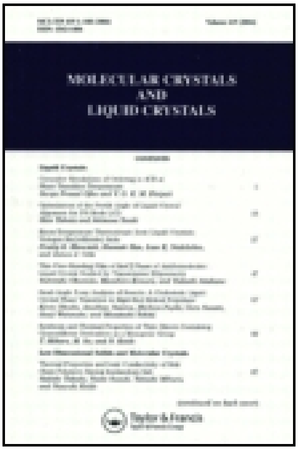

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Preparation and Liquid Crystalline Behaviour of a Series of Semifluorinated Allylic Monomers

Elisabeth Taffin de Givenchy [a] , Frédéric Guittard [a] , Laurent Caillier [a] , Juan Munuera [a] & Serge Geribaldi [a]

[a] Laboratoire de Chimie des Matériaux Organiques et Métalliques (C.M.O.M.), Faculté des Sciences, Université de Nice Sophia-Antipolis, Parc Valrose, Nice Cedex, France

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Preparation and Liquid Crystalline Behaviour of a Series of Semifluorinated Allylic Monomers

Elisabeth Taffin de Givenchy
Frédéric Guittard
Laurent Caillier
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Serge Geribaldi
Laboratoire de Chimie des Matériaux Organiques et Métalliques (C.M.O.M.), Faculté des Sciences, Université de Nice Sophia-Antipolis, Parc Valrose, Nice Cedex, France

A series of smectic liquid-crystalline 4,4′-biphenyl derivatives incorporating a perfluorinated segment and an allylic part have been prepared and their mesomorphic properties investigated. The preparation of these compounds has been done from 2-F-butylethyl iodide, the 2-F-hexylethyl iodide or the 2-F-octylpropanoic acid. The physical properties of these novel fluorinated materials are commented and illustrated in comparison with four homologous allylic series previously described. The choice of the molecular design of these monomers allows us to obtain dimorphism and high mesomorphic range determined from differential thermal analysis and the light microscopy.

Keywords: dimorphism; fluorinated; molecular design; smectic

1. INTRODUCTION

The introduction of fluorinated parts, which are not compatible, in a polymer, can produce a segregation into distinct microdomains that is favourable to the appearance of a well organized phase such as mainly smectic liquid crystal phases [1–4]. Furthermore, one of the most important parameter for the use as L.C. devices is the wide temperature range of mesomorphism, with enantiotropy and

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Address correspondence to Frédéric Guittard, Laboratoire de Chimie des Matériaux Organiques et Métalliques (C.M.O.M.), Faculté des Sciences, Université de Nice Sophia-Antipolis, Parc Valrose, 06108 Nice Cedex 2, France. E-mail: guittard@unice.fr

reproducibility, during the phase transition phenomena, but also the chemical and thermal stability. Perfluorinated tails are also chemically stable, possess very low viscosity and can increase the stability of the resulting mesophases. It is worth noting that the nature of the spacer, bounding the perfluorinated tails to the rigid core can govern and furthermore “exacerbate” the pro-smectogenic effect of *F*-alkylated chains [5–11]. This kind of arrangement can be used for surface treatment to reach for example low surface energy materials [12–14]. So, the preparation of fluorinated liquid crystal polymers (LCPs) is of a great-interest class of materials because they combine the anisotropy of liquid crystalline mesophases, the intrinsic remarkable properties of the polymer backbone (mechanical properties and glassy state as an example) and the peculiar properties of fluorinated part. In order to prepare this kind of structure, it is important to well design the monomers which exhibit LC properties. In this study we present omega unsaturated monomers as raw materials for homopolymerization or for grafting polyhydrogenosiloxane backbone. In order to find out the best molecular arrangement parameters inside the monomer, we have taken into account previous comparison of fluorinated vinylic monomers described in the literature [15,16]. In fact, the systematic variation of molecular structure combined with determination of key physico-chemical properties is a cornerstone for establishing structure property relationship in mesomorphic field.

