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3,4-Difluoropyrrole-, 3,3,4,4-tetrafluoropyrrolidine- and pyrrolidine-based liquid crystals

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ABSTRACT

A new class of liquid crystals was formed with *N*-heterocycles as the terminal group, such groups as a 3,4-difluoropyrrole, 3,3,4,4-tetrafluoropyrrolidine, or pyrrolidine. Their properties were modified by varying the terminal heterocycles and/or the length of the alkyl chains on the cyclohexane liquid crystal building block. A comparison of the non-fluorinated and fluorinated pyrrolidine and fluorinated pyrrole as terminal group in the cyclohexane liquid crystals was studied. The mesophase behaviour was affected by altering the polarity of the terminal *N*-heterocycle. Compounds **n/m-4H** having the terminal pyrrolidine show a nematic phase. Comparatively, compounds **3/2-4F** and **5/2-4F**, having a fluorinated pyrrolidine, exhibit SmG phase. With 3,4-difluoropyrrole as terminal group, **n/m-2F** exhibit the broadest nematic phase range and good thermal stability, thus meeting the criterion for high performance liquid crystals materials.

1. Introduction

The development of stable mesophases with broad mesomorphic ranges [1–3] and low viscosities [4–8] continues to be of great interest. Liquid crystal compounds with fluorine and fluorinated alkyl substituents with such physical properties offer significant advantages over currently used liquid crystal materials [9–12]. The location of fluoro substituents include terminal group [13], linking arm [14], lateral and core position [15–17]. The introduction of a fluorine atom or fluorinated group into liquid crystals systems will change the properties of these materials, such as broadening the nematic phase range, decreasing smectic phase range, lowering the melting point and increasing the dielectric anisotropy [18,19].

For display applications, broad nematic phase range and good chemical stability are essential factors, however complicated interdependent relationship exists among dielectric anisotropy, viscosity, birefringence, threshold voltage and response time [20]. Liquid crystals (LCs) with strongly positive dielectric anisotropy help lower both the threshold voltage and power consumption [21], but excessive strongly positive dielectric anisotropy often lead to the increasing of viscosity, which will delay the response time [22]. Therefore, compounds that exhibit broad nematic phase range, high dielectric anisotropy, moderate birefringence, and low viscosity are promising for display applications.

The substituents, 3,4-difluorobenzene and 3,4,5-trifluorobenzene, are chemically stable and are able to react with a variety of liquid crystal building blocks. This makes them promising candidates in the development of new liquid crystal materials. There are reports of many 3,4-difluorophenol and 3,4,5-trifluorophenol derivatives as TFT (thin film transistor) liquid crystal materials. Some of these reported liquid crystal molecules [18,23,24] are shown in Scheme 1. Using 3,4,5-trifluorophenol as a building block one can achieve a high and stable dielectric anisotropy yet maintain a low viscosity.

Generally, the synthesis of 3,4,5-trifluorophenol often uses the grignard reagents as the starting material and the reaction should be conducted under nitrogen or argon atmospheres, using air-free techniques [25]. These stringent reaction conditions make the preparation process difficult. It is possible that 3,4,5-trifluorobenzene in the LCs can be replaced by the fluorinated heterocycles, inviting a study of structure and the change in properties of these fluorinated liquid crystals (FLCs). Some of FLCs have been found to display outstanding liquid crystal properties and open the way to future perspective applications in optoelectronics [26,27]. A liquid crystal display device using a liquid crystal composition containing the 3,4-disubstituted pyrrole and drivable at low voltage was

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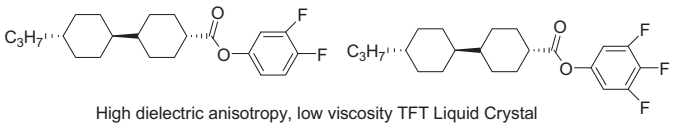


Scheme 1. 3,4-Difluorophenol, 3,4,5-trifluorophenol based liquid crystals.

