SUPPORTING INFORMATION

Synthesis and Thermal Behavior of Chiral Dimers: Occurrence of Highly Frustrated and Cholesteric Liquid Crystal Phases

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Contents

I. General

All the chemicals were obtained from either Sigma Aldrich Chemicals (Pvt.) Ltd or Lancaster Company and used as received. All the solvents were purified and dried by standard methods and the crude samples were purified by column chromatographic technique using either silica gel (230-400 mesh) or neutral aluminium oxide as a stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254). The absorption spectra were recorded on a Perkin-Elmer Lambda 20 UV-Vis spectrometer. IR spectra were recorded using Perkin Elmer Spectrum 1000 FT-IR spectrometer. 1H NMR spectra were recorded using either a Bruker AMX-400 (400 MHz) or a Bruker Aveance series DPX-200 (200MHz) spectrometer and the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a Jeol-JMS-600H spectrometer in FAB+ mode using 3-nitrobenzyl alcohol as a liquid matrix. Elemental analyses were done using Eurovector model EA 3000 CHNS analyzer. The identification of the mesophases and the transition temperatures of the compounds were initially determined using a polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90). The transition temperatures and associated enthalpies were determined by differential scanning calorimetry (Perkin Elmer DSC7). X-Ray diffraction studies were carried on powder samples in Lindemann capillaries with CuKα radiation using an Image Plate Detector (MAC Science, Japan) equipped with a double mirror focusing optics.

II. General procedure for the synthesis of intermediates and final compounds (Scheme I).

II.1 4-*n*-Alkoxy benzaldehydes (3a-c) and 4-*n*-alkoxycinnamic acid (6a-c)

These intermediates were synthesized using the procedure described previously.[1]

General procedure for the synthesis of 3,4-*n*-dialkoxy benzaldehyde (4a-c).

A mixture of 3,4-dihydroxy benzaldehyde (36.20 mmol, 1 equiv.), anhyd. K_2CO_3 (144.80 mmol, 4 equiv.) and *n*- bromoalkane (79.64 mmol, 2.2 eq) was taken in dry DMF and stirred at 80 °C for 12 hours under nitrogen atmosphere. The cooled reaction mixture was poured into ice-water and extracted with dichloromethane (2 × 25 ml). The combined extracts were washed with water, brine, dried over anhyd. Na_2SO_4 and concentrated. The crude product was purified by column chromatography using neutral alumina. Elution with hexanes followed by 5-10% ethyl acetate-hexanes yielded the desired intermediates.

4a: R_f = 0.48 in 10% EtOAc-hexanes; a colorless solid, m.p.: 54 °C yield: 86 %; IR (KBr pellet): ν_{max} in cm^{-1} 2924, 2850, 1683, 1673, 1164; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 9.83 (s, 1H, CHO), 7.40-7.43 (m, 2H, Ar), 6.95 (d, 1H, *J* = 8 Hz), 4.07 (q, 4H, *J* = 6.4 Hz, 2 × OCH_2), 0.85-1.9 (m, 30H, 12 × CH_2, 2 × CH_3); MS (FAB+): m/z calcd for $C_{23}H_{39}O_3$ (M+1): 363.3. Found: 363.1.

4b: R_f = 0.48 in 10% EtOAc-hexanes; a colorless solid, m.p.: 64 °C; yield: 80 %; IR (KBr pellet): ν_{max} in cm^{-1} 2922, 2850, 1683, 1672, 1134; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 9.83 (s, 1H, CHO), 7.39-7.44 (m, 2H, Ar), 6.95 (d, 1H, *J* = 8 Hz), 4.02- 4.11 (q, 4H, *J* = 6.4 Hz, 2 × OCH_2), 0.85-1.9 (m, 38H, 16 × CH_2, 2 × CH_3); MS (FAB+): m/z calcd for $C_{27}H_{47}O_3$ (M+1): 419.3. Found: 419.5.

4c: R_f = 0.49 in 10% EtOAc-hexanes; a colorless solid, m.p.:70 °C; yield: 82 %; IR (KBr pellet): ν_{max} in cm^{-1} 2919, 2850, 1683, 1671, 1134; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 9.83 (s, 1H, CHO), 7.39-7.44 (m, 2H, Ar), 6.95 (d, 1H, *J* = 8 Hz), 4.02- 4.11 (q, 4H, *J* = 6.4 Hz, 2 × OCH_2), 0.85-1.9 (m, 46H, 20 × CH_2, 2 × CH_3); MS (FAB+): m/z calcd for $C_{31}H_{55}O_3$ (M+1): 475.4. Found: 475.4.

II.2 General procedure for the synthesis of 3,4-*n*-dialkoxy cinnamic acid (7a-c).

A mixture of 3,4-*n*-dialkoxy benzaldehyde (**4a-c**) (5.51 mmol, 1 equiv.), malonic acid (8.27 mmol, 1.5 equiv.), pyridine and catalytic amount of piperidine were refluxed for 10 hours at 120°C. The reaction mixture was cooled and neutralized with 20% (aq) HCl to get a white precipitate. The crude material was filtered and washed with water. The product was further purified by recrystallization from EtOAc: EtOH (1:9).

7a: R_f = 0.30 in 30% CH_2Cl_2-hexanes; a colorless solid ; yield: 75 %; m.p.: 129 °C; IR (neat): ν_{max} in cm^{-1} 3018, 2923, 1684, 1623, 1172; ^{1}H NMR (400MHz, $CDCl_3$): δ 12.56 (s, 1H, 1 × OH), 7.28 (d, 1H, *J* = 15.8 Hz 1 × olefinic), 7.10 (m, 2H, Ar), 6.87 (d, *J* = 8.0 Hz. 1H, Ar), 6.31 (d, 1H, *J* = 15.9 Hz 1 × olefinic), 4.04 (t, *J* = 6.5 Hz, 4H, 2 × OCH_2), 1.86-0.87 (m, 30H, 12 × CH_2, 2 × CH_3); MS (FAB+): m/z calcd for $C_{25}H_{41}O_3$ (M+1): 405.3. Found: 405.4.

