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Synthesis and properties of novel 1,1-difluoropropoxy-linked liquid crystalline compounds of negative dielectric anisotropy

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A series of liquid crystalline compounds having the difluoropropyleneoxy moiety (–$OCF_2C_2H_4$–) as a linking group has been synthesized. The physical properties, i.e. dielectric anisotropy, birefringence, viscosity and phase transition temperatures, have been measured. This novel class of compounds shows a larger negative dielectric anisotropy than the corresponding compounds having a propyleneoxy (–OC_3H_6–) linking group. Their dielectric properties may be explained by the combined effect of fluorine atoms with large electron negativities and the electron donating feature of an oxygen atom substituted on the same carbon atom. The semi-empirical quantum calculation method (AM1) also confirmed this dielectric behaviour of the difluoropropyleneoxy linkage group.

1. Introduction

Liquid crystalline compounds with large negative dielectric anisotropy ($\Delta\varepsilon$) are essential for the recently developed display driving modes, IPS [1–3] and MVA [4]. These modes have the significant advantages of wider viewing angles and good contrast. In these circumstances, according to the basis of the display cell, the MVA mode requires LC material having negative dielectric anisotropy. Thus, the development of dielectrically negative LC compounds with excellent properties is essential.

Recently, many liquid crystalline compounds having various linking groups have been synthesized and their physical properties measured. In particular, for positive $\Delta\varepsilon$ materials, compounds with the difluoromethyleneoxy moiety (–CF_2O–) are well known to show low viscosity (η) due to the low intermolecular aggregation energy, but large dielectric anisotropy ($\Delta\varepsilon$) due to the dipole moment of the two fluorine atoms [5,21]. To investigate whether a similar molecular interaction would be expected for a dielectrically negative liquid crystalline compound, we studied the introduction of a novel linking group, 1,1-difluoropropylenoxy moiety (–$OCF_2C_2H_4$–), into the conventional negative LC structure with the 2, 3-difluoro-1, 4-phenylene group. In this paper, we report some physical properties and evaluate the potential of this novel series of compounds for display devices.

2. Results and discussion

2.1. *Synthesis*

Liquid crystalline compounds having a 1,1-difluoropropyleneoxy group (**9a**, **9b**, **12a**–**12f**, **15a**–**15d**) were synthesized as follows. First, etherification associated with HBr elimination of the phenols (**7a**, **7b**, **10a**–**10d**, **13a**, **13b**) [6–11] with 1,1-difluoropropene derivatives (**6a**, **6b**), using KOH as base in toluene, gave allyl ether (**8a**, **8b**, **11a**–**11f**, **14a**–**14d**). Following this, catalytic hydrogenation with 5% Pd/C under a H_2 atmosphere gave the desired materials (**9a**, **9b**, **12a**–**12f**, **15a**–**15d**), respectively (see schemes 1–2). 1,1-difluoro-1,2-dibromo-3-(2,3-difluoro-4-alkyloxyphenyl)propane (**6a**, **6b**) were synthesized by a multi-step procedure (scheme 1). Compounds (**6a**, **6b**) were synthesized by the Wittig reaction from the aldehydes (**4a**, **4b**) derived from the 2,3-difluorophenol (**1**) [12] using tris(dimethylamino)phosphine [$P(N(CH_3)_2)_3$] and dibromodifluoromethane (CF_2Br_2) [13–17], and bromine addition in CH_2Cl_2 at -20°C.

Chemical purities of the synthesized compounds were confirmed by GC analysis. All the compounds are chemically stable. Their clearing temperatures did not change even after heating (150°C, 1 h) and under UV irradiation (20 min with a 500 W, high-pressure Hg lamp).

2.2. *Physical properties*

The phase sequences and the transition enthalpies of the compounds are shown in Tables 1–3. In addition, for