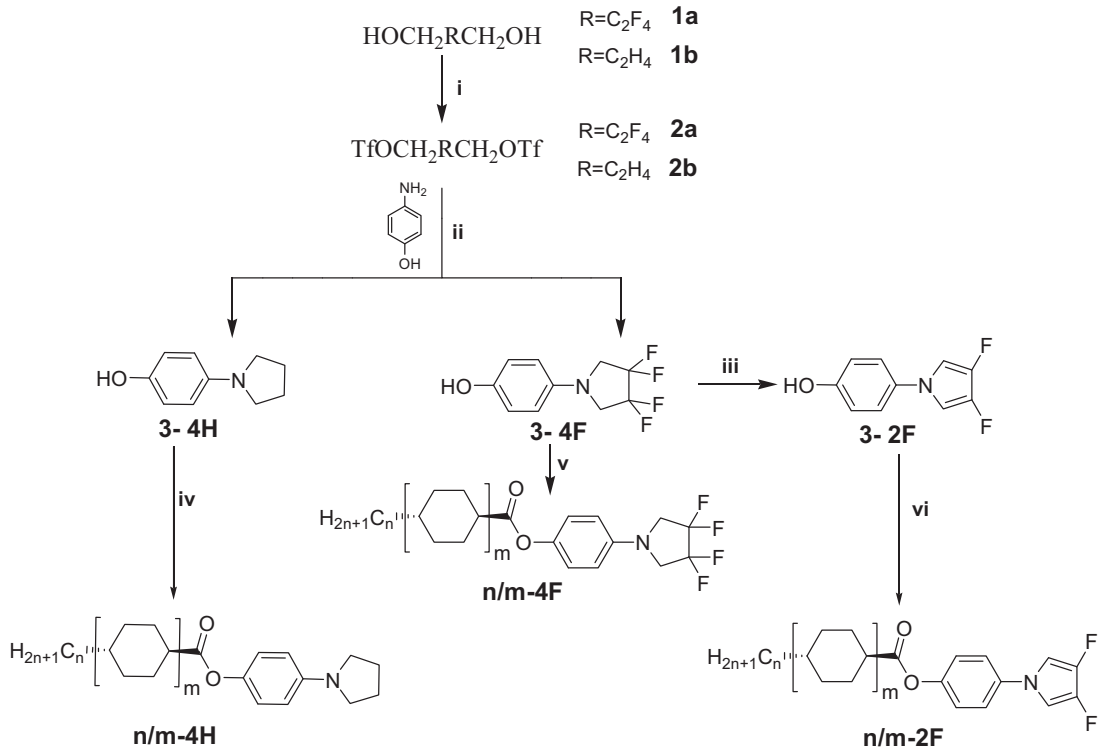
reported by Chisso Corporation [28]. Modification of the *N*-heterocycles structure and/or the length of the alkyl chains on the cyclohexane building block has shown marked influences in the properties of these liquid crystals. In this work, we report a series of cyclohexane-based liquid crystals with pyrrolidine, 3,3,4,4-tetrafluoropyrrolidine, and 3,4-difluoropyrrole as terminal group in an effort to establish the impact of the fluorinated *N*-heterocycle on the liquid crystal physical and chemical properties. Varying the terminal *N*-heterocycles from pyrrolidine to 3,3,4,4-tetrafluoropyrrolidine, further defluorination to the aromatic 3,4-difluoropyrrole, it is possible to increase or decrease the polarity and the interlayer force which affects the mesophase behaviour and physical properties.

2. Results and discussion

2.1. Synthesis

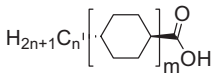
Novel liquid crystals **n/m-4H** and their fluorinated derivatives **n/m-4F**, **n/m-2F** were synthesized as shown in Scheme 2. In the previous experiments, the aryl amines react with the trifluoromethanesulfonic acid polyfluoroalkyldiyl ester to give *N*-based fluoro-heterocycles 4-(3,3,4,4-tetrafluoropyrrolidin-1-yl)-benzenamine in high yield [29]. The trifluoromethanesulfonic acid alkyldiyl and polyfluoroalkyldiyl esters **2a-b**, were reacted with 4-aminophenol in the presence of Et_3N in CH_3CH_2OH to give 4-pyrrolidin-1-yl-phenol, **3-4H**, and 4-(3,3,4,4-tetrafluoropyrrolidin-1-yl) phenol, **3-4F**, respectively.

The 3,4-difluoropyrrole was synthesized by the double elimination H-F reaction of 3,3,4,4-tetrafluoropyrrolidine with equimolar *t*-BuOK in DMSO as solvent at room temperature for 30 min as previously reported [30]. When 4-(3,3,4,4-tetrafluoropyrrolidin-1-yl) phenol, **3-4F** was reacted with *t*-BuONa, a higher concentration of the base (4 M), a higher reaction temperature (100 °C) and a longer reaction time (12 h) were required to drive the reaction to completion. The product 4-(1H-3,4-difluoropyrrole-1-yl) phenol, **3-2F**, was conveniently isolated by flash chromatography on silica gel with ethyl acetate-petroleum ether (1:5) as an eluent to give a white solid in 80% yield. Next, the cyclohexane-based liquid crystal building block *trans*-4′-alkyl-(1,1′-mono or bicyclohexyl)-4-carboxylic acid (3CA, 5CA, 3CCA, and 5CCA) was esterified with the corresponding phenol, 4-pyrrolidin-1-yl-phenol, **3-4H**, 4-(3,3,4,4-tetrafluoropyrrolidin-1-yl) phenol, **3-4F**, and 4-(1H-3,4-difluoropyrrole-1-yl) phenol, **3-2F**, using dicyclohexylcarbodiimide (DCC) and *N*,*N*-dimethylaminopyridine (DMAP) in dichloromethane to give **n/m-4H**, **n/m-4F**, **n/m-2F** in high yield. This is



Reagents and conditions: i: $(CF_3SO_2)_2O$, CH_2Cl_2, RT, 12h. ii: Et_3N, EtOH, 90 °C, 24h.

iii : t-BuONa, DMSO, 100 °C, 12h. iv, v, vi : 3CA, or 3CCA, or 5CA, or 5CCA, DCC, DMAP, $CHCl_3$, 80 °C, 12h.