The aim of this work is to design and describe the synthesis of new biphenyl compounds (see Fig. 1) precursors of highly fluorinated polymers. These compounds will present a biphenyl mesogenic core, linked to a various-length fluorinated tail through an ester linker. The L.C. phases of these compounds were characterized by a combination of

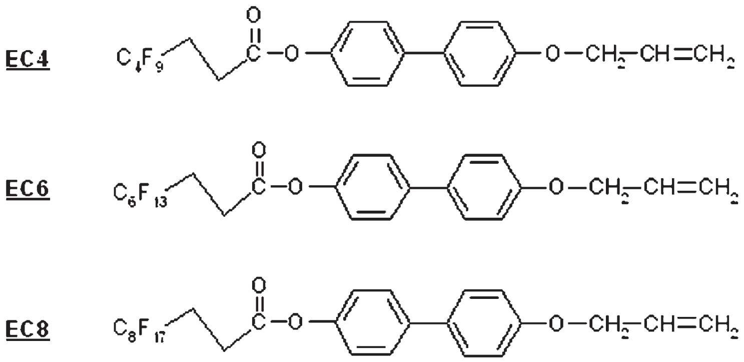


FIGURE 1 Investigated allylic monomers.

differential scanning calorimetry (D.S.C.) and optical polarized microscopy (P.O.M.) methods.

2. EXPERIMENTAL PART

2.1. Materials

All the chemicals were purchased from Aldrich and Acros Chemical Co. and were used without any further purification. Unless specified as dry, the solvents were unpurified reagent grade. The procedure for the preparation of 2-*F*-alkylpropanoic acids are described elsewhere [17]. Perfluorinated raw materials were given by Atofina.

2.2. Methods

Confirmation of the structures was obtained by Nuclear Magnetic Resonance (N.M.R.) and Mass Spectrometry (M.S.). N.M.R. spectroscopy was carried out using a Bruker AC 200 MHz spectrometer. Spectra were recorded using deuterated solvent with TMS as internal reference for ^{1}H N.M.R. and $CFCl_3$ for ^{19}F N.M.R.. M.S. was carried out using a Thermo Finnigan spectrometer and an EI mode at 70 eV. The purity of the monomers was determined by thin layer chromatography. The initial phase assignments and corresponding transition temperatures were determined using an Olympus BX 60 optical microscope equipped with crossed polarizers. The samples were thermostated by means of a Linkam Scientific Instruments LTS 350 heating unit and TMS 94 temperature control by the same manufacturer. Temperatures and enthalpies of transition were investigated by D.S.C. using a Perkin Elmer DSC7 instrument. Samples of 5–10 mg were placed in aluminium capsules and heated in a static nitrogen atmosphere. The heating and cooling curves were obtained at the rate of 10°C min^{-1}. The phase transition temperatures of the monomers were extrapolated as the onset temperatures.

2.3. Synthesis

The synthesis of 4-[4-(Allyloxyphenyl)]phenyl-3-(perfluoro-n-alkyl)-propanoate (**EC4**, **EC6** and **EC8**) was carried out in two steps as showed in Figure 2. Yields for all compounds are reported in Table 1.

4-(4-Allyloxyphenyl)phenol (2)

In a 100 mL round bottom flask equipped with a condenser, 20 mmol of sodium hydroxide was diluted in 9 mL of water. Then 10 mmol of

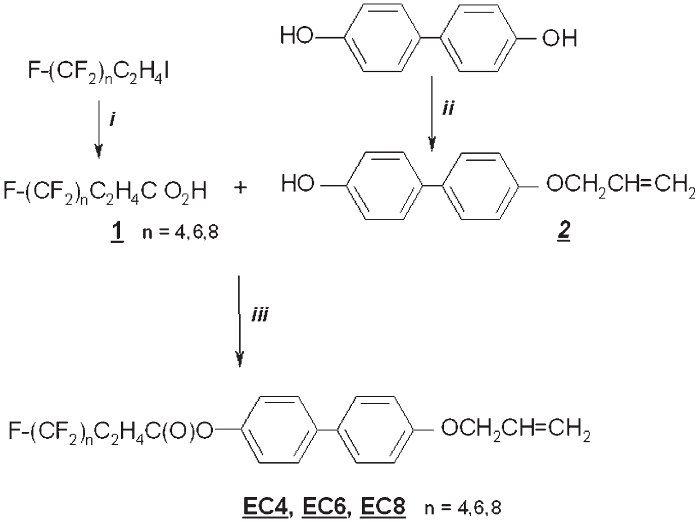


FIGURE 2 Synthetic pathway to monomers. Reagents and conditions: (i) Mg, Et_2O, CO_2, (ii) Br $CH_2CH{=}CH_2$, NaOH, H_2O/EtOH reflux then HCl, (iii) DCC, DMAP, 12 h, rt.

