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Deniz Vardar, Huriye Akdas-Kiliç, Hale Ocak, Olivier Jeannin, Franck

Camerel, Belkiz Bilgin Eran

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1	Pyridine Based Chiral Smectogens: Effects of Polar		
2	End Groups on Liquid Crystal Properties		
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5	Deniz Vardar ¹ , Hurive Akdas-Kılıc ^{1,2} , Hale Ocak ^{1*} , Olivier Jeannin ² , Franck Camerel ² , Belkız		
6	Bilgin Eran ^{1*}		
7			
8	¹ Yildiz Technical University, Department of Chemistry, 34220 Esenler, Istanbul, Turkey		
9	² Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes		
10			
11	*Corresponding Author: <u>bbilgin@yildiz.edu.tr</u> , <u>hocak@yildiz.edu.tr</u>		
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15	Abstract:		
16	In this study, novel chiral pyridine-based rod-like mesogens, consisting of a chloro or bromo		
17	group substituted pyridine head core which is connected to one or two aromatic rings through		
18	ester linkers and a flexible (S)-2-methylbutoxy or (S)-3,7-dimethyloctyloxy chiral end chain		
19	have been synthesized. The liquid crystal properties of new compounds were investigated by		
20	various experimental techniques such as DSC, POM and SAXS. Depending of the nature of		
21	the halogen end group, the derivatives with two aromatic rings are non-mesogenic compounds		
22	whereas a smectic A phase (SmA) enantiotropically occurs for the members with three		
23	aromatic rings of the series. Additionally, chloro group substituted compound composed of		
24	three aromatic rings carrying a (S) -2-methylbutoxy end chain exhibits an enantiotropic chiral		
25	nematic phase (N*).		
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33	Keywords: Liquid crystal, rod-like molecules, chirality, pyridine-based cores.		

34 **1.Introduction**

Liquid crystals are advanced organic materials which have found a wide usage in indicator 35 technology, organic semiconductor, sensors, bioactive materials and optical device 36 applications.[1,2,3,4] Studies of the structure-mesogenity relationship in liquid crystals have 37 led to significant improvements in the design of mesogenic molecules.[5,6] Molecular design 38 plays an important role in the emergence of liquid crystalline properties and a rational design 39 based on established molecular guidelines can allow for a rapid optimization of the liquid 40 crystalline properties, in term of structural organization and thermal range, for the target 41 42 application.[7,8] Within the different classes of LCs, rod-like (calamitic) liquid crystals, 43 characterized by their simple molecular structure and sensitivity to external stimulating effects 44 such as electric and magnetic fields, are intensively studied and incorporated in many LC materials.[9,10,11] 45

46 The calamitic structures usually consist of central rigid core, which ensure chemical anisotropy to the structure, with flexible chains at the end positions. Their liquid crystal 47 48 properties can be tuned by varying the aromatic core, the type and length of end chains and incorporating of branched units or molecular chirality.[12,13] In the design of a calamitic 49 50 liquid crystal molecule, the number of aromatic rings that determine the length of the molecule, the type of binding units, the presence of polar substituents on the aromatic core, 51 and the type of the flexible aliphatic ends chains are the major factors that determine the 52 53 emergence of mesomorphic properties. The most commonly used terminal groups in calamitic molecules are long alkyl and alkyloxy chains. By providing flexibility feature to the rigid core 54 unit, they also play an important role in decreasing the melting point of the molecule and also 55 contribute to mesophase formation. In addition, any polar end group (cyano or halogen, etc.) 56 in the structure, helps the formation of a more regular mesophase because it has high polarity 57 and can contribute to molecular stacking, which can positively influence the mesophase 58 59 formation.[14]

The introduction of a chiral center placed on the central core, on the terminal chains or on the flexible linking units can lead to liquid crystals which exhibit different properties than structurally related to those of non-chiral analogous.[15,16,17,18,19] A helical arrangement of the molecules can emerge, leading to a polar organization of the chiral molecules, which is one of the main ways to obtain light-responsive liquid crystal materials for applications in high-resolution displays and electro-optical devices.[7,20,21] Besides, helical LC phases can also arise from achiral molecules with a bent geometry.[22,23,24]

The introduction of a heteroatom in the molecular structure are decisive factors for the 67 formation in a particular type of molecular organization at a specific temperature range. In 68 particular, the number and the position into the aromatic ring affects its polarizability and 69 sometimes the geometric shape of the molecule, and as a result, the physical properties of the 70 mesogen such as the phase transition temperatures and/or the dielectric properties.[25] Six-71 membered N-heterocyclic systems such as pyridine is one of the simplest heterocyclic 72 73 aromatics used as a core system in the design of liquid crystalline molecules.[26,27,28,29,30] The position of the nitrogen atom in the pyridine fragment and its position in the molecular 74 75 core considerably influence the liquid crystalline properties of pyridine derivatives[31] and has a significant impact on the dispersion forces, the dipole moment, the polarizability of the 76 77 molecule and, inevitably, on the dielectric nature of the mesogen.[32]

