; MALDI-MS: isotopic cluster at *m/z* 2352.3 ($M+Na^+$, 100%);






EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea
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5661.1
2426.3
1531.3
1911.1
2160.2
% Intensity
Mass (m/z)
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3280.4
4520.6
5760.8
7001.0
Printed: 10:40, October 11, 2011
Acquired: 10:38:00, October 11, 2011
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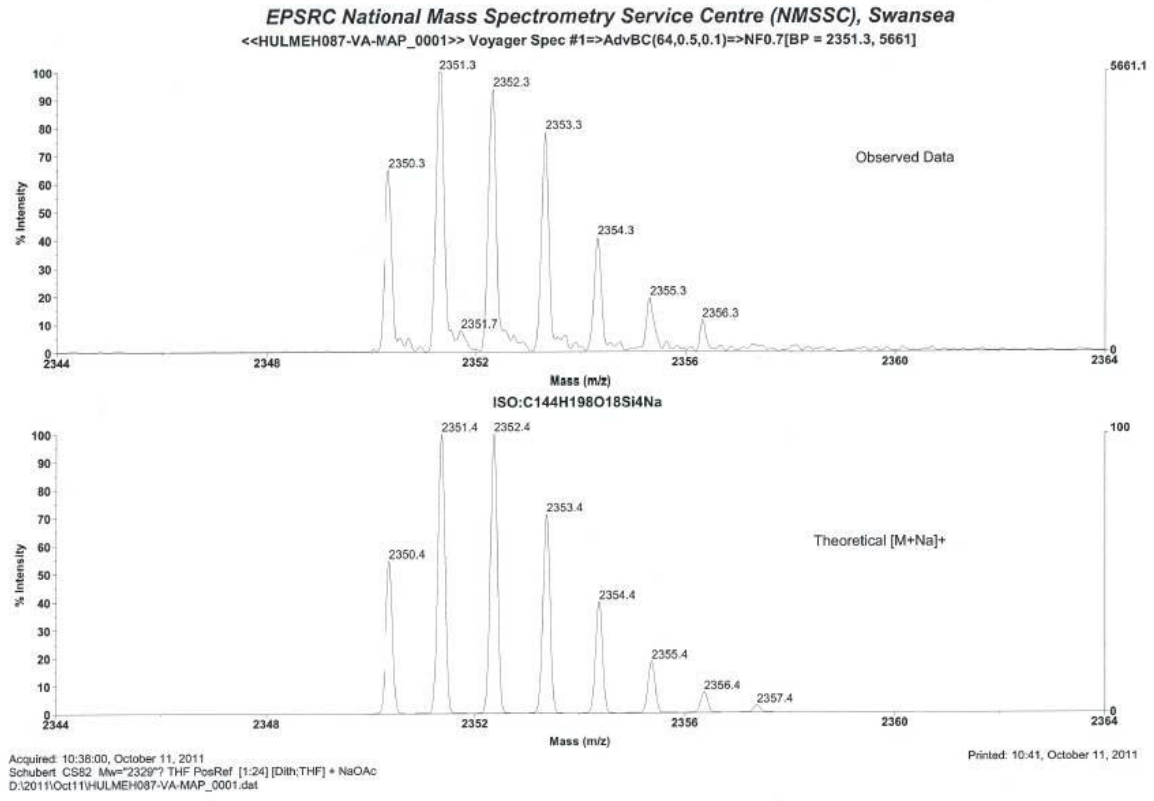
EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea
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2352.3
2353.3
2350.3
2354.3
2355.3
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2351.7
5661.1
Observed Data
% Intensity
Mass (m/z)
ISO:C144H198O18Si4Na
