Highly Frustrated Liquid Crystal Phases in Optically Active Dimers: Synthesis and Rich Phase Transitional Behavior

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I. Experimental

Ia. General Information

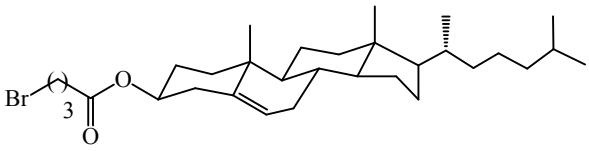
The starting chemicals such as cholesterol, 4-hydroxybenzaldehyde, 4-nitrophenol, 4-bromobutyric acid, 5-bromovaleric acid, 6-bromocaproic acid and 8-bromocaprylic acid were procured from an overseas company, and were used as received. The bulk solvents were purchased from the local sources which were purified by standard methods. Thin layer chromatography (TLC) plates, consisting of a thin layer of silica gel (Merck, Kieselgel60, F254) on an aluminium foil backing, were used to monitor the progress and completion of reactions; TLC plates were also employed to assess the purity of the intermediates. Column chromatography technique was used to purify the intermediates wherein silica gel (100-200 mesh) and neutral alumina were used as stationary phases. UV-Vis spectroscopy was performed using a Perkin Elmer Lambda 20 UV-Vis spectrometer. Perkin Elmer Spectrum 1000 FT-IR spectrometer was employed to record IR spectra of the samples using KBr pellets; the X-axes of IR spectra are plotted in wavenumber (cm^{-1}) unit. ^{1}H and ^{13}C NMR spectra of the samples were recorded in $CDCl_3$ at ambient temperature on a Bruker AMX-400 (400 MHz) spectrometer. The chemical shifts (δ) are reported in parts per million using the solvent residual peak as an internal standard. Coupling constants (*J* values) are reported in Hz. FAB mass spectra were recorded on a JEOL JMS-600H mass spectrometer where 3-nitrobenzyl alcohol was used as a liquid matrix and a Perkin Elmer Elemental Analyzer Series II 2400 and Carlo-Erba Flash 1112 analyzers were used for elemental analysis. The thermal properties of the dimers and some of the key intemediates were examined with the help of an Olympus BX50 (Model BX50F4) optical polarizing microscope, attached to a

digital camera and a Mettler FP82HT hot stage programmed by an FP90 Central Processor, and Perkin-Elmer Diamond differential scanning calorimeter (DSC). Prior to use the DSC was calibrated using pure indium as a standard. DSC thermograms were recorded at a scanning rate of 5 °C/min. X-Ray diffraction (XRD) studies with $CuK_{\propto}$ (λ = 0.15418 nm) radiation were carried out using a powder X-ray diffractometer viz., PANalytical X'Pert PRO MP machine consisting of a focusing elliptical mirror and a fast resolution detector (PIXCEL); the chosen sample for this study was placed into a Lindemann glass capillary (0.5 mm diameter), and the capillary was then carefully flame sealed at both the ends. CD spectra were obtained with the help of Jasco J-810 spectropolorimeter.

Ib. General Procedure for the synthesis of cholesteryl ω-bromoalkanoates (**1a-d**)

In a round bottom flask ω-bromoalkanoic acid (12.9 mmol, 1 equiv.) was taken, 12ml of oxalyl chloride was added and stirred at rt for 4h under nitrogen atmosphere. The excess of oxalyl chloride was distilled out under reduced pressure and the ω-bromoalkanoyl chloride obtained was dried under *vacuo* and added dropwise to a solution of cholesterol (5g, 12.9 mmol, 1 equiv.) in pyridine (6 ml) and dry THF (50 ml) at 0^{o} C. The reaction mixture was warmed to rt and stirred for 12 h. The reaction mixture was filtered on celite bed and the filtrate was concentrated to obtain a pale yellow mass which was dissolved in a mixture of CH_2Cl_2 and Et_2O (20:80). The organic layer was thoroughly washed with water, brine and dried over anhyd. Na_2SO_4. The crude mass obtained upon evaporation of the solvent was purified by column chromatography using neutral alumina. Elution with a mixture of 30% CH_2Cl_2-hexanes afforded the pure product.

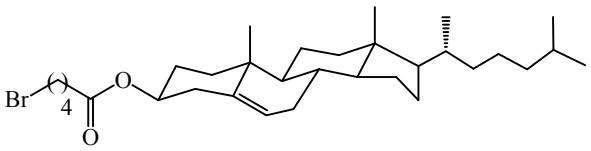
Cholesteryl 4-bromobutanoate: **1a**



R_f = 0.33 in 30% CH_2Cl_2-hexanes; a white solid; yield: 5.67g, 82 %; m.p.: 87.6 °C; IR (KBr Pellet): ν_{max} in cm^{-1} 2948, 2866, 1733, 1465, 1171, 1027; ^{1}H NMR (400MHz, $CDCl_3$): δ 5.38 (brd, *J* = 4.0 Hz, 1H, 1 × olefinic), 4.66 (m, 1H, 1 × CHOCO), 3.48 (t, *J* = 6.4 Hz, 2H, 1 × CH_2Br), 2.49 (m, 4H, 2 × allylic CH_2), 2.03-1.05 (m, 28H, 11 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.8 Hz, 3H, 1 × CH_3), 0.88 (d, *J* = 1.6 Hz, 3H, 1 × CH_3), 0.86 (d, *J* = 2.0

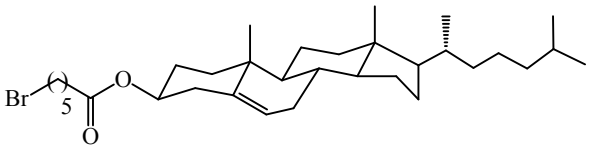
Hz, 3H, 1 × CH_3), 0.68 (s, 3H, 1 × CH_3); MS (FAB+): m/z calcd for $C_{31}H_{53}BrO_2$ (M+2) : 536.3. Found: 536.2.

1b: Cholesteryl 5-bromopentanoate



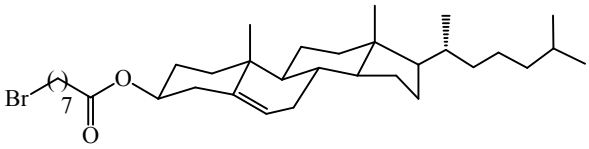
R_f = 0.33 in 30% CH_2Cl_2-hexanes; a white solid; yield: 5.96g, 84 %; m.p.: 100.57 °C; IR (KBr Pellet): ν_{max} in cm^{-1} 2944, 2868, 1733, 1463, 1174, 1000; ^1H NMR (400MHz, $CDCl_3$): δ 5.38 (brd, *J* = 4.0 Hz, 1H, 1 × olefinic), 4.63 (m, 1H, 1 × CHOCO), 3.42 (t, *J* = 6.8 Hz, 2H, 1 × CH_2Br), 2.32 (m, 4H, 2 × allylic CH_2), 2.02-1.06 (m, 30H, 12 × 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* = 1.8 Hz, 3H, 1 × CH_3), 0.86 (d, *J* = 1.8 Hz, 3H, 1 × CH_3), 0.68 (s, 3H, 1 × CH_3); MS (FAB+): m/z calcd for $C_{32}H_{54}BrO_2$ (M+1): 549.3. Found: 549.3.

1c: Cholesteryl 6-bromohexanoate



R_f = 0.33 in 30% CH_2Cl_2-hexanes; a white solid; yield: 6.33g, 87 %; m.p.: 100.57 ^oC; IR (KBr Pellet): ν_{max} in cm^{-1} 2949, 2863, 1733, 1465, 1175, 1020; ^1H NMR (400MHz, $CDCl_3$): δ 5.38 (brd, *J* = 4.0 Hz, 1H, 1 × olefinic), 4.65 (m, 1H, 1 × CHOCO), 3.42 (t, *J* = 8.0 Hz, 2H, 1 × CH_2Br), 2.32 (m, 4H, 2 × allylic CH_2), 2.03-1.04 (m, 32H, 13 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 4.0 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), 0.68 (s, 3H, 1 × CH_3); MS (FAB+): m/z calcd for $C_{33}H_{56}BrO_2$: 563.3. Found: 563.4.

1d: Cholesteryl 8-bromooctanoate

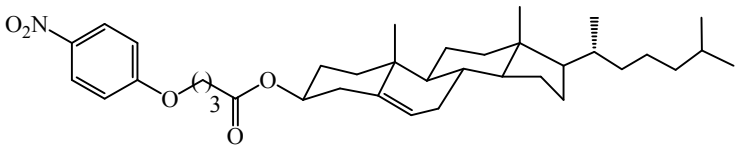


R_f = 0.33 in 30% CH_2Cl_2-hexanes; a white solid; yield: 6.73g, 88 %; m.p.: 86.31 ^oC; IR (KBr Pellet): ν_{max} in cm^{-1} 2947, 2866, 1733, 1465, 1171, 1026; ^1H NMR (400 MHz, $CDCl_3$): δ 5.38 (brd, J = 3.4 Hz, 1H, 1 × olefinic), 4.63 (m, 1H, 1 × CHOCO), 3.42 (t, J = 8.0 Hz, 2H, 1 × CH_2Br), 2.32 (m, 4H, 2 × allylic CH_2), 2.02-1.04 (m, 36H, 15 × CH_2, 6 × CH), 1.02 (s, 3H, 1 × CH_3), 0.92 (d, J = 4.0 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), 0.68 (s, 3H, 1 × CH_3); MS (FAB+): m/z calcd for $C_{35}H_{59}BrO_2$: 590.37. Found: 590.11.

