Electronic Supplementary Material (ESI) for Soft Matter.

Interplay of Chirality and Restricted Rotation: Stabilisation of Chiral, Frustrated Mesophase Over a Wide Thermal Range.

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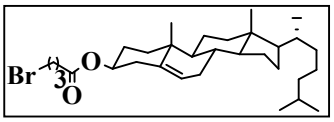
Experimental Details

The required chemical such as 4-hydroxybenzaldehyde, Carbon Tetrabromide, n-BuLi, Triphenyl Phosphine, DCC (dicyclohexyl carbodiimide), cholesterol, 8-bromooctanoic acid 6-bromohexanoic acid and 5-bromovaleric acid, 4-bromobutyric acid obtained from Sigma-Aldrich and were used as received. The commercial organic solvents used were distilled prior to use. The LR grade organic solvents used in synthesis were purified and dried following standard drying protocols. Thin-layer chromatography (TLC) was carried out using TLC plates consisting of a thin layer of silica gel (Merck, Kieselgel60, F254) on an aluminium foil support. This technique was used to monitor the progress/ completion of reactions as well as for examining the purity of the intermediates. The spots on the eluted TLC were visualized by using UV light at 254 nm or $KMnO_4$ stains. The column chromatography was carried out using glass columns loaded with either Merck silica gel (60-120/100–200 mesh) or neutral alumina. UV-Vis spectra were recorded using either a Perkin– Elmer's Lambda 750, 2015 NIR spectrometer or a Perkin Elmer's, Lambda 20 UV-Vis spectrophotometer. IR spectra of the samples were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. Bruker AMX-400 spectrometer operating at 400 MHz was used to record room temperature ^{1}H and ^{13}C NMR spectra of the sample ($CDCl_3$ solution) were recorded using a Bruker AMX-400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts (δ) have been presented in parts per million (ppm) relative to TMS using the residual $CHCl_3$ peak in $CDCl_3$ solution as internal standard; δ H 7.26 and δ C 77.0 relative to TMS. NMR peaks multiplicities are presented as s (singlet), d (doublet), t (triplet) and m (multiplet). Coupling constants (J) are given in Hertz (Hz). Elemental analysis was carried out using a Perkin Elmer Elemental Analyzer Series II 2400 analyzer. CD spectra were obtained with the help of Jasco J-810 spectropolarimeter. The mesomorphic properties of the materials were evaluated using an Olympus BX50 (Model BX50F4) polarizing optical microscope (POM), attached to a Mettler FP82HT hot stage (attached to FP90 central processor) as well as to a digital camera. Differential scanning calorimeter (DSC) traces were recorded at a scanning rate of 5°C/min using Perkin-Elmer Diamond DSC equipment that was calibrated before use, using pure indium as a standard. X-Ray diffraction (XRD) measurements were undertaken with CuK∝ (λ=0.15418 nm) radiation using a PANalytical Empyrean machine. The powder samples placed in Lindemann capillaries (0.5 mm diameter) were used for XRD.

Scheme 1

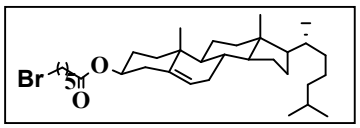
General synthetic procedure for the synthesis of cholesteryl ω-bromoalkanoates (1a-d).

ω-bromoalkanoic acid (1 equiv.) was reacted with the oxalyl chloride (12 ml) in room temperature under an inert (nitrogen) atmosphere. The unreacted oxalyly chloride was removed using distillation; the product ω-bromoalkanoyl chloride was dried completely under *vacuo*. The dry ω-bromoalkanoyl chloride thus obtained was added slowly at 0° C to a pyridinic (6 ml) solution of cholesterol (1 equiv.) in dry THF (50 ml). The mixture was slowly warmed up to rt, where it was stirred for a further 12 hrs. The celtite bed filtration was carried out on the reaction mixture, and the solvent was evaporated from the filtrate to obtain a pale yellow mass. The crude product thus obtained was dissolved in 20:80 mixture of CH_2Cl_2 and Et_2O. The organic layer was washed with abundant distilled water and brine (saturated NaCl) solutions and dried using anhydrous Na_2SO_4. The product thus obtained after evaporating the organic solvent was further purified by column chromatography using neutral alumina. A 30% mixture of CH_2Cl_2-hexanes was used as the eluant to generate a pure product. (Yield: 82-87%)

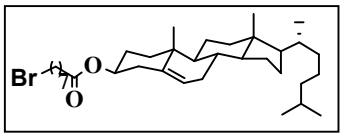


1a: R_f= 0.33 in 30% CH_2Cl_2 : Hexanes; a white solid; yield: 82 %; m.p.: 87-88 °C; IR (KBr Pellet): ν_{max} in cm^{-1}: 2950, 2890, 1739, 1567; ^1H NMR (400MHz, $CDCl_3$): δ 5.37 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.65 (m, 1H, 1 × CHOCO), 3.74 (t, *J* = 6.5 Hz, 2H, 1 × CH_2Br), 2.48 (m, 4H, 2 × allylic CH_2), 2.03-1.05 (m, 28H, 11 × CH_2, 6 × CH), 1.01 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.4 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 1.4 Hz, 3H, 1 × CH_3), 0.85 (d, *J* = 1.4 Hz, 3H, 1 × CH_3), 0.67 (s, 3H, 1 × CH_3); Anal. calcd for $C_{31}H_{51}BrO_2$: C, 69.50; H, 9.59. Found: C, 69.73; H, 9.42.

1b: R_f= 0.30 in 30% CH_2Cl_2 : hexanes; a white solid; yield: 82 %; m.p.: 100-101 °C; IR (KBr Pellet): ν_{max} in cm^{-1}: 2949, 2860, 1725, 1563; ^1H NMR (400MHz, $CDCl_3$): δ 5.38 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.62 (m, 1H, 1 × CHOCO), 3.43 (t, *J* = 6.5 Hz, 2H, 1 × CH_2Br), 2.33 (m, 4H, 2 × allylic CH_2), 2.03-1.01 (m, 30H, 12 × CH_2, 6 × CH), 1.01 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 1.6 Hz, 3H, 1 × CH_3), 0.86 (d, *J* = 1.8 Hz, 3H, 1 × CH_3), 0.68 (s, 3H, 1 × CH_3 Anal. calcd for $C_{32}H_{53}BrO_2$: C, 69.91; H, 9.71. Found: C, 69.86; H, 9.75.



1c: R_f= 0.25 in 30% CH_2Cl_2 : Hexanes; a white solid; yield: 87 %; m.p.: 119-120 °C; IR (KBr Pellet): ν_{max} in cm^{-1}: 2944, 2864, 1730, 1557; ^1H NMR (400MHz, $CDCl_3$): δ 5.38 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.63 (m, 1H, 1 × CHOCO), 3.42 (t, *J* = 6.8 Hz, 2H, 1 × CH_2Br), 2.31 (m, 4H, 2 × allylic CH_2), 2.03-1.04 (m, 32H, 13 × CH_2, 6 × CH), 1.01 (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), 0.85 (d, *J* = 1.8 Hz, 3H, 1 × CH_3), 0.67 (s, 3H, 1 × CH_3); Anal. calcd for $C_{33}H_{55}BrO_2$: C, 70.30; H, 9.56. Found: C, 70.66; H, 9.56.

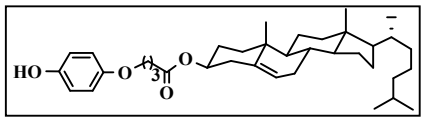


1d: R_f= 0.31 in 30% CH_2Cl_2 : Hexanes; a white solid; yield: 88 %; m.p.: 86.31 °C; IR (KBr Pellet): ν_{max} in cm^{-1}: 2949, 2868, 1742, 1567; ^1H NMR (400 MHz, $CDCl_3$): δ 5.37 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.62 (m, 1H, 1 × CHOCO), 3.40 (t, *J* = 6.8 Hz, 2H, 1 × CH_2Br), 2.31 (m, 4H, 2 × allylic CH_2), 2.02-1.03 (m, 36H, 15 × CH_2, 6 × CH), 1.01 (s, 3H, 1 × CH_3), 0.92 (d, *J* = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, *J* = 1.7 Hz, 3H, 1 × CH_3),

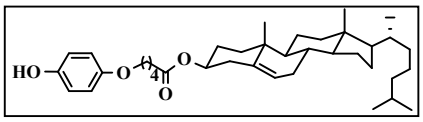
0.85 (d, J = 1.6 Hz, 3H, 1 × CH_3), 0.67 (s, 3H, 1 × CH_3); Anal. calcd for $C_{35}H_{59}BrO_2$: C, 71.03; H, 10.84. Found: C, 71.08; H, 10.99.

General procedure for the synthesis of cholesteryl *n*-(4'-hydroxy phenyl-4-oxy) alkanoates (II.1.2a-d)

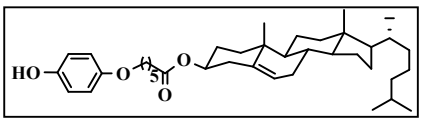
The 2-butanone solution of cholesteryl ω-bromoalkanoates (1.1 equiv.), ethyl 4-hydroxyphenol (1equiv.), and anhydrous K_2CO_3 (2.2 equiv.) were refluxed at 80 °C for 24 h under nitrogen environment. Once the reaction was complete, the reaction mixture was added to ice-cold water and was subjected to solvent extraction using ethyl acetate. The organic layer was washed repeatedly with distilled water and brine and was dried using anhydrous. Na_2SO_4. The crude product was obtained by concentrating the organic layer and the purification was done using column chromatography with silica (100-200 mesh) as a stationary phase. (Yield: 78-82%)



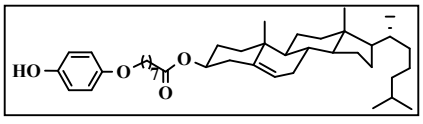
2a: R_f= 0.28 in 20% EtOAc : Hexanes; a white solid; yield: 78 %; m.p.: 152.1 °C; IR (KBr Pellet): ν_{max} in cm^{-1} 2948, 2867, 1711, 1511, 1230; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78-6.72 (m, 4H, Ar), 5.38 (brd, J = 3.8 Hz, 1H, 1 × olefinic), 4.64 (m, 1H, 1 × CHOCO), 3.93 (t, J = 6.8 Hz, 2H, 1 × OCH_2), 2.34 (m, 4H, 2 × allylic CH_2), 2.04-1.07 (m, 28H, 11 × CH_2, 6 × CH), 1.04 (s, 3H, 1 × CH_3), 0.90 (d, J = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, J = 1.7 Hz, 3H, 1 × CH_3), 0.85 (d, J = 1.6 Hz, 3H, 1 × CH_3), 0.68 (s, 3H, 1 × CH_3); MS (FAB$^+$): m/z calcd for $C_{37}H_{56}O_4$: 564.4. Found: 564.1.



2b: R_f= 0.28 in 20% EtOAc : Hexanes; a white solid; yield: 79 %; m.p.: 124.2 °C; IR (KBr Pellet): ν_{max} in cm^{-1} 2934, 2868, 1710, 1518, 1231; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79-6.74 (m, 4H, Ar), 5 .37 (brd, J = 3.8 Hz, 1H, 1 × olefinic), 4.66 (m, 1H, 1 × CHOCO), 3.92 (t, J = 6.8 Hz, 2H, 1 × OCH_2), 2.34 (m, 4H, 2 × allylic CH_2), 2.03-1.04 (m, 30H, 12 × CH_2, 6 × CH), 1.01 (s, 3H, 1 × CH_3), 0.92 (d, J = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, J = 1.6 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 $C_{38}H_{58}O_4$: 578.4. Found: 578.6.



2c: R_f= 0.28 in 20% EtOAc : Hexanes; a white solid; yield: 81 %; m.p.: 122.0 °C; IR (KBr Pellet): ν_{max} in cm^{-1} 2937, 2864, 1714, 1514, 1228; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80-6.76 (m, 4H, Ar), 5.38 (brd, J = 3.8 Hz, 1H, 1 × olefinic), 4.64 (m, 1H, 1 × CHOCO), 3.90 (t, J = 6.8 Hz, 2H, 1 × OCH_2), 2.35 (m, 4H, 2 × allylic CH_2), 2.02-1.06 (m, 32H, 13 × CH_2, 6 × CH), 1.00 (s, 3H, 1 × CH_3), 0.92 (d, J = 6.5 Hz, 3H, 1 × CH_3), 0.87 (d, J = 1.6 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 $C_{39}H_{60}O_4$: 592.4. Found: 593.1.

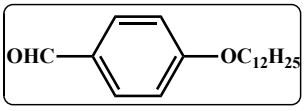


2d: R_f= 0.28 in 20% EtOAc : Hexanes; a white solid; yield: 82 %; m.p.: 120.0 °C; IR (KBr Pellet): ν_{max} in cm^{-1} 2938, 2860, 1715, 1510, 1227; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89-6.70 (m, 4H, Ar), 5.37 (brd, J = 3.8 Hz, 1H, 1 × olefinic), 4.65 (m, 1H, 1 × CHOCO), 3.91 (t, J = 6.8 Hz, 2H, 1 × OCH_2), 2.35 (m, 4H, 2 × allylic CH_2), 2.02-1.04 (m, 36H, 15 × CH_2, 6 × CH), 1.00 (s, 3H, 1 × CH_3), 0.92 (d, J = 6.5 Hz,

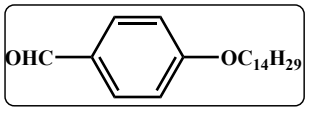
3H, 1 × CH_3), 0.87 (d, *J* = 1.6 Hz, 3H, 1 × CH_3), 0.86 (d, *J* = 1.8 Hz, 3H, 1 × CH_3), 0.68 (s, 3H, 1 × CH_3); MS (FAB^+): m/z calcd for $C_{41}H_{64}O_4$: 620.4, Found: 621.0.

General procedure for the synthesis of 4-(*n*-alkoxy)benzaldehydes (3a-d)

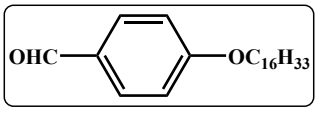
A mixture of 4-hydroxybenzaldehyde (1g, 8.19 mmol, 1eq.), *n*-alkylbromide (9.01 mmol, 1.1 eq.), anhydrous K_2CO_3 (9.01 mmol, 1.1 eq.) and DMF was refluxed in an inert atmosphere for 12 h. After cooling, the reaction mixture was poured into ice-cold water and the product was extracted with dichloromethane (50 mL×3). The combined organic layers were washed with cold aqueous 5% NaOH solution (25 mL×3), water (25 mL×3), brine and dried over anhydrous Na_2SO_4. The solvent was removed in *vacuo* and the crude product obtained was purified by column chromatography on silica gel (100-200 mesh) using 10% EtOAc-hexanes as an eluent. (yield: 78-85%)



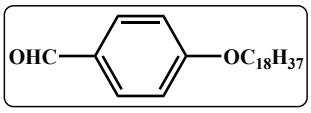
3a: R_f = 0.53 in 30% CH_2Cl_2 : Hexanes; a colorless liquid; yield: 83.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} : 2959, 2874, 1699, 1602, 1509, 1313, 1259, 1161 and 836; ^1H NMR (400 MHz, $CDCl_3$): δ 9.9 (s, 1H, -CHO), 7.82 (d, *J* = 8.4 Hz, 2H, Ar), 6.99 (d, *J* = 8.4 Hz, 2H, Ar), 4.04 (t, *J* = 6.4 Hz, 2H, -OCH_2), 1.88-1.31 (m, 20H, 10 × CH_2), 0.87 (t, *J* = 6.6 Hz, 3H, -CH_3); MS (FAB^+): m/z for $C_{19}H_{30}O_2$ (M+1), Calculated: 290.1; Found: 290.6.



3b: R_f = 0.54 in 30% CH_2Cl_2 : Hexanes; a colorless liquid; yield: 84.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} : 2956, 2879, 1699, 1601, 1263, 1157 and 1113; ^1H NMR (400 MHz, $CDCl_3$): δ 9.8 (s, 1H, -CHO), 7.84 (d, *J* = 8.8 Hz, 2H, Ar), 6.97 (d, *J* = 8.8 Hz, 2H, Ar), 4.05 (t, *J* = 6.4 Hz, 2H, -OCH_2), 1.87-1.29 (m, 24H, 12×CH_2) and 0.88 (t, *J* = 6.6 Hz, 3H, -CH_3); MS (FAB^+): m/z for $C_{21}H_{34}O_2$ (M+1), Calculated: 319.3; Found: 319.4.



3c: R_f = 0.53 (in 30% CH_2Cl_2 : Hexanes; a colorless liquid; yield: 85.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} : 2957, 2873, 1698, 1604, 1510, 1313, 1259, 1162 and 835; ^1H NMR (400 MHz, $CDCl_3$): δ 9.9 (s, 1H, -CHO), 7.82 (d, *J* = 8.8 Hz, 2H, Ar), 6.99 (d, *J* = 8.8 Hz, 2H, Ar), 4.04 (t, *J* = 6.4 Hz, 2H, -OCH_2), 1.83-1.31 (m, 28H, 14×CH_2) and 0.87 (t, *J* = 6.6 Hz, 3H, -CH_3); MS (FAB^+): m/z for $C_{23}H_{38}O_2$, Calculated: 358.3; Found: 358.4.

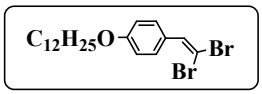


3d: R_f = 0.55 in 30% CH_2Cl_2 : Hexanes; a colorless liquid; yield: 83.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} 2963, 2870, 1701, 1607, 1260, 1167 and 1117; ^1H NMR (400 MHz, $CDCl_3$): δ 9.8 (s, 1H, -CHO), 7.83 (d, *J* = 8.8 Hz, 2H, Ar), 6.98 (d, *J* = 8.8 Hz, 2H, Ar), 4.05 (t, *J* = 6.4 Hz, 2H, -OCH_2), 1.88-1.30 (m, 32H, 16×CH_2) and 0.89 (t, *J* = 6.6 Hz, 3H, -CH_3); MS (FAB^+): m/z for $C_{25}H_{42}O_2$, Calculated: 375.3; Found: 375.5.

