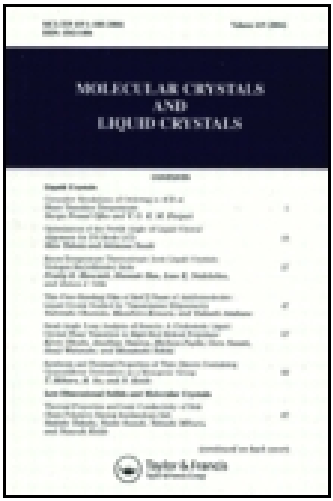

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Synthesis and Mesomorphic Properties of Some Fluoro-Substituted Benzoates

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Synthesis and Mesomorphic Properties of Some Fluoro-Substituted Benzoates

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Several series of fluoro-substituted benzoate liquid crystals have been synthesized. The results showed that the SmA phase is enhanced with the increasing of the degree of fluoro-substitution on the *para*- and *meta*-postion of the terminal phenyl groups. And the molecules which have same molecular structural formula show nearly the same melting points. It is also discussed about the effect of the ester bond's direction on the mesomorphic properties.

INTRODUCTION

For many years fluoro-substitution in mesogens has been used as a useful way of modifying the transition temperatures and/or the mesomorphase types of the parent systems. The fluoro-substituent is ideal in that it combines the properties of large electronegativity and small size so that it significantly affects the physical properties of molecules without eliminating the possibility of mesophase formation. The effect of lateral fluoro-substitution in liquid crystals is very well-reported and summarized[1-13]. In these years many patents have been published on systems with fluoro substituents in a terminal phenyl ring, and the terminal fluoro substituted liquid crystals have been widely used in nematic mixtures for TFT applications. In our group many compounds have been synthesized in this field. And it was found that not only the *para*-fluoro substitution but also the *meta*-fluoro substitution of the terminal phenyl group enhances the formation of SmA phase[14]. The molecular structure shown as below(**I**).

To further study this phenomena, we prepared the molecules below(**II**). The synthesis of series **345F*n*** has been published elsewhere[15].

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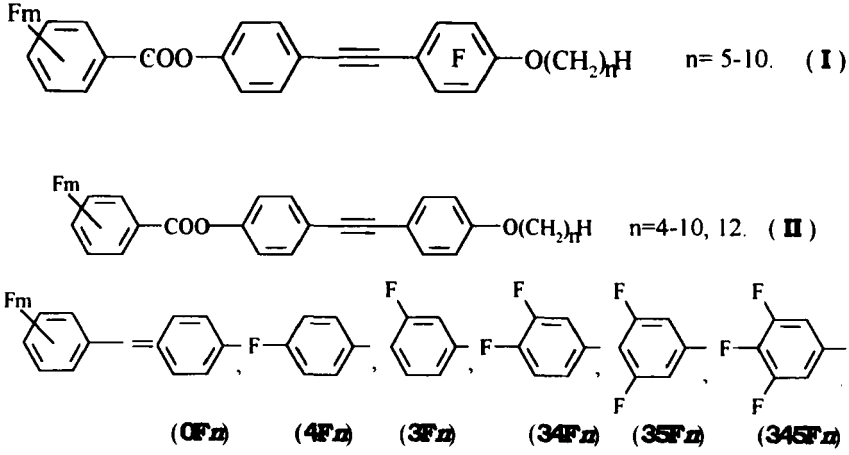
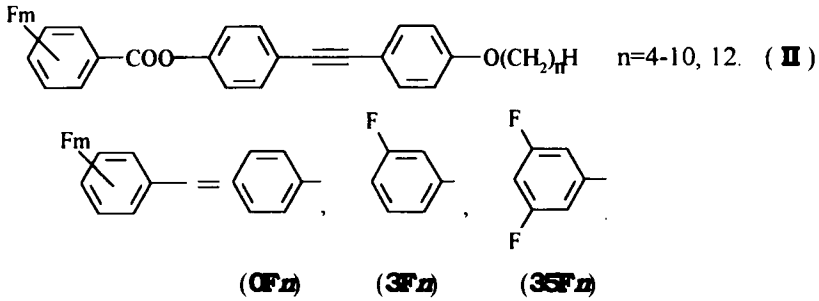


RESULTS AND DISCUSSION

The transition temperatures of the compounds, **0F*n*** ([4-(4′-*n*-alkyloxyphenyl)-acetylenyl]-phenyl benzoate), **4F*n*** ([4-(4′-*n*-alkyloxyphenyl)acetylenyl]phenyl 4-fluorobenzoate), **3F*n*** ([4-(4′-*n*-alkyloxyphenyl)acetylenyl]phenyl 3-fluorobenzoate), **34F*n***([4-(4′-*n*-alkyloxyphenyl)acetylenyl]phenyl 3,4-difluorobenzoate), **35F*n*** ([4-(4-*n*-alkyloxyphenyl)acetylenyl]phenyl 3,5-difluorobenzoate), **345F*n*** ([4-(4-*n*-alkyloxyphenyl)acetylenyl]phenyl 3,4,5-trifluorobenzoate) are presented in **Table I** and **Table II**. In all these series most of them show enantiotropic nematic and/or smectic A phases, only **34F*n*** series show monotropic SmB phase. Due to such short mesomorphic ranges, several transition temperatures of the compounds **4F*10*** and **35F*9*** cannot be determined by DSC.