Ic. General procedure for the synthesis of cholesteryl ω-(4-nitrophenoxy)alkanoates (**2a-d**)

To a solution of cholesteryl ω-bromoalkanoate (**1a / 1b / 1c / 1d**) (1g, 1.9 mmol, 1 equiv.) in butanone was added 4-nitrophenol (2.1 mmol, 1 equiv) and anhyd. K_2CO_3 (2.1 mmol, 1.1 equiv). The reaction mixture was refluxed at 80 ^oC for 12h. The reaction mixture was poured into ice cold water and extracted with CH_2Cl_2. The organic layer was washed with 5 % (aq) NaOH solution (25ml × 3), water (25ml × 3), brine and dried over anhyd, Na_2SO_4. The organic layer was concentrated and the crude obtained was purified by column chromatography using silica gel (100-200 mesh). Elution with 10% ethylacetate-hexanes furnished the pure product.

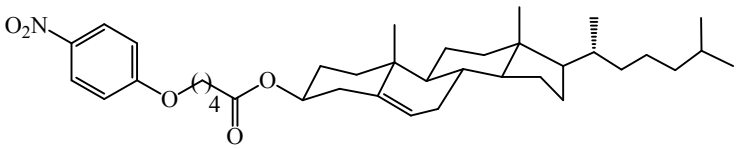
2a: Cholesteryl 4-(4-nitrophenoxy)butanoate



R_f = 0.43 in 30% CH_2Cl_2-hexanes; white solid; yield: 0.9 g, 82% IR (Neat): ν_{max} in cm^{-1} 2946, 2867, 1733, 1592, 1510, 1378,1338, 1178, 1111; ^1H NMR (400MHz, $CDCl_3$) : δ 8.20 (d, 2H, J = 6.8 Hz, Ar), 6.96 (d, J = 7.2 Hz, 2H, Ar), 5.38 (brd, J = 3.6 Hz, 1H, 1 × olefinic), 4.68-4.60 (m, 1H, 1 × CHOCO), 4.13 (t, 2H, J = 6.4 Hz, 1 × OCH_2), 2.52-2.30 (m, 4H, 2 ×

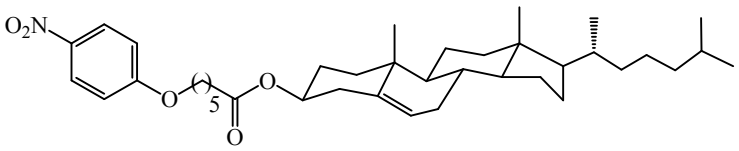
allylic CH_2); 2.16 – 0.68 (m, 43H, 6 × CH, 11 × CH_2, 5 × CH_3); Anal. calcd for $C_{37}H_{55}NO_5$: C, 74.83; H, 9.34; N, 2.36; Found: C, 74.25; H, 8.97; N, 2.72.

2b: Cholesteryl 5-(4-nitrophenoxy)pentanoate



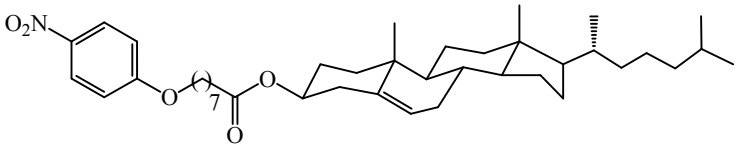
R_f = 0.44 in 30% CH_2Cl_2-hexanes; white solid; yield: 0.9 g, 84%; IR (Neat): ν_{max} in cm^{-1} 2946, 2867, 1733, 1592, 1510, 1386, 1338, 1178, 1111; ^1H NMR (400MHz, $CDCl_3$) : δ 8.20 (d, 2H, *J* = 6.8 Hz, Ar), 6.95 (d, *J* = 7.2 Hz, 2H, Ar), 5.37 (brd, *J* = 3.6 Hz, 1H, 1 × olefinic), 4.66-4.58 (m, 1H, 1 × CHOCO), 4.09 (t, 2H, *J* = 6.0 Hz, 1 × OCH_2), 2.39-2.30 (m, 4H, 2 × allylic CH_2), 2.03 – 0.68 (m, 45H, 6 × CH, 12 × CH_2, 5 × CH_3); Anal. calcd for $C_{38}H_{57}NO_5$: C, 75.08; H, 9.45; N, 2.3; Found: C, 75.27; H, 9.547; N, 3.07.

2c: Cholesteryl 6-(4-nitrophenoxy)hexanoate



R_f = 0.44 in 30% CH_2Cl_2-hexanes; white solid; yield: 0.9g, 80%; IR (Neat): ν_{max} in cm^{-1} 2946, 2867, 1732, 1592, 1511, 1386, 1338, 1178, 1111; ^1H NMR (400MHz, $CDCl_3$) : δ 8.20 (d, 2H, *J* = 7.2 Hz, Ar), 6.94 (d, *J* = 6.8 Hz, 2H, Ar), 5.37 (brd, *J* = 4.0 Hz, 1H, 1 × olefinic), 4.66-4.58 (m, 1H, 1 × CHOCO), 4.07 (t, 2H, *J* = 6.4 Hz, 1 × OCH_2), 2.34-2.30 (m, 4H, 2 × allylic CH_2), 2.00 – 0.68 (m, 47H, 6 × CH, 13 × CH_2, 5 × CH_3); Anal. calcd for $C_{39}H_{59}NO_5$: C, 75.32; H, 9.56; N, 2.25; Found: C, 76.06; H, 9.29; N, 3.09.

2d: Cholesteryl 8-(4-nitrophenoxy)octanoate.



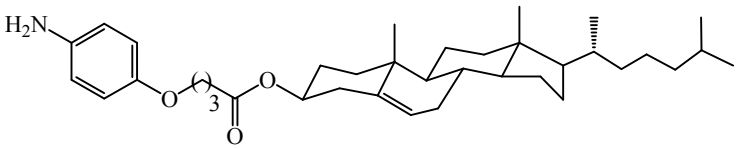
R_f = 0.45 in 30% CH_2Cl_2-hexanes; white solid; yield: 0.8g, 76%; IR (Neat): ν_{max} in cm^{-1} 2944, 2868, 1732, 1593, 1510, 1337, 1180, 1110; ^1H NMR (400MHz, $CDCl_3$) : δ 8.20 (d, 2H, *J* = 7.2 Hz, Ar), 6.95 (d, *J* = 7.2 Hz, 2H, Ar), 5.37 (brd, *J* = 4.0 Hz, 1H, 1 × olefinic), 4.65-

4.57 (m, 1H, 1 × CHOCO), 4.06 (t, 2H, J = 6.4 Hz, 1 × OCH_2), 2.32-2.26 (m, 4H, 2 × allylic CH_2), 1.99 – 0.68 (m, 51H, 6 × CH, 15 × CH_2, 5 × CH_3); Anal. calcd for $C_{41}H_{63}NO_5$: C, 75.77; H, 9.77; N, 2.16; Found: C, 75.15; H, 9.72; N, 2.58.

Id. General procedures for the synthesis of cholesteryl ω-(4-aminophenoxy)alkanoates (**3a-d**)

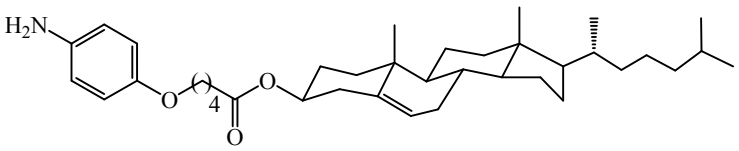
Nitro compound (**2a / 2b / 2c /2d**) (0.5g) was taken in THF solution. To this was added 10% Pd-C (10% weight of the starting material). The reaction mixture was degassed and stirred under H_2 gas (1 atmospheric pressure, balloon) for 4h at rt. The reaction mixture was filtered over celite bed, concentrated and the solid obtained was recrystallized from hexanes to afford a off-white solid.