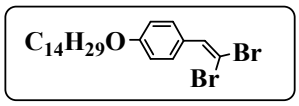
General procedure for the synthesis of 1-(2,2-dibromovinyl)-4-(alkoxy)benzene (4a-d:)

Zn dust (2 eq., 15.2 mmol) and triphenyl phosphine (2 eq., 15.2 eq mmol) were dissolved in dry DCM (dicholoromethane) and maintained at 0 °C. Carbon tetrabromide (2 eq., 15.2 mmol) was dissolved in dry DCM and injected slowly into the mixture maintained at 0 °C. The mixture was stirred for 15 mins at the same temperature, warmed to room temperature, and maintained for another 15 mins. 4-(*n*-alkoxy)benzaldehyde (1 eq.) was dissolved in dry

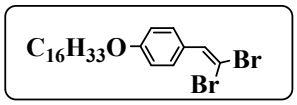
DCM and injected into the reaction mixture, and the mixture was stirred for 24 h. After the completion of the reaction, the precipitate was filtered, and the filtrate was treated with hexanes, where the white precipitate formed was filtered. This procedure was repeated multiple times to remove almost all the unreacted reagents. Finally, the filtrate was evaporated, and the pure compound was obtained *via* column chromatography using hexanes as eluent. (Yield: 81-84%)



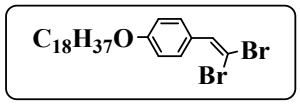
4a: R_f = 0.52 in Hexanes; a white solid; yield: 81.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} 2917, 2848, 1605, 1508, 1467, 1304, 1259, 1177, 1019 and 865 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 4 Hz, 2H, Ar), 7.40 (s, 1H, C_6H_5-C=CH), 6.88 (d, *J* = 4 Hz, 2H, Ar), 3.97 (t, *J* = 4 Hz, 2H, -OCH_2), 1.79-0.87 (m, 23H, 1×CH_3 10×CH_2); Anal. calcd for $C_{20}H_{30}Br_2O$: C, 53.83; H, 6.78. Found: C, 54.04; H, 7.11.



4b: R_f = 0.53 in Hexanes; a white solid; yield: 84.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} 2924, 2853, 1607, 1508, 1466, 1305, 1249, 1177 and 869; ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.51 (d, *J* = 8 Hz, 2H, Ar), 7.40 (s, 1H, C_6H_5-C=CH), 6.89 (d, *J* = 8 Hz, 2H, Ar), 3.97 (t, *J* = 4 Hz, 2H, -OCH_2), 1.80-0.88 (m, 27H, 1×CH_3 12×CH_2); Anal. calcd for $C_{22}H_{34}Br_2O$: C, 55.71; H, 7.23. Found: C, 56.12; H, 7.58.



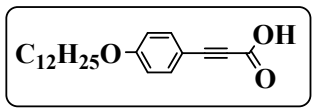
4c: R_f = 0.55 in Hexanes; a white solid; yield: 83.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} 2919, 2849, 1606, 1568, 1508, 1304, 1259, 1170, 1022 and 867; ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.50 (d, *J* = 8 Hz, 2H, Ar), 7.41 (s, 1H, C_6H_5-C=CH), 6.87 (d, *J* = 8 Hz, 2H, Ar), 3.98 (t, *J* = 4 Hz, 2H, -OCH_2), 1.80-0.86 (m, 31H, 1×CH_3 13×CH_2); Anal. calcd for $C_{24}H_{38}Br_2O$: C, 57.38; H, 7.62. Found: C, 57.72; H, 7.99.



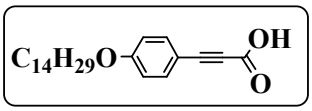
4d: R_f = 0.55 in Hexanes; a white solid; yield: 84.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} 2920, 2849, 1606, 1567, 1510, 1305, 1261, 1169, 1021 and 864; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8 Hz, 2H, Ar), 7.40 (s, 1H, C_6H_5-C=CH), 6.87 (d, *J* = 8 Hz, 2H, Ar), 3.96 (t, *J* = 4 Hz, 2H, -OCH_2), 1.81-0.87 (m, 35H, 1×CH_3 16×CH_2); Anal. calcd for $C_{26}H_{42}Br_2O$: C, 58.87; H, 7.98. Found: C, 59.23; H, 8.31.

General procedure for the synthesis of 3-(4-(alkoxy)phenyl)propiolic acid (5a-d)

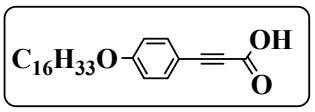
1-(2,2-dibromovinyl)-4-alkoxybenzene (1 eq.) was dissolved in dry THF and cooled to -78° C for 30 mins. 1.6 M n-BuLi in hexanes (2 eq.) was injected slowly and allowed to stir at the same temperature for 1 hr. The reaction mixture was warmed to room temperature and stirred for an hour. Further, the mixture was again cooled to -60 °C, and Dry ice (solid CO_2, 5g) was added and slowly warmed to room temperature. The reaction mixture was poured into water and treated with 2 M HCl till the solution was acidic. It was extracted with EtOAc, and the organic layer was washed with water and dried over Na_2SO_4. The solvent was evaporated, and the crude product was purified *via* silica gel column chromatography using 15% EtOAc-Hexanes. (Yield: 69-71%)



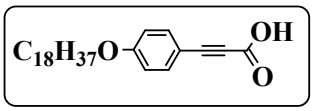
5a: R_f = 0.59 in EtOAc; an off-white solid; yield: 71 %; IR (KBr Pellet): ν_{max} in cm^{-1} 3422, 2926, 2854, 2200, 1673, 1601, 1416, 1253, 1210, 1167, 1016 and 833; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8 Hz, 2H, Ar), 6.88 (d, *J* = 8 Hz, 2H, Ar), 4.05 (t, *J* = 6 Hz, 2H, -OCH_2), 1.81-1.28 (m, 20 H, 10 ×CH_2) and 0.87 (m, 3H, -CH_3); Anal. calcd for $C_{21}H_{30}O_3$: C, 76.33; H, 9.15. Found: C, 76.54; H, 9.31.



5b: R_f = 0.61 in EtOAc; an off-white solid; yield: 69.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} 3420, 2920, 2849, 2197, 1668, 1601, 1415, 1212, 1167, 1008 and 828 ; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8 Hz, 2H, Ar), 6.89 (d, *J* = 8 Hz, 2H, Ar), 4.00 (t, *J* = 8 Hz, 2H, -OCH_2), 1.82-1.28 (m, 24 H, 12 ×CH_2) and 0.90 (t, J = 6 Hz, 3H, -CH_3); Anal. calcd for $C_{23}H_{34}O_3$: C, 77.05; H, 9.56. Found: C, 77.32; H, 9.81.



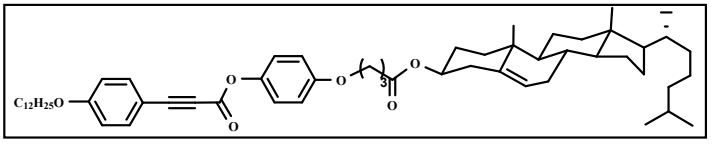
5c: R_f = 0.61 in EtOAc; an off-white solid; yield: 70.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} 3430, 2921, 2850, 2195, 1665, 1600, 1413, 1209, 1164, 1017 and 836; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8 Hz, 2H, Ar), 6.89 (d, *J* = 8 Hz, 2H, Ar), 4.00 (t, *J* = 8 Hz, 2H, -OCH_2), 1.80-1.26 (m, 28 H, 14 ×CH_2) and 0.90 (t, J = 8 Hz, 3H, -CH_3); Anal. calcd for $C_{25}H_{38}O_3$: C, 77.68; H, 9.91. Found: C, 77.83; H, 10.12



5d: R_f = 0.59 in EtOAc; an off-white solid; yield: 71.0 %; IR (KBr Pellet): ν_{max} in cm^{-1} 3443, 2917, 2848, 2196, 1665, 1600, 1509, 1416, 1210, 1167 and 838; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8 Hz, 2H, Ar), 6.89 (d, *J* = 8 Hz, 2H, Ar), 4.00 (t, *J* = 8 Hz, 2H, -OCH_2), 1.82-1.26 (m, 32 H, 16 ×CH_2) and 0.90 (t, J = 8 Hz, 3H, -CH_3); Anal. calcd for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found: C, 78.48; H, 10.41

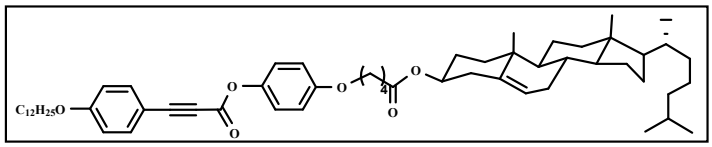
General procedure for the synthesis of cholesteryl 4-(4-((3-(4-(alkyloxy)phenyl)prop -ioloyl)oxy)phenoxy)alkanoate (CPPD-*n*,*m* Series)

3-(4-(alkyloxy)phenyl)propiolic acid (3.5 mmol, 1 eq.) and cholesteryl *n*-(4'-hydroxy phenyl-4-oxy) hexanoates (4.0 mmol, 1 eq.) were dissolved in dry THF and stirred under an inert (nitrogen) atmosphere. DCC (4.7 mmol, 1.2 eq.) and a catalytic amount of DMAP, were added the reaction mixture was stirred at room temperature for 24 hours. The by-product dicylohexyl urea formed as a white precipitate was removed through celite filtration, and the filtrate was concentrated to obtain the crude product. The crude product thus obtained was purified using column chromatography with silica gel (230-400 mesh) as stationary phase and 10% EtOAc-hexanes as an eluent. (Yield: 77-84%)

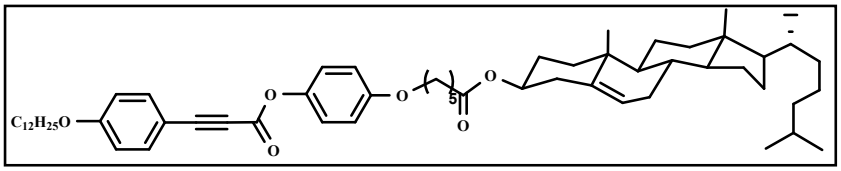


CPPD-3,12: R_f = 0.69 in 30% EtOAc : Hexanes; a white solid; yield: 80.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 2926, 2852, 2196, 1720, 1601, 1502, 1436, 1280, 1185, 1143, 834; UV-Vis: λ_{max} = 298 nm, ε = 1.7 × 10^4 L mol^{-1} cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5 .38 (brd, *J* = 3.8 Hz, 1H, 1 × olefinic), 4.64 - 4.62 (m, 1H, 1 × CHOCO), 4.01 - 3.97 (m, 4H, 2 × OCH_2), 2.34-0.68 (m, 70 H, 6 × CH_3, 23 × CH_2, 6 × CH) ; ^{13}C NMR

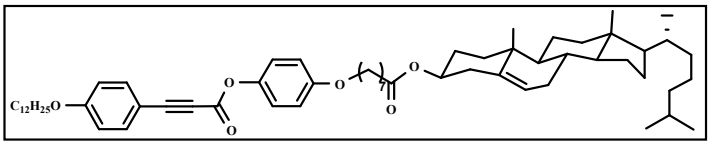
(100 MHz, $CDCl_3$): 172.6, 161.5, 156.9, 153.2, 143.4, 139.7, 134.9, 122.4, 115.2, 114.9, 110.8, 89.9, 79.9, 74.2, 68.3, 67.3, 56.8, 56.2, 50.1, 39.6, 35.8, 31.9, 29.7, 29.6, 29.4, 29.1, 26.0, 22.9, 19.4, 18.8, 11.9; Anal. calcd for $C_{58}H_{84}O_6$: C, 79.41; H, 9.65. Found: C, 79.00; H, 10.00.



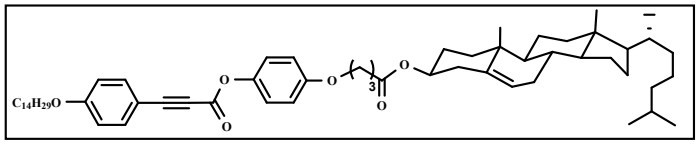
CPPD-4,12: R_f = 0.68 in 30% EtOAc : Hexanes; a white solid; yield: 80.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3433, 2929, 2852, 2198, 1739, 1722, 1602, 1501, 1467, 1380, 1256, 1188, 833 ; UV-Vis: λ_{max} = 297 nm, ε = 2.8 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.63 - 4.62 (m, 1H, 1 × CHOCO), 4.00 - 3.92 (m, 4H, 2 × OCH_2), 2.30-0.66 (m, 72 H, 6 × CH_3, 24 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 173.3, 161.5, 157.2, 153.2, 143.6, 139.8, 135.3, 122.3, 115.2, 114.9, 110.8, 89.8, 79.9, 68.4, 56.8, 56.2, 50.1, 39.8, 29.7, 29.6, 29.4, 26.0, 22.8, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{59}H_{86}O_6$: C, 79.50; H, 9.73. Found: C, 79.12; H, 9.35.



CPPD-5,12: R_f = 0.69 in 30% EtOAc : Hexanes; a white solid; yield: 81.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3432, 2926, 2851, 2204, 1716, 1601, 1505, 1469, 1286, 1188, 835; UV-Vis: λ_{max} = 300 nm, ε = 2.9 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.63 - 4.61 (m, 1H, 1 × CHOCO), 4.00 - 3.93 (m, 4H, 2 × OCH_2), 2.33 - 2.30 (m, 4H, 1 × allylic, -COOCH), 1.57 - 0.67 (m, 70 H, 6 × CH_3, 23 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 173.1, 161.5, 157.1, 153.2, 143.7, 139.7, 135.3, 122.3, 115.2, 114.9, 110.8, 89.9, 79.9, 68.3, 68.1, 56.8, 56.2, 50.1, 39.6, 35.8, 31.9, 29.7, 29.6, 29.4, 29.1, 26.0, 25.7, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{60}H_{88}O_6$: C, 79.60; H, 9.80. Found: C, 79.21; H, 10.09.

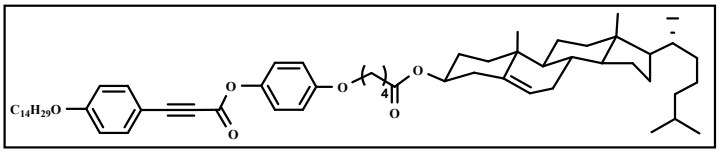


CPPD-7,12: R_f = 0.65 in 30% EtOAc : Hexanes; a white solid; yield: 83.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3448, 2920, 2850, 2215, 1737 1712, 1603, 1510, 1468, 1249, 1184, 829 ; UV-Vis: λ_{max} = 299 nm, ε = 2.0 × 10^4 L mol^{-1} cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.63 - 4.61 (m, 1H, 1 × CHOCO), 4.00 - 3.92 (m, 4H, 2 × OCH_2), 2.32 - 2.26 (m, 4H, 1 × allylic, -COOCH), 1.99 - 0.67 (m, 74 H, 6 × CH_3, 25 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 173.3, 161.5, 157.2, 153.2, 143.6, 139.8, 135.3, 122.3, 115.2, 114.9, 110.8, 89.9, 79.9, 68.4, 56.8, 56.2, 50.1, 39.6, 31.9, 29.7, 29.6, 29.4, 29.0, 26.0, 25.9, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{62}H_{92}O_6$: C, 79.78; H, 9.94. Found: C, 79.44; H, 9.52.

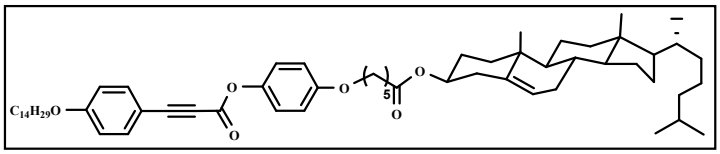


CPPD-3,14: R_f = 0.67 in 30% EtOAc : Hexanes; a white solid; yield: 82.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3435, 2926, 2851, 2197, 1722,

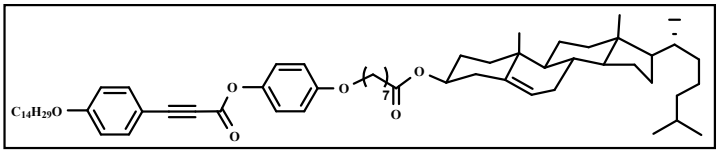
1602, 1502, 1288, 1185, 834 ; UV-Vis: λ_{max} = 295 nm, ε = 2.7 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.91-6.88 (m, 4H, Ar), 5.37 (brs, 1H, 1 × olefinic), 4.63 - 4.60 (m, 1H, 1 × CHOCO), 3.99 - 3.93 (m, 4H, 2 × OCH_2), 2.51- 2.31 (m, 4H, 1 × allylic, -COOCH), 2.12- 0.68 (m, 70 H, 6 × CH_3, 23 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 172.6, 161.5, 157.0, 153.2, 143.8, 139.7, 135.3, 122.4, 115.2, 114.9, 110.8, 89.9, 79.9, 68.4, 56.8, 56.2, 50.1, 39.6, 29.7, 29.6, 29.4, 26.0, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{60}H_{88}O_6$: C, 79.60; H, 9.80. Found: C, 79.31; H, 9.45.