Compounds **0F*n*** exhibit only nematic phases, whereas **3F*n*** and **4F*n*** show nematic phases with very narrow monotropic or enantiotropic SmA phases being shown with longer alkoxy chains. In the **34F*n*** series both broad-range smectic A and nematic phases are found. This series also exhibits short range smectic B phases at larger chain lenghths. The **345F*n*** series is more favorable to form SmA phases than the series **34F*n***. When n≥9, only the SmA phase is found. And both the **3F*n*** and **35F*n*** series show narrow mesomorphic phase ranges. But compounds **35F*n*** are more favourable to form SmA phases.

TABLE I Phase transition temperatures(°C) of the compounds **0F*n*, 3F*n*** and **35F*n***[*]

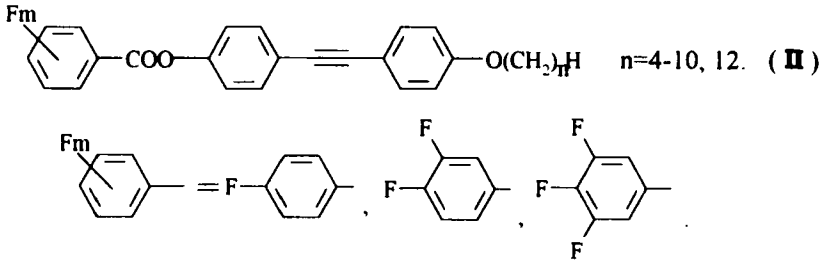


(**0F*n***) (**3F*n***) (**35F*n***)

name	*n*	*Phase transition temperatures/°C*
0F6	6	Cr 102.4 N 150.2 I 149.1 N 90.6 Recr
0F7	7	Cr 103.1 N 141.3 I 140.2 N 87.3 Recr
0F8	8	Cr 101.7 N 140.6 I 139.2 N 82.8 Recr
0F9	9	Cr 115.4 N 134.9 I 133.8 N 94.3 Recr
0F10	10	Cr 105.3 N 133.7 I 132.6 N 86.4 Recr
3F4	4	Cr 123.5 N 151.2 I 149.6 N 104.1 Recr
3F5	5	Cr 111.7 N 141.2 I 139.9 N 99.0 Recr
3F6	6	Cr 109.5 N 143.4 I 142.6 N 96.9 Recr
3F7	7	Cr 113.6 N 136.1 I 134.8 N 94.4 Recr
3F8	8	Cr 111.8 N 136.5 I 135.4 N 90.4 Recr
3F9	9	Cr 116.2 N 131.6 I 129.9 N 96.3 Recr
3F10	10	Cr 114.8 N 131.4 I 130.0 N 103.2 S_A 98.3 Recr
3F12	12	Cr 117.0 N 127.5 I 126.0 N 110.5 S_A 96.8 Recr
35F4	4	Cr 113.2 N 134.9 I 133.5 N 107.3 Recr
35F5	5	Cr 111.5 N 125.6 I 124.1 N 106.0 S_A 99.0 Recr
35F6	6	Cr 104.2 S_A 118.9 N 130.8 I 129.2 N 117.2 S_A 98.5 Recr
35F7	7	Cr 95.3 S_A 119.8 N 126.2 I 124.9 N 118.6 S_A 90.1 Recr
35F8	8	Cr 94.6 S_A 124.7 N 127.7 I 126.3 N 123.1 S_A 86.2 Recr
35F9	9	Cr 98.2 S_A 123.9[**] N 124.0 I 122.1 N 121.7[**] S_A 80.8 Recr
35F10	10	Cr 97.3 S_A 125.7 I 124.4 S_A 85.3 Recr
35F12	12	Cr 100.9 S_A 124.1 I 122.4 S_A 86.3 Recr

[*] Cr, Crystal; S_A, Smectic A; N, Nematic; Recr, Recrystal.
[**] : data obtained by polymicroscopy

TABLE II Phase transition temperatures(°C) of the compounds **4F*n*, 34F*n*** and **345F*n***[*]