3a: Cholesteryl 4-(4-aminophenoxy)butanoate



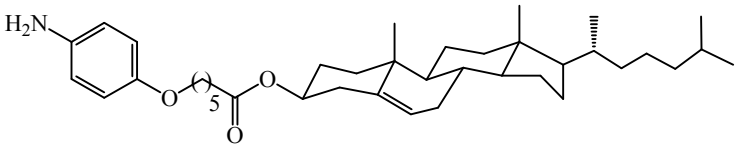
R_f = 0.49 in 50% CH_2Cl_2-hexanes; white solid; yield: 0.42g, 87%; IR (Neat): ν_{max} in cm^{-1} 3376, 2937, 2868, 1726, 1179, 1103; ^1H NMR (400MHz, $CDCl_3$) : δ 6.73 (d, 2H, J = 6.8 Hz, Ar), 6.64 (d, J = 6.8 Hz, 2H, Ar), 5.37 (brd, J = 3.6 Hz, 1H, 1 × olefinic), 4.63-4.60 (m, 1H, 1 × CHOCO), 3.91 (t, 2H, J = 6.0 Hz, 1 × OCH_2), 3.42 (brs, 2H, 1 × NH_2), 2.35-2.30 (m, 4H, 2 × allylic CH_2), 1.99 – 0.68 (m, 43H, 6 × CH, 11 × CH_2, 5 × CH_3); Anal. calcd for $C_{37}H_{57}NO_3$: C, 78.81; H, 10.19; N, 2.48; Found: C, 78.31; H, 10.25; N, 2.72.

3b: Cholesteryl 5-(4-aminophenoxy)pentanoate



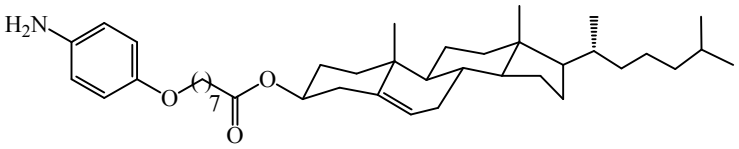
R_f = 0.49 in 50% CH_2Cl_2-hexanes; white solid; yield: 0.44g, 92 %; IR (Neat): ν_{max} in cm^{-1} 3376, 2938, 2869, 1726, 1179, 1103; ^1H NMR (400MHz, $CDCl_3$) : δ 6.74 (d, 2H, J = 6.4 Hz, Ar), 6.65 (d, J = 6.8 Hz, 2H, Ar), 5.37 (brd, J = 3.6 Hz, 1H, 1 × olefinic), 4.66-4.57 (m, 1H, 1 × CHOCO), 3.89 (t, 2H, J = 6.4 Hz, 1 × OCH_2), 2.32-2.28 (m, 4H, 2 × allylic CH_2), 1.99 – 0.68 (m, 45H, 6 × CH, 12 × CH_2, 5 × CH_3); Anal. calcd for $C_{38}H_{59}NO_3$: C, 78.98; H, 10.29; N, 2.42; Found: C, 79.30; H, 10.82; N, 2.36.

3c: Cholesteryl 6-(4-aminophenoxy)hexanoate.



R_f = 0.50 in 50% CH_2Cl_2-hexanes; white solid; yield: 0.43g, 90 %; IR (Neat): ν_{max} in cm^{-1} 3374, 2940, 2869, 1726, 1179, 1102; ^1H NMR (400MHz, $CDCl_3$) : δ 6.66 (d, 2H, *J* = 6.4 Hz, Ar), 6.57 (d, *J* = 6.4 Hz, 2H, Ar), 5.30 (brd, *J* = 4.0 Hz, 1H, 1 × olefinic), 4.58 -4.52 (m, 1H, 1 × CHOCO), 3.85 (t, 2H, *J* = 6.4 Hz, 1 × OCH_2), 2.28 - 2.23 (m, 4H, 2 × allylic CH_2), 1.92 – 0.61 (m, 47H, 6 × CH, 13 × CH_2, 5 × CH_3); Anal. calcd for $C_{39}H_{61}NO_3$: C, 79.14; H, 10.39; N, 2.37; Found: C, 79.41; H, 10.63; N, 2.38.

3d: Cholesteryl 8-(4-aminophenoxy)octanoate.

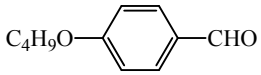


R_f = 0.51 in 50% CH_2Cl_2-hexanes; white solid; yield: 0.45g, 94 %; IR (Neat): ν_{max} in cm^{-1} 3374, 2940, 2869, 1726, 1179, 1102; ^1H NMR (400MHz, $CDCl_3$) : δ 6.75 (d, 2H, *J* = 6.8 Hz, Ar), 6.67 (d, *J* = 6.4 Hz, 2H, Ar), 5.38 (brd, *J* = 3.6 Hz, 1H, 1 × olefinic), 4.65-4.57 (m, 1H, 1 × CHOCO), 3.90 (t, 2H, *J* = 6.4 Hz, 1 × OCH_2), 2.32-2.25 (m, 4H, 2 × allylic CH_2), 1.99 – 0.68 (m, 51H, 6 × CH, 15 × CH_2, 5 × CH_3); Anal. calcd for $C_{41}H_{65}NO_3$: C, 79.43; H, 10.57; N, 2.26; Found: C, 79.71; H, 10.44; N, 2.59.

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

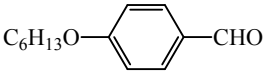
To a solution of 4-hydroxybenzaldehyde (1g, 8.19mmol, 1 equiv.) in butanone was added *n*-alkoxybromide (9.01 mmol,1.1 equiv) and anhyd. K_2CO_3 (9.01 mmol, 1.1 equiv). The reaction mixture was refluxed at 80 ^oC for 12h. The reaction mixture was poured into ice cold water and extracted with CH_2Cl_2. The organic layer was washed with 5 % (aq) NaOH solution (25ml × 3), water (25ml × 3), brine and dried over anhyd, Na_2SO_4. The organic layer was concentrated and the crude obtained was purified by column chromatography using silica gel (100-200 mesh). Elution with 10% ethylacetate-hexanes furnished the pure product.

4a: 4-(*n*-Butyloxy)benzaldehyde.



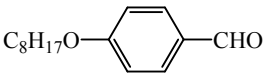
R_f = 0.51 in 30% CH_2Cl_2-hexanes; pale yellow liquid; yield: 1.1g, 75%; IR (Neat): ν_{max} in cm^{-1} 2959, 2874, 1695, 1383, 1230, 1128, 1112; ^1H NMR (400MHz, $CDCl_3$) : δ 9.88 (s, 1H, 1 × CHO), 7.84 (d, *J* = 6.8 Hz, 2H, Ar), 7.00 (d, *J* = 6.8 Hz, 2H, Ar), 4.07 (t, J = 6.4 Hz, 2H, 1 × OCH_2), 1.84-1.46 (m, 4H, 2 × CH_2), 0.99 (t, *J* = 7.6 Hz, 3H, 1 × CH_3); MS(FAB^+): m/z Calcd. for $C_{11}H_{14}O_2$: 178.1; Found: 178.3.

4b: 4-(*n*-Hexyloxy)benzaldehyde



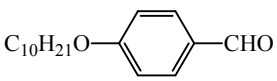
R_f = 0.51 in 30% CH_2Cl_2-hexanes; pale yellow liquid; yield: 1.3g, 79%; IR (Neat): ν_{max} in cm^{-1} 2959, 2873, 1696, 1230 and 1112; ^1H NMR (400MHz, $CDCl_3$) : δ 9.88 (s, 1H, 1 × CHO), 7.84 (d, *J* = 6.8 Hz, 2H, Ar), 7.00 (d, *J* = 6.8 Hz, 2H, Ar), 4.06 (t, *J* = 6.8 Hz, 2H, 1 × OCH_2), 1.85-1.29 (m, 8H, 4 × CH_2), 0.91 (t, *J* = 6.8 Hz, 3H, 1 × CH_3); MS(FAB^+): m/z Calcd. for $C_{13}H_{19}O_2$(M+1) : 207.1; Found: 207.2.

4c: 4-(*n*-Octyloxy)benzaldehyde



R_f = 0.51 in 30% CH_2Cl_2-hexanes; pale yellow liquid; yield: 1.5g, 77%; IR (Neat): ν_{max} in cm^{-1} 2959, 2873, 1695, 1231, 1128, 1113; ^1H NMR (400MHz, $CDCl_3$) : δ 9.88 (s, 1H, 1 × CHO), 7.84 (d, *J* = 6.8 Hz, 2H, Ar), 7.01 (d, *J* = 6.8 Hz, 2H, Ar), 4.05 (t, *J* = 6.8 Hz, 2H, 1 × OCH_2), 1.85-1.28 (m, 12H, 6 × CH_2), 0.90 (t, *J* = 6.8 Hz, 3H, 1 × CH_3); MS(FAB^+): m/z Calcd. for $C_{15}H_{23}O_2$(M+1) : 235.2; Found: 235.2.

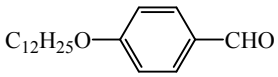
4d: 4-(*n*-Decyloxy)benzaldehyde.



R_f = 0.52 in 30% CH_2Cl_2-hexanes; pale yellow liquid; yield: 1.6g, 75%; IR (Neat): ν_{max} in cm^{-1} 2926, 2855, 1670, 1215, 1160, 1109; ^1H NMR (400MHz, $CDCl_3$) : δ 9.88 (s, 1H, 1 × CHO), 7.84 (d, *J* = 8.8 Hz, 2H, Ar), 7.01 (d, *J* = 6.8 Hz, 2H, Ar), 4.05 (t, *J* = 6.4 Hz, 2H, 1 ×

OCH_2), 1.83-1.30 (m, 16H, 8 × CH_2), 0.90 (t, J = 6.8 Hz, 3H, 1 × CH_3); MS(FAB$^+$): m/z Calcd. for $C_{17}H_{26}O_2$: 262.2; Found: 262.5.