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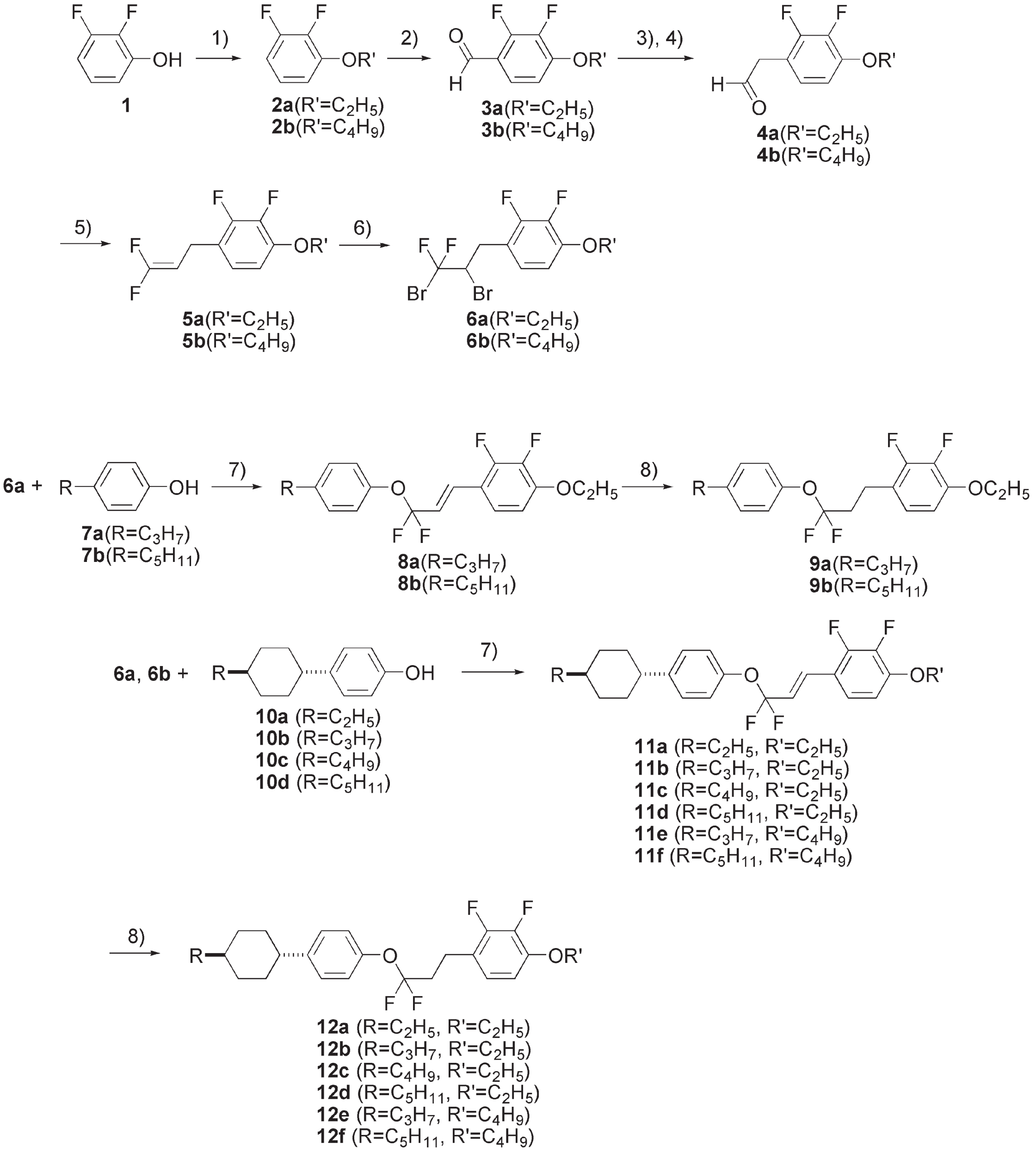
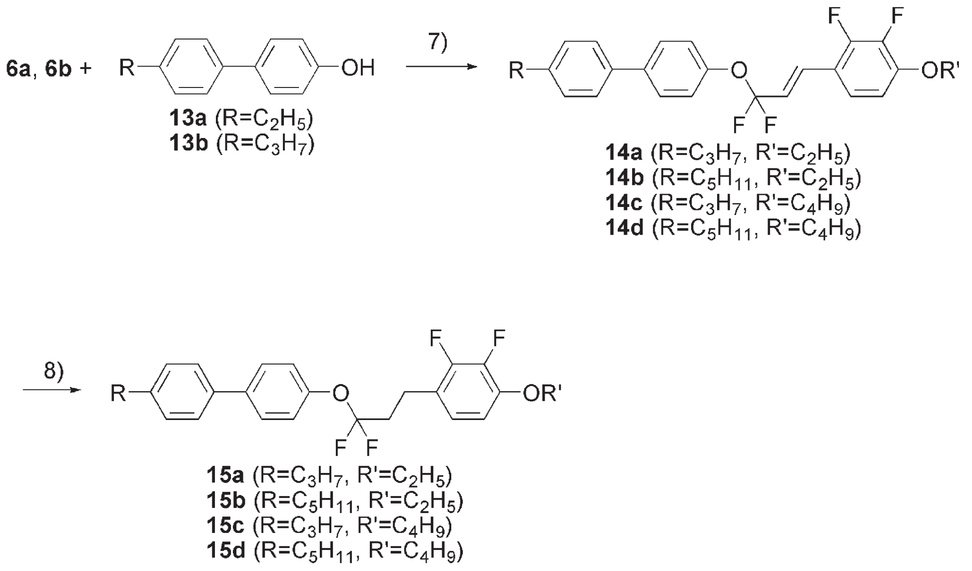


Scheme 1. Synthesis of two rings derivatives (**9a**–**9b**) and three rings derivatives (**12a**–**12f**) having 1,1-difluoropropoxy linkage group. 1) R'I, K_2CO_3, MEK; 2) *sec*−BuLi, DMF, THF; 3) $CH_3OCH_2PPh_3^+Cl^-$, *t*-BuOK, THF; 4) 6N-HCl, acetone; 5) $P(N(CH_3)_2)_3$, CF_2Br_2, 6) Br_2, CH_2Cl_2; 7) KOH, toluene; 8) H_2 5%-Pd/C, EtOH/toluene (1:1).

reference, data for 2-ethoxy-2,3-difluorobenzene derivatives having a 1,1-difluoromethoxy linking group (**r1**) [18] and a propyloxy linking group (**r2**) [19] are also shown in the Table 2.

The two-ring compounds, **9a** and **9b** (figure 1), exhibited melting points of 32.3°C and 39.7°C, respectively, in the heating process and did not show any mesophase on cooling to −50°C. Except for compound **12a**, all the three-ring systems, the biphenylcyclohexane derivatives (**12b**–**12f**) and the terphenyl derivatives (**15a**–**15d**) showed enantiotropic nematic phases. The compound **12a** showed a monotropic nematic phase. The biphenyl cyclohexane derivatives (**12b**–**12d**) exhibited lower melting points and slightly higher N–I transition temperatures, and comparatively wider nematic temperature ranges. The terphenyl compounds (**15a**–**15d**) exhibited higher melting points and slightly higher N–I transition temperatures, or slightly narrower nematic temperature ranges, in comparison with the corresponding biphenyl cyclohexane derivatives



Scheme 2. Synthesis of three rings derivatives (**15a**–**15d**) having 1,1-difluoropropoxy linkage group.

Table 1. Transition temperatures (°C) and associated enthalpies of transition (kJ mol^{-1}) of the two-ring derivatives (**9a**, **9b**).

Compound	Cr	I
9a	• 32.3[a](26.8)[b]	•
9b	• 39.7 (34.5)	•

[a] A Cr–Cr transition was observed during the first heating cycle on DSC at 27.8°C (1.69). [b] Data in parentheses indicate the transition enthalpies

Table 2. Transition temperatures (°C) and associated enthalpies of transition (kJ mol^{-1}) of the three-ring derivatives (**12a**–**12f**).

Compound	Cr	N	I	Ref.
12a	• 83.5 (35.9)[a]	(• 90.2 (0.75))	•	
12b	• 50.0 (25.9)	• 101.5 (2.20)	•	
12c	• 47.1 (23.0)	• 96.1 (1.44)	•	
12d	• 49.9 (29.4)	• 104.9 (1.70)	•	
12e	• 76.3 (31.7)	• 92.4 (1.58)	•	
12f	• 75.3 (39.2)	• 97.3 (1.73)	•	
r1	• 51.1 (17.6)	• 116.8 (1.24)	•	[18]
r2	• 81.5 (32.3)	• 84.1 (1.60)	•	[19]

[a] Data in parentheses indicate the transition enthalpies.

Table 3. Transition temperatures (°C) and associated enthalpies of transition (kJ mol^{-1}) of the three-ring derivatives (**15a**–**15d**).