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2352.4
2353.4
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2357.4
Theoretical [M+Na]+
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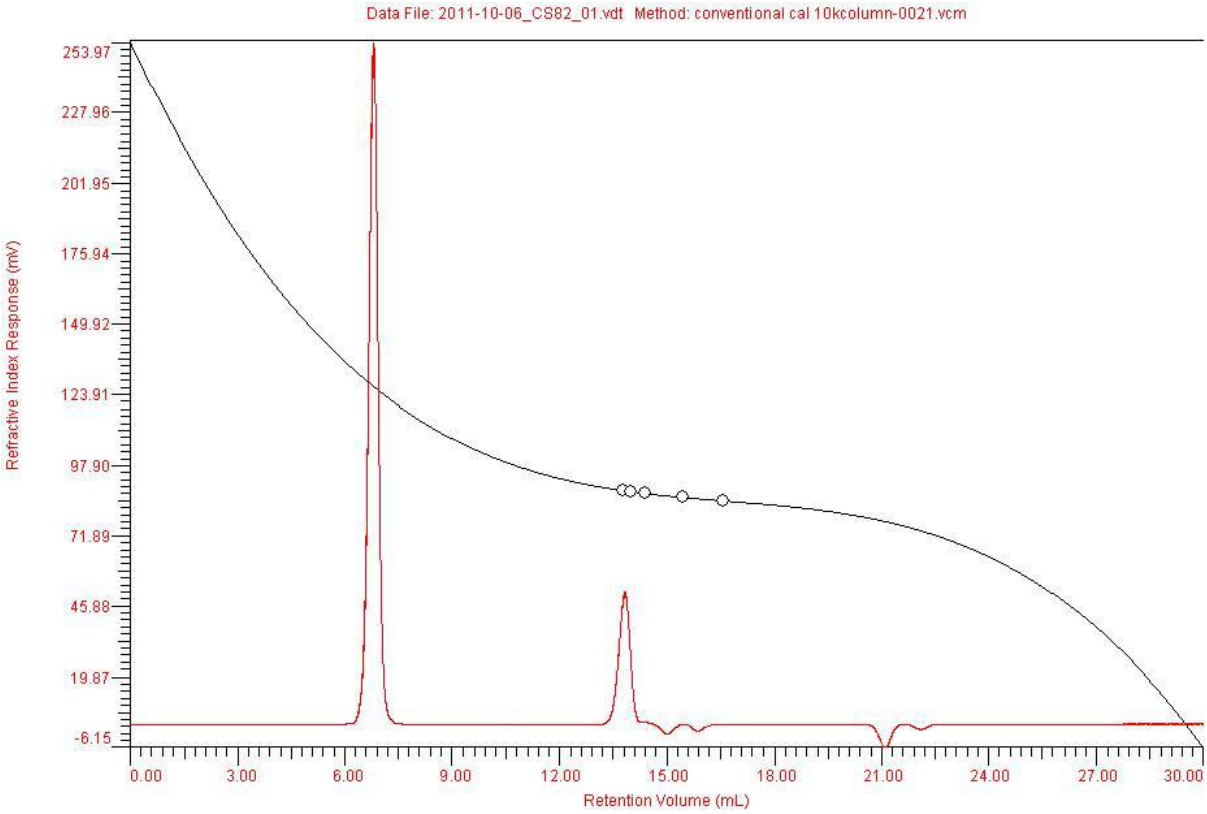
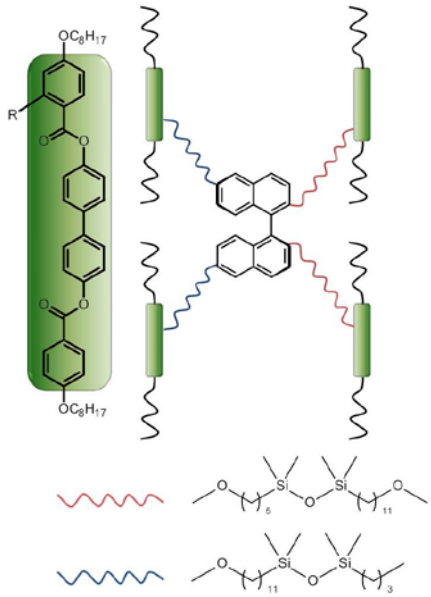
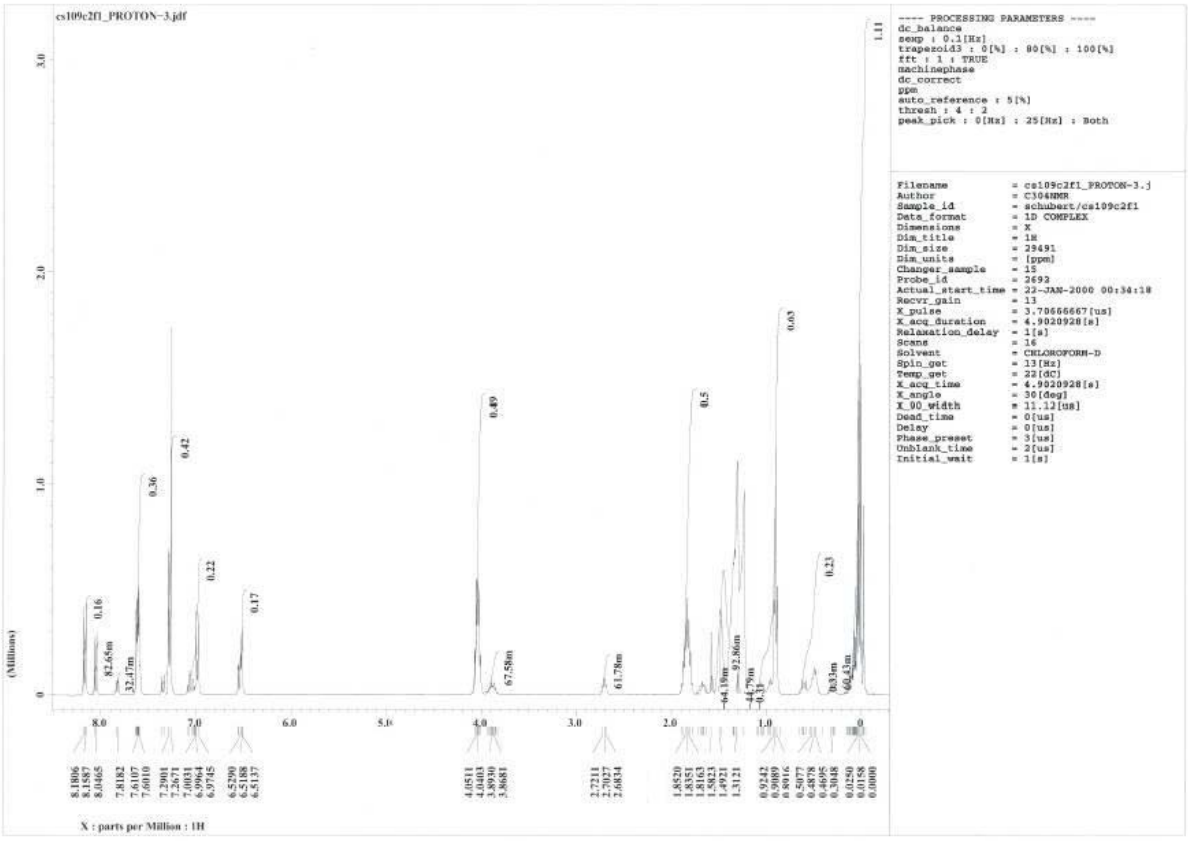
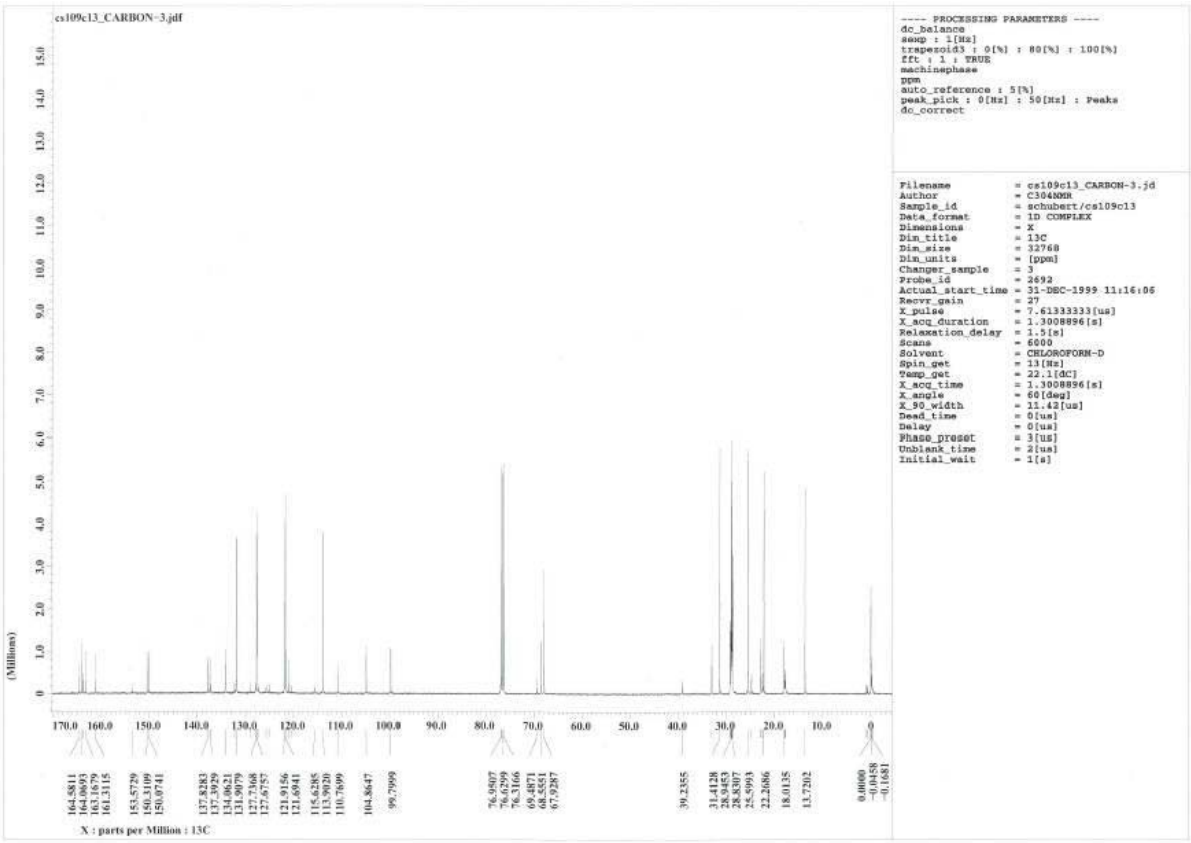