4e: 4-(*n*-Dodecyloxy)benzaldehyde.

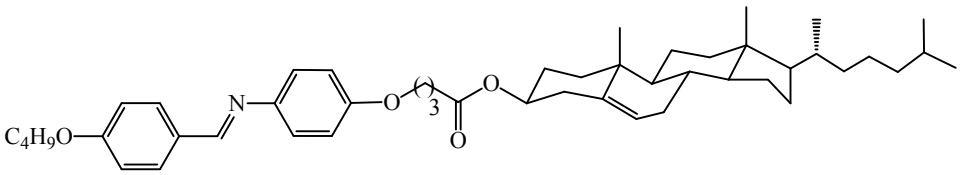


R_f = 0.52 in 30% CH_2Cl_2-hexanes; pale yellow liquid; yield: 1.8g, 74%; IR (Neat): ν_{max} in cm^{-1} 2927, 2855, 1694, 1230, 1160 and 1110; ^{1}H NMR (400MHz, $CDCl_3$) : δ 9.88 (s, 1H, 1 × CHO), 7.83 (d, J = 6.8 Hz, 2H, Ar), 7.00 (d, J = 6.8 Hz, 2H, Ar), 4.06 (t, J = 6.6 Hz, 2H, 1 × OCH_2), 1.83-1.33 (m, 20H, 10 × CH_2), 0.90 (t, J = 7.1 Hz, 3H, 1 × CH_3); MS(FAB$^+$): m/z Calcd. for $C_{19}H_{30}O_2$: 290.2; Found: 290.6.

If: General procedures for the synthesis of cholesteryl 4-(4-((4-*n*-alkoxylbenzylidene)-amino)phenoxy)alkanoates (**DSB-n,R**)

A mixture of cholesteryl ω-(4-aminophenoxy)alkanoate (**3a** / **3b** / **3c**/ **3d**) (0.126 mmol, 1 equiv), 4-*n*-alkoxyl benzaldehydes (0.63 mmol, 1.5 equiv) and catalytic amount of glacial acetic acid (2 drops) in absolute ethanol was refluxed for 1h. The dull yellow solid material obtained on cooling was filtered, washed continually with hot ethanol and further purified by repeated recrystallization from a mixture of CH_2Cl_2:EtOH (1:9) to obtain off-white pure solids.

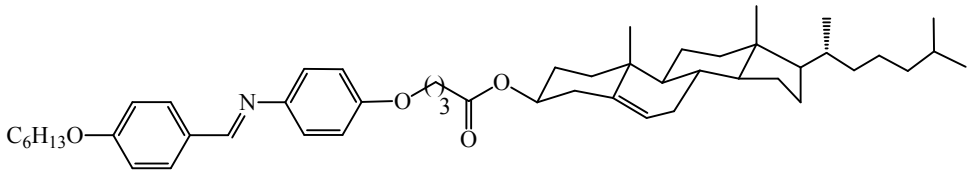
DSB-3,4: Cholesteryl 4-(4-((4-butoxylbenzylidene)amino)phenoxy)butanoate



Yield: 0.063g, 82%; IR (Neat): ν_{max} in cm^{-1} 2955, 2869, 1732, 1608, 1179, 1112; UV-Vis: λ_{max} = 335 nm, ε = 1.56 × 10^3 L mol $^{-1}$ cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.83 (d, J = 8.8 Hz, 2H, Ar), 7.20 (d, J = 9.2 Hz, 2H, Ar), 6.98 (d, J = 8.8 Hz, 2H, Ar), 6.92 (d, J = 8.8 Hz, 2H, Ar), 5.39 (brd, J = 4.0 Hz, 1H, olefinic), 4.68 (m, 1H, 1 × CHOCO), 4.05 (m, 4H, 2 × OCH_2), 2.53-2.12 (m, 4H, 2 × allylic CH_2), 1.99-0.68 (m, 50H, 6 × CH, 13 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.6, 161.6, 157.9, 157.2, 145.4, 139.7, 130.2, 129.3, 122.7, 122.0, 115.0, 114.7, 74.1, 67.9, 67.1, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.2, 29.0, 28.2, 28.0, 27.8, 24.8, 24.3, 23.8, 22.8, 22.6,

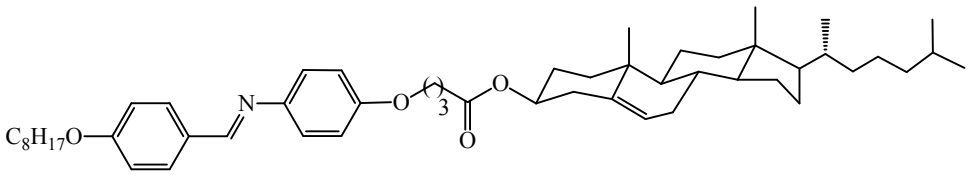
21.0, 19.3, 19.2, 18.7, 13.8, 11.9; Anal. calcd for $C_{48}H_{69}NO_4$: C, 79.62; H, 9.61; N, 1.93; Found: C, 80.11; H, 9.65; N, 2.50.

DSB-3,6: Cholesteryl 4-(4-((4-hexyloxybenzylidene)amino)phenoxy)butanoate



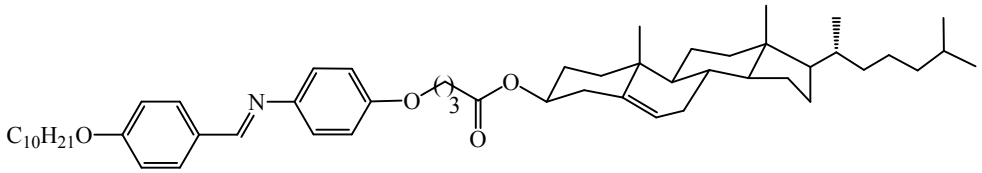
Yield: 0.067g, 84%; IR (Neat): ν_{max} in cm^{-1} 2954, 2869, 1732, 1608, 1178, 1112; UV-Vis: λ_{max} = 334 nm, ε = 2.28 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 7.2 Hz, 2H, Ar), 7.19 (d, *J* = 6.8 Hz, 2H, Ar), 6.99 (d, *J* = 7.2 Hz, 2H, Ar), 6.91 (d, *J* = 6.4 Hz, 2H, Ar), 5.38 (brd, *J* = 4.8 Hz, 1H, olefinic), 4.68 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.52-2.31 (m, 4H, 2 × allylic CH_2), 2.12-0.68 (m, 54H, 6 × CH, 15 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.6, 161.6, 158.0, 157.2, 145.4, 139.7, 130.2, 129.3, 122.7, 122.0, 115.0, 114.7, 74.1, 68.2, 67.1, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.6, 31.2, 29.2, 28.2, 28.0, 27.8, 25.7, 24.8, 24.3, 23.8, 1.86; 22.8, 22.6, 22.5, 21.0, 19.3, 18.7, 14.0, 11.9; Anal. calcd for $C_{50}H_{73}NO_4$: C, 79.85; H, 9.78; N, 1.86; Found : C, 80.46; H, 9.90; N, 2.31.

DSB-3,8: Cholesteryl 4-(4-((4-octyloxylbenzylidene)amino)phenoxy)butanoate



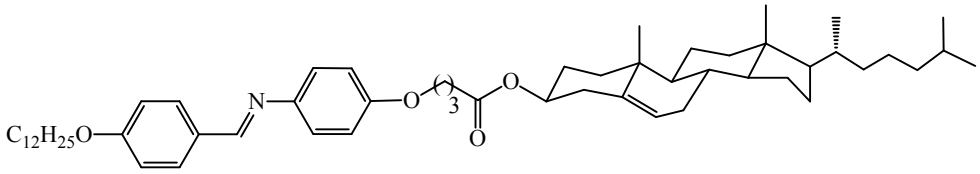
Yield: 0.070g, 85%; IR (Neat): ν_{max} in cm^{-1} 2952, 2870, 1732, 1608, 1178, 1111; UV-Vis: λ_{max} = 335 nm, ε = 2.13 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 6.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 6.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4.0 Hz, 1H, olefinic), 4.68 (m, 1H, 1 × CHOCO), 4.04 (m, 4H, 2 × OCH_2), 2.52-2.31 (m, 4H, 2 × allylic CH_2), 2.12-0.68 (m, 58H, 6 × CH, 17 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.1, 161.2, 157.5, 156.7, 145.0, 139.2, 129.7, 128.8, 122.2, 121.6, 114.5, 114.2, 73.6, 67.7, 66.6, 56.2, 55.7, 49.6, 41.9, 39.3, 39.1, 37.7, 36.5, 36.1, 35.7, 35.3, 31.4, 31.3, 30.7, 28.9, 28.8, 28.7, 27.8, 27.5, 27.3, 25.6, 24.3, 23.8, 23.4, 22.3, 22.2, 22.1, 20.6, 18.8, 18.2, 13.6, 11.4; Anal. calcd for $C_{52}H_{77}NO_4$: C, 80.05; H, 9.95; N, 1.80; Found: C, 80.33; H, 10.30; N, 1.73.