7b: R_f = 0.34 in 30% CH_2Cl_2-hexanes; a colorless solid ; yield: 80 %; m.p.: 128 °C; IR (neat): ν_{max} in cm^{-1} 3018, 2919, 1660, 1621, 1173; ^{1}H NMR (400MHz, $CDCl_3$): δ 12.54 (s, 1H, 1 × OH), 7.72 (d, 1H, *J* = 15.8 Hz 1 × olefinic), 7.10 (m, 2H, Ar), 6.87 (d, *J* = 8.0 Hz. 1H, Ar), 6.31 (d, 1H, *J* = 15.9 Hz 1 × olefinic), 4.04 (t, *J* = 6.4 Hz, 4H, 2 × OCH_2), 1.86-0.87 (m, 38H, 16 × CH_2, 2 × CH_3); MS (FAB+): m/z calcd for $C_{29}H_{50}O_4$ (M+2): 462.4. Found: 462.8.

7c: R_f = 0.35 in 30% CH_2Cl_2-hexanes; a colorless solid ; yield: 83 %; m.p.: 127 °C; IR (neat): ν_{max} in cm^{-1} 3022, 2983, 1723, 1660, 1141; ^{1}H NMR (400MHz, $CDCl_3$): δ 12.59 (s, 1H, 1 × OH), 7.73 (d, 1H, *J* = 15.8 Hz 1 × olefinic), 7.10 (m, 2H, Ar), 6.87 (d, *J* = 8.2 Hz. 1H, Ar), 6.31 (d, 1H, *J* = 15.9 Hz 1 × olefinic), 4.05 (t, *J* = 6.5 Hz, 4H, 2 × OCH_2), 1.87-0.86 (m, 46H, 20 × CH_2, 2 × CH_3); MS (FAB+): m/z calcd for $C_{33}H_{57}O_4$ (M+1): 516.4. Found: 516.7.

II.3 Procedure for the synthesis of 2,3,4 *n*-tridodecyloxy cinnamic acid (8).

A mixture 2,3,4-*n*-tridodecyloxy benzaldehyde (**5**)[2] (2g, 3.03 mmol, 1 equiv.), malonic acid (0.47g, 4.55 mmol, 1.5 equiv.), pyridine and catalytic amount of piperidine was flask refluxed for 10 hours at 120 °C. The reaction mixture was cooled and neutralized with ice-cold 20% (aq) HCl to get a precipitate. The crude material was filtered and washed with water. The product was further purified by recrystallization from EtOAc: EtOH (1:9).

8: R_f = 0.58 in 30% CH_2Cl_2-hexanes; a colorless solid; yield: 70 %; IR (KBr pellet): ν_{max} in cm^{-1} 3024, 2984, 1725, 1680, 1142; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 12.26 (s, 1H, 1 × OH), 7.73 (d, 1H, *J* = 16.0 Hz 1 × olefinic), 7.56 (d, 1H, *J* = 8.0 Hz, Ar), 6.78 (d, 1H, *J* =9.4 Hz, Ar), 6.34 (d, 1H, *J* = 15.8 Hz 1 × olefinic), 4.4 (t, 2H, *J* = 6.4 Hz, 1 × OCH_2), 3.93- 4.04(m, 4H, 2 × OCH_2), 1.28 -1.78 (m, 60H, 30 × CH_2), 0.87 (t, 9H, *J* = 6.1 Hz, 3 × CH_3); MS (FAB+): m/z calcd for $C_{45}H_{81}O_4$ (M+1): 701.6. Found: 701.3.

II.4 General procedure for the synthesis of the cholesteryl ω-[4-(4'-*n*-alkoxycinnamoyloxy)phenoxy]alkanoates (MDC-n,R series).

A mixture of cholesteryl ω-(4'-hydroxyphenoxy) alkanoate (**2a-d**)[3] (0.27 mmol, 1 equiv.), 4-*n*-alkoxy cinnamic acid (**6a-c**) (0.275 mmol, 1 equiv.) and 4-dimethylamino pyridine (DMAP) (0.02 mmol, 0.05 equiv.) was dissolved in dry CH_2Cl_2 under nitrogen atmosphere. To the above clear solution, *N,N'*-dicyclohexylcarbodiimide (DCC) (0.40 mmol, 1.5 equiv.) dissolved in dry CH_2Cl_2 was added slowly while maintaining the temperature below 15 °C and stirred for 4 hours at room temperature. Dicyclohexylurea precipitate was filtered off and washed thoroughly with dry CH_2Cl_2.The combined filtrates were washed with water and dried over Na_2SO_4. The crude product was purified by column chromatography using neutral alumina. Elution with 10% EtOAc-hexanes afforded the product which was further purified by recrystallization from EtOH and CH_2Cl_2 (9:1) to yield a pure colorless solid.

MDC-3,10: R_f = 0.58 in 20% EtOAc-hexanes; a colorless solid; yield: 64 %; IR (KBr pellet): ν_{max} in cm^{-1} 2932, 2851, 1731, 1634, 1604, 1256, 1134, 1054; UV–Vis: λ_{max} = 316.24 nm, $\in$ = 3.08×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.52 (d, *J* = 8.7 Hz, 2H, Ar), 7.06 (d, *J* = 6.9 Hz, 2H, Ar), 6.92-6.88 (m, 4H, Ar), 6.49 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.64-4.62 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 5.8 Hz, 4H, 2 × OCH_2), 2.51-1.08 (m, 48H, 21 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.85 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{56}H_{82}O_6$: 850.6. Found: 850.8; Anal. calcd for $C_{56}H_{82}O_6$: C, 79.01; H, 9.71. Found: C, 79.18; H, 9.95.

