Condensation of Free Volume in Structures of Nematic and Hexatic Liquid Crystals

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1.1. General Techniques

Miscellaneous solvents were purchased from Fisher Scientific dried by sequential percolation through columns of activated alumina and copper Q5 catalyst prior to use. Chemical intermediates were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography (TLC) using an appropriate solvent system. Silica coated aluminium TLC plates used were purchased from Merck (Kieselgel 60 F-254) and visualised using UV light at wavelengths of both 254 nm and 365 nm. Column chromatography was performed using flash grade silica from Fluorochem (40 - 63μm particle size). Yields refer to chromatographically (HPLC) and spectroscopically (^{1}H NMR and ^{13}C{^{1}H} NMR) homogenous material.

1.2. Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (^{1}H) and 100.5 MHz (^{13}C{^{1}H}) as solutions in deuterated chloroform.

1.3. Mass Spectrometry (MS)

Mass spectra were recorded on a Bruker micrOTOF MS-Agilent series 1200LC spectrometer. We thank Mr. Karl Heaton of the University of York for acquiring MS data.

1.4. High Performance Liquid Chromatography (HPLC)

High-performance liquid chromatography was performed on a Shimadzu Prominence modular HPLC system comprising a LC-20A quaternary solvent pump, a DGU-20A$_5$ degasser, a SIL-20A autosampler, a CBM-20A communication bus, a CTO-20A column oven, and a SPO-20A dual wavelength UV-vis detector operating at 220/250 nm. The column used was an Alltech C18 bonded reverse-phase silica column with a 5 μm pore size,

an internal diameter of 10 mm and a length of 250 mm. In all cases the mobile phase used was neat acetonitrile, purchased from Fisher Scientific UK.

1.5. Polarised Optical Microscopy (POM)

Polarised optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hotstage controlled by a Mettler FP90 central processor. Photomicrographs were captured *via* an InfinityX-21 MP digital camera mounted atop the microscope.

1.6. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed on a Mettler DSC822^e fitted with an autosampler operating with Mettler Star^e software and calibrated before use against an indium standard (onset = 156.55 ± 0.2 °C, ΔH = 28.45 ± 0.40 Jg^{-1}) under an atmosphere of dry nitrogen.

1.7. Small Angle X-ray Scattering (SAXS)

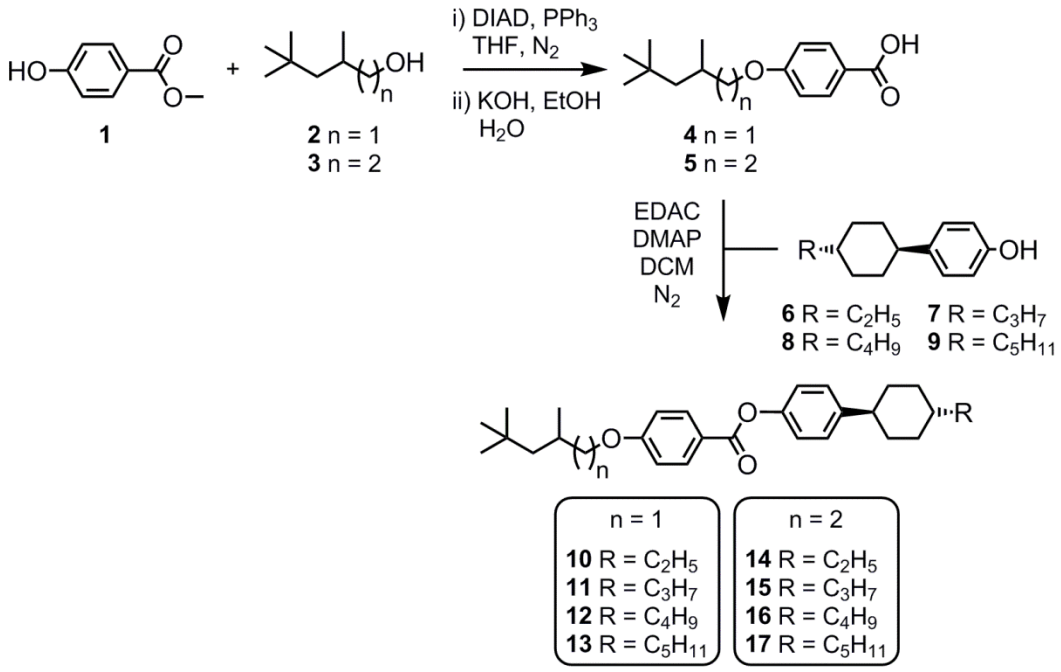
Small angle X-ray scattering was performed using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. The radiation used was copper Kα (λ = 0.154056 nm) from a 1 μS microfocus source. A silver behenate standard was used to calibrate d-spacings and determine instrumental broadening. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample. Samples were filled into 0.9 mm O.D. capillary tubes (approx. I.D. ~0.85 mm) and aligned with a pair of 1T magnets, with the field strength at the sample position being approximately 0.6T Diffraction patterns were collected as a function of temperature and the data processed using Matlab as follows. Two-dimensional scattering patterns were collected on cooling from the isotropic liquid until crystallisation in ~ 1.2 °C intervals. These were radially averaged (0.05 ° step size) to give scattered intensity as a function of 2θ for each frame. Fitting of this integrated data with a Voigt function (in all cases $R^2 > 0.99$) allowed the peak position and FWHM to be determined for both the small- and wide- angle peaks; the FWHM was corrected for instrumental broadening then used to determine correlation lengths parallel and perpendicular to the director. FWHM and d-spacing values were converted into 2θ allowing us to obtain domain sizes from the Scherrer equation. All data processing was carried out using custom Matlab scripts which may be made available on request from the corresponding author.

1.8. Computational Chemistry

Quantum chemical calculations were performed using the Gaussian 09 revision e.01 suite of programmes. [1]

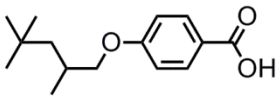
1.9. Single Crystal X-ray Diffraction

Single-crystal diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Cu-K_α radiation (λ = 1.54184 Å' using a EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with "Crysalis".[2] Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. [3] OLEX2 [4] was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithms used for structure solution were Superflip charge-flipping" [5] for **10** and "ShelXT dual-space" [6] for **14**. Refinement by full-matrix least-squares used the SHELXL-97 [7] algorithm within OLEX2. [4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. Both structures exhibited disorder of the branched alkyl chain. For **10**, the 2,4,4-trimethylpentanol group was disordered and modelled in two positions with refined occupancies of 0.766:0.234(3), the ADP of the disordered atom pairs were constrained to be the same. For **14**, the 3,5,5-trimethylhexanol group was disordered and modelled in two positions with refined occupancies of 0.731:0.269(4). The C_{22}-O_3 and C_{22}-O_{3a} bond lengths were restrained to be equal, C_{22a}-C_{23a} was restrained to be 1.52 angstroms and the ADP of C_{22} and C_{22A} constrained to be equal.