3CA: n=3, m=1. 5CA: n=5, m=1.

3CCA: n=3, m=2. 5CCA: n=5, m=2

4H, 4F, 2F represent pyrrolidine, 3,3,4,4-tetrafluoropyrrolidine, and 3,4- difluoropyrrole respectively

Scheme 2. Synthesis of *N*-heterocycles liquid crystals.

Table 1
Thermal behaviour of the new compounds.

Compounds	Transition temperatures (°C)[a] [Enthalpies of transition] ($J g^{-1}$)		T_d (°C)[b]
3/2-2F	Cr 157.5 [10.58], N 289.5 [1.89]	Iso	314
5/2-2F	Cr 97.1 [4.00], Cr′ 131.0 [6.20], N 282.0 [1.00]	Iso	324
3/1-2F	Cr 103.5 [10.98], N 133.6 [1.42]	Iso	265
5/1-2F	Cr 94.0 [10.58], Cr′ 110.0 [0.64], N 137.0 [0.68]	Iso	272
3/2-4F	Cr 53.8 [3.49], Cr′ 91.60 [6.20], SmG 208.6 [6.08]	Iso	313
5/2-4F	Cr 113.0 [2.93], SmG 207.0 [6.95]	Iso	328
3/1-4F	Cr 141.3[5.02]	Iso	293
5/1-4F	Cr 136.2 [4.98]	Iso	309
3/2-4H	Cr 165.2 [6.30], N 276.2 [0.98]	Iso	349
5/2-4H	Cr 159.3 [10.64], N 267.3 [1.86]	Iso	340
3/1-4H	Cr 73.2 [1.12], Cr′ 102.2 [5.25], N 114.2 [1.68]	Iso	298
5/1-4H	Cr 101.8 [6.0], N 116.8 [0.88]	Iso	306

[a] Cr, SmG, N, Iso indicate crystal, smectic phase G, nematic phase and isotropic phase, respectively.
[b] Decomposition temperature.

the first example of the cyclohexane-based liquid crystals with *N*-heterocycles, pyrrolidine, 3,3,4,4-tetrafluoropyrrolidine, and 3,4-difluoropyrrole, as terminal group, most of which display broad mesomorphic range and high thermal stability.

2.2. Liquid crystalline properties

As shown in Table 1, the new compounds containing *N*-heterocycles as the end group display good liquid crystal properties. The three factors which affect the mesomorphic behaviour include: (1) the structure of the *N*-heterocycles; (2) the polyfluoroalkyl or fluorine substituent group on the *N*-heterocycles; and (3) the nature of the cyclohexane liquid crystal building block.

Transition temperatures and enthalpies of transition for compounds **n/m-4F**, **n/m-2F** and **n/m-4H** are given in Table 1. All the synthesized compounds show thermotropic liquid crystalline phases except compounds **3/1-4F** and **5/1-4F**, whereby the mesomorphism type is dramatically dependent on the type of *N*-heterocycles. Investigations by DSC and POM show compounds **3/1-4F** and **5/1-4F** melt into isotropic liquids at 141.3 °C and 136.2 °C directly and no texture of liquid crystal being observed. The series of **n/m-4H** and **n/m-2F** with terminal pyrrolidine and 3,4-difluoropyrrole showed a typical nematic phase. Their nematic phase was evidenced based on its schlieren texture as shown in Fig. 1. The mosaic texture of SmG can be seen in **n/m-4F** which is the **n/m-4H** fluoroalkyl derivatives, e.g., **5/2-4F** (Cr 113 °C, SmG 207 °C) and **3/2-4F** (Cr 53.8 °C, Cr′ 91.6 °C, SmG 208 °C). An example of such a texture is given in the supporting information.

Compounds **3/2-4F**, **5/1-2F**, **5/2-2F**, and **3/1-4H** show three endothermic peaks in the heating cycle, e.g., **3/2-4F** (Cr 53.8 °C, Cr′ 91.6 °C, SmG 208 °C), **5/1-2F** (Cr 94 °C, Cr′ 110 °C, N 137 °C), **5/2-2F** (Cr 97 °C, Cr′ 131 °C, N 282 °C), **3/1-4H** (Cr 73 °C, Cr′ 102 °C, N 114 °C); a Cr–Cr′ transition was seen before the appearance of a mesophase phase. The result was verified by POM as there was no mesophase between the Cr–Cr′ transition temperature ranges.