MDC-4,10: R_f = 0.58 in 20% EtOAc-hexanes; a colorless solid; yield: 61 %; IR (KBr pellet): ν_{max} in cm^{-1} 2932, 2851, 1731, 1634, 1604, 1256, 1135, 1054; UV–Vis: λ_{max} = 316.41 nm, $\in$ = 3.44×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.53 (d, *J* = 8.7 Hz, 2H, Ar), 7.07 (d, *J* = 7.0 Hz, 2H, Ar), 6.92-6.88 (m, 4H, Ar), 6.49 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.64-4.61 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.5 Hz, 4H, 2 × OCH_2), 2.36-1.08 (m, 50H, 22 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.85 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{57}H_{85}O_6$ (M+1): 865.6. Found: 865.41; Anal. calcd for $C_{57}H_{84}O_6$: C, 79.12; H, 9.78. Found: C, 78.88; H, 10.03.

MDC-5,10: R_f = 0.59 in 20% EtOAc-hexanes; a colorless solid; yield: 64 %; IR (KBr pellet): ν_{max} in cm^{-1} 2923, 2851, 1730, 1630, 1602, 1256, 1137, 1092; UV–Vis: λ_{max} = 316.66 nm, $\in$ = 3.20×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.53 (d, *J* = 8.8 Hz, 2H, Ar), 7.06 (d, *J* = 6.9 Hz, 2H, Ar), 6.92-6.87 (m, 4H, Ar), 6.49 (d, *J* = 16.0 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.64-4.63 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.6 Hz, 4H, 2 × OCH_2), 2.32-1.08 (m, 52H, 23 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.6 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.85 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{58}H_{86}O_6$: 878.6. Found: 878.4; Anal. calcd for $C_{58}H_{86}O_6$: C, 79.22; H, 9.86. Found: C, 79.44; H, 9.63.

MDC-7,10: R_f = 0.59 in 20% EtOAc-hexanes; a colorless solid; yield: 69 %; IR (KBr pellet): ν_{max} in cm^{-1} 2934, 2853, 1733, 1630, 1600, 1255, 1137, 1002; UV–Vis: λ_{max} = 316.15 nm, $\in$ = 4.89×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.53 (d, *J* = 8.6 Hz, 2H, Ar), 7.06 (d, *J* = 8.9 Hz, 2H, Ar), 6.92-6.87 (m, 4H, Ar), 6.49 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.9 Hz, 1H, 1 × olefinic), 4.65-4.61 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.6 Hz, 4H, 2 × OCH_2), 2.32-1.05 (m, 56H, 25 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.6 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 1.6 Hz, 3H, 1 × CH_3), 0.86 (d, *J* = 1.6 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{60}H_{90}O_6$: 906.6. Found: 906.0; Anal. calcd for $C_{60}H_{90}O_6$: C, 79.42; H, 10.00. Found: C, 79.12; H, 9.94.

MDC-3,12: R_f = 0.68 in 20% EtOAc-hexanes; a colorless solid; yield: 69 %; IR (KBr pellet): ν_{max} in cm^{-1} 2927, 2851, 1732, 1636, 1602, 1252, 1197, 1142; UV–Vis: λ_{max} = 316.80 nm, $\in$ = 3.66×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.52 (d, *J* = 8.7 Hz, 2H, Ar), 7.05 (d, *J* = 8.9 Hz, 2H, Ar), 6.99-6.83 (m, 4H, Ar), 6.49 (d, *J* =

16.0 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 4.8 Hz, 1H, 1 × olefinic), 4.64-4.61 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.8 Hz, 4H, 2 × OCH_2), 2.51-1.08 (m, 52H, 23 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 2.1 Hz, 3H, 1 × CH_3), 0.85 (d, *J* = 2.0 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{58}H_{86}O_6$: 878.6. Found: 878.7; Anal. calcd for $C_{58}H_{86}O_6$: C, 79.22; H, 9.86. Found: C, 79.43; H, 9.83.

MDC-4,12: R_f = 0.68 in 20% EtOAc-hexanes; a colorless solid; yield: 60 %; IR (KBr pellet): ν_{max} in cm^{-1} 2927, 2851, 1730, 1628, 1603, 1257, 1193, 1138; UV–Vis: λ_{max} = 316.67 nm, $\in$ = 2.83×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.52 (d, *J* = 8.7 Hz, 2H, Ar), 7.07 (d, *J* = 9.0 Hz, 2H, Ar), 6.92-6.80 (m, 4H, Ar), 6.49 (d, *J* = 16.0 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 4.5 Hz, 1H, 1 × olefinic), 4.64-4.62 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.6 Hz, 4H, 2 × OCH_2), 2.36-1.08 (m, 54H, 24 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.6 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 2.1 Hz, 3H, 1 × CH_3), 0.86 (d, *J* = 2.1 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 172.62, 165.99, 161.36, 156.57, 146.02, 144.47, 139.73, 129.90, 126.83, 122.56, 122.32, 115.10, 114.98, 114.67, 73.89, 68.4, 67.87, 56.74, 56.17, 50.11, 42.35, 39.78, 39.51, 38.17, 37.02, 36.61, 36.21, 35.74, 34.26, 31.86, 29.52, 29.13, 28.67, 28.16, 27.96, 27.83; MS (FAB+): m/z calcd for $C_{59}H_{88}O_6$: 892.6. Found: 892.7; Anal. calcd for $C_{59}H_{88}O_6$: C, 79.33; H, 9.93. Found: C, 79.09; H, 10.03.

