

**Nonsymmetric dimers comprising chalcone and cholesterol entities:
An investigation on structure-property correlations**

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Supporting Information

I. Experimental Section

I.1. Materials and methods

Chemicals were obtained from Fluka, Aldrich, Lancaster and local chemical companies, and were used without any purification; solvents were dried following the standard procedures. Chromatography was performed using silica gel (60-120 and 100-200 mesh). Aluminium sheets pre-coated with silica gel (Merck, Kieselgel60, F₂₅₄) were used for thin layer chromatography, IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. The spectral positions are given in wave number (cm⁻¹) unit. NMR spectra were recorded using either a Bruker DRX -500 (500 MHz) or Bruker AMX-400 (400 MHz) spectrometer or Bruker Avance series DPX-200(200 MHz) spectrometer. For ¹H NMR spectra, the chemical shifts are reported in ppm relative to TMS as an internal standard. Coupling constants are expressed in Hz. Microanalyses were performed using a Euro EA3000 model elemental analyzer. Mass spectra were determined on JEOL JMS-600H spectrometer in FAB⁺ mode using 3-nitrobenzylalcohol as a liquid matrix.

X-Ray diffraction studies were carried on powder samples in Lindemann capillaries with CuK_α radiation using an Image Plate Detector (MAC Science, Japan) equipped with a double mirror focusing optics. The mesogenic compounds were investigated for their liquid crystalline behavior by employing an optical polarizing microscope (Leica DMLP) equipped with a programmable hot stage (Mettler FP90) and differential scanning calorimeter (Perkin Elmer DSC7). Abovementioned optical polarizing microscope equipped with a programmable hot stage and differential scanning calorimeter were used to determine the melting points of non-mesomorphic compounds.

I.2. Syntheses

I.2.1. General procedure for the synthesis of 4-*n*-alkoxy benzaldehydes (2a-e)

A mixture of 4-hydroxy benzaldehyde (5 g, 40.9 mmol, 1equiv.), *n*-alkylbromide (41.4 mmol, 1.2 equiv.), anhydrous K₂CO₃ (11.3 g, 81.9 mmol, 2 equiv.) and butanone was heated under reflux in an inert atmosphere for 12 h. After cooling, the reaction mixture was poured into ice-cold water and the product was extracted into dichloromethane (CH₂Cl₂) (50ml × 3). The combined organic layers were washed with cold aqueous NaOH solution (25 ml × 3), water (25 ml × 3), brine, dried over anhydrous Na₂SO₄ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel (100-200 mesh) with a 10% mixture of ethyl acetate-hexanes as the eluent.

2a. A colorless liquid; *R_f* = 0.5 (30% CH₂Cl₂-hexanes); yield: 7.7 g (80 %); IR (KBr Pellet): ν_{\max} in cm⁻¹ 2958, 2873, 1696, 1601, 1508, 1312, 1259, 1160 and 833; ¹H NMR (400 MHz, CDCl₃): δ 9.9 (s, 1H, 1 × CHO), 7.82 (d, *J* = 8.4 Hz, 2H, Ar), 6.99 (d, *J* = 8.8 Hz, 2H, Ar), 4.04 (t, *J* = 6.4 Hz, 2H, 1 × OCH₂), 1.88-1.31 (m, 12H, 6 × CH₂), 0.87 (t, *J* = 6.6 Hz, 3H, 1 × CH₃); MS (FAB+): *m/z* for C₁₅H₂₃O₂(M+1), Calculated: 235.2, Found: 235.2.

2b. A colorless liquid; *R_f* = 0.5 (30% CH₂Cl₂-hexanes); yield: 8.3 g (82 %); IR (KBr Pellet): ν_{\max} in cm⁻¹ 2959, 2877, 1699, 1601, 1510, 1312, 1259, 1160 and 833; ¹H NMR (400 MHz, CDCl₃): δ 9.9 (s, 1H, 1 × CHO), 7.82 (d, *J* = 8.4 Hz, 2H, Ar), 6.99 (d, *J* = 8.8 Hz, 2H, Ar), 4.04 (t, *J* = 6.4 Hz, 2H, 1 × OCH₂), 1.88-1.31 (m, 14H, 7 × CH₂), 0.87 (t, *J* = 6.6 Hz, 3H, 1 × CH₃); MS (FAB+): *m/z* for C₁₆H₂₅O₂(M+1), Calculated: 249.2, Found: 249.2.

2c. A colorless liquid; *R_f* = 0.52 (30% CH₂Cl₂-hexanes); yield: 9.1 g (85 %); IR (KBr Pellet): ν_{\max} in cm⁻¹ 2960, 2878, 1698, 1605, 1510, 1314, 1260, 1162 and 835; ¹H NMR (400 MHz, CDCl₃): δ 9.9 (s, 1H, 1 × CHO), 7.82 (d, *J* = 8.4 Hz, 2H, Ar), 6.99 (d, *J* =

8.8 Hz, 2H, Ar), 4.04 (t, $J = 6.4$ Hz, 2H, $1 \times \text{OCH}_2$), 1.88-1.31 (m, 16H, $8 \times \text{CH}_2$), 0.87 (t, $J = 6.6$ Hz, 3H, $1 \times \text{CH}_3$); MS (FAB+): m/z for $\text{C}_{17}\text{H}_{27}\text{O}_2(\text{M}+1)$, Calculated: 263.2, Found: 263.2.

2d. A low melting solid; $R_f = 0.52$ (30% CH_2Cl_2 -hexanes); yield: 8.8 g (78 %); IR (KBr Pellet): ν_{max} in cm^{-1} 2962, 2877, 1700, 1606, 1511, 1315, 1262, 1164 and 838; ^1H NMR (400 MHz, CDCl_3): δ 9.9 (s, 1H, $1 \times \text{CHO}$), 7.82 (d, $J = 8.4$ Hz, 2H, Ar), 6.99 (d, $J = 8.8$ Hz, 2H, Ar), 4.04 (t, $J = 6.4$ Hz, 2H, $1 \times \text{OCH}_2$), 1.88-1.31 (m, 18H, $9 \times \text{CH}_2$), 0.87 (t, $J = 6.6$ Hz, 3H, $1 \times \text{CH}_3$); MS (FAB+): m/z for $\text{C}_{18}\text{H}_{29}\text{O}_2(\text{M}+1)$, Calculated: 277.2, Found: 277.2.

2e. A low melting solid; $R_f = 0.53$ (30% CH_2Cl_2 -hexanes); yield: 10.1 g (85 %); IR (KBr Pellet): ν_{max} in cm^{-1} 2959, 2874, 1699, 1602, 1509, 1313, 1259, 1161 and 836; ^1H NMR (400 MHz, CDCl_3): δ 9.9 (s, 1H, $1 \times \text{CHO}$), 7.82 (d, $J = 8.4$ Hz, 2H, Ar), 6.99 (d, $J = 8.8$ Hz, 2H, Ar), 4.04 (t, $J = 6.4$ Hz, 2H, $1 \times \text{OCH}_2$), 1.88-1.31 (m, 20H, $10 \times \text{CH}_2$), 0.87 (t, $J = 6.6$ Hz, 3H, $1 \times \text{CH}_3$); MS (FAB+): m/z for $\text{C}_{19}\text{H}_{31}\text{O}_2(\text{M}+1)$, Calculated: 291.2, Found: 291.2.

I.2.2. General procedure for the synthesis of hydroxy chalcones 3a-e

A mixture of the appropriate aldehyde (**2a-e**) (2.93 g, 12.5 mmol, 1.0 equiv.) and 3-hydroxyacetophenone (1.7 g, 12.5 mmol, 1.0 equiv.) was dissolved in methanol (25 ml). To this, a solution of KOH (2.52 g, 45 mmol, 3.6 equiv.) in minimum quantity of methanol was added with vigorous stirring at ambient temperature. The resultant reaction mixture was heated under reflux for 12 h; excess of methanol was removed and the residue was acidified with cold 1N HCl solution. A pale yellow solid separated was filtered, dissolved in CH_2Cl_2 and dried over anhydrous Na_2SO_4 . Evaporation of CH_2Cl_2 yielded the crude chalcone that was purified by column chromatography on silica gel (60-120) with a 10% mixture of ethyl acetate-hexanes as the eluent.

3a. A yellow solid; $R_f = 0.31$ (10% EtOAc-hexanes); yield: 3.43 g (78%); m.p.: 99 °C IR (KBr Pellet) ν_{\max} in cm^{-1} : 3379, 2925, 1651, 1563, 1510, 1444, 1296, 1250, 1170, 830, 789 and 575; $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 7.8 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.6-7.61 (bd, $J = 8.6$ Hz, 4H, Ar), 7.38 (t, $J = 8.2$ Hz, 15.6 Hz, 2H, 1 \times olefinic H, 1 \times Ar), 7.1 (dd, $J = 1.8$ Hz, 8.1 Hz, 1H, Ar), 6.92 (d, $J = 8.6$ Hz, 2H, Ar), 5.7 (s, 1H, 1 \times OH), 4.0 (t, $J = 6.4$ Hz, 2H, 1 \times OCH_2), 1.87-0.86 (m, 15H, 6 \times CH_2 , 1 \times CH_3); MS (FAB+): m/z for $\text{C}_{23}\text{H}_{29}\text{O}_3(\text{M}+1)$, Calculated: 353.2, Found: 353.2

3b. A yellow solid; $R_f = 0.32$ (10% EtOAc-hexanes), yield: 3.48 g (76%); m.p.: 108 °C IR (KBr Pellet) ν_{\max} in cm^{-1} : 3382, 2921, 2849, 1656, 1564, 1510, 1448, 1296, 1253, 1170, 825, 792 and 575; $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 7.8 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.54-7.61 (bd, $J = 8.6$ Hz, 4H, 4 \times Ar), 7.38 (t, $J = 8.2$ Hz, 15.6 Hz, 2H, 1 \times olefinic H, 1 \times Ar), 7.1 (dd, $J = 2.2$ Hz, 7.8 Hz, 1H, Ar), 6.92 (d, $J = 8.6$ Hz, 2H, Ar), 5.4 (s, 1H, 1 \times OH), 4.0 (t, $J = 6.4$ Hz, 2H, 1 \times OCH_2), 1.87-0.86 (m, 17H, 7 \times CH_2 , 1 \times CH_3); MS (FAB+): m/z for $\text{C}_{24}\text{H}_{30}\text{O}_3$, Calculated: 366.2, Found: 366.8.

3c. A cream colored solid; $R_f = 0.32$ (10% EtOAc-hexanes); yield: 3.57 g (75%); m.p.: 101 °C; IR (KBr Pellet) ν_{\max} in cm^{-1} : 3375, 2922, 2851, 1661, 1580, 1566, 1510, 1447, 1295, 1253, 1168, 827, and 575; $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 7.8 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.54-7.61 (bd, $J = 8.6$ Hz, 4H, Ar), 7.38 (t, $J = 8.2$ Hz, 15.6 Hz, 2H, 1 \times olefinic H, 1 \times Ar), 7.1 (dd, $J = 2.2$ Hz, 7.8 Hz, 1H, Ar), 6.92 (d, $J = 8.6$ Hz, 2H, Ar), 5.4 (s, 1H, 1 \times OH), 4.0 (t, $J = 6.4$ Hz, 2H, 1 \times OCH_2), 1.84-0.85 (m, 19H, 8 \times CH_2 , 1 \times CH_3); MS (FAB+): m/z for $\text{C}_{25}\text{H}_{33}\text{O}_3(\text{M}+1)$, Calculated: 381.2, Found: 381.2.

3d. A cream colored solid; $R_f = 0.33$ (10% EtOAc-hexanes); yield: 3.85 g (78%); m.p.: 118 °C; IR (KBr Pellet) ν_{\max} in cm^{-1} : 3382, 2920, 2850, 1656, 1564, 1566, 1511, 1448, 1296, 1253, 1170, 984, 825 and 575; $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 7.8 (d, $J =$

15.6 Hz, 1H, 1 × olefinic H), 7.54-7.61 (bd, $J = 8.6$ Hz, 4H, Ar), 7.38 (t, $J = 8.2$ Hz, 15.6 Hz, 2H, 1 × olefinic H, 1 × Ar), 7.1 (dd, $J = 2.2$ Hz, 7.8 Hz, 1H, Ar), 6.92 (d, $J = 8.6$ Hz, 2H, Ar), 5.4 (s, 1H, 1 × OH), 4.0 (t, $J = 6.4$ Hz, 2H, 1 × OCH₂), 1.84-0.85 (m, 21H, 9 × CH₂, 1 × CH₃); MS (FAB+): m/z for C₂₆H₃₅O₃(M+1), Calculated: 395.5, Found: 395.3.

3e. A cream colored solid; $R_f = 0.36$ (70% CH₂Cl₂-hexanes); yield: 4.1 g (80%); m.p.: 104 °C; IR (KBr Pellet) ν_{\max} in cm⁻¹: 3376, 2921, 2850, 1660, 1580, 1566, 1510, 1448, 1295, 1252, 1168, 986, 827 and 576; ¹H NMR (200 MHz, CDCl₃): δ 7.8 (d, $J = 15.6$ Hz, 1H, 1 × olefinic H), 7.54-7.61 (bd, $J = 8.6$ Hz, 4H, Ar), 7.38 (t, $J = 8.2$ Hz, 15.6 Hz, 2H, 1 × olefinic H, 1 × Ar), 7.1 (dd, $J = 2.2$ Hz, 7.8 Hz, 1H, Ar), 6.92 (d, $J = 8.6$ Hz, 2H, Ar), 5.4 (s, 1H, 1 × OH), 4.0 (t, $J = 6.4$ Hz, 2H, 1 × OCH₂), 1.81-0.85 (m, 23H, 10 × CH₂, 1 × CH₃); MS (FAB+): m/z for C₂₇H₃₇O₃(M+1), Calculated: 409.3, Found: 409.3

I.2.3. General procedures for the synthesis of dimers of series-1 (3DC-n,m series)

A mixture of the appropriate cholesteryl ω -bromoalkanoate (**1a-d**) (0.26 mmol, 1equiv.), hydroxy chalcone (**3a-e**) (0.26 mmol, 1equiv.), anhydrous K₂CO₃ (0.072 g, 0.52 mmol, 4 equiv.) and dry DMF (5-6 ml) was heated at 80 °C for 12 h under nitrogen atmosphere. The reaction mixture was allowed to attain room temperature and poured into ice-cold water. The product was extracted into CH₂Cl₂ (30ml × 3) and dried over Na₂SO₄. The crude compound obtained after the evaporation of CH₂Cl₂ was purified by column chromatography (neutral alumina) using a mixture of 10% CH₂Cl₂-hexanes as an eluent. Off-white solid obtained was further purified by repeated recrystallization in a mixture of CH₂Cl₂-hexanes (1:9) until a constant clearing (isotropic) temperature was obtained.