Compound	Cr	N	I
15a	• 98.3 (34.4)[a]	• 113.1 (2.30)	•
15b	• 107.6 (34.4)[b]	• 108.5 (2.31)	•
15c	• 70.8 (33.9)	• 103.0 (1.44)	•
15d	• 75.0 (36.6)	• 99.9 (1.96)	•

[a] Data in the parentheses indicate the transition enthalpies [b] A Cr–Cr transition was observed during the first heating cycle on DSC at 72.2°C (0.61).

(**12b**–**12f**). From the comparison of the clearing point between compound **r2** (115.9°C) having the –OCF_2– moiety and compound **12b** (101.5°C), the compound with a –$OCF_2C_2H_4$– linking group showed about a 15°C lower clearing temperature.

The reduction of the clearing temperature was assumed to be caused by a decrease of thermal stability of the nematic phase due to introduction of a flexible and elongated –$OCF_2C_2H_4$– group which consists of –OCF_2– and –C_2H_4– moieties.

The dielectric anisotropies ($\Delta\varepsilon$) and the optical anisotropies (Δn) and the viscosity (η) of the synthesized compounds were estimated by the linear extrapolation method using a nematic host mixture having $\Delta\varepsilon$ of -1.3 (see section 4). The data are shown in Tables 4–6. All the difluoropropoxy derivatives exhibited a very large negative $\Delta\varepsilon$ ranging from -3.99 to -5.88. Comparison between compound **12b** (-5.53) and compound **r2** (-4.09) clearly indicates that the compound having a –$OCF_2C_2H_4$– moiety exhibits slightly larger negative $\Delta\varepsilon$. The $\Delta\varepsilon$ of compound **r1** having a –OCF_2– moiety has almost the same values (-5.53 and -5.59). From this fact, it seems that the dipole moments of the C–F bond on the –$OCF_2C_2H_4$– moiety are directed along the short axis of the molecules and nearly parallel to the dipole moments of the 2,3-difluorophenyl groups.

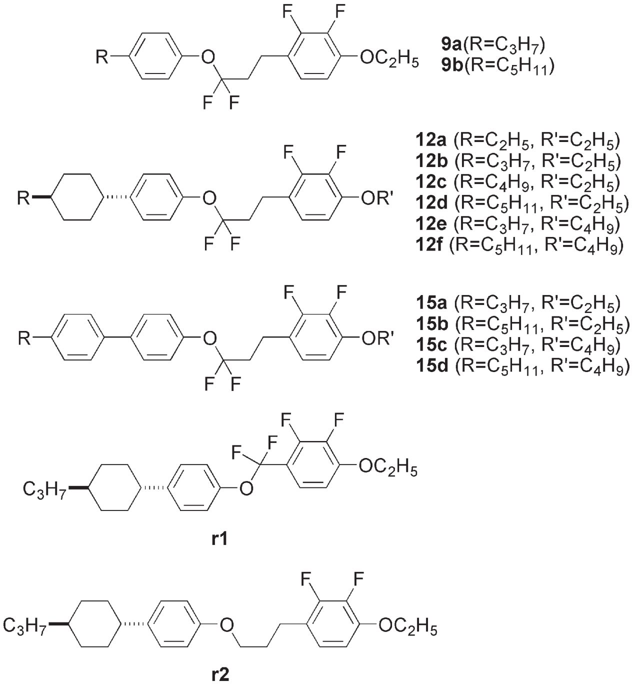


Figure 1. Chemical structure of 1,1-difluoropropoxy derivatives (**9a**–**9b**, **12a**–**12f** and **15a**–**15d**) and reference compounds **r1** and **r2**.

Table 4. Data extrapolated from mixtures containing 15 wt% of two-ring derivatives (**9a**, **9b**) in nematic host mixture consisting of cyclohexylcarboxylate derivatives (85 wt%).

Compound	$T_{NI}{}^{a}$/°C	T_{NI}/°C	$\Delta\varepsilon$	Δn	η/mPa S
9a	59.7	−24.7	−4.70	0.085	21.3
9b	60.6	−18.7	−5.08	0.087	32.7
host	74.6	–	−1.30	0.087	18.8

^{a}Experimental data from mixtures.

Table 5. Data extrapolated from mixtures containing 15 wt% of the three-ring derivatives (**12a**–**12f**) in nematic host mixture consisting of cyclohexylcarboxylate derivatives (85 wt%).

Compound	$T_{NI}{}^{a}$/°C	T_{NI}/°C	$\Delta\varepsilon$	Δn	η/mPa S
12a	74.7	75.3	−5.00	0.102	49.4
12b	78.2	98.6	−5.53	0.120	46.8
12c	77.5	93.9	−5.69	0.110	50.1
12d	79.1	104.6	−4.25	0.108	49.0
12^{e}	77.1	91.3	−4.34	0.110	48.1
12f	77.9	96.6	−4.00	0.100	52.7
r1	80.8	115.9	−5.59	0.134	46.3
r2	76.5	87.3	−4.09	0.120	69.0
host	74.6	–	−1.30	0.087	18.8

^{a}Experimental data from mixtures.

The extrapolated Δn values of the compounds synthesized are in the range 0.085 to 0.179. The two-ring systems, **9a** and **9b**, exhibit relatively small Δn values (0.085 and 0.087); three-ring systems (**11a**–**14d**) exhibit relatively large Δn values (0.102–0.179). Terphenyl compounds (**15a**–**15d**) exhibit the largest Δn values (0.150–0.179), due to their highly conjugated π-electron systems.

Table 6. Data extrapolated from mixtures containing 15 wt% of the three-ring derivatives (**15a**–**15d**) in nematic host mixture consisting of cyclohexylcarboxylate derivatives (85 wt%).

Compound	$T_{NI}{}^{a}$/°C	T_{NI}/°C	$\Delta\varepsilon$	Δn	η/mPa S
14a	79.6	107.9	−3.99	0.179	49.9
14b	77.7	105.9	−5.88	0.175	54.0
14c	78.2	98.6	−4.41	0.167	55.9
14d	78.3	99.3	−4.14	0.150	57.1
host	74.6	–	−1.30	0.087	18.8

^{a}Experimental data from mixtures.

The extrapolated viscosity (η) of the compounds synthesized is in the range 21.3 to 55.9 mPa s. The two-ring systems. **9a** and **9b**. show small η values (21.3 and 32.7 mPa s); in three-ring systems (**12a**–**15d**), terphenyl compounds (**15a**–**15d**) show relatively large η values (49.9–57.1 mPa s). Compound **12b** having a –$OCF_2C_2H_4$– moiety and corresponding compound **r1** having a –OCF_2– moiety show very similar values (46.8 and 46.3 mPa s).

