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Synthesis and liquid crystalline properties of novel compounds containing a 3-fluoro-4-cyanophenoxy group

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A series of novel compounds containing a 3-fluoro-4-cyanophenoxy group were synthesized and fully characterized by IR and ^{1}H NMR, and their mesomorphic properties were studied. Seven compounds exhibited enantiotropic nematic phases and three compounds exhibited monotropic nematic phases, as confirmed by differential scanning calorimetry and polarizing optical microscopy. Selected properties of the liquid crystalline compounds synthesized were calculated by *ab initio* methods at a HF/6-31G level. The bond lengths, bond angles and dihedral angles of the fragments with the same structure change little between the compounds. All the compounds with a terminal alkoxy chain approached a planar structure.

1. Introduction

Liquid crystals are a class of substances whose properties are intermediate between those of liquids and crystals under specific conditions. Liquid crystal compounds have been shown to yield easily controllable organized monolayers [1, 2] and multilayers [3–5] at an air–water interface. Their organization at the air–water interface depends on interactions between liquid crystal (LC) molecules, and on LC molecule/aqueous subphase interactions as well as on the state of compression of the film. As display materials, liquid crystals possess many distinctive advantages [6–8].

In recent years much attention and effort have been devoted to the development of new liquid crystalline compounds which possess low melting points, high clearing points and suitable mesophase ranges. The work on cinnamic acid esters by Jones and Ratto [9] showed that these are low melting-point compounds with wide nematic ranges and rather high nematic–isotropic transition temperatures. The research on cinnamates as photo-alignment materials by Zhang *et al.* [10] has shown that these compounds can withstand high temperature. These properties make cinnamic acid ester an important fragment in liquid crystals with significant application potential in liquid crystal displays.

Recently, fluoro-substituted liquid crystals have become of interest [11–15] because they generally exhibit excellent properties compared with the corresponding unsubstitued compounds, such as lower viscosity, high voltage mean retention and high specific resistance. It is known that the nematic–isotropic transition temperatures of compounds containing a fluorine atom at the *ortho*- or *meta*-position with respect to the terminal cyano group on a phenyl ring are only slightly lower than for the corresponding esters with a terminal fluorine atom [16, 17]. However, the viscosity and driving voltage required for the new esters are remarkably higher than those for the analogous non-fluoro-substituted phenyl esters.

The effect of lateral substituents on the liquid crystal transition temperatures of a wide range of compounds has been studied systematically [18–20]. The vast majority of the liquid crystals studied were acids or bore terminal alkyl or alkoxy chains. A number of compounds, based on 2-fluoro-4-hydroxybenzonitrile, have been used widely in LCDs worldwide, and exhibit excellent properties [21–25]. In contrast, only a small number of compounds bearing a terminal CN function and a lateral substituent have been reported [26–28]. To study the effect of lateral substitution on liquid crystals incorporating F and CN groups in a terminal position, we synthesized a series of derivatives of 2-fluoro-4-hydroxybenzonitrile. The F atom was chosen as the lateral substituent, because F-substituted liquid crystals generally exhibit nematic–isotropic transition temperatures only a little below those of the corresponding compounds with a H atom in place of the F atom [16].

2. General techniques

Melting points were measured on a WRR melting point apparatus, with the thermometer uncorrected. Infrared

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(IR) spectra were recorded on a Nicolet 510P FTIR spectrophotometer using KBr pellets. ^{1}H NMR spectra were recorded on a Rigaku JNM-ECP 600 spectrometer using DMSO-d$_6$ as solvent, using TMS as internal standard. Phase transition temperatures were measured using a Netzch DSC-204 differential scanning calorimeter with a heating and cooling rates of 5°C min^{-1}. The temperatures at the maximum in DSC enthalpic peaks were taken as the phase transition temperatures. An Olympus BX-51 polarizing microscope equipped with a heating stage was used to observe various mesophases, again with heating and cooling rates of 5°C min^{-1}. The three-dimensional structures of the compounds were constructed using the Chem3D package, and the MM2 force field was applied to search for the lower energy conformations for each molecule, The *ab initio* method was performed to optimize the low energy conformation of the compounds at HF/6-31G level. For all optimized configurations, there was no imaginary frequency in the vibrational analysis.