MDC-5,12: R_f = 0.69 in 20% EtOAc-hexanes; a colorless solid; yield: 64 %; IR (KBr pellet): ν_{max} in cm^{-1} 2928, 2851, 1733, 1635, 1602, 1253, 1158, 1136; UV–Vis: λ_{max} = 316.74 nm, $\in$ = 1.96×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.53 (d, *J* = 8.7 Hz, 2H, Ar), 7.07 (d, *J* = 9.0 Hz, 2H, Ar), 6.92-6.89 (m, 4H, Ar), 6.49 (d, *J* = 16.0 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 4.5 Hz, 1H, 1 × olefinic), 4.66-4.63 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.6 Hz, 4H, 2 × OCH_2), 2.33-1.08 (m, 56H, 25 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.6 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 2.1 Hz, 3H, 1 × CH_3), 0.86 (d, *J* = 2.1 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{60}H_{90}O_6$: 906.6. Found: 906.5; Anal. calcd for $C_{60}H_{90}O_6$: C, 79.42; H, 10.00. Found: C, 79.48; H, 10.27.

MDC-7,12: R_f = 0.70 in 20% EtOAc-hexanes; a colorless solid; yield: 68 %; IR (KBr pellet): ν_{max} in cm^{-1} 2919, 2850, 1734, 1635, 1604, 1261, 1150, 1130 UV–Vis: λ_{max} = 316.81 nm, $\in$ = 3.04×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.53 (d, *J* = 8.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.92-6.88 (m, 4H, Ar), 6.49 (d, *J* = 16.0 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 4.2 Hz, 1H, 1 × olefinic), 4.63-4.61 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.6 Hz, 4H, 2 × OCH_2), 2.32-1.08 (m, 60H, 27 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 2.2 Hz, 3H, 1 × CH_3), 0.86 (d, *J* = 2.2 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{62}H_{95}O_6$ (M+1): 935.7. Found: 935.3; Anal. calcd for $C_{62}H_{94}O_6$: C, 79.61; H, 10.13. Found: C, 79.88; H, 10.31.

MDC-3,16: R_f = 0.60 in 20% EtOAc-hexanes; a colorless solid; yield: 62 %; IR (KBr pellet): ν_{max} in cm^{-1} 2923, 2850, 1731, 1633, 1602, 1254, 1196, 1143; UV–Vis: λ_{max} = 315.92 nm, $\in$ = 2.21×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.53 (d, *J* = 8.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.92-6.88 (m, 4H, Ar), 6.49 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 3.6 Hz, 1H, 1 × olefinic), 4.64-4.62 (m, 1H, 1 ×

CHOCO), 3.99 (t, *J* = 6.5 Hz, 4H, 2 × OCH_2), 2.51-1.08 (m, 60H, 27 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 2.1 Hz, 3H, 1 × CH_3), 0.85 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{62}H_{94}O_6$: 934.7. Found: 934.1; Anal. calcd for $C_{62}H_{94}O_6$: C, 79.61; H, 10.13. Found: C, 79.89; H, 10.13.

MDC-4,16: R_f = 0.64 in 20% EtOAc-hexanes; a colorless solid; yield: 66 %; IR (KBr pellet): ν_{max} in cm^{-1} 2921, 2850, 1727, 1633, 1597, 1250, 1181, 1132; UV–Vis: λ_{max} = 316.38 nm, ∈ = 1.90 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.53 (d, *J* = 8.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.8 Hz, 2H, Ar), 6.92-6.88 (m, 4H, Ar), 6.49 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 3.6 Hz, 1H, 1 × olefinic), 4.64-4.61 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.6 Hz, 4H, 2 × OCH_2), 2.36-1.09 (m, 62H, 28 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 1.76 Hz, 3H, 1 × CH_3), 0.85 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{63}H_{96}O_6$: 948.7. Found: 948.3; Anal. calcd for $C_{63}H_{96}O_6$: C, 79.70; H, 10.19. Found: C, 79.42; H, 10.25.

MDC-5,16: R_f = 0.70 in 20% EtOAc-hexanes; a colorless solid; yield: 70 %; IR (KBr pellet): ν_{max} in cm^{-1} 2922, 2851, 1725, 1654, 1570, 1254, 1190, 1132; UV–Vis: λ_{max} = 316.21 nm, ∈ = 2.4 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.53 (d, *J* = 8.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.92-6.88 (m, 4H, Ar), 6.49 (d, *J* = 16.0 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 3.4 Hz, 1H, 1 × olefinic), 4.64-4.61 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.6 Hz, 4H, 2 × OCH_2), 2.33-1.09 (m, 64H, 29 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.6 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 2.1 Hz, 3H, 1 × CH_3), 0.85 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{64}H_{99}O_6$ (M+1): 964.5. Found: 964.8; Anal. calcd for $C_{64}H_{98}O_6$: C, 79.78; H, 10.25. Found: C, 80.03; H, 9.96.

MDC-7,16: R_f = 0.74 in 20% EtOAc-hexanes; a colorless solid; yield: 73 %; IR (KBr pellet): ν_{max} in cm^{-1} 2925, 2841, 1727, 1644, 1570, 1256, 1190, 1122; UV–Vis: λ_{max} = 316.19 nm, ∈ = 2.5 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.82 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.53 (d, *J* = 8.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.92-6.89 (m, 4H, Ar), 6.49 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 3.7 Hz, 1H, 1 × olefinic), 4.62-4.60 (m, 1H, 1 × CHOCO), 3.99 (t, *J* = 6.5 Hz, 4H, 2 × OCH_2), 2.32-1.07 (m, 68H, 31 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.85 (d, *J* = 1.7 Hz, 3H, 1 × CH_3), 0.67 (s, 6H, 2 × CH_3); MS (FAB+): m/z calcd for $C_{66}H_{102}O_6$: 990.7. Found: 990.8; Anal. calcd for $C_{66}H_{102}O_6$: C, 79.95; H, 10.37. Found: C, 80.05; H, 10.09.