(**4F*n***) (**34F*n***) (**345F*n***)

name	*n*	*Phase transition temperatures/°C*
4F7	7	Cr 117.5 N 201.7 I 200.2 N 95.0 Recr
4F8	8	Cr 115.3 N 196.6 I 195.7 N 96.1 Recr
4F9	9	Cr 119.3 N 188.7 I 187.4 N 95.8 S_A 94.1 Recr
4F10	10	Cr 117.7 S_A 118.3[**] N 184.7 I 183.4 N 118.6 S_A 98.0 Recr
34F4	4	Cr 123.4 N 207.8 I 206.4 N 96.1 Recr
34F5	5	Cr 115.6 S_A 122.8 N 195.4 I 194.1 N 121.0 S_A 91.4 Recr
34F6	6	Cr 107.8 S_A 137.0 N 191.3 I 189.9 N 135.5 S_A 87.8 S_B 84.4 Recr
34F7	7	Cr 93.4 S_A 149.5 N 183.6 I 182.4 N 148.0 S_A 78.4 S_B 75.7 Recr
34F8	8	Cr 94.3 S_A 155.9 N 180.2 I 178.8 N 154.6 S_A 81.2 S_B 73.0 Recr
34F9	9	Cr 101.2 S_A 159.1 N 174.0 I 172.9 N 157.7 S_A 81.9 S_B 73.3 Recr
34F10	10	Cr 96.5 S_A 161.3 N 171.2 I 169.6 N 160.0 S_A 83.8 S_B 73.9 Recr
34F12	12	Cr 99.6 S_A 161.3 N 163.8 I 162.5 N 159.8 S_A 84.5 S_B 79.3 Recr
345F6	6	Cr 96.5 S_A 158.0 N 171.5 I 170.0 N 156.5 S_A 72.9 Recr
345F7	7	Cr 87.9 S_A 161.6 N 166.6 I 165.2 N 160.0 S_A 66.6 Recr
345F8	8	Cr 84.2 S_A 162.8 N 164.3 I 163.1 N 161.5 S_A 69.9 Recr
345F9	9	Cr 87.3 S_A 159.6 I 158.1 S_A 72.2 Recr
345F12	12	Cr 89.2 S_A 154.9 I 153.6 S_A 154.9 I 153.6 S_A 78.8 Recr

[*] Cr, Crystal; S_A, Smectic A; N, Nematic; Recr, Recrystal.
[**] : data obtained by polymicroscopy.

It is generally accepted that replacement of a terminal *para*-hydrogen in a molecule by another substituent enhances the potential of the system to form liquid crystals. If we consider series **4F*n*, 34F*n*** and **345F*n*** to be the derivatives of the parents series **0F*n*, 3F*n*** and **35F*n*** with a *para*-fluoro substitutent, the *para*-fluorine atoms may conjugate with the carbonyl carbon through the intervening aro-

matic ring, which would involve a highly polar structure. Then the clearing points of the **4F*n*, 34F*n*** and **345F*n*** series would be expected to higher than their correspounding parents[16]. This is shown to be the cause in **Fig. 1**.

From the **Fig. 1**, it can also be seen that the clearing points are droping with increasing the degree of the *meta*-fluoro substitution. But there is a little different between the two groups, **groupl** (series **4F*n*, 34F*n*** and **345F*n***) and **group 2** (series **0F*n*, 3F*n*** and **35F*n***). Firstly, it can be seen from **group 1**, that a second lateral fluoro-substituent in the acid causes a further depression in the clearing point which is approximately equivalent to that of the first substitution. Secondly, it can be seen from **group 2**, that a second lateral fluoro-substituent in the acid causes a larger depression of clearing points than that caused by a single fluoro-substituent in the acid. Although this phenomena cannot be explainted clearly now, we believe that this can be rationalised by considering how *meta*-fluoro-substitution affects the breadth of the molecule[4] and how *para*-fluoro substituent affects the polarity of the benzoates.

