Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

A New Way to Access Chiral Liquid Crystals: Organocatalyst-Mediated Synthesis of Chiral Rod-Like Liquid Crystals

Li Wang [a], Xiao-Jun Liu [a], Ping Huang [a], Qing-Ping Gong [a], Yong-Hong Li [a], Bi-Qin Wang [a] & Ke-Qing Zhao [a]

[a] Department of Chemistry and Materials Science, Sichuan Normal University, Chengdu, Sichuan, China

Version of record first published: 30 Jun 2011

To cite this article: Li Wang, Xiao-Jun Liu, Ping Huang, Qing-Ping Gong, Yong-Hong Li, Bi-Qin Wang & Ke-Qing Zhao (2011): A New Way to Access Chiral Liquid Crystals: Organocatalyst-Mediated Synthesis of Chiral Rod-Like Liquid Crystals, Molecular Crystals and Liquid Crystals, 541:1, 53/[291]-59/[297]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.570138

Mol. Cryst. Liq. Cryst., Vol. 541: pp. 53/[291]–59/[297], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.570138

Taylor & Francis
Taylor & Francis Group

A New Way to Access Chiral Liquid Crystals: Organocatalyst-Mediated Synthesis of Chiral Rod-Like Liquid Crystals

LI WANG, XIAO-JUN LIU, PING HUANG, QING-PING GONG, YONG-HONG LI, BI-QIN WANG, AND KE-QING ZHAO

Department of Chemistry and Materials Science, Sichuan Normal University, Chengdu, Sichuan, China

In this article, an asymmetric organocatalytic way to prepare chiral liquid crystals from non-chiral starting materials was described. By using L-proline as the organocatalyst, several new chiral rod-like liquid crystals that are elusive with traditional methods were prepared. In addition, a series of novel enone-containing rod-like liquid crystals were also obtained as side-products. Mesomorphic properties of all new compounds were studied by Polarized Optical Microscope and Differential Scanning Calorimetry.

Keywords Chiral rod-like liquid crystals; enone-containing mesogens; L-proline; organocatalysis

1. Introduction

Chiral liquid crystal (CLC) is an important family of liquid crystals. This is because CLCs, compared to non-chiral mesogens, normally exhibit unconventional molecular stackings and mesomorphic properties [1]. Besides, CLCs could be applied in displays with "fast switching, high contrast and large viewing angles" [2] due to their spontaneous polarization (P_S) properties.

Traditionally, CLCs were prepared by "chiral-pool" [3] methods. However, the scarcity, and hence high costs of chiral fragments in "chiral pool" largely restricted the research and development of CLCs. As a result, a new method to prepare CLCs from readily available, inexpensive starting materials is very indispensable.

The new method to prepare CLCs, as we expected, should satisfy several requirements: 1) non-chiral, therefore common and inexpensive starting materials; 2) highly concise synthetic routes; and 3) the process should be easily handled and environmentally friendly. On our way to search such a method, organocatalytic asymmetric induction has drawn our attention [4]. Organocatalysts are usually stable, easily accessible, cheap and non-toxic [4]. Besides, asymmetric organocatalysis has been

Address correspondence to Ke-Qing Zhao, Department of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610066, Sichuan, China. Tel.: +86-2884764743; Fax: +86-2884764743; E-mail: kqzhao@sicnu.edu.cn

studied intensively in recent decades and has already been applied to a wide range of non-chiral starting materials [4]. Consequently, with all these merits and convenience of asymmetric organocatalysis, we envisioned that, through this way, chirality could be introduced into liquid crystals quite efficiently, which hence may largely expand the knowledge of CLCs.

2. Experimental Methods

As the starting stage of the research project, we decided to use the most common and best studied organocatalytic reaction—L-proline-catalyzed asymmetric aldolization between ketones and aldehydes [5]—to prepare a chiral rod-like liquid crystals **4** and enone-bearing rod-like liquid crystals **5**∼**10**. The synthetic routes are described in Figures 1 and 2. Very noticeably, the L-proline-catalyzed aldol condensation reaction provided us enones with (*E*)-configurations exclusively. Though the similar stereoselective enone formations have been reported by Li *et al.* [6] aldol condensations of such bulky aldehydes in our cases have never been reported. Furthermore, L-proline-catalyzed aldol addition of ketones and eletron-donating group substituted, highly bulky benzaldehyde derivatives was also reported first time in this article even though the high reaction temperature (35°C) and high catalytic loading in our method provided low enantioselectivity.