HO
O
O
1
+
OH
n
2 n = 1
3 n = 2
i) DIAD, PPh3
THF, N2
ii) KOH, EtOH
H2O
OH
O
n
4 n = 1
5 n = 2
EDAC
DMAP
DCM
N2
R
OH
6 R = C2H5
7 R = C3H7
8 R = C4H9
9 R = C5H11
O
O
n
O
O
R
n = 1
10 R = C2H5
11 R = C3H7
12 R = C4H9
13 R = C5H11
n = 2
14 R = C2H5
15 R = C3H7
16 R = C4H9
17 R = C5H11

Scheme 1

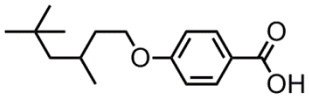
1.2. Synthetic Details and Chemical Characterisation



4-(2,4,4-Trimethylpentyloxy)benzoic acid (4)

To a stirred solution of 2,4,4-trimethylpentan-1-ol (5 g, 38.46 mmol), triphenyl phosphine (10.1 g, 38.46 mmol) and methyl 4-hydroxybenzoate (6.4 g, 42.31 mmol) in anhydrous THF (125 ml), under an atmosphere of dry nitrogen, was added neat DIAD (7.8 g, 7.6 ml, 38.46 mmol) dropwise over a period of 0.5h. The resulting solution was stirred for 6h, and the solvent removed *in vacuo*. Ethanol (100 ml) was added to the crude residue and the solution was heated under reflux before the addition of 4M sodium hydroxide solution (30 ml). The solution was heated under reflux for 16 h, cooled to r.t. and diluted with water (100 ml) and filtered. The filtrate was acidified to pH 1 with 36% HCl, the resulting precipitate collected by filtration and recrystallised from ethanol giving the title compound as translucent needles.

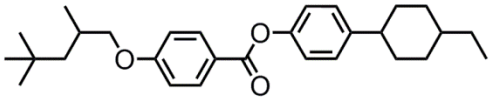
Yield:	7.4 g (73%)
Melting Point:	106.3 °C
^{1}H NMR (400 MHz, $CDCl_3$):	0.79 (9H, S), 0.88 (3H, d, $J_{H\text{-}H}$ = 6.4 Hz), 0.94 – 1.03 (1H, m), 1.17 – 1.24 (1H, m), 1.42 – 1.54 (1H, m), 1.58 – 1.68 (2H, m), 3.96 (2H, t, $J_{H\text{-}H}$ = 6.4), 6.90 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 7.80 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.9 Hz).
MS M/Z (ESI+):	273.1462 ($C_{15}H_{22}NaO_3$, cacld. for $C_{15}H_{23}O_3$: 273.1461 M+Na), 251.1650 ($C_{15}H_{23}O_3$, calcd. for $C_{15}H_{23}O_3$: 251.1642, M+H)
FT-IR (v max, cm^{-1}):	547, 640, 771, 840, 941, 1026, 1118, 1157, 1249, 1296, 1427, 1604, 1674, 2553, 2669, 2826, 2947



4-(3,5,5-Trimethylhexyloxy)benzoic acid (5)

Quantities used: 3,5,5-Trimethylhexan-1-ol (15 g, 18.2 ml, 0.113 mol), methyl 4-hydroxybenzoate (17 g, 0.112 mol), PPh_3 (27.9 g, 0.106 mol), DIAD (21.5 g, 0.106 mol), THF (200 ml), then aqueous 4M NaOH (100 ml), EtOH (300 ml). The experimental procedure was as described in the synthesis of compound 4, giving the title compound as white plates.

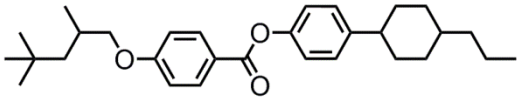
Yield:	19.7 g (76%)
Melting Point:	122.2 °C
^{1}H NMR (400 MHz, DMSO-D6):	0.79 (9H, s), 0.88 (3H, d, J_{H-H} = 6.4 Hz), 0.94 – 1.03 (1H, m Hz), 1.17 – 1.24 (1H, m), 1.42 – 1.54 (1H, M), 1.58 – 1.68 (2H, m), 3.96 (2H, t, J_{H-H} = 6.4 Hz), 6.90 (2H, ddd, J_{H-H} = 2.1 Hz, J_{H-H} = 2.8 Hz, J_{H-H} = 8.9 Hz), 7.80 (2H, ddd, J_{H-H} = 2.1 Hz, J_{H-H} = 2.8 Hz, J_{H-H} = 8.9 Hz)
MS M/Z (ESI+):	287.1609 ($C_{16}H_{24}NaO_3$, calcd. for $C_{16}H_{24}NaO_3$: 287.1618, M + Na), 265.1787 ($C_{16}H_{25}O_3$, calcd. for $C_{16}H_{25}O_3$: 265.1798, M + H)
FT-IR (v max, cm^{-1}):	503, 553, 632, 650, 693, 763, 771, 827, 844, 889, 943, 968, 997, 1012, 1053, 1109, 1128, 1166, 1201, 1251, 1296, 1321, 1363, 1390, 1429, 1473, 1514, 1579, 1604, 1674, 2868, 2895, 2953



4-(4-Ethylcyclohexyl)phenyl 4-((2,4,4-trimethylpentyl)oxy)benzoate (10)

Compound **4** (400 mg, 1.6 mmol), compound **6** (391 mg, 1.92 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol) were dissolved into dry DCM (4 ml) in an oven dried vial, and the resulting solution stirred for 16h. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (10:1) to give the title compound as white needles.

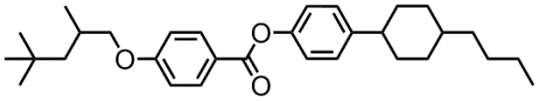
Yield:	0.47 g (67%)
^{1}H NMR (400 MHz, $CDCl_3$):	0.81 – 1.42 (22H, m), 1.77 – 1.87 (4H, m), 1.89 – 2.01 (1H, m), 2.41 (1H, tt, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 12.4 Hz), 3.66 (1H, dd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 3.77 (1H, dd, $J_{H\text{-}H}$ = 5.8 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 6.87 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 7.02 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 7.17 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 8.06 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.9 Hz)
^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$):	11.53, 19.93, 29.50, 29.85, 29.95, 33.12, 34.37, 39.03, 44.07, 47.28, 74.34, 114.23, 121.36, 121.65, 127.70, 132.19, 145.21, 148.94, 163.51, 165.12
MS M/Z (ESI+):	475.2608 ($C_{29}H_{40}KO_3$, calcd. for $C_{29}H_{40}KO_3$: 475.2609, M + K) 459.2860 ($C_{29}H_{40}NaO_3$, calcd. for $C_{29}H_{40}NaO_3$: 459.2870, M + Na) 437.3036 ($C_{29}H_{21}O_3$, calcd. for $C_{29}H_{41}O_3$: 437.3050, M + H)
FT-IR (v max, cm^{-1}):	516, 542, 605, 630, 659, 690, 763, 802, 844, 877, 939, 968, 1004, 1074, 1105, 1166, 1201, 1257, 1317, 1446, 1465, 1510, 1604, 1720, 2848, 2870, 2891, 2918, 2953.
Assay (RP-HPLC):	99.3%



4-(4-Propylcyclohexyl)phenyl 4-((2,4,4-trimethylpentyl)oxy)benzoate (11)

Quantities used: **4** (400 mg, 1.6 mmol), compound **7** (418 mg, 1.92 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound **10**. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (17:1) to give the title compound as white needles.

