

Supplementary Information

Title: Nematic twist-bend phase with nanoscale modulation of molecular orientation

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Affiliations:

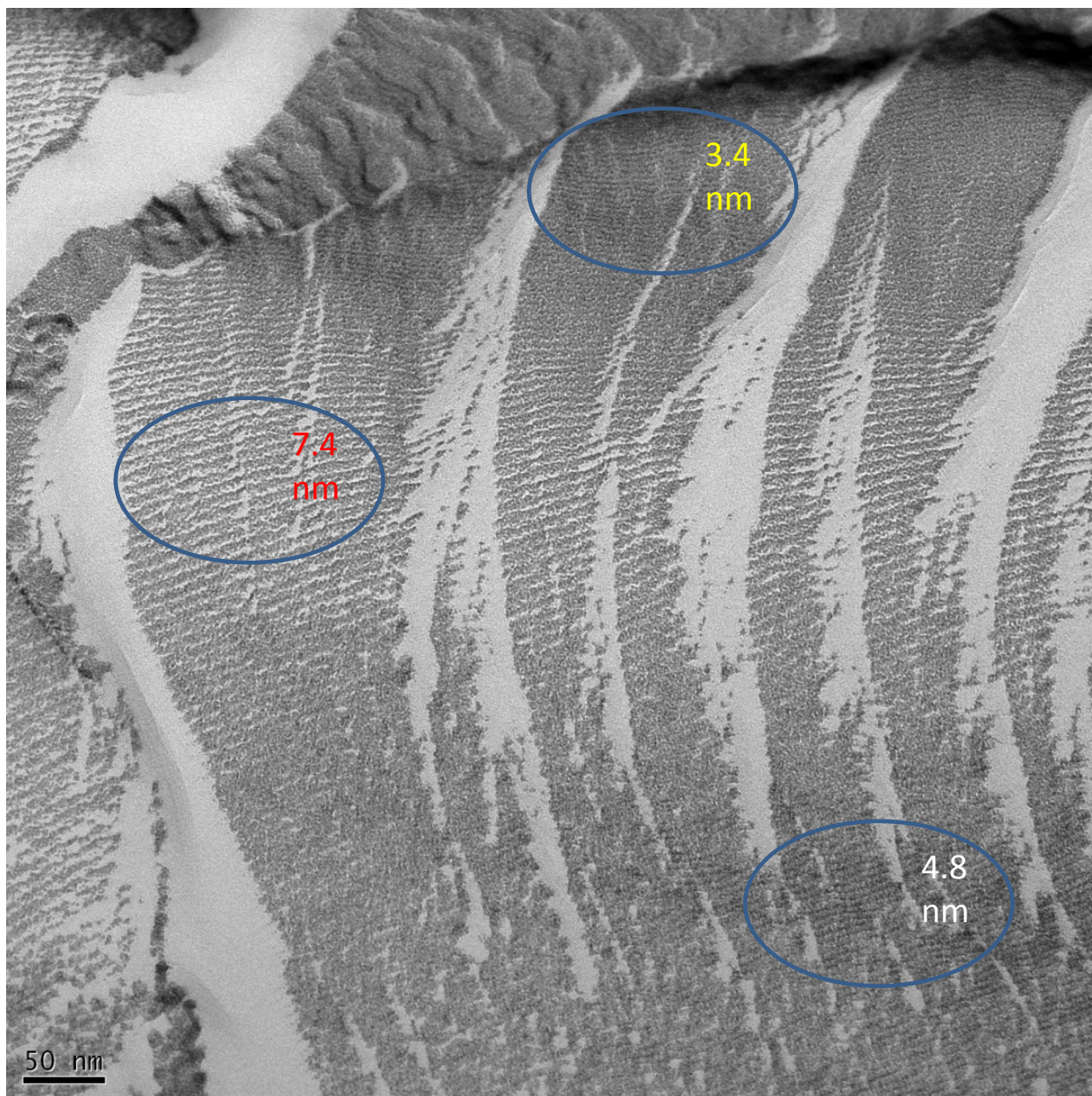