4-(4-hydroxyphenyl)phenol was added slowly and allowed to react at room temperature. After 20 minutes, 10 mol of allylbromide was added dropwise and the solution was stirred under reflux for 8 hours. After cooling down, the solution was filtrated to remove the remaining 4,4′-biphenolate. The resulting white solid was poured into a 10% HCl aqueous solution, stirred for 20 minutes and the solution was filtrated again. The 4-(4-Allyloxyphenyl)phenol so isolated (The purification of the 4-(4-Allyloxyphenyl)phenol intermediate is based from the difference of solubility between the mono and the disubstituted compounds) was recrystallized from ethanol. Yield 45%.

TABLE 1 Yields for Allylic Monomers

Cpds	R_F value	Yield %	Overall %
1a	4	54	–
1b	6	40	–
2	–	40	–
EC4	4	75	30
EC6	6	81	33
EC8	8	90	36

^{1}H NMR ($CDCl_3$/TMS, δ ppm, J Hz), 4,62 (2H, $O\underline{CH}_2CHCH_2$, d, J = 5,3), 5,35 (1H, $O\underline{CH}_2CHCH_2$, dd, J = 10,5 J = 1,5), 5,48 (1H, $OCH_2CH\underline{CH}_2$, dd, J = 17,3 J = 1,5), 6,08 (1H, $OCH_2\underline{CH}CH_2$, m, J = 10,5 J = 17,3 J = 5,3), 7,00 to 7,5 ($8H_{ar}$).

4-[4-(Allyloxyphenyl)]phenyl-3-(perfluoro-n-alkyl)propanoate (EC4, EC6 and EC8)

Esterification of 2 with 2-*F*-alkylpropanoic acids previously prepared (2-*F*-butylpropanoic acid and 2-*F*-hexylpropanoic acid) or commercially available (2-*F*-octylpropanoic acid) was performed using dicyclohexylcarbodiimide (DCC) catalyzed by 4-(*N,N*-dimethylamino)-pyridine. In a typical experiment, a suspension of 11 mmol of 2-*F*-alkylpropanoic acids and 10 mmol of 4-(4-allyloxyphenyl)phenol (**2**) in 30 mL dry dichloromethane was prepared. Then 11 mmol of dicyclohexylcarbodiimide (DCC) and 1,1 mmol of 4-(N,N-dimethylamino)pyridine were added and the solution was stirred at room temperature for 3 hours. The solution was filtrated to eliminate the dicyclohexylurea and the solvent was removed under vacuum. The 4-[4-(allyloxyphenyl)]phenyl-3-(perfluoro-n-alkyl)propanoate (**EC4** ~ **EC8**) were purified by column chromatography over silicagel using dichloromethane as the eluant.

For **EC8**: ^{1}H NMR ($CDCl_3$/TMS, δ ppm, J Hz), 2,60 (2H, $CF_2\underline{CH}_2$, tt, J = 8,1 J = 18,4), 2,95 (2H, $CF_2CH_2\underline{CH}2$, t, J = 8,1), 4,63 (2H, $\underline{OCH}_2CHCH_2$, d, J = 5,3), 5,32 (1H, $OCH_2CH\underline{CH}_2$, dd, J = 10,5 J = 1,5), 5,47 (1H, $OCH_2CH\underline{CH}_2$, dd, J = 17,3 J = 1,5), 6,08 (1H, $OCH_2\underline{CH}CH_2$, m, J = 10,5 J = 17,3, J = 5,3), 7,00 ($2H_{ar}$, d, J = 8,8), 7,15 ($2H_{ar}$, d, J = 8,7), 7,51 ($2H_{ar}$, d, J = 8,8), 7,58 ($2H_{ar}$, d, J = 8,7) ^{19}F N.M.R. ($CDCl_3/CFCl_3$, δ ppm), -82 (CF_3, m), -115.5 [$(CF_2)_\alpha$, m], -123 [$(CF_2)_{\beta,\gamma,\delta}$, m], -124 [$(CF_2)_\varepsilon$, m], -124.5 [$(CF_2)_\zeta$, m], -127 [$(CF_2)_\eta$, m] MS (70 eV) m/z (%), 41 (100%), 69 (41,3%), 77 (35,1%), 185 (22,1%), 660 (11,6%), 700 (29,5%).