II.5 General procedure for the synthesis of the cholesteryl ω-[4-(3',4'-*n*-dialkoxycinnamoyloxy)phenoxy]alkanoates (DDC-n,R series).

A mixture of cholesteryl ω-(4'-hydroxyphenoxy) alkanoate (**2a-d**)[3] (0.36 mmol, 1 equiv.), 3,4-*n*-dialkoxy cinnamic acid (**7a-c**) (0.36 mmol, 1 equiv.) and 4-dimethylamino pyridine (DMAP) (0.02 mmol, 0.05 equiv.) was dissolved in dry CH_2Cl_2 under nitrogen atmosphere. To the above clear solution, DCC (0.54 mmol, 1.5 equiv.) dissolved in dry CH_2Cl_2 was added slowly while maintaining the temperature below 15 °C and stirred for 4 hours at room temperature. Dicyclohexylurea precipitate was filtered off and washed

thoroughly with CH_2Cl_2.The combined filtrates were washed with water and dried over Na_2SO_4. The crude product was purified by column chromatography using neutral alumina. Elution with 10% EtOAc-hexane afforded the product which was further purified by recrystallization from EtOH and CH_2Cl2 (9:1) to yield a pure colorless solid.

DDC-3,8: R_f = 0.76 in 20% EtOAc-hexanes; a colorless solid; yield: 67 %; IR (KBr pellet): ν_{max} in cm^{-1} 2923, 2850, 1720, 1631, 1596, 1215, 1196, 1133; UV–Vis: λ_{max} = 331.92 nm, $\in$ = 2.21 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.48 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.64-4.61 (m, 1H, 1 × CHOCO), 4.05-3.99 (m, 6H, 3 × OCH_2), 2.52-0.67 (m, 77H, 7 × CH_3, 25 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{62}H_{94}O_7$: 950.7. Found: 950.1; Anal. calcd for $C_{62}H_{94}O_7$: C, 78.27; H, 9.96. Found: C, 78.29; H, 9.89.

DDC-4,8: R_f = 0.78 in 20% EtOAc-hexanes; a colorless solid; yield: 69 %; IR (KBr pellet): ν_{max} in cm^{-1} 2943, 2840, 1729, 1633, 1599, 1205, 1194, 1133; UV–Vis: λ_{max} = 331.84 nm, $\in$ = 2.17 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.91-6.86 (m, 3H, Ar), 6.48 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.4 Hz, 1H, 1 × olefinic), 4.65-4.62 (m, 1H, 1 × CHOCO), 4.05-3.96 (m, 6H, 3 × OCH_2), 2.51-0.67 (m, 79H, 7 × CH_3, 26 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{63}H_{97}O_7$ (M+1): 965.7. Found: 965.7; Anal. calcd for $C_{63}H_{96}O_7$: C, 78.38; H, 10.02. Found: C, 78.65; H, 10.15.

DDC-5,8: R_f = 0.83 in 20% EtOAc-hexanes; a colorless solid; yield: 66 %; IR (KBr pellet): ν_{max} in cm^{-1} 2931, 2851, 1727, 1629, 1593, 1262, 1189, 1130; UV–Vis: λ_{max} = 331.78 nm, $\in$ = 4.39 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.47 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.4 Hz, 1H, 1 × olefinic), 4.63-4.62 (m, 1H, 1 × CHOCO), 4.05-3.93 (m, 6H, 3 × OCH_2), 2.33-0.67 (m, 81H, 7 × CH_3, 27 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{64}H_{99}O_7$ (M+1): 979.7. Found: 979.5; Anal. calcd for $C_{64}H_{98}O_7$: C, 78.48; H, 10.08. Found: C, 78.62; H, 9.93.

DDC-7,8: R_f = 0.86 in 20% EtOAc-hexanes; a colorless solid; yield: (64%); IR (KBr pellet): ν_{max} in cm^{-1} 2930, 2859, 1724, 1625, 1593, 1262, 1190, 1131; UV–Vis: λ_{max} = 331.08 nm, $\in$ = 1.35 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.47 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 4.0 Hz, 1H, 1 × olefinic), 4.63-4.61 (m, 1H, 1 × CHOCO), 4.05-3.92 (m, 6H, 3 × OCH_2), 2.32-0.67 (m, 85H, 7 × CH_3, 29 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{66}H_{103}O_7$ (M+1): 1007.7. Found: 1007.7; Anal. calcd for $C_{66}H_{102}O_7$: C, 78.68; H, 10.20. Found: C, 78.75; H, 10.26.

DDC-3,10: R_f = 0.68 in 20% EtOAc-hexanes; a colorless solid; yield: 67 %; IR (KBr pellet): ν_{max} in cm^{-1} 2924, 2851, 1719, 1625, 1596, 1265, 1191, 1132; UV–Vis: λ_{max} = 331.14 nm, $\in$ = 2.01 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.8 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.47 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.6 Hz, 1H, 1 × olefinic), 4.64-4.62 (m, 1H, 1 ×

CHOCO), 4.05-3.98 (m, 6H, 3 × OCH_2), 2.51-0.67 (m, 85H, 7 × CH_3, 29 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{66}H_{103}O_7$ (M+1): 1007.7. Found: 1007.7; Anal. calcd for $C_{66}H_{102}O_7$: C, 78.68; H, 10.20. Found: C, 78.41; H, 9.95.

