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Cyanoalkyl difluoro-terphenyl-carboxylate chiral dopants

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ABSTRACT

A liquid crystal like difluoroterphenyl chiral dopant was synthesized to match the dimensions of a host chiral dopant mixture. The melting point of the chiral dopants was decreased by increasing the length of the alkyl chain. The melting point of the chiral dopants also decreased when fluorine was on the same ring as the ester i.e. at 2″, 3″ position. These dopants were formulated with terphenyl host mixture and liquid crystal properties were assessed. New dopants, when added to the host mixture, maintain SmA[1] but the SmC[2] phase was reduced markedly. There was a decrease in spontaneous polarisation when fluorine was on the same ring as the ester i.e. at 2″, 3″ position. As the molecular weight of the chiral dopant increased (pentyl → heptyl → nonyl), spontaneous polarisation decreased.

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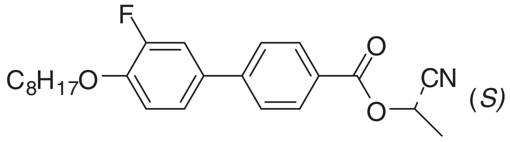
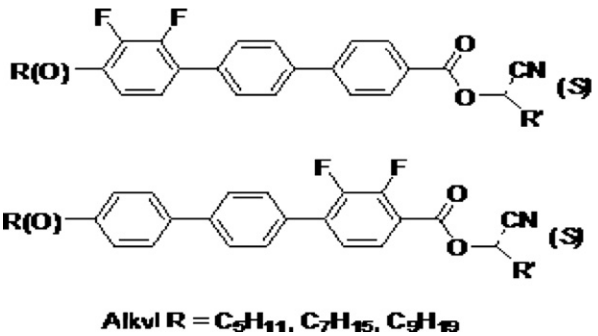
1. Introduction

A chiral dopant (BE80F2N[3]) that has proved to be successful is the octyloxyfluorobiphenyl ester which has a chiral cyanohydrin as the branched asymmetric group.



This molecule, when added to an achiral FLC[4] host mixture (5–12% w/w) provides an FLC mixture with a reasonable compromise of liquid crystalline and electro-optic properties. Enhancement of the dopants' mesogenic properties can be obtained from using a terphenyl [1,2] structure and further improvement may be obtained from increasing the length of the chain attached to the cyanohydrin. The increased chain length may, however also increase polarisation and decrease the pitch length of the material. The study of ferroelectric liquid crystals (FLCs) has fast developed into multidisciplinary field involving physicists, electrical engineers, computer engineers, and chemists. As in nematic technology, the FLC material is not a single component, but a mixture of many compounds. It is best to employ an achiral room temperature 'host' SmC with a broad LC phase temperature range, low viscosity, good stability etc. and to dope this with a chiral material. One example of a chiral dopant is (BE80F2N) which has proven increase in the Ps and decrease in the pitch length. The latter effects result from the restricted rotation caused by lengthening the chain. Syntheses of the longer chain cyanohydrin esters involve a different route, starting from amino acids. The synthetic targets chosen, will examine the effect of the position of the ortho-difluoro substituent and the chain length. The synthetic routes involve directed lithiation and Suzuki palladium catalysed cross coupling of boronic acids with arylhalides as a key component [3]. Target chiral dopants are given below.



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[1] Smectic A.
[2] Smectic C.
[3] Octyloxyfluorobiphenyl ester.
[4] Ferroelectric liquid crystal.

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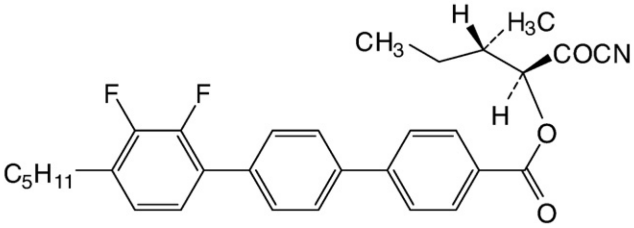
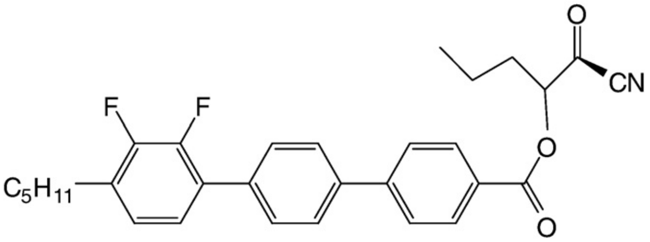


(S)-(−)-1-cyno-2-methylbutyl-4-pentyl-difluoroterphenyl-4′-carboxylate



(S)-(−)-1-cyno-2-methylbutyl-4-pentyl difluoroterphenyl-4′-carboxylate

2. Synthesis details of ferroelectric liquid crystals

The initial aim of this work was to synthesize ortho difluoro substituted materials that possess a central terphenyl core and to incorporate a chiral centre in the terminal chain. Eight materials were prepared, five of which possess fluorine on the alkyl side and the other three on the chiral side. In six dopants a chiral centre was introduced using commercially available (S)-lactamide. L-leucine and L-norvaline were also used to induce a chiral centre in the ortho difluoro-substituted materials to produce two dopants.

2.1. Synthesis schemes

Here are six schemes to elaborate the synthesis of all intermediate compounds as well as dopants. In Fig. 1 synthesis of bromo-biphenyl cynohydrin ester is given which is an intermediate compound for the synthesis of 4-heptyl-2,3-difluoro terphenyl nitrile and 4-nonyl-2,3-difluoroterphenyl nitrile [4]. In Fig. 2, synthesis of 4-heptyl-2,3-difluoro terphenyl nitrile (D7), 4-nonyl-2,3-difluoro terphenyl nitrile (D9), 4-pentyl-2″,3″-difluoro terphenyl nitrile (D5R) and 4-heptyl-2″,3″-difluoro terphenyl nitrile (D7R) are presented while Fig. 3 gives the synthesis route for 4-pentyl-2,3-difluoro terphenyl nitrile (D5)[4] and Fig. 4 for 4-nonyl-2″,3″-difluoro terphenyl nitrile (D5R). Figs. 5 [5] and 6 provide the synthesis route for dopants (S)-(−)-1-cyno-pentyl-4-pentyl difluoroterphenyl-4′-carboxylate (D52) and (S)-(−)-1-cyno-2-methylbutyl-4-pentyl difluoroterphenyl-4′-carboxylate (D53) respectively [6].

2.1.1. 4-pentyl-2,3-difluoro terphenyl carbonyl nitrile (D5)

2.1.1.1. Quantities. 4-pentyl-2,3-difluoro terphenyl carbonyl amide (1 g, 12.16 mmol, 473 g/mol), $POCl_3$ (1.33 ml,14.5 mmol,153 g/mol) and dry DMF (27.5 ml).