A general procedure for the L-proline-catalyzed aldolization. To a mixture of an aldehyde substrate **3** or **11** (1.0 equiv.) in acetone (0.02 mol/L) added L-proline (1.0 equiv.). The reaction was then heated to 35°C, and was monitored by thin-layer

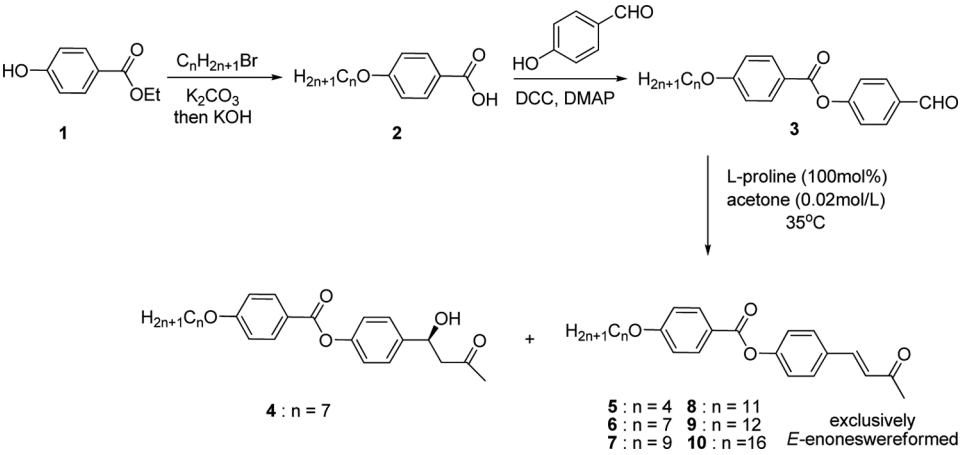

Figure 1. Synthetic routes for the L-proline-catalyzed asymmetric aldolization.

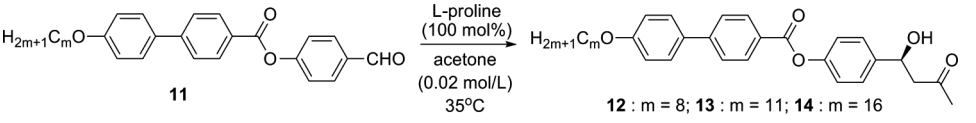

Figure 2. L-proline-catalyzed asymmetric aldolization of aldehydes **11**.

chromatography. Upon completion, the reaction was concentrated, purified by column chromatography. The desired aldol products (**4, 12∼14**)or enone compounds (**5∼10**) were recrystallized from ethanol as white solids.

(E)-4-(3-Oxobut-1-enyl)phenyl 4-butoxybenzoate, 5 (13% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.14 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 16.2$ Hz, 1H), 7.26 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 6.70 (d, $J = 16.2$ Hz, 1H), 4.06 (t, $J = 6.6$ Hz, 2H), 2.40 (s, 3H), 1.86–1.78 (m, 2H), 1.55–1.48 (m, 2H), 1.00 (t, $J = 7.2$ Hz, 3H).

(E)-4-(3-Oxobut-1-enyl)phenyl 4-heptoxybenzoate, 6. (28% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.14 (d, $J = 9.0$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 16.2$ Hz, 1H), 7.26 (d, $J = 7.8$ Hz, 2H), 6.98 (d, $J = 8.4$ Hz, 2H), 6.70 (d, $J = 16.2$ Hz, 1H), 4.05 (t, $J = 6.6$ Hz, 2H), 2.40 (s, 3H), 1.86–1.79 (m, 2H), 1.50–1.44 (m, 2H),1.42–1.30 (m, 6H), 0.88 (t, $J = 7.2$ Hz, 3H).