DDC-4,10: R_f = 0.70 in 20% EtOAc-hexanes; a colorless solid; yield: 69 %; IR (KBr pellet): ν_{max} in cm^{-1} 2925, 2841, 1739, 1629, 1602, 1255, 1190, 1130; UV–Vis: λ_{max} = 332.14 nm, ∈ = 2.18 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.8 Hz, 2H, Ar), 7.07 (d, *J* = 8.8 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.48 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 5.6 Hz, 1H, 1 × olefinic), 4.64-4.62 (m, 1H, 1 × CHOCO), 4.05-3.96 (m, 6H, 3 × OCH_2), 2.51-0.67 (m, 87H, 7 × CH_3, 30 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{67}H_{105}O_7$ (M+1): 1021.7. Found: 1021.9; Anal. calcd for $C_{67}H_{104}O_7$: C, 78.78; H, 10.26. Found: C, 79.02; H, 10.05.

DDC-5,10: R_f = 0.70 in 20% EtOAc-hexanes; a colorless solid; yield: 72 %; IR (KBr pellet): ν_{max} in cm^{-1} 2926, 2851, 1740, 1630, 1602, 1257, 1191, 1134; UV–Vis: λ_{max} = 330.10 nm, ∈ = 1.21 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.80 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.8 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.48 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.63-4.61 (m, 1H, 1 × CHOCO), 4.05-3.93 (m, 6H, 3 × OCH_2), 2.33-0.67 (m, 89H, 7 × CH_3, 31 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{68}H_{106}O_7$: 1035.8. Found: 1035.4; Anal. calcd for $C_{68}H_{106}O_7$: C, 78.87; H, 10.32. Found: C, 79.05; H, 10.14.

DDC-7,10: R_f = 0.72 in 20% EtOAc-hexanes; a colorless solid; yield: 74 %; IR (KBr pellet): ν_{max} in cm^{-1} 2924, 2852, 1721, 1631, 1594, 1259, 1190, 1131; UV–Vis: λ_{max} = 331.18 nm, ∈ = 3.85 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.80 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.6 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.48 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.6 Hz, 1H, 1 × olefinic), 4.65-4.61 (m, 1H, 1 × CHOCO), 4.05-3.92 (m, 6H, 3 × OCH_2), 2.33-0.67 (m, 93H, 7 × CH_3, 33 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{70}H_{110}O_7$: 1062.8. Found: 1062.7; Anal. calcd for $C_{70}H_{110}O_7$: C, 79.05; H, 10.42. Found: C, 78.99; H, 10.55.

DDC-3,12: R_f = 0.76 in 20% EtOAc-hexanes; a colorless solid; yield: 65 %; IR (KBr pellet): ν_{max} in cm^{-1} 2928, 2854, 1721, 1632, 1596, 1215, 1192, 1132; UV–Vis: λ_{max} = 332.95 nm, ∈ = 1.97 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.7 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.47 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.6 Hz, 1H, 1 × olefinic), 4.64-4.62 (m, 1H, 1 × CHOCO), 4.05-3.99 (m, 6H, 3 × OCH_2), 2.51-0.67 (m, 93H, 7 × CH_3, 33 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{70}H_{110}O_7$: 1062.8. Found: 1062.7; Anal. calcd for $C_{70}H_{110}O_7$: C, 79.05; H, 10.42. Found: C, 78.98; H, 10.58.

DDC-4,12: R_f = 0.78 in 20% EtOAc-hexanes; a colorless solid; yield: 60 %; IR (KBr pellet): ν_{max} in cm^{-1} 2938, 2864, 1725, 1633, 1599, 1229, 1196, 1134; UV–Vis: λ_{max} = 333.91 nm, ∈ = 2.68 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.6 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.47 (d, *J* = 15.9 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.4 Hz, 1H, 1 × olefinic), 4.64-4.60 (m, 1H, 1 × CHOCO), 4.05-3.96 (m, 6H, 3 × OCH_2), 2.36-0.67 (m, 95H, 7 × CH_3, 34 × CH_2, 6 × CH); ^{13}C

NMR (100 MHz, $CDCl_3$): 172.91, 166.19, 156.59, 151.72, 149.21, 146.55, 144.31, 139.69, 127.02, 123.03, 122.70, 122.44, 115.05, 114.62, 112.19, 73.94, 69.33, 69.08, 67.79, 56.71, 56.14, 50.03, 42.34, 39.75, 39.55, 38.19, 37.02, 36.63, 36.21, 35.84, 34.31, 31.98, 31.94, 31.88, 29.76, 29.72, 29.69, 29.67, 29.47, 29.43, 29.25, 29.14, 28.69, 28.28, 28.06, 27.85, 26.06, 26.04, 24.33, 23.86, 22.88, 22.75, 21.75, 21.06, 19.38, 18.75, 14.19, 11.90; MS (FAB+): m/z calcd for $C_{71}H_{112}O_7$: 1076.8. Found: 1075.2; Anal. calcd for $C_{71}H_{112}O_7$: C, 79.13; H, 10.23. Found: C, 79.21; H, 10.48.

DDC-5,12: R_f = 0.80 in 20% EtOAc-hexanes; a colorless solid; yield: 66 %; IR (KBr pellet): ν_{max} in cm^{-1} 2928, 2854, 1721, 1632, 1596, 1215, 1192, 1133; UV–Vis: λ_{max} = 333.96 nm, $\in$ = 8.81 × 10^3 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.8 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.47 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 4.2 Hz, 1H, 1 × olefinic), 4.64-4.61 (m, 1H, 1 × CHOCO), 4.05-3.93 (m, 6H, 3 × OCH_2), 2.33-0.67 (m, 97H, 7 × CH_3, 35 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{72}H_{114}O_7$: 1090.9. Found: 1090.6; Anal. calcd for $C_{72}H_{114}O_7$: C, 79.22; H, 10.53. Found: C, 79.41; H, 10.26.