Herein we report the design, synthesis and characterization of new pyridine-based calamitic 78 79 mesogens, consisting of a chloro or bromo group substituted pyridine head core which is connected to one or two aromatic rings through ester linkers and carrying a (S)-2-80 81 methylbutoxy or a (S)-3,7-dimethyloctyloxy chiral side chain. The effect of structural variations on mesomorphic properties have been discussed based on some viewpoints: the 82 83 introduction of two chiral chains with different length, the number of aromatic rings in the rigid core unit, the attaching of a pyridine ring into the core unit and the presence of polar end 84 groups such as bromo and chloro. Their thermal and liquid crystal properties were 85 investigated by differential scanning calorimetry (DSC), optical polarizing microscopy 86 (POM) and Small-angle X-ray scattering (SAXS). 87

88

89 **2. Experimental**

90 **2.1 Materials and instrumentation**

New chiral compounds (4a,b, 7a,b and 8a,b) were characterized by ¹H NMR and ¹³C NMR
(Bruker Avance III 500 spectrometer, in CDCl₃ solution, with tetramethylsilane as external
standard). Microanalysis was performed using a Thermo Fischer Scientific FlashEA 1112
Series elemental analyzer.

The mesomorphic properties of compounds were investigated by using a Mettler FP-82 HT hot stage and control unit in conjunction with a Leica DM2700P polarizing microscope. DSCthermograms of chiral imine compounds were recorded on a Perkin-Elmer DSC-6 with heating and cooling rate of 10 °C.min⁻¹ under nitrogen atmosphere.

X-ray scattering experiments (SAXS) were performed using a Microstar Bruker rotating 99 anode X-ray generator operated at 40 kV and 40 mA with monochromatic Cu K α radiation (λ 100 = 1.541 Å) and point collimation. The patterns were collected with a Mar345 Image-Plate 101 detector (Marresearch, Norderstedt, Germany). The exposure time at each temperature was 102 3600 s and the heating or cooling speed between two temperatures was 10 $^{\circ}$ C.min⁻¹. The 103 samples were held in Lindeman glass capillaries (1.5 mm diameter). The capillaries were 104 placed inside a Linkam HFX350-Capillary X-Ray stage which allow measurements from -196 105 °C up to 350 °C with an accuracy of 0.1 °C. 106

(S)-(-)- β -Citronellol (Aldrich, $\geq 99.0\%$, [α] $\frac{20}{589} = -5.3^{\circ}$, neat), (S)-(-)-2-methyl-1-butanol 107 (Fluka), p-toluenesulfonyl chloride (Merck), 4-benzyloxyphenol (Alfa Aesar), ethyl 4-108 hydroxybenzoate (Alfa Aesar), benzyl chloride (Merck), K₂CO₃ (Merck), sodium hydroxide 109 110 pellets (Merck), N,N'-dicyclohexylcarbodiimide (Merck), 4-(dimethylamino)pyridine (Merck), 10% Pd/C (Alfa Aesar), methyl 5-bromopyridine-2-carboxylate (ABCR), methyl 6-111 chloropyridine-3-carboxylate (Aldrich), were purchased from commercial sources and used as 112 received. Ethanol (Merck), 2-butanone (Merck) and THF (Merck %99) were purchased 113 commercially as dry solvents and were used without further purification. Anhydrous solvent 114 CH₂Cl₂ was dried over di-phosphorus pentoxide (Merck) and distilled under a N₂ atmosphere. 115 Solvents used in the purification step such as crystallization and column chromatography 116 (hexane (H), ethyl acetate (EA), chloroform, dichloromethane and ethanol) were distilled. 117 Analytical thin-layer chromatography (TLC) was carried out on aluminium plates coated with 118 silica gel 60 F254 (Merck) for intermediates and aluminium plates coated with aluminium 119 120 oxide 60 F254, neutral (Merck) for target imine compounds. Column chromatography was performed using silica gel 60 (Merck, pore size 60 Å, 230-400 mesh particle size). 121

122

123 2.2 Synthesis and Characterization

124

125 The synthesis of new pyridine based chiral calamitic compounds 4a,b and compounds 7a,b126 and 8a,b are presented in Scheme 1.

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Scheme 1. Synthesis of the new pyridine based chiral calamitic compounds 4a,b, 7a,b and8a,b.