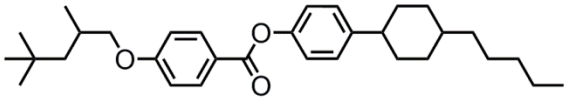
Yield:	0.38 g (52%)
^{1}H NMR (400 MHz, $CDCl_3$):	0.82 (3H, t, $J_{H\text{-}H}$ = 7.0 Hz), 0.86 (9H, s), 0.89 – 1.41 (12H, m), 1.75 – 1.87 (4H, m), 1.89 – 2.01 (1H, m), 2.40 (1H, tt, $J_{H\text{-}H}$ = 3.4 Hz, $J_{H\text{-}H}$ = 12.2 Hz), 3.65 (1H, dd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}H}$ = 9.2 Hz), 3.77 (1H, dd, $J_{H\text{-}H}$ = 5.8 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 6.87 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 7.03 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 7.16 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 8.05 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.9 Hz)
^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$):	14.40, 19.92, 20.01, 29.50, 29.85, 30.96, 33.51, 34.38, 36.96, 39.68, 44.06, 47.28, 74.34, 114.22, 121.36, 121.65, 127.69, 132.19, 145.21, 148.93, 163.51, 165.11
MS M/Z (ESI+):	489.2758 ($C_{30}H_{42}KO_3$, calcd. for $C_{30}H_{42}KO_3$: 489.2766, M + K) 473.3020 ($C_{30}H_{42}NaO_3$, cacld. for $C_{30}H_{42}NaO_3$: 473.3026, M + Na)
FT-IR (v max, cm^{-1}):	513, 536, 605, 632, 661, 692, 763, 800, 842, 875, 970, 1012, 1026, 7076, 1165, 1205, 1251, 1313, 1363, 1446, 1467, 1510, 1602, 1720, 2848, 2891, 2954.
Assay (RP-HPLC):	99.9%



4-(4-Butylcyclohexyl)phenyl 4-((2,4,4-trimethylpentyl)oxy)benzoate (12)

Quantities used: **4** (400 mg, 1.6 mmol), compound **8** (445 mg, 1.92 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound **10**. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

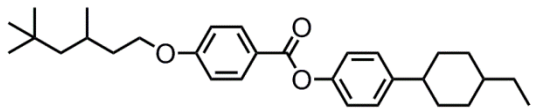
Yield:	0.26 g (35%)
^{1}H NMR (400 MHz, $CDCl_3$):	0.80 – 1.42 (26H, m), 1.76 – 1.88 (4H, m), 1.90 – 2.00 (1H, m), 2.41 (1H, tt, $J_{H\text{-}H}$ = 3.4 Hz, $J_{H\text{-}H}$ = 12.4 Hz), 3.66 (1H, dd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}H}$ = 9.2 Hz), 3.77 (1H, dd, $J_{H\text{-}H}$ = 6.1 Hz, $J_{H\text{-}H}$ = 9.2 Hz), 6.88 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 7.03 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 7.18 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 8.05 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 8.9 Hz)
^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$):	14.16, 19.93, 23.00, 29.22, 29.51, 29.86, 30.97, 33.56, 34.40, 37.08, 37.24, 44.07, 47.29, 74.35, 114.23, 121.36, 121.65, 127.70, 132.19, 145.23, 148.94, 163.51, 165.12
MS M/Z (ESI+):	487.3168 ($C_{31}H_{44}NaO_3$, cacld. for $C_{31}H_{44}NaO_3$: 487.6792, M + Na) 465.3353 ($C_{31}H_{45}O_3$, cacld. for $C_{31}H_{45}O_3$: 465.6975, M + H)
FT-IR (v max, cm^{-1}):	511, 538, 607, 632, 661, 692, 763, 800, 846, 877, 975, 1016, 1066, 1165, 1195, 1253, 1317, 1361, 1465, 1510, 1602, 1724, 2852, 2918, 2954.
Assay (RP-HPLC):	99.9%



4-(4-Pentylcyclohexyl)phenyl 4-((2,4,4-trimethylpentyl)oxy)benzoate (13)

Quantities used: **4** (400 mg, 1.6 mmol), compound **9** (472 mg, 1.92 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound **10**. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

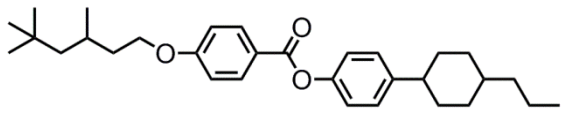
Yield:	0.66 g (87%)
^{1}H NMR (400 MHz, $CDCl_3$):	0.80 – 1.42 (28H, m), 1.75 – 1.87 (4H, m), 1.89 – 2.00 (1H, m), 2.40 (1H, tt, $J_{H\text{-}H}$ = 3.0 Hz, $J_{H\text{-}H}$ = 12.1 Hz), 3.65 (1H, dd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 3.75 (1H, dd, $J_{H\text{-}H}$ = 6.1 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 6.87 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 7.02 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 7.18 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 8.06 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.9 Hz)
^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$):	14.12, 19.92, 22.70, 26.63, 29.50, 29.86, 30.96, 32.19, 33.56, 34.40, 37.26, 37.35, 44.07, 47.29, 74.34, 114.23, 121.36, 121.65, 127.69, 132.19, 145.21, 148.94, 163.51, 165.10
MS M/Z (ESI+):	501.3320 ($C_{32}H_{46}NaO_3$, cacld. for $C_{32}H_{46}NaO_3$: 501.3339, M + Na) 479.3515 ($C_{32}H_{47}O_3$, cacld. for $C_{32}H_{47}O_3$: 479.7245, M + H)
FT-IR (v max, cm^{-1}):	538, 607, 632, 692, 763, 800, 846, 877, 1016, 1066, 1165, 1195, 1253, 1317, 1361, 1465, 1510, 1602, 1724, 2852, 2954.
Assay (RP-HPLC):	99.9%



4-(4-Ethylcyclohexyl)phenyl 4-((3,5,5-trimethylhexyl)oxy)benzoate (14)