3DC-3,8. A cream colored solid; $R_f = 0.34$ (10% EtOAc-hexanes); yield: 0.164 g (78%); UV-Vis: $\lambda_{\max} = 341.7$ nm, $\epsilon = 2.5 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 250.8$ nm, $\epsilon = 2.1 \times 10^4$ L mol⁻¹cm⁻¹; IR (KBr Pellet) ν_{\max} in cm⁻¹: 2938, 2851, 1734, 1655, 1584, 1568, 1510, 1473, 1438, 1293, 1252, 1168, 827, 790, 574; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.58-7.60 (m, 2H, 1 \times Ar, 1 \times olefinic H), 7.52 (s, 1H, 1 \times Ar), 7.4 (d, $J = 6.8$ Hz, 2H, Ar), 7.38 (d, $J = 8.7$ Hz, 1H, Ar), 7.11 (dd, $J = 2.2$ Hz, 8.1 Hz, 1H, Ar), 6.92 (d, $J = 8.8$ Hz, 2H, Ar), 5.3 (d, $J = 4.0$ Hz, 1H, 1 \times olefinic H), 4.61-4.65 (m, 1H, 1 \times CHOCO), 4.09 (t, $J = 6.1$ Hz, 2H, 1 \times OCH₂), 4.0 (t, $J = 6.5$ Hz, 2H, 1 \times OCH₂), 2.51 (t, $J = 7.2$ Hz, 2H, 1 \times CH₂), 2.17-0.67 (m, 45H, 1 \times CH₃, 18 \times CH₂, 6 \times CH), 1.01 (s, 3H, 1 \times CH₃), 0.91 (d, $J = 6.48$ Hz, 3H, 1 \times CH₃), 0.87 (d, $J = 1.5$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.6$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 190.23, 172.41, 161.43, 159.26, 144.74, 140.16, 139.74, 130.19, 129.49, 127.62, 122.64, 120.99, 119.96, 119.33, 115.07, 113.93, 74.16, 68.33, 67.25, 56.81, 56.34, 50.2, 42.42, 39.86, 39.58, 38.23, 37.08, 36.67, 36.28, 35.79, 31.96, 31.78, 31.18, 29.31, 29.20, 28.19, 28.0; MS (FAB+): m/z for C₅₄H₇₉O₅(M+1), Calculated: 807.6. Found: 807.6; Anal. calcd for C₅₄H₇₈O₅ (found) %: C 80.35 (80.75) and H 9.74 (9.30).

3DC-3,9. A cream colored solid; $R_f = 0.34$ (10%EtOAc-hexanes); yield: 0.164 g (77%); UV-Vis: $\lambda_{\max} = 345$ nm, $\epsilon = 20.9 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 247$ nm, $\epsilon = 1.9 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2935, 2851, 1723, 1659, 1573, 1512, 1446, 1293, 1248, 1174, 1041, 828, 576; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.58-7.60 (m, 2H, 1 \times Ar, 1 \times olefinic H), 7.53 (s, 1H, Ar), 7.4 (d, $J = 7.4$ Hz, 2H, Ar), 7.38 (d, $J = 8.2$ Hz, 1H, Ar), 7.11 (d, $J = 2.1$ Hz, 1H, 1 \times Ar), 6.92 (d, $J = 8.8$ Hz, 2H, Ar), 5.36 (d, $J = 4.2$ Hz, 1H, 1 \times olefinic H), 4.63-4.65 (m, 1H, 1 \times CHOCO), 4.09 (t, $J = 6.2$ Hz, 2H, 1 \times OCH₂), 4.0 (t, $J = 6.6$ Hz, 2H, 1 \times OCH₂), 2.52 (t, $J = 7.2$ Hz, 2H, 1 \times CH₂), 2.14-0.67 (m, 50H, 2 \times CH₃, 19 \times CH₂, 6 \times CH), 1.01 (s, 3H, 1 \times CH₃), 0.87 (d, $J = 1.8$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.8$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for C₅₅H₈₀O₅, Calculated: 820.6. Found: 820.4; Anal. calcd for C₅₅H₈₀O₅(found) %: C 80.44 (80.2) and H 9.82 (9.8).

3DC-3,10. A cream colored solid; $R_f = 0.33$ (10%EtOAc-hexanes); yield: 0.169 g (78%); UV-Vis: $\lambda_{\max} = 342$ nm, $\epsilon = 1.36 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 251.3$ nm, $\epsilon = 1.21 \times 10^4$ L mol⁻¹cm⁻¹; IR (KBr Pellet) ν_{\max} in cm⁻¹: 2935, 2852, 1723, 1659, 1591, 1573, 1512, 1446, 1293, 1248, 1174, 1042, 829, 576; ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.60 (d, $J = 8.7$ Hz, 1H, Ar) 7.59 (d, $J = 11.7$ Hz, 1 \times olefinic H), 7.52 (s, 1H, Ar), 7.4 (d, $J = 7.4$ Hz, 2H, Ar), 7.38 (d, $J = 8.2$ Hz, 1H, Ar), 7.1 (dd, $J = 2.1$ Hz, 8 Hz, 1H, Ar), 6.92 (d, $J = 8.8$ Hz, 2H, Ar), 5.36 (d, $J = 4.2$ Hz, 1H, 1 \times olefinic H), 4.63-4.65 (m, 1H, 1 \times CHOCO), 4.09 (t, $J = 6.2$ Hz, 2H, 1 \times OCH₂), 4.0 (t, $J = 6.6$ Hz, 2H, 1 \times OCH₂), 2.52 (t, $J = 7.2$ Hz, 2H, 1 \times CH₂), 2.14-0.67(m, 52H, 2 \times CH₃, 20 \times CH₂, 6 \times CH), 1.01 (s, 3H, 1 \times CH₃), 0.87 (d, $J = 1.8$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.8$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); MS (FAB⁺): m/z for C₅₆H₈₃O₅(M+1), Calculated: 835.6, Found: 835.6; Anal. calcd for C₅₆H₈₂O₅ (found) %: C 80.53 (80.6) and H 9.90 (9.9).

3DC-3,11. A cream colored solid; $R_f = 0.36$ (10%EtOAc-hexanes); yield: 0.172 g (78%); UV-Vis: $\lambda_{\max} = 342.4$ nm, $\epsilon = 2.4 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 243.1$ nm, $\epsilon = 1.6 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2936, 2851, 1723, 1656, 1591, 1571, 1511, 1293, 1248, 1172, 982, 830, 785 and 576; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.60 (d, $J = 8.7$ Hz, 1H, Ar) 7.58 (d, $J = 12$ Hz, 1 \times olefinic H), 7.52 (s, 1H, Ar), 7.41 (d, $J = 8.4$ Hz, 2H, Ar), 7.38 (d, $J = 8.3$ Hz, 1H, Ar), 7.11 (dd, $J = 1.9$ Hz, 8 Hz, 1H, Ar), 6.92 (d, $J = 8.7$ Hz, 2H, Ar), 5.36 (d, $J = 3.7$ Hz, 1H, 1 \times olefinic H), 4.63-4.65 (m, 1H, 1 \times CHOCO), 4.09 (t, $J = 6.0$ Hz, 2H, 1 \times OCH₂), 3.99 (t, $J = 6.5$ Hz, 2H, 1 \times OCH₂), 2.51 (t, $J = 7.2$ Hz, 2H, 1 \times CH₂), 2.32-0.67(m, 54H, 2 \times CH₃, 21 \times CH₂, 6 \times CH), 1.01 (s, 3H, 1 \times CH₃), 0.87 (d, $J = 1.6$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.5$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); MS (FAB⁺): m/z for C₅₇H₈₅O₅(M+1), Calculated: 849.6, Found: 849.6; Anal. calcd for C₅₇H₈₄O₅ (found) %: C 80.61 (80.5) and H 9.97 (9.7).

3DC-3,12. A cream colored solid; $R_f = 0.37$ (10%EtOAc-hexanes); yield: 0.193 g (86 %); UV-Vis: $\lambda_{\max} = 342.4$ nm, $\epsilon = 1.63 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 248.2$ nm, $\epsilon = 1.4 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2925, 2851, 1724, 1659, 1572, 1512, 1444, 1293, 1248, 1174, 829 and 576; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.60 (d, $J = 8.7$ Hz, 1H, Ar) 7.59 (d, $J = 12$ Hz, 1H, 1 \times olefinic H), 7.52 (s, 1H, Ar), 7.39 (d, $J = 7.1$ Hz, 1H, Ar), 7.37 (d, $J = 8.5$ Hz, 1H, Ar), 7.11 (dd, $J = 1.9$ Hz, 8 Hz, 2H, Ar), 6.92 (d, $J = 8.7$ Hz, 2H, Ar), 5.34 (d, $J = 4.0$ Hz, 1H, 1 \times olefinic H), 4.61-4.65 (m, 1H, 1 \times CHOCO), 4.09 (t, $J = 6.6$ Hz, 2H, 1 \times OCH₂), 4.0 (t, $J = 6.1$ Hz, 2H, 1 \times OCH₂), 2.51 (t, $J = 7.2$ Hz, 2H, 1 \times CH₂), 2.2-0.67 (m, 53H, 1 \times CH₃, 22 \times CH₂, 6 \times CH), 1.01 (s, 3H, 1 \times CH₃), 0.88 (d, $J = 2.8$ Hz, 3H, 1 \times CH₃), 0.87 (d, $J = 2.4$ Hz, 3H, 1 \times CH₃), 0.85 (d, $J = 1.7$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for C₅₈H₈₇O₅(M+1), Calculated: 863.6. Found: 863.4; Anal. calcd for C₅₈H₈₆O₅ (found) %: C 80.69 (80.7) and H 10.04 (9.8).

3DC-4,8. A colorless solid; $R_f = 0.30$ (10%EtOAc-hexanes); yield: 0.149 g (70%); UV-Vis: $\lambda_{\max} = 346.9$ nm, $\epsilon = 1.8 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 247.1$ nm, $\epsilon = 1.5 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹:2934, 2866, 2365, 1726, 1659, 1591, 1569, 1512, 1448, 1290, 1249, 1174, 1043, 829, 786 and 572; ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.59 (d, $J = 6.9$ Hz, 2H, Ar) 7.56 (d, $J = 15.9$ Hz, 1H, 1 \times olefinic H), 7.51 (s, 1H, Ar), 7.39 (d, $J = 6.5$ Hz, 1H, Ar), 7.38 (d, $J = 9.0$ Hz, 1H, Ar), 7.09 (dd, $J = 1.9$ Hz, 7.8 Hz, 1H, Ar), 6.91 (d, $J = 8.7$ Hz, 2H, Ar), 5.36 (d, $J = 3.6$ Hz, 1H, 1 \times olefinic H), 4.63 (m, 1H, 1 \times CHOCO), 4.04 (m, 2H, 1 \times OCH₂), 3.99 (t, $J = 6.6$ Hz, 2H, 1 \times OCH₂), 2.37(t, $J = 6.3$ Hz, 2H, 1 \times CH₂) 2.31-0.67 (m, 47H, 1 \times CH₃, 19 \times CH₂, 6 \times CH), 1.01 (s, 3H, 1 \times CH₃), 0.90 (d, $J = 6.4$ Hz, 3H, 1 \times CH₃), 0.87 (d, $J = 1.8$ Hz, 3H, 1 \times CH₃), 0.85 (d, $J = 1.9$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 190.31, 172.77, 161.42, 159.34, 144.78, 140.08, 139.76, 130.24, 129.5, 127.56,122.64, 120.90, 119.88, 119.40, 115.03, 113.76, 73.98, 68.31, 67.75, 56.79, 56.28, 50.16, 42.40, 39.83, 39.56, 38.23, 37.07, 36.67, 36.26, 35.81, 34.32, 31.81, 29.34, 29.21, 28.68, 28.23, 28.03, 27.89, 26.04,

24.31; MS (FAB+): m/z for $C_{55}H_{81}O_5(M+1)$ Calculated: 821.6, Found: 821.7; Anal. calcd for $C_{55}H_{80}O_5$ (found) %: C 80.44 (80.4); H 9.82 (9.8).

3DC-4.9. A colorless solid; $R_f = 0.32$ (10%EtOAc-hexanes); yield: 0.167 g (77%); UV-Vis: $\lambda_{max} = 342$ nm, $\epsilon = 0.1 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{max} = 255.4$ nm, $\epsilon = 0.06 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{max} in cm⁻¹:2934, 1726, 1660, 1592, 1569, 1512, 1448, 1291, 1250, 1173, 1042, 829, 787 and 574; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.58 (d, $J = 8.6$ Hz, 2H, Ar) 7.56 (d, $J = 17.9$ Hz, 1H, 1 \times olefinic H), 7.51 (s, 1H, Ar), 7.4 (dd, $J = 6.5$ Hz, 2.5 Hz, 1H, Ar), 7.38 (dd, $J = 9.0$ Hz, 3.8 Hz, 1H, Ar), 7.1 (dd, $J = 1.9$ Hz, 7.8 Hz, 1H, Ar), 6.92 (d, $J = 8.7$ Hz, 2H, Ar), 5.37 (d, $J = 3.6$ Hz, 1H, 1 \times olefinic H), 4.63 (m, 1H, 1 \times CHOCO), 3.99-4.06 (m, 4H, 2 \times OCH₂), 2.38 (t, $J = 4.4$ Hz, 2H, 1 \times CH₂), 2.02-0.67(m, 49H, 1 \times CH₃, 20 \times CH₂, 6 \times CH), 1.01 (s, 3H, 1 \times CH₃), 0.91 (d, $J = 6.6$ Hz, 3H, 1 \times CH₃), 0.87 (d, $J = 1.6$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.6$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for $C_{56}H_{83}O_5 (M+1)$ Calculated: 835.6, Found: 835.4; Anal.calcd for $C_{56}H_{82}O_5$ (found) %: C 80.53 (80.7); H 9.9 (9.9).

3DC-4.10. A cream colored solid; $R_f = 0.32$ (10%EtOAc-hexanes); yield: 0.168 g (76%); UV-Vis: $\lambda_{max} = 342.2$ nm, $\epsilon = 1.7 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{max} = 246.8$ nm, $\epsilon = 1.5 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{max} in cm⁻¹:2928, 1732, 1658, 1590, 1569, 1511, 1448, 1291, 1250, 1173, 1017, 826 and 573; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 12.6$ Hz, 1H, 1 \times olefinic H), 7.59 (d, $J = 6.8$ Hz, 2H, 2 \times Ar) 7.58 (d, $J = 17.9$ Hz, 1H, 1 \times olefinic H), 7.52 (s, 1H, 1 \times Ar), 7.39 (d, $J = 8.1$ Hz, 1H, 1 \times Ar), 7.38 (dd, $J = 8.1$ Hz, 1H, Ar), 7.10 (dd, $J = 2.1$ Hz, 8 Hz, 1H, Ar), 6.92 (d, $J = 6.9$ Hz, 2H, Ar), 5.37 (d, $J = 4.2$ Hz, 1H, 1 \times olefinic H), 4.63 (m, 1H, 1 \times CHOCO), 3.99-4.06 (m, 4H, 2 \times OCH₂), 2.38(t, $J = 5.3$ Hz, 2H, 1 \times CH₂) 2.3-0.67(m, 48H, 1 \times CH₃, 21 \times CH₂, 6 \times CH), 1.01 (s, 3H, 1 \times CH₃), 0.91 (d, $J = 5.2$ Hz, 3H, 1 \times CH₃), 0.89 (d, $J = 5.4$ Hz, 3H, 1 \times CH₃),0.87 (d, $J = 1.4$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.6$ Hz, 3H, 1 \times

CH₃), 0.67 (s, 3H, 1 × CH₃); MS (FAB+): m/z for C₅₇H₈₄O₅, Calculated: 848.6, Found: 848.9; Anal.calcd for C₅₇H₈₄O₅ (found) %: C 80.61 (80.5); H 9.9 (9.9) .

3DC-4,11. A colorless solid; *R_f* = 0.39 (10%EtOAc-hexanes); yield: 0.179 g (80%); UV-Vis: λ_{max} = 341.2nm, ε = 1.2 × 10⁴ L mol⁻¹cm⁻¹, λ_{max} = 250.9 nm, ε = 1.1 × 10⁴ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{max} in cm⁻¹:2926, 1731, 1655, 1592, 1570, 1511, 1467, 1450, 1290, 1249, 1173, 1044, 784 and 572; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 12.6 Hz, 1H, 1 × olefinic H), 7.59 (d, *J* = 7.0 Hz, 2H, 2 × Ar) 7.58 (d, *J* = 12.4 Hz, 1H, 1 × olefinic H), 7.52 (s, 1H, Ar), 7.4 (d, *J* = 6.4 Hz, 1H, Ar), 7.38 (d, *J* = 6.4 Hz, 1H, Ar), 7.10 (dd, *J* = 1.8 Hz, 6.4 Hz, 1H, Ar), 6.92 (d, *J* = 7.0 Hz, 2H, Ar), 5.36 (d, *J* = 3.2 Hz, 1H, 1 × olefinic H), 4.62 (m, 1H, 1 × CHOCO), 4.06 (t, *J* = 4.4 Hz, 2H, 1 × OCH₂), 4.0 (t, *J* = 5.2 Hz, 2H, 1×OCH₂), 2.38 (d, *J* = 5.4 Hz, 2H, 1 × CH₂) 2.37 - 0.67 (m, 53H, 1 × CH₃, 22× CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.91 (d, *J* = 5.2 Hz, 3H, 1 × CH₃), 0.87 (d, *J* = 1.8 Hz, 3H, 1× CH₃), 0.86 (d, *J* = 3.5 Hz, 3H, 1× CH₃), 0.67 (s, 3H, 1 × CH₃); MS (FAB+): m/z for C₅₈H₈₆O₅, Calculated: 862.6, Found: 862.4; Anal.calcd for C₅₈H₈₆O₅ (found) %:C 80.69 (80.7); H 10.04 (10.5).