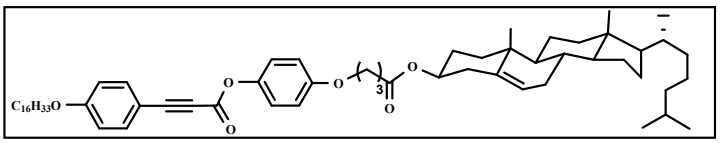
CPPD-4,14: R_f = 0.65 in 30% EtOAc : Hexanes; a white solid; yield: 78.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3447, 2924, 2852, 2198, 1734, 1722, 1603, 1505, 1467, 1286, 1187, 834 ; UV-Vis: λ_{max} = 301 nm, ε = 2.6 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.65 - 4.60 (m, 1H, 1 × CHOCO), 4.00 - 3.96 (m, 4H, 2 × OCH_2), 2.47- 2.31 (m, 4H, 1 × allylic, -COOCH), 2.02- 0.67 (m, 72 H, 6 × CH_3, 24 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 172.9, 161.5, 157.1, 153.2, 143.7, 139.7, 135.3, 122.4, 115.2, 114.9, 110.3, 89.9, 79.9, 68.4, 67.9, 56.8, 56.2, 50.1, 39.6, 29.7, 29.6, 29.4, 26.0, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{61}H_{90}O_6$: C, 79.69; H, 9.87. Found: C, 79.77; H, 9.58.



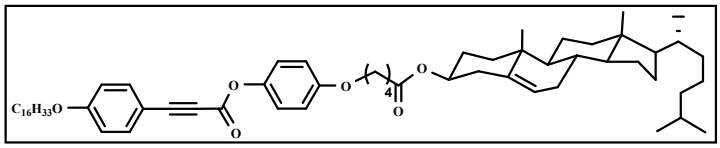
CPPD-5,14: R_f = 0.66 in 30% EtOAc : Hexanes; a white solid; yield: 79.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3433, 2926, 2851, 2206, 1724, 1601, 1506, 1287, 1164, 833 ; UV-Vis: λ_{max} = 297 nm, ε = 2.7 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.63 - 4.62 (m, 1H, 1 × CHOCO), 4.00 - 3.93 (m, 4H, 2 × OCH_2), 2.33 - 2.30 (m, 4H, 1 × allylic, -COOCH), 1.86 - 0.67 (m, 74 H, 6 × CH_3, 25 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 173.1, 161.5, 157.1, 153.2, 143.7, 139.8, 135.3, 122.7, 122.3, 114.9, 110.8, 89.9, 80.2, 68.3, 68.1, 56.7, 56.2, 50.1, 39.6, 32.9, 32.0, 29.8, 29.7, 29.6, 29.4, 29.1, 28.1, 26.0, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{62}H_{92}O_6$: C, 79.78; H, 9.94. Found: C, 79.52; H, 9.54.



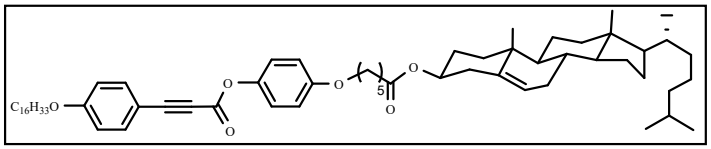
CPPD-7,14: R_f = 0.68 in 30% EtOAc : Hexanes; a white solid; yield: 77.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3431, 3826, 2852, 2204, 1723, 1602, 1506, 1468, 1290, 1187, 833 ; UV-Vis: λ_{max} = 298 nm, ε = 2.5 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.63 - 4.61 (m, 1H, 1 × CHOCO), 3.99 - 3.93 (m, 4H, 2 × OCH_2), 2.33 - 2.17 (m, 4H, 1 × allylic, -COOCH), 1.56 - 0.68 (m, 78 H, 6 × CH_3, 27 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 172.6, 161.5, 156.9, 153.1, 143.8, 139.7, 135.2, 122.3, 115.2, 114.9, 110.8, 89.9, 79.9, 68.3, 67.3, 56.7, 56.2, 50.1, 39.6, 31.9, 29.6, 29.4, 29.1, 28.2, 28.0, 27.8, 25.9, 24.7, 22.8, 22.6, 19.3, 18.7, 10.2; Anal. calcd for $C_{64}H_{96}O_6$: C, 79.95; H, 10.06. Found: C, 79.48; H, 9.78.



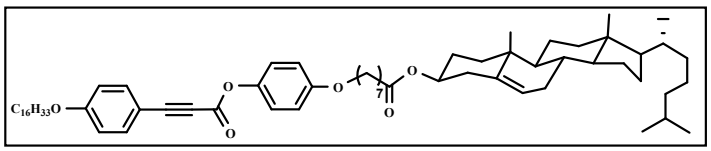
CPPD-3,16: R_f = 0.71 in 30% EtOAc : Hexanes; a white solid; yield: 84.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3430, 3824, 2846, 2201, 1727, 1602, 1501, 1467, 1294, 1185, 831 ; UV-Vis: λ_{max} = 300 nm, ε = 1.3 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.91-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.63 - 4.61 (m, 1H, 1 × CHOCO), 4.01 - 3.97 (m, 4H, 2 × OCH_2), 2.51- 2.31 (m, 4H, 1 × allylic, -COOCH), 2.12- 0.68 (m, 74 H, 6 × CH_3, 23 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 172.6, 161.5, 156.9, 153.2, 143.8, 139.7, 135.3, 122.8, 115.2, 115.0, 110.8, 89.9, 79.9, 68.3, 67.2, 56.8, 50.1, 39.9, 29.8, 29.6, 26.4, 26.0, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{62}H_{92}O_6$: C, 79.78; H, 9.94. Found: C, 79.37; H, 9.58.



CPPD-4,16: R_f = 0.70 in 30% EtOAc : Hexanes; a white solid; yield: 80.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3443, 2925, 2852, 2198, 1724, 1602, 1505, 1468, 1285, 1187, 834 ; UV-Vis: λ_{max} = 298 nm, ε = 2.2 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.37 (brs, 1H, 1 × olefinic), 4.63 - 4.61 (m, 1H, 1 × CHOCO), 4.00 - 3.96 (m, 4H, 2 × OCH_2), 2.39-2.31 (m, 4H, 1 × allylic, -COOCH), 2.02- 0.68 (m, 76 H, 6 × CH_3, 26 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 172.9, 161.5, 157.1, 153.2, 143.7, 139.7, 135.3, 122.3, 115.2, 114.9, 110.8, 89.9, 79.9, 68.3, 67.9, 56.8, 56.2, 50.1, 39.6, 29.8, 29.7, 29.6, 29.4, 26.0, 22.9, 22.6, 19.4, 18.9, 11.9; Anal. calcd for $C_{63}H_{94}O_6$: C, 79.87; H, 10.00. Found: C, 71.04; H, 10.83.

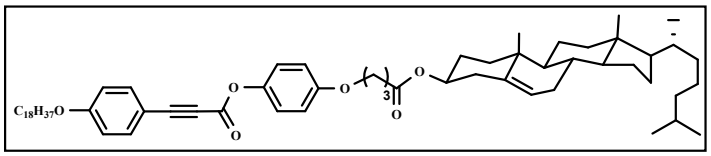


CPPD-5,16: R_f = 0.67 in 30% EtOAc : Hexanes; a white solid; yield: 77.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3432, 2924, 2850, 2208, 1722, 1601, 1505, 1469, 1286, 1196, 833 ; UV-Vis: λ_{max} = 296 nm, ε = 3.5 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.63 - 4.61 (m, 1H, 1 × CHOCO), 4.00 - 3.93 (m, 4H, 2 × OCH_2), 2.32 - 2.30 (m, 4H, 1 × allylic, -COOCH), 1.55 - 0.68 (m, 78 H, 6 × CH_3, 27 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 173.1, 161.5, 157.1, 153.2, 143.7, 139.8, 135.3, 122.7, 122.4, 114.9, 110.8, 89.9, 79.9, 68.4, 68.1, 50.1, 39.6, 32.0, 29.8, 29.7, 29.6, 29.4, 26.0, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{64}H_{96}O_6$: C, 79.95; H, 10.06. Found: C, 79.63; H, 9.63.

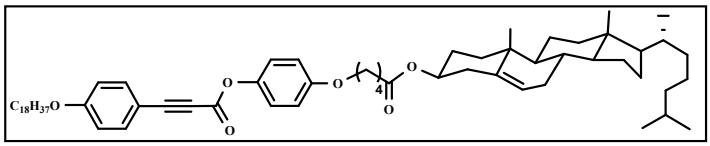


CPPD-7,16: R_f = 0.68 in 30% EtOAc : Hexanes; a white solid; yield: 79.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3447, 2926, 2852, 2198, 1733, 1716, 1601, 1504, 1468, 1255, 1185, 833 ; UV-Vis: λ_{max} = 295 nm, ε = 2.8 × 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.10 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.65 - 4.62 (m, 1H, 1 × CHOCO), 4.00 - 3.97 (m, 4H, 2 × OCH_2), 2.49 - 2.41 (m, 4H, 1 × allylic, -COOCH), 1.55 - 0.68 (m, 82 H, 6 × CH_3, 29 × CH_2, 6 × CH); ^{13}C

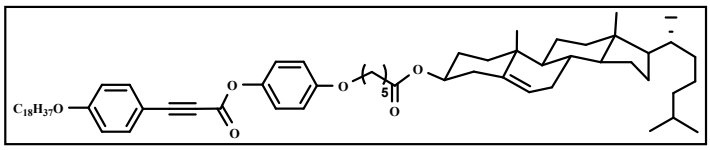
NMR (100 MHz, $CDCl_3$): 172.6, 161.5, 156.9, 153.1, 143.8, 139.7, 135.2, 122.3, 115.2, 114.9, 110.8, 89.9, 79.9, 68.3, 67.3, 56.7, 56.2, 50.1, 39.6, 31.9, 29.6, 29.4, 29.1, 28.2, 28.0, 27.8, 25.9, 24.7, 22.8, 22.6, 19.3, 18.7, 10.2; Anal. calcd for $C_{66}H_{100}O_6$: C, 80.11; H, 10.19. Found: C, 79.78; H, 10.01.



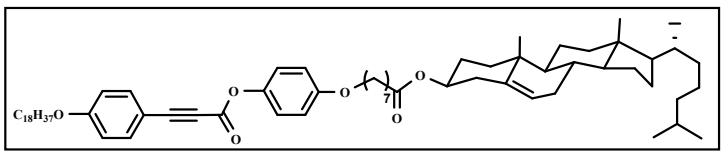
CPPD-3,18: R_f = 0.69 in 30% EtOAc : Hexanes; a white solid; yield: 83.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3436, 2924, 2851, 2198, 1721, 1602, 1503, 1470, 1280, 1185, 834; UV-Vis: λ_{max} = 297 nm, $\varepsilon = 3.0 \times 10^4$ L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.10 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.64 - 4.61 (m, 1H, 1 × CHOCO), 4.00 - 3.96 (m, 4H, 2 × OCH_2), 2.35 - 2.28 (m, 4H, 1 × allylic, -COOCH), 1.83 - 0.68 (m, 78 H, 6 × CH_3, 27 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 173.3, 161.5, 157.2, 153.2, 143.6, 135.2, 122.6, 122.3, 115.2, 114.9, 110.8, 89.6, 79.9, 68.4, 68.3, 56.7, 56.2, 50.1, 39.6, 31.9, 29.7, 29.6, 29.4, 29.0, 28.3, 26.0, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{64}H_{96}O_6$: C, 80.11; H, 10.19. Found: C, 80.11; H, 9.89. MS(FAB^+): m/z Calcd. for $C_{64}H_{96}O_6$ (M+1): 961.44; Found: 962.1.



CPPD-4,18: R_f = 0.70 in 30% EtOAc : Hexanes; a white solid; yield: 81.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}; 3433, 2923, 2852, 2194, 1721, 1601, 1504, 1469, 1284, 1186, 835 ; UV-Vis: λ_{max} = 299 nm, $\varepsilon = 2.6 \times 10^4$ L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.37 (brs, 1H, 1 × olefinic), 4.64 - 4.60 (m, 1H, 1 × CHOCO), 4.00 - 3.92 (m, 4H, 2 × OCH_2), 2.32- 2.26 (m, 4H, 1 × allylic, -COOCH), 2.02- 0.67 (m, 80 H, 6 × CH_3, 28 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 173.3, 161.5, 157.2, 153.2, 143.6, 139.8, 135.3, 122.3, 115.2, 114.9, 110.8, 89.9, 79.9, 68.3, 56.8, 56.2, 50.1, 39.6, 29.8, 29.7, 29.6, 29.4, 26.0, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{65}H_{98}O_6$: C, 80.03; H, 10.13. Found: C, 79.69; H, 9.81.



CPPD-5,18: R_f = 0.71 in 30% EtOAc : Hexanes; a white solid; yield: 82.0 %; IR (KBr Pellet): ν_{max} in cm^{-1}: 3428, 2922, 2851, 2205, 1720, 1601, 1504, 1469, 1285, 1187, 837; UV-Vis: λ_{max} = 299 nm, $\varepsilon = 2.0 \times 10^4$ L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.64 - 4.60 (m, 1H, 1 × CHOCO), 4.00 - 3.93 (m, 4H, 2 × OCH_2), 2.33 - 2.27 (m, 4H, 1 × allylic, -COOCH), 2.02- 0.68 (m, 82 H, 6 × CH_3, 29 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$): 173.1, 161.5, 157.2, 153.2, 143.7, 139.8, 135.3, 122.3, 115.2, 114.9, 110.8, 89.9, 79.8, 68.4, 68.1, 56.8, 56.2, 50.1, 39.6, 29.8, 29.7, 29.6, 29.4, 26.0, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{66}H_{100}O_6$: C, 80.11; H, 10.19. Found: C, 79.81; H, 9.98.



CPPD-7,18: R_f = 0.70 in 30% EtOAc : Hexanes; a white solid; yield: 80.0 %; IR (KBr Pellet):

ν_{max} in cm^{-1}: 3426, 2928, 2847, 2208, 1724, 1604, 1501, 1473, 1286, 1185, 835; UV-Vis: λ_{max} = 300 nm, $\varepsilon = 3.1 \times 10^4$ L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, 2H, *J* = 8 Hz, Ar), 7.09 (d, 2H, *J* = 8 Hz, Ar), 6.90-6.88 (m, 4H, Ar), 5.38 (brs, 1H, 1 × olefinic), 4.62 - 4.61 (m, 1H, 1 × CHOCO), 4.00 - 3.92 (m, 4H, 2 × OCH_2), 2.32 - 2.26 (m, 4H, 1 × allylic, -COOCH), 2.00 - 0.67 (m, 86 H, 6 × CH_3, 31 × CH_2, 6 × CH); ^{13}C NMR (100 MHz, $CDCl_3$); 172.6, 161.5, 156.9, 153.2, 143.8, 139.7, 135.3, 122.8, 122.4, 115.2, 110.8, 89.9, 79.9, 68.3, 67.2, 50.1, 32.0, 29.7, 29.6, 29.4, 26.0, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $C_{68}H_{104}O_6$: C, 80.26; H, 10.30. Found: C, 79.97; H, 10.0