2.1.1.2. Procedure. Dry DMF was cooled to 0 °C. $POCl_3$ was added slowly by syringe under nitrogen keeping the temperature below 5 °C. It was stirred for 20 min and turned coloured. Pentyl-2,3-difluoro terphenyl carbonyl amide was added in portion and stirred for 20 h at room temperature. The solution was poured in ice and water mixture, swirled around and was placed to settle down. A precipitate was

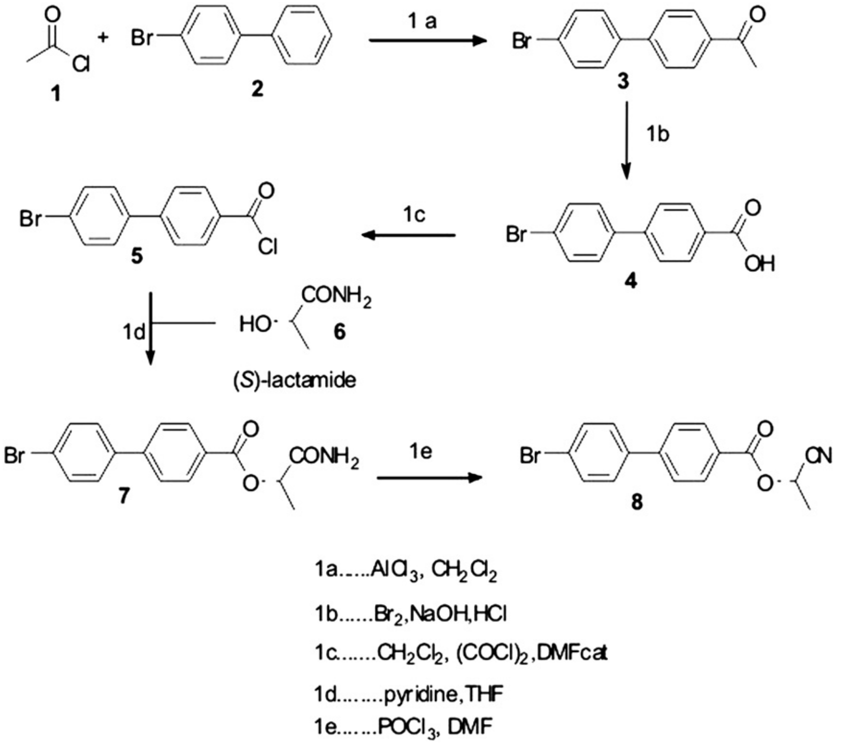


Fig. 1. Synthesis steps of biphenyl cyanohydrin ester.