3DC-4,12. A cream colored solid; *R_f* = 0.40 (10%EtOAc-hexanes); yield: 0.178 g (78%); UV-Vis: λ_{max} = 344.9 nm, ε = 1.3 × 10⁴ L mol⁻¹cm⁻¹, λ_{max} = 245.7 nm, ε = 1.3 × 10⁶ L mol⁻¹cm⁻¹, IR(KBr Pellet) ν_{max} in cm⁻¹: 2926, 2852, 1724, 1660, 1573, 1511, 1446, 1294, 1248, 1176, 830 and 578; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 15.6 Hz, 1H, 1 × olefinic H), 7.59 (d, *J* = 6.8 Hz, 2H, Ar) 7.58 (d, *J* = 12.2 Hz, 1 × olefinic H), 7.52 (s, 1H, Ar), 7.39 (d, *J* = 7.2 Hz, 1H, Ar), 7.38 (d, *J* = 8.2 Hz, 1H, 1 × Ar), 7.1 (dd, *J* = 2.0 Hz, 8 Hz, 1H, 1 × Ar), 6.92 (d, *J* = 6.9 Hz, 2H, 2 × Ar), 5.37 (bd, *J* = 3.6 Hz, 1H, 1 × olefinic H), 4.61-4.65 (m, 1H, 1 × CHOCO), 3.99- 4.1 (m, 4H, 2 × OCH₂), 2.38 (t, *J* = 5.4 Hz, 2H, 1 × CH₂), 2.36-0.67(m, 52H, 23×CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.91 (d, *J* = 5.2 Hz, 3H, 1× CH₃), 0.88 (d, *J* = 5.3 Hz, 3H, 1× CH₃), 0.87 (d, *J* = 1.6 Hz, 3H, 1 × CH₃), 0.86 (d, *J* = 1.6 Hz, 3H, 1 × CH₃), 0.67 (s, 3H,

1×CH₃); MS (FAB+): m/z for C₅₉H₈₉O₅(M+1) Calculated: 877.7, Found: 877.5; Anal. calcd for C₅₉H₈₈O₅ (found) %: C 80.77 (80.9) and H 10.11 (10.4).

3DC-5,8. A cream colored solid; $R_f = 0.39$ (10%EtOAc-hexanes); yield: 0.174 g (80%); UV-Vis: $\lambda_{\max} = 342.5$ nm, $\epsilon = 0.9 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 246.5$ nm, $\epsilon = 0.8 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2942, 2867, 2853, 1736, 1651, 1576, 1508, 1291, 1249, 1164, 1040, 827, 784 and 574; ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, $J = 15.6$ Hz, 1H, 1× olefinic H), 7.58 (d, $J = 8.6$ Hz, 2H, Ar) 7.57 (d, $J = 14.8$ Hz, 1× olefinic H), 7.52 (s, 1H, Ar), 7.38 (d, $J = 7.5$ Hz, 1H, 1× Ar), 7.36 (d, $J = 8.1$ Hz, 1H, Ar), 7.1 (d, $J = 2.4$ Hz, 6 Hz, 1H, Ar), 6.91 (d, $J = 8.7$ Hz, 2H, Ar), 5.35 (bd, $J = 3.8$ Hz, 1H, 1× olefinic H), 4.62(m, 1H, 1× CHOCO), 3.99- 4.03 (m, 4H, 2× OCH₂), 2.31(t, $J = 7.5$ Hz, 2H, 1× CH₂), 2.14-0.67(m, 49H, 20×CH₂, 6× CH, 1× CH₃), 1.01 (s, 3H, 1× CH₃), 0.89 (d, $J = 4.9$ Hz, 3H, 1× CH₃), 0.86 (d, $J = 1.6$ Hz, 3H, 1× CH₃), 0.84 (d, $J = 1.6$ Hz, 3H, 1× CH₃), 0.66 (s, 3H, 1× CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 190.26, 172.91, 159.35, 144.70, 139.70, 130.17, 129.41, 122.55, 120.78, 119.79, 119.30, 114.95, 113.69, 73.81, 68.23, 67.92, 56.71, 56.20, 50.08, 42.32, 39.76, 39.51, 38.16, 37.00, 36.59, 36.19, 35.75, 34.55, 31.88, 31.75, 29.28, 29.15, 28.88, 28.17, 27.96, 27.82, 25.97, 25.6; MS (FAB+): m/z for C₅₆H₈₃O₅(M+1) Calculated: 835.6, Found: 835.8; Anal. calcd for C₅₆H₈₂O₅ (found) %: C 80.53 (80.3); H 9.90 (10).

3DC-5,9. A cream colored solid; $R_f = 0.37$ (10%EtOAc-hexanes); yield: 0.172 g (78%); UV-Vis: $\lambda_{\max} = 349$ nm, $\epsilon = 1.5 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 239.1$ nm, $\epsilon = 1.6 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2942, 2854, 1736, 1651, 1566, 1509, 1291, 1250, 1165, 1039, 828, 785 and 574; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 12.6$ Hz, 1H, 1× olefinic H), 7.59 (d, $J = 7.0$ Hz, 2H, Ar) 7.58 (d, $J = 13.6$ Hz, 1× olefinic H), 7.51 (s, 1H, Ar), 7.38 (d, $J = 5.6$ Hz, 1H, Ar), 7.37(d, $J = 6.9$ Hz, 1H, Ar), 7.1 (dd, $J = 2.2$ Hz, 6.6 Hz, 1H, Ar), 6.92 (d, $J = 6.8$ Hz, 2H, Ar), 5.37 (bd, $J = 3.4$ Hz, 1H, 1× olefinic H), 4.63 (m, 1H, 1× CHOCO), 4.03 (t, $J = 5.2$ Hz, 2H, 1×

OCH₂), 4.0 (t, $J = 5.24$ Hz, 2H, 1 × OCH₂), 2.34-0.67 (m, 50H, 22 × CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.94 (d, $J = 4.1$ Hz, 3H, 1 × CH₃), 0.91 (d, $J = 5.2$ Hz, 3H, 1 × CH₃), 0.87 (d, $J = 1.3$ Hz, 3H, 1 × CH₃), 0.86 (d, $J = 1.4$ Hz, 3H, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); MS (FAB+): m/z for C₅₇H₈₅O₅(M+1) Calculated: 849.6, Found: 849.6; Anal. calcd for C₅₇H₈₄O₅ (found) %:C 80.61 (80.8); H 9.97 (9.9).

3DC-5,10. A yellow colored solid; $R_f = 0.37$ (10%EtOAc-hexanes); yield: 0.177 g (79%); UV-Vis: $\lambda_{\max} = 341.7$ nm, $\epsilon = 1.6 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 245.3$ nm, $\epsilon = 1.5 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2940, 2853, 1737, 1652, 1566, 1509, 1291, 1250, 1166, 1039, 828, 784 and 574; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 12.5$ Hz, 1H, 1 × olefinic H), 7.59 (d, $J = 7.0$ Hz, 2H, Ar) 7.57 (d, $J = 13.6$ Hz, 1 × olefinic H), 7.51 (s, 1H, Ar), 7.39(d, $J = 5.5$ Hz, 1H, Ar), 7.38 (d, $J = 6.9$ Hz, 1H, Ar), 7.1 (dd, $J = 1.8$ Hz, 6.5 Hz, 1H, Ar), 6.92 (d, $J = 7.0$ Hz, 2H, Ar), 5.37(d, $J = 4.2$ Hz, 1H, 1 × olefinic H), 4.63 (m, 1H, 1 × CHOCO), 4.04 (t, $J = 5.1$ Hz, 2H, 1 × OCH₂), 4.0 (t, $J = 5.20$ Hz, 2H, 1 × OCH₂), 2.34-0.67 (m, 58H, 23 × CH₂, 6 × CH, 2 × CH₃), 1.01 (s, 3H, 1 × CH₃), 0.88 (d, $J = 4.6$ Hz, 3H, 1 × CH₃), 0.86 (d, $J = 3.6$ Hz, 3H, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); MS (FAB+): m/z for C₅₈H₈₆O₅, Calculated: 862.6, Found: 862.9; Anal. calcd for C₅₉H₈₆O₅ (found) %:C 80.69 (80.7); H 10.04 (10).

3DC-5,11. A cream colored solid; $R_f = 0.40$ (10%EtOAc-hexanes); yield: 0.194 g (85%); UV-Vis: $\lambda_{\max} = 342.2$ nm, $\epsilon = 1.6 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 242.6$ nm, $\epsilon = 1.4 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2928, 2852, 1729, 1655, 1589, 1512, 1290, 1251, 1170, 1042, 829 and 786; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 12.5$ Hz, 1H, 1 × olefinic H), 7.59 (d, $J = 7.0$ Hz, 2H, Ar), 7.58 (d, $J = 13.5$ Hz, 1 × olefinic H), 7.51 (s, 1H, Ar), 7.39 (d, $J = 5.5$ Hz, 1H, Ar), 7.38(d, $J = 7.0$ Hz, 1H, Ar), 7.1 (dd, $J = 1.9$ Hz, 6.5 Hz, 1H, Ar), 6.92 (d, $J = 6.9$ Hz, 2H, Ar), 5.37(d, $J = 3.2$ Hz, 1H, 1 × olefinic H), 4.63 (m, 1H, 1 × CHOCO), 4.04 (t, $J = 5.04$ Hz, 2H, 1 × OCH₂), 4.0 (t, $J = 5.2$ Hz, 2H, 1 × OCH₂), 2.34-0.67(m, 57H, 24 × CH₂, 6 × CH, 1 × CH₃), 1.01 (s, 3H, 1 × CH₃), 0.92 (d, $J = 5.2$ Hz, 3H, 1 × CH₃), 0.87 (d, $J = 1.7$ Hz, 3H, 1 ×

CH₃), 0.86 (d, $J = 1.7$ Hz, 3H, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); MS (FAB+): m/z for C₅₉H₈₉O₅(M+1) Calculated: 877.8, Found: 877.6; Anal. calcd for C₅₉H₈₈O₅ (found) %: C 80.77(81); H 10.11(10).

3DC-5,12. A yellow colored solid; $R_f = 0.42$ (10%EtOAc-hexanes); yield: 0.171 g (74%); UV-Vis: $\lambda_{\max} = 345$ nm, $\epsilon = 3.2 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 246.8$ nm, $\epsilon = 2.6 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2929, 2853, 1730, 1656, 1590, 1514, 1291, 1252, 1172, 1043, 830 and 787; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 12.5$ Hz, 1H, 1×olefinic H), 7.59 (d, $J = 7.0$ Hz, 2H, Ar), 7.58 (d, $J = 13.4$ Hz, 1 × olefinic H), 7.51 (s, 1H, 1 × Ar), 7.39(d, $J = 5.6$ Hz, 1H, Ar), 7.37(d, $J = 6.9$ Hz, 1H, Ar), 7.1 (dd, $J = 1.9$ Hz, 6.5 Hz, 1H, Ar), 6.92 (d, $J = 7.0$ Hz, 2H, Ar), 5.37(d, $J = 3.5$ Hz, 1H, 1 × olefinic H), 4.62 (m, 1H, 1 × CHOCO), 4.04 (t, $J = 5.1$ Hz, 2H, 1 × OCH₂), 4.0 (t, $J = 5.2$ Hz, 2H, 1 × OCH₂), 2.34-0.67(m, 56H, 25 × CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.91 (d, $J = 5.2$ Hz, 3H, 1 × CH₃), 0.89 (d, $J = 5.2$ Hz, 3H, 1 × CH₃), 0.87 (d, $J = 1.8$ Hz, 3H, 1 × CH₃), 0.86 (d, $J = 1.7$ Hz, 3H, 1 × CH₃), 0.67(s, 3H, 1 × CH₃); MS (FAB+): m/z for C₆₀H₉₁O₅(M+1) Calculated: 891.7, Found: 891.6; Anal. calcd for C₆₀H₉₀O₅ (found) %: C 80.85 (80.5); H 10.18 (10.5).

3DC-7,8. A white colored solid; $R_f = 0.35$ (10%EtOAc-hexanes); yield: 0.191 g (85%); UV-Vis: $\lambda_{\max} = 342.2$ nm, $\epsilon = 1.9 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 248.4$ nm, $\epsilon = 1.2 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2933, 2867, 2360, 2343, 1728, 1659, 1572, 1511, 1291, 1250, 1173, 1027, 826 and 668; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 12.6$ Hz, 1H, 1 × olefinic H), 7.59 (d, $J = 7.0$ Hz, 2H, Ar) 7.57 (d, $J = 14.8$ Hz, 1 × olefinic H), 7.52 (s, 1H, Ar), 7.38 (d, $J = 6.3$ Hz, 1H, Ar), 7.36 (d, $J = 6.3$ Hz, 1H, Ar), 7.11 (dd, $J = 1.8$ Hz, 6.4 Hz, 1H, Ar), 6.92 (d, $J = 7$ Hz, 2H, Ar), 5.36 (bd, $J = 3.1$ Hz, 1H, 1 × olefinic H), 4.61(m, 1H, 1×CHOCO), 3.99- 4.04 (m, 4H, 2 × OCH₂), 2.32-0.67 (m, 55H, 23 × CH₂, 6 × CH, 1 × CH₃), 1.01 (s, 3H, 1 × CH₃), 0.91 (d, $J = 5.2$ Hz, 3H, 1 × CH₃), 0.87 (d, $J = 1.8$ Hz, 3H, 1× CH₃), 0.86 (d, $J = 1.8$ Hz, 3H, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 190.32,

172.78, 161.42, 160.23, 144.73, 140.07, 139.82, 130.22, 129.46, 127.57, 122.59, 120.79, 119.92, 119.41, 115.04, 113.78, 73.78, 68.27, 56.79, 56.28, 50.16, 42.40, 39.84, 39.58, 38.24, 37.08, 36.67, 36.26, 35.81, 34.70, 31.96, 31.81, 29.71, 29.34, 29.21, 29.02, 28.23, 28.03, 27.89, 26.04; MS (FAB+): m/z for C₅₈H₈₆O₅, Calculated: 862.6, Found: 862.3; Anal. calcd for C₅₈H₈₆O₅ (found) %: C 80.69 (81); H 10.04 (9.9).

3DC-7,9. A colorless solid; $R_f = 0.34$ (10%EtOAc-hexanes); yield: 0.178 g (78%); UV-Vis: $\lambda_{\max} = 341$ nm, $\epsilon = 2.3 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 251.2$ nm, $\epsilon = 2.1 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2944, 2856, 1738, 1650, 1567, 1510, 1292, 1250, 1166, 1040, 830, 786 and 576; ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, $J = 15.8$ Hz, 1H, 1 \times olefinic H), 7.58 (d, $J = 8.6$ Hz, 2H, Ar) 7.57 (d, $J = 15.6$ Hz, 1 \times olefinic H), 7.51 (s, 1H, Ar), 7.38 (d, $J = 8.2$ Hz, 1H, Ar), 7.36(d, $J = 7.5$ Hz, 1H, Ar), 7.08 (dd, $J = 2.1$ Hz, 6.6 Hz, 1H, Ar), 6.91 (d, $J = 8.2$ Hz, 2H, Ar), 5.31(bd, $J = 3.2$ Hz, 1H, 1 \times olefinic H), 4.61(m, 1H, 1 \times CHOCO), 3.97-4.03 (m, 4H, 2 \times OCH₂), 2.34-0.67 (m, 57H, 24 \times CH₂, 6 \times CH, 1 \times CH₃), 1.01 (s, 3H, 1 \times CH₃), 0.88 (d, $J = 6.6$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.7$ Hz, 3H, 1 \times CH₃), 0.84 (d, $J = 1.6$ Hz, 3H, 1 \times CH₃), 0.66 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for C₅₉H₈₉O₅(M+1) Calculated: 877.7, Found: 877.8; Anal. calcd for C₅₉H₈₈O₅ (found) %: C 80.77 (80.8); H 10.11 (10).