New pyridine based chiral compounds **4a**,**b** and **7a**,**b** with three aromatic cores, in which the 148 pyridine ring substituted with a bromo or chloro polar end group have been prepared by the 149 esterification of 4-Alkyloxyphenyl-4-hydroxybenzoates (3a, b) and 5-bromopyridine-2-150 carboxylic acid (1) or 6-chloropyridine-3-carboxylic acid (5), which were obtained basic 151 hydrolysis in EtOH with NaOH(aq), using N,N'-dicyclohexylcarbodiimide (DCC) and 4-152 (dimethylamino)pyridine (DMAP) as catalyst in dry CH₂Cl₂. As described previously[33], 153 (S)-4-(2-methylbutoxy)phenyl 4-hydroxybenzoate (3a)and (S)-4-(3,7-154 Dimethyloctyloxy)phenyl 4-hydroxybenzoate (3b)[33], have been synthesized starting from 155 (S)-2-methylbutanol, which was tosylated to yield (S)-2-methylbutyl-1-tosylate[13] and (S)-(-156)- β -citronellol, which was firstly hydrogenated (H₂, Pd/C in MeOH) to give (S)-3,7-dimethyl-157 1-octanol and then converted to (S)-3,7-dimethyloctyl-1-bromide (conc. aqu. HBr, conc. 158 H_2SO_4 [34], respectively. The etherification of (S)-2-methylbutyl-1-tosylate or (S)-3,7-159 160 dimethyloctyl-1-bromide with 4-benzyloxyphenol, followed by hydrogenolytic debenzylation yielded to the corresponding 4-alkyloxyphenols 6a and 6b.[35,36] The esterification of the 161 162 obtained 4-alkyloxyphenols with 4-benzyloxybenzoic acid[37] using N,N'dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) yielded (S)-4-(2-163 methylbutoxy)phenyl 4-benzyloxybenzoate (2a) or (S)-4-(3,7-Dimethyloctyloxy)phenyl 4-164

- benzyloxybenzoate (2b) and followed by deprotection of the benzyl group under
 hydrogenolytic reaction conditions leads to 4-Alkyloxyphenyl-4-hydroxybenzoates (3a, b).
- 167 The esterification of 6-chloropyridine-3-carboxylic acid (5) with the corresponding 4-
- 168 alkyloxyphenol **6a,b** using the same procedure yielded to 4-((S)-2-methylbutoxy) phenyl 6-
- 169 chloronicotinate (8a) and 4-((S)-3,7-dimethyloctyloxy)phenyl 6-chloronicotinate (8b),
 170 respectively.
- 171 Spectroscopic data and preparation procedures of (*S*)-4-(3,7-Dimethyloctyloxy)phenyl 4-172 benzyloxybenzoate (**2b**), (*S*)-4-(3,7-Dimethyloctyloxy)phenyl 4-hydroxybenzoate (**3b**) and 173 (*S*)-4-(3,7-Dimethyloctyloxy)phenol (**6b**) were given in Guzeller et al.[33] The procedure for 174 the synthesis of **3a** and spectroscopic data of **2a**, **3a**, **6a** as well as 5-bromopyridine-2-175 carboxylic acid (**1**) or 6-chloropyridine-3-carboxylic acid (**5**) were given in supplementary 176 information (SI) file.
- ____

178 The procedure for the synthesis of the final compounds 4a,b, 7a,b and 8a,b:

- 179 For the synthesis of **4a**,**b** and **7a**,**b**, to a mixture of 1.5 mmol of 5-bromopyridine-2-carboxylic acid (1) or 6-chloropyridine-3-carboxylic acid (5) and 1.5 mmol of (S)-4-(2-180 methylbutoxy)phenyl 4-hydroxybenzoate (3a) or (S)-4-(3,7-Dimethyloctyloxy)phenyl 4-181 hydroxybenzoate (3b)[33] in 20 mL of dichloromethane, N,N'-dicyclohexylcarbodiimide (2.5 182 mmol) and 4-(dimethylamino)pyridine (0.12 mmol) were added. The mixture was stirred 183 under argon atmosphere at room temperature for 24 hours and the reaction progress was 184 monitored by TLC (H: EA / 3: 1). The reaction mixture was filtered over silica gel and the 185 solvent was removed under reduced pressure. The crude product was purified by column 186 187 chromatography on silica gel eluting with hexane/ethylacetate mixtures (H: EA / 3: 1) and finally washed with ethanol. 188
- The synthesis of compounds **8a,b** has been carried out by the esterification of 6chloropyridine-3-carboxylic acid (5) and the corresponding 4-alkyloxyphenols **6a** and **6b**[33] using the same procedure in that of target products **4a,b** and **7a,b**.
- 192

4-[4-((S)-2-Methylbutoxy)phenoxycarbonyl]phenyl 5-bromopicolinate (4a)

- 194 **Yield**: 35 %; colorless crystals. ¹**H NMR** (500 MHz, CDCl₃): δ (ppm) = 8.84 (d, $J \approx 1.9$ Hz,
- 195 1H, Ar-CH), 8.23 (d, $J \approx 8.7$ Hz, 2H, Ar-CH), 8.12 (d, $J \approx 8.3$ Hz, 1H, Ar-CH), 8.02 (dd, $J_1 \approx$
- 196 8.3, $J_2 \approx 2.3$ Hz, 1H, Ar-CH), 7.34 (d, $J \approx 8.7$ Hz, 2H, Ar-CH), 7.04 (d, $J \approx 9.0$ Hz, 2H, Ar-
- 197 CH), 6.87 (d, $J \approx 9.0$ Hz, 2H Ar-CH), 3.76, 3.67 (2dd, $J_1 \approx 8.9$, $J_2 \approx 6.0$ Hz, 2H, OCH₂), 1.81-