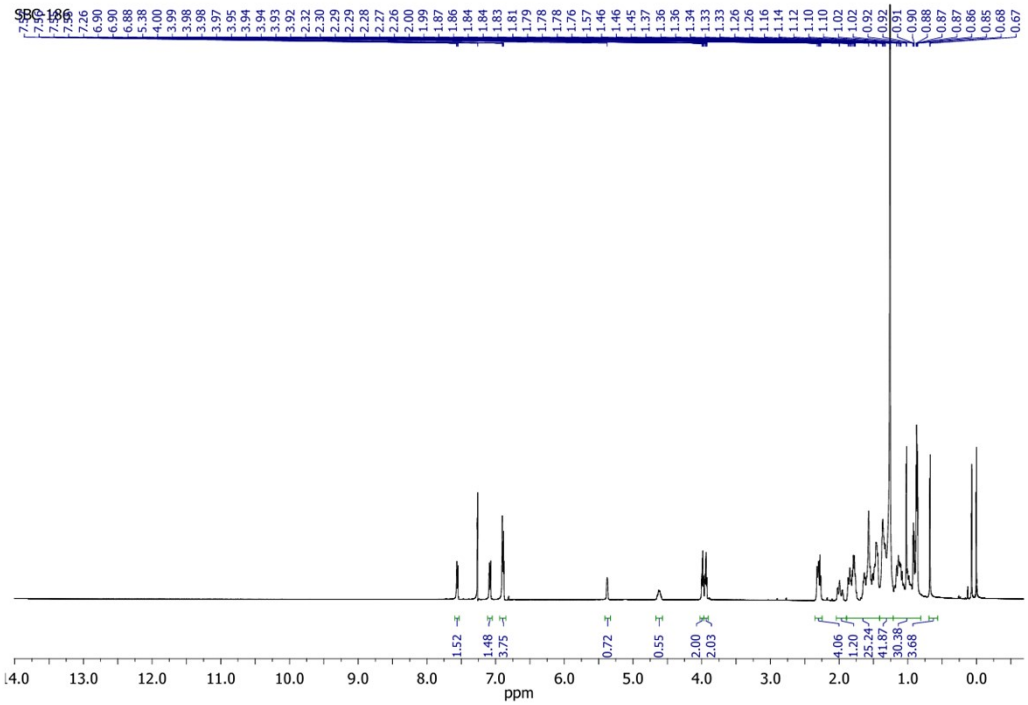


Figure S1: 1H NMR Spectrum of the dimer CPPD-3,12

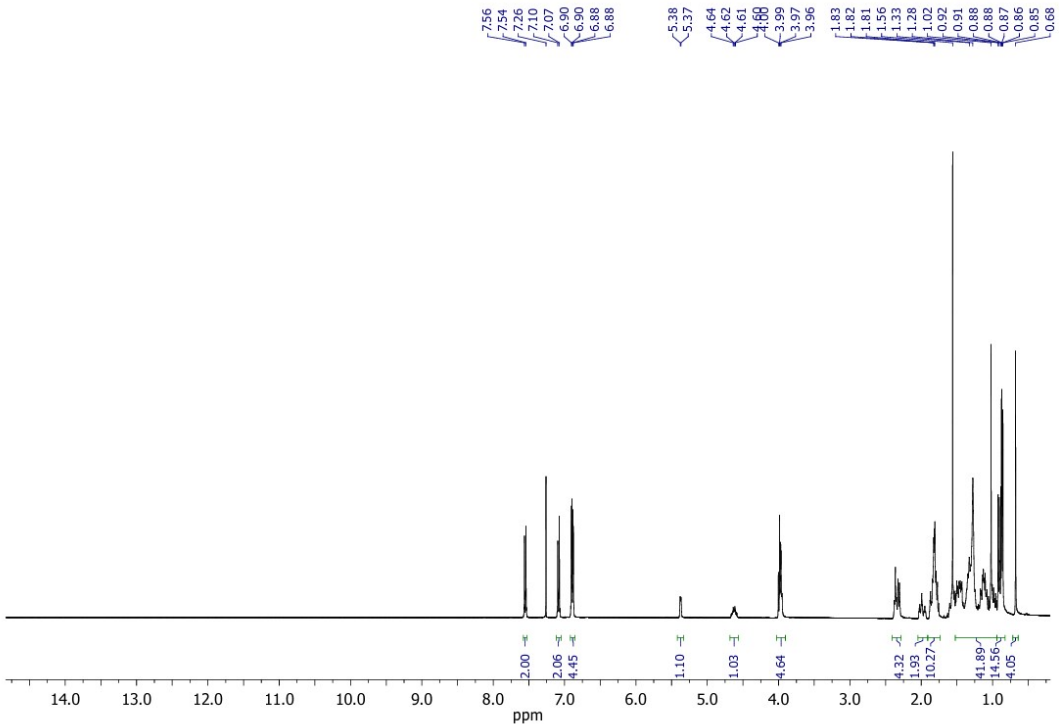


Figure S2: 1H NMR Spectrum of the dimer CPPD-3,14

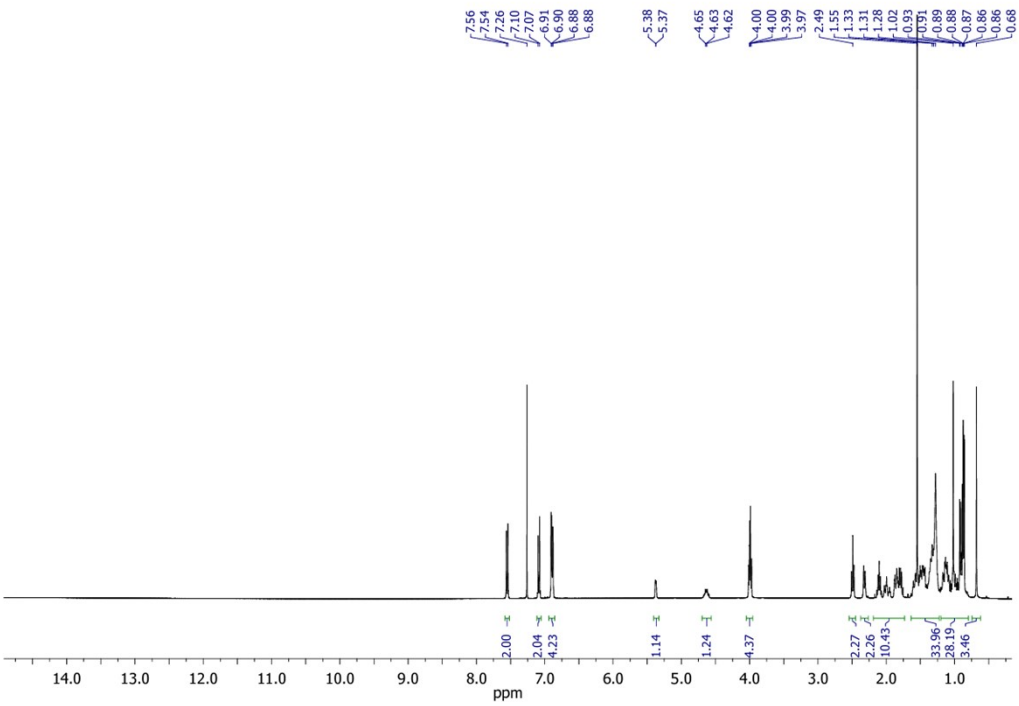


Figure S3: 1H NMR Spectrum of the dimer CPPD-3,16

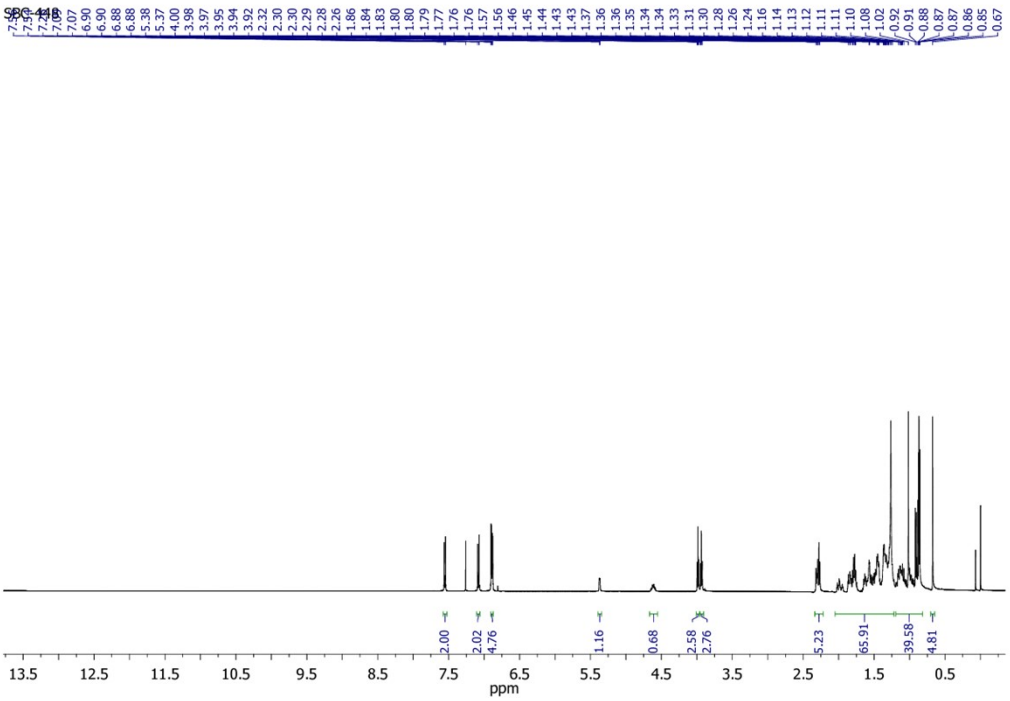


Figure S4: 1H NMR Spectrum of the dimer CPPD-3,18

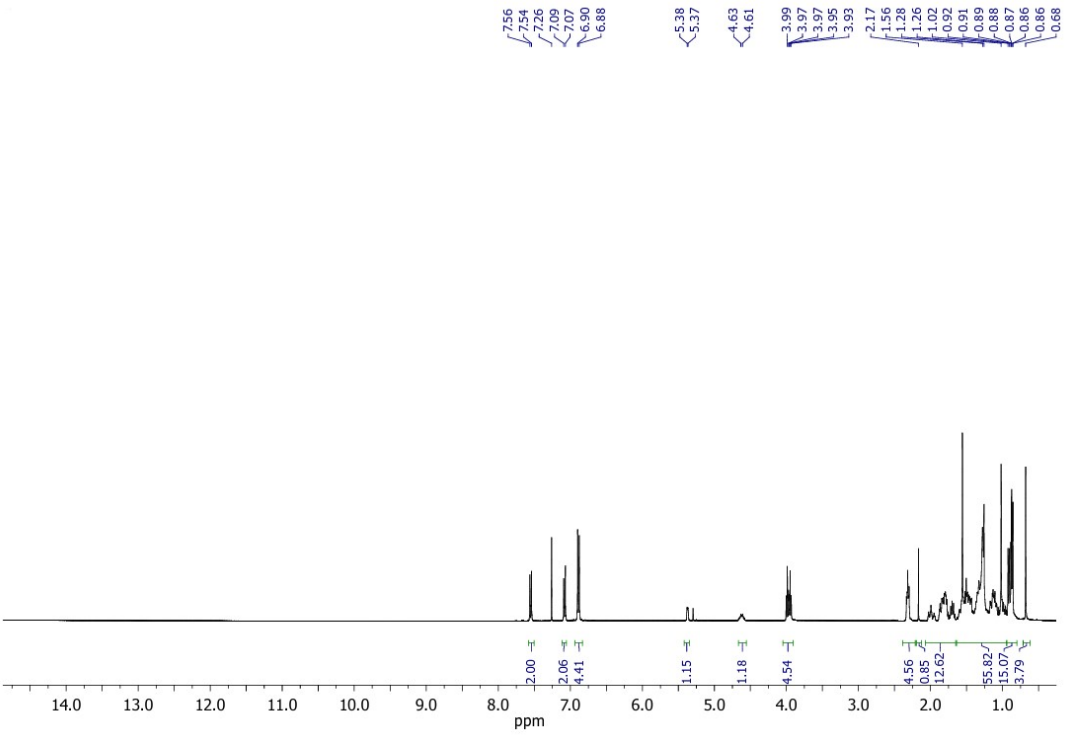


Figure S5: 1H NMR Spectrum of the dimer CPPD-4,12

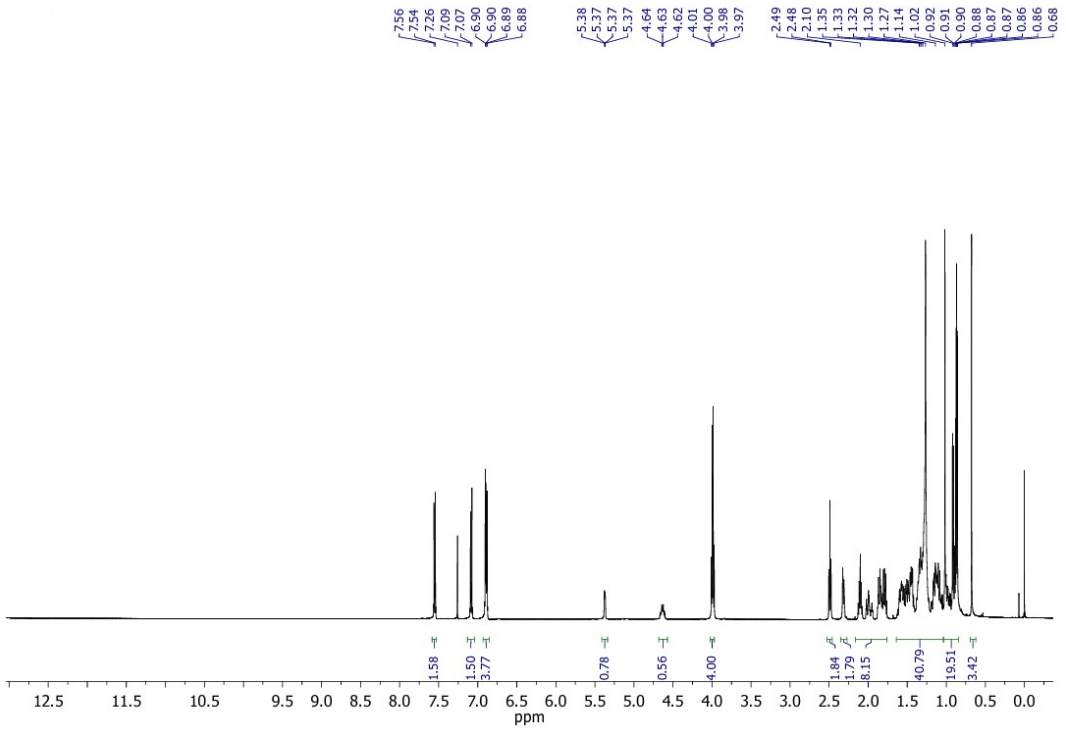


Figure S6: 1H NMR Spectrum of the dimer CPPD-4,14

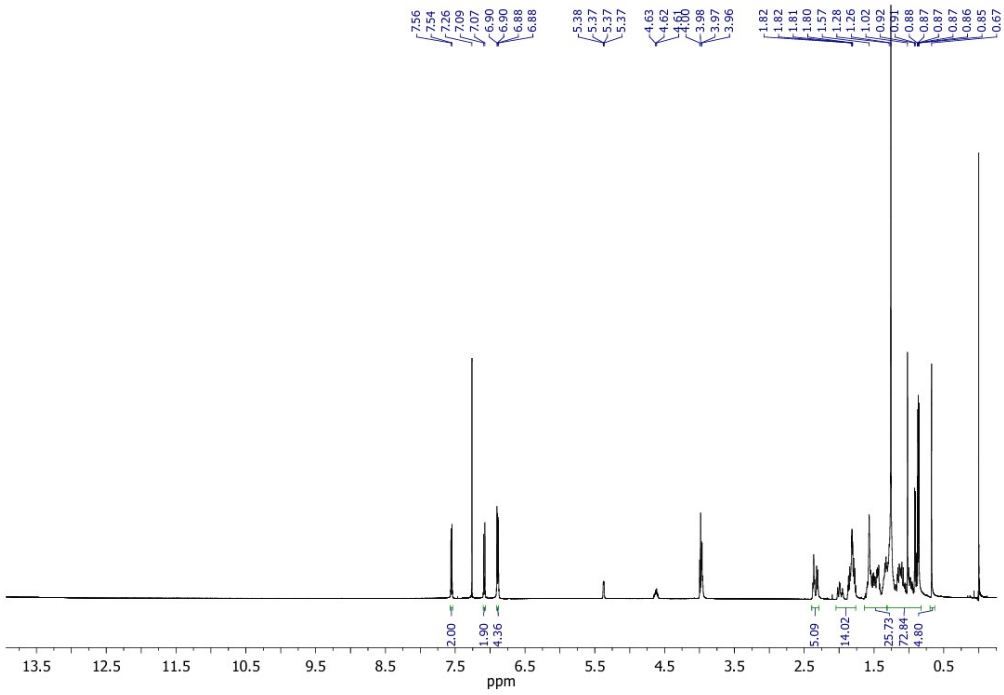


Figure S7: 1H NMR Spectrum of the dimer CPPD-4,16

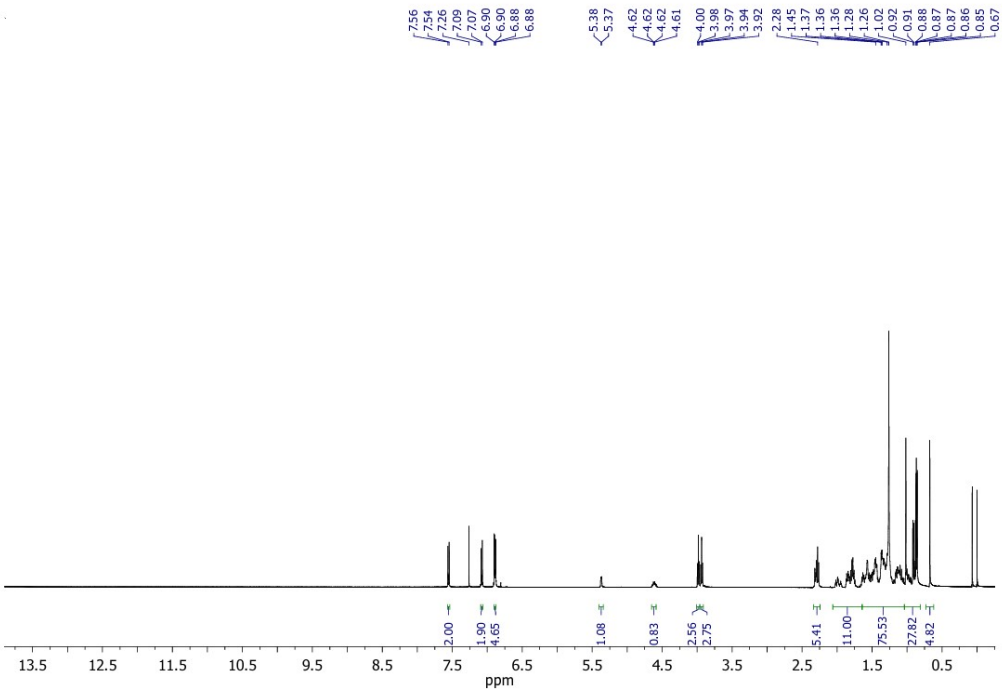


Figure S8: 1H NMR Spectrum of the dimer CPPD-4,14

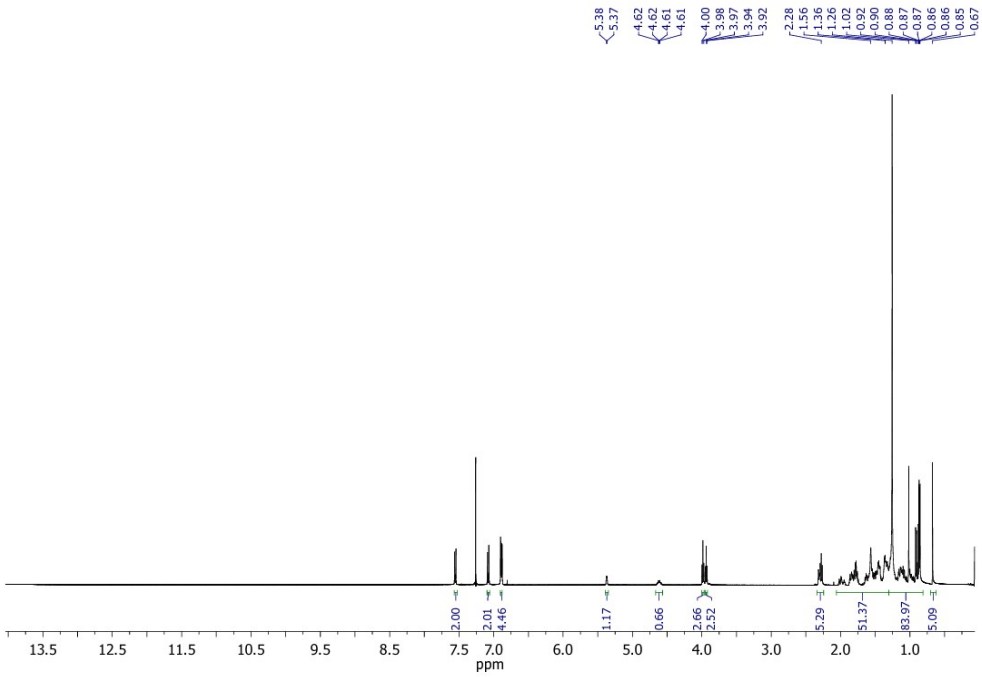


Figure S9: 1H NMR Spectrum of the dimer CPPD-5,12

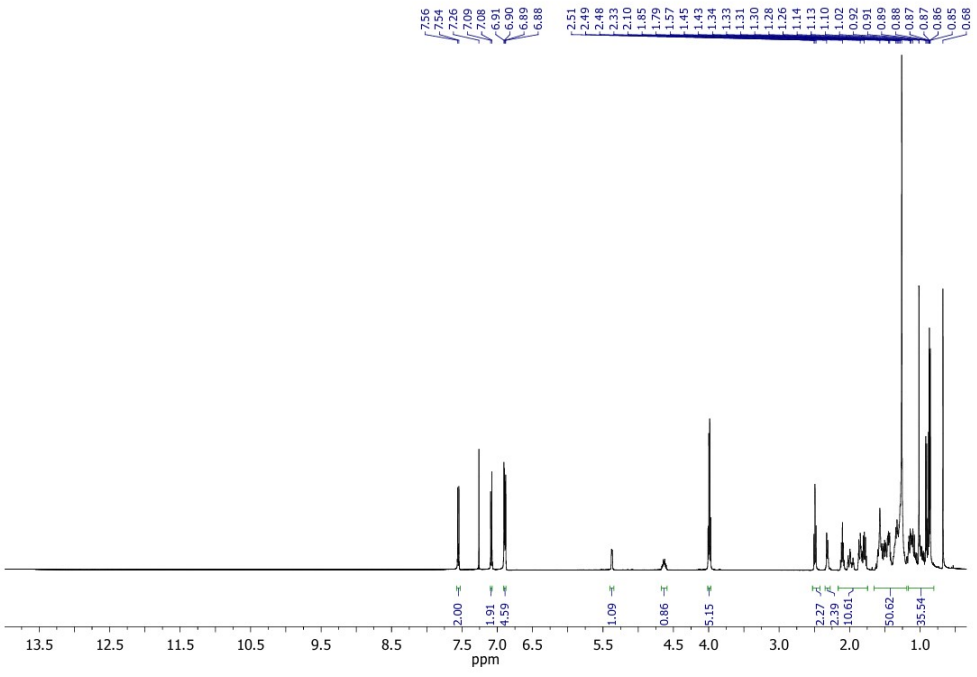


Figure S10: 1H NMR Spectrum of the dimer CPPD-5,14

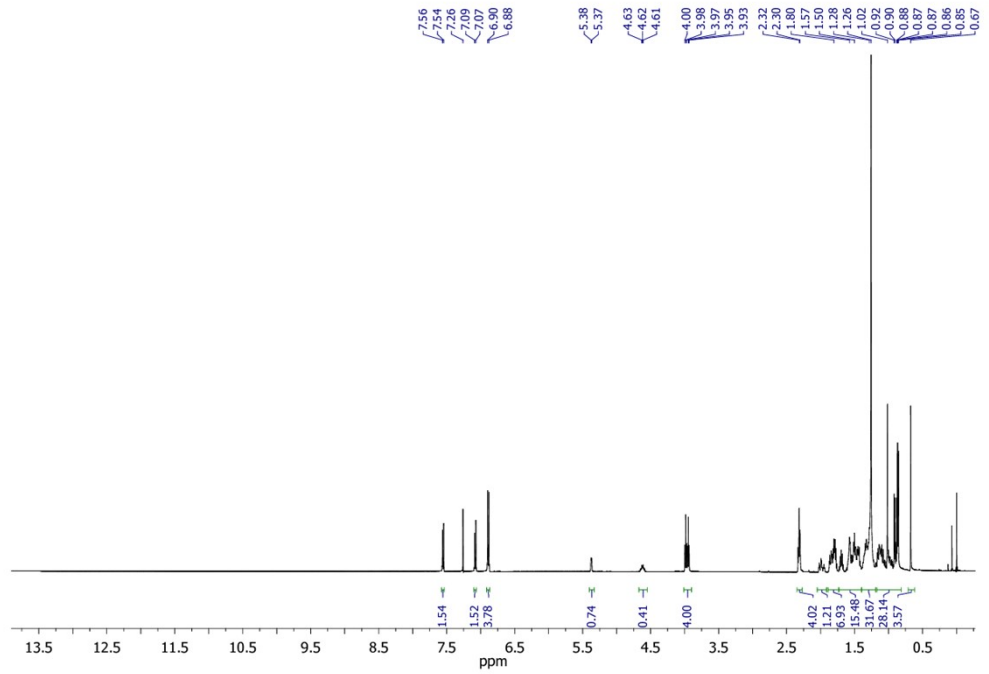


Figure S11: 1H NMR Spectrum of the dimer CPPD-5,16

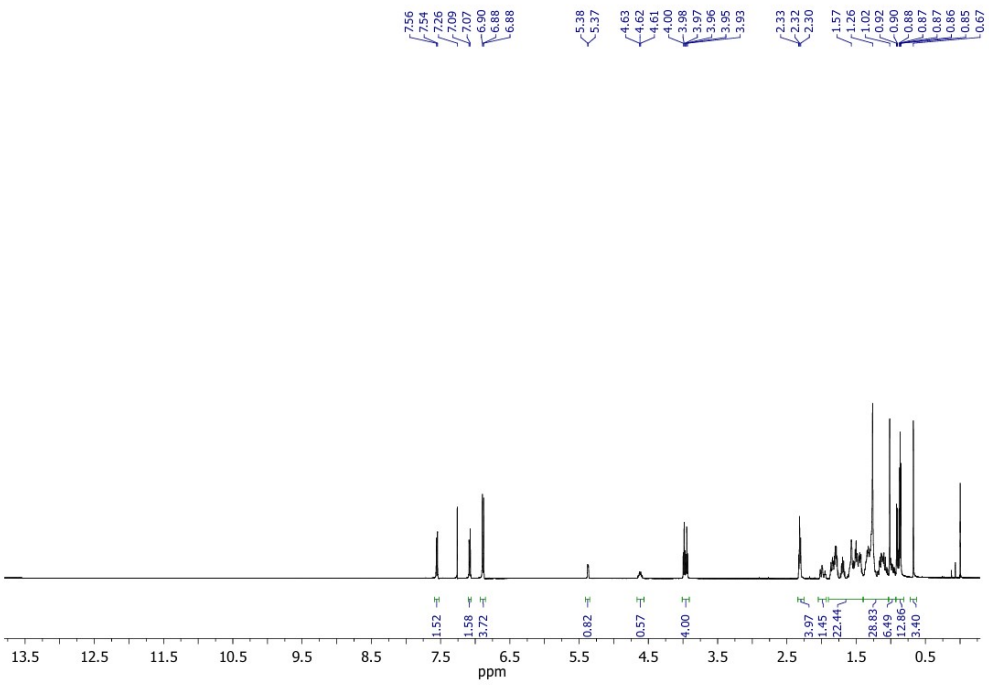