Comparison of viscosity (η) between compound **12b** (46.8 mPa s) and compound **r2** (69.0 mPa s) clearly indicates that introduction of a –$OCF_2C_2H_4$– moiety characterized by the combination of an ether linkage and fluorine substitution on the same carbon atom adjoining the ether oxygen atom reduces viscosity. This comparison indicates that the –$OCF_2C_2H_4$– moiety has similar effect as the –OCF_2– moiety in reducing the viscosity of liquid crystalline compounds.

2.3. *Molecular modelling*

To compare the most stable conformational electronic condition of the compound **12b** having a –$OCF_2C_2H_4$– linkage with corresponding compound **r2** having a –OC_3H_6– linkage, a semi-empirical quantum chemical method (MOPAC Ver.6 AM1 PRECISE XYZ NOINTER VECTORS BONDS POLRA [20]) has been applied. The experimental $\Delta\varepsilon$ values of compounds **12b** and **r2** are shown in Table 7 with the calculated total dipole moments μ, the angle of the total dipole moment

Table 7. Calculated values and experimental values of compounds **12b** and **r2**.

Compound	μ/D	β/°	α_{ave}/a.u.	$\Delta\alpha$/a.u.	$\Delta\varepsilon$
12b	3.96	87.6	148.6	161.1	−5.53
r2	3.85	87.9	242.9	169.8	−4.09

β, the average polarizability α_{ave} and polarizability anisotropy $\Delta\alpha$ of their most stable conformation.

β represents the angle between the direction of the total dipole and the moment of inertia of the molecule. The maximum β of 90° would indicate that the dipole moment is exactly parallel to the short axis of the molecule. The β values of **12b** (87.6°), and **r2** (87.9°) are almost 90°, and thus the appropriate angle for liquid crystal compounds having negative $\Delta\varepsilon$. Moreover, the μ value of **12b** having a $–OCF_2C_2H_4–$ moiety is slightly larger than that of **r2** having a $–OC_3H_6–$ moiety.

Figure 2 shows the optimized structure of compound **12b**. The two fluorine atoms of the $–OCF_2C_2H_4–$ moiety are almost vertical to the face of 2,3-difluorophenylene ring. Figure 3 shows the optimized structure of compound **r2**. The two hydrogen atoms bonding carbon atoms adjacent to the oxygen atoms of the $–OC_3H_6–$ moiety are almost vertical to the face of 2,3-difluorophenylene ring. The shapes of the most stable conformations that have been calculated, **r2** having a $–OC_3H_6–$ moiety and **12b** having a $–OCF_2C_2H_4–$ moiety, are almost the same. The comparison of the calculated total dipole moments μ, the angle of the total dipole moment β and the most stable conformation suggest that compound **12b** having a $–OCF_2C_2H_4–$ moiety exhibits a larger negative $\Delta\varepsilon$ compared with **r2** having a $–OC_3H_6–$ moiety; this is caused by the difference of the size of the dipole moment caused by the existence of two fluorine atoms on $–OCF_2C_2H_4–$ moiety.

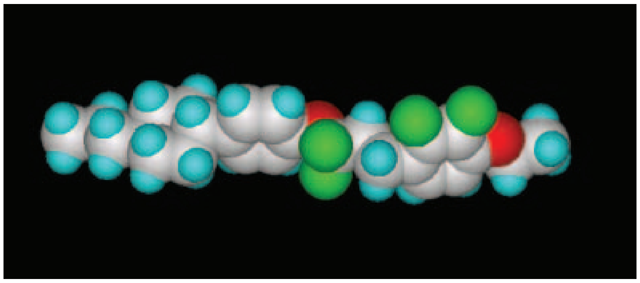


Figure 2. Optimized structure of compound **12b**.

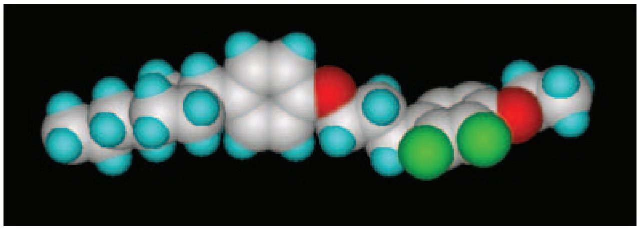


Figure 3. Optimized structure of compound **r2**.

3. Conclusions

A novel series of liquid crystalline compounds having a 1,1-difluoropropylenoxy moiety has been studied. Most of the three ring compounds with 1,1-difluoropropylenoxy derivatives show enantiotropic nematic phases and high clearing temperatures. This series exhibits large negative $\Delta\varepsilon$, higher clearing point, wider nematic temperature range and lower viscosity compared with the corresponding propyleneoxy derivatives. These compounds are chemically and thermally very stable. The series of liquid crystalline 1,1-difluoropropylenoxy derivatives should be useful materials as a component that could improve the performance of LCDs.

4. Experimental section

4.1. *Instrumentation and materials*

The synthesized compounds were characterized by the following conditions and using the following instruments. Phase transition temperatures: Perkin Elmer DSC 7 and Diamond DSC differential scanning calorimetry and Nikkon Optiphot polarization microscope with Mettler FP82 hot stage. ^1H NMR: Bruker DRX500 (500 MHz); TMS as an internal reference. ^{13}C NMR: Bruker DRX500 (126 MHz); TMS as an internal reference. ^{19}F NMR: Bruker DRX500 (470 MHz); $CFCl_3$ as an internal reference. MS: JEOL JMS-Automass II-150 (70 eV, EI). GC: Shimadzu GC-14A fitted with a capillary column: Shimadzu HiCap (CBP1-M50-025). The measurements of the physical properties of the nematic mixtures containing synthesized compounds were performed using the following instruments and under the following conditions: dielectric anisotropy ($\Delta\varepsilon$) measured at 25°C (Hewlett Packard 4284A LCR meter); optical anisotropy (Δn) measured at 25°C (Atago 4T & 2T Abbe refractometer); viscosity (η) measured at 20°C (Lauda Viscoboy viscometer). The nematic host mixture consisted of phenyl cyclohexanecarboxylates, i.e. 4-methoxyphenyl *trans*-4-*n*-pentylcyclohexanecarboxylate, 4-ethoxyphenyl *trans*-4-*n*-propylcyclohexanecarboxylate, 4-ethoxyphenyl *trans*-4-*n*-butylcyclohexanecarboxylate, 4-ethoxyphenyl *trans*-4-*n*-pentylcyclohexanecarboxylate, and 4-butoxyphenyl *trans*-4-*n*-propylcyclohexanecarboxylate (12:10:12:8:16 by weight). The physical properties of the host mixture were $T_{NI}=74.6°C$, $\Delta\varepsilon=-1.3$, $\Delta n=0.087$ and $\eta=18.8$ mPa s.