198 1.77 (m, 1H, C*H*), 1.24-1.16 (m, 2H, C*H*₂), 0.95 (d, *J* ≈ 6.7 Hz, 3H, C*H*₃), 0.89 (t, *J* ≈ 7.5 Hz, 199 3H, C*H*₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 164.70, 162.78 (COO), 157.16, 154.72, 145.35, 144.07, 127.77, 126.01 (Ar-C), 151.50, 140.02, 131.90, 127.09, 122.30, 121.89, 115.14 (Ar-CH), 73.29 (OCH₂), 34.70 (CH), 26.12 (CH₂), 16.52, 11.31 (CH₃). **FT-IR**: γ (cm⁻¹) = 1758, 1735 (C=O stretching), 1603-1505 (Ar-C=C stretching). C₂₄H₂₂BrNO₅ (484.35);

- 203 Anal. Calc. (%): C, 59.52; H, 4.58; N, 2.89. Found (%): C, 59.23; H, 4.91; N, 3.03.
- 204

4-[4-((S)-3,7-Dimethyloctyloxy)phenoxycarbonyl]phenyl 5-bromopicolinate (4b)

- **Yield**: 34 %; colorless crystals. ¹**H NMR** (500 MHz, CDCl₃): δ (ppm) = 8.84 (d, $J \approx 1.8$ Hz, 206 207 1H, Ar-CH), 8.23 (d, $J \approx 8.8$ Hz, 2H, Ar-CH), 8.12 (d, $J \approx 8.6$ Hz, 1H, Ar-CH), 8.02 (dd, $J_1 \approx$ 8.3, $J_2 \approx 2.3$ Hz, 1H, Ar-CH), 7.34 (d, $J \approx 8.8$ Hz, 2H, Ar-CH), 7.05 (d, $J \approx 9.0$ Hz, 2H, Ar-208 209 CH), 6.87 (d, $J \approx 9.0$ Hz, 2H, Ar-CH), 3.98-3.86 (m, 2H, OCH₂), 1.81-1.70 (m, 1H, CH), 1.57-1.08 (m, 9H, CH, CH₂), 0.88 (d, $J \approx 6.6$ Hz, 3H, CH₃), 0.81 (d, $J \approx 6.6$ Hz; 6H, CH₃). 210 211 ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 164.69, 162.79 (COO), 156.97, 154.72, 145.34, 144.10, 127.77, 126.01 (Ar-C), 151.50, 140.03, 131.90, 127.09, 122.32, 121.90, 115.13 (Ar-212 CH), 66.74 (OCH₂), 39.24, 37.27, 36.20, 24.66 (CH₂), 29.83, 27.97 (CH), 22.71, 22.61, 19.64 213 (CH₃). **FT-IR:** γ (cm⁻¹) = 1734 (2 C=O stretching), 1593-1506 (Ar-C=C stretching). 214 C₂₉H₃₂BrNO₅ (554.48); Anal. Calc. (%): C, 62.82; H, 5.82; N, 2.53. Found (%): C, 63.13; H, 215 5.90; N, 2.21. 216
- 217

218 **4-[4-((S)-2-Methylbutoxy)phenoxycarbonyl]phenyl 6-chloronicotinate (7a)**

Yield: 45 %; colorless crystals. ¹**H NMR** (500 MHz, CDCl₃): δ (ppm) = 9.20 (d, $J \approx 2.4$ Hz, 219 1H, Ar-CH), 8.42 (dd, $J_1 \approx 8.3$ Hz, $J_2 \approx 2.4$ Hz, 1H, Ar-CH), 8.31 (d, $J \approx 8.8$ Hz, 2H, Ar-CH), 220 7.53 (d, *J* ≈ 8.3 Hz, 1H, Ar-CH), 7.39 (d, *J* ≈ 8.8 Hz, 2H, Ar-CH), 7.12 (d, *J* ≈ 9.0 Hz, 2H, Ar-221 CH), 6.95 (d, $J \approx 9.0$ Hz, 2H, Ar-CH), 3.83, 3.75 (2dd, $J_1 \approx 8.9$ Hz, $J_2 \approx 6.0$ Hz, 2H, OCH₂), 222 1.93-1.82 (m, 1H, CH), 1.66-1.50, 1.35-1.23 (2m, 2H, CH₂), 1.03 (d, $J \approx 6.7$ Hz, 3H, CH₃), 223 0.96 (t, $J \approx 7.5$ Hz, 3H, CH_3). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 164.64, 162.54 224 (COO), 157.19, 156.72, 154.27, 144.04, 127.85, 124.13 (Ar-C), 151.72, 140.09, 131.94, 225 124.54, 122.29, 121.76, 115.15 (Ar-CH), 73.30 (OCH₂), 34.71 (CH), 26.12 (CH₂), 16.52, 226 227 11.31 (CH₃). **FT-IR:** γ (cm⁻¹) = 1738, 1712 (C=O stretching), 1605-1507 (Ar-C=C stretching). C₂₄H₂₂CINO₅ (439.89); Anal. Calc. (%): C, 65.53; H, 5.04; N, 3.18. Found (%): 228 C, 65.66; H, 5.16; N, 2.97. Full MS (ESI) (electrospray ionization) (+): m/z (%) = 440 (100) 229 230 $[M^+]$, 260 (87) $[M^+-C_{11}H_{15}O_2]$, 140 (25) $[C_6H_3CINO]$.