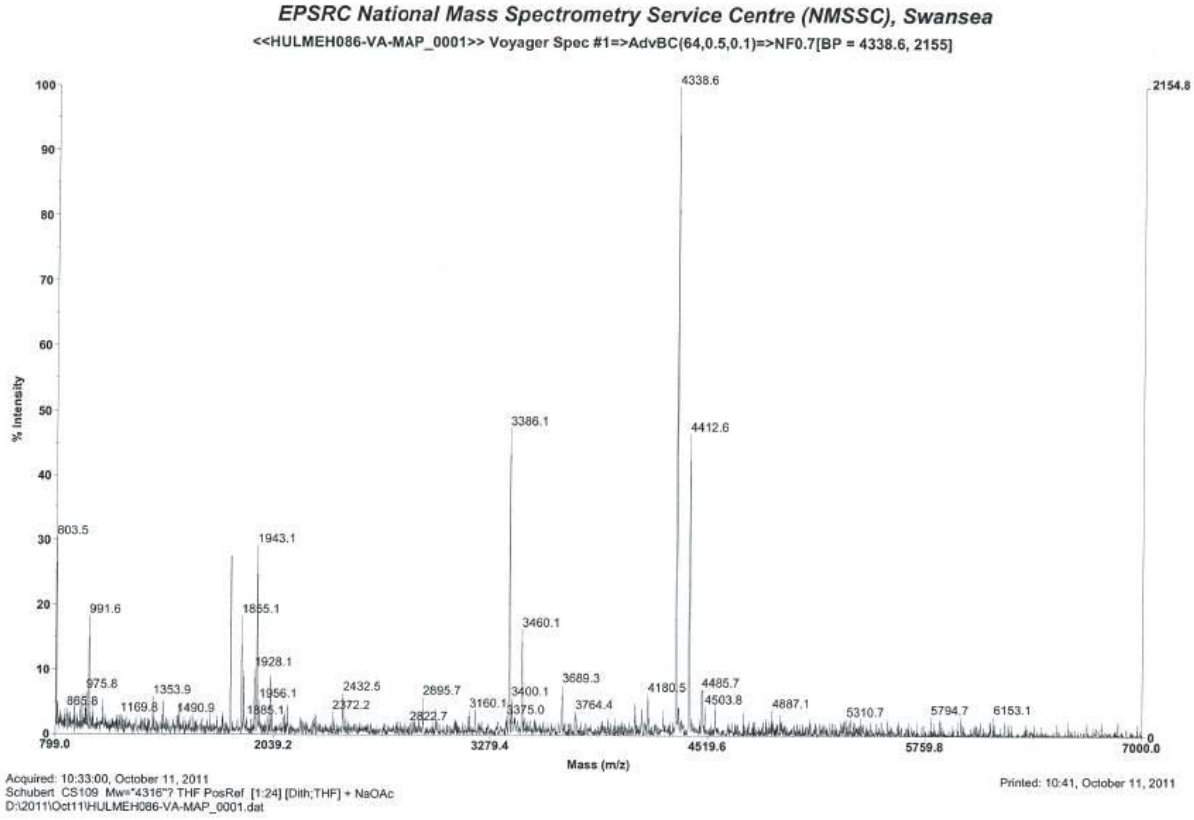
Tetramer (2)