The nematic phase range of the liquid crystals with a 3,4-difluoropyrrole as terminal group are broader than those with pyrrolidine with the same cyclohexane building block, e.g., **3/2-2F** (Cr 157.5 °C, N 289.5 °C), which is broader than **3/2-4H** (Cr 165.2 °C, N 276.2 °C). Replacing the one-ring cyclohexane building block (3CA, 5CA) with two-ring cyclohexane (3CCA, 5CCA) results in an increase in the nematic phase range, e.g., **3/2-2F** (Cr 157.5 °C, N 289.5 °C) and **3/1-2F** (Cr 103.5 °C, N 133.6 °C). Two-ring cyclohexanes show a broad mesomorphism range from 100 °C to 151 °C. As a result, the two-ring cyclohexane elongates the molecule to give the appropriate length to width ratio, which is propitious to the forming and stability of mesomorphism.

The introduction of fluorine atoms into liquid crystal molecular causes the change in physical properties. In general, the new compounds with 3,4-difluoropyrrole as terminal group exhibit the highest clearing point, e.g., comparing with the analogous 3,3,4,4-tetrafluoropyrrolidine, and pyrrolidine terminal compounds, e.g., **5/2-2F** and **5/2-4F**, at Cp. 282.5 °C and 207 °C respectively while **5/2-4H** has Cp. 267.3 °C. The lower melting temperature and higher clearing point is advantageous for potential application.

Thermal stabilities, which range from 270 °C to 350 °C and depend on the heterocycle and the cyclohexane building block, were determined by thermal gravimetric analysis (TGA). Data show that the decomposition temperatures were higher than the clearing point for these compounds. The decomposition temperatures of the new compounds are shown in Table 1. In general, the new compounds with one-ring cyclohexane are thermally less stable than their two-ring cyclohexane analogue. The new compounds with 3,3,4,4-tetrafluoropyrrolidine, and 3,4-difluoropyrrole as terminal group show similar thermal stability and are mesophase stable to high temperature.

The typical structures of the liquid crystals **3/2-4H**, **3/2-4F**, and **3/2-2F**, with the same cyclohexane building block and different *N*-heterocycles as terminal group, were investigated by X-Ray diffraction. The diffraction patterns obtained for **3/2-2F** and **3/2-4H** are given in the supporting information. The **3/2-2F** and **3/2-4H**, with 3,4-difluoropyrrole and pyrrolidine terminal group, only a wide diffraction peak was observed in the wide angle region and no diffraction peak was found in the small angle region. This indicates that no lamellar ordering exists in the mesophase. The diffraction

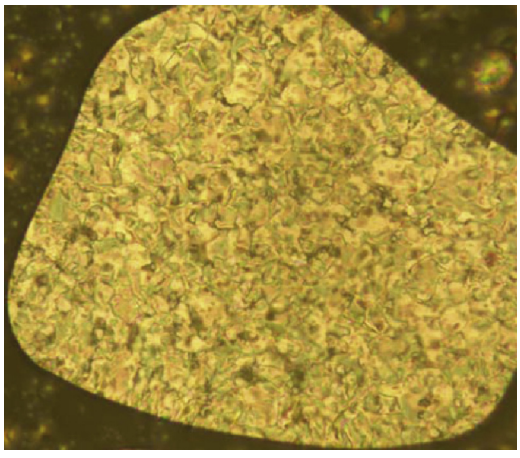


Figure 1. POM texture for **3/2-2F** at 240 °C.

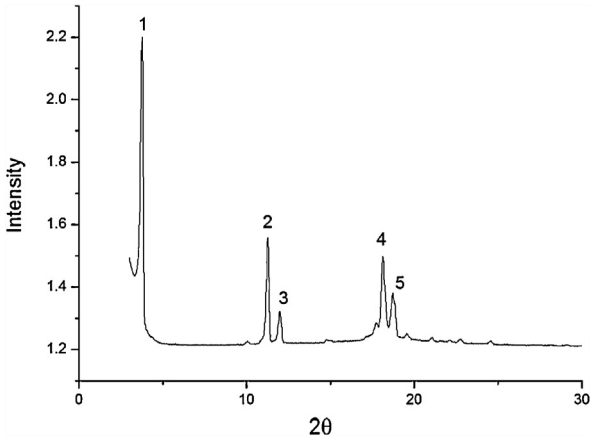


Figure 2. XRD diffraction pattern for **3/2-4F** recorded at 150 °C.

pattern of **3/2-4F** is given in the Fig. 2. In the case of **3/2-4F** with 3,3,4,4-tetrafluoropyrrolidine as terminal group, a strong sharp scattering at 3.77° corresponding to the d spacing of 23.4 Å was given in the small angle region. In the wide angle region, four scattering at 11.27°, 12.00°, 18.50°, and 18.70° corresponding to the d spacing of 7.85 Å, 7.34 Å, 4.80 Å, and 4.70 Å respectively were obtained. The SmG showed several sharp diffraction peaks in the wide angle region in previous reports [31–33]. The SmG Phase was assigned for **3/2-4F** by the photomicrographs optical texture as well as X-ray diffraction (XRD) spectrum characterization.