Figure S12: 1H NMR Spectrum of the dimer CPPD-5,18

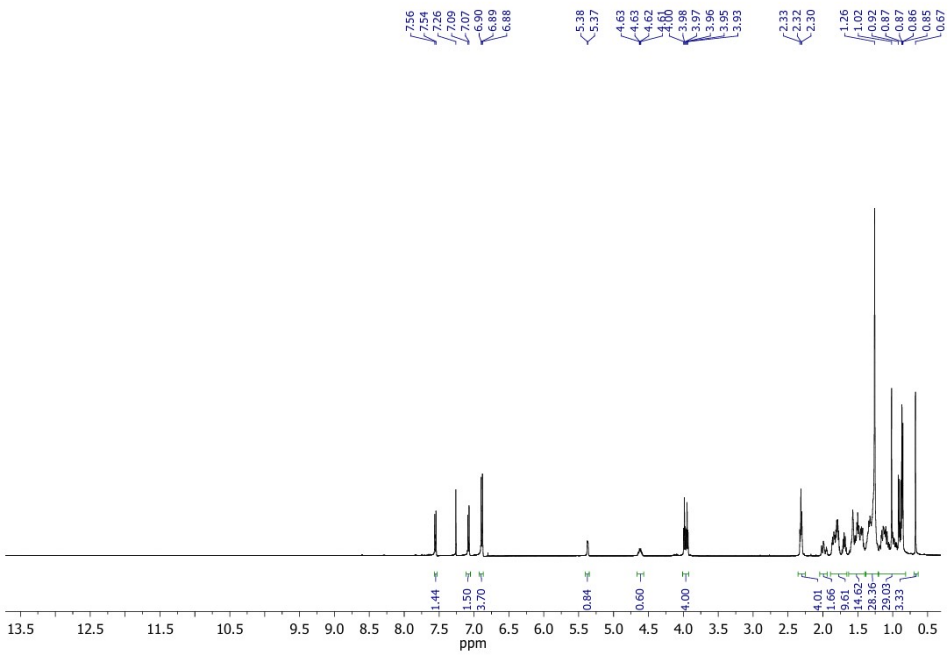


Figure S13: 1H NMR Spectrum of the dimer CPPD-7,12

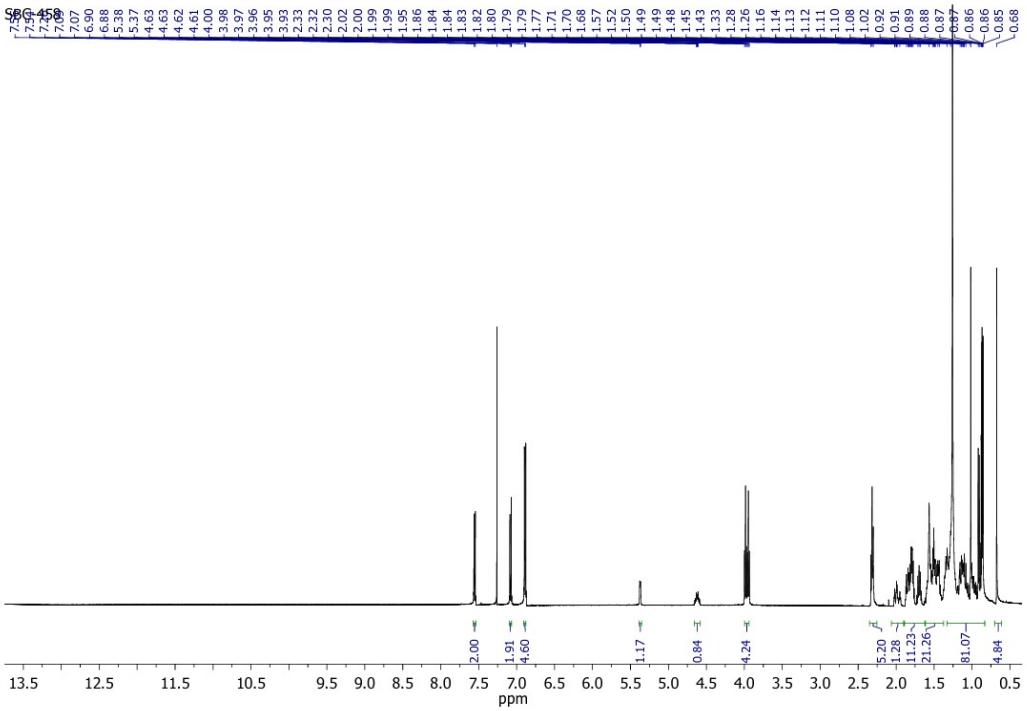


Figure S14: 1H NMR Spectrum of the dimer CPPD-7,14

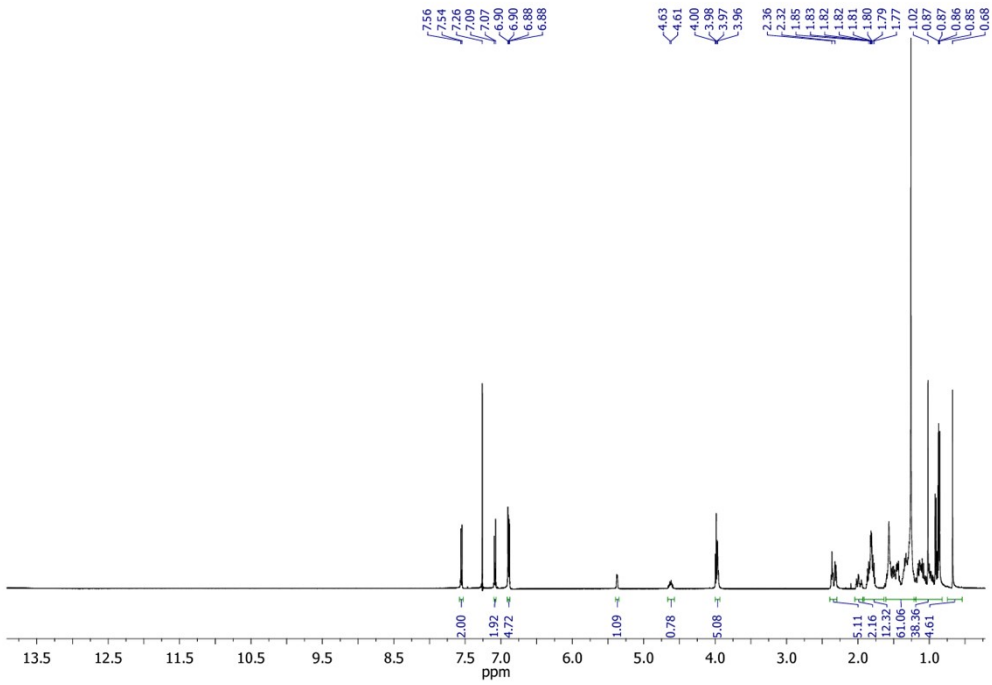


Figure S15: 1H NMR Spectrum of the dimer CPPD-7,16

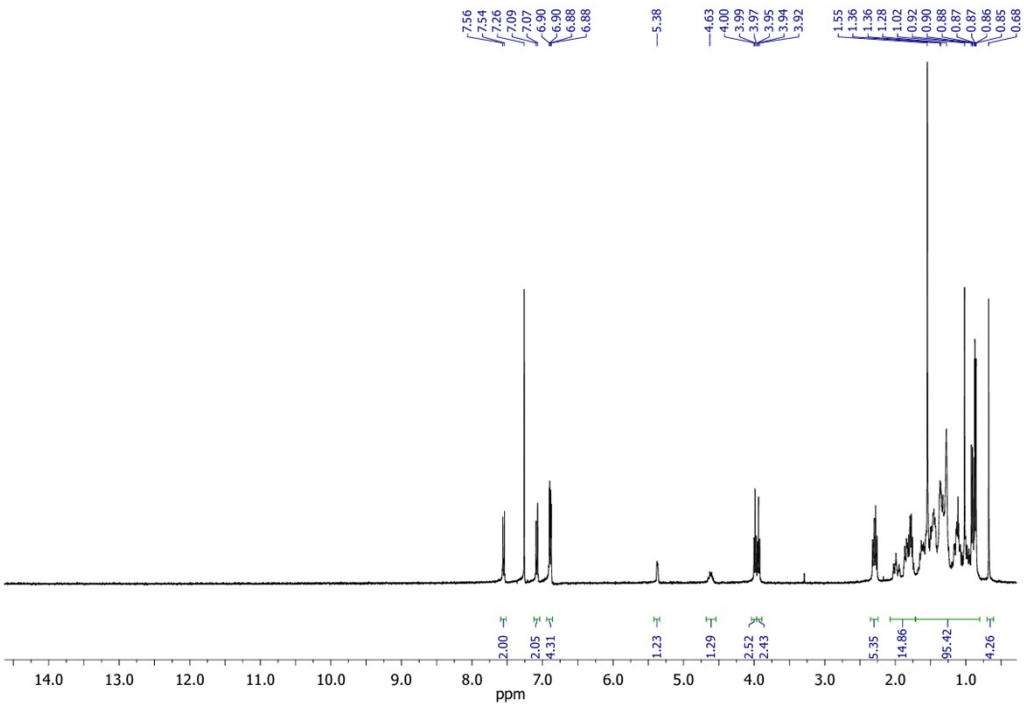


Figure S16: 1H NMR Spectrum of the dimer CPPD-7,18

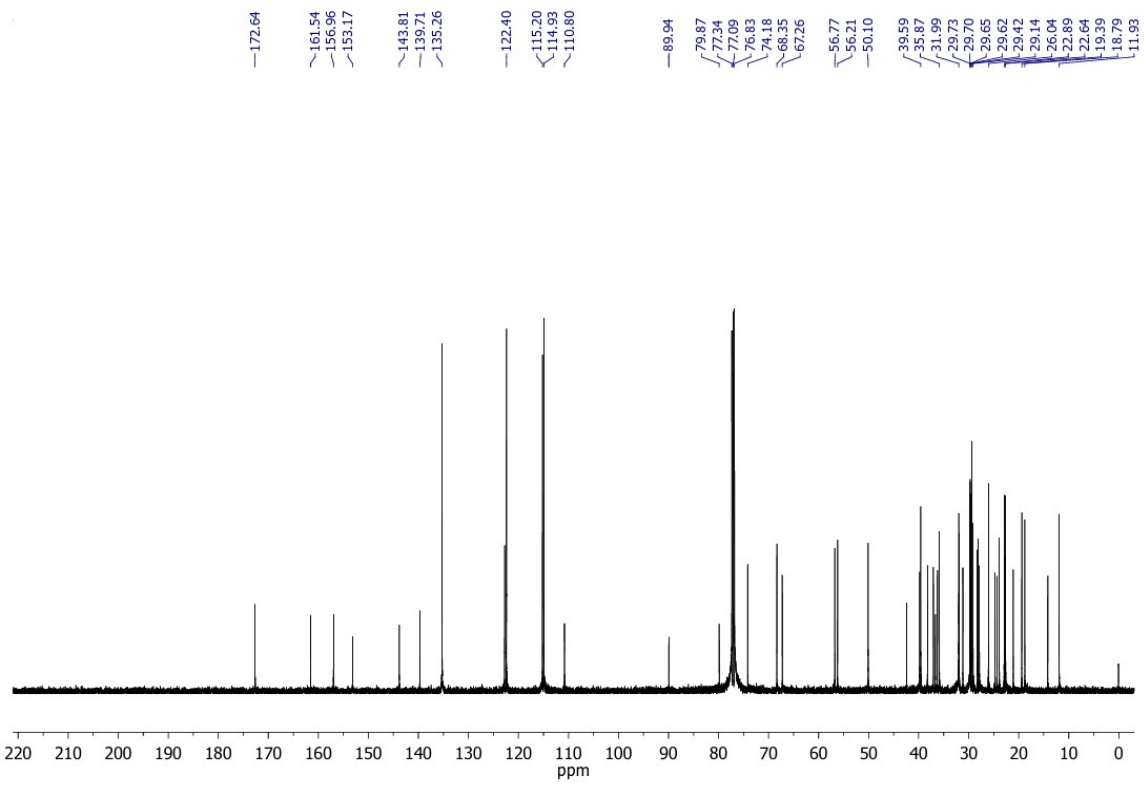


Figure S17: 13C NMR Spectrum of the dimer CPPD-3,12

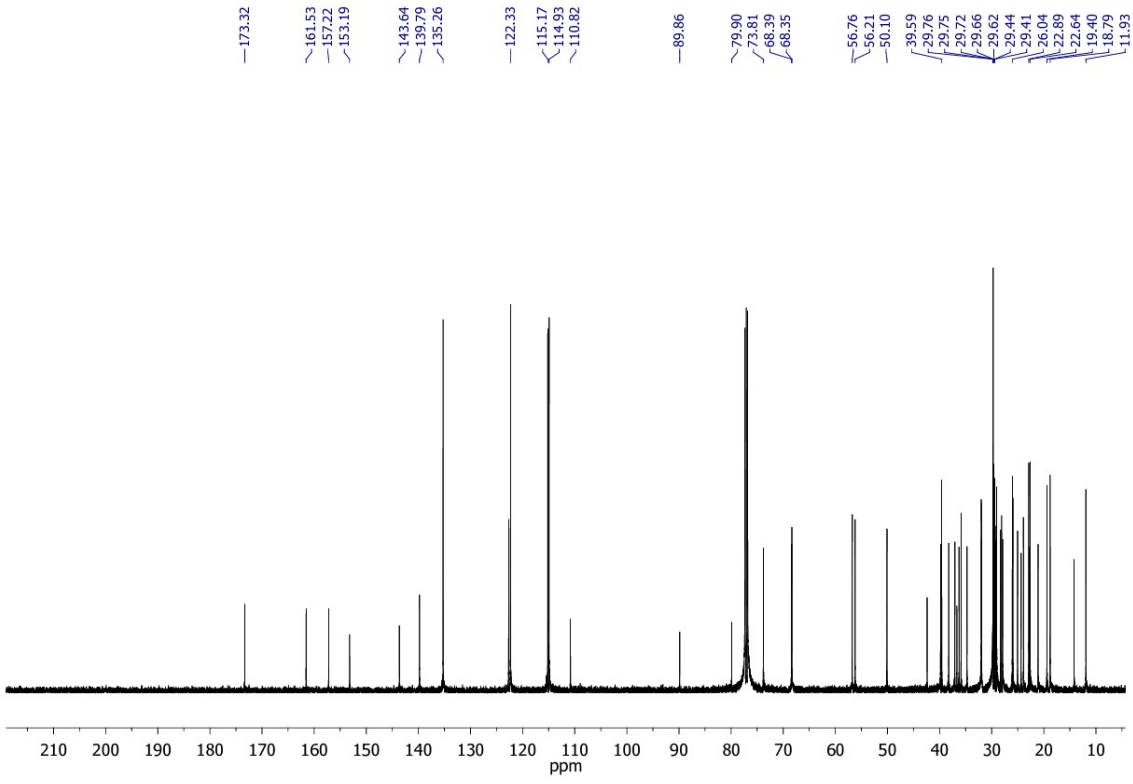


Figure S18: 13C NMR Spectrum of the dimer CPPD-4,12

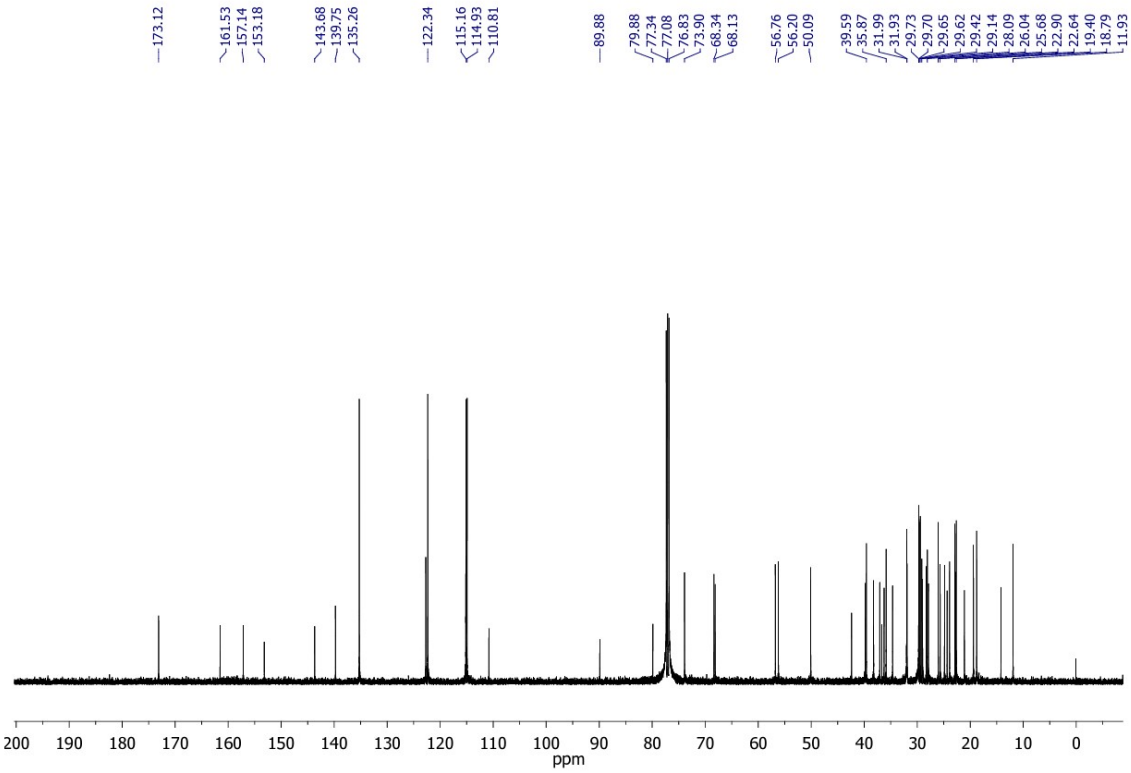


Figure S19: 13C NMR Spectrum of the dimer CPPD-5,12

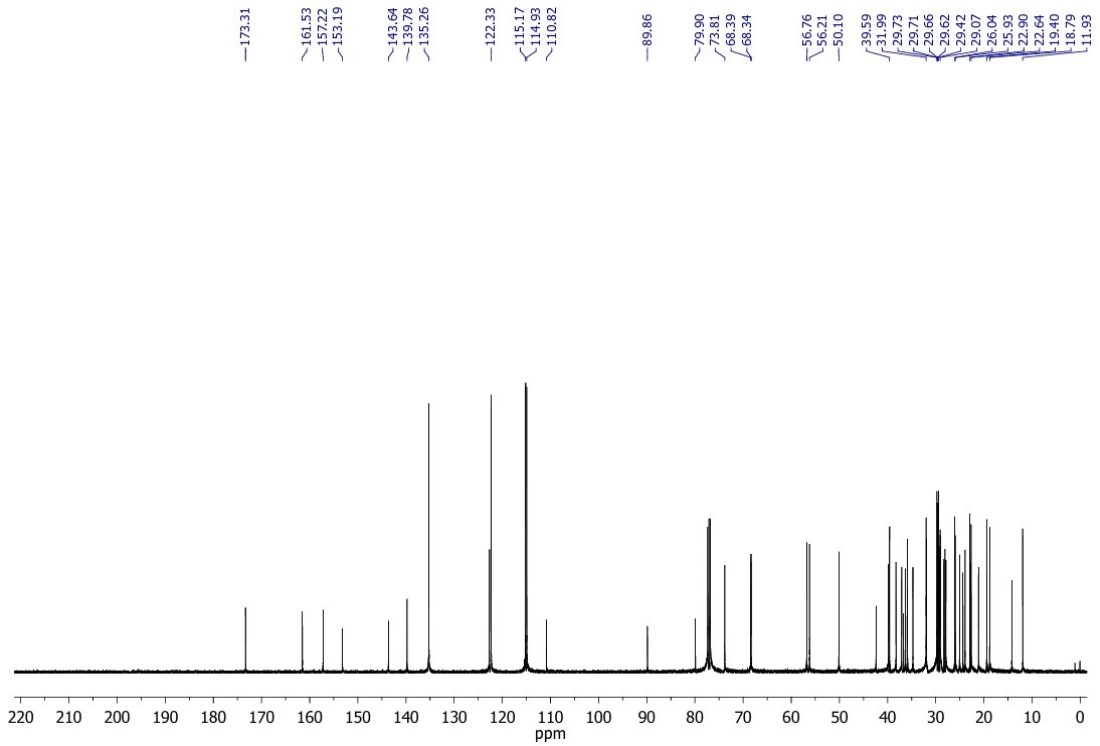


Figure S20: 13C NMR Spectrum of the dimer CPPD-7,12

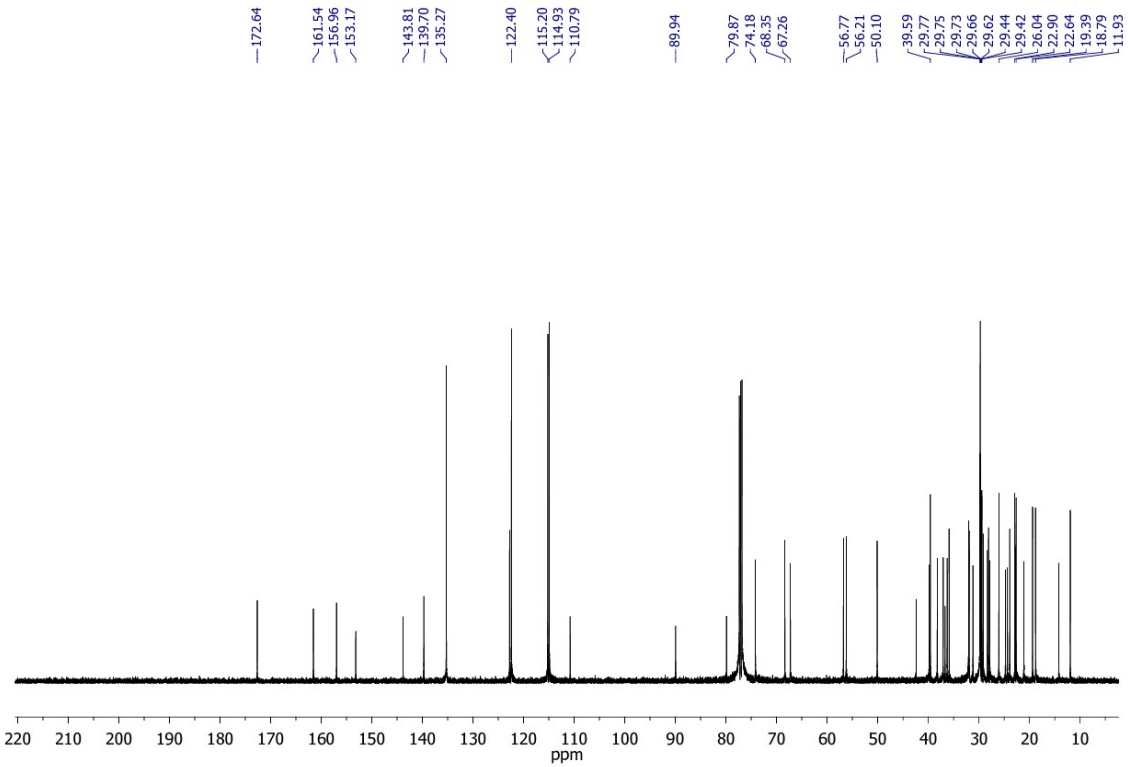


Figure S21: 13C NMR Spectrum of the dimer CPPD-3,14

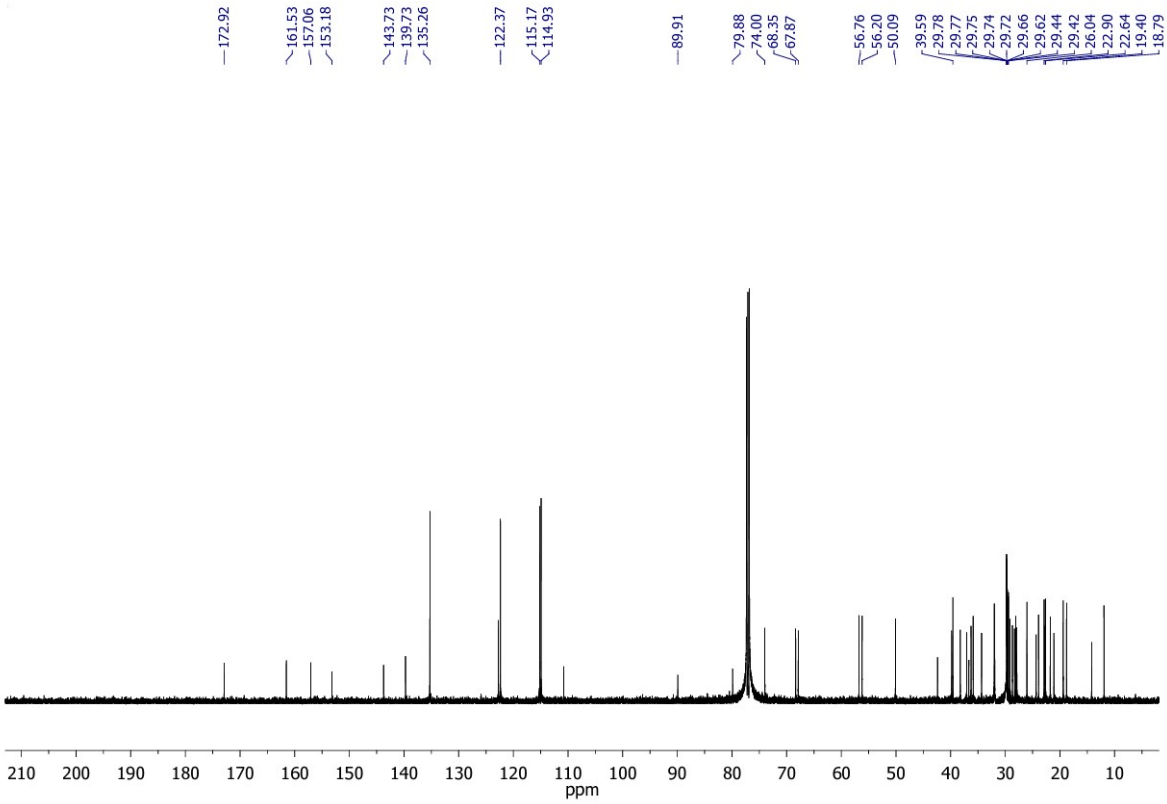


Figure S22: 13C NMR Spectrum of the dimer CPPD-4,14

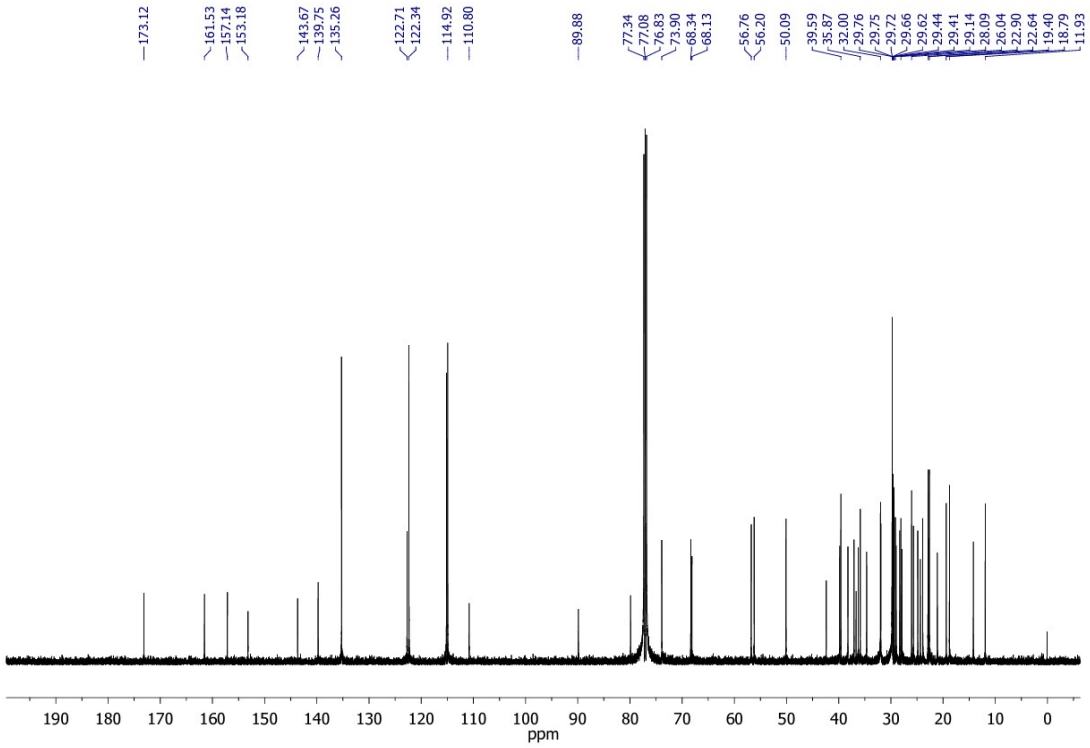