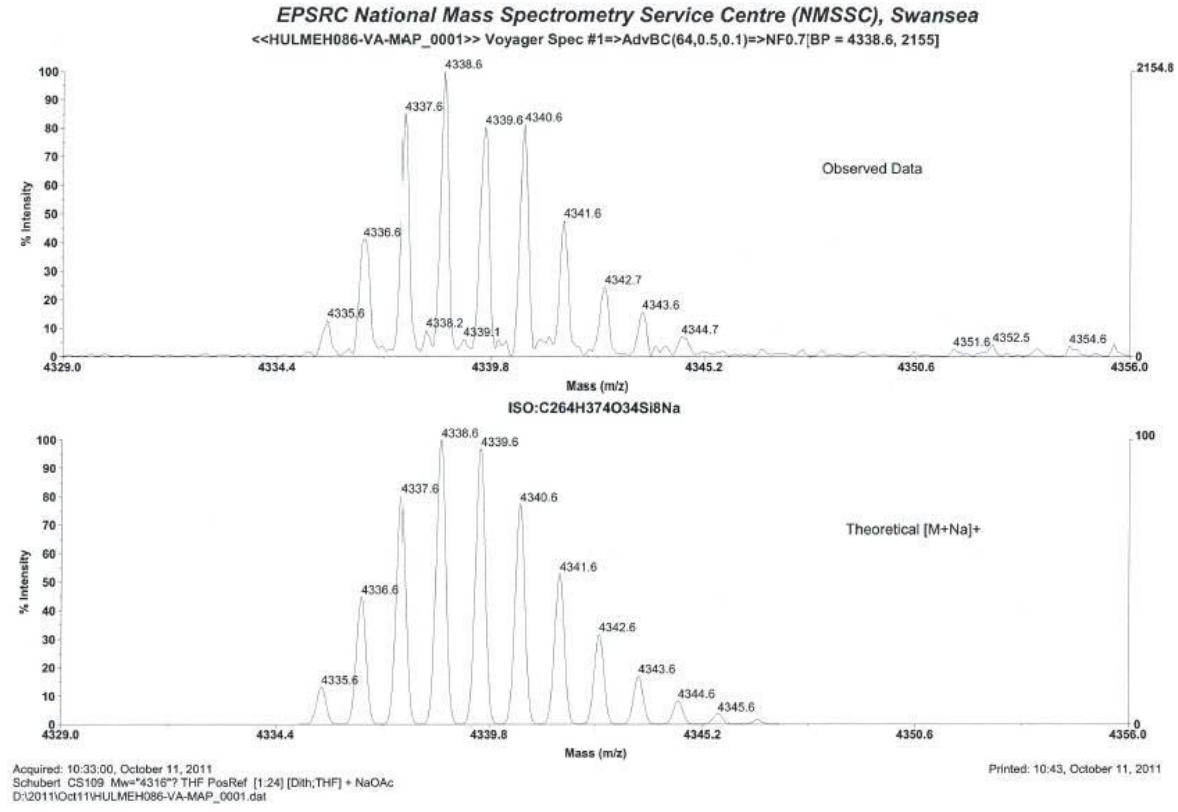


To a solution of (*S*)-6,6'-di(prop-2-enyl)-2,2'-di(4-pentenyloxy)-1,1'-binaphthalene **7** (0.032 g, 0.064 mmol) in anhydrous toluene (10 mL) was added 4-octyloxy-biphenyl-4-yl 4-octyloxy-2-[11-(1,1,3,3-tetramethyldisiloxanyl)-undec-1-yloxybenzoate **8** (0.31 g, 0.32 mmol). A stream of anhydrous air was passed through the solution for 5 minutes before adding Karstedt's catalyst (10 µL, ~2% in xylenes) and stirring for 16 hours at ambient temperature. The solvent was removed under reduced pressure and the crude product purified initially by silica gel column chromatography (Hexane/DCM 1:2, 3:2) and then by subsequent graduated silica gel column chromatography (MeCN, MeCN/DCM 1:4) to afford the *title compound* as white solid (0.16 g, 57%), $[\alpha]_D^{22}$ -1.20 (*c* 0.01, chloroform). δ_H (400 MHz, $CDCl_3$) 8.16 (8H, d, *J* 9.8), 8.04 (4H, d, *J* 9.6), 7.81 (2H, d, *J* 10.0), 7.60 (18H, m), 7.33 (2H, d, *J* 10.0), 7.27 (18H, d, *J* 9.8), 7.16 (2H, m), 6.98 (8H, d, *J* 9.9), 6.51 (8H, m), 4.04 (24H, m), 3.88 (4H, m), 2.70 (4H, m), 1.83 (24H, m), 1.29 (4H, m), 1.09-0.93 (160H, m), 0.91 (24H, t, *J* 7.2), 0.47-0.51 (12H, m), 0.01-0.02 (48H, m); δ_C (101 MHz, $CDCl_3$) 165.08, 164.57, 164.21, 163.67, 161.81, 154.08, 150.81, 150.58, 138.33, 137.90, 134.56, 132.79, 132.41, 129.51, 128.24, 128.17, 127.73, 126.25, 125.29, 122.41, 122.20, 121.59, 120.97, 116.13, 114.40, 111.27, 105.37, 100.30, 69.99, 69.06, 68.43, 39.74, 33.59, 31.91, 29.79, 29.75, 29.70, 29.54, 29.49, 29.44, 29.33, 29.24, 29.21, 26.10, 25.34, 23.40, 23.35, 22.99, 22.77, 18.51, 18.39, 18.30, 14.22, 1.42. 1.31, 0.50; MALDI-MS: isotopic cluster at *m/z* 4338.6 ($M+Na^+$, 100%).






EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea
<<HULMEH086-VA-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>NF0.7[BP = 4338.6, 2155]
% Intensity
Mass (m/z)
4338.6
2154.8
4412.6
3386.1
803.5
1943.1
991.6
1855.1
3460.1
1928.1
975.8
1353.9
2432.5
2895.7
3689.3
4180.5
4485.7
865.6
1169.8
1490.9
1956.1
1885.1
2372.2
2822.7
3160.1
3400.1
3375.0
3764.4
4503.8
4887.1
5310.7
5794.7
6153.1
799.0
2039.2
3279.4
4519.6
5759.8
7000.0
Acquired: 10:33:00, October 11, 2011
Schubert CS109 Mw="4316"? THF PosRef [1:24] [Dith;THF] + NaOAc
D:\2011\Oct11\HULMEH086-VA-MAP_0001.dat
Printed: 10:41, October 11, 2011


EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea
<<HULMEH086-VA-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>NF0.7[BP = 4338.6, 2155]
Observed Data
% Intensity
Mass (m/z)
4338.6
2154.8
4337.6
4339.6
4340.6
4341.6
4336.6
4342.7
4343.6
4335.6
4338.2
4339.1
4344.7
4351.6
4352.5
4354.6
4329.0
4334.4
4339.8
4345.2
4350.6
4356.0
ISO:C264H374O34Si8Na
Theoretical [M+Na]+
4336.6
4339.6
4337.6
4340.6
4341.6
4336.6
4342.6
4343.6
4335.6
4344.6
4345.6
Acquired: 10:33:00, October 11, 2011
Schubert CS109 Mw="4316"? THF PosRef [1:24] [Dith;THF] + NaOAc
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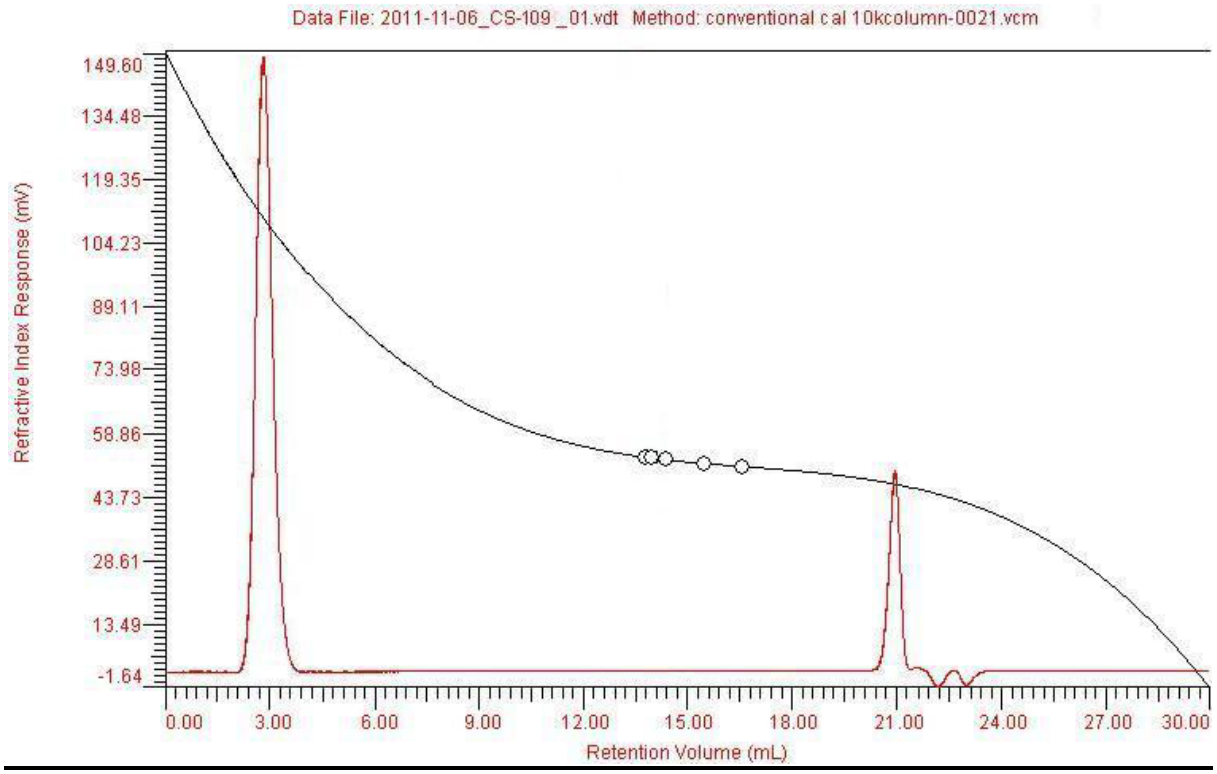
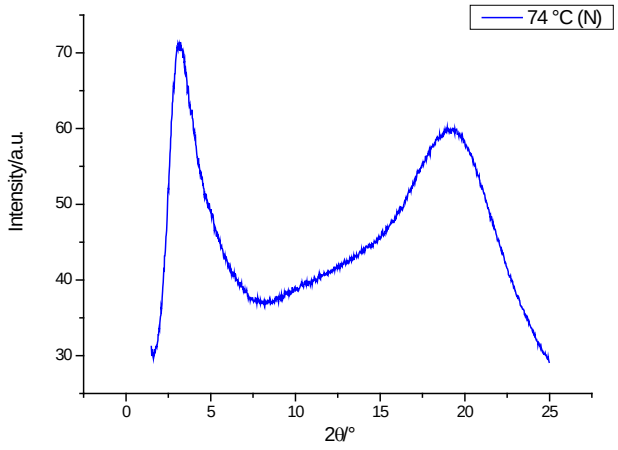
Printed: 10:43, October 11, 2011

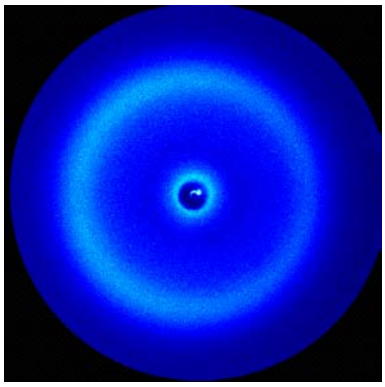


Liquid Crystal Analysis

X-ray Diffraction (XRD)

Dimer **1**

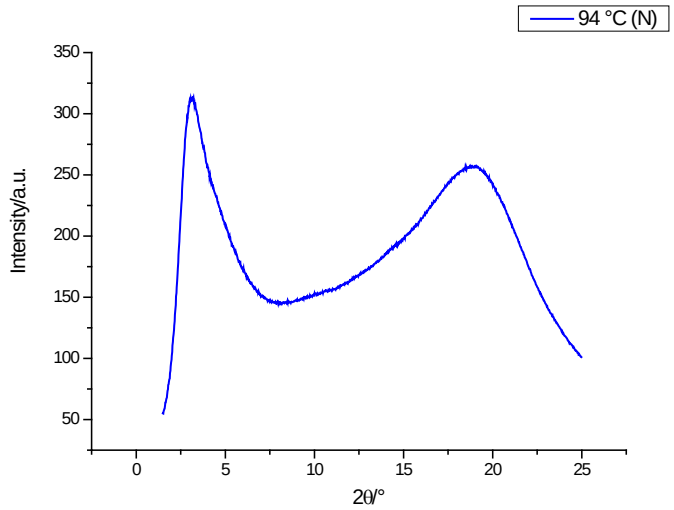


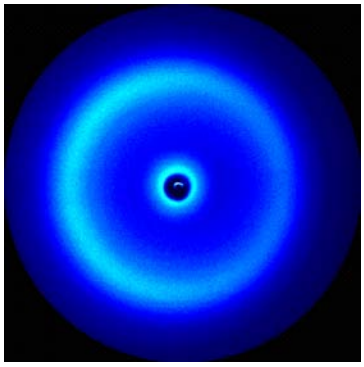


On cooling
Temp = 74 °C
Nematic
Distance detector to sample = 300 mm
Exposure time = 300 sec