3. Conclusion

A new class of *N*-heterocycles based liquid crystals were synthesized that employed 3,4-difluoropyrrole, 3,3,4,4-tetrafluoropyrrolidine, and pyrrolidine as terminal group. Their melting points, decomposition temperatures, clearing points, mesomorphism type were determined. The properties of these liquid crystals can be adjusted by using different *N*-heterocycles, cyclohexane building blocks, fluoroalkyl and fluorine substituents on the *N*-heterocycles. They show a wide mesophase range and are mesophase stable to high temperatures. The mesophase behaviour was affected by altering the terminal *N*-heterocycle. Compounds **n/m-4H** having the terminal pyrrolidine show a broad nematic range. With 3,4-difluoropyrrole as terminal group, **n/m-2F** exhibit the broadest nematic range and good thermal stability. Compounds **3/2-4F** and **5/2-4F**, bearing fluorinated pyrrolidine, exhibit SmG Phase. The two CF_2 groups increase the molecular polarity. It would favour the enhancement of interlayer interactions which contribute to the formation of layer arrangement smectic phase. New compounds with one-ring cyclohexane building block are thermally less stable than their two-ring cyclohexane analogue. The fluorinated heterocycles can replace the expensive 3,4-difluorobenzene and 3,4,5-trifluorobenzene in LCs to form promising liquid crystal materials.

4. Experimental

4.1. General considerations

All the reagents used were analytical reagents purchased from commercial sources and used as received. ^{1}H and ^{19}F were recorded on a 400 MHz nuclear magnetic resonance spectrometer operating at 400 and 376 MHz respectively. Chemical shifts were reported relative to Me_4Si for ^{1}H and CCl_3F for ^{19}F. The solvent was either $CDCl_3$ unless otherwise specified. Thermogravimetric analysis (TGA) measurements were performed at a heating rate of 10 °C min^{-1} with a Netzsch STA409PC (Germany) instrument. The DSC was recorded at a scan rate of 2 °C min^{-1} on a Netzsch DSC200PC apparatus. Optical micrographs were observed with a polarizing optical microscope (POM) (*Nikon* LINKAM-THMSE600) equipped with a heating plate (HCS601). Variable-temperature X-ray diffraction (XRD) experiments were performed on a Bruker D8 Advance X-ray diffractometer (using Cu Kα1 radiation of a wavelength of 1.54 Å) with temperature controller. Elemental analyses were performed on an EXETER CE-440 Elemental Analyzer.

4.2. General procedure for the preparation of trifluoromethanesulfonic acid 2,2,3,3-tretrafluoro-1,4-butanediyl ester **2a** and trifluoromethanesulfonic acid 1,4-butanedily ester **2b**

2,2,3,3-Tetrafluoro-1,4-butanediol **1a**, or 1,4-butanediol **1b** (1 mmol), pyridine (3 mmol) and dichloromethylene (20 mL) were stirred at room temperature. After 30 min, trifluoromethanesulfonic anhydride (2.5 mmol) in 10 mL dichloromethylene was slowly added over 1 h. The mixture was stirred for 12 h, then washed with water (3 × 30 mL), and dried over anhydrous sodium sulfate. The solvent was removed under vacuum to give trifluoromethanesulfonic acid 2,2,3,3-tretrafluoro-1,4-butanedily ester.

4.3. General procedure for the preparation of 4-(3,3,4,4-tetrafluoropyrrolidin-1-yl) phenol (**3-4F**)

Trifluoromethanesulfonic acid 2,2,3,3,-tretrafluoro-1,4-butanediyl ester **2a** (5 mmol), 4-aminophenol (5 mmol), and Et_3N (12.5 mmol) in 15 mL ethanol were placed in a Pyrex glass tube, sealed, heated at 90 °C for 24 h. After cooling, the organic solvent was removed under reduced pressure. 30 mL of dichloromethane was added to the residue and was then washed with water (3 × 30 mL), dried over anhydrous Na_2SO_4. After the solvent was removed, the crude product was chromatographed on silica gel with ethyl acetate-petroleum ether (1:5) as an eluent to give white solid. 75% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 6.81 (d, J = 8.6 Hz, 2H), 6.44 (d, J = 8.8 Hz, 2H), 3.74 (t, J = 10.4 Hz, 4H). ^{19}F NMR ($CDCl_3$) δ (ppm): −121.95 (m, 4F). MS (ESI) m/z: 234.91(M^+). Anal. Calcd (%) for $C_{10}H_9F_4NO$ (235.18): C, 51.07; H, 3.86; N, 5.96. Found: C, 51.06; H, 3.83; N, 5.97.