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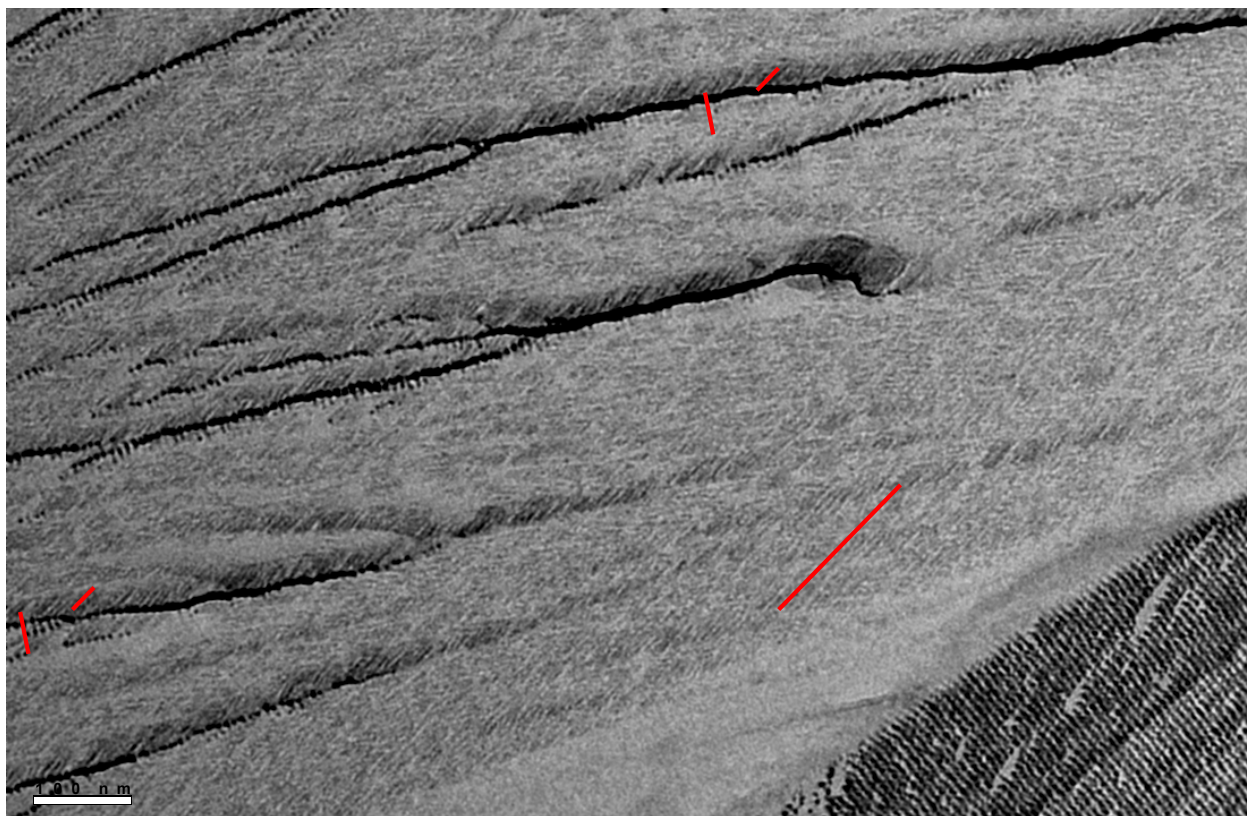
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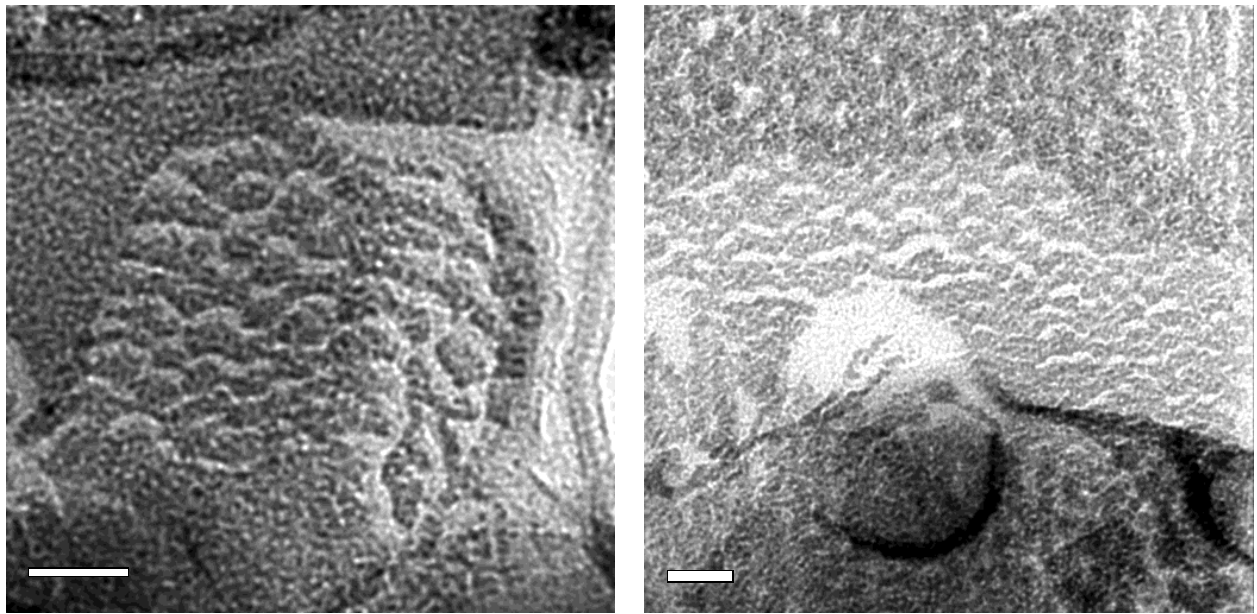
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