DSB-3,10: Cholesteryl 4-(4-((4-decyloxylbenzylidene)amino)phenoxy)butanoate



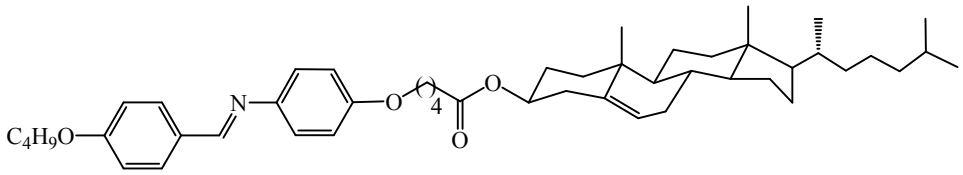
Yield: 0.068g, 80%; IR (Neat): ν_{max} in cm^{-1} 2955, 2869, 1732, 1608, 1178, 1112; UV-Vis: λ_{max} = 335 nm, ε = 7.99 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.4 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.38 (brd, J = 4.0 Hz, 1H, olefinic), 4.65 (m, 1H, 1 × CHOCO), 4.04 (m, 4H, 2 × OCH_2), 2.52-2.31 (m, 4H, 2 × allylic CH_2), 2.14-0.68 (m, 62H, 6 × CH, 19 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.9, 161.6, 157.9, 157.3, 145.3, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.9, 67.9, 67.8, 56.7, 56.2, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.3, 31.9, 31.2, 28.7, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.6, 21.8, 21.0, 19.3, 19.2, 18.7, 14.0, 11.9; Anal. calcd for $C_{54}H_{81}NO_4$: C, 80.25; H, 10.10; N, 1.73; Found: C, 79.85; H, 10.43; N, 1.58.

DSB-3,12: Cholesteryl 4-(4-((4-dodecyloxylbenzylidene)amino)phenoxy)butanoate.



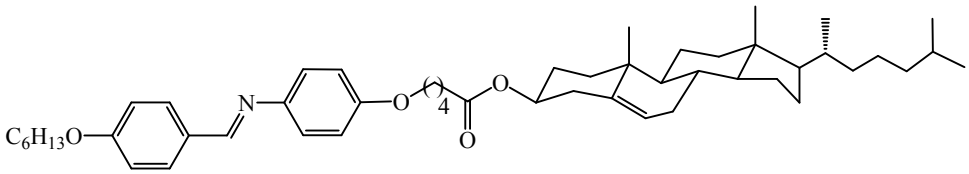
Yield: 0.066g, 83%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 334 nm, ε = 7.67 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.37 (brd, *J* = 4.4 Hz, 1H, olefinic), 4.66 (m, 1H, 1 × CHOCO), 4.08 (m, 4H, 2 × OCH_2), 2.39-2.30 (m, 4H, 2 × allylic CH_2), 2.0-0.68 (m, 66H, 6 × CH, 21 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.9, 161.6, 157.9, 145.3, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.9, 68.2, 67.7, 56.7, 56.2, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.3, 31.9, 31.8, 31.6, 29.2, 28.7, 28.2, 28.0, 27.8, 25.7, 24.3, 23.8, 22.8, 22.6, 21.7, 21.0, 19.3, 18.7, 14.0 and 11.9; Anal. calcd for $C_{56}H_{85}NO_4$: C, 80.43; H, 10.24; N, 1.67; Found: C, 80.26; H, 10.29; N, 1.83.

DSB-4,4: Cholesteryl 5-(4-((4-butoxylbenzylidene)amino)phenoxy)pentanoate



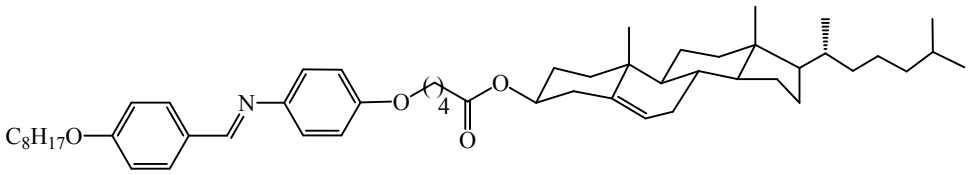
Yield: 0.064g, 72%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 335 nm, ε = 1.07 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 6.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 6.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4.0 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.04 (m, 4H, 2 × OCH_2), 2.37-2.30 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 52H, 6 × $CH_,$ 14 × $CH_2,$ 6 × CH_3); ^{13}C NMR (100MHz): 172.4, 161.2, 157.4, 156.8, 144.8, 139.2, 129.7, 128.8, 122.2, 121.6, 114.5, 114.2, 73.4, 67.4, 67.2, 56.2, 55.7, 49.6, 41.9, 39.3, 39.1, 37.7, 36.5, 36.1, 35.7, 35.3, 33.8, 31.4, 30.8, 28.2, 27.8, 27.5, 27.3, 23.8, 23.4, 22.3, 22.1, 21.3, 20.6, 18.8, 18.2, 13.4, 11.4; Anal. calcd for $C_{49}H_{71}NO_4$: C, 79.74; H, 9.70; N, 1.90; Found: C, 79.98; H, 9.93; N, 2.35.

DSB-4,6: Cholesteryl 5-(4-((4-hexyloxylbenzylidene)amino)phenoxy)pentanoate



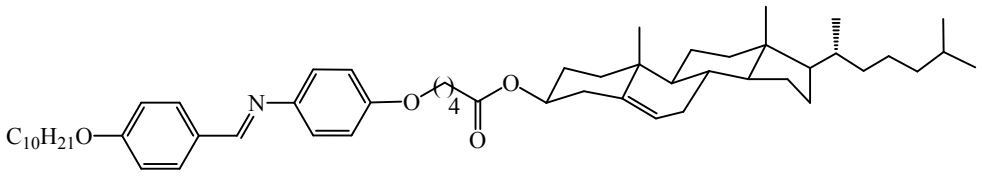
Yield: 0.069g, 75%; IR (Neat): ν_{max} in cm^{-1} 2931, 2857, 1736, 1606, 1168, 1110; UV-Vis: λ_{max} = 335 nm, ε = 2.67 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.4 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.4 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.37 (brd, *J* = 4.0 Hz, 1H, olefinic), 4.66 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.37-2.30 (m, 4H, 2 × allylic CH_2), 1.99-0.67 (m, 56H, 6 × $CH_,$ 16 × $CH_2,$ 6 × CH_3); ^{13}C NMR (100MHz): 172.9, 161.6, 157.9, 145.3, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.9, 68.2, 67.7, 56.7, 56.2, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.3, 31.9, 31.6, 29.2, 28.7, 28.2, 28.0, 27.8, 25.7, 24.3, 23.8, 22.8, 22.6, 21.7, 21.0, 19.3, 18.7, 14.0, 11.8; Anal. calcd for $C_{51}H_{75}NO_4$: C, 79.95; H, 9.87; N, 1.83; Found: C, 80.45; H, 9.50; N, 2.09.

DSB-4,8: Cholesteryl 5-(4-((4-octyloxylbenzylidene)amino)phenoxy)pentanoate



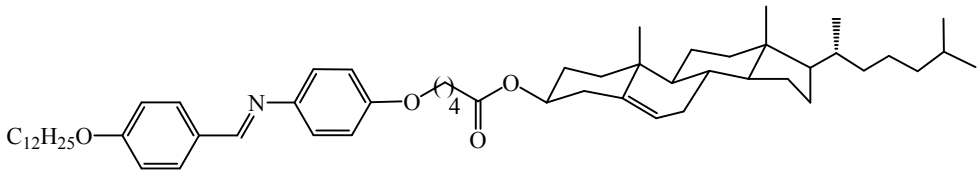
Yield: 0.074g, 77%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 336 nm, ε = 2.92 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.4 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.37 (brd, *J* = 4.4Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.39-2.30 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 60H, 6 × CH_3, 18 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.8, 161.6, 157.9, 157.3, 145.3, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.9, 68.2, 67.7, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.3, 31.9, 31.8, 29.4, 29.2, 28.7, 28.2, 28.0, 27.8, 26.0, 24.3, 23.8, 22.6, 21.8, 21.0, 19.3, 18.7, 14.1, 11.9; Anal. calcd for $C_{53}H_{79}NO_4$: C, 80.15; H, 10.03; N, 1.76; Found: C, 80.48; H, 10.28; N, 1.87.