(E)-4-(3-Oxobut-1-enyl)phenyl 4-nonyloxybenzoate, 7. (26% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.14 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 16.2$ Hz, 1H), 7.26 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 6.70 (d, $J = 16.2$ Hz, 1H), 4.05 (t, $J = 6.6$ Hz, 2H), 2.40 (s, 3H), 1.85–1.80 (m, 2H), 1.50–1.44 (m, 2H), 1.38–1.26 (m, 10H), 0.88 (t, $J = 6.6$ Hz, 3H).

(E)-4-(3-Oxobut-1-enyl)phenyl 4-undecyloxybenzoate, 8. (27% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.13 (d, $J = 9.0$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 16.2$ Hz, 1H), 7.26 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 6.70 (d, $J = 16.2$ Hz, 1H), 4.05 (t, $J = 6.6$ Hz, 2H), 2.40 (s, 3H), 1.85–1.80 (m, 2H), 1.50–1.44 (m, 2H), 1.39–1.26 (m, 14H), 0.89 (t, $J = 6.6$ Hz, 3H).

(E)-4-(3-Oxobut-1-enyl)phenyl 4-dodecyloxybenzoate, 9. (20% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.13 (d, $J = 9.0$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 16.2$ Hz, 1H), 7.26 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 6.70 (d, $J = 16.2$ Hz, 1H), 4.05 (t, $J = 6.6$ Hz, 2H), 2.40 (s, 3H), 1.85–1.80 (m, 2H), 1.50–1.45 (m, 2H), 1.38–1.22 (m, 16H), 0.88 (t, $J = 6.6$ Hz, 3H).

(E)-4-(3-Oxobut-1-enyl)phenyl 4-hexadecyloxybenzoate, 10. (22% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.13 (d, $J = 9.0$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 16.2$ Hz, 1H), 7.26 (d, $J = 9.0$ Hz, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 6.70 (d, $J = 16.2$ Hz, 1H), 4.05 (t, $J = 6.6$ Hz, 2H), 2.40 (s, 3H), 1.85–1.79 (m, 2H), 1.51–1.44 (m, 2H), 1.39–1.22 (m, 24H), 0.88 (t, $J = 6.6$ Hz, 3H).

4-(1-Hydroxy-3-oxobutyl)phenyl 4-(heptyloxy)benzoate, 4. (20% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.13 (d, $J = 9.0$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.97(d, $J = 8.4$ Hz, 2H), 5.19 (dd, $J = 3.0$, 9.0 Hz, 1H), 4.04 (t, $J = 6.6$ Hz, 2H), 3.01 (br, 1H), 2.90 (dd, $J = 9.0$, 17.4 Hz, 1H), 2.84 (dd, $J = 3.6$, 18.0 Hz, 1H), 2.22 (s, 3H), 1.85–1.78 (m, 2H), 1.51–1.44 (m, 2H), 1.40–1.27 (m, 6H), 0.90 (t, $J = 6.6$ Hz, 3H).

4-(1-Hydroxy-3-oxobutyl)phenyl 4′-(octyloxy)biphenyl-4-carboxylate, 12. (18% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.23 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 9.0$ Hz, 2H), 5.21 (dd, $J = 3.0$, 9.0 Hz, 1H), 4.02 (t, $J = 6.0$ Hz, 2H), 3.33 (br, 1H), 2.91 (dd, $J = 9.0$, 17.4 Hz, 1H), 2.86 (dd, $J = 3.0$,

17.4 Hz, 1H), 2.22 (s, 3H), 1.85–1.78 (m, 2H), 1.51–1.44 (m, 2H), 1.40–1.24 (m, 8H), 0.90 (t, $J = 6.6$ Hz, 3H).

4-(1-Hydroxy-3-oxobutyl)phenyl 4′-(undecyloxy)biphenyl-4-carboxylate, 13. (22% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.23 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 7.8$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 5.21 (dd, $J = 6.6$, 6.6 Hz, 1H), 4.02 (t, $J = 6.0$ Hz, 2H), 3.33 (br, 1H), 2.91 (dd, $J = 9.0$, 17.4 Hz, 1H),2.86 (dd, $J = 2.4$, 17.4 Hz, 1H), 2.23 (s, 3H), 1.84–1.78 (m, 2H), 1.51–1.45 (m, 2H), 1.39–1.24 (m, 14H), 0.89 (t, $J = 6.6$ Hz, 3H).