Figure S23: 13C NMR Spectrum of the dimer CPPD-5,14

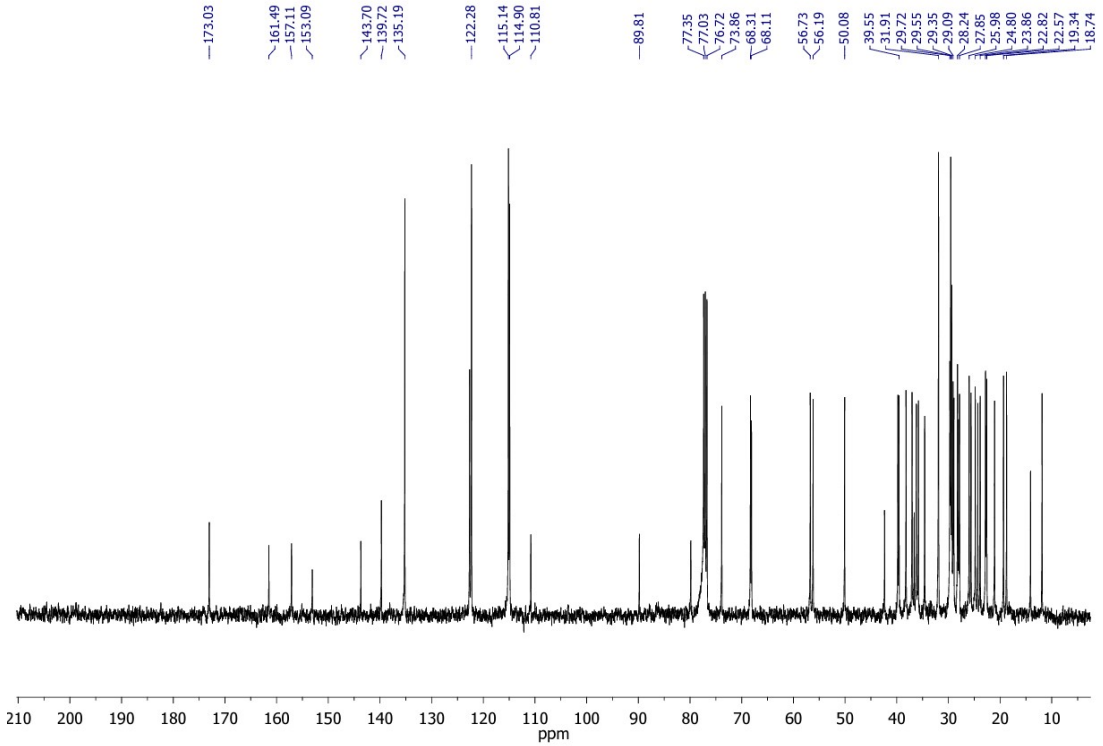


Figure S24: 13C NMR Spectrum of the dimer CPPD-7,14

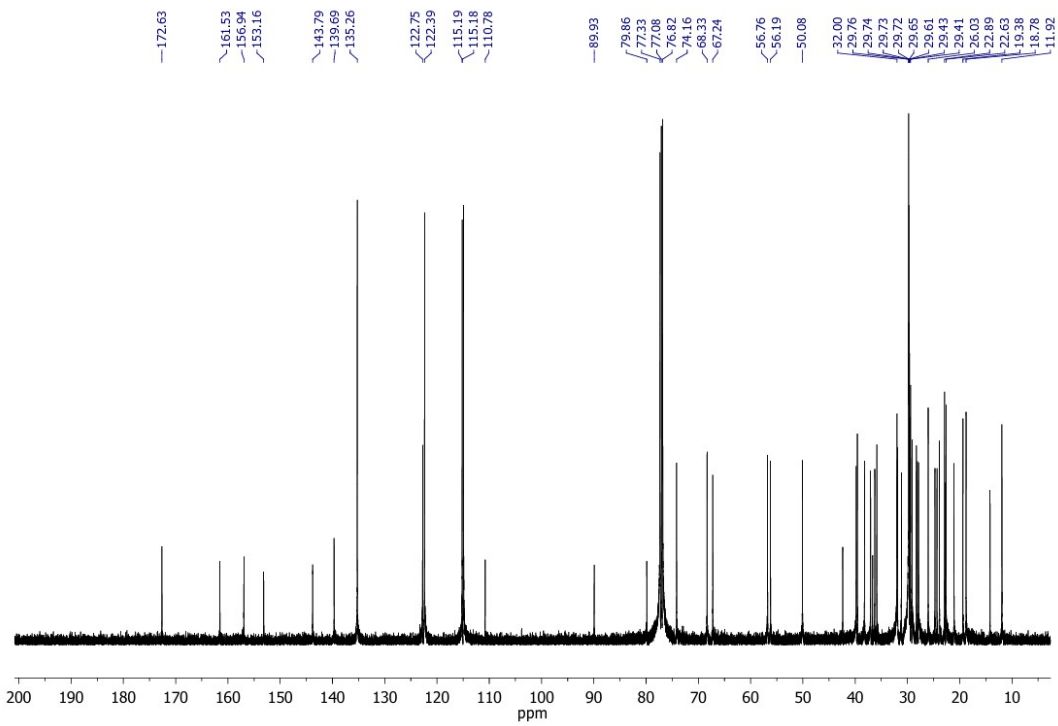


Figure S25: 13C NMR Spectrum of the dimer CPPD-3,16

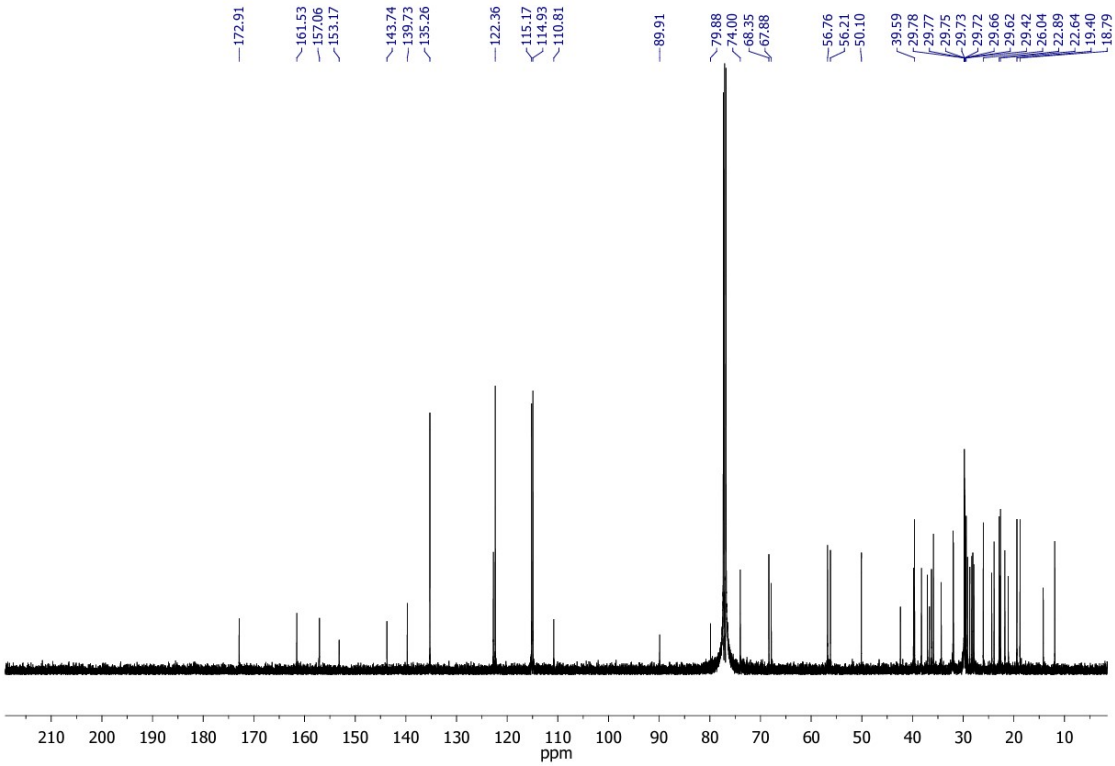


Figure S26: 13C NMR Spectrum of the dimer CPPD-4,16

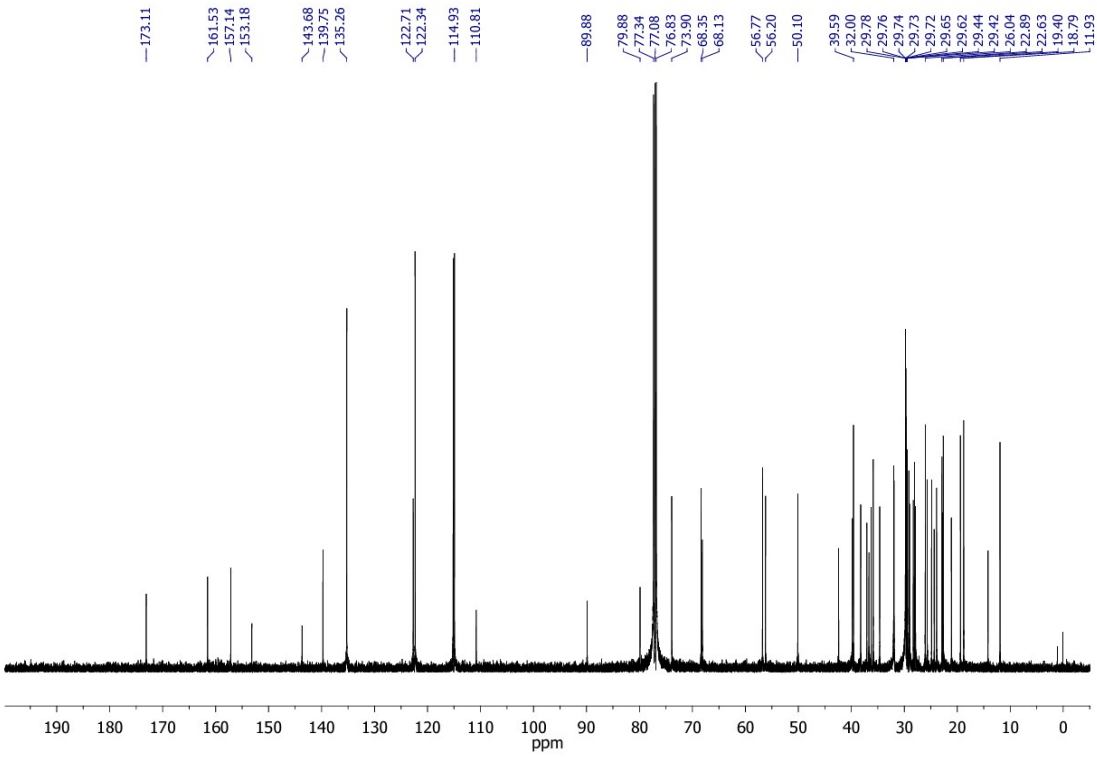


Figure S27: 13C NMR Spectrum of the dimer CPPD-5,16

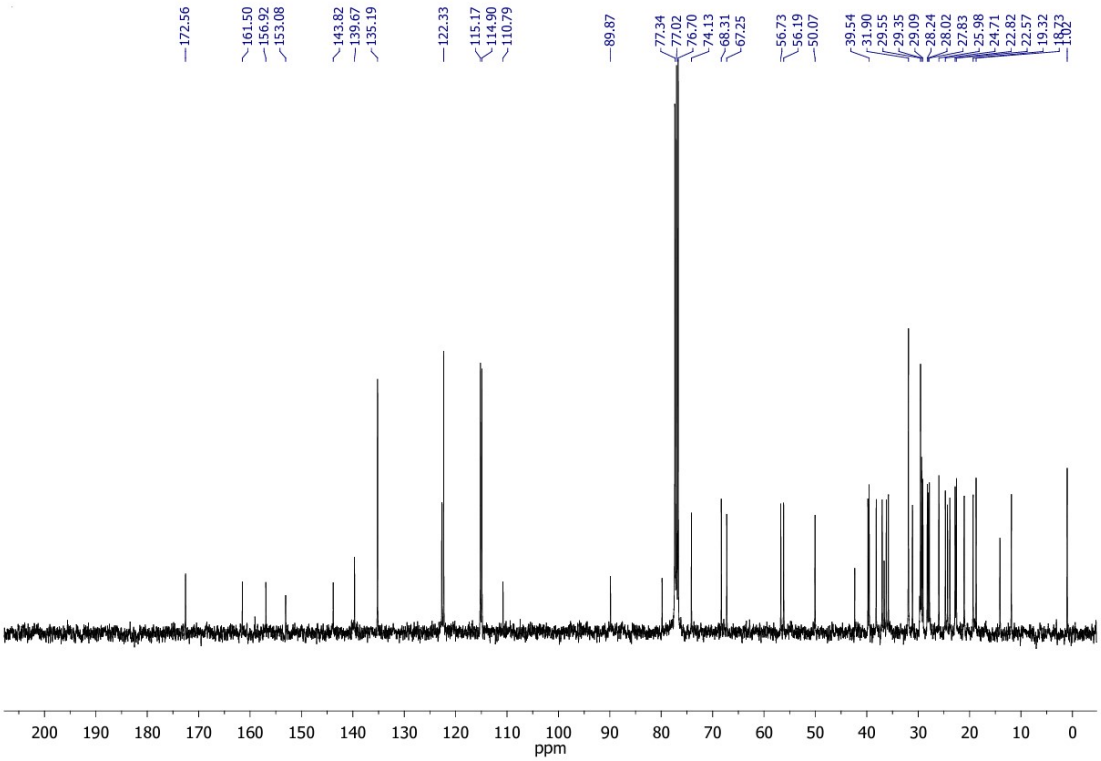


Figure S28: 13C NMR Spectrum of the dimer CPPD-7,16

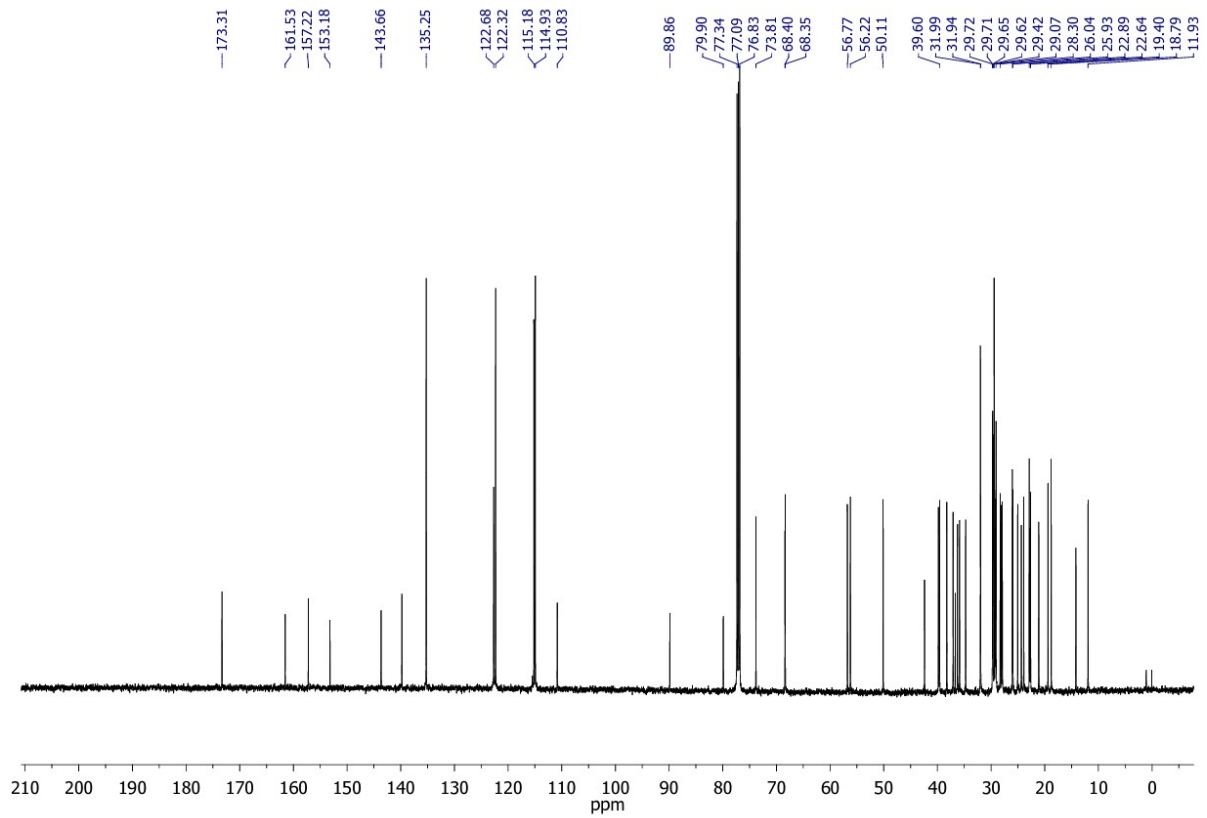


Figure S29: 13C NMR Spectrum of the dimer CPPD-3,18

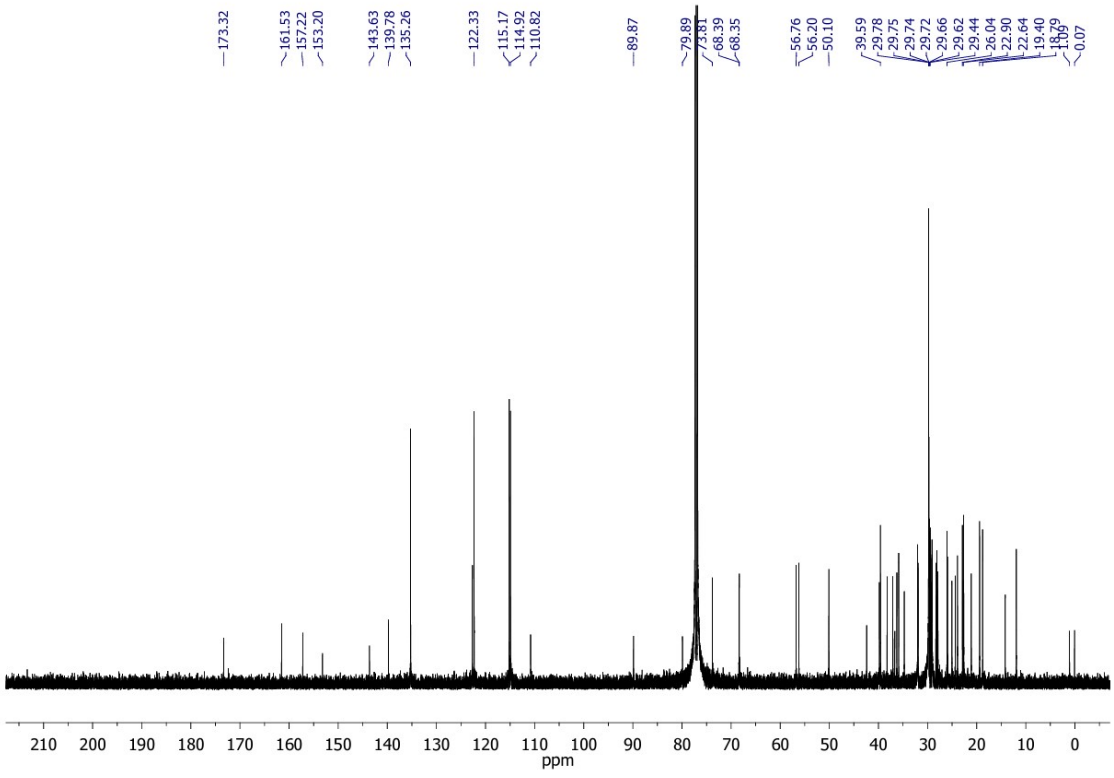


Figure S30: 13C NMR Spectrum of the dimer CPPD-4,18

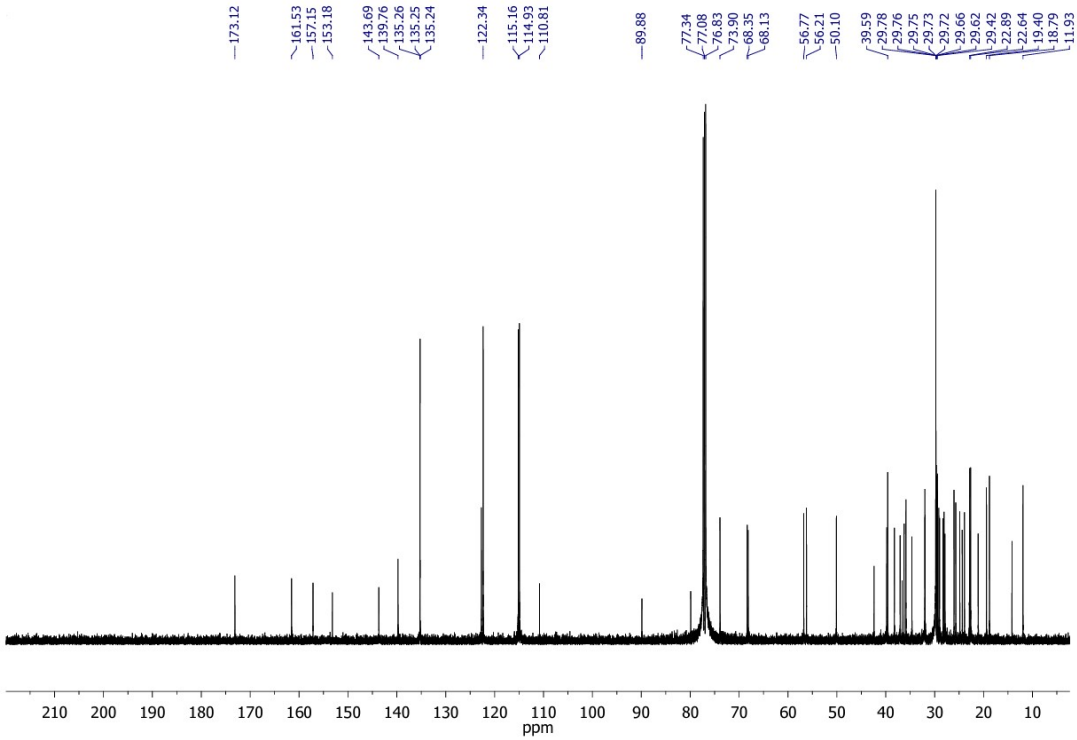


Figure S31: 13C NMR Spectrum of the dimer CPPD-5,18

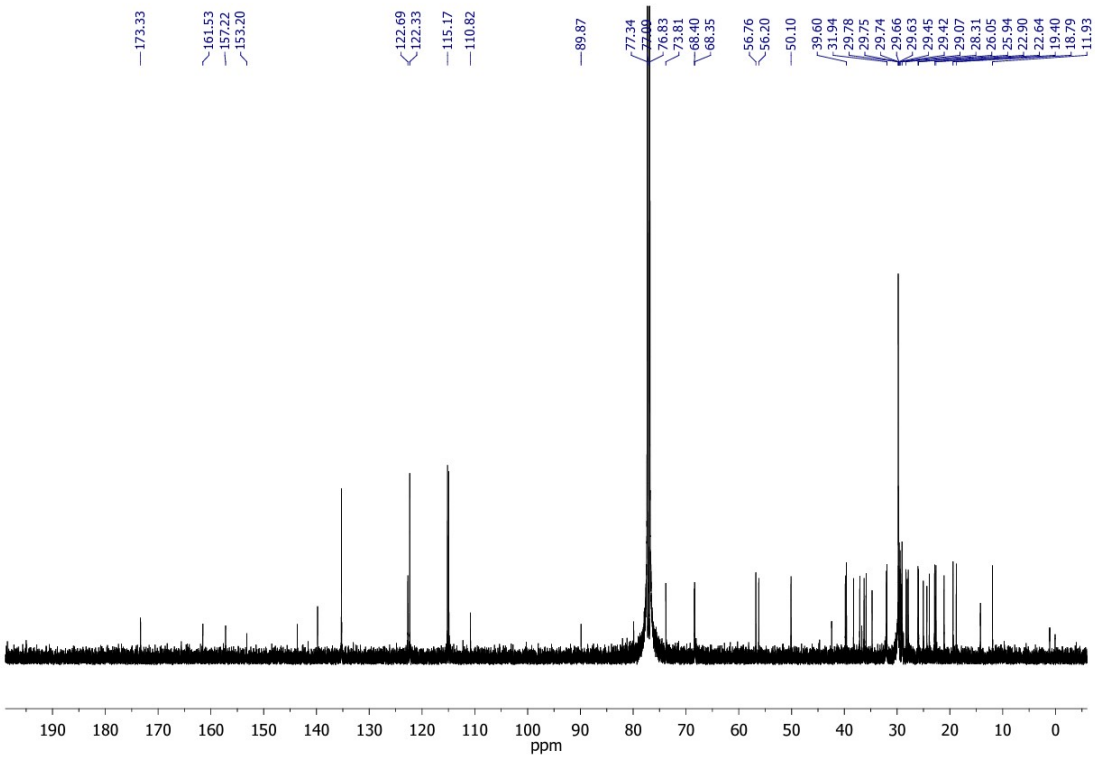


Figure S32: 13C NMR Spectrum of the dimer CPPD-7,18

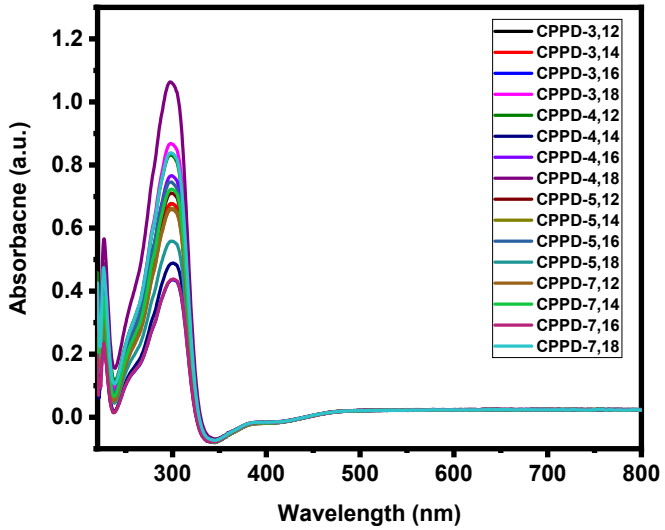


Figure S33: UV-Vis Spectra of the CPPD dimers in DCM.

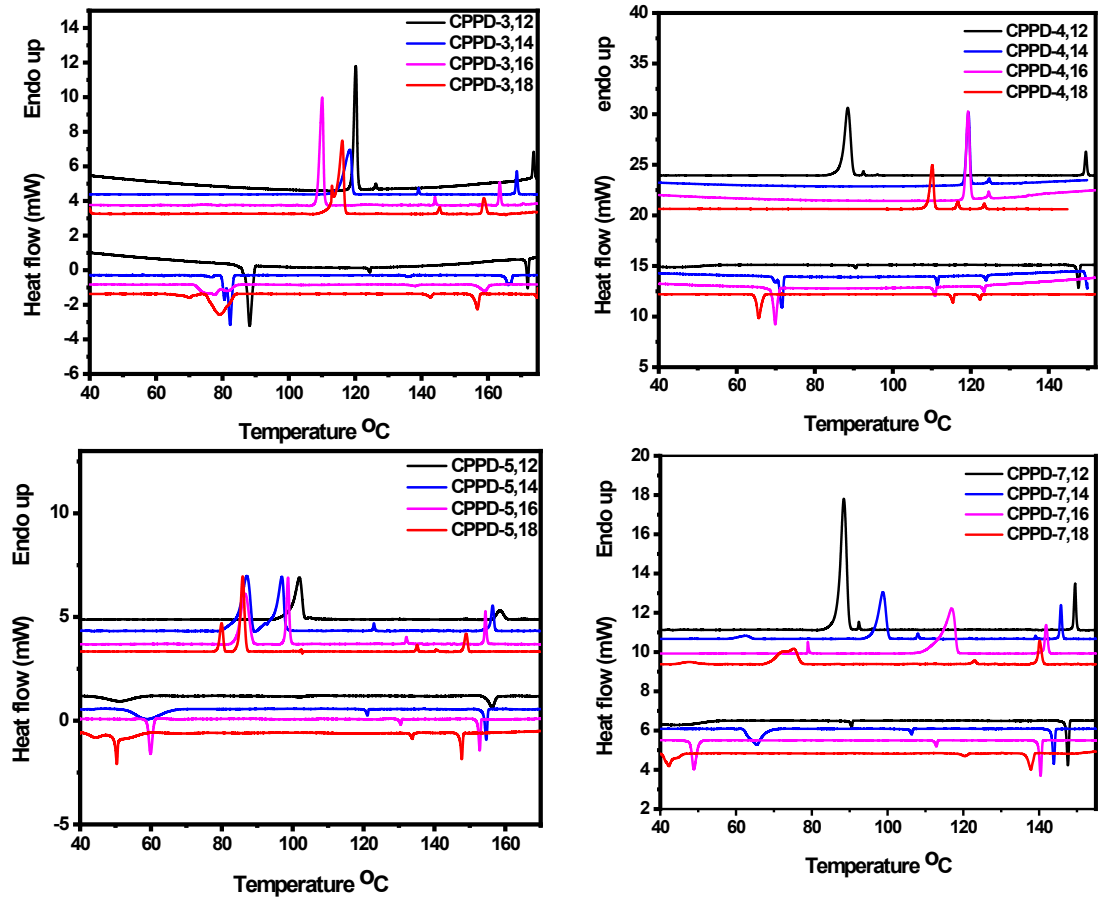