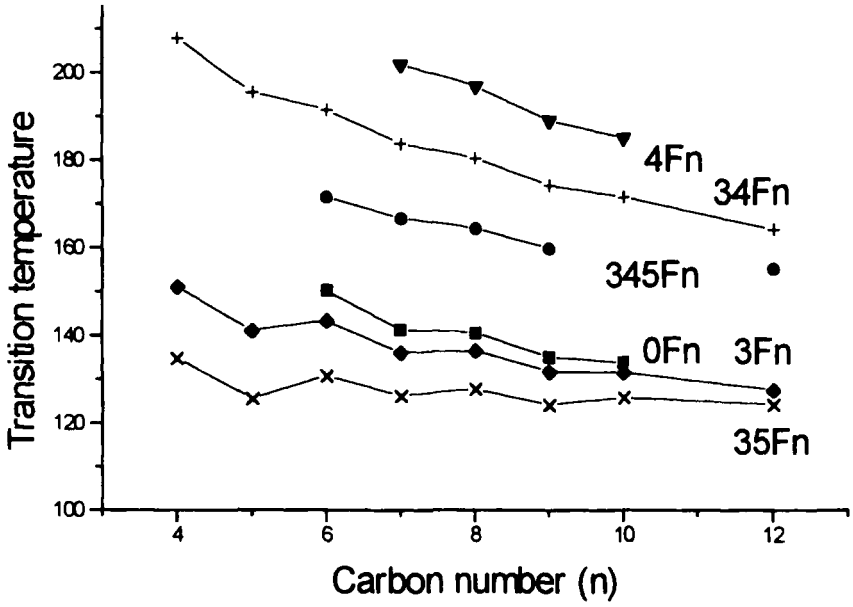


FIGURE 1 The number of the carbon atoms in the alkoxy chain versus the clearing points of the six series listed in the Table I and Table II

From **Fig. 2**, it can be seen that the molecules which have same molecular structural formula show nearly the same melting points, and with the increase of fluoro-substitution, the melting points decrease with the exception of the series

0F*n*, the reson for this may be the degree of fluoro-substitution affects the molecular packing in the solid phase. The different between the mono-fluoro-substitution series **4F*n***(or **3F*n***) and the none-fluoro-substitution series **0F*n***, the melting point increase may be rationalised as the fact that the fluorine atom increases the polarity of the molecule. Furthermore, from the **Table I**and **Table II**, it is found that increasing the degree of the fluoro substitution on the terminal phenyl group increases the formation of smectic A phase. This means that with the increase of fluoro-substitution in the terminal phenyl group the terminal-terminal attractions are disrupted step by step. Then the melting points are reduced.

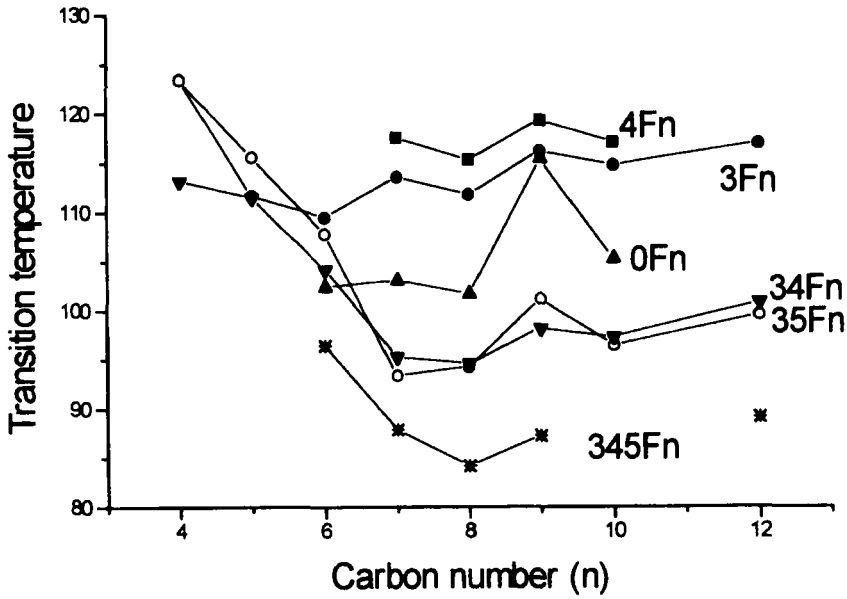


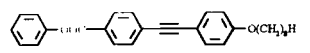
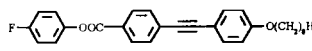
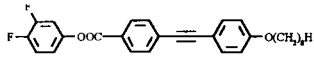
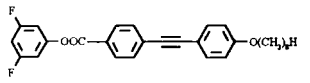
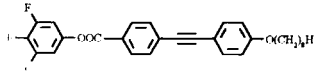
FIGURE 2 The number of the carbon atoms in the alkoxy chain versus the melting points of the six series listed in the Table I and Table II

It is the second time to be found that not only the *para*-fluoro substitution but also the *meta*-fluoro substitution enhances the formation of smectic A phase[14]. The reason of this phenomena must be the disruption of intermolecular crystalline packing by the fluoro substituent. As we have discussed the phenomena may be formed by the existence of microphase seperation when the number of the fluorine atoms increased to some degree[14]. This phenomena can also be explained as follows. The fluorine atom combines the properties of large electronegativity and small size. Then the fluoro-substituent shows much negative charge. With the increasing of the degree of fluoro-substituents in the terminal phenyl ring, the

distance between terminal groups is increased. Then the terminal-terminal attraction is weakened, and smectic phase formation is more likely.