4-[4-((*S*)-3,7-Dimethyloctyloxy)phenoxycarbonyl]phenyl 6-chloronicotinate (7b)

Yield: 45 %; colorless crystals. ¹**H NMR** (500 MHz, CDCl₃): δ (ppm) = 9.20 (d, $J \approx 2.4$, 1H, 232 Ar-CH), 8.42 (dd, $J_1 \approx 8.3$ Hz, $J_2 \approx 2.4$ Hz, 1H, Ar-CH), 8.31 (d, $J \approx 8.8$ Hz, 2H, Ar-CH), 233 7.53 (d, $J \approx 8.3$, 1H, Ar-CH), 7.39 (d, $J \approx 8.8$ Hz, 2H, Ar-CH), 7.13 (d, $J \approx 9.0$ Hz, 2H, Ar-234 CH), 6.95 (d, $J \approx 9.0$ Hz, 2H, Ar-CH), 4.09-3.89 (m, 2H, OCH₂), 1.88-1.78 (m, 1H, CH), 235 1.65-1.13 (m, 9H, CH, 4 CH₂), 0.95 (d, $J \approx 6.6$ Hz, 3H, CH₃), 0.88 (d, $J \approx 6.1$ Hz, 6H, CH₃). 236 ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 164.64, 162.55 (COO), 156.99, 156.67, 154.26, 237 144.05, 127.84, 124.12 (Ar-C), 151.73, 140.10, 131.95, 124.55, 122.31, 121.77, 115.13 (Ar-238 CH), 66.73 (OCH₂), 39.24, 37.27, 36.19, 24.66 (CH₂), 29.82, 27.98 (CH), 22.72, 22.64, 19.64 239 (*CH*₃). **FT-IR:** γ (cm⁻¹) = 1736, 1724 (C=O stretching), 1605-1507 (Ar-C=C stretching). 240 C₂₉H₃₂CINO₅ (510.03); Anal. Calc. (%): C, 68.29; H, 6.32; N, 2.75. Found (%): C, 68.00; H, 241 6.30; N, 2.70. Full MS (ESI) (electrospray ionization) (+): m/z (%) = 512 (18) [M⁺+2H], 260 242

- 243 (100) $[M^+-C_{16}H_{25}O_2]$, 140 (65) $[C_6H_3CINO]$.
- 244

245 **4-((S)-2-Methylbutoxy)phenyl 6-chloronicotinate (8a)**

Yield: 48 %; colorless crystals. ¹**H NMR** (500 MHz, CDCl₃): δ (ppm) = 9.09 (d, $J \approx 2.4$ Hz, 246 1H, Ar-CH), 8.31 (dd, $J_1 \approx 8.3$, $J_2 = 2.4$ Hz, 1H, Ar-CH), 7.42 (d, $J \approx 8.3$ Hz, 1H, Ar-CH), 247 7.04 (d, $J \approx 9.0$ Hz, 2 Ar-CH), 6.87 (d, $J \approx 9.0$ Hz, 2H, Ar-CH), 3.75, 3.67 (2dd, $J_1 \approx 8.9$, 248 $J_2 \approx 6.0$ Hz, 2H, OCH₂), 1.83-1.78 (m, 1H, CH), 1.24-1.18 (m, 2H, CH₂), 0.95 (d, $J \approx 6.7$ Hz, 249 3H, CH₃), 0.89 (t, $J \approx 7.4$ Hz, 3H, CH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 163.48 250 (COO), 158.11, 155.97, 142.27, 124.71 (Ar-C), 151.64, 139.19, 124.86, 122.15, 115.21 (Ar-251 CH), 71.92 (OCH₂), 34.72 (CH), 26.13 (CH₂), 17.49, 11.34 (CH₃). **FT-IR:** γ (cm⁻¹) = 1728 252 (C=O stretching), 1583-1504 (Ar-C=C stretching). C₁₇H₁₈ClNO₃ (319.79); Anal. Calc. (%): 253 254 C, 63.85; H, 5.67; N, 4.38. Found (%): C, 64.12; H, 5.91; N, 4.17.