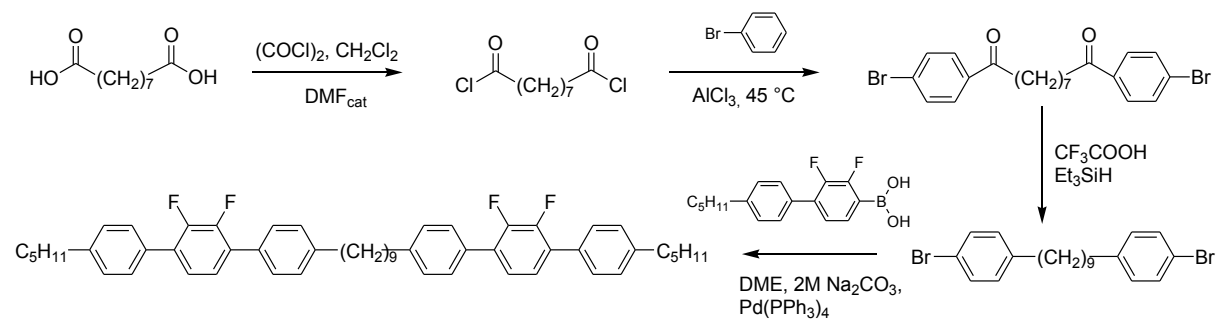
Supplementary Figure S1. | FFTEM texture of M1. Magnified image of a local area in Fig.5b, with unusually small periods of 7.4, 4.8, and 3.4 nm. Scale bar 50 nm.