3DC-7,10. A colorless solid; $R_f = 0.39$ (10%EtOAc-hexanes); yield: 0.181 g (78%); UV-Vis: $\lambda_{\max} = 343.9$ nm, $\epsilon = 20.6 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 249.8$ nm, $\epsilon = 12.3 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2928, 2852, 1727, 1656, 1570, 1512, 1292, 1248, 1174, 1029, 986 and 832; ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, $J = 15.8$ Hz, 1H, 1 \times olefinic H), 7.58 (d, $J = 8.6$ Hz, 2H, Ar) 7.57 (d, $J = 15.5$ Hz, 1 \times olefinic H), 7.51 (s, 1H, Ar), 7.4(d, $J = 8.0$ Hz, 1H, Ar), 7.37(d, $J = 7.4$ Hz, 1H, Ar), 7.1 (dd, $J = 2.4$ Hz, 6.8 Hz, 1H, Ar), 6.91 (d, $J = 8.7$ Hz, 2H, Ar), 5.36 (bd, $J = 4.2$ Hz, 1H, 1 \times olefinic H), 4.63-4.65 (m, 1H, 1 \times CHOCO), 3.98-4.03 (m, 4H, 2 \times OCH₂), 2.28-0.67(m, 59H, 25 \times CH₂, 6 \times CH, 1 \times CH₃), 1.01 (s, 3H, 1 \times CH₃), 0.91(d, $J = 6.6$ Hz, 3H, 1 \times CH₃), 0.87 (d, $J = 4.0$ Hz, 3H, 1 \times CH₃), 0.85 (d, $J = 5.0$ Hz, 3H, 1 \times CH₃),

0.66 (s, 3H, 1 × CH₃); MS (FAB⁺): m/z for C₆₀H₉₀O₅, Calculated: 890.7, Found: 890.9; Anal. calcd for C₆₀H₉₀O₅ (found) %: C 80.85 (81.2%); H 10.18 (9.8).

3DC-7,11. A colorless solid; *R_f* = 0.4 (10%EtOAc-hexanes); yield: 0.169 g (72%); UV-Vis: λ_{max} = 341 nm, ε = 1.5 × 10⁴ L mol⁻¹cm⁻¹, λ_{max} = 247.1 nm, ε = 1.4 × 10⁴ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{max} in cm⁻¹: 2927, 2852, 1726, 1656, 1570, 1513, 1446, 1292, 1248, 1174, 1030, 986 and 832; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 15.6 Hz, 1H, 1 × olefinic H), 7.59 (d, *J* = 8.6 Hz, 2H, Ar) 7.58 (d, *J* = 15.2 Hz, 1 × olefinic H), 7.52 (s, 1H, Ar), 7.39(d, *J* = 8.2 Hz, 1H, Ar), 7.38 (d, *J* = 7.5 Hz, 1H, Ar), 7.1 (dd, *J* = 2.2 Hz, 8.1 Hz, 1H, Ar), 6.92 (d, *J* = 8.7 Hz, 2H, Ar), 5.37(d, *J* = 3.6 Hz, 1H, 1 × olefinic H), 4.57-4.62 (m, 1H, 1 × CHOCO), 4.02 (t, *J* = 6.4 Hz, 2H, 1 × OCH₂), 4.0 (t, *J* = 6.4 Hz, 2H, 1 × OCH₂), 2.29-0.67(m, 61H, 26 × CH₂, 6 × CH, 1 × CH₃), 1.01 (s, 3H, 1 × CH₃), 0.91(d, *J* = 6.6 Hz, 3H, 1 × CH₃), 0.87 (d, *J* = 1.7 Hz, 3H, 1 × CH₃), 0.85 (d, *J* = 1.6 Hz, 3H, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); MS (FAB⁺): m/z for C₆₁H₉₃O₅(M+1) Calculated: 905.7, Found: 905.4; Anal. calcd for C₆₁H₉₂O₅ (found) %: C 80.92(80.5); H 10.24 (10).

3DC-7,12. A colorless solid; *R_f* = 0.41 (10%EtOAc-hexanes); yield: 0.2 g (85%); UV-Vis: λ_{max} = 345.2 nm, ε = 1.6 × 10⁴ L mol⁻¹cm⁻¹, λ_{max} = 245.8 nm, ε = 1.3 × 10⁴ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{max} in cm⁻¹: 2928, 2854, 1727, 1657, 1571, 1514, 1447, 1292, 1248, 1176, 1032, 988 and 834; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 15.6 Hz, 1H, 1 × olefinic H), 7.59 (d, *J* = 8.6 Hz, 2H, Ar), 7.57 (d, *J* = 18.1 Hz, 1 × olefinic H), 7.51 (s, 1H, Ar), 7.41(d, *J* = 8.4 Hz, 1H, Ar), 7.38 (d, *J* = 7.2 Hz, 1H, Ar), 7.1 (dd, *J* = 2.2 Hz, 8.0 Hz, 1H, Ar), 6.92 (d, *J* = 8.7 Hz, 2H, Ar), 5.37(d, *J* = 3.6 Hz, 1H, 1 × olefinic H), 4.6-4.62 (m, 1H, 1 × CHOCO), 4.03 (t, *J* = 6.4 Hz, 2H, 1 × OCH₂), 4.0 (t, *J* = 4.2 Hz, 2H, 1 × OCH₂), 2.26-0.67(m, 63H, 27 × CH₂, 6 × CH, 1 × CH₃), 1.01 (s, 3H, 1 × CH₃), 0.89(d, *J* = 8.6 Hz, 3H, 1 × CH₃), 0.87 (d, *J* = 1.7 Hz, 3H, 1 × CH₃), 0.85 (d, *J* = 1.7 Hz, 3H, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 190.27, 173.12, 161.30, 159.38, 144.67, 139.92, 139.69, 130.15, 129.38,

127.42, 122.51, 120.70, 119.73, 119.33, 114.90, 113.6, 73.68, 68.13, 56.66, 56.13, 50.02, 42.28, 39.71, 39.47, 38.12, 36.96, 36.55, 36.14, 35.72, 34.6, 31.84, 29.5, 29.27, 29.10, 28.93, 28.15, 27.94, 27.78, 25.93, 25.80, 24.9, 24.22, 23.78, 22.71, 22.59, 22.47, 20.98, 19.24, 18.65, 15.42, 14.0, 11.78; MS (FAB+): m/z for C₆₂H₉₅O₅(M+1) Calculated: 919.7, Found: 919.7; Anal. calcd for C₆₂H₉₄O₅ (found) %: C 80.99 (80.9); H 10.31 (10.6).

I.2.4. Synthesis of 3-*n*-octyloxy acetophenone (5)

This compound was prepared using a procedure analogous to that described above for the synthesis of 4-alkoxy benzaldehydes (**2a-e**). Precursors and their quantities used: *n*-octyl bromide (22.0 mmol, 1.2 equiv.), 3-hydroxy acetophenone (3 g, 21.8 mmol, 1 equiv.), anhydrous K₂CO₃ (6.1 g, 44.1 mmol, 2 equiv.) and butanone (10 ml). A colorless liquid; *R_f* = 0.66 (20% EtOAc-hexanes); yield: 4.33 g (80 %); IR (KBr Pellet) ν_{\max} in cm⁻¹: 3018, 2929, 2857, 1654, 1576, 1441, 1336, 1256, 1169, 831 and 758; ¹H NMR (200 MHz, CDCl₃): δ 7.9 (d, *J* = 8.3 Hz, 2H, 2 × Ar), 7.02 (d, *J* = 8.2 Hz, 2H, Ar), 4.02 (t, *J* = 6.4 Hz, 2H, 1 × OCH₂), 2.5 (s, 3H, 1 × COCH₃), 1.80-0.86 (m, 15H, 6 × CH₂, 1 × CH₃); MS (FAB+): m/z for C₁₆H₂₅O₂(M+1) Calculated: 249.2, Found: 249.2.

I.2.5. Synthesis of hydroxy chalcone 6

Compound **6** was synthesized using a synthetic procedure similar to that described above for the preparation of chalcones (**3a-e**). Precursors and their quantities used: 4-hydroxy benzaldehyde (1.48 g, 12.1 mmol, 1equiv.), 3-*n*-octyloxy acetophenone (**5**) (3 g, 12.1 mmol, 1equiv.) and KOH (2.44 g, 43.5 mmol, 3.6 equiv.) and methanol (20 ml). Column chromatography: silica gel (60-120 mesh) and 10% ethylacetate-hexanes as eluent. A yellow solid; *R_f* = 0.25 (2:8 EtOAc-hexanes); yield: 3.33 g, 78 %; m.p.: 74°C ; IR (KBr Pellet) ν_{\max} in cm⁻¹: 3338, 2929, 2857, 1654, 1576,

1514, 1441, 1336, 1296, 1256, 1169, 831, 758 and 668; ^1H NMR (200 MHz, CDCl_3): δ 7.8 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.57 (d, $J = 8.6$ Hz, 4H, Ar), 7.39 (t, $J = 7.6$ Hz, 15.8 Hz, 2H, 1 \times olefinic H, Ar), 7.12 (d, $J = 7.8$ Hz, 1H, Ar), 6.88 (d, $J = 8.4$ Hz, 2H, Ar), 5.16 (s, 1H, 1 \times OH), 3.95-4.1 (t, $J = 6.4$ Hz, 2H, 1 \times OCH_2), 1.85-0.86 (m, 15H, 6 \times CH_2 , 1 \times CH_3); MS (FAB+): m/z for $\text{C}_{23}\text{H}_{29}\text{O}_3(\text{M}+1)$ Calculated: 353.2, Found: 353.2; Anal. calcd for $\text{C}_{23}\text{H}_{28}\text{O}_3$: C, 78.38; H, 8.01. Found: C, 78.5; H, 8.4.

1.2.6. Synthesis of dimers of series-2 (3RDC-n,m)

These dimers were prepared and purified in a similar way to that described above for compounds of series-1 (see section 2.3B). Precursors and their quantities used: cholesteryl ω -bromoalkanoate (**1a-d**) (0.26 mmol, 1equiv.), hydroxy chalcone **6** (0.092 g, 0.26 mmol, 1equiv.), anhydrous K_2CO_3 (0.072 g, 0.52 mmol, 4 equiv.) and dry DMF (5-6 ml).

3RDC-3,8: A colorless solid; $R_f = 0.48$ (20% EtOAc-hexanes); yield: 0.167 g, (80%); UV-Vis: $\lambda_{\text{max}} = 338.3$ nm, $\epsilon = 1.5 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$, $\lambda_{\text{max}} = 246.8$ nm, $\epsilon = 1.5 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$, IR (KBr Pellet) ν_{max} in cm^{-1} : 2934, 2868, 1728, 1660, 1588, 1512, 1468, 1252, 1177, 1027, 984 and 827; ^1H NMR (400 MHz, CDCl_3): δ 7.78 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.59 (d, $J = 8.6$ Hz, 2H, Ar), 7.57 (d, $J = 15.6$ Hz, 1 \times olefinic H), 7.52 (s, 1H, Ar), 7.4 (d, $J = 8.3$ Hz, 1H, Ar), 7.35 (d, $J = 7.3$ Hz, 1H, Ar), 7.1 (dd, $J = 2.4$ Hz, 5.8 Hz, 1H, Ar), 6.92 (d, $J = 8.7$ Hz, 2H, Ar), 5.36 (bd, $J = 3.6$ Hz, 1H, 1 \times olefinic H), 4.6-4.64 (m, 1H, 1 \times CHOCO), 3.99-4.1 (m, 4H, 2 \times OCH_2), 2.5-0.67 (m, 50H, 19 \times CH_2 , 6 \times CH, 2 \times CH_3), 1.01 (s, 3H, 1 \times CH_3), 0.87 (d, $J = 1.6$ Hz, 3H, 1 \times CH_3), 0.85 (d, $J = 1.7$ Hz, 3H, 1 \times CH_3), 0.67 (s, 3H, 1 \times CH_3); MS (FAB+): m/z for $\text{C}_{54}\text{H}_{79}\text{O}_5(\text{M}+1)$ Calculated: 807.6, Found: 807.2; Anal. calcd for $\text{C}_{54}\text{H}_{78}\text{O}_5$ (found) %: C 80.35 (80.6); H 9.74 (9.7).

3RDC-4,8: A colorless solid; $R_f = 0.48$ (20% EtOAc-hexanes); yield: 0.169 g (79%); UV-Vis: $\lambda_{\max} = 339$ nm, $\epsilon = 1.7 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 250$ nm, $\epsilon = 1.6 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2936, 2869, 1730, 1662, 1590, 1512, 1470, 1254, 1178, 1027, 984 and 830; ¹H NMR (400 MHz, CDCl₃): δ 7.8 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.58 (d, $J = 8.7$ Hz, 2H, Ar) 7.57 (d, $J = 15.3$ Hz, 1 \times olefinic H), 7.52 (s, 1H, Ar), 7.39 (d, $J = 8.2$ Hz, 1H, Ar), 7.37 (d, $J = 7.4$ Hz, 1H, Ar), 7.1 (dd, $J = 1.8$ Hz, 6.4 Hz, 1H, Ar), 6.91 (d, $J = 8.8$ Hz, 2H, Ar), 5.37 (bd, $J = 4.1$ Hz, 1H, 1 \times olefinic H), 4.6-4.64 (m, 1H, 1 \times CHOCO), 4-4.1 (m, 4H, 2 \times OCH₂), 2.37-0.67 (m, 49H, 20 \times CH₂, 6 \times CH, 1 \times CH₃), 1.02 (s, 3H, 1 \times CH₃), 0.91 (d, $J = 6.4$ Hz, 3H, 1 \times CH₃), 0.87 (d, $J = 1.6$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.7$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for C₅₅H₈₁O₅(M+1) Calculated: 821.6, Found: 821.5; Anal.calcd for C₅₅H₈₀O₅ (found) %:C 80.44 (80.4); H 9.82 (9.9).

3RDC-5,8: A colorless solid; $R_f = 0.48$ (20% EtOAc-hexanes); yield: 0.174 g (80%); UV-Vis: $\lambda_{\max} = 341$ nm, $\epsilon = 1.4 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 249.2$ nm, $\epsilon = 3.7 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2936, 2867, 1727, 1657, 1582, 1511, 1472, 1258, 1175, 1028, 824 and 793; ¹H NMR (400 MHz, CDCl₃): δ 7.8 (d, $J = 12.6$ Hz, 1H, 1 \times olefinic H), 7.58 (d, $J = 8.7$ Hz, 2H, Ar) 7.57 (d, $J = 15.3$ Hz, 1 \times olefinic H), 7.52 (s, 1H, Ar), 7.39(d, $J = 6.2$ Hz, 1H, Ar), 7.37(d, $J = 6.4$ Hz, 1H, Ar), 7.1 (dd, $J = 1.8$ Hz, 6.5 Hz, 1H, Ar), 6.9 (d, $J = 7.0$ Hz, 2H, Ar), 5.37 (bd, $J = 4.2$ Hz, 1H, 1 \times olefinic H), 4.63 (m, 1H, 1 \times CHOCO), 4-4.04 (m, 4H, 2 \times OCH₂), 2.34-0.67 (m, 48H, 21 \times CH₂, 6 \times CH), 1.01 (s, 3H, 1 \times CH₃), 0.96 (d, $J = 4.2$ Hz, 3H, 1 \times CH₃), 0.94 (d, $J = 4.3$ Hz, 3H, 1 \times CH₃), 0.87 (d, $J = 1.8$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.7$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for C₅₆H₈₃O₅(M+1) Calculated: 835.6, Found: 835.7; Anal.calcd for C₅₆H₈₂O₅ (found) %: C 80.53 (80.3); H 9.90 (10).