4.4. General procedure for the preparation of 4-(1H-3,4-difluoropyrrole-1-yl) phenol (**3-2F**)

4-(3,3,4,4-Tetrafluoropyrrolidin-1-yl) phenol **3-4F** (2 mmol), sodium tert-butoxide (16 mmol) in 10 mL dimethyl sulfoxide were placed in a Pyrex glass tube, sealed, heated at 100 °C for 12 h. After cooling, 30 mL dichloromethane was added to the reaction mixture and then washed with water (3 × 30 mL) and dried over anhydrous Na_2SO_4. After the solvent was removed, the crude product was chromatographed on silica gel with ethyl acetate–petroleum ether (1:5) as an eluent to give white solid. 80% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.14 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.61 (s, 2H), 4.89 (s, 1H). ^{19}F NMR ($CDCl_3$) δ (ppm): −178.29 (s, 2F). MS (ESI) m/z: 196.27(M^++H^+). Anal. Calcd (%) for: $C_{10}H_7F_2NO$ (195.17): C, 61.54; H, 3.62; N, 7.18. Found: C, 61.55; H, 3.64; N, 7.16.

4.5. General procedure for the preparation of 4-pyrrolidin-1-yl-phenol (3-4H)

Trifluoromethanesulfonic acid 1,4-butanediyl ester **2b** (5 mmol), 4-aminophenol (5 mmol), and Et_3N (12.5 mmol) in 15 mL ethanol were placed in a Pyrex glass tube, sealed, heated at 90 °C for 24 h. After cooling, the organic solvent was removed under reduced pressure to the residue was added 30 mL dichloromethane then washed with water (3 × 30 mL), dried over anhydrous Na_2SO_4. After the solvent was removed, the crude product was chromatographed on silica gel with ethyl acetate–petroleum ether (1:5) as an eluent to give white solid, 78% yield. ^{1}H NMR (DMSO) δ (ppm): 8.48(s, 1H), 6.62 (d, J = 8.8, 2H), 6.39 (d, J = 8.8, 2H), 3.10 (t, J = 7.2, 4H), 1.90 (m, 4H). MS (ESI) m/z: 164.20 (M^++H^+).

4.6. General procedure for the preparation of n/m-4F, n/m-2F and n/m-4H

4-(3,3,4,4-Tetrafluoropyrrolidin-1-yl) phenol **3-4F**, 4-(1H-3,4-difluoropyrrole-1-yl) phenol **3-2F** or 4-pyrrolidin-1-yl-phenol **3-4H** (1 mmol), *trans*-4-(*trans*-4-*n*-alkylcyclohexyl)cyclohexanecarboxylic acid or *trans*-4-*n*-alkylcyclohexanecarboxylic acid (1 mmol), *N*,*N*′-dicyclohexyl carbodiimide (DCC) (1 mmol), 4-dimethylaminopyridine (DMAP) (0.05 mmol) in 10 mL chloroform were placed in a Pyrex glass tube, sealed, heated at 80 °C for 12 h.

After cooling, the white solid was filtrated off, the solvent was removed under vacuum, and then the crude product was chromatographed on silica gel with dichloromethylene–petroleum ether (2:1) as an eluent to give **n/m-4F**, **n/m-2F** and **n/m-4H**.

Trans-4-(*trans*-4-*n*-propylcyclohexyl)cyclohexanecarboxylic acid 4′-(3,3,4,4-tetrafluoropyrrolidin-1-yl) phenyl ester (**3/2-4F**). 87% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 6.99 (d, J = 8.7 Hz, 2H), 6.51 (d, J = 8.8 Hz, 2H), 3.86–3.75 (m, 4H), 2.4–2.38 (m, 1H), 2.14 (d, J = 12.4 Hz, 2H), 1.85 (d, J = 10.4 Hz, 2H), 1.74 (t, J = 14.7 Hz, 4H), 1.51 (t, J = 12.3 Hz, 2H), 1.30 (m, J = 13.7, 6.9 Hz, 2H), 1.18–1.07 (m, 6H), 1.04–0.95 (m, 3H), 0.87 (t, J = 7.2 Hz, 5H). ^{19}F NMR ($CDCl_3$) δ (ppm): −122.69 (m, 4F). MS (ESI) m/z: 469.50 (M^+). Anal. Calcd (%) for: $C_{26}H_{35}F_4NO_2$ (469.56): C, 66.51; H, 7.51; N, 2.98. Found: C, 66.47; H, 7.46; N, 3.00.

Trans-4-(*trans*-4-*n*-propylcyclohexyl)cyclohexanecarboxylic acid 4′-(1H-3,4-difluoropyrrole-1-yl) phenyl ester **(3/2-2F)**. 85% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 7.24 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 6.68 (s, 2H), 2.46 (t, J = 12.2 Hz, 1H), 2.15 (d, J = 12.3 Hz, 2H), 1.86 (d, J = 10.3 Hz, 2H), 1.74 (t, J = 14.6 Hz, 4H), 1.53 (q, J = 12.0 Hz, 2H), 1.31 (m, 2H), 1.19–0.96 (m, 9H), 0.87 (t, J = 7.1 Hz, 5H). ^{19}F NMR ($CDCl_3$) δ (ppm): −177.34 (s, 2F). MS (ESI) m/z: 452.10 (M^++Na^+). Anal. Calcd (%) for: $C_{26}H_{33}F_2NO_2$ (429.54): C, 72.70; H, 7.74; N, 3.26. Found: C, 72.34; H, 7.73; N, 3.29.