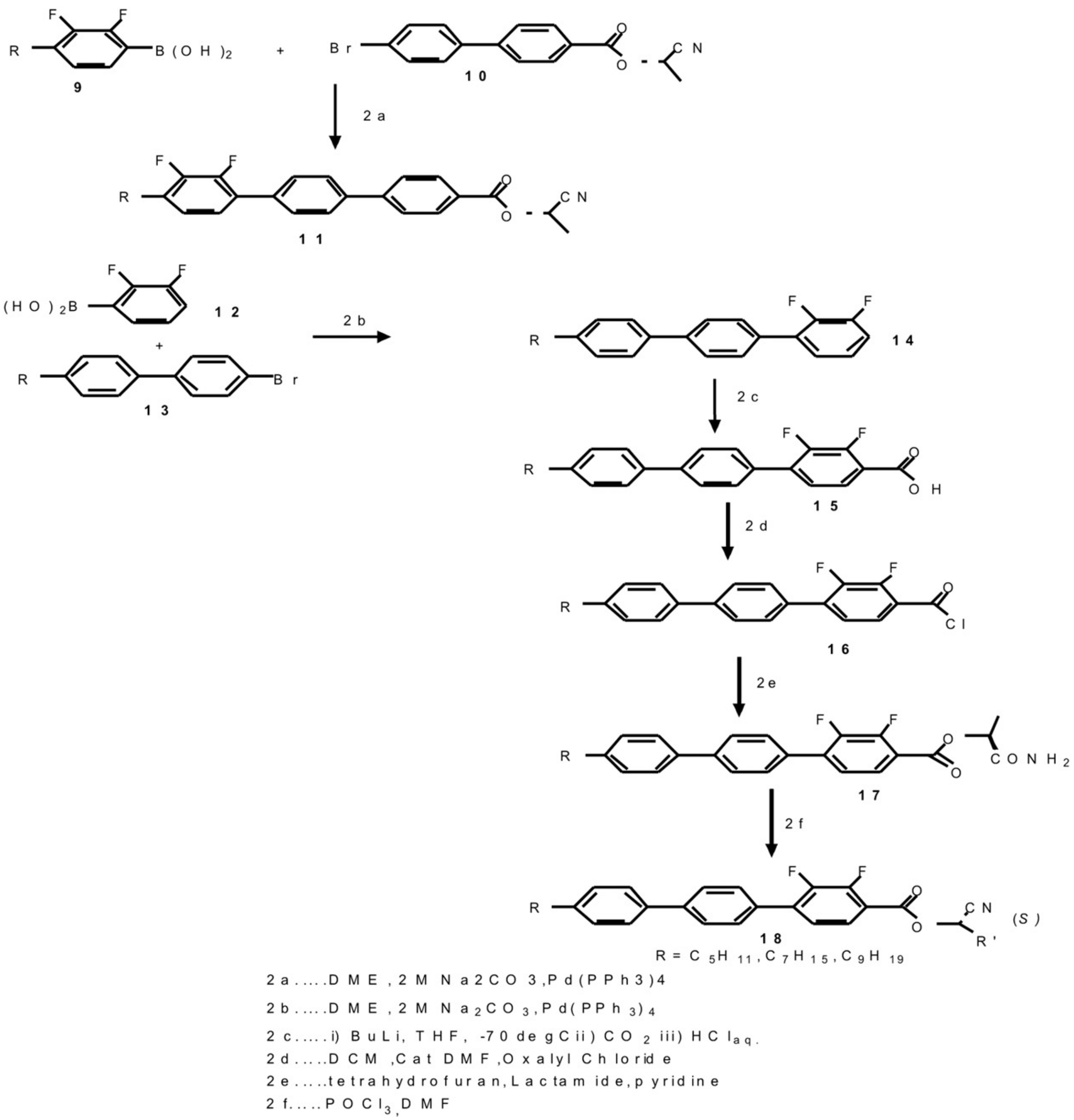


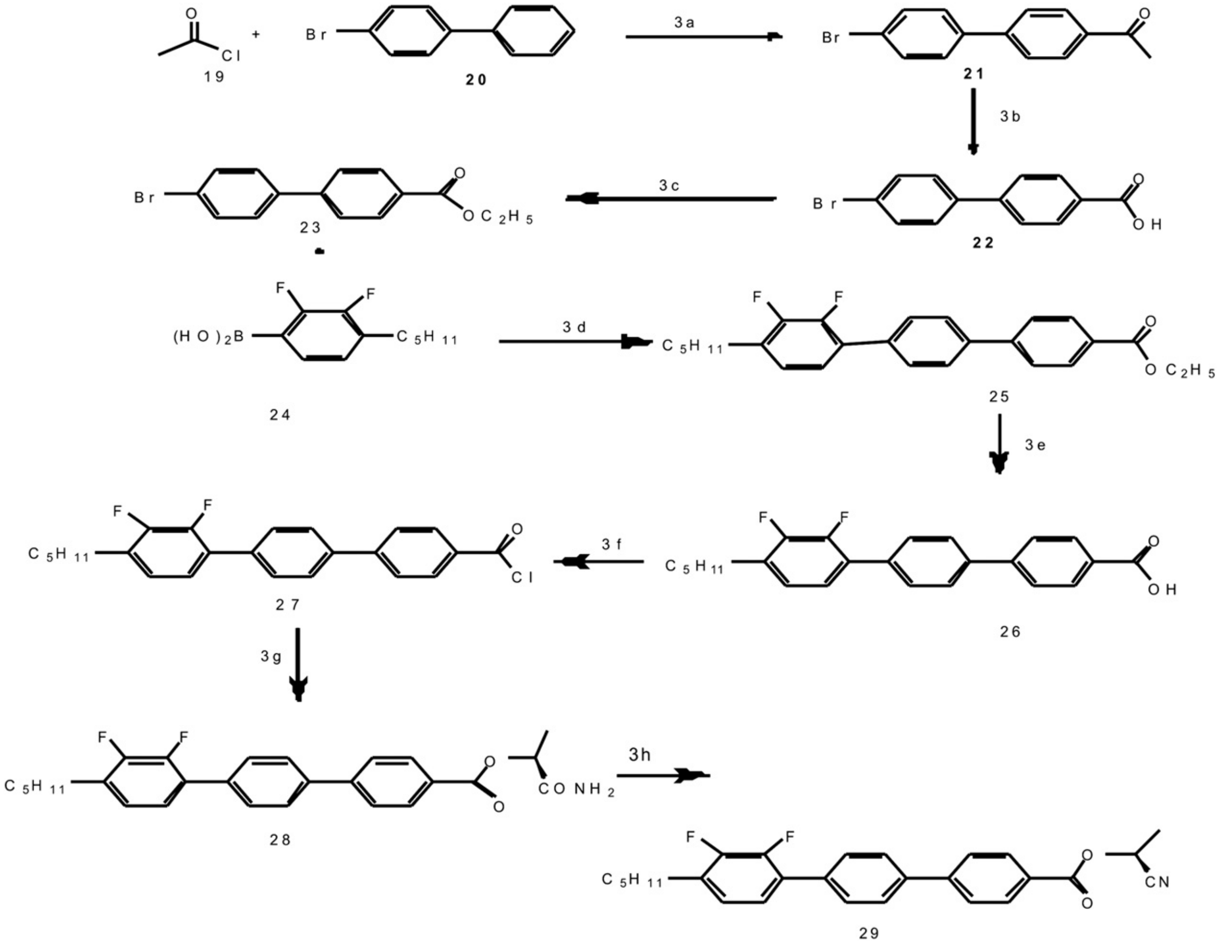
Fig. 2. Synthesis steps of 4-akyl-2″,3″ difluoro terphenyl nitrile using coupling reactions [1].

obtained. It was then filtered by micro-filtration by dissolving in THF. The solvent was removed in vacuo to get the dry product. Then it was re-crystallised twice through acenitrile. It was put in desiccators overnight.

Yield (0.17 g, 18.18%); M.P. 131.8 °C (from acenitrile); elemental analysis: calc. for (found: C, 74.67; H, 6.04; N, 3.10. $C_{29}H_{29}F_2NO_2$ requires C, 74.81; H, 5.81; N, 3.23%); m/z 433 (M^+, 100%), 376, 363, 323, 306, 277, 153; transitions/°C K 106.1 (48.2 J/g) SmA* 132.1 (83.21 J/g) I; IR(KBr)υ_{max}/cm^{-1} 2928(CH), 1728 s(CO), 1458, 1263, 1095, 810, 771; δ_H(400 MHz; $CDCl_3$) 0.92 (3H, t, J7, $C\underline{\boldsymbol{H}}_3CH_2$), 1.35–1.39 (4H, m), 1.66(2H, quint, J7.5, $ArCH_2C\underline{\boldsymbol{H}}_2$), 1.81(3H, d, J7, Me), 2.71 (2H, t, J 7.4, $ArCH_2$), 5.69 (1H, q, J7, CHMe), 7.02 (1H, ddd, J6.8, 6.6, 1.5, 20H), 7.16 (1H, ddd, J6.8, 6.4, 1.6, 19H), 7.66 (2H, dd, J 8.4, 1.3, 6- and 18-H), 7.72 (2H, d, J 8.4, 1- and 17-H), 7.75 (2H, d, J 8.6, 10- and 14-H), 8.15 (2H, d, J8.6, 11 and 13H); δ_F(376;$CDCl_3$) 143.30 (1F, dd, $J_{F,F}$20.81, $J_{F,H}$6.9), 143.88 (1F, dd, $J_{F,F}$18.5, $J_{F,H}$6.9); δ_C(100.5; $CDCl_3$) 13.99, 19.01, 22.45, 28.77, 29.71, 31.44, 57.77 ($\underline{\mathbf{C}}$HMe), 117.59 (CN), 124.11 (dd, $J_{C,F}$3.1, 2.3), 124.88 (dd, $J_{C,F}$4.6, 4.5), 127.1, 127.2, 127.4, 127.6, 129.4, 129.5, 130.6, 131.3, 131.5, 135.2 (d, $J_{C,F}$ 2.3), 139, 146.09, 164.57 (CO).

2.1.2. 4-heptyl-2,3-difluoro terphenyl carbonyl nitrile (D7)

2.1.2.1. Quantities and procedure. (S)-1-cynoethyl-4-bromo diphenyl-4′-carboxylate (1 g, 3.03 mmol, 330 g/mol), 2,3-diflouro-4-nanoyl phenyl boronic acid (2.56 g, 10 mmol, 256 g/mol), potassium phosphate (1.93 g, 9.09 mmol, 212.28 g/mol) and dioxan (40 ml) were added under dry nitrogen at room temperature. The flask was flushed by nitrogen three times and then tetrakis (triphenyl phosphine) palladium (0) (0.162 g, 0.1401 mmol, 1156 g/mol) was added. The stirred mixture was heated under reflux (ca. 140 °C) for 23 h (i.e., until g.l.c/t.l.c. analysis revealed a complete reaction). The



3a……AlCl$_3$, CH$_2$Cl$_2$
3b……Br$_2$,NaOH,Hcl
3c……Ethanol, H$_2$SO$_4$
3d……DME,2M Na$_2$CO$_3$,pd(pph$_3$)$_4$
3e……Sodium hydroxide ,Ethanol
3f……Oxalyl Chloride ,DCM ,Cat DMF
3g……tetrahydrofuran ,Lactamide , Pyridine
3h……POCl$_3$,DMF

Fig. 3. Synthesis steps of 4-pentyl-2,3 difluoro terphenyl nitrile using coupling reactions [1].

mixture was filtered by hypo flow and the solvent was evaporated to get the dry product. The dry product was purified by addition to a packed chromatography column of silica gel [silica gel, DCM: hexane: 20:80] to yield a white product. Product was re-crystallised twice through acenitrile. It was cooled quickly in liquid nitrogen to avoid it becoming gel. It was filtered by pressure. It was again filtered by micro-filtration by dissolving in THF to remove the dust particles and was evaporated to get the dry product. It was put in the desiccators overnight.