Supplementary Figure S2. | FFTEM texture of M1. Magnified image of a local area in Fig.5b, showing a chiral structure similar to the one observed by Chen et al in Ref.19. Scale bar 100 nm.



Supplementary Figure S3. | FFTEM texture of M1. Enlarged views of Bouligand arches of type II. Scale bars 20 nm.

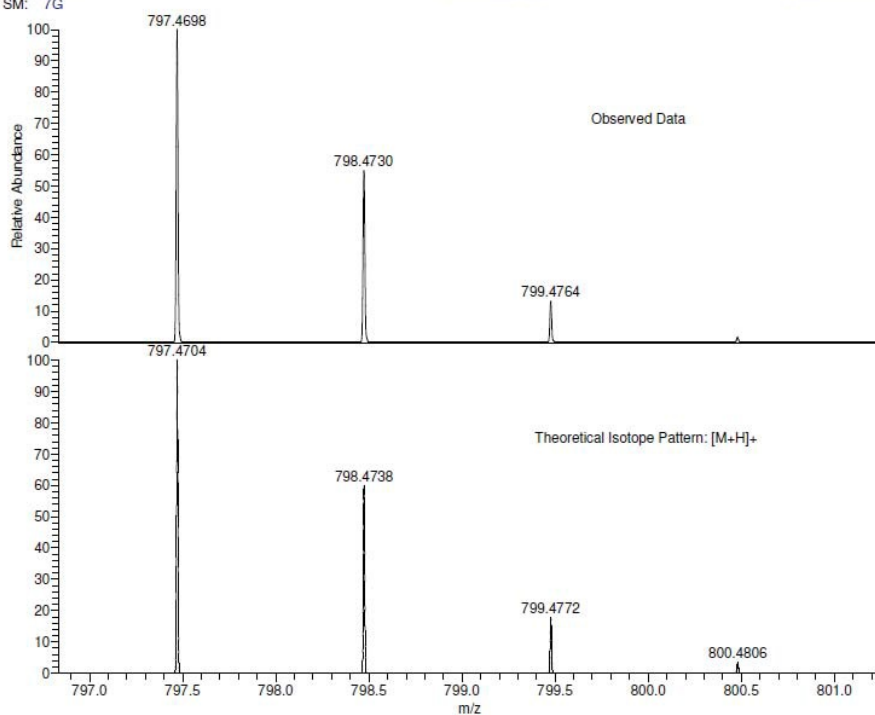


Supplementary Figure S4. | Synthesis of 1,5-Bis(2',3'-difluoro-4''-pentyl-[1,1':4,1''-terphenyl]-4-yl)nonane (DTC5C9).

DTC5C9 MW=797?
ASAP(DCM)
SM: 7G

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LTQ Orbitrap XL

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NL:
4.84E6
HULMEH208-PG-HASP#127-
140 RT: 7.14-7.87 AV: 14 T:
FTMS + p APCI corona Full ms
[100.00-1200.00]

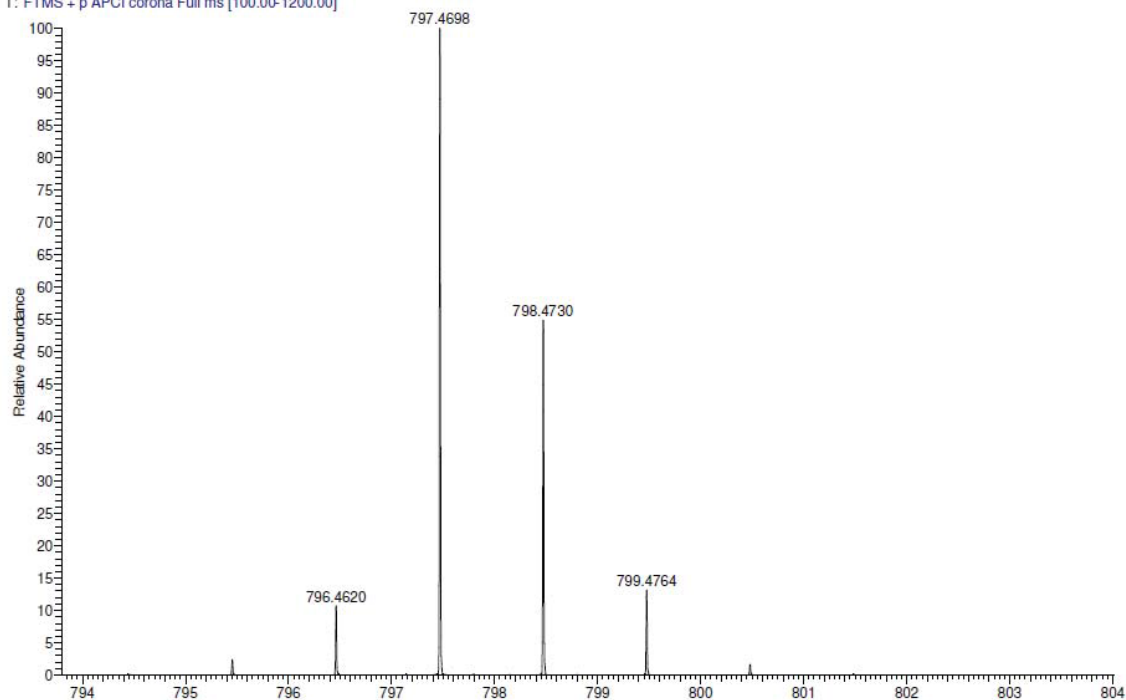
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C₂₅H₄₁F₄
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr .@FWHM

