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# Liquid Crystalline 2-Cyclopropylcyclopropyl Derivatives – Synthesis and Evaluation of the Properties

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Liquid crystalline compounds containing (2-cyclopropylcyclopropyl)alkyl moieties in their side chains have been synthesized for the first time. Some of them showed mesophases SmA and SmB as well as N phases. In comparison to compounds with simple alkyl side chains, the new ones with the bicyclopropyl moieties were found to shift the phase transition temperatures to a lower temperature region. The dielectric and optical anisotropies of the compounds mainly depended on their mesogenic substructures.

Keywords Cyclopropane, synthesis, phase transition

## INTRODUCTION

Several liquid crystalline compounds containing only one terminal monosubstituted or internal 1,2-disubstituted cyclopropane moiety in their side chain have been reported [1–3]. However, liquid crystalline compounds having bicyclopropyl or higher oligocyclopropyl groups in their side chain have not been reported.*

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*The properties of the recently isolated natural products with quatercyclopropyl or even quinquecyclopropyl groupings in their fatty acid moieties are undoubtedly influenced by their peculiar structures [4, 5].

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The bicyclopropyl (2-cyclopropylcyclopropyl) moiety would not simply be a novel structural element in liquid crystalline compounds. It can also be expected to influence the rigidity due to its decreased degrees of freedom for internal rotation, thus resulting in different conformational preferences compared to an *n*-alkyl chain.** This feature would be expected to influence the order parameter and possibly favor liquid crystallinity over a wider temperature range. Based on the new convenient accessibility of bicyclopropylidene [7, 8], and the fact that all sorts of monosubstituted bicyclopropylidene derivatives can easily be prepared by deprotonation and subsequent electrophilic substitution [9] we have recently developed a synthetic access to alcohols and acids with a terminal bicyclopropyl moiety [10]. As one of the possible applications of these new building blocks, we have prepared a number of liquid crystalline compounds containing the novel 2-cyclopropylcyclopropyl moiety and evaluated their physical properties.

## SYNTHESIS

The novel liquid crystalline compounds **3** and **4** with *trans*-configurated terminal 2-cyclopropylcyclopropyl moieties were synthesized as outlined in Scheme 1. Bicyclopropylidenylalkanols (**1**, $n = 1$, 3, and 5), which were prepared by reactions of lithiated bicyclopropylidene with ethylene oxide ($n = 1$) and with $\omega$-tetrahydropyranyloxyalkyl iodides ($n = 3,5$), respectively, were reduced with lithium in liquid ammonia (Birch conditions) to give $\omega$-(*trans*-2-cyclopropylcyclopropyl)alkanols **2** [10].

The alcohols **2** were either transformed to the corresponding bromides by treatment with *N*-bromosuccinimide/triphenylphosphine, which in turn reacted with appropriate mesogenic phenols ($K_2C0_3$, EtOH, reflux) to yield the corresponding ethers, or they were oxidized with Jones reagent to give carboxylic acids, which were subsequently esterified with appropriate mesogenic phenols (DCC, DMAP, $CH_2Cl_2$) to give the corresponding ester derivatives **4**. The esters **6** with *cis*-configurated 2-cyclopropylcyclopropyl end groups were prepared from the corresponding bicyclopropylacetic acid obtained by Jones oxidation of the *cis*-configurated 2-(2′-cyclopropylcyclopropyl)ethanol **5** (Scheme 2).

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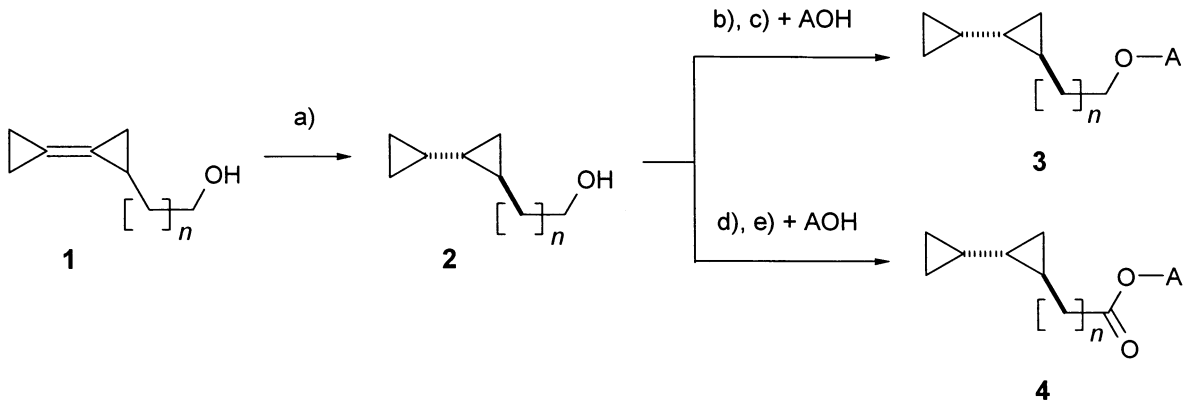
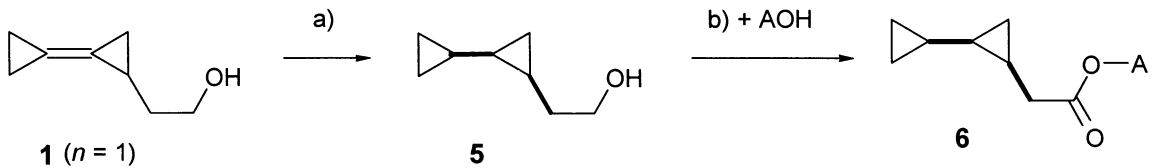
**Unsubstituted bicyc1opropyl at room temperature exists as an equilibrium mixture of ≅40% *ap* (*s-trans*) and ≅60% *sc* (gauche) conformer with a free enthalpy difference of 0.15 kcal · mol$^{-1}$ in favor of the *sc* conformer [6]. In *n*-butane, the conformational equilibrium favors the *ap* conformer by 0.9 kcal · mol$^{-1}$.




SCHEME 1 a) Li, liq. $NH_3$, −78→0°C. b) $PPh_3$, NBS. c) $K_2CO_3$, EtOH, Δ. d) Jones reagent, acetone, 0°C. e) DCC, DMAP, $CH_2Cl_2$. AOH = 4-(4-cyanophenyl)phenol, 4-(4-propylphenyl)phenol, 4-(4-pentylphenyl)phenol, 4-(5-octylpyrimid-2-yl)phenol, 4-[4-(4-propylcyclohexyl)cyclohexyl]phenol, 2,3-difluoro-4-[4-(4-propylcyclohexyl)-cyclohexyl]phenol. For details see Tables 1 and 2.




SCHEME 2 a) $H_2$, Lindlar cat. b) DCC, DMAP, $CH_2Cl_2$. AOH = 4-(4-cyanophenyl)phenol, 4-(4-propylphenyl)phenol, 4-(4-pentylphenyl)phenol, 4-(5-octylpyrimid-2-yl)phenol, 4-[4-(4-propylcyclohexyl)cyclohexyl]phenol, 2,3-difluoro-4-[4-(4-propylcyclohexyl)-cyclohexyl]phenol. For details see Table 3.