4.2. *Synthesis*

Representative structural data are provided for each type of final product and intermediate prepared.

4.2.1. 2,3-difluoroethoxybenzene, 2a. A solution of 2,3-difluorophenol (**1**) (103.3 g, 793.9 mmol) in 2-butanone

(770 ml) was added K_2CO_3 (128 g, 923 mmol) and a solution of iodoethane (180 g, 1154 mmol) in 2-butanone (350 ml) then the suspension mixture was stirred at refluxed for 3 h. Water (200 ml) and toluene (100 ml) were added to the reaction mixture at room temperature, and the separated organic layer was washed with 2N NaOH (100 ml), brine (100 ml) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by distillation under reduced pressure, b.p. 90–93°C at 5.33kPa, to yield 115.4 g (729.7 mmol, 92%) of **2a** as colourless liquid. ^{1}H NMR δ (ppm): 1.44 (t, J=7.0 Hz, 3H), 4.10 (q, J=7.0 Hz, 2H), 6.70–6.76 (m, 2H), 6.92–6.97 (m, 1H). ^{13}C NMR δ (ppm): 16.4, 67.0, 110.6 (d, $^2J_{CF}$=17.9 Hz), 111.4 (d, $^4J_{CF}$=2.1 Hz), 124.9 (dd, $^3J_{CF}$=8.8 Hz, $^4J_{CF}$=5.4 Hz), 143.1 (dd, $^1J_{CF}$=247 Hz, $^2J_{CF}$=13.9 Hz), 150.4 (dd, $^3J_{CF}$=8.2 Hz, $^4J_{CF}$=3.3 Hz), 153.2 (dd, $^1J_{CF}$=246 Hz, $^2J_{CF}$=10.8 Hz). ^{19}F NMR δ (ppm): −138.3 (ddd, $^3J_{HF}$=8.9 Hz, $^4J_{HF}$=6.1 Hz, $^3J_{FF}$=19.8 Hz), −160.5 (ddd, $^2J_{HF}$=10.8 Hz, $^3J_{HF}$=7.1 Hz, $^3J_{FF}$=24.5Hz).

4.2.2. 2,3-difluoro-4-ethoxybenzenecarboaldehyde, 3a. A solution of 2,3-difluoroethoxybenzene (**2a**) (90.0 g, 569.3 mmol) in THF (300 ml) was added 0.96 mol l^{-1} *sec*-BuLi in hexane (890 ml, 854 mmol) at −68°C, and the reaction mixture was stirred for 2 h at −68°C. To the reaction mixture was added a solution of DMF (62.4 g, 854 mmol) in THF (210 ml) at −68°C, and the reaction mixture was stirred for 1 h at −68°C and at room temperature overnight. Water (200 ml) and toluene (100 ml) were added to the reaction mixture at room temperature, and the separated organic layer was washed with brine (100 ml) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (500 g), eluting with ethyl acetate/heptane (1/1) to yield 87.5 g (470.0 mmol, 82.1%) of **3a** as colourless crystals. ^{1}H NMR δ (ppm): 1.51 (t, J=7.0 Hz, 3H), 4.23 (q, J=7.0 Hz, 2H), 6.83–6.87 (m, 1H), 7.59–7.62 (m, 1H). ^{13}C NMR δ (ppm): 13.6, 64.7, 108.1 (d, $^4J_{CF}$=2.89 Hz), 117.5 (d, $^3J_{CF}$=6.3 Hz), 122.8 (dd, $^3J_{CF}$=3.5 Hz, $^4J_{CF}$=2.9 Hz), 139.5 (dd, $^1J_{CF}$=250 Hz, $^2J_{CF}$=13.2 Hz), 152.5 (dd, $^1J_{CF}$=259 Hz, $^2J_{CF}$=10.8Hz), 152.9 (dd, $^3J_{CF}$=7.6 Hz, $^4J_{CF}$=3.9Hz), 187.8. ^{19}F NMR δ (ppm): −146.4 (dd, $^4J_{HF}$=7.1 Hz, $^3J_{FF}$=19.8 Hz), −159.5 (ddd, $^4J_{HF}$=8.0 Hz, $^5J_{HF}$=1.9 Hz $^3J_{FF}$=19.8 Hz).

4.2.3. 2-(2,3-difluoro-4-ethoxyphenyl)acetaldehyde, 4a. A suspension mixture of methoxymethyltriphenylphosphonium chloride (209.4 g, 610.9 mmol) in THF (840 ml) was added potassium *tert*-butoxide (68.5 g, 610.9 mmol) at −40°C, and the reaction mixture was stirred for 1 h at −40°C. To the reaction mixture was added a solution of 2,3-difluoro-4-ethoxybenzenecarbaldehyde (**3a**) (87.5 g, 469.9 mmol) in THF (430 ml) at −40°C, and the reaction mixture was stirred for 1 h at −40°C and at room temperature overnight. Water (200 ml) and toluene (100 ml) were added to the reaction mixture at room temperature, and the separated organic layer was washed with brine (100 ml) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and heptane (200 mL) was added to the residue, and the suspension mixture was stirred for 2 h at 50°C. The precipitated solid was removed by filtration, and the cake was washed twice with heptane (50 ml). The solvent of the filtrate was removed under reduced pressure, and the suspension purified by column chromatography on silica gel (80 g), eluting with heptane to yield vinyl ether compound as intermediate. To the solution of vinyl ether compound in acetone (600 ml) was added 6N HCl aq. (300 ml) and the reaction mixture was stirred at ambient temperature for overnight. To the reaction mixture was added water (200 ml) and toluene (100 ml) and the separated organic layer was washed with brine (100 ml) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to yield 66.1 g (330.3 mmol) (70.3%) of **4a** as colourless crystals. ^{1}H NMR δ (ppm): 1.46 (t, J=7.0 Hz, 3H), 3.71 (t, J=1.5 Hz, 2H), 4.12 (q, J=7.0 Hz, 2H), 6.73 (td, J=7.0 Hz, $^4J_{HF}$=2.0 Hz, 1H), 6.84 (td, J=8.0 Hz, $^4J_{HF}$=2.0 Hz, 1H), 9.74 (q, J=1.5 Hz). ^{13}C NMR δ (ppm): 15.1, 43.6, 65.8, 110.0 (d, $^3J_{CF}$=2.5 Hz), 113.3 (d, $^2J_{CF}$=13.8 Hz), 125.0 (t, $^3J_{CF}$=4.8 Hz), 141.9 (dd, $^1J_{CF}$=148 Hz, $^2J_{CF}$=14.5 Hz), 148.4 (dd, $^2J_{CF}$=8.5 Hz, $^3J_{CF}$=3.6 Hz), 150.4 (dd, $^1J_{CF}$=247 Hz, $^2J_{CF}$=10.8 Hz), 198.1. ^{19}F NMR δ (ppm): −140.8 (dd, $^4J_{HF}$=7.5 Hz, $^3J_{FF}$=19.8 Hz), −159.0 (ddd, $^4J_{HF}$=11.3 Hz, $^5J_{HF}$=2.4 Hz $^3J_{FF}$=23.5 Hz).