DTC5C9 MW=797?
ASAP(DCM)

EPSRC National Facility Swansea
LTQ Orbitrap XL

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16/09/2013 08:13:23

HULMEH208-PG-HASP #127-140 RT: 7.14-7.87 AV: 14 SM: 7G NL: 4.84E6
T: FTMS + p APCI corona Full ms [100.00-1200.00]



Supplementary Figure S5. | High resolution mass spectra of 1,5-Bis(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)nonane (DTC5C9).

Supplementary Methods

Synthesis of 1,5-Bis(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)nonane

Preparation of nonanedioyl dichloride: Nonanedioic acid (17 g, 0.09 mol) was dissolved in dry dichloromethane (200 ml) under nitrogen. Oxalyl chloride (30 ml, 44.3 g, 0.35 mol) was added followed by dry *N, N'*-dimethylformamide (1 drop) and gentle stirring. The nitrogen supply was turned off and the reaction was monitored by the evolution of gas. The reaction was stirred overnight and then refluxed for 2 hours until gas evolution had ceased. The solution was evaporated by vacuum distillation to yield crude nonanedioyl dichloride which was used immediately in the Friedel-Crafts acylation described below. Due to the instability of acyl chlorides the crude product was used immediately; no NMR spectra were recorded.

Preparation of 1,7-bis(4-bromophenyl)nonane-1,7-dione: Bromobenzene (50 ml, 74.75 g, 0.47 mol) was added to powdered aluminium chloride (25 g, 0.187 mol) and rapidly stirred under nitrogen for 1 hour. The crude nonanedioyl dichloride was dissolved in bromobenzene (30 ml, 44.85 g, 0.285 mol) and was added dropwise over a period of one hour. The temperature of the reaction was maintained below 45 °C during the addition. The reaction mixture was maintained at 40 °C and stirred overnight. The reaction was allowed to cool to ambient temperature and poured into a solution of concentrated hydrochloric acid (150ml) in ice water (600 ml). A small portion of dichloromethane was added to dissolve the suspended solids. The aqueous layer was extracted with dichloromethane several times and the organic extracts were dried over magnesium sulphate with rapid stirring overnight. The dichloromethane was evaporated under reduced pressure. The crude solid was recrystallised from ethanol four times to yield 1,5-bis-(4-bromophenyl)nonane-1,5-dione. The yield was found to be 18.4 g, 44 %

¹H NMR (CDCl₃, *J*/Hz, 400 MHz): δ 7.81 (4H, d, *J* = 8.6); 7.59 (4H, d, *J* = 8.6); 2.92 (4H, t, *J* = 7.3); 1.69-1.76 (4H, m); 1.42-1.35 (6H, m).