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4-((S)-3,7-Dimethyloctyloxy)phenyl 6-chloronicotinate (8b)

Yield: 60 %; colorless crystals. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 9.08 (d, *J* ≈ 2.4 Hz, 1H, Ar-C*H*), 8.31 (dd, $J_1 \approx 8.3$, $J_2 \approx 2.4$ Hz, 1H Ar-C*H*), 7.42 (d, $J \approx 8.3$ Hz, 1H, Ar-C*H*), 7.05 (d, $J \approx 9.1$ Hz; 2H, Ar-C*H*), 6.87 (d, $J \approx 9.1$ Hz, 2H, Ar-C*H*), 3.93-3.89 (m, 2H, OC*H*₂), 1.79-1.70 (m, 1H, C*H*), 1.31-1.08 (m, 9H, C*H*, C*H*₂), 0.88 (d, $J \approx 6.6$ Hz, 3H, C*H*₃), 0.80 (d, $J \approx 6.1$ Hz, 6H, C*H*₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 163.45 (COO), 157.25, 156.25, 143.59, 124.70 (Ar-C), 151.64, 140.05, 124.39, 122.16, 115.21 (Ar-CH), 66.78 (OCH₂), 39.25, 37.28, 36.19, 34.94 (CH₂), 29.84, 27.99 (CH) 24.67, 22.62, 19.66 (CH₃). FT- IR: γ (cm⁻¹) = 1713 (C=O stretching), 1586-1507 (Ar-C=C stretching). C₂₂H₂₈ClNO₃
(389.91); Anal. Calc. (%): C, 67.77; H, 7.24; N, 3.59. Found (%): C, 67.74; H, 7.27; N, 3.48.
3. Results and Discussions

268

269 **3.1 Liquid crystalline properties**

270

The mesomorphic properties of the pyridine based chiral compounds **4**, **7** and **8** were investigated by using optical polarizing microscope (POM) and differential scanning calorimeter (DSC). The phase transitions temperatures observed on heating and cooling cycles and corresponding transition enthalpies of the compounds are given in Table 1. The peak temperatures are given in degree Celsius and the numbers in parentheses indicate the transition enthalpy (ΔH). The mesomorphic behavior of all the compounds is summarized in Fig. 2.

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Table 1 Mesophase, phase transition temperatures (°C) and the corresponding transition enthalpies $(\Delta H \text{ kJ/mol})^a$ of the compounds **4a,b**; **7a,b** and **8a,b**.

×–{	$Y = Z \qquad 0 \qquad$	
	a: R* =* (S)	b: R* =*
	Heating	Cooling
4a	Cr 137.46 (25.90) Iso	Iso 118.59 (21.70) Cr

4b	Cr ₁ 107.02 (0.86) Cr ₂ 130.05 (29.97) SmA	Iso 154.85 (2.42) SmA 118.04 (31.09)
	156.49 (2.40) Iso	Cr ₂ 101.65 (0.76) Cr ₁
7a	Cr 141.66 (38.10) SmA 174.46 (1.55)	Iso 192.47 (0.45) N* 172.18 (1.75) SmA
	N [*] 194.15 (0.33) Iso	125.16 (36.43) Cr
7b	Cr 132.55 (38.37) SmA 188.01 (4.62) Iso	Iso 185.65 (4.64) SmA 120.83 (32.44) Cr
8 a	Cr 54.70 ^b Iso	Iso 46.00 ^b Cr
8b	Cr 70.00 ^b Iso	Iso 51.00 ^b Cr

^a Perkin-Elmer DSC-6; enthalpy values in italics in brackets taken from the 2nd heating and cooling scans at a rate of 10 °C.min⁻¹; Abbreviations: Cr = crystalline, SmA = smectic A mesophase, N* = chiral nematic phase, Iso = isotropic liquid phase. ^b These transitions were determined by PM.

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286 On cooling, compound 4a composed of three aromatic rings substituted a bromo polar end 287 group as well as (S)-2-methylbutoxy group shows only one reversible transition around 137 288 °C, which corresponds to a crystal-to-isotropic phase transition by POM (see Fig.S27). On contrary, three transitions were detected in the DSC traces both during the heating and cooling 289 290 runs for the compound **4b** which is the analog substituted with (S)-3,7-dimethyloctyloxy chiral moiety of compound 4a. On heating, a phase transition sequence of crystal Cr₁- Cr₂-291 292 SmA-Iso between 107 °C and 156 °C and the same reverse phase transition sequence with 293 three exotherms were observed on cooling (Table 1 and Fig. 1). Depending on the presence of 294 short branched end chain, compound 4a is non-mesogenic whereas compound 4b exhibits enantiotropic SmA mesophase appearing with an ordinary fan-shaped texture (see Fig. 2a). 295

Compounds 7a derived from 6-chloronicotinic acid substituted with (S)-2-methylbutoxy 296 chiral moiety exhibits enantiotropic SmA phase as well as chiral nematic (N^*) phase. On 297 cooling from isotropic phase, oily streaks texture of N* phase firstly appeared at 192 °C and 298 then homeotropic texture of SmA phase emerged at 172 °C. It should be noted here that the 299 enthalpy change during N*-Iso transition or vice versa transition is very small value. This is 300 301 presumably a result from the short branched chain which increases the molecular biaxiality and so reduces the order change at the transition.[38] The homeotropic texture of SmA phase 302 303 converted to the focal conic pattern after shearing the sample (see Fig. 2b).