4-(1-Hydroxy-3-oxobutyl)phenyl 4′-(hexadecyloxy)biphenyl-4-carboxylate, 14. (19% Yield, White Solid.). ^{1}H NMR (600 MHz, $CDCl_3$) δ8.23 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 9.0$ Hz, 2H), 5.21 (dd, $J = 3.0$, 8.4 Hz, 1H), 4.02 (t, $J = 6.0$ Hz, 2H), 3.35 (br, 1H), 2.91(dd, $J = 9.0$, 17.4 Hz, 1H),2.86 (dd, $J = 3.6$, 17.4 Hz, 1H),2.23 (s, 3H), 1.83–1.78 (m, 2H), 1.56–1.47 (m, 2H), 1.38–1.22 (m, 24H), 0.88 (t, $J = 6.6$ Hz, 3H).

3. Results and Discussion

3.1. *Mesomorphic Studies of the Chiral Compound 4 and Enone-containing Rod-Like Liquid Crystals (5∼10)*

POM and DSC investigations of the chiral compound **4** did not show any mesomorphic properties, even though its starting aldehyde was reported to exhibit liquid crystal behaviors [8]. This was not surprising, since the introduction of chirality would cause uneven molecular plane, and hence, not-well-organized molecular stackings, which is harmful to liquid crystal phases formation [1].

In sharp contrast, however, the new enone-containing compounds (**5∼10**) showed excellent liquid crystal properties (phase transition temperatures were included in Table 1). These enone-containing liquid crystals (ELCs) exhibited higher melting points and wider mesomorphic ranges than their aldehyde precursors [8]. This might be due to the strengthened intermolecular π-π interactions, and hence elevated level of molecular stackings that were brought by enone functionalities.

Table 1. Thermotropic properties of the ELCs

$CH_3COCH{=}CHC_6H_4OOCC_6H_4OC_nH_{2n+1}$, [n = 4, 7, 9, 11, 12, 16]

		Mesophases and transition temperatures and enthalpy changes	
Compd.	n	Second heating/°C (ΔH, KJ/mol)	First cooling/°C (ΔH, KJ/mol)
5	**4**	K119(84.5)N139(1.3)I	I139(2.0)N93(75.8)K
6	**7**	K112(62.2)S_A125(2.9)N133(1.34)I	I132(1.5)N125(2.6)S_A75(51.8)K
7	**9**	K57(17.4)S_B108(68.1)S_A134(9.5)I	I134(9.7)S_A88(62.7)S_B38(20.6)K
8	**11**	K52(34.0)S_B106(64.3)S_A136(10.5)I	I136(10.1)S_A74(54.9)S_B44(33.1)K
9	**12**	K54(42.4)S_B104(66.8)S_A136(10.6)I	I136(10.8)S_A80(62.7)S_B47(41.9)K
10	**16**	K76(49.6)S_B102(67.3)S_A134(12.0)I	I135(11.9)S_A87(68.3)S_B70(46.9)K

K: Crystal phase; S: Smectic phase; N: Nematic phase; I: Isotropic phase.

Table 2. Thermotropic properties of CLCs

$CH_3COCH_2CHOHC_6H_4OOCC_6H_4C_6H_4OC_mH_{2m+1}$, [n = 8, 11, 16]

		Mesophases and transition temperatures	
Compd.	n	Second heating/°C (ΔH, KJ/mol)	First cooling/°C (ΔH, KJ/mol)
12	**8**	K79(36.0)S_A205(1.1)S_C*(1.8)223I	I223(1.8)S_C*206(1.0)S_A76(32.44)K
13	**11**	K128(98.8)S209(13.0)I	I215(8.9)S81(78.1)K
14	**16**	K123(95.3)S_C*208(12.7)I	I213(9.9)S_C*91(84.3)K

Cry: Crystal phase; S: Smectic Phase; N: Nematic Phase; I: Isotropic phase.

Besides, by varying the length of the terminal alkyl chain, the ELCs' melting points and the width of mesomorphic ranges were first increased (n = 4∼12), then started to fall (n = 12 and 16), which is typical to most rod-like liquid crystals.