All reagents were obtained commercially, and used without further purification. Tetrahydrofuran (THF) and pyridine (Py) were dried immediately before use. The series of novel compounds containing a 2-fluoro-4-hydroxybenzonitrile side group were synthesized as shown in scheme 1.

3. Results and discussion

3.1. *Liquid crystalline behaviour*

In this study, 15 new cinnamic acid esters were synthesized, 10 of which exhibited liquid crystalline properties. The phase transition temperatures recorded by DSC are summarized in table 1. On heating a pristine sample of compounds **2a–c** with electron-withdrawing groups (–F, –Cl or –NO$_2$) on the 4-position of the benzene ring, we observed no liquid crystalline textures by transmitted polarized optical microscopy. This was because the core of the synthesized compounds had two strong electron-withdrawing groups (–F and –CN) at one end, while the other end was also occupied by electron-withdrawing groups. When the alkoxy group on the benzene ring of the cinnamic acid ester is small, such as in the case of methoxy or ethoxy, the compound still did not exhibit liquid crystalline properties, because the affinity between the two ends of the molecule is relatively large, and unfavorable to the formation of a liquid crystalline phase. Only when the electron-donating alkoxy group is large enough to suitably reduce the affinity, do these compounds exhibit mesophases. Thus it was observed that compounds **2d** and **2e** were not liquid crystals.

Typical DSC traces of the liquid crystalline compounds are shown in figure 1. On heating a pristine sample, the material started to melt. As the temperature was raised further, the material appeared to be in its mesomorphic state. On cooling, the clearing point occurred at a lower temperature, indicating that the material had undergone slight supercooling. The melting points and the clearing points on heating those compounds with an *n*-alkoxy group substitutent are plotted in figure 2, and their mesophase ranges summarized in figure 3.

Compared with the series of substituted benzoic acid esters of 2-fluoro-4-hydroxybezonitrile reported elsewhere [16, 28], the melting points of each of the esters reported here are all much higher than their counterparts, presumably because the attractions between aromatic cores in the cinnamic acid esters are much higher than those between benzoic ester cores. The benzoic acid esters with methoxy- to *n*-heptoxy-subsutituents were all monotropic liquid crystals, while the *n*-propoxy- to octoxy-substituted cinnamic acid esters are all enantiotropic liquid crystals exhibiting nematic phases, showing that there are relatively high axial interactions between these molecules. On the other hand, compared with the series of substituted biphenylcarboxylic acid esters, the melting points and the clearing points of the esters reported here are slightly lower than their counterparts, because the interactions between cinnamic ester cores are lower than those between biphenylcarboxylic acid ester cores.