Quantities used: **5** (200 mg, 0.77 mmol), compound **6** (160 mg, 0.77 mmol), EDAC (170 mg, 0.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound **10**. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

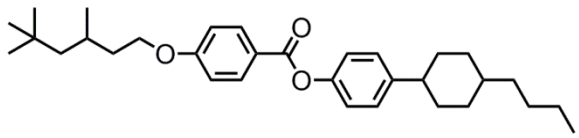
Yield:	300 mg (87%)
^{1}H NMR (400 MHz, $CDCl_3$):	0.90 (9H, s), 0.99 (2H, d, $J_{H\text{-}H}$ = 6.7 Hz), 1.31 – 1.01 (5H, m), 1.54 – 1.38 (2H, m), 1.66 (1H, quint, $J_{H\text{-}H}$ = 6.4 Hz), 1.94 – 1.71 (6H, m), 2.48 (1H, tt, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 12.2 Hz), 4.05 (2H, t, $J_{H\text{-}H}$ = 6.4 Hz), 6.96 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.9 Hz), 7.09 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 7.23 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 8.12 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.9 Hz)
^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$):	11.53, 22.76, 26.08, 29.92, 29.95, 31.13, 33.12, 34.36, 38.25, 39.02, 44.07, 51.02, 66.52, 114.20, 121.35, 121.67, 127.70, 132.20, 145.22, 148.93, 163.38, 165.13
MS M/Z (ESI+):	473.3019 ($C_{30}H_{42}NaO_3$, calcd. for $C_{30}H_{42}NaO_3$: 473.3026, M + Na) 451.3183 ($C_{30}H_{43}O_3$, cacld. for $C_{30}H_{43}O_3$: 451.6705, M + H)
FT-IR (v max, cm^{-1}):	501, 540, 601, 655, 763, 972, 1072, 1165, 1257, 1465, 1512, 1581, 1604, 1728, 2846, 2908, 2954
Assay (RP-HPLC):	98.6%



4-(4-Propylcyclohexyl)phenyl 4-((3,5,5-trimethylhexyl)oxy)benzoate (15)

Quantities used: **5** (200 mg, 0.77 mmol), compound **7** (160 mg, 0.77 mmol), EDAC (170 mg, 0.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound **10**. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

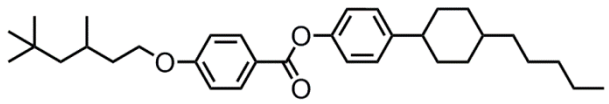
Yield:	320 mg (89%)
^{1}H NMR (400 MHz, $CDCl_3$):	0.93 – 0.85 (12H, m), 0.99 (2H, d, $J_{H\text{-}H}$ = 6.6 Hz), 1.54 – 1.02 (5H, m), 1.93 – 1.60 (7H, m), 2.47 (1H, tt, $J_{H\text{-}H}$ = 3.3 Hz, $J_{H\text{-}H}$ = 12.1 Hz), 4.05 (2H, t, $J_{H\text{-}H}$ = 6.6 Hz Hz), 6.95 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.8 Hz), 7.09 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 7.23 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 8.12 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.8 Hz, $J_{H\text{-}H}$ = 8.8 Hz).
^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$):	14.40, 20.01, 22.76, 26.08, 29.92, 31.13, 33.52, 34.39, 36.96, 38.25, 39.68, 44.07, 51.02, 66.52, 114.19, 121.36, 121.68, 127.70, 132.20, 145.23, 148.93, 163.38, 165.12
MS M/Z (ESI+):	465.3379 ($C_{30}H_{45}O_3$, cacld. for $C_{30}H_{45}O_3$: 465.3363, M + H)
FT-IR (v max, cm^{-1}):	540, 609, 655, 686, 763, 848, 972, 1010, 1072, 1165, 1195, 1257, 1465, 1512, 1581, 1604, 1720, 2846, 2916
Assay (RP-HPLC):	99.7%



4-(4-Buttylcyclohexyl)phenyl 4-((3,5,5-trimethylhexyl)oxy)benzoate (16)

Quantities used: **5** (200 mg, 0.77 mmol), compound **8** (170 mg, 0.77 mmol), EDAC (170 mg, 0.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound **10**. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (14:1) to give the title compound as white needles.

Yield:	310 mg (84%)
^{1}H NMR (400 MHz, $CDCl_3$):	0.99 (2H, d, $J_{H\text{-}H}$ = 6.6 Hz), 0.89 (12H, s), 1.11 (1H, d, $J_{H\text{-}H}$ = 5.5), 1.14 (1H, d, $J_{H\text{-}H}$ = 5.9 Hz), 1.32 – 1.20 (8H, m), 1.54 – 1.37 (3H, m), 1.65 (1H, quint, $J_{H\text{-}H}$ = 6.6 Hz), 1.93 – 1.70 (6H, m), 2.52 – 2.42 (1H, tt, $J_{H\text{-}H}$ = 2.9 Hz, $J_{H\text{-}H}$ = 12.2 Hz), 4.05 (2H, t, $J_{H\text{-}H}$ = 6.6 Hz), 6.96 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.8 Hz), 7.09 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.5 Hz), 7.23 (2H, ddd $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.8 Hz), 8.12 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.8 Hz).
$^{13}C\{^{1}H\}$ NMR (100.5 MHz, $CDCl_3$):	14.16, 22.76, 23.00, 26.08, 29.22, 29.92, 31.13, 33.56, 34.40, 37.08, 37.24, 38.25, 44.07, 51.02, 66.52, 114.20, 121.36, 121.67, 127.70, 132.20, 145.23, 148.93, 163.38, 165.12
MS M/Z (ESI+):	479.2757 ($C_{30}H_{47}O_3$, cacld. for $C_{30}H_{47}O_3$: 479.7245, M + H)
FT-IR (v max, cm^{-1}):	501, 540, 663, 686, 763, 810, 848, 871, 1010, 1072, 1165, 1195, 1257, 1465, 1512, 1604, 1720, 2846, 2916
Assay (RP-HPLC):	98.1%



4-(4-Pentylcyclohexyl)phenyl 4-((3,5,5-trimethylhexyl)oxy)benzoate (17)

Quantities used: **5** (400 mg, 1.6 mmol), compound **9** (377 mg, 1.6 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound **10**. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