3RDC-7,8: A colorless solid $R_f = 0.52$ (20% EtOAc-hexanes); yield: 0.180 g (80%); UV-Vis: $\lambda_{\max} = 341.8$ nm, $\epsilon = 1.7 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 249$ nm, $\epsilon = 1.4 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2931, 2853, 1729, 1653, 1580, 1514, 1470,

1440, 1262, 1174, 1018, 822 and 740; ^1H NMR (400 MHz, CDCl_3): δ 7.8 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.59 (d, $J = 8.6$ Hz, 2H, Ar), 7.57 (d, $J = 15.0$ Hz, 1 \times olefinic H), 7.52 (s, 1H, Ar), 7.4 (d, $J = 8.2$ Hz, 1H, Ar), 7.38 (d, $J = 7.4$ Hz, 1H, Ar), 7.12 (dd, $J = 2$ Hz, 6.8 Hz, 1H, Ar), 6.9 (d, $J = 8.7$ Hz, 2H, Ar), 5.36 (bd, $J = 3.6$ Hz, 1H, 1 \times olefinic H), 4.57- 4.63 (m, 1H, 1 \times CHOCO), 4.03 (t, $J = 6.6$ Hz, 2H, 1 \times OCH_2), 3.99 (t, $J = 6.6$ Hz, 2H, 1 \times OCH_2), 2.34-0.67(m, 55H, 23 \times CH_2 , 6 \times CH, 1 \times CH_3), 1.01 (s, 3H, 1 \times CH_3), 0.90 (d, $J = 6.5$ Hz, 3H, 1 \times CH_3), 0.87 (d, $J = 1.7$ Hz, 3H, 1 \times CH_3), 0.85 (d, $J = 1.7$ Hz, 3H, 1 \times CH_3), 0.67 (s, 3H, 1 \times CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 190.29, 173.10, 161.25, 159.42, 144.65, 139.91, 139.67, 130.15, 129.37, 127.46, 122.54, 120.67, 119.76, 119.35, 114.89, 113.61, 73.69, 68.25, 68.06, 56.66, 56.13, 50.02, 42.28, 39.70, 39.47, 38.13, 36.96, 36.56, 36.14, 35.72, 34.57, 31.84, 31.74, 29.27, 29.17, 29.01, 28.90, 28.14, 27.94, 27.78, 25.98, 25.75, 24.87, 24.22, 23.78, 22.72, 22.57, 22.47, 20.98, 19.24, 18.65, 13.98, 11.78; MS(FAB+): m/z for $\text{C}_{58}\text{H}_{86}\text{O}_5$, Calculated: 862.6, Found: 862.1; Anal.calcd for $\text{C}_{58}\text{H}_{86}\text{O}_5$ (found) %:C 80.69 (80.4); H 10.04 (9.9).

I.2.7. Synthesis of 4-bromo-4'-(*n*-octyloxy)biphenyl (7):

This compound was prepared using a procedure similar to that described for the synthesis of aldehyde **5**. Precursors and their quantities used: *n*-octylbromide (0.77 g, 4.0 mmol, 1.2 equiv.), 4-bromo-4'-hydroxy biphenyl (1 g, 4.0 mmol, 1equiv.), anhydrous K_2CO_3 (1.1 g, 8.0 mmol, 2 equiv.) and butanone. Column chromatography: silica gel (100-200 mesh) and 10% EtOAc-hexanes as an eluent. A colorless solid; $R_f = 0.8$ (10% EtOAc-hexanes); yield: 1.34 g, 85%; m.p.: 125 $^\circ\text{C}$ IR (KBr Pellet) ν_{max} in cm^{-1} : 3419, 2920, 2853, 1605, 1523, 1474, 1288, 1253, 1198, 996, 812 and 789; ^1H NMR (200 MHz, CDCl_3): δ 7.53 (d, $J = 8.4$ Hz, 2H, Ar), 7.47 (d, $J = 9.0$ Hz, 2H, Ar), 7.44 (d, $J = 8.6$ Hz, 2H, Ar), 6.96 (d, $J = 8.6$ Hz, 2H, Ar), 3.99 (t, $J = 6.6$ Hz, 2H, 1 \times OCH_2), 1.84-0.86 (m, 15H, 6 \times CH_2 , 1 \times CH_3); MS (FAB+): m/z for $\text{C}_{20}\text{H}_{25}\text{BrO}_3$ Calculated: 392.1, Found: 392.1.

I.2.8. Synthesis of 4-formyl-4'-(*n*-octyloxy)biphenyl (**8**):

To a solution of compound **7** (4.33 g, 11 mmol, 1equiv.) in dry THF (15 ml) at -78 °C was added drop wise a 1.6 M solution of *n*-butyllithium (13 mmol, 1.2 equiv) in hexanes under an inert atmosphere. After stirring for 2.5 h, a solution of dry DMF (1.3 ml, 17 mmol, 1.5 equiv) in dry THF was added drop wise at -78 °C. The reaction mixture was allowed to warm up to room temperature and continued to stir for 12 h. The reaction mixture was acidified with cold 1N HCl (30 ml) and stirred for 1 h. The crude product was extracted into ethyl acetate (2 × 50 ml) and the combined organic extracts were washed with water (2 × 100 ml) and dried over anhydrous Na₂SO₄. Solvent was then removed *in vacuo* and the crude material was purified by column chromatography on silica gel (60-120) using 30% CH₂Cl₂-hexanes as an eluent. A colourless solid; $R_f = 0.57$ (5% EtOAc-CH₂Cl₂); yield: 2.39 g (70%); m.p. 155 °C IR (KBr Pellet) ν_{\max} in cm⁻¹: 2955, 2922, 2855, 2364, 1601, 1477, 1293, 1253, 1185, 1122, 1029, 847 and 774; ¹H NMR (200 MHz, CDCl₃): δ 10.0 (s, 1H, CHO), 7.92 (d, $J = 8.3$ Hz, 2H, Ar), 7.72 (d, $J = 8.2$ Hz, 2H, Ar), 7.58 (d, $J = 8.0$ Hz, 2H, Ar), 7.0 (d, $J = 8.8$ Hz, 2H, Ar), 4.01 (t, $J = 6.6$ Hz, 2H, 1 × OCH₂), 1.85-0.88 (m, 15H, 6 × CH₂, 1 × CH₃); MS (FAB+): m/z for C₂₁H₂₇O₂(M+1) Calculated: 311.2, Found: 311.2.

I.2.9. Synthesis of hydroxy chalcone **9**

Compound **9** was prepared by a procedure as described for the synthesis of chalcones **3a-e**. Precursors and their quantities used: 4-formyl-4'-(*n*-octyloxy)biphenyl (**8**) (0.372 g, 1.2 mmol, 1.0 equiv.), 3-hydroxy acetophenone (0.163 g, 1.2 mmol, 1 equiv.), KOH (0.236 g, 4.2 mmol, 3.6 equiv.) and methanol (25 ml). Column chromatography: silica gel (60-120) and 15% ethylacetate-hexanes as eluent. A yellow solid; $R_f = 0.4$ (5% EtOAc-CH₂Cl₂); yield: 0.37 g (72%); m.p.: 91 °C ; IR (KBr Pellet) ν_{\max} in cm⁻¹: 3345, 2929, 2400, 1676, 1598, 1586, 1450, 1287, 1252, 1184, 884 and 669; ¹H NMR (200 MHz, CDCl₃): δ 7.85 (d, $J = 15.6$ Hz, 1H, 1 × olefinic H), 7.7

(d, $J = 8.4$ Hz, 2H, Ar), 7.6 (d, $J = 9.2$ Hz, 2H, Ar), 7.48-7.72(m, 4H, Ar), 7.4 (t, 2H, $J = 15.6$ Hz, 8.0 Hz, 1 \times olefinic H, 1 \times Ar), 7.09 (d, $J = 7.1$ Hz, 1H, Ar), 7.0 (d, $J = 8.6$ Hz, 2H, Ar), 5.3(s, 1H, 1 \times OH), 4.01 (t, $J = 6.4$ Hz, 2H, 1 \times OCH₂), 1.85-0.86 (m, 15 H, 6 \times CH₂, 1 \times CH₃); MS (FAB+): m/z for C₂₉H₃₃O₃(M+1) Calculated: 429.2, Found: 429.2.

1.2.10. Synthesis of dimers of series-3 (3BDC-n,m series)

These target compounds were synthesized and purified in an analogous way to that described above for dimers of series-1 (see section 2.3B). Precursors and their quantities used: cholesteryl ω -bromoalkanoate (**1a-d**) (0.26 mmol, 1equiv.), hydroxy chalcone **9** (0.111 g, 0.26 mmol, 1equiv.), anhydrous K₂CO₃ (0.072 g, 0.52 mmol, 4 equiv.) and dry DMF (5-6 ml).

3BDC-3,8: A yellow solid; $R_f = 0.33$ (20% EtOAc-hexanes); yield: 0.179 g (78%); UV-Vis: $\lambda_{\max} = 349.6$ nm, $\epsilon = 1.8 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 268.9$ nm, $\epsilon = 1.7 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2933, 2868, 2852, 1712, 1585, 1574, 1498, 1467, 1254, 1193, 1172, 1042 and 822; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.7 (d, $J = 8.2$ Hz, 2H, Ar) 7.61 (d, $J = 8.1$ Hz, 2H, Ar), 7.56 (d, $J = 6.7$ Hz, 4H, Ar), 7.53 (d, $J = 13.6$ Hz, 1H, 1 \times olefinic H), 7.41(t, $J = 8.0$ Hz, 1H, Ar), 7.12 (dd, $J = 2.4$ Hz, 6.1 Hz, 1H, Ar), 6.98 (d, $J = 8.6$ Hz, 2H, Ar), 5.36 (bd, $J = 4.2$ Hz, 1H, 1 \times olefinic H), 4.63-4.65 (m, 1H, 1 \times CHOCO), 4.1 (t, $J = 6.0$ Hz, 2H, 1 \times OCH₂), 4.0 (t, $J = 6.5$ Hz, 2H, 1 \times OCH₂), 2.52-0.67(m, 50H, 19 \times CH₂, 6 \times CH, 2 \times CH₃), 1.01 (s, 3H, 1 \times CH₃), 0.87 (d, $J = 1.4$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.4$ Hz, 3H, 1 \times CH₃), 0.66 (s, 3H, 1 \times CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 190.13, 172.46, 159.14, 144.51, 142.99, 139.58, 133.16, 132.31, 129.54, 128.96, 128.01, 126.96, 122.63, 121.55, 121.0, 119.48, 114.94, 113.72, 74.09, 68.14, 67.07, 56.63, 56.13, 49.99, 42.27, 39.69, 39.47, 38.11, 36.94, 36.54, 36.15, 35.72, 31.81, 31.07, 29.22, 28.15, 27.94, 27.94, 27.77, 25.99, 24.61, 24.21, 23.79, 22.72, 22.48,

20.97, 19.23, 18.66, 13.99, 11.78; MS (FAB+): m/z for $C_{60}H_{83}O_5(M+1)$ Calculated: 883.6, Found: 883.6; Anal.calcd for $C_{60}H_{82}O_5$ (found) %: C 81.59 (81.5); H 9.36 (9.4).

3BDC-4,8: A yellow solid; $R_f = 0.33$ (20% EtOAc-hexanes); yield: 0.179 g (77%); UV-Vis: $\lambda_{max} = 347.9$ nm, $\epsilon = 1.6 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{max} = 269$ nm, $\epsilon = 1.6 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{max} in cm⁻¹: 2932, 2868, 2852, 1732, 1574, 1499, 1286, 1253, 1169, 779 and 653; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, $J = 15.8$ Hz, 1H, 1 \times olefinic H), 7.7 (d, $J = 8.3$ Hz, 2H, Ar) 7.61 (d, $J = 8.3$ Hz, 2H, Ar), 7.55 (d, $J = 8.3$ Hz, 4H, Ar), 7.53 (d, $J = 13.6$ Hz, 1H, 1 \times olefinic H) , 7.41(t, $J = 8.0$ Hz, 1H, Ar) , 7.12 (dd, $J = 2.3$ Hz, 8.4 Hz, 1H, Ar), 6.98 (d, $J = 8.7$ Hz, 2H, Ar), 5.36 (bd, $J = 4.2$ Hz, 1H, 1 \times olefinic H), 4.61-4.63 (m, 1H, 1 \times CHOCO), 3.97-4.02 (m, 4H, 2 \times OCH₂), 2.32-0.67(m, 52H, 20 \times CH₂, 6 \times CH, 2 \times CH₃), 1.01 (s, 3H, 1 \times CH₃), 0.87 (d, $J = 1.6$ Hz, 3H, 1 \times CH₃), 0.85 (d, $J = 1.6$ Hz, 3H, 1 \times CH₃), 0.66 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for $C_{61}H_{85}O_5(M+1)$ Calculated: 897.6, Found: 897.9; Anal.calcd for $C_{61}H_{84}O_5$ (found) %: C 81.65 (81.3); H 9.44 (9.5).

3BDC-5,8: A yellow solid; $R_f = 0.34$ (20% EtOAc-hexanes); yield: 0.175 g (74%); UV-Vis: $\lambda_{max} = 349.8$ nm, $\epsilon = 2.2 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{max} = 267.4$ nm, $\epsilon = 2.2 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{max} in cm⁻¹: 2935, 2867, 1734, 1589, 1576, 1498, 1250, 1174, 785 and 653; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, $J = 15.5$ Hz, 1H, 1 \times olefinic H), 7.69 (d, $J = 8.2$ Hz, 2H, Ar) 7.61 (d, $J = 8.1$ Hz, 2H, Ar) , 7.56 (d, $J = 8.7$ Hz, 4H, Ar), 7.53 (d, 1H, $J = 15.6$ Hz, 1H, 1 \times olefinic H) , 7.41(t, $J = 7.9$ Hz, 1H, Ar), 7.11 (dd, $J = 2.1$ Hz, 6.2 Hz, 1H, Ar), 6.98 (d, $J = 8.6$ Hz, 2H, Ar), 5.36 (bd, $J = 4.2$ Hz, 1H, 1 \times olefinic H), 4.63 (m, 1H, 1 \times CHOCO), 3.97-4.1 (m, 4H, 2 \times OCH₂), 2.34-0.67 (m, 51H, 21 \times CH₂, 6 \times CH, 1 \times CH₃), 1.01 (s, 3H, 1 \times CH₃), 0.89 (d, $J = 5.9$ Hz, 3H, 1 \times CH₃), 0.87 (d, $J = 1.5$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.52$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for $C_{62}H_{87}O_5(M+1)$ Calculated: 911.7, Found: 911.4; Anal.calcd for $C_{62}H_{86}O_5$ (found) %: C 81.71 (81.6); H 9.51 (9.8).