The latter was prepared by catalytic hydrogenation of bicyclopropylidenylethanol **1** ($n = 1$) over Lindlar catalyst. With this poisoned palladium catalyst the hydrogenation was selective for the strained double bond without opening of any of the cyclopropane rings (Scheme 1) [11]. Catalytic hydrogenations of **1** ($n = 1$) using Pd/C and $Pd/BaSO_4$ catalysts, however, gave mixtures of **5** and ring-opened products. In Schemes 1 and 2, "A" stands for the following mesogenic groups: **a**) 4′-cyanobiphenyl; **b**) 4′-propylbiphenyl; **c**) 4′-pentylbiphenyl; **d**) 4-(5-octylpyrimid-2-yl)phenyl; **e**) 4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]phenyl; **f**) 2,3-difluoro-4-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]phenyl.



## RESULTS AND DISCUSSION

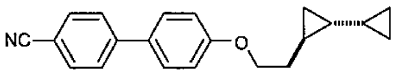
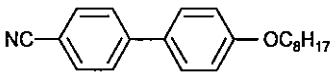
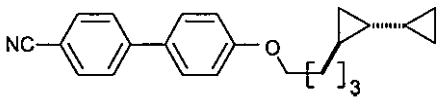
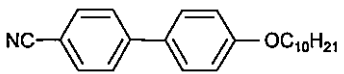
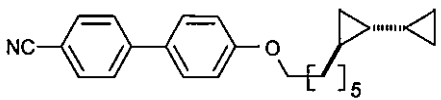
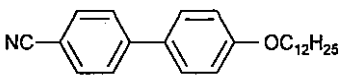
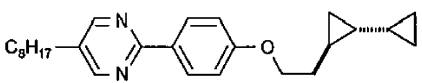
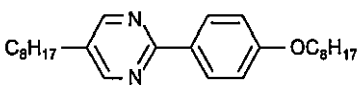
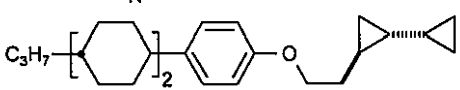
The phase transition temperatures of the ethers with *trans*-configurated 2-cyclopropylcyclopropyl end groups in their side chains are summarized in Table 1. When the 2-cyclopropylcyclopropyl moiety is too close to the mesogenic group as in compound **3a**-1, the liquid crystallinity is suppressed, so that only a melting point is exhibited, and no mesophase was found up to room temperature during the cooling process. However, compound **3a**-3, having four methylene groups between the bicyclopropyl unit and the mesogenic core, shows the C – SmA – N – I phase sequence around room temperature. An extension of the spacer, as in **3a**-5, with six methylene groups, stabilizes the SmA phase and decreases the temperature range of the N phase.

The pyrimidylphenyl derivative **3d** and the bicyclohexylphenyl compound **3e** show N phases with smectic phases SmA or SmB, respectively, even though the bicyclopropyl unit is as close to the mesogenic core as in **3a**-1. The transition temperatures of the novel compounds **3a**-1, **3a**-3, **3a**-5, and **3d** are all distributed in the lower temperature region compared to those of the compounds **ref-1**, **ref-2**, **ref-3**, and **ref-4** with *n*-alkyl chains.

Conversion of one methylene to a carbonyl group in the side chain strongly diminishes the liquid crystallinity (Table 2). The esters **4a** and **4d** do not show any mesomorphic phases during the heating and cooling processes up to room temperature, and only the compound **4d**-3, with an extended spacer between the core and the bicyclopropyl unit, exhibits a monotropic SmA phase.

Comparison of the transition sequences for the ether **3d** and the ester **4d** clearly indicates the difference of the two kinds of side chains in influencing the liquid crystalline properties. The alkylbiphenyl bicyclopropylacetates **4b** and **4c**, however, display more highly ordered smectic phases SmB. The

TABLE 1 Transition temperatures (°C) of the synthesized novel liquid crystalline ethers with *trans*-(2-cyclopropylcyclopropyl) end groups

| | *Compound* | *C* | *SmB* | *SmC* | *SmA* | *N* | *I* | *Ref.* |
|---|---|---|---|---|---|---|---|---|
| **3a-1** |  | • 69.9 | | | | | • | |
| **ref-1** |  | • 54.5 | | | • 67.0 | • 80.0 | • | [17] |
| **3a-3** |  | • < r. t. | | | • 22.0 | • 24.1 | • | |
| **ref-2** |  | • 59.5 | | | • 84.0 | | • | [18] |
| **3a-5** |  | • < r. t. | | | • 49.9 | | • | |
| **ref-3** |  | • 70.0 | | | • 90.0 | | • | [18] |
| **3d** |  | • < r. t. | | | • 15.9 | • 18.7 | • | |
| **ref-4** |  | • 29.0 | | • 56.0 | • 62.0 | • 69.0 | • | [19] |
| **3e** |  | • < r. t. | • 140.2 | | | • 143.2 | • | |

esters containing three rings in the mesogenic core, i. e., compounds **4e**-1, **4e**-3, and **4f**, exhibit C–SmB–N–I phase sequences again. The comparison of the transition temperatures of the novel compounds and the corresponding compounds with *n*-alkyl chains **ref-5**, **ref-6**, and **ref-7** shows again the shifting of the transition temperatures to a lower temperature region.

A comparison of compounds **4** having *trans*-configurated 2-cyclopropylcyclopropyl end groups, with the corresponding esters having *cis*-configurated bicyclopropyl end groups, is extremely interesting and important. It is well known that liquid crystallinity, particularly phase sequences, of liquid crystals with alkenyl side chains are strongly influenced by the configuration of the internal double bond in the side chain [12–16]. In all known cases, one of the two configurations (either *trans* or *cis*, depending on the position of the double bond) induces remarkably lower melting points and a poorer mesogenic potential compared to the respective diastereomer.

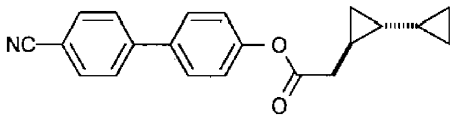
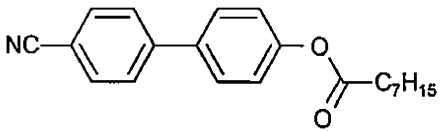
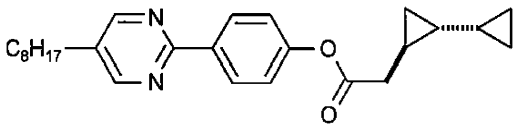
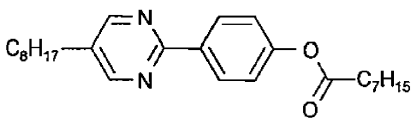
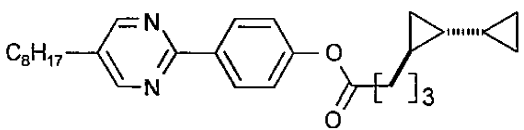
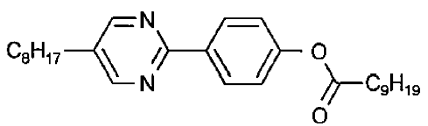
The *cis*- and *trans*-bicyclopropylacetates of two kinds of biphenyl derivatives, namely *p*-cyano- **6a** and **4a**, and *p*-(*n*-pentyl)biphenyl esters **6c** and **4c**, were investigated (Table 3). Surprisingly, in each case the *cis*-bicyclopropyl derivatives **6a** and **6c** have the higher melting point, and thus even **6c** shows no mesophase, whereas the corresponding *trans*-diastereomer **4c** displays an SmB phase. The length/breadth ratios (L/B ratios) of the compounds **6c** and **4c** have been estimated according to MOPAC-AM1 calculations [23]. Figure 1 shows the computed molecular structures of compounds **6c** and **4c** with their calculated L/B ratios. The estimated L/B ratio of compound **6c** is 3.16, which may be too small for the formation of a mesophase, while the L/B ratio of **4c** is 3.56.