Yield:	0.55 g (70%)
^{1}H NMR (400 MHz, $CDCl_3$):	0.77 – 1.90 (35H, m), 2.41 (1H, tt, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 12.2 Hz), 3.98 (2H, t, $J_{H\text{-}H}$ = 7.0 Hz), 6.89 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.6 Hz, $J_{H\text{-}H}$ = 9.2 Hz), 7.03 (2H, ddd, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.8 Hz), 7.17 (2H, ddd $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.8 Hz), 8.06 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.6 Hz, $J_{H\text{-}H}$ = 9.2 Hz).
^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$):	14.12, 22.70, 22.76, 26.07, 26.63, 29.91, 31.12, 32.19, 33.55, 34.39, 37.25, 37.35, 38.25, 44.06, 51.01, 66.51, 114.19, 121.35, 121.67, 127.68, 132.19, 145.21, 148.93, 163.38, 165.10
MS M/Z (ESI+):	515.3480 ($C_{33}H_{48}NaO_3$, calcd. for $C_{33}H_{48}NaO_3$: 515.3496, M + Na), 493.3657 ($C_{33}H_{49}O_3$, calcd. for $C_{33}H_{49}O_3$: 493.3676, M + H)
FT-IR (v max, cm^{-1}):	501, 663, 686, 763, 810, 848, 1010, 1072, 1165, 1195, 1257, 1465, 1512, 1604, 1720, 2846, 2916
Assay (RP-HPLC):	99.9%

2. Supplimental Figures

2.1. Supplemental SAXS Data

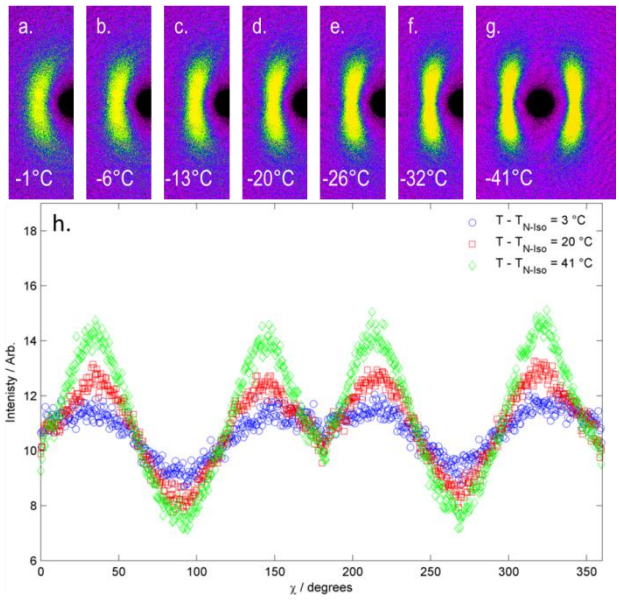


Figure SI-1: The nematic phase of compound **13** as studied by SAXS. (a-g), evolution of the small-angle scattering peak for a magnetically aligned sample of **13** as a function of the indicated reduced temperartures, and (h) plot of integrated diffraction intensity for the small angle peak as a function of the angle χ for compound **13** at three different reduced temperatures.

2.2. Supplemental Single Crystal X-ray Diffraction Data

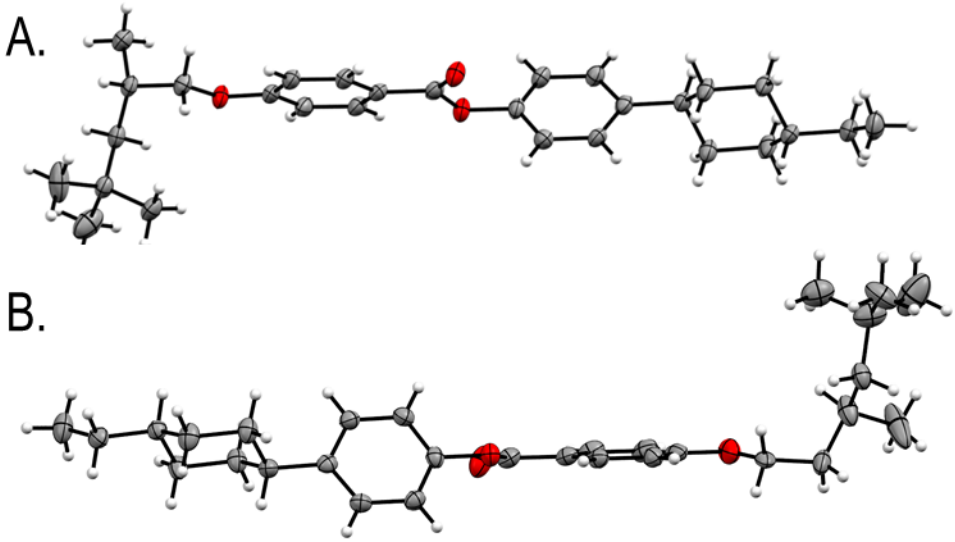


Figure SI-2: Thermal elipsoid model (50% probability level) of the structure of (a) compound **10** and (b) compound **14** obtained by X-ray diffraction on single crystals grown from neat ethanol with a thermal gradient. For **10** the angle between the plane of the two phenyl rings is 58.76(9) °, and for **14** it is 58.18(2) °. For **10** the plane of the major form of the bulky end group (mean of 25 atoms) is at an angle of 84.59(6)° from the plane of the mesogenic unit (mean of 46 atoms) while for **14** the end group (mean of 28 atoms) is at an angle of 80.96(6) ° from the plane of the mesogenic unit (mean of 46 atoms).

2.3. Supplemental Mixture Data

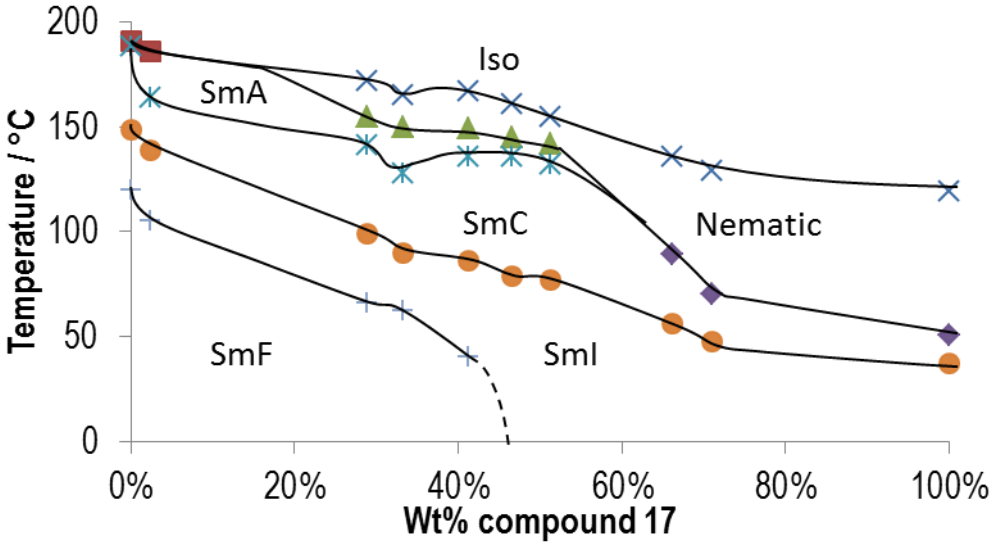


Figure SI-3: Transiton temperatures (°C) of binary mixtures of **17** with *bis* decylterephthalaniline (TBDA)