Trans-4-*n*-propylcyclohexanecarboxylic acid 4′-(3,3,4,4-tetrafluoropyrrolidin-1-yl) phenyl ester (**3/1-4F**). 85% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 6.99 (d, J = 8.9 Hz, 2H), 6.51 (d, J = 8.9 Hz, 2H), 3.80 (m, 4H), 2.45 (m, 1H), 2.12 (d, J = 11.6 Hz, 2H), 1.86 (d, J = 13.6 Hz, 2H), 1.54 (m, 2H), 1.41–1.14 (m, 6H), 1.08–0.85 (m, 4H). ^{19}F NMR ($CDCl_3$) δ (ppm): −122.69 (m, 4F). MS (ESI) m/z: 388.2 (M^++H^+). Anal. Calcd (%) for: $C_{20}H_{25}F_4NO_2$ (387.41): C, 62.00; H, 6.50; N, 3.62. Found: C, 62.02; H, 6.54; N, 3.63.

Trans-4-*n*-propylcyclohexanecarboxylic acid 4′-(3,4-difluoropyrrole-1-yl) phenyl ester (**3/1-2F**). 86% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 7.24 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 6.68 (s, 2H), 2.48 (t, J = 12.1 Hz, 1H), 2.13 (d, J = 12.4 Hz, 2H), 1.88 (d, J = 12.5 Hz, 2H), 1.63–1.48 (m, 2H), 1.40–1.26 (m, 3H), 1.25–1.15 (m, 2H), 0.98 (d, J = 12.7 Hz, 2H), 0.90 (t, J = 7.1 Hz, 3H). ^{19}F NMR ($CDCl_3$) δ (ppm): −177.34 (s, 2F). MS (ESI) m/z: 347.85 (M^+). Anal. Calcd (%) for: $C_{20}H_{23}F_2NO_2$ (347.80): C, 69.15; H, 6.67; N, 4.03. Found: C, 69.12; H, 6.65; N, 4.04.

Trans-4-(*trans*-4-*n*-pentylcyclohexyl)cyclohexanecarboxylic acid 4′-(3,3,4,4-tetrafluoropyrrolidin-1-yl) phenyl ester (**5/2-4F**). 82% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 6.99 (d, J = 8.9 Hz, 2H), 6.50 (d, J = 8.9 Hz, 2H), 3.80 (m, 4H), 2.43 (m, J = 1H), 2.13 (d, J = 11.5 Hz, 2H), 1.95–1.75 (m, 4H), 1.71 (d, J = 13.4 Hz, 3H), 1.61–1.15 (m, 11H), 1.16 (s, 2H), 1.07 (m, 10H), 0.88 (t, J = 6.9 Hz, 6H). ^{19}F NMR ($CDCl_3$) δ (ppm): −122.69 (m, 4F). MS (ESI) m/z: 498.30 (M^+ + H^+). Anal. Calcd (%) for: $C_{28}H_{39}F_4NO_2$ (497.29): C, 67.58; H, 7.90; N, 2.81. Found: C, 67.55; H, 7.92; N, 2.84.

Trans-4-(*trans*-4-*n*-pentylcyclohexyl)cyclohexanecarboxylic acid 4′-(3,4-difluoropyrrole-1-yl) phenyl ester (**5/2-2F**). 82% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 7.26 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 6.70 (s, 2H), 2.45 (m, J = 1H), 2.12 (d, J = 11.5 Hz, 2H), 1.95–1.75 (m, 4H), 1.71 (d, J = 13.4 Hz, 3H), 1.60–1.14 (m, 11H), 1.16 (s, 2H), 1.08(m, 10H), 0.89(t, J = 6.9 Hz. ^{19}F NMR ($CDCl_3$) δ (ppm): −177.34 (s, 2F). MS (ESI) m/z: 480.18 (M^++Na^+). Anal. Calcd (%) for: $C_{28}H_{37}F_2NO_2$ (457.28): C, 73.49; H, 8.15; N, 3.06. Found: C, 73.31; H, 8.10; N, 3.07.

Trans-4-*n*-pentylcyclohexanecarboxylic acid 4′-(3,3,4,4-tetrafluoropyrrolidin-1-yl) phenyl ester (**5/1-4F**). 80% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 6.99 (d, J = 8.6 Hz, 2H), 6.51 (d, J = 8.6 Hz, 2H), 3.81 (t, J = 10.0 Hz, 4H), 2.45 (t, J = 12.2 Hz, 1H), 2.12 (d, J = 12.2 Hz, 2H), 1.87 (d, J = 12.4 Hz, 2H), 1.56 (t, J = 11.6 Hz, 2H), 1.37–1.16 (m, 9H), 1.04–0.94 (m, 2H), 0.89 (t, J = 6.7 Hz, 3H). ^{19}F NMR ($CDCl_3$) δ (ppm): −122.69 (m, 4F). MS (ESI) m/z: 415.5 (M^+). Anal. Calcd (%) for: $C_{22}H_{29}F_4NO_2$ (415.46): C, 63.60; H, 7.04; N, 3.37. Found: C, 63.62; H, 7.05; N, 3.40.