4.2.4. 1,1-difluoro-3-(2,3-difluoro-4-ethoxyphenyl) propene, 5a. A solution of dibromodifluoromethane (103.9 g, 495.3 mmol) in THF (300 ml) was added dropwise a solution of tris(diethylamino)phosphine (245.0 g, 990.6 mmol) at 0–20°C over 2 h, and the reaction mixture was stirred for 1 h at 5°C. To the reaction mixture was added a solution of 2-(2,3-difluoro-4-ethoxyphenyl)acetaldehyde (**4a**) (66.1 g, 330.2 mmol) in THF (65 ml) at 5–10°C over 1.5 h, and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture (200 ml) was poured into the mixture of 3N HCl aq. and *n*-heptane at 0°C and the separated organic layer was washed with 3N HCl aq. (300 ml), brine (500 ml) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the suspension purified by column chromatography on silica gel (100 g), eluting with *n*-heptane and distillation under reduced pressure, b.p. 85°C at 0.26 kPa, to yield 43.8 g (186.9 mmol) of **5a** as pale yellow liquid. ^{1}H NMR δ (ppm): 1.44 (t, $J=7.0$ Hz, 3H), 3.28 (dd, $J=8.0$ Hz, $^{3}J=1.0$ Hz, 2H), 4.09 (q, $J=7.0$ Hz, 2H), 4.34 (tdd, $J=8.0$ Hz, $^{3}J_{E\text{-HF}}=24.5$ Hz, $^{3}J_{Z\text{-HF}}=2.0$ Hz, 1H), 6.66 (td, $J=9.0$ Hz $^{4}J_{HF}=2.0$ Hz, 1H), 6.82 (td, $J=8.5$ Hz $^{4}J_{HF}=2.5$ Hz, 1H). ^{13}C NMR δ (ppm): 16.1, 22.7, 66.7, 110.7 (d, $^{3}J_{CF}=3.0$ Hz), 121.4 (d, $^{2}J_{CF}=13.3$ Hz), 124.2 (t, $^{3}J_{CF}=4.8$ Hz), 139.2, 142.8 (dd, $^{1}J_{CF}=247.3$ Hz, $^{2}J_{CF}=14.3$ Hz), 148.5 (dd, $^{2}J_{CF}=8.3$ Hz, $^{3}J_{CF}=2.5$ Hz), 151.0 (dd, $^{1}J_{CF}=246.8$ Hz, $^{2}J_{CF}=10.8$ Hz), 158.1 (t, $^{1}J_{CF}=286.1$ Hz). ^{19}F NMR δ (ppm): −88.6 (d, $^{2}J_{FF}=44.2$ Hz), −91.3 (dd, $^{3}J_{\text{E-HF}}=24.5$ Hz, $^{3}J_{FF}=44.7$ Hz), −142.5 (dd, $^{4}J_{HF}=7.1$ Hz, $^{3}J_{FF}=19.3$ Hz), −159.7 (dd, $^{3}J_{HF}=7.5$ Hz, $^{3}J_{FF}=20.2$ Hz).

4.2.5. 1,2-dibromo-1,1-difluoro-3-(2,3-difluoro-4-ethoxyphenyl)propane, 6a. A solution of 1,1-difluoro-3-(2,3-difluoro-4-ethoxyphenyl)propene (**5a**) (43.8 g, 186.9 mmol) in CH_2Cl_2 (800 ml) was added dropwise a solution of bromine (35.8 g, 224.3 mmol) in CH_2Cl_2 (80 ml) at −60°C, and the reaction mixture was stirred for 1 h at −60°C, and overnight at room temperature. To the reaction mixture was added a saturated aqueous solution of sodium hydrogen sulfite (250 ml) at room temperature, and the separated organic layer was washed with brine (500 ml) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the suspension purified by column chromatography on silica gel (100 g), eluting with *n*-heptane/toluene (1/1) to yield 65.4 g (166.0 mmol) of **6a** as pale yellow liquid. ^{1}H NMR δ (ppm): 1.46 (t, $J=7.0$ Hz, 3H), 3.02 (dd, $J=14.5$ Hz, $^{3}J=11.0$Hz, 1H), 3.71 (dd, $J=14.5$ Hz, $^{3}J=3.00$ Hz, 1H), 4.12 (q, $J=7.0$ Hz, 2H), 4.34 (tdd, $J=11.0$ Hz, $^{4}J_{HF}=5.0$ Hz, 3.0 Hz), 6.71 (td, $J=7.0$ Hz, $^{4}J_{HF}=2.0$ Hz, 1H), 6.91 (td, $J=8.5$ Hz $^{4}J_{HF}=2.5$ Hz, 1H). ^{13}C NMR δ (ppm): 13.8, 32.5, 54.2 (t, $^{2}J_{CF}=23.8$ Hz), 64.3, 108.2 (d, $^{3}J_{CF}=3.0$ Hz), 115.4 (d, $^{2}J_{CF}=12.5$ Hz), 119.6 (t, $^{1}J_{CF}=306.9$ Hz), 124.0 (t, $^{3}J_{CF}=4.8$ Hz), 140.4 (dd, $^{1}J_{CF}=248.1$ Hz, $^{2}J_{CF}=13.3$ Hz), 147.1 (dd, $^{3}J_{CF}=8.18$ Hz, $^{4}J_{CF}=3.4$ Hz), 149.1 (dd, $^{1}J_{CF}=247.1$ Hz, $^{2}J_{CF}=10.9$ Hz). ^{19}F NMR δ (ppm): −46.9 (dd, $^{2}J_{FF}=160.0$ Hz, $^{3}J_{HF}=4.7$ Hz), −53.3 (dd, $^{2}J_{FF}=159.5$ Hz, $^{3}J_{HF}=11.8$ Hz), −141.6 (dd, $^{4}J_{HF}=7.5$ Hz, $^{3}J_{FF}=19.3$ Hz), −159.2 (dd, $^{4}J_{HF}=7.5$ Hz, $^{3}J_{FF}=19.8$ Hz).