3. RESULTS AND DISCUSSION

The choice of the molecular parameters of this series of monomers was determined from previous works described in the literature [15,16]. These compounds are listed in Figure 3. The corresponding mesomorphic properties are reported in Figure 4. Each monomers named Ax, Bx, Cx and Dx differ to each other by one molecular parameter. The correlation between their mesomorphic properties allows us to consider the series described in the present work and coded ECx. The value "x", described in the Figure 4, equal to 4, 6 or 8, corresponds to the fluorinated methylene units in the *F*-alkyl tail.

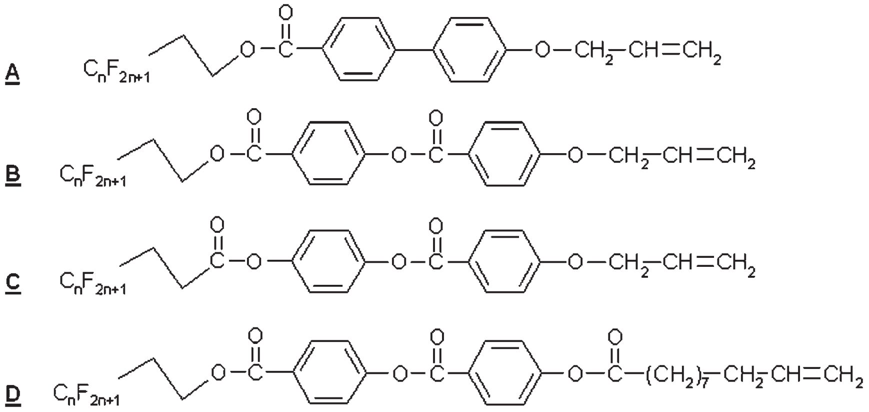


FIGURE 3 Allylic monomers used for comparison [15,16].

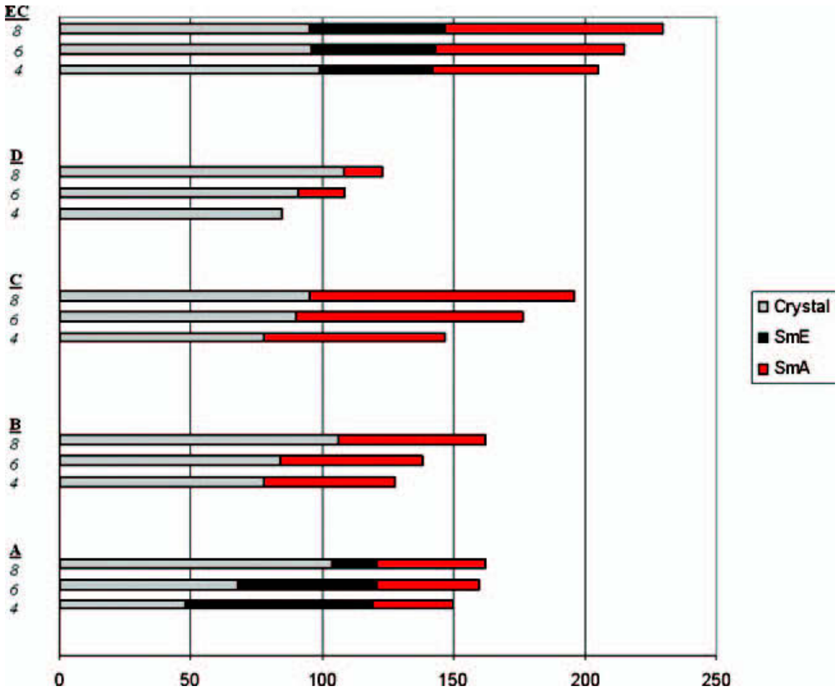
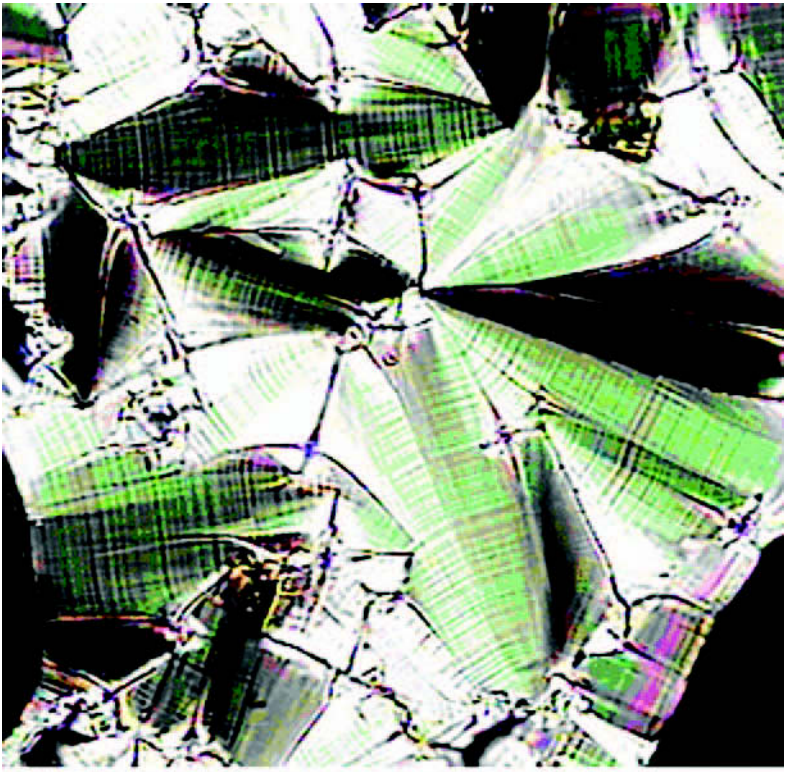