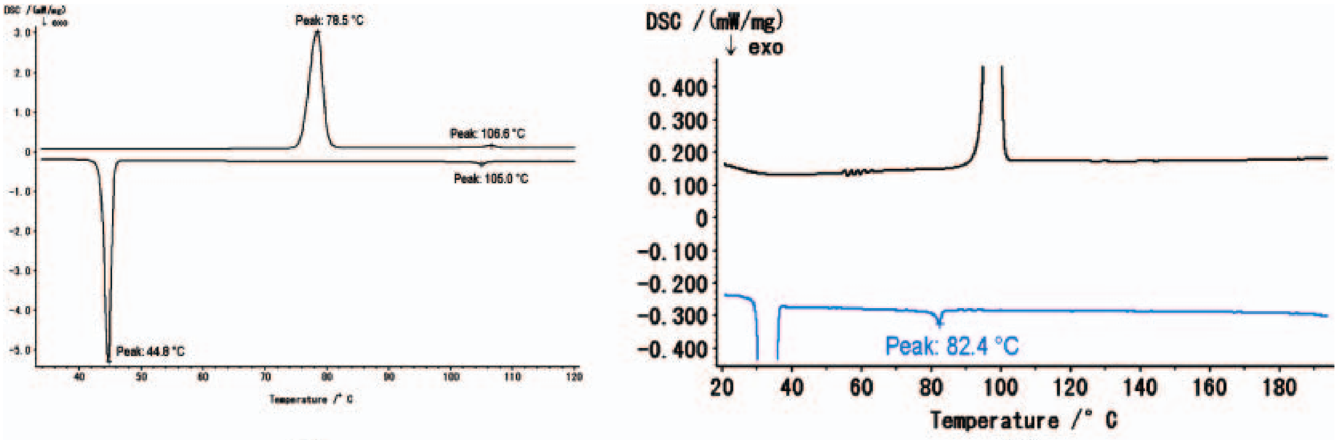
1 a-o **2 a-o**

a, R = F; **b**, R = Cl; **c**, R = NO$_2$; **d**, R = OMe; **e**, R = OEt; **f**, R = OCH$_2$CH$_2$CH$_3$; **g**, R = O(CH$_2$)$_3$CH$_3$; **h**, R = O(CH$_2$)$_4$CH$_3$; **i**, R = O(CH$_2$)$_5$CH$_3$; **j**, R = O(CH$_2$)$_6$CH$_3$; **k**, R = O(CH$_2$)$_7$CH$_3$; **l**, R = O(CH$_2$)$_9$CH$_3$; **m**, R = OCH$_2$CH(CH$_3$)$_2$; **n**, R = O(CH$_2$)$_2$CH(CH$_3$)$_2$; **o**, R = OCH$_2$C$_6$H$_5$.

Scheme 1. Synthesis of substituted cinnamic acid esters of 2-fluoro-4-hydroxybenzonitrile

Table 1. Melting and clearing temperatures, phase ranges and liquid crystalline phase type. T_M=melting point, T_{1C}=clearing point on heating, T_{2C}=clearing point on cooling, T_{Cr}=recrystallizing point, ΔT=mesophase range during heating. Temperatures in brackets indicate monotropic transitions.

	Phase transition					
	Heating		Cooling			
Compound	T_M/°C	T_{1C}/°C	T_{2C}/°C	T_{Cr}/°C	ΔT/°C	Phase type
2 a	137	—	—	107	—	—
2 b	149	—	—	90	—	—
2 c	190	—	—	161	—	—
2 d	165	—	—	148	—	—
2 e	125	—	—	118	—	—
2 f	102	113	112	88	9	Nematic
2 g	89	113	113	47	24	Nematic
2 h	79	106	105	48	27	Nematic
2 i	78	107	105	45	29	Nematic
2 j	69	104	103	48	35	Nematic
2 k	93	105	104	85	12	Nematic
2 l	85	108	106	67	23	Nematic
2 m	83	—	(71)	52	(19)	Nematic
2 n	99	—	(82)	32	(50)	Nematic
2 o	149	—	(132)	89	(43)	Nematic



(*a*) (*b*)

Figure 1. Typical DSC traces of the liquid crystalline compounds (*a*) **2i**, showing the typical DSC trace of an enantiotropic liquid crystal, (*b*) **2m**, showing the typical DSC trace of a monotropic liquid crystal

The two esters with branched terminal alkoxy chains, **2m** and **2n**, were monotropic liquid crystalline compounds, unlike the other compounds in this series, which were enantiotropic LCs. Furthermore, their melting points and clearing points are lower than those of their isomers with linear terminal alkoxy chains, compounds **2g** and **2h**. This is because the branching of the terminal chain increased the breadth of the molecule, and because the flexibility of the terminal chain inhibited the approach of neighbouring molecules, thus lowering their interactions and, leading to the lowering of the melting and clearing points.

The clearing points of the enantiotropic liquid crystals, i.e. the esters with linear terminal alkoxy chains, did not vary significantly, revealing that the clearing point, was mainly determined by the interactions between the cores of the molecules, i.e. the cinnamic acid ester of 3-fluoro-4-cyanophenyl. This differs from the behaviour of other typical series of liquid crystalline compounds, in which the clearing points change much more when the terminal alkoxy chains increase in length, again implying that the interactions between the cinnamic acid ester cores are relatively stronger than those between molecular cores