Yield (0.42 g, 30.88%); M.P.122 °C (from acenitrile) elemental analysis: calc. for (found: C, 75.22; H, 6.54; N, 2.93. $C_{29}H_{29}F_2NO_2$ requires C, 75.47; H, 6.33; N, 3.03%); m/z 461 (M^+, 100%), 408, 391, 376, 363, 323, 277, 153; transitions/°C K 121 I (47.51 J/g); IR (KBr) υ_{max}/cm^{-1} 2924 (CH), 1724 vs, (CO), 1606, 1487, 1464, 1398, 1317, 1274, 1206, 1181, 1110, 1039, 1004, 895, 846, 810, 767; δ_H(400 MHz; CDCl$_3$), 0.89 (3H, t, $C\underline{\boldsymbol{H}}_3C\underline{\boldsymbol{H}}_2$), 1.28–1.43 (8H, m), 1.66 (2H, quint, J7.79, $ArC\underline{\boldsymbol{H}}_2C\underline{\boldsymbol{H}}_2$), 1.81 (3H, d, J 6.78, Me), 2.71 (2H, t, J 7.51, ArCH$_2$), 5.69 (1H, q, J 6.96, $C\underline{\boldsymbol{H}}$Me), 7.03 (1H, ddd, J 6.78, 6.6, 1.5, 20H), 7.15 (1H, ddd, J 6.78, 6.6, 1.5, 19H), 7.67 (2H, dd, J 6.78, 1.47, 6- and 18-H), 7.72 (2H, d, J 8.3, 1- and 17-H), 7.75 (2H, d, J 8.3,10- and 14-H), 8.15 (2H, d, J 8.3,11- and 13-H); δ_F(376; CDCl$_3$) −143.29 (1F, dd, $J_{F,F}$20.81, $J_{F,H}$6.9)–143.88 (1F, dd, $J_{F,F}$20.81, $J_{F,H}$6.9), δ_C(100.5; CDCl$_3$), 14.1, 19.01, 22.65, 28.81, 29.08, 29.25, 30.04, 31.77, 57.76 ($\underline{\boldsymbol{C}}$HMe), 117.6(CN), 124.1 (dd, $J_{C,F}$3.8, 2.3), 124.88 (dd, $J_{C,F}$4.6, 3.8), 127.06, 127.21, 127.44, 127.58, 129.43, 129.46, 130.59, 131.32, 131.46, 135.2, 139.0, 146.09, 164.57 (CO).

2.1.3. 4-nanoyl-2,3-difluoro terphenyl carbonyl nitrile (D9)

2.1.3.1. Quantities. (S)-1-cynoethyl-4-bromo diphenyl-4′-carboxylate (0.1.39 g, 4.21 mmol, 330 g/mol), 2,3-diflouro-4-nanoyl phenyl boronic acid (2.92 g, 10.28 mmol, 284 g/mol), potassium phosphate (2.68 g, 12.63 mmol, 212.28 g/mol) tetrakis (triphenyl phosphine) palladium (0) (0.093 g, 0.0804 mmol, 1156 g/mol)and dioxan (60 ml).

2.1.3.2. Procedure. The experimental procedure was as described for the compound D7 except that when dry product was re-crystallised through acenitrile, it turned into gel. So it was purified by addition to a packed chromatography column of silica gel [silica gel, DCM:hexane: 75:25] to yield a white product. It was then filtered by micro-filtration by dissolving in THF and was evaporated to get the dry product. It was put in the desiccators overnight.

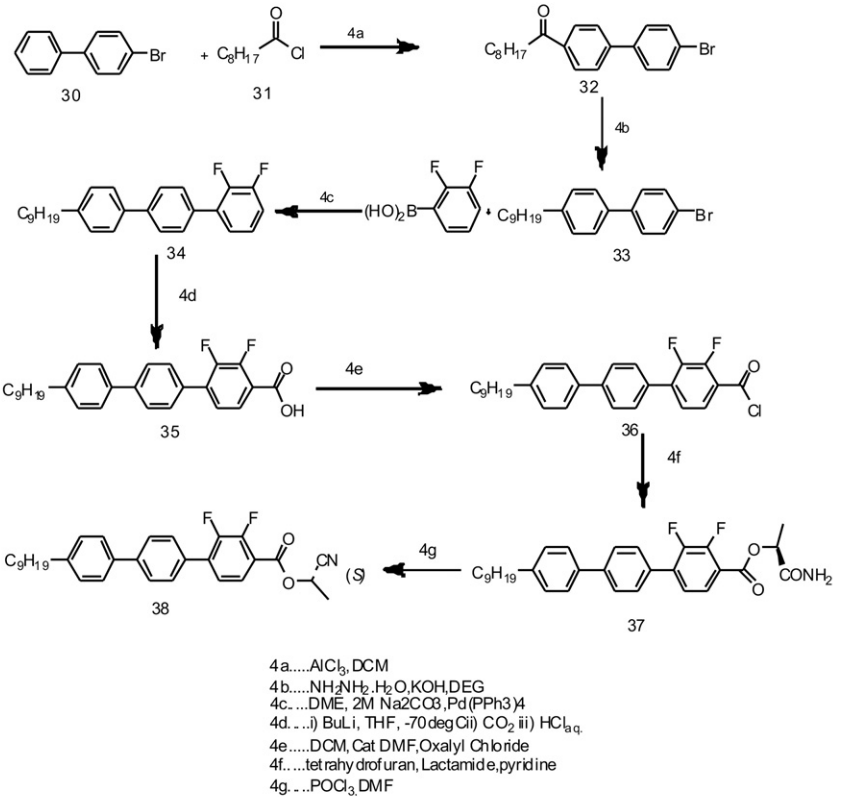


Fig. 4. Synthesis steps of 4-nonyl-2″,3″ difluoro terphenyl nitrile using coupling reactions.