FIGURE 4 Comparison of the LC ranges of the mesophases for compounds **Ax**, **Bx**, **Cx**, **Dx** et **EC** (x = 4, 6, 8).

TABLE 2 Transition Temperatures for Monomers Observed on Heating from D.S.C. (Scanning Rate 10°C min^{-1})

	Transition Temperature (°C)						
Cpds	C		S_E		S_A		I
EC4	●	99	●	142	●	205	●
EC6	●	96	●	143	●	215	●
EC8	●	95	●	147	●	230	●

C, crystal, S_A, S_E: Smectic A and E respectively, I, isotropic.



(a)

FIGURE 5 Optical polarizing micrograph displayed by **EC8** on cooling from isotropic melt: (a) temperature 126°C, ×33 same position of the sample as in Figure 5b, (b) temperature 198°C, ×33.

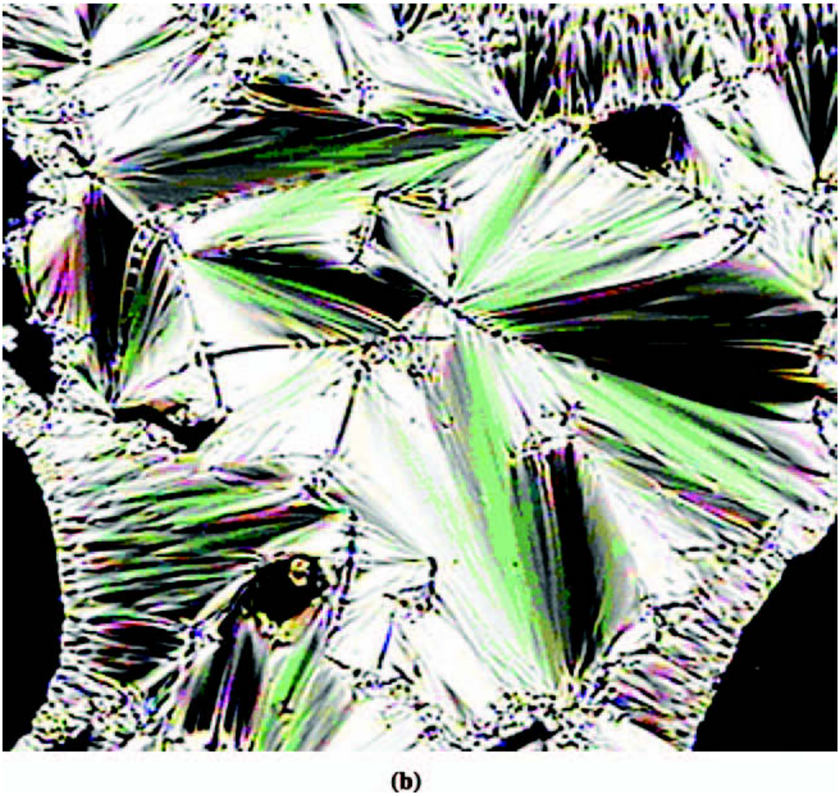


FIGURE 5 Continued.