The dielectric anisotropies ($\Delta\epsilon$) and optical anisotropies ($\Delta n$) of representative compounds are listed in Table 4. The values were obtained by extrapolations using the base mixture A or ZLI-1132 (see Experimental section below). The values are not significantly influenced by the novel 2-cyclopropylcyclopropyl moiety, but mainly by their mesogenic groups. The compounds **3e**, **4c**, **4e**-3, and **6c** show moderate values of $\Delta\epsilon$ and $\Delta n$, and compound **6a** exhibits large values of $\Delta\epsilon$ and $\Delta n$ because of the terminal CN substitution. The compound **4f** showed a large negative $\Delta\epsilon$ due to the fluorine substitution, with an orientation perpendicular to the chain.

## CONCLUSION

Novel liquid crystalline compounds having 2-cyclopropylcyclopropyl end groups in their side chains were synthesized, and their properties were

TABLE 2 Transition temperatures (°C) of the synthesized novel liquid crystalline esters with *trans*. (2-cyclopropylcyclopropyl) end groups

| | *Compound* | *C* | *SmB* | *SmC* | *SmA* | *N* | *I* | *Ref.* |
|---|---|---|---|---|---|---|---|---|
| **4a** |  | • 43.1 | | | | | • | |
| **ref-5** |  | • 78.0 | | | | (• 75.0) | • | [20] |
| **4d** |  | • 34.7 | | | | | • | |
| **ref-6** |  | • 51.0 | | • 52.0 | • 54.0 | • 56.0 | • | [21] |
| **4d-3** |  | • 35.5 | | | (• 29.9) | | • | |
| **ref-7** |  | • 42.0 | | • 55.5 | | • 59.8 | • | [22] |

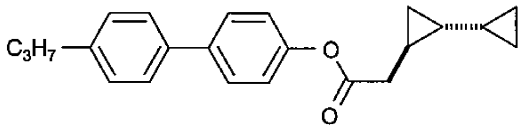
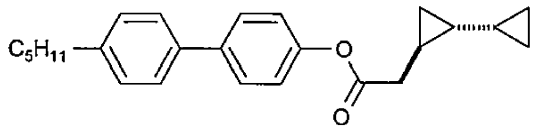
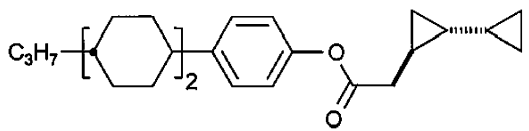
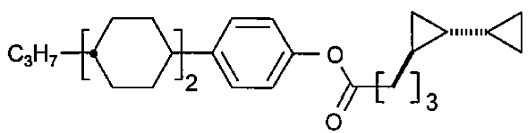
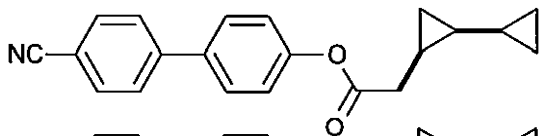
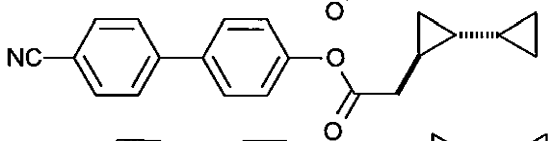
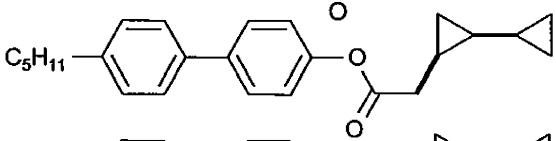
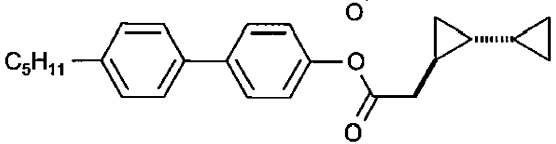
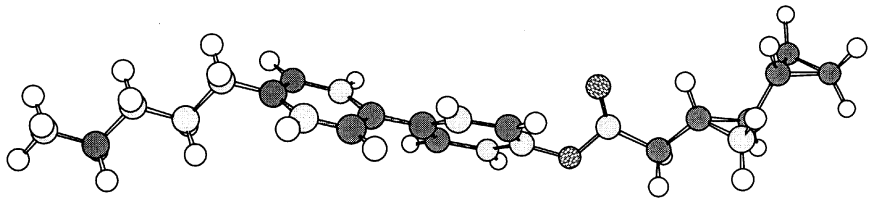
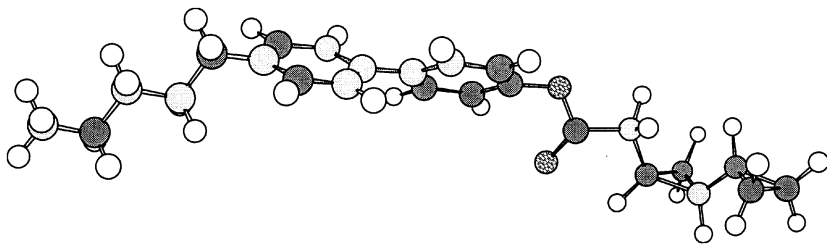
| | | | | | |
|---|---|---|---|---|---|
| **4b** |  | • < r. t. | • 49.1 | | • |
| **4c** |  | • < r. t. | • 53.7 | | • |
| **4e-1** |  | • < r. t. | • 149.0 | • 160.4 | • |
| **4e-3** |  | • < r. t. | • 160.8 | • 162.7 | • |
| **4f** |  | • < r. t. | • 65.3 | • 137.6 | • |

TABLE 3 Comparison of transition temperatures (°C) of *trans*- and *cis*-configurated bicyclopropyl derivatives

| | *Compound* | *C* | *SmB* | *I* |
|---|---|---|---|---|
| **6a** |  | • 73.8 | | • |
| **4a** |  | • 43.1 | | • |
| **6c** |  | • 48.0 | | • |
| **4c** |  | • < r. t. | • 53.7 | • |