4.2.6. 1-[1,1-difluoro-3-(2,3-difluoro-4-ethoxyphenyl)-2-propenyloxy]-4-propylbenzene, 8a. A solution of 4-propylphenol (**7a**) (3.11 g, 22.8 mmol), potassium hydroxide (85%) (4.52 g 68.5 mmol), TBAB (1.10 g, 3.43 mmol) in toluene (60 ml) was stirred at reflux for 1 h. A solution of 1,2-dibromo-1,1-difluoro-3-(2,3-difluoro-4-ethoxyphenyl)propane (**6a**) (9.00 g 22.8 mmol) in toluene (30 ml) was added dropwise to the reaction mixture at 80°C, and the reaction mixture was refluxed for 1 h. To the reaction mixture was added water (100 ml) at room temperature, and the separated organic layer was washed with brine (500 ml) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the suspension purified by column chromatography on silica gel (100 g), eluting with *n*-heptane/toluene (1/1) to yield 5.24 g (16.4 mmol) of **8a** as colourless crystal. ^{1}H NMR δ (ppm): 0.97 (t, $J=7.5$ Hz, 3H), 1.47 (t, $J=7.0$ Hz, 3H), 1.66 (m, $J=7.5$ Hz, 2H), 2.60 (t, $J=7.5$ Hz, 2H), 4.13 (q, $J=7.0$ Hz, 2H), 6.36 (dd, $J=16.0$ Hz, $^{4}J_{HF}=6.5$ Hz, 1H), 6.73 (td, $J=9.0$ Hz, 4JHF=1.5 Hz, 1H), 7.11–7.21 (m, 6H). ^{19}F NMR δ (ppm): −66.4 (d,$^{3}J_{HF}=6.6$ Hz), −142.4 (dd, $^{4}J_{HF}=7.5$ Hz, $^{3}J_{FF}=19.8$ Hz), −159.7 (dd, $^{4}J_{HF}=7.5$ Hz, $^{3}J_{FF}=19.3$ Hz).

4.2.7. 1-[1,1-difluoro-3-(2,3-difluoro-4-ethoxyphenyl)-2-propyloxy]-4-propylbenzene, 9a. A mixture of 1-[1,1-difluoro-3-(2,3-difluoro-4-ethoxyphenyl)]-2-propenyloxy-4-propylbenzene (**9a**) (3.11 g, 10.4 mmol), 5% Pd/C (0.17 g), toluene (10 ml) and EtOH (10 ml) was stirred under H_2 atmosphere at ambient temperature for 16 h. The catalyst was removed by filtration and obtained filtrate was concentrated. The residue was purified from column chromatography on silica gel (10 g), eluting with *n*-heptane followed by recrystallization by EtOH to yield 2.47 g (7.66 mmol) of **9a** as colourless crystal. ^{1}H NMR δ (ppm): 0.97 (t, $J=7.5$ Hz, 3H), 1.47 (t, $J=7.0$ Hz, 3H), 1.66 (m, $J=7.5$ Hz, 2H), 2.43–2.49 (m, 2H), 2.60 (t, $J=7.5$ Hz, 2H), 2.98 (t, $J=8.0$ Hz, 2H), 4.13 (q, $J=7.0$ Hz, 2H), 6.70 (td, $J=9.0$ Hz, $^{4}J_{HF}=1.5$ Hz, 1H), 6.90 (td, $J=8.0$ Hz, $^{4}J_{HF}=2.0$ Hz, 1H), 7.10–7.18 (m, 4H). ^{13}C NMR δ (ppm): 14.2, 15.1, 22.6, 24.9, 36.5 (t, $^{2}J_{CF}=28.9$ Hz), 37.7, 65.7, 109.8 (d, $^{3}J_{CF}=3.0$ Hz), 121.0 (d, $^{2}J_{CF}=13.5$ Hz), 121.9, 123.8 (t, $^{3}J_{CF}=4.9$ Hz), 124.8 (t, $^{1}J_{CF}=266.0$ Hz), 129.6, 140.3, 141.6 (dd, $^{1}J_{CF}=247.1$ Hz, $^{2}J_{CF}=14.5$ Hz), 147.4, 148.5, 150.3 (dd, $^{1}J_{CF}=245.9$ Hz, $^{2}J_{CF}=10.7$ Hz). ^{19}F NMR δ (ppm): −71.2 (t, $^{3}J_{HF}=10.4$ Hz), −142.4 (dd, $^{4}J_{HF}=7.5$ Hz, $^{3}J_{FF}=19.8$ Hz), −159.7 (dd, $^{4}J_{HF}=7.5$ Hz, $^{3}J_{FF}=19.3$ Hz). MS *m*/*z* (%)=136 (100) [$C_3H_7C_6H_4O^+$], 143 (100) [$CH_3C_6H_2F_2O^+$], 171(90) [$C_2H_4OC_6H_2F_2CH_2^+$], 371 (70) [M^+].