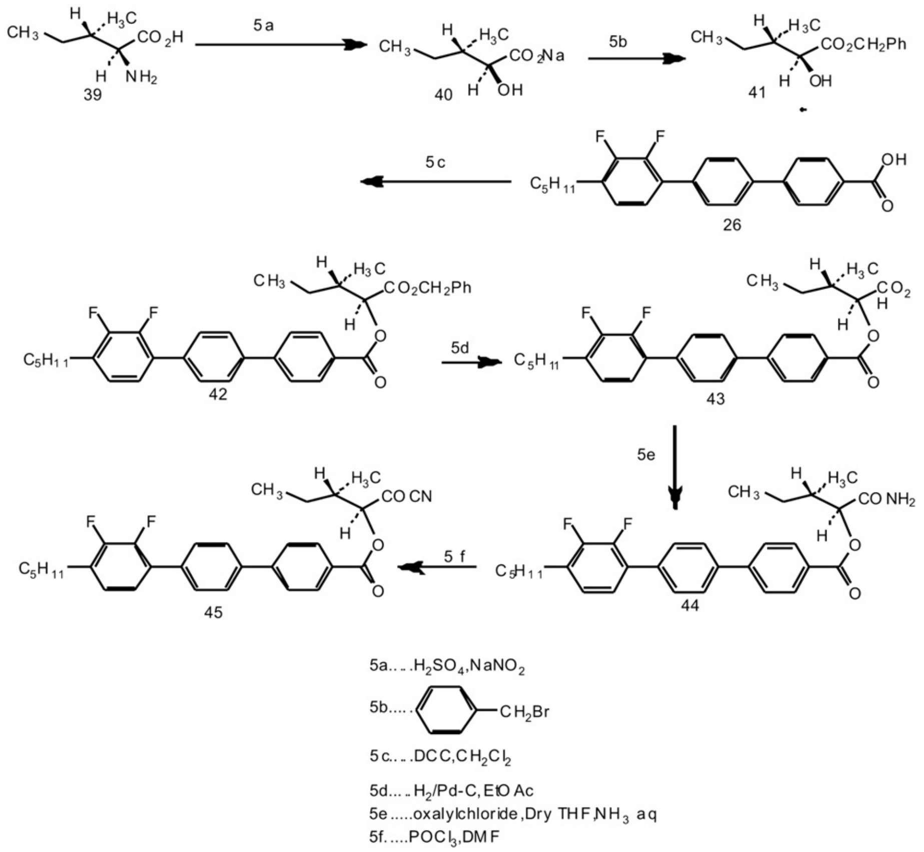


Fig. 5. Synthesis route for (S)-(−)-1-cyno-2-methylbutyl-4-pentyl-difluoroterphenyl-4′-carboxylate [2].

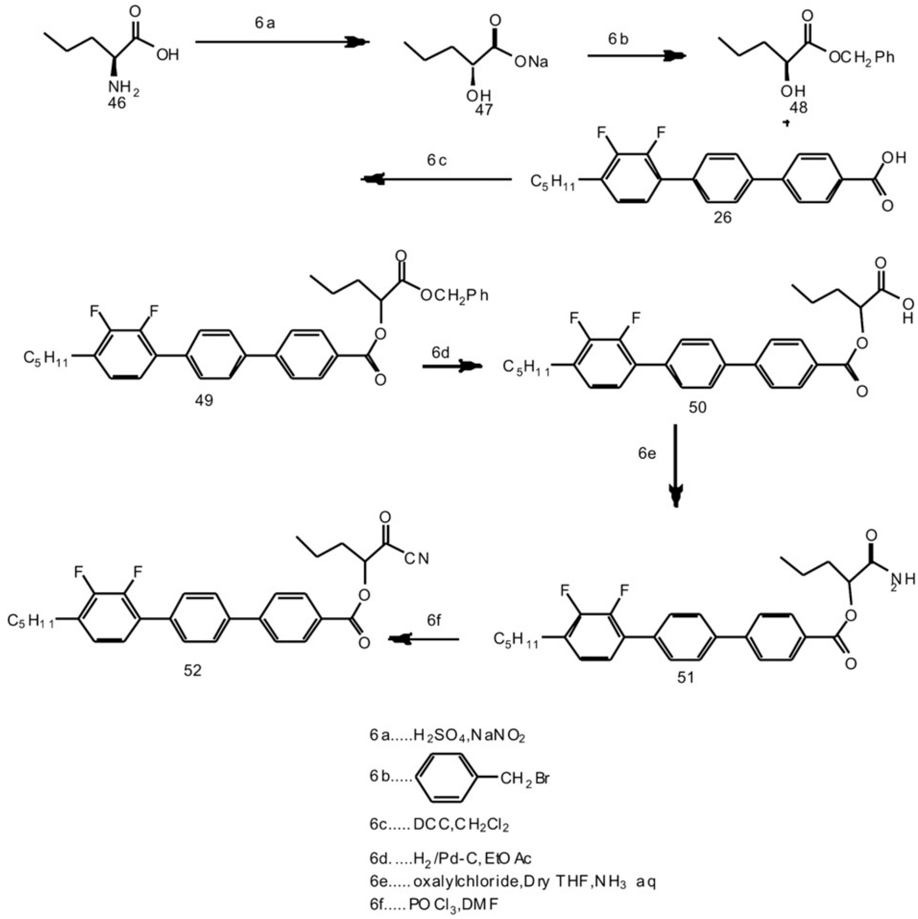


Fig. 6. Synthesis route for (S)-(−)-1-cyno-pentyl-4-pentyl-difluoroterphenyl-4′-carboxylate.

Yield (1.05 g, 50.97%); M.P. 119 °C; elemental analysis: calc. for (found: C, 76.19; H, 7.12; N, 2.73. $C_{31}H_{33}F_2NO_2$ requires C, 76.05; H, 6.79; N, 2.86%); m/z 489 (M^+ 100%), 376, 323, 277, 153; transitions/°C K 118 I (37.83 J/g).

IR(KBr)υ_{max}/cm^1 2923(CH), 1724vs (CO), 1607, 1487, 1464, 1397, 1317, 1274, 1206, 1181, 1110, 1039, 1004, 895, 846, 810, 767; δ_H(400 MHz; $CDCl_3$) 0.89 (3H, t, J6.96, $C\underline{\boldsymbol{H}}_3C\underline{\boldsymbol{H}}_2$), 1.24–1.39 (8H, m), 1.65 (2H, quint, J7.3, $ArC\underline{\boldsymbol{H}}_2C\underline{\boldsymbol{H}}_2$), 1.81 (3H, d, J6.8, Me), 2.71 (2H, t, J7.7, $ArC\underline{\boldsymbol{H}}_2$), 5.69 (1H, q, J7, $C\underline{\boldsymbol{H}}Me$), 7.02 (1H, ddd, J 6.6, 6.4, 1.5, 20H), 7.16 (1H, ddd, J 7, 6.6, 1.7, 19H), 7.66 (2H, dd, J 8.4, 1.5, 6- and 18-H), 7.72 (2H, d, J 8.6, 1- and 17-H), 7.75 (2H, d, J 8.6, 10- and 14-H), 8.15 (2H, d, J 8.6, 11- and 13-H); δ_F(376; $CDCl_3$) −143.29 (1F, dd, $J_{F,F}$20.81, $J_{F,H}$6.9), −143.88(1F, dd, $J_{F,F}$ 20.81, $J_{F,H}$6.9); δ_C(100.5; $CDCl_3$) 14.11, 19.01, 22.67, 28.81, 29.28, 29.31, 29.41, 29.51, 30.04, 31.87, 57.76 ($\underline{\boldsymbol{C}}HMe$), 117.59(CN), 124.10 (dd, $J_{C,F}$3.8, 2.3), 124.88 (dd, $J_{C,F}$4.6), 127.06, 127.20, 127.44, 127.57, 129.43, 129.46, 130.59, 131.33, 131.46, 135.2, 139.01, 146.09, 164.57 (CO).

2.1.4. 4-pentyl-2″,3″-difluoro terphenyl carbonyl nitrile (D5R)

2.1.4.1. Quantities. 4-pentyl-2″,3″-difluoro terphenyl carbonyl amide (1.2 g, 2.59 mmol, 463 g/mol), $POCl_3$ (1.59 ml, 17.095 mmol, 153 g/mol) and dry DMF (33 ml).