DDC-7,12: R_f = 0.82 in 20% EtOAc-hexanes; a colorless solid; yield: 70 %; IR (KBr pellet): ν_{max} in cm^{-1} 2932, 2844, 1723, 1613, 1601, 1225, 1198, 1143; UV–Vis: λ_{max} = 331.04 nm, $\in$ = 1.58 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.8 Hz, 1H, 1 × olefinic), 7.13 (d, *J* = 7.8 Hz, 2H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90-6.86 (m, 3H, Ar), 6.48 (d, *J* = 15.7 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 4.3 Hz, 1H, 1 × olefinic), 4.64-4.60 (m, 1H, 1 × CHOCO), 4.05-3.92 (m, 6H, 3 × OCH_2), 2.32-0.67 (m, 101H, 7 × CH_3, 37 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{74}H_{118}O_7$: 1118.8. Found: 1118.7; Anal. calcd for $C_{74}H_{118}O_7$: C, 79.38; H, 10.62. Found: C, 79.46; H, 10.40.

II.6 General procedure for the synthesis of the cholesteryl ω-[4-(2',3',4'-*n*-dodecyloxycinnamoyloxy)phenoxy]alkanoates (TDC-n,12 series).

A mixture of cholesteryl ω-(4'-hydroxyphenoxy) alkanoate (**2a-d**)[3] (0.18 mmol, 1 equiv.), 2,3,4-*n*-tridodecyloxy cinnamic acid (**8**) (0.18 mmol, 1 equiv.) and 4-dimethylamino pyridine (DMAP) (0.0091 mmol, 0.05 equiv.) was dissolved in dry CH_2Cl_2 under nitrogen atmosphere. To the above clear solution, DCC (0.27 mmol, 1.5 equiv.) dissolved in dry CH_2Cl_2 was added slowly while maintaining the temperature below 15 ^oC and stirred for 4 hours at room temperature. Dicyclohexylurea precipitate was filtered off and washed thoroughly with CH_2Cl_2. The combined filtrates were washed with water and dried over Na_2SO_4. The crude product was purified by column chromatography using neutral alumina. Elution with 10% EtOAc-hexanes afforded the product which was further purified by recrystallization from EtOH: CH_2Cl_2 (9:1) to yield a pure colorless solid.

TDC-3,12: R_f = 0.72 in 20% EtOAc-hexanes; a colorless solid; yield: 62 %; IR (KBr pellet): ν_{max} in cm^{-1} 2923, 2851, 1729, 1630, 1591, 1250, 1193, 1134; UV–Vis: λ_{max} = 319.89 nm, $\in$ = 2.94 × 10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.11 (d, *J* = 16.1 Hz, 1H, 1 × olefinic), 7.30 (d, *J* = 8.8 Hz, 1H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.89 (d, *J* = 8.9 Hz, 2H, Ar), 6.69

(d, *J* = 8.8 Hz, 1H, Ar), 6.57 (d, *J* = 16.1 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.6 Hz, 1H, 1 × olefinic), 4.64-4.60 (m, 1H, 1 × CHOCO), 4.08 (t, 2H, *J* = 6.5 Hz, 1 × OCH_2), 4.05- 3.95 (m, 6H, 3 × OCH_2), 2.51-0.67 (m, 116H, 8 × CH_3, 43 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{82}H_{134}O_8$: 1247.9. Found: 1247.3; Anal. calcd for $C_{82}H_{134}O_8$: C, 78.92; H, 10.82. Found: C, 78.88; H, 11.02.

TDC-4,12: R_f = 0.74 in 20% EtOAc-hexanes; a colorless solid; yield: 62 %; IR (KBr pellet): ν_{max} in cm^{-1} 2925, 2856, 1734, 1638, 1581, 1239, 1195, 1139; UV–Vis: λ_{max} = 319.85 nm, $\in$ = 2.33×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.11 (d, *J* = 16.1 Hz, 1H, 1 × olefinic), 7.30 (d, *J* = 8.8 Hz, 1H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.89 (d, *J* = 9.0 Hz, 2H, Ar), 6.69 (d, *J* = 8.8 Hz, 1H, Ar), 6.57 (d, *J* = 16.1 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.5 Hz, 1H, 1 × olefinic), 4.64-4.60 (m, 1H, 1 × CHOCO), 4.08 (t, 2H, *J* = 6.6 Hz, 1 × OCH_2), 4.05- 3.92 (m, 6H, 3 × OCH_2), 2.32-0.67 (m, 118H, 8 × CH_3, 44 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{83}H_{136}O_8$: 1262.0. Found: 1262.4; Anal. calcd for $C_{83}H_{136}O_8$: C, 79.00; H, 10.52. Found: C, 79.30; H, 10.28.