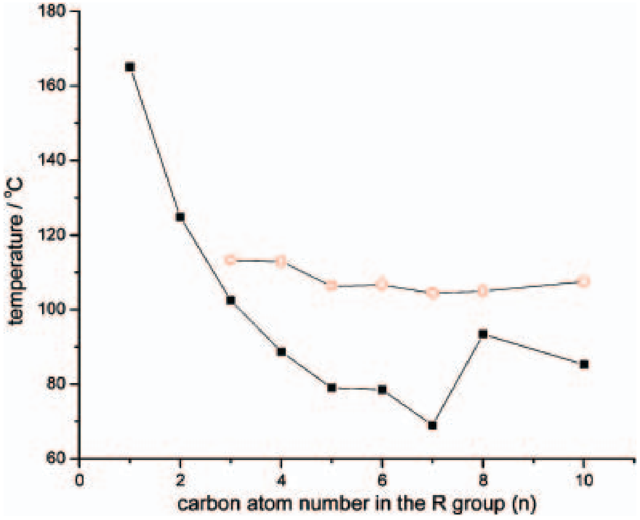


Figure 2. Relationship between the number of carbon atoms in the alkoxy chain and the transition temperatures of the target compounds: T_M (■), T_{1c} (○).

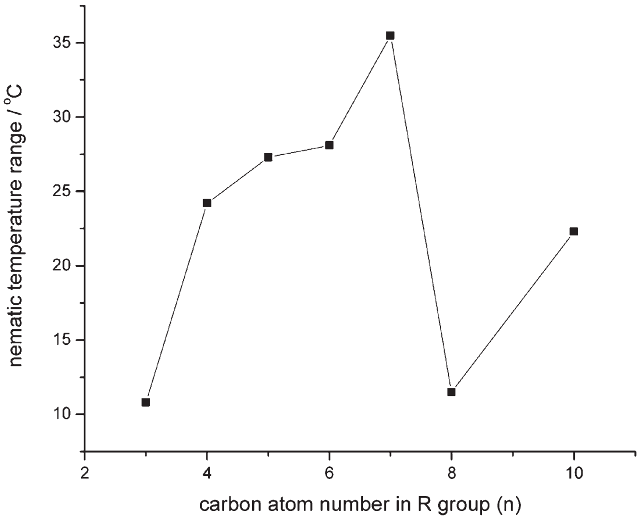


Figure 3. Relationship between the number of carbon atoms in the alkoxy chain and the nematic range of the target compounds.

which are not highly polarizable. As to the relationship between the melting points and the number of carbon atoms (represented by *n*) in the alkoxy group, it was observed that the melting point initially decreases as *n* increases (when $n<6$) and then increases in an alternating fashion (when $n>6$). This phenomenon can be explained thus: when *n* is relatively small, the melting points depend on the interactions between molecules of the cinnamic acid ester of 3-fluoro-4-cyanophenyl, which are relatively strong; when the alkoxy group is larger, this attraction is diluted, and so the melting points become lower. When the alkoxy group is sufficently large ($n>6$), however the long carbon chains begin to dominate the interactions between the molecules, and hence the melting points increase in an alternating fashion as seen, for example, in a series of straight chain alkanes.

3.2. *The textures of the liquid crystalline compounds*

The liquid crystalline textures were observed by polarizing optical microscopy. A small sample was ground and placed on the heating stage of the microscope and then heated at a rate of 5°C min^{-1}. It was observed that all 10 liquid crystalline compounds exhibit a schlieren texture in their mesophase ranges, indicating them all to be nematic liquid crystals. Typical textures of these liquid crystalline compounds are shown in figure 4.

In the case of compound **2i**, the sample exhibited needle-like crystals under the microscope at 20°C. It was then heated on the heating stage at a rate of 5°C min^{-1}. The sample melted at 78°C, the crystals disappeared rapidly and turned into a schlieren texture, figure 4 (*a*). The schlieren texture disappeared to give a totally black field of view at 107°C. The sample was further heated to 120°C, held for 5 min, and then cooled at a rate of 5°C min^{-1}. The schlieren texture reappeared at 105°C, and the sample recrystallized at 45°C. The phase behaviour of compounds **2 f–l** showed that they were all enantiotropic nematic liquid crystals.

When compound **2n** was heated at a rate of 5°C min^{-1}, the needle-like crystals melted at 99°C, and disappeared giving a totally black field of view. The sample was heated to 120°C and then cooled at a rate of 5°C min^{-1}; a schlieren texture, figure 4 (*b*) appeared at 83°C and the sample recrystallized at 34°C. This phase behaviour showed that **2n** was a monotropic nematic liquid crystalline compound. Compounds **2m–o** were monotropic nematic liquid crystals.