3.2. *Revision of Our Design and Mesomorphic Studies of Chiral Rod-Like Liquid Crystals (12∼14)*

The absence of liquid crystal properties of **4** could be ascribed to its presumed uneven molecular plane, and hence disordered molecular stackings [1]. This hypothesis provided us a clue that other functional groups which were able to enhance and further stabilize molecular stackings should be added into **4**.

After deliberate considerations, we decided to introduce one more phenyl moiety into the chiral molecule **4**, and then three bisphenyl-derived benzaldehydes **11** were synthesized (Fig. 2), which were then utilized for the preparation of chiral aldol products **12∼14**.

Very gratifyingly, our revised design has been successful: POM and DSC studies showed that all new chiral compounds **12∼14** beared with excellent mesomorphic

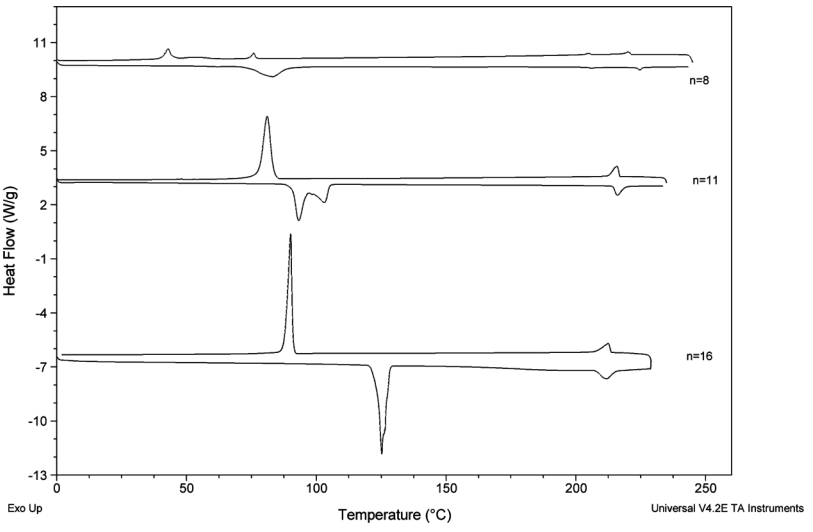

Figure 3. DSC traces of the CLCs.

properties. Besides, with the lengthening of the terminal alkyl chain, these CLCs showed higher melting points but narrower mesomorphic ranges. Phase transition temperatures and enthalpy changes of the CLCs were generalized in Table 2; their DSC traces were shown in Figure 3; and selected POM photographs were shown in Figure 4. It should be noted that the two peaks observed during the cooling process of **12** (n = 8, Fig. 3) could be associated with a monotropic phase transition and a crystallization, respectively. Vice versa, the two peaks observed during the heating process of **13** (n = 11, Fig. 3) could be explained as a crystal to S_A phase transition followed by a monotropic phase transition. Moreover, it is very noteworthy to mention that the newly prepared CLCs are elusive with traditional "chiral-pool" methods. Most importantly, this new methodology can generate CLCs that have a substituent with high polarity (e.g., hydroxy) on the stereogenic center. This is of interest, because the dipole moment of **12** and **14** (Table 2) may result into high spontaneous polarization (Ps) as presumed S_C^* phases were observed (Fig. 4) [1].