However, compound **7b** carrying longer and more branched chain by two methyl groups 304 305 shows reversible transitions Cr-SmA-Iso which were detected in the DSC traces during the heating and the cooling runs. This result agrees with the work of Laschat et al.[39] who 306 reported that homologous series of chloro- and bromo-terminated 5-phenylpyrimidine 307 308 mesogens also form exclusively SmA phases and with the report of Goodby et al. that a 309 chloro end-group acts as a strong SmA-promoter.[40,41] Additionally, compound 7b, which has a (S)-3,7-dimethyloctyloxy chiral moiety and a chloro polar head, shows richer 310 311 mesomorphism and mesophase stability as compared with the mesomorphic behavior observed for pyridine-based calamitic esters carrying same chiral moiety.[42] On the other 312 hand, it can be said that the use of a longer terminal alkyl chain in the members with three 313 aromatic rings clearly allows to stabilize the formation SmA phase over larger temperature 314 range in comparison of the introduction of shorter branched chain such as (S)-2-methylbutoxy 315

316 group at the terminal. One point should be mentioned here that longer terminal chains reduce 317 the melting point by providing mobility and flexibility in the structure and this case allows 318 designing mesogens with desired properties for many applications.

319 Herein, we would also like to focus on the comparison between compounds 4a and 7a which 320 structurally differs by the nature of the halogen atom on the pyridine group and the position of the nitrogen. It is known that the nature of halogen groups plays a significant role in the intra-321 and inter-molecular interactions[43] which affect the packing of the molecules, that 322 predominantly influences mesophase stability. The main reason is not the strong polar 323 324 interactions at interfaces, as previously postulated in the literature.[44] Instead, the evidence 325 suggests that the effect is due to the electron-withdrawing effect of the chloro end-group, 326 which should reduce electrostatic repulsion between the alkoxy chains and increase attractive van der Waals interactions between aromatic cores in the SmA phase.[45] Also, one point 327 328 should also be considered that the size and shape of the substituent which able to interact with the mesogenic unit. Van der Waals volume of a substituent bounded to a phenyl ring shows a 329 330 linear dependence on phase transition.[46] In our case, the polar bromine of compound 4a leads to a non-mesogenic behavior due to the lower electron-withdrawing effect of bromine 331 332 than that of chlorine as compared to compound **7a** showing liquid crystallinity.

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Fig. 1. DSC thermograms of compounds **4b** and **7a,b** on 2^{nd} heating and cooling (10 °C min⁻¹).



Fig. 2. Optical textures of mesophases of compounds 4b and 7a,b as observed between crossed polarizers (indicated by arrows) in ordinary glassplates on cooling (magnification

- ×100); (a) fan-shaped texture of SmA mesophase of compound **4b** obtained at T = 151 °C; (b) focal conic texture after shearing the homeotropic pattern of SmA mesophase of compound **7a** obtained at T = 148 °C; (c) oily-streak texture of N* phase of compound **7a** obtained at T =184 °C; (d) fan-shaped texture of SmA mesophase of compound **7b** obtained at T = 160 °C.
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Compounds **8a** and **8b** show reversible crystal-isotropic transition that corresponds to a nonmesogenic behavior (see Table 1 and Fig.S28). This behavior indicates that only two aromatic rings are not sufficient to obtain liquid crystallinity. Surprisingly, melting point of compound **8b** with more branched and longer chain ~15 °C higher than that of compound **8a**.

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364 3.2 SAXS Measurements

The mesophases of compounds 7a and 7b derived from 6-chloronicotinic acid were 365 366 confirmed by XRD analysis. The SAXS patterns recorded on 7b compound confirm the presence of two reversible phase transitions around 130 and 180 °C. The SAXS pattern of the 367 high temperature phase is typical of an isotropic state with a broad halo in the small angles 368 region (34.4 Å) and a broad halo in the wide angles region (4.9 Å), arising from the mean 369 distances between the long and the short molecular axes, respectively, in a disordered state 370 (Fig. 3a and 3b). Below 130 °C, the SAXS patterns are typical of a crystalline phase with 371 many sharp diffraction peaks in the small and wide angles regions (Fig. 3c). On contrary, the 372 SAXS patterns recorded between 130 and 180 °C are characterized by the presence of two 373 sharp reflections in the small angles region and a broad halo in the wide-angle region. Based 374 on the POM observations, showing the formation of SmA phase, the reflections observed at 375 376 33.4 and 16.7 Å in the small angle region were indexed as the (001) and (002) reflections of a lamellar phase. In the wide-angle region, the broad halo centered at 4.75 Å was associated to 377 the mean distance between the alkyl chains in a molten state and confirms the liquid 378 crystalline nature of the phase. The size of the molecule is a fully extended state was 379 estimated to 27.5 Å using a Chem3D molecular model. The lamellar period d = 33.4 Å is only 380 slightly larger than the molecular length (Fig. 3d). Thus, the smectic phase is constituted of 381 382 monolayers of molecules slightly shifted along the director.