2.2. Supplemental XRD data

2.2.1. Structure 10

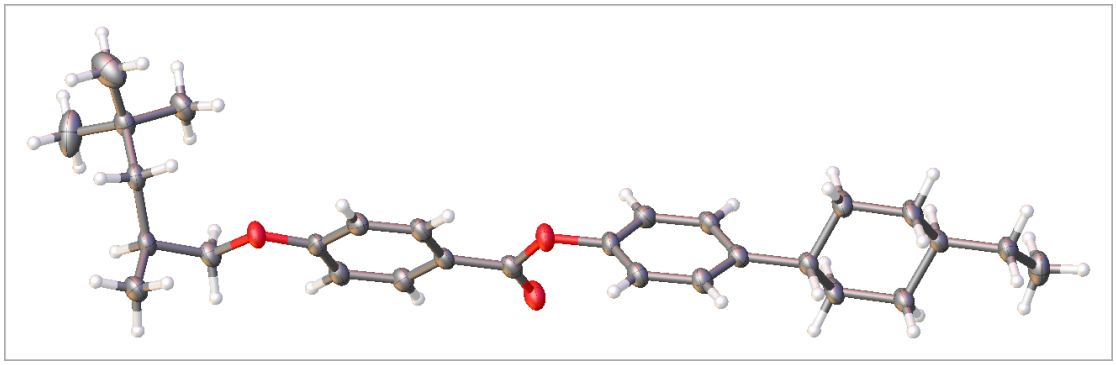


Table 1 Crystal data and structure refinement for 10.

Identification code	jwg1609
Empirical formula	$C_{29}H_{40}O_3$
Formula weight	436.61
Temperature/K	109.9(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.7608(8)
b/Å	5.5364(2)
c/Å	28.2495(12)
α/°	90
β/°	106.554(5)
γ/°	90
Volume/Å^3	2512.7(2)
Z	4
ρ_{calc}g/cm^3	1.154
μ/mm^{-1}	0.564
F(000)	952.0
Crystal size/mm^3	0.251 × 0.075 × 0.046
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	7.242 to 142.068
Index ranges	$-15 \leq h \leq 20$, $-6 \leq k \leq 5$, $-34 \leq l \leq 34$
Reflections collected	10843
Independent reflections	4772 [R_{int} = 0.0504, R_{sigma} = 0.0493]
Data/restraints/parameters	4772/0/306
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0743, wR_2 = 0.1900
Final R indexes [all data]	R_1 = 0.0951, wR_2 = 0.2121
Largest diff. peak/hole / e $Å^{-3}$	0.35/-0.37

Table 2 Bond Lengths for 10.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C12	1.413(2)	C16	C21	1.387(3)
O1	C15	1.366(3)	C17	C18	1.380(3)
O2	C15	1.203(3)	C18	C19	1.384(3)
C1	C2	1.512(4)	C19	C20	1.390(3)
C2	C3	1.520(3)	C19	O3	1.359(4)
C3	C4	1.519(3)	C19	O3A	1.425(12)
C3	C8	1.527(3)	C20	C21	1.388(3)
C4	C5	1.532(3)	C25	C26	1.511(4)
C5	C6	1.532(3)	C25	C27	1.521(4)
C6	C7	1.535(3)	C25	C28	1.528(3)
C6	C9	1.515(3)	C25	C24	1.553(4)
C7	C8	1.521(3)	C25	C24A	1.572(10)
C9	C10	1.386(3)	C29	C23	1.541(4)
C9	C14	1.395(3)	C29	C23A	1.522(10)

C10	C11	1.396(3)	O3	C22	1.440(4)
C11	C12	1.378(3)	C22	C23	1.516(4)
C12	C13	1.374(3)	C23	C24	1.538(4)
C13	C14	1.384(3)	O3A	C22A	1.430(14)
C15	C16	1.476(3)	C22A	C23A	1.527(12)
C16	C17	1.396(3)	C23A	C24A	1.499(15)

Table 3 Bond Angles for 10.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C15	O1	C12	117.82(18)	C17	C18	C19	120.6(2)
C1	C2	C3	115.0(2)	C18	C19	C20	119.9(2)
C2	C3	C8	112.70(19)	C18	C19	O3A	133.8(4)
C4	C3	C2	111.4(2)	C20	C19	O3A	106.3(4)
C4	C3	C8	109.83(19)	O3	C19	C18	112.2(2)
C3	C4	C5	112.7(2)	O3	C19	C20	128.0(2)
C6	C5	C4	111.39(19)	C21	C20	C19	119.3(2)
C5	C6	C7	109.71(18)	C16	C21	C20	121.2(2)
C9	C6	C5	112.47(18)	C26	C25	C27	108.2(2)
C9	C6	C7	112.76(19)	C26	C25	C28	110.3(2)
C8	C7	C6	111.9(2)	C26	C25	C24	114.5(2)
C7	C8	C3	112.21(19)	C26	C25	C24A	85.9(4)
C10	C9	C6	120.3(2)	C27	C25	C28	109.3(2)
C10	C9	C14	118.0(2)	C27	C25	C24	101.7(2)
C14	C9	C6	121.6(2)	C27	C25	C24A	131.0(5)
C9	C10	C11	121.5(2)	C28	C25	C24	112.4(2)
C12	C11	C10	118.4(2)	C28	C25	C24A	108.8(4)
C11	C12	O1	116.7(2)	C19	O3	C22	116.3(2)
C13	C12	O1	121.4(2)	O3	C22	C23	107.9(3)

C13	C12	C11	121.8(2)		C22	C23	C29	110.3(2)
C12	C13	C14	119.0(2)		C22	C23	C24	115.1(2)
C13	C14	C9	121.3(2)		C24	C23	C29	108.4(3)
O1	C15	C16	111.1(2)		C23	C24	C25	119.9(3)
O2	C15	O1	123.1(2)		C19	O3A	C22A	108.7(8)
O2	C15	C16	125.8(2)		O3A	C22A	C23A	107.7(9)
C17	C16	C15	122.2(2)		C29	C23A	C22A	110.0(7)
C21	C16	C15	119.0(2)		C24A	C23A	C29	110.6(7)
C21	C16	C17	118.8(2)		C24A	C23A	C22A	117.6(9)
C18	C17	C16	120.2(2)		C23A	C24A	C25	118.5(8)