To further study the formation of the liquid crystalline phases in this types of compounds, we have also synthsized five compounds shown in **Table III**. Although these compounds are only different in the direction of ester bond from the analogous compounds shown in **Table I** and **Table II**, the former compounds show more stable mesophases than the latter. For smectic phase formation, lateral attractions are essential, and they must be considerably greater than the terminal attractions. Each of the compounds list in the **Table 3** has conjugation between the alkoxy and carboxy groups; this should increase the polarity of the carbonyl oxygen, thus leading to an increased intermolecular dipole-dipole interaction. Explaning why the compounds in the **Table III** tend to form smectic phases preferently than the correspounding compounds in the **Table I** and **Table II**[16]. From the mesomorphic properties listed in the **Table III**, it is also found that not only the *para*-fluoro substitution but also the *meta*-fluoro substitution enhances the formation of smectic A phase.

TABLE III Phase transition temperatures(°C) of the other five compounds

compounds	*phase transition temperature/°C*
	Cr101.7S_A121.3N142.4I141.4N120.2S_A85.5S_B 81.7Recr
	Cr115.0S_A176.7N194.0I192.6N175.4S_A100.9Recr
	Cr105.7S_A174.1N176.4I175.1N172.2S_A86.9Recr
	Cr92.5S_A139.0I136.9S_A90.7S_C69.6S_{X1}64.0S_{X2} 62.8Recr
	Cr105.3S_A160.6I159.0S_A88.9Recr

Experimental

The structures of the final products and intermidiates were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer, using KBr pellets of solids or films of liquids. ^{1}H NMR spectra, with TMS as the internal standard and $CDCl_3$ as the solvent, were run in Fx-90Q (90 MHz) or Bruker 300 (300 MHz). ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as

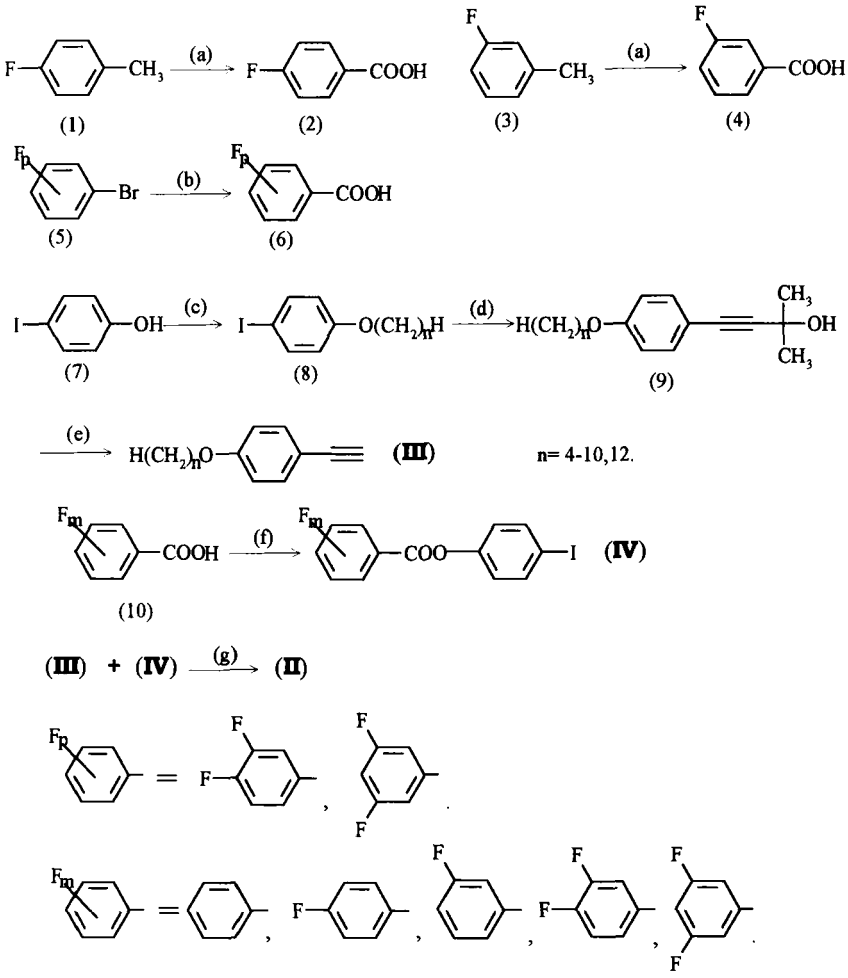
external standard and CDCl3 as the solvent, were recorded on a Varian EM 360L (60 MHz) specrometer (high field positive). MS spectra were measured with a Finnigan-4021 spectroscope. The phase transition temperatures of the target compounds were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). The transition tempratures reported in this paper were the peak values of the transition on DSC traces.