**4c** L/B = 3.56



**6c** L/B = 3.16

FIGURE 1. Optimized structures of the bicyclopropyl derivatives **4c** with *trans*-configuration and **6c** with *cis*-configuration of the internal cyclopropyl group, respectively (L/B = Length/Breadth ratio).

evaluated. Due to the decreased conformational flexibility of the novel moiety, the new compounds have a higher tendency to be crystalline. However, compounds with longer spacers between the bicyclopropyl moiety and the mesogenic groups or with appropriately selected mesogenic groups

TABLE 4 Dielectric ($\Delta\varepsilon$) and optical anisotropy ($\Delta n$) of the synthesized compounds[a]

| *Compound* | $\Delta\varepsilon$ | $\Delta n$ |
|---|---|---|
| **3e** | 3.7 | 0.077 |
| **4c** | 3.7 | 0.070 |
| **4e**−3 | 3.7 | 0.077 |
| **4f** | −3.7[b] | 0.087[b] |
| **6a** | 10.3 | 0.137 |
| **6c** | 3.0 | 0.064 |

[a]Extrapolated, 15% in ZLI-1132 (see Experimental section of this article) unless otherwise indicated.
[b]Extrapolated, 10% in the base mixture A (see Experimental section of this article).

do exhibit mesophases SmA, SmB, and N. Their $\Delta\epsilon$ and $\Delta n$ values were mainly influenced by their mesogenic substructures and not significantly affected by the novel moiety in the side chains.

## EXPERIMENTAL

The transition temperatures of the synthesized novel liquid crystalline compounds were measured with a polarizing microscope, Nikon XTP-11, in conjunction with a Mettler hot stage FP 82 and a control unit FP 80. The physical properties, dielectric anisotropy and optical anisotropy, were evaluated by an extrapolation technique using a nematic base mixture A comprising phenylcyclohexanecarboxylates, namely 4-ethoxyphenyl *trans*-4-propylcyclohexanecarboxylate, 4-butoxyphenyl *trans*-4-propylcyclohexane carboxylate, 4-ethoxyphenyl *trans*-4-butylcyclohexanecarboxylate, 4-methoxyphenyl *trans*-4-pentylcyclohexanecarboxylate, and 4-ethoxyphenyl *trans*-4-pentylcyclohexanecarboxylate in the weight ratio of 10:16:12:12:8 (clearing point 76°C, $\Delta\epsilon$ − l.23), or ZLI-1132® (Merck GmbH). Dielectric anisotropy and optical anisotropy of nematic mixtures containing the synthesized compounds were measured with a HEWLETT PACKARD 4284A LCR meter and an ATAGO 4T & 2T Abbe refractometer, respectively.

All new compounds were purified by column chromatography on silica gel or by recrystallization. Their chemical structures were fully confirmed by spectroscopic techniques, i.e., IR [Bruker IFS 66 (FT-IR)], $^{1}$H NMR [Bruker AM 250 (250 MHz)], $^{13}$C NMR [Bruker AM 250 (62.9 MHz)], and mass spectrometry (Varian MAT CH 7). Their molecular formulas were established by elemental analysis.

### Synthesis of 4-cyano-4′-[2-(trans-2-cyclopropylcyclopropyl)-ethyloxy]-1,1′-biphenyl (3a-1)

#### *(1) 2-trans-2-Cyclopropylcyclopropyl)ethyl bromide*

To a solution of *trans*-2-(cyclopropylcyclopropyl)ethanol [10] (503 mg, 3.99 mmol) in dichloromethane (15 mL) was added triphenylphosphine (1.26 g, 4.80 mmol) and NBS (1.42 g, 7.98 mmol). The reaction mixture was stirred for 2 min and poured into ice-cooled water. Workup and column purification on silica gel ($R_f$ = 0.79, pentane/diethyl ether 5/1) gave 2-(*trans*-2-cyclopropylcyclopropyl)ethyl bromide (559 mg, 74%) as a colorless oil.

IR (KBr): $\nu$ 3076 cm $^{-1}$, 2997, 2961, 2924, 2861, 1456, 1428, 1260, 1211, 1016; $^{1}$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.01–0.06 (m, 2 H), 0.13–0.46 (m, 4 H),

0.53–0.67 (m, 2 H), 0.74–0.89 (m, 1 H), 1.67–1.82 (m, 2 H), 3.37 (t, *J* 7.1 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.87, 2.98, 9.56 (each, $CH_2$), 11.97, 15.68, 20.2 (each, CH), 33.75 ($CH_2$), 37.38 ($CH_2Br$); MS(70 eV, EI), *m*/*z* (%): 200/188 (21/23) [$M^+$], 109 (100).

### *(2) 4-Cyano-4′-[2-(trans-2-cyclopropylcyclopropyl)ethyloxy]-1,1′-biphenyl (3a-1)*

A mixture of 2-(*trans*-2-cyclopropylcyclopropyl)ethyl bromide (309 mg, 1.63 mmol), 4-(4-cyanophenyl)phenol(334 mg,1.71 mmol), $K_2CO_3$ (248 mg, 1.79 mmol) and ethanol (10 mL) was heated under reflux for 3 h. The usual workup followed by column chromatography on silica gel ($R_f$ = 0.34, pentane/diethyl ether 5/1) and recrystallization (MeOH) gave 96 mg (20%) of **3a**-1 as colorless crystals.

IR (KBr): *v* 3076 cm$^{-1}$,3063, 2997, 2950, 2929, 2222 (ArC≡N), 1605, 1494, 1250, 1013, 828; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.03–0.58 (m, 2 H), 0.19–0.38 (m, 4 H), 0.58–0.71 (m, 2 H), 0.78–0.87 (m, 1 H), 1.69 (q, *J* 6.6 Hz, 2 H), 4.03 (t, *J* 6.6 Hz, 2 H), 7.00 (d, *J* 8.8 Hz, 2 H), 7.52 (d, *J* 8.8 Hz, 2 H), 7.63 (d, *J* 13.6 Hz, 2 H), 7.66 (d, *J* 13.6 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.82, 2.97, 9.53 (each, $CH_2$), 12.01, 13.36, 20.26 (each, CH), 33.55 ($CH_2$), 67.94 ($CH_2O$), 109.82 (C), 114.93 (CH), 119.02 (C), 126.90, 128.18 (each, CH), 131.05 (C), 132.42 (CH), 145.96, 159.62 (each, C); MS (70 eV, EI), *m*/*z* (%): 303 (28) [$M^+$], 234 (22) [$M^+ - C_5H_9$], 195 (66) [$M^+ - C_8H_{12}$], 178(20), 166(26), 140(18), 93(24), 79(27), 67 (100).

### 4-Cyano-4′-[α;-(trans-2-cyclopropylcyclopropyl)acetoxy]-1,1′-biphenyl (4a)

A mixture of α-(*trans*-2-cyclopropylcyclopropyl)acetic acid [10] (190 mg, 1.36 mmol), 4-(4-cyanophenyl)phenol (318 mg, 1.63 mmol), DCC (336 mg, 1.63 mmol), DMAP (16 mg, 0.131 mmol) and dichloromethane (5 mL) was stirred for 5 h. The usual workup followed by column chromatography on silica gel ($R_f$ = 0.85, pentane/diethyl ether 1/1) and recrystallization (MeOH) gave **4a** (182 mg, 42%) as colorless crystals.