Table 4 Torsion Angles for 10.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
O1	C12	C13	C14	178.2(2)	C15	O1	C12	C13	69.2(3)
O1	C15	C16	C17	-7.3(3)	C15	C16	C17	C18	-179.5(2)
O1	C15	C16	C21	173.47(19)	C15	C16	C21	C20	179.6(2)
O2	C15	C16	C17	172.7(2)	C16	C17	C18	C19	-0.3(3)
O2	C15	C16	C21	-6.5(3)	C17	C16	C21	C20	0.4(3)
C1	C2	C3	C4	-172.2(2)	C17	C18	C19	C20	0.7(3)
C1	C2	C3	C8	63.8(3)	C17	C18	C19	O3	-179.9(2)
C2	C3	C4	C5	179.85(19)	C17	C18	C19	O3A	-179.6(8)
C2	C3	C8	C7	179.5(2)	C18	C19	C20	C21	-0.5(3)
C3	C4	C5	C6	55.9(3)	C18	C19	O3	C22	179.3(2)
C4	C3	C8	C7	54.6(3)	C18	C19	O3A	C22A	1.1(13)
C4	C5	C6	C7	-54.7(3)	C19	C20	C21	C16	0.0(3)
C4	C5	C6	C9	178.9(2)	C19	O3	C22	C23	175.7(3)
C5	C6	C7	C8	55.4(3)	C19	O3A	C22A	C23A	-174.3(8)
C5	C6	C9	C10	-107.7(2)	C20	C19	O3	C22	-1.3(4)

C5	C6	C9	C14	71.3(3)	C20	C19	O3A	C22A	-179.1(7)
C6	C7	C8	C3	-56.3(3)	C21	C16	C17	C18	-0.3(3)
C6	C9	C10	C11	-179.0(2)	C26	C25	C24	C23	57.4(3)
C6	C9	C14	C13	178.8(2)	C26	C25	C24A	C23A	-161.4(8)
C7	C6	C9	C10	127.6(2)	C27	C25	C24	C23	173.8(2)
C7	C6	C9	C14	-53.4(3)	C27	C25	C24A	C23A	-50.7(10)
C8	C3	C4	C5	-54.6(3)	C28	C25	C24	C23	-69.5(3)
C9	C6	C7	C8	-178.44(18)	C28	C25	C24A	C23A	88.5(8)
C9	C10	C11	C12	0.4(3)	C29	C23	C24	C25	-162.0(2)
C10	C9	C14	C13	-2.2(3)	C29	C23A	C24A	C25	167.2(6)
C10	C11	C12	O1	-178.60(19)	O3	C19	C20	C21	-179.9(3)
C10	C11	C12	C13	-2.6(3)	O3	C22	C23	C29	-69.9(3)
C11	C12	C13	C14	2.4(3)	O3	C22	C23	C24	53.1(4)
C12	O1	C15	O2	-3.1(3)	C22	C23	C24	C25	74.0(3)
C12	O1	C15	C16	176.91(18)	O3A	C19	C20	C21	179.6(6)
C12	C13	C14	C9	0.0(3)	O3A	C22A	C23A	C29	69.6(11)
C14	C9	C10	C11	1.9(3)	O3A	C22A	C23A	C24A	-58.2(12)
C15	O1	C12	C11	-114.8(2)	C22A	C23A	C24A	C25	-65.3(12)

2.2.2. Structure 14

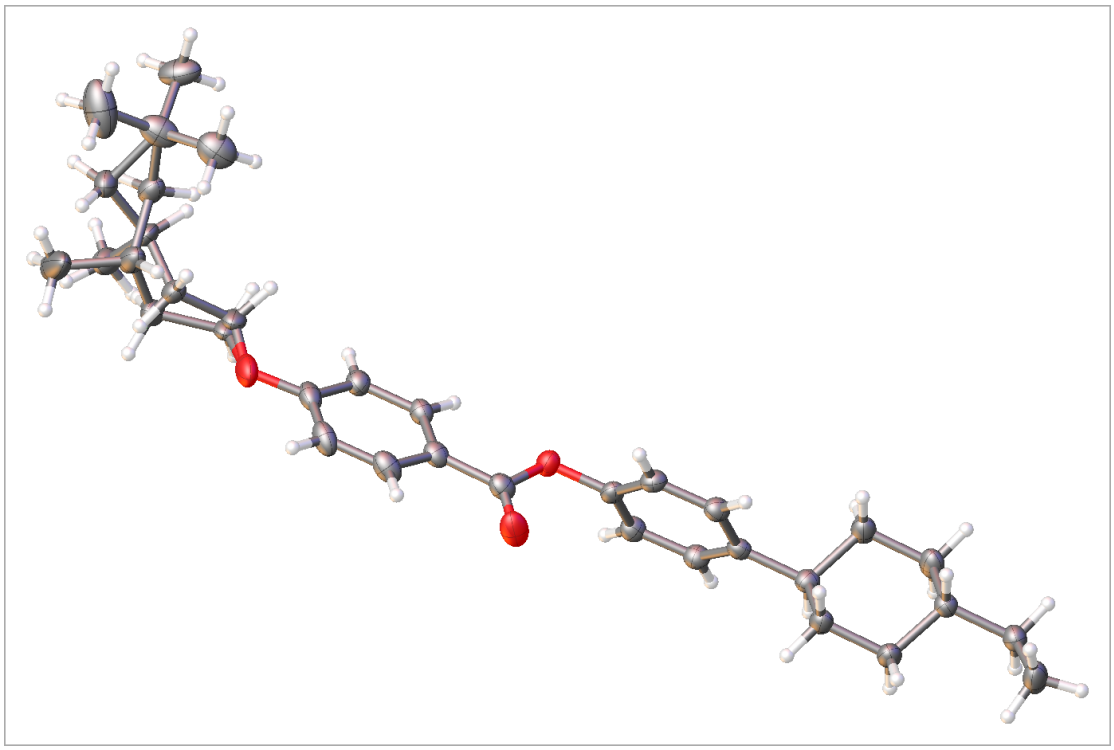


Table 1 Crystal data and structure refinement for 14.

Identification code	jwg1608
Empirical formula	$C_{30}H_{42}O_3$
Formula weight	450.63
Temperature/K	110.05(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.3302(6)
b/Å	5.5649(2)
c/Å	29.6423(9)
α/°	90
β/°	104.367(3)
γ/°	90
Volume/Å^3	2609.53(16)
Z	4

ρ_{calc}g/cm^3	1.147
μ/mm^{-1}	0.557
F(000)	984.0
Crystal size/mm^3	0.433 × 0.088 × 0.038
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.54 to 134.106
Index ranges	-19 ≤ h ≤ 14, -6 ≤ k ≤ 6, -26 ≤ l ≤ 35
Reflections collected	9357
Independent reflections	4663 [R_{int} = 0.0319, R_{sigma} = 0.0346]
Data/restraints/parameters	4663/2/348
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0683, wR_2 = 0.1701
Final R indexes [all data]	R_1 = 0.0807, wR_2 = 0.1793
Largest diff. peak/hole / e Å^{-3}	0.26/-0.38