Preparation of 1,5-bis-(4-bromophenyl)nonane: 1,5-Bis-(4-bromophenyl)heptane-1,5-dione (8.8 g, 0.02 mol) was dissolved in trifluoroacetic acid (30.75 ml, 45.79 g, 0.40 mol). Triethylsilane (16.6 ml, 12.09 g, 0.10 mol) was added dropwise over a period of one hour with rapid stirring and cooling in a water bath. The reaction mixture became turbid white after 1 hour. The reaction

was stirred at ambient temperature for 48 hours. The reaction mixture was poured into a mixture of ice and water. Hexane was added and the aqueous layer was extracted in hexane four times. The organic extracts were combined and were dried over magnesium sulphate overnight. The solvent was then evaporated. The crude product was separated by column (silica) chromatography and yielded 1,5-bis-(4-bromophenyl)heptane. The mobile phase was a hexane/dichloromethane gradient starting with pure hexane finishing at 35 % dichloromethane. The yield was found to be 3.17 g, 36.2 %

^1H NMR (CDCl_3 , J/Hz , 400 MHz): δ 7.38 (4H, d, $J = 8.4$); 7.04 (4H, d, $J = 8.6$); 2.55 (4H, t, $J = 7.7$); 1.53-1.61 (4H, m); 1.24-1.35 (10H, m).

Preparation of 1,5-bis(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)nonane: A solution of 1,5-bis-(4-bromophenyl)nonane (0.48 g, 0.01 mol) and (2,3-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)boronic acid (1.0 g, 0.03 mol) in a mixture of 1,2-dimethoxyethane (12 ml) and saturated aqueous solution of sodium hydrogen carbonate (18 ml) was thoroughly degassed with argon for 1 hour. Tetrakis(triphenylphosphine)palladium(0) 50 mg was added. The reaction was refluxed at 125 °C for 12 hours under stirring. The reaction was allowed to cool to room temperature. Water was added to the reaction. The aqueous solution was extracted with dichloromethane four times and dried over magnesium sulphate overnight. The solvent was evaporated and the crude product was separated by column chromatography and yielded 1,5-bis(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)nonane. The mobile phase was a hexane/dichloromethane gradient starting with pure hexane, finishing at 50 % dichloromethane. The yield was found to be 0.66 g, 70 %.

^1H NMR; δ_{H} (CDCl_3 , J/Hz , 400 MHz): δ 7.38 (4H, d, $J = 8.4$); 7.04 (4H, d, $J = 8.6$); 2.55 (4H, t, $J = 7.7$); 1.53-1.61 (4H, m); 1.24-1.35 (10H, m);

^{13}C NMR; δ_{C} ; (100MHz; J/Hz ; CDCl_3) 148.48 (dd, $^1\text{J}(\text{C-F}) = 250.6\text{Hz}$, $^2\text{J}(\text{C-F}) = 15.4\text{Hz}$), 143.08, 131.97, 129.47 (m), 128.70, 128.67, 124.55 (m), 35.71, 35.69, 31.55, 31.39, 31.10, 29.46, 29.32, 22.55, 14.04;

^{19}F NMR δ_{F} (377MHz; CDCl_3) -143.22;

MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{55}\text{H}_{60}\text{F}_4+\text{H}$: 796.4704; found: 797.4698. The mass spectra are shown in Supplementary Fig. S5.

The compound MCT5 (CAS registry number 121218-76-6) was purchased from Kingston Chemicals Ltd, Hull, UK and used without further purification. . This compound was first reported in Supplementary Reference 36.

Supplementary Reference

36. Gray, G. W., Hird, M., Lacery, D. & Toyne, K. J. The synthesis and transition temperatures of some 4,4'' dialkyl and 4,4'' alkoxyalkyl 1,1': 4',1'' terphenyls with 2,3 or 2',3' difluoro substituents and of their biphenyl analogues. *J. Chem. Soc. Perkin Trans. 2*, 2041-2053 (1989).