DSB-4,10: Cholesteryl 5-(4-((4-decyloxylbenzylidene)amino)phenoxy)pentanoate



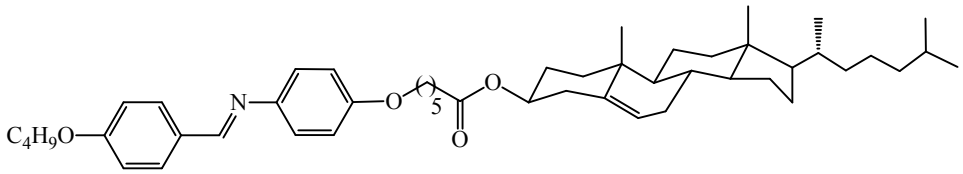
Yield: 0.066g, 66%; IR (Neat): ν_{max} in cm^{-1} 2931, 2857, 1736, 1606, 1168, 1108; UV-Vis: λ_{max} = 335 nm, ε = 3.81 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.37 (brd, *J* = 3.6 Hz, 1H, olefinic), 4.66 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.39-2.30 (m, 4H, 2 × allylic CH_2), 2.03-0.68 (m, 64H, 6 × CH_3, 20 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.9, 161.6, 157.9, 157.3, 145.3, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.9, 68.2, 67.7, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.3, 31.9, 29.6, 29.4, 29.3, 29.2, 28.7, 28.2, 28.0, 27.8, 26.0, 24.3, 23.8, 22.8, 22.7, 22.6, 21.8, 21.0, 19.3, 18.7, 14.1, 11.9; Anal. calcd for $C_{55}H_{83}NO_4$: C, 80.34; H, 10.17; N, 1.70; Found: C, 80.54; H, 10.03; N, 1.88.

DSB-4,12: Cholesteryl 5-(4-((4-dodecyloxylbenzylidene)amino)phenoxy)pentanoate



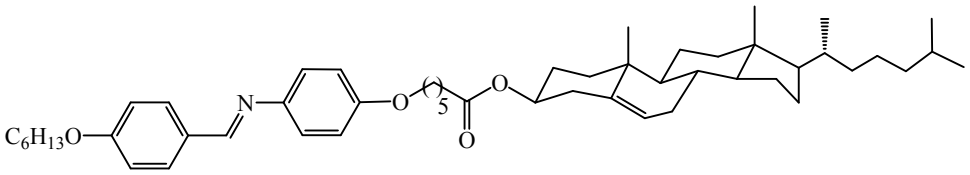
Yield: 0.070g, 68%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 336 nm, ε = 3.79 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 9.2 Hz, 2H, Ar), 5.37 (brd, J = 3.6 Hz, 1H, olefinic), 4.66 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.39-2.30 (m, 4H, 2 × allylic CH_2), 2.03-0.68 (m, 68H, 6 × CH, 22 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.9, 161.6, 157.9, 157.3, 145.3, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.9, 68.2, 67.7, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.3, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 28.7, 28.2, 28.0, 27.8, 26.0, 24.3, 23.8, 22.8, 22.7, 22.6, 21.8, 21.0, 19.3, 18.7, 14.1, 11.9; Anal. calcd for $C_{57}H_{87}NO_4$: C, 82.06; H, 10.51; N, 1.68; Found: C, 81.63; H, 10.12; N, 2.13.

DSB-5,4: Cholesteryl 6-(4-((4-butoxylbenzylidene)amino)phenoxy)hexanoate



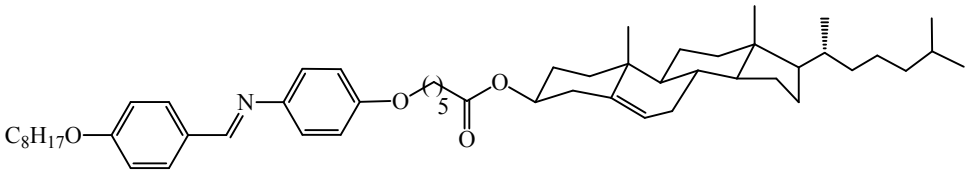
Yield: 0.045g, 72%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 335 nm, ε = 8.49 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.04 (m, 4H, 2 × OCH_2), 2.34-2.30 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 54H, 6 × CH, 15 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 173.04, 161.6, 157.9, 157.4, 145.2, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.8, 67.9, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.2, 29.0, 28.2, 28.0, 27.8, 25.6, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 19.2, 18.7, 13.8, 11.9; Anal. calcd for $C_{50}H_{73}NO_4$: C, 79.85; H, 9.78; N, 1.86; Found: C, 80.30; H, 9.61; N, 2.31.

DSB-5,6: Cholesteryl 6-(4-((4-hexylbenzylidene)amino)phenoxy)hexanoate.



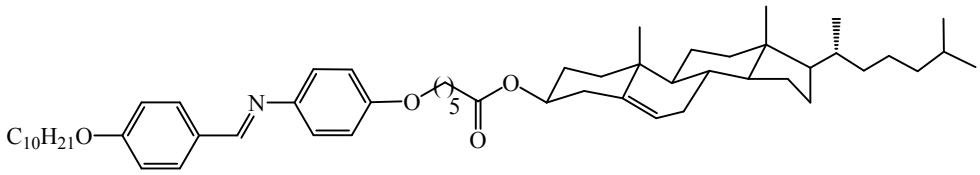
Yield: 0.043g, 66%; IR (Neat): ν_{max} in cm^{-1} 2937, 2857, 1735, 1606, 1169, 1111; UV-Vis: λ_{max} = 337 nm, ε = 1.7 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4.4 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.34-2.30 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 58H, 6 × CH_3, 17 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 173.0, 161.6, 157.9, 157.4, 145.2, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.8, 68.2, 67.9, 56.7, 56.2, 50.1, 42.3, 39.8, 39.6, 38.2, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.6, 29.2, 29.0, 28.2, 28.0, 27.8, 25.7, 25.6, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 14.0, 11.9; Anal. calcd for $C_{52}H_{77}NO_4$: C, 80.05; H, 9.95; N, 1.80; Found: C, 80.35; H, 10.21; N, 2.33.

DSB-5,8: Cholesteryl 6-(4-((4-octyloxylbenzylidene)amino)phenoxy)hexanoate.



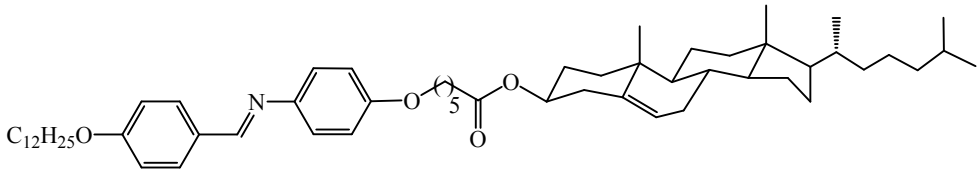
Yield: 0.046g, 68%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 335 nm, ε = 2.15 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 9.2 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4.0 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.34-2.30 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 62H, 6 × CH_3, 19 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 173.1, 161.7, 157.9, 157.4, 145.3, 139.7, 130.2, 129.3, 122.6, 122.1, 115.0, 114.7, 73.9, 68.2, 68.0, 56.7, 56.2, 50.1, 42.4, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.8, 29.4, 29.2, 29.0, 28.3, 28.0, 27.9, 26.1, 25.7, 24.8, 24.3, 23.9, 22.9, 22.8, 22.7, 22.6, 22.5, 21.1, 19.3, 18.7, 14.1, 11.9; Anal. calcd for $C_{54}H_{81}NO_4$: C, 80.25; H, 10.10; N, 1.73; Found: C, 80.01; H, 10.30; N, 1.94.

DSB-5,10: Cholesteryl 6-(4-((4-decyloxylbenzylidene)amino)phenoxy)hexanoate



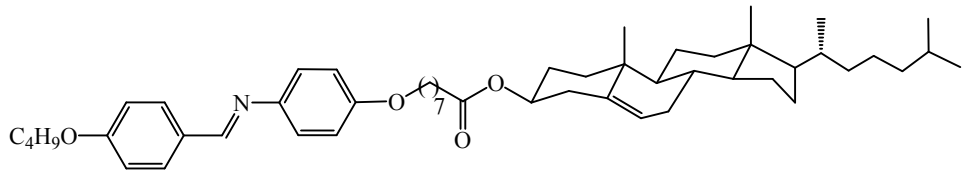
Yield: 0.050g, 71%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 350 nm, ε = 4.45 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4.0 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.34-2.30 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 66H, 6 × CH, 21 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 173.1, 161.7, 157.9, 157.4, 145.3, 139.7, 130.2, 129.3, 122.6, 122.1, 115.0, 114.7, 73.9, 68.2, 68.0, 56.7, 56.2, 50.1, 42.4, 39.8, 39.6, 38.2, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 29.6, 29.4, 29.3, 29.2, 29.0, 28.3, 28.0, 27.9, 26.0, 25.7, 24.8, 24.3, 23.9, 22.8, 22.7, 22.6, 21.1, 19.3, 18.7, 14.1, 11.9; Anal. calcd for $C_{56}H_{85}NO_4$: C, 80.43; H, 10.24; N, 1.67; Found: C, 80.70; H, 10.40; N, 1.72.