IR (KBr): *v* 3067 cm$^{-1}$, 2999, 2222 (ArC≡N), 1753 (C=O), 1605, 1493, 1170, 1158, 1126, 830; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.07–0.12 (m, 2 H), 0.32–0.47 (m, 4 H), 0.80–0.95 (m, 3 H), 2.47 (dd, *J* 15.8 Hz, 7.5 Hz, 1 H), 2.54 (dd, *J* 15.8 Hz, 6.7 Hz, 1 H), 7.21 (d, *J* 8.7 Hz, 2 H), 7.57 (d, *J* 8.7 Hz, 2 H), 7.62 (d, *J* 8.7 Hz, 2 H), 7.69 (d, *J* 8.7 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.81, 2.85, 9.74 (each, $CH_2$), 11.70, 11.83, 20.22 (each, CH), 38.74 ($CH_2CO$), 110.77 (C), 118.71 (CN), 122.18, 127.48, 128.15, 132.46 (each,

CH), 136.54, 144.54, 151.05 (each, C), 171.36 ($CO_2$); MS (70 eV, EI), *m/z* (%): 317 (4) [$M^+$], 195 (100) [$M^+ - C_7H_{10}CO$], 166 (7), 122 (10), 95 (12); Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.42; H, 5.84; N, 4.53.

According to the same procedures as used for the syntheses of compounds **3a**-1 and **4a**, the novel liquid crystalline compounds listed in Tables 1, 2, and 3 were prepared using 2-(*trans*-2-cyclopropylcyclopropyl)ethanol, 4-(*trans*-2-cyclopropylcyclopropyl)butanol, and 6-(*trans*-2-cyclopropylcyclopropyl)hexanol as the starting materials.



### 4-Cyano-4′-[4-(trans-2-cyclopropylcyclopropyl)butyloxy]-11′-biphenyl (3a-3)

Smectic at room temperature (287 mg, 60%). $R_f = 0.43$ (pentane/diethyl ether 5/1). IR (KBr): *v* 3074 $cm^{-1}$, 3039, 2996, 2936, 2855, 2225 (ArC≡N), 1604, 1494, 1250, 1180, 1014, 822; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.02–0.36 (m, 6 H), 0.41–0.58 (m, 2 H), 0.73–0.89 (m, 1 H), 1.21–1.60 (m, 4 H), 1.77–1.88 (m, 2 H), 3.99 (t, *J* 6.5 Hz, 2 H), 6.98 (d, *J* 8.7 Hz, 2 H), 7.52 (d, *J* 8.7 Hz, 2 H), 7.62 (d, *J* 8.5 Hz, 2 H), 7.67 (d, *J* 8.5 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.86, 2.95, 9.83 (each, $CH_2$), 12.18, 16.53, 20.35 (each, CH), 25.95, 28.89, 33.70 (each, $CH_2$), 68.06 ($CH_2O$), 109.86 (C), 114.96 (CH), 119.04 (CN), 126.94, 128.21 (each, CH), 131.08 (C), 132.45 (CH), 145.14, 159.68 (each, C); MS (70 eV, CI), *m/z* (%): 680 (15) [$2MNH_4^+$], 366 (48) [$MNH_4^+ + NH_3$], 349 (100) [$MNH_4^+$]; Anal. Calcd for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.16; H, 7.84; N, 4.35.

### 4-Cyano-4′-[6-(trans-2-cyclopropylcyclopropyl)hexyloxy]-1,1′-biphenyl (3a-5)

Smectic at room temperature (427 mg, 63%). $R_f = 0.40$ (pentane/diethyl ether 5/1). IR (KBr): *v* 3076 $cm^{-1}$, 2996, 2920, 2851, 2225 (ArC≡N), 1604, 1495, 1251, 821; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.01–0.20 (m, 3 H), 0.22–0.54 (m, 4 H), 0.73–0.79 (m, 1 H), 1.07–1.57 (m, 9 H), 1.78–1.84 (m, 2 H), 4.00 (t, *J* 6.5 Hz, 2 H), 6.98 (d, *J* 8.7 Hz, 2 H), 7.52 (d, *J* 8.7 Hz, 2 H), 7.64 (d, *J* 8.7 Hz, 2 H), 7.68 (d, *J* 8.7 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.75, 2.80, 8.82 (each, $CH_2$), 12.06, 16.45, 20.17 (each, CH), 25.80, 28.93, 28.96, 29.28, 33.78 (each, $CH_2$), 67.78 ($CH_2O$), 109.66 (C), 114.75 (CH), 118.75 (CN), 126.63, 127.95 (each, CH), 130.72 (C), 132.19 (CH), 144.80, 159.53 (each, C); MS (70 eV, EI), *m/z* (%): 359 (4) [$M^+$], 279 (6), 195 (100) [$M^+ - C_{12}H_{20}$], 166 (7), 140 (4); Anal. Calcd for $C_{25}H_{29}NO$: C, 83.52; H, 8.13; N, 3.90. Found: C, 83.31; H, 8.28; N, 3.88.

### 4-[2-(trans-2-Cyclopropylcyclopropyl)ethyloxy]-1-(5-octylpyrimid-2-yl)benzene (3d)

Colorless oil (223 mg, 43%). $R_f = 0.35$ (pentane/diethyl ether = 5/1). IR(KBr): $\nu$ 3074 $cm^{-1}$, 2995, 2924, 2853, 1607, 1584, 1430, 1253, 1168, 799; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 0.01–0.04 (m, 2 H), 0.17–0.34 (m, 4 H), 0.58–0.67 (m, 2 H), 0.79–0.88 (m, 4 H), 1.21–1.41 (m, 10 H), 1.60–1.70 (m, 4 H), 2.55 (t, $J$ 7.3 Hz, 2 H), 4.03 (t, $J$ 6.6 Hz, 2 H), 6.97 (d, $J$ 8.9 Hz, 2 H), 8.34 (d, $J$ 8.9 Hz, 2 H), 8.54 (s, 2 H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.79, 2.97, 9.52 (each, $CH_2$), 12.06, 13.43 (each, CH), 14.06 ($CH_3$), 20.26 (CH), 22.60, 28.94, 29.11, 29.22, 30.02, 30.72, 31.72, 33.61 (each, $CH_2$), 67.83 ($CH_2O$), 114.26, 129.27 (each, CH), 130.00, 131.95 (each, C), 156.81 (CH), 161.01, 162.32 (each, C); MS (70 eV, EI), $m/z$ (%): 393 (27), 392 (100) [$M^+$], 391 (40), 368 (24), 324 (32), 323 (82) [$M^+ - C_5H_9$], 284 (41), 185 (49); Anal. Calcd for $C_{26}H_{36}N_2O$: C, 79.55; H, 9.24; N, 7.14. Found: C, 79.56; H, 9.21; N, 7.04.