Figure S34. DSC thermograms recorded during the first heating−cooling cycles at a rate of 5 °C for the mesogens

Table S1. XRD data of the N* and TGBC* phases exhibited by **CPPD-5,12**

Dimer (L/Å)	LC phase	Temperature (ºC)	Layer spacing – d (Low angle position)/ Å	Wide-angle position/ Å	d_1/L	Tilt angle (º) $\theta = \cos^{-1}(d_1/L)$
CPPD-5,12 (53.02)	N*	155	-	5.14	---	-
		140	-	5.01	---	-
		120	-	4.91	-	-
	TGBC*	90	36.98	4.81	0.69	46.3
		70	35.98	4.79	0.67	47.9

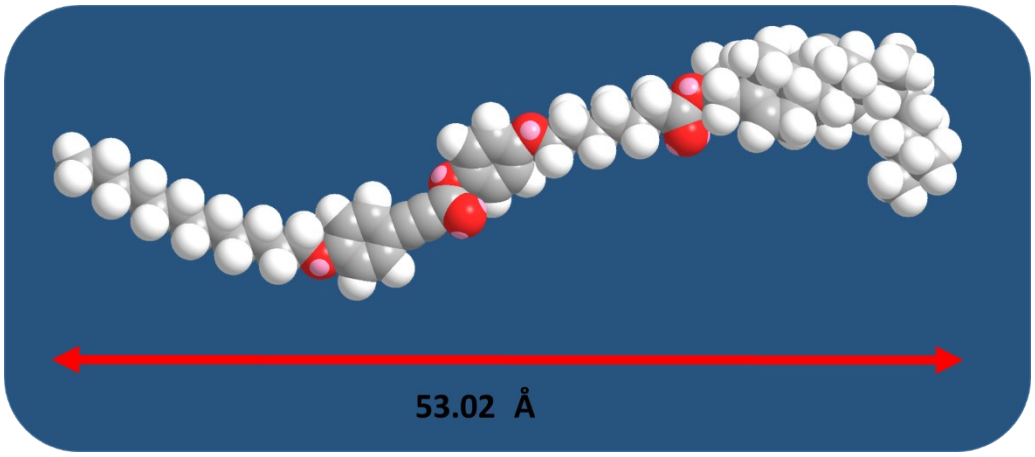


Figure S35: Energy minimised all-*trans* structure of CPPD-5,12 indicating the molecular length

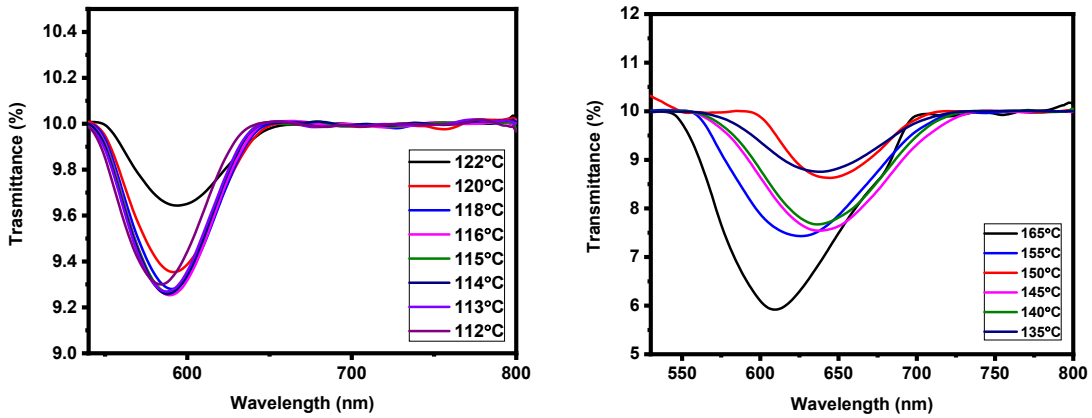


Figure S36. Selective reflection (UV-Vis) spectrum recorded as a function of temperature for the N* phase of the dimers (a) **CPPD-5,12** (b) **CPPD-7,12**

Table S2. CD spectroscopic data obtained in N* phase as a function of temperature for the mesogens helix while the transmitted light possess opposite handedness.

Dimer	Phase	Temperature (°C)	CD	
			λ_{max} (nm)	CD (mdeg)
CPPD-3,12	N*	165	585, 307	456.2,-1561.3
		155	605, 310	760.3, -2000
		150	604, 307	1310.8, -2000