2 θ	θ	*d*-value (nm)
3.2347	1.6174	2.7313
18.9870	9.4935	0.4674

Tetramer **2**

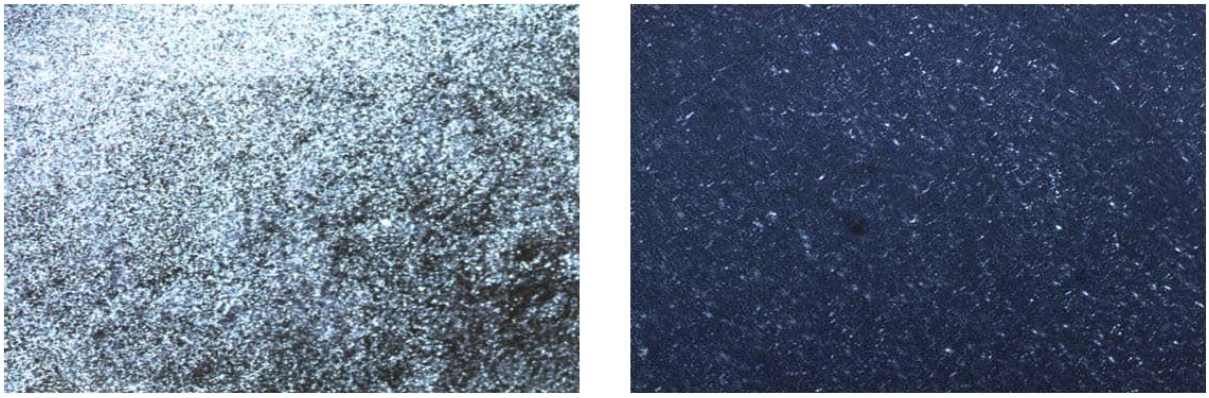




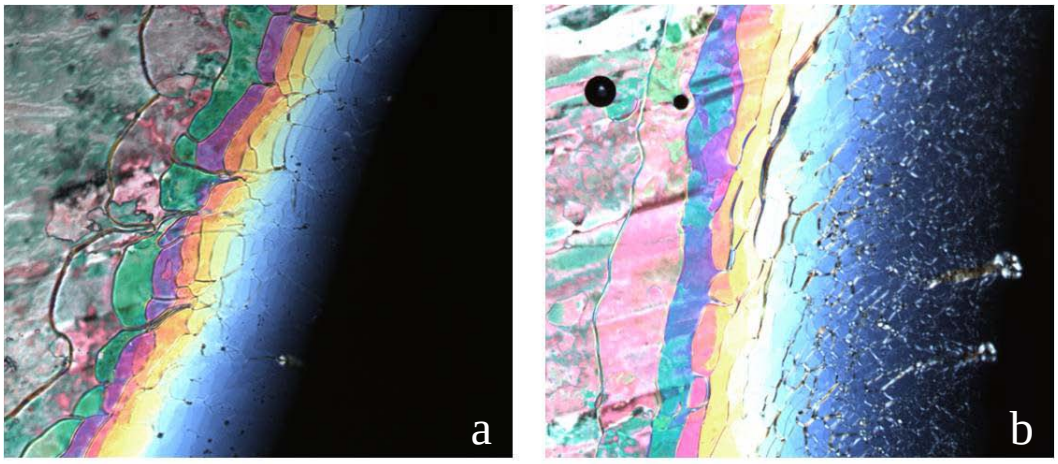
On cooling
Temp = 94 °C
Nematic
Distance detector to sample = 300 mm
Exposure time = 300 sec

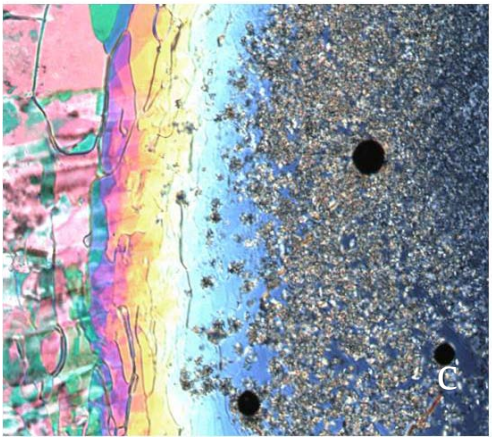
2 θ	θ	*d*-value (nm)
3.1792	1.5896	2.7790
18.7310	9.3655	0.4737

Optical Polarising Microscopy (OPM)

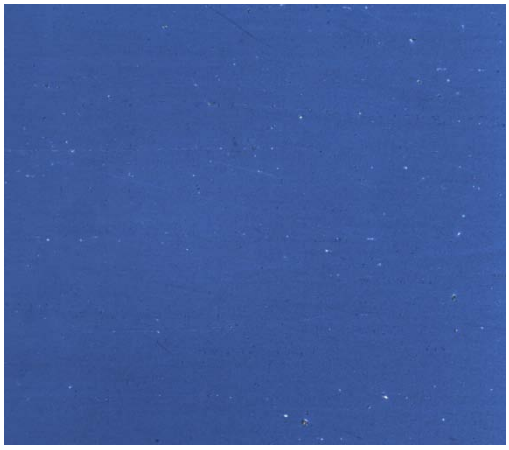


Optical polarising microscopy textures of dimer **1** (left) at 77°C and tetramer **2** (right) at 85°C