### 4-[2-(trans-2-Cyclopropylcyclopropyl)ethyloxy]-1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]benzene (3e)

Smectic at room temperature (189 mg, 47%). $R_f = 0.78$ (pentane/diethyl ether 5/1). IR (KBr): $\nu$ 3077 $cm^{-1}$, 2998, 2913, 2847, 1612, 1512, 1246, 1042; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 0.02–0.07 (m, 2 H), 0.17–0.34 (m, 4 H), 0.61–0.66 (m, 2 H), 0.79–1.57 (m, 20 H), 1.60–1.90 (m, 9 H), 2.39 (t, $J$ 9.3 Hz, 1 H), 3.96 (t, $J$ 6.8 Hz, 2 H), 6.83 (d, $J$ 8.6 Hz, 2 H), 7.11 (d, $J$ 8.6 Hz, 2 H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.86, 3.05, 9.55 (each, $CH_2$), 12.11, 12.87 (each, CH), 14.44 ($CH_3$), 20.05 ($CH_2$), 20.32 (CH), 30.08, 30.39, 33.59, 33.82, 34.83 (each, $CH_2$), 37.62 (CH), 39.83 ($CH_2$), 42.90, 43.41, 43.47 (each, CH), 67.75 ($CH_2O$), 114.15, 127.49 (each, CH), 139.81, 157.13 (each, C); MS (70 eV, CI), $m/z$ (%): 443 (10) [$MNH_4^+ + NH_3$], 426 (100) [$MNH_4^+$], 408 (12) [$M^+$]; Anal. Calcd for $C_{29}H_{44}O$: C, 85.23; H, 10.85. Found: C, 85.43; H, 10.82.

### 4-[α-(trans-2-Cyclopropylcyclopropyl)acetoxy]-1-(5-octylpyrimid-2-yl)benzene (4d)

Colorless solid (260 mg, 47%). $R_f = 0.14$ (pentane/diethyl ether 5/1). IR (KBr): $\nu$ 3076 $cm^{-1}$, 2997, 2925, 2853, 1761 (C=O), 1585, 1546, 1430, 1202, 1160, 1129, 797, 654; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 0.06–0.12 (m, 2 H), 0.22–0.41 (m, 4 H), 0.76–0.92 (m, 5 H), 1.21–1.32 (m, 12 H), 1.63–1.64 (m,

1 H), 2.41 (dd, *J* 15.8 Hz, 7.5 Hz, 1 H, $CH_2O$), 2.52 (dd, *J* 15.8 Hz, 7.0 Hz, 1 H, $CH_2O$), 2.60 (t, *J* 7.5 Hz, 2 H), 7.21 (d, *J* 8.9 Hz, 2 H), 8.44 (d, *J* 8.9 Hz, 2 H), 8.61 (s, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.81, 2.89, 8.72 (each, $CH_2$), 11.76, 11.91 (each, CH), 14.01 ($CH_3$), 20.26 (CH), 22.55, 28.96, 29.09, 29.21, 30.06, 30.67, 31.72, 38.88 (each, $CH_2$), 121.54, 129.01 (each, CH), 132.86, 135.10, 152.52 (each, C), 156.91 (CH), 161.69 (C), 171.24 ($CO_2$); MS (70 eV, CI), *m/z* (%): 407 (100) [$M^+ + H$], 383 (11), 287 (6), 285 (19), 269 (9); Anal. Calcd for $C_{26}H_{34}N_2O_2$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.63; H, 8.70; N, 6.94.



### 4-[4-(trans-2-Cyclopropylcyclopropyl)butanoyloxy]-1-(5-octylpyrimid-2-yl)benzene (4d-3)

Colorless solid (540 mg, 65%). $R_f = 0.30$ (pentane/diethyl ether 5/1). IR (KBr): *v* 3077 $cm^{-1}$, 2997, 2928, 2853, 1758 (C=O), 1585, 1546, 1430, 1203, 1160, 1140, 1013, 798, 653; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.03–0.37 (m, 5 H), 0.45–0.59 (m, 1 H), 0.77–0.90 (m, 4 H), 1.27–1.50 (m, 14 H), 1.59–1.76 (m, 3 H), 1.78–1.87 (m, 1 H), 2.54–2.64 (m, 4 H), 7.19 (d, *J* 8.7 Hz, 2 H), 8.43 (d, *J* 8.7 Hz, 2 H), 8.60 (s, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.73, 2.97, 9.63 (each, $CH_2$), 12.09 (CH), 13.95 ($CH_3$), 16.23, 20.34 (each, CH), 22.50, 24.76, 28.90, 29.04, 29.15, 29.99, 30.59, 31.67, 33.24, 33.89 (each, $CH_2$), 121.45, 128.94 (each, CH), 132.76, 135.02, 152.45 (each, C), 156.82 (CH), 161.61 (C), 171.76 ($CO_2$); MS (70 eV, CI), *m/z* (%): 452 (2) [$MNH_4^+$], 435 (100) [$M^+ + H$], 411 (42) [$MNH\}_4^+ - C_3H_5$], 285 (26) [$MNH_4^+ - C_9H_{15}CO_2$], 269 (32).

### 4-[α-(trans-2-Cyclopropylcyclopropyl)acetoxy]-4′-propyl-1,1′-biphenyl (4b)

Smectic at room temperature (153 mg, 58%). $R_f = 0.56$ (pentane/diethyl ether 5/1). IR (KBr): *v* 3074 $cm^{-1}$, 2998, 2954, 2928, 2868, 1749 (C=O), 1494, 1204, 1170, 1157, 1004, 834, 810; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.08–0.13 (m, 2 H), 0.34–0.46 (m, 5 H), 0.81–0.92 (m, 2 H), 0.97 (q, *J* 7.4 Hz, 3 H), 1.67 (t, *J* 7.4 Hz, 2 H), 2.38 (dd, *J* 15.8 Hz, 7.5 Hz, 1 H), 2.53 (dd, *J* 15.8 Hz, 6.8 Hz, 1 H), 2.64 (t, *J* 7.4 Hz, 2 H), 7.14 (d, *J* 8.6 Hz, 2 H), 7.23 (d, *J* 8.1 Hz, 2 H), 7.48 (d, *J* 8.1 Hz, 2 H), 7.57 (d, *J* 8.6 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.91, 2.95, 9.85 (each, $CH_2$), 11.84, 12.37 (each, CH), 13.88 ($CH_3$), 20.35 (CH), 24.55, 37.65, 38.96 (each, $CH_2$), 121.76, 126.91, 127.95, 128.89 (each, CH), 137.73, 138.85, 141.91, 149.90 (each, C), 171.72 ($CO_2$); MS (70 eV, CI), *m/z* (%): 686 (7) [$2MNH_4^+$], 369

(5) [$MNH_4^+ + NH_3$], 352 (100) [$MNH_4^+$]; Anal. Calcd for $C_{23}H_{26}O_2$: C, 82.60; H, 7.84. Found: C, 82.85; H, 8.04.