2.1.4.2. Procedure. The experimental procedure was as described for the preparation of 4-pentyl-2,3-difluoro terphenyl carbonyl nitrile except that it was filtered and washed with water. The dry product was recrystallised through isopropanol.

Yield (0.6 g, 55.05%); M.P.103.2 °C (from isopropanol); elemental analysis: calc. for (found: C, 75.01; H, 5.86; N, 3.09. $C_{27}H_{25}F_2NO_2$ requires C, 74.81; H, 5.81; N, 3.23%); m/z 433 (M^+, 100%), 390, 376, 363, 335, 323, 278, 165, 153; transitions/°C SmC* 102.8 (15.85 J/g) SmA* 164.9 (16.45 J/g)I.

IR(KBr)υ_{max}/cm^{-1} 2925 (CH), 1723vs (CO), 1623, 1506, 1459, 1399, 1313, 1295, 1212, 1141, 1096, 1038, 808, 775; δ_H(400 MHz; $CDCl_3$) 0.91 (3H, t, J7.2, $C\underline{\boldsymbol{H}}_3C\underline{\boldsymbol{H}}_2$), 1.34–1.38 (4H, m), 1.66 (2H, quint, J7.5, $ArC\underline{\boldsymbol{H}}_2C\underline{\boldsymbol{H}}_2$), 1.82 (3H, d, J7, Me), 2.66 (2H, t, J7.7, $ArC\underline{\boldsymbol{H}}_2$), 5.67 (1H, q, J 7, $C\underline{\boldsymbol{H}}Me$), 7.29 (2H, d, J 8.4), 7.36 (1H, ddd, J 8.5, 8.4, 1.6), 7.57 (2H, d, J 8.2), 7.65 (2H, dd, J 8.4, 1.6), 7.72 (2H, d, J 8.6), 7.80 (1H, ddd, J 8.5, 6.2, 1.6); δ_F(376 MHz; $CDCl_3$), −132.39 (1F, dd, $J_{F,F}$ 25.4, $J_{F,H}$ 6.9), −141.00 (1F, dd, $J_{F,F}$ 25.4, $J_{F,H}$ 6.9); δ_C(100.5; $CDCl_3$) 14.04, 18.9, 22.57, 31.17, 31.56, 35.61, 58.16 ($\underline{\boldsymbol{C}}HMe$), 116.86 (d, $J_{C,F}$6.1), 117.19 (CN), 124.52 (dd, $J_{C,F}$3.8, 2.3), 126.38 (d, $J_{C,F}$4.6), 126.97, 127.32, 129.01, 129.29 (d, $J_{C,F}$3.84), 131.93 (d, $J_{C,F}$3.84), 136.15, 136.25, 137.41, 142.11, 142.85, 161.68 (dd, $J_{C,F}$ 3.8, 3.1, CO).

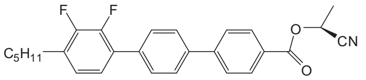
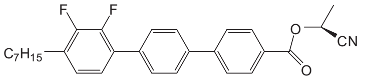
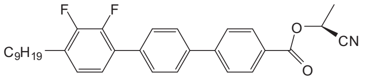
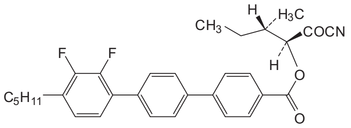
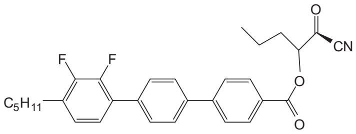
2.1.5. 4-heptyl-2″,3″-difluoro terphenyl carbonyl nitrile (D7R)

2.1.5.1. Quantities. 4-heptyl-2″,3″-difluoro terphenyl carbonyl amide (0.8 g, 1.69 mmol, 473 g/mol), $POCl_3$ (1.06 ml, 11.40 mmol, 153 g/mol) and dry DMF (22 ml).

2.1.5.2. Procedure. The experimental procedure was as described for the preparation of 4-pentyl-2″,3″-difluoro terphenyl carbonyl nitrile.

Yield (0.57 g, 75%); M.P. 95.8 °C (fromisopropanol); elemental analysis: (found: C, 74.49; H, 6.41; N, 2.72. Calc. for $C_{29}H_{29}F_2NO_2$: C, 75.47; H, 6.33; N, 3.03%); m/z 461 (M^+, 100%), 391, 376, 363, 323,

Table 1
Transition temperatures (°C) and enthalpy change taken by optical polarising microscope and differential scanning calorimeter for the 4-alkyl-2, 3-difluoro terphenyl nitrile, (S)-(−)-1-cyno-2-methylbutyl-4-pentyl -difluoroterphenyl-4′-carboxylate and (S)-(−)-1-cyno-2-methylbutyl-4-pentyl difluoroterphenyl-4′-carboxylate.

Structure	Mesomorphic behaviour
	Melting point: 131.6 °C Transitions/°C K 106.1(48.2 J/g) SmA* 132.1 (83.21 J/g) I
	Melting point:121 ° C Transitions/°C K 121 (47.51 J/g) I
	Melting point:118.9 °C Transitions/°C K 118 (37.83 J/g) I
	Melting point:72.54 °C (14.39 J/g) Transitions/°C K 102.8 °C (55.82 J/g) I
	Melting point: °C Transitions/°C K–I

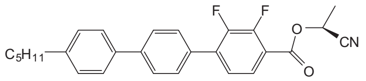
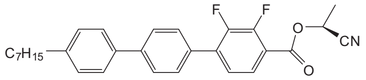
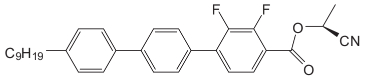
278, 165, 153; transitions/°C SmC* 95.2 (14.61 J/g) SmA* 145.5 (14.85 J/g)I.

IR(KBr)υ_{max}/cm^{-1} 2923 (CH), 1733s (CO), 1653, 1635, 1623, 1559, 1507, 1458, 1399, 1313, 1212, 1142, 1037, 808, 775; δ_H(400 MHz; $CDCl_3$) 0.89 (3H, t, J7.1, CH_3CH_2), 1.24–1.42 (8H, m), 1.66 (2H, quint, J 7.7, $ArCH_2C\underline{\boldsymbol{H}}_2$), 1.81(3H, d, J 7, Me), 2.66 (2H, t, J7.5, $ArCH_2$), 5.67 (1H, q, J 7, $\underline{C}$HMe), 7.29 (2H, d, J 8.4) 7.36 (1H, ddd, 6.8, J 6.6, 1.6), 7.56 (2H, d, J 8.2), 7.65 (2H, dd, J 7, 1.6), 7.72 (2H, d, J 8.6), 7.8 (1H, ddd, J 6.4, 2.0); δ_F(376;$CDCl_3$) −132.4 (1F, dd, $J_{F,F}$18.5, $J_{F,H}$6.9), 141.01 (1F, dd, $J_{F,F}$20.8, $J_{F,H}$6.9); δ_C(100.5; $CDCl_3$) 14.10, 18.89, 22.67, 29.18, 29.33, 31.48, 31.81, 35.64, 58.15 ($\underline{\mathbf{C}}$HMe), 116.85 (d$J_{C,F}$6.9), 117.18, 124.51 (dd, $J_{C,F}$3.8, 3.1), 126.35 (dd, $J_{C,F}$3.8, 3.1), 126.95, 127.31, 129.00, 129.27 (d$J_{C,F}$3.1), 131.93, 136.15, 136.25, 137.39, 142.10, 142.86, 161.67 (dd, $J_{C,F}$6.1, 3.8).