TDC-5,12: R_f = 0.76 in 20% EtOAc-hexanes; a colorless solid; yield: 67 %; IR (KBr pellet): ν_{max} in cm^{-1} 2916, 2848, 1728, 1639, 1591, 1297, 1191, 1139; UV–Vis: λ_{max} = 319.93 nm, $\in$ = 2.23×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.07 (d, *J* = 16.1 Hz, 1H, 1 × olefinic), 7.30 (d, *J* = 8.8 Hz, 1H, Ar), 7.07 (d, *J* = 8.8 Hz, 2H, Ar), 6.89 (d, *J* = 8.9 Hz, 2H, Ar), 6.69 (d, *J* = 8.6 Hz, 1H, Ar), 6.57 (d, *J* = 16.1 Hz, 1H, 1 × olefinic), 5.37 (brd, *J* = 3.5 Hz, 1H, 1 × olefinic), 4.64-4.62 (m, 1H, 1 × CHOCO), 4.08 (t, 2H, *J* = 6.4 Hz, 1 × OCH_2), 4.05-3.93 (m, 6H, 3 × OCH_2), 2.34-0.67 (m, 120H, 8 × CH_3, 45 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 173.12, 169.21, 166.42, 162.94, 156.59, 155.76, 153.13, 144.41, 141.83, 139.71, 132.01, 122.97, 122.67, 115.54, 114.99, 108.37, 73.75, 72.70, 68.79, 68.06, 56.71, 56.14, 53.12, 50.04, 47.07, 42.34, 39.75, 39.55, 38.19, 37.02, 36.63, 36.21, 35.84, 34.63, 31.88, 30.36, 29.74, 29.71, 29.62, 29.56, 29.44, 29.43, 29.29, 29.01, 28.27, 28.06, 27.85, 26.19, 26.15, 25.66, 24.84, 24.32, 23.86, 22.87, 22.75, 22.61, 21.06, 19.37, 18.75, 14.96, 14.18, 11.89; MS (FAB+): m/z calcd for $C_{84}H_{139}O_8$ (M+1): 1276.0. Found: 1276.8; Anal. calcd for $C_{84}H_{138}O_8$: C, 79.07; H, 10.90. Found: C, 79.25; H, 11.19.

TDC-7,12: R_f = 0.80 in 20% EtOAc-hexanes; a colorless solid; yield: 65 %; IR (KBr pellet): ν_{max} in cm^{-1} 2916, 2848, 1728, 1639, 1591, 1297, 1191, 1139; UV–Vis: λ_{max} = 319.93 nm, $\in$ = 2.23×10^4 L $mol^{-1}cm^{-1}$; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.10 (d, *J* = 16.2 Hz, 1H, 1 × olefinic), 7.30 (d, *J* = 8.8 Hz, 1H, Ar), 7.07 (d, *J* = 8.9 Hz, 2H, Ar), 6.90 (d, *J* = 8.9 Hz, 2H, Ar), 6.69 (d, *J* = 8.9 Hz, 1H, Ar), 6.57 (d, *J* = 16.1 Hz, 1H, 1 × olefinic), 5.38 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.64-4.61 (m, 1H, 1 × CHOCO), 4.09 (t, 2H, *J* = 6.6 Hz, 1 × OCH_2), 4.05- 3.97 (m, 6H, 3 × OCH_2), 2.33-0.67 (m, 124H, 8 × CH_3, 47 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{86}H_{142}O_8$: 1303.1. Found: 1303.6; Anal. calcd for $C_{86}H_{142}O_8$: C, 79.21; H, 10.98. Found: C, 79.50; H, 10.31.

III. Additional textures and XRD profiles

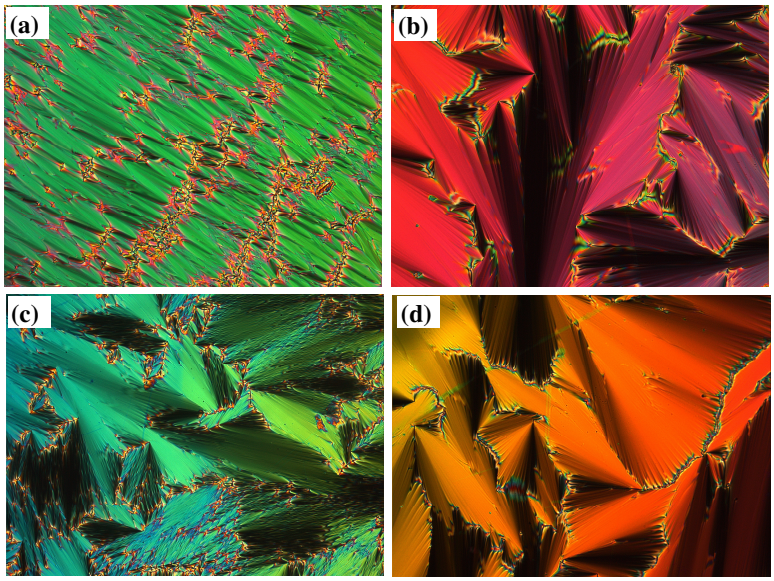

Figure S1. Microphotographs of the textures observed in a homogeneously aligned SmA phase of dimer **MDC-7,10** at (a) 140 °C, (b) 133 °C, (c) 104 °C, (d) 93 °C.

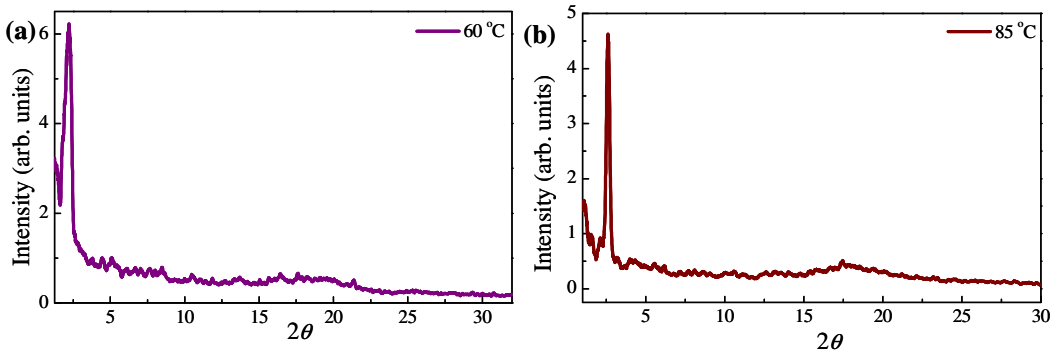

Figure S2. Intensity *vs* 2θ profiles derived from the 2D XRD pattern of TGBC* phase dimers (a) **MDC-3,16** at 60 ^{o}C and (b) **DDC-3,8** at 85 ^{o}C.

References

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