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Fig. 3. SAXS pattern of **7b** compound recorded at different temperatures (a) T = 200 °C; (b) T = 170 C°; (c) T = 200 °C (2rd heating) and d) Proposed organization for **7b** in the SmA mesophase at 170 °C (extended length ~ 27.5 Å (Dreiding model); atom: white = hydrogen, grey = carbon, blue = nitrogen, green = chloride, red = oxygen).

From the XRD data, an organization model can be proposed and his presented in Fig. 3d. The
lamellar distance moderately increases by less than 1% between 140 and 170 °C and a layer
thermal expansion coefficient +0.01 Å.K⁻¹ can be calculated for **7b** in the SmA phase.



Fig. 4. (a) SAXS patterns recorded on 7a compound upon heating (b) Selected temperaturedependent SAXS patterns recorded on 7a compound upon cooling (insert: zoom of the area 68 ° in 2θ of the curve at 175 °C).

The SAXS patterns of compound 7a measured at 205 °C is characteristic of an isotropic state 433 with one broad peak in the small angles region centered at 28.5 Å and another one in the wide 434 angles region at 4.8 °C. Upon cooling, a clear narrowing of the diffraction peak in the small 435 angles region is observed around 195 °C and is in line with the formation of a nematic phase 436 with a subtle ordering of the rod-like molecules (see Fig. 4). By POM observations, this phase 437 was assigned as a chiral nematic phase (N*). Upon further cooling, another phase transition is 438 clearly detected between 185 and 175 °C. The first order reflection centered at 26.3 Å at 175 439 °C became really sharp and a second order reflections appeared at 13.2 Å. These two 440 reflections, based on the POM observations, can be indexed as the first two (001) and (002) 441 reflections of a lamellar phase. The broad halo centered at associated to the carbon chains in a 442 molted state, confirms that the compound is in a liquid crystalline state. The compound 443 remains in this smectic phase down to 140°C and a slight decrease of the interlayers distance 444 is observed with a layer thermal contraction coefficient of -0.01 Å.K⁻¹. The interlayers 445 446 distance is comparable to the length of the molecule in a fully extended conformation l = 24.5 $Å \sim d$, meaning that the SmA phase is formed of monolayers of molecules arranged in slightly 447 shifted head-to-tail fashion like 7b compound (See model Fig. 3d). At 120 °C, the compound 448 is clearly in a crystalline state and several sharp diffraction peaks are observed on the whole 449 2θ range. On heating, the reverse phase transition sequence is observed and the compounds 450 transit from a crystalline phase to the SmA phase at 135-145 °C, then from the SmA phase to 451 the N* phase at 170-180 °C and finally from the N* phase to the isotropic phase at 195-205 452

^oC. Thus, all the transitions are perfectly reversible and the phase transition temperatures
detected by SAXS are fully consistent with the temperature measured by DSC.

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456 4. Conclusion

In this article, we have synthesized and characterized new pyridine based rod-like compounds 457 composed of a chloro- or bromo-pyridine polar head linked to one or two benzene rings 458 through ester linkers and a flexible a (S)-2-methylbutoxy or (S)-3,7-dimethyloctyloxy chiral 459 end chain on the other side. The chain length and the type of the halogen atom have been 460 461 varied to understand the relationship between the structure and mesogenic properties. The chlorine substituted two aromatic rings derivatives exhibit non-mesogenic behavior, whereas 462 463 members with three aromatic rings carrying a (S)-3,7-dimethyloctyloxy or (S)-2methylbutoxy group exhibit SmA phase. A chiral nematic phase (N*) was also observed for 464 465 the derivative with a (S)-2-methylbutoxy terminal chain. Additionally, the replacement of chlorine with bromine atom as well as the position of nitrogen atom in the pyridine ring lead 466 467 to disappearing of liquid crystallinity for derivative carrying the same chiral moiety. However, it can be said that the mesophase stability decreases for bromine substituted analog 468 469 terminated with (S)-3,7-dimethyloctyloxy group. The mesophases of compounds derived from 470 6-chloronicotinic acid were confirmed by XRD measurement. The organization in the SmA mesophase of (S)-3,7-dimethyloctyloxy substituted analog is constituted of monolayers of 471 molecules slightly shifted along the director. What's emerges from our work is that the 472 occurence of liquid crystalline phase strongly depends on the nature of the halogen atoms and 473 474 the introduction of the chlorine atom into the structure due to its more electron-withdrawing 475 effect is more favorable.

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482 Appendix A. Supplementary data

483 Electronic supplementary information (ESI) is available.

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