3.3. *Theoretical calculations on the liquid crystalline compounds*

Some properties of the liquid crystalline compounds synthesized were calculated using theoretical methods. The three-dimensional structures of the compounds were constructed using the Chem3D package, and the MM2 force field was applied to search for the lower energy conformations for each molecule, The *ab initio* method was performed to optimize the low energy conformation of the compounds at the HF/6-31G level. For all optimized configurations, there was no imaginary frequency in the vibrational analysis. All of the quantum chemistry calculation were performed using the Gaussian98 package on a Pentium IV PC.

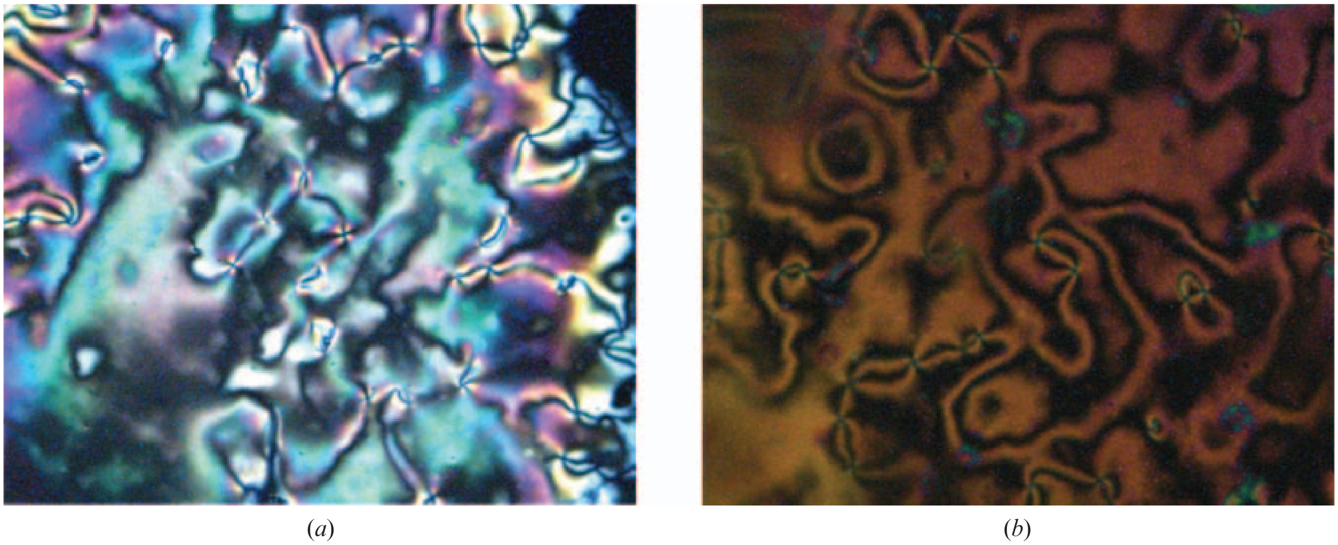

(*a*) (*b*)

Figure 4. Typical polarizing optical micrographs of the liquid crystalline compounds (*a*) **2i** on heating, nematic schlieren texture, 100.0°C; (*b*) **2n** on cooling, schlieren texture, 75.0°C.

The main geometrical parameters (bond length, bond angle, dihedral angle), the ratio L/W of length (L) and width (W), net charges of the main atoms, the total energy E, energy level of frontal molecule orbital (E_{HOMO}, E_{LUMO} and $\Delta E=E_{\mathrm{LUMO}}-E_{\mathrm{HOMO}}$), dipole moment μ and stable configuration for compounds **2f–o** were calculated.

The carbon atom number of the alkoxy chain attached to the benzene ring had only a small effect on the geometrical parameters of the compounds based on our results. The bond lengths, bond angles and dihedral angles of the fragments having the same structure showed little change. All the compounds with a terminal alkoxy chain approached a planar structure.

The ratio of length to width (L/W) of the molecule is an important parameter that affects liquid crystalline properties of compounds. The L/W of the compounds varied from 3.59 to 5.84. The length was calculated between the nitrogen atom in the cyano group attached to the benzene ring and the hydrogen atom attached to the carbon atom in the alkoxy group; the width was from the oxygen atom of the carbonyl group to the hydrogen atom of the corresponding benzene ring. The width of the nine compounds was almost identical, while the length of the title compounds varied according to the different length of substitutant group R. The larger the L/W of the molecule, the greater the viscosity of the compound, while the dielectric anisotropy of the molecule decreased. Among the title compounds, the molecule with the largest L/W was compound **2k**. The molecular L/W values were all sufficiently large to make the formation a liquid crystalline possible.