2.1.6. 4-nonyl-2″-3″-difluoroterphenyl carbonyl nitrile (D9R)

2.1.6.1. Quantities. 4-nonyl-2″-3″-difluoroterphenyl carbonyl amide (3 g, 5.9 mmol, 508 g/mol), $POCl_3$ (3.7 ml, 39.8 mmol, 153 g/mol) and dry DMF (85 ml).

Table 2
Transition temperatures (°C) and enthalpy change taken by optical polarising microscope and differential scanning calorimeter for the 4-alkyl-2″,3″-difluoro terphenyl nitrile.

Structure	Mesomorphic behaviour
	Melting point: 103.2 °C Transitions/°C SmC* 102.8 (15.85 J/g) SmA* 164.9 (16.45 J/g) I
	Melting point: 95.78 °C Transitions/°C SmC* 95.2 (14.61 J/g) SmA* 145.5 (14.85 J/g) I I
	Melting point:85.43 °C (13.93 J/g) Transitions/°C K 82.9 (13.93 2 J/g) SmY 94.9 (0.40 J/g) SmX 100.99 (0.44 J/g) SmA 131.6 (11.42 J/g) I

2.1.6.2. Procedure. The experimental procedure is as described by 4-pentyl-2″,3″-difluoro terphenyl carbonyl nitrile.

Yield (1.12 g, 38.62%); M.P 85.43 °C (13.93 J/g) (from isopropanol); transition temperature/° C K 79.46 (13.65 J/g) SmX 94.9 (0.30 J/g) SmA 131.6 (11.42 J/g) I; Elemental analysis: calc. for (found: C, H, N. $C_{31}H_{33}F_2NO_2$ requires C, 76.05; H, 6.79; N,2.86%); δ_H(400 MHz; $CDCl_3$) 0.88 (3H, t, J7.0, $C\underline{\boldsymbol{H}}_3CH_2$), 1.24–1.41 (13H, m), 1.66 (2H, quint, J7.7, $ArCH_2C\underline{\boldsymbol{H}}_2$), 1.80–1.88 (3H, m), 2.66 (2H, t, J 7.9, $ArCH_2$), 5.67 (1H, q, J 7), 7.29 (2H, d, J 8.4), 7.36 (1H, ddd, J 8.4, 6.4, 1.6), 7.56 (2H, d, J8.2), 7.64 (2H, dd, J8.6, 1.6), 7.71 (2H, d, J8.6), 7.80 (1H, ddd, J8.4, 6.4, 1.8); δ_F(376; $CDCl_3$) 132.40 (1F, dd, $J_{F,F}$20.81, $J_{F,H}$6.9), 141.00 (1F, dd, $J_{F,F}$20.81, $J_{F,H}$6.9); δ_C(100.5; $CDCl_3$) 14.09, 18.87, 22.66, 29.33 (d, J3.8), 29.53 (d, J3.1), 31.15, 31.88, 35.63, 58.15, 116.85 (d, J6.9), 117.17, 124.50 (dd, $J_{C,F}$4.6, 2.3), 126.36 (dd, $J_{C,F}$4.6, 3.1), 126.94, 127.30, 128.98, 129.27 (d, $J_{C,F}$3.1), 131.92, 136.13, 136.24, 137.38, 142.09, 142.85, 152.78, 161.67.

2.1.7. (S)-(−)-1-cyno-2-methylbutyl-4-pentyldifluoroterphenyl-4′-carboxylate (D53)

2.1.7.1. Quantities. (S)-1-carbamoyl-2-methylbutyl-4-pentyl difluoroterphenyl-4′-carboxylate (1 g, 2.02 mmol, 494 g/mol), $POCl_3$ (1.27 ml,1 3.65 mmol, 153 g/mol) and dry DMF (30 ml).

2.1.7.2. Procedure. The experimental procedure is the same as described for 4-pentyl-2″,3″-difluoro terphenyl carbonyl nitrile.

Yield (0.71 g, 73.96%), M.P 102.8 °C (from ethanol);transition/°C melting point 72.54 °C (from ethanol) (14.39 J/g) K 103.2 (55.82 J/g) I;

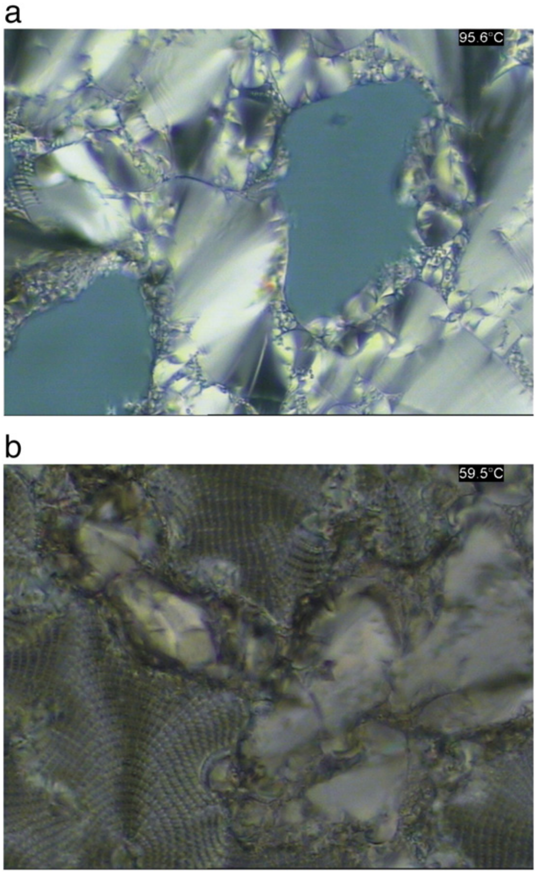


Fig. 7. (a) Mixture of 7% D7R in HM1; focal conic texture of the SmA* phase which arises because of an energetically favoured packing of the lamellar structure to give a system of curved, equidistant layers and (b) mixture of 7% D7R in HM1; the scheliring texture of SmC* phase.

elemental analysis: (found: C, 75.77; H, 6.57; N, 2.95. calc. for $C_{30}H_{31}F_2NO_2$: C, H, N, %); δ_H(400 MHz; $CDCl_3$) 0.92 (3H, t, J 7.1), 1.04 (3H, t, J 7.5), 1.23 (3H, d, J 6.8), 1.33–1.52 (5H, m), 1.63–1.74 (3H, m), 2.05–2.17 (1H, m), 2.70 (2H, t, J 7.9), 5.58 (1H, d, J 5.5), 7.02 (1H, ddd, $J_{C,F}$8.1, 6.6, 1.6), 7.15 (1H, ddd, $J_{C,F}$8.4, 6.4, 1.8), 7.66 (2H, dd, $J_{C,F}$8.6, 1.5), 7.72 (2H, d, $J_{C,F}$8.4), 7.75 (2H, d, $J_{C,F}$8.6), 8.14 (2H, d, $J_{C,F}$8.6); δ_F(376; $CDCl_3$) −143.29 (1F, dd, $J_{F,F}$20.81, $J_{F,H}$4.6), 143.87 (1F, dd, $J_{F,F}$20.8, $J_{F,H}$6.9); δ_C(100.5; $CDCl_3$) 11.21, 14.01, 14.69, 22.46, 25.16, 28.79, 29.73, 31.45, 37.60, 66.00, 116.04, 124.13 (dd, $J_{C,F}$3.8, 2.3), 124.9 (dd, $J_{C,F}$4.6, 3.8), 127.11–127.69 (m), 129.47 (d, $J_{C,F}$ 3.1), 130.57, 131.34, 131.47, 135.20, 139.07, 146.09, 164.66, 170.99 (CO).