3BDC-7,8: A yellow solid; $R_f = 0.34$ (20% EtOAc-hexanes); yield: 0.182 g (75%); UV-Vis: $\lambda_{\max} = 345$ nm, $\epsilon = 1.3 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 268.5$ nm, $\epsilon = 1.3 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2932, 2868, 1732, 1589, 1574, 1499, 1253, 1190, 779 and 654; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, $J = 15.6$ Hz, 1H, 1 \times olefinic H), 7.7 (d, $J = 8.3$ Hz, 2H, Ar), 7.62 (d, $J = 8.1$ Hz, 2H, Ar), 7.55-7.59 (m, 6H, Ar), 7.49 (d, 1H, $J = 13.2$ Hz, 1H, 1 \times olefinic H), 7.41(t, $J = 7.9$ Hz, 1H, Ar), 7.12 (dd, $J = 1.9$ Hz, 7.8 Hz, 1H, Ar), 6.99 (d, $J = 8.7$ Hz, 2H, Ar), 5.37(bd, $J = 4.2$ Hz, 1H, 1 \times olefinic H), 4.57-4.63 (m, 1H, 1 \times CHOCO), 3.97-4.1 (m, 4H, 2 \times OCH₂), 2.32-0.67(m, 56 H, 22 \times CH₂, 6 \times CH, 2 \times CH₃), 1.01 (s, 3H, 1 \times CH₃), 0.87 (d, $J = 1.8$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.7$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for C₆₄H₉₁O₅(M+1) Calculated: 939.7, Found: 939.7; Anal.calcd for C₆₄H₉₀O₅ (found) %: C 81.83 (81.8); H 9.66 (9.5).

1.2.11. Synthesis of 1,2-difluoro-3-(*n*-octyloxy) benzene (10)

This compound was synthesized in a similar way to that described for the preparation of 4-alkoxy benzaldehydes (**2a-e**). Precursors and their quantities used: *n*-octylbromide (3 g, 15.4 mmol, 1.2 equiv.), 1,2-difluoro-3-hydroxy benzene, (2 g, 15.4 mmol, 1 equiv.), anhydrous K₂CO₃ (4.24 g, 30.7 mmol, 2 equiv.) and butanone (15 ml). Column chromatography: silica gel (60-120 mesh) and 5% ethylacetate-hexanes as the eluent. A colorless liquid; $R_f = 0.44$ (10% CH₂Cl₂-hexanes); yield: 3.47 g (93%); IR (Neat) ν_{\max} in cm⁻¹ 3435, 3046, 2928, 2857, 1619, and 1597; ¹H NMR (200 MHz, CDCl₃): δ 6.94 (m, 1H, Ar), 6.71 (m, 2H, Ar), 4.02 (t, $J = 6.6$ Hz, 2H, 1 \times OCH₂), 1.81 (m, 2H, 1 \times CH₂), 1.4-1.2 (m, 10H, 5 \times CH₂) and 0.88 (t, $J = 6.5$ Hz, 3H, 1 \times CH₃); MS (FAB+): m/z for C₁₄H₂₀F₂O, Calculated: 242.2, Found: 242.4.

1.2.12. Synthesis of 2,3-difluoro-4-(*n*-octyloxy)phenylboronic acid (11)

n-Butyllithium (1.6 M solution in hexanes; 13 mmol, 1.2 equiv.) was added dropwise to a solution of **10** (2.67 g, 11 mmol, 1equiv.) in dry THF (15ml) at -78 °C under dry nitrogen atmosphere. The reaction mixture was stirred at this temperature for 2.5 h before a previously cooled (-5 °C) solution of tri-isopropyl borate (3.2 g, 17 mmol, 1.5 equiv) in dry THF was added drop wise to the reaction flask at -78 °C. The reaction mixture was allowed to warm to room temperature overnight and stirred with 10 % aqueous HCl (30 ml) for 1 h. The crude product was extracted into ether (2 × 50 ml) and the combined organic extracts were washed with water (2 × 100 ml) and dried over anhydrous Na₂SO₄. The crude product obtained after evaporating solvent *in vacuo* was recrystallized twice from CH₂Cl₂. A colourless solid; *R_f* = 0.42 (50% EtOAc-hexanes); yield: 2.7 g (88 %); IR (KBr pellet) ν_{\max} in cm⁻¹: 3337, 2927, 2857, 1627, 1573 and 1520; ¹H NMR (200 MHz, CDCl₃): δ 7.48 (m, 1H, Ar), 6.77 (m, 1H, Ar), 4.92 (brs, 2H, 2 × OH), 4.07 (t, *J* = 6.58 Hz, 2H, 1 × OCH₂), 1.79 (m, 2H, 1 × CH₂), 1.5-1.3 (m, 10H, 5 × CH₂) and 0.88 (t, *J* = 6.54 Hz, 3H, 1 × CH₃).MS (FAB+): *m/z* for C₁₄H₂₂BO₃F₂ (M+1), Calculated: 287.2. Found: 287.1.

1.2.13. Synthesis of 2',3'-difluoro-4'-(*n*-octyloxy)biphenyl-4-carbaldehyde (12**)**

Boronic acid (**11**) (1 g, 3.5 mmol, 1.05 equiv.), 4-bromo benzaldehyde (0.61 g, 3.3 mmol, 1 equiv.), 2M Na₂CO₃ (aq) solution (4 ml), benzene (10 ml) and ethanol (10 ml) were taken in a 100 ml single necked RBF and degassed for 15 minutes by purging nitrogen. After adding tetrakis-(triphenyl phosphine) palladium (0) the reaction mixture was heated under reflux for 12 h. The reaction mixture was allowed to attain room temperature and was poured into cold water (50 ml). The mixture was extracted with ethyl acetate (2 × 50 ml) and the combined organic extracts were washed with brine (2 × 50 ml) and dried over anhydrous Na₂SO₄. The solvent was removed *in vacuo* and the crude product obtained was purified by column chromatography using silica gel (100-200 mesh), and 8% EtOAc-hexanes and 15% EtOAc-hexanes as eluents. The product was further purified by repeated recrystallization with hexanes. A colorless solid; *R_f* = 0.68 (7:3 CH₂Cl₂-EtOAc);

yield: 0.849 g (70%); m.p.: 78 °C. IR (KBr Pellet) ν_{\max} in cm^{-1} : 2955, 2921, 2853, 1696, 1606, 1526, 1470, 1393, 1214, 1177, 800 and 692; ^1H NMR (200 MHz, CDCl_3): δ 10.1 (s, 1H, CHO), 7.95 (d, $J = 8.0$ Hz, 2H, Ar), 7.69 (d, $J = 6.2$ Hz, 2H, Ar), 7.1-7.19 (m, 1H, Ar), 6.83 (t, $J = 7.3$ Hz, 1H, Ar), 4.1 (t, $J = 6.0$ Hz, 2H, $1 \times \text{OCH}_2$), 1.93-0.86 (m, 15H, $6 \times \text{CH}_2$, $1 \times \text{CH}_3$); MS (FAB+): m/z for $\text{C}_{21}\text{H}_{25}\text{O}_2\text{F}_2(\text{M}+1)$ Calculated: 347.2. Found: 347.2.

I.2.14. Synthesis of hydroxy chalcone 13

Compound **13** was prepared by a similar procedure as described for the preparation of chalcones (**2a-e**). Precursors and their quantities used: aldehyde (**12**) (1.7 g, 4.9 mmol, 1.0 equiv.), 3-hydroxy acetophenone (0.67 g, 4.9 mmol, 1equiv.), KOH (1 g, 17.7 mmol, 3.6 equiv.) and methanol (30 ml). Column chromatography: silica gel (60-120 mesh) and 10% EtOAc-hexanes as the eluent. A yellow solid; $R_f = 0.3$ (70% CH_2Cl_2 -EtOAc); yield: 1.82 g (80%); m.p.: 112 °C; IR (KBr Pellet) ν_{\max} in cm^{-1} : 3424, 2922, 2853, 1658, 1575, 1505, 1470, 1232, 1184, 1106, 891, 740 and 674; ^1H NMR (200 MHz, CDCl_3): δ 7.85 (d, $J = 15.7$ Hz, 1H, $1 \times \text{olefinic H}$), 7.72 (d, $J = 8.2$ Hz, 1H, Ar), 7.66 (d, $J = 13.2$ Hz, 1H, $1 \times \text{olefinic H}$), 7.5-7.59 (m, 5H, Ar) 7.4 (t, 1H, $J = 7.8$ Hz, Ar), 7.1-7.18 (m, 2H, Ar), 6.82 (d, $J = 7.3$ Hz, 1H, Ar), 5.2 (s, 1H, $1 \times \text{OH}$), 4.1 (t, $J = 6.4$ Hz, 2H, $1 \times \text{OCH}_2$), 1.89-0.86 (m, 15H, $6 \times \text{CH}_2$, $1 \times \text{CH}_3$); MS (FAB+): m/z for $\text{C}_{29}\text{H}_{30}\text{O}_3\text{F}_2$, Calculated: 464.2, Found: 464.6.

I.2.15. Synthesis of dimers of Series-4 (3BFDC-n,m series)

These target dimers were synthesized and purified in an analogous way to that noted above for dimers of series-1 (see section **2.3B**). Precursors and their quantities used: cholesteryl ω -bromoalkanoate (**1a-d**) (0.26 mmol, 1equiv.), hydroxy chalcone **13** (0.12 g, 0.26 mmol, 1equiv.), anhydrous K_2CO_3 (0.072 g, 0.52 mmol, 4 equiv.) and dry DMF (5-6 ml).

3BFDC-3,8: A cream solid; $R_f = 0.29$ (20% EtOAc-hexanes); yield: 0.182 g (76%); UV-Vis: $\lambda_{\max} = 325.8$ nm, $\epsilon = 1.8 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 262.1$ nm, $\epsilon = 1.9 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2932, 2869, 2364, 1735, 1592, 1504, 1256, 1186, 896 and 799; ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, $J = 15.6$ Hz, 1H, 1× olefinic H), 7.72 (d, $J = 8.4$ Hz, 2H, Ar) 7.49-7.61 (m, 5H, 1 × olefinic H, 4 × Ar), 7.41(t, $J = 8.0$ Hz, 1H, Ar), 7.11-7.2 (m, 2H, Ar), 6.8-6.84 (m, 1H, Ar), 5.36 (bd, $J = 4.2$ Hz, 1H, 1 × olefinic H), 4.61-4.63 (m, 1H, 1 × CHOCO), 4.06-4.1 (m, 4H, 2× OCH₂), 2.51(t, $J = 6.8$ Hz, 2H, 1× CH₂), 2.32-0.67(m, 45H, 18 × CH₂, 6 × CH, 1× CH₃), 1.01 (s, 3H, 1 × CH₃), 0.89 (d, $J = 2.2$ Hz, 3H, 1 × CH₃), 0.87 (d, $J = 1.8$ Hz, 3H, 1× CH₃), 0.85 (d, $J = 1.8$ Hz, 3H, 1 × CH₃), 0.66 (s, 3H, 1 × CH₃); MS (FAB+): m/z for C₆₀H₈₀F₂O₅, Calculated: 918.6, Found: 918.6; Anal.calcd for C₆₀H₈₀F₂O₅ (found) %:C 78.39 (78.3); H 8.77 (8.4).

3BFDC-4,8: A cream solid; $R_f = 0.29$ (20% EtOAc-hexanes); yield: 0.189 g (78%); UV-Vis: $\lambda_{\max} = 338$ nm, $\epsilon = 1.6 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 246$ nm, $\epsilon = 1.3 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2946, 2867, 2365, 1713, 1590, 1504, 1467, 1256, 1187, 1076, 952 and 794; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, $J = 15.6$ Hz, 1H, 1×olefinic H), 7.72 (d, $J = 8.3$ Hz, 2H, Ar) 7.54-7.58 (m, 5H, 1×olefinic H, 4 × Ar), 7.41(t, $J = 6.4$ Hz, 1H, Ar), 7.1-7.14 (m, 2H, Ar), 6.8-6.84 (m, 1H, Ar), 5.37(bd, $J = 4.4$ Hz, 1H, 1×olefinic H), 4.56-4.61(m, 1H, 1×CHOCO), 4.09 (t, $J = 6.6$ Hz, 2H, 1 × OCH₂), 4.04 (t, $J = 6.6$ Hz, 2H, 1× OCH₂), 2.42-0.67(m, 46H, 20 × CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.91 (d, $J = 6.5$ Hz, 3H, 1× CH₃) 0.89 (d, $J = 2.7$ Hz, 3H, 1× CH₃), 0.87 (d, $J = 1.8$ Hz, 3H, 1 × CH₃), 0.85 (d, $J = 1.7$ Hz, 3H, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); MS (FAB+): m/z for C₆₁H₈₃F₂O₅(M+1) Calculated: 933.6, Found: 933.6; Anal.calcd for C₆₁H₈₃F₂O₅ (found) %:78.50(78.3); H 8.86(8.7).

3BFDC-5,8: A cream solid; $R_f = 0.30$ (20% EtOAc-hexanes); yield: 0.184 g (75%); UV-Vis: $\lambda_{\max} = 321$ nm, $\epsilon = 1.5 \times 10^4$ L mol⁻¹cm⁻¹, $\lambda_{\max} = 262$ nm, $\epsilon = 1.8 \times 10^4$ L mol⁻¹cm⁻¹, IR (KBr Pellet) ν_{\max} in cm⁻¹: 2934, 2868, 2363, 1729, 1592, 1503, 1468,

1439, 1256, 1183, 1076 and 792; ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 12.6$ Hz, 1H, 1 \times olefinic H), 7.72 (d, $J = 6.6$ Hz, 2H, Ar) 7.58-7.6 (m, 4H, Ar), 7.54 (d, $J = 12.6$ Hz, 1 \times olefinic H), 7.41(t, $J = 6.4$ Hz, 1H, Ar), 7.1-7.14 (m, 2H, Ar), 6.8-6.84 (m, 1H, Ar), 5.37 (bd, $J = 4.3$ Hz, 1H, 1 \times olefinic H), 4.56-4.61(m, 1H, 1 \times CHOCO), 4.09 (t, $J = 5.2$ Hz, 2H, 1 \times OCH₂), 4.05 (t, $J = 5.1$ Hz, 2H, 1 \times OCH₂), 2.35-0.67 (m, 51H, 21 \times CH₂, 6 \times CH, 1 \times CH₃), 1.01 (s, 3H, 1 \times CH₃), 0.87 (d, $J = 1.7$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.7$ Hz, 3H, 1 \times CH₃), 0.85 (d, $J = 1.7$ Hz, 3H, 1 \times CH₃), 0.67 (s, 3H, 1 \times CH₃); ^{13}C NMR (100 MHz, CDCl_3): δ 190.08, 172.92, 159.37, 148.37, 144.05, 139.65, 137.09, 134.14, 129.51,129.14, 128.59, 123.39, 122.55, 122.33,121.95, 120.86, 119.60,113.69, 109.75,73.78, 69.97, 67.90, 56.66, 56.14, 50.02, 42.28, 39.70, 39.47, 38.12, 36.95, 36.55, 36.15, 35.72, 34.52, 31.84, 31.72, 29.21, 29.11, 28.84, 28.15, 27.94, 27.79, 25.81, 25.56, 24.72, 24.21, 23.79, 22.72, 22.56, 22.48, 20.98, 19.23, 18.65, 13.98, 11.78; MS (FAB+): m/z for $\text{C}_{62}\text{H}_{85}\text{F}_2\text{O}_5(\text{M}+1)$ Calculated: 947.6, Found: 947.6; Anal.calcd for $\text{C}_{62}\text{H}_{84}\text{F}_2\text{O}_5$ (found) %: C 78.61(78.6); H 8.94(8.7).