		145	605, 307	1439.0, -2000
		140	601, 308	1609.2, -2000
		135	605, 307	1770.3, -2000
		130	607, 307	1957.6, -2000
		125	610, 307	1963.5, -2000
CPPD-4,12	N*	120	320	486.7
		118	322, 381	718.9, 1305.2
		115	322, 392	818.6, 1342.2
		105	322, 411	1196.9, 1248.4
		103	322, 413	1379.9, 1336.9
		98	333, 415	1728.4, 1641.7
		97	332, 415	1842.0, 1809.4
		96	333, 416	1950.0, 1981.4
		95	334, 417	1999.7, 1896.0
CPPD-5,12	N*	160	538, 323	3.60, -250
		155	542, 325	170.5, -280
		150	536, 329	771.2, -521
		145	539, 322	1131.3, -542
		140	538, 326	1195.4, -550
		130	537, 326	530.9, -580
		120	538, 325	1652.6, -593
		110	540, 322	1818.5, -615
		105	542, 322	1979.5, -632
CPPD-7,12	N*	148	556, 343	673.1, -35.0
		147	553, 342	647.5, -34.7
		145	574, 342	1038.4, 35.7
		142	574, 341	1370.1, 55.1
		139	578, 340	1457.2, 84.5
		136	583, 342	1544.0, 118.0
		130	585, 341	1598.6, 132.4
		125	588, 343	1660.3, 173.6
		120	592, 342	1727.0, 207.3
		115	597, 342	1790.9, 241.8
		110	600, 340	1858.2, 270.2
		105	604, 341	1928.5, 287.8
		95	614, 345	1981.4, 291.1
		93	627, 347	1999.2, 299.6