3. Results and discussions

3.1. 4-alkyl-2,3-difluoro terphenyl nitrile

Table 1 shows the transition temperatures and handedness of any helical phases formed from a series of three 4-alkyl-2,3-difluoro terphenyl nitrile which differ only due to the length of alkyl chain attached to it.

4-heptyl-2,3-difluoro terphenyl nitrile and 4-nanoyl-2,3-difluoro terphenyl nitrile did not pose a problem since a chiral dopant need not necessarily be mesogenic as the chiral structure can still induce chirality into phases of an achiral host mixture. 4-heptyl-2, 3-difluoro terphenyl nitrile and 4-nanoyl-2, 3-difluoro terphenyl nitrile did not exhibited any mesomorphic behaviour due to their comparative long terminal chain length than 4-pentyl-2, 3-difluoro terphenyl nitrile. The lack of any liquid crystal phase, however does not pose any problem in the potential behaviour of compounds as chiral dopant in ferroelectric mixtures, various weight percentage composition mixtures were prepared and analysed by optical microscope in the HM1.

3.2. 4-alkyl-2″,3″-difluoro terphenyl nitrile

Table 2 shows the transition temperatures and handedness of any helical phases formed from a series comprising three 4-alkyl-2″,3″-difluoro terphenyl nitriles which differ only due to the length of the alkyl chain attached to it.

From the results obtained it is apparent that the length of the alkyl chain has a considerable effect on the melting point, transition temperatures and mesophase morphology. As the length of the alkyl chain to the nitriles increases, the melting point decreases which is evident by comparing the three compounds although materials are purely smectogenic materials, exhibiting a SmC* phase and having a SmA* phase at high temperatures.

Liquid crystal phases were viewed through optical polarising microscope and the results are given in Fig. 7(a, b).

3.3. Mixture comparison with respect to ferroelectric properties

The automatic liquid crystal tester was used to measure the ferroelectric liquid crystal properties of various mixtures prepared during this study. Fig. 8 shows various ferroelectric mixtures that contain 3% or 7% chiral dopants in achiral host mixture HM1.

The spontaneous polarisation increases as the alkyl chain length attached to the chiral dopant increases. When the di fluorine is attached to the 2″–3″-position i.e. towards the chiral centre then the polarisation has small values as compared to the fluorine attached to the alkyl side i.e. at the 2–3 position. At the same time the spontaneous polarisation increases with the increase of the percentage of the chiral dopant while the viscosity increases with the increase of alkyl length. Viscosity for the dopants having fluorine on the chiral side has lesser value than the dopants having fluorine on the alkyl side. Viscosity decreases with increase of % of dopant.

4. Conclusions

Eight chiral dopants were successfully synthesized. The melting point of the dopants decreased as the length of alkyl chain to dopant increased. When difluorine was on the same ring as the ester i.e. at 2″, 3″ position then melting point is lower as compared to dopants when difluorine was on the 2″, 3″ position. Spontaneous polarisation increases while viscosity decreases with increase of % of dopant. The spontaneous polarisation and viscosity increase as the alkyl chain length attached to the chiral dopant increases [6].

Abbreviations

D5	4-pentyl-2,3 difluoro terphenyl nitrile
D7	4-heptyl-2,3 difluoro terphenyl nitrile
D9	4-nonyl-2,3 difluoro terphenyl nitrile
D5R	4-pentyl-2″,3″ difluoro terphenyl nitrile

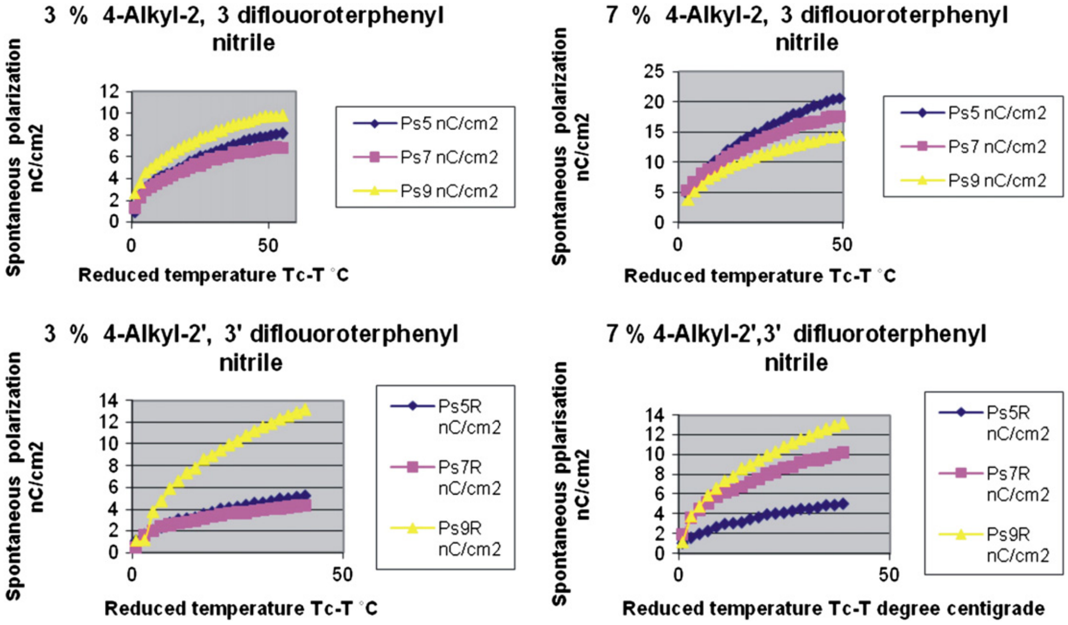


Fig. 8. Shows variation of polarisation with T_c–T °C of mixture of 4-(pentyl, heptyl, nonyl)-2,3 difluoro terphenyl nitrile and 4-(pentyl, heptyl, nonyl)-2″,3″ difluoro terphenyl nitrile in HM1.

D7R	4-heptyl-2″,3″ difluoro terphenyl nitrile
D9R	4-nonyl-2″,3″ difluoro terphenyl nitrile
D52	(S)-(—)-1-cyno-2-methylbutyl-4-pentyl-difluoroterphenyl-4′-carboxylate
D53	(S)-(—)-1-cyno-2-methylbutyl-4-pentyl difluoroterphenyl-4′-carboxylate
DMF	Diethylformamide
THF	tetrahydrofuran

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