3BFDC-7,8: A cream solid; $R_f = 0.38$ (20% EtOAc-hexanes); yield: 0.186 g (74%); UV-Vis: $\lambda_{\text{max}} = 325.7$ nm, $\epsilon = 1.7 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$, $\lambda_{\text{max}} = 262$ nm, $\epsilon = 1.9 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$, IR (KBr Pellet) ν_{max} in cm^{-1} : 2934, 2867, 1732, 1593, 1576, 1470, 1296, 1254, 1173, 1078 and 777; ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 15.7$ Hz, 1H, 1 \times olefinic H), 7.72 (d, $J = 8.3$ Hz, 2H, Ar) 7.52-7.6 (m, 5H, 4 \times Ar, 1 \times olefinic H), 7.41(t, $J = 8.0$ Hz, 1H, Ar), 7.1-7.12 (m, 2H, Ar), 6.8-6.83 (m, 1H, Ar), 5.35 (bd, $J = 4.3$ Hz, 1H, 1 \times olefinic H), 4.56-4.61(m, 1H, 1 \times CHOCO), 4.08 (t, $J = 6.6$ Hz, 2H, 1 \times OCH₂), 4.03 (t, $J = 6.4$ Hz, 2H, 1 \times OCH₂), 2.32-0.67(m, 55H, 23 \times CH₂, 6 \times CH, 1 \times CH₃), 1.01 (s, 3H, 1 \times CH₃), 0.92 (d, $J = 6.5$ Hz, 3H, 1 \times CH₃), 0.89 (d, $J = 2.7$ Hz, 3H, 1 \times CH₃), 0.86 (d, $J = 1.7$ Hz, 3H, 1 \times CH₃), 0.66 (s, 3H, 1 \times CH₃); MS (FAB+): m/z for $\text{C}_{64}\text{H}_{89}\text{F}_2\text{O}_5(\text{M}+1)$ Calculated: 975.7. Found: 975.1; Anal.calcd for $\text{C}_{64}\text{H}_{88}\text{F}_2\text{O}_5$ (found) %: C 78.81(78.5); H 9.09(9.4).

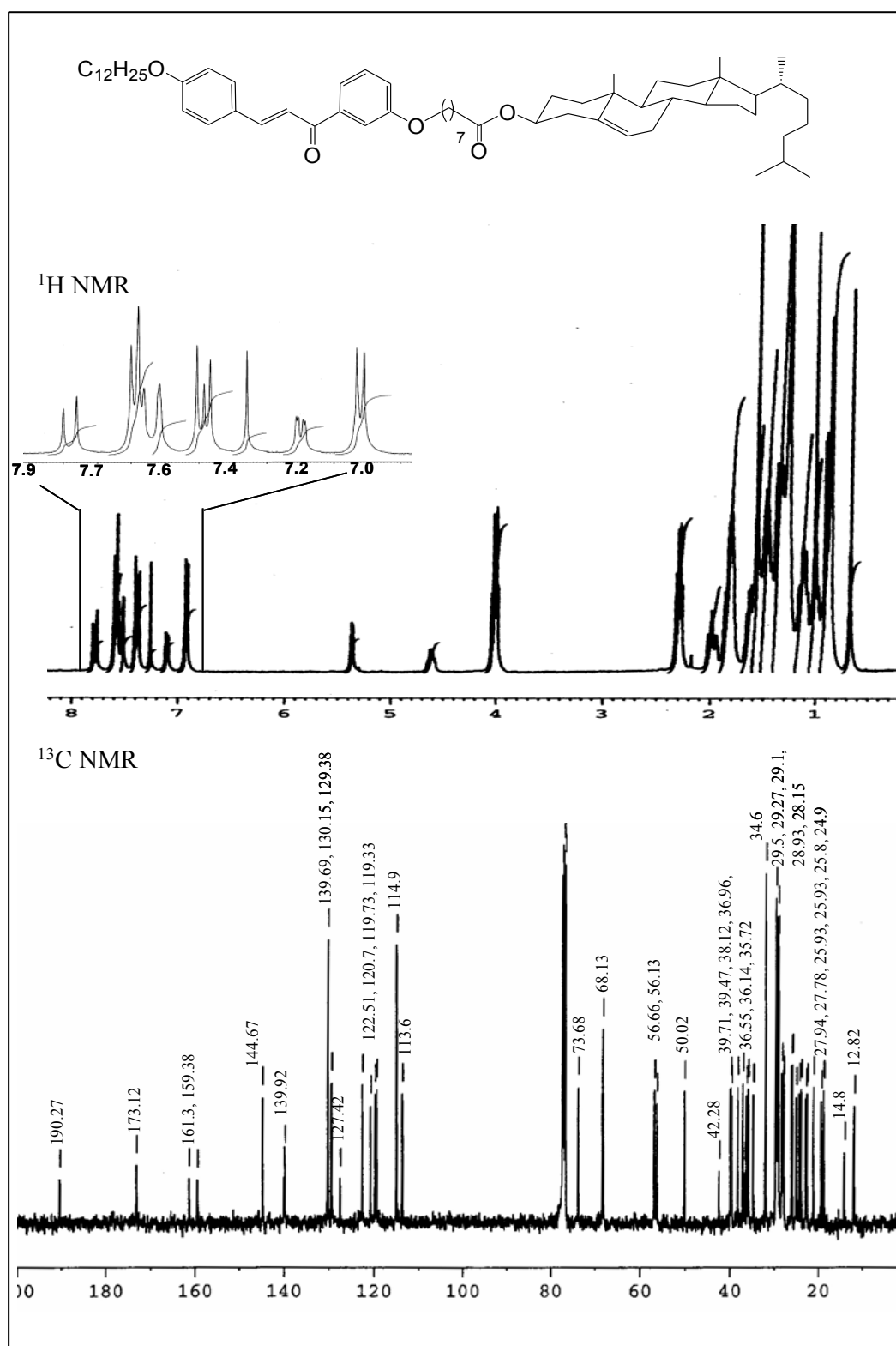


Figure S1. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra of **3DC-7,12** in CDCl₃

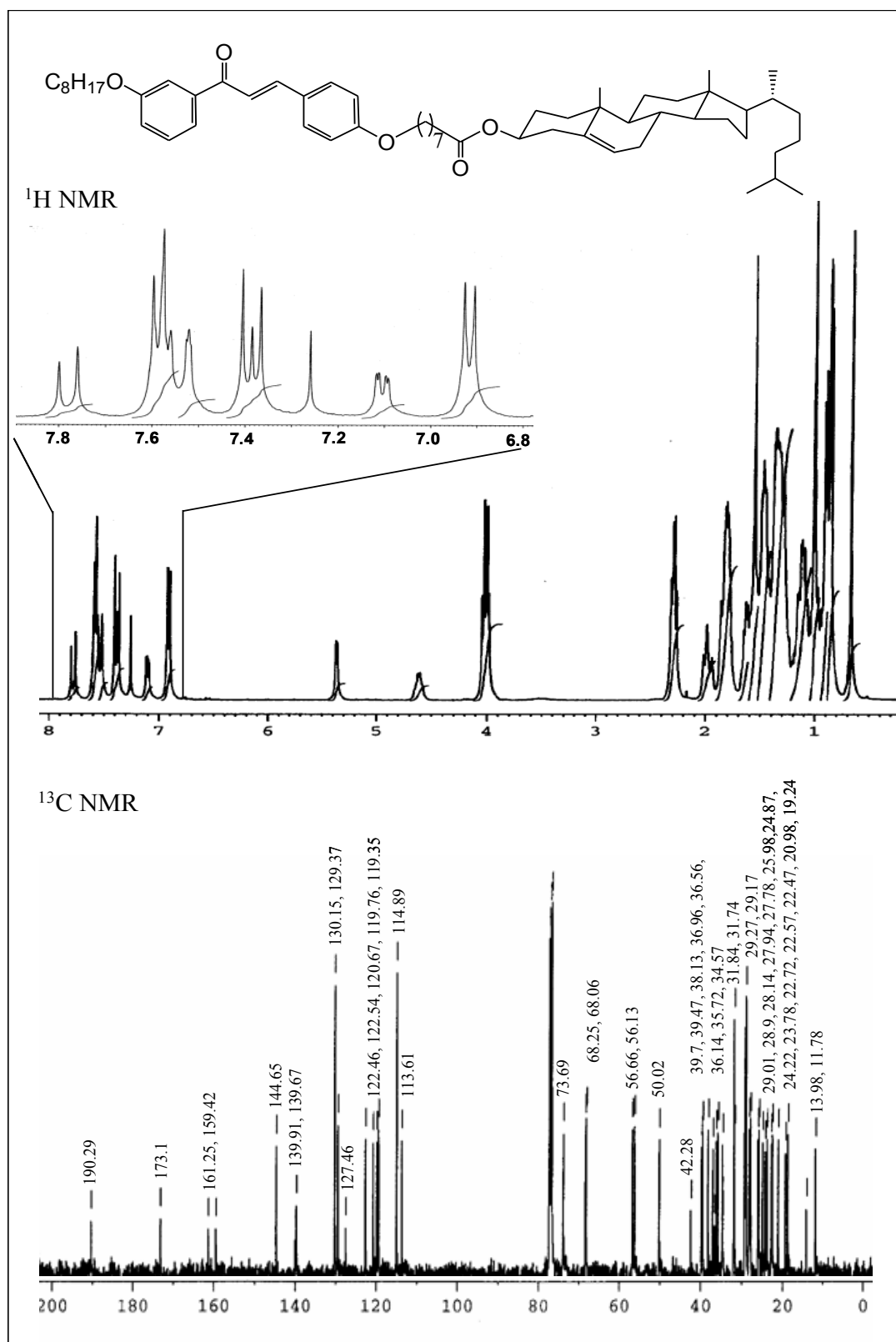


Figure S2. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra of **3RDC-7,8** in CDCl₃

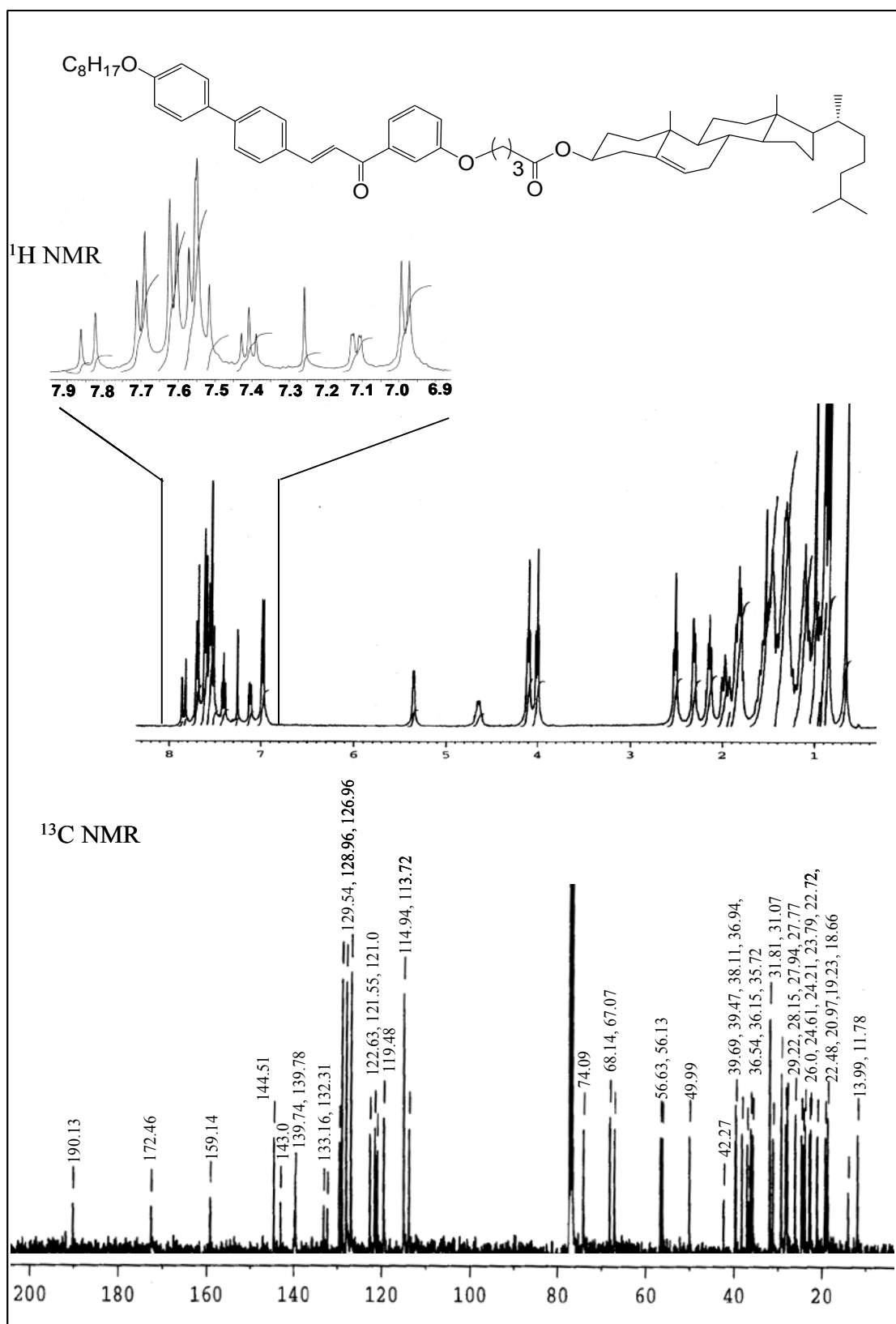


Figure S3. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra of **3BDC-3,8** in CDCl₃

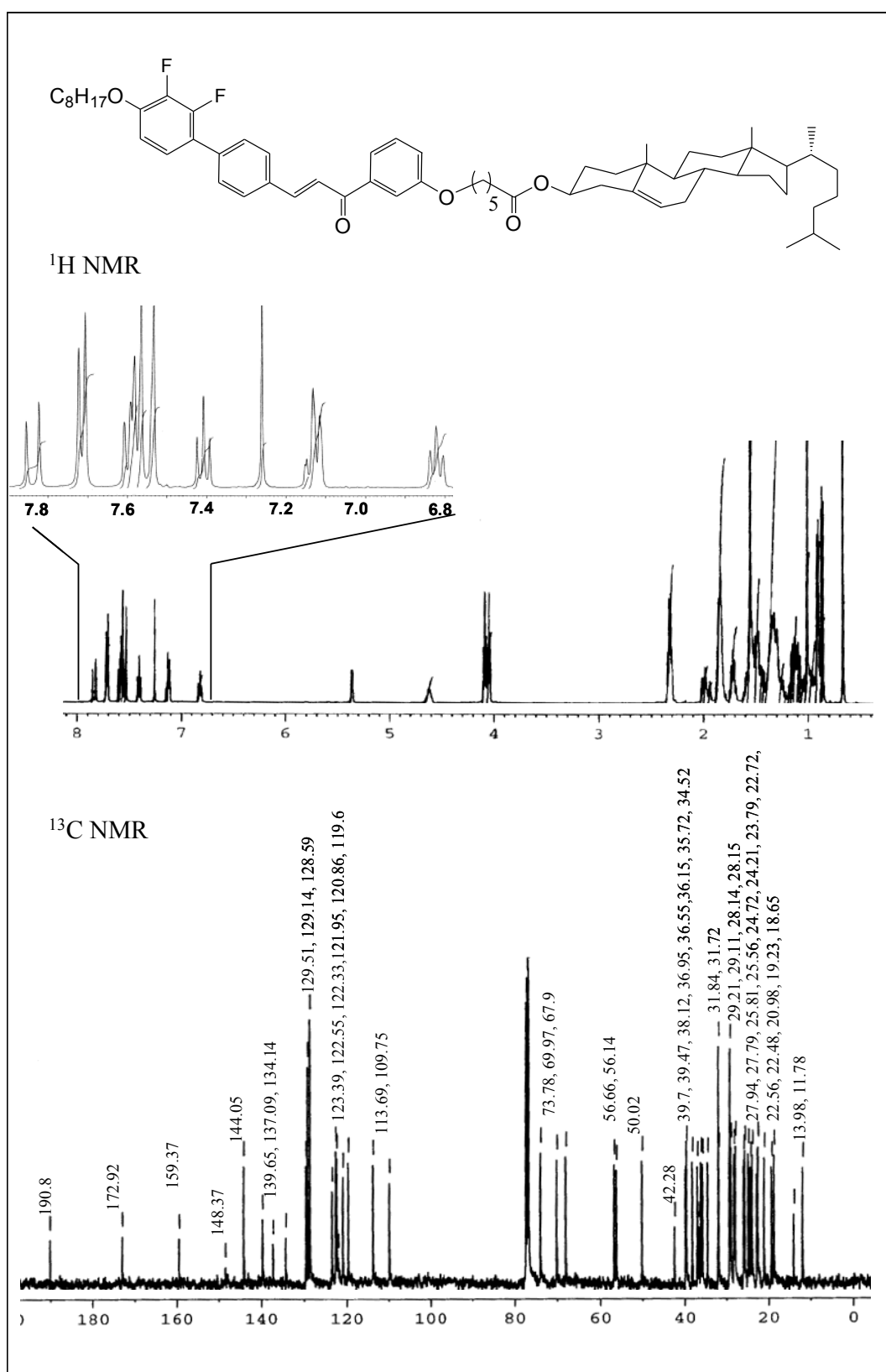


Figure S4. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra of **3FDC-5,8** in CDCl₃

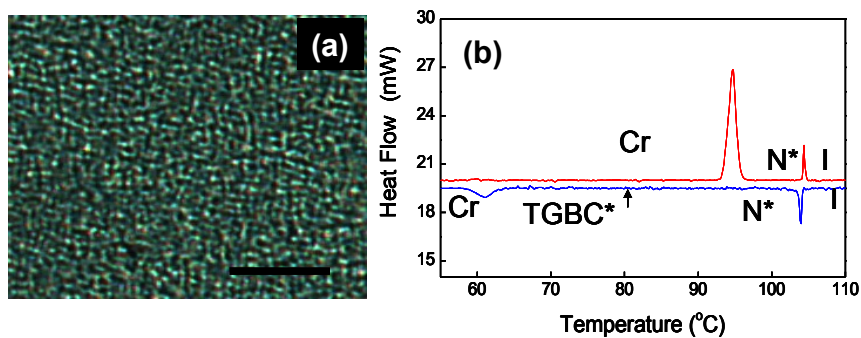


Figure S5. (a) Photomicrograph of square grid texture of TGBC* obtained (at 65 °C) on cooling the N* phase of **3DC-7,12** and (b) DSC traces of the first heating (red trace) and cooling (blue trace) cycles obtained for **3DC-7,12** at a rate of 5 °C min⁻¹. (Bar: 100 μm).