### 4-[α-(trans-2-Cyclopropylcyclopropyl)acetoxy]-4′-pentyl-1,1′-biphenyl (4c)

Smectic at room temperature (320 mg, 65%). $R_f = 0.38$ (pentane/diethyl ether 5/1). IR (KBr): $\nu$ 3075 $cm^{-1}$, 2999, 2953, 2921, 2852, 1750 (C=O), 1495, 1205, 1171, 1157, 831; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 0.10–0.15 (m, 2 H), 0.34–0.49 (m, 4 H), 0.80–1.00 (m, 6 H), 1.33–1.39 (m, 4 H), 1.60–1.73 (m, 2 H), 2.40 (dd, $J$ 15.8 Hz, 7.5 Hz, 1 H), 2.55 (dd, $J$ 15.8 Hz, 6.7 Hz, 1 H), 2.66 (t, $J$ 7.3 Hz, 2 H), 7.17 (d, $J$ 8.5 Hz, 2 H), 7.26 (d, $J$ 8.0 Hz, 2 H), 7.50 (d, $J$ 8.0 Hz, 2 H), 7.60 (d, $J$ 8.5 Hz, 2 H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.89, 2.93, 9.82 (each, $CH_2$), 11.81, 12.00 (CH), 14.01 ($CH_3$), 20.32 (CH), 22.57, 31.14, 31.50, 35.52, 38.92 (each, $CH_2$), 121.72, 126.89, 127.91, 128.80 (each, CH), 137.65, 138.82, 141.14, 149.87 (each, C), 171.67 ($CO_2$); MS (70 eV, CI), $m/z$ (%): 742 (9) [$2MNH_4^+$], 380 (100) [$MNH_4^+$]; Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83, H, 8.34. Found: C, 82.68, H, 8.10.

### 4-[α-(trans-2-Cyclopropylcyclopropyl)acetoxy]-1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]benzene (4e-1)

Smectic at room temperature (185 mg, 77%). $R_f = 0.72$ (pentane/diethyl ether 5/1). IR (KBr): $\nu$ 3071 $cm^{-1}$, 2996, 2949, 2915, 2841, 1766 (C=O), 1508, 1323, 1195, 1164, 1145, 1121, 1015; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 0.07–0.10 (m, 2 H), 0.32–0.44 (m, 4 H), 0.76–1.42 (m, 22 H), 1.74–1.93 (m, 7 H), 2.33 (dd, $J$ 15.8 Hz, 7.6 Hz, 1 H), 2.44 (m, 1 H), 2.51 (dd, $J$ 15.8 Hz, 6.8 Hz, 1 H), 6.98 (d, $J$ 8.5 Hz, 2 H), 7.19 (d, $J$ 8.5 Hz, 2 H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.93 (2 $CH_2$), 9.82 ($CH_2$), 11.83, 12.38 (each, CH), 14.43 ($CH_3$), 20.02 ($CH_2$), 20.31 (CH), 30.06, 30.29, 33.58, 34.63 (each, $CH_2$), 37.59 (CH), 38.94, 39.89 (each, $CH_2$), 42.86, 43.37, 44.07, 121.13, 127.66 (each, CH), 145.30, 148.61 (each, C), 171.82 ($CO_2$); MS (70 eV, CI), $m/z$ (%): 862 (3) [$2MNH_4^+$], 440 (100) [$MNH_4^+$], 416 (16); Anal. Calcd for $C_{29}H_{42}O_2$: C, 82.41; H, 10.02. Found: C, 82.63; H, 10.13.

### 4-[4-(trans-2-Cyclopropylcyclopropyl)butanoyloxy]-1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]benzene (4e-3)

Smectic at room temperature (481 mg, 89%). $R_f = 0.73$ (pentane/diethyl ether 5/1). IR (KBr): $\nu$ 3078 $cm^{-1}$, 2999, 2915, 2848, 1757 (C=O), 1508,

1447, 1204, 1170, 1141, 1015, 837, 539; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.02–0.57 (m, 7 H), 0.74–1.56 (m, 23 H), 1.74–1.92 (m, 9 H), 2.38–2.50 (m, 1 H), 2.56 (t, *J* 7.4 Hz, 2 H), 6.96 (d, *J* 8.5 Hz, 2 H), 7.18 (d, *J* 8.5 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.79, 3.01, 9.76 (each, $CH_2$), 12.15 (CH), 14.37 ($CH_3$), 16.29 (CH), 19.98 ($CH_2$), 20.40 (CH), 24.90, 30.01, 30.24, 33.32, 33.52, 34.57, 34.83 (each, $CH_2$), 37.55 (CH), 39.76 ($CH_2$), 42.80, 43.32, 44.01, 121.05, 127.53 (each, CH), 145.10, 148.56 (each, C), 172.28 ($CO_2$); MS (70 eV, CI), *m/z* (%): 485 (4) [$MNH_4^+ + NH_3$], 469 (35), 468 (100) [$MNH_4^+$], 445 (12), 444 (36), 388 (10); Anal. Calcd for $C_{31}H_{46}O_2$: C, 82.61; H, 10.29. Found: C, 82.79; H, 10.13.

### 1-[α-(trans-2-Cyclopropylcyclopropyl)acetoxy]-2,3-difluoro-4-(trans-4-(trans-4-propylcyclohexyl)cyclohexyl]benzene (4f)

Smectic at room temperature (248 mg, 95%). $R_f = 0.72$ (pentane/diethyl ether 5/1). IR (KBr): *v* 2905 cm$^{-1}$, 2847, 1749 (C=O), 1502, 1473, 1292, 1262, 1204, 1120, 1041; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.07–0.11 (m, 2 H), 0.33–0.43 (m, 4 H), 0.77–1.57 (m, 22 H), 1.74–1.90 (m, 7 H), 2.39 (dd, *J* 15.9 Hz, 7.5 Hz, 1 H), 2.56 (dd, *J* 15.9 Hz, 7.5 Hz, 1 H), 2.78 (t, *J* 11.7 Hz, 1 H), 6.79–6.98 (m, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.80, 2.94, 9.80 (each, $CH_2$), 11.76, 12.29 (CH), 14.42 ($CH_3$), 20.02 ($CH_2$), 20.39 (CH), 30.02, 30.09, 33.03, 33.54 (each, $CH_2$), 37.17, 37.58 (each, CH), 38.37, 39.79 (each, $CH_2$), 42.80, 43.31, 117.77, 120.93 (each, CH), 133.90, 134.10 (C), 143.02 (dd, *J* 250 Hz, 15.3 Hz), 148.99 (dd, *J* 247 Hz, 10.4 Hz), 170.46 ($CO_2$); MS (70 eV, CI), *m/z* (%): 493 (8) [$MNH_4^+ + NH_3$], 477 (32), 476 (100) [$MNH_4^+$], 458 (20) [$M^+$]; Anal. Calcd for $C_{29}H_{40}F_2O_2$: C, 75.95, H, 8.79. Found: C, 75.98, H, 8.88.