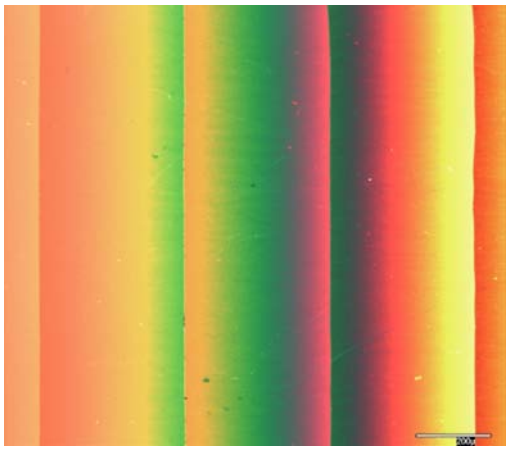
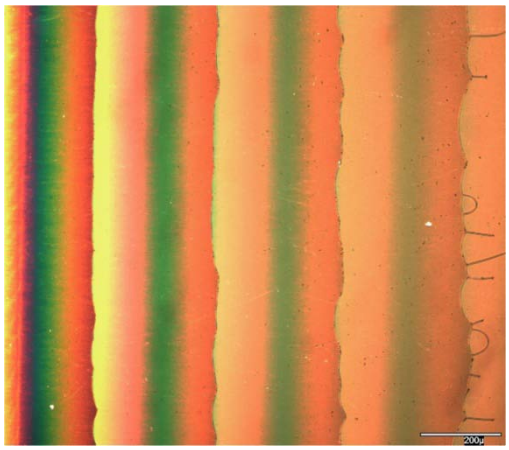




Optical polarising microscopy textures of contact experiment between compound **1** and nematic precursor **8** at (a) 96 °C – nematic mesogen and isotropic compound **1**; (b) 85 °C – nematic mesogen and chiral nematic compound **1**; (c) 47 °C – nematic mesogen and crystalline compound **1**

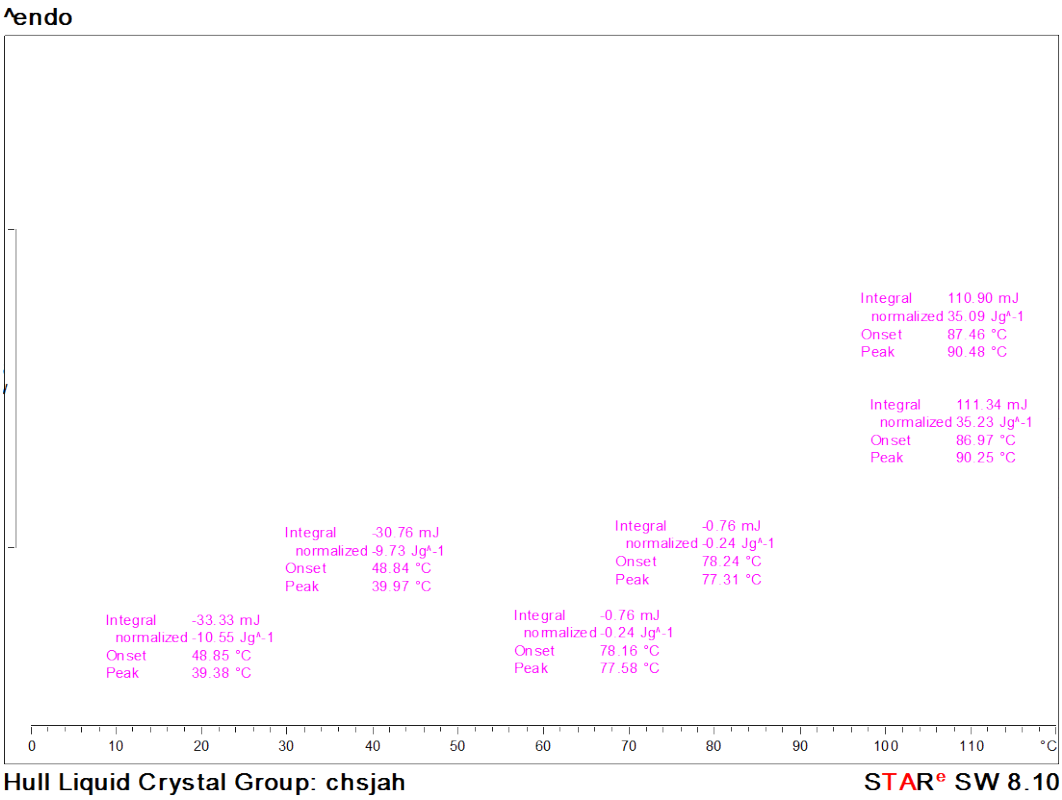
OPM textures of compounds **1** (left) at 70 °C and **2** (right) at 90 °C in electro-optical polyimide coated planar aligned cells (2.0 μm thickness) on cooling.

Helical twisting power measurements of compounds **1** (left) and **2** (right) using Grandjean-Cano wedge cells (0.3 mm, tanθ 0.0083) in ~5% w/w concentration in 4-pentyl-4'-cyanobiphenyl (5CB) at ambient temperature

Differential Scanning Calorimetry (DSC)

Compound **1**



Compound **2**