4.2.8. 1-[1,1-difluoro-3-(2,3-difluoro-4-ethoxyphenyl)-2-propenyloxy]-4-(4-ethylcyclohexyl)benzene, 11a. Following the method employed for the synthesis of **8a**, 3.37 g (33.9%). ^{1}H NMR δ (ppm): 0.907 (t,

$J=7.5$ Hz, 3H), 0.994–1.05 (m, 2H), 1.16–1.23 (m, 1H), 1.24–1.29 (m, $J=7.5$ Hz, 2H), 1.37–1.45 (m, 2H), 1.44 (t, $J=7.0$ Hz, 3H), 1.87–1.89 (m, 4H), 2.46 (tt, $^3J_{aa}=12.0$ Hz, $^3J_{ae}=3.0$ Hz, 1H), 4.10 (q, $J=7.0$ Hz, 2H), 6.36 (dd, $J=16.0$ Hz, $^4J_{HF}=6.50$ Hz, 1H), 6.73 (td, $J=9.0$ Hz, $^4J_{HF}=1.5$ Hz, 1H), 7.11–7.21 (m, 6 H). ^{19}F NMR δ (ppm): -66.4 (d,$^3J_{HF}=6.6$ Hz), -142.4 (dd, $^4J_{HF}=7.5$ Hz, $^3J_{FF}=19.8$ Hz), -159.7 (dd, $^4J_{HF}=7.5$ Hz, $^3J_{FF}=19.8$ Hz).

4.2.9. 1-[1,1-difluoro-3-(2,3-difluoro-4-ethoxyphenyl)-2-propyloxy]-4-(4-ethylcyclohexyl)benzene, 12a. Following the method employed for the synthesis of **9a**, 2.99 g (90.4%). ^{1}H NMR δ (ppm): 0.907 (t, $J=7.5$ Hz, 3H), 0.994–1.05 (m, 2H), 1.16–1.23 (m, 1H), 1.24–1.29 (m, $J=7.5$ Hz, 2H), 1.37–1.45 (m, 2H), 1.44 (t, $J=7.0$ Hz, 3H), 1.87–1.89 (m, 4H), 2.38–2.48 (m, 3H), 2.94 (t, $J=8.0$ Hz, 2H), 4.10 (q, $J=7.0$ Hz, 2H), 6.67 (td, $J=8.0$ Hz, $^4J_{HF}=2.0$ Hz, 1H), 6.87 (td, $J=8.0$ Hz, $^4J_{HF}=2.0$ Hz, 1H), 7.07–7.17 (m, 4H). ^{13}C NMR δ (ppm): 11.5, 14.8, 22.2, 30.0, 33.1, 34.4, 36.2 (t, $^2J_{CF}=29.3$ Hz), 39.1, 44.0, 65.4, 119.4, 120.7 (d, $^3J_{CF}=13.2$ Hz), 121.5, 123.4 (t, $^3J_{CF}=4.9$ Hz), 124.4 (t, $^1J_{CF}=265.5$ Hz), 127.6, 141.6 (dd, $^1J_{CF}=247.2$ Hz, $^2J_{CF}=14.3$ Hz), 145.1, 147.0 (dd, $^3J_{CF}=8.4$ Hz, $^4J_{CF}=2.4$ Hz), 148.2, 149.9 (dd, $^1J_{CF}=247.0$ Hz, $^2J_{CF}=9.70$ Hz). ^{19}F NMR δ (ppm): -71.2 (t,$^3J_{HF}=10.8$ Hz), -142.4 (dd, $^4J_{HF}=7.5$ Hz, $^3J_{FF}=19.8$ Hz), -159.7 (dd, $^4J_{HF}=8.0$ Hz, $^3J_{FF}=20.2$ Hz). MS *m/z* (%)=143 (100) [$\mathrm{CH_3C_6H_2F_2O^+}$], 171(60) [$\mathrm{C_2H_4OC_6H_2F_2CH_2^+}$], 204 (40) [$\mathrm{C_2H_5C_6H_{10}C_6H_4O^+}$], 439 (20) [M$^+$].

4.2.10. 1-[1,1-difluoro-3-(2,3-difluoro-4-ethyloxyphenyl)-2-propenyloxy]-4-(4-propylphenyl)benzene, 14a. Following the method employed for the synthesis of **8a**, 14.9 g (69.4%). ^{1}H NMR δ (ppm): 0.972 (t, $J=7.0$ Hz, 3H), 1.44 (t, $J=7.0$ Hz, 3H), 1.68 (m, $J=7.6$ Hz, 3H), 2.63 (t, $J=7.5$ Hz, 2H), 4.10 (q, $J=7.0$ Hz, 2H), 6.36 (dd, $J=16.0$ Hz, $^4J_{HF}=6.50$ Hz, 1H), 6.73 (td, $J=9.00$ Hz, $^4J_{HF}=1.50$ Hz, 1H), 7.11–7.21 (m, 6 H), 7.47–7.55(m, 4H). ^{19}F NMR δ (ppm): -66.4 (d, $^3J_{HF}=6.58$ Hz), -142.4 (dd, $^4J_{HF}=7.62$ Hz, $^3J_{FF}=19.9$ Hz), -159.7 (dd, $^4J_{HF}=7.62$ Hz, $^3J_{FF}=19.9$ Hz).

4.2.11. 1-[1,1-difluoro-3-(2,3-difluoro-4-ethyloxphenyl)-2-propyloxy]-4-(4-propylphenyl)benzene, 15a. Following the method employed for the synthesis of **9a**, 6.90 g (46.3%). ^{1}H NMR δ (ppm): 0.972 (t, $J=7.0$ Hz, 3H), 1.44 (t, $J=7.0$ Hz, 3H), 1.68 (m, $J=7.6$ Hz, 2H), 2.42–2.49(m, 2H), 2.63 (t, $J=7.5$ Hz, 2H), 2.97 (t, $J=7.9$ Hz, 2H), 4.10 (q, $J=7.0$ Hz, 2 H), 6.68 (td, $J=7.1$ Hz, $^4J_{HF}=1.8$ Hz), 6.88 (td, $J=8.5$ Hz, $^4J_{HF}=2.2$ Hz), 7.21–7.25 (m, 4H), 7.47–7.55 (m, 4H). ^{19}F NMR δ (ppm): -71.2 (t,$^3J_{HF}=11.5$ Hz), -142.4 (dd, $^4J_{HF}=7.6$ Hz, $^3J_{FF}=19.9$ Hz), -159.7 (dd, $^4J_{HF}=7.6$ Hz, $^3J_{FF}=19.9$ Hz). MS *m/z* (%)=143 (100) [$\mathrm{CH_3C_6H_2F_2O^+}$], 172(50) [$\mathrm{C_2H_5OC_6H_2F_2CH_2^+}$], 212 (100) [$\mathrm{C_3H_7C_6H_4C_6H_4O^+}$], 446 (70) [M$^+$].

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