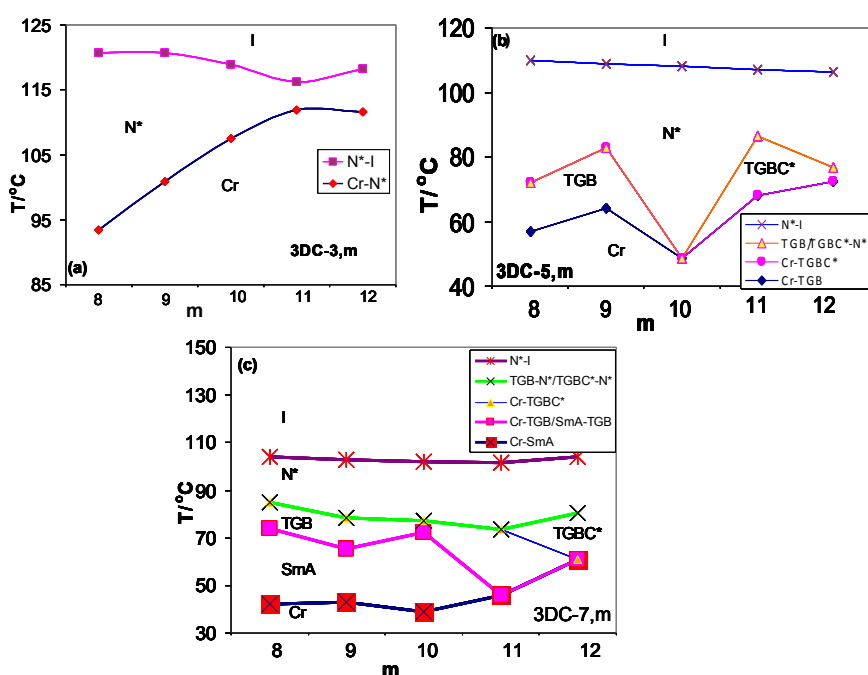


Figure S6. Plots of transition temperatures as a function of alkoxy tail length (**m**) for the compounds (a) **3DC-3,m** series, (b) **3DC-5,m** series and (c) **3DC-7,m** series.

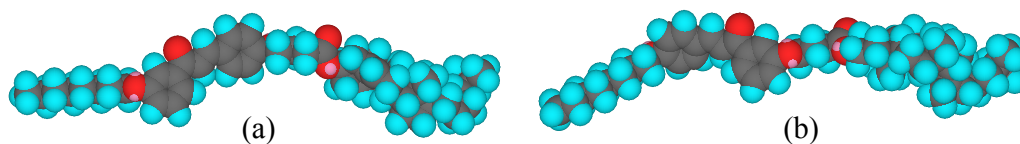


Figure S7. Energy minimized structures of dimers (a) **3RDC-3,8** and (b) **3DC-3,8**. Note that the former dimer is relatively linear when compared to the latter one.

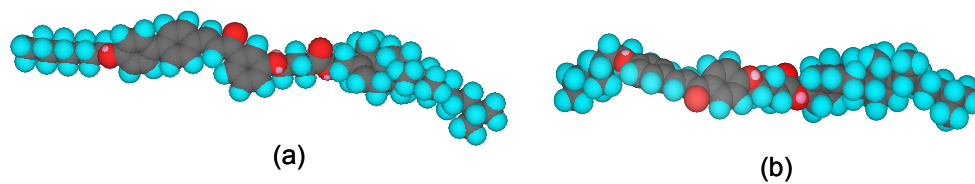


Figure S8. Energy minimized structures of dimers (a) **3BDC-3,8** and (b) **3DC-3,8**; Notice that the former dimer is little longer than the latter.

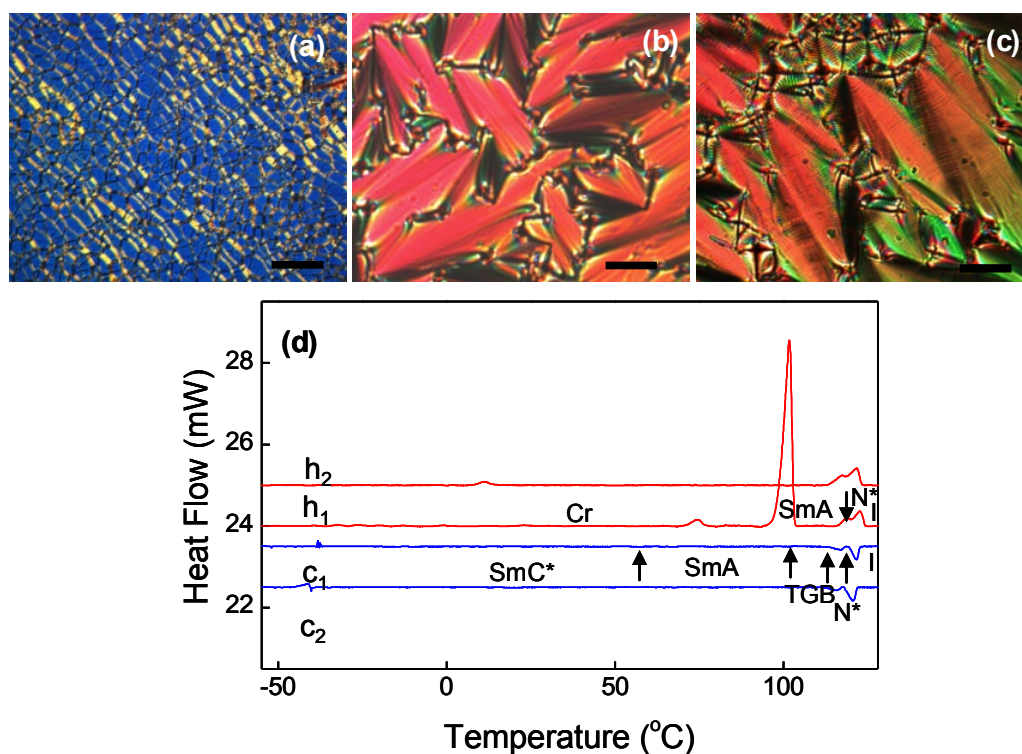


Figure S9. Photomicrographs of the textures observed for the mesophases of dimer **3RDC-5,8**: (a) oily streak (planar) texture of N* phase (at 118 °C), (b) focal conic texture of SmA phase (at 80.7 °C) obtained on cooling from N* (c) focal conics with chiral lines (at 50 °C) obtained for SmC* phase on cooling from SmA phase (Bar: 100 μm). (d) DSC traces of first and second heating and cooling cycles obtained for **3RDC-5,8** at a rate of 5 °C min⁻¹ [h₁ = first heating (red trace), h₂ second heating, c₁ = first cooling (blue trace), c₂ = second cooling]

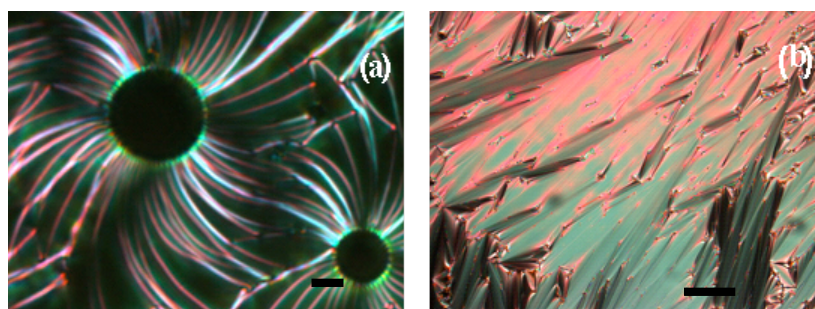


Figure S10. Photomicrographs of the filamentary texture of TGB phase growing around the air packets of homeotropic SmA phase (at 145 °C) (a) and focal-conic texture of the homogeneously aligned SmA phase at 110 °C (b) of dimer **3BDC-3,8**. (Bar: 100 μm).

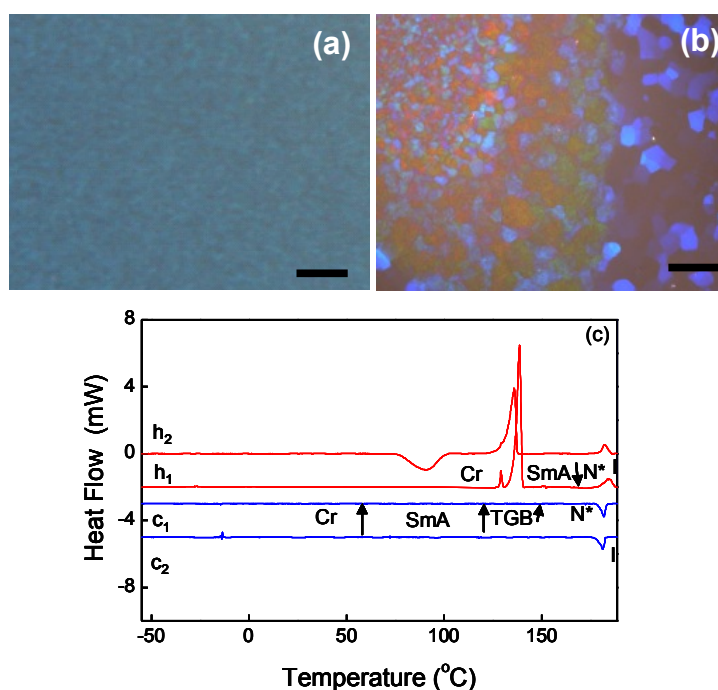


Figure S11. Photomicrographs of foggy texture of BPIII obtained at 153 °C (a), platelet texture of cubic blue phase (either BPI or BPII) obtained at 152 °C (b) for dimer **3BDC-4,8** and DSC traces of first and second heating (red trace) and cooling cycles obtained for **3BDC-5,8** (c). (Bar: 100 μm).

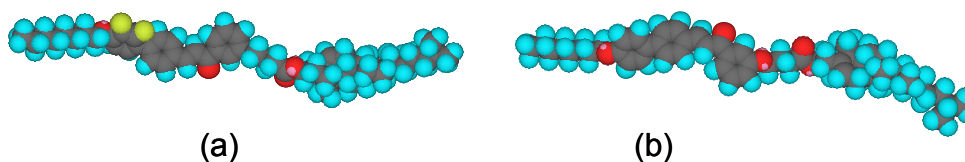


Figure S12. Energy minimized structures of dimers (a) **3FDC-3,8** and (b) **3BDC-3,8** showing the effect of lateral fluoro substitution on the molecular conformation.

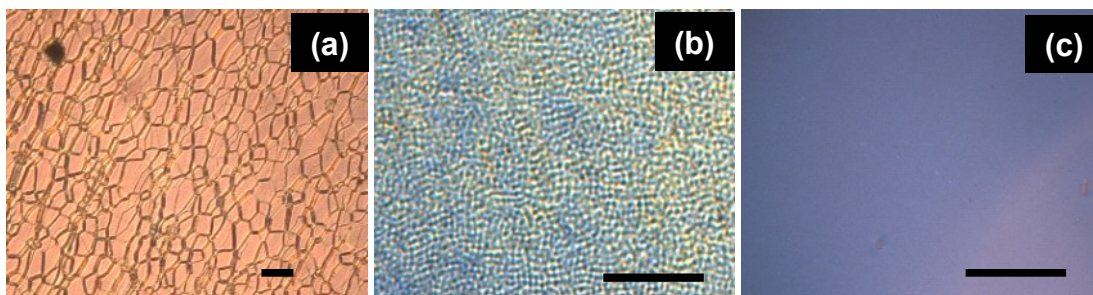


Figure S13. Photomicrographs of optical textures obtained for the (a) oily streak texture of N* phase at 158.3 °C of dimer **3FDC-3,8**, (b) square grid pattern of TGBC* phase at 107 °C of dimer **3FDC-3,8** and (c) foggy texture of BPIII at 136 °C of dimer **3FDC-4,8**. (Bar: 100 μ m).

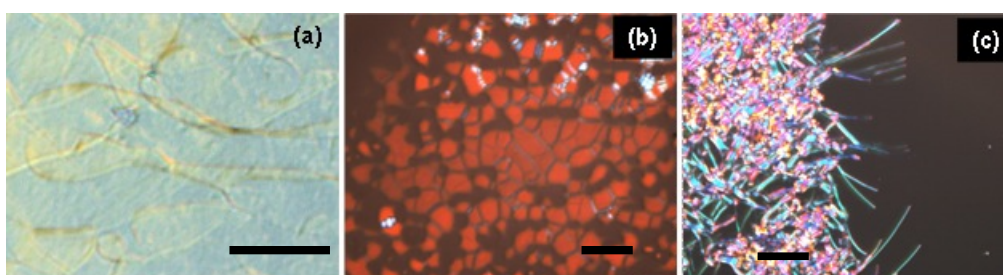


Figure S14. Photomicrographs of the planar texture obtained for the TGB of dimer **3FDC-5,8** at 120 °C (a), the platelet texture of BPI/II of dimer **3FDC-7,8** at 146 °C (b), and the texture corresponding to SmA (right portion; dark field of view), TGB (middle portion: filaments) and N* (left portion: non-specific, but on shear gives planar texture) appearing simultaneously on heating from the homeotropic SmA phase of dimer **3FDC-7,8** (c). (Bar: 100 μ m).

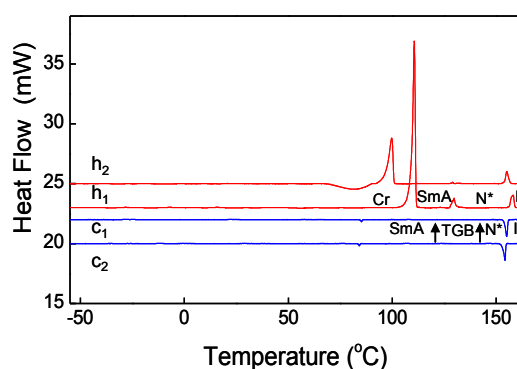


Figure S15. DSC thermograms of dimer **3FDC-5,8**.