The net charge of the oxygen atom in the alkoxy chain was negative, and that of the C atom in the benzene ring connected to the alkoxy group positive when the substituent group R was an alkoxy chain. The net charges of the C atom increased slightly from 0.426281 to 0.426678 when the C number of the substituting group R was increased, and the negative change increased also lightly. For the isomeric compounds **2g** and **2m**, **2h** and **2n**, the net charges of the C atom in the benzene ring connected to the isoalkoxy group increases from 0.426305 to 0.428777, and from 0.426591 to 0.427048, respectively. The net charges of the fluorine and nitrogen atoms were negative. Comparing the nine compounds, it can be seen that the electronegativity of F and N varied slightly. Due to the apposing charges that were present at the two ends of the molecules, there were sufficient axial interations between the molecules for the substance to exhibit a nematic phase.

The stable energies of compounds **2f–k** decreased when the number of carbon atoms in the alkoxy group increased, which illustrated the increasing stability of the corresponding molecules. For compound **2o**, the total energy was the lowest of all the 10 compounds ($E_{15}=-1487.7$ A.U.) and the stability was the highest, i.e. the total stability of the molecule was greatest when the substituent group R was benzyl phenylate. In addition, for isomeric compounds **2g** and **2m**, **2h** and **2n**, the stable energies were much the same.

The dipole moment was an important parameter affecting the melting point and dielectric anisotropy of the liquid crystal compounds. The molecular symmetry was a little changed when the C number of the alkoxy chain was modified, and the dipole moment was also little affected.

The electron transition energy, $\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$, affects on the ultraviolet/visible spectrum of a molecule. The smaller the value of ΔE, the stronger the UV activity of the molecule. The ΔE of compound **2o** was the minimum and the activity was very strong. In addition, the first ionization energy, affects the molecular properties. The higher the E_{HOMO}, the smaller the ionization energy of the molecule, and the electron is more easily lost. The E_{HOMO} of compounds **2f–k** in creased steadily, and was maximum for **2o**, which was consistent with the activity.

4. Synthesis of the substituted cinnamic acid esters of 2-fluoro-4-cyanobenzonitrile

A mixture of 3-fluoro-4-cyanophend (0.01 mol) and the required cinnamic acid **1** (0.01 mol), (1,3-dicyclohexylcarbodiimide (2.06 g), dried THF (20 ml) and 4-dimethylaminopyridine (0.04 g) was stirred at room temperature for 3 h. The precipitate was filtered off and the filtrate poured into crushed ice (100 g). After a white solid appeared, the mixture was filtered and washed with water, then dried to give **2** as a colourless solid. The crude product was purified by column chromatography (silica gel, petroleum ether/EtOAc, 1/8) to give a solid with constant melting point. The data for each compound is provided, only representative examples are given for the series of homologues **2d–l**.

2a: white powder, yield 25%, m.p. 137.0°C. IR: 2241 (C≡N); 1743 (C=O); 1601, 1511, 1496 (carbon framework of phenyl rings); 1269, 1131 (C–O–C). ^{1}H NMR: 6.90 (proton 1, d, 1H), 7.94 (proton 2,4, m, 3H), 7.32–7.37 (proton 3,5, m, 3H), 7.64 (d, proton 6, 1H), 8.06 (proton 7, d, 1H).

2b: white powder, yield 46%, m.p. 149.1°C. IR: 2229 (C≡N); 1737 (C=O); 1615, 1586, 1492 (carbon framework of phenyl rings); 1258, 1119 (C–O–C). ^{1}H NMR: 6.95 (proton 1, d, 1H), 7.54 (proton 2, m, 2H), 7.88 (proton 3, m, 2H), 7.37 (proton 4, m, 1H), 7.64 (d, proton 5, 1H), 7.93 (d, proton 6, 1H), 8.06 (proton 7, d, 1H).