DSB-5,12: Cholesteryl 6-(4-((4-dodecyloxylbenzylidene)amino)phenoxy)hexanoate



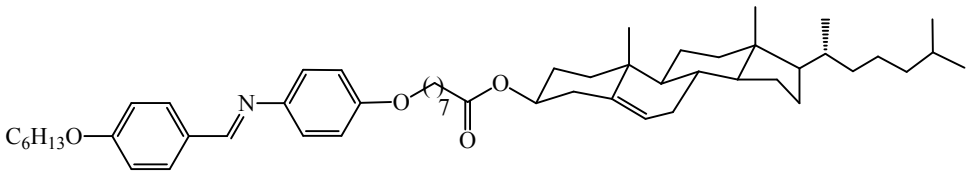
Yield: 0.058g, 80%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 336 nm, ε = 1.73 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4.0 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.34-2.30 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 70H, 6 × CH, 23 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 173.1, 161.7, 157.9, 157.4, 145.3, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.8, 68.2, 67.9, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 29.7, 29.6, 29.4, 29.2, 29.0, 28.2, 28.0, 27.8, 26.0, 25.6, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 14.1, 11.9; Anal. calcd for $C_{58}H_{89}NO_4$: C, 80.60; H, 10.38; N, 1.62; Found: C, 81.03; H, 10.36; N, 1.78.

DSB-7,4: Cholesteryl 8-(4-((4-butoxylbenzylidene)amino)phenoxy)octanoate



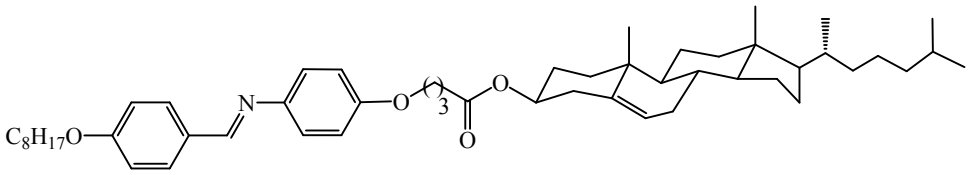
Yield: 0.064g, 78%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 335 nm, ε = 1.85 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4.8Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.32-2.26 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 58H, 6 × CH, 17 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 173.0, 161.6, 157.9, 157.4, 145.2, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.8, 67.9, 56.7, 56.2, 50.1, 42.3, 39.6, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.2, 29.0, 28.2, 28.0, 27.8, 25.6, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 19.2, 18.7, 13.8, 11.9; Anal. calcd for $C_{52}H_{77}NO_4$: C, 80.05; H, 9.95; N, 1.80; Found: C, 80.06; H, 10.29; N, 1.97.

DSB-7,6: Cholesteryl 8-(4-((4-hexyloxylbenzylidene)amino)phenoxy)octanoate



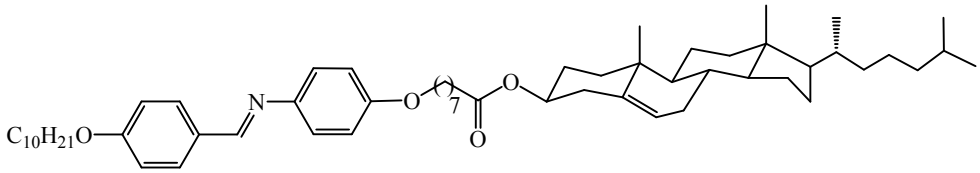
Yield: 0.060g, 71%; IR (Neat): ν_{max} in cm^{-1} 2935, 2852, 1736, 1606, 1171, 1108; UV-Vis: λ_{max} = 335 nm, ε = 1.51 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 9.2 Hz, 2H, Ar), 5.38 (brd, *J* = 4.4 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.32-2.26 (m, 4H, 2 × allylic CH_2), 2.17-0.68 (m, 62H, 6 × CH, 19 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 173.0, 161.6, 157.9, 157.4, 145.2, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.8, 68.2, 67.9, 56.7, 56.2, 50.1, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.6, 29.2, 29.0, 28.2, 28.0, 27.8, 25.7, 25.6, 24.8, 24.3, 23.8, 22.8, 22.6, 22.5, 21.0, 19.3, 18.7, 14.0, 11.9; Anal. calcd for $C_{54}H_{81}NO_4$: C, 80.25; H, 10.10; N, 1.73; Found: C, 80.58; H, 10.43; N, 1.98.

DSB-7,8: Cholesteryl 8-(4-((4-octyloxylbenzylidene)amino)phenoxy)octanoate



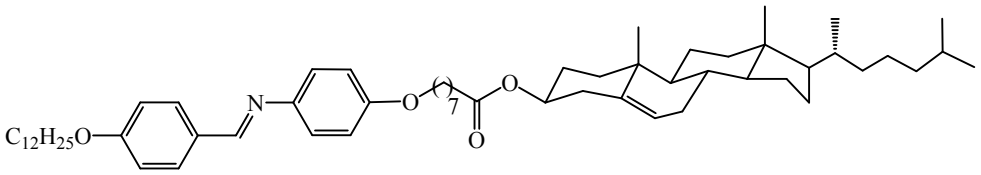
Yield: 0.066g, 75%; IR (Neat): ν_{max} in cm^{-1} 2921, 2850, 1734, 1604, 1168, 1112; UV-Vis: λ_{max} = 337 nm, ε = 1.85 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4.8 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.32-2.26 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 66H, 6 × CH, 21 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 173.0, 161.6, 157.9, 157.4, 145.2, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.8, 67.9, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.2, 29.0, 28.2, 28.0, 27.8, 25.6, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 19.2, 18.7, 13.8, 11.9; Anal. calcd for $C_{56}H_{85}NO_4$: C, 80.43; H, 10.24; N, 1.67; Found: C, 80.72; H, 10.52; N, 1.54.

DSB-7,10: Cholesteryl 8-(4-((4-decyloxylbenzylidene)amino)phenoxy)octanoate



Yield: 0.072g, 79%; IR (Neat): ν_{max} in cm^{-1} 2921, 2850, 1736, 1605, 1170, 1109; UV-Vis: λ_{max} = 336 nm, ε = 1.90 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 9.2 Hz, 2H, Ar), 5.38 (brd, *J* = 4.4 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.32-2.26 (m, 4H, 2 × allylic CH_2), 2.16-0.68 (m, 70H, 6 × CH, 23 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.9, 161.7, 157.9, 157.3, 145.3, 139.7, 130.2, 129.3, 122.7, 122.1, 115.0, 114.7, 73.9, 68.2, 67.7, 56.7, 56.2, 50.1, 42.4, 39.8, 39.6, 38.2, 37.0, 36.6, 36.2, 35.8, 34.4, 31.9, 31.6, 29.2, 28.7, 28.3, 28.0, 27.9, 25.7, 24.3, 23.9, 22.8, 22.6, 21.8, 21.1, 19.4, 18.7, 14.0, 11.9; Anal. calcd for $C_{58}H_{89}NO_4$: C, 80.60; H, 10.38; N, 1.62; Found: C, 80.41; H, 10.21; N, 1.59.

DSB-7,12: Cholesteryl 8-(4-((4-dodecyloxylbenzylidene)amino)phenoxy)octanoate



Yield: 0.064g, 68%; IR (Neat): ν_{max} in cm^{-1} 2921, 2850, 1736, 1605, 1170, 1109; UV-Vis: λ_{max} = 337 nm, ε = 2.05 × 10^3 L mol^{-1} cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) : δ 8.39 (s, 1H, 1 × CH=N), 7.82 (d, *J* = 8.4 Hz, 2H, Ar), 7.19 (d, *J* = 9.2 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 5.38 (brd, *J* = 4.8 Hz, 1H, olefinic), 4.63 (m, 1H, 1 × CHOCO), 4.03 (m, 4H, 2 × OCH_2), 2.32-2.26 (m, 4H, 2 × allylic CH_2), 2.02-0.68 (m, 74H, 6 × CH, 25 × CH_2, 6 × CH_3); ^{13}C NMR (100MHz): 172.9, 161.6, 157.9, 157.3, 145.3, 139.7, 130.2, 129.3, 122.6, 122.0, 115.0, 114.7, 73.9, 68.2, 67.7, 56.7, 56.2, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.3, 31.9, 31.8, 29.3, 29.2, 28.7, 28.2, 28.0, 27.8, 26.0, 24.3, 23.8, 22.8, 22.6, 21.7, 21.0, 19.3, 18.7, 14.1, 11.9; Anal. calcd for $C_{60}H_{93}NO_4$: C, 80.75; H, 10.50; N, 1.57; Found: C, 81.03; H, 10.81; N, 1.96.