Hence, ECx allylic compounds were studied by Polarizing Optical Microscopy (P.O.M.) and Differential Scanning Calorimetry (D.S.C.) on heating and cooling with a scanning rate of 10°C/min. Our aim was to study the mesomorphic properties of our 4-[4-(allyoxyphenyl)]-phenyl-3-(perfluoro-n-alkyl)propanoate and to compare there L.C. domains with previously synthetized allylic compounds (Fig. 3). The Polarized Optical Microscopy (POM) studies showed that **EC4** to **EC8** exhibit a smectogenic thermotropic mesomorphism. The phase transition temperatures are given in Table 2.

We can notice a wide mesomorphic smectogenic range. From miscibility studies with internal references previously published [10], the assignment of mesophases is of type Smectic E and A (see Figs. 5a and 5b). Transition temperature seems to be as a function of the number of fluoromethylene units. Increasing the semi fluorinated chain

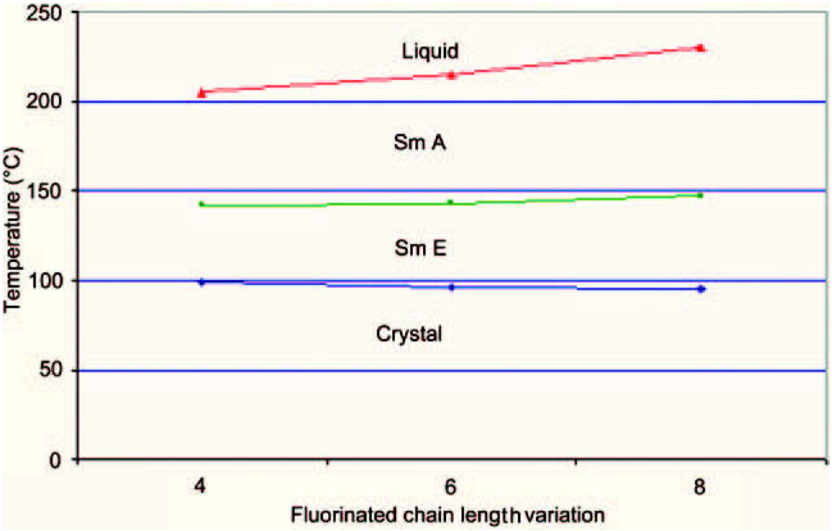


FIGURE 6 Influence the fluorinated chains lengths on the mesomorphic properties.

length, does not cause a significant variation of the melting temperature but leads to the rise of the clearing point. The comparison of the LC range against fluorinated tails length is more complex. Indeed, if the global L.C. range increases from 106°C for **EC4** to 135°C for **EC8**, the fluorinated chain length does not show any influence on the first mesophase (from 95° to 147° for all compounds) while the smectic A phase increases with the number of perfluoromethylene units (see Fig. 6). The increasing of fluorinated tail favourably affects the clearing point.

We can compare our structures to those previously synthetized as allylic monomers analogues and presented in Figures 3 and 4. Two mesophases are observed for biphenyl derivatives compounds (**A** and **EC**). The mesogenic core is an important element for the apparition of several large and more organize mesophases. In contrast to **A**, the liquid crystal range of **EC** monomers increases with the fluorinated chain length. The widest mesomorphic range was obtained from EC series.

CONCLUSION

The synthesis of a series of allylic monomers differing only by the length of the perfluoroalkyl tail has been realized. All members of this series exhibit liquid crystalline phase of type smectic A and E. The molecular conception of these monomers from homologous compounds previously described in the literature allows us to reach dimorphism and wide range smectic mesomorphism. This kind of structure is of a great interest for precursor of side chain liquid crystalline polymers.

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