The liquid crystal molecules studied were synthesized following the route as shown in **Scheme 1**.

The oxiadation of 1-fluoro-4-methylbenzene and 1-fluoro-3-methylbenzene by $K_2Cr_2O_7$ in concentrated H_2SO_4/water solution afforded 4-fluorobenzoic acid (2) and 3-fluorobenzoic acid (**4**)[17]. The other two difluorobenzoic acids were obtained from the corresponding bromo derivatives[15]. Then the mild one pot esterification between 4-iodophenol and the benzoic acid in the presence of both dicyclohexylcarbodiimide(DCC) and DMAP catalyst in dried THF gave the compounds (**IV**). Finally, the target LC molecules were obtained easily by the coupling reaction between compounds (**III**)[18] and (**IV**) under the catalyst of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in dried triethylamine according to the literature[19]. As an example, the synthesis of compound **4F*8*** is described below.

4-(4'-n-Octyloxyphenyl)acetylenyl]phenyl 4-fluorobenzoate (4F8)

A typical procedure: under dry nitrogen, to a mixture of compound 4-*n*-octyloxyphenylacetylene (121 mg, 0.525 mmol), 4-iodiophenol 4-fluorobenzoates (150 mg, 0.438 mmol), bis(triphenylphosphine) palladium dichloride (3 mg), copper(I) iodide (5 mg) triphenylphosphine (8 mg), was added 10 ml of anhydrous triethylamine. The reasulting mixture was refluxed while stirring for 2 h. Analysis by TLC revealed a complete reaction. Then the formed precipitate was filtered off and washed with ether and the filtrate washed with water, dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was purified by column chromatogrraphy on silica gel using petroleum ether (bp 60–90 °C)-ethyl acetate (20:1) as eluent to give a pale yellow crystal which was recrystallized from acetone-methol to yield white flaky crystals of compound (**4F*8***) Yield: 183mg (93.8%); Mp 115.3 °C. IR υ_{max}(KBr, cm^{-1}): 2929, 2853, 1729, 1605, 1516, 1251, 1179 cm^{-1}. $\delta_H(CDCl_3)$, 0.88(t, 3H, CH_3), 1.32–1.88(m, 12H, 6XCH_2), 3.96(t, J=6.0Hz, 2H, 2×RCH_2O), 6.78–7.63(m, 10H, ArH), 8.08–8.31(m, 2H, ArH) ppm, ^{19}F NMR δ_F (60MHz, $CDCl_3$, TFA): 26.31(s, F) ppm. MS m/z (rel. int.): 444(M^+, 34.76), 332($C_6H_4FCOOC_6H_4$-≡-$C_6H_4OH^+$, 2.70), 123($C_6H_4FCO^+$, 100.00). Elem. anal. Calcd for $C_{29}H_{29}FO_3$: C, 78.35%; H, 6.58%; F, 4.27%. Found: C, 78.29%; H, 6.55%; F, 4.28%.



SCHEME I (a) $K_2Cr_2O_7$, H_2SO_4; (b) 1) Mg, ether, 2) CO_2, 3) H_3^+O; (c) KOH, C_2H_5OH, H_2O, $Br(CH_2)nH$; (d) $HOC(CH_3)_2$-C≡CH, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF/Et_3N; (e) KOH, $C_6H_5CH_3$, reflux; (f) DCC/DMAP, THF, *p*-I-C_6H_4OH, r.t.; (g) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF/Et_3N

The same procedure was used to prepare the other compounds.

4-(4'-n-Hexyloxyphenyl)acetylenyl]phenyl benzoate (0F6)

IR (KBr) υ_{max}: 2950, 2853, 2214, 1736, 1605, 1508, 1253, 1179, 836 cm^{-1}. ^1H NMR δ_H (300MHz; $CDCl_3$; TMS): 0.93(t, J=6.7, 3H, CH_3), 1.36–1.85(m, 8H, $4XCH_2$), 3.98(t, J=6.6Hz, 2H, RCH_2O), 6.89(d, J=8.8Hz, 2H, ArH), 7.23(d,

J=8.6, 2H, ArH), 7.46–7.68(m, 7H, ArH), 8.22(d, J=7.3Hz, 2H, ArH) ppm. MS m/z (rel. int.): 398(M^+, 9.37), 105($C_6H_4CO^+$, 100.00). Elem. anal. Calcd for $C_{27}H_{26}O_3$: C, 81.38; H, 6.58%. Found: C, 81.71; H, 6.57%.