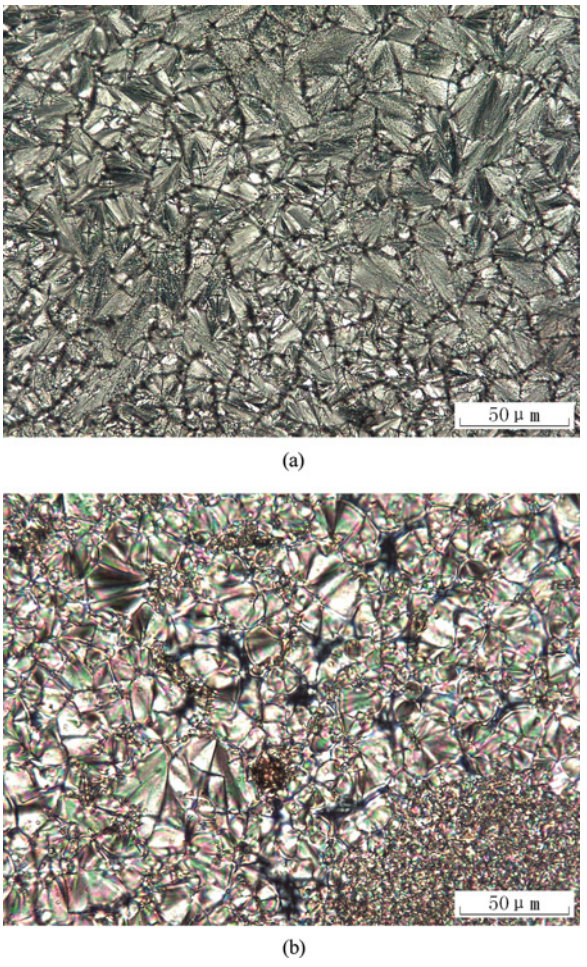

Figure 4. Selected POM photographs of the CLCs. (a) POM graph of **13** at 148°C; (b) POM graph of **14** at 157°C. (Figure appears in color online.)

4. Conclusions and Perspectives

In summary, we have successfully developed an unprecedented, organocatalytic method to synthesize chiral rod-like liquid crystals, starting from inexpensive, readily available and environmentally benign materials. Besides, a series of novel enone-containing rod-like mesogens were also prepared using this method. Improvements of the methodology and preparations of other categories of chiral liquid crystals are currently under investigations. Our future work will be focused on the study of spontaneous polarization properties of the newly synthesized chiral liquid crystals. Furthermore, our ultimate goal is to synthesize chiral liquid crystals from non-chiral and non-mesogenic starting materials.

Acknowledgment

We would like to thank the National Natural Science Foundation of China (No. 20872104 and No. 50973076) for generous financial support.

References

[1] Demus, D., *et al.* (1998). In: *Handbook of Liquid Crystals*, Gooby, J. W., Gray, G. W., & Spiess, H. W. (Eds.), Wiley-VCH: Weinheim, Chapter 5, 115.

[2] (a) Dierking, I. (2003). *Textures of Liquid Crystals*, Wiley-VCH: Weinheim, Chapter 7, 100; (b) Meyer, R. B., Liébert, L., Strzelecki, L., & Keller, P. (1975). *J. Phys. Lett.*, *36*, L69; (c) Durand, G., & Martinot-Lagarde, Ph. (1980). *Ferroelectrics*, *24*, 89.

[3] For a detailed explanation of "chiral-pool" method: Clayden, J., *et al.* (2001). *Organic Chemistry*, Oxford University Press: New York, Chapter 45, 1222.

[4] For a recent review of organocatalysis in asymmetric synthesis: (a) Pellisier, H. (2007). *Tetrahedron*, *63*, 9267; (b) Hayashi, Y. (2005). *J. Syn. Org. Chem. Jpn.*, *63*, 464; (c) Seayad, J., & List, B. (2005). *Org. Biomol. Chem.*, *3*, 719.

[5] For examples of L-proline-catalyzed aldolization between ketones, and aldehydes see: List, B., Lerner, R. A., & Barbas, C. F. (2000). *J. Am. Chem. Soc.*, *122*, 2395; List, B. (2002). *Tetrahedron*, *58*, 5573.

[6] Wang, J.-F., Lei, M., Li, Q., Ge, Z.-M., & Li, R.-T. (2009). *Tetrahedron*, *65*, 4826.

[7] (a) Alkylation of ethyl-4-hydroxybenzoate then hydrolysis was performed following the procedure reported by Shoichi, K., Hiroyuki, M., Machiko, F., Shigeharu, N., Koichi, S., & Kazuya, S. (2008). *Chem. Mater.*, *20*, 3675; (b) Esterification of 4-alkoxybenzoic acid, and 4-hydroxybenzaldehyde was performed following the procedure reported by Christina, K., Amaranatha, R. R., Anton, H., Ute, B., & Carsten, T. (2006). *J. Am. Chem. Soc.*, *128*, 3051.

[8] Malthete, J., Canceill, J., Gabard, J., & Jacques, J. (1981). *Tetrahedron*, *37*, 2815.