### Synthesis of 4-cyano-4′-[α-(cis-2-cyclopropylcyclopropyl)acetoxy]-1,1′-biphenyl (6a)

#### *(1) Synthesis of cis-2-(cyclopropylcyclopropyl)ethanol*

A mixture of bicyclopropylidenylethanol **1** ($n = 1$) (475 mg, 3.83 mmol), Lindlar catalyst (220 mg), and MeOH (10 mL) was stirred under hydrogen atmosphere for 12 h. The catalyst was removed by filtration, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel ($R_f = 0.29$, pentane/diethyl ether 1/1) to give cis-2-(cyclopropylcyclopropyl)ethanol (269 mg, 56%) as a colorless oil.

IR (Film): *v* 3328 cm$^{-1}$, 3077, 2997, 2931, 2870, 1451, 1427, 1292, 1051, 1015, 842, 821; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.14–0.16 (m, 2 H),

0.41–0.58 (m, 6 H), 0.70–0.76 (m, 1 H), (1.59 (s, 1 H), 1.65 (q, *J* 6.8 Hz, 1 H), 1.70 (q, *J* 6.8 Hz, 1 H), 3.76 (t, *J* 6.8 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 4.14, 4.32, 8.85 (each, $CH_2$), 8.93, 12.63, 18.39 (each, CH), 32.13, 63.02 (each, $CH_2$); MS (70 eV, CI), *m/z* (%): 178 (4), 161 (8) [$MNH_4^+ + NH_3$], 144 (100) [$MNH_4^+$], 127 (15), 126 (15), 109 (50).

### *(2) α-(cis-2-Cyclopropylcyclopropyl)acetic acid*

To a solution of *cis*-2-(cyclopropylcyclopropyl)ethanol (250 mg, 1.98 mmol) in acetone (9 mL), Jones reagent was added at 6°C until the reddish color persisted. The usual workup gave α-(*cis*-2-cyclopropylcyclopropyl)acetic acid (276 mg, 99%) as a colorless oil.

$R_f = 0.32$ (pentane/diethyl ether = 1/1). IR (film): *v* 3077 cm$^{-1}$, 3000, 1710 (C=O), 1418, 1296, 1184, 1018, 935, 823; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ −0.06 to 0.01 (m, 1 H), 0.05–0.18 (m, 2 H), 0.33–0.49 (m, 2 H), 0.51–0.66 (m, 2 H), 0.75–0.86 (m, 1 H), 1.03–1.18 (m, 1 H), 2.45 (dd, *J* 16.7 Hz, 1 H), 2.48 (dd, *J* 16.7 Hz, 7.5 Hz, 1 H), 12.05 (brs, 1 H, OH); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 4.02, 4.23 (each, $CH_2$), 8.66 (CH), 8.91 ($CH_2$), 11.74, 18.17 (each, CH), 33.99 ($CH_2$), 159.30 ($CO_2$); MS (70 eV, EI), *m/z* (%): 140 (8) [$M^+$], 95 (33), 80 (100) [$M^+ - C_2H_4O_2$], 67 (68), 59 (60), 54 (69), 43 (95); Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.77, H, 8.90.

### *(3) 4-Cyano-4′-[α-(cis-2-cyclopropylcyclopropyl)acetoxy]-1,1′-biphenyl (6a)*

A mixture of α-(*cis*-2-cyclopropylcyclopropyl)acetic acid (180 mg, 1.29 mmol), 4-(4-cyanophenyl)phenol (275 mg, 1.41 mmol), DCC (320 mg, 1.55 mmol), DMAP (16 mg, 0.131 mmol) and dichloromethane (10 mL) was stirred for 15 h. The usual workup followed by column chromatography on silica gel ($R_f = 0.60$, pentane/diethyl ether 1/1) and recrystallization (MeOH) gave **6a** (91 mg, 22%) as colorless crystals.

IR (KBr): *v* 3065 cm$^{-1}$, 2987, 2227 (ArC≡N), 1749 (C=O), 1600, 1493, 1390, 1320, 1169, 1152, 1113, 845, 826; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.08 (q, *J* 5.2 Hz, 1 H), 0.20–0.22 (m, 2 H), 0.55 (t, *J* 7.5 Hz, 2 H), 0.63–0.75 (m, 2 H), 0.81–0.92 (m, 1 H), 1.18–1.29 (m, 1 H), 2.70 (d, *J* 7.5 Hz, 2 H), 7.22 (d, *J* 8.7 Hz, 2 H), 7.62 (d, *J* 8.7 Hz, 2 H), 7.60 (d, *J* 8.5 Hz, 2 H), 7.71 (d, *J* 8.5 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 4.06, 4.24 (each, $CH_2$), 8.71 (CH), 9.02 ($CH_2$), 11.87, 18.27 (each, CH), 34.34 ($CH_2CO$), 110.81 (CN), 118.74 (C), 122.21, 127.52, 128.17, 132.50 (each, CH), 136.53, 144.61, 151.18 (each, C), 172.06 ($CO_2$); MS (70 eV, EI), *m/z* (%): 317 (7) [$M^+$], 195 (100)

$[M^+ - C_7H_{10}CO]$, 166 (9), 140 (8), 122 (13), 95 (18); Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47, H, 6.03, N, 4.41. Found: C, 79.39, H, 5.97, N, 4.35.

### 4-[α-(cis-2-Cyclopropylcyclopropyl)acetoxy]-4′-pentyl-1,1′-biphenyl (6c)

According to the procedures for the synthesis of **6a**, compound **6c** was prepared from α-(*cis*-2-cyclopropylcyclopropyl)acetic acid and 4-(4-cyanophenyl)phenol.

Colorless solid (128 mg, 32%). $R_f = 0.65$ (pentane/diethyl ether 5/1). IR (KBr): $\nu$ 3073 $cm^{-1}$, 2998, 2951, 2924, 2854, 1759 (C=O), 1495, 1321, 1203, 1166, 1146, 1125, 1005, 808; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 0.05–0.11 (m, 2 H), 0.20–0.22 (m, 2 H), 0.47–0.55 (m, 2 H), 0.66–0.75 (m, 2 H), 0.83–0.93 (m, 4 H), 1.25–1.37 (m, 4 H), 1.55–1.68 (m, 2 H), 2.64 (t, *J* 8.1 Hz, 2 H), 2.69 (d, *J* 7.3 Hz, 2 H), 7.16 (d, *J* 8.5 Hz, 2 H), 7.24 (d, *J* 8.1 Hz, 2 H), 7.41 (d, *J* 8.1 Hz, 2 H), 7.57 (d, *J* 8.5 Hz, 2 H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 4.11, 4.28 (each, $CH_2$), 8.71 (CH), 9.05 ($CH_2$), 11.79 (CH), 13.97 ($CH_3$), 18.33 (CH), 22.49, 31.10, 31.47, 34.41, 35.48 (each, $CH_2$), 121.69, 126.84, 127.83, 128.75 (each, CH), 137.64, 138.70, 142.04, 149.96 (each, C), 172.21 ($CO_2$); MS (70 eV, EI), *m/z* (%): 362 (13) $[M^+]$, 240 (100) $[M^+ - C_7H_{10}CO]$, 183 (47); Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.06; H, 8.37.



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