2c: yellowish powder, yield 30%, m.p. 189.8°C. IR: 2237 (C≡N); 1730 (C=O); 1606, 1582, 1500 (framework of phenyl rings); 1270, 1157 (C–O–C). ^{1}H NMR: 7.15 (proton 1, d, 1H), 8.30 (proton 2, m, 2H), 8.13 (proton 3, m, 2H), 8.06 (proton 4∼5, m, 2H), 7.40 (d, proton 6, 1H), 7.67 (proton 7, d, 1H).

2d: white powder, yield 20%, m.p. 165.1°C. IR: 2239 (C≡N); 1743 (C=O); 1605, 1575, 1515 (framework of phenyl rings); 1259,1129 (C–O–C). ^{1}H NMR: 3.82 (–CH_3, s, 3H), 6.76 (proton 1, d, 1H), 7.03 (proton 2, m, 2H), 7.80 (proton 3, m, 2H), 7.35 (proton 4, m, 1H), 7.62 (d, proton 5, 1H), 7.88 (d, proton 6, 1H), 8.04 (proton 7, d, 1H).

2e: white powder, yield 16%, m.p. 124.8°C. IR: 2229 (C≡N); 1728 (C=O); 1602, 1752, 1512 (framework of phenyl rings); 1253, 1151 (C–O–C). ^{1}H NMR: 1.34 (–CH_3, t, 3H), 4.10 (–CH_2–, m, 2H), 6.74 (proton 1, d, 1H), 7.01 (proton 2, m, 2H), 7.78 (proton 3∼5, m, 3H), 7.62 (proton 4, m, 1H), 7.87 (m, proton 6, 1H), 8.04 (proton 7, d, 1H).

2l: colourless needle crystals, yield 13%, m.p. 85.2°C. IR: 2231 (C≡N); 1723 (C=O); 1601, 1571, 1512 (framework of phenyl rings); 1259, 1113 (C–O–C). ^{1}H NMR: 0.86 (CH_3–, t, 3H); 1.26–1.72 (Me–CH_2–, m, 14H) 4.03 (Ar–CH_2–, m, 2H), 6.74 (proton 1, d, 1H), 7.01 (proton 2, m, 2H), 7.78 (proton 3, m, 2H), 7.35 (proton 4, m, 1H), 7.62 (d, proton 5, 1H), 7.87 (d, proton 6, 1H), 8.04 (proton 7, d, 1H).

2m: white needle crystals, yield 18%, m.p. 83.0°C. IR: 2239 (C≡N); 1732 (C=O); 1600, 1572, 1499 (framework of phenyl rings); 1258, 1126 (C–O–C). ^{1}H NMR: 0.99 (CH_3–, d, 6H), 2.03 (Me_2CH–, m, 1H), 3.82 (Ar–CH_2–, m, 2H), 6.74 (proton 1, d, 1H), 7.01 (proton 2, m, 2H), 7.78 (proton 3, m, 2H), 7.35 (proton 4, m, 1H), 7.61 (d, proton 5, 1H), 7.87 (d, proton 6, 1H), 8.05 (proton 7, d, 1H).

2n: white needle crystals, yield 17%, m.p. 98.9°C. IR: 2231 (C≡N); 1729 (C=O); 1602, 1572, 1499 (framework of phenyl rings); 1254, 1116 (C–O–C). ^{1}H NMR: 0.94 (CH_3–, t, 6H); 1.63 (Ar–CH_2–, m, 2H); 1.78 (Me_2CH–, m, 1H); 4.06 (Ar–CH_2–, m, 2H); 6.74 (proton 1, d, 1H), 7.02 (proton 2, m, 2H), 7.78 (proton 3, m, 2H), 7.35 (proton 4, m, 1H), 7.62 (d, proton 5, 1H), 7.87 (d, proton 6, 1H), 8.05 (proton 7, d, 1H).

2o: colourless needle crystals, yield 14%, m.p. 148.7°C. IR: 2236 (C≡N); 1711 (C=O); 1601, 1572, 1513 (framework of phenyl rings); 1255, 1114 (C–O–C). ^{1}H NMR: 5.19 (Ar–CH_2–, m, 2H); 6.76 (proton 1, d, 1H); 7.10–7.87 (Ar–H, m, 12H), 8.04 (proton 7, d, 1H).

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