Table S1: Phase transition temperatures (°C)[a] and enthalpies of transitions (kJ mol^{-1}) of intermediates

Compounds	Phase Sequence
	Heating
	Cooling
2a	Cr 133.6 (20.5) I
	I 130.3 (0.6) N* 117.2 (0.6) [b] TGB-SmA 89 (1.2) Cr
2b	Cr 106.9 (0.5) N* 125 (0.6) I
	I 123.9 (0.7) N* 113.2 [c] TGB-SmA 106 (0.5) Cr
2c	Cr 136.3 (19.1) I
	I 124.4 (0.7) N* 102.4 (11.3) Cr
2d	Cr 94 (0.5) N* 106.8 (2) I
	I 106.4 (1.2) N* 54.0 [c] Cr
3a	Cr 120.9 (17) SmA-TGB-N* 126.6 (2) I
	I 125.7 (1.6) N*-TGB 124.2 (0.8) SmA 99.6 (21.1) Cr
3b	Cr 121.7 (24.6) SmA-TGB-N* 127.9 (2.3) I
	I 126.9 (2.4) N*-TGB-SmA 102.7 (21.4) Cr
3c	Cr 94.6 (16.9) SmA-TGB-N* 105 (1) I
	I 104 (0.8) N*-TGB 98.4 (0.4) SmA 50.0 (11.5) Cr
3d	Cr 108.26 (34.7) SmA-TGB-N* 112.65 (1.1) I
	I 111.74 (1.1) N*-TGB 100.2 SmA 66.90 (22.5) Cr

[a] Transition temperatures determined by both POM and peak values of the DSC traces during the first heating/cooling cycles at 5 °C /min rate. [b] TGB−N * transition was observed under the microscope, but this was not resolved in the DSC scan and hence the ΔH value represents the combined enthalpy for both TGB−N* transition. [c] The transitions were observed under the microscope, but this was not resolved in the DSC scan.

The nitro compounds **2a-d** show the N* phase commonly; it is enantiotropic only in the case of dimers **2b** and **2d**. Compounds **2a** and **2b** show monotropic TGB and SmA phases

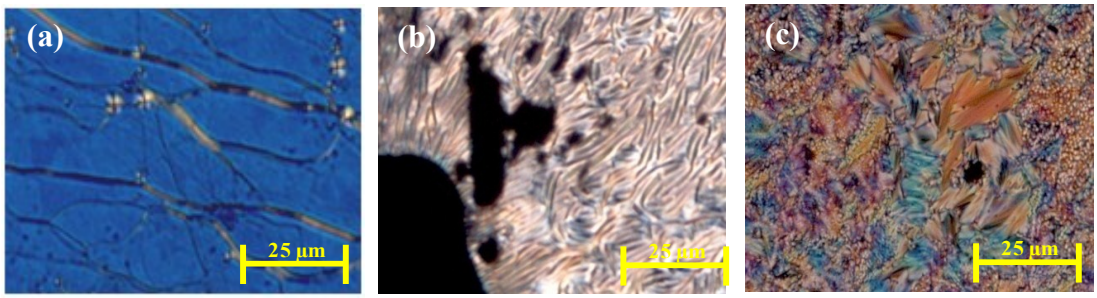


Figure S1. Photomicrographs of the optical textures of LC phases obtained for **IV-2a**: (a) the Grandjean planar texture of N* phase (129 °C), (b) the filament texture of the TGB phase (114 °C) and (c) focal-conic texture of the homogeneously aligned SmA phase (100 °C).

compounds also the TGB phase exist over a very short thermal range. The existence of these mesophases was clearly identified by observing their characteristic textural patterns under POM. For example, when a sample of compound **2a** was held between two untreated glass

slides and cooled slowly from the isotropic state, a focal-conic texture of the N* phase was observed; when pressed gently, the textural pattern sharply changes to a Grandjean planar pattern [23] as shown in Fig. 1a. On cooling the unperturbed sample, at 117.2 °C the field of view fills with a pattern consisting of both filament and planar textures which is the characteristic of the TGB phase (Fig. 1b). [23] On cooling further, the pattern immediately changes to a focal-conic fan coexistent with a *pseudo*-isotropic texture, which is typical of the SmA phase. The existence of the SmA phase was further evidenced based on the observation of a characteristic focal-conic texture (Fig. 1c) in slides treated for planar orientation and a dark field of view for slides treated for homeotropic orientation. Four series of target dimers were examined for their phase transitional properties and the details of these studies with analysis of the results are presented in the following sections.

Table S2: The all-*trans* molecular length [*L (*Å)] and the spacings d_1 corresponding to the low-angle reflections of XRD pattern of SmX phase belonging to dimer **DSB-4,8**; d_1/L ratio is also given.

Dimer [*L* (Å)]	Temperature (°C)	d_1 (Å) Layer spacing	d_1/L
DSB-4,8 (42)	90	39.7	0.95
	95	40.3	0.96
	100	40.9	0.97
	105	41.8	1.0
	110	42.6	1.01
	115	43.5	1.03
	120	44.8	1.07

Table S3: The all-*trans* molecular length [*L* (Å)], the spacings d_1 corresponding to the low-angle reflections of XRD pattern of TGB and/or TGBC* phases of dimers **DSB-7,10** and **DSB-7,12**; d_1/L ratio is also given.

Dimer [*L* (Å)]	LC phase	Temperature / °C	d_1 (Layer spacing)	d_1 / *L*
DSB-7,10 [52.2]	TGB	145	52.36	1.00
		143	52.67	1.00
		141	52.71	1.00
		139	52.22	1.00
		137	51.58	0.98
		135	52.17	0.99
		133	52.47	1.00
	TGBC*	131	50.31	0.96
		129	49.84	0.95
		127	49.30	0.94
		125	48.88	0.93
		123	48.52	0.92
		121	48.24	0.92
		119	47.59	0.91
		117	47.24	0.90
		115	47.09	0.90
		113	46.53	0.89
		111	46.34	0.88
DSB-7,12 [57.4]	TGBC*	154	55.11	0.96
		152	54.94	0.95
		150	55.09	0.95
		148	55.05	0.95
		146	54.99	0.95
		144	55.03	0.95
		142	55.07	0.95
		140	54.74	0.95
		138	53.67	0.93
		136	52.86	0.92
		134	52.21	0.90
		132	51.68	0.90
		130	51.16	0.89
		128	50.69	0.88
		126	50.24	0.87
		124	49.78	0.86
		122	49.41	0.86
		120	49.10	0.85
		118	48.66	0.84
		116	48.29	0.84
		114	47.92	0.83
		112	47.61	0.82
		110	47.25	0.82

Table S4: Temperature-dependent CD data for the chiral nematic phase of dimers

Dimer	Phase	Temperature (°C)	CD	
			λ_{max} (nm)	CD (mdeg)
DSB-3,4	I	225	---	---
	N*	210	456.5, 375.8, 314.1, 257.6	39.1, -300.2, -33.2, 44.3
		205	456.4, 375.8, 314.4, 258.4	39.0, -297.1, -37.6, 33.3
		200	455.0, 374.1, 313.1, 256.1	36.6, -285.1, -41.3, 40.3
		195	455.5, 373.0, 315.7, 257.1	35.1, -286.7, -46.04, 44.6
		190	456.5, 373.9, 314.3, 256.9	34.6, -281.9, -49.8, 51.2
		185	456.5, 376.0, 215.0, 256.8	33.2, -280.2, -29.2, 34.5
		180	456.5, 376.5, 310.6, 256.1	33.0, -281.7, -22.9, 34.4
		175	456.0, 376.3, 310.7, 258.3	32.74, -277.3, -21.3, 33.3
		170	460.0, 377.0, 310.5, 256.9	31.1, -269.2, -17.6, 26.4
DSB-4,4	I	175	---	---
	N*	165	494.7, 405.4	64.43, 126.0
		155	495.0, 405.3	63.16, 122.3
		145	494.8, 405.3	61.11, 117.
		135	496.0, 405.6	60.05, 114.2
		125	495.9, 405.5	56.9, 107.1
		115	496.4, 405.2	55.5, 103.2
		105	496.4, 406.1	53.8, 99.6
		95	496.7, 406.1	51.9, 95.6
		85	496.2, 405.6	49.03, 88.6
		75	496.1, 405.6	46.2, 82.8
DSB-5,4	I	210	---	---
	N*	205	360.3, 309.1, 260.7	-1732.3, -687.4, 527.5
		200	361.9, 309.2, 260.7	-1633.0, -608.6, 509.2
		195	363.9, 309.4, 260.5	-1540.6, -530.2, 472.3
		190	365.6, 309.7, 261.0	-1464.2, -468.9, 465.6
		185	367.0, 309.0, 260.1	-1415.0, -444.7, 444.3
		180	366.0, 310.0, 260.5	-1377.4, -433.8, 430.0
		175	367.7, 310.2, 261.0	-1341.7, 432.8, 422.5
		170	367.8, 309.4, 260.5	-1279.0, -410.3, 420.8
DSB-7,4,	I	190	---	---
	N*	185	599.8,390.7, 257.1	-20.7, -251.3, 17.0
		180	601.7,390.3, 257.8	4.9, -84.6, 9.3
		175	598.6,390.9,257.0	21.6, -49.2,6.6
		170	598.2, 391.2, 256.8	34.2, -31.2, 5.6
		165	598.1, 387.6, 257.4	44.9, -17.3, 4.8