Table 2 Bond Lengths for 14

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.522(4)	C17	C18	1.394(3)
C2	C3	1.532(3)	C18	C19	1.384(3)
C3	C4	1.517(3)	C19	C20	1.390(4)
C3	C8	1.529(3)	C19	O3	1.370(3)
C4	C5	1.525(3)	C20	C21	1.374(4)
C5	C6	1.533(3)	C22	C23	1.539(8)
C6	C7	1.530(3)	C22	O3	1.457(5)
C6	C9	1.510(3)	C22A	C23A	1.523(18)
C7	C8	1.524(3)	C22A	O3	1.439(9)
C9	C10	1.390(3)	C23	C24	1.536(6)
C9	C14	1.397(3)	C23A	C24A	1.505(13)

C10	C11	1.387(3)		C24	C25	1.534(5)	
C11	C12	1.377(3)		C24	C30	1.544(5)	
C12	C13	1.374(3)		C24A	C25A	1.534(13)	
C12	O1	1.414(3)		C24A	C30A	1.535(14)	
C13	C14	1.389(3)		C25	C26	1.572(5)	
C15	C16	1.479(3)		C25A	C26	1.602(9)	
C15	O1	1.362(3)		C26	C27	1.520(4)	
C15	O2	1.200(3)		C26	C28	1.517(4)	
C16	C17	1.383(3)		C26	C29	1.516(5)	
C16	C21	1.399(3)					

Table 3 Bond Angles for 14.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	C2	C3	114.6(2)	C18	C19	C20	120.0(2)
C4	C3	C2	110.73(19)	O3	C19	C18	124.5(2)
C4	C3	C8	109.77(19)	O3	C19	C20	115.5(2)
C8	C3	C2	112.98(18)	C21	C20	C19	120.0(2)
C3	C4	C5	113.2(2)	C20	C21	C16	120.9(2)
C4	C5	C6	111.45(19)	O3	C22	C23	110.9(5)
C7	C6	C5	109.53(19)	O3	C22A	C23A	92.9(9)
C9	C6	C5	112.21(18)	C24	C23	C22	116.8(4)
C9	C6	C7	113.32(19)	C24A	C23A	C22A	101.6(7)
C8	C7	C6	111.8(2)	C23	C24	C30	107.1(4)
C7	C8	C3	112.02(18)	C25	C24	C23	110.1(4)
C10	C9	C6	120.6(2)	C25	C24	C30	111.1(3)
C10	C9	C14	117.8(2)	C23A	C24A	C25A	114.4(10)
C14	C9	C6	121.6(2)	C23A	C24A	C30A	110.7(9)
C11	C10	C9	121.8(2)	C25A	C24A	C30A	109.2(7)

C12	C11	C10	118.4(2)		C24	C25	C26	119.8(3)
C11	C12	O1	117.5(2)		C24A	C25A	C26	105.1(7)
C13	C12	C11	121.9(2)		C27	C26	C25	106.5(3)
C13	C12	O1	120.5(2)		C27	C26	C25A	123.8(4)
C12	C13	C14	119.0(2)		C28	C26	C25	103.9(2)
C13	C14	C9	121.1(2)		C28	C26	C25A	119.2(5)
O1	C15	C16	112.21(19)		C28	C26	C27	109.2(3)
O2	C15	C16	124.5(2)		C29	C26	C25	120.7(3)
O2	C15	O1	123.3(2)		C29	C26	C25A	83.1(4)
C17	C16	C15	123.3(2)		C29	C26	C27	109.1(3)
C17	C16	C21	118.6(2)		C29	C26	C28	107.1(3)
C21	C16	C15	118.1(2)		C15	O1	C12	116.67(17)
C16	C17	C18	120.9(2)		C19	O3	C22	117.4(4)
C19	C18	C17	119.6(2)		C19	O3	C22A	119.6(9)

Table 4 Torsion Angles for 14.

A	**B**	**C**	**D**	**Angle/˚**	**A**	**B**	**C**	**D**	**Angle/˚**
C1	C2	C3	C4	176.1(2)	C17	C18	C19	O3	-179.9(2)
C1	C2	C3	C8	-60.3(3)	C18	C19	C20	C21	0.2(4)
C2	C3	C4	C5	179.4(2)	C18	C19	O3	C22	5.5(4)
C2	C3	C8	C7	-178.4(2)	C18	C19	O3	C22A	-9.8(12)
C3	C4	C5	C6	-55.5(3)	C19	C20	C21	C16	-0.3(4)
C4	C3	C8	C7	-54.2(3)	C20	C19	O3	C22	-174.2(3)
C4	C5	C6	C7	54.9(3)	C20	C19	O3	C22A	170.5(12)
C4	C5	C6	C9	-178.4(2)	C21	C16	C17	C18	-0.4(3)
C5	C6	C7	C8	-56.0(3)	C22	C23	C24	C25	76.4(5)
C5	C6	C9	C10	106.8(2)	C22	C23	C24	C30	-162.7(4)
C5	C6	C9	C14	-72.5(3)	C22A	C23A	C24A	C25A	-161.4(13)

C6	C7	C8	C3	56.8(3)	C22A	C23A	C24A	C30A	74.8(14)
C6	C9	C10	C11	178.6(2)	C23	C22	O3	C19	173.5(3)
C6	C9	C14	C13	-178.8(2)	C23	C24	C25	C26	-159.0(3)
C7	C6	C9	C10	-128.5(2)	C23A	C22A	O3	C19	-154.7(7)
C7	C6	C9	C14	52.2(3)	C23A	C24A	C25A	C26	87.4(10)
C8	C3	C4	C5	54.0(3)	C24	C25	C26	C27	63.5(4)
C9	C6	C7	C8	177.90(19)	C24	C25	C26	C28	178.8(3)
C9	C10	C11	C12	0.0(3)	C24	C25	C26	C29	-61.3(4)
C10	C9	C14	C13	1.9(3)	C24A	C25A	C26	C27	-58.9(9)
C10	C11	C12	C13	2.3(3)	C24A	C25A	C26	C28	87.0(8)
C10	C11	C12	O1	178.68(19)	C24A	C25A	C26	C29	-167.3(8)
C11	C12	C13	C14	-2.5(3)	C30	C24	C25	C26	82.5(5)
C11	C12	O1	C15	114.6(2)	C30A	C24A	C25A	C26	-147.9(8)
C12	C13	C14	C9	0.3(3)	O1	C12	C13	C14	-178.71(19)
C13	C12	O1	C15	-69.0(3)	O1	C15	C16	C17	8.2(3)
C14	C9	C10	C11	-2.1(3)	O1	C15	C16	C21	-171.7(2)
C15	C16	C17	C18	179.7(2)	O2	C15	C16	C17	-171.6(2)
C15	C16	C21	C20	-179.7(2)	O2	C15	C16	C21	8.5(4)
C16	C15	O1	C12	-178.46(18)	O2	C15	O1	C12	1.3(3)
C16	C17	C18	C19	0.3(3)	O3	C19	C20	C21	180.0(2)
C17	C16	C21	C20	0.4(4)	O3	C22	C23	C24	72.3(5)
C17	C18	C19	C20	-0.2(3)	O3	C22A	C23A	C24A	-179.4(11)

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