Trans-4-*n*-pentylcyclohexanecarboxylic acid 4′-(3,4-difluoropyrrole-1-yl) phenyl ester (**5/1-2F**). 80% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 7.24 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.68 (s, 2H), 2.45 (t, J = 12.2 Hz, 1H), 2.12 (d, J = 12.2 Hz, 2H), 1.87 (d, J = 12.4 Hz, 2H), 1.56 (t, J = 11.6 Hz, 2H), 1.37–1.16 (m, 9H), 1.04–0.94 (m, 2H), 0.89 (t, J = 6.7 Hz, 3H). ^{19}F NMR ($CDCl_3$) δ (ppm): −122.69 (m, 4F). MS (ESI) m/z: 375.3 (M^+). Anal. Calcd (%) for: $C_{22}H_{27}F_2NO_2$ (375.2): C, 70.38; H, 7.25; N, 3.73. Found: C, 70.31; H, 7.21; N, 3.72.

Trans-4-(*trans*-4-*n*-propylcyclohexyl)cyclohexanecarboxylic acid 4′-(pyrrolidin-1-yl) phenyl ester (**3/2-4H**). 78% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 6.90 (d, J = 8.5 Hz, 2H), 6.51 (d, J = 7.5 Hz, 2H), 3.26 (t, J = 12.3 Hz, 4H), 2.41 (t, J = 12.1 Hz, 1H), 2.13 (d, J = 12.3 Hz, 2H), 1.99 (m, 4H), 1.84 (d, J = 10.5 Hz, 2H), 1.73 (t, J = 14.2 Hz, 4H), 1.52 (m, 3H), 1.34–1.26 (m, 2H), 1.7–0.96 (m, 9H), 0.89–0.85 (m, 4H). MS (ESI) m/z: 398.56 (M^++H^+). Anal. Calcd (%) for: $C_{26}H_{39}NO_2$ (397.59): C, 78.54; H, 9.89; N, 3.52. Found: C, 78.59; H, 9.90; N, 3.55.

Trans-4-(*trans*-4-*n*-pentylcyclohexyl)cyclohexanecarboxylic acid 4′-(pyrrolidin-1-yl) phenyl ester (**5/2-4H**). 76% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 6.90 (d, J = 8.2 Hz, 2H), 6.51 (d, J = 8.1 Hz, 2H), 3.26 (t, J = 12.3 Hz, 4H), 2.42 (t, J = 12.1 Hz, 1H), 2.14 (d, J = 12.5 Hz, 2H), 1.99 (m, 4H), 1.88–1.65 (m, 7H), 1.52 (m, 2H), 1.36–1.19 (m, 15H), 1.17–0.84 (m, 4H). MS (ESI) m/z: 426.57 (M^+). Anal. Calcd (%) for: $C_{28}H_{43}NO_2$ (426.65): C, 79.01; H, 10.18; N, 3.29. Found: C, 78.90; H, 10.01; N, 3.05.

Trans-4-*n*-propylcyclohexanecarboxylic acid 4′-(pyrrolidin-1-yl) phenyl ester (**3/1-4H**). 79% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 6.91 (d, J = 8.4 Hz, 2H), 6.52 (d, J =7.3 Hz, 2H), 3.26 (t, J = 12.1 Hz, 4H), 2.44 (t, J = 12.1 Hz, 1H), 2.12 (d, J = 12.5 Hz, 2H), 2.00 (m, 4H), 1.86 (d, J = 12.1 Hz, 2H), 1.55 (m, 2H), 1.31 (m, 4H), 1.23–1.14 (m, 2H), 0.94 (m, 4H). MS (ESI) m/z: 315.55 (M^+). Anal. Calcd (%) for: $C_{20}H_{29}NO_2$ (315.45): C, 76.15; H, 9.27; N, 4.44. Found: C, 76.40; H, 10.30; N, 4.61.

Trans-4-*n*-pentylcyclohexanecarboxylic acid 4′-(pyrrolidin-1-yl) phenyl ester (**5/1-4H**). 75% yield; white solid; ^{1}H NMR ($CDCl_3$) δ (ppm): 6.90 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 7.8 Hz, 2H), 3.26 (t, J = 12.1 Hz, 4H), 2.44 (t, J = 12.1 Hz, 1H), 2.11 (d, J = 12.5 Hz, 2H), 2.00 (m, 4H), 1.86 (d, J = 12.5 Hz, 2H), 1.61–1.50 (m, 2H), 1.37–1.15 (m, 10H), 0.93 (m, 4H). MS (ESI) m/z: 344.44 (M^+ + H^+). Anal. Calcd (%) for: $C_{22}H_{33}NO_2$ (343.50): C, 76.92; H, 9.68; N, 4.08. Found: C, 76.60; H, 9.58; N, 4.12.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2013.07.022.

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