4-(4'-n-Butyloxyphenyl)acetylenyl]phenyl 3-fluorobenzoate (3F4)

Mp. 123.5°C. IR (KBr) υ_{max}: 2955, 2870(s, C-H), 1730(vs, C=O), 1606(s, C_6H_4), 1514(vs, C_6H_4F), 1251, 1179(s, C-O-C) cm^{-1}. ^1H NMR δ_H (90MHz; $CDCl_3$; TMS): 1.00(t, 3H, CH_3), 1.26–1.86(m, 4H, $2XCH_2$), 3.98(t, J=6.0Hz, 2H, RCH_2O), 6.82–6.93(m, 2H, ArH), 7.16–7.63(m, 8H, ArH), 8.12–8.34(m, 2H, ArH) ppm, ^{19}F NMR δ_F(60MHz, $CDCl_3$, TFA): 34.70(s, F)ppm. MS m/z (rel. int.): 387(M^+-1, 33.56), 123(C_6H_4FCO, 100.00). Elem. anal. Calcd for $C_{25}H_{21}FO_3$: C, 77.30 H, 5.45; F, 4.89%. Found: C, 77.37; H, 5.40; F, 4.74%.

4-(4'-n-Butyloxyphenyl)acetylenyl]phenyl 3,4-difluorobenzoate (34F4)

Mp. 123.4°C. IR (KBr) υ_{max}: 2934, 2874 1729, 1605, 1514, 1467, 1247, 1162, 877, 831, 801cm^{-1}. ^1H NMR δ_H (90MHz; $CDCl_3$; TMS): 1.00(t, 3H, CH_3), 1.26–1.86(m, 4H, $2XCH_2$), 3.99(t. J=6.0Hz, 2H, RCH_2O), 6.82–6.92(m, 2H, ArH), 7.14–7.62(m, H, ArH), 7.92–8.13(m, 2H, ArH) ppm, ^{19}F NMR δ_F(60MHz, $CDCl_3$, TFA): 51.60(m, F), 58.80(m, F)ppm. MS m/z (rel. int.): 406(M^+, 13.04), 265(M^+- $C_6H_3F_2CO$, 1.63), 141 ($C_6H_3F_2CO$, 100.00). Elem. anal. Calcd for $C_{25}H_{20}F_2O_3$: C, 73.88 H, 4.96; F, 9.35%. Found: C, 73.87; H, 4.82; F, 9.00%.

4-(4'-n-Pentyloxyphenyl)acetylenyl]phenyl 3,5-difluorobenzoate (35F5)

Mp. 111.5°C. IR (KBr) 2930, 2857(s, C-H), 2217(s, C≡C), 1741(vs, C=O), 1598(s, C_6H_4), 1514(vs, $C_6H_3F_2$), 1224, 1166(s, C-O-C)cm^{-1}. ^1H NMR δ_H (90MHz; $CDCl_3$; TMS): 0.95(t, 3H, CH_3), 1.27–1.85(m, 6H, $3XCH_2$), 3.96(t, J=6.0Hz, 2H, RCH_2O), 6.83–6.93(m, 2H, ArH), 7.10–7.26(m, 3H, ArH), 7.43–7.78(m, 6H, ArH) ppm, ^{19}F NMR δ_F(60MHz, $CDCl_3$, TFA): 30.66(s, F)ppm. MS m/z (rel. int.): 420, 349, 141. Elem. anal. Calcd for $C_{26}H_{22}F_2O_3$: C, 74.27 H, 5.27; F, 9.04%. Found: C, 74.31; H, 5.41; F, 8.69%.

The other compounds in series **0F*n*, 3F*n*, 4F*n*, 34F*n*** and **35F*n*** had the same type of NMR spectrum. The M.P., IR, MS and E.A. of the other compounds were shown in **Table IV**.

The synthesis of series **345F*n*** has been published elsewhere[15].

TABLE IV The M.P., IR, MS and E.A. of the compounds synthesized in this paper

	M.P. (°C)	IR	MS	E.A.	
				Calcd.	Found
)	117.5	2929, 2856, 1729, 1605, 1516, 1252, 1179	430, 332, 123	C, 78.12; H, 6.32; F, 4.41	C, 78.12; H, C, 78.36; H F, 4.49
	119.3	2917, 2850, 1729, 1605, 1515, 1252, 1179	458, 332, 123	C, 78.58; H, 6.81; F, 4.14	C, 78.37; H, 6.81; F, 3.
	117.7	2917, 2850, 1729, 1605, 1515, 1252, 1179	472, 332, 123	C, 78.79; H, 7.04; F, 4.02	C, 78.77; H. 7.05; F, 3
	103.1	2929, 2855, 1729, 1606, 1508, 1251, 1179	412, 105	C, 81.52; H, 6.84	C, 81.46; H, 6.82
	101.7	2953, 2852, 1736, 1606, 1508, 1252, 1179	427, 105	C, 81.66; H, 7.09	C, 81.62; H, 6.89
	115.4	2917, 2851, 2218, 1739, 1606, 1250, 1174	440, 105	C, 81.78; H, 7.32	C, 81.84; H, 7.19
	105.3	2953, 2850, 1729, 1606, 1508, 1252, 1179	354, 105	C, 81.90; H, 7.54	C, 81.75; H, 7.40
	111.7	2931, 2866, 1729, 1605, 1517, 1253, 1179	402, 332, 123	C, 77.59; H, 5.76; F, 4.72	C, 77.59; H, 5.70; F, 4.
	109.5	2931, 2862, 1730, 1606, 1516, 1253, 1179	416, 332, 123	C, 77.86; H, 6.05; F, 4.56	C, 77.68; H, 6.07; F, 4.
	113.6	2929, 2856, 1729, 1606, 1516, 1252, 1179	430, 332, 123	C, 78.12; H, 6.32; F, 4.41	C, 77.88; H, 6.19; F, 4.
	111.8	2929, 2852, 1729, 1607, 1516, 1252, 1179	444, 332, 123	C, 78.35; H, 6.58; F, 4.27	C, 78.20; H, 6.52; F, 3.
	116.2	2917, 2850, 1729, 1605, 1516, 1253, 1179	458, 123	C, 78.58; H, 6.81; F, 4.14	C, 78.68; H, 6.92; F, 4.
)	114.8	2917, 2850, 1729, 1607, 1517, 1253, 1179	472, 123	C, 78.79; H, 7.04; F, 4.02	C, 78.90; H, 7.17; F, 4.
)	117.0	2916, 2849, 1729, 1607, 1517, 1253, 1179	500, 123	C, 79.17; H, 7.45; F, 3.79	C, 79.54; H, 7.62; F, 3.
3)	115.6	2935, 2870, 1729, 1606, 1566, 1248, 1163	420, 279, 141	C, 74.27; H, 5.27; F, 9.04	C, 74.39; H, 5.17; F, 8.
3)	107.8	2934, 1729, 1607, 1517, 1248, 1163	434, 293, 141	C, 74.64; H, 5.57; F, 8.75	C, 74.57; H, 5.47; F, 8.
3)	93.4	2933, 2857, 1733, 1605, 1567, 1252, 1164	448, 307, 141	C, 74.98; H, 5.84; F, 8.47	C, 75.18; H, 5.73; F, 8.
3)	94.3	2920, 2854, 1733, 1606, 1512, 1253, 1164	462, 321, 141	C, 75.31; H, 6.10; F, 8.21	C, 75.32; H, 6.01; F, 8.

M.P. (°C)	*IR*	*MS*	*E.A.*	
			Calcd.	*Found*
101.2	2920, 2851, 1733, 1606, 1512, 1255, 1164	476, 141	C, 75.61; H, 6.35; F, 7.97	C, 75.73; H, 6.30; F, 7.
96.5	2918, 2851, 1732, 1605, 1512, 1253, 1164	490, 141	C, 75.90; H, 6.57; F, 7.75	C, 75.89; H, 6.52; F, 7.
99.6	2935, 2870, 1729, 1606, 1566, 1248, 1163	518, 141	C, 76.42; H, 7.00; F, 7.33	C, 76.40; H, 6.92; F, 7.
113.2	2954, 2870, 2218, 1741, 1598, 1224, 1176	405, 349, 141	C, 73.88; H, 4.96; F, 9.35	C, 73.95; H, 4.80; F, 9.
104.2	2932, 2218, 1740, 1603, 1513, 1227, 1164	434, 349, 141	C, 74.64; H, 5.57; F, 8.75	C, 74.51; H, 5.53; F, 8.
95.3	2931, 2857, 2217, 1739, 1603, 1250, 1175	448, 350, 141	C, 74.98; H, 5.84; F, 8.47	C, 75.00; H, 5.82; F, 8.
94.6	2922, 2854, 2217, 1739, 1602, 1251, 1175	462, 350, 141	C, 75.31; H, 6.10; F, 8.21	C,; H,; F, 8.12
98.2	2920, 2851, 2217, 1739, 1602, 1252, 1175	476, 350, 141	C, 75.61; H, 6.35; F, 7.97	C, 75.71; H, 6.29; F, 7.
97.3	2920, 2851, 2217, 1739, 1601, 1252, 1175	490, 350, 141	C, 75.90; H, 6.57; F, 7.75	C, 75.92; H, 6.58; F, 7.
100.9	2918, 2850, 2217, 1739, 1598, 1251, 1176	518, 350, 141	C, 76.42; H, 7.00; F, 7.33	C, 76.